

STUDIES ON SELECTED MONO- AND TETRANUCLEAR GROUP 8 CARBONYL
COMPOUNDS

by

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"Studies on Selected Mono- and Tetranuclear Group 8 Carbonyl Compounds"

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ABSTRACT

The compounds $M(\text{CO})_4\text{L}$ ($M=\text{Fe}, \text{Ru}, \text{Os}$, $\text{L}=\text{EPh}_3$, $\text{E}=\text{P}, \text{As}, \text{Sb}$, $\text{L}=\text{PMe}_3$, $\text{P}(\text{OCH}_2)_3\text{CMe}$; $M=\text{Ru}, \text{Os}$, $\text{L}=\text{SbMe}_3$) have been synthesized from L and $M(\text{CO})_5$. In $\text{Ru}(\text{CO})_4\text{AsPh}_3$ and $\text{Ru}(\text{CO})_4\text{SbMe}_3$, crystal structures revealed the unique ligand is in an axial position of the trigonal-bipyramidal coordination sphere, whereas, in $\text{Os}(\text{CO})_4\text{SbPh}_3$, SbPh_3 is in an equatorial site. Infrared spectroscopy showed the presence of both axial and equatorial isomers in solution for many of the complexes; interconversion is rapid on the ^{13}C NMR time scale. The tendency to give the less common equatorial isomer is $\text{Ru} > \text{Os} \gg \text{Fe}$, $\text{Sb} > \text{As} > \text{P}$, $\text{Ph} > \text{Me}$, and $\text{P}(\text{OCH}_2)_3\text{CMe} > \text{PMe}_3, \text{PPh}_3$. The ordering of the group 15 elements is rationalized in terms of their σ -donor rather than π -acceptor ability (π bonding may be important in determining the other trends). This is the first time an axial-equatorial switchover has been observed in a closely related series of five-coordinate compounds.

The clusters $\text{Os}_4(\text{CO})_n\text{PMe}_3$ ($n=15, 14, 13$) have been synthesized and their crystal structures determined. This series constitutes the first example where a 64 electron cluster displays sequential ligand loss to a 62 and then to a 60 electron species. The $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$ (1) cluster is the first reported with an unsupported donor-acceptor metal-metal bond. In $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$ (2) the Os_4 skeleton is a planar rhomboid with two long and two short Os-Os bonds. This asymmetry is discussed

in terms of a novel bonding model using three-centre-two-electron bonds. The structure of 2 is compared to that of $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$ (3) which has also been synthesized and characterized. Although 3 is isoelectronic with 2, it has an Os_4 butterfly structure with a dihedral angle of 113° . The $\text{Os}_4(\text{CO})_{13}\text{PMe}_3$ (4) compound is the only reported group 8 tetrahedral cluster with 14 two-electron donor ligands.

The fluxional properties of the clusters have been investigated by variable temperature ^{13}C NMR spectroscopy. In solution 1 undergoes CO ligand exchange probably via several different processes. In contrast to 3 which is rigid, 2 exhibits remarkable nonrigidity which is accounted for by an unusual dynamic rearrangement of the metal skeleton. Cluster 4 is highly fluxional even at -120°C .

This unique group of molecules will be of interest to chemists investigating structural and fluxional properties of clusters.

DEDICATION

For Nicole, for whom there has never been enough time.

QUOTATION

"Concern for man himself and his fate must always form the chief interest of all technical endeavors, concern for the great unsolved problems of the organization of labor and the distribution of goods--in order that the creations of our mind shall be a blessing and not a curse to mankind. Never forget this in the midst of your diagrams and equations."

. Albert Einstein

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TABLE OF CONTENTS

Approval	ii
Abstract	iii
Dedication	v
Quotation	vi
Acknowledgements	vii
List of Tables	x
List of Figures	xiii
A. AXIAL-EQUATORIAL ISOMERISM IN COMPLEXES $M(CO)_4L$ (M=Fe, Ru, Os; L=GROUP 15 LIGAND)	
.....	1
1. Introduction	2
1.1 Overview	2
1.2 Literature Survey	5
1.3 Project Description	18
2. Results	20
2.1 Structural Studies	21
2.2 Infrared Studies	32
2.3 NMR Studies	38
3. Discussion	42
3.1 Steric Considerations	42
3.2 Electronic Properties of the Ligands	47
3.3 Influence of the Central Metal	52
3.4 Summary	55
3.5 Future Directions	58
4. Experimental Procedures	60
4.1 Materials and Instrumentation	60

4.2	Synthesis Methods	61
4.3	Crystal Structure Determinations	65
B..	SYNTHESIS, STRUCTURE AND CHARACTERIZATION OF Os ₄ (CO) _n PMe ₃ (n=15, 14, 13) AND (μ-H) ₂ Os ₄ (CO) ₁₃ PMe ₃	71
1.	Introduction	72
1.1	Theoretical Approaches	72
1.2	Project Description	91
2.	Results and Discussion	93
2.1	Os ₄ (CO) ₁₅ PMe ₃	95
2.2	Os ₄ (CO) ₁₄ PMe ₃	108
2.3	(μ-H) ₂ Os ₄ (CO) ₁₃ PMe ₃	120
2.4	Os ₄ (CO) ₁₃ PMe ₃	130
2.5	Summary and Conclusions	139
3.	Experimental Procedures	143
3.1	Materials and Instrumentation	143
3.2	Synthetic Methods	144
3.3	Crystal Structure Determinations	148
	Appendix	158
	References	247

LIST OF TABLES

Table	Page
A.1.1 Previously Known $M(\text{CO})_4\text{L}$ Derivatives.	15
A.2.1 Selected Molecular Dimensions for $\text{Ru}(\text{CO})_4\text{AsPh}_3$	22
A.2.2 Selected Molecular Dimensions for $\text{Ru}(\text{CO})_4\text{SbMe}_3$	25
A.2.3 Selected Molecular Dimensions for $\text{Os}(\text{CO})_4\text{SbPh}_3$	27
A.2.4 M-C Distances in $\text{Fe}(\text{CO})_5$ and $M(\text{CO})_4\text{L}$ Compounds	29
A.2.5 Infrared, ^{13}C NMR and Melting Point Data for $M(\text{CO})_4\text{L}$ Compounds	33
A.3.1 Ligand Bond Angles for $M(\text{CO})_4\text{ER}_3$ Complexes	55
A.4.1 Analytical and Mass Spectral Data for New $M(\text{CO})_4\text{L}$ Derivatives	62
A.4.2 Diffractometer Collection and Refinement Parameters for $M(\text{CO})_4\text{L}$ Compounds	66
A.4.3 Crystallographic Data for $\text{Ru}(\text{CO})_4\text{AsPh}_3$, $\text{Os}(\text{CO})_4\text{SbPh}_3$, $\text{Ru}(\text{CO})_4\text{SbMe}_3$ and $\text{Os}(\text{CO})_4\text{AsPh}_3$	69
B.1.1 Group 8 Tetranuclear Clusters with 60 Valence Electrons .	86
B.1.2 Group 8 Butterfly Structures	88
B.1.3 Tetranuclear Group 8 Clusters with 64 Valence Electrons .	90
B.2.1 Selected Molecular Dimensions for $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$	96
B.2.2 Selected Molecular Dimensions of $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$	109

B.2.3	Selected Molecular Dimensions for $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$..	121
B.2.4	Selected Molecular Dimensions for $\text{Os}_4(\text{CO})_{13}\text{PMe}_3$	131
B.3.1	Analytical and Mass Spectral Data for Os_4 Compounds	144
B.3.2	CO Stretching Frequencies, ^1H NMR Resonances and Melting Data for Os_4 Compounds	146
B.3.3	Crystallographic Data For Os_4 Compounds	149
B.3.4	Data Collection Parameters for Os_4 Compounds	152
S.1	Fractional Coordinates for $\text{Ru}(\text{CO})_4\text{AsPh}_3$	159
S.2	Thermal Parameters for $\text{Ru}(\text{CO})_4\text{AsPh}_3$	160
S.3	Bond Lengths and Angles for the Phenyl Groups of $\text{Ru}(\text{CO})_4\text{AsPh}_3$	161
S.4	Structure Factors for $\text{Ru}(\text{CO})_4\text{AsPh}_3$	162
S.5	Fractional Coordinates for $\text{Ru}(\text{CO})_4\text{SbMe}_3$	169
S.6	Thermal Parameters for $\text{Ru}(\text{CO})_4\text{SbMe}_3$	169
S.7	Structure Factors for $\text{Ru}(\text{CO})_4\text{SbMe}_3$	170
S.8	Fractional Coordinates for $\text{Os}(\text{CO})_4\text{SbPh}_3$	174
S.9	Thermal Parameters for $\text{Os}(\text{CO})_4\text{SbPh}_3$	175
S.10	Bond Lengths and Angles for the Phenyl Groups of $\text{Os}(\text{CO})_4\text{SbPh}_3$	176
S.11	Structure Factors for $\text{Os}(\text{CO})_4\text{SbPh}_3$	177
S.12	Fractional Coordinates for $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$, Molecule 1 ...	189
S.13	Fractional Coordinates for $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$, Molecule 2 ...	190
S.14	Thermal Parameters for $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$, Molecule 1	191

S.15	Thermal Parameters for $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$, Molecule 2	192
S.16	Fractional Coordinates for Hydrogen Atoms of $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$	192
S.17	Structure Factors for $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$	193
S.18	Fractional Coordinates for $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$	212
S.19	Thermal Parameters for $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$	213
S.20	Structure Factors for $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$	214
S.21	Fractional Coordinates for $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$	224
S.22	Thermal Parameters for $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$	225
S.23	Structure Factors for $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$	226
S.24	Fractional Coordinates for $\text{Os}_4(\text{CO})_{13}\text{PMe}_3$	236
S.25	Thermal Parameters for $\text{Os}_4(\text{CO})_{13}\text{PMe}_3$	237
S.26	Structure Factors for $\text{Os}_4(\text{CO})_{13}\text{PMe}_3$	238

LIST OF FIGURES

Figure	Page
A.1.1 Trigonal Bipyramidal Geometry	2
A.1.2 Molecular Orbital Interaction Diagram for ML_5 Complexes ..	6
A.1.3 Molecular Orbitals Filled by d Electrons of $M(CO)_5$ Complexes	8
A.1.4 Molecular Orbital Diagram for π -Interactions of an ML_5 Fragment with a π -acceptor Ligand.	10
A.2.1 Thermal Ellipsoid Diagram for $Ru(CO)_4AsPh_3$	22
A.2.2 Thermal Ellipsoid Diagram for $Ru(CO)_4SbMe_3$	24
A.2.3 Thermal Ellipsoid Diagram for $Os(CO)_4SbPh_3$	26
A.2.4 Definition of Structural Angles for Five Coordinate Compounds	31
A.2.5 Solution Infrared Spectra of a) $Ru(CO)_4SbPh_3$, b) $Ru(CO)_4AsPh_3$ and c) $Ru(CO)_4PPh_3$	34
A.2.6 Solution Infrared Spectra of a) $Os(CO)_4SbPh_3$ and b) $Fe(CO)_4SbPh_3$	35
A.2.7 Solution Infrared Spectra of a) $Ru(CO)_4SbMe_3$ and b) $Ru(CO)_4P(OCH_2)_3CMe$	36
A.2.8 Solid State Infrared Spectra of a) $Ru(CO)_4SbPh_3$ and b) $Os(CO)_4SbPh_3$	37
A.2.9 Berry Pseudorotation Mechanism and Some Possible Reaction Coordinates	40

A.3.1	Newman Projections for $M(\text{CO})_4\text{ER}_3$ Compounds	44
B.1.1	Geometries of Tetranuclear Group 8 Clusters	73
B.1.2	Geometry of $\text{HOs}_3\text{Re}(\text{CO})_{15}$	76
B.1.3	Frontier Orbitals for $[\text{M}(\text{CO})_4]^{2+}$ and $\text{M}(\text{CO})_3$	81
B.1.4	The Isolobal Analogy as Applied to $\text{Os}(\text{CO})_4$ and $\text{Os}(\text{CO})_3$ Fragments	83
B.2.1	Thermal Ellipsoid Diagram for $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$, Molecule 2 .	96
B.2.2	Os-Os Bond Lengths in $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$	99
B.2.3	Variable Temperature ^{13}C NMR Spectra of $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$..	103
B.2.4	Fluxional Processes of $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$	105
B.2.5	Fluxional Processes and ^{13}C NMR Spectrum of $\text{Os}_3(\text{CO})_{11}\text{P}(\text{OMe})_3$	106
B.2.6	Thermal Ellipsoid Diagram for $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$	109
B.2.7	Bonding Model for $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$	112
B.2.8	Molecular Orbital Diagram for $[\text{Os}_4(\text{CO})_{16}]^{2+}$	114
B.2.9	Application of the Isolobal Analogy to $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$...	115
B.2.10	^{13}C NMR Spectra of $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$	115
B.2.11	Fluxional Mechanisms for $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$	118
B.2.12	Thermal Ellipsoid Diagrams for $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$	121

B.2.13	¹ H NMR Spectrum and Hydride Ligand Positions for (μ -H) ₂ Os ₄ (CO) ₁₃ PMe ₃	124
B.2.14	Octahedral Geometry of the Hinge Vertices of Butterfly Structures	126
B.2.15	¹³ C NMR Spectra for (μ -H) ₂ Os ₄ (CO) ₁₃ PMe ₃	129
B.2.16	Thermal Ellipsoid Diagram for Os ₄ (CO) ₁₃ PMe ₃	131
B.2.17	Possible Resonance Structures for Os ₄ (CO) ₁₃ PMe ₃	136
B.2.18	¹³ C NMR Spectra of Os ₄ (CO) ₁₃ PMe ₃	138

PART A

AXIAL-EQUATORIAL ISOMERISM IN COMPLEXES $M(CO)_4L$

(M=Fe, Ru, Os; L=GROUP 15 LIGAND)

CHAPTER 1
INTRODUCTION

1.1 Overview

Five-coordinate, transition metal complexes of the type ML_5 (M =transition metal, L =two electron donor ligand) exist in two ideal geometries, the trigonal bipyramid (TBP) and the square pyramid. In either geometry, a monosubstituted complex ML_4L' may take one of two isomeric forms. In a square pyramid, the unique ligand L' may appear at either an apical or basal position. In a TBP either axially or equatorially substituted geometries are possible (see Figure A.1.1). Most organometallic complexes of d^8 metals adopt a trigonal bipyramidal configuration and the site preference of the unique ligand in this form has been the subject of considerable theoretical and experimental interest. Several models describing the inherent

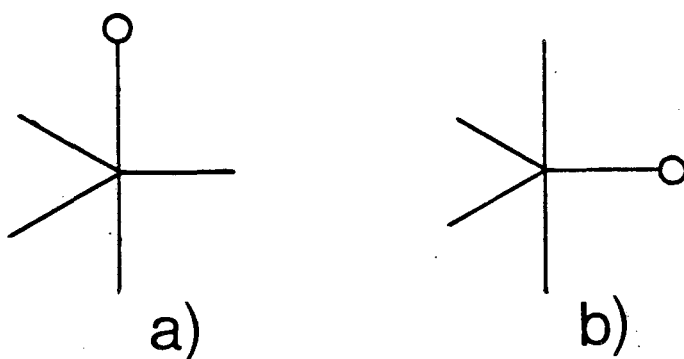


Figure A.1.1. Trigonal Bipyramidal Geometry. The unique ligand is in the a)axial and b)equatorial site.

differences of the M-L bonds in ML_5 have also been proposed.^{1,2,3} Interest has been expressed not only in the stable molecules^{4,5,6,7,8} but also in intermediates of dissociative reactions of octahedral complexes⁹ as well as of associative reactions of tetrahedral complexes.¹⁰

Nonrigidity involving axial-equatorial exchange has been observed for many TBP ML_4L' complexes, and the Berry pseudorotation mechanism has often been proposed as the exchange mechanism.¹¹ Both theoretical^{12,13} and experimental¹⁴ studies indicate the barrier to nonrigidity is low so that which isomer is adopted by a given complex can be attributed to thermodynamic rather than kinetic constraints. Infrared spectroscopy reveals which isomer predominates in solution; an axial $M(CO)_4L$ complex typically has three bands in the carbonyl stretching region while an equatorial $M(CO)_4L$ complex has four.¹⁵ The short time scale of this technique (10^{-11} s)¹⁶ allows detection of both isomeric forms if they are present in solution.

A theme common to many studies is that a ligand possessing better π -acceptor properties is more likely to be found in the equatorial site.¹⁷ Indeed, a search of the literature revealed numerous examples of strong π -acceptors such as CO, PF_3 , or NO in the equatorial position of a TBP (see Table A.1.1, page 15). However, in most cases the unique ligand, a weak π -acceptor was found in the axial site. Also, the large majority of the known complexes contained a first row transition metal as the central atom. Other (theoretical) studies indicated that the σ -donor

ability^{1,18} or the steric requirements² of the unique ligand might also be important in determining the site preference.

As the following literature survey illustrates there was little experimental evidence to support or refute these ideas. Also there was almost no discussion as to whether the period of the transition metal row could influence ligand site preference.

1.2 Literature Survey

1.2.1 *Theoretical Papers*

Without doubt, the most significant theoretical work on transition metal pentacoordination to appear in recent years is that of Rossi and Hoffmann.¹ As their work is so germane to this study, the appropriate sections are summarized here in some detail.

The authors cautioned that the extended Hückel calculations on which their model is based do not take into account steric or electrostatic effects. It might also be added that the calculations were performed on ML_5 species where M was a third row transition metal (Pt). What effect changing M to a first or second row metal might have had on their conclusions was not discussed.

The consideration of the electronic effects began with a molecular orbital interaction diagram (reproduced in Figure A.1.2). for a trigonal bipyramidal ML_5 species assuming π bonding ligands are absent. The low lying e' , a_2'' and a_1' orbitals can be viewed as filled by ligand electrons; their nature is such that for d^0 systems the axial bonds are weaker than the equatorial ones. As metal d electrons are added the e'' orbitals are filled first. Since this set is rigorously non-bonding, there is no effect on bond strength. The next orbitals to be filled, the e' set are weakly metal-equatorial antibonding. The antibonding nature arises from mixing of not

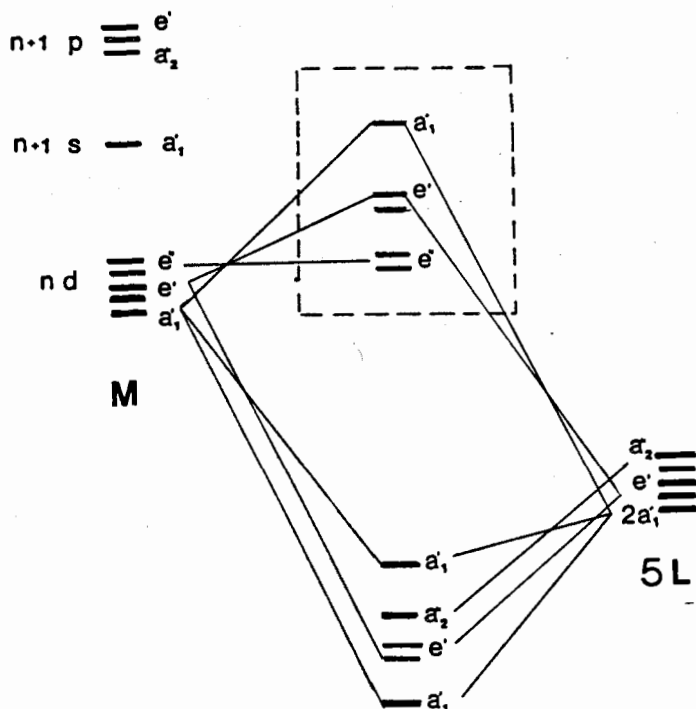


Figure A.1.2. Molecular Orbital Interaction Diagram for ML_5 Complexes. The interactions shown here are for σ interactions only, π -bonding interactions are considered subsequently. (After Rossi and Hoffmann.¹)

only ligand σ and metal nd orbitals but metal $(n+1)p$ orbitals as well. The $(n+1)p$ orbital mixing has the effect of hybridizing the orbitals away from the ligands thus weakening the antibonding interaction and stabilizing the orbital. Nevertheless, addition of metal d electrons to this e' set results in weakening of the metal-equatorial ligand bonds to the extent that for the cases where the central metal has d^6-d^8

configuration, they are calculated to be weaker than the metal-axial ligand bonds. The last orbital to be filled, having a_1' symmetry, is strongly metal-axial ligand antibonding so that in a d^{10} complex, the axial bonds are once again predicted to be weaker, (see Figure A.1.3).

It is assumed that a strong σ -donor would take up the position where it would form the most stable, lowest energy bond. That is, strong σ -donor ligands are more likely to be found at equatorial sites in complexes in which the central metal has d^0 - d^4 and d^{10} electronic configuration and at axial sites if the central metal has d^6 - d^8 electronic configuration. Conversely, weak σ -donors are more likely found in an equatorial site in a complex having a central metal of d^6 to d^8 configuration.

Consideration of the effects of π bonding on the site preference of the ligands takes into account the change of symmetry of the molecule, and therefore of the orbitals, that results from substitution of only one ligand. A normal two electron donor, π -acceptor ligand, has two low-lying unoccupied orbitals of π symmetry. If the ligand occupies an axial site the molecular symmetry is changed from D_{3h} to C_{3v} and the π -acceptor orbitals on the ligand transform as e_x and e_y . If the ligand is equatorial the complex has C_{2v} symmetry and the ligand π orbitals transform as b_1 and b_2 . In this case these orbitals line up parallel and perpendicular to the original 3-fold axis of the trigonal bipyramid, respectively. The

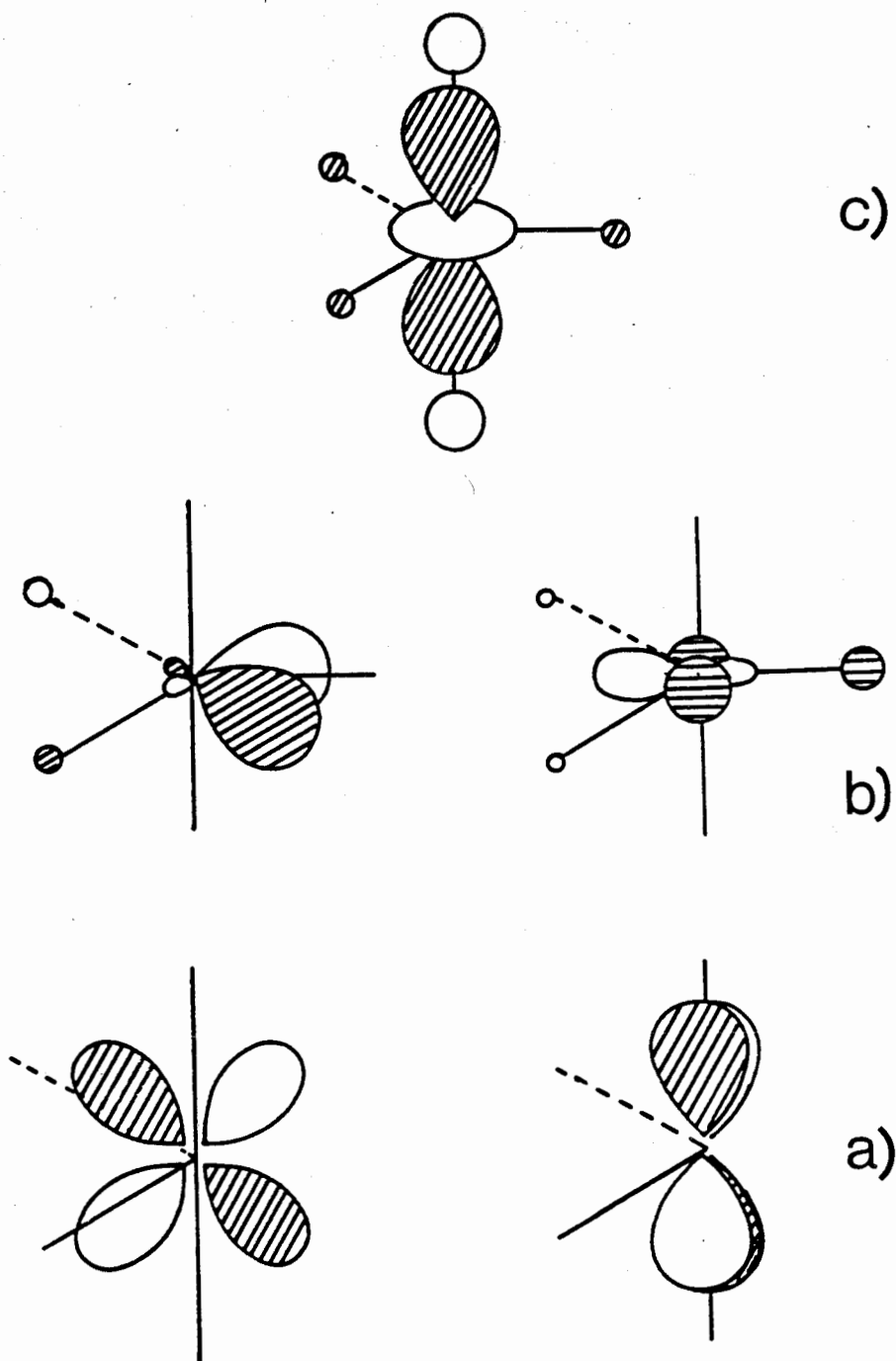


Figure A.1.3. Molecular Orbitals Filled by d Electrons of $M(CO)_5$ Complexes. The e'' orbitals shown in a) are filled first, then the e' orbitals shown in b) and finally the a_1' orbital shown in c). (After Rossi and Hoffmann.¹)

orbitals of the ML_4 framework also transform differently with the change of molecular point group. From a consideration of the π interactions of the unique ligand orbitals and ML_4 framework metal d orbitals that are allowed by symmetry, Rossi and Hoffmann concluded that the equatorial perpendicular interaction is stronger than the equatorial parallel interaction which is about equal to the axial interaction. These features are displayed in the MO diagram, given in Figure A.1.4. It was concluded that when the central metal has d^8 electronic configuration a π -acceptor ligand will favour an equatorial site.

Prediction of the site preference of a real ligand must take into account both σ and π bonding. For example conclusions drawn regarding $d^8 M(CO)_4L$ complexes must attempt an evaluation of the relative importance of these factors since CO and many other common ligands are poor σ -donors (preferring equatorial sites) and good π -acceptors (also preferring equatorial sites). Any ligand which is both a poorer σ -donor and a better π -acceptor than CO would be predicted to occupy an equatorial site. But if only one of these conditions is satisfied the situation is less clear. For example, what would be the site preference of a very poor σ -donor ligand in the presence of very good π -acceptor ligands, i.e., are σ or π effects dominant? The crystal structures analyzed by the authors showed longer equatorial bonds for $ML_5 d^8$ systems (i.e. dominance of the σ effect). However there were no consistent trends for the ML_4L'

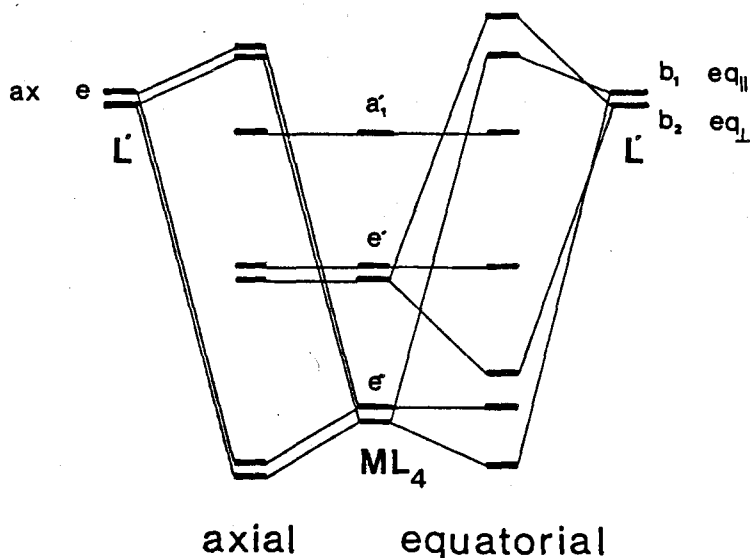


Figure A.1.4. Molecular Orbital Diagram for π -Interactions of an ML_4 Fragment with a π -acceptor Ligand. (After Rossi and Hoffmann.¹)

systems with d^8 configurations.

In summary, the work of Rossi and Hoffmann indicates that a weak σ -donor, or a strong π -acceptor ligand will occupy an equatorial site in the d^8 case; conversely a strong σ -donor, or weak π -acceptor will prefer the axial site. The prediction of the site preference of any particular ligand rests on an evaluation of the relative importance of these two types of bonding.

Another theoretical paper on pentacoordination is that of Burdett¹⁸ who considered the angular overlap of the metal d and ligand σ orbitals only. He concluded that for a low-spin d^8 configuration the stronger σ -donor will prefer the axial position, and also that "within the d orbital manifold the axial bond strength was greater than the equatorial." Since there was no consideration of the effect of π bonding on site preference the author readily admitted "our scheme is not the whole story."

Shustorovich has written a number of papers based on perturbation theory, on substitution effects of the σ bonded components in molecules of various geometries.^{3,19,20} He concluded that for d^8 metals, the axial site is favoured for a strong σ -donor. Once again, the effect of π bonding was not considered.

Since the question of site preference of the ligands cannot be separated from the inherently unequal nature of the axial and equatorial bonds of a TBP complex, several MO calculations on $Fe(CO)_5$ and closely related molecules are also of interest.^{12,13,21,22} The results underscore the difficulties of theoretical studies on pentacoordinate molecules. That is, the energy differences of the various conformations are small, and subject to error. The axial bonds of $Fe(CO)_5$ have been calculated to be weaker,²¹ stronger but much longer,¹³ and marginally longer²² than the equatorial bonds. Experimental lengths as determined in an electron diffraction study are 1.807(6)Å for the $Fe-C_{ax}$ distance and 1.827(6)Å for the $Fe-C_{eq}$

distance.²³ The most recent calculations¹² (using an SCF method) show that a subtle change in the assumed 3d energy level brings the calculated lengths for the axial and equatorial Fe-C bonds (1.82Å and 1.83Å respectively) into close correspondence with the experimental values. This results from both a decrease in the p_x and p_y contribution to equatorial Fe-C bonds and an increased d_{z^2} bonding contribution to the a_1 orbital. Thus the symmetry overlap model of Rossi and Hoffmann in which the d orbitals make their main contribution to the e'' and e' orbitals is only valid as a first approximation and the d orbital contribution to the lower lying bonding orbitals must also be taken into account for more precise predictions.

Unfortunately even this improved picture of the bonding in $\text{Fe}(\text{CO})_5$ does not provide a satisfactory explanation as to why a weak σ -donor ligand, such as SbPh_3 , should be in an axial position in $\text{Fe}(\text{CO})_4\text{SbPh}_3$ ²⁴ but in an equatorial site in $\text{Ru}(\text{CO})_4\text{SbPh}_3$.⁶ Actually, $\text{Fe}(\text{CO})_4\text{SbPh}_3$ would be predicted to exist as the equatorial isomer on the basis of this model, since the equatorial bonds have the weaker σ component.

The situation with regard to steric factors is complicated since it is unclear whether axial or equatorial sites are more sterically hindered. Lichtenberger and Brown¹⁴ have shown that for symmetric ER_3 ligands (the type used in this study) the equatorial position is more crowded. Thus ligands with large cone angles should prefer the axial position. Keiter²⁵ and Cowley²⁶ have pointed out that for large asymmetric ligands such

as $\text{PPh}(\text{PPh}_2)_2$ and $\text{P}_2(2,4,6\text{-t-Bu}_3\text{C}_6\text{H}_2)_2$ steric strain is actually eased in the equatorial position.

Favas and Kepert have developed more subtle steric reasoning based on a mathematical summation of all possible ligand-ligand interactions.² They base their calculations on the ratio (R) of the effective bond length of the unique ligand to that of the other four ligands. The effective bond length is the distance from the metal atom to a theoretical point location of the bonding electron pair. When the one effective bond length associated with the unique ligand is shorter than the other four (e.g., $R=0.8$) the equatorial isomer is predicted to be stable. However, when $R=1.2$ the axial isomer is predicted. The crossover from the equatorial to axial form occurs at about $R=1.00$. For very low or high values of R the predicted stereochemistry approaches an apically substituted square pyramid or a capped tetrahedron, respectively. The R values were calculated for a number of different geometries, described in terms of the OC-M-CO and OC-M-L angles, and the results presented graphically. Thus if the structure of a complex is known its R value can be read off the appropriate graph.

Unfortunately nearly all the examples of $\text{M}(\text{CO})_4\text{L}$ type compounds cited by Favas and Kepert are axially substituted and have R values ≈ 1.00 . For example, the authors calculated the R value for $\text{Fe}(\text{CO})_4\text{L}$ compounds to be ≈ 1.00 and thus explained the low barrier to axial-equatorial rearrangement found in ^{13}C NMR studies.²⁷ However, this does little to predict the axial

substitution of the cited examples. Nor can it explain the change in site preference for the SbPh_3 ligand when iron is replaced by ruthenium in $\text{M}(\text{CO})_4\text{SbPh}_3$ ($\text{M}=\text{Fe}, \text{Ru}$).

In $\text{eq-Mn}(\text{CO})_4\text{NO}^{2+}$ there is no significant distortion of the equatorial carbonyls and again an R value of ≈ 1.0 would be predicted. This is in contradiction to the statement of Favais and Kepert that the known geometry of this compound (equatorial substitution) implies "greater repulsion (lower R values) from the nitrosyl ligand than from the other four unidentate ligands."²

In summary, it can be said that not enough work has been done to build up a sizeable set of self-consistent R values and in most cases, the R values are calculated from the structure, rather than the structure predicted on the basis of known R values. This has led to some contradictory results. The work of these authors is rarely cited by other workers in the field suggesting their method has not gained wide acceptance.

1.2.2 Experimental Studies

Table A.1.1 lists 46 known d^8 transition metal complexes of the type $\text{M}(\text{CO})_4\text{L}$. Analysis of these data and the related literature points out that both experimental confirmation and a wide understanding of the theoretical predictions summarized above are lacking. Most of the complexes are of a first row transition metal and the unique ligand, a relatively poor π -acceptor, occupies an axial position. While this is

Table A.1.1. Previously Known $M(\text{CO})_4\text{L}$ Derivatives.

Compound	Substitution Site	Ref.
$[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$	axial ^a	29
$\text{Mn}(\text{CO})_4\text{NO}$	equatorial ^a	28
$[\text{Fe}(\text{CO})_4\text{CN}]^-$	axial ^a	8
$\text{Fe}(\text{CO})_4\text{L}$ (L=PPh ₃ , AsPh ₃ , SbPh ₃ , PPh ₂ Me, PPhMe ₂ , P(C ₆ H ₁₁) ₃ , P(n-Bu) ₃ , P(OPh) ₃ , P(OEt) ₃ , P(OMe) ₃)	axial	30
$\text{Fe}(\text{CO})_4\text{L}$ (L=PPh ₃ , CNMe, CNEt, CNPh, CNBu ^t)	axial	31
$\text{Fe}(\text{CO})_4\text{P}\{(\text{N}(\text{SiMe}_3)_2)\text{C}(\text{SiMe}_3)_2\}$	equatorial	32
$\text{Fe}(\text{CO})_4\text{SbMe}_3$, $\text{Fe}(\text{CO})_4\text{AsMe}_3$	axial ^a	33
$\text{Fe}(\text{CO})_4\text{L}$ (L=PEt ₃ , Ph ₂ P(CH ₂) ₂ PPh ₂ , C ₂ H ₅ NC)	axial	34
$\text{Fe}(\text{CO})_4\text{L}$ (L=C ₅ H ₅ N, C ₅ H ₄ N ₂)	axial	35
$\text{Fe}(\text{CO})_4\text{PCl}_3$	mixture	36
$\text{Fe}(\text{CO})_4\text{PF}_3$	mixture	37
$\text{Fe}(\text{CO})_4\text{L}$ L=PF ₂ [(OC)(CF ₃) ₂ CN] L=PF[(OC)(CF ₃) ₂ CN] ₂ L=P[(OC)(CF ₃) ₂ CN] ₃ L=PF ₂ OCNC ₂ (CF ₃) ₄ O	mixture mostly equatorial equatorial mixture	7
$\text{Fe}(\text{CO})_4\text{P}(\text{NMe}_2)_3$	axial ^a	38
$\text{Fe}(\text{CO})_4(\eta^1\text{-PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)$	axial ^a	25
$\text{Fe}(\text{CO})_4\text{SC}_3\text{Ph}_2$	axial	2
$[\text{Fe}(\text{CO})_4\text{SnR}_2]^{2-}$	axial	39

$\text{Ru}(\text{CO})_4\text{L}$ (L=PPh ₃ , PMePh ₂ , PBU ₃)	axial	40
$\text{Ru}(\text{CO})_4\text{P}(\text{OCH}_3)_3$	axial ^a	41
$\text{Ru}(\text{CO})_4\text{SbPh}_3$	equatorial ^a	6
$\text{Ru}(\text{CO})_4\text{PF}_3$	mixture ^b	42
$\text{Os}(\text{CO})_4\text{PPh}_3$	axial	43
$\text{Co}(\text{CO})_4\text{SiR}_3$ (R=H, F, Cl)	axial ^a	14,44
$\text{Co}(\text{CO})_4\text{GeCl}_3$	axial	2
$\text{Co}(\text{CO})_4\text{AuPPh}_3$	axial	2

^aSolid state crystal structure determined by X-ray crystallography.

^bVery poorly characterized.

consistent with the theories outlined above it can only be taken as partial confirmation of them as there are so few equatorial isomers. Also very little attempt has been made to discuss both the π and σ properties of the unique ligands. Indeed, π bonding arguments alone have been used by a number of authors to explain site preference.^{8, 29, 38} Several other studies dealt with other aspects of the chemistry of $\text{M}(\text{CO})_4\text{L}$ complexes rather than the observed geometry.^{30, 31, 33, 34, 44}

Reasoning based on π -bonding alone or in conjunction with steric factors was also used in a few cases where equatorial isomers were found.^{7, 45} In these examples, $\text{Fe}(\text{CO})_4\text{P}[(\text{OC})(\text{CF}_3)_2\text{CN}]_3$ and $\text{Fe}(\text{CO})_4\text{PF}_3$, the unusually high values of the carbonyl stretching frequencies were consistent

with the unique ligand having exceptional π -acceptor ability.

Steric arguments alone were used to explain why the unique ligand in both $\text{Fe}(\text{CO})_4\text{P}_2(2,4,6\text{-t-Bu}_3\text{C}_6\text{H}_2)_2$ ²⁶ and $\text{Fe}(\text{CO})_4\text{P}\{\text{N}(\text{SiMe}_3)_2\}\{\text{C}(\text{SiMe}_3)_2\}$ ³² adopts an equatorial position. In both cases the ligand is large and asymmetric.

The compound $\text{eq-Mn}(\text{CO})_4\text{NO}$ is the subject of some controversy in the literature; the original authors²⁸ suggested the data were not consistent with NO being a better π -acceptor than CO while later workers⁸ claimed the opposite.

A few authors did note that the relative σ -donor/ π -acceptor ratio of the ligands is important in determining the geometry.^{25, 35} However in no case was there any attempt to rate the relative importance of these factors separately.

The situation for the nine listed compounds of the second and third row metals is no better. Of these, seven are axially substituted, and no explanation was given for the site preference.^{40, 41, 43} Of the remaining two, $\text{Ru}(\text{CO})_4\text{PF}_3$ probably exists as a mixture of isomers in solution but it was very poorly characterized.⁴² The other complex, $\text{Ru}(\text{CO})_4\text{SbPh}_3$, was shown to exist as the equatorial form in the solid state, but the authors were unable to rationalize that observation.⁶ It will be shown later that their interpretation of the solution infrared spectrum of this compound was incorrect.

In summary, it can be said that the preference of strong π -acceptor ligands to occupy equatorial sites while weak π -acceptors are found in axial positions is widely accepted and illustrated by numerous examples. The role of σ bonding in influencing site preference is well documented in the theoretical literature but rarely cited in papers concerned with synthetic chemistry. Little effort has been made to rank the relative importance of the two types of bonding, i.e. to predict the site preference of a weak σ -donor in the presence of strong π -acceptors. The possibility of first, second, or third row transition metals having different tendencies to give equatorial or axial isomers has received little attention.

1.3 Project Description

It was decided to undertake a study of the site preference of the unique ligand in d^8 transition metal complexes of the iron triad of the type $M(\text{CO})_4\text{L}$ ($M=\text{Fe}, \text{Ru}, \text{Os}$; $\text{L}=\text{group 15 ligand}$). These complexes seemed a suitable target group since they exist as TBP's and from the one study on $\text{Ru}(\text{CO})_4\text{SbPh}_3$ were expected to exhibit axial-equatorial isomerism.

Interest in this project was stimulated by the knowledge that relatively few second and third row TBP complexes were known, and few of these were equatorially substituted. The structure of $\text{Ru}(\text{CO})_4\text{SbPh}_3$ was of special interest since it contained a second row transition metal and the unique ligand

(not known as a strong π acid) was equatorial.⁶ In the Fe analogue it was axial.²⁴ Convenient synthetic routes to $\text{Ru}(\text{CO})_5$ and $\text{Os}(\text{CO})_5$ had been developed in this laboratory^{4,6} and it was thought that this would allow facile synthesis of $\text{Ru}(\text{CO})_4\text{L}$ and $\text{Os}(\text{CO})_4\text{L}$ derivatives. It was hoped that new equatorial isomers could be synthesized and that this would lead to a better understanding of the question of site preference in general. The existence of $\text{eq-Ru}(\text{CO})_4\text{SbPh}_3$ suggested that attempts to synthesize $\text{Os}(\text{CO})_4\text{SbPh}_3$ might be a useful starting point. As the work proceeded it became apparent that compounds of the type $\text{M}(\text{CO})_4\text{L}$ ($\text{M}=\text{Fe}, \text{Ru}, \text{Os}$; $\text{L}=\text{ER}_3$, $\text{E}=\text{P}, \text{As}, \text{Sb}$; $\text{R}=\text{Ph}, \text{Me}$; $\text{L}=\text{P}(\text{OCH}_2)_3\text{CMe}$) would be synthetically accessible and this would allow a systematic study of the influence of both the ligand and the central metal on the site preference.

CHAPTER 2

RESULTS

Several derivatives of the type $M(\text{CO})_4\text{L}$ ($M=\text{Fe}, \text{Ru}, \text{Os}$; $\text{L}=\text{group 15 ligand}$) have been prepared.⁴⁷ The ruthenium trimethylphosphine derivative, $\text{Ru}(\text{CO})_4\text{PMe}_3$, was prepared by the action of PMe_3 on $\text{Ru}_3(\text{CO})_{12}$ at 120°C under 75 atmospheres of CO , a method used previously for $\text{Ru}(\text{CO})_4\text{P}(\text{OMe}_3)$.⁴¹ The osmium analogue was synthesized in a similar manner only under more forcing conditions (280°C , 200 atm CO). All other derivatives were prepared in hexane from $M(\text{CO})_5$ and the appropriate ligand. With $\text{Ru}(\text{CO})_5$ the reaction proceeded at a convenient rate at room temperature whereas for $\text{Os}(\text{CO})_5$ temperatures of 80°C or above were necessary. This illustrates the greater lability of carbonyls when bonded to the second row transition metal, a property previously observed with this group of metals in $M(\text{CO})_4(\text{SiCl}_3)_2$ derivatives.⁴⁸ For osmium, and to a lesser extent, ruthenium, there were competing reactions in the formation of the $M(\text{CO})_4\text{L}$ complexes which gave $M_3(\text{CO})_{12}$ and other clusters. The poor yields of $\text{Os}(\text{CO})_4\text{L}$ were marginally improved by carrying out the reactions under carbon monoxide. The colour of the complexes ranged from the orange $\text{Ru}(\text{CO})_4\text{SbPh}_3$ to the white $M(\text{CO})_4\text{PMe}_3$ species. They could be handled in air for short periods but decomposed upon prolonged exposure.

2.1 Structural Studies

The structures of $\text{ax-Ru(CO)}_4\text{AsPh}_3$, $\text{ax-Ru(CO)}_4\text{SbMe}_3$ and $\text{eq-Os(CO)}_4\text{SbPh}_3$ were determined by conventional X-ray diffraction techniques. Views of each molecule showing the thermal ellipsoids and the atomic numbering scheme for each are given in Figures A.2.1, A.2.2 and A.2.3 respectively; selected bond lengths and angles are given in Tables A.2.1, A.2.2 and A.2.3. Although the structure was not determined, the compound $\text{Os(CO)}_4\text{AsPh}_3$ was found to be isostructural with $\text{Ru(CO)}_4\text{AsPh}_3$. It can be seen that of the compounds studied here, $\text{Ru(CO)}_4\text{AsPh}_3$, $\text{Os(CO)}_4\text{AsPh}_3$ and $\text{Ru(CO)}_4\text{SbMe}_3$ adopt the axial form in the solid state while only $\text{Os(CO)}_4\text{SbPh}_3$ (as determined in this study) and $\text{Ru(CO)}_4\text{SbPh}_3$ (as determined by Forbes and coworkers⁶) adopt the equatorial form. This represents the first occasion where a site preference switchover for a closely related series of five-coordinate complexes has been observed. The reasons for this will be discussed subsequently, however there are several other points of interest about the structures which are considered now.

The Os-Sb bond length of $2.612(2)\text{\AA}$ ⁴⁹ appears to be the first reported in the literature for a molecular compound. It may be compared with the Os-Sb bond lengths in OsSb_2 ($2.639(3)\text{\AA}$ and $2.644(4)\text{\AA}$),⁵⁰ and the Ru-Sb distance of $2.623(4)\text{\AA}$ in $\text{Ru(CO)}_4\text{SbPh}_3$.^{6, 51} The Ru-Sb distance of $2.619(1)\text{\AA}$ found for $\text{Ru(CO)}_4\text{SbMe}_3$ may likewise be compared to these lengths. The

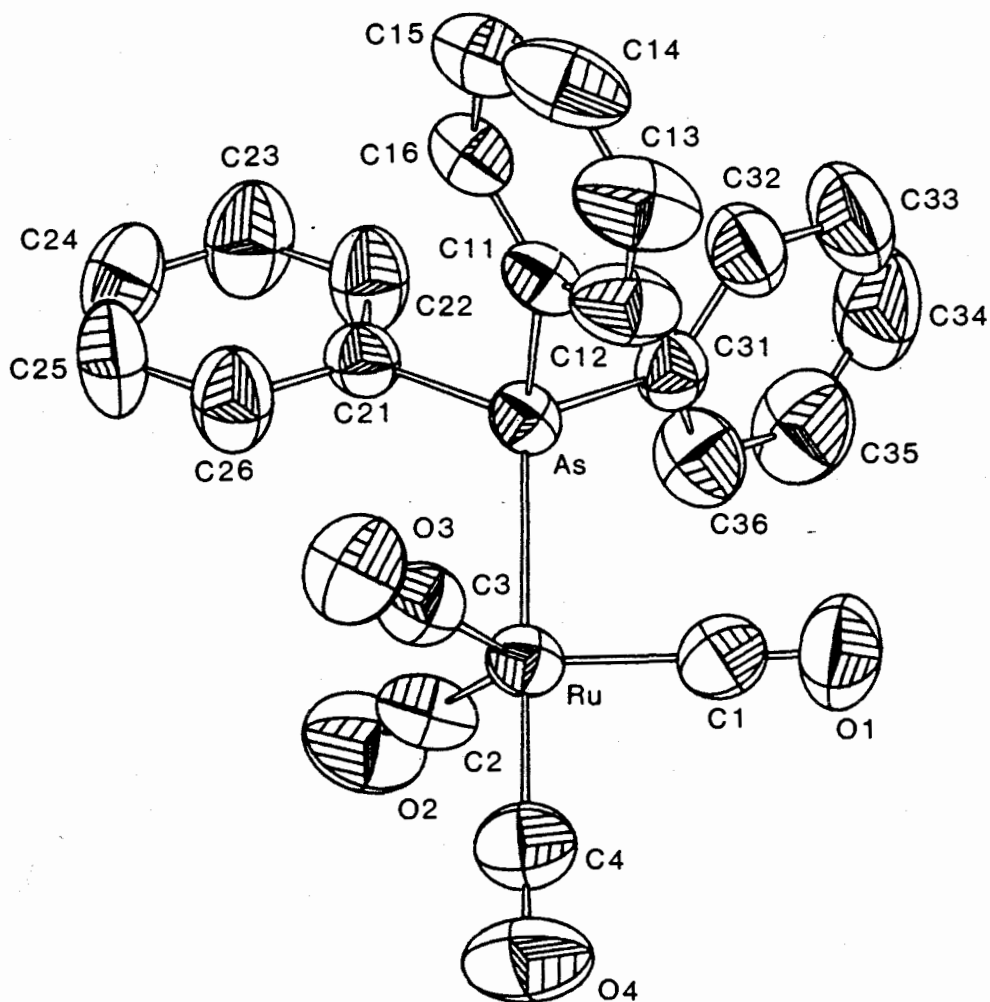


Figure A.2.1. Thermal Ellipsoid Diagram for Ru(CO)₄AsPh₃

Table A.2.1 Selected Molecular Dimensions for Ru(CO)₄AsPh₃.

a) Bond Lengths

Atoms	Length (Å)	Corrected Length (Å)
Ru-As	2.461(1)	2.507 ^a
Ru-C(1)	1.918(5)	1.930 ^b
Ru-C(2)	1.915(5)	1.921 ^b
Ru-C(3)	1.921(5)	1.932 ^b
Ru-C(4)	1.890(5)	1.906 ^b
C(1)-O(1)	1.140(7)	1.153 ^c
C(2)-O(2)	1.147(6)	1.160 ^c
C(3)-O(3)	1.132(7)	1.146 ^c
C(4)-O(4)	1.153(6)	1.168 ^c
As-C(11)	1.938(5)	
As-C(21)	1.932(5)	
As-C(31)	1.925(5)	

b) Bond Angles

Bond	Angle (°)	Bond	Angle (°)
C(1)-Ru-C(2)	117.9(2)	O(2)-C(2)-Ru	178.6(4)
C(1)-Ru-C(3)	118.5(2)	O(3)-C(3)-Ru	178.1(5)
C(1)-Ru-C(4)	92.5(2)	O(4)-C(4)-Ru	179.2(5)
C(2)-Ru-C(3)	123.4(2)	C(11)-As-C(21)	103.1(2)
C(2)-Ru-C(4)	90.0(2)	C(11)-As-C(31)	103.0(2)
C(3)-Ru-C(4)	91.5(2)	C(21)-As-C(31)	103.3(2)
As-Ru-C(1)	89.0(1)	C _{Ph} -As-C _{Ph} ^d	103.1
As-Ru-C(2)	89.1(1)	Ru-As-C(11)	115.4(1)

As-Ru-C(3)	88.0(1)	Ru-As-C(21)	115.1(1)
As-Ru-C(4)	178.5(2)	Ru-As-C(31)	115.2(1)
O(1)-C(1)-Ru	177.9(5)	Ru-As-C _{Ph} ^d	115.2

c) Torsion Angles
Bonds

Angle (°)

C(11)-As-Ru-C(3)	34.24
C(21)-As-Ru-C(2)	37.67
C(31)-As-Ru-C(1)	35.57

^aAtoms assumed to move independently.

^bSecond atom assumed to ride on the first.

^cBoth atoms assumed to ride on Ru.

^dMean value.

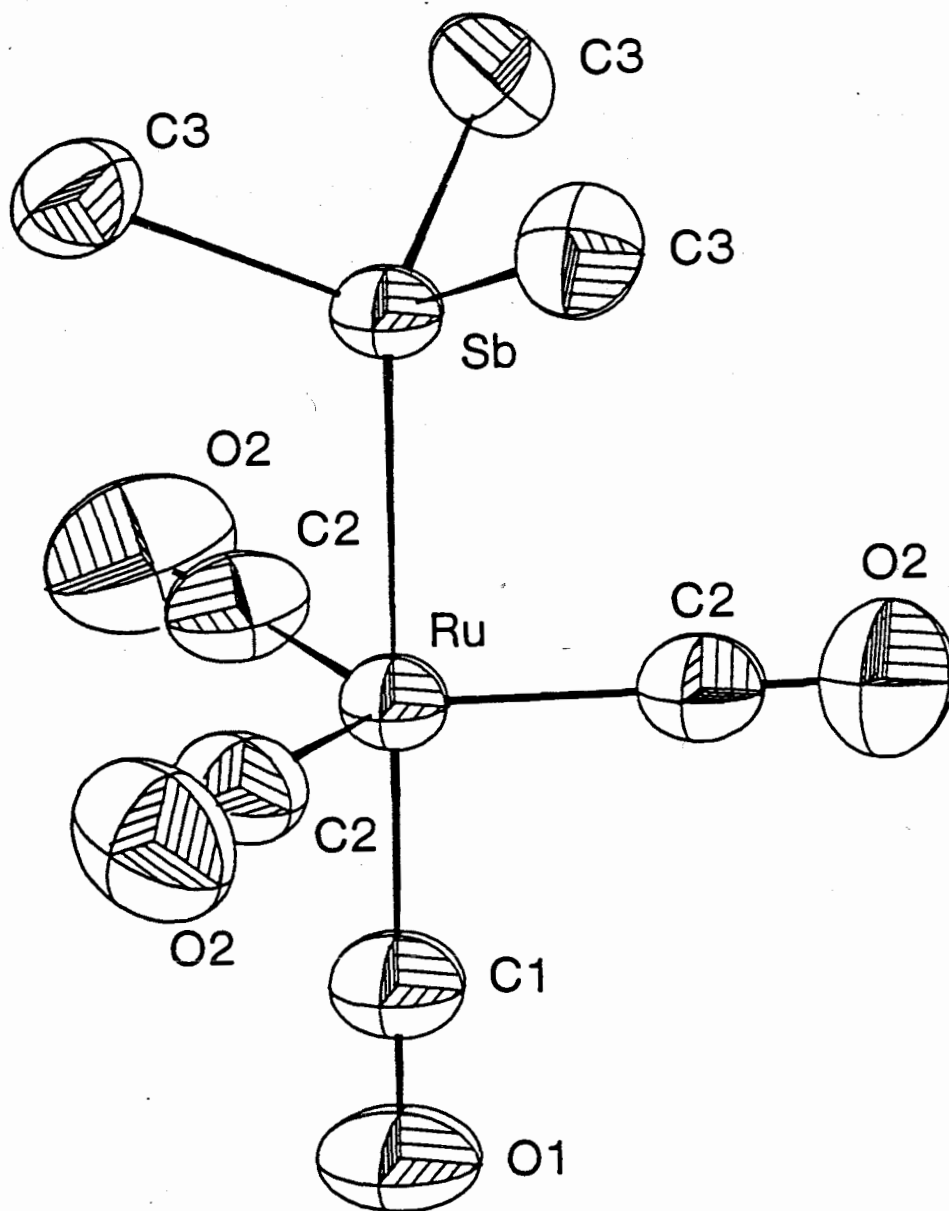


Figure A.2.2. Thermal Ellipsoid Diagram for Ru(CO)₄SbMe₃

Table A.2.2. Selected Molecular Dimensions for Ru(CO)₄SbMe₃

a) Bond Lengths

Atoms	Length (Å)	Corrected Length (Å)
Ru-Sb	2.6187(9)	2.6578 ^a
Ru-C(1)	1.89(2)	1.90 ^b
Ru-C(2)	1.92(1)	1.94 ^b
Sb-C(3)	2.140(7)	
C(1)-O(1)	1.16(2)	1.17 ^c
C(2)-C(2)	1.13(1)	1.15 ^c

b) Bond Angles

Bond	Angle (°)
C(1)-Ru-C(2)	91.9(2)
C(2)-Ru-C(2)	119.9(3)
Ru-Sb-C(1)	180.0(-)
Ru-Sb-C(3)	115.7(2)
C(3)-Sb-C(3)	102.6(3)
Ru-C(2)-O(2)	178.3(9)

^aAtoms assumed to move independently.

^bSecond assumed to ride on first atom.

^cBoth atoms assumed to ride on Ru.

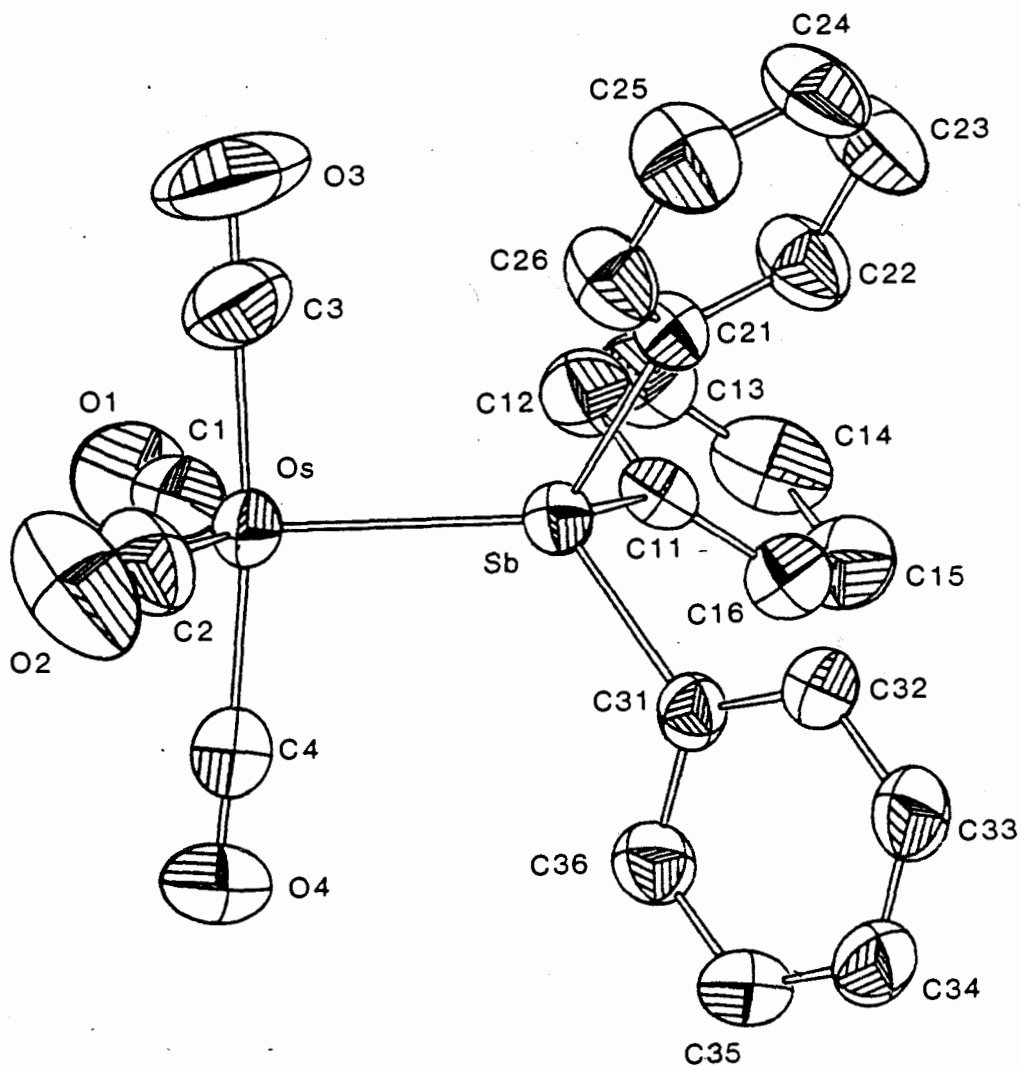


Figure A.2.3. Thermal Ellipsoid Diagram for $\text{Os}(\text{CO})_4\text{SbPh}_3$.

Table A.2.3. Selected Molecular Dimensions for Os(CO)₄SbPh₃.

a) Bond Lengths

Atoms	Length (Å)	Corrected Length (Å)
Os-Sb	2.612(2)	2.649 ^a
Os-C(1)	1.926(5)	1.934 ^b
Os-C(2)	1.911(7)	1.933 ^b
Os-C(3)	1.952(6)	1.980 ^b
Os-C(4)	1.939(6)	1.945 ^b
C(1)-O(1)	1.134(7)	1.148 ^c
C(2)-O(2)	1.148(8)	1.164 ^c
C(3)-O(3)	1.117(8)	1.138 ^c
C(4)-O(4)	1.134(7)	1.150 ^c
Sb-C(11)	2.131(5)	
Sb-C(21)	2.136(5)	
Sb-C(31)	2.124(5)	

b) Bond Angles

Bond	Angle (°)	Bond	Angle (°)
C(1)-Os-C(2)	136.4(3)	O(2)-C(2)-Os	175.6(6)
C(1)-Os-C(3)	90.7(3)	O(3)-C(3)-Os	178.6(8)
C(1)-Os-C(4)	88.8(2)	O(4)-C(4)-Os	177.1(5)
C(2)-Os-C(3)	88.6(3)	C(11)-Sb-Os	114.0(1)
C(2)-Os-C(4)	87.6(3)	C(21)-Sb-Os	118.4(1)
C(3)-Os-C(4)	173.8(3)	C(31)-Sb-Os	121.2(1)
Sb-Os-C(1)	107.0(2)	C _{Ph} -Sb-Os ^d	117.9
Sb-Os-C(2)	116.6(2)	C(11)-Sb-C(21)	100.1(2)

Sb-Os-C(3)	90.7(2)	C(11)-Sb-C(31)	99.0(2)
Sb-Os-C(4)	95.4(2)	C(21)-Sb-C(31)	100.5(2)
O(1)-C(1)-Os	176.9(5)	C _{Ph} -Sb-C _{Ph} ^d	99.9

c) Torsion Angles
Bonds

	Angle (°)
C(21)-Sb-Os-C(3)	22.97
C(31)-Sb-Os-C(4)	31.03

^aAtoms assumed to move independently.

^bSecond atom assumed to ride on the first.

^cBoth atoms assumed to ride on Ru.

^dMean value.

Ru-As bond length of 2.461Å is somewhat longer than the Ru-As bond lengths in the literature which are in the range 2.401(3)-2.445(2)Å.^{52,53} However, the literature values are for bidentate arsenic ligands in cluster compounds so that it would be unwise to attach any significance to the differences. The C(1)-Os-Sb angle (107.0(2)°) in eq-Os(CO)₄SbPh₃ is significantly smaller than the C(2)-Os-Sb angle (116.6(2)°). This difference is difficult to rationalize. A similar inequality of seemingly equivalent angles was also present in Co(PPh₂Me)₂Cl₂NO.⁵⁴

There has been considerable discussion^{8,28,29,38} regarding differences in M-C_{eq} and M-C_{ax} bonds in Fe(CO)₄L and similar complexes. When L=phosphine the bonds are shortened as compared to those of the parent pentacarbonyl²³ with greater contraction of the

Table A.2.4. M-C Distances in Fe(CO)₅ and M(CO)₄L Compounds

Compound	M-C _{eq} (Å) ^a	M-C _{ax} (Å)	Ref.
Fe(CO) ₅ ^b	1.827(6)	1.807(6)	23
Fe(CO) ₅ ^c	1.795(20)	1.795(20)	55
Fe(CO) ₄ PPh ₃	1.795(2)	1.795(2)	29
Fe(CO) ₄ P(NMe ₂) ₃	1.787(5)	1.793(6)	38
Fe(CO) ₄ SbPh ₃	1.787(4)	1.765(4)	24
Fe(CO) ₄ Sb(Bu ^t) ₃	1.794(7)	1.748(8)	56
[Fe(CO) ₄ CN] ⁻	1.768(8)	1.723(8)	8
Ru(CO) ₄ AsPh ₃	1.918(5)	1.909(5)	this work
Ru(CO) ₄ SbMe ₃	1.92(1)	1.89(2)	this work
Ru(CO) ₄ SbPh ₃	1.932(6)	1.929(6) ^a	6
Os(CO) ₄ SbPh ₃	1.919(6)	1.946(6) ^a	this work

^aMean value

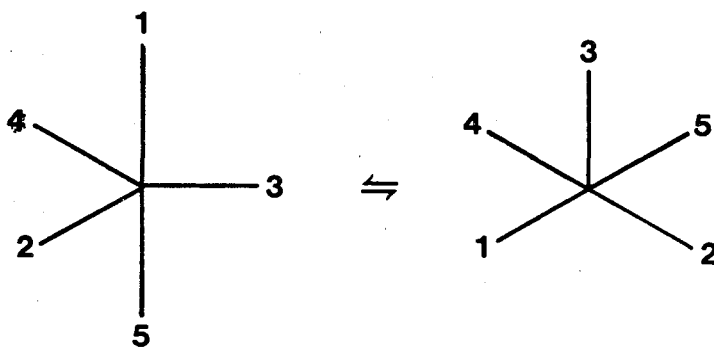
^bElectron diffraction study

^cX-ray diffraction study

Fe-C_{eq} bonds as compared to the Fe-C_{ax} bond (see Table A.2.4). The normal explanation for these observations is that replacement of the strongly π-accepting CO by a poorer π-bonding ligand reduces competition for the metal π electron density so that the other CO ligands, particularly the equatorial ones, may form stronger Fe-C π bonds. This can be seen in the structures of Fe(CO)₄PPh₃ and Fe(CO)₄P(NMe₂)₃ both of which have nearly equal Fe-C_{eq} and Fe-C_{ax} bond lengths. When the ligand is SbPh₃,

$\text{Sb}(t\text{-Bu})_3$ or CN^- , the overall shortening of the Fe-C bonds can be seen, but the axial and equatorial bonds are significantly different. Presumably any directional π bonding effect causing shortening of Fe-C_{eq} bonds is accompanied by a reduced trans influence of the unique ligand causing shortening of the Fe-C_{ax} bond as well. For the compounds studied here comparisons with the parent carbonyls cannot be made since the structures of $\text{Ru}(\text{CO})_5$ and $\text{Os}(\text{CO})_5$ are not known. In the compounds $\text{Ru}(\text{CO})_4\text{AsPh}_3$ and $\text{Ru}(\text{CO})_4\text{SbMe}_3$ the mean M-C_{eq} length is longer than the M-C_{ax} length, while in $\text{Os}(\text{CO})_4\text{SbPh}_3$ the opposite is true. However, in these compounds and in eq- $\text{Ru}(\text{CO})_4\text{SbPh}_3$ and in $\text{Fe}(\text{CO})_4\text{PPh}_3$ noted above, the distances are not significantly different. In light of this, and the fact that the X-ray structure of $\text{Fe}(\text{CO})_5$ had large estimated standard deviations and showed nearly equal Fe-C_{eq} and Fe-C_{ax} lengths⁵⁵ which were shorter than the distances found in the electron diffraction study, it seems hazardous to draw any firm conclusions on this question.

Finally it should be noted that although the distortion from TBP geometry in the equatorially substituted complexes is significant, assignment of square pyramid geometry would not be appropriate. According to criteria developed by Holmes,⁵⁷ $\text{Os}(\text{CO})_4\text{SbPh}_3$ has an axial angle, θ_{15} , of 173.8° , and an equatorial angle, θ_{24} , of 136.4° and a dihedral angle, δ_{24} , of 36.6° (see Figure A.2.4). This places the complex considerably more than half-way along a Berry type coordinate along which the



$$\theta_{15} = 180^\circ$$

$$\theta_{24} = 120^\circ$$

$$\theta_{15} = \theta_{24}$$

Figure A.2.4. Definition of Structural Angles for Five Coordinate Compounds. The angle δ_{24} is that between the normals of the 1,2,4 and 2,4,5 planes. (After Holmes.⁵⁷)

δ_{24} angles varies smoothly from 0° for a square pyramid to 53.1° for an ideal trigonal bipyramid.

2.2 Infrared Studies

Solution infrared spectra in the carbonyl stretching region are illustrated in Figures A.2.5, A.2.6 and A.2.7 and summarized in Table A.2.5. The assignment of peaks to either the axial or equatorial isomer was done on the following basis. When only three carbonyl stretches were present these were assigned to the axial isomer, in accord with the characteristic pattern for $M(CO)_4L$ complexes of C_{3v} symmetry.^{15, 58} Similar peaks in solutions of compounds displaying more than three carbonyl stretches were also assigned to the axial isomer with the additional peaks being assigned to the equatorial isomer. No absorptions were assigned to possible isomers adopting a square pyramid geometry since few d^8 complexes of this type are known and theoretical predictions have been made to suggest this form is unlikely.⁵⁹ Furthermore, in the solid state $M(CO)_4SbPh_3$ ($M=Ru, Os$) adopt the equatorial form; it is just these species which show the most intense absorptions of the second isomer in solution. The maximum number of peaks assigned to the equatorial isomer in any solution was three although four infrared active CO stretches are expected for an $M(CO)_4L$ molecule displaying C_{2v} symmetry. It is thought that, since the infrared spectrum of no solution indicated the presence of the equatorial isomer to the exclusion of the axial isomer, the unobserved peak, or peaks, of the equatorial form were degenerate with those due to the axial molecule. The solid state infrared spectra of both eq-Ru(CO)₄SbPh₃ and

Table A.2.5. Infrared, ^{13}C NMR and Melting Point Data for $\text{M}(\text{CO})_4\text{L}$ Compounds.

Compound	$\nu(\text{CO})\text{cm}^{-1}\text{a}$		^{13}C NMR ^b (ppm)		m. p. °C ^c
	eq ^d	ax ^e	eq	ax	
$\text{Fe}(\text{CO})_4\text{PMe}_3$		2051		1937	214.2(20.8)
$\text{Fe}(\text{CO})_4\text{P}(\text{OCH}_3)_3\text{CMe}$		2070		1970	212.2(25.5)
$\text{Fe}(\text{CO})_4\text{PPh}_3$		2052		1947	209.0(18.7)
$\text{Fe}(\text{CO})_4\text{AsPh}_3$		2051		1947	213.7
$\text{Fe}(\text{CO})_4\text{SbPh}_3$		2048		1946	212.7
$\text{Ru}(\text{CO})_4\text{PMe}_3$		2061		1947	205.3(2.4)
$\text{Ru}(\text{CO})_4\text{P}(\text{OCH}_3)_3\text{CMe}$	2093	2076	2014	1976	203.3(10.5)
$\text{Ru}(\text{CO})_4\text{PPh}_3$		2062		1955	204.6(3.5)
$\text{Ru}(\text{CO})_4\text{AsPh}_3$	2079	2061	1999	1958	204.7
$\text{Ru}(\text{CO})_4\text{SbMe}_3$	2071	2060	1988	1965	203.4
$\text{Ru}(\text{CO})_4\text{SbPh}_3$	2078	2060	1999	1967	207.4
$\text{Os}(\text{CO})_4\text{PMe}_3$		2061		1939	189.9(4.5)
$\text{Os}(\text{CO})_4\text{P}(\text{OCH}_3)_3\text{CMe}$	2092	2076	2009	1967	186.7(12.5)
$\text{Os}(\text{CO})_4\text{PPh}_3$		2061		1946	189.4(6.0)
$\text{Os}(\text{CO})_4\text{AsPh}_3$	2077	2061	1991	1947	188.7
$\text{Os}(\text{CO})_4\text{SbMe}_3$	2069	2058	1977	1942	188.2
$\text{Os}(\text{CO})_4\text{SbPh}_3$	2076	2060	1992	1950	190.1
$\text{Ru}(\text{CO})_4\text{SbPh}_3$ ^f	2078		1997	1980, 1949	
$\text{Os}(\text{CO})_4\text{SbPh}_3$ ^f	2076		1987	1973, 1937	

^aAll solution spectra recorded in hexane.

^bSpectra recorded at room temperature in $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ (1:5) or CD_2Cl_2 soln.; Jpc (Hz) in parenthesis.

^cNew compounds only.

^dEquatorial isomer.

^eAxial isomer.

^fSolid state spectrum in KBr disk.

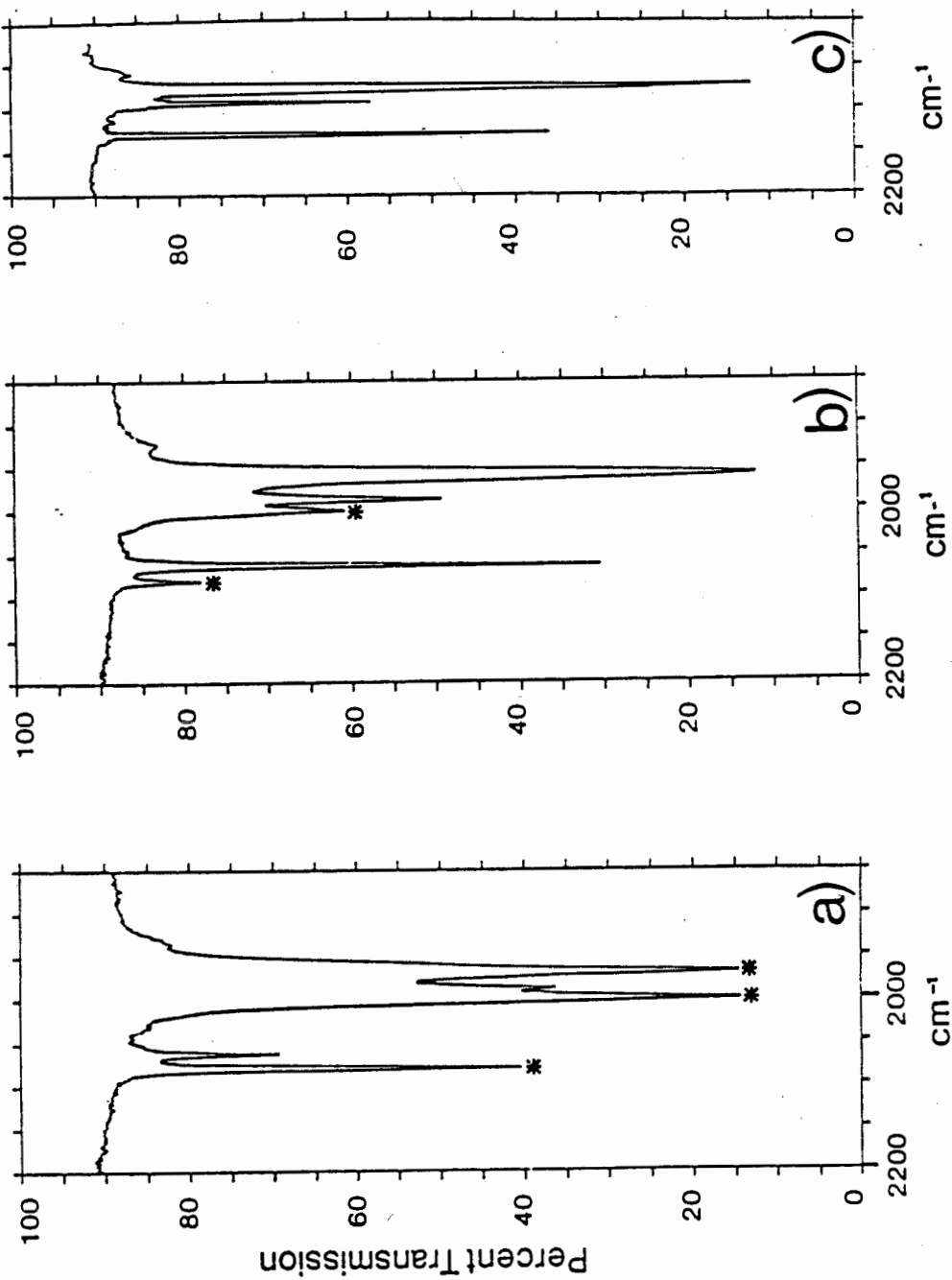


Figure A.2.5. Solution Infrared Spectra of a) $\text{Ru}(\text{CO})_4\text{SbPh}_3$, b) $\text{Ru}(\text{CO})_4\text{AsPh}_3$ and c) $\text{Ru}(\text{CO})_4\text{PPh}_3$. Bands due to the equatorial isomer are marked with an asterisk. The wavenumber scale of spectrum c) is reduced by a factor of two compared to that of a) and b).

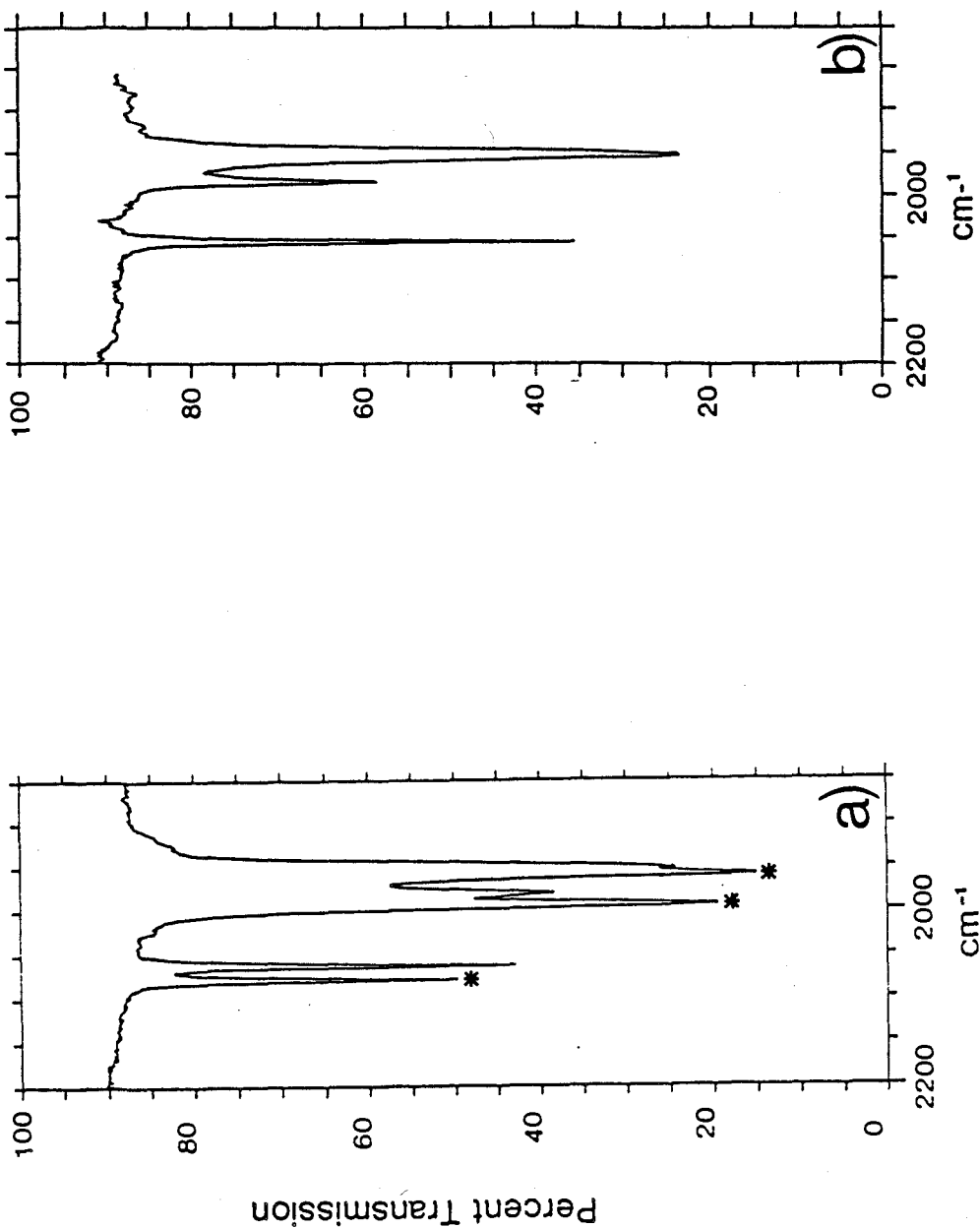


Figure A.2.6. Solution Infrared Spectra of a) $\text{Os}(\text{CO})_4\text{SbPh}_3$ and b) $\text{Fe}(\text{CO})_4\text{SbPh}_3$. Bands due to the equatorial isomer are marked with an asterisk.

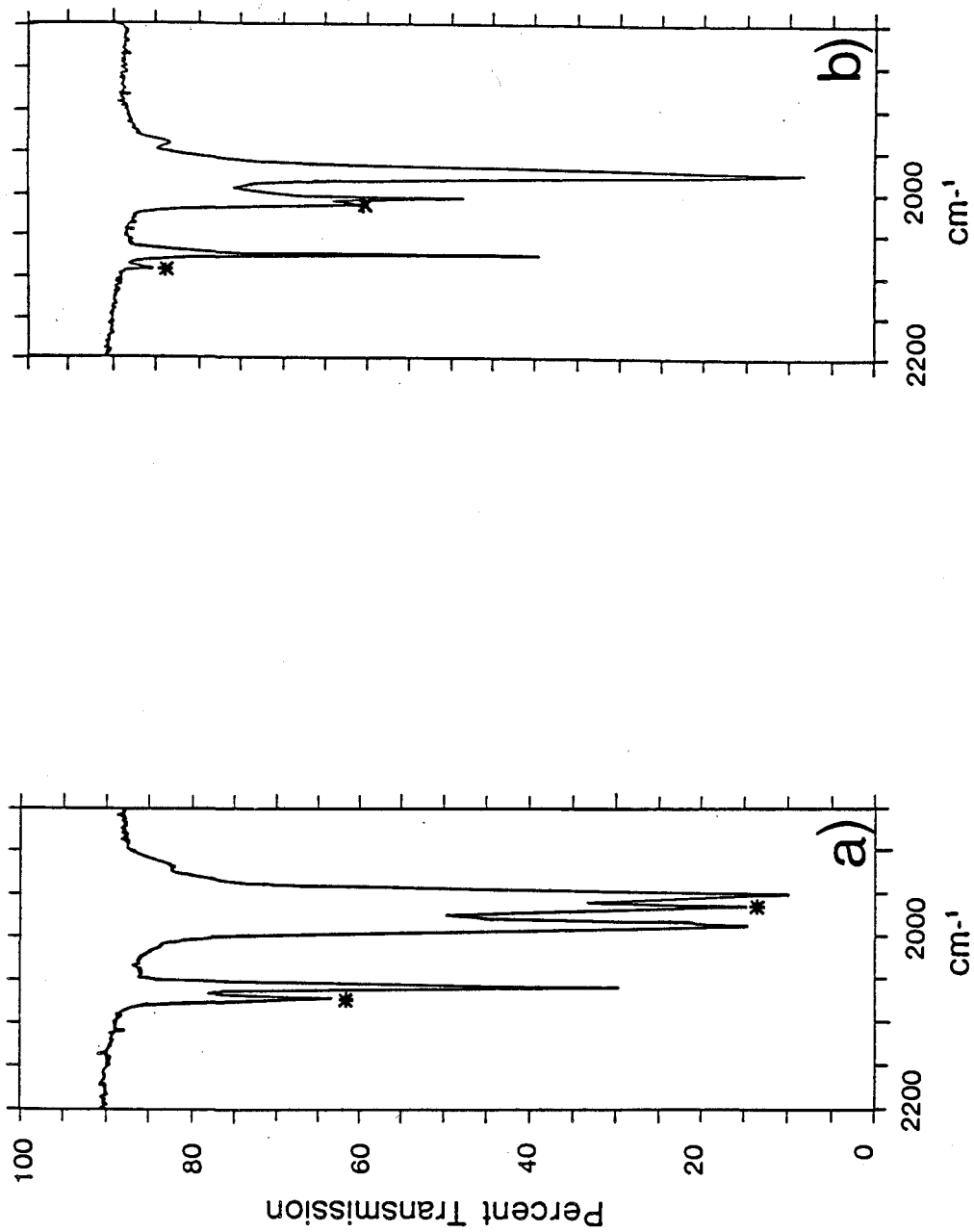


Figure A.2.7. Solution Infrared Spectra of a) Ru(CO)₄SbMe₃ and b) Ru(CO)₄P(OCH₂)₃CMe. Bands due to the equatorial isomer are marked with an asterisk.

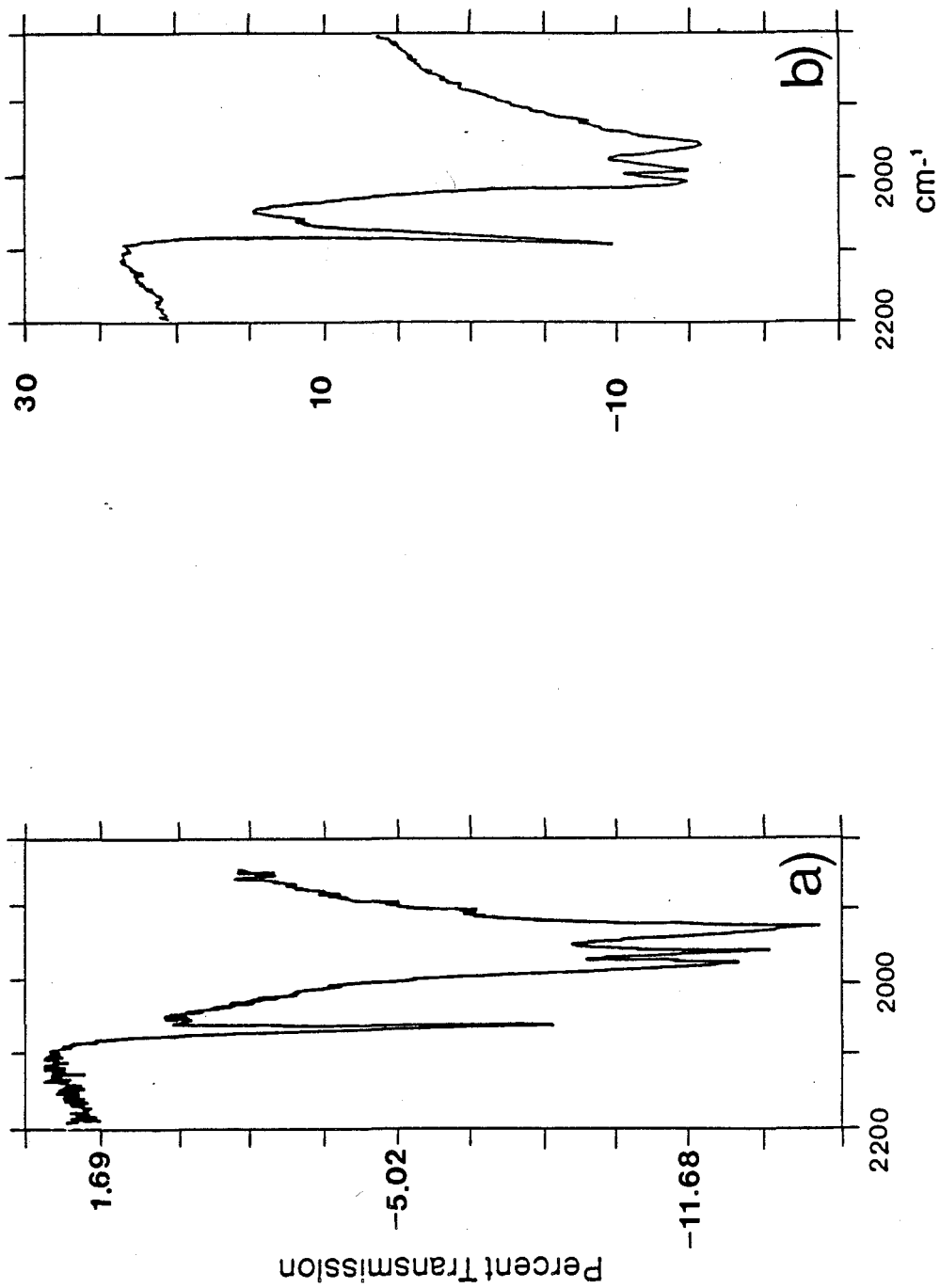


Figure A.2.8. Solid State Infrared Spectra of a) $\text{Ru}(\text{CO})_4\text{SbPh}_3$ and b) $\text{Os}(\text{CO})_4\text{SbPh}_3$.

eq-Os(CO)₄SbPh₃ did display four bands (Figure A.2.8.) These solid state spectra confirm that the structures determined by X-ray diffraction were representative of the bulk solid state structure and were not the chance result of single crystal analysis.

The short time scale¹⁶ of infrared spectroscopy allowed the existence of two isomers in solution to be displayed for all the Ru and Os derivatives except when L was PMe₃, see Table A.2.5. It was hoped that low temperature studies using the method of Hartman and co-workers⁶⁰ would reveal a shift in the equilibrium of the two isomers and hence allow the calculation of thermodynamic parameters. Accordingly the area of the absorbance peaks of Ru(CO)₄SbPh₃ at 2078 cm⁻¹(ax) and 2060 cm⁻¹(eq) were measured at temperatures ranging from ambient to -90 °C. Similar attempts were made for Os(CO)₄SbPh₃ and Ru(CO)₄SbMe₃, but no linear relationship between the band areas could be detected and this avenue of investigation was abandoned.

2.3 NMR Studies

While the solution infrared spectra clearly displayed the presence of two isomers in solution for many of the M(CO)₄L complexes, the ¹³C NMR spectra revealed only a single resonance in all cases, except that ³¹P coupling was observed when the complex contained a phosphorus donor ligand. (The J_{P-C} values

are noted in brackets in Table A.2.5.) The indication is clearly that not only are the axial and equatorial carbonyls exchanging rapidly in each isomer but also the isomeric forms must be rapidly interconverting. This would be the expected result if the exchange occurred by the Berry pseudorotation (BPR) mechanism.¹¹ Such a mechanism has been previously proposed many times to account for the nonrigidity of five coordinate molecules.^{45,61} It seems likely to be occurring in the complexes studied here because the equatorial isomer can be detected for many of the species. If a BPR mechanism were operative the free energy change upon rearrangement could be represented as in Figure A.2.9. It would be expected that the energy difference between the equatorially substituted molecule (3) and the axial isomer (1 and 5) would be reflected in the ratio of isomers displayed in the infrared spectra. Where the ax/eq ratio is nearly one, the energy level of the equatorial form would be nearly equal to that of the axial form (case A). When only the axial form can be detected in solution the energy difference would be large, (case B) i.e., the equatorial form is best considered as an intermediate. Slowed exchange would be expected if the initial activation barrier were large (cases C and D), or if the equatorial isomer were highly unfavoured (case E).

Whereas it was previously noted that $\text{Fe}(\text{CO})_4\text{PPh}_3$ ⁶² and several other $\text{Fe}(\text{CO})_4\text{L}^7$ complexes showed no signs of slowed exchange at low temperatures it was hoped that this would not be

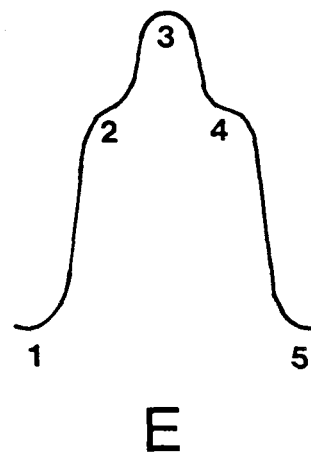
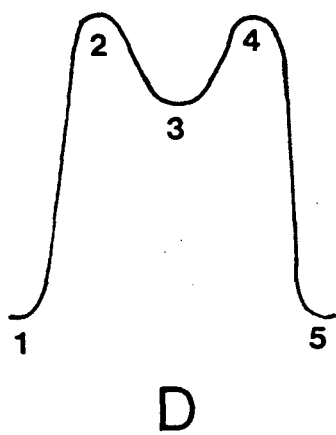
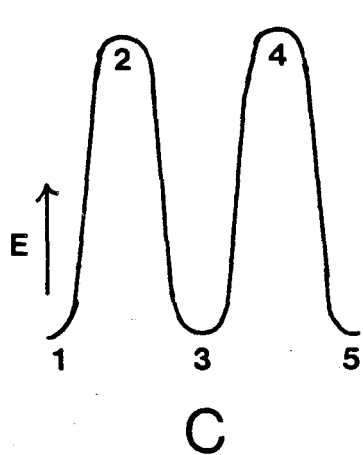
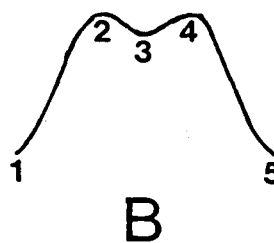
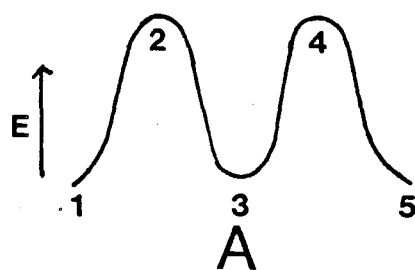
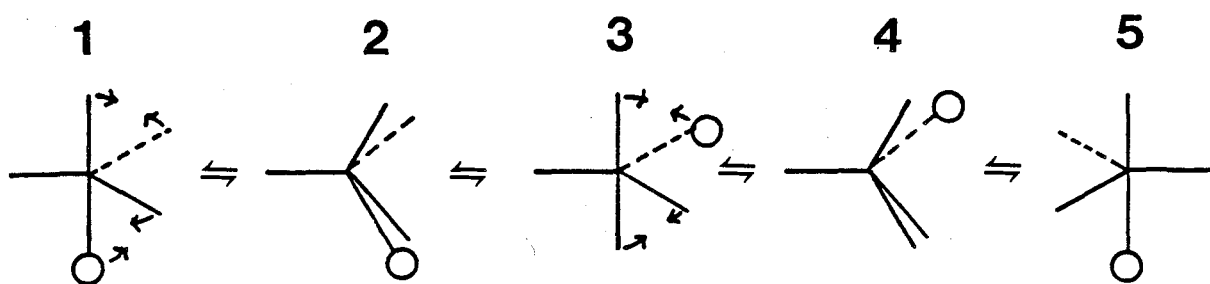


Figure A.2.9. Berry Pseudorotation Mechanism and Some Possible Reaction Coordinates. (After Lichtenberger and Brown,¹⁴)

the case for the Ru and Os derivatives. Much higher barriers to nonrigidity had been observed for an octahedral system of $M(\text{CO})_4(\text{EMe}_3)_2$ ($E=\text{Si, Ge, Sn, Pb}$) complexes when $M=\text{Ru}$ or Os than when $M=\text{Fe}$.⁶³ In this case both cis and trans isomers could be detected in the ^{13}C NMR spectra indicating a reaction diagram as in C would be applicable. A variable temperature ^{13}C NMR study on a series of $\text{ax-Co}(\text{CO})_4\text{EX}_3$ ($E=\text{C, Si, Ge, Sn, Pb}$; $X=\text{F, Cl, CH}_3, \text{CH}_2\text{C}_6\text{H}_5, \text{C}_6\text{H}_5$) derivatives found slow exchange at low temperatures.¹⁴ Coalescence temperatures varying from -10°C to $<-160^\circ\text{C}$ were observed. (In this case only the axial form was detected in the low temperature limit so that the diagrams D or E might apply.) It was found that higher barriers to non-rigidity were associated with smaller group 14 donor atoms. For example, $\text{Co}(\text{CO})_4\text{CF}_3$ had a coalescence temperature of -10°C .

The solution ^{13}C NMR spectra of $\text{Ru}(\text{CO})_4\text{P}(\text{OCH}_2)_3\text{CMe}_3$, $\text{Ru}(\text{CO})_4\text{SbPh}_3$ and $\text{Os}(\text{CO})_4\text{SbPh}_3$ were studied to very low temperatures (-100°C , -110°C , and -100°C respectively), but in all cases the carbonyl resonance remained a sharp singlet or doublet, (the ^{13}CO signal for $\text{Ru}(\text{CO})_4\text{P}(\text{OCH}_2)_3\text{CMe}$ is coupled to P). Therefore kinetic parameters for axial-equatorial exchange could not be obtained. Valuable mechanistic information could have been obtained had the exchange been slowed on the NMR time scale because the Berry pseudorotation mechanism predicts simultaneous collapse of the signals of each isomer. This has yet to be observed for any system.

CHAPTER 3

DISCUSSION

It can be seen from Figures A.2.1 to A.2.3, A.2.5 to A.2.7 and Table A.2.5 that the tendency to give equatorial isomer is $\text{Ph}_3\text{Sb} > \text{Ph}_3\text{As} > \text{Ph}_3\text{P}$ and $\text{Ru} > \text{Os} > \text{Fe}$. Also, as far as the substituents on the ligand are concerned, $(\text{OCH}_2)_3\text{CMe}$ must be considered the most likely to give an equatorial isomer since it alone displays the existence of that form in solution when attached to phosphorus. The ordering for the ligand substituents is then $\text{SbPh}_3 > \text{SbMe}_3$ (As ligands would probably display similar behaviour) and $\text{P}(\text{OCH}_2)_3\text{CMe} > \text{PPh}_3, \text{PMe}_3$. The site preference switchover from axial to equatorial isomers in the solid state occurs for $\text{M}=\text{Ru}, \text{Os}$ when the unique ligand is SbPh_3 . It was found that it was exactly those compounds which displayed the most intense solution IR bands for the equatorial isomer that adopted this form in the solid state.

It is clear that the tendency to give equatorial isomer depends both on the nature of the ligand and on the central metal. Each of these factors is discussed below, in terms of both steric and electronic (σ and π bonding) considerations.

3.1 Steric Considerations

It seems fairly easy to discount steric factors as the cause of the observed switchover of the solid state configurations and

of the variation of the axial/equatorial isomer ratio in solution. As mentioned earlier, Lichtenberger and Brown¹⁴ have shown that ER₃ type ligands are more sterically crowded in the equatorial position than in the axial position, even though only two close encounters with CO groups at 90° are expected for the unique ligand when it is in an equatorial position. The reason is the inability of the three R groups to adopt a fully staggered conformation with respect to the two CO ligands. This is illustrated in the Newman projections in Figure A.3.1. We also find that the closest non-bonded contacts do indeed occur in the equatorial compound Os(CO)₄SbPh₃, (C(1)···H(12)=3.09Å). Furthermore, calculations on a model of eq-Os(CO)₄AsPh₃ using coordinates from ax-Ru(CO)₄AsPh₃ and eq-Os(CO)₄SbPh₃ indicate two contacts between the group 15 ligand and carbonyls that are slightly less than the sum of the van der Waals radii for the atoms involved (C(1)···H(12)=2.79Å; C(4)···H(36)=2.83Å).⁶⁴ Within ax-Ru(CO)₄AsPh₃ the comparable contacts are at this sum (C(3)···H(26)=3.16Å.) (The closest nonbonded contacts between the hydrogens and oxygens were O(1)···H(32)=3.02Å for ax-Ru(CO)₄AsPh₃ and O(1)···H(12)=3.04Å for eq-Os(CO)₄SbPh₃.)

Given that the equatorial site is more sterically crowded it is to be expected that a ligand having a larger cone angle would be more likely to occupy the axial position. In the case of Ru(CO)₄SbR₃ (R=Me, Ph) the reverse is found. When R=Me (estimated cone angle=118°) the compound crystallizes as the

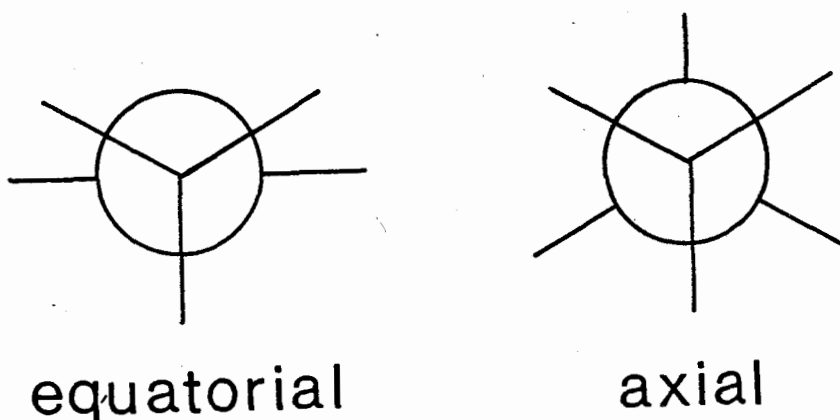


Figure A.3.1. Newman Projections for $M(CO)_4ER_3$ Compounds (After Lichtenberger and Brown.¹⁴)

axial isomer whereas when $R=Ph$ (estimated cone angle= 145°) the equatorial isomer is observed. (The cone angles of these ligands were considered to be equal to the corresponding phosphorus analogues.⁶⁵) The solution IR spectra are consistent with there being more axial isomer in solution for $R=Me$ than for $R=Ph$. Large ligands are known to occupy both equatorial sites, as in $Fe(CO)_4P[OC(CF_3)_2CN]_3$,⁷ and axial sites as in $Fe(CO)_4[P(t-Bu)_3]$.⁶⁶ In the former case the cone angle is at least 160° while in the latter it is 182° .⁶⁵ Ligands with small cone angles are also found in both sites. The compound $Fe(CO)_4P(OMe)_3$ exists entirely in the axial form, while a

statistical distribution of isomers is found for $\text{Fe}(\text{CO})_4\text{PF}_3$.⁶⁷ The cone angles are 107° for $\text{P}(\text{OMe}_3)$ ⁶⁶ and 104° for PF_3 .⁶⁷ Also different site preferences are found for ligands which have approximately the same cone angle; i.e. PPh_3 and AsPh_3 prefer the axial site in $\text{M}(\text{CO})_5\text{L}$ ($\text{M}=\text{Fe}, \text{Ru}, \text{Os}$) while SbPh_3 occupies an equatorial position in both $\text{Ru}(\text{CO})_4\text{SbPh}_3$ and $\text{Os}(\text{CO})_4\text{SbPh}_3$ in the solid state. The cone angle in all three cases is 145° .⁶⁸ We conclude that arguments based on the steric requirements of the ligands may be discounted as an explanation for axial-equatorial isomerism regardless of whether the axial or equatorial site is considered the more crowded.

As far as the central metal is concerned, it would be expected that iron (having the smallest covalent radius of the three metals) would be most affected by steric factors. And while it is true that all the iron compounds studied here displayed only the axial isomer in solution, the examples of other workers cited above show this is not always the case.

A more subtle steric argument based on calculating a minimum total repulsion energy summed over all the M-L bonds is the subject of the review by Favas and Kepert² noted in the introduction. It will be remembered that they base their calculations on the ratio (R) of the effective bond lengths of the unique ligand to the other four ligands and that for $\text{M}(\text{CO})_4\text{L}$ complexes the distortion of the C-M-C bond angles was calculated for different R values and the results were presented in graphical form. Thus the theoretical R values can be deduced

if the structure is known. In $ax\text{-Ru}(\text{CO})_4\text{AsPh}_3$ and $ax\text{-Ru}(\text{CO})_4\text{SbMe}_3$, there is only a slight bending of the equatorial carbonyls toward the non-carbonyl ligand. This would be in accord with $R \approx 1.00$ and no clear prediction of site preference. For the compounds $eq\text{-Ru}(\text{CO})_4\text{SbPh}_3$ and $eq\text{-Os}(\text{CO})_4\text{SbPh}_3$, the bending of the carbonyl ligands is quite pronounced and would lead to a predicted R value of ≈ 0.85 in accord with the site preference found. However this R value is intuitively very unsatisfying in that it would be expected that the M-C bonding electrons would be closer to the metal nucleus than the M-Sb bonding electrons, leading to an R value > 1.0 . The distortion of the equatorial bond angles from the ideal 120° could then be seen as the result of the greater repulsion between the electrons in the M-C bonds (which also have a large, diffuse, π component) than between these electrons and those in the M-Sb bond.

One final point is that it appears highly unlikely that crystal packing forces contribute to the switchover of isomeric forms in the solid state. If this were the case the close correlation with the solution infrared spectra would not be expected. Furthermore, the four species studied here, $\text{M}(\text{CO})_4\text{AsPh}_3$ and $\text{M}(\text{CO})_4\text{SbPh}_3$ ($\text{M}=\text{Ru}, \text{Os}$), as well as $\text{Fe}(\text{CO})_4\text{EPh}_3$, $\text{E}=\text{P}^{29}$ and Sb^{24} crystallize in the same space group ($P\bar{1}$), regardless of the isomeric form adopted. Packing forces may be the determining factor in the compound $\text{Fe}(\text{CO})_4\text{PPh}(\text{PPh}_2)_2$ which crystallizes as the equatorial isomer but displays only an axial

carbonyl stretching pattern in solution.⁶⁹

3.2 Electronic Properties of the Ligands

It is generally recognized^{70,71} that while the π -acceptor properties of the group 15 ligands do not vary appreciably on descending the group, the σ -donor ability decreases in the order $\text{PR}_3 > \text{AsR}_3 > \text{SbR}_3$.^{71,72} Since some of the conclusions of this work are based on this premise it is worth exploring it in some detail.

It has been established that the carbonyl stretching frequencies of closely related species of the type $\text{M}(\text{CO})_x\text{L}$ increase with increasing π -acceptor properties of L but do not vary as much with the σ -donor properties.⁷³ From Table A.2.5 it can be seen that the CO stretching frequencies of $\text{M}(\text{CO})_4\text{EPH}_3$ (E=P,As,Sb) for the axial isomer are all very similar indicating no appreciable variation of the π -acidity of the ligands. This is consistent with earlier studies wherein it was taken to indicate near equality of the π -acceptor qualities of these ligands.^{74,75}

Considerable experimental evidence^{68,76,77,78} has been presented to show that the donor strength of group 15 ligands follows the order $\text{PR}_3 > \text{AsR}_3 > \text{SbR}_3$. A quantitative understanding of the relative σ -donor strength of the ligands studied here can be gained from an analysis of the heats of formation of a number of LBX_3 adducts. Mente and Mills⁷⁶ found ΔH values of -68.6,

-46.2 and -26.8 kcal/mol for the reaction of BCl_3 with Me_3P , Me_3As and Me_3Sb respectively. Values for BH_3 were closely related at -79.9 and -49.6 kcal/mol for Me_3P and Me_3As . (The reaction between Me_3Sb and BH_3 was anomalous.) Other investigators^{7,9} have found the ΔH of OCBH_3 to be -25.1 kcal/mol; a value approximately equal to that expected for Me_3SbBH_3 . Since no π interaction is expected between the group 15 donor atom and the B atom we may take these measurements as an indication of donor strength. Because of the weaker inductive effect of the phenyl group compared to the methyl group, the SbPh_3 ligand would be expected to be a weaker donor than SbMe_3 and hence a weaker donor than CO. This would explain why a switchover of site preference in the solid state occurs when the unique ligand is changed from SbMe_3 to SbPh_3 . A rough estimate of the magnitude of the change of donor strength that occurs when Ph groups are substituted for Me groups can be seen from the values of the ΔH values found for the reaction of ER_3 ligands with $\text{trans} [\text{CH}_3\text{L}'_2(\text{THF})\text{Pt}][\text{PF}_6]$ ($\text{L}' = \text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)$).^{6,8} The values for PMe_3 and PPh_3 were -26.2 and -19.5 kcal/mol respectively while those for AsMe_3 and AsPh_3 were -15.4 and -12.8 kcal/mol. (The value for SbPh_3 was -6.1 kcal/mol, no value was recorded for SbMe_3 .) Any strengthening of the π component in the L-Pt bond in the compounds studied above would offset the trend displayed. The fact that the trend so clearly exists must be taken as an indication of the weakening donor strength.

A more recent study⁸⁰ based on ^{13}C chemical shifts in NMR spectra concluded that the ordering of the donor/acceptor ratio of these ligands is $\text{SbR}_3 > \text{PR}_3 > \text{AsR}_3$. However, this conclusion must be viewed with some caution since it is based only on the correlation between the ^{13}C NMR chemical shift (δCO) in $\text{LNi}(\text{CO})_3$ complexes and the relative donor/acceptor character of L. The ordering is as above only when $\text{R}=\text{Ph}$, and differs when $\text{R}=\text{Me}$. From the ^{13}C NMR data obtained in this study (Table A.2.5) an order of $\text{AsPh}_3 > \text{SbPh}_3 > \text{PPh}_3$ is indicated, based on the $\text{Fe}(\text{CO})_4\text{L}$ complexes which exist only in the axial form. Yet other orderings are possible if the data of Buchner and Schenk⁸¹ are used. It seems that while such methods may be valid when applied to P donor ligands, they cannot be extended to other group 15 ligands. In 1965 it was noted⁸² that ^{13}C chemical shifts of transition metal complexes were poorly understood. This comment was reiterated in 1974⁸³ and still seems valid in 1986.

A structural study of $\text{Cr}(\text{CO})_5\text{EPh}_3$ ($\text{E}=\text{P}, \text{As}, \text{Sb}, \text{Bi}$) complexes concluded from decreasing C-E-C angles and relatively shortened M-E bond lengths that the M-E bonds had more s character on descending the group.⁸⁴ From these results it was concluded that the bond order increased on going to the element lower in the group. (The distortion of the group 15 ligand from tetrahedral geometry can also be seen in the crystal structures determined here and by others.^{6, 43}) The explanation that the E-C bonds have enhanced p-character while the M-E bonds

have enhanced s-character is well accepted. It has been pointed out, however, that increased s character of the lone pair of such ligands makes it less available for bonding.⁸¹ Furthermore, a recent theoretical study⁸⁵ indicated the lone pair on PF_3 was less diffuse and had more s character than that of PMe_3 . It is well known that PF_3 is less basic than PMe_3 .

While it is generally accepted that a shorter bond indicates a stronger bond it should be remembered that the Cr-E bonds of the heavier analogues are only shortened relative to the covalent radii of the donor atom. This would be the expected result of the lone pair having more s character and does not necessarily indicate increased bond order. Such an effect might be expected to be quite large when the donor atom is Sb or Bi since their covalent radii are considerably larger than that of P. The variation of bond length can thus be explained (at least in part) by the more compact nature of the orbital having the greater s character. Other workers have found that shorter bonds do not necessarily mean stronger bonds. Bryan and Kuchowski⁸⁶ concluded that Me_3PBH_3 was a more stable adduct than F_3PBH_3 even though the latter molecule had a significantly shorter P-B bond. Similarly, in $\text{PtCl}_2(\text{PEt}_3)(\text{PF}_3)$ the Pt- PEt_3 bond length (2.272(3)Å) was longer than the Pt- PF_3 length (2.141(3)Å) even though the Pt- PF_3 bond was thought to have lower intrinsic strength than the Pt- PEt_3 bond.⁸⁷

We conclude that it is the σ -donor strength of most of the ligands studied here that determines their site preference in

$M(CO)_4L$ complexes, i.e., the stronger σ -donors prefer the axial position while the weaker σ -donors favour the equatorial site even in the presence of strong π -acceptor ligands (such as CO). This is in accord with the theoretical studies discussed in the introduction but at variance with the usual explanation that it is the π -acceptor properties of the ligand that determines the site preference.

The commonly held view that good π -acceptor ligands prefer the equatorial site, is not disputed. However, if it were the determining factor in the molecules studied here it would be reflected in higher CO stretching frequencies for the axial isomers of those complexes with a significant amount of equatorial isomer in solution. As noted earlier the CO stretching frequencies of all the $M(CO)_4EPh_3$ ($E=P, As, Sb$) complexes (axial isomer) are all very similar. Only for $M(CO)_4P(OCH_2)_3CMe$ ($M=Fe, Ru, Os$) are the bands due to the axial isomer shifted to higher frequencies and in this case the occurrence of some equatorial isomer for $M=Ru$ and Os may be rationalized accordingly, using π bonding arguments. The same can be said for other examples of $M(CO)_4L$ compounds reported in the literature which have a large fraction of equatorial isomer in solution such as $M(CO)_4PF_3$ ($M=Fe^{2+}, Ru^{4+}$) and $Fe(CO)_4P[OC(CF_3)_2CN]_3$ ⁷. That the carbonyl stretching frequencies of $M(CO)_4SbPh_3$ complexes do not occur at high frequencies indicates that $SbPh_3$ is not a better π -acceptor than CO; therefore π bonding arguments cannot be used to explain why

$\text{Ru}(\text{CO})_4\text{SbPh}_3$ and $\text{Os}(\text{CO})_4\text{SbPh}_3$ exist predominantly as the equatorial form.

3.3 Influence of the Central Metal

As was stated earlier the tendency of the transition metals to give the equatorial isomer was $\text{Ru} > \text{Os} \gg \text{Fe}$. In fact, there was no example for the group 15 ligands studied here of a $\text{Fe}(\text{CO})_4\text{L}$ derivative which gave detectable amounts of the equatorial isomer in solution. This trend is difficult to rationalize especially for the ruthenium and osmium complexes where the energy differences between the two isomers were small. Several possible explanations were considered and are now discussed. Unfortunately they do not account for the observations.

1) According to simple MO theory, ligand orbitals which are closest in energy to the symmetry matched metal orbitals form the strongest bonds. The ligand σ -donor orbitals are necessarily lower in energy than those of the metal while the opposite is true for the π orbitals. The increased energy of the valence metal orbitals on going from Fe, to Ru and/or Os should lead to stronger π bonds and weaker σ bonds. The energy levels of the valence orbitals are about equal for Ru and Os since the effect of increased atomic number is offset by the lanthanide contraction. Thus any ligand should have a greater tendency to occupy the equatorial position in ruthenium and

osmium complexes. However this effect should be approximately the same for CO as for the other ligand, so that no difference in site preference should result when the central metal is changed.

The available evidence suggests that the amount of π bonding to the CO ligands follows the order Fe-CO > Os-CO > Ru-CO, that is, the infrared CO stretching frequencies in complexes studied here and in the parent carbonyls follow the order, Ru-CO > Os-CO > Fe-CO. Also Ru(CO)₅ was the least stable of the three pentacarbonyls.⁴⁶ However, the differences in the infrared stretching frequencies are not great, and it is difficult to understand why the same order would not also be true for M-ER₃ bonds. In that case there would be no change in the difference between the M-CO and M-ER₃ bond strengths as M varied.

2) Other factors which have been used to explain differences in M-L bonding as the metal is replaced by heavier members of the triad are atomic size,⁸⁸ the lanthanide contraction⁸⁹ and relativity effects.⁹⁰ Each of these explain trends in M-L bonding as M is varied. But once again, a difference between M-CO and M-ER₃ bonding cannot be easily rationalized.

3) Arguments based on the hardness and softness of metals and ligands⁹¹ might lead to the conclusion that the soft SbPh₃ ligand should form stronger bonds to ruthenium and osmium than to iron. This in turn would lead to the prediction that there would be less of the equatorial form for the M(CO)₄SbPh₃

complexes of the heavier metals, contrary to what is observed.

4) A careful study of the $M-Sb-C_{Ph}$ and $C_{Ph}-Sb-C_{Ph}$ bond angles for the three compounds $M(CO)_4SbPh_3$ ($M=Fe, Ru, Os$) revealed that all the $M-Sb-C_{Ph}$ angles are enlarged from the tetrahedral angle of 109.5° and follow the order $Ru \geq Os > Fe$ for M . Consequently all the $C_{Ph}-Sb-C_{Ph}$ are reduced from the tetrahedral angle and follow the order $Fe > Os \geq Ru$. (see Table A.3.1.) In accord with the above discussion, this may be taken to mean that all the $M-Sb$ bonds have enhanced s character while the $Sb-C_{Ph}$ bonds have enhanced p character. The s character of the $M-Sb$ bond would follow the order $Ru-Sb > Os-Sb > Fe-Sb$. The logical extension of the statement that increased s character of the lone pair on ER_3 ligands makes them less available for bonding,⁸¹ leads to the conclusion that $M-ER_3$ σ bonds with greater s character are weaker would be consistent with the observed trend for the site preference. This line of reasoning is weak however, in that it only correlates two sets of observations and explains neither. Also, it would lead one to predict that the $Ru-Sb-C_{Me}$ and $Ru-As-C_{Ph}$ angles of $Ru(CO)_4SbMe_3$ and $Ru(CO)_4AsPh_3$ would be larger than the $Fe-Sb-C_{Ph}$ angle in $Fe(CO)_4SbPh_3$. As can be seen from Table A.3.1 they are smaller.

It is concluded that a deeper understanding of the influence of the central metal on the site preference of a unique group 15 ligand awaits more detailed molecular orbital calculations. Simple symmetry overlap arguments do not suffice. Quite subtle yet significant differences could be expected from varying the

Table A.3.1. Ligand Bond Angles for $M(\text{CO})_4\text{ER}_3$ Complexes.

Compound	M-E-C _{ph} Angle (°) ^a	C _{ph} -E-C _{ph} Angle(°) ^a	Ref.
Fe(CO) ₄ SbPh ₃	116.0-116.8	101.6-102.0	24
Ru(CO) ₄ SbPh ₃	113.8-121.7	98.7-99.9	6
Os(CO) ₄ SbPh ₃	114.0-121.2	99.0-100.5	this work
Ru(CO) ₄ SbMe ₃	115.7(2)	102.6(3)	this work
Ru(CO) ₄ AsPh ₃	115.1-115.4	103.0-103.3	this work

^aRange where appropriate.

MO approach. This has been discussed by Blyholder and Springs in their study on $\text{Fe}(\text{CO})_5$.¹²

3.4 Summary

It has been previously predicted that better π -acceptors and weaker σ -donor ligands have a greater tendency to occupy the equatorial site in a d^8 transition metal TBP complex of the type $\text{ML}_4\text{L}'$.¹ Since good π -acceptor ligands are usually poor σ -donors and vice versa, changes in site preference have been difficult to attribute unambiguously to either the σ or π properties of the unique ligand. In many synthetic papers the site preferences were discussed only in terms of the π bonding ability of the unique ligand.¹⁷

The majority of known complexes of the type $\text{ML}_4\text{L}'$ were of first row transition metals wherein the unique ligand occupied

an axial position. A few other examples existed which had a very strong π -acceptor ligand in the equatorial site. That the carbonyl stretching frequencies of these complexes were shifted to higher wave numbers was consistent with unusual π bonding ability of the ligands (i.e., PF_3 and $\text{P}[\text{OC}(\text{CF}_3)_2\text{CN}]_3$ in the iron tetracarbonyl compounds.)

The complex $\text{Ru}(\text{CO})_4\text{SbPh}_3$ was, therefore, unusual and interesting in that it contained both a second row transition metal and a unique ligand (SbPh_3), not known as an exceptional π acid, in an equatorial position. This anomaly was the main impetus for the present study.

The new and known complexes synthesized and characterized here were all of the type $\text{M}(\text{CO})_4\text{L}$ ($\text{M}=\text{Fe}, \text{Ru}, \text{Os}$; $\text{L}=\text{group 15 ligand}$). This has allowed a systematic study of the influence of the central metal, the group 15 donor atom, and the ligand substituents on the site preference. Axial-equatorial isomerism was observed for a number of these complexes. The solution and solid state CO stretching frequencies and the crystal structures are all consistent with the tendency to give the equatorial isomer as $\text{Sb} > \text{As} > \text{P}$, $\text{Ph} > \text{Me}$, $\text{P}(\text{OCH}_2)_3\text{CMe} > \text{PPh}_3, \text{PMe}_3$ and $\text{Ru} > \text{Os} > \text{Fe}$. The switchover to the equatorial form in the solid state occurred between $\text{Ru}(\text{CO})_4\text{AsPh}_3$ and $\text{Ru}(\text{CO})_4\text{SbPh}_3$, and $\text{Ru}(\text{CO})_4\text{SbMe}_3$ and $\text{Ru}(\text{CO})_4\text{SbPh}_3$. The osmium analogues displayed similar behaviour.

Group 15 ligands with the same substituents are similar in size⁶⁸ and in their π bonding properties,^{70,71} but their basicity decreases markedly on descending the period.^{70,75,76,77,78} The observed site preference trend for the group 15 ligands with the same substituents has, therefore, been rationalized on the basis that weaker σ -donor ligands prefer the equatorial site even in the presence of strong π -acceptors such as CO. The same explanation was used with regard to EMe_3 and EPh_3 ligands since the Me group is known to increase the σ basicity of any ligand to which it is attached. Reasoning based on π bonding is more relevant when applied to the $\text{P}(\text{OCH}_2)_3\text{CMe}$ ligand. The $\text{M}(\text{CO})_4\text{P}(\text{OCH}_2)_3\text{CMe}$ ($\text{M}=\text{Ru}, \text{Os}$) complexes were the only ones with a phosphorus ligand to exhibit a detectable amount of the equatorial isomer in solution. It was noted that the CO stretching frequencies of these complexes were shifted to considerably higher wavenumbers compared to those found for $\text{M}(\text{CO})_4\text{PMe}_3$. It thus seems reasonable that existence of a small amount of equatorial isomer when the unique ligand was $\text{P}(\text{OCH}_2)_3\text{CMe}$ ligand may be rationalized in terms of the good π bonding ability of that ligand. However, it should be remembered that this phosphite ligand is also expected to be a weak σ -donor.

The influence of the central metal on the ligand site preference is certainly one of the most interesting and unexpected findings of this study. Unfortunately, it has been difficult to account for the observation in terms of σ bonding,

variation in valence orbital energies, or any other possible explanation. Arguments based on π bonding can be made in view of the lability of CO ligands attached to Ru and the CO stretching frequencies of Ru-CO>Os-CO>Fe-CO. But this rationalization is weak at best because it does not predict a different change in the nature of the M-CO bond as compared to the M-ER₃ bond.

Steric factors have been discussed and ruled out as a major contribution for the complexes studied here. They are probably important in other cases where the steric requirement of the unique ligand is extreme, e.g. in Fe(CO)₄P{N(SiMe₃)₂}{C(SiMe₃)₂}³² and Fe(CO)₄P₂(2,4,6-t-Bu₃C₆H₂)₂.²⁶

The ¹³C NMR spectra displayed only one signal for each compound studied. This is indicative of rapid axial-equatorial exchange and rapid equilibrium between the isomers. The Berry pseudorotation mechanism accounts for both observations. Low temperature studies indicated the barrier to rearrangement is low.

3.5 Future Directions

It is felt that the insight into the factors determining site preference in TBP derivatives of d⁸ transition metals has been considerably enhanced by this study. However the nature of the influence of the central metal is still poorly

understood. Structural characterization of $\text{Ru}(\text{CO})_5$ and/or $\text{Os}(\text{CO})_5$ would allow detailed MO calculations to be carried out on these molecules. This might point out interesting differences between their electronic structures which could help account for the changes in molecular geometry that occur when Ru or Os is substituted for Fe in the $\text{M}(\text{CO})_4\text{L}$ complexes studied here.

Another approach would be to investigate whether the metals of other triads influence the geometry of $\text{ML}_4\text{L}'$ complexes in a similar way. Numerous complexes of the type $\text{Co}(\text{CO})_4\text{XR}_3$ (X=group 14 atom; R=alkyl, aryl, H) are known. However, the rhodium and iridium analogues are unknown. Synthesis and characterization of such complexes might prove extremely interesting because axial-equatorial exchange in $\text{Co}(\text{CO})_4\text{EX}_3$ complexes can be slowed down on the ^{13}C NMR time-scale.¹⁴

CHAPTER 4

EXPERIMENTAL PROCEDURES

4.1 Materials and Instrumentation

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Reactions under moderate CO pressure were carried out in a 200-mL general-purpose bomb from Parr Instrument Co. Hexane was refluxed over potassium and THF over potassium benzophenone ketyl; both were distilled and stored under nitrogen before use. The pentacarbonyls of ruthenium and osmium were prepared by literature methods;^{4,6} $\text{Fe}(\text{CO})_5$ was commercially available. The group 15 ligand, $\text{P}(\text{OCH}_2)_3\text{CMe}$, was synthesized by the method of Heitsch and Verkade^{9,2} by Mr. R. F. Alex; it was sublimed before use. Other ligands were commercially available. The iron complexes $\text{Fe}(\text{CO})_4\text{L}$ were prepared by literature^{3,4} methods or minor variations thereof. The method previously used to prepare $\text{Ru}(\text{CO})_4\text{P}(\text{OMe})_3$ from $\text{Ru}_3(\text{CO})_{12}$ was used for $\text{Ru}(\text{CO})_4\text{PMe}_3$.^{4,1}

Infrared spectra were obtained with a Perkin-Elmer 983 spectrophotometer; NMR spectra with a Bruker 400-MHz instrument and mass spectra with a Hewlett Packard 5985 GC-MS system with an ionization voltage of 70eV. Microanalysis were performed by Mr. M. K. Yang of the Microanalytical Laboratory of Simon Fraser University. Analytical and mass spectral data for new

compounds are given in Table A.4.1; infrared, ^{13}C NMR and melting point data in Table A.2.5. Yields were calculated by comparing the weight of product (pure by infrared spectroscopy) to that expected for 100% yield.

Solutions of $\text{Ru}(\text{CO})_5$ and $\text{Os}(\text{CO})_5$ were handled with extreme caution in view of the well known toxic properties of $\text{Fe}(\text{CO})_5$. The ligands PMe_3 and SbMe_3 were handled in the inert atmosphere of a dry box since they ignite spontaneously in air.

Because of the nature of the preparations of $\text{Ru}(\text{CO})_5$ and $\text{Os}(\text{CO})_5$, the concentrations of the hexane solutions of these compounds could only be determined approximately. For most preparations described below the concentration of $\text{Ru}(\text{CO})_5$ in hexane was $\approx 2 \times 10^{-3} \text{M}$, for $\text{Os}(\text{CO})_5$ it was $\approx 7 \times 10^{-3} \text{M}$. Typical reactions using these starting materials involved 25mL of solution.

4.2 Synthesis Methods

4.2.1 *Preparation of $\text{Ru}(\text{CO})_4\text{P}(\text{OCH}_2)_3\text{CMe}$*

A solution of $\text{Ru}(\text{CO})_5$ and a slight excess of $\text{P}(\text{OCH}_2)_3\text{CMe}$ was stirred in the dark at room temperature for 18 h during which time a pale yellow precipitate formed. The mother liquor was then removed and the precipitate washed with hexane (3x5mL). The precipitate was recrystallized from a large volume of hexane to give the product as pale yellow needles. The yield was 43%.

Table A.4.1. Analytical and Mass Spectral Data for New $M(\text{CO})_4\text{L}$ Derivatives.

Compound	%Calcd.		%Found		Mass Spectrum ^a
	C	H	C	H	
$\text{Ru}(\text{CO})_4\text{P}(\text{OCH}_2)_3\text{CMe}$	29.92	2.51	29.95	2.50	362 (P ⁺)
$\text{Ru}(\text{CO})_4\text{PMe}_3$	29.07	3.14	29.01	3.16	290 (P ⁺)
$\text{Ru}(\text{CO})_4\text{AsPh}_3$	50.89	2.91	50.92	2.89	dec.
$\text{Ru}(\text{CO})_4\text{SbMe}_3$	22.13	2.39	22.19	2.19	382 (P ⁺)
$\text{Os}(\text{CO})_4\text{P}(\text{OCH}_2)_3\text{CMe}$	24.15	2.01	23.99	1.90	452 (P ⁺)
$\text{Os}(\text{CO})_4\text{PMe}_3$	22.22	2.40	22.25	2.40	380 (P ⁺)
$\text{Os}(\text{CO})_4\text{AsPh}_3$	43.43	2.48	43.51	2.57	610 (P ⁺)
$\text{Os}(\text{CO})_4\text{SbMe}_3$	17.91	1.92	17.89	1.93	470 (P ⁺)
$\text{Os}(\text{CO})_4\text{SbPh}_3$	40.32	2.31	40.43	2.58	656 (P ⁺)

^aMost intense peak of parent ion envelope; in all cases the parent ion agreed with that simulated by computer.

4.2.2 Preparation of $\text{Ru}(\text{CO})_4\text{EPh}_3$ (E=P, As, Sb)

A hexane solution of $\text{Ru}(\text{CO})_5$ with an approximate two-fold molar excess of the ligand was stirred under CO pressure (25 atm) at room temperature for 18 h. After this period the gas was released and the solvent removed on the vacuum line to leave a yellow-orange powder. Recrystallization of the powder twice from hexane gave the pure $\text{Ru}(\text{CO})_4\text{EPh}_3$ product. The yield was 41% for $\text{Ru}(\text{CO})_4\text{AsPh}_3$ and 39% for $\text{Ru}(\text{CO})_4\text{SbPh}_3$. The arsenic derivative was thermally unstable and slowly decomposed when

stored at room temperature. Preparation of $\text{Ru}(\text{CO})_4\text{PPh}_3$ from $\text{Ru}(\text{CO})_5$ and PPh_3 has been reported previously.⁴³

4.2.3 Preparation of $\text{Ru}(\text{CO})_4\text{SbMe}_3$

A solution of $\text{Ru}(\text{CO})_5$ in hexane was placed in a Carius tube. The tube was cooled to -196°C and evacuated; the solution was degassed with one freeze-thaw cycle. With the vessel at room temperature an approximately equimolar quantity of SbMe_3 was added and the tube pressurized with CO (2 atm). The solution was then stirred in the dark at room temperature for 5 h. After this period the gases were released, the solution transferred to a Schlenk tube and evaporated to dryness at 0°C . The pure, pale yellow product was obtained by sublimation (static atmosphere, <0.02 mm) to a cold-water probe. The yield was 41%.

4.2.4 Preparation of $\text{Os}(\text{CO})_4\text{PMe}_3$

METHOD 1. The compound was prepared in excellent yield by the reaction of equimolar quantities of PMe_3 and $\text{Os}(\text{CO})_5$ in hexane at 120°C under CO pressure (40 atm) for 16 h. The white compound was purified by sublimation at 35°C , <0.02 mm, to a probe at -78°C .

METHOD 2. This derivative was also prepared (in excellent yield) by heating $\text{Os}_3(\text{CO})_{12}$ and PMe_3 (1:3 molar ratio) in hexane at 280°C under CO (200 atm) for 48 h. The compound was isolated as in Method 1. (This reaction was first carried out by Dr. P. Rushman.)

4.2.5 Preparation of $\text{Os}(\text{CO})_4\text{SbMe}_3$

Approximately equimolar quantities of $\text{Os}(\text{CO})_5$ and SbMe_3 in hexane solution were heated at 80 °C under CO (33 atm) for 16 h. After the reaction vessel had been cooled and the CO released, the solution was transferred to a Schlenk tube and evaporated to dryness on the vacuum line. The pure, pale yellow $\text{Os}(\text{CO})_4\text{SbMe}_3$ (11% yield) was isolated by sublimation from the residue onto a cold water probe at static vacuum (<0.02 mm).

4.2.6 Preparation of $\text{Os}(\text{CO})_4\text{EPh}_3$ (E=As, Sb)

Approximately equimolar quantities of $\text{Os}(\text{CO})_5$ and EPh_3 in hexane were heated at 90 °C under CO (25 atm). The resulting solution was evacuated to dryness. This procedure removed unreacted $\text{Os}(\text{CO})_5$ as well as solvent. The remaining solid was dissolved in a minimum of hexane and chromatographed on a silica gel column (20 x 2.5 cm), with an eluent of hexane:THF (11:1). (Although occasional exposure of the solutions to air appeared not to affect the chromatography, the other conditions were found to be critical to the successful isolation of the desired product.) During the chromatography three bands formed, the first two were yellow, and the third very pale yellow to almost colourless. The first and third bands, $\text{Os}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{11}\text{EPh}_3$ respectively, were discarded. The second band was the product, $\text{Os}(\text{CO})_4\text{EPh}_3$, which was recrystallized from hexane to give pale yellow crystals. The yield was 15% for $\text{Os}(\text{CO})\text{SbPh}_3$ and 7% for $\text{Os}(\text{CO})\text{AsPh}_3$. The triphenylphosphine

analogue, $\text{Os}(\text{CO})_4\text{PPh}_3$, was prepared similarly, in much better yield.⁴³

4.3 Crystal Structure Determinations

4.3.1 $\text{Ru}(\text{CO})_4\text{AsPh}_3$ and $\text{Os}(\text{CO})_4\text{SbPh}_3$

Details are given here for the crystallographic analysis of $\text{Ru}(\text{CO})_4\text{AsPh}_3$ with the differences for $\text{Os}(\text{CO})_4\text{SbPh}_3$ noted in parentheses.

Pale yellow, plate-like crystals suitable for X-ray analysis were grown from hexane. Oscillation, Weissenberg and precession photographs were taken with Cu K radiation. These indicated the space group to be $\text{P}\bar{1}$ or $\text{P}1$ and gave approximate cell dimensions. The space group was subsequently determined to be $\text{P}\bar{1}$ by the structure solution. Accurate cell dimensions were determined by a least-squares refinement of 24 (22) reflections in the range $2\theta=16.2-25.4^\circ$ ($30.9-42.4^\circ$) on a Picker FACS-I four circle automated diffractometer which employed graphite monochromated $\text{Mo K}\alpha$ radiation, $\lambda=0.71069 \text{ \AA}$.

Details of the data collection are given in Table A.4.2, other crystallographic data in Table A.4.3. The data were collected at $20\pm 1^\circ \text{C}$. Stationary-crystal stationary-counter background counts for 10% of the scan time were taken at each side of the scan. Peak-profile analysis was performed on all reflections to derive the intensity, I , and the associated error, $\sigma(I)$.⁹³ Two standards were measured after every 70

Table A.4.2. Diffractometer Collection and Refinement Parameters for $M(CO)_4L$ Compounds.

	Ru(CO) ₄ AsPh ₃	Os(CO) ₄ SbPh ₃	Ru(CO) ₄ SbMe ₃
scan method	ω -2 θ	ω -2 θ	ω -2 θ
scan range, 2 θ , deg	3.5-40.0	3.5-40.0	3.0-50.0
scan width, 2 θ , deg	1.40	1.20	1.30
scan rate, 2 θ , deg/min	2	3	1.3-6.6
collection range	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
transmission coefficient range	0.594-0.932	0.365-0.644	0.913-1.000 ^a
unique reflections	2018	3754	582
observed reflections ($I > 2.3\sigma$)	1650	3115	523
variables	253	298	39
R_1 ^b	0.0203	0.0192	0.0233
R_2 ^c	0.0213	0.0205	0.0295
gof	1.0463	1.3989	0.9806
largest shift ^d	0.15	0.36	0.00

^a Empirical absorption correction, see text.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

^c $R_2 = [\sum (|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$

^d Largest shift/error in the final cycle of refinement.

reflections; they gave no indication of decomposition. The data were corrected for Lorentz and polarization effects and an analytical absorption correction⁹⁴ was also applied.

The structures were solved by Patterson and Fourier methods. All non-hydrogen atoms were located from successive electron density difference maps. The final refinement was by block-diagonal least-squares methods with anisotropic parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated (or previously refined) positions. Unit weights were used throughout for both structures. There were no significant trends in the average $\Sigma \omega ||F_o| - |F_c||^2$ as a function of $|F_o|$ and $\sin\theta/\lambda$ in the final error analysis. Atomic scattering factors including anomalous dispersion for non-hydrogen atoms were taken from reference 95.⁹⁵ ORTEP views, with 50% thermal ellipsoids, of $\text{Ru}(\text{CO})_4\text{AsPh}_3$ and $\text{Os}(\text{CO})_4\text{SbPh}_3$ are given in Figures A.2.1 and A.2.3 respectively; these also give the labelling scheme employed for each molecule. Final coordinates for all atoms of both molecules, anisotropic thermal parameters for the non-hydrogen atoms, thermal parameters for the hydrogen atoms and structure factors are listed in the appendix. Selected bond lengths and angles for $\text{Ru}(\text{CO})_4\text{AsPh}_3$ are given in Table A.2.1; for $\text{Os}(\text{CO})_4\text{SbPh}_3$ in Table A.2.3. The computer programs used were those developed by Larson and Gabe.⁹⁶

4.3.2 $Os(CO)_4AsPh_3$

Space group and approximate cell dimensions were determined as for $Ru(CO)_4AsPh_3$. Accurate cell dimensions were obtained in a manner similar to that used for $Ru(CO)_4SbMe_3$; the 2θ scan range was $16.2-25.4^\circ$ for 25 accurately centred reflections. The standard deviations of the cell dimensions were slightly higher than desirable for data collection; an examination of the peak profiles also indicated the crystal was not of sufficiently high quality for a structure determination. Cell dimensions (see Table A.4.3) and the space group revealed the compound is isostructural with $Ru(CO)_4AsPh_3$.

4.3.3 $Ru(CO)_4SbMe_3$

Pale yellow crystals suitable for X-ray analysis were obtained by slow sublimation in a sealed, evacuated tube. Weissenberg photographs (Cu, $\lambda=1.5418 \text{ \AA}$) were used to assign the space group as R3 or $R\bar{3}$. The compound was then assumed to be isostructural with $Fe(CO)_4SbMe_3$ ³³ (space group R3) and the cell dimensions of this compound were used as a first approximation for the ruthenium analogue. Accurate cell dimensions were determined by least-squares refinement of 25 accurately centred reflections ($2\theta=20-25^\circ$, Mo $K_{\alpha 1}$, $\lambda=0.7093 \text{ \AA}$). Crystal data are given in Table A.4.2. Diffraction data were collected at $20\pm 1^\circ \text{C}$. on an Enraf-Nonius CAD4-F diffractometer using a graphite monochromator. Background measurements were made by extending the scan range by 25% at each side of the scan. Measurement of two standard reflections every hour showed no significant

Table A.4.3. Crystallographic Data for $\text{Ru}(\text{CO})_4\text{AsPh}_3$, $\text{Os}(\text{CO})_4\text{SbPh}_3$, $\text{Ru}(\text{CO})_4\text{SbMe}_3$ and $\text{Os}(\text{CO})_4\text{AsPh}_3$.

	$\text{Ru}(\text{CO})_4\text{AsPh}_3$	$\text{Os}(\text{CO})_4\text{SbPh}_3$	$\text{Ru}(\text{CO})_4\text{SbMe}_3$	$\text{Os}(\text{CO})_4\text{AsPh}_3$
formula wt.	519.4	655.3	380.0	608.4
space group	$\overline{P}1$	$\overline{P}1$	R3	$\overline{P}1$
crystal system	triclinic	triclinic	hexagonal	triclinic
a, Å	10.605(3)	11.123(2)	10.378(1)	10.633(6)
b, Å	11.068(4)	11.284(4)	-	11.029(7)
c, Å	9.979(3)	12.714(4)	9.632(1)	9.979(6)
α , deg	113.57(3)	129.29(2)	90	113.43(5)
β , deg	93.14(3)	102.35(2)	120	93.24(5)
γ , deg	91.47(3)	102.45(2)	120	91.60(5)
Volume, Å ³	1070.6	1068.5	898.3	1070.3
Z	2	2	3	2
d_{calc} , g/cm ³	1.611	2.037	2.057	
d_{found} , g/cm ³	1.50	1.99	2.10	
μ (Mo K_{α}), cm ⁻¹	22.70	71.81	33.99	
crystal size, mm	0.24x0.22x0.030	0.076x0.11x0.22	0.61x0.37x0.14	

crystal decay, instability in the detection chain or variation in generator output. Lorentz polarization and a semi-empirical absorption⁹⁷ corrections were applied.

The non-hydrogen positional parameters from $\text{Fe}(\text{CO})_4\text{SbMe}_3$ ³³ were employed as the initial model. Refinement proceeded quickly by full matrix least-squares methods with anisotropic temperature factors used in the final cycles. Hydrogen atoms were not included in the calculations. When inverse coordinates were employed the residual R, dropped from 0.0248 to 0.0233 therefore they were used for subsequent refinement. The weighting scheme $\omega = [\sigma^2(F) + 0.0006F^2]^{-1}$ was shown to be correct on the basis of trends in $\omega\Delta^2$ as a function of $|F_o|$ and $\sin\theta/\lambda$. The 1,-1,0 reflection was omitted from the refinement because it was judged to suffer from extinction (final $KF_o = 229.43$, $F_c = 260.88$). Details of the data collection and final refinement parameters are given in Table A.4.2. Atomic scattering factors which included anomalous dispersion were taken from reference 95. An ORTEP view, with the atomic labelling scheme, of $\text{Ru}(\text{CO})_4\text{SbMe}_3$ is shown in Figure A.2.2. Selected bond lengths and angles are given in Table A.2.2. Final atomic coordinates, anisotropic thermal parameters and structure factor listings are listed in the appendix. The computer programs in this determination were from, "The Vax 750/780 Crystal Structure System".⁹⁸

PART B

**SYNTHESIS, STRUCTURE AND CHARACTERIZATION OF
 $\text{Os}_4(\text{CO})_n\text{PMe}_3$ (n=15, 14, 13) AND $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$**

CHAPTER 1

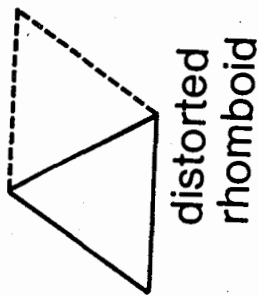
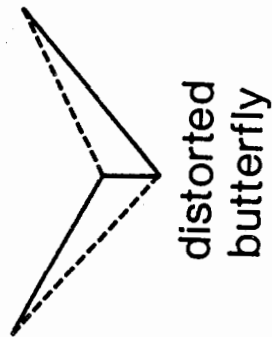
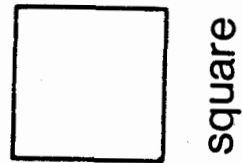
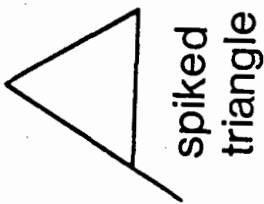
INTRODUCTION

1.1 Theoretical Approaches

Chemists remain interested in transition metal clusters even though previously hoped for industrial catalytic applications have been slow in coming. The continued fascination stems from the large number of bonding modes, structures, fluxional processes and reactivities that clusters exhibit which present a challenge to both the theoretician and the experimentalist. The group 8 metals have proven a particularly fruitful area of study; over a thousand clusters are known with nuclearities ranging from three to ten⁹⁹ and geometries from chains¹⁰⁰ to very compact deltahedra.¹⁰¹ Of special interest to this study are Group 8 tetranuclear clusters; these exhibit spiked triangle,¹⁰² tetrahedral,¹⁰³ butterfly,¹⁰⁴ planar rhomboidal¹⁰⁵ and other^{101, 106} geometries, see Figure B.1.1.

Several different approaches are used to rationalize or predict these structural variations but the discussion here will be limited to those most frequently encountered: the Effective Atomic Number (EAN) or 18-Electron Rule, Polyhedral Skeletal Electron Pair Theory (PSEPT), the isolobal analogy and some specific molecular orbital treatments. The first of these, the well known^{70, 107} EAN or 18-Electron Rule is often used to explain the structures of mono-, di- and trinuclear transition

64 electrons
spiked triangle



62 electrons
butterfly



60 electrons
tetrahedron

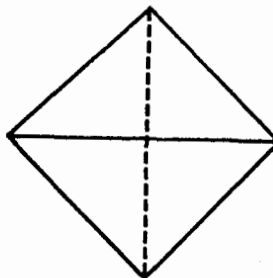


Figure B.1.1. Geometries of Tetranuclear Group 8 Clusters.

metal complexes containing π -acceptor ligands. According to this approach valence electrons are assigned to the metal atoms, each of which is considered separately. Since a transition metal atom has nine valence orbitals, a stable structure is predicted only if a total of 18 electrons can be assigned to each metal atom. If there are not enough electrons available from the metal atom d orbitals and from the ligands then metal-metal bonding occurs. These bonds usually contribute one electron to each metal atom involved. For tetranuclear complexes the predicted number of cluster metal-metal bonds is given by the formula: $nb=(72-ne)/2$, where nb is the number of metal-metal bonds and ne is the number of electrons assignable to the complex from the ligands, charge and metal valence electrons. Thus a 64 electron tetranuclear complex is expected to have four metal-metal bonds and a square or spiked triangle geometry. The predicted number of bonds (and shapes) for 62 and 60 electron complexes are five (butterfly) and six (tetrahedron) respectively.

Churchill and Hollander used the 18-Electron Rule to explain the geometry of $\text{HOs}_3\text{Re}(\text{CO})_{15}$, which has a planar rhomboidal structure.¹⁰⁸ The two $\text{Os}(\text{CO})_4$ moieties were viewed as 16 electron fragments needing two metal-metal bonds each and they thus bridge the $\text{HOs}(\text{CO})_3$ and $\text{Re}(\text{CO})_4$ fragments. The latter two fragments are 15 electron species needing three metal-metal bonds and hence the extra bond between them (see Figure B.1.2). The total number of valence electrons associated with the

cluster is 62.

Adams and co-workers also used the 18-Electron Rule in their discussion of the tetrahedral molecule $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-S})$.¹⁰⁹ Each $\text{Os}(\text{CO})_3$ fragment was seen as having 14 electrons; an additional three are obtained from the three metal-metal bonds in which each osmium atom partakes. The sulphur ligand donates four electrons to the cluster, thus each osmium atom obtains an 18 electron configuration. The total number of electrons is 60 so that a tetrahedral structure is predicted, in agreement with experiment. However, it is difficult to understand on the basis of localized two-center, two-electron bonds how a $\mu_3\text{-S}$ ligand, capping one face of a tetrahedron can contribute one electron to each of four osmium atoms.

A similar difficulty exists in describing the bonding in $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-S})_2$ which has a butterfly structure. Each osmium atom obtains an eighteen electron configuration only if each $\mu_3\text{-S}$ ligand contributes three electrons to the cluster. This is in contradiction to the normal description of sulphur as a four electron donor. Adams and Yang view the sulphur ligands as contributing four electrons and refer to the cluster as 'electron rich'.¹¹⁰ That is, it has 64 electrons but five metal-metal interactions. The authors believe the extra electrons cause weakening (and lengthening) of two of the Os-Os bonds which are consequently very reactive. It is difficult to view these elongated bonds as normal two-center-two-electron bonds.

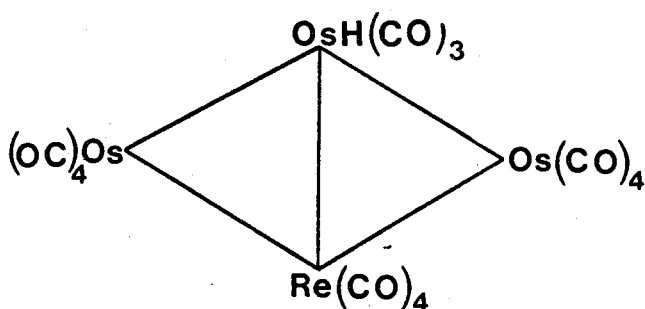


Figure B.1.2. Geometry of $\text{HOs}_3\text{Re}(\text{CO})_{15}$.

A large number of cluster compounds, particularly those of high nuclearity, cannot be adequately described using only the 18-Electron Rule and simple two-center-two-electron bonds. The tetrahedral cluster $\text{H}_4\text{Re}_4(\text{CO})_{12}$ is electron deficient and is more appropriately described as having four, four-center Re_3H bonds.¹¹¹ Each of the clusters, $\text{Rh}_6(\text{CO})_{16}$, $[\text{Co}_6(\text{CO})_{14}]^{4-}$, and $\text{H}_2\text{Ru}_6(\text{CO})_{18}$ has two electrons too many to be accommodated by twelve two-center-two-electron bonds in its octahedral core.¹¹² A more suitable approach for these and other clusters is based on molecular orbital calculations which can be applied to transition metal clusters in a simplified version, namely the Polyhedral Skeletal Electron Pair Theory (PSEPT).

This theory was developed and applied to transition metal clusters almost simultaneously by Wade¹¹³ and by Mingos.¹¹⁴ According to these early versions of PSEPT each metal

contributes three atomic orbitals to the bonding molecular orbitals of the cluster. A cluster containing n metal atoms therefore has $3n$ atomic orbitals from which the cluster molecular orbitals can be formed. It is considered that one orbital from each vertex atom, that is n orbitals, point toward the center of the cluster to form one strongly bonding and $n-1$ non-bonding or antibonding molecular orbitals. The remaining $2n$ orbitals are dispersed radially and combine to form n bonding and n antibonding orbitals. The result is $n+1$ bonding molecular orbitals.

The number of electrons donated by a vertex varies with the metal and number and type of ligands. For group 8 metals, $M(CO)_3$ vertices contribute two electrons and $M(CO)_4$ vertices, four electrons. Bridging carbonyl ligands contribute two electrons and bridging or terminal hydrides one electron to cluster bonding. PSEPT predicts that when $n+1$ electron pairs are available to fill the $n+1$ bonding orbitals a stable compact deltahedron with n vertices i.e., a 'closo' structure, results. If $n+2$ electron pairs are present the appropriate deltahedron has $n+1$ vertices, one of which is unoccupied. This results in a more open structure, designated 'nido' which has one vertex missing. Thus an M_5 cluster with 7 electron pairs such as $Fe_5(CO)_{15}C$ is expected to, and does, adopt a square pyramidal geometry, i.e., an octahedron with one vertex missing.¹¹⁵ This may be compared to $Os_5(CO)_{16}$ which has 6 electron pairs ($n+1$) and a trigonal bipyramid (closo) geometry.¹¹⁶ Complexes with $n+3$

electron pairs exhibit even more open 'arachno' geometries which are based on deltahedra with two vertices missing. For example, in $\text{H}_3\text{Os}_4(\text{CO})_{12}\text{I}$ which has seven electron pairs, the osmium atoms display a butterfly arrangement which is considered as an octahedron with two cis vertices missing.¹¹⁷ A rarely used extension of this theory designates complexes with $n+4$ electron pairs as 'hypho' structures; deltahedra with three vertices missing.

Despite the advantage of PSEPT that it shifts the focus of attention from the individual metal atoms to the cluster as a whole, application of the theory to tetranuclear clusters is problematic. The view that the tetrahedral geometries of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$,¹¹⁸ $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$,¹¹⁹ and $\text{Os}_4(\mu_3\text{-NCH})(\text{CO})_{12}$,¹²⁰ (for example), which have six skeletal electron pairs apiece, are trigonal bipyramids with one vertex missing has been described as 'artificial'.¹²¹ Certainly the idea that spiked triangles such as $\text{H}_2\text{Os}_4(\text{CO})_{15}$ or $\text{H}_3\text{Os}_4\text{Br}(\text{CO})_{13}$ ¹⁰² which contain 8 skeletal pairs are hypho pentagonal bipyramids, is of little use. Mingos attempted to deal with part of the problem by defining an 'electron precise' cluster as one having the same number of bonding pairs as M-M vectors. This definition was then applied to tetrahedral clusters with six electron pairs.¹¹⁴ Confusion is still evident, however, in that he later referred to such clusters as 'closo' structures.¹²²

Another weakness of this theory is the rule that each metal atom makes available three atomic orbitals for cluster bonding

regardless of the number of terminal ligands bonded to it. Later calculations have shown that, in many cases, an $\text{Os}(\text{CO})_4$ fragment contributes only two orbitals to cluster bonding.¹²²

Recent modifications of PSEPT have made some attempt to deal with these issues. Johnson and Benfield,¹⁰⁷ for example, suggested that an $\text{M}(\text{CO})_4$ ($\text{M}=\text{Fe}, \text{Ru}, \text{Os}$) fragment contributes two electrons and two atomic orbitals to cluster bonding. This concept is intuitively satisfying where the $\text{Os}(\text{CO})_4$ fragment is found in an edge bridging position as in $\text{H}_2\text{Os}_5(\text{CO})_{16}$,¹²³ but less so where the $\text{Os}(\text{CO})_4$ fragment is more highly coordinated. For example, $\text{Os}_5(\text{CO})_{16}$, which was cited in the paper, has an $\text{Os}(\text{CO})_4$ fragment with a total connectivity of eight, but this was not discussed at all.

A far more comprehensive discussion is that of Evans and Mingos.¹²² Their paper on the extension of PSEPT to nonconical fragments described the application of extended Hückel molecular orbital (EHMO) calculations to carbonyl clusters containing $\text{Os}(\text{CO})_4$ and T-shaped $\text{Os}(\text{CO})_3$ vertices. Specific calculations were performed for several tetranuclear configurations that bear a close relationship to those studied here. The authors showed that the isoelectronic C_{2v} $[\text{Os}(\text{CO})_4]^{2+}$ and T-shaped $\text{Os}(\text{CO})_3$ fragments are also isolobal, i.e., they have frontier orbitals of similar, but not identical, energy and shape. The $\text{Os}(\text{CO})_4$ fragment is similar to the $[\text{Os}(\text{CO})_4]^{2+}$ fragment but has two more electrons. The frontier orbitals a_1 and b_2 , hybrid s-z and hybrid xy respectively, are illustrated in Figure B.1.3., which

shows that the order of the orbitals differs for the two fragments. The nature of the frontier orbitals also differs in that the b_2 orbital in $\text{Os}(\text{CO})_3$ is calculated to be 17% metal in character while in $\text{Os}(\text{CO})_4$ it is 53%. This led the authors to predict that T-shaped $\text{Os}(\text{CO})_3$ fragments are "likely to be less effective in cluster bonding" and also "distorted from planar geometry in order that the overlap with the a_1 orbital be maximized". On the other hand, the $\text{Os}(\text{CO})_4$ fragments were calculated to have the correct symmetry and bonding characteristics to form planar systems. As an illustration, the authors performed calculations on the hypothetical planar cluster, $[\text{Os}_4(\text{CO})_{16}]^{2+}$ while the planar structures, $\text{HOs}_3\text{Re}(\text{CO})_{15}$ and $[\text{Re}_4(\text{CO})_{16}]^{2-}$ were cited as known examples. Taken together these two concepts mean that 62 electron clusters with $\text{M}(\text{CO})_3$ groups at the hinges are more likely to be butterflies while those with $\text{M}(\text{CO})_4$ groups may be planar. It should also be noted that a cluster containing an excess of electrons for a close polyhedron and having an $\text{M}(\text{CO})_4$ vertex is more likely to adopt an edge-bridged rather than a nido or arachno structure, as in $\text{H}_2\text{Os}_5(\text{CO})_{16}$, cited above.

The authors considered polyhedra wherein the electron count for a close structure was not exceeded and were led to several conclusions. First, $\text{Os}(\text{CO})_4$ fragments are likely to maintain their C_{2v} symmetry since deformation to C_{4v} is calculated to require 2.6eV. Second, the a_1 orbital of the $\text{M}(\text{CO})_4$ is only 28% localized on the metal meaning it is largely $\text{CO } \pi^*$ in character.

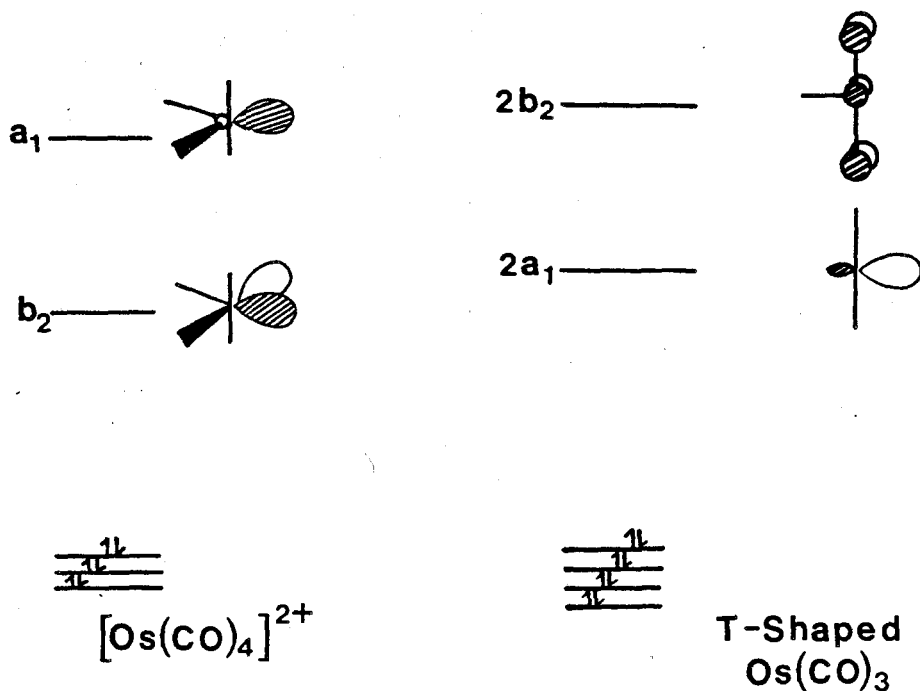


Figure B.1.3. Frontier Orbitals for $[M(CO)_4]^{2+}$ and $M(CO)_3$.

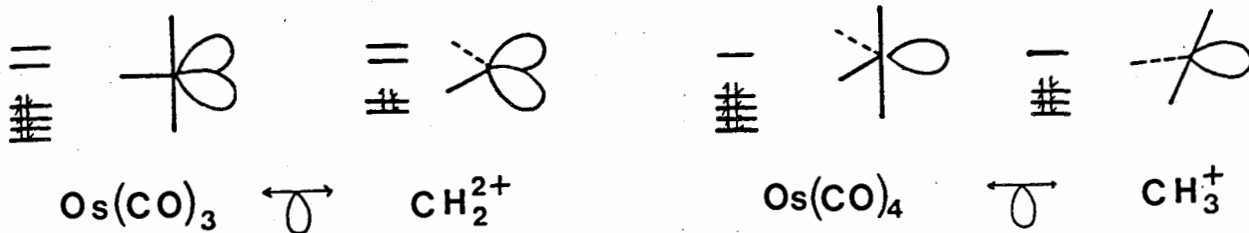
(After Evans and Mingos.¹²²)

In order to make up for a deficiency of electron density, the carbonyl ligands were predicted to take part in semi-bridging interactions with other metal atoms. Specific overlap population calculations for a tetrahedral cluster with one $Os(CO)_4$ group gave 0.23 and 0.25 for $M'-C$ overlap, depending on the conformer. Finally the authors predicted that even with additional metal-metal bonding arising from weak interaction of the cluster with the $M(CO)_4$ b_1 orbital, an $M(CO)_4$ fragment will be less effective in a nonplanar cluster environment than a conical $M(CO)_3$ fragment. That being the case, bonds involving $Os(CO)_4$ fragments are expected to be longer than those involving only conical $Os(CO)_3$ fragments. The authors go so far as to

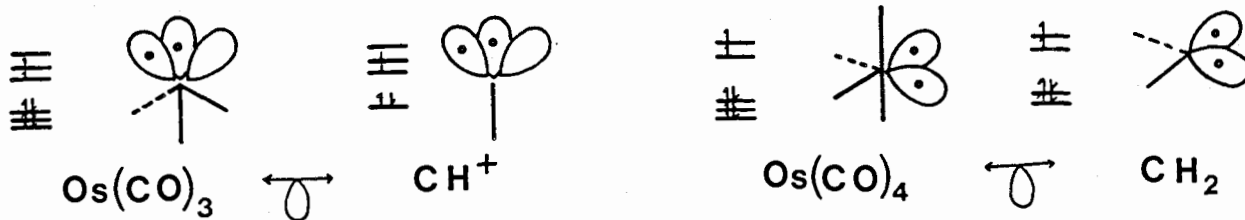
predict that closed polyhedra with more than one $M(\text{CO})_4$ vertex are "unlikely to be stable."

Although PSEPT is widely used to rationalize the structures of many medium-sized clusters, other approaches have also been employed. Hoffmann used EHMO calculations to develop an isolobal analogy between transition metal and organic fragments.¹²⁴ According to this analogy the number of electrons and orbitals a transition metal fragment has available depends on the coordination number of the transition metal. An $\text{Os}(\text{CO})_4$ fragment, for example, can be isolobal to several different organic fragments depending on whether the osmium atom is 5, 6 or 7 coordinate, as in Figure B.1.4. This method has limited predictive powers but it does have flexibility and is therefore useful in rationalizing structures after the fact.

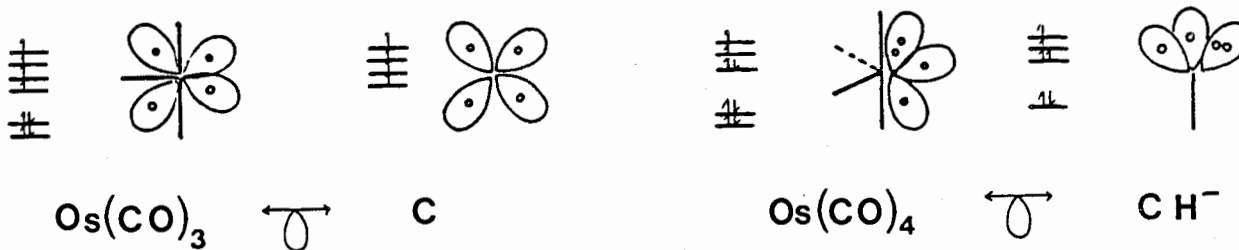
Lauher also used extended Hückel calculations on bare metal clusters to investigate their bonding.¹²⁵ The four metal atoms of a tetranuclear cluster contribute nine orbitals each and generate 36 molecular orbitals. According to Lauher, six of these orbitals are antibonding in molecules of T_d symmetry, thus 30 orbitals are bonding and 60 valence electrons are necessary for a stable structure to be formed. Changing the symmetry to C_{2v} (butterfly geometry) results in one antibonding orbital being lowered in energy so that 62 cluster valence electrons are necessary. Square (D_{4h}) symmetry is shown to require 64 electrons. No calculations were performed for a spiked triangle. While these conclusions are consistent with those of



5 coordinate



6 coordinate



7 coordinate

Figure B.1.4. The Isolobal Analogy as Applied to $\text{Os}(\text{CO})_4$ and $\text{Os}(\text{CO})_3$ Fragments. The ' \leftarrow ' character means 'is isolobal with'. (After Hoffmann,^{1,2,4})

PSEPT and the 18-Electron Rule, it can be seen that this method cannot take into account any possible localized or unequal metal-metal bonds.

In an alternative scheme relating the electron count to structure, Teo emphasized the number of vertices, faces and 'missing' antibonding orbitals a cluster possesses.^{126, 127} The conclusions drawn regarding tetranuclear clusters are similar to those described above i.e., a four vertex, four face cluster (tetrahedron) needs 60 cluster electrons, and reduction of the number of faces (i.e., changing to butterfly or planar geometry) requires additional electrons. Like Lauher, Teo was concerned only with the total number of valence electrons of a cluster and not with the influence the ligands attached to a particular vertex have on localized bonding. Nor did he make any attempt to account for the variation in the structures of 62 or 64 electron species.

As can be seen there are several different approaches to understanding the structure and bonding in tetranuclear clusters, all of which give similar predictions. That is, tetranuclear clusters containing 60 valence electrons should be tetrahedra, while those containing 62 electrons should be butterflies or planar rhomboidal structures. To our knowledge no author has dealt extensively with 64 electron clusters, but it is accepted that only four metal-metal interactions are expected for these species.¹²⁵ That these general predictions are valid can be seen from the examples cited in Tables B.1.1,

B.1.2 and B.1.3. The most notable exceptions are 64 electron clusters which can be not only squares and spiked triangles, but distorted butterflies as well. There are also a few examples in the literature of 60 electron butterflies such as $[\text{Fe}_4(\text{CO})_{12}\text{CCO}_2\text{Me}]^-$ ¹²⁸ and $\text{Os}_4(\text{CO})_{12}(\text{C}_2\text{H}_2)$ ¹²⁹ but they are not relevant to this study.

Table B.1.1. Group 8 Tetrahedral Clusters with 60 Valence Electrons.

Compound	Comments	Ref.
$[\text{Fe}_4(\text{CO})_{13}]^{2-}$	has one μ_3 -CO ligand and three three weakly semi-bridging CO's	103
$\text{H}_2\text{FeRu}_3(\text{CO})_{13}$	three terminal CO's on each Ru, two terminal CO's on Fe, two asymmetric CO bridges on Fe-Ru bonds	130
$[\text{FeRu}_3(\text{CO})_{12}\text{NO}]^-$	NO is terminal on Fe, three CO's are μ_2	131
$\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$	isomeric forms in solution, NMR evidence that metal framework undergoes minor reorganization in solution at temperatures above -45°C	119
$[\text{HFeOs}_3(\text{CO})_{13}]^-$	two CO's bridge Fe and Os bonds, H bridges Os-Os bond	132
$\text{H}_2\text{FeOs}_3(\text{CO})_{13}$	two bridging CO's on Fe-Os bonds	132
$\text{H}_2\text{Ru}_4(\text{CO})_{13}$	H's probably bridge long Ru-Ru bonds	133
$[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$	two isomers in solid state, rapid isomerism of H positions in solution	118, 134
$[\text{H}_2\text{Ru}_4(\text{CO})_{12}]^{2-}$	NMR evidence for CO bridges at $\approx -80^\circ\text{C}$	135
$\text{H}_4\text{Ru}_4(\text{CO})_{12}$	H's probably bridge long Ru-Ru bonds	136
$\text{H}_4\text{Ru}_4(\text{CO})_{10}\text{PPh}_3$	long Ru-Ru bonds bridged by H's	137
$[\text{HOs}_4(\text{CO})_{13}]^-$	has a bridging CO which is rare for Os clusters	138
$[\text{H}_2\text{Os}_4(\text{CO})_{12}\text{I}]^-$	I is terminal	139

$\text{H}_3\text{Os}_4(\text{CO})_{11}\text{NO}$	NO is terminal, long Os-Os bonds and displacement of CO groups indicate position of bridging H's	140
$\text{HOs}_4\text{AuPet}_3(\text{CO})_{13}$	one bridging CO, AuPet ₃ group is μ_2	141
$\text{H}_3\text{Os}_4\text{AuPet}_3(\text{CO})_{13}$	no bridging CO, AuPet ₃ group is μ_2	141
$\text{Os}_4\text{NCH}_3(\text{CO})_{13}$	NCH ₃ caps one face and is 4 e donor	120
$\text{H}_3\text{Os}_4(\text{CO})_{11}\text{C}_6\text{H}_9$	cyclohexene ring σ -bonded to one Os and π -bonded to another	142
$\text{H}_3\text{Os}_4(\text{CO})_{11}\text{CHCHPh}$	H's located by neutron diffraction, one H bridges short Os-Os bond	143
$\text{H}_4\text{Os}_4(\text{CO})_{11}\text{P}(\text{OMe})_3$	the H's bridge long Os-Os bonds	144
$\text{H}_4\text{Os}_4(\text{CO})_{11}\text{NCMe}$	as for $\text{H}_4\text{Os}_4(\text{CO})_{11}\text{P}(\text{OMe})_3$	145
$\text{H}_2\text{Os}_4(\text{CO})_{12}\text{CHCH}_2\text{Ph}$	CHCH ₂ Ph is μ_2 only, 2 e donor	146

Table B.1.2. Group 8 Butterfly Structures.

Compound	Comments	Ref.
$[\text{HFe}_4(\text{CO})_{12}]^-$	one π -CO, H bridges the hinge, $\phi=117^\circ$, converts to tetrahedron with all terminal CO's when warmed.	147,148
$[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$	^{13}C NMR evidence for butterfly structure	149
$[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$	N is μ_4 to Fe's, Fe-N-Fe unit almost linear, $\phi=78.2^\circ$	150
$\text{HFe}_4\text{N}(\text{CO})_{12}$	N is μ_4 to Fe's, Fe-N-Fe unit almost linear, $\phi=101^\circ$	151
$\text{Fe}_4\text{N}(\text{CO})_{11}\text{NO}$	spectroscopic evidence only for butterfly structure	150
$[\text{HFe}_4(\text{CO})_{12}\text{C}]^-$	C is μ_4 , $\phi=104^\circ$	152
$\text{HFe}_4(\text{CO})_{12}(\eta^2\text{-COCH}_3)$	$\eta^2\text{-COCH}_3$ group is 5 e donor	152
$\text{HFe}_4(\eta^2\text{-CH})(\text{CO})_{12}$	in $\eta^2\text{-CH}$ group the C is μ_4 to all Fe's, the H is μ_2 between C and one Fe, $\phi=110.6^\circ$	153
$\text{Fe}_4\text{AuPET}_3(\text{CO})_{12}\text{COCH}_3$	as for $\text{HFe}_4(\text{CO})_{12}(\eta^2\text{-COCH}_3)$	154
$[\text{Fe}_4(\text{CO})_{13}\text{A}]^-$ A=AuEt ₃ , AuPh ₃ , HgCH ₃	two isomers as for $[\text{HFe}_4(\text{CO})_{13}]^-$, in tetrahedral form A is μ_3 on a face	154,155
$\text{Ru}_4(\text{CO})_{13}\text{PPh}$	$\mu_3\text{PPh}$ group bridges both wing tips and one hinge Ru $\phi=111.24^\circ$	156
$[\text{Ru}_4(\text{CO})_{13}\text{Cl}]^-$	Cl bridges wing tips, $\phi=91.0^\circ$	157
$\text{H}_3\text{Ru}_4\text{N}(\text{CO})_{11}$	one H bridges hinge, other two H's bridge hinge-wing tips, N is μ_4 to Ru's, $\phi=108.6(108.2)^\circ$ ^b	158
$\text{HRu}_4\text{N}(\text{CO})_{12-x}$ $[\text{P}(\text{OMe})_3]_x$ x=1,2,3	N is μ_4 to Ru's, ϕ not given ^a	159

$\text{Os}_4(\text{CO})_{13}\text{S}$	S is μ_3 to one closed triangular face, i.e., no bridge across wing tips or hinge, nearly flat, $\phi=170.0(176.5)^\circ$ ^b	160
$[\text{Os}_4(\text{CO})_{12}\text{N}]^-$	isostructural with $[\text{Fe}_4(\text{CO})_{12}\text{N}]^-$ $\phi=105.4^\circ$	158
$\text{H}_3\text{Os}_4(\text{CO})_{12}\text{I}$	I bridges the wing tips, H's located by neutron diffraction, ϕ not given ^a	117
$\text{H}_3\text{Os}_4(\text{CO})_{12}\text{NO}$	NO bridges the wing tips, ϕ not given ^a	159
$[\text{H}_3\text{Os}_4(\text{CO})_{12}(\text{NCMe})_2]^+$	one H bridges the hinge, no bridge across the wing tips, $\phi=112.2(1)^\circ$	104
$\text{H}_3\text{Os}_4(\text{CO})_{12}\text{OH}$	OH is 3 e donor, OH bridges the wing tips, $\phi=92.5^\circ$	161
$\text{H}_3\text{Os}_4(\text{CO})_{12}\text{OPO}_3\text{H}$	wing tips bridged by OPO_3H , $\phi=92.5(92.2)^\circ$ ^b	161
$[\text{H}_4\text{Os}_4(\text{CO})_{12}\text{OH}]^+$	hinge not bridged, OH bridges wing tips, $\phi=82.3^\circ$	161

^aWhere the dihedral angle, ϕ , is noted as 'not given' the crystal structure diagram clearly indicated a butterfly structure.

^bTwo molecules in the asymmetric unit.

Table B.1.3. Tetranuclear Group 8 Clusters with 64 Valence Electrons.

Compound	Comment	Ref.
$\text{Fe}_4(\text{CO})_{11}(\text{NEt})(\text{ONeEt})$	square, NEt is μ_4 , ONeEt is μ_4	162
$\text{Fe}_4(\text{CO})_{12}(\text{PR})_2$	square, PR ligands are μ_4 , first two easily lose CO	106
$\text{Fe}_4(\text{CO})_{11}\text{P}(\text{OMe})_3(\text{PR})_2$		
$\text{Fe}_4(\text{CO})_{10}(\text{P}(\text{OMe})_3)_2(\text{PR})_2$		
$\text{FeRu}_3(\text{CO})_{13}(\text{PPh}_2)_2$	distorted planar rhomboid, all Ru-Ru bonds elongated, peripheral Ru-Ru bonds bridged by PPh_2 ligands	163
$\text{Ru}_4(\text{CO})_{13}(\text{C}\equiv\text{C}^t\text{Bu})(\text{PPh})_2$	nearly planar rhomboid, $\phi=176.93^\circ$	164
$\text{Ru}_4(\text{CO})_8(\text{PPh}_2)_2(\text{C}\equiv\text{C}^t\text{Bu})_2$ ($\text{PPh}_2\text{C}\equiv\text{C}^t\text{Bu}$)	butterfly, $\phi=167.04^\circ$	164
$\text{Ru}_4(\text{CO})_{10}(\text{PPh}_2)(\text{C}=\text{CHPr}^i)$ (OH)	butterfly, $\phi=141.49^\circ$	164
$\text{Ru}_4(\text{CO})_{10}(\text{OEt})(\text{PPh}_2)$ ($\text{C}=\text{CHPr}^i$)	butterfly, $\phi=143.69^\circ$	165
$\text{H}_2\text{Os}_4(\text{CO})_{15}, \text{H}_3\text{Os}_4\text{Br}(\text{CO})_{13}$	spiked triangles, all Os-Os bonds normal covalent bonds	102
$\text{Os}_4(\text{CO})_{12}(\text{CS})\text{S}$	distorted square or butterfly unit not bonded across the hinge, the S is μ_3 , it caps one face, CS on other side of the framework	166
$\text{Os}_4(\text{CO})_{12}\text{S}_2$	butterfly, S ligands are μ_3 and bridge both wing tips and one hinge atom apiece, two weak metal-metal interactions	110
$\text{Os}_4(\text{CO})_{12}\text{Se}_2$	see comments for $\text{Os}_4(\text{CO})_{12}\text{S}_2$, can be described as nido pentagonal bipyramid	167

1.2 Project Description

The study here described began as an attempt to synthesize a cluster containing an unsupported, donor-acceptor metal-metal bond. In such a bond one metal is considered as donating two electrons to the other metal in order that both metals achieve an 18-electron count. In most organometallic complexes with metal-metal bonds the bond is considered as a normal covalent bond, i.e., each metal contributes one electron to the bond. Bridged donor-acceptor metal-metal bonds had been proposed several times¹⁶⁸ but alternate electron counting schemes could be applied to many of the examples. Several dimeric compounds synthesized in our laboratory had metal-metal bonds that could be unambiguously assigned as donor-acceptor bonds,^{169, 170, 171} but until this study no cluster containing an unsupported donor-acceptor metal-metal bond had been synthesized. It was thought that the synthesis of cluster compounds with one or more such bonds could provide a systematic route to larger clusters. Rational routes to high nuclearity clusters are known¹⁷² but these are rare; for example, many large osmium clusters are still obtained, in poor yields, by pyrolysis of $\text{Os}_3(\text{CO})_{12}$ or its derivatives.^{99, 173, 174} The mechanisms of these building up reactions are still not well understood.

Until the present work, there was no reported fully characterized example of a 64 electron cluster displaying sequential ligand loss to give a 62 and then a 60 electron

species.^{102, 175} Here we report just such a series of compounds in the synthesis and characterization of the three clusters $\text{Os}_4(\text{CO})_n\text{PMe}_3$ ($n=15, 14, 13$). The 62 electron butterfly structure $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$ has also been synthesized and characterized. All four clusters have gross frameworks in accord with the theories outlined in the previous discussion. However, each has unique and interesting aspects not predicted by theory. The fluxional properties of these molecules were also investigated by variable temperature ^{13}C NMR spectroscopy. For two of the compounds novel exchange mechanisms are proposed. We believe the mechanism put forward for $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$ has not been previously proposed.

CHAPTER 2

RESULTS AND DISCUSSION

The reaction of $\text{Os}_3(\text{CO})_{11}\text{MeCN}$ with $\text{Os}(\text{CO})_4\text{PMe}_3$ proceeded at a convenient rate in hexane at 60 °C to produce $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$, a brilliant orange compound. Subsequent structural studies revealed it to be a spiked triangle in which $\text{Os}(\text{CO})_4\text{PMe}_3$, an 18 electron moiety acts as a two electron donor to the $\text{Os}_3(\text{CO})_{11}$ species.¹⁷⁶

This initial success led to a similar attempt with $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and $\text{Os}(\text{CO})_4\text{PMe}_3$. The unsaturated cluster $\text{H}_2\text{Os}_3(\text{CO})_{10}$ was known to be very reactive and many ligand addition reactions with it had been reported.¹⁷⁷ Surprisingly, the product of this reaction was not $\text{H}_2\text{Os}_4(\text{CO})_{14}\text{PMe}_3$ but rather $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$ as before. Indeed, the reaction in hexane was complete at room temperature in one hour. A 57% yield could be obtained if excess $\text{Os}(\text{CO})_4\text{PMe}_3$ was present.

A further attempt to obtain a new cluster with a donor-acceptor bond was made by adding Me_3NO to $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$ in CH_2Cl_2 in the presence of $\text{Os}(\text{CO})_4\text{PMe}_3$. It was hoped that substitution of a CO ligand by an $\text{Os}(\text{CO})_4\text{PMe}_3$ would occur producing a doubly spiked triangle, $\text{Os}_5(\text{CO})_{18}(\text{PMe}_3)_2$. Instead, simple CO ligand loss occurred and the product was $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$. This compound has the interesting property that it appears deep red in CH_2Cl_2 solution and distinctly green in hexane. Novel features were displayed in the variable

temperature ^{13}C NMR spectra of this compound so the structure was determined by X-ray analysis.

Results of mass spectra of both these compounds showed the most abundant peak in the highest mass envelope to be at 1202 m^+/e , i.e., $[\text{P-2CO}]^+$ and $[\text{P-CO}]^+$ respectively suggesting the compound $\text{Os}_4(\text{CO})_{13}\text{PMe}_3$ might be synthetically accessible. Indeed, this deep burgundy compound was obtained in 34% yield when a hexane solution of $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$ was heated at 90 °C for 24 h.

During the investigation of the reaction of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and $\text{Os}(\text{CO})_4\text{PMe}_3$, it was noted that addition of Me_3NO to the reaction mixture produced several products. Isolation of bright red $\text{H}_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$ was possible using chromatographic techniques. Although this complex is isoelectronic with $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$, its structure and fluxional properties are quite different.

These differences along with other aspects of the chemistry of these four tetranuclear osmium clusters are the basis of this discussion.

2.1 Os₄(CO)₁₅PMe₃

2.1.1 *Structure and Bonding*

The structure of Os₄(CO)₁₅PMe₃ (1) as determined by X-ray crystallography shows there are two molecules in the asymmetric unit but the differences between them are not chemically significant (see Figure B.2.1 and Table B.2.1). The metal atom framework of 1 is best described as a 'spiked triangle' in which the 18 electron moiety Os(CO)₄PMe₃ donates two electrons to the Os₃(CO)₁₁ fragment. There are no unusual bond lengths or angles; all carbonyl ligands are terminal and the the closest non-bonded Os-C contact is Os(12)··C(113) at 3.32(3)Å. This is consistent with the IR solution spectrum in CH₂Cl₂ which exhibits only terminal carbonyl stretches (see Table B.3.2 page 146). According to the 18-Electron Rule each osmium atom has its required complement of 18 electrons.

Similar spiked triangle structures have been observed for (μ-H)Os₃Re(CO)₁₅NCMe¹⁷⁵ and (μ-H)HOs₄(CO)₁₅¹⁰², but this is the first example containing a dative, or donor-acceptor, metal-metal bond. The dative metal-metal bond in 1 has no supporting metal-metal bonds nor is there evidence of even weak interaction between the Os(11) (or Os(21)) carbonyl ligands and Os(12) (or Os(22)).

While this type of unsupported dative bond is previously unknown for cluster compounds it has been reported for a number of dimeric complexes synthesized in this laboratory.^{169, 170, 171}

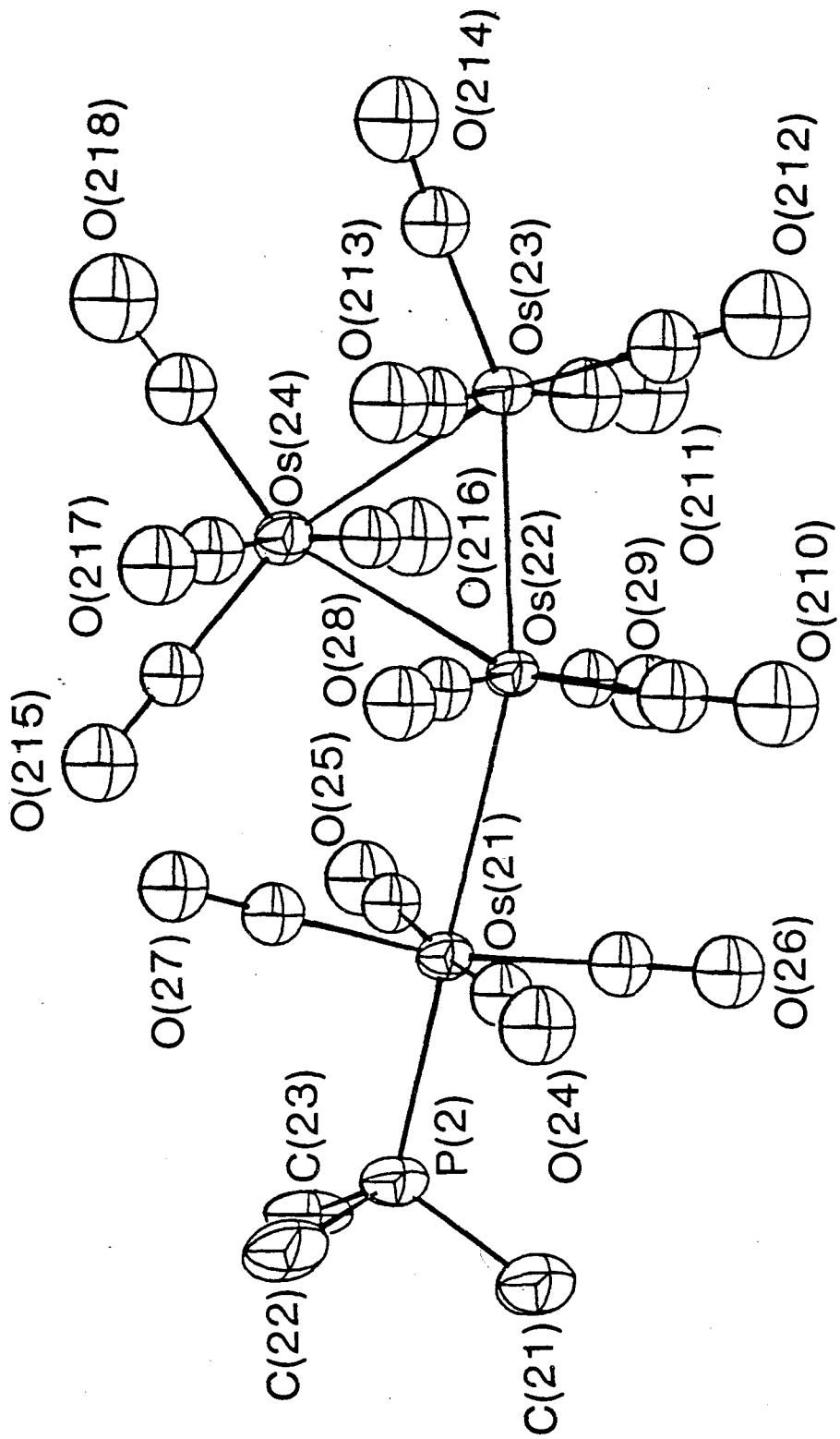


Figure B.2.1. Thermal Ellipsoid Diagram for $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$.

Table B.2.1. Selected Molecular Dimensions for Os₄(CO)₁₅PMe₃**a) Bond Lengths--Molecule 1.**

Atoms	Bond Length (Å)	Atoms	Bond Length (Å)
Os(11)-Os(12)	2.939(1)	Os(14)-C(118)	1.91(2)
Os(11)-P(1)	2.354(5)	P(1)-C(11)	1.83(2)
Os(11)-C(14)	1.92(2)	P(1)-C(12)	1.79(2)
Os(11)-C(15)	1.92(2)	P(1)-C(13)	1.83(2)
Os(11)-C(16)	1.92(2)	C(14)-O(14)	1.15(2)
Os(11)-C(17)	1.91(2)	C(15)-O(15)	1.16(2)
Os(12)-Os(13)	2.849(1)	C(16)-O(16)	1.15(2)
Os(12)-Os(14)	2.923(1)	C(17)-O(17)	1.15(2)
Os(12)-C(18)	1.91(2)	C(18)-O(18)	1.16(2)
Os(12)-C(19)	1.89(2)	C(19)-O(19)	1.17(2)
Os(12)-C(110)	1.81(2)	C(110)-O(110)	1.18(2)
Os(13)-Os(14)	2.894(1)	C(111)-O(111)	1.13(2)
Os(13)-C(111)	1.93(2)	C(112)-O(112)	1.17(3)
Os(13)-C(112)	1.85(2)	C(113)-O(113)	1.15(2)
Os(13)-C(113)	1.92(2)	C(114)-O(114)	1.19(3)
Os(13)-C(114)	1.84(2)	C(115)-O(115)	1.14(2)
Os(14)-C(115)	1.89(2)	C(116)-O(116)	1.16(3)
Os(14)-C(116)	1.87(2)	C(117)-O(117)	1.15(3)
Os(14)-C(117)	1.88(2)	C(118)-O(118)	1.16(2)

b) Bond Angles--Molecule 1.

Bonds	Angle (°)	Bonds	Angle (°)
Os(11)-Os(12)-Os(13)	165.32(3)	Os(14)-Os(12)-C(110)	157.3(6)
Os(13)-Os(12)-Os(14)	60.17(3)	C(18)-Os(12)-C(19)	173.1(8)
Os(12)-Os(13)-Os(14)	61.19(3)	Os(14)-Os(13)-C(112)	157.4(7)
Os(12)-Os(14)-Os(13)	58.64(3)	Os(14)-Os(13)-C(114)	99.7(7)
Os(12)-Os(11)-P(1)	174.0(1)	C(111)-Os(13)-C(113)	175.6(9)
Os(12)-Os(11)-C(14)	88.3(6)	Os(13)-Os(14)-C(115)	162.5(6)
Os(12)-Os(11)-C(15)	84.1(6)	Os(12)-Os(14)-C(118)	89.2(6)
Os(12)-Os(11)-C(16)	88.0(5)	C(116)-Os(14)-C(117)	91.8(9)
Os(12)-Os(11)-C(17)	84.9(5)	Os(11)-P(1)-C(11)	113.4(7)
C(14)-Os(11)-C(15)	171.3(8)	Os(11)-P(1)-C(12)	114.3(7)
C(16)-Os(11)-C(17)	172.8(8)	Os(11)-P(1)-C(13)	114.9(7)

c) Bond Lengths--Molecule 2.

Atoms	Bond Length (Å)	Atoms	Bond Length (Å)
Os(21)-Os(22)	2.937(1)	Os(24)-C(218)	1.88(2)
Os(21)-P(2)	2.355(5)	P(2)-C(21)	1.81(2)
Os(21)-C(24)	1.94(2)	P(2)-C(22)	1.79(2)
Os(21)-C(25)	1.93(2)	P(2)-C(23)	1.82(2)
Os(21)-C(26)	1.93(2)	C(24)-O(24)	1.13(2)
Os(21)-C(27)	1.94(2)	C(25)-O(25)	1.14(2)
Os(22)-Os(23)	2.855(1)	C(26)-O(26)	1.16(2)
Os(22)-Os(24)	2.930(1)	C(27)-O(27)	1.13(2)
Os(22)-C(28)	1.93(2)	C(28)-O(28)	1.13(2)
Os(22)-C(29)	1.90(2)	C(29)-O(29)	1.17(2)

Os(22)-C(210)	1.83(2)	C(210)-O(210)	1.17(2)
Os(23)-Os(24)	2.894(1)	C(211)-O(211)	1.16(2)
Os(23)-C(211)	1.91(2)	C(212)-O(212)	1.18(2)
Os(23)-C(212)	1.84(2)	C(213)-O(213)	1.15(2)
Os(23)-C(213)	1.92(2)	C(214)-O(214)	1.14(2)
Os(23)-C(214)	1.90(2)	C(215)-O(215)	1.18(2)
Os(24)-C(215)	1.85(2)	C(216)-O(216)	1.17(2)
Os(24)-C(216)	1.92(2)	C(217)-O(217)	1.14(2)
Os(24)-C(217)	1.91(2)	C(218)-O(218)	1.17(2)

d) Bond Angles--Molecule 2.

Bonds	Angle (°)	Bond	Angle (°)
Os(21)-Os(22)-Os(23)	163.05(3)	Os(24)-Os(22)-C(210)	159.3(6)
Os(23)-Os(22)-Os(24)	60.02(2)	C(28)-Os(22)-C(29)	173.8(7)
Os(22)-Os(23)-Os(24)	61.28(3)	Os(24)-Os(23)-C(212)	163.2(6)
Os(22)-Os(24)-Os(23)	58.70(2)	Os(22)-Os(23)-C(214)	156.9(6)
Os(22)-Os(21)-P(2)	177.3(1)	C(211)-Os(23)-C(213)	173.9(8)
Os(22)-Os(21)-C(24)	90.6(5)	Os(23)-Os(24)-C(215)	162.8(6)
Os(22)-Os(21)-C(25)	84.5(5)	Os(22)-Os(24)-C(218)	154.6(6)
Os(22)-Os(21)-C(26)	82.21(6)	C(216)-Os(24)-C(217)	174.5(8)
Os(22)-Os(21)-C(27)	87.0(5)	Os(21)-P(2)-C(21)	113.6(7)
C(24)-Os(21)-C(25)	175.1(7)	Os(21)-P(2)-C(22)	113.4(7)
C(26)-Os(21)-C(27)	169.2(7)	Os(21)-P(2)-C(23)	114.4(6)

Investigation of the structure, reactivity, and fluxional properties of these compounds has established the following:

1) Dative metal-metal bonds are slightly longer than normal covalent bonds between the same metals.

2) The $\text{Os}(\text{CO})_4\text{PMe}_3$ complex is a weak donor ligand, comparable in strength to CO.

3) These complexes are either sparingly soluble or insoluble in hexane but all dissolve readily in CH_2Cl_2 . This is probably a consequence of the polar nature of the donor-acceptor bond.

4) Compounds with donor-acceptor bonds are fluxional; they exhibit intramolecular carbonyl exchange. A mechanism consistent with the variable temperature ^{13}C NMR spectra is bridge-terminal carbonyl exchange across the dative bond.

Complex 1 exhibits all the above characteristics. From Figure B.2.2 which shows the Os-Os bond lengths in Å within each of the two independent molecules it can be seen that the

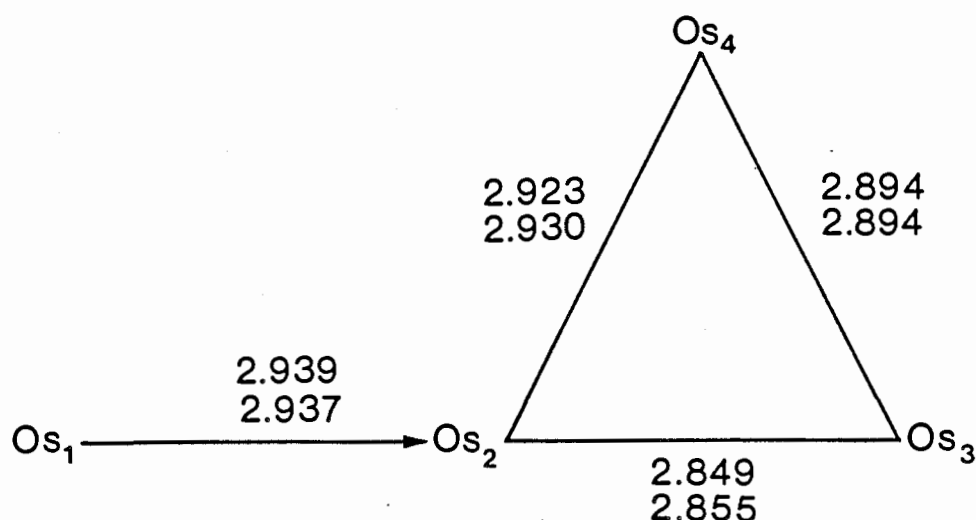


Figure B.2.2. Os-Os Bond Lengths in $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$. There are two independent molecules in the asymmetric unit.

donor-acceptor bond in each molecule is $\approx 0.06\text{\AA}$ longer than the average Os-Os bond length of 2.877\AA in $\text{Os}_3(\text{CO})_{12}$.¹⁷⁸ (The standard deviation in each length is 0.001\AA). While unbridged Os-Os bond lengths in osmium clusters vary, they rarely exceed 2.91\AA , especially when the osmium atoms are six-coordinate.¹⁷⁹

The Os(12)-Os(13) (or Os(22)-Os(23)) bond which is trans to the dative metal-metal bond is short compared to those in $\text{Os}_3(\text{CO})_{12}$, indicating $\text{Os}(\text{CO})_4\text{PMe}_3$ is a weak donor ligand.¹⁸⁰ It is known that strong σ -donors lengthen the M-L bond in the position trans to the donor ligand in monomeric complexes¹⁸¹ and Adams has extended this idea in his proposal that the trans influence of ligands affects the length of metal-metal bonds in osmium clusters.¹⁸⁰ It was observed that the Os-Os bonds trans to PMe_2Ph and CS were $2.856(1)\text{\AA}$ and $2.830(2)\text{\AA}$ in $\text{Os}_3(\mu_3\text{-S})(\text{CO})_8\text{L}$ complexes compared to a length of $2.814(1)\text{\AA}$ when $\text{L}=\text{CO}$. It follows that a comparatively short Os-Os bond indicates the ligand in the trans position is a weak σ -donor.

The Os(13)-Os(14) (or Os(23)-Os(24)) bond is of comparable length to those in $\text{Os}_3(\text{CO})_{12}$, while the bond cis to the dative bond, Os(12)-Os(14) (or Os(22)-Os(24)), is somewhat lengthened. This may be a result of the shortening of the Os(12)-Os(13) (or Os(22)-Os(23)) bond. This type of reciprocal relationship between bond lengths was suggested in regard to $\text{Os}_3(\mu_3\text{-S})_2(\text{CO})_8\text{PMe}_2\text{Ph}$ by Adams and coworkers who speculated that the weakening of one bond is accompanied by a decrease in metal-metal overlap.¹⁸⁰ This in turn permits increased overlap

between one of the atoms involved in the weak bond and a third metal atom. Presumably the reverse is equally reasonable, i.e., strengthening of one bond, with increased orbital overlap could lead to a longer neighbouring bond.

Further evidence that $\text{Os}(\text{CO})_4\text{PMe}_3$ is a weak donor ligand comes from thermal decomposition and ligand substitution studies. When a solution of 1 was stirred overnight at room temperature (25 °C) it decomposed. Both $\text{Os}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{11}\text{PMe}_3$ were identified as decomposition products by IR spectroscopy.¹⁸² (Decomposition of 1 during synthesis was avoided by carrying out the reaction in hexane, in which 1 precipitates.) Reaction of 1 with PPh_3 in solution quickly produced $\text{Os}_3(\text{CO})_{11}\text{PPh}_3$ and $\text{Os}(\text{CO})_4\text{PMe}_3$.

We have described the bonding in 1 as that of a triangular cluster having one unusual ligand, $\text{Os}(\text{CO})_4\text{PMe}_3$. However, 1 may also be considered a tetranuclear cluster with 64 electrons that is predicted to have four metal-metal bonds. Both a spiked triangle and a square fulfill this requirement and both configurations are known. As mentioned in the introduction, there are also a number of 64 electron butterfly structures; these have two or three elongated metal-metal bonds.

Neither the 18-Electron Rule nor PSEPT is useful in predicting the specific geometry of a particular 64 electron compound. An alternative proposal is that the bridging characteristics of the ligands strongly influence the geometry

of the metal atom framework.¹⁰² For example, the square clusters cited in Table B.1.1 and elsewhere^{183,184} all have two face bridging ligands, perhaps this μ_4 bonding is able to overcome diagonal interactions that could produce strain in square complexes. Butterfly clusters which have 64 electrons also have ligands that are edge or face bridging and may consequently prevent the complete rupture of metal-metal bonds. The known spiked triangles have ligands which do not constrain the structure in this way even though some have bridging hydrides or halogens. It therefore seems that the spiked triangle is the preferred, or lowest energy configuration and other geometries are adopted when there are ligands present that prevent the molecule from opening up to the fullest extent possible.

2.1.2 Fluxional Properties of $Os_4(CO)_{15}PMe_3$

The ^{13}C NMR spectrum at $-67^\circ C$ of a ^{13}CO enriched sample of 1 is consistent with the solid state structure. It has five resonances of relative intensity one at $\delta=183.9, 180.1, 173.0, 171.6$ and 171.0 ppm; three resonances of relative intensity two at $\delta=198.4, 187.7$ and 184.0 ppm; and one resonance of relative intensity four at $\delta=181.6$ ppm (see Figure B.2.3). The resonance at $\delta=181.6$ ppm is assigned to the carbonyl groups on the $Os(CO)_4PMe_3$ ligand which rotates about the $Os(11)-Os(12)$ (or $Os(21)-Os(22)$) axis in solution; those of relative intensity one and two are assigned to the equatorial and axial carbonyls respectively of the $Os_3(CO)_{11}$ fragment. When the solution was warmed to $-26^\circ C$ two axial signals and two equatorial signals

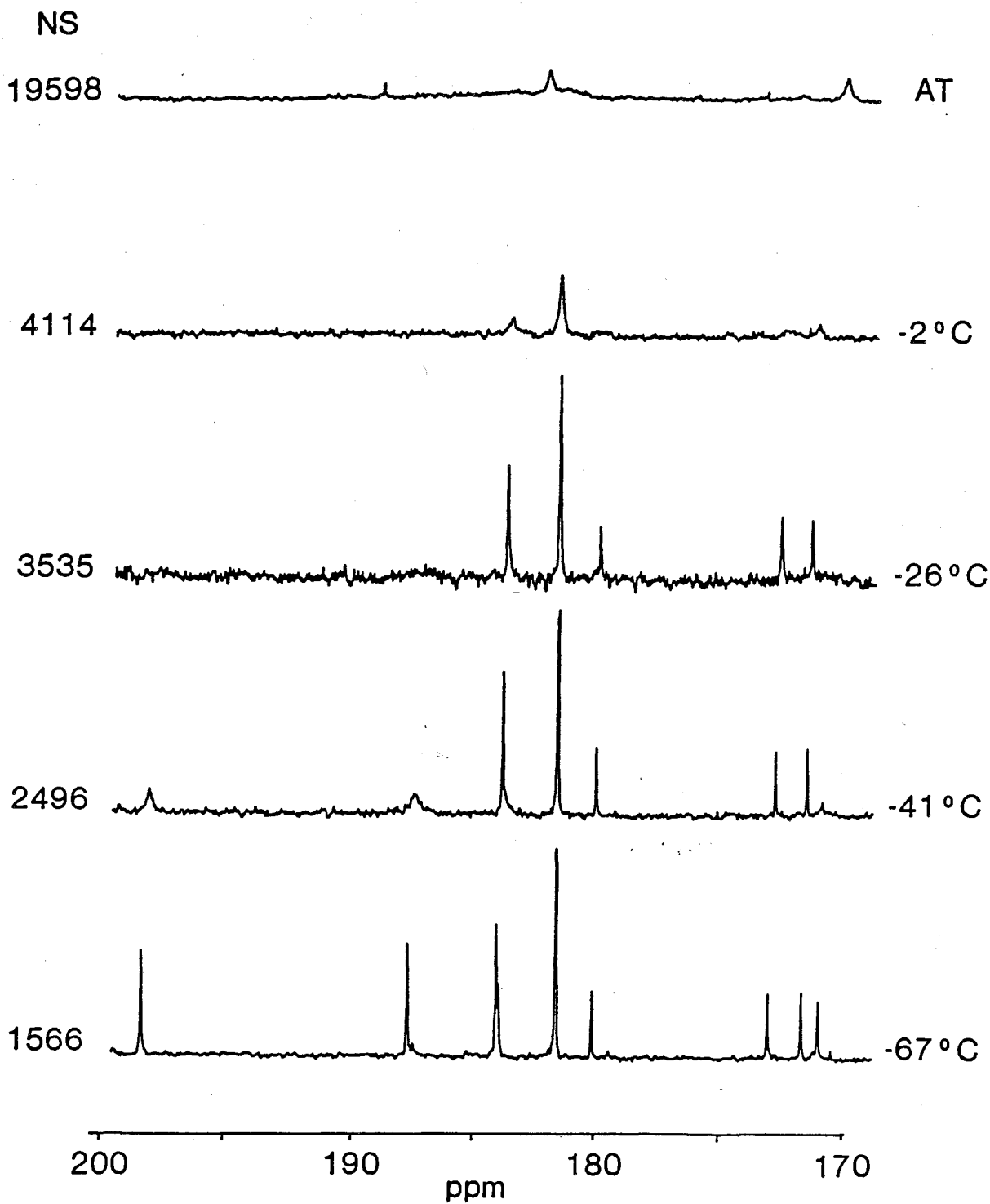
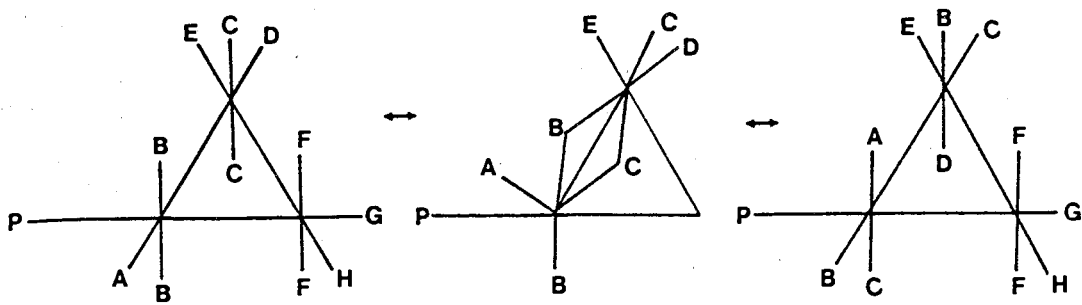


Figure B.2.3. Variable Temperature ^{13}C NMR Spectra of $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$. 'NS' means 'number of scans'.

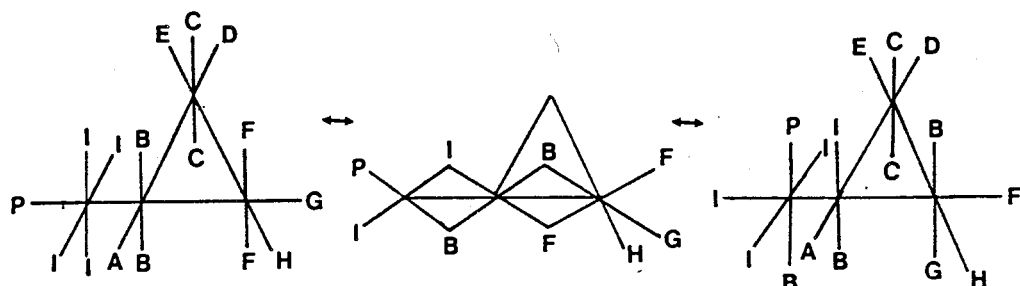
broadened and collapsed into the baseline. Further warming resulted in collapse of the remaining signals. At ambient temperature (20 °C) the only peaks present in the spectrum were the very weak signals due to the decomposition products $\text{Os}(\text{CO})_4\text{PMe}_3$ and $\text{Os}_3(\text{CO})_{12}$. Decomposition was more extensive on further warming and precluded investigation of the ^{13}C NMR spectrum of 1 at a higher temperature. Apart from the decomposition, the collapse process was reversible.

Mechanistic proposals which account for these observations are as follows:

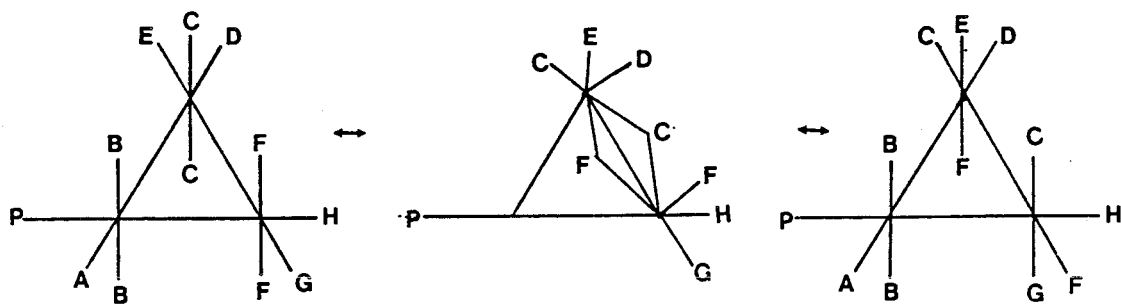
1) At temperatures between -67 °C and -26 °C the process A shown in Figure B.2.4 occurs. In the intermediate, two carbonyls bridge the Os-Os bond cis to the $\text{Os}(\text{CO})_4\text{PMe}_3$ ligand. Bridge-terminal exchange causes collapse of carbonyl signals A, B, C and D. This mechanism has been proposed for $\text{Os}_3(\text{CO})_{11}\text{L}$ ($\text{L}=\text{PEt}_3$,¹⁸⁵ $\text{P}(\text{OMe}_3)$ ¹⁸⁶). It appears that the extra electron density on the osmium atom donated from L, or left there because of weak back-bonding, facilitates carbonyl exchange with the osmium atom cis to the $\text{L}\rightarrow\text{Os}$ bond. Ligand exchange along the trans Os-Os bond might also be expected, but would this bring L into an axial position, which appears to an energetically unfavourable process. Investigations in this laboratory of the ^{13}C NMR spectra of $\text{Os}_3(\text{CO})_{11}\text{P}(\text{OMe})_3$ have confirmed that at -10 °C there is only one sharp equatorial carbonyl signal, all others are broadened (see Figure B.2.5).¹⁸⁶ This observation is accounted for if bridge-terminal exchange does not take place



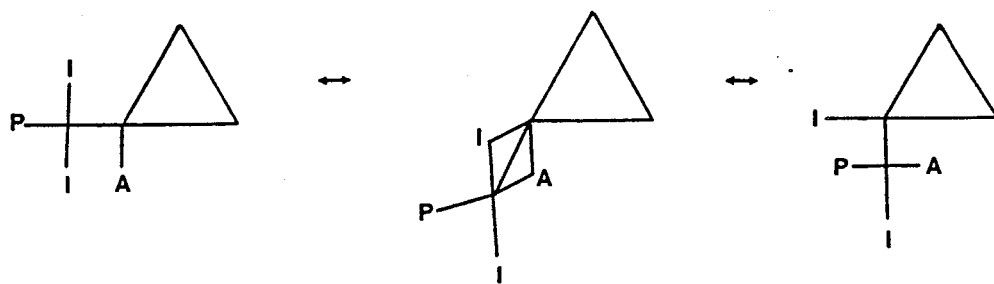
Mechanism A



Mechanism B



Mechanism C



Mechanism D

Figure B.2.4. Fluxional Processes of $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$.

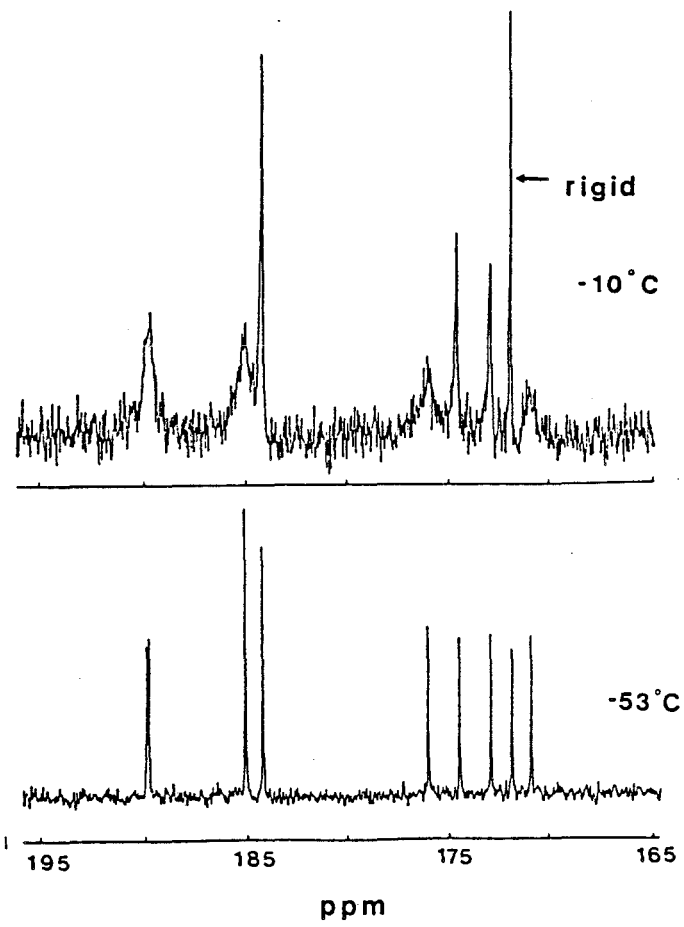
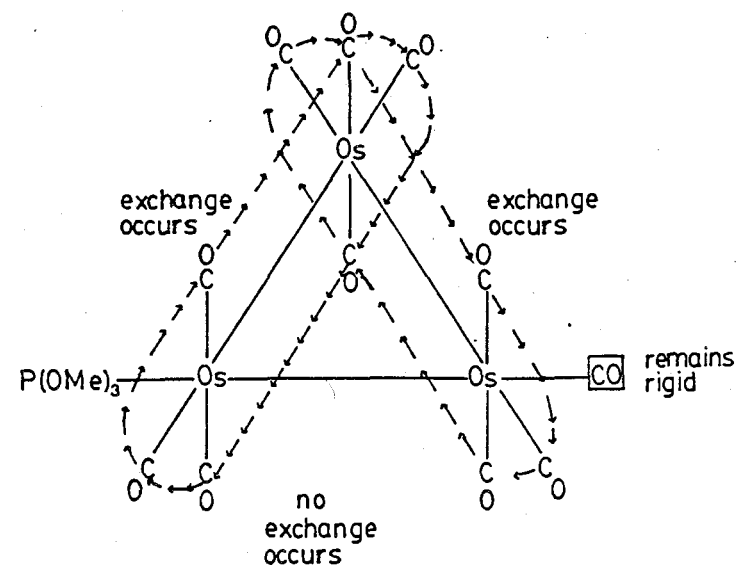


Figure B.2.5. Fluxional Processes and ¹³C NMR Spectrum of Os₃(CO)₁₁P(OMe)₃.

along the Os-Os bond trans to $P(OMe)_3$, but does occur along the other two Os-Os bonds. Such processes always leave the $P(OMe)_3$ ligand in an equatorial position. Therefore the CO ligand in the trans three bond position to $P(OMe)_3$, also does not exchange with, or become equivalent to, any other CO group, and the peak assigned to it does not broaden.

2) At temperatures above $-26\text{ }^\circ\text{C}$, two processes, B and C, illustrated in Figure B.2.4 occur. The first, B, involves simultaneous bridge terminal exchange across the dative Os-Os bond and across the Os-Os bond trans to the dative bond. Such a mechanism accounts for the collapse of signals due to carbonyl ligands B, F, G and I. In order to account for collapse of the other signals mechanism C is proposed. That this exchange occurs more slowly than A is consistent with the observations made for $Os_3(CO)_{11}P(OMe)_3$.

An alternative mechanism which accounts for the spectra observed at $-26\text{ }^\circ\text{C}$ and at $0\text{ }^\circ\text{C}$ is exchange across the dative Os-Os bond involving carbonyls A and I and a change of position of the $Os(CO)_4PMe_3$ group (mechanism D in Figure B.2.4). However, when 1 was prepared from $Os_3(CO)_{11}MeCN$ and ^{13}C enriched $Os(CO)_4PMe_3$, the ^{13}C NMR spectrum revealed that the ^{13}C label was equally distributed over all carbonyl sites within the molecule. This cannot occur unless mechanism C is also operative. Without a high temperature limiting spectrum it is not possible to distinguish between the A,B,C and A,C,D possibilities.

It is interesting to note that both B and D mechanisms give rise to a second isomer of 1 with the PMe_3 ligand in an axial position. There are a number of weak peaks in the ^{13}C NMR spectrum of 1 taken at -67°C , suggesting that such an isomer is present. The ^{13}C NMR spectra of two other compounds which have donor-acceptor metal-metal bonds, $(\text{Me}_3\text{P}_x(\text{CO})_{5-x}\text{OsW}(\text{CO})_5)$ ($x=1,2$), also indicated the presence of two isomers in solution.^{169,187}

2.2 $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$

2.2.1 *Structure and Bonding*

According to the bonding models discussed in the introduction, a 62 electron tetranuclear complex such as $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$ (2) is expected to adopt a butterfly arrangement of metal atoms. Such a geometry accommodates five nearly equal metal-metal bonds and allows variation of the dihedral angle between the metal atom triangles depending upon the number and bonding characteristics of the ligands. The crystal structure of 2 revealed it is not a butterfly. Rather, as can be seen from Figure B.2.6 and Table B.2.2, molecules of 2 are very nearly planar in the solid state; the dihedral angle between the planes $\text{Os}(1)\text{-Os}(2)\text{-Os}(3)$ and $\text{Os}(1)\text{-Os}(3)\text{-Os}(4)$ is $177.10(3)^\circ$. The solution ^{13}C NMR spectrum at low temperature (see Figure B.2.10, page 115) exhibits four signals of relative intensity two which are assigned to the four different pairs of axial carbonyl ligands. The axial carbonyls on any given osmium atom can be equivalent only if the molecule is planar. It is

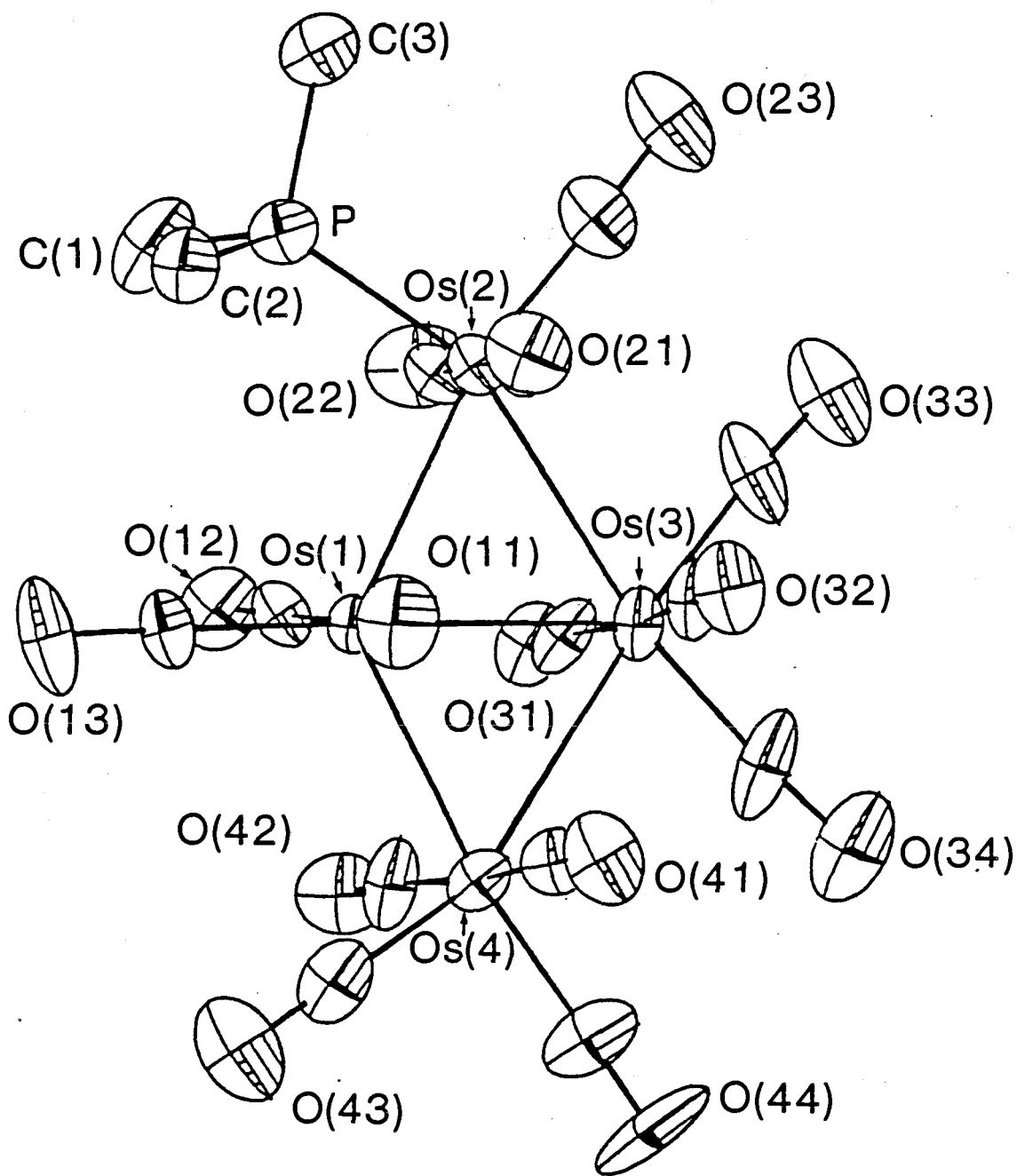


Figure B.2.6. Thermal Ellipsoid Diagram for $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$.

Table B.2.2 Selected Molecular Dimensions for Os₄(CO)₁₄PMe₃.

a) Bond Lengths

Atoms	Bond Length (Å)	Atoms	Bond Length (Å)
Os(1)-Os(2)	2.779(2)	Os(4)-C(44)	1.93(2)
Os(1)-Os(3)	2.935(2)	P(1)-C(1)	1.79(2)
Os(1)-Os(4)	2.784(2)	P(1)-C(2)	1.78(2)
Os(2)-Os(3)	3.013(2)	P(1)-C(3)	1.80(3)
Os(3)-Os(4)	2.982(2)	C(11)-O(11)	1.13(3)
Os(2)-P(1)	2.320(6)	C(12)-O(12)	1.16(3)
Os(1)-C(11)	1.92(2)	C(13)-O(13)	1.16(2)
Os(1)-C(12)	1.88(2)	C(21)-O(21)	1.14(2)
Os(1)-C(13)	1.86(2)	C(22)-O(22)	1.12(3)
Os(2)-C(21)	1.95(2)	C(23)-O(23)	1.16(3)
Os(2)-C(22)	1.92(2)	C(31)-O(31)	1.13(3)
Os(2)-C(23)	1.89(2)	C(32)-O(32)	1.08(3)
Os(3)-C(31)	1.93(2)	C(33)-O(33)	1.14(3)
Os(3)-C(32)	2.02(2)	C(34)-O(34)	1.18(3)
Os(3)-C(33)	1.88(2)	C(41)-O(41)	1.13(3)
Os(3)-C(34)	1.87(2)	C(42)-O(42)	1.14(3)
Os(4)-C(41)	1.97(3)	C(43)-O(43)	1.19(3)
Os(4)-C(42)	1.93(3)	C(44)-O(44)	1.12(3)
Os(4)-C(43)	1.82(3)		

b) Bond Angles

Bonds	Angle (°)	Bonds	Angle (°)
Os(2)-Os(1)-Os(3)	63.57(3)	Os(1)-Os(2)-P(1)	97.7(2)
Os(2)-Os(1)-Os(4)	126.28(5)	Os(1)-Os(2)-C(23)	165.7(7)
Os(3)-Os(1)-Os(4)	62.79(3)	Os(2)-Os(3)-C(33)	74.1(8)
Os(1)-Os(2)-Os(3)	60.74(5)	Os(2)-Os(3)-C(34)	170.9(8)
Os(2)-Os(3)-Os(1)	55.69(3)	Os(3)-Os(4)-C(43)	155.5(7)
Os(2)-Os(3)-Os(4)	111.76(5)	Os(1)-Os(4)-C(44)	168.0(8)
Os(1)-Os(3)-Os(4)	56.12(3)	Os(4)-Os(1)-C(13)	116.0(7)
Os(3)-Os(4)-Os(1)	61.09(4)	Os(2)-Os(1)-C(13)	117.7(7)
C(11)-Os(1)-C(12)	170.0(8)	Os(2)-P(1)-C(1)	114.8(9)
C(21)-Os(2)-C(22)	177.8(8)	Os(2)-P(1)-C(2)	117.0(7)
C(31)-Os(3)-C(32)	172.4(8)	Os(2)-P(1)-C(3)	114.0(8)
C(41)-Os(4)-C(42)	174.2(9)		

concluded that 2 is planar from a chemical point of view and the small deviation of the dihedral angle from 180° arises from solid state effects. This structure exists despite the presence of a T-shaped $\text{Os}(\text{CO})_3$ fragment, in conflict with the prediction of Evans and Mingos discussed earlier.¹²²

We believe the planar geometry is related to the lack of bridging ligands. There is no indication in the crystal structure of any weakly semi-bridging interaction between a carbonyl ligand and a neighbouring non-bonded Os atom. The closest non-bonded Os-C contact is $\text{Os}(2)\cdots\text{C}(33)$ at $3.08(2)\text{\AA}$. Furthermore, the solution infrared spectrum displayed only

terminal carbonyl stretches, see Table B.3.2. Because 2 is isoelectronic with $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$ (3), a butterfly with two bridging ligands, further discussion of this point is postponed until the structure of 3 has been described.

Another interesting aspect of the structure of 2 is its asymmetry. The fifteen terminal ligands are not evenly distributed among the four osmium atoms; one of the hinge atoms, Os(1), has only three carbonyl ligands while each of the other three metal atoms has four ligands apiece. Contrary to the prediction of Evans and Mingos, the peripheral bonds involving the T-shaped $\text{Os}(\text{CO})_3$ fragment are much shorter than the other Os-Os vectors. The Os(1)-Os(2), Os(1)-Os(4) distances are 2.779(2)Å and 2.784(2)Å respectively, while the other two peripheral bonds are very long; i.e., Os(2)-Os(3)=3.013(2)Å and Os(3)-Os(4)=2.982(2)Å. The short diagonal Os(1)-Os(3) vector is of more typical length, 2.935(2)Å. These values can be compared to the average Os-Os distance in $\text{Os}_3(\text{CO})_{12}$ i.e., 2.877(3)Å.¹⁷⁸ Both $\text{Os}_3(\text{CO})_{12}$ and 2 are planar clusters and three of the four vertices in 2, like those in $\text{Os}_3(\text{CO})_{12}$, have four terminal ligands.

In order to account for the long and short bonds in 2 and ensure that each osmium atom obeys the 18-Electron Rule we propose the bonding model illustrated in Figure B.2.7. It has a single bond between the $\text{Os}(\text{CO})_3$ fragment and each of the other three vertices. In addition there are two three-centre-two-electron bonds, each encompassing the wing tips

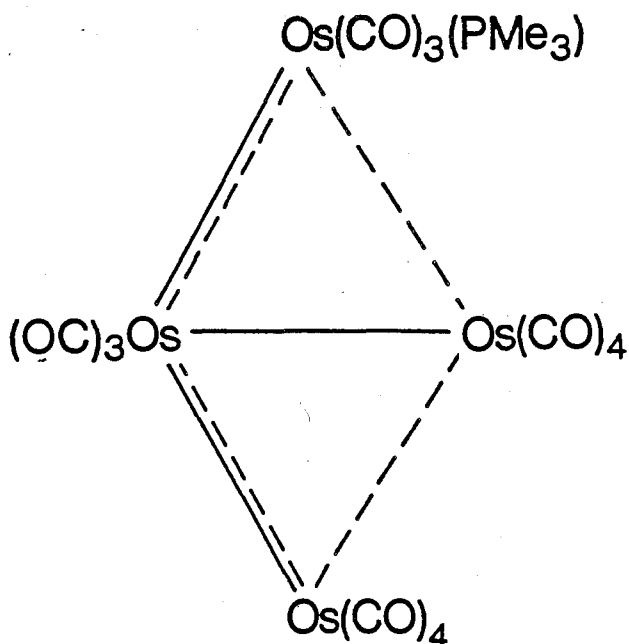


Figure B.2.7. Bonding Model for $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$.

and one hinge vertex. The short Os-Os vectors are thereby assigned a bond order of 1.5 and the long Os-Os vectors an order of 0.5, while the hinge vertices are connected by a normal single bond.

We would be interested to see if detailed molecular orbital calculations would support or refute this proposed bonding model, as simpler approaches have not proven helpful. For example we have attempted to apply PSEPT to 2, but the results are unsatisfactory. If, in accord with the view of Evans and Mingos, the T-shaped $\text{Os}(\text{CO})_3$ fragments donates two orbitals and no electrons to cluster bonding while the C_{2v} OsL_4 fragments donate two orbitals and one electron pair, there are only three bonding interactions. This is shown in the scheme developed for

$[\text{Os}_4(\text{CO})_{16}]^{2+}$; (Figure B.2.8) a hypothetical molecule isoelectronic with 2.¹²² Three bonds hardly seems enough to hold so stable a tetranuclear species together. Also, the $[\text{Os}_4(\text{CO})_{16}]^{2+}$ molecule is not predicted to be asymmetric, no localized bonding is anticipated.

A rather liberal application of the isolobal analogy¹²⁴ with the T-shaped $\text{Os}(\text{CO})_3$ fragment deemed to provide three orbitals and two electrons in a manner similar to a conical $\text{Os}(\text{CO})_3$ fragment (see page 83) does result in a structure with five bonding interactions including a dative covalent bond across the hinge (see Figure B.2.9). The model also satisfies the 18-Electron Rule for all the osmium atoms but all the bonds are normal single bonds. Like PSEPT, this model fails to predict the observed asymmetry in 2.

2.2.2 Fluxional Properties

A ^{13}C enriched sample of 2 in $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$ solution at -115°C exhibited a ^{13}C NMR spectrum in the carbonyl region consistent with the structure found in the solid state, i.e., four resonances of relative intensity two (at $\delta=211.9, 202.0$ ($J_{\text{P-C}}=8.6\text{Hz}$), 192.5 and 171.9 ppm), assigned to the axial carbonyls; and six resonances of relative intensity one (at $\delta=192.2, 176.9, 174.7, 172.7, 171.0$ and 166.4 ppm) assigned to equatorial carbonyls, see Figure B.2.10. The axial signal at $\delta=202.0$ ppm can be assigned to the carbonyls bonded to Os(2) by virtue of the carbon-phosphorus coupling, but no phosphorus

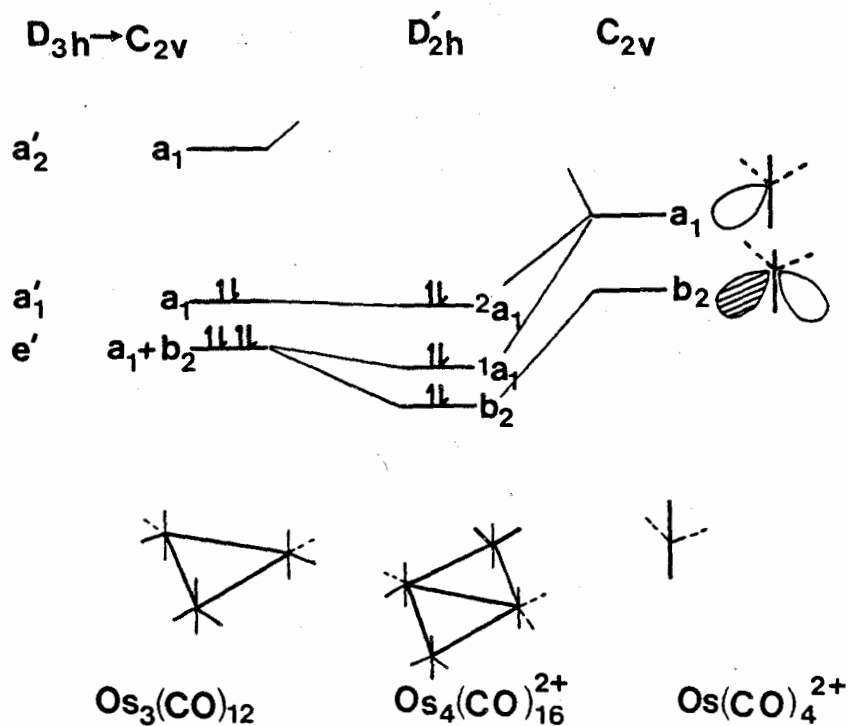


Figure B.2.8. Molecular Orbital Diagram for $[Os_4(CO)_{16}]^{2+}$. (After Evans and Mingos¹²³)

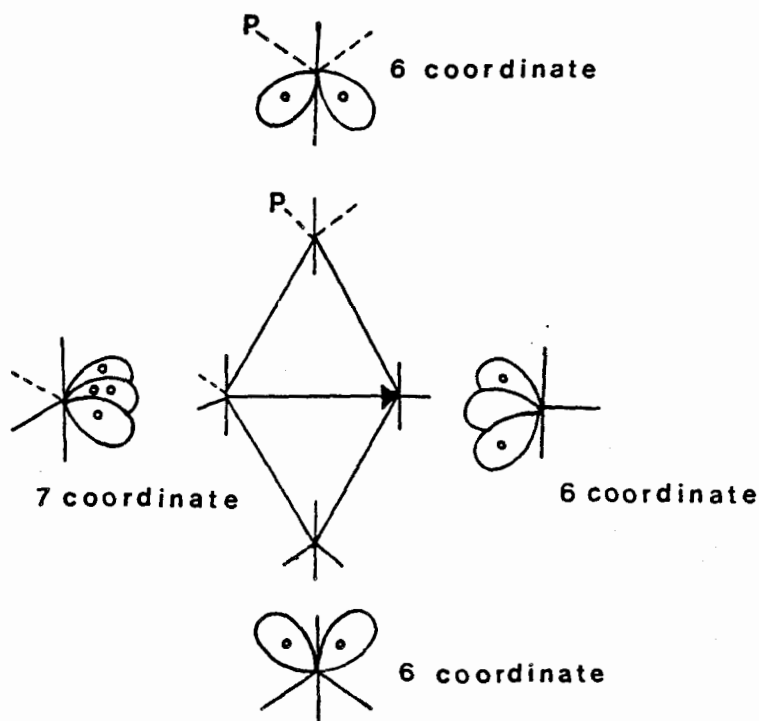


Figure B.2.9. Application of the Isolobal Analogy to $Os_4(CO)_{14}PMe_3$.

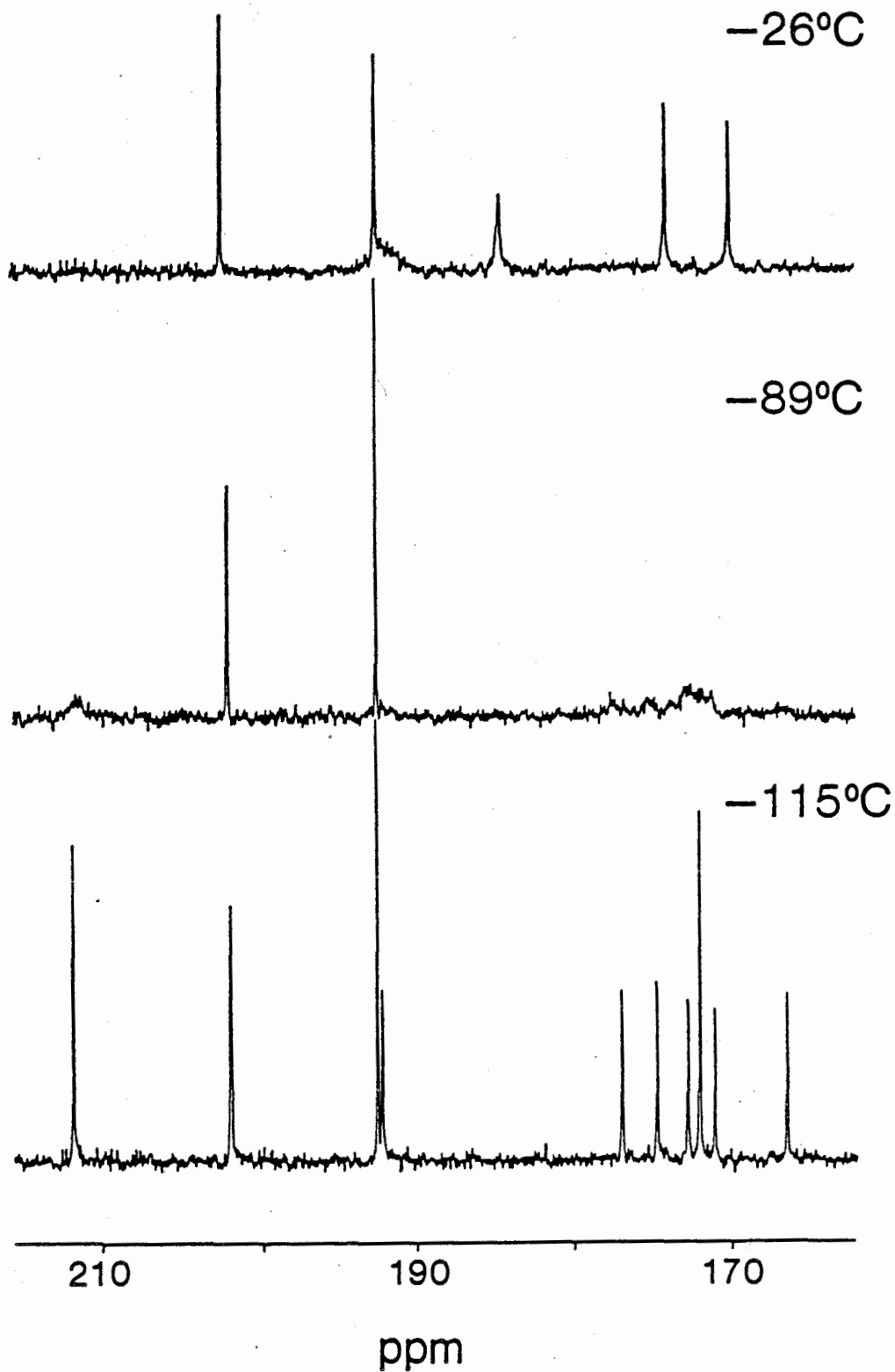


Figure B.2.10. ^{13}C NMR Spectra of $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$.

coupling was observed for any of the equatorial resonances. This lack of equatorial carbon-phosphorus coupling has been noted for other osmium clusters.^{185, 186}

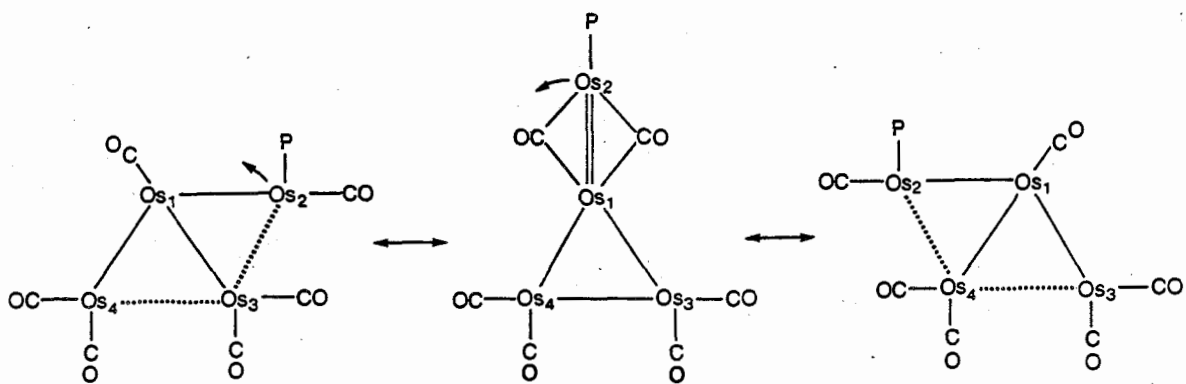
When the solution was warmed to $-87\text{ }^{\circ}\text{C}$, eight of the signals broadened and collapsed into the baseline; the two remaining signals were due to axial carbonyls including those bonded to Os(2). The spectrum obtained with the sample at $-26\text{ }^{\circ}\text{C}$ has three additional peaks at $\delta=183.6$, 173.1 and 169.0 ppm, as well as a broad resonance just upfield of the signal at $\delta=191.6$ ppm.¹⁸⁸ These four signals are at the average value of the chemical shifts of the original signals taken in pairs. The broad signal at approximately $\delta=190$ ppm arises from the coalescence of the two axial peaks, while the other three new peaks come from the pair-wise collapse of the original six equatorial signals.

Various fluxional mechanisms have been proposed for osmium clusters,^{101, 189} but none of these can explain the variable temperature ^{13}C NMR spectra of 2. For example, three-fold twist and bridge-terminal carbonyl exchange mechanisms cause axial and equatorial signals to average. A simple merry-go-round rearrangement (as in step I of Mechanism B, Figure B.2.11) produces a second isomer of 2 with the PMe_3 ligand trans to the $\text{Os}(\text{CO})_3$ fragment rather than to an $\text{Os}(\text{CO})_4$ fragment. There is no evidence for such a second isomer in the spectrum at $-115\text{ }^{\circ}\text{C}$. Furthermore, this mechanism would not cause pair-wise coalescence of the original signals, rather signals would appear

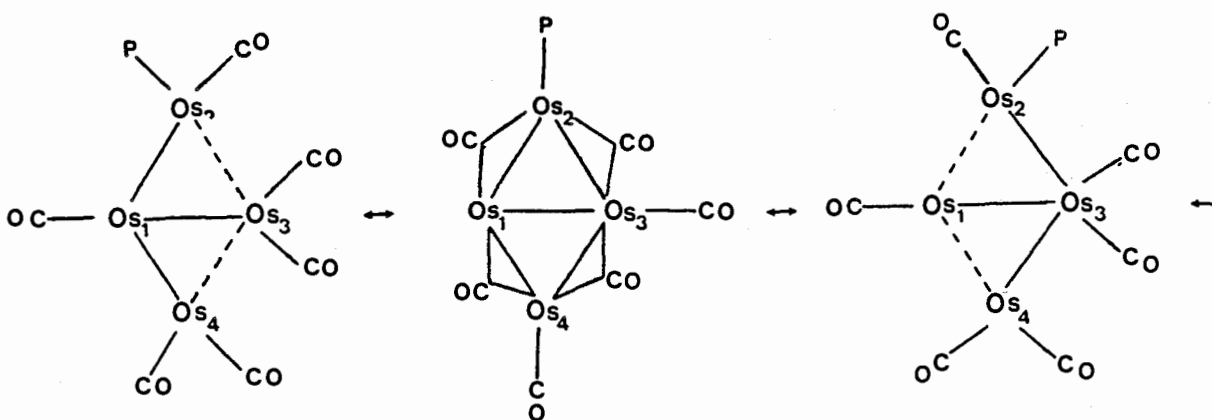
at values averaging those assignable to the individual isomers. Mechanism A, shown in Figure B.2.11, correctly accounts for the observed spectra, it predicts the following exchanges: C(13) with C(23), C(33) with C(43), C(34) with C(44), and C(31),C(32) with C(41), C(42). The axial carbons of Os(1) {C(11), C(12)} and Os(2) {C(21),C(22)} remain unaffected by the process. The double bond between Os(1) and Os(2) in the intermediate is proposed in order to fulfill the requirements of the 18-Electron Rule for both Os atoms. Similar configurations have been reported elsewhere.¹⁹⁰ It is probable that the extreme weakness of the Os(2)-Os(3) bond lowers the activation barrier to non-rigidity and allows exchange to continue at temperatures down to approximately -100 °C. It would be interesting to see what effect substitution of the PMe₃ with weaker σ -donors might have on the exchange rate.

This novel 'windshield wiper' mechanism involves a significant rearrangement of the metal skeleton. Skeletal reorganization has been previously proposed for metal clusters but was either unspecified^{191,192} or included only subtle changes in bond lengths.¹⁹³ A recent study has concluded, however, that Pt-Os bond breaking and making probably occurs in PtOs₃(CO)₉(PMe₂Ph)₂(μ_3 -S)₂.¹⁹⁴ Recently, Johnson has suggested that such mechanisms are more common than previously thought.¹⁹⁵

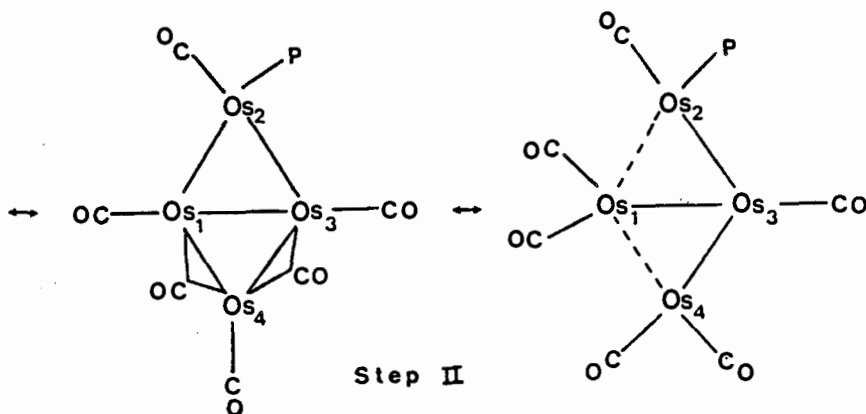
Because the mechanism A is so unusual, an exhaustive search was made for other explanations of the ¹³C NMR spectra, but only one emerged. Mechanism B (Figure B.2.11) shows a two step



Mechanism A



Step I



Step II

Mechanism B

Figure B.2.11. Fluxional Mechanisms for $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$. (Axial carbonyls have been omitted for clarity.)

merry-go-round rearrangement wherein only equatorial carbonyls take part in bridging but the axial carbons C(11), C(12) exchange with C(31), C(32) by virtue of the change in the number of ligands on Os(1) and Os(3). Equatorial carbonyl signal averaging predicted by this mechanism is C(13) with C(23), C(34) with C(44), and C(33) with C(43). This scheme is consistent with the observed spectra but is thought unlikely to be correct for the following reasons:

1)The mechanism has two steps, each of which must occur at the same rate, otherwise signal averaging would occur between the structure found in the solid state and the intermediate II. It is unlikely that step I which involves four bridging carbonyls would occur at the same speed as step II which involves only two.

2)The mechanism involves carbonyls bridging the extremely long Os(2)-Os(3) and Os(3)-Os(4) bonds.

3)The intermediates of both steps do not obey the 18-Electron Rule.

4)If such merry-go-round mechanisms have low activation barriers, one would be expected to operate in $\text{Os}_3(\text{CO})_{11}\text{PEt}_3$, but this is not observed.¹⁸⁵

The ^{13}C spectrum of 2 with the sample at 0 °C showed the peaks at $\delta=201.6, 183.6, 173.1$ and 169.0 ppm had broadened. An attempt was made to investigate the second fluxional process operating at higher temperatures but a spectrum for the fast exchange limit could not be obtained as the sample underwent

some sort of reaction (perhaps with the solvent). A sharp peak at $\delta=189.9$ ppm appeared in the room temperature spectrum which was assigned to the decomposition product $\text{Os}(\text{CO})_4\text{PMe}_3$.

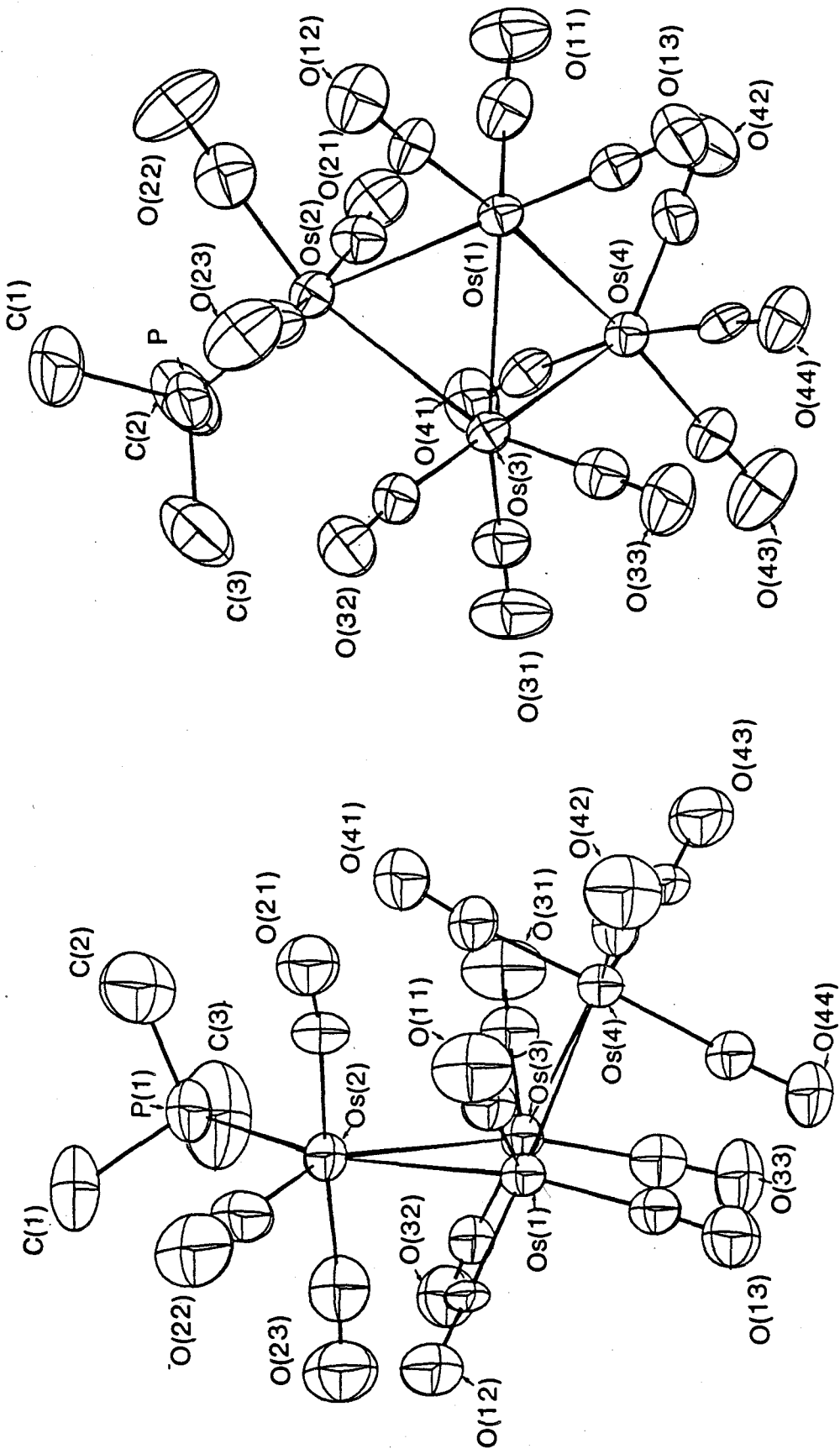
2.3 $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$

2.3.1 *Structure and Bonding*

Like 2, $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$ (3) is a 62 electron species, but the X-ray structure determination revealed it has a butterfly framework with a dihedral angle of $112.74(3)^\circ$ between the Os_3 triangles (Figure B.2.12 and Table B.2.3.) The PMe_3 group is attached to one of the wing-tips, Os(2), and all the carbonyl ligands are terminal. The closest non-bonded Os-C contact is $\text{Os}(2)\cdots\text{O}(12)$ 3.17Å.

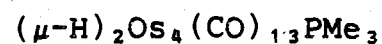
As a consequence of the bend at the hinge the terminal ligands at the wing-tips are forced into close contact. In 3 the affected carbonyl ligands are skewed to alleviate the resulting non-bonded interactions, (Figure B.2.12.) The dihedral angle between the $\text{Os}(2)\text{-Os}(4)\text{-C}(41)$ and $\text{Os}(4)\text{-Os}(2)\text{-C}(21)$ planes is $51.1(9)^\circ$ and the $\text{C}(21)\cdots\text{C}(41)$ distance is 2.87(2)Å. This distance is considered a 'close contact' since the van der Waals radius of carbon, if taken as half the interplanar distance in graphite, is 1.67Å.¹⁹⁶

The hydride ligands in 3 were not located in the X-ray diffraction investigation, however, the ^1H NMR spectrum had two signals in the bridging hydride region, a doublet of doublets at



121a

Figure B.2.12. Thermal Ellipsoid Diagrams for $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$.

Table B.2.3. Selected Molecular Dimensions for**a) Bond Lengths**

Bond	Length (Å)	Bond	Length (Å)
Os(1)-Os(2)	2.868(1)	Os(4)-C(43)	1.90(2)
Os(1)-Os(3)	2.886(1)	Os(4)-C(44)	1.94(2)
Os(1)-Os(4)	2.939(1)	P(1)-C(1)	1.82(2)
Os(2)-Os(3)	3.115(1)	P(1)-C(2)	1.79(3)
Os(3)-Os(4)	2.850(1)	P(1)-C(3)	1.80(3)
Os(2)-P(1)	2.342(4)	C(11)-O(11)	1.17(3)
Os(1)-C(11)	1.86(2)	C(12)-O(12)	1.15(2)
Os(1)-C(12)	1.87(1)	C(13)-O(13)	1.12(2)
Os(1)-C(13)	1.91(2)	C(21)-O(21)	1.14(2)
Os(2)-C(21)	1.94(2)	C(22)-O(22)	1.13(3)
Os(2)-C(22)	1.93(2)	C(23)-O(23)	1.16(2)
Os(2)-C(23)	1.91(2)	C(31)-O(31)	1.15(2)
Os(3)-C(31)	1.89(2)	C(32)-O(32)	1.13(2)
Os(3)-C(32)	1.93(2)	C(33)-O(33)	1.13(3)
Os(3)-C(33)	1.89(2)	C(41)-O(41)	1.15(2)
Os(4)-C(41)	1.92(2)	C(42)-O(42)	1.15(2)
Os(4)-C(42)	1.89(2)	C(43)-O(43)	1.13(2)
		C(44)-O(44)	1.16(2)

b) Bond Angles (°)

Bond	Angle (°)	Bond	Angle (°)
Os(2)-Os(1)-Os(3)	65.56(2)	Os(2)-Os(1)-C(13)	170.1(5)
Os(2)-Os(1)-Os(4)	94.86(3)	Os(1)-Os(2)-C(22)	100.6(5)
Os(3)-Os(1)-Os(4)	58.59(3)	Os(3)-Os(2)-P(1)	106.4(1)
Os(1)-Os(2)-Os(3)	57.48(2)	Os(2)-Os(3)-C(31)	110.1(6)
Os(2)-Os(3)-Os(1)	56.96(2)	Os(2)-Os(3)-C(32)	89.4(5)
Os(2)-Os(3)-Os(4)	91.50(3)	Os(2)-Os(3)-C(33)	158.8(6)
Os(1)-Os(3)-Os(4)	61.64(3)	Os(3)-Os(4)-C(43)	107.8(5)
Os(3)-Os(4)-Os(1)	59.77(2)	Os(1)-Os(4)-C(42)	91.9(5)
C(21)-Os(2)-C(23)	169.1(7)	Os(2)-P(1)-C(1)	113.3(9)
C(41)-Os(4)-C(44)	168.4(7)	Os(2)-P(1)-C(2)	114.6(7)
Os(2)-Os(1)-C(11)	93.7(6)	Os(2)-P(1)-C(3)	116.2(8)
Os(2)-Os(1)-C(12)	81.0(5)		

$\delta = -20.4$ ppm, H_A , ($J_{H-H} = 1.23$ Hz and $J_{P-H} = 10.2$ Hz) and an unresolved doublet at $\delta = -18.3$ ppm, H_B . The small J_{P-H} value is consistent with H_A bridging the Os(2)-Os(3) vector, i.e., cis to the PMe_3 ligand. Trans J_{P-H} values are of the order of 150 Hz.^{197, 198, 199} Consistent with this positioning is the Os(2)-Os(3) distance which is extremely long, 3.115(1) Å. Long Os-Os vectors have been previously associated with Os(μ -H)Os configurations as in $H_2Os_3(CO)_{11}$, which has an H-bridged Os-Os vector of 2.9886(9) Å.¹⁷⁹ Other long Os-Os vectors that are H-bridged have been noted for the butterfly clusters $H_3Os_4(CO)_{12}(NCMe)_2$ in which the bridged Os-Os distances are

3.130(2)Å, 3.145(2)Å and 2.937(2)Å,¹⁰⁴ and $\text{H}_3\text{Os}_4(\text{CO})_{12}\text{I}$ in which the bridged Os-Os distances are 3.055(1)Å and 2.927(2)Å¹¹⁷

The location of the second bridging hydrogen cannot be determined unambiguously. There are no other Os-Os vectors which, by being conspicuously long, would indicate the presence of an Os(μ -H)Os linkage. Since the two hydrogens are coupled H_B probably bridges either the Os(1)-Os(3) or the Os(3)-Os(4) vector. The Os(1)-Os(3) distance is significantly longer, i.e., 2.886(1)Å cf. 2.850(1)Å, and therefore this position is favoured, i.e., H_B bridges the hinge. It should be noted however, that the Os-Os distance assigned to this Os(μ -H)Os grouping is very short. Further evidence in support of the positioning of this hydride is presented in the section on the ¹³C NMR spectra of this complex.

The position of bridging hydride ligands can sometimes be inferred from the distortion of M-M-CO angles cis to the hydride bridge.¹⁷⁸ For this compound, however, it was thought that such distortion could be a result of the skewing of the CO(21) and CO(41) ligands noted earlier. If this were the case the displacement of the CO ligands could not be relied upon to indicate the position of the hydride ligands.

Comparison of the isoelectronic structures 2 and 3 leads to the question of why 2 is planar but 3 is bent, or more generally, 'What determines the dihedral angle of such compounds?' As indicated earlier, we believe the answer lies in

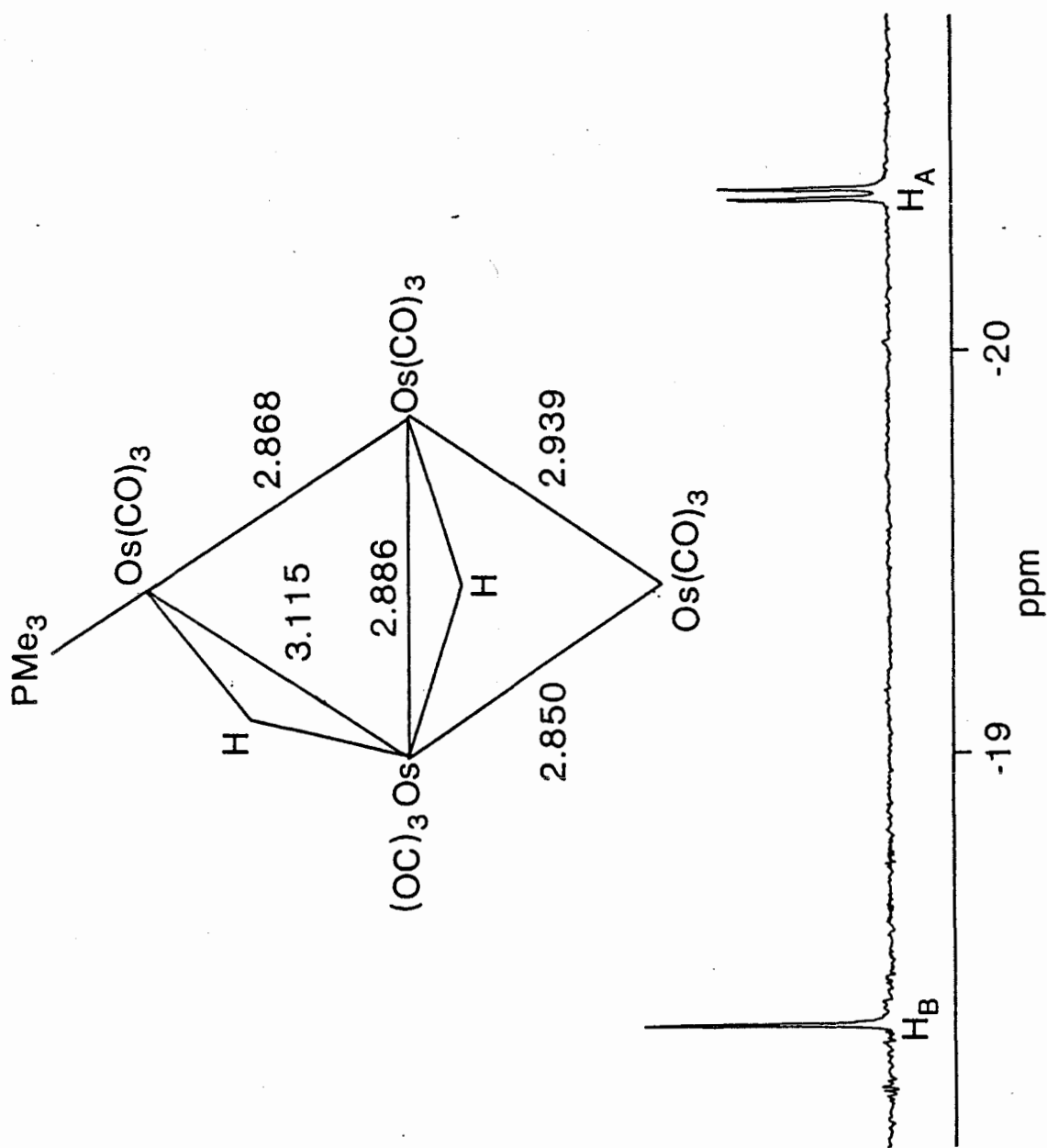


Figure B.2.13. ^1H NMR Spectrum and Hydride Ligand Positions for $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$.

the presence and position of bridging ligands. Two other flat 62 electron clusters are known, $\text{ReOs}_3\text{H}(\text{CO})_{15}$ and $[\text{Re}_4(\text{CO})_{16}]^{2-}$; both lack bridging ligands.^{108,200} The same is true for the larger planar structures $\text{Os}_5(\text{CO})_{19}$ ²⁰¹ and $\text{Os}_5(\text{CO})_{17}[\text{P}(\text{OMe})_3]_4$.²⁰² On the other hand the twenty-three butterfly clusters listed in Table B.1.2 all have a bridging ligand across the hinge, across the wing-tips, or both. Some flat 62 or 64 electron structures with bridging ligands are known, but these bridges are either on a face or along a peripheral edge.

It is easy to understand that the wing-tips must be drawn closer together when bridged, otherwise the distance between them would be too long for bonding with the bridging ligand to take place. The Os(2)-Os(4) distance in 2, for example, is 4.962(3)Å, while typical wing-tip spans in $[\text{Os}_4(\text{CO})_{12}(\mu_4\text{-N})]^-$ and $[(\mu\text{-H})_4\text{Os}_4(\text{CO})_{12}(\mu\text{-OH})]^+$ are 3.903Å¹⁵⁸ and 3.537Å,¹⁶¹ respectively. Bending at the hinge allows the wing-tip osmiums to maintain pseudo-octahedral geometry in that the bridge atom-wing-tip osmium-terminal carbonyl angle is close to 180°. Such angles in $(\mu\text{-H})_3\text{Os}_4\text{I}(\text{CO})_{13}$ and $[(\mu\text{-H})_4\text{Os}_4(\text{CO})_{12}\text{OH}]^+$ are 172.5(1)° and 174.2(4)° respectively.^{117,161} (The geometry is only pseudo-octahedral because the angles of the osmium triangles must be approximately 60°.)

Similar maintenance of nearly octahedral geometry occurs for the hinge osmium atoms if they are bridged by a hydride ligand, as is often the case. Such M- μH -M' configurations are often

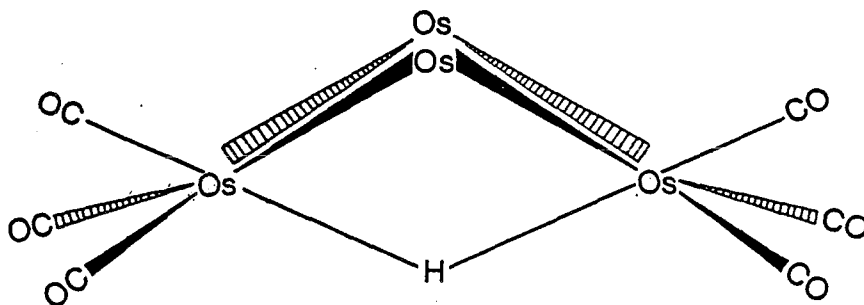
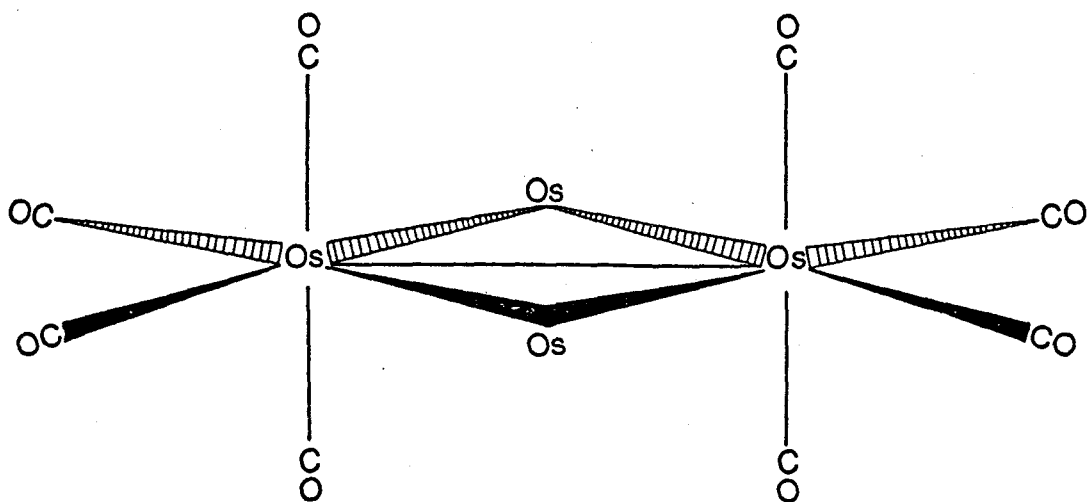


Figure B.2.14. Octahedral Geometry of the Hinge Vertices of Butterfly Structures.

represented as three-centre-two-electron bonds with little or no direct metal-metal interaction.^{203,204} Octahedral geometry can be maintained at the hinge vertices if the terminal ligands are bonded trans and cis to the bridging hydride. Only by bending can a butterfly achieve this, otherwise the terminal ligands must make very small angles with each other or the peripheral M-M vectors. In $(\mu\text{-H})_3\text{Os}_4\text{I}(\text{CO})_{13}$, the hydride ligands were located by neutron diffraction, and the H(2)-Os(2)-C(22) i.e., $\mu\text{-H-M-CO}_{\text{trans}}$ angle is $172.5(1)^\circ$.¹¹⁷ The octahedral geometry must be energetically favoured otherwise the bending of the Os_4 framework in 3 would be prevented by the steric interaction between C(21) and C(41), noted earlier.

We conclude that it is the wing-tip or hinge bridging ligands that force the metal framework to adopt a butterfly geometry; if neither is present the molecule will be flat. The electronic and steric properties of the hinge or wing-tip bridge ligands may determine the exact dihedral angle. In this regard, it is interesting to note that the cluster cation $[(\mu\text{-H})_3\text{Os}_4(\text{CO})_{12}(\text{NCMe})_2]^+$; which has a similar structure to 3 in that the hinge is hydrogen bridged but the wing-tips are not connected, has a dihedral angle of 112.2° , very close to that of 3.¹⁰⁴

2.3.2 ^{13}C NMR Studies

Unlike the other complexes in this study, 3 does not appear to undergo rapid ligand exchange at temperatures close to ambient. A $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum run on a ^{13}CO enriched sample of 3 held at 0 °C revealed thirteen sharp resonances, as expected from the solid state structure (Figure B.2.15). It is possible that the bridging hydrogens block the carbonyl ligand exchange. The peaks of low intensity at $\delta=190.3$ and $\delta=188.0$ ppm can be assigned to the pseudo-axial carbonyls on Os(2), consistent with previous assignments of low field signals to axial carbonyls in planar osmium clusters.^{102,185,186} The low intensity of these signals is due to unresolved coupling to the phosphorus atom. The low field signals at $\delta=191.3$ and 186.7 ppm were tentatively assigned to the pseudo-axial carbonyls on Os(4), but the origin of the other peaks could not be unambiguously determined.

In order to help determine the position of the bridging hydrogens, gated and selectively hydrogen decoupled ^{13}C NMR spectra were obtained on 3 with the sample at 0 °C. The gated spectrum showed that the three carbon peaks at $\delta=175.5$, 174.4 and 171.4 ppm exhibited coupling to hydrogen. The peak at $\delta=176.8$ ppm was reduced in intensity from that in the $^{13}\text{C}\{^1\text{H}\}$ spectrum of 3. Selective decoupling of H_A at -20.4 ppm gave a singlet signal at $\delta=174.4$ ppm, while the signal at $\delta=176.8$ ppm sharpened marginally. The same procedure applied to H_B at -18.3 ppm resulted in singlets for the $\delta=175.5$ and 171.4 ppm

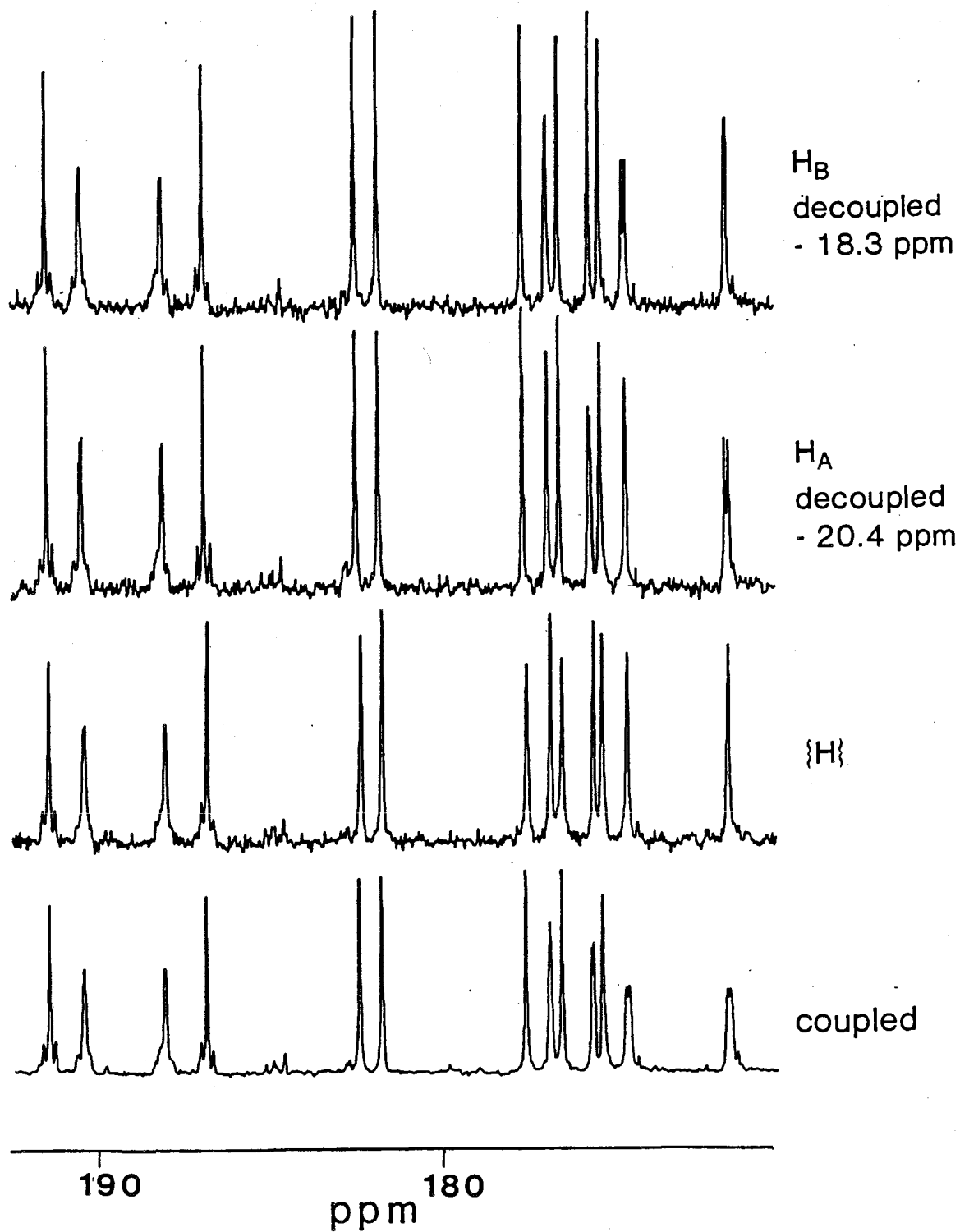


Figure B.2.15. ^{13}C NMR Spectra for $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$

resonances, see Figure B.2.15. The data are consistent with the presence of the bridging hydrides along the Os(2)-Os(3) (H_A) and Os(1)-Os(3) (H_B) vectors, except that the weakness of the coupling of H_A to one of the carbonyl signals is not explained. Placement of H_A along the Os(1)-Os(2) vector would explain why it shows strong coupling to only one carbonyl but then it would be expected to exhibit strong trans coupling to the phosphorus atom, which is not observed.

An alternative position of H_B , i.e., along the Os(3)-Os(4) vector, is also in accord with the observed H-C couplings, but this location is not consistent with the length of the Os(3)-Os(4) vector which is only 2.850(1)Å. Placement of H_B along the much longer Os(1)-Os(4) vector (2.939(1)Å) is ruled out because the two hydrogen signals are coupled in the 1H NMR spectrum.

2.4 Os₄(CO)₁₃PMe₃

2.4.1 *Structure and Bonding*

The major stimulus for investigating the structure of Os₄(CO)₁₃PMe₃ (4) was the desire to examine the validity of the scheme of structural changes that occur with sequential ligand loss. It can be seen, however, from Figure B.2.16 and Table B.2.4 that this complex has several interesting aspects in its own right. As expected, the metal atom framework consists of a tetrahedron, but the vertices are more unusual: one Os(CO)₃PMe₃

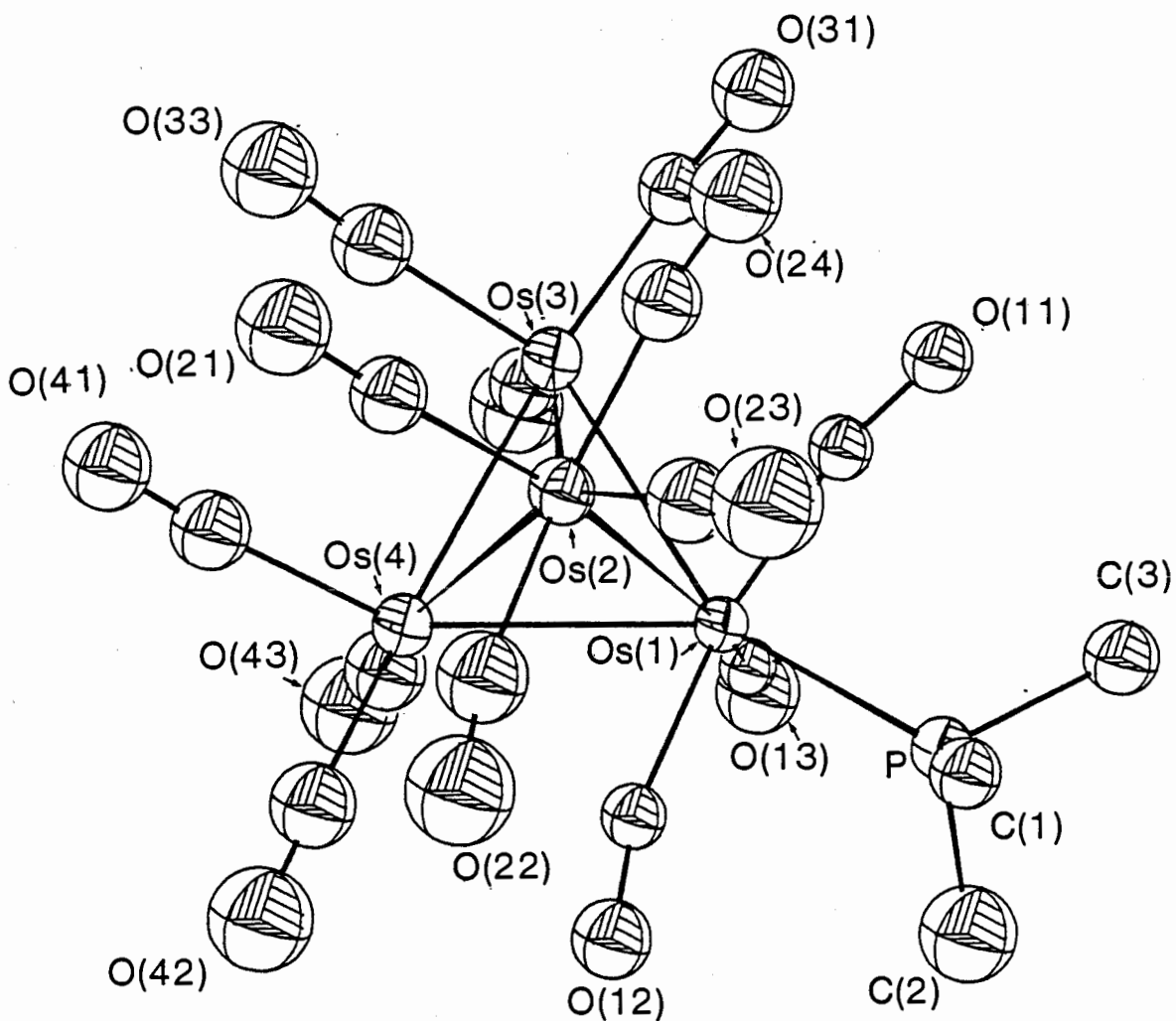


Figure B.2.16. Thermal Ellipsoid Diagram for $\text{Os}_4(\text{CO})_{13}\text{PMe}_3$.

Table B.2.4. Selected Molecular Dimensions for Os₄(CO)₁₃PMe₃.

a) Bond Lengths.

Atoms	Bond Length (Å)	Atoms	Bond Length (Å)
Os(1)-Os(2)	2.861(2)	Os(4)-C(42)	1.88(3)
Os(1)-Os(3)	2.831(1)	Os(4)-C(43)	1.89(3)
Os(1)-Os(4)	2.842(1)	P(1)-C(1)	1.73(3)
Os(2)-Os(3)	2.857(2)	P(1)-C(2)	1.83(3)
Os(2)-Os(4)	2.869(1)	P(1)-C(3)	1.85(3)
Os(3)-Os(4)	2.765(1)	C(11)-O(11)	1.18(3)
Os(1)-P(1)	2.361(6)	C(12)-O(12)	1.15(3)
Os(1)-C(11)	1.91(2)	C(13)-O(13)	1.20(3)
Os(1)-C(12)	1.92(3)	C(21)-O(21)	1.17(4)
Os(1)-C(13)	1.87(2)	C(22)-O(22)	1.17(5)
Os(2)-C(21)	1.90(3)	C(23)-O(23)	1.13(4)
Os(2)-C(22)	1.87(4)	C(24)-O(24)	1.17(4)
Os(2)-C(23)	1.92(3)	C(31)-O(31)	1.15(3)
Os(2)-C(24)	1.94(3)	C(32)-O(32)	1.17(4)
Os(3)-C(31)	1.89(3)	C(33)-O(33)	1.12(4)
Os(3)-C(32)	1.85(3)	C(41)-O(41)	1.07(4)
Os(3)-C(33)	1.90(3)	C(42)-O(42)	1.18(4)
Os(4)-C(41)	1.90(3)	C(43)-O(43)	1.16(4)

b) Weak Interactions

Atoms	Distance Å
Os(3)--C(11)	2.73(2)
Os(3)--C(24)	2.57(3)
Os(4)--C(12)	2.68(2)
Os(4)--C(22)	2.80(4)

c) Bond Angles

Bonds	Angle (°)	Bonds	Angle (°)
Os(2)-Os(1)-Os(3)	60.24(4)	Os(4)-Os(2)-C(21)	94.4(8)
Os(2)-Os(1)-Os(4)	60.41(4)	Os(4)-Os(2)-C(22)	69(1)
Os(3)-Os(1)-Os(4)	58.34(3)	Os(3)-Os(2)-C(24)	61.2(9)
Os(1)-Os(2)-Os(3)	59.35(4)	Os(1)-Os(2)-C(23)	108(1)
Os(1)-Os(2)-Os(4)	59.45(4)	Os(4)-Os(1)-C(12)	65.3(7)
Os(3)-Os(2)-Os(4)	57.75(4)	Os(2)-Os(3)-C(32)	148.3(8)
Os(1)-Os(3)-Os(2)	60.41(4)	Os(4)-Os(3)-C(33)	92.1(9)
Os(1)-Os(3)-Os(4)	61.02(3)	Os(1)-Os(3)-C(31)	112.5(8)
Os(2)-Os(3)-Os(4)	61.35(4)	Os(2)-Os(4)-C(43)	150(1)
Os(1)-Os(4)-Os(2)	60.14(4)	Os(3)-Os(4)-C(41)	93.7(9)
Os(1)-Os(4)-Os(3)	60.64(3)	Os(1)-Os(4)-C(42)	115(1)
Os(2)-Os(4)-Os(3)	60.90(4)	Os(1)-P(1)-C(1)	117(1)
Os(2)-Os(1)-P(1)	111.8(2)	Os(1)-P(1)-C(2)	113(1)
Os(3)-Os(1)-C(11)	66.9(7)	Os(1)-P(1)-C(3)	115(1)
Os(2)-Os(1)-C(13)	152.4(7)		

fragment, one $\text{Os}(\text{CO})_4$ fragment and two $\text{Os}(\text{CO})_3$ fragments. This appears to be the first recorded example of a closed polyhedron having two vertices with four terminal two-electron donor ligands. In contrast to the prediction of Mingos and Evans¹²² neither steric nor electronic effects appear to make this compound unstable. It can be stored under N_2 , at room temperature, for several months without decomposition. Indeed, the other compounds 1 and 2 showed loss of CO under the ionization conditions of mass spectroscopy while 4 did not, indicating it may be the most stable of the three. Complex 4 has the highest melting point of the series, 183 °C (see Table B.2.5.) Further evidence of stability comes from the Os-Os bond lengths. The shortest Os-Os bond [$\text{Os}(3)\text{-Os}(4)$, 2.765(1)Å] is between the two $\text{Os}(\text{CO})_3$ fragments, while the other five bonds are all within 0.02Å of their mean value of 2.852Å. Churchill has pointed out that such values should be compared to similar unbridged bond lengths in other tetrahedra.²⁰⁵ The complex $\text{H}_2\text{Os}_3\text{Co}(\text{CO})_{16}(\eta^5\text{-C}_5\text{H}_5)^{205}$ for example, has an unbridged Os-Os bond between two $\text{Os}(\text{CO})_3$ fragments, of 2.778(1)Å°, similar to the $\text{Os}(3)\text{-Os}(4)$ bond length determined here. The cluster $[\text{H}_2\text{Os}_4(\text{CO})_{12}]^{2-}$ has unbridged Os-Os bonds of 2.797(2), 2.811(2), 2.792(2) and 2.792(2)Å,²⁰⁶ while those in $[\text{HOs}_4(\text{CO})_{13}]^-$ are 2.817(2), 2.807(2), 2.773(2) and 2.774(2)Å.¹³⁸ The unique inequivalent unbridged Os-Os distance in the neutral complex $\text{H}_2\text{Os}_4(\text{CO})_{11}\text{CNMe}$ is 2.822(1)Å.¹⁴⁵ The bonds involving the $\text{Os}(\text{CO})_4$ and $\text{Os}(\text{CO})_3\text{PMe}_3$ fragments in 4 are significantly longer than any of these lengths, perhaps reflecting their diminished

cluster bonding capacity, relative to that of an $\text{Os}(\text{CO})_3$ fragment. However, the differences are not so great as to imply any of the Os-Os bonds in **4** are particularly weak. The crystallographically inequivalent bonds in $\text{Os}_5(\text{CO})_{16}$ which involve the $\text{Os}(\text{CO})_4$ fragment are significantly longer at 2.889(3)Å and 2.866(4)Å.¹¹⁶ One might predict the Os(1)-Os(2) bond in **4** to be especially lengthened since both osmium atoms have four ligands, but it is not particularly long at 2.861(2)Å.

In agreement with Mingos and Evans' calculations,¹²² the OsL_4 fragments maintain nearly C_{2v} symmetry and there exists evidence for weakly semi-bridging interactions between four of the carbon atoms bonded to Os(1) and Os(2) and neighbouring osmium atoms [Os(3)···C(11)=2.73(2)Å, Os(3)···C(24)=2.57(3)Å, Os(4)···C(12)=2.68(2)Å and Os(4)···C(22)=2.80(4)Å; the corresponding Os-C-O angles are listed in Table B.2.4.] These semi-bridging interactions, however weak, add to the overall stability of the complex. As Mingos noted, such interactions have been previously observed in $\text{Os}_5(\text{CO})_{16}$,¹¹⁶ $(\mu\text{-H})_2\text{Ru}_4(\text{CO})_{13}$ ¹³³ and $(\mu\text{-H})_2\text{FeRu}_3(\text{CO})_{13}$.¹³⁰ It is of interest that other similar structures such as $[(\mu\text{-H})\text{Os}_4(\text{CO})_{13}]^-$ ¹³⁸ and $(\mu\text{-H})_2\text{FeOs}_3(\text{CO})_{13}$ ²⁰⁷ have fully bridging CO ligands rather than $\text{M}(\text{CO})_4$ vertices, but the reasons for such variation in structure are not understood.

It can be seen that PSEPT in its more sophisticated form is applicable to this complex, in spite of the fact that its ability to exist was questioned. Predictions regarding the

symmetry of OsL_4 vertices, their weakly semi-bridging interactions and the relative strength of the metal framework bonds are all in accord with the results determined here.¹²² While a bonding scheme of the osmium carbonyl cluster $\text{Os}_4(\text{CO})_{14}$, which would be analogous to 4 was not developed by Mingos and Evans, there can be little doubt such calculations would result in the prediction of six cluster bonding orbitals containing twelve electrons.

We have used the isolobal analogy to develop a simple localized bonding picture for 4.¹²⁴ According to this approach, the $\text{Os}(\text{CO})_3$ fragments, which have a total coordination of six, contribute three orbitals containing two electrons to the cluster, while the other two fragments, $\text{Os}(\text{CO})_4$ and $\text{Os}(\text{CO})_3\text{PMe}_3$, which are seven coordinate contribute three orbitals containing four electrons. Thus the resonance structures shown in Figure B.2.16 may be proposed for 4, in which each osmium atom achieves an 18 electron configuration. The model shows donor-acceptor bonds from the vertices having four ligands to those having three. The expectation that these bonds would be slightly longer than normal covalent bonds is in accord with the lengths determined here. The electron density built up on Os(3) and Os(4) is relieved by the semi-bridging action of the carbonyl ligands.

The main difference between this approach and PSEPT is the assumption that the frontier orbitals are almost degenerate rather than separated by an energy gap large enough to maintain

the electrons in pairs. This difference is minor especially in view of the fact that the EHMO method, on which both the isolobal analogy and PSEPT are based, is well known to be subject to error regarding the computed energy levels of the orbitals. Hence, there is no strong reason to prefer one model over the other.

2.4.2 Fluxional Properties

Variable temperature ^{13}C NMR spectra revealed that the barrier to internuclear carbonyl exchange is very low in 4. The room temperature spectrum had only one resonance, a sharp singlet at $\delta=181.1$ ppm. This signal shifted slightly upfield as the sample was cooled; at -125 °C, the lowest temperature

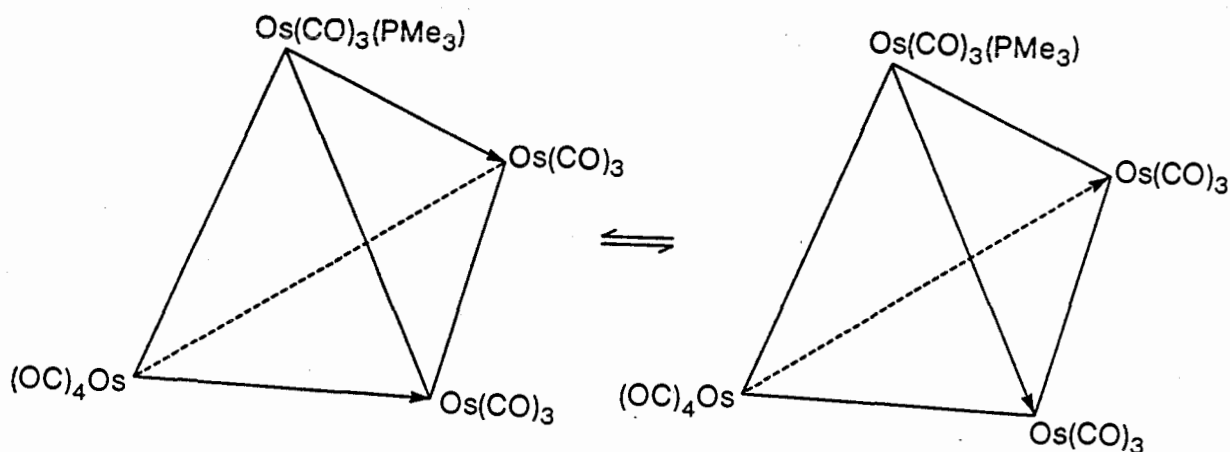


Figure B.2.17. Possible Resonance Structures for $\text{Os}_4(\text{CO})_{13}\text{PMe}_3$.

attained, the peak was at $\delta=179$ ppm, and was considerably broadened (Figure B.2.17). These data are consistent with rapid exchange of all carbonyl ligands on the four osmium atoms probably via a bridge-terminal mechanism. Local exchange at separate vertices is not ruled out, but must occur in conjunction with internuclear exchange if the existence of only one carbonyl signal is to be explained. It is probable that the weak semi-bridging interactions between non-bonded Os and C atoms facilitate bridge-terminal carbonyl exchange.

When the sample was cooled to -91 °C, two other small peaks at $\delta=202.0$ and 195.2 ppm appeared in the spectrum. The spectrum obtained with the sample at -125 °C had a total of ten additional peaks, all of which were attributable to complex 2. Compound 4 is almost certainly not reverting back to 2 at this temperature. Rather it is probable that the two complexes were both present in solution because they were not completely separated during synthesis. Pure samples of 4 were obtained by chromatography on a silica gel column, a procedure which required that the column eluent be monitored by IR spectroscopy because the bands due to 2 and 4 overlapped somewhat. This was very difficult with samples that had been enriched with ^{13}C because of the large number of CO stretches. The reason that the signals due to 2 did not appear in the higher temperature ^{13}C spectrum is that this complex was present in only trace amounts in the sample. The presence of sharp resonances due to 2 in the spectrum taken with the sample at -125 °C confirms that

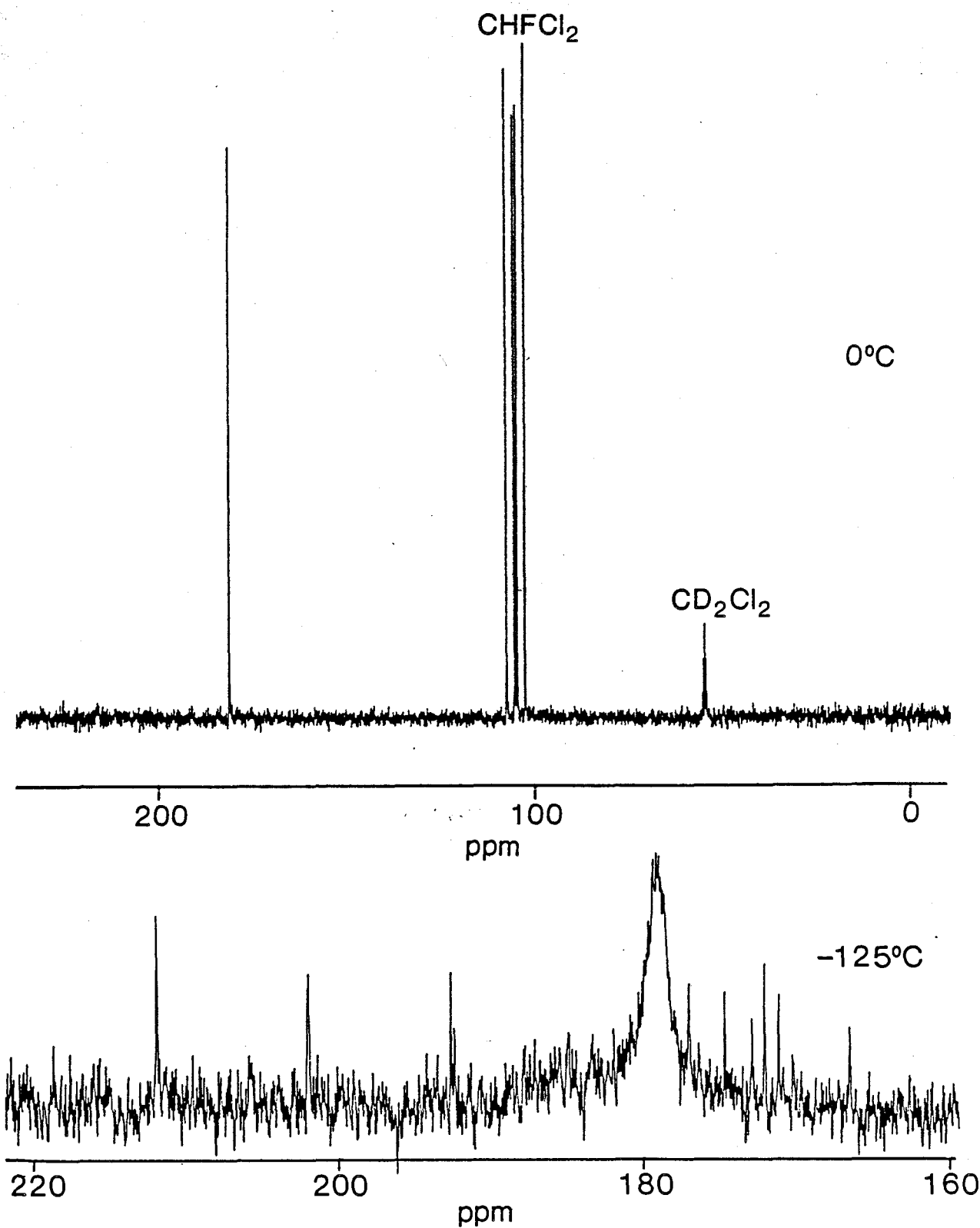


Figure B.2.18. ^{13}C NMR Spectra of $\text{Os}_4(\text{CO})_{13}\text{PMe}_3$. (The scale is expanded on the lower spectrum.)

the broadening of the signal due to 4 was indeed due to slowed exchange and not to loss of field homogeneity of the spectrometer or solvent viscosity.

2.5 Summary and Conclusions

The $\text{Os}_4(\text{CO})_n\text{PMe}_3$ ($n=15,14,13$) series constitutes the first fully characterized example where a 64 electron complex displays sequential ligand loss to 62 and then to a 60 electron species. The gross skeletal features of each of the three clusters conforms to that predicted by the current bonding theories. Nevertheless, many of the details of the structures are unexpected. The 64 electron species $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$ (1) has a dative covalent metal-metal bond, i.e., $\text{Os}(\text{CO})_4\text{PMe}_3$ acts as a two electron donor ligand in the cluster. The bonding is best described in terms of a triangular cluster with twelve two electron donor ligands, one of which is unusual.

Unlike most 62 electron species, $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$ (2) is flat, and its peripheral framework is asymmetric. A novel bonding model involving Os-Os bond orders of 1.5 and 0.5 has been proposed to account for the unusual bond lengths. Similar non-integral bond orders may be applicable to other osmium clusters that have Os-Os bonds of unusual lengths.

The structure of 2 has been compared to that of $(\mu_2\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$ (3) which has the more common butterfly framework with a dihedral angle of 112.2° . A hydrogen ligand

bridging the hinge has been proposed as the reason 3 is bent.

The 60 electron tetrahedral complex $\text{Os}_4(\text{CO})_{13}\text{PMe}_3$ (4) is stable despite a forecast to the contrary. We believe it is the first reported closed cluster with two ML_4 vertices.

As was noted earlier 4 is the most stable of the series. The rapid decomposition of 1 in solution at room temperature shows it to be the least stable. A temperature of 90 °C is necessary to cause ligand loss from 2 at a reasonable rate. The mass spectra are consistent with this ranking in that 1 and 2 show as the peaks of highest mass, ions due to the parent ion of 4⁺. It may be that increased metal-metal interactions inhibit decomposition; the 'spike' osmium in 1 takes part in only one metal-metal bond while each osmium in 4 is bonded to three others. Also, complex 4 may resist further ligand loss as there is no facile framework reorganization available that can make up for the loss of two more electrons. Further CO ligand loss from 4 was not studied although it did appear that it melted without decomposition at 183 °C.

The ¹³C NMR spectra reveal that while 3 is nearly rigid at room temperature all members of the series $\text{Os}_4(\text{CO})_n\text{PMe}_3$ (n=15, 14, 13) undergo rapid ligand exchange. Furthermore the barrier to non-rigidity is lowered as the complexes become more compact. The low temperature limiting spectra for 1 was reached at -67 °C, for 2 at -115 °C while 4 was still fluxional at the latter temperature, which is about the lowest accessible to us.

The well known bridge-terminal carbonyl exchange mechanism accounts for the observed spectra of 1 provided that exchange involving the carbonyls of the $\text{Os}(\text{CO})_4\text{PMe}_3$ ligand is assumed to occur concurrently with carbonyl exchange on the osmium triangle at temperatures above -26°C . We believe the remarkable fluxional behaviour of 2 involves not only ligand exchange but skeletal rearrangement as well. The 'windshield wiper' mechanism proposed here is unique. The extremely low barrier to the non-rigidity exhibited by the tetrahedral complex 4 may be a consequence of the weak semi-bridging C-Os interactions. The lack of a low temperature limiting spectra for 4 prohibited development of a definite proposal for the ligand exchange mechanism.

There are several reasons why the bonding theories discussed in the introduction cannot predict the fine detail of these structures. Neither Lauher nor Teo take into account any ligand influence on localized bonding. The values calculated for the orbital energy levels using the EHMO method are a qualitative guide at best. Wooley has pointed out that the fundamental assumption of the EHMO method, i.e., that the resonance integral is proportional to the overlap integral, is invalid.²⁰⁸ As a result, models based on EHMO calculations greatly underestimate the d orbital contribution to cluster bonding.

If accurate bonding models for osmium clusters are to be developed, relativistic effects must be considered. Drs. Malli and Arratia-Perez of this department and others have shown that

the d orbitals of third row transition metals are destabilized while the s orbitals are stabilized by relativity effects.^{209,210,211} As a result, there is considerable s-d orbital mixing. It is unfortunate that full relativistic calculations are currently possible only on molecules of high symmetry, but such calculations are planned for the Os(CO)₄ and Os(CO)₃ fragments.²¹²

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Materials and Instrumentation

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere using standard Schlenk techniques. Hexane was refluxed over potassium and methylene chloride over phosphorus pentoxide; they were distilled and stored under nitrogen before use. The complexes $\text{H}_2\text{Os}_3(\text{CO})_{10}$, $\text{Os}_3(\text{CO})_{11}\text{MeCN}$ and $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ were prepared by literature methods,^{213, 214, 215} and $\text{Os}(\text{CO})_4\text{PMe}_3$ was prepared as in Part A. The reagent Me_3NO was sublimed, then dissolved in MeOH before use.

Infrared spectra were obtained with a Perkin-Elmer 983 spectrophotometer; NMR spectra with a Bruker 400-MHz instrument and mass spectra with a Kratos MS-50 using a direct insertion probe at 220-250 °C and electron impact with an ionization voltage of 70eV. Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University. Analytical and mass spectral data are given in Table B.3.1. The infrared stretching frequencies in the carbonyl region, melting points and ^1H NMR resonances are listed in Table B.3.2.

Table B.3.1. Analytical and Mass Spectral Data for Os₄ Compounds.

Compound	%Calcd.		%Found		Mass Spectrum ^a
	C	H	C	H	
Os ₄ (CO) ₁₅ PMe ₃	17.20	0.72	17.09	0.76	1202 (P-2CO) ⁺
Os ₄ (CO) ₁₄ PMe ₃	16.60	0.74	16.84	0.67	1202 (P-CO) ⁺
(μ-H) ₂ Os ₄ (CO) ₁₃ PMe ₃	15.98	0.92	16.12	0.82	1176 (P-CO) ⁺
Os ₄ (CO) ₁₃ PMe ₃	16.00	0.76	16.11	0.79	1202 (P ⁺)

^a

Most intense peak of parent ion envelope; in all cases the parent ion agreed with that simulated by computer.

3.2 Synthetic Methods

3.2.1 *Preparation of Os₄(CO)₁₅PMe₃*

METHOD I. A solution of of H₂Os₃(CO)₁₀ in hexane (200 mg, .27 mmol in 25 mL) was stirred at room temperature with a large excess of Os(CO)₄PMe₃ (230 mg, .60 mmol) for approximately 2 h. Evolved gases were allowed to escape through an oil bubbler. During this time Os₄(CO)₁₅PMe₃ precipitated from solution as an orange powder. The supernatant liquid was decanted and the product washed with hexane (≈3x5 mL), dried on a vacuum line and then dissolved in a minimum of hot CH₂Cl₂ (≈10 mL). Hexane was added to precipitate the product. The yield was 194 mg (.15 mmol, 57%) yield. The analytical sample was recrystallized from CH₂Cl₂.

METHOD II. A hexane solution of $\text{Os}_3(\text{CO})_{11}\text{MeCN}$ (130 mg) and excess $\text{Os}(\text{CO})_4\text{PMe}_3$ (55 mg), was stirred at 60 °C for 2 h. The supernatant liquid was decanted and the orange precipitate, $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$, dried on a vacuum line. The yield was about 40% and was not improved by longer reaction times.

3.2.2 Preparation of $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$

METHOD I. To a solution of $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$ in CH_2Cl_2 (typically 100 mg, .079 mmol in 25 mL), Me_3NO in MeOH was added until the infrared band at 2086 cm^{-1} had just disappeared. During this time the colour of the solution changed from orange to deep red. The solution was filtered through a short silica column ($\approx 10 \times 2.5$ cm) and evacuated to dryness. The product was then extracted into hot hexane (3x20 mL). Removal of solvent gave the dark red crystalline product $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$; the yield was 80 mg (0.065 mmol, 80%). The analytical sample was recrystallized from hot hexane.

METHOD II. A toluene solution of $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ (≈ 30 mg in 10 mL) and excess $\text{Os}(\text{CO})_4\text{PMe}_3$ (150 mg) was degassed with two freeze-thaw cycles and stirred at room temperature overnight. The solvent was removed on the vacuum line and the excess $\text{Os}(\text{CO})_4\text{PMe}_3$ sublimed at 40 °C onto a cold water probe to leave the crude product $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$, which was purified as in Method I.

Table B.3.2. CO Stretching Frequencies, ¹H NMR Resonances and Melting Point Data for Os₄ Compounds.

Compound	ν CO (cm ⁻¹)	δ ¹ H NMR (ppm) ^a	m p (°C)
Os ₄ (CO) ₁₂ PMe ₃	2115vw, 2086m, 2048s, 2033s, 2005m(asym), 1974w, 1961w, 1916w(br)	0.57, (10.4)	148
Os ₄ (CO) ₁₂ PMe ₃	2116w, 2069s, 2046m, 2035vs, 2028 (sh), 2014m, 2004w, 1986vw, 1978m, 1951vw, 1927w	0.95, (10.2)	128
(μ -H) ₂ Os ₄ (CO) ₁₂ PMe ₃	2101w, 2069s, 2052s, 2030s, 2016s, 2003s, 1985m, 1976w	1.03, (10.2)	204
Os ₄ (CO) ₁₂ PMe ₃	2091m, 2048vs, 2016s, 1992m	1.02, (10.6)	183

^a δ -H values are in parenthesis.

^b Infrared spectrum in CH₂Cl₂ solution.

^c Infrared spectrum in hexane solution.

3.2.3 Preparation of $(\mu-H)_2Os_4(CO)_{13}PMe_3$

A CH_2Cl_2 solution of $H_2Os_3(CO)_{10}$ (100 mg, .12mmol in 15 mL) was stirred with a slight excess of $Os(CO)_4PMe_3$ (25 mg, .13 mmol). A solution of Me_3NO in MeOH was added dropwise until the purple colour was discharged and the infrared bands at 2094, 2074 and 2060 cm^{-1} had disappeared. The resulting red solution was then filtered through a short silica gel column (10x2.5 cm) and evacuated to dryness. The product was extracted with cold hexane (4x5 mL) and chromatographed on a silica gel column (30x2.5 cm) with 1:2 CH_2Cl_2 /hexane as the eluent. The first band, a faint yellow, was not indentified. The second band, which was orange, was the product and was followed by a broad dark brown band identified as $Os_4(CO)_{14}PMe_3$. Further bands were discarded without identification. The yield was 31 mg (.025 mmol, 26%) and the analytical sample was recrystallized from a 3:4 CH_2Cl_2 /hexane mixture.

3.2.4 Preparation of $Os_4(CO)_{13}PMe_3$

A hexane solution of $Os_4(CO)_{14}PMe_3$ (85 mg, .071 mmol in 20 mL) was placed in a sealed tube and degassed with two freeze-thaw cycles. It was then stirred at 90 °C for approximately 24h with frequent degassing (every 2h, when possible). The reaction was followed by infrared spectroscopy and when it appeared no further changes in the relative intensities of the CO bands were taking place the sample was

cooled and chromatographed on a silica gel column (30x2.5 cm) with 9:1 hexane/CH₂Cl₂ as the eluent. The first band, (light yellow) was identified by infrared spectroscopy as Os₃(CO)₁₁PMe₃¹⁸²; the second, brown-purple band was the product, and was collected in fractions as it was not well separated from the third band, Os₄(CO)₁₄PMe₃. Two further bands, light orange and purple, were not identified. The yield was 29 mg (.024 mmol, 34%) and the analytical sample was recrystallized from hexane.

3.3 Crystal Structure Determinations

3.3.1 *General*

The following procedure was followed for each of the four compounds. Details for the individual complexes are given subsequently. A crystal of suitable size (see Table B.3.3) was mounted on an Enraf-Nonius CAD4-F diffractometer. Use of the diffractometer 'Search', 'Index' and 'Transformation' routines allowed approximate cell dimensions to be assigned on the basis of 25 high θ angle reflections. The NRC 'Creduc' routine was used to check for possible alternate Bravais lattices.⁹⁸ Subsequent examination of the systematic absences and Laue symmetry allowed these particular monoclinic space groups to be determined unambiguously. The triclinic space group was confirmed during structure refinement. Diffraction data were collected at 20 \pm 1 °C using graphite monochromated Mo-K α_1 ($\lambda=0.7930\text{\AA}$) radiation. Background measurements were made by

Table B.3.3. Crystallographic Data for Os₄ Compounds.

	Os ₄ (CO) ₁₂ PMe ₆	Os ₄ (CO) ₁₂ (PMe) ₆	(μ -H) ₂ Os ₄ (CO) ₁₂ (PMe) ₆	Os ₄ (CO) ₁₂ (PMe) ₆
Formula Wt.	1258	1230	1204	1202
Colour	orange	deep red	red	burgandy
Solvent	CH ₂ Cl ₂	hexane	hexane/CH ₂ Cl ₂	hexane
Space Group	P $\bar{1}$	P2 ₁ /a	P2 ₁ /n ^c	P2 ₁ /c
Crystal System	triclinic	monoclinic	monoclinic	monoclinic
a, Å	12.473(2)	13.525(5)	15.541(6)	15.470(2)
b, Å	13.325(2)	12.969(6)	11.013(3)	10.193(1)
c, Å	17.547(2)	14.825(5)	16.280(4)	16.527(2)
α , deg	109.05(1)	--	--	--
β , deg	90.44(1)	99.14(3)	114.10(3)	113.452(9)
γ , deg	94.60(1)	--	--	--
V, Å ³	2745	2567	2560	2390
Z	4	4	4	4
d _{calc} , g/cm ³	3.036	3.185	3.153	3.337
μ (Mo K α) cm ⁻¹	186	199 ^b	199	213
Crystal Size, mm	0.11x0.29x0.28	0.34x0.16x0.11	0.11x0.18x0.27	0.24x0.19x0.08

^aAlternate P2₁/c no.14.

^bAn experimentally based absorption correction was applied, see text.

^cP2₁/n, non-standard setting for P2₁/c; equivalent positions are: x,y,z; 1/2-x,1/2+y,1/2-z; -x,-y,-z; 1/2+x,1/2-y,1/2+z.

extending the scan range by 25% at each side of the scan. Monitoring of two standard reflections every one or two hours revealed no significant crystal decay. A Lorentz polarization correction was applied. Accurate cell dimensions were assigned on the basis of 25 [24 for $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$ and 19 for $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$] carefully centered high angle ($2\theta > 21^\circ$) reflections widely scattered in reciprocal space. Psi scans were run for a number of reflections (typically about six) throughout the 2θ range of data collection and having chi near 90° . Crystal faces were measured and indexed using a locally modified optical telescope with a filar eyepiece and the diffractometer 'Micros' and 'Micror' routines.

The osmium atoms were located by electron density methods and other non-hydrogen atoms by alternating Fourier difference maps with least squares refinement. Since the linear absorption coefficients were so large, $\approx 200 \text{ cm}^{-1}$, great care was taken with the absorption correction. Analytical corrections were applied to those reflections for which psi scans had been obtained and the results were compared to those of the empirical method. Small adjustments in the values of the crystal dimensions were made when necessary, to ensure that the intensity variation as determined by the analytical method matched that of the empirical method. In general, the analytical correction was preferred to the empirical one; see the following individual structure determinations for details. The strong inner data

showed evidence for extinction in all four structures as $|KF_0|$ values were less than $|F_c|$ values. Extinction was added as a refinable parameter if its size, significance and the improvement in the agreement so warranted, otherwise those reflections suffering most noticeably from extinction were removed from the refinement process (see Table B.3.3).²¹⁶ Unit weights were used during the initial stages of refinement for all four structures. After anisotropic refinement the weight, ω , for each reflection was set to be $\omega = [\sigma^2(F) + KF^2]^{-1}$ and the value of K was adjusted to remove trends in the average $\omega\Delta^2$ values as a function of $|F_0|$ and $\sin\theta/\lambda$ in the error analysis. There were no significant trends in the final error analyses. In each case the largest peaks in the final Fourier difference map were in the vicinity of the osmium atoms. Crystallographic data are given in Table B.3.3 and details of data collection in Table B.3.4. Atomic scattering factors which included anomalous dispersion were taken from reference 95. Diagrams of the molecules as computed by the SNOOPI program²¹⁷ are shown in Figures B.2.1, B.2.6, B.2.10 and B.2.16. Bond lengths and angles are given in Tables B.2.1 to B.2.4. Final atomic coordinates, anisotropic thermal parameters and structure factors are listed in the appendix. The computer programs used were from "The Vax 750/780 Crystal Structure System."⁹⁸

Table B.3.4. Data Collection Parameters for Os₄ Compounds.

	Os ₄ (CO) ₁₂ PMe ₆	Os ₄ (CO) ₁₂ PMe ₆	(μ-H) ₂ Os ₄ (CO) ₁₂ PMe ₆	Os ₄ (CO) ₁₂ PMe ₆
scan method	ω-2θ	ω-2θ	ω-2θ	ω-2θ
scan range, 2θ, deg	0.0-45.0	0.0-45.0	0.0-45.0	0.0-45.0
scan width, 2θ, deg	1.3	1.3	1.3	1.3
scan rate, 2θ, deg/min	1.4-6.6	1.4-6.6	1.4-6.6	1.4-6.6
collection range	±h, ±k, +l	±h, ±k, +l	±h, ±k, +l	±h, ±k, +l
transmission coefficient range	0.120-1.00 ^a	0.0555-0.146	0.0141-0.164	0.0249-0.422
unique reflections	7167	3331	3544	3104
observed reflections ^b	5172	2424	2503	2060
variables in final model	386	325	308	163
R ₁ ^c	0.0367	0.0385	0.0325	0.0470
R ₂ ^d	0.0407	0.0479	0.0380	0.0601
K factor in wt. scheme	0.0004	0.0008	0.0004	0.0006
gof	1.3508	1.3112	1.4231	1.6416
largest shift ^e	0.03	0.00	0.00	0.02
map σ e/Å ³ f	0.25	0.27	0.23	0.39
largest peak e/Å ³ g	1.55	1.59	1.79	2.18
extinction parameter (X10 ⁻³) ^h	22(1.3)	--	6.7(1.3)	23(2.6)

^aEmpirical absorption correction, see text.

^bI > 2.3σ(I) except for (μ-H)₂Os₄(CO)₁₂PMe₆ for which I > 3.0 σ(I).

$$CR_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$dR_2 = \frac{|\sum \omega(|F_o| - |F_c|)^2 / \sum \omega |F_o|^2}{\sum \omega |F_o|^2}$$

^eLargest shift/error in the final cycle of refinement.

^fStandard deviation of the final Fourier difference map.

^gLargest peak in the final Fourier difference map.

^hParameter is g in the formula $F_c' = k|F_c| (1 + g|F_c|^{2Lp_2/p_1})^{-1/2}$

where F_c' is the corrected, calculated structure factor.

k is a scale factor, Lp is the Lorentz polarization factor

and $P_n = 1 + \cos^n 2\theta$.

3.3.2 $Os_4(CO)_{15}PMe_3$

After all the atoms had been located, refinement proceeded quickly with only the osmium atoms having anisotropic thermal parameters ($R_1=0.082$). Since the crystal had been cut to appropriate size it was necessary to define some 16 crystal faces with indexes as high as 25 in order that an analytical absorption correction⁹⁷ could be applied. Extinction was added as a refinable parameter.⁹⁶ (It was noted, in particular, that the 1,0,2 and 2,0,0 reflections had much better agreement after this procedure)²¹⁸ ($R_1=0.041$). Initial positions of hydrogen atoms on the methyl carbons in each of the two molecules in the asymmetric unit were located in a Fourier difference map using inner data only. These were used to calculate the positions of the second and third hydrogen atoms of the methyl groups. This procedure was applied to five of the six methyl groups; hydrogen atoms on the sixth methyl group could not be located. In view of the difficulty in defining crystal faces it was decided to try an empirical absorption correction,⁹⁴ which proved advantageous ($R_1=0.038$). At this point the phosphorus and methyl carbon atoms were allowed to vary anisotropically and the weighting scheme was adjusted ($R_1=0.037$). Finally the structure was refined to completion using block diagonal methods and the positions of the hydrogen atoms were recalculated.

3.3.3 $Os_4(CO)_{14}PMe_3$

Isotropic refinement of all non-hydrogen atoms proceeded quickly ($R_1=0.088$), however correction for absorption proved difficult. The variations of intensity as measured by the psi scans were not consistent for the different reflections, nor was there any match with the analytical correction. It was not surprising, therefore, that neither the empirical⁹⁴ nor the analytical⁹⁷ correction improved the value of the residual, even though the measurement of crystal dimensions was carefully checked. Since the transmission factors for the analytical correction appeared to be too small (0.00529-0.06219) it was decided to decrease the absorption coefficient from the calculated value of 199 cm^{-1} in a systematic way. It was found that a μ value of 100 cm^{-1} gave the best results ($R_1=0.064$). The reason for this difficulty was very probably that the crystal had re-entrant angles making it impossible for the computer program to handle the absorption correction properly. All non-hydrogen atoms were allowed to vary anisotropically ($R_1=0.0393$), and then the weighting scheme was adjusted ($R_1=0.039$). Hydrogen atoms were included at calculated positions²¹⁹ with a single isotropic temperature ($R_1=0.039$). Addition of extinction as a refinable parameter did not improve the agreement and gave an unreasonably small extinction coefficient ($2.4(.26) \times 10^{-8}$), but four reflections were removed from the refinement as they suffered from extinction.²²⁰ The data were then refined to completion using full matrix least

squares.

3.3.4 $(\mu-H)_2Os_4(CO)_{13}PMe_3$

Full-matrix least-squares refinement with only the osmium and phosphorus atoms located and with these atoms assigned isotropic thermal parameters gave a residual (R_1) value of 0.19. Application of an analytical absorption correction greatly improved the agreement ($R_1=0.11$) as did location of the other non-hydrogen atoms ($R_1=0.052$). Anisotropic temperature factors were then added and the weighting scheme was adjusted. Methyl hydrogen atom positions were generated from initial positions located on a Fourier difference map generated using inner data only ($R_1=0.036$). The $-2,2,2$ reflection was omitted from structure refinement as it had an anomalously large $\omega\Delta^2$ value i.e., 441. (The next highest $\omega\Delta^2$ value was 74.) Because the error analysis showed the weak data had a large average $\omega\Delta^2$ it was decided to flag unobserved those reflections for which $I \leq 3\sigma(I)$. This procedure reduced the number of observed reflections from 2597 to 2503 and the residual (R_1) value to 0.033. Attempts to locate the bridging hydrogens using difference Fourier synthesis on inner data only were not successful. Final convergence was achieved using full matrix least-squares refinement.

3.3.5 $Os_4(CO)_{13}PMe_3$

Initial phasing difficulties were overcome by application of an analytical absorption correction. This was necessary because the transmission coefficients ranged from 0.0249 to 0.422. The heavy and light atoms were then easily located, and refined with anisotropic thermal parameters assigned to the osmium atoms only ($R_1=0.051$). At this point the phosphorus and oxygen atoms were allowed anisotropic thermal parameters and attempts were made to locate the hydrogen atoms using Fourier difference synthesis on inner data only. This proved to be a non-trivial matter. Initially only one hydrogen atom could be located. The methyl carbon atoms were allowed anisotropic parameters and two hydrogen atoms were added at calculated positions. Full matrix refinement reduced the R_1 value to 0.047. The weighting scheme was then adjusted and the -5,3,8 reflection which had an anomalously high $\omega\Delta^2$ value of 401 was eliminated from the refinement process. (No other reflection had an $\omega\Delta^2$ value greater than 150.) At this point it was possible to locate two more hydrogen positions from the difference synthesis and consequently calculate the position of the remaining four ($R_1=0.046$). Analysis of low angle strong data revealed several reflections having large $\omega\Delta^2$ values for which the observed structure factors were smaller than the calculated values suggesting the data might suffer from extinction. This, combined with the fact that not all thermal parameters for the oxygen and carbon atoms were well behaved led

to the decision to return to isotropic parameters for these atoms. Full matrix refinement produced an R_1 value of 0.047. Addition of extinction as a refinable parameter reduced the residual R_1 to 0.045. Further investigation of the weighting scheme led to a K value of 0.0006 being assigned. A second attempt at allowing the oxygen atoms anisotropic thermal parameters was made but the results were no better than those of the first trial. It was decided to leave all oxygen and carbon atoms isotropic. The hydrogen atom positions were then recalculated and the structure was refined to completion by full matrix least squares. One large peak ($2.2e/\text{\AA}^3$, 5.6σ) in the final Fourier difference map was located inside the tetrahedron of osmium atoms at a distance of $1.319(1)\text{\AA}$ from Os(4), but there was no evidence to suggest it had any chemical significance.

APPENDIX

Supplemental Tables

Table S.1. Fractional Coordinates for Ru(CO)₄AsPh₃

ATOM	X	Y	Z	BISO
RU	0.35373(4)	0.19970(4)	0.23603(5)	4.57(2)
AS	0.20818(5)	0.31855(5)	0.13740(5)	4.18(2)
C1	0.2193(5)	0.0705(5)	0.2070(6)	6.2(3)
O1	0.1387(4)	-0.0043(4)	0.1941(5)	9.0(3)
C2	0.3699(5)	0.3512(5)	0.4186(6)	5.5(3)
O2	0.3770(4)	0.4417(4)	0.5281(4)	7.0(2)
C3	0.4571(5)	0.1771(5)	0.0764(6)	6.1(3)
O3	0.5152(4)	0.1628(5)	-0.0202(5)	8.7(3)
C4	0.4686(5)	0.1122(5)	0.3134(6)	6.4(3)
O4	0.5392(4)	0.0582(4)	0.3591(5)	9.7(3)
C11	0.1925(4)	0.2555(5)	-0.0744(5)	4.6(3)
C12	0.1768(5)	0.1237(6)	-0.1561(6)	6.3(3)
C13	0.1618(6)	0.0733(6)	-0.3085(6)	7.7(4)
C14	0.1657(6)	0.1601(8)	-0.3737(6)	8.9(6)
C15	0.1809(6)	0.2903(7)	-0.2955(7)	9.3(5)
C16	0.1940(5)	0.3399(6)	-0.1438(6)	6.7(4)
C21	0.2510(4)	0.5048(5)	0.2005(5)	4.8(3)
C22	0.1593(5)	0.5956(5)	0.2319(5)	5.4(3)
C23	0.1908(6)	0.7290(5)	0.2790(6)	6.7(4)
C24	0.3150(7)	0.7693(6)	0.2932(7)	8.2(5)
C25	0.4056(6)	0.6821(7)	0.2627(8)	9.4(5)
C26	0.3747(5)	0.5474(6)	0.2164(7)	7.3(4)
C31	0.0355(4)	0.3147(4)	0.1864(5)	4.2(2)
C32	-0.0632(5)	0.2969(6)	0.0869(6)	6.2(4)
C33	-0.1869(5)	0.2937(7)	0.1231(7)	7.5(5)
C34	-0.2120(5)	0.3095(6)	0.2592(7)	6.8(4)
C35	-0.1163(6)	0.3277(7)	0.3604(6)	8.0(5)
C36	0.0083(5)	0.3305(6)	0.3245(6)	6.7(4)
H12	0.171(4)	0.066(4)	-0.118(5)	8.(0)
H13	0.158(5)	-0.018(5)	-0.365(5)	8.(0)
H14	0.152(4)	0.126(5)	-0.461(5)	8.(0)
H15	0.178(5)	0.359(5)	-0.335(5)	8.(0)
H16	0.207(4)	0.432(4)	-0.089(5)	8.(0)
H22	0.080(4)	0.570(4)	0.221(4)	8.(0)
H23	0.128(4)	0.791(4)	0.305(5)	8.(0)
H24	0.328(4)	0.857(5)	0.332(5)	8.(0)
H25	0.479(5)	0.681(5)	0.247(5)	8.(0)
H26	0.437(4)	0.486(4)	0.189(5)	8.(0)
H32	-0.051(4)	0.286(4)	-0.001(4)	8.(0)
H33	-0.251(4)	0.289(5)	0.060(5)	8.(0)
H34	-0.294(4)	0.308(4)	0.285(5)	8.(0)
H35	-0.128(4)	0.334(4)	0.437(5)	8.(0)
H36	0.067(4)	0.347(4)	0.387(5)	8.(0)

Table S.2. Thermal Parameters for Ru(CO)₄AsPh₃

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ru	5.53(2)	5.80(3)	6.03(3)	0.27(2)	-0.13(2)	2.77(2)
As	5.21(3)	5.55(3)	5.12(3)	-0.02(2)	0.00(2)	2.6(3)
C1	8.4(4)	6.6(4)	8.7(4)	-0.2(3)	-1.2(3)	4.2(3)
C2	5.9(3)	7.5(4)	7.5(4)	0.0(3)	-0.5(3)	3.2(3)
C3	6.1(3)	8.7(4)	8.6(4)	1.2(3)	0.4(3)	3.9(3)
C4	8.2(3)	7.6(3)	8.3(4)	-0.4(3)	-1.4(3)	2.8(3)
O1	10.9(3)	8.3(3)	14.8(4)	-2.8(2)	-1.2(3)	6.0(3)
O2	10.2(3)	8.8(3)	7.9(3)	-0.4(2)	-0.1(2)	-1.0(2)
O3	8.5(3)	14.5(4)	10.0(3)	1.5(3)	3.3(2)	5.2(3)
O4	12.5(4)	11.6(4)	12.8(4)	3.3(3)	-3.2(3)	5.5(3)
C11	4.8(3)	6.7(3)	5.6(3)	0.3(2)	0.5(2)	2.6(3)
C12	9.5(4)	8.5(4)	5.9(4)	-0.4(3)	-0.3(3)	2.3(3)
C13	12.2(5)	10.2(5)	6.8(4)	0.7(4)	0.3(4)	0.7(4)
C14	11.4(5)	16.8(7)	5.6(4)	2.3(5)	1.6(4)	3.4(4)
C15	11.2(4)	16.9(3)	8.2(5)	1.0(5)	1.8(4)	7.5(5)
C16	7.7(4)	10.4(3)	7.2(4)	0.6(3)	1.0(3)	5.0(4)
C21	6.3(3)	6.3(3)	5.6(3)	-0.4(3)	-0.8(2)	3.4(3)
C22	8.0(4)	6.2(3)	6.3(3)	-0.5(3)	-0.1(3)	3.2(3)
C23	11.0(5)	6.7(4)	7.5(4)	0.2(3)	-0.8(3)	3.4(3)
C24	14.2(6)	6.4(4)	10.5(5)	-2.5(4)	-4.2(4)	4.5(4)
C25	8.4(5)	10.4(5)	17.8(5)	-2.9(4)	-3.2(4)	8.3(5)
C26	7.4(4)	7.4(4)	13.0(4)	-1.1(3)	-1.5(4)	5.8(4)
C31	6.1(3)	5.4(3)	4.4(3)	0.4(2)	0.1(2)	1.9(2)
C32	6.0(3)	11.1(5)	6.3(3)	-0.8(3)	0.4(3)	3.3(3)
C33	6.1(4)	13.5(6)	8.7(4)	-0.6(4)	0.5(3)	3.6(4)
C34	5.5(4)	10.3(5)	10.2(5)	-0.4(3)	2.2(3)	2.9(4)
C35	9.9(5)	13.5(6)	7.1(4)	0.5(4)	3.4(3)	4.4(4)
C36	7.3(4)	12.2(5)	5.9(4)	0.4(3)	0.5(3)	3.6(4)

U_{ij} values have been multiplied by 100.

Table S.3. Bond Lengths and Angles for the Phenyl Groups of $\text{Ru}(\text{CO})_4\text{AsPh}_3$

a) Bond Lengths (Å).

C(11)-C(12)	1.357(7)
C(12)-C(13)	1.392(8)
C(13)-C(14)	1.361(10)
C(14)-C(15)	1.337(10)
C(15)-C(16)	1.386(8)
C(16)-C(11)	1.368(7)
C(21)-C(22)	1.374(7)
C(22)-C(23)	1.383(7)
C(23)-C(24)	1.362(9)
C(24)-C(25)	1.339(10)
C(25)-C(26)	1.397(8)
C(26)-C(21)	1.362(7)
C(31)-C(32)	1.356(7)
C(32)-C(33)	1.383(7)
C(33)-C(34)	1.341(9)
C(34)-C(35)	1.344(9)
C(35)-C(36)	1.391(8)
C(36)-C(31)	1.366(7)

b) Bond Angles (°)

C(11)-C(12)-C(13)	121.3(5)
C(12)-C(13)-C(14)	118.0(6)
C(13)-C(14)-C(15)	121.6(6)
C(14)-C(15)-C(16)	120.0(6)
C(15)-C(16)-C(11)	119.9(6)
C(16)-C(11)-C(12)	119.0(5)
C(21)-C(22)-C(23)	121.1(5)
C(22)-C(23)-C(24)	118.8(5)
C(23)-C(24)-C(25)	120.9(5)
C(24)-C(25)-C(26)	120.6(6)
C(26)-C(21)-C(22)	119.1(5)
C(31)-C(32)-C(33)	121.4(5)
C(32)-C(33)-C(34)	120.3(5)
C(33)-C(34)-C(35)	119.7(5)
C(34)-C(35)-C(36)	120.3(5)
C(35)-C(36)-C(31)	120.8(5)
C(36)-C(31)-C(32)	117.6(5)

Table S.4. Structure Factors for $\text{Ru}(\text{CO})_4\text{AsPh}_3$

COLUMNS ARE 10FD,10FC, 10SIG

H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG		
1	201	192	1	-6	132	123	3	2	237	242	3	2	0	82	-6	6	106	101	4	8	420	411	4		
2	892	917	2	-3	249	250	3	3	496	501	4	3	0	89	84	7	89	86	4	9	94	96	6		
3	579	557	2	-2	429	435	5	5	2	152	151	4	2	280	278	8	280	278	4	10	117	123	5		
4	341	346	3	-1	1082	1088	2	6	5	219	214	4	3	300	308	9	87	92	3	1	H, 1,	1	5		
5	793	779	3	0	870	863	2	0	68	68	7	5	5	469	471	H,	164	171	5	-10	105	106	5		
6	522	535	3	1	147	136	2	-6	147	136	2	5	6	86	88	-7	291	302	4	-9	258	263	4		
7	695	690	3	2	374	367	4	-5	374	367	4	6	7	121	114	-6	291	302	4	-8	207	213	4		
8	181	165	4	3	161	169	4	4	161	169	4	8	8	86	86	-5	694	699	3	-7	590	597	3		
9	H, 0,	1	5	-3	310	308	4	-3	310	308	4	4	8	H, 1,	-5	-4	66	64	4	-5	447	444	3		
-10	105	104	5	5	84	87	5	-1	84	87	5	5	-8	218	218	H,	733	731	4	-4	155	134	3		
-9	263	264	4	1	317	318	4	1	317	318	4	4	-7	184	179	0	504	492	2	-3	558	541	2		
-8	490	494	4	6	374	371	4	2	374	371	4	4	-6	103	107	1	529	536	2	-2	259	268	2		
-7	218	231	4	7	331	338	4	2	374	371	4	4	-5	243	244	2	862	850	2	-1	377	375	2		
-6	529	535	5	9	114	111	5	3	198	207	4	4	-4	80	79	4	771	760	2	0	1071	1051	1		
-5	602	594	3	-9	64	59	8	4	199	189	4	4	-3	617	613	3	6	59	59	2	2	208	197	2	
-4	322	314	2	-8	308	299	4	-2	167	162	4	4	-2	131	132	3	7	67	70	6	2	279	274	2	
-3	1331	1333	2	-7	80	72	5	-4	69	49	6	4	-1	481	472	3	8	341	341	3	3	126	133	3	
-2	1328	1333	1	-6	56	60	6	5	0	243	234	5	3	0	106	113	3	9	316	309	4	4	54	43	4
-1	636	599	1	-5	119	120	4	0	1	95	91	3	1	95	91	3	H,	1,	-1	6	254	271	3		
0	954	924	1	-4	431	431	3	1	67	57	6	6	2	138	134	3	94	99	6	7	489	478	4		
1	613	600	2	-3	754	755	3	2	290	290	4	4	3	293	305	3	4	407	406	8	7	210	211	4	
2	622	624	2	-1	1067	1051	2	3	74	57	6	6	6	741	738	3	4	432	433	4	8	233	226	5	
3	186	178	3	0	82	101	3	3	H,	1,	9	4	6	269	268	4	5	371	374	9	9	H, 1,	2	4	
4	555	556	3	1	68	77	3	0	210	203	4	4	6	210	203	4	H,	1,	-4	2	242	236	4		
5	459	458	3	2	296	280	3	2	1	137	142	4	-6	128	127	4	810	803	2	-9	856	857	2		
6	283	282	4	3	666	669	3	1	139	136	5	5	-5	527	527	3	355	364	2	-8	341	348	4		
7	193	197	4	4	495	500	3	3	H,	1,	8	3	-4	690	695	3	452	445	2	-7	262	264	4		
8	116	116	5	5	308	314	3	-3	74	77	6	6	-3	467	465	3	109	85	2	-6	474	471	3		
9	46	35	10	6	390	392	3	-2	118	117	5	5	-2	493	498	3	1	1039	1019	1	-5	104	80	4	
-10	H, 0,	2	5	8	134	139	5	-1	337	338	4	4	-1	96	72	3	2	259	257	2	-2	856	857	2	
-9	135	130	5	-8	117	129	5	0	111	115	5	5	0	214	202	2	3	1156	1151	2	-1	434	436	2	
-8	287	289	4	-6	66	63	6	1	265	261	5	5	1	308	288	2	4	259	247	3	0	792	768	2	
-7	275	283	4	-5	518	525	3	2	88	100	5	5	2	761	769	2	5	67	64	4	1	433	427	2	
-6	122	126	4	-4	76	76	5	4	87	93	5	5	3	497	497	3	7	538	546	3	2	207	196	2	
-5	245	244	3	-3	617	607	3	5	160	158	5	5	4	491	501	3	8	232	238	4	4	363	363	3	
-4	422	417	2	-2	310	317	3	-3	H,	1,	7	4	5	436	433	3	9	337	343	4	5	485	502	3	
-3	813	810	2	1	269	266	3	-2	429	437	4	4	7	91	87	5	10	186	184	5	6	245	258	4	
-2	1577	1571	2	3	108	109	4	-1	257	264	4	4	9	193	182	5	H,	1,	0	7	400	403	4		
-1	613	594	2	4	408	406	3	0	420	409	3	3	-8	129	130	5	H,	1,	-3	5	8	162	171	5	
0	418	409	2	5	238	246	4	1	79	75	5	5	-7	57	60	6	337	335	4	-8	411	411	3		
1	167	174	2	6	95	108	5	3	86	87	5	5	-6	463	463	3	463	463	4	-7	330	333	4		
2	765	774	3	7	H, 0,	6	5	4	253	249	4	4	-5	76	77	4	5	764	766	3	-6	150	154	4	
3	310	302	3	-7	114	111	4	5	221	228	4	4	-4	609	623	3	609	623	3	-5	132	136	3		
4	501	502	3	6	100	106	5	4	206	205	4	4	-3	664	661	2	3	341	325	2	-3	557	552	3	
5	244	246	4	-6	100	106	5	7	281	266	4	4	-2	58	63	3	1	797	799	1	-1	1252	1247	2	
6	99	113	5	-4	486	479	3	0	H,	1,	6	5	-1	366	347	2	0	117	121	1	0	480	483	2	
7	244	246	4	-5	116	111	4	-7	101	104	4	4	0	365	345	2	1	1431	1467	2	1	214	202	2	
8	97	101	6	-3	130	125	4	-5	87	86	5	5	1	574	563	2	2	642	648	2	2	122	119	3	
9	H, 0,	3	4	-2	194	208	3	-4	363	367	3	3	2	76	82	3	4	131	122	3	3	160	166	3	
-9	284	280	4	-1	229	227	3	-3	90	94	5	5	3	818	818	2	5	63	69	4	4	320	330	3	
-8	119	120	5	0	106	101	4	-2	513	510	3	3	4	335	338	3	6	453	454	3	6	578	575	3	
-7	279	271	4	1	212	218	3	-1	269	269	3	3	5	315	308	3	7	115	111	4	7	137	138	4	

COLUMNS ARE 10FD,10FC, 10SIG

COLUMNS ARE 10FO,10FC, 10SIG

H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	
8	172	171	3	-3	160	152	4	0	853	853	3	0	369	351	2	-4	290	297	3	-4	71	80	5	
-9	285	281	4	1	182	190	4	4	49	72	5	1	236	241	2	-3	74	84	4	-3	315	320	3	
-7	355	360	5	2	142	140	5	4	426	430	3	4	206	205	3	-2	159	169	3	-2	821	821	3	
-6	101	100	4	H, 2,-9	H, 2,-9	H, 2,-9	5	5	801	806	3	3	1320	1326	2	-1	285	285	2	-1	821	821	3	
-5	48	41	6	-1	246	240	5	6	53	33	4	4	558	548	3	0	605	597	2	3	198	198	3	
-4	412	418	3	0	102	105	4	7	133	133	4	5	415	402	3	2	1330	1328	2	3	151	147	4	
-3	390	402	3	1	231	232	4	6	H, 2,-4	H, 2,-4	4	6	258	258	3	3	311	307	2	5	253	257	4	
-2	902	908	3	2	193	200	5	-8	322	327	4	8	174	134	5	5	171	177	3	6	499	501	4	
-1	117	113	3	-4	H, 2,-8	H, 2,-8	5	-7	78	70	5	7	194	203	4	5	195	202	3	4	H, 2, 5	H, 2, 5	4	
1	97	87	3	-4	151	151	4	-6	83	75	4	9	192	201	5	6	230	233	4	-4	46	18	6	
2	128	130	3	-2	314	319	4	-5	204	205	3	5	H, 2,-1	H, 2,-1	5	8	383	375	4	-7	170	162	4	
3	233	230	3	-1	153	151	4	-4	211	217	3	3	261	250	5	5	343	337	4	-3	471	481	3	
4	509	512	3	0	458	473	4	-3	832	826	3	3	121	124	5	4	H, 2, 2	H, 2, 2	4	-2	415	414	3	
5	397	401	3	1	126	132	4	-2	260	262	3	3	204	213	4	-8	188	189	4	-1	217	224	3	
6	184	186	4	-1	974	959	4	-6	315	322	3	3	315	322	3	-7	431	432	4	0	361	356	4	
7	269	264	4	2	207	208	4	0	91	108	3	3	681	699	3	-5	110	113	4	2	202	203	4	
-8	184	189	5	5	138	134	5	1	73	70	3	3	140	139	3	-4	644	632	3	3	73	79	5	
-6	109	112	5	2	291	283	4	2	82	70	3	3	1038	1036	2	-3	164	165	3	4	429	435	4	
-5	64	61	6	-5	73	67	4	3	477	484	3	3	911	912	2	-1	798	797	2	5	263	260	4	
-4	458	469	3	-2	278	279	4	4	582	585	3	4	427	411	2	0	694	685	2	6	245	249	4	
-3	362	364	3	-1	505	508	3	6	287	297	3	5	447	450	2	1	283	277	3	7	158	156	5	
-2	351	360	3	0	233	238	4	7	385	386	3	3	986	974	2	2	709	708	3	3	H, 2, 6	H, 2, 6	4	
-1	524	525	3	1	456	463	3	8	58	68	7	2	1389	1384	2	3	218	226	3	4	299	308	4	
0	115	117	4	3	160	166	4	9	H, 2,-3	H, 2,-3	7	3	139	143	5	4	132	127	3	-3	64	52	6	
1	117	114	4	4	160	166	4	5	175	172	5	5	922	894	3	4	456	462	3	6	388	383	4	
2	506	510	3	5	276	278	4	-8	121	122	5	5	192	192	3	5	456	462	3	-1	219	218	4	
3	153	151	4	6	188	179	4	-6	80	84	4	4	349	356	4	7	349	356	4	2	78	70	5	
4	360	356	4	7	64	74	8	-5	459	455	3	3	378	382	4	8	290	299	4	3	322	325	4	
5	259	248	4	-4	H, 2,-6	H, 2,-6	4	-4	199	196	3	3	227	221	4	9	212	201	5	5	236	242	4	
6	257	257	4	-7	281	283	4	-3	575	575	2	2	H, 2, 0	H, 2, 0	7	-9	129	122	5	-5	145	152	5	
-3	553	561	3	-6	78	74	5	-2	846	847	2	2	91	97	5	-8	147	154	5	-3	297	289	4	
-2	163	170	4	-5	116	113	4	-1	114	110	2	2	466	469	4	-7	327	322	4	-1	187	180	4	
-1	105	100	4	-3	330	328	3	0	865	857	3	3	463	456	3	-6	428	432	4	2	231	236	4	
0	442	440	3	-2	368	377	3	1	59	65	3	3	761	760	3	-5	62	60	5	3	178	179	4	
1	149	160	4	-1	682	684	3	2	480	482	2	2	311	327	3	-4	60	56	5	5	H, 3,-9	H, 3,-9	4	
2	400	401	4	0	548	566	3	3	311	290	2	2	208	198	2	-3	90	102	3	0	243	244	4	
3	97	86	5	1	255	258	4	4	949	953	3	3	249	253	2	-2	445	446	3	1	258	274	4	
4	119	127	5	2	183	183	3	5	434	438	3	3	262	264	2	-1	292	282	3	2	215	209	4	
5	81	83	6	4	409	413	3	6	155	163	4	4	682	690	2	0	682	690	2	3	225	215	4	
6	170	176	7	5	213	216	4	7	136	133	4	4	1360	1375	2	1	459	471	3	3	H, 3,-8	H, 3,-8	4	
7	329	327	4	6	328	333	4	8	132	133	5	5	289	277	2	2	210	207	3	3	187	185	5	
8	114	119	5	9	233	232	4	9	234	240	5	5	671	651	3	3	61	53	4	-4	85	82	6	
9	170	178	6	-9	H, 2,-2	H, 2,-2	5	4	141	138	5	5	550	557	3	3	4	233	228	3	-3	142	147	4
10	74	76	7	-8	183	175	4	6	169	165	4	4	147	138	3	4	489	487	3	-1	331	333	4	
11	329	327	4	-7	57	58	6	7	471	480	4	4	87	90	6	6	66	64	6	0	108	110	4	
12	210	206	4	-6	190	198	4	-6	295	294	4	4	453	456	4	7	453	456	4	1	368	367	4	
13	52	57	7	-5	83	93	4	-5	318	318	3	3	305	309	4	8	88	83	6	6	275	281	4	
14	126	122	4	-4	276	277	3	-4	785	791	3	3	H, 2, 1	H, 2, 1	4	8	H, 2, 4	H, 2, 4	4	2	131	135	4	
15	146	145	4	-3	91	81	4	-3	563	557	2	2	279	279	4	4	294	287	5	5	65	67	6	
16	270	271	4	-2	948	958	4	-2	461	458	2	2	75	76	6	-7	129	124	5	6	110	111	5	
17	257	245	4	-1	522	524	3	-1	898	895	2	2	518	524	3	-6	350	348	4	4	H, 3,-7	H, 3,-7	4	

COLUMNS ARE 10FD,10FC, 10SIG

COLUMNS ARE 10FD,10FC, 10SIG

4	H	3	197	198	4	7	309	304	4	SIG	4	H	7	71	73	6	6	6	SIG	6	H	3	2	2	136	147	5	5	5	476	469	3	3	SIG	3			
2	-2	312	318	3	-9	8	125	120	5	5	8	8	9	94	103	5	5	5	5	5	5	8	3	228	2	0	132	147	5	5	5	476	469	3	3	SIG	3	
1	-1	146	139	4	-8	4	436	433	4	4	5	5	9	183	186	5	5	5	5	5	5	5	3	3	3	0	722	723	3	3	3	722	723	3	3	SIG	3	
1	1	573	595	3	-6	4	145	169	4	4	6	6	8	79	73	6	6	6	6	6	6	-8	185	186	4	321	324	4	4	4	300	316	3	3	SIG	3		
2	2	441	443	3	-4	5	97	99	4	4	4	4	-6	342	344	4	4	4	4	4	4	-6	221	212	2	274	280	4	4	4	118	116	4	4	SIG	4		
5	5	253	255	4	-3	3	883	879	2	2	3	3	-5	636	635	3	3	3	3	3	3	-5	437	436	4	4	436	447	4	4	4	135	142	4	4	SIG	4	
6	6	211	205	4	-2	4	683	688	2	2	2	2	-3	811	831	3	3	3	3	3	3	-2	107	103	3	3	141	142	5	5	5	435	447	3	3	SIG	3	
7	7	308	305	4	-1	1	890	879	2	2	2	2	-1	824	831	3	3	3	3	3	3	-1	603	603	4	4	193	184	4	4	4	316	313	4	4	SIG	4	
-7	-7	137	139	5	1	0	91	85	3	3	3	3	0	374	357	2	2	2	2	2	2	0	370	361	3	3	4	8	8	103	107	5	5	SIG	5			
-6	-6	345	339	4	2	2	130	122	2	2	2	2	2	1090	1087	2	2	2	2	2	2	2	4	472	472	4	4	228	228	4	4	4	322	328	4	4	SIG	4
-3	-3	51	56	6	3	3	656	658	2	2	2	2	3	596	596	3	3	3	3	3	3	3	218	222	3	3	86	86	5	5	5	120	112	5	5	SIG	5	
-2	-2	449	455	3	4	4	555	551	3	3	3	3	4	676	659	3	3	3	3	3	3	5	122	126	4	4	181	181	4	4	4	367	371	4	4	SIG	4	
-1	-1	545	549	3	5	5	482	487	2	2	2	2	6	460	473	3	3	3	3	3	3	6	424	430	4	4	160	157	4	4	4	193	200	3	3	SIG	3	
0	0	341	341	3	6	6	479	475	3	3	3	3	8	234	238	3	3	3	3	3	3	7	150	142	5	5	212	213	3	3	3	492	495	3	3	SIG	3	
1	1	457	466	3	3	3	3	3	3	3	3	3	9	343	354	3	3	3	3	3	3	8	256	263	5	5	187	187	4	4	4	492	495	3	3	SIG	3	
2	2	102	98	4	-9	9	269	271	5	5	5	5	3	135	134	4	4	4	4	4	4	-7	296	286	4	4	684	684	2	2	2	681	684	2	2	SIG	2	
4	4	72	65	5	-8	8	189	190	4	4	4	4	-9	127	130	5	5	5	5	5	5	-6	227	219	4	4	223	223	3	3	3	220	223	3	3	SIG	3	
5	5	395	405	4	-7	7	194	199	4	4	4	4	-8	91	92	5	5	5	5	5	5	-5	132	139	4	4	434	434	3	3	3	395	403	3	3	SIG	3	
6	6	165	169	4	-6	6	108	117	4	4	4	4	-7	293	292	4	4	4	4	4	4	-4	105	103	4	4	434	434	3	3	3	432	434	3	3	SIG	3	
7	7	169	161	4	-5	5	549	554	3	3	3	3	-6	83	78	5	5	5	5	5	5	-3	213	212	3	3	144	144	4	4	4	135	144	4	4	SIG	4	
8	8	209	201	5	-4	4	89	88	3	3	3	3	-5	755	762	3	3	3	3	3	3	-2	250	257	4	4	200	200	3	3	3	196	200	3	3	SIG	3	
-8	-8	311	315	4	-3	3	1375	1381	2	2	2	2	-4	528	542	3	3	3	3	3	3	0	795	803	3	3	312	312	3	3	3	304	312	3	3	SIG	3	
-7	-7	296	290	4	-2	2	1089	1084	2	2	2	2	-3	171	180	3	3	3	3	3	3	-3	340	339	3	3	617	617	3	3	3	619	617	3	3	SIG	3	
-6	-6	187	192	4	-1	1	342	335	2	2	2	2	-2	145	149	3	3	3	3	3	3	2	300	303	3	3	78	78	6	6	6	707	78	6	6	SIG	6	
-5	-5	96	98	4	0	0	485	477	2	2	2	2	0	617	607	2	2	2	2	2	2	4	151	144	4	4	199	199	4	4	4	203	199	4	4	SIG	4	
-3	-3	542	546	3	2	2	200	209	2	2	2	2	1	671	665	2	2	2	2	2	2	5	325	323	4	4	434	434	3	3	3	432	434	3	3	SIG	3	
-2	-2	152	151	3	3	3	198	205	2	2	2	2	2	1357	1258	2	2	2	2	2	2	6	138	145	5	5	246	246	4	4	4	242	246	4	4	SIG	4	
-1	-1	712	718	3	4	4	975	973	3	3	3	3	4	97	100	4	4	4	4	4	4	7	377	387	4	4	420	420	4	4	4	410	420	4	4	SIG	4	
0	0	530	533	3	5	5	237	232	3	3	3	3	6	178	182	4	4	4	4	4	4	-6	260	245	4	4	167	167	5	5	5	164	167	4	4	SIG	4	
1	1	110	108	3	6	6	54	42	6	6	6	6	7	307	306	4	4	4	4	4	4	-4	136	131	4	4	73	73	4	4	4	72	73	4	4	SIG	4	
2	2	76	74	4	7	7	60	45	7	7	7	7	8	197	198	5	5	5	5	5	5	-3	194	200	4	4	481	481	3	3	3	468	481	3	3	SIG	3	
5	5	59	55	6	8	8	106	109	5	5	5	5	9	269	259	5	5	5	5	5	5	-2	338	339	3	3	967	967	2	2	2	972	967	2	2	SIG	2	
6	6	483	482	4	9	9	338	238	4	4	4	4	-9	61	51	7	7	7	7	7	7	-1	584	574	3	3	161	161	3	3	3	160	161	3	3	SIG	3	
8	8	157	154	5	-9	9	233	234	5	5	5	5	-8	115	113	5	5	5	5	5	5	0	112	113	4	4	765	765	2	2	2	766	765	2	2	SIG	2	
-9	-9	298	297	4	-7	7	281	285	4	4	4	4	-6	231	229	4	4	4	4	4	4	3	192	185	4	4	146	146	3	3	3	147	146	3	3	SIG	3	
-7	-7	441	435	4	-6	6	344	358	3	3	3	3	-5	413	429	4	4	4	4	4	4	4	134	139	4	4	106	106	3	3	3	120	106	3	3	SIG	3	
-6	-6	151	149	4	-5	5	88	91	4	4	4	4	-4	376	378	3	3	3	3	3	3	6	241	232	4	4	591	591	3	3	3	586	591	3	3	SIG	3	
-5	-5	217	213	3	-4	4	185	185	2	2	2	2	-2	162	169	3	3	3	3	3	3	5	168	172	4	4	284	284	4	4	4	268	284	4	4	SIG	4	
-4	-4	389	390	3	-3	3	645	842	2	2	2	2	-1	122	121	3	3	3	3	3	3	-3	288	287	4	4	354	354	4	4	4	365	354	4	4	SIG	4	
-3	-3	218	229	3	-2	2	327	343	2	2	2	2	0	461	458	2	2	2	2	2	2	0	216	212	4	4	86	86	6	6	6	192	189	4	4	SIG	4	
-2	-2	735	729	3	0	0	330	329	2	2	2	2	1	786	787	2	2	2	2	2	2	-1	194	191	4	4	395	395	5	5	5	390	395	5	5	SIG	5	
-1	-1	110	116	3	1	1	342	343	2	2	2	2	2	175	171	3	3	3	3	3	3	0	216	212	4	4	86	86	4	4	4	87	86	4	4	SIG	4	
0	0	583	582	2	2	2	394	381	2	2	2	2	3	436	448	3	3	3	3	3	3	3	0	68	61	6	6	385	385	3	3	3	57	52	5	5	SIG	5
2	2	215	229	3	3	3	701	682	2	2	2	2	4	177	180	3	3	3	3	3	3	4	206	199	4	4	577	577	3	3	3	566	577	3	3	SIG	3	
3	3	53	55	4	4	4	57	56	3	3	3	3	5	127	133	3	3	3	3	3	3	4	77	74	4	4	385	385	3	3	3	392	385	3	3	SIG	3	
4	4	368	379	3	5	5	352	362	3	3	3	3	6	116	118	3	3	3	3	3	3	-2	289	284	4	4	827	827	2	2	2	823	827	2	2	SIG	2	
5	5	515	518	3	6	6	81	78	5	5	5	5	7	289	287	4	4	4	4	4	4	-1	108	109	5	5	714	714	4	4	4	701	714	4	4	SIG	4	

COLUMNS ARE 10FD,10FC, 10SIG

H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	
3	354	352	4	6	340	331	4	-5	114	119	5	-2	89	82	6	1	292	293	3	
4	124	125	5	7	113	122	5	-1	75	70	6	3	436	430	3	3	512	254	3	
5	222	216	4	8	282	256	5	-3	190	170	5	4	134	141	4	4	194	102	4	
-6	213	204	4	-8	80	84	6	-1	110	119	5	5	191	192	5	-4	165	167	5	
-5	255	242	4	-7	351	341	4	0	89	80	6	-7	105	111	5	-3	170	161	5	
-4	252	251	4	-6	129	130	4	1	120	119	3	3	311	305	4	-2	513	500	4	
-3	389	380	4	-5	347	348	4	2	250	246	3	-1	264	263	4	0	353	357	4	
-2	200	196	4	-4	266	269	3	3	253	251	3	-3	115	109	5	2	89	82	5	
1	405	399	4	-3	70	76	4	4	211	208	4	0	94	79	5	-4	271	269	4	
2	159	158	4	-2	542	551	3	5	429	421	4	2	187	192	4	-3	154	143	4	
3	416	416	4	0	821	817	3	6	82	80	7	3	115	109	5	-2	139	140	4	
4	250	250	4	1	136	138	4	1	131	129	5	4	313	325	4	-1	451	456	3	
5	174	177	4	2	416	410	3	7	131	129	5	4	313	325	4	-1	451	456	3	
H, 6, -6	146	149	3	3	146	149	3	-0	222	210	5	-5	242	228	4	1	494	501	3	
-7	218	215	5	4	66	61	5	-5	204	202	4	3	312	305	3	-3	247	254	3	
-5	349	347	4	5	264	262	4	-4	395	396	4	-3	246	256	4	4	131	134	4	
-4	107	108	5	6	132	134	5	-3	363	358	4	-2	346	345	4	6	154	153	4	
-3	365	366	3	7	424	413	4	-2	208	210	4	-1	73	89	6	H, 7, -2	4	96	103	6
-2	154	157	4	H, 6, -2	4	4	4	-1	433	440	4	2	304	299	4	-7	370	370	4	
-1	130	132	4	8	294	295	5	2	63	68	5	3	273	283	4	-5	397	396	4	
0	397	394	3	-7	88	107	6	3	512	499	3	4	308	308	4	-4	118	110	4	
1	275	278	3	-6	349	346	4	4	352	358	4	5	189	187	4	-3	91	98	4	
2	610	610	3	-3	64	61	4	5	115	119	6	-2	259	265	3	-1	145	149	5	
3	70	71	5	-2	425	425	3	6	212	210	5	-6	298	295	4	-4	410	408	4	
4	320	325	4	-1	801	813	3	6	H, 6, 2	2	7	-4	192	188	4	0	638	638	3	
5	122	132	5	0	340	353	3	3	69	64	4	-3	286	281	4	2	319	327	3	
6	124	120	5	1	553	557	3	7	295	297	4	-5	295	297	4	4	75	79	5	
7	H, 6, -5	212	4	3	34	25	7	-5	119	125	4	-1	147	135	4	6	224	210	4	
-7	207	212	4	4	92	83	4	-3	415	414	4	1	370	359	3	7	235	248	5	
-6	391	385	5	5	485	472	3	-2	400	392	4	3	533	538	4	-7	181	181	5	
-5	95	96	5	6	344	352	4	-1	97	95	5	5	242	241	4	-6	347	346	4	
-4	445	450	5	7	163	164	5	1	76	74	4	-7	168	163	5	-3	100	91	4	
-3	71	75	5	8	214	214	5	2	418	418	4	-7	181	181	5	-1	74	81	6	
-2	132	123	3	H, 6, -1	215	205	5	4	351	343	4	-7	168	163	5	-3	100	91	4	
-1	104	109	4	-8	215	205	5	5	194	198	5	-6	199	201	4	-2	435	432	3	
0	615	611	3	-7	283	276	4	6	H, 6, 3	3	5	-5	426	421	4	-1	411	426	3	
1	554	554	3	-6	66	72	6	-6	171	173	5	-3	358	353	3	0	553	559	3	
2	208	208	3	-5	82	67	5	-4	412	397	4	-2	134	132	4	1	296	288	3	
3	471	463	3	-4	94	96	4	-3	92	88	6	-1	133	137	4	5	254	252	4	
4	110	107	4	-3	388	387	3	-2	239	241	4	0	250	253	3	6	76	74	6	
7	230	234	4	-2	141	140	3	0	239	241	4	0	250	253	3	6	76	74	6	
H, 6, -4	221	214	5	-1	737	744	3	2	62	58	6	1	253	253	3	7	259	233	5	
-8	221	214	5	0	552	556	4	4	2	159	161	2	476	486	4	-7	186	177	5	
-7	185	178	4	1	75	77	4	3	374	375	5	4	355	358	4	-7	177	171	5	
-6	299	298	4	3	108	118	4	5	112	121	5	7	113	111	5	-6	177	171	5	
-5	400	397	3	4	416	425	3	6	H, 6, 4	4	5	-7	250	241	4	-4	82	82	6	
-4	66	60	5	5	73	80	6	-5	219	216	5	-6	300	286	4	-3	368	367	4	
-3	71	69	4	6	375	367	4	-4	153	137	5	-5	245	247	4	-1	556	569	3	
-1	494	504	3	7	197	195	5	-3	219	206	4	-4	429	431	3	0	158	158	4	
0	383	387	3	8	H, 6, 0	0	6	1	299	295	4	-2	85	78	4	1	164	165	4	
1	709	707	3	-8	100	91	6	2	178	167	4	-1	62	71	5	2	101	104	4	
2	541	547	3	-7	224	217	5	3	190	204	5	0	315	320	3	3	172	165	4	

COLUMNS ARE 10FD,10FC, 10SIG

COLUMNS ARE 10FO,10FC, 10SIG

COLUMNS ARE 10FO,10FC, 10SIG

H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	
5	203	193	4	2	364	358	4	-3	76	76	6	-3	111	118	6	0	111	118	6	
-6	234	228	4	6	296	292	5	-2	332	330	4	-1	171	169	4	3	56	41	8	
-4	354	348	4	-6	214	208	5	-1	166	168	4	2	98	85	5	-3	H, 10,	-3	5	
-3	77	67	5	-4	77	79	7	2	201	196	4	3	70	63	6	-2	141	140	5	
-2	265	265	4	-3	89	90	6	3	335	331	4	5	170	166	4	2	250	258	4	
-1	112	113	4	-2	210	208	4	5	H, 9,	181	5	-3	H, 10,	-4	5	2	170	206	5	
0	98	105	5	-1	116	122	5	-5	207	199	4	-2	65	73	7	3	168	193	5	
1	256	258	4	0	441	440	4	-4	329	328	4	-1	175	174	4	0	H, 10,	-2	5	
2	168	170	4	1	282	289	4	-3	439	428	4	-4	139	144	4	0	111	118	6	
3	440	434	4	2	86	93	6	-2	68	62	6	3	336	328	4	3	H, 10,	-3	8	
6	71	71	6	3	55	62	7	1	336	328	4	2	190	211	4	-3	141	140	5	
H, 8,	-4	-4	4	5	285	274	5	3	291	289	4	3	291	289	4	2	250	258	4	
-6	199	191	4	-5	95	82	6	4	199	192	4	4	199	192	4	3	H, 10,	-4	7	
-5	265	264	4	-4	109	104	6	5	72	74	7	5	H, 9,	-2	4	0	156	159	5	
-4	131	127	5	-3	146	134	5	7	275	270	4	-5	275	270	4	5	143	146	5	
-3	381	378	4	-2	87	81	6	-5	148	147	5	-4	148	147	5	4	148	146	4	
0	71	71	5	-1	324	325	5	-3	132	139	5	-2	142	146	4	3	132	135	5	
1	374	374	3	0	77	71	7	-2	142	146	4	-2	136	135	4	2	170	206	5	
2	305	313	4	1	206	209	5	-2	136	135	4	-1	136	135	4	3	168	193	5	
3	212	203	4	4	142	148	5	5	0	348	353	4	0	348	353	4	3	H, 10,	-2	5
4	298	300	4	H, 8,	2	2	4	4	199	192	4	4	199	192	4	-1	175	174	4	
H, 8,	-3	-3	4	-3	196	181	5	5	1	78	82	6	1	78	82	6	0	156	159	5
-6	133	133	5	-2	199	193	5	5	2	357	357	4	2	357	357	4	2	170	206	5
-5	312	314	4	-1	141	143	5	3	49	82	9	3	49	82	9	4	132	135	5	
-4	324	320	4	0	204	191	5	4	132	135	5	4	132	135	5	4	132	135	5	
-3	170	166	4	H, 9,	-7	-7	4	H, 9,	-1	-1	5	H, 9,	-1	-1	5	H, 9,	-1	-1	5	
-2	151	160	4	-3	95	91	5	-4	161	159	5	-4	161	159	5	-4	161	159	5	
0	395	391	3	-2	420	408	4	-3	145	149	4	-3	145	149	4	-3	145	149	4	
1	152	160	4	0	279	272	4	-2	123	124	5	-2	123	124	5	-2	123	124	5	
2	516	525	4	1	102	90	5	-1	97	95	5	-1	97	95	5	-1	97	95	5	
3	324	323	4	3	115	117	5	0	298	303	4	0	298	303	4	0	298	303	4	
4	196	195	4	H, 9,	-6	-6	4	H, 9,	-6	-6	4	1	318	326	4	1	318	326	4	
6	100	96	6	-4	228	221	4	3	174	168	5	3	174	168	5	3	174	168	5	
H, 8,	-2	-2	4	-3	314	300	4	-4	H, 9,	0	4	-4	H, 9,	0	4	-4	H, 9,	0	4	
-6	336	337	4	-2	240	240	4	-4	54	53	9	-4	54	53	9	-4	54	53	9	
-4	333	337	4	-1	315	319	4	-2	48	46	4	-2	48	46	4	-2	48	46	4	
-3	129	138	4	3	248	244	4	-1	243	251	4	-1	243	251	4	-1	243	251	4	
-2	44	46	7	4	132	142	5	0	177	182	5	0	177	182	5	0	177	182	5	
-1	339	347	3	H, 9,	-5	-5	4	1	233	223	4	1	233	223	4	1	233	223	4	
0	219	223	4	-5	221	214	4	2	189	191	5	2	189	191	5	2	189	191	5	
1	536	537	3	-4	129	130	5	H, 9,	1	1	8	H, 9,	1	1	8	H, 9,	1	1	8	
3	270	277	4	-3	339	346	4	-3	77	74	8	-3	77	74	8	-3	77	74	8	
5	158	162	5	-2	214	209	4	-2	211	202	5	-2	211	202	5	-2	211	202	5	
6	162	162	5	-1	208	205	4	0	295	300	5	0	295	300	5	0	295	300	5	
H, 8,	-1	-1	6	0	82	74	6	H, 10,	-6	-6	6	H, 10,	-6	-6	6	H, 10,	-6	-6	6	
-6	122	117	5	1	135	127	4	-2	220	214	4	-2	220	214	4	-2	220	214	4	
-5	270	273	4	2	216	217	4	-1	95	97	6	-1	95	97	6	-1	95	97	6	
-4	70	47	6	4	274	272	4	0	244	243	4	0	244	243	4	0	244	243	4	
-1	257	253	4	H, 9,	-4	-4	4	H, 10,	-5	-5	4	H, 10,	-5	-5	4	H, 10,	-5	-5	4	
0	372	363	4	-5	113	112	6	-3	95	99	6	-3	95	99	6	-3	95	99	6	
1	197	199	4	-4	328	333	4	-2	188	189	4	-2	188	189	4	-2	188	189	4	

Table S.5. Fractional Coordinates for Ru(CO)₄SbMe₃

atom	x	y	z
Ru	0.(-)	0.(-)	0.(-)
Sb	0.(-)	0.(-)	-0.27183(9)
C(1)	0.(-)	0.(-)	0.196(2)
C(2)	-0.206(1)	-0.052(1)	-0.0066(8)
C(3)	-0.176(1)	-0.194(1)	-0.3682(9)
O(1)	0.0(-)	0.0(-)	0.317(1)
O(2)	-0.326(8)	-0.080(1)	-0.0091(9)

Table S.6. Thermal Parameters for Ru(CO)₄SbMe₃

ATOM	U11	U22	U33	U12	U13	U23
RU	4.91(4)	4.91(0)	3.81(9)	2.45(0)	0.00(0)	0.00(0)
SB	5.34(4)	5.34(0)	3.48(7)	2.67(0)	0.00(0)	0.00(0)
C1	7.6(5)	7.6(0)	4.6(6)	3.8(0)	0.0(0)	0.0(0)
C2	6.3(4)	8.8(5)	4.8(3)	4.0(4)	0.1(3)	0.6(3)
C3	6.8(4)	6.6(4)	6.7(5)	2.2(3)	-0.9(3)	-1.7(3)
O1	11.3(6)	11.3(0)	3.9(4)	5.6(0)	0.0(0)	0.0(0)
O2	6.4(4)	15.2(6)	10.7(5)	5.2(4)	0.8(3)	1.4(5)

TEMP=-2(PI)**2(U11*H*H*ASTAR*ASTAR+---+2*U12*H*K*ASTAR*BSTAR+---)

THE UIJ VALUES HAVE BEEN MULTIPLIED BY 100.

Table S.7. Structure Factors for $\text{Ru}(\text{CO})_4\text{SbMe}_3$

COLUMNS ARE 10FO,10FC, 10SIG

K	NFO	FC	SIG	K	NFO	FC	SIG	K	NFO	FC	SIG	K	NFO	FC	SIG	K	NFO	FC	SIG	K	NFO	FC	SIG		
1	186	200	7	9	157	152	8	8	-2, K,	2	9	8	-2, K,	2	9	8	-2, K,	2	9	8	0	46	34	24*	
1	2300	2609	1*	1	727	753	2	11	64	181*	13	0	11, K,	3	3	11	0	1542	1508	2	11	129	142	10	
4	1565	1579	4	4	451	454	3	4	451	454	3	4	10, K,	3	4	4	0	836	866	2	4	3, K,	3	3	
7	732	716	3	13	153	151	9	3	242	255	2	3	-1, K,	2	3	6	6	478	484	4	6	478	484	4	
10	308	316	5	2	196	190	6	6	218	222	4	6	-6, K,	1	6	6	9	185	196	7	9	185	196	7	
2	498	485	3	7	6	K,	1	3	6	K,	1	3	6	K,	1	3	6	6	478	484	4	6	478	484	4
11	180	195	8	11	573	574	3	9	573	574	3	9	70	76	13	12	218	226	7	12	218	226	7		
5	1149	1141	2	14	295	294	13	5	279	274	5	12	58	38	20*	10	352	366	4	10	352	366	4		
8	553	538	4	8	126	124	11	8	126	124	11	8	0,	K,	2	10	181	176	8	10	181	176	8		
11	180	195	8	11	7,	K,	1	1	7,	K,	1	1	419	371	1	13	326	324	2	13	326	324	2		
2	2191	2247	2	3	0	552	533	3	4	326	324	2	4	326	324	2	4	326	324	2	4	326	324	2	
3	1385	1406	2	12	331	356	4	7	204	207	5	8	204	207	5	8	511	491	3	8	511	491	3		
3	695	696	3	6	134	142	10	10	97	80	11	11	11	309	316	11	11	309	316	11	11	309	316	11	
6	288	267	5	10	271	271	5	10	271	271	5	10	1, K,	2	14	128	131	11	14	128	131	11			
9	1861	1854	2	13	151	157	9	1	309	299	7	2	885	844	2	9	-6, K,	3	9	-6, K,	3	9	-6, K,	3	
1	1861	1854	2	13	151	157	9	1	309	299	7	2	885	844	2	9	-6, K,	3	9	-6, K,	3	9	-6, K,	3	
4	861	843	3	5	831	846	2	2	259	252	6	4	259	252	6	4	259	252	6	4	259	252	6		
4	473	467	4	8	573	564	3	5	113	115	12	5	113	115	12	5	113	115	12	5	113	115	12		
10	154	166	9	11	277	274	5	11	277	274	5	11	277	274	5	11	277	274	5	11	277	274	5		
2	1327	1270	2	3	493	513	2	3	493	513	2	3	493	513	2	3	493	513	2	3	493	513	2		
5	628	612	3	6	797	780	2	6	797	780	2	6	797	780	2	6	797	780	2	6	797	780	2		
8	233	237	6	9	358	340	7	12	18	K,	2	12	18	K,	2	12	18	K,	2	12	18	K,	2	12	
3	374	642	5	7	667	650	3	10	61	38	16*	10	61	38	16*	10	61	38	16*	10	61	38	16*		
6	323	325	5	7	667	650	3	10	61	38	16*	10	61	38	16*	10	61	38	16*	10	61	38	16*		
1	768	745	3	13	122	115	11	11	59	33	16*	11	59	33	16*	11	59	33	16*	11	59	33	16*		
4	447	432	4	14	80	19	14	8	5, K,	2	14	8	5, K,	2	14	8	5, K,	2	14	8	5, K,	2	14	8	
7	175	184	9	2	1433	1543	1	7	143	141	6	7	143	141	6	7	143	141	6	7	143	141	6		
2	494	490	4	8	459	456	3	9	116	104	8	9	116	104	8	9	116	104	8	9	116	104	8		
5	249	238	6	11	152	155	8	12	64	47	15*	12	64	47	15*	12	64	47	15*	12	64	47	15*		
0	535	528	4	0	1618	1616	1	7	143	141	6	7	143	141	6	7	143	141	6	7	143	141	6		
3	326	323	5	3	997	1005	2	10	112	109	9	10	112	109	9	10	112	109	9	10	112	109	9		
1	355	346	5	9	292	286	5	13	48	19	25*	13	48	19	25*	13	48	19	25*	13	48	19	25*		
4	168	165	9	12	98	113	14	8	187	188	5	8	187	188	5	8	187	188	5	8	187	188	5		
2	189	198	8	1	1507	1527	2	14	47	24	25*	14	47	24	25*	14	47	24	25*	14	47	24	25*		
0	205	212	7	7	459	468	3	6	188	186	4	6	188	186	4	6	188	186	4	6	188	186	4		
12	148	154	9	10	149	155	9	12	6	18	178*	12	6	18	178*	12	6	18	178*	12	6	18	178*		
13	153	142	9	5	422	428	3	4	367	352	2	4	367	352	2	4	367	352	2	4	367	352	2		
11	240	241	6	8	247	238	5	7	185	187	5	7	185	187	5	7	185	187	5	7	185	187	5		
14	70	109	19*	0	979	969	1	13	56	25	21*	13	56	25	21*	13	56	25	21*	13	56	25	21*		
9	341	330	4	6	631	636	3	5	290	291	3	5	290	291	3	5	290	291	3	5	290	291	3		

COLUMNS ARE 10FO,10FC, 10SIG

COLUMNS ARE 10FO,10FC, 10SIG

K	NFO	FC	SIG	K	NFO	FC	SIG	K	NFO	FC	SIG	K	NFO	FC	SIG
7	3, K, 8	239	6	8	3, K, 9	58	182*	3	240	238	6	3	0, K, 12	247	6
2	4, K, 8	537	4	3	125	131	8	1	270	273	6	3	314	316	5
5	278	279	5	6	111	125	9	4	145	139	9	0	228	232	6
0	541	536	4	1	6	70	184*	2	6, K, 10	6, K, 10	8	1	1, K, 12	179	8
3	350	343	5	4	4, K, 9	166	6	0	2, 181	176	8	4	4, K, 12	272	7
6	202	199	7	7	169	64	24*	0	7, K, 10	7, K, 10	7	1	203	199	7
1	408	410	4	5	5, K, 9	110	10	7	-6, K, 11	-6, K, 11	6	2	2, K, 12	2, K, 12	7
4	226	223	7	0	106	70	45*	7	260	246	6	8	326	310	5
2	229	238	6	3	6, K, 9	126	9	6	236	227	7	4	394	392	4
0	272	266	5	1	7, K, 9	68	16*	4	-4, K, 11	-4, K, 11	5	7	286	288	6
3	185	182	8	2	7, K, 9	46	190*	5	379	378	5	8	323	221	7
1	189	186	8	0	9, K, 9	37	23*	8	223	221	7	3	411	428	4
10	-8, K, 9	46	45*	8	-6, K, 10	10	7	6	339	335	5	6	0, K, 11	0, K, 11	4
8	-7, K, 9	63	18*	6	182	173	7	3	411	428	4	1	513	521	4
9	-6, K, 9	63	175*	9	-5, K, 10	242	6	5	327	316	5	4	382	390	5
7	120	121	9	7	247	242	6	7	234	230	7	2	395	412	4
10	7	47	182*	5	175	162	8	3	472	470	4	5	2, K, 11	2, K, 11	5
5	141	139	7	8	-4, K, 10	194	5	2	330	341	5	0	420	417	5
8	80	86	13	3	322	314	7	4	280	274	6	4	4, K, 11	4, K, 11	5
6	-3, K, 9	119	8	6	433	439	4	0	366	357	5	3	363	363	5
9	122	119	14	9	276	273	9	6	220	219	7	6	3, K, 11	3, K, 11	5
4	-2, K, 9	95	7	4	151	142	9	1	410	417	5	1	410	417	5
7	126	118	8	7	-1, K, 10	10	7	4	280	274	6	4	280	274	6
10	34	45	34*	2	0, K, 10	10	4	2	4, K, 11	4, K, 11	5	2	330	341	5
2	167	163	6	5	354	379	4	1	269	267	6	1	269	267	6
5	165	166	6	8	285	292	5	5	5, K, 11	5, K, 11	6	5	211	195	6
8	80	72	14	0	124	129	10	0	366	357	5	3	216	226	8
0	0, K, 9	9	4	3	462	459	4	1	6, K, 11	6, K, 11	6	1	269	267	6
3	308	303	4	6	300	308	5	5	188	195	8	6	188	195	8
6	109	114	9	3	233	226	6	5	211	195	6	4	224	215	6
9	7	60	191*	1	2, K, 10	10	4	6	-3, K, 12	-3, K, 12	8	4	224	215	6
1	1, K, 9	9	5	4	351	354	5	6	188	195	8	2	265	259	5
4	234	237	7	7	294	290	9	2	265	259	5	5	214	215	7
1	145	147	7	4	143	132	9	4	-1, K, 12	-1, K, 12	5	2	265	259	5
7	76	64	14	2	3, K, 10	10	5	7	214	215	7	5	214	215	7
2	190	187	6	5	291	298	7	0	0, K, 12	0, K, 12	5	5	0, K, 12	0, K, 12	5
5	6	63	171*	0	203	198	7	0	347	350	5	0	347	350	5

Table S.8. Fractional Coordinates for Os(CO)₄SbPh₃

ATOM	X	Y	Z	BISO
OS	0.67903(2)	0.44175(3)	0.21107(2)	3.35(1)
SB	0.82775(3)	0.69625(4)	0.50892(3)	3.13(1)
C1	0.5342(6)	0.4872(8)	0.1543(7)	5.3(3)
C2	0.7344(8)	0.2647(8)	0.1069(7)	6.8(5)
C3	0.5592(7)	0.3104(9)	0.2312(8)	6.5(4)
C4	0.7885(6)	0.5495(7)	0.1677(6)	4.3(3)
O1	0.4473(5)	0.5078(7)	0.1140(6)	8.3(3)
O2	0.7634(7)	0.1558(7)	0.0360(6)	11.7(5)
O3	0.4920(6)	0.2333(9)	0.2420(8)	12.0(5)
O4	0.8507(5)	0.6056(6)	0.1364(5)	7.2(3)
C11	0.7652(5)	0.8940(6)	0.6142(5)	3.9(2)
C12	0.6238(6)	0.8461(8)	0.5595(6)	5.0(3)
C13	0.5798(6)	0.9708(9)	0.6204(7)	6.2(4)
C14	0.6749(7)	1.1420(9)	0.7331(8)	7.8(4)
C15	0.8158(6)	1.1920(7)	0.7904(7)	5.6(3)
C16	0.8601(5)	1.0679(7)	0.7306(6)	4.3(2)
C21	0.8263(5)	0.6416(6)	0.6418(5)	3.8(2)
C22	0.8276(7)	0.7558(7)	0.7808(6)	5.9(4)
C23	0.8282(8)	0.7170(9)	0.8642(8)	8.0(5)
C24	0.8277(8)	0.5698(9)	0.8124(8)	7.7(4)
C25	0.8271(8)	0.4556(9)	0.6753(8)	7.7(5)
C26	0.8266(7)	0.4895(7)	0.5878(7)	5.8(4)
C31	1.0440(5)	0.8531(6)	0.6123(5)	3.1(2)
C32	1.1363(5)	0.9006(7)	0.7390(6)	3.8(2)
C33	1.2762(5)	1.0091(8)	0.8101(6)	4.4(3)
C34	1.3246(5)	1.0726(7)	0.7557(6)	4.3(3)
C35	1.2343(6)	1.0236(8)	0.6285(7)	5.2(3)
C36	1.0945(5)	0.9146(7)	0.5565(6)	4.5(3)
H12	0.551(5)	-0.717(6)	0.471(5)	5.(0)
H13	0.483(6)	0.929(7)	0.577(6)	6.(0)
H14	0.638(6)	1.225(8)	0.771(7)	8.(0)
H15	0.887(6)	1.312(7)	0.868(6)	6.(0)
H16	0.963(5)	1.108(6)	0.773(5)	5.(0)
H22	0.828(5)	0.852(7)	0.813(6)	6.(0)
H23	0.834(6)	0.798(8)	0.955(7)	8.(0)
H24	0.826(6)	0.547(8)	0.868(7)	8.(0)
H25	0.838(6)	0.357(8)	0.640(7)	8.(0)
H26	0.828(5)	0.406(7)	0.488(6)	6.(0)
H32	1.100(5)	0.851(6)	0.769(5)	4.(0)
H33	1.344(5)	1.041(6)	0.897(5)	5.(0)
H34	1.407(5)	1.143(6)	0.798(5)	5.(0)
H35	1.266(5)	1.067(6)	0.593(5)	5.(0)
H36	1.037(5)	0.885(6)	0.471(5)	4.(0)

Table S.9. Thermal Parameters for $\text{Os}(\text{CO})_4\text{SbPh}_3$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Os	4.41(1)	4.59(1)	3.20(1)	1.10(1)	1.11(1)	2.78(1)
Sb	3.38(2)	4.35(2)	3.66(2)	1.65(1)	1.60(1)	2.77(2)
C1	6.2(3)	7.6(4)	6.4(4)	2.6(3)	3.1(3)	5.3(3)
C2	12.2(6)	7.2(4)	6.6(4)	4.9(4)	4.6(4)	5.4(4)
C3	5.9(4)	9.6(5)	9.2(5)	0.8(4)	1.5(4)	7.3(5)
C4	5.9(3)	5.4(3)	4.8(3)	1.9(3)	2.0(3)	3.2(3)
C4	5.9(3)	13.3(4)	11.0(4)	6.0(3)	4.1(3)	9.6(4)
O2	22.4(7)	11.6(4)	10.7(4)	11.8(5)	10.0(5)	8.7(4)
O3	9.1(4)	17.3	19.4(7)	0.6(4)	4.1(4)	15.8(6)
O4	9.5(3)	8.8(3)	8.8(3)	2.2(3)	5.1(3)	6.5(3)
C11	4.8(3)	5.4(3)	4.6(3)	2.9(2)	2.8(2)	3.9(2)
C12	5.2(3)	7.2(4)	6.6(4)	3.3(3)	3.2(3)	4.9(3)
C13	5.7(3)	9.3(5)	8.3(4)	4.7(3)	4.2(3)	6.4(3)
C14	9.3(5)	9.7(5)	10.7(5)	7.3(4)	7.2(4)	8.3(5)
C15	7.7(4)	5.5(3)	7.9(4)	3.6(3)	4.3(3)	4.7(3)
C16	5.3(3)	5.3(3)	5.8(3)	2.8(3)	2.8(3)	3.9(3)
C21	5.1(3)	4.8(3)	4.2(3)	2.5(2)	2.5(3)	3.3(2)
C22	10.9(5)	5.5(3)	6.0(3)	4.6(3)	5.1(4)	4.3(3)
C23	14.1(7)	8.8(5)	7.4(4)	7.0(5)	7.3(0)	6.4(4)
C24	11.4(5)	9.5(5)	8.1(4)	5.7(4)	6.1(4)	7.5(4)
C25	12.5(6)	7.5(4)	9.1(5)	5.8(4)	5.5(4)	6.7(4)
C26	9.9(5)	6.0(3)	6.2(4)	5.0(4)	4.7(3)	4.4(3)
C31	4.0(2)	4.1(2)	3.8(2)	1.9(2)	1.9(2)	2.5(2)
C32	4.4(3)	5.5(3)	4.6(3)	1.4(2)	1.5(2)	3.4(3)
C33	4.7(3)	7.4(4)	4.7(3)	1.9(3)	1.1(2)	4.0(3)
C34	4.1(3)	6.7(4)	5.7(3)	1.5(3)	2.1(3)	3.6(3)
C35	6.0(3)	7.0(4)	7.0(4)	2.6(3)	3.7(3)	5.2(3)
C36	4.9(3)	7.0(4)	5.3(3)	2.5(3)	2.2(3)	4.6(3)

U_{ij} values have been multiplied by 100.

Table S.10. Bond Lengths and Angles for the Phenyl Groups of $\text{Os}(\text{CO})_4\text{SbPh}_3$.

a) Bond Lengths (Å).

C(11)-C(12)	1.392(7)
C(12)-C(13)	1.379(8)
C(13)-C(14)	1.367(10)
C(14)-C(15)	1.384(9)
C(15)-C(16)	1.375(8)
C(16)-C(11)	1.384(7)
C(21)-C(22)	1.371(7)
C(22)-C(23)	1.380(8)
C(23)-C(24)	1.343(9)
C(24)-C(25)	1.359(9)
C(25)-C(26)	1.385(8)
C(26)-C(21)	1.388(7)
C(31)-C(32)	1.379(7)
C(32)-C(33)	1.383(7)
C(33)-C(34)	1.378(8)
C(34)-C(35)	1.365(8)
C(35)-C(36)	1.388(7)

b) Bond Angles (°).

C(11)-C(12)-C(13)	120.1(5)
C(12)-C(13)-C(14)	120.0(5)
C(13)-C(14)-C(15)	120.6(5)
C(14)-C(15)-C(16)	119.5(5)
C(15)-C(16)-C(11)	120.6(5)
C(16)-C(11)-C(12)	119.1(5)
C(21)-C(22)-C(23)	119.4(5)
C(22)-C(23)-C(24)	121.4(6)
C(23)-C(24)-C(25)	119.9(5)
C(24)-C(25)-C(26)	120.6(6)
C(25)-C(26)-C(21)	119.1(5)
C(26)-C(21)-C(22)	119.6(5)
C(31)-C(32)-C(33)	120.5(5)
C(32)-C(33)-C(34)	120.3(5)
C(33)-C(34)-C(35)	119.6(5)
C(34)-C(35)-C(36)	120.5(5)
C(35)-C(36)-C(31)	120.4(5)
C(36)-C(31)-C(32)	118.7(4)

Table S.11. Structure Factors for $\text{Os}(\text{CO})_4\text{SbPh}_3$

COLUMNS ARE 10FO,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	
-13	194	200	8	-3	177	171	7	0	-10	2	L	0	224	223	7	2	558	552	6	
5	233	251	8	-1	404	409	8	4	207	201	8	2	208	207	8	3	788	816	6	
-13	281	277	8	4	298	290	8	5	426	426	6	3	230	242	8	6	579	569	6	
5	188	172	9	5	187	184	10	5	88	80	11	-6	-10	8	7	7	272	285	7	
-13	124	136	11	-1	-11	6	L	3	401	395	7	-4	199	198	7	9	263	244	8	
3	246	250	9	-3	404	405	6	8	99	128	13	-4	225	222	6	-6	100	96	L	
4	165	172	11	-2	164	150	7	9	147	152	10	-3	237	238	6	-5	357	347	6	
5	78	61	16	-1	98	91	7	7	-10	3	L	-2	168	169	8	-4	444	443	6	
-13	109	116	10	3	274	280	9	-4	205	214	7	1	185	187	8	-1	579	585	5	
3	439	426	6	1	345	336	7	-3	343	345	6	-1	225	237	8	0	149	154	6	
-13	304	315	6	4	267	262	9	-2	343	345	6	-7	163	163	8	1	276	271	6	
1	117	129	11	-1	-11	7	L	1	-10	9	L	-10	-10	9	L	2	354	354	6	
-12	280	274	7	-5	151	159	8	8	0	229	225	5	311	313	7	3	308	324	6	
2	114	111	12	-3	172	174	8	1	146	142	7	-3	389	394	7	4	185	194	8	
3	362	349	7	-1	187	179	8	2	502	503	6	-2	218	211	7	5	143	140	8	
6	306	296	7	1	324	314	7	4	198	189	7	0	194	198	9	5	378	389	6	
7	236	252	8	2	369	373	6	1	98	87	12	5	347	348	9	6	237	234	7	
-12	128	114	9	3	128	114	9	2	190	181	9	6	245	254	7	-10	4	L	L	
1	244	251	8	5	405	388	6	-5	304	309	L	7	106	98	13	-6	237	234	7	
3	137	150	10	7	80	83	13	-4	97	91	10	8	193	186	9	-5	204	212	7	
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5	181	177	8	9	-2	274	287	8	-3	441	434	6	1	618	636	-9	542	541	5	
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-12	275	268	7	1	9	9	L	-2	583	581	5	2	2	447	449	0	447	449	5	
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6	210	218	9	-4	336	318	7	3	166	157	7	-4	471	459	5	5	352	352	6	
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COLUMNS ARE 10FO,10FC, 10SIG

COLUMNS ARE 10FO,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	
-5	352	352	6	2	502	501	5	3	3	3	5	-7	128	134	7	1	1366	1378	4	1	128	134	7	
-4	316	304	6	3	167	188	5	3	3	3	6	-6	870	869	5	3	345	335	5	6	564	561	5	
-3	82	63	12	4	796	792	5	4	4	4	6	-5	176	112	6	5	201	196	6	7	271	269	6	
-1	239	231	8	5	721	725	5	5	5	5	6	-4	253	258	6	6	426	426	6	8	267	246	6	
-7	11	L		6	96	102	6	6	6	6	7	-2	343	343	7	9	426	426	6	9	426	426	6	
-10	207	205	7	7	295	306	6	6	6	6	7	0	131	129	6	9	378	376	7	9	378	376	7	
-8	114	121	9	8	584	580	6	-10	1	1	8	1	240	237	8	8	287	288	7	8	287	288	7	
-7	215	173	7	9	159	153	8	-9	2	2	5	2	154	148	10	-7	405	400	6	6	405	400	6	
-6	170	173	8	8	-6	3	L	-8	4	4	5	-6	104	104	9	-6	204	206	6	6	204	206	6	
-5	148	140	9	-9	348	347	7	-7	7	7	6	-11	104	75	9	-5	749	747	5	5	749	747	5	
-3	277	263	8	-8	120	125	8	-8	4	4	4	-10	216	238	7	-4	450	451	4	4	450	451	4	
-7	313	322	7	-7	122	118	8	-4	1	1	5	-9	494	486	6	-3	450	450	4	4	450	450	4	
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-4	166	165	10	-5	198	187	5	-2	5	5	4	-6	245	234	6	-1	234	240	3	3	234	240	3	
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1	159	163	6	-3	899	907	4	0	4	4	5	-2	428	433	7	1	204	201	5	5	204	201	5	
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-1	296	292	4	-3	345	344	4	-11	142	133	7	7	204	193	3	3	254	263	4	4	254	263	4	
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COLUMNS ARE 10FO, 10FC, 10SIG

L	-5	1	3	3	4	-5	1	2	-10	-9	-4	1	1	2	3	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813	814	815	816	817	818	819	820	821	822	823	824	825	826	827	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851	852	853	854	855	856	857	858	859	860	861	862	863	864	865	866	867	868	869	870	871	872	873	874	875	876	877	878	879	880	881	882	883	884	885	886	887	888	889	890	891	892	893	894	895	896	897	898	899	900	901	902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921	922	923	924	925	926	927	928	929	930	931	932	933	934	935	936	937	938	939	940	941	942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961	962	963	964	965	966	967	968	969	970	971	972	973	974	975	976	977	978	979	980	981	982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000
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COLUMNS ARE 10FO, 10FC, 10SIG

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COLUMNS ARE 10FO,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG
4	3	3	6	1	338	330	6	-4	541	521	6	-10	415	416	6	1	802	806	4
4	175	181	6	2	263	252	6	-3	246	247	7	-9	123	127	8	2	789	779	5
6	502	503	6	4	336	335	7	-1	288	271	7	-8	60	68	12	3	484	479	5
7	121	112	10	7	3	7	8	-8	284	288	8	-8	790	782	5	4	79	72	7
8	157	161	9	-12	430	424	7	-3	11, 11, L		8	-8	196	199	5	5	551	563	6
-11	346	340	7	-10	341	344	5	-12	124	120	9	-6	983	987	3	6	65	67	14
-10	238	225	6	-8	570	577	4	-10	182	165	7	-4	865	854	3	7	112	126	13
-9	137	140	7	-7	461	469	4	-11	483	469	6	-5	993	987	3	-2	5, L		
-8	681	676	4	-6	204	203	4	-8	338	335	9	-3	1289	1273	3	-12	198	210	8
-6	650	661	4	-5	1070	1077	4	-7	308	314	6	-1	157	143	3	-11	433	440	6
-5	312	310	4	-4	83	75	8	-4	113	119	9	0	2038	2097	3	-9	632	640	5
-4	606	602	3	-3	288	300	4	-6	379	361	7	3	1239	1256	4	-8	477	473	4
-3	762	754	3	-2	767	752	5	-4	3, 12, L		7	3	505	519	4	-7	518	524	4
-2	325	332	3	-1	529	532	5	-13	209	199	7	4	436	446	4	-6	662	660	3
-1	1143	1118	3	0	282	297	6	-11	163	163	7	5	763	762	5	-5	158	159	4
0	685	672	4	2	514	501	6	-10	184	188	8	6	255	250	6	-4	1086	1092	3
1	1359	1368	4	3	119	127	11	-9	185	184	7	7	391	395	6	-3	59	69	6
2	189	187	5	-3	173	184	8	-8	184	180	7	8	204	199	7	-2	597	595	3
3	121	129	8	-13	173	184	8	-6	310	306	7	9	312	315	8	-1	696	685	4
4	762	770	5	-12	504	500	6	-10	268	276	7	-11	136	132	8	0	613	610	4
5	181	175	7	-10	122	115	7	-9	208	190	8	2	178	164	7	2	215	213	6
6	271	283	7	-9	680	673	5	-7	128	127	10	3	747	754	9	3	176	171	7
7	145	145	10	-8	538	538	5	-9	2, 0, L		10	8	632	616	6	5	176	171	9
-3	692	695	5	-7	196	195	5	-8	396	400	5	6	313	302	8	6	313	302	8
-10	692	695	5	-6	493	500	4	1	1540	1506	2	-7	415	406	4	-13	119	120	9
-9	384	382	5	-5	927	933	4	2	925	884	2	-6	569	565	4	-12	146	158	8
-8	230	224	5	-4	74	74	8	4	1547		3	-5	1230	1235	3	-11	146	158	8
-7	624	624	4	-2	658	658	5	6	342	339	6	-4	238	223	3	-10	77	81	5
-6	884	891	4	-1	313	315	6	7	891	899	5	-3	285	280	3	-9	63	81	10
-5	106	105	5	1	262	256	7	8	604	605	5	-2	1672	1662	2	-8	929	920	4
-4	327	312	3	2	377	387	7	9	197	190	6	-1	951	931	3	-7	589	592	5
-3	1458	1450	3	-3	9, L		9	10	186	182	8	0	164	158	4	-6	703	697	5
-2	696	679	3	-13	184	189	8	11	421	413	7	1	1211	1211	4	-7	666	668	4
-1	100	95	6	-12	390	367	6	-10	-2, 1, L		7	2	1194	1218	4	-4	95	109	9
0	838	837	4	-11	171	175	6	-8	471	471	7	3	170	179	5	-3	344	344	6
1	972	983	5	-10	121	117	7	-7	112	106	8	4	135	134	7	-6	350	344	6
2	110	118	9	-9	521	520	5	-7	845	840	5	5	961	959	5	-5	577	579	3
3	121	115	8	-7	379	370	5	-6	864	855	4	6	174	180	7	-4	1532	1522	4
4	554	554	6	-6	346	351	5	-5	381	376	4	7	109	121	10	-1	1094	1107	4
5	154	163	9	-5	387	376	5	-4	429	431	4	8	352	364	8	0	552	541	5
-3	6, L		6	-4	397	402	5	-3	1925	1942	3	-2	4, L		4	1	250	257	6
-11	103	108	9	-3	103	90	9	-2	444	439	2	-12	404	399	7	2	396	404	6
-10	708	702	5	-2	335	339	6	-1	444	421	2	-10	90	101	10	3	597	591	6
-9	95	92	8	-1	74	74	12	0	1859	1885	2	-9	866	865	5	-13	182	180	7
-8	355	350	4	0	293	288	7	1	1428	1465	3	-8	234	243	5	-12	291	290	6
-7	708	717	4	1	125	104	09	2	142	128	5	-7	240	239	4	-11	554	552	5
-6	843	835	4	-3	10, L		4	3	886	887	3	-6	1254	1258	3	-10	246	240	5
-5	357	369	4	-11	448	445	5	-5	1177	1164	3	-8	923	923	4	-8	923	923	4
-4	177	176	4	-10	254	253	6	5	75	51	9	-4	245	245	4	-7	426	428	4
-3	732	733	4	-9	99	95	7	7	793	804	5	-3	201	207	3	-6	405	410	4
-2	57	65	8	-8	380	377	5	8	268	263	6	-2	1689	1669	7	-5	537	529	8
-1	413	409	5	-7	544	537	5	9	205	218	7	-1	421	389	3	-4	769	766	4
0	515	523	5	-6	112	116	8	10	218	221	9	0	439	436	4	-3	454	451	4

COLUMNS ARE 10FO,10FC, 10SIG

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L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG
-9	478	484	5	-6	1303	1277	3	-13	257	248	7	-14	82	86	11	-10	403	399	6
-8	323	323	6	-4	1538	1518	3	-12	145	151	2	-11	368	360	6	-8	112	88	9
-7	220	207	6	-2	435	424	2	-10	730	731	5	-12	337	336	6	-7	312	306	7
-6	222	213	7	-2	330	326	2	-10	2073	2110	3	-12	257	237	5	-6	305	307	7
-5	459	445	6	-1	2073	2110	3	-9	156	154	5	-11	257	237	5	-6	305	307	7
-5	162	175	8	0	811	791	3	-8	65	79	8	-11	257	237	5	-6	305	307	7
-13	310	307	7	2	1420	1444	4	-7	1185	1195	4	-10	236	239	5	-1	13	13	L
-12	355	356	6	3	1181	1195	4	-6	578	572	3	-9	708	713	4	-12	106	115	10
-8	152	157	7	4	548	543	5	-5	436	440	4	-8	123	122	6	-11	92	99	11
-6	179	185	9	5	284	292	5	-4	928	911	3	-7	194	192	6	-10	298	295	7
-5	222	229	8	6	855	860	5	-3	1255	1250	3	-6	681	679	4	0	0	0	L
-5	222	229	8	6	855	860	5	-3	1255	1250	3	-6	681	679	4	0	0	0	L
-2	70	84	14	9	306	308	8	-1	191	182	4	-5	288	280	5	1	658	627	2
-12	197	201	7	-12	341	336	7	0	931	947	4	-4	473	465	5	2	1028	982	2
-9	142	129	8	-11	241	250	7	2	285	287	6	-2	422	424	6	3	1834	1856	3
1	1703	1778	2	-10	337	329	6	3	294	282	6	-1	232	255	7	5	518	511	4
3	119	103	3	-9	213	214	6	4	329	334	7	1	248	243	7	7	946	943	5
3	973	936	3	-8	784	783	4	5	172	178	9	9	199	211	7	8	162	152	7
4	635	633	3	-7	182	185	5	5	1	6	L	-14	199	211	7	9	100	98	11
5	772	769	4	-6	401	404	3	-12	361	365	6	-13	220	222	7	10	384	376	7
6	539	544	4	-5	879	881	3	-11	275	278	6	-12	83	88	10	0	1	L	L
7	122	135	7	-4	248	227	3	-10	346	339	5	-11	601	610	5	-11	400	395	7
8	526	523	5	-3	614	594	2	-9	579	576	4	-9	167	159	6	-10	352	350	6
10	290	299	7	-2	161	156	6	-8	163	162	5	-8	633	627	5	-9	244	251	6
-1	163	183	9	-1	495	485	3	-7	580	586	4	-7	343	340	5	-8	231	220	6
-9	219	217	7	0	606	602	3	-6	234	232	4	-6	267	272	5	-7	894	891	4
-8	588	584	5	-2	800	797	4	-4	396	400	4	-4	671	663	5	-4	1044	1017	3
-7	264	269	5	3	115	99	7	-3	49	47	8	-1	438	435	6	-3	1508	1498	2
-6	486	493	4	4	801	810	5	-2	918	927	4	0	202	197	8	-2	895	866	2
-5	514	502	4	5	109	112	9	-1	174	182	6	-14	178	177	7	0	516	474	1
-4	1196	1188	3	6	295	290	6	0	363	356	5	-13	78	72	10	1	1261	1268	3
-3	396	366	3	7	355	349	7	1	420	421	6	-12	318	325	6	2	676	637	4
-2	472	463	2	8	183	203	10	2	538	531	6	-11	543	552	5	3	1110	1108	3
-1	1782	1790	2	-1	4	L	8	2	-1	7	L	-11	599	595	5	5	688	676	4
0	833	818	2	-12	170	167	8	-14	151	161	9	-8	599	595	5	5	688	676	4
1	530	532	3	-11	208	187	7	-13	340	336	6	-7	208	216	6	6	320	327	5
2	1261	1279	3	-10	710	692	5	-12	561	558	6	-6	229	232	6	7	443	434	4
3	1712	1722	3	-8	336	339	4	-11	239	232	5	-5	333	327	6	8	336	340	7
4	378	386	4	-7	1090	1098	4	-10	156	158	6	-5	457	455	9	9	227	229	8
5	85	98	7	-6	890	881	3	-9	1020	1023	4	-1	299	296	8	0	2	L	L
6	938	950	5	-5	396	407	3	-8	368	369	4	-1	11	11	L	-1	229	229	7
7	254	251	6	-4	718	703	3	-7	186	192	4	-13	171	177	7	7	590	595	5
8	118	131	8	-3	1364	1346	3	-6	1064	1047	4	-12	173	168	7	7	131	116	6
9	395	390	7	-2	118	114	4	-5	1046	1045	4	-11	217	212	6	-7	309	319	4
-11	415	399	7	0	1247	1263	4	-4	204	219	5	-10	216	220	7	7	960	949	3
-10	121	116	8	2	860	849	4	-3	283	292	5	-9	107	102	9	6	976	952	3
-9	197	195	6	3	449	459	5	-2	1038	1047	5	-8	240	240	10	-4	241	235	3
-8	1047	1028	5	4	827	823	6	0	143	143	8	-7	99	108	10	-3	1214	1187	2
-7	317	319	4	5	78	56	12	1	468	487	6	-6	235	235	7	-2	2146	2142	2

COLUMNS ARE 10FD,10FC, 10SIG

COLUMNS ARE 10FD,10FC, 10SIG

-5	1331	1319	3	82	1013	86	8	1	124	109	3, L	2	-9	435	439	5	3	227	229	7	7	199	209	8	SIG		
-4	1336	1343	3	-6	485	487	4	0	288	273	3	3	-7	1010	995	4	4	171	158	9	9	369	364	7	FC		
-2	172	182	3	-5	209	202	5	2	1856	1885	3	3	-6	432	428	3	5	306	288	8	8	1, 10, L	1, 10, L	6	L		
-1	1349	1357	4	-3	639	636	5	3	775	750	3	3	-5	329	332	3	-13	425	433	6	6	116	109	8	SIG		
0	376	375	5	-2	769	757	5	4	615	602	4	4	-4	1647	1611	3	-12	364	370	5	5	11	10	6	FC		
1	90	93	9	0	488	481	8	6	377	383	4	4	-3	1575	1560	3	-11	130	125	7	7	153	170	6	SIG		
2	785	785	5	1	129	128	9	9	943	946	5	5	-2	402	386	2	3	565	579	4	4	142	153	7	FC		
3	541	538	6	0	9, L			1	505	501	7	7	-1	382	379	3	3	1069	1072	4	4	306	301	5	L		
4	119	127	9	-14	377	385	6	-11	304	287	7	7	0	1457	1490	4	4	175	178	5	5	197	196	7	SIG		
5	159	148	10	-13	84	85	10	-10	163	158	7	7	1	196	204	5	5	95	88	5	5	156	157	8	FC		
-13	110	106	9	-12	228	224	6	-9	406	396	6	6	3	226	236	5	-6	1072	1068	4	4	265	272	7	SIG		
-12	540	531	5	-11	302	300	5	-8	864	871	5	5	4	794	809	5	-5	484	490	4	4	263	252	7	FC		
-11	550	560	5	-10	457	469	5	-5	235	225	4	4	5	664	674	6	6	267	262	4	4	1, 11, L	1, 11, L	7	L		
-10	240	239	5	-9	328	328	5	-6	1344	1339	3	3	6	149	164	10	-2	1033	1034	5	5	148	164	8	SIG		
-9	420	418	4	-5	736	721	5	-4	450	643	3	3	7	416	422	8	8	718	708	6	6	180	181	7	FC		
-8	988	989	4	-4	347	339	6	-2	354	329	2	2	1, 4, L				2	249	241	7	7	205	209	7	SIG		
-7	54	49	8	-3	309	328	7	-1	2005	2086	2	2	-13	81	66	11	3	121	116	11	11	460	457	6	L		
-6	180	179	4	-2	317	328	7	0	161	147	3	3	-12	76	93	12	12	1, 7, L		6	6	439	426	6	FC		
-5	978	970	3	0	208	213	8	1	596	597	3	3	-11	593	592	5	5	585	601	5	5	176	195	9	SIG		
-4	579	578	4	0, 10, L				2	1759	1799	4	4	-10	496	493	5	-12	233	233	6	6	106	104	11	FC		
-3	546	542	4	-14	175	177	7	3	611	609	4	4	-9	169	168	5	-11	393	401	5	5	147	148	10	L		
-2	381	372	5	-13	208	207	6	4	476	466	4	4	-8	607	607	4	-10	513	511	5	5	1, 12, L	1, 12, L	10	SIG		
-1	893	916	5	-12	345	346	6	5	671	669	5	5	-6	1590	1601	3	-9	735	736	4	4	322	316	6	FC		
0	182	177	6	-11	141	133	7	6	784	785	5	5	-5	121	123	3	-8	375	376	4	4	302	304	6	SIG		
1	221	229	7	-9	631	622	5	7	110	111	9	9	-4	1371	1360	3	-6	1070	1075	4	4	128	136	9	FC		
2	497	504	6	-8	168	174	7	9	410	406	8	8	-3	895	884	3	-4	349	339	5	5	328	306	7	L		
3	111	114	11	-7	154	163	7	1, 2, L			7	7	-2	674	652	3	-3	521	529	5	5	2, 0, L	2, 0, L	7	SIG		
4	269	273	8	-6	440	437	6	-12	421	414	7	7	-1	599	606	4	-2	446	442	5	5	1807	1907	2	FC		
-14	134	156	7, L	-5	397	385	6	-11	102	93	9	9	0	1411	1436	4	-1	363	379	6	6	1082	1060	3	L		
-13	223	228	10	-4	118	111	9	-10	280	285	6	6	2	166	143	7	1	455	446	6	6	2	105	115	5	SIG	
-12	417	422	5	-3	160	156	9	-9	566	559	5	5	3	643	646	6	-13	248	248	6	6	3	1458	1453	4	FC	
-10	708	700	5	-2	375	375	7	-8	777	765	4	4	5	299	294	7	-12	320	322	5	5	5	554	544	5	L	
-9	111	103	6	0, 11, L				-7	402	401	6	6	6	126	122	11	-10	324	325	5	5	6	655	643	6	SIG	
-8	404	411	6	-13	371	369	6	-6	69	58	3	3	1, 5, L			8	-8	656	654	4	4	7	356	346	6	FC	
-7	654	653	4	-11	102	115	8	-4	843	828	2	2	-13	131	119	8	8	585	574	5	5	2, 1, L	2, 1, L	6	L		
-6	599	608	4	-10	245	242	7	-3	1098	1066	2	2	-12	132	131	8	8	370	365	6	6	392	388	6	SIG		
-5	499	504	4	-9	542	550	5	-2	680	656	2	2	-11	587	589	5	-5	585	574	5	5	2, 1, L	2, 1, L	6	FC		
-4	201	217	5	-7	81	102	12	-1	952	941	2	2	-10	253	249	5	-4	565	562	5	5	296	311	7	L		
-3	860	844	5	-6	389	378	6	0	708	708	3	3	-9	686	689	4	-3	166	168	7	7	180	187	7	SIG		
-1	116	112	9	-5	220	205	8	1	154	149	5	5	-8	115	107	5	-2	106	94	10	10	455	460	5	FC		
1	240	226	7	-4	134	140	10	2	943	969	4	4	-7	552	562	3	-1	512	516	7	7	323	324	5	L		
2	165	153	8	0, 12, L				3	194	192	5	5	-6	663	655	3	1	101	103	11	11	218	228	5	SIG		
3	199	175	8	-13	235	233	7	4	588	583	5	5	-5	532	517	3	3	1, 9, L		4	4	1160	1160	4	FC		
0	414	427	6	-12	65	64	13	5	445	439	6	6	-4	530	537	3	-12	498	510	5	5	250	255	4	L		
-14	414	427	6	-11	271	265	7	6	210	208	7	7	-3	91	89	6	-11	389	399	5	5	4	862	839	3	SIG	
-13	317	324	6	-9	166	150	7	7	478	469	6	6	-2	824	825	4	-9	295	283	5	5	-3	643	626	2	FC	
-12	106	116	9	-8	209	200	7	1, 3, L			5	5	-1	267	259	5	-8	692	694	5	5	-2	801	781	2	L	
-11	438	428	5	-7	118	115	11	-12	252	239	7	7	0	320	336	5	-5	699	687	5	5	-1	1127	1077	2	SIG	
-10	689	695	5	-11	312	322	7	-10	462	457	5	5	-10	674	682	6	-4	414	398	6	6	0	281	272	4	FC	
																										3	L

COLUMNS ARE 10F0,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG
2	337	335	4	-9	284	278	5	-7	1030	1035	4	4	282	282	6	1	754	768	6	6	233	226	7
3	197	207	5	-8	860	864	4	-5	145	153	6	6	412	413	8	-14	445	445	6	8	445	445	6
4	765	769	5	-7	84	75	6	-4	945	942	5	5	758	763	7	-11	65	71	11	5	65	71	11
5	687	683	5	-6	75	60	6	-3	638	641	5	5	758	763	7	-11	65	71	11	5	65	71	11
6	226	210	6	-4	1600	1576	3	-2	222	224	7	7	312	312	5	-10	851	846	4	5	851	846	4
7	165	169	8	-4	721	714	3	-1	275	267	6	6	223	223	5	-9	568	577	4	5	568	577	4
8	529	525	7	-3	488	484	3	0	559	548	6	6	848	852	4	-8	346	345	4	4	346	345	4
-12	94	98	11	-2	912	894	4	-8	344	328	7	7	1093	1085	3	-7	619	608	4	3	619	608	4
-11	96	103	10	-1	1369	1408	4	-15	187	187	7	7	185	182	4	-6	1078	1076	4	4	1078	1076	4
-10	532	521	5	2	936	932	6	-11	444	454	6	6	149	149	5	-4	194	193	5	5	194	193	5
-9	662	669	5	3	312	317	6	-10	560	557	5	5	1792	1769	3	-4	138	127	6	3	138	127	6
-8	147	145	6	4	223	210	7	-9	242	241	5	5	352	347	3	-3	873	873	5	3	873	873	5
-7	389	381	4	5	258	252	8	-8	328	316	5	5	181	189	4	-2	251	254	6	4	251	254	6
-6	1468	1460	3	2	722	726	4	-7	722	726	4	4	1270	1270	4	-1	307	313	6	4	307	313	6
-5	308	304	3	-12	761	775	5	-6	110	98	4	4	822	838	7	0	306	302	7	7	306	302	7
-4	423	413	3	-11	325	337	5	-5	97	104	9	9	204	201	5	1	406	385	7	5	406	385	7
-3	2269	2261	2	-10	820	294	4	-4	523	529	7	7	715	727	6	2	139	150	11	6	139	150	11
-2	1128	1101	2	-9	817	820	5	-2	343	349	7	7	129	120	10	-14	205	201	7	7	205	201	7
-1	667	657	3	-8	1104	1109	4	-1	190	185	8	8	327	331	8	-13	289	309	6	6	289	309	6
0	1113	1120	4	-7	458	447	4	0	222	226	8	8	331	331	4	-12	291	283	6	6	291	283	6
1	1408	1451	4	-6	201	203	4	-6	201	203	4	4	147	145	8	-11	189	190	6	6	189	190	6
2	187	185	5	-5	1410	1407	3	-4	161	152	7	7	479	479	5	-10	465	470	5	5	465	470	5
3	93	94	8	-4	388	386	6	-13	358	353	6	6	218	223	5	-9	114	121	6	6	114	121	6
4	845	850	5	-3	569	553	4	-12	177	195	6	6	363	371	4	-8	618	606	4	4	618	606	4
5	446	447	6	-2	770	768	4	-11	230	237	6	6	695	705	3	-8	187	181	5	5	187	181	5
6	251	259	7	-1	796	805	5	-10	174	180	5	5	711	707	3	-6	277	281	5	5	277	281	5
7	202	186	8	0	356	357	8	-9	531	537	5	5	625	632	3	-5	715	713	5	5	715	713	5
-13	358	366	7	2	612	608	6	-7	148	140	6	6	186	186	4	-4	335	342	6	6	335	342	6
-12	117	110	9	4	173	164	9	-6	573	566	5	5	1047	1047	3	-3	370	368	6	6	370	368	6
-11	182	181	7	2	6	6	7	-5	331	328	6	6	628	628	4	-2	297	302	6	6	297	302	6
-10	698	696	5	-14	190	194	4	-4	206	206	7	7	605	605	5	-1	503	504	7	7	503	504	7
-9	451	452	5	-12	447	464	5	-3	211	205	8	8	282	282	5	0	202	200	6	6	202	200	6
-8	473	476	4	-11	148	147	7	-2	362	380	7	7	634	639	6	1	634	639	6	6	634	639	6
-7	414	413	4	-10	536	542	5	-2	2	10	10	10	324	324	8	3	329	328	7	7	329	328	7
-6	1584	1579	3	-9	509	506	4	-13	463	476	6	6	257	257	8	4	246	257	8	8	246	257	8
-5	476	461	3	-8	160	173	5	-12	189	198	6	6	3	3	5	3	3	3	5	5	3	3	5
-4	1019	992	3	-7	815	817	4	-11	109	101	8	8	46	46	6	-14	74	74	6	6	74	74	6
-3	1625	1615	3	-5	582	583	4	-10	464	463	5	5	481	481	6	-13	473	481	6	6	473	481	6
-2	170	163	4	-4	429	422	4	-9	507	519	8	8	135	135	8	-5	703	704	5	5	703	704	5
-1	537	944	4	-3	694	698	5	-8	101	104	8	8	212	212	5	-4	198	202	7	7	198	202	7
0	326	323	5	-2	425	427	5	-7	97	83	9	9	467	467	4	-4	144	147	8	8	144	147	8
1	464	472	5	0	660	659	6	-6	444	437	6	6	697	697	4	-2	366	369	7	7	366	369	7
2	545	545	5	3	215	219	8	-4	79	76	12	12	338	338	4	-1	325	320	7	7	325	320	7
3	276	278	6	3	313	296	8	-3	267	276	8	8	77	77	6	-7	81	77	6	6	81	77	6
4	340	337	7	2	7	7	7	-4	1401	1396	3	3	1343	1343	4	-6	1335	1343	4	4	1335	1343	4
5	111	102	10	-14	427	421	6	-13	361	361	6	6	224	224	3	-5	234	224	4	4	234	224	4
6	350	336	7	-13	132	145	8	-11	221	224	7	7	138	138	5	-13	134	137	8	8	134	137	8
-13	149	157	9	-11	603	616	5	-10	310	303	6	6	1022	1022	4	-3	1025	1022	5	5	1025	1022	5
-12	432	421	6	-9	568	566	5	-8	127	131	9	9	614	614	5	-2	300	290	6	6	300	290	6
-11	352	351	5	-8	396	397	4	-6	241	238	8	8	371	371	6	0	371	371	6	6	371	371	6

COLUMNS ARE 10F0,10FC, 10SIG

COLUMNS ARE 10FO,10FC, 10SIG

COLUMNS ARE 10FO,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG
-7	253	245	6	-8	294	297	4	-8	118	111	6	-2	261	252	7	-5	381	382	7	-4	268	262	5
-5	388	385	6	-7	881	881	3	-8	795	803	4	-6	536	542	10	-6	720	717	4	-3	803	798	5
-3	172	172	10	-6	536	542	10	-5	555	549	3	-5	555	549	3	-6	720	717	4	-1	148	155	8
-2	210	213	9	-5	555	549	3	-6	384	369	4	-4	384	369	4	-5	647	643	4	0	514	513	7
-1	364	357	6	-4	371	370	4	-3	1213	1198	3	-4	871	856	4	-10	551	559	5	1	313	316	7
-14	323	334	6	-3	1213	1198	3	-4	371	370	4	-3	210	207	6	-9	324	324	6	2	160	158	10
-12	145	152	8	-2	371	370	4	-2	608	622	5	-8	243	235	6	-8	243	235	6	6	282	288	6
-10	297	310	6	0	864	888	5	-1	173	188	7	-7	229	226	6	-7	229	226	6	6	158	158	8
-9	152	159	8	1	344	355	5	0	503	499	6	-6	556	565	6	-6	556	565	6	6	245	245	6
-8	145	134	7	2	605	626	5	1	214	219	8	-3	370	368	7	-13	170	163	7	8	125	125	7
-7	408	407	6	4	531	520	6	2	142	125	9	-3	370	368	7	-13	170	163	7	8	121	121	7
-5	97	106	12	5	148	143	8	3	353	356	8	-13	284	292	7	-11	491	498	5	-9	250	254	5
-4	295	291	8	6	205	207	9	4	353	356	8	-13	284	292	7	-11	491	498	5	-9	250	254	5
-3	11	11	8	4	3	4	3	14	351	339	9	-14	351	339	9	-14	351	339	9	4	338	344	5
-11	329	332	7	-12	492	491	6	-13	96	109	6	-13	169	177	7	-8	1045	1047	5	-7	412	400	5
-11	428	415	6	-11	162	162	7	-11	565	578	5	-8	260	260	6	-7	246	233	4	-5	536	529	5
-10	246	251	7	-10	445	447	5	-10	326	328	5	-8	260	260	6	-7	246	233	4	-4	169	162	7
-8	213	201	7	-9	506	506	4	-9	191	202	5	-7	238	231	7	-5	611	602	4	-3	302	308	6
-7	347	334	7	-8	747	749	4	-8	590	589	4	-5	200	206	9	-4	705	696	4	-2	350	348	7
-3	12	12	7	-7	582	587	4	-7	885	888	4	-5	200	206	9	-4	705	696	4	-1	189	209	8
-11	241	234	7	-6	165	159	4	-6	111	120	6	-12	276	286	7	-1	744	741	5	0	244	249	8
0	506	508	4	-4	143	138	4	-4	244	244	5	-11	101	107	10	-1	744	741	5	7	161	164	8
1	1524	1516	4	-3	317	311	4	-4	993	994	5	-9	266	260	7	1	477	472	6	-13	165	169	8
2	257	250	4	-2	1035	1028	4	-2	212	210	6	-8	312	310	7	2	336	342	7	-12	588	598	5
3	125	131	5	-1	663	688	5	-1	506	511	6	0	247	257	5	4	335	326	8	-10	122	125	7
4	997	987	5	1	366	371	5	0	440	441	6	0	247	257	5	4	335	326	8	-9	676	681	5
5	337	335	5	1	278	269	6	1	118	108	10	2	596	579	4	-14	127	136	10	-7	235	228	5
6	378	381	6	2	783	784	6	2	783	784	6	3	506	498	5	-13	314	306	6	-6	278	268	5
7	245	235	7	5	435	430	7	-14	308	309	6	5	572	568	6	-12	109	115	9	-5	636	631	5
8	409	403	8	4	4	4	4	-13	84	93	11	7	193	179	8	-10	611	616	5	-2	484	476	7
-10	712	702	6	-12	605	605	6	-12	206	211	6	-12	178	175	8	-9	147	155	5	-1	221	236	9
-9	381	373	5	-10	185	193	6	-10	149	157	6	-11	653	657	5	-8	425	421	4	-14	104	85	9
-8	158	164	5	-9	888	888	4	-9	77	82	8	-9	367	366	6	-7	631	619	4	-13	279	295	7
-7	902	886	4	-8	660	669	4	-8	633	630	5	-8	467	470	5	-6	953	955	4	-12	447	458	6
-6	1304	1289	4	-7	410	410	4	-7	514	521	5	-7	552	544	4	-4	176	178	5	-11	157	168	7
-5	286	271	4	-6	805	781	4	-6	316	305	5	-6	470	474	4	-3	1090	1091	5	-9	571	581	5
-4	197	190	3	-5	1412	1416	4	-4	641	644	5	-4	869	861	3	-2	242	244	6	-7	167	181	7
-3	1685	1664	3	-4	160	155	5	-2	184	186	6	-2	519	517	3	-1	264	275	6	-6	429	412	6
-2	766	748	3	-3	54	57	11	-1	361	355	7	-1	850	838	4	0	512	514	6	-5	381	386	6
-1	292	311	3	-2	1041	1047	5	0	165	170	10	0	679	701	5	1	535	538	6	-4	158	156	9
0	1286	1323	4	-1	504	513	4	4	4	8	10	1	474	479	5	2	121	127	11	-14	242	239	7
1	1188	1211	4	0	253	245	6	-15	227	230	7	1	338	339	5	5	340	340	6	-13	167	165	7
2	171	173	6	1	413	415	6	-14	141	140	8	3	780	783	6	-14	340	340	6	-13	167	165	7
3	211	223	6	2	598	594	6	-13	333	335	6	5	165	166	8	-13	391	388	7	-12	114	115	9
4	707	712	5	3	119	110	10	-10	280	287	6	6	403	397	7	-11	224	231	5	-11	405	407	6
6	127	120	9	4	4	5	4	-10	360	372	5	5	5	2	8	-10	754	767	5	-10	99	115	9
7	375	383	8	-14	170	174	8	-9	363	382	5	5	2	193	193	8	265	268	6	-8	260	263	6
-11	163	165	7	-13	203	208	7	-8	222	224	6	-11	606	604	6	-8	169	168	5	-8	231	223	6
-10	709	716	5	-11	278	279	5	-6	449	460	5	-8	1027	1028	4	-7	851	851	4	-7	336	341	6
								-4	189	180	8	-7	515	510	4	-6	807	804	4	-6	140	145	9

COLUMNS ARE 10FD,10FD, 10SIG

COLUMNS ARE 10FD,10FD, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG
-4	343	353	8	-10	134	130	6	-5	437	434	6	-4	770	762	4	-10	306	314	6
-14	278	264	7	-8	267	259	5	-4	489	483	6	-3	273	257	5	-9	270	278	6
-12	144	151	8	-7	187	183	5	-1	405	417	7	-1	949	983	5	-6	518	529	5
-11	429	430	6	-6	1057	1047	4	-1	6	7, L	7	-1	189	185	7	-5	274	288	6
-10	93	112	10	-5	1053	1052	4	-13	257	264	6	0	108	118	11	-4	210	211	7
-8	368	353	7	-4	255	265	7	-12	217	214	7	2	708	715	6	-3	182	172	8
-7	273	279	8	-3	351	340	5	-11	248	258	6	7	346	456	7	-2	329	330	7
-11	219	218	8	-2	1167	1179	5	-10	411	417	5	4	164	160	9	-3	217	224	9
0	1306	1310	4	0	184	208	8	-8	446	439	5	-12	344	353	6	-12	332	338	6
1	640	638	5	2	387	379	7	-6	333	334	6	-10	108	115	8	-10	90	96	11
3	380	382	5	3	159	175	9	-5	185	189	7	-9	358	369	5	-9	570	584	5
4	819	808	6	-13	374	386	6	-3	338	348	7	-6	209	207	5	-6	564	563	5
-11	228	259	7	-11	279	284	6	-14	231	251	7	-4	393	388	4	-3	140	141	9
-10	530	529	5	-10	185	184	6	-13	362	362	6	-3	481	484	5	-7	336	341	6
-8	104	115	8	-9	654	653	4	-11	99	93	9	-2	288	279	6	-12	336	341	6
-7	985	974	4	-8	80	80	8	-10	627	631	5	0	139	145	9	-10	257	257	6
-6	433	420	4	-7	145	142	6	-8	172	168	7	0	163	173	9	-9	640	636	5
-5	465	457	4	-6	858	856	4	-7	504	505	6	1	163	173	9	-9	640	636	5
-4	628	619	4	-5	212	203	5	-6	369	386	6	2	441	437	7	-6	469	454	6
-3	907	889	4	-4	622	614	5	-5	107	113	10	-13	91	111	13	-13	236	240	7
-2	337	342	4	-3	172	176	7	-4	164	160	9	-12	256	269	7	-9	166	157	7
-1	144	141	7	-2	447	457	6	-14	262	275	7	-11	84	97	10	-12	240	248	8
0	1057	1094	5	-1	333	351	6	-14	262	275	7	-11	84	97	10	-12	240	248	8
1	169	164	7	0	183	194	8	-13	240	245	7	-10	410	409	5	-12	240	248	8
2	331	329	6	1	362	361	7	-12	113	115	9	-8	222	207	5	-11	349	337	6
3	412	414	6	6	5, L	5, L	7	-11	116	133	9	-7	599	593	4	-8	370	364	7
4	281	284	7	-14	214	204	8	-10	368	383	7	-6	488	483	4	0	765	773	5
5	287	279	8	-13	192	209	8	-9	106	98	9	-5	380	375	4	0	765	773	5
-12	240	239	7	-11	591	595	5	-6	368	364	7	-4	223	222	6	1	140	138	8
-11	244	258	6	-9	74	73	10	-11	123	129	11	-3	750	754	5	2	109	131	10
-10	266	274	6	-8	734	726	4	-12	282	282	7	-1	113	113	9	4	143	141	9
-9	470	467	5	-7	463	454	5	-10	90	104	11	0	620	623	6	-11	245	250	7
-7	475	477	4	-5	371	358	5	-9	283	272	7	1	287	280	8	-9	111	110	9
-6	409	403	4	-4	776	766	5	0	175	186	6	7, L	169	161	7	-9	335	321	6
-5	748	735	4	-3	101	119	10	1	466	464	5	-11	426	443	5	-8	121	143	8
-4	361	344	4	-2	98	119	10	2	306	300	6	-10	461	468	5	-7	404	404	5
-3	144	141	5	-1	545	551	7	3	484	481	6	-8	184	185	6	-6	546	537	5
-2	895	901	5	0	265	270	8	4	204	203	7	-7	683	671	4	-5	443	424	4
-1	228	220	7	1	138	127	9	7, L	7, L	1, L	5	-6	300	299	5	-4	475	471	4
0	311	313	6	6, L	210	206	7	-5	137	136	7	-3	160	163	6	-3	129	144	10
1	574	574	6	-14	220	225	7	-11	374	375	7	-4	613	615	5	-2	677	673	6
2	574	590	6	-13	119	108	9	-10	107	120	10	-3	703	700	6	-1	175	182	9
3	163	162	9	-12	382	393	6	-8	843	827	5	-2	164	135	8	0	273	282	7
6, L	248	265	7	-11	589	603	5	-7	296	292	5	0	550	557	7	1	480	491	6
-13	440	435	6	-8	664	667	5	-6	147	139	6	7, L	209	209	6	2	227	229	8
-12	440	435	6	-7	157	172	6	-5	914	909	4	-12	209	209	6	3	209	211	9

Table S.12. Fractional Coordinates for Os₄(CO)₁₅PMe₃,
Molecule 1

ATOM	X	Y	Z	BISO
OS(11)	0.28363(5)	0.95360(6)	0.11918(4)	2.59(3)
OS(12)	0.27094(5)	1.18189(6)	0.20523(4)	2.55(3)
OS(13)	0.24664(6)	1.40409(6)	0.24823(4)	3.20(3)
OS(14)	0.20324(5)	1.27036(6)	0.08238(4)	2.93(4)
P(1)	0.2743(3)	0.7686(4)	0.0516(3)	3.12(22)
C(11)	0.1433(15)	0.7001(15)	0.0572(13)	4.7(12)
C(12)	0.2939(15)	0.7320(16)	-0.0548(12)	4.4(11)
C(13)	0.3712(15)	0.6975(16)	0.0888(13)	5.7(14)
C(14)	0.3459(13)	0.9913(15)	0.0316(11)	3.9(4)
C(15)	0.2309(13)	0.9367(15)	0.2169(11)	3.6(4)
C(16)	0.4266(13)	0.9688(15)	0.1648(10)	3.5(4)
C(17)	0.1412(12)	0.9574(14)	0.0796(10)	3.3(3)
C(18)	0.1233(13)	1.1504(15)	0.2239(10)	3.6(4)
C(19)	0.4172(14)	1.1952(16)	0.1804(12)	4.6(4)
C(110)	0.3111(13)	1.1818(15)	0.3048(11)	4.0(4)
C(111)	0.0978(14)	1.3757(16)	0.2698(12)	4.6(4)
C(112)	0.2815(15)	1.4373(17)	0.3570(12)	5.0(4)
C(113)	0.3951(15)	1.4207(18)	0.2224(12)	5.2(5)
C(114)	0.2219(16)	1.5342(18)	0.2395(13)	5.7(5)
C(115)	0.1827(14)	1.1508(16)	-0.0120(11)	4.1(4)
C(116)	0.1755(17)	1.3764(19)	0.0385(14)	6.0(5)
C(117)	0.3513(16)	1.2846(19)	0.0636(13)	5.8(5)
C(118)	0.0571(14)	1.2478(16)	0.1087(12)	4.5(4)
O(14)	0.3865(10)	1.0141(11)	-0.0197(8)	5.3(3)
O(15)	0.2024(11)	0.9256(12)	0.2767(9)	6.3(3)
O(16)	0.5126(10)	0.9853(12)	0.1930(8)	5.5(3)
O(17)	0.0560(9)	0.9634(10)	0.0577(8)	4.6(3)
O(18)	0.0351(11)	1.1262(12)	0.2355(9)	6.2(3)
O(19)	0.3100(11)	1.2016(13)	0.1711(9)	6.7(4)
O(110)	0.3378(11)	1.1869(13)	0.3704(9)	6.8(4)
O(111)	0.0114(11)	1.3645(13)	0.2857(9)	6.7(4)
O(112)	0.3004(13)	1.4580(14)	0.4263(10)	8.0(4)
O(113)	0.4845(12)	1.4352(13)	0.2115(10)	7.1(4)
O(114)	0.2055(11)	1.6207(13)	0.2362(9)	6.9(4)
O(115)	0.1722(11)	1.0781(12)	-0.0687(9)	6.0(3)
O(116)	0.1635(14)	1.4396(16)	0.0071(11)	9.3(5)
O(117)	0.4385(13)	1.2901(15)	0.0442(11)	8.5(5)
O(118)	-0.0333(11)	1.2290(12)	0.1170(9)	6.0(3)

BISO=8PI**2(U11+U22+U33)/3

Table S.13. Fractional Coordinates for Os₄(CO)₁₅PMe₃,
Molecule 2

ATOM	X	Y	Z	BISO
OS(21)	0.77334(5)	0.03464(5)	0.37813(4)	2.40(3)
OS(22)	0.81459(5)	-0.18932(5)	0.30054(4)	2.28(3)
OS(23)	0.80617(5)	-0.41600(6)	0.25594(4)	2.79(3)
OS(24)	0.66744(5)	-0.30249(6)	0.38046(4)	2.65(3)
F(2)	0.7459(4)	0.2145(4)	0.4453(3)	3.23(23)
C(21)	0.8585(16)	0.3065(16)	0.4408(14)	5.3(14)
C(22)	0.6284(16)	0.2564(16)	0.4089(13)	5.3(12)
C(23)	0.7250(16)	0.2469(14)	0.5530(12)	4.4(11)
C(24)	0.7665(13)	0.0554(15)	0.2738(10)	3.5(4)
C(25)	0.7813(12)	0.0013(14)	0.4769(10)	3.1(3)
C(26)	0.9282(13)	0.0545(15)	0.3819(10)	3.6(4)
C(27)	0.6212(12)	-0.0130(14)	0.3627(10)	3.3(3)
C(28)	0.7083(13)	-0.1934(14)	0.2187(10)	3.4(3)
C(29)	0.9227(12)	-0.1695(13)	0.3825(10)	2.9(3)
C(210)	0.9167(14)	-0.1682(16)	0.2320(11)	4.3(4)
C(211)	0.9182(14)	-0.3966(17)	0.3358(12)	4.6(4)
C(212)	0.9092(14)	-0.4482(16)	0.1789(12)	4.6(4)
C(213)	0.7013(14)	-0.4227(16)	0.1737(11)	4.2(4)
C(214)	0.7612(14)	-0.5534(16)	0.2602(11)	4.3(4)
C(215)	0.5986(13)	-0.1955(14)	0.4531(10)	3.4(3)
C(216)	0.7814(12)	-0.2872(14)	0.4589(10)	3.2(3)
C(217)	0.5625(13)	-0.3083(15)	0.2990(11)	3.8(4)
C(218)	0.6005(14)	-0.4240(16)	0.3979(11)	4.3(4)
O(24)	0.7657(10)	0.0755(11)	0.2159(8)	5.2(3)
O(25)	0.7891(9)	-0.0126(10)	0.5375(8)	4.7(3)
O(26)	1.0214(9)	0.0687(10)	0.3826(7)	4.4(3)
O(27)	0.5330(9)	-0.0430(10)	0.3527(7)	4.2(3)
O(28)	0.6469(9)	-0.1910(11)	0.1716(8)	4.7(3)
O(29)	0.9958(9)	-0.1491(10)	0.4296(8)	4.6(3)
O(210)	0.9814(11)	-0.1600(12)	0.1863(9)	6.0(3)
O(211)	0.9921(11)	-0.3910(13)	0.3781(9)	6.5(4)
O(212)	0.9733(11)	-0.4719(13)	0.1283(9)	6.8(4)
O(213)	0.6366(10)	-0.4324(11)	0.1242(8)	5.5(3)
O(214)	0.7368(11)	-0.6369(12)	0.2622(9)	6.2(3)
O(215)	0.5510(10)	-0.1268(11)	0.4954(8)	4.9(3)
O(216)	0.8455(10)	-0.2780(11)	0.5101(8)	5.2(3)
O(217)	0.4940(10)	-0.3062(11)	0.2566(8)	5.3(3)
O(218)	0.5552(11)	-0.4990(13)	0.4082(9)	6.7(4)

$$\text{BISO} = 8\text{PI} \times 2 (\text{U}_{11} + \text{U}_{22} + \text{U}_{33}) / 3$$

Table S.14. Thermal Parameters for $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$, Molecule 1

ATOM	U11	U22	U33	U12	U13	U23
OS(11)	3.40(3)	3.30(4)	3.14(4)	0.45(3)	-0.10(3)	1.04(3)
OS(12)	3.67(4)	3.09(4)	2.94(4)	0.13(3)	-0.06(3)	0.95(3)
OS(13)	5.38(4)	2.88(4)	3.90(4)	-0.22(3)	0.00(3)	0.59(4)
OS(14)	4.02(4)	3.86(5)	3.24(4)	0.21(3)	-0.08(3)	1.40(4)
P(1)	4.7(3)	3.2(3)	4.0(3)	0.9(2)	0.1(2)	1.1(2)
C(11)	6.2(12)	3.8(13)	8.0(15)	-0.7(10)	0.8(10)	2.7(12)
C(12)	6.7(13)	4.6(14)	5.8(14)	1.5(11)	-0.1(10)	-1.3(11)
C(13)	6.2(13)	5.2(14)	10.3(18)	2.5(11)	-1.3(12)	4.5(14)
C(14)	4.9(5)					
C(15)	4.6(5)					
C(16)	4.5(4)					
C(17)	4.2(4)					
C(18)	4.5(5)					
C(19)	5.8(5)					
C(110)	5.1(5)					
C(111)	5.8(5)					
C(112)	6.3(6)					
C(113)	6.5(6)					
C(114)	7.2(6)					
C(115)	5.1(5)					
C(116)	7.7(7)					
C(117)	7.3(6)					
C(118)	5.6(5)					
O(14)	6.8(4)					
O(15)	8.0(4)					
O(16)	6.9(4)					
O(17)	5.8(3)					
O(18)	7.8(4)					
O(19)	8.4(5)					
O(110)	8.6(5)					
O(111)	8.5(5)					
O(112)	10.1(5)					
O(113)	9.0(5)					
O(114)	8.7(5)					
O(115)	7.5(4)					
O(116)	11.8(6)					
O(117)	10.7(6)					
O(118)	7.6(4)					

Table S.15. Thermal Parameters for $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$, Molecule 2

ATOM	U11	U22	U33	U12	U13	U23
OS(21)	3.80(4)	2.56(4)	2.75(4)	0.34(3)	0.05(3)	0.55(3)
OS(22)	3.28(3)	2.37(4)	3.01(4)	0.26(3)	0.11(3)	0.55(3)
OS(23)	3.72(4)	3.20(4)	3.16(4)	-0.09(3)	0.01(3)	1.05(3)
OS(24)	4.52(4)	2.48(4)	3.58(4)	0.47(3)	-0.25(3)	0.28(3)
F(2)	5.4(3)	2.7(3)	4.2(3)	0.5(2)	0.3(2)	0.6(2)
C(21)	6.9(14)	4.4(14)	9.1(17)	-0.8(11)	1.0(12)	1.8(13)
C(22)	7.6(14)	4.7(14)	7.9(16)	0.5(11)	0.4(11)	3.5(13)
C(23)	9.4(15)	2.4(11)	5.4(13)	2.0(10)	0.6(11)	0.3(10)
C(24)	4.5(4)					
C(25)	3.9(4)					
C(26)	4.5(5)					
C(27)	4.2(4)					
C(28)	4.3(4)					
C(29)	3.6(4)					
C(210)	5.5(5)					
C(211)	4.3(4)					
C(212)	4.1(4)					
C(213)	4.9(5)					
C(214)	5.4(5)					
C(215)	5.8(5)					
C(216)	5.8(5)					
C(217)	5.3(5)					
C(218)	5.4(5)					
O(24)	6.6(4)					
O(25)	5.9(4)					
O(26)	5.6(3)					
O(27)	5.3(3)					
O(28)	5.9(4)					
O(29)	5.8(3)					
O(210)	7.7(4)					
O(211)	6.2(4)					
O(212)	6.6(4)					
O(213)	6.7(4)					
O(214)	8.5(5)					
O(215)	8.2(4)					
O(216)	8.6(5)					
O(217)	6.9(4)					
O(218)	7.9(4)					

TEMP=-2*(PI)**2*(U11*H*H*ASTAR*ASTAR+---+'2*U12*H*K*ASTAR*BSTAR+---)

THE UIJ VALUES HAVE BEEN MULTIPLIED BY 100.

Table S.16. Fractional Coordinates for Hydrogen Atoms of $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$

ATOM	X	Y	Z	B
H(111)	0.1433	0.6230	0.0367	5.
H(112)	0.1186	0.7221	0.1132	5.
H(113)	0.0976	0.7268	0.0238	5.
H(121)	0.2991	0.6551	-0.0810	5.
H(122)	0.2303	0.7563	-0.0738	5.
H(123)	0.3610	0.7693	-0.0660	5.
H(211)	0.8794	0.2964	0.3849	5.
H(212)	0.9228	0.3017	0.4710	5.
H(213)	0.8292	0.3769	0.4652	5.
H(221)	0.5631	0.2115	0.4110	5.
H(222)	0.6267	0.3306	0.4463	5.
H(223)	0.6353	0.2537	0.3528	5.
H(231)	0.6977	0.3189	0.5736	5.
H(232)	0.7951	0.2527	0.5805	5.
H(233)	0.6743	0.1892	0.5550	5.

Table S.17. Structure Factors for $\text{Os}_4(\text{CO})_{15}\text{PMe}_3$

COLUMNS ARE 10FD,10FC, 10SIG

L	KFD	FC	SIG	L	KFD	FC	SIG	L	KFD	FC	SIG	L	KFD	FC	SIG	L	KFD	FC	SIG
-5	2	2	14	-11	1502	1554	20	-15	388	479	76	-10	502	553	74	-7	331	3310	11
-6	2502	2488	12	-9	1215	1174	21	-14	412	422	71	-13	713	745	41	-17	1307	1233	31
-5	3629	3672	10	-8	2799	2779	14	-10	532	579	35	-12	809	804	25	-16	508	521	64
-3	861	802	16	-7	378	312	54	-14	713	745	41	-13	713	745	41	-15	1412	1459	26
-2	1864	1820	14	-6	1034	1036	20	-12	607	604	46	-10	502	553	74	-14	1258	1270	27
-1	1004	1004	14	-5	701	700	28	-11	1161	1213	31	-9	790	749	35	-13	1425	1425	23
0	742	711	18	-3	1207	1228	18	-10	532	579	35	-9	772	776	89	-11	1629	1634	19
1	3091	3094	10	-2	809	804	25	-8	854	818	34	-6	487	416	76	-9	2929	2848	13
2	1044	1031	14	-1	954	1024	22	-7	759	732	43	-5	992	950	30	-8	3331	3310	12
3	756	721	20	0	1826	1845	15	-6	1669	1669	23	-4	1780	1869	42	-7	3607	3570	11
4	1010	1042	17	6	1669	1669	23	-2	2349	2413	19	-3	1780	1869	42	-6	1954	1936	12
5	4668	4690	11	6	2008	2002	22	0	2991	3036	18	-4	-	-	-	-6	1954	1936	12
6	844	866	23	8	668	604	54	1	2991	3036	18	-4	-	-	-	-5	973	985	16
8	630	656	36	9	2161	2151	24	2	518	451	65	1	2909	2876	9	-4	1204	1165	13
9	2282	2276	16	9	538	658	81	3	787	822	46	3	3794	3662	9	-3	3112	3028	9
10	641	702	42	12	1007	984	39	4	819	810	46	4	1175	1180	14	-2	2496	2358	9
12	969	981	35	12	670	667	47	5	1076	1105	38	5	830	873	18	-1	1740	1709	10
15	1472	1437	31	-17	1429	1415	25	6	1367	1409	33	6	3768	3791	10	0	1740	1709	10
-17	1034	994	35	-16	1396	1407	22	7	1252	1302	37	7	939	956	19	1	755	769	17
-16	910	949	37	-13	1396	1407	22	7	1252	1302	37	7	939	956	19	1	755	769	17
-13	924	994	32	-12	1597	1611	20	8	1130	1188	31	8	1874	1944	14	2	845	854	16
-12	967	933	28	-11	874	861	30	9	1166	1182	22	9	1129	1142	20	3	2920	2944	10
-11	2931	2917	14	-9	2861	2917	14	10	1129	1142	20	10	1129	1142	20	3	2920	2944	10
-9	1619	1554	16	-8	1122	1137	23	11	699	716	43	11	1418	1441	21	4	1518	1502	13
-7	452	351	37	-7	1633	1722	17	12	480	493	61	12	1062	1023	32	5	1410	1536	16
-6	662	668	25	-6	834	855	27	13	886	933	36	13	1062	1023	32	5	1410	1536	16
-5	408	282	34	-5	1556	1538	17	14	3221	3321	17	14	1050	1121	35	6	1276	1248	17
-4	645	662	23	-4	951	981	24	15	683	700	48	15	1050	1121	35	6	1276	1248	17
-3	1292	1289	13	-3	697	713	21	16	3397	3472	17	16	1365	1370	29	7	4579	4611	12
-2	261	275	48	-2	1304	1292	20	17	704	781	46	17	1365	1370	29	7	4579	4611	12
-1	890	899	17	-1	630	564	36	18	692	646	46	18	1365	1370	29	7	4579	4611	12
3	686	720	24	0	2378	2275	16	19	431	509	76	19	1365	1370	29	7	4579	4611	12
4	1904	1915	13	2	378	191	66	20	431	509	76	20	1365	1370	29	7	4579	4611	12
5	3219	3214	12	3	2428	2401	18	21	1358	1357	30	21	1365	1370	29	7	4579	4611	12
6	706	647	30	4	1394	1423	25	22	936	965	41	22	1365	1370	29	7	4579	4611	12
7	3427	3530	14	5	622	666	53	23	956	963	44	23	1365	1370	29	7	4579	4611	12
9	656	647	42	6	1178	1248	36	24	502	540	86	24	1365	1370	29	7	4579	4611	12
10	1918	1883	21	-5	953	928	31	25	618	703	56	25	1365	1370	29	7	4579	4611	12
11	1735	1740	24	-14	1433	1537	23	26	642	590	51	26	1365	1370	29	7	4579	4611	12
12	1078	1071	34	-13	2071	2159	18	27	1161	1213	31	27	1365	1370	29	7	4579	4611	12
13	1716	1773	27	-11	2071	2159	18	28	2840	2853	19	28	1365	1370	29	7	4579	4611	12
-17	1538	1484	26	-10	668	697	39	29	582	643	57	29	1365	1370	29	7	4579	4611	12
-16	729	741	42	-9	518	572	49	30	992	1027	36	30	1365	1370	29	7	4579	4611	12
-15	1668	1556	22	-8	1051	1078	25	31	992	1027	36	31	1365	1370	29	7	4579	4611	12
-14	1518	1553	22	-7	2000	2028	17	32	1735	1812	25	32	1365	1370	29	7	4579	4611	12
-13	739	687	37	-6	511	916	15	33	581	587	60	33	1365	1370	29	7	4579	4611	12
-12	1332	1377	22	-5	1011	916	15	34	1570	1576	42	34	1365	1370	29	7	4579	4611	12
-11	1747	1732	17	-4	713	719	34	35	929	936	67	35	1365	1370	29	7	4579	4611	12
-10	439	395	48	-3	376	370	64	36	592	639	67	36	1365	1370	29	7	4579	4611	12
-9	452	435	43	-1	2775	2857	16	37	1897	2009	30	37	1365	1370	29	7	4579	4611	12
-8	2802	2802	12	0	511	443	64	38	5	12, 12, 1	72	38	1365	1370	29	7	4579	4611	12
-8	2802	2802	12	3	3187	3171	18	39	498	534	81	39	1365	1370	29	7	4579	4611	12

COLUMNS ARE 10FD,10FC, 10SIG

COLUMNS ARE 10FD,10FC, 10SIG

1	1900	1911	11	11	0	836	864	22	3	2134	2139	19	-16	693	685	49	0	1203	1139	-7	2344	2302	11	SIG
2	3489	3365	10	10	2	667	742	27	4	711	673	45	-15	1827	1874	23	1	2143	2171	-5	3426	3385	10	FC
3	2926	2854	11	11	5	1138	1154	19	6	2761	2782	20	-14	957	880	35	3	1898	1687	-4	5184	5125	9	L
4	2070	2021	13	13	5	1500	1526	19	6	3121	3165	20	-13	995	1055	34	3	1388	1398	-4	4087	968	13	SIG
5	3173	3222	12	12	7	2444	2436	35	7	2170	2279	25	-11	809	940	40	4	2637	2655	-1	1087	313	27	FC
6	1098	1009	21	21	8	911	867	35	7	890	862	47	-11	790	757	40	5	1940	1956	0	1534	1471	9	L
8	1400	1400	22	22	11	753	755	46	8	890	862	47	-9	1847	1902	22	6	1185	1132	1	1759	1761	9	SIG
10	1242	1190	29	29	11	1219	1199	34	11	800	774	41	-8	800	774	41	8	2899	2968	2	1112	1127	13	FC
11	529	457	37	37	12	1128	1162	40	12	1445	1530	40	-7	1800	1821	23	9	1243	1281	3	890	830	17	L
12	1163	1219	37	37	12	862	843	52					-6	587	571	56	10	1212	1271	4	771	769	20	SIG
13	1176	1219	39	39	17	941	930	34	-17	941	930	34	-5	1984	1992	22	11	575	507	5	2448	2452	12	FC
14	728	665	59	59	16	1076	1130	31	-16	532	406	54	-3	2222	2314	22	12	2151	2121	8	483	471	50	L
15	827	781	58	58	14	730	811	41	-15	961	1036	32	-2	1246	1331	31	13	1084	1136	9	1384	1356	24	SIG
-16	1618	1624	23	23	-14	1009	1049	28	-14	597	596	46	-2	470	401	75	14	763	865	10	1834	1888	23	FC
-14	1136	1176	27	27	-12	745	658	33	-13	1412	1418	23	-12	977	971	41	14			11	1174	1215	35	L
-13	2225	2290	18	18	-10	489	423	46	-10	617	608	41	-9	1431	1476	31	15	451	461	-17	451	461	81	SIG
-12	1749	1737	18	18	-8	2458	2423	14	-8	732	2162	17	-4	925	986	45	16	454	649	-15	1744	1773	29	FC
-10	2402	2404	14	14	-7	2715	2737	13	-7	944	991	28	-6	665	699	66	17	2725	2773	-14	908	907	55	L
-9	2436	2395	13	13	-6	1902	1955	14	-6	1157	1169	24	-5	797	917	48	18	2144	2106	-13	1033	1038	30	SIG
-8	1076	1103	18	18	-5	2540	2585	12	-5	2209	2166	16	-4	531	657	67	19	932	946	-8	963	978	39	FC
-7	275	203	54	54	-3	1483	1479	15	-3	430	504	25	-13	1022	1068	37	20	3399	3342	-7	597	692	56	L
-6	1177	1127	15	15	-2	2783	2791	12	-2	1068	1046	25	-12	410	292	76	21	3335	3285	-6	418	515	69	SIG
-3	4146	4254	9	9	-1	729	748	26	-1	943	968	30	-9	946	981	38	22	520	530	-8	947	947	17	FC
-2	1513	1512	12	12	0	493	550	38	0	1306	1338	25	-8	861	905	45	23	4783	4671	-7	389	332	39	L
-1	2782	2846	10	10	2	1691	1731	16	2	1414	1420	16	-7	879	906	47	24	2836	2773	-3	947	947	17	SIG
0	1344	1319	13	13	3	2093	2088	16	3	2062	2017	35	-5	1098	1106	40	25	2836	2773	-4	578	542	23	FC
1	1024	958	18	18	5	425	558	69	5	643	689	60	-2	473	422	89	26	1087	1093	-11	1741	1640	10	L
2	1084	1046	19	19	6	229	242	22	6	726	728	60	-1	482	516	90	27	921	873	-9	351	323	47	SIG
3	1064	1046	14	14	8	1584	1649	29	8	1085	1084	30	-15	879	906	47	28	894	830	-8	389	332	39	FC
6	1043	1030	25	25	9	1627	1655	29	9	1627	1655	29	-13	879	906	47	29	598	627	-7	947	947	17	L
7	1376	1361	23	23	10	1058	1108	42	-13	376	139	71	-11	1098	1106	40	30	3102	3128	2	578	542	23	SIG
9	1579	1622	25	25	11	1215	1216	40	-12	926	930	32	-10	473	422	89	31	1076	1077	-4	463	508	27	FC
10	2411	2356	21	21	-4	1663	1679	23	-11	633	670	46	-13	1960	2020	26	32	490	511	-2	1911	1806	10	L
11	1206	1230	36	36	-17	703	766	43	-10	717	718	41	-11	954	958	40	33	1076	1077	7	1770	1730	20	SIG
12	617	533	65	65	-16	703	766	43	-9	465	456	58	-10	453	290	76	34	1522	1551	8	1530	1505	13	FC
13	606	798	75	75	-15	652	771	42	-9	1814	1796	19	-11	954	958	40	35	1076	1077	8	1741	1640	10	L
14	1383	1419	39	39	-14	1052	1101	28	-5	2130	2220	19	-9	435	518	84	36	3675	3726	-4	5136	5066	11	SIG
-17	1127	1104	30	30	-13	901	915	30	-4	1788	1810	21	-4	1184	1211	35	37	1080	1150	10	2973	2903	13	FC
-13	1282	1318	23	23	-12	881	877	31	-3	1350	1313	25	-3	577	707	73	38	885	872	5	2509	2494	15	L
-12	980	1034	26	26	-11	3787	3866	14	-2	1436	1438	25	-1	1099	1044	42	39	1094	1114	14	433	416	66	SIG
-11	1677	1643	17	17	-9	2968	3047	14	-1	1626	1586	23	-1	1843	1828	31	40	758	725	16	726	692	46	FC
-9	606	625	32	32	-7	1442	1494	19	0	982	1031	34	-4	952	889	45	41	938	939	10	3131	3197	20	L
-8	630	645	29	29	-6	680	700	31	1	598	641	57	-11	1338	1389	35	42	638	566	-17	1770	1782	29	SIG
-6	966	1041	19	19	-4	467	521	43	3	896	892	43	-8	675	517	57	43	825	767	-16	2220	2285	27	FC
-5	1950	1932	12	12	-3	2254	2276	15	6	698	661	57	-7	698	693	58	44	1057	1034	-12	701	609	65	L
-4	600	570	26	26	-2	1604	1593	17	7	1040	1188	44	-6	746	689	55	45	1183	1155	-11	830	806	42	SIG
-3	1436	1463	14	14	-1	1749	693	30	8	802	925	58	-5	448	456	88	46	630	528	-10	925	899	35	FC
-2	1940	1910	12	12	0	825	817	29	9	813	858	59	-3	1430	1486	35	47	421	374	-17	1266	1277	27	L
-1	5461	5489	10	10	1	1252	1244	23	-4	10	10	10	-1	2457	2421	25	48	1460	1406	-8	1912	1959	20	SIG

COLUMNS ARE 10FO,10FC, 10SIG

14	-3	4	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	
-14	2205	1436	13	1339	1406	42	-13	928	927	31	-3	1047	1114	40	7	800	810	23	
-13	876	829	30	1509	1453	39	-11	2661	2769	16	4	1359	1322	34	8	2477	2467	14	
-12	1143	1140	23	-3	6	L	-9	375	298	65	5	505	606	83	11	1251	1217	34	
-11	2838	2815	13	1185	1112	58	-8	901	892	31	6	726	647	60	12	950	873	49	
-10	961	955	22	-16	1542	1553	-7	2282	2295	17	7	881	883	53	13	764	543	66	
-9	368	316	46	-15	1192	1303	-6	1224	1120	24	-3	11	L	L	14	1253	1191	47	
-8	2522	2533	12	-13	719	748	-5	742	803	36	-15	1681	1777	27	16	1056	1025	58	
-7	2600	2540	11	-11	2876	2965	-3	410	439	61	-13	1026	1038	37	17	593	550	101	
-6	1385	1414	13	-10	1222	1204	-1	774	800	37	-11	676	551	51	-2	L	L	L	
-5	1092	1083	14	-9	2058	2109	-1	1548	1542	22	-10	1310	1361	30	-16	1545	1538	28	
-4	729	710	19	-8	1774	1740	0	1044	1059	31	-7	727	772	24	-15	1356	1338	29	
-3	748	745	18	-6	1009	1021	2	635	708	53	-7	727	772	52	-13	737	744	44	
-2	488	501	27	-4	2532	2573	3	2967	2953	20	-6	532	468	69	-12	3142	3138	16	
-1	3441	3471	9	-3	863	854	2	1267	1266	33	-5	1826	1881	26	-11	2374	2413	16	
0	3328	3395	10	-1	1431	1391	5	1900	1991	26	-1	878	874	47	-10	1768	1815	17	
1	3615	3694	10	0	2450	2437	4	1761	1819	28	1	576	487	66	-9	473	462	41	
2	5804	5798	11	1	391	420	7	860	829	50	2	717	634	57	-8	1444	1518	16	
3	517	504	36	2	1686	1656	8	901	972	50	4	709	630	61	-7	855	814	20	
4	1307	1353	19	3	944	908	9	736	804	62	5	1233	1140	40	-6	3887	3812	10	
5	422	497	54	4	1140	1170	10	866	833	54	6	503	517	88	-5	5305	5183	9	
6	1195	1209	27	6	2285	2344	11	960	963	54	-3	12	L	L	-3	6346	6124	8	
7	1195	1209	27	7	1749	1791	17	-3	9	L	-14	453	508	88	-3	2034	2022	8	
8	2668	2763	20	7	1749	1791	17	1389	1456	27	-13	558	553	71	-3	3275	3166	6	
9	1152	1140	34	8	1663	1754	30	16	449	502	-11	984	1102	43	-1	1212	1202	8	
10	908	924	52	9	1031	1085	45	-16	449	502	-10	935	988	44	1	906	918	14	
11	886	901	52	-3	7	L	-13	608	531	47	-10	699	787	57	3	906	918	14	
12	1666	1690	33	-18	849	825	38	-10	842	844	-8	733	790	53	4	3350	3301	9	
13	1320	1335	41	-17	727	612	42	1882	1870	20	-2	1102	1174	40	6	697	681	27	
15	935	980	60	-16	1125	1192	28	-5	1576	1661	-6	1420	1388	31	7	1087	1075	22	
-14	456	487	57	-15	652	663	42	-3	1957	2058	-2	1102	1174	40	7	1087	1075	22	
-13	975	960	27	-12	993	1021	28	-2	3000	2982	-1	458	405	86	8	2862	2735	16	
-12	1214	1219	21	-11	511	470	46	0	2642	2763	0	1140	1152	40	10	2261	2265	22	
-11	1613	1630	17	-10	694	717	34	1	2305	2397	1	1693	1706	31	11	1966	1996	28	
-10	1946	1928	15	-9	3682	3740	13	3	462	426	81	803	784	59	14	969	912	57	
-9	2925	2995	12	-8	1862	1859	16	4	1150	1179	38	473	203	94	15	978	983	60	
-8	649	688	27	-7	2401	2451	15	5	1201	1242	37	-3	13	L	16	924	917	66	
-7	608	563	27	-6	1220	1212	20	6	1998	2042	28	956	950	46	17	731	569	82	
-6	2433	2467	11	-5	1395	1437	18	7	1067	1061	42	961	938	45	-2	L	L	L	
-5	1880	1892	12	-4	854	898	26	9	775	761	61	673	731	64	-18	445	462	83	
-4	3581	3561	10	-3	491	496	43	-7	486	657	88	825	672	52	-15	1123	1195	32	
-3	4369	4472	10	-1	1136	1169	23	-16	774	777	45	1145	1159	42	-14	1999	1992	21	
-2	1402	1409	14	0	922	988	29	-14	790	927	45	1	1483	1509	37	-13	2777	2745	17
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1	396	394	41	3	1999	2124	21	-12	1025	1088	34	-8	493	365	88	-11	1241	1194	21
2	1856	1859	14	4	2837	2850	19	-11	864	880	40	-5	510	680	96	-10	2035	2034	15
3	483	471	45	5	517	572	70	-6	3268	3442	18	-4	1023	918	49	-9	883	928	22
4	372	410	64	7	1406	1333	33	-5	1238	1235	31	-4	192	0	L	-8	3890	3886	11
5	427	403	70	8	2166	2229	26	-5	3253	3342	19	1	2	0	L	-7	3638	3600	10
6	1144	1019	32	9	1195	1246	40	-4	2334	2326	22	1	1902	1842	6	-6	721	678	19
7	564	614	73	11	563	475	82	-3	597	676	59	2	2547	2539	6	-6	428	414	31
9	550	512	73	-17	936	1022	36	-2	1156	1169	34	3	1759	1801	13	-3	2866	2871	7
12	1260	1301	41	-15	803	773	36	0	897	891	46	6	5083	4982	10	-2	2472	2497	7

COLUMNS ARE 10FD,10FC, 10SIG

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-2	286	176	50	-7	2541	2570	13	-2	2161	2233	19	-12	1464	1478	32	-13	1464	1478	32	
-1	2009	1974	11	-6	5833	6047	12	-1	1779	1814	22	-10	1194	1219	36	-10	1194	1219	36	
0	2908	2910	11	-5	2004	2057	14	0	2690	2770	19	-9	1194	1217	37	-8	1194	1217	37	
1	2084	2060	13	-4	3172	3250	13	1	2383	2507	21	-8	2200	2324	25	-8	2200	2324	25	
2	2572	2587	13	-3	1568	1621	16	2	1799	1805	25	-7	2577	2707	23	-7	2577	2707	23	
3	2864	2883	14	-2	2093	2059	15	3	1133	1211	36	-6	505	433	39	-6	505	433	39	
4	4509	4518	14	0	1978	2007	17	4	1488	1464	30	-5	1310	1250	74	-5	1310	1250	74	
5	942	955	30	1	754	746	34	7	465	331	91	-4	487	326	82	-4	487	326	82	
7	477	3432	16	2	3342	3432	16	7	-2	9	L	-2	1037	1056	41	-2	1037	1056	41	
8	464	503	80	3	401	423	70	3	1032	1034	34	-1	624	513	64	-1	624	513	64	
9	1163	1114	38	4	1331	1384	28	4	1203	1214	29	-2	12	L	-2	12	L	-2		
10	2767	2774	24	5	1230	1193	31	5	1059	1101	33	-13	1795	1841	29	-13	1795	1841	29	
11	1724	1750	34	6	967	978	41	6	542	580	59	-12	1516	1581	33	-12	1516	1581	33	
12	983	914	58	8	1730	1685	30	8	12	431	425	73	-11	739	808	59	-11	739	808	59
13	861	852	60	9	1844	1768	30	9	622	626	53	-10	1432	1443	34	-10	1432	1443	34	
14	1240	1093	46	10	2470	2381	27	10	2487	2502	19	-8	1200	1137	39	-8	1200	1137	39	
15	1158	1134	52	12	1141	1194	47	12	1197	1181	29	-6	609	630	71	-6	609	630	71	
-17	376	181	74	-18	1758	1729	23	-18	908	944	37	-5	530	383	79	-5	530	383	79	
-16	974	920	30	-17	1963	1984	20	-17	1586	1578	24	-4	1876	1918	28	-4	1876	1918	28	
-15	712	725	38	-16	1300	1269	25	-16	2320	2429	21	-3	814	872	54	-3	814	872	54	
-14	627	674	40	-15	797	832	35	-15	1711	1698	24	-1	496	486	83	-1	496	486	83	
-13	399	415	57	-14	1560	1547	20	-14	2337	2403	22	0	613	749	69	0	613	749	69	
-12	1094	1097	23	-13	3382	3458	15	-13	2031	2025	24	1	539	573	80	1	539	573	80	
-11	2400	2434	14	-10	2383	2353	16	-10	2031	2025	24	2	1598	1600	33	2	1598	1600	33	
-10	1427	1444	17	-9	2314	2388	16	-9	2282	2288	28	3	2282	2288	28	3	2282	2288	28	
-8	537	555	32	-8	1507	1552	19	-8	1856	1836	26	4	1987	2009	31	4	1987	2009	31	
-7	1807	1867	14	-7	1568	1628	19	-7	671	740	61	-11	1010	1066	48	-11	1010	1066	48	
-6	293	232	52	-6	300	416	45	-6	746	740	60	-10	1010	1066	48	-10	1010	1066	48	
-5	931	964	19	-4	1501	1526	19	-4	1582	1521	33	-9	977	931	49	-9	977	931	49	
-4	3286	3328	11	-3	1944	1909	17	-3	1504	1528	35	-7	1081	994	43	-7	1081	994	43	
-3	2085	2155	12	-2	1023	1053	26	-2	516	531	68	-6	1440	1421	35	-6	1440	1421	35	
-2	4036	4052	11	0	1998	2042	19	-14	1871	1137	36	-3	1096	935	43	-3	1096	935	43	
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6	672	813	52	12	1270	1203	44	-3	2262	2302	23	-7	609	567	79	-7	609	567	79	
8	632	616	63	8	-2	8	L	-2	3093	3122	21	-6	1506	1421	37	-6	1506	1421	37	
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-18	1172	1193	29	-13	751	867	40	3	554	487	74	3	925	887	11	-1	553	599	15	
-17	632	634	46	-10	1776	1889	20	4	1200	1312	39	3	877	877	11	0	2873	2872	7	
-15	1116	1098	26	-9	2231	2325	18	5	1351	1333	36	4	894	859	41	1	412	434	28	
-14	1498	1523	21	-8	1297	1329	24	6	695	649	64	5	538	500	40	2	1274	1230	15	
-12	1245	1265	21	-7	694	645	39	8	1062	970	47	6	1299	1278	23	2	748	797	35	
-10	558	555	39	-6	1319	1326	24	-14	741	766	55	7	461	427	66	4	748	797	35	
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COLUMNS ARE 10FD,10FC, 10SIG

COLUMNS ARE 10FD,10FC, 10SIG

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1	3234	3212	14	8	2597	2424	24	-15	739	673	48	0	487	470	84	-9	4740	4866	17	-4	3985	3947	11
2	8572	8510	14	11	1097	1030	46	-13	585	567	62	3	735	689	58	-8	3369	3377	13	-11	2063	2060	15
3	1288	1388	24	12	826	805	63	-12	1961	1941	24	4	673	705	66	-7	789	769	24	-10	1927	1879	14
6	851	858	41	12	7	7	63	-11	534	470	68	6	1449	1479	38	-6	4057	4001	10	-8	5223	5293	10
8	1946	1882	26	-18	733	822	44	-10	420	266	83	-1	12	12	12	-5	1857	1820	11	-7	962	965	17
9	1730	1639	30	-16	691	756	43	-9	676	712	55	-11	1063	1057	47	-5	4740	4866	17	-4	3985	3947	11
11	818	679	60	-15	1380	1421	24	-8	3304	3264	19	-10	2195	2067	28	-3	382	365	17	-4	3985	3947	11
12	1515	1392	38	-10	1317	1240	24	-4	445	151	80	-9	1051	942	47	-2	5132	5185	6	-2	1920	1932	14
13	1347	1271	42	-9	3005	3058	16	-3	1845	1759	25	-8	1744	1711	32	-1	213	62	41	-1	603	597	35
15	932	843	61	-8	2410	2480	17	-2	5229	4938	18	-7	486	221	83	-0	1354	1445	10	0	1404	1421	19
-1	755	787	37	-7	1677	1651	20	-1	3023	2922	20	-6	1410	1367	35	1	281	319	44	2	6411	6616	14
-16	755	787	37	-6	3111	3133	16	0	4852	4657	18	-5	690	728	65	2	1153	1183	15	3	2928	3110	16
-15	396	432	66	-2	1550	1587	23	1	852	851	49	-4	558	521	78	3	443	487	41	5	527	394	54
-14	828	853	31	0	1143	1147	29	3	507	481	80	-3	633	619	70	4	2420	2420	14	5	527	394	54
-13	1042	1058	24	1	854	921	39	-2	1419	1411	35	-2	1419	1368	35	5	1528	1479	19	6	3140	3184	18
-12	2935	2852	13	2	739	619	45	6	1773	1688	30	0	1093	1157	41	6	709	741	36	7	1197	1152	30
-11	631	633	33	3	692	638	52	1	1330	1423	38	1	1330	1423	38	8	699	639	39	8	2130	2125	22
-10	1951	1946	14	4	2114	2063	24	9	1209	1114	42	2	1629	1673	33	3	1717	1665	21	9	2179	2100	24
-9	2312	2356	14	5	1663	1584	28	-1	957	919	45	-1	1063	1120	48	16	1039	927	52	10	654	562	65
-8	485	366	38	6	619	657	68	-17	1000	1019	41	-13	1200	1128	46	9	5553	1568	25	10	654	562	65
-7	592	546	32	7	1616	1515	32	-16	614	618	64	-12	502	516	99	11	912	925	46	12	1180	1069	44
-6	3985	3985	12	8	3189	3045	23	-15	444	370	85	-8	1130	959	42	12	3723	3531	20	13	845	952	63
-5	1955	1993	14	9	1491	1481	36	-3	464	553	85	-3	466	26	89	14	1327	1217	38	14	2282	2188	30
-4	4214	4201	12	10	1190	1228	43	-13	1906	1964	27	0	844	696	55	15	1684	1607	34	16	1313	1279	47
-3	2824	2851	13	11	802	800	62	-12	1194	1263	38	1	1063	1120	48	16	1039	927	52	16	1313	1279	47
-2	332	244	64	12	1154	1000	46	-11	957	919	45	1	1063	1120	48	16	1039	927	52	16	1313	1279	47
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1	830	817	31	-18	729	738	46	-8	1593	1595	31	-5	1461	1304	38	-16	2228	2200	23	-14	1988	1951	18
2	406	251	64	-17	1269	1350	29	-7	1690	1748	29	-4	2058	1894	30	-14	1590	1530	26	-13	1688	1679	18
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6	1034	960	38	-12	2624	2639	19	-4	2609	2580	23	1	311	184	18	-9	1117	1077	19	-10	3191	3150	14
12	2027	1900	31	-11	1745	1767	23	-3	1097	1104	40	2	4001	4142	7	-8	3792	3819	11	-8	803	803	25
14	950	951	59	-9	413	121	76	-2	1061	1004	41	3	878	855	15	-7	527	498	27	-6	1254	1286	21
-17	1371	1369	24	-7	1007	991	34	0	1905	1851	27	4	341	295	47	-6	3252	3143	9	-4	1857	1759	18
-16	1810	1870	20	-6	1744	1810	23	1	898	925	48	5	651	646	32	-5	419	457	29	-3	377	131	71
-15	382	506	69	-5	971	1043	36	3	498	528	83	6	4262	4280	12	-4	2709	2712	9	-2	1727	1789	19
-14	1701	1780	20	-4	467	470	67	4	854	812	50	8	2852	2786	15	-2	2639	2712	10	0	1738	1807	19
-11	1686	1687	18	-2	614	578	53	6	844	839	53	9	1056	1048	28	1	6056	641	31	1	1062	1177	29
-9	1354	1412	20	-1	412	249	76	7	970	957	49	10	896	945	36	2	742	726	30	2	5096	5102	15
-8	2806	2832	14	0	2068	2118	22	8	610	416	76	11	1197	1175	31	3	523	362	47	3	748	776	39
-7	816	848	29	1	1336	1350	30	-1	1197	1175	31	12	1749	1669	26	4	1920	1908	18	4	5659	5770	15
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-5	754	773	32	3	1070	987	38	-15	1302	1313	37	14	902	872	50	6	2987	2987	16	6	1478	1476	27
-4	5218	5373	13	4	3115	3043	31	-13	635	737	69	16	2245	2167	28	7	1797	1805	22	7	1461	1488	29
-3	1343	1407	21	5	1201	1170	38	-12	743	865	61	17	1079	1018	49	8	3933	3863	17	8	2013	1980	26
-2	2442	2411	16	6	2211	2164	26	-10	2143	2151	28	-18	521	450	90	10	541	555	73	10	2256	2378	28
0	2873	2964	16	7	1056	1060	45	-9	612	656	75	-16	1302	1236	35	13	927	828	52	11	1446	1405	37
2	1898	1940	21	8	1299	1259	39	-8	569	409	78	-16	1302	1236	35	13	927	828	52	11	1446	1405	37
3	1762	1787	22	10	1860	1808	32	-7	497	326	86	-15	1152	1062	37	14	970	990	54	-18	1307	1259	28
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COLUMNS ARE 10FO,10FC, 10SIG

COLUMNS ARE 10FO,10FC, 10SIG

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-13	432	493	55	-14	1441	1403	27	4	780	788	55	5	0	13	85	0	13	85	55	16	767	869	71	
-12	1234	1247	22	-12	2149	2138	22	6	868	872	53	6	868	872	53	6	868	872	53	6	868	872	53	
-11	585	588	41	-11	1282	1264	31	7	1452	1484	36	7	1452	1484	36	7	1452	1484	36	7	1452	1484	36	
-10	2487	2711	15	-10	1369	1403	30	8	1607	1516	34	8	1607	1516	34	8	1607	1516	34	8	1607	1516	34	
-7	805	800	33	-9	804	789	45	9	504	312	92	9	504	312	92	9	504	312	92	9	504	312	92	
-6	1210	1229	24	-8	1374	1355	29	0	101	101	101	0	101	101	101	0	101	101	101	0	101	101	101	
-4	4224	4202	15	-6	854	896	42	-17	547	631	83	-15	942	965	52	1	1021	1009	50	-11	1345	1350	32	
-3	1242	1305	27	-4	1687	1614	24	-4	627	611	74	1	1021	1009	50	0	14	14	50	-8	5406	5405	16	
-2	7401	7047	14	-2	1280	1291	29	-13	499	492	94	-13	499	492	94	0	14	14	50	-8	5406	5405	16	
-1	396	425	71	-1	1371	1327	27	-13	499	492	94	-7	645	627	78	0	14	14	50	-8	5406	5405	16	
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2	1900	1860	19	1	874	1033	40	-11	513	663	97	-4	774	673	66	-6	1611	1563	38	0	663	642	7	
3	1741	1715	22	2	845	828	41	-8	684	763	68	-3	818	750	63	-4	774	673	66	-6	1611	1563	38	
4	2358	2316	20	3	986	990	38	-6	989	963	46	-6	989	963	46	0	663	642	7	7	629	646	22	
6	1452	1424	30	4	2352	2423	23	-4	1952	1904	27	0	663	642	7	0	663	642	7	7	629	646	22	
7	983	936	41	5	753	706	54	-3	882	841	49	1	395	428	14	1	395	428	14	1	395	428	14	
9	1227	1121	38	6	3594	3519	21	-2	3975	3638	20	2	7904	7797	6	2	7904	7797	6	3	1576	1577	15	
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12	525	483	92	8	1546	1456	35	0	1406	1359	35	4	1254	1248	12	6	565	520	27	3	1968	1975	17	
13	714	510	70	9	906	900	53	0	1514	1565	34	5	3545	3596	10	8	3458	3491	16	5	1072	1039	29	
14	2151	2071	32	11	547	584	92	5	1250	1245	39	6	613	687	29	9	2801	2863	18	7	764	775	44	
-18	1087	1019	30	12	697	689	77	8	510	590	97	8	2889	2928	13	10	4281	4333	18	8	1136	1087	34	
-16	732	771	40	-16	688	736	54	0	11	11	11	9	1192	1199	22	11	483	601	84	9	1729	1694	27	
-15	1501	1491	23	-15	681	683	56	-14	1284	1291	43	10	2452	2452	16	12	756	821	54	10	1154	1169	39	
-14	1693	1717	21	-14	1257	1301	34	-13	1014	958	52	14	1930	1951	25	15	1234	1178	41	12	1174	1125	42	
-12	2990	3022	17	-12	1557	1532	30	-11	523	676	95	15	1394	1339	32	16	2643	2530	27	1	540	473	60	
-10	731	754	42	-10	2613	2587	22	-10	2154	2072	30	-10	2154	2072	30	1	1	1	1	1	1	540	473	60
-9	1544	1575	23	-9	657	593	60	-9	1224	1091	43	-18	1305	1255	48	-18	2159	2097	29	-15	1011	1025	29	
-8	1337	1307	26	-8	1386	1323	32	-8	3673	3411	23	-14	1733	1620	34	-17	539	566	82	-15	1011	1025	29	
-7	1243	1221	27	-6	1330	1285	31	-7	1123	955	43	-13	707	696	68	-16	2158	2145	26	-12	3296	3368	28	
-6	6286	6398	16	-4	1203	1123	32	-6	1178	1148	42	-10	607	552	67	-14	1176	1123	35	-10	2021	2073	27	
-5	1325	1242	27	-2	2336	2191	22	-4	483	37	87	-8	1063	918	35	-13	1511	1516	26	-8	512	685	76	
-4	3931	3837	16	-1	1080	983	35	-2	544	451	78	-6	1128	1029	20	-12	1959	1916	20	-6	2962	2945	18	
-2	2842	2750	17	0	3456	3370	19	0	825	825	52	-4	2194	2128	8	8	-10	4872	4858	11	-4	3886	3939	15
-1	979	834	31	2	2254	2235	23	0	704	700	64	-3	1145	1121	9	9	942	941	35	-3	1885	1846	19	
0	791	715	38	5	879	869	51	5	890	834	52	-2	6286	6249	6	6	524	587	57	-2	802	855	35	
1	1970	1960	18	6	1316	1343	38	6	1000	916	49	-1	860	889	9	9	6	3872	3926	14	-1	913	882	30
2	3022	3037	18	0	9	9	49	0	12	12	58	0	6413	6023	6	-4	1554	1568	18	0	2846	2930	15	
3	585	590	56	-17	846	892	49	-13	965	1016	58	1	1048	1084	9	-3	977	967	22	1	1966	2000	18	
4	920	941	38	-15	784	855	55	-12	1819	1753	35	1	678	653	16	9	11	11	11	2	1317	1399	24	
5	1756	1847	26	-14	1798	1833	30	-11	628	554	81	3	1596	1533	11	-2	4114	4218	11	5	1319	1322	28	
7	870	881	48	-13	484	396	86	-10	1654	1610	37	5	1019	1015	18	0	528	460	34	6	1584	1544	27	
8	1857	1788	29	-10	3314	3311	72	-8	1651	1490	34	5	1166	1133	18	1	1254	1182	17	7	982	944	27	
9	1300	1301	40	-10	612	527	72	-7	516	652	92	6	2192	2154	13	4	5827	5929	13	8	2110	2080	25	
10	3309	3186	24	-6	1622	1450	29	-6	1140	1033	43	8	465	528	14	5	1009	1070	27	9	804	852	56	
11	518	716	94	-4	2555	2370	22	-4	2005	1877	29	8	465	528	14	5	1009	1070	27	9	804	852	56	
12	2012	2007	32	-3	932	821	43	-3	1289	1216	38	10	1572	1634	23	7	2760	2721	17	12	2442	2447	28	
13	568	548	93	-2	1672	1526	28	-2	691	587	64	11	1359	1357	28	8	1462	1561	26	13	536	409	94	
-18	1986	1997	22	-1	766	623	52	-1	785	734	57	13	794	681	50	10	937	946	42	-18	533	578	58	

COLUMNS ARE 10FO,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG
-17	849	894	38	-4	1804	1759	25	-7	919	835	54	-12	1908	1847	26
-16	1393	1335	27	-2	756	705	49	-6	2604	2367	25	-10	2147	2148	17
-14	2391	2507	24	-1	903	845	42	-3	1689	1498	32	-8	3133	3057	11
-10	1770	1694	30	-2	481	360	92	-7	260	288	52	-7	260	288	52
-8	1760	1734	27	1	1295	1359	33	-1	839	785	55	-6	2547	2531	9
-4	6206	6043	16	2	3045	3139	21	2	1014	1036	46	-4	2903	2817	8
-3	1200	1165	28	3	867	855	47	-3	1937	1863	32	-3	1609	1608	9
-2	3624	3665	16	4	4352	4260	31	-12	595	232	89	-2	2029	1986	7
-1	1290	1235	26	6	1644	1628	30	-10	2722	2348	27	-1	2678	2614	7
0	1396	1428	25	10	2313	2157	29	-9	985	890	55	0	1710	1507	8
1	854	823	36	11	553	192	93	-8	2277	2137	30	3	1515	1452	12
2	1085	1154	32	1	9	1	9	-8	1043	962	48	4	999	1030	18
3	1444	1498	27	-17	578	575	91	-5	1012	916	47	5	2788	2768	11
4	1431	1472	28	-16	1143	1080	50	-5	801	743	58	6	974	985	20
6	721	706	54	-14	675	669	84	-4	801	743	58	6	974	985	20
7	1027	1062	43	-12	2241	2097	30	-3	992	916	48	7	1207	1236	19
8	1605	1574	32	-8	4031	3507	21	-2	1022	967	47	8	531	531	41
9	758	792	61	-7	1192	1124	40	-1	1034	986	47	9	2069	2176	18
11	731	692	67	-6	933	813	47	1	862	796	53	10	2540	2511	17
12	1951	1899	33	-5	453	481	90	2	822	759	57	11	921	927	35
				-4	605	551	67	1	13	1	13	12	1840	1810	23
-16	920	892	48	-2	4642	4264	19	-8	884	683	55	13	490	540	74
-15	909	876	51	-1	1644	1571	29	-7	549	438	83	14	472	532	77
-12	2214	2230	30	0	3882	3820	20	-6	726	635	68	15	744	854	55
-10	2686	2566	25	2	780	843	54	-5	913	732	54	16	923	887	47
-8	2438	2305	24	3	1301	1246	36	-4	670	598	71	17	2	2	2
-7	454	166	84	4	473	481	91	-3	1087	964	47	-18	680	653	100
-6	3158	2880	19	5	1002	1022	47	0	1644	1614	34	-17	983	904	67
-5	1106	1067	35	6	791	684	56	-6	2843	2776	31	-16	2843	2776	31
-2	532	304	59	7	784	768	59	-5	1086	1025	58	-15	1086	1025	58
-1	942	808	37	8	662	613	72	-5	1399	1229	40	-14	1340	1310	43
0	888	913	38	9	522	572	94	-4	2456	2210	29	-13	679	609	62
1	1478	1489	26	1	10	1	10	-12	857	721	40	-12	857	721	40
3	1080	1078	36	-16	531	19	104	0	9519	9452	6	-10	2475	2543	13
4	631	607	60	-14	827	814	71	1	1028	940	9	-9	610	643	28
5	1292	1306	35	-12	1418	1232	43	2	3049	2925	7	-8	2633	2736	11
6	2018	2028	27	-10	1802	1656	34	3	2947	2917	8	-7	383	373	35
8	2808	2747	25	-9	847	767	61	4	396	414	34	-6	3202	3140	10
10	1541	1539	36	-8	1820	1630	32	5	743	718	21	-5	880	858	18
11	985	1008	53	-6	1883	1729	29	6	1795	1765	13	-4	4027	3941	9
12	1696	1626	37	-5	695	629	63	7	1808	1892	14	-3	2402	2024	10
				-4	1985	1836	28	8	1525	1557	16	-2	1402	1297	11
-18	1250	1236	39	-3	1216	1058	38	10	636	629	39	-1	248	79	45
-17	886	925	55	0	1330	1354	36	11	1801	1798	10	1	2134	2177	14
-15	741	745	68	1	863	769	51	12	1404	1398	25	2	522	434	29
-14	2458	2434	29	3	894	921	50	13	1129	1096	32	3	1228	1216	16
-12	3494	3225	25	5	628	679	72	15	539	601	67	4	543	508	32
-11	561	364	90	6	898	853	53	16	2134	2135	25	5	408	504	44
-10	990	835	51	8	827	869	63	17	1115	1150	41	6	2821	2806	13
-8	1611	1524	32	1	11	1	1	7	3037	3059	14	9	1073	1101	38
-7	559	508	75	-14	889	726	65	-17	825	849	77	8	3613	3629	15
-6	1758	1534	27	-10	1914	1783	33	-16	795	779	75	9	580	608	50
-5	637	576	60	-8	611	620	81	-14	1274	1138	47	10	1321	1287	27

COLUMNS ARE 10FO,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG
-16	1605	1509	36	-12	1908	1847	26	-16	1640	1626	40	-16	1640	1626	40
-14	2054	2011	28	-10	2147	2148	17	-14	1340	1310	43	-14	2134	2148	16
-13	883	841	48	-8	3133	3057	11	-12	981	1024	31	-12	981	1024	31
-12	1130	1084	37	-7	260	288	52	-9	1140	1144	24	-4	3275	3318	16
-10	3516	3548	18	-15	779	729	72	-5	563	577	37	-3	600	723	46
-8	1631	1571	21	-14	1891	1809	28	-4	1271	1255	18	-2	2028	2053	18
-7	834	818	33	-12	382	263	58	-3	3143	3105	12	-1	1257	1239	24
-5	665	696	36	-10	1375	1364	17	-2	2335	2325	13	2	1881	1918	20
-4	4638	4715	13	-9	1241	1242	18	-1	316	334	63	3	953	983	34
-3	327	205	65	-8	5294	5433	11	0	579	617	34	4	519	468	62
-2	5979	6084	13	-6	704	698	26	1	2134	2177	14	5	1039	969	36
-1	2499	2511	14	-4	3730	3723	20	2	4668	4699	12	8	466	475	90
0	3684	3807	13	-3	445	441	37	3	2678	2768	11	10	2735	2693	25
1	1830	1807	17	-2	809	768	21	4	690	688	40	11	1286	1227	41
2	1615	1582	20	-1	2076	2070	12	5	398	233	71	12	2020	2045	32
3	1615	1582	20	-1	2076	2070	12	5	398	233	71	12	2020	2045	32
4	690	688	40	0	1566	1535	14	6	2233	2196	16	13	759	788	70
5	398	233	71	0	1036	1082	19	7	994	1057	38	14	2443	2400	30
6	2652	2590	19	1	1036	1082	19	7	994	1057	38	14	2443	2400	30
7	994	1057	38	2	2398	2411	12	8	3170	3224	17	15	850	715	56
8	994	1057	38	2	2398	2411	12	8	3170	3224	17	15	850	715	56
9	1009	993	42	3	4721	775	28	9	1108	1087	36	-16	900	884	73
10	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
11	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
12	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
13	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
14	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
15	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
16	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
17	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
18	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
19	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
20	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
21	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
22	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
23	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
24	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
25	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
26	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
27	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
28	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
29	1774	1763	29	4	721	775	28	9	1108	1087	36	-16	900	884	73
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COLUMNS ARE 10FD,10FC, 10SIG

COLUMNS ARE 10FD,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	
-3	1390	1317	37	5	1630	1636	14	1	4	545	587	30	-2	3703	3674	13	4	2172	2171	23	4	1865	1854	26
-1	600	547	75	6	1788	1870	15	2	762	728	24	3	4101	4139	30	5	1033	1033	40	6	1033	897	40	
2	1434	1482	38	9	886	858	29	3	759	763	26	4	1781	1822	17	7	1031	988	42	8	1055	1063	43	
3	12	608	80	10	1812	1778	20	4	508	532	39	5	905	904	28	8	1061	1063	43	11	861	815	56	
-12	710	2075	31	11	1990	2003	20	5	605	639	36	6	1156	1196	23	9	965	947	29	10	965	947	29	
-10	2253	2075	31	13	1261	1293	29	6	1156	1196	23	4	965	947	29	10	965	947	29	11	861	815	56	
-8	1672	1573	36	14	448	502	77	7	1988	2087	18	6	2788	2867	18	16	586	560	75	-15	586	560	75	
-5	769	686	62	4	2	2	4	8	2759	2804	17	8	763	672	46	18	15	507	620	86	-13	644	747	66
-3	849	745	56	-17	1048	1048	37	9	2189	2236	20	10	1571	1566	29	6	4	6	6	6	6	6	6	6
-1	879	810	56	-16	2373	2448	21	10	1405	1403	27	2	4	885	885	42	4	885	885	42	-12	1348	1318	33
2	497	329	92	-15	1118	1156	29	11	1209	1155	32	27	-17	884	885	42	4	885	885	42	-10	2415	2398	23
3	13	648	68	-14	575	580	49	13	1370	1443	32	32	-16	603	596	58	16	603	596	58	-9	1397	1411	30
3	13	648	68	-13	540	479	46	14	866	888	49	49	-15	965	999	38	14	866	888	49	-8	432	509	81
-11	874	770	68	-12	1389	1479	20	15	887	877	52	52	-14	1178	1181	32	15	887	877	52	-7	779	772	45
-10	824	656	66	-10	1164	908	19	4	4	4	4	4	-14	1178	1181	32	15	887	877	52	-6	1500	1477	27
-9	1258	1117	46	-9	576	633	32	16	1342	1454	25	25	-12	2600	2614	19	16	1342	1454	25	-5	2119	2137	22
-6	1612	1414	36	-8	1392	1384	15	-14	1923	1869	18	18	-10	989	1039	33	17	784	691	43	-3	784	691	43
-3	714	648	70	-7	568	560	29	-13	1538	1609	21	21	-8	893	988	38	17	784	691	43	-2	924	862	38
0	5106	4978	8	-6	3109	3122	11	-12	1038	984	26	26	-7	2552	2657	17	1	1012	1096	38	-2	924	862	38
2	1939	1960	10	-5	1458	1455	13	-11	763	793	34	34	-9	1540	1503	23	2	1012	1096	38	-1	1012	1096	38
2	1767	1780	11	-4	3738	3622	10	-9	2740	2777	14	14	-6	2204	2144	17	3	1849	1689	27	2	1849	1689	27
3	885	840	17	-3	4637	4536	9	-7	1262	1248	19	19	-5	555	509	45	4	1201	1216	38	4	1201	1216	38
7	1065	1077	20	-2	726	686	21	-6	1748	1775	15	15	-4	1386	1423	21	5	1299	1349	36	5	1299	1349	36
8	334	280	58	-1	1171	1169	15	-4	2580	2650	13	13	-3	682	757	27	6	3312	3340	23	6	3312	3340	23
9	525	365	43	0	1413	1373	13	-4	1984	1951	14	14	-2	955	949	27	7	1314	1346	38	7	1314	1346	38
10	1414	1400	21	1	2736	2756	11	-1	918	903	21	21	-1	376	351	64	8	1107	1144	47	8	1107	1144	47
11	859	843	33	2	306	444	51	0	1065	1082	20	20	1	1396	1433	23	9	1107	1144	47	9	1107	1144	47
12	795	817	39	3	1493	1491	14	1	3890	3944	12	12	2	392	349	69	10	1100	1101	45	10	1100	1101	45
14	610	596	54	4	2685	2672	12	2	5157	5140	12	12	3	416	423	67	11	1453	1442	36	11	1453	1442	36
15	1280	1261	31	6	1111	1136	21	3	3983	4087	13	13	4	686	735	45	12	1453	1442	36	12	1453	1442	36
16	1459	1434	30	7	2527	2520	15	4	2664	2780	15	15	5	407	431	76	13	1110	1113	42	13	1110	1113	42
4	1	1	52	8	2533	2645	16	5	1070	1054	26	26	6	444	614	81	14	1110	1113	42	14	1110	1113	42
-17	790	795	52	9	831	903	35	6	942	1029	26	26	7	942	1029	26	15	1467	1425	33	15	1467	1425	33
-16	679	681	54	10	2018	2046	20	7	942	1029	26	26	8	1586	1546	30	16	1467	1425	33	16	1467	1425	33
-14	1424	1413	25	11	972	1012	35	8	2291	2303	20	20	9	1586	1546	30	17	776	717	52	17	776	717	52
-13	922	972	32	12	1857	1929	24	9	972	982	38	38	10	1299	1344	37	18	776	717	52	18	776	717	52
-12	1305	1283	22	13	1027	943	36	10	1428	1402	29	29	11	1167	1148	42	19	776	717	52	19	776	717	52
-11	2455	2524	15	14	926	841	42	11	747	704	50	50	12	1116	1127	45	20	776	717	52	20	776	717	52
-10	1090	1041	21	15	1026	930	42	12	1026	1089	33	33	-17	1242	1225	36	21	776	717	52	21	776	717	52
-9	488	476	38	-16	667	651	43	-18	1026	1089	33	33	-14	518	513	73	22	776	717	52	22	776	717	52
-8	2214	2198	12	-15	605	651	46	-17	480	383	62	62	-13	901	955	44	23	776	717	52	23	776	717	52
-7	376	305	40	-14	2119	2150	18	-16	1597	1637	24	24	-12	847	962	46	24	776	717	52	24	776	717	52
-6	1771	1824	12	-14	1415	1454	25	-14	1415	1454	25	25	-11	464	328	73	25	776	717	52	25	776	717	52
-5	4127	4185	9	-11	1597	1593	18	-13	617	564	49	49	-9	1429	1419	27	26	776	717	52	26	776	717	52
-5	4127	4185	9	-10	1137	1102	21	-11	742	788	40	40	-7	2618	2645	18	27	776	717	52	27	776	717	52
-3	1808	1737	11	-9	2033	2511	14	-11	936	958	32	32	-6	2504	2520	18	28	776	717	52	28	776	717	52
-2	1953	1917	10	-8	4032	4025	12	-10	2896	2887	16	16	-5	2396	2405	19	29	776	717	52	29	776	717	52
-1	4737	4704	9	-6	446	416	38	-9	374	465	69	69	-4	393	456	73	30	776	717	52	30	776	717	52
0	2911	2806	9	-4	976	978	18	-8	1912	1918	17	17	-3	1251	1189	25	31	776	717	52	31	776	717	52
1	2379	2257	10	-3	636	651	25	-7	2997	3094	14	14	-2	1908	1905	20	32	776	717	52	32	776	717	52
2	689	701	21	-2	1206	1192	16	-6	1094	1125	23	23	0	1363	1417	25	33	776	717	52	33	776	717	52
3	1431	1418	13	-1	1415	1450	14	-5	892	907	26	26	1	660	668	47	34	776	717	52	34	776	717	52
4	1352	1337	14	0	288	380	53	-3	1899	1987	16	16	2	878	834	38	35	776	717	52	35	776	717	52

COLUMNS ARE 10FO,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG
-6	1143	1222	41	-10	842	789	26	-16	1736	1731	21	-10	752	745	36	-7	2735	2786	18	-3	1083	1089	43
-5	1576	1494	31	-8	3182	3258	12	-14	392	179	68	-9	2244	2321	17	-6	1150	1154	29	-2	2143	2153	26
-4	3305	3362	23	-8	1190	1210	18	-14	758	681	35	-8	785	812	33	-5	1449	1529	25	-1	1905	1918	38
-3	2163	2198	27	-6	1276	1288	15	-13	723	726	37	-7	678	675	36	-3	1411	1460	25	0	1218	1225	38
-2	2441	2508	26	-4	1547	1464	13	-11	1690	1758	19	-6	1102	1135	23	-3	1368	1419	25	1	1269	1234	37
2	592	659	74	-3	6199	6240	10	-10	1687	1714	18	-5	1176	1210	22	-2	1530	1447	23	2	818	928	55
4	1810	1825	32	-2	4597	4584	10	-9	1387	1375	14	-4	561	492	38	-2	2588	2645	19	-12	824	800	63
5	496	82	92	-1	4551	4501	10	-7	1926	1976	19	-4	1235	1258	21	2	825	849	40	-11	1063	1016	48
4	1103	1013	16	-6	1201	1210	18	-1	1059	1107	24	-1	1059	1107	24	3	435	258	76	-9	831	855	57
20	765	780	20	-5	572	452	31	0	2609	2681	15	5	445	412	45	5	445	412	85	-6	1266	1268	40
29	544	518	29	-4	1311	1266	16	1	3939	4023	14	6	2243	2325	24	4	2243	2325	24	-5	1654	1631	32
4	2953	2974	12	-2	510	407	32	2	3193	3310	15	7	2081	2153	26	-4	2443	2339	26	-4	2443	2339	26
5	1413	1461	16	0	418	401	41	3	1676	1775	20	8	1536	1520	32	-3	878	962	54	-3	878	962	54
6	1721	1742	16	1	1892	1916	14	4	667	613	41	9	2320	2383	27	0	881	863	52	0	881	863	52
8	709	640	34	2	1316	1270	17	5	458	496	62	5	81	553	81	2	1395	1429	39	2	1395	1429	39
9	1178	1159	25	3	2040	2090	15	7	739	715	45	-15	491	553	81	5	81	553	81	-15	491	553	81
10	569	423	48	5	3019	3149	14	8	2380	2468	22	-14	920	920	45	-14	920	920	45	-14	920	920	45
11	502	429	59	6	1041	1054	26	10	697	748	54	-12	1354	1411	32	-10	1502	1526	39	-10	1502	1526	39
12	1416	1434	26	7	1512	1507	21	12	1003	963	44	-8	605	781	60	6	605	781	60	-8	605	781	60
13	1895	1914	23	8	788	748	37	8	788	748	37	-17	917	940	40	5	1916	1681	23	1	2201	2200	12
14	427	500	81	9	520	564	60	9	520	564	60	-15	1473	1435	27	-4	1961	1936	22	3	848	881	21
15	1923	1914	26	10	676	640	48	10	676	640	48	-14	799	787	43	-3	1400	1424	27	5	1839	1794	14
5	2	2	2	14	605	695	67	14	605	695	67	-13	967	997	36	-2	1691	1641	24	10	1325	1325	24
33	882	882	33	-17	788	791	38	-12	981	924	34	1	911	902	41	11	2014	2035	20	15	1815	1740	25
18	2411	1538	22	-16	390	506	73	-11	742	718	43	2	1019	1040	39	14	607	552	55	15	1815	1740	25
33	770	770	33	-12	877	844	32	-10	1277	1290	26	3	2093	2119	25	15	1740	1740	25	15	1740	1740	25
15	2276	2210	15	-11	2707	2726	16	-9	375	371	74	4	3078	3074	22	5	1740	1740	25	15	1740	1740	25
17	1547	1547	17	-10	829	821	31	-8	1036	1091	30	5	1308	1332	35	-15	1125	1172	29	15	1740	1740	25
15	1715	1715	15	-9	1320	1315	21	-7	2339	2374	18	6	461	404	88	-14	709	741	40	15	1740	1740	25
15	1694	1694	15	-8	1182	1146	22	-6	2027	1960	18	7	480	550	90	-12	849	918	51	-8	492	503	40
15	2922	2922	11	-7	3436	3532	13	-4	2396	2496	16	8	1081	1164	45	-11	3347	3365	14	-7	1290	1309	17
11	3023	3051	11	-6	1298	1327	19	-5	1041	1005	21	-3	1642	1606	19	5	9	9	9	-9	827	865	28
16	1214	1214	16	-5	1041	1005	21	-3	1642	1606	19	-3	1642	1606	19	-13	1630	1638	31	-8	492	503	40
35	408	408	35	-4	758	766	27	-2	1059	1613	20	-2	1059	1613	20	-12	849	918	51	-7	1290	1309	17
21	666	666	21	-3	931	906	22	-1	1089	1109	26	-1	1089	1109	26	-10	822	934	51	-5	2386	2361	12
11	2799	2799	11	-1	2594	2634	13	0	846	840	32	0	846	840	32	26	26	26	26	-13	1630	1638	31
20	780	780	20	0	2347	2399	14	2	1160	1170	27	2	1160	1170	27	-9	818	839	49	-9	818	839	49
34	340	340	34	1	2894	2921	14	4	397	401	75	4	397	401	75	-8	1305	1252	33	-4	1887	1937	13
11	3106	3106	11	3	1153	1194	23	6	1367	1412	29	6	1367	1412	29	-5	941	897	42	-3	1152	1083	16
16	1481	1480	16	4	2476	2594	16	7	1091	1118	36	6	1367	1412	29	-4	1342	1351	32	-2	278	444	11
19	1171	1171	19	5	2125	2138	18	8	585	608	64	7	1091	1118	36	-3	1192	1187	35	-1	4440	4448	11
29	692	692	29	7	1526	1570	23	11	1453	1485	35	8	585	608	64	-2	1106	1116	37	0	2594	2586	11
18	1676	1676	18	8	930	969	36	11	1453	1485	35	-1	1231	1280	36	1	3148	3078	11	1	3148	3078	11
18	1676	1676	18	8	930	969	36	11	1453	1485	35	11	1453	1485	35	2	1676	1724	14	2	1676	1724	14
20	1538	1538	20	6	1466	1538	20	10	1058	1117	35	5	7	7	7	3	352	266	47	3	352	266	47
35	1538	1538	35	7	1466	1538	20	10	1058	1117	35	-16	1376	1375	32	3	1094	1065	40	4	1173	1159	19
44	1949	1949	44	8	1848	1949	20	11	879	837	43	-15	1949	1991	25	5	10	10	10	-13	1456	1449	37
23	2996	2997	17	12	779	743	50	-14	1016	1019	38	-14	1016	1019	38	-12	1378	1391	37	6	2050	2026	16
26	2735	2768	18	13	1471	1425	32	-13	1038	1065	37	-13	1038	1065	37	-11	1370	1421	36	7	1086	1106	23
23	1889	1889	23	13	1471	1425	32	-13	1038	1065	37	-11	1370	1421	36	8	592	619	43	8	592	619	43
59	834	834	59	11	1809	1889	23	5	5	5	5	-11	1169	1204	33	-9	896	808	48	10	522	477	54
45	834	834	45	12	775	834	45	-16	1335	1181	29	-11	439	462	76	-8	707	717	60	11	1552	1586	24
47	985	1015	38	13	985	1015	38	-14	1318	1343	26	-10	1394	1422	28	-6	1093	1132	42	12	413	125	73
19	526	466	69	14	526	466	69	-12	1324	1363	26	-9	2396	2436	20	-5	1052	1069	43	13	1637	1607	25
24	1188	1188	24	14	526	466	69	-12	1324	1363	26	-9	2396	2436	20	-5	1052	1069	43	13	1637	1607	25
5	5	5	5	-11	632	579	44	-11	632	579	44	-8	2878	2902	18	-4	675	607	61	14	1064	953	36

COLUMNS ARE 10FD, 10FC, 10SIG

COLUMNS ARE 10FD, 10FC, 10SIG

15	1025	904	39	-7	1162	1178	23	5	971	969	6, 10, L	6	1632	1646	19	1285	1299	FC	19		
-16	1093	1059	29	-4	2106	2035	15	9	2087	2102	L	-13	970	997	48	1407	1421	FC	25		
-15	610	653	47	-3	2430	2434	15	6	6	7, L	-12	746	809	60	392	418	495	FC	60		
-13	603	601	44	-4	1843	2159	27	-15	685	746	L	-11	1520	1510	33	2836	2864	FC	15		
-12	690	656	37	0	562	854	38	-10	541	613	L	-9	1657	1706	30	1170	1189	FC	23		
-11	639	595	38	1	2730	2812	15	-7	2553	2605	L	-5	1347	1372	35	1893	1929	FC	17		
-10	547	518	41	2	3476	3577	14	-6	2672	2668	L	-3	1964	1963	27	1634	1706	FC	48		
-9	2106	2123	15	3	3881	3951	14	-5	2756	2795	L	-2	1573	1565	31	1574	1644	FC	41		
-7	963	966	22	4	842	817	32	-4	412	379	L	-1	2280	2374	17	1597	1644	FC	19		
-5	2198	2325	13	5	2295	2328	18	-2	1954	1920	L	0	499	459	364	1214	1238	FC	23		
-4	1690	1639	14	6	1132	1159	28	-1	848	849	L	3	949	859	49	3	589	614	FC	44	
-3	3934	4032	11	8	1243	1276	29	0	1610	1582	L	4	1435	1521	37	7	1842	1859	FC	20	
-2	1634	1649	14	10	1263	1277	31	2	1682	1689	L	6, 11, L	6	752	745	29	2857	2915	FC	17	
-1	626	577	27	11	1095	1114	36	4	631	677	L	-11	1083	1015	46	5	2431	2453	FC	19	
0	1017	1016	19	6, 5, L	1051	1024	32	5	991	1039	L	-6	1248	1257	40	8	968	992	FC	36	
1	1019	1034	20	-16	515	594	61	8	864	913	L	-2	1206	1216	41	1	2293	2181	FC	7, 5, L	
3	969	979	22	-15	391	226	73	9	802	723	L	-1	487	381	91	1	928	975	FC	35	
4	3096	3147	13	-13	687	562	42	8, L	6, 8, L	L	0	823	810	55	2	2065	2092	FC	55		
6	1038	978	25	-11	1268	1276	25	-15	974	961	L	-7	892	997	57	6	1810	1888	FC	79	
7	1149	1154	25	-10	1075	1072	27	-13	1018	1057	L	-3	563	655	84	7	1592	1577	FC	25	
8	1479	1455	22	-9	1075	1072	27	-13	1018	1057	L	-3	563	655	84	7	1592	1577	FC	35	
10	1183	1239	30	-8	1523	1523	21	-12	593	703	L	0	1349	1293	16	10	599	709	FC	24	
11	990	1073	35	-7	2995	2973	15	-10	952	1001	L	1	3883	3841	11	11	1149	1161	FC	38	
12	1220	1219	31	-6	1591	1637	20	-9	1236	1265	L	0	1349	1293	16	10	599	709	FC	24	
13	1443	1478	30	-5	1017	927	26	-8	1287	1332	L	3	4322	4312	12	12	887	906	FC	32	
14	598	631	64	-3	1732	1761	18	-5	1581	1572	L	3	4322	4312	12	12	887	906	FC	22	
-15	1067	1117	29	-2	788	796	31	-4	427	545	L	5	738	703	29	13	876	828	FC	16	
-14	1171	1124	26	-1	3096	3205	15	-2	1667	1718	L	6	1145	1154	22	6	1145	1154	FC	43	
-11	2351	2323	16	0	2784	2866	15	0	1376	1388	L	8	358	359	67	-15	611	565	FC	38	
-10	974	1017	28	1	574	656	45	1	534	515	L	9	2145	2072	18	-13	414	397	FC	16	
-9	3518	3572	14	3	885	900	31	2	853	884	L	10	668	631	43	-12	560	478	FC	19	
-8	1760	1725	17	4	1143	1155	26	4	954	1004	L	11	753	814	41	-11	1477	1482	FC	26	
-5	831	863	25	6	2036	2066	21	5	1676	1678	L	12	1148	1170	30	-10	571	487	FC	73	
-4	891	882	23	8	1009	1036	36	6	2041	2084	L	13	1597	1588	25	-9	1354	1302	FC	35	
-2	1688	1709	15	9	492	419	70	7	1350	1353	L	-13	1721	1801	21	-8	347	446	FC	29	
2	1335	1328	18	10	722	734	54	9	6, 9, L	6, 9, L	L	-12	668	750	41	-6	510	494	FC	46	
4	828	885	30	6, L	430	88	75	-14	854	905	L	-11	423	606	60	-5	677	653	FC	14	
5	1922	1889	18	-16	430	88	75	-11	1294	1326	L	-10	1019	1097	27	-4	1464	1424	FC	44	
7	4233	4270	15	-15	1294	1331	30	-9	462	180	L	-9	4015	4034	13	-3	842	848	FC	33	
8	1120	1141	30	-14	1015	986	34	-8	1378	1441	L	-8	1053	1069	24	-2	1085	1062	FC	18	
9	1719	1708	23	-13	1813	1797	23	-6	642	650	L	-7	1299	1240	19	-1	1171	1152	FC	22	
11	482	504	68	-12	698	728	46	-5	600	504	L	-6	736	717	28	0	615	623	FC	48	
13	1827	1838	27	-10	421	83	71	-3	467	571	L	-5	688	614	29	-3	688	670	FC	29	
-16	603	655	50	-9	1213	1206	37	-2	1437	1511	L	-3	5116	5108	12	3	1277	1329	FC	41	
-14	979	1031	31	-8	983	952	31	-1	1311	1372	L	-2	2990	2984	12	4	1280	1308	FC	27	
-13	1598	1586	22	-6	993	1010	30	1	2721	2864	L	-1	4036	3974	12	5	3421	3408	FC	17	
-12	1143	1203	28	-3	1649	1675	21	2	1122	1060	L	0	1127	1140	19	6	379	289	FC	29	
-11	1273	1273	25	-1	1933	1933	19	3	803	818	L	3	803	818	26	12	457	543	FC	78	
-9	3162	3158	15	0	692	631	40	4	914	930	L	4	2367	2412	15	7, 4, L	2	1227	1277	FC	27
-8	413	283	57	1	711	708	40	4	6, 10, L	6, 10, L	L	5	728	687	31	-11	2557	2552	FC	36	

COLUMNS ARE 10FD,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	
4	649	635	49	0	770	1734	55	-1	580	540	37	-14	678	627	49	-5	657	669	51	7	1121	1147	28	
5	1043	1095	35	1	341	287	63	3	1341	583	49	-12	616	583	49	-3	806	829	43	11	437	663	46	
6	978	1028	38	3	1329	1312	21	-9	1366	1430	25	-2	1280	1301	30	12	795	758	46	12	795	758	46	
7	1257	1221	32	4	2214	2211	17	-7	1458	1432	23	-7	1458	1432	23	36	9	2	9	12	795	758	46	
7	7	7	11, L	5	384	461	66	6	746	780	39	-6	746	780	39	36	1701	1773	28	-14	817	793	39	
-15	2055	2075	25	-7	1250	1241	39	4	1083	1090	28	-4	1083	1090	28	28	5	1815	1801	28	-13	1227	1214	28
-14	922	922	41	-5	1677	1758	32	7	389	257	72	-3	2050	2067	19	19	8	9	9	-12	567	580	50	
-13	1391	1388	29	-4	1315	1410	39	8	543	456	54	-1	1038	974	28	28	-11	1134	1102	38	-11	999	953	40
-9	1769	1767	23	-2	517	492	83	9	1163	1217	30	-1	1958	2004	19	19	-9	673	633	56	-10	559	568	39
-8	2006	2077	22	8	0	0	0, L	11	1224	1284	31	0	1478	1418	23	23	0	1478	1418	28	-8	696	702	40
-7	1753	1777	23	0	970	948	23	8	8	3, L	31	0	1478	1418	23	23	0	1478	1418	28	-8	696	702	40
-6	1259	1236	28	1	2220	2187	14	-15	1549	1520	25	3	882	1030	32	32	7	902	879	42	-7	1142	1149	26
-5	798	912	42	2	605	588	34	-11	1358	1407	24	6	1115	1054	32	32	-5	1355	1463	32	-6	702	601	37
-4	1248	1287	28	3	1857	1884	16	-10	904	900	32	7	690	703	50	50	-1	867	868	46	-5	589	626	43
-3	1263	1249	28	4	1478	1472	19	-9	2744	2756	16	9	600	557	60	60	7	600	557	60	-4	1866	1903	18
-2	1446	1462	26	5	3121	3110	14	-7	864	855	30	8	6	6	6, L	85	2	470	113	85	-2	1116	1124	24
0	2265	2391	21	6	1091	1080	24	-5	1255	1259	22	-14	546	563	64	64	3	1325	1305	36	-1	759	755	33
1	910	854	38	7	537	498	46	-5	1255	1259	22	-13	1969	2005	23	23	8	10, L	8	10, L	1	1327	1329	22
3	810	826	43	8	363	337	73	-4	2134	2129	16	-12	561	590	59	59	-9	1179	1187	39	2	705	675	36
5	436	205	60	11	2036	2011	21	-3	618	589	38	-10	980	1120	35	35	-7	791	736	52	3	565	580	46
6	672	622	56	13	425	265	75	-2	1756	1726	18	-8	581	667	53	53	-6	683	718	60	6	709	689	41
7	1607	1617	29	8	1	1, L	65	-1	1732	1677	18	-6	411	284	71	71	-5	927	928	46	7	1226	1252	28
-10	794	872	45	-13	418	376	65	2	993	953	27	-4	524	592	58	58	-3	1042	1093	42	9	912	917	37
-9	699	734	50	-8	1107	1090	25	5	843	775	32	-3	1469	1487	25	25	-2	536	610	79	10	946	890	37
-9	1359	1352	31	-7	1702	1671	18	3	1613	1676	22	-2	589	611	52	52	-1	784	773	55	9	9	3, L	9
-6	546	485	61	-6	1024	968	24	6	554	618	54	-1	3061	3136	18	18	0	9	0, L	0	13	627	552	49
-5	573	568	57	-5	529	520	42	7	3871	4012	17	0	880	857	36	36	1	3034	2992	14	-12	790	820	38
-4	1156	1176	32	-4	2093	1987	15	9	1132	1150	32	3	1681	1122	33	33	2	1681	1562	18	-11	696	646	41
-3	987	1014	37	-1	3193	3144	13	10	875	840	39	5	1255	1307	32	32	3	4013	3913	14	-8	478	392	57
-2	1178	1194	32	0	1101	1113	21	15	448	423	69	7	659	652	55	55	4	1163	1113	24	-7	1928	1957	20
0	595	702	58	1	3154	3116	14	-15	448	423	69	7	659	652	55	55	4	1163	1113	24	-7	1928	1957	20
1	1505	1586	28	2	1823	1826	16	-14	392	34	71	-13	1399	1436	30	30	7	643	668	42	-5	1312	1347	24
3	1282	1833	27	3	1427	1469	19	-13	1117	1159	30	-13	1399	1436	30	30	9	2036	2049	21	-4	930	892	30
4	930	948	44	4	959	954	26	-12	1190	1237	28	-12	871	838	41	41	10	669	722	47	-3	1393	1324	22
5	347	450	44	5	347	450	44	-11	835	879	37	-10	618	609	55	55	11	1019	998	34	-2	1135	1104	25
6	1127	1127	25	6	1127	1127	25	-9	1750	1812	21	-10	797	751	42	42	12	639	679	53	-1	1401	1429	22
7	599	567	44	7	599	567	44	-8	558	556	49	-7	1690	1740	24	24	9	1	1, L	9	0	750	778	36
8	775	801	37	8	775	801	37	-6	518	525	52	-8	1690	1740	24	24	9	1	1, L	9	0	750	778	36
9	1328	1339	26	9	1328	1339	26	-7	1496	1538	21	-6	1139	1232	31	31	-11	740	764	37	2	525	584	51
10	661	656	46	-5	1933	1888	18	-5	1745	1788	24	-5	1745	1788	24	24	-9	2343	2335	17	3	364	146	70
11	710	751	46	-4	1706	1657	19	-2	956	1014	37	-2	956	1014	37	37	-8	366	484	71	4	1032	1071	30
12	416	436	78	-4	1593	1586	20	0	1077	1101	33	0	1077	1101	33	33	-7	990	979	28	5	2289	2344	19
13	1074	1063	36	-2	1168	1093	24	1	409	457	81	-6	1484	1476	21	21	-6	1484	1476	21	9	2151	2188	23
15	402	256	71	-1	1131	1038	25	2	1371	1461	28	-5	623	629	39	39	2	1371	1461	28	-5	623	629	39
-11	1348	1341	55	-11	869	937	32	4	894	894	30	4	431	548	83	83	-4	1456	1450	20	-12	768	681	41
-10	778	762	55	-10	572	518	46	2	1084	1097	27	7	570	638	70	70	-3	2287	2279	16	-11	1555	1537	23
-9	485	435	81	-9	1353	1352	22	3	2627	2687	18	8	8	8, L	8	8	-2	858	930	30	-10	928	954	34
-8	1457	1509	33	-7	998	902	25	6	2168	2199	20	-11	1057	1096	38	38	-1	2118	2064	16	-9	680	692	43
-6	661	657	59	-6	983	955	26	5	492	462	61	-9	1046	1023	36	36	3	643	562	38	-8	371	330	73
-3	1014	1037	42	-5	3041	3033	14	10	865	900	44	-8	1110	1128	34	34	4	1633	1582	20	-6	384	1064	31
-2	1346	1365	34	-3	3062	2963	14	8	5	5, L	8	-7	440	737	80	80	6	837	907	34	-5	541	490	50

COLUMNS ARE 10FD,10FC, 10SIG

COLUMNS ARE 10FO,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG		
-4	1499	1484	22	3	796	831	46	-3	1412	1490	23	-1	1011	1019	33	2	917	944	32		
-2	1642	1678	21	9	9	8	40	-2	497	576	54	1	1506	1529	25	7	1040	992	33		
-1	540	521	52	-10	972	911	50	-1	958	982	30	2	492	474	63	8	891	895	39		
1	570	609	50	-9	1326	1323	31	0	877	852	32	3	846	850	40	-10	410	559	77		
2	495	428	57	-8	784	878	48	1	878	908	32	4	997	964	36	-9	491	543	62		
3	491	466	59	-7	971	929	38	2	613	671	45	5	459	315	71	-7	1169	1081	28		
5	1850	1964	23	-5	1225	1294	32	3	1585	1595	22	-11	426	439	81	-6	407	412	69		
6	582	564	55	-3	608	503	55	4	729	689	39	-10	963	963	38	-5	731	605	40		
7	1982	2050	23	-1	1045	1071	38	6	593	576	50	-9	653	653	52	-4	1375	1368	25		
8	543	550	63	3	1071	1134	41	8	488	462	65	-8	608	541	55	-3	1907	1860	21		
-12	1272	1209	29	-9	741	688	53	9	1116	1068	33	-7	768	747	43	-2	1375	1392	25		
-11	820	884	41	-7	1162	1238	38	-4	397	251	78	-3	645	657	51	1	1332	1353	35		
-10	1100	1171	31	-6	1128	1150	38	-11	571	496	53	-4	345	345	78	0	760	768	38		
-7	1546	1584	23	-3	693	698	55	-10	623	560	48	-2	695	736	47	5	985	925	34		
-6	412	523	71	-1	1054	965	40	-9	1427	1387	24	-1	2556	2611	20	6	392	53	74		
-5	614	593	47	0	496	207	76	-7	1410	1379	24	0	684	700	48	8	854	808	42		
-4	981	966	32	10	0	0	46	-5	607	612	46	2	627	506	52	11	3	3	44		
-3	482	425	60	0	810	814	32	-4	1439	1516	24	3	1034	1069	37	-10	736	694	44		
-2	968	958	33	1	1435	1443	22	-3	873	847	33	5	928	918	41	-7	946	951	34		
-1	2745	2817	18	3	1464	1488	22	-2	1202	1243	26	10	7	7	1083	998	30	0	1823	1767	22
0	903	875	35	5	1122	1166	27	-1	1914	1914	20	-10	680	630	53	-3	1840	1775	22		
1	2309	2405	20	5	2418	2446	18	1	1880	1936	20	-9	901	812	41	-3	487	488	59		
5	823	827	42	6	958	952	31	3	643	710	46	-8	892	936	42	-2	1007	887	30		
6	514	554	66	7	393	471	73	4	697	712	42	-7	1297	1275	31	-1	982	1014	32		
7	1081	1041	35	8	896	886	34	5	484	611	62	-5	1043	1051	36	0	982	996	33		
8	583	526	62	9	647	590	48	6	739	690	44	-2	572	573	60	1	1650	1598	23		
-13	769	790	48	11	1577	1582	26	7	2720	2729	49	-2	418	130	78	2	890	822	35		
-12	1090	1099	35	-12	904	884	36	8	716	679	49	-2	846	854	43	3	1072	1047	31		
-11	1730	1736	24	-11	1030	1005	31	9	586	655	61	3	776	798	48	4	661	624	48		
-10	664	583	49	-8	588	636	46	-12	1184	1111	31	10	8	786	845	51	11	1028	1038	34	
-9	1147	1152	31	-7	1129	1169	27	-10	1220	1202	29	-8	766	845	51	-10	520	460	63		
-8	547	543	57	-6	902	963	32	-9	846	838	37	-7	1017	981	39	-8	664	693	48		
-5	1376	1472	27	-5	590	612	46	-5	764	827	40	-6	953	974	41	-6	616	661	51		
-3	2728	2770	19	-4	1227	1274	25	-3	898	966	35	-4	449	642	83	-4	706	732	45		
1	1592	1673	25	-3	854	850	32	-2	724	789	42	-3	1519	1534	30	-2	393	340	75		
2	1119	1165	32	-2	998	1017	28	-1	1056	1036	30	-2	642	629	58	-1	813	842	40		
3	1046	1055	34	-1	1319	1337	23	0	1170	1154	28	0	995	1008	29	1	708	733	45		
4	1106	1110	34	0	465	496	55	2	940	972	34	0	951	977	31	2	409	336	73		
5	1295	1309	31	1	1624	1657	20	3	911	896	35	2	1222	1222	25	4	1341	1404	29		
6	445	548	80	2	1030	992	28	5	1151	1122	31	3	2322	2315	18	5	1314	1272	30		
7	641	729	60	3	1272	1304	25	7	448	635	79	3	618	573	46	7	1989	2016	23		
-10	629	631	55	9	1594	1556	25	10	5	5	45	4	888	915	36	-6	566	466	55		
-9	1032	1025	35	10	1437	1377	28	-12	787	775	45	7	1308	1276	29	-6	822	809	41		
-8	880	919	40	-12	1010	952	33	-11	418	121	78	9	11	1	29	-2	866	866	55		
-7	637	669	53	-11	1346	1343	27	-9	1010	952	33	-11	418	121	78	-2	866	866	55		
-6	1033	1112	35	-9	618	622	46	-8	1689	1671	24	-9	1023	993	32	-1	1899	1918	23		
-3	491	565	66	-8	393	368	69	-5	871	866	37	-7	529	437	53	0	804	850	43		
-2	718	710	46	-7	486	503	57	-4	731	771	42	-5	664	622	26	1	1733	1754	25		
0	1193	1194	30	-6	1505	1516	23	-3	1161	1261	29	-4	1216	1197	26	2	977	940	36		
1	912	959	39	-5	2677	2620	17	-2	1013	980	32	-3	592	621	47	-8	750	713	48		

COLUMNS ARE 10FD,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG
-5	1156	1192	34	3	1211	1134	30	-3	1136	1085	31
-1	736	690	49	13	13	1	L	-2	1021	1024	35
0	13	0	L	-2	901	904	38	0	977	980	35
	1196	1137	30	2	1730	1656	24				

Table S.18. Fractional Coordinates for $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$

ATOM	X	Y	Z
OS(1)	0.30601(5)	0.46157(6)	0.31561(5)
OS(2)	0.24561(6)	0.64841(6)	0.23286(5)
OS(3)	0.20186(5)	0.45139(7)	0.12628(5)
OS(4)	0.28547(6)	0.26800(6)	0.23360(6)
P(1)	0.2911(4)	0.7534(4)	0.3594(4)
C(1)	0.217(2)	0.738(2)	0.448(2)
C(2)	0.416(2)	0.740(2)	0.420(1)
C(3)	0.285(2)	0.889(2)	0.334(2)
C(11)	0.437(2)	0.475(2)	0.282(1)
C(12)	0.188(1)	0.459(2)	0.368(1)
C(13)	0.368(2)	0.465(2)	0.437(1)
C(21)	0.380(2)	0.661(2)	0.202(1)
C(22)	0.114(2)	0.630(2)	0.264(1)
C(23)	0.196(2)	0.755(2)	0.150(2)
C(31)	0.083(2)	0.432(2)	0.181(1)
C(32)	0.334(2)	0.480(2)	0.085(1)
C(33)	0.141(2)	0.557(2)	0.050(1)
C(34)	0.167(2)	0.342(2)	0.044(2)
C(41)	0.405(2)	0.293(2)	0.176(2)
C(42)	0.172(2)	0.256(2)	0.297(1)
C(43)	0.362(2)	0.201(2)	0.328(2)
C(44)	0.248(2)	0.147(2)	0.161(2)
O(11)	0.519(1)	0.482(1)	0.277(1)
O(12)	0.123(1)	0.458(1)	0.411(1)
O(13)	0.402(1)	0.463(2)	0.514(1)
O(21)	0.460(1)	0.676(1)	0.189(1)
O(22)	0.035(1)	0.629(1)	0.279(1)
O(23)	0.169(1)	0.823(2)	0.102(1)
O(31)	0.009(1)	0.420(1)	0.207(1)
O(32)	0.403(1)	0.496(1)	0.058(1)
O(33)	0.093(1)	0.612(2)	0.001(1)
O(34)	0.142(1)	0.278(2)	-0.011(1)
O(41)	0.474(1)	0.300(1)	0.142(1)
O(42)	0.104(1)	0.243(1)	0.333(1)
O(43)	0.408(1)	0.155(1)	0.391(1)
O(44)	0.224(2)	0.076(2)	0.121(2)
H(11)	0.229(0)	0.793(0)	0.493(0)
H(12)	0.145(0)	0.742(0)	0.424(0)
H(13)	0.228(0)	0.674(0)	0.479(0)
H(21)	0.431(0)	0.798(0)	0.463(0)
H(22)	0.464(0)	0.743(0)	0.379(0)
H(23)	0.424(0)	0.679(0)	0.454(0)
H(31)	0.304(0)	0.933(0)	0.387(0)
H(32)	0.327(0)	0.910(0)	0.290(0)
H(33)	0.217(0)	0.913(0)	0.307(0)

Table S.19. Thermal Parameters for Os₄(CO)₁₄PMe₃

ATOM	U11	U22	U33	U12	U13	U23
OS(1)	3.41(4)	3.34(5)	2.81(4)	-0.21(3)	0.10(3)	-0.06(4)
OS(2)	3.54(4)	3.78(5)	3.38(5)	0.44(3)	0.93(3)	0.53(4)
OS(3)	3.54(4)	5.43(6)	2.53(4)	-0.11(4)	0.23(3)	-0.27(4)
OS(4)	4.06(5)	3.79(5)	4.27(5)	-0.06(4)	0.83(3)	-0.89(4)
P(1)	4.7(3)	4.1(3)	4.7(3)	-0.2(3)	1.0(2)	-0.2(3)
C(1)	11.9(23)	8.8(21)	6.3(17)	-2.8(17)	4.8(16)	-3.1(16)
C(2)	6.4(14)	5.8(15)	4.3(12)	-0.9(11)	1.1(10)	-0.2(12)
C(3)	10.8(21)	5.2(17)	6.1(16)	0.1(14)	1.7(15)	-0.7(13)
C(11)	6.3(15)	3.6(13)	4.3(12)	0.2(11)	2.5(11)	1.3(10)
C(12)	4.2(11)	4.3(13)	3.5(11)	-0.3(10)	0.4(9)	1.1(10)
C(13)	6.7(14)	6.0(15)	2.8(12)	-2.8(12)	0.4(10)	0.9(11)
C(21)	6.9(16)	4.6(14)	3.0(11)	-0.7(11)	3.0(10)	1.5(10)
C(22)	5.0(14)	3.7(12)	4.2(12)	1.5(10)	1.4(10)	1.1(10)
C(23)	4.7(13)	6.5(16)	6.2(15)	1.2(11)	1.8(11)	1.6(14)
C(31)	3.9(12)	5.4(15)	4.3(12)	0.2(10)	0.4(10)	-2.2(11)
C(32)	6.2(15)	6.3(16)	2.5(11)	1.2(12)	0.8(11)	-0.2(11)
C(33)	5.4(14)	9.7(21)	4.4(13)	2.4(14)	1.6(11)	3.7(15)
C(34)	5.5(15)	12.1(24)	4.2(13)	-1.1(15)	0.7(11)	-4.0(16)
C(41)	6.2(15)	4.3(14)	5.5(14)	1.5(12)	-0.7(12)	-0.2(12)
C(42)	5.3(14)	8.2(19)	3.0(12)	1.5(13)	-1.7(10)	-1.3(12)
C(43)	4.6(13)	6.8(17)	5.8(15)	0.4(12)	2.0(11)	-1.7(13)
C(44)	5.8(15)	5.9(17)	9.4(20)	-1.8(12)	2.7(14)	-3.2(16)
O(11)	5.1(10)	8.6(13)	6.9(11)	-0.9(9)	1.6(8)	-0.1(9)
O(12)	5.9(10)	6.8(12)	6.5(10)	-0.3(8)	1.4(9)	-0.8(9)
O(13)	8.6(12)	13.8(18)	3.1(9)	-3.2(11)	-0.4(8)	2.9(11)
O(21)	5.7(9)	6.7(11)	7.7(11)	-1.3(8)	4.4(9)	0.6(9)
O(22)	4.3(9)	6.9(12)	12.0(15)	1.2(8)	4.2(10)	-0.3(10)
O(23)	9.6(14)	9.7(15)	7.6(13)	2.6(12)	0.3(10)	4.4(12)
O(31)	4.6(9)	6.9(11)	5.3(9)	-0.9(8)	1.1(7)	-1.2(8)
O(32)	5.1(9)	8.5(12)	5.1(10)	0.0(8)	3.1(8)	0.6(8)
O(33)	7.0(11)	11.5(16)	6.4(11)	2.4(11)	-1.8(9)	3.8(11)
O(34)	9.0(13)	11.4(16)	6.6(12)	-2.6(12)	1.7(10)	-3.4(12)
O(41)	6.5(11)	8.5(13)	6.7(11)	0.6(9)	3.7(9)	1.5(10)
O(42)	4.6(9)	6.4(11)	8.7(12)	0.5(8)	2.1(9)	0.0(10)
O(43)	7.8(12)	10.7(16)	7.8(12)	3.9(11)	2.6(10)	3.1(12)
O(44)	18.0(22)	7.6(14)	13.0(19)	-4.2(15)	3.4(16)	-8.1(15)

TEMP=-2(PI)**2(U11*H*H*ASTAR*ASTAR+---+'2*U12*H*K*ASTAR*BSTAR+---)

THE UIJ VALUES HAVE BEEN MULTIPLIED BY 100.

Table S.20. Structure Factors for $\text{Os}_4(\text{CO})_{14}\text{PMe}_3$

COLUMNS ARE 10F0,10FC, 10SIG

H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	
4	3986	4388	8	11	728	758	34	0	4090	4288	17	-14	523	479	58	-4	2122	2168	12	1	422	309	45	
6	1074	1094	14	12	1999	2094	20	1	2124	2108	20	-12	1045	1025	28	-3	999	998	16	4	970	982	19	
8	1302	1464	16	1	1808	1857	15	3	3658	3633	17	-10	2176	2136	16	-2	1406	1404	14	5	716	709	27	
10	2352	2543	16	3	917	891	17	4	2003	1884	19	-8	1436	1493	13	0	782	781	27	7	714	668	33	
12	1297	1388	24	5	1484	1448	18	7	654	661	41	-6	607	629	19	3	995	991	16	10	1332	1117	26	
2	1022	1068	9	6	755	745	28	9	1038	996	33	-2	333	331	32	5	2179	2211	13	11	377	157	72	
4	1468	1569	10	7	1264	1246	21	10	793	715	43	-12	1045	1025	28	5	1264	1246	19	12	881	840	36	
6	1702	1856	12	9	738	776	32	2	582	603	49	-8	1951	1973	14	-1	369	346	47	7	714	668	33	
7	313	286	40	0	530	522	34	3	682	632	43	-6	1436	1493	13	0	782	781	27	7	714	668	33	
8	1429	1529	15	0	6328	6916	13	5	781	761	35	-5	714	693	18	2	1862	1866	11	9	366	264	69	
9	714	789	27	1	647	645	29	7	600	567	45	-4	466	483	24	2	1862	1866	11	9	366	264	69	
10	1039	1088	23	2	3540	3553	12	3	1130	1118	29	-3	607	629	19	3	995	991	16	10	1332	1117	26	
11	676	710	35	3	1220	1262	19	4	1130	1118	29	-2	333	331	32	5	2179	2211	13	11	377	157	72	
12	561	583	42	5	873	918	28	2	795	774	37	2	498	480	23	5	1264	1246	19	12	881	840	36	
13	395	451	61	6	830	824	29	6	791	738	37	2	1432	1324	11	6	2683	2625	15	15	H 7, 1			
0	502	445	20	7	1509	1451	20	7	818	760	37	3	546	523	26	7	887	867	26	12	1080	1027	33	
1	649	629	15	8	1930	1865	20	4	1191	1145	14	4	1191	1145	14	8	1823	1737	18	-11	1860	1829	23	
2	297	307	37	9	1787	1714	20	5	913	836	35	5	1109	1088	15	9	953	956	26	-10	1392	1421	25	
4	1262	1251	12	11	1648	1554	22	-12	443	453	58	6	2161	2198	12	10	997	982	26	-9	1811	1846	20	
5	2336	2500	10	12	1381	1345	26	-10	332	68	58	7	1234	1252	16	11	423	429	56	-8	915	913	29	
6	2262	2340	11	12	H 7, 0			-8	1163	1130	17	8	1300	1343	18	12	554	543	46	-5	441	670	32	
7	3002	3097	12	3	348	314	48	-6	1870	1872	11	9	755	797	28	8	H 5, 1			-13	1080	1088	22	
8	2113	2330	14	5	507	524	37	-4	2761	2777	9	10	1136	1188	23	-13	707	657	45	-4	1080	1088	22	
9	2919	3212	14	6	699	726	32	2	2819	2769	7	11	693	708	34	-12	1220	1195	28	-2	2000	1996	16	
10	1673	1773	18	7	930	888	29	-2	443	415	17	12	406	507	58	-11	747	751	36	-1	558	549	39	
11	2067	2274	18	8	793	844	35	4	1014	1084	13	13	416	440	60	-10	1210	1274	24	-10	1550	1570	19	
12	430	482	54	9	733	692	39	6	1853	1950	12	13	H 3, 1			-9	993	968	24	2	517	548	37	
13	1277	1372	24	10	1048	1017	32	8	1172	1248	18	-13	1540	1495	25	-7	496	432	36	3	727	716	26	
1	747	725	20	11	721	622	42	14	1611	1532	25	-12	899	898	32	-6	2255	2332	14	4	1776	1808	16	
2	287	281	39	12	634	568	48	-13	851	830	36	-10	1903	1880	19	-5	696	697	24	5	1101	1151	21	
3	398	354	34	2	375	430	55	-12	1909	1855	20	-9	1346	1300	21	-4	4905	5279	12	6	2763	2867	16	
4	2088	2043	12	3	1167	1141	21	-11	1568	1513	20	-8	2634	2713	15	-3	1436	1452	15	7	1908	1874	19	
5	419	395	33	4	749	728	29	-10	2564	2548	15	-8	868	875	23	-2	6215	6699	12	8	2598	2731	18	
6	2157	2237	13	5	2229	2218	16	-9	1140	1122	19	-7	1675	1710	15	-1	1777	1703	16	8	1840	1865	20	
8	1498	1573	17	6	1381	1358	19	-8	2136	2201	14	-5	1221	1273	14	0	7855	8454	13	10	1334	1328	25	
10	1193	1219	22	7	2455	2417	18	-7	431	473	32	-2	1074	1082	15	1	2395	2352	13	11	1421	1343	25	
11	341	402	65	8	1157	1132	29	-6	1279	1343	13	-2	1074	1082	15	1	2395	2352	13	11	1421	1343	25	
12	435	466	54	9	2257	2239	20	-5	3109	3244	10	-1	904	849	20	3	997	975	17	-11	642	617	49	
0	3581	3597	11	10	764	699	39	-3	4715	4978	8	0	421	340	40	4	1598	1704	15	-10	722	754	42	
1	4678	4697	12	11	1306	1221	28	-2	884	877	12	1	1031	1036	14	6	618	642	35	-9	887	885	33	
2	1961	1973	11	2	827	860	30	1	5634	5557	6	2	1819	1783	10	7	486	486	43	-8	1267	1296	25	
3	1997	2062	11	3	904	856	28	3	1067	990	12	5	4709	4488	12	10	953	990	30	-4	794	781	30	
4	514	513	32	4	1239	1200	23	3	2318	2282	11	7	3786	3748	13	11	578	582	46	-7	663	666	39	
5	725	660	25	5	1185	1123	23	5	1019	976	13	8	1337	1323	23	9	845	809	31	-6	1101	1147	25	
6	1962	1957	15	6	1269	1245	23	5	992	1008	14	8	2959	3016	14	11	578	582	46	-4	794	781	30	
7	766	752	25	7	1290	1293	24	6	1471	1512	13	8	3786	3748	13	11	578	582	46	1	432	415	49	
8	2845	2912	15	8	720	734	41	7	2187	2401	13	9	3182	3166	15	-13	669	629	50	2	727	772	32	
9	1351	1373	20	9	1122	1037	31	8	1757	1868	15	10	1289	1336	22	-12	387	402	75	-10	602	631	47	
10	2768	2944	16	10	1754	1825	17	9	1754	1825	17	11	1386	1383	21	-11	606	604	43	-11	457	412	55	

COLUMNS ARE 10FO, 10FC,

H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	
9	478	552	58	3	1318	1305	72	2	4142	3974	9	11	1044	1027	29	-1	914	905	27	
11	540	503	52	4	553	527	59	3	3084	2824	11	12	967	919	32	0	929	957	26	
10	1679	1752	25	5	1736	1624	25	5	3961	3769	12	13	1471	1485	26	3	837	864	25	
-8	1759	1798	23	14	1071	1066	31	7	4792	4607	12	-12	H 5, 2			4	390	327	47	
-7	505	534	33	-12	1402	1345	27	8	7	3054	3027	14	-9	934	860	33	5	1060	1088	22
-6	961	966	30	-10	821	851	23	8	8	2438	2437	15	-9	970	1010	26	7	1716	1667	21
-5	1150	1171	26	-8	1820	1866	15	11	9	2199	2229	17	-8	1131	1145	23	8	642	592	43
-3	1604	1612	22	-6	4697	4923	11	12	11	907	895	30	-7	1332	1325	20	9	1430	1455	24
-2	958	899	28	0	7479	7967	6	12	12	1165	1138	26	-6	2737	2778	14	10	806	839	36
-1	1546	1505	22	2	3155	2775	8	-13	0	601	582	51	-4	3492	3553	13	12	1249	1223	28
0	754	814	34	4	768	748	16	-12	0	806	857	37	-3	361	356	52	H 8, 2			54
1	784	780	31	6	1873	1943	12	-11	0	428	421	57	-2	2715	2597	15	-11	1001	976	34
4	1070	1074	24	8	1359	1476	17	-10	0	1218	1207	22	-1	896	811	25	-9	1058	1061	29
5	1181	1092	23	12	616	663	42	-9	0	552	450	37	0	1662	1690	16	-7	587	522	47
6	1940	1793	18	-13	1146	1110	28	-8	1246	1275	19	1	990	1034	18	-1	1087	1157	26	
7	1073	1060	28	-11	956	941	28	-6	731	736	23	3	1174	1073	16	0	1247	1259	23	
8	2021	1919	20	-9	391	368	47	-5	767	839	20	4	841	858	21	1	2737	2674	17	
9	522	484	60	-3	1952	1785	11	-3	415	379	35	5	1316	1293	19	2	2148	2187	17	
10	1405	1399	26	-2	2193	2088	11	-2	616	559	30	6	1092	1091	24	3	3265	3349	15	
-9	921	937	37	-7	1062	1049	18	-1	775	721	26	7	774	781	30	4	2279	2318	16	
-8	413	347	76	-6	2277	2300	12	1	806	806	17	8	1022	1069	27	5	3660	3785	15	
-5	1456	1453	25	-5	2396	2389	11	2	738	729	18	9	510	428	49	6	1637	1680	20	
-4	1682	1693	23	-4	3545	3564	10	3	544	310	27	-13	1054	1012	36	8	1049	1023	30	
-3	944	933	34	-3	1952	1785	11	4	364	321	45	-12	1256	1210	28	9	1492	1475	24	
-3	1203	1195	28	-2	2193	2088	11	5	1376	1342	16	-11	997	1046	38	H 9, 2				2
-2	724	673	43	-1	1738	1592	9	6	555	469	34	-10	1323	1354	24	0	674	706	51	
-1	637	707	46	0	955	851	10	7	436	396	46	-10	1054	1090	25	-9	889	853	36	
1	1050	1060	29	1	626	501	15	8	814	841	30	-8	1054	1090	25	-8	919	918	34	
3	1311	1294	25	2	795	762	17	10	617	628	41	-7	1753	1781	19	-7	798	727	38	
5	1505	1465	21	3	1096	966	14	-6	536	551	40	-6	4050	4085	14	-6	1446	1523	25	
7	1118	1134	27	4	1268	1190	13	-4	568	510	36	-4	4980	5124	14	-4	1178	1216	27	
9	582	559	53	5	735	689	19	-12	2184	2123	20	-5	4050	4085	14	-2	602	662	47	
H 11, 1				6	2213	2196	13	-10	2420	2432	17	-3	4980	5124	14	-2	602	662	47	
-8	413	347	76	7	378	353	40	-8	1998	2056	17	-2	332	188	66	0	682	658	37	
-5	425	483	64	8	2087	2132	15	-7	2133	2177	15	-1	4346	4352	15	2	1184	1125	24	
-5	1524	1555	26	10	1743	1769	18	-6	303	307	54	1	2888	2859	14	4	1384	1355	21	
-4	732	793	44	12	1105	1089	27	-5	3336	3464	13	3	540	508	29	5	680	667	36	
-3	2916	3007	20	13	494	391	54	-4	1095	1088	18	4	706	744	26	6	1324	1333	24	
-2	878	890	38	-3	3289	3329	12	5	1101	1105	21	5	1101	1105	21	7	622	665	43	
-1	3572	3665	19	-14	590	536	52	-2	1175	1124	21	6	1244	1277	22	8	773	735	37	
0	985	1015	32	-13	1834	1792	22	0	3410	3306	13	7	1613	1704	20	9	677	609	45	
1	2912	2906	19	-12	502	580	53	0	697	646	25	8	1151	1189	25	9	H 10, 2			2
2	727	709	39	-11	1975	1973	19	1	435	486	31	9	692	763	40	-9	848	897	42	
3	1510	1454	24	-9	2191	2223	16	2	256	215	49	10	1297	1293	37	-8	995	1044	35	
4	399	388	64	-7	931	965	20	3	1406	1363	15	12	889	834	37	-6	2303	2338	22	
7	766	774	37	-6	1039	1040	16	4	1551	1543	15	5	846	783	39	-5	846	783	39	
H 12, 1				-5	258	272	49	5	2653	2518	14	-12	671	688	50	-4	3165	3060	20	
-2	380	266	76	-4	1947	1930	12	6	2644	2673	15	-10	777	829	38	-3	1511	1523	27	
7	693	699	46	-3	366	333	39	7	2230	2144	16	-7	632	664	39	-2	3319	3388	19	
H 13, 1				-1	634	608	24	8	2576	2449	17	-5	1115	1119	24	-1	1570	1593	23	
-2	397	186	73	0	2193	2099	9	9	504	477	49	-4	371	324	59	0	2439	2495	19	
1	691	630	43	1	2177	2173	9	10	1702	1737	23	-3	1405	1452	21	1	1397	1366	24	

COLUMNS ARE 10FD,10FC, 10SIG

COLUMNS ARE 10FD,10FC, 10SIG

-4	1076	1027	18	3	4517	4451	11	11	42	838	3	926	902	42	-2	450	397	3	1670	1704	17	20	
-3	3770	3684	11	5	4962	4799	12	24	24	1319	9	1354	1360	31	-1	1109	1120	3	1106	1067	17	41	
-1	1644	1476	10	6	3611	3611	14	17	46	570	8	1411	1434	29	0	833	809	3	1977	1821	15	15	
0	407	360	24	7	2990	2871	15	27	17	2822	6	1878	1787	23	1	1678	1787	23	2249	2131	12	12	
1	336	247	31	8	1393	1267	21	16	23	3166	5	2058	1915	23	2	910	835	40	2279	2154	11	11	
2	1578	1486	12	10	764	696	37	24	23	1310	4	1954	1897	24	3	2391	2290	23	4196	4193	9	9	
5	2181	2014	13	12	1682	1633	24	29	17	2590	2	406	419	73	4	933	815	39	4221	4264	10	10	
6	1079	1001	19	13	609	619	53	25	25	1075	1	999	987	33	3	H 0,	4	10	7016	7206	10	10	
7	948	921	21	3	336	343	49	49	24	1415	1	1415	1431	24	-12	357	347	66	2734	2655	12	12	
8	1153	1111	20	20	653	636	26	26	30	924	2	924	922	30	-10	1383	1351	19	4398	3942	12	12	
9	676	629	33	11	426	395	62	16	18	2030	3	2030	2022	18	-8	3257	3423	14	2060	2093	14	14	
10	1009	1024	27	10	1023	997	28	28	23	1307	4	1307	1276	23	-6	3806	4006	13	2128	2103	15	15	
11	1858	1806	20	20	359	383	64	21	22	1473	5	1473	1472	22	-4	4408	4465	12	7100	994	23	23	
12	825	788	36	8	1721	1806	19	19	24	1631	6	1378	1432	24	-2	1929	1874	11	470	261	53	53	
13	1828	1784	24	7	1231	1197	19	38	51	733	7	532	558	51	0	1342	1363	11	1600	1410	22	22	
-14	988	971	34	8	1663	1725	22	38	22	1663	8	1193	1171	55	6	1344	1345	17	1891	1782	24	24	
-13	613	586	46	10	1384	1402	25	25	43	1384	10	554	481	55	10	2193	2136	16	H 3,	4	70	70	
-12	815	778	33	12	772	762	43	43	29	772	12	425	358	83	-11	1916	1901	23	874	918	29	29	
-10	607	679	40	9	557	595	35	29	29	1332	9	1190	1187	35	-14	776	671	38	509	470	42	42	
-7	1401	1346	17	10	1205	1194	16	16	67	434	-10	1100	1081	36	-13	491	499	55	4	1256	1260	18	18
-5	1293	1246	16	1	425	525	34	27	27	1289	-9	1499	1500	29	-11	526	587	46	3	926	879	23	23
-4	842	800	22	2	2017	2071	13	26	26	1290	-8	1713	1641	27	-10	866	861	29	2	1728	1588	15	15
-2	549	461	33	3	818	836	20	29	29	1031	-7	1360	1361	30	-9	2443	2489	16	2333	2212	13	13	
0	1454	1390	11	4	2366	2364	14	20	20	1840	-6	1840	1811	20	-4	1650	1624	27	0	1708	1678	13	13
1	1776	1731	10	6	2031	2042	16	35	35	786	-5	471	542	68	-8	2204	2332	16	0	1708	1678	13	13
2	1375	1263	13	8	1787	1682	19	20	20	1800	-3	1174	1131	28	-7	3278	3271	14	1	4215	4281	10	10
3	3234	3079	11	9	836	782	34	40	40	635	-3	1019	1005	32	-5	2766	2712	14	3	2964	2965	11	11
4	1119	1069	17	10	1098	1068	30	32	32	771	-1	1019	1005	32	-5	2766	2712	14	3	2300	2255	13	13
5	1881	1857	14	11	915	831	34	34	17	2283	3	1063	1058	28	-4	2437	2456	13	4	1181	1146	19	19
6	350	268	50	12	574	550	56	56	22	1044	1	683	608	37	-3	1344	1271	17	5	1390	1375	18	18
7	1760	1596	17	13	822	757	42	14	14	3818	2	531	564	52	-1	991	995	17	6	465	431	40	40
8	1000	950	25	13	H 5,	3	42	22	22	1061	3	531	564	52	0	732	690	18	8	1357	1319	22	22
9	1157	1126	24	13	820	831	42	14	14	3740	4	1235	1234	36	1	2324	2228	10	10	1018	936	34	34
10	1165	1085	25	11	779	771	37	22	22	1163	5	939	973	42	2	1863	1793	12	12	H 4,	4	4	
11	739	688	38	10	367	298	71	17	17	2739	6	2155	2037	24	3	2173	2061	12	-13	780	781	41	41
12	723	753	43	9	686	701	38	38	28	1096	7	1197	1125	33	4	2156	2165	13	-12	1657	1621	22	22
13	386	299	76	8	1960	1936	19	38	38	673	8	2207	2191	33	5	702	701	25	-11	1319	1309	26	26
-13	1403	1354	26	6	3886	4004	15	15	43	767	9	824	899	40	-2	2823	2648	14	-10	1501	1468	23	23
-11	882	924	33	5	485	482	45	74	74	385	10	1665	1699	24	8	2458	2342	16	-9	2422	2473	18	18
-10	962	931	28	4	597	5174	14	66	66	440	11	620	584	46	9	1244	1200	25	-8	1071	1095	26	26
-9	737	765	31	3	3721	3683	14	30	30	H 8,	1	953	891	33	10	1733	1580	21	-7	2678	2701	16	16
-8	1713	1750	18	1	759	745	30	41	41	565	-10	565	539	57	11	1193	1134	28	-6	520	505	41	41
-6	1626	1732	15	0	3635	3728	13	25	25	667	-3	667	619	41	6	728	765	52	-5	3014	2934	15	15
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-2	1170	1068	20	3	510	535	32	32	25	881	-1	601	652	51	-11	861	876	31	-11	2905	2954	12	12
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2	6519	6874	10	12	H 6,	3	45	45	45	645	9	1043	967	32	5	1043	967	32	-7	515	523	38	38

COLUMNS ARE 10FO,10FC, 10SIG

COLUMNS ARE 10FO,10FC, 10SIG

6	1078	1031	23	23	830	947	31	31	1010	947	5	5	8	860	883	30	30	478	431	62	18	
7	374	438	58	17	2262	258	74	74	380	258	40	40	9	354	320	25	25	-6	898	732	38	
8	478	457	50	33	1637	976	33	33	1006	976	16	16	11	618	529	50	50	-5	1788	1801	20	
9	1735	1665	21	17	2007	4	17	17	H 11, 4	4	19	19	12	1324	1223	29	29	-4	736	819	36	
11	2261	2092	20	24	1048	2077	26	26	2109	2077	1000	1000	3	1084	5	45	45	-3	431	492	57	
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-10	1779	1765	22	41	644	523	54	54	610	523	28	28	-11	1250	1273	27	27	-1	956	1005	26	
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-7	1101	1138	27	27	1253	1346	53	53	560	577	18	18	-8	1536	1500	22	22	3	1112	1203	21	
-6	3988	3968	16	39	833	896	36	36	834	896	44	44	12	759	672	45	45	6	1634	1250	22	
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3	704	725	26	24	1458	1500	24	24	0	884	888	38	38	-4	2489	2438	15	15	0	1882	1870	14
4	1710	1767	16	19	2403	2566	19	19	2	1489	1385	27	27	-3	914	858	21	21	1	2465	2559	13
5	436	526	49	28	2428	2552	28	28	4	1326	1307	28	28	-2	3857	3746	12	12	3	1228	1275	37
6	1004	993	28	16	3989	4077	16	16	H 13, 4	4	30	30	-1	2355	2297	12	12	2	1368	1384	18	
7	416	455	57	17	2307	2326	17	17	-3	917	989	39	39	-1	4980	4980	10	10	5	633	589	36
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-12	823	860	41	38	2592	2664	17	17	2	433	370	81	81	3	2339	2310	13	13	8	885	938	31
-10	906	957	36	25	695	703	38	38	3	857	778	43	43	4	935	900	22	22	9	2127	2153	20
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-8	1385	1428	25	39	543	617	56	56	-12	1208	1229	24	24	6	876	877	30	30	11	1659	1610	24
-7	2437	2398	19	39	H 9, 4	4	39	39	-10	2442	2535	16	16	7	749	760	30	30	12	871	779	38
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-3	1817	1824	19	32	554	515	59	59	-2	334	269	39	39	-10	937	906	34	34	4	2286	2452	17
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2	375	409	46	27	1633	1655	23	23	6	1121	1059	21	21	-10	1356	1348	24	24	-4	1957	1916	18
3	823	810	24	20	1198	1224	27	27	8	1356	1257	22	22	-8	1498	1452	20	20	-3	611	646	40
6	360	460	69	36	1836	1820	30	30	10	1491	1356	23	23	-6	321	350	59	59	-2	1561	1509	20
7	988	955	31	23	731	779	36	36	12	893	860	38	38	-5	1154	1134	20	20	-1	524	516	38
9	1456	1525	23	45	1319	1320	23	23	H 1, 5	5	26	26	-4	1808	1767	17	17	0	1002	1002	21	
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-8	921	897	36	62	1781	1839	19	19	-10	1781	1839	19	19	1	4882	5038	11	11	7	532	516	49
-7	1347	1354	27	28	602	542	62	62	-9	2026	2137	17	17	2	4679	4755	11	11	8	2187	2295	19
-6	523	480	53	25	1756	1590	28	28	-8	2536	2693	16	16	3	3765	3698	12	12	10	2017	2003	21
-5	627	590	54	35	2027	2000	35	35	-7	2358	2456	16	16	4	2848	2813	14	14	11	393	228	73
-4	732	733	35	26	627	590	54	54	-6	1890	1945	16	16	5	2207	2147	16	16	5	H 6, 5	5	31
-3	942	948	35	26	1804	1329	17	17	-5	1304	1329	17	17	6	762	736	28	28	-11	1499	1504	28
-2	2023	2016	18	56	543	617	56	56	-4	1127	1084	19	19	7	550	566	40	40	-9	2613	2468	20

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H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG
9	950	1014	36	-12	525	628	50	-8	2839	2861	19	-6	453	456	66
10	409	534	76	-10	442	525	54	-7	444	376	57	-4	1093	1036	33
-10	883	838	42	-6	374	373	48	-5	1924	1958	20	-3	1563	1540	26
-9	1592	1624	29	-4	662	589	26	-4	431	332	52	-2	929	1056	41
-7	1435	1414	28	0	1059	1092	16	-2	673	650	38	-1	2245	2300	21
-5	560	590	57	2	3099	2920	12	-11	1173	1209	39	0	1087	1011	25
-2	456	494	62	4	3461	3416	13	-10	961	906	30	4	1570	1577	18
-1	1209	1278	28	6	3710	3594	14	-9	768	904	31	2	1145	1087	26
0	888	901	35	8	3587	3342	16	-6	1825	1853	22	3	2424	2476	18
1	1621	1571	22	10	2337	2096	20	-5	2090	2164	17	10	1133	1135	29
2	1181	1240	26	12	476	494	71	-4	3870	3681	15	9	450	276	69
3	1114	1129	26	H 1,	6		14	-3	4505	4395	14	-12	1192	1192	34
4	1047	992	37	-13	1494	1593	25	-2	5099	5030	13	-11	406	337	78
6	731	656	36	-11	2048	2139	20	-1	3931	3788	12	-10	1265	1326	30
7	547	599	53	-10	564	654	44	0	3555	3538	12	-9	625	628	49
9	1276	1209	32	-9	2380	2409	17	1	3322	3400	12	-8	1846	1877	23
-9	978	991	41	-8	939	957	27	2	1996	2040	14	-7	700	621	39
-8	1717	1701	26	-7	1577	1583	18	3	1223	1232	19	-6	2099	2121	20
-7	856	863	42	-5	495	397	37	4	432	444	46	-4	1760	1716	21
-6	1511	1465	28	-4	685	609	27	6	1528	1590	20	-2	625	710	43
-5	735	644	46	-3	2248	2231	13	8	2067	2125	28	0	339	308	62
-4	689	643	48	-1	2322	2364	14	9	825	749	34	1	532	518	38
0	446	527	68	0	984	1002	17	10	1558	1468	24	3	1244	1400	22
1	475	486	60	1	1485	1462	14	12	710	651	48	4	1069	1169	25
2	575	570	47	2	1698	1683	14	5	1522	1580	22	-8	739	737	50
6	438	481	65	4	1766	1779	15	6	528	581	53	-6	633	587	53
8	938	884	37	5	1810	1843	16	-12	1232	1258	30	2	762	761	39
-8	903	898	44	6	1423	1410	19	-11	1143	1161	30	9	1662	1815	23
-7	842	745	46	7	2707	2602	16	-10	1474	1411	24	10	422	418	68
-6	1158	1146	35	8	1402	1264	22	-9	1598	1576	23	-12	1290	1245	33
-5	786	818	48	9	2478	2273	19	-8	1712	1704	21	-10	863	867	40
-4	941	984	39	10	1309	1215	26	-7	1378	1385	22	-7	533	466	54
-3	657	657	48	11	1275	1222	29	-6	1540	1525	19	-5	1136	1147	29
-2	595	611	51	12	1004	861	35	-5	676	665	33	-6	365	208	73
-1	489	475	59	-13	882	962	36	-4	1581	1577	21	-5	400	235	80
5	895	905	35	-12	684	779	42	-3	528	489	43	-4	2872	2929	19
-5	831	737	45	-11	930	965	32	-2	1358	1307	20	-2	3176	3224	19
-3	573	579	57	10	1118	1195	27	0	801	828	25	0	2882	2913	17
-2	1017	1065	35	-9	1118	1159	25	1	965	1051	21	1	1127	1252	27
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2	712	693	48	-7	1686	1736	18	5	849	741	30	3	1352	1340	22
3	909	874	38	-5	2095	2158	16	6	744	731	33	4	710	753	36
5	1116	1135	33	-4	1049	1029	23	7	1462	1607	33	5	1003	1043	29
-3	838	798	44	-3	2734	2671	14	8	649	569	39	6	1804	1795	21
-2	1693	1654	41	-2	2455	2358	13	9	1436	1485	24	7	846	895	38
-1	895	874	47	-1	1736	1673	13	11	1044	1030	34	8	1837	1826	23
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1	2068	2089	26	3	1653	1613	12	-12	1877	1813	25	10	1233	1290	29
					3721	3687	12	-10	2514	2471	20	-9	400	308	77
					739	698	26	-9	473	495	61	-8	400	308	77
												-12	1940	2041	21
												-10	1734	1783	20
												-13	661	616	49
												-12	576	421	52

COLUMNS ARE 10FD,10FC, 10SIG

COLUMNS ARE 10FD,10FC, 10SIG

H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG
-9	1313	1347	23	-11	372	140	73	-2	1053	1013	36	-12	955	926	34	-10	836	830	36
-8	2652	2732	17	-8	516	569	54	2	1009	1064	35	-11	574	615	48	-4	1988	1906	22
-7	2291	2364	18	-7	475	456	56	4	933	913	34	-10	1512	1498	22	-3	679	659	44
-6	4115	4075	16	-6	862	911	35	5	528	577	58	-9	388	503	68	-2	3912	3831	17
-5	2161	2150	19	-5	532	551	54	6	584	521	54	-8	1547	1536	22	-1	847	833	34
-4	3699	3639	15	-4	1148	1114	29	7	671	698	42	-7	671	698	42	0	4335	4471	17
-3	1472	1514	19	-3	446	471	60	-7	1066	1099	37	-6	1041	1033	29	1	1018	979	29
-2	2022	2034	16	-2	1269	1178	24	-6	683	597	54	-5	534	550	49	2	3750	3973	17
-2	2014	2035	18	-1	348	222	68	-5	1063	1092	39	-3	975	951	26	3	630	643	46
3	795	715	33	0	998	968	28	-4	1033	1046	24	-2	1093	1046	24	4	2338	2330	20
4	2621	2555	18	2	1371	1424	23	-2	921	906	41	-1	833	853	29	6	643	643	52
6	1364	1391	23	3	631	698	45	0	780	788	42	0	1802	1813	19	7	387	359	75
7	787	772	34	4	1542	1555	24	5	454	474	70	1	818	812	30	8	692	638	45
9	1374	1275	25	5	918	930	36	6	434	535	80	2	1719	1771	21	6	10	6	10
10	618	617	51	6	1333	1346	30	6	434	535	80	3	622	592	41	-10	1089	1053	31
-10	666	708	40	7	696	730	45	-3	427	439	84	4	1675	1625	22	-9	711	664	44
-8	735	759	36	8	626	680	51	-2	894	962	44	5	452	268	55	-8	1082	1114	31
-6	995	1001	30	9	427	502	71	-1	678	749	53	6	911	877	31	-7	495	518	59
-5	455	488	60	-10	589	542	51	0	1775	1743	26	11	1209	1241	28	-6	639	695	50
-4	668	602	37	-9	679	735	44	2	2095	2121	23	-11	1124	1097	28	3	628	615	47
-3	967	997	28	-7	1221	1302	29	3	742	793	46	-9	1833	1733	20	5	711	814	46
-2	318	91	63	-5	810	816	41	4	1751	1742	26	-8	1923	1883	20	7	611	575	57
-1	1260	1253	21	-3	589	666	54	4	1751	1742	26	-8	1923	1883	20	7	611	575	57
1	1609	1700	19	-1	3054	3249	18	1	676	644	56	-5	2260	2219	19	0	10	10	10
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3	931	953	28	-1	2163	2254	21	4	1751	1742	26	-6	2435	2392	19	-8	1721	1705	24
4	1256	1278	25	4	653	643	46	1	676	644	56	-5	2260	2219	19	-7	1102	1087	33
5	699	656	40	5	2006	2113	22	-4	838	824	28	-2	647	645	50	-6	1907	1818	25
6	1104	1197	29	6	882	855	40	-2	1535	1472	22	0	464	490	50	-4	1282	1223	34
7	463	507	56	7	628	661	55	4	1449	1486	23	1	452	457	52	0	944	1027	35
8	699	779	41	8	906	950	39	6	1160	1206	26	4	384	401	75	4	1331	1384	26
10	553	509	57	8	827	807	36	8	827	807	36	5	706	586	41	5	640	681	51
-12	642	626	47	-10	510	562	62	9	1217	1269	28	7	1111	1160	29	7	1114	1083	37
-10	691	624	40	-9	1219	1276	31	12	1217	1269	28	8	679	692	43	-9	578	573	61
-9	708	734	39	-8	799	828	42	-11	886	831	31	9	1481	1480	26	-8	471	576	73
-8	1050	1044	29	-7	1372	1329	28	-10	1032	1046	29	9	1481	1480	26	-6	423	526	83
-7	1882	1949	21	-6	401	432	80	-9	1071	1088	27	-11	1167	1200	29	-3	1101	967	37
-6	1040	1025	29	-5	859	835	43	-8	1143	1169	26	-10	1058	1078	30	-1	1247	1305	31
-5	2376	2199	20	-2	776	692	42	-7	1177	1212	27	-9	1411	1466	25	0	735	790	44
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-3	922	903	29	2	792	809	37	-3	1504	1486	20	-7	1660	1652	22	2	798	832	40
-1	785	710	30	6	480	454	66	-2	892	864	26	-6	1189	1084	28	3	927	1042	35
0	679	714	35	8	453	371	70	-1	3252	3328	15	-5	1385	1310	26	4	779	832	43
1	2451	2600	16	0	1114	1093	23	0	1114	1093	23	-3	673	625	39	5	709	695	47
2	822	853	33	1	3673	3770	16	-2	825	827	33	-3	825	827	33	6	653	667	54
3	3037	3132	17	2	462	482	54	1	517	568	48	-2	825	827	33	9	10	10	10
5	2290	2265	21	-8	1366	1351	30	2	462	482	54	-7	703	644	52	-7	703	644	52
6	716	773	43	-7	2339	2349	23	3	3331	3202	17	-6	1084	1049	37	-6	1084	1049	37
7	1059	1063	30	-6	2095	2022	24	5	564	446	53	-5	646	618	59	-5	646	618	59
8	1362	1372	26	-5	2897	2828	23	6	1109	1130	26	6	835	863	38	-1	580	673	60
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				-3	2317	2257	26	9	1248	1174	28	-11	448	430	65	-8	1273	1261	26

COLUMNS ARE 10FD,10FC, 10SIG

COLUMNS ARE 10FD,10FC, 10SIG

H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG
-6	1064	1067	31	-8	920	976	46	-7	649	619	45	-3	1367	1359	30
-5	723	631	39	-7	714	672	46	-7	649	619	45	-4	1791	828	33
-3	1376	1389	24	-6	408	221	78	-5	1296	1281	26	-8	562	628	57
-2	772	757	34	-5	687	748	54	-4	964	1000	32	-7	942	908	36
-1	1234	1243	25	-4	438	465	82	-3	1392	1360	24	-5	1220	1181	29
0	1477	1509	22	-3	588	635	59	-2	1435	1337	22	-4	925	918	34
1	1040	1101	28	-1	1006	1091	37	-1	1093	1096	29	-3	1046	1089	31
2	1406	1433	24	-1	403	593	78	0	1360	1339	25	-2	946	910	33
3	688	648	41	0	954	944	36	1	592	599	47	-1	438	553	66
4	1304	1257	27	2	814	862	39	2	620	645	47	0	640	695	47
6	717	709	42	4	698	706	48	7	525	530	59	-4	519	769	77
	H 4,	11			H 3,	12			H 3,	12		-3	1126	1120	39
-11	456	504	66	-7	1413	1394	30	-9	1118	1115	30	-2	649	711	58
-10	1279	1300	28	-6	713	727	53	-7	936	915	34	-1	824	810	46
-9	683	644	42	-5	644	42	35	-5	420	351	67	-8	751	751	43
-8	812	916	37	-3	546	497	68	0	695	733	40	1	612	562	56
-6	534	456	56	3	673	696	48	1	723	775	40	2	637	623	56
-5	645	598	48		H 9,	11		2	1025	1104	31	-4	463	430	67
-3	1673	1707	23	-6	958	907	43	3	1570	1598	25	-3	1348	1364	28
-2	1008	918	30	-5	737	735	55	4	1330	1330	29	-2	497	559	83
-1	2192	2256	20	-4	1180	1163	39	5	1721	1796	25	-1	644	573	48
0	928	925	32	-2	786	803	51	6	1347	1372	28	3	611	670	55
1	1851	1875	21	1	556	621	63	7	1627	1458	25	4	1024	1038	37
3	876	842	35		H 10,	11		H 4,	12			5	1145	1166	35
4	709	746	45	-3	788	824	57	-10	506	628	61	-8	943	876	37
6	1163	1164	31	-2	1998	1948	29	-9	1233	1249	28	-7	693	739	50
7	701	712	45	-1	998	991	42	-8	972	985	34	-6	1578	1576	28
	H 5,	11			H 0,	12		-7	599	575	49	6	818	766	39
-10	825	851	40	-10	810	835	35	-6	1562	1508	26	H 1,	13		
-9	414	444	70	-6	890	823	32	-5	384	249	75	-4	1748	1645	25
-8	703	668	42	-4	1745	1707	20	-4	1546	1571	26	-8	1371	1314	26
-7	631	662	48	-2	1293	1242	24	-3	945	943	34	-7	949	908	32
-5	818	858	43	2	718	692	43	-2	895	899	35	-6	1570	1489	23
-4	726	690	45	4	1376	1312	24	-1	685	781	44	-5	1642	1636	23
-3	651	677	48	6	1851	1920	23	1	434	477	65	-4	1413	1358	24
-2	602	677	54		H 1,	12		2	413	382	67	-3	1413	1461	25
-2	565	554	52	-11	385	556	76	4	813	885	42	-2	771	809	38
3	624	632	48	-10	1066	1079	31	6	997	972	36	-1	761	805	38
4	1038	1006	33	-8	728	702	39	6	H 5,	12		-3	2105	2086	24
5	919	946	33	-7	754	736	38	-8	583	684	55	3	1326	1310	29
6	1201	1247	33	-5	2208	2137	20	-6	2323	2190	23	4	948	955	35
7	603	699	55	-4	700	690	40	-4	3586	3451	20	5	1303	1374	29
	H 6,	11		-3	2927	2948	17	-3	865	799	39	6	1151	1107	30
-9	711	695	43	-2	929	887	30	-2	3667	3652	19	H 2,	13		
-8	396	277	73	-1	2528	2562	18	-1	804	826	42	-9	644	564	46
-5	1599	1440	28	0	762	790	37	0	2713	2748	20	-7	629	508	45
-3	2717	2717	21	1	1592	1523	22	1	666	727	45	-6	545	465	53
-1	3098	3128	20	2	377	219	72	2	1749	1757	23	-1	678	641	43
1	2535	2678	21	4	907	923	35	6	971	988	40	0	1078	1039	29
3	1541	1674	26	5	1034	1053	31	H 6,	12			1	1098	1091	30
4	639	694	50	6	1235	1305	28	-8	601	561	54	-3	1440	1461	28
6	953	999	42	7	1131	1215	31	-6	446	443	76	3	1468	1434	28
	H 7,	11			H 2,	12		-5	1309	1306	33	4	2007	1951	23

COLUMNS ARE 10FO, 10FC, 10SIG

H	KFO	FC	SIG	H	KFO	FC	SIG	H	KFO	FC	SIG
-2	H 6, 14	545	65	-5	885	941	38	-1	991	942	35
1	977	1012	40	-1	799	740	39	0	1522	1520	28
	H 0, 15			0	1129	1132	33	1	991	923	38
-6	1228	1195	29	1	1705	1700	27	2	1593	1536	29
-4	1406	1377	27	2	839	808	47		H 3, 15		
-2	1434	1395	26		H 2, 15			-5	467	429	70
0	924	866	39	-5	833	867	41	-2	641	661	52
2	644	765	60	-4	756	688	43	-1	972	957	37
	H 1, 15			-3	1012	996	34	0	907	950	41
-6	1071	982	32	-2	1126	1130	32	1	1101	1130	36

Table S.21. Fractional Coordinates for $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$

ATOM	X	Y	Z
OS(1)	0.33486(4)	0.10071(5)	0.05491(4)
OS(2)	0.30382(4)	-0.14812(5)	0.08784(4)
OS(3)	0.26492(4)	-0.05045(5)	-0.10381(4)
OS(4)	0.14666(4)	0.13670(5)	-0.08784(4)
P(1)	0.2452(4)	-0.3469(4)	0.0686(4)
C(1)	0.320(2)	-0.452(2)	0.154(2)
C(2)	0.136(2)	-0.363(2)	0.080(2)
C(3)	0.227(2)	-0.419(2)	-0.036(2)
C(11)	0.291(1)	0.161(2)	0.137(1)
O(11)	0.269(1)	0.206(1)	0.191(1)
C(12)	0.454(1)	0.065(1)	0.144(1)
O(12)	0.526(1)	0.046(1)	0.201(1)
C(13)	0.374(1)	0.256(2)	0.031(1)
O(13)	0.403(1)	0.346(1)	0.022(1)
C(21)	0.204(1)	-0.081(2)	0.115(1)
O(21)	0.150(1)	-0.047(1)	0.141(1)
C(22)	0.376(1)	-0.157(2)	0.216(2)
O(22)	0.418(1)	-0.160(2)	0.292(1)
C(23)	0.416(2)	-0.189(2)	0.075(1)
O(23)	0.488(1)	-0.217(1)	0.076(1)
C(32)	0.344(1)	-0.176(1)	-0.117(1)
O(32)	0.386(1)	-0.249(1)	-0.132(1)
C(31)	0.153(1)	-0.119(2)	-0.190(1)
O(31)	0.085(1)	-0.160(1)	-0.243(1)
C(33)	0.279(1)	0.046(2)	-0.194(1)
O(33)	0.289(1)	0.101(1)	-0.248(1)
C(41)	0.086(1)	-0.001(2)	-0.063(1)
O(41)	0.042(1)	-0.082(1)	-0.055(1)
C(42)	0.116(1)	0.252(2)	-0.018(1)
O(42)	0.097(1)	0.320(1)	0.025(1)
C(43)	0.042(1)	0.151(1)	-0.201(1)
O(43)	-0.024(1)	0.161(1)	-0.264(1)
C(44)	0.211(1)	0.254(2)	-0.131(1)
O(44)	0.246(1)	0.324(1)	-0.161(1)
H(11)	0.305(0)	-0.529(0)	0.121(0)
H(12)	0.308(0)	-0.459(0)	0.208(0)
H(13)	0.388(0)	-0.437(0)	0.175(0)
H(21)	0.093(0)	-0.322(0)	0.036(0)
H(22)	0.151(0)	-0.340(0)	0.146(0)
H(23)	0.127(0)	-0.457(0)	0.083(0)
H(31)	0.282(0)	-0.437(0)	-0.034(0)
H(32)	0.188(0)	-0.357(0)	-0.087(0)
H(33)	0.179(0)	-0.486(0)	-0.048(0)

Table S.22. Thermal Parameters for $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$

ATOM	U11	U22	U33	U12	U13	U23
OS(1)	3.33(4)	3.97(4)	3.18(4)	-0.03(3)	1.34(3)	-0.24(3)
OS(2)	4.20(4)	4.03(4)	3.52(4)	0.68(3)	2.00(3)	0.42(3)
OS(3)	3.81(4)	3.62(3)	2.99(4)	0.39(3)	1.54(3)	-0.03(3)
OS(4)	3.45(4)	3.71(4)	3.73(4)	0.41(3)	1.36(3)	0.03(3)
F(1)	7.3(3)	3.5(2)	5.9(3)	0.4(2)	3.6(3)	0.8(2)
C(1)	13.5(22)	6.9(14)	9.2(19)	3.4(14)	5.2(17)	3.6(13)
C(2)	9.5(18)	5.2(12)	15.0(26)	-0.6(11)	5.1(19)	-1.4(14)
C(3)	22.0(34)	5.4(13)	10.2(21)	-2.5(16)	8.4(23)	-1.8(14)
C(11)	4.6(11)	6.8(12)	5.9(13)	1.1(9)	1.9(10)	1.1(11)
O(11)	9.1(11)	11.1(11)	5.6(9)	0.3(9)	4.1(9)	-3.1(9)
C(12)	1.7(9)	5.6(10)	4.7(11)	0.7(7)	-0.5(8)	1.4(9)
O(12)	4.8(8)	8.3(9)	7.8(10)	0.0(7)	0.5(8)	1.0(8)
C(13)	4.1(9)	5.3(10)	3.6(9)	0.5(8)	1.8(8)	-0.2(8)
O(13)	7.2(9)	5.1(8)	8.1(11)	-2.2(7)	2.3(8)	0.0(7)
C(21)	3.2(9)	5.5(10)	4.9(11)	-0.9(8)	0.8(9)	-0.9(9)
O(21)	6.6(9)	8.3(9)	5.8(9)	2.3(7)	3.1(8)	0.3(7)
C(22)	5.0(11)	6.9(12)	8.3(16)	0.0(9)	5.6(12)	0.4(12)
O(22)	10.1(13)	17.0(17)	2.9(8)	-0.1(11)	1.7(8)	1.4(10)
C(23)	8.2(15)	6.5(12)	4.2(11)	0.2(10)	4.4(11)	-1.2(9)
O(23)	6.6(9)	13.3(13)	7.2(10)	4.0(9)	4.3(8)	0.8(8)
C(32)	4.4(9)	4.4(9)	4.3(10)	0.3(8)	2.3(9)	0.4(8)
O(32)	7.2(8)	5.6(7)	7.2(9)	2.5(7)	4.4(8)	-0.2(7)
C(31)	4.9(11)	5.9(11)	4.7(11)	0.6(9)	1.6(10)	-0.9(10)
O(31)	6.8(10)	10.8(11)	6.5(10)	-2.2(8)	1.0(8)	-4.3(9)
C(33)	5.3(12)	5.4(11)	5.4(13)	1.2(9)	1.6(10)	-0.4(10)
O(33)	10.7(12)	7.8(9)	6.2(10)	1.8(8)	5.1(9)	3.0(8)
C(41)	5.2(11)	6.3(11)	2.8(9)	2.3(9)	1.6(9)	0.4(9)
O(41)	6.3(8)	5.6(8)	7.9(10)	-0.5(6)	4.6(8)	0.9(7)
C(42)	5.4(11)	3.8(10)	5.8(12)	0.5(8)	-0.1(10)	0.6(9)
O(42)	9.5(11)	7.5(9)	10.1(13)	-0.1(8)	6.1(10)	-2.5(9)
C(43)	2.7(9)	5.7(10)	4.8(11)	1.0(8)	-0.9(9)	1.0(9)
O(43)	5.8(10)	13.7(13)	7.4(11)	-1.3(9)	-2.1(9)	4.0(10)
C(44)	4.3(10)	5.7(10)	1.7(8)	1.1(8)	-0.5(8)	-0.2(8)
O(44)	7.9(10)	7.0(8)	5.5(9)	-0.8(7)	2.8(8)	2.5(7)

TEMP=-2(PI)**2(U11*H*H*ASTAR*ASTAR+---+2*U12*H*K*ASTAR*ESTAR+---)

THE UIJ VALUES HAVE BEEN MULTIPLIED BY 100.

Table S.23. Structure Factors for $(\mu\text{-H})_2\text{Os}_4(\text{CO})_{13}\text{PMe}_3$

COLUMNS ARE 10FD, 10FC, 10SIG

L	KFD	FC	SIG	L	KFD	FC	SIG	L	KFD	FC	SIG	L	KFD	FC	SIG
3	515	540	28	4	2950	3048	11	11	1211	1211	15	8	1582	1588	21
4	797	760	21	6	1168	1160	24	2	2147	2237	10	15	9	1052	1043
5	1146	1176	18	12	484	560	67	3	1128	1184	12	11	10	1352	1338
8	1017	912	28	16	1351	1357	26	3	503	477	29	12	11	790	784
9	1426	1380	26	10	10	1	1	5	3456	3427	16	13	14	1981	1945
10	871	815	39	1	302	328	37	4	574	565	27	16	13	1356	1361
11	858	854	40	2	1194	1211	10	6	1275	1236	20	18	15	1220	1176
13	1215	1128	32	3	1859	1881	7	7	1768	1714	18	18	9	57	5
14	560	423	63	4	511	512	21	9	904	868	31	14	8	3489	3498
15	2012	2023	28	5	1978	1909	13	10	1145	1151	29	40	1	1537	1542
1	1803	1806	14	6	333	391	30	13	948	948	39	33	2	388	367
2	932	914	19	8	607	638	34	14	576	517	58	23	3	2450	2450
4	683	679	25	9	538	587	42	15	806	809	47	24	5	3364	3377
5	1179	1218	19	13	733	719	43	1	519	477	30	27	8	9	2310
6	438	352	43	15	536	549	52	4	676	701	27	32	10	795	824
7	1152	1142	23	17	1212	1196	29	5	1265	1220	17	31	11	1730	1693
11	731	671	45	10	10	2	1	6	1139	1072	20	2	12	1025	959
12	914	858	39	1	2374	2433	8	7	711	713	32	27	15	1292	1232
13	634	593	56	2	774	792	12	8	418	409	24	24	6	1098	1088
14	929	917	41	3	1807	1869	8	9	768	741	33	21	7	1261	1301
2	1131	1128	18	5	1470	1468	8	11	1454	1452	25	11	1	1534	1570
3	1697	1693	14	6	716	686	25	13	570	586	56	15	2	556	554
4	844	837	23	7	1052	1036	20	3	663	624	27	22	3	1598	1613
5	1938	1884	15	8	929	923	22	4	520	527	34	22	4	3400	3435
6	1638	1585	17	9	713	724	41	5	721	695	27	25	6	2472	2476
8	935	952	28	11	609	695	54	6	1066	1010	21	21	8	693	639
9	1297	1270	24	12	622	625	59	10	1079	1139	28	22	9	1865	1835
11	1830	1734	22	15	567	654	60	12	1247	1172	27	30	10	1971	1941
12	474	398	63	10	10	3	1	15	1262	1289	30	32	11	727	800
1	459	516	39	3	866	843	11	16	325	226	53	33	13	813	793
2	636	645	29	4	389	399	24	1	388	159	29	29	2	1724	1753
3	461	448	38	5	404	336	27	2	1668	1729	11	11	3	1485	1491
4	2327	2303	14	6	1022	935	16	3	386	437	29	29	4	1519	1477
5	783	803	27	7	775	737	24	8	1259	1219	23	11	5	1672	1625
6	1606	1621	18	8	759	740	38	11	958	892	31	13	6	369	359
8	1012	933	26	9	858	887	36	5	575	566	35	17	8	1992	2003
10	2554	2461	19	14	1182	1190	34	7	594	616	35	19	8	1922	2003
11	763	732	39	16	774	751	52	3	544	476	36	36	10	1733	1716
12	1118	1108	31	10	10	4	1	9	806	776	36	36	11	449	443
1	1250	1188	19	1	1841	1892	12	5	11720	1811	25	25	11	499	443
2	1039	1022	22	3	468	504	34	7	1734	1657	20	25	12	1150	1128
4	645	645	32	4	934	944	18	8	558	485	46	26	3	401	397
5	1366	1376	19	5	1095	1093	17	16	2427	2493	15	44	4	492	436
6	804	752	29	6	1561	1529	11	3	2641	2486	11	44	5	674	678
7	618	580	38	7	994	945	25	5	1040	1086	23	11	6	724	747
8	731	692	36	8	1745	1698	20	4	1609	1603	13	13	7	879	871
9	1263	1213	25	11	701	721	47	7	2657	2858	15	13	9	587	648
10	643	734	43	13	708	621	46	13	3059	3200	19	22	10	9	9
1	459	516	39	2	1955	2024	8	17	1820	1788	23	34	1	1181	1124
2	636	645	29	3	866	843	11	1	325	226	53	33	2	1719	1611
3	461	448	38	4	389	399	24	2	587	623	32	33	3	9	6
4	2327	2303	14	6	1022	935	16	5	558	559	35	35	4	2162	2069
5	783	803	27	7	775	737	24	6	777	773	28	33	5	901	844
6	1606	1621	18	8	759	740	38	7	667	624	27	35	6	687	639
8	1012	933	26	9	858	887	36	8	1079	1139	28	36	7	2286	2277
10	2554	2461	19	14	1182	1190	34	9	594	616	35	36	8	1362	1340
11	763	732	39	16	774	751	52	10	544	476	36	36	9	2556	2631
12	1118	1108	31	10	10	4	1	4	719	686	29	39	10	1320	1369
1	1250	1188	19	1	1841	1892	12	5	611	607	35	35	11	832	630
2	1039	1022	22	3	468	504	34	7	1734	1657	20	45	12	705	646
4	645	645	32	4	934	944	18	8	558	485	46	26	13	595	526
5	1366	1376	19	5	1095	1093	17	16	2427	2493	15	44	14	832	801
6	804	752	29	6	1561	1529	11	3	2641	2486	11	44	15	898	821
7	618	580	38	7	994	945	25	5	1040	1086	23	11	17	3	3
8	731	692	36	8	1745	1698	20	4	1609	1603	13	13	1	1606	1610
9	1263	1213	25	11	701	721	47	7	2657	2858	15	44	2	1616	1670
10	643	734	43	13	708	621	46	13	3059	3200	19	22	3	548	504
1	459	516	39	2	1955	2024	8	17	1820	1788	23	34	4	1010	985
2	636	645	29	3	866	843	11	1	325	226	53	33	5	2358	2121
3	461	448	38	4	389	399	24	2	587	623	32	33	6	2258	215
4	2327	2303	14	6	1022	935	16	5	558	559	35	35	7	475	379
5	783	803	27	7	775	737	24	6	777	773	28	36	8	475	379
6	1606	1621	18	8	759	740	38	7	667	624	27	37	9	475	379
8	1012	933	26	9	858	887	36	8	1079	1139	28	38	10	475	379
10	2554	2461	19	14	1182	1190	34	9	594	616	35	39	11	475	379
11	763	732	39	16	774	751	52	10	544	476	36	39	12	475	379
12	1118	1108	31	10	10	4	1	4	719	686	29	39	13	475	379

COLUMNS ARE 10FO,10FC, 10SIG

1	1884	1908	11	11	416	532	62	1	2726	2859	3	1	10	2612	2592	6,	14	1587	1665	23	8	1093	1119	FC	SIG				
2	1971	2041	10	12	550	525	50	2	1079	1134	9	1	11	494	454	18	15	15	534	533	23	9	1764	1703	FC	SIG			
3	276	199	40	1	438	472	40	3	1865	1878	11	1	13	1307	1286	29	17	17	565	543	48	10	1432	1420	FC	SIG			
4	1222	1160	14	3	441	317	39	4	276	310	41	1	14	1609	1588	28	1	1	1919	2009	8	11	721	723	FC	SIG			
5	1939	1911	13	4	395	368	46	5	706	710	23	2	15	827	780	44	2	2	1353	1327	9	14	1362	1309	FC	SIG			
6	612	539	30	5	639	649	31	6	928	920	23	3	16	1654	1688	10	3	3	1534	1688	10	15	545	469	FC	SIG			
7	1874	1841	17	6	479	534	45	7	461	477	45	1	17	993	990	17	4	4	2198	2100	12	1	1016	997	FC	SIG			
8	452	325	51	8	851	803	29	8	887	886	28	2	18	1881	1892	13	5	5	2038	1971	14	2	1254	1271	FC	SIG			
9	649	684	44	8	597	527	39	9	1245	1228	24	3	19	1245	1228	24	6	6	451	665	30	4	1943	1955	FC	SIG			
10	1085	1058	31	11	1840	1803	32	11	1840	1803	32	3	20	4	652	671	26	7	7	4865	4480	14	5	943	913	FC	SIG		
11	733	783	44	1	576	552	35	12	1205	1204	30	4	21	5	1257	1302	17	8	8	2247	2247	17	6	475	415	FC	SIG		
12	716	758	47	6	784	727	32	13	1267	1232	30	5	22	6	1468	1492	18	9	9	1859	1867	20	8	1863	1939	FC	SIG		
13	788	796	47	7	623	569	41	14	937	854	38	6	23	7	732	719	30	10	10	1920	1941	22	9	1441	1525	FC	SIG		
14	1366	1433	13	1	4603	4715	17	15	1564	1640	10	7	24	8	1047	1025	23	11	11	1298	1327	29	10	2187	2171	FC	SIG		
15	1404	1424	13	3	3222	2425	15	16	338	320	29	8	25	9	1679	1636	19	12	12	2673	2674	32	11	981	993	FC	SIG		
16	2136	2167	11	5	3044	3141	20	17	622	624	18	9	26	10	897	869	31	13	13	1068	1044	31	12	576	501	FC	SIG		
17	1386	1358	14	7	2993	3158	18	18	4	2728	2768	11	11	14	1130	1093	28	14	14	1068	1044	31	13	745	741	FC	SIG		
18	1945	1815	14	9	1552	1611	23	19	5	856	825	19	12	15	902	883	37	15	15	590	466	45	14	965	880	FC	SIG		
19	1882	1854	15	11	3566	3754	18	20	6	533	519	32	13	16	7	8	3	1	3006	3118	8	15	1810	1762	FC	SIG			
20	362	364	58	13	1540	1542	23	21	7	720	667	28	14	17	1146	1203	18	1	1	1146	1188	10	1	1315	1309	FC	SIG		
21	977	950	29	15	1942	2106	21	22	8	1770	1743	19	15	18	2	1146	1203	18	2	2	1303	1285	10	2	1756	1775	FC	SIG	
22	1645	1631	27	17	2879	2881	20	23	10	1017	1043	29	16	19	3	718	708	26	3	3	985	949	15	3	1226	1219	FC	SIG	
23	1370	1365	27	1	1818	1863	10	24	11	1400	1352	25	17	20	4	545	544	34	4	4	2932	2850	12	4	679	639	FC	SIG	
24	815	806	40	1	1818	1863	10	25	12	1074	1115	32	21	21	5	547	450	35	5	5	3265	3118	14	5	2102	2080	FC	SIG	
25	839	912	40	2	3112	3293	8	26	13	982	942	34	22	22	6	1954	1903	17	6	6	1324	1327	19	6	371	372	FC	SIG	
26	874	843	40	3	3019	2961	10	27	14	1887	1836	25	23	23	7	457	407	49	7	7	2078	2096	18	7	1578	1511	FC	SIG	
27	1132	1132	15	4	605	647	29	28	8	1340	1330	22	24	24	8	1340	1330	22	8	8	1362	1334	22	8	833	878	FC	SIG	
28	1945	966	16	5	1861	1845	16	29	9	822	794	31	25	25	9	822	794	31	9	9	1027	1040	28	9	1518	1432	FC	SIG	
29	1884	1888	14	6	2408	2373	16	30	1	409	404	27	26	26	1	2133	2097	15	10	10	1094	1116	29	10	472	410	FC	SIG	
30	1633	1574	15	7	1443	1446	23	31	2	498	513	23	27	27	2	2133	2097	15	11	11	2193	2164	21	11	950	922	FC	SIG	
31	1096	1093	20	8	2277	2349	22	32	3	3941	4099	10	28	28	3	617	546	31	12	12	1490	1485	28	12	8	8	FC	SIG	
32	554	495	36	9	2281	2327	24	33	4	704	706	20	29	29	4	544	579	39	13	13	865	846	41	13	1959	1955	FC	SIG	
33	424	387	50	10	2063	2130	22	34	5	3077	3008	12	30	30	5	2383	2309	16	14	14	1490	1485	28	14	2255	2266	FC	SIG	
34	1479	1437	21	11	1951	2111	22	35	6	599	584	29	31	31	6	599	584	29	15	15	1787	1821	9	15	768	765	FC	SIG	
35	1341	1358	24	12	1951	2111	22	36	7	2532	2524	15	32	32	7	2532	2524	15	16	16	623	623	16	16	991	1008	FC	SIG	
36	1873	1894	22	13	1306	1301	25	37	8	929	914	26	33	33	8	585	512	43	17	17	645	623	16	17	2255	2266	FC	SIG	
37	1062	1090	30	14	2186	2237	21	38	9	3820	3852	16	34	34	9	2293	2136	12	18	18	2097	2168	19	18	991	1008	FC	SIG	
38	760	707	21	15	1905	919	34	39	10	601	611	47	35	35	10	3430	3591	17	19	19	1327	1281	18	19	960	928	FC	SIG	
39	794	787	21	16	762	815	13	40	11	1161	1151	30	36	36	11	1161	1151	30	20	20	1089	1128	24	20	496	534	FC	SIG	
40	540	516	29	1	3483	3585	8	41	12	2104	2021	23	37	37	12	1472	1524	23	21	21	1014	1051	28	21	1174	1198	FC	SIG	
41	1271	1237	18	2	3982	3833	11	42	13	1941	1876	26	38	38	13	1941	1876	26	22	22	579	500	44	22	1613	1660	FC	SIG	
42	459	494	46	3	784	829	26	43	1	1218	1263	14	39	39	14	2922	3007	8	23	23	1794	1739	22	23	1334	1280	FC	SIG	
43	1212	1258	24	4	1982	1942	18	44	2	2598	2443	11	40	40	1	2598	2443	11	24	24	515	392	57	24	486	495	FC	SIG	
44	825	739	32	5	852	841	33	45	3	535	548	25	41	41	2	2067	1928	12	25	25	606	488	51	25	881	875	FC	SIG	
45	1222	1205	27	6	3302	3283	19	46	4	4010	4068	11	42	42	3	2262	2288	17	26	26	514	509	65	26	481	457	FC	SIG	
46	479	439	33	7	676	646	47	47	5	1944	1994	14	43	43	4	2670	2727	19	27	27	2263	2318	10	27	891	875	FC	SIG	
47	1036	1031	19	8	1724	1741	27	48	6	440	473	41	44	44	5	2689	2742	21	28	28	1238	1237	13	28	607	668	FC	SIG	
48	439	446	41	9	1082	1050	31	49	7	1865	1826	16	45	45	6	2889	2742	21	29	29	4	1025	1053	16	29	477	460	FC	SIG
49	1036	1031	19	10	1248	1240	28	50	8	3002	2995	15	46	46	7	1980	2047	21	30	30	6	1190	1134	18	30	532	526	FC	SIG
50	439	446	41	11	549	497	52	51	9	758	781	33	47	47	8	1445	1484	25	31	31	7	1990	1994	16	31	507	479	FC	SIG

COLUMNS ARE 10FO,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG
6	1002	947	19	7	726	756	28	14	988	936	35	1	1188	1168	19	3	1765	1767	10	3	1765	1767	10
7	1076	1099	20	8	1980	1949	27	5	3649	3658	11	4	720	720	31	5	883	878	18	5	883	878	18
8	1505	1490	18	9	615	579	37	6	517	495	31	1	449	448	21	6	807	790	22	6	807	790	22
9	1849	1840	18	10	507	477	46	2	886	905	14	2	886	905	14	7	1580	1572	18	7	1580	1572	18
10	604	586	41	12	810	811	36	3	2910	2927	10	3	2910	2927	10	8	462	476	48	8	462	476	48
11	1881	1930	21	13	1083	1061	31	4	777	780	19	4	777	780	19	9	1891	1936	20	9	1891	1936	20
12	1686	1673	25	1	1357	1439	14	5	914	912	32	5	1804	1500	14	10	665	665	38	10	665	665	38
13	453	488	68	2	1324	1349	15	11	3729	3835	30	6	601	665	35	11	725	725	39	11	725	725	39
14	713	775	45	3	1383	1358	15	12	1111	1090	28	7	2685	2720	14	14	832	816	38	14	832	816	38
2	1352	1363	9	4	1383	1358	15	14	1729	1694	21	8	3539	3633	14	15	695	763	45	15	695	763	45
3	1434	1375	10	5	641	624	30	15	2451	2417	18	9	969	992	22	1	1007	1050	11	1	1007	1050	11
4	3032	2961	10	7	1394	1424	19	16	412	413	60	11	1173	1188	21	3	524	513	21	3	524	513	21
5	791	732	26	11	1227	1216	46	1	4047	4164	6	12	1672	1713	19	4	1061	1008	14	4	1061	1008	14
6	1389	1429	23	1	1160	1153	17	3	4393	4312	8	13	876	861	6	5	987	965	17	5	987	965	17
7	11245	1184	25	2	490	557	33	5	1530	1527	14	14	2037	1957	7	6	1350	1314	16	6	1350	1314	16
8	1098	1104	31	3	622	569	33	6	1329	1251	16	1	1776	1836	11	7	495	429	35	7	495	429	35
9	664	604	47	4	980	1021	23	7	2684	2770	14	2	1463	1419	12	8	1305	1321	21	8	1305	1321	21
10	738	758	13	5	428	379	51	8	765	745	28	3	2300	2248	11	9	998	1018	26	9	998	1018	26
11	1225	1231	16	6	1365	1374	23	9	2816	2834	16	6	2072	2151	15	10	1042	1001	29	10	1042	1001	29
12	1039	1054	12	10	1374	1374	23	10	2996	3073	16	7	2194	2250	16	11	669	655	44	11	669	655	44
13	317	351	37	1	375	388	43	12	1894	1880	23	8	1972	2010	18	12	1022	962	34	12	1022	962	34
14	343	375	40	3	553	544	33	13	1762	1770	24	9	1842	1845	18	14	1201	1256	11	14	1201	1256	11
15	1687	1690	16	4	689	725	33	14	826	835	36	11	567	522	45	1	2028	2085	10	1	2028	2085	10
1	990	946	24	5	1238	1241	24	15	1118	1083	28	12	661	600	41	2	3186	3091	7	2	3186	3091	7
2	1218	1195	23	6	956	939	23	16	2248	2165	20	13	2068	1976	22	3	1480	1436	24	3	1480	1436	24
3	1529	1483	22	7	709	694	30	1	1616	1575	8	1	2269	2366	12	4	2998	2996	10	4	2998	2996	10
4	625	586	45	8	2617	8290	14	2	5672	5888	9	2	2018	1999	12	5	834	819	15	5	834	819	15
5	988	972	32	9	1059	972	26	3	2802	2848	7	3	2251	2238	13	6	1856	1885	15	6	1856	1885	15
6	1462	1405	25	10	1823	1913	17	4	3068	3028	10	4	2353	2404	14	7	1856	1885	15	7	1856	1885	15
7	780	706	44	11	2276	2287	15	5	1665	1590	13	5	2064	2119	17	8	2390	2394	16	8	2390	2394	16
8	1875	1942	10	12	572	511	36	6	1424	1472	16	6	1737	1704	18	9	1205	1214	24	9	1205	1214	24
9	350	345	29	13	388	432	60	7	852	844	24	7	1106	1118	27	10	2792	2877	19	10	2792	2877	19
10	486	462	27	14	5862	5847	5	8	3375	3390	15	8	625	585	44	11	1072	1046	28	11	1072	1046	28
11	546	561	27	1	731	684	13	9	450	374	49	9	1106	1118	27	12	907	943	30	12	907	943	30
12	1015	987	18	2	3244	3178	9	10	1837	1825	20	10	625	585	44	13	1067	1102	26	13	1067	1102	26
13	1894	1865	15	3	3377	3308	10	11	564	589	47	11	412	413	36	14	850	801	31	14	850	801	31
14	1234	1296	21	4	533	512	34	12	812	754	37	1	412	413	36	1	482	502	17	1	482	502	17
15	2158	2153	17	5	1838	1798	16	13	647	612	45	3	1414	1392	16	2	1553	1517	8	2	1553	1517	8
16	978	976	31	6	1417	1451	26	4	1090	1077	33	4	2091	2065	15	3	3533	3495	9	3	3533	3495	9
17	1259	1242	27	7	1492	1522	21	5	2119	2123	16	5	545	480	37	6	2214	2247	12	6	2214	2247	12
18	1269	1219	30	8	1643	1787	20	6	2639	2668	10	6	1115	1186	25	7	1128	1072	19	7	1128	1072	19
19	71	71	11	9	665	712	37	7	4485	4517	10	7	545	480	37	8	491	560	40	8	491	560	40
20	1652	1697	11	10	3308	3458	16	8	1075	1087	17	8	1115	1186	25	9	2935	3028	16	9	2935	3028	16
21	2402	2530	11	11	643	624	37	9	965	1001	17	9	1107	1081	27	10	1882	1898	22	10	1882	1898	22
22	1201	1215	15	12	1643	1787	20	10	1075	1087	17	10	498	516	33	11	842	861	33	11	842	861	33
23	1224	1238	16	13	665	712	37	11	1075	1087	17	11	843	833	22	12	928	962	36	12	928	962	36
24	417	411	39	14	934	924	27	12	1949	2008	18	12	1472	1502	18	13	1059	1029	9	13	1059	1029	9
25	1201	1215	15	15	792	775	31	13	1174	1127	24	13	755	739	29	14	1333	1346	9	14	1333	1346	9
26	1224	1238	16	16	2013	1982	20	14	2090	2088	20	14	2000	2032	18	15	1059	1029	9	15	1059	1029	9
27	417	411	39	1	2087	2151	5	15	893	863	33	15	503	565	47	16	1333	1346	9	16	1333	1346	9

COLUMNS ARE 10FD,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	
5	453	432	43	7	2577	2717	14	6	1892	1993	15	1	1	1	1	7	469	432	44	
10	849	839	33	8	699	792	30	8	1357	1424	21	2	202	2142	17	8	428	350	52	
2	540	581	33	9	466	453	45	10	782	772	32	9	1359	1356	20	10	787	777	36	
3	837	835	24	10	587	616	41	11	1494	1479	23	10	937	995	25	12	1235	1208	28	
6	447	424	47	12	444	350	63	12	1458	1506	26	11	921	950	27	13	797	757	40	
1	1208	1246	20	13	1321	1295	26	12	866	883	16	12	2360	2402	16	14	854	870	39	
2	964	966	23	14	1469	1427	23	14	834	868	18	14	834	868	18	15	602	591	38	
3	472	397	42	0	0	4	6	2	888	911	18	15	404	442	7	2	1008	956	14	
4	1088	1087	24	1	2465	2637	7	3	1935	1971	13	0	444	442	7	4	2487	2417	13	
5	533	510	42	2	2443	2721	8	5	1753	1775	15	1	1300	1259	8	5	473	418	34	
2	5485	5290	8	3	4518	4713	9	6	866	905	24	2	435	348	26	7	2322	2227	15	
4	4456	4731	9	4	795	844	16	8	1028	1024	24	3	1606	1598	12	8	880	888	25	
6	6789	7297	9	5	1908	1966	13	4	1086	1109	24	4	679	665	22	10	859	845	32	
8	1983	2132	11	6	3898	4022	13	10	365	250	60	6	573	526	32	11	828	841	35	
10	1941	2042	11	7	1772	1717	16	11	916	938	30	7	1561	1525	18	13	933	938	39	
12	1451	1485	13	8	2271	2385	16	8	0	9	9	8	2020	1916	18	13	1	7	7	14
14	525	463	28	9	1839	1868	18	1	292	231	47	9	1149	1140	26	0	922	925	10	
1	7382	7611	5	10	872	804	36	2	2086	2145	13	10	1876	1897	21	1	2338	2565	11	
2	2153	2226	7	11	872	804	36	3	1076	1068	19	11	1031	1038	27	3	739	693	21	
3	1178	1246	12	12	1320	1359	27	4	1076	1068	19	13	1169	1245	23	5	2678	2823	13	
4	1820	1888	12	13	872	804	36	5	1179	1243	20	14	1009	1009	26	6	474	504	38	
5	5064	5352	12	14	538	510	55	6	486	492	39	1	1	3	3	7	1635	1683	18	
6	1496	1566	18	0	0	5	8	6	866	883	16	1	1255	1154	8	8	513	557	43	
7	1496	1566	18	1	2630	2779	8	7	1195	1171	22	2	1	1	1	9	579	510	45	
8	2459	2873	17	2	5127	5581	8	8	1195	1171	22	1	3007	2815	9	11	579	510	45	
9	625	743	33	3	953	938	14	9	1561	1596	21	2	4	951	968	17	12	544	591	54
10	1948	2024	17	4	3966	4154	10	10	0	10	10	6	477	346	37	12	544	591	54	
11	1618	1585	19	5	993	987	16	0	2043	2105	13	7	1291	1211	20	0	2248	2339	8	
12	649	623	34	6	1471	1532	16	1	482	493	33	8	1301	1243	21	20	856	904	19	
14	2022	2033	13	7	1450	1480	18	3	874	859	23	8	1988	1821	20	3	1213	1203	17	
15	833	826	22	8	4026	4106	15	3	874	859	23	11	967	931	30	3	1213	1203	17	
0	790	724	6	9	1139	1138	25	4	1910	1930	17	13	766	787	36	4	1049	1080	20	
1	806	796	8	10	1649	1620	22	6	1554	1551	19	15	1099	1074	27	5	671	639	29	
2	339	259	24	11	1578	1532	25	7	595	589	37	15	1	4	4	8	705	706	32	
3	691	685	18	12	1812	1732	25	8	715	720	33	1	1	1	1	9	371	314	58	
4	1133	1155	14	13	0	6	25	0	11	11	11	1	1065	1091	10	9	371	314	58	
5	549	599	28	14	495	504	17	1	1104	1121	20	2	578	542	17	1	1	9	9	10
6	2605	2754	14	0	421	421	20	2	628	610	31	3	3364	3332	10	2	932	976	19	
7	2371	2551	18	1	2211	2293	9	3	759	798	29	3	1390	1352	14	1	1310	1311	16	
8	649	623	34	2	378	349	26	4	855	806	28	4	1983	1829	15	2	351	326	48	
9	2371	2551	18	3	2785	2904	10	5	1670	1662	20	5	1431	1462	21	3	1364	1370	18	
10	1948	2024	17	4	740	743	19	6	1	0	0	6	858	900	29	4	1364	1370	18	
11	1618	1585	19	5	447	465	31	7	998	945	23	9	1580	1559	22	7	721	743	31	
12	725	672	34	6	1042	1051	18	8	2500	2536	14	10	9	454	485	53	9	454	485	53
13	2180	2162	18	7	3228	3414	14	9	2500	2536	14	11	954	992	31	1	1	10	10	10
14	836	833	31	8	2167	2256	18	10	2879	2880	14	12	723	710	41	0	599	609	20	
15	2537	2451	17	9	1376	1427	24	11	2604	2689	15	13	1012	993	32	1	1012	1018	20	
0	2506	2611	6	10	1376	1427	24	12	2070	2110	17	14	1	5	5	3	1364	1370	18	
1	1351	1356	9	11	980	996	31	13	1	1	4	0	205	253	25	1	1365	1375	10	
2	1819	1819	11	12	1554	1502	24	14	764	750	4	0	1365	1375	10	2	605	615	34	
3	2481	2567	12	13	2222	2169	23	1	617	576	13	1	950	927	13	6	499	449	41	
4	1819	1819	11	0	0	7	23	2	920	894	14	2	950	927	13	7	499	556	44	
5	2481	2567	12	1	934	994	14	3	1411	1310	13	3	1	11	11	7	499	556	44	
				2	1351	1356	9	4	2062	1939	12	4	1364	1370	18	8	405	415	34	
				3	4836	479	26	5	646	585	28	5	1740	1648	15	9	1644	1644	22	
				4	723	755	22	6	4836	479	26	6	1	1	1	10	1483	1491	23	
				5	1349	1374	16	7	1376	1332	19	7	1244	1204	19	11	770	761	36	
								8	1376	1332	19	8	1	1	1	12	835	859	34	
								9	1376	1332	19	9	1	1	1	13	2	4	4	4
								10	1376	1332	19	10	1	1	1	14	1	1	1	1
								11	1376	1332	19	11	1	1	1	15	1	1	1	1
								12	1376	1332	19	12	1	1	1	16	1	1	1	1
								13	1376	1332	19	13	1	1	1	17	1	1	1	1
								14	1376	1332	19	14	1	1	1	18	1	1	1	1
								15	1376	1332	19	15	1	1	1	19	1	1	1	1
								16	1376	1332	19	16	1	1	1	20	1	1	1	1
								17	1376	1332	19	17	1	1	1	21	1	1	1	1
								18	1376	1332	19	18	1	1	1	22	1	1	1	1
								19	1376	1332	19	19	1	1	1	23	1	1	1	1
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								21	1376	1332	19	21	1	1	1	25	1	1	1	1
								22	1376	1332	19	22	1	1	1	26	1	1	1	1
								23	1376	1332	19	23	1	1	1	27	1	1	1	1
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								25	1376	1332	19	25	1	1	1	29	1	1	1	1
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								28	1376	1332	19	28	1	1	1	32	1	1	1	1
								29	1376	1332	19	29	1	1	1	33	1	1	1	1
								30	1376	1332	19	30	1	1	1	34	1	1	1	1
								31	1376	1332	19	31	1	1	1	35	1	1	1	1
								32	1376	1332	19	32	1	1	1	36	1	1	1	1
								33	1376	1332	19	33	1	1	1	37	1	1	1	1
								34	1376	1332	19	34	1	1	1	38	1	1	1	1
								35	1376	1332	19	35	1	1	1	39	1	1		

COLUMNS ARE 10FD,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	
1	3200	3166	8	0	2274	2376	9	0	1317	1338	6	0	3271	3115	9	0	1317	1338	6	
2	2326	2223	10	1	976	1061	19	1	3271	3115	9	1	1035	1023	26	2	2426	2352	12	
3	3413	3341	11	2	1941	2013	14	2	3163	3131	10	2	828	890	33	3	3321	3202	13	
4	3924	3898	12	5	704	703	29	3	1869	1781	14	3	1064	1059	31	4	2086	1960	16	
5	639	620	30	6	1329	1318	20	4	1521	1487	16	4	1244	1305	10	5	755	780	29	
6	2299	2244	16	8	1090	1097	25	5	480	451	40	5	1206	1156	23	6	1195	1220	23	
7	3275	3113	16	9	1121	1154	27	6	965	941	24	6	2072	2076	17	7	2427	2357	18	
8	503	429	47	2	10	L	19	3	2194	2082	19	3	1948	1963	15	4	2086	1960	16	
9	1861	1868	20	0	1478	1566	11	4	746	755	35	4	2167	2231	16	5	755	780	29	
10	1280	1280	25	1	866	848	22	10	862	853	33	5	733	718	29	1	4316	4206	10	
12	768	719	37	4	1533	1494	18	12	687	693	38	6	2072	2076	17	2	2426	2352	12	
13	1252	1198	27	5	652	676	33	13	794	755	32	7	876	867	28	3	3321	3202	13	
0	2405	2473	6	6	578	605	38	3	1756	1766	6	9	1128	1115	27	4	2086	1960	16	
2	4584	4600	10	7	638	639	37	10	2308	2304	19	10	1230	1216	26	5	755	780	29	
3	2002	1962	12	0	822	844	18	1	2292	2315	9	3	1047	1063	18	6	1195	1220	23	
4	1449	1418	15	1	506	506	38	2	1932	1939	11	1	1227	1211	18	7	2427	2357	18	
5	2097	2055	14	2	867	852	26	3	3138	3160	12	2	1079	1048	21	8	2598	2588	18	
6	3271	3236	15	3	995	961	25	4	801	736	23	4	1293	1299	21	9	980	1051	30	
7	1157	1108	24	3	0	L	25	5	762	708	28	7	1064	1086	25	10	1415	1413	24	
8	3372	3365	17	1	2195	2085	17	7	2006	1972	19	8	1088	1058	26	8	1088	1058	26	
12	2440	2300	20	3	1338	1297	18	8	695	694	37	8	3	10	L	0	2487	2547	6	
1	2427	2399	10	5	465	345	26	11	956	925	31	0	363	334	32	0	2090	2097	11	
2	577	515	22	7	718	726	26	12	636	524	42	1	595	655	31	2	4386	4318	11	
3	1686	1598	14	9	2099	2101	16	13	479	430	61	2	640	603	29	3	1184	1143	17	
4	652	597	25	13	753	706	29	3	5	L	7	3	680	634	30	3	2301	2225	15	
5	1694	1640	16	0	1290	1326	7	0	1290	1326	7	0	739	742	19	5	1415	1341	20	
6	770	774	28	0	2564	2555	5	1	267	159	37	2	813	814	28	6	1070	990	26	
7	2761	2844	16	1	3300	3206	10	4	1487	1418	13	2	691	676	33	7	2789	2846	18	
8	1211	1216	23	2	1091	1062	18	5	349	326	50	3	4	0	L	8	1987	1866	20	
10	813	859	35	3	3478	3267	12	6	604	574	36	2	5129	4920	13	9	957	903	30	
11	2098	2048	22	4	458	338	40	8	1402	1400	24	4	4662	4567	13	10	678	694	40	
0	1394	1411	8	5	692	615	32	9	794	814	36	6	1248	1223	19	11	1002	930	29	
1	1120	1081	15	7	750	693	30	10	1464	1431	24	8	2536	2410	15	0	1916	1960	7	
2	486	539	30	8	444	502	47	12	543	577	53	10	2731	2755	15	1	2247	2180	11	
3	1893	1887	14	10	1400	1445	20	3	6	L	17	12	436	380	46	2	1896	1847	13	
4	462	430	36	11	660	711	33	0	410	388	17	4	1455	1422	6	3	2309	2294	13	
5	729	714	26	12	1199	1258	22	3	503	460	27	0	1455	1422	6	4	533	558	34	
6	845	848	25	3	2	L	15	3	674	665	24	1	706	690	24	5	905	932	25	
7	1003	1011	23	0	1983	1913	5	4	1687	1610	15	3	3561	3493	13	6	2161	2227	17	
9	1430	1396	22	1	676	651	19	5	459	425	40	4	2016	1916	17	8	865	856	33	
10	1180	1160	25	2	3738	3528	11	6	1084	1076	22	5	2555	2509	17	9	786	819	36	
11	476	510	57	3	1360	1315	15	8	561	567	42	6	815	793	32	6	1212	1172	26	
1	2504	2648	12	6	939	898	25	10	705	726	40	7	560	453	40	10	451	485	62	
2	1440	1493	15	7	1211	1176	23	11	619	601	48	8	1954	1845	18	12	1820	1702	23	
3	1089	1064	19	8	478	361	49	9	2534	2678	16	9	2534	2678	16	4	6	L	4	
4	970	956	21	9	472	500	53	10	545	555	16	10	1726	1685	18	1	969	984	16	
5	660	603	29	10	1096	1177	26	11	292	342	44	11	1478	1516	19	2	560	517	28	
7	1212	1210	21	11	813	803	30	12	1410	1359	15	12	602	601	36	3	369	280	46	
9	882	930	30	13	846	818	29	3	1833	1766	15	0	1825	1870	5	4	998	990	41	
				14	1119	1065	24	4	1229	1240	18	5	2	1734	1704	13	5	1288	1351	22
								5	2563	2638	15	2	2	1734	1704	13	6	684	634	35

COLUMNS ARE 10FO,10FC, 10SIG

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG		
9	539	613	40	10	507	470	54	6	455	370	48	3	1637	1587	18	747	671	36			
11	480	509	43	5	5	7	7	3	2263	2347	16	10	1142	1135	29	8	2386	2414	18		
13	561	560	39	0	984	961	11	7	2185	2298	20	5	1732	1800	19	0	2254	2279	8		
0	475	4809	6	2	2312	2318	14	10	1033	1045	26	12	681	668	36	1	941	887	21		
1	1436	1296	15	3	1107	1077	20	12	681	668	36	0	335	355	34	2	2465	2469	15		
2	1943	1856	15	4	864	874	25	0	516	511	14	0	1114	1080	20	3	1479	1351	20		
3	2661	2545	15	5	962	959	23	0	1312	4192	14	2	1345	1397	20	5	2545	2475	18		
4	1827	1777	17	6	1209	1238	23	1	4312	4192	14	2	1492	1452	20	6	2335	2402	20		
5	846	834	28	8	1276	1251	25	2	888	862	24	4	842	843	31	7	1105	1103	28		
6	2263	2174	18	9	1222	1204	26	3	988	948	25	5	842	843	31	8	1452	1355	23		
7	1695	706	38	1	1141	1201	18	5	2384	2275	17	0	825	860	38	9	708	708	40		
8	1015	976	25	2	1324	1315	18	6	1919	1972	19	0	546	531	38	7	7	5	195	18	
9	477	519	46	3	1561	1548	17	7	1873	1898	21	1	584	559	39	0	285	195	30	0	
10	1743	1818	6	4	1833	1843	17	8	1901	1803	20	1	496	505	45	1	3241	3097	14	1	
11	4160	3932	11	5	727	710	32	9	1136	1123	27	3	403	478	58	2	1324	1265	19	2	
12	3211	3177	13	6	1470	1514	22	10	3643	3700	7	4	4534	4495	15	3	2324	2351	16	3	
13	1170	1121	20	7	1064	1130	29	11	2156	2114	14	1	4534	4495	15	4	1314	1340	22	4	
14	1886	1779	19	8	446	473	26	2	1053	949	26	5	4155	4005	15	5	936	916	29	5	
15	2641	2553	17	9	506	542	39	3	1003	1005	27	6	1967	1866	17	6	812	806	35	6	
16	1326	1376	23	0	486	473	26	7	2006	2033	20	7	2164	2071	18	7	2038	1993	21	7	
17	2029	2014	19	1	1305	1307	20	8	1295	1238	25	8	4361	4269	17	8	648	622	44	8	
18	1573	1597	23	2	5	10	22	9	895	979	37	9	2164	2071	18	9	719	712	38	9	
19	2148	2187	6	3	553	583	23	10	850	612	42	0	4361	4269	17	10	1314	1340	22	10	
20	2577	2501	12	4	605	625	33	11	478	454	17	1	4361	4269	17	11	1314	1340	22	11	
21	3216	3101	12	5	701	662	21	12	478	454	17	2	2446	2496	9	12	1314	1340	22	12	
22	1049	995	20	6	384	302	51	13	1643	1588	15	3	983	971	23	13	1913	1920	15	13	
23	773	752	29	7	384	302	51	14	5783	741	31	4	2390	2357	17	14	2353	2435	15	14	
24	1929	1880	19	8	0	0	0	15	1041	1035	30	5	2164	2071	18	15	1101	1045	22	15	
25	1172	1249	25	9	2160	2133	19	16	650	612	42	6	4361	4269	17	16	826	834	29	16	
26	2706	2704	18	10	1664	1662	18	17	510	453	52	7	4361	4269	17	17	674	623	35	17	
27	1103	1155	27	11	1385	1354	20	18	460	412	35	8	1427	1440	9	18	1607	1543	17	18	
28	1300	1292	25	12	1543	1517	18	19	546	572	34	9	764	705	28	19	1490	1490	39	19	
29	685	667	42	13	1165	1128	21	20	783	741	31	10	1709	1637	18	20	1204	1165	23	20	
30	896	948	10	14	363	389	23	21	450	514	46	11	2011	1849	17	21	542	456	48	21	
31	1146	1108	15	15	818	817	26	22	784	810	30	12	2592	2566	18	22	1492	1480	23	22	
32	1931	1922	16	16	657	625	34	23	439	424	59	13	881	872	32	23	1467	1399	23	23	
33	812	763	26	17	818	817	26	24	6	7	429	424	14	1116	1123	11	24	1608	1646	10	24
34	1415	1382	50	18	818	817	26	25	116	1123	11	15	871	878	15	25	521	512	50	25	
35	1467	1475	22	19	681	668	36	26	1912	1926	14	16	721	717	37	26	366	366	46	26	
36	907	899	32	20	1462	1471	20	27	952	962	22	17	674	641	36	27	792	779	32	27	
37	1107	1141	28	21	1316	1285	20	28	1843	1930	17	18	407	382	55	28	871	878	15	28	
38	422	432	62	22	1049	1009	29	29	1167	1140	24	19	1788	1812	17	29	1188	1195	13	29	
39	693	677	13	23	791	849	30	30	6	8	7	20	1367	1354	17	30	1977	1942	24	30	
40	1524	1491	14	24	815	805	29	31	1016	1009	29	21	391	430	54	31	1070	1096	25	31	
41	582	545	30	25	6	2	12	32	638	649	37	22	430	430	54	32	437	472	54	32	
42	1669	1599	16	26	658	685	12	27	1796	1779	20	23	1914	1975	19	33	710	710	38	33	
43	507	514	41	27	1618	1581	18	28	2129	2156	9	24	2053	2067	20	34	1316	1321	22	34	
44				28				29	1030	984	22	25	1024	1023	29	35	386	415	59	35	

COLUMNS ARE 10FD,10FC, 10SIG

COLUMNS ARE 10FD,10FC, 10SIG

L	KFD	FC	SIG	L	KFD	FC	SIG	L	KFD	FC	SIG	L	KFD	FC	SIG	
0	568	615	22	2	1463	1462	33	3	611	623	45	1	983	1048	27	
1	1252	1200	20	3	770	787	33	4	693	691	38	2	967	950	28	
3	1668	1620	19	4	557	474	45	5	922	947	33	3	799	809	34	
4	831	804	31	5	1945	1957	22	10	10	5	L	4	822	843	34	
5	681	685	40	7	2006	1966	22	0	1273	1045	15	11	11	7	L	
0	722	749	20	0	2533	2609	9	1	1021	1358	22	0	1327	1303	14	
2	918	944	28	1	560	520	38	2	495	550	49	1	1293	1275	23	
8	10	L	28	2	2351	2328	17	3	902	875	30	2	1166	1226	26	
0	591	597	26	3	437	486	55	4	1079	1097	28	12	0	L		
9	0	L	26	5	494	441	50	10	10	6	L	0	977	1012	32	
1	1911	1866	20	6	1461	1440	25	0	933	946	16	2	1243	1342	25	
3	4373	4586	15	9	7	L	26	2	1045	1084	26	6	838	862	32	
5	1376	1449	22	0	334	376	35	3	897	975	30	1	1127	1131	28	
7	1743	1881	20	1	1137	1146	23	10	0	7	L	2	655	785	46	
9	3176	3227	17	2	949	962	26	0	334	234	37	2	797	853	39	
0	590	618	24	3	1016	1050	26	1	723	733	33	3	1084	1063	28	
1	1908	1868	19	4	925	986	30	2	769	746	32	4	593	641	43	
2	3012	2980	18	9	9	L	16	11	0	L	21	6	12	2	L	
3	881	832	32	0	947	932	16	1	1871	2026	21	12	0	829	852	21
4	2671	2707	20	1	697	648	32	3	1651	1664	19	0	1032	1068	29	
7	664	711	35	3	494	409	47	5	784	876	32	1	1603	1565	23	
8	2301	2422	18	4	931	919	30	7	2454	2590	18	3	1673	1706	25	
0	2486	2507	10	0	1413	1363	14	1	622	586	45	6	593	641	43	
2	2470	2371	18	1	810	793	31	2	1389	1444	34	12	0	829	852	21
3	453	468	52	10	0	L	22	3	858	905	26	2	12	2	L	
4	592	540	43	0	1929	1902	18	4	614	588	43	3	1269	1327	28	
7	648	591	40	2	2446	2518	18	5	980	975	28	0	13	2	L	
8	577	513	43	4	721	808	34	6	1301	1377	24	1	823	858	36	
9	571	580	43	6	439	604	52	6	11	2	L	2	1469	1544	25	
0	321	270	33	8	719	759	35	0	2491	2588	11	3	1479	1544	25	
1	685	648	37	10	10	L	19	1	808	912	35	4	1479	1544	25	
2	1874	1912	19	0	940	979	19	4	1088	1083	29	1	724	742	40	
3	796	762	33	1	2412	2498	18	6	680	584	42	3	1269	1327	28	
4	1512	1483	22	3	1410	1401	25	6	680	584	42	0	13	2	L	
5	758	744	36	7	704	618	41	0	2126	2150	11	11	829	852	21	
7	605	601	44	4	618	674	40	1	530	468	50	2	1736	1719	21	
8	941	939	32	0	1296	1243	13	4	412	430	63	4	1603	1565	23	
0	2088	2159	9	1	769	834	32	6	1408	1414	26	11	11	4	L	
1	1802	1807	18	2	1566	1590	22	0	677	738	21	11	4	L		
2	1343	1355	19	3	799	804	34	0	2202	2299	19	19	11	4	L	
3	2211	2253	19	5	1037	1050	30	1	2202	2299	19	31	967	881	31	
4	918	892	32	7	900	864	32	5	1457	1491	25	5	1457	1491	25	
5	469	436	56	0	1754	1803	11	6	1224	1221	28	6	111	5	L	
6	2076	2081	20	1	552	471	45	0	978	945	16	0	978	945	16	
7	1081	1061	30	4	925	951	31	0	1354	1351	22	1	1354	1351	22	
8	962	947	33	5	773	783	36	3	555	506	44	3	555	506	44	
0	1262	1280	12	6	961	942	31	4	738	797	40	4	738	797	40	
				9	10	4	L	5	1783	1766	23	5	1783	1766	23	

Table S.24. Fractional Coordinates for Os₄(CO)₁₃PMe₄

ATOM	X	Y	Z	BISO
OS(1)	0.72624(6)	0.06807(9)	0.16526(7)	2.11(5)
OS(2)	0.81211(7)	0.08846(10)	0.35340(7)	2.91(5)
OS(3)	0.84245(7)	0.28599(10)	0.24489(7)	2.76(6)
OS(4)	0.66698(7)	0.26834(10)	0.25142(8)	2.92(6)
P	0.7071(4)	-0.1526(6)	0.1181(5)	2.8(4)
C(1)	0.726(2)	-0.272(2)	0.197(2)	3.3(5)
C(2)	0.591(2)	-0.187(3)	0.032(3)	6.1(8)
C(3)	0.783(2)	-0.207(3)	0.062(2)	3.6(6)
C(11)	0.851(2)	0.051(2)	0.169(2)	2.8(5)
O(11)	0.921(1)	0.019(2)	0.162(1)	3.2(3)
C(12)	0.605(2)	0.040(2)	0.167(2)	2.8(5)
O(12)	0.534(1)	-0.003(2)	0.164(1)	4.2(4)
C(13)	0.676(1)	0.141(2)	0.052(2)	2.1(4)
O(13)	0.642(1)	0.193(2)	-0.019(1)	4.6(4)
C(21)	0.849(2)	0.188(3)	0.459(2)	3.9(6)
O(21)	0.875(1)	0.254(2)	0.522(2)	5.9(5)
C(22)	0.697(2)	0.049(3)	0.361(3)	5.6(8)
O(22)	0.637(2)	-0.006(3)	0.374(2)	7.9(7)
C(23)	0.857(2)	-0.083(3)	0.400(2)	4.8(7)
O(23)	0.885(2)	-0.183(3)	0.425(2)	8.4(7)
C(24)	0.936(2)	0.104(3)	0.351(2)	4.3(6)
O(24)	1.014(1)	0.079(2)	0.365(2)	5.6(5)
C(31)	0.958(2)	0.282(2)	0.232(2)	3.3(5)
O(31)	1.026(1)	0.276(2)	0.219(1)	4.4(4)
C(32)	0.792(2)	0.398(2)	0.150(2)	3.3(5)
O(32)	0.757(1)	0.462(2)	0.086(2)	5.8(5)
C(33)	0.879(2)	0.425(3)	0.328(2)	4.2(6)
O(33)	0.905(2)	0.508(2)	0.377(2)	6.0(5)
C(41)	0.690(2)	0.411(3)	0.332(2)	4.1(6)
O(41)	0.707(1)	0.500(2)	0.369(2)	5.1(5)
C(42)	0.556(2)	0.233(3)	0.268(2)	4.8(7)
O(42)	0.487(2)	0.207(2)	0.278(2)	7.2(6)
C(43)	0.606(2)	0.370(3)	0.148(2)	4.3(6)
O(43)	0.561(2)	0.441(2)	0.093(2)	6.2(5)
H(11)	0.673(0)	-0.366(0)	0.155(0)	5.(0)
H(12)	0.705(0)	-0.238(0)	0.248(0)	4.(0)
H(13)	0.798(0)	-0.302(0)	0.226(0)	4.(0)
H(21)	0.566(0)	-0.098(0)	-0.008(0)	7.(0)
H(22)	0.591(0)	-0.269(0)	-0.013(0)	5.(0)
H(23)	0.542(0)	-0.209(0)	0.062(0)	7.(0)
H(31)	0.789(0)	-0.128(0)	0.025(0)	5.(0)
H(32)	0.745(0)	-0.287(0)	0.020(0)	5.(0)
H(33)	0.854(0)	-0.245(0)	0.103(0)	5.(0)

Table S.25. Thermal Parameters for $\text{Os}_4(\text{CO})_{13}\text{PMe}_4$

ATOM	U11	U22	U33	U12	U13	U23
OS(1)	2.58(5)	2.76(5)	2.66(6)	0.01(4)	1.08(5)	-0.30(5)
OS(2)	3.83(6)	4.58(7)	2.66(7)	-0.40(5)	1.44(5)	-0.08(5)
OS(3)	3.28(6)	3.55(6)	3.65(7)	-0.83(4)	1.94(5)	-0.67(5)
OS(4)	3.28(6)	3.72(6)	4.10(7)	-0.04(5)	2.12(5)	-0.82(5)
F	3.3(3)	3.3(4)	3.9(5)	0.1(3)	1.3(3)	-0.5(3)
C(1)	4.2(7)					
C(2)	7.8(10)					
C(3)	4.6(7)					
C(11)	3.5(6)					
O(11)	4.1(4)					
C(12)	3.6(6)					
O(12)	5.3(5)					
C(13)	2.7(6)					
O(13)	5.8(5)					
C(21)	5.0(8)					
O(21)	7.5(6)					
C(22)	7.1(10)					
O(22)	10.1(9)					
C(23)	6.1(9)					
O(23)	10.6(9)					
C(24)	5.5(8)					
O(24)	7.1(6)					
C(31)	4.2(7)					
O(31)	5.6(5)					
C(32)	4.2(7)					
O(32)	7.3(6)					
C(33)	5.4(8)					
O(33)	7.6(7)					
C(41)	5.3(8)					
O(41)	6.5(6)					
C(42)	6.1(9)					
O(42)	9.1(8)					
C(43)	5.5(8)					
O(43)	7.8(7)					

TEMP=-2(PI)**2(U11*H*H*ASTAR*ASTAR+---+2*U12*H*K*ASTAR*BSTAR+---)

THE UIJ VALUES HAVE BEEN MULTIPLIED BY 100.

Table S.26. Structure Factors for $\text{Os}_4(\text{CO})_{13}\text{PMe}_4$

COLUMNS ARE 10FD,10FC, 10SIG

L	KFD	FC	SIG	L	KFD	FC	SIG	L	KFD	FC	SIG	L	KFD	FC	SIG
10	1911	1865	45	4	630	620	39	10	1069	1038	41	11	1640	1597	43
3	1274	1217	31	6	831	838	32	5	1051	1085	35	11	1692	1742	39
4	1077	1061	31	12	1070	1087	36	7	786	833	38	14	1046	903	57
7	1838	1835	43	14	141	1	42	4	473	534	55	16	1363	1243	64
9	999	1022	36	1	1820	1841	42	9	657	739	54	16	1363	1243	64
10	1129	1058	34	2	571	556	45	10	1069	1038	41	1	677	727	39
11	649	754	64	3	850	879	31	11	1640	1597	43	1	677	727	39
4	1728	1680	40	5	1101	1139	26	12	1261	1137	47	2	1889	1739	36
6	1515	1495	37	7	1667	1632	39	13	1041	975	64	3	836	907	30
7	620	654	52	8	392	386	70	13	1041	975	64	3	836	907	30
8	1248	1215	33	11	1527	1515	38	2	1131	1130	29	8	2075	2081	49
9	775	760	47	12	763	803	55	3	850	850	32	9	1165	1112	37
10	1180	1080	36	13	1209	1099	43	4	531	539	49	10	2652	2673	57
2	2250	2272	43	7	692	702	44	5	526	517	53	11	1894	1850	53
4	1030	890	29	11	821	795	54	6	609	617	58	12	2289	2145	59
6	1470	1508	40	13	760	672	75	8	486	691	59	13	809	932	88
8	1229	1215	27	14	1216	1899	47	10	1854	1816	56	12	1640	1672	40
10	1283	1221	31	2	1629	1569	38	12	2116	1899	47	2	1640	1672	40
12	2541	2505	50	6	1936	1996	47	1	1129	1172	36	3	611	559	41
3	514	446	50	9	644	646	67	2	656	673	42	4	513	599	52
4	882	926	33	10	684	638	73	5	1969	2016	46	7	905	945	47
5	555	581	47	12	1295	1186	59	6	854	800	56	9	995	991	63
6	880	861	35	4	1429	1429	44	7	1129	1172	36	10	2013	1998	60
7	538	568	53	3	484	370	55	8	1295	1186	59	11	750	603	99
8	842	832	35	5	459	387	61	9	1129	1172	36	12	1970	1773	54
10	1025	1033	37	5	450	512	74	10	974	744	113	1	796	873	44
11	551	516	64	11	1204	1047	79	2	973	935	33	1	796	873	44
12	1558	1505	37	2	1423	1347	33	4	1468	1373	60	2	1795	1830	41
1	1485	1404	33	5	1135	1200	61	5	1084	984	96	3	1776	1790	40
2	703	605	41	7	1495	1439	71	6	1146	1036	113	4	1372	1349	34
3	988	930	31	7	1495	1439	71	7	131	121	108	5	2014	1946	53
5	636	651	44	13	0	0	49	8	893	880	49	7	1558	1377	57
6	1460	1471	32	4	1020	1056	26	1	1162	1124	30	8	1306	1198	78
7	1496	1485	34	4	1213	1217	29	3	818	827	47	9	1479	1458	44
8	1672	1677	43	6	2690	2899	36	6	1228	1183	84	10	1905	1604	74
11	970	913	47	8	1181	1210	26	12	1780	1744	58	11	1675	1581	42
2	766	810	41	10	706	720	41	13	690	749	99	12	1732	1680	47
4	721	799	42	12	922	843	40	14	920	1011	74	14	796	809	108
6	947	977	35	1	137	1	31	4	3187	3301	31	1	1525	1625	37
8	947	1004	44	2	1099	1164	34	6	3227	3415	32	2	508	398	52
9	806	743	54	4	1078	1062	25	8	3227	3415	32	5	3035	2119	107
11	861	919	64	5	442	486	52	10	526	556	55	7	1667	1647	103
3	1017	930	33	6	1694	1747	41	14	2097	2011	45	6	1667	1647	103
				6	1694	1747	41	16	2763	2712	70	1	983	917	35
				10	504	653	67	1	12	1	1	2	812	827	36
				11	1165	1173	36	2	581	605	39	3	668	640	49

COLUMNS ARE 10FD,10FC, 10SIG

L	KFO	FC	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG	
13	843	782	74	5692	5538	26	2	5692	5538	26	2	5692	5538	26	2	5692	5538	26	
2	1566	1622	36	5408	5047	46	4	5408	5047	46	4	5408	5047	46	4	5408	5047	46	
3	1242	1267	27	2408	2177	60	10	2011	2049	51	15	951	989	45	4	480	512	39	
4	1492	1492	37	3220	3020	68	11	1546	1559	43	16	2065	2145	53	5	1442	1493	36	
5	1838	1869	41	1286	1134	63	13	1582	1511	47	16	2065	2145	53	6	843	852	29	
7	1394	1384	30	1425	1361	42	14	831	765	88	1	1061	973	25	12	619	596	80	
1	2029	2069	38	1541	1680	52	1	988	1000	28	2	2496	2220	67	13	620	301	95	
2	603	706	40	1102	1194	40	2	555	471	39	3	1180	1136	106	1	3285	3342	30	
3	2908	2928	34	12	3316	3679	51	3	1685	713	38	4	832	851	58	3	3768	3909	30
5	2195	2235	39	13	2969	3317	53	5	1208	1278	32	14	598	711	66	5	2225	2277	37
6	497	371	53	14	3011	3269	52	6	891	882	32	16	791	873	52	6	1175	1171	26
8	1010	962	36	15	1509	1606	34	10	974	989	42	1	1166	1244	27	8	1109	1160	30
9	785	757	49	16	1465	1553	35	10	974	989	42	1	1166	1244	27	11	2168	2196	54
10	807	815	53	17	686	571	62	1	2380	2338	35	1	5915	6349	23	13	2916	2903	67
11	827	765	55	1	277	299	48	1	1336	1490	36	3	1516	1433	35	1	979	1012	27
13	2260	2218	65	2	277	299	48	3	3212	3222	34	4	5290	5589	35	1	979	1012	27
1	955	930	28	3	637	546	53	4	1159	1123	28	5	2040	1977	50	2	1038	998	26
3	1284	1343	31	4	2253	2273	54	5	2198	2246	39	6	1567	1338	39	3	673	667	36
4	636	623	41	9	932	851	51	7	732	711	41	7	2531	2427	55	4	1168	1171	33
5	542	475	47	11	1245	1460	41	8	930	914	36	9	2021	1992	53	6	887	847	31
8	818	842	41	12	545	565	77	11	1530	1531	41	10	2108	2072	49	10	701	770	50
10	1462	1480	33	1	530	524	28	12	1120	1084	50	11	967	1137	50	10	634	605	59
11	1088	1037	45	2	3610	3698	25	12	1120	1084	50	12	4191	4592	50	11	1066	1007	42
2	979	970	31	3	728	682	27	1	970	1001	30	13	804	730	56	13	804	730	56
4	1148	1124	28	4	3507	3731	33	5	566	490	49	14	3151	3480	52	14	3151	3480	52
5	1240	1214	34	5	1441	1421	36	6	618	742	54	16	652	831	64	2	1519	1449	40
7	1477	1540	45	6	1973	2024	46	8	618	742	54	17	759	845	55	3	1299	1290	25
8	1002	922	36	7	4782	4816	46	9	1040	1062	39	1	1000	921	25	4	644	655	41
9	1249	1258	35	8	1548	1481	38	1	654	631	44	2	1308	1327	29	5	1883	1913	44
2	1193	1280	25	9	3873	3842	60	2	566	490	49	3	1357	1321	33	6	868	882	35
4	1817	1817	24	10	1760	1723	46	5	1035	1062	35	5	471	409	45	7	1959	1910	46
6	5429	5361	26	11	934	944	69	2	2441	2417	18	7	1424	1396	39	8	1197	1181	31
8	7670	7453	35	12	2345	2421	57	4	442	370	30	8	938	892	44	8	1197	1181	31
10	4415	4304	45	14	1719	1883	48	6	1625	1615	35	9	1006	882	49	9	2476	2454	55
16	1587	1584	38	16	847	1024	55	8	1729	1578	38	10	1594	1562	41	10	2014	2032	58
1	1256	1258	25	1	635	666	26	10	1047	894	46	11	694	625	90	12	2257	2171	46
2	567	585	20	2	558	438	30	12	1237	1088	52	13	716	773	70	13	919	825	60
3	2839	2739	22	3	1094	1152	26	14	1256	1281	44	15	537	539	82	14	1297	1319	43
4	899	899	28	4	1094	1152	26	1	4070	4002	17	1	843	887	21	4	602	551	48
5	720	802	31	5	1054	1010	38	2	2576	2476	20	4	1395	1474	33	2	1846	1716	17
6	1648	1552	42	6	793	862	56	3	6065	6008	22	5	2043	2187	34	6	6099	5831	30
7	977	929	38	7	1050	967	52	4	4991	4703	28	6	3321	3340	34	8	4492	6102	42
8	1399	1222	36	8	1076	1075	54	6	4925	4452	28	7	3898	4086	38	10	2089	2030	52
10	1082	953	56	9	2982	3062	29	7	4243	3918	48	8	3605	3541	43	14	620	707	68
12	794	754	62	10	1076	1075	54	8	6029	5782	52	9	3560	3572	48	16	1930	2180	52
16	717	701	57	11	2041	2069	38	9	1496	1424	58	10	1676	1672	39	1	1149	1107	23
				1	2982	3062	29	10	3649	3681	54	11	808	881	67	3	1199	1078	26
				3	2684	2785	31	11	2041	2069	38	12	681	771	82	10	485	563	75
				5	1671	1774	38	12	681	771	82	15	681	771	82	1	2385	2451	28

COLUMNS ARE 10FD,10FC, 10SIG

L	KFD	FC	SIG	L	KFD	FC	SIG	L	KFD	FC	SIG
0	11, 3, L	27	6	1285	1153	45	0	1568	1581	40	0
0	2479 2538	29	1	1412	1476	40	1	1298	1331	21	13, 0, L
1	904 941	41	1	1169	1212	34	4	1697	1674	40	4
2	1987 2088	54	5	1382	1361	36	5	13, 1, L			
3	497 384	43	6	1133	1100	44	0	1187	1229	20	13, 1, L
4	1785 1720	54	0	1928	1950	29	2	995	1024	34	2
5	615 529	35	1	552	606	50	4	780	731	47	4
6	1276 1341	29	2	1952	2004	44	0	13, 2, L			
0	1287 1291	35	3	775	777	41	0	1205	1246	20	0
1	1356 1417	32	4	1658	1671	41	1	1342	1359	33	1
2	839 804	37	5	771	799	50	4	526	461	66	4
5	1485 1473	29	0	12, 3, L			0	13, 3, L			
11, 5, L			0	12, 3, L			0	972	985	24	0
0	889 916	35	2	2492	2630	28	2	1006	1060	34	2
1	1382 1347	63	4	1089	1153	29	0	13, 4, L			
2	420 530	39	0	913	850	38	0	794	755	30	0
3	1366 1384	37	1	12, 4, L			0	13, 5, L			
4	518 564	37	0	1455	1481	27	1	13, 5, L			
5	1024 1024	23	1	883	834	32	1	767	748	41	1
11, 6, L			2	962	968	31	0	14, 1, L			
0	1015 994	56	3	644	665	49	0	696	685	30	0
11, 6, L			4	805	759	42	1	627	637	47	1
1	487 584	38	0	12, 5, L			2	14, 2, L			
11, 7, L			0	730	749	36	0	623	611	50	2
1	1507 1554	25	1	573	615	47	0	14, 3, L			
12, 0, L			3	698	729	47	0	1389	1367	25	0
0	1490 1472	35	0	12, 6, L			0	15, 0, L			
2	1600 1735	35	0	564	537	47	0	1268	1299	22	0
4	1566 1516	35									

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218. Without Extinction

	kF_o	F_c	$\omega\Delta^2$
1,0,2	656	779	88
2,0,0	766	944	135

With Extinction

1,0,2	790	779	0.48
2,0,0	952	944	0.16

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220. These four reflections were:

	kF_o	F_c
2,0,0	710	987
-1,1,1	702	757
-2,0,2	818	835
-4,0,2	867	1015