BROMINE DERIVATIVES OF RUTHENIUM AND OSMIUM CARBONYLS

by

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ABSTRACT

Bromonium ions of group 8 metal carbonyl compounds $M_3(CO)_{12}$ (M = Ru, Os) and $Os(CO)_5$ have been synthesized and evidence has been provided that these ions are, unexpectedly, not intermediates in the bromination of the respective metal carbonyls.

Addition of $[Ad_2Br][TFPB]$ (Ad_2 = adamantylideneadamantane; TFPB = tetrakis-(3,5-bis-(trifluoromethyl)phenyl)borate, $[\{3,5\text{-}(CF_3)_2C_6H_3\}B]_4^-$) to $M_3(CO)_{12}$ in CH_2Cl_2 at or below room temperature readily affords $[M_3(CO)_{12}Br][TFPB]$, which on addition of hexane gives air-stable, red-orange (M = Ru) or pale-yellow (M = Os) crystals. The structures of the two cations as determined by X-ray crystallography reveal they have markedly different structures: the ruthenium derivative can be considered as an organometallic analogue of the bromonium ion of ethylene, $[C_2H_4Br]^+$, whereas the osmium cation can be thought of as the corresponding analogue of cyclopropane, $[C_3H_6Br]^+$.

The product from the treatment of $[Os_3(CO)_{12}Br]^+$ in CH_2Cl_2 at room temperature with $[(C_2H_5)_4N]Br$ is *cis,cis*-$Os_3(CO)_{12}(Br)_2$, and not *cis,trans*-$Os_3(CO)_{12}(Br)_2$, the first product of the reaction of Br_2 with $Os_3(CO)_{12}$. On the other hand, $[Ru_3(CO)_{12}Br]^+$ under the same conditions did not yield *cis,cis*-$Ru_3(CO)_{12}(Br)_2$; the products have yet to be identified. The first detectable product (by ^{13}C NMR spectroscopy) in the reaction of $Ru_3(CO)_{12}$ with Br_2 at -50 °C is the previously unknown *cis,cis*-$Ru_3(CO)_{12}(Br)_2$, the structure of which was confirmed by X-ray crystallography.

The reaction of $Os(CO)_5$ with $[Ad_2Br][TFPB]$ affords the hitherto unknown $[Os(CO)_5Br][TFPB]$ which (by ^{13}C NMR spectroscopy) has an octahedral structure. The compounds $Os(CO)_5$ and $Os(CO)_4(PMe_3)$ were also reacted with Br_2 at low temperature to yield complexes of the formulation $Os(CO)_5.Br_2$ and $[Os(CO)_4(Br)(PMe_3)][Br_3]$. Variable temperature ^{13}C NMR studies of $Os(CO)_5.Br_2$ indicate the presence of two isomers in solution. One of the isomers is tentatively identified as the acyl bromide derivative, $Os(CO)_4[C(O)Br](Br)$; the other isomer is of unknown structure. Infrared studies show that Cl_2 and I_2 also yield the products analogous to the bromination. A remarkable aspect of this part of the study is the characterization of $[Os(CO)_5Br]^+$ and $Os(CO)_5.Br_2$ and the finding that $Os(CO)_5.Br_2$ is not the ionic compound $[Os(CO)_5Br][Br]$ as had been previously assumed. Interestingly, $Os(CO)_5.Br_2$ on reaction with NaTFPB yielded $[Os(CO)_5Br]^+$ which on treatment with $[(C_2H_5)_4N]Br$ gives $Os(CO)_5.Br_2$. On the basis of infrared and NMR studies, the phosphine-substituted complex is formulated as the ionic compound $[Os(CO)_4(Br)(PMe_3)][Br_3]$, the analogue of $[Os(CO)_5Br]TFPB$.

DEDICATION

To my parents,

husband

and

'little' Ashina

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During the past two years I have learned much from my senior supervisors, Professors R. K. Pomeroy, and A. J. Bennet. I acknowledge them with a sense of gratitude for giving me valuable guidance throughout this project.

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LIST OF ABBREVIATIONS AND SYMBOLS

cis	latin: on this side
trans	latin: across
cm^{-1}	wavenumber
δ	chemical shift, scale NMR.
ν	frequency
deg	degrees
FT	Fourier transform
FAB	fast atom bombardment
h	hour
Hz	hertz, sec^{-1}
HOMO	highest occupied molecular orbital
IR	infrared
LUMO	lowest unoccupied molecular orbital
m	relative intensity of the peak is medium (IR spectra)
NMR	nuclear magnetic resonance
PMe_3	$P(CH_3)_3$, trimethyl phosphine
TFPB	tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate $[(3,5\text{-}(CF_3)C_6H_3]_4B$
OTf	$CF_3SO_3^-$
ppm	parts per million
min	minute

vs	relative intensity of the peak is very strong (IR spectra)
s	relative intensity of the peak is strong (IR spectra)
w	relative intensity of the peak is weak (IR spectra)
vw	relative intensity of the peak is very weak (IR spectra)

LIST OF NUMBERED COMPLEXES

(**2.1**)	$[Ru_3(CO)_{12}Br]$TFPB
(**2.2**)	$[Os_3(CO)_{12}Br]$TFPB
(**2.3**)	$[Ru_3(CO)_{12}Br_2]$
(**3.1**)	$[Os(CO)_5Br]$TFPB
(**3.2A**)	$[Os(CO)_5.Br_2]$, isomer **A**
(**3.2B**)	$[Os(CO)_5.Br_2]$, isomer **B**
(**3.3**)	$[Os(CO)_4(PMe_3)(Br)][Br_3]$

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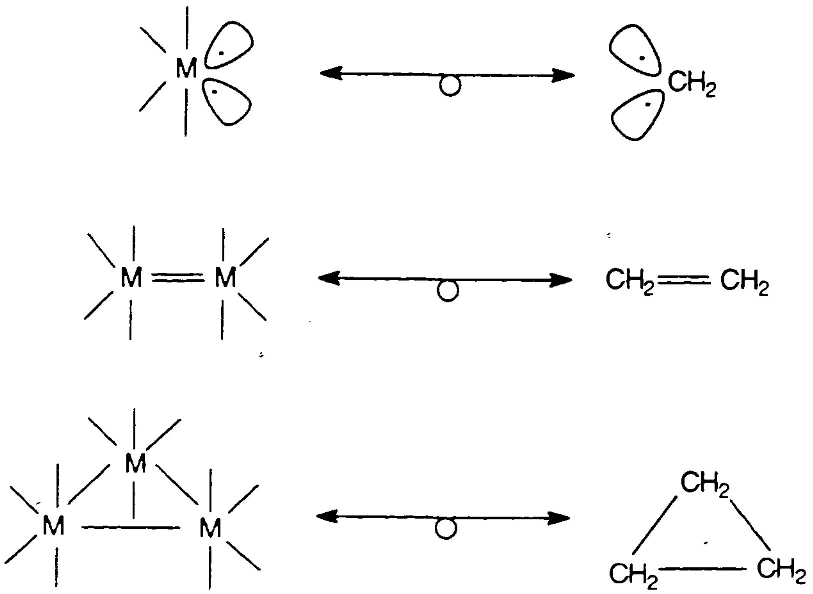
CHAPTER 1

INTRODUCTION

Metal carbonyl chemistry is an important class of organometallic chemistry and metal carbonyl complexes have found widespread use as catalysts and reagents in organic synthesis. For example, cobalt carbonyl ($Co_2(CO)_8$) is used industrially as a hydroformylation catalyst and Collman's reagent ($Na_2Fe(CO)_4.1.5$ dioxane) is extensively used for inserting a carbonyl group into an organic molecule.[1] The chemistry of binary metal carbonyls is therefore of fundamental importance in organometallic chemistry.

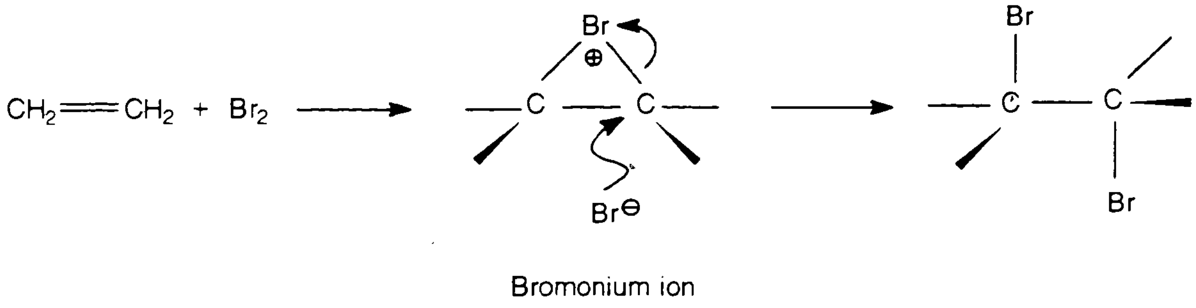
The concept of isolobal analogy which lies behind much of the chemistry described in this thesis is first discussed. This concept in organometallic chemistry was made popular by Hoffmann. He described how organic and inorganic fragments are related to each other in his Noble lecture "Building bridges between inorganic and organic fragments".[2] The isolobal analogy states that "two chemical species are said to be isolobal when the number, symmetry properties, approximate energies, and shapes of the frontier orbitals are similar, and the number of electrons in them are the same."[2] This concept has helped inorganic chemists to think of transition metal compounds (with all the associated electrons and orbitals) in terms of much more easily understood organic analogues. The isolobal fragments important in this work are the methylene fragment, CH_2, and the group 8 metal tetracarbonyl fragments, $M(CO)_4$ (M = Fe, Ru, Os), and these are shown in Scheme 1.1.

The primary focus of our studies was to characterize the bromonium ions of group 8 metal carbonyls. However, before the more complex reactions of metal carbonyls with bromine can be understood it is essential to grasp the mechanism for the bromination of



Scheme 1.1 Illustration of the Isolobal Analogy between CH_2 and $M(CO)_4$ (M = Fe, Ru, Os). Carbonyl ligands have been omitted for clarity.

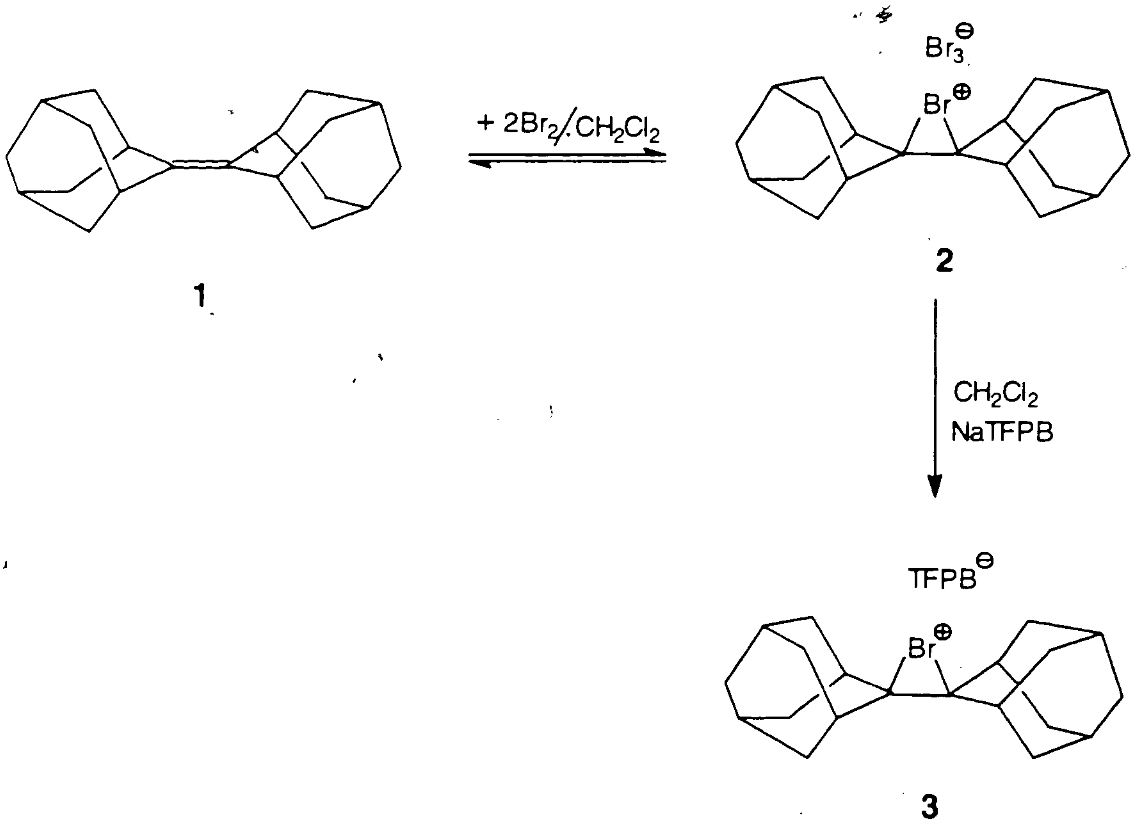
alkenes which is one of the fundamental reactions of organic chemistry. The question that arises from the study of bromination of alkenes is, is the addition of bromine concerted; and is there an open carbonium ion intermediate or a cyclic halonium ion intermediate? The results from the stereochemical studies on alkene bromination are summarizd as follows. For bromination, the anti addition product is formed if there is no substituent that would stabilize a carbonium ion center. But when one of the alkene substituents is an aryl group the syn product formation becomes detectable. The generally accepted mechanism of the electrophilic addition of halogens to an olefinic double bond is shown in Scheme 1.2 in which a three membered ring intermediate is briefly formed, which then reacts with Br^- or Br_3^- to give an anti-dibromide product.[3] The addition of Br^+ to the alkene results in a bromonium ion.[3, 4] It explains why the nucleophilic addition of bromide occurs from the back-side to open up the ring with the rupture of a C-Br bond giving the overall anti addition product.



Scheme 1.2 Proposed mechanism for the anti-dibromide product via bromonium ion.

The use of sterically congested alkenes has allowed the isolation and characterization of several intrinsically reactive intermediates formed during the electrophilic addition reaction, *i.e.*, $[Ad_2Br]Br_3^-$, $[Ad_2Br][OTf]$ and $[Ad_2I][OTf]$.[5, 6, 11b] The normal product forming steps are slowed down or stopped altogether due to severe crowding at the stage of the intermediate. For example, Strating and coworkers[5] in 1969 reported that the sterically hindered alkene, adamantylideneadamantane (Ad=Ad) (**1**) when reacted with bromine yields a stable bromonium ion as the tribromide salt (**2**) (Scheme 1.3). This ion has been characterized by single crystal X-ray diffraction which shows the Van der Waals radii of the back side hydrogen atoms effectively overlap (Figure 1.1).[7] Despite much discussion,[7, 8] there is no simple answer to the question of whether the crystal structure is a σ or π-complex.

Brown et al described this distinction as "a semantic one and has no real meaning".[8] The counter ion Br_3^- forms a close contact with the Br^+ ion suggestive of an intimate ion pair. The overall structure reveals that there is severe crowding at the side opposite the Br^+ ion which prevents access of a nucleophile to the ion. This unusual feature is the likely source of the stability of the ion-pair. The olefin Ad=Ad is unique among presently investigated olefins in that its structure absolutely impedes the progress of Br_2 addition beyond the stage of bromonium ion-formation. The olefin Ad=Ad is also known to yield a chloronium ion in the reaction of Ad_2 with Cl_2 which then rearranges to form a monosubstituted product.[9]



Scheme 1.3 Preparation of $[Ad_2Br]TFPB$

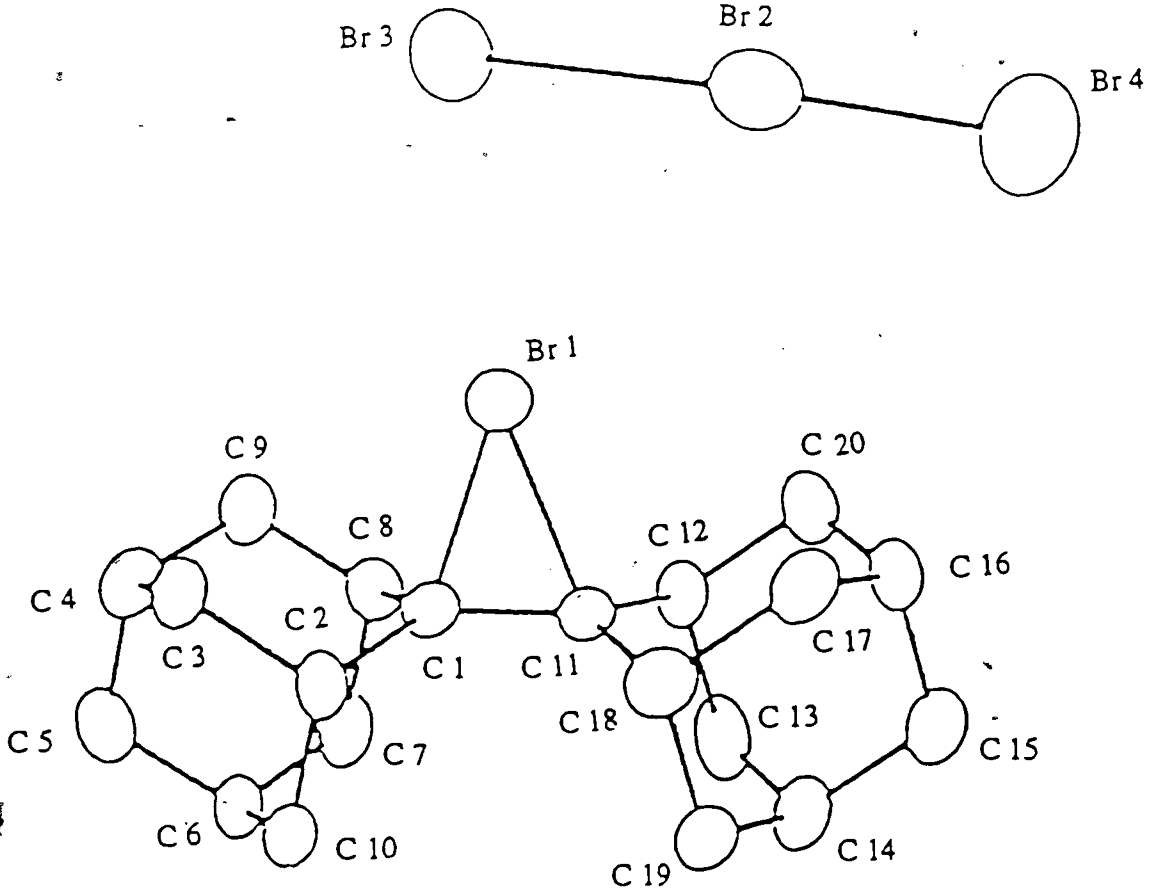
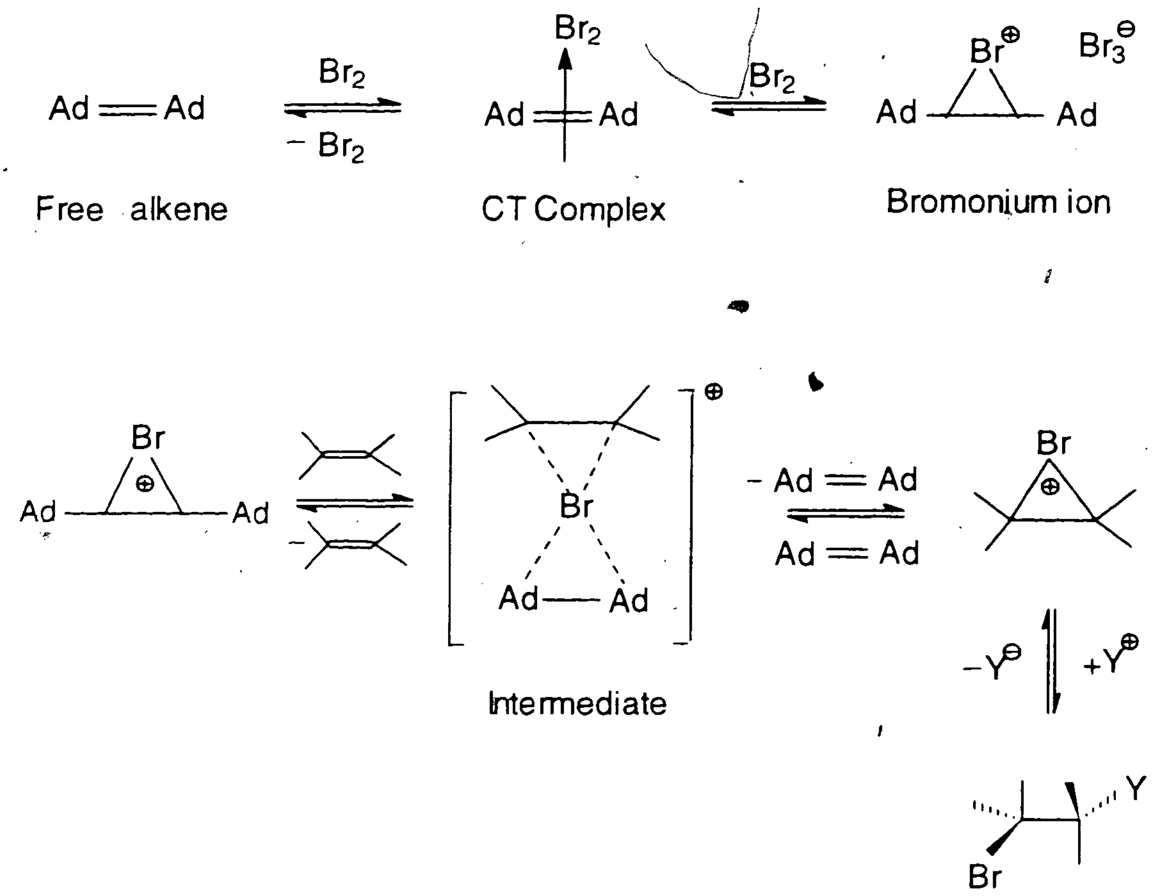


Figure 1.1 Molecular structure of $[Ad_2Br][Br_3]$

The counterion, Br_3^-, which is strongly nucleophilic can attack the Br of the bromonium ion; this mode of reactivity leads to reversal and the formation of bromine and the initial alkene (Ad=Ad).[7] The Br_3^- ion can, however, be replaced by an anion that is non-nucleophilic and prevents self decomposition and which is also non-susceptible to electrophilic attack.[10] The anion, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) is less reactive to electrophilic attack than the widely used PF_6^-, ClO_4^- and BF_4^- anions. The counterion [TFPB] has four aromatic rings that allow extensive electron delocalisation over the entire molecule resulting in marked non-nucleophilicity. Moreover, the presence of two electron withdrawing CF_3 moieties on each ring makes the anion highly resistant to electrophilic attack. This is the reason why compound **3** (Scheme 1.3) possesses unusual stability.

Recently Brown and coworkers have reported the ability of the bromonium ion of adamantylideneadamantane as the triflate salt [(Ad_2Br) (OTf)] to transfer Br^+ to acceptor olefins.[11] Halide transfer in alkenes is believed to occur via a charge transfer intermediate as indicated in Scheme 1.4. In view of the ability of $[Ad_2Br]^+$ to transfer Br^+ to olefins and the isolobal relationship between CH_2 and organometallic fragments, it was anticipated that $[Ad_2Br]^+$ would transfer Br^+ to organometallic molecules. We, accordingly, decided to isolate and structurally characterize the bromonium ion derivatives of some of the group 8 metal carbonyls as the TFPB {tetrakis[3,5-bis(trifluoromethyl)phenyl]borate} salts.[7, 10, 11]

The group 8 metal carbonyls studied were $Os(CO)_5$ and $M_3(CO)_{12}$ (M = Ru, Os). The latter complexes have the triangular arrangement shown in Scheme 1.1 and are thus isolobal analogues of cyclopropane. It was important to compare the similarity or diversity of the bromonium ion structures of these metal complexes studied. The trinuclear clusters were



Scheme 1.4 Mechanism showing halide transfer.

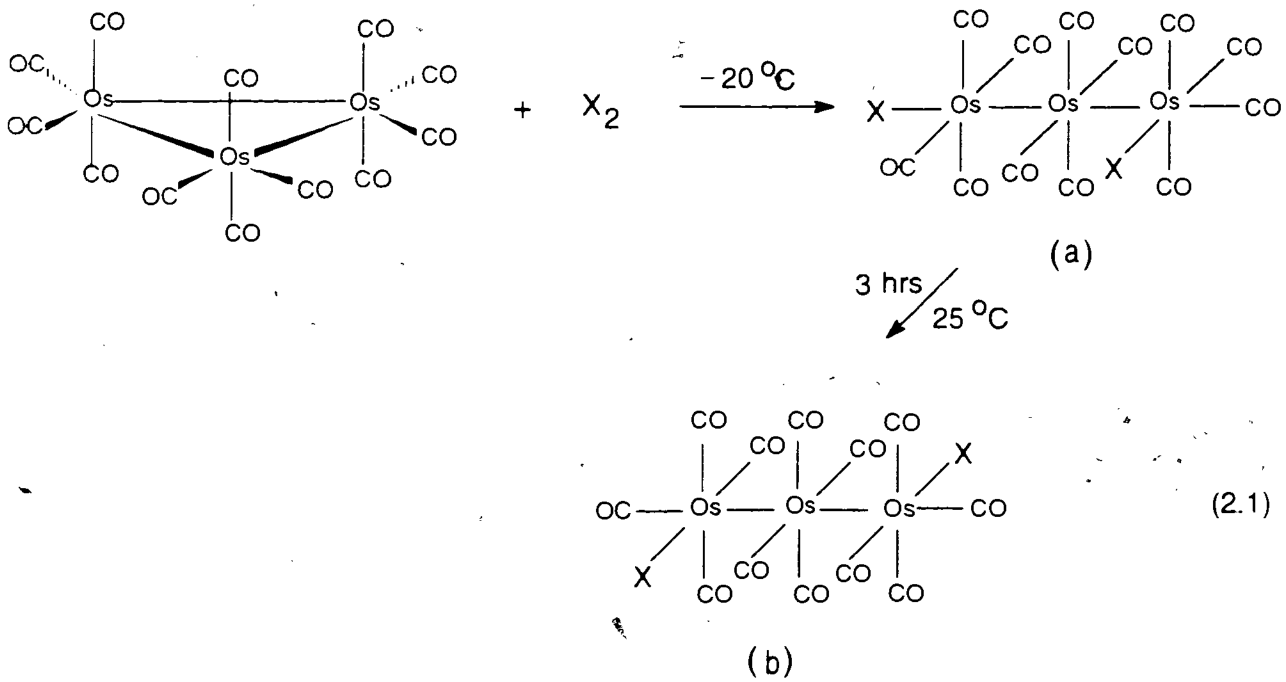
first studied since previous work by Pomeroy and coworkers indicated that it would be a fruitful area of endeavor.[12] The preparation and characterization of these bromonium ion complexes *i.e.*, $[M_3(CO)_{12}Br]^+$ and $[Os(CO)_5Br]^+$ are described in Chapters 2 and 3, respectively. Also described in Chapter 3 are the reactions of Br_2 with $Os(CO)_5$ and $Os(CO)_4(PMe_3)$. It should be pointed out that the organometallic compounds investigated in this study (*i.e.*, $M_3(CO)_{12}$, and $Os(CO)_5$) are not isolobal analogues of ethylene. Therefore, a metal-carbene complex (*e.g.*, $(OC)_4WCPh_2$) which is an isolobal analogue of C_2H_4 would be expected to give a stable bromonium derivative when reacted with $[Ad_2Br][TFPB]$.

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF $[M_3(CO)_{12}Br][TFPB]$ (M= Ru, Os) AND $Ru_3(CO)_{12}Br_2$

2.1 Introduction

The initial reaction of $Os_3(CO)_{12}$ with halogens is the cleavage of one osmium-osmium bond resulting in the formation of $Os_3(CO)_{12}X_2$ (X = Cl, Br, I) (Eq. 2.1, X = Br), but if the reactions are allowed to continue beyond this stage, dinuclear derivatives are obtained.[13] The structure of *cis,cis*-$Os_3(CO)_{12}I_2$ has been established by X-ray



(2.1)

(a) *cis,trans*-$Os_3(CO)_{12}Br_2$

(b) *cis,cis*-$Os_3(CO)_{12}Br_2$

crystallography.[14] The detailed mechanism of the reaction of $Os_3(CO)_{12}$ with halogens is not well understood and has been previously described as complicated.[13] Pomeroy and coworkers have shown that the reaction of iodine with $Os_3(CO)_{12}$ proceeds via the $[Os_3(CO)_{12}(I)]^+$ cation, and it was suggested that bromination and chlorination of $Os_3(CO)_{12}$ proceeded through similar intermediates that have very short lifetimes.[12] The first observable product (by ^{13}C NMR spectroscopy) in the bromination of $Os_3(CO)_{12}$ in CD_2Cl_2/CH_2Cl_2 at -20 °C is *cis,trans*-$Os_3(CO)_{12}Br_2$ (**a** in Eq. 2.1) which in solution at room temperature isomerizes over 3 hours to *cis,cis*-$Os_3(CO)_{12}Br_2$ (**b** in Eq. 2.1).[12]

The halogenation of the ruthenium analogue, $Ru_3(CO)_{12}$ (which is isostructural to $Os_3(CO)_{12}$), has been reported to yield $Ru_3(CO)_{12}X_6$, $Ru_2(CO)_6X_4$ and *cis*-$Ru(CO)_4X_2$.[15] In this chapter we report a reinvestigation of this reaction where it was found that the first detectable product in the reaction of $Ru_3(CO)_{12}$ with Br_2 is the previously unknown *cis,cis*-$Ru_3(CO)_{12}Br_2$. It has been reported that the iodination of $Fe_3(CO)_{12}$ gives *cis*-$Fe(CO)_4I_2$ and *trans,trans*-$Fe_2(CO)_8I_2$ in extremely low yield (~2%).[16] The reaction of $Fe_3(CO)_{12}$ with $[Ad_2Br]^+$ has also been investigated in this study.

Brown and coworkers have reported that the bromonium ion of adamantylideneadamantane (*i.e.*, $[Ad_2Br]^+$), as the triflate salt, can transfer Br^+ to acceptor olefins.[11] Given this information, and that $M_3(CO)_{12}$ is isolobal with cyclopropane it was thought that $[Ad_2Br]^+$ could transfer a Br^+ to $M_3(CO)_{12}$ (M = Os, Ru) yielding $[M_3(CO)_{12}Br]^+$ as isolable salts. An initial study by Dr. Weibin Wang revealed that the reaction of $[Ad_2Br]^+$ with $Os_3(CO)_{12}$ does indeed yield bromoniumdodecacarbonyltriosmium (+1) ion, $[Os_3Br]^+$, as the TFPB salt, (TFPB = $B[3,5\text{-}(CF_3)_2C_6H_3]_4$). The product was isolated as a pale-yellow, air-stable, crystalline solid. In this chapter, the use of the bromonium ion reagent to prepare the $[M_3(CO)_{12}Br]^+$ (M = Os, Ru) ions and the determination of their crystal structures is reported along with the reactivity of $[M_3(CO)_{12}Br]^+$ with $[Et_4N]Br$ or $[Et_4N]Br_3$.

The results of this chapter have recently been published as a communication.[17]

2.2 Results and Discussion

2.2.1 Preparation of the $[M_3(CO)_{12}Br]^+$ (M = Ru, Os) Ions

The preliminary study by Dr. Weibin Wang indicated the formation of a pale yellow compound, $[Os_3(CO)_{12}Br][TFPB]$ (**2.2**), from $Os_3(CO)_{12}$ and $[Ad_2Br][TFPB]$. This result was confirmed by repeating the reaction of $Os_3(CO)_{12}$ with $[Ad_2Br]TFPB$ using identical reaction conditions (2.5 h, 25 °C) as employed previously. Similarly, the orange compound, $[Ru_3(CO)_{12}Br][TFPB]$ (**2.1**) was prepared from the reaction of $Ru_3(CO)_{12}$ and $[Ad_2Br][TFPB]$ in CH_2Cl_2 (2 h, 0 °C). Both **2.1** and **2.2** are thermally and air stable.

2.2.2 Structures of $[M_3(CO)_{12}Br]^+$ Ions

The molecular structures of **2.1** and **2.2** were determined using X-ray crystallography by Dr. Raymond Batchelor and Dr. Weiben Wang.

Structure of $[Ru_3(CO)_{12}Br]$ [TFPB] (2.1)

The molecular structure of the cation (**2.1**) is shown in Figure 2.1; selected bond lengths and bond angles are listed in Table 2.1. The molecular structure of **2.1** consists of a bent chain of three ruthenium atoms [(Ru(1)Ru(2)Ru(3) = 157.19 (4) °], one Ru-Ru bond of which is bridged by the bromonium ion. The Ru atom not bound to the bromine atom has five carbonyls coordinated to it. The lack of any bridging carbonyl is evident from the Figure

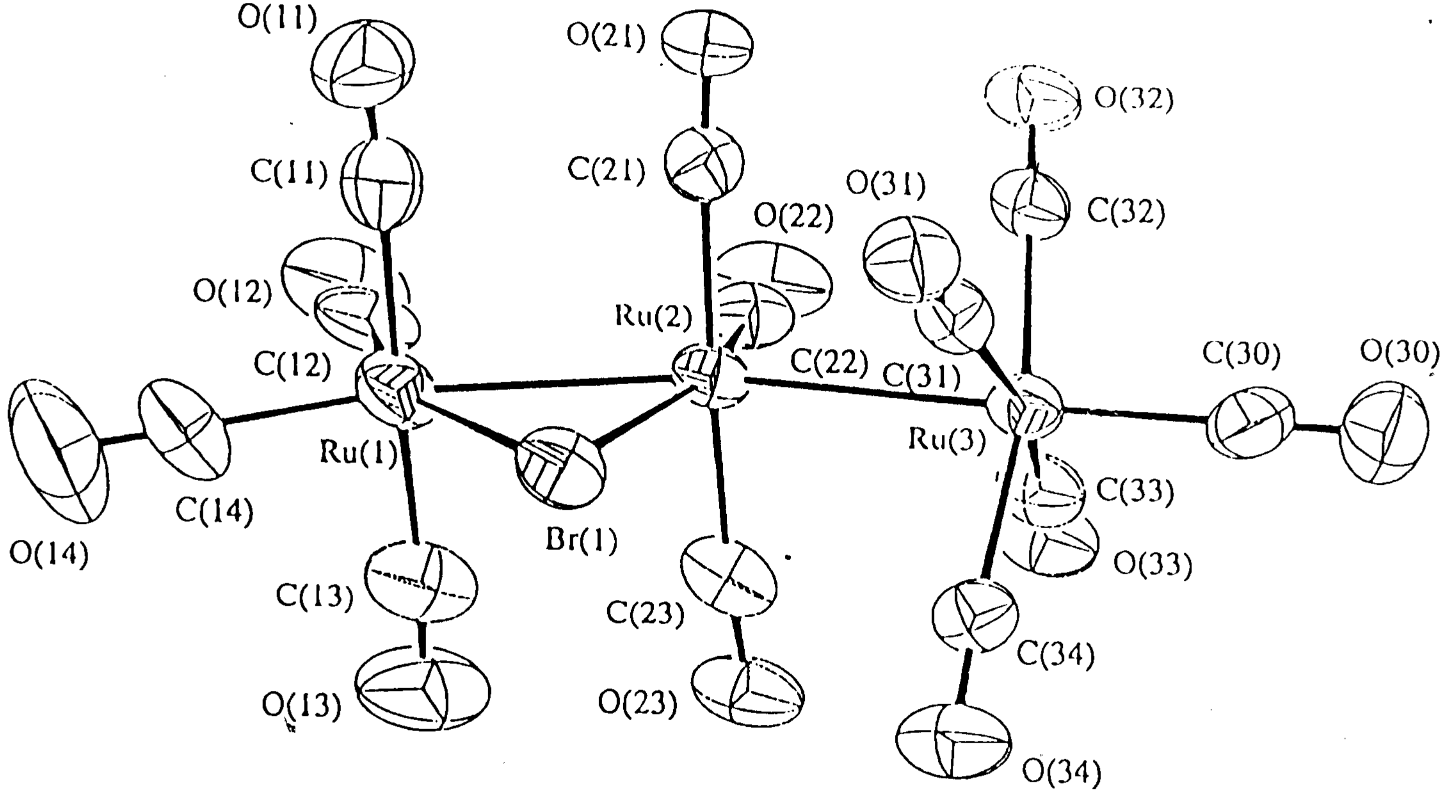


Figure 2.1 Molecular structure of $[Ru_3(CO)_{12}Br][TFPB]$ (2.1).

Table 2.1 Selected bond lengths (Å) and bond angles (deg) for $[Ru_3(CO)_{12}Br][TFPB]$

Bond Lengths (Å)	
Ru(1) - Ru(2)	2.8067(14)
Ru(2) - Ru(3)	2.8907(14)
Ru(1) - Br	2.5428(15)
Ru(2) - Br	2.5611(13)
Ru - C (range)	1.855(11) - 1.992(9)
C - O (range)	1.098(12) - 1.142(18)

Bond Angles (deg)	
Ru(1) - Ru(2) - Ru(3)	157.57(7)
Ru(1) - Ru(2) - Br	56.47(7)
Ru(1) - Br - Ru(2)	66.69(7)
Ru(2) - Ru(1) - Br	56.84(6)
Ru(3) - Ru(2) - Br	101.10(7)

2.1. An electron count at each metal center indicates that the $Ru(CO)_5$ moiety is an 18-electron species, and thus the metal-metal bond involving the Ru atom of this fragment is an unusual donor-acceptor (dative) metal-metal bond.[18] It is the first example of a molecular structure where $Ru(CO)_5$ acts as a donor ligand, although $Os(CO)_5$ is known to act as a two electron donor ligand in such complexes as $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$.[18a, 19] The cation **2.1** may therefore be considered as derived from $[Ru_2(\mu\text{-}Br)(CO)_8]^+$ in which one of the carbonyl ligands has been replaced by $Ru(CO)_5$. This indicates that $[Ru_2(\mu\text{-}Br)(CO)_7]^+$ unit in **2.1** is an extremely strong acceptor unit. Since $Ru(CO)_4$ is isolobal with CH_2,[2] the $[Ru_2(\mu\text{-}Br)(CO)_8]^+$ ion is therefore an organometallic analogue of the classical bromonium ion of ethylene, $[C_2H_4Br]^+$. The Ru(μ-Br)Ru unit in the cation may be considered as consisting of either a closed three-center, two-electron RuBrRu bond, or comprised of two two-center, two-electron Ru-Br bonds, in each case augmented by a Ru-Ru bond. The Ru-Ru bond length of the Ru(μ-Br)Ru unit is short at 2.8067(14) Å. The unbridged, Ru-Ru dative bond is more typical of Ru-Ru bonds at 2.8907(14) Å. For example, in $Ru_3(CO)_{12}$ the average Ru-Ru bond length is 2.8515(4) Å;[20] in $Ru_3(CO)_{12}Br_2$, it is 2.8823(4) Å.[17, 20] The Ru-Br distance of 2.5519(14) in **2.1** compares well with that found in $Ru_3(CO)_{12}Br_2$ (2.5564(5) Å) described below.

Structure of $[Os_3(CO)_{12}Br][TFPB]$ (2.2)

The molecular structure of cation (**2.2**) is shown in Figure 2.2 and selected bond lengths and bond angles of the structure are listed in Table 2.2. The $[Os_3Br]^+$ unit is a nearly planar four membered ring with only two Os-Os bonds. One Os-Os bond [2.952(3) Å] is slightly shorter than the other Os-Os bond [2.964(3) Å]; the difference in the bond lengths is attributed to packing forces and is barely significant at 4σ (σ is the standard deviation in the lengths). These bond lengths are longer than the average Os-Os bond distance in $Os_3(CO)_{12}$ [2.877(3) Å].[21] In *cis,cis*-$Os_3(CO)_{12}I_2$ the Os-Os bonds are crystallographically equivalent at 2.935(2) Å.[14] In the cation **2.2** the third Os-Os vector is completely nonbonding at a distance of 4.011(3) Å. The Os-Br distance of 2.568(4) Å in **2.2** is shorter than the Os-Br (terminal) distance of 2.592(3) Å in $Os_3(CO)_{10}Br_2[P(OMe)_3]_2$,[22] but is longer than those found in $[Os_2Br_{10}]^{2-}$ (average Os-Br (terminal) = 2.454(5) Å)[23] and $OsBr_3(PPh_3)_2(CH_3CN)$ (average

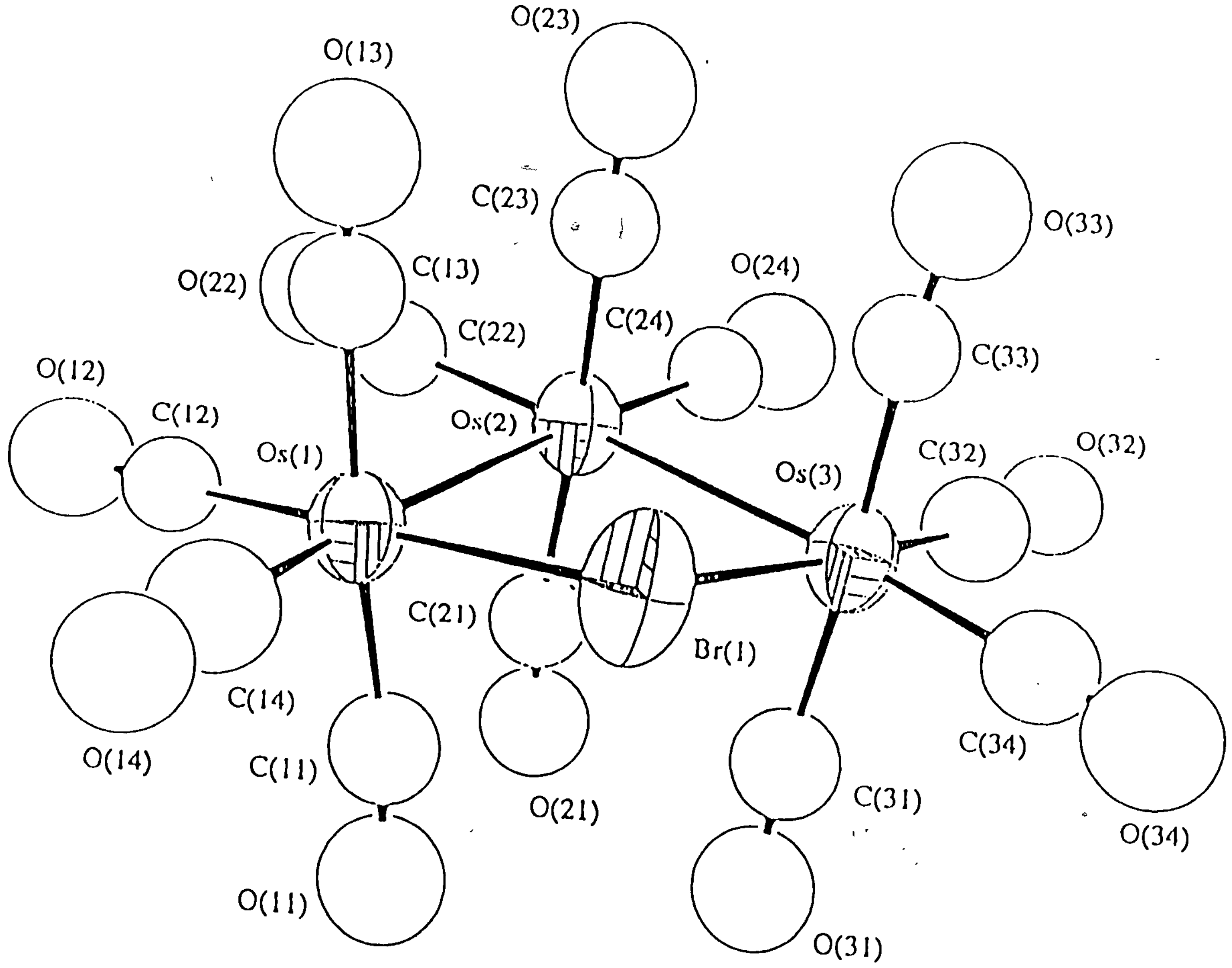


Figure 2.2 Molecular structure of $[Os_3(CO)_{12}Br][TFPB]$ (2.2).

2.493(1) Å).[23] Inasmuch as $Os(CO)_4$ is isolobal with CH_2,[2] the structure is an organometallic model for that of $[C_3H_6Br]^+$, the bromonium ion adduct of cyclopropane. The structure of the latter cation is unknown, but the geometry most favoured does, indeed, have a configuration analogous to that found for **2.2**.[24]

Table 2.2 Selected bond lengths (Å) and bond angles (deg) for $[Os_3(CO)_{12}Br][TFPB]$

Bond Lengths (Å)			
Os(1) - Os(2)	2.952(3)	(C - O)	1.07(4)-1.18(4)
Os(2) - Os(3)	2.964(3)	$(C - O)_{av}$	1.13(3)
Os(1) - - Os(3)	4.011(3) (non-bonding)	(Os - C)	1.89(4)-1.99(4)
Os(1) - Br	2.568(4)	$(Os - C)_{av}$	1.93(2)
Os(3) - Br	2.567(4)		

Bond Angles (deg)	
Os(1) - Os(2) - Os(3)	85.37(6)
Os(1) - Br - Os(3)	102.7(1)
Os(2) - Os(1) - Br	85.0(1)
Os(2) - Os(3) - Br	84.8(1)

2.2.3 Spectroscopic properties of $[M_3(CO)_{12}Br]$ ions

The infrared spectra (carbonyl region) of **2.1** and **2.2** in CH_2Cl_2 are shown in Figure 2.3. The spectra exhibit CO stretching bands attributable only to terminal carbonyls consistent with the solid-state structures.

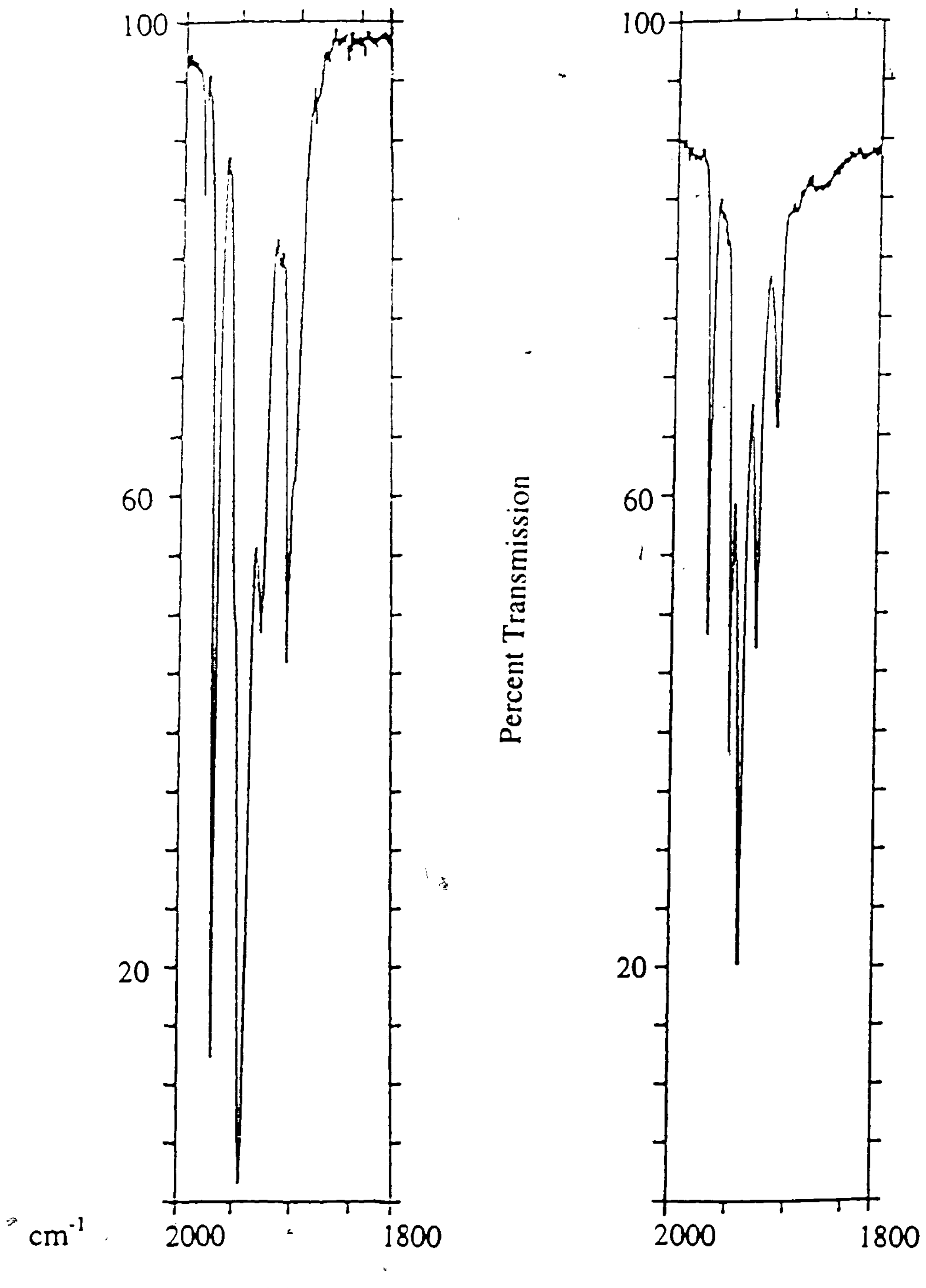


Figure 2.3 IR spectrum (carbonyl region) of (a) $[Ru_3(CO)_{12}Br]^+$ (**2.1**) and (b) $[Os_3(CO)_{12}Br]^+$ (**2.2**) in CH_2Cl_2.

The ^{13}C NMR spectrum of **2.1** (~30-40% ^{13}CO enriched) (Figure 2.4) in CH_2Cl_2/CD_2Cl_2 at 0 °C indicates that the predominant form of the cation in solution also has the same structure as found in the solid state and with rigid carbonyls. The expected number of signals for **2.1** is seven in the ratio of 1:4:2:1:2:1:1 and this is observed in the ^{13}C NMR spectrum of the ion. The signal at δ 175.9 can be assigned to the carbonyl **a** (Figure 2.4) on the donor Ru atom and which is trans to the donor-acceptor bond. It has previously been established that resonances of this type (*i.e.*, trans to dative metal-metal bonds) occur at high field.[18a, 25, 26] The most intense resonance at δ 190.4 can be unambiguously assigned to the four radial carbonyls on the donor $Ru(CO)_5$ fragment (*i.e.*, the carbonyls labeled **b**). Carbonyls **c** and **e** should have equal intensity. Based on this assumption, the signal at δ 189.2 and 200.1 can be assigned to carbonyls **c** and **e**. It is tentatively assumed that the axial carbonyls **e** bound to the Ru atom not attached to the $Ru(CO)_5$ donor group give rise to the downfield resonance (*i.e.*, at 200.1 ppm) while the carbonyls **c** which are bound to the central atom are assigned to the upfield resonance at 189.2 ppm. The remaining three resonances at δ 178.9, 188.1, 196.1 of intensity one can then be assigned to carbonyls **d** (trans to bromine and bound to the central Ru atom and hence furthest upfield), **f** (trans to bromine but on the terminal Ru atom and hence downfield) and **g** (cis to bromine and on the terminal Ru atom and hence furthest downfield). A more definitive assignment is not possible at this time.

On cooling the sample to -60 °C the ^{13}C NMR spectrum of **2.1** also exhibited four minor resonances at δ 196.3, 192.9, 188.1, and 173.7 attributed to the presence of a second form of **2.1** in solution (Figure 2.4). On warming to 0 °C, these minor peaks (marked with an asterisk) collapsed to the baseline indicative of carbonyl exchange in the second isomer. At

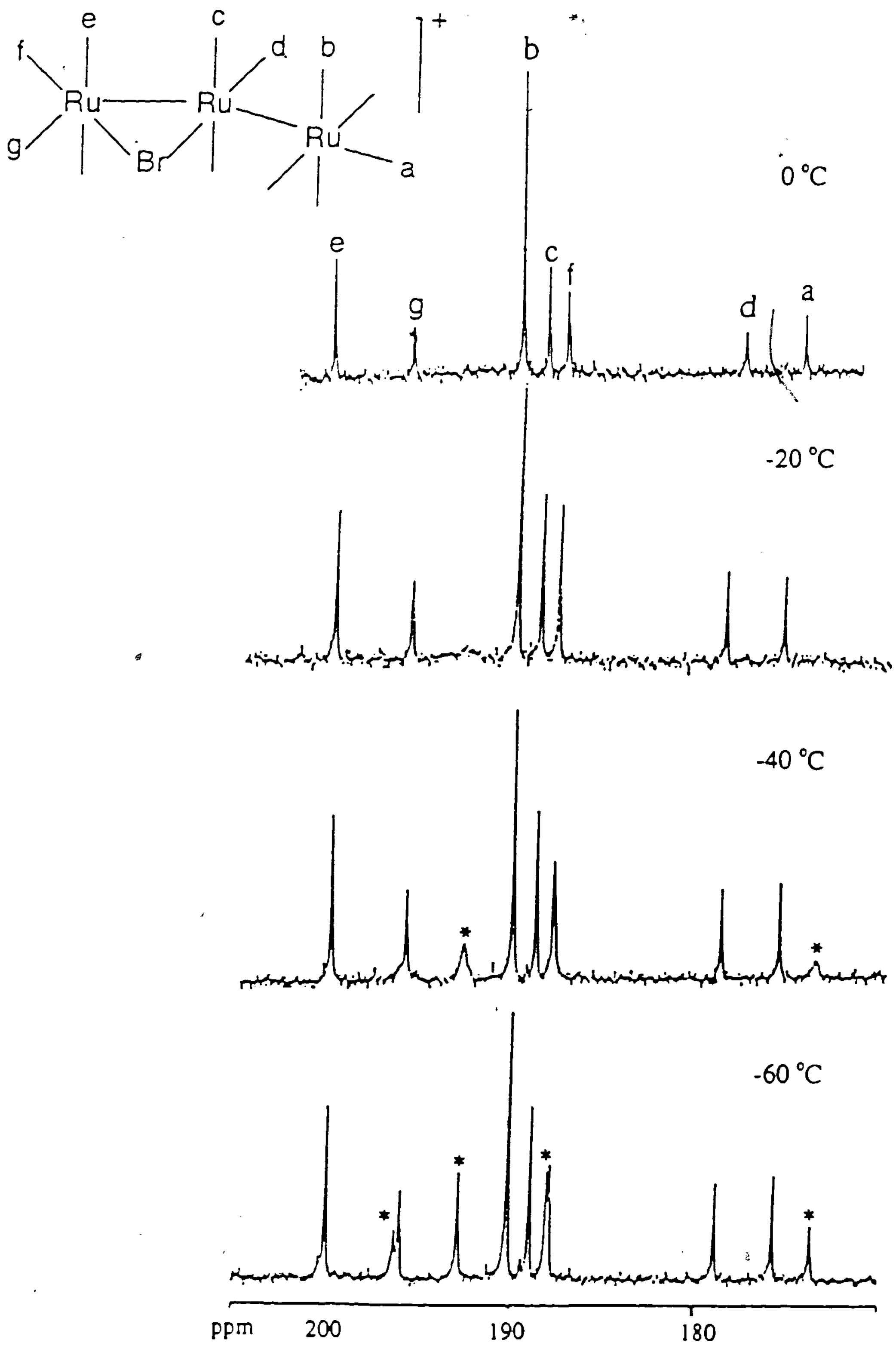


Figure 2.4 Variable temperature ^{13}C NMR of [Ru$_3$(CO)$_{12}$Br][TFPB] (**2.1**) in CH$_2$Cl$_2$/CD$_2$Cl$_2$ (3:1); the signals marked with an asterisk are due to a minor isomer of **2.1**.

present the structure of the second isomer is unknown.

The ^{13}C NMR spectrum of the cation **2.2** (~30% ^{13}CO enriched) in CH_2Cl_2/CD_2Cl_2 is shown in Figure 2.5. The major signals observed are consistent with one form in solution which has the same structure as found in the solid state. The extremely weak signals in the spectrum cannot be assigned at this time but they are not due to $Os_3(CO)_{12}$. The spectral assignment of **2.1** is based on the signal intensities and the characteristic chemical shift region of certain types of carbonyls.[27] The signal at δ 177.0 of greatest intensity can be unambiguously assigned to the axial carbonyls a on the two Os atoms associated with the Br

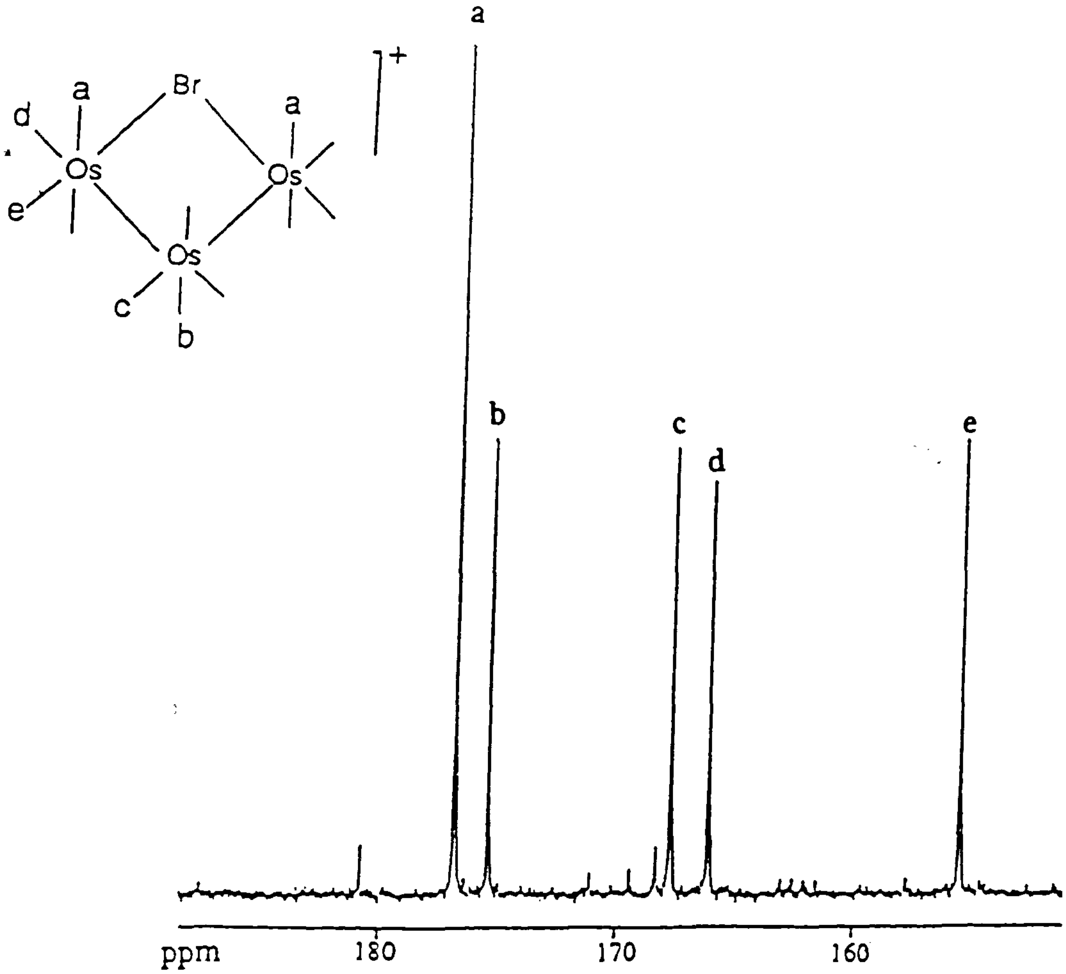


Figure 2.5 ^{13}C NMR spectrum of $[Os_3(CO)_{12}Br][TFPB]$ at 25 °C in CH_2Cl_2/CD_2Cl_2

bridge. The other four resonances have almost the same intensity. The highest field signal at δ 155.1 is assigned to the two CO groups **e** trans to Br atom. It has been previously observed that the resonances trans to electronegative ligands such as Br are shifted upfield.[26] Assignment of the signals attributable to carbonyls **b**, **c** and **d** is less certain. If, however, it is assumed that the ^{13}C resonances due to the axial carbonyls are to lower field than those of the equatorial carbonyls, and that the signals associated with an osmium atom (bound to a halogen atom) are shifted upfield then the assignment is as follows: δ 175.4 due to **b**, 167.7 due to **c**, and 166.0 due to **d**.[12, 27b]

2.2.4 Reactions of $[M_3(CO)_{12}Br]^+$ (M = Ru, Os) with $[Et_4N]Br$ or $[Et_4N][Br_3^-]$

The IR spectrum of the products obtained from the treatment of **2.1** with either bromide or tribromide ions is different from that of *cis,cis*-$Ru_3(CO)_{12}Br_2$ (reported below). The products of the reaction have not, as yet, been completely characterized. The ^{13}C NMR spectra of the reaction mixture at various temperatures are shown in Figure 2.6. The spectra are consistent with the presence of more than one product. Warming of the sample to 20 °C caused a nearly complete disappearence of the signals associated with one of the products. From the ^{13}C NMR and IR data, the initial products of the reaction of **2.1** with $[Et_4N]Br$ are tentatively identified as $(OC)_4Ru(\mu\text{-}Br)Ru(CO)_3Br$ and $Ru(CO)_5$ (*i.e.*, displacement of the weak donor ligand $Ru(CO)_5$ from **2.1** by Br^-). The $Ru(CO)_5$ loses CO to give $Ru_3(CO)_{12}$ (which is known to readily occur under the reaction conditions).[28] The CO liberated then converts $(OC)_4Ru(\mu\text{-}Br)Ru(CO)_3Br$ to *cis,cis*-$Ru_2(CO)_8Br_2$ which on warming in solution to 20 °C converts to *trans,trans*-$Ru_2(CO)_8Br_2$. Some of these conclusions are based on the literature data given in Table 2.3. The $(OC)_4Ru(\mu\text{-}Br)Ru(CO)_3Br$ is expected to have five

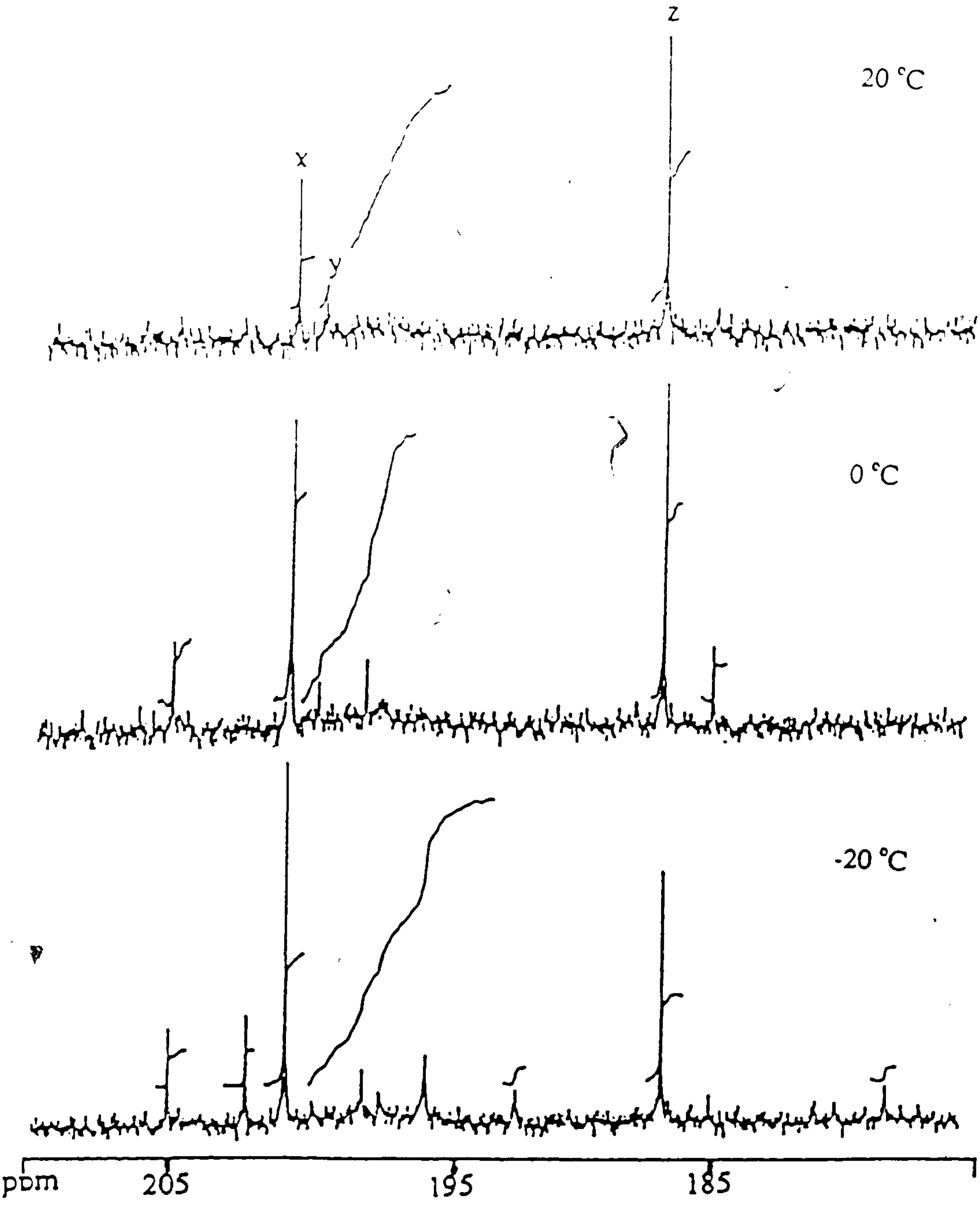


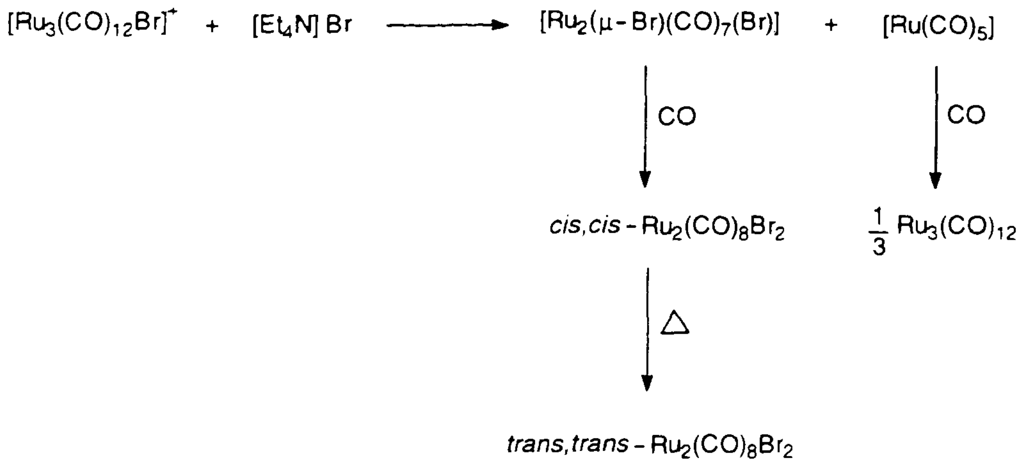
Figure 2.6 ^{13}C NMR spectra of $[Ru_3(CO)_{12}Br]^+$ with $[Et_4N]Br$ at variable temperature in CH_2Cl_2/CD_2Cl_2. For assignments x, y and z see Table 2.3.

Table 2.3. Literature and observed data for Ru-Carbonyl compounds

	ν(CO),[a] cm^{-1}	^{13}C NMR[c] ppm	Observed ^{13}C NMR[c] ppm	
$Ru(CO)_5$	2036.5[28] 2001.5	200.6	200.66	(**x**)
$Ru_3(CO)_{12}$	2059.5[29, 30] 2028.5 2011.0	199.7	199.61	(**y**)
$Ru_2(CO)_8Br_2$	2083.0[b, 31] 2112.5 2046.0	–	186.59,	(**z**)

[a] CH_2Cl_2 solution. [b] Similar to the data of $Os_2(CO)_8Br_2$.
[c] Recorded at 100.6 MHz, CD_2Cl_2/CH_2Cl_2 solution.

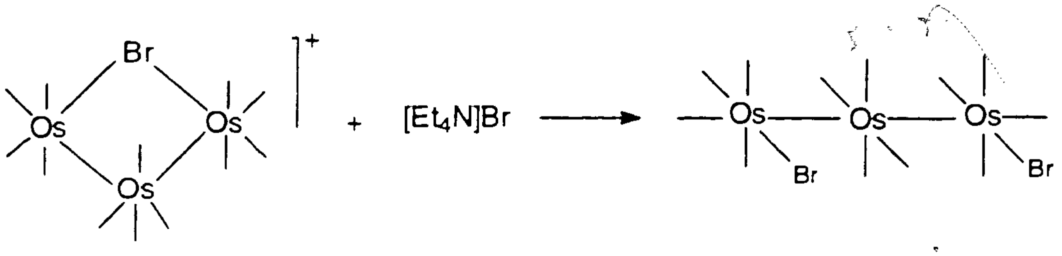
^{13}C NMR resonances in 2:2:1:1:1 ratio and a number of weak signals are observed including one at a highfield as expected for a CO trans to a Br atom at δ 202.03, 197.0, 195.24, 191.81, 177.69 in a spectrum at -20 °C. The *cis,cis*-$Ru_2(CO)_8Br_2$ molecule is expected to give three ^{13}C NMR resonances in 2:1:1 ratio and three are observed in approximate correct ratio in the spectrum at 0 °C; the chemical shifts are δ 205.16, 197.86, 184.49. In the spectrum at 20 °C there are three signals one of which (at δ 200.66) is assigned to $Ru(CO)_5$. The signal at δ 199.61 is assigned to $Ru_3(CO)_{12}$ (which is known to be highly fluxional in solution at room temperature). The remaining signal at δ 186.59 is assigned to *trans,trans*-$Ru_2(CO)_8Br_2$ (which should have one ^{13}C NMR signal in the high field region due to the presence of the Br atom). The two strong signals are in ~1:2 ratio as expected from the proposed mechanism. These results are shown in Eq. 2.2. It is planned to study this reaction in more detail in an attempt to further characterize the products.



(2.2)

Such a mechanism would explain how $Fe_2(CO)_8I_2$ is formed from the reaction of $Fe_3(CO)_{12}$ and I_2. It is expected that $Fe_2(CO)_8I_2$ would react with excess I_2 to yield *cis*-$Fe(CO)_4I_2$.[16] The addition of $[Ad_2Br]$TFPB in $Fe_3(CO)_{12}$ in solution, surprisingly, gave no reaction. There are two possible reasons for this: It may be that the metal atoms in $Fe_3(CO)_{12}$ are protected from attack by the bulky $[Ad_2Br]^+$ ion by the surrounding carbonyl ligands. It has been previously found that whereas $SnCl_4$ reacts readily with $M_3(CO)_{12}$ (M = Ru, Os) in benzene at room temperature to yield *cis,trans*-$M_3(CO)_{12}(Cl)(SnCl_3)$, no reaction takes place between $Fe_3(CO)_{12}$ and $SnCl_4$.[32] A second reason is that $Fe_3(CO)_{12}$ may be a poorer Br^+ acceptor than Ad_2 and hence transfer does not take place. It is known that basicity increases on going from the first row transition metal complex to the third row analogue.

In contrast to **2.1**, **2.2** in solution reacts immediately with $[Et_4N]Br$ or $[Et_4N]Br_3$ at room temperature to yield *cis,cis*-$Os_3(CO)_{12}Br_2$ (Eq. 2.3), that is, the product is not the *cis,trans*-isomer. For this reason, **2.2** is *not* an intermediate in the bromination of $Os_3(CO)_{12}$. As mentioned in the introduction, *cis,trans*-$Os_3(CO)_{12}Br_2$ is the first observable product in the bromination and this isomer slowly isomerizes to the cis,cis form in solution at room temperature.



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2.3 Synthesis and Characterization of $Ru_3(CO)_{12}Br_2$ (2.3)

2.3.1 Preparation of $Ru_3(CO)_{12}Br_2$ (2.3)

Dropwise addition of Br_2 (CH_2Cl_2 solution) to a CH_2Cl_2 solution of $Ru_3(CO)_{12}$ maintained at 0 °C gave an orange solution from which the orange compound, $Ru_3(CO)_{12}Br_2$ (**2.3**) was isolated in good yield (60%).

2.3.2 Structure of $Ru_3(CO)_{12}Br_2$ (2.3)

The molecular structure of **2.3** is shown in Figure 2.7. Selected bond lengths and bond angles are listed in Table 2.4. The molecular structure of **2.3** has a crystallographically imposed two-fold axis that passes through Ru(2) (the mid point between C(21) and C(22)); the Ru-Ru-Ru angle is therefore 180°. It consists of a linear chain of three ruthenium atoms bonded to each other by unbridged Ru-Ru bond. The spine of molecule **2.3** comprises a linear O-C-Ru-Ru-Ru-C-O sequence. The two bromide ligands bonded to the terminal

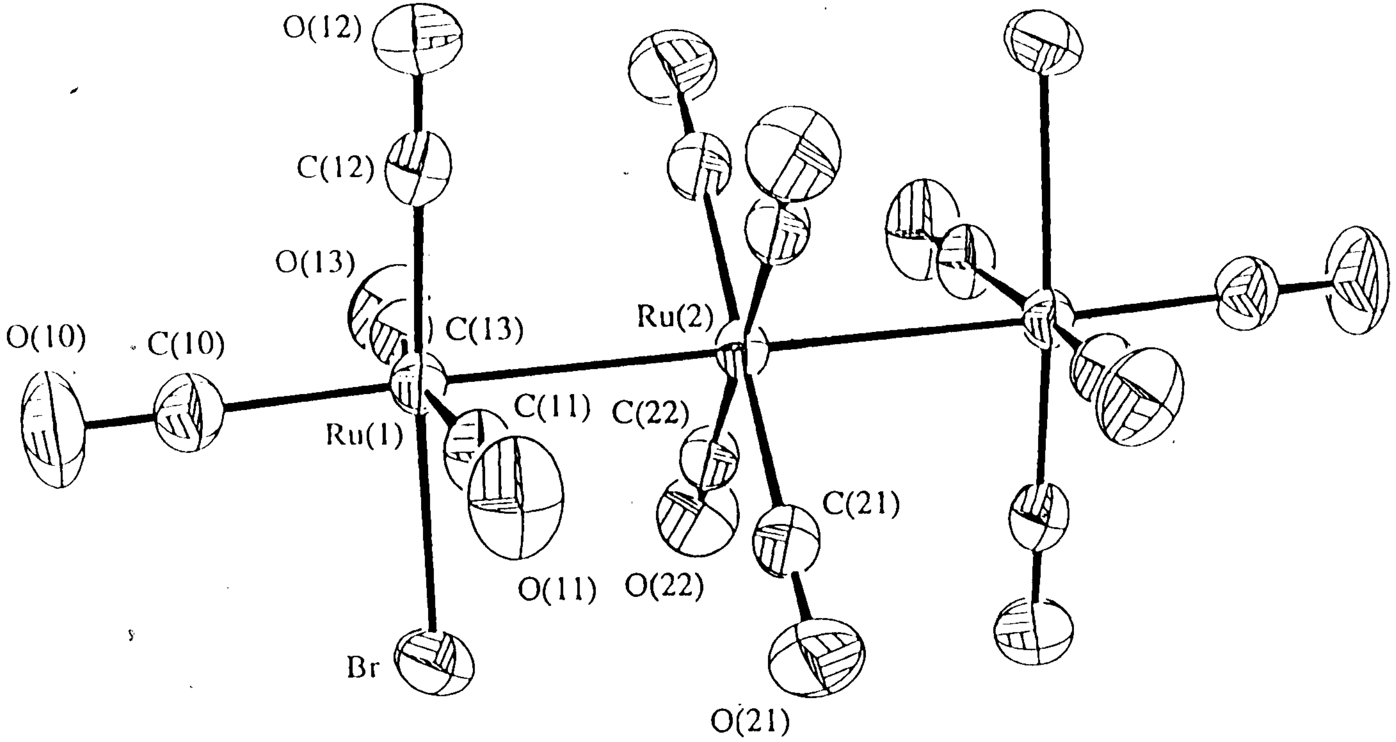


Figure 2.7 Molecular structure of *cis,cis*-$Ru_3(CO)_{12}Br_2$ (**2.3**).

Table 2.4 Selected bond lengths (Å) and bond angles (deg) for $Ru_3(CO)_{12}Br_2$

Bond Lengths (Å)	
Ru(1) - Ru(2)	2.8823(4)
Ru(1) - Br	2.5564(5)
Ru - C	1.894(4) - 1.977(3)
C - O	1.094(5) - 1.125(5)

Bond angles (deg)	
Ru(2) - Ru(1) - C(10)	178.06(12)
Ru(2) - Ru(1) - C(11)	85.79(13)
Ru(2) - Ru(1) - C(13)	84.70(12)
Br - Ru(1) - C(10)	87.46(11)
Br - Ru(1) - C(11)	87.46(11)
Br - Ru(1) - C(12)	176.71(13)
Br - Ru(1) - C(13)	88.14(10)

ruthenium atoms occupy positions as far away from each other as possible; they have a cis,cis arrangement with respect to the Ru-Ru chain. Four radial carbonyl ligands are bound to the central ruthenium atom. Each ruthenium atom in the chain obeys the 18-electron rule. The Ru-Ru distance in $Ru_3(CO)_{12}Br_2$ of 2.8823(4) Å may be compared to the average Ru-Ru distance in $Ru_3(CO)_{12}$ of 2.8515(4) Å,[20] which is taken as a normal Ru-Ru single bond distance. The structure of **2.3** is isostructural with that of $Os_3(CO)_{12}I_2$ although the Os-Os bond at 2.935(2) Å in the latter molecule is significantly longer than the Ru-Ru bond length in **2.3**.

2.3.3 Spectroscopic Properties of 2.3

The infrared spectrum of *cis,cis*-$Ru_3(CO)_{12}Br_2$ **(2.3)** in CH_2Cl_2 (Figure 2.8) shows three CO-stretching bands. This spectrum is consistent with the solid state structure; it is also similar to the IR spectrum of *cis,cis*-$Os_3(CO)_{12}Br_2$.[12] The small difference in the CO stretching frequencies may be attributed to the change in the metal center.

The ^{13}C NMR spectrum of ^{13}C-enriched (~30-40%) sample of **2.3** in CH_2Cl_2/CD_2Cl_2 at -50 °C is shown in Figure 2.9. The four signals in a 2:2:1:1 ratio are consistent with the solid state structure. It is interesting to note that **2.3** has the cis,cis configuration. For $Os_3(CO)_{12}Br_2$ the cis,trans isomer was formed initially in the reaction of $Os_3(CO)_{12}$ and Br_2, but it isomerized completely in CH_2Cl_2 to the cis,cis form over 3 h.[12] When Br_2 in CH_2Cl_2 was added to $Ru_3(CO)_{12}$ (^{13}CO-enriched) in CD_2Cl_2/CH_2Cl_2 at -50 °C, the first product observed by ^{13}C NMR spectroscopy was *cis,cis*-$Ru_3(CO)_{12}Br_2$ (Figure 2.9). In other words, if the cis,trans-isomer is formed initially it isomerizes rapidly even at -50 °C.

It is also noteworthy that the ^{13}C NMR spectrum of **2.3** indicates equivalence of the radial carbonyls on the central Ru atom which in turn indicates free rotation about the Ru-Ru bonds. The spectral assignment of the ^{13}C NMR signals of **2.3** is quite straightforward and is based on the signal intensities and the chemical shifts of the resonances.[27] The resonance at δ 201.9 of intensity four is assigned to the four radial carbonyls on the central Ru atom since this Ru atom does not have a Br atom directly attached to it (*e.g.*, the ^{13}C NMR resonance of $Ru_3(CO)_{12}$ is at δ 199.7, Table 2.3). As mentioned previously, resonances of CO ligands bound to metal atoms that are also bound to a Br atom are shifted upfield. The resonance at δ 195.1 also of intensity four can therefore be unambiguously assigned to the axial carbonyls **b**

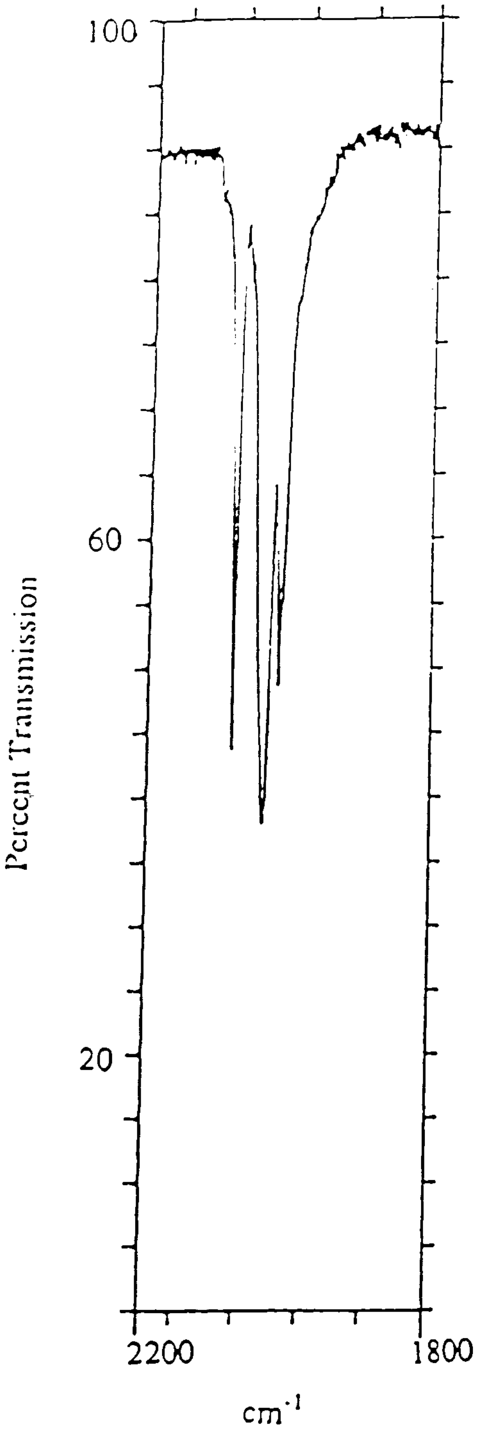


Figure 2.8 IR spectrum (carbonyl region) of *cis,cis*-$Ru_3(CO)_{12}Br_2$ in CH_2Cl_2.

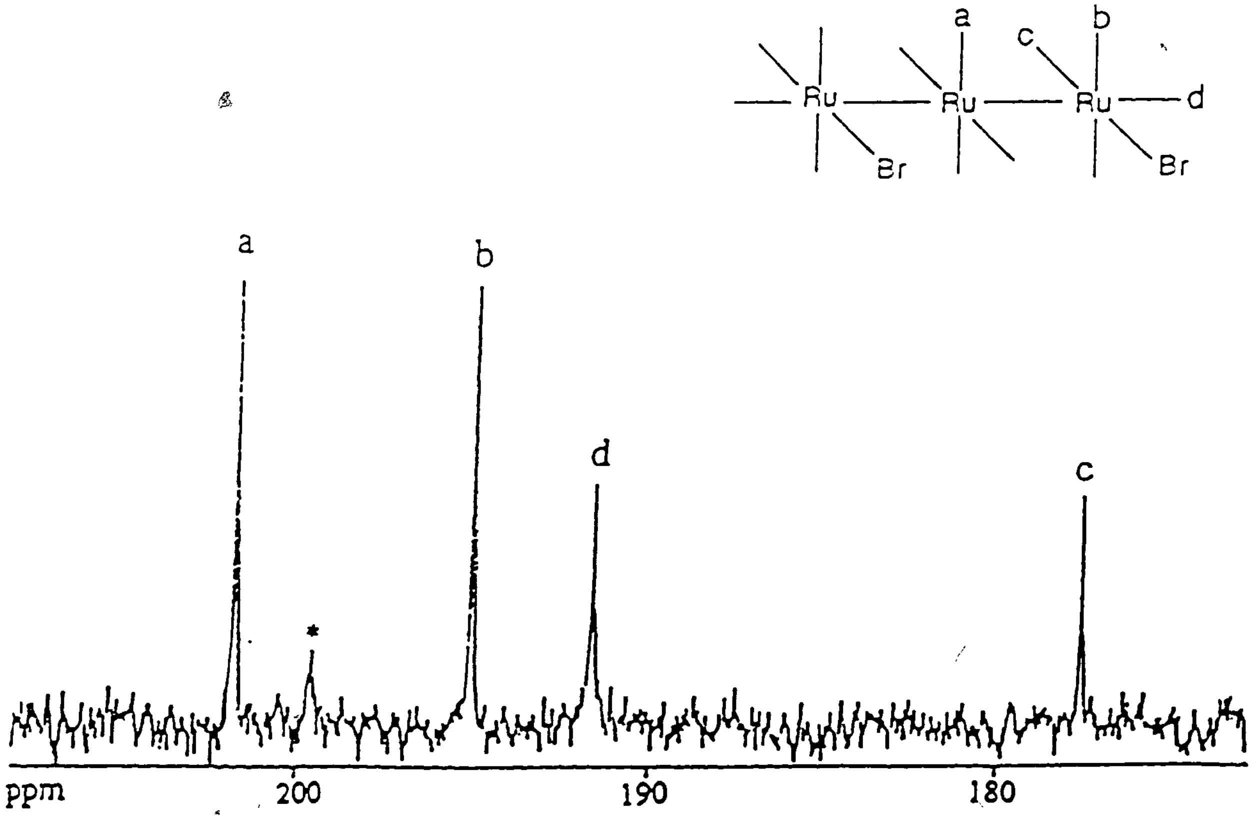


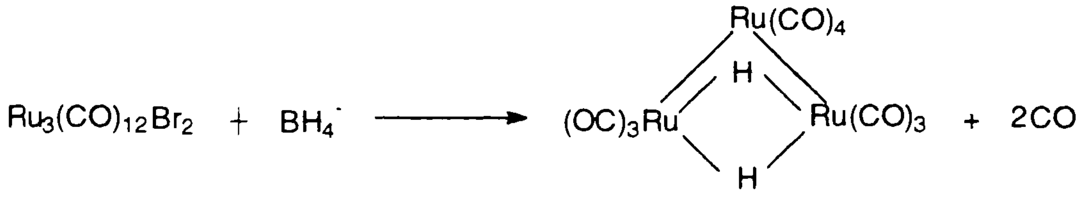
Figure 2.9 The ^{13}C NMR spectrum as obtained by adding Br_2 to $Ru_3(CO)_{12}$ (^{13}CO enriched) in CH_2Cl_2/CD_2Cl_2 at -50 °C. Unreacted $Ru_3(CO)_{12}$ (which is highly fluxional in solution) is marked with an asterisk.

on the outer Ru atoms (which do have a Br atom bound to them). The resonance at δ 177.6 of intensity two can be assigned to the two carbonyls trans to bromine. Finally, the resonance at δ 191.60 is assigned to the two equatorial carbonyls **d**. In the spectrum, a minor signal at δ 199.5 is due to excess $Ru_3(CO)_{12}$ (marked with asterisk).

2.4 Conclusion

The bromonium derivatives of $M_3(CO)_{12}$ with the anion TFPB can be conveniently synthesized from $M_3(CO)_{12}$, (M = Os, Ru) and $[Ad_2Br][TFPB]$ at or below room temperature. This represents the first time where the $[Ad_2Br]^+$ reagent has been used to form bromonium ion derivatives of organometallic complexes. Four important observations have been made with regard to $[M_3(CO)_{12}Br]^+$ ions. First, the Ru and Os cations exhibit markedly different structures in the solid state. Reasons for this intriguing difference are unknown at present. Second, it appears that the **2.1** exists in two isomeric forms in solution; one of which is rigid and the other fluxional. Third, evidence has been presented that **2.1** and **2.2** are *not* intermediates in the respective brominations of $M_3(CO)_{12}$ as originally suggested. Fourth, the spectroscopic studies showed that the reactivity of **2.1** with bromide ion is very different from that of **2.2**. The last reaction will be the subject of further study. Furthermore, the linear triruthenium complex **2.3** has been prepared in which the two bromine atoms occupy cis positions to each other. The cis-trans isomer was not observed in this reaction as it was in the corresponding reaction of $Os_3(CO)_{12}$ and Br_2. Once again, the reason for this difference is unknown at present. It may be that the *cis,trans*-$Ru_3(CO)_{12}Br_2$ isomerizes rapidly at -50 °C or that the reaction of Br_2 with $Ru_3(CO)_{12}$ proceeds by a different mechanism to that of the Os congener.

Compound **2.3** may be a valuable precursor to other triruthenium compounds. For example, the reaction of [BH$_4$]$^-$ may yield the unknown, Ru$_3$(μ-H)$_2$(CO)$_{10}$ (Eq. 2.4). The Os analogue, Os$_3$(μ-H)$_2$(CO)$_{10}$ of this compound is an extremely valuable starting material.[31, 33]



(2.4)

2.5 Experimental

2.5.1 General Methods

The following general procedures were applied to all experimental work reported in this chapter unless otherwise stated. Manipulations of starting materials and products were carried out under an inert atmosphere of nitrogen with the use of Schlenk-tube techniques. The autoclave used was a 200 mL Parr general purpose bomb.

2.5.2 Materials

Hexane was refluxed over potassium, distilled and stored under nitrogen before use. Acetonitrile, methanol and dichloromethane were treated similarly, except CaH$_2$ was used as the drying agent. Petroleum ether was distilled from potassium permanganate. 1,2-dimethoxyethane (DME) was obtained from Aldrich Chemicals Company and was allowed to stand over molecular sieves (type 4A) for several days and then refluxed over potassium and distilled. The solvent was used on the same day to minimize the formation of peroxides. The NMR solvent was CH_2Cl_2/CD_2Cl_2 (3:1) which was stored in a dry box. Carbon-13 CO used in the labeling of complexes with ^{13}CO was obtained commercially from Cambridge Isotope Laboratories. Lithium wire was obtained from Alpha Products. Dodecacarbonyltriosmium ($Os_3(CO)_{12}$) (Oxchem), tetraethylammonium bromide ($[(C_2H_5)_4N]Br$) (Eastman) and bromine (Anachaemia) were also obtained commercially. Dodecacarbonyltriruthenium, $Ru_3(CO)_{12}$ (Alpha), was prepared from $RuCl_3.xH_2O$ by a literature method.[30] The preparation of tetraethylammonium tribromide $[(C_2H_5)_4N]Br_3$ is described below.[34] The preparation of Ad_2[35] and $[Ad_2Br]TFPB$[36] have been previously reported. The preparations are included here for completeness.

2.5.3 Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 983 IR spectrophotometer; the internal calibration of the instrument was periodically checked against the known absorption frequencies of gaseous CO and found accurate to ± 1 cm^{-1}. Samples were contained in cells with NaCl windows. All ^{13}C NMR data were recorded at the specified temperatures on a Bruker AMX 400 instrument at an operating frequency of 100.6 MHz. Microanalyses were carried out by the Microanalytical Laboratory at Simon Fraser University by M. Yang.

2.5.4 Synthesis

2.5.4.1 Preparation of Adamantylideneadamantane (Ad$_2$)

A 3-L, three-necked flask was dried and fitted with three rubber septa. Anhydrous titanium trichloride (100 g, 0.648 mol) was added to the weighed flask in a dry box. The flask was reweighed and fitted with a mechanical stirrer equipped with a glass shaft and a teflon paddle. One of the rubber septa was replaced by a reflux condenser through which a stream of nitrogen was flowing. 1, 2-Dimethoxyethane (950 mL) was added through the remaining septum to the flask with a syringe. After the addition of DME was complete the remaining rubber septum was replaced with a glass stopper. Small pieces of lithium wire (13.50 g, 2.25 mol) were washed in methanol followed by petroleum ether, and they were then added to the stirred suspension. The mixture was heated at reflux under positive N$_2$ pressure for 1 h using an oil bath; the colour of the solution at this point had changed from gray-green to gray-black. After this period, 2-adamantanone (24.32 g, 0.162 mol) was added and the mixture was heated at reflux for 18 h, after which, stirring was maintained as the mixture was allowed to cool to room temperature. Petroleum ether (950 mL) was added in 150 mL portions at 5-min intervals. The addition of petroleum ether caused a viscous black precipitate to be formed and left milky-white solution. The stirrer was disconnected and the solution was filtered through a sintered glass funnel containing 80 g of Florisil. The remaining black material in the flask was washed with 75 mL portions of petroleum ether and poured onto the same pad of Florisil. The filter pad was then washed with 630 mL of petroleum ether. The solvent was removed on a rotary evaporator to yield a white crystalline solid (18-20 g). This crude product was dissolved in 1 L of CCl$_4$ and filtered. A yellow precipitate of $[Ad_2Br]Br_3$ formed when bromine (15 mL) was added to the filtrate. The precipitate was filtered and Ad_2 was regenerated by adding cyclohexene (20 mL) and methanol. The white precipitate that formed was filtered under vacuum, and pure white crystals of Ad_2 were obtained by sublimation of this residue at 120 °C. Yield (17 g, 75%).

2.5.4.2 Preparation of Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Na[TFPB])[10]

A 250-mL 3-necked flask fitted with a condenser/N_2 inlet and 50-mL addition funnel was charged with Mg turnings (1.0 g, 41 mmol) and 10 mL of ether. 3,5-Bis(trifluoromethyl)-1-bromobenzene (6.3 mL, 36 mmol) and 40 mL of ether were placed in the addition funnel and added dropwise to the flask over a period of 1 h so as to maintain a moderate reflux. After about 4 h stirring, $NaBF_4$ (1.0 g, 8.5 mmol), dried (at ~110 °C for 1 h under vacuum) was added and the mixture stirred for another 12 h, producing a light tan suspension. The suspension was slowly poured into 50 mL of a saturated solution of NaCl, and the brown ether layer separated by using a separating funnel. The ether layer was removed under vacuum giving a thick, dark brown oil. The oil was washed with 20 mL of benzene and dried under vacuum which yielded a brown solid. The solid was then rinsed with 5 mL CH_2Cl_2 and dried at 110 °C for 6 h yielding 4.8 g of Na[TFPB] (60% yield).

2.5.4.3 Preparation of adamantylideneadamantane bromonium ion $[Ad_2Br][TFPB]$

A 100 mL round-bottom flask was charged with Ad_2 (500 mg, 1.87 mmol), stir bar, Na[TFPB] (1.7 g, 2 mmol) and excess bromine (~1 mL) in 40 mL dry CH_2Cl_2. The mixture was sonicated for about 10 h after which the dark yellow precipitate of $[Ad_2Br]Br_3$ had

1

completely dissolved; further sonication (3 h) induced the formation of a pale yellow precipitate of NaBr. After this time, the solution was rapidly filtered and the clear brown filtrate was transferred to another 100 mL round-bottom flask for recrystallization. Dry hexane (50 mL) was added to yield beige needles of [Ad_2Br][TFPB] (1.6 g, 90% Yield).

2.5.4.3 Preparation of tetraethylammonium tribromide [$(Et_4N)Br_3$]

To [$(C_2H_5)_4N$]Br (200 mg, 0.952 mmol) in MeCN (30 mL) was added bromine (152 mg, 0.952 mmol) dropwise at room temperature. The initial colourless solution went red-yellow. The mixture was further stirred overnight with no apparent change. The solvent and excess bromine were removed under vacuum and the residue was washed two times with hexane. Recrystallization from methanol yielded the orange-red compound [$(C_2H_5)_4N$]Br_3. Yield (270 mg, 77 %).

2.5.4.4 Preparation of $Ru_3(CO)_{12}$

A literature method was followed for the preparation of $Ru_3(CO)_{12}$.[30] A solution of $RuCl_3.xH_2O$ (2.0 g) in methanol (150 mL) in an autoclave, was pressurized to 60 atm with CO. The solution was heated at 125 °C for 20 h. The reaction mixture was allowed to cool, the CO vented, and the bright orange crystals of $Ru_3(CO)_{12}$ (1.3 g) were collected by vacuum filteration. A small amount of black product, presumed to be RuO_2 was obtained on the filter paper. IR (Hexane) $\nu(CO)cm^{-1}$: 2060.5(vs), 2031(s), 2011.5(m)

2.5.4.5 Preparation of ^{13}CO-labeled $Ru_3(CO)_{12}$

An evacuated Carius tube fitted with a Teflon valve and equipped with a Teflon-coated magnetic stir bar, was charged with $Ru_3(CO)_{12}$ (50 mg, 0.078 mmol), toluene (15 mL) and subjected to three cycles of freeze-pump-thaw. The vessel was then pressurized with 2 atm of CO (99% ^{13}C-enriched). The tube was then heated to ~100 °C in an oil bath for 50 h; it was then transferred to a Schlenk tube, cooled and more toluene was added. After this it was placed in the refrigerator at -20 °C. The orange product was collected. The ^{13}CO enrichment was typically 30-40% ^{13}CO-enriched, as calculated by the computer simulation of the mass spectra of the complex with the program (MS) written by Dr. W. K. Leong at SFU.

2.5.4.6 Preparation of $[Ru_3(CO)_{12}Br]$TFPB (2.1)

To $Ru_3(CO)_{12}$ (60.0 mg, 0.094 mmol) in CH_2Cl_2 (20 mL) was added $[Ad_2Br][TFPB]$ (113 mg, 0.094 mmol) at 0 °C. The mixture was stirred for about 2 h. The reaction was followed by infrared spectroscopy. An IR spectrum in CH_2Cl_2 (νCO region) of the reaction solution indicated only the presence of compound **2.1**. The solvent was removed on the vacuum line to give an orange compound which was recrystallized from CH_2Cl_2/hexane to afford orange crystals (100 mg, 68% Yield). IR (CH_2Cl_2) νCO : 2165(w), 2137.5(s), 2087(vs), 2055(w), 2012(m), ^{13}C NMR (CH_2Cl_2/CD_2Cl_2, 0 °C) : δ 200.1 (2C), 196.1 (2C), 190 (4C), 189.2 (1C), 188.1 (1C), 178.9 (1C), 175.9 (1C).

Elemental analysis : (Found)	*33.37% C*	*0.79% H*
(Calculated for $C_{44}H_{12}BBrF_{24}O_{12}Ru_3$)	*33.39% C*	*0.76% H*

The ^{13}CO-enriched compound **2.1** was synthesized in an identical way from ^{13}CO-enriched $Ru_3(CO)_{12}$ (30-40% ^{13}C).

2.5.4.7 Reaction of 2.1 with $[(C_2H_5)_4N]Br$

To **2.1** (40 mg, 0.025 mmol) in CH_2Cl_2 (15 mL) was added $[Et_4N]Br$ (6 mg, 0.028 mmol) at 0 °C. The solution turned from orange to pale yellow soon after the addition; the solution was allowed to stir at 0 °C for ~1.5 h. The reaction was followed by infrared spectroscopy (ν(CO) region). The solvent was removed on the vacuum line to give a yellow residue. Attempted recrystallization of the yellow compound from CH_2Cl_2/hexane caused it to turn green. IR (CH_2Cl_2) of yellow solution: 2135(w), 2112.5(m), 2074.5(s), 2031(s).

2.5.4.8 Preparation of $[Os_3(CO)_{12}Br][TFPB]$ (2.2)

(This reaction was first carried out by Dr. Weibin Wang at SFU). A solution of $Os_3(CO)_{12}$ (25 mg, 0.027 mmol) and $[Ad_2Br]^+$ (33 mg, 0.027 mmol) in CH_2Cl_2 was stirred at 25 °C for 2.5 h. An infrared spectrum in the carbonyl stretching region of the pale yellow solution at this stage indicated complete conversion to product. The solvent was removed on the vacuum line and the solid recrystallized from an approximate 1:1 mixture of hexane and CH_2Cl_2 to give the product as pale-yellow, air-stable crystals. Yield = ~73%, 28 mg. IR (CH_2Cl_2) ν(CO): 2137(m), 2098.5(s), 2081(vs), 2055(m), 2022(w). ^{13}C NMR (carbonyl region only) (CH_2Cl_2/CD_2Cl_2, 25 °C): δ 177.0 (4C), 175.4 (2C), 167.7 (2C), 166.0 (2C), 155.1 (2C).

Elemental analysis : (Found)	*28.57% C*	*0.66% H*
(Calculated for $C_{44}H_{12}BBrF_{24}O_{12}Os_3$)	*28.74% C*	*0.66% H*

The ^{13}CO-enriched compound was synthesized from ^{13}CO-enriched $Os_3(CO)_{12}$ (~30% ^{13}C).

2.5.4.9 Reaction of 2.2 with $[(C_2H_5)_4N]Br$

To **2.2** (10 mg, 0.0054 mmol) was added $[Et_4N]Br$ (2 mg, 0.0095 mmol) in CH_2Cl_2 (10 mL) at room temperature. The reaction was essentially instantaneous when followed by infrared spectroscopy. Hexane was added to the solution to bring about precipitation of the product. The compound as identified by infrared spectroscopy was *cis,cis*-$Os_3(CO)_{12}Br_2$. The reaction vessel and contents were then placed in the freezer at -20 °C for about 4 h to complete precipitation. The solvent was removed with a syringe and the compound was dried on the vacuum line. IR (CH_2Cl_2) ν(CO) : 2118(s), 2062.5(vs), 2029(m), Literature values for $Os_3(CO)_{12}Br_2$[12] (ν(CO) region): 2148.5(vw), 2118.5(s), 2061.5(vs, br.), 2030.5(s), 2001.5(w).

2.5.4.10 Reaction of 2.2 with $[(C_2H_5)_4N]Br_3$

The reaction of **2.2** (20 mg, 0.011 mmol) in CH_2Cl_2 (20 mL) with $[Et_4N]Br_3$ (4 mg, 0.011 mmol) at 0 °C was carried out in the similar manner as described in 2.5.4.9. The product obtained was also *cis,cis*-$Os_3(CO)_{12}Br_2$.[12]

2.5.4.11 Preparation of $Ru_3(CO)_{12}Br_2$ (2.3)

To $Ru_3(CO)_{12}$ (100 mg, 0.156 mmol) in CH_2Cl_2 (20 mL) was added Br_2 (1 eq in CH_2Cl_2) dropwise while stirring at -50 °C. The reaction was followed by infra-red spectroscopy. An IR spectrum (νCO region) of the solution at this stage indicated only the presence of $Ru_3(CO)_{12}Br_2$. The solvent was removed under vacuum. The crude solid was recrystallized from CH_2Cl_2/hexane to afford orange crystals of $Ru_3(CO)_{12}Br_2$ (72 mg, Yield

~60%). IR (CH_2Cl_2) ν(CO): 2112.5(s), 2061.5(vs), 2039.5(m), ^{13}C NMR (CH_2Cl_2/CD_2Cl_2): δ 201.9 (4C), 195.1 (4C), 191.6 (2C), 177.6 (2C).

Elemental analysis : (Found)	*18.16% C*	*0.00% H*
(Calculated for $C_{12}Br_2O_{12}Ru_3$)	*18.04% C*	*0.00% H*

The ^{13}CO-labeled $Ru_3(CO)_{12}Br_2$ was synthesized from ^{13}CO labeled $Ru_3(CO)_{12}$ in an identical manner.

CHAPTER 3

SYNTHESIS AND PARTIAL CHARACTERIZATION OF [Os(CO)$_5$Br]TFPB, "Os(CO)$_5$.Br$_2$", AND [Os(CO)$_4$(PMe$_3$)(Br)]Br$_3^-$

3.1 Introduction

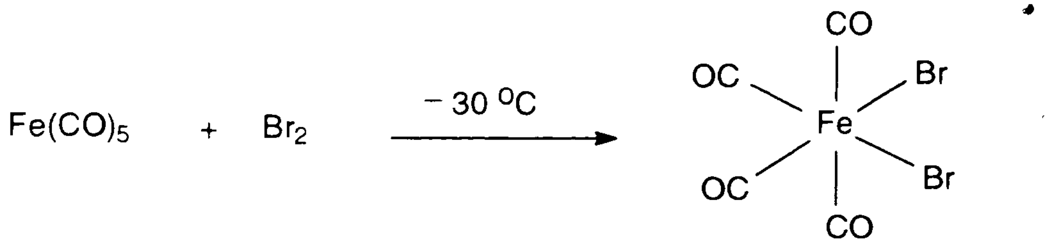
The only previous study involving the halogenation of Os(CO)$_5$ was a preliminary study on the addition of chlorine to Os(CO)$_5$ at -78 °C (Eq. 3.1) reported by Pomeroy and coworkers in 1987.[28b] The product of the reaction was an air-stable crystalline solid at room temperature and had the composition Os(CO)$_5$.Cl$_2$; it was believed to be [Os(CO)$_5$Cl]Cl.[28b] Based on the findings from this study reported here this formulation is almost certainly incorrect.

$$\mathrm{Os(CO)_5} + \mathrm{Cl_2} \xrightarrow{-78\ ^{\circ}\mathrm{C}} \text{"[Os(CO)}_5\text{Cl][Cl]"} \qquad (3.1)$$

The reaction of the first-row transition metal analogue of Os(CO)$_5$ (*i.e.*, Fe(CO)$_5$) with bromine at low temperatures has been studied by Noack.[37] Two unstable intermediate products were inferred from the bands in the carbonyl region of the infrared spectrum of the reaction solution. For the first, the structure [Fe(CO)$_5$Br]Br was proposed and for second, Fe(CO)$_4$(COBr)Br (Eq. 3.2). The latter structure was based on observation that it exhibits a band at 1665 cm^{-1} which is characteristic of the acyl group.[37] The product obtained by

$$\mathrm{Fe(CO)_5} + \mathrm{Br_2} \xrightarrow{-80\ ^{\circ}\mathrm{C}} \mathrm{[Fe(CO)_5(Br)]Br} + \mathrm{Fe(CO)_4(COBr)Br} \qquad (3.2)$$

carrying out the reaction at -30 °C is *cis*-$Fe(CO)_4(Br)_2$[37, 38] (Eq. 3.3). On the other hand, low temperature IR studies in CH_2Cl_2 by Farona and Camp indicated the presence of only one intermediate of composition $Fe(CO)_5.(Br)_2$; they proposed the ionic formulation $[Fe(CO)_5Br]Br$ for the compound (Eq. 3.2).[38] Their results are considerably different from those carried out in $CHCl_3/CH_2Cl_2$ solution by Noack.[37, 38] Dobson et al.[39]studied the mechanism of the thermal oxidative-elimination reaction between $Fe(CO)_5$ and I_2, and found evidence for the successive formation of two adducts of formula $Fe(CO)_5.I_2$; each adduct



(3.3)

then yields *cis*-$Fe(CO)_4(I)_2$ through the loss of CO. Salts of the cationic complexes $Fe(CO)_5H^+$, $Fe(CO)_5Cl^+$, $Fe(CO)_5Br^+$ and $Fe(CO)_5NO^+$ are known and these have been characterized by infrared and ultraviolet absorption spectroscopy, for example, (ν(CO) for $Fe(CO)_5Br^+$: 2200(m), 2155(s), 2110 and 2100(s).[40] Caldderazzo and L'Eplattenier[28a] have reported the formation of *cis*-$Os(CO)_4(Br)_2$ from the reaction of $Os(CO)_4(H)_2$ with CBr_4. Our results did not reveal evidence for this compound from the reaction of $Os(CO)_5$ and Br_2 at room temperature.

Osmium carbonyl complexes are usually more stable than the corresponding iron complexes. Given this information and the availability of [Ad_2Br][TFPB], it was decided to attempt the preparation of the $[Os(CO)_5(Br)]^+$ cation and investigate its reaction with Br^- in order to more fully understand the bromination of group 8 pentacarbonyls. (It was expected that the reaction of $Os(CO)_5$ with $[Ad_2Br]^+$ would provide $[Os(CO)_5Br]^+$ as the stable TFPB salt). The reaction of $Os(CO)_5$ with Br_2 has also been studied to ascertain whether $[Os(CO)_5Br]^+Br^-$ is an intermediate or product of the reaction.

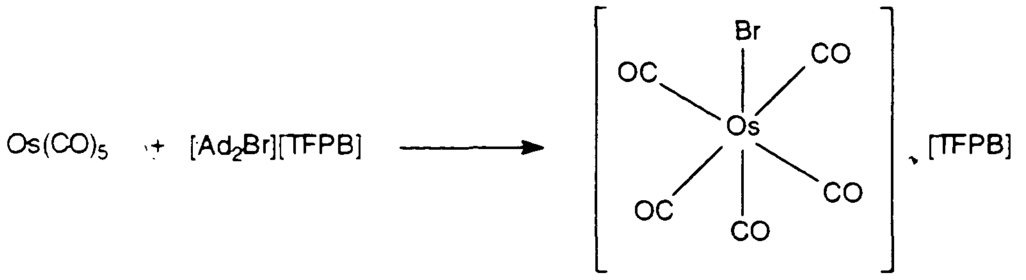
This chapter deals with reactions of $Os(CO)_5$ with both Br_2, and $[Ad_2Br]$TFPB. In addition, the reaction of a phosphine derivative of $Os(CO)_5$ *i.e.*, $[Os(CO)_4(PMe_3)]$ with Br_2 is also discussed. A preliminary investigation of the reaction of $Os(CO)_5$ with chlorine and iodine is also described.

3.2 Results and Discussion

3.2.1 Synthesis and Characterization of $[Os(CO)_5Br]$TFPB (3.1)

3.2.1.1 Preparation of $[Os(CO)_5Br]$TFPB (3.1)

Addition of a solution of $[Ad_2Br]$TFPB in CH_2Cl_2 to $Os(CO)_5$ in hexane at -78 °C afforded a light tan precipitate of **3.1** (Eq. 3.4). After isolation and recrystallization of the



3.1

(3.4)

precipitate from CH_2Cl_2/hexane, compound **3.1** was obtained as an off-white crystalline solid which was stable for short periods in air. The C/H analysis of **3.1** is consistent with the formulation $[Os(CO)_5(Br)][TFPB]$.

3.2.1.2 Spectroscopic properties of 3.1

It was initially thought that the product of the reaction of $Os(CO)_5$ with $[Ad_2Br]TFPB$ was $[Os(CO)_5(Br)_2]^{2+}$. However, the chemical analysis and a careful comparison of the spectroscopic properties of the compound with those in literature, were not consistent with this view. The properties which confirmed the compound **3.1** as $[Os(CO)_5Br]TFPB$ are discussed here. The infrared spectrum of $[Os(CO)_5Br]TFPB$ (**3.1**) (ν(CO) cm^{-1}: 2222(w), 2152(vs), 2120(m) in CH_2Cl_2) is shown in Figure 3.1. The pattern of bands of **3.1** is consistent with C_{4v} symmetry and very similar to that of $Re(CO)_5Br$ (ν(CO) cm^{-1}: 2146(w), 2040(vs), 1987(m)),[41] but the CO absorbance bands appear at much higher wavenumbers in the **3.1** complex. The high CO stretching frequencies of **3.1** are very unusual. Most metal carbonyl compounds have CO stretching frequencies below that of free CO (2143 cm^{-1}). This can be explained by the back bonding of the filled metal d-orbitals to the π^* (antibonding) molecular orbital on CO (Figure 3.2, and 3.3). The positions of the CO stretches in **3.1** are similar to those of the recently prepared $[Os(CO)_6]^{2+}$ (ν(CO) IR:, 2190 cm^{-1}, Raman: 2259 cm^{-1}, 2218).[42] The osmium atom in both **3.1** and $[Os(CO)_6]^{2+}$ has a formal oxidation state of (II). In $[Os(CO)_6]^{2+}$ and **3.1**, the high frequency CO stretches are consistent with the view that there is very little back bonding to the π^* molecular orbitals on CO because the d-orbitals are contracted by the positive charge on the Os atom (MO diagram in Figure 3.4). Since the bonding MO's (A_{1g}, T_{1u}, E_g) remove electron density from the σ_5

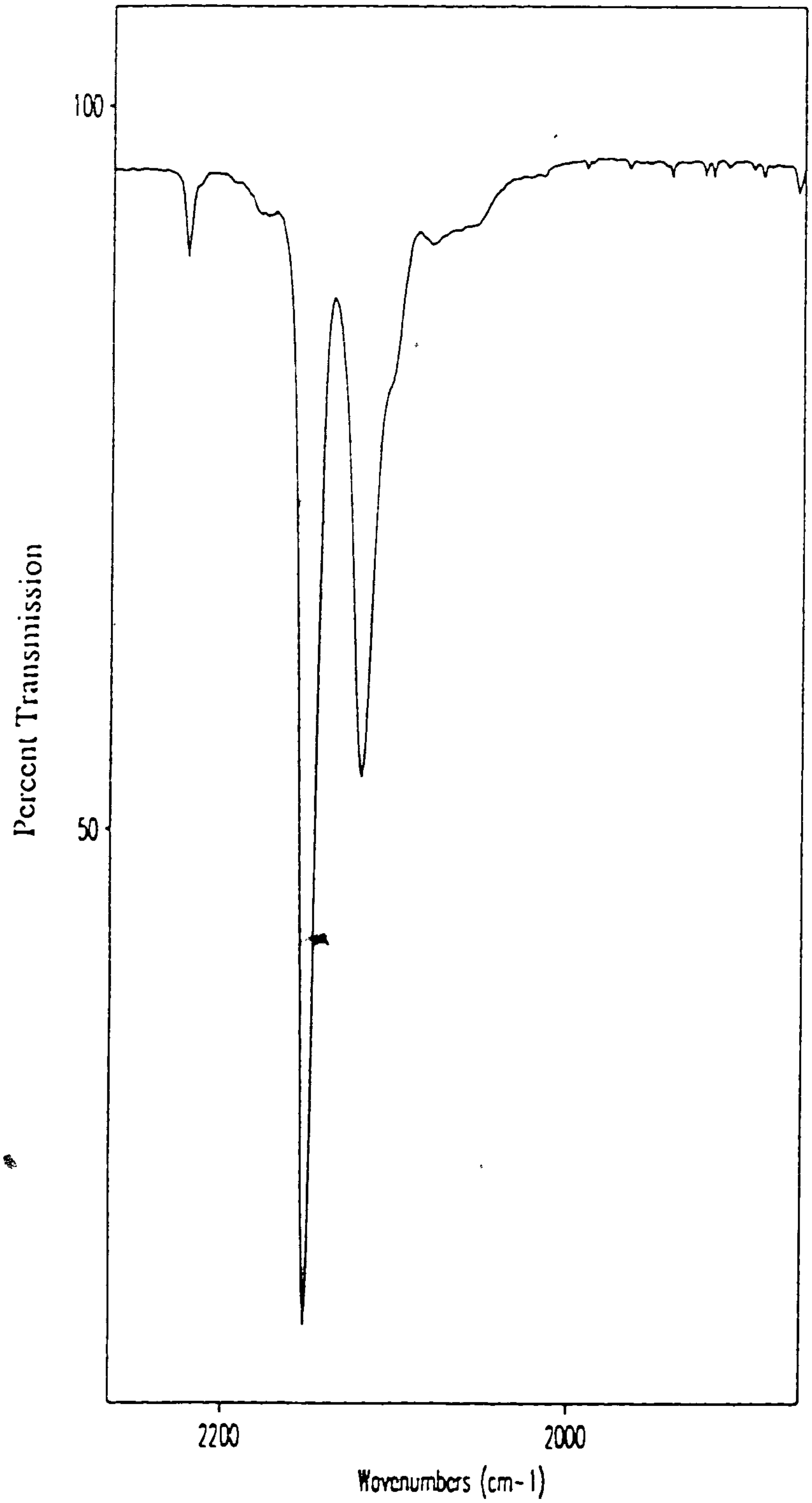


Figure 3.1 IR spectrum (carbonyl region) of $[Os(CO)_5Br][TFPB]$ in CH_2Cl_2.

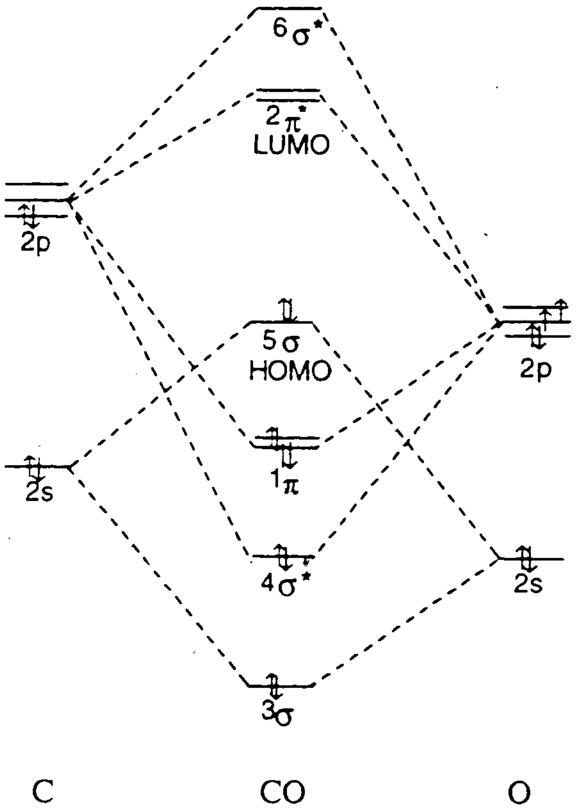


Figure 3.2 Molecular orbitals of CO. The 1σ and 2σ orbitals arise from the 1s interactions and are not shown.

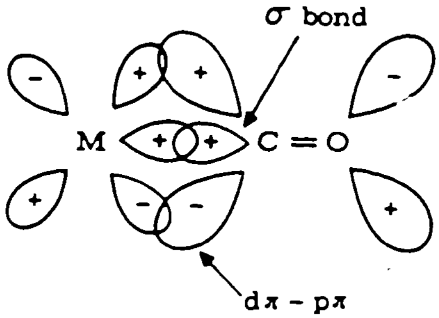


Figure 3.3 Molecular orbital picture of M-CO bonding.

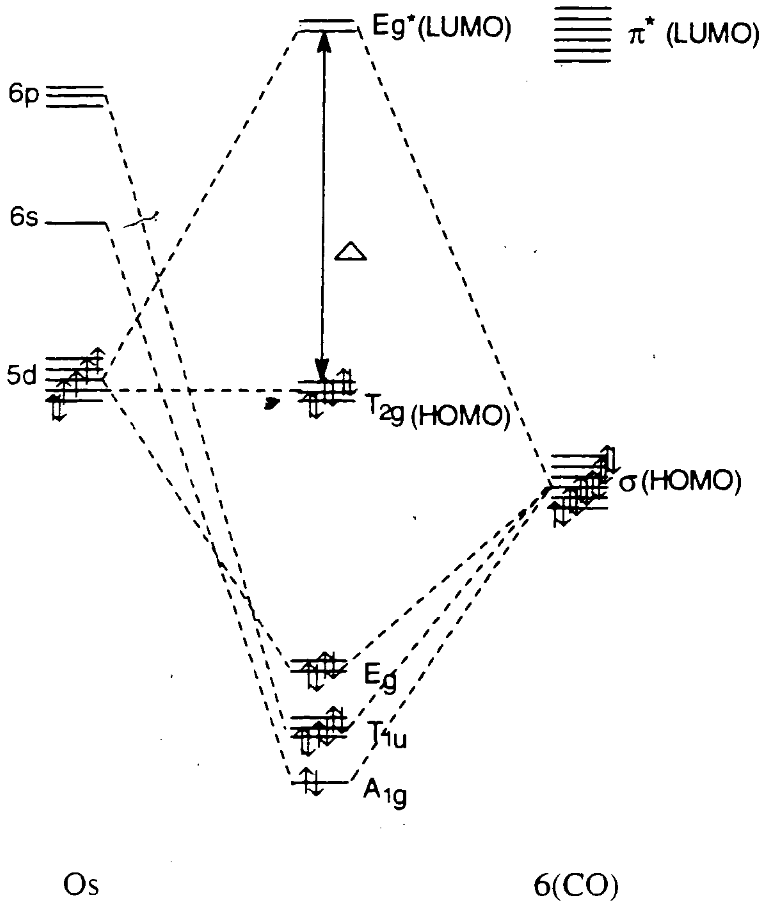


Figure 3.4 Suggested Molecular orbital diagram for $[Os(CO)_6]^{2+}$

(HOMO) molecular orbitals on the CO ligands and σ_5 molecular orbital is slightly antibonding in character, this donation increases the CO bond strengths which in turn increases the CO stretching frequencies.

The ^{13}C NMR spectrum of **3.1** in CH_2Cl_2/CD_2Cl_2 recorded at 0 °C is shown in Figure 3.5. The number of CO resonances expected for **3.1** is two in a 4:1 ratio and these are observed at δ 156.3 and 154.0, respectively (see also Table 3.1). The spectrum is consistent with the presence of only one form of **3.1** in solution. The resonances of the carbonyls are shifted upfield, rather than downfield compared to $Os(CO)_5$. This is contrary to what one would expect from simple bonding arguments: the presence of a positive charge on the complex **3.1** should result in deshielding at the carbon atoms and hence a downfield shift. The shift in the opposite direction to what is expected from the simple bonding arguments is typical for the ^{13}C NMR spectra of metal carbonyl complexes. For example, the presence of the strongly electron donating PMe_3 ligand in $Os(CO)_4(PMe_3)$ causes a downfield, rather than upfield, shift in the ^{13}C NMR resonance of the carbonyl ligands compared to the corresponding signal in $Os(CO)_5$ (Table 3.1).[43] The upfield shift of the CO resonances in $[Os(CO)_5(Br)]^+$ can be rationalized in terms of changes in the paramagnetic term which in turn changes the chemical shift. This term, which is more important than the diamagnetic term for ^{13}C contains $(\Delta E)^{-1}$ (the HOMO-LUMO gap), and p and d orbital imbalance factors.[43, 44] It may be that in $[Os(CO)_5(Br)]^+$, the ΔE term is larger than that in $Os(CO)_5$ causing the upfield shift. Consistent with this view is that the cation $[Os(CO)_6]^{2+}$ is colourless whereas $Os(CO)_5$ is yellow. This may indicate strong σ-bonding in **3.1** and $[Os(CO)_6]^{2+}$ that results in Eg* being raised in energy. The shift upfield cannot be due to p or d imbalance since the ^{13}C NMR resonance in $[Os(CO)_6]^{2+}$ is shifted even further upfield than that in **3.1** and this ion is, of course, symmetric. Table 3.1 gives the ^{13}C NMR chemical shifts for $Os(CO)_4(PMe_3)$,[19, 45] $Os(CO)_5$,[28b] $[Os(CO)_6]^{2+}$[42] and $[Os(CO)_5Br]^+$.

The spectral assignment of the compound **3.1** is straightforward based on the CO resonance intensities, and the characteristic region in which they appear.[27] The resonance at δ 156.3 of relative intensity four can be assigned to carbonyls **a** (Figures 3.5 and 3.6) which are cis to bromine atom. The signal at δ 154.0 of relative intensity one can be unambiguously

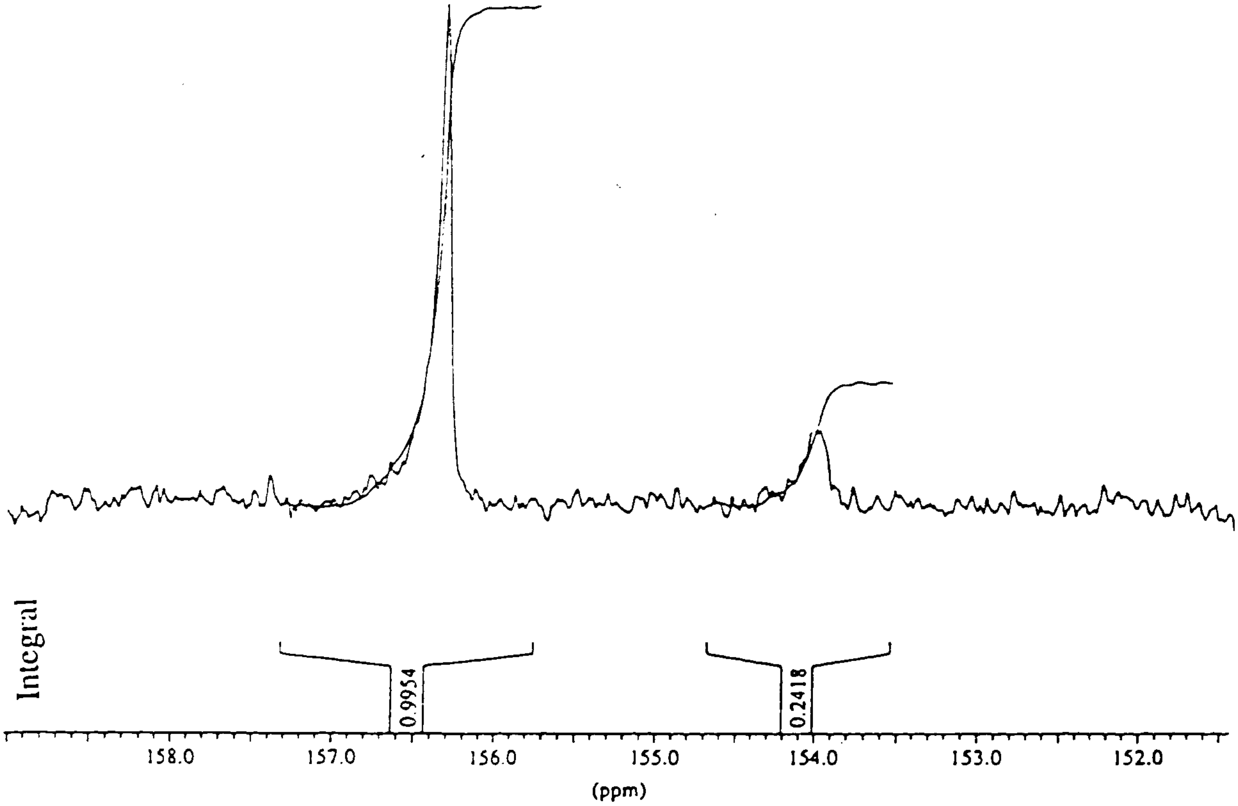


Figure 3.5 ^{13}C NMR spectrum of [Os(CO)$_5$Br]TFPB (carbonyl region) at 0 °C in CH$_2$Cl$_2$/CD$_2$Cl$_2$ (3:1)

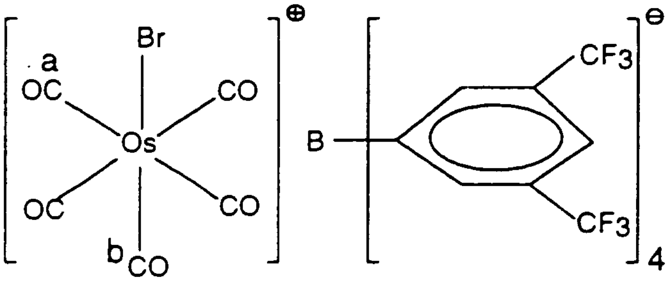


Figure 3.6 Proposed structure for [Os(CO)$_5$Br][TFPB]

assigned to carbonyl **b** which is trans to the bromine atom.

The MS (FAB) of **3.1** exhibits a parent peak [P^+] for the cation at 411 m/z and at 383 m/z due to [P-CO]$^+$. Crystals of compound **3.1** have been sent for crystal structure determination to St. Mary's University, Halifax.

Table 3.1 ^{13}C NMR spectra of some metal carbonyl compounds

Compound	^{13}C NMR, δ, ppm
$Os(CO)_4(PMe_3)$	189.9
$Os(CO)_5$	182.6
$[Os(CO)_5(Br)]^+$	156.3, 154.0
$[Os(CO)_6]^{2+}$	147.3

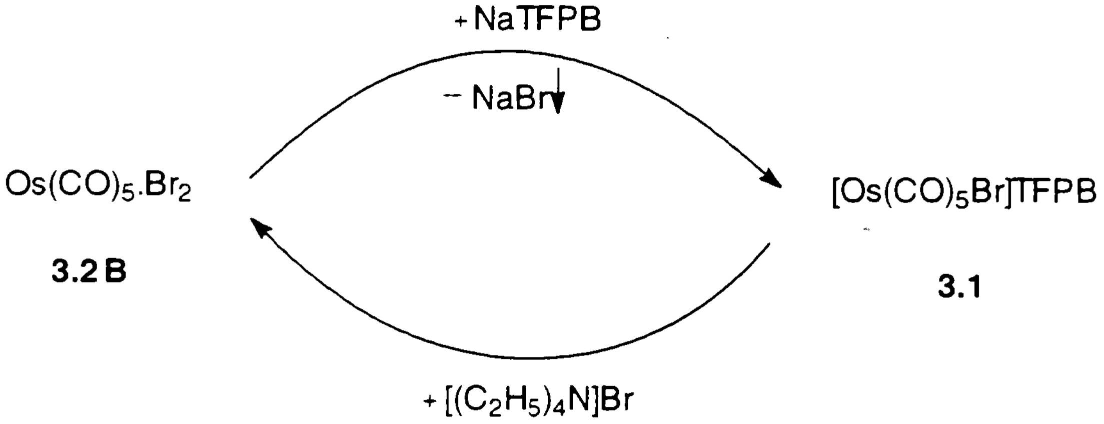
3.2.2 Synthesis and partial characterization of $Os(CO)_5.Br_2$ (3.2)

3.2.2.1 Preparation of $Os(CO)_5.Br_2$ (3.2)

Dropwise addition of Br_2 solution in CH_2Cl_2 to a hexane solution of $Os(CO)_5$ at -78 °C afforded an off-white, air-sensitive solid. Elemental analysis of this compound was consistent with the formulation $Os(CO)_5.Br_2$ (**3.2**). Crystals suitable for X-ray crystallography have not yet been obtained. The infrared spectrum of **3.2** in the carbonyl stretching region (Figure 3.10) indicates that it is not *cis*-$Os(CO)_4Br_2$ reported earlier by Calderazzo and L'Eplattenier.[28a, 46] Furthermore, the IR and ^{13}C NMR spectrum of **3.2** clearly show that it is not [$Os(CO)_5(Br)$](Br). Preliminary IR and ^{13}C NMR spectroscopic studies of **3.2** are given at the end of this chapter. These studies suggest **3.2** is in fact a mixture of two isomers, **3.2A** and **3.2B**.

3.2.3 Investigation of the interconversion of 3.1 and 3.2B

The interconversion of **3.1** to **3.2B** and of **3.2B** to **3.1** was studied by infrared and NMR spectroscopy. To a solution of **3.1** in CH_2Cl_2 at room temperature was added tetraethylammonium bromide and the reaction was monitored by IR spectroscopy. An almost immediate conversion of **3.1** to compound **3.2B** was observed. On the other hand, addition of the sodium salt of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) to **3.2B** in CH_2Cl_2 at room temperature readily yielded compound **3.1,** as also indicated by IR spectroscopy. (The sodium salt, NaTFPB was added because it was originally thought that **3.2B** was the ionic compound $[Os(CO)_5Br]Br$ and that NaTFPB would replace Br^- with $TFPB^-$). The reactions were also followed by ^{13}C NMR spectroscopy which confirmed the interconversion between **3.2B** and **3.1**; the interconversion reactions are summarized in Scheme 3.1.

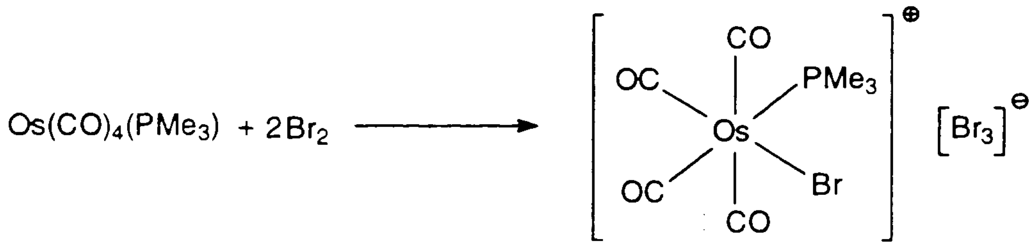


Scheme 3.1 Interconversion of 3.1 and 3.2B.

3.2.4 Synthesis and Characterization of [$Os(CO)_4(PMe_3)Br]Br_3$ (3.3)

3.2.4.1 Preparation of [$Os(CO)_4(PMe_3)Br]Br_3$ (3.3)

Addition of a solution of bromine in CH_2Cl_2 to $Os(CO)_4(PMe_3)$ in CH_2Cl_2 while stirring at room temperature immediately caused the colourless solution of $Os(CO)_4(PMe_3)$ to turn yellow. The carbonyl stretches of the starting material in the IR spectrum of the reaction solution were replaced by four new CO stretching bands. Evaporation of the solvent yielded a yellow solid that was recrystallized from CH_2Cl_2 to give an air-stable yellow crystalline solid. The C/H analysis of the solid was consistent with the formulation $Os(CO)_4(PMe_3).(Br)_4$. By comparison of the IR spectrum with compounds **3.1** and **3.2**, the product is formulated as $[Os(CO)_4(PMe_3)(Br)][Br_3]$ (Eq. 3.2), *i.e.*, **3.3** is an analogue of the cation **3.1**.



(3.5)

3.3

3.2.4.2 Spectroscopic properties of 3.3

The infrared spectrum (CO stretching region) of the compound **3.3[Br_3]** in CH_2Cl_2 is shown in Figure 3.7. The compound is formulated as *cis*-$[Os(CO)_4(PMe_3)Br]Br_3$ (**3.3[Br_3]**)

on the basis of its spectroscopic properties. Four infrared active CO-stretches in the 2000–2200 cm^{-1} region are expected for a molecule of the type *cis*-$M(CO)_4(X)(Y)$ with C_s symmetry and four bands are observed for **3.3**.[47] (The very weak band at 2019.4 cm^{-1} is due to a vibration that involves ^{13}CO). Four carbonyl stretches are the maximum number allowed for $Os(CO)_4(X)(Y)$ molecule regardless of the symmetry of X and Y. A *trans*-$M(CO)_4(X)(Y)$ configuration would be expected to give only one infrared-active carbonyl stretch. In Table 3.2, the shifts in the CO stretching frequencies on going from $Os(CO)_4(PMe_3)$ to the brominated product **3.3** are compared to the corresponding shifts of $Os(CO)_5/[Os(CO)_5Br]^+$and $Os(CO)_4(CNBu^t)/[Os(CO)_4(CNBu^t)(H)]^+$ pairs of complexes. Table 3.2 shows that there is a shift of approximately 120 cm^{-1} on going from the neutral to the positively charged species and this is also observed in $Os(CO)_4(PMe_3)/[Os(CO)_4(PMe_3)(Br)]^+$ pair.

Table 3.2 The IR ν(CO) absorption data for $Os(CO)_5$ and its derivatives.

Compound	IR absorptions, ν(CO) bands, cm^{-1}			
$Os(CO)_5$[28b]		2035 (s)	1993 (s)	
$[Os(CO)_5(Br)]^+$	2222 (w)	2152 (vs)	2120 (s)	
$Os(CO)_5.Br_2$	2176 (w)	2102 (s)	2054 (m)	1670.5 (w)
$Os(CO)_4(CNBu^t)$[19]	2062 (s)	1990 (m, sh)	1951 (vs, br)	
$[Os(CO)_4(CNBu^t)(H)]^+$ [19]	2176 (m)	2126 (s)	2102 (vs, br)	
$Os(CO)_4(PMe_3)$[45]	2061 (s)	1980 (m)	1939 (vs)	
$[Os(CO)_4(PMe_3)(Br)]^+$	2182 (m)	2128 (w)	2107 (vs)	2080 (s)

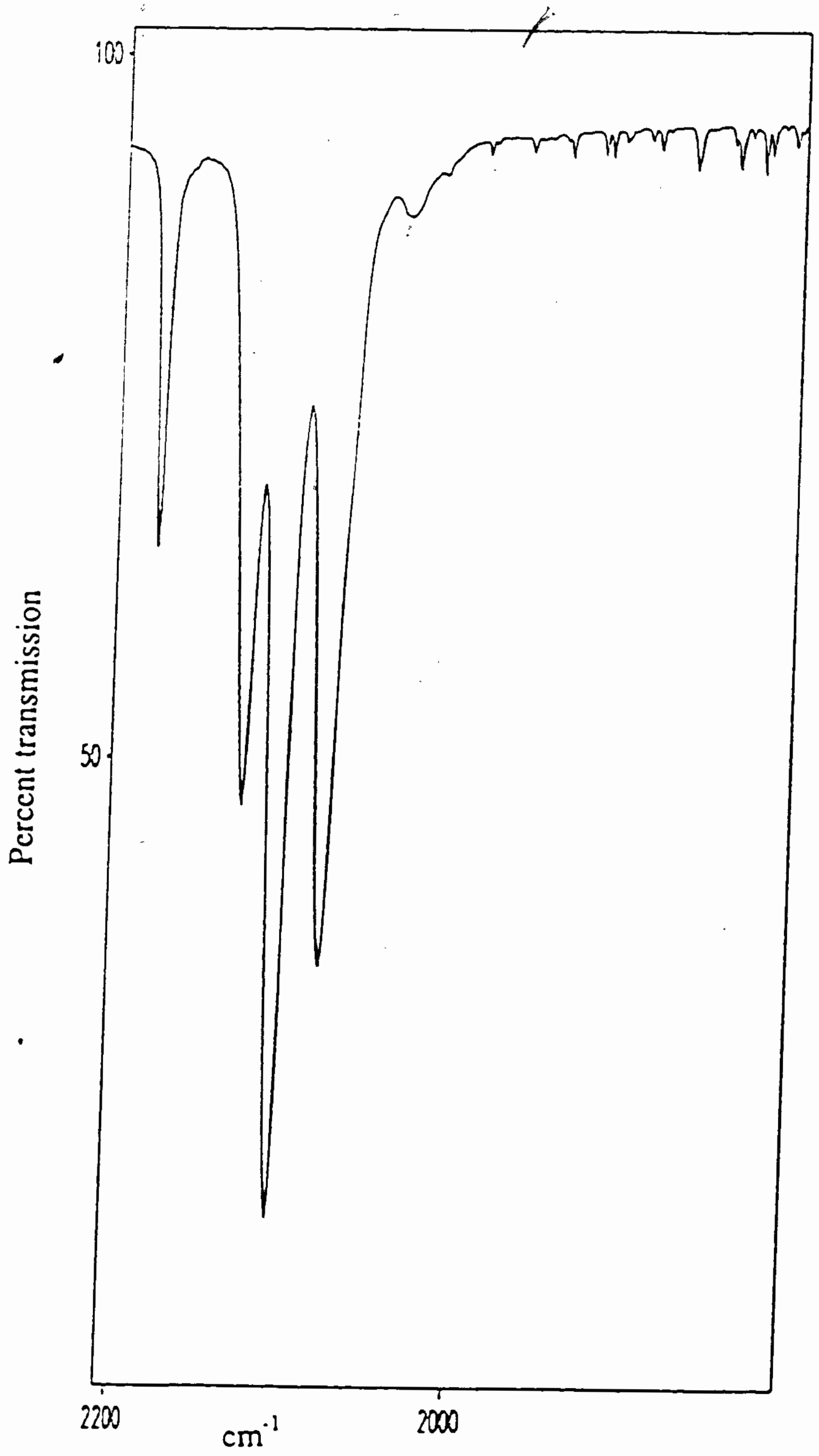


Figure 3.7 IR spectrum (carbonyl region) of $[Os(CO)_4(PMe_3)Br]Br_3$ in CH_2Cl_2.

This increase in the frequencies of the CO stretches is therefore consistent with a positively charged species and not a neutral species such as $Os(CO)_5.Br_2$.

The $^{13}C\{^1H\}$ NMR spectrum of **3.3** is also consistent with the ionic formulation. The spectrum of $[Os(CO)_4(PMe_3)Br]Br_3$ recorded at room temperature is shown in Figure 3.8. Based on the characteristic region of the carbonyls,[27] and the intensities of the signals, the spectrum of **3.3** can be assigned as indicated by the letters **a** through **c**. The doublet of intensity two at δ 163.8 is assigned to the resonances due to the axial carbonyls labeled **a** which are equivalent, and exhibit a small cis J_{PC} coupling (10 Hz). The resonance at δ 159.6 is assigned to one half of the doublet due to the carbonyl labeled **b** (trans to the phosphorus atom) centered at δ 159.3 with a large trans-J_{PC} coupling of 59 Hz; the other half of the doublet is at δ 159.0 but is degenerate with half of the doublet of the remaining resonance. The signal at δ 158.9 is attributed to one half of the doublet of the resonance centered at δ 158.9 due to the carbonyl labeled **c** with a small cis-J_{PC} coupling of 15 Hz. The signal at δ 159.0 of intensity two is due to the overlapping of two resonances due to the cis and trans ^{13}C-^{31}P couplings. An alternative assignment would be to assign the signal at δ 159.0 to a carbonyl **c** (J_{PC} = 0 Hz) and the signals at δ 159.6 and 158.9 as due to the doublet due to carbonyl **b** (with a trans J_{PC} of ~75 Hz). This is thought less likely as carbonyls **a** and **c** should have similar couplings.

The ^{13}C NMR spectrum is not consistent with an acyl bromide formulation, $Os(CO)_3(PMe_3)(COBr)(Br)$, (see the discussion in the next section). One would expect for the fac isomer three doublets of intensity one in the $^{13}C\{^1H\}$ NMR spectrum, one of which would have a large trans-J_{PC} coupling; for each of the three mer isomers two doublets would

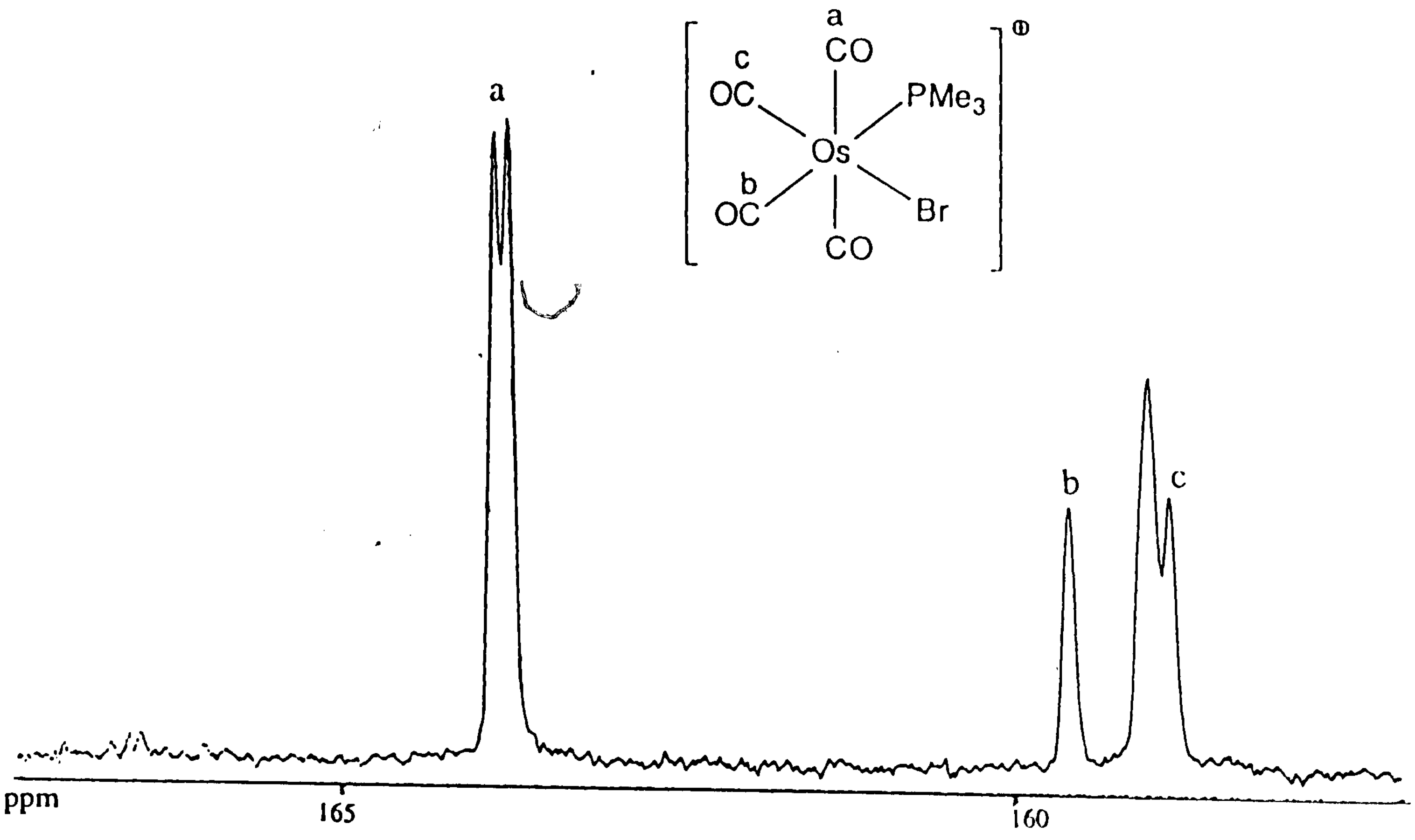


Figure 3.8 $^{13}C\{^1H\}$ NMR spectrum of $[Os(CO)_4(PMe_3)(Br)]Br_3$ at room temperature in CH_2Cl_2/CD_2Cl_2

be expected in a 2:1 ratio with one of the signals of one isomer exhibiting a large trans J_{PC} coupling. As found for the $Os(CO)_5$/$[Os(CO)_5(Br)]^+$ pair there is a dramatic upfield shift in the ^{13}C NMR resonance on going to the positively charged species. The ^{13}C NMR resonance of the nonrigid $Os(CO)_4(PMe_3)$ is at 189.9 ppm. Note also that the chemical shifts of **3.3** are downfield to those of **3.1** even though on going from **3.1** to **3.3** a carbonyl ligand has been replaced with the strongly electron-donating PMe_3 ligand.

The ^1H, $^1H\{^{31}P\}$and $^{31}P\{^1H\}$ spectra of **3.3** are shown in Figure 3.9. The ^1H NMR spectrum shows a doublet (J_{PH} = 11.3 Hz) centered at δ 2.27. The same sample at the same temperature showed only one signal at δ 2.26 in the $^1H\{^{31}P\}$ spectrum (Figure 3.9). The$^{31}P\{^1H\}$ NMR spectrum at room temperature showed only one signal at δ -46.0 indicating the presence of only one isomer of the compound present in solution.

The PMe_3 ligand is a stronger σ donor/poorer π acceptor when compared to CO. There is thus more electron density at the Os atom in $Os(CO)_4(PMe_3)$ compared to that in $Os(CO)_5$. That the reaction of $Os(CO)_4(PMe_3)$ with Br_2 yields the ionic complex $[Os(CO)_4(PMe_3)(Br)]^+$ can therefore be attributed to the presence of the electron donating PMe_3 ligand which stabilizes the positive charge on the ionic derivative and hence is the thermodynamically preferred product rather than the brominated derivative $Os(CO)_4(PMe_3).Br_2$. In the bromination of $Os(CO)_5$, there is presumably not sufficient electron density on the osmium atom to stabilize $[Os(CO)_5(Br)]^+$ relative to $Os(CO)_5.Br_2$. This suggests that an $Os(CO)_4L$ compound where L is a weaker donor ligand than PMe_3 (such as $P(C_6F_5)_3$) may give the brominated complex, and because of the presence of the donor ligand the complex would more likely to form crystals suitable for a crystallographic study.

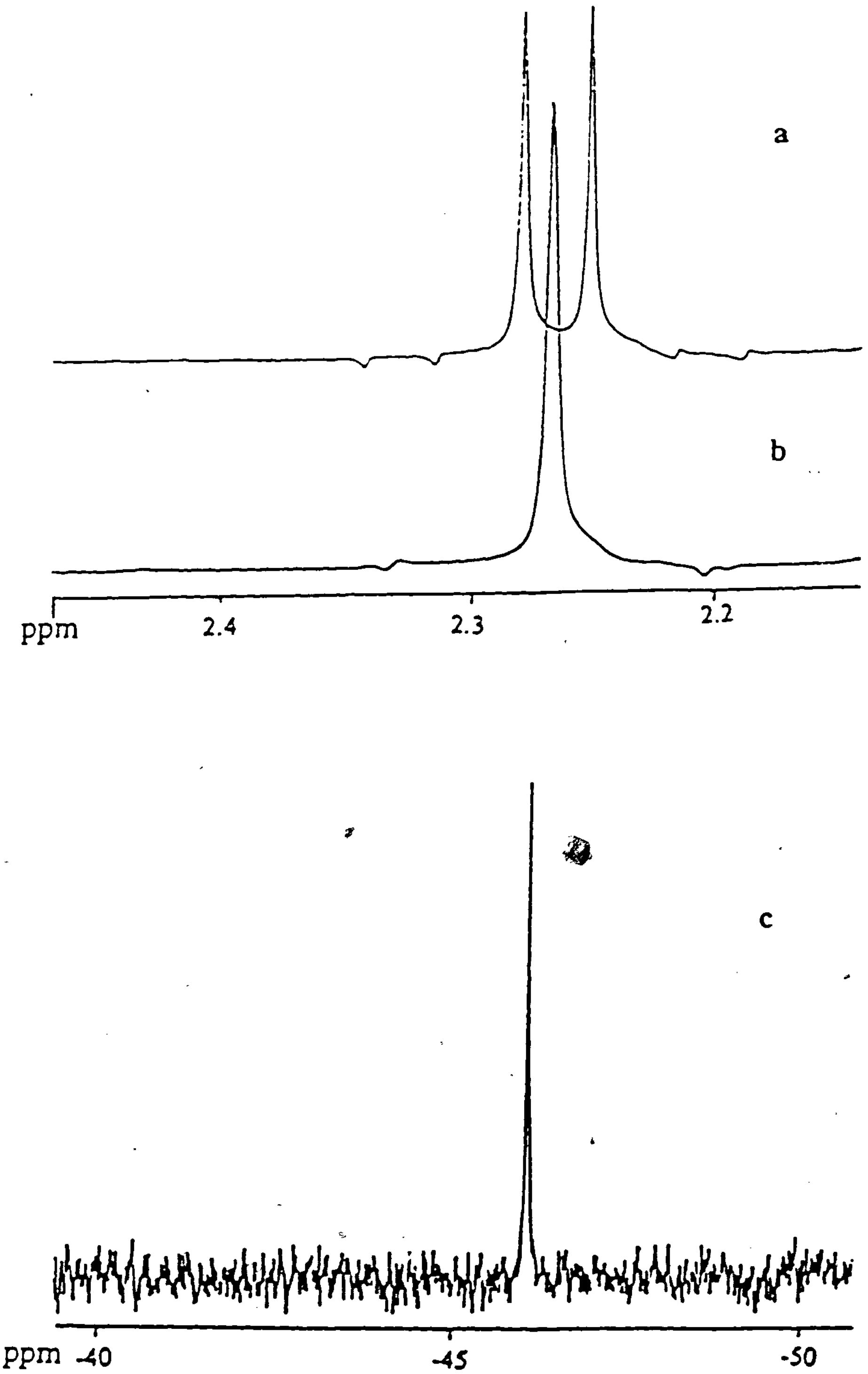
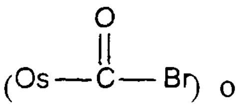
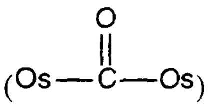


Figure 3.9 a) ^{1}H b) ^{1}H {^{31}P} c) ^{31}P{^{1}H} NMR of [Os(CO)$_4$(PMe$_3$)(Br)]Br$_3$ at room temperature in CD$_2$Cl$_2$.

3.2.5 Preliminary spectroscopic studies on $Os(CO)_5.Br_2$ (3.2)

The infrared spectrum of **3.2** in CH_2Cl_2 after various times is shown in Figure 3.10. It has a ν(CO) pattern similar to **3.1** but the positions of the carbonyl bands appear at far lower wavenumbers. Therefore, the structure can not be $[Os(CO)_5(Br)]Br$ as was anticipated. The IR spectrum shows CO absorbance bands in region 1650-1750 cm^{-1} which is consistent with either an acyl bromide  $(\mathrm{Os{-}\overset{\overset{O}{\|}}{C}{-}Br})$ or a bridging carbonyl  $(\mathrm{Os{-}\overset{\overset{O}{\|}}{C}{-}Os})$, the latter possibility is considered unlikely as not many osmium complexes are known with bridging carbonyl ligands. Spectrum (1) in Figure 3.10 has a band at 1722 cm^{-1} which disappears in about 3 h (see 3 in Fig. 3.10) and a band at 1670 cm^{-1} that has increased in intensity (see also page 69). The peak marked with an asterisk may be due to the starting material. The analysis of the spectra indicates the presence of two compounds **3.2A** and **3.2B** at the beginning of the reaction. Although the spectra need to be redetermined, apparently **A** and **B** have a similar IR pattern in the region 2000-2200 cm^{-1}, but **A** exhibits a strong band at 1722 cm^{-1} while **B** has two weaker bands at 1671 and 1603 cm^{-1}. It is not clear if the band at 1603 cm^{-1} is genuine (see the spectrum on page 69). Preliminary evidence indicates that **A** converts to **B** completely in CH_2Cl_2 after 3 h. Compound **3.2B** is tentatively assigned as the acyl bromide derivative *cis*-$Os(CO)_4(COBr)(Br)$. The structure of **3.2A** is unknown.

The ^{13}C NMR spectrum of **3.2** (~10% enriched in ^{13}CO) at -40 °C is shown in Figure 3.11. A satisfactory interpretation of the ^{13}C NMR spectra of **3.2** is currently not possible. The spectrum shows signals at δ 165.2, 163.9 and 161.7 which are tentatively assigned to **3.2B** as follows. The resonance at δ 165.2 of relative intensity two is attributed to the two axial carbonyls **a** which are equivalent. Likewise, the signals at δ 163.9, that is a multiplet,

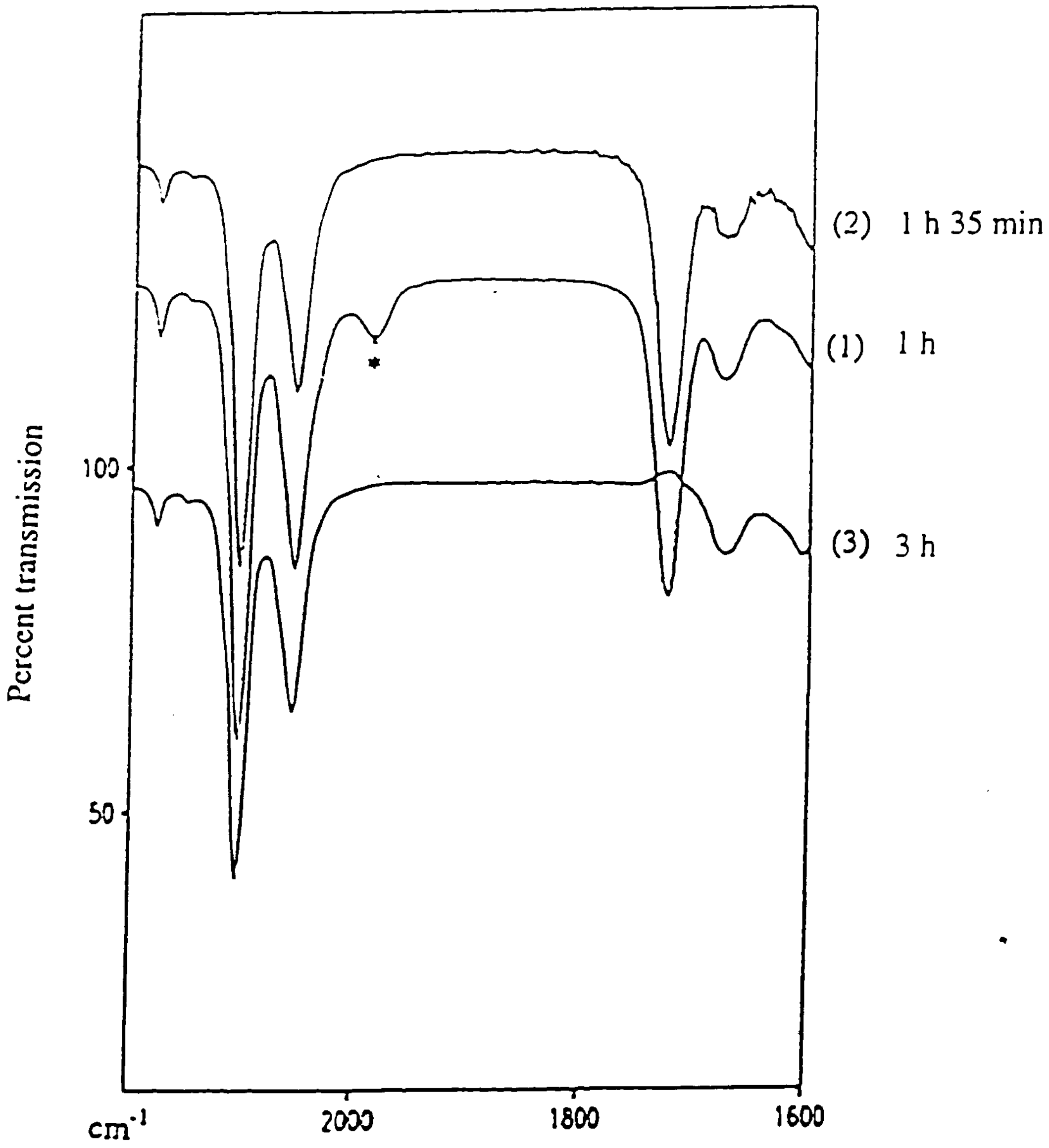


Figure 3.10 IR spectra (1), (2) and (3) (carbonyl region) of $Os(CO)_5.Br_2$ (**3.2**) at different time intervals. See Figure 3.14 (page 69) for an IR spectrum of pure **3.2B**.

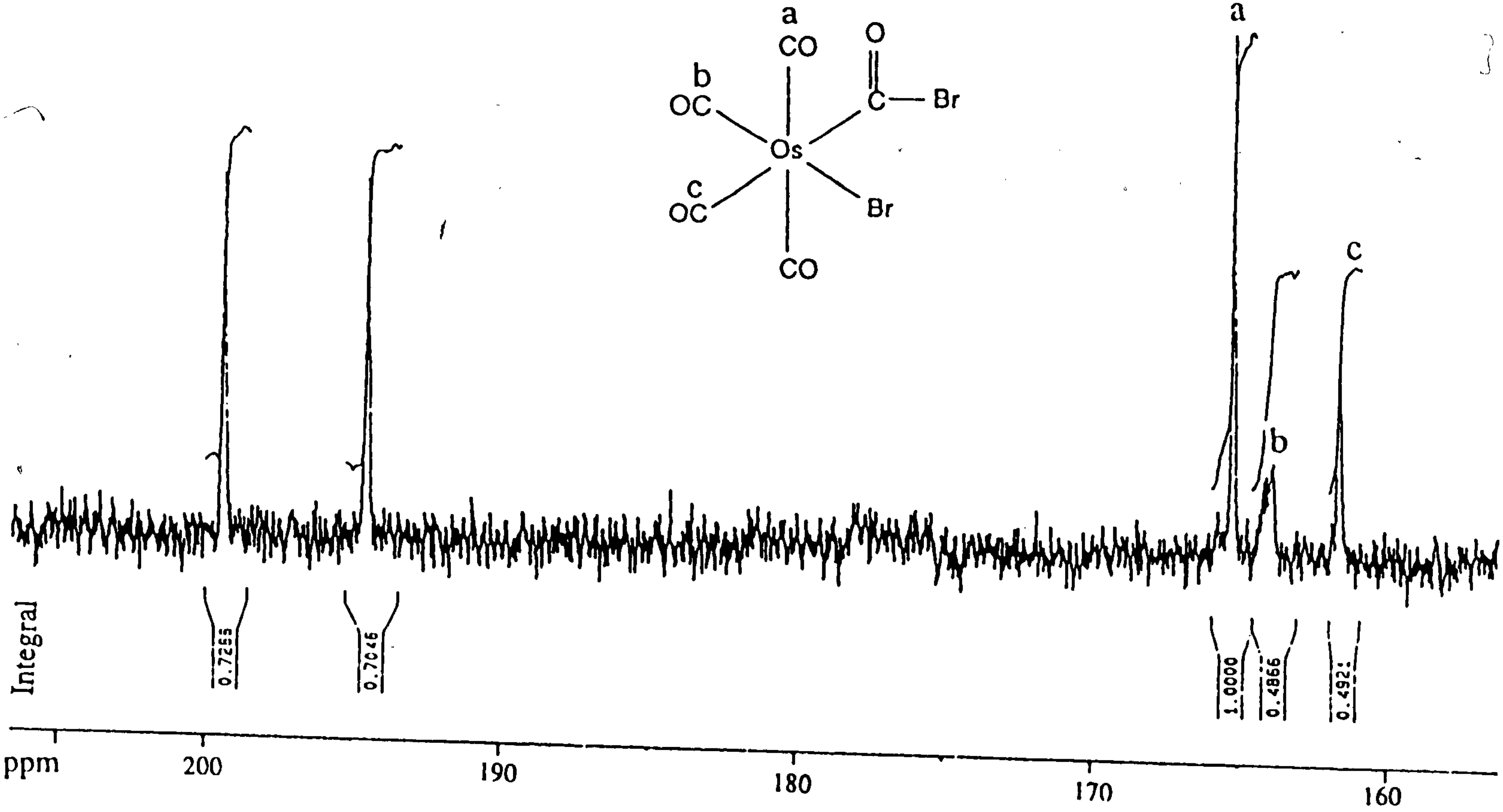
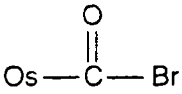
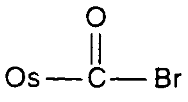
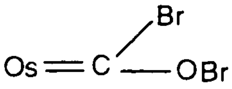


Figure 3.11 ^{13}C NMR of $Os(CO)_5.Br_2$ in CH_2Cl_2/CD_2Cl_2 at -40 °C.

and 161.7 are attributed to carbonyls **b** and **c,** respectively. The multiplicity of the resonance at δ 163.9 is tentatively attributed to the J-coupling of the carbonyl carbon to the two isotopes of Br (^{79}Br, spin 3/2 with a natural abundance of 50.54% and ^{81}Br spin 3/2 with a natural abundance of 49.46%). Each isotope would give (2nI+1) or four resonances for a total of 8 resonances of roughly equal intensity. The J-coupling of bromine to the other carbonyl carbon atoms is not observed since they are cis rather than trans to the bromine ligand. It is known that trans coupling is typically an order of magnitude larger than comparable cis coupling. It should, however, be pointed out that studies in this group have never observed coupling to bromine before (it self decouples because of quadrupolar effects). As discussed for $[Os(CO)_5Br]^+$, these are the unusual chemical shifts for Os-CO species (which are normally in the range of δ 170-195 ppm). It is proposed that the CO resonance due to the  $Os{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Br$ unit was not seen since it was outside the chemical shift region investigated (0-200 ppm). A resonance outside the region of observation would be "folded in" to the observed region and would not have the phase of the other resonances that occur in the region. Obviously, the spectra need to be repeated in the region 200-380 ppm where the resonance of an Os-C(O)Br group might be expected to come.[48]

As mentioned earlier, the identity of the species **3.2A** giving rise to the other carbonyl signals is at present unknown. The region in which these two resonances occur is typical of $Os(CO)_{5-x}(L)_x$ where L is an *electron donating* ligand *e.g.*, for $Os(CO)_4(PMe_3)$ the ^{13}C NMR resonance occurs at δ 189.9 (Table 3.1).[19] It is difficult to visualize how addition of two electron withdrawing bromine atoms to $Os(CO)_5$ could give rise to a species with such low field resonances. Note the resonances assigned to **3.2A** are some 30 ppm downfield to those of **3.2B**. Since the two resonances are of equal intensity at different temperatures, compound **A** appears to be rigid. It is probable that a third resonance (of half the intensity since there are 5 carbonyl groups in the starting complex) is present, but it too was outside the region of study. It has also been observed (Figure 3.12) that the intensities of the resonances attributed to **3.2A** relative to those due to **3.2B** varied with the sample. It is believed that **3.2A** is the kinetic product of the bromination and that on standing in CH_2Cl_2 solution at room temperature it isomerizes to **3.2B** (or an equilibrium mixture that highly favors **3.2B**). There was evidence for this in the IR spectra of a fresh sample that was left standing in CH_2Cl_2 as discussed earlier. Once again, more experiments are needed now that it is realized that **3.2** is a mixture of two forms. The identity of **3.2A** is particularly intriguing and we do not wish to speculate on its structure at this time. It may be possible to grow crystals of pure **3.2A** by carrying out the addition of Br_2 to $Os(CO)_5$ slowly at low temperature. Crystals of **3.2B** might be obtained by allowing the sample of **3.2** to completely isomerize before attempting to grow crystals. The ^{13}C NMR spectra of **3.2** will be thoroughly investigated from 200-380 ppm where resonances due to  $\mathrm{Os{-}C({=}O){-}Br}$ (or even the carbene unit  $\mathrm{Os{=}C(Br){-}OBr}$) would be expected to occur.[48]

The formation of the compound **3.2** with the formulation $Os(CO)_5.Br_2$ was an unanticipated result; the bromonium ion derivative $[Os(CO)_5(Br)][Br]$ or $[Os(CO)_5(Br)][Br_3]$ was the expected product from the reaction of Br_2 with $Os(CO)_5$. Noack has proposed that the bromination of $Fe(CO)_5$ to give *cis*-$Fe(CO)_4(Br)_2$ proceeds via an acyl bromide intermediate (shown in Scheme 3.2),[37] but this conversion took place above -30 °C.

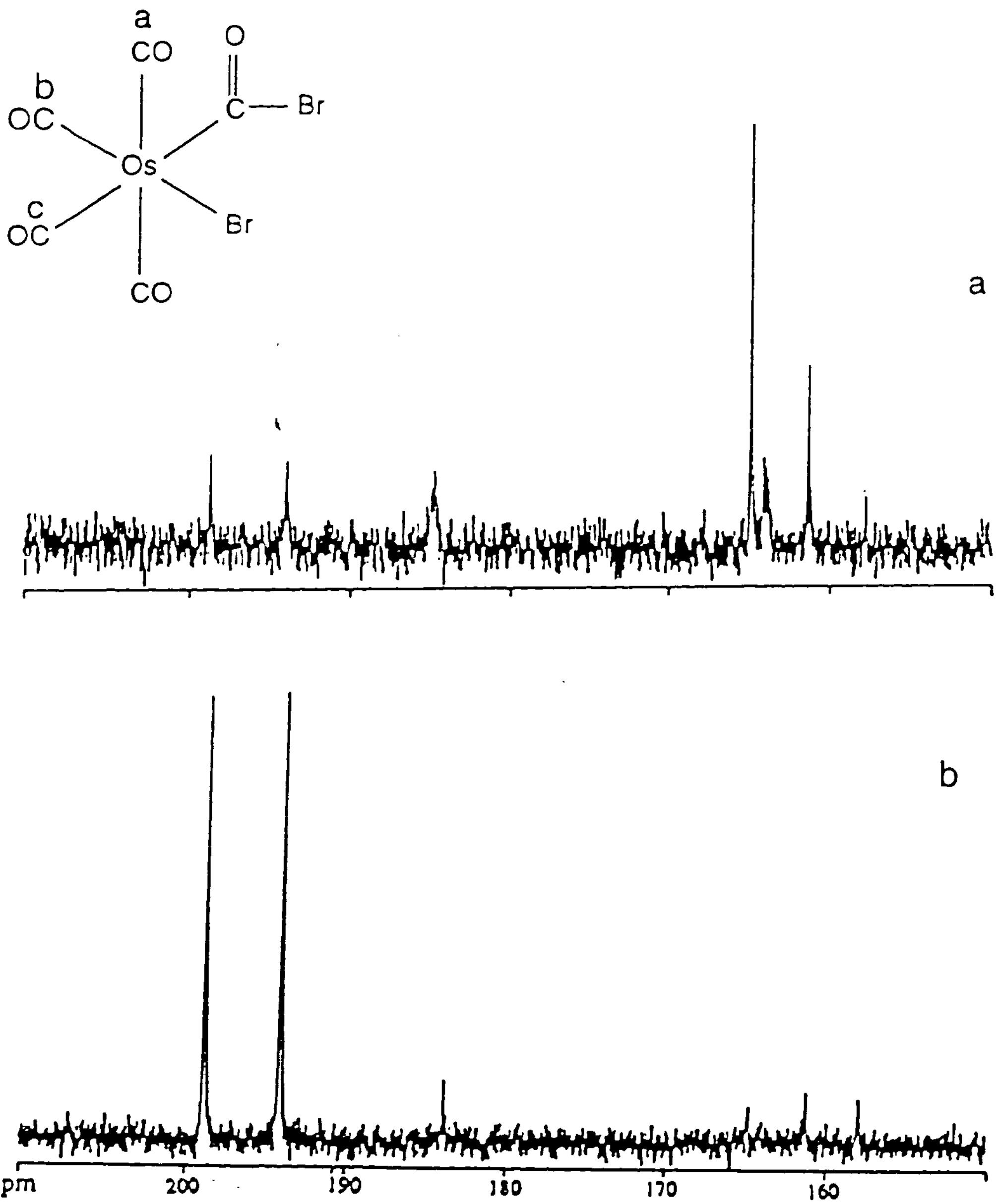
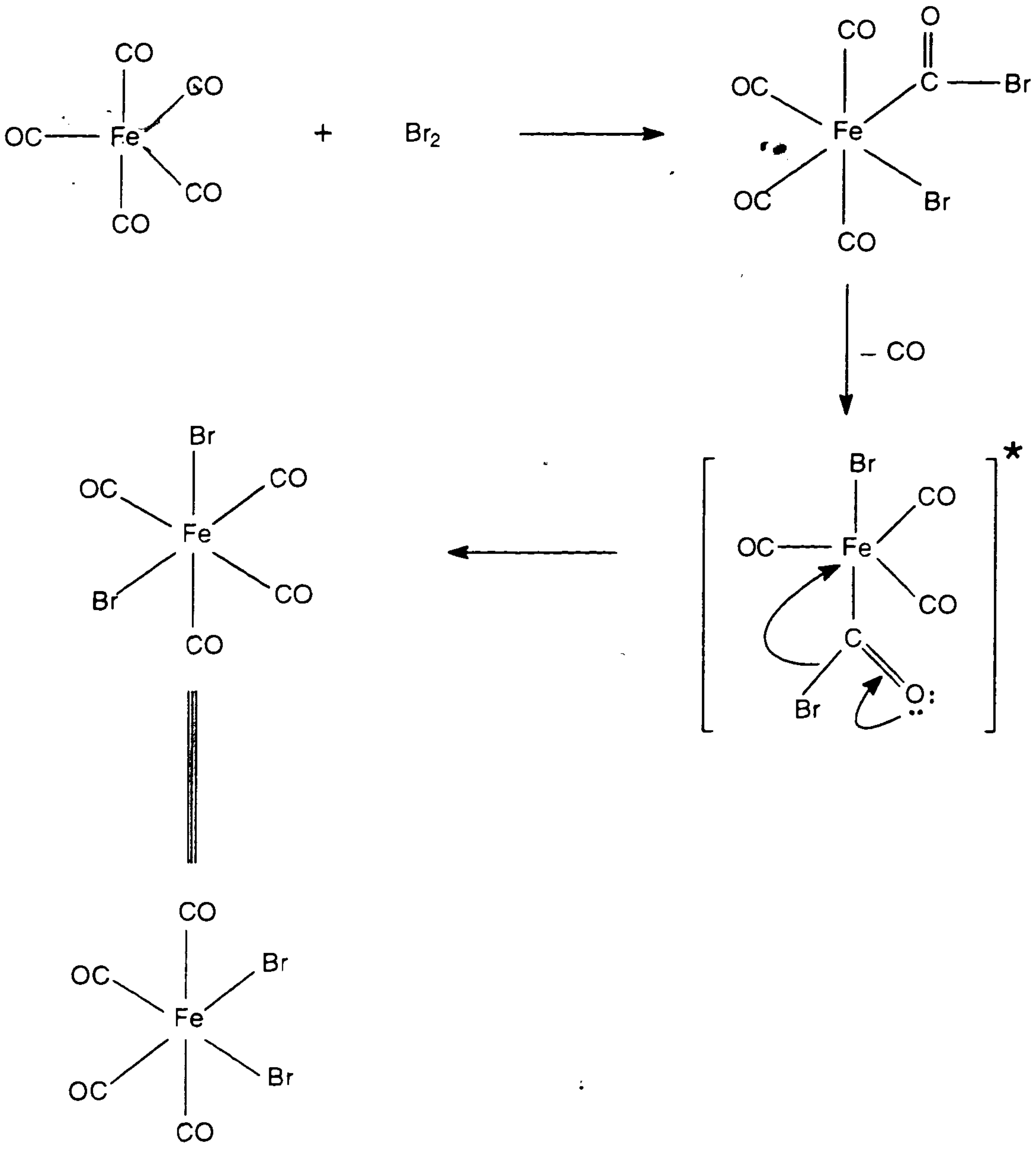


Figure 3.12 ^{13}C NMR spectra of $Os(CO)_5.Br_2$ (a) in $CHFCl_2/CD_2Cl_2$ at -120 °C (b) in CH_2Cl_2/CD_2Cl_2 at -95 °C.



Scheme 3.2 Proposed mechanism for the formation of $Fe(CO)_4Br_2$

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* other isomers are possible but poor π-acceptors prefer axial sites.

Furthermore, our results provide no indication of *cis*-$Os(CO)_4(Br)_2$ in the reaction (that has been prepared by other methods in the Pomeroy's laboratory). This can be attributed to the stronger M-C bonding in the third row transition metal carbonyl complex. The structure proposed for the compound **3.2B** is shown in Figure 3.13. It is the cis form and analogous to the Fe compound proposed by Noack.[37]

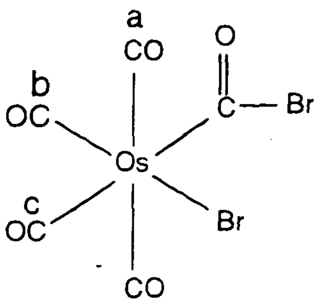
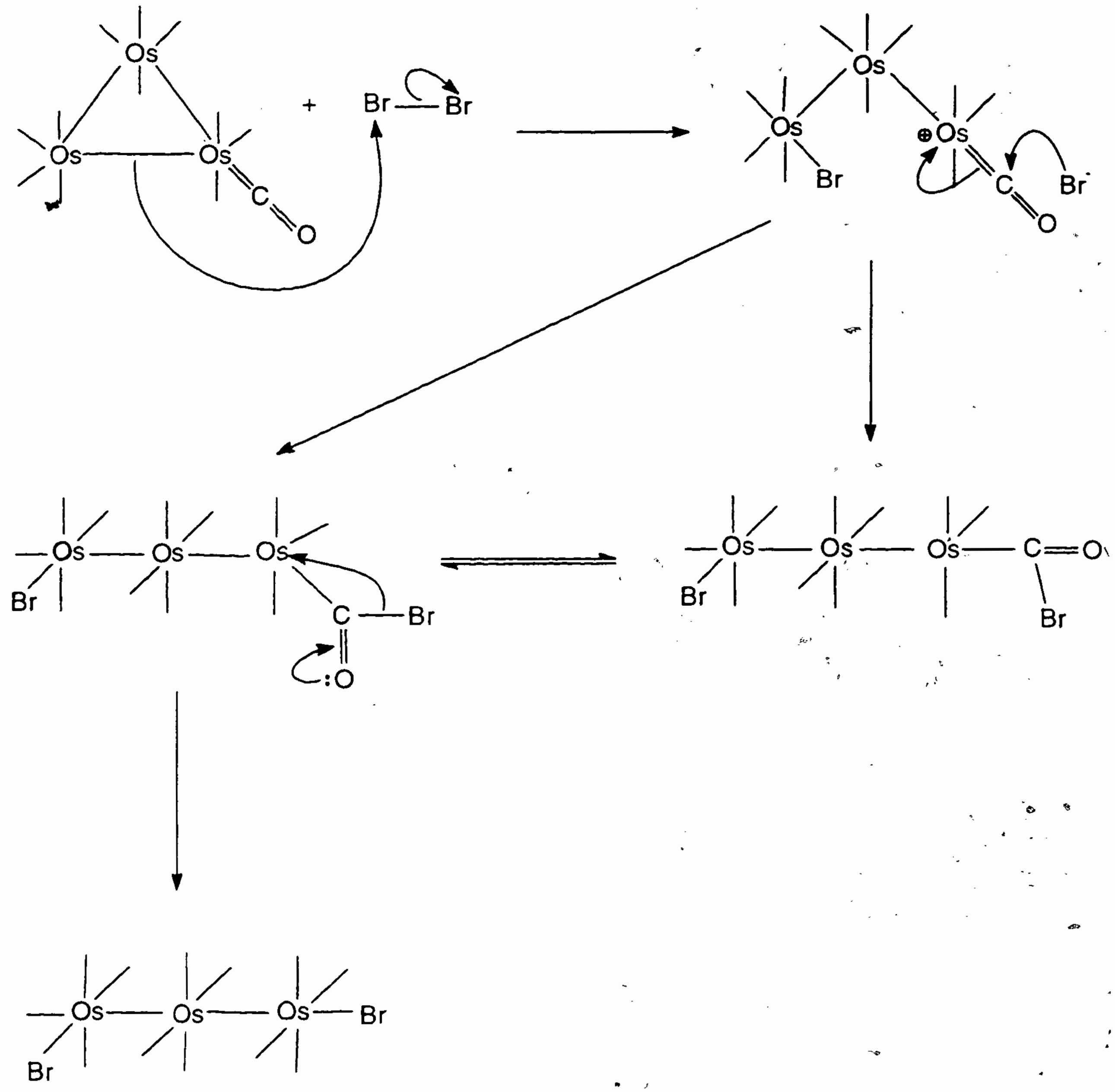


Figure 3.13 Proposed structure for $Os(CO)_5.Br_2$ (**3.2B**)

An acyl bromide intermediate might also explain why the *trans,cis-* rather than the *cis,cis*-$Os_3(CO)_{12}(Br)_2$ compound is the initial product of the bromination of $Os_3(CO)_{12}$, as described in Chapter 2 of this thesis. An acyl bromide intermediate could readily yield the trans product since there would be free rotation about the Os-C(O)Br bond. This is shown in Scheme 3.3.

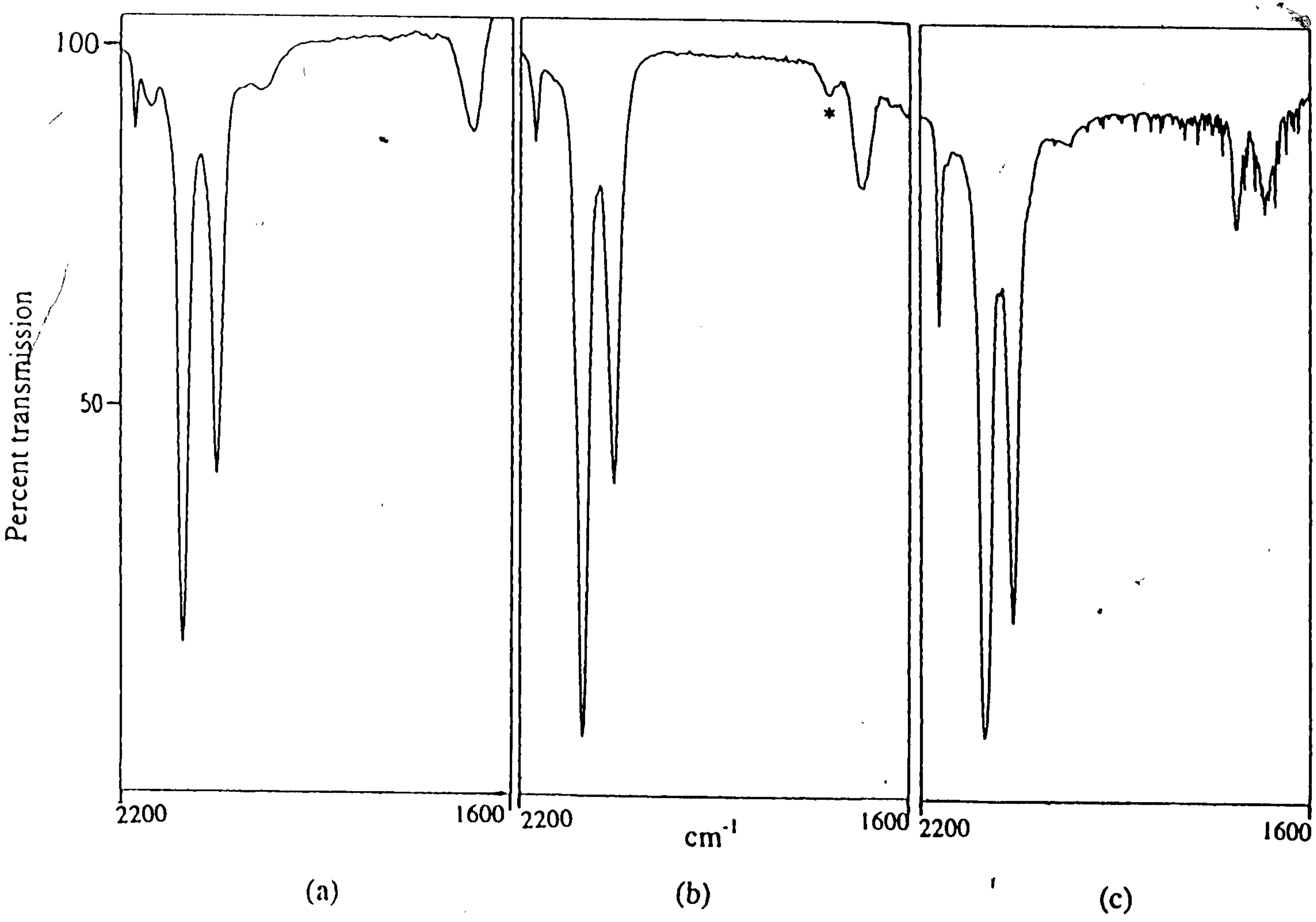


Scheme 3.3 Proposed mechanism for the bromination of $Os_3(CO)_{12}$ to give *trans,cis*-$Os_3(CO)_{12}Br_2$.

Note that five coordinate complexes such as the terminal Os-$Os(CO)_3(COBr)$ unit are invariably nonrigid and undergo rapid ax-eq ligand exchange so that the intermediate could rapidly isomerize to the equatorial isomer if the COBr unit were initially formed in an axial position.

3.2.6 Preliminary study of the reactions of $Os(CO)_5$ with Cl_2 and I_2

Preliminary results indicate that the reaction of $Os(CO)_5$ with Cl_2 and I_2 yields products analogous to $Os(CO)_5.Br_2$. Osmium pentacarbonyl was treated with Cl_2, and I_2 under similar reaction conditions used for the bromination reaction. The infrared spectra of the products obtained are shown in Figure 3.14. The $Os(CO)_5.Cl_2$ complex was originally formulated as $[Os(CO)_5(Cl)]Cl$, but this is almost certainly not the case. The IR spectrum in the carbonyl region (Figure 3.14) closely resembles that of $Os(CO)_5.Br_2$ (**3.2B**) and not $[Os(CO)_5Br]^+$ (**3.1**). Indeed, the original notes of Dr. Rushman, who first prepared $Os(CO)_5.Cl_2$, reports a CO stretch in the IR spectrum at 1720 cm^{-1} which disappeared upon recrystallization of the compound and was probably dismissed as an artifact (*e.g.*, due to wash acetone).[28b] It was customary at the time to only record IR spectra of new compounds between the region 2200-1800 cm^{-1} where the CO stretches of terminal carbonyl ligands occur (there are very few osmium compounds known with bridging carbonyl ligands). It therefore appears that $Os(CO)_5.Cl_2$ also exists in two forms analogous to **3.2A** and **B**. As previously mentioned, crystals of $Os(CO)_5.Br_2$ suitable for X-ray crystallography could not be obtained. It may be that $Os(CO)_5.X_2$ (X = Cl, Br, and I) would give crystalline products suitable for analysis by X-ray crystallography especially now that it is realized that two isomers are possible. That $Os(CO)_5.I_2$ exhibits two bands in the 1600-1700 cm^{-1} region of



(a) (b) (c)

Figure 3.14 IR spectra (carbonyl region) (a) chlorination (b) bromination (c) iodination products of $Os(CO)_5$. *Some 3.2A may still be present.

the IR spectrum indicates both forms are present. On the other hand, $Os(CO)_5.Cl_2$ apparently has one band in this region and may therefore be the best compound to attempt to grow crystal of a crystallographic study.

As expected, there is a wavenumber decrease in the CO absorbances in the infrared spectra on going from the chloro to the iodo derivative. This can be explained as due to a higher degree of $d\pi$-π^* bonding from the metal to the carbon monoxide groups in the iodo derivative. This results from the increased electron density at the metal center due to the lower electronegativity of I compared to Cl (or Br). The IR spectra of these derivatives are similar to those reported for $Fe(CO)_5.Br_2$ (ν(CO): 2152(m), 2090(s), 2066(w), 1665(w) cm^{-1}).[37]

3.3 Conclusion

The initial product from the bromination of $Os(CO)_5$ was not the expected ionic compound $[Os(CO)_5Br]Br$ but $Os(CO)_5.Br_2$ (**3.2**). The cation $[Os(CO)_5Br][TFPB]$ was obtained by a different route from $Os(CO)_5$ and $[Ad_2Br]TFPB$ in the dark at low temperature and its formulation confirmed by infrared and ^{13}C NMR studies. An important finding of this investigation therefore is that the cation $[Os(CO)_5Br]^+$ (**3.1**) is *not* an intermediate in the bromination of $Os(CO)_5$.

Evidence has been presented that **3.2** exists in two isomeric forms in solution which was not realized when the experiments were carried out. More detailed studies are, therefore, required to determine the nature of the initial products of the reaction of bromine with $Os(CO)_5$. This and other aspects of the halogenation of group 8 pentacarbonyls will be the subject of a future investigation.

A phosphine analogue of the cation **3.1** has also been prepared from a phosphine-substituted pentacarbonyl of osmium. In this case, the bromonium ion can be prepared by using Br_2 rather $[Ad_2Br]^+$.

3.4 Experimental

3.4.1 General Methods

The following general procedures were applied to all experimental work reported in this chapter unless otherwise stated. Manipulations of starting materials and products were carried out in the dark under an inert atmosphere of nitrogen with the use of Schlenk-tube techniques.

3.4.2 Materials

Hexane was refluxed over potassium, distilled and stored under nitrogen before use. Dichloromethane was treated similarly, except CaH_2 was used as the drying agent. The NMR solvents were CD_2Cl_2 and CH_2Cl_2/CD_2Cl_2 (3:1) which were stored in a dry box. Carbon-13 CO (99% ^{13}C and 10% ^{18}O) was used in the labeling of complexes with ^{13}CO. Osmium pentacarbonyl, $Os(CO)_5$ was prepared from $Os_3(CO)_{12}$ at ~350 °C under CO (200 atm at room temperature) according to the literature method.[28b] Pentacarbonylosmium is a liquid at room temperature and difficult to isolate and manipulate in the pure state. For this reason the solutions of $Os(CO)_5$ were employed. The concentration of the solution of $Os(CO)_5$ that was produced from the reaction was calculated from the amount of $Os_3(CO)_{12}$ that was left unreacted. By this method it was estimated that 1 mL of the hexane solution contained about

0.008 g of $Os(CO)_5$. Bromine (Anachaemia) and tetraethylammonium bromide $[(C_2H_5)_4N]Br$ (Eastman) were obtained commercially. The adamantylideneadamantane bromonium salt of TFPB was prepared as described in Chapter 2. The compound $Os(CO)_4(PMe_3)$ was prepared from $Os(CO)_5$ by a literature procedure.[49]

3.4.3 Instrumentation

An external medium-pressure mercury discharge lamp (200W, Hanovia Model 654 A36) surrounded by a water-cooled jacket was employed for the UV irradiation experiments. The distance between the sample and the lamp was approximately 5 cm. Infrared spectra were recorded on a Bomem Michelson model 120 FT spectrophotometer. Samples were contained in cells with NaCl windows. All ^1H, ^{31}P, and ^{13}C NMR data were recorded at the specified temperatures on a Bruker AMX 400 instrument at an operating frequencies of 400.13, 162.0 and 100.6, MHz, respectively. Mass spectra were obtained with a Hewlett-Packard Model 5985 mass spectrometer. Spectra were determined in the FAB mode (Xenon). Microanalyses were performed in the Microanalytical Laboratory at Simon Fraser University by M. Yang.

3.4.4 Preparation of $[Os(CO)_5Br]TFPB$ (3.1)

The dropwise addition of a solution of $[Ad_2Br][TFPB]$ (80 mg, 0.066 mmol) in CH_2Cl_2 to $Os(CO)_5$/hexane (22 mg, 0.066 mmol) while stirring at -78 °C, resulted in the formation of a light tan precipitate. The reaction mixture was left to stand for 10 min at which time the solvent was decanted from the precipitate. An infrared spectrum at this time showed the formation of a new product with no bands due to the starting material remaining.

The pure compound was obtained as off-white crystals by recrystallization from CH_2Cl_2. Yield (55 mg, 65%). IR(CH_2Cl_2) ν(CO): 2222(w), 2152(vs), 2120(s), cm^{-1}, ^{13}C NMR (CH_2Cl_2/CD_2Cl_2, 0 °C): δ 154.2 (4 C), 152.0 (1 C). MS (FAB, m/z): 411 $[M]^+$, 383 $[M-CO]^+$

Elemental analysis : *(Found)* *34.74% C* *0.97% H*

(Calculated for $C_{37}H_{12}BBrF_{24}O_5Os$*)* *34.90% C* *0.94% H*

The ^{13}CO-enriched compound **3.1** was synthesized in an identical way from ^{13}CO-enriched $Os(CO)_5$ (see below).

3.4.5 Preparation of ^{13}CO-enriched $Os(CO)_5$

An evacuated Pyrex Carius tube fitted with a Teflon valve was charged with $Os(CO)_5$ solution in hexane (30 mL) and subjected to three cycles of freeze-pump-thaw. The vessel was then pressurized with 2 atm of ^{13}C-enriched CO. The stirred and air-cooled solution was irradiated with a 200W Hanovia medium pressure mercury lamp through a filter ($\lambda \geq 400$ nm) for 29 h. The resulting yellow solution was evacuated and $Os(CO)_5$/hexane was separated from $Os_3(CO)_{12}$ by vacuum transfer. The concentration of $Os(CO)_5$ was approximately 1×10^{-2} M, and the material was ~10% ^{13}C labeled.

3.4.6 Reaction of $[Os(CO)_5Br][TFPB]$ (3.1) with $[(C_2H_5)_4N]Br$

To **3.1** (10 mg, 0.0078 mmol) was added $[Et_4N]Br$ (3.0 mg, 0.014 mmol) at room temperature and an infrared spectrum was taken as soon as possible after the addition. The spectrum revealed bands only due to $Os(CO)_5.Br_2$ (**3.2B**) *i.e.*, the reaction was essentially instantaneous. IR(CH_2Cl_2) ν(CO) cm^{-1}: 2176(w), 2103(vs), 2055(s), 1670.5(w).

3.4.7 Preparation of $Os(CO)_5.Br_2$ (3.2)

To a solution of $Os(CO)_5$ in hexane (10 mL, 80 mg, 0.242 mmol) at -78 °C was added, dropwise, Br_2 (0.009 mL, 20 mg) as a solution in CH_2Cl_2. A light tan precipitate formed which was allowed to stand for 10 min at which time the solvent was decanted from the solid. The compound was then recrystallized from CH_2Cl_2. Several attempts to grow suitable crystals of **3.2** for X-ray analysis were unsuccessful. Yield (70 mg, 59%) IR (CH_2Cl_2) of **3.2B** ν(CO) cm^{-1}: 2176(w), 2103(vs), 2055(s), 1670.5(w), ^{13}C NMR (CH_2Cl_2/CD_2Cl_2, -40 °C): δ 199.4 (2C), 194.5 (2C) due to **3.2A**, 165.2 (2C), 163.9 (1C), 161.7 (1C) due to **3.2B**. A satisfactory mass spectrum was not obtained by EI and FAB mode.

Elemental analysis : (Found) *12.01% C* *0.00% H*

(Calculated for $C_5Br_2O_5Os$) *12.25% C* *0.00% H*

3.4.8 Reaction of $Os(CO)_5.Br_2$ (3.2) with Na[TFPB]

To $Os(CO)_5.Br_2$ (30 mg, 0.060 mmol) was added Na[TFPB] (54 mg, 0.060 mmol). The infrared spectrum which was taken soon after the addition of Na[TFPB] showed bands due to compound **3.1**. IR(CH_2Cl_2) ν(CO): 2222(w), 2150(vs), 2119(s).

3.4.9 Preparation of [$Os(CO)_4(PMe_3)$]Br_3 (3.3)

The solution of Br_2 in CH_2Cl_2, (1 eq, 0.004 mL) was added dropwise to a vigorously stirred solution of $Os(CO)_4(PMe_3)$ (30 mg, 0.079 mmol) in CH_2Cl_2 (20 mL) at -78 °C until the colourless solution went pale-yellow and the starting material was completely consumed (by IR spectroscopy). The solvent was removed under vacuum, and the crude product was purified by recrystallization from CH_2Cl_2 to give air-stable yellow crystals. Yield (32 mg, 75%) IR (CH_2Cl_2) ν(CO): 2182(m), 2128(m), 2107(vs), 2080(s) cm^{-1}, ^1H NMR (CD_2Cl_2, rt): δ 2.26 (J_{PH} = 11.3 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ -46.0; $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, rt): δ 163.8 (J_{PC} = 10 Hz), 159.3 (J_{PC} = 59 Hz), 158.9 (J_{PC} = 15 Hz).

Elemental analysis : (Found)		*12.21% C*	*1.17% H*
	(Calculated for $C_7H_9Br_4O_4OsP$)	*12.06% C*	*1.30% H*

The ^{13}CO-enriched compound **3.3** was synthesized in an identical way from ^{13}CO-enriched $Os(CO)_4(PMe_3)$.

3.4.10 The ^{13}CO enrichment of $Os(CO)_4(PMe_3)$

A solution of $Os(CO)_4(PMe_3)$ (40 mg) in C_6H_6 (25 mL) was placed in an evacuated Pyrex Carius tube and subjected to three cycles of freeze-pump-thaw. The vessel was then pressurized with 2 atm of ^{13}C-enriched CO. The stirred and air-cooled solution was irradiated with Hanovia medium pressure mercury lamp through a filter ($\lambda \geq$ 400 nm) for six days (144 h). The yellow solution was then transferred to a Schlenk tube and the solvent was evaporated under vacuum. The resulting yellow solid was then sublimed to a probe at -78 °C. Yield (15 mg, 38%, ~10% labeled).

REFERENCES

1. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of organotransition Metal Chemistry* University Science books: Mill Valley, CA, **1987**, Parts II and III.
2. Hoffman, R. *Angew. Chem. Int. Ed.* **1982**, *21*, 711.
3. Carey, F. A.; Sundberg, R. J. *Advanced Organic chemistry*; Second Edition: **1984,** Part A.
4. Nagorski, R. W.; Brown, R. S. *J. Am. Chem. Soc.* **1992**, *114*, 7773.
5. Strating, J.; Wieringa, J. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1969**, 907.
6. Brown, R. S. *Acc. Chem. Res.* **1997**, *30*, 131.
7. Slebocka, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504.
8. Ruasse, M. F. *Advances in Physical Organic Chemistry*, **1993**, *28*, 207.
9. Strating, J.; Wieringa, J. H.; Wynberg H. *Tetrahedron Letters*, **1970**, *52*, 4579.
10. Bahr, S. R.; Boudjouk, P. *J. Org. Chem.* **1992**, *57*, 5545.
11. Brown, R. S.; Nagorski, R. W.; Bennet, A.J.; McClung, R. E. D.; Aarts, G. H. M.; Klobukowski, M.; McDonald, R.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1994**, *116*, 2448.
12. Sanati, H. K.; Becalska, A.; Ma, A. K.; Pomeroy, R. K. *J. Chem. Soc., Chem. Commun.* **1990**, 198.
13. Sutton, E. E. *Synthetic and Structural Investigation into Homo- and Hetero-, Di- and Tri-nuclear Complexes Containing Osmium*, Ph. D Thesis, University of Cape Town, January **1986.**
14. Cook, N.; Smart, L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1744.

15. Johnson, B. F. G.; Johnston, R. D.; Lewis, J. *J. Chem. Soc. (A)*, **1990**, 798.

16. Cotton, F. A.; Johnson, B. F. G. *Inorg. Chem.* **1967**, *11*, 2113.

17. Nagra, H. K.; Batchelor, R. J.; Bennet, A. J.; Einstein, F. W. B.; Lathioor, E. C.; Pomeroy, R. K.; Wang, W. *J. Am. Chem. Soc.* **1996**, *118*, 1207.

18. (a) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P. W.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 854. (b) Nakatsuji, H.; Hada, M.; Kawashima, A. *Inorg. Chem.* **1992**, *31*, 1740.

19. Male, J. L. *The Investigation of Transition Metal Complexes Containing a Dative Metal-Metal Bond*, Ph.D Thesis, Simon Fraser University, September **1996.**

20. Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

21. Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

22. Chen, Y. S.; Wang, S.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1986**, *25*, 1118.

23. Cotton, F. A.; Duraj, S. A.; Hincley, C. C.; Matusz, M.; Roth, W. J. *Inorg. Chem.* ***1984***, *23*, 3080.

24. Lambert, B.; Chelius, E. C.; Schulz, W. J.; Carpenter, N. E. *J. Am. Chem. Soc.* **1990**, *112*, 3156.

25. Einstein, F. W. B.; Johnston, V. J.; Ma, A. K.; Pomeroy, R. K. *Organometallics* **1990,** *9*, 52.

26. Davis, H. B.; Einstein, F. W. B.; Glavina, P. G.; Jones, T.; Pomeroy, R. K.; Rushman, P. *Organometallics* **1989**, *8*, 1030.

27. (a) Alex, R. F.; Pomeroy, R. K. *Organometallics* **1987**, *6*, 2437. (b) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic; New York, **1981**, and

references therein.

28. (a) Calderazzo, F.; L'Eplattenier, F.; *Inorg. Chem.* **1967**, 6, 1220. (b) Rushman, P. G. N.; Buuren, V.; Shiralian, M.; Pomeroy, R. K. *Organometallics* **1983**, *2*, 693.
29. Aime, S.; Botta, M.; Gobetto, R.; Osello, D. *J. Chem. Soc., Dalton Trans.* **1988**, 792.
30. Bruce, M. I.; Matisons, J. G.; Wallis, R. C.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2365.
31. Moss, J. R.; Graham, W. A. G. *J. Chem. Soc., Dalton Trans.* **1977**, 89.
32. Becalska, A.; Pomeroy, R. K.; Graham, W. A. G. *Can. J. Chem.* **1989**, *67*, 1236
33. Moss, J. R.; Graham, W. A. G. *Inorganic Chemistry*, **1977**, *16*, 75.
34. Finkelstein, M.; Hart, S. A.; Moore, W. M.; Ross, S. D.; Eberson, L. *J. Org. Chem.* **1986**, *51*, 3548.
35. Fleming, M. P.; McMurray, J. E. *Organic Syntheses*, *60*, 113.
36. Lathioor, E. C.; Bennet, A. J. Unpublished results.
37. Noack, K.; *J. Organomet. Chem.* **1968**, *13*, 411.
38. Farona, M. F.; Camp, G. R. *Inorg. Chim. Acta* **1969**, *3*, 395.
39. Dobson, G. R.; Jernigan, R. T.; Chang, P. *J. Organomet. Chem.* **1973**, *54*, C33.
40. Iqbal, Z.; Waddington, T. C. *J. Chem. Soc.,(A)*, **1968**, 2958.
41. Cotton, F.A.; Kraihanzel, C.S. *Inorg. Chem.* **1963**, *2*, 533.
42. Wang, C.; Bley, B.; Jollenbeck, G. B.; Lewis, A. R.; Siu, S. C.; Willner, H.; Aubke, F. *J. Chem. Soc., Chem. Commun.* **1995**, 2071
43. Harris, R. K. Nuclear Magnetic Resonance Spectroscopy-A Physicochemical View, Longman Scientific and Technical: Hong Kong, **1986**, p 184.

44. Yoder, C. H.; and Schaeffer, C. D. *Introduction to Multinuclear NMR*, Benjamin/Cummings: Menlo Park, **1987**, p 82.

45. Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* **1985**, *24*, 2777.

46. Calderazzo, F.; L'Eplattenier, F. *Inorg. Chem.* **1968**, *7*, 1290.

47. Adams, D. M. *Metal-Ligand and Related Vibrations,* St. Martin's: New York, **1968**; p 98-101.

48. Gordon, A. J.; Ford, R. A. *The Chemists Companion,* John Wiley and Sons, 1972, p 252-290.

49. Davis, H. B. *Binuclear and Trinuclear Compounds Containing Osmium and Group 6 Metal Atoms*, Ph. D. Thesis, Simon Fraser University, Jan. **1991**.