THE INVESTIGATION OF TRANSITION METAL COMPLEXES CONTAINING A DATIVE METAL-METAL BOND

by

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B.Sc. (Hons.) Thames Polytechnic (Greenwich University), England 1988

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THE INVESTIGATION OF TRANSITION METAL COMPLEXES CONTAINING A DATIVE METAL-METAL BOND

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ABSTRACT

New and previously known compounds with an unbridged, donor-acceptor (dative) metal-metal bond have for the first time been systematically studied with a number of techniques. (In this unusual class of compounds one metal fragment is considered to donate two electrons to an unsaturated metal fragment in forming the metal-metal bond.)

The photochemistry of the complex \((\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\) (2.1), a molecule with a donor-acceptor metal-metal bond, was examined in detail and the results are consistent with the view that the photoprocess involved is heterolytic cleavage of the metal-metal bond. This is in contrast to the homolytic cleavage found in the photolysis of complexes with a nondative covalent metal-metal bond. Control experiments to probe possible alternative photoprocesses for 2.1 failed to yield any evidence to support alternative pathways. All detected photoproducts were independently synthesized or identified from data in the literature. This led to the synthesis and structural characterization of \(\text{mer-cis-}\) and \(\text{fac-Os(CO)}_5(\text{PMe}_3)(\text{Cl})_2\) and the study of their interconversion.

In complexes that have \(\text{Os(CO)}_4(\text{CNBu}^\text{t})\) as the 18-electron, donor fragment, it was found that the \(^{13}\text{C}\) NMR resonance of the two carbonyl ligands \(\text{trans}\) to one another and \(\text{cis}\) to the metal-metal bond varied considerably upon the identity of the 16-electron, acceptor fragment. The chemical shift of this resonance is believed to be indicative of the acceptor ability of the 16-electron fragment. Some examples of acceptor moieties used were: \(\text{Os(CO)}_3(\text{GeCl}_3)(\text{Cl}), \text{Ru(CO)}_3(\text{SiCl}_3)_2, \text{Ru(CO)}_3(\text{SiCl}_3)(\text{Br}), \text{Re(CO)}_4(\text{X})(\text{X}=\text{Cl, Br, I}).\) A similar study was carried out on analogous complexes with \(\text{Os(CO)}_4(\text{PMe}_3)\) as the donor fragment by using both \(^{31}\text{P(}^1\text{H)}\) and \(^{13}\text{C(}^1\text{H)}\) NMR spectroscopy, but it was found that the
chemical shift of the $^{31}$P resonance was less sensitive to the identity of the acceptor fragment.

Syntheses of complexes with weak (and strong) 18-electron, donor fragments with the strong acceptor Ru(CO)$_3$(SiCl)$_3$ unit were studied. Complexes having the following donors were prepared: (Cp*)Ir(CO)$_2$ (Cp* = η$^5$-C$_5$Me$_5$), Os(CO)$_4$(P$_c$) (two isomers; P$_c$ = P(OCH$_2$)$_3$CMe), Os(CO)$_4$(CNBu'), Ru(CO)$_4$(PMe$_3$), Os(CO)$_4$(PMe$_3$). The compounds (Me$_3$P)(OC)$_4$MRu(CO)$_3$(SiCl)$_3$ (M = Ru, Os) were characterized by X-ray crystallography. This is the first time a complex in which the weak donor Ru(CO)$_4$(PMe$_3$) acts as a ligand has been structurally characterized. (The analogous iron derivative could not be prepared.)
DEDICATION

To those who made it possible and are ever patient,

Edgar William Male and Freda Mary Male

and "mi esposa perfecta".
“...People are out there doing bad things to each other.

It’s because they are being dehumanized.

It is time to take the humanity back into the center of the ring, and follow that for a time.

Greed, it ain’t going anywhere.

The richest person in the world is the most unhappy one.

They should have that in a big billboard across Times Square.

You know, think on that.

Without people you are nothing...”

ACKNOWLEDGMENTS

I would like to thank my supervisor, Dr. Roland K. Pomeroy for providing me with the means to develop my research at Simon Fraser University, the latitude to pursue alternate avenues of research, and for his insights into organometallic chemistry.

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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Å</td>
<td>angstrom unit, (1 \times 10^{-10}) m</td>
</tr>
<tr>
<td>Acc</td>
<td>an acceptor fragment</td>
</tr>
<tr>
<td>Ar</td>
<td>aryl or aromatic</td>
</tr>
<tr>
<td>ax</td>
<td>axial</td>
</tr>
<tr>
<td>(br)</td>
<td>broad (spectra)</td>
</tr>
<tr>
<td>Bu'</td>
<td>iso-butyl ((\text{CH}_2\text{C(H)}\text{(CH}_3)_2)</td>
</tr>
<tr>
<td>Bu&quot;</td>
<td>(n)-butyl ((\text{CH}_2\text{(CH}_2)_2\text{CH}_3))</td>
</tr>
<tr>
<td>Bu'</td>
<td>tertiary butyl ((\text{C(CH}_3)_3))</td>
</tr>
<tr>
<td>CI</td>
<td>chemical ionization</td>
</tr>
<tr>
<td>cis</td>
<td>(Latin: on this side)</td>
</tr>
<tr>
<td>cm⁻¹</td>
<td>wavenumber</td>
</tr>
<tr>
<td>COD</td>
<td>1,5-cyclooctadiene ((\text{C}<em>8\text{H}</em>{12}))</td>
</tr>
<tr>
<td>COE</td>
<td>cis-cyclooctene ((\text{C}<em>8\text{H}</em>{14}))</td>
</tr>
<tr>
<td>Cp</td>
<td>(\eta^5)-cyclopentadienyl ((\eta^5\text{-C}_5\text{H}_5))</td>
</tr>
<tr>
<td>Cp*</td>
<td>(\eta^5)-pentamethylcyclopentadienyl ((\eta^5\text{-C}_5\text{Me}_5))</td>
</tr>
<tr>
<td>Cy</td>
<td>cyclohexyl ((\text{C}<em>6\text{H}</em>{11}))</td>
</tr>
<tr>
<td>d</td>
<td>doublet (spectra)</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift, scale (NMR), dimensionless</td>
</tr>
<tr>
<td>deg</td>
<td>degrees</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide ([\text{HCON(\text{CH}_3)}]_2)</td>
</tr>
<tr>
<td>dmpe</td>
<td>(\text{bis(dimethylphosphino)}\text{ethane (Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2))</td>
</tr>
<tr>
<td>Dnr</td>
<td>a donor fragment</td>
</tr>
<tr>
<td>dppm</td>
<td>(\text{bis(diphenylphosphino)}\text{methane (Ph}_2\text{PCH}_2\text{PPh}_2))</td>
</tr>
<tr>
<td>ε</td>
<td>molar absorptivity, (\text{L mol}^{-1}\ \text{cm}^{-1})</td>
</tr>
<tr>
<td>(\eta)_{abs}</td>
<td>absolute viscosity, (\text{Pa s})</td>
</tr>
<tr>
<td>(E_{1/2})</td>
<td>half-wave reduction potential</td>
</tr>
<tr>
<td>EI</td>
<td>electron impact</td>
</tr>
<tr>
<td>eq</td>
<td>equatorial</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl (CH$_2$CH$_3$)</td>
</tr>
<tr>
<td>φ</td>
<td>quantum yield</td>
</tr>
<tr>
<td>FAB</td>
<td>fast atom bombardment</td>
</tr>
<tr>
<td>fac</td>
<td>facial</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier transform</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>h</td>
<td>Planck’s constant</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz, sec$^{-1}$</td>
</tr>
<tr>
<td>I$_a$</td>
<td>light intensity, einsteins s$^{-1}$</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>L</td>
<td>unidentate ligand</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>λ</td>
<td>wavelength, nm</td>
</tr>
<tr>
<td>m</td>
<td>multiplet (spectra)</td>
</tr>
<tr>
<td>(m)</td>
<td>the relative intensity of the peak is medium (spectra)</td>
</tr>
<tr>
<td>M</td>
<td>Molarity, mol L$^{-1}$</td>
</tr>
<tr>
<td>Me</td>
<td>methyl (CH$_3$)</td>
</tr>
<tr>
<td>mer</td>
<td>meridional</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>mp</td>
<td>melting point</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectroscopy</td>
</tr>
<tr>
<td>m/z</td>
<td>mass-to-charge ratio</td>
</tr>
<tr>
<td>ν</td>
<td>frequency</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOBA</td>
<td>$m$-nitrobenzyl alcohol ($n$-NO$_2$C$_6$H$_4$CH$_2$OH)</td>
</tr>
<tr>
<td>NOESY</td>
<td>Nuclear Overhauser Effect Correlation Spectroscopy</td>
</tr>
<tr>
<td>OMe</td>
<td>methoxy (OCH$_3$)</td>
</tr>
<tr>
<td>o-tol</td>
<td>ortho-tolyl (o-C$_6$H$_4$CH$_3$)</td>
</tr>
<tr>
<td>P$_c$</td>
<td>caged phosphite [P(OCH$_2$)$_3$CCH$_3$]</td>
</tr>
</tbody>
</table>
Ph  phenyl (C₆H₅)
ppm  parts per million
PPN⁺  bis(triphenylphosphine)iminium ([{(C₆H₅)₃P}₂N]⁺)
PR₃  tertiary phosphine ligand
Prᵢ  iso-propyl (C(H)(CH₃)₂)
Prᵢ⁻  n-propyl (CH₂CH₂CH₃)
p-tol  para-tolyl (p-C₆H₄CH₃)
Py  pyridine, C₅H₅N
ρ  density, g cm⁻³
R  alkyl
rm. temp.  room temperature
s  singlet (spectra)
second
(s)  the relative intensity of the peak is strong (spectra)
sec-Bu  secondary butyl (C(H)(CH₃)CH₂CH₃)
(sh)  shoulder (spectra)
t  triplet (spectra)
TBAP  tetrabutylammonium perchlorate ([Bu⁴N][ClO₄])
THF  tetrahydrofuran (C₄H₈O)
TMIO  1,1,3,3-tetramethylisoindoline-2-oxyl
TMS  tetramethylsilane (Si(CH₃)₄)
trans  Latin: across
UV-vis  ultraviolet-visible
(vbr)  very broad (spectra)
(vs)  the relative intensity of the peak is very strong (spectra)
(vw)  the relative intensity of the peak is very weak (spectra)
w  the relative intensity of the peak is weak (spectra)
LIST OF NUMBERED COMPLEXES

(2.1) \((\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\)

(\text{fac-2.2}) \(\text{fac-Os(CO)}_3(\text{PMe}_3)(\text{Cl})_2\)

(\text{mer-cis-2.2}) \(\text{mer-cis-Os(CO)}_3(\text{PMe}_3)(\text{Cl})_2\)

(\text{fac-2.3}) \(\text{fac-Os(CO)}_3(\text{PMe}_3)(\text{CCl}_3)(\text{Cl})\)

([\text{Bu}''\text{4N}]_2[2.4]) \([\text{Bu}''\text{4N}]_2[\text{W}_2(\text{CO})_{10}]\)

(3.1) \(\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3\)

(3.2) \([\text{Os}(\text{CO})_2(\text{PMe}_3)(\text{Cl})(\mu-\text{Cl})]_2\)

(4.1) \((\text{Me}_3\text{P})(\text{OC})_4\text{OsCr(CO)}_5\)

(4.2) \((\text{Me}_3\text{P})(\text{OC})_4\text{OsMo(CO)}_5\)

(4.3) \((\text{OC})_4(\text{Bu}''\text{NC})\text{OsCr(CO)}_5\)

(4.4) \((\text{OC})_4(\text{Bu}''\text{NC})\text{OsMo(CO)}_5\)

(4.5) \((\text{OC})_4(\text{Bu}''\text{NC})\text{OsW(CO)}_5\)

(4.6) \((\text{OC})_4(\text{Bu}''\text{NC})\text{OsOs(CO)}_3(\text{GeCl}_3)(\text{Cl})\)

(4.7) \((\text{OC})_4(\text{Bu}''\text{NC})\text{OsRu(CO)}_3(\text{SiCl}_3)_2\)

(4.8) \((\text{OC})_4(\text{Bu}''\text{NC})\text{OsRu(CO)}_3(\text{SiCl}_3)(\text{Br})\)

(4.9) \((\text{OC})_4(\text{Bu}''\text{NC})\text{OsRe(CO)}_4(\text{Cl})\)

(4.10) \((\text{OC})_4(\text{Bu}''\text{NC})\text{OsRe(CO)}_4(\text{Br})\)

(4.11) \((\text{OC})_4(\text{Bu}''\text{NC})\text{OsRe(CO)}_4(\text{I})\)

([4.12][\text{BCl}_4]) \([\text{Os(CO)}_4(\text{CNBu}''(\text{H}))][\text{BCl}_4]\)

(4.13) \((\text{Me}_3\text{P})(\text{OC})_4\text{OsRe(CO)}_4(\text{Br})\)

(4.14) \((\text{Me}_3\text{P})(\text{OC})_4\text{OsRu(CO)}_3(\text{SiCl}_3)_2\)

(4.15) \((\text{Me}_3\text{P})(\text{OC})_4\text{OsRu(CO)}_3(\text{SiCl}_3)(\text{Br})\)

(4.16) \((\text{Me}_3\text{P})(\text{OC})_4\text{OsRe(CO)}_4(\text{Cl})\)

(4.17) \((\text{Me}_3\text{P})(\text{OC})_4\text{OsRe(CO)}_4(\text{I})\)

(4.18) \((\text{H})(\text{Me}_2\text{P})(\text{OC})_3\text{OsRe(CO)}_5\)

(4.19) \((\text{Cl})(\text{Me}_3\text{P})(\text{OC})_3\text{OsRe(CO)}_5\)

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CHAPTER 1

Complexes with a donor-acceptor metal-metal bond

1.1 Introduction

The compounds that are central to this thesis are binuclear transition metal complexes containing a donor-acceptor metal-metal bond. To understand this class of compounds and the contentions that surround these molecules, various related concepts will be briefly surveyed. Initially, complexes with a nondative metal-metal bond are discussed. The concept of Lewis acid/Lewis base is then discussed and along with the types of complexes containing a Lewis acid/Lewis base interaction. Finally, binuclear transition metal complexes containing an unbridged, donor-acceptor metal-metal bond are reviewed.

The chemistry of binuclear inorganic complexes can be dominated by the nature of the metal-metal bonding. Thus the role of the metal-metal interaction can be of tantamount importance. In 1844 Peligot described a compound, Cr₂(O₂CCH₃)₄·2H₂O, that is now known to contain a multiple metal-metal bond. It was only with the emergence of X-ray crystallography in the 1930’s that it was possible to gather evidence for direct metal-metal interactions. The first crystal structure determination of a binuclear metal carbonyl, Fe₂(CO)₉, was carried out in 1939. In 1947 Linus Pauling suggested that a covalent bond existed between the two iron atoms in Fe₂(CO)₉. The crystal structure of this molecule was later reexamined and confirmed to be the first example of a bridged binuclear metal carbonyl. With the discovery of [(Cp)Mo(CO)₃]₂ and M₂(CO)₁₀ (M = Mn, Re) and the determination of their molecular structures in 1956 and 1957, respectively, the existence of
compounds with an unbridged, nondative covalent metal-metal bond was established. This was significant since prior to this point whenever a metal-metal interaction was proposed in a molecule it was always bridged by ligands and therefore a degree of doubt was introduced about whether a metal-metal interaction was indeed present. Binuclear inorganic compounds containing an unbridged, nondative covalent metal-metal bond are now exceedingly numerous.\(^1,2,7\)

The terms Lewis acid and Lewis base are defined as: “A Lewis acid is a molecule or ion whose incomplete electronic arrangement allows it to bind to another species by accepting an electron pair from that species. A Lewis base is a molecule or ion capable of donating an electron pair to a Lewis acid and resulting in the formation of a coordinate covalent bond.”\(^8\) Another term for a coordinate covalent bond is a dative covalent bond. The Lewis acid/Lewis base descriptors were later modified thus, a Lewis base is an electron donor and conversely a Lewis acid is an electron acceptor.\(^8\) A typical main group example is the ammonia-borane, H\(_3\)NBH\(_3\) adduct, and this is compared to the nondative covalent bond in the isoelectronic system, ethane, see Figure 1.1.

Some transition metal complexes are also known to act as Lewis bases. An extension of the main group electron Lewis acid-Lewis base adducts area was to use a transition metal as an electron donor to the electron deficient group 13 moiety. Some examples are: (Cp\(_2\))(H)\(_2\)MBX\(_3\), (Cp)HReBX\(_3\) (M = Mo, W; X = F, Cl),\(^9\) [M][(OC)\(_5\)nM'BX\(_3\)] (M = Na, K, Rb, Cs, R\(_4\)N; M' = Mn, Re, Tc, Co, Rh, Ir; R = Et, Bu\(^i\), Pr\(^i\); X = H, F; n = 0, 1),\(^10\) [PPN][(OC)\(_4\)CoEPH\(_3\)], [Et\(_4\)N][(Cp)(OC)\(_2\)FeEPH\(_3\)] (E = In, Ga, Al), [Pr\(_n\)N][(OC)\(_3\)MnInPH\(_3\)], [Bu\(_n\)N][(Cp)(OC)\(_3\)WInPH\(_3\)].\(^11\)
This was extended to the use of a coordinatively unsaturated group 11 or 12 species as the Lewis acid, with a transition metal complex acting as the electron donor. Some examples of such adducts are, (Cp)(Me₃P)₂CoA [A = Zn(PMe₃)(Cl)₂, Cu(PMe₃)₂(Cl), Hg(Cl)₂],¹³ [(2,6-(Me₂NCH₂)₂C₆H₃)Pt(μ-{(p-tol)NYNR})MX₃] (Y = CH, N; R = Me, Et, Pr; M = Ag, X = Br, M = Hg, X₂ = Br, Cl),¹⁴ [(PhO)₃P]₂(F₃C₆)₂RhAg(PPh₃),¹⁵ (OC)₂(L)₂{[MeO(O)C]₂C₂S₂C}FeHg(Cl)₂ (L = PMe₂Ph, PMe₃, P(OMe)₃, PPh₃).¹⁶ The complexes (L)₂(OC)₂{[MeO(O)C]₂C₂S₂C}FeHg(Cl)₂¹⁶ are particularly interesting since only with the utilization of the Lewis acid to reduce the excess electron density on the Fe center are these complexes attainable. The authors proposed that the formation of a donor-acceptor interaction could be a general method for the stabilization of electron rich, metal complexes.
A further extension of this concept would be to have both the electron donor and electron acceptor as transition metal complexes. Compounds of this type will be discussed in classes rather than in a historical approach. The first class of compounds to be considered will be those that contain a donor-acceptor metal-metal bond and bridging entities. One of the first compounds proposed to contain a donor-acceptor metal-metal bond between two transition metal fragments was Fe₂(CO)₆[C₄(CH₃)₂(OH)₂]. The chemical bonding of this molecule was believed to be as shown in representation I in Figure 1.2. It was later realized to be the first example of a molecule containing a semibridging carbonyl, Fe₂(μ-CO)(CO)₅[C₄(CH₃)₂(OH)₂] as shown in representation II in Figure 1.2. Theoretical calculations support this view of the metal-metal bonding and furthermore indicate a “very strong Fe-C interaction only σ in nature” in the ferracyclopentadienyl ring. These calculations therefore do not support the alternative bonding picture where an Fe=C is invoked and shown in representation III in Figure 1.2. Further analogues have been prepared and lend weight to this argument, such as, Fe₂(μ-CO)(CO)₅[C₄(C₄H₈)₂], which resembles representation II, and PtFe(CO)₃(COD) [μ-PhCC(H)C(H)CPh], which resembles representation I. Nevertheless, as with other compounds containing nondative metal-metal bonds with bridging ligands, vide infra, there exists an ambiguity as to the exact nature of the metal-metal interaction.

Since the first report of a complex with a dative metal-metal bond bridged by ligands, a considerable number of further such organometallic complexes have been reported. They cannot, however, be regarded as common. Studies of some further examples will now be discussed.
Figure 1.2 The representations of the bonding in the complex Fe$_2$(CO)$_6$[C$_4$(CH$_3$)$_2$(OH)$_2$].

Theoretical calculations have been carried out on several of the bridged systems in an attempt to understand the bonding interaction between the metal atoms. Williams et al. proposed that complexes with either asymmetrically bridging $\pi$-acid ligands such as (CO) as in [(Aryl)(OC)Cr(\(\mu\)-CO)$_2$Rh(CO)(Aryl')] (Aryl' = \(\eta^5\)-C$_6$H$_6$, \(\eta^5\)-1,3,5-Me$_3$C$_6$H$_3$, \(\eta^6\)-C$_6$Me$_6$; Aryl' = Cp*, \(\eta^5\)-C$_9$H$_7$)\(^{18}\), unsaturated hydrocarbons as in [(Cp)(OC)M(\(\eta^1\),\(\eta^5\),\(\mu\)-(C$_5$H$_4$)Mn(CO)$_4$ (M = Mo, W)\(^{19}\), or bridging $\pi$-donor ligands such as, phosphido ligands as in [(Me$_3$P)Pt(\(\mu\)-PPh$_2$)$_2$M(Aryl)$_2$ (M = Th, Zr, Hf; Aryl = Cp*, Cp)\(^{20}\)] or sulfido groups as in [Fe(\(\mu\)-\(\eta^5\)-SC$_5$H$_4$)$_2$Pd(PPh$_3$)]0.5C$_6$H$_5$CH$_3$\(^{21}\)] could be classified and discussed together.\(^{12}\) It was suggested that in these compounds "the direct metal-metal donor-acceptor bonding is overshadowed by interactions that take place through the bridging ligands."\(^{12,20b,22}\) This proposal was corroborated by theoretical calculations contained in reference 20a on the phosphido bridged species. A major point from these studies is that, as previously mentioned, the presence of the bridging entities often obscures the issue of the nature of the metal-metal bonding.
A second class of compounds where dative metal-metal bonds have been proposed are certain metal cluster compounds. (The Johnson definition of a cluster, that is, a molecular compound with three or more metal atoms with some bonding interactions between the metal centers will be used here\(^\text{23}\)). Some examples of clusters which contain a putative donor-acceptor metal-metal bond are: Os\(_6\)(CO)\(_{18}\) as shown in Figure 1.3,\(^\text{24}\) Ru\(_5\)(\(\mu_5\)-C\(_2\)PPh\(_2\))(\(\mu\)-PPh\(_2\))(CO)\(_{15}\),\(^\text{25}\) Pt\(_3\)Fe\(_2\)(CO)\(_{12}\)(COD)\(_2\), Pt\(_3\)Fe\(_2\)(CO)\(_7\)(COD)(\(\mu_3\)-PhC\(_2\)Ph\(_3\))(\(\mu\)-PhC\(_2\)Ph),\(^\text{17e}\) (Ph\(_3\)P)(OC)\(_3\)Re(\(\mu\)-H)Os\(_3\)(CO)\(_{11}\), (Cp\(^*\))(OC)\(_2\)OsOs\(_3\)(\(\mu\)-H)(CO)\(_{10}\),\(^\text{26}\) Os\(_5\)(CO)\(_{15}\)(eq-PMe\(_3\)),\(^\text{27}\) and [(OC)\(_5\)\(_n\)(L)\(_n\)Os]Os\(_3\)(CO)\(_{11}\) (L = PMe\(_3\), \(n = 1\) as shown in Figure 1.3,\(^\text{28a}\) L = P\(_c\), \(n = 1\),\(^\text{28b}\) L = CNBu', \(n = 1,2\)).

**Figure 1.3** Metal cluster compounds with a donor-acceptor metal-metal bond: (a) as an integral part of the metal cluster framework, Os\(_6\)(CO)\(_{18}\) and (b) exo to the metal cluster skeleton, (Me\(_3\)P)(OC)\(_4\)OsOs\(_3\)(CO)\(_{12}\).

These clusters may be further subdivided into two subsections; those in which the donor-acceptor metal-metal bond is an integral part of the metal cluster skeleton,\(^\text{17e,24-27}\) and those in which the donor-acceptor metal-metal bond is on the exterior of the metal cluster skeleton.\(^\text{28}\) A delocalized bonding picture (the polyhedral skeletal electron pair theory) is
usually employed in describing cluster compounds of nuclearity five or greater. Since the donor-acceptor interaction is a localized picture, this may not be the preferred model to describe the bonding in the first subsection of metal clusters. As it is these cluster compounds may be viewed as containing bridging entities and thus the elucidation of the nature of the metal-metal interactions may not be easy, or possible, for the reasons mentioned previously with the bridged binuclear complexes. In the second subsection of clusters, with the donor-acceptor interaction exo to the cluster, the electron pair is probably not delocalized into the cluster framework and the donor-acceptor formalism is therefore probably a more accurate picture.

Transition metal complexes that are charged and contain a putative donor-acceptor metal-metal bond have also been prepared. For example Anders and Graham suggested that the unbrided compounds \[\text{[Et}_4\text{N}][(\text{OC})_5\text{M}'](\text{CO})_5] \quad (M = \text{Mn, Re; } M' = \text{Cr, Mo, W})
\]

consisted of a \[\text{[(OC)}_5\text{M}:]-\] fragment acting as a Lewis base to the \(\text{M'(CO)}_5\) fragment after displacing CO from the \(\text{M'(CO)}_6\) reactant. Theoretical calculations have attempted to clarify this metal-metal bonding scheme. It was suggested in \[\text{[Et}_4\text{N}][(\text{OC})_3\text{ReW(CO)}_5] \]

that there was little charge delocalization over the M-M bond and, furthermore, that it was localized on the tungsten fragment. This is therefore not consistent with a donor-acceptor metal-metal bond. While the closely related unbridged system of, \[\text{[PPN]}^+[\text{(L)}_n(\text{X})\text{FeM(CO)}_{9-n}]^- \quad (M = \text{Cr, W; } X = \text{H, AuPPh}_3, \text{CH}_3; L = \text{PPh}_3, \text{P(OOMe)}_3, \text{PMe}_3, \text{PET}_3, \text{P(OEt)}_3; n = 0, 1)\]

has also been the subject of theoretical calculations. These calculations, in a converse manner, clearly suggest \[\text{[(H)(OC)}_4\text{FeMo(CO)}_5]^- \] does have a donor-acceptor metal-metal bond. Theoretical calculations on the binuclear cationic system with the phosphino bridging ligands, \[\text{[Pt}_2\text{Me}_3(\mu-\text{dppm})_2][\text{PF}_6] \]

indicated it to
contain a donor-acceptor metal-metal bond with the bridging ligands not providing “electron communication between the metals”.\textsuperscript{12} This is in contrast to similar compounds with phosphido ligands [for example (Me\textsubscript{3}P)Pt(\mu-PPh\textsubscript{2})\textsubscript{2}Th(Aryl)\textsubscript{2} (Aryl = C\textsubscript{p}* , C\textsubscript{p})\textsuperscript{20}] where calculations indicate the bridging ligands do influence the nature of the metal-metal bond.\textsuperscript{12} Molecular orbital calculations on [(Cp)\textsubscript{2}Ti(SCH\textsubscript{2}CH\textsubscript{2}SCH\textsubscript{2})\textsubscript{2}CH\textsubscript{2}Cu][PF\textsubscript{6}],\textsuperscript{33} with bridging sulfido ligands indicate it does have a weak donor-acceptor metal-metal interaction, but this plays only a secondary role relative to the interactions via the bridging entities.\textsuperscript{12,34} {This is analogous to the uncharged sulfido bridged system, [Fe\textsubscript{μ-η}\textsuperscript{5-η}\textsuperscript{1}-SC\textsubscript{5}H\textsubscript{4})\textsubscript{2}Pd(PPh\textsubscript{3})]0.5C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}\textsuperscript{21}, mentioned previously).}

An unusual bioinorganic example of a cationic complex believed to contain a bridged donor-acceptor metal-metal bond is trans-[(NH\textsubscript{3})\textsubscript{2}Pt(1-MeC'-N3, N4)\textsubscript{2}Pd(NH\textsubscript{3})]\textsuperscript{2+} [NO\textsubscript{3}]\textsuperscript{-}2.3H\textsubscript{2}O (1-MeC'-N3, N4 = 1-methylcytosinate anion with metals binding via N3 and the deprotonated amine), as shown in Figure 1.4.\textsuperscript{35}
Figure 1.4 The cationic component of trans-[(NH₃)₂Pt(1-MeC'=N₃, N₄)₂Pd(NH₃)]⁺ [NO₃]⁻·3H₂O (1-MeC'-N₃, N₄ = 1-methylcytosinate anion with metals binding via N₃ and the deprotonated amine).

Two further systems that merit mention are [(MeNC)₂Ni(µ-dppm)₂Pd(CNMe)][PF₆]³⁶ and [(Cl)Pt(µ-dppm)₂Pt(L)][ClO₄] (L = (4-chlorophenyl)(4-pyridyl)-acetylene).³⁷ For the first compound, ³¹P{¹H} NOESY NMR spectroscopy was utilized to monitor the isomerization between the thermodynamically less stable species with a dative, covalent metal-metal bond and its isomer with a nondative covalent metal-metal bond. In the second system, [(Cl)Pt(µ-dppm)₂Pt(L)][ClO₄], (see Figure 1.5) with a donor-acceptor metal-metal bond, was utilized as a multielectron transfer agent to an organic fragment. The aim was to create a luminescent donor-acceptor metal complex as a novel route to photocatalysts for energy storage reactions.
When all of these binuclear compounds with donor-acceptor metal-metal bonds are considered, the different fields of chemistry that they came from are quite diverse. Generally it would seem, as in the case of the complexes with bridging entities, that the theoretical calculations carried out on charged species do not always clarify the bonding picture. One could argue that placement of the charge in different locations in the molecule may yield a different formalism for the metal-metal interaction.

Binuclear complexes in which there is less ambiguity as to the description of the metal-metal interaction are those compounds that are neutral and where the metal-metal bond is unbridged. Even in such neutral complexes where the donor-acceptor metal-metal bond is unbridged, there appears to be two subsets. The first subset are those complexes that are a result of a charged transition metal fragment that displaces a halide from an uncharged metal fragment. Three examples of this class of complex are: (OC)$_4$CoRh(CO)(PEt$_3$)$_2$, (OC)$_2$(Cp)RuZr(Cp)$_2$(X) [X = CH$_3$, Cl, O-Bu']$^{39}$ and (Cp)(OC)$_2$RuTh(Cp$^*$)$_2$(X) (X = Cl, I).$^{40}$ Based on the chemistry and/or geometry of these systems, the metal-metal bonds are formulated as anionic donor-cationic acceptor bonds. Theoretical calculations$^{41}$ suggest a donor-acceptor metal-metal bond is present and for the
latter two molecules, the bond is best considered as \([(\text{Cp})_2(\text{I})\text{M}]^+[\text{Ru}(\text{CO})_2(\text{Cp})]^- (\text{M} = \text{Th}, \text{Zr})\). Furthermore, \([\text{Ru}(\text{CO})_2(\text{Cp})]^-\) can be considered an "organometallic pseudohalide". The bonding description remains, however, ambiguous since in the uncharged bimetallic complex it is possible to arrive at a scheme that does not require a cation and an anion that then leads to assigning the metal-metal interaction as a nondative covalent bond. Once again, there is ambiguity in the description of the metal-metal bond in these molecules.

The second subset of complexes are neutral bimetallic molecules containing an unbridged metal-metal bond and synthesized from two neutral mononuclear transition metal fragments. Any ambiguity over placement of charge is, therefore, avoided. The first species of this type to be synthesized were \((\text{Cp})_2(\text{H})_2\text{MM'}(\text{CO})_5 (\text{M} = \text{Mo}, \text{W}; \text{M'} = \text{Cr}, \text{Mo}, \text{W})\).\(^{42}\) Comparing this system to the previous work mentioned above that indicates the \((\text{Cp})\text{M}(\text{H})^-\) molecules can act as a Lewis base towards group 13 Lewis acids,\(^9\) the formalism of a donor-acceptor metal-metal bond in these \text{MM'} complexes, therefore, seems reasonable. The question about the positions of the hydrides in these complexes\(^{42}\) was later laid to rest by Legzdins and coworkers\(^{43}\) who reanalyzed the \(^1\text{H}\) NMR data and stated the hydrides are "unquestionably" static in solution on the NMR timescale and nonbridging. Unfortunately, there are no structural determinations of these molecules. The first structural characterization of a neutral, binuclear transition metal complex containing an unbridged donor-acceptor metal-metal bond came in 1983 when Pomeroy and coworkers reported the synthesis and molecular structure of \((\text{OC})_5\text{OsOs}(\text{CO})_3(\text{GeCl}_3)(\text{Cl})\), see Figure 1.6.\(^{44}\)
The complex was shown by X-ray crystallography to have an unbridged Os-Os bond and the Os(CO)$_5$ species, an 18-electron fragment, can be seen to be acting as a 2-electron donor ligand to the 16-electron Os(CO)$_3$(GeCl$_3$)(Cl) acceptor moiety.

Subsequently analogous complexes were synthesized by Pomeroy and coworkers and other groups, see Table 1.1.

In a further extension of this work, Pomeroy and coworkers synthesized several intriguing complexes believed to contain two donor-acceptor metal-metal bonds in tandem (i.e., Os→Os→W), with no bridging interactions, viz., (L)$_2$(OC)$_3$OsOs(CO)$_4$W(CO)$_5$, (L)(OC)$_4$OsOs(CO)$_3$(L)W(CO)$_5$ (L = P$_5$, CNBu$_5^{52a}$). This was an unprecedented bonding mode for transition metal complexes.

Figure 1.6 Molecular structure of (OC)$_5$OsOs(CO)$_3$(GeCl$_3$)(Cl)
Table 1.1 Neutral transition metal complexes with an unbridged, donor-acceptor metal-metal bond that are derived from two uncharged reactants.

<table>
<thead>
<tr>
<th>Complexes with an unbridged, neutral donor-acceptor metal-metal bond.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(OC)₅OsRu(CO)₃(SiCl₃)(X) (X = Br, SiCl₃)</td>
<td>45</td>
</tr>
<tr>
<td>(Me₃P)(OC)₄OsRu(CO)₃(SiCl₃)₂</td>
<td>45</td>
</tr>
<tr>
<td>(Me₃P)(OC)₄RuRu(CO)₃(SiCl₃)(Br)</td>
<td>45</td>
</tr>
<tr>
<td>(Cp*)(OC)₂IrW(CO)₅</td>
<td>46</td>
</tr>
<tr>
<td>(Cp*)(OC)[(Pr'O)₃P]IrRh(Cl)(CO)[P(OPr')₃]</td>
<td>47</td>
</tr>
<tr>
<td>(Cp*)(OC)(OC)₄OsRe(CO)₄(Br)</td>
<td>48</td>
</tr>
<tr>
<td>(η⁵-Aryl)(OC)(L)M Pt(C₆F₅)₂(CO) (Aryl = Cp, Cp*; M = Co, Rh; L = CO, PPh₃)</td>
<td>49</td>
</tr>
<tr>
<td>(L)(OC)₄OsM(CO)₅ (M = Cr, Mo, W; L = PMe₃, PPh₃, PMePh₂, PMe₂Ph, P(OMe)₃, Pc)</td>
<td>50</td>
</tr>
<tr>
<td>(OC)₅-n(L)nOsM(CO)₅ (M = Cr, Mo, W; L = CNBu', n = 1, 2)</td>
<td>51</td>
</tr>
</tbody>
</table>

Once again, theoretical calculations have been carried out on some of these systems, that is, (OC)₅OsOs(CO)₃(Cl)(Y) (Y = GeCl₃, Cl)¹² and (OC)₅OsM(CO)₅ (M = Cr, W).¹²,⁵³ The results strongly suggest the metal-metal interaction should be considered a donor-acceptor interaction. Indeed, it was suggested¹² that the donor-acceptor interaction in these systems was one of the strongest when compared to compounds such as [Pt₂Me₃(μ-dppm)₂]⁺[PF₆]⁻.³²
1.2 Thesis

This thesis will only be concerned with this latter class of complexes, namely, neutral, binuclear transition metal complexes with an unbridged, donor-acceptor metal-metal bond. These molecules lack the ambiguities concerning the metal-metal bonding that exist for those molecules that are charged or where the metal-metal bond is bridged by ligands. In Chapter 2 the photochemistry of \((\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\) (2.1), a complex with a donor-acceptor metal-metal bond, is described. Since we have suggested that the metal-metal bonding in 2.1 is different from such complexes as \((\text{OC})_5\text{ReRe(CO)}_5\), the photochemistry of 2.1 might also be expected to differ from that exhibited by molecules with nondative covalent metal-metal bonds. Chapter 3 describes the synthesis and characterization of complexes pertinent to the photoproducts of Chapter 2. From all the prior work on neutral, unbridged binuclear complexes containing donor-acceptor metal-metal bonds, little comparative chemistry of the complexes had been carried out.\(^{41,43-51}\) Chapters 4 and 5 attempt to redress this situation. In Chapter 4 the synthesis of a series of new binuclear transition metal complexes containing a donor-acceptor metal-metal bond are described with \(\text{Os(CO)}_4(\text{CNBu}^\prime)\) and \(\text{Os(CO)}_4(\text{PMe}_3)\) as the donor fragments. When \(\text{Os(CO)}_4(\text{CNBu}^\prime)\) is the donor fragment there is a carbonyl ligand \textit{trans} to the donor-acceptor metal-metal bond, and its \(^{13}\text{C}\{^1\text{H}\}\) NMR resonance is at an unusually high field and varies significantly with alteration of the acceptor fragment.\(^{51}\) It was therefore thought that a comparison of the \(^{13}\text{C}\{^1\text{H}\}\) NMR resonance of this \textit{trans}-carbonyl ligand or the other carbonyl groups in these complexes might provide a probe for defining the ‘acceptor strength’ of the various acceptor fragments. In an analogous fashion the \(^{31}\text{P}\{^1\text{H}\}\) NMR chemical shifts of the phosphorus resonance in molecules with a donor-acceptor metal-
metal bond and Os(CO)$_4$(PMe$_3$) as the donor fragment might corroborate the findings with the Os(CO)$_4$(CNBu') system.

Syntheses of compounds with various 18-electron, donor fragments with the strong acceptor Ru(CO)$_3$(SiCl$_3$)$_2$ unit were studied and reported in Chapter 5. Complexes having the following donors were prepared: (Cp*)Ir(CO)$_2$, Os(CO)$_4$P$_c$ [two isomers, P$_c$ = P(OCH$_2$)$_3$CCH$_3$], Os(CO)$_4$(CNBu'), Ru(CO)$_4$(PMe$_3$), Os(CO)$_4$(PMe$_3$). The comparative chemistry and the $^{13}$C($^1$H) NMR chemical shifts of the carbonyl ligands on the acceptor fragment of this group of complexes were employed to investigate the 'donor strength' of the donor fragments.
Investigation of the photochemistry of (Me₃P)(OC)₄OsW(CO)₅ (2.1)

2.1 Introduction

Metal-metal bonds have two modes of cleavage upon photolysis: homolytic cleavage, (eq 2.1), where the moieties formed are radicals, and heterolytic cleavage, (eq 2.2), where one moiety retains both electrons associated with the bond.

\[
\begin{align*}
(L)_nM-M'(L)_m & \xrightarrow{h\nu} (L)_nM^* + *M'(L)_m \\
(L)_nM-M'(L)_m & \xrightarrow{h\nu} (L)_nM: + M'(L)_m
\end{align*}
\] (2.1) (2.2)

Another photochemical pathway allowable to a bimetallic complex is the dissociation of a ligand, typically CO (eq 2.3) with retention of the metal-metal bond.\(^5^4\)

\[
(L)_nM-M'(L)_m \xrightarrow{h\nu} (L)_nM-M'(L)_{m-1} + L
\] (2.3)

Both homolytic metal-metal bond cleavage and ligand dissociation are commonly observed processes in the photolysis of bimetallic organometallic compounds.\(^5^4\) Heterolytic cleavage of the metal-metal bond on the other hand remains an elusive process. It is noteworthy that, in all previous cases where photochemical heterolyses have been claimed, definitive evidence for heterolysis was either lacking or upon reexamination of the system it has been shown that the heterolytic process was actually homolysis followed by an electron transfer. Thus Cox et al. suggested that the disproportionation reactions of (Cp)₂M₂(CO)₆ (M = Mo, W) and Mn₂(CO)₁₀ dimers occurred by a heterolytic primary photoprocess.\(^5^5\)
Further mechanistic investigation, however, strongly suggested that the initial photoprocess was metal-metal bond homolysis followed by rapid uptake of the solvent or ligand into one of the metal radical fragments. Following this, electron transfer between the metal radical fragments occurs to yield the same final photoproducts as determined earlier.\textsuperscript{56,57} Turner and coworkers examined the photochemistry of CpFe(CO)(\(\mu\)-CO)\(_2\)Co(CO)\(_3\) in a matrix at 10 K.\textsuperscript{58} When the argon matrix was doped with 10\% CO an unidentified intermediate was formed, that appeared not be [CpFe(CO)\(_2\), Co(CO)\(_4\)] and hence a disproportionation mechanism was disfavored. The intermediate subsequently yielded [CpFe(CO)\(_3\)]\(^+\) and [Co(CO)\(_4\)]\(^-\). Upon irradiation under similar conditions in a pure CO matrix, however, different final photoproducts were observed, one of these products was assigned to the radical fragment, [Co(CO)\(_4\)]\(^+\). This was proposed to arise from the intermediate, [Co(CO)\(_4\)]\(^-\) and not from the initial homolysis of the bimetallic species since the [CpFe(CO)\(_2\)]\(^+\) radical or derivatives of this radical were not observed. In a later paper the authors stated, "In inert gas matrices, homolysis of the M-M is not usually observable, because the bulky radicals produced are held close together in the matrix cage and forced to recombine."\textsuperscript{59} Thus, in all of these studies the pathway of initial homolysis of the metal-metal bond followed by a component of the matrix acting as a ligand to produce the disproportionation products could not be completely ruled out. This is particularly true when it is pointed out that it has been found for similar systems such as (OC)\(_4\)CoM(CO)\(_3\)(LL) (M = Mn, Re; LL = 2,2'-bipyridine, 2-pyridinecarbaldehyde N-isopropylimine) that the heterolytic products are the result of photochemical homolysis followed by direct electron transfer between geminate cage radicals.\textsuperscript{60}
Finally, in the aforementioned later paper by Turner and coworkers it was speculated that in a CO matrix at 12 K photolysis of Os$_2$(CO)$_9$ might initially proceed via heterolytic metal-metal bond cleavage to form Os(CO)$_4$ and Os(CO)$_5$.\textsuperscript{59} Although in an Ar matrix the initial photoprocess was shown to be CO loss and formation of Os$_2$(CO)$_8$, this species was also observed when the photolysis of Os$_2$(CO)$_9$ was carried out under similar conditions in a CO matrix. The species, Os$_2$(CO)$_8$ could therefore undergo cleavage of the metal-metal bond and then coordinate a CO molecule to give Os(CO)$_5$. Both mechanisms equally account for the final photoproduct of Os(CO)$_5$. As with the preceding system, however, it was not possible to distinguish between the two routes by direct experimental evidence.

Although metal-metal bond heterolyses are equivocal, there is ample precedent for photochemical heterolyses in reactions not involving metal-metal bonds. For example, metal-ligand bond cleavage reactions such as CO or phosphine loss (eq 2.3)\textsuperscript{61} are typically heterolytic. Since such metal-ligand bonds are dative in nature, a bimetallic system with a dative metal-metal bond, it was reasoned, might undergo heterolytic cleavage upon photolysis. A dative metal-metal bond by its nature will have a bond that is polar. It had previously been suggested that “Significant ionic contribution to the M-M' bond will likely result in a situation where M-M' bond cleavage is heterolytic” when talking about the photolysis of bimetallic systems.\textsuperscript{62} That is, to say, that heterobinuclear complexes composed of two, mononuclear metal fragments of different electron configuration and electronegativities would have a polar metal-metal bond and probably would be predisposed towards heterolytic cleavage of the metal-metal bond.\textsuperscript{63}

What constitutes a metal-metal dative (donor-acceptor) bond? When one transition metal fragment having a full electron quota can be envisaged as donating two of its
electrons to an unsaturated metallic fragment then the resulting bond is considered a dative metal-metal bond. Both nondative and dative covalent metal-metal bonds are thought to have a pair of electrons holding the two metal fragments together, see Figure 1.1. The distinction between a dative covalent and a nondative covalent bond is that upon supplying energy to either bond they should yield different products. Each process would proceed upon the lowest ground state energy surface and assuming there was no crossing over to another surface, eventually the metal-metal bond would be cleaved and the fragments would be an infinite distance apart. For the complex containing a dative bond, at this point one fragment would have a full complement of electrons whereas the other would be an unsaturated species; the two electrons associated with the bond reside on the former fragment. On the other hand, separation of the nondative covalent bond would yield radicals. Thus heating the complex proposed to contain a dative metal-metal bond in the presence of a two electron donor ligand and trapping the unsaturated fragment may assist in the assignment of a metal-metal bond as a dative bond.

In 1983 Pomeroy and coworkers reported the synthesis and structural characterization of $(OC)_5OsOs(CO)_3(GeCl)_3(Cl)$ and demonstrated that the unbridged complex was formed from $Os(CO)_5$ and $Os(CO)_3(GeCl)_3(Cl)$. It was proposed that $Os(CO)_5$, a stable 18 electron molecule, was acting as a Lewis base to the unsaturated $Os(CO)_3(GeCl)_3(Cl)$ moiety. When the reaction was repeated under similar conditions but with the good donor ligand $PPh_3$ present the only complex formed was $Os(CO)_3(PPh_3)(GeCl)_3(Cl)$. This supports the idea that $Os(CO)_5$ is acting as a two electron donor and is therefore a phosphine mimic. Since that report Pomeroy’s group and other
groups have prepared many other examples of neutral, unbridged complexes with dative metal-metal bonds.\textsuperscript{44-51}

It had previously been shown that it was possible to produce clusters from complexes with unbridged, dative metal-metal bonds upon photolysis in Pyrex, as shown in eq 2.4.\textsuperscript{66} Formation of clusters via the photolysis of bimetallic complexes is not often observed and it may be the consequence of having a dative metal-metal bond rather than a nondative metal-metal bond in the precursor complex. The mechanism that was tentatively proposed to account for the metal cluster formation involved the initial heterolytic cleavage of the metal-metal bond in (R\textsubscript{2}P)(OC)\textsubscript{4}OsM(CO)\textsubscript{5} upon photolysis.

\[
\text{(R\textsubscript{2}P)(OC)\textsubscript{4}OsM(CO)\textsubscript{5}} \xrightarrow{h\nu \lambda \geq 275 \text{ nm}} \text{(OC)\textsubscript{3}M[Os(CO)\textsubscript{3}(PR\textsubscript{3})]_2}
\]

\[\text{M = Cr, Mo, W; PR\textsubscript{3} = PMe_3, P(OMe)\textsubscript{3}, P_c}\]

Thermal heterolytic cleavage of a metal-metal bond has been demonstrated, for example, in the complexes (Cp)(Me\textsubscript{3}P)\textsubscript{2}CoA [A = Zn(Cl)\textsubscript{2}(PMe\textsubscript{3}), Cu(Cl)(PMe\textsubscript{3})\textsubscript{2}],\textsuperscript{67} (OC)\textsubscript{4}CoRh(CO)(PE\textsubscript{3})\textsubscript{2},\textsuperscript{38} (Cp)(H)\textsubscript{2}MM'(CO)\textsubscript{5} (M = Mo, W; M' = Cr, Mo, W)\textsuperscript{42} and several of the neutral unbridged complexes with a dative metal-metal bond, see Table 1.1.\textsuperscript{45-47,49,50} Indeed, as mentioned previously, it may be a key experiment to aid in the analysis of the nature of a metal-metal bond.

Because heterolyses are common in the thermolysis of compounds with a dative metal-metal bond we were prompted to thoroughly investigate the photochemistry of a complex with an unbridged, dative metal-metal bond. Herein the photolysis of (Me\textsubscript{3}P)(OC)\textsubscript{4}OsW(CO)\textsubscript{5} (2.1) a complex with a putative dative metal-metal bond is described and a thorough study of the mechanisms involved was undertaken. A preliminary account of our findings has appeared.\textsuperscript{68}
2.2 Results and Discussion

As mentioned in the introduction to Chapter 2, there are three possible primary pathways for the photolysis of a binuclear metal complex namely, heterolytic cleavage of the metal-metal bond, homolytic cleavage of the metal-metal bond, and metal-ligand dissociation.

If heterolytic cleavage of the metal-metal bond in \((\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\) (2.1) was to occur it would produce fragments such as \(\text{Os(CO)}_4(\text{PMe}_3)\) (the saturated 18-electron fragment) and \([\text{W(CO)}_5]\) (the unsaturated 16-electron fragment.) The species \(\text{Os(CO)}_4(\text{PMe}_3)\) is a stable, previously characterized species.\(^{69}\) Although \([\text{W(CO)}_5]\) may not be directly observable at room temperature it could be trapped with a suitable ligand such as \(\text{PPh}_3\) to yield the known complex \(\text{W(CO)}_5(\text{PPh}_3)\).\(^{70}\)

If homolytic cleavage of the metal-metal bond in 2.1 took place then the observable products might be \([\text{Os(CO)}_4(\text{PMe}_3)]^+\) and \([\text{W(CO)}_5]^−\). Both fragments are radicals and as such would be expected to react with radical traps to yield isolable products. Although the chemistry of \([\text{Os(CO)}_4(\text{PMe}_3)]^+\) is unknown, in the presence of a chlorinated compound as a radical trap it might be expected to form \([\text{Os(CO)}_4(\text{PMe}_3)(\text{Cl})]^+\). The analogous pentacarbonyl complex, \([\text{Os(CO)}_5\text{Cl}]^+\), is known and stable at room temperature in solution.\(^{71}\) The reaction of \([\text{W(CO)}_5]^−\) with typical radical traps such as \(\text{CCl}_4\) or \(\text{C}_6\text{H}_5\text{CH}_2\text{Cl}\) would be expected to yield \([\text{W(CO)}_5(\text{Cl})]^−\), a known complex.\(^{72}\)

If dissociation of a ligand, for instance \(\text{CO}\), were the primary photoprocess then \([\text{OsW(CO)}_8(\text{PMe}_3)]\) might be an observable species. If not observable, then in the presence of a ligand (L), the complex \([\text{OsW(CO)}_8(\text{PMe}_3)(L)]\) might be expected to be isolable. The measurement of the quantum yield might also supply the required mechanistic information.
The UV-vis absorption spectrum of 2.1 exhibits a peak with a maximum at 368 nm ($\varepsilon = 2.79 \times 10^3 \pm 1.9 \times 10^2$ L mol$^{-1}$ cm$^{-1}$) in deoxygenated C$_6$H$_6$ at 298 K, while in deoxygenated CH$_2$Cl$_2$ the peak maximum is observed at 364 nm ($\varepsilon = 2.8 \times 10^3$ L mol$^{-1}$ cm$^{-1}$) at room temperature. By analogy to other binuclear complexes with unbridged, metal-metal bonds this band is assigned to a $\sigma \rightarrow \sigma^*$ transition associated with the metal-metal bond.$^{54,73}$ For example, the UV-vis absorption spectrum of (Cp)(OC)$_3$MoFe(CO)$_2$(Cp) in C$_6$H$_6$ at 298 K exhibits a transition at 398 nm ($\varepsilon = 1.23 \times 10^4$ L mol$^{-1}$ cm$^{-1}$) while (Cp)(OC)$_3$WFe(CO)$_2$(Cp) in C$_6$H$_6$ at 298 K, exhibits a transition at 388 nm ($\varepsilon = 1.21 \times 10^4$ L mol$^{-1}$ cm$^{-1}$) both assigned to the $\sigma \rightarrow \sigma^*$ absorption associated with the M-Fe (M = Mo, W) bond.$^{73}$ One might expect the absorption maximum for this transition to shift to an even higher energy on substituting a heavier Os atom for the Fe atom in the hypothetical molecule, (Cp)(OC)$_3$WOs(CO)$_2$(Cp) (which would follow the trend illustrated in the Mo-Fe and W-Fe complexes previously mentioned) and might be expected to have similar energy $\sigma \rightarrow \sigma^*$ transition associated with the metal-metal bond as the complex 2.1.$^{54,73}$ Likewise, the complexes [(H)FeM(CO)$_9$]$^-$ (M = Cr, Mo, W), with a putative donor-acceptor metal-metal bond, exhibit a strong absorption in the near-UV (315-330 nm, $\varepsilon = 10^4$ L mol$^{-1}$ cm$^{-1}$).$^{30}$ These energy maxima were also ascribed to a $\sigma \rightarrow \sigma^*$ transition of the M-M bond by analogy to [M$_2$(CO)$_{10}$]$^{2-}$ (M = Cr, W) systems.$^{30}$ Our assignment of the absorption at 368 nm in C$_6$H$_6$, in the UV-vis absorption spectrum of 2.1 to the $\sigma \rightarrow \sigma^*$ transition of the Os-W bond therefore has ample precedence.
2.2.1 Experiments to explore the possibility of heterolytic cleavage

The IR $\nu$(CO) absorption bands in C$_6$H$_6$ at room temperature of 2.1 and all the ensuing photoproducts are shown in Table 2.1. Photolysis ($\lambda \geq 400$ nm) of 2.1 (1.66 x $10^{-3}$ M) in the presence of PPh$_3$ (1.91 x $10^{-1}$ M) in deoxygenated benzene proceeded according to eq 2.5 (see Figure 2.1). Photolyses were carried out at $\lambda \geq 400$ nm so as to irradiate complex 2.1 in the low energy tail of the electronic absorption band at 368 nm in order to reduce the possibility of multiple excitation pathways (leading, for example, to CO loss as well as metal-metal bond cleavage).

\[
\text{(Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5 + \text{PPh}_3 \xrightarrow{\text{hv} (\lambda \geq 400 \text{ nm})} \text{Os(CO)}_4\text{(PMe}_3) + \text{Os(CO)}_3\text{(PMe}_3)\text{(PPh}_3) + \text{W(CO)}_5\text{(PPh}_3) + \text{W(CO)}_6
\]

46% 49% 81% 8%

The photoproducts were identified by comparison with the infrared spectra of the compounds prepared independently, or with spectra reported in the literature.\textsuperscript{69,70,74} The concentrations of the species observed in the IR spectra were determined from the molar absorptivities that were in turn determined from known concentrations of the compounds in IR cells of known path length, for further details see Section 2.4.2.
Table 2.1  IR v(CO) absorption data for (Me₃P)(OC)₄OsW(CO)₅ (2.1) and all photoproducts in C₆H₆ at room temperature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR absorptions v(CO) bands, cm⁻¹ (ε, L mol⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Me₃P)(OC)₄OsW(CO)₅</td>
<td>2092 (340), 2041 (1970), 2007 (6980), 1912 (7520), 1894 (2490)</td>
</tr>
<tr>
<td>Os(CO)₄(PMe₃)</td>
<td>2058 (2110), 1974 (1360), 1930 (5300)</td>
</tr>
<tr>
<td>Os(CO)₃(PMe₃)(PPh₃)</td>
<td>1881 (6870)</td>
</tr>
<tr>
<td>fac-Os(CO)₃(PMe₃)(Cl)₂</td>
<td>2125 (1390), 2050 (2660), 2004 (2390)</td>
</tr>
<tr>
<td>W(CO)₆</td>
<td>1976 (15500)</td>
</tr>
<tr>
<td>W(CO)₅(PPh₃)</td>
<td>2071 (1730), 1981 (423), 1937 (10500)</td>
</tr>
</tbody>
</table>
Figure 2.1 Infrared spectra of the photolysis ($\lambda \geq 400$ nm) of 2.1 in C$_6$H$_6$ in the presence of PPh$_3$. The timescale of the reaction was 0-28 min utilizing a 200W high pressure mercury arc lamp.

It was found that there is a nearly quantitative conversion of the starting material into the products shown in equation 2.5. A control experiment (see Figure 2.2) showed that Os(CO)$_4$(PMe$_3$) (1.15 x $10^{-2}$ M) (at 400 nm, $\varepsilon = 20$ L mol$^{-1}$ cm$^{-1}$ in C$_6$H$_6$) in the presence of PPh$_3$ (1.52 x $10^{-1}$ M) is photochemically converted to Os(CO)$_3$(PMe$_3$)(PPh$_3$) (3.40 x $10^{-3}$ M, 30% conversion) under similar reaction conditions. This suggests that the photoproduct, Os(CO)$_3$(PMe$_3$)(PPh$_3$) is predominantly formed in a secondary photochemical reaction, shown in eq 2.6.
Os(CO)$_4$(PMe$_3$) + PPh$_3$ $\xrightarrow{h\nu (\lambda \geq 400 \text{ nm}) \ N_2}$ Os(CO)$_3$(PMe$_3$)(PPh$_3$) + CO \hspace{1cm} (2.6)

**Figure 2.2** Infrared spectra of the photolysis ($\lambda \geq 400$ nm) of Os(CO)$_4$(PMe$_3$) in C$_6$H$_6$ in the presence of PPh$_3$. The timescale of the reaction was 0-104 min utilizing a 200W high pressure mercury arc lamp.

If the unsaturated, 16-electron fragment [W(CO)$_5$], is formed, it would be expected to react with PPh$_3$ rapidly to yield W(CO)$_5$(PPh$_3$).$^{75}$ (The mechanism for the formation of the minor product, W(CO)$_6$ (8%), will be discussed later.) An irradiation ($\lambda \geq 400$ nm) of W(CO)$_6$ (3.55 x 10$^{-3}$ M) with PPh$_3$ (6.34 x 10$^{-2}$ M) in deoxygenated C$_6$H$_6$ at room temperature showed no formation of W(CO)$_5$(PPh$_3$) after 32 min of photolysis [W(CO)$_6$, at 400 nm, $\varepsilon$ = 2 L mol$^{-1}$ cm$^{-1}$ in C$_6$H$_6$]. This strongly suggests that no photochemical reaction occurred at this wavelength for the complex. When the irradiative wavelength was altered
to $\lambda \geq 335$ nm, which corresponds to an $^1A_{1g} \rightarrow ^1T_{1g}$ transition in W(CO)$_6$ photochemical reactions were observed, see eqs 2.7 and 2.8 (products were identified by IR spectroscopy).

\[
\begin{align*}
W(CO)_6 + PPh_3 & \xrightleftharpoons[\text{N}_2]{h\nu (\lambda \geq 335 \text{ nm})} W(CO)_5(PPh_3) + CO \quad (2.7) \\
W(CO)_5(PPh_3) & \xrightleftharpoons[\text{N}_2]{h\nu (\lambda \geq 335 \text{ nm})} W(CO)_4(PPh_3)_2 + CO \quad (2.8)
\end{align*}
\]

Therefore in the irradiation ($\lambda \geq 400$ nm) of 2.1, contributions to the products from secondary photochemical reactions of W(CO)$_6$ can be considered negligible.

The results from this photochemical reaction are most readily interpreted in terms of a heterolytic primary photoprocess to yield Os(CO)$_4$(PMe$_3$) and [W(CO)$_5$] as the photoproducts.

Prior qualitative studies had demonstrated that 2.1 reacts slowly with PPh$_3$ in deoxygenated CH$_2$Cl$_2$ at room temperature to yield Os(CO)$_4$(PMe$_3$) and W(CO)$_5$(PPh$_3$), the products consistent with heterolytic cleavage of the metal-metal bond. These experiments were, however, carried out under ambient laboratory light and therefore possible photolysis combined with thermolysis cannot be entirely discounted. This reaction was therefore repeated under careful thermolysis conditions with measures taken to eliminate the possibility of photolysis. The thermal reaction of 2.1 ($1.1 \times 10^{-3}$ M) with PPh$_3$ ($6.0 \times 10^{-2}$ M) was carried out in deoxygenated C$_6$H$_6$, under N$_2$, in the dark at both room temperature and 313 K. No products were observed in the IR spectra of the control reaction at room temperature until 27 h 30 min and the starting material, 2.1, was still clearly visible in the IR spectrum after 9 days. At 313 K traces of Os(CO)$_4$(PMe$_3$) and W(CO)$_5$(PPh$_3$) were
detected by IR spectroscopy after 3 h and the IR absorptions of the starting material, 2.1, were undetectable after 66 h (see Figure 2.3). Even the longest photochemical experiments with 2.1 described in this chapter were complete within 2 h and thus the contribution of the thermal reaction pathway to the products can be considered negligible. Note that the thermal experiments yield results that also consistent with our definition of a dative metal-metal bond and therefore add additional support to the proposal that the metal-metal bond in complex 2.1 is a dative interaction.

![Figure 2.3](image)

Figure 2.3 The thermal control reaction of 2.1, in C₆H₆, in the presence of an excess of PPh₃, at 313 K followed by IR spectroscopy. The timescale of the reaction was 0-66 h.
The photolysis of 2.1 (9.08 x 10^{-4} M) alone in deoxygenated benzene proceeded in accordance to eq 2.9 (as shown in Figure 2.4). In no instance was any W(CO)_{5}(\eta^2-C_6H_6) observed in the IR spectra.\textsuperscript{78}

\begin{align*}
(\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5 & \xrightarrow{\text{hv} \ (\lambda \geq 400 \text{ nm})} \quad \text{Os(OC)}_4(\text{PMe}_3) \quad + \quad \text{W(CO)}_6 \\
2.1 & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
\end{align*}

(2.9)

\textbf{Figure 2.4} Infrared spectra of the irradiation (\(\lambda \geq 400 \text{ nm}\)) of 2.1 in C_6H_6 at room temperature. Timescale of the photolysis was 0-720 s utilizing a 200W high pressure mercury arc lamp.

The acceptor transition metal moiety generated upon the photolysis of 2.1 is presumably identical to the electron deficient fragment generated in the decomposition of the complex, [MeFeW(CO)_{9}]\textsuperscript{30b}. In this latter system, the formation of W(CO)_{6} is believed
to result from the decomposition of the [W(CO)₅] fragment, similar chemistry for complex 2.1 would result in a maximum yield of 83% of W(CO)₆, as shown in eq 2.10. This yield of W(CO)₆ is not allowing for the Lewis acid, [W(CO)₅] to abstract a CO ligand from other complexes or from a CO resulting from secondary photochemistry of the osmium species (see Figure 2.2).⁷⁹

\[
6 \text{W(CO)}_5 \rightarrow 5 \text{W(CO)}_6 + [\text{W}] \quad (2.10)
\]

The complex 2.1 has been shown to decompose in CH₂Cl₂ at room temperature to Os₃(CO)₉(PMe₃)₃ and W(CO)₆ when exposed to air and under ambient light.⁵⁰,⁷⁴ It was observed that this reaction pathway was slowed considerably upon the removal of traces of oxygen from the solution. In our experiments deoxygenated C₆H₆ was used in all cases and at no time was the cluster complex, Os₃(CO)₉(PMe₃)₃ detected by IR spectroscopy.

2.2.2 Experiments to explore the possibility of homolytic cleavage

2.2.2.1 Experiments with the radical trap C₆H₅CH₂Cl

The products in eqs 2.5 and 2.9 could conceivably be the result of a homolytic cleavage of the metal-metal bond followed by a fast electron transfer. To probe this possibility, a solution of 2.1 (1.47 x 10⁻³ M) in deoxygenated C₆H₆ was irradiated (λ ≥ 400 nm) in the presence of an excess of the good radical trap C₆H₅CH₂Cl (1.47 x 10⁻² M).⁸⁰ The photoproducts were identical to those in eq 2.9 except there were lower yields of W(CO)₆ (57%) and Os(CO)₄(PMe₃) (43%); no other photoproducts were observed. Furthermore, no bibenzyl was detected (an expected sideproduct if radicals are indeed
trapped by the benzyl halide radical trap). Thus the experiment did not result in any product that could be attributed to the trapping of a radical species.

### 2.2.2.2 Experiments with the radical trap CCl₄

Other radical traps were also utilized. Complex 2.1 (2.18 x 10⁻³ M) was irradiated (λ ≥ 400 nm) in the presence of an excess of CCl₄ (5.68 x 10⁻² M) in deoxygenated C₆H₆. On this occasion different photoproducts were observed: W(CO)₆ (56%) and fac-Os(CO)₃(PMe₃)(Cl)₂ (fac-2.2) (72%) (see Chapter 3 for the characterization of this compound) as shown in Figure 2.5.

The photochemical control reaction of the irradiation (λ ≥ 400 nm) of Os(CO)₄(PMe₃) (5.64 x 10⁻³ M) in the presence of an excess of CCl₄ (5.53 x 10⁻² M) in deoxygenated C₆H₆ was carried out. The IR spectra showed complete conversion of Os(CO)₄(PMe₃) to a sole photoprodut with the IR ν(CO) bands of: 2119(m), 2055(m), 2010(m) (m = medium intensity) after 32 min of irradiation. The bands did not alter at all after a further 2 h 40 min in the dark, at room temperature. This was clearly a different compound from fac-2.2 observed in the irradiation of 2.1 in the presence of CCl₄ (see Figure 2.5). The new species was tentatively assigned as ‘Os(CO)₃(PMe₃)(Cl)(CCl₃)’ (fac-2.3) (see Chapter 3 for the chemistry and further control reactions concerning this species).
Figure 2.5 Infrared spectra of the photolysis ($\lambda \geq 400$ nm) of 2.1 in C$_6$H$_6$ in the presence of CCl$_4$. Timescale of photolysis was 0-13 min with a 200W high pressure mercury arc lamp.

Thermal control reactions were carried out in which 2.1 (1.47 x $10^{-3}$ M) was stirred in the dark with CCl$_4$ (1.45 x $10^{-1}$ M) in deoxygenated C$_6$H$_6$ under N$_2$. No change in 2.1 was detected until 3 h 30 min when trace amounts of fac-2.2 and W(CO)$_6$ were detected in the solution. Even after 58 h at room temperature in the dark the reaction was far from complete: IR $v$(CO) bands due to 2.1 were clearly visible. Likewise, Os(CO)$_4$(PMe$_3$) (1.79 x $10^{-3}$ M) was stirred in the dark with CCl$_4$ (1.45 x $10^{-1}$ M) in deoxygenated C$_6$H$_6$ under N$_2$. The complex fac-2.3 was observed in an IR spectrum of the solution immediately after mixing; there were no signs of Os(CO)$_4$(PMe$_3$) after 58 h. Interestingly, in the IR spectrum of Os(CO)$_4$(PMe$_3$) after 58 h indicated that the initial product, fac-2.3 had converted over this time period to fac-2.2 (for further work that investigates this conversion see Chapter 3).
This was indicated by the small changes in the positions of the IR v(CO) bands on going from the starting complex into the other species, see Figure 2.6. Because the CO stretches of \( \text{fac-2.3} \) and \( \text{fac-2.2} \) occur at similar frequencies in the IR spectra this effect was not apparent after 10 h.

![Figure 2.6](image)

**Figure 2.6** The thermal control of \( \text{Os(CO)}_4(\text{PMe}_3) \) in \( \text{C}_6\text{H}_6 \) at room temperature in the dark in the presence of \( \text{CCl}_4 \). The initial species \( \text{Os(CO)}_4(\text{PMe}_3) \); ↓; the species tentatively identified as ‘\( \text{Os(CO)}_3(\text{PMe}_3)(\text{CCl}_3)(\text{Cl}) \)’ \( \text{fac-2.3} \): ↑; the final species \( \text{fac-Os(CO)}_3(\text{PMe}_3)(\text{Cl})_2 \) \( \text{fac-2.2} \): ↑. The Timescale of the reaction was 0-58 h.

This result prompted the additional experiment of photolysing \( (\lambda \geq 335 \text{ nm}) \) \( \text{W(CO)}_6 \) \( (1.99 \times 10^{-3} \text{ M}) \) and \( \text{Os(CO)}_4(\text{PMe}_3) \) \( (2.02 \times 10^{-3} \text{ M}) \) in deoxygenated \( \text{C}_6\text{H}_6 \) with \( \text{CCl}_4 \) \( (2.36 \times 10^{-1} \text{ M}) \) (this wavelength was chosen to generate [\( \text{W(CO)}_5 \)] in situ, as in eq 2.7).
The experiment was designed to see if the [W(CO)₅] fragment promotes the different reaction pathways observed for the photochemical reaction of 2.1 with CCl₄ as compared to Os(CO)₄(PMe₃) with CCl₄. The IR ν(CO) absorption bands due to Os(CO)₄(PMe₃) were undetectable after 2 min. The initial, observed photoproduct was tentatively assigned to \textit{fac}-2.3 that then converted to \textit{fac}-2.2 within 56 min. Substantial amounts of W(CO)₆ were still remaining after this time, see Figure 2.7.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.7.png}
\caption{The photochemical control reaction of Os(CO)₄(PMe₃) and W(CO)₆ in C₆H₆ in the presence of CCl₄, irradiation at \( \lambda \geq 335 \) nm. Timescale of the reaction was 0-56 min utilizing a 200W high pressure mercury arc lamp.}
\end{figure}

In the photolysis of 2.1 (\( \lambda \geq 400 \) nm) in the presence of an excess of CCl₄ no products that could be considered the result of radical fragments containing tungsten were trapped. Indeed, the only photoproduct containing tungsten detected by IR spectroscopy...
was W(CO)\textsubscript{6}. No other species, which might have been expected, such as [W(CO)\textsubscript{5}Cl\textsuperscript{-}] (see Table 2.2), [W(CO)\textsubscript{4}(Cl)\textsubscript{2}]\textsuperscript{81} or [W(CO)\textsubscript{5}Cl]\textsuperscript{82} were detected, although this does not completely rule out the presence of any such species. The sole photoprodoot containing osmium detected by IR spectroscopy was \textit{fac-2.2}. Thermal reactions of 2.1 with CCl\textsubscript{4} in deoxygenated C\textsubscript{6}H\textsubscript{6}, in the absence of light, at room temperature demonstrated that the same products are produced as in the photochemical reaction only the thermal pathway is much slower. Hence the products observed when 2.1 is photolysed in the presence of CCl\textsubscript{4} are due to a photochemical process alone and not a thermochemical pathway.

As mentioned previously, the photochemical reaction of 2.1 in the presence of an excess of C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}Cl gave Os(CO)\textsubscript{4}(PMe\textsubscript{3}) and W(CO)\textsubscript{6}, which are different products to those produced from the photolysis of 2.1 with CCl\textsubscript{4} under similar conditions. That the radical trapping reagents CCl\textsubscript{4} and C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}Cl gave different products may be related to their first half-wave reduction potentials (E\textsubscript{1/2}) in DMF versus a dropping mercury electrode. For CCl\textsubscript{4} (1 \times 10\textsuperscript{-3} M, 1.75 \times 10\textsuperscript{-1} M [Bu\textsubscript{4}N][Br] as supporting electrolyte) E\textsubscript{1/2} = -0.25 V,\textsuperscript{83} and for C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}Cl (2 \times 10\textsuperscript{-1} M [Bu\textsubscript{4}N][ClO\textsubscript{4}] as supporting electrolyte) E\textsubscript{1/2} = -2.20 V.\textsuperscript{84} Half-wave reduction potentials can be related to the electron affinities of the species,\textsuperscript{85} and therefore CCl\textsubscript{4} clearly has a greater electron affinity than C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}Cl.

Before discussing the present results the photolysis of W(CO)\textsubscript{6} in the presence of an excess of CCl\textsubscript{4} in a hydrocarbon solvent is discussed. This reaction has stimulated considerable interest on the identity of the species formed, and which species is the active catalyst in olefin metathesis.\textsuperscript{81,82,86} One of the postulated intermediates is [W(CO)\textsubscript{5}Cl]\textsuperscript{+} which is believed to be formed in conjunction with COCl\textsubscript{2} and ['CCl\textsubscript{3}]. The proposed mechanism, to yield the aforementioned products, proceeds via a donor-acceptor interaction
and then to a charge transfer complex, if the donor entity was $\text{W(CO)_6}$ the mechanism might be as shown in eq 2.11.

$$\text{W(CO)_6} + \text{A} \rightleftharpoons [\text{W(CO)_6} \cdots \text{A}] \xrightarrow{hv} [\text{W(CO)_6}^\cdots \text{A}^\cdots]$$

The position of the equilibrium was suggested to be strongly influenced by the strength of the donor (D) and the strength of the acceptor (A): the better either component is the more the right-hand side of the equilibrium is favored. It was demonstrated that as the acceptor entity was varied, while the donor entity remained constant, the electron transfer reaction only proceeded when the electron affinity for the acceptor (A) was sufficiently large. For example, $\text{CCl}_4$ (electron affinity 2.12 eV) reacted via electron transfer whilst $\text{CH}_2\text{Cl}_2$ (electron affinity 1.32 eV) did not. It is therefore proposed the difference in the reaction of $\text{CCl}_4$ and $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ with 2.1 could be ascribed to the different electron affinities of the two radical trapping species. Furthermore, it has been shown that COCl$_2$ can be produced from the photolysis of W(CO)$_6$ in the presence of CCl$_4$ while the probability of phosgene arising from the monochlorocarbon, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, would appear to be much lower. There is no precedent of the latter reaction at present. This would suggest if COCl$_2$ is indeed the species influencing the reaction pathway then CCl$_4$ would be able promote this route while $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ would not favor such an interaction.

There are several species that could act as the donor component (D, eq 2.11) in the photolysis of the donor-acceptor adduct namely, $\text{C}_6\text{H}_6$, $\text{W(CO)_6}$, [$\text{W(CO)_5}$], $\text{Os(CO)_4(PMe}_3)$, [$\text{Os(CO)_3(PMe}_3)$]. As described above, there is a difference in the initial products from the photolysis of 2.1 in $\text{C}_6\text{H}_6$ in the presence of CCl$_4$ as compared to the products formed in the corresponding photolysis of $\text{Os(CO)_4(PMe}_3)$. The clear difference
in the reactions is in the reaction of 2.1 in the presence of CCl₄ a tungsten fragment is also present, this is definitely lacking in the photolysis of Os(CO)₄(PMe₃) in the presence of CCl₄. The control reaction of the photolysis (λ ≥ 335 nm) of Os(CO)₄(PMe₃) together with W(CO)₆ in C₆H₆ in the presence of an excess of CCl₄ clearly suggests that W(CO)₆ or a photoexcited tungsten species produced in situ, plays a key role in the relatively rapid formation of fac-2.2. Recall that fac-2.2 was not produced in the photolysis (λ ≥ 400 nm) of Os(CO)₄(PMe₃) in C₆H₆ in the presence of CCl₄ and in the thermal reaction of Os(CO)₄(PMe₃) in C₆H₆ in the presence of CCl₄ fac-2.2 was not observed after 10 h at room temperature, in the dark.

In the previous studies on the photolysis of W(CO)₆ in the presence of CCl₄ it was proposed that [W(CO)₅Cl]⁺ is formed but was unspecific as to exactly how [W(CO)₅Cl]⁺ and COCl₂ arose. The possibility that either one or both of these molecules are present in the photolysis of 2.1 in the presence of CCl₄ cannot be ruled out. It has been demonstrated that Os(CO)₄(PMe₃) can act as a nucleophile/Lewis base and might be expected to react with COCl₂ (a well-known acylating agent) to give 2.2. The chemistry of the unstable 17-electron species [W(CO)₅Cl]⁺ is also unknown; it might also be able to chlorinate Os(CO)₄(PMe₃). Alternatively, [CCl₃]⁺ or [Cl]⁻, formed from [CCl₄]⁻, could also conceivably chlorinate Os(CO)₄(PMe₃).

The photochemical and thermal reactions of Os(CO)₄(PMe₃) in C₆H₆, in the presence of CCl₄ gave a different, as yet only tentatively identified, initial product fac-2.3 to that produced in the analogous reactions of 2.1. It had previously been shown that the photolysis of Os(CO)₄(PMe₃) in deoxygenated C₆H₆, in the presence of an excess of PPh₃ gave Os(CO)₃(PMe₃)(PPh₃) (see Figure 2.2). The most probable pathway for this reaction
is the initial loss of CO to generate the unsaturated fragment \([\text{Os}(\text{CO})_3(\text{PMe}_3)]\), followed by coordination of \(\text{PPh}_3\) (see eq 2.6), a reaction previously demonstrated for \(\text{Fe}(\text{CO})_4(\text{PMe}_3)\).\(^{88}\) It appears reasonable that \([\text{Os}(\text{CO})_3(\text{PMe}_3)]\) is also formed when \(\text{Os}(\text{CO})_4(\text{PMe}_3)\) is irradiated in the presence of \(\text{CCl}_4\). Previous work has shown that the irradiation (\(\lambda > 350\) nm) of \(\text{Fe}(\text{CO})_5\) in the presence of \(\text{CCl}_4\) yields the intermediate \([\text{Fe}(\text{CO})_4(\text{CCl}_3)(\text{Cl})]\), that is, oxidative-addition of \(\text{CCl}_4\) occurs.\(^{89}\) Thus the alternate oxidative-addition reaction pathway was proposed. (It was also found that monohalocarbons displayed different reactivity towards \(\text{Fe}(\text{CO})_5\) on photolysis, as opposed to \(\text{CCl}_4\) under analogous reaction conditions.)

It therefore seems reasonable that the initial product produced in the photolysis of \(\text{Os}(\text{CO})_4(\text{PMe}_3)\) in the presence of \(\text{CCl}_4\) is \(\text{fac-2.3}\) which subsequently decomposes to \(\text{fac-2.2}\). It is known that complexes with the \(\text{M-CCl}_3\) component are unstable and readily decompose to the corresponding \(\text{M-Cl}\) derivative.\(^{90}\) That different products are observed on the irradiation of \(2.1\) with \(\text{CCl}_4\) or \(\text{Os}(\text{CO})_4(\text{PMe}_3)\) with \(\text{CCl}_4\) under similar conditions indicates that the photoexcited osmium fragments in both reactions are most probably not identical. This supports the view that it is the \([\text{W}(\text{CO})_5]\) unit that alters the reactivity of \(\text{Os}(\text{CO})_4(\text{PMe}_3)\). This may be through either an interaction of \(\text{CCl}_4\) with a tungsten species or one of the several reactive tungsten containing fragments, including a carbonyl bridged bimetallic species, \((\text{vide infra})\).

2.2.2.3 Experiments with the radical trap 1,1,3,3-tetramethylisooindoline-2-oxyl.

A further radical trap utilized was 1,1,3,3-tetramethylisooindoline-2-oxyl, TMIO.\(^{91}\) This stable nitroxide radical trap, TMIO is a superior radical trap to \(\text{CCl}_4\) and \(\text{C}_6\text{H}_5\text{CH}_2\text{Cl}\).
Upon interaction with a photogenerated radical TMIO does not generate further radicals that could then undergo additional chemistry. Furthermore, with the radical species [(MeCp)Mo(CO)3]⁺, in C₆H₆ at 296 K, TMIO reacts 77 times faster than does CCl₄.¹² Photolysis (λ ≥ 400 nm) of 2.1 (1.53 x 10⁻³ M) in deoxygenated C₆H₆ at room temperature in the presence of an excess of TMIO (6.86 x 10⁻³ M) proceeded in accordance with eq 2.9. The only photoproducts observed were W(CO)₆ (22%), and Os(CO)₄(PMe₃) (75%) which are the same as the products produced in the photolysis of 2.1 in the absence of any other reagent and similar to that produced in the irradiation of 2.1 with C₆H₅CH₂Cl. Because benzene has an intense absorption in the IR spectrum close to the single ν(CO) absorption of W(CO)₆, sometimes there is a difficulty measuring the absorbance of the latter signal in this solvent. This in turn makes it difficult to measure the concentration of W(CO)₆ produced. It is therefore expected that the concentrations of W(CO)₆ produced in the various photolysis reactions are subject to a larger error and that the different concentrations should not be taken as indicating a major change in the reaction pathway.

For the photolysis (λ ≥ 400 nm) of 2.1 in C₆H₆ in the presence of an excess of the radical traps C₆H₅CH₂Cl and TMIO the results are not consistent with radicals being produced. Although these negative results do not completely rule out the possibility of homolytic cleavage of the metal-metal bond, the results do not support such a mechanism.

2.2.3 Experiments to probe whether radical traps would interact with [W(CO)₅]⁻

As a control reaction to probe whether the radical traps would trap the species, [W(CO)₅]⁻, if it was formed, [Bu⁺₄N]₂[W₂(CO)₁₀] ([Bu⁺₄N]₂[2.4]) (for details of the synthesis of this compound see Chapter 3; for IR ν(CO) data see Table 2.2) was irradiated
(λ ≥ 420 nm) in CH3CN in the presence of radical traps. Acetonitrile was used as a solvent in preference to C6H6 since [Bu4N]2[2.4] is only sparingly soluble in C6H6 and does not give a satisfactory IR spectrum. It had previously been proposed that [Bu4N]2[2.4] cleaves to yield [W(CO)5]− radicals upon photolysis or electrochemical oxidation.93,94 Irradiation (λ ≥ 420 nm) of [Bu4N]2[2.4] (0.011 M) in deoxygenated CH3CN in the presence of an excess of C6H5CH2Cl (0.89 M) for 1.5 min yields [W(CO)5Cl]− as the only metal carbonyl containing product, as identified by IR spectroscopy (see Table 2.2 and Figure 2.8). Upon further photolysis other IR ν(CO) absorption peaks emerged which were assigned to W(CO)5(CH3CN); these were slowly followed by the appearance of still further weak, IR ν(CO) bands, which were identified as due to W(CO)4(CH3CN)2 (see Table 2.2). The photolysis was halted after 72 min of irradiation. The yellow compound, [Et4N][W(CO)5Cl], is known to have a lower energy electronic absorption band maximum at 417 nm (ε = 3.10 x 103 L mol⁻¹ cm⁻¹) in methanol.95 Thus, the complex [Bu4N][W(CO)5Cl] is not expected to display vastly different absorption characteristics in CH3CN due to the slight modification of the cation or the solvent. Irradiation at λ ≥ 420 nm, in the aforementioned reaction, would therefore photoexcite the complex [W(CO)5Cl]−. Irradiation (λ ≥ 436 nm) of [W(CO)5Br]− at 280 K, in CO saturated CHCl3 is known to yield W(CO)6.96 The analogous reaction where CH3CN is the entering ligand into [W(CO)5] would, therefore, appear plausible, particularly since the concentration of CH3CN is greater than that of CO. The complex, W(CO)5(CH3CN) could then undergo further photochemical substitution to yield W(CO)4(CH3CN)2. It is known that upon photolysis of W(CO)6, at higher energy wavelengths, a mixture of W(CO)5(CH3CN) and W(CO)4(CH3CN)2 is formed quickly.97 The proposed mechanism for the photolysis
(λ ≥ 420 nm) of [Bu₄N][2.4] [UV-vis absorption band maxima at 347 nm (ε = 7.21 x 10³ L mol⁻¹ cm⁻¹) and 390 nm (shoulder, ε = 4.84 x 10³ L mol⁻¹ cm⁻¹) in CH₃CN]⁹³ in
deoxygenated CH₃CN in the presence of C₆H₅CH₂Cl is thus initial trapping of the
photogenerated [W(CO)₅]⁻ to form [W(CO)₅Cl]⁻. This is followed by the secondary
photochemistry of [W(CO)₅Cl]⁻ to yield W(CO)₅(CH₃CN) and with prolonged irradiation
further substitution takes place to yield a small amount of W(CO)₄(CH₃CN)₂.
Table 2.2 The IR ν(CO) absorption data for [Bu⁺₄N]₂[W₂(CO)₁₀] ([Bu⁺₄N]₂[2.4]) and most of the products observed in CH₃CN at room temperature upon interaction with the radical traps C₆H₅CH₂Cl, CCl₄ and TMIO.

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR absorptions ν(CO) bands, cm⁻¹</th>
<th>IR media</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bu⁺₄N]₂[W₂(CO)₁₀]</td>
<td>1940(m), 1891(vs), 1788(s)ᵃ</td>
<td>CH₃CN</td>
<td>this work, 93</td>
</tr>
<tr>
<td>W(CO)₆</td>
<td>1975(s)</td>
<td>CH₃CN</td>
<td>this work, 93</td>
</tr>
<tr>
<td>[Et₄N][W(CO)₅Cl]</td>
<td>2061(w), 1904(s), 1869(m)</td>
<td>KBr</td>
<td>72</td>
</tr>
<tr>
<td>[Bu⁺₄N][W(CO)₅Cl]</td>
<td>2064(w), 1919(s), 1846(m)</td>
<td>CH₃CN</td>
<td>this work</td>
</tr>
<tr>
<td>[Et₄N][W(CO)₅Br]</td>
<td>2064(w), 1904(s), 1868(m)</td>
<td>KBr</td>
<td>72</td>
</tr>
<tr>
<td>W(CO)₅(CH₃CN)</td>
<td>2085(w), 1948(vs), 1931(s)</td>
<td>C₆H₁₄</td>
<td>97a</td>
</tr>
<tr>
<td></td>
<td>2075, 1940</td>
<td>CH₃CN</td>
<td>97a</td>
</tr>
<tr>
<td></td>
<td>2078(w), 1939(s)</td>
<td>CH₃CN</td>
<td>this work</td>
</tr>
<tr>
<td>cis-W(CO)₄(CH₃CN)₂</td>
<td>2024(m), 1900(vs), 1842(s)</td>
<td>CH₃CN</td>
<td>97a</td>
</tr>
<tr>
<td>trans-W(CO)₄(CH₃CN)₂</td>
<td>1898(s)</td>
<td>CH₃CN</td>
<td>93</td>
</tr>
<tr>
<td>W(CO)₄(CH₃CN)₂</td>
<td>2020(vw), 1898(m), 1840(w)</td>
<td>CH₃CN</td>
<td>this work</td>
</tr>
</tbody>
</table>

ᵃ Relative intensities of the IR absorption bands in this study and throughout the text; vw = very weak, w = weak, m = medium, s = strong, vs = very strong.
Figure 2.8 The irradiation ($\lambda \geq 420$ nm) of $[\text{Bu}^\theta \text{N}]_2[W_2(CO)_{10}]$ ($[\text{Bu}^\theta \text{N}]_2[2.4]$) in CH$_3$CN in the presence of an excess of C$_6$H$_5$CH$_2$Cl. ↓ $[\text{Bu}^\theta \text{N}]_2[2.4]$, † initial photoproduc, ↑ secondary photochemistry beginning. Timescale of the photolysis was 0-4 min utilizing a 100W high pressure mercury arc lamp.
The photochemical reaction of \([\text{Bu}^n\text{N}]_2[2.4]\) was next attempted in \(\text{CH}_3\text{CN}\) in the presence of \(\text{CCl}_4\). To a solution of \([\text{Bu}^n\text{N}]_2[2.4]\) (9.8 \(\times\) 10\(^{-3}\) M) in deoxygenated \(\text{CH}_3\text{CN}\), at room temperature, an excess of \(\text{CCl}_4\) (9.4 \(\times\) 10\(^{-1}\) M) was added with the exclusion of light. With zero time of irradiation or exposure to any light, except red light, an IR spectrum of the solution clearly showed absorption bands due to \(\text{W}(\text{CO})_6\), \([\text{W}(\text{CO})_5\text{Cl}]^-\) and a small shoulder due to \(\text{W}(\text{CO})_5(\text{CH}_3\text{CN})\) (IR \(\nu(\text{CO})\) absorption bands as designated in Table 2.2). An almost instantaneous thermal reaction, therefore, seems to occur. The reaction of the dimeric complex with the radical trap, \(\text{CCl}_4\), once again differs from the interaction of the complex with the radical trap, \(\text{C}_6\text{H}_5\text{CH}_2\text{Cl}\).

It has been reported that the electrochemical oxidation of \([\text{Bu}^n\text{N}]_2[2.4]\) in \(\text{THF}\), in the presence of an excess of \(\text{CH}_2\text{Cl}_2\) with a supporting electrolyte of tetrabutylammonium perchlorate, \(\text{TBAP}\), \([\text{Bu}^n\text{N}][\text{ClO}_4]\), and an \(\text{Ag}/\text{AgNO}_3\) reference electrode, gave \(\text{W}(\text{CO})_5(\text{THF})\) and \([\text{W}(\text{CO})_5\text{Cl}]^-\) as the products.\(^{94}\) The electron affinity of \(\text{CCl}_4\) (2.12 eV, first \(E_{1/2} = -0.25\) V in DMF with \([\text{Bu}^n\text{N}][\text{Br}]\) as supporting electrolyte) is much greater than \(\text{CH}_2\text{Cl}_2\) (1.32 eV, first \(E_{1/2} = -2.14\) V in DMF with \([\text{Bu}^n\text{N}][\text{Br}]\) as supporting electrolyte).\(^{83,85}\) Thus if there was an electron transfer reaction and the process involved an oxidation/reduction couple, \(\text{CCl}_4\) would be expected to promote the process more than \(\text{CH}_2\text{Cl}_2\). Furthermore, the reaction of \([\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{Cl}]\) in chlorobenzene in the presence of an excess of \(\text{ZrCl}_4\) and \(\text{pent-2-ene}\) in \(n\)-heptane, in the dark has been suggested to proceed via a charge-transfer type complex.\(^{88}\) It was further suggested that the reaction was optimized with a good donor, a good acceptor and a polar solvent.\(^{88}\) One possible explanation for the products observed would be that \([\text{Bu}^n\text{N}]_2[2.4]\) forms a charge-transfer complex with \(\text{CCl}_4\) in the polar solvent \(\text{CH}_3\text{CN}\), in the dark which yields \([\text{W}(\text{CO})_5\text{Cl}]^-\) and
W(CO)$_5$(CH$_3$CN) analogous to the electrochemical reaction of [Bu$^+$$_4$N]$_2$[2.4] and CH$_2$Cl$_2$ mentioned above. It had previously been found that after the photolysis of W(CO)$_6$ in CH$_3$CN, that, if the reaction mixture was allowed to remain in the dark at room temperature, substantial quantities of W(CO)$_6$ were reformed$^{97a}$. This implies that an equilibrium exists between the species, W(CO)$_6$/W(CO)$_5$(CH$_3$CN) (as shown in eq 2.12) and this may explain the presence of W(CO)$_6$ in the reaction of [Bu$^+$$_4$N]$_2$[2.4] in CH$_3$CN in the presence of CCl$_4$.

$$W(CO)_6 + CH_3CN \rightleftharpoons W(CO)_5(CH_3CN) + CO \quad (2.12)$$

Finally, [Bu$^+$$_4$N]$_2$[2.4] (1.2 x 10$^{-2}$ M) was irradiated ($\lambda \geq 420$ nm) in deoxygenated CH$_3$CN in the presence of TMIO (6.8 x 10$^{-2}$ M). After 5 min of photolysis the IR v(CO) absorption bands due to [Bu$^+$$_4$N]$_2$[2.4] were no longer detectable in the IR spectrum, at which point the peaks due to a small amount of W(CO)$_6$ and three new IR v(CO) absorption bands at, 1915 (m), 1834 (m, v.br), 1790 (w, br) were observed. Upon irradiation for a further 47 min the three new IR v(CO) absorption bands were reduced in intensity while the IR v(CO) absorption band for W(CO)$_6$ increased in intensity and bands due to W(CO)$_5$(CH$_3$CN) were seen to grow in, (as well as weak bands attributed to W(CO)$_4$(CH$_3$CN)$_2$). It had been previously demonstrated that TMIO can act as a monodentate ligand as in (Cp)Fe(CO)$_2$(TMIO), (IR v(CO): 2012, 1916 cm$^{-1}$ in THF) or as a bidentate ligand as in (MeCp)Mo(CO)$_2$(TMIO), (IR v(CO): 1944, 1834 cm$^{-1}$ in toluene)$^{92}$. These three new CO stretching absorptions are therefore tentatively attributed to the complex [W(CO)$_4$(η$^1$-TMIO)]$^-$, as shown in Figure 2.9a, by analogy to [PPN][W(CO)$_4$(PPh$_3$)(SCH$_3$)] (IR v(CO): 2003, 1881-1876, 1801 cm$^{-1}$ in THF)$^{98}$ and
\[\text{[Et}_4\text{N}\{\text{W(CO)}_4[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{S}]\}\] (IR v(CO): 1982, 1845, 1792 cm\(^{-1}\) in CH\(_2\)Cl\(_2\)).\(^9\) A species such as, \[\text{[W(CO)}_5(\eta-\text{TMIO})]^{-}\] (shown in Figure 2.9b) was ruled out since it would be expected to give CO stretches in the IR spectrum similar to \[\text{[PPN][W(CO)}_5\text{OC(O)C(CH}_3)_3\}] (IR v(CO): 2058(w), 1906(s), 1841(m) cm\(^{-1}\) in THF).\(^10\)

![Chemical structures](image)

**Figure 2.9** The two most probable complexes produced by the reaction of [W(CO)]\(^{\text{III}}\) and the radical trap TMIO. (a) \[\text{[W(CO)}_4(\eta^2-\text{TMIO})]^{-}\] (b) \[\text{[W(CO)}_5(\eta-\text{TMIO})]^{-}\].

The tungsten complex tentatively identified as \[\text{[W(CO)}_4(\eta^2-\text{TMIO})]^{-}\] might be expected to react, in a similar manner to \[\text{[W(CO)}_5\text{Br}]^{-}\], upon further irradiation in CH\(_3\)CN to give \[\text{W(CO)}_5(\text{CH}_3\text{CN})\] and \[\text{W(CO)}_4(\text{CH}_3\text{CN})_2\]. These results are therefore, consistent with the view that TMIO acts as a radical trap for the photogenerated radical, \[\text{[W(CO)}_5]^{-}\].
2.2.4 Experiments to explore the possibility of metal-ligand dissociation

Photolysis ($\lambda \geq 400$ nm) of 2.1 (2.96 x 10$^{-3}$ M) in a CO saturated C$_6$H$_6$ solution (7.4 x 10$^{-3}$ M)$^{101}$ at room temperature yielded Os(CO)$_4$(PMe$_3$) (81%) and W(CO)$_6$ (74%) in an analogous manner to eq 2.9 (see Figure 2.10).

Figure 2.10 Irradiation ($\lambda \geq 400$ nm) of 2.1 (2.96 x 10$^{-3}$ M) at room temperature in a C$_6$H$_6$ solution saturated with CO (7.4 x 10$^{-3}$ M). Timescale of the reaction was 0-900 s utilizing a 200W high pressure mercury arc lamp.

When 2.1 was irradiated ($\lambda \geq 400$ nm) in the absence of any ligand only 66% of W(CO)$_6$ was recovered (eq 2.9). In the presence of CO this was increased to 74% and is similar to the irradiation of 2.1 in the presence of PPh$_3$ where 89% of tungsten containing products were recovered (eq 2.5). The concentration of 2.1 is far greater in the present reaction, with CO, than it was in the reaction without CO (eq. 2.9), and yet the progress
of the former reaction appeared as fast or faster than the latter reaction (compare Figure 2.4 with that of Figure 2.10).

Quantum yield measurements were carried out on the irradiation ($\lambda = 368$ nm) of 2.1 (average value $2.90 \times 10^{-4}$ M) in C$_6$H$_6$ under various conditions in order to probe the mechanism. The quantum yields were measured at 368 nm in order to obtain the maximum absorption possible for the species 2.1 while seeking to avoid problems with absorptions due to products (for W(CO)$_6$ at 368 nm, $\varepsilon = 220$ L mol$^{-1}$ cm$^{-1}$, for Os(CO)$_4$(PMe$_3$) at 368 nm, $\varepsilon = 98$ L mol$^{-1}$ cm$^{-1}$ both in C$_6$H$_6$, at room temperature). Less than 15% of the bimetallic complex 2.1 was allowed to react in these measurements. Irradiation ($\lambda = 368$ nm) of 2.1 in deoxygenated benzene under 1.0 x 10$^5$ Pa (1.0 atm) of N$_2$ at 296 ± 1 K yielded Os(CO)$_4$(PMe$_3$) and W(CO)$_6$ with a quantum yield for the disappearance of 2.1 of 0.13 ± 0.01 (see Figure 2.11). The irradiation of 2.1 in deoxygenated C$_6$H$_6$ under 1.0 x 10$^5$ Pa (1.0 atm) of CO at 296 ± 1 K again gave the products Os(CO)$_4$(PMe$_3$) and W(CO)$_6$, but with a quantum yield for the disappearance of 2.1 of 0.28 ± 0.05, (see Figure 2.11). It would be expected that if the initial photoprocess was loss of a CO ligand, or the PMe$_3$ ligand, that in the presence of an excess of a free ligand such as CO or PPh$_3$ (as in eq 2.5) the initial process would be inhibited and the quantum yield for the disappearance of 2.1 would be reduced.
That the quantum yield under CO *increases* strongly suggests that the initial photochemical reaction of 2.1 is not M-CO bond cleavage. Furthermore, the irradiation of 2.1 in deoxygenated C₆H₆ in the presence of an excess of PPh₃, (eq 2.5) did not yield
[OsW(CO)₈(PMe₃)(PPh₃)] which might be expected if M-CO dissociation was the preferred photochemical pathway. These results lend further support to the view that the preferred reaction pathway, upon the photolysis of 2.1 is heterolytic cleavage of the metal-metal bond. In the presence of CO the recombination of heterolytic fragments would be inhibited, since the [W(CO)₃] would be trapped by CO. This would increase the quantum yield for the disappearance of 2.1 relative to the reaction carried out under similar conditions in the absence of CO, as observed.

2.2.5  Experiments to probe the mechanism of the formation of the minor product, W(CO)₆, in the photolysis of 2.1 in the presence of PPh₃.

As indicated in eq 2.5, the minor tungsten-containing product, W(CO)₆, was formed in about 8% yield upon the irradiation of 2.1 in C₆H₆, at room temperature even in the presence of a large excess of PPh₃ ([2.1]:[PPh₃] 1:115, [PPh₃] = 1.91 x 10⁻¹ M). The ratio of the concentrations was altered and the reaction repeated under similar conditions ([2.1]:[PPh₃] 1:10, [PPh₃] = 1.83 x 10⁻² M) and the yield of W(CO)₆ was essentially unchanged at 7%.

It has been demonstrated that secondary photochemistry of Os(CO)₄(PMe₃) occurs under these reaction conditions (see Figure 2.2) where a product consistent with the photodissociation of a CO ligand from Os(CO)₄(PMe₃) is observed. It has been proposed that irradiation (λ = 405 ± 10 nm) of W(CO)₅(PPh₃) in CHCl₃ in the presence (or absence) of PPh₃ proceeds via two photochemical pathways that are both equally possible namely, photodissociation of either a carbonyl or the PPh₃ ligand,¹⁰² that is, the photolysis
of W(CO)$_5$(PPh$_3$) could yield [W(CO)$_5$] and PPh$_3$. In the photolysis of 2.1 in the presence of PPh$_3$ the species, [W(CO)$_5$] could be formed and then react with the CO liberated from Os(CO)$_4$(PMe$_3$), and hence account for the formation of small amounts of W(CO)$_6$ that are observed. In order to test this possibility the irradiation ($\lambda \geq 400$ nm) of Os(CO)$_4$(PMe$_3$) (1.81 x $10^{-3}$ M) and W(CO)$_5$(PPh$_3$) (1.58 x $10^{-3}$ M) in C$_6$H$_6$, at room temperature, in the presence of an excess of PPh$_3$ (1.85 x $10^{-1}$ M) was carried out. The results are shown in Figure 2.12.

![Figure 2.12](image)

**Figure 2.12** Photolysis of Os(CO)$_4$(PMe$_3$), W(CO)$_5$(PPh$_3$), and PPh$_3$ in C$_6$H$_6$ ($\lambda \geq 400$ nm). The timescale of the reaction was 0-23 h utilizing a 100W High pressure mercury arc lamp.

The progress of the reaction was slow relative to the irradiation of 2.1 under similar conditions (see Figure 2.1), even allowing for the different powers of the lamps. The new
IR absorption bands in Figure 2.12 were assigned to Os(CO)$_3$(PMe$_3$)(PPh$_3$)$_7$ and W(CO)$_4$(PPh$_3$)$_2$ and there is no evidence of the production of W(CO)$_6$. If small amounts of W(CO)$_6$ were present it would have been detected since the molar absorption coefficient of the IR absorption at 1976 cm$^{-1}$ of W(CO)$_6$ is large in C$_6$H$_6$ (see Table 2.1). This result strongly suggests that photodissociation of PPh$_3$ from W(CO)$_5$(PPh$_3$) to yield W(CO)$_6$ is not a significant route.

An alternative mechanism for the formation of W(CO)$_6$ is that it is formed in a geminate cage reaction, involving CO abstraction by [W(CO)$_5$] from Os(CO)$_4$(PMe$_3$) in the caged intermediate [Os(CO)$_4$(PMe$_3$), W(CO)$_5$]. The high reactivity of [W(CO)$_5$] and its ability to abstract ligands from other moieties is well preceded (see references 30b, 75, 78, and 79). To probe this possibility the photolysis (λ ≥ 400 nm) of 2.1 (1.22 x 10$^{-3}$ M) was repeated in a more viscous medium of biphenyl (2.87 M) in C$_6$H$_6$, at 298 K, (kinematic viscosity 1.2 x 10$^{-6}$ m$^2$ s$^{-1}$, absolute viscosity 1.2 mPa.s as compared to C$_6$H$_6$ absolute viscosity 0.601 mPa.s at 298 K and 0.564 at 303 K) in the presence of an excess of PPh$_3$ (1.36 x 10$^{-1}$ M). It would be expected that if production of W(CO)$_6$ is via the reaction of geminate cage species then in a more viscous medium, cage escape would be hindered and the yield of W(CO)$_6$ should be increased. The reaction in the more viscous solvent gave the same photoproducts and the yield of W(CO)$_6$ was unchanged at 8%. The reaction was carried out under similar conditions but with mineral oil added to C$_6$H$_6$ to create the more viscous medium (mineral oil 30.3% v/v in C$_6$H$_6$ at 301 K, kinematic viscosity 1.3 x 10$^{-6}$ m$^2$ s$^{-1}$, absolute viscosity 1.1 mPa.s). When this solvent system was used the yield of W(CO)$_6$ was again 8%. In the latter reaction concerns arose over the possibility of preferential solvation of the photoproducts due to the differences in polarity and shape of
mineral oil and C₆H₆. This problem was believed to be alleviated with the biphenyl/C₆H₆ solvent system since the molecules are similar analogous to the solvent pairing of paraffin oil with C₆H₁₄ in reference 103. The experiments in a more viscous medium strongly suggest that it is unlikely that CO abstraction that occurs in a caged intermediate is responsible for the formation of the minor amounts of W(CO)₆.

There are two isomers of \((\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\) 2.1, in solution, one with the phosphine ligand trans to the metal-metal bond (major isomer) and the other with the phosphine ligand cis to the metal-metal bond (minor isomer) see Scheme 2.1.\(^{50,74}\) The isomers have been shown to be in dynamic equilibrium in solution at room temperature.\(^{50,74}\)

The ratio of the isomers was determined by the integration of the two sets of doublets in the \(^1\text{H}\) NMR spectrum in C₆D₆ over the range 299-279 K. At 299K, the \(^1\text{H}\) NMR spectrum of 2.1 showed the minor isomer with \(\delta = 0.83\) (d, Me, 9H, \(^2J\text{P-H} = 10.2\) Hz), and the major isomer with \(\delta = 0.63\) (d, Me, 9H, \(^2J\text{P-H} = 10.3\) Hz). The major:minor isomer ratio was determined to be 2.6:1.0. At 279 K, the major:minor isomer ratio was 2.7:1.0. There seems, therefore, to be little variation in the ratio of the isomers in the temperature range 279-299 K, the temperature range expected during the photolysis of 2.1. For this reason, the determination of the potentially different molar absorption coefficients of the two isomers of 2.1 in this solvent was not possible. Carrying out the studies at a higher temperature would increase the probability of thermal reactions occurring in conjunction with photochemical reactions.
Scheme 2.1  Proposed mechanism for the isomerization of 2.1.

It is expected that both isomers of 2.1 would have similar molecular orbitals and therefore irradiation of the two isomers of 2.1 would produce two different Franck-Condon states. The two Franck-Condon states could relax differently, one to give the major products, Os(CO)$_4$(PMe$_3$) and [W(CO)$_5$] and the other to give [(Me$_3$P)(OC)$_3$Os(μ-CO)]W(CO)$_3]$. This intermediate with the single bridging CO ligand could then cleave the bridging CO ligand to yield the minor product W(CO)$_6$ and [Os(CO)$_3$(PMe$_3$)] (route b, Scheme 2.2). The latter unsaturated complex would react with PPh$_3$ and the resultant product would not be distinguishable from the secondary photochemistry of Os(CO)$_4$(PMe$_3$), see eq 2.6. This mechanism is consistent with the results from the reaction carried out in a more viscous medium because a caged pair is not required. It should be pointed out that the singly bridged intermediate could cleave the bridging CO ligand the other way (route a, Scheme 2.2) to produce Os(CO)$_4$(PMe$_3$) and [W(CO)$_5$], that is, it could

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also account for the major products formed in the photolysis and this route cannot be
ignored.

![Scheme 2.2 Proposed mechanism for the relaxed excited state of 2.1.]

The relative energies of the Franck-Condon states and the products would probably
determine the populations of the two pathways. Clearly pathway b in Scheme 2.2 does not
account for all the W(CO)$_6$ formed in the photolysis of 2.1 in the absence of an incoming
ligand, where 66% W(CO)$_6$ was recovered (eq 2.9). It plays only a minor role. The major
production of W(CO)$_6$ (eq 2.9) is believed to be from the reaction of [W(CO)$_5$] with CO
arising from partial decomposition of [W(CO)$_5$]$^{30b}$ (eq 2.10) or by [W(CO)$_5$] abstracting a
CO from other moieties present.$^{79}$ As to which Franck-Condon state produces the relaxed,
excited state intermediate with the singly bridging CO, there is no direct evidence for the
proposed intermediate [(Me$_3$P)(OC)$_3$Os(μ-CO)W(CO)$_5$] and hence any further comments
would be speculative. The intermediate might be detected by flash photolysis of 2.1.
Tentatively, the Franck-Condon state arising from the irradiation of the minor isomer of
2.1, with the phosphine ligand cis to the Os-W bond, is proposed to yield the singly bridged intermediate which then yields the minor product W(CO)₆.

It should also be mentioned that a doubly bridged intermediate [(Me₃P)(OC)₃Os(μ-CO)₂W(CO)₄] with two bridging CO ligands is also possible (Scheme 2.2). A similar thermally excited transition state species on the ground state energy surface, although containing an Os-W dative metal-metal bond, was proposed to account for the nonrigidity and thermal decomposition products of (R₃P)(OC)₄OsM(CO)₅ (M = Cr, Mo, W).⁵⁰ From the species with the two carbonyl bridges there are again two decomposition pathways. Symmetric cleavage of the Os(μ-CO)₂W unit (pathway a) which would yield Os(CO)₄(PMe₃) and [W(CO)₅] and asymmetric cleavage (pathway b) to give W(CO)₆ and [Os(CO)₃(PMe₃)], see Scheme 2.2.

As before the formation of W(CO)₆ by route b would be independent of the presence of PPh₃ and viscosity of the medium. There is precedent for the proposal of asymmetric cleavage of a bimetallic species with two bridging CO ligands in both thermal¹⁰⁷ and photochemical reactions.¹⁰⁸

2.3 Conclusion

The thermal (at room temperature and 303 K) reactions of 2.1, in C₆H₆, in the dark, in the presence of an excess of PPh₃ yield products that are consistent with heterolytic cleavage of the metal-metal bond. This provides further support that the Os-W bond in the complex (Me₃P)(OC)₄OsW(CO)₅, 2.1, is indeed a dative covalent interaction.

The irradiation (λ ≥ 400 nm) of 2.1 in C₆H₆, in the presence of an excess of PPh₃ yielded predominantly Os(CO)₄(PMe₃), W(CO)₅(PPh₃) and a secondary photochemical
product Os(CO)$_3$(PMe$_3$)(PPh$_3$). The initial products are also consistent with heterolytic cleavage of the metal-metal bond in 2.1. A minor product of W(CO)$_6$ can be ascribed to heterolysis via an alternate route to form W(CO)$_6$ and the unsaturated fragment [Os(CO)$_3$(PMe$_3$)] which is presumably trapped by PPh$_3$ to form more Os(CO)$_3$(PMe$_3$)(PPh$_3$). Attempts to trap radicals which would be produced from homolytic cleavage of the metal-metal bond were unsuccessful. Although this does not eliminate this reaction route, it strongly suggests it is not the preferred route of reaction for 2.1. Quantum yield determinations for the disappearance of 2.1 upon irradiation ($\lambda = 368$ nm) in C$_6$H$_6$, under N$_2$ or CO demonstrated that the quantum yield increased in the presence of CO. This result strongly suggests that metal-ligand photodissociation is not the preferred reaction pathway in the photolysis of 2.1. The evidence presented here is consistent with the view that the first observable photoprocess in the irradiation of (Me$_3$P)(OC)$_4$OsW(CO)$_5$ at $\lambda \geq 368$ nm is heterolytic cleavage of the dative covalent Os-W bond in 2.1. This is believed to be the first example where strong evidence of the photolysis of a metal-metal bond to then yield fragments consistent with heterolytic cleavage has been observed. We are of the opinion that this study opens a myriad of opportunities for future photochemical work on complexes with dative metal-metal bonds. This work may also serve to distinguish between dative covalent and nondative covalent metal-metal bonds.
2.4 Experimental

2.4.1 General Methods

All manipulations were performed under nitrogen or argon by using standard Schlenk, drybox, or vacuum line techniques unless stated otherwise. Drybox manipulations were carried out in a nitrogen filled Vacuum Atmospheres HE-493 Dri-Lab with attached Dri-Train.

2.4.2 Materials

Tetrahydrofuran (Baker) was freshly distilled as needed from potassium benzophenone ketyl. Hexanes (BDH) and benzene (Baker) were distilled from potassium. Dichloromethane (Anachemia) and acetonitrile (BDH) were distilled from calcium hydride. Carbon tetrachloride (Baker) was distilled from P₂O₅ twice and used immediately with the minimum amount of exposure to light. Benzyl chloride (BDH) was refluxed with MgSO₄ and then fractionally distilled under reduced pressure, collecting the middle fraction. All solvents were distilled and stored under nitrogen.

Trimethylphosphine (Strem) was used as purchased while triphenylphosphine (Aldrich) was recrystallized from hexanes; both phosphines were stored under nitrogen and in the dark. TMIO was freshly sublimed at 308 K, and 1.3 x 10⁻² Pa prior to usage. Bibenzyl (Aldrich) was recrystallized from 30-60° petroleum ether; mineral oil (Spectrum) (345/350 viscosity, specific gravity at 298 K 0.865-0.925) was stirred with sodium overnight then filtered under N₂ and finally subjected to three freeze-pump-thaw cycles prior to usage. Carbon monoxide gas (Linde/Union Carbide, C. P. grade) was used as
provided. The metal carbonyls W(CO)_6 (Strem) and Os_3(CO)_{12} (Oxkem) were used as purchased. The complexes \((\text{Me}_3\text{P})(\text{OC})_4\text{OsW(CO)}_5\), \((2.1)\),\(^{50}\) Os(CO)_3(PMe_3)(PPh_3)^{74} were prepared as previously recorded in the literature, the phosphine derivative, W(CO)_5(PPh_3) was prepared from W(CO)_5(THF)^{30,50} and PPh_3, the excess starting material W(CO)_6 was removed by sublimation and W(CO)_5(PPh_3) was recrystallized from C_6H_{14}/CH_2Cl_2 analogous to prior work.\(^{70}\) The mononuclear complex Os(CO)_4(PMe_3)^{69} was prepared according to the literature method except that a Parr 4021 500 mL rocker type pressure vessel coupled with a Parr 4841 temperature controller was used. This allows greater temperature control and hence precision and safety of the reaction. When pressures that exceeded \(9.65 \times 10^6\) Pa (95.3 atm) were required for the reaction, an Aminco nitrogen-operated diaphragm-type compressor (model J46-14025) was employed. The temperature for a typical reaction was \(633 \pm 24\) K and the pressure of CO gas at this temperature was \(5.102 \times 10^7 \pm 3.4 \times 10^5\) Pa (503.7 \pm 3.4 atm) (or \(2.275 \times 10^7 \pm 3.4 \times 10^5\) Pa (224.6 \pm 3.4 atm) at 295 K prior to the reaction) these values are quite different to the original values in the literature.\(^{69}\) The preparation and characterization of other complexes such as: \([\text{Bu}^n\text{N}]_2\text{W}_2(\text{CO})_{10}\) \(([\text{Bu}^n\text{N}]_2[2.4])\), Os_3(CO)_9(PMe_3)_3, \(\text{fac-Os(CO)}_3(\text{PMe}_3)(\text{Cl})_2\) (fac-2.2), and ‘Os(CO)_3(PMe_3)(CCl_3)(Cl)’ (2.3) will be discussed in Chapter 3.

### 2.4.3 Instrumentation

Infrared spectra were measured by using either a Bomem Michelson model 120 FT-IR instrument with spectral calc software, a Nicolet 5DXB FT-IR spectrometer, a Nicolet Magna 550 FT IR spectrometer with Omnic 1.2a software, or a Perkin-Elmer 983G IR spectrophotometer. Samples were prepared as solutions usually in NaCl (path length
0.0965 mm or 0.442 mm) or CaF$_2$ (path length 0.116 or 0.105 mm) cells. For mechanistic work a known amount of solid was dissolved in a deoxygenated solution containing known quantities of other reagents, if appropriate, and transferred to an IR cell via a gastight syringe.

UV-vis spectra were measured in solution with either a Perkin-Elmer Lambda 6 series UV-vis spectrophotometer, a (Varian) Cary 210 UV-vis spectrophotometer or a Hewlett-Packard 8452A diode array spectrophotometer.

All NMR data were recorded at various specified temperatures on a Bruker AMX 400 instrument at an operating frequency of 400.13 MHz for $^1$H nuclei. The $^1$H NMR chemical shifts are reported in ppm downfield (positive) of tetramethylsilane.

The variable temperature $^1$H NMR spectra of 2.1 in C$_6$D$_6$ (Isotec) at 299 K, 294 K, 289 K, 284 K, 279 K were allowed 20 minutes to equilibrate at the desired temperature in the 5 mm tube prior to collection of the data. The temperature was controlled using a B-VT 1000 variable temperature unit and dried air at 273 K. The thermocouple had been calibrated at: 77, 195, 273 and 373 K and demonstrated to have an error in the thermocouple of ± 0.6 K in the temperature range 314-183 K. Temperature values on the instrument were corroborated by measuring peak separations for a standard Bruker sealed sample of methanol and converting these values into temperature by the literature method. The temperature values were found to be accurate to ± 1 K. The sweep width was 5.0 ppm with the solvent peaks folded in to reduce the sweep width. The time domain was 32 k with a size of 64 k and 256 scans per spectrum to reduce the signal-to-noise ratio and increase the resolution.
Synthetic photochemical reactions were carried out with a 200W Hanovia medium-pressure mercury lamp (model 654 A36) as the UV-vis source in a water and air cooled quartz jacket. The sample solution was typically in a Pyrex glass, Carius tube and was magnetically stirred and air cooled at room temperature and there was \( \sim 5 \) cm between the source and the edge of the reaction vessel. All solutions were subjected to several (three) freeze-pump-thaw cycles prior to photolysis.

Mechanistic photochemical reactions were carried out with a Oriel 200W or a Oriel 100W high-pressure mercury arc lamp as the UV-vis source, in conjunction with a 10 cm water filter with Pyrex windows to reduce IR emissions. Corning glass filters were used for broad band irradiations: CS 3-73 (\( \lambda \geq 420 \) nm), CS 3-74 (\( \lambda \geq 400 \) nm), CS 3-75 (\( \lambda \geq 365 \) nm), CS 4-72 (\( \lambda \geq 335 \) nm). Reaction solutions for mechanistic experiments were scrupulously protected from extraneous light.

Quantum yield determinations were carried out with an Oriel 200W high-pressure mercury arc lamp coupled with a Beckman DU monochromator and a Merlin™ radiometer system, model 70100 produced by the Oriel Corp.\(^{110}\) Light intensity was determined by actinometry using Aberchrome 540 in toluene (\( \phi_{368} = 0.20 \)).\(^{111}\) The Teflon sealed UV-vis cuvettes used for the quantum yield determinations were 1 cm in pathlength and had freeze-pump-thaw side arms and magnetic stirrers. A volume of 4.00 mL of the reaction solution was pipeted into the UV-vis cuvette side-arm and subjected to a minimum of four cycles of freeze-pump-thaw whereupon the solutions were allowed to warm to room temperature and either CO or N\(_2\) (O\(_2\) scrubbed and dried) (1.0 \times 10\(^5\) Pa, 1 atm) were introduced into the vessel. The quantum yields at 368 nm (lamp intensities were typically \( I_a = 2.3 \times 10^{10} \) einsteins s\(^{-1}\) at this wavelength) were determined by the initial (<15%) rates of
disappearance of the UV-vis absorption band maximum at 368 nm (assigned to a $\sigma \rightarrow \sigma^*$ transition) in complex 2.1. It has been demonstrated (see Figure 2.3 and Section 2.2.2) that there were no measurable dark reactions during the timescale of the quantum yield experiments. The stirred UV-vis cells were maintained at 296 ± 1 K with a flow of compressed air through the cell holder during the photolysis to prevent warming and thermal reaction. All quantum yields were corrected with a linear correction factor for non-absorption.

Kinematic viscosities of the solutions were measured with a calibrated Cannon-Fenske viscometer and corrected to absolute viscosities. The mixed solvent systems were prepared in a darkened dry box as were the viscosity determinations of the thoroughly mixed, temperature equilibrated solvent systems.

Yields of the products were determined by comparing product peaks in the IR spectra of reaction solutions to those of authentic samples of known concentrations in IR cells of known path length by two methods. The concentrations of complexes 2.1 and fac-2.2 were determined from the absorption intensities of v(CO) bands and the molar absorption coefficients of these bands that had been previously determined. Absorption corrections were made for non-zero baselines. From solutions of known concentration of Os(CO)$_4$(PMe$_3$), W(CO)$_6$, W(CO)$_5$(PPh$_3$), Os(CO)$_3$(PMe$_3$)(PPh$_3$) it was possible to calculate the central 30% area of an absorption peak of a CO stretch in the IR spectrum. It was then possible to compare this with the corresponding peak area in the IR spectrum of the reaction mixture by using Omnic 1.2a software which then allowed the concentrations of the products from the reactions to be determined.
CHAPTER 3

Preparation and investigation of proposed photoproducts

3.1 Introduction

This chapter is of a supportive nature for Chapter 2; it contains the preparative details, chemistry or mechanistic evidence to substantiate the identity of compounds either used in or used as precursors to make complexes described in Chapter 2. The chemistry exhibited by some of these complexes is interesting in its own right and therefore merits a separate chapter.

3.2 Results and Discussion

3.2.1 The preparation of \([\text{Bu}^n_4\text{N}]_2[\text{W}_2(\text{CO})_{10}]\) ([\text{Bu}^n_4\text{N}]_2[2.4]).

The earlier procedure used to prepare \([\text{Na}]_2[\text{W}_2(\text{CO})_{10}]\) ([\text{Na}]_2[2.4]) (via \(\text{W}(\text{CO})_6\), sodium and 2,2'-bipyridine in THF requires a long reaction time (72 h) and the yield is not totally satisfactory (23%).\(^9\)) An alternative procedure for the preparation of [2.4] via potassium intercalated into graphite (C\(_6\)K) has appeared; it is a shorter and more selective route to the anionic dimer but the scant description of the method has probably prevented the more widespread use of the procedure.\(^1\)) An elaboration of the procedure is presented in the experimental section. By the use of the latter method the bright yellow, air sensitive, dimeric complex \([\text{Bu}^n_4\text{N}]_2[\text{W}_2(\text{CO})_{10}]\) ([\text{Bu}^n_4\text{N}]_2[2.4]) was prepared.\(^1\)) The time period for
the preparation of $[\text{K}_{2}\text{[2.4]}$ is much reduced via this route (3-4 h) and the purity and yield of $[\text{Bu}^n\text{N}_{2}\text{[2.4]}$ are much improved (56% yield) over the earlier method.

### 3.2.2. The preparation of Os$_3$(CO)$_9$(PMe$_3$)$_3$ (3.1).

The preparation of Os$_3$(CO)$_9$(PMe$_3$)$_3$ (3.1) has been previously reported$^{114}$ but it is made in conjunction with Os$_3$(CO)$_{12-n}$(PMe$_3$)$_n$ ($n = 1,2$) and the yield was 11%. An alternative method which produces the trisubstituted cluster as the only cluster species is described in the experimental section. It is analogous to the preparation of Os$_3$(CO)$_9$(PPh$_3$)$_3$$^{115}$ and Os$_3$(CO)$_9$(PET$_3$)$_3$$^{116}$ and produced similar products to those reported by Bellachioma et al.$^{117}$ The side products were Os(CO)$_4$(PMe$_3$) and Os(CO)$_3$(PMe$_3$)$_2$$^{69,74,114-116}$ (as identified by IR spectroscopy) and could both be individually separated by either sublimation or column chromatography. (Both side products are useful as donor-fragments in the preparation of complexes with a donor-acceptor metal-metal bond.)$^{50,74}$ The orange, crystalline compound, 3.1 was obtained in 31% yield. In an analogous manner to Os$_3$(CO)$_9$[P(OMe)$_3$]$_3$$^{118}$ and Os$_3$(CO)$_9$(PET$_3$)$_3$$^{119}$ the complex 3.1 has been shown to exhibit nonrigidity on the NMR timescale (1 - $10^{-6}$ s)$^{120}$ see Figure 3.1. From studies on similar complexes the static structure of 3.1 is believed to be that shown below (Figure 3.2).$^{118,119,121}$
Figure 3.1 Variable-temperature $^{13}C\{^1H\}$ NMR spectra of Os$_3$(CO)$_9$(PMe$_3$)$_3$ in CD$_2$Cl$_2$/CH$_2$Cl$_2$, 1/3.

Figure 3.2 The structure of Os$_3$(CO)$_9$(PMe$_3$)$_3$ (3.1).
3.2.2.1 The $^{13}$C($^1$H) NMR spectroscopic properties of Os$_3$(CO)$_9$(PMe$_3$)$_3$ (3.1).

In CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1:3) at 233 K, 3.1 exhibits two sharp singlets in the carbonyl region of the $^{13}$C($^1$H) NMR spectrum at 196.68 ppm and 183.55 ppm with intensities in a ratio of 2:1, hence the signals are readily attributed to axial and equatorial carbonyls respectively (Figure 3.1) at lower temperatures the phosphorus-carbon coupling, $^2J_{P,C}$ would be observable (analogous to Os$_3$(CO)$_9$[P(OMe)$_3$]$_3$] at 208 K in C$_7$D$_8$ where $^2J_{P,C} = 10.3$ Hz). At 298 K the peaks have broadened considerably, indicative of a carbonyl exchange process. A mechanism of synchronous phosphine libration (that is, the PMe$_3$ ligands always remain in equatorial sites) at all three osmium atoms, analogous to the mechanism proposed for Os$_3$(CO)$_9$[P(OMe)$_3$]$_3$, is believed to be operative. This would allow all the carbonyl ligands to exchange. A terminal-bridge carbonyl exchange mechanism, normally proposed for the interchange of carbonyl ligands in metal cluster complexes, is blocked since it would require PMe$_3$ to occupy an axial site which is believed to be energetically unfavorable for steric reasons.

3.2.3 The preparation of mer-cis-Os(CO)$_3$(PMe$_3$)(Cl)$_2$ (mer-cis-2.2).

It was proposed in Chapter 2, Section 2.2.2, that Os(CO)$_3$(PMe$_3$)(Cl)$_2$ (2.2) was formed upon the irradiation ($\lambda \geq 400$ nm) of (Me$_3$P)(OC)$_4$OsW(CO)$_5$ (2.1) in C$_6$H$_6$ in the presence of CCl$_4$. To confirm the identity of this product it was desirable to prepare and characterize this species via an alternative reaction route. The complexes Os(CO)$_3$(PPh$_3$)(Cl)$_2$ and Os(CO)$_3$(PEn$_3$)(Cl)$_2$ had been previously prepared by the reaction of the appropriate phosphine trisubstituted osmium cluster, Os$_3$(CO)$_9$(PR$_3$)$_3$ with Cl$_2$. The numbers of IR $\nu$(CO) bands reported for each complex suggested, however, that
more than one isomer was present in solution and the stereochemistry of these molecules had not been addressed. The utilization of the reaction of 3.1 with Cl₂ therefore appeared a viable pathway to 2.2.

To a solution of 3.1 in C₆H₅CH₃ an excess of Cl₂ dissolved in C₆H₅CH₃ was added at 273 K. The mixture instantly changed from a clear, orange solution to an opaque, deep red-orange mixture and then changed again to a pale yellow solution (presumably due to the excess Cl₂) along with the formation of a white precipitate. Upon recrystallization of the white solid, colorless needles of 2.2 were obtained in excellent yield. There are three possible isomers of the formula Os(CO)₃(PMe₃)(Cl)₂ (2.2) namely, fac, mer-cis and mer-trans. These are shown in Figure 3.4 later in the chapter. In order to establish the geometry of the product isolated in this study the structure was determined by X-ray diffraction.†

3.2.3.1 The molecular structure of mer-cis-Os(CO)₃(PMe₃)(Cl)₂ (mer-cis-2.2).

The structure revealed the configuration of the molecule in the solid state to be mer-cis-Os(CO)₃(PMe₃)(Cl)₂ (mer-cis-2.2). The molecular structure is shown in Figure 3.3 and selected bond lengths and bond angles are shown in Tables 3.1 and 3.2, respectively.

† All X-ray diffraction studies reported in this thesis were carried out in Professor F. W. B. Einstein’s laboratory under his supervision by either Dr. W. K. Leong or Dr. W. Wang.
Figure 3.3  A molecular structure of mer-cis-Os(CO)$_3$(PMe$_3$)(Cl)$_2$ (mer-cis-2.2).
Table 3.1 Selected bond lengths of *mer-cis*-Os(CO)$_3$(PMe$_3$)(Cl)$_2$ (*mer-cis-2.2*).

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
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</tr>
</thead>
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<tr>
<td>Os(1) - P(1)</td>
<td>2.341(1)</td>
</tr>
<tr>
<td>Os(1) - Cl(1)</td>
<td>2.427(1)</td>
</tr>
<tr>
<td>Os(1) - Cl(2)</td>
<td>2.457(1)</td>
</tr>
<tr>
<td>Os(1) - C(11)</td>
<td>1.978(6)</td>
</tr>
<tr>
<td>Os(1) - C(12)</td>
<td>1.957(6)</td>
</tr>
<tr>
<td>Os(1) - C(13)</td>
<td>1.856(5)</td>
</tr>
</tbody>
</table>

A notable feature of the structure is the Os-CO bond length [1.856(5) Å] for the carbonyl *trans* to the Cl atom is substantially shorter than either of the other Os-CO distances, [1.957(6) and 1.978(6) Å] which are *trans* to each other. This has been observed in other systems such as: (Br)$_2$Os$_3$(CO)$_{10}$[P(OMe)$_3$]$_2$,$^{122}$ Os$_3$(μ-Cl)$_2$(CO)$_6$,$^{123}$ and

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Table 3.2 Selected bond angles of *mer-cis*-Os(CO)$_3$(PMe$_3$)(Cl)$_2$ (*mer-cis-2.2*).

<table>
<thead>
<tr>
<th>Bond Angles (deg)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1) - Os(1) - Cl(1)</td>
<td>87.36(4)</td>
</tr>
<tr>
<td>P(1) - Os(1) - C(12)</td>
<td>90.5(1)</td>
</tr>
<tr>
<td>P(1) - Os(1) - C(13)</td>
<td>94.0(2)</td>
</tr>
<tr>
<td>P(1) - Os(1) - C(11)</td>
<td>91.0(1)</td>
</tr>
<tr>
<td>P(1) - Os(1) - Cl(2)</td>
<td>174.61(4)</td>
</tr>
<tr>
<td>C(11) - Os(1) - C(12)</td>
<td>176.6(2)</td>
</tr>
<tr>
<td>C(11) - Os(1) - C(13)</td>
<td>91.5(2)</td>
</tr>
<tr>
<td>C(12) - Os(1) - C(13)</td>
<td>91.5(2)</td>
</tr>
</tbody>
</table>

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A notable feature of the structure is the Os-CO bond length [1.856(5) Å] for the carbonyl *trans* to the Cl atom is substantially shorter than either of the other Os-CO distances, [1.957(6) and 1.978(6) Å] which are *trans* to each other. This has been observed in other systems such as: (Br)$_2$Os$_3$(CO)$_{10}$[P(OMe)$_3$]$_2$,$^{122}$ Os$_3$(μ-Cl)$_2$(CO)$_6$,$^{123}$ and

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*Footnote:* Here and elsewhere in this thesis estimated standard deviations in the least significant figure are given in parentheses.

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These differences in Os-CO bond lengths may be rationalized by σ or π bonding arguments.\textsuperscript{124} The CO ligand is expected to be a better σ-donor ligand than the Cl atom and thus the Os-CO σ-overlap is greater at the expense of the trans Os-Cl σ-overlap and this results in a shorter M-CO bond trans to a Cl atom relative to a case where the two CO’s are trans to each other.\textsuperscript{124} From a consideration of the π-interactions, it is expected that the two CO ligands trans to each other compete equally for the back-bonding from the filled metal d-orbitals, while the CO trans to the Cl receives more d-π back donation from the metal since Cl is a π-donor ligand. This results in more double bond character to the Os-CO trans to Cl and results in a shorter Os-CO bond. The filled orbitals on the metal and chlorine might even exert some repulsion which would further support the observation that the Os-Cl bond trans to the CO ligand is longer with a concomitant shorter Os-CO bond trans to the Cl atom.

The Os-Cl bond lengths (2.427(1) and 2.457(1) Å) in \textit{mer-cis-2.2} are similar to those observed in the literature namely, \textit{fac-[Os(PEt\textsubscript{2}Ph)\textsubscript{3}(Cl)\textsubscript{3}].CH\textsubscript{2}Cl\textsubscript{2}} [2.442(3)-2.449(2) Å]\textsuperscript{125} and \textit{(OC)\textsubscript{3}OsOs(CO)\textsubscript{3}(GeCl\textsubscript{3})(Cl)} [2.435(7)-2.459(8) Å].\textsuperscript{44} Similar arguments as given above may be used to rationalize the different Os-Cl bond lengths in \textit{mer-cis-2.2}. The Os-P bond length is also similar to those reported in the literature such as in \textit{Os(CO)\textsubscript{2}(PMe\textsubscript{3})\textsubscript{2}(CH\textsubscript{3})(I)} [2.365(4)-2.373(4) Å],\textsuperscript{117} \textit{(Br)(Me\textsubscript{3}P)(OC)\textsubscript{3}OsRe(CO)\textsubscript{5}} [2.347(5) Å].\textsuperscript{48}

The osmium atom has close to octahedral coordination with the cis-P-Os-L angles all in the range; 87.36(4)-94.0(2)°, and cis-Cl(2)-Os-L angles are in the range: 87.37(1)-91.3(2)°. All of the Os-C-O bonds are almost linear, with angles ranging from; 177.6(5)-178.3(5)°.
3.2.3.2 The spectroscopic properties of mer-cis-Os(CO)$_3$(PMe$_3$)(Cl)$_2$ (mer-cis-2.2).

The v(CO) region of the IR spectrum of 2.2, in CH$_2$Cl$_2$, showed three bands at: 2145 (vw), 2066 (s), 2019 (m) cm$^{-1}$ which is very similar to the IR spectrum (v(CO) bands) reported for Os(CO)$_3$(PEt$_3$)(Cl)$_2$ in cyclohexane: 2144 (w), 2070 (vs), 2023 (s) cm$^{-1}$. As mentioned earlier, there are three possible structural isomers of 2.2, as shown in Figure 3.4. The very weak, IR CO stretch at the highest frequency is attributed to a symmetric v(CO) band. The intensity of this band suggests that an isomer with two CO ligands that are trans to one another, for which the dipole moment change would be small. This is therefore consistent with a mer-cis- or mer-trans- isomer.

The IR spectral bands of the complex in nujol at 310 (m) and 279 (s) cm$^{-1}$ were assigned to v(Os-Cl) bands by analogy to other systems, namely, Os(CO)$_2$(PPh$_3$)$_2$(Cl)$_2$ [IR, solid, v(Os-Cl): 306 (m), 284 (m) cm$^{-1}$],$^{115b}$ Os(CO)$_3$(PEt$_3$)(Cl)$_2$ [IR, nujol, v(Os-Cl): 312 (s), 289 (s) cm$^{-1}$].$^{116}$ This result strongly suggests that the molecule is not the mer-trans-isomer since, although group theory predicts two IR v(Os-Cl) bands for each isomer, the symmetric A$_1$ (Os-Cl) stretch would be expected to be very weak or of negligible intensity with the two Cl atoms trans to each other. The nujol IR spectral results, are therefore also consistent with a mer-cis arrangement of the ligands.

The $^{13}$C{$^1$H} NMR spectrum of the $^{13}$CO-labeled complex in CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1:3) at 233 K, showed in the carbonyl region of the spectrum two doublets at 167.2 ppm (1C, $^2J_{P.C} = 6.9$ Hz) and 172.4 ppm (2C, $^2J_{P.C} = 7.6$ Hz). Both of these resonances exhibit a small, two bond, carbon-phosphorus coupling typical of a CO ligand cis to a phosphine ligand: Os$_4$(CO)$_{15}$(PMe$_3$) $\delta$ 181.6 (d, CO, 4C, $^2J_{P.C} = 4.1$ Hz),$^{28}$ Os$_3$(CO)$_{10}$(PEt$_3$)$_2$ $\delta$ 197.1 (d, CO, 2C, $^2J_{P.C} = 7$ Hz), $\delta$ 196.2 (d, CO, 2C, $^2J_{P.C} \approx 7$ Hz).$^{119}$ This indicates that both the
carbonyl ligands are cis to the PMe₃ ligand and in agreement with a the mer-cis-arrangement. On the basis of their relative intensities, the higher field resonance (of intensity 1) is assigned to the CO ligand trans to the Cl ligand while the lower field resonance (of intensity 2) is assigned to the two CO ligands trans to each other.

Point group symmetry:

\[
\begin{align*}
\text{mer-cis-} & : C_s \\
\text{mer-trans-} & : C_{2v} \\
\text{fac-} & : C_s
\end{align*}
\]

The expected IR \( \nu(\text{CO}) \) bands: 2A' + A''

The expected IR \( \nu(\text{Os-Cl}) \) bands: 2A'

Figure 3.4 The possible structural isomers of Os(CO)₃(PMe₃)(Cl)₂

3.2.4 The preparation of fac-Os(CO)₃(PMe₃)(Cl)₂ (fac-2.2).

The IR spectrum in the carbonyl stretching region of mer-cis-2.2 was not the same as that given by the product from the photolysis of 2.1 in the presence of CCl₄. The objective to produce this 2.2 species had therefore not been achieved by this synthesis. The IR spectrum of a previously prepared analogue, Os(CO)₃(PPh₃)(Cl)₂, suggested, however, that other isomers of these molecules may be readily obtainable. The IR spectrum of the PPh₃ complex is 2123(w), 2048(s), 2017(w), 1978(s) in nujol. This idea was particularly appealing when the IR spectrum of the photoproduct, 2.2, (2126(m), 2050(s), 2004(s) cm⁻¹ in C₆H₆) was compared to that of the PPh₃ compound (compare the three higher frequency \( \nu(\text{CO}) \) bands in the IR spectrum of Os(CO)₃(PPh₃)(Cl)₂ with the photoproduct). It was also known that a related molecule namely, Ru(CO)₃(Br)₂(OPPh₃)
had the *fac* configuration.\textsuperscript{127} For the latter molecule, it was suggested that the CO ligands prefer not to be *trans* to one another but instead prefer to be *trans* to a weaker $\pi$-acceptor ligand, such as Br or (OPPh$_3$) and therefore a *fac*-arrangement is expected to be thermodynamically the most stable.\textsuperscript{127} This configuration was also suggested for the complex Os(CO)$_3$(PPh$_3$)(H)$_2$.\textsuperscript{128} In view of this evidence the possible isomerization of *mer-cis-2.2* was investigated.

A solution of *mer-cis-2.2* in THF was allowed to stir at room temperature, in the dark under N$_2$, for nine days. After this time, an IR spectrum of the solution revealed that the IR $\nu$(CO) bands due to *mer-cis-2.2* no longer remained and new bands due to a mixture of at least two complexes were obtained. Column chromatography of the mixture afforded two products, the major product was recrystallized from C$_6$H$_4$/C$_6$H$_5$CH$_3$ to afford colorless needles of a second isomer of 2.2. The minor product is believed to be [Os(CO)$_2$(PMe$_3$)(Cl)(μ-Cl)]$_2$ (3.2) and is discussed below.

### 3.2.4.1 The molecular structure of *fac-Os(CO)$_3$(PMe$_3$)(Cl)$_2* (fac-2.2).

The crystal structure of the second isomer was determined by X-ray crystallography to establish unambiguously its geometry and to compare bond lengths to the *mer-cis* form. The configuration of the second isomer was indeed determined to be the *fac* form (i.e., *fac-Os(CO)$_3$(PMe$_3$)(Cl)$_2* (fac-2.2)). The molecular structure is shown in Figure 3.5 and selected bond lengths and bond angles are listed in Tables 3.3 and 3.4, respectively.
Figure 3.5 A molecular structure of $\text{fac-}\text{Os(CO)}_3(\text{PMe}_3)(\text{Cl})_2$ ($\text{fac-2.2}$).
Table 3.3 Selected bond lengths of fac-Os(CO)$_3$(PMe$_3$)(Cl)$_2$ (fac-2.2).

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>Molecule 1</th>
<th>Molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(1) - Cl(11)</td>
<td>2.422(2)</td>
<td>Os(2) - Cl(21)</td>
</tr>
<tr>
<td>Os(1) - Cl(12)</td>
<td>2.425(1)</td>
<td>Os(2) - Cl(22)</td>
</tr>
<tr>
<td>Os(1) - P(1)</td>
<td>2.400(1)</td>
<td>Os(2) - P(2)</td>
</tr>
<tr>
<td>Os(1) - C(11)</td>
<td>1.891(7)</td>
<td>Os(2) - C(21)</td>
</tr>
<tr>
<td>Os(1) - C(12)</td>
<td>1.913(6)</td>
<td>Os(2) - C(22)</td>
</tr>
<tr>
<td>Os(1) - C(13)</td>
<td>1.958(7)</td>
<td>Os(2) - C(23)</td>
</tr>
</tbody>
</table>

The unit cell of the molecular structure contains two independent molecules. In fac-2.2 both the Cl atoms are trans to a CO ligand and hence the Os-Cl distances [2.418(2)-2.426(2) Å, see Table 3.3] are very similar to the Os-Cl bond length [2.427(1) Å] in mer-cis-2.2 which has the CO ligand trans to the Os-Cl bond, also see Table 3.1. For the carbonyls trans to a Cl, and the Os-C bond lengths are Os-C(lm) (l, m = 1-2) [1.881(7)-1.913(6) Å]. These values lie between those observed in the mer-cis-isomer [for Os-C(13) 1.856(5) Å, trans to a Cl atom; and for Os-C(1n) (n = 1, 2) 1.978(6) and 1.957(6) Å, trans to a CO ligand]. It is not clear why the Os-C bond lengths in the fac-isomer are not more similar to the Os-C bond length which is trans to a Cl atom in the mer-cis-isomer but elongation due to steric interactions in the fac form or packing forces may be operative (see below). It is expected that a chlorine ligand is more bulky than a carbonyl group. The third carbonyl ligand in fac-2.2 which is trans to a PMe$_3$ group has a bond length [Os-C(n3), n = 1, 2; 1.958(7) Å] which is similar to the Os-C bond lengths of the two CO ligands trans to
Table 3.4 Selected bond angles of \textit{fac}-\textit{Os(CO)}\textsubscript{3}(\textit{PMe}_{3})(\textit{Cl})\textsubscript{2} (\textit{fac-2.2}).

<table>
<thead>
<tr>
<th>Bond Angles (deg)</th>
<th>Molecule 1</th>
<th>Molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(11) - Os(1) - Cl(12)</td>
<td>90.24(6)</td>
<td>Cl(21) - Os(2) - Cl(22)</td>
</tr>
<tr>
<td>Cl(11) - Os(1) - P(1)</td>
<td>86.56(5)</td>
<td>Cl(21) - Os(2) - P(2)</td>
</tr>
<tr>
<td>Cl(11) - Os(1) - C(12)</td>
<td>88.6(2)</td>
<td>Cl(21) - Os(2) - C(22)</td>
</tr>
<tr>
<td>Cl(12) - Os(1) - P(1)</td>
<td>87.00(6)</td>
<td>Cl(22) - Os(2) - P(2)</td>
</tr>
<tr>
<td>Cl(12) - Os(1) - C(13)</td>
<td>86.4(2)</td>
<td>Cl(22) - Os(2) - C(23)</td>
</tr>
<tr>
<td>P(1) - Os(1) - C(11)</td>
<td>91.6(2)</td>
<td>P(2) - Os(2) - C(21)</td>
</tr>
<tr>
<td>P(1) - Os(1) - C(12)</td>
<td>93.0(2)</td>
<td>P(2) - Os(2) - C(22)</td>
</tr>
<tr>
<td>C(11) - Os(1) - C(12)</td>
<td>90.8(3)</td>
<td>C(21) - Os(2) - C(22)</td>
</tr>
<tr>
<td>C(11) - Os(1) - C(13)</td>
<td>93.9(3)</td>
<td>C(21) - Os(2) - C(23)</td>
</tr>
<tr>
<td>C(12) - Os(1) - C(13)</td>
<td>93.5(3)</td>
<td>C(22) - Os(2) - C(23)</td>
</tr>
<tr>
<td>Cl(11) - Os(1) - C(11)</td>
<td>178.0(2)</td>
<td>Cl(21) - Os(2) - C(21)</td>
</tr>
<tr>
<td>Cl(11) - Os(1) - C(13)</td>
<td>88.0(2)</td>
<td>Cl(21) - Os(2) - C(23)</td>
</tr>
<tr>
<td>Cl(12) - Os(1) - C(11)</td>
<td>90.4(2)</td>
<td>Cl(22) - Os(2) - C(21)</td>
</tr>
<tr>
<td>Cl(12) - Os(1) - C(12)</td>
<td>178.8(2)</td>
<td>Cl(22) - Os(2) - C(22)</td>
</tr>
<tr>
<td>P(1) - Os(1) - C(13)</td>
<td>171.4(2)</td>
<td>P(2) - Os(2) - C(23)</td>
</tr>
</tbody>
</table>

Each other, in the \textit{mer-cis}-isomer, mentioned above. This would be unexpected from electronic arguments since the \(\sigma\)-donor/\(\pi\)-acceptor properties of CO and \textit{PMe}_{3} are very different. This again suggests that steric interactions or packing interactions play an important part in determining the bond lengths.
It is interesting to compare the two Os-P bond lengths of the two isomeric forms of 2.2. In the fac-isomer the Os-P bond which is trans to a CO ligand is 2.400(1) and 2.402(2) Å whereas in the mer-cis-isomer, where the Os-P bond is trans to a Cl atom the Os-P bond length 2.341(1) Å. The Os-P distance in the fac isomer is amongst the longest Os-P (PMe₃) lengths reported. The long Os-P bond in the fac isomer as compared to that in the mer-cis form may be attributed to the differing trans influences of the PMe₃ and Cl ligands for reasons already discussed. It may, however, be a least partly due to the greater steric interactions in the fac form. In eq-Os₅(CO)₁₅(PMe₃) the PMe₃ group occupies a sterically crowded site and the Os-P bond length [2.396(4) Å] reflects this; in ax-Os₅(CO)₁₅(PMe₃) the Os-P distance is 2.318(4) Å.²⁷

The osmium atom has an approximately octahedral coordination with the cis-P-Os-L angles all in the range; 85.17(6) - 93.0(2)°, and cis-C(n3)-Os-L, (n = 1 or 2), angles are in the range: 86.4(2) - 93.9(3)°. All of the Os-C-O bonds are almost linear, with angles ranging from, 176.7(6) - 179.3(6)°.

3.2.4.2 The spectroscopic properties of fac-Os(CO)₃(PMe₃)(Cl)₂ (fac-2.2).

The IR spectrum of fac-2.2 in C₆H₆ exhibits three bands at 2126(m), 2050(s), 2004(s) cm⁻¹, which are identical to the bands observed for the product obtained from the irradiation (λ ≥ 400 nm) of 2.1 in C₆H₆ in the presence of CCl₄. Use of similar arguments to those used in the discussion above on the configuration of mer-cis-2.2 suggests the IR data is consistent with a fac-arrangement, see Figure 3.4. The greater intensity of the CO stretch at highest frequency compared to that of the mer-cis isomer is consistent with no trans OC-Os-CO arrangement of ligands in the present molecule. The pattern and intensity
of the IR v(CO) bands is analogous to that of the complex fac-Ru(CO)$_3$(C$_5$H$_5$N)(Cl)$_2$.\textsuperscript{129} The IR spectrum of the \textit{fac-2.2} isomer in nujol exhibited two bands at 318(s) and 296(s) cm$^{-1}$, assigned to v(Os-Cl) by comparison to Os-Cl stretches in the literature\textsuperscript{115b,116,129} and \textit{mer-cis-2.2}. That both bands are intense is consistent with the Cl ligands being mutually \textit{cis} consistent with the \textit{fac} arrangement.

The $^{13}$C\{$^1$H\} NMR spectrum of the $^{13}$CO-labeled \textit{fac}-complex in CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1:3), at 233 K, showed in the carbonyl region two doublets at 167.2 ppm (2C, $^2$J$_{P,C} =$ 9.2 Hz) and 168.0 ppm (1C, $^2$J$_{P,C} =$107.6 Hz). The chemical shift of the resonance at 167.2 ppm of relative intensity 2 is identical to that of the resonance of the CO ligand \textit{trans} to a Cl atom and \textit{cis} to a PMe$_3$ group in the complex, \textit{mer-cis-2.2}. Both resonances have a small two bond carbon-phosphorus coupling characteristic of a \textit{cis} coupling. The downfield resonance of the \textit{fac} isomer at 168.0 ppm of relative intensity 1 exhibits a large two bond carbon-phosphorus coupling ($^2$J$_{P,C} =$ 107.6 Hz) characteristic of a \textit{trans} coupling. As a comparison the $^{13}$C\{$^1$H\} NMR spectrum of the form of (P$_c$(OC)$_4$OsM(CO)$_5$ (M = Cr, W) with the P$_c$ ligand \textit{cis} to the Os-M bond and \textit{trans} to a CO ligand, the two bond carbon-phosphorus couplings are 120.9 (M = Cr) and 122.0 Hz (M = W).\textsuperscript{50} The $^{13}$C\{$^1$H\} NMR spectrum in the carbonyl region for \textit{fac-2.2} is therefore unambiguous and confirms that the configuration of the second isomer of 2.2 in solution is the \textit{fac}-isomer.

\subsection*{3.2.5 The preparation of [Os(CO)$_2$(PMe$_3$)(Cl)(μ-Cl)$_2$] (3.2).}

In the preparation of \textit{fac-2.2} from \textit{mer-cis-2.2}, described above, a minor product was also formed. To optimize and characterize this new species a solution of \textit{mer-cis-2.2} in C$_6$H$_5$CH$_3$/CH$_3$CN was stirred, in the dark under N$_2$, at 323 K, for 18 h. After this period the
only ν(CO) bands in the IR spectrum of the product, in CH₂Cl₂, were 2050(s), 1983(s) cm⁻¹. These bands are attributed to [Os(CO)₂(PMe₃)(Cl)(μ-Cl)]₂ (3.2). The white product was recrystallized from C₆H₅CH₃/CH₂Cl₂ to give small, white, star-shaped crystals of the complex, 3.2 in a 54% yield. Repeated attempts to obtain a crystal of this complex that was suitable for X-ray crystallography were unsuccessful.

3.2.5.1 The spectroscopic and physical properties of [Os(CO)₂(PMe₃)(Cl)(μ-Cl)]₂ (3.2).

It was originally thought that this product from the thermolysis of mer-cis-2.2 was the third isomer of 2.2, namely, the mer-trans form. The chemical analysis and spectroscopic properties were not consistent with this view. The latter properties are discussed here. The ν(CO) region of the IR spectrum of the dimeric complex in CH₂Cl₂, shows a simple pattern of two strong bands at 2050(s), and 1983(s) cm⁻¹, which is very similar to the IR spectrum for [Os(CO)₂(PPh₃)(Cl)(μ-Cl)]₂: 2051(s), 1981(s) cm⁻¹, in CHCl₃.¹¹⁶ The IR spectrum of the PMe₃ complex in nujol had bands at 314(m), 273(m), 242(m) cm⁻¹ which were assigned to ν(Os-Cl) vibrations by analogy to [Os(CO)₂(PPh₃)(Cl)(μ-Cl)]₂ [IR, nujol, ν(Os-Cl): 321(s), 280(s), 242(m) cm⁻¹]. In a ruthenium analogue of [Ru(CO)₃(Cl)(μ-Cl)]₂ there are also three ν(Ru-Cl) bands in the IR spectrum at 331, 290, 260 cm⁻¹ which are assigned as one terminal and two bridged ν(Ru-Cl) frequencies, respectively.¹²⁹-¹³² This is in marked contrast to the two ν(Os-Cl) bands in the IR spectrum for Os(CO)₃(PR₃)(Cl)₂ (R = Me, Et,¹¹⁶ Ph¹¹⁵b), and the similar complex Ru(CO)₃(C₅H₅N)(Cl)₂.¹³² Presumably both complexes, [Os(CO)₂(PR₃)(Cl)(μ-Cl)]₂ (R = Me, Ph¹¹⁵b) are structurally similar to the unsubstituted complex, Ru₂(CO)₆(Cl)₄ which contains two bridging and two terminal chlorine atoms. A more comprehensive
discussion of the structural isomers of Ru$_2$(CO)$_6$(X)$_4$ (X = Cl, Br) will be considered later on in the text. The crystal structure of [Ru(CO)$_3$(Br)(μ-Br)]$_2$ shows the configuration in Figure 3.6.$^{129-133}$

![Figure 3.6](image)

**Figure 3.6** The solid state and solution structure of [Ru(CO)$_3$(Cl)(μ-Cl)]$_2$

The MS (EI) exhibits a peak envelope with a maximum at 753 m/z, which can be assigned to [M-Cl]$^+$. In a melting point (mp) determination of 3.2, the compound started to decompose at 530 K which was markedly different from both isomeric forms of 2.2. The mononuclear compounds changed from colorless, clear needles to an opaque, white powder at 392 K and showed no further changes to 473 K. This behavior may be compared to that of Os(CO)$_3$(PPh$_3$)(Cl)$_2$ which has a mp of 363-364 K and [Os(CO)$_2$(PPh$_3$)(Cl)$_2$]$_2$ which has a mp of 563-568 K.$^{116}$ The ruthenium analogue, Ru(CO)$_3$(PPh$_3$)(Cl)$_2$, is known to give [Ru(CO)$_2$(PPh$_3$)(Cl)$_2$]$_2$ when warmed in solution.$^{131}$ Loss of CO probably also occurs in the melting point determinations of 2.2. To examine this possibility a mixture of fac-2.2 and 3.2 (≈1:1) was heated in CH$_3$CN, at 309 K, for 20 h, under 2.2 x 10$^5$ Pa (2.2 atm) of CO. The reaction was monitored by IR spectroscopy and spectra are shown in Figure 3.7.
Figure 3.7  IR spectra of the reaction of a mixture of $\text{fac-Os(CO)}_3(\text{PMe}_3)(\text{Cl})_2$ (fac-2.2) (*) and $[\text{Os(CO)}_2(\text{PMe}_3)(\text{Cl})(\mu-\text{Cl})]_2$ (3.2) (#) (initially ~ 1:1) in CH$_3$CN, at 309 K, under 2.2 x $10^5$ Pa (2.2 atm) CO. The solid line is the initial spectrum; the dotted line is the spectrum after 20 h.

If the loss of a CO ligand from fac-2.2 is the process occurring on thermolysis then the CO would be expected to inhibit the reaction. This was demonstrated as shown in Figure 3.7. Furthermore, it was shown that the process is reversible: carbon monoxide reacts with 3.2, to give as the sole observable product, fac-2.2. This result supports the proposed identity of the dimeric species. No other changes were observed in the IR spectrum after a further 23 h 30 min of heating under the conditions. This suggests that for
this particular set of conditions (309 K, CO, CH₃CN) the two osmium complexes are in equilibrium. Similar equilibria have been established for [Ru(CO)₃(Cl)]₂/Ru(CO)₄(Cl)₂, and [Ru(CO)(PMe₂Ph)₂(Cl)(μ-Cl)]₂/all-cis-Ru(CO)₃(PMe₂Ph)(Cl)₂, for explanation of this configuration see Figure 3.12.

The ruthenium compound, [Ru(CO)₂(PPh₃)(Cl)(μ-Cl)]₂, has been reported and it was suggested that the structural arrangement was based on the known structure of [Ru(CO)₃(Cl)(μ-Cl)]₂, see Figure 3.6. The spectroscopic evidence indicates [Ru(CO)₂(PPh₃)(Cl)(μ-Cl)]₂ exists as only one isomer in solution. The available evidence indicates there are, however, two isomers of 3.2 present in solution. The ¹H NMR spectrum in CD₃CN at 308 K of 3.2 shows two sets of doublets at 1.76 ppm (²J₁₁ = 11.7 Hz) and 1.80 ppm (²J₁₁ = 11.7 Hz) in the ratio 3:1, respectively. The corresponding ³¹P{¹H} NMR spectrum shows two singlets at -30.73 and -30.37 ppm also in the ratio 3:1, respectively. This indicates that there are two isomers present in a 3:1 ratio. Furthermore, the PMe₃ groups in the two isomers are not too dissimilar from one another. Repeated recrystallizations and different preparations of the dimeric compound did not alter the NMR spectra of the mixture, suggesting the additional peaks are not due to impurities. The three most likely structural arrangements of the complex, 3.2, (i.e., that maintain the Os₂Cl₄ core) are shown in Figure 3.8. Structures with two CO ligands trans to one another are thought not preferred for electronic reasons (e.g., as used for Ru(CO)₃(Br)₂(OPh₃)).
Figure 3.8 Some structural isomers of \([\text{Os(CO)}_2(\text{PMe}_3)(\text{Cl})(\mu-\text{Cl})]_2\) (3.2) showing the point group symmetry, the expected \(v(\text{CO})\) bands (top line) and the expected \(v(\text{Os-Cl})\) bands (lower line) in the IR spectrum, as predicted from group theory for each isomer.

The structure A, in Figure 3.8 is believed unlikely since although it is possible that the number of \(v(\text{CO})\) and \(v(\text{Os-Cl})\) bands in the IR spectrum could be less than predicted it would seem less probable to occur for both types of vibrations. The \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum, in CD$_3$CN at 308 K, of 3.2 was unfortunately of poor quality but showed three sets of doublets in the carbonyl region of the spectrum at \(\delta\) 170.5 \((^2J_{\text{P.C}} = 10.0\ \text{Hz})\), 170.9 \((^2J_{\text{P.C}} = 11.0\ \text{Hz})\) and 171.9 ppm \((^2J_{\text{P.C}} = 5.8\ \text{Hz})\) in the ratio 4:11:12, respectively, with the latter two resonances being relatively broad. The two resonances at \(\delta\) 170.9 and 171.9 ppm of approximately equal relative intensity are attributed to the major isomer, and
the peak at δ 170.5 ppm due to the minor isomer, with the second resonance of the minor isomer being accidentally degenerate with a broad resonance from the major isomer. There is no evidence in the $^{13}$C{$^1$H} NMR spectrum of a large two bond carbon-phosphorus coupling, as observed in fac-2.2, that would suggest an isomer with a CO ligand trans to a PMe$_3$ group. The resonances assigned to the major isomer may be attributed to carbonyl ligands in two slightly different environments both of which are cis to a PMe$_3$ ligand. Further information, unfortunately, cannot be garnered from the $^{13}$C{$^1$H} NMR spectrum of 3.2.

Combining all the results discussed above, the two structures C and B (Figure 3.8) are believed to be the most likely forms for 3.2. In both cases the PMe$_3$ group is cis to both CO ligands; in structure B, the PMe$_3$ ligand is trans to a bridging Cl atom, while in structure C, it is trans to a terminal Cl atom. Both structures would give rise to two different $^{31}$P{$^1$H} and $^1$H NMR environments, yet in the IR spectrum the different ν(CO) bands for the two isomers would probably not be discernible in polar solvents such as CH$_2$Cl$_2$. It should, however, be noted that structure B can be formed from the fusion of two all cis-Os(CO)$_2$(PMe$_3$)(Cl)$_2$ units (where the Os atoms have octahedral coordination), present in the precursor fac-2.2. On the other hand, structure C contains a trans Cl-Os-PMe$_3$ (with the Cl nonbridging) that is not present in fac-2.2. For this reason, if rearrangement of the unsaturated fragment is neglected, structure B is tentatively believed to be the major isomer.
3.2.6 Investigation of the interconversion of the isomers of the complex Os(CO)$_3$(PMe$_3$)(Cl)$_2$ (2.2).

The conversion of *mer-cis-2.2* to *fac-2.2* and the possible role of 3.2 in the conversion was studied by NMR spectroscopy. A solution of *mer-cis-2.2* in CD$_3$CN at 308 K, with exclusion of light, was followed over time by $^{31}$P{$^1$H} and $^1$H NMR spectroscopy. The $^{31}$P{$^1$H} NMR spectra are shown in Figures 3.9 and 3.10. The $^{31}$P{$^1$H} NMR spectra were more informative because of the simplicity of the spectra, and because the $^1$H NMR resonance of *mer-cis-2.2* is coincident with a resonance of the solvent (CD$_3$CN, 1.93, pentet, $^2$J$_{D,H} = 2.5$ Hz). Assignments of the resonances were confirmed by comparing with the chemical shifts of the appropriate authentic compounds under the same conditions. The solutions were also examined with IR spectroscopy after the acquisition of the NMR spectra, see Table 3.5.

In the heating of *mer-cis-2.2* in CD$_3$CN at 308 K, the first significant change occurred after 2 h, when three new $^{31}$P{$^1$H} NMR resonances were observed. These are assigned to *fac-2.2* and the two isomeric forms of 3.2. After 4 h the resonances assigned to the three new species are quite distinct, see Figure 3.9. Over the time period of 0-18 h the major process observed is the conversion of *mer-cis-2.2* to *fac-2.2* with a minor process, the formation 3.2, see Figures 3.9 and 3.11.
Figure 3.9 The $^{31}$P{$^1$H} NMR spectra of \textit{mer-cis}-Os(CO)$_3$(PMe$_3$)(Cl)$_2$ (\textit{mer-cis-2.2}) in CD$_3$CN at 308 K over the time period 0-18 h. The peak marked with $\perp$ is assigned to the \textit{mer-cis} form; the peak marked with * is assigned to the \textit{fac} isomer; the signals marked with # are attributed to the two isomers of [Os(CO)$_2$(PMe$_3$)(Cl)(\mu-Cl)$_2$] (3.2).
Figure 3.10 The $^{31}\text{P}^{[\text{H}]}$ NMR spectra of mer-cis-Os(CO)$_3$(PMe$_3$)(Cl)$_2$ (mer-cis-2.2) in CD$_3$CN at 308 K over the time period 18-283 h. The peak marked with $\perp$ is assigned to the mer-cis form; the peak marked with $\ast$ is assigned to the fac isomer; the signals marked with $\#$ are attributed to the two isomers of [Os(CO)$_2$(PMe$_3$)(Cl)(\text{\mu}-Cl)]$_2$ (3.2).
Table 3.5 The $^1$H and $^{31}$P($^1$H) NMR and IR spectroscopic results of all the complexes pertinent to the heating of *mer-cis*-Os(CO)$_3$(PMe$_3$)(Cl)$_2$ (*mer-cis-2.2*) in CD$_3$CN at 308 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H NMR, ppm$^a$</th>
<th>$^{31}$P($^1$H) NMR, ppm$^a$</th>
<th>IR ν(CO) bands, $^b$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>mer-cis</em>-Os(CO)$_3$(PMe$_3$)(Cl)$_2$</td>
<td>1.93(d, CH$<em>3$, $^2$J$</em>{P,H}$ = 11.6 Hz)</td>
<td>-36.10(s, PMe$_3$)</td>
<td>2145(vw), 2066(s), 2019(m)</td>
</tr>
<tr>
<td>*fac-Os(CO)$_3$(PMe$_3$)(Cl)$_2$</td>
<td>1.77(d, CH$<em>3$, $^2$J$</em>{P,H}$ = 11.5 Hz)</td>
<td>-31.78(s, PMe$_3$)</td>
<td>2127(m), 2054(s), 2012(m)</td>
</tr>
<tr>
<td>[Os(CO)$_2$(PMe$_3$)(μ-Cl)(Cl)]$_2$</td>
<td>1.76(d, CH$<em>3$, $^2$J$</em>{P,H}$ = 11.8 Hz), 1.80 (d, CH$<em>3$, $^2$J$</em>{P,H}$ = 11.4 Hz)</td>
<td>-30.74(s,PM$_3$)</td>
<td>2047(s), 1971(s)</td>
</tr>
<tr>
<td>Os$_3$(CO)$_9$(PMe$_3$)$_3$</td>
<td>1.81(d, CH$<em>3$, $^2$J$</em>{P,H}$ = 10.2 Hz)</td>
<td>-58.20(s, PM$_3$)</td>
<td>1977(sh,m), 1965(vs,br), 1920(s)</td>
</tr>
<tr>
<td>PMe$_3$</td>
<td>0.97(d, CH$<em>3$, $^2$J$</em>{P,H}$ = 1.6 Hz)</td>
<td>-60.53(s, PM$_3$)</td>
<td></td>
</tr>
<tr>
<td>OPMe$_3$</td>
<td>1.38(d, CH$<em>3$, $^2$J$</em>{P,H}$ = 13.2 Hz)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>2.21(s, H$_2$O)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ In CD$_3$CN at 308 K. $^b$ In CH$_2$Cl$_2$ at room temperature (i.e., samples were removed from the reaction solution, CD$_3$CN removed and the remaining solid dissolved in CH$_2$Cl$_2$).
Figure 3.11 A plot of the integrated peak area the $^{31}\text{P}\{^1\text{H}\}$ NMR resonance of $\text{mer-cis-}$
$\text{Os(CO)}_3(\text{PMe}_3)(\text{Cl})_2$ (mer-cis-2.2), $\text{fac-}$
$\text{Os(CO)}_3(\text{PMe}_3)(\text{Cl})_2$ (fac-2.2) or
$[\text{Os(CO)}_2(\text{PMe}_3)(\text{Cl})(\mu-\text{Cl})]_2$ (3.2) in CD$_3$CN, at 308 K with respect to time.

After 47 h the $^{31}\text{P}\{^1\text{H}\}$ NMR resonance due to $\text{mer-cis-2.2}$ was undetectable (Figure
3.10). The $^{31}\text{P}\{^1\text{H}\}$ NMR resonance due to $\text{fac-2.2}$ was also drastically reduced and the
major signals present were due to the two isomeric forms of 3.2. After 283 h the only
detectable resonances were those due to 3.2. An IR spectrum of the ν(CO) region of this
sample in CH$_2$Cl$_2$ showed only two bands at, 2047(s) and 1971(s) (Table 3.5). Samples of
PMe$_3$, OPMe$_3$, H$_2$O, 3.1 were examined with $^{31}\text{P}\{^1\text{H}\}$ and $^1\text{H}$ NMR to determine if these
species were present in the reaction of $\text{mer-cis-2.2}$ in CD$_3$CN, at 308 K, see Table 3.5. All
of these control experiments demonstrated that no other species except mer-cis-, fac-2.2 and 3.2 were present.

![Chemical Structures]

**Figure 3.12** The structures of the isomers of Ru(CO)$_2$(PMe$_2$Ph)(Cl)$_2$.\textsuperscript{132}

It has previously been established that all-trans-Ru(CO)$_2$(PMe$_2$Ph)$_2$(Cl)$_2$ isomerizes to the thermodynamic product, cis- Ru(CO)$_2$(PMe$_2$Ph)$_2$(Cl)$_2$ (Figure 3.12).\textsuperscript{132} Furthermore, it was demonstrated that in CH$_3$CN the all-trans-Ru(CO)$_2$(PMe$_2$Ph)(Cl)$_2$ species forms Ru(CO)(PMe$_2$Ph)(NCMe)(Cl)$_2$ exclusively in the cis-arrangement.\textsuperscript{132} In the present study there was no $^1$H, $^{31}$P({$^1$H}) NMR and IR spectroscopic evidence for Os(CO)$_2$(PMe$_3$)(NCCD$_3$)(Cl)$_2$ in the isomerization of mer-cis-2.2 in CD$_3$CN. Obviously more detailed studies are required but, although not strong evidence, that Os(CO)$_2$(PMe$_3$)(NCCD$_2$)(Cl)$_2$ is not observed suggests that the isomerization of mer-cis-2.2 to fac-2.2 goes via a nondissociative mechanism. If this is the case, the most probable mechanism for the rearrangement is the trigonal twist mechanism, shown in Figure 3.13.

Trigonal twist mechanisms have been implicated in the isomerization of a number of related complexes, for example Cr(CO)$_2$(CY)[P(OMe)$_3$]$_3$ (Y = S, Se).\textsuperscript{134} Ru(CO)(H)$_2$(PPh$_3$)$_3$.\textsuperscript{135}
Figure 3.13 The trigonal twist mechanism to account for the conversion of mer-cis to fac-Os(CO)$_3$(PMe$_3$)(Cl)$_2$.

As in [Cs]$^+$(Os(CO)$_3$(Cl)$_3$)$^-$_{136}, Os(CO)$_2$(PPh$_3$)$_2$(Cl)$_2$,$_{115b}$ and Ru(CO)$_2$(PMe$_2$Ph)$_2$(Cl)$_2$,$_{132}$ the thermodynamically preferred form of 2.2 is the isomer with the carbonyl ligands mutually cis to each other, that is fac-2.2. This configuration minimizes the competition by the carbonyl ligands for the $\pi$-electron density at the metal center. In other words, in the most stable form of 2.2 there is either a weak $\pi$-acceptor ligand (PMe$_3$) or $\pi$-donor ligand (Cl) trans to each of the $\pi$-acceptor carbonyl groups.

Furthermore, the results suggest that 3.2 is formed from fac-2.2 via initial loss of a CO ligand to give [Os(CO)$_2$(PMe$_3$)(Cl)$_2$] that is probably stabilized by solvent interaction. Rapid dimerization of the solvated fragments would then yield the observed product.

3.2.7 Tentative identification of the complex, fac-Os(CO)$_3$(PMe$_3$)(CCl$_3$)(Cl) (fac-2.3).

The irradiation ($\lambda \geq 400$ nm) of Os(CO)$_4$(PMe$_3$) in C$_6$H$_6$ in the presence of CCl$_4$, or stirring a solution of Os(CO)$_4$(PMe$_3$) in C$_6$H$_6$ in the presence of CCl$_4$ at room temperature, in the absence of light for 18 h, gives a product with three $\nu$(CO) bands in the IR spectrum at 2118(m), 2054(s), 2010(s) cm$^{-1}$ in C$_6$H$_6$. The frequencies and intensities of these bands
are extremely similar to those of \textbf{fac-2.2} in C$_6$H$_6$ (2126(m), 2050(s), 2004(s) cm$^{-1}$). It also resembles the spectrum of Fe(CO)$_3$(PPh$_3$)(C$_3$F$_7$)(I): 2103(w), 2051(s), 2035(m) (in C$_2$Cl$_4$).$^{137}$ It is therefore tentatively proposed that the new species is \textit{‘fac-Os(CO)$_3$(PM$_3$)(CCl$_3$)(Cl)’} (\textbf{fac-2.3}). Repeated attempts to purify this compound for thorough characterization were unsuccessful. Complexes such as [M(CCl$_3$)(Cl)(CO)(PPh$_3$)$_3$] (M = Ru, Os) have been proposed as intermediate species in the production of M(Cl)$_2$(=CCl$_2$(CO)(PPh$_3$)$_2$ but have resisted all attempts at isolation.$^{90}$ The instability of these CCl$_3$ intermediates was suggested to be due to spontaneous chloride loss or some other rearrangement occurring.$^{90c}$ In order to garner information about the identity of the proposed species, the complex was generated in situ and examined with $^1$H NMR spectroscopy, (Table 3.6). When Os(CO)$_4$(PM$_3$) was irradiated ($\lambda \geq 400$ nm) in C$_6$H$_6$ for 3 h no other species were observed except the starting material. This strongly suggests that Os(CO)$_3$(PM$_3$)(H)(C$_6$H$_5$) (which might then lead to Os(CO)$_3$(PM$_3$)(Cl)(C$_6$H$_5$) in the presence of CCl$_4$) was not formed this experiment also indicates that Os(CO)$_3$(PM$_3$) (\textit{\eta}$_2$-C$_6$H$_6$) was also probably not produced. The photolysis ($\lambda \geq 400$ nm) of Os(CO)$_4$(PM$_3$) in C$_6$H$_6$ in the presence of an excess of CCl$_4$ (10 drops) for 2 h showed by $^1$H NMR and IR spectroscopy that a new compound was formed. This could, as mentioned previously, be tentatively assigned as \textbf{fac-2.3}. On standing for 2 days in the dark at room temperature, it converted to \textbf{fac-2.2}, as demonstrated by IR spectroscopy. That the photogenerated species readily converts to the complex, \textbf{fac-2.2} might suggest that the compounds are similar. The irradiation ($\lambda \geq 400$ nm) of Os(CO)$_4$(PM$_3$) in C$_6$H$_6$, in the presence of an excess of CH$_2$Cl$_2$ (10 drops) for 2 h showed no reaction by $^1$H NMR and IR spectroscopy. The $^1$H NMR
Table 3.6 Experiments to investigate the products of the photolysis ($\lambda \geq 400$ nm) of Os(CO)$_4$(PMe$_3$) in C$_6$H$_6$ in the presence of CCl$_4$.

<table>
<thead>
<tr>
<th>Compound(s)</th>
<th>$^1$H NMR, $^a$ ppm Before photolysis</th>
<th>$^1$H NMR, $^b$ ppm After Photolysis</th>
<th>IR v(CO) bands after photolysis, $^a$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(CO)$_4$(PMe$_3$)</td>
<td>0.93 (d, CH$<em>3$, $^2$J$</em>{P-H}$ = 10.4 Hz)</td>
<td>0.92 (d, CH$<em>3$, $^2$J$</em>{P-H}$ = 10.4 Hz)</td>
<td>2058(m), 1975(m), 1931(s)</td>
</tr>
<tr>
<td>Os(CO)$_4$(PMe$_3$) + CCl$_4$</td>
<td>1.02 (d, CH$<em>3$, $^2$J$</em>{P-H}$ = 10.3 Hz))</td>
<td>1.04 (d, CH$<em>3$, $^2$J$</em>{P-H}$ = 10.4 Hz))</td>
<td>2118(m), 2054(s), 2010(s)</td>
</tr>
<tr>
<td>Os(CO)$_4$(PMe$_3$) + CH$_2$Cl$_2$</td>
<td>1.04 (d, CH$<em>3$, $^2$J$</em>{P-H}$ = 10.4 Hz)</td>
<td>1.04 (d, CH$<em>3$, $^2$J$</em>{P-H}$ = 10.4 Hz)</td>
<td>2058(m), 1975(m), 1930(s)</td>
</tr>
<tr>
<td>Os$_3$(CO)$_9$(PMe$_3$)$_3$</td>
<td>1.43 (d, CH$<em>3$, $^2$J$</em>{P-H}$ = 9.9 Hz)</td>
<td></td>
<td>2049(vw), 1978(w,sh), 1968(vs), 1978(sh), 1923(s), 1915(w,sh)</td>
</tr>
<tr>
<td>mer-cis-</td>
<td>0.76 (d, CH$<em>3$, $^2$J$</em>{P-H}$ = 10.9 Hz)</td>
<td></td>
<td>2064(s), 2010(m)</td>
</tr>
<tr>
<td>Os(CO)$_3$(PMe$_3$)(Cl)$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fac-Os(CO)$_3$(PMe$_3$)(Cl)$_2$</td>
<td>0.99 (d, CH$<em>3$, $^2$J$</em>{P-H}$ = 11.2 Hz)</td>
<td></td>
<td>2126(m), 2049(s), 2004(s)</td>
</tr>
</tbody>
</table>

$^a$ In C$_6$H$_6$ at room temperature. $^b$ The duration of the photolysis is given prior to the NMR data.
spectra of 3.1, *mer-cis*- and *fac-2.2* in C\textsubscript{6}H\textsubscript{6} indicate that none of these complexes are initially formed upon the irradiation of Os(CO)\textsubscript{4}(PMe\textsubscript{3}) in C\textsubscript{6}H\textsubscript{6}, in the presence of CCl\textsubscript{4}. Both the IR and \textsuperscript{1}H NMR spectrum of the initial photoproduct do, however, suggest that it is similar to *fac-2.2*.

An alternate possibility is the initial photoproduct is Os(CO)\textsubscript{2}(PMe\textsubscript{3})(CC\textsubscript{1}2)(Cl)\textsubscript{2}. The species Fe(CO)\textsubscript{5}(CC\textsubscript{1}2)(Cl)\textsubscript{2} is proposed as the product of the photochemical reaction of Fe(CO)\textsubscript{5} with CCl\textsubscript{4}.\textsuperscript{89} The compound Os(CO)(PPh\textsubscript{3})\textsubscript{2}(CC\textsubscript{1}2)(Cl)\textsubscript{2} is also well characterized.\textsuperscript{90b} Such a complex, however, would be expected to exhibit two ν(CO) bands in the solution IR spectrum which is not the case. Likewise, a dimeric species such as 3.2 if present, would also be expected to show two ν(CO) bands in the solution IR spectrum and hence this compound can also be eliminated from further consideration. Other possibilities are [Os(CO)\textsubscript{4}(PMe\textsubscript{3})(X)]\textsuperscript{+}[Cl]\textsuperscript{-} (X = CCl\textsubscript{3}, Cl). These compounds would be analogous to the complex, [Os(CO)\textsubscript{4}(PMe\textsubscript{3})(CH\textsubscript{3})]\textsuperscript{+}[I]\textsuperscript{-}, whose IR spectrum ν(CO) bands are 2158(s), 2098(s), 2071(vs) cm\textsuperscript{-1} in CH\textsubscript{2}Cl\textsubscript{2}.\textsuperscript{117} The ligands CCl\textsubscript{3} and Cl are more electron withdrawing than the CH\textsubscript{3} group and therefore the IR ν(CO) frequencies would be expected to be much higher than those for the methyl derivative which is not observed. Given that Os(CO)\textsubscript{3}(PMe\textsubscript{3})(CH\textsubscript{3})(Cl) has IR ν(CO) bands at, 2097(s), 2027(s), 1982(s) cm\textsuperscript{-1} in \textit{n}-hexane\textsuperscript{117} it would seem to further support the idea that the identity of the photoproduct is Os(CO)\textsubscript{3}(PMe\textsubscript{3})(CC\textsubscript{1}3)(Cl) (i.e., a similar spectrum to the methyl derivative but with the ν(CO) bands at higher frequencies).

The \textsuperscript{13}C{\textsuperscript{1}H} NMR spectrum of \textsuperscript{13}CO-labeled Os(CO)\textsubscript{4}(PMe\textsubscript{3}) in C\textsubscript{6}D\textsubscript{6} at room temperature in the presence of an excess of CCl\textsubscript{4} (10 drops), was run before and after irradiation (λ ≥ 400 nm) for 3 h. The rather poor \textsuperscript{13}C{\textsuperscript{1}H} NMR spectrum of the product,
showed that the carbonyl resonance (189.6 ppm) due to Os(CO)$_4$(PMe$_3$) had been replaced by three major resonances at $\delta$ 169.3 (CO, $^2J_{P-C} = 100.6$ Hz), 170.2 (CO, $^2J_{P-C} = 7.6$ Hz), 170.8 (CO, $^2J_{P-C} = 7.8$ Hz). Unfortunately, the poor signal-to-noise ratio prohibited a meaningful integration of the peak areas of the signals. The spectrum is, however, consistent with fac-2.3. The chemical shifts are similar to those observed for 3.2 and mer-cis- and fac-2.2, even allowing for the change in solvents, and the relatively large two bond carbon-phosphorus coupling indicates a CO ligand trans to the PMe$_3$ group.

Although a complete characterization of fac-2.3 has not been possible the available spectroscopic evidence supports this formulation. It has also been shown, that the new species observed is probably not 3.2, Os(CO)$_3$(PMe$_3$)(H)(C$_6$H$_5$), Os(CO)$_3$(PMe$_3$)(Cl)(C$_6$H$_5$), Os(CO)$_3$(PMe$_3$)(\eta^2-C_6H$_6$), Os(CO)$_2$(PMe$_3$)(CCl$_2$)(Cl)$_2$, or [Os(CO)$_4$(PMe$_3$)(X)]$^+$[Cl]$^-$ (X = CCl$_3$, Cl).

3.3 Conclusion

In this chapter, descriptions of the preparation of [Bu$^t$$_4$N]$_2$[2.4] and 3.1 (with improved yields), and the new complexes mer-cis-2.2, fac-2.2 and 3.2 are described. The stereochemistry of the new molecules has been determined in the solid state (for the mononuclear complexes) by X-ray crystallography, and in solution by IR and NMR spectroscopy. The characterization of fac-2.2 was essential for the mechanistic work described in Chapter 2. The complex, mer-cis-2.2 has been demonstrated by an NMR study to convert into fac-2.2 which then loses a CO ligand to form 3.2. The species formed upon the irradiation ($\lambda \geq 400$ nm) of Os(CO)$_4$(PMe$_3$) in C$_6$H$_6$ in the presence of CCl$_4$ has been
tentatively identified as **fac-2.3** again, a species of importance to the mechanistic discussions in Chapter 2.

### 3.4 Experimental

#### 3.4.1 General Methods

Manipulations, solvent purification, and routine spectroscopic measurements were carried out as described in Chapter 2 (Section 2.4). Only previously unmentioned experimental details will be mentioned from this point in the text onwards.

#### 3.4.2 Materials

Toluene (Mallinckrodt) was distilled from potassium; 1,4-dimethylbenzene (Aldrich) was distilled from sodium. Propan-2-ol (BDH) was refluxed with CaO and distilled; and then further refluxed with CaH₂ and distilled again. Tetrabutylammonium iodide [Bu⁴N][I] (Aldrich) was recrystallized from C₆H₆ and stored in a dessicator. The NMR solvents were CD₂Cl₂ (Cambridge Isotope Laboratories), CD₂Cl₂/CH₂Cl₂ (1:3), CD₃CN (Matheson), and C₇D₈ (Merck Sharpe Dohme). They were stored in the dry box and used as received. Carbon-13 CO (Isotec; 99.5 atom % ^13C and 10.1 atom % ^18O) was used in the labeling of complexes with ^13CO. Samples to be examined with ^1H NMR spectroscopy before and after photolysis were contained in NMR tubes (Wilmad) fitted with a J. Young valve.
3.4.3 Instrumentation

All NMR data were recorded at the specified temperatures on a Bruker AMX 400 instrument at an operating frequency of 161.98 and 100.61 MHz for $^{31}$P and $^{13}$C nuclei, respectively. Carbon-13 NMR chemical shifts are reported in ppm downfield (positive) of tetramethylsilane. The chemical shifts for $^{31}$P NMR are referenced to external 85% H$_3$PO$_4$. A cooling unit containing liquid nitrogen and a heater coil was attached to the NMR probe and was used to attain the desired temperatures at 273 K or lower.

Mass spectra (MS) were obtained with a Hewlett-Packard Model 5985 mass spectrometer. Spectra were determined in the EI (70 eV), CI (isobutane) or FAB mode (FAB, Phrasor Scientific Inc. accessory, m-nitrobenzyl alcohol, xenon). For molecules of molecular mass above 1000 $m/z$ the MS were obtained on a Kratos-MS-50 instrument (at the University of British Columbia, regional facility). The pattern of the envelope of ions for the parent ion or the species of highest mass matched the computer simulated pattern for all complexes considered. Microanalyses were performed by the Simon Fraser University Microanalytical Laboratory.

3.4.4 Syntheses

Although details have been given in prior publications of the preparation and characterization of $[\text{Bu}''\text{N}]_2[2.4]$\textsuperscript{93} and 3.1,\textsuperscript{114} modified procedures are given here for thoroughness and as future reference.

**Preparation of $[\text{Bu}''\text{N}]_2[\text{W}_2(\text{CO})_{10}]$ ($[\text{Bu}''\text{N}]_2[2.4]$).** Graphite flakes (Aldrich, 0.414g, 3.45 x $10^{-2}$ mol) were placed in a Pyrex Carius tube, under Ar, with a glass stir bar
and heated to 433 K with stirring, in a graphite flake bath, for 20 min. To the vessel at room temperature was added fleshly cut potassium (MCB, 0.165 g, 4.22 mmol) in a dry box to give the potassium-graphite laminate, C₈K. To C₈K, under Ar, THF (5 mL) was added and the slurry stirred at room temperature. A solution of W(CO)₆ (8.26 x 10⁻² M) in THF (50 mL) was added to the C₈K slurry via a cannula and stirred at room temperature under Ar for 1-2 h, until the evolution of CO ceased and the solid was observed to go from bronze to silver-gray in color. The slurry was filtered under Ar into a Schlenk tube via a cannula to yield a yellow-orange solution of [K]₂[2.4] and unreacted W(CO)₆. The solvent was removed on the vacuum line and the W(CO)₆ extracted by sublimation (1.3 Pa) to a cold water probe. The residual [K]₂[2.4] was redissolved in deoxygenated THF (20 mL) and transferred via cannula to a solution of [Bu‴₂N][I] (1.55 g, 4.20 mmol) in deoxygenated THF (70 mL) and stirred for 16 h at room temperature in the dark under Ar. The mixture was filtered to remove KI. The solvent was removed on the vacuum line. Propan-2-ol was added to the remaining yellow-orange solid, {[Bu‴₂N]₂[2.4]} is virtually insoluble in propan-2-ol whereas [Bu‴₂N][I] is extremely soluble and any KI is soluble. The slurry was filtered and the residual [Bu‴₂N]₂[2.4] washed with fresh propan-2-ol, vigourously dried and collected. Bright yellow, air sensitive, powderous [Bu‴₂N]₂[2.4] (1.30 g, 56% yield) was identified by comparison to the literature, IR spectrum (CH₃CN), ν(CO): 1940(m), 1891(vs), 1788(s) cm⁻¹; (THF), ν(CO): 1941(m), 1888(vs), 1789(s) cm⁻¹.93

Preparation of Os₅(CO)₉(PMe₃)₃ (3.1). A slurry of Os₅(CO)₁₂ (0.700 g, 0.772 mmol) in 1,4-dimethylbenzene (10 mL) was prepared in a Pyrex Carius tube, to which was added PMe₃ (0.30 mL, 2.90 mmol) and additional 1,4-dimethylbenzene (10 mL). The reaction vessel was sealed under N₂ and heated at 403 K with stirring for 6 h to give a clear,
deep-orange solution. The solvent and excess PMe3 were removed under vacuum. The products of the reaction were: 3.1, Os(CO)₄(PMe₃) and Os(CO)₃(PMe₃)₂, as identified by IR spectroscopy. The complex Os(CO)₄(PMe₃) (0.150 g) was obtained by sublimation (1.3 Pa) at 293-313 K to a probe cooled by cold water or it could also be separated by column chromatography (silica gel, 20 x 1 cm, C₆H₁₄/CH₂Cl₂). The mononuclear product Os(CO)₃(PMe₃) was abstracted by sublimation (1.3 Pa) at 343-363 K to a probe at 195 K. Attempted chromatography on a silica gel column (silica gel, 20 x 1 cm, C₆H₁₄/CH₂Cl₂) was unsuccessful. (It is known that Os(CO)₃(PMe₃), reacts with O₂ to produce Os(CO)₂[O(CO)O](PMe₃)₂.) The crude 3.1 obtained after removal of Os(CO)₄(PMe₃) and Os(CO)₃(PMe₃)₂ was purified by recrystallization from C₆H₁₄/C₆H₅CH₃. In this way 3.1 (0.250 g, 31% yield) was obtained as orange air-stable crystals. For the ¹³C{¹H} NMR experiments ¹³CO-labeled 3.1 was prepared in an identical manner to the unlabeled cluster except ¹³CO-labeled Os₃(CO)₁₂ was employed (typically 46-49% ¹³C-enriched; see Appendix A-1 for further explanation of how the enrichment was determined by mass spectroscopy). For 3.1: IR (C₆H₁₄), ν(CO): 1988(m,sh), 1975(s), 1932(m), 1920(m,sh) cm⁻¹; (CH₂Cl₂), ν(CO): 1977(sh,m), 1965(vs,br), 1920(s) cm⁻¹; ¹H NMR (CD₂Cl₂, 233 K): δ 1.78 (d, PMe₃, ²J_P-H = 10.0 Hz); ³¹P{¹H} NMR (CD₂Cl₂, 233 K): δ -58.62 (s, PMe₃); ¹³C{¹H} NMR (CD₂Cl₂/CH₂Cl₂ 1:3, 233 K): δ 23.19 (d, PMe₃, ¹J_P-C = 37.2 Hz), 183.55 (s, 3C, CO), 196.68 (s, 6C, CO); MS (EI, m/z): 1052 (M⁺); Anal. Calcd. for C₁₈H₂₇O₉Os₃P₃: C, 20.57; H, 2.59. Found: C, 20.72; H, 2.61.

Preparation of mer-cis-Os(CO)₃(PMe₃)(Cl)₂ (mer-cis-2.2). To 3.1 (0.090 g, 0.086 mmol) in C₆H₅CH₃ (15 mL) was added 4 mL of a saturated solution of Cl₂ in C₆H₅CH₃ at 273 K. The solution instantly went opaque red-orange and then rapidly (≈ 10 s) altered to a
pale yellow solution (presumably due to the excess Cl₂) along with a fine white precipitate. The mixture was stirred for a further 10 min with no apparent change, the solvent was reduced to a minimum by evacuation and C₆H₁₄ (10 mL) was added to the mixture to complete the precipitation. An IR spectrum in CH₂Cl₂ (ν(CO) region) of the supernatant indicated the presence of fac-2.2 and trace amounts of 3.2 in the solution. The supernatant was removed and the remaining white solid washed several times with C₆H₁₄. The crude white solid was recrystallized from THF/C₆H₁₄ to afford colorless crystals of mer-cis-2.2 (0.095 g, 88% yield). The ¹³CO-labeled mer-cis-2.2 was prepared in an identical manner from ¹³CO-labeled 3.1. For mer-cis-2.2: IR (CH₂Cl₂), ν(CO): 2145(vw), 2066(s), 2019(m) cm⁻¹; (C₆H₆), ν(CO): 2064(s), 2010(m) cm⁻¹; (nujol), ν(Os-Cl): 310(m), 279(s) cm⁻¹; ¹H NMR (CD₂Cl₂, rm. temp.): δ 1.96 (d, CH₃, ²J₃₋₅ =11.0 Hz); ³¹P{¹H} (CD₂Cl₂, rm. temp.): δ -38.42 (s, PMe₃); ¹³C{¹H} (CD₂Cl₂/CH₂Cl₂ 1:3, 233 K): δ 18.12 (d, CH₃, ¹J₃₋₅ = 42.3 Hz), 167.23 (d, 1C, CO, ²J₃₋₅ = 6.9 Hz), 172.42 (d, 2C, CO, ²J₃₋₅ = 7.6 Hz); MS (El, m/z): 422 (M⁺); mp: at 392 K the colorless crystals became opaque and there was no further change to 423 K; Anal. Calcd. for C₆H₉Cl₂O₃OsP: C, 17.11; H, 2.15. Found: C, 17.14; H, 2.09.

Preparation of fac-Os(CO)₃(PMe₃)(Cl)₂ (fac-2.2). A solution of mer-cis-2.2 (0.140 g, 0.332 mmol) in THF (15 mL) was allowed to stir at room temperature in the dark under N₂ for 9 days. After this time the IR ν(CO) bands due to mer-cis-2.2 were no longer present in the solution and had been replaced by the IR ν(CO) bands of fac-2.2, and much weaker bands due to 3.2 (see below). The solution was evaporated to dryness under vacuum. The remaining white solid was chromatographed on a silica gel column (1 x 20 cm); the fac-2.2 was eluted with CH₂Cl₂/C₆H₁₄ (4/1) and the 3.2 (0.010 g, 8%) with CH₂Cl₂. The crude, white solid of fac-2.2 (0.095 g, 68%) was recrystallized from
C₆H₄/C₆H₅CH₃ to afford colorless crystals. The ¹³CO-labeled fac-2.2 was prepared in an identical manner from ¹³CO-labeled mer-cis-2.2. For fac-2.2: IR (C₆H₁₄), ν(CO): 2126(m), 2048(m), 2005(m) cm⁻¹; (CH₂Cl₂), ν(CO): 2127(m), 2054(s), 2012(m) cm⁻¹; (CH₃CN), ν(CO): 2128(m), 2054(s), 2012(s) cm⁻¹; (C₆H₆), ν(CO): 2126(m), 2050(s), 2004(s) cm⁻¹; (nujol), ν(Os-Cl): 318(s), 296(s) cm⁻¹; ¹H NMR (CD₂Cl₂, rm. temp.): δ 1.81 (d, CH₃, ²Jₚ,H = 11.2 Hz); ³¹P{¹H} (CD₂Cl₂, rm. temp.): δ -33.59 (s, PMe₃); ¹³C{¹H} (CD₂Cl₂/CH₂Cl₂ 1:3, 233 K): δ 12.60 (d, CH₃, ¹Jₚ,C = 40.4 Hz), 167.22 (d, 2C, CO, ²Jₚ,C = 9.2 Hz), 167.96 (d, 1C, CO, ²Jₚ,C = 107.6 Hz); MS (EI, m/z): 422 (M⁺), (CI, m/z): 387 [(M-Cl)⁺]; mp: at 392 K the colorless crystals became opaque and there was no further change to 473 K; Anal. Calcd. for C₆H₅Cl₂O₃OsP: C, 17.11; H, 2.15. Found: C, 17.30; H, 2.16.

Preparation of [Os(CO)₂(PMe₃)(Cl)(µ-Cl)]₂ (3.2). A solution of mer-cis-2.2 (0.020 g, 0.048 mmol) in C₆H₅CH₃/CH₃CN (15 mL, 2/1 v/v, respectively) was stirred in the dark at 323 K for 18 h. After this period, the IR ν(CO) bands for mer-cis-2.2 were no longer present in the solution and the sole product, as suggested by the IR ν(CO) bands present, was 3.2. The solution was evaporated to dryness on the vacuum line and the white solid recrystallized from C₆H₅CH₃/CH₂Cl₂ to afford small white star-shaped crystals of 3.2 (0.010 g, 54% yield). Repeated attempts to grow crystals suitable for crystallographic analysis were unsuccessful. The ¹³CO-labeled 3.2 was prepared from ¹³CO-labeled mer-cis-2.2. For 3.2: IR (CH₂Cl₂), ν(CO): 2050(s), 1983(s) cm⁻¹; (CH₃CN), ν(CO): 2047(s), 1971(s) cm⁻¹; (nujol), ν(Os-Cl): 314(m), 273(m), 242(m) cm⁻¹; ¹H NMR (CD₃CN, 308 K): δ 1.76 (d, CH₃, ²Jₚ,H = 11.7 Hz), 1.80 (d, CH₃, ²Jₚ,H = 11.7 Hz), the relative ratio of the integrated areas of the peaks was 3:1, respectively; ³¹P{¹H} (CD₃CN, 308 K): δ -30.73 (s,
PMe₃), -30.37 (s, PMe₃), the relative ratio of the integrated areas of the peaks was 3:1, respectively; $^{13}$C{$^1$H} (CD₂Cl₂/CH₂Cl₂ 1:3, 233 K): δ 15.5 (d, PMe₃, $^1J_{P/C}$ = 43.1 Hz), 170.5 (d, 4C, CO, $^2J_{P/C}$ = 10.0 Hz), 170.9 (d, br, 11C, CO, $^2J_{P/C}$ = 11.0 Hz), 171.9 (d, br, 12C, CO, $^2J_{P/C}$ = 5.8 Hz); Mass Spec. (E. I., m/z): 753 (M⁺-Cl); mp: 530 K decomposition; Anal. Calcd. for C₁₀H₁₆Cl₄O₄Os₂P₂: C, 15.27; H, 2.31. Found: C, 15.75; H, 2.38.

Experiments to investigate the identity of the species proposed as 'fac-Os(CO)$_3$(PMe₃)(Cl)$_2$' (fac-2.3). Typically 5 x 10⁻³ - 1.0 x 10⁻² g of Os(CO)$_4$(PMe₃) were placed in a vial, in the dry box, in minimal light and to this was added C₆H₆ (0.5 mL) and, depending on the experiment, an excess (10 drops) of CCl₄. This mixture was then filtered and transferred to a 5 mm NMR tube fitted with a J. Young valve. The room temperature sample was maintained in the absence of light and a $^1$H NMR spectrum obtained of the sample with a presaturation pulse program on a Bruker AMX 400 spectrometer. The air-cooled sample was then photolysed (200W medium pressure mercury arc lamp, water and air cooled) through a CS 3-74 filter (λ ≥ 400 nm) for 2-3 h. The $^1$H NMR spectrum was reacquired. Immediately following this procedure an IR spectrum of the sample was obtained in C₆H₆.

Molecular structure of mer-cis-Os(CO)$_3$(PMe₃)(Cl)$_2$ (mer-cis-2.2). X-ray quality crystals of mer-cis-2.2 proved difficult to grow as the complex has a tendency to form crystals that are of the appropriate size in only two dimensions (i.e., platelike). This problem was overcome by dissolving mer-cis-2.2 in a minimum amount of THF in an NMR tube and layering C₆H₁₄ on top of the THF and placing the NMR tube within a Schlenk tube filled with N₂ in the freezer (at ~ 233 K). The crystal structure analysis of mer-cis-2.2 was determined by Professor F. W. B. Einstein and Dr. W. K. Leong at Simon
Fraser University. The crystal structure was determined to be monoclinic, with the space group $P2_1/n$ and an asymmetric unit containing one crystallographically distinct molecule.

**Molecular structure of $\text{fac-Os(CO)}_3(\text{PMe}_3)(\text{Cl})_2$ ($\text{fac-2.2}$).** X-ray quality crystals of $\text{fac-2.2}$ also proved difficult to grow for the same reasons as the $\text{mer-cis}$ isomer. This problem was overcome by dissolving the compound in a minimum amount of $\text{C}_6\text{H}_5\text{CH}_3$ in an NMR tube and placing the NMR tube within a Schlenk flask charged with $\text{C}_6\text{H}_{14}$. The vessel and the contents were frozen and evacuated and allowed to warm slowly to room temperature, allowed to stand for a day at room temperature before placing the Schlenk tube in the freezer ($\sim 233$ K) to afford suitable crystals. The crystal structure analysis of $\text{fac-2.2}$ was also determined by Professor F. W. B. Einstein and Dr. W. K. Leong at Simon Fraser University. The crystal structure was determined to be monoclinic, with the space group $P2_1/n$ and a unit cell containing two crystallographically distinct molecules.
CHAPTER 4

Investigation of the acceptor ability of acceptor fragments

4.1 Introduction

Several complexes with a donor-acceptor metal-metal bond have been prepared in our laboratory but there were very few studies of a comparative nature between these compounds under exacting conditions. Unlike the complexes (Me₃P)(OC)₄OsM(CO)₅ (M = Cr, Mo, W) (2.1, 4.1, 4.2) in the compounds (OC)₄(Bu'NC)OsM(CO)₅ (4.3-4.5) the noncarbonyl ligand (CNBu') ligand is cis to the dative M-M bond and therefore there is a CO ligand trans to this bond. The ¹³C NMR resonance of this CO ligand appears at unusually high fields relative to the resonances of all the other carbonyl ligands in these complexes.

For mononuclear complexes the basicities of metal fragments M(CO)ₓ(L)ᵧ had been probed by enthalpies of protonation, the IR CO stretching frequencies, the ¹³C NMR chemical shifts of the carbonyl ligands, the ³¹P NMR chemical shift of phosphorus containing ligands, and the wavelength of the UV-absorption of transitions associated with the metal center.

In [(Dnr)M(CO)₅] (Dnr = cis-[(H)W(CO)₄P(OMe)₃], [(H)W(CO)₅]⁻, [(H)Cr(CO)₅]⁻, trans-[(H)Fe(CO)₃P(OMe)₃], [Mn(CO)₅]⁻, [(H)Fe(CO)₄]⁻; M = Cr, W) complexes which contain a donor-acceptor metal-metal bond the relative ligating ability of the donor fragments had been examined using competition reactions and IR CO stretching frequencies.
From theoretical calculations on \((OC)_5OsM(CO)_5\) \((M = \text{Cr, W})\) it was suggested that "When the dative metal-metal bond is formed, the electron transfer is not restricted to the metal-metal region, but occurs from the whole Os(CO)_5 to the whole of M(CO)_5 \((M = \text{W, Cr})\) including all the radial CO ligands."\(^{53}\) This suggests that all the ligands on both the donor and acceptor fragments might provide a relative measure of the dative interaction.

In the literature a scale of both a donor number and an acceptor number has been proposed based on the interaction of solvents with a specific donor or acceptor complex, with the higher the numerical value, the better donor or acceptor.\(^{159,160}\) The donor number was defined as the molar enthalpy value for the reaction of the donor with SbCl_5 or the \(^{23}\)Na NMR chemical shift of NaClO_4 in the respective solvent.\(^{159}\) While the acceptor number was based on the \(^{31}\)P NMR chemical shift in Et_3PO in the respective solvent.\(^{159}\) In the development of the acceptor number it was suggested that the \(^{31}\)P NMR chemical shift in the complex Et_3PO was ideal because the probe nucleus was remote from the actual center of interaction and the phosphorus atom occupies a well defined site.\(^{159}\)

In our binuclear complexes there is a donor-acceptor metal-metal interaction. It was thought, analogously, by using the identical donor fragment \(((OC)_4(Bu^1NC)Os\) or \((\text{Me}_3\text{P})(OC)_4Os)\) in each binuclear species the carbonyl and/or isocyanide or phosphine sites would be well defined and invariant while remote from the actual Os-Acc (Acc = acceptor metal fragment) interaction. This idea considered in conjunction with the shift to high field (relative to all the other carbonyl ligands \(^{13}\)C NMR resonances) of the \(^{13}\)C NMR resonance of the CO ligand \textit{trans} to the metal-metal bond in 4.3-4.5 might be viewed to be an indication of the acceptor ability of the acceptor fragment. New complexes with a donor-acceptor metal-metal bond with both \((OC)_4(Bu^1NC)Os\) and \((\text{Me}_3\text{P})(OC)_4Os\) as the
donor fragments have therefore been synthesized to test this proposal. The acceptor moieties were systematically altered and the systems examined with $^1$H, $^{13}$C, $^{31}$P NMR, IR, UV-vis spectroscopies in order to try to establish the relative acceptor abilities of the acceptor fragments. A development of such a model would enable us to assess which were the relatively better acceptor fragments, and ultimately lead to the optimization of the strength of the dative metal-metal bond.

4.2 Results and Discussion

4.2.1 Complexes with a donor-acceptor metal-metal bond with (CO)$_4$(CNBu')Os as the donor fragment.

4.2.1.1 The preparation of Os(CO)$_4$(CNBu').

Two preparations of Os(CO)$_4$(CNBu') have previously been reported in the literature.$^{51,161}$ It was prepared either via Os(CO)$_4$(η$^2$-COE) to which CNBu' was added or from the catalyzed (the catalyst was CoCl$_2$.2H$_2$O) reaction of Os(CO)$_5$ with CNBu'. Both routes gave a 28% yield of Os(CO)$_4$(CNBu'). An alternative, simple route for large scale preparations of Os(CO)$_4$(CNBu') with a slightly improved yield (35% yield) is presented herein. The pale cream complex, Os(CO)$_4$(CNBu') was prepared by heating Os(CO)$_5$ in the presence of CNBu' at 381 K for 24 h, under CO pressure.
4.2.1.2 The $^{13}$C-enrichment of Os(CO)$_4$(PMe$_3$), Os(CO)$_4$(CNBu$^t$) and other mononuclear donor fragments.

In cases where an unstable complex containing a donor-acceptor metal-metal bond has an acceptor fragment that cannot be $^{13}$C-enriched, the $^{13}$C-labeling of the donor moiety becomes imperative for obtaining a $^{13}$C NMR spectrum of the compound. The $^{13}$C-enrichment of Os(CO)$_4$(PMe$_3$) has been briefly reported in the literature. This involved the photolysis of a C$_6$H$_{14}$ solution of Os(CO)$_4$(PMe$_3$) under $^{13}$CO pressure in a Pyrex reaction vessel for $\geq 5$ h and the yield was typically $\leq 40\%$.\textsuperscript{50a} In Chapter 2, it was proposed that Os(CO)$_4$(PMe$_3$) loses a CO ligand upon irradiation ($\lambda \geq 400$ nm) in C$_6$H$_6$, see eq 2.6 and Figure 2.2. This suggested that if a solution of Os(CO)$_4$(PMe$_3$) in C$_6$H$_6$ was irradiated ($\lambda \geq 400$ nm) under $^{13}$C-enriched CO ($2.2 \times 10^5$ Pa; 2.2 atm) then a mild, selective route to $^{13}$C-labeled Os(CO)$_4$(PMe$_3$) might be effected. This new procedure has been found to be successful and the yield of the $^{13}$CO-enriched product is much improved of previous methods, see Table 4.1.

A thermal route to prepare $^{13}$CO-enriched Os(CO)$_4$(CNBu$^t$), by heating a C$_6$H$_{14}$ solution of Os(CO)$_4$(CNBu$^t$) at 343 K for 64 h under $^{13}$C-enriched CO with a yield of 47% of the labeled product was known.\textsuperscript{162} The $^{13}$CO-enrichment of Cp*Ir(CO)$_2$ has also been previously reported in the literature (by stirring a C$_5$H$_{12}$ solution of Cp*Ir(CO)$_2$ under $^{13}$CO).\textsuperscript{47} A new procedure, reported herein, provides an alternative and often improved route and indicates the potential general applicability of the method, see Table 4.1 and Section 4.4.4.
Table 4.1 The $^{13}$CO-enrichment of various mononuclear donor fragments utilizing selective photolysis ($\lambda \geq 400$ nm) in C$_6$H$_6$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$h^a$</th>
<th>$mol^{-1}$</th>
<th>$cm^{-1}$</th>
<th>$m/\epsilon$</th>
<th>$m/\epsilon$</th>
<th>minimization</th>
<th>% $^{13}$CO- %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(CO)$_4$(CNBu$^-$)</td>
<td>29</td>
<td>10</td>
<td>387</td>
<td>390</td>
<td>$\leq 0.173$</td>
<td>70-79</td>
<td>58</td>
</tr>
<tr>
<td>Os(CO)$_4$(PMe$_3$)</td>
<td>133</td>
<td>20</td>
<td>380</td>
<td>380</td>
<td>$\leq 0.067$</td>
<td>7-11</td>
<td>87</td>
</tr>
<tr>
<td>Ru(CO)$_4$(PMe$_3$)</td>
<td>12</td>
<td>17</td>
<td>290</td>
<td>290</td>
<td>$\leq 0.048$</td>
<td>11-14</td>
<td>86</td>
</tr>
<tr>
<td>Os(CO)$_4$(Pc)</td>
<td>140</td>
<td>$\sim 0$</td>
<td>452</td>
<td>452</td>
<td>0.233</td>
<td>22-26</td>
<td>73</td>
</tr>
<tr>
<td>(Cp$^*$)Ir(CO)$_2$</td>
<td>5</td>
<td>131</td>
<td>384</td>
<td>386</td>
<td>0.055</td>
<td>86-93</td>
<td>74</td>
</tr>
</tbody>
</table>

$^a$ Time of irradiation ($\lambda \geq 400$ nm) in C$_6$H$_6$ at room temperature. $^b$ At 400 nm in C$_6$H$_6$. $^c$ MS (El) $M^+$ is the largest relative abundance of the parent ion envelope of peaks. $^d$ The amount of incorporation of $^{13}$CO in the sample was determined by computer simulation of the envelope of peaks of the parent ion in the mass spectrum. This is described in detail in Appendix A-1.

4.2.1.3 The preparation of Os(CO)$_4$(GeCl)$_3$(Cl).

Analogous to the preparation of Fe(CO)$_4$(SnCl)$_3$(Cl) from Fe(CO)$_5$ and SnCl$_4$, it was hoped that a straightforward reaction of Os(CO)$_5$ with GeCl$_4$ would result in the formation of Os(CO)$_4$(GeCl)$_3$(Cl) as the sole product, but this was not the case. A solution of Os(CO)$_5$ in C$_6$H$_{14}$ with a slight excess of GeCl$_4$ in a high pressure vessel and was heated at 348 K for 22 h, under CO pressure. The use of CO pressure was to prevent loss of CO in the mononuclear complex and dimerization of the species to presumably yield [Os(CO)$_5$(GeCl)$_3$(μ-Cl)]$_2$ as proposed for the analogous compound Ru(CO)$_4$(SnCl)$_3$(Cl). The resultant reaction mixture was found to be a combination of Os(CO)$_4$(GeCl)$_3$(Cl) and
The source of the hydride ligand in the complex, Os(CO)$_4$(GeCl$_3$)(H), is, at present, unknown. The C. P. grade CO used in this reaction, however, contained trace amounts of H$_2$. At this time, it is not fully understood how the reaction proceeds to yield this product. The hydride complex, Os(CO)$_4$(GeCl$_3$)(H) was converted to the desired product, Os(CO)$_4$(GeCl$_3$)(Cl) by stirring the reaction mixture in a solution of CH$_2$Cl$_2$/CCl$_4$ for seven days at room temperature. The pure off-white Os(CO)$_4$(GeCl$_3$)(Cl) (0.515 g, 33% yield) was finally obtained upon sublimation.

4.2.1.4 The $^{13}$C-enrichment of Os(CO)$_4$(GeCl$_3$)(Cl).

The $^{13}$C-enriched Os(CO)$_4$(GeCl$_3$)(Cl) was prepared by heating a C$_6$H$_6$ solution of Os(CO)$_4$(GeCl$_3$)(Cl) at 323 K under $^{13}$C-enriched CO (1.4 x 10$^5$ Pa) for 10 days. A $^{13}$C($^1$H) NMR spectrum in CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1/3) at room temperature of $^{13}$C-enriched Os(CO)$_4$(GeCl$_3$)(Cl) exhibits four singlet resonances in the carbonyl region of the spectrum at, 160.01, 160.66, 163.54 and 165.56 ppm, with the integrated areas in the ratio, 2:32:2:3, see Figure 4.1.

The very intense signal, 160.66 ppm, with a relative integrated area of 32, is attributed to the carbonyl ligand trans to the GeCl$_3$ group. The resonance at 163.54 ppm, with a relative integrated area of two, is assigned to the carbonyl ligand trans to the Cl atom while the resonance at 165.56 ppm, with a relative integrated area of three, is ascribed to the two carbonyl ligands trans to one another. The assignment of the upfield $^{13}$C NMR resonance at 160.02 ppm, with a relative integrated area of two, is uncertain. It may be due to a $^{13}$C-$^{18}$O ligand trans to the GeCl$_3$ group: the $^{13}$C-enriched CO used to $^{13}$C-label
Os(CO)$_4$(GeCl$_3$)(Cl) was specified as 99.5 atom % $^{13}$C and 10.1 atom % $^{18}$O by the manufacturers, and secondary isotopic shift effects are quite well known.$^{166}$

The carbonyl region of the $^{13}$C-$^1$H NMR spectrum of $^{13}$C-enriched Os(CO)$_4$(GeCl$_3$)(Cl).

![Figure 4.1](image)

Figure 4.1 The carbonyl region of the $^{13}$C-$^1$H NMR spectrum of $^{13}$C-enriched Os(CO)$_4$(GeCl$_3$)(Cl).

The large disparity in the relative integrated areas of the peaks is attributed to a stereospecific exchange of the $^{12}$CO ligand trans to the GeCl$_3$ group by a $^{13}$C-enriched CO. A similar stereospecific exchange of both of the CO ligands trans to an ECl$_3$ group has been reported for the complexes cis-Ru(CO)$_4$(ECI$_3$)$_2$ (E = Si, Ge).$^{167}$ An IR spectrum of the ν(CO) region of the reaction solution showed very little difference in the relative intensities of the absorption bands after one day compared to after 10 days at 323 K, under $^{13}$C-enriched CO, which suggests the reaction was virtually complete after one day. As postulated in the literature,$^{44}$ the carbonyl ligand trans to the GeCl$_3$ group is particularly labile due to not only the trans effect from the GeCl$_3$ ligand but also the cis effect of the chloro group, as was observed in the analogous complexes cis-Ru(CO)$_4$(SiMeCl$_2$)(X) (X =
halide) where the labile CO ligand is both trans to the SiRCl₂ group and cis to a halide ligand.¹⁶ It was suggested that in the molecule (OC)₅OsOs(CO)₃(GeCl₃)(Cl) the donor fragment, Os(CO)₅, occupies the site trans to the GeCl₃ group,⁴⁴ consistent with the stereospecific loss of CO in Os(CO)₄(GeCl₃)(Cl). This lability of the CO trans to the GeCl₃ group assists in the formation of the complex with a dative covalent metal-metal bond and has allowed for the preparation of other molecules with a donor-acceptor metal-metal bond (described below). The stereospecific ¹³CO exchange in Os(CO)₄(GeCl₃)(Cl), however, does not allow ¹³CO-enrichment of the Os(CO)₃(GeCl₃)(Cl) acceptor fragment CO sites in molecules of the type (Dnr)Os(CO)₃(GeCl₃)(Cl) (Dnr = an organometallic donor fragment) since it is the ¹³CO that is substituted by the Donor fragment. This case and similar molecules emphasizes the importance of being able to ¹³CO-enrich the mononuclear metal donor fragment, a procedure not usually practiced in this laboratory.⁴⁵,⁴⁶,⁴⁸,⁵⁰,⁵¹

4.2.1.5 The preparation of complexes with a donor-acceptor metal-metal bond that have Os(CO)₄(CNBu') as the donor fragment.

The new complexes (OC)₅(Bu'NC)Os(Acc) [Acc = Os(CO)₃(GeCl₃)(Cl), Ru(CO)₅(SiCl₃)₂, Ru(CO)₅(SiCl₃)(Br), Re(CO)₄(X) (X = Cl, Br, I)] (4.6-4.11) and [Os(CO)₄(CNBu')(H)][BCl₄] ([4.12][BCl₄]) were prepared by various procedures. The complex 4.12 is included in this collection of compounds since it was produced from the attempted synthesis of (Bu'NC)(OC)₄OsBCl₃ and one possible way to view the molecule is (Bu'NC)(OC)₄Os(H⁺).

The complex (Bu'NC)(OC)₄OsOs(CO)₃(GeCl₃)(Cl) (4.6) was prepared from heating a C₆H₁₄ solution of Os(CO)₄(CNBu') and Os(CO)₄(GeCl₃)(Cl) under vacuum at 323 K to
produce the aforementioned binuclear complex in a 63% yield. The complexes 
\[(\text{Bu}'\text{NC})(\text{OC})_4\text{OsRu(CO)}_3(\text{SiCl}_3)(Y)\ (Y = \text{SiCl}_3, \text{Br})\ (4.7, 4.8)\]
were obtained upon stirring a \(\text{C}_6\text{H}_{14}\) solution of the respective \(\text{Ru(CO)}_4(\text{SiCl}_3)(Y)\) complex and \(\text{Os(CO)}_4(\text{CNBu}')\) at room temperature under vacuum, in 50% and 78% yields, respectively. Heating a \(\text{C}_6\text{H}_5\text{CH}_3\) solution of \([\text{Re(CO)}_4X]_2\ (X = \text{Cl, Br, I})\) and \(\text{Os(CO)}_4(\text{CNBu}')\) at 318 K and subsequent cooling of the filtered reaction solution afforded the complexes 
\[(\text{Bu}'\text{NC})(\text{OC})_4\text{OsRe(CO)}_4(X)\ (4.9-4.11)\] as yellow crystals in 38%, 27% and 44% yields, respectively. The complex \([4.12][\text{BCl}_4]\) was obtained by the vacuum transfer of an excess of freshly purified \(\text{BCl}_3\) into a vessel containing a \(\text{C}_6\text{H}_{14}\) solution of \(\text{Os(CO)}_4(\text{CNBu}')\). The source of the \(\text{HCl}\) is unclear. Measures were taken to remove \(\text{HCl}\) from \(\text{BCl}_3\) as suggested in the literature,\textsuperscript{169} but may not have been stringent enough, or the solvent was not completely dry although it was freshly distilled from potassium under \(\text{N}_2\). It has also been pointed out by Shriver and Drezdon that silicone stopcock grease reacts with \(\text{BCl}_3\) to produce \(\text{HCl}\) or \(\text{H}_2\text{O}\) by some unknown route and this may, therefore, be the source of the hydrogen and chloride.\textsuperscript{170}

\textbf{4.2.1.6 The molecular structure of }\((\text{OC})_4(\text{Bu}'\text{NC})\text{OsOs(CO)}_3(\text{GeCl}_3)(\text{Cl})'0.5(\text{C}_6\text{H}_5\text{CH}_3)\) 
\((4.6)\).

The structure of \((\text{OC})_4(\text{Bu}'\text{NC})\text{OsOs(CO)}_3(\text{GeCl}_3)(\text{Cl})'0.5(\text{C}_6\text{H}_5\text{CH}_3)\) \((4.6)\) was determined by X-ray crystallography by Professor F. W. B. Einstein and Dr. W. Wang at Simon Fraser University. A view of the molecule is shown in Figure 4.2; selected bond lengths and bond angles are given in Tables 4.2 and 4.3, respectively.
Figure 4.2 Molecular structure of \((Bu'NC)(OC)_4OsOs(CO)_3(GeCl_3)(Cl)^{0.5}(C_6H_5CH_3)\).
Table 4.2  Selected bond lengths from the molecular structure of 
(OC)$_4$(Bu'NC)OsOs(CO)$_3$(GeCl$_3$)(Cl)'0.5(C$_6$H$_3$CH)$_3$ (4.6).

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(1) - Os(2)</td>
</tr>
<tr>
<td>Os(2) - Ge(1)</td>
</tr>
<tr>
<td>Os(2) - Cl(1)*</td>
</tr>
<tr>
<td>Os(2) - Cl(11)*</td>
</tr>
<tr>
<td>Os(1) - C(1)</td>
</tr>
<tr>
<td>Os(1) - C(11)</td>
</tr>
<tr>
<td>Os(1) - C(12)</td>
</tr>
<tr>
<td>Os(1) - C(13)</td>
</tr>
<tr>
<td>Os(1) - C(14)</td>
</tr>
<tr>
<td>Os(2) - C(21)</td>
</tr>
<tr>
<td>Os(2) - C(22)</td>
</tr>
<tr>
<td>Os(2) - C(23)*</td>
</tr>
<tr>
<td>Os(2) - C(231)*</td>
</tr>
</tbody>
</table>

* Molecule was partly disordered with the unique Cl(1) atom and the C(23)-O(23) group cis to it occupying common sites which were numbered Cl(11), C(231) and O(231).

As can be seen in Figure 4.2, this is another example of Os(CO)$_4$(CNBu') acting as a two-electron donor ligand towards the 16-electron acceptor fragment Os(CO)$_3$(GeCl$_3$)(Cl) via an unbridged, dative metal-metal bond. As observed in the analogous systems (OC)$_4$(Bu'NC)OsOs$_3$(CO)$_{11}^{28c}$ and (OC)$_4$(Bu'NC)OsCr(CO)$_5$ (4.3)$^{51}$ the isocyanide ligand is cis to the metal-metal bond, in contrast to (L)(OC)$_4$OsOs$_3$(CO)$_{11}$ (L = PMe$_3$, P$_c$, P$_{28b}$) and (Me$_2$P)(OC)$_4$OsOsM(CO)$_5$ (M = W, Cr, Mo) (2.1, 4.1, 4.2)$^{50}$ where the phosphorus-containing ligand is trans to the osmium--osmium bond. The osmium-oscium bond length in 4.6 is 2.916(1) Å which is similar to the respective bond in (OC)$_4$(Bu'NC)OsOs$_3$(CO)$_{11}$ 2.918(2) Å$^{28c}$ and (OC)$_5$OsOs(CO)$_3$(GeCl$_3$)(Cl) 2.916(2)-2.931(1) Å$^{44}$ The dimensions of the Os(CO)$_4$(CNBu') ligand are similar to those of the Os(CO)$_4$(CNBu') ligand in
(OC)₄(Bu'NC)OsOs₃(CO)₁₁,²⁸c and 4.₃.⁵₁ As seen in other molecules,²⁸c,⁵₁ the Os-C bond length to the isocyanide group is marginally longer than the corresponding Os-C bond length to the carbonyl ligand trans to the isocyanide group on the same osmium atom, that is, 2.04(2) Å versus 1.93(2) Å, respectively. This is consistent with the view that the CO ligand is a better π-acceptor than the CNBu' ligand.¹⁷¹

<table>
<thead>
<tr>
<th>Bond Angles (deg)</th>
<th>C(11) - Os(1) - Os(2) 83.6(5)</th>
<th>C(12) - Os(1) - C(11) 93.4(8)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(12) - Os(1) - Os(2) 176.6(6)</td>
<td>C(13) - Os(1) - C(11) 170.2(7)</td>
</tr>
<tr>
<td></td>
<td>C(13) - Os(1) - Os(2) 87.0(5)</td>
<td>C(13) - Os(1) - C(12) 96.1(8)</td>
</tr>
<tr>
<td></td>
<td>C(14) - Os(1) - Os(2) 85.5(6)</td>
<td>C(14) - Os(1) - C(11) 90.4(9)</td>
</tr>
<tr>
<td></td>
<td>C(1) - Os(1) - Os(2) 87.6(5)</td>
<td>C(14) - Os(1) - C(12) 92.8(8)</td>
</tr>
<tr>
<td></td>
<td>C(1) - Os(1) - C(11) 91.3(8)</td>
<td>C(14) - Os(1) - C(13) 91.5(9)</td>
</tr>
<tr>
<td></td>
<td>C(1) - Os(1) - C(12) 94.2(7)</td>
<td>Ge(1) - Os(2) - Os(1) 174.54(8)</td>
</tr>
<tr>
<td></td>
<td>C(1) - Os(1) - C(13) 85.6(8)</td>
<td>N(1) - C(1) - Os(1) 174.8(20)</td>
</tr>
<tr>
<td></td>
<td>C(1) - Os(1) - C(14) 172.7(8)</td>
<td></td>
</tr>
</tbody>
</table>

As found for other complexes with an unbridged, dative metal-metal bond⁴₈,⁵₀ there is a slight inward leaning of the two equatorial carbonyl ligands that are trans to one another on the donor metal atom, towards the acceptor metal atom. In the complex 4.₆ the Os(2)-Os(1)-C(1n) angles (n =1,3) are 83.6(5) and 87.0(5)°, respectively. This leaning is
less than that observed in 4.3 [Cr-Os-C(3) 80.0(2)°] and more similar to that observed in
(OC)₅OsOs(CO)₃(GeCl₃)(Cl) [Os(n2)-Os(n1)-C(nm) (n = 1-3; m = 1-4) 82.2(8)-87.4(9)°],
(see Figure 1.6 for the molecular structure and the numbering scheme). The inward
leaning is not present in the trans equatorial carbonyls of the acceptor half of the molecule
[Os(1)-Os(2)-C(2n) (n = 1, 3) 88.8(5) and 92.9(13)°], see Table 4.3, which was also
observed for 4.3 and (OC)₅OsOs(CO)₃(GeCl₃)(Cl). The dimensions of the
Os(CO)₃(GeCl₃)(Cl) fragment in the complex 4.6 are similar to those of the
Os(CO)₃(GeCl₃)(Cl) moiety in (OC)₅OsOs(CO)₃(GeCl₃)(Cl), with two exceptions: the
Os(2)-Cl(1) bond length is 2.41(1) Å in 4.6 which is shorter than observed in
(OC)₅OsOs(CO)₃(GeCl₃)(Cl) (2.435(7), 2.448(8) and 2.459(8) Å), and the Os(2)-C bond
lengths to a carbonyl ligand are all similar 1.90(2)-1.94(2) Å. Further comment on the
Os(CO)₃(GeCl₃)(Cl) fragment of the molecule 4.6 cannot be made because of the disorder
in the structure. (The atoms Cl(1), C(23), O(23) have a 66±2% site occupancy and the two
ligands interchange positions to become Cl(11), C(231) and O(231), respectively, with an
occupancy of 34±2%).

4.2.1.7 The molecular structure of [Os(CO)₄(CNBu')(H)][BCl₄] ([4.12][BCl₄]).

The structure of [Os(CO)₄(CNBu')(H)][BCl₄] ([4.12][BCl₄]) was determined by X-
ray crystallography by Professor F. W. B. Einstein and Dr. W. Wang at Simon Fraser
University. A view of the molecule is shown in Figure 4.3; selected bond lengths and bond
angles are shown in Tables 4.4 and 4.5, respectively.
Figure 4.3 Molecular structure of [Os(CO)$_4$(CNBu')(H)][BCl$_4$].
Table 4.4  Selected bond lengths from the molecular structure of [Os(CO)\(_4\)(CNBu')\(\text{H}\)]\([\text{BCl}_4]\) ([4.12]\([\text{BCl}_4]\)).

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(1) - C(11)</td>
<td>1.964(9)</td>
<td>N(1) - C(1)</td>
</tr>
<tr>
<td>Os(1) - C(12)</td>
<td>2.003(9)</td>
<td>N(1) - C(2)</td>
</tr>
<tr>
<td>Os(1) - C(13)</td>
<td>1.986(9)</td>
<td>C(2) - C(3)</td>
</tr>
<tr>
<td>Os(1) - C(14)</td>
<td>1.974(9)</td>
<td>C(2) - C(4)</td>
</tr>
<tr>
<td>Os(1) - C(1)</td>
<td>2.061(8)</td>
<td>C(2) - C(5)</td>
</tr>
</tbody>
</table>

Table 4.5  Selected bond angles from the molecular structure of [Os(CO)\(_4\)(CNBu')\(\text{H}\)]\([\text{BCl}_4]\) ([4.12]\([\text{BCl}_4]\)).

<table>
<thead>
<tr>
<th>Bond Angles (deg)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C(12) - Os(1) - C(11)</td>
<td>95.7(3)</td>
<td>C(1) - Os(1) - C(13)</td>
</tr>
<tr>
<td>C(13) - Os(1) - C(11)</td>
<td>170.9(3)</td>
<td>C(1) - Os(1) - C(14)</td>
</tr>
<tr>
<td>C(13) - Os(1) - C(12)</td>
<td>93.4(3)</td>
<td>C(2) - N(1) - C(1)</td>
</tr>
<tr>
<td>C(14) - Os(1) - C(11)</td>
<td>89.3(3)</td>
<td>N(1) - C(1) - Os(1)</td>
</tr>
<tr>
<td>C(14) - Os(1) - C(12)</td>
<td>97.9(4)</td>
<td>C(3) - C(2) - N(1)</td>
</tr>
<tr>
<td>C(14) - Os(1) - C(13)</td>
<td>89.4(4)</td>
<td>C(4) - C(2) - N(1)</td>
</tr>
<tr>
<td>C(1) - Os(1) - C(11)</td>
<td>86.0(3)</td>
<td>C(5) - C(2) - N(1)</td>
</tr>
<tr>
<td>C(1) - Os(1) - C(12)</td>
<td>91.9(3)</td>
<td></td>
</tr>
</tbody>
</table>

The Os-C bond lengths of the carbonyl ligands in the molecule [4.12] range from 1.964(9)-2.061(8) Å, which are longer than the respective bonds in 4.6 (1.87(2)-1.93(2) Å)
and 4.3 (1.934(12)-1.972(7) Å).\textsuperscript{51} In [4.12] there is presumably less electron density available for π-backboning to the ligands due to the positive charge and this results in longer metal-ligand bonds.\textsuperscript{171} This has been observed in other systems such as W(CO)\textsubscript{6}/[W(CO)\textsubscript{6}]\textsuperscript{+}.\textsuperscript{171a} The Os-C(12) bond length (2.003(9) Å) in [4.12] is marginally longer than the other Os-C bond lengths to the carbonyl ligands (1.986(9)-1.964(9) Å).

Although the difference is not significant statistically it is consistent with the view that the H ligand has a greater trans influence than either the CO or CNR ligands.\textsuperscript{124a,172} The Os-C bond length to the isocyanide group (Os-C(1) 2.061(8) Å) is similar to that in 4.6 (2.04(2) Å, see Table 4.2) and (OC)\textsubscript{4}(Bu'NC)OsOs\textsubscript{3}(CO)\textsubscript{11} (2.04(4) Å).\textsuperscript{28c} That the effect of the positive charge on the Os-C bond length to the isocyanide group is smaller than that on the Os-C bond length to the carbonyl ligands is consistent with the view that the RNC group is a better σ-donor, but a poorer π-acceptor than the CO ligand.\textsuperscript{171} The positive charge in [4.12] reduces the amount of π-donation from the metal center which has a larger effect on the CO ligands than the isocyanide group. The osmium atom in [4.12] has an approximate octahedral coordination with the cis-C(12)-Os-L angles in the range 91.9(3)-97.9(4)°, see Table 4.5. There is a slight leaning towards the least sterically demanding site (H) as exemplified by the angle C(1)-Os-C(14) of 169.5(3)°. The angle of the C(2)-N(1)-C(1) unit (176.7(8)°) is close to a linear arrangement as seen in the other systems, 4.3,\textsuperscript{51} 4.6 (see Table 4.3), and Os\textsubscript{3}(μ-H)\textsubscript{2}(CO)\textsubscript{9}(CNBu').\textsuperscript{173} All of the Os-C-O bonds are almost linear, with angles ranging from 173.1(8)-176.6(7)°.
4.2.1.8 The spectroscopic properties of complexes with a donor-acceptor metal-metal bond and Os(CO)$_4$(CNBu') as the donor fragment.

The $^1$H NMR chemical shifts and $\nu$(CN), $\nu$(CO) bands in the IR spectra of the new compounds together with the corresponding data for Os(CO)$_4$(CNBu')$^{51,161}$ are shown in Table 4.6.

As might be expected the $^1$H resonance for the methyl groups in the cationic complex [4.12] is downfield (deshielded, higher frequency) relative to the chemical shifts of the other complexes. This is consistent, once again, with the view that the cationic complex has less electron density than the neutral species. The relative ratios of the integrals of the methyl and hydride $^1$H NMR resonances of [4.12] are 13:1 and not 9:1. This suggests that the different proton nuclei in the complex, [4.12] have different relaxation times due to their different environments.

The $^1$H NMR chemical shifts of the methyl resonance of the complexes with a donor-acceptor metal-metal bond are too close to one another to be able to speculate on any trends (see Table 4.6).

For the Os(CO)$_4$(CNBu') fragment in molecules of the type, cis-(OC)$_4$(Bu'NC)Os(Acc) (Acc = acceptor moiety, treating this whole group as a singular point), one might expect four IR active $\nu$(CO) bands.$^{51}$ For the acceptor fragments it might be expected to observe either three IR active bands in the molecules of the type, mer-(Dnr)Ru(CO)$_3$(SiCl$_3$)(Y) (Y = SiCl$_3$, Br), mer-(Dnr)Os(CO)$_3$(GeCl$_3$)(Cl) or a maximum of four IR active $\nu$(CO) bands in, cis-(Dnr)Re(CO)$_4$(X) (X = Cl, Br, I; Dnr = donor moiety) molecules.
The IR spectra were recorded in CH₂Cl₂, since unlike 4.3-4.5 the complexes in Table 4.6 are not sufficiently soluble in C₆H₁₄ to afford an IR spectrum. This insolubility suggests that the present (OC)₄(Bu'NC)Os(Acc) (Acc = an acceptor fragment) compounds, in Table 4.6, are more polar than the molecules 4.3-4.5. The disadvantage of recording IR spectra in CH₂Cl₂, however, is that it is a more polar solvent and hence interacts more strongly with the complexes which results in broadening of the IR bands. This can result in overlapping of v(CO) bands such that the number of IR v(CO) bands observed is less than expected. This in turn prohibits a detailed analysis of the IR spectra of the complexes.¹⁷⁴

The v(CN) band of the complexes appears as a single peak in a region characteristic of v(CN) absorptions and although broad the assignment of the band is therefore straightforward. It was hoped that the v(CN) band might exhibit a shift in frequency that could be correlated to the acceptor strength of the acceptor fragment. Unfortunately, there is too little variation in the v(CN) band frequencies of the series of complexes (Table 4.6) to allow such an analysis.

As pointed out previously for 4.3-4.5, the carbonyl (and isocyanide) stretching frequencies shift to higher values on going from the free, mononuclear complex Os(CO)₄(CN Bu') to coordinated to another metal fragment, (see Table 4.6), that is, not allowing for the change in coordination and geometry.⁵¹
Table 4.6 Infrared spectra (ν(CN), ν(CO) regions) and ¹H NMR spectra of complexes with a donor-acceptor metal-metal bond and Os(CO)₄(CNBu') as the donor fragment.

<table>
<thead>
<tr>
<th>Compound a</th>
<th>¹H NMR, b</th>
<th>IR, c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ, ppm</td>
<td>ν(CN), cm⁻¹</td>
</tr>
<tr>
<td>(Dnr)Os(CO)₃(GeCl₃)(Cl)</td>
<td>1.56</td>
<td>2224(w, asym)</td>
</tr>
<tr>
<td>(Dnr)Ru(CO)₃(SiCl₃)₂</td>
<td>1.55</td>
<td>2219(m)</td>
</tr>
<tr>
<td>(Dnr)Ru(CO)₃(SiCl₃)(Br)</td>
<td>1.51</td>
<td>2217(w, asym)</td>
</tr>
<tr>
<td>(Dnr)Re(CO)₄(Cl)</td>
<td>1.52</td>
<td>2217(w, br)</td>
</tr>
<tr>
<td>(Dnr)Re(CO)₄(Br)</td>
<td>1.52</td>
<td>2219(w, br)</td>
</tr>
<tr>
<td>(Dnr)Re(CO)₄(I)</td>
<td>1.53</td>
<td>2218(w, br)</td>
</tr>
<tr>
<td>[(Dnr)H]+</td>
<td>1.62(CH₃), 2252(w, br)</td>
<td>2176(m), 2126(s), 2102(vs, br)</td>
</tr>
<tr>
<td>Os(CO)₄(CNBu') d</td>
<td>1.49</td>
<td>2202(m)</td>
</tr>
</tbody>
</table>

a (Dnr) = (OC)₄(Bu'NC)Os. b Recorded in CD₂Cl₂ at 233K, all peaks are singlets due to the CH₃ resonances unless specified otherwise. c Recorded in CH₂Cl₂, at room temperature with a resolution of ± 2 cm⁻¹. d This mononuclear complex is included for a comparison.
Both the (El) and (Cl) mass spectra of the new compounds suggest that the metal-
metal donor-acceptor bonds in 4.9-4.11 are weaker than those in 4.6, 4.7, and 4.8. This is
because in the spectra of complexes with Re(CO)₄(X) as the acceptor moiety there are
intense ion fragments that arise from cleavage of the metal-metal bond.

The $^{13}$C{¹H} NMR chemical shifts for the new complexes together with the
previously prepared compounds, Os(CO)₄(CNBu′) and 4.3-4.5 are reported in Table
4.7.$^{51,161}$ All samples were recorded under similar conditions to allow the accurate
comparison of the different acceptor fragments.

The donor fragment, (OC)₄(Bu′NC)Os, in the derivatives show three $^{13}$C NMR
chemical resonances in the relative integral ratio 1:1:2, in the range 159-187 ppm, see Table
4.7, which is consistent with the structures observed in the solid state by X-ray
crystallography, that is with the isocyanide ligand cis to the dative metal-metal bond.$^{28c,51}$

There was no evidence in the $^{13}$C{¹H} NMR spectra for the isomer with the (CNBu′) group
trans to the metal-metal bond. For the complexes (L)(OC)₄OsM(CO)₅ (M = Cr, Mo, W; L
= phosphine, phosphite) the major isomer in solution has the phosphorus containing ligand
trans to the metal-metal bond.$^{50}$ That the isocyanide ligand occupies a different site is
interpreted as the less sterically demanding CNBu′ ligand (cone angle $68^\circ$, $70^\circ$)$^{175}$ occupies
the electronically preferred and sterically allowed site cis to the metal-metal bond,
exclusively.$^{28c,51,176}$ This is the electronically preferred site since the poorer $\pi$-acceptor
ligand, CNBu′, is trans to a carbonyl ligand. The sterically more demanding PR₃ ligand
(cone angles: P(OCH₂)₃CCH₃, 101°; P(OMe)₃, 107°; PMe₃, 118°)$^{141}$ is forced for steric
reasons to occupy the site trans to the metal-metal bond most of the time.
In all complexes that contain a carbonyl ligand trans to a donor-acceptor metal-metal bond, the $^{13}$C NMR resonance of the carbonyl carbon of this ligand occurs at unusually high fields (~159-167 ppm, see Table 4.7), that is, it is shielded (at a lower frequency) relative to the other carbonyl carbon resonances in the donor fragment.\cite{28c,44,45,50-52}

In previous studies the $^{13}$C NMR chemical shift of the carbonyl trans to the noncarbonyl ligand was observed upfield from its cis carbonyl neighbors in systems where the noncarbonyl ligands are one electron donors namely, Re(CO)$_5$(X) (a few examples are, X = CH$_3$, C$_6$H$_5$, Br, SiCl$_3$, SiMe$_3$, GeMe$_3$, SnMe$_3$) and M(CO)$_4$[(EMe$_{3-n}$)(Cl)$_n$]$_2$ (M = Fe, Ru, Os; E = Si, Ge, Sn, Pb; n = 1-3).\cite{142,177} For these mononuclear systems the $^{13}$C NMR chemical shift of the carbonyl carbons trans to the noncarbonyl ligands are in the range ~178-183 ppm for rhenium complexes\cite{142} and ~167-173 ppm for osmium complexes\cite{177} which illustrates how high field (low frequency) the respective carbonyl carbon resonances are in the complexes with a donor-acceptor metal-metal bond.
Table 4.7 The $^{13}\text{C}^{{1}\text{H}}$ NMR spectra of complexes with a donor-acceptor metal-metal bond and Os(CO)$_4$(CNBu') as the donor fragment.

<table>
<thead>
<tr>
<th>Compound$^a$</th>
<th>$^{13}\text{C}^{{1}\text{H}}$ NMR$^b$</th>
<th>$\delta$(CH$_3$)$^c$</th>
<th>$\delta$(CO)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Dnr)Os(CO)$_3$(GeCl$_3$)(Cl)</td>
<td>29.42 159.34 171.46 174.37 172.35 (1C), 182.59 (2C)$^e$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Dnr)Ru(CO)$_3$(SiCl$_3$)$_2$</td>
<td>29.36 160.29 174.08 178.08 196.73 (1C), 197.97 (2C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Dnr)Ru(CO)$_3$(SiCl$_3$)(Br)</td>
<td>29.44 161.65 175.46 179.86 194.54 (1C), 197.23 (2C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Dnr)Re(CO)$_4$(Cl)</td>
<td>29.49 164.18 175.72 180.17 186.03 (1C), 188.75 (1C), 194.00 (2C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Dnr)Re(CO)$_4$(Br)</td>
<td>29.47 163.57 175.96 180.31 185.29 (1C), 188.54 (1C), 192.65 (2C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Dnr)Re(CO)$_4$(I)</td>
<td>29.46 162.70 176.44 180.68 184.22 (1C), 188.08 (1C), 190.38 (2C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Dnr)W(CO)$_5$</td>
<td>29.20 165.35 177.40 183.63 201.90 (4C), (125.4), 203.54 (1C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Dnr)Mo(CO)$_5$</td>
<td>29.22 166.44 179.27 186.63 209.86 (4C), 215.79 (1C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Dnr)Cr(CO)$_5$</td>
<td>29.16 165.06 179.66 186.77 222.35 (4C), 229.22 (1C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(Dnr)H]$^+$</td>
<td>29.56 163.64 164.24 (3C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os(CO)$_4$(CNBu')$^g$</td>
<td>29.81 187.49 (4C, 116.7)$^h$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The donor fragment (Dnr) = (OC)$_4$(Bu'NC)Os.  
$^b$ Recorded in CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1:3) at 233K, in ppm.  
$^c$ All the methyl resonances are singlets.  
$^d$ There are four carbonyl ligands, the particular carbonyl ligand being assigned is marked with the asterisk, the others are marked with a period and A symbolizes the acceptor fragment of the molecule.  
$^e$ The relative integrated areas are given in parentheses as numbers of carbons.  
$^f$ The second number in the parentheses is a one bond tungsten-carbon coupling ($^{1}J_{w,c}$) in Hz.  
$^g$ This mononuclear complex is included for a comparison.  
$^h$ The second number in parentheses is a one bond osmium-carbon coupling ($^{1}J_{o,c}$) in Hz.
For the $^{13}\text{C}\{^{1}\text{H}\}$ NMR spectrum of the complex 4.6 only the donor fragment, $(\text{OC})_4(\text{Bu}^\prime\text{NC})\text{Os}$, was $^{13}\text{C}$-enriched. The $^{13}\text{CO}$-enrichment of Os(\text{CO})_4(\text{GeCl}_3)(\text{Cl})$, as previously discussed, is stereospecific and the single $^{13}\text{C}$-label is lost upon the formation of the binuclear complex. There was no evidence of the $^{13}\text{C}$-label scrambling between the two fragments of the binuclear complex, as has previously been observed for (\text{L})(\text{OC})_4\text{OsM(CO)}_5 (M = \text{Cr, Mo, W}; \text{L} = \text{phosphine, phosphite, CNBu}^\prime), and \text{Cp*}(\text{OC})_2\text{IrW(CO)}_5.^{46,50,51}$ The $^{13}\text{C}$ NMR resonances for the carbonyl carbons in the acceptor fragment of 4.6 were due to natural abundance $^{13}\text{C}$ nuclei and hence the signal intensities were weak. The weak $^{13}\text{C}$ carbonyl carbon resonance at 182.59 ppm is assigned to the two carbonyl carbons $\text{trans}$ to one another in Os(\text{CO})_3(\text{GeCl}_3)(\text{Cl})$, while a very low intensity carbonyl carbon resonance at 172.35 ppm is tentatively assigned as the carbonyl carbon $\text{trans}$ to the chlorine atom. These assignments are consistent with the chemicals shifts ($\delta$ 179.8 (2), 170.3 (1) ppm) for the acceptor fragment in $(\text{OC})_5\text{OsOs(OC)}_3(\text{GeCl}_3)(\text{Cl}).^{44}$

The complexes 4.7 and 4.8 were prepared from $^{13}\text{CO}$-enriched donor and acceptor fragments. The two carbonyl carbon resonances, in a relative integral ratio of 1:2, in the range ~194-198 ppm (see in Figure 4.4) are unambiguously assigned to the ruthenium acceptor fragment, see Table 4.7.
Figure 4.4 The $^{13}\text{C}^{1\text{H}}$ NMR spectrum of (Bu'NC)(OC)$_4$OsRu(CO)$_3$(SiCl)$_2$ in CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1/3) at 233 K.

In 4.7 both the (CNBu') ligand and one of the SiCl$_3$ groups are *cis* to the metal-metal bond (Figure 4.5a). It was therefore thought there might be restricted rotation about the metal-metal bond. There was, however, no detectable broadening or splitting of the carbonyl carbon resonances in the $^{13}\text{C}^{1\text{H}}$ NMR spectrum of 4.7 in CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1/3) down to 183 K. This indicates that there is at least rapid oscillation about the metal-metal bond so as to render each pair of carbonyl ligands that are *cis* to the noncarbonyl substituent equivalent.
Figure 4.5 The idealized structures of (a) (Bu'NC)(OC)$_4$OsRu(CO)$_3$(SiCl)$_2$ (4.7) and (b) (Bu'NC)(OC)$_4$OsRe(CO)$_4$(X) (X = Cl, Br, I) (4.9-4.11).

For the complexes 4.9-4.11 (Figure 4.5b) the $^{13}$C NMR carbonyl resonances of the rhenium acceptor fragments exhibit three peaks in a 1:1:2 relative integral ratio, in the range $\delta \sim 184$-194 ppm, see Table 4.7. The most downfield (high frequency) $^{13}$C resonance of intensity two is readily assigned to the two carbonyl carbons that are trans to one another. The most upfield (low frequency) carbonyl carbon resonance is assigned to the carbonyl ligand trans to the metal-metal bond analogous to (Me$_3$P)(OC)$_4$OsRe(CO)$_4$(Br) (4.13) where the respective upfield carbonyl resonance on the rhenium acceptor fragment exhibited a three bond carbon-phosphorus coupling consistent with the carbonyl being trans to the metal-metal bond.$^{48}$ The remaining carbonyl resonance ($\delta \sim 188$ ppm, see Table 4.7) is therefore assigned to the carbonyl carbon trans the halide atom. The solution structure of the acceptor fragment of these molecules is consistent with the structure observed in the solid state by X-ray crystallography for 4.13, that is, with the halide ligand cis to the metal-
metal bond (Figure 4.5b). There was no evidence in the $^{13}$C NMR spectra for the isomer with the halide ligand trans to the metal-metal bond.

The $^{13}$C NMR spectra of 4.3-4.5 have previously been assigned. Unlike the donor fragments described above where the $^{13}$C($^1$H) NMR resonance of the trans carbonyl carbon is upfield from the cis carbonyl resonances, in M(CO)$_5$ (M = Cr, Mo, W) units, the resonance of the trans carbonyl is downfield from that of the cis carbonyls. This is also observed for M(CO)$_5$L complexes (M = Cr, Mo, W; L = a two electron donor). There is also an upfield shift of the carbonyl resonances on going to the metal lower in the same chemical group, as in (Ph$_3$P)M(CO)$_5$, 2.1, 4.1, and 4.2.

The $^{13}$C($^1$H) NMR spectrum of the complex [4.12] was collected in three different solvent systems (CD$_2$Cl$_2$, CD$_3$CN, CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1/3)) in an attempt to separate the three different carbon-13 carbonyl resonances expected in the spectrum. The $^{13}$C($^1$H) NMR spectra are consistent with the upfield carbonyl resonance with a relative integral intensity of one as being assigned to the CO ligand trans to the hydride group. The downfield carbonyl resonance is believed to be comprised of two carbonyl resonances that overlap to give a single resonance of relative intensity three. In some spectra this resonance was asymmetric suggesting that it was composed of two peaks. In the $^1$H-coupled $^{13}$C NMR spectrum of [4.12] in CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1/3) at 233K the high field resonance at 164.48 ppm, (of relative integral intensity one), appeared as a doublet ($^2J_{C,H} = 19.1$ Hz) while the downfield resonance consisted of a major peak at 164.20 ppm, with a shoulder at 164.14 ppm (a combined relative integral intensity of three). This is consistent with the view that the upfield resonance is due to the CO ligand trans to the hydride ligand with a large two bond, carbon-hydrogen coupling ($^2J_{C,H}$). Furthermore, the shoulder seen on the
downfield resonance is evidence for a smaller two bond cis carbon-hydrogen coupling. The trans $^2J_{C-H}$ coupling in [4.12] of 19.1 Hz is typical for such couplings. For example, the green isomer of Os$_3$(μ-H)$_2$(CO)$_5$(CNBu') is reported as having the trans $^2J_{C-H}$ couplings of 11.7 and 11.6 Hz. Similarly, Os(CO)$_4$(GeCl$_3$(H) exhibits a trans $^2J_{C-H}$ coupling of 14.7 Hz with cis $^2J_{C-H}$ couplings of 7.5 and 6.0 Hz.

The $^{13}$C($^1$H) NMR spectrum of Os(CO)$_4$(CNBu') was obtained under identical conditions to those of the binuclear complexes. The mononuclear complex exhibits a singular carbonyl resonance in the spectrum, consistent with fluxional behavior that renders the carbonyl ligands equivalent. If the difference in the geometry of Os(CO)$_4$(CNBu') as a free mononuclear complex and upon coordination in a binuclear complex, has a negligible influence on the chemical shift, the $^{13}$C NMR resonance of the carbonyls of Os(CO)$_4$(CNBu') (187.49 ppm) is downfield relative to the resonances of the (OC)$_4$(Bu'NC)Os fragment in the binuclear complexes (see Table 4.7). This might suggest less electron density on the Os fragment in binuclear complexes relative to the mononuclear species if a simple interpretation of the chemical shift (see later in the text for details) is employed. This is consistent with the trends in the IR carbonyl and isocyanide stretching frequencies of the free and complexed Os(CO)$_4$(CNBu') unit.

As noted in Table 4.7, the carbonyl resonance of Os(CO)$_4$(CNBu') exhibited a detectable coupling to $^{187}$Os (spin $\frac{1}{2}$, 1.6% natural abundance) of 116.7 Hz. Such couplings have been observed in a few other systems, such as, trans-(P$_2$)(OC)$_4$OsW(CO)$_5$ ($^1J_{Os-C} = 91.5$ Hz) and trans-2.1 ($^1J_{Os-C} = 92$ Hz). The larger size of the Os-C coupling in the trigonal bipyramidal Os(CO)$_4$(CNBu') (20% s-character, sp$^3$d) is consistent with the larger s-character in the Os-C bonds compared to that in the octahedral environment of
(L)(OC)$_4$Os(Acc) (L = PMe$_3$, P$_c$; Acc = acceptor moiety) (12.5% s-character, sp$^3$d$^2$). Coupling between nuclei through bonds is considered to utilize $\sigma$-electrons and there is therefore a dependence on the s-character of the bond.$^{178}$

It has been shown in ($\eta^5$-Cp)Fe(CO)$_2$(Y) [Y = Cl, Br, I, C$_6$H$_5$, CH$_3$, Sn(CH$_3$)$_3$, Ge(CH$_3$)$_3$, Si(CH$_3$)$_3$], and (OC)$_5$MC(X)R' (M = Cr, W; R' = CH$_3$, Ph; X = NH$_2$, OR; R = CH$_3$, C$_2$H$_5$)$^{145}$ that the complex with the most electron-withdrawing ligand X or Y, in a series of complexes, exhibits the carbonyl-carbon resonance at the highest field in the $^{13}$C{H} NMR spectrum. In Re(CO)$_5$(X) [X = CH$_3$, C$_6$H$_5$, Br, SiCl$_3$, Si(CH$_3$)$_3$, Ge(CH$_3$)$_3$] the $^{13}$C NMR resonance of the carbonyl ligands cis to the unique ligand exhibit a linear correlation in their $^{13}$C NMR chemical shifts and IR force constants, with the more highly shielded carbonyl carbons belonging to ligands with the higher force constants.$^{142}$ The results of this latter study support the findings of the two prior systems. It was also suggested that the linear correlation between the $^{13}$C NMR chemical shift of the cis carbonyl ligands with the IR carbonyl stretching force constants could be extended to include data of the same correlation for the complexes W(CO)$_5$L [L = P(OD)$_3$, P(O-n-C$_4$H$_9$)$_3$, SbPh$_3$, AsPh$_3$, BiPh$_3$, PPh$_3$].$^{142,149}$ Although this exact correlation between the two sets of data may be serendipitous, both individual series of compounds have definitive trends. Presumably, the basis for this comparison of these two distinct sets of data was the comparison of the effect of the increased donor ability of a ligand to shift the carbonyl carbon resonance to a lower field in the $^{13}$C NMR spectrum as has also been observed in Ni(CO)$_3$(L), M(CO)$_5$(L) (M = Cr, Mo, W; L = phosphine, phosphite, arsine, stibine). (Note this shift is opposite to what is observed when L is an electron-withdrawing ligand).$^{143,146}$

The relative chemical shift of the carbonyl resonance in these series of complexes has
been used as a measure of the electronic effect parameter of the ligand, L, analogous to Tolman's electronic parameter derived from the IR spectra of Ni(CO)$_3$L complexes.$^{141}$

All the above systems are mononuclear. If the binuclear organometallic complexes with a donor-acceptor metal-metal bond are considered as (L)(OC)$_4$Os(Acc) (L = CNBu', a phosphine or a phosphite; Acc = the varied acceptor fragment and is treated as a sole entity) the analogy with the mononuclear complexes is apparent. It was thought the chemical shifts of the carbonyls of the donor moiety could be used as a measure of the acceptor ability of 16-electron fragments in the binuclear complexes with a donor-acceptor metal-metal bond. It is true that the nature of the bond between the donor fragment and the acceptor moiety is different to the typical mononuclear metal carbonyl system with a metal to single electron withdrawing species (X or Y)$^{142,144,145}$ but the model may still be useful. The results of the $^{13}$C NMR studies of these complexes are given in Table 4.7. The $^{13}$C NMR resonances for the carbonyl carbons in the binuclear complexes are all upfield of the carbonyl carbon resonance for the free donor fragment which, of course, has no acceptor moiety withdrawing electron density from the Os(CO)$_4$(CNBu') donor fragment.

The binuclear complexes in Table 4.7 are ordered according to the increasing chemical shift in the $^{13}$C NMR of the carbonyl carbons cis to the metal-metal bond. The ordering would be slightly different if the $^{13}$C NMR chemical shift of the carbonyl carbon trans to the metal-metal was used but it has been shown in several of the aforementioned systems that the correlation of the electronic effect parameter with this particular carbonyl resonance is not as good and has been ascribed to additional π-character involved with this particular carbonyl ligand.$^{140,142,143,146-149,179}$ The greatest variation in the $^{13}$C NMR chemical shifts of the respective carbonyl carbons of the donor moiety, (OC)$_4$(Bu'NC)Os,
was the chemical shift of the two carbonyl ligands trans to one another (the change in the chemical shifts was 12.40 ppm). This initially seemed surprising, since it was anticipated that it would have been the carbonyl trans to the metal-metal bond that would have shown the largest variation since trans influences are usually larger than cis influences in metal complexes, but the change in the chemical shifts of this ligand was 7.10 ppm. This lack of variation in the chemical shift of the carbonyl trans to the metal-metal bond can possibly be ascribed to the additional π-interaction that this ligand has as postulated for the M(CO)₅(L) complexes mentioned above.¹⁴⁰,¹⁴²,¹⁴³,¹⁴⁶-¹⁵⁰,¹⁷⁹ The ranges of the change in chemical shifts in the present complexes ranges are greater than the total ranges of the carbonyl ¹³C NMR chemical shifts which were observed for the molybdenum carbonyl complexes Mo(CO)₅(L) (L = a wide variety of thirty-one phosphorus containing ligands) which had chemical shift ranges of 6.38 ppm and 4.58 ppm for the cis and trans carbonyl ligands, respectively.¹⁴⁶

It has been pointed out that the utilization of ¹³C NMR chemical shifts of carbonyl carbons to examine the electronic parameters of a ligand cannot differentiate between a weaker σ-donor and a stronger π-acceptor ligand.¹⁴⁸ Both effects shift the ¹³C NMR chemical resonance of the carbonyl carbon upfield and both weaker σ-donor and a stronger π-acceptor properties tend to occur together.¹⁴⁸ In the case of the binuclear organometallic complexes the σ-interaction is viewed as a dative metal-metal bond while any π-interaction would presumably be a repulsive interaction between two sets of filled d-orbitals (see Figure 5.2). Hence, in this series of binuclear compounds it may be possible to assign the changes in chemical shifts as predominantly due to σ-interactions.

Simplistically, the strongest acceptor should cause the ¹³C NMR resonance of the carbonyl ligands on the donor fragment, (OC)₄(Bu'NC)Os, to shift to the highest field. If
this is the case then Os(CO)$_3$(GeCl$_3$)(Cl) is the strongest acceptor fragment of those measured. This observation is in keeping with the exceptional stability of (OC)$_5$OsOs(CO)$_3$(GeCl$_3$)(Cl)$^{44}$ as compared to (OC)$_5$OsRu(CO)$_3$(SiCl$_3$)(Y) (Y = SiCl$_3$, Br)$^{45}$ and (OC)$_5$OsCr(CO)$_5$. This difference between the acceptor ability of the most potent acceptor, Os(CO)$_3$(GeCl$_3$)(Cl) and the second strongest Ru(CO)$_3$(SiCl$_3$)$_2$ unit is illustrated in Chapter 5: with the compound Cp*(OC)$_2$IrOs(CO)$_3$(GeCl$_3$)(Cl) which is stable whereas Cp*(OC)$_2$IrRu(CO)$_3$(SiCl$_3$)$_2$ is thermally unstable. Similarly, (OC)$_5$OsOs(CO)$_3$(GeCl$_3$)(Cl) showed no detectable reaction in solution with PPh$_3$ over a 12 h period at 338 K$^{44}$ while a solution of (OC)$_5$OsRu(CO)$_3$(SiCl$_3$)(Br) and PPh$_3$ at room temperature rapidly produced Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)(Br) and Os(CO)$_5$$^{45}$ indicating Os(CO)$_3$(GeCl$_3$)(Cl) has, indeed, a greater acceptor ability than Ru(CO)$_3$(SiCl$_3$)(Y) (Y = SiCl$_3$, Br).

For the complexes (L)(OC)$_4$OsM(CO)$_5$ (L = a phosphorus containing ligand; M = Cr, Mo, W) it was suggested that the order of stability of the acceptor fragments was W > Mo > Cr.$^{50,74}$ This agrees with the order based on the $^{13}$C NMR chemical shifts reported here (Table 4.7). A cautionary note should be mentioned in this comparison: thermal stabilities are a composite of both the ground state and the transition state effects whereas, the $^{13}$C NMR measurements consider solely ground state effects.

The data was studied to see whether the approximate electronegativity of the acceptor fragment might correlate with the $^{13}$C NMR chemical shift of the carbonyl carbons of the donor fragment. A correlation between the electronegativity of substituents on an atom in a metal carbonyl complex with the IR stretching frequencies of the carbonyl groups has previously been proposed; the correlation of IR stretching frequencies of the carbonyl
groups with $^{13}$C NMR chemical shifts of the carbonyl carbons has as discussed above been shown to exhibit a linear relationship.\textsuperscript{142-150} Therefore putting the two arguments together would not seem unreasonable.\textsuperscript{144} The electronegativity of the ligand \textit{trans} to the metal-metal bond in the acceptor fragment was considered first since this is probably the dominant effect. The electronegativity of the other ligands in the acceptor unit were considered next (within a series). Finally, the electronegativity of the central metal atom within a series was taken into account. The group electronegativities were calculated using Mulliken-Jaffe atomic electronegativities and converted to the Pauling scale of electronegativities ($\chi_p$); see Appendix A-2 for further details.\textsuperscript{181} The ordering based on the $^{13}$C NMR chemical shifts in the present series of binuclear complexes in Table 4.7 would seem to correlate with the ordering of the approximate electronegativities of the acceptor fragments. The only exception to the trend was for Ru(CO)$_3$(SiCl)$_3$(Br) fragments. The respective Pauling electronegativities of the two unique ligands were, $\chi_p$ Br (14\% s) = 2.95 and $\chi_p$ SiCl$_3$ = 2.83 while the $^{13}$C NMR resonance of the two carbonyl ligands \textit{trans} to one another in (OC)$_4$(Bu'NC)Os were 178.08 and 179.86 ppm, respectively (see Table 4.7).\textsuperscript{181} It has been suggested that the Mulliken-Jaffe $b$ parameters are an inverse measure of the charge capacity [Br, $b_r$ = 10.41; SiCl$_3$, $b_r$ = 2.50],\textsuperscript{181b} and that groups are more effective reservoirs of charge capacity than atoms. This suggests that the SiCl$_3$ group is a better charge acceptor than Br even though the Br atom has a slightly higher electronegativity.\textsuperscript{181b} Alternatively, it may be that since SiCl$_3$ is thought to be a $\pi$-acceptor ligand while Br is a $\pi$-donor species the net electron density accepted by SiCl$_3$ is greater than Br.\textsuperscript{140,167} If either of these ideas are in effect then the correlation between the $^{13}$C chemical shift of the \textit{cis} carbonyl carbons in the donor fragment
(OC)$_4$(Bu'NC)Os in the $^{13}$C NMR spectra (see Table 4.7) and the electronegativity of the acceptor fragments is valid for all the complexes. It should be stated here that the electronegativity is only one of the components determining the $^{13}$C NMR chemical shift of the carbonyl ligands; electronegativities are based on single bonds and may not reflect π-interactions.$^{181}$ When this is taken in conjunction with the fact that NMR theory of chemical shifts is still progressing and at this time is not fully understood for organometallic systems it may not be accurate to consider these scales/trends quantitative.$^{182,183}$ This should not detract from the use of $^{13}$C NMR chemical shifts of the carbonyl ligands as a measure of the acceptor ability of the acceptor moiety. Correlations of this sort in other organometallic systems have been extremely useful.$^{142-150}$

As previously mentioned, the $^{13}$C NMR chemical shifts of the cis-carbonyl ligands in for example, M(CO)$_4$(L) correlate with the IR stretching force constants of the carbonyl ligands to yield a linear relationship and hence the $^{13}$C NMR chemical shift can be used as a measure of the electronic parameter of the noncarbonyl ligand, L.$^{142-150}$ With the present series of binuclear complexes a thorough analysis of the IR carbonyl stretching modes was prohibited, for reasons already discussed.

It was thought that there may also be a correlation between the $^{13}$C NMR chemical shift of the two carbonyls trans to one another and cis to the metal-metal bond on the donor fragment, Os(CO)$_4$(CNBu') (see Table 4.7) and the force constants in the IR spectra for the stretching modes of the carbonyl ligands in the mononuclear cis-Ru(CO)$_4$(SiCl)$_2$,$^{167}$ Re(CO)$_5$(X) (X = Cl, Br, I),$^{184a}$ M(CO)$_6$ (M = Cr, Mo, W)$^{185}$ from the literature. It was thought the force constants in the mononuclear complexes would indicate the acceptor ability of the compound before it lost one carbonyl group to become an acceptor fragment.
This was not the case, no correlation was observed, as to whether this may be due to the fact that the two probes (NMR and IR) that were used were on two different sets of molecules (binuclear and mononuclear compounds, respectively), at this juncture, can not be elaborated upon.

The UV-vis spectra of the new compounds together with the previously prepared complexes 4.3-4.5\textsuperscript{51,161} for comparison, are shown in Table 4.8.

As previously mentioned in the text (see Section 2.2), the longest wavelength (lowest energy) band is assigned to a $\sigma \rightarrow \sigma^*$ transition associated with the metal-metal bond.\textsuperscript{30a,c,54,73,74} The complexes [(H)FeM(CO)$_9$]$^-$ (M = Cr, Mo, W), which are thought to contain a dative metal-metal bond, exhibit two bands in the UV-vis spectra at 315-330 nm ($\epsilon \sim 10^4$ L mol$^{-1}$ cm$^{-1}$) and 380-410 nm ($\epsilon \sim 10^3$ L mol$^{-1}$ cm$^{-1}$) which were assigned to the $\sigma \rightarrow \sigma^*$ and $d\pi \rightarrow \sigma^*$ transitions, respectively.\textsuperscript{30a,c} It is believed the assignment of the longest wavelength band in our systems to the $\sigma \rightarrow \sigma^*$ transition rather than to a $d\pi \rightarrow \sigma^*$ transition is correct since it is in agreement with work in the literature and our system is slightly different (uncharged).\textsuperscript{54,73,74} The assignment of the $\sigma \rightarrow \sigma^*$ to the lowest energy absorption is also in agreement with what one might expect based on the simplistic idea of a transition between the smallest energy gap (the HOMO and LUMO) from theoretical calculations for the complexes (OC)$_5$OsCr(CO)$_5$\textsuperscript{53} and (OC)$_5$OsW(CO)$_5$.\textsuperscript{12} In our compounds, it is not known why two bands of almost equal molar absorptivity are observed and the identity of the second transition. It is purely speculative to suggest that there could be due to spin-orbit coupling or mixing of other states to result in this other band in the UV-vis spectra. It is known that spin-orbit coupling is strongest for third row transition metals and there is evidence of spin-orbit coupling in Os(CO)$_4$(L) (L = CO, PMe$_3$).\textsuperscript{187,188} With 4.7 a single
band is observed in this region of the UV-vis spectrum (see Table 4.8) presumably in this case the two bands are coincident which would explain the larger molar absorptivity of this compound when compared to the other species in Table 4.8 and suggest the complex is analogous to the other compounds. The UV-vis spectra 4.3 and 4.4 exhibit only one band while the tungsten

Table 4.8 The UV-vis absorption spectra of complexes with (OC)$_4$(Bu'NC)Os as the donor fragment.

<table>
<thead>
<tr>
<th>Compound$^a$</th>
<th>UV-vis absorption,$^b$ nm ($\epsilon$, L mol$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Dnr)Os(CO)$_3$(GeCl)$_3$(Cl)</td>
<td>350(1.3 x 10$^4$), 308(1.6 x 10$^4$)</td>
</tr>
<tr>
<td>(Dnr)Ru(CO)$_3$(SiCl)$_2$</td>
<td>324(9.1 x 10$^3$)</td>
</tr>
<tr>
<td>(Dnr)Ru(CO)$_3$(SiCl)$_3$(Br)</td>
<td>368(1.2 x 10$^3$), 334(1.3 x 10$^3$)</td>
</tr>
<tr>
<td>(Dnr)Re(CO)$_3$Cl</td>
<td>358(3.1 x 10$^3$), 334(3.7 x 10$^3$)</td>
</tr>
<tr>
<td>(Dnr)Re(CO)$_3$Br</td>
<td>362(2.7 x 10$^3$), 338(3.5 x 10$^3$)</td>
</tr>
<tr>
<td>(Dnr)Re(CO)$_3$I</td>
<td>370(2.5 x 10$^3$), 334$^c$(4.4 x 10$^3$)</td>
</tr>
<tr>
<td>(Dnr)W(CO)$_5$</td>
<td>364(2.8 x 10$^3$), 318$^c$(3.6 x 10$^3$)</td>
</tr>
<tr>
<td>(Dnr)Mo(CO)$_5$</td>
<td>362(2.5 x 10$^3$)</td>
</tr>
<tr>
<td>(Dnr)Cr(CO)$_5$</td>
<td>400(1.7 x 10$^3$)</td>
</tr>
</tbody>
</table>

$^a$ (Dnr) = (OC)$_4$(Bu'NC)Os. $^b$ In CH$_2$Cl$_2$ at room temperature. $^c$ Broad shoulder and the peak maximum was located utilizing ideas in the literature.$^{186}$

analogue exhibits a second band as a shoulder at 318 nm, the second bands for the chromium and molybdenum species are presumably present but too broad to observe. For further examples and discussion of UV-vis absorptions of complexes with a donor-acceptor
metal-metal bond which are similar to those presented here see later in the text (Tables 4.12 and 5.8).

For the complexes \([(H)(L)_{n}(OC)_{4-n}FeW(CO)_{5}]^{-}\), \((L = P(OMe)_3; n = 0, 1)\) it was suggested the wavelength of the \(\sigma \rightarrow \sigma^*\) transition in the UV-vis spectra should indicate the polarity of the dative metal-metal bond\(^{30a,c}\). Expanding on this proposal it was thought that the \(\sigma \rightarrow \sigma^*\) transition might be a useful probe to investigate within the present series which acceptor had the greatest acceptor ability. Simplistically, it was thought that the better the overlap between the molecular orbitals that combine to form the metal-metal dative bond the larger the energy required for the \(\sigma \rightarrow \sigma^*\) excitation and the shorter the wavelength observed for the transition in the UV-vis spectrum. This is provided the donor moiety is the same in each case (i.e., \((OC)_4(Bu'NC)Os\)). Although, the \(\sigma \rightarrow \sigma^*\) transition associated with the metal-metal bond is not a measure of the metal-metal bond strength but may illustrate trends in the energies of heterolytic cleavage\(^{189}\).

Previously it had been found for \([MoO_{4-n}S_n]^2\) \((n = 0-4)\) and \([MoSe_4]^2\) that there was a linear correlation between \(^{95}\)Mo NMR chemical shifts and the inverse of the lowest optically allowed transition energies \((d \rightarrow d^*\) transitions) in the UV-vis spectra\(^ {156}\). Similarly, in octahedral Co(III) complexes with oxygen and nitrogen ligands a correlation exists between \(^{59}\)Co NMR chemical shifts and the lowest energy \(d \rightarrow d\) electronic transition\(^ {157}\). It was therefore thought that there might be a correlation between the UV-vis \(\sigma \rightarrow \sigma^*\) transition associated with the metal-metal bond in \((OC)_4(Bu'NC)Os(Acc)\) (Acc = an acceptor fragment) complexes and the \(^{13}\)C NMR chemical shift of the carbonyl ligands on the same donor moiety in a series of complexes as the acceptor fragment was varied. No
such correlation was, however, observed indicating that the bonding in these complexes is more complex that the simplistic ideas presented herein.

4.2.2 Complexes with Os(CO)$_4$(PMe$_3$) as the donor fragment.

4.2.2.1 Preparation of the new complexes with Os(CO)$_4$(PMe$_3$) as the donor fragment.

The complexes (Me$_3$P)(OC)$_4$OsRu(CO)$_3$(SiCl$_3$)Y (Y = SiCl$_3$, Br) (4.14, 4.15) were obtained upon stirring a C$_6$H$_{14}$ solution of the appropriate Ru(CO)$_4$(SiCl$_3$)Y complex and Os(CO)$_4$(PMe$_3$) at room temperature under vacuum, and were obtained in 72% and 94% yields, respectively (also see eq 5.1). The molecular structure of 4.14 was determined by X-ray crystallography and will be discussed in Chapter 5 along with the ruthenium analogue, (Me$_3$P)(OC)$_4$RuRu(CO)$_3$(SiCl$_3$)$_2$.

Heating of a 1,2-C$_2$H$_4$Cl$_2$ solution of [Re(CO)$_4$X]$_2$ (X = Br, Cl, I) and Os(CO)$_4$(PMe$_3$) at 323 K, afforded the complexes, (Me$_3$P)(OC)$_4$OsRe(CO)$_4$(X) (4.13, 4.16, 4.17) which upon subsequent recrystallization gave the complexes as pale yellow crystals in 53%, 54% and 44% yields, respectively. The starting materials, [Re(CO)$_4$X]$_2$ were recrystallized from C$_6$H$_6$ or C$_6$H$_5$CH$_3$ and not CHCl$_3$ to prevent the formation of the anion analogous to [(μ-X)$_3$Re$_2$(CO)$_6$]$^-$. This anion was sometimes observed by IR spectroscopy in the synthesis of 4.13, 4.16 and 4.17 when this precaution was not taken. Another precaution implemented was the filtration of the dried 1,2-C$_2$H$_4$Cl$_2$ through basic alumina, before use of the solvent in the syntheses. This was carried out to remove any HCl that might be present and which might also have promoted a similar reaction to give [Re$_2$(CO)$_6$(μ-X)$_3$]$^-$. 
The preparation of \((\text{H})(\text{Me}_3\text{P})(\text{OC})_3\text{OsRe}(\text{CO})_5\) (4.18) has been reported previously and was obtained in this study in a 58% yield but the duration of the reaction varied dramatically with different repetitions of the procedure (eq 4.1).\(^{48}\)

\[
\text{Os(CO)}_4(\text{PMe}_3) + (\text{H})\text{Re(CO)}_5 \xrightarrow{343 \text{ K}} \text{Vacuum} \xrightarrow{\geq 140 \text{ h}} (\text{H})(\text{Me}_3\text{P})(\text{OC})_3\text{OsRe(CO)}_5 + \text{CO} \quad (4.1)
\]

In the system, \((\text{H})\text{Os}_2(\text{CO})_8(\text{R})\) with \(\text{CCl}_4\) the reaction rate was not reproducible and this behavior was attributed to a radical-chain mechanism.\(^{192}\) It has been previously proposed in the literature that the formation of 4.18 could proceed via the radical intermediate \([\text{(Me}_3\text{P})(\text{OC})_3\text{OsRe(CO)}_5]\) and the observation reported here is consistent with this mechanism.\(^{48}\)

The complexes, \((\text{X})(\text{Me}_3\text{P})(\text{OC})_3\text{OsRe(CO)}_5\) \((\text{X} = \text{Cl, Br, I})\) (4.19-4.21) were prepared by stirring a \(\text{C}_6\text{H}_{14}\) solution of 4.18 at room temperature with an excess of \(\text{CCl}_4\), \(\text{CBr}_4\) or \(\text{CH}_2\text{I}_2\). The subsequent recrystallizations of the products afforded the complexes, 4.19-4.21 in 74%, 75% and 86% yields, respectively.
4.2.2.2 Investigation of the possible interconversion \((\text{Me}_3\text{P})(\text{OC})_4\text{OsRe(CO)}_4(\text{X})\) (4.16, 4.13, 4.17) and \((\text{X})(\text{Me}_3\text{P})(\text{OC})_3\text{OsRe(CO)}_5\) \((\text{X} = \text{Cl, Br, I})\) (4.19-4.21).

Previously it had been found that \((\text{Me}_3\text{P})(\text{OC})_4\text{OsMn(CO)}_4(\text{Br})\) isomerized to \((\text{Br})(\text{Me}_3\text{P})(\text{OC})_3\text{OsMn(CO)}_5\) at room temperature in \(\text{CH}_2\text{Cl}_2\)\(^45\). On 4.13, 4.16, or 4.17 under \(\text{N}_2\), in the absence of light, in either \(\text{CH}_2\text{Cl}_2\), \(\text{C}_6\text{H}_6\), \(\text{C}_6\text{H}_5\text{CH}_3\) or \(1,2\text{-C}_2\text{H}_4\text{Cl}_2\) at temperatures in the range from room temperature to 353 K over a time period of 12 h - 450 h, the only new products observed in solution were \(\text{Os(CO)}_4(\text{PMe}_3), \text{Re(CO)}_5(\text{X})\) and \([\text{Re(CO)}_4\text{X}]_2\). A much reduced amount of the starting material typically, still remained. (All species were identified by the IR spectra of the reaction solutions)\(^69,190,193\). At no time was there any IR spectral evidence to suggest the complexes 4.17-4.21 were present in the reaction mixture, which is consistent with the preliminary findings for the bromo analogue.\(^45\). This difference in behavior between the rhenium complexes and manganese analogues might be due to the view that Re-X bonds being stronger than the Mn-X bonds in similar manner to Re-H bonds and Mn-H bonds.\(^192\) (The \(\text{Mn(CO)}_5(\text{X})\) compounds are more reactive than the \(\text{Re(CO)}_5(\text{X})\) complexes).\(^194\)

The possible isomerization in the other direction (that is, from a complex with a nondative covalent metal-metal bond to a complex with a dative covalent bond) was also examined. The complex 4.19 was stirred in \(\text{CH}_2\text{Cl}_2\) or \(\text{C}_6\text{H}_5\text{CH}_3\) at room temperature, under \(\text{N}_2\) for up to 300 h and the reaction solution monitored by IR spectroscopy. In \(\text{C}_6\text{H}_5\text{CH}_3\) the IR \(v(\text{CO})\) bands due to 4.19 were seen to decrease in intensity and the only new peaks observed were those assigned to \(\text{Re(CO)}_5\text{Cl}\); while in \(\text{CH}_2\text{Cl}_2\) an IR spectrum of the solution as the reaction proceeded revealed bands due to \(\text{Re(CO)}_5\text{Cl}\) and \(\text{fac-Os(CO)}_3(\text{PMe}_3)(\text{Cl})_2\) (fac-2.2).\(^193\) Both sets of reactions, therefore, show there is no
interconversion of the species \((\text{Me}_3\text{P})(\text{OC})_4\text{OsRe}(	ext{CO})_4(\text{X})\) 4.16, 4.13, 4.17 and 4.19-4.21. All that was observed were the products consistent with the cleavage of the Os-Re bond in each molecule.

4.2.2.3 Spectroscopic properties of complexes with \(\text{Os}(	ext{CO})_4(\text{PMe}_3)\) as the donor fragment.

The \(^1\text{H}\) NMR chemical shifts and IR \(v(\text{CO})\) bands of the new compounds, together with those of \(\text{Os}(	ext{CO})_4(\text{PMe}_3)\), \(^2\text{H}\) \(2.1\), \(^5\text{O}\) \(4.1\), \(^5\text{O}\) \(4.2\), \(^5\text{O}\) \(4.13\), \(^4\text{H}\) \(4.14\), \(^4\text{H}\) \(4.18\), \(4.2\), and \(4.20\) are shown in Table 4.9. The complexes 4.16, 4.13, 4.17 are viewed as containing a dative covalent metal-metal bond whereas the corresponding complexes 4.19-4.21 are considered to contain a nondative covalent metal-metal bond. As previously pointed out, this allows a comparison of the two types of metal-metal bonding in the molecules with the minimum amount of changes. \(^4\text{H}\) The IR spectra \(v(\text{CO})\) of the complexes (in Table 4.9), were recorded in \(\text{CH}_2\text{Cl}_2\) in which all the compounds were soluble. The complexes 4.19-4.21 (and \(\text{Os}(	ext{CO})_4(\text{PMe}_3)\) are, however, soluble in the less polar solvent, \(\text{C}_6\text{H}_{14}\). This observation is consistent with the earlier observation that complexes with a dative covalent metal-metal bond are less soluble in nonpolar solvents due to the increased polarity of the metal-metal bond. \(^4\text{H}\) \(^4\text{H}\)

Use of \(\text{CH}_2\text{Cl}_2\) as a solvent for the IR spectra results in broadening of the CO stretching bands and precludes a thorough analysis of the IR spectra. \(^1\text{H}\) For the donor fragment in the molecules of the formula \(\text{trans}-(\text{Me}_3\text{P})(\text{OC})_4\text{Os}((\text{Acc})\) (Acc = acceptor moiety, treating this whole group as a point) one might expect two IR active \(v(\text{CO})\) bands; for the acceptor fragments in the complexes of the type; \(\text{mer}-(\text{Dnr})\text{Ru}(	ext{CO})_3(\text{SiCl}_3)(\text{Y})\) (Y =
SiCl$_3$, Br; Dnr = donor moiety, treating those whole group as a point), (Dnr)M(CO)$_5$ (M = Cr, Mo, W) and cis-(Dnr)Re(CO)$_4$(X) (X = Cl, Br, I) it might be expected to observe three, three and four IR active v(CO) bands, respectively. Clearly these numbers of IR v(CO) bands are not observed in all the IR spectra of the complexes, see Table 4.9, suggesting that there some an overlap of some of the v(CO) bands.

In some the studies of IR spectra of complexes with dative metal-metal bonds, it was postulated that the CO stretches above \(-2000\) cm\(^{-1}\) could be assigned to the donor moiety and those below \(-2000\) cm\(^{-1}\) to the acceptor fragment (see (Me$_3$P)(OC)$_4$OsM(CO)$_5$ (M = W, Cr, Mo) (2.1, 4.1, 4.2) ( in Table 4.9) because of the charge separation in the donor-acceptor metal-metal bond (i.e., M(\(\delta^+\))\(\rightarrow\)M(\(\delta^-\))).\(^{50,51}\) It is well known that a positive charge on a metal carbonyl molecule causes an increase in the CO stretching frequencies whereas a negative charge shifts the CO stretches to lower frequencies. Unfortunately in some of the complexes recorded in Table 4.9, this distinction was not so well defined.
Table 4.9 The IR spectra (v(CO) region) and $^1$H NMR spectra of complexes with Os(CO)$_4$(PM$_3$) as the donor fragment and some related structural isomers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H NMR,$^a$ δ, ppm</th>
<th>IR,$^b$ v(CO), cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRu(CO)$_3$(SiCl)$_2$</td>
<td>2.16 (10.7)</td>
<td>2124(w), 2069(w,sh), 2038(vs), 2012(vw,sh)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRu(CO)$_3$(SiCl)$_3$(Br)</td>
<td>2.10 (10.7)</td>
<td>2124(vw), 2079(w), 2055(w,sh), 2041(vs), 2031(s,sh)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRe(CO)$_4$(Cl)</td>
<td>2.02 (10.5)</td>
<td>2119(vw), 2070(m), 2051(w,sh), 2024(vs), 1974(m), 1914(m)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRe(CO)$_4$(Br)</td>
<td>2.02 (10.5)</td>
<td>2119(vw), 2069(m), 2050(w,sh), 2026(vs), 1974(m), 1915(m)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRe(CO)$_4$(I)</td>
<td>2.03 (10.5)</td>
<td>2117(vw), 2066(m), 2051(w,sh), 2027(vs), 1974(m), 1916(m)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsW(CO)$_5$</td>
<td>1.99 (10.7), 1.88 (10.4)$^c$</td>
<td>2094(w), 2041(m,sh), 2009(vs), 1913(vs), 1880(m,sh)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsMo(CO)$_5$</td>
<td>1.97 (10.7), 1.86 (10.4)$^c$</td>
<td>2090(w), 2043(m,sh), 2004(vs), 1920(s), 1883(m,sh)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsCr(CO)$_5$</td>
<td>2.00 (10.7), 1.84 (10.4)$^c$</td>
<td>2092(w), 2025(m,sh), 2011(vs), 1912(s), 1885(m,sh)</td>
</tr>
<tr>
<td>(H)(Me$_2$P)(OC)$_3$OsRe(CO)$_5$$^d$</td>
<td>1.91 (CH$_3$, 10.5), -10.59 (H, 19.0)</td>
<td>2106(m), 2036(m), 1999(vs,br), 1958(m,br)</td>
</tr>
<tr>
<td>(Cl)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$$^d$</td>
<td>1.91 (10.8)</td>
<td>2116(m), 2055(m), 2035(w,sh), 2012(vs), 2004(vs), 1969(m,br)</td>
</tr>
<tr>
<td>(Br)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$$^d$</td>
<td>1.95 (10.7)</td>
<td>2115(m), 2053(m), 2034(w,sh), 2004(s), 1970(m,br)</td>
</tr>
<tr>
<td>(I)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$$^d$</td>
<td>2.04 (10.3)</td>
<td>2115(m), 2051(m), 2036(w,sh), 2010(s,br), 1967(m,br)</td>
</tr>
<tr>
<td>Os(CO)$_4$(PM$_3$)$^e$</td>
<td>1.82 (10.5)</td>
<td>2058(m), 1973(m,sh), 1931(vs)</td>
</tr>
</tbody>
</table>
Footnotes to Table 4.9.

a The $^1$H NMR spectra were in CD$_2$Cl$_2$ at 233 K, the coupling constant, $^2J_{P-H}$ is given in parentheses. b The IR spectra were in CH$_2$Cl$_2$ at room temperature with a resolution of ± 2 cm$^{-1}$. c The second resonance is assigned to the isomer with the phosphine cis to the metal-metal bond. d Complex contains a nondative covalent metal-metal bond. e The previously reported mononuclear complex is given for direct comparison.$^{69}$

The $^1$H NMR resonances of the PMe$_3$ group in the complexes with a donor-acceptor metal-metal bond in Table 4.9 show little variation in the chemical shift with alteration of the acceptor fragment. This can be attributed to the proton nuclei being too removed from the metal-metal interaction to experience a large variation on changing the acceptor moiety. Unlike 2.1, 4.1, 4.2, the compounds 4.13-4.17 exhibit no evidence in the $^1$H NMR spectra for a second isomer (i.e., with the PMe$_3$ group cis to the metal-metal bond).

The complexes containing a nondative covalent metal-metal bond, 4.18-4.20 exhibit a proton resonance somewhat to higher field (increased shielding) to that of the structural isomer containing a donor-acceptor metal-metal bond. This suggests there is less electron density being removed or given from the PMe$_3$ group to the bimetallic complex in the compounds containing the nondative covalent metal-metal bond.
Table 4.10 The $^{13}$C-$^1$H NMR spectra of complexes with a Os(CO)$_4$(PMe$_3$) as the donor fragment and some related isomers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{13}$C-$^1$H NMR$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$(CH$_3$)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRu(CO)$_3$(SiCl$_3$)$_2$</td>
<td>21.80 (38.9)$^b$</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRu(CO)$_3$(SiCl$_3$)(Br)</td>
<td>22.13 (38.9)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRe(CO)$_4$(Cl)</td>
<td>22.42 (37.6)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRe(CO)$_4$(Br)</td>
<td>22.36 (37.8)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRe(CO)$_4$(I)</td>
<td>22.30 (37.9)</td>
</tr>
<tr>
<td>(H)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$</td>
<td>23.37 (38.0)</td>
</tr>
<tr>
<td>(Cl)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$</td>
<td>17.14 (37.4)</td>
</tr>
<tr>
<td>(Br)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$</td>
<td>17.85 (37.9)</td>
</tr>
<tr>
<td>(I)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$</td>
<td>19.31 (38.7)</td>
</tr>
<tr>
<td>Os(CO)$_4$(PMe$_3$)$^e$</td>
<td>21.19 (39.1)</td>
</tr>
</tbody>
</table>

$^a$ All $^{13}$C-$^1$H NMR spectra were recorded in CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1:3) at 233 K.  
$^b$ The coupling constant, $^1J_{P-C}$ in Hz in parentheses.  
$^c$ The carbonyl resonances are described as singlets (s) or doublets (d), the relative integrated area is given and where applicable the carbon-phosphorus coupling, $^2J_{P-C}$ in Hz is given in the parentheses.  
$^d$ These are complexes containing a nondative covalent metal-metal bond.  
$^e$ For a direct comparison.  
$^f$ The third number in parentheses is a osmium-carbon coupling ($^1J_{Os-C}$) in Hz.
The $^{13}$C($^1$H) NMR chemical shifts for the new complexes together with those of the previously prepared compounds Os(CO)$_4$(PMe$_3$)$_2$, $^{2,1,50,74}$ 4.1, $^{50,74}$ 4.2, $^{50,74}$ 4.13, $^{48}$ 4.14, $^{45}$ 4.18, $^{48}$ and 4.20$^{48}$ are shown in Table 4.10. All samples were recorded under similar conditions to allow an accurate comparison of the acceptor fragments.

As in the binuclear complexes with (OC)$_4$(Bu'NC)Os as the donor fragment the $^{13}$C NMR resonance of the carbonyls of the free ligand Os(CO)$_4$(PMe$_3$) (189.50 ppm) is downfield relative to the resonances of the (Me$_3$P)(OC)Os fragment in the binuclear complexes (see Table 4.10). This is consistent with less electron density on the Os fragments in binuclear complexes and is consistent with the IR carbonyl stretching frequencies of the various species (see Table 4.9). Analogous to Os(CO)$_4$(CNBu') (see Table 4.7) the carbonyl resonance of Os(CO)$_4$(PMe$_3$) exhibits a detectable coupling ($^1J_{Os-C} = 122.0$ Hz) to $^{187}$Os.

The $^{13}$C NMR resonances of the carbonyls of the donor fragments (Me$_3$P)(OC)$_4$Os, all exhibit a doublet (carbon to phosphorus coupling, $^2J_{P-C}$) in the range 181-184 ppm, (see Table 4.10) of relative intensity four (see Figure 4.6). This is consistent with the structure observed in the solid state by crystallography, that is, with the phosphine ligand trans to the dative metal-metal bond.$^{50,74}$ There was no evidence in the spectra for the isomer with the (PMe$_3$) group cis to the metal-metal bond as found for the (L)(OC)$_4$OsM(CO)$_5$ (M = Cr, Mo, W; L = phosphine, phosphite) complexes.$^{50,74}$ Presumably, the difference in behavior between 2.1, 4.1, 4.2 and the other complexes in Table 4.10 with a dative metal-metal bond can be ascribed to the difference of the acceptor moieties.

The $^{13}$C NMR spectra of the acceptor fragments in (Dnr')Ru(CO)$_3$(SiCl$_3$)(Y) (Dnr' = (Me$_3$P)(OC)$_4$Os; Y = SiCl$_3$, Br) (4.14, 4.15) and (Dnr')Re(CO)$_4$(X) (X = Br, Cl, I) (4.13,
4.16, 4.17) (see Table 4.10) were assigned as described in Section 4.2.1.8 and are similar to the analogous compounds with (OC)$_4$(Bu'NC)Os as the donor moiety, see Table 4.7.

The $^{13}$C NMR spectra of complexes 4.18-4.21, with nondative metal-metal bonds, are also shown in Table 4.10. For the osmium fragment two resonances with phosphorus-carbon couplings ($^{2}J_{P-C}$) were observed, one signal of relative intensity 1 in the range 175-185 ppm and, the other of relative intensity 2 in the range 185-192 ppm. The rhenium moieties showed either one (for the hydride complex) or two broad resonances (for the halide complexes). The latter signals were in a ratio of 1:4. This suggests that the solution structures are the same as that observed in the solid state for 4.20 by X-ray crystallography, that is, on the osmium fragment the phosphine $trans$ and the halide or hydride $cis$ to the metal-metal bond (see Figure 4.6).$^{48}$ There was no evidence in the $^{13}$C NMR spectra of the complexes of any other isomer.

![Figure 4.6 The idealized structures of (a) (Me$_3$P)(OC)$_4$OsRe(CO)$_4$(X) (X = Cl, Br, I) (4.16, 4.13, 4.17) and (b) (X)(Me$_3$P)(OC)$_4$OsRe(CO)$_5$ (4.19-4.21).](image)

Analogous to the ideas put forth in Section 4.2.1.8, it was thought a correlation between the $^{13}$C NMR resonances on the donor fragment, (Me$_3$P)(OC)$_4$Os, and the accepting ability of the acceptor moiety might be in effect. If this were the case, the
resonances might be expected to shift to lower field as the accepting ability of the acceptor fragment decreased. The \(^{13}\)C NMR resonances of the four CO ligands cis to the metal-metal bond on the donor fragment range from 181.85-183.97 ppm. In Table 4.10 these resonances are ordered according to increasing chemical shift in the \(^{13}\)C NMR of the carbonyl carbons on the donor fragment cis to the metal-metal bond. This gives an order of decreasing acceptor ability of Ru(CO)\(_3\)(SiCl)\(_2\), Ru(CO)\(_3\)(SiCl)\(_3\)(Br), Re(CO)\(_4\)(Cl), Re(CO)\(_4\)(Br), Re(CO)\(_4\)(I). This ordering is exactly the same as seen for the analogous complexes with (OC)\(_4\)(Bu'NC)Os as the donor moiety, see Table 4.7. Furthermore, for \(2.1\), \(4.1\), \(4.2\) (although the \(^{13}\)C\(^{1}\)H) NMR spectra of these complexes were collected under different conditions), the ordering of the acceptor fragments for these compounds is: W(CO)\(_5\), Mo(CO)\(_5\), Cr(CO)\(_5\); which is also the same as observed in Table 4.7.\(^{50,74}\)

Similarly, if the simplistic model of approximate electronegativity of the acceptor fragment (Section 4.2.1.8) is used, there appears to be correlation between the \(^{13}\)C NMR chemical shift of the cis carbonyl carbons in the donor fragment (Me\(_3\)P)(OC)\(_4\)Os and the electronegativity of the acceptor fragments (see Table 4.10).

The \(^{31}\)P\(^{1}\)H) NMR chemical shifts for the new complexes together with those of the previously prepared compounds, Os(CO)\(_4\)(PMe)\(_3\),\(^{69}\) \(2.1\),\(^{50,74}\) \(4.1\),\(^{50,74}\) \(4.2\),\(^{50,74}\) \(4.13,48\) \(4.14,45\) \(4.18,48\) and \(4.20\)\(^{48}\) are shown in Table 4.11. All samples were recorded under similar conditions to allow direct comparisons of the different acceptor fragments.
Table 4.11 The $^{31}\text{P}$$^1\text{H}$ NMR of complexes with Os(CO)$_4$(PMe$_3$) as the donor fragment and some related structural isomers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{31}\text{P}$$^1\text{H}$ NMR, $\delta$(PMe$_3$)$_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRu(CO)$_3$(SiCl)$_2$</td>
<td>-49.85</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRu(CO)$_3$(SiCl)$_3$(Br)</td>
<td>-50.96</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRe(CO)$_4$(Cl)</td>
<td>-52.01</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRe(CO)$_4$(Br)</td>
<td>-52.35</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRe(CO)$_4$(I)</td>
<td>-52.74</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsCr(CO)$_5$</td>
<td>-50.33, -62.32$^c$ (23:1)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsMo(CO)$_5$</td>
<td>-51.16, -62.16$^c$ (6:1)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsW(CO)$_5$</td>
<td>-51.24, -62.76$^c$ (14:1)</td>
</tr>
<tr>
<td>(Cl)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$$^b$</td>
<td>-37.62</td>
</tr>
<tr>
<td>(Br)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$$^b$</td>
<td>-43.54</td>
</tr>
<tr>
<td>(I)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$$^b$</td>
<td>-52.79</td>
</tr>
<tr>
<td>Os(CO)$_4$(PMe$_3$)</td>
<td>-52.00</td>
</tr>
</tbody>
</table>

$^a$ All $^{31}\text{P}$$^1\text{H}$ NMR spectra were recorded in CD$_2$Cl$_2$ at 233K in ppm. $^c$ These are complexes with a nondative covalent metal-metal bond. $^c$ For the minor isomer with the phosphine ligand cis to the metal-metal bond, the ratio of major isomer:minor isomer is given in parentheses.

The complexes in Table 4.11 typically contain a single resonance in the $^{31}\text{P}$$^1\text{H}$ NMR spectra and therefore aids in the detection of any phosphorus containing impurities or other isomeric forms. The values for the isomeric ratios of the complexes 2.1, 4.1, 4.2 are somewhat different to the values reported in the literature$^{50,74}$ since these present values were collected under slightly different conditions of solvent and temperature. In no other systems with (Me$_3$P)(OC)$_4$Os as the donor fragment was there any evidence in the $^{31}$P NMR spectra to suggest the presence of other isomers in the solution. The $^{31}\text{P}$$^1\text{H}$ NMR chemical shifts for complexes with an Os-Re dative covalent bond show only small
variation whereas for those of complexes with nondative covalent metal-metal bonds there is a marked variation. This is presumably due to the adjacent location of the halide ligand and possibly the nature of the Os-Re bond.

The $^{31}$P NMR resonance of the free donor fragment Os(CO)$_4$(PMe$_3$) is not very different to those of complexes with dative metal-metal bonds. This suggests less shift of electron density upon coordination to give the binuclear species (Me$_3$P)(OC)$_4$Os(Acc) (Acc = an acceptor fragment). This is unlike the trend that was observed in the IR v(CO) stretching frequencies and the $^1$H and $^{13}$C NMR chemical shifts of Os(CO)$_4$(PMe$_3$) in the complexed binuclear species and uncomplexed form.

It was thought that the $^{31}$P NMR resonances of the PMe$_3$ ligand in the complexes with a dative metal-metal bond could also be used to probe the acceptor ability of the acceptor fragments, in the same way that the $^{13}$C NMR resonances of the carbonyl ligands on the same donor fragments (see previously in the text, and Tables 4.7 and 4.10). The C-P-C bond angles in 2.1, 50.74 $^{4.1} 50.74^{4.13}$, 48 and 4.14, are remarkably similar and range from 102.3(6)-105.5(5)$^\circ$ which might suggest the solution geometries should also be virtually identical. This is important since it has been suggested that altering the geometry around the $^{31}$P nucleus can drastically change the $^{31}$P NMR chemical shift of the species.$^{152-155}$

In the literature there are two different models for the trends observed in $^{31}$P NMR chemical shifts. With the series of complexes [$\eta^6$-C$_6$H$_5$(X)]Cr(CO)$_2$(PPh$_3$) (X = H, CH$_3$, C(CH$_3$)$_3$, OCH$_3$, N(CH$_3$)$_2$, Si(CH$_3$)$_3$, F, Cl, Br, COCH$_3$, CHO, CO$_2$CH$_3$, C$_6$H$_5$, CF$_3$) the IR carbonyl stretching force constants were shown to correlated well with the $^{31}$P NMR chemical shifts.$^{151}$ Furthermore, it was proposed that “Electron donating ring substituents
cause a downfield shift of the phosphorus resonance while electron withdrawing groups shift the resonance upfield.” This was consistent with work previously done on the system M(CO)\(_{m-n}(PA_3)_n\) (M = Cr, Mo, W; m = 6; 1 < n < 4; A = F, Cl, OCH\(_3\), SCH\(_3\), N(CH\(_3\))\(_2\), CH\(_3\), C\(_2\)H\(_5\)).

\[
\text{Figure 4.7} \quad \text{Proposed structure of the Mo(CO)\(_4\)((PPh_2O)_2Y(R)(R')) (Y(R) = P(O), Si(Me); R' = alkyl, haloalkyl, aryl) complexes.}^{152}
\]

In the suite of compounds Mo(CO)\(_4\)((PPh_2O)_2Y(R)(R')) (Y(R) = P(O), Si(Me); R' = alkyl, haloalkyl, aryl) the \(^{13}\)C, \(^{17}\)O, \(^{29}\)Si and \(^{31}\)P NMR spectra were collected (see Figure 4.7).\(^{152}\) The Correlations between the chemical shifts of the various resonances were, with very few exceptions, shown to be excellent. Care had been taken in the construction of the system to limit rotation around the Mo-P bond and to maintain the same three groups around the phosphorus utilizing the chelate ring, this ensured only the electron \(\sigma\)-donor/\(\pi\)-acceptor properties of the phosphorus substituents were varied and not the geometries as well. It was proposed “Increased electron density at the diphenylphosphinite phosphorus should result in increased \(\pi\)-back donation of electron density from the metal \(d\) orbitals into the carbonyl \(\pi^*\) orbitals with a commensurate increase in electron density at the carbonyl oxygen and decrease in electron density at the carbonyl carbon.” This translates to, as the
electron density of the substituent on the phosphorus was increased the diphenylphosphinite $^{31}\text{P}$ and carbonyl $^{17}\text{O}$ NMR resonances were observed to be relatively shielded (shifted upfield) with concomitant deshielding (shifting downfield) of the carbonyl $^{13}\text{C}$ NMR resonances. This work is believed to be the first study in which it was possible to correlate the changes in electron density observed in carbonyl ligands directly to changes in electron density at the phosphorus nucleus.

Clearly these two models oppose one another. In the case of $[\eta^6\text{C}_6\text{H}_5(\text{X})]\text{Cr(}\text{CO})_2(\text{PPh}_3)$ the metal is in a pseudo-octahedral environment and does not directly correlate the $^{31}\text{P}$ NMR chemical shifts with $^{13}\text{C}$ NMR chemical shifts of the carbonyl ligands while in $\text{Mo(}\text{CO})_4((\text{PPh}_2\text{O})_2\text{Y(R)(R'))}$ a true octahedral orientation exists and a precise correlation was found.

With the binuclear complexes with a dative metal-metal bond the system may be closer to a true octahedral environment and it was thought that using the same donor fragment in all complexes would maintain the geometry and connectivity around the phosphorus to allow a good correlation to be observed. If the acceptor ability of the acceptor fragment increases, it might be expected that the electron density at the Os metal center would decrease and there would be less $\pi$-back-donation to the $^{13}\text{C}$ carbonyl and electron density would increase at the $^{13}\text{C}$ nucleus (with a concomitant decrease of the electron density at the $^{17}\text{O}$ atom). Presumably there would also be less electron density at the $^{31}\text{P}$ phosphine center which would yield a inverse relationship between the NMR chemical shifts of $^{31}\text{P}$ with $^{13}\text{C}$ resonances. An approximate inverse relationship between the $^{13}\text{C}$ and $^{31}\text{P}$ NMR chemical shifts was observed in this system (see Tables 4.10 and 4.11). From the $^{31}\text{P}$ NMR chemical shifts the ordering of acceptor ability of the acceptor
fragments would be in decreasing order, \( \text{Ru} \left( \text{CO} \right)_3 \left( \text{SiCl}_3 \right)_2 \), \( \text{Cr} \left( \text{CO} \right)_5 \), \( \text{Ru} \left( \text{CO} \right)_3 \left( \text{SiCl}_3 \right) \left( \text{Br} \right) \), \( \text{Mo} \left( \text{CO} \right)_5 \), \( \text{W} \left( \text{CO} \right)_5 \), \( \text{Re} \left( \text{CO} \right)_4 \left( \text{Cl} \right) \), \( \text{Re} \left( \text{CO} \right)_4 \left( \text{Br} \right) \), \( \text{Re} \left( \text{CO} \right)_4 \left( \text{I} \right) \) which is markedly different from the series proposed utilizing \( ^{13}\text{C} \) NMR as the probe or approximate electronegativities of the acceptor fragments (see previously in the text).

It should be noted that previous studies have often indicated an apparent lack of correlation of \( ^{31}\text{P} \) NMR chemical shifts with the chemical shifts of other NMR nuclei when used as probes of electron density.\(^{152,155}\) Furthermore, in some of these studies, arguments involving the \( \pi \)-accepting ability of the phosphorus containing ligand were invoked. In one case\(^{153}\) a model with a metal-phosphorus \( d_\pi-d_\pi \) overlap was used but a model with the metal \( d \) orbital interacting with the phosphine P-R \( \sigma^* \) orbitals is equally valid.\(^{195}\) It might be that the use of the latter model could cause the arguments to be re-evaluated. In the \( ^{13}\text{C} \) NMR spectra of complexes with \( \left( \text{OC} \right)_4 \left( \text{Bu}' \text{NC} \right) \text{Os} \) as the donor fragment (Section 4.2.1.8) a poor correlation was observed with the chemical shift of the carbonyl ligand \textit{trans} to the metal-metal bond but a better correlation was found with the chemical shifts of the CO groups \textit{cis} to the metal-metal bond. Given this a better correlation might have been observed if the phosphine ligand was also \textit{cis} to the metal-metal bond. At this time it is thought that the \( ^{31}\text{P} \) NMR chemical shift of the phosphine ligand does not provide a sensitive probe to the acceptor ability of the acceptor fragments.

The UV-vis spectra of the new compounds together with the previously prepared complexes 2.1,\(^{50}\) 4.1,\(^{50}\) 4.2\(^{50}\) and 4.13\(^{48}\) for comparison, are shown in Table 4.12.

As previously mentioned in the text (Sections 2.2 and 4.2.1.8) the longest wavelength (lowest energy) band is assigned to a \( \sigma \rightarrow \sigma^* \) transition associated with the dative metal-metal bond.\(^{30a,c,54,73,74}\) At present it is not known why two bands of almost
equal molar absorptivity are observed in some cases; and it is tentatively attributed to spin-orbit coupling effects or mixing of other states. It is not thought that the absorption bands are due to charge transfer transitions since in the complexes 2.1, 4.13 and 4.17 the maxima of the UV-vis absorption bands ($\lambda_{\text{max}}$) did not change substantially upon changing the polarity of the solvent (from C$_6$H$_6$ to CH$_2$Cl$_2$).$^{196}$ As with 4.7, the complex 4.14 exhibits a single band in this region of the UV-vis spectrum (see Tables 4.8 and 4.12). Presumably, in this case, the two bands are coincident which would explain the larger molar absorptivity of this compound compared to that of the other species (Table 4.12). Similarly, the UV-vis spectra of (L)(OC)$_4$OsM(CO)$_5$ (M = Cr, Mo; L = CNBu', PMe$_3$) (4.1-4.4) (Tables 4.8 and 4.12) exhibit only one band while the tungsten analogues exhibit a second band as a shoulder at 318 nm ($L = \text{CNBu'}$) and 334 nm ($L = \text{PMe}_3$). The second bands for the chromium and molybdenum species are presumably present, but too broad to observe.

For 4.19-4.21 with a nondative covalent metal-metal bond, the lower energy transition in the UV-vis absorption spectra was assigned to a $\sigma\pi \rightarrow \sigma^*$ transition, with the higher energy and more intense transition as due to a $\sigma \rightarrow \sigma^*$ absorption. This assignment is in accord with studies in the literature.$^{197}$

As found before, (Section 4.2.1.8) there was no correlation of the bands assigned to $\sigma \rightarrow \sigma^*$ transition associated with the metal-metal bond and the $^{13}$C NMR chemical shift of the carbonyl ligands on the donor moiety in this series of complexes.
Table 4.12 The UV-vis absorption spectra of complexes with (Me₃P)(OC)₄Os as the donor fragment and some related structural isomers.

<table>
<thead>
<tr>
<th>Compoundᵃ</th>
<th>UV-vis absorption,ᵇ nm (ε, L mol⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Dnr')Ru(CO)₃(SiCl₃)₂</td>
<td>330(2.2 x 10⁴)</td>
</tr>
<tr>
<td>(Dnr')Ru(CO)₃(SiCl₃)(Br)</td>
<td>374(1.4 x 10⁴), 336(1.4 x 10⁴)</td>
</tr>
<tr>
<td>(Dnr')Re(CO)₄Cl</td>
<td>358(3.2 x 10³), 333(4.1 x 10³)</td>
</tr>
<tr>
<td>(Dnr')Re(CO)₄Br</td>
<td>359(3.3 x 10³), 334(4.6 x 10³)</td>
</tr>
<tr>
<td>(Dnr')Re(CO)₄I</td>
<td>370(3.8 x 10³), 340(6.0 x 10³)</td>
</tr>
<tr>
<td>(Dnr')W(CO)₅</td>
<td>364(2.8 x 10³), 334ᵈ(2.9 x 10³)</td>
</tr>
<tr>
<td>(Dnr')Mo(CO)₅</td>
<td>362(2.4 x 10³)</td>
</tr>
<tr>
<td>(Dnr')Cr(CO)₅</td>
<td>402(1.7 x 10³)</td>
</tr>
<tr>
<td>(Dnr')W(CO)₅ᶜ</td>
<td>368(2.8 x 10³), 334ᵈ(2.7 x 10³)</td>
</tr>
<tr>
<td>(Dnr')Re(CO)₄Brᶜ</td>
<td>366(≤ 1.8 x 10³),ˢ 338(≤ 2.6 x 10³)</td>
</tr>
<tr>
<td>(Dnr')Re(CO)₄Fᶜ</td>
<td>378(2.0 x 10³), 342(3.7 x 10³)</td>
</tr>
<tr>
<td>(Cl)(Me₃P)(OC)₃OsRe(CO)₅</td>
<td>378(1.6 x 10³), 322(1.2 x 10⁴)</td>
</tr>
<tr>
<td>(Br)(Me₃P)(OC)₃OsRe(CO)₅</td>
<td>378(1.5 x 10³), 325(1.3 x 10⁴)</td>
</tr>
<tr>
<td>(I)(Me₃P)(OC)₃OsRe(CO)₅</td>
<td>388(1.1 x 10³), 334(9.0 x 10³)</td>
</tr>
</tbody>
</table>

ᵃ (Dnr') = (Me₃P)(OC)₄Os. ᵇ Recorded in CH₂Cl₂ at room temperature. ᵈ Recorded in C₆H₆ at room temperature. ᵉ Broad shoulder and the peak maximum was located utilizing ideas in the literature. ᵖ Problems with solubility prohibited a quantitative determination of the molar absorptivity.
4.3 Conclusion

A series of binuclear complexes with an unbridged dative metal-metal bond and with either (OC)_4(ButNC)Os or (Me_3P)(OC)_4Os as the donor moiety have been prepared. The complexes have been investigated with IR, ^1H, ^13C{^1H}, ^31P{^1H} NMR and UV-vis spectroscopies together with X-ray crystallography determinations of (Bu^tNC)(OC)_4OsOs(CO)_3(GeCl_3)(Cl).0.5(C_6H_5CH_3) (4.6) and [Os(CO)_4(CNBu^t)(H)][BCl_4] ([4.12][BCl_4]). Most of the techniques are apparently insensitive to the acceptor ability of the acceptor fragments in these complexes, but the ^13C NMR of the carbonyl ligands (cis to the metal-metal bond) on the donor moiety is a sensitive probe to the acceptor fragments. The extent of the shift upfield of the resonance of the carbonyl ligands on the 18-electron donor fragment is believed to be a measure of the acceptor ability of the 16-electron moiety. From the ^13C{^1H} NMR data, the 16-electron acceptor moieties were ordered in decreasing acceptor ability as: Os(CO)_3(GeCl_3)(Cl), Ru(CO)_3(SiCl_3)_2, Ru(CO)_3(SiCl_3)(Br), Re(CO)_4(Cl), Re(CO)_4(Br), Re(CO)_4(I), W(CO)_5, Mo(CO)_5, Cr(CO)_5. This ordering is generally in agreement with both the approximate relative electronegativities of the acceptor groups and the qualitative observations concerning the relative stabilities of the binuclear complexes formed from these acceptor fragments.

From work outlined in Chapter 2 a general procedure has been developed for the ^13CO-labeling of donor fragments which uses mild conditions and provides high yields of the ^13CO-enriched complex. This should be extremely useful in the study of ^13CO scrambling mechanisms that might occur in these complexes. This aspect is developed further in Chapter 5.
4.4 Experimental

4.4.1 General Methods

Manipulations, solvent purification and routine spectroscopic measurements were carried out as described in the sections 2.4 and 3.4, in their respective Chapters. Only previously unreferred to experimental details will be mentioned here.

4.4.2 Materials

The compounds CNBu' (Aldrich), HSiCl3 (Aldrich), and GeCl4 (Alpha), Re2(CO)10 (Strem), Br2 (Anachemia), CH2I2 (Aldrich) were used as supplied. The compound CBr4 (BDH) was sublimed at room temperature, under static vacuum (~1.3 Pa) to a probe cooled to 195 K in the absence of light, prior to use. The solvent, 1,2-dichloroethane (Anachemia) was stirred over NaOH under N2 overnight and then refluxed with and distilled from P2O5. Boron trichloride (Matheson) was purified by distillation under vacuum (1.3 x 10⁻² Pa) from a vessel at 245 K to a cold trap at 195 K where it was subjected to a further 15 min dynamic vacuum, to remove volatile impurities, this process was then repeated three times.169 The ¹³CO-labelled complexes, (L)(OC)₄OsM(CO)₅ (M = Cr, Mo, W; L = PMe₃, CNBu') (2.1, 4.1-4.5) were prepared from ¹³CO-enriched M(CO)₅(THF) and unlabelled Os(CO)₄(PMe₃) or Os(CO)₄(CNBu') as described in the literature.50,51,74,161 The complex, Os(CO)₅ was also prepared according to the literature71 except the temperature for the reaction was typically 638 ± 24 K (and not 553-563 K as previously reported) and the pressure of the gas at the working temperature, was about 4.8 x 10⁷. The concentration of the solution of Os(CO)₅ in C₆H₁₄ that was produced from the reaction was calculated by absorbance in the UV-vis
spectrum. In C₆H₁₄, Os(CO)₅ has two shoulders in the spectrum at 272 nm (ε = 3.04 x 10³ L mol⁻¹ cm⁻¹) and 242 nm (ε = 3.86 x 10³ L mol⁻¹ cm⁻¹) as determined by Dr. H. B. Davis. In a typical procedure use of 2.00 g of Os₃(CO)₁₂ in 200 mL of C₆H₁₄ yielded a solution of Os(CO)₅ in C₆H₁₄ of 1.82 x 10⁻² M (i.e., 69% conversion). The starting material Ru₃(CO)₁₂ was prepared from RuCl₃.xH₂O by a literature method.¹⁹⁸ The compounds cis-Ru(CO)₄(SiCl₃)₂,¹⁹⁹ trans-Ru(CO)₄(SiCl₃)(Br),¹⁶₈ HRe(CO)₅,²⁰⁰ Re(CO)₅(X)¹⁹³ [Re(CO)₄X]₂ (X = Cl, Br, I)¹⁹⁰ were prepared as described in the literature. The ¹³CO-enriched complexes [Re(CO)₄X]₂, HRe(CO)₅, Re(CO)₅X (X = Cl, Br, I) were prepared by literature methods.¹⁸⁴,²⁰¹

### 4.4.3 Instrumentation

The ¹³C{¹H} NMR spectra of the binuclear ¹³CO-enriched complexes were recorded at 233 K in CD₂Cl₂/CH₂Cl₂ (1/3), the number of scans was 1000, the sweep width was 248 ppm, with a time domain and computer area size of 3.2 x 10⁴, the pulse angle was 38°, and the acquisition time 0.65538 s. Concentrations of the binuclear complexes were approximately 1 x 10⁻³ M. Using the resonance of the carbonyl carbon cis to the CNBu¹ ligand (the peak with smallest relative integrated area) the signal/noise ratio was determined and found to range from 1:9 to 1:41.²⁰² In cases where several spectra of a particular complex were obtained, chemical shift values were reproducible to ± 0.02 ppm. The ¹³C{¹H} NMR chemical shifts are quoted to two decimal places based on this reproducibility and analogous to those in references 145,146 and 177. The details of the NMR experiments are given to allow the chemical shifts of the complexes to be reproduced, as was done in the literature.¹⁴²
In a similar fashion the $^{31}\text{P}[^1\text{H}]$ NMR spectra were obtained at 233 K in CD$_2$Cl$_2$; the number of scans was 2000, the sweep width was 248 ppm, with a time domain of $1.6 \times 10^4$ and a computer area size of $3.2 \times 10^4$; the pulse angle was 41°, and the acquisition time 0.30402 s. Concentrations of the samples were approximately $1 \times 10^{-2}$ M. Using the PMe$_3$ phosphorus resonance the signal/noise ratio was determined and found to range from 1:41 to 1:107. In cases where several spectra of a particular complex were obtained, chemical shift values were also reproducible to ± 0.02 ppm.

The UV-vis absorption spectra of the binuclear complexes were recorded on a Hewlett-Packard 8452A diode array spectrophotometer at room temperature in either CH$_2$Cl$_2$ or C$_6$H$_6$ with a resolution of ± 2 nm. Only the longer wavelength absorptions were measured. The wavelength of the peak maximum ($\lambda_{\text{max}}$) for absorption bands with a broad shoulder were assigned utilizing ideas in the literature. For an examples of typical precisions in the molar absorptivity, the molar absorptivity for (OC)$_4$(Bu$^\text{NC}$)OsRu(CO)$_3$(SiCl$_3$)(Br) (4.8) in CH$_2$Cl$_2$, at 368 nm, $\varepsilon = 1210 \pm 89$ L mol$^{-1}$cm$^{-1}$ and at 334 nm, $\varepsilon = 1327 \pm 83$ L mol$^{-1}$cm$^{-1}$, and the molar absorptivity for (Me$_3$P)(OC)$_4$OsW(CO)$_5$ (2.1) in C$_6$H$_6$, at 368 nm, $\varepsilon = 2790 \pm 190$ L mol$^{-1}$cm$^{-1}$ and at 334 nm, $\varepsilon = 2730 \pm 190$ L mol$^{-1}$cm$^{-1}$.

4.4.4 Syntheses

Although details have been given in prior publications of the preparation and characterization of (Me$_3$P)(OC)$_4$OsRe(CO)$_4$(Br) (4.13), (Me$_3$P)(OC)$_4$OsRu(CO)$_3$(SiCl$_3$)$_2$, (4.14) and (X)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$ (X = H, Br) (4.18, 4.20), modified procedures or
characterizations are given here for thoroughness and as a future reference. The complexes 
\((OC)_4(Bu'NC)OsRe(CO)_4(X)\) \((X = Cl, Br, I)\) \((4.9-4.11)\) were prepared by Mr. D. F. Green.

**Preparation of Os(CO)\(_4\)(CNBu').** Two preparations of Os(CO)\(_4\)(CNBu') have been reported in the literature.\(^{51,161}\) An alternative, simple route for large scale preparations, with a slightly improved yield is reported here. A 500 mL Parr 4021 rocker type, pressure vessel was charged with 200 mL of an Os(CO)\(_5\) solution in C\(_6\)H\(_{14}\) \((1.39 \times 10^{-2} \text{ M})\) to which CNBu' \((0.45 \text{ mL, } 4.0 \times 10^{-3} \text{ mol})\) was added. The pressure vessel was flushed once with CO, and then pressurized with \(4.5 \times 10^6 \text{ Pa (44 atm)}\) of CO gas at 293 K. The vessel was then heated to 381 ± 11 K for 24 h with the pressure vessel stationary in an upright position. After the reaction was allowed to cool the contents of the reaction vessel were transferred to a large Schlenk tube. The reaction vessel was washed several times with hexanes and the washings also transferred to the Schlenk tube and the solvent was removed on a vacuum line. The remaining yellow solid was then sublimed to either a probe cooled with cold water or dry ice under dynamic vacuum \((1.3 \text{ Pa})\) at 298 or 309 K. Cream colored Os(CO)\(_4\)(CNBu') \((0.470 \text{ g, 35% yield})\) was obtained as the sublimate.

**Preparation of \(^{13}\)CO-enriched Os(CO)\(_4\)(CNBu').** A Pyrex Carius tube (fitted with a Teflon valve) was charged with Os(CO)\(_4\)(CNBu') \((120 \text{ mg, 0.31 mmol}), C_6H_6 (50 \text{ mL})\) and subjected to three cycles of freeze-pump-thaw. The vessel was then pressurized with \(2.2 \times 10^5 \text{ Pa (2.2 atm)}\) of \(^{13}\)C-enriched CO \((99.5 \text{ atom }% \^{13}\text{C} \text{ and } 10.1 \text{ atom }% \^{18}\text{O})\) and sealed. The stirred and air cooled solution was irradiated with a 200W Hanovia medium pressure mercury lamp through a filter \((\lambda \geq 400 \text{ nm})\) for 29 h. The resulting yellow solution was evacuated and the remaining solid sublimed at room temperature under a dynamic vacuum \((1.3 \text{ Pa})\) to a water cooled probe. A cream sublimate of \(^{13}\)CO-labeled
Os(CO)$_4$(CNBu') (typically 70 mg, 58% yield) was collected. The $^{13}$CO-enrichment was typically 70-79% $^{13}$CO-enriched, as calculated by the computer simulation of the MS of the complex, (for details of this determination see Appendix A-1). For Os(CO)$_4$(CNBu'):

$^{13}$C$^1$H NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 233 K): $\delta$ 29.81 (s, CH$_3$), 187.49 (s, CO, $^1J_{Os-C} = 116.7$ Hz).

This procedure was used as a general method for the $^{13}$C-enrichment of mononuclear donor fragments: Os(CO)$_4$(PMe$_3$) (133 h photolysis, 7-11% $^{13}$C-enrichment, 87% yield), Os(CO)$_4$(PMe$_3$): $^{13}$C$^1$H NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 233 K): $\delta$ 21.19 (d, CH$_3$, $^1J_{P-C} = 39.1$ Hz), 189.50 (d, CO, $^2J_{P-C} = 4.0$ Hz, $^1J_{Os-C} = 122.0$ Hz); Ru(CO)$_4$(PMe$_3$) (12 h photolysis, 11-14% $^{13}$C-enrichment, 86% yield), Ru(CO)$_4$(PMe$_3$): $^{13}$C$^1$H NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 233 K): $\delta$ 21.35 (d, CH$_3$, $^1J_{P-C} = 33.6$ Hz), 204.84 (s, CO); Os(CO)$_4$[P(OCH$_2$)$_3$CMe] (140 h photolysis, 22-26% $^{13}$C-enrichment, 73% yield), Os(CO)$_4$[P(OCH$_2$)$_3$CMe]: $^{13}$C$^1$H NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 233 K): $\delta$ 15.45 (s, P(OCH$_2$)$_3$CCH$_3$), 32.44 (d, P(OCH$_2$)$_3$CCH$_3$, $^2J_{P-C} = 37.2$ Hz), 76.35 (d, P(OCH$_2$)$_3$CCH$_3$, $^3J_{P-C} = 6.8$ Hz), 186.67 (d, CO, $^2J_{P-C} = 13.0$ Hz, $^1J_{Os-C} = 115.6$ Hz); Cp*Ir(CO)$_2$ (5 h photolysis, 86-93% $^{13}$C-enrichment, 74% yield), $^{13}$C$^1$H NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 233 K): $\delta$ 10.43 (s, C$_5$(CH$_3$)$_5$), 97.36 (s, C$_5$(CH$_3$)$_5$), 177.93 (s, CO). Slight differences to the procedure were employed for M(CO)$_4$(PMe$_3$) (M = Ru, Os): sublimed at 313 K to a probe cooled to 195 K, and for Os(CO)$_4$[P(OCH$_2$)$_3$CMe] which was purified by column chromatography and recrystallization.

Preparation of Os(CO)$_4$(GeCl$_3$)(Cl). A solution of Os(CO)$_5$ in C$_6$H$_{14}$ (1.51 x 10$^{-2}$ M, 200 mL) was placed in a glass liner inside a Parr 4021 500 mL rocker type pressure vessel. An additional amount of C$_6$H$_{14}$ (100 mL) was added to the Os(CO)$_5$ solution and a further 30
mL of C₆H₁₄ was placed between the inside of the pressure vessel and the outside of the glass liner. To the Os(CO)₅ solution was then added GeCl₄ (6.0 mL, 5.2 x 10⁻² mol) and the pressure vessel sealed. The pressure vessel was flushed once with CO and then pressurized to 9.0 x 10⁶ Pa (89 atm) with CO at room temperature; the reaction vessel was stationary in the upright position and heated to 348 K for 22 h. After the pressure vessel was allowed to cool and the excess gases vented, a yellow solution (containing Os(CO)₄(GeCl₃)(H) and a little Os(CO)₄(GeCl₃)(Cl)) and white crystals (Os(CO)₄(GeCl₃)(Cl)) were afforded. The species were identified by IR spectroscopy and comparison to the spectra to those of the previously reported, Fe(CO)₄(SnCl₃)(Cl),¹⁶³ Os(CO)₄(SnCl₃)(H),²⁰³ Os(CO)₄(SiCl₃)(H),²⁰⁴ Os(CO)₄(GeCl₃)(H), and Os(CO)₄(GeCl₃)(Cl).¹⁶⁵ The supernatant solution together with multiple C₆H₁₄ washes of the pressure vessel and solids, were placed in a Schlenk tube, and the solvent was removed on the vacuum line. The remaining solid was sublimed at 338 K under dynamic vacuum (1.3 Pa) to a water-cooled probe. The white sublimate, a mixture of Os(CO)₄(GeCl₃)(H), and Os(CO)₄(GeCl₃)(Cl) (total 0.45 g) was collected and dissolved in CCl₄ (30 mL) and CH₂Cl₂ (10 mL) and stirred for seven days at room temperature, under N₂ in ambient light. After this time an IR spectrum of the solution showed no ν(CO) bands assignable to Os(CO)₄(GeCl₃)(H). The vessel was evacuated to dryness and the remaining solid sublimed at 338 K, under dynamic vacuum (1.3 Pa) to a water-cooled probe. The off-white sublimate was collected to typically afford a 24% yield of Os(CO)₄(GeCl₃)(Cl) (0.38 g). The hexane insoluble materials from the reaction were taken separately and sublimed at 338 K, under dynamic vacuum (1.3 Pa) to a water-cooled probe. In some preparations an IR spectrum of the sublimate showed the ν(CO) bands due to Os(CO)₄(GeCl₃)(H) and therefore the process of stirring the compound in a solution of CCl₄/CH₂Cl₂ was carried out.
In some cases the sublimate was spectroscopically pure Os(CO)$_4$(GeCl$_3$)(Cl) (typically 135 mg, 9% yield). Occasionally the sublimate was contaminated with Os(CO)$_4$(Cl)$_2$,\textsuperscript{128} this complex was converted to [Os(CO)$_3$(Cl)$_2$]$_2$\textsuperscript{205} by bubbling N$_2$ through the solution containing the Os(CO)$_4$(Cl)$_2$ species. This was then followed by removal of the solvent on the vacuum line and sublimation of the remaining solid at 338 K, under dynamic vacuum (1.3 Pa), under these conditions [Os(CO)$_3$(Cl)$_2$]$_2$ did not readily sublime, and pure Os(CO)$_4$(GeCl$_3$)(Cl) was obtained as the sublimate. For Os(CO)$_4$(GeCl$_3$)(Cl): IR (CH$_2$Cl$_2$), ν(CO): 2179(m), 2118(sh,m), 2108(vs), 2069(s) cm$^{-1}$; MS (EI, m/z): 518 (M$^+$), 481 (M$^+$-Cl).

**Preparation of $^{13}$CO-enriched Os(CO)$_4$(GeCl$_3$)(Cl).** The complex Os(CO)$_4$(GeCl$_3$)(Cl) (48 mg, 9.3 x 10$^{-2}$ mmol) was dissolved in C$_6$H$_6$ (15 mL) in a Carius tube (fitted with a Teflon valve). The solution was subjected to three freeze-pump-thaw cycles and then placed under 1.4 x 10$^5$ Pa (1.4 atm) of $^{13}$C-enriched CO gas (99.5 atom % $^{13}$C; 10.1 atom % $^{18}$O). The sealed vessel was heated at 323 K, in the absence of light, for 10 days. After such time the solution was transferred to a Schlenk tube and the solvent evacuated, the remaining solid was sublimed at 333 K under dynamic vacuum (1.3 Pa), to a water-cooled probe. The off-white sublimate of $^{13}$CO-labelled Os(CO)$_4$(GeCl$_3$)(Cl) was collected (31 mg, 65% yield). $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, rm temp): δ 160.01 (s, br, CO), 160.66 (s, CO), 163.54 (s, CO), 165.56 (s, CO) in the ratio 2:32:2:3, respectively. IR (C$_6$H$_6$), ν(CO): 2172(m), 2108(vs), 2085(s), 2070(vw,sh), 2052(s), 2018(w) cm$^{-1}$ (as compared to the initial $^{13}$CO-unenriched Os(CO)$_4$(GeCl$_3$)(Cl) IR (C$_6$H$_6$), ν(CO): 2176(m), 2106(vs), 2064(s) cm$^{-1}$).
Preparation of (OC)$_4$(Bu'NC)OsOs(CO)$_3$(GeCl$_3$)(Cl) (4.6). A round-bottom flask capped with a Teflon valve was charged with Os(CO)$_4$(CNBu') (50 mg, 0.13 mmol), Os(CO)$_4$(GeCl$_3$)(Cl) (46 mg, 8.9 x 10$^{-2}$ mmol) and C$_6$H$_{14}$ (20 mL). The contents of the reaction vessel were subjected to three cycles of freeze-pump-thaw and heated at 323 K, in the absence of light, under vacuum for 19 h. This afforded a yellow solution and a yellow precipitate. The reaction vessel and its contents were cooled to 273 K and the supernatant removed by pipet and the yellow solid was washed with C$_6$H$_{14}$ at 273 K until an IR spectrum of the wash liquid no longer showed absorption bands due to the starting material. The yellow solid, crude (OC)$_4$(Bu'NC)OsOs(CO)$_3$(GeCl$_3$)(Cl) (4.6), was dissolved in CH$_2$Cl$_2$, filtered and the solution was reduced to a minimum volume whereupon C$_6$H$_{14}$ was placed on top of the CH$_2$Cl$_2$ solution, as a layer. The solution was stored at ~233 K which afforded pale yellow, star-shaped crystals of 4.6 (49 mg, 63% yield). The $^{13}$CO-enriched 4.6 was prepared in similar manner from $^{13}$CO-labeled Os(CO)$_4$(CNBu') and unenriched Os(CO)$_4$(GeCl$_3$)(Cl). For 4.6: IR (CH$_2$Cl$_2$), v(CN): 2224(w,asym) cm$^{-1}$; v(CO): 2137(s), 2095(m,sh), 2075(w,sh), 2062(vs), 2025(s), 1994(m) cm$^{-1}$; $^1$H NMR (CD$_2$Cl$_2$, 233 K): δ 1.56 (s, CH$_3$); $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 233 K): δ 29.42 (s, CH$_3$), 159.34 (s, 1C, CO), 171.46 (s, 1C, CO), 172.35 (tentatively, s, 1C, CO), 174.37 (s, 2C, CO), 182.63 (s, 2C, CO); MS (EI, m/z): 875 (M$^+$), 840 (M$^+$-Cl), 819 (M$^+$-2CO); (Cl, m/z): 838/840 (M$^+$-Cl); UV-vis absorption spectrum (CH$_2$Cl$_2$) $\lambda_{max}$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$) 308 (1.6 x 10$^4$), 350 (1.3 x 10$^4$); Anal. Calcd. for C$_{12}$H$_9$Cl$_4$GeNO$_7$Os$_2$: C, 16.49; H, 1.04; N, 1.60. Found: C, 16.60; H, 1.02; N, 1.80.

Preparation of (OC)$_4$(Bu'NC)OsRu(CO)$_3$(SiCl$_3$)$_2$ (4.7). A flame-dried, round-bottom flask capped with a Teflon valve was charged with cis-Ru(CO)$_4$(SiCl)$_3$$_2$ (92 mg,
0.19 mmol), Os(CO)$_4$(CNBu') (72 mg, 0.19 mmol) and C$_6$H$_{14}$ (20 mL). The contents of the reaction vessel were subjected to three cycles of freeze-pump-thaw and then stirred in the absence of light, at room temperature, under vacuum for 18 h. After this time period a colorless, clear supernatant and a pale yellow precipitate had resulted. The supernatant was removed from the solid; the latter was washed several times with C$_6$H$_{14}$ until the starting materials were no longer detected in the IR spectrum of the washes. The crude pale yellow, (OC)$_4$(Bu'NC)OsRu(CO)$_3$(SiCl)$_2$ (4.7), was dissolved in a minimum amount of 1,2-C$_2$H$_4$Cl$_2$, to which was added C$_6$H$_{14}$ as a layer above the solution of the product. The solution was stored at ~233 K which afforded pale yellow crystals of 4.7 (80 mg, 50% yield). The $^{13}$CO-enriched 4.7 was prepared in similar manner from $^{13}$CO-labeled Os(CO)$_4$(CNBu') and $^{13}$CO-enriched cis-Ru(CO)$_4$(SiCl)$_3$ (all sites equally enriched). For 4.7: IR (CH$_2$Cl$_2$), v(CN): 2219(m) cm$^{-1}$; v(CO): 2126(s), 2078(vs), 2054(vs), 2032(w,sh), 2015(m,sh) cm$^{-1}$; $^1$H NMR (CD$_2$Cl$_2$, 233 K): $\delta$ 1.55 (s, CH$_3$); $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 233 K): $\delta$ 29.36 (s, CH$_3$), 160.29 (s, 1C, CO), 174.08 (s, 1C, CO), 178.08 (s, 2C, CO), 196.73 (s, 1C, CO), 198.97 (s, 2C, CO); MS (EI, m/z): 841 (M$^+$), 785 (M$^+$.2CO); (Cl, m/z): 841 (M$^+$), 804/806 (M$^+$-Cl); UV-vis absorption spectrum (CH$_2$Cl$_2$) $\lambda_{max}$, nm ($e$, M$^{-1}$ cm$^{-1}$) 324 (9.1 x 10$^3$); Anal. Calcd. for C$_{12}$H$_9$Cl$_6$NO$_7$OsRuSi$_2$: C, 17.17; H, 1.08; N, 1.67. Found: C, 17.31; H, 1.12; N, 1.65.

Preparation of (OC)$_4$(Bu'NC)OsRu(CO)$_3$(SiCl)$_3$(Br) (4.8). A round-bottom flask capped with a Teflon valve was charged with trans-Ru(CO)$_4$(SiCl)$_3$(Br) (54 mg, 0.13 mmol), Os(CO)$_4$(CNBu') (49 mg, 0.13 mmol) and C$_6$H$_{14}$ (25 mL). The reaction was carried out under identical conditions to those mentioned in the preparation of 4.7. The supernatant solution above the resultant pale yellow precipitate not only contained the starting materials
but also [Ru(CO)₃(SiCl₃)(Br)]₂, as identified by IR spectrum. The solvent was decanted and the pale yellow solid washed several times with fresh C₆H₁₄ to remove any starting materials and [Ru(CO)₃(SiCl₃)(Br)]₂. The crude, pale yellow (OC)₄(Bu'NC)OsRu(CO)₃(SiCl₃)(Br) (4.8) was dissolved in a minimum amount of CH₂Cl₂ at 195 K, to which was added C₆H₁₄, at 195 K, to precipitate the pale yellow product rapidly. The supernatant was removed and the pale yellow powder washed with fresh C₆H₁₄. Finally the powder was dried on the vacuum line to yield pale yellow 4.8 (80 mg, 78% yield). The ¹³CO-enriched 4.8 was prepared in similar manner, from ¹³CO-labelled Os(CO)₄(CNBu') and ¹³CO-enriched trans-Ru(CO)₄(SiCl₃)(Br). The ¹³CO-enriched [Ru(CO)₄(SiCl₃)]₂, used to prepare ¹³CO-enriched trans-Ru(CO)₄(SiCl₃)(Br), was prepared from ¹³CO-labeled Ru₃(CO)₁₂ and HSiCl₃ under ¹³C-labeled CO. (The ¹³CO-labeled Ru₃(CO)₁₂ was prepared in an analogous manner to the preparation of ¹³CO-enriched Os₃(CO)₁₂, except that a temperature of 363 K was used.) For 4.8: IR (CH₂Cl₂), ν(CN): 2217 (w, asym) cm⁻¹; ν(CO): 2125 (m), 2087 (m), 2049 (vs), 2030 (vw, sh), 2005 (w, sh) cm⁻¹; ¹H NMR (CD₂Cl₂, 233 K): δ 1.51 (s, CH₃); ¹³C(¹H) NMR (CD₂Cl₂/CH₂Cl₂ 1/3, 233 K): δ 29.44 (s, CH₃), 161.65 (s, 1C, CO), 175.46 (s, 1C, CO), 179.86 (s, 2C, CO), 194.54 (s, 1C, CO), 197.23 (s, 2C, CO); MS (EI, m/z): 785/787 (M⁺), 729/731 (M⁺-2CO); (Cl, m/z): 785/787 (M⁺), 842/844 (M⁺+C₄H₉); UV-vis absorption spectrum (CH₂Cl₂) λ_max, nm (ε, M⁻¹ cm⁻¹) 334 (1.3 x 10³), 368 (1.2 x 10³); Anal. Calcd. for C₁₂H₇BrCl₃NO₇OsRuSi: C, 18.36; H, 1.16; N, 1.78. Found: C, 18.41; H, 1.23; N, 1.74.

Preparation of (OC)₄(Bu'NC)OsRe(CO)₄(Cl) (4.9). A flame-dried, round-bottom flask capped with a Teflon valve was charged with Os(CO)₄(CNBu') (44 mg, 0.11 mmol), [Re(CO)₄Cl]₂ (36 mg, 5.4 x 10⁻² mmol) and C₆H₅CH₃ (15 mL). The contents of the
reaction vessel were subjected to three freeze-pump-thaw cycles and then placed under N2 (~1.0 x 10^5 Pa). The reaction vessel was heated at 318 K with stirring for about 20 h. This procedure afforded a yellow solution and a yellow precipitate. The entire contents of the flask were transferred to a Schlenk tube and the solvent removed by decantation. The yellow solid was rinsed several times with fresh C6H14 to remove excess Os(CO)4(CNBu') and then dissolved in a minimum amount of C6H5CH3 and C6H14 added carefully as a layer on top of the solution. The contents of the Schlenk tube were allowed to cool to ~233 K. Yellow crystals of (OC)4(Bu'NC)OsRe(CO)4(Cl) (4.9) (30 mg, 39% yield) were obtained.

The 13CO-enriched 4.9 was prepared in a similar manner from 13CO-labeled [Re(CO)4Cl]2 and 13CO-labeled Os(CO)4(CNBu'). For 4.9: IR (CH2Cl2), ν(CN): 2217 (w, br) cm⁻¹; ν(CO): 2119 (m), 2074 (s), 2039 (vs), 1978 (s), 1914 (s) cm⁻¹; 1H NMR (CD2Cl2, 233 K): δ 1.52 (s, CH3); 13C{1H} NMR (CD2Cl2/CH2Cl2 1/3, 233 K): δ 29.49 (s, CH3), 164.18 (s, 1C, CO), 175.72 (s, 1C, CO), 180.17 (s, 2C, CO), 186.03 (s, 1C, CO), 188.75 (s, 1C, CO), 194.00 (s, 2C, CO); MS (EI, m/z): 719 (M⁺), 691 (M⁺-CO); (Cl, m/z): 388 [M⁺-Re(CO)4Cl+1]; UV-vis absorption spectrum (CH2Cl2) λmax, nm (ε, M⁻¹ cm⁻¹) 334 (3.7 x 10³), 358 (3.1 x 10³); Anal. Calcd. for C13H9C1N080sRe: C, 21.71; H, 1.26; N, 1.95. Found: C, 21.80; H, 1.23; N, 1.95.

Preparation of (OC)4(Bu'NC)OsRe(CO)4(Br) (4.10). The procedure for the preparation of the complex, (OC)4(Bu'NC)OsRe(CO)4(Br) (4.10) was similar to the preparative method used for the production of 4.9. In one reaction Os(CO)4(CNBu') (32 mg, 0.083 mmol) and [Re(CO)4Br]2 (30 mg, 0.040 mmol) in C6H5CH3 (15 mL) were employed, which afforded yellow crystals of 4.10 (16 mg, 27% yield) upon recrystallization. The 13CO-enriched 4.10 was prepared in a similar manner from 13CO-
labeled \([\text{Re(CO)}_4\text{Br}]_2\) and \(^{13}\text{CO}\)-labeled \(\text{Os(CO)}_4(\text{CNBu})\). For 4.10: IR (CH\(_2\)Cl\(_2\)), \(\nu(\text{CN})\): 2219 (w, br) cm\(^{-1}\); \(\nu(\text{CO})\): 2118 (m), 2073 (s), 2040 (vs), 1980 (s, br), 1915 (s) cm\(^{-1}\); \(^1\text{H}\) NMR (CD\(_2\)Cl\(_2\), 233 K): 8 1.52 (s, CH\(_3\)); \(^{13}\text{C}\{^{1}\text{H}\}\) NMR (CD\(_2\)Cl\(_2/\text{CH}_2\text{Cl}_2, 1/3\), 233 K): 8 29.47 (s, CH\(_3\)), 163.57 (s, 1C, CO), 175.96 (s, 1C, CO), 180.31 (s, 2C, CO), 185.29 (s, 1C, CO), 188.54 (s, 1C, CO), 192.65 (s, 2C, CO); MS (EI, m/z): 765 (M\(^+\)), 737 (M\(^+\)-CO); (Cl, m/z): 764/766 (M\(^+\)), 388 [M\(^+\)-Re(\text{CO})\(_4\)Br]+1, 407 [Re(\text{CO})\(_5\)Br]+1; UV-vis absorption spectrum (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}, \text{nm} (\varepsilon, M^{-1} \text{ cm}^{-1})\) 338 (3.5 \times 10\(^3\)), 362 (2.7 \times 10\(^3\)); Anal. Calcd. for C\(_{13}\)H\(_9\)BrNO\(_8\)OsRe: C, 20.45; H, 1.19; N, 1.83. Found: C, 20.91; H, 1.33; N, 1.87.

**Preparation of (OC)\(_4\)(Bu'NC)OsRe(OC)\(_4\)(I) (4.11).** The procedure for the preparation of the complex, (OC)\(_4\)(Bu'NC)OsRe(OC)\(_4\)(I) (4.11) was similar to the preparative method used for the preparation of 4.9. In one reaction Os(CO)\(_4\)(CNBu') (29 mg, 7.5 \times 10\(^{-2}\) mmol) and [Re(CO)\(_4\)]\(_2\) (30 mg, 3.5 \times 10\(^{-2}\) mmol) in C\(_6\)H\(_5\)CH\(_3\) (15 mL) were employed and this gave yellow crystals of 4.11 (25 mg, 44% yield) upon recrystallization. The \(^{13}\text{CO}\)-enriched 4.11 was prepared in a similar manner from \(^{13}\text{CO}\)-labeled [Re(\text{CO})\(_4\)]\(_2\) and \(^{13}\text{CO}\)-labeled Os(CO)\(_4\)(CNBu'). For 4.11: IR (CH\(_2\)Cl\(_2\)), \(\nu(\text{CN})\): 2218 (w, br) cm\(^{-1}\); \(\nu(\text{CO})\): 2118 (m), 2070 (s), 2040 (vs), 1978 (s, br), 1917 (s) cm\(^{-1}\); \(^1\text{H}\) NMR (CD\(_2\)Cl\(_2\), 233 K): 8 1.53 (s, CH\(_3\)); \(^{13}\text{C}\{^{1}\text{H}\}\) NMR (CD\(_2\)Cl\(_2/\text{CH}_2\text{Cl}_2, 1/3\), 233 K): 8 29.46 (s, CH\(_3\)), 162.70 (s, 1C, CO), 176.44 (s, 1C, CO), 180.68 (s, 2C, CO), 184.22 (s, 1C, CO), 188.08 (s, 1C, CO), 190.38 (s, 2C, CO); MS (EI, m/z): 426 [M\(^+\)-Os(\text{CO})\(_4\)(CNBu')]; UV-vis absorption spectrum (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}, \text{nm} (\varepsilon, M^{-1} \text{ cm}^{-1})\) 334 (broad shoulder) (4.4 \times 10\(^3\)), 370 (2.5 \times 10\(^3\)); Anal. Calcd. for C\(_{13}\)H\(_9\)INO\(_8\)OsRe: C, 19.26; H, 1.12; N, 1.73. Found: C, 19.39; H, 1.05; N, 1.66.
Preparation of \([\text{Os(CO)}_4(\text{CNBu}')(\text{H})][\text{BCl}_4]\) ([4.12][\text{BCl}_4]). A flame-dried Carius tube with a Teflon valve was charged with Os(CO)_4(CNBu') (50 mg, 0.13 mmol) and C_6H_14 (15 mL) and the solution subjected to three freeze-pump-thaw cycles. The vessel was then attached to a high vacuum line (1.3 x 10^-2 Pa). An excess of freshly purified BCl_3 (~1 mL, ~1 x 10^-2 mol) was vacuum transferred into the Carius tube at 77 K and sealed. The vessel and contents were allowed to warm to 278 K in the absence of light and the solution stirred for 18 h. This afforded a cream precipitate and a colorless, clear solution. The solvent and excess BCl_3 were removed on the vacuum line (1.3 x 10^-2 Pa) and the remaining cream solid washed several times with fresh C_6H_14, to remove any unreacted starting material. The cream solid was transferred in the dry box to an H-shaped-vessel that was capped with two Teflon valves and the solid was dissolved in a minimum amount of 1,2-C_2H_4Cl_2; to the other side of the H-shaped vessel was added C_6H_14. Both sides of the crystallization vessel were subjected to three cycles of freeze-pump-thaw and left under vacuum. The vessel and the contents were allowed to warm to room temperature, the side containing the [Os(CO)_4(CNBu')(H)][BCl_4] ([4.12][BCl_4]) solution was placed in a Dewar of H_2O at room temperature while the other side containing C_6H_14 was left in air at ambient air temperature. The solvents were allowed to equilibrate for several days at room temperature before placing the crystallization vessel in the freezer (~233 K). Clear, cream, needle-shaped crystals of [4.12][BCl_4] were obtained. The \(^{13}\text{CO}\)-labeled complex was prepared in a similar manner from \(^{13}\text{CO}\)-enriched Os(CO)_4(CNBu'). For [4.12][BCl_4]: IR (CH_2Cl_2), ν(CN): 2252(w,br) cm\(^{-1}\); ν(CO): 2176(m), 2126(s), 2102(vs,br) cm\(^{-1}\); \(^1\)H NMR (CD_2Cl_2, 233 K): δ 1.62 (s, CH_3), -7.65 (s, H) in the ratio 13:1, respectively; \(^{13}\text{C}\text{\{}^1\text{H}\}\) NMR (CD_2Cl_2/CH_2Cl_2 1:3, 233 K): δ 29.56 (s, CH_3), 163.64 (s, 1C, CO), 164.14 (s, sh, CO),
164.20 (s, CO) the last two carbonyl resonances had a combined relative integrated area of three; $^{13}$C NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 233 K): δ 163.48 (d, 1C, CO, $^2J_{C-H} = 19.1$ Hz), 164.20 (s, sh, 3C, CO); $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 233 K): δ 30.29 (s, 3C, CH$_3$), 165.00 (s, 1C, CO), 165.20 (s, 2C, CO), 166.00 (s, 1C, CO); $^{13}$C($^1$H) NMR (CD$_2$CN, 233 K): δ 166.30 (s, 1C, sh, CO), 166.45 (s, 2C, CO), 166.83 (s, 1C, CO); MS (EI, m/z): 387 (M$^+$-H); (CI, m/z): 388 (M$^+$), 332 (M$^+$-2CO); (FAB, m/z): 388 (M$^+$), 332 (M$^+$-2CO); Anal. Calcd. for C$_9$H$_{10}$BCl$_4$NO$_4$Os: C, 20.06; H, 1.87; N, 2.60. Found: C, 20.19; H, 1.87; N, 2.98.

Preparation (Me$_3$P)(OC)$_4$OsRe(CO)$_4$(Br) (4.13). The preparation of (Me$_3$P)(OC)$_4$OsRe(CO)$_4$(Br) (4.13) has been previously described but is reported here for completeness.$^{48}$ A flame-dried round-bottom flask capped with a Teflon valve was charged with [Re(CO)$_4$Br]$_2$ (96 mg, 0.13 mmol), Os(OC)$_4$(PMe$_3$) (96 mg, 0.25 mmol), and 1,2-C$_2$H$_4$Cl$_2$ (15 mL), and the resulting mixture heated at 323 K with stirring. The reaction was complete in approximately 13 h. Pale yellow crystals of 4.13 (104 mg, 54% yield) were obtained upon recrystallization from 1,2-C$_2$H$_4$Cl$_2$/C$_6$H$_{14}$. The $^{13}$CO-enriched 4.13 was prepared in a similar manner from $^{13}$CO-labeled [Re(CO)$_4$Br]$_2$ and $^{13}$C-enriched Os(OC)$_4$(PMe$_3$). For 4.13: IR (CH$_2$Cl$_2$), v(CO): 2119(vw), 2069(m), 2050(w,sh), 2026(vs), 1974(m), 1915(m) cm$^{-1}$; $^1$H NMR (CD$_2$Cl$_2$, 233 K): δ 2.02 (d, CH$_3$, $^2J_{P-H} = 10.5$ Hz); $^{31}$P($^1$H) NMR (CD$_2$Cl$_2$, 233 K): δ -52.35 (s, PMe$_3$); $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 233 K): δ 22.36 (d, CH$_3$, $^1J_{P-C} = 37.8$ Hz), 183.50 (d, 4C, CO, $^2J_{P-C} = 3.7$ Hz), 186.00 (s, 1C, CO), 188.53 (s, 1C, CO), 193.12 (s, 2C, CO); MS (EI, m/z): 756/758 (M$^+$), 728/730 (M$^+$-CO); (CI, m/z): 757/759 (M$^+$+1), 729/731 (M$^+$-CO+1); UV-vis absorption spectrum (CH$_2$Cl$_2$) $\lambda_{max}$, nm (ε, M$^{-1}$ cm$^{-1}$) 334 (4.6 x 10$^{3}$), 359 (3.3 x 10$^{3}$); (C$_6$H$_6$) 338 (≤ 2.6 x 10$^{3}$),
Preparation of (Me₃P)(OC)₄OsRu(CO)₃(SiCl₃)₂ (4.14). A brief description of the preparation and characterization of (Me₃P)(OC)₄OsRu(CO)₃(SiCl₃)₂ (4.14) has previously appeared in the literature. An elaboration of the procedure and thorough characterization of the complex are presented herein. A flame-dried round-bottom flask with a Teflon valve was charged with cis-Ru(CO)₄(SiCl₃)₂ (82 mg, 0.17 mmol), Os(CO)₄(PMe₃) (65 mg, 0.17 mmol), C₆H₁₄ (20 mL) and the solution stirred at room temperature. The reaction was complete after 16 h. After such time a pale yellow precipitate and colorless supernatant had formed. Pale yellow crystals of 4.14 (102 mg, 72% yield) were obtained upon recrystallization from 1,2-C₂H₂Cl₂/C₆H₁₄. The ¹³CO-enriched 4.14 was prepared in a similar manner from ¹³CO-labeled cis-Ru(CO)₄(SiCl₃)₂ (all sites equally enriched) and ¹³CO-labeled Os(CO)₄(PMe₃); the ¹³CO-enriched complex 4.14 was also prepared from ¹³CO-labeled Os(CO)₄(PMe₃) and unenriched cis-Ru(CO)₄(SiCl₃)₂. For 4.14: IR (CH₂Cl₂), ν(CO): 2124 (w), 2069 (w, sh), 2038 (vs), 2012 (w, sh) cm⁻¹; 'H NMR (CD₂Cl₂, 233 K): δ 2.16 (d, CH₃, 2Jₚ-H = 10.7 Hz); ³¹P{'H} NMR (CD₂Cl₂, 233 K): δ -49.85 (s, PMe₃); ¹³C{'H} NMR (CD₂Cl₂/CH₂Cl₂ 1/3, 233 K): δ 21.80 (d, CH₃, 1Jₚ-C = 38.9 Hz), 181.85 (d, 4C, CO), 196.44 (s, 1C, CO), 198.27 (s, 2C, CO); MS (El, m/z): 834 (M⁺), 806 (M⁺-CO); UV-vis absorption spectrum (CH₂Cl₂) λmax, nm (ε, M⁻¹ cm⁻¹) 330 (2.2 x 10⁴); Anal. Calcd. for C₁₀H₉Cl₆O₇OsPRuSi₂: C, 14.43; H, 1.09. Found: C, 14.55; H, 1.10.

² Molecular structure of (Me₃P)(OC)₄OsRu(CO)₃(SiCl₃)₂ (4.14). The molecular structure (Me₃P)(OC)₄OsRu(CO)₃(SiCl₃)₂ (4.14) is discussed in Chapter 5 along with that of the ruthenium analogue, (Me₃P)(OC)₄RuRu(CO)₃(SiCl₃)₂.
Preparation of (Me₃P)(OC)₄OsRu(CO)₃(SiCl₃)(Br) (4.15). The complex (Me₃P)(OC)₄OsRu(CO)₃(SiCl₃)(Br) (4.15) has previously been mentioned but experimental details or characterization were not presented; they are therefore presented here. A flame-dried round-bottom flask capped with a Teflon valve was charged with trans-Ru(CO)₄(SiCl₃)(Br) (71 mg, 0.17 mmol), Os(CO)₄(PMe₃) (52 mg, 0.14 mmol) and C₆H₁₄ (15 mL) and the reaction mixture was stirred for 16 h. After this period a pale yellow precipitate and a colorless supernatant had resulted. The supernatant solution, which contained [Ru(CO)₃(SiCl₃)(Br)]₂ as identified by the IR spectrum, was removed and the solid washed several times with warm C₆H₁₄ until no species was detectable in the IR spectrum v(CO) region of the washes. The pale yellow powder of 4.15 (100 mg, 94% yield) was not recrystallized in order to prevent dissociation or isomerization of the bimetallic species. The ¹³C₀-enriched 4.15 was prepared in a similar manner from ¹³CO-labeled trans-Ru(CO)₄(SiCl₃)(Br) and ¹³CO-labeled Os(CO)₄(PMe₃). For 4.15: IR (CH₂Cl₂), v(CO): 2124(vw), 2079(w), 2055(sh), 2041(vs), 2031(s, sh) cm⁻¹; ¹H NMR (CD₂Cl₂, 233 K): δ 2.10 (d, CH₃, 2Jₚ-H = 10.7 Hz); ¹³P{¹H} NMR (CD₂Cl₂, 233 K): δ -50.96 (s, PMe₃); ¹³C{¹H} NMR (CD₂Cl₂/CD₂Cl₂ 1/3, 233 K): δ 22.13 (d, CH₃, 1Jₚ-C = 38.9 Hz), 183.15 (d, 4C, CO, 2Jₚ-C = 4.6 Hz), 194.57 (s, 1C, CO), 197.72 (s, 2C, CO); MS (EI, m/z): 778/780 (M⁺); (Cl, m/z): 381 [M⁺-Ru(CO)₃(SiCl₃)(Br)+1]; UV-vis absorption spectrum (CH₂Cl₂) λₘₚₐₓ, nm (ε, M⁻¹ cm⁻¹) 336 (1.4 x 10⁴), 374 (1.4 x 10⁴); Anal. Calcd. for C₁₀H₉BrCl₃O₇P₃RuSi: C, 15.44; H, 1.17. Found: C, 15.65; H, 1.19.

Preparation of (Me₃P)(OC)₄OsRe(CO)₄(Cl) (4.16). A flame-dried, round-bottom flask capped with a Teflon valve was charged with Os(CO)₄(PMe₃) (100 mg, 0.26 mmol), [Re(CO)₄Cl]₂ (88 mg, 0.13 mmol), and 1,2-C₂H₄Cl₂ (20 mL). The solvent had been filtered...
under N₂, through dried basic alumina prior to use, to remove any HCl present. The contents of the flask were subjected to three cycles of freeze-pump-thaw and then heated at 323 K, with stirring, in the absence of light for approximately 4 h. After such time a clear yellow solution had resulted; the solution was transferred to a Schlenk tube and the solvent removed on the vacuum line. The remaining pale yellow solid was sublimed twice at 313 K under dynamic vacuum (1.3 Pa) to a probe cooled to 195 K, to remove Os(CO)₄(PMe₃) and Re(CO)₅(Cl). The crude (Me₃P)(OC)₄OsRe(CO)₄(Cl) (4.16) was then washed with warm, C₆H₁₄ until an IR spectrum of the supernatant no longer showed any ν(CO) bands. The pale yellow solid was then dissolved in a minimum amount of 1,2-C₂H₄Cl₂, which had previously been filtered through dried, basic alumina, and then C₆H₁₄ was carefully layered on top of the solution and the mixture cooled to ~233 K. Pale yellow crystals of 4.16 (100 mg, 53% yield) were afforded. The ¹³CO-enriched 4.16 was prepared in a similar manner from ¹³CO-labeled [Re(CO)₄Cl]₂ and unenriched Os(CO)₄(PMe₃). For 4.16: IR (CH₂Cl₂), ν(CO): 2119(vw), 2070(m), 2051(w,sh), 2024(vs), 1974(m), 1914(m) cm⁻¹; ¹H NMR (CD₂Cl₂, 233 K): δ 2.02 (d, CH₃, ²Jₚ,H = 10.5 Hz); ³¹P{¹H} NMR (CD₂Cl₂, 233 K): δ -52.01 (s, PMe₃); ¹³C{¹H} NMR (CD₂Cl₂/CH₂Cl₂ 1/3, 233 K): δ 22.42 (d, CH₃, ¹Jₚ,C = 37.6 Hz), 183.28 (d, 4C, CO, ²Jₚ,C = 3.5 Hz), 186.68 (s, 1C, CO), 188.73 (s, 1C, CO), 194.52 (s, 2C, CO); MS (EI, m/z): 712 (M⁺), 684/686 (M⁺-CO); (Cl, m/z): 713 (M⁺+1), 685/687 (M⁺-CO+1); UV-vis absorption spectrum (CH₂Cl₂) λmax, nm (ε, M⁻¹ cm⁻¹) 333 (4.1 x 10³), 358 (3.2 x 10³); Anal. Calcd. for C₁₁H₉ClO₈OsPRe: C, 18.56; H, 1.27. Found: C, 18.80; H, 1.30.

**Preparation of (Me₃P)(OC)₄OsRe(CO)₄(I) (4.17).** A flame-dried round-bottom flask capped with a Teflon valve was charged with [Re(CO)₄I]₂ (128 mg, 0.15 mmol),
Os(CO)$_4$(PMe$_3$) (120 mg, 0.32 mmol), 1,2-C$_2$H$_4$Cl$_2$ (15 mL) and the solution stirred at 323 K for 20 h. Yellow crystals of (Me$_3$P)(OC)$_4$OsRe(CO)$_4$(I) (4.17) (110 mg, 44% yield) were obtained upon recrystallization from 1,2-C$_2$H$_4$Cl$_2$/C$_6$H$_{14}$. The $^{13}$CO-enriched 4.17 was prepared in a similar manner from $^{13}$CO-labeled [Re(CO)$_4$I]$_2$ and unenriched Os(CO)$_4$(PMe$_3$). For 4.17: IR (CH$_2$Cl$_2$), v(CO): 2117(vw), 2066(m), 2051(w,sh), 2027(vs), 1974(m), 1916(m) cm$^{-1}$; $^1$H NMR (CD$_2$Cl$_2$, 233 K): $\delta$ 2.03 (d, CH$_3$, $^2$$J_{P-H}$ = 10.5 Hz); $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 233 K): $\delta$ -52.74 (s, PMe$_3$); $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 233 K): $\delta$ 22.30 (d, CH$_3$, $^1$$J_{P-C}$ = 37.9 Hz), 183.97 (d, 4C, CO, $^2$$J_{P-C}$ = 3.8 Hz), 184.97 (s, 1C, CO, br), 188.02 (s, 1C, CO), 190.70 (s, 2C, CO); MS (EI, m/z): 804/806 (M$^+$); (CI, m/z): 805 (M$^+$+1), 777 (M$^+$-CO+1); UV-vis absorption spectrum (CH$_2$Cl$_2$) $\lambda_{\text{max}}$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$) 340 (6.0 x 10$^3$), 370 (3.8 x 10$^3$); (C$_6$H$_6$) 342 (3.7 x 10$^3$), 378 (2.0 x 10$^3$); Anal. Calcd. for C$_{11}$H$_9$IO$_8$OsPRe: C, 16.44; H, 1.13. Found: C, 16.62; H, 1.19.

Preparation of (H)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$ (4.18). The preparation of (H)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$ (4.18) has been reported before, but the procedure was modified and is therefore reported here for completeness. A round-bottom flask with a Teflon valve was charged with Os(CO)$_4$(PMe$_3$) (0.532 g, 1.41 mmol), Re(CO)$_5$(H) (0.20 mL, 1.41 mmol) and C$_6$H$_{14}$ (20 mL). The contents of the flask were subjected to three cycles of freeze-pump-thaw; the vessel and contents were heated under vacuum in the absence of light at 343 K for 140 h. The duration of the reaction, however, varied dramatically with different preparations and hence an IR spectrum of the reaction solution were routinely obtained to follow the progress of the reaction. After completion of the reaction, a pale yellow solution was afforded. The solution was transferred to a Schlenk tube together with several C$_6$H$_{14}$ washings and the solvent removed on the vacuum line.
The solid was sublimed initially at room temperature, in the absence of light, under dynamic vacuum (1.3 Pa) to a probe cooled to 195 K. This removed any HRe(CO)$_5$, Os(CO)$_4$(PMe$_3$) and Re$_2$(CO)$_{10}$ (the sublimates were identified from their IR spectra)\textsuperscript{69,193,200} Further sublimation under dynamic vacuum (1.3 Pa) at 313 K, to a probe cooled to 195 K removed the remaining HRe(CO)$_5$ and Os(CO)$_4$(PMe$_3$) but also some 4.18. The remaining yellow solid was recrystallized from a large volume of C$_6$H$_{14}$ or from C$_6$H$_5$CH$_3$/C$_6$H$_{14}$ to afford a yellow powder of 4.18 (0.53 g, 58% yield). The $^{13}$CO-enriched 4.18 was prepared in a similar manner from $^{13}$CO-labeled HRe(CO)$_5$ and unenriched Os(CO)$_4$(PMe$_3$). For 4.18: IR (C$_6$H$_{14}$), v(CO): 2108(m), 2037(m), 2008(s,sh), 204(vs), 1988(w,sh), 1967(m) cm$^{-1}$; (CH$_2$Cl$_2$), v(CO): 2106(m), 2036(m), 1999(vs,br), 1958(m,br) cm$^{-1}$; $^1$H NMR (C$_6$D$_5$CD$_3$, rm. temp): $\delta$ -10.38 (d, H, $^2$J$_{P-H}$ = 19.4 Hz), 1.10 (d, CH$_3$, $^2$J$_{P-H}$ = 10.3 Hz);\textsuperscript{48} (CD$_2$Cl$_2$, 233 K): $\delta$ -10.59 (d, H, $^2$J$_{P-H}$ = 19.0 Hz), 1.91 (d, CH$_3$, $^2$J$_{P-H}$ = 10.5 Hz); $^{31}$P$^1$H NMR (C$_6$D$_5$CD$_3$, rm. temp): $\delta$ -48.9 (s, PMe$_3$);\textsuperscript{48} $^{13}$C$^1$H NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 233 K): $\delta$ 23.37 (d, CH$_3$, $^1$J$_{P-C}$ = 38.0 Hz), 184.14 (d, 1C, CO, $^2$J$_{P-C}$ = 3.2 Hz), 188.34 (d, 2C, CO, $^2$J$_{P-C}$ = 7.0 Hz) 190.69 (s, 4C, CO, vbr); MS (EI, m/z): 678 (M$^+$);\textsuperscript{48} Anal. Calcd. for C$_{11}$H$_{10}$O$_8$OsPRe: C, 19.50; H, 1.49. Found: C, 19.77; H, 1.37.\textsuperscript{48}

**Preparation of (Cl)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$ (4.19).** A Schlenk tube was charged with 4.18 (100 mg, 0.148 mmol), CCl$_4$ (17$\mu$L, 0.18 mmol) and C$_6$H$_{14}$ (20 mL). The contents of the flask were stirred under N$_2$, at room temperature, in the absence of light for 8-19 h. After this time a pale yellow solution, and a pale yellow precipitate was afforded and there were no longer any IR v(CO) absorption bands due to 4.18 in the IR spectrum of the reaction solution. The solvent and excess CCl$_4$ were removed on the vacuum line. The remaining pale yellow solid was dissolved in a minimum amount of 1,2-C$_2$H$_4$Cl$_2$, which
had previously been filtered through dried basic alumina. To the filtered solution was added C\textsubscript{6}H\textsubscript{14} as a top layer and the Schlenk tube cooled slowly to ~233 K. Pale yellow crystals of (Cl)(Me\textsubscript{3}P)(OC)\textsubscript{3}OsRe(CO)\textsubscript{5} (4.19) (78 mg, 74% yield) were obtained. The \textsuperscript{13}CO-enriched complex was prepared in a similar manner from \textsuperscript{13}CO-labeled 4.18. For 4.19: IR (C\textsubscript{6}H\textsubscript{14}), ν(CO): 2117(m), 2056(m), 2040(m), 2012(vs), 1977(w,sh), 1975(s) cm\textsuperscript{-1}; (CH\textsubscript{2}Cl\textsubscript{2}): ν(CO) 2116(m), 2055(m), 2035(w,sh), 2012(vs), 2004(vs), 1969(m,br) cm\textsuperscript{-1}; \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3}, rm. temp): δ 1.11 (d, CH\textsubscript{3}, \textsuperscript{3}J\textsubscript{P-H} = 10.5 Hz); (CD\textsubscript{2}Cl\textsubscript{2}, 233 K): δ 1.91 (d, CH\textsubscript{3}, \textsuperscript{3}J\textsubscript{P-H} = 10.8 Hz); \textsuperscript{31}P{\textsuperscript{1}H} NMR (C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3}, rm. temp): δ -40.84 (s, PMe\textsubscript{3}); (CD\textsubscript{2}Cl\textsubscript{2}, 233 K): δ -37.62 (s, PMe\textsubscript{3}); \textsuperscript{13}C{\textsuperscript{1}H} NMR (CD\textsubscript{2}Cl\textsubscript{2}/CH\textsubscript{2}Cl\textsubscript{2} 1/3, 233 K): δ 17.14 (d, CH\textsubscript{3}, \textsuperscript{1}J\textsubscript{P-C} = 37.4 Hz), 176.58 (d, 1C, CO, \textsuperscript{2}J\textsubscript{P-C} = 3.2 Hz), 183.32 (s, 1C, CO, vbr), 190.67 (s, 4C, CO, vbr), 191.55 (d, 2C, CO, \textsuperscript{2}J\textsubscript{P-C} = 5.0 Hz); MS (EI, m/z): 712/714 (M\textsuperscript{+}), 684/686 (M\textsuperscript{+}-CO); UV-vis absorption spectrum (CH\textsubscript{2}Cl\textsubscript{2}) \textlambda\textsubscript{max}, nm (ε, M\textsuperscript{-1} cm\textsuperscript{-1}) 322 (1.2 x 10\textsuperscript{4}), 378 (1.6 x 10\textsuperscript{3}); Anal. Calcd. for C\textsubscript{11}H\textsubscript{9}ClO\textsubscript{8}OsPRe: C, 18.56; H, 1.27. Found: C, 18.70; H, 1.27.

**Preparation of** (Br)(Me\textsubscript{3}P)(OC)\textsubscript{3}OsRe(CO)\textsubscript{5} (4.20). The preparation of (Br)(Me\textsubscript{3}P)(OC)\textsubscript{3}OsRe(CO)\textsubscript{5} (4.20) has previously been reported, but is described herein for completeness.\textsuperscript{48} A Schlenk tube was charged with 4.18 (90 mg, 0.13 mmol), freshly sublimed CBr\textsubscript{4} (53 mg, 0.16 mmol), and C\textsubscript{6}H\textsubscript{14} (20 mL) and stirred at room temperature. The reaction was complete in 30 min as determined by IR spectroscopy. The solvent was removed on the vacuum line and excess CBr\textsubscript{4} removed by sublimation. Yellow crystals of 4.20 (75 mg, 75% yield) were obtained upon recrystallization from 1,2-C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2}/C\textsubscript{6}H\textsubscript{14}. The \textsuperscript{13}CO-enriched 4.20 was prepared in a similar manner from \textsuperscript{13}CO-labeled 4.18. For 4.20: IR (C\textsubscript{6}H\textsubscript{14}), ν(CO): 2117(m), 2055(m), 2040(m), 2013(vs), 2009(vs), 1997(vw,sh),
1976(s) cm⁻¹; (CH₂Cl₂), ν(CO): 2115(m), 2053(m), 2034(w,sh), 2011(s), 2004(s), 1970(m,br) cm⁻¹; ¹H NMR (C₆D₅CD₃, rm. temp): δ 1.17 (d, CH₃, ²Jₚ-H = 10.4 Hz); (CD₂Cl₂, 233 K): δ 1.95 (d, CH₃, ²Jₚ-H = 10.7 Hz); ³¹P{¹H} NMR (C₆D₅CD₃, rm. temp): δ -47.1 (s, PMe₃); (CD₂Cl₂, 233 K): δ -43.54 (s, PMe₃); ¹³C{¹H} NMR (CD₂Cl₂/CH₂Cl₂ 1/3, 233 K): δ 17.85 (d, CH₃, ¹Jₚ-C = 37.9 Hz), 176.27 (d, 1C, CO, ²Jₚ-C = 4.0 Hz), 183.06 (s, 1C, CO, vbr), 189.22 (d, 2C, CO, ²Jₚ-C = 5.0 Hz), 190.87 (s, 4C, CO, vbr); MS (EI, m/z): 756/758 (M⁺); UV-vis absorption spectrum (CH₂Cl₂) λ_max, nm (ε, M⁻¹ cm⁻¹) 325 (1.3 x 10⁴), 378 (1.5 x 10³); Anal. Calcd. for C₁₁H₉BrO₈OsRe: C, 17.47; H, 1.20. Found: C, 17.49; H, 1.19.

**Preparation of (I)(Me₃P)(OC)₃OsRe(CO)₅ (4.21).** A Schlenk tube was charged with 4.18 (100 mg, 0.148 mmol), CH₂I₂ (14 µL, 0.18 mmol), and C₆H₁₄ (20 mL) and the solution stirred for 8-10 h. The solvent and excess CH₂I₂ were removed under vacuum. Bright yellow, needle like crystals of (I)(Me₃P)(OC)₃OsRe(CO)₅ (4.21) (102 mg, 86% yield) were obtained upon recrystallization from 1,2-C₂H₄Cl₂/C₆H₁₄. The ¹⁳CO-enriched 4.21 was prepared in a similar manner from ¹³CO-labeled 4.18. For 4.21: IR (C₆H₁₄), ν(CO): 2116(m), 2052(m), 2040(m), 2010(vs), 1996(vw,sh), 1977(s) cm⁻¹; (CH₂Cl₂), ν(CO): 2115(m), 2051(m), 2036(w,sh), 2010(s,br), 1967(m,br) cm⁻¹; ¹H NMR (C₆D₅CD₃, rm. temp): δ 1.26 (d, CH₃, ²Jₚ-H = 10.3 Hz); (CD₂Cl₂, 233 K): δ 2.04 (d, CH₃, ²Jₚ-H = 10.3 Hz); ³¹P{¹H} NMR (C₆D₅CD₃, rm. temp): δ -56.6 (s, PMe₃); (CD₂Cl₂, 233 K): δ -52.79 (s, PMe₃); ¹³C{¹H} NMR (CD₂Cl₂/CH₂Cl₂ 1/3, 233 K): δ 19.31 (d, CH₃, ¹Jₚ-C = 38.7 Hz), 175.45 (d, 1C, CO, ²Jₚ-C = 4.0 Hz), 182.52 (s, 1C, CO, vbr), 185.31 (d, 2C, CO, ²Jₚ-C = 5.0 Hz), 191.24 (s, 4C, CO, vbr); MS (EI, m/z): 804 (M⁺), 776 (M⁺-CO); UV-vis absorption
spectrum \((CH_2Cl_2) \lambda_{max}, \text{nm (e, M}^{-1} \text{cm}^{-1})\) 334 \((9.0 \times 10^3)\), 388 \((1.1 \times 10^3)\); Anal. Calcd. for \(C_{11}H_9IO_8OsPRe\): C, 16.44; H, 1.13. Found: C, 16.60; H, 1.14.

**Molecular structure of \((OC)_4(Bu'NC)OsOs(CO)_3(GeCl_3)(Cl)\) (4.6).** X-ray quality crystals of \((OC)_4(Bu'NC)OsOs(CO)_3(GeCl_3)(Cl)\) (4.6) proved difficult to grow as the complex had the tendency to form crystals that were too small. This problem was overcome by dissolving 4.6 in a minimum amount of 1,2-\(C_2H_4Cl_2\) in a Schlenk tube and layering \(C_6H_5CH_3\) on top of the solution. The vessel and the contents were allowed to cool slowly in the freezer (-233 K) and produced pale yellow needle like crystals of 4.6. The crystal structure analysis of 4.6 was determined by Professor F. W. B. Einstein and Dr. W. Wang at Simon Fraser University. The crystal structure was determined to be monoclinic, with the space group \(P2_1/n\). The asymmetric unit contains one 4.6 molecule and half a toluene molecule. A \(^1\text{H NMR}\) spectrum of some of the crystals of the complex, 4.6, recrystallized from the solvent system \(C_6H_5CH_3/1,2-C_2H_4Cl_2\), exhibited proton resonances due to \(C_6H_5CH_3\). There was disorder in the molecule with the C(23)-O(23) carbonyl and Cl(1) atom (66\(\pm\)2\% site occupancy) interchanged; the minor component was designated C(23), O(23) and Cl(1), respectively (34\(\pm\)2\% site occupancy).

**Molecular structure of \([\text{Os}(CO)_4(CNBu}'(H)][BCl_4] ([4.12][BCl_4])\).** The crystal structure analysis of \([\text{Os}(CO)_4(CNBu}'(H)][BCl_4] ([4.12][BCl_4])\) was carried out by Professor F. W. B. Einstein and Dr. W. Wang at Simon Fraser University. The structure was determined to be monoclinic, with the space group \(P2_1/c\). The asymmetric unit contains one crystallographically distinct \([4.12]\) cation and one \([BCl_4]^\text{-}\) anion. The position of the terminal hydrogen atom investigated using the HYDEX program and the lowest site energy was found to be trans to C(12).\(^{206}\)
CHAPTER 5

Investigation of the donor ability of donor fragments

5.1 Introduction

In Chapter 4 a series of complexes with a donor-acceptor metal-metal bond and either (OC)$_4$(Bu'NC)Os or (Me$_3$P)(OC)$_4$Os as the donor fragment were prepared and examined to probe whether the difference in the acceptor abilities of the acceptor moieties could be determined.

An analogous study of the donor ability of the donor fragments in these types of complexes was considered to be useful since prior work had shown that the donor fragment with the greatest electron density at the metal were not necessarily the species with the greatest donor ability. For example (Me$_3$P)(OC)$_4$Os is believed to be a better donor fragment than (Me$_3$P)$_2$(OC)$_3$Os, even though the IR $\nu$(CO) frequencies of these five coordinate complexes indicate there is more electron density on the metal in the later complex.$^{50,51,69,74,161}$

In this chapter complexes with a dative metal-metal bond and Ru(CO)$_3$(SiCl)$_3$$_2$ as the acceptor fragment are described. Previously in Chapter 4 evidence was presented that indicated that Ru(CO)$_3$(SiCl)$_3$$_2$ had the second highest acceptor ability of the species examined. The reasons this species was chosen over the acceptor fragment, Os(CO)$_3$(GeCl)$_3$(Cl) (the species with the highest relative acceptor ability) were, (i) the relative ease of preparation of cis-Ru(CO)$_4$(SiCl)$_3$$_2$ (see Section 4.4 and reference 199); (ii) the ready generation of the 16-electron species Ru(CO)$_3$(SiCl)$_3$$_2$ (see Section 4.4 and
reference 199); (iii) less chance of isomerization of the complex with a donor-acceptor bond since SiCl$_3$ does not migrate as readily as Cl, (an isomerization with Cl could lead to a complex with a nondative metal-metal bond analogous to (Br)(Me$_3$P)(OC)$_3$OsRe(CO)$_5$ (4.20); (iv) the ease of $^{13}$CO-enrichment of the acceptor fragment (see Section 4.2.1.4 and reference 167). The complexes with a dative metal-metal bond and Ru(CO)$_3$(SiCl)$_3$ as the acceptor fragment have been examined with IR, $^1$H, $^{31}$P{$^1$H}, $^{13}$C{$^1$H} NMR and UV-vis spectroscopies and in two cases with X-ray crystallography.

5.2 Results and Discussion

5.2.1 Complexes with Ru(CO)$_3$(SiCl)$_3$$_2$ as the acceptor fragment.

5.2.1.1 Preparation of the complexes with Ru(CO)$_3$(SiCl)$_3$$_2$ as the acceptor fragment.

The new complexes (Dnr)Ru(CO)$_3$(SiCl)$_3$$_2$ [Dnr = (OC)$_4$(Bu'NC)Os, (PMe$_3$)(OC)$_4$Os, (P$_c$)(OC)$_4$Os, (Me$_3$P)(OC)$_4$Ru, Cp*(OC)$_2$Ir] (4.7, 4.14, 5.1-5.3) and Cp*(OC)$_2$IrOs(CO)$_3$(GeCl$_3$)(Cl) (5.4) were prepared (eq 5.1 and 5.2).

$$\text{Dnr} + \text{cis-Ru(CO)$_3$(SiCl)$_3$$_2$} \xrightarrow{\text{rm. temp}} \text{Dnr} \rightarrow \text{Ru(CO)$_3$(SiCl)$_3$$_2$ + CO} \quad (5.1)$$

$$\text{Dnr} = (OC)$_4$(Bu'NC)Os, (Me$_3$P)(OC)$_4$Os, (P$_c$)(OC)$_4$Os, (Me$_3$P)(OC)$_4$Ru, Cp*(OC)$_2$Ir$$

$$\text{Cp*Ir(CO)$_2$ + cis-Os(CO)$_4$(GeCl$_3$)(Cl)} \xrightarrow{323 \text{ K}} \text{Cp*(OC)$_2$IrOs(CO)$_3$(GeCl$_3$)(Cl) + CO} \quad (5.2)$$

The complex 5.4 is included in this collection of compounds in order to allow a direct comparison between the two acceptor fragments (Ru(CO)$_3$(SiCl)$_3$$_2$ and Os(CO)$_3$(GeCl$_3$)(Cl)) with the same donor fragment Cp*(OC)$_2$Ir.
The complex \( \text{Cp}^*(\text{OC})_2\text{IrOs(CO)}_3\text{(GeCl}_3\text{(Cl)} \) was prepared (54% yield) by heating a \( C_6H_{14} \) solution of \( \text{Cp}^*\text{Ir(CO)}_2 \) and \( \text{Os(CO)}_4\text{(GeCl}_3\text{(Cl)} \) under vacuum at 323 K. The complexes \( (\text{Dnr})\text{Ru(CO)}_3\text{(SiCl}_3\text{)}_2 \) (\( \text{Dnr} = (\text{OC})_4\text{(Bu′NC)O}_s, (\text{PMe}_3\text{(OC)}_4\text{Os}, (\text{P}_c\text{(OC)}_4\text{Os, (Me}_3\text{P)(OC)}_4\text{Ru, Cp}^*(\text{OC})_2\text{Ir} \) (4.7, 4.14, 5.1-5.3) were obtained upon stirring a \( C_6H_{14} \) solution of the respective donor fragment and \( \text{cis-Ru(CO)}_4\text{(SiCl}_3\text{)}_2 \) at room temperature under vacuum. The products were obtained in yields that range from 50-82%. In cases where the product was considered unstable [for example, \( \text{Cp}^*(\text{OC})_2\text{IrRu(CO)}_3\text{(SiCl}_3\text{)}_2 \) (5.3)], or that there was a possibility of two isomeric forms (that is, with the phosphorus containing ligand being \text{cis} or \text{trans} to the metal-metal bond) it was solely manipulated in \( C_6H_{14} \).

Several attempts were made to prepare the complex \( \text{(Me}_3\text{P)(OC)}_4\text{FeRu(CO)}_3\text{(SiCl}_3\text{)}_2 \) both by using the method described above or by utilizing a nitrogen purge (to prohibit the back reaction). After 48h in both cases there was no evidence of a reaction. Attempts were made to prepare the complexes with \( \text{Fe(CO)}_4\text{(CNBu′)} \) and \( \text{CpIr(CO)}_2 \) as the donor units with \( \text{cis-Ru(CO)}_4\text{(SiCl}_3\text{)}_2 \) as the acceptor fragment but were also unsuccessful.
5.2.1.2 The molecular structure of (Me₃P)(OC)₄RuRu(CO)₃(SiCl₃)₂ (5.2)

The molecular structure of (Me₃P)(OC)₄RuRu(CO)₃(SiCl₃)₂ (5.2) was determined by X-ray crystallography by Professor F. W. B. Einstein and Dr. W. K. Leong. A view of the molecule is shown in Figure 5.1; selected bond lengths and bond angles are given in Tables 5.1 and 5.2, respectively. There are two crystallographically distinct molecules in the unit cell and hence there are two sets of bond lengths and bond angles.

Table 5.1  Selected bond lengths from the molecular structure of (Me₃P)(OC)₄RuRu(CO)₃(SiCl₃)₂ (5.2).

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Molecule 1</th>
<th>Molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1) - Ru(2)</td>
<td>2.995(1)</td>
<td>2.975(1)</td>
</tr>
<tr>
<td>Ru(1) - P(1)</td>
<td>2.370(3)</td>
<td>2.376(3)</td>
</tr>
<tr>
<td>Ru(1) - C(11)</td>
<td>1.94(1)</td>
<td>1.92(1)</td>
</tr>
<tr>
<td>Ru(1) - C(12)</td>
<td>1.93(1)</td>
<td>1.95(1)</td>
</tr>
<tr>
<td>Ru(1) - C(13)</td>
<td>1.94(1)</td>
<td>1.97(1)</td>
</tr>
<tr>
<td>Ru(1) - C(14)</td>
<td>1.95(1)</td>
<td>1.97(1)</td>
</tr>
<tr>
<td>Ru(2) - Si(1)</td>
<td>2.338(3)</td>
<td>2.342(3)</td>
</tr>
<tr>
<td>Ru(2) - Si(2)</td>
<td>2.420(4)</td>
<td>2.413(4)</td>
</tr>
<tr>
<td>Ru(2) - C(21)</td>
<td>1.92(1)</td>
<td>1.93(1)</td>
</tr>
<tr>
<td>Ru(2) - C(22)</td>
<td>1.91(1)</td>
<td>2.01(1)</td>
</tr>
<tr>
<td>Ru(2) - C(23)</td>
<td>1.92(1)</td>
<td>1.93(1)</td>
</tr>
</tbody>
</table>
This is the first example of a molecular structure of an uncharged complex with an unbridged dative metal-metal bond where both the donor and acceptor atoms are a second row transition metal. It is the second example (the first example was Cp(OC)₂RhPt(C₅F₅)₂(CO) prepared by Usón and coworkers)\textsuperscript{49} of a molecular structure of an uncharged complex with an unbridged dative metal-metal bond with a second row transition metal fragment as the donor moiety.

\textbf{Figure 5.1} Molecular structure of $\text{(Me}_3\text{P)}\text{(OC)}_4\text{RuRu(CO)}_3\text{(SiCl)}_2$ (5.2).
Table 5.2 Selected bond angles for (Me₃P)(OC)₄RuRu(CO)₃(SiCl₃)₂ (5.2).

<table>
<thead>
<tr>
<th>Bond Angles (deg)</th>
<th>Molecule 1</th>
<th>Molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(2) - Ru(1) - P(1)</td>
<td>176.6(1)</td>
<td>Ru(4) - Ru(3) - P(2)</td>
</tr>
<tr>
<td>Ru(2) - Ru(1) - C(11)</td>
<td>90.0(3)</td>
<td>Ru(4) - Ru(3) - C(31)</td>
</tr>
<tr>
<td>Ru(2) - Ru(1) - C(12)</td>
<td>88.4(3)</td>
<td>Ru(4) - Ru(3) - C(32)</td>
</tr>
<tr>
<td>Ru(2) - Ru(1) - C(13)</td>
<td>83.1(3)</td>
<td>Ru(4) - Ru(3) - C(33)</td>
</tr>
<tr>
<td>Ru(2) - Ru(1) - C(14)</td>
<td>84.7(3)</td>
<td>Ru(4) - Ru(3) - C(34)</td>
</tr>
<tr>
<td>C(11) - Ru(1) - C(13)</td>
<td>172.7(4)</td>
<td>C(31) - Ru(3) - C(33)</td>
</tr>
<tr>
<td>C(12) - Ru(1) - C(14)</td>
<td>172.8(4)</td>
<td>C(32) - Ru(3) - C(34)</td>
</tr>
<tr>
<td>Si(1) - Ru(2) - Si(2)</td>
<td>90.8(1)</td>
<td>Si(3) - Ru(4) - Si(4)</td>
</tr>
<tr>
<td>Si(1) - Ru(2) - C(21)</td>
<td>93.6(3)</td>
<td>Si(3) - Ru(4) - C(41)</td>
</tr>
<tr>
<td>Si(1) - Ru(2) - C(22)</td>
<td>87.5(3)</td>
<td>Si(3) - Ru(4) - C(42)</td>
</tr>
<tr>
<td>Si(1) - Ru(2) - C(23)</td>
<td>88.5(3)</td>
<td>Si(3) - Ru(4) - C(43)</td>
</tr>
<tr>
<td>Si(2) - Ru(2) - C(21)</td>
<td>84.5(4)</td>
<td>Si(4) - Ru(4) - C(41)</td>
</tr>
<tr>
<td>Si(2) - Ru(2) - C(22)</td>
<td>178.3(3)</td>
<td>Si(4) - Ru(4) - C(42)</td>
</tr>
<tr>
<td>Si(2) - Ru(2) - C(23)</td>
<td>87.6(4)</td>
<td>Si(4) - Ru(4) - C(43)</td>
</tr>
<tr>
<td>C(21) - Ru(2) - C(23)</td>
<td>171.9(5)</td>
<td>C(41) - Ru(4) - C(43)</td>
</tr>
</tbody>
</table>

The ruthenium-ruthenium bond lengths in the two independent molecules of 5.2 are 2.975(1) and 2.995(1) Å. These bond lengths are significantly longer than most other Ru-Ru bond distances reported in the literature and significantly different from each other. Some Ru-Ru bond lengths reported are, in Ru₃(CO)₁₂ 2.855 Å (average value).
Ru₃(CO)₉(PMe₃)₃ 2.859 Å (average value);[Ru₂(CO)₈]²⁻ 2.936(1) Å;[Ru₂(SiMe₃)(CO)₄(μ-η³,η⁴-C₅H₈SiMe₃)] 2.909(2) Å; (μ-η⁵,η³-C₅H₄C(C₆H₅)₂)Ru₂(CO)₅ 2.845(1) Å; (μ-η⁵,η⁵-H₂C₅-C₅H₄)Ru₂(CO)₄ 2.821(1) Å;[Ru(CO)₄SnMe₃]₂ 2.943(1) Å and [Ru₃(CO)₁₂(Br)]⁺ 2.8901(1) Å. The Ru-Ru bond in the last charged complex, [Ru₃(CO)₁₂(Br)]⁺, is a dative Ru-Ru bond. A more similar Ru-Ru bond length (3.009(1) Å) is present in one of the isomers of Ru₅(μ₅-C₂PPh₂)(μ-PPh₂)(CO)₁₅ which is also proposed to be a Ru-Ru dative bond.²⁵

The ruthenium-phosphorus bond lengths in 5.2 are 2.370(3) and 2.376(3) Å which are longer than the respective bonds in Ru₃(CO)₉(PMe₃)₃ 2.330 Å (average value);[Ru₂(CO)₈]²⁻ and (OC)₄OsSi(STol-p)[Ru(Cp*)(PMe₃)₂] 2.285(3)-2.303(3) Å.²¹⁵

The ruthenium-carbon bond lengths in 5.2 of the donor fragment, (Me₃P)(OC)₄Ru are 1.92(1)-1.97(1) Å which are similar to Ru-CO distances in the literature, for example, Ru₃(CO)₉(PMe₃)₃ 1.920 Å (average value of axial carbonyl ligands);Ru₃(CO)₁₂ 1.942(4) Å (average value of axial carbonyl ligands);Ru(CO)₄[P(OCH₃)₃] 1.928(7)-1.938(6) Å,²¹⁶ and [Ru(CO)₄SnMe₃]₂ 1.932(5)-1.947(7) Å.²¹³

The ruthenium-carbon bond lengths in 5.2 of the acceptor moiety, Ru(CO)₃(SiCl₃)₂ are 1.91(1)-2.01(1) Å. When the Ru-C bond lengths and the total distance between Ru-C-O is considered together there are no differences between the Ru-C bond lengths. These Ru-C bond lengths are similar to those in cis-Ru(CO)₄(GeCl₃)₂ (1.96(4)-2.04(4) Å),²¹⁷ and this supports the idea that SiCl₃ and GeCl₃ have similar π-accepting abilities and trans influences as CO ligands even though they have a greater kinetic trans effect.¹⁶⁷,¹⁹⁹c,²¹⁷-²¹⁹

The ruthenium-silicon bond lengths for the Ru-Si bond trans to the metal-metal bond in 5.2 are 2.338(3) and 2.342(3) Å which is significantly shorter than the Ru-Si bond
*cis* to the metal-metal bond at 2.413(4) and 2.420(4) Å. For comparison the Ru-Si bond lengths in \((p-t\text{-Bu}_2\text{C}_6\text{H}_4)\text{Ru(CO)(SiCl}_3\text{)}_2\) are 2.338(1) and 2.340(1) Å.\textsuperscript{218} It is known that the SiCl\(_3\) ligand is a particularly good \(\pi\)-acceptor ligand.\textsuperscript{167} The SiCl\(_3\) group *cis* to the metal-metal bond in 5.2 is *trans* to a CO group and there is competition with the CO entity for the \(\pi\)-electron density which could result in a long Ru-Si bond (2.413(4) and 2.420(4) Å) with little double bond character. On the other hand, the SiCl\(_3\) group *trans* to the metal-metal bond does not have such competition for the \(\pi\)-electron density and is therefore much shorter (2.338(3) and 2.342(3) Å). Furthermore, it has been observed in \(\text{Cp}^*(\text{OC})_2\text{IrW(CO)}_5\),\textsuperscript{46} \((\text{Me}_3\text{P})(\text{OC})_4\text{OsM(CO)}_5\) \((\text{M} = \text{W}, \text{Cr})\) \((2.1, 4.1),\textsuperscript{50}\) \((\text{OC})_5\text{a(Bu’NC)}_n\text{OsCr(CO)}_5\) \((n = 1, 2)\textsuperscript{51}\) and \((\text{Me}_3\text{P})(\text{OC})_4\text{OsRe(CO)}_4\text{(Br)}\) \((4.13)\textsuperscript{48}\) that the ligand on the acceptor fragment *trans* to the dative metal-metal bond has a shorter bond than other identical ligands on the same fragment. It was suggested that the group on the acceptor fragment *trans* to the metal-metal bond might also assist in the dative metal-metal interaction by reducing the electron density in the filled \(d\)-orbitals on the metal atoms, an interaction that results in a repulsion between the metal atoms, see Figure 5.2.\textsuperscript{50,51}

![Figure 5.2](image)

**Figure 5.2** One of the repulsive interactions between the filled \(d\)-orbitals involved in the dative metal-metal bond and the role of SiCl\(_3\) in reducing the interaction.
As found for other complexes with an unbridged, dative metal-metal bond there is a slight inward leaning of the equatorial carbonyl ligands on the donor metal atom towards the acceptor metal atom in 5.2. The Ru(n)-Ru(m)-C(mk) angles \((n = 2,4; m = 1,3; k = 1-4)\) are 82.9(3)-91.0(4)° (Table 5.2) which are similar to the respective angles in \((\text{Me}_3\text{P})(\text{OC})_4\text{OsOs}_3(\text{CO})_{11}\) 84.1(6)-90.2(5)°. This also suggests that in 5.2 there are no significant steric interactions between the SiCl\(_3\) group that is cis to the metal-metal bond and the CO ligands on the donor fragment.

As observed with similar systems such as \((\text{OC})_4(\text{Bu}^\prime\text{NC})\text{OsOs}(\text{CO})_3(\text{GeCl}_3)(\text{Cl})\) (4.6) (Table 4.3) and \((\text{OC})_2\text{OsOs}(\text{CO})_3(\text{GeCl}_3)(\text{Cl})\), inward leaning of the equatorial carbonyl ligands on the acceptor half of the molecule is not present in 5.2 (Table 5.2). The ruthenium atom of the acceptor moiety (Ru(n) \((n = 2,4)\)) has close to an octahedral coordination, with no evidence of SiCl\(_3\) groups exerting additional steric interactions to distort the environment around the ruthenium atom. As observed in cis-Ru(CO)\(_4\)(GeCl\(_3\))\(_2\), \((p\text{-}t\text{-Bu}_2\text{C}_6\text{H}_4)\text{Ru}(\text{CO})(\text{SiCl}_3)\)_2 and CpFe(CO)(H)(SiCl\(_3\))\(_2\), there is distortion of the tetrahedral geometry of the SiCl\(_3\) groups, in 5.2 causing the average Ru-Si-Cl angle to be 116.9°, with the average Cl-Si-Cl angle equal to 101.0°.

5.2.1.3 The molecular structure of \((\text{Me}_3\text{P})(\text{OC})_4\text{OsRu}(\text{CO})_3(\text{SiCl}_3)_2\) (4.14)

The molecular structure of \((\text{Me}_3\text{P})(\text{OC})_4\text{OsRu}(\text{CO})_3(\text{SiCl}_3)_2\) (4.14) was also determined by X-ray crystallography by Professor F. W. B. Einstein and Dr. W. K. Leong; and allows a direct comparison with 5.2. A view of the molecule is shown in Figure 5.3; selected bond lengths and bond angles are given in Tables 5.3 and 5.4, respectively. The compound 4.14
is isostructural with 5.2 and therefore also has two crystallographically independent molecules in the unit cell.

![Molecular structure of (Me₃P)(OC)₄OsRu(CO)₃(SiCl₃)₂ (4.14).](image)

**Figure 5.3** Molecular structure of (Me₃P)(OC)₄OsRu(CO)₃(SiCl₃)₂ (4.14).

As can be seen in Figure 5.3, this is another example of (Me₃P)(OC)₄Os acting as a two-electron donor ligand towards the 16-electron acceptor fragment, Ru(CO)₅(SiCl₃)₂, via an unbridged, dative metal-metal bond. As observed in similar molecules the phosphorus ligand is trans to the metal-metal bond, e.g., as in (Me₃P)(OC)₄OsOs₃(CO)₁₁,²⁸a (Me₃P)(OC)₄OsM(CO)₅ (M = W, Cr) (2.1, 4.1),⁵⁰ and (Me₃P)(OC)₄OsRe(CO)₄(Br) (4.13).⁴⁸ This is in contrast to (OC)₄(Bu¹NC)OsCr(CO)₅ (4.3)⁵¹ and
(OC)$_4$(Bu’NC)OsOs(CO)$_3$(GeCl$_3$)(Cl) (4.6)$^{44}$ (Figure 4.2) where the noncarbonyl ligand (CNBu’) is cis to the metal-metal bond.

The osmium-ruthenium bond lengths in the two independent molecules of 4.14 are 2.984(1) and 3.014(1) Å. These bond lengths are longer than the Ru-Ru bonds in Ru$_3$(CO)$_{12}$ 2.855 Å (average value)$^{207}$ and Ru$_3$(CO)$_9$(PMe$_3$)$_3$ 2.859 Å (average value)$^{208}$ the Os-Os bonds in Os$_3$(CO)$_{12}$ 2.877(3) Å (average value)$^{222}$ (OC)$_5$OsOs(CO)$_3$(GeCl$_3$)(Cl) 2.916(2), 2.927(2) and 2.931(1) Å,$^{44}$ and (OC)$_4$(Bu’NC)OsOs(CO)$_3$(GeCl$_3$)(Cl) (4.6) 2.916(1) Å (Table 4.2); or the unbridged Os-Ru bonds in [(µ-H)$_2$RuOs$_3$(CO)$_{13}$] 2.803(2)-2.810(1) Å,$^{223}$ and [RuOs$_4$(µ-H)$_4$(η$^5$-C$_6$H$_6$)(CO)$_{11}$] 2.774(3)-2.803(3) Å.$^{224}$ Since most of the above bond lengths refer to cluster compounds in which it is known that bond lengths are shorter than similar bonds in dinuclear compounds the comparison may not be completely valid.$^{225}$ However, in (OC)$_5$-n(Bu’C)$_n$OsOs(CO)$_3$(GeCl$_3$)(Cl) (n = 0, 1) both compounds have a dative Os-Os interaction, the bond lengths of which are shorter than in 4.14. There is hardly any significant difference in the bond lengths of the Os-Ru interaction (2.984(1) and 3.014(1) Å) in 4.14 and the analogous Ru-Ru interactions (2.975(1) and 2.995(1) Å) in 5.2. The covalent radii of ruthenium and osmium are approximately the same, due to the lanthanide contraction and relativistic effects, therefore, it might be expected that Ru-Ru and Os-Ru bond lengths would be similar.$^{226}$ It has been suggested that dative metal-metal bonds that have a second row transition metal as the donor atom are less stable than their third row counterparts.$^{50b}$ That the Ru-Ru and Os-Ru bonds in these two complexes are comparable might suggest that this instability is due to transition state stabilization effects rather than due to ground state destabilization. Such a view is
consistent with a theoretical study on complexes with a dative metal-metal bond 
\[ ([\text{OC}]_5\text{OsM(CO)}_5 \ (M = \text{Cr, W}) \] that are less stable than the nondative covalent metal-metal 
bonds \[ ([\text{OC}]_3\text{MM(CO)}_5 \ (M = \text{Mn, Re}) \] because of the geometrical relaxation energy on 
going from square-pyramidal \text{Os(CO)}_5 to trigonal-bipyramidal \text{Os(CO)}_5. \(^{53}\)

The dimensions of the \((\text{Me}_3\text{P})(\text{OC})_4\text{Os} \) fragment in \textbf{4.14} (see Table 5.3) are similar 
to those of the \((\text{Me}_3\text{P})(\text{OC})_4\text{Os} \) ligand in \((\text{Me}_3\text{P})(\text{OC})_4\text{Os}_{\text{3}}\text{(CO)}_{\text{11}}, \(^{28a}\) 
\((\text{Me}_3\text{P})(\text{OC})_4\text{Os(CO)}_5 \ (M = \text{W, Cr}) \ (\textbf{2.1}, \textbf{4.1}), \(^{50}\) and \((\text{Me}_3\text{P})(\text{OC})_4\text{OsRe(CO)}_4\text{Br} \ (\textbf{4.13}) \(^{48}\)

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Molecule 1</th>
<th>Molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(1) - Ru(2)</td>
<td>3.014(1)</td>
<td>Os(3) - Ru(4)</td>
</tr>
<tr>
<td>Os(1) - P(1)</td>
<td>2.344(4)</td>
<td>Os(3) - P(2)</td>
</tr>
<tr>
<td>Os(1) - C(11)</td>
<td>1.94(1)</td>
<td>Os(3) - C(31)</td>
</tr>
<tr>
<td>Os(1) - C(12)</td>
<td>1.95(2)</td>
<td>Os(3) - C(32)</td>
</tr>
<tr>
<td>Os(1) - C(13)</td>
<td>1.92(1)</td>
<td>Os(3) - C(33)</td>
</tr>
<tr>
<td>Os(1) - C(14)</td>
<td>1.92(2)</td>
<td>Os(3) - C(34)</td>
</tr>
<tr>
<td>Ru(2) - Si(1)</td>
<td>2.338(5)</td>
<td>Ru(4) - Si(3)</td>
</tr>
<tr>
<td>Ru(2) - Si(2)</td>
<td>2.399(5)</td>
<td>Ru(4) - Si(4)</td>
</tr>
<tr>
<td>Ru(2) - C(21)</td>
<td>1.93(1)</td>
<td>Ru(4) - C(41)</td>
</tr>
<tr>
<td>Ru(2) - C(22)</td>
<td>1.92(2)</td>
<td>Ru(4) - C(42)</td>
</tr>
<tr>
<td>Ru(2) - C(23)</td>
<td>1.91(1)</td>
<td>Ru(4) - C(43)</td>
</tr>
</tbody>
</table>
The Os-C (1.92(2)-1.96(2) Å) and Os-P (2.344(4)-2.381(4) Å) bond lengths in 4.14 are also similar to those in the donor fragment of 5.2 (see Table 5.1).

Table 5.4 Selected bond angles of (Me₃P)(OC)₄OsRu(CO)₃(SiCl)₂ (4.14).

<table>
<thead>
<tr>
<th>Bond Angles (deg)</th>
<th>Molecule 1</th>
<th>Molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(2) - Os(1) - P(1)</td>
<td>176.8(1)</td>
<td>Ru(4) - Os(3) - P(2)</td>
</tr>
<tr>
<td>Ru(2) - Os(1) - C(11)</td>
<td>89.3(4)</td>
<td>Ru(4) - Os(3) - C(31)</td>
</tr>
<tr>
<td>Ru(2) - Os(1) - C(12)</td>
<td>87.7(4)</td>
<td>Ru(4) - Os(3) - C(32)</td>
</tr>
<tr>
<td>Ru(2) - Os(1) - C(13)</td>
<td>82.6(4)</td>
<td>Ru(4) - Os(3) - C(33)</td>
</tr>
<tr>
<td>Ru(2) - Os(1) - C(14)</td>
<td>85.6(4)</td>
<td>Ru(4) - Os(3) - C(34)</td>
</tr>
<tr>
<td>C(11) - Os(1) - C(13)</td>
<td>171.0(6)</td>
<td>C(31) - Os(3) - C(33)</td>
</tr>
<tr>
<td>C(12) - Os(1) - C(14)</td>
<td>173.1(6)</td>
<td>C(32) - Os(3) - C(34)</td>
</tr>
<tr>
<td>Si(1) - Ru(2) - Si(2)</td>
<td>91.1(2)</td>
<td>Si(3) - Ru(4) - Si(4)</td>
</tr>
<tr>
<td>Si(1) - Ru(2) - C(21)</td>
<td>94.5(4)</td>
<td>Si(3) - Ru(4) - C(41)</td>
</tr>
<tr>
<td>Si(1) - Ru(2) - C(22)</td>
<td>86.7(4)</td>
<td>Si(3) - Ru(4) - C(42)</td>
</tr>
<tr>
<td>Si(1) - Ru(2) - C(23)</td>
<td>89.8(4)</td>
<td>Si(3) - Ru(4) - C(43)</td>
</tr>
<tr>
<td>Si(2) - Ru(2) - C(21)</td>
<td>85.5(5)</td>
<td>Si(4) - Ru(4) - C(41)</td>
</tr>
<tr>
<td>Si(2) - Ru(2) - C(22)</td>
<td>177.7(4)</td>
<td>Si(4) - Ru(4) - C(42)</td>
</tr>
<tr>
<td>Si(2) - Ru(2) - C(23)</td>
<td>87.3(5)</td>
<td>Si(4) - Ru(4) - C(43)</td>
</tr>
<tr>
<td>C(21) - Ru(2) - C(23)</td>
<td>171.7(7)</td>
<td>C(41) - Ru(4) - C(43)</td>
</tr>
</tbody>
</table>
The ruthenium-silicon bond lengths in **4.14** are 2.338(5) and 2.349(4) Å (for the Ru-Si bond *trans* to the metal-metal bond) and 2.399(5) and 2.413(5) Å (for the Ru-Si bond *cis* to the metal-metal bond) which are no different to the Ru-Si bond lengths in **5.2** (Table 5.1).

The ruthenium-carbon bond lengths of the acceptor fragment, Ru(CO)\(_3\)(SiCl\(_3\))\(_2\) in **4.14** are in the range 1.89(1)-1.97(2) Å. When the Ru-C bond lengths and the total distances between Ru-C-O are considered together there are no differences between the Ru-C bond lengths or Os-C bond lengths in this molecule or when compared to all the Ru-C bond lengths in **5.2** (Table 5.1).

As also found for **5.2**, (Table 5.2) there is a slight inward leaning of the equatorial carbonyl ligands on the donor metal atom, towards the acceptor metal atom in **4.14**; these angles range from 82.6(4) to 90.2(5)° (see Table 5.4). This suggests that in **4.14** there are no steric interactions between the SiCl\(_3\) group *cis* to the metal-metal bond and the CO ligands on the donor fragment.

These bond angles around the Ru atom in the acceptor fragment of **4.14** are similar to those observed in **5.2** (see Table 5.2). The ruthenium atom Ru(n) (n= 2,4) has close to octahedral coordination, with no evidence for distortion by the bulky SiCl\(_3\) groups. As also observed in **5.2**, there is distortion of the tetrahedral geometry of the SiCl\(_3\) groups of **4.14** (the average Ru-Si-Cl angle is 116.9°, with the average Cl-Si-Cl angle equal to 101.0°).
5.2.1.4 Spectroscopic properties of the (Dnr)Ru(CO)₃(SiCl)₂ complexes (Dnr = a donor fragment).

The ¹H NMR chemical shifts and IR ν(CO) bands of the new compounds together with data of some previously prepared complexes, (OC)₅OsRu(CO)₃(SiCl)₂ (5.5)⁴⁵ and Os(CO)₄(L) (L = PMe₃, P₅)⁶⁹ are given for comparison in Table 5.5. The ¹H NMR resonances for (P₅)(OC)₄OsRu(CO)₃(SiCl)₂ (5.1) are downfield (deshielded) relative to those of the uncoordinated Os(CO)₄(P₅) (see Table 5.5). Similar behavior is observed in Os(CO)₄(L) (L = CNBu', PMe₃) (see Tables 4.6 and 4.9, respectively). This is consistent with the view that the electron density on the osmium fragment is reduced in the binuclear complex. As in (P₅)(OC)₄Mo(CO)₅ (M = Cr, W)⁵⁰ it was found that there were two isomers of 5.1 in solution, one with the P₅ ligand cis to the metal-metal bond and one with the P₅ group trans to the metal-metal bond. Upon careful examination of several preparations and recrystallizations of 5.1 it was shown by both ¹H and ³¹P(¹H) NMR spectroscopy (see Tables 5.5 and 5.6) that the cis isomer was formed initially and then isomerized to the trans form (see later in the text for further details). This is in contrast to the (L)(OC)₄OsM(CO)₅ (L = phosphine, phosphite; M = Cr, Mo, W) derivatives where the two isomers are in dynamic equilibrium.⁵⁰ The ¹H NMR resonances for the trans isomer are further downfield than the resonances for the cis isomer (as seen in other analogous systems).⁵⁰ This suggests less electron density at the ¹H nuclei in the trans form and presumably indicates that more electron density is donated to the osmium center in the trans isomer relative to that in the cis isomer. It has been previously suggested that the cis position to the metal-metal bond is the electronically preferred position while the trans position is sterically preferred.⁵⁰,⁵¹,⁷⁴,¹⁶¹
Table 5.5 The IR spectra (v(CO) region) and $^1$H NMR spectra of (Dnr)Ru(CO)$_3$(SiCl)$_2$ (Dnr = a donor fragment) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H NMR, $^a$ δ, ppm</th>
<th>IR, $^b$ v(CO), cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Bu'NC)(OC)$_4$OsRu(CO)$_3$(SiCl)$_2$</td>
<td>1.55</td>
<td>2126(s), 2078(s), 2054(vs), 2032(w,sh), 2015(m,sh)</td>
</tr>
<tr>
<td>cis-(P$_c$)(OC)$_4$OsRu(CO)$_3$(SiCl)$_2$</td>
<td>0.87 (CH$_3$), 4.44</td>
<td>2130(m), 2081(w,sh), (CH$<em>2$, $^3$J$</em>{P-H}$ = 5.0 Hz) 2070(vw,sh), 2054(vs), 2020(w,sh)</td>
</tr>
<tr>
<td>trans-(P$_c$)(OC)$_4$OsRu(CO)$_3$(SiCl)$_2$</td>
<td>0.93 (CH$_3$), 4.50</td>
<td>2124(vw), 2073(vw,sh), (CH$<em>2$, $^3$J$</em>{P-H}$ = 5.1 Hz) 2056(vs), 2016(w,sh)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$OsRu(CO)$_3$(SiCl)$_2$</td>
<td>2.16 (10.7)</td>
<td>2124(w), 2069(w,sh), 2038(vs), 2012(vw,sh)</td>
</tr>
<tr>
<td>(OC)$_2$OsRu(CO)$_3$(SiCl)$_2$</td>
<td></td>
<td>2159(m), 2119(vw), 2091(s), 2074(vs), 2028(s)</td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$RuRu(CO)$_3$(SiCl)$_2$</td>
<td>1.95 (10.5)</td>
<td>2122(w), 2068(w,sh), 2044(vs), 2013(w,sh)</td>
</tr>
<tr>
<td>(Cp*)(OC)$_2$IrRu(CO)$_3$(SiCl)$_2$</td>
<td>2.24</td>
<td>2095(w), 2079(vw,sh), 2043(s), 2022(m,sh), 2009(vw,sh)$^c$</td>
</tr>
<tr>
<td>(Cp*)(OC)$_2$IrOs(CO)$_3$(GeCl)$_3$(Cl)</td>
<td>2.29</td>
<td>2113(w), 2061(m,sh), 2041(vs), 2020(vw,sh), 1993(m)</td>
</tr>
<tr>
<td>Os(CO)$_4$(PMe$_3$)</td>
<td>1.82 (10.5)</td>
<td>2058(m), 1973(m,sh), 1931(vs)</td>
</tr>
<tr>
<td>Os(CO)$_4$(P$_c$)</td>
<td>0.80 (CH$_3$), 4.32</td>
<td>2076(m), 1999(m,sh), 1956(vs)</td>
</tr>
<tr>
<td></td>
<td>(CH$<em>2$, $^3$J$</em>{P-H}$ = 4.9 Hz)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ In CD$_2$Cl$_2$ at 233 K, the coupling constant ($^2$J$_{P-H}$) is given in parentheses where applicable. $^b$ In CH$_2$Cl$_2$ at room temperature. $^c$ Solution initially at 233 K (see Figure 5.4).

The mechanism of cis to trans isomerization probably involves CO migration as shown in Scheme 5.1. This is believed to be the mechanism of isomerization in
(Me₃P)(OC)₄OsM(CO)₅ (M = W, Cr, Mo) (2.1, 4.1, 4.2)⁵⁰ although a trigonal twist mechanism (analogous to that proposed for (Bu'NC)₂(OC)₃OsCr(CO)₅)⁵¹ or fragmentation of the binuclear complex into a geminate pair followed by rearrangement within a solvent cage cannot be completely ruled out.⁵⁰-⁵² In 2.1, 4.1 and 4.2 all the CO ligands can exchange during isomerization.⁵⁰ In order for an SiCl₃ group to remain trans to the metal-metal bond the isomerization by a CO exchange mechanism must take place in the manner shown in Scheme 5.1. In other words the carbonyl ligands that are mutually trans and on the Ru(CO)₃(SiCl₃)₂ moiety maintain their identity during isomerization. (Further experiments to test this observation are planned).

Scheme 5.1 A proposed mechanism for the isomerization of (P₅)(OC)₄MRu(CO)₃(SiCl₃)₂ (5.1).

It is also of interest to note, that unlike the compounds 2.1, 4.1 and 4.2,⁵⁰ 4.14 and 5.2 showed evidence of only one isomer at all times by ¹H and ³¹P{¹H} NMR spectroscopy (see Tables 5.5 and 5.6), even when the latter complexes were prepared under careful conditions to try to observe any initial (cis) product formed.

The complex 5.3 immediately decomposes at room temperature in a CH₂Cl₂ solution to unidentified product(s). The product(s) is(are) not cis-Ru(CO)₄(SiCl₃)₂,¹⁶⁷,¹⁹⁹ [Cp*Ir(CO)]₂,²²⁷a or Cp*Ir(CO)₂²²⁷ by comparison to the IR spectroscopic data on these
complexes. To obtain the IR spectrum (ν(CO) bands) of 5.3 a solution of the complex was prepared at 233K. The normal spectrum (CH₂Cl₂ as the reference) and the difference spectra (the initial spectrum as the reference spectrum) were obtained as a function of time to ascertain which peaks were due to the initial compound and which were the decomposition product(s), (see Figure 5.4 for the difference spectra). (Note that in Figure 5.4, the IR difference spectra, the IR ν(CO) bands ascribed to the starting material 5.3 grow in as negative peaks over time while the decomposition product(s) grow in as positive peaks over the 35 min time period as the solution warmed from 233K to room temperature). This experiment indicated the IR ν(CO) bands of 5.3 in CH₂Cl₂ are: 2095(w), 2079(vw,sh), 2043(s), 2022(m,sh), 2009(vw,sh) cm⁻¹ (all the negative peaks in Figure 5.4 and 2079 cm⁻¹ from the normal spectra), while the decomposition products are: 2120(m), 2078(m,sh), 2043(s), 2016(w,sh) cm⁻¹ (the positive peaks in Figure 5.4 and 2043 and 2016 cm⁻¹ from the normal spectra).

To assist in the characterization of 5.3 the complex 5.4 was prepared. Both ¹H NMR spectra of these complexes exhibit a single ¹H NMR resonance for the methyl groups (Table 5.5) with similar chemical shifts to that of Cp*(OC)₂IrW(CO)₅.⁴⁶

The complex 5.4 does not decompose in a CH₂Cl₂ solution and has IR ν(CO) bands (Table 5.5) that are similar to those proposed for 5.3 adding support to the assignment of this thermally unstable Ru compound.

The relative stabilities of the two acceptor fragments Ru(CO)₅(SiCl₃)₂ and Os(CO)₅(GeCl₃)(Cl) with the donor moiety Cp*(OC)₂Ir is another illustration of the greater

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⁴ Subsequent work at SFU indicates that the unknown product is the result of the reaction of 5.3 with CH₂Cl₂ and may be [Cp*Ir(CO)₂(CH₂Cl)][Ru(CO)₅(SiCl₃)₂(Cl)] by comparison to [Cp*Ir(CO)₂(CH₂Cl)][Re₄(CO)₆(μ-Cl)]₃.²²⁸
acceptor ability of the latter unit compared to that of Ru(CO)$_3$(SiCl)$_3$. This is consistent with the earlier $^{13}$C NMR studies described in Chapter 4 (Section 4.2.1.8) and with the greater stability of (OC)$_5$OsOs(CO)$_3$(GeCl)$_3$(Cl) compared to (OC)$_5$OsRu(CO)$_3$(SiCl)$_3$ (5.5).

![Figure 5.4](image.png)

**Figure 5.4** Difference IR spectra of Cp*(OC)$_2$IrRu(CO)$_3$(SiCl)$_3$ (5.3) starting at 233 K and decomposing to an unknown product(s) on warming to ambient temperature over a 35 min period.

If the donor moiety (Dnr) in *mer-*[(Dnr)Ru(CO)$_3$(SiCl)$_3$], and *mer-*[(Dnr)Os(CO)$_3$(GeCl)$_3$(Cl)] is treated as a symmetrical noncarbonyl ligand then one expects three IR active v(CO) bands for the two acceptor moieties. For the donor fragments (Dnr) the following number of IR active v(CO) bands are expected: *trans-*[(L)(OC)$_4$M(Acc), two bands, *cis-*[(OC)$_4$(L)Os(Acc), four bands; (OC)$_5$Os(Acc), three bands and Cp*(OC)$_2$Ir(Acc),
two bands \((\text{Acc} = \text{acceptor moiety})^{46,50,51}\). The IR spectra were recorded in \(\text{CH}_2\text{Cl}_2\) which has the disadvantage of interacting with the complexes and broadening the IR bands. Because of this bands may overlap and the number of IR \(\nu(\text{CO})\) bands (see Table 5.5) may be less than expected. In the IR spectra of the two isomers of 5.1 there are fewer IR \(\nu(\text{CO})\) bands observed for the \textit{trans} isomer (Table 5.5) in agreement with its higher symmetry. For \((\text{L})\text{(OC)}_4\text{OsM(CO)}_5\) \((\text{M} = \text{Cr, Mo, W}; \text{L} = \text{a phosphorus containing ligand},^{50}\text{CNBu}^{51})\) and \(\text{Cp}^*(\text{OC})_2\text{IrW(CO)}_5^{46}\) the IR CO stretching frequencies at greater than 2000 cm\(^{-1}\) are believed to mainly involve the donor fragment, and those at less than 2000 cm\(^{-1}\) are assigned to the acceptor fragment. This is consistent with the expected donor \((\delta^+)\) - acceptor \((\delta^-)\) polarity of the complexes. The intense IR \(\nu(\text{CO})\) band in the range \(1910-1930\) cm\(^{-1}\) is assigned to the \(\text{E}_1\) \(\nu(\text{CO})\) mode of the \(\text{M(CO)}_5\) acceptor fragment.\(^{51}\) In the binuclear molecules with \(\text{Ru(CO)}_3(\text{SiCl}_3)_2\) as the acceptor fragment, however, a clear distinction between the IR \(\nu(\text{CO})\) bands of the donor and acceptor fragments is not evident (see Table 5.5) and prohibits a greater analysis of the IR \(\nu(\text{CO})\) bands.\(^{174}\)

The \(^{31}\text{P}\{^1\text{H}\}\) NMR chemical shifts of the new compounds together with those for \(\text{Os(CO)}_4(\text{L})\) \((\text{L} = \text{PMe}_3, \text{P}_c)^{69}\) are shown in Table 5.6. As observed in the \(^1\text{H}\) NMR spectra (Tables 4.9 and 5.5), the \(^{31}\text{P}\{^1\text{H}\}\) NMR resonances for 5.1 and 4.14 are downfield (deshielded) relative to those of the uncoordinated \(\text{Os(CO)}_4(\text{P}_c)\) and \(\text{Os(CO)}_4(\text{PMe}_3)\). Interpretation of this chemical shift is difficult since (as discussed in Chapter 4) the \(^{31}\text{P}\{^1\text{H}\}\) NMR resonance for \(\text{Os(CO)}_4(\text{PMe}_3)\) is not different or suggestive of less electron density on coordination in the binuclear species \((\text{Me}_3\text{P})(\text{OC})_4\text{Os(Acc)}\) \((\text{Acc} = \text{an acceptor fragment})\) (Table 4.11). Furthermore, and as mentioned previously, the \(^{31}\text{P}\) NMR chemical shift can vary dramatically upon alteration of the geometry surrounding the \(^{31}\text{P}\) nucleus,\(^{152-155}\) and it
Table 5.6 The $^{31}$P{$^1$H} NMR of complexes with Ru(CO)$_3$(SiCl$_3$)$_2$ as the acceptor fragment.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{31}$P{$^1$H} NMR, $\delta^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$trans$-(Me$_3$P)(OC)$_4$OsRu(CO)$_3$(SiCl$_3$)$_2$</td>
<td>-49.85</td>
</tr>
<tr>
<td>$cis$-(P$_c$)(OC)$_4$OsRu(CO)$_3$(SiCl$_3$)$_2$</td>
<td>31.25</td>
</tr>
<tr>
<td>$trans$-(P$_c$)(OC)$_4$Ru(CO)$_3$(SiCl$_3$)$_2$</td>
<td>32.87</td>
</tr>
<tr>
<td>$trans$-(Me$_3$P)(OC)$_4$RuRu(CO)$_3$(SiCl$_3$)$_2$</td>
<td>-15.81</td>
</tr>
<tr>
<td>Os(CO)$_4$(P$_c$)</td>
<td>15.85</td>
</tr>
<tr>
<td>Os(CO)$_4$(PMe$_3$)</td>
<td>-52.00</td>
</tr>
</tbody>
</table>

$^a$ In CD$_2$Cl$_2$ at 233K in ppm.

is thought that the $^{31}$P NMR chemical shift of the phosphorus nucleus does not provide a sensitive probe to the acceptor ability of the acceptor fragments. A simple model correlating electron density at the $^{31}$P nucleus with chemical shift is not apparent in the present complexes, thereby, prohibiting further analysis of the data.

The $^{13}$C{$^1$H} NMR chemical shifts for the new complexes are reported in Table 5.7 together with the $^{13}$C NMR chemical shifts for M(CO)$_4$(PMe$_3$) (M = Ru, Os), Cp*Ir(CO)$_2$ and 5.45,69,227 All spectra were recorded under similar conditions to allow the comparison of the different donor fragments. As expected, the two acceptor fragments, Ru(CO)$_3$(SiCl$_3$)$_2$ and Os(CO)$_3$(GeCl$_3$)(Cl) show two $^{13}$C NMR resonances in the carbonyl region in a 1:2 ratio in the ranges 193-200 ppm (ruthenium fragments) and 172-181 ppm (osmium fragments) and are similar to analogous species,44,45 (Tables 4.7 and 4.10). This is consistent with the solid-state structures, which have the three CO ligands in a meridional
arrangement, and *cis* to the metal-metal bond (Figures 5.1 and 5.3). There was no evidence in the $^{13}$C{H} NMR spectra for any other isomer (e.g., with the CO ligands in a facial configuration). In all the molecular structures of binuclear complexes with Os(CO)$_3$(GeCl$_3$)(Cl) as the acceptor fragment it is the GeCl$_3$ ligand that is *trans* to the metal-metal bond (Figures 1.6 and 4.2). In the complexes (L)(OC)$_4$OsRe(CO)$_4$(X) (L = CNBu', PMe$_3$; X = Cl, Br, I) (4.9-4.11, 4.13, 4.16, 4.17) the $^{13}$C{H} NMR spectra (see Tables 4.7 and 4.10) shows that the halide ligand is *cis* to the metal-metal bond, in all cases. This is also consistent with the X-ray crystallographic determination of the structure of 4.13.$^{48}$ This might suggest that the preference of ligands to be *trans* to the metal-metal bond in the acceptor fragment Os(CO)$_3$(GeCl$_3$)(Cl) is GeCl$_3$ > CO > X. This is a transition from strong π-acceptor ligands (GeCl$_3$, CO) to a strong π-donor ligand (Cl).$^{140,167,218,229}$ It has previously been suggested, complexes of this type appear to be most stable when the ligand *trans* to the metal-metal bond is a π-acceptor ligand, this reduces repulsive interactions between the two sets of filled d-orbitals on the two transition metal centers (Figure 5.2). It would also be favorable to have a ligand that was a σ-acceptor on the acceptor half of the molecule *trans* to the M-M bond.$^{50,51}$ Both these σ/π requirements are met in GeCl$_3$ and SiCl$_3$ ligands.
Table 5.7 The $^{13}$C-$^1$H NMR spectra of complexes with Ru(CO)$_3$(SiCl)$_2$ as the acceptor fragment.

<table>
<thead>
<tr>
<th>Compound$^a$</th>
<th>$^{13}$C-$^1$H NMR$^b$</th>
<th>$\delta$(CH$_3$)$^c$</th>
<th>$\delta$(CO)$^d$</th>
<th>Donor fragment</th>
<th>Acceptor fragment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Me$_3$P)(OC)$_4$Ru(Acc)</td>
<td>20.85 (30.2)</td>
<td>198.95 (s, 4C)</td>
<td>197.09</td>
<td>199.03</td>
<td></td>
</tr>
<tr>
<td>(OC)$_4$(Bu'NC)Os(Acc)</td>
<td>29.36</td>
<td>160.29 (s, 1C), 174.08</td>
<td>196.73</td>
<td>198.97</td>
<td></td>
</tr>
<tr>
<td>(Me$_3$P)(OC)$_4$Os(Acc)</td>
<td>21.80 (38.9)</td>
<td>181.85 (d, 4C, 4.0)</td>
<td>196.44</td>
<td>198.27</td>
<td></td>
</tr>
<tr>
<td>trans-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(P$_c$)(OC)$_4$Os(Acc)$^e$</td>
<td>9.60 (s, CH$_3$), 77.46</td>
<td>177.44 (d, 4C, 8.3)</td>
<td>196.11</td>
<td>197.85</td>
<td></td>
</tr>
<tr>
<td>(P$_c$)(OC)$_4$Os(Acc)$^e$</td>
<td>br, C</td>
<td></td>
<td>(s, 1C) (s, 2C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-(P$_c$)(OC)$_4$Os(Acc)$^e$</td>
<td>77.63 (br, C)</td>
<td>161.75 (d, 1C, 12.0), 174.62 (d, 1C, 120.7), 178.11 (d, 2C, 17.1)</td>
<td>195.25</td>
<td>197.27</td>
<td></td>
</tr>
<tr>
<td>(OC)$_5$Os(Acc)$^f$</td>
<td></td>
<td>158.6(s,1C), 173.4(s,4C)</td>
<td>194.2</td>
<td>196.0</td>
<td></td>
</tr>
<tr>
<td>(Cp*)(OC)$_2$Ir(Acc)</td>
<td>10.02 (s, CH$_3$), 102.47 (s, C$_5$(CH$_3$)$_5$)</td>
<td>169.60 (s, vbr, 2C)</td>
<td>193.94</td>
<td>196.75</td>
<td></td>
</tr>
<tr>
<td>(Cp*)(OC)$_2$Ir(Acc2)</td>
<td>10.20 (s, CH$_3$), 102.49 (s, C$_5$(CH$_3$)$_5$)</td>
<td>167.43 (s, 2C)</td>
<td>172.98</td>
<td>180.47</td>
<td></td>
</tr>
<tr>
<td>Os(CO)$_4$(PMe$_3$)</td>
<td>21.19 (39.1)</td>
<td>189.50 (d, 4C, 4.0)</td>
<td>(s, 1C) (s, 2C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os(CO)$_4$(P$_c$)$^e$</td>
<td>15.45 (s, CH$_3$), 32.44 (d, CH$_2$, 37.2), 76.35 (d, C, 6.8)</td>
<td>186.67 (d, 4C, 13.0)</td>
<td>(s, vbr, (s, 2C) 1C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru(CO)$_4$(PMe$_3$)</td>
<td>21.35 (33.6)</td>
<td>204.84 (s, 4C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp*Ir(CO)$_2$</td>
<td>10.43 (s, CH$_3$), 97.36 (s, C$_5$(CH$_3$)$_5$)</td>
<td>177.93 (s, 2C)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Footnotes to Table 5.7

a (Acc) = Ru(CO)3(SiCl)2, (Acc2) = Os(CO)3(GeCl3)(Cl). b In CD2Cl2/CH2Cl2 (1/3) at 233 K. c The coupling constant, JPC in Hz is given in parentheses. d The carbonyl resonances are described as singlets (s) or doublets (d), the relative intensity is given and, where applicable, the two bond carbon-phosphorus coupling, 2JPC is the last number in the parentheses. e PC = P(OCH2)3CCH3. f From reference 45 recorded at 253K in an unspecified ratio of CD2Cl2/CH2Cl2.

It had been found previously that Os(CO)4(PMe3) and cis-Ru(CO)4(SiCl3)2 could be equally enriched with 13CO in all carbonyl sites equally.50a,167 On the other hand, the only labile CO in Os(CO)4(GeCl3)(Cl) is that which is trans to the GeCl3 group and this 13CO label is lost in the formation of the (Dnr)Os(CO)3(GeCl3)(Cl) complexes (also see Section 4.2.1.4). For these reasons 13C NMR spectra could be obtained on complexes 13CO-enriched in all carbonyl sites except for the (Dnr)Os(CO)3(GeCl3)(Cl) complexes. In the 13C NMR spectra of the cis-(OC)4(L)OsRu(CO)3(SiCl3)2 (L = CNBu', PC) (4.7, cis-5.1) complexes the three carbonyl resonances of the osmium donor fragments (in a relative ratio of 1:1:2) were observed in the chemical shift range −160-179 ppm, (Table 5.7). The assignments are analogous to those shown in Table 4.7, i.e., the resonance of intensity one that is furthest upfield is assigned to the carbonyl trans to the dative metal-metal bond. In the trans-(L)(OC)4MRu(CO)3(SiCl3)2 (M = Os, Ru; L = PMe3, PC) (4.14, 5.2, trans-5.1) complexes the donor moiety exhibits a single carbonyl resonance in the 13C NMR spectrum in the chemical shift range −177-199 ppm (Tables 5.7 and 4.10).

The spectrum of 5.3 was obtained at temperatures of 233 K and lower to reduce decomposition. A spectrum of 5.3 in CD2Cl2/CH2Cl2 at 233 K was initially collected and then the sample was allowed to warm to ambient temperature over a 2 h period. The sample was cooled to 233 K again and a second spectrum obtained. The 13C NMR carbonyl
resonances in the initial spectrum were virtually gone and replaced by two resonances at 188.00 and 191.84 ppm in an intensity ratio of 2:5, respectively. There was also a new resonance in the methyl region at 10.29 ppm. As mentioned previously, the decomposition products are only tentatively identified, at this point, but are not Cp*Ir(CO)₂ (Table 5.7), from this $^{13}$C NMR spectrum (in agreement with IR spectral data).

The $^{13}$C NMR spectrum of 5.4 (Table 5.7) is similar to that of 5.3, but with the resonances of the carbonyls on the Os atom shifted upfield relative to those on the Ru atom as is generally observed for metal carbonyl complexes.$^{143,146,177}$ The $^{13}$C NMR spectra of Cp*(OC)$_2$IrW(CO)$_5$ and Cp*Ir(CO)$_2$ also support the assignments of the signals in the spectrum of 5.3.

Interestingly, all the carbonyl sites in 5.4 were equally enriched (recall that in the synthesis of 5.4 only Cp*Ir(CO)$_2$ was $^{13}$CO enriched). This observation indicates carbonyl exchange has occurred in the product. It should be noted that in (L)(OC)$_4$OsM(CO)$_5$ (M = Cr, Mo, W; L = phosphine, phosphite, CNBu')$^{50,51}$ the carbonyls are rigid on the NMR timescale by $^{13}$C NMR spectroscopy in solution at room temperature, but the carbonyls in Cp*(OC)$_2$IrW(CO)$_5$ are fluxional. The carbonyls in (L)(OC)$_4$OsM(CO)$_5$ (M = Cr, Mo, W; L = phosphine, phosphite, CNBu') do, however, undergo slow exchange at room temperature but this is not fast enough to cause line broadening.$^{50,51}$ The group GeCl$_3$ is believed to be unable to act as a bridging ligand and there was no evidence of Cl migration to the iridium fragment. The GeCl$_3$/Cl ligands, however, do not have to migrate for CO exchange to occur: a simple bridge-terminal CO exchange might be expected to cause isomerization to the form with the GeCl$_3$ group cis to the Ir-Os bond but the concentration of this isomer was too low to detect. (This is discussed in more detail later in this section).
Utilizing the arguments on the $^{13}$C NMR carbonyl resonances for the same donor fragment, outlined previously in Chapter 4, it would appear that from the spectra of the complexes 5.3 and 5.4 that Os(CO)$_3$(GeCl$_3$)(Cl) has a greater acceptor ability than Ru(CO)$_3$(SiCl$_3$)$_2$ in this type of complex (Tables 4.7 and 5.7).

As before in the $^{13}$C{$_{\text{H}}$} NMR spectra there is an upfield shift in the carbonyl resonances of Os(CO)$_4$(CNBu'), M(CO)$_4$(PMe$_3$) (M = Ru, Os), Os(CO)$_4$(P$_2$), and Cp*Ir(CO)$_2$ upon the formation of the binuclear complexes, (see Tables 4.7, 4.10 and 5.7). If the difference in the geometry of the free mononuclear complexes and upon coordination, is considered a negligible influence, this is consistent with donation of electron density away from the donor fragment on formation of the binuclear complex (analogous to the shift of v(CO) bands in the IR spectra).

For reasons previously discussed, it was thought a correlation between the $^{13}$C NMR chemical shifts of the carbonyl ligands of the Ru(CO)$_3$(SiCl$_3$)$_2$ fragment and the donating ability of the donor fragment might exist i.e., the resonances might shift to lower field as the donating ability of the donor fragment increases. The $^{13}$C NMR chemical shifts of the two CO ligands trans to one another on the acceptor fragment range from 196.75 to 199.03 ppm, while the shifts of the CO ligands trans to the SiCl$_3$ group range from 193.94-197.09 ppm, (Table 5.7). The $^{13}$C NMR chemical shifts in Table 5.7 suggest the following order of decreasing donor ability (Me$_3$P)(OC)$_4$Ru > (OC)$_4$(Bu'NC)Os > (Me$_3$P)(OC)$_4$Os > trans-(P$_2$)(OC)$_4$Os > cis-(P$_2$)(OC)$_4$Os > Cp*(OC)$_2$Ir with (OC)$_3$Os similar to Cp*(OC)$_2$Ir in donor abilities (the chemical shifts of 5.5 are taken from the literature where the experimental conditions were not quite the same as used in this study).$^{45}$ That Cp*(OC)$_2$Ir is one of the weakest donors is in keeping with the fact that 5.3 decomposes rapidly in solution at room
temperature, and with prior work on this species as a donor ligand.\textsuperscript{46} Similarly, \textbf{5.5} dissociates readily in solution at room temperature which indicates that Os(CO)\textsubscript{5} is also a weak donor.\textsuperscript{45} The species \textbf{4.14}, \textbf{5.1} and \textbf{5.2} are much more stable in solution than \textbf{5.3} as observed by \textsuperscript{31}P\{\textsuperscript{1}H\}, \textsuperscript{1}H and \textsuperscript{13}C\{\textsuperscript{1}H\} NMR spectroscopic studies. Furthermore, \textit{cis}-\textbf{5.1} isomerizes to the \textit{trans} form indicating that the \textit{trans} species was preferred thermodynamically (Section 5.2.1.5). These observations are also consistent with the \textsuperscript{13}C NMR data that indicate that the \textit{trans}-(P\textsubscript{c})(OC)\textsubscript{4}Os species is a better donor than the \textit{cis} isomer.

In a preliminary study a CH\textsubscript{2}Cl\textsubscript{2} solution of \textbf{4.14} (1.17 x 10\textsuperscript{-3} M) or \textbf{5.2} (9.69 x 10\textsuperscript{-4} M) and excess PPh\textsubscript{3} (1.56 x 10\textsuperscript{-1} M) was stirred in the absence of light at 313 K. After 9 h \textbf{4.14} could not be detected in the IR spectrum while the corresponding ruthenium species, \textbf{5.2} was still observable after 12 h. Surprisingly, this suggests that the species with the ruthenium donor fragment was more stable than the complex with the osmium donor fragment. This agrees with the \textsuperscript{13}C NMR data (Table 5.7). It is, however, counter to the observation that the (Me\textsubscript{3}P)(OC)\textsubscript{4}RuM(CO)\textsubscript{5} (M = Cr, Mo, W) complexes formed only at low temperatures and decomposed at ambient temperature, whereas the osmium analogues were stable in solution at room temperature.\textsuperscript{50} It is possible that due to different orbital energies and different overlap, that the stability of the complexes of this type depend on both the donor and acceptor fragments. For example, Ru(CO)\textsubscript{4}(PMe\textsubscript{3}) may form a stable complex with Ru(CO)\textsubscript{5}(SiCl\textsubscript{3})\textsubscript{2} but an unstable complex with M(CO)\textsubscript{5} (M = Cr, Mo, W) but the reverse would be true for Os(CO)\textsubscript{4}(PMe\textsubscript{3}). Alternatively, that a binuclear species more readily dissociates might be due to kinetic instability resulting from stabilization of the transition state while the donor abilities of the donor fragments as derived from the
$^{13}$C NMR data is based solely upon the ground state stability (i.e., a thermodynamic property). Obviously more studies of this nature on complexes with dative metal-metal bonds are needed.

### 5.2.1.5 Investigation of fluxionality of the new Complexes.

The $^{13}$C NMR resonances of some of the carbonyl ligands in the spectrum of 5.3 at 233 K were relatively broad (Figure 5.5). This suggested that there might be a dynamic process present such as the interchange of CO ligands between the donor and acceptor fragments, or possibly some form of restricted rotation about bonds in the molecule. In Cp*(CO)$_2$IrW(CO)$_5$ all the CO ligands rapidly exchange at room temperature and the exchange is only slowed at 176 K where there are three distinct carbonyl environments in the $^{13}$C NMR spectrum. (In Cp*(OC)[(i-PrO)$_3$P]IrRh(CO)[P(O-i-Pr)$_3$] there was no evidence of ligand exchange even at 333 K). A variable temperature (233-193 K) $^{13}$C NMR study of 5.3 in CD$_2$Cl$_2$/CH$_2$Cl$_2$ was therefore carried out and the results are shown in Figure 5.5.

The spectra shown in Figure 5.5 are consistent with the view that the carbonyl ligands on the iridium fragment interchange with only the carbonyl trans to the SiCl$_3$ on the ruthenium fragment, while the two CO groups trans to one another on the ruthenium moiety do not participate in the fluxional process. As mentioned previously, for 5.4 all carbonyl sites become equally labeled when it was prepared from $^{13}$CO-labeled Cp*Ir(CO)$_2$ and $^{13}$CO-unenriched cis-Os(CO)$_4$(GeCl$_3$)(Cl). To account for the interchange of CO ligands in the two complexes Scheme 5.2 is proposed.
Figure 5.5 Variable-temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of Cp*(OC)$_2$IrRu(CO)$_3$(SiCl)$_2$ (5.3) in CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1/3) at 203, 213, 223, 233 K.

In Scheme 5.2 species a interconverts to species b by a rotation about the Ir-M bond and species a and b interconvert to species c and d, respectively, via a carbonyl bridged intermediate as proposed in other similar systems.\textsuperscript{46,50}
Scheme 5.2 A proposed mechanism for the $^{13}$CO scrambling in 
\[ \text{Cp}^*(\text{OC})_2\text{IrM}(\text{CO})_3(\text{ECl}_3)(\text{X}) \] \((M = \text{Ru, Os}; E = \text{Si, Ge}; X = \text{SiCl}_3, \text{Cl}) \) (5.3 and 5.4).

For 5.3 the conversion of a to c regenerates the same species, \((M = \text{Ru}; E = \text{Si}; X = \text{SiCl}_3\) and a and c are identical). The pathway b to d generates a species with a CO ligand trans to the Ir-Ru dative bond and the two SiCl$_3$ groups mutually cis to one another and evidently does not occur on the NMR timescale for 5.3.$^{120}$ It was suggested previously that the preference of ligands to be trans to the metal-metal bond in the acceptor fragment.
Os(CO)$_3$(GeCl$_3$)(Cl) is GeCl$_3$ > CO > Cl. Since the SiCl$_3$ ligand is similar to GeCl$_3$ the preference of ligands to occupy this site is believed to be GeCl$_3$ ~ SiCl$_3$ > CO > Cl.$^{140,167,218,229}$. This suggests, the species a and c are favored over d, which agrees with Ru(CO)$_3$(SiCl$_3$)$_2$(L) (L = a phosphorus containing ligand) where only the meridional isomer was observed.$^{199b,230}$. Since the signal due to the mutually $trans$ carbonyls on the Ru(CO)$_3$(SiCl$_3$)$_2$ of the Ir-Ru derivative remains sharp processes represented by pathway B (i.e., b→d) do not occur on the NMR timescale in the Ir-Ru complex.$^{120}$

For 5.4 (i.e., M= Os, E = Ge, X = Cl) there was no evidence of any fluxional process on the NMR timescale, but nevertheless all CO sites became enriched when the complex was prepared from $^{13}$CO-enriched Cp*Ir(CO)$_2$ and unenriched cis-Os(CO)$_4$(GeCl$_3$)(Cl). This of course, is indicative of a slow carbonyl exchange. In this case Route A (a→c) on Scheme 5.2, generates a species with Cl $trans$ to the Ir-Os bond and GeCl$_3$ cis to the metal-metal bond. It is thought that such a species (c) for the complex 5.4 would be disfavored. While in route B (b→d), a molecule with both GeCl$_3$ and Cl cis to the Ir-Os bond and a CO ligand is $trans$ to the metal-metal bond would be formed. In order for complete scrambling to occur the mechanism shown as route B (b→d) must be combined with that in A (a→c) or route B occurs in conjunction with some other mechanism such as a trigonal twist mechanism to result in the complete scrambling of the label. It is not necessary to detect the isomer with the CO $trans$ to the Ir-Os bond (d). It may be present in an undetectable concentration but still provide for complete CO exchange.

It should also be noted that the complex 5.4 was prepared at 323 K (and not ambient temperature as for 5.3). At this point it is not known if this difference in preparation is a contributing factor to the difference in the fluxionality of the two complexes.
The carbonyl region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $(\text{Me}_3\text{P})(\text{OC})_4\text{OsRu(}\text{CO})_3(\text{SiCl}_3)_2$ (4.14) in CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1/3) at 233 K prepared from (a) $^{13}\text{CO}$-enriched Os(\text{CO})$_4$(\text{PMe}_3) and $^{13}\text{CO}$-enriched $\text{cis-Ru(}\text{CO})_4(\text{SiCl}_3)_2$ and (b) $^{13}\text{CO}$-labeled Os(\text{CO})$_4$(\text{PMe}_3) and unenriched $\text{cis-Ru(}\text{CO})_4(\text{SiCl}_3)_2$.

A $^{13}\text{C}$ NMR spectrum of 4.14, with both halves $^{13}\text{CO}$-enriched, in CD$_2$Cl$_2$/CH$_2$Cl$_2$ at 233 K is shown in Figure 5.6a. A similar spectrum of 4.14 in which only the donor fragment, $(\text{Me}_3\text{P})(\text{OC})_4\text{Os}$ was $^{13}\text{CO}$-enriched is shown as Figure 5.6b. It is clear from the spectra that there is no evidence of the $^{13}\text{CO}$ ligands migrating from the osmium moiety to the ruthenium fragment in the compound. This is in contrast to 5.3 (partial exchange) and
in 2.1, 4.1-4.5 and Cp*(OC)2IrW(CO)5.46,50,51 This difference can be attributed to the reluctance of the PMe3 ligand to adopt a site cis to the Os-Ru bond in 4.14 which would be required for a bridging mechanism to occur. It is probable that with both the PMe3 group (cone angle 118°) and the SiCl3 ligand cis to the metal-metal bond there could be steric interactions between these bulky ligands that would destabilize this isomer.141 That the 13CO has remained on the osmium in the product indicates that the formation of 2.14 does not involve the initial formation of the cis isomer as observed in the Pc analogue (see below).

As in 4.7 (Section 4.2.1.8) it was thought that there might be restricted rotation about the metal-metal bond in 4.14 and (Me3P)(OC)4RuRu(CO)3(SiCl3)2. There was, however, no detectable broadening or splitting of the carbonyl carbon resonances in the 13C{1H} NMR spectra of 4.14 and (Me3P)(OC)4RuRu(CO)3(SiCl3)2 in CD2Cl2/CH2Cl2 down to 183 K. This indicates that there is at least rapid oscillation about the metal-metal bond so as to render the carbonyl ligands on the donor fragment, (Me3P)(OC)4M equivalent. A large excess of PPh3 was added to the NMR samples and they were allowed to stand in the dark at ambient temperature for 4 h. The samples were then cooled to 233K and the 13C{1H} NMR spectra recollected. In both cases no new carbonyl resonances were observed. This indicates that dissociation of the metal-metal bond had not occurred since M(CO)4(PMe3) or mer-Ru(CO)3(PPh3)(SiCl3)2 would have been expected to be formed.69 The UV-vis spectra of the new compounds together with those of (OC)2OsOs(CO)3(GeCl3)(Cl),44 and (OC)2OsRu(CO)3(SiCl3)245 are given in Table 5.8. As in the molecules described in Chapter 4 the lowest energy band is assigned to the σ → σ*
Table 5.8 The UV-vis absorption spectra of complexes with Ru(CO)$_3$(SiCl)$_3$ as the acceptor fragment.

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV-vis absorption, $^a$ nm ($\epsilon$, L mol$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Bu'NC)(OC)$_4$OsRu(CO)$_3$(SiCl)$_3$</td>
<td>324(9.1 x 10$^3$)</td>
</tr>
<tr>
<td>trans-</td>
<td>324(1.0 x 10$^4$)</td>
</tr>
<tr>
<td>(P$_2$)(OC)$_4$OsRu(CO)$_3$(SiCl)$_3$</td>
<td>330(2.2 x 10$^4$)</td>
</tr>
<tr>
<td>(Me$_2$P)(OC)$_4$OsRu(CO)$_3$(SiCl)$_3$</td>
<td>370(1.5 x 10$^3$), 290$^b$(3.1 x 10$^3$)</td>
</tr>
<tr>
<td>(OC)$_5$OsRu(CO)$_3$(SiCl)$_3$</td>
<td>336(2.6 x 10$^4$)</td>
</tr>
<tr>
<td>(Me$_2$P)(OC)$_4$RuRu(CO)$_3$(SiCl)$_3$</td>
<td>344(1.3 x 10$^4$), 302$^b$(1.5 x 10$^4$)</td>
</tr>
</tbody>
</table>

$^a$ In CH$_2$Cl$_2$ at room temperature. $^b$ Broad shoulder and the peak maximum was located utilizing ideas in the literature.\(^{186}\)

As found for 4.7 and 4.14 (Chapter 4) the molar absorptivities of the species with a single absorption band (5.1 and 5.2) are approximately a power of ten larger than the other species where two bands are exhibited (Tables 4.8, 4.12 and 5.8). This suggests that where a single absorption is observed it is the result of two bands that are overlapped. The two bands are the result of splitting of a single band and is tentatively attributed to spin-orbit coupling or mixing of other states.

Analogous to the ideas put forth in Chapter 4 (Sections 4.2.1.8 and 4.2.2.3) it was simplistically thought that keeping the acceptor moiety molecular orbitals the same and varying the donor fragment molecular orbitals the system might be receptive to being
probed. (The combined molecular orbitals that formed the metal-metal dative bond would reflect the relative donor ability of the donor fragments in the transitions in the UV-vis spectrum associated with the metal-metal bond.) As with the molecules discussed in Chapter 4 there was no correlation between the \( \lambda_{\text{max}} \) of the UV-vis absorption and the \(^{13}\text{C}\) NMR resonances in the complexes.

5.2.1.6 The Isomerization of \((\text{P}_c)(\text{OC})_4\text{OsRu(CO)}_3(\text{SiCl})_2\) (5.1).

The conversion of \(\text{cis-}(\text{P}_c)(\text{OC})_4\text{OsRu(CO)}_3(\text{SiCl})_2\) (\textit{cis-5.1}) to \(\text{trans-}(\text{P}_c)(\text{OC})_4\text{OsRu(CO)}_3(\text{SiCl})_2\) (\textit{trans-5.1}) was studied with NMR spectroscopy. The isomerization of \textit{cis-5.1} in \(\text{CD}_2\text{Cl}_2\) at 303 K, (with the exclusion of light) was followed over time by \(^{31}\text{P}\{^1\text{H}\}\) and \(^1\text{H}\) NMR spectroscopy. The \(^1\text{H}\) NMR spectra are shown in Figure 5.7; the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra gave similar results. Because of the lower sensitivity of \(^{31}\text{P}\{^1\text{H}\}\) NMR spectroscopy only the \textit{trans} isomer could be detected after 4 h. Assignments of the resonances were confirmed by comparison to the chemical shifts of pure samples of the appropriate isomers. At no time during the experiments were resonances due to free \(\text{Os(CO)}_4(\text{P}_c)\) detected which would have indicated dissociation of the metal-metal bond.

A \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum of \textit{cis-5.1} (both fragments \(^{13}\text{CO}\)-enriched) in \(\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2\) was collected at 233 K. The solution was then allowed to warm to ambient temperature in the dark and remain at this temperature for 12 h whereupon it was cooled to 233 K and the \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum was recollected. The \(^{13}\text{C}\{^1\text{H}\}\) NMR spectra showed initially only trace amounts of the \textit{trans} isomer. After 12 h only trace amounts of the \textit{cis} form remained, thereby, confirming the results obtained by \(^1\text{H}\) and \(^{31}\text{P}\{^1\text{H}\}\) NMR spectroscopy. There is essentially no change between the \(^1\text{H}\) NMR spectra collected after
6 h 15 min and after 14 h 45 min at 303 K in CD$_2$Cl$_2$. This indicates an equilibrium between the isomers has been established after 6 h 15 min.

Figure 5.7 The $^1$H NMR spectra cis-(P$_3$)(OC)$_4$OsRu(CO)$_3$(SiCl)$_2$ (cis-5.1) in CD$_2$Cl$_2$, at 303 K over the time period 31 min-14 h 45 min. The peaks marked with # are assigned to the cis form and the peaks marked with * are assigned to the trans isomer.
A solution of recrystallized trans-5.1 in CD$_2$Cl$_2$ was allowed to sit at ambient temperature in the dark for 20 h. The solution was then examined with $^{31}$P{$^1$H} and $^1$H NMR spectroscopy (at 303 K). The resulting spectra indicated that both the trans (major form) and the cis (minor form) isomers were present in ratios that were similar to those observed in the isomerization of the cis isomer. These findings establish that an equilibrium between the two isomeric forms does indeed exist in solution and that it heavily favors the trans form. Interestingly, the cis form is the kinetically preferred form whereas we believe that 4.14 is formed directly with the phosphine trans to the metal-metal bond.

The compound 4.14 was prepared under similar conditions to 5.1 to try to observe an initial cis product. A solution of 4.14, with the exclusion of light was followed by NMR spectroscopy. In all $^{31}$P{$^1$H} and $^1$H NMR spectra of the product in CD$_2$Cl$_2$ at 303 K over a 0-10 h period there was only evidence for the trans isomer.

Presumably, the PMe$_3$ ligand with its larger cone angle (PMe$_3$, 118°; Pc, 101°)$^{141}$ would have greater steric interactions with the SiCl$_3$ group cis to the metal-metal bond and this would reduce the stability of a cis isomer in 4.14. For (L)(OC)$_4$OsW(CO)$_5$ in solution (CH$_2$Cl$_2$ or CHCl$_3$) when L = Pc the cis:trans ratio was 1:1.5, whereas, when L = PMe$_3$ the ratio was 1:3.3 suggesting there is, indeed, a great preference for the cis isomer when L = Pc. This must be viewed with caution since the opposite trend is observed in the Cr analogues.$^{50b}$

Alternatively, it is possible that in the formation of 4.14 and 5.1 it is the trigonal bipyramidal reactant Os(CO)$_4$(L) (L = PMe$_3$, Pc) that influences whether the cis form of the binuclear species is formed. In Os(CO)$_4$(Pc) the isomer with Pc in an equatorial position is present in solution whereas no such isomer is observed in Os(CO)$_4$(PMe$_3$) (PMe$_3$ occupies
an axial site).\(^69\) It may be that the \textit{cis} isomer of \textbf{5.1} is formed via the \textit{eq}-\text{Os}(\text{CO})_4(P_e) which cannot take place in \text{Os}(\text{CO})_4(P\text{Me}_3).

### 5.3 Conclusion

A series of complexes with dative metal-metal bonds and with Ru(\text{CO})_3(\text{SiCl}_3)_2 as the acceptor fragment have been prepared. The complexes have been investigated by IR, \(^1\text{H}, \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \Quad...
The complex \((P_c)(OC)_4OsRu(CO)_3(SiCl)_2\) (5.1) is formed with the phosphite group \(cis\) to the metal-metal bond and then in solution it isomerizes to the more stable \(trans\) form as demonstrated by \(^{13}C\{^1H\}, ^1H\) and \(^{31}P\{^1H\}\) NMR spectroscopy.

### 5.4 Further work

It might have been informative to examine the \(^{29}Si\) NMR of the \((Dnr)Ru(CO)_3(SiCl)_2\) complexes, but the need for low temperature work, a relatively extended acquisition time and the need for larger amounts of the complexes for \(^{29}Si\) NMR spectral determination prevented such a study. Now that the syntheses have been defined it might be considered for future work.

It would interesting to study the effect of the phosphorus containing ligand \((L)(OC)_4OsRu(CO)_3(SiCl)_2\) (\(L =\) phosphine, phosphite). These could now be synthesized and this would lead to the elucidation of what properties of \(L\) determine whether the ligand \(L\) is \(cis\) or \(trans\) to the metal-metal bond and at what rate isomerization occurs.

Furthermore, it would be interesting to prepare \((P_c)(OC)_4OsRu(CO)_3(SiCl)_2\) (5.1) from specifically \(^{13}CO\)-labeled fragments such as; \((P_c)(OC)_4Os\) (all sites), \(Ru(CO)_3(SiCl)_2\) (all sites) or with \(^{13}CO\) in the site \(trans\) to the \(SiCl\) group in \(Ru(CO)_3(SiCl)_2\). This latter complex would not be difficult to make since \(cis-Ru(CO)_4(SiCl)_2\) undergoes stereospecific exchange in solution with \(^{13}CO\) at room temperature.\(^{167}\) Only those sites \(trans\) to the silyl ligands become labeled. Studies of the isomerization of \(cis\)-5.1 with stereospecifically \(^{13}CO\)-labeled sites would provide information on whether the isomerization precedes via a terminal-bridged intermediate or a trigonal-twist of the donor fragment.
To follow up the idea that Ru containing donor fragments apparently possess greater donor ability with the specific acceptor fragment Ru(CO)$_3$(SiCl)$_3$ it would be most informative to react Ru(CO)$_5$, Ru(CO)$_4$(CNBu'), Ru(CO)$_4$(P$_c$) with the aforementioned acceptor fragment and compare their properties with the Os analogues.

5.5 Experimental

5.5.1 General Methods

Manipulations, solvent purification and routine spectroscopic measurements were carried out as described in the Sections 2.4, 3.4 and 4.4, in their respective Chapters. Only previously unreferred to experimental details will be mentioned from this point in the text onwards.

5.5.2 Materials

The compounds P(OCH$_2$)$_3$CCH$_3$ (P$_c$)$_{233}$ Os(CO)$_4$(P$_c$)$_{69}$ CpIr(CO)$_2$$_{234}$ Cp*Ir(CO)$_2$$_{227}$ Ru(CO)$_4$PMe$_3$$_{69}$ Fe(CO)$_4$PMe$_3$$_{69}$ were prepared as described in the literature.

5.5.3 Syntheses

Preparation of Fe(CO)$_4$(CNBu'). Although Fe(CO)$_4$(CNBu') has previously been prepared from the catalyzed (CoCl$_2$.2H$_2$O) reaction of Fe(CO)$_5$ and CNBu', an alternate route to this complex was utilized. A 200 mL general-purpose bomb (Parr Instruments Co.) was charged with Fe(CO)$_5$ (1 mL, 7.6 x 10$^{-3}$ mol), CNBu' (0.85 mL, 7.5 x 10$^{-3}$ mol) and
C_{6}H_{14} (20 mL). The pressure vessel was flushed twice with CO gas and then pressurized with 3.8 \times 10^{6} \text{ Pa} (38 \text{ atm}) of CO gas at 293 K. The reaction vessel was then heated to 383 K for 16 h. After the reaction vessel was allowed to cool the entire contents of the bomb and C_{6}H_{14} washings were transferred to a Schlenk tube and the solvent removed on the vacuum line. The remaining yellow solid was then sublimed under dynamic vacuum (1.3 Pa) at 298-309 K to either a probe cooled with cold water or dry ice. Fine yellow crystals of Fe(CO)_{4}(CNBu') (1.8 g, 96\% yield) were obtained as the sublimate.

**Preparation of (Bu^tNC)(OC)_{4}OsRu(CO)(SiCl)_{3} (4.7).** The preparation and characterization of this compound has previously been described in Section 4.4.

**Possible isomerization of (Me_3P)(OC)_{4}OsRu(CO)(SiCl)_{3} (4.14).** (The preparation and characterization of this compound has previously been described in Section 4.4). In order to examine the possibility of isomers the complex was prepared from Os(CO)_{4}(PMe_3) (21 mg, 5.6 \times 10^{-2} \text{ mmol}), cis-Ru(CO)_{4}(SiCl)_{3} (24 mg, 5.0 \times 10^{-2} \text{ mmol}) in C_{6}H_{14} (15 mL). After the reaction the precipitate was without crystallization subjected to multiple washes with fresh C_{6}H_{14} aliquots to furnish a pale yellow powder of (Me_3P)(OC)_{4}OsRu(CO)(SiCl)_{3} (4.14) (34 mg, 82\% yield). The ^{13}CO-enriched 4.14 was prepared in a similar manner from ^{13}CO-labeled cis-Ru(CO)_{4}(SiCl)_{3} (all sites equally enriched)^{167} and ^{13}CO-labeled Os(CO)_{4}(PMe_3). A sample was also prepared from ^{13}CO-labeled Os(CO)_{4}(PMe_3) and unenriched cis-Ru(CO)_{4}(SiCl)_{3}.

**Preparation of (P_5)(OC)_{4}OsRu(CO)(SiCl)_{3} (5.1).** A reaction vessel was charged with cis-Ru(CO)_{4}(SiCl)_{3} (92 mg, 0.19 mmol), Os(CO)_{4}(P_5) (60 mg, 0.13 mmol), C_{6}H_{14} (25 mL) and the solution stirred at room temperature for 48 h. After such time a pale yellow precipitate and colorless supernatant resulted. Pale yellow crystals of 5.1 (84 mg, 50\%
yield) were obtained upon recrystallization from \(1,2-C_2H_2C_6H_{14}\). In order to examine the possibility of isomeric structures the complex was prepared from Os(CO)\(_4\)(P\(_{c}\)) (31 mg, 6.9 x 10\(^{-2}\) mmol), cis-Ru(CO)\(_4\)(SiCl\(_3\))\(_2\) (30 mg, 6.2 x 10\(^{-2}\) mmol) and \(C_6H_{14}\) (15 mL). The product (without recrystallization), was then subjected to multiple washes with fresh \(C_6H_{14}\) aliquots to furnish a pale yellow powder of 5.1 (40 mg, 74% yield). The \(^{13}\)CO-enriched 5.1 was prepared in a similar manner from \(^{13}\)CO-labeled cis-Ru(CO)\(_4\)(SiCl\(_3\))\(_2\) (all sites equally enriched)\(^{167}\) and \(^{13}\)CO-labeled Os(CO)\(_4\)(P\(_{c}\)). For cis-5.1: IR (CH\(_2\)Cl\(_2\)): \(v(CO)\) 2130(m), 2081(w,sh), 2070(vw,sh), 2054(vs), 2020(w,sh) cm\(^{-1}\); \(^1\)H NMR (CD\(_2\)Cl\(_2\), 233 K): \(\delta\) 0.87 (s, \(CH_3\)), 4.44 (d, \(CH_2\), \(\^3J_{H-P} = 5.0\) Hz); \(^1\)H NMR (CD\(_2\)Cl\(_2\), 303 K): \(\delta\) 0.89 (s, \(CH_3\)), 4.45 (d, \(CH_2\), \(\^3J_{H-P} = 4.9\) Hz); \(^{31}\)P\(^{\{1\}H}\) NMR (CD\(_2\)Cl\(_2\), 233 K): \(\delta\) 31.25 (s, \(P_c\)); \(^{31}\)P\(^{\{1\}H}\) NMR (CD\(_2\)Cl\(_2\), 303 K): \(\delta\) 29.56 (s, \(P_c\)); \(^{13}\)C\(^{\{1\}H}\) NMR (CD\(_2\)Cl\(_2\)/CH\(_2\)Cl\(_2\) 1/3, 233 K): \(\delta\) 77.63 (br, P(OCH\(_2\))\(_3\)CCH\(_3\)), 161.75 (d, 1C, CO, \(\^2J_{C-P} = 12.0\) Hz), 174.62 (d, 1C, CO, \(\^2J_{C-P} = 120.7\) Hz), 178.11 (d, 2C, CO, \(\^2J_{C-P} = 17.1\) Hz), 195.25 (s, 1C, CO), 197.27 (s, 2C, CO). For trans-5.1: IR (CH\(_2\)Cl\(_2\)): \(v(CO)\) 2124(vw), 2073(vw,sh), 2056(vs), 2016(w,sh) cm\(^{-1}\); \(^1\)H NMR (CD\(_2\)Cl\(_2\), 233 K): \(\delta\) 0.93 (s, \(CH_3\)), 4.50 (d, \(CH_2\), \(\^3J_{P-H} = 5.1\) Hz); \(^1\)H NMR (CD\(_2\)Cl\(_2\), 303 K): \(\delta\) 0.95 (s, \(CH_3\)), 4.52 (d, \(CH_2\), \(\^3J_{P-H} = 4.9\) Hz); \(^{31}\)P\(^{\{1\}H}\) NMR (CD\(_2\)Cl\(_2\), 233 K): \(\delta\) 32.87 (s, \(P_c\)); \(^{31}\)P\(^{\{1\}H}\) NMR (CD\(_2\)Cl\(_2\), 303 K): \(\delta\) 32.57 (s, \(P_c\)); \(^{13}\)C\(^{\{1\}H}\) NMR (CD\(_2\)Cl\(_2\)/CH\(_2\)Cl\(_2\) 1/3, 233 K): \(\delta\) 9.60 (s, P(OCH\(_2\))\(_3\)CCH\(_3\)), 77.46 (br, P(OCH\(_2\))\(_3\)CCH\(_3\)), 177.44 (d, 4C, CO, \(\^2J_{P-C} = 8.3\) Hz), 196.11 (s, 1C, CO), 197.85 (s, 2C, CO); MS (El, m/z): 792/794 (M\(^+\)-4CO); (CI, m/z): 869 (M\(^+\)-Cl), 813 (M\(^+\)-2CO-Cl); Anal. Calcd. for C\(_{12}\)H\(_9\)Cl\(_6\)O\(_{10}\)OsPRuSi\(_2\): C, 16.50; H, 1.04. Found: C, 16.70; H, 1.15.

Preparation of (Me\(_3\)P)(OC)\(_4\)RuRu(CO)\(_3\)(SiCl\(_3\))\(_2\) (5.2). The preparation of (Me\(_3\)P)(OC)\(_4\)RuRu(CO)\(_3\)(SiCl\(_3\))\(_2\) (5.2) was similar to that used for
(Bu'NC)(OC)₄OsRu(CO)₃(SiCl)₂ (4.7) and (Me₃P)(OC)₄OsRu(CO)₃(SiCl)₂ (4.14) and as described previously in the text (see Section 4.4 for details). A reaction vessel was charged with cis-Ru(CO)₄(SiCl)₂ (25 mg, 5.2 x 10⁻² mmol), Ru(CO)₄(PMe₃) (17 mg, 5.9 x 10⁻² mmol), C₆H₁₄ (25 mL) and the solution stirred for 21 h. After such time a yellow precipitate and colorless supernatant resulted. Pale yellow crystals of 5.2 (26 mg, 67% yield) were obtained upon recrystallization from 1,2-C₂H₄Cl₂/C₆H₁₄. The ¹³C⁰-enriched 5.2 was prepared in a similar manner, as mentioned above, from ¹³C⁰-labeled cis-Ru(CO)₄(SiCl)₂ (all sites equally enriched)¹⁶⁷ and ¹³C⁰-labeled Ru(CO)₄(PMe₃). For 5.2: IR (CH₂Cl₂): ν(CO) 2122(w), 2068(w,sh), 2044(vs), 2013(w,sh) cm⁻¹; ¹H NMR (CD₂Cl₂, 233 K): δ 1.95 (d, CH₃, ²J_H-P = 10.5 Hz); ³¹P{¹H} NMR (CD₂Cl₂, 233 K): δ -15.81 (s, PMe₃); ¹³C{¹H} NMR (CD₂Cl₂/CH₂Cl₂ 1/3, 233 K): δ 20.85 (d, CH₃, ²J_C-P = 30.2 Hz), 197.09 (s, 1C, CO), 198.95 (s, 4C, CO), 199.03 (s, sh, 2C, CO); (CD₂Cl₂/CH₂Cl₂ 1/3, 183 K): δ 20.35 (d, CH₃, ²J_C-P = 30.2 Hz), 196.80 (s, 1C, CO), 198.27 (d, 4C, CO, ²J_C-P = 7.0 Hz), 198.55 (s, br, 2C, CO); MS (Cl, m/z): 597 (M⁺-4CO-Cl); Anal. Calcd. for C₁₀H₉Cl₆O₇PR₂Si₂: C, 16.16; H, 1.22. Found: C, 16.38; H, 1.18.

**Preparation of Cp*(OC)₂IrRu(CO)₃(SiCl)₂ (5.3).** A round-bottom flask capped with a Teflon valve was charged with cis-Ru(CO)₄(SiCl)₂ (50 mg, 0.10 mmol), Cp*Ir(CO)₂ (44 mg, 0.12 mmol), and C₆H₁₄ (15 mL). The reaction did not go to completion; both starting materials were present by IR spectroscopy after a reaction time of 48 h. After such time a yellow precipitate and yellow supernatant resulted; the solid was subjected to multiple washes with fresh C₆H₁₄ aliquots to furnish a yellow powder of 5.3 (46 mg, 53% yield). To measure spectroscopic features of this thermally unstable compound in solution additonal precautions were taken. For the ¹³C NMR of the complex,
solutions were prepared at 203 K, with the exclusion of light, and inserted into a $^{13}$C NMR probe at 233 K. The $^{13}$CO-enriched 5.3 was prepared in a similar manner from $^{13}$CO-labeled cis-Ru(CO)$_4$(SiCl)$_3$ (all sites equally enriched)$^{167}$ and $^{13}$CO-labeled Cp*Ir(CO)$_2$. For 5.3: IR (CH$_2$Cl$_2$): v(CO) 2095(w), 2079(vw,sh), 2043(s), 2022(m,sh) 2009(vw,sh) cm$^{-1}$; $^1$H NMR (CD$_2$Cl$_2$, 233 K): $\delta$ 2.24 (s, CH$_3$); $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 233 K): $\delta$ 10.02 (s, CH$_3$), 102.47 [s, C$_5$(CH$_3$)$_5$], 169.60 (s, vbr, 2C, CO), 193.94 (s, vbr, 1C, CO), 196.75 (s, 2C, CO); (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 183 K): $\delta$ 169.16 (s, 2C, CO), 193.57 (s, 1C, CO), 196.45 (s, 2C, CO); MS (EI, m/z): 454 [M$^+$-Cp*Ir(CO)$_2$]; (CI, m/z): 455 [M$^+$-Cp*Ir(CO)$_2$+1], 385 [M$^+$-Ru(CO)$_3$(SiCl)$_3$+1]; Anal. Calcd. for C$_{15}$H$_{15}$Cl$_6$Ir$_2$Ru$_2$Si$_2$: C, 21.51; H, 1.81. Found: C, 21.69; H, 1.83.

**Preparation of Cp*(OC)$_2$IrOs(CO)$_3$(GeCl$_3$)(Cl) (5.4).** A reaction vessel was charged with Os(CO)$_4$(GeCl$_3$)(Cl) (62 mg, 0.12 mmol), Cp*Ir(CO)$_2$ (50 mg, 0.13 mmol), and C$_6$H$_{14}$ (20 mL). The contents of the reaction vessel were degassed and heated under a static vacuum for 21h at 323 K. After such time a yellow precipitate and yellow supernatant resulted; the supernatant was removed and the precipitate washed several times with fresh C$_6$H$_{14}$ aliquots to remove excess starting materials. Yellow crystals of 5.4 (57 mg, 54% yield) were obtained upon recrystallization from 1,2-C$_2$H$_4$Cl$_2$/C$_6$H$_{14}$. The $^{13}$CO-enriched 5.4 was prepared in a similar manner, from unenriched Os(CO)$_4$(GeCl$_3$)(Cl) and $^{13}$CO-labeled Cp*Ir(CO)$_2$. For 5.4: IR (CH$_2$Cl$_2$): v(CO) 2113(w), 2061(m,sh), 2041(vs), 2020(vw,sh), 1993(m) cm$^{-1}$; $^1$H NMR (CD$_2$Cl$_2$, 233 K): $\delta$ 2.29 (s, CH$_3$); $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ 1/3, 233 K): $\delta$ 10.20 (s, CH$_3$), 102.49 [s, C$_5$(CH$_3$)$_5$], 167.43 (s, 2C, CO), 172.98 (s, 1C, CO), 180.47 (s, 2C, CO); MS (EI, m/z): 384 [M$^+$-Os(CO)$_3$(GeCl$_3$)(Cl)];
Preparation of (OC)$_5$OsRu(CO)$_3$(SiCl)$_2$ (5.5). A brief description of the preparation and characterization of (OC)$_5$OsRu(CO)$_3$(SiCl)$_2$ (5.5) has previously appeared in the literature. The complex was prepared in an analogous manner to the complex (Me$_3$P)(OC)$_4$OsRu(CO)$_3$(SiCl)$_3$(Br) (4.15) in Section 4.4. The reaction does not go to completion, both starting materials were present after a typical reaction time of 48 h. The pale yellow powder of 5.5 was obtained in a 30% yield. For 5.5: IR (CH$_2$Cl$_2$): v(CO) 2159(m), 2119(vw), 2091(s), 2074(vs), 2028(s) cm$^{-1}$; MS (EI, m/z): 786 (M$^+$), 730 (M$^+$-2CO); (CI, m/z): 455 (M$^+$-Os(CO)$_3$+1), 333 (M$^+$-Ru(CO)$_3$(SiCl)$_3$_2+1); Anal. Calcd. for C$_8$Cl$_6$O$_8$OsRuSi$_2$: C, 12.25. Found: C, 12.01.

Molecular structure of (Me$_3$P)(OC)$_4$OsRu(CO)$_3$(SiCl)$_2$ (4.14). Crystals of (Me$_3$P)(OC)$_4$OsRu(CO)$_3$(SiCl)$_2$ (4.14) of a suitable size for X-ray crystallography proved difficult to grow. The problem was overcome by dissolving 4.14 in a minimum amount of 1,2-C$_2$H$_4$Cl$_2$ in an NMR tube which was placed in a Schlenk tube containing C$_6$H$_{14}$ whereupon the Schlenk tube was sealed and the pressure in the vessel reduced. The solvent system was allowed to equilibrate at room temperature, in the absence of light, for a few days and then placed in the freezer (~233 K); this procedure afforded crystal suitable for the X-ray study. The crystal structure analysis of 4.14 was carried out by Professor F. W. B. Einstein and Dr. W. K. Leong at Simon Fraser University. The crystal structure was determined to be monoclinic, with a space group of $P2_1$ and a unit cell containing two crystallographically distinct molecules.
Molecular structure of (Me₃P)(OC)₄RuRu(CO)₃(SiCl₃)₂ (5.2). The X-ray quality crystals of (Me₃P)(OC)₄RuRu(CO)₃(SiCl₃)₂ (5.2) were obtained serendipitously by dissolving a sample in a minimum amount of CD₂Cl₂ in an NMR tube placed in cold bath at 233K and then in an NMR spectrometer at 233K. The crystal structure analysis of 5.2 was carried out by Professor F. W. B. Einstein and Dr. W. K. Leong at Simon Fraser University. The crystal structure was determined to be monoclinic, with a space group of \( P2_1 \) and a unit cell containing two crystallographically distinct molecules.
APPENDICES

The results generated from the computer simulation of the mass spectra of the $^{13}$CO-enriched complexes are discussed in Chapters 3 and 4. A description of the computer program used to simulate the mass spectra, and an example of a simulated and observed mass spectrum are given in Appendix A-1.

The discussion of the $^{13}$C NMR chemical shifts of carbonyl carbons on the donor fragment $(OC)_4(Bu'NC)Os$ in binuclear complexes containing a donor-acceptor metal-metal bond in Chapter 4 invoked a discussion of electronegativities of groups and atoms. A description of how the electronegativities of species were calculated and an ordering of the binuclear complexes is given in Appendix A-2.

Attempted preparations of binuclear complexes from various donor fragments and the acceptor fragment Os(CO)$_3$(GeCl$_3$)(Cl) are given in Appendix 3.
The mass spectra (MS) were simulated using an ‘in house’ computer program written by Dr. W. K. Leong. The mass spectrometer was calibrated prior to running the spectra of the complexes and both the enriched and the unenriched samples were run to check the assignments. The MS of $^{13}$C-labeled species are simulated using a modified version of the program which prompts for the identity and numbers of each element, using the ‘dummy’ elements C* and O* for $^{13}$C and $^{18}$O, respectively. The amount of $^{18}$O enrichment is assumed to be 10% of the input percentage of $^{13}$C-enrichment, as specified by the manufacturers and the $^{13}$C-labeling is assumed to be equally distributed over all sites.

The program has two modes; one mode to simulate the MS of the labeled species and prompts for the identity and number of the elements present and the percentage of $^{13}$C-enrichment. The second mode can be used as a simplistic tool to obtain the range of $^{13}$C-enrichments of the molecule that best fit what is observed in the MS. The subroutine for the second mode calculates the best-fit for a range of assumed percent $^{13}$C-enrichments. This subroutine besides prompting for the identity and number of the elements asks for the peak of largest abundance in the envelope of peaks observed and to give the four peaks above and below the most abundant peak a ranking number according to their respective relative abundances. The ranking numbers are entered and the subroutine uses the simple expression, eq A-1.1, to quickly approach a range of minima.

$$\sum \left( \frac{\text{observed rank} - \text{simulated rank}}{\text{observed rank}} \right)^2$$

(A-1.1)

The ranges of $^{13}$C-enrichment quoted in this text are then 2.5 x minimized difference in ranking order to give greater confidence in the values. It should be pointed out that this
is by no means a rigorous mathematical determination of the percent of $^{13}$C-enrichment of the complex, it is however, a useful tool to quickly obtain a range of values for the percent of $^{13}$C-enrichment to a level of precision that is greater than was previously possible. An example of the simulation produced from this simple computer program is given in Figure A-1.1, and Table A-1.1 for $^{13}$C-enriched Os$_3$(CO)$_{12}$ (which was calculated to be 46-49% $^{13}$C-enriched, minimization function = 0.076, the most abundant peak of the parent ion M$^+$ for the unlabeled species was 908 m/z, and 914 m/z for the $^{13}$C-enriched species.)

![Figure A-1.1](image)

**Figure A-1.1** The parent envelope of peaks in the mass spectrum (EI) of $^{13}$C-enriched Os$_3$(CO)$_{12}$, (a) the observed envelope of peaks, (b) the envelope of peaks simulated for 48% $^{13}$C-enrichment.
Table A-1.1  The nine most abundant peaks in the mass spectrum of $^{13}\text{C}$-enriched Os$_3$(CO)$_{12}$, directly comparing the observed mass spectrum with the spectrum simulated for 48% $^{13}\text{C}$-enrichment.

<table>
<thead>
<tr>
<th>m/z</th>
<th>rel abund, %$^a$</th>
<th>ranking</th>
<th>rel abund, %$^a$</th>
<th>ranking</th>
</tr>
</thead>
<tbody>
<tr>
<td>910</td>
<td>56.8</td>
<td>9</td>
<td>59.4</td>
<td>8</td>
</tr>
<tr>
<td>911</td>
<td>72.6</td>
<td>7</td>
<td>75.3</td>
<td>6</td>
</tr>
<tr>
<td>912</td>
<td>84.2</td>
<td>4</td>
<td>88.9</td>
<td>4</td>
</tr>
<tr>
<td>913</td>
<td>97.3</td>
<td>2</td>
<td>97.7</td>
<td>2</td>
</tr>
<tr>
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<td>100.0</td>
<td>1</td>
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<td>1</td>
</tr>
<tr>
<td>915</td>
<td>94.6</td>
<td>3</td>
<td>95.2</td>
<td>3</td>
</tr>
<tr>
<td>916</td>
<td>83.4</td>
<td>5</td>
<td>84.2</td>
<td>5</td>
</tr>
<tr>
<td>917</td>
<td>77.6</td>
<td>6</td>
<td>69.1</td>
<td>7</td>
</tr>
<tr>
<td>918</td>
<td>59.5</td>
<td>8</td>
<td>52.4</td>
<td>9</td>
</tr>
</tbody>
</table>

$^a$ relative abundance, normalized to 100% if not already in that format.
The calculations of group electronegativities and the use of Mulliken-Jaffe parameters has been previously reported in the literature but they are included to clarify the discussion in the thesis.\textsuperscript{181}

The equations used to calculate the Mulliken-Jaffe group electronegativities \((a_G)\) and the Mulliken-Jaffe \((b_G)\) parameters are:

\[
a_G = \frac{\sum (va/b)}{\sum (v/b)} \quad \text{A-2.1}
\]

\[
b_G = \frac{1}{\sum (v/b)} \quad \text{A-2.2}
\]

where: \(v\) represents the number of atoms of a particular element in the group

\(a\) or \(\chi_{MJ}\) represents the inherent Mulliken-Jaffe electronegativity

\(b\) the Mulliken-Jaffe \(b\) parameter or the charge coefficient

An example of the method is the calculation of the Mulliken-Jaffe group terms \(a_G\) and \(b_G\) for the ligand SiF\(_3\):

For F the assumed valent state is the "typical" singly bonded valence state for periodic group 17, 14.3\% s (valence 1) and hence \(a = 15.30, b = 17.81\).\textsuperscript{181}

For Si the assumed valent state is tetrahedral, sp\(^3\), 25\% s (valence 4) and hence \(a = 7.30, b = 7.13\).\textsuperscript{181}

\[
a_G = \frac{\sum \left( \frac{1 \times 7.30}{7.13} + \frac{3 \times 15.30}{17.81} \right)}{\sum \left( \frac{1}{7.13} + \frac{3}{17.81} \right)} = 11.67
\]
The Mulliken-Jaffe atomic electronegativities \( (a \text{ or } \chi_{MJ}) \) or group electronegativities \( (a_G) \) were converted to the Pauling electronegativity \( (\chi_p) \) by using the equation:

\[
b_G = \left( \frac{1}{7.13} + \frac{3}{17.81} \right) = 3.24
\]

The conversion was carried out in order to allow a greater comparison with the Pauling electronegativity scale.

The values used for the comparisons of the acceptor fragments were used as in the literature\(^{181}\) or calculated using the above equations are shown in Table A-2.1.

The electronegativity of the acceptor fragment was considered in the order, looking at the electronegativity of the ligand trans to the metal-metal bond first, which is possibly the dominant interaction, the electronegativity of the other ligands, within a series and finally the electronegativity of the central metal atom, within a series. Hence the first three acceptor fragments were ordered, \( \text{Os(CO)}_3 \text{(GeCl}_3 \text{)(Cl)} \), \( \text{Ru(CO)}_3 \text{(SiCl}_3 \text{)(Br)} \), \( \text{Ru(CO)}_3 \text{(SiCl}_3 \text{)}_2 \). But it should be considered that the Mulliken-Jaffe \( b_G \) parameter or the charge coefficient for groups are generally much lower than the Mulliken-Jaffe atomic \( b \) parameters.\(^{181a,b}\) This taken in conjunction with the idea that the Mulliken-Jaffe \( b \) parameter or the charge coefficient is an inverse measure of charge capacity or polarizability (the ability to donate or withdraw charge as a function of electronegativity change) hence it is shown that groups are better charge donors or acceptors than singular atoms \( (\text{Br, } l/b = 0.096; \text{SiCl}_3, l/b = 0.40).^{181a,b} \) Hence allowing the better charge accepting
Table A-2.1 The electronegativities ($\chi_{MJ}$ and $\chi_{P}$) and Mulliken-Jaffe $b$ parameter used for the comparison of the acceptor fragments in the series of binuclear complexes with $(OC)_4(Bu'NC)Os$ as the donor fragment.

<table>
<thead>
<tr>
<th>Group or atom</th>
<th>$\chi_{MJ}$ or $a$</th>
<th>$b$ or $\chi_{P}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>or $a_G$</td>
<td>$b_G$</td>
</tr>
<tr>
<td>GeCl$_3$</td>
<td>9.80</td>
<td>2.56</td>
</tr>
<tr>
<td>Cl</td>
<td>10.95</td>
<td>11.55</td>
</tr>
<tr>
<td>SiCl$_3$</td>
<td>9.67</td>
<td>2.50</td>
</tr>
<tr>
<td>Br</td>
<td>10.25</td>
<td>10.41</td>
</tr>
<tr>
<td>I</td>
<td>9.29</td>
<td>9.33</td>
</tr>
<tr>
<td>Os</td>
<td></td>
<td>2.2$^a$</td>
</tr>
<tr>
<td>Ru</td>
<td></td>
<td>2.2$^a$</td>
</tr>
<tr>
<td>Re</td>
<td></td>
<td>1.9$^a$</td>
</tr>
<tr>
<td>W</td>
<td></td>
<td>2.36$^a$</td>
</tr>
<tr>
<td>Mo</td>
<td></td>
<td>2.16$^a$</td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td>1.66$^a$</td>
</tr>
</tbody>
</table>

$^a$ These Pauling electronegativities were obtained from reference 181c, the oxidation state in the literature is not always the same as in the binuclear complex containing a donor-acceptor metal-metal bond but for comparisons the oxidation state was kept constant to illustrate any trends involved.

It is notable that the ability to compensate for the slightly lower electronegativity of SiCl$_3$ compared to Br the first three acceptor fragments were ordered, Os(CO)$_3$(GeCl$_3$)(Cl), Ru(CO)$_3$(SiCl$_3$)$_2$, Ru(CO)$_3$(SiCl$_3$)(Br). This comparison of the GeCl$_3$ group with the SiCl$_3$ ligand is in keeping with the IR data found for Mn(CO)$_5$(GeCl$_3$) as compared to Mn(CO)$_5$(SiCl$_3$) and
the complexes cis-Ru(CO)₄(ECl₃)₂ (E = Si, Ge).¹⁴⁰,¹⁶⁷,²¹⁸,²²⁹ The next series of acceptor fragments, which were without a strongly electron withdrawing group trans to the metal-metal bond, Re(CO)₄Cl, Re(CO)₄Br, Re(CO)₄I, are in the order expected from the differing halide atom. The final three compounds were ordered according to the Pauling electronegativity value (χₑ) in reference ₁₈₁c, with the metal atoms in an oxidation state of +2 which is not identical to the oxidation state of the same metals in the binuclear complexes, but the trend is quite clear. Hence the ordering of decreasing approximate electronegativity was suggested to be: Os(CO)₃(GeCl₃)(Cl), Ru(CO)₃(SiCl₃)₂, Ru(CO)₃(SiCl₃)(Br), Re(CO)₄Cl, Re(CO)₄Br, Re(CO)₄I, W(CO)₅, Mo(CO)₅, Cr(CO)₅.
A-3: Appendix for Chapter 4

Since the acceptor fragment Os(CO)₃(GeCl₃)(Cl) was proposed (Chapter 4) to be the best acceptor moiety, attempts were made to prepare binuclear complexes with this acceptor unit. Two such complexes, (OC)₄(Bu'NC)OsOs(CO)₃(GeCl₃)(Cl) (4.6) and Cp*(OC)₂IrOs(CO)₃(GeCl₃)(Cl) (5.4), were prepared. Other attempts to prepare complexes of this type are described here. They are mostly preliminary results from exploratory reactions.

**Reaction of Os(CO)₄(PMe₃) with Os(CO)₄(GeCl₃)(Cl).** A round-bottom flask capped with a Teflon valve was charged with Os(CO)₄(PMe₃) (44 mg, 0.12 mmol), Os(CO)₄(GeCl₃)(Cl) (50 mg, 9.7 x 10⁻² mmol) and C₆H₁₄ (20 mL). The contents of the flask were subjected to three cycles of freeze-pump-thaw and heated at 323 K in the absence of light under vacuum for 18 h. This afforded a colorless solution and a yellow precipitate. The reaction vessel and its contents were cooled to room temperature and the supernatant removed by pipet and the yellow solid was washed with C₆H₁₄ until an IR spectrum of the wash liquid no longer showed absorption bands due to the starting material. The pale yellow powder was not recrystallized in order to prevent dissociation or isomerization of the bimetallic species. The ¹³CO-enriched product was prepared in a similar manner from ¹³CO-labeled Os(CO)₄(PMe₃) and unenriched Os(CO)₄(GeCl₃)(Cl). The product was subsequently identified as (Cl)(Me₃P)(OC)₃OsOs(CO)₄(Cl) as described below.

The ν(CO) region of the IR spectrum of (Cl)(Me₃P)(OC)₃OsOs(CO)₄(Cl) was similar to that of (Me₃P)(OC)₄OsRu(CO)₃(SiCl₃)(Br) (4.15) (Table 4.9). Likewise the ¹H NMR resonance for (Cl)(Me₃P)(OC)₃OsOs(CO)₄(Cl) was similar to those for the
complexes 4.15 and (Me₃P)(OC)₄OsRe(CO)₄(X) (X = Br, Cl, I) (4.13, 4.16, 4.17) (Table 4.9). It was the $^{31}$P{$^1$H} NMR resonance of (Cl)(Me₃P)(OC)₃OsOs(CO)₄(Cl) that first suggested that the complex has an (Cl)(Me₃P)(OC)₃Os fragment and is not the expected product (Me₃P)(OC)₄OsOs(CO)₃(GeCl₃)(Cl). The chemical shift of the phosphorus resonance (-36.31 ppm) is similar to that observed for (Cl)(Me₃P)(OC)₃OsRe(CO)₅ (4.19) (-37.62 ppm) and is markedly different from shifts for (Me₃P)(OC)₄Os(Acc) (Acc = an acceptor fragment) (i.e., -49.85 - -52.74 ppm, see Table 4.11).

Figure A-3.1 The idealized structure of (Cl)(Me₃P)(OC)₃Os(CO)₄(Cl) (M = Ru, Os) with labeling scheme for the carbonyl ligands.

The carbonyl region of the $^{13}$C{$^1$H} NMR spectrum of (Cl)(Me₃P)(OC)₃OsOs(CO)₄(Cl) also supports the configuration of the complex proposed in Figure A-3.1. The two resonances for the (Cl)(Me₃P)(OC)₃Os fragment of the molecule are assigned as the two resonances with phosphorus-carbon couplings ($^2J_{P,C}$) one with relative intensity 1 at 173.89 ppm and the other with relative intensity 2 at 185.08 ppm to the C₉O and C₆O ligands respectively, see Figure A-3.1. This assignment is consistent with the $^{13}$C NMR spectrum of the carbonyl ligands in a similar environment found in 4.19 (Table 4.10).
The Os(CO)$_4$(Cl) fragment was not initially $^{13}$CO-labeled and would only become $^{13}$CO-enriched upon a terminal-bridge carbonyl exchange mechanism with the other half of the molecule. It might, therefore, be expected that the intensities of the other carbonyl ligands may not be in the ratio 1:2:1, if there is preferential labeling of specific sites as observed in Cp*(OC)$_2$IrRu(CO)$_3$(SiCl)$_3$$_2$ (5.3) (Scheme 5.2). The actual intensities of the three carbonyl resonances for the Os(CO)$_4$(Cl) fragment were 4:2:1. The tentative assignment of the peaks are, the singlet at 178.41 ppm with an intensity of 4 is assigned to C$_6$O (see Figure A-3.1). This requires that there is preferential $^{13}$CO-labeling of this site. Although this designation is counter to the assignment for 4.16 (Chapter 4), it is in agreement with that for complexes such as mer-cis- (mer-cis-2.2) (Chapter 3), fac-Os(CO)$_3$(PMe$_3$)(Cl)$_2$ (fac-2.2) (Chapter 3), ax, eq-, eq, eq-Os$_3$(CO)$_{12}$(Cl)$_2$,$_{236}$ Os$_3$(CO)$_{10}$(PR$_3$)$_2$ (PR$_3$ = PH$_2$Me, P(OMe)$_3$)$_{122}$ where the resonance of the carbonyl trans to the halide ligand is upfield from those of other carbonyl ligands. The doublet with a phosphorus-carbon coupling ($^3J_{P,C}$) at 179.19 ppm with a relative intensity of 2 is assigned as C$_6$O (refer to Figure A-3.1) analogous to the assignment in 4.13.$^{48}$ The final singlet carbonyl resonance with intensity 1 at 179.79 ppm is therefore attributed to C$_6$O (see Figure A-3.1).

It would appear that at some point in the reaction of Os(CO)$_4$(PMe$_3$) and Os(CO)$_4$(GeCl$_3$)(Cl) that GeCl$_2$ was ejected as well as a CO group. A similar process of ejection of SnCl$_2$ from Ru$_2$(CO)$_6$(SnCl$_3$)$_2$(μ-Cl)$_2$ has been observed.$^{164}$ At present the mechanism for this process is not known.

For (Cl)(Me$_3$P)(OC)$_3$OsOs(CO)$_4$(Cl): IR (CH$_2$Cl$_2$) ν(CO): 2122(w,sh), 2082(w,sh), 2046(vs), 2014(w,sh), 1988(w,sh) (cm$^{-1}$); $^1$H NMR (CD$_2$Cl$_2$, 233 K): δ 2.01 (d, 9H, CH$_3$, 237
\[ ^2J_{\text{P-H}} = 11.08 \text{ Hz}; \quad ^{31}\text{P}\{^1\text{H}\} \text{ NMR (CD}_2\text{Cl}_2, 233K): \delta = 36.31 \text{ (s, PMe}_3\}; \quad ^{13}\text{C}\{^1\text{H}\} \text{ NMR (CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2 1/3, \text{ rm. temp.): } \delta = 17.99 \text{ (d, CH}_3, ^1J_{\text{P-C}} = 39.7 \text{ Hz}), 173.89 \text{ (d, 1C, CO, } ^2J_{\text{P-C}} = 4.0 \text{ Hz), 178.41 \text{ (s, CO), 179.19 \text{ (d, CO, } ^3J_{\text{P-C}} = 5.0 \text{ Hz), 179.79 \text{ (s, CO), 185.08 \text{ (d, 2C, CO, } ^2J_{\text{P-C}} = 7.0 \text{ Hz); MS (EI, m/z): 724 (M')}, \quad 668/770 (M'-2\text{ CO}); \quad \text{Anal. Calcd. for } \text{C}_{10}\text{H}_9\text{Cl}_2\text{O}_7\text{Os}_2\text{P: C}, 16.60; \quad \text{H}, 1.25. \quad \text{Found: C}, 16.34; \quad \text{H}, 1.41. \]

**Reaction of Ru(CO)\textsubscript{4}(PMe\textsubscript{3}) with Os(CO)\textsubscript{4}(GeCl\textsubscript{3})(Cl).** A round-bottom flask capped with a Teflon valve was charged with Ru(CO)\textsubscript{4}(PMe\textsubscript{3}) (57 mg, 0.20 mmol), Os(CO)\textsubscript{4}(GeCl\textsubscript{3})(Cl) (40 mg, 8.9 x 10\textsuperscript{-2} mmol) and C\textsubscript{6}H\textsubscript{14} (15 mL). The contents of the flask were subjected to three cycles of freeze-pump-thaw and heated at 323 K in the absence of light under vacuum for 17 h. This afforded a clear yellow/orange solution and a yellow precipitate. The reaction vessel and its contents were cooled to room temperature and the supernatant removed by pipet and the yellow solid was washed with C\textsubscript{6}H\textsubscript{14} until an IR spectrum of the wash liquid no longer showed absorption bands due to the starting material. The pale yellow powder of (Cl)(Me\textsubscript{3}P)(OC)\textsubscript{3}RuOs(CO)\textsubscript{4}(Cl) (45 mg, 80% yield) was obtained upon recrystallized from CH\textsubscript{2}Cl\textsubscript{2}/C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}/C\textsubscript{6}H\textsubscript{14}. The \textsuperscript{13}CO-enriched (Cl)(Me\textsubscript{3}P)(OC)\textsubscript{3}RuOs(CO)\textsubscript{4}(Cl) was prepared in a similar manner from \textsuperscript{13}CO-labeled Ru(CO)\textsubscript{4}(PMe\textsubscript{3}) and unenriched Os(CO)\textsubscript{4}(GeCl\textsubscript{3})(Cl).

The ν(CO) region of the IR spectrum of (Cl)(Me\textsubscript{3}P)(OC)\textsubscript{3}RuOs(CO)\textsubscript{4}(Cl) does not appear drastically different from the analogous spectrum for (Me\textsubscript{3}P)(OC)\textsubscript{4}RuRu(CO)\textsubscript{3}(SiCl\textsubscript{3})(Br).\textsuperscript{45} The chemical shift of the \textsuperscript{1}H NMR resonance of (Cl)(Me\textsubscript{3}P)(OC)\textsubscript{3}RuOs(CO)\textsubscript{4}(Cl) is similar to that in (Me\textsubscript{3}P)(OC)\textsubscript{4}RuRu(CO)\textsubscript{3}(SiCl\textsubscript{3})\textsubscript{2} (5.2) (Table 5.5). As with the Os analogue, it was the chemical shift of the \textsuperscript{31}P\{\textsuperscript{1}H\} NMR resonance of (Cl)(Me\textsubscript{3}P)(OC)\textsubscript{3}RuOs(CO)\textsubscript{4}(Cl) that first suggested the complex has an
(Cl)(Me₃P)(OC)₃Ru and not an (Me₃P)(OC)₄Ru fragment. The phosphorus resonance is at -3.51 ppm which is markedly different from that of (Me₃P)(OC)₄RuRu(CO)₃(SiCl₃)₂ (5.2) at -15.81 ppm (Table 5.6).

The carbonyl region of the $^{13}$C{¹H} NMR spectrum of (Cl)(Me₃P)(OC)₃RuOs(CO)₄(Cl) also supports this configuration of the complex. The two signals, with phosphorus-carbon couplings ($^2J_{P,C}$), one with relative intensity 2 at 195.30 ppm and the other with relative intensity 3 at 199.62 ppm are assigned to the C₈O and C₉O ligands, respectively, see Figure A-3.1. This assignment is consistent with that for (Br)(Me₃P)(OC)₃RuRu(CO)₄(SiCl₃).⁴⁵ The intensities of the three carbonyl resonances for the Os(CO)₄(Cl) fragment were 2:1:1. The doublet at 204.34 ppm (due to phosphorus coupling) is confidently assigned to C₈O (see Figure A-3.1). The signal of intensity 2 (179.49 ppm) is tentatively attributed to C₉O and that of the remaining signal of intensity 1 (191.76 ppm) to C₁₀O (Figure A-3.1). There could, however, be preferential enrichment of carbonyls as proposed for the osmium analogue which could lead to the reverse assignment for the last two signals.

For (Cl)(Me₃P)(OC)₃RuOs(CO)₄(Cl): IR (CH₂Cl₂) v(CO): 2084(w,sh), 2048(vs), 2002(w,sh) (cm⁻¹); ¹H NMR (CD₂Cl₂, 233 K): δ 1.86 (d, 9H, CH₃, $^2J_{P,H} = 10.80$ Hz); $^{31}$P{¹H} NMR (CD₂Cl₂, 233K): δ -3.51 (s, PMe₃); $^{13}$C{¹H} NMR (CD₂Cl₂/CH₂Cl₂ 1/3, rm. temp.): δ 18.22 (d, CH₃, $^1J_{P,C} = 33.6$ Hz), 179.49 (s, CO), 191.76 (s, CO), 195.30 (d, 1C, CO, $^2J_{P,C} = 6.9$ Hz), 199.62 (d, 2C, CO, $^2J_{P,C} = 9.2$ Hz), 204.34 (d, CO, $^3J_{P,C} = 9.2$ Hz); MS (EI, m/z): 635 (M⁺-1); (Cl, m/z): 635 (M⁺-1); Anal. Calcd. for C₁₆H₉Cl₂O₇OsPRu: C, 18.94; H, 1.43. Found: C, 17.10; H, 1.38.
Molecular structure of \((\text{Cl})(\text{Me}_3\text{P})(\text{OC})_3\text{RuOs}(\text{CO})_4(\text{Cl})\). X-ray quality crystals of \((\text{Cl})(\text{Me}_3\text{P})(\text{OC})_3\text{RuOs}(\text{CO})_4(\text{Cl})\) were obtained upon multiple recrystallizations from \(\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}\). Even then the yellow crystals of \((\text{Cl})(\text{Me}_3\text{P})(\text{OC})_3\text{RuOs}(\text{CO})_4(\text{Cl})\) had to be manually separated from trace amounts of orange crystals, believed to be \([(\text{Me}_3\text{P})(\text{OC})_2\text{Ru}(\mu-\text{Cl})]_2\text{Os}(\text{CO})_4\) (see below). The crystal structure analysis of \((\text{Cl})(\text{Me}_3\text{P})(\text{OC})_3\text{RuOs}(\text{CO})_4(\text{Cl})\) was carried out by Professor F. W. B. Einstein and Dr. W. Wang at Simon Fraser University. The structure was determined to be monoclinic, with the space group \(P2_1/c\). A view of the molecule is shown in Figure A-3.2; selected bond lengths and bond angles are given in Tables A-3.1 and A-3.2, respectively.

As can be seen in Figure A-3.2 this is a molecule with a nondative covalent ruthenium-osmium bond. As observed in similar molecules the phosphine ligand is trans to
the metal-metal bond e.g., as in (Br)(Me₃P)(OC)₃OsRe(CO)₅ (4.20),
(Me₃P)(OC)₄MRu(CO)₃(SiCl₃)₂ (M = Ru, Os) (5.2, 4.14) (Figures 5.1 and 5.3, respectively).

The ruthenium-osmium bond length in (Cl)(Me₃P)(OC)₃RuOs(CO)₄(Cl) is 2.909(1) Å (Table A-3.1) which is significantly shorter than the dative covalent Ru-Os bond in 4.14 (2.984(1) and 3.014(1) Å) (Table 5.3) or the dative covalent Ru-Ru bond in 5.2 (2.975(1) and 2.995(1) Å) (Table 5.1). Other unbridged Ru-Os bond lengths reported in the literature are 2.803(2)-2.810(1) Å in [(µ-H)₂RuOs₃(CO)₁₃] and 2.774(3)-2.803(3) Å in [RuOs₄(µ-H)₄(η⁶-C₆H₆)(CO)₁₁]. These distances are in cluster compounds in which it is known that the bond lengths are usually shorter than similar bonds in binuclear compounds.²²⁵

That a nondative metal-metal bond is shorter than a similar dative covalent metal-metal bond has been observed before in 4.13 (Os-Re 3.006(1) Å) compared to 4.20 (Os-Re 2.977(1) Å). It was thought that the difference in the Os-Re bond lengths in 4.13 and 4.20 could be attributed to the different electronic character of each metal-metal bond. If the differences in the ligands in (Cl)(Me₃P)(OC)₃RuOs(CO)₄(Cl) and (Me₃P)(OC)₄OsRu(CO)₃(SiCl₃)₂ (4.14) are considered insubstantial, then the significant difference in the Ru-Os bond lengths in the two compounds might also be ascribed to the different nature of the metal-metal bond in these molecules.

The ruthenium-phosphorus (2.364(2) Å) and ruthenium-carbon (Ru-C(2n); n = 1, 2; 1.949(9) and 1.95(1) Å) bond lengths in (Cl)(Me₃P)(OC)₃RuOs(CO)₄(Cl) (see Table A-3.1) are similar to those in 4.14 (see Table 5.4). The Ru-C(23) bond length (1.86(1) Å) is shorter than the other Ru-C(2n) bond lengths since it is trans to a Cl atom (while C(21) and C(22) are trans to one another) as was observed in mer-cis-Os(CO)₃(PMe₃)(Cl)₂ mer-cis-
2.2) (see Section 3.2.3.1). A similar phenomenon is also observed in the Os(CO)$_4$(Cl) fragment of (Cl)(Me$_3$P)(OC)$_3$RuOs(CO)$_4$(Cl): whereas the Os-C(1m) (m = 1, 3, 4; 1.97(1), 1.98(1), 1.97(1) Å) bond lengths are virtually identical, the Os-C(12) (1.91(1) Å) bond length is shorter and C(12) is the CO ligand that is trans to a Cl atom.

The osmium-chlorine bond length (2.445(3) Å) is similar to those found in 4.6 (2.41(1) and 2.40(3) Å) (Table 4.2) and (OC)$_3$OsOs(CO)$_3$GeCl$_3$(Cl) (2.448(8), 2.435(7) and 2.459(8) Å). The osmium-chlorine bond length (2.445(3) Å) is similar to those found in 4.6 (2.41(1) and 2.40(3) Å) (Table 4.2) and (OC)$_3$OsOs(CO)$_3$GeCl$_3$(Cl) (2.448(8), 2.435(7) and 2.459(8) Å).

As in 4.20 there is a slight inward leaning of the carbonyl ligands towards the metal-metal bond. On the ruthenium fragment, the only carbonyl ligand to lean towards the osmium is C(22) (C(22) - Ru(1) - Os(1) 85.8(3)°) (see Table A-3.2). (The angles of the other carbonyl ligands are C(2n) - Ru(1) - Os(1) (n = 1, 3) 89.0(3) and 90.4(3)°. It is more noticeable on the osmium fragment where the respective C(1m) - Os(1) - Ru(1) (m = 1-3) angles range from 83.1(3)-85.7(3)°, see Table A3-2.

Table A-3.1  Selected bond lengths of (Cl)(Me$_3$P)(OC)$_3$RuOs(CO)$_4$(Cl).

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Os(1) - Ru(1)</th>
<th>Ru(1) - Cl(2)</th>
<th>Os(1) - Cl(1)</th>
<th>Ru(1) - P(1)</th>
<th>Os(1) - C(11)</th>
<th>Ru(1) - C(21)</th>
<th>Os(1) - C(12)</th>
<th>Ru(1) - C(22)</th>
<th>Os(1) - C(13)</th>
<th>Ru(1) - C(23)</th>
<th>Os(1) - C(14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(1) - Ru(1)</td>
<td>2.909(1)</td>
<td>2.439(2)</td>
<td>2.445(3)</td>
<td>2.364(2)</td>
<td>1.97(1)</td>
<td>1.949(9)</td>
<td>1.91(1)</td>
<td>1.95(1)</td>
<td>1.98(1)</td>
<td>1.86(1)</td>
<td>1.97(1)</td>
</tr>
</tbody>
</table>
Table A-3.2  Selected bond angles of (Cl)(Me3P)(OC)3RuOs(CO)4(Cl).

<table>
<thead>
<tr>
<th>Bond Angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(1) - Os(1) - Ru(1)</td>
</tr>
<tr>
<td>Cl(2) - Ru(1) - Os(1)</td>
</tr>
<tr>
<td>C(11) - Os(1) - Cl(1)</td>
</tr>
<tr>
<td>Cl(2) - Ru(1) - P(1)</td>
</tr>
<tr>
<td>C(11) - Os(1) - C(12)</td>
</tr>
<tr>
<td>Cl(2) - Ru(1) - C(21)</td>
</tr>
<tr>
<td>C(11) - Os(1) - C(13)</td>
</tr>
<tr>
<td>Cl(2) - Ru(1) - C(22)</td>
</tr>
<tr>
<td>C(11) - Os(1) - Ru(1)</td>
</tr>
<tr>
<td>Cl(2) - Ru(1) - C(23)</td>
</tr>
<tr>
<td>C(12) - Os(1) - Ru(1)</td>
</tr>
<tr>
<td>C(21) - Ru(1) - Os(1)</td>
</tr>
<tr>
<td>C(13) - Os(1) - Ru(1)</td>
</tr>
<tr>
<td>C(22) - Ru(1) - Os(1)</td>
</tr>
<tr>
<td>C(14) - Os(1) - Ru(1)</td>
</tr>
<tr>
<td>C(23) - Ru(1) - Os(1)</td>
</tr>
<tr>
<td>P(1) - Ru(1) - Os(1)</td>
</tr>
</tbody>
</table>

In one preparation of (Cl)(Me3P)(OC)3RuOs(CO)4(Cl) that involved multiple recrystallizations of (Cl)(Me3P)(OC)3RuOs(CO)4(Cl) from CH2Cl2/C6H14, [(Me3P)(OC)2Ru(μ-Cl)]2Os(CO)4 was obtained in trace amounts as orange crystals that were suitable for an X-ray structural determination (described below). Attempts to prepare [(Me3P)(OC)2Ru(μ-Cl)]2Os(CO)4 in larger quantities were unsuccessful. The mechanism of formation of [Ru(CO)2(PMe3)(μ-Cl)]2Os(CO) is unknown.

An all osmium analogue of [Ru(CO)2(PMe3)(μ-Cl)]2Os(CO)4 is known, that is, Os3(CO)8(PPh3)(μ-Cl)2 which was prepared by the reaction of Os3(CO)10(μ-Cl)2 with PPh3.116 The carbonyl region of IR spectrum of [Ru(CO)2(PMe3)(μ-Cl)]2Os(CO)4 (2070(s), 2016(s), 1989(s), 1948 (w,sh) cm⁻¹) is somewhat similar to that of Os3(CO)8(PPh3)(μ-Cl)2 (2079(s), 2014(s), 2004(s), 1967(w), 1943(m) cm⁻¹).116 Unlike the mass spectrum of
Os₃(CO)₈(PPh₃)(µ-Cl)₂ where there was no evidence of the parent peak, the mass spectrum of \([\text{Ru(CO)}₂(\text{PMe₃})(\mu-\text{Cl})]₂\text{Os(CO)}₄\) exhibited a parent peak and peaks assignable to the loss of one and two CO ligands.

For \([\text{(Me₃P)}(\text{OC})₂\text{Ru(µ-Cl)}]₂\text{Os(CO)}₄\): IR (CH₂Cl₂) ν(CO): 2070(s), 2016(s), 1989(s), 1948 (w,sh) (cm⁻¹); MS (EI, m/z): 840/841 (M⁺), 812/813 (M⁺-CO), 784/785 (M⁺-2CO); (Cl, m/z): 841 (M⁺+1).

**Molecular structure of \([\text{(Me₃P)}(\text{OC})₂\text{Ru(µ-Cl)}]₂\text{Os(CO)}₄\).** The crystal structure analysis of \([\text{(Me₃P)}(\text{OC})₂\text{Ru(µ-Cl)}]₂\text{Os(CO)}₄\) was carried out by Professor F. W. B. Einstein and Dr. W. Wang at Simon Fraser University. The structure was determined to be monoclinic, with the space group \(P2_1/n\) and a unit cell containing two crystallographically distinct molecules. Furthermore, the methyl carbon atoms of the trimethylphosphine groups were found to occur in two general positions resulting in two partially occupied orientations of these groups.

As can be seen in Figure A-3.3 the two ruthenium and one osmium atom approximately define an isosceles triangle. The osmium atom has four terminal carbonyl ligands while the ruthenium centers have two terminal carbonyl groups, one phosphine ligand, and are bridged by two chloride ligands. A single crystal X-ray study was not carried out on \(\text{Os₃(CO)}₈(\text{PPh₃})(\mu-\text{Cl})₂\); the closest analogue characterized crystallographically is \(\text{Os₃(CO)}₁₀(\mu-\text{Cl})₂\).\(^{123}\) The osmium-ruthenium bond lengths are 2.861(3) and 2.876(3) (molecule 1) and 2.872(3) and 2.874(3) Å (molecule 2; see Table A-3.3). These distances are longer than the Os-Os distances in \(\text{Os₃(CO)}₁₀(\mu-\text{Cl})₂\) (2.849(2), 2.855(2), 2.846(2), 2.850(2) Å; two independent molecules in the unit cell).\(^{123}\) The Ru - Os - Ru bond angles are 67.64(8)° (molecule 1) and 67.81(8)° (molecule 2; see
Table A-3.4) which is smaller than the respective angles in Os$_3$(CO)$_{10}$($\mu$-Cl)$_2$ (69.06(4)$^\circ$ and 69.83(4)$^\circ$).$^{123}$

Figure A-3.3 Molecular structure of [Ru(CO)$_2$(PMe$_3$)(\(\mu\)-Cl)]$_2$Os(CO)$_4$. 
Table A-3.3  Selected bond lengths of \([\text{Ru(CO)}_2(\text{PMe}_3)(\mu-\text{Cl})])_2\text{Os(CO)}_4\).

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Molecule 1</th>
<th>Molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(1) - Ru(1)</td>
<td>2.861(3)</td>
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<tr>
<td>Os(1) - Ru(2)</td>
<td>2.876(3)</td>
<td>Os(2) - Ru(4)</td>
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<td>Os(1) - C(114)</td>
<td>1.84(4)</td>
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Table A-3.4  Selected bond angles of \([\text{Ru(CO)}_2(\text{PMe}_3)(\mu-\text{Cl})]\)_2\text{Os(CO)}_4.

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<th>Bond Angles (deg)</th>
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<tbody>
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</tr>
<tr>
<td>C(121) - Ru(1) - C(122)</td>
<td>91.9(14)</td>
<td>C(221) - Ru(3) - C(222)</td>
</tr>
<tr>
<td>Ru(1) - Cl(11) - Ru(2)</td>
<td>79.8(2)</td>
<td>Ru(3) - Cl(21) - Ru(4)</td>
</tr>
<tr>
<td>Ru(1) - Cl(12) - Ru(2)</td>
<td>81.1(2)</td>
<td>Ru(3) - Cl(22) - Ru(4)</td>
</tr>
</tbody>
</table>
The bridging Cl atoms are bound to the metallic core via Ru(n) (n = 1, 3) and Ru(m) (m = 2, 4) with an average bond length of 2.473(13) Å (see Table A-3.3) and an average Ru -Cl - Ru bond angle of 80.6(6)° (see Table A-3.4) which is a longer average M-Cl bond length (2.461(3) Å) and a smaller average M - Cl - M bond angle (82.04(8)°) than in Os₃(CO)₁₀(μ-Cl)₂.¹²³

**Reaction of Fe(CO)₄(PMe₃) with Os(CO)₄(GeCl₃)(Cl).** A round-bottom flask capped with a Teflon valve was charged with Fe(CO)₄(PMe₃) (28 mg, 0.16 mmol), Os(CO)₄(GeCl₃)(Cl) (50 mg, 9.7 x 10⁻² mmol) and C₆H₁₄ (20 mL). The contents of the flask were subjected to three cycles of freeze-pump-thaw and heated at 323 K in the absence of light under vacuum for 5 days. This afforded a colorless solution and a white and orange precipitate. An IR spectrum of the precipitate in CH₂Cl₂ showed ν(CO) bands due to Fe(CO)₄(PMe₃), Os(CO)₄(GeCl₃)(Cl) and some new bands (2135(w), 2068(m), 2029(w) cm⁻¹). A further 20 mL of C₆H₁₄ was added to the flask and the contents subjected to three cycles of freeze-pump-thaw and heated at 333 K in the absence of light under vacuum for a further 7 days. This finally afforded a pale yellow solution above an orange solid. An IR spectrum of the supernatant solution indicated Fe(CO)₄(PMe₃) was present. The entire contents of the flask were transferred to a Schlenk tube and the solvent removed under vacuum. The Fe(CO)₄(PMe₃) was removed by heating the flask to 323 K under vacuum and subliming the Fe(CO)₄(PMe₃) to a cold finger (195 K). The residue after sublimation was washed with fresh C₆H₁₄ to yield a yellow/orange powder whose IR spectrum ν(CO) bands were 2136(w), 2069(w,sh), 2058(s), 2002(m) cm⁻¹ in CH₂Cl₂. Attempted recrystallization from warm toluene produced an oil with the same IR spectrum ν(CO) bands. The IR spectrum ν(CO) bands for the unidentified compound do not
resemble those of \((\text{OC})_4(\text{Bu'}\text{NC})\text{OsOs(\text{CO})_3(\text{GeCl}_3)(\text{Cl})}\) (Table 4.6) or \((\text{OC})_5\text{OsOs(\text{CO})_3(\text{GeCl}_3)(\text{Cl})}\)^4^4 but have some similarity to those of \((\text{Cl})(\text{Me}_3\text{P})(\text{OC})_3\text{MOs(\text{CO})_4(\text{Cl})}\) (see above).

**Reaction of Fe(\text{CO})_4(\text{CNBu'}) with Os(\text{CO})_4(\text{GeCl}_3)(\text{Cl}).** A round-bottom flask capped with a Teflon valve was charged with Fe(\text{CO})_4(\text{CNBu'}) \((30 \text{ mg, 0.12 mmol})\), Os(\text{CO})_4(\text{GeCl}_3)(\text{Cl}) \((50 \text{ mg, 9.7 x 10^{-2} mmol})\) and C_6H_14 \((30 \text{ mL})\). The contents of the flask were subjected to three cycles of freeze-pump-thaw and heated at 323 K in the absence of light under vacuum for 18 h. This afforded a yellow solution and a yellow precipitate. The supernatant solution was removed and the remaining solid washed with fresh C_6H_14. An IR spectrum of the crude product in CH_2Cl_2 showed three new v(CO) bands \((2133(m), 2072(w,sh) \text{ and } 2050(s) \text{ cm}^{-1})\). The solid was transferred to a Schlenk tube to allow a removal of any excess Fe(\text{CO})_4(\text{CNBu'}) by sublimation of the mononuclear complex to a cooled probe \((195 \text{ K})\) while the vessel was heated at 333 K. An IR spectrum of the residue in CH_2Cl_2 showed v(CN) and v(CO) bands at 2223(w, br), 2127(s), 2063(w, sh), 2046(s), 2010(w, sh) cm^{-1}. The IR v(CO) bands of this unknown complex do not resemble those of \((\text{OC})_4(\text{Bu'}\text{NC})\text{OsOs(\text{CO})_3(\text{GeCl}_3)(\text{Cl})}\) (Table 4.6) or \((\text{OC})_5\text{OsOs(\text{CO})_3(\text{GeCl}_3)(\text{Cl})}\)^4^4

**Reaction of Os(\text{CO})_3(\text{PMe}_3)_2 with Os(\text{CO})_4(\text{GeCl}_3)(\text{Cl}).** A round-bottom flask capped with a Teflon valve was charged with Os(\text{CO})_3(\text{PMe}_3)_2 \((50 \text{ mg, 0.12 mmol})\), Os(\text{CO})_4(\text{GeCl}_3)(\text{Cl}) \((50 \text{ mg, 9.7 x 10^{-2} mmol})\) and C_6H_14 \((20 \text{ mL})\). The contents of the flask were subjected to three cycles of freeze-pump-thaw and heated at 323 K in the absence of light under vacuum for 18 h. This afforded a colorless solution and a yellow oil. An IR spectrum of the supernatant solution indicated the presence of Os(\text{CO})_3(\text{PMe}_3)_2 and
trace amounts of Os(CO)$_2$(PMe$_3$)$_2$(Cl)$_2$. The supernatant solution was removed and the remaining oil washed with fresh C$_6$H$_{14}$. An IR spectrum of the crude product in CH$_2$Cl$_2$ showed $\nu$(CO) bands at: 2120(w), 2068(w, sh), 2055(m, sh), 2035(s) cm$^{-1}$. The IR $\nu$(CO) bands of this unknown complex do not resemble those of (OC)$_4$(Bu$^1$NC)OsOs(CO)$_3$(GeCl$_3$)(Cl) (Table 4.6) or (OC)$_5$OsOs(CO)$_3$(GeCl$_3$)(Cl). Upon subjecting the yellow oil to sublimation conditions (heating the vessel to 333 K while cooling a probe to 195 K) an IR of the sublimate showed the presence of Os(CO)$_2$(PMe$_3$)$_2$(Cl)$_2$ and Os(CO)$_4$(Cl)$_2$. Recrystallization of the yellow oil from CH$_2$Cl$_2$/C$_6$H$_{14}$ gave only yellow oil.

**Reaction of Os(CO)$_4$(GeCl$_3$)(Cl) with cis-cyclooctene (COE).** Using results outlined in Section 4.2.1.4 it was thought the CO trans to GeCl$_3$ in Os(CO)$_4$(GeCl$_3$)(Cl) could be replaced by COE. The COE would then act as a labile ligand to which it was hoped donor fragments could add under mild reaction conditions.

A round-bottom flask capped with a Teflon valve was charged with Os(CO)$_4$(GeCl$_3$)(Cl) (50 mg, 9.7 x 10$^{-2}$ mmol) and cis-cyclooctene (COE) (20 mL). The contents of the flask were subjected to three cycles of freeze-pump-thaw and heated at 323 K in the absence of light under vacuum for 1-3 days. This afforded a colorless solution. (If the Os(CO)$_3$(COE)(GeCl$_3$)(Cl) was to be used in another preparative step the COE would be removed under vacuum and the solid redissolved in C$_6$H$_6$ to be added to a solution of the donor fragment). The solution was filtered, transferred to a Schlenk tube, C$_6$H$_{14}$ (40 mL) layered on top of the solution and placed in the freezer which afforded white crystals.
Figure A-3.4  One possible orientation of cis-cyclooctene with a labeling scheme for the carbon and hydrogen atoms to assist the $^1$H and $^{13}$C NMR resonance assignments.

The IR spectrum of Os(CO)$_3$(COE)(GeCl$_3$)(Cl) shows two strong bands and two weak shoulders in the $\nu$(CO) region of the spectrum, in several solvents and for multiple preparations. This suggests that Os(CO)$_3$(COE)(GeCl$_3$)(Cl) is not the sole species in solution (three IR active $\nu$(CO) bands are expected from group theory). The elemental analysis, however, suggests that the compound is quite pure. The $^1$H and particularly the $^{13}$C NMR resonances suggest that the COE ligand is present but is coordinated to the Os center (by comparison to the free ligand)$^{237,238}$ and there are three carbonyl ligands in two environments.

For Os(CO)$_3$(COE)(GeCl$_3$)(Cl): IR (COE) $\nu$(CO): 2130(vw), 2076(vs), 2056(vw,sh), 2025(s) (cm$^{-1}$); (CH$_2$Cl$_2$) $\nu$(CO): 2135(w), 2079(s), 2061(m,sh), 2034(m) (cm$^{-1}$); (C$_6$D$_6$) $\nu$(CO): 2139(vw), 2078(vs), 2051(vw,sh), 2027(m) (cm$^{-1}$); $^1$H NMR (CD$_2$Cl$_2$, rm. temp) (see Figure A-3.4 for labeling of the atoms): $\delta$ 1.50-1.60 (m, 2H, (C$_{\alpha}$HC$_{\beta}$H$_2$C$_\gamma$H$_1$/H$_2$C$_8$H$_1$/H$_2$)$_2$), 1.76-1.61 (m, 4H, (C$_{\alpha}$HC$_{\beta}$H$_2$C$_\gamma$H$_1$/H$_2$C$_8$H$_1$/H$_2$)$_2$), 1.99 (m, 2H, (C$_{\alpha}$HC$_{\beta}$H$_2$C$_\gamma$H$_1$/H$_2$C$_8$H$_1$/H$_2$)$_2$), 2.29 (m, 2H, (C$_{\alpha}$HC$_{\beta}$H$_2$C$_\gamma$H$_1$/H$_2$C$_8$H$_1$/H$_2$)$_2$), 2.80 (m, 2H, (C$_{\alpha}$HC$_{\beta}$H$_2$C$_\gamma$H$_1$/H$_2$C$_8$H$_1$/H$_2$)$_2$), 5.38 (m, 2H, (C$_{\alpha}$HC$_{\beta}$H$_2$C$_\gamma$H$_1$/H$_2$C$_8$H$_1$/H$_2$)$_2$); $^{13}$C($^1$H) NMR (C$_6$D$_6$, rm.
temp.) (see Figure A-3.4 for labeling of the atoms): δ 25.09 (s, 2C, (C_6H_CpH_2C_7H_2C_8H_2)_2),
28.20 (s, 2C, (C_6H_CpH_2C_7H_2C_8H_2)_2), 31.05 (s, 2C, (C_6H_CpH_2C_7H_2C_8H_2)_2), 102.05 (s, 2C,
(C_6H_CpH_2C_7H_2C_8H_2)_2), 172.48 (s, 1C, CO), 173.83 (s, 2C, CO); MS (EI, m/z): 453 (M^+ -
COE-Cl); Anal. Calcd. for C_{11}H_{14}Cl_4GeO_3Os: C, 22.06; H, 2.36. Found: C, 22.30; H, 2.45.

(Note free cis-COE ^1H NMR (CD_2Cl_2, rm. temp): δ 1.43-1.56 (m, 8H,
(C_6H_CpH_2C_7H_1/H_2C_8H_1/H_2)_2), 2.13 (m, 4H, (C_6H_CpH_1/H_2C_7H_2C_8H_2)_2), 5.62 (m, 2H,
(C_6H_CpH_2C_7H_2C_8H_2)_2) which concurs with the literature).^{237}

**Reaction of Fe(CO)_4(PMe_3) with Os(CO)_3(COE)(GeCl_3)(Cl).** A round-bottom
flask capped with a Teflon valve was charged with Fe(CO)_4(PMe_3) (24 mg, 9.8 x 10^{-2}
mmol), Os(CO)_3(COE)(GeCl_3)(Cl) (9.3 x 10^{-2} mmol, 56 mg, presuming all the
Os(CO)_4(GeCl_3)(Cl) reacted) and C_6H_{14}/C_6H_6 (4/11 mL). The contents of the flask were
stirred at room temperature under N_2 in the absence of light for 4 days. This afforded a
cream colored solution and a fine cream precipitate. In both components of the product
mixture the sole species observed in the IR spectra were Fe(CO)_4(PMe_3),
Os(CO)_4(GeCl_3)(Cl) and Os(CO)_3(COE)(GeCl_3)(Cl).

**Reaction of Os(CO)_4(PMe_3) with Os(CO)_3(COE)(GeCl_3)(Cl).** A round-bottom
flask capped with a Teflon valve was charged with Os(CO)_4(PMe_3) (37 mg, 9.8 x 10^{-2}
mmol), Os(CO)_3(COE)(GeCl_3)(Cl) (9.7 x 10^{-2} mmol, 58 mg, presuming all the
Os(CO)_4(GeCl_3)(Cl) reacted) and C_6H_{14}/C_6H_6 (4/11 mL). The contents of the flask were
stirred at room temperature under N_2 in the absence of light for 18 h. This afforded a pale
yellow solution and yellow oil. The supernatant was removed and the oil washed with
C_6H_{14}. An IR spectrum of the yellow oil in CH_2Cl_2 showed ν(CO) bands identical to those
of (Cl)(Me_3P)(OC)_3OsOs(CO)_4(Cl) (see above).

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Reaction of Rh(CO)₄(PMe₃) with Os(CO)₃(COE)(GeCl₃)(Cl). A round-bottom flask capped with a Teflon valve was charged with Rh(CO)₄(PMe₃) (24 mg, 8.1 x 10⁻² mmol), Os(CO)₃(COE)(GeCl₃)(Cl) (8.1 x 10⁻² mmol, 49 mg, presuming all the Os(CO)₄(GeCl₃)(Cl) reacted) and C₆H₁₄/C₆H₆ (4/11 mL). The contents of the flask were stirred at room temperature under N₂ in the absence of light for 2 days. This afforded a yellow solution and a yellow precipitate. The supernatant was removed and the yellow solid was washed with C₆H₁₄. An IR spectrum of the crude solid in CH₂Cl₂ showed ν(CO) bands at 2082 (w, sh), 2051 (vs), 2032 (vw, sh), 1993 (w, sh). The two higher ν(CO) frequencies are very similar to those of (Cl)(Me₃P)(OC)₃RuOs(CO)₄(Cl) (see above) and was thought to be a crude sample of this compound.

Reaction of Os(CO)₅ with Os(CO)₃(COE)(GeCl₃)(Cl). A round-bottom flask capped with a Teflon valve was charged with Os(CO)₅ (56 mg in 14 mL of C₆H₁₄, 0.17 mmol), Os(CO)₃(COE)(GeCl₃)(Cl) (9.7 x 10⁻² mmol, 58 mg, presuming all the Os(CO)₄(GeCl₃)(Cl) reacted) and C₆H₁₄ (10 mL). The contents of the flask were stirred at room temperature under N₂ in the absence of light for 2 days. This afforded a yellow colored solution and a cream precipitate. The supernatant was removed and the cream solid was washed with C₆H₁₄. An IR spectrum of the crude solid showed it to be (OC)₅OsOs(CO)₃(GeCl₃)(Cl). Upon recrystallization from C₆H₁₄/CH₂Cl₂ pure (OC)₅OsOs(CO)₃(GeCl₃)(Cl) was obtained (30 mg, 38% yield).

Reaction of Fe(CO)₄(CNBu') with Os(CO)₃(COE)(GeCl₃)(Cl). A round-bottom flask capped with a Teflon valve was charged with Fe(CO)₄(CNBu') (24 mg, 9.6 x 10⁻² mmol), Os(CO)₃(COE)(GeCl₃)(Cl) (9.1 x 10⁻² mmol, 54 mg, presuming all the Os(CO)₄(GeCl₃)(Cl) reacted) and C₆H₁₄/C₆H₆ (4/11 mL). The contents of the flask were
stirred at room temperature under N₂ in the absence of light for 20 h. This afforded a yellow solution and a yellow precipitate. The supernatant solution was removed and the solid washed with C₆H₁₄. Upon recrystallization of the sample from CH₂Cl₂/C₆H₁₄ afforded a pale yellow solid. An IR spectrum of the sample in CH₂Cl₂ showed an ν(CN) band 2229(w) and ν(CO) frequencies 2135(m), 2086(w,sh), 2061(s), 2047(vw,sh). This IR spectrum does not resemble that of (OC)₅OsOs(CO)₃(GeCl₃)(Cl)⁴⁴ but the higher frequency (CO) stretches and the ν(CN) band do resemble those in (OC)₄(Bu'NC)OsOs(CO)₃(GeCl₃)(Cl) (Table 4.6). The C, H and N analysis of the product (C, 14.20; H, 1.63; N, 1.28) did not agree with either (Bu'NC)(OC)₄FeOs(CO)₃(Cl)₂ (C, 24.18; H, 1.52; N, 2.35) or (Bu'NC)(OC)₄FeOs(CO)₃(GeCl₃)(Cl) (C, 19.49; H, 1.23; N, 1.89).
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