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TO MY MOTHER

THE UNIVERSITY OF ALBERTA

SILICON, GERMANIUM AND TIN DERIVATIVES OF RUTHENIUM AND OSMIUM CARBONYLS

by

ROLAND KENNETH POMEROY

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF

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DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled

"SILICON, GERMANIUM AND TIN DERIVATIVES
OF RUTHENIUM AND OSMIUM CARBONYLS"

submitted by ROLAND KENNETH POMEROY in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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November 29, 1971
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ABSTRACT

The reaction of dodecacarbonyltriruthenium, $Ru_3(CO)_{12}$, with group IV tetrahalides has been studied. Several types of compounds were prepared depending on the conditions and tetrahalide employed e.g., $Ru_3(CO)_{12}SnCl_4$, $[Ru(CO)_4(SiCl_3)]_2$, $Ru(CO)_4I_2$, $[Ru(CO)_3Cl_2]_2$, $Ru_2(CO)_5MX_6$ and $Ru(CO)_4(MX_3)_2$; (M = Si, Ge or Sn; X = halogen). The $Ru_2(CO)_5MX_6$ derivatives are rare examples of compounds containing three halogen bridges. In contrast to the iron analogues, the $Ru(CO)_4(MX_3)_2$ compounds appeared more stable as the *trans*-isomers consistent with the view that the MX_3 group is as good a π-acceptor as CO, when bonded to ruthenium. The factors affecting the relative proportion of the *cis*-and *trans*-isomers were investigated by the synthesis of a number of silyl derivatives of both ruthenium and osmium.

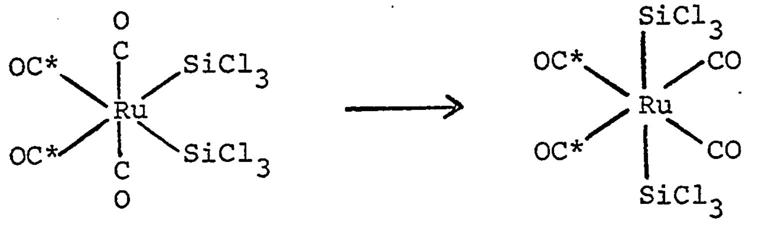
The exchange of ^{13}CO with *cis*-$Ru(CO)_4(SiCl_3)_2$ was studied near room temperature. It was shown that the substitution was first-order dissociative and that only the two CO groups *trans* to the $SiCl_3$ groups were labile. The complete stereospecificity of this exchange makes it unique in carbonyl chemistry at the present time. That the first labelled CO remained in the equatorial position upon coordination of the second ^{13}CO establishes the stereochemical rigidity of the five-coordinative intermediate. The *trans*-isomer did not exchange with ^{13}CO under similar conditions; however, upon irradiation with ultraviolet light it also

gave *cis*-$Ru(CO)_2(^{13}CO)_2(SiCl_3)_2$ (1) labelled in the equatorial position.

The rate of isomerization of *cis*-$Ru(CO)_4(SiCl_3)_2$ to the corresponding *trans*-form, in the range 70-100°, was studied. Activation parameters $\Delta H^{\ddagger} = 24.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -7$ eu were found. The latter result is consistent with a non-dissociative process.

The nmr spectrum of *cis*-and *trans*-$Os(CO)_4(SiMe_3)_2$ was examined. The two signals assignable to the *cis*-and *trans*-isomers collapsed to a single peak at temperatures above 50°. Detailed analysis of the spectra gave $\Delta H^{\ddagger} = 17.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = 1.6$ eu for the process. Under the same conditions, $Os(CO)_4(SiMe_3)_2$ did not exchange with ^{13}CO. The evidence appears to indicate that this is a rare example of a stereochemically, non-rigid octahedral molecule.

In order to elucidate the mechanism, the isomerization of 1 was undertaken. The initial product was identified as 2.



1 **2**

The stereochemistry of **2** is consistent with a three-fold twist and not with a migration or two-fold twist mechanism. This is the first case in which evidence for such a three-fold or Bailar twist has been presented for a non-chelated, octahedral system.

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November 29, 1971

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CHAPTER 1

INTRODUCTION

The synthesis and chemistry of compounds containing covalent metal-metal bonds has burgeoned at a rate parallel to that of all scientific knowledge. In 1965, in the particular area of bonds between two dissimilar metals there were 'perhaps only a few dozen' and the subject could be dismissed in a few lines.[1] In 1968 a review [2] listed over four hundred and fifty compounds which contained a group IV metal bonded to a transition metal. By 1970, a further three hundred and sixty had been prepared.[3] In light of these and other reviews [4,5] it is unnecessary to summarize the whole field of organometallic compounds containing metal-metal bonds. Instead only two areas, which are particularly relevant to the work presented in this thesis, will be covered.

The first section of this Chapter will concern itself with group IV derivatives of the iron triad: iron, ruthenium and osmium. Group IV shall mean silicon, germanium, tin and lead. It is well known that the first period member of a chemical group is best considered apart from its heavier congeners.[1] This is true for the organometallic chemistry of carbon - very few analogues exist between it and the other elements of group IV. Silicon on the other hand is, in this field, conveniently considered as a metal: its transition metal derivatives are very similar to those of germanium and tin. Also included in this section is a part on the parent carbonyls. This is covered not only for its relevance to the thesis as a whole but to illustrate some of the interesting structural problems encountered in this field.

In many ways this first section will be found to be representative of the whole topic of organometallic compounds containing covalent metal-metal bonds. Most synthetic methods for preparing these compounds are to be found there. Diverse structural types are also encountered amongst these compounds.

The second section of the Chapter will review the physical studies on the nature of the group IV-transition metal bond. As will be seen this is a subject of some controversy.

SECTION I

The Effective Atomic Number Rule

Before discussing the parent carbonyls, mention should be made of an important though somewhat empirical rule known as the effective atomic number (EAN) rule.[6,7] A carbon monoxide group is regarded as a source of two valence electrons, so that in the simple 'binary' carbonyls M'(CO)y with one metallic atom in the molecule the EAN of the metal (atomic number +2y) is always the atomic number of the next noble gas, e.g., 36 in $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$, and 86 in $W(CO)_6$ and $Os(CO)_5$. Not only do the binary carbonyls obey this rule but also the vast majority of organometallic compounds. It has been very useful in preparative work in both accounting for and even predicting the stoichiometries of complexes. This rule will be illustrated from time to time in this review; however it should not be forgotten that it is not infallible and several notable exceptions exist e.g., $V(CO)_6$, $Rh_6(CO)_{16}$ and $(C_5H_5)_2Ni$.

The Pentacarbonyls, $Fe(CO)_5$, $Ru(CO)_5$ and $Os(CO)_5$

Iron pentacarbonyl, the second carbonyl to be discovered, was first prepared in 1891.[8] The first reports of the ruthenium [9] and osmium [10] analogues appeared in 1936 and 1943 respectively. However it was not until 1967 that these last two compounds were reinvestigated and more fully characterized.[11]

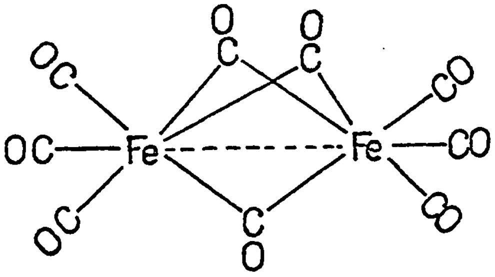
The structure of $Fe(CO)_5$ has been firmly established as trigonal bipyramidal. There has been considerable discussion as to whether or not there are two kinds of Fe-C bond distance in $Fe(CO)_5$. The most recent electron diffraction study [7] confirms that in the gas phase, although there is no distortion from D_{3h} symmetry, Fe-C (equatorial) [1.8331 ± 0.0024 Å] is somewhat longer than Fe-C (axial) [1.8062 ± 0.0031 Å]. It should be mentioned in passing that the X-ray crystallographic study [12] of $Fe(CO)_5$ establishes that the bonding is Fe-C-O rather than Fe-O-C. The question of whether in metal carbonyls the structures involve M-(OC)y linkages rather than M-(CO)y was sometimes raised.

From their infrared spectra the pentacarbonyls of ruthenium and osmium very probably have trigonal bipyramidal structures also.[11]

All three pentacarbonyls are volatile liquids. They decompose when heated or irradiated to give polynuclear carbonyls.

The Enneacarbonyls $Fe_2(CO)_9$, $Ru_2(CO)_9$ and $Os_2(CO)_9$

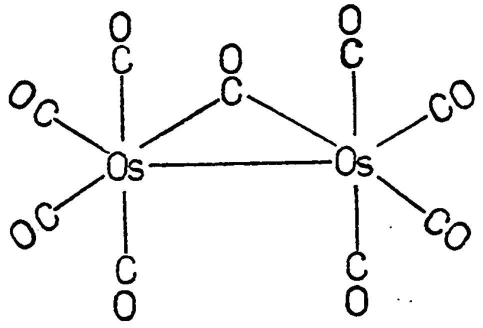
Enneacarbonyldiiron like $Fe(CO)_5$ has been known for decades whereas the enneacarbonyls of ruthenium and osmium have only been reported in the last year. The structure of enneacarbonyldiiron (1.1) can be described in terms of two octahedra sharing a common face formed by the carbon atoms of the bridging carbonyl groups.



1.1

The insolubility of this compound is somewhat of an enigma and prevents a study of the infrared spectrum in solution. It is also surprising that the carbonyl sublimes so much less readily than does octacarbonyldicobalt. Nevertheless, the molecular structure in the crystal has been definitely established.[13] It is customarily assumed that each terminal CO group contributes two electrons to the iron atom to which it is attached, and that each bridging molecule contributes one electron to each of the metal atoms. Hence each iron atom shares nine ligand electrons which together with its own eight electrons gives seventeen in all. Since the molecule is diamagnetic it is assumed that the odd electrons become paired in a metal-metal bond. This is consistent with the observed iron-iron distance (2.46 Å) which is at the lower range of metal-metal distances found in other iron complexes in which such bonding has been invoked.

The ruthenium and osmium analogues of $Fe_2(CO)_9$ have been elusive. Substances formulated initially as $Ru_2(CO)_9$ [9] and $Os_2(CO)_9$ [10] were later shown by X-ray crystallography to be $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ [14]. However, very recently Moss and Graham have found [15] that $Os(CO)_5$ upon ultraviolet irradiation at -40° gives $Os_2(CO)_9$. Unlike $Fe_2(CO)_9$ this compound is soluble in hydrocarbon solvents. The infrared spectrum appeared to favour the structure given in 1.2 as that which $Os_2(CO)_9$ adopts in solution.

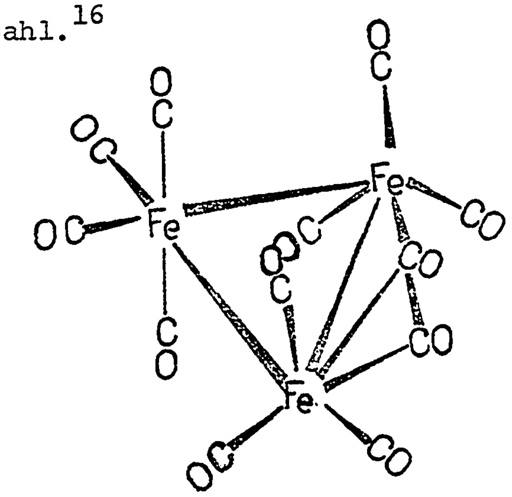


1.2

Although spectroscopic evidence was obtained for $Ru_2(CO)_9$ it was too unstable to be isolated.

The Dodecarbonyls $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$

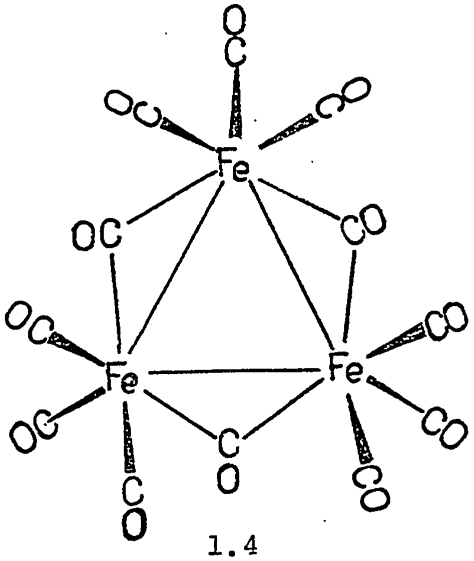
The question of the structure of $Fe_3(CO)_{12}$ in both the solid state and in solution has been a subject of controversy for a number of years. The solid state structure, which was complicated by disorder, has been finally solved by Wei and Dahl.[16]



1.3

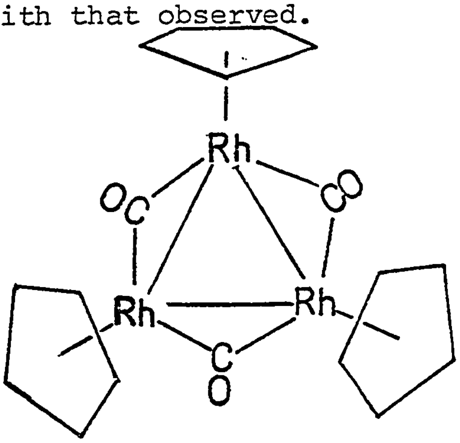
The structure (1.3) may be regarded as being derived from that of $Fe_2(CO)_9$ by replacing one of the bridging CO groups by an $Fe(CO)_4$ group. The latter is bonded by two iron-iron bonds 2.67 Å in length. The other metal-metal bond is 2.56 Å long, and the two bridging carbonyl groups are somewhat unsymmetrically located.

The ir spectrum of $Fe_3(CO)_{12}$ in solution shows bands in the bridging carbonyl region which are much weaker than would be expected if the solid state structure were maintained in solution. Moreover, the two observed terminal carbonyl bands are far fewer than the nine expected. It has been suggested,[16] that the predominant form in solution is that shown in 1.4.

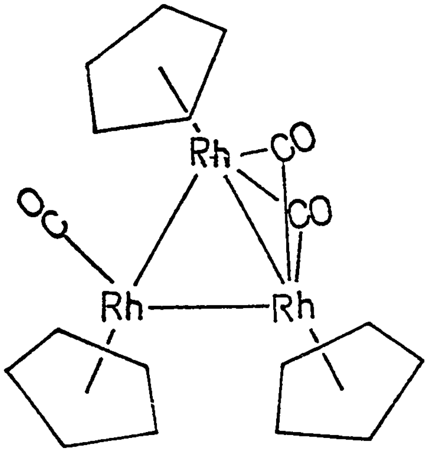


1.4

This suggestion was based on the fact that the related $[CpRh(CO)]_3$ shows bridged and partially bridged structures in the solid state - as established by X-ray crystallography (1.5 and 1.6). Such a structure in solution would greatly reduce the number of ir active terminal bands, in agreement with that observed.

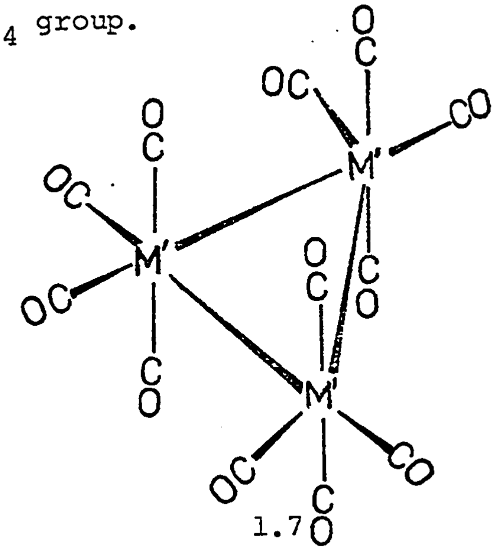


1.5



1.6

The structures of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ are much less complicated. These molecules have been shown by X-ray crystallography [14,17] to have the symmetric D_{3h} structure shown in 1.7. This structure could be thought of as replacing the CO group in the structure suggested for $Os_2(CO)_9$ by a $M'(CO)_4$ group.

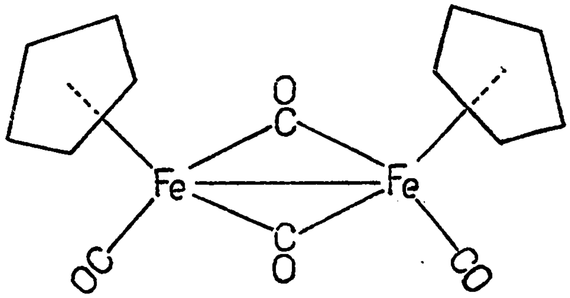


1.7

The infrared spectra of these compounds are consistent with view that the solid state structures are maintained in solution.[18]

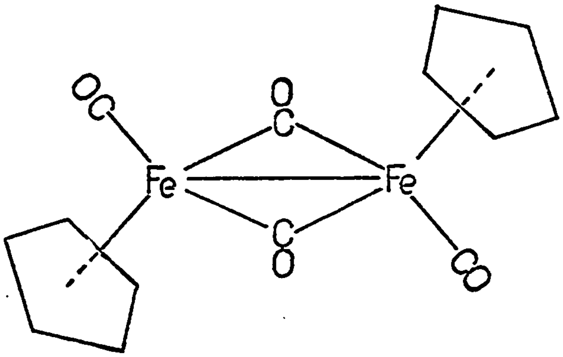
The Cyclopentadienyl Metal Dicarbonyl Dimers – $[(\pi\text{-}C_5H_5)M'(CO)_2]_2$ (M′= Fe, Ru or Os).

The cyclopentadienyl metal dicarbonyl dimers, although not strictly carbonyls, will be discussed since they are common starting materials and also show structural features of interest. The configuration shown in 1.8 was established [19] for $[C_5H_5Fe(CO)_2]_2$ as obtained by recrystallization from ligroin.

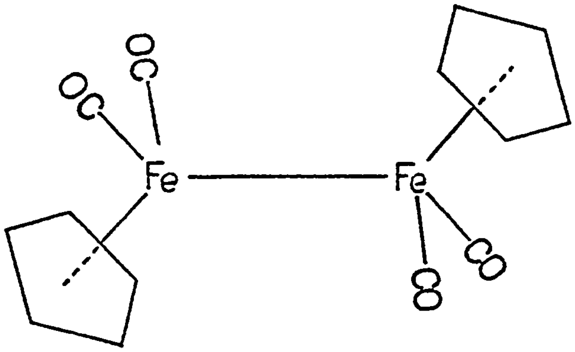


1.8

The infrared spectrum of the solution indicated that more than one isomer was present. It was originally suggested [20] that the *cis*-structure (as found for the solid) was in equilibrium with the unbridged form (1.10). However, it is now believed that the *cis*-form is in equilibrium with the *trans*-form (1.9) presumably with the unbridged form as an intermediate.[21]



1.9



1.10

The *trans*-form has in fact been isolated, by recrystallizing solutions of the compound at -78°, and its structure confirmed by X-ray analysis.[22] The ruthenium analogue behaves similarly [23] although the osmium compound is thought to have the unbridged structure both in solution and the solid state.[20]

GROUP IV DERIVATIVES OF THE IRON TRIAD

Some General Comments.

These compounds vary from the air sensitive volatile liquid $(OC)_4Fe(SiCl_3)H$ [24] to the thermally stable crystalline solids such as $(OC)_4Ru(SnPh_3)_2$ (mpt. 180-182°).[25]

In general lead derivatives are far less common than those of the other group IV elements. This may be because the starting materials are thermally unstable e.g., $PbCl_4$ decomposes much above room temperature into $PbCl_2$ and Cl_2. Also there is the possibility that the products decompose more easily.

The process

$$M' - X + MX_2 \rightleftarrows M' - MX_3$$

M' = Fe, Ru or Os

M = Si, Ge, Sn or Pb

X = halogen

may be compared to

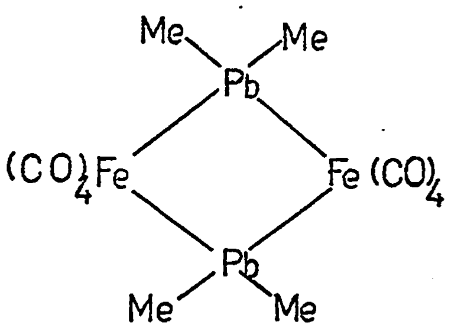
$$X_2 + MX_2 \rightleftarrows MX_4$$

This is known [1] to lie to the left for lead. It appears that the energy gained in formation of two more M-X bonds is not enough to compensate for the $M^{II} \rightarrow M^{IV}$ promotion energy. Of course, with silicon this equilibrium lies completely in the opposite direction. This type of decomposition is known to take place in $(Ph_3P)_2PtCl(Ph_3Pb)^3$ i.e.

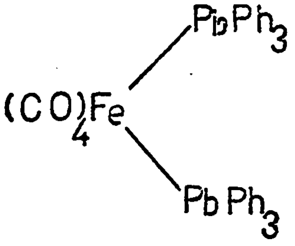
$$(Ph_3P)_2PtCl(Ph_3Pb) \rightarrow (Ph_3P)_2PtClPh + [Ph_2Pb]$$

Evidence concerning the loss of MX_2 from $M'-MX_3$ systems will be presented in this thesis.

It is interesting that although the lead derivatives are rare they played an important part in the history of the subject of covalent, metal-metal bonds. The first suggestion of the possibility of metal-metal bonding appears to have been made in 1947 by Hein and Heuser who postulated structures 1.11 and 1.12 for $[(OC)_4FePbMe_2]_2$ and $(OC)_4Fe(PbPh_3)_2$.[26]



1.11



1.12

As is general in the field of organometallic chemistry far more work has been carried out on iron than on the second and third row congeners. Because of their scarcity in nature, and the complicated methods needed for their extraction, ruthenium and osmium are expensive. Also, until the last five years, convenient methods of preparation of the carbonyls were not known. These aspects are reflected in the current prices of carbonyls (Table 1.1). Where analogous compounds of the iron group exist, however, it is usually found that the derivatives of ruthenium and osmium are, if anything, more stable than those of iron.

Compounds Where the Group IV Ligand is Monodentate

Mononuclear Derivatives.

Many compounds are known which have the stoichiometry $M'(CO)_4XX'$ (M' = Fe, Ru or Os), with $X(X')$ a one-electron donor. Note the $M'(CO)_4$ moiety, which may be considered as arising from either the removal of a CO group from $M'(CO)_5$ or from degradation of $M'_3(CO)_{12}$, is two electrons short of the noble gas configuration.

When $X(X')$ is a ligand where a group IV element is the donor atom it usually takes the form MR_3 where M = Si, Ge, Sn or Pb and R is an organic group or halogen. Compounds are known where $X = X' = MR_3$, where X and X' are different MR_3 type ligands and where $X = MR_3$ but X' is some other one-electron donor such as halide or hydride. Representative compounds in these categories are listed in Table 1.2.

There are two structural possibilities for an octahedral complex of formula $M'(CO)_4XX'$, namely *cis* and *trans*. These are shown in 1.13 and 1.14 respectively.

TABLE 1.1 [27]

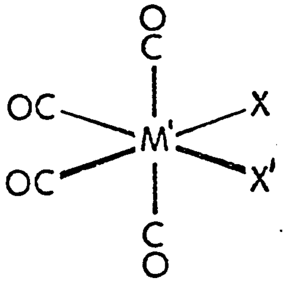
Cost of the Carbonyls of the Iron Triad

Compound	Quantity	Price
$Fe(CO)_5$	1 lb (454 g)	$15.00
$Fe_3(CO)_{12}$	100 g	$45.00
$Ru_3(CO)_{12}$	1 g	$20.00
$Os_3(CO)_{12}$	0.5 g	$75.00

TABLE 1.2

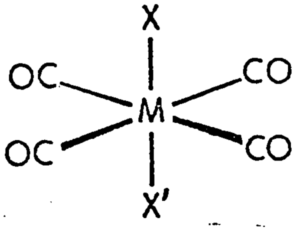
Examples of Compounds of the Type $M'(CO)_4(MR_3)_2$ and $M'(CO)_4(MR_3)X$

	Compound	Ref.
cis -	$(OC)_4Fe(SiCl_3)(H)$	24
cis -	$(OC)_4Fe(SnCl_3)(Cl)$	28
cis -	$(OC)_4Ru(SiMe_3)(I)$	29
cis -	$(OC)_4Os(SiMe_3)(Me)$	30
cis -	$(OC)_4Os(SiMe_3)(CF_2CF_2H)$	30
cis -	$(OC)_4Fe(SiH_3)_2$	31
trans -	$(OC)_4Fe(GeI_3)_2$	28
cis -	$(OC)_4Fe(SnPh_3)_2$	25
trans -	$(OC)_4Ru(SnPh_3)_2$	25
cis- and *trans*-	$(OC)_4Os(SiMe_3)_2$	30
cis- and *trans*-	$(OC)_4Os(SnMe_3)_2$	30
cis- and *trans*-	$(OC)_4Ru(SiMe_3)(SnMe_3)$	32
cis- and *trans*-	$(OC)_4Ru(SiMe_3)(GeBu_3)$	32



cis

1.13



trans

1.14

The *cis* – form is the geometry found for most complexes of this type although the occurrence of *trans* – $M'(CO)_4(MR_3)_2$ derivatives and studies related to them will form a substantial part of this thesis. In this review the *cis*-configuration will be assumed unless otherwise stated.

There are four main ways of preparing these compounds.

(1) Metathetical reactions involving a carbonyl metal anion and a group IV halide e.g.

$$2H_3SiI + Fe(CO)_4^{2-} \rightarrow (OC)_4Fe(SiH_3)_2 + 2I^- \qquad 31$$

$$2Me_3SnCl + Fe(CO)_4^{2-} \rightarrow (OC)_4Fe(SnMe_3)_2 + 2Cl^- \qquad 33$$

$$2Ph_3PbCl + Fe(CO)_4^{2-} \rightarrow (OC)_4Fe(PbPh_3)_2 + 2Cl^- \qquad 34$$

The corresponding osmium anion $Os(CO)_4^{2-}$ is as yet unknown, although $Ru(CO)_4^{2-}$ has been synthesized by reduction of $Ru_3(CO)_{12}$ with sodium in liquid ammonia.[25] Group IV derivatives have been prepared from this anion:

$Ru(CO)_4^{2-} + 2R_3SnCl \rightarrow (OC)_4Ru(SnR_3)_2$ 25

(2) Oxidative elimination reactions. This involves the ejection of a carbon monoxide ligand (usually) and raising of the formal oxidation number of the central atom from zero to two upon coordination of X and X' e.g.,

$Fe(CO)_5 + SnBr_4 \rightarrow (OC)_4Fe(SnBr_3)(Br) + CO$ 26

$Fe(CO)_5 + Cl_3SiH \xrightarrow{h\nu} (OC)_4Fe(SiCl_3)(H) + CO$ 24

A rare case where a ligand other than carbon monoxide is eliminated is the reaction:

$(Ph_3P)_2Fe(CO)_3 + SnCl_4 \rightarrow Ph_3P(OC)_3Fe(SnCl_3)(Cl) + Ph_3P$ 28

(3) Reactions involving transition metal hydrides.

$(OC)_4OsH_2 + SnCl_4 \rightarrow (OC)_4Os(SnCl_3)(H) + HCl$ 35

$2Ph_3PbOH + (OC)_4FeH_2 \rightarrow (OC)_4Fe(PbPh_3)_2 + 2H_2O$ 35

$(OC)_4Os(SiMe_3)(H) + Me_3SiH \rightarrow$ *cis*- and *trans*- $(OC)_4Os(SiMe_3)_2 + H_2$ 30

(4) Cleavage of transition metal-metal bonds.

$Os_3(CO)_{12} + 3Me_3SiH \rightarrow 3(OC)_4Os(SiMe_3)H$ 30

$Os_3(CO)_{12} + 6Me_3GeH \rightarrow$ 3 *cis*- and *trans*- $Os(CO)_4(GeMe_3)_2 + 3H_2$ 36

$Ru_3(CO)_{12} + 6R_3SnH \rightarrow 3(OC)_4Ru(SnMe_3)_2 + 3H_2$ 24

Other mononuclear compounds containing ligands besides CO are known, e.g. phosphine complexes:

$Ph_3PFe(CO)_4 + SnCl_4 \rightarrow (Ph_3P)Fe(CO)_3(SnCl_3)(Cl)$ 28

$(Ph_3P)_2Ru(CO)_3 + Me_3SiH \xrightarrow{h\nu} (Ph_3P)_2Ru(SiMe_3)_2(CO)_2$ 32

Also in this class are the cyclopentadienyl products which have the general formula $(C_5H_5)M'(CO)_2MR_3$ - the C_5H_5 group (Cp) acting as a five electron donor.

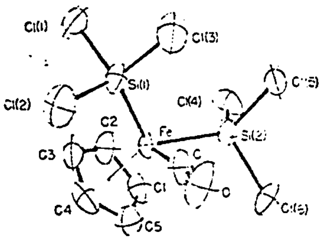
These can be prepared by methods analogous to the carbonyls:

$CpFe(CO)_2^- + Ph_3SnCl \rightarrow CpFe(CO)_2SnPh_3$ 33

$[CpFe(CO)_2]_2 + Cl_3SiH \rightarrow CpFe(CO)_2SiCl_3$ 38

$CpFe(CO)_2SiCl_3 + Cl_3SiH \rightarrow CpFe(CO)(SiCl_3)_2(H)$ 24

The last mentioned compound is a strong acid. Its structure has been determined [39] and is shown in Fig. 1.15. The hydrogen was not located but it is presumably *trans* to the carbon monoxide at the base of a square pyramid, in which the cyclopentadienyl ring forms the apex.



1.15

Other methods for preparing these cyclopentadienyl products are insertions between metal-halogen bonds:

$$CpRu(CO)_2Cl + SnCl_2 \rightarrow CpRu(CO)_2SnCl_3 \qquad 40$$

and metathetical reactions on compounds already containing the metal-metal bond:

$$CpFe(CO)_2(SiHMe_2) + CCl_4 \rightarrow CpFe(CO)_2(SiClMe_2) \qquad 41$$

$$CpFe(CO)_2SnCl_3 + SnBr_2 \rightarrow CpFe(CO)_2SnBr_3 \qquad 42$$

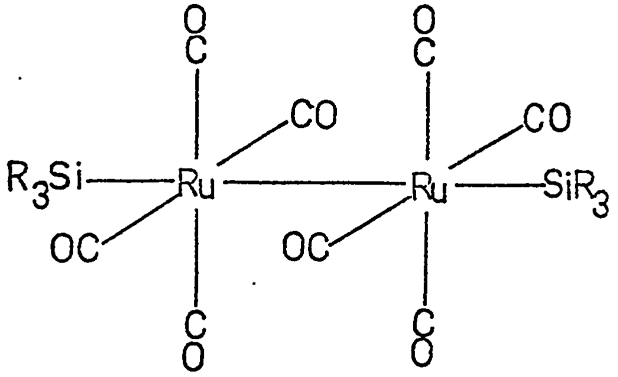
Polynuclear Compounds

Carbonyl compounds of the iron triad which contain homonuclear, transition metal-metal bonds have the general formula

$$X-[M'(CO)_4]_n-X'$$

It is found that the strength of these metal-metal bonds increases on going down the periodic table so that it might be expected that such derivatives will be more common for ruthenium and osmium. Compounds are known with n = 3 (X = Cl [43] or H [44]) and with n = 4 (X = H)[44], however, the only species known where X(X') is a M R_3 ligand has n = 2.

Reaction of R_3SiH with $Ru_3(CO)_{12}$ gives $[Ru(CO)_4SiR_3]_2$[32] which on the basis of its infrared spectrum was assigned an all *trans*-structure:



1.16

It was found that the methyl derivative could be cleaved, like $Mn_2(CO)_{10}$, to yield the anion $Me_3SiRu(CO)_4^-$. This product considerably expands the scope of Si-Ru chemistry. An example of its utility is given in the reaction:

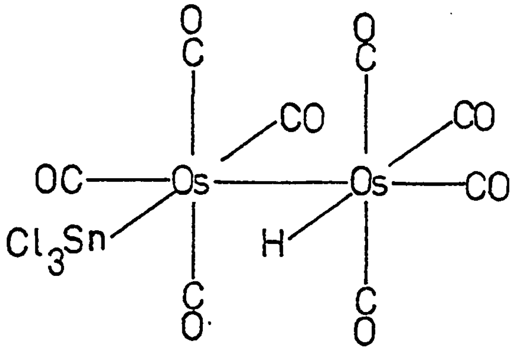
$$Me_3SiRu(CO)_4^- + Mn(CO)_5Br \rightarrow \textit{trans}\text{-}Me_3SiRu(CO)_4Mn(CO)_5 \qquad 32$$

This molecule contains a transition metal-metal bond between elements of two different periods.

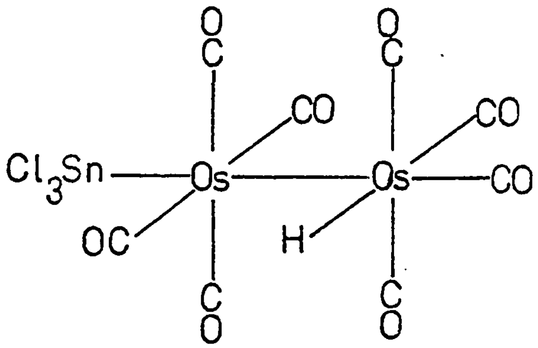
Although similar chemistry does not exist for iron, the derivative $[Fe(CO)_4SiCl_3]_2$ is known.[45] This was the unusual product from the reaction between $(OC)_4Fe(SiCl_3)(H)$ and tetrafluoroethylene. Unlike the ruthenium complex the infrared spectrum appeared to indicate that the Cl_3Si groups were *cis* to the Fe-Fe bond.

Reaction of $Os_2(CO)_8H_2$ with $SnCl_4$ gave $HOs_2(CO)_8SnCl_3$.[35]

Infrared and nmr studies could not distinguish between the structures 1.17 and 1.18



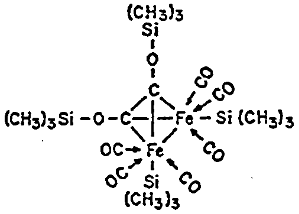
1.17



1.18

The compound [45] $Hg[Ru(CO)_4GeMe_3]_2$ has been prepared from $[Me_3GeRu(CO)_4^-]$; it is believed to contain a pentanuclear chain of metal atoms.

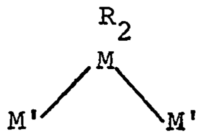
A compound having the empirical composition $[(CH_3)_3Si]_2Fe(CO)_4$ has been obtained by reaction of $(CH_3)_3SiI$ with $Na_2Fe(CO)_4$ in tetrahydrofuran.[47] However, it was shown that this complex was dimeric, the spectroscopic and chemical properties being consistent with structure 1.19.



1.19

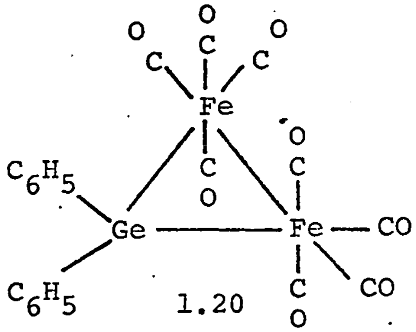
Compounds Where the Group IV Ligand is Bidentate

A group IV ligand can simultaneously act as a one electron donor to two transition metals forming a bridge:



Again R is usually an organic group or halogen.

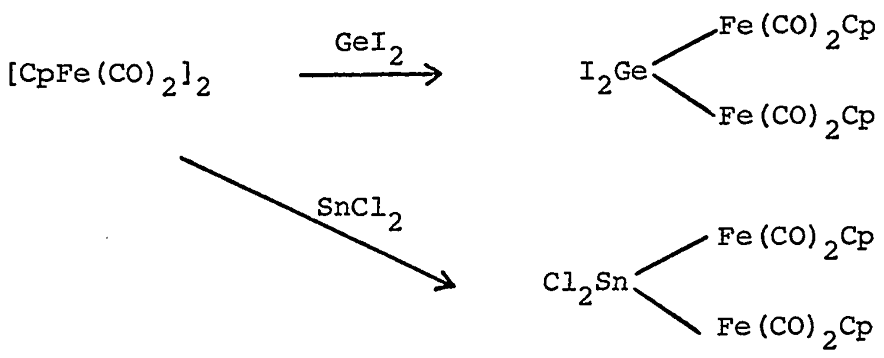
A single such bridge has been postulated in one of the products isolated in the reaction of Ph_2GeH_2 with $Fe_3(CO)_{12}$ [48]



1.20

This compound may be compared to the structure suggested for $Os_2(CO)_9$ with the Ph_2Ge moiety replacing the bridging CO group. Several other compounds exist where the analogy between a bridging R_2M and carbonyl group is apparent.

Single bridges of this type have been formed by the insertion of divalent halides of group IV between the Fe-Fe bond of $[CpFe(CO)_2]_2$ e.g.,



49

49

The number of compounds of this type has been greatly extended by replacing the halide with some other group e.g.,

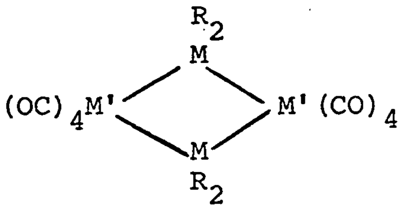
$$I_2Ge[Fe(CO)_2Cp]_2 + 2MeLi \rightarrow 2LiI + Me_2Ge[Fe(CO)_2Cp]_2 \qquad 49$$

$$Cl_2Sn[Fe(CO)_2Cp]_2 + NaBH_4 \rightarrow H_2Sn[Fe(CO)_2Cp]_2 \qquad 49$$

A further rather exotic example of this reaction is given below, it contains a tin atom bound to four transition metals.

$$[CpFe(CO)_2]_2SnCl_2 + [CpMo(CO)_3^-] \longrightarrow$$
$$[Cp(OC)_2Fe]_2Sn[Mo(CO)_3Cp]_2 \qquad 50$$

The most common case where a group IV element is bidentate are the doubly bridged compounds having the general formula:



These four membered metal rings arise in a variety of ways as shown below:

$Fe(CO)_4^{2-} + R_2MX_2 \rightarrow [(OC)_4FeMR_2]_2$ 5

(M = Ge or Sn) (X = halide, R = alkyl group)

$R_2Sn(C{\equiv}CR')_2 + Fe_3(CO)_{12} \xrightarrow{110^\circ} [(OC)_4FeSnR_2]_2$ 52

$R_2SnR''_2 + Fe(CO)_5 \rightarrow [(CO)_4FeSnR_2]_2$ 53

(R" = vinyl or phenyl).

$Fe(CO)_5 + Fe(CO)_4(GeX_3)_2 \xrightarrow{\Delta} [Fe(CO)_4GeX_2]_2$ 28

(X = Cl, Br, I)

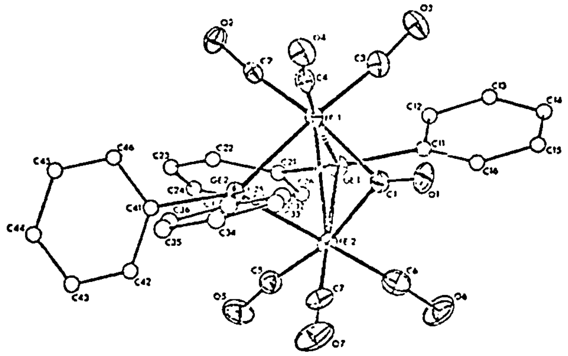
$R_2GeH_2 + Fe_3(CO)_{12} \rightarrow [Fe(CO)_4GeR_2]_2$ 48

$Cl_3SiH + Fe(CO)_5 \rightarrow [Fe(CO)_4SiCl_2]_2$ 38

Although the ruthenium analogues to $[Fe(CO)_4SnR_2]_2$ could not be prepared by the reaction R_2SnCl_2 with $Ru(CO)_4^{2-}$ they have been prepared by the rather peculiar path:

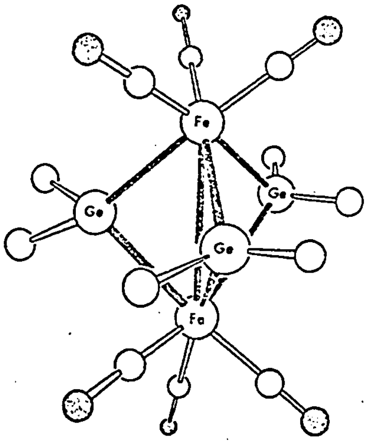
$[Me_3SiRu(CO)_4]^- + (CH_3)_2SnCl_2 \rightarrow [(CH_3)_2SnRu(CO)_4]_2$ 32

On heating $[Ph_2GeFe(CO)_4]_2$ a compound having the formula $[Ph_2Ge]_2Fe_2(CO)_7$ is isolated.[48] This has the structure shown (as established[54] by X-ray crystallography):



1.21

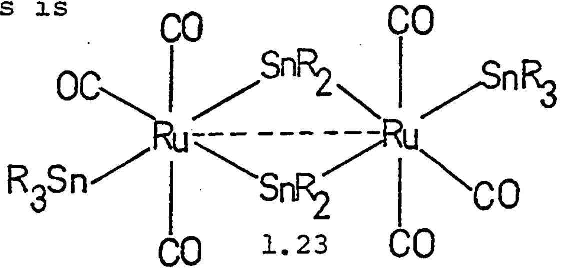
The similarity of this compound with $Fe_2(CO)_9$ is obvious. The molecule $[(CO)_3Fe]_2(GeMe_2)_3$ (1.22) which may be considered as replacing all three bridging CO groups with Me_2Ge groups is formed in the reaction of Me_2GeH_2 with $Fe_3(CO)_{12}$.[55]



1.22

The X-ray study [55] revealed extremely acute Fe-Ge-Fe bond angles (69.8° compared to the normal tetrahedral value of 109°). The Fe-Fe bond length of 2.744 Å was near the upper limit of measured iron-iron distances for such compounds, a fact that was explained as a consequence of the steric limits introduced by the three bridging germanium atoms. Ruthenium and osmium analogues of this compound have recently been prepared.[45]

Another complex containing a four membered ring of metal atoms is

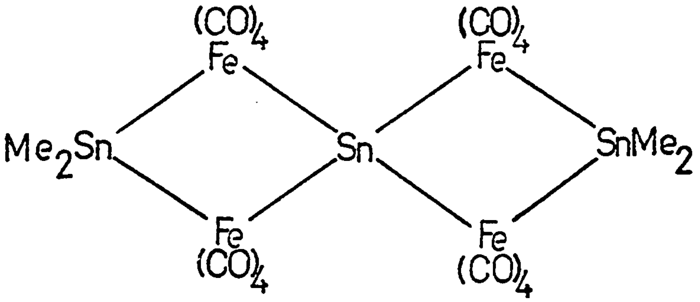


1.23

formed in low yields in the reaction between $Ru_3(CO)_{12}$ and R_3SnH (R=an organic group).[25] Although it was suggested that the ruthenium atoms attained the noble gas number of electrons by interaction via the d-orbitals of the bridging tin atoms, the X-ray structure [57] of the methyl derivative revealed a Ru-Ru distance of 3.12 Å which is not inconsistent with a direct Ru-Ru bond. The germanium analogue has recently been reported.[45]

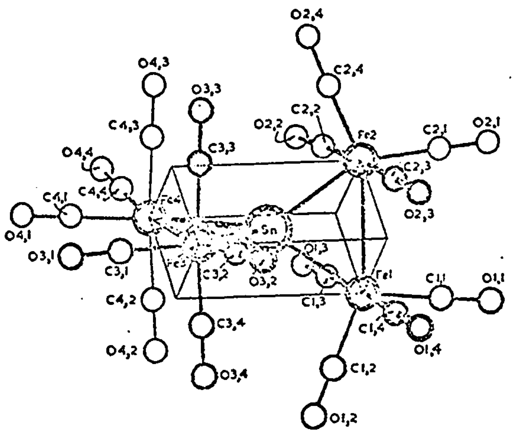
Compounds Where the Group IV Atom is Bound to More than Two Transition Metals

A compound which may be classified in both this and the previous section is



1.24

This is formed in low yield in the reaction of trimethyltin hydride with ironpentacarbonyl.[58] Perhaps more interesting is $Sn[Fe(CO)_4]_4$, formed in similar yield in the same reaction. A structural determination [59] revealed the following configuration:



1.25

Two different iron-iron bond lengths (4.65 and 2.87 Å) and two different Fe-Sn-Fe bond angles (133° and 69°) strongly suggested direct Fe-Fe bonds between pairs of iron atoms (as indicated in 1.25).

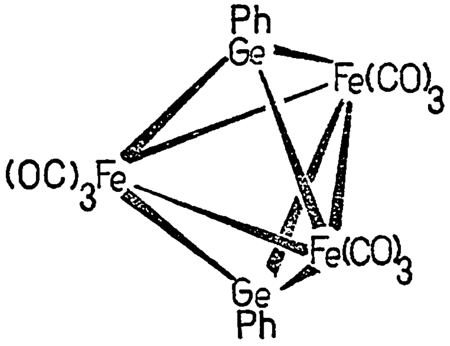
Other reactions producing a tin atom bonded to four iron atoms are:

$$SnCl_4 + 4Fe(CO)_3(NO)^- \rightarrow Sn[Fe(CO)_3(NO)]_4 + 4Cl^- \qquad 60$$

$$SnCl_4 + 4CpFe(CO)_2^- \rightarrow Sn[Fe(CO)_2Cp]_4 + 4Cl^- \qquad 61$$

The intermediates $ClSn[Fe(CO)_3(NO)]_3$ and $Cl_2Sn[Fe(CO)_2Cp]_2$ were isolated from the first and second of these reactions, respectively.

A cluster compound containing a germanium atom simultaneously bonded to three iron atoms has been synthesized from $PhGeH_3$ and $Fe(CO)_5$.[62] This is believed to have the geometry:

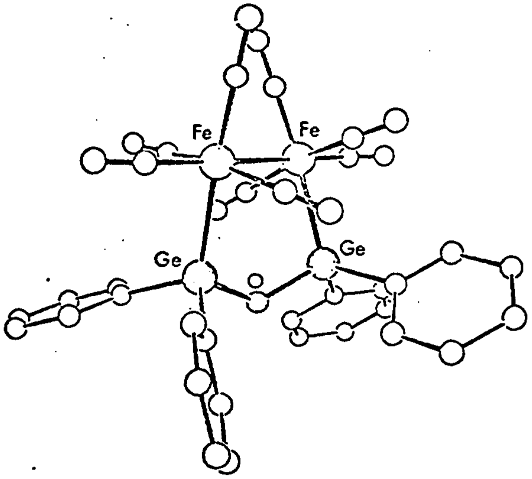


1.26

Rings Containing Both a Group IV Element and a Transition Metal

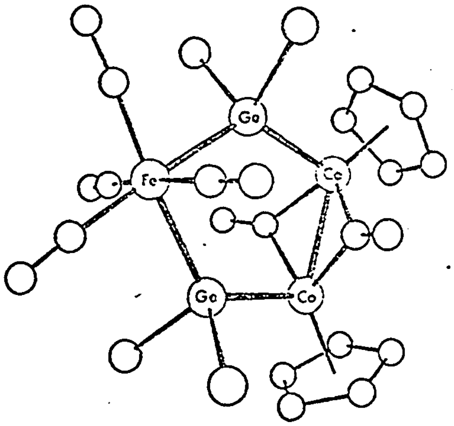
Besides the four membered rings mentioned earlier, there are a few compounds containing five or more atoms in which some or all of the constituents are either a group IV element or a member of the iron triad.

Although the structure of $[(OC)_3Fe]_2(GePh_2)_2CO$ has been confirmed by X-ray analysis [54] the solution infrared spectrum showed more terminal CO absorptions than would be expected for such a structure. It has now been shown that this is due to spontaneous decomposition to $[(OC)_4FeGePh_2]_2O$.[62] The structure of this compound has been determined, crystallographically, and has revealed a five membered ring [63]:



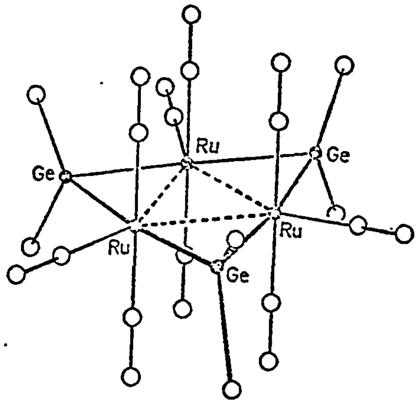
1.27

Reaction of $Cp(OC)Co(GeCl_3)_2$ with $Fe(CO)_5$ gave the somewhat unexpected, novel, metal-metal heterocycle $[CpCo(CO)]_2(GeCl_2)_2Fe(CO)_4$.[64] This was shown by X-ray diffraction to have the following structure:



1.28

Finally in this section it has been found that six membered rings are formed in the pyrolysis of $(Me_3Ge)_2M'(CO)_4$ (M' = Ru or Os).[46] A diffraction study of the ruthenium compound revealed the geometry:



1.29

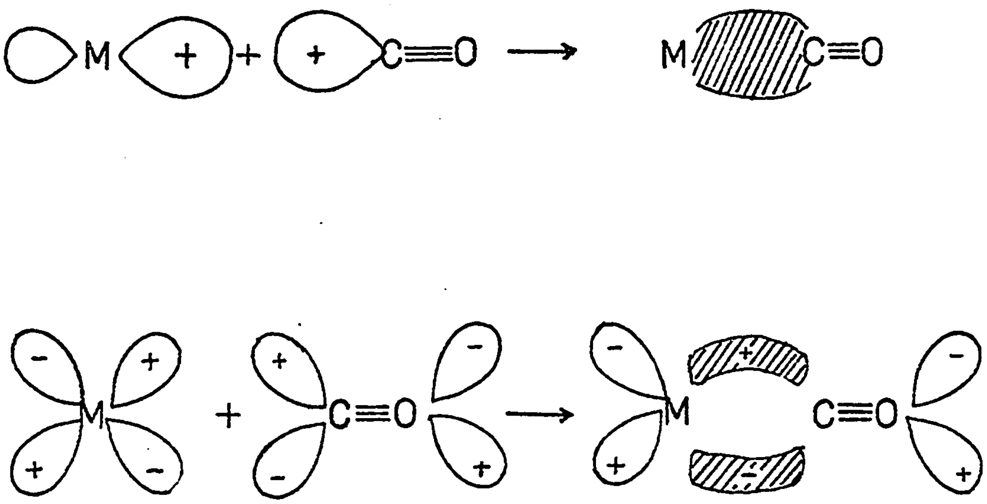
SECTION II

THE NATURE OF THE GROUP IV - TRANSITION METAL BOND

Before discussing the nature of the group IV-transition metal bond an outline of the current theory concerning the bonding between carbon monoxide and the transition metal is in order.[1,7]

The ability of the CO group to stabilize metal atoms in low-positive, zero, or low-negative oxidation states is believed to be due to a so called 'synergic' bonding effect. A metal-carbon σ bond is formed by overlap of a filled sp hybrid orbital of carbon and a vacant hybrid orbital of the metal, for example, dsp^3 of Fe in $Fe(CO)_5$. In addition, π-bonds are formed by overlap of filled d-orbitals of the metal with antibonding orbitals of the CO group. As a consequence, charge transfer in the σ bond is in the opposite direction to that in the π-bond, and the latter is considered to be crucial in serving to remove negative charge on the metal. This bonding situation is illustrated in 1.30.

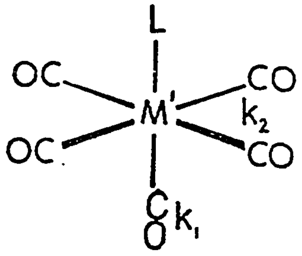
The bond between the group IV element and the transition metal is similarly thought to consist of a σ bond and a π-bond. The group IV element has empty d-orbitals which have the right symmetry and (possibly) the right energy for overlap with the filled d-orbitals on the central metal. This is also analogous to the formal σ donor, π-acceptor system assumed to operate in tertiary phosphine



1.30

and arsine complexes [1] (R_3Ge^- and R_3As are iso-electronic). A considerable amount of work has been carried out in order to evaluate the importance of the π-contribution to the metal-metal bond.

Graham [65] has made a detailed study of the carbonyl-stretching, force constants (k_1 and k_2) of derivatives of the type

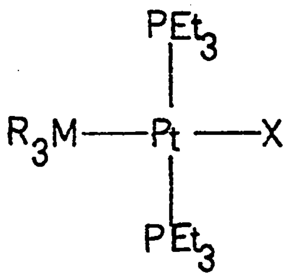


M' = Mn or Re

1.31

It is found that k_1 and k_2 do not change to the same extent on changing L. By making relatively simple assumptions about how the σ and π properties should affect the force constants it was possible to set up a chart where each X derivative was ranked according to its σ- and π-capability. The chart is shown in Fig. 1.1. It can be seen that the R_3M ligands have considerable π-acceptor character. Another important conclusion of this study was that the overall order of ligands did not change on going from Mn to Re.

Earlier infrared studies of the Pt-H [66] and Pt-Cl [67,68] stretch in derivatives



X = Cl or H
M = Si or Ge

1.32

concluded that the MR_3 group had a high *trans*-bond weakening effect due to a strong Pt-Si (or Pt-Ge) σ bond. The ^{19}F nmr of a closely related system [69] (1.33) showed that the $SnCl_3$ was a rather exceptional ligand in having strong π-acceptor but weak σ-character. Carbon monoxide is thought to have similar bonding properties.

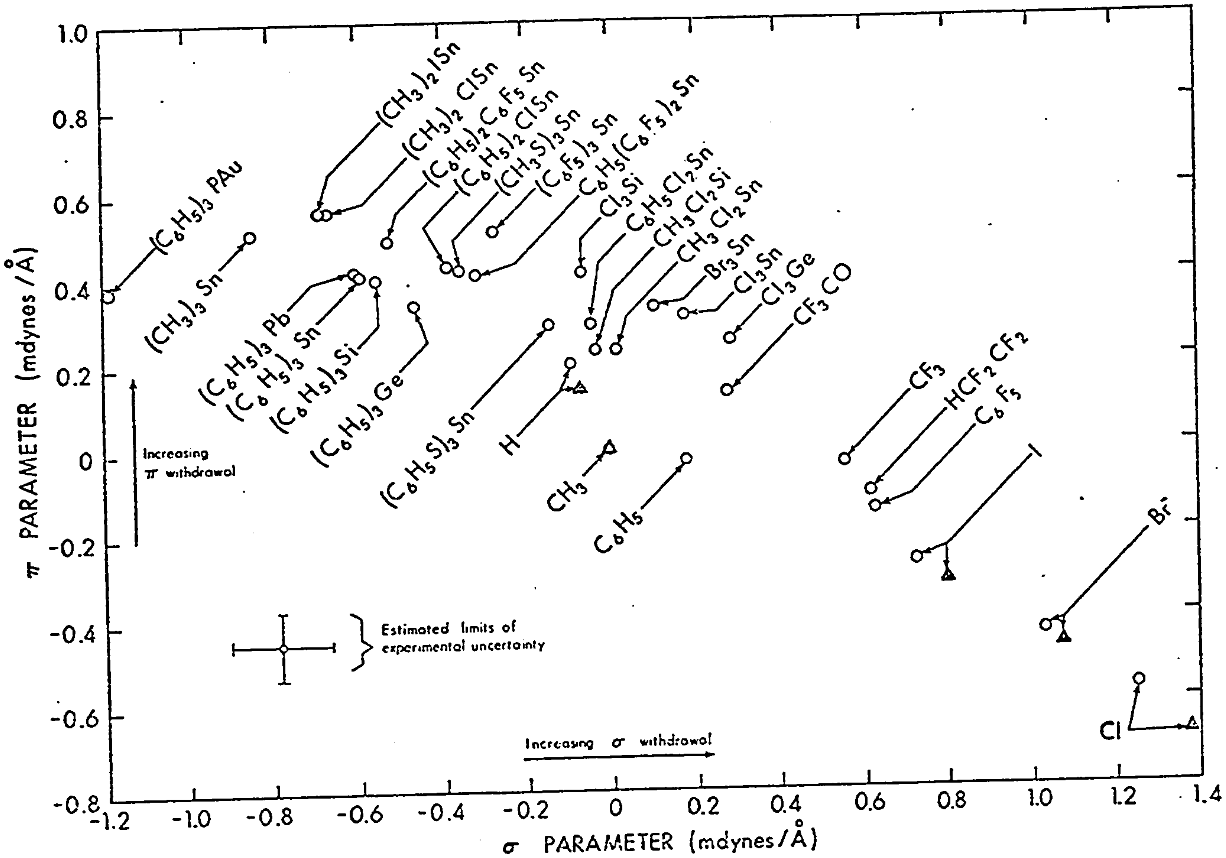
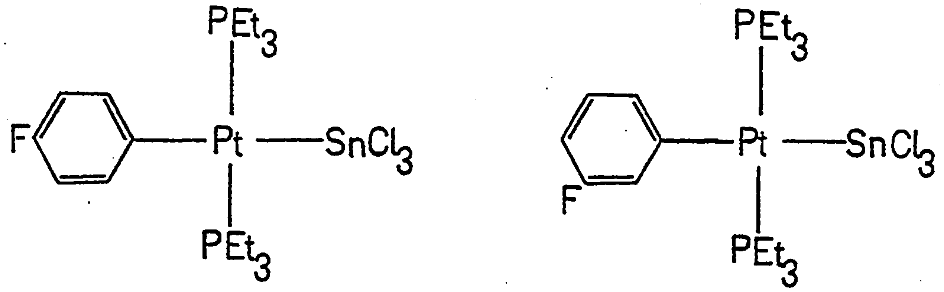


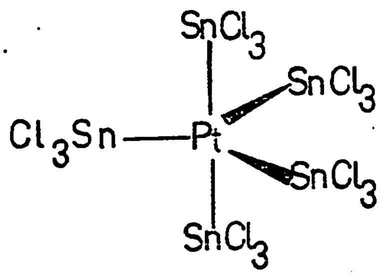
FIGURE 1.1 Relative σ- and π- parameters for pentacarbonylmanganese derivatives.



1.33

Subsequent studies [38] have shown that the Cl_3Sn group is not unique and that there is little difference between Cl_3Si, Cl_3Ge and Cl_3Sn as ligands.

Caution should be exercised when making comparisons between two very different systems and applying the results to yet a third. It should not be forgotten that there is no theoretical justification to relate force constants to bond strength [70], although it is found empirically that this is invariably the case. Also the *trans*-effect originally applied to a kinetic effect and not to static structures.[71] With such factors in mind, it would not be unexpected if, say, the rate of substitution of the ligands in question did not follow exactly the order predicted from considerations of bonding in the ground state. The π-acceptor properties of $SnCl_3$ when bonded to platinum may be much greater than when bonded to manganese because the d-orbitals on the tin are closer in energy to the filled d-orbitals on platinum. The exceptional nature of $SnCl_3$ when bonded to platinum is illustrated in the compound $[Pt(SnCl_3)_5]^{3-}$ (1.36).[72] This is one of the few five co-ordinate platinum complexes - it also has the noble gas number of electrons.



1.36

If there were appreciable π-bonding between the group IV element and the transition metal it would be expected that the bond length would be shorter than that expected for the hypothetical single bond length. A difficulty arises, however, in estimating the covalent radii of the transition metal in low oxidation states. For example, a value of 1.46 Å - half the Mn-Mn distance in $Mn_2(CO)_{10}$ - has been recommended [73] for the single-bond covalent radius of manganese in compounds such as $R_3SiMn(CO)_5$. However, the values of 1.31 and 1.38 Å have been obtained for this parameter from diffraction studies on $HMn(CO)_5$ [74] and $ClMn(CO)_5$.[75] These probably arise because the covalent radius is not a fixed, hard core but can vary from compound to compound. Some authors [76] did not consider the change, albeit formal in the oxidation state on going from $Mn_2(CO)_{10}$ to $R_3SiMn(CO)_5$. Even with these limitations it is found that there appears to be a significant contraction in the metal-group IV element bond. This is shown in Table 1.3.[76] The covalent radius of group IV atom is usually taken as half the distance of the M-M bond in R_3M-MR_3 compounds.

It is perhaps pertinent at this stage to discuss the rather moot point of oxidation states in these organometallic compounds. The oxidation state of manganese in $Mn_2(CO)_{10}$ is taken to be zero. However, the oxidation state of manganese in a compound such as $(OC)_5Mn-SnPh_2-Mn(CO)_5$ could be taken as +I, 0, or -I depending on how one views the bonding in this compound.[77] To avoid this difficulty ligands like $SnCl_3$ are formally regarded as uninegative i.e. $^-SnCl_3$, so that, similar to $Mn(CO)_5Cl$, Mn in $Mn(CO)_5SnCl_3$ is considered as being in the +I state. It is again stressed that this concept is a formal one and works if the rules are adhered to. The utility of the whole idea of oxidation states concerning these compounds is, however, sometimes dubious. Consider, for instance the two reactions:

$$2Mn(CO)_5^- + Sn^{IV}Cl_4 \rightarrow ((OC)_5Mn)SnCl_2 + 2Cl^-$$

$$Mn_2(CO)_{10} + Sn^{II}Cl_2 \rightarrow ((OC)_5Mn)SnCl_2$$

TABLE 1.3[75]

Contractions in the Group IV - Transition Metal Bond Lengths

Compound	Expt. length, Å	Calcd. length, Å†	Contraction. Å
$H_3SiCo(CO)_4$	2.38	2.49	0.11
$F_3SiCo(CO)_4$	2.23	2.48	0.25
$Cl_3SiCo(CO)_4$	2.25	2.48	0.23
$(CH_3)_3Si\text{-}Mn(CO)_5$	2.50	2.54(2.63)	0.04(0.13)
$(C_6H_5)_3Ge\text{-}Mn(CO)_5$	2.53	2.57(2.66)	0.04(0.13)
$(CH_3)_3Sn\text{-}Mn(CO)_5$	2.67	2.76(2.85)	0.09(0.18)
$(C_6H_5)_3Sn\text{-}Mn(CO)_5$	2.67	2.76(2.85)	0.09(0.18)
trans-$(C_6H_5)_3Sn\text{-}Mn(CO)_4P(C_6H_5)_3$	2.63	2.76(2.85	0.13(0.22)

† Values not in parentheses were calculated using a manganese radius of 1.46 Å, those in parentheses using a value of 1.37 Å.

In the product the tin atom is regarded as being in the zero oxidation state, an oxidation state previously 'unknown' for tin.[1] This assignment is also difficult to agree with in view of the modes of synthesis. Furthermore, Fenton and Zuckerman [78] have studied a number of chlorotin derivatives of transition metals by Mössbauer spectroscopy and in all cases the results appeared to indicate that the tin atom was in the +IV oxidation state (even in $[Pt(SnCl_3)_5]^{3-}$). Consistent with this observation was the mean Sn-Cl distance of 2.40 Å found in $Cl_3SnIr(C_8H_{12})_2$ (calculated for Sn^{IV}-Cl, 2.39 Å and for Sn^{II}-Cl 2.62 Å). Comparable distances are also observed for Sn-Cl in bipy-$Mo(CO)_3(SnMeCl_2)Cl$ (mean 2.40 Å [79]), $Ru_2(CO)_5SnCl_6$ (2.35 Å [80]) and in π-$C_5H_5Fe(CO)_2(SnCl_3)$ (2.36 Å).[81]

Structural studies of $[Fe(\pi\text{-}C_5H_5)(CO)_2(SnR_3)]$ type derivatives (R = Cl [81], Br [82], Ph [83] and $SnR_3 = SnCl_2Ph$ [84]) were interpreted in that there was free rotation about the Fe-Sn bond. This was taken to mean that $d\pi$-$d\pi$ interaction was not involved in this bond since the π-orbitals in question would lack the cylindrical symmetry compatible with this free rotation about the bond axis. This is difficult to see, for if the cyclopentadienyl ligand is assumed to occupy three coordination sites, then the iron atom would have an octahedral configuration. In such a situation there would be two orthogonal π-orbitals, in planes containing the

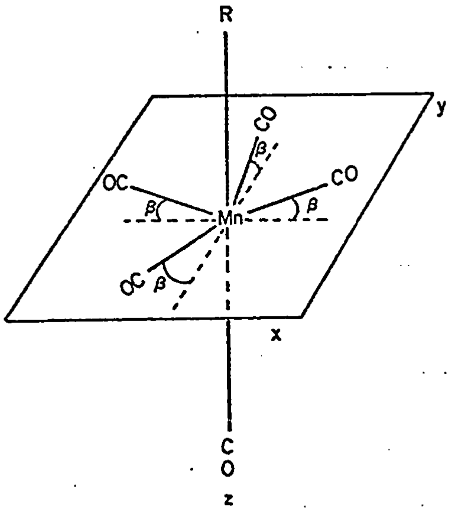
Fe-Sn bond. These, although not completely degenerate, would have suitable symmetry to allow π-overlap with empty tin d-orbitals with simultaneous rotation of Sn about the Fe-Sn bond axis.

Molecular orbital calculations [76] on $F_3SiCo(CO)_4$ predicted relatively small, yet significant, Co-Si π-bonding; analogous calculations for $Cl_3SiCo(CO)_4$ gave significantly less π-interaction in the Si-Co bond, σ-bonding accounting for about 97% of the bonding.

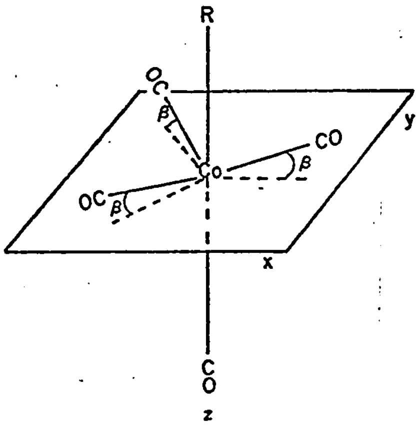
Nuclear quadrupole resonance [85] and mass spectral studies [86] on these two and related compounds were not inconsistent with Co-Si multiple bonding. The latter work gave surprisingly high values of approximately 100 kcal mole^{-1} as the strength of the Co-Si bond in these derivatives.

A relative increase in s-electron density in tin-transition-metal bonds is indicated by certain ir spectroscopic measurements of carbonyl stretching frequencies in such compounds [87,88], by ^{119}Sn nmr studies of $SnMe_3$ derivatives [89] and by observations of the quadrupole splitting and isotope shift effects in ^{119}Sn Mössbauer spectra.[90]

The possibility that there is direct interaction between the group IV element and the equatorial CO groups, in derivatives of the type $R_3MCo(CO)_4$ and $R_3MMn(CO)_5$ has been discussed.[75] This postulate is consistent with evidence on these compounds currently available. A structural finding that lends weight to this argument is the displacement of the equatorial CO groups towards the substituent as illustrated in 1.37 and 1.38



1.37



1.38

The extent of this displacement is shown in Table 1.4.[75] The last compound in this Table appears to indicate that it is not repulsion between the equatorial and axial CO groups that is causing this distortion, as has been suggested.[91] It is possible, however, that $P(C_6H_5)_3$ could impose steric repulsion on the equatorial CO groups to the same extent as an axial CO. It must be mentioned that other species, not containing a group IV element, of the type $RCo(CO)_4$ and $RMn(CO)_5$ also show this effect. However,

TABLE 1.4 [76]

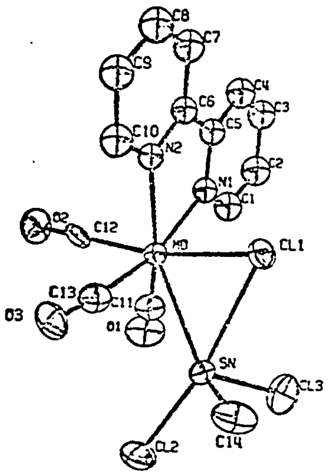
Displacement of Equatorial CO Groups in Some $RCo(CO)_4$ and $RMn(CO)_5$ Derivatives

Compound	Average R-M-Coeq bond angle deg	Displacement β°
$H_3Si\text{-}Co(CO)_4$	81.7	8.3
$F_3SiCo(CO)_4$	85.4	4.6
$Cl_3SiCo(CO)_4$	85.2	4.8
$(CH_3)_3SiMn(CO)_5$	84.5	5.5
$(CH_3)_3SnMn(CO)_5$	84.4	5.6
$(C_6H_5)_3SnMn(CO)_5$	86.7	3.3
trans-$(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3$	85.7	4.3

molecular orbital calculations [92] on $Mn(CO)_5L$ (L = Cl, Br, I, H) indicated that a ligand-ligand interaction bringing about an electron-donor effect from ligand L to *cis*-carbonyls may be important. Such a direct bonding interaction fails to explain the large *trans*-effects found for MR_3 ligands in square planar complexes.

It is quite possible that both the bonding interaction with the *cis*-ligands and the π-bonding mechanism are both operative in group IV compounds of the transition metals. Evidence will be presented in this thesis that, although favoring the π-bonding hypothesis, will support this view.

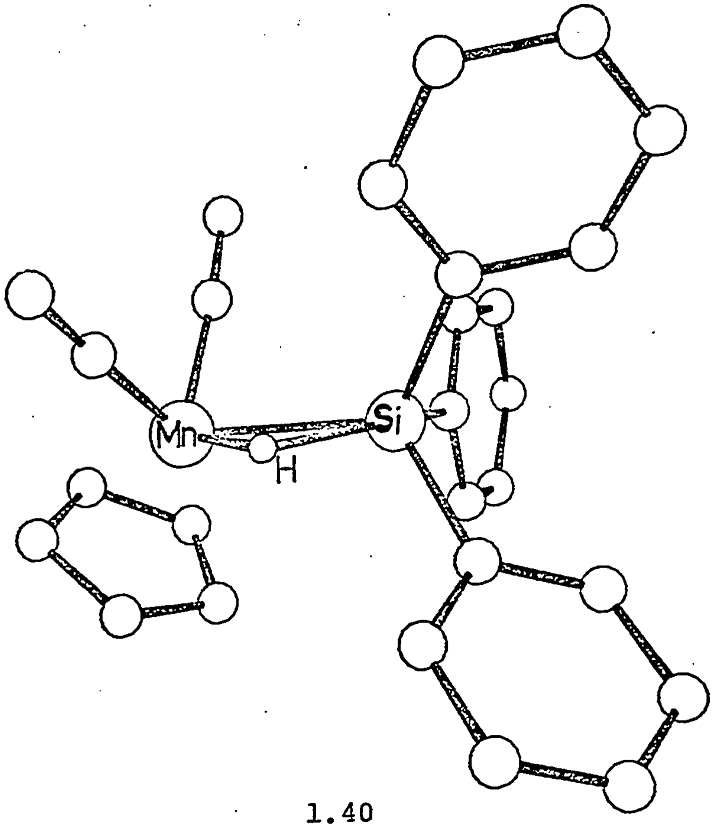
Although interaction of the group IV element with neighbouring CO groups is a matter of contention, there are several cases where a group IV atom is bonded to another ligand while simultaneously being bonded to a transition metal. The structure [79] of bipy $Mo(CO)_3Cl(SnCl_2Me)$ has the geometry shown in 1.39



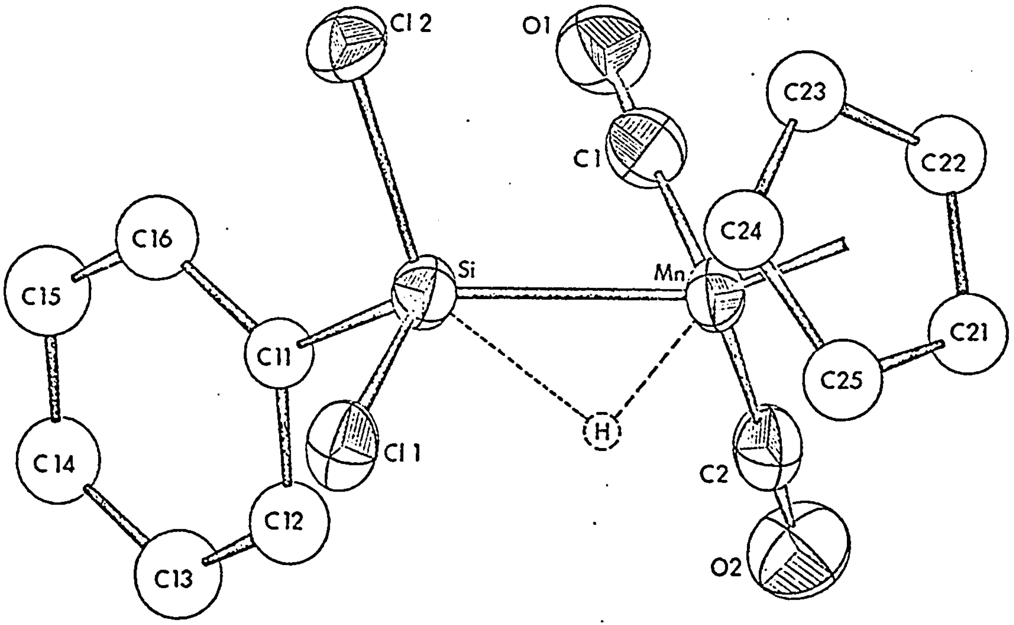
1.39

The bond length (2.805 Å) between tin and the unique chlorine atom, although longer than normal Sn-Cl lengths (2.35-2.45 Å), is considerably shorter than the van der Waals radii for the two elements. It has also been found that $SnCl_4$ may be displaced from the related bipy-$Mo(CO)_3(SnCl_3)Cl$ by basic phosphines.[93]

A similar type of interaction between hydrogen and silicon is found in crystallographic studies of $(\pi\text{-}C_5H_5)Mn(CO)_2(SiPh_3)H$ [94] and $(\pi\text{-}C_5H_5)Mn(CO)_2(SiCl_2Ph)H$ [95] (1.40 and 1.41 respectively). The hydrogen was located in both cases. It was originally



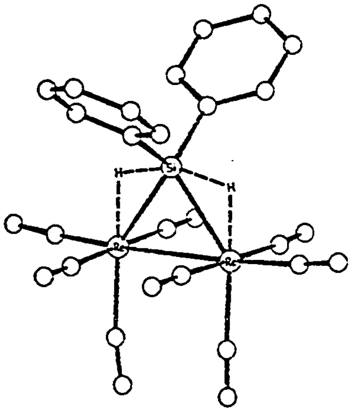
1.40



1.41

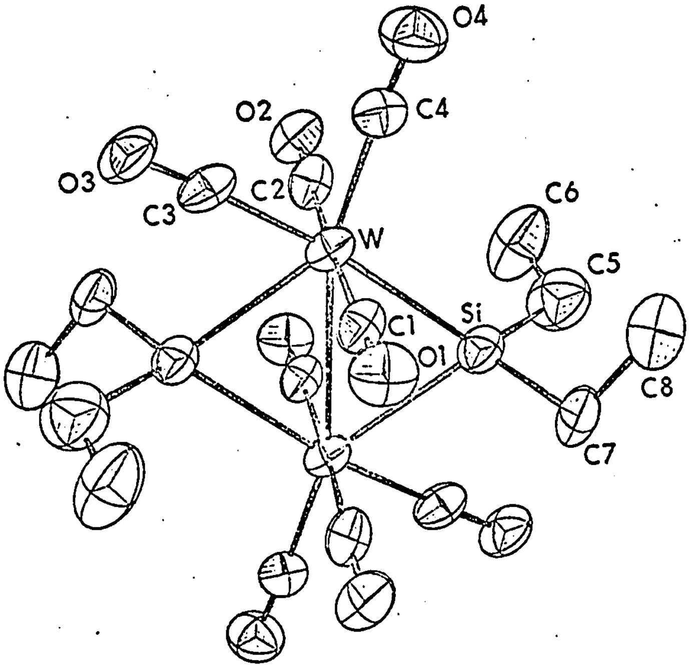
thought that the absence of an infrared-active, terminal Mn-H stretch in 1.40 was due to the bridging nature of hydride ligand. It is now believed that there is, by coincidence, no net dipole moment change due to the electronic environment of the unique hydrogen in the molecule. This is supported by the observation of an absorption in the Raman spectrum that can be assigned to such a stretch and also by the fact that 1.41 shows an infrared active Mn-H stretch. The kinetics of displacement of Ph_3SiH from 1.40, by a variety of ligands, has been investigated.[96]

A number of other compounds which may have the same bonding situation have been synthesized by Hoyano and Graham.[97] Thus in the compound $Re_2(CO)_8(H_2SiPh_2)$ the hydrogen atoms were placed in the conspicuously vacant sixth coordination site of each rhenium atom as shown in 1.42.[98] However more recent structural considerations of this and the compounds $Re_2(CO)_6(H_2SiR_2)_2$ and $Re_2(CO)_7(HSiR_2)_2$ [99] have led to the conclusion that perhaps the hydrogen ligands do not interact with the silicon.



1.42

In the more sterically crowded $W_2(CO)_8(HSiR_2)_2$ (1.43) one pair of W-Si bond lengths is distincly longer than the other suggesting that this compound should be formulated with a three-center two-electron bond.[95]



1.43

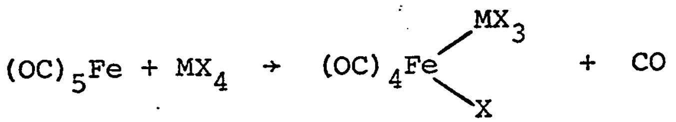
In conclusion, it can be seen from this review, and as will become apparent in this thesis, group IV derivatives of transition metals offer some intriguing and exciting problems in both structure and bonding.

CHAPTER 2

THE REACTION OF GROUP IV TETRAHALIDES WITH DODECACARBONYLTRIRUTHENIUM

INTRODUCTION

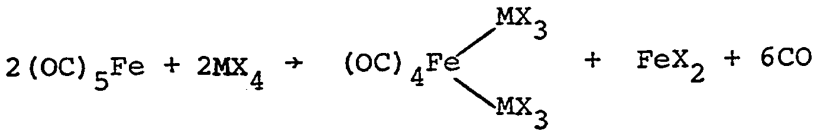
Kummer and Graham have reported [28] the reaction of tin and germanium tetrahalides (MX_4) with iron pentacarbonyl. When the reaction was carried out below or only slightly above room temperature (depending on the tetrahalide), compounds with one Fe-M bond were formed:



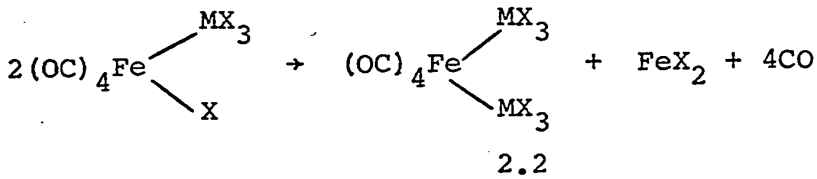
$$(OC)_5Fe + MX_4 \rightarrow (OC)_4Fe(MX_3)(X) + CO$$

2.1

Reactions at higher temperatures, or heating type 2.1 products in an appropriate solvent, produced derivatives with a sequence of M-Fe-M bonds:



$$2(OC)_5Fe + 2MX_4 \rightarrow (OC)_4Fe(MX_3)_2 + FeX_2 + 6CO$$



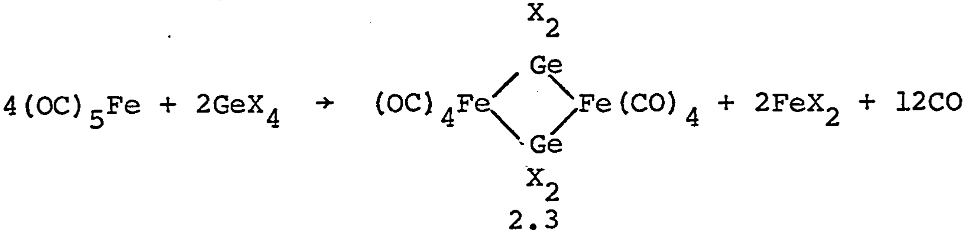
$$2(OC)_4Fe(MX_3)(X) \rightarrow (OC)_4Fe(MX_3)_2 + FeX_2 + 4CO$$

2.2

Type 2.1 compounds were only observed in the *cis*-form; these unsymmetrical derivatives were not very stable thermally, tending to rearrange or disproportionate to the symmetrical 2.2 type especially in solution.

For compounds of class 2.2 *cis*-and *trans*-forms were observed. In the two cases where both isomers of a particular compound were isolated, $(OC)_4Fe(GeCl_3)_2$ and $(OC)_4Fe(SnCl_3)_2$, the *cis*-form was the more stable and the *trans*-form isomerized in solution in a short time. For the tribromogermanium and triiodogermanium compounds, only the *trans*-isomer was detected. These facts were accommodated by regarding the *cis*-form as the electronically preferred structure, since it avoids as nearly as possible a condition in which mutually *trans*-carbonyl groups are competing for π-electron density of the iron. Steric hindrance was then invoked to explain the 'anomalous' stability of *trans*-$(OC)_4Fe(GeI_3)_2$. These compounds were among the first *trans*-disubstituted derivatives of the iron group carbonyls to be reported.

Under more vigorous conditions (80-90°, sealed tubes), iron pentacarbonyl reacted with germanium tetrahalides (but not those of tin) to form compounds of type 2.3, having a four-membered ring of metal atoms:



2.3

Although not reported, it was observed in the same study that dodecacarbonyltriiron also afforded the latter products under slightly more vigorous conditions.

It has become increasingly evident [100] that the chemistry of $Fe_3(CO)_{12}$ is in many respects different from its second row congener - dodecacarbonyltriruthenium. It therefore seemed worthwhile to extend this reaction to $Ru_3(CO)_{12}$ so that a comparison with iron would be possible.

RESULTS AND DISCUSSION

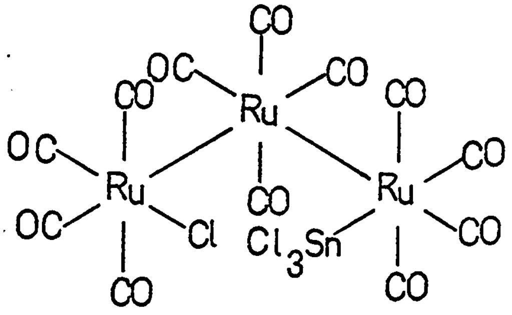
PART I

REACTIONS CARRIED OUT UNDER AN INERT ATMOSPHERE

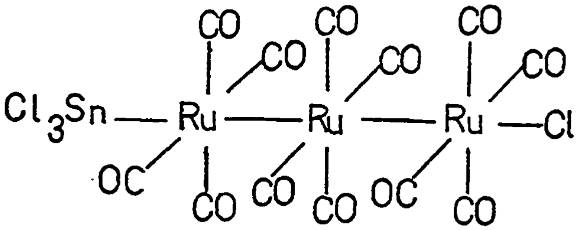
Dodecacarbonyltriruthenium has been found to undergo reaction with tin(IV) and germanium(IV) tetrahalides according to Scheme A. Compounds 2.5, 2.6 and 2.7 were not isolated in this study, although evidence for these reasonable intermediates will be given in subsequent parts of this Chapter.

Speculations on Structure of $Ru_3(CO)_{12}SnCl_4$

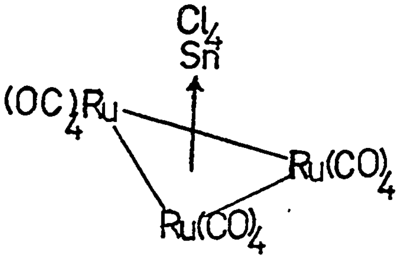
The initial product 2.4 could be isolated only in the case of tin tetrachloride. At present the structure of this interesting, photochromic compound is regarded as uncertain and the following discussion must be considered of a speculative nature at the present time.



2.9a

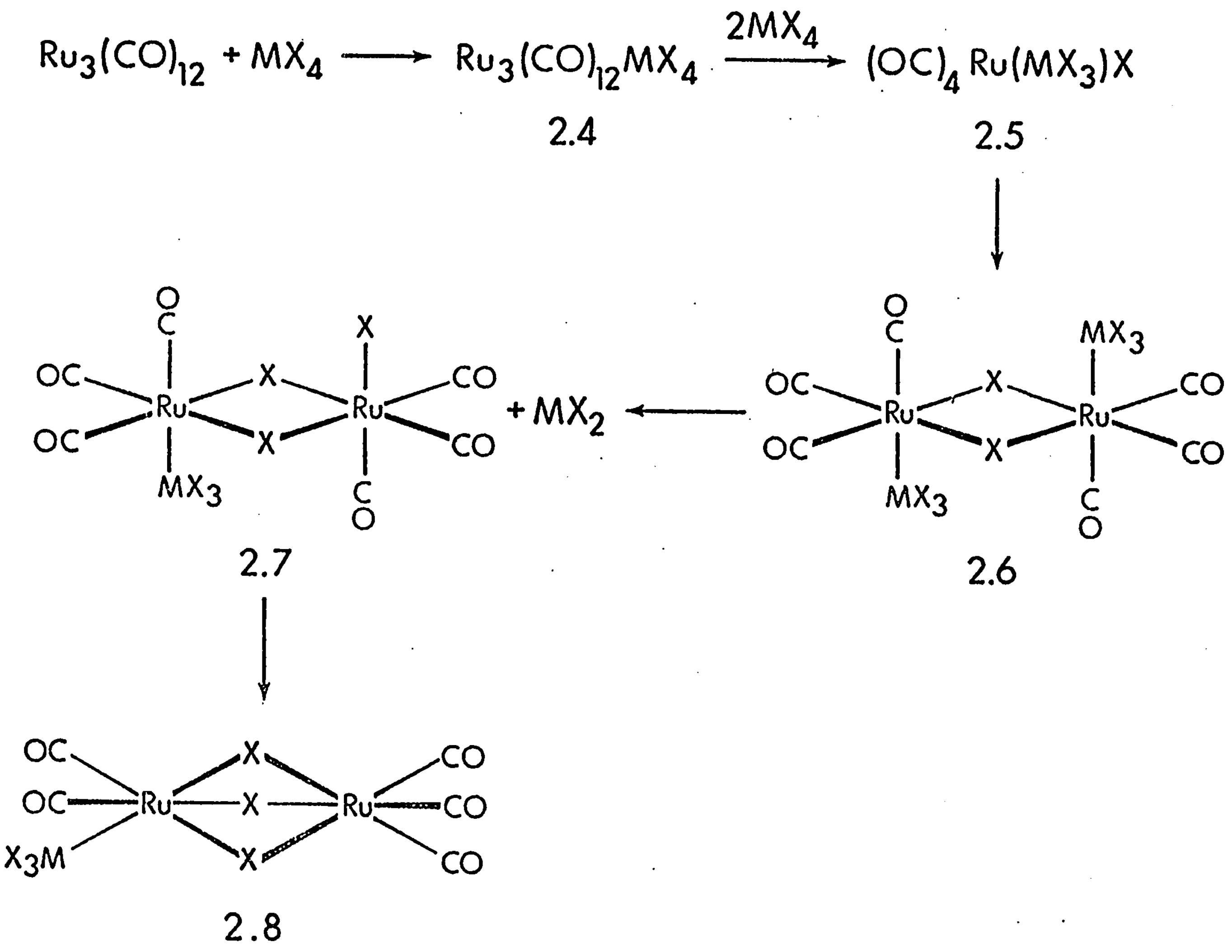


2.9b



2.9c

SCHEME A


Ru3(CO)12 + MX4
Ru3(CO)12MX4
2MX4
(OC)4 Ru(MX3)X
2.4
2.5
2.6
+ MX2
2.7
2.8
OC
CO
X
MX3
X3M
Ru

If ruthenium-ruthenium bond cleavage has occurred, a staggered version of 2.9b is possible. This structure has C_{4v} symmetry taking the Cl_3Sn group as cylindrical, and six infrared carbonyl stretching bands are permitted. Six bands and a shoulder are observed (Fig. 2.1), which might result from lower actual symmetry. Note that a configuration such as 2.9a has at most C_{2v} symmetry for which one would predict eleven infrared carbonyl stretching modes. Formation of the all-*trans* structure 2.9b would involve isomerization at three metal atoms since the parent $Ru_3(CO)_{12}$ has an all-*cis* arrangement; yet the formation of $Ru_3(CO)_{12}SnCl_4$ occurs under mild conditions in a short period of time. Under comparable conditions, $Fe_3(CO)_{12}$ does not react at all in two days; even though its solution structure may differ, one might have expected an analogous product if simple cleavage of the metal-metal bond were involved.

These considerations led to the proposal of the alternate structure 2.9c, in which the triangle of transition metals serves as a Lewis base, with $SnCl_4$ a Lewis acid. Seven infrared bands are predicted for this C_{2v} structure. The basicity of $Ru_3(CO)_{12}$ towards a proton has recently been demonstrated [101] with the isolation of $[HRu_3(CO)_{12}]^+PF_6^-$. The failure of the other tetrahalides (e.g., $SnBr_4$ and SnI_4) to form similar compounds could be due to their weaker Lewis acidity.[102] Other evidence that this species may be

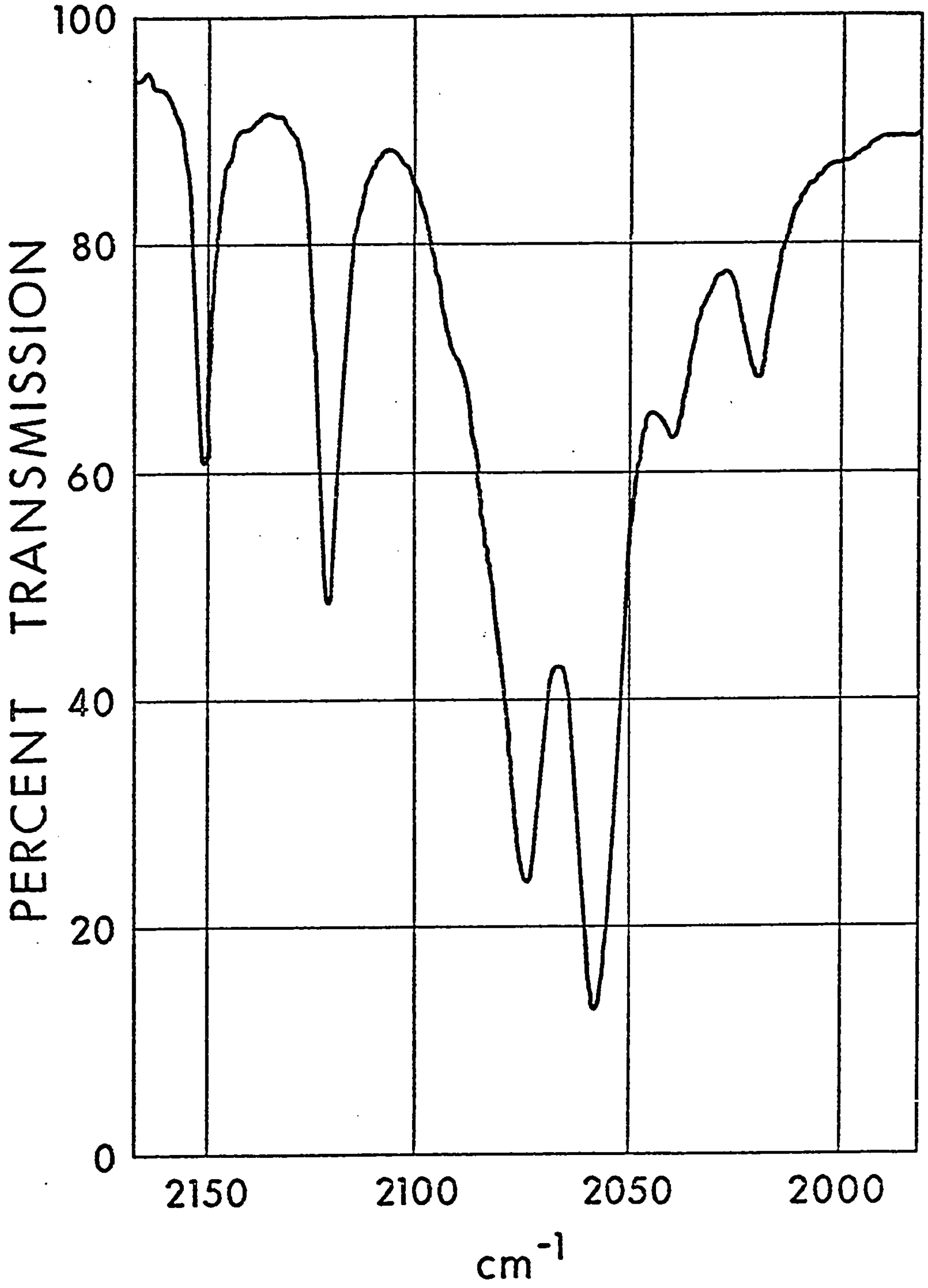


FIGURE 2.1 Infrared spectrum of $Ru_3(CO)_{12}SnCl_4$ (CH_2Cl_2 solution).

an adduct is the failure to observe a Ru-Sn stretch in the Raman spectrum (Chapter 7). Note too that $Ru_3(CO)_{12}SiCl_4$ was not obtained from the reaction of $Ru_3(CO)_{12}$ and $SiCl_4$ although other derivatives containing Ru-Ru bonds were.

Unfortunately it has not been possible to obtain crystals of $Ru_3(CO)_{12}SnCl_4$ or its osmium analogue that are suitable for X-ray crystallography nor was it possible to elucidate the structure by the chemical reactions of these derivatives. Thus the reaction of $Ru_3(CO)_{12}SnCl_4$ with pyridine did not produce $Ru_3(CO)_{12}$ which might have been expected if $Ru_3(CO)_{12}SnCl_4$ were the adduct of a Lewis acid and a Lewis base. Attempts to insert $SnCl_2$ into $Os_3(CO)_{12}Cl_2$ - thought to have a chain of osmium atoms [43] - were unsuccessful.

Although a mass spectrum of $Ru_3(CO)_{12}SnCl_4$ could not be obtained, such a spectrum was observed for the osmium analogue.[35,147c] The spectrum is reported in detail for the first time in Table 2.1. The spectrum is extremely complicated owing to large numbers of different isotopes involved: Os(four), Sn(seven) and Cl(two). This wide spread of peaks made it difficult to assign some regions, since peaks due to one ion overlapped with another, e.g., $(P'-Cl)^+$ and $(P'-CO)^+$.

Although not conclusive, the mass spectral evidence does favor the adduct formulation for $Os_3(CO)_{12}SnCl_4$. It

TABLE 2.1

Mass Spectrum of $Os_3(CO)_{12}SnCl_4$

Peak	Approximate Intensity	Assignment*
1166	12	$Os_3(CO)_{12}SnCl_4$
1133	17	$Os_3(CO)_{12}SnCl_3$
1082	21	$Os_3(CO)_9SnCl_4$
1050	10	$Os_3(CO)_9SnCl_3$
1028	22	$Os_3(CO)_7SnCl_4$
1000	14	$Os_3(CO)_6SnCl_4$
968	6	$Os_3(CO)_5SnCl_4$
939	7	$Os_3(CO)_4SnCl_4$
894	12	$Os_3(CO)_2SnCl_4$
888	16	$Os_3(CO)_3SnCl_3$
859	19	$Os_3(CO)SnCl_4$
838	59	$Os_3(CO)_7Cl_2$
810	30	$Os_3(CO)_6Cl_2$
803	27	$Os_3(CO)_7Cl$
799	31	$Os_3(CO)_8$
784	33	$Os_3(CO)_5Cl_2$
756	33	$Os_3(CO)_4Cl_2$
747	45	$Os_3(CO)_5Cl$
726	31	$Os_3(CO)_3Cl_2$
722	31	$Os_3(CO)_4Cl$
720	30	
698	19	$Os_3(CO)_2Cl_2$

continued.......

TABLE 2.1 (continued)

Peak	Approximate Intensity	Assignment*
691	23	$Os_3(CO)_3Cl$
664	28	$Os_3(CO)_2Cl$
641	120	$Os_2(CO)_8Cl$
620	51	$Os_2(CO)_6Cl_2$
613	150	$Os_2(CO)_2Cl$
592	50	$Os_2(CO)_5Cl_2$
585	115	$Os_2(CO)_6Cl$
564	45	$Os_2(CO)_4Cl_2$
557	85	$Os_2(CO)_5Cl$
536	50	$Os_2(CO)_3Cl_2$
530	45	$(Os_2(CO)_4Cl$
508	22	$Os_2(CO)_2Cl_2$
501	50	$Os_2(CO)_3Cl$
499	50	
489	8	Os_2Cl_3?
482	25	$Os_2(CO)Cl_2$
480	25	
473	26	$Os_2(CO)_2Cl$
466	11	$Os_2(CO)_3$
452	27	Os_2Cl_2
436	10	$Os_2(CO)_2$
431	7	Os_2CCl
429	7	

continued.....

TABLE 2.1 (continued)

Peak	Approximate Intensity	Assignment*
417	19	Os_2Cl
401	8	$Os_2(CO)$
394†	4	$[Os_3(CO)_5Cl_2]^{2+}$
394	4	Os_2C
382	13	Os_2
374	29	$Os(CO)_4Cl_2$
363†	3	$[Os_3(CO)_3Cl_2]^{2+}$
346	16	$Os(CO)_3Cl_2$
339	7	$Os(CO)_4Cl$
332	17	$Os(CO)_5$
318	9	$Os(CO)_2Cl_2$
311	26	$Os(CO)_3Cl$
304	15	$Os(CO)_4$
290	9	$Os(CO)Cl_2$
283	11	$Os(CO)_2Cl$
276	7	$Os(CO)_3$
262	9	$OsCl_2$
260	17	$SnCl_4$
248	7	$Os(CO)_2$
239	4	$OSnCl_3$
227	13	$OsCl$
225	130	$SnCl_3$
204	5	OsC

continued.........

TABLE 2.1 (continued)

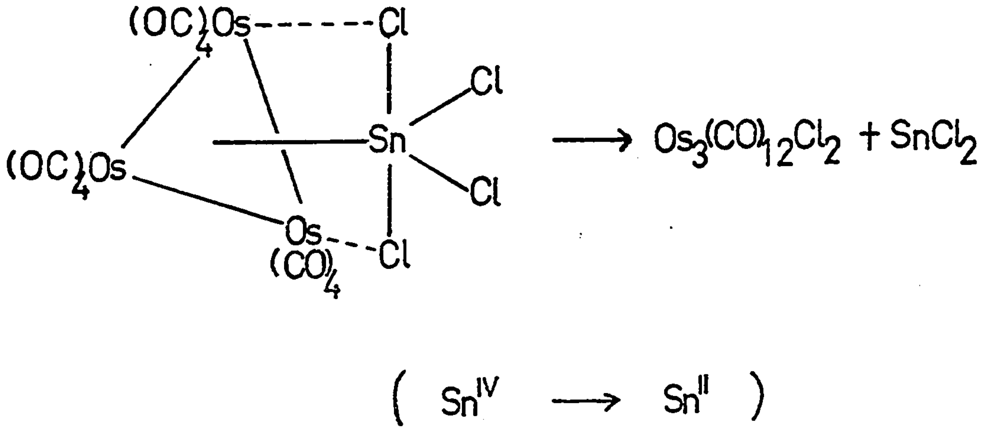
Peak	Approximate Intensity	Assignment
192	15	Os
190	90	$SnCl_2$
155	260	SnCl
136	24	SnO
120	50	Sn

---

* Where more than one possibility existed for an assignment (e.g., the mass of Os is approximately the same as that of $SnCl_2$) a consideration of the pattern enabled the correct assignment to be made.

† Peaks also observed at half unit intervals indicating that these are double charged ions.

might have been expected that if $Os_3(CO)_{12}SnCl_4$ were the product of a Lewis acid with a Lewis base then ions $(Os_3(CO)_{12})^+$ and $(SnCl_4)^+$ might have been very abundant. The latter peak was present but no peaks which could reasonably be assigned to $(Os_3(CO)_{12})^+$ were observed. The occurrence of the type $(Os_3(CO)_{11}Cl_2)^+$ and $(Os_2(CO)_nCl_2)^+$ may, however, be explained by the following process II.1

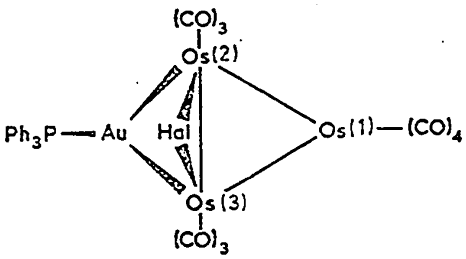


II.1

A similar mechanism would give $Os_2(CO)_nCl_2$ species. In such a structure it is possible that an oxygen on a carbonyl group would be in close proximity and hence formation of ions containing Sn-O would be facilitated as observed.

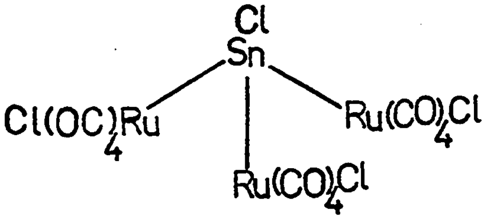
A structure containing Cl_3Sn-Os_3-Cl system might be expected to yield ions containing Os-Sn linkages. Also one might expect that it would be difficult for such a structure to give $[Os_2(CO)_nCl_2]^+$ ions or $(SnCl_4)^+$.

The observation of a parent ion in this compound does confirm that this compound is not $Os_3(CO)_{10}SnCl_4$. A compound originally thought [104] to have a four membered linear metal chain of composition $Cl-Os(CO)_4-Os(CO)_4-Os(CO)_4-AuPPh_3$ has subsequently been shown to have structure 2.10.[105]

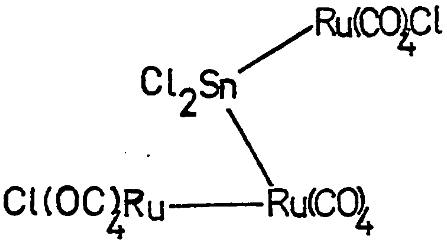


2.10

Other structures for $Ru_3(CO)_{12}SnCl_4$ which obey the EAN rule are shown in 2.9d - 2.9e.



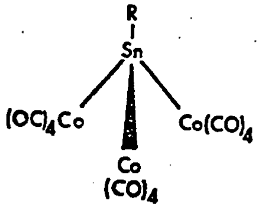
2.9d



2.9e

There are a number of isomers of each case. However, arrangements such as 2.9d and 2.9e can be excluded for the following reasons. Except for a configuration 2.9d with all ligand chlorines *trans* to the tin, group theory would predict more than the seven infrared carbonyl bands observed. Such structures are not consistent with the mass spectral data. There is evidence that Cl-Os$(CO)_4$-Os$(CO)_4$-$SnCl_3$, which still contains an osmium-osmium bond, can be isolated from the reaction of $Os_3(CO)_{12}$ with $SnCl_4$. Both $Ru_3(CO)_{12}SnCl_4$ and its osmium analogue are formed under mild conditions where cleavage of two or three of the transition metal-metal bonds might not be expected. If rupture of these bonds does occur then it is difficult to explain why it does not take place for $Fe_3(CO)_{12}$.

Structures 2.9d or 2.9e however might explain the chemical reactions of these compounds. Molecules are known which contain tin bonded to three transition metal atoms:



2.11

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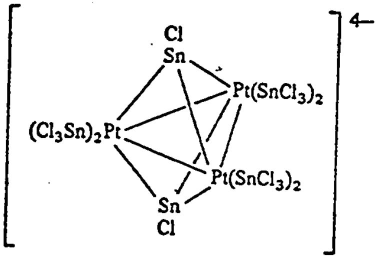


2.12

ref.107

The infrared spectrum of $(CH_3)Sn[Co(CO)_4]_3$ and $Ru_3(CO)_{12}SnCl_4$ are somewhat similar in the carbonyl region, but this might also be expected if $Ru_3(CO)_{12}SnCl_4$ had the adduct formulation.

A possible method of distinguishing between the various structural possibilities for $Ru_3(CO)_{12}SnCl_4$ would be the use of ^{35}Cl nqr or tin Mössbauer.

The same product, i.e., $Ru_3(CO)_{12}SnCl_4$ was observed in the reaction of $PhSnCl_3$ with $Ru_3(CO)_{12}$. Such a phenomenon has been noted before [28,108] and is believed to involve ligand exchange after the reaction of $PhSnCl_3$ with the transition metal according to II.2.

$$M'\text{-}SnCl_2Ph + PhSnCl_3 \rightarrow M'\text{-}SnCl_3 + Ph_2SnCl_2 \qquad \text{II.2}$$

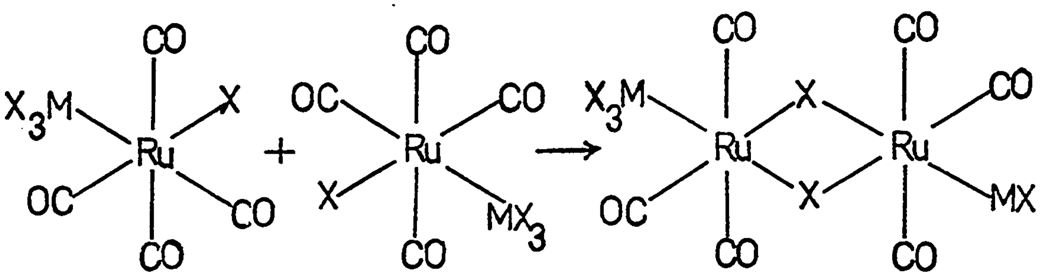
However an alternative mechanism, in the present case, could involve ligand exchange before reaction with $Ru_3(CO)_{12}$, as shown in II.3.

$$\left.\begin{array}{l} PhSnCl_3 + PhSnCl_3 \rightleftarrows Ph_2SnCl_2 + SnCl_4 \\ SnCl_4 + Ru_3(CO)_{12} \rightarrow Ru_3(CO)_{12}SnCl_4 \end{array}\right. \qquad \text{II.3}$$

Support for II.2 is the fact that $MeSnCl_3$ does not appear to react with $Ru_3(CO)_{12}$ which would not have been expected, if the reaction proceeded by initial attack at the transition metal by the organotin trichloride. The methyl group in $MeSnCl_3$ does not undergo ligand exchange reactions at these mild temperatures.

The $Ru_2(CO)_5MX_6$ Derivatives

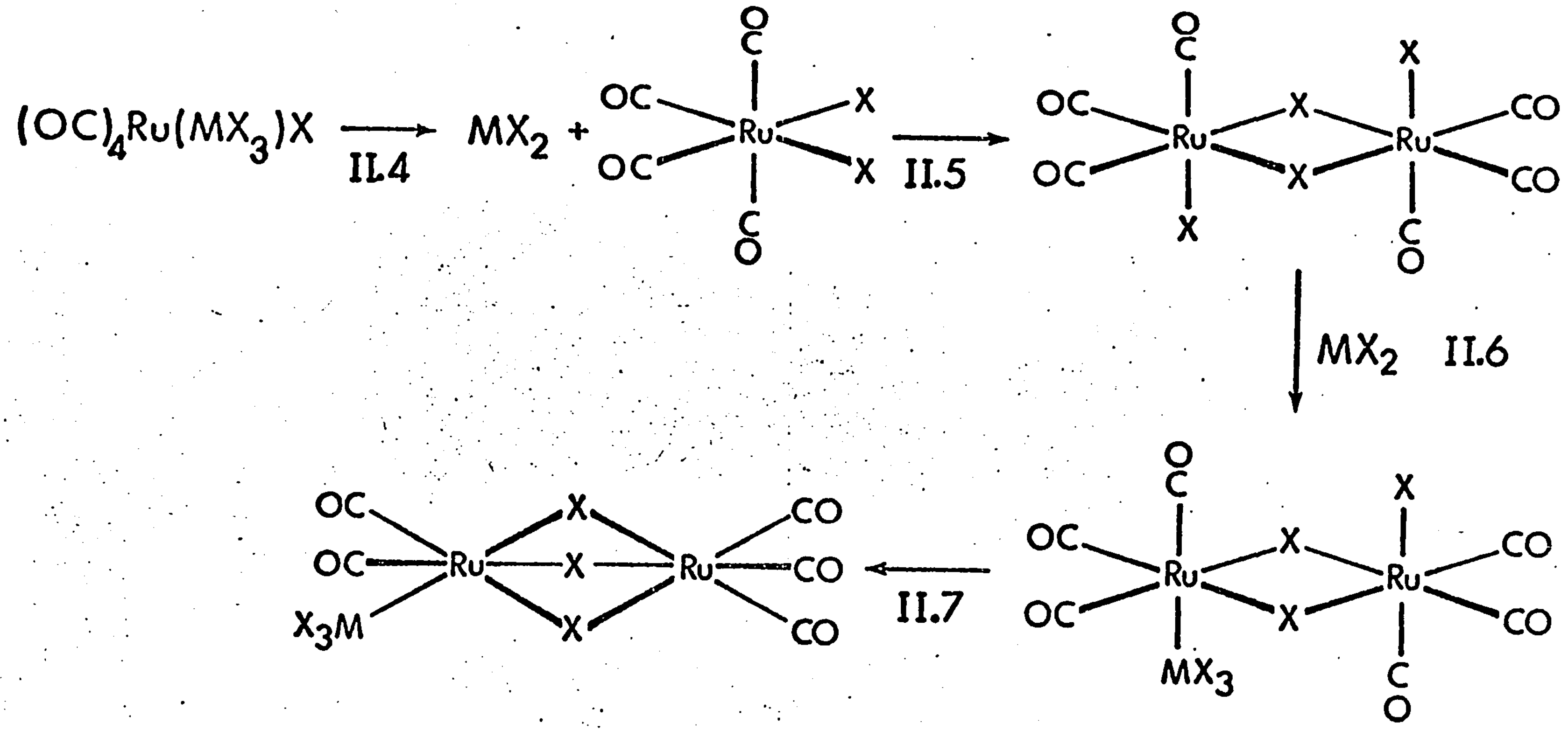
Reaction of MX_4 with $Ru_3(CO)_{12}$ at higher temperatures would be expected to produce $Ru(CO)_4(X)(MX_3)$ analogous to iron. Subsequent dimerization as previously outlined (2.4-2.8) would give the product isolated. The formation of the third halogen bridge probably takes place because of the high *trans*-effect of the MX_3 group *trans* to the carbon monoxide group being displaced. Further work presented in this thesis will show that the MX_3 group has a high *trans*-effect-higher in some cases than CO. In view of this result a second mechanism for the formation of $Ru_2(CO)_5MX_6$ may be formulated (Scheme B). If the MX_3 group had a greater *trans*-effect than CO then the following course would be expected for the dimerization:



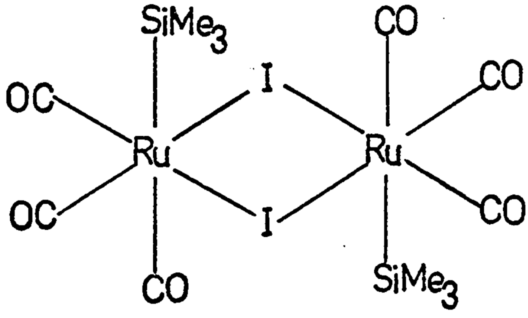
2.13

Indeed there is evidence for two isomeric forms of $[Me_3SiRu(CO)_3X]_2$ resulting from the dimerization of

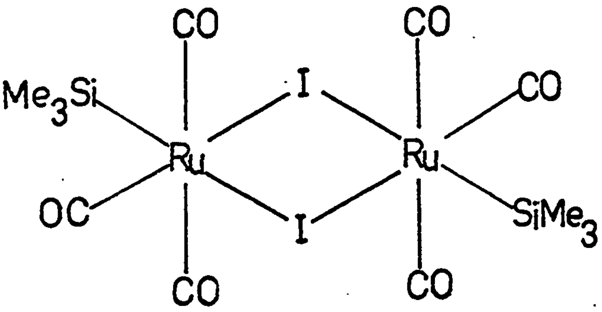
SCHEME B



$Me_3SiRu(CO)_4I$.[29] These two forms are thought to be 2.14 and 2.15. The monomer $Me_3SiRu(CO)_4I$ exists as the *trans*-isomer, dimerization of which would be expected to produce 2.15.



2.14

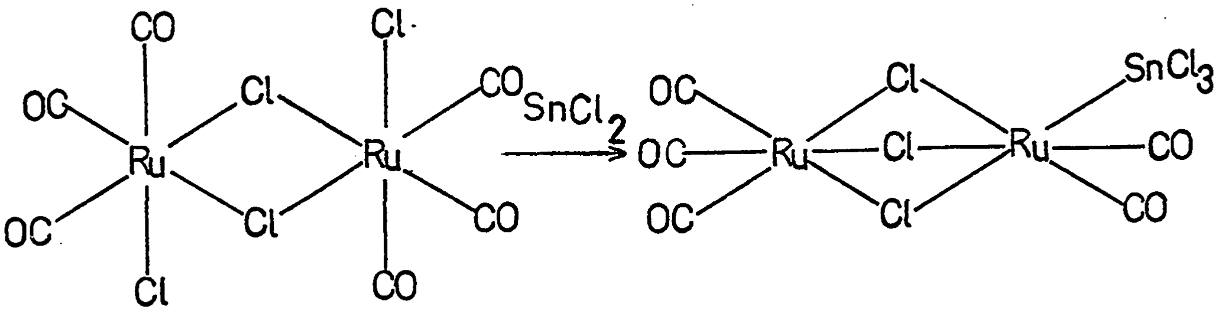


2.15

In view of the structure of $Me_3SiRu(CO)_4I$ the stable form of $Ru(CO)_4X(MX_3)$ might also be predicted to be *trans* and hence a dimerization product similar to 2.15 would be expected. However, it is impossible to form a third halogen bridge if it is *trans* to one of the others, suggesting that the reaction goes *via* the mechanism II.4-II.7. Intramolecular rearrangement of 2.15 into 2.14 by a mechanism to be discussed in subsequent Chapters of this thesis cannot be completely ruled out.

Other evidence to support the Scheme B mechanism of formation of $Ru_2(CO)_5MX_6$ is the following: elision of MX_2 groups from $Ru-MX_3$ systems is known to take place (see later in this Chapter); process II.5 is known to occur at these temperatures [109]; and finally steps II.6 and II.7 have been shown to take place for $[Ru(CO)_3Cl_2]_2$

and $SnCl_2$ i.e.,



The explanation of the different course of the overall reaction compared to iron probably lies not in the increased strength of the metal-metal bond but in the increased strength of the ruthenium-halogen bond and the stability of the tetracarbonyl halides. The reaction of $Fe(CO)_5$ with MX_4 is believed to go *via* II.9 and II.10.

$$\begin{array}{c} Fe(CO)_4X(MX_3) \rightleftarrows (OC)_4FeX_2 + MX_2 \\ \downarrow \\ FeX_2 + 4CO \end{array} \qquad II.9$$

$$Fe(CO)_4X(MX_3) + MX_2 \rightleftarrows Fe(CO)_4(MX_3)_2 \qquad II.10$$

For ruthenium carbonyl, as explained, equations II.11 and II.12 are thought operative.

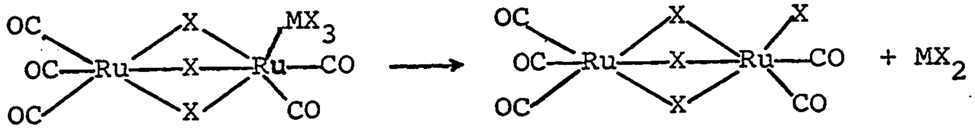
$$\begin{array}{c} Ru(CO)_4X(MX_3) \rightleftarrows (OC)_4RuX_2 + MX_2 \\ \downarrow \\ [Ru(CO)_3X_2]_2 \end{array} \qquad II.11$$

$$[Ru(CO)_3X_2]_2 + MX_2 \rightarrow Ru_2(CO)_5MX_6 + CO \qquad \text{II.12}$$

In the iron case the MX_2 produced can only react with $Fe(CO)_4X(MX_3)$ to give $Fe(CO)_4(MX_3)_2$, the equilibrium II.10 presumably lying to the right. With ruthenium the MX_2 has a choice of undergoing reaction II.12 or a pathway analogous to II.10. The former scheme is operative probably because (a) the reaction is irreversible under the conditions (CO released) and (b) the stronger Ru-X bond makes it more difficult to insert MX_2 into this bond. This second point will be developed more fully in the second part of this Chapter.

The $Ru_2(CO)_5MX_6$ derivatives are air-stable, crystalline solids which range in color from white for $Ru_2(CO)_5GeCl_6$ to deep red for $Ru_2(CO)_5SnI_6$. The bromides and iodides do however darken when exposed to direct sunlight.

The mass spectra of the chlorides and bromides showed strong parent peaks which agreed well with those patterns simulated by the computer. Interestingly, an intense peak (even for the iodides) was that due to the ion $(P-MX_2)^+$ i.e., the following process occurs in the electron beam:



II.13

For X = Cl or Br, $(P-MX_2)^+$ was the strongest peak, for X = I the most intense peak was $(P-I)^+$. Attempts to bring about loss of MX_2 by heating or irradiating solutions of $Ru_2(CO)_5SnI_6$ were unsuccessful.

The molecular structure of $Ru_2(CO)_5SnCl_6$ has been established by an X-ray diffraction study.[80] This is shown in Fig. 2.2. Selected bond lengths are given in Table 2.2. Three other structures have recently been published in which two ruthenium atoms are bridged by three chlorine atoms.[110-112] Delocalization of the odd electron in $[(n-C_4H_9)_3P]_4Ru_2Cl_5$ has been suggested to account for the Ru-Ru distance (3.115 Å); a distance of 3.12 Å has been taken as evidence of a Ru-Ru bond in $[((CH_3)_3Sn)((CH_3)_2Sn)Ru(CO)_3]_2$.[57] The Ru-Ru separation in the present diamagnetic compound was found to be almost as short (3.157 Å), although no metal-metal interaction need be invoked to satisfy the EAN rule. These observations support the recent comment by Dahl *et al.*[113] that in general metal-metal distances in ligand-bridged complexes do not provide a valid estimate of either metal radii or metal-metal bond orders. These distances are very much longer than the Ru-Ru distance found in the parent carbonyl (2.848 Å).[17]

In the present structure, the Ru-Cl distance *trans* to $SnCl_3$ is the same as the other two Ru-Cl distances for the ruthenium atoms involved, implying that Cl_3Sn and CO have similar *trans*-effects or, more precisely, that the *trans*-bond weakening effect of the two ligands as

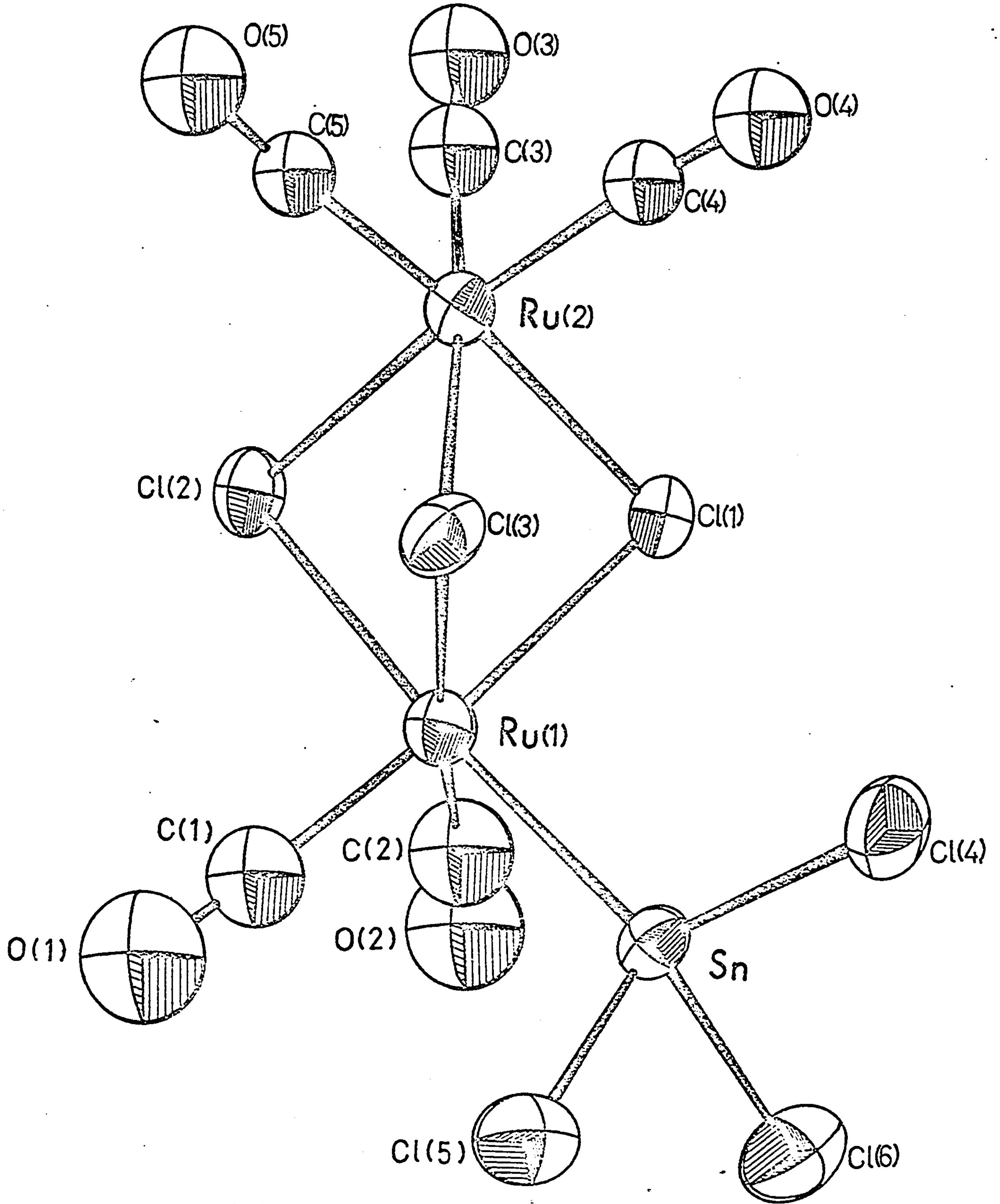


FIGURE 2.2 Structure of $Ru_2(CO)_5SnCl_6$

TABLE 2.2

Selected Bond Lengths (Å) for $Ru_2(CO)_5SnCl_6$

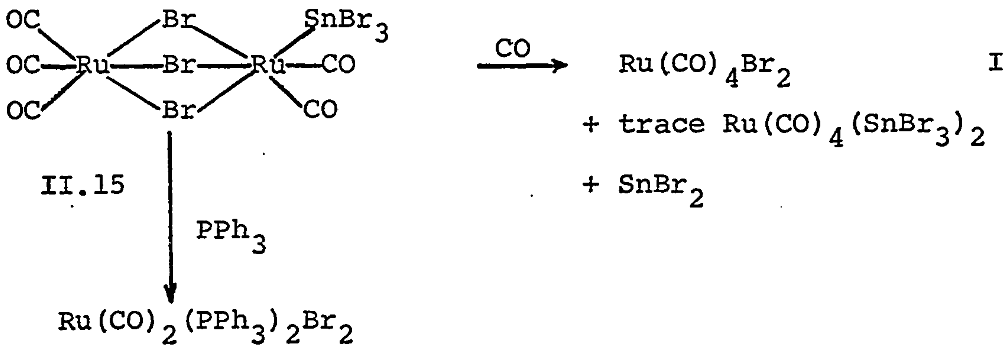
Sn-Ru(1)	2.565(4)
Ru(1)-Ru(2)	3.157(4)
Sn-Cl(4)	2.34(1)
Sn-Cl(5)	2.35(1)
Sn-Cl(6)	2.35(1)
Ru(1)-Cl(1)	2.44(1)
Ru(1)-Cl(2)	2.46(1)
Ru(1)-Cl(3)	2.45(1)
Ru(2)-Cl(1)	2.42(1)
Ru(2)-Cl(2)	2.39(1)
Ru(2)-Cl(3)	2.44(1)
Ru(1)-C(1)	1.90(5)
Ru(1)-C(2)	1.83(6)
Ru(2)-C(3)	1.80(4)
Ru(2)-C(4)	1.97(4)
Ru(2)-C(5)	1.87(4)
C(1)-O(1)	1.13(6)
C(2)-O(2)	1.17(7)
C(3)-O(3)	1.23(6)
C(4)-O(4)	1.09(5)
C(5)-O(5)	1.14(5)

Mean Values

Sn-Cl	2.35	C-O	1.15
Ru-C	1.87	Ru-Cl	2.43

(figures in parentheses are standard errors) judged from this compound are the same. The mean Sn-Cl (2.35 Å) distance is also consistent with this being an Sn(IV) compound.[78]

Further support for the structure of $Ru_2(CO)_5SnBr_6$ is provided in its reactions with CO and Ph_3P (II.14 and II.15 respectively).



II.14

II.15

The formation of $Ru(CO)_2(PPh_3)_2Br_2$ and $Ru(CO)_4Br_2$ demonstrates the tendency for Ru-$SnBr_3$ to dissociate into Ru-Br and $SnBr_2$. No evidence was found for $Ru(CO)_4(Br)(SnBr_3)$ in reaction II.14.

The overall symmetry of the $Ru_2(CO)_5MX_6$ class of compound is only C_s, from which one would, from group theory, predict five infrared-active CO stretching modes. That only a maximum of four bands are observed (Fig. 2.3,2.4) can be explained in terms of the local symmetry of the individual ruthenium atoms. If the bridging halogens are all equivalent with respect to the -$Ru(CO)_3$ half of the molecule, then one would only expect two ir active modes for such an entity and hence a total of four bands for the whole molecule. This equivalence has been shown to be almost the case

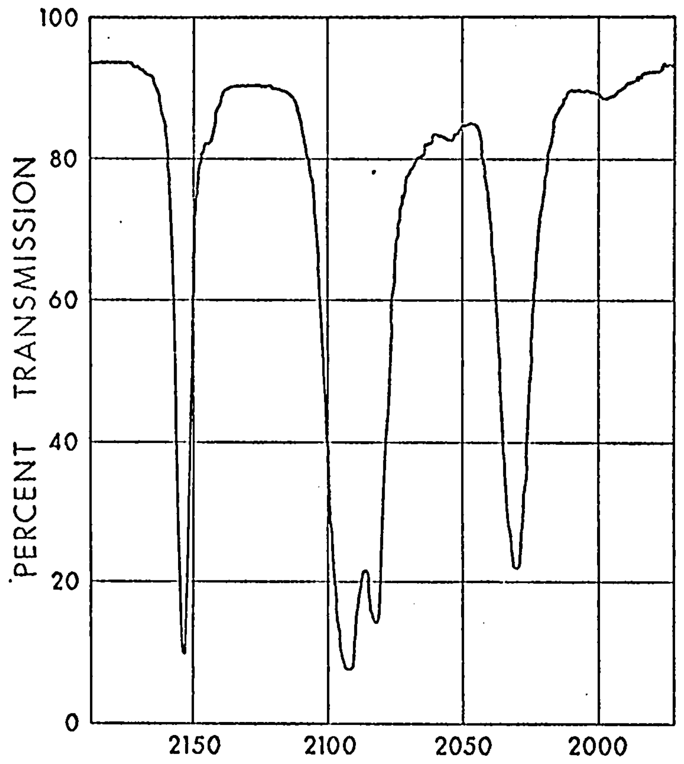


FIGURE 2.3 Infrared Spectrum of $Ru_2(CO)_5SnCl_6$ (CH_2Cl_2 solution).

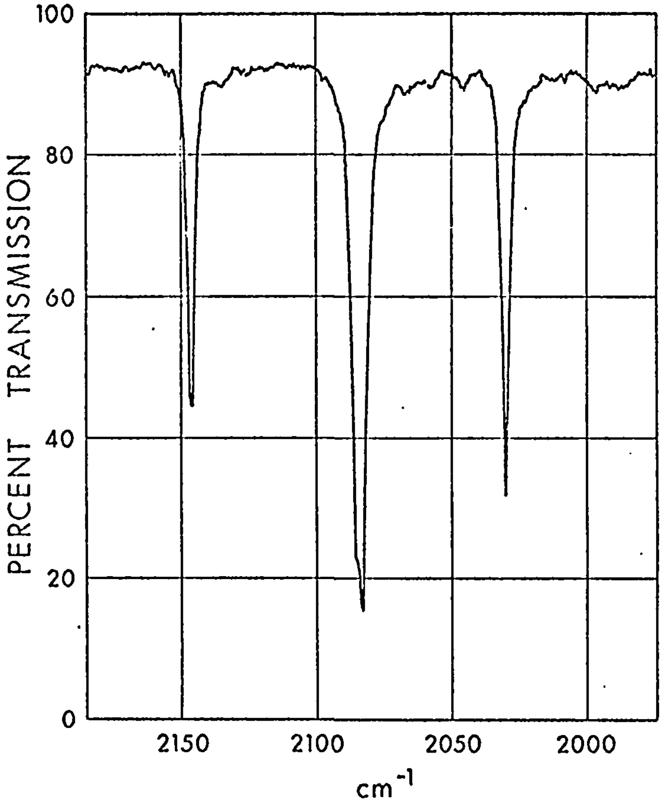


FIGURE 2.4 Infrared Spectrum of $Ru_2(CO)_5GeCl_6$ (cyclohexane solution)

in the structure of solid $Ru_2(CO)_5SnCl_6$.[80]

The occurrence of three bridging halogen atoms between two metals is relatively rare especially when the halogen is bromine or iodine. To our knowledge, the $Ru_2(CO)_5MX_6$ derivatives provide the only well-authenticated examples of a triple bridge of halogens in carbonyl chemistry.

The reaction of silicon tetrachloride with dodecacarbonyltriruthenium is more complicated than those just described for germanium and tin. By carrying out the reaction in evacuated sealed tubes between 100-150° a number of products were formed. Removal of solvent and sublimation of these products at room temperature gave a minute trace of *trans*-$Ru(CO)_4(SiCl_3)_2$ identified by its infrared and mass spectra. Sublimation in an evacuated sealed tube, along which a temperature gradient of about 60° to room temperature was maintained, gave three types of crystals. The pale yellow and colorless crystals which previous experiments had shown sublime at almost exactly the same temperature (35° < 0.01 mm) were separated by hand. The pale yellow crystals were identified by mass and infrared spectroscopy as the known [31] compound $[Ru(CO)_4SiCl_3]_2$, and the colorless crystals as $Ru_2(CO)_5SiCl_6$. The orange crystals were identified later as $Ru_3(CO)_{10}Cl_2$. A plausible mechanism for the formation of these compounds is given in Scheme C.

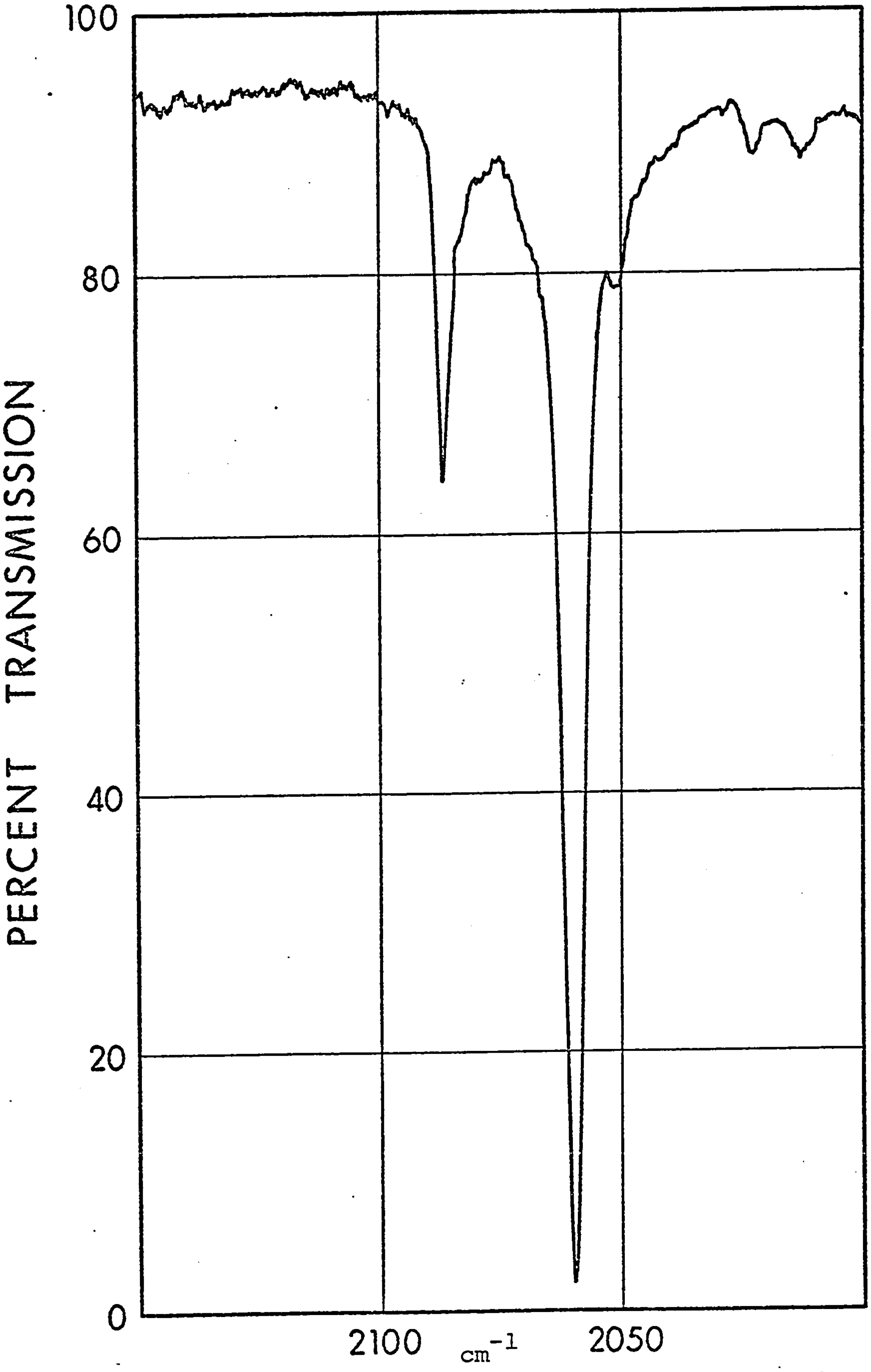
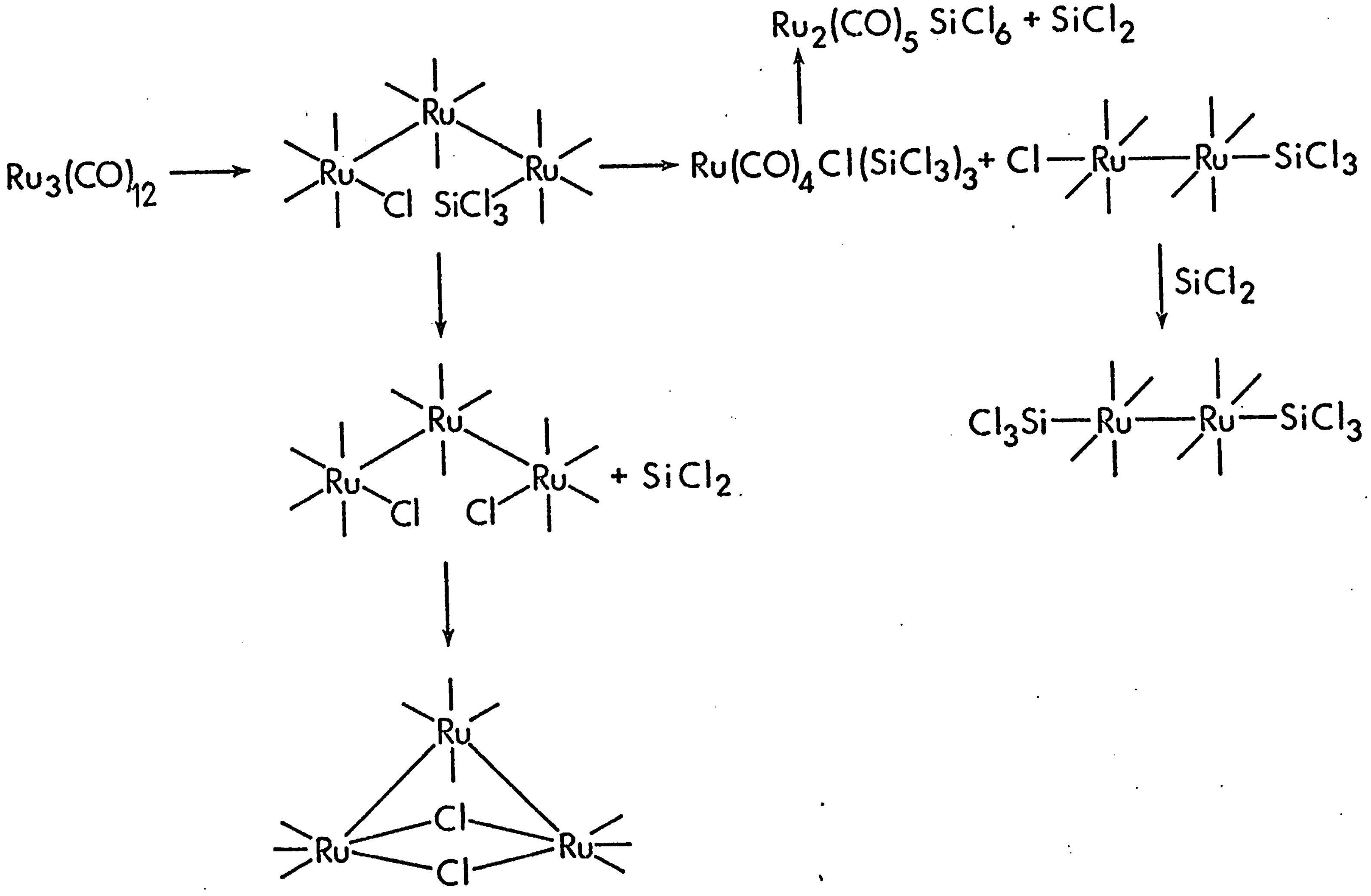


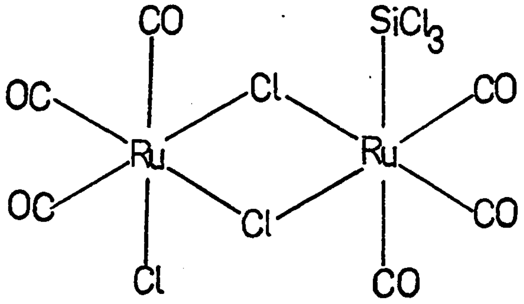
FIGURE 2.5 Infrared spectrum of $[Ru(CO)_4SiCl_3]_2$
(cyclohexane solution).

SCHEME C



$Ru_3(CO)_{12}$
Ru
Cl
$SiCl_3$
$Ru(CO)_4Cl(SiCl_3)_3$ + Cl
$SiCl_3$
$Ru_2(CO)_5\ SiCl_6 + SiCl_2$
$SiCl_2$
Cl_3Si
$SiCl_3$
+ $SiCl_2$
Cl

There was evidence of further products, formed in small amounts, especially when the reaction was carried out for longer periods of time (approximately two weeks). However, in all cases the only method of isolation was by hand picking, of the crystals, under the microscope; it was found that chromatography could not be used for separation of compounds containing Ru-MX_3 groups. One of these products, which was separated as deeper yellow crystals, had a two band infrared spectrum (2090 cm^{-1}, 2054 cm^{-1} heptane). This was suspected to be $Ru_2(CO)_6SiCl_6$ (2.16).



2.16

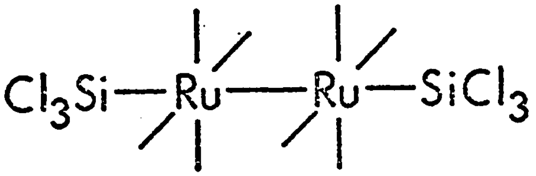
Further evidence for such derivatives will be presented in the second part of this Chapter.

Reaction with the solvent could also have taken place to give some of these minor products. The following reactions are known for $Ru_3(CO)_{12}$:[114]

$$Ru_3(CO)_{12} + C_6H_3Me_3 \rightarrow Ru_6C(CO)_{14}C_6H_3Me_3$$
$$Ru_3(CO)_{12} + nC_9H_{20} \rightarrow Ru_6C(CO)_{17} + H_2Ru_4(CO)_{13}$$

It will be shown later that $Ru(CO)_4(GeCl_3)_2$ reacts with benzene under special conditions to give $C_6H_6Ru(CO)(GeCl_3)_2$. However, solvent did not appear to interfere with the formation of the $Ru_2(CO)_5MX_6$ derivatives.

Alternative syntheses for $Ru(CO)_4(SiCl_3)_2$, $Ru_2(CO)_5SiCl_6$ and $Ru_3(CO)_{12}Cl_2$ have been found. A preparation of $Ru_2(CO)_8(SiCl_3)_2$ has appeared in the literature.[32] This involves the reaction of Cl_3SiH with $Ru_3(CO)_{12}$ at 80°, in a sealed tube. The structure of the compound is believed to be

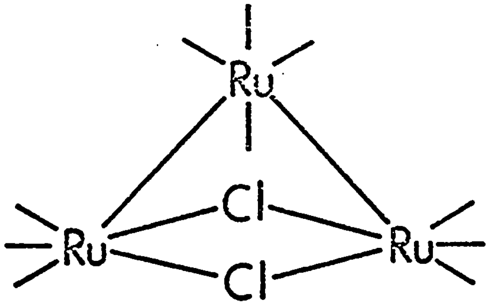


2.17

It was found in the present work that if Cl_3SiH and $Ru_3(CO)_{12}$ in benzene were stirred under a nitrogen atmosphere, at room temperature, for three weeks then the major product was $Ru_2(CO)_5SiCl_6$. Other products were $[Ru(CO)_3Cl_2]_2$ and $Ru_2(CO)_8(SiCl_3)_2$. Reaction of Cl_3SiH and $Ru_3(CO)_{12}$ under CO pressure at 180° gave *cis-* and *trans-*$Ru(CO)_4(SiCl_3)_2$ in excellent yield (see Chapter 3).

Silicon tetrachloride and $Ru_3(CO)_{12}$ under 70 atmospheres of carbon monoxide at 125°, gave $Ru_3(CO)_{10}Cl_2$ in good yield, the other product being $[Ru(CO)_3Cl_2]_2$. This latter substance is insoluble in heptane and easily separated from

$Ru_3(CO)_{10}Cl_2$. The new compound, $Ru_3(CO)_{10}Cl_2$, was characterized by complete elemental analysis. A mass spectrum could not be obtained for this compound. Although $Ru_3(CO)_{10}Cl_2$ did not sublime under high vacuum, it did when heated in a sealed, evacuated tube. It is probable that some $Ru_3(CO)_{10}Cl_2$ decomposed and the resulting small pressure of CO was sufficient to stabilize the sublimation. The air-sensitive $Ru_3(CO)_{10}Cl_2$ is an orange, crystalline solid; it is the first trimeric carbonyl halide of ruthenium; the osmium analogue is however known.[115] The infrared spectra of these compounds are similar (Table 2.3) and they are thought to have the same structure (2.18).[116]



2.18

It is to be noted, however, that the infrared spectrum (Fig. 2.6) of the ruthenium compound does have more bands than the osmium product. Some of the bands of $Ru_3(CO)_{10}Cl_2$ are very close to those of $Ru_3(CO)_{12}$, and it is possible that some $Ru_3(CO)_{12}$ was present as an impurity. This is con-

TABLE 2.3

Infrared Spectra of M'$_3$(CO)$_{10}$Cl$_2$ Species

$Ru_3(CO)_{10}Cl_2$ (in heptane)	2114vvw, 2088s, 2078s, 2062vvw, 2033vs, 2027m, 2010w, 2002m, 1999m
$Os_3(CO)_{10}Cl_2$ (in cyclohexane[115])	2114w, 2084s, 2071s 2029s, 2016s, 1993, 1988w
$Ru_3(CO)_{12}$ (in heptane)	2060vs, 2030s, 2016vw, 2011m.

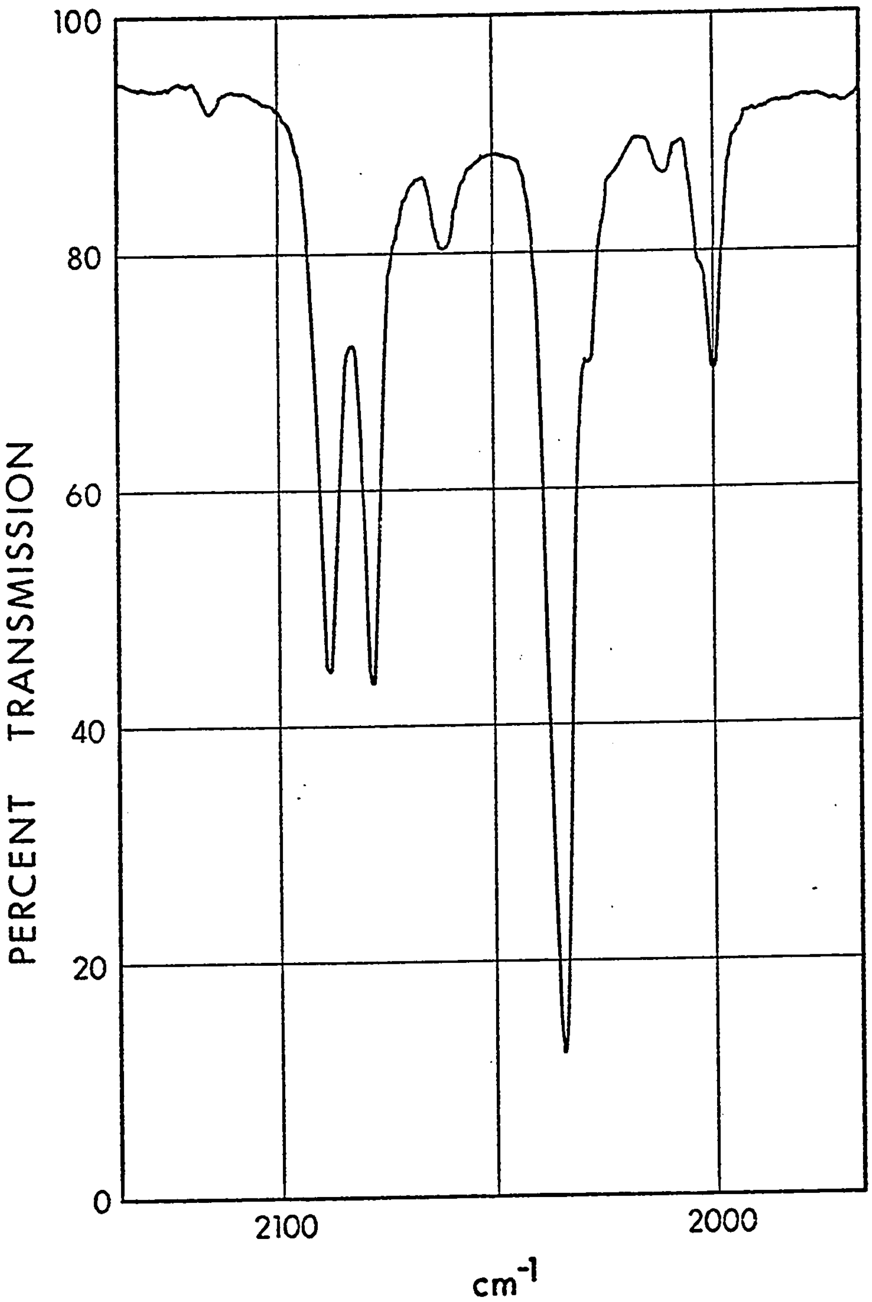


FIGURE 2.6 Infrared Spectrum of $Ru_3(CO)_{10}Cl_2$ (heptane solution).

sidered unlikely since the overall pattern and intensity of the absorptions remained the same even after three recrystallizations from hexane. Sublimation did not alter the spectrum either. It is quite possible that the carbonyl stretching modes associated with the unique ruthenium atom are degenerate with those of $Ru_3(CO)_{12}$. Group theory predicts for a structure such as 2.19 (of C_{2v} symmetry) a maximum of nine infrared-active carbonyl stretching fundamentals and, indeed, nine are observed for the ruthenium compound.

Also of interest is the fact that the product was $Ru_3(CO)_{10}Cl_2$ and not $Ru_3(CO)_{12}Cl_2$, even though the synthesis was carried out under CO pressure. This is especially so when the preparation [115] of $Os_3(CO)_{10}Cl_2$ is considered:

$$Os_3(CO)_{12} + Cl_2 \rightarrow Os_3(CO)_{12}Cl_2 \underset{CO}{\overset{heat}{\rightleftarrows}} Os_3(CO)_{10}Cl_2 \qquad \text{II.16}$$

Although the reaction of silicon tetrachloride with $Ru_3(CO)_{12}$ appears to have limitations for synthetic use, it is interesting, since it represents one of the first times that silicon tetrachloride has been induced to react with a metal carbonyl to give derivatives containing metal-silicon bonds. The reason for this difference between silicon, and tin and germanium, may lie in the much higher M-Cl bond strength of silicon (Table 2.4).

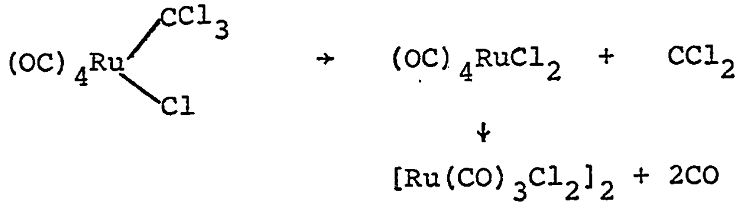
TABLE 2.4 [117]

M-Cl Bond Strengths

Bond	Bond Strength* (kcal mol^{-1})
C-Cl	93
Si-Cl	105
Ge-Cl	82?
Sn-Cl	75?

* Bond strengths, or bond dissociation energies, are not equal to, and may differ considerably from, mean bond energies derived solely from thermochemical data on molecules and atoms.

The reaction of $Ru_3(CO)_{12}$ and carbon tetrachloride (note the C-Cl bond strength, Table 2.4) at 135°, in sealed tubes, gives $[Ru(CO)_3Cl_2]_2$ in good yield. The nature of this carbonyl chloride dimer will be discussed in part II of this Chapter. A reasonable pathway for the formation of this compound is:



$$(OC)_4Ru(CCl_3)(Cl) \rightarrow (OC)_4RuCl_2 + CCl_2 \qquad \text{II.17}$$
$$\downarrow$$
$$[Ru(CO)_3Cl_2]_2 + 2CO$$

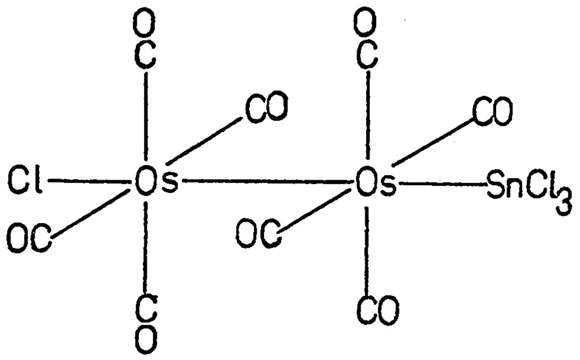
It is possible that the reason for the instability of the $Ru\text{-}CCl_3$ bond is due to lack of orbitals of the right energy on carbon that are capable of π-bonding with those on ruthenium. In support of the proposed course of the reaction II.17 is the isolation, from the reaction mixture, of C_2Cl_6. This product may be considered the result of insertion of the very reactive carbene, $:CCl_2$, into a C-Cl bond of CCl_4:

$$Cl_3C\text{-}Cl + :CCl_2 \rightarrow Cl_3C\text{-}CCl_3 \qquad \text{II.18}$$

The reaction of $Ru_3(CO)_{12}$ with $CHCl_3$ to yield $[Ru(CO)_3Cl_2]_2$ appeared while this work was in progress. The report [118] also included a brief mention of the reaction with CCl_4.

A preliminary study of the reaction of $Os_3(CO)_{12}$ with $SnCl_4$ and $GeCl_4$ to give $Os_2(CO)_5MCl_6$ (M = Sn or Ge) derivatives was carried out. It was found that, under more forcing conditions, products having the expected infrared and mass spectroscopic properties could be isolated. However, even though these compounds were purified first by recrystallization and then by sublimation, barely acceptable analytical results were obtained for carbon. Difficulty was experienced in the synthesis of the tin compound. It was found that reaction of $Os_3(CO)_{12}$ and $SnCl_4$ in sealed tubes, under a variety of conditions, gave only $[Os(CO)_3Cl_2]_2$ and *trans*-$Os(CO)_4(SnCl_3)_2$ unless it was carried out on a minute scale. It is presumed that when the experiment was carried out on a large scale there was a build up of CO pressure which favoured the production of these last products over $Os_2(CO)_5SnCl_6$. There were infrared indications that in the reaction of $Os_3(CO)_{12}$ and $SnCl_4$ in a Schlenk tube, $[Os(CO)_3Cl_2]_2$ was formed and was slowly converted to $Os_2(CO)_5SnCl_6$.

There was also evidence in the same reaction for $Os_2(CO)_6SnCl_4$ (2.19). Thus, when the reaction was stopped in the early stages, a compound could be isolated which exhibited one weak and one strong carbonyl stretching band consistent with a structure like 2.19. The mass spectrum



2.19

also agreed with such a formulation. Unfortunately insufficient material was isolated for analysis. One cannot exclude the possibility that this compound was $[Os(CO)_4SnCl_3]_2$, analogous to $[Ru(CO)_4SiCl_3]_2$, and that the heaviest peak in its mass spectrum corresponded to loss of $SnCl_2$ from the parent ion (c.f., the mass spectrum of $Ru_2(CO)_5SnCl_6$).

PART II

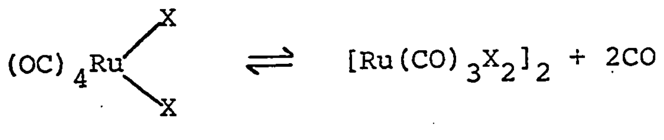
REACTIONS UNDER CO PRESSURE

It was reasoned that if the reaction of tin or germanium tetrahalides with $Ru_3(CO)_{12}$ were carried out under high CO pressure the bridging reactions (Schemes A and B) might be prevented and the formation of derivatives of the type $Ru(CO)_4(MX_3)_2$ would be favored.

This indeed was found to be the case. However, the products do depend on the exact conditions employed; this is shown in Table 2.5 for the particular case of $GeCl_4$. These results are interpreted as follows. The initial product $Ru(CO)_4X(MX_3)$ loses MX_2 as previously described:

$$Ru(CO)_4X(MX_3) \rightleftarrows Ru(CO)_4X_2 + MX_2 \qquad \text{II.19}$$

The fate of the $Ru(CO)_4X_2$ species depends on the nature of X. If X is iodide, $Ru(CO)_4I_2$ appears to be stable under the conditions used and no further reaction takes place. However for the bromide and chloride the dimerization process II.20 takes place:



$$(OC)_4RuX_2 \rightleftharpoons [Ru(CO)_3X_2]_2 + 2CO$$

II.20

This proceeds completely to the right for chloride if sufficient time is allowed; $Ru(CO)_4Cl_2$ is detected in the

TABLE 2.5

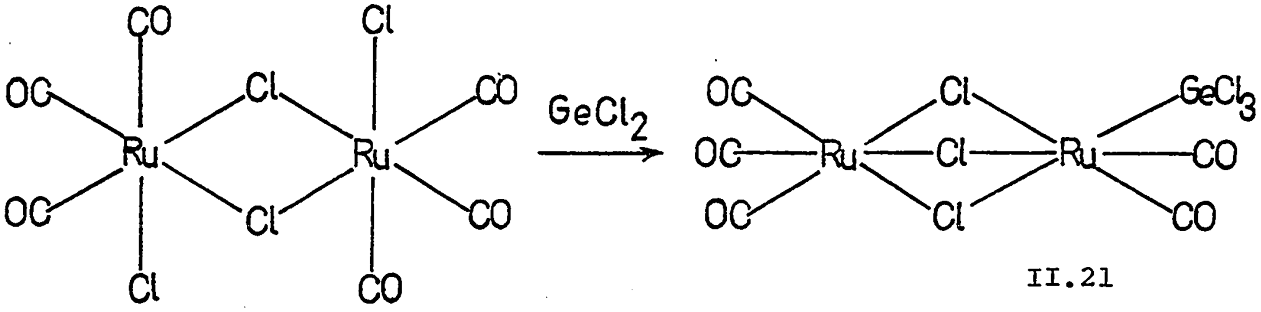
Products of the Reaction Between $GeCl_4$ and $Ru_3(CO)_{12}$

$Ru_3(CO)_{12}$ (mmol)	$GeCl_4$ (mmol)	Temp. (°C)	Time (hr)	Products (identified by IR spectroscopy)
0.5	6.8	120	4	$Ru_3(CO)_{12}$, $[Ru(CO)_3Cl_2]_2$
0.5	6.8	120-130	22	$Ru_2(CO)_5GeCl_6$
0.5	13.6	150	2	$Ru_2(CO)_5GeCl_6{}^*$, $Ru(CO)_4Cl_2$, $[Ru(CO)_3Cl_2]_2$ trace $Ru_2(CO)_5GeCl_6$
0.5	6.8	150	4	$Ru_2(CO)_6GeCl_6{}^*$, $[Ru(CO)_3Cl_2]_2$, *trans*-$Ru(CO)_4(GeCl_3)_2$
0.5	6.8	150	22	$Ru_2(CO)_5GeCl_6$, *trans*-$Ru(CO)_4(GeCl_3)_2$
0.5	6.8	180	4	*cis/trans*-$Ru(CO)_4(GeCl_3)_2$, $Ru_2(CO)_5GeCl_6$ $[Ru(CO)_3Cl_2]_2$
0.5	34	135	12	$[Ru(CO)_3Cl_2]_2$, trace of other products.

Reactions carried out in inert hydrocarbon solvent e.g. heptane under approximately 70 atmospheres of carbon monoxide.

* Compound not fully characterized.

early stages. When MX_4 is $GeCl_4$, a large excess of this reagent appears to suppress any further reaction and $[Ru(CO)_3Cl_2]_2$ is isolated. If only a slight excess is used, then the final product isolated at 135° is $Ru_2(CO)_5GeCl_6$:

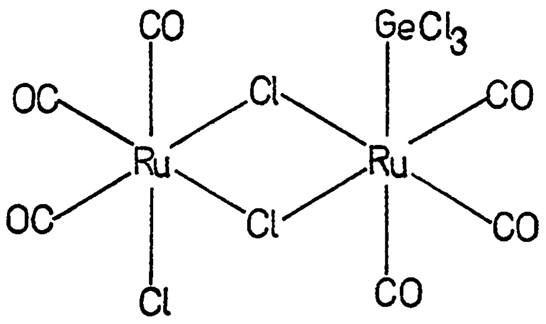


II.21

This last process appears irreversible under 70 atmospheres of carbon monoxide, in contrast to the bromides and iodides. That $GeCl_2$ is the reactive species was concluded from the fact that $[Ru(CO)_3Cl_2]_2$ did not react with $GeCl_4$ under identical conditions. The reason why a large excess of $GeCl_4$ prevents formation of $Ru_2(CO)_5GeCl_6$ is perhaps due to the tetrachloride acting as a scavenger for $GeCl_2$ in an analogous fashion to CCl_4 i.e.,

$$GeCl_4 + GeCl_2 \rightarrow Ge_2Cl_6 \qquad \text{II.22}$$

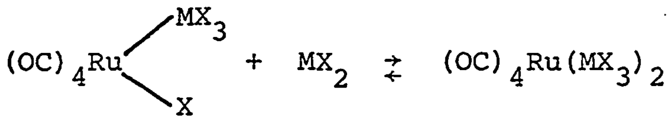
An intermediate in the formation of $Ru_2(CO)_5GeCl_6$ from $[Ru(CO)_3Cl_2]_2$ is probably 2.20.



2,20

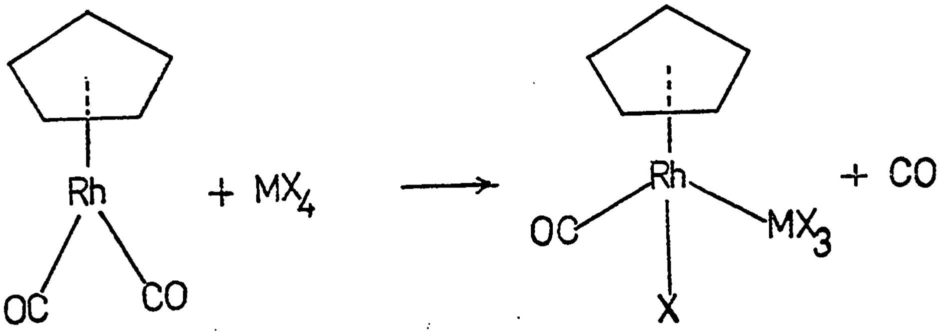
Evidence was found, in some of the reactions, for such a compound with the observation of two bands in the infrared spectrum of the mixture, in positions (2096, 2062 cm^{-1}) expected for such a derivative. This compound decomposed fairly rapidly in solution or under vacuum to give $Ru_2(CO)_5GeCl_6$.

When the reaction between tin or germanium tetrahalides and dodecacarbonyltriruthenium was carried out at 150°, (under 70 atmospheres of CO), $Ru(CO)_4(MX_3)_2$ compounds were isolated in the cases where X = Cl or Br. These substances were isolated in approximately the 50% yield expected if the insertion reaction II.23 takes



$$(OC)_4Ru\begin{matrix} MX_3 \\ X \end{matrix} + MX_2 \rightleftarrows (OC)_4Ru(MX_3)_2 \qquad \text{II.23}$$

place at this temperature. As has been elaborated in the introduction to this Chapter, II.23 takes place at much lower temperatures when the central atom is iron. The difference between this and the present case is probably, as has been mentioned before, due to the stronger Ru-X bond. Similar results have been obtained with the reaction of MX_4 with $(\pi\text{-}C_5H_5)Rh(CO)_2$.[119] Although $(\pi\text{-}C_5H_5)Co(CO)(MX_3)_2$ derivatives could be isolated,[108] employment of the same conditions gave rhodium compounds containing only one $Rh\text{-}MX_3$ bond:



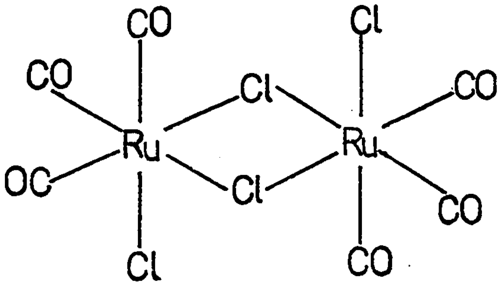
It appears, in contrast to the chlorides and bromides, that the equilibrium II.23 lies to the left when X is iodine. This is somewhat analogous to $Ru(CO)_4(HgX)_2$ species [120] - the iodide could not be prepared even though the corresponding iron compound exists. Attempts to replace chlorine by iodine in $Ru(CO)_4(MCl_3)_2$ only led to decomposition. Further evidence that II.23 is reversible is shown by the following: solutions of $Ru(CO)_4(MX_3)_2$ decompose, when heated in evacuated sealed tubes at 140°, into $Ru_2(CO)_5MX_6$; a dichloromethane solution of $Ru(CO)_4(SnBr_3)_2$, when allowed to stand, slowly disproportionated to $Ru(CO)_4Br_2$ and $SnBr_2$.

The occurrence of $Ru(CO)_4(MX_3)_2$ derivatives as the *trans*-isomers will be discussed in a subsequent section of this Chapter. However it is convenient at this stage to mention that in the one case where the *cis*-isomer was isolated, ($Ru(CO)_4(GeCl_3)_2$), it was established that the *cis*-and *trans*-forms were in equilibrium at about 150° (see the Experimental Section for details). Both isomers appeared stable in solution at room temperature.

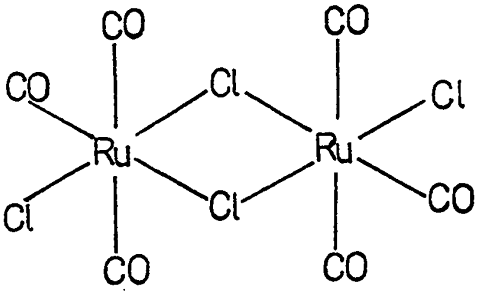
The interaction of MX_4 with $Ru_3(CO)_{12}$ under CO pressure is further complicated by the formation of $Ru(CO)_5$ under the conditions involved. It was found that conversion of $Ru_3(CO)_{12}$ to $Ru(CO)_5$ is 90% at 100° and 140 atmospheres of CO after twenty four hours. It is possible that the reaction of $Ru(CO)_5$ with MX_4 could take a different course to $Ru_3(CO)_{12}$. Thus the initial product of $Ru(CO)_5$ and MX_4 would be expected to be *cis*-$Ru(CO)_4X(MX_3)$ whereas possibly *trans*-$Ru(CO)_4X(MX_3)$ would result from $Ru_3(CO)_{12}$ plus MX_4, especially if the latter reaction proceeded *via* some X-$Ru(CO)_4$-$Ru(CO)_4$-MX_3 intermediate. Indeed, reaction at room temperature of $SnCl_4$ with $Ru(CO)_5$ gave a product with an infrared spectrum consistent with *cis*-$Ru(CO)_4(SnCl_3)Cl$, which decomposed on warming to give *trans*-$Ru(CO)_4(SnCl_3)_2$ and $Ru_2(CO)_5SnCl_6$. Its extreme instability prevented isolation. The very unstable nature of other $(OC)_4RuX(MR_3)$ derivatives has been reported.[28]

On the Supposed Isomers of $[Ru(CO)_3Cl_2]_2$

Bruce and Stone [121] have reported the preparation of $[Ru(CO)_3Cl_2]_2$ which they believed existed as two isomers 2.21 and 2.22:



2.21



2.22

Absorptions (in $CHCl_3$) at 2144vs, 2084vs and 2009w cm^{-1} were assigned to the *trans*-form (2.22) and bands at 2138vs, 2063vs and 2021m cm^{-1} to the *cis*-form (2.21).

Lewis and coworkers [122] reported similar results but went further to say that the two isomers could be separated by chromatography on silica. They designated the α-isomer to the compound showing absorptions at 2136s, 2075s, 2013w cm^{-1} (in $CHCl_3$) and the β-isomer to that which had bands at 2141s, 2079vs, 2006w cm^{-1} (again in $CHCl_3$).

However, the compound formulated as $[Ru(CO)_3Cl_2]_2$ in this study shows only two absorptions in the region 1800-2200 cm^{-1} in dichloromethane namely 2144s and 2084s cm^{-1}. This is in agreement with Bracci *et al.*,[118] who also did not observe any absorptions in the region 2000-2030 cm^{-1} for this compound. In carbon tetrachloride the low energy band is resolved into two bands with peaks at 2139s, 2082s and 2076s cm^{-1} (see Fig. 2.7a). These results are consistent with only one structure for $[Ru(CO)_3Cl_2]_2$ which is almost certainly 2.21, a configuration that has been confirmed by an X-ray crystallographic study [123] on $[Ru(CO)_3Br_2]_2$ and also the structure one might expect to be the more stable, since it does not have CO groups *trans* to one another.

However, it was confirmed that there was a change in the infrared spectrum of $[Ru(CO)_3Cl_2]_2$ in chloroform: initial bands at 2142 and 2084 cm^{-1} are (in dilute solution) replaced within about an hour by bands at 2137s, 2074s and 2065sh cm^{-1} (Fig. 2.7b). This, contrary to previous reports, is thought to be due to a reaction of $[Ru(CO)_3Cl_2]_2$ with the ethanol normally present, to the extent of approximately 0.75%, in commercial chloroform. Thus an infrared spectrum in ethanol-free chloroform shows a two-band spectrum (Fig. 2.7c) which is similar to that obtained in dichloromethane and which does not vary with time. Ethanol-free chloroform was prepared by either the method given by Vogel [124] or, more simply, by passing commercial chloroform down a column of alumina or silica. This last procedure could possibly explain the results

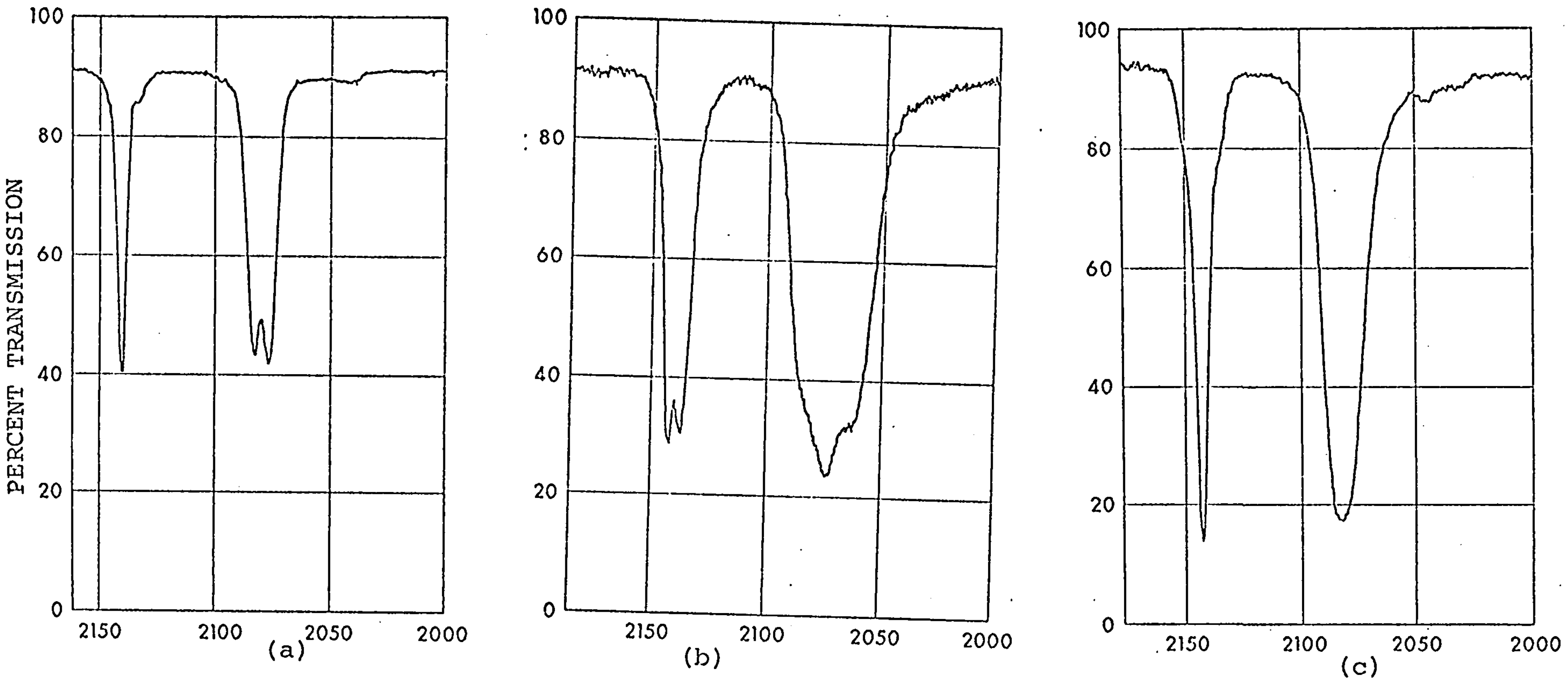


FIGURE 2.7 Infrared spectra of $[Ru(CO)_3Cl_2]_2$
(a) in carbon tetrachloride
(b) in commercial chloroform after ca. 10 min.
(c) in ethanol-free chloroform

of Lewis and coworkers.[122] The molecular weight of $[Ru(CO)_3Cl_2]_2$ (calculated 512) was found to be 319 and 321 in commercial chloroform whilst in ethanol-free chloroform it was found to be 526 and 536. Addition of ethanol to solution of $[Ru(CO)_3Cl_2]_2$ in pure chloroform causes an immediate change to the three-band spectrum. The exact position of these bands depends on the amount of ethanol added; in pure ethanol only two bands are observed i.e., 2122m, 2054s but both are extremely broad.

Dilution and infrared examination after several hours of a concentrated solution in commercial chloroform showed that dimeric $[Ru(CO)_3Cl_2]_2$ was still present, even though the solution contained excess ethanol. Removal of solvent from dilute solutions gave only $[Ru(CO)_3Cl_2]_2$ - as evidenced by the infrared spectrum of the product in CH_2Cl_2. These results are consistent with an equilibrium between $[Ru(CO)_3Cl_2]_2$ and an ethanol adduct (II.24).

$$[Ru(CO)_3Cl_2]_2 + 2EtOH \rightleftharpoons 2[EtOH]Ru(CO)_3Cl_2$$

II.24

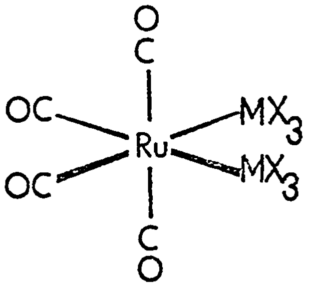
Similar behaviour has also been observed for $[Os(CO)_3Cl_2]_2$. Thus, solutions in commercial chloroform show peaks at 2135 and 2061 cm^{-1} which are replaced (more slowly than in the case of ruthenium) by bands ascribed to $(EtOH)Os(CO)_3Cl_2$, at 2128, 2050 and 2034 cm^{-1}. However, in ethanol-free chloroform no such transformation occurs. The results of Bruce *et al.*[125] are consistent with this interpretation if the ethanol adduct is, in this case, stable in the solid state.

It is assumed that the spectra [122] in chloroform of $[Ru(CO)_3Br_2]_2$ and $[Ru(CO)_3I_2]_2$ may be attributed to the same phenomenon.

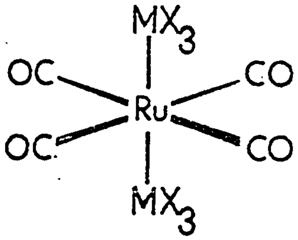
Coordination of the ethanol undoubtedly takes place through the oxygen in a similar fashion to tetrahydrofuran in $(C_4H_8O)Ru(CO)_3Cl_2$.[121]

On the *Trans* Isomers of $Ru(CO)_4(MX_3)_2$

The $Ru(CO)_4(MX_3)_2$ (X = Cl or Br) derivatives may either have a *cis*- or *trans*-configuration. These possibilities are shown in 2.23 and 2.24 respectively.



cis
2.23



trans
2.24

If C_{2v} symmetry is assumed for the *cis*-structure, a maximum of four infrared-active carbonyl stretching fundamentals are predicted ($2A_1 + B_1 + B_2$). If the symmetry of the MX_3 group is neglected, the *trans*- isomer has D_{4h} symmetry, for which group theory predicts just one infrared-active carbonyl stretching vibration (E_u). Thus in cases of *cis-trans* isomerization, the infrared makes an unambiguous distinction between the two forms (see for example Fig. 2.8 and 2.9).

That the $Ru(CO)_4(MX_3)_2$ compounds isolated here were *trans* isomers, as evidenced by a single sharp carbonyl resonance in the infrared, is surprising. Only in the case of $Ru(CO)_4(GeCl_3)_2$ was the *cis*-isomer isolated, and then

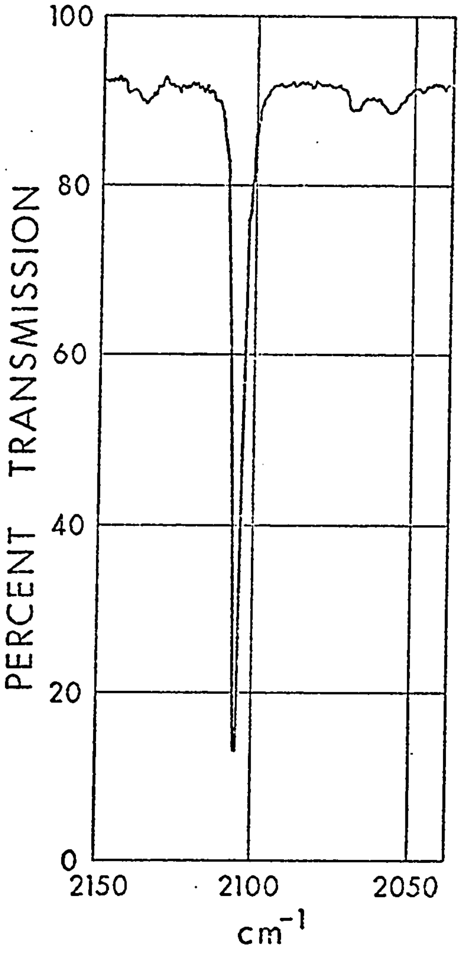


FIGURE 2.8

Infrared spectrum of *trans*-Ru(CO)$_4$(GeCl$_3$)$_2$ (cyclohexane solution).

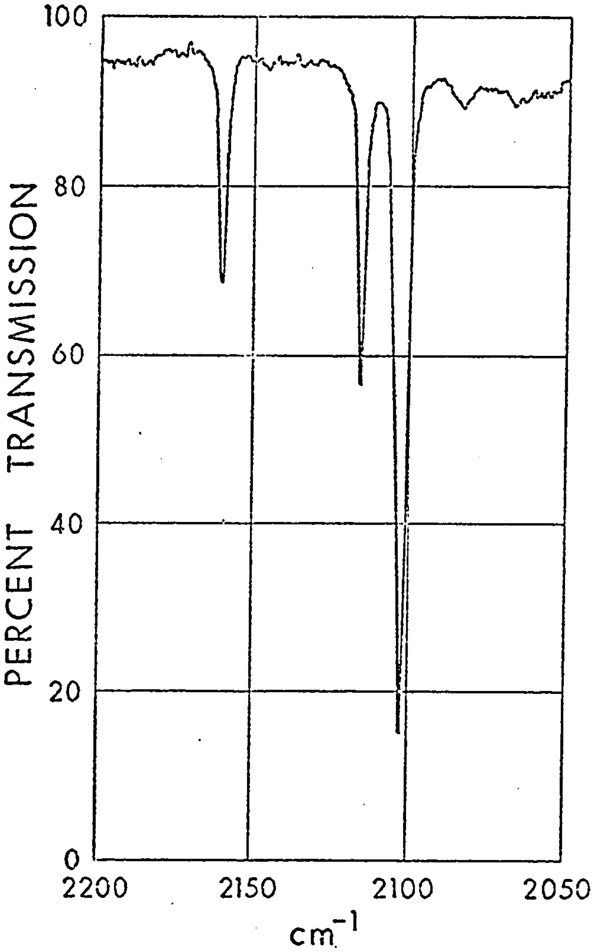


FIGURE 2.9

Infrared spectrum of *cis*-Ru(CO)$_4$(GeCl$_3$)$_2$ (cyclohexane solution).

only in trace amounts. This is in contrast to the iron analogues [28] where the *cis*-isomers appeared to be the stable form. In the case of $Fe(CO)_4(MCl_3)_2$ (M = Sn or Ge) the *trans* isomers were isolated but these appeared to isomerize fairly quickly to the *cis* form in solution. In order to explain the 'anomolous' stability of *trans*-$Fe(CO)_4(GeX_3)_2$ (X = Br or I) steric hindrance was invoked. However, such arguments cannot be used to account for the stability of the *trans*-isomers in the present case since steric hinderance would be expected to be less with the larger ruthenium atom.

Several alternative explanations may be offered for this phenomenon. If one assumes that the MX_3 group, when bonded to ruthenium, has π-acceptor properties comparable to CO then both *cis*-and *trans*-conformations would be equally preferred from the electronic standpoint and steric factors would determine the structure. Stone and coworkers [25] have suggested that a possible reason for the stability of *trans*-$Ru(CO)_4(SnPh_3)_2$ is that electron delocalization *via* Ru-Sn dπ-dπ bonding can be more extensive with a linear Sn_2Ru sequence, than with a *cis*-configuration. It is difficult to see how this can be so. It also fails to consider the π-bonding of the carbonyl groups. If the SnX_3 moiety were a significantly better π-bonder than CO then it would be expected that the *cis*-conformation would again be the most stable since in this situation it avoids as far as possible two SnX_3 competing for the same π-density on the central atom.

If the MX_3 group were as good a π-acceptor as CO then it might be expected that the *trans*-bond weakening effects of both ligands would be comparable. This has already been illustrated for $Ru_2(CO)_5SnCl_6$ but this is even more evident in the bond lengths found [126] by X-ray crystallography, for *cis*-and *trans*-$Ru(CO)_4(GeCl_3)_2$. The structures are shown in Fig. 28 and 29. Detailed information of the parameters in these molecules is given in Tables 2.6-2.12. Riding corrections are very rarely applied to bond lengths and so uncorrected lengths are used here for comparison with other structures.

It can be seen from the bond lengths given in Table 2.6 and 2.9 that bond lengths whether *trans* to a $GeCl_3$ or CO group are, within experimental error, equal. It should be mentioned here that the differences between the Ru-C bond lengths in the two *cis*-molecules are not significant.

If $GeCl_3$ is a strong π-acceptor then π-bonding between the CO groups and ruthenium should be less than in other comparable compounds i.e., the Ru-C bond in the present structures should more closely approach a single bond. In agreement with this the Ru-C distances are longer than in other crystallographic studies so far reported of molecules which contain the Ru-CO entity:

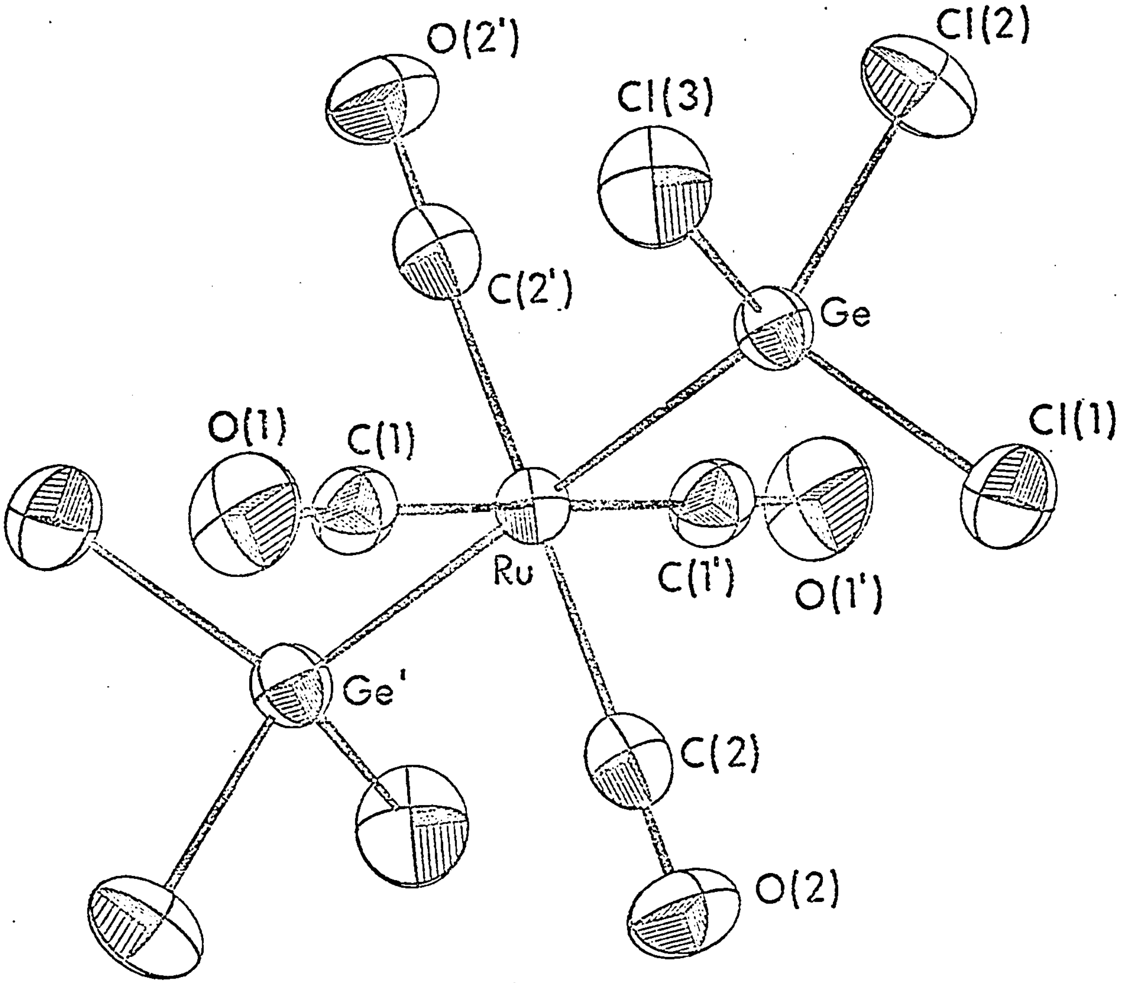


FIGURE 2.10 Structure of *trans*-Ru$(CO)_4(GeCl_3)_2$

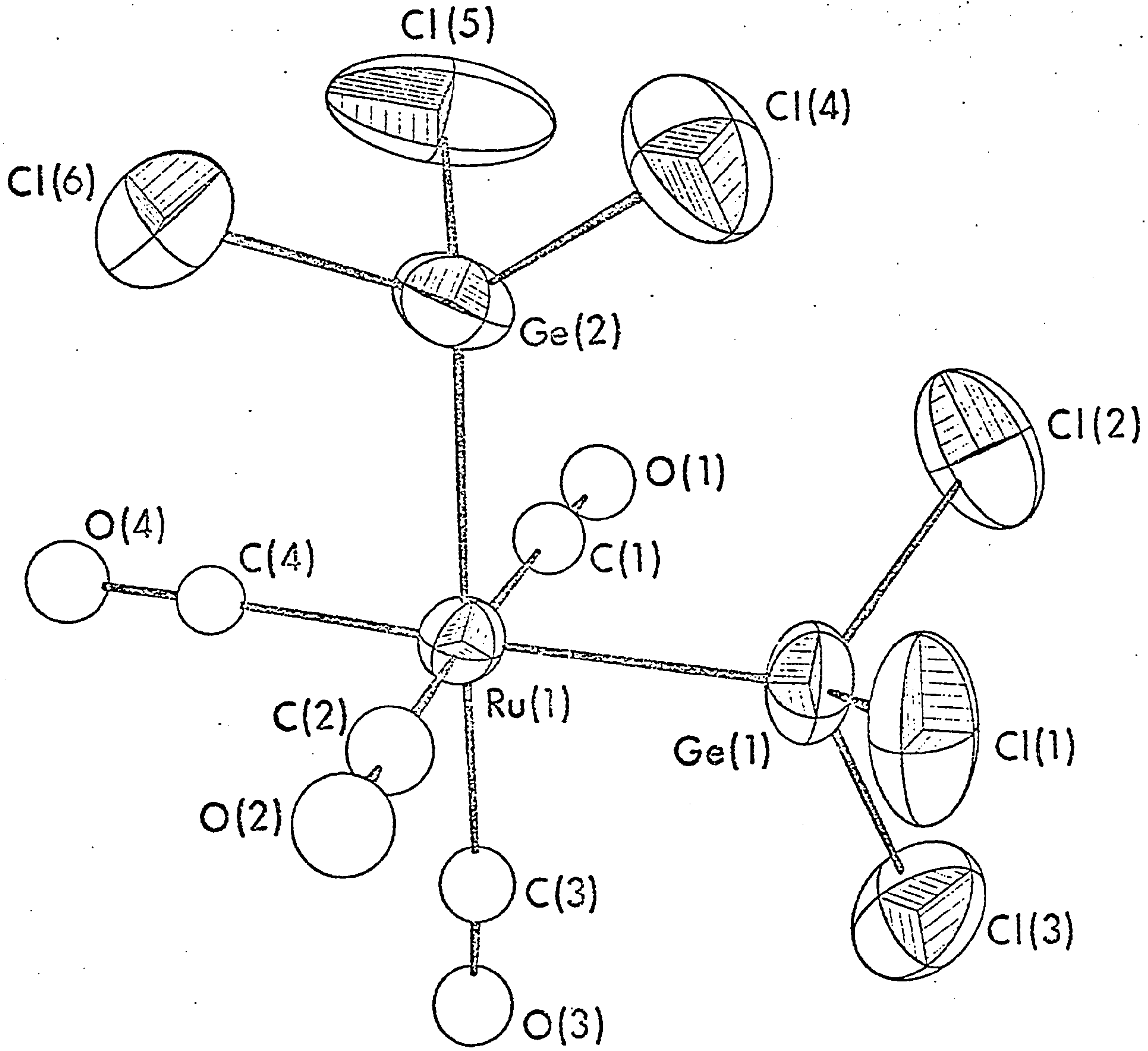


FIGURE 2.11 Structure of *cis*-$Ru(CO)_4(GeCl_3)_2$

TABLE 2.6

Bond Lengths of *trans*-$Ru(CO)_4(GeCl_3)_2$ With and Without Riding Corrections

Atoms	Distance	Corrected Distance
Ru-Ge	2.477(1)[a]	2.481(1)
Ru-C(1)	1.976(6)	1.980(6)
Ru-C(2)	1.980(6)	1.981(6)
Ge-Cl(1)	2.145(2)	2.166(2)
Ge-Cl(2)	2.160(2)	2.179(2)
Ge-Cl(3)	2.153(2)	2.171(2)
C(1)-O(1)	1.114(6)	1.154(7)
C(2)-O(2)	1.115(6)	1.151(7)

---

a = Numbers in parentheses are estimated standard deviations occurring in the last digit listed.

TABLE 2.7

Intramolecular Angles of *trans*-$Ru(CO)_4(GeCl_3)_2$

Atoms	Angle	Atoms	Angle
Ge-Ru-C(1)	90.0(1)[a]	Ru-C(1)-O(1)	179.3(5)
Ge-Ru-C(2)	89.8(1)	Ru-C(2)-O(2)	179.3(5)
C(1)-Ru-C(2)	88.9(2)		
Ru-Ge-Cl(1)	117.00(5)	Cl(1)-Ge-Cl(2)	102.7(1)
Ru-Ge-Cl(2)	114.33(5)	Cl(1)-Ge-Cl(3)	104.4(1)
Ru-Ge-Cl(3)	114.11(5)	Cl(2)-Ge-Cl(3)	102.6(1)

---

a = Numbers in parentheses are estimated standard deviations occurring in last digit listed

TABLE 2.8

Intramolecular Non-bonded Contacts (<4.0 Å) of *trans*-$Ru(CO)_4(GeCl_3)_2$

Atoms	Distance
Cl(1)....Cl(2)	3.36
Cl(1)....Cl(3)	3.40
Cl(2)....Cl(3)	3.37
Cl(1) - C(2)	3.54
Cl(2) - C(1)'	3.67
Cl(2) - C(2)'	3.67
Cl(3) - C(1)	3.42

TABLE 2.9

Intermolecular Non-bonded Contacts (<3.6 Å) for *trans*-$Ru(CO)_4(GeCl_3)_2$

Atoms	Distance	Symmetry postion of second atom		
Cl(1)-O(1)	3.42	½+x,	½-y,	½+z
Cl(1)-Cl(1)	3.52	-x,	1-y,	-z
Cl(2)-O(2)	3.45	½+x,	½-y,	½+z
Cl(3)-O(2)	3.35	-½+x,	½-y,	½+z
Cl(3)-C(2)	3.53	-½+x	½-y,	½+z
Cl(3)-C(1)	3.57	-½+x,	½+y,	½-z
Cl(3)-O(2)	3.60	x,	y,	1+z
O(1)-O(1)	3.06	-1-x,	-y,	-z
O(1)-O(2)	3.32	-½-x,	-½+y,	-½-z

TABLE 2.10

Selected Intramolecular Distances for *cis*-Ru(CO)$_4$(GeCl$_3$)$_2$

(i) Bondlengths in Å (standard deviations given in parentheses).

Atoms	Uncorrected distance	Corrected[a] distance	Atoms	Uncorrected distance	Corrected[a] distance
Ru(1)-Ge(1)	2.477(4)	2.487(5)	Ru(2)-Ge(3)	2.461(4)	2.466(5)
Ru(1)-Ge(2)	2.478(5)	2.488(6)	Ru(2)-Ge(4)	2.477(5)	2.484(5)
Ge(1)-Cl(1)	2.11(1)	2.18(1)	Ge(3)-Cl(7)	2.15(1)	2.19(1)
Ge(1)-Cl(2)	2.14(1)	2.19(1)	Ge(3)-Cl(8)	2.16(1)	2.19(1)
Ge(1)-Cl(3)	2.14(1)	2.18(1)	Ge(3)-Cl(9)	2.17(1)	2.19(1)
Ge(2)-Cl(4)	2.13(1)	2.17(1)	Ge(4)-Cl(10)	2.15(1)	2.18(1)
Ge(2)-Cl(5)	2.12(1)	2.20(1)	Ge(4)-Cl(11)	2.14(1)	2.19(1)
Ge(2)-Cl(6)	2.18(1)	2.22(1)	Ge(4)-Cl(12)	2.14(1)	2.17(1)
Ru(1)-C(1)	1.99(4)	2.03(4)	Ru(2)-C(5)	1.93(3)	1.96(4)
Ru(1)-C(2)	2.02(3)	2.04(4)	Ru(2)-C(6)	1.92(3)	1.96(4)
Ru(1)-C(3)	1.96(4)	2.00(5)	Ru(2)-C(7)	1.95(3)	1.97(4)
Ru(1)-C(4)	1.97(3)	1.99(4)	Ru(2)-C(8)	1.92(4)	1.97(4)
C(1)-O(1)	1.10(3)	-	C(5)-O(5)	1.16(3)	-
C(2)-O(2)	1.07(3)	-	C(6)-O(6)	1.16(3)	-
C(3)-O(3)	1.12(3)	-	C(7)-O(7)	1.14(3)	-
C(4)-O(4)	1.17(3)	-	C(8)-O(8)	1.13(4)	-

[a] Second atom assumed to ride on first.

(continued.......)

TABLE 2.10 (continued)

(ii) Non-bonded contacts (Å)

Atoms	Distance	Atoms	Distance	Atoms	Distance
Cl(1)-Cl(2)	3.36	Cl(11)-Cl(12)	3.37	C(1)-C(2)	2.88
Cl(1)-Cl(3)	3.38	Cl(2)-Cl(4)	3.60	C(1)-C(3)	2.84
Cl(2)-Cl(3)	3.33	Cl(1)-C(2)	3.33	C(1)-C(4)	2.84
Cl(4)-Cl(5)	3.35	Cl(2)-C(2)	3.53	C(2)-C(4)	2.91
Cl(4)-Cl(6)	3.28	Cl(5)-C(1)	3.42	C(3)-C(4)	2.90
Cl(5)-Cl(6)	3.34	Cl(6)-C(2)	3.56	C(5)-C(7)	2.81
Cl(7)-Cl(8)	3.37	Cl(6)-C(4)	3.57	C(5)-C(8)	2.73
Cl(7)-Cl(9)	3.38	Cl(7)-C(5)	3.41	C(6)-C(7)	2.79
Cl(8)-Cl(9)	3.35	Cl(8)-C(7)	3.26	C(6)-C(8)	2.79
Cl(10)-Cl(11)	3.34	Cl(11)-C(8)	3.35	C(7)-C(8)	2.87
Cl(10)-Cl(12)	3.31	Cl(12)-C(5)	3.61		

TABLE 2.11

Intramolecular Angles of *cis*-$Ru(CO)_4(GeCl_3)_2$

Atoms	Angle (°)	Atoms	Angle (%)
Ge(1)-Ru(1)-Ge(2)	91.5(2)	Ge(3)-Ru(2)-Ge(4)	90.5(1)
Ge(1)-Ru(1)-C(1)	87(1)	Ge(3)-Ru(2)-C(5)	89(1)
Ge(1)-Ru(1)-C(2)	87(1)	Ge(3)-Ru(2)-C(6)	88(1)
Ge(1)-Ru(1)-C(3)	87(1)	Ge(3)-Ru(2)-C(7)	88(1)
Ge(1)-Ru(1)-C(4)	178(1)	Ge(3)-Ru(2)-C(8)	178(1)
Ge(2)-Ru(1)-C(1)	90(1)	Ge(4)-Ru(2)-C(5)	87(1)
Ge(2)-Ru(1)-C(2)	86(1)	Ge(4)-Ru(2)-C(6)	88(1)
Ge(2)-Ru(1)-C(3)	178(1)	Ge(4)-Ru(2)-C(7)	177(1)
Ge(2)-Ru(1)-C(4)	87(1)	Ge(4)-Ru(2)-C(8)	88(1)
C(1)-Ru(1)-C(2)	173(1)	C(5)-Ru(2)-C(6)	174(2)
C(1)-Ru(1)-C(3)	92(2)	C(5)-Ru(2)-C(7)	93(1)
C(1)-Ru(1)-C(4)	92(1)	C(5)-Ru(2)-C(8)	90(2)
C(2)-Ru(1)-C(3)	93(1)	C(6)-Ru(2)-C(7)	93(2)
C(2)-Ru(1)-C(4)	94(1)	C(6)-Ru(2)-C(8)	93(2)
C(3)-Ru(1)-C(4)	95(1)	C(7)-Ru(2)-C(8)	96(2)
Ru(1)-Ge(1)-Cl(1)	115.1(3)	Ru(2)-Ge(3)-Cl(7)	117.3(3)
Ru(1)-Ge(1)-Cl(2)	114.7(3)	Ru(2)-Ge(3)-Cl(8)	112.3(3)
Ru(1)-Ge(1)-Cl(3)	114.2(3)	Ru(2)-Ge(3)-Cl(9)	118.5(3)
Ru(1)-Ge(2)-Cl(4)	122.1(4)	Ru(2)-Ge(4)-Cl(10)	118.1(3)
Ru(1)-Ge(2)-Cl(5)	114.2(4)	Ru(2)-Ge(4)-Cl(11)	114.8(3)
Ru(1)-Ge(2)-Cl(6)	112.8(3)	Ru(2)-Ge(4)-Cl(12)	114.4(3)
Cl(1)-Ge(1)-Cl(2)	103.3(4)	Cl(7)-Ge(3)-Cl(8)	102.5(4)
Cl(1)-Ge(1)-Cl(3)	105.1(4)	Cl(7)-Ge(3)-Cl(9)	102.7(4)
Cl(2)-Ge(1)-Cl(3)	103.1(4)	Cl(8)-Ge(3)-Cl(9)	101.1(4)
Cl(4)-Ge(2)-Cl(5)	104.1(4)	Cl(10)-Ge(4)-Cl(11)	102.3(4)
Cl(4)-Ge(2)-Cl(6)	99.1(4)	Cl(10)-Ge(4)-Cl(12)	101.4(4)
Cl(5)-Ge(2)-Cl(6)	101.7(5)	Cl(11)-Ge(4)-Cl(12)	103.9(4)

(continued....)

TABLE 2.11 (continued)

Ru(1)-C(1)-O(1)	174(4)	Ru(2)-C(5)-O(5)	175(3)
Ru(1)-C(2)-O(2)	178(3)	Ru(2)-C(6)-O(6)	176(3)
Ru(1)-C(3)-O(3)	173(4)	Ru(2)-C(7)-O(7)	178(4)
Ru(1)-C(4)-O(4)	178(3)	Ru(2)-C(8)-O(8)	177(3)

Standard deviations are in parentheses and refer to the last digit quoted.

TABLE 2.12

Selected (<3.6 Å) Intermolecular Contacts for

cis-Ru(CO)$_4$GeCl$_3$)$_2$

Atoms	Distance (Å)	Position of Second Atom
Cl(1)-O(5)	3.41	x, y, 1+z
Cl(1)-O(7)	3.38	x, y, 1+z
Cl(2)-O(6)	3.41	1+x, y, 1+z
Cl(2)-O(7)	3.36	1+x, y, 1+z
Cl(4)-O(6)	3.57	-x, +y, -z
Cl(4)-O(8)	3.52	-x, +y, -z
Cl(5)-O(5)	3.43	1-x, +y, -z
Cl(6)-O(4)	3.55	1-x, +y, -z
Cl(7)-O(7)	3.31	-x, +y, -1-z
Cl(8)-O(7)	3.44	-x, +y, -1-z
Cl(8)-O(8)	3.49	-x, +y, -1-z
Cl(9)-O(2)	3.39	-x, +Y, -z
Cl(9)-O(3)	3.56	-x, y, -z
Cl(10)-O(1)	3.53	-1+x, y, z
Cl(10)-O(3)	3.46	-x, +y, -z
Cl(10)-O(4)	3.48	-1+x, y, z
Cl(11)-O(2)	3.47	x, y, z
Cl(12)-O(4)	3.33	x, y, z
Cl(1)-C(5)	3.53	x, y, 1+z
Cl(1)-C(7)	3.54	x, y, 1+z

(continued........)

Table 2.12 (continued)

Atoms	Distance (Å)	Position of Second Atom
Cl(2)-C(7)	3.57	1+x, y, 1+z
Cl(8)-C(7)	3.50	-x, +y, -1-z
Cl(8)-C(8)	3.52	-x, +y, -1-z
Cl(9)-C(2)	3.57	-x, +y, -z
Cl(9)-C(9)	3.60	-x, +y, -z
Cl(12)-C(2)	3.57	x, y, z
Cl(12)-C(4)	3.53	x, y, z
Cl(6)-Cl(12)	3.51	x, y, z
Cl(7)-Cl(3)	3.58	1-x, +y, -z
Cl(5)-Cl(11)	3.47	1-x, +y, -z
O(1)-O(7)	3.45	1+x, y, 1+z
O(4)-O(6)	3.33	1+x, y, z
C(2)-O(8)	3.57	-x, +y, -z
O(6)-O(3)	3.43	-x, +y, -z

1.92 Å for $Ru_3(CO)_{12}$	17
1.93 Å for $[Ru(CO)_3Br_2]_2$	123
1.89 Å for $Ru_2(CO)_5SnCl_6$	80
1.87 Å for $[(Me_3Sn)(OC)_3RuSnMe_2]_2$	57

Also the CO bond length of 1.115 Å found for the *trans*-compound is shorter than in other transition metal carbonyl compounds (~1.15 Å)[1] consistent with greater triple bond character. The present two structures may be compared with those of $Cr(CO)_5P(Ph_3)_3$ and $Cr(CO)_5P(OPh)_3$ (Table 2.13)[127] where the π-bonding capability of the ligands involved is believed to be CO > $P(OC_6H_5)_3$ > $P(C_6H_5)_3$.

Also consistent with a strong π-bonding character for the $GeCl_3$ ligand are the very high CO stretching frequencies observed for *cis*- and *trans*-$Ru(CO)_4(GeCl_3)_2$ (Table 2.1). According to the presently accepted description of the bonding (see Chapter 1), as the extent of back donation from Ru to CO decreases the M-C bond becomes weaker, the C-O bond becomes stronger and the C-O stretching frequency increases.

Although the strong π bonding concept is, at present, the most attractive explanation for the occurrence of stable *trans*-isomers, there are some inconsistencies. If there is less π-bonding in the Ru-C bonds of *trans*-$Ru(CO)_4(GeCl_3)_2$ than in typical metal carbonyls, it might be expected that these bonds would be rather weak. Yet this is not the case

TABLE 2.13 [127]

Some Bond Lengths for $Cr(CO)_5PPh_3$ and $Cr(CO)_5P(OPh)_3$

Bond	Phosphite	Phosphine
Cr-P	2.309(1)	2.422(1)
Cr-C *(trans)*	1.861(4)	1.844(4)
C-O *(trans)*	1.136(6)	1.154(5)
Cr-C *(cis, av)*	1.896(4)	1.880(4)
C-O *(cis, av)*	1.131(6)	1.147(6)

(numbers in parentheses are standard deviations) since *trans*-$Ru(CO)_4(GeCl_3)_2$ is an air stable, crystalline solid, high melting for an organometallic compound (236°) and does not exchange with ^{13}CO in solution (see Chapter 4).

Compounds are known which have very high CO stretching frequencies and yet appear stable as the *cis*-isomer, e.g., *cis*-$Ru(CO)_4Br_2$ (2181w, 2125s, 2112s, 20812).[122] Likewise *trans*-isomers are known, and do not isomerize, which have relatively low CO stretching fundamentals e.g., *trans*-$Ru(CO)_4(SnPh_3)_2$ (2097vw, 2055vw, 2029s).[25] There may be steric factors involved in this last case although, if this were the dominating factor, it should be more extreme in the case of $Fe(CO)_4(SnPh_3)_2$; yet the latter compound seems stable in the *cis*-configuration.

Of course, it should not be forgotten that more than one factor influences carbonyl stretching frequencies.[65]

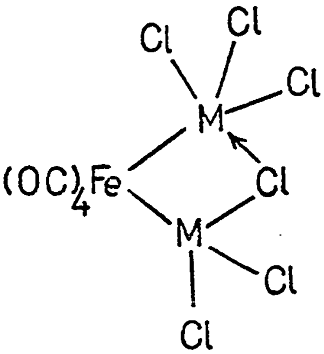
It might be expected that the π-acceptor properties of the MX_3 group when bonded to a particular transition metal would vary considerably with the identiy of M due to the different energies of the d-orbitals involved. However, as noted in this and other studies,[38] there is little difference between Cl_3Si, Cl_3Ge and Cl_3Sn as ligands. The relative proportions of *cis*-and *trans*-isomers found for a particular group IV element may be explained on the size of the MX_3 ligands (details of $Ru(CO)_4(SiCl_3)_2$ will be presented in Chapter 3). The carbonyl stretching frequencies in the series *trans*-$Ru(CO)_4(MCl_3)_2$ (M = Si, Ge or Sn) are almost invariant and the small difference between the individual frequencies may be attributed to the different electronegativities of M.[65,128] Similarly, on going from iron to ruthenium to osmium, one might expect the *cis*-isomer to be stable for some cases, yet this appears not to be so - the *trans*-isomer becomes increasingly favored.

As previously stated if the π-acceptor properties of MX_3 were better than CO then one would predict that the *cis*-isomer would again become the stable form i.e., only for a narrow spectrum of π-acid character would the *trans*-isomers be stable.

With regard to the formation of the *trans*-isomer on going down the periodic table, it appears from the work of Pańkowski and Bigorgne that $Os(CO)_4I_2$ is stable as the *trans*-isomer, implying that the iodide ligand is as good a π-acceptor when bonded to osmium as carbon monoxide; this, of course, is completely incompatible with current ideas of bonding in these compounds.

Bonding interaction of the MX_3 moiety with neighbouring carbon monoxide groups has been postulated in other compounds,[76] (Chapter 1). This could account for the stability of the *trans*-isomers since in such a configuration the MX_3 group can interact with all four carbonyls, as opposed to only two in the *cis*-form. However, it is difficult to see why this does not take place in the case of iron since here the group IV atom should be in even closer contact with the CO groups.

It should be mentioned here that other interactions have been suggested [28] in regard to this type of compound. In order to explain the greater solubility of *cis*-$(OC)_4Fe(MCl_3)_2$ as compared to its *trans*-analogue, an intramolecular coordination process shown in 2.30 was put forward. Such interaction might favor one isomer over the other;



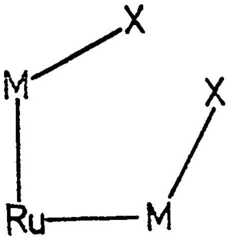
2.30

however, in the case of *cis*-and *trans*-$Ru(CO)_4(GeCl_3)_2$ no such bonding took place, although they show similar properties to the iron compounds with regard to solubility.

The structural determination of the *cis*-isomer went further to show that the $GeCl_3$ group was in fact a rather compact ligand when bonded to ruthenium and that interaction between chlorine atoms does not provide a source of steric repulsion.[126]

From the structures of *cis*-and *trans*-$Ru(CO)_4(GeCl_3)_2$ it was not possible to say that the latter molecule was sterically the most unhindered.

Caution must be used when discussing the steric interactions within the *cis*-molecule. There are two opposing effects on going to a group IV element lower in the periodic table. One is the increase in the Ru-M bond (see 2.31) which would be expected to lessen interaction between neighbouring X groups. An opposing effect is the increase in M-X distance



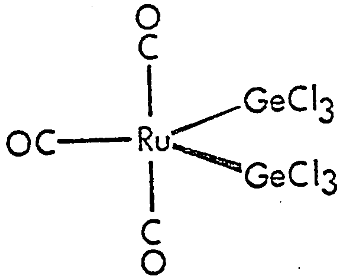
2.31

which may cause the repulsion between X groups to become important (especially for large X groups). For example it cannot from a cursory consideration be said that there is less steric hindrance in *cis*-$Ru(CO)_4(SiCl_3)_2$ than in *cis*-$Ru(CO)_4(SnCl_3)_2$.

The last point may explain why $Fe(CO)_4(SnBr_3)_2$ appears stable as the *cis*-form whereas the germanium analogue is stable as the *trans*-molecule.

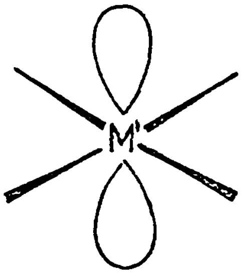
It is noted that in many of these compounds of 'anomalous' stereochemistry the groups which are attached to the central atom are fairly electronegative. It may be that these electronegative ligands remove electron density from the transition metal *via* an inductive mechanism, making π-bonding less important in these compounds. In such a situation one could visualize that π-bonding would be unimportant and again steric requirements would dictate a particular configuration. This theory does not assume that the π-acceptor character of MX_3 is comparable to CO, but rather that in these particular compounds the π-character in all bonds is less important.

In Chapter 4, evidence will be presented that the stable configuration for the five-coordinate intermediate $[Ru(CO)_3(GeCl_3)_2]$ has the Cl_3Ge ligands in the equatorial positions (2.32). This may be considered as the 'better'

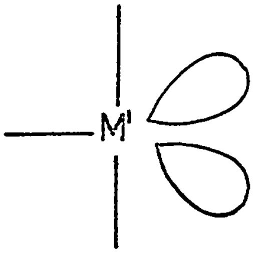


2.32

π-bonding group, Cl_3Ge, occupying the equatorial positions as is found for stable five-coordinate compounds of iron[130] e.g. $Fe(CO)_3(Ph_3)_2$. This proposed structure has the Cl_3Ge moieties *cis* to each other in contrast to the octahedral form where the system is more stable in a *trans* configuration This is reminiscent of positions adopted by lone pairs of electrons according to the Valence Shell Electron Pair Repulsion Theory (VSEPR)[131] i.e.,



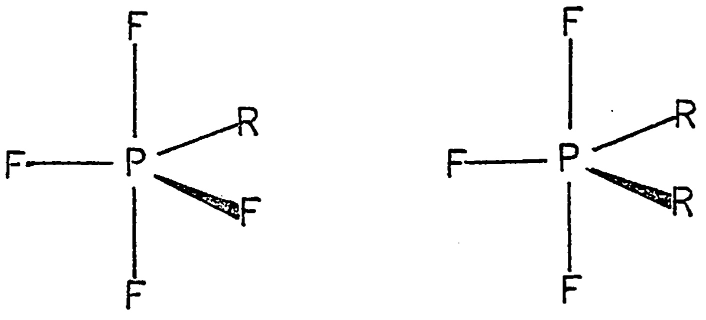
2.33



2.34

This prompts the idea that perhaps in these present compounds it is the bond pair - bond pair repulsions which determine the observed geometries.

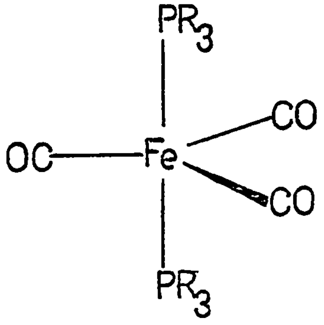
In a molecule which contains no lone-pairs of electrons it might be expected that the bond pairs which most resemble lone pairs would seek those positions in the various polyhedra that lone-pairs take up. Bonds to electronegative elements are believed to contain more p-character i.e., they are more directional.[132] Bonds to less electronegative elements are more diffuse and might be expected to behave more like lone-pairs. In agreement with this idea it is found that in five-coordinate compounds (particularly those of phosphorus) the more electronegative elements go into the axial positions and the less electronegative (like lone pairs) into the equatorial positions e.g.,



2.35

This idea has been suggested before.[131c]

Consider a bond in which π-density makes an important contribution. Such a linkage would have more diffuse electron density than one in which no π-bonding was associated. Thus it would be expected that π-bonds would behave in a similar manner to lone-pairs in their steric requirements. Hence a rationale for why the better π-bonding ligands enter the equatorial positions in five-coordinate compounds e.g.,



In agreement with this idea are the bond angle deformations found in carbonyl complexes. For example as mentioned in Chapter 1, in $Mn(CO)_5L$ and $Co(CO)_4L$ the equatorial carbonyls are displaced towards the L group.[76] As discussed in that

Chapter, this has been attributed to bonding interaction between L (when L is MX_3) and the carbonyls; however, repulsion between axial CO group and the other CO ligands is an alternative explanation. If the MX_3 group were as good (or better) π-acceptor as CO this theory would again anticipate the *trans*-configuration as the most stable in octahedral complexes. However, in the event that the MX_3 group was a much better π-acid than CO, then the present hypothesis would still predict the *trans*-geometry in contrast to the conventional π-bonding ideas which would lead one to expect the *cis* form.

The tendency to form the *trans*-isomer as one goes down the periodic table may also be explained. On going from a first-row transition element to a second-row member there is an increase in the M-C distance. It is possible that the maximum π-electron density is further from the central atom in second-row elements and hence repulsive forces between neighbouring M-CO groups would be reduced. It is also possible that there is less π-overlap with second-row elements because the orbitals on the metal do not match so closely those π*-orbitals on the carbon monoxide. In contrast to this last situation, it is quite likely that there is better π-overlap in some of the $M'-MX_3$ bonds when M' is changed from a first into a second-row transition metal. Hence one might expect such bonds to behave more like lone-pairs.

An explanation of why $Os(CO)_4I_2$ appears stable as the *trans*-isomer may be offered. Here it is proposed that the Os-I does contain electron density of a π-nature, arising from donation from the filled p-orbitals on iodine to the d-orbitals of osmium. Such a bonding situation has been suggested before for halogens in carbonyl compounds.[65]

EXPERIMENTAL

General Techniques:

Unless otherwise stated reactions were carried out under a nitrogen atmosphere using Schlenk-tube apparatus. Hydrocarbon solvents were dried by distilling them from calcium hydride and storing them before use over sodium. Dichloromethane was dried using P_2O_5, distilled, and stored over $CaCl_2$ in the dark. The sealed tubes used in this work were constructed of thick-walled Pyrex glass with a volume of about 80 ml. These were sealed with a standard Teflon valve and placed in a cylindrical furnace such that the Teflon seal protruded from the entrance and was unaffected by the high temperature of some of the reactions. This method had the advantage over conventional Carius tubes of being able to use the tubes described here repeatedly. Also with the present technique it was possible to take samples during the course of a reaction. This method is, however, less safe and precautions against possible explosion were taken. Reactions requiring high carbon monoxide pressure were carried out in a 200 ml Parr autoclave. The previously evacuated bomb was filled to the required pressure using the pressure of the tank.

Melting points were observed microscopically usihg a Kofler hot stage. Microanalyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Ellsach über Engelskirchen, West Germany, by Pascher Mickroanalytisches Laboratorium, Bonn and by the microanalytical laboratory of this department. Molecular weights determined by osmotic pressure were carried out either by Bernhardt (for $[Ru(CO)_3Cl_2]_2$) or by the analytical laboratory of this department. The magnetic properties of $Ru_2(CO)_5SnCl_6$ were investigated by Mr. D. Day of this department. Mass spectra were taken with an Associated Electrical Industries MS-9 or MS-12 instrument, using direct introduction of solid samples. In many cases computer simulated patterns were used to facilitate the interpretation of mass spectra. The program employed for this purpose was written by Drs. R. S. Gay and E. H. Brooks of this department. Infrared spectra in the carbonyl stretching region were measured using a Perkin-Elmer Model 337 (grating) spectrometer equipped with a Hewlett Packard Model 7127A recorder for scale expansion. The expanded spectrum obtained (100 cm^{-1} = 13 cm of chart paper) was calibrated by introducing a gas cell containing carbon monoxide into the sample beam at the appropriate time during the running of the spectrum. The resulting spectrum was then placed on a previously calibrated, illuminated scale and the known peak of CO band number 31 aligned at the appropriate place on this scale and the values of the unknown absorptions read off. The scale was checked from time to time by using this procedure for gas samples of DCl and DBr. The results obtained were compared with the accepted values[148]; in no case was the difference between the observed and the literature values greater than 1 cm^{-1}.

The starting material used in the preparation of $Ru_3(CO)_{12}$ was $RuCl_3.\sim 3H_2O$ as obtained from either A. D. Mackay, Inc., 198 Broadway, New York, N.Y. 10038 or Engelhard, 113 Astor St., Newark, New Jersey 07114; it contained 38-40% ruthenium. The method used for the synthesis of $Ru_3(CO)_{12}$ is essentially that of Bruce and Stone [121], however it does differ in some subtle ways from the original and so is reported here in detail. These differences were found to be essential for good yields of the carbonyl. Two low pressure synthesis of $Ru_3(CO)_{12}$ have recently appeared in the literature.[149] Published procedures [133] were used for the preparation of germanium(IV) iodide, and tin IV bromide and iodide. Other reagents were available commercially and used without further purification.

Analytical, spectroscopic and other pertinent data for the compounds described here are given in Tables 2.14-2.18. Representative infrared spectra have been shown.

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

The zinc metal used was in the form of a perforated sheet, known to the trade as 'fanning mill sheet'. A sheet approximately 4 in x 40 in was rolled into a tight spool and fitted into the top half of a 480 ml autoclave. In the bottom half was placed $RuCl_3 \cdot \sim 3H_2O$ (7.0 g) in methanol (200 ml). The autoclave was pressurized with approximately 30 atm. of carbon monoxide and heated to 65°. When these conditions had been achieved rocking of the bomb was commenced i.e., the zinc sheet and methanolic solution were brought into contact. Rocking was continued for 24-30 hr. The reaction vessel was then cooled and the gas vented. The methanol was decanted, from the sheet and other insoluble matter, and used again. The perforated sheet, which had crystals of $Ru_3(CO)_{12}$ stuck to it, and all insoluble material from the bottom of the autoclave were transferred to an 800 ml beaker. The contents were then extracted with two 500 ml portions of boiling benzene (fume hood). The extracts were filtered and allowed to stand at 6° overnight. The benzene was then removed and the $Ru_3(CO)_{12}$ washed with n-hexane and dried under vacuum. Yields of 60-75% (3.5-4.5 g) were generally obtained.

Preparation of $Ru(CO)_5$ from $Ru_3(CO)_{12}$.

An autoclave containing $Ru_3(CO)_{12}$ (0.64 g, 1.0 mmol) in heptane (20 ml) was pressurized with carbon monoxide (140 atm) and heated at 100° for 24 hr. The vessel was cooled and the carbon monoxide vented. The solution was distilled under high vacuum, with the exclusion of light, through a trap kept at -198°. Under these conditions heptane and $Ru(CO)_5$ collected in the trap together. The product was characterized by its infrared spectrum (2038s, 2002s in heptane, Lit:[134] 2035 and 1999 cm^{-1}). From the $Ru_3(CO)_{12}$ remaining in the autoclave after the distillation it was estimated that the reaction was 90% complete. Even by storing the initially colorless solutions of $Ru(CO)_5$ in the refrigerator with the exclusion of light, decomposition to $Ru_3(CO)_{12}$ occurred. This was in contrast to $Os(CO)_5$ which appeared stable under comparable conditions.

Preparation of $Ru_3(CO)_{12}SnCl_4$.

A suspension of $Ru_3(CO)_{12}$ (0.64 g, 1 mmol) in benzene (25 ml) was stirred with $SnCl_4$ (1 ml, 8.6 mmol) at room temperature. After 40 min (there was no appreciable evolution of gas during this time) a fine yellow solid had formed. Benzene was removed and the product washed twice with 25 ml portions of n-hexane and dried under vacuum. The yield was almost quantitative. The analytical sample was obtained in the form of yellow platelets by recrystallization from $CH2Cl_2$-n-hexane at -78°.

The compound decomposes when kept in CH_2Cl_2 for long periods. Solutions of $Ru_3(CO)_{12}SnCl_4$ in CH_2Cl_2 are initially green but rapidly turn yellow on exposure to light. The green color is partially restored by storage in the dark.

The compound is stable for short periods in air but decomposes above 80° without melting. It was too insoluble for a molecular weight determination and insufficiently volatile, below its decomposition temperature, for a mass spectrum.

Preparation of Tri-μ-iodo(triiodotin)pentacarbonyldiruthenium.

A solution of $Ru_3(CO)_{12}$ (0.64 g, 1 mmol) and SnI_4 (1.9 g, 3 mmol) in toluene (25 ml) was stirred at 100° for four hours. The solution was filtered hot to remove a precipitate consisting mainly of SnI_2 but also containing some carbonyl compound, probably $[Ru(CO)_2I_2]_n$. The filtrate was allowed to stand in the refrigerator overnight whereupon red, crystalline, $Ru_2(CO)_5SnI_6$ (1.4 g, 78%) was obtained. The compound was washed with n-hexane and dried under vacuum. It may be recrystallized from CH_2Cl_2-n-hexane or from benzene.

The mother liquor was evaporated to dryness and the resulting residue extracted with n-hexane. An infrared spectrum of this extract showed only the carbonyl stretching bands of *cis*-$Ru(CO)_4I_2$.

The bromide $\underline{Ru_2(CO)_5SnBr_6}$ was prepared in a similar manner.

In the reactions of GeI_4 and $GeBr_4$ there was an initial formation of an unidentified precipitate. However, continued stirring for four days gave the desired products

$Ru_2(CO)_5GeBr_6$ and $Ru_2(CO)_5GeI_6$. The workup procedure was similar to that of the SnI_4 compound. Both bromides may be sublimed at ca. 135°/0.01 mm.

Preparation of Tri-μ-chloro(trichlorotin)pentacarbonyldiruthenium, $Ru_2(CO)_5SnCl_6$.

A xylene solution (25 ml) of $Ru_3(CO)_{12}$ (0.64 g, 1.0 mmol) and tin(IV) chloride (1.0 ml, 8.6 mmol) was stirred at 135° for 90 min. The hot solution was then filtered to remove tin(II) chloride (0.28 g, 1.48 mmol) and placed in the refrigerator. The essentially pure $Ru_2(CO)_5SnCl_6$ (0.95 g, 94%) was washed with n-hexane and dried under vacuum. The compound may be recrystallized from CH_2Cl_2-n-hexane or sublimed at 110°/0.01 mm.

Attempts to prepare $Ru_2(CO)_5SnCl_6$ at 100° led to the formation of small amounts of *trans*-$Ru(CO)_4(SnCl_3)_2$ which could not be conveniently separated from $Ru_2(CO)_5SnCl_6$.

A magnetic study, by the Faraday method, revealed $Ru_2(CO)_5SnCl_6$ to be diamagnetic.

Preparation of Tri-μ-chloro(trichlorogermanium)pentacarbonyldiruthenium and *cis* and *trans*-bis(trichlorogermanium)tetracarbonylruthenium.

Germanium (IV) chloride (3.0 ml, 26 mmol) and $Ru_3(CO)_{12}$

Leaf 132 omitted in page numbering.

(1.92 g, 3 mmol) in 20 ml of benzene were heated to 150° in a sealed tube. After 24 hr, the tube was slowly cooled and excess $GeCl_4$ and solvent removed under vacuum. The resulting product was extracted with five 50 ml portions of ice-cold CH_2Cl_2. The insoluble material which, at this stage, showed only one carbonyl stretching band in the infrared, was recrystallized from hot CH_2Cl_2 to give white, crystalline *trans*-$Ru(CO)_4(GeCl_3)_2$ (1.2 g, 24%).

The CH_2Cl_2 extracts were combined and solvent removed on the rotary evaporator. Slow sublimation of the remaining solid at 35°/0.01 mm gave *cis*-$Ru(CO)_4(GeCl_3)_2$ (36 mg, 0.7%). Very careful sublimation at 65° then gave more *trans*-$Ru(CO)_4(GeCl_3)_2$ (0.33 g, 6.4%). Finally, sublimation at 105°/0.01 mm gave pure $Ru_2(CO)_5GeCl_6$ (1.83 g, 48%).

That the *cis*- and *trans*-isomers were in equilibrium at 150° was shown by the following observations:

(1) The composition of the products was not changed by allowing the reaction to proceed for a longer time.

(2) Heating a solution of *cis*-$Ru(CO)_4(GeCl_3)_2$ under CO pressure (>4 atm) to 150° resulted in its conversion almost entirely to the *trans*-isomer.

(3) Heating the pure *trans*-compound under similar conditions produced a small amount of the *cis* compound. This was shown by evaporating the sample to dryness

and extracting with n-hexane, in which the *cis* compound is more soluble. An infrared spectrum of this extract also showed that some $Ru_2(CO)_5GeCl_6$ had also been formed. (Heating *trans*-$Ru(CO)_4(GeCl_3)_2$ to 150° in the absence of CO and in an inert solvent produces $Ru_2(CO)_5GeCl_6$.

Differential thermal analysis, using a DuPont 900 Differential Thermal Analyser, of *trans*-$Ru(CO)_4(GeCl_3)_2$ revealed no abnormalities below its melting point i.e., there was no lamda point.

Irradiation of solutions of *trans*-$Ru(CO)_4(GeCl_3)_2$ under a CO atmosphere gives the *cis*-isomer exclusively. This did not appear to be a good method for producing the *cis*-isomer in large quantities since prolonged irradiation caused decomposition (see however ref. 36 - note yield). Both compounds appear to be stable in solution under normal conditions and show no signs of interconverting. The *cis*-compound is more soluble in non-polar solvents than the *trans*-isomer.

In contrast to the tin analogue, $Ru_2(CO)_5GeCl_6$ is quite soluble in non-polar solvents.

<u>*Trans*-$Ru(CO)_4(GeBr_3)_2$</u> was prepared as was *trans*-$Ru(CO)_4(GeCl_3)_2$, except that the entire product was separated from $Ru_2(CO)_5GeBr_6$ by sublimation at 80°/0.01 mm. Although there was no evidence for *cis*-$Ru(CO)_4(GeBr_3)_2$, an

infrared spectrum of the reaction mixture showed a third product with two infrared bands (at 2096 and 2066 cm^{-1}, CH_2Cl_2 solution). This compound believed to be $Ru_2(CO)_6GeBr_6$ has not yet been isolated.

A similar reaction with GeI_4 failed to produce any $Ru(CO)_4(GeI_3)_2$ although again a product having two bands in the infrared (2082 and 2055 cm^{-1}, CH_2Cl_2 solution) was observed. However it decomposed during workup.

Preparation of *Trans*-$Ru(CO)_4(SnCl_3)_2$.

A solution of $Ru_3(CO)_{12}$ (0.64 g, 1 mmol) and $SnCl_4$ (3 ml, 26 mmol) in benzene (20 ml) was pressurized in an autoclave with carbon monoxide (70 atm). It was then heated at 150° overnight. The autoclave was cooled to ca 50°, the gas vented, and the solution filtered from the almost pure *trans*-$Ru(CO)_4(SnCl_3)_2$ (0.75 g, 37.5%) which was washed with hexane and dried under vacuum. Further cooling of the filtrate gave additional *trans*-$Ru(CO)_4(SnCl_3)_2$ (0.22 g, 11%). A contaminant of $[Ru(CO)_3Cl_2]_2$ present in small amounts was removed by washing with cold CH_2Cl_2. The analytical sample of *trans*-$Ru(CO)_4(SnCl_3)_2$ was obtained by recrystallization from hot CH_2Cl_2.

An infrared spectrum of the mother liquor was complicated but the main component was identified as $[Ru(CO)_3Cl_2]_2$. One of the minor products, $Ru(CO)_4Cl_2$, could also be identified from its infrared spectrum, but as found by other workers, this compound could not be isolated.

Trans-$Ru(CO)_4(SnCl_3)_2$ is insoluble in non-polar organic solvents and sparingly soluble in polar solvents. Some indication of ths solubility is that ca 150 ml of boiling CH_2Cl_2 were required to dissolve 0.45 g of the compound. *Trans*-$Ru(CO)_4(SnCl_3)_2$ may be sublimed at 110°/0.01 mm.

Trans-$Ru(CO)_4(SnBr_3)_2$ was prepared similarly except that after the initial filtration, the mother liquor was evaporated to dryness under vacuum and the residue sublimed at 80°/0.01 mm to remove $Ru(CO)_4Br_2$. Sublimation at 135° then gave pure *trans*-$Ru(CO)_4(SnBr_3)_2$.

Reaction of SnI_4 and $Ru_3(CO)_{12}$ under high CO pressure.

Dodecacarbonyltriruthenium (0.64 g, 1 mmol) and tin(IV) iodide (1.9 g, 3 mmol) in benzene (50 ml) were heated at 100°, under CO pressure (70 atm), for 12 hr. On cooling and venting the gas the product was found to consist almost entirely of $Ru(CO)_4I_2$ and SnI_2. The solution of $Ru(CO)_4I_2$ was filtered to remove SnI_2, and the solvent was removed under vacuum. Pure $Ru(CO)_4I_2$ could then be obtained either by recrystallization from n-hexane at -78° or by sublimation at 80°/0.01 mm. Use of higher temperatures failed to produce any $Ru(CO)_4(SnI_3)_2$. However, in these latter reactions there was evidence for *trans*-$Ru(CO)_4I_2$ (ν_{CO} = 2088

cm^{-1}, cyclohexane) in agreement with the work of Pańkowski and Bigorgne.[129]

GeI_4 reacted similarly while $GeBr_4$ gave mixtures of $Ru(CO)_4Br_2$ and $[Ru(CO)_3Br_2]_2$ which could be separated by sublimation of the monomer at 80°/0.01 mm; extraction of the remaining solid with CH_2Cl_2 gave the dimer.

Preparation of $[Ru(CO)_3Cl_2]_2$ from $GeCl_4$.

A solution of $Ru_3(CO)_{12}$ (0.64 g, 1 mmol) and $GeCl_4$ (3 ml, 26 mmol) in n-heptane 20 ml was heated overnight at 135° under carbon monoxide. The autoclave was then cooled and the gases vented. The solution was allowed to stand overnight in the refrigerator. Filtration gave a grey product which on sublimation at 105°/0.01 mm gave pure white $[Ru(CO)_3Cl_2]_2$ (0.68 g, 88%).

Subsequent preparations of this compound by this method have shown that yields are dependent on the exact conditions employed. Samples often contain $Ru_2(CO)_5GeCl_6$ which can however be removed by extraction into n-heptane.

The reaction of $Ru_3(CO)_{12}$ with $GeCl_4$ under CO pressure was studied under a variety of conditions. The results are given in Table 2.5.

Preparation of $[Ru(CO)_3Cl_2]_2$ from CCl_4.

An evacuated sealed tube containing $Ru_3(CO)_{12}$ (0.64 g, 1 mmol) and CCl_4 (25 ml) was heated at 160° for 22 hr. The sealed tube was allowed to cool to room temperature. The excess CCl_4 was then carefully removed at the water pump. The residue was then sublimed at 25°/0.01 mm in a closed container containing a cold water finger. The C_2Cl_6 (0.12 g) obtained was identified by a comparison with an authentic sample - infrared spectrum in the range 1300-400 cm^{-1}, mp, 187° (in sealed capillary), mass spectrum $(C_2Cl_5)^+$ (highest ion observed) and analysis (calcd for C_2Cl_6 C = 10.15, H = 0.0, found C = 9.63, H = 0.08).

After sublimation at room temperature the remaining product was sublimed at 110°/0.01 mm to give $[Ru(CO)_3Cl_2]_2$ (0.43 g, 57%).

In another experiment $Ru_3(CO)_{12}$ (0.32 g, 0.5 mmol) and CCl_4 (1 ml, 10 mmol) in 15 ml heptane were heated at 150° in an evacuated sealed tube for 16.5 hr. The yield of $[Ru(CO)_3Cl_2]_2$, which is insoluble in heptane, was 92%.

A similar yield was obtained when the reaction was carried out under 40 atm of carbon monoxide at 180°.

The behaviour of $[Ru(CO)_3Cl_2]_2$ in commercial chloroform has been discussed.

Preparation of $Ru_3(CO)_{10}Cl_2$.

A solution of $Ru_3(CO)_{12}$ (0.64 g, 1 mmol) and $SiCl_4$ (5 ml, 37.5 mmol) in heptane (30 ml) were heated at 125°, under 70 atm of carbon monoxide for 42 hr. The autoclave was allowed to cool and the gas vented. The solution was transferred to a Schlenk-tube under nitrogen and cooled to -78°. On the bottom of the reaction vessel a product, identified as $[Ru(CO)_3Cl_2]_2$ (0.10 g), from its infrared spectrum, was found.

After standing at -78° for several hours the heptane and excess $SiCl_4$ were separated from the product in the form of yellow-orange platelets. The product was recrystallized three times from hexane at -78°. There appeared to be no change in the infrared spectrum of $Ru_3(CO)_{10}Cl_2$ after these recrystallizations.

$Ru_3(CO)_{10}Cl_2$ is a yellow-orange crystalline solid which decomposes in air. It is however stable when stored under nitrogen or vacuum. Although it did not sublime under high vacuum, it did when heated at 60° in an evacuated sealed tube one end of which was maintained at room temperature (see discussion). After this procedure $Ru_3(CO)_{10}Cl_2$ was obtained as orange crystals.

The Reaction of $Ru_3(CO)_{12}$ with $SiCl_4$.

Silicon tetrachloride (3 ml, 26 mmol) and $Ru_3(CO)_{12}$ (0.64 g, 1 mmol) in heptane (10 ml) were heated in an evacuated sealed tube for two weeks. The tube was then slowly cooled to room temperature. The heptane solution was removed from a product consisting of white and yellow crystals. An infrared spectrum in heptane of the hand-picked yellow crystals revealed two bands (2090s, 2054s cm^{-1}).

This compound was tentatively assigned as $Ru_2(CO)_6SiCl_6$ (see discussion). It rapidly decomposed in solution and could not be obtained in sufficient quantity for definitive identification.

The heptane solution was evaporated to dryness and the residue combined with the solid precipitate. The resulting matter was sublimed at room temperature onto a probe at -78°. A minute amount of colorless crystals of *trans*-$Ru(CO)_4(SiCl_3)_2$ were obtained. This was identified by its infrared spectrum (2090 cm^{-1}, heptane) and its mass spectrum (calc 482, found: 482) (see Chapter 3).

Attempts to sublime the products at higher temperatures (~35°) resulted in mixtures being obtained. To partially overcome this the solid material was placed in an evacuated sealed tube along which a temperature gradient between 60-25° was maintained. In this way very slow sublimation took place giving three types of crystals. Two forms, pale yellow and colorless, accumulated in the same area of the tube and a small quantity were separated by hand. The pale yellow variety were identified as $[Ru(CO)_3SiCl_3]_2$ by infrared spectroscopy (2087m, 2059vs, 2051vw, (heptane) lit.[32] 2086w, 2056s, 2050wsh cm^{-1} (cyclohexane)) and by mass spectroscopy (calcd mass for parent ion = 696, obs. = 696). The colorless crystals were identified as $Ru_2(CO)_5SiCl_6$ by infrared spectroscopy. The third type of crystals was orange and identified as $Ru_3(CO)_{10}Cl_2$ by infrared spectroscopy.

Attempts to favor one product over the other by using a variety of conditions eg., temperatures up to 180°, reaction times of upwards of two weeks, were unsuccessful. In fact, in some of these reactions evidence for yet more products, as indicated by infrared analysis, was found.

Preparation of $Ru_2(CO)_5SiCl_6$.

A solution of $Ru_3(CO)_{12}$ (0.64 g, 1 mmol) and Cl_3SiH (2 ml, 20 mmol) in hexane (30 ml) was stirred for 21 days. Solvent and excess Cl_3SiH were removed under vacuum leaving a white solid. This was extracted with two 25 ml portions of hexane. The remaining product was identified as $[Ru(CO)_3Cl_2]_2$. The two hexane fractions were evaporated to dryness and the remaining material extracted with 10 ml of ice-cold hexane which removed in impurity believed to be $[Ru(CO)_4SiCl_3]_2$. The remaining product was dried and sublimed at 70°/0.01 mm to give $Ru_2(CO)_5SiCl_6$ (0.20 g, 23%).

Reaction of $Ru_2(CO)_5SnBr_6$ with Ph_3P.

To a solution of $Ru_2(CO)_5SnBr_6$ (0.47 g, 0.5 mmol) in benzene (25 ml) was added Ph_3P (0.52 g, 2.0 mmol) in benzene (25 ml). The resulting solution was refluxed for 30 min, allowed to cool partially and decanted from a small quantity of yellow oil which had formed. An infrared spectrum of the reaction solution at this stage showed that the only product present was $Ru(CO)_2(Ph_3P)_2Br_2$. Removal of the benzene and two recrystallizations from CH_2Cl_2-n-hexane gave the pure product.

Other compounds of the type $Ru_2(CO)_5MX_6$ reacted with Ph_3P similarly.

Reaction of $Ru_2(CO)_5SnBr_6$ with Carbon Monoxide.

An autoclave containing a solution of $Ru_2(CO)_5SnBr_6$ in benzene was pressurized with carbon monoxide (70 atm) and heated at 100° overnight. The reaction vessel was then cooled and the gas vented. An infrared spectrum of the reaction mixture showed that it contained mainly *cis*-$Ru(CO)_4Br_2$ plus a small amount of *trans*-$Ru(CO)_4(SnBr_3)_2$. Tin(II) bromide was also isolated. The products were the same using only 10 atm of CO at room temperature although the reaction took approximately a week to go to completion.

Reaction of $[Ru(CO)_3Cl_2]_2$ with $SnCl_2$.

An evacuated sealed tube containing $[Ru(CO)_3Cl_2]_2$ (0.256 g, 0.5 mmol) and $SnCl_2$ (0.095 g, 0.5 mmol) in benzene was heated at 150° for 13 hr. The reaction was then allowed to cool to room temperature and an infrared spectrum was taken of the solution. This revealed that some $[Ru(CO)_3Cl_2]_2$ was still present and so the tube was once again evacuated and heated for a further 20 hr. An infrared spectrum taken of the cooled reaction mixture at this stage revealed only $Ru_2(CO)_5SnCl_6$ present. The warm solution was filtered and hexane (10 ml) added and allowed to cool in the refrigerator. Crystals of $Ru_2(CO)_5SnCl_6$ (0.30 g, 89%) were washed with hexane and dried under vacuum.

Preparation of $Os_2(CO)_5GeCl_6$.

An evacuated sealed tube containing $Os_3(CO)_{12}$ (0.225 g, 0.25 mmol) and $GeCl_4$ (0.5 ml) in benzene (10 ml) were heated at 170° for 17 hr. The tube was allowed to cool and the solution evaporated to dryness. The solid material was sublimed at 65°/0.01 mm to remove *trans*-$Os(CO)_4(GeCl_3)_2$. After this procedure the remaining product was sublimed at 110°/0.01 to give $Os_2(CO)_5GeCl_6$. Recrystallization from CH_2Cl_2-pentane and a further slow sublimation failed to give a product with a satisfactory carbon analysis; mp 177-179. *Anal.* Calcd. for $Os_2(CO)_5GeCl_6$: C, 7.45; H, 0.0. Found: C, 8.26; H, 0.15. Mol. wt: found by mass spectrometry, 805; calcd. 805.8.

Preparation of $Os_2(CO)_5SnCl_6$. Method I.

An evacuated sealed tube containing $Os_3(CO)_{12}$ (0.091 g, 0.01 mmol) and $SnCl_4$ (0.25 ml) in benzene (10 ml) was heated at 150° for 20 hr. The solution was allowed to cool to approximately 60°, filtered (under nitrogen) and placed in the refrigerator. The white crystalline product of $Os_2(CO)_5SnCl_6$ (0.072 g, 66%) was washed with pentane and dried under vacuum. It appeared spectroscopically pure.

Attempts to repeat this reaction on a larger scale, in the same sealed tube (80 ml volume) were unsuccessful.

Method II.

A solution of $Os_3(CO)_{12}$ (0.225 g, 0.25 mmol) and $SnCl_4$ (0.5 ml) in toluene (10 ml) was heated at 110° for 7 days. The solution, which contained much decomposition material, was filtered hot and placed in the refrigerator. The resulting crude product was washed with hexane and dried under vacuum. The compound was recrystallized from CH_2Cl_2-pentane and then sublimed at 115°/0.01 mm to give the pure product (0.18 g, 56%); mp 194-195°. *Anal.* Calcd. for $Os_2(CO)_5SnCl_6$: C, 7.05; H, 0.0. Found: C, 7.88; H, 0.0. Mol. wt: found by mass spectrometry, 851; calcd, 851.

Preparation of $Os_2(CO)_8SnCl_4$.

(This experiment was first carried out by Dr. J. R. Moss). A xylene solution)20 ml) of $Os_3(CO)_{12}$ (0.225 g, 0.25 mmol) and $SnCl_4$ (0.5 ml, 2.2 mmol) were heated in an oil bath at 120° for two hours. The solution was then placed in the refrigerator overnight. The crude product was washed with n-hexane and dried under vacuum. Two recrystallizations from CH_2Cl_2-n-hexane gave a small amount of white crystalline product (ν_{CO} = 2068 cm^{-1} CH_2Cl_2 solution); mp ~200 decomp. Mol. wt: found by mass spectrometry, 866; calcd, 865.

TABLE 2.14

Analytical Data for $Ru_2(CO)_5MX_6$ Compounds

				Calculated %					Found %			
Compound	M.P. °C	Color	Mol. Wt.	C	H	O	X	Mol.Wt.[g]	C	H	O	X
$Ru_3(CO)_{12}SnCl_4$	d>80[b]	Yellow	——	16.0	0.0	21.3	15.8	——	16.2 15.9	0.3 0.1	21.2 20.9	15.5[a] 15.4[c]
$Ru_2(CO)_5SnCl_6$	d178	Pale Yellow	673.6	8.9	0.0	11.9	31.6	674	9.0	0.2	12.1	31.6
$Ru_2(CO)_5SnBr_6$	d193	Yellow	940.3	6.4	0.0	8.5	51.0	942	6.5	0.1	8.5	49.9
$Ru_2(CO)_5SnI_6$	d188	Red	1222.3	4.9	0.0	6.5	62.3	1095	5.1	0.1	6.7	61.5[e]
$Ru_2(CO)_5GeCl_6$	d185	White	627.5	9.6	0.0	12.8	33.9	627	9.7	0.0	12.8	33.6
$Ru_2(CO)_5GeBr_6$	d194	Yellow	894.2	6.7	0.0	9.0	53.6	895	6.9	0.2	9.1	54.4[f]
$Ru_2(CO)_5GeI_6$	d>200[b]	Orange	1176.2	5.1	0.0	6.8	64.7	1049	5.9	0.0	6.9	64.4
$Ru_2(CO)_5SiCl_6$	d142	White	583.0	10.3	0.0	13.7	36.5	584	10.8	0.1	13.7	34.9

X = halogen; a = as obtained from $PhSnCl_3$ reaction; b = without melting; c = Ru Calc., 13.2, found 12.7; d = decomposes; e = Ru, Calc. = 16.5, Found 15.2; Sn Calc = 9.7, Found = 9.9; f = Mol. Wt. Calc = 894, Found (CH_2Br_2) = 861; g = as found by mass spectrometry, most abundant ion; h = corresponds to parent ion minus iodine.

TABLE 2.15

Analytical Data for $Ru(CO)_4(MX_3)_2$ Derivatives and Carbonyl Halides

Compound	M.P. °C	Color	Mol.Wt.	Calculated % C	H	O	X	Mol.Wt.	Found % C	H	O	X
trans-$Ru(CO)_4(SnCl_3)_2$	d201	White	663.2	7.2	0.0	9.7	32.1	664	7.2	0.2	9.7	32.1
trans-$Ru(CO)_4(SnBr_3)_2$	d181	Yellow	929.9	5.2	0.0	6.9	51.6	932	5.2	0.2	7.1	51.4
trans-$Ru(CO)_4(GeCl_3)_2$	236[j]	White	571.0	8.4	0.0	11.2	37.3	571	8.6	0.0	12.0	37.3
cis-$Ru(CO)_4(GeCl_3)_2$[m]	95	White	571.0	8.4	0.0	11.2	37.3	571	8.6	0.0	12.1	37.0
trans-$Ru(CO)_4(GeBr_3)_2$	213	White	837.7	5.7	0.0	7.6	57.2	840	5.9	0.0	7.9	57.2
$Ru_3(CO)_{10}Cl_2$	d>75[b]	Yellow/ Orange	-	18.4	0.0	24.5	10.8	-	18.8	-	24.2	10.9[k]
$[Ru(CO)_3Cl_2]_2$	-	White	512.0	14.1	0.0	18.8	27.7	512	14.0	0.0	19.1	28.2
$[Ru(CO)_3Br_2]_2$	-	Pale Yellow	689.9	10.4	0.0	-	-	691	10.5	0.3	-	-
$Ru(CO)_4Br_2$	-	White	372.9	12.9	0.0	17.2	-	373	13.2	0.2	17.0	-
$Ru(CO)_4I_2$	-	Yellow	466.9	10.3	0.0	13.7	54.4	469	10.4	0.2	13.7	54.3
$Ru(CO)_2(P(C_6H_5)_3)_2Br_2$	270[l]	White	-	54.2	3.6	-	-	-	54.2	3.3	-	-

j = sealed capillary, k = Ru Calc. 46.3, Found 45.00; Si Calc, 0.0, Found, 1.19. l = Lit.[135] m p 270°; m = Lit.[148] m p 90-100°. See Chapter 5, Part A concerning melting points of these compounds.

TABLE 2.16

Compound	Infrared Spectrum (2200-1800 cm^{-1})	
$Ru_3(CO)_{12}SnCl_4$ [c]	2150m, 2120m, 2089sh, 2073s, 2057s, 2039w, 2019w	a
$Ru_2(CO)_5SnCl_6$ [c]	2154s, 2094s, 2084s, 2031s	a
$Ru_2(CO)_5SnBr_6$	2147s, 2087s, 2078s, 2026s	a
	2140s, 2087s, 2076s, 2025s	b
$Ru_2(CO)_5SnI_6$	2133s, 2072sh, 2069s, 2018s	a
	2126s, 2068s, 2019s	b
$Ru_2(CO)_5GeCl_6$	2152s, 2090sh, 2088s, 2032s	a
	2146m, 2085sh, 2083s, 2031s	b
$Ru_2(CO)_5GeBr_6$	2146s, 2083s, 2029m	a
	2140m, 2080s, 2078s, 2029s	b
$Ru_2(CO)_5GeI_6$	2132s, 2073s, 2022m	a
	2125s, 2073s, 2067s, 2024s	b
$Ru_2(CO)_5SiCl_6$	2144s, 2081vs, 2080vs, 2023s	b
$Os_2(CO)_5SnCl_6$ [c]	2148s, 2073vs, 2012m	a
$Os_2(CO)_5GeCl_6$	2147m, 2073s, 2012m	a

a = CH_2Cl_2 solution, b = cyclohexane solution

c = insoluble in cyclohexane

w = weak, m = medium, s = strong, sh = shoulder

TABLE 2.17

Infrared Data for Ru(CO)$_4$(MX$_3$)$_2$ Compounds

Compound	Infrared Spectrum (2200-1800 cm^{-1})	
trans-Ru(CO)$_4$(SnCl$_3$)$_2$	2106s	a
trans-Ru(CO)$_4$(SnBr$_3$)$_2$	2101s	a
cis-Ru(CO)$_4$(GeCl$_3$)$_2$^{c}	2160w, 2116m, 2103s	b
trans-Ru(CO)$_4$(GeCl$_3$)$_2$	2105s 2111s	b a
trans-Ru(CO)$_4$(GeBr$_3$)$_2$	2103s 2105s	b a

a = CH_2Cl_2 solution: b = cyclohexane solution

c = Lit.[36] = 2162w, 2117m, 2104s.

TABLE 2.18

Infrared Data for Ruthenium Carbonyl Halides

Compound		Infrared Spectrum (2200-1800 cm^{-1})						Ref.
cis-$Ru(CO)_4Cl_2$ [c]		2187w,	2132vs,	2115m,	2083m		a	
	Lit:	2185w,	2135s,	2104s,	2077s		e	122
cis-$Ru(CO)_4Br_2$		2181w,	2125s,	2112s,	2081s		a	
	Lit:	2175m,	2133s,	2104s,	2071s		b	122
	Lit:	2177m,	2123vs,	2105s,	2073s		f	134
cis-$Ru(CO)_4I_2$		2159m,	2106s,	2096s,	2068s		b	
	Lit:	2161m,	2107vs,	2096s,	2066s		b	122
	Lit:	2160m,	2119vw,	2105vs,	2095s,	2066s	h	134
$[Ru(CO)_3Cl_2]_2$ [d]		2139m,	2082m,	2076m			f	
		2142s,	2082s,				a	
	Lit:	2141s,	2079vs,	2006w,			g	122
	Lit:	2144s,	2084vs,	2009w,			g	121
$[Ru(CO)_3Br_2]_2$ [d]			2137s,	2078s,			a	
	Lit:	2136s,	2075s,	2013w,			g	122
$Ru(CO)_2(PPh_3)_2Br_2$			2058s,	1997s,			a	
	Lit:		2061s,	1980s,			i	135

(continued.......)

FOOTNOTES TO TABLE 2.18

a = CH_2Cl_2 solution

b = cyclohexane solution

c = compound not isolated

d = see discussion concerning infrared spectra

e = ether solution

f = carbon tetrachloride solution

g = chloroform solution

h = heptane solution

i = nujol mull

CHAPTER 3

PREPARATION OF M'(CO)$_4$(SiX$_3$)$_2$ COMPOUNDS

INTRODUCTION

The occurrence of stable *trans*-isomers of the type Ru(CO)$_4$(MX$_3$)$_2$ prompted further investigation into the synthesis of such derivatives. It was hoped that by doing this it would be possible to determine how factors such as the size and electronegativity of the MX$_3$ group influenced the formation of the *trans*-isomer. Also pertinent was the effect of changing the central atom to osmium.

From a survey of the literature some predictions can be made concerning this. Both *trans*-Fe(CO)$_4$(GeCl$_3$)$_2$ and *trans*-Fe(CO)$_4$(SnCl$_3$)$_2$ have been prepared although as already pointed out they fairly rapidly isomerized in solution.[28] The existence of *trans*-Fe(CO)$_4$(SiCl$_3$)$_2$ had been claimed [51] but it now appears that this was in fact, *cis*-Fe(CO)$_4$(SiCl$_3$)H.[36] On the basis of ir spectroscopy, compounds Ru(CO)$_4$(SnR$_3$)$_2$ (R = Me, Et, i-Pr, t-But, Ph or PhCH$_2$) existed as *cis*- or *trans*-isomers; the *trans*-form was favored by the larger substituents.[25] Although Ru(CO)$_4$(SnPh$_3$)$_2$ existed with *trans*-geometry, Fe(CO)$_4$(SnPh$_3$)$_2$ was entirely *cis*. This tendency to favor the *trans*-form on going to the transition metal lower in the periodic table is also found for derivatives of the type M'(CO)$_4$(MMe$_3$)$_2$ (M' = Ru [32], or Os [30], M = (Si or Sn). In the case of ruthenium the compounds appeared to be entirely *cis* whereas for osmium both *cis*- and *trans*-forms were observed.

At the time this work was carried out it was not known whether the formation of the different proportions of *cis*- and *trans*-molecules arose from a dynamic equilibrium or from different rates of formation i.e., a kinetic effect. There are examples of one isomer being kinetically preferred whilst the other is thermodynamically the more stable.[71, 137] With this reservation in mind it was to be expected that on going from iron to ruthenium to osmium, the *trans*-geometry would be the preferred configuration for derivatives of the type $(M'(CO)_4(MR_3)_2$. Also the *trans*-isomer appeared to be favored by increasing the size of the MR_3 group. The results of Chapter 2 show that increasing electronegativity of R also favors the *trans*-isomer.

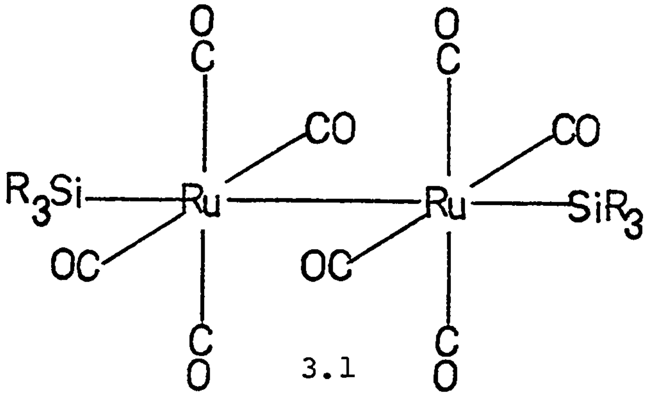
Research was undertaken to substantiate these ideas. In particular it seemed likely that a profitable area would be the synthesis of $Ru(CO)_4(SiR_3)_2$ and $Os(CO)_4(SiR_3)_2$ compounds since it would be expected that in some cases the *cis*-form could be obtained in sufficient quantity for physical study.

It was known that silanes react with transition metal carbonyls giving products containing SiR_3 groups.[138] A reason why silanes may be so useful in the synthesis of such compounds is the fact the the Si-H bond strength is 71.4 kcal mol^{-1} [117] compared to a value for Si-Cl of 105 kcal. This allows compounds to be synthesized under milder conditions where they do not decompose. For example, $Fe(CO)_5$ and Cl_3SiH react at 140-150° to give $(Cl_3Si)_2Fe(CO)_4$ in high yield. However, if the reaction is carried out at temperatures above 160° the major product is $[Cl_2SiFe(CO)_4]_2$.[138] Also another advantage of silanes is that if a transition metal-hydrogen bond is formed in an intermediate stage then one would expect it to react with more silane according to III.1.

$$M'\text{-}H + R_3SiH \rightarrow M'\text{-}SiR_3 + H_2 \qquad \text{III.1}$$

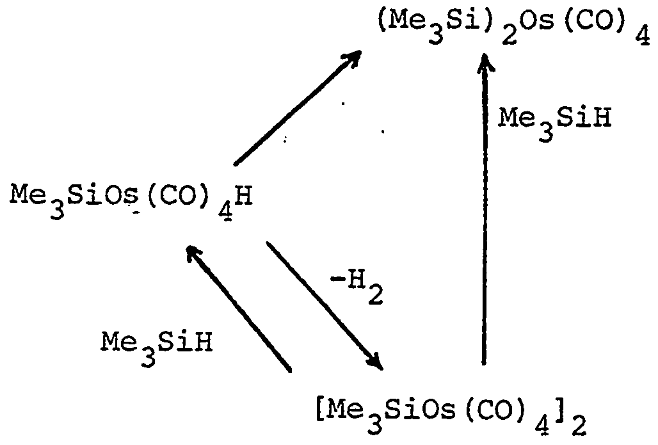
It has been pointed out in Chapter 2 that the transition metal-halogen bond is not so easily broken and can undergo bridging reactions.

The reaction of silanes with $Ru_3(CO)_{12}$ [32] and $Os_3(CO)_{12}$ [30] has been studied. Compounds having the structure 3.1 were isolated in high yields in the reaction between triorganosilanes and dodecacarbonyltriruthenium at *ca.* 80°.



3.1

Only when R = Me was a low yield (0–1%) of the expected $(Me_3Si)_2Ru(CO)_4$ obtained in addition. Treatment of $Os_3(CO)_{12}$ with R_3SiH (R = Me or Et) in hexane at 140° gave analogous silyl-osmium complexes $(R_3Si)_2Os(CO)_4$ and $[R_3SiOs(CO)_4]_2$ as well as the trialkylsilyl(tetracarbonyl)osmium hydrides, $R_3SiOs(CO)_4H$. The conditions of the reaction could be varied so as to control the proportions of the three products obtained, which were inter-related according to III.3



III.3

It was hoped that by carrying out the above reactions under even more forcing conditions that only $M'(CO)_4(SiR_3)_2$ species would be obtained.

RESULTS AND DISCUSSION

It has been found that silanes, X_3SiH, (X = Cl or F) react with $Ru_3(CO)_{12}$ at 175° - 200°, under carbon monoxide pressure, to give excellent yields of $Ru(CO)_4(SiX_3)_2$ compounds. This method was also found ideal not only for the corresponding osmium analogues but also derivatives of the type $Os(CO)_4(SiMe_{3-x}Cl_x)_2$.

Trends in the Relative Stabilities of *cis*-and *trans*-$M'(CO)_4(MX_3)_2$ Compounds

The products isolated in this study existed as either *cis*-or *trans*-molecules or a mixture of both. In the last case, examples were found where the isomers could be physically separated and in others where they could not. This latter phenomenon and its implications constitutes Chapter 5 of this thesis.

Details of the relative amounts of *cis*-and *trans*-isomers isolated are given in Table 3.1. These figures must be treated with caution and in no way should they be taken as quantitative results. It is probable that there is rapid temperature-dependent equilibrium between *cis*-and *trans*-forms under the reaction conditions but for most cases it is not known at what temperature the dynamic equilibrium is stopped on cooling. Other factors could distort the yields of *cis*-and *trans*-isomers: it is quite possible that the less soluble *trans*-isomer could crystal-

TABLE 3.1

Relative Amounts of *cis*-and *trans*-Isomers, for $M'(CO)_4(MX_3)_2$

Compounds*

Compound	*Cis* (Approx.%)	*Trans* (Approx.%)	Ref.
$Ru(CO)_4(SiF_3)_2$	100	0	b
$Os(CO)_4(SiF_3)_2$[c]	91	9	b
$Fe(CO)_4(SiCl_3)_2$	100	0	136
$Ru(CO)_4(SiCl_3)_2$[c]	23	77	b
$Os(CO)_4(SiCl_3)_2$	0	100	b
$Fe(CO)_4(GeCl_3)_2$[c]	100	a	28
$Ru(CO)_4(GeCl_3)_2$[c]	2.4	97.6	b
$Os(CO)_4(GeCl_3)_2$	0	100	b
$Fe(CO)_4(SnCl_3)_2$[c]	100	a	28
$Ru(CO)_4(SnCl_3)_2$	0	100	b
$Os(CO)_4(SnCl_3)_2$	0	100	b
$Fe(CO)_4(GeBr_3)_2$	0	100	28
$Ru(CO)_4(GeBr_3)_2$	0	100	b
$Fe(CO)_4(SnBr_3)_2$	100	0	28
$Ru(CO)_4(SnBr_3)_2$	0	100	b
$Fe(CO)_4(SnPh_3)_2$	100	0	25
$Ru(CO)_4(SnPh_3)_2$	0	100	25
$Ru(CO)_4(SiMe_3)_2$	0	100	32
$Os(CO)_4(SiMe_3)_2$[d]	43	57	b(30)
$Os(CO)_4(SiMe_2Cl)_2$[d]	33	67	b

(continued)

TABLE 3.1 (continued)

Compound	*cis* (Approx.%)	*trans* (Approx.%)	Ref.
$Ru(CO)_4(SiMeCl_2)_2$	0	100	b
$Os(CO)_4(SiMeCl_2)_2$[c]	16	84	b
$Ru(CO)_4(SnMe_3)_2$	100	0	25
$Os(CO)_4(SnMe_3)_2$[d]	31	69	b(30)
$Os(CO)_4(SiMe_3)(SnMe_3)$	50	50	32

---

[*] Based on yields

a=*trans* isomerizes to *cis* form in solution

b=this work

c=isomers can be separated at room temperature

d=isomers cannot be separated at room temperature.

lize out of the reaction solution upsetting the equilibrium. This is certainly the case for $Ru(CO)_4(SiCl_3)_2$ where a more exact study (Chapter 5) reveals that the ratio of *trans* to *cis* is *ca.* 2:1 whereas on the basis of yields obtained it is (Table 3.1) 3.4:1. Losses during work-up would also affect the results.

Even with all these complications the yields do convey an approximate indication of the trends pointed out in the Introduction. Other compounds pertinent to this series, with the appropriate reference, are included for completeness in the Table.

It appears, in these derivatives, that there is a definite tendency to favor the *trans*-isomer on going to the transition metal lower in the periodic table. This is no better illustrated than in the series:

$Fe(CO)_4(SiCl_3)_2$	completely *cis*
$Ru(CO)_4(SiCl_3)_2$	*trans:cis* = *ca.* 2:1
$Os(CO)_4(SiCl_3)_2$	completely *trans*

The trend on changing the group IV element is not clear. The *cis:trans* ratios of 1:2 for $Ru(CO)_4(SiCl_3)_2$ and 1:40 for $Ru(CO)_4(GeCl_3)_2$ along with the fact that $Ru(CO)_4(SnCl_3)_2$ is only *trans* might be taken to indicate that the tendency is again to give the *trans*-form on going down the periodic table. In contrast to this result are the pairs of compounds *trans*-$Fe(CO)_4(GeBr_3)_2$ and *cis*-

$Fe(CO)_4(SnBr_3)_2$, and $Os(CO)_4(SiMe_3)_2$ (*cis:trans*, 1:1.32) and $Os(CO)_4(SnMe_3)_2$ (1:0.44). Currently no generalities can be detected as the group IV element is varied. Part of the reason for this may be the opposing steric effects of lengthening the M'-M and M-X bonds.

The effect of changing the substituents on the group IV atom is clearer. Provided that their electronegativity remains approximately the same, increasing the size of the groups in $M(CO)_4(MX_3)_2$ favors the formation of the *trans*-isomer, as might be expected from purely steric arguments.

However, in the derivatives, $Os(CO)_4(SiMe_{3-x}Cl_x)_2$, successive replacement of methyl groups by chlorine causes a greater amount of the *trans*-isomer to be formed. This replacement should, if anything, decrease the bulk of the ligand so that the trend to more *trans*-isomer is contrary to steric considerations. This progression is most probably related to the increased substituent electronegativity and can be rationalized on the assumption that the more electronegative substituents contract the empty d-orbitals on silicon. This may result in a better overlap with the filled d-orbitals on osmium, leading (Chapter 2) to a preference for the *trans*-isomer. This, of course, assumes that the vacant 3d-orbitals on silicon are higher in energy than the filled 5d-orbitals on osmium.

The effect of changing the electronegativity of the

X atoms is not as simple as the previous discussion might suggest, since $Os(CO)_4(SiF_3)_2$ is mainly *cis*. This may be explained by the much smaller steric repulsions in the fluorine derivative, or on the assumption that SiF_3 is a poorer π-acceptor than the other silyl ligands, or by a combination of these effects. Support for the idea that the SiF_3 group is a poorer π-acceptor than $SiCl_3$ is found in the carbonyl stretching frequencies of *cis*-$Ru(CO)_4(SiF_3)_2$ (2152w, 2101m, 2094m, 2081s) which are almost identical to those of *cis*-$Ru(CO)_4(SiCl_3)_2$ (2150m, 2103s, 2094w, 2084vs). It is found that in derivatives of the type *cis*-$Ru(CO)_4X_2$ that as X becomes more electronegative, the stretching frequencies are raised (consider the series X = I, Br, Cl Table 2.18). One would therefore expect the CO stretching frequencies to be higher for the SiF_3 derivative. That this is not the case can be explained if SiF_3 is a poorer π-acceptor than $SiCl_3$. This poorer π-character may arise in two ways. It is possible that in F_3Si the d-orbitals are contracted to such an extent that they are too small to overlap with the d-orbitals on the transition metal. Alternatively back-bonding between the filled p-orbitals on fluorine with the d-orbitals on silicon reduces the availability of these latter orbitals for dπ-dπ bonding with osmium. These suggestions concerning the π-acceptor properties of the F_3Si and Cl_3Si ligands when bonded to Ru or Os are in contrast to the results of molecular-orbital calculations on $F_3SiCo(CO)_4$ and $Cl_3SiCo(CO)_4$.[76]

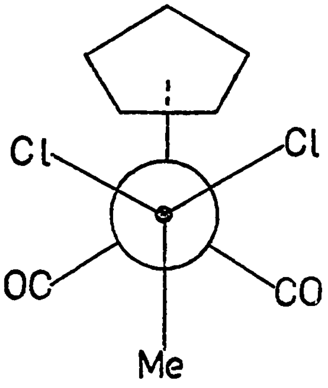
The points raised above serve to illustrate that a delicate balance between some very subtle factors influence the formation of one isomer over the other.

Physical and Spectroscopic Properties of $M'(CO)_4(SiX_3)_2$ Compounds.

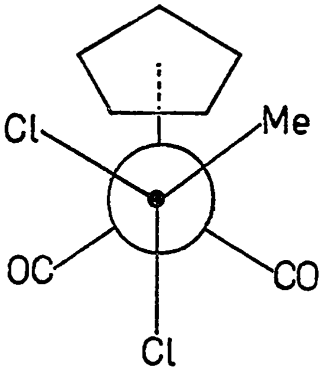
In all cases where separation of the two isomers was achieved it was done by fractional sublimation - the *cis*-form subliming at the lower temperature except in the case of $Os(CO)_4(SiF_3)_2$ where, peculiarly, the *trans* -isomer sublimed at the lower temperature. Except for $Os(CO)_4(MMe_3)_2$ (M = Si or Sn) which are yellow liquids at room temperature, the compounds described here are colorless solids which can be handled for short periods in air but do decompose when exposed to air for longer periods. This is especially true for the ruthenium derivatives; $Ru(CO)_4(SiF_3)_2$ in particular turns red in air. All compounds are stable under vacuum, however.

When the substituents on the silicon are different, e.g., in the cases of $ClMe_2Si$ and Cl_2MeSi, the infrared spectrum is complicated by conformational effects. This phenomenon was first explained by Jetz and Graham[38] who observed four terminal CO stretches in the compound

$(Cl_2MeSi)Fe(CO)_2C_5H_5$, whereas only two would be predicted from group theory. This was attributed to the presence of two conformations of the molecule, shown in Newman projection as 3.2 and 3.3.



3.2



3.3

Consideration of *cis*-$Ru(CO)_4(SiMeCl_2)_2$ shows that there would be a number of conformations for this molecule which would give a complicated infrared spectrum. Indeed *cis*-$Fe(CO)_4(SiMeCl_2)_2$ which had been previously synthesized [138] shows six terminal CO stretches where, of course, only four are predicted. It was therefore difficult to say whether $Ru(CO)_4(SiMeCl_2)_2$, from its infrared spectrum existed as a mixture of *cis*-and *trans*-, or only as the *cis*-form. (The spectrum showed five terminal CO stretches, Fig. 3.1). It was concluded that only the *cis*-form was present by the fact that the compound sub-

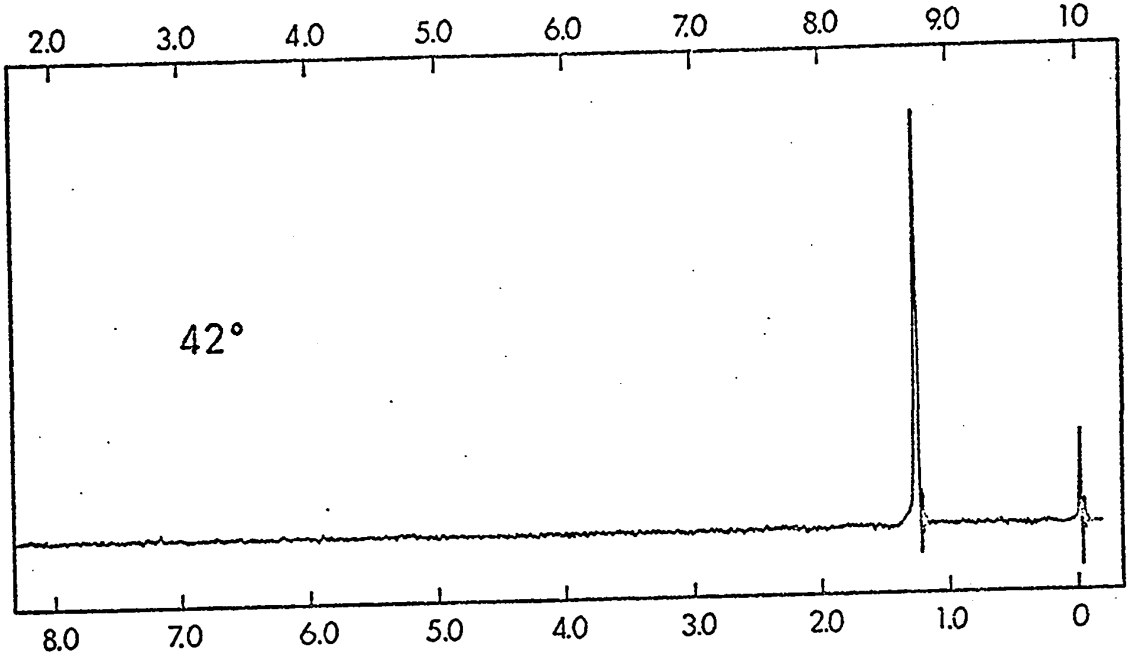
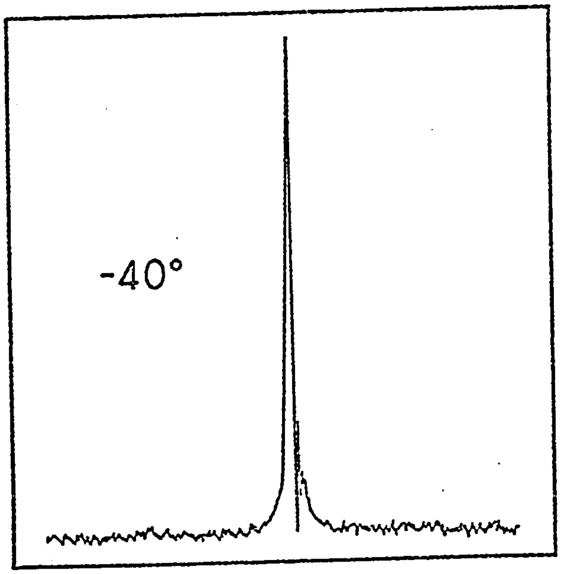
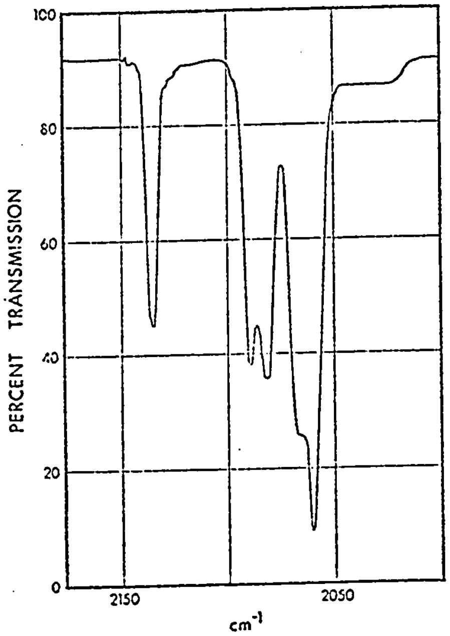


FIGURE 3.1 3.1(a) Nmr spectrum of *cis*-Ru(CO)$_4$(SiMeCl$_2$)$_2$ in CDCl$_3$.

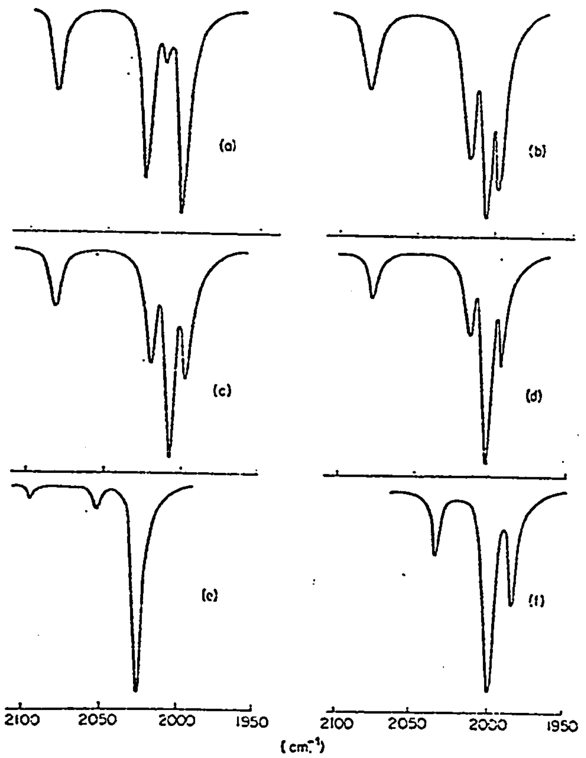


3.1(b) Nmr spectrum at -40°



3.1(c) Infrared spectrum of *cis*-Ru(CO)$_4$(SiMeCl$_2$)$_2$ in heptane limed with no change in its infrared spectrum, and because the nmr spectrum exhibited only a single peak which remained sharp even at -60°. Although this evidence does not rule out a rapid equilibrium between *cis*- and *trans*-forms at this low temperature, it is considered unlikely, in view of the other *cis-trans* isomerizations encountered in this study (see Chapter 5). It seems likely that $Ru(CO)_4(SiMe_2Cl)_2$, which was not synthesized in this study, would have *cis*-geometry in view of the fact that both $Ru(CO)_4(SiMe_3)_2$ and $Ru(CO)_4(SiMeCl_2)_2$ have *cis*-structures.

It is convenient at this stage to discuss some of the results of Knox and Stone concerning these derivatives. The infrared spectra of some $Ru(CO)_4(SnR_3)_2$ compounds as reported by these workers are reproduced in Fig. 3.2. On these results they concluded that as the size of R increased there was more of the *trans*-form present. Although this interpretation is probably correct (especially for $R = CH_2Ph$ and Ph) it is not conclusive since the same results might be produced by *cis* alone. Thus, only four bands are observed though five might be predicted (four for *cis* and one for the *trans*). It might be expected from empirical considerations that the E_u mode of the *trans*-compound would be degenerate with the B_1 mode of the *cis*-molecule.[139] In the majority of cases studied here this has proved not to be exactly true - they are,



I.r. spectra in the carbonyl stretching region:
(a) $(Me_3Sn)_2Ru(CO)_4$, (b) $(Et_3Sn)_2Ru(CO)_4$, (c) $(Pr_3Sn)_2Ru(CO)_4$,
(d) $(Bu_3Sn)_2Ru(CO)_4$, (e) $(Ph_3Sn)_2Ru(CO)_4$, and
(f) $Me_{10}Sn_4Ru_2(CO)_6$

FIGURE 3.2 Infrared spectra of $Ru(CO)_4(SnR_3)_2$ derivatives (taken from ref. 25).

however, very close in energy. Intensity considerations were also put forward [140] to support the argument but even consideration of the $M'(CO)_4X_2$ spectra presented in this thesis show that the intensities do not follow a regular pattern. Spectra could be complicated by conformation effects in the ethyl, isopropyl and benzyl derivatives in a similar manner to that observed in $(MeO)_3SiFe(CO)_2Cp$.[138]

Nmr spectra would have provided much more conclusive evidence about the composition of these compounds. The nmr of $Ru(CO)_4(SnMe_3)_2$ which is reported here consisted of a single sharp peak even at -60° in agreement with their view that this compound is completely *cis*. An example of the unreliability of predicting *cis-trans* ratios from infrared data is the case of $Os(CO)_4(SnMe_3)_2$ where the ir spectrum (Fig. 3.3) indicated pure *cis*, whereas the nmr revealed a significant proportion of *trans* (Fig. 5.4).

Knox and Stone assigned the most intense signal in the nmr spectrum of $Os(CO)_4(SiMe_3)_2$ to the *trans*-isomer.[30] This was based on the observation of three weak (due to *cis*) and one strong band (assigned to the *trans*) in the infrared spectrum of $Os(CO)_4(SiMe_3)_2$. However, it has been found (see Chapter 5) in studies of the separate isomers that the extinction coefficient of the single infrared band of *trans*-$Ru(CO)_4(SiCl_3)_2$ is very much

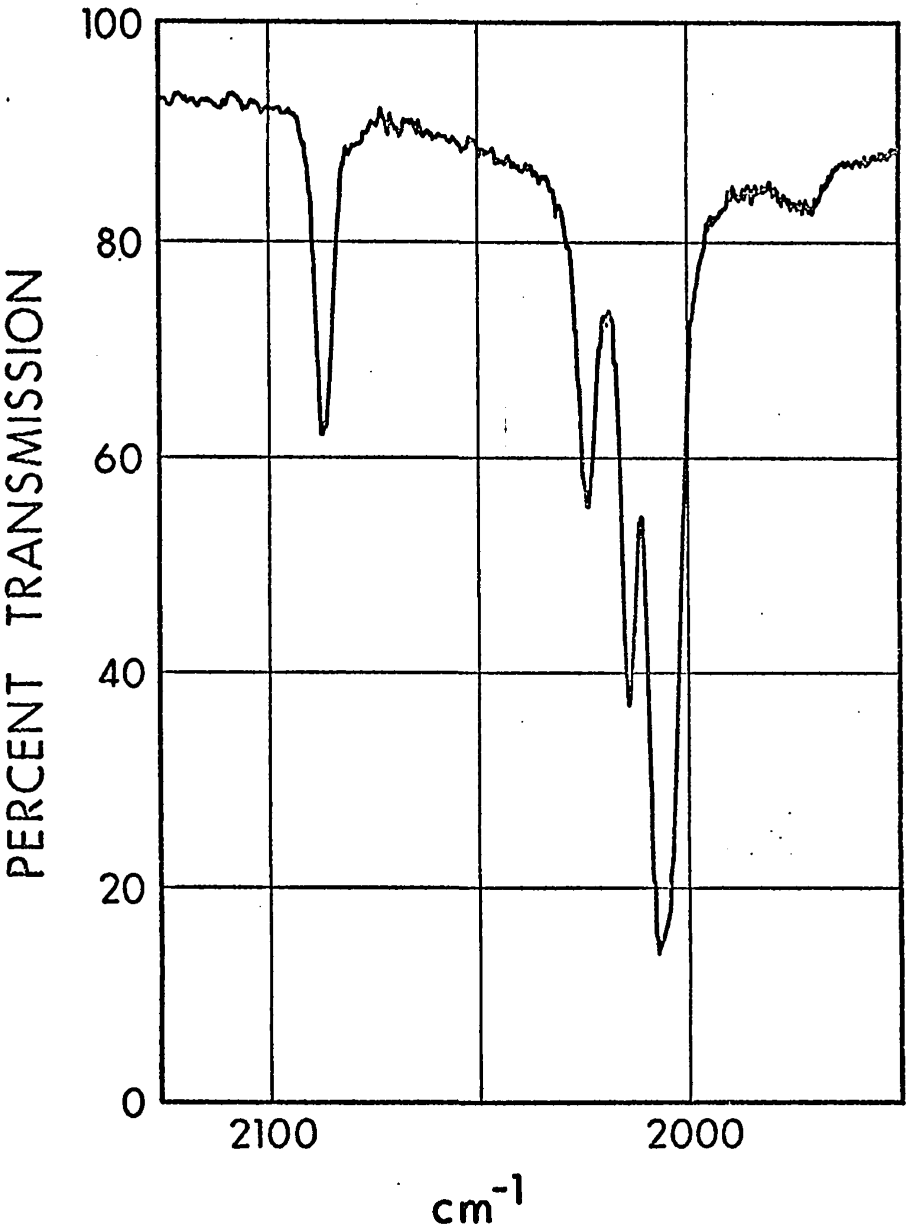


FIGURE 3.3 Infrared spectrum of $Os(CO)_4(SnMe_3)_2$ (heptane solution)

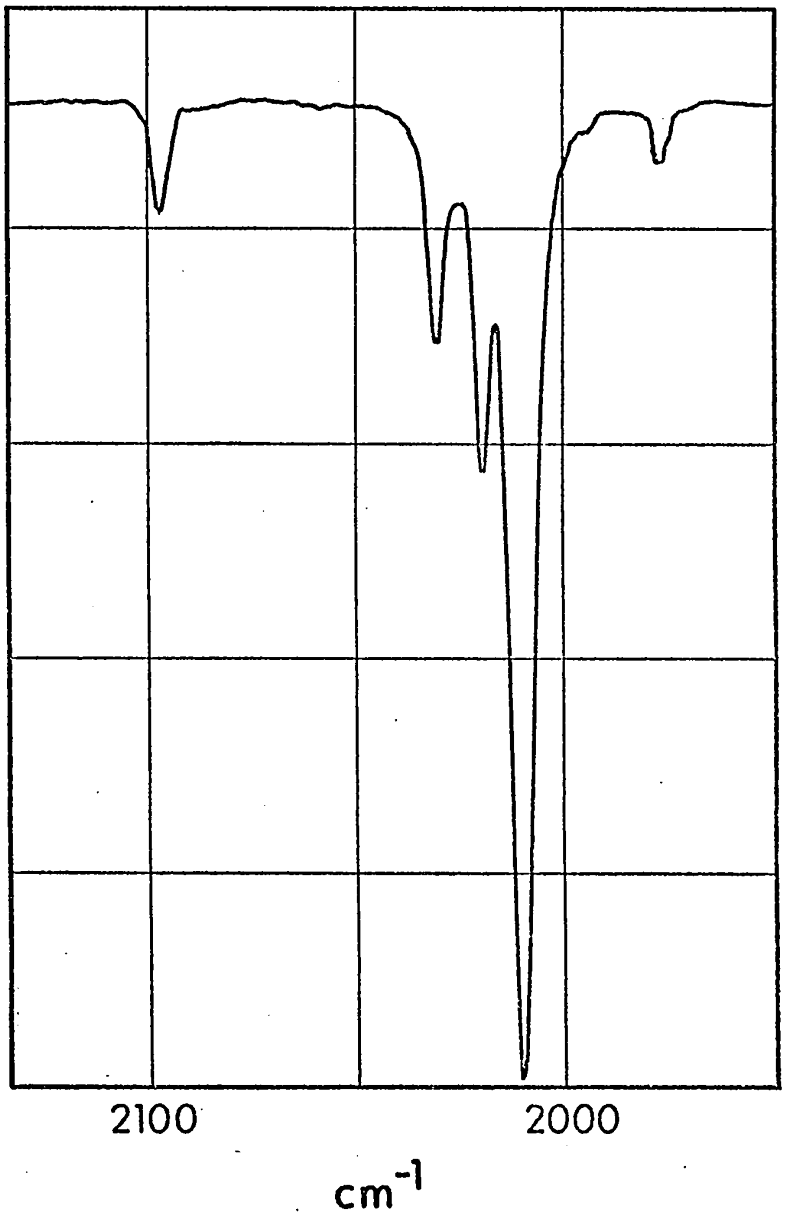
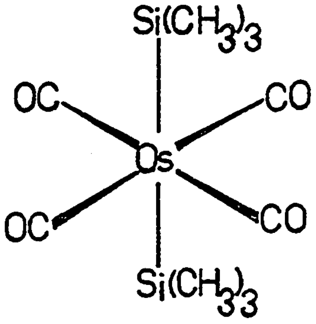
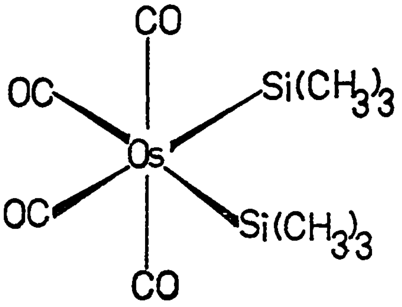


FIGURE 3.4 Infrared spectrum of $Os(CO)_4(SiMe_3)_2$ (heptane solution)

greater than any band of the corresponding *cis*-isomer. Hence, in *cis-trans* mixtures, a stronger band for the *trans* compound does not necessarily mean that it is present in greater amount than the *cis*. That the assignment is nevertheless correct is shown by two pieces of evidence. Low temperature studies (see Chapter 5) of the nmr spectrum of $Os(CO)_4(SiMe_3)_2$ reveal that the proportion of isomers is temperature-dependent, the signal assigned to the *cis* form increasing at lower temperatures. Infrared bands due to the *cis*-isomer also increase in intensity on cooling. Furthermore, in the isomers of $Os(CO)_4(SiMeCl_2)_2$, which can be physically separated at room temperature, the *trans*-compound exhibits an nmr signal at lower field than the *cis*-derivative (Fig. 3.5).



trans
3.4



cis
3.5

Consider the resonances in *cis*- and *trans*-$Os(CO)_4(SiMe_3)_2$ in more detail. As pointed out in Chapter 1 the transition metal-silicon bond is believed to contain σ- and π -

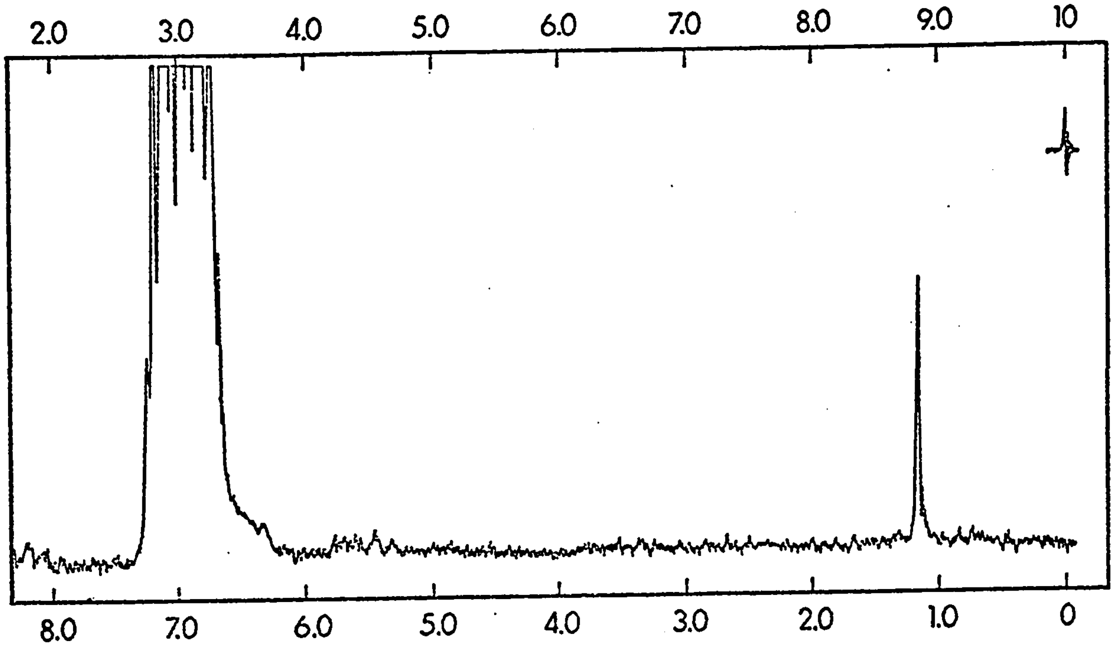


FIGURE 3.5(a) Nmr spectrum of *trans*-Os(CO)$_4$(SiMeCl$_2$)$_2$ (dichlorobenzene solution).

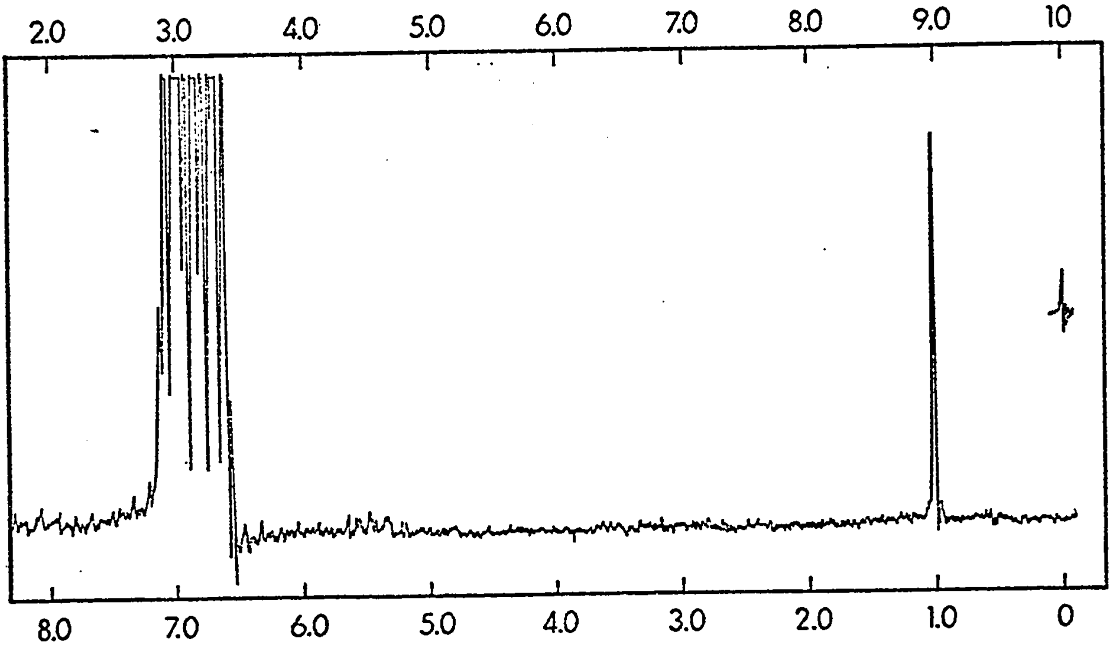


FIGURE 3.5(b) Nmr spectrum of *cis*-Os(CO)$_4$(SiMeCl$_2$)$_2$ (dichlorobenzene solution).

contributions. If it is assumed that a purely inductive effect would be isotropic, [65,141] then, in the case where π-bonding is negligible, we would expect the nmr signals of both *cis*-and *trans*-$Os(CO)_4(Si(CH_3)_3)_2$ to occur at the same energy i.e., the inductive effect exerted upon a ligand will be the same whether the substituent is *cis* or *trans* to that ligand. As stated the two resonances do not appear at the same field strength; the difference between the two signals may result, at least in part, from the difference in *trans* - effects of $SiMe_3$ and CO i.e., the non-isotropic effect on the *trans*-ligand. This phenomenon is tentatively ascribed to π-bonding. Since the *trans*-molecule resonates at a lower field than the *cis*, this is taken to mean that the $SiMe_3$ group has a larger *trans*-effect than CO implying that in this compound the Me_3Si group is the better π-acceptor. Similar arguments can be applied to the other *cis*- and *trans*-derivatives described in this Chapter.

The above ideas must, at the present stage, be considered exploratory and subject to modification as knowledge about these and related compound becomes more abundant. Thus, although the *trans*-effect in four coordinate transition metal complexes has been fairly well delineated, studies on octahedral systems and in particular those of organometallic compounds are scarce. It may well be that there is an electrostatic mutual polarization process operative in the present compounds similar to that in square-planar complexes i.e., an inductive effect directional in character. The chemical shift depends on many factors [142] in a way that is not fully understood and hence it may not be valid relating to the *trans*-effect although it has been done before.[67,69]

If these two points do not seriously affect the argument then the chemical shift data could prove valuable in assessing some of the theories concerning these derivatives. In many ways the separation of the σ-and π-effects in the present treatment is reminiscent of the method used in the determination of the Graham σ-and π-parameters.[65] One might therefore expect a linear relationship between the two. It might also be possible to correlate the difference in the two nmr signals with the *cis:trans* ratio. As pointed out in Chapter 2 the *trans* form might be favored as the π-bonding capacity of SiR_3 is increased. No attempt has been made to investigate these relationships here since for valid study a much larger series of compounds would have to be examined.

In view of the fact that $Ru(CO)_4(MCl_3)_2$ (M = Ge or Sn) derivatives may be useful for synthetic purposes (see Chapter 6) alternative methods of preparation were sought to give these products in higher yield than the routes in Chapter 2. It was found that the reactions outlined in III.3 and III.4 gave $Ru(CO)_4(GeCl_3)_2$ and

$Ru(CO)_4(SnCl_3)_2$ respectively in excellent yield

$$Ru_3(CO)_{12} + 6Cl_3GeH \xrightarrow[150°]{CO} 3Ru(CO)_4(GeCl_3)_2 + 3H_2 \qquad III.3$$

$$Ru_3(CO)_{12} + 3SnCl_2 + 3SnCl_4 \xrightarrow[150°]{CO} 3Ru(CO)_4(SnCl_3)_2 \qquad III.4$$

These methods also proved suitable for the corresponding osmium complexes. In the case of $Os(CO)_4(MCl_3)_2$ (M = Si, Ge or Sn) only the *trans*-isomers were isolated. In the reaction between Cl_3SiH and $Os_3(CO)_{12}$ there was infrared evidence for trace amounts of a compound having a *cis*-$Os(CO)_4X_2$ type structure, this was probably due to $Os(CO)_4(SiCl_3)H$. A minor product in the reaction of $Fe_3(CO)_{12}$ and Cl_3SiH at 140° is $Fe(CO)_4(SiCl_3)H$.[136] Attempts to prepare *cis*-$Os(CO)_4(SiCl_3)_2$ by irradiating or heating the corresponding *trans*-compound under carbon monoxide were unsuccessful.

The preparation of *trans*-$Ru(CO)_4(GePh_3)_2$ was carried out because the compound was desired for an X-ray diffraction study. However, this derivative provides another facet to this interesting series of compounds. The initial diffraction results for the lattice parameters, coupled with the density measurements, indicated that the molecule should be formulated as $Ru(CO)_4(GePh_3)_2.CH_2Cl_2$. This explained the previously puzzling analytical results.

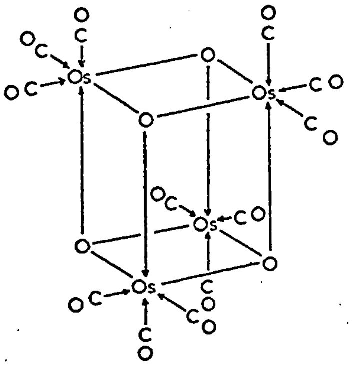
Further confirmation of a molecule of dichloromethane as a solvent of crystallization was provided by the nmr spectrum of this compound (in $CDCl_3$) which showed a peak in both the correct ratio and region expected for such an adduct. That the compound appears to etch when exposed for long periods in air may be due to loss of this molecule of solvation from the surface of the crystal. It is interesting that $Ru(CO)_4(SnPh_3)_2$ and $Ru(CO)_4(Sn(CH_2Ph)_3)_2$ although recrystallized from dichloromethane-hexane, in a similar manner to $Ru(CO)_4(GePh_3)_2$, did not appear to contain CH_2Cl_2.[25] Of course, the other compounds reported here could not involve CH_2Cl_2 of crystallization since they were purified by sublimation, a method found unsuitable for $Ru(CO)_4(GePh_3)_2$. That a molecule of solvent is retained even in the crystalline state may indicate a relatively strong interaction between *trans*-$Ru(CO)_4(GePh_3)_2$ and solvent molecules whilst in solution.

During purification of $Os_3(CO)_{12}$, $Os_4(CO)_{12}O_4$ was obtained as a white crystalline solid. This compound had been previously reported as having a four band infrared spectrum in the carbonyl stretching region.[143] The mass spectrum, which contained $(Os_3(CO)_n)^{2+}$ (n=0.11) ions, was interpreted as due to the dissociation:

$$OsO_4.Os_3(CO)_{11}{}^{+} \rightarrow Os_3(CO)_{11}{}^{2+} + OsO_4{}^{-} \qquad \text{III.5}$$

Both these results are inconsistent with the structure

(3.6) which has recently been established for $Os_4(CO)_{12}O_4$ by X-ray crystallography.[144]



3.6

The $Os_4(CO)_{12}O_4$ isolated in this study, however showed only two bands in the infrared region in question (Fig. 3.6) consistent with the symmetry of the molecule. This spectrum may be compared with that of $Ir_4(CO)_{12}$ and $Re_4H_4(CO)_{12}$ [145] which also show only two bands and are believed to have a tetrahedral structure. The mass spectrum of $Os_4(CO)_{12}O_4$ in the present study did not show $(Os_3(CO)_n)^{2+}$ ions as reported, only peaks due to $(Os(CO)_nO_4)^{x+}$ (n=1-12, x=1 or 2), $Os_3O_2^+$, Os_3O^+ and Os_2^+ were observed above mass 200. It is probable that the original $Os_4(CO)_{12}O_4$ contained $Os_3(CO)_{12}$ as an impurity.

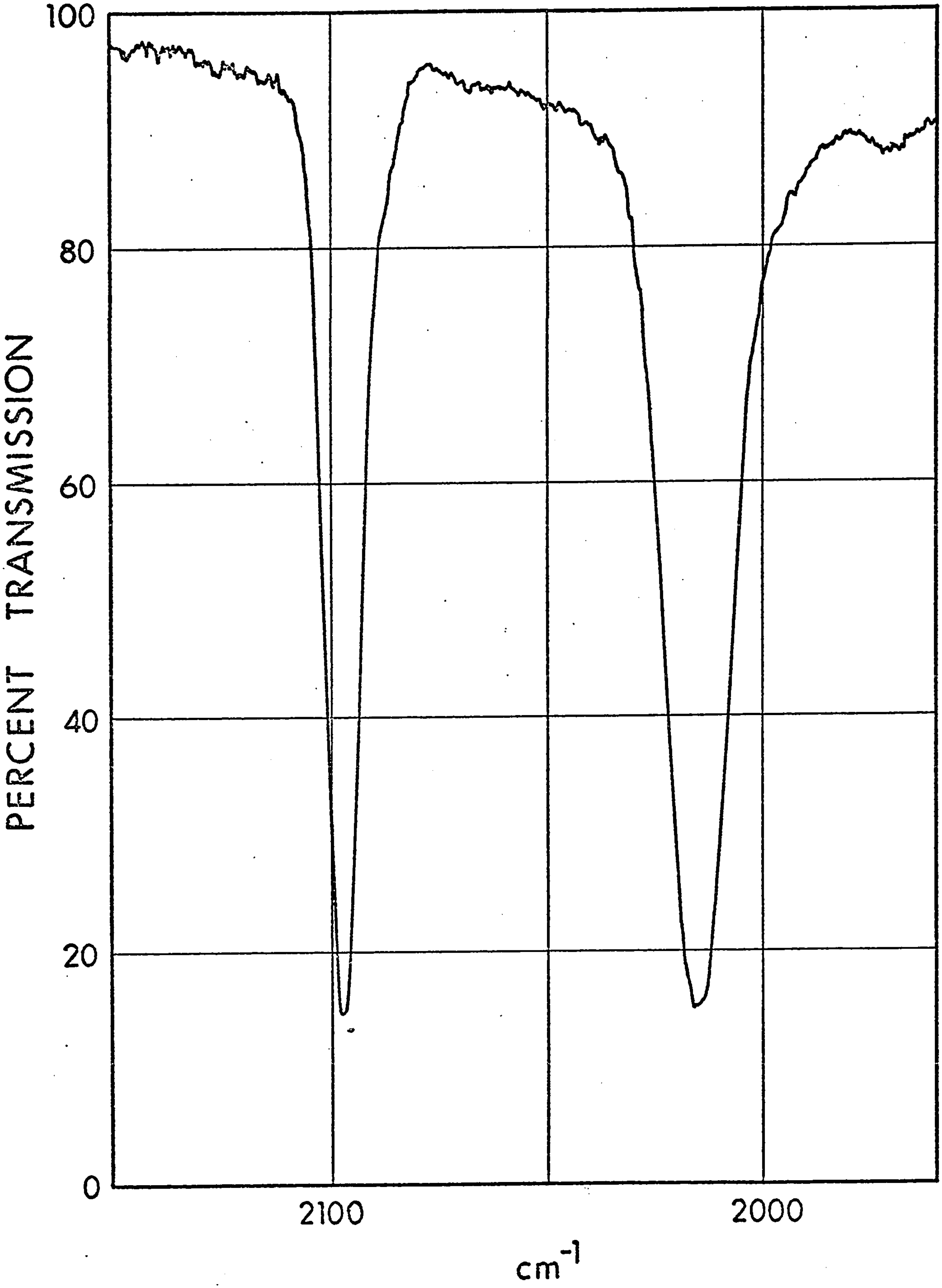


FIGURE 3.6 Infrared spectrum of $Os_4O_4(CO)_{12}$ (CH_2Cl_2 solution)

Similar observations have very recently been made by Bradford and Nyholm.[145]

EXPERIMENTAL

The proton nmr spectra were recorded using a Varian A 56/60 spectrometer with TMS as an external standard. The external standard was used for two reasons. Many of the compounds (e.g., $Os(CO)_4(SiMe_3)_2$) were air sensitive and were sealed under vacuum, in the nmr tubes, before running the spectra and also the resonances of these particular derivatives come, as one would expect, fairly close to $Si(CH_3)_4$ and thus there was a possibility of an internal standard complicating the spectra. Fluorine nmr were run on the same instrument using $CFCl_3$ as internal standard. Other experimental techniques employed have been outlined in Chapter 2.

Dodecacarbonyltriosmium was obtained as a by-product from the preparation of *cis*-$Os(CO)_4H_2$ and of $Os(CO)_5$.[147] It was purified by recrystallization from toluene and careful sublimation at 80°/0.01. This latter process served to separate $Os_3(CO)_{12}$ from $Os_4(CO)_{12}O_4$.

Preparation of *cis*—and *trans*-$Ru(CO)_4(SiCl_3)_2$.

An autoclave containing $Ru_3(CO)_{12}$ (1.28 g, 2 mmol) and Cl_3SiH (2 ml, 20 mmol) in n-heptane (30 ml) was pressurized with approximately 70 atmospheres of carbon monoxide. The vessel was heated for 18 hr at 175°. The autoclave was then allowed to cool and the gas vented. The solution was transferred to a Schlenk-tube under nitrogen and placed in dry ice. On the bottom of the bomb pure, white, crystalline *trans*-$Ru(CO)_4(SiCl_3)_2$ (1.8 g) was obtained. These crystals were washed with n-hexane and dried with a stream of nitrogen.

The solution, after standing several hours in dry ice, gave white crystals which were sublimed at room-temperature (27°) onto a cold water probe (13°) at 0.01 mm. The product *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.6 g) was obtained as colorless crystals. Sublimation of the remaining material at 60°/0.01 mm yielded a further batch of *trans*-$Ru(CO)_4(SiCl_3)_2$ (0.2 g). This latter product was used for the analytical sample. Total yield of *cis*- and *trans*-$Ru(CO)_4(SiCl_3)_2$ was 90% theoretical. An infrared spectrum of the mother liquor after the above treatment showed traces of a third product, believed to be $Ru(CO)_4(SiCl_3)H$, besides a small amount of *cis*- and *trans*-$Ru(CO)_4(SiCl_3)_2$.

The method described above was essentially that used for the preparation of the other silicon derivatives except that the reaction was carried out on such a scale that 0.5 mmol of the parent carbonyl was used. Yields in all cases were 90% or better. Procedures peculiar to an individual reaction are given in the following pages. Analytical data is given in Table 3.2, infrared and nmr data in Table 3.3.

Comments on Individual Preparations

cis-$Ru(CO)_4(SiF_3)_2$

In this and other preparations involving F_3SiH, the evacuated autoclave was pressurized with F_3SiH (3 atm) before adding the carbon monoxide. The compound sublimes at 45°/0.01 mm. It is barely soluble in heptane and slowly decomposes in solution. In view of this, nmr results of this (and the osmium analogue) should be treated with caution; solutions had to be heated to obtain a concentration suitable for nmr. Although stable under vacuum *cis*-$Ru(CO)_4(SiF_3)_2$ turns red in moist air within hours.

cis-$Ru(CO)_4(SiMeCl_2)_2$

This compound is a low melting solid (ca 60°) which sublimes at room temperature/0.01 mm. It can be handled for short periods in air.

trans-$Ru(CO)_4(GePh_3)_2.CH_2Cl_2$

This compound did not sublime at 100°/0.01 mm. It was recrystallized from CH_2Cl_2-n-hexane. It appeared reasonably stable in air undergoing superficial etching after 1-2 days.

cis-$Ru(CO)_4(SnMe_3)_2$ and $Os(CO)_4(SnMe_3)_2$

Although the method described above gave excellent yields of silyl derivatives, only poor yields were obtained when the preparation of $M'(CO)_4(SnMe_3)_2$ (M = Ru, Os) was attempted. This is probably because these derivatives (and Me_3SnH) decompose at the temperature employed.[140] The liquid compounds could however be separated from the decomposition products by sublimation at 27°/0.01 mm. They were characterized by comparing their infrared spectrum with those reported in the literature.[25,30]

$Os(CO)_4(SiMe_3)_2$

This compound was characterized by infrared and nmr spectroscopy [30], and also by mass spectroscopy. This compound decomposed in air and in dibromomethane solutions exposed to air into an as yet unidentified product.

The compounds $Fe(CO)_4(SiMe_3)_2$ and $Ru(CO)_4(SiMe_3)_2$ could not be prepared by the method used to prepare the osmium analogue.

$Os(CO)_4(SiMe_2Cl)_2$

This solid could not be resolved into isomers by sublimation at 27°/0.01 mm. When the reaction was carried out at 175° instead of 200°, there was evidence for $[ClMe_2Os(CO)_3]_2$: a strong band in the infrared at 2026 cm^{-1}.

cis-and *trans*-$Os(CO_4)(SiMeCl_2)_2$

The *cis*-isomer was separated from the *trans* by sublimation at 27°/0.01 mm. The *trans*-isomer sublimes at

55°/0.01 mm. The compounds appeared reasonably air stable.

cis-and *trans*-$Os(CO)_4(SiF_3)_2$

The *trans*-isomer (which was formed in very low yield) sublimed at 27°/0.01 mm, the *cis*-isomer at 50°/0.01 mm. The compounds are far more stable than the ruthenium species; they do not appear to decompose in air.

trans-$Os(CO)_4(SiCl_3)_2$

Present in trace amounts in the reaction mixture was a compound having an infrared spectrum 2154w, 2096m, 2081vs, 2076sh(?). This could have been *cis*-$Os(CO)_4(SiCl_3)_2$ although it is more probable that it was *cis*-$Os(CO)_4(SiCl_3)H$. The air-stable *trans*-$Os(CO)_4(SiCl_3)_2$ may be sublimed at 75°/0.01 mm. Attempts to convert *trans*-$Os(CO)_4(SiCl_3)_2$ into the *cis* isomer by heating or irradiating it under a CO atmosphere were unsuccessful.

trans-$Os(CO)_4(GeCl_3)_2$

The reaction was carried out at 135°. The air-stable product was recrystallized from CH_2Cl_2-n-hexane.

trans-$Os(CO)_4(SnCl_3)_2$

Compound was recrystallized from CH_2Cl_2.

Preparation of *trans*-$Ru(CO)_4(GeCl_3)_2$ from $Ru_3(CO)_{12}$ and Cl_3GeH.

An autoclave containing $Ru_3(CO)_{12}$ (0.32 g, 0.5 mmol) and Cl_3GeH (0.5 ml) in n-heptane (15 ml) was pressurized with carbon monoxide (70 atm) and heated at 150° for 19 hr. The vessel was allowed to cool and the gases released. The mother liquor was removed from crystalline *trans*-$Ru(CO)_4(GeCl_3)_2$ (0.80 g, 99%) which was washed with n-hexane and dried with a stream of nitrogen. An infrared spectrum of the reaction solution showed traces of *cis*-$Ru(CO)_4(GeCl_3)_2$.

The osmium analogue *trans*-$Os(CO)_4(GeCl_3)_2$ was prepared in a similar manner.

Preparation of *trans*-$Ru(CO)_4(SnCl_3)_2$ from the reaction of $Ru_3(CO)_{12}$ with $SnCl_2$ and $SnCl_4$.

To $Ru_3(CO)_{12}$ (0.32 g, 1 mmol) and $SnCl_2$ (0.30 g, 1.6 mmol) in benzene (15 ml) was added $SnCl_4$ (1 ml, 8.6 mmol). The autoclave was pressurized with carbon monoxide (70 atm) and heated to 145° for 12 hr. It was then cooled, the gases liberated and the mother liquor removed from *trans*-$Ru(CO)_4(SnCl_3)_2$ (0.83 g, 82%) which was washed with n-hexane and dried with a stream of nitrogen. The compound was recrystallized from CH_2Cl_2 to remove any traces of $SnCl_2$.

The osmium compound *trans*-$Os(CO)_4(SnCl_3)_2$ was similarly prepared.

TABLE 3.2

Analytical Data for $M'(CO)_4(MX_3)_2$ Compounds

Compound	Calculated					Found				
	Mol.Wt.	C	H	O	X	Mol.Wt.[a]	C	H	O	X
cis-$Ru(CO)_4(SiF_3)_2$	383.3	12.53	0	16.70	29.74	384	12.54	0	-	28.02
cis-$Ru(CO)_4(SiCl_3)_2$	482.0	9.97	0	13.28	44.13	482	10.03	0	12.64	45.39
trans-$Ru(CO)_4(SiCl_3)_2$	482.0	9.97	0	13.28	44.13	482	10.27	0	12.61	45.38
cis-$Ru(CO)_4(SiMeCl_2)_2$	441	16.34	1.37	14.51	32.14		16.60	1.30	14.93	31.61
trans-$Ru(CO)_4(GePh_3)_2.CH_2Cl_2$	905.9	54.36	3.56	7.06	7.83	820 822[c]	54.35	3.58	-	7.87
cis-$Os(CO)_4(SiF_3)_2$	472.4	10.17	0	13.51	24.13	474	10.21	-	-	22.55
trans-$Os(CO)_4(SiF_3)_2$	472.4	10.17	0	13.51	24.13	474	9.86	-	-	-
trans-$Os(CO)_4(SiCl_3)_2$	571.1	8.41	0	11.21	37.25	572	8.62	-	11.62	36.19
trans-$Os(CO)_4(GeCl_3)_2$	660.1	7.28	0	9.69	32.22	660	7.26	-	9.57	31.95
trans-$Os(CO)_4(SnCl_3)_2$	752.3	6.39	0	8.51	28.27	752	6.59	0.30	-	28.21
cis and *trans*-$Os(CO)_4(SiMe_2Cl)_2$	489.5	19.63	2.47	13.08	14.49	490	19.85	3.35	-	14.43
cis-$Os(CO)_4(SiMeCl_2)_2$	530.3	13.59	1.14	12.06	26.74	530	13.71	-	11.86	25.85
trans-$Os(CO)_4(SiMeCl_2)_2$	530.3	13.59	1.14	12.06	26.74	530	13.11	-	11.64	26.37

X = halogen, a = as observed mass spectrometrically (most intense peak)

b = not measured, c = calc for $Ru(CO)_4(GePh_3)_2$ = 820.9

TABLE 3.3

Infrared and Nmr Data for M'$(CO)_4(MX_3)_2$ Compounds

Compound	Infrared Spectrum, 2200-2000 cm^{-1} (heptane solution)	Nmr Spectrum	Solvent
cis-Ru$(CO)_4(SiF_3)_2$	2152w, 2101m, 2094m, 2081s	82.30 ppm[b]	$CDCl_3$
cis-Ru$(CO)_4(SiCl_3)_2$	2150m, 2103s, 2094s, 2084vs	-	
trans-Ru$(CO)_4(SiCl_3)_2$	2089vs, (2093vs, CH_2Cl_2 soln)	-	
cis-Ru$(CO)_4(SiMeCl_2)_2$	2136m, 2089m, 2082m, 2066sh, 2060s,	8.72 τ[g]	$CDCl_3$
trans-Ru$(CO)_4(GePh_3)_2 \cdot CH_2Cl_2$	2063vw, 2034s[a]	2.11 (multiplet) 4.74[h]	$CDCl_3$
cis-Ru$(CO)_4(SnMe_3)_2$	2084s, 2024s, 2015w, 2106[d]	9.20 τ[g]	CH_2Br_2
Os$(CO)_4(SiMe_3)_2$[c]	2098w, 2031w, 2020w, 2011s[e]	9.39 τ, 9.48 τ[i]	CH_2Br_2
Os$(CO)_4(SiMe_2Cl)_2$	2120w, 2061w, 2033s	8.54 τ 8.62 τ	CH_2Br_2
cis-Os$(CO)_4(SiMeCl_2)_2$	2140m,[a] 2083m,[a] 2067m,[a] 2059s[a]	8.98 τ	1,2-dichlorobenzene
trans-Os$(CO)_4(SiMeCl_2)_2$	2094vw, 2059vs[a]	8.83 τ	1,2-dichlorobenzene
Os$(CO)_4(SnMe_3)_2$	2088w, 2025m, 2014m, 2006s[f]	9.54, 9.62[j]	CH_2Br_2
cis-Os$(CO)_4(SiF_3)_2$	2156w, 2094m, 2080sh, 2078vs	82.87 ppm[b]	$CDCl_3$

continued.......

TABLE 3. (continued)

trans-Os(CO)$_4$(SiF$_3$)$_2$	2079s		82.64 ppm[b]	CDCl$_3$
trans-Os(CO)$_4$(SiCl$_3$)$_2$	2081vs	(2084vs, CH$_2$Cl$_2$ soln)	-	
trans-Os(CO)$_4$(GeCl$_3$)$_2$	2095vs	(2099vs, CH$_2$Cl$_2$ soln)	-	
trans-Os(CO)$_4$(SnCl$_3$)$_2$	2095vs	(CH$_2$Cl$_2$ soln)		

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w = weak, m = medium, s = strong, sh = shoulder; a = broad asymmetric; b = upfield from CFCl$_3$; c = Mol. wt. calcd = 448, found by mass spectrometry = 450; d = lit.[25] = 2084s, 2024s, 2012w, 2003s; e = lit.[30] = 2099w, 2031w, 2020w, 2011s; f = lit.[30] = 2088w, 2025m, 2014m, 2007s; g = spectrum unchanged -60°; h = ratio of peaks 16:1, calcd. 15:1; CH$_2$Cl$_2$ lit.[198] = 4.67 τ (CCl$_4$ soln); i = lit.[30] = 9.38, 9.47 τ; j = lit.[30] = 9.47, 9.55 τ.

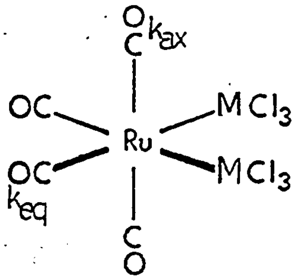
CHAPTER 4

STUDIES ON ^{13}CO EXCHANGE OF $M'(CO)_4X_2$ COMPOUNDS

INTRODUCTION

The existence of stable *trans*-isomers of $Ru(CO)_4(MCl_3)_2$ (M = Si, Ge or Sn) indicated that the group IV ligand had a somewhat eccentric character and that these derivatives merited more detailed physical study. As described in Chapter 2 there was no discernable difference in the ruthenium-carbon or ruthenium-germanium distances in either *cis*-or *trans*-$Ru(CO)_4(GeCl_3)_2$. This implied that the *trans*-bond weakening effects of $GeCl_3$ and CO were comparable. However, it might be expected that the structural parameters would be rather insensitive to subtle differences in ground state *trans*-effects.

A more informative piece of information might be the CO stretching force constants k_{eq} and k_{ax} of the *cis*-derivatives (4.1). In accordance with normal practice in these *cis* - carbonyl systems, the MCl_3 groups are taken to be in the equatorial plane, as the drawings suggest.



4.1

The absolute and relative magnitude of the two constants can be related to the σ- and π-character of the MCl_3 moiety, besides giving information on the *trans* properties of the two ligands. That the three frequencies of $Ru(CO)_4(GeCl_3)_2$ were all above 2100 cm^{-1} implied that the k values would be amongst the highest encountered.

Besides the two primary force constants k_{eq} and k_{ax}, there are also three interaction constants: $k_{ax,ax}$, $k_{eq,eq}$ and $k_{ax,eq}$. Since there are, at most, four CO stretching absorptions it is impossible from this data alone to solve exactly the equations relating the frequencies with force constants. Several approximate procedures exist for the solution of this problem, the most popular being the so-called Cotton-Kraihanzel method.[150] This assumes $k_{ax} > k_{eq}$ and $k_{eq,eq} = k_{eq,ax} = 0.5\ k_{ax,ax}$. Besides its approximate nature, the Cotton-Kraihanzel procedure is unsuitable for application to the present system. That k_{ax} is assumed to be greater than k_{eq} necessarily implies that the MCl_3 group should be a poorer π-acceptor than carbon monoxide which from previous discussion may not be the case. Coupled with this was the accidental degeneracy of two of the bands in the spectrum of *cis*-$Ru(CO)_4(GeCl_3)_2$ - giving only three observable frequencies.

Replacing a coordinated ^{12}CO molecule with ^{13}CO will result in a shift to lower wavelengths of the frequencies of those modes involving the substituted molecule. This is, of course, due to the increased mass resulting from exchanging carbon-13 for carbon-12. However, the force constants are presumed to remain fixed, and hence with this additional ^{13}CO data can be calculated without any *a priori* assumptions about the interaction constants.

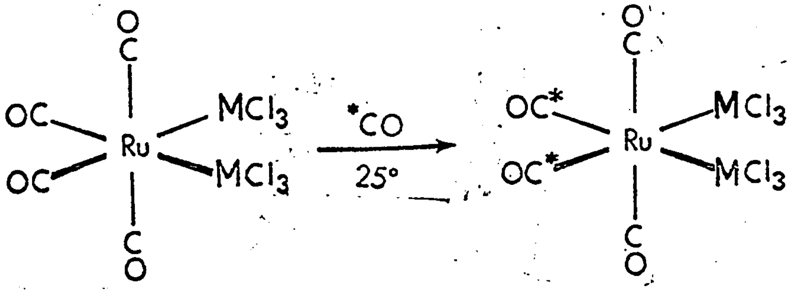
Although this method is superior to the Cotton-Kraihanzel treatment, it does assume that the carbonyl stretching modes do not mix with any of the other modes of the molecule. Since the stretching fundamentals of carbon monoxide ligands are much higher in energy than the other modes of the molecule (see Chapter 7) this is thought not to be a serious limitation.[151] Also, no account is taken of the anharmonicity of the vibrations. Agreement between the calculated and observed spectra is, however, quite remarkable and is often within the experimental accuracy of the frequencies ($\pm$ 1 cm^{-1}).

The above discussion outlines the reasons why the ^{13}CO studies were initiated. As this work progressed it became apparent that the substitution of *cis*-$Ru(CO)_4(MCl_3)_2$ (M = Si or Ge) was stereospecific. Because of this, the calculation of force constants became of secondary importance and the exact nature of the CO substitution was studied in its own right.

RESULTS AND DISCUSSION

Stereospecific Nature of the Exchange of *Cis*-Ru(CO)$_4$(MCl$_3$)$_2$

The ^{13}CO substitution of *cis*-Ru(CO)$_4$(MCl$_3$)$_2$ (M = Si or Ge) has been found to be stereospecific: only those CO groups *trans* to MCl$_3$ are replaced. This is shown in IV.1



IV.1

This conclusion comes from the results (Table 4.5) that the new bands arising from the ^{13}CO exchange can only be fitted if it is assumed that only the equatorial positions are substituted. No absorptions were observed to grow in positions calculated for axial substitution; weak bands are observed in the unsubstituted product which can be attributed to vibrations involving naturally occurring ^{13}C in the axial position.

Although final confirmation that the exchange is stereospecific in the equatorial position relies on the spectrum fitting procedure, qualitatively the nature of the replacement can be seen by comparing the spectra of Ru(CO)$_4$(SiCl$_3$)$_2$ and Ru(CO)$_4$I$_2$ (Fig. 4.1 and 4.2 respectively).

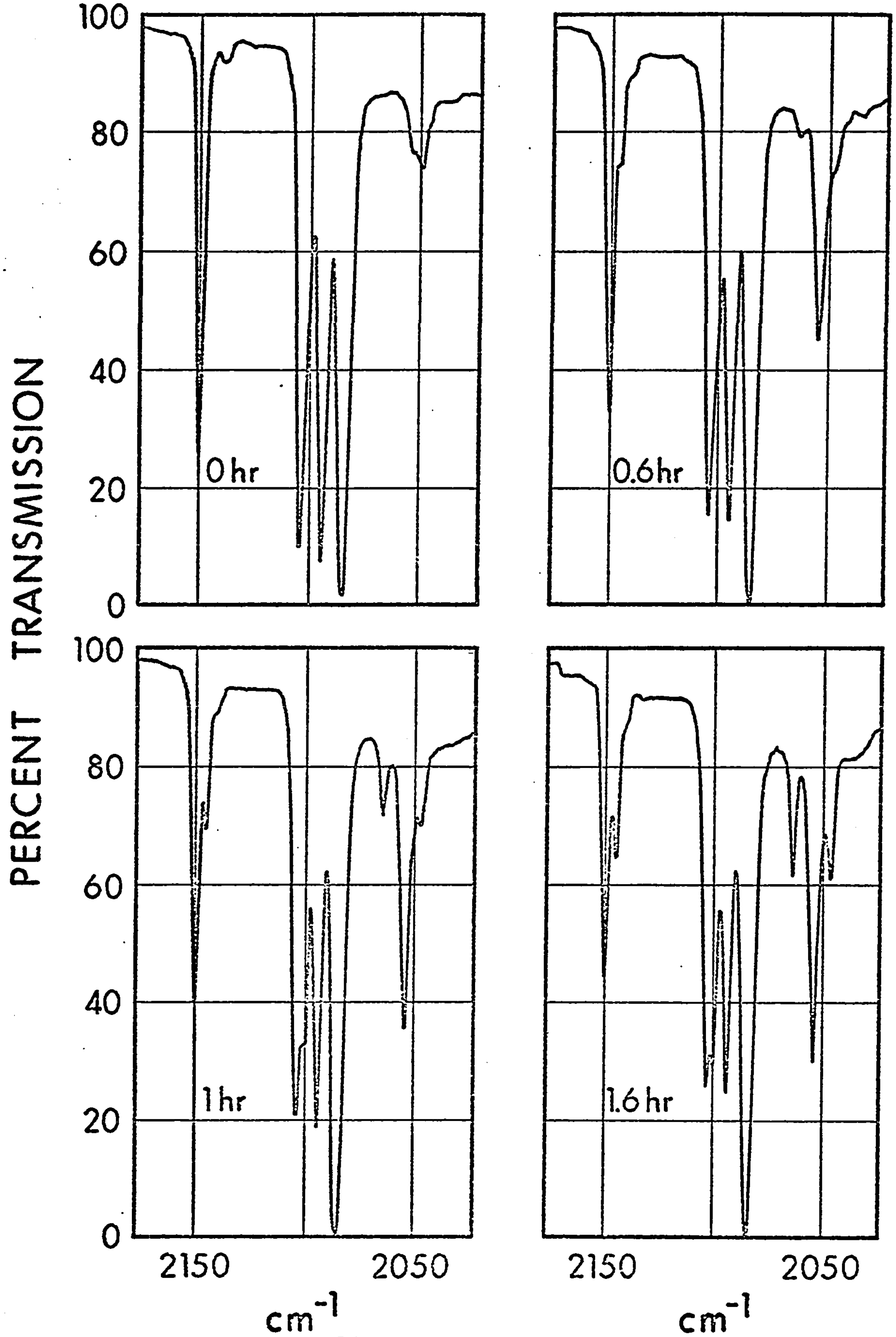


FIGURE 4.1 The ^{13}CO Exchange of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$

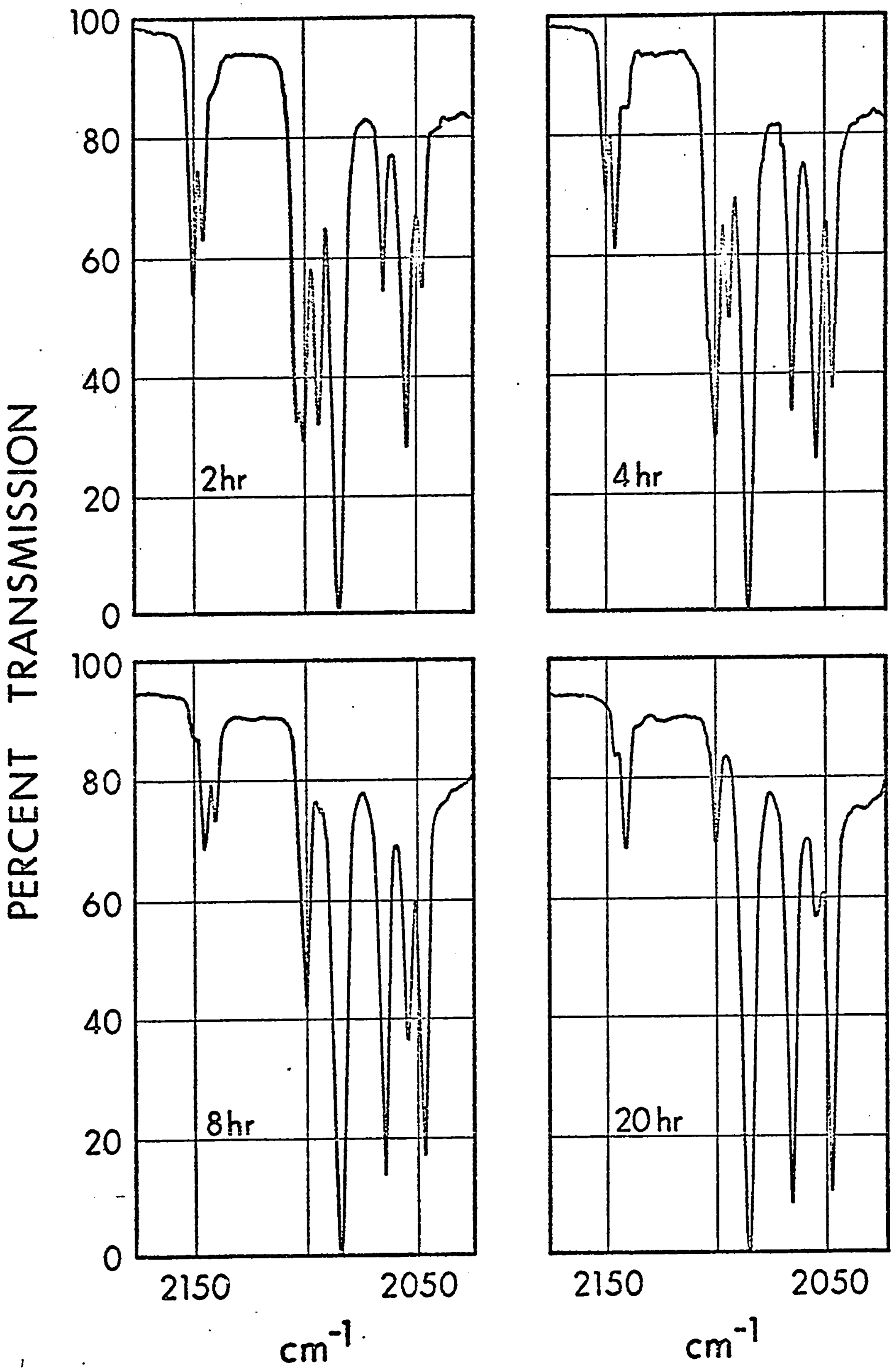


FIGURE 4.1 continued

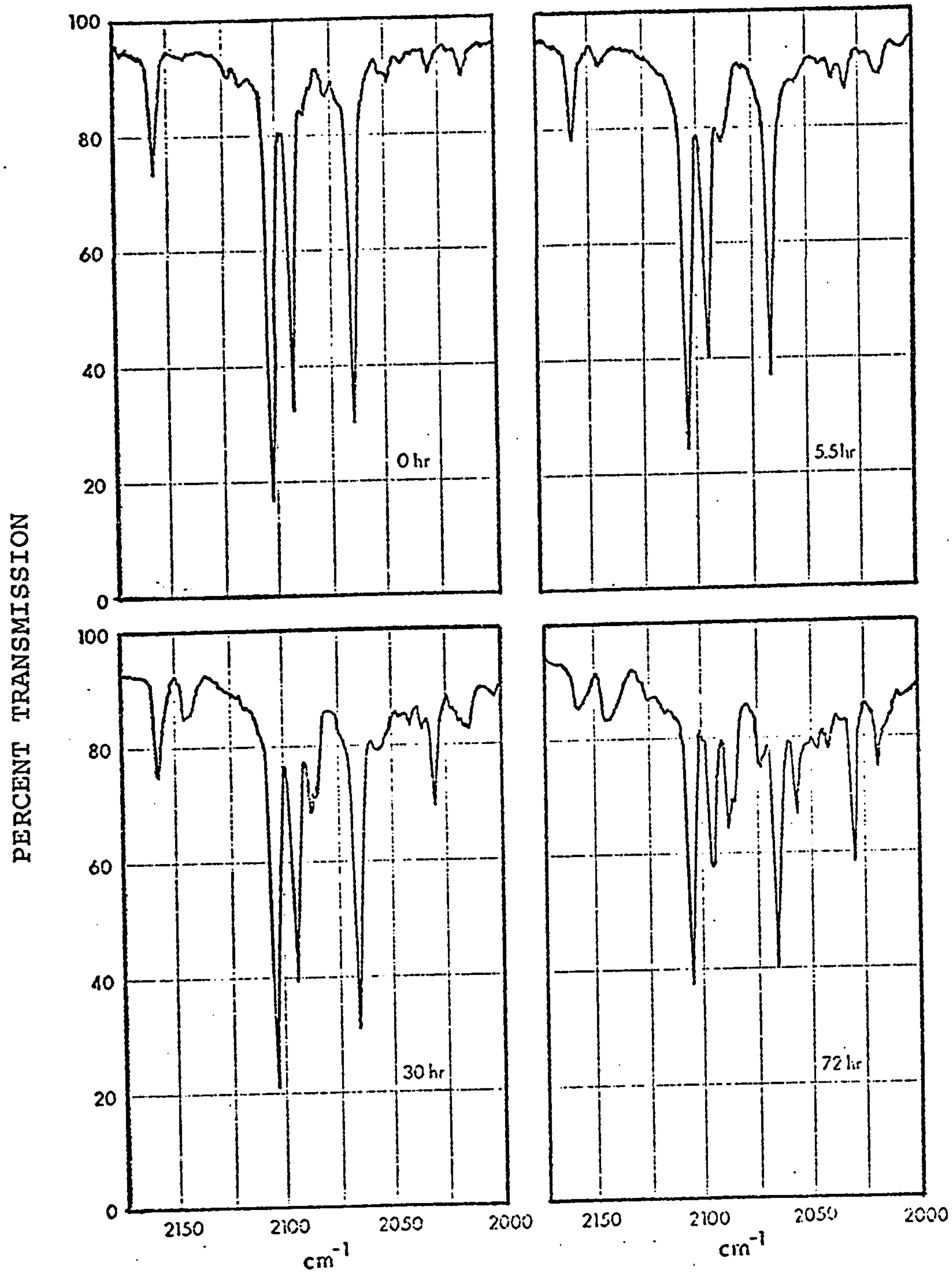
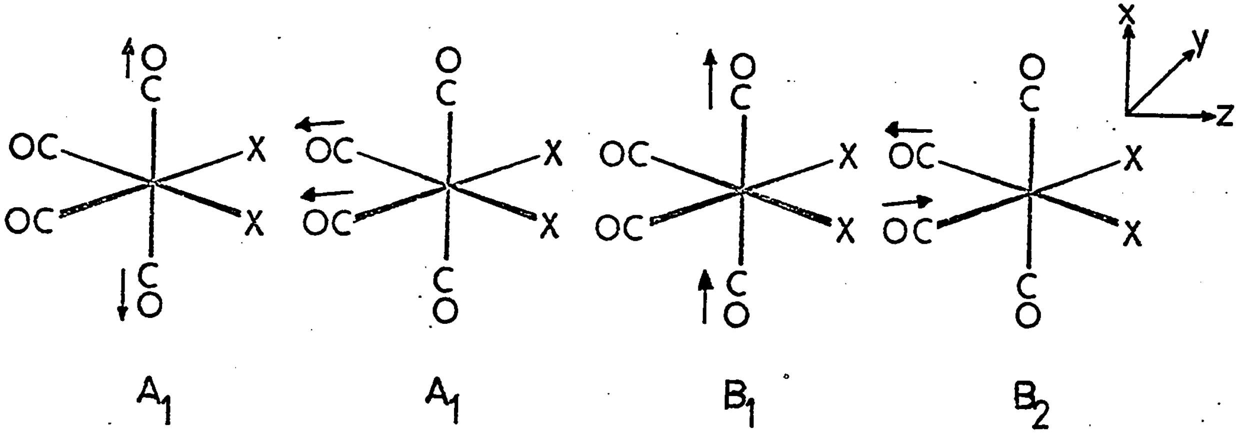


FIGURE 4.2 The ^{13}CO Exchange of *cis*-$Ru(CO)_4I_2$ (taken from Ref. 151).

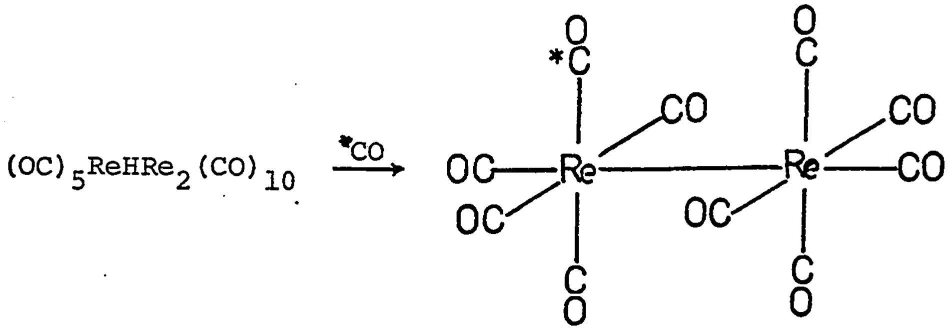
The four ir-active CO stretches for $Ru(CO)_4X_2$ (symmetry C_{2v}) are depicted below with their various symmetry labels.



Since they have the same symmetry, the two A_1 modes are coupled together so that either axial or equatorial substitution will cause a shift in these frequencies. The B_1 mode does not involve the equatorial CO groups and will therefore not be affected by substitution of ^{13}CO in this position.

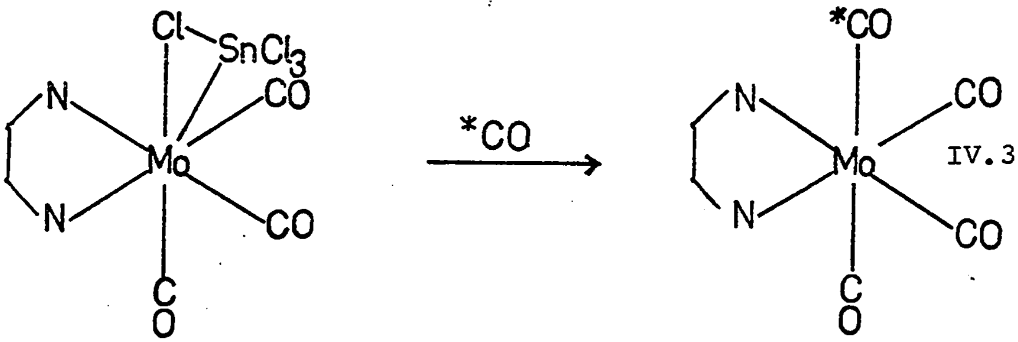
This is what is observed in the spectrum of *cis*-$Ru(CO)_4(SiCl_3)_2$; the lowest energy band remains at the same intensity whilst the other bands gradually disappear with simultaneous growth of new bands. With $Ru(CO)_4I_2$ all four bands decrease in intensity during exchange. There are also many more ^{13}CO bands in the case of the iodide corresponding to both axial and equatorial substitution.

This completely stereospecific substitution of carbon monoxide makes it unique in carbonyl chemistry at the present time. Stereospecific replacement of other ligands by ^{13}CO has been reported. Thus $Re_2(CO)_{10}$ labelled in the equatorial position has been prepared by reaction IV.2 [152]



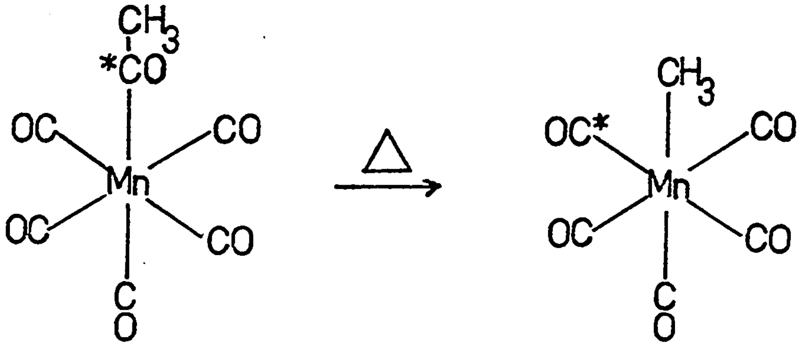
IV.2

Recently, from these laboratories, it has been found that the reaction of labelled CO with $bipyMo(CO)_3SnCl_4$ gives $bipyMo(CO)_4$ labelled in the axial position only (IV.3)[93]



IV.3

$Mn(CO)_5CH_3$ stereospecifically labelled in the equatorial position has been formed by decarbonylation of $CH_3\overset{*}{C}OMn(CO)_5$ (IV.4).[153]


IV.4

In order to observe preferential enrichment in specific sites, not only must the introduction at a specific site be kinetically favored, but, as pointed out by Brown,[154] nondissociative exchange between sites must be slow; that is, the molecule in question must be stereochemically rigid under the conditions of the experiment. In most reported cases, (eg. $XMn(CO)_5$,[155] $I_2Fe(CO)_4$ [156,157]) the labelled carbon monoxide is distributed statistically among the non-equivalent sites of the product molecule. Two systems have recently been reported which appear to meet these criteria: ortho-phenanthrolinetetracarbonylchromium [158] and piperidine-pentacarbonylmolybdenum.[159] In both compounds, carbonyl groups *trans* to the nitrogen ligands exchanged more slowly by a factor of 3 or 4. Very recently it has shown by careful study that the axial carbonyl of $Mn(CO)_5Br$ exchanges 0.74 times slower than the equatorial group.[160a]

In all cases where preferential enrichment has been achieved there was no subsequent scrambling between the labelled and unlabelled positions; indeed the spectrum of enriched $(OC)_4Ru(SiCl_3)_2$ was unchanged after a week, except for loss of intensity due to decomposition. This implies that in the ground state the structures are rigid.

The Relative *trans*-Effects of CO, $SiCl_3$ and $GeCl_3$.

There was no reaction of ^{13}CO with *trans*-$Ru(CO)_4(MCl_3)_2$

under normal conditions. This result, along with the fact that it was the carbonyls *trans* to the MCl_3 group that exchanged, implies that the *trans*-effect of MCl_3 is greater in this system than that of CO. Further, since the substitution in $Ru(CO)_4(SiCl_3)_2$ is very much faster than in the germanium analogue it is possible to say that the *trans*-effect of $SiCl_3$ is greater in these compounds than that of Cl_3Ge.

By comparison of the CO stretching force constants found for the relevant molecules (Table 4.1) one might have predicted the reverse order. From the conventional picture of the bonding of carbon monoxide to a transition metal (Chapter 1) the less π-bonding that occurs the more triple bond character the CO has and thus the higher the force constant. Normally, without this synergic effect of back-bonding, the metal-carbon bond is considered to be weakened; hence the higher the CO stretching force constant the weaker the metal-carbon bond. In previous cases where there has been a preference of *CO substitution, it has always been found that it is the CO group *trans* to another CO group that exchanges faster. The same is found for substitution of CO with phosphines and other donor ligands. For example the reaction of $[Mn(CO)_4I]_2$ with pyridine gives $Mn(CO)_3py_2I$ with the stereochemistry shown in eq. IV.5.

TABLE 4.1

CO Stretching Force Constants for M'(CO)$_4$ X$_2$ Derivatives

Compound	k_{eq} (mdynes Å^{-1})	k_{ax} (mdynes Å^{-1})	Ref.
cis-$Ru(CO)_4(GeCl_3)_2$	18.07	18.25	a/151
trans-$Ru(CO)_4(GeCl_3)_2$	18.33^b		a
cis-$Ru(CO)_4(SiCl_3)_2$	17.91	17.96	a
trans-$Ru(CO)_4(SiCl_3)_2$	18.02		a
cis-$Fe(CO)_4(SiCl_3)_2$	17.31	17.76	151
cis-$Fe(CO)_4Br_2$	17.62	18.26	151
cis-$Fe(CO)_4I_2$	17.42	17.83	151
cis-$Ru(CO)_4I_2$	17.47	18.36	a/151
cis-$Os(CO)_4I_2$	17.32	18.23	a
cis-$Os(CO)_4H_2$	17.35	17.54	a
$Mn(CO)_5H$	16.45	16.93	161
$Mn(CO)_5Cl$	16.22	17.50	155
$Mn(CO)_5Br$	16.26	17.41	155
$Mn(CO)_5I$	16.30	17.28	155

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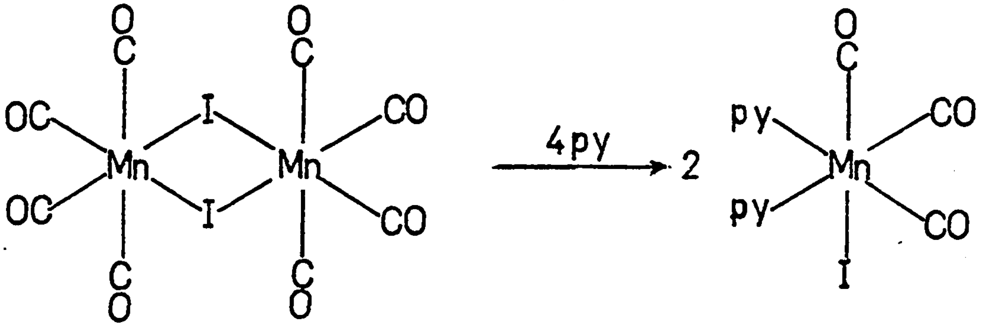
[a] this work

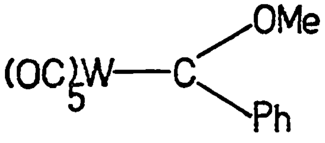
[b] approximate result, CH_2Cl_2 solution.



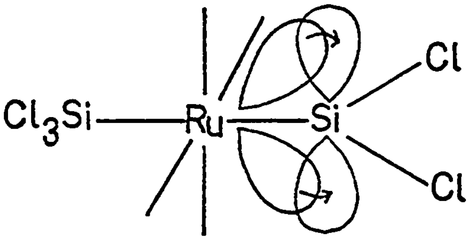
IV.5

The present compounds to not follow this order - although the differences are small-the CO group with the lowest force constant is the most labile. It is possible that in the present compounds a different situation exists. From the high values of the force constants it is probable that there is very little π-density transmitted to the CO groups. This suggests that σ-bonding is much more important in determining the force constants in these derivatives. It has been shown [162] that CO absorbed on zinc oxide absorbs in the infrared at 2200 cm^{-1}, compared to the stretching frequency of free gaseous CO of 2143 cm^{-1}. This adsorption on zinc oxide is believed to involve a situation whereby the CO molecule is purely σ-bonded to the surface. Thus σ-bonding appears to cause an increase in the force constant; a similar conclusion has been reached by Dobson.[163] If a situation exists where σ-bonding is the major contribution affecting the force constant, a higher force constant would be taken to mean a stronger σ-bond. If this interpretation is correct then the *trans*-effects are in agreement with the force constants, i.e., the *trans*-effects in these derivatives decrease in the order $SiCl_3 > GeCl_3 > CO$. Once again it is stated that there is no theoretical reason why force constants and bond strength should be related [70] although it is normally assumed to be the case.

The mass spectra of *cis*-and *trans*-$Ru(CO)_4(SiCl_3)_2$ (Table 4.2 and 4.3 respectively) are also in agreement with the $SiCl_3$ group having a larger *trans*-effect than CO. Thus in the *cis*-molecule the parent peak (P^+) and $(P-CO)^+$ are very weak whereas $(P-2CO)^+$ is the strongest peak in the spectrum. It could be argued that this was due to loss of the axial CO groups; however, in the spectrum of the *trans*-isomer, $(P-Cl)^+$ and $(P-SiCl_3)^+$ are strong ions i.e., the $SiCl_3$ groups are acting upon on one another. The analogous germanium compounds show similar behaviour although not quite so markedly as one might expect. It is interesting to speculate that the structure of $(P-Cl)^+$ may be stabilized in a similar fashion to the carbene derivatives of transition metals, an example of which is given in 4.2.[164] The positive charge on silicon could be stabilized by π-density on the ruthenium (4.3)



4.2



4.3

TABLE 4.2

Mass Spectrum of *cis*-$Ru(CO)_4(SiCl_3)_2$

m/a	Rel. Abund.	Assignment
482	2.1	$Ru(CO)_4(SiCl_3)_2^+$
454	34	$Ru(CO)_3(SiCl_3)_2^+$
426	100	$Ru(CO)_2(SiCl_3)_2^+$
398	30	$Ru(CO)(SiCl_3)_2^+$
370	11	$Ru(SiCl_3)_2^+$
363	11	$Ru(CO)(SiCl_3)(SiCl_2)^+$
349	5	$Ru(CO)_4(SiCl_3)^+$
335	9	$Ru(SiCl_3)(SiCl_2)^+$
321	14	$Ru(CO)_3(SiCl_3)^+$
293	16	$Ru(CO)_2(SiCl_3)^+$
284	13	$Ru(CO)_3(SiCl_2)^+$
256	25	$Ri(CO)_2(SiCl_2)^+$
237	20	$Ru(CO)(SiCl_3)^+$
230	58	$Ru(CO)(SiCl_2)^+$
202	75	$Ru(SiCl_2)^+$
170	39	$RuCl_2^+$
165	46	$RuSiCl^+$
135	93	$RuCl^+$

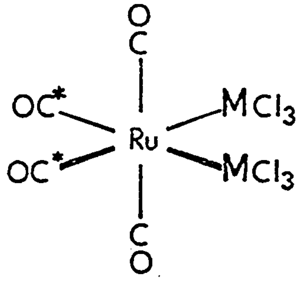
TABLE 4.3

Mass Spectrum of *trans*-$Ru(CO)_4(SiCl_3)_2$

m/a	Rel. Abund.	Assignment
482	18	$Ru(CO)_4(SiCl_3)_2^+$
447	10	$Ru(CO)_4(SiCl_3)(SiCl_2)^+$
426	2.4	$Ru(CO)_2(SiCl_3)_2$
398	7.8	$Ru(CO)(SiCl_3)_2^+$
391	3.7	$Ru(CO)_2(SiCl_3)(SiCl_2)^+$
370	5.4	$Ru(SiCl_3)_2^+$
363	7.1	$Ru(CO)(SiCl_3)(SiCl_2)^+$
349	49	$Ru(CO)_4(SiCl_3)^+$
334	4.9	$Ru(SiCl_3)(SiCl_2)^+$
321	100	$Ru(CO)_3(SiCl_3)^+$
293	24	$Ru(CO)_2(SiCl_2)^+$
265	9.0	$Ru(CO)(SiCl_3)^+$
258	4.1	$Ru(CO)_2(SiCl_2)^+$
237	16	$Ru(SiCl_3)^+$
230	29	$Ru(CO)(SiCl_2)^+$
202	32	$Ru(SiCl_2)-$
170	21	$RuCl_2^+$
165	24	$Ru(SiCl)^+$
135	29	$RuCl^+$

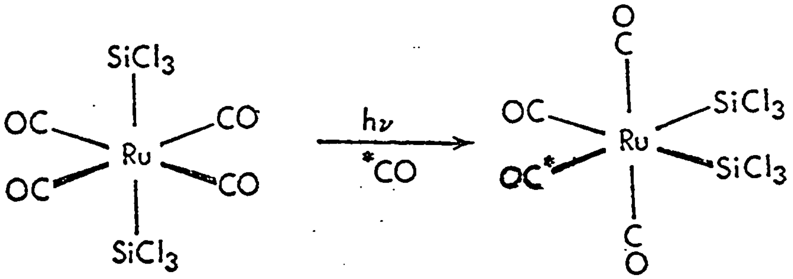
The Exchange of *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$.

As has already been pointed out *trans*-Ru(CO)$_4$(MCl$_3$)$_2$ (M = Si or Ge) was ordinarily inert to ^{13}CO. However, upon irradiation with ultraviolet light, the product was found to be the same as that which was obtained on exchanging the *cis*-compound namely 4.4.



4.4

During the isomerization of the unenriched *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$ under ^{13}CO, the first new bands to appear were those of equatorially monosubstituted *cis* (see Fig. 4.3. Therefore the *trans* goes directly to enriched *cis* (IV.6) and is not converted to unenriched *cis* with subse-



IV.6

quent ^{13}CO exchange. If the isomerization was like that given in IV.7 we would have expected to see absorptions

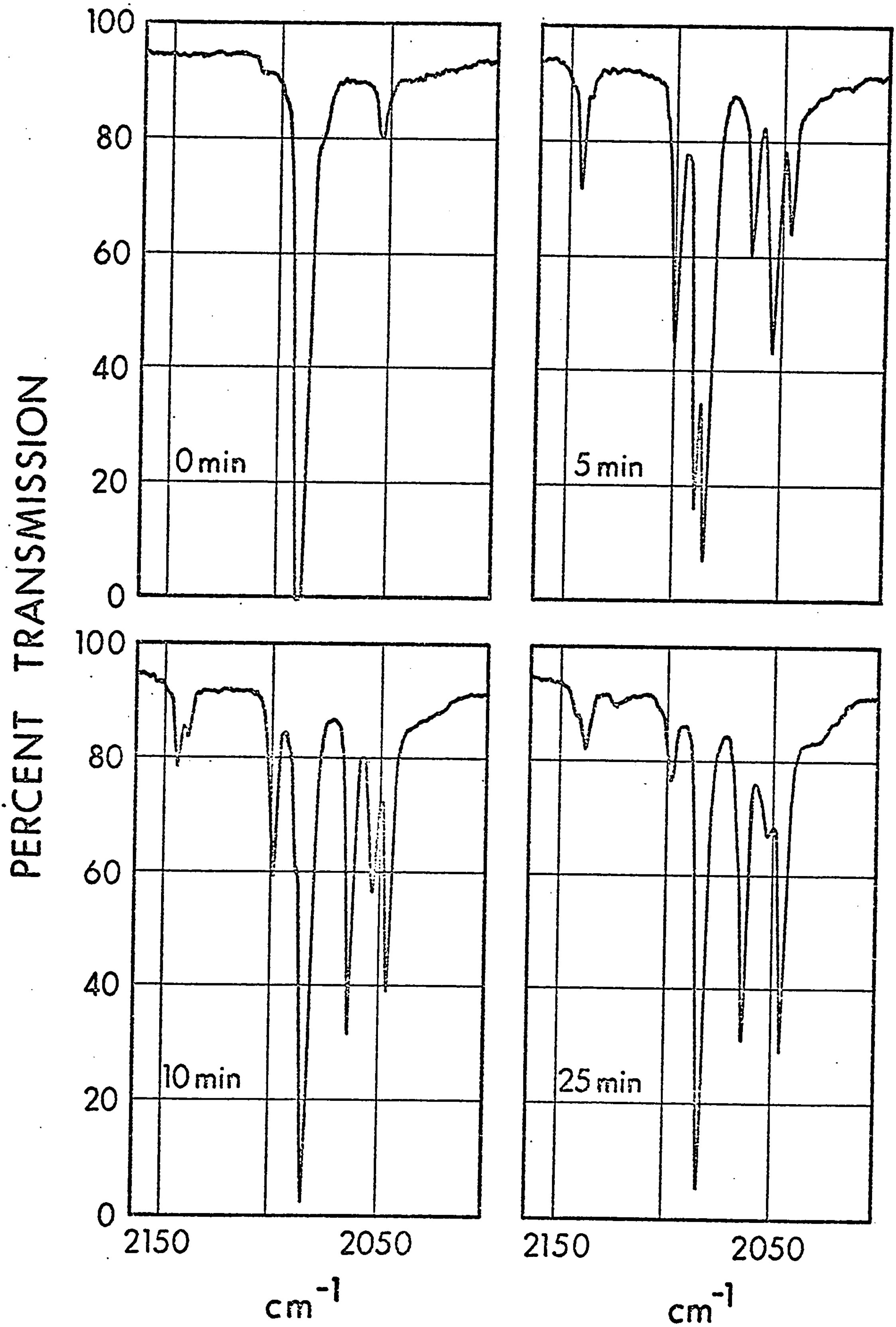
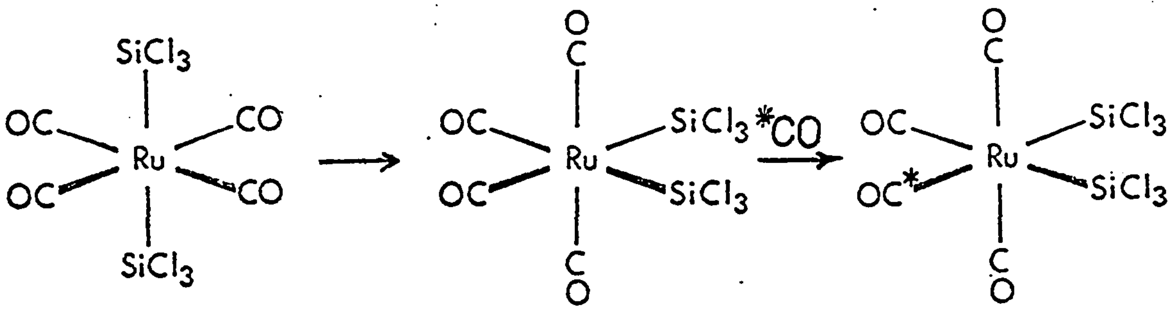


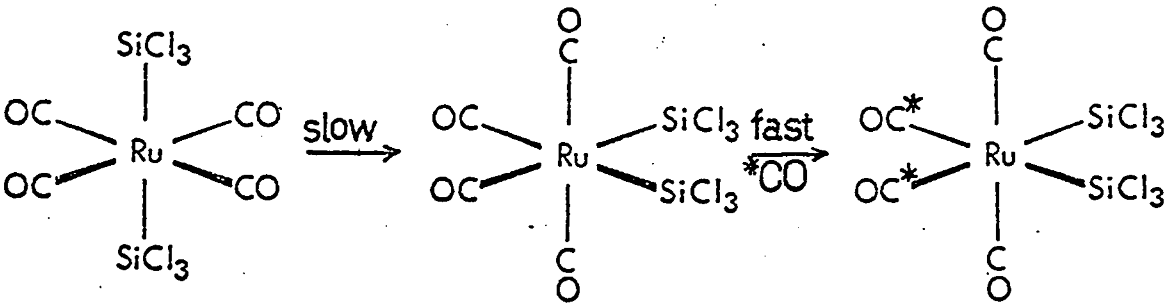
FIGURE 4.3 The ^{13}CO Exchange of *trans*-$Ru(CO)_4(SiCl_3)_2$.

due to unenriched *cis*. It would not have been



IV.7

possible to say that IV.7 was not the mechanism if disubstituted *cis* had been the first product observed since a path such as IV.8 would also fit such results.



V.8

This surprising result has important implications for the understanding of the five-coordinate intermediate in dissociative metal carbonyl reactions. Discussion will be restricted to $Ru(CO)_4(SiCl_3)_2$ since this was studied in most detail. Arguments presented here probably apply to $Ru(CO)_4(GeCl_3)_2$, also.

The Kinetics of ^{13}CO Exchange of *cis*-$Ru(CO)_4(SiCl_3)_2$.

Before considering the nature of the five-coordinate intermediate, evidence is presented here to show that the exchange of *cis*-$Ru(CO)_4(SiCl_3)_2$ proceeds *via* a dissociative mechanism. Indeed, without such evidence it is questionable whether the ensuing discussion would be valid. That *cis*-$Ru(CO)_4(SiCl_3)_2$ undergoes ^{13}CO substitution by way of a five-coordinate species is supported by the rate law which is independent of carbon monoxide concentration i.e.,

$$\text{Rate} = k[Ru(CO)_4(SiCl_3)_2] \qquad \text{IV.9}$$

This was proven by showing (Table 4.4) that the rate was the same under different partial pressures of ^{13}CO (of constant enrichment). These different pressures of CO were achieved by dilution with nitrogen. The straight-line plots also show that the reaction is first order in *cis*-$Ru(CO)_4(SiCl_3)_2$.

The rate law IV.9 cannot be proved by measuring the rates under an atmosphere consisting only of carbon monoxide in which the ratio ^{12}CO:^{13}CO is varied. Considerations show that even if the reaction is zero order in carbon monoxide the rate will appear to depend upon the partial pressure of ^{13}CO. For this reason rates obtained using 95.5% enriched carbon monoxide were corrected to 100% ^{13}CO

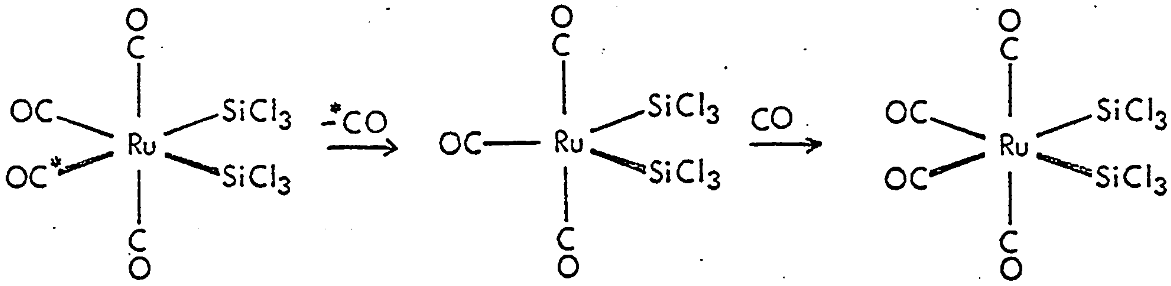
TABLE 4.4

Rates of ^{13}CO Exchange for *cis*-$Ru(CO)_4(SiCl_3)_2$

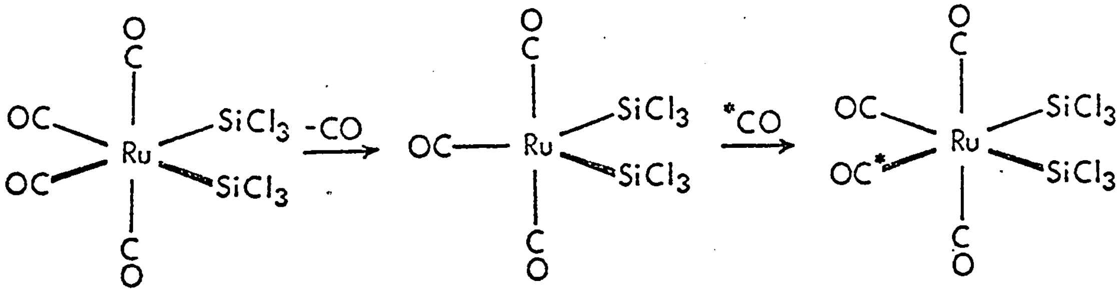
Temp.	Atmosphere % ^{13}CO	Observed Rate sec^{-1}	Corrected Rate (100% ^{13}CO) sec^{-1}
26.4	95.5	1.04×10^{-4}	mean 1.06×10^{-5}
26.6	60.0	1.03×10^{-4}	
26.6	40.0	1.00×10^{-4}	
26.6	20.0	0.99×10^{-4}	
20.2	40.0	3.51×10^{-5}	3.67×10^{-5}
34.8	40.0	3.23×10^{-4}	3.38×10^{-4}

by multiplying by the statistical factor 100/95.5.

Another problem introduced by use of carbon monoxide of low enrichment is that, as the exchange progresses, the reaction of singly labelled *cis*-$Ru(CO)_4(SiCl_3)_2$ with ^{12}CO to give unlabelled product will become significant and departure from first order plots will be observed. Note that the rate for reaction IV.10 is half that for IV.11



IV.10



IV.11

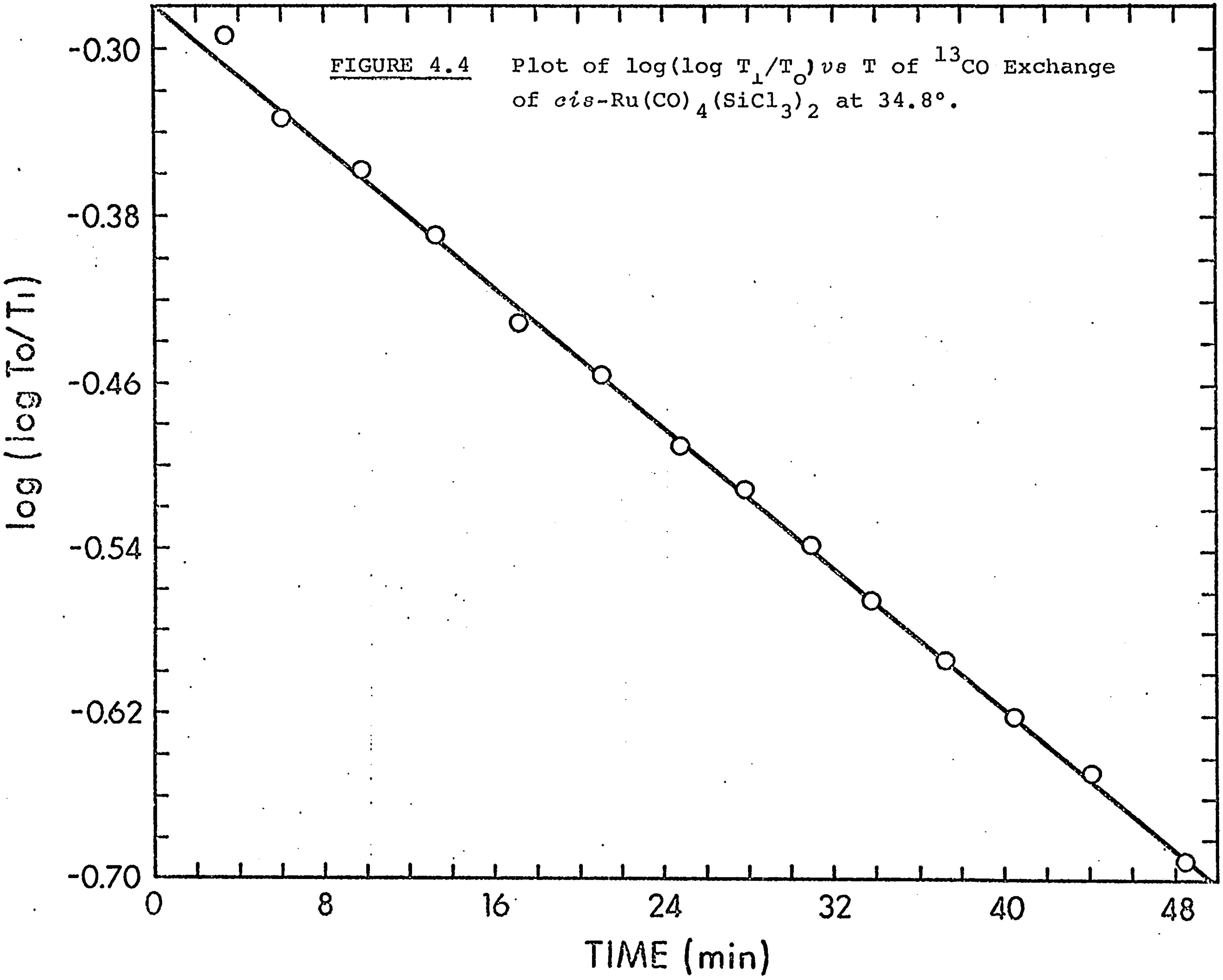
again due to statistical factors: there is twice the chance of CO being lost in IV.11 as to *CO in IV.10. Using 95.5% enriched CO, no departure from linear first order plots was observed in the early stages of the exchange, (Fig. 4.4).

The rate of reaction IV.10 would not be exactly half that of IV.11 because of the isotope effect of replacing ^{12}C with ^{13}C. The rate of reaction IV.11 would not vary if the substitution in the second step were by ^{12}CO instead of ^{13}CO since it is the first step which determines the rate.

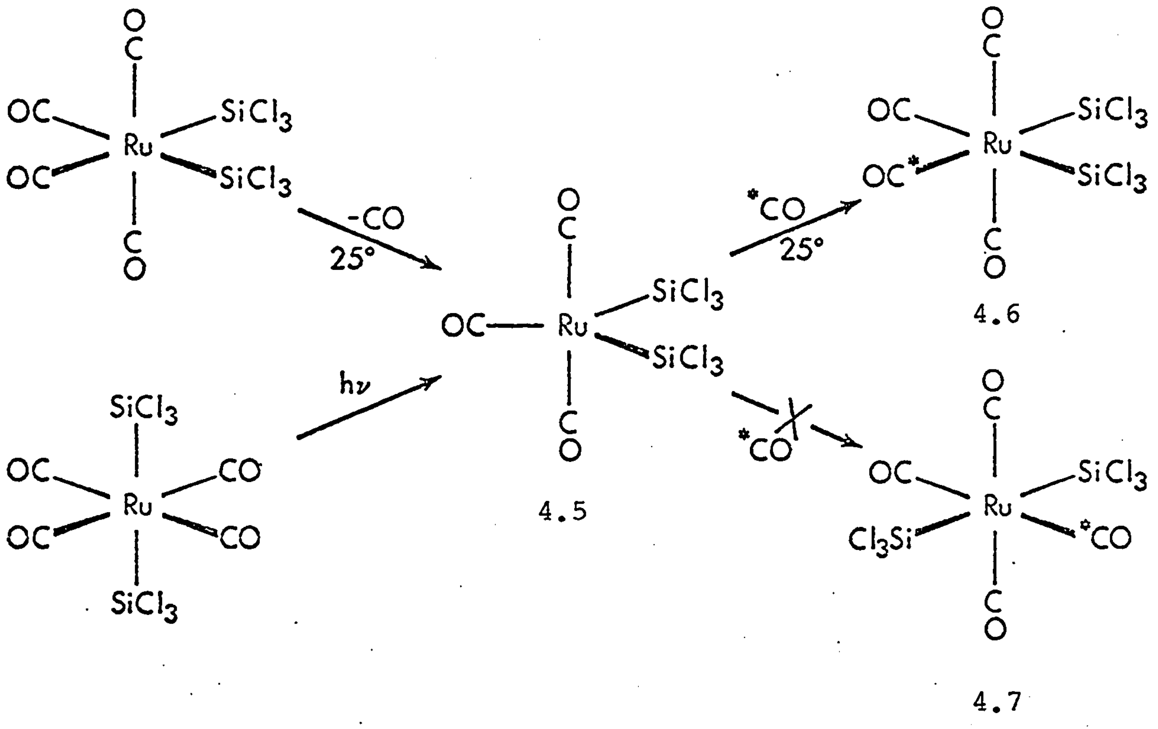
By studying the rate of exchange of ^{13}CO at three different temperatures (20.2°, 26.6° and 34.8°) it was possible to calculate activation parameters of $\Delta H^{\ddagger} = 26.7 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = 3 \pm 3$ eu. This latter result is not inconsistent with a dissociative mechanism.

The Mechanism of the ^{13}CO Exchange of $Ru(CO)_4(SiCl_3)_2$.

The mechanism of the ^{13}CO substitution of *cis-* and *trans*-$Ru(CO)_4(SiCl_3)_2$ can be rationalized in terms of a common five-coordinate having the geometry designated in 4.5 with both trichlorosilyl groups in equatorial positions of the trigonal bipyramid, as indicated in the following scheme. The favored intermediate 4.5 might appear to be capable of reaction with ^{13}CO to form the enriched *trans*-isomer 4.7 (with loss of stereospecificity in subsequent reactions), but microscopic reversibility implies that since



<u>FIGURE 4.4</u> Plot of log(log T_1/T_o) *vs* T of ^{13}CO Exchange of *cis*-$Ru(CO)_4(SiCl_3)_2$ at 34.8°.

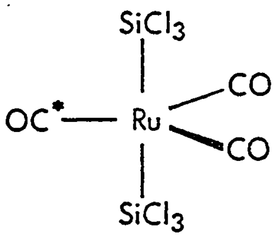


SCHEME D

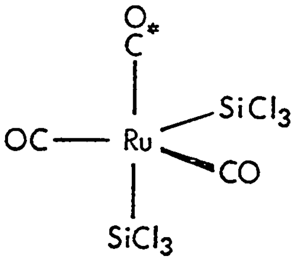
the barrier for *trans* → 4.5 is much greater than that for *cis* → 4.5, the barrier for 4.5 → 4.7 is much greater than that for 4.5 → 4.6. Intuitively, this result may have been expected since the larger $SiCl_3$ groups would block the reentry of CO *via* the 4.5 → 4.7 pathway.

In general, a five-coordinate intermediate may be stereochemically nonrigid in ways which exchange the initially axial and equatorial carbonyls, yet still react with labelled carbon monoxide to give a stereospecifically singly-labelled product; this consequence of microscopic reversibility was first pointed out in this context by Brown.[154] However, in the present case stereospecificity persists as a second ^{13}CO is introduced. This establishes that the initially axial and equatorial sets of carbonyl groups are at all times differentiated in the five-coordinate intermediate.

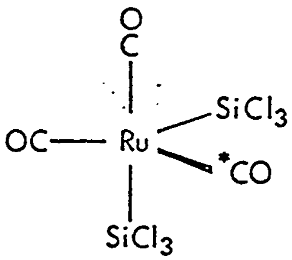
Accordingly, there must be restrictions on the non-rigid processes which the intermediate can undergo. Of the other isomeric five-coordinate structures to which singly labelled 4.5 might be converted by the Berry mechanism[165], 4.8 can be excluded since all carbonyls are equivalent. Isomer 4.9 cannot be rigorously excluded but it is probably not involved since its conversion to forms such as 4.10 with scrambling of carbonyls from the two initial sites, would be expected to be facile. This suggests that there are significant energy differences among the isomeric five-coordinate intermediates with 4.5 the most stable and the others essentially inaccessible.



4.8

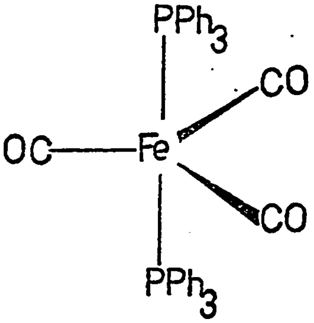


4.9



4.10

Arguments of the sort advanced by Muetterties [166] for other types of five-coordinate intermediates may be applicable here as well. The fact that *trans*-$Ru(CO)_4(SiCl_3)_2$ goes to the *cis*-form under ultraviolet irradiation, even though this is not favored thermodynamically (see Chapter 5), could be explained in terms of the relative stabilities of the five-coordinate intermediates. Among the phosphoranes, it is established that the equatorial positions are preferred by the more electropositive substituents.[167] It is not clear in the present case whether the same principle can be applied i.e., that a trichlorosilyl group is more electropositive than a carbonyl. On the other hand, it has been suggested [130] for Fe(0) compounds that poorer π-bonding ligands favor axial sites e.g., $Fe(CO)_3(PPh_3)_2$ [168] has structure 4.11. On the other hand in $Fe(CO)_3(PF_3)_2$,



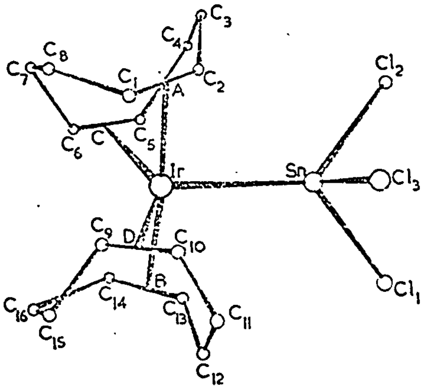
4.11

where PF_3 is considered to have comparable π-properties to CO, there is a dynamic equilibrium between the axial and equatorial isomers.[169] That 4.5 is the stable five-coordinate intermediate implies that the $SiCl_3$ (and $GeCl_3$) is a better π-acceptor than CO. This result is in harmony with many of the other observations delineated in this thesis although this is perhaps the most dramatic.

It is found (Chapter 5) that the ratio of *cis*-to *trans*-isomer for $Ru(CO)_4(SiCl_3)_2$ is approximately 1:2 at room temperature in heptane. On this basis it might have been expected that for the silyl case the five-coordinate intermediates 4.8 and 4.10 might have been present at least to some extent. That this is not the case is shown by no change in the spectrum of exchanged *cis*-$Ru(CO)_4(SiCl_3)_2$, under ^{13}CO, even after one week.

This suggests that in the five-coordinate intermediate there is even more preference for the ligands in particular positions than in the octahedral ground state.

In view of the trend to *trans*-isomers as one goes to a transition metal lower in the periodic table it might be expected that as yet unsynthesized $Cl_3MIr(CO)_4$ (M = Si, Ge or Sn) derivatives may exist as the equatorial isomers even though in the cobalt analogues the MCl_3 moiety is axial. Note that $Cl_3SnIr(C_8H_{12})_2$ (4.12) is considered to have the Cl_3Sn in an equatorial position.[170]



4.12

Speculation on the Mechanism of ^{13}CO Exchange of Other $M'(CO)_4X_2$ Species.

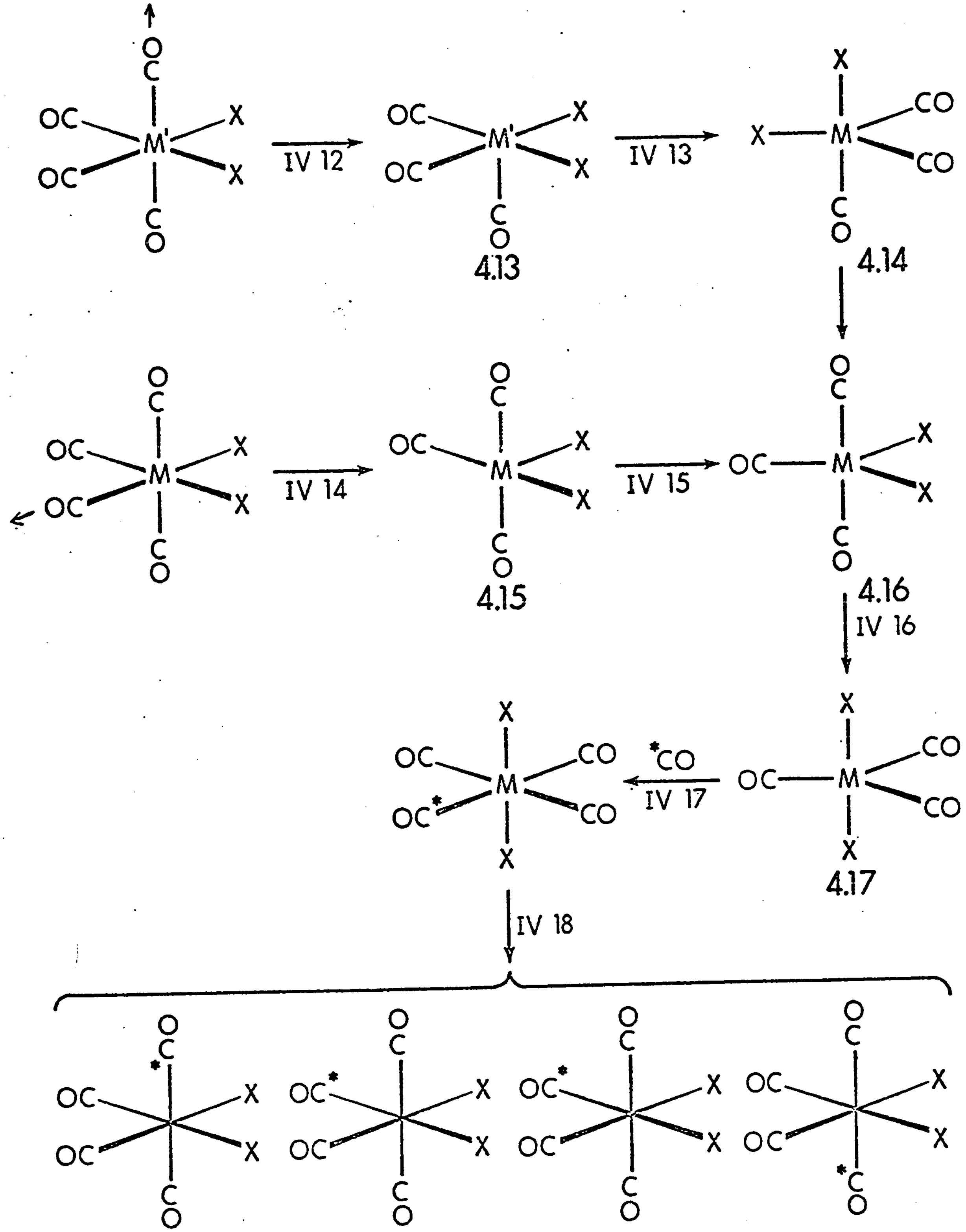
$Fe(CO)_4I_2$ and $Ru(CO)_4I_2$

Let us now apply these ideas to other *cis*-$M'(CO)_4X_2$ species (M' = Fe, Ru or Os, X = a one electron donor). If X is a poorer π-acceptor than carbon monoxide - as most ligands are thought to be - it might be expected that $M'(CO)_4X_2$ would be stable as the *cis*-form whereas the five coordinate intermediate [$M'(CO)_3X_2$] would be stable with the X groups in the axial position i.e., *trans* to each other. Hence if the *trans*-isomer of $M'(CO)_4X_2$ is capable of existence a method of synthesis might be the irradiation of the *cis*-molecule under a carbon monoxide atmosphere. Besides the stability of the *trans*-form, this method would depend on the stability of the five-coordinate intermediate since it could decompose or dimerize.

This is just what is observed for *cis*-$Fe(CO)_4I_2$ and *cis*-$Ru(CO)_4I_2$. When either of these compounds was irradiated, in solution, the *trans*-isomer was formed.[129] The reaction was not carried out under a carbon monoxide atmosphere although it was probably present since decomposition occurred simultaneously with the isomerization. Solutions of *trans*-$Fe(CO)_4I_2$ in the dark isomerize back to the *cis*-form. On the arguments presented here it is unlikely that this latter rearrangement proceeds by way of dissociative mechanism, i.e., it is probably intramolecular (see Chapter 5).

The formation of the *trans*-isomer can be explained on the basis of the stability of the five-coordinate intermediate. It could also explain the random nature of the ^{13}CO exchange of *cis*-$Ru(CO)_4I_2$ (or $Fe(CO)_4I_2$). Thus one could imagine a mechanism as shown in Scheme E for the exchange.

SCHEME E


M'
IV 12
4.13
IV 13
4.14
M
IV 14
4.15
IV 15
4.16
IV 16
4.17
*CO
IV 17
IV 18
OC
CO
X
*

For this to be an acceptable pathway, the rearrangement IV.18 would have to be rapid compared to the exchange. Although the equilibrium IV.16 has been established,[129]

$$cis\text{-Fe(CO)}_4\text{I}_2 \underset{\text{dark}}{\overset{h\nu}{\rightleftarrows}} trans\text{-Fe(CO)}_4\text{I}_2 \qquad \text{IV.19}$$

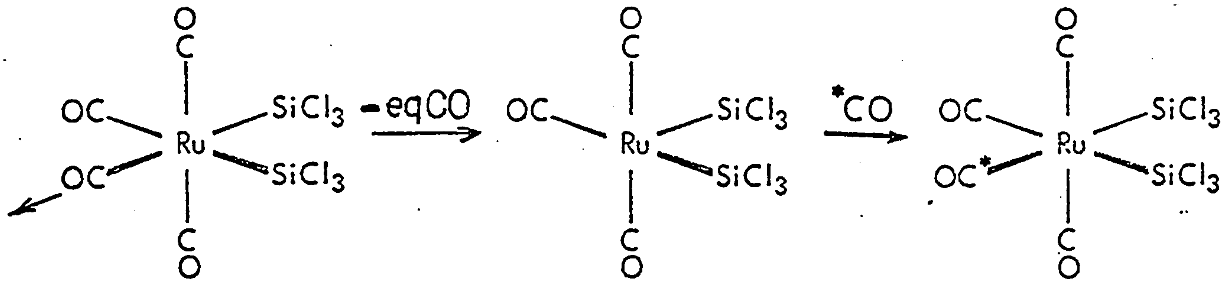
the rate of the *trans* → *cis* isomerization was not given and therefore it is uncertain whether the rate of isomerization of the *trans*-form is fast compared to the exchange. Even though the *trans*-form can be isolated pure and its infrared spectrum measured, its behavior under exchange conditions has not been studied. It may be that in the dark the *trans*-form goes rapidly over to *cis*-form. No bands were reported [156,157] in the papers on the *CO exchange of *cis*-Fe(CO)$_4$I$_2$ which could be assigned to substituted *trans*-derivatives. There was however an absorption observed during the ^{13}CO exchange of *cis*-Ru(CO)$_4$I$_2$ which could be attributed to *trans*-Ru(CO)$_4$I$_2$. If this isomer does isomerize under the conditions more rapidly than the exchange, then Scheme E is a viable mechanism for exchange.

There are, however, a number of other ways in which the random nature of the exchange in these compounds can be achieved. One possibility is that both the equatorial and axial CO groups exchange at the same rate. This at first seems unlikely since the CO stretching force constants for the two types of CO groups are quite different, (Table 4.1) consistent with different M-C bond strengths. We would also not expect the carbonyl and iodide ligand to have the same *trans*-effects.

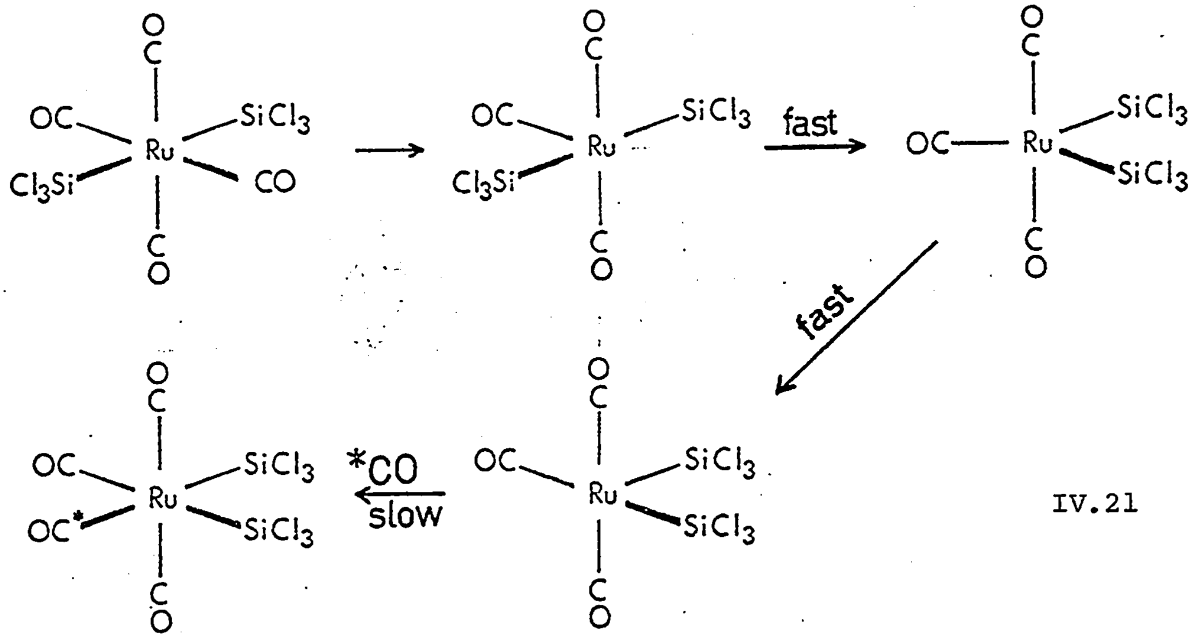
In light of the evidence presented earlier it is possible to comment on the above statements. As has been pointed out the force constants in $Ru(CO)_4(MCl_3)_2$ compounds do not give any indication as to whether the CO groups will exchange or not. This is even more evident when the force constants are compared with those of the manganese and iron compounds listed in Table 4.1, all of which undergo both axial and equatorial exchange.

It has been shown that for $Ru(CO)_4(SiCl_3)_2$ the five-coordinate intermediate appears to be of prime importance in dictating the course of the exchange. It is possible that the five-coordinate intermediate is also of importance in determining which CO group is lost.

This assumes that the intermediate of the exchange is trigonal bipyramidal. It is noted that the exchange of *cis*-$Ru(CO)_4(SiCl_3)_2$ could be explained as involving only a square-based pyramid (IV.20). However, the exchange and isomerization of *trans*-$Ru(CO)_4(SiCl_3)_2$ by any reasonable pathway must involve a trigonal bipyramidal intermediate. This form could have only a very transitory existence (IV.21).



IV.20

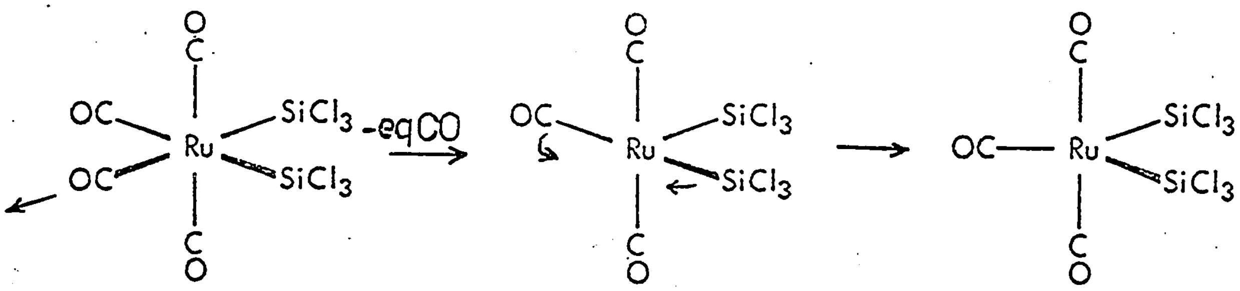


IV.21

This is considered unlikely; there is an accumulation of evidence which shows that the preferred configuration for $M'L_5$ species, both in the ground and excited state, is trigonal bipyramidal. At present we favor a concerted mechanism of simultaneous formation of the trigonal pyramidal intermediate as the carbon monoxide is lost. If the square pyramidal intermediate initially formed from *trans*-$Ru(CO)_4(SiCl_3)_2$ had a finite life-time, then we would have expected at least some enriched *trans*-$Ru(CO)_4(SiCl_3)_2$ to be formed, which was not the case.

As has been shown, there appears to be considerable energy difference between the various possible isomers of the intermediate $[Ru(CO)_3(SiCl_3)_2]$. In such a situation a free energy diagram for exchange of the type given in Fig. 4.5 could be imagined.

The equatorial CO groups are lost preferentially because it is only in this way that the stable form can be obtained (IV.22).



IV.22

The other possibility IV.23 does not occur since it results in a less stable isomer:

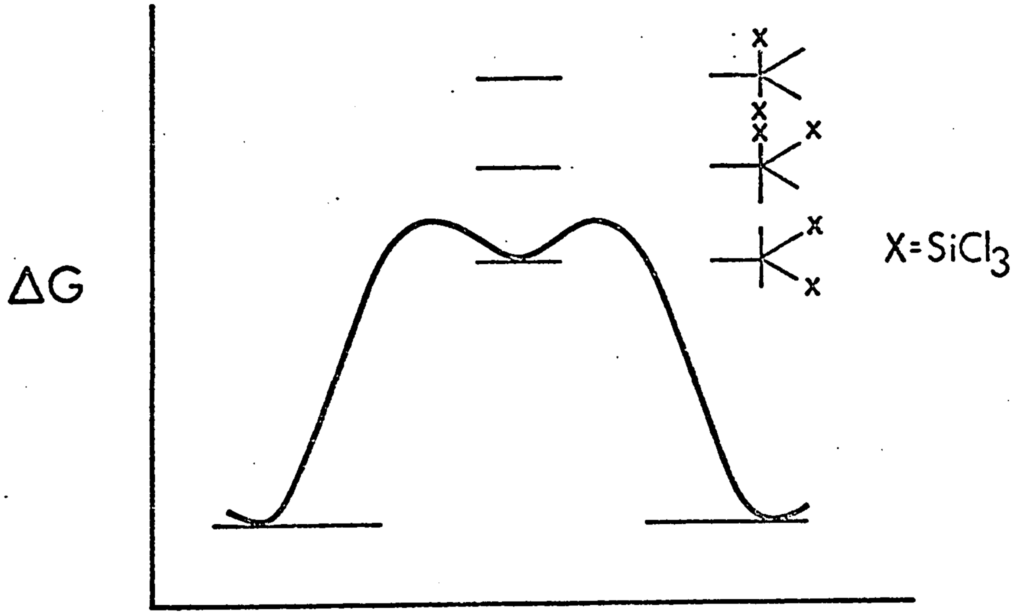


FIGURE 4.5 Free Energy Diagram for Exchange of $Ru(CO)_4(SiCl_3)_2$

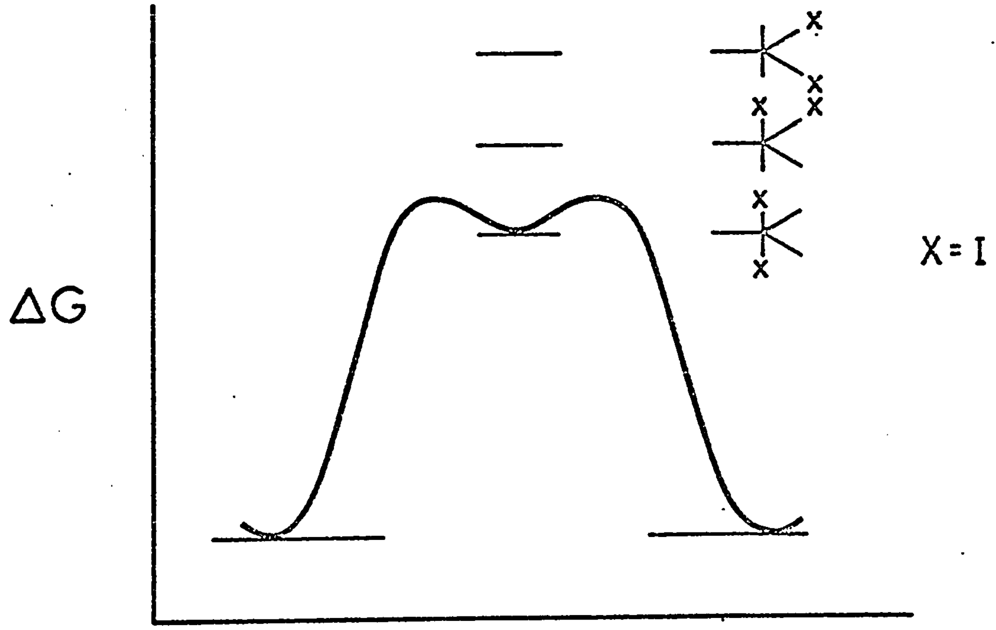
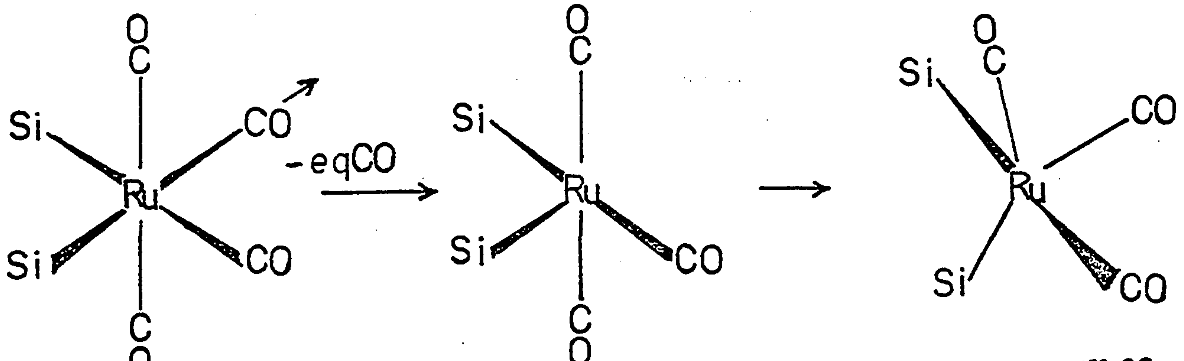
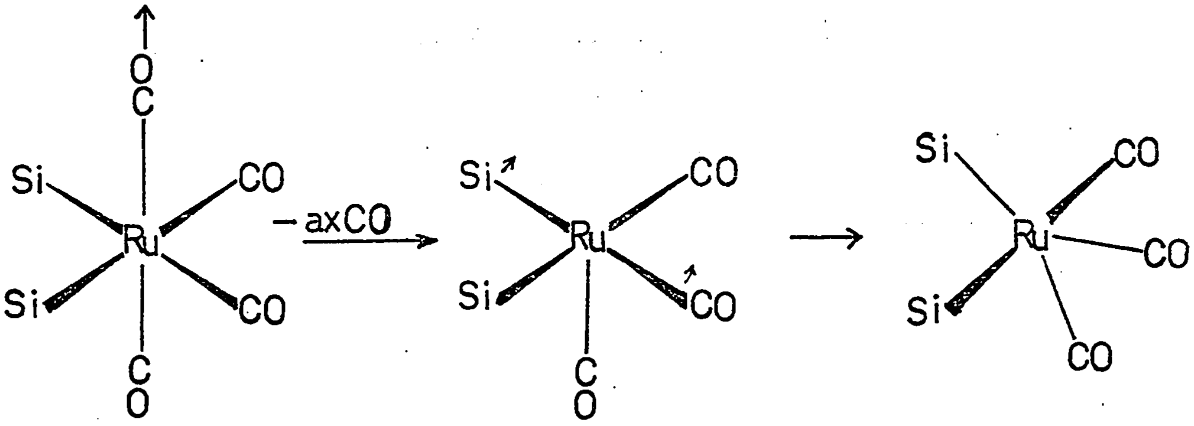


FIGURE 4.6 Free Energy Diagram for Exchange of $Ru(CO)_4I_2$



IV.23

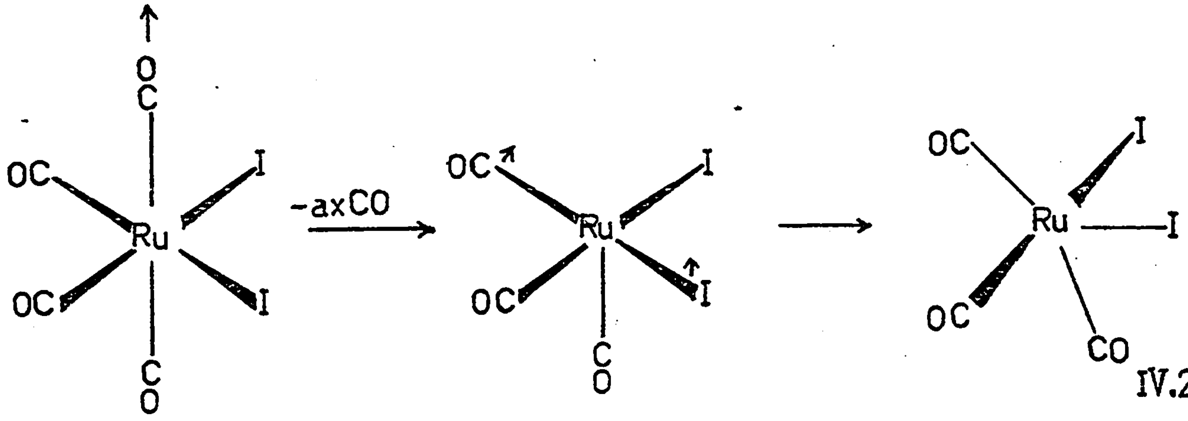
Loss of an axial carbonyl can only result in the same less stable form with an axial $SiCl_3$ group (reaction IV.24).



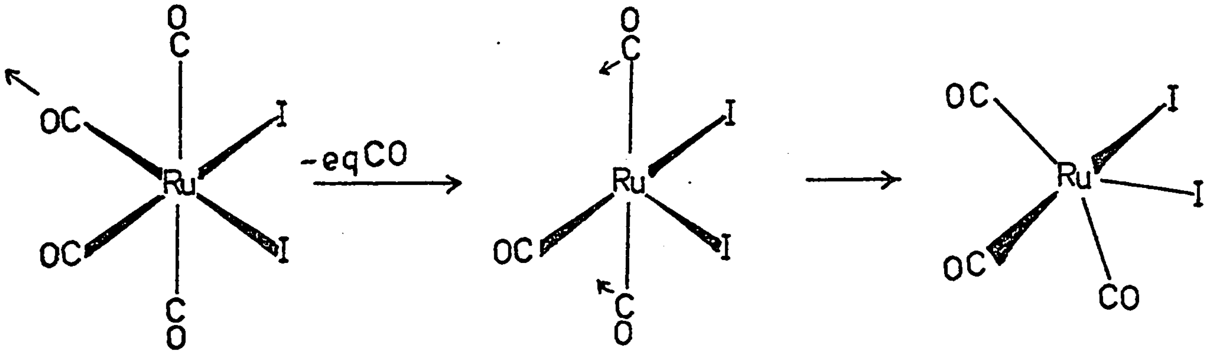
IV.24

This assumes that there is no major rearrangement of the ligands, which appears reasonable since such atomic motion would require considerable energy. It is visualized that only those ligands *cis* to the departing CO group move to partially fill the vacant site.

Now let us consider an example such as *cis*-$Ru(CO)_4I_2$. In such a case a free energy diagram could be envisaged where the order of energy of the intermediates is inverted (Fig. 4.6). Loss of either an axial or equatorial CO group cannot lead, in a single concerted step, to the most stable form. What is presumed to be the next most stable isomer (4.18) with one iodine axial, can result from loss of either type of CO (IV.25; IV.26)

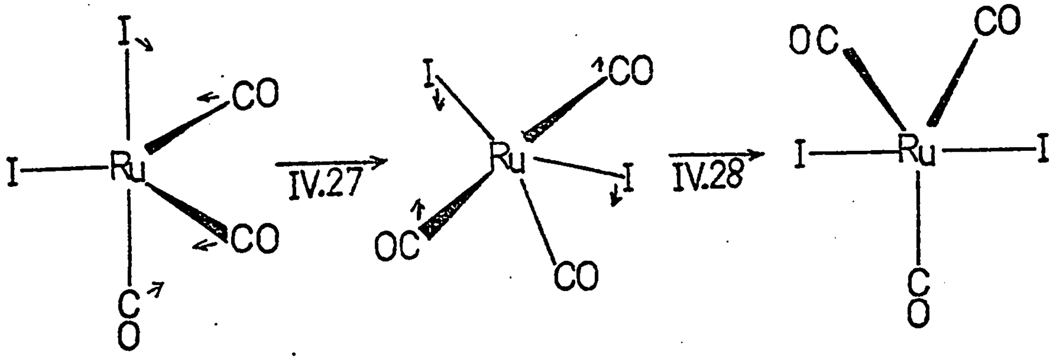


IV.25



IV.26

The only way 4.18 can rearrange to the more stable diaxial form 4.20 by a Berry mechanism [165] is *via* the most unstable isomer 4.19 (IV. 27 and IV.28).



4.18 4.19 4.20

The energy required for IV.27 may be sufficiently high so that it does not take place under normal thermal conditions. It may, however, be achieved in irradiation experiments i.e., *via* Scheme E.

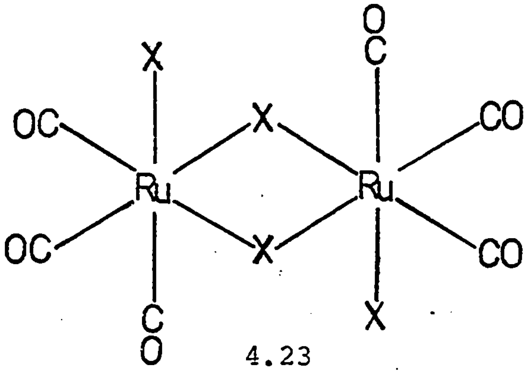
However both equatorial and axial exchange might take place without involving 4.20, since it has been shown in both situations formation of the next most stable intermediate 4.18 can easily take place. If all other factors are equal then we expect, by statistical arguments, that the axial will exchange twice as fast as the equatorial CO groups. Such a 2:1 preference may not be detected using the current technique. It also assumes that all other factors are equal which certainly will not be the case. Steric effects and relative bond strengths are expected to play an important part in determining which CO group is lost.

As pointed out by Brown [154], another mechanism by which random exchange can be achieved is by an intramolecular rearrangement of the octahedral ground state. This would have to be rapid compared to the rate of exchange. Although such rearrangements in octahedral complexes are rare, it will be shown (Chapter 5) that $Os(CO)_4(SiMe_3)_2$ is stereochemically non-rigid at room temperature. Also $Ru(CO)_4(SiCl_3)_2$ appears to behave in a similar manner but above 70°. In both these cases the process involves *cis-trans* isomerization and the *trans*-form of $Ru(CO)_4I_2$ is not normally present in solutions of the *cis*-compound. A mechanism which exchanges the carbonyl groups but keeps the iodines *cis* cannot be excluded.

There is evidence that the exchange of *cis*-$Fe(CO)_4Br_2$ proceeds *via* initial loss of Br_2.[172] Early studies [171] revealed that the exchange depended on the concentration of carbon monoxide, and further work [172] showed that it was inhibited by the presence of Br_2. Furthermore, the exchange of CO was found to be approximately equal to the exchange with $^*Br_2$. This suggested that the two types of replacement involved the formation of the same active intermediate $[Fe(CO)_4]$ for which CO and Br_2 must compete.[172]

The generality of this reaction is doubtful. Although simultaneous loss of two ligands followed by attack by CO is known [93,96] (Chapter 1), they involved ligands that were associated in the solid state. No such interaction was observed in the crystal structure of *cis*-$Ru(CO)_4I_2$.[173] The isoelectronic $Mn(CO)_5Br$ also shows almost random exchange[161], where loss of X_2 is, of course, impossible. Furthermore no decomposition products which might result from an $Fe(CO)_4$ moiety were observed (e.g., $Fe_3(CO)_{12}$, $Fe(CO)_5$).

Indeed *cis*-$Ru(CO)_4X_2$ (X = Br or I) decomposes by a first order process, into $[Ru(CO)_3X_2]_2$ (4.23). That the entropy of activation was positive also supported the

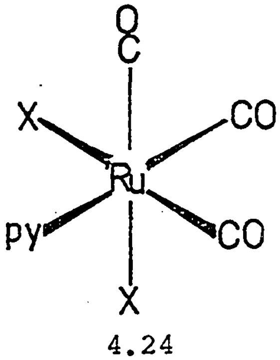


4.23

mechanism IV.29.[109]

$$Ru(CO)_4X_2 \xrightarrow{-CO} Ru(CO)_3X_2 \qquad IV.29$$

It was also found that $Ru(CO)_4X_2$ reacts with two electron-donors such as pyridine to give compounds of the type 4.24.[109]



4.24

Both 4.23 and 4.24 are consistent with the axial CO group being lost preferentially.

cis-$Fe(CO)_4(SiCl_3)_2$

Rapid isomerization of the *trans*-form (Scheme E)) is perhaps a more likely mechanism in the random exchange of *cis*-$Fe(CO)_4(SiCl_3)_2$. The greater stability of the *cis*-form implies that $SiCl_3$ is a somewhat poorer π-acceptor than CO but in view of the properties of $Ru(CO)_4(SiCl_3)_2$ this difference may not be great. This suggests that for the intermediate $[Fe(CO)_3(SiCl_3)_2]$ the most stable form would be one with the $SiCl_3$ groups *trans* to each other but the energy difference between the various isomers may be small. The exchange only took place under ultraviolet irradiation [174] so that energy might be available for the formation of the *trans*-form of $[Fe(CO)_3(SiCl_3)_2]$. Since *trans*-$Ru(CO)_4(SiCl_3)_2$ isomerizes (Chapter 5) at a much lower temperature than *trans*-$Ru(CO)_4(GeCl_3)_2$, it might be expected that *trans*-$Fe(CO)_4(SiCl_3)_2$ would isomerize at temperatures below room temperature since this is the point at which *trans*-$Fe(CO)_4(GeCl_3)_2$ rearranges.

cis-$Os(CO)_4I_2$

From the work of Bigorgne and Pańkowski [129] it appears that $Os(CO)_4I_2$ is stable as the *trans*-form. Thus the *cis*-isomer is obtained by heating *trans*-$Os(CO)_4I_2$ (under CO pressure) whereas the reverse is true for iron and ruthenium. Also irradiation of the *trans*-compound produces the *cis*, again opposite to what is found for other members of the iron triad. These rather surprising results would at first appear to suggest that iodine is a better π-acceptor than CO. These observations can, however, be rationalized in terms of repulsion of bond pairs as outlined in Chapter 2. The irradiation experiment did suggest that ^{13}CO exchange of *cis*-$Os(CO)_4I_2$ may be stereospecific. However, it was found that the exchange did not take place unless the solution was irradiated and then the exchange was found to be non-stereospecific within the limitations of the experiment.

It is difficult to say why *cis*-$Os(CO)_4I_2$ does not exchange in the dark whereas the ruthenium and iron compounds do. Perhaps because the σ- and π-orbitals of iodine are closer in energy to those of osmium there is better overlap in the Os-I bond. Such a situation may cause a strengthening of the Os-C bonds since it has been suggested that the synergic character of the transition-metal halogen bond is in the opposite direction to that of the transition-metal carbon bond [65] i.e., π-density is donated from the π-orbitals of iodine to those of osmium which in turn is conveyed to the π* orbitals on CO (4.24). The force constant (Table 4.1) of the equatorial CO group

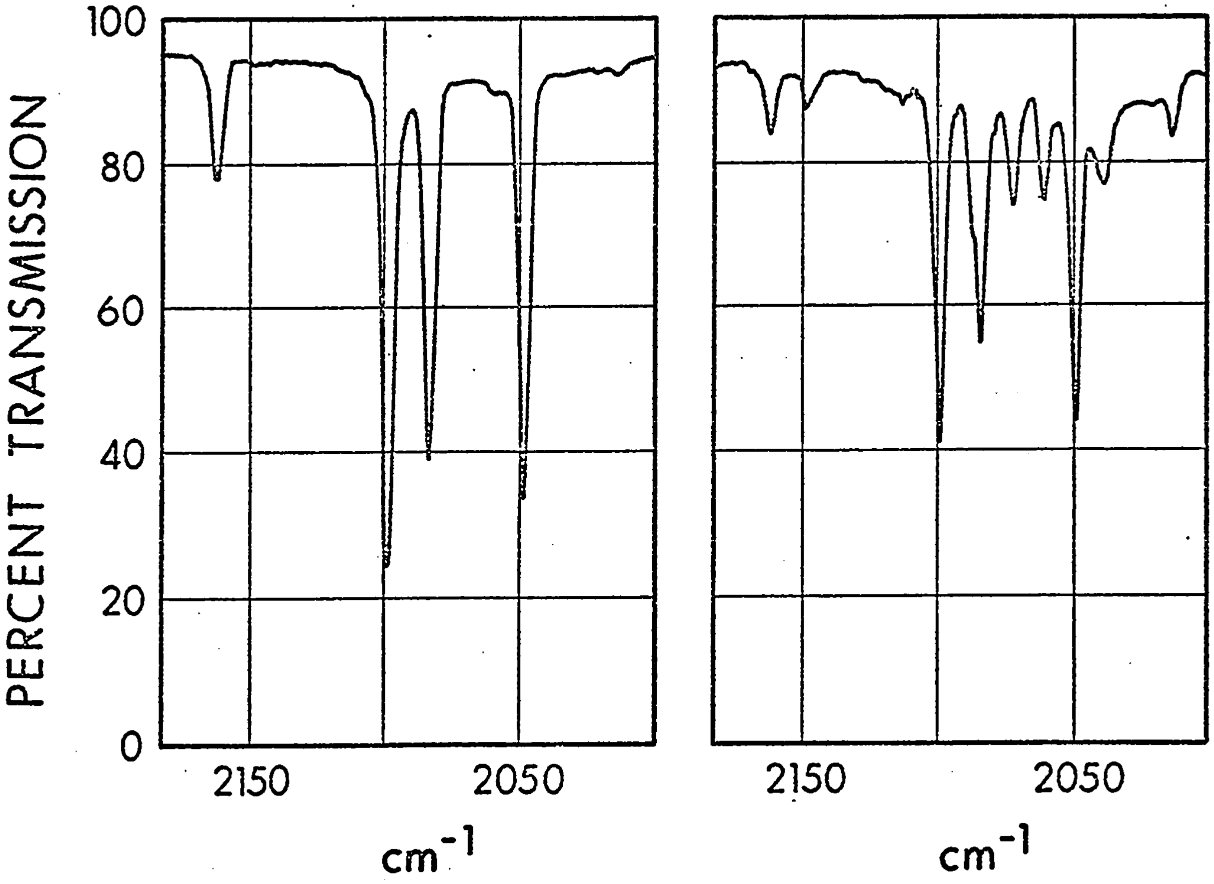
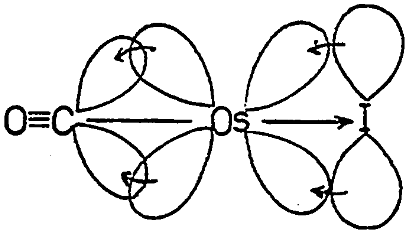


FIGURE 4.7 The ^{13}CO Exchange of *cis*-$Os(CO)_4I_2$

in *cis*-$Os(CO)_4I_2$ is somewhat lower than the same constant



4.25

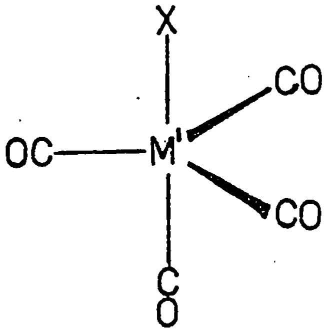
for the iron and ruthenium analogues in agreement with this hypothesis. The non-stereospecific nature of the exchange suggests that energy differences between the various forms of the intermediate $[Os(CO)_3I_2]$ may be negligible.

cis-$Os(CO)_4H_2$

The hydride ligand in square planar systems is believed [175] to have a large *trans*-effect; however *cis*-$Os(CO)_4H_2$ did not exchange with ^{13}CO under normal conditions (irradiation caused decomposition).

$M'(CO)_5X$ Compounds

If we consider the nature of the five-coordinate intermediate to $XM'(CO)_5$ systems we come to the conclusion that if X is a poor π-acceptor then the five-coordinate intermediate shown in 4.26 would be the most stable. Reaction



4.26

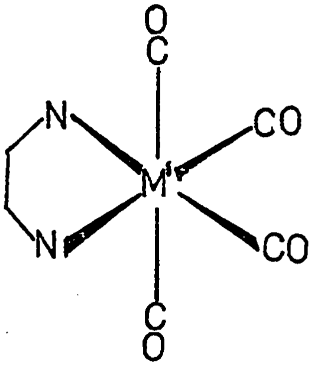
of this intermediate with ^{13}CO would give a stereospecifically labelled product in the equatorial position. Early studies on the exchange of $XMn(CO)_5$ (X = Cl, Br, I [155] or H [161]) indicated that they were completely random. However, recently Berry and Brown [160(a)] have shown, by careful study, that in $Mn(CO)_5Br$ the rate of thermal exchange of the axial site was 0.74 times that for radial substitution; in the photochemical reaction there was little or no preference for radial over axial substitution. Another study [160(b)] by these workers indicated that the ratio of the rate of axial to equatorial substitution was consistent with a hydride migration mechanism.

Darensbourg and coworkers [159] have found with $PipMo(CO)_5$ (Pip - piperidine) that the equatorial position exchanges approximately three times faster than the axial position.

There may be a common explanation for the non-exchange of fluorines in R_2PF_3 [166] and the non-exchange of carbonyls in [$Ru(CO)_3(SiCl_3)_2$]; one might expect that stereospecific double exchange in a molecule of $XM'(CO)_5$ type would not be possible, since the intermediate [$XM'(CO)_4$] would resemble RPF_4 in its ability to exchange axial and equatorial ligands without traversing high-energy isomeric forms. Unfortunately the attempted ^{13}CO exchange of $Cl_3SiRe(CO)_5$ was unsuccessful. The compound did not exchange under normal conditions and ultraviolet irradiation gave new CO absorptions which could only be attributed to decomposition products.

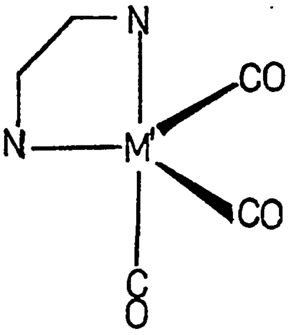
cis-$M'L_2(CO)_4$ Species.

In a species such as 4.27 we would expect 4.28 to be



4.27

the stable intermediate. On arguments already outlined this intermediate can be reached either by loss of an equatorial or axial CO. We might expect the exchange would be random although ground state considerations might dictate preference of one site over another. Studies [158] of (*o*-phen)$Cr(CO)_4$



4.28

showed that the rate of substitution at the equatorial position was more than four times that of the axial.

Conclusions

The factors which appear to hold for the ^{13}CO exchange of $Ru(CO)_4(SiCl_3)_2$ have been applied (with rather free rein) to other known systems. Although these ideas can explain the currently available information on ^{13}CO substitutions, they may be found not to apply on closer scrutiny.

The need for more data of an exact nature is obvious. Such questions as, is the reaction independent of CO concentration, is there any preference at all of one site over the other (in non-stereospecific exchanges), are rarely answered.

The manner of substitution of the second labelled CO gives much information on the nature of the intermediate. We have seen that the incorporation of the second labelled

CO in *cis*-$Ru(CO)_4(SiCl_3)_2$ is stereospecific from which it is deduced that the intermediate is rigid. Of equal interest would be a system where the exchange of the first labelled molecule was stereospecific but the second was non-stereospecific. As Brown has pointed out [154] no information about the fluxional nature of the intermediate can be obtained by the mode of replacement of the first CO.

Also, the possibility of non-rigidity in the octahedral ground state cannot be ruled out especially in view of the results that will be presented in the following Chapter. It is anticipated that ^{13}C nmr will play a key role in these investigations, although it will not be able to detect rearrangements that are slow on the nmr time scale but faster than the rate of exchange.

EXPERIMENTAL

Starting Materials:

The synthesis of most of the compounds used in this investigation have been described in Chapter 2 or 3 of this thesis. Published procedures were used for the preparation of $Cl_3SiRe(CO)_5$ [138] and $Os(CO)_4H_2$ [134] (sample kindly provided by Dr. J. R. Moss). The method of Calderazzo and L'Eplattenier", used to prepare *cis*-$Ru(CO)_4I_2$, was employed to prepare *cis*-$Os(CO)_4I_2$ i.e., addition of iodine to $Os(CO)_5$, the product was purified by sublimation under high vacuum. Heptane was dried by distilling over calcium hydride and storing over sodium before use. The ^{13}CO was obtained from Monsanto Research Corporation, Miarnisburg, Ohio; it had an initial isotopic enrichment of 95.5% ^{13}CO as determined by mass spectroscopy.

^{13}CO Enrichment Reactions.

The enriched carbon monoxide was manipulated in a glass vacuum system of conventional design, by means of a Toepler pump. Exchange reactions were performed in bulbs which could be connected to the vacuum system by ball joints. The vessels were also equipped with a Teflon valve so that, once filled with enriched CO, they could be transferred to other parts of the laboratory. Samples for ir analysis were withdrawn, with the aid of a 1 ml syringe, through a serum cap covering a small side arm on the bulb.

After the exchange reactions the diluted ^{13}CO was returned to storage bulbs for further use.

The general procedure was the same for all exchange reactions studied. A sample of the compound in question (ca. 5 mg, ca 0.01 mmol) was dissolved in heptane (5 ml) and placed in the reaction flask which was equipped with a magnetic stirring bar. The flask and contents were cooled to -78° and evacuated under high vacuum. Stirring during this procedure ensured that the solution was degassed without possible decomposition of the sample. With the flask maintained at -78°, the enriched carbon monoxide was transferred from the storage bulb to the vessel by means of the Toepler pump. Enough enriched CO was used so as to give a pressure of slightly greater than atmospheric, so that any leakage during sampling was outwards.

The reaction bulb was sealed, removed from the vacuum system and allowed to warm to room temperature. Aliquots, of approximately 0.2 ml, were withdrawn at convenient times for infrared sampling. Stirring was maintained throughout the exchange to ensure equilibrium between the solution and the enriched carbon monoxide (which was present in vast excess).

A Hanovia Utility Lamp (616A) placed a few centimeters from the flask was employed in the experiments which required irradiation with ultraviolet light.

Details of the individual exchange reactions are given below. Results are given in Table 4. , and also shown in the appropriate figures. Dr. R. S. Gay carried out the thermal exchange reactions on *cis*-$Ru(CO)_4I_2$ and *cis*-$Ru(CO)_4(GeCl_3)_2$.[151] It was in the latter reaction that the stereospecific nature of the exchange of $Ru(CO)_4(MCl_3)_2$ compounds was first noted. Since these reactions form an integral part of this study they are included here in detail.

Calculation of Force Constants.

The force constant computations were made by the usual energy-factored vibrational analysis using local versions of Schachtschneider's program FPERT. These calculations were carried out by Dr. G. O. Evans of this department on the IBM 360/67 computer at the University of Alberta. Results are given in Table 4.5.

The Kinetics of ^{13}CO Exchange.

Freshly sublimed *cis*-$Ru(CO)_4(SiCl_3)_2$ was dissolved in heptane (7 ml) so as to give a solution in which the highest energy band (2150 cm^{-1}) had a percentage transmission of approximately 25% (ca. 2.5 mg/ml). The bulb was filled with 95.5% ^{13}CO in the same way as described for the routine exchange experiments. Dilution of the samples with nitrogen was carried out by first pressurizing the reaction vessel with a previously calculated amount of 95.5% enriched carbon monoxide and then bringing the total pressure to 750 mm with nitrogen. By 60% ^{13}CO (Table 4.4) it is meant 450 mm ^{13}CO, 20 mm of ^{12}CO and 280 mm of N_2 (total pressure 750 mm). The flasks were kept in dry ice until rate studies commenced.

The reactions were carried out in a specially constructed water-bath through which water from a constant temperature reservoir was rapidly pumped. The bath was of such a construction so as to allow stirring of the solution by means of a magnetic stirrer situated beneath the bath and was shallow enough to be able to remove samples from the reaction flask by means of an extended side-arm. The vessel was shielded from direct light.

The rate of exchange was studied by watching the disappearance of the high energy band of the unsubstituted compound in a similar manner to that described for the *cis→trans* isomerization (discussed in detail in Chapter 5). By comparing some of the curves with those simulated by a DuPont 310 Curve Resolver it appeared that the percentage transmission of the high energy band at 2150 cm^{-1} was unaffected by the growth of a product band at 2145 cm^{-1}.

The treatment of the results was exactly the same as given in Chapter 5. The results are given in Table 4.4. From the rates at the three different temperatures it was possible to calculate activation parameters of $\Delta H^{\ddagger} = 26.7 \pm 1.0$ kcal $mole^{-1}$ and $\Delta S^{\ddagger} = 3 \pm 3$ eu.

cis-$Ru(CO)_4(GeCl_3)_2$

This reaction was carried out using ca. 50% enriched CO. In one reaction it took 430 hr to go to completion (Fig. 4.8).[151] During this time a weak band due to a decomposition product appeared at 2094 cm^{-1}. This band also appeared in similar samples kept under ^{12}CO. An attempt to repeat the exchange was unsuccessful.[174] The successful exchange may have been brought about by catalysis by an impurity. However, it may be that in this exchange the stirrer caused significant heating of the solution thus accelerating the reaction.

trans-$Ru(CO)_4(GeCl_3)_2$

There was no observable exchange with ^{13}CO under normal conditions after two days.

Irradiation with ultraviolet light under 61% ^{13}CO caused the stereospecifically labelled *cis*-product to be formed i.e., a spectrum similar to that shown in Fig. 4.8 (430 hr) was obtained.

Ultraviolet irradiation of *cis*-$Ru(CO)_4(GeCl_3)_2$ produced the same effect in approximately the same time (35 min).

The force constants reported here contain a minor correction to those reported in the original work.[151]

cis-$Ru(CO)_4(SiCl_3)_2$

The exchange is shown in Fig 4.1. The reaction took approximately 18 hr to go to completion. The rate of ^{13}CO substitution appeared unaffected by carrying it out in the dark.

There was no further exchange on heating the solution to 55° after 4 hr. A sample left under ^{13}CO for 7 days showed no change except for loss of intensity due to decomposition.

trans-$Ru(CO)_4(SiCl_3)_2$

There was no apparent exchange after stirring a sample of *trans*-$Ru(CO)_4(SiCl_3)_2$ under ^{13}CO for two days. There was also no exchange on heating a solution of *trans*-$Ru(CO)_4(SiCl_3)_2$ to 50° under a ^{13}CO atmosphere.

Irradiation of the solutions rapidly gave the stereospecifically labelled *cis*-product; this is shown in Fig. 4.3 . This substitution took place at a much faster rate than in the case of *trans*-$Ru(CO)_4(GeCl_3)_2$.

cis-$Ru(CO)_4I_2$

The reaction was carried out under 50% ^{13}CO in the dark, to avoid formation of the *trans*-isomer. However a band was observed at 2088 cm^{-1} which is close to that reported [129] for *trans*-$Ru(CO)_4I_2$ (2089.5 cm^{-1}). Moreover this frequency does not fit the calculated results with the accuracy normally found in these experiments.[151] It was therefore assigned to the unsubstituted *trans*-molecule and omitted in the calculation of a new set of force constants for *cis*-$Ru(CO)_4I_2$.

cis-$Os(CO)_4I_2$

There was no discernable replacement of CO in $Os(CO)_4I_2$ after it was kept under ^{13}CO for 2 days. The solution was irradiated to achieve exchange (Fig. 4.7).

cis- $Os(CO)_4H_2$

This compound did not exchange with ^{13}CO after 24 hr. Irradiation caused the solution to become cloudy, no new CO bands were observed.

The force constants were calculated from the frequencies of the unsubstituted molecule (see Fig. 4.9), and from the frequencies of ^{13}CO modes due to the 4% of the monosubstituted product occurring in natural abundance.

$Re(CO)_5SiCl_3$

No exchange was detected after 24 hr. Irradiation did cause new bands to appear but these bands could only be reasonably assigned to decomposition products.

cis-$Ru(CO)_4(SiF_3)_2$

This compound was too unstable in solution to be studied.

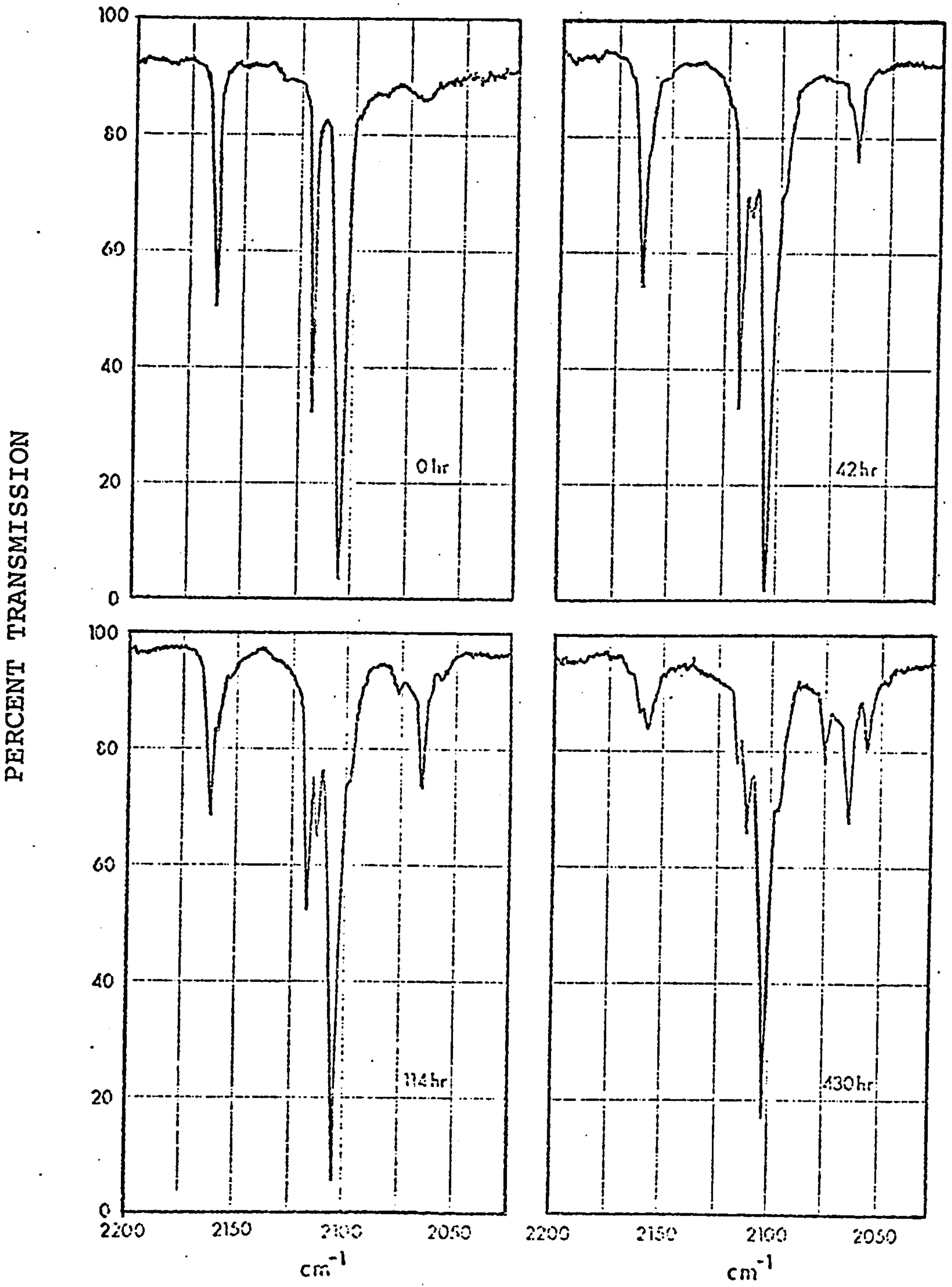


FIGURE 4.8 The ^{13}CO Exchange of *cis*-$Ru(CO)_4(GeCl_3)_2$

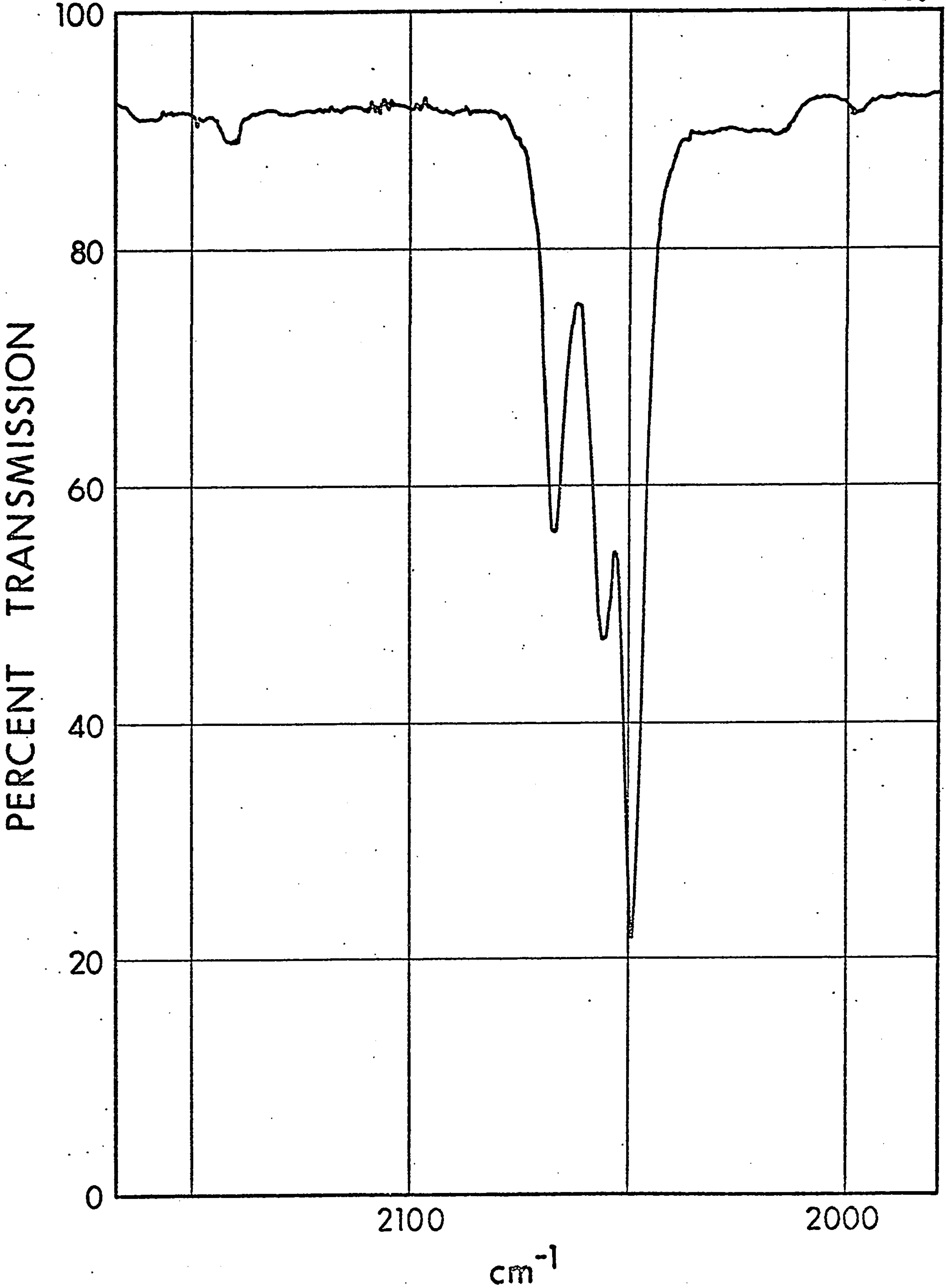


FIGURE 4.9 The Infrared Spectrum of *cis*-Os(CO)$_4$H$_2$ (heptane solution).

TABLE 4.5

Force Constants, Observed and Calculated Band Positions for Some *cis*-M'$(CO)_4X_2$ Derivatives

	Observed Frequencies (cm^{-1}) Assignment[a]				Calculated Frequencies (cm^{-1}) Assignment[a]				Force Constants				
Compound	A_1	A_1	B_1	B_2	A_1	A_1	B_1	B_2	k_{eq}	k_{ax}	$k_{eq,eq}$	$k_{eq,ax}$	$k_{ax,ax}$
cis-$Ru(CO)_4(GeCl_3)_2$ unsub.	2161	2116	2103	2103	2160.8	2116	2103	2103	18.07	18.25	0.22	0.17	0.39
cis-$Ru(CO)_4(GeCl_3)_2$ eq. monosub.	2157	2111.5	2063.8	-	2157.2	2111.3	2063.9	2103					
cis-$Ru(CO)_4(GeCl_3)_2$ eq. disub.	-	2075.5	-	2055.5	2153.8	2075.6	2103.0	2055.8					
cis-$Ru(CO)_4(SiCl_3)_2$ unsub.	2150	2103	2084	2093.5	2149.6	2102.8	2084.2	2093.3	17.91	17.96	0.22	0.19	0.42
cis-$Ru(CO)_4(SiCl_3)_2$[b] ax. monosub.	2140	-	2051	2093.5	2139.9	2099.2	2050.4	2093.3					
cis-$Ru(CO)_4(SiCl_3)_2$ eq. monosub.	2145	2100	2054	2084	2145.0	2099.4	2054.2	2084.2					
cis-$Ru(CO)_4(SiCl_3)_2$ eq. disub.	2140	2064	2084	2046	2140.5	2064.6	2084.2	2046.6					
cis-$Ru(CO)_4I_2$ unsub.	2159	2093	2104	2065	2160	2093.5	2104.8	2065.8	17.47	18.36	0.24	0.06	0.47
cis-$Ru(CO)_4I_2$ ax. monosub.	2146	-	2073	-	2145	2093.7	2072.2	2065.5					
cis-$Ru(CO)_4I_2$ eq. monosub.	-	2084	2030	-	2159.8	2083.4	2029.4	2104.8					

cis-Os(CO)$_4$I$_2$ unsub.	2163	2083	2098	2048	2162.8	2082.7	2097.8	2047.7	17.32	18.23	0.39	0.24	0.46
cis-Os(CO)$_4$I$_2$ ax. monosub	2149	-	2061	-	2149.2	2085.6	2061.3	2047.7					
cis-Os(CO)$_4$I$_2$ eq. monosub	-	2072	2014	-	2160.4	2072.2	2014.4	2097.8					
cis-Os(CO)$_4$H$_2$ unsub.	2141	2068	2056	2048	2141.0	2068.0	2048.1	2056.0	17.35	17.54	0.28	0.28	0.60
cis-Os(CO)$_4$H$_2$[b] ax. monosub.	2129	-	2017	-	2129.0	2064.9	2016.9	2056.0					

---

a = The symmetry labels, A_1, A_1, B_1 and B_2 become A', A', A', and A" respectively in the monosubstituted molecules.

b = Observed as weak bands in the unenriched compound.

CHAPTER 5

INVESTIGATION OF THE *cis-trans* ISOMERIZATION OF $Ru(CO)_4(SiCl_3)_2$ and $Os(CO)_4(SiMe_3)_2$

PART A

The Equilibrium and Kinetics of Isomerization of *cis*-and *trans*-$Ru(CO)_4(SiCl_3)_2$

Introduction

In Chapter 2 experimental observations were presented which indicated that *cis*-and *trans*-$Ru(CO)_4(GeCl_3)_2$ were in dynamic equilibrium at temperatures above ca. 140°. Only qualitative observations were possible, however, because (a) only a minute amount of *cis* was present at equilibrium and, (b) the inconvenient experimental conditions needed to achieve equilibrium (high temperature and carbon monoxide pressure). This was in contrast to *trans*-$Fe(CO)_4(GeCl_3)_2$ which isomerized to the *cis*-form even at room temperature (in solution).[28] Comparable studies soon revealed that $Ru(CO)_4(SiCl_3)_2$ was intermediate in character: equilibrium was attained at observable rates at temperatures of ca. 75° and above. Facile separation of the two isomers of $Ru(CO)_4(SiCl_3)_2$ at room temperature, in useful quantities suggested that a more exact study of the equilibrium and kinetics of isomerization of this compound might be feasible

The ^{13}CO exchange results suggested this might be a profitable area of research. It is easy to conceive of an isomerization proceeding by a dissociative mechanism involving a five-coordinate intermediate, yet the conclusions reached from the ^{13}CO exchange experiments suggested that this did not take place for the present compound. Thus the *cis*-isomer appeared to form a five-coordinate intermediate without any concomitant isomerization. The *trans*-form, although isolated in greater yield than the *cis*, isomerized completely to the *cis*-form when irradiated. Furthermore the *trans* - compound did not exchange with ^{13}CO under normal conditions. These results appeared to indicate that if the *trans*-form ever formed a five-coordinate species it would go completely over to the *cis*-molecule.

Loss of a $SiCl_3$ moiety during isomerization also seemed an unlikely possibility, as did a bimolecular process. It was surmised that the rearrangement might be intramolecular i.e., that the molecule was stereochemically non-rigid, although on a slower time scale than one usually associates with this phenomenon.

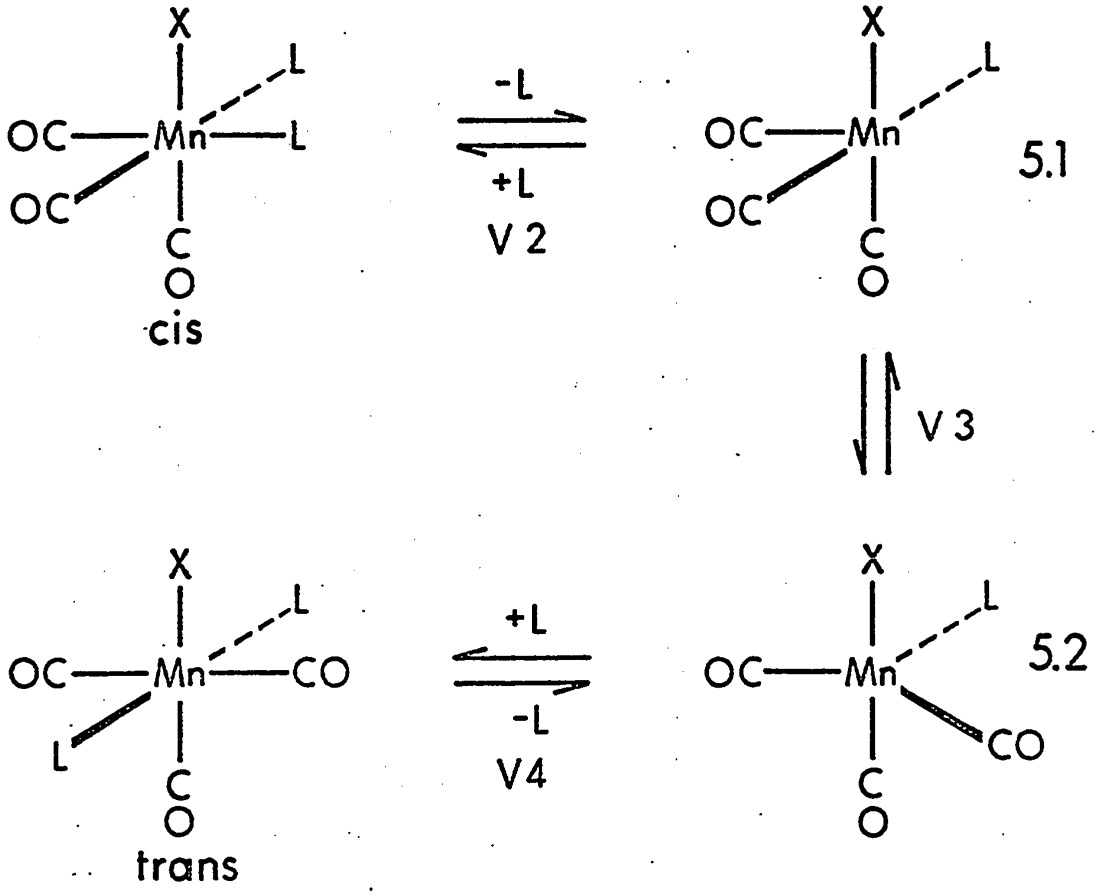
Very few *cis-trans* isomerizations have been studied in carbonyl chemistry although numerous examples exist outside this field.[71] The cases in coordination chemistry e.g., $(Co(en)_2Cl_2)^+$, appear to involve a dissociative step. The results [137] of a kinetic study into the *cis-trans* isomerization of $Mn(CO)_3L_2Br$ (L = phosphine) are discussed here in some detail as they have some bearing on this investigation. It was found that the rate of ligand interchange by equation V.1 was about ten times faster than the rate of *cis-trans* isomerization.

$$cis\text{-}Mn(CO)_3[P(OPh)_3]_2Br + 2P(OC_4H_9)_3 \rightarrow$$
$$cis\text{-}Mn(CO)_3[P(OC_4H_9)_3]_2Br + 2P(OPh)_3 \qquad (V.1)$$

Furthermore the rate did not depend on the ligand concentration. This suggested that a dissociation process might provide a path for isomerization, with the five-coordinate intermediate returning to the *cis*-isomer approximately eleven times for every twelve dissociations.

The probable mechanism is shown in Scheme F. The structure of the active intermediate(s) is not known, but a tetragonal pyramid (5.1) can readily permit ligand interchange without accompanying isomerization. However, if this form has time to generate a trigonal bipyramidal structure (5.2) before the ligand return, it then appears the ligand return could take place in the trigonal plane at a remote position from the bulky ligand already there and give rise to the *trans*-isomer. This hypothesis was supported by the observation that the compounds containing the best π-bonding ligands had the lowest activation energies for isomerization, and it is just these ligands that are

SCHEME F


X
L
OC
Mn
L
OC
C
O
cis
-L
+L
V 2
X
L
OC
Mn
OC
C
O
5.1
V 3
X
L
OC
Mn
CO
L
C
O
trans
+L
-L
V4
X
L
OC
Mn
CO
C
O
5.2

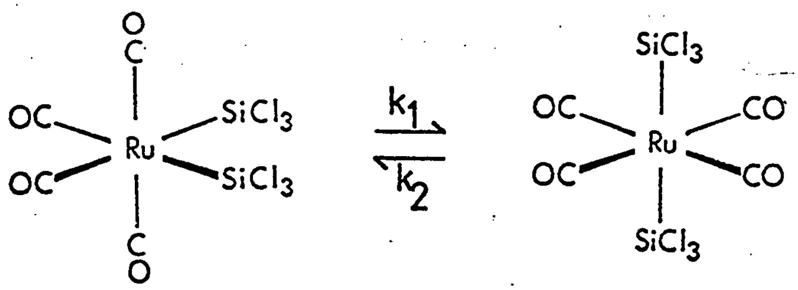
expected to have the greatest stabilizing influence of a trigonal bipyramidal structure.

It should be pointed out that the attack on the five-coordinate intermediate to give the *trans*-isomer does not violate the principle of microscopic reversibility since both the *cis*- and *trans*-forms dissociate under the conditions, unlike $Ru(CO)_4(SiCl_3)_2$ where only the *cis*-dissociates.

Also to be noted is that the results may be explained entirely on the basis of a trigonal bipyramidal intermediate in a similar manner discussed for $[Ru(CO)_3(SiCl_3)_2]$.

RESULTS AND DISCUSSION

The isomerization V.5, in octane, has been studied kinetically using infrared spectroscopy at temperatures of 73.6°, 86.4° and 100.2°. This was carried out by observing the disappearance of the highest energy band (Fig. 4.1) of the initially pure *cis*-compound as it came to equilibrium. Details are given in the experimental section, the results in Table 5.1. A typical rate plot obtained is shown in Fig. 5.1. It can be seen that initially the plot is a straight line confirming that this is a first order process. Obviously as the concentration of the *trans*-form becomes appreciable the back reaction k_2 is significant and the plot departs from linearity becoming horizontal at equilibrium.



V.5

By studying the rates of reaction over a temperature range it was possible to calculate values for the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 24.9 ± 0.9 kcal mol^{-1} and -7 ± 3 eu respectively.

TABLE 5.1

Rates of Isomerization for *cis*-$Ru(CO)_4(SiCl_3)_2$ (in n-Octane)

Temperature °C	Rate sec^{-1}
73.6	4.17×10^{-5}
86.4	1.70×10^{-4}
100.2	5.92×10^{-4}

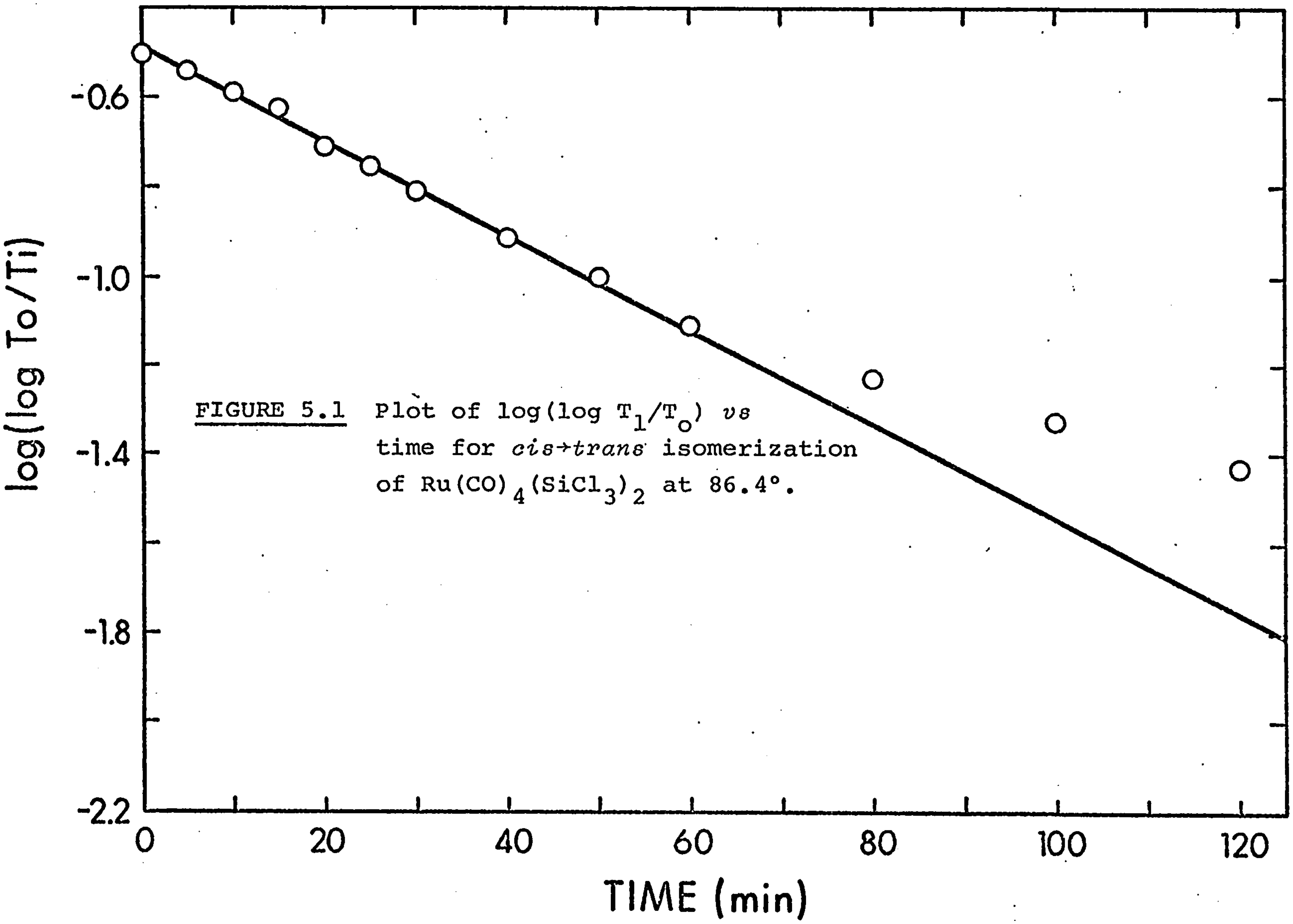


FIGURE 5.1 Plot of log(log T_1/T_o) *vs* time for *cis→trans* isomerization of $Ru(CO)_4(SiCl_3)_2$ at 86.4°.

The equilibrium constant (K) for V.5 was also studied in decalin over a greater range of temperature (73.8° - 158.2°). The results show (Table 5.2) that the equilibrium constant varied only slightly with temperature, the *cis*-form becoming the more stable at higher temperature. From a plot of log K vs $\frac{1}{T}$ it was possible to say that ΔH for the isomerization was very approximately 0.1 kcal mol^{-1} (in decalin). From this latter result a ΔS value of 0.2 eu could be estimated. Although the equilibrium constant appeared to be the same in octane, qualitative observation of the equilibrium in the more polar solvent 1,2-dichlorobenzene showed far more *cis* present. The relative proportion of the two isomers in this solvent was estimated as about 1:1. It might be expected that the more polar *cis*-form would be more favored in polar solvents. Indeed, the difference of 0.1 kcal mol^{-1} between the *cis* and the *trans* form in decalin is so small that it might be explained purely in terms of solvent interaction.

The exact mechanism of the isomerization will be discussed in detail in the third part of this Chapter. At this stage it is possible to say that the $\Delta S^{\ddagger}$ value of -7 eu is consistent with an intramolecular process [176] i.e., the transition state is more ordered than either of the products.

Support for an intramolecular rearrangement is provided

TABLE 5.2

Equilibrium Constants for the *cis*-$Ru(CO)_4(SiCl_3)_2 \rightleftarrows$ *trans*-$Ru(CO)_4(SiCl_3)_2$ System (in Decalin)

Temperature °C	$K_{trans/cis}$
73.8	1.92
84.6	1.82
125.8	1.79
153.6	1.69
158.2	1.64

by the fact that the isomerization takes place in the solid state. Samples of either isomer, when heated as the solid above 70°, isomerized to give a mixture of both isomers. It appeared that the rate of isomerization in the solid state was of the same order as in solution.

It is unlikely that CO dissociation takes place in the solid state in view of the fact that *cis*-$Ru(CO)_4(SiCl_3)_2$ can be sublimed, and is stable for long periods of time, under high vacuum; the unstable nature of this compound in air probably results from attack on the Si-Cl bonds by moisture and not by CO dissociation.

The isomerization in the solid state caused some dramatic effects to be observed when taking the melting point of *cis*-$Ru(CO)_4(SiCl_3)_2$. Thus if a sample of *cis*-$Ru(CO)_4(SiCl_3)_2$ in a sealed capillary was rapidly heated it melted reasonably sharply at ca. 100°; the exact melting point depending on the rate of heating. If, however, a similar sample was heated slowly no such change took place; instead the sample appeared to become a semi-solid at 125°. which finally melted at 160-166°. A sample of the *trans*-isomer under similar conditions melted at 164-166°.

An infrared sample of the melted material showed that the ratio of *cis:trans* was very approximately 5:6.

PART B

Nmr Study of $Os(CO)_4(SiMe_3)_2$ and Related Derivatives.

Introduction

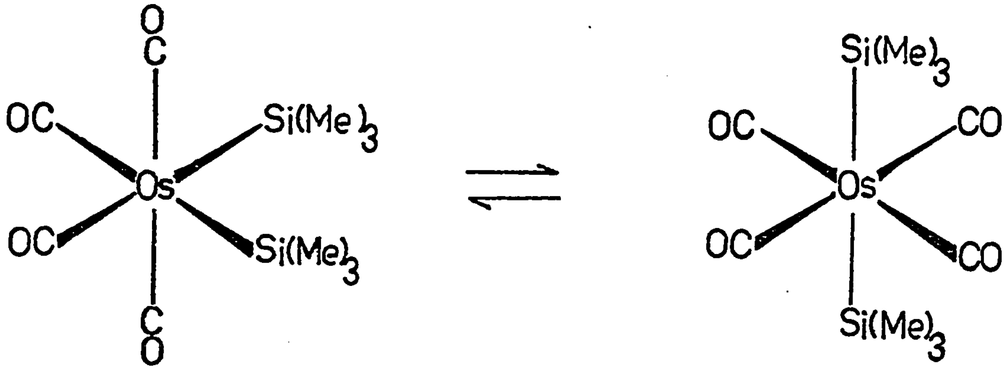
From the evidence presented in Part A of this Chapter it appeared that $Ru(CO)_4(SiCl_3)_2$ was stereochemically non-rigid. Since it is extremely unusual for non-chelated, octahedral complexes to exhibit this phenomenon, a quest for further examples was undertaken. In particular, compounds were sought to which the nmr technique could be applied.

The compound $Os(CO)_4(SiMe_3)_2$ first synthesized by Knox and Stone [30] seemed ideally suited for this study. From the infrared and nmr spectra of this substance it was concluded [30] that it was a mixture of *cis*- and *trans*-isomers in the ratio of 1:1.5. More important was the fact that these isomers could not be physically separated by conventional techniques. This suggested that the rate of isomerization, at room temperature, was greater than 10^{-2} sec^{-1}, the limit at which physical resolution of isomers is normally considered possible.

It seemed that this, and related systems, warranted more thorough nmr investigation. The synthesis of the compounds discussed here has been presented in Chapter 3.

RESULTS AND DISCUSSION

It has been found that the nmr spectrum of $Os(CO)_4(SiMe_3)_2$ in dibromomethane does indeed exhibit features consistent with fluxional behaviour. At temperatures slightly above room temperature the two signals, at τ 9.37 and τ 9.48, assignable to the *cis*- and *trans*-form respectively, begin to broaden and finally coalesce to a single peak above ca. 65°. The process is completely reversible. Furthermore the spectrum is unchanged upon a ten fold dilution, suggesting that the process is not bimolecular. Also, when a sample of $Os(CO)_4(SiMe_3)_2$ was kept under ^{13}CO at 55° for 165 minutes, no significant ^{13}CO enrichment of the compound was observed in the infrared. These observations are entirely consistent with the intramolecular rearrangement V.6:



V.6

By comparison of the observed spectra (Fig. 5.2a) with those simulated by the computer (Fig. 5.2b) it was

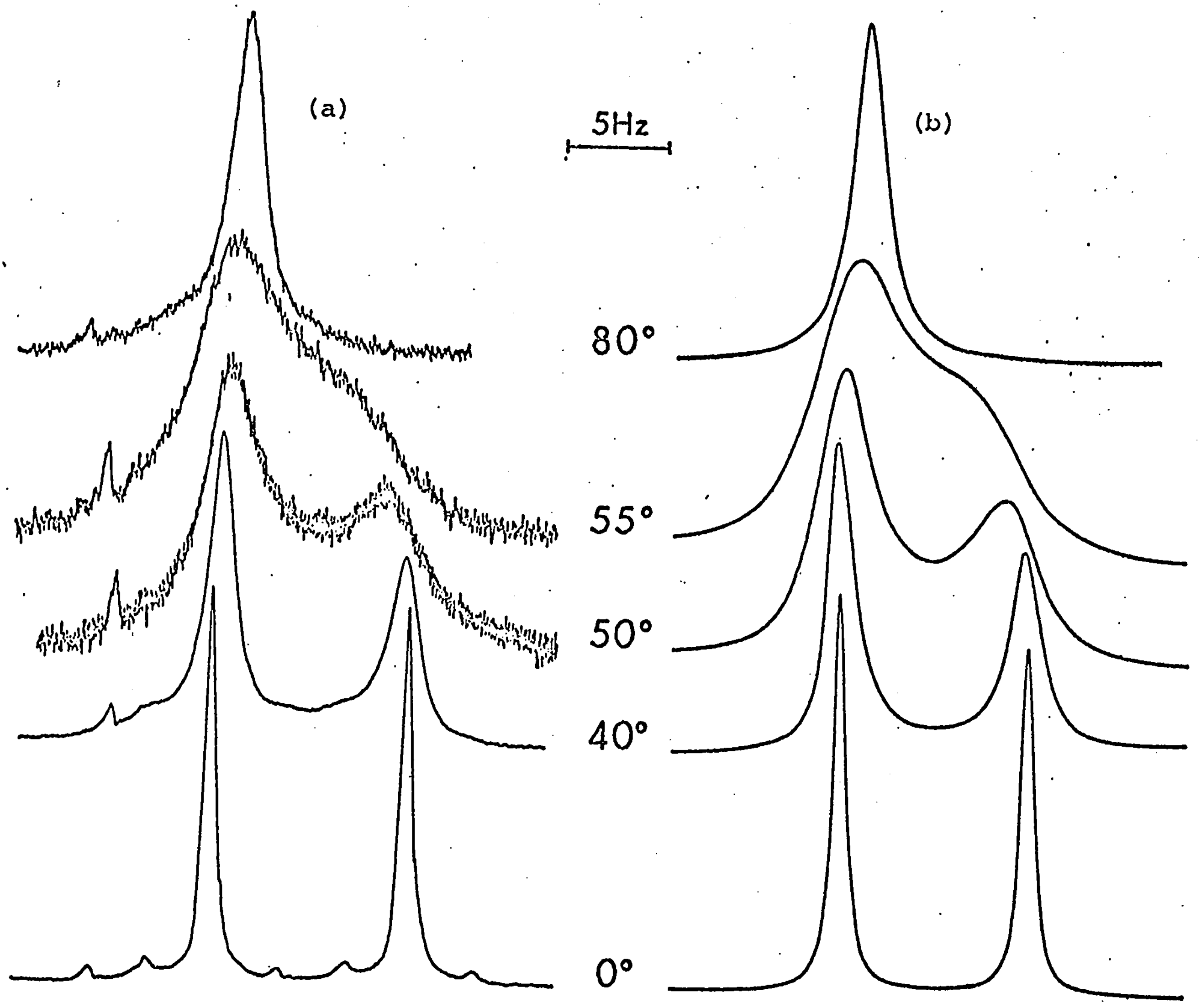


FIGURE 5.2 Observed (a) and Calculated (b) Nmr Spectra for $Os(CO)_4(SiMe_3)_2$

TABLE 5.3

Rates of Isomerization of $Os(CO)_4(SiMe_3)_2$

Temp. °C	$\tau_A{}^a$	$P_B{}^b$	Rate sec^{-1} *cis→trans*
30	0.690	0.438	1.86
40	0.358	0.431	3.69
50	0.122	0.421	11.2(7)
55	0.0685	0.417	20.4(1)
60	0.0472	0.412	30.2(3)
65	0.0344	0.408	42.1(8)
70	0.0228	0.404	64.7(0)
75	0.0157	0.400	95.5(5)
80	0.0131	0.395	116(.9)

---

a = lifetime of *trans*-isomer

b = population of *cis*-isomer, as obtained from extrapolation of the plot of log K vs $\frac{1}{T}$.

TABLE 5.4

Equilibrium Constant for $Os(CO)_4(SiMe_3)_2$ in CH_2Br_2

cis $\rightleftharpoons$ *trans*

Temperature °C	Equilibrium Constant
-40	0.85
-30	0.93
-20	0.94
-10	1.04
0	1.12
10	1.14
20	1.22
30	1.37

possible to calculate the rate of isomerization (Table 5.3) at several different temperatures in the range 30°-80°. These rates led to the activation parameters $\Delta H^{\ddagger} = 17.9 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger}$ 1.6 ± 2 eu, for the process. Allowance was made in the calculated nmr spectra for changes in the equilibrium ratio of *cis:trans* isomers. Relative intensities of the two proton nmr peaks between -40° and + +30° led to the thermodynamic values of $\Delta H° = 0.8$ kcal mol^{-1} and $\Delta S° = 3.1$ eu for process V.6.

In order to gain further insight to the factors affecting this rearrangement process other derivatives of a similar type were studied. The result of replacing one of the methyl groups on the silicon with chlorine, i.e., $Os(CO)_4(SiMe_2Cl)_2$, caused the coalescence temperature to increase by some 70° (Fig. 5.3). Although this result is only qualitative, it indicates that electronic factors are important in determining the rate of isomerization. We would expect that the steric requirements of a chlorine atom would, if anything, be smaller than those of a methyl group. As pointed out in Chapter 3, if a second CH_3 group is replaced by chlorine then the two isomers can be physically separated at room temperature. The tin compound $Os(CO)_4(SnMe_3)_2$ exhibited very similar behaviour to its silicon analogue. The two nmr signals collapsed at approximately the same temperature (Fig. 5.4).

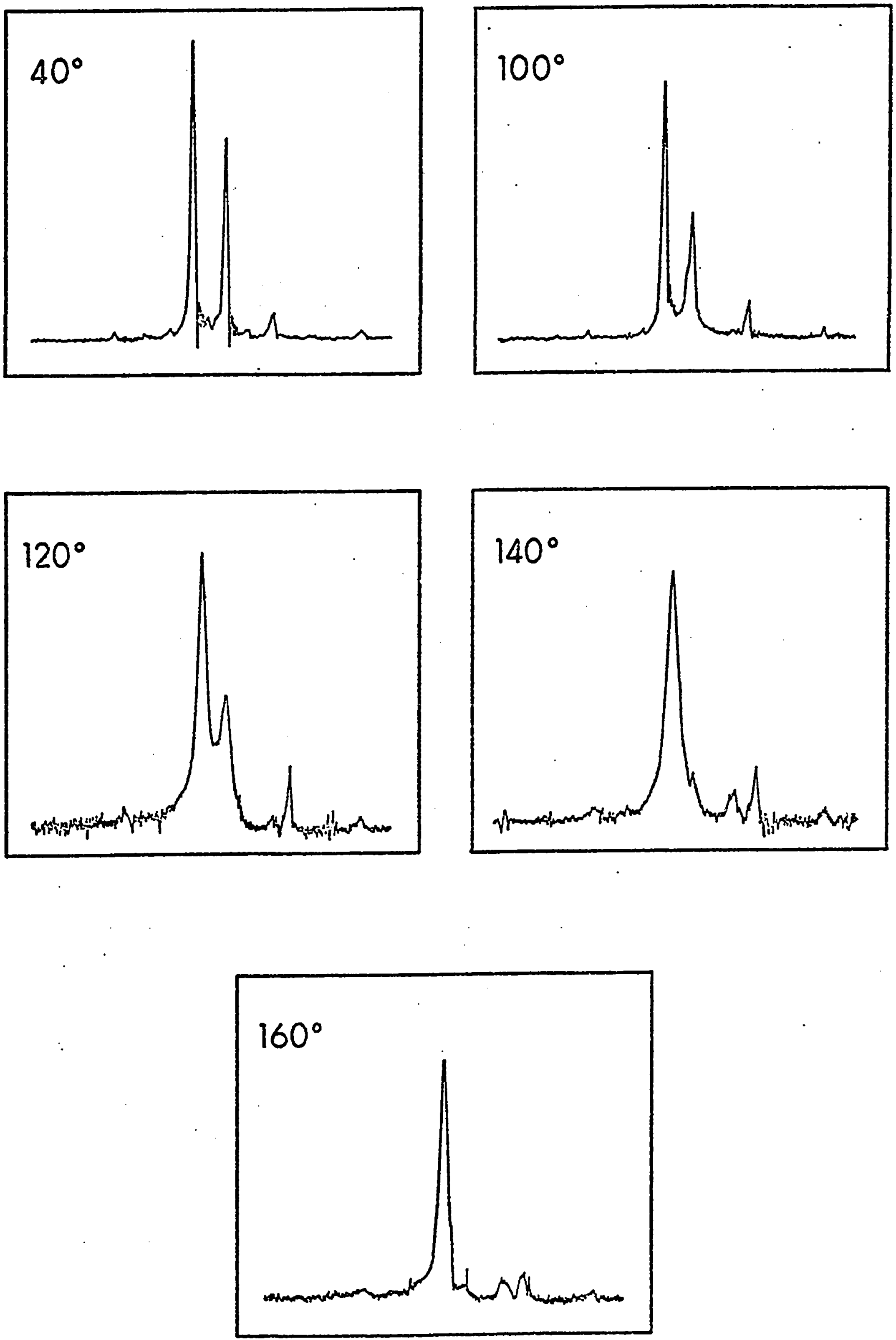


FIGURE 5.3 Nmr Spectra of $Os(CO)_4(SiMe_2Cl)_2$
(dichlorobenzene solution)

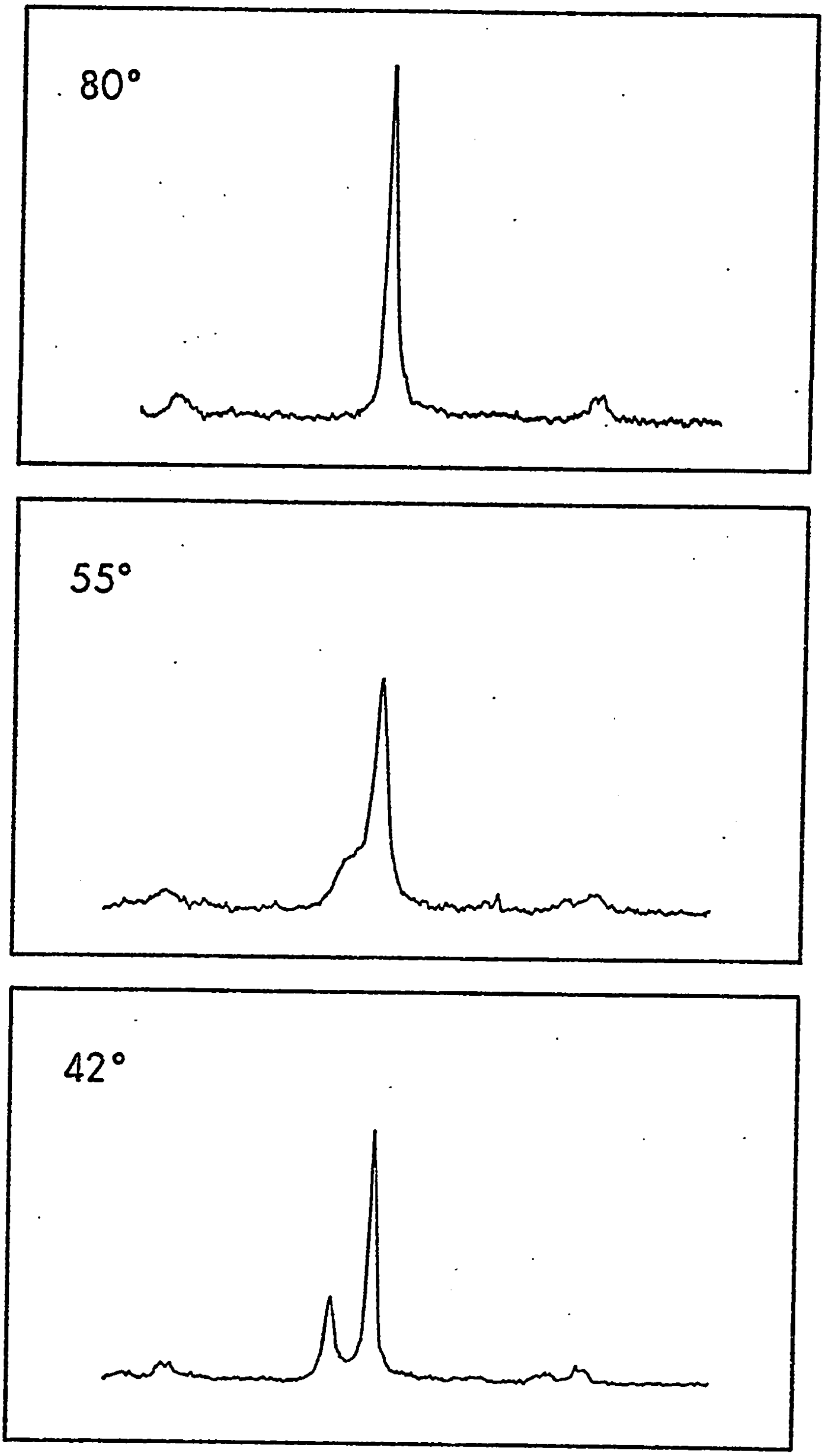
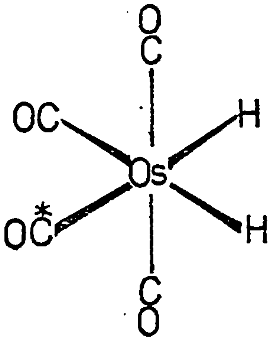


FIGURE 5.4 Nmr spectra of $Os(CO)_4(SnMe_3)_2$, note Sn coupling before and after collapse.

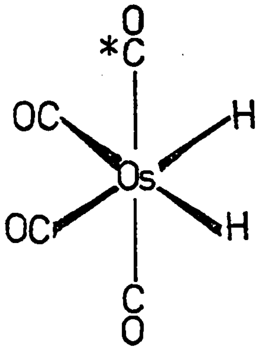
The nmr spectrum of *cis*-$Os(CO)_4H_2$ was studied. If the molecule was rigid under the conditions studied we would have expected to see three ^{13}C-Os-H couplings in the ratio 1:1:2 as shown below.



*trans*J(^{1}H, ^{13}C)

*cis*J(^{1}H, ^{13}C)

5.3



cis'J(^{1}H, ^{13}C)

5.4

Molecules such as 5.3 and 5.4 are present to the extent of 2%. If the molecule is non-rigid these three couplings should collapse to a single peak. Also, ^{187}Os with spin 1/2 would be similarly be expected to couple with hydrogen; ^{187}Os is present to the extent of 1.64% in naturally occurring osmium.[117]

As can be seen in Fig. 5.5 two couplings are observed (41.2 and 8.2 Hz) in a very approximate ratio of 1.5:1. This spectrum was the same at room temperature and at 75°.

Unfortunately this does not tell us if the molecule is non-rigid or not. It may mean that the 40.7 Hz coupling is due to ^{187} Os-H and the other to an average of ^{13}C-H couplings because of fast exchange. It could mean that the molecule is rigid and the other couplings are small and buried under the main peak or the couplings are accidentally degenerate. The knowledge of ^{13}C-M-H coupling is in a primitive state [177] and the absolute magnitude of ^{13}C-M-H coupling constant cannot in general be used to assign stereochemistry. To our knowledge no ^{187}Os-H couplings have been reported for comparison with the present system.

It is anticipated the ^{13}C nmr will resolve the question of non-rigidity in *cis*-$Os(CO)_4H_2$ and other systems.

The synthesis of $(Ph_3P)(OC)_3Os(SiMe_3)_2$ was carried out in the hope that ^{31}P coupling to the methyl signals could be seen both before and after collapse - proof that this was indeed an intramolecular rearrangement. Heating triphenylphosphine with $Os(CO)_4(SiMe_3)_2$ for seven hours at 80°, produced no apparent reaction. This is again consistent with a non-dissociative mechanism for the isomerization $Os(CO)_4(SiMe_3)_2$; if this compound did lose a carbonyl group it might be expected that PPh_3 would readily substitute for a carbon monoxide ligand. Irradiation of a solution of $Os(CO)_4(SiMe_3)_2$ and PPh_3 gave a mixture of products. However, by far the main component appeared to be 5.5.

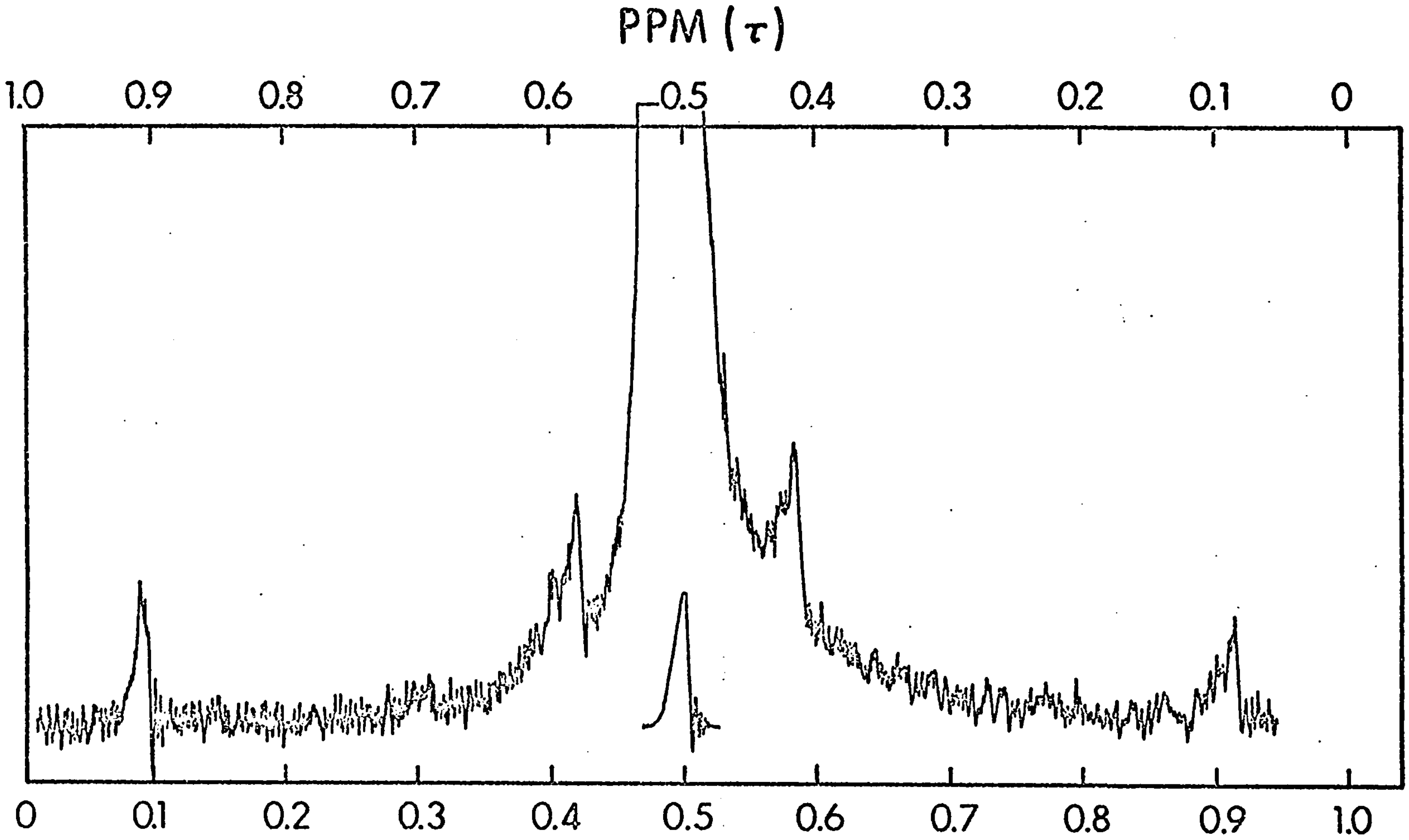
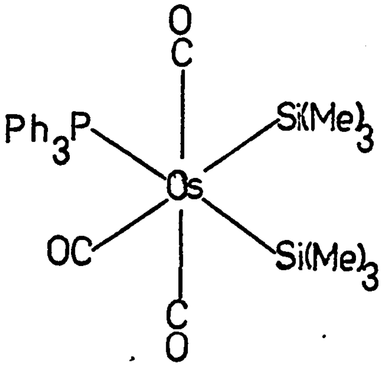
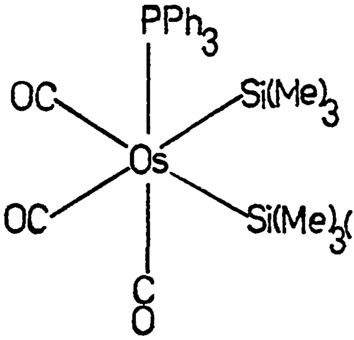


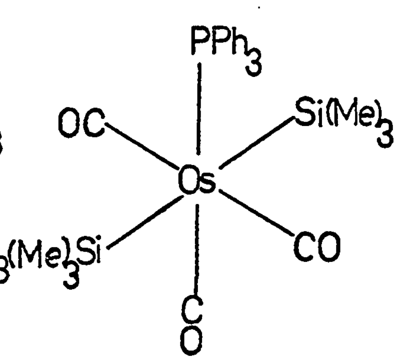
FIGURE 5.5 Nmr spectrum of *cis*-Os(CO)$_4$H$_2$ (benzene solution).



5.5



5.6



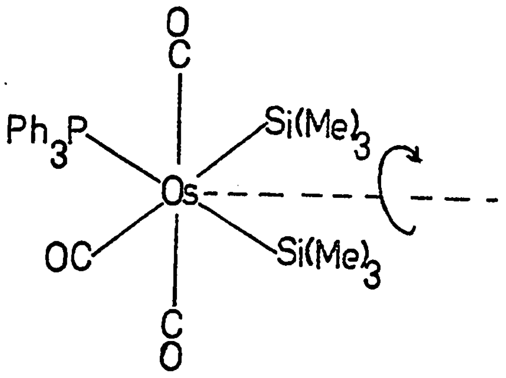
5.7

This structure was assigned on the basis of its infrared and nmr spectrum. The three well-defined bands in the infrared carbonyl stretching region had a pattern similar to *trans*-$Mo(CO)_3[P(OMe)_3]_3$ which is known to have a structure like 5.5; complexes having geometries as in 5.6 and 5.7 usually show only two bands.[178] The nmr spectrum exhibited two strong resonances in the silicon-methyl region in the ratio of 1:1. One of these signals was split into a doublet the other was a singlet. This agrees with configuration 5.5 with one Me_3Si group *trans* to phosphorus and strongly coupled and the other Me_3Si *cis* with negligible coupling. Although the compound was not isolated pure, its composition was confirmed by mass spectrometry.

Unfortunately, even though collapse of the signals in the nmr spectrum was observed, it did not take place until above 120° at which point peaks due to decomposition products were seen to grow. Since much higher temperatures than 120° would be necessary to give sharp peaks where a chance of observing any phosphorus coupling would be possible, this study was abandoned. By the use of some other phosphine ligand (e.g., PF_3) this problem might be solved.

That the nmr spectrum of this compound did not collapse until 120° might be interpreted in two ways. The first possibility is that the more bulky PPh_3 group hinders the attainment of the transition state. Secondly because the *trans*-effect of PPh_3 is generally thought to be less than CO one might expect the Os-Si bond *trans* to PPh_3 to be stronger than in $Os(CO)_4(SiMe_3)_2$. If breaking or stretching of this bond were involved in the intermediate then this would result in a slower process.

The previous discussion assumes that the rearrangement in $Ph_3P(OC)_3Os(SiMe_3)_2$ is the same as in $Os(CO)_4(SiMe_3)_2$ but this is not necessarily so. On the nmr evidence the only requirement is that the two types of methyl groups become equivalent. This may go *via* a short-lived intermediate where the $SiMe_3$ ligands are mutually *trans* as depicted in 5.7 or by some other mechanism e.g., a two fold twist (5.6).



5.6

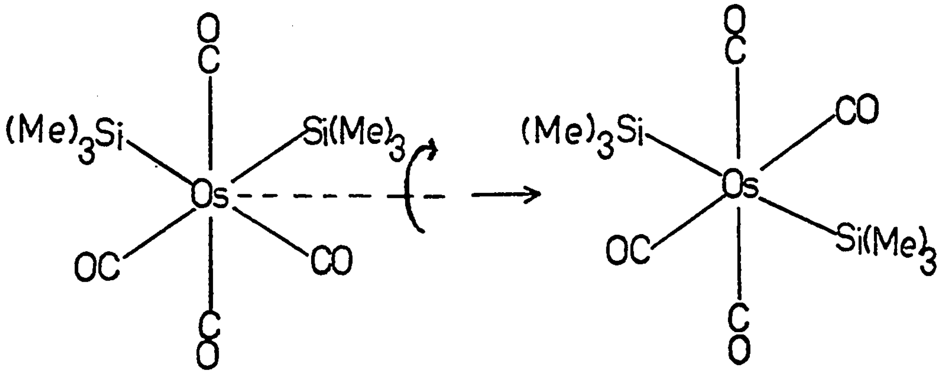
Possible Mechanisms for *cis-trans* Isomerization of $Os(CO)_4(SiMe_3)_2$

The only other case of a non-chelated octahedral system that has been reported [179] to be stereochemically non-rigid is the L_4FeH_2 class of compounds, (L is phosphine e.g., $P(OPh)_3$, PPh_2Me). The nmr spectra of these compounds are temperature dependent and the limiting high-temperature spectra show apparent equivalent coupling of hydrogen and phosphorus nuclei.

A mechanism known as 'tetrahedral tunnelling' was proposed to explain the fluxional behaviour of these complexes. In this process the phosphine ligands are distorted to a P_4Fe pseudotetrahedral transition state. The hydrogen atoms were then considered to traverse face edge positions. Support for this hypothesis was found in the solid state structure of $H_2Fe[PhP(OC_2H_5)_2]_4$ determined [180] by X-ray crystallography, which showed that the iron-phosphorus geometry is nearly midway between that expected for octahedral and tetrahedral dispositions, i.e., the ground state is distorted towards tetrahedral symmetry.

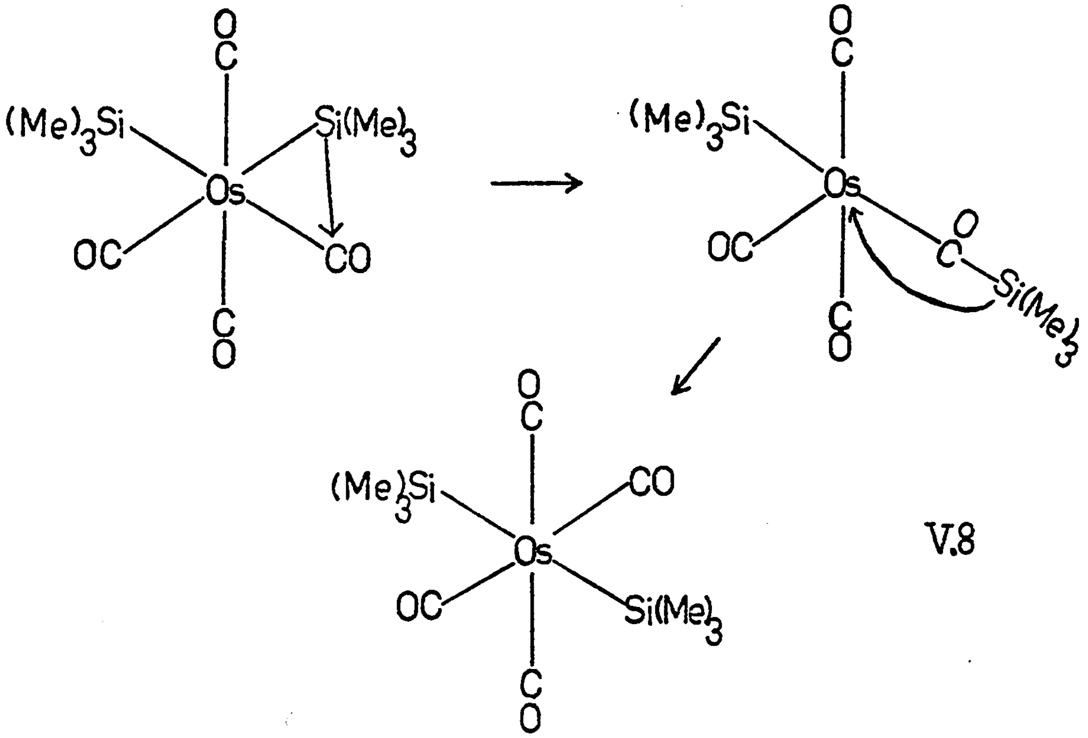
Because of the much larger size of the ligands, tunnelling is unlikely to occur in $Os(CO)_4(SiMe_3)_2$. Significant distortion from regular octahedral geometry is not expected in view of the known structures [126] of *cis*-and *trans*-$Ru(CO)_4(GeCl_3)_2$.

There are however, a number of intramolecular pathways by which a *cis*, monodentate, octahedral system can convert to the corresponding *trans*-form, and vice versa. A two fold twist similar to 5.6 and shown below (V.7) will achieve this.



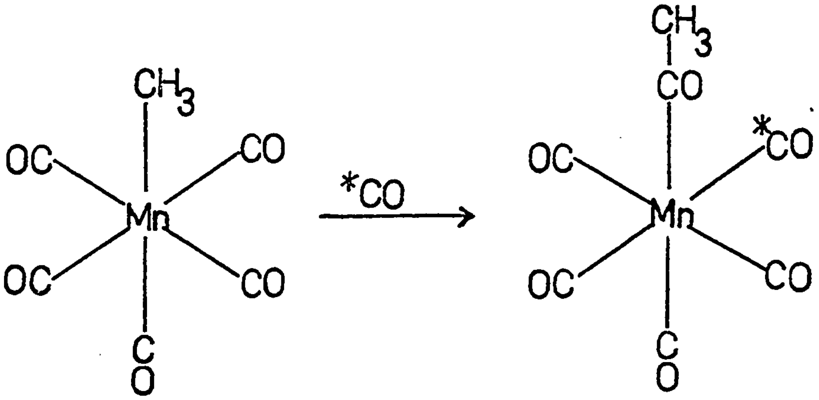
V.7

A $SiMe_3$ migration is another possibility (V.8).



V.8

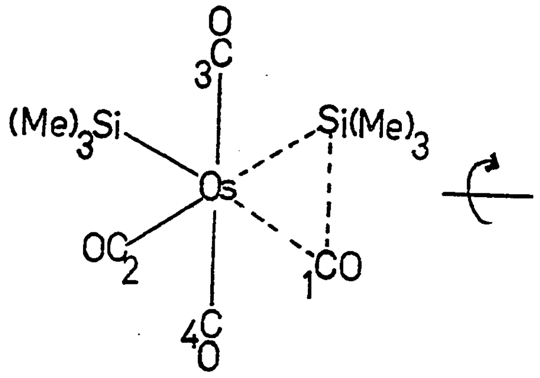
However, this is considered unlikely in view of the fact that there was no exchange with ^{13}CO during isomerization. In $CH_3Mn(CO)_5$, where such a migration is believed operative, exchange with labelled CO did take place (V.9) [181]



V.9

Whereas compounds are known [6] containing a $\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-M}$ (M = transition metal) linkage there are no known examples of $\mathrm{Me_3Si-\overset{O}{\overset{\|}{C}}-M}$ cases in the literature, suggesting that such systems are unstable.

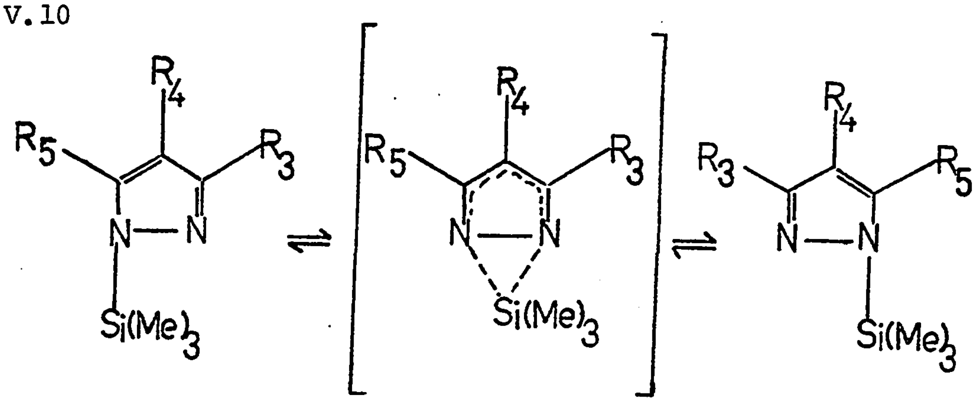
A more attractive intermediate might be a transition state which is a hybrid between the two possiblities just discussed i.e., a kind of pseudo five-coordinate, acyl-type intermediate shown in 5.9.



5.9

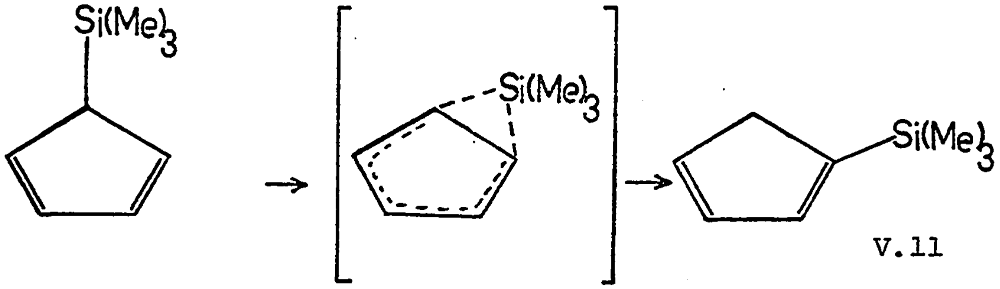
The CO group labelled 1 is both *cis* and *trans* to $SiMe_3$. The high *trans*-effect of the $SiMe_3$ group might facilitate $Os-C_1$ stretching. Exchanging positions of $SiMe_3$ with C_3O does not result in the *trans*-form. This argument cannot be applied to the reverse process since in the *trans*-derivative all carbonyls are equivalent.

Intermediates involving five-coordinate silicon are not new in organometallic chemistry. A recent example [182] of a tautomerism believed to involve such an intermediate is V.10



V.10

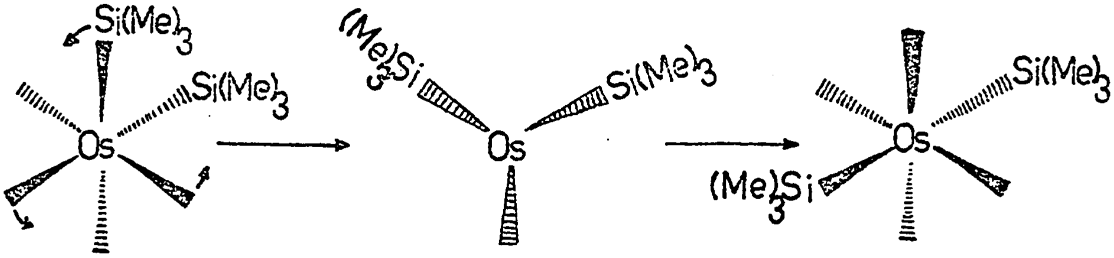
A better known case is the (πC_5H_5)MMe_3 (M = Si, Ge or Sn) species. These compounds exhibit variable temperature nmr consistent with the fluxional behaviour V.II



V.11

It was found that the rate increased Sn > Ge > Si which may mean that tin has a greater tendency to form the five-coordinate intermediate. As stated there was little difference in coalescence temperature of $Os(CO)_4(SiMe_3)_2$ and $Os(CO)_4(SnMe_3)_2$. Also, $(C_5H_5)SiMeCl_2$ undergoes this so-called 1,2 shift at a rate similar to the trimethyl derivative [184] (cf. $Os(CO)_4(SiMeCl_2)_2$). It should, however, be mentioned here that $CF_3Mn(CO)_5$ does not undergo migration as does $CH_3Mn(CO)_5$.

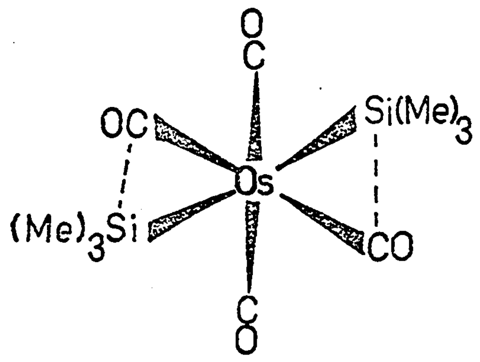
Besides the two-fold twists just described, isomerization can be brought about by a three-fold or trigonal twist. In 1958, although such a mechanism had been independently proposed before, Bailar suggested [185] such a twist to account for the racemization of such complexes as $[Co(en)_3]^{3+}$ and $[Co(en)_2X_2]^+$. This mechanism which is often known as the Bailar twist is shown in V.12.



V.12

Similar twist mechanisms, which differ in the mode of twist and in the exact configuration of the intermediate, have been proposed by Rây and Dutt, [185] and Springer and Sievers.[187] Consideration [187] of molecular models show that the transition state is very similar to trigonal prismatic intermediate of V.12 (5.8).

Five-coordinate silicon may also be invoked in the stabilization of 5.8; if there were bonding between silicon and the adjacent CO groups, then this would stabilize the trigonal prismatic state as given in 5.11.



5.11

A trigonal twist mechanism is not generally thought to be an attractive one energetically.[188] Only very recently have two cases been reported [189,190] in which such a mechanism has been proposed. In these, distortion towards a trigonal prismatic configuration was probably present in the ground state. In most isomerizations of chelated complexes it appears that bond-breaking is important.

The 'turnstile' rotation mechanism recently proposed [167] for five-coordinate phosphorus compounds is considered to be a form of trigonal twist when applied to octahedral systems.

PART C

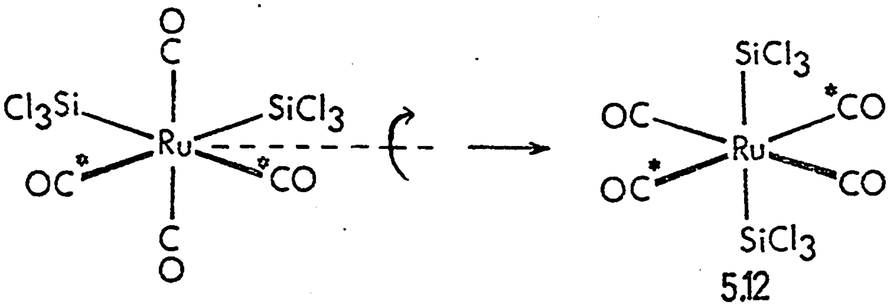
The Isomerization of *cis*-$Ru(CO)_2(^{13}CO)_2(SiCl_3)_2$

Introduction

Since stereochemical non-rigidity in octahedral complexes is of such unusual occurrence, possible methods of elucidation of the mechanism of rearrangement were sought. For this purpose the isomerization of labelled *cis*-$Ru(CO)_4(SiCl_3)_2$ was studied.

Let us consider the isomerization of *cis*-$Ru(CO)_4(SiCl_3)_2$ in which the equatorial carbonyls have been replaced by ^{13}CO.

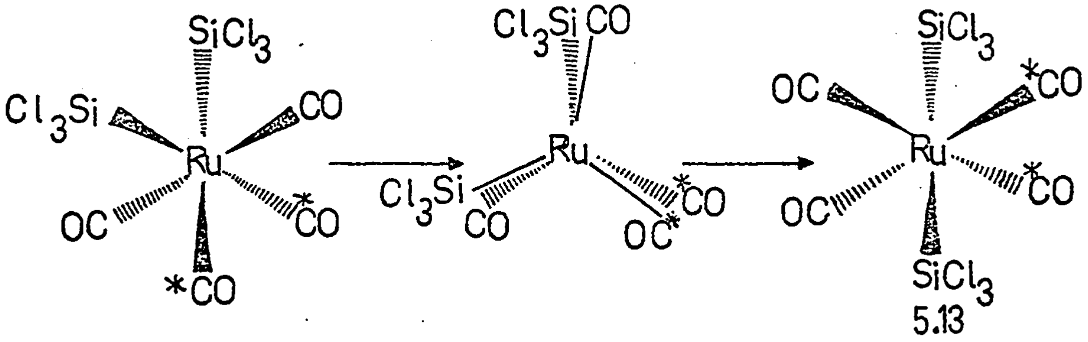
If the mechanism of the rearrangement is a two-fold twist or migration (V.13) then the labelled CO groups would end up *trans* to one another in the product i.e.,



5.12

V.13

However, if the *cis* → *trans* process proceeds *via* a trigonal prismatic intermediate then the labelled CO groups will be *cis* to each other in the resulting *trans*-$Ru(CO)_4(SiCl_3)_2$ (V.14).



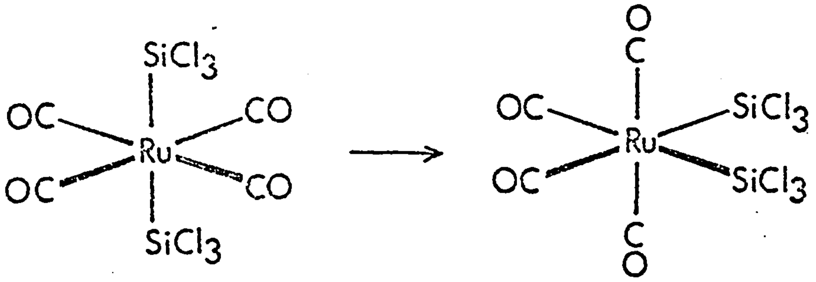
5.13

V.14

The various possible types of three-fold twists [186,189] cannot be distinguished in this system since the end product is the same in all three cases.

The two *trans*-derivatives 5.12 and 5.13 can be distinguished since they will absorb at different frequencies in the infrared. These frequencies may be calculated from the appropriate force constants for *trans*-$Ru(CO)_4(SiCl_3)_2$. These force constants may in turn be estimated from a knowledge of the stretching frequencies of the unsubstituted and monosubstituted molecules.

The two structures 5.12 and 5.13 are the possible initial products; of course, as the isomerization proceeds the back-reaction V.15 will become significant.



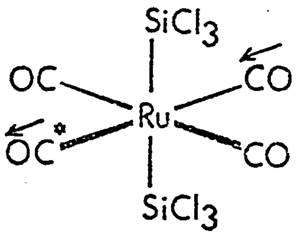
V.15

It was therefore essential to study the reaction in its early stages.

RESULTS AND DISCUSSION

The isomerization of labelled *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ was carried out at 80-85° under an atmosphere consisting of 95.5% ^{13}CO. As can be seen in Table 5.5 and Fig. 5.6, the results are consistent with the initial product having the labelled CO groups *cis* to each other (5.13). This is in agreement with the *cis-trans* rearrangement proceeding by a trigonal twist mechanism. This is the first case where evidence indicates that such a process occurs in a non-chelated, octahedral system.

The possibility that some other mechanism makes a minor contribution to the isomerization cannot be entirely ruled out. Although a weak band at 2089 cm^{-1} is observed in the early stages of the reaction, this can be assigned as due to a mode (5.14) of the monosubstituted *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$ present in small quantities.



5.14

A good indication that in the first stages of the isomerization there are no species containing two ^{13}CO

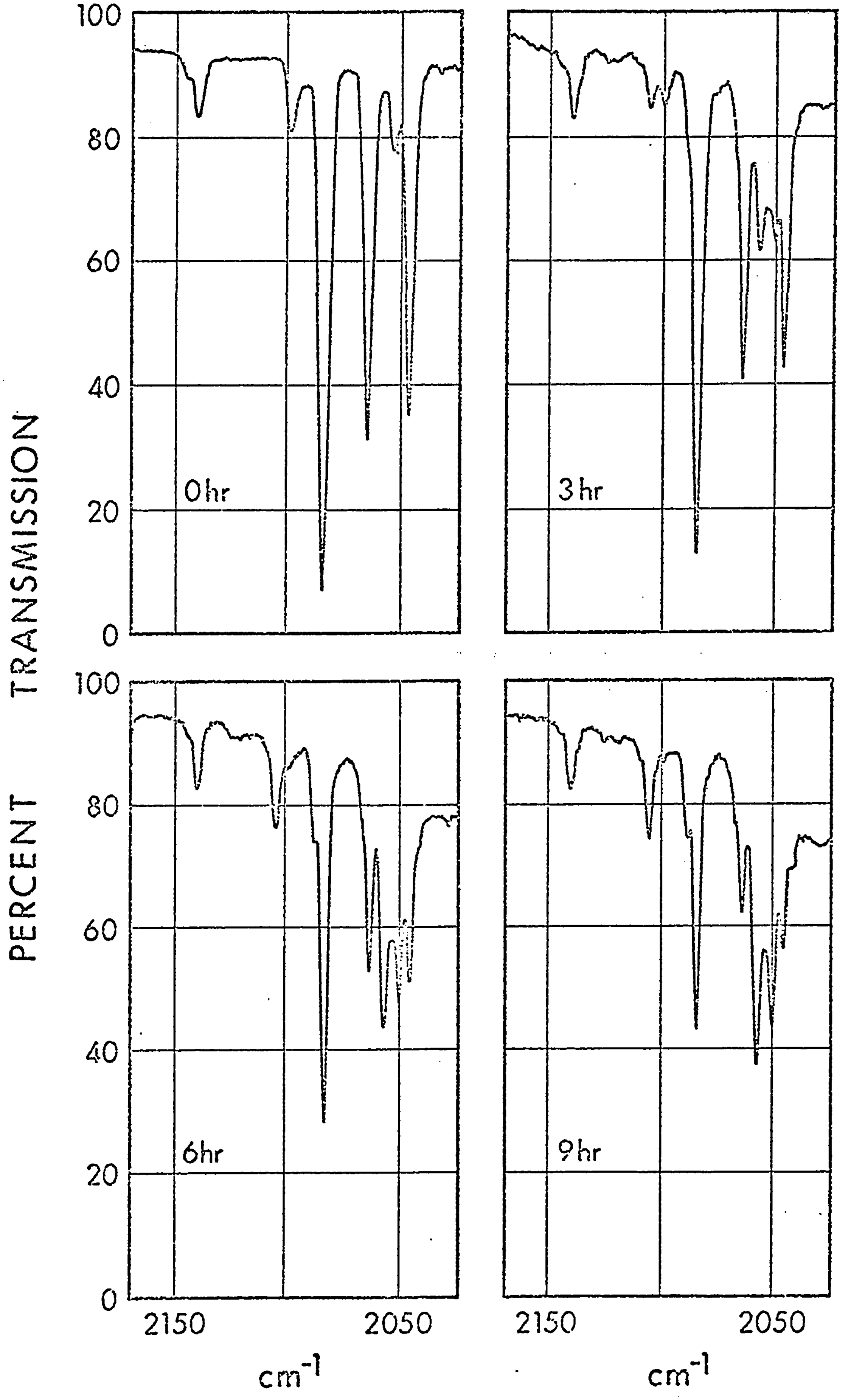


FIGURE 5.6 Infrared Spectra During Exchange of *cis*-Ru(CO)$_2$(^{13}CO)$_2$(SiCl$_3$)$_2$

TABLE 5.5

Infrared Frequencies of the Product of the Isomerization of Labelled *cis*-$Ru(CO)_4(SiCl_3)_2$

Observed Bands[a] (cm^{-1})	2140	2106	2058	2051
Calculated (C_{2v})[b] (cm^{-1})	2140.7	2101.1	2057.9	2049.6
Calculated (D_{2h})[b] (cm^{-1})	2142.9[c]	2088.6	2074.7[c]	2042.0[d]

---

a = no other new bands observed in the initial stages of the reaction.

b = calculated from force constants obtained from frequencies of the unenriched product i.e., $k = 18.07$, $k'_{cis} = 0.29$, $k'_{trans} = 0.46$; this assumes band at 2109 cm^{-1} is attributable to the B_1 mode of the unsubstituted molecule.

c = not active in the infrared

d = observed in the later stages

C_{2v} structure has labelled molecules *cis*, the D_{2h} structure has them *trans*.

TABLE 5.6

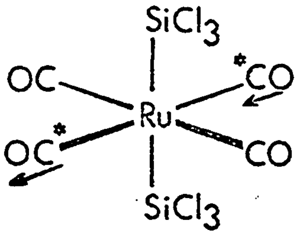
Calculated and Observed Stretching Frequencies for *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$ Species

	Unsubstituted	Monosubstituted		Disubstituted (C_{2v})			
Observed Bands (cm^{-1})	2088.5	2109	2054.5	2140	2106	2058	2051
Calculated[a] (cm^{-1})	2088.3	2109.5	2054.6	2140.0	2105.8	2057.6	2051.6

---

a = force constants are $k = 18.02$, $k'_{cis} = 0.18$, $k'_{trans} = 0.41$; calcd for A_1 mode of unsub. *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$ = 2115.9 cm^{-1}.

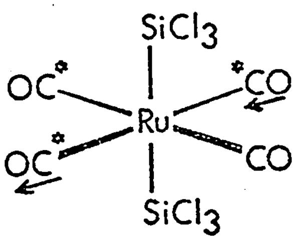
groups *trans* to each other is the absence of a peak at 2042 cm^{-1} due to the mode depicted in 5.15. As the reaction pro-



5.15

gressed, a band at this value did appear which in the final stages was the strongest band in the spectrum. This is because at equilibrium under 95.5% ^{13}CO, there would be mainly tri- and tetra-substituted species and in such molecules a mode such as 5.15 would be present.

The failure to observe the absorption at 2042 cm^{-1} in the initial stages gives us even more insight into the whole process. If exchange of *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$ with ^{13}CO was significant at the temperature of isomerization, then we would expect an absorption at 2042 cm^{-1} due to 5.16.

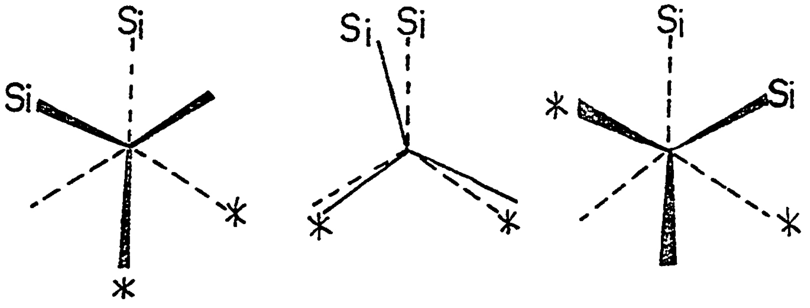


5.16

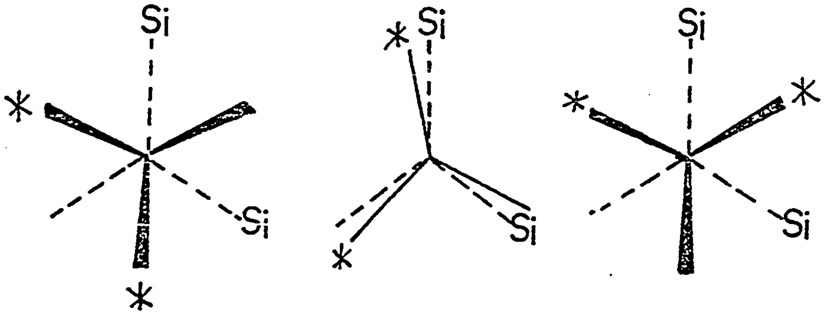
As stated in Chapter 4, no observable exchange of ^{13}CO with *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$ took place below 50°.

Also, if the isomerization of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ proceeded by a dissociative mechanism (Scheme G) we would expect a random distribution of the labelled molecules in the product and hence a band at 2042 cm^{-1}. That the isomerization did not proceed by a dissociative step was supported by the fact that irradiating *cis-trans* mixtures under ^{12}CO at equilibrium at 85° caused an immediate shift to the *cis*-form.

Besides the three-fold twist which brings about isomerization (V.14) there are other types (V.16 and V.17) of three-fold twists which, though not bringing about isomerization, do exchange the equatorial and axial carbonyl groups.

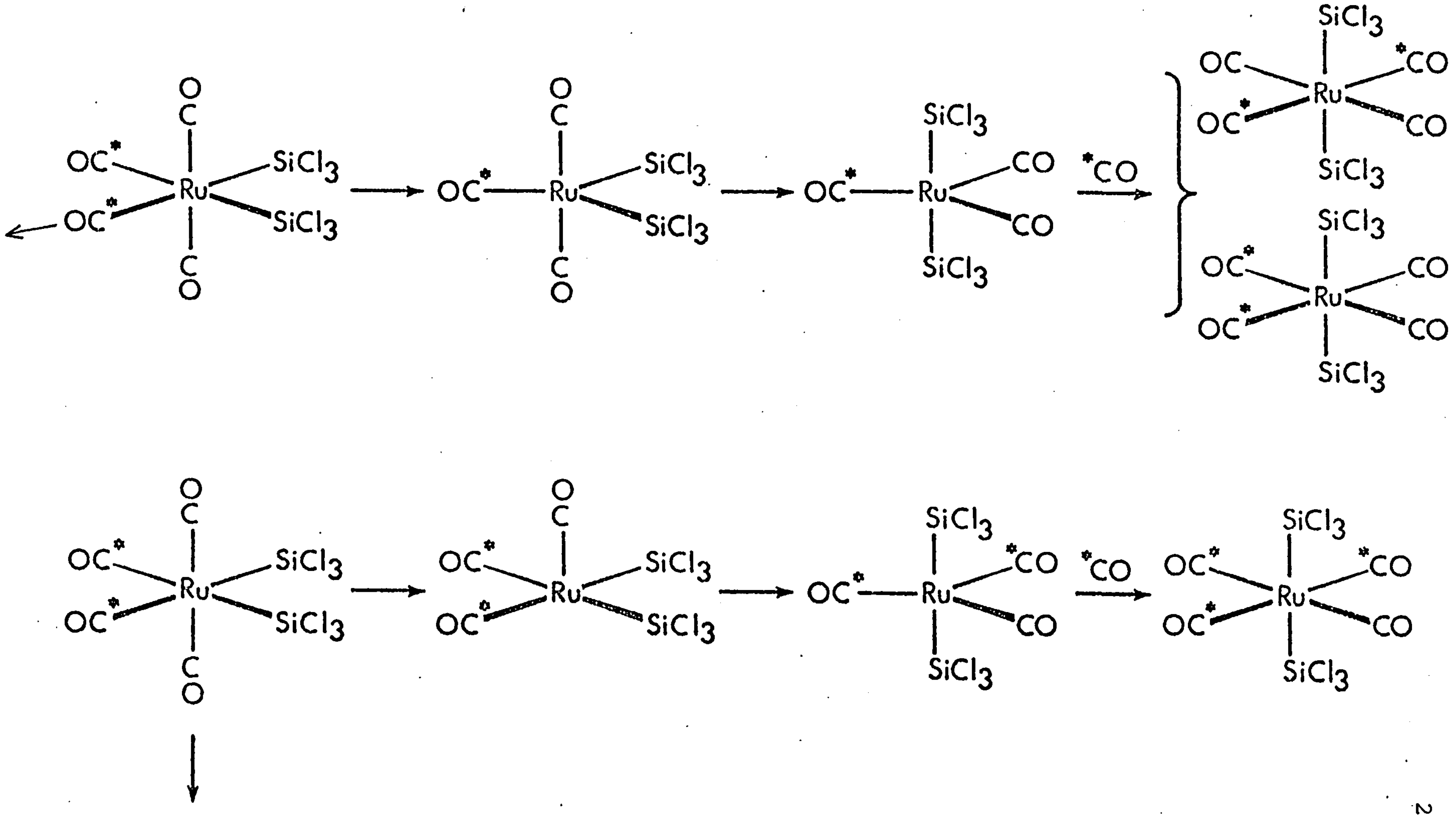


IV.16



IV.17

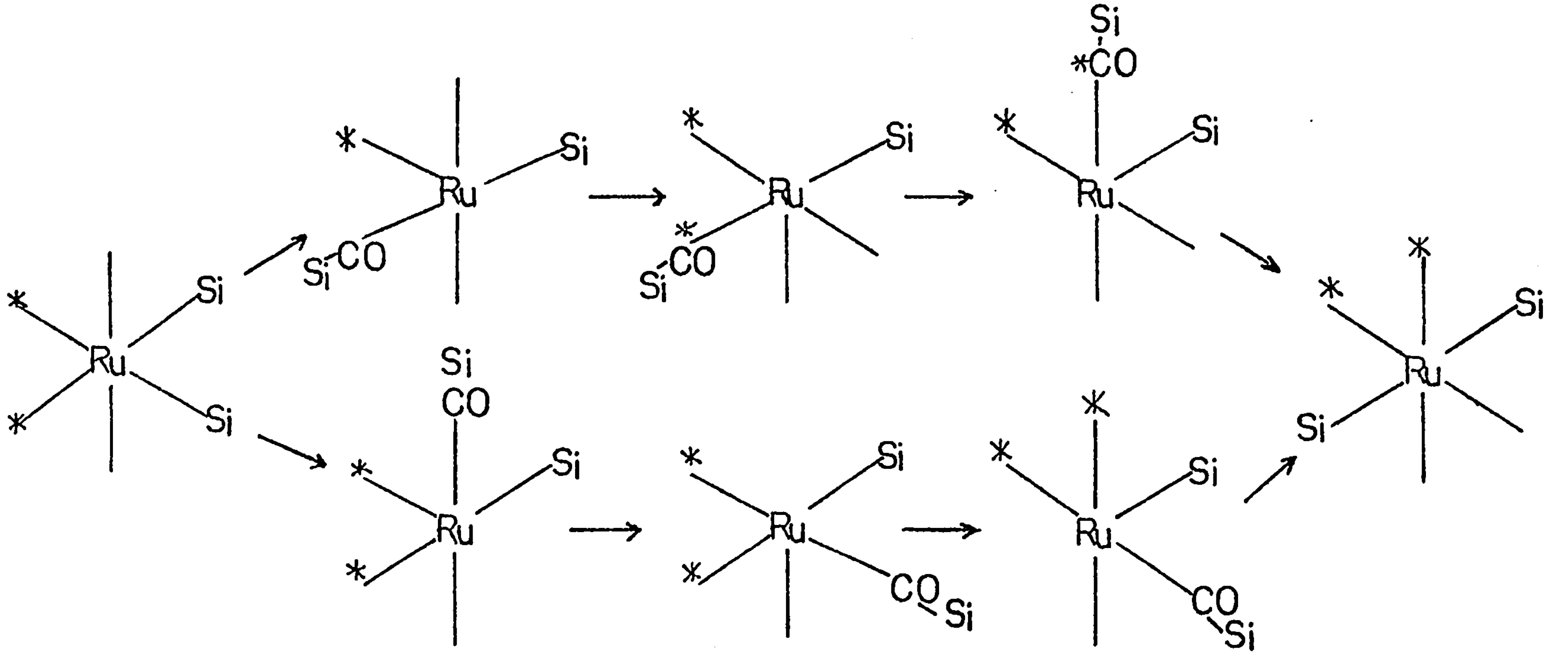
SCHEME G



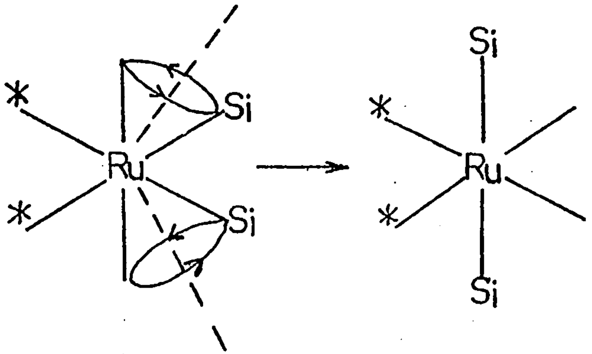
Since no new bands appeared at positions expected for an axially-substituted *cis*-molecule during the initial stages of the isomerization, it is possible to say that these twists do not take place to any significant extent. It is easy to see why V.16 might not be energetically favorable since in the transition state the bulky $SiCl_3$ groups are in close proximity. However, the transition state of V.17 is very similar to the transition state of the Bailar twist which brings about isomerization. This transition state might also be stabilized by bonding interaction between the silicon and the nearest carbonyl groups, as described in Part B of this Chapter. A reason why the twist V.14 is of lower energy than V.17 might be because V.14 lowers the repulsion between the more bulky $SiCl_3$ groups i.e., the driving force is the steric interaction between the $SiCl_3$ groups.

Other mechanisms which might account for the observed result are shown in Scheme H. The isomerization path V.18 is considered highly unlikely since the five-coordinate intermediate would be expected to exchange with ^{13}CO; there are also similar paths of equal probability which would give a *cis*-product with ^{13}CO in the axial position (e.g., V.20).

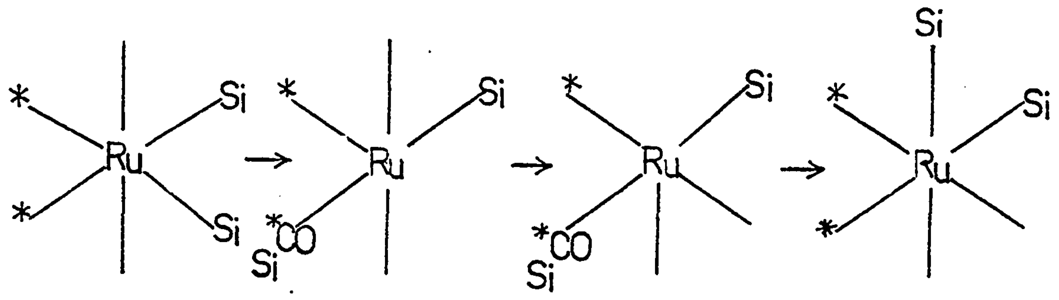
SCHEME H



IV.18



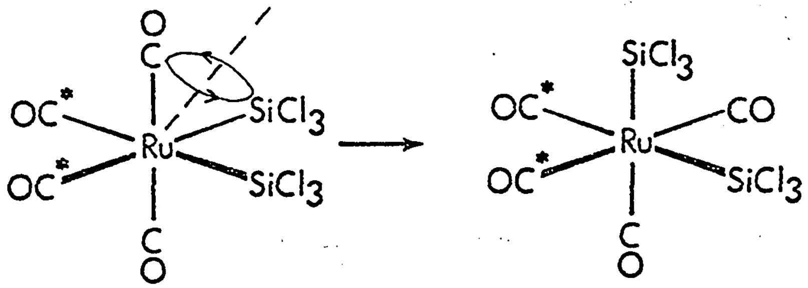
IV.19



V.20

Also the mechanism of rearrangement in five-coordinate compounds is believed to involve simultaneous movement of pairs of ligands.

It is difficult to see why a mechanism such as V.18 or V.19 would be of lower energy than the simple migration step (V.13) mentioned in the introduction. If a mechanism such as V.19 were operative it might be expected that one two-fold twist involving a $SiMe_3$ and an axial CO group would be just as probable (V.21); this would give a *cis*-molecule with a labelled axial carbonyl, which does not take place.



V.21

Conclusion

The results given in this Chapter have significant implication in the field of metal carbonyl chemistry and, indeed, inorganic chemistry in general. The trigonal twist has been thought to be a high energy process, especially for non-chelated, octahedral molecules. Up until 1970, no octahedral complexes were known which underwent non-dissociative rearrangement.[179] In the cases that exist [180,189] distortion of the octahedral ground state was shown to be present. In view of the properties of the compounds described here fluxional behaviour in non-chelated, octahedral systems must now be considered a possibility. Just how widespread this occurrence is remains to be seen.

EXPERIMENTAL

Kinetics of Isomerization of *cis*-$Ru(CO)_4(SiCl_3)_2$.

The solvent used in the rate studies was n-octane, which had been freshly distilled from calcium hydride. Decalin distilled from sodium at reduced pressure, was used in the equilibrium investigation. Freshly sublimed *cis*-$Ru(CO)_4(SiCl_3)_2$ was used in all reactions which were carried out in 10 ml standard volumetric flasks, fitted with a tap and side arm. Reactions were performed in a constant-temperature oil bath, the temperature of which was controlled to ± 0.1°. An atmosphere of carbon monoxide was maintained throughout the experiments.

The high energy infrared band (2150 cm^{-1}) of *cis*-$Ru(CO)_4(SiCl_3)_2$ and the band of the *trans*-isomer (2089 cm^{-1} were shown to obey Beer's Law. Molar absorption coefficients of 5.1×10^3 and 4.7×10^4 $mole^{-1}$ cm^2 respectively were estimated for the bands; this assumed a path length of 0.05 cm.

Rates of isomerization were determined by watching the disappearance of the high energy band of the *cis*-isomer. Initial solutions (5.0 ml) contained sufficient *cis*-$Ru(CO)_4(SiCl_3)_2$ so that the band at 2150 cm^{-1} had a percentage transmission of ca 25% (i.e., approximately 2.3 mg ml^{-1}). Aliquots were withdrawn at convenient times by means of a 1 ml syringe and the transmittance (T_1) of the 2150 cm^{-1} band measured. Since the transmittance of the baseline (T_0) could not be measured at zero *cis* concentration, it was taken to be the baseline just preceeding the high energy band for each reading.

A typical plot is shown in Fig. 5.1 of $\log(\log T_0/T_1)$ against time (i.e., $\log(A-A_o)$ vs time, A is absorbance). As can be seen the plot is initially a straight line confirming the first order nature of the reaction. The results for these initial first order rates (k_{obsd}) are given in Table 5.1.

The activation enthalpy ($\Delta H^{\ddagger}$) of 24.9 ± 0.9 kcal mol $^{-1}$ was calculated from the reactive gradient of the plot of $\ln k_1/T$ against $\frac{1}{T}$, where k_1 is the average value of k_{obsd}. The entropy of activation (-7 ± 3 eu) was found from the equation

$$\Delta H^{\ddagger} = \Delta G^{\ddagger} + T\Delta S^{\ddagger}$$

where $\Delta G^{\ddagger}$ is calculated from the relationship

$$k_{obsd} = \frac{kT}{h} e^{-(\frac{\Delta G^{\ddagger}}{RT})}$$

where k is Boltzmann's constant and h is Planck's constant.

Measurement of the Equilibrium Constant

A known weight (12.0 - 20.0 mg) of *cis*-$Ru(CO)_4(SiCl_3)_2$ in decalin (5.00 ml) was allowed to come to equilibrium. An infrared spectrum of the solution was then taken and the concentration of the *cis*- isomer found using the Beer's Law plot. A 1.00 ml sample of the solution was diluted to 10.00 ml and an infrared spectrum taken of it. From this latter spectrum the concentration of the *trans*-isomer could be found in a similar manner to the *cis*. The absorptions due to the *cis* form in the diluted samples were weak so that interference of these bands in the measurement of the absorbance of the *trans*-isomer was small. Thus although T_0 for the *trans*-compound could not be measured exactly it could be estimated fairly accurately.

It was found in most cases that the sum of the concentrations of the *cis*-and *trans*-forms at equilibrium was equal within experimental error to the initial *cis* concentration. The exceptions were the results of the equilibrium above 150° where it was found that the concentrations at equilibrium were slightly lower than the initial concentration suggesting that some decomposition had taken place.

The results of the equilibrium study are given in Table 5.2.

Nmr Study of $Os(CO)_4(SiMe_3)_2$

Freshly sublimed $Os(CO)_4(SiMe_3)_2$ was dissolved in dibromomethane; the solution was then degassed and sealed in an nmr tube under high vacuum. This was necessary since it was found that solutions of $Os(CO)_4(SiMe_3)_2$ in dibromomethane when exposed to air decomposed to an, as yet, unidentified product.

Nmr spectra were run on a Varian HA100 instrument. The temperature was measured using a thermocouple which had been previously calibrated and was believed to be accurate to ± 1°.

From the integration of the respective *cis*-and *trans*-signals it was possible to calculate the equilibrium constant (k) at 10° intervals in the range -40 - +30 (Table 5.4). From the slope of a plot of log K vs $\frac{1}{T}$ a value of 0.8 kcal mol^{-1} was found for ΔH° for the equilibrium *cis* $\rightleftarrows$ *trans*. A value for ΔS° of 3.1 eu was found from the standard thermodynamic equations:

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -RT \ln K$$

From the plot of log K vs $\frac{1}{T}$ it was possible to estimate the relative proportion of *cis*- and *trans*-forms in the region of collapse (30-80°).

The rate constants for the reaction were evaluated from the lifetimes which were obtained by matching computer-simulated spectra with the experimental spectra. The computer program used for this purpose was written by Dr. D. L. Rabenstein of this department and was similar to that described in ref. 190. Drs. D. L. Rabenstein and S. Libich assisted in the nmr line shape calculations. The chemical shift difference between the two signals was found to be slightly temperature-dependent and so a value of 9.3 Hz was used in the calculations; this was the difference found in the region just before collapse of the signals.

The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated as described previously.

Results are given in Table 5.3. Some representative observed and calculated spectra are shown in Fig. 5.2.

Nmr Spectra of $Os(CO)_4(SiMe_2Cl)_2$ and $Os(CO)_4(SnMe_3)_2$

Nmr samples were prepared similarly only in the case of $Os(CO)_4(SiMe_2Cl)_2$, 1,2-dichlorobenzene (dried with P_2O_5) was used as a solvent. The spectra were recorded on the 56/60 machine (see Chapter 2). The results for $Os(CO)_4(SiMeCl_2)_2$ and $Os(CO)_4(SnMe_3)_2$ are shown in Fig. 5.3 and 5.4. respectively.

Nmr Study of *cis*-$Os(CO)_4H_2$

The method [134] of Calderazzo and L'Eplattenier was used to prepare *cis*-$Os(CO)_4H_2$ except that pentane was used as a solvent instead of heptane. The pentane was removed under vacuum and a sample of the hydride condensed into an nmr tube cooled in liquid nitrogen, using high vacuum techniques. An approximately equal volume of benzene was added to the sample and the tube sealed under vacuum.

The nmr was run at room temperature and at 75° on the HA 100 instrument as previously described. The results are discussed in the appropriate section of this Chapter.

Attempted ^{13}CO Exchange with $Os(CO)_4(SiMe_3)_2$

The procedure was essentially that described in Chapter 4 except that a slightly more concentrated solution was used. In this way the weak modes due to ^{13}CO present in natural abundance could be clearly seen.

The continuously stirred sample was heated at 55° for 165 minutes. An infrared spectrum after this procedure revealed no significant change in the spectrum.

Preparation of $Os(CO)_3(PPh_3)(SiMe_3)_2$

A solution of $Os(CO)_4(SiMe_3)_2$ (0.13 g, 0.30 mmol) and PPh_3 (0.079 g, 0.30 mmol) in heptane (15 ml) was heated at 80° for 7 hr. There appeared to be no reaction (by ir analysis). The solution was then irradiated for 2 hr. Removal of solvent left a sticky solid. The compound could not be purified by sublimation. The infrared of this solid showed bands at 2049m, 1980s, 1968vs cm^{-1} and weak bands at 2070 and 2010 cm^{-1}. The mass spectrum showed a strong peak at 684 (calcd for $(Ph_3P)Os(CO)_3(SiMe_3)_2$ is 682), plus a weak peak at 756. The nmr spectrum in dichlorobenzene showed a singlet at 9.96 τ and a doublet at 9.58 τ in the ratio of 1:1, besides other minor peaks. These peaks were observed to collapse at 120°. On raising the temperature to 165° the signal consisted of a fairly broad peak.

However, the intensity of this signal was weak and new resonances were seen to appear in the spectrum. An nmr spectrum of the cooled solution showed that considerable decomposition had taken place.

Isomerization of Equatorially Labelled *cis*-$Ru(CO)_4(SiCl_3)_2$

A sample of *cis*-$Ru(CO)_4(SiCl_3)_2$ in which the equatorial CO groups had been replaced by ^{13}CO was prepared as previously described. The solution was placed in an oil-bath at 80-85°. The atmosphere of 95.5% ^{13}CO was maintained throughout the experiment; the solution was stirred continuously. Infrared spectra were taken of the solution after each hour, for 11 hr. At this stage the main band in the spectrum was at 2043 cm^{-1}.

Results are given in Table 5.6 and some representative spectra are shown in Fig 5.6 . It was found that $Ru(CO)_4(SiCl_3)_2$ slowly attacked the infrared cells (NaBr) and it is this which causes the base line to become somewhat depressed in and around the region of 2040 cm^{-1}.

Calculation of the Stretching Frequencies of *trans*-$Ru(CO)_2(^{13}CO)_2(SiCl_3)_2$

In *trans*-$Ru(CO)_4(SiCl_3)_2$ there are three force constants which determine the CO stretching frequencies namely the primary stretching force constant, k, and the two interaction constants k'_{cis} and k'_{trans}. In order to determine these accurately at least three frequencies must be known and correctly assigned.

Concentrated solutions of *trans*-$Ru(CO)_4(SiCl_3)_2$ show two additional weak bands at 2109 and 2054.5 cm^{-1} besides the main E_u band at 2088.5 cm^{-1} (see Chapter 7 for a more complete discussion). The absorption at 2054.5 cm^{-1} is confidently assigned to a mode which is similar to the components of the E_u but involves one ^{13}CO molecule. This peak is observed because there is some 1% naturally occurring ^{13}C, thus monosubstituted *trans*-$Ru(CO)_4(SiCl_3)_2$ should be present to the extent of 4% in unenriched products. The vibration at 2109 cm^{-1} was assigned to the B_{1g} mode of the unsubstituted molecule.

From these frequencies and assignments it was possible to calculate the force constants for *trans*-$Ru(CO)_4(SiCl_3)_2$ and hence the carbonyl stretching frequencies for the possible isomers of *trans*-$Ru(CO)_2(SiCl_3)_2$. The results are given in Table 5.6.

However, it was realized that a better fit of all the available data could be obtained if the band at 2109 cm^{-1} was assigned to an A_1 mode of the monosubstituted molecule. When this had been done agreement between the observed and predicted bands for all possible *trans*-$Ru(CO)_4(SiCl_3)_2$ species was excellent as can be seen from Table 5.7.

The computations outlined above were kindly performed by Dr. G. O. Evans of this department. The calculations of frequencies from force constants were carried out using a program known as VSEC.

It could be argued that the band at 2042 cm^{-1} due to the molecule with two ^{13}CO ligands *trans* to one another is weak in the infrared. This is thought to be extremely improbable since this band corresponds to one of the components of the E_u mode of the unsubstituted compound and this latter mode is extremely intense in the infrared. Also a band at 2043 cm^{-1} becomes the strongest absorption in the spectrum as the reaction progresses, for reasons already stated.

CHAPTER 6

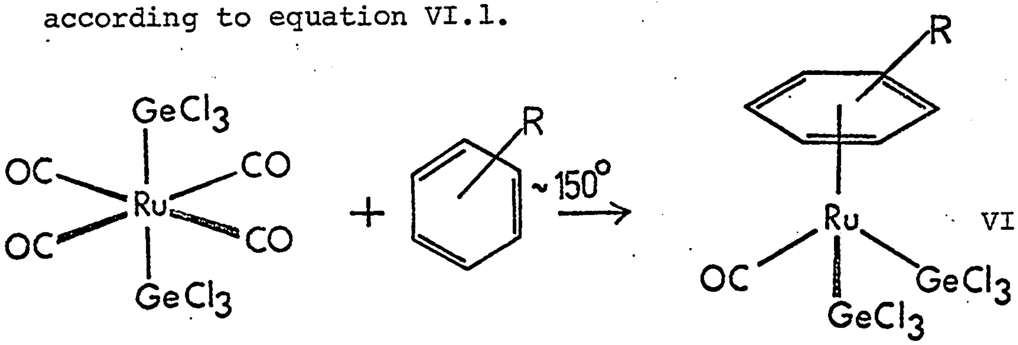
ARENE DERIVATIVES OF $Ru(CO)_4(GeCl_3)_2$

INTRODUCTION

It has been seen, from both the X-ray results and the force constant calculations, that in *cis*-and *trans*-$Ru(CO)_4(GeCl_3)_2$ the *trans*-effects of Cl_3Ge and CO are very much the same. In other words these molecules have some resemblance to the isoelectronic $Mo(CO)_6$. It therefore seemed worthwhile to study some of the reactions of *trans*-$Ru(CO)_4(GeCl_3)_2$ which are exhibited by $Mo(CO)_6$.

RESULTS AND DISCUSSION

It has been found that *trans*-Ru(CO)$_4$(GeCl$_3$)$_2$ reacts with arenes to give (arene)Ru(CO)(GeCl$_3$)$_2$ derivatives according to equation VI.1.



VI.1

This is entirely analogous to the reaction of molybdenum hexacarbonyl with arene to give (arene)Mo(CO)$_3$ complexes.[6,192,193]

The reactions of type V.1 were carried out in evacuated sealed tubes for the low boiling ligands whereas simple refluxing in the appropriate ligand was found to be sufficient for the xylene and mesitylene derivatives.

The reaction takes place at the same temperature at which isomerization occurs (Chapter 2). It has been shown that in *cis*-Ru(CO)$_4$(GeCl$_3$)$_2$ the GeCl$_3$ groups labilize the *trans*-CO groups (Chapter 4). A reasonable mechanism for the formation of these substances is that given in Scheme I . Also consistent with the scheme was the fact that (C$_6$H$_6$)Ru(CO)(SiCl$_3$)$_2$ could be obtained at 80° from the reaction of benzene with *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$. At this

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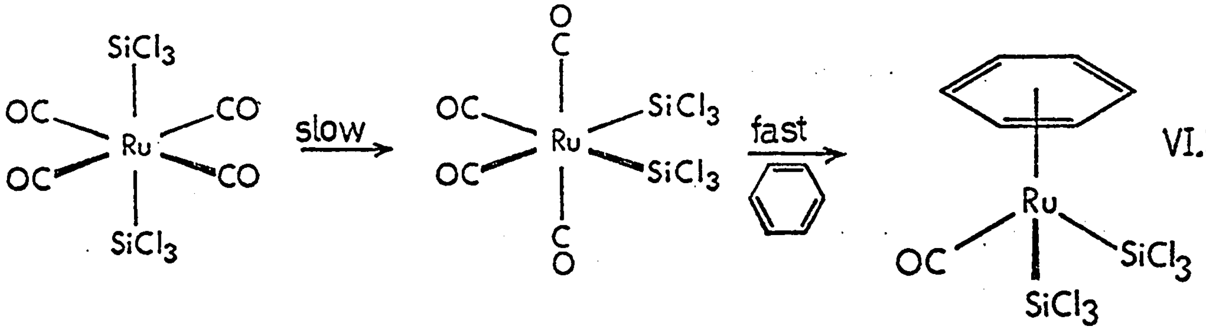
temperature *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$ isomerizes to the *cis*-form and as has been seen in Chapter 4 the SiCl$_3$ has a larger *trans* labilizing effect in these systems than in GeCl$_3$. Furthermore, infrared spectra taken during the course of this reaction showed only bands due to *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$ and (C$_6$H$_6$)Ru(CO)(GeCl$_3$)$_2$ indicating that the reaction went according to VI.2.

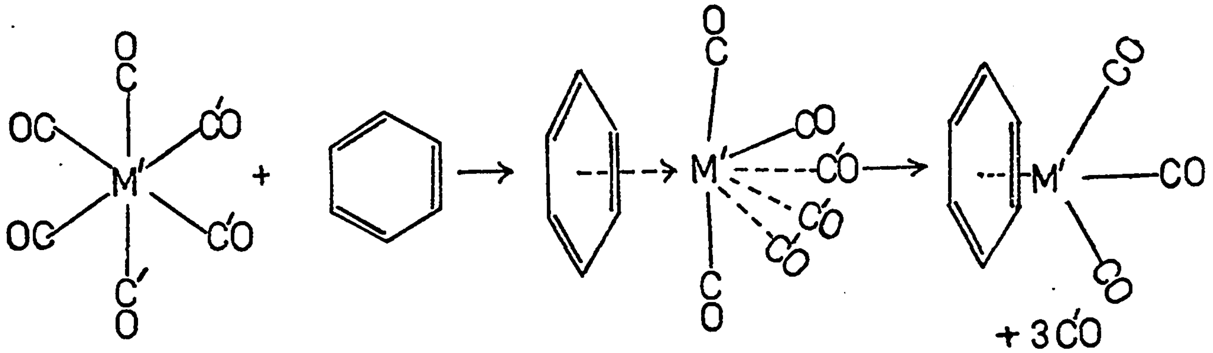


VI.2

Also, it has been found that in a similar reaction with Ru(CO)$_4$(SnCl$_3$)$_2$, for which no *cis* - form has been observed, that only decomposition into Ru$_2$(CO)$_5$SnCl$_6$ took place.

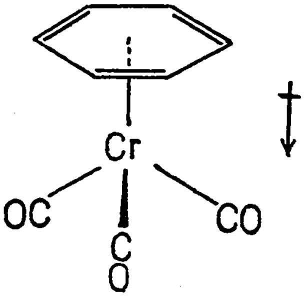
That derivatives of the type (arene)Ru(CO)(GeBr$_3$)$_2$ could be prepared albeit in low yield may indicate that the *cis*-form of Ru(CO)$_4$(GeBr$_3$)$_2$ is capable of existence.

There is kinetic evidence to indicate that the reaction between arenes and Mo(CO)$_6$ proceeds via an 'inversion' mechanism (VI.3).[194] Such a mechanism cannot be ruled out in the present case.



VI.3

The compounds (arene)Ru(CO)$(GeCl_3)_2$ are all either colorless or pale yellow solids which appeared air-stable except for some samples of the benzene derivative which underwent superficial decomposition. Even though the molecular weight of (C_6H_6)Ru(CO)$(GeCl_3)_2$ is less than that of Ru$(CO)_4(GeCl_3)_2$ it is insoluble in non-polar solvents and does not sublime under high vacuum. These compounds also have remarkable thermal stability: they do not appear to undergo any decomposition before their melting points which are above 200°. Dipole-dipole interaction may account for this behaviour. Arenecarbonylchromium(O) complexes have been found [195] to have large dipole moments with the axial component pointing from the arene towards the metal (6.1) The dipole moments of the present compounds might be



6.1

expected to be even greater in view of the electronegative $GeCl_3$ groups.

The melting points of the present compounds (Table 6.1) reflect the symmetry of the arene ligand and are compared with both the free ligand and the corresponding (arene)$Cr(CO)_3$ compounds.

The mass spectrum of $C_6H_6Ru(CO)(GeCl_3)_2$ (Table 6.2) and its mesitylene analogue show only a weak parent ion but a strong peak due to loss of one chlorine atom i.e., $[(C_6H_6)Ru(CO)(GeCl_3)(GeCl_2)]^+$. This may be compared with $(C_5H_5)Fe(CO)H(SiCl_3)_2$, (P), for which the heaviest ion observed in the mass spectrum was $(P-Cl)^+$.

In most cases the compounds were too insoluble for nmr study; however, for the more symmetrical benzene and mesitylene derivatives spectra were obtained. The resonances of the ring protons are shifted upfield compared to that of the free ligand. This has been previously explained as due to perturbation of the aromatic ring

TABLE 6.1

Melting Points of the Arene Derivatives

Arene	(Arene)Ru(CO)(GeCl$_3$)$_2$ (mp °C)	Arene[117] (mp °C)	(Arene)Co(CO)$_3$[196] (mp °C)
Benzene	>300	5.5	165.5-166.5
Toluene	236	-95	82 - 83
o-Xylene	221 - 222	-25.18	90 - 91.4
m-Xylene	246 - 248	-47.87	107 - 108
p-Xylene	240 - 242	13.26	99 - 100
Mesitylene	>300	-44.7	117.5-178

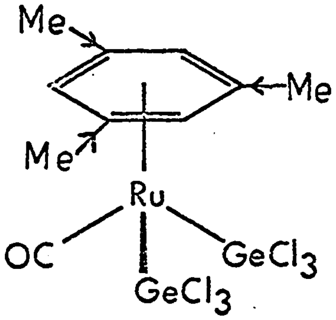
TABLE 6.2

Mass Spectrum of (Benzene)Ru(CO)$(GeCl_3)_2$

Peak	Approximate Intensity	Assignment
566	2.3	$(C_6H_6)Ru(CO)(GeCl_3)_2$
531	87	$(C_6H_6)Ru(CO)(GeCl_3)(GeCl_2)$
422	71	$(C_6H_6)Ru(CO)GeCl_3$
387	81	$(C_6H_6)Ru(CO)GeCl_2$
359	45	$(C_6H_6)RuGeCl_2$
352	71	$(C_6H_6)Ru(CO)GeCl$
324	100	$(C_6H_6)RuGeCl$
281	11	$RuGeCl_3$
274	11	$Ru(CO)GeCl_2$
250	38	$(C_6H_6)RuCl_2$
243	42	$(C_6H_6)Ru(CO)Cl$
215	35	$(C_6H_6)RuCl$
208	45	$(C_6H_6)Ru(CO)$
180	25	$(C_6H_6)Ru$

current by π-bond formation to the metal.[197] Note the methyl signal in $((CH_3)_3C_6H_3)Ru(CO)(GeCl_3)_2$ is at lower field than the methyl signal in uncoordinated mesitylene (Fig. 6.1).

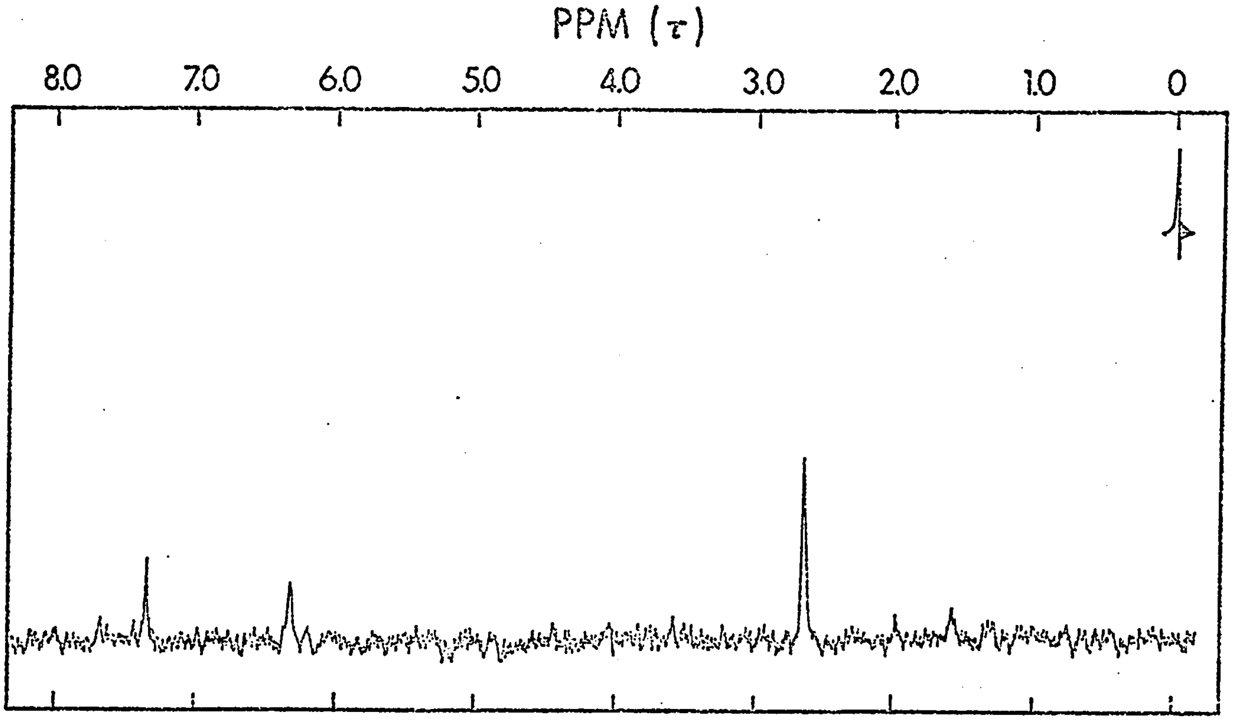
It is apparent from Table 6.3 that progressive substitution of the hydrogens on the arene by methyl groups causes a lowering of the CO stretching frequency. This is consistent with the greater inductive effect of the methyl groups pushing more electron density onto the arene ring and this density being partially transmitted to the carbonyl group *via* the ruthenium atom (6.2)



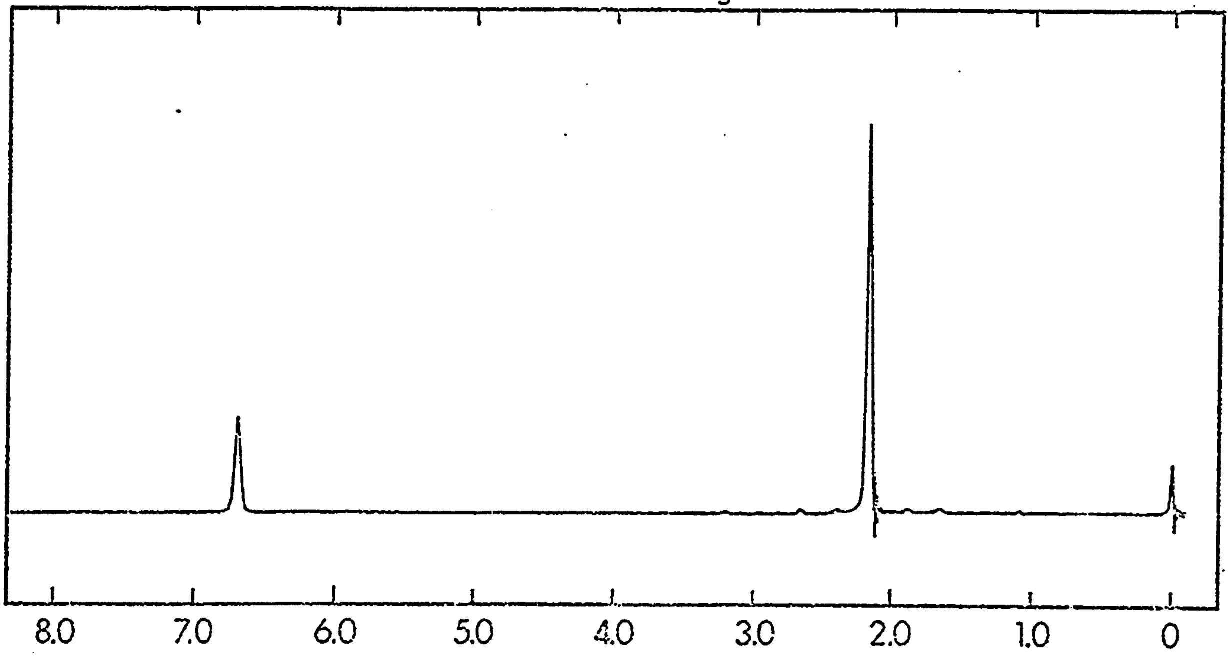
6.2

For the dimethyl benzenes the CO stretching frequency appeared almost insensitive to the exact position of the methyl groups i.e., the *ortho-*, *meta-* and *para*-xylene derivatives had approximately the same CO stretching frequency.

Although a number of attempts were made to prepare the hexamethyl derivative, none afforded this compound in



<u>FIGURE 6 (a)</u> Nmr spectrum of $((CH_3)_3C_6H_3)Ru(CO)(GeCl_3)_2$ in $CDCl_3$, peak at low field is due to $CHCl_3$.



<u>FIGURE 6 (b)</u> Nmr spectrum of mesitylene

TABLE 6.3

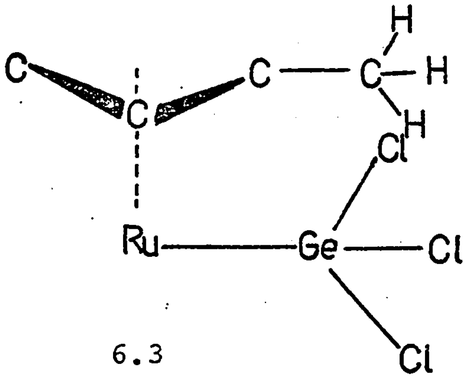
Infrared Spectra of (Arene)Ru(CO)$(GeCl_3)_2$ Derivatives

Compound	Infrared Spectrum (2200 - 2000 cm^{-1})	
	CH_2Cl_2 solution (cm^{-1})	Nujol mull (cm^{-1})
$(C_6H_6)Ru(CO)(GeCl_3)_2$	2040	2048
$(CH_3)C_6H_5Ru(CO)(GeCl_3)_2$	2037	2035(?), 2030, 2020
(o-$(CH_3)_2C_6H_4$)Ru(CO)$(GeCl_3)_2$	2031	2026
(m-$(CH_3)_2C_6H_4$)Ru(CO)$(GeCl_3)_2$	2032	2018
(p-$(CH_3)_2C_6H_4$)Ru(CO)$(GeCl_3)_2$	2034	2037, 2024
$((CH_3)_3C_6H_3)Ru(CO)(GeCl_3)_2$	2029	2027, 2020
$(C_6H_6)Ru(CO)(SiCl_3)_2$	2016	-
$(C_6H_6)Ru(CO)(GeBr_3)_2$[a]	2037	-
$((CH_3)_3C_6H_3)Ru(CO)(GeBr_3)_2$	2027	-

---

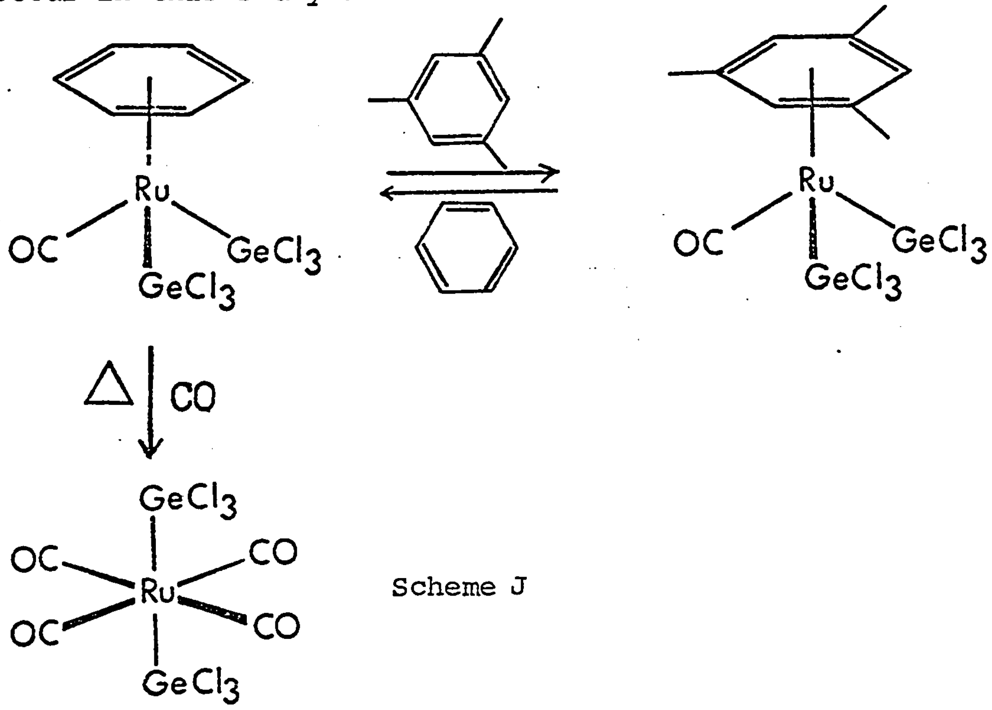
[a] Compound not characterized.

sufficient quantity for characterization. There was observed in some cases, however, an absorption in the infrared at 2019 cm^{-1}, a position one might expect for such a compound. A reason for the failure to prepare this compound may be that there is too much steric hindrance between the methyl hydrogens and the chlorine atoms as shown in 6.3.



6.3

Some chemical reactions of $(C_6H_6)Ru(CO)(GeCl_3)_2$ found to occur in this study are shown in Scheme J.

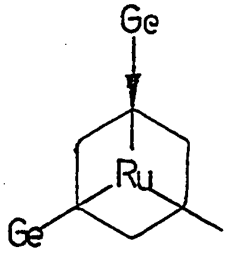


Scheme J

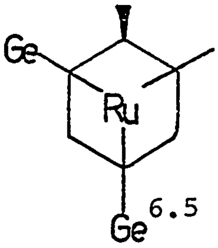
Rotational Isomers of (Arene)Ru(CO)$(GeCl_3)_2$

As is normally found for these and the related cyclopentadiene derivatives, the aromatic ring protons exhibit a single sharp peak in the nmr. Such an observation is consistent with rapid rotation of the ring about an axis through the middle of the ring and the ruthenium atom.

In the solid state, motion of the ring does not take place and hence different conformations of the ring with respect to the other half of the molecule are possible. These possibilities are illustrated for $(CH_3C_6H_5)Ru(CO)(GeCl_3)_2$ (6.4 - 6.10). The molecules 6.4 - 6.7 are the so-called



6.4



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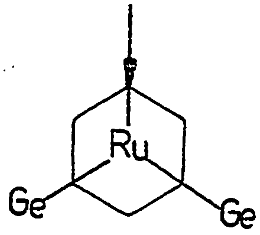
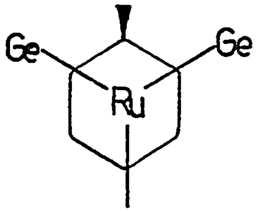
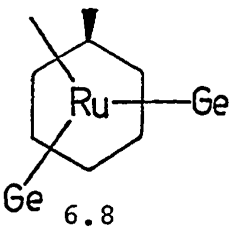


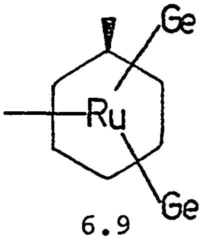
6.6



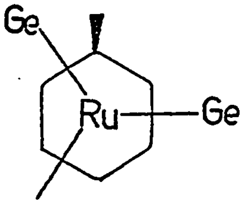
6.7



6.8



6.9

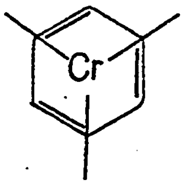


6.10

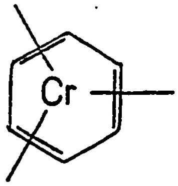
eclipsed and 6.8 - 6.10 the staggered forms; there are optical isomers of 6.8 and 6.10.

In solution all different forms would be present to some extent and this could result in the broad band observed. That there is more than one isomer present in the solid state for some of these derivatives is shown by the solid state infrared spectra for these compounds (Table 6.3 and see Fig. 6.2).

It is difficult to say which forms are the most favorable. It has been found that benzene and hexamethyl benzene chromium tricarbonyl have the staggered conformation 6.12. However, (anisole)$Cr(CO)_3$ and (*o*-toluidine)$Cr(CO)_3$ have the



6.11



6.12

eclipsed conformation 6.11. It has been suggested that the eclipsed configurations arise since the ring substituents are electron-releasing and are *ortho-para* directing. The relatively high electron density on the *ortho* and *para* carbons favors them being held *trans* to the π-acid carbonyl groups. This electronic effect would, however, compete with steric repulsion between the ring substituents and the metal CO groups.

If we apply the above arguments to $(CH_3C_6H_5)Ru(CO)(GeCl_3)_2$ we might expect the eclipsed form to be slightly more favored since the methyl group is electron-releasing. Molecular models, assuming normal bond parameters, show that steric repulsion would be quite considerable in cases such as 6.4. Since the methyl group is *ortho-para* directing, 6.5 and 6.7 would not be expected to be preferred configurations. Since previous results have concluded that the π-acceptor properties of $GeCl_3$ and CO are similar we might expect 6.6 to be the only form present in the solid state. It is found, however, that there are at least two and possibly three CO stretches in the solid state (Fig. 6.2). This may mean that some of the staggered forms are present; methyl groups are not strongly *ortho-para* directing. Of the possible staggered forms 6.8 appears most likely.

Infrared spectra in the solid state are broad and bands are often not resolved. It might also be expected that the CO stretching frequencies of the different possible conformers might be close in energy, making the resolution problem worse. Other effects such as crystal splitting (see for example Chapter 7) may cause extra bands in the solid state; the benzene and *meta*-xylene derivatives did, however, show only one CO stretch in the infrared.

In the *ortho*-xylene derivative the inductive effects

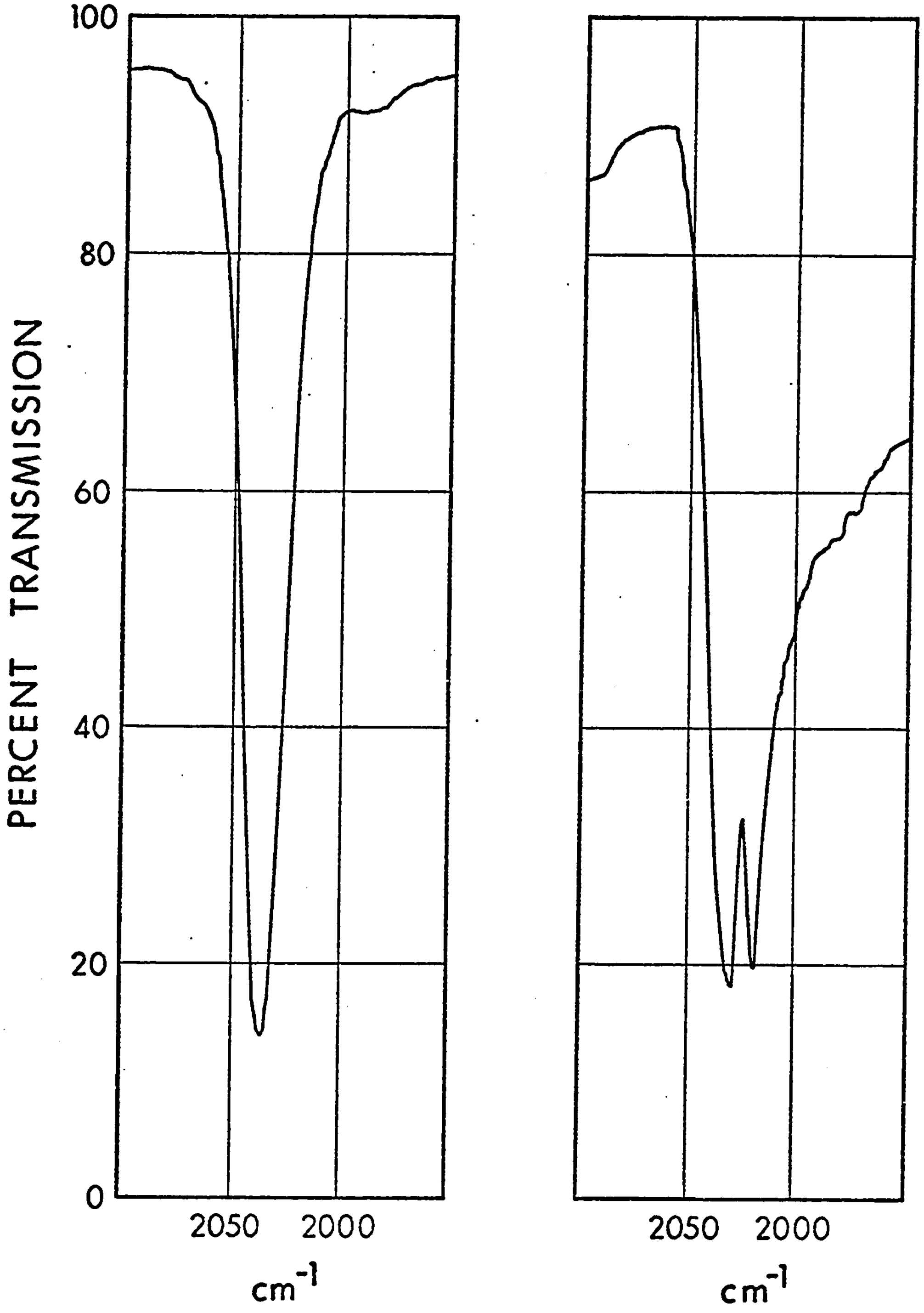
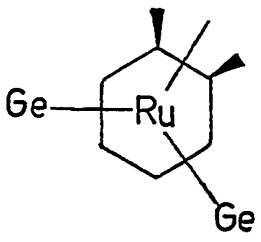
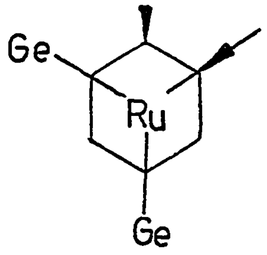


FIGURE 6.2 Infrared Spectra of $(CH_3C_6H_5)Ru(CO)(GeCl_3)_2$

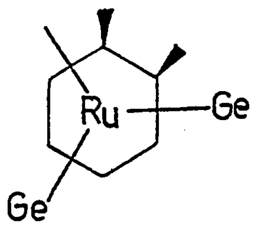
of the two methyl groups will cancel; therefore the eclipsed configurations will not be preferred. It is expected that steric arguments will be important in this case. On this basis 6.13 - 6.15 might be expected to be stable. Only a single CO stretch is observed in the solid state. This may mean that there is accidental degeneracy or that only one form is present. If the latter is the case then it is expected that 6.13 would be the preferred conformer since this has the minimum steric interaction.



6.13

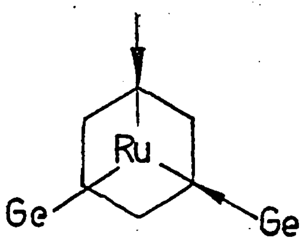


6.14



6.15

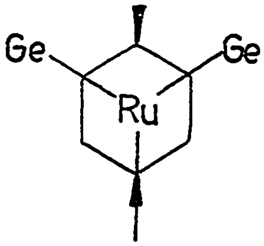
By arguing along similar lines it is possible to predict stable configurations for the other derivatives synthesized in this study. For the *meta*-xylene compound we might expect, since the inductive effects of the methyl groups enhance one another, that an eclipsed form might be more favored than in the toluene derivative i.e., 6.16 would be the only preferred configuration. The structure 6.16 does have a $GeCl_3$ in close proximity to a methyl group and hence a staggered form cannot be ruled out. However, that only one band is found in the CO stretching region



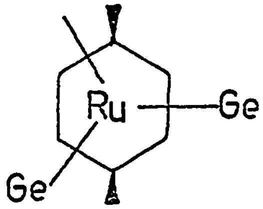
6.16

implies that only structure 6.16 is present.

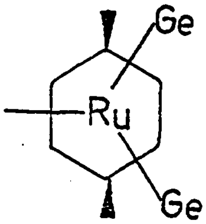
For the *para*-xylene derivative 6.17 - 6.19 are reasonable structures. The geometry given in 6.19 may be less



6.17



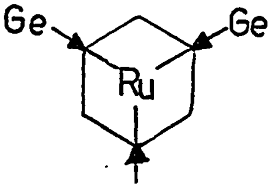
6.18



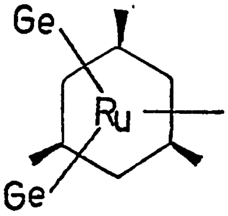
6.19

favorable due to close contacts between $GeCl_3$ and methyl groups. Only two CO stretches are observed in the solid state.

Similarly two absorptions are observed for the mesitylene compound. These may be due to forms given in 6.20 and 6.21. Although steric interaction may be great in 6.20, the increased bonding by having the π-groups *trans* to the unsubstituted carbons may compensate for this. If only steric

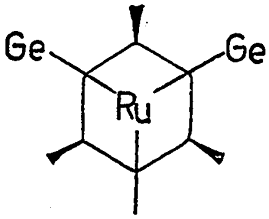


6.20



6.21

interactions dictated which structure was preferred, we could only expect one reasonable geometry (6.22).



6.22

That two stretches are observed indicates that other effects are present.

Reaction of $Ru(CO)_4(GeCl_3)_2$ with Dienes

The reaction of $Ru(CO)_4(GeCl_3)_2$ (and to a lesser extent $Ru(CO)_4(SiCl_3)_2$) with dienes was studied. In all cases intractable polymeric products were obtained.

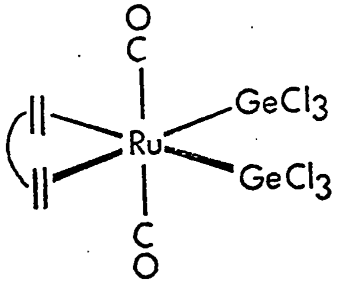
This is in itself a very interesting result. The mechanism of olefin polymerization is by no means clearly understood and many possibilities have been discussed. At the present time the majority of evidence supports an ionic polymerization mechanism. There is general agreement that the polymerization involves growth at the metal by an insertion mechanism (VI. 6).[6]

$$M'\text{-}R \xrightarrow{CH_2=CH_2} M'CH_2CH_2R \xrightarrow{C'H_2=C'H_2} M'\text{-}C'H_2\text{-}C'H_2CH_2CH_2R$$

IV.6

The necessity of a vacant site on the transition metal has been stressed, for instance in the polymerization of olefins using Ziegler-Natta catalysts. This is believed to involve a path as shown in Scheme K .[6]

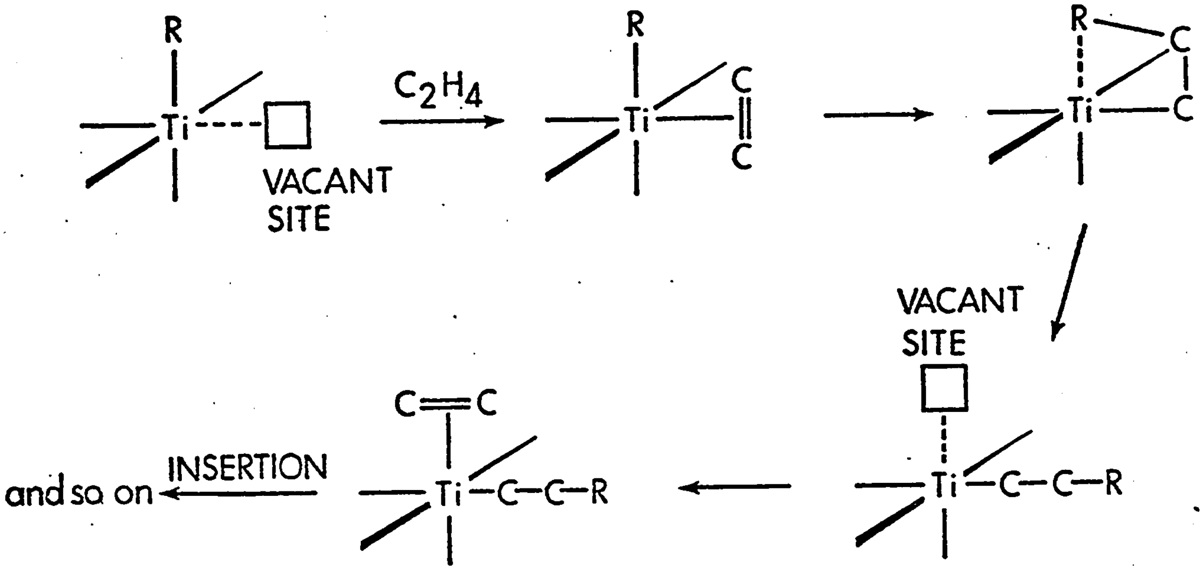
It is interesting to speculate that a similar situation exists for *cis*-$Ru(CO)_4(SiCl_3)_2$. It is envisaged that the diolefin is coordinated in the equatorial plane at sites known to be labile from ^{13}CO studies (6.23). It is possible that because of the large *trans*-effect of the $GeCl_3$ group one



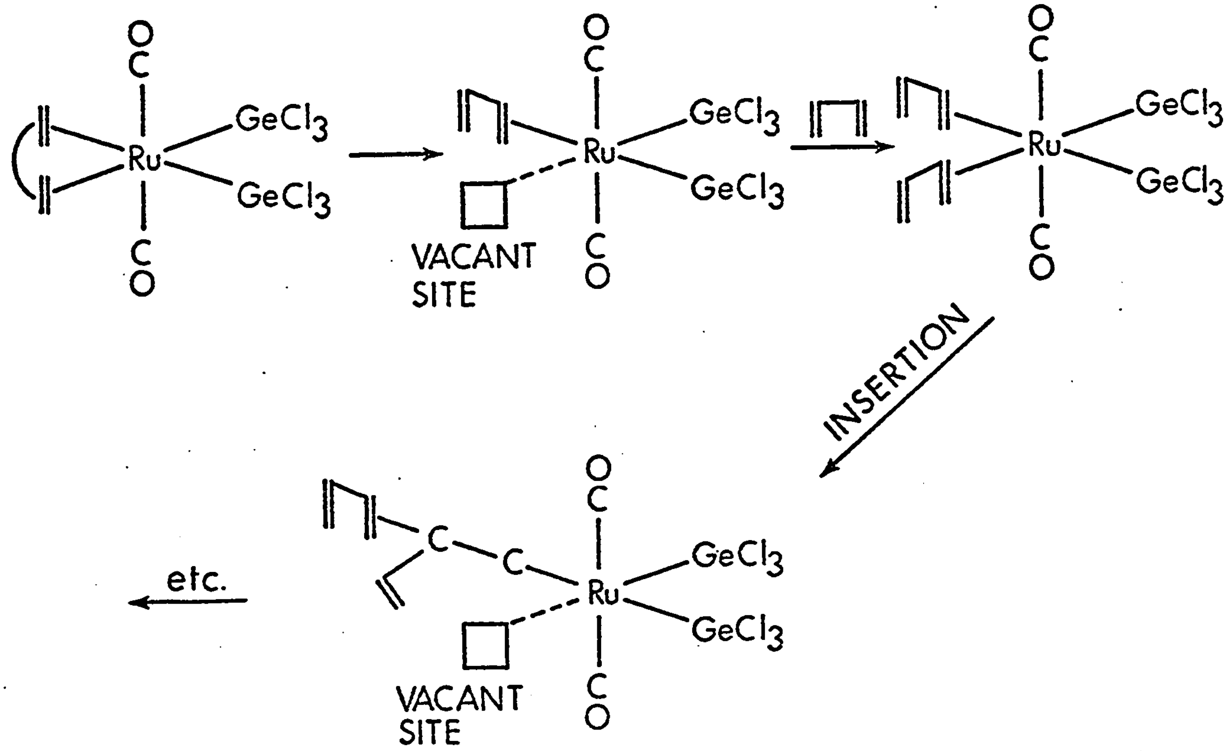
6.23

of the double bonds becomes detached leaving a vacant site

SCHEME L



SCHEME K

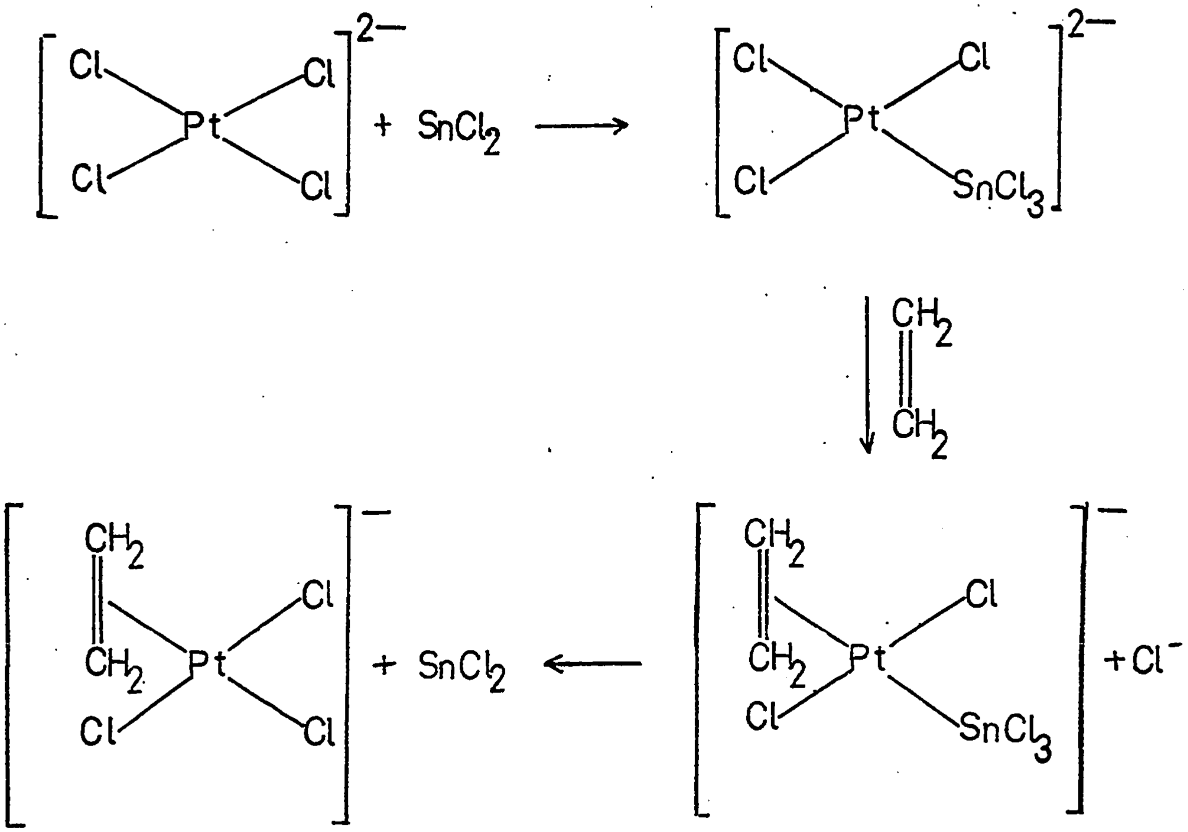


for coordination of another diolefin. Polymerization would then follow as shown in Scheme L .

Not unrelated to the above is the use of $SnCl_2$ as a catalyst in the preparation of transition metal olefin compounds.[6] An example is the preparation of Zeise's salt (VI.)

$$PtCl_4^{2-} + C_2H_4 \xrightarrow{SnCl_2} [C_2H_4PtCl_3]^-$$

A reasonable mechanism for the formation of the salt is the following:



Such insertion and elimination of $SnCl_2$ into a transition metal bond have been documented in this thesis. The high *trans*-effect of $SnCl_3$ has also been discussed. It should be pointed out that $[Cl_2Pt(SnCl_3)_2]^{2-}$ has been isolated from the reaction of $[PtCl_4]^{2-}$ and $SnCl_2$.[103]

EXPERIMENTAL

Techniques outlined in Chapter 2 were employed here. Infrared data is listed in Table 6.3., analytical data in Table 6.4.

Preparation of $(C_6H_6)Ru(CO)(GeCl_3)_2$.

Benzene (25 ml) and *trans*-$Ru(CO)_4(GeCl_3)_2$ (0.57 g, 1.0 mmol) were heated in an evacuated sealed tube at 150° for six days. Approximately every twelve hours during this period the tube was cooled (care!) and reevacuated. After this time the tube was allowed to stand at ca 6° for 24 hr. The benzene was then removed from the large, pale yellow needles of the product, $(C_6H_6)Ru(CO)(GeCl_3)_2$ (0.41 g, 72%). The crystals were washed with two portions of hexane (10 ml) and dried under vacuum. The compound appeared pure by ir spectroscopy; it can, however, be recrystallized from either benzene or CH_2Cl_2-hexane, if needed; mp >300°; nmr: 3.38 τ (CH_2Cl_2 solution), benzene [198], 2.734 τ.

An infrared spectrum of the remaining benzene mother liquor showed that it contained $Ru_2(CO)_5GeCl_6$ besides more product.

The corresponding toluene derivative, $(CH_3C_6H_5)Ru(CO)(GeCl_3)_2$ was prepared in the same manner. An attempt to prepare $(C_6H_6)Ru(CO)(GeBr_3)_2$ by the same method led to isolation of 25 mg of greenish-yellow crystals which had the expected ir spectrum (2037 cm^{-1}, CH_2Cl_2 solution). This crude product did not give satisfactory analytical data however. An infrared spectrum of the benzene solution showed mainly $Ru_2(CO)_5GeBr_6$. A similar experiment using *trans*-$Ru(CO)_4(SnCl_3)_2$ gave only $Ru_2(CO)_5SnCl_6$.

Preparation of $(C_6H_6)Ru(CO)(SiCl_3)_2$.

Benzene (10 ml) and *trans*-$Ru(CO)_4(SiCl_3)_2$ (0.241 g, 0.5 mmol) were refluxed under a nitrogen atmosphere for 48 hr. Infrared spectra taken during this time showed only starting material and product i.e., no *cis*-$Ru(CO)_4(SiCl_3)_2$ was present. After the two days the solution was filtered and evaporated to dryness to give an almost quantitative yield of crude product. The analytical sample, in the form of white crystals, was obtained from two recrystallizations from CH_2Cl_2-n-heptane; mp 203° decomp. nmr: 3.42 τ ($CDCl_3$ solution).

Preparation of $[(CH_3)_3C_6H_3]Ru(CO)(GeCl_3)_2$.

A solution of *trans*-$Ru(CO)_4(GeCl_3)_2$ (0.57 g, 1.0 mmol) in mesitylene was refluxed for 11 hr. The solution was then filtered and placed in the refrigerator overnight. The product $[(CH_3)_3C_6H_3]Ru(CO)(GeCl_3)_2$ (0.45 g, 75%) was separated from mesitylene, washed with hexane and dried under vacuum. It may be crystallized from benzene or CH_2Cl_2-n-hexane to give the pure compound, mp >300°; nmr:

3.68, 7.36 τ (in ratio 1:3 ; $CDCl_3$ solution); mesitylene [198] 3.356 τ, 7.778 τ.

It is essential in the above reaction not to let the reaction proceed much longer than 11 hr as decomposition to unknown products takes place, resulting in lower yields.

The xylene derivatives were prepared in a similar manner only with reflux times of 70 - 90 hour. Nmr spectra of these compounds could not be obtained due to their insolubility.

The bromo derivative $[(CH_3)_3C_6H_3]Ru(CO)(GeBr_3)_2$ was prepared in the same way as the chloro analogue; the yield, however, was low (12%).

Reaction of $(C_6H_6)Ru(CO)(GeCl_3)_2$ with Carbon Monoxide

An autoclave containing $(C_6H_6)Ru(CO)(GeCl_3)_2$ (0.057 g) in heptane was pressurized with carbon monoxide (50 atm) and heated at 150° for 24 hr. The autoclave was cooled and the gas vented. An infrared spectrum of the heptane solution showed only *trans*-$Ru(CO)_4(GeCl_3)_2$.

Reaction of $(C_6H_6)Ru(CO)(GeCl_3)_2$ with Mesitylene

A solution of $(C_6H_6)Ru(CO)(GeCl_3)_2$ (0.057 g, 0.1 mmol) in mesitylene (10 ml) was refluxed for 20 min, filtered and allowed to cool. Crystals of $[(CH_3)_3C_6H_3]Ru(CO)(GeCl_3)_2$ (0.040 g, 66%) were washed with n-hexane and dried under vacuum. The product was identified by its infrared spectrum in CH_2Cl_2.

In a similar reaction $[(CH_3)_3C_6H_3]Ru(CO)(GeCl_3)_2$ was heated in benzene at 150° in an evacuated sealed tube for twelve hours. The product was found to be $(C_6H_6)Ru(CO)(GeCl_3)_2$.

Reaction of Norbornadiene with *trans*-$Ru(CO)_3(GeCl_3)_2$.

An evacuated sealed tube containing *trans*-$Ru(CO)_4(GeCl_3)_2$ and norbornadiene (25 ml) was heated at 140° overnight. On cooling, the tube was found to contain a solid, brown mass of clear, jelly-like material which was insoluble in n-hexane, CH_2Cl_2, acetone, HCl and HNO_3-HF solution.

Reaction with other dienes was similar.

TABLE 6.4

Analytical Data for Arene Derivatives

Compound	Calculated %				Found %			
	C	H	O	X	C	H	O	X
$(C_6H_6)Ru(CO)(GeCl_3)_2$[a]	14.88	1.07	2.83	37.64	15.01	1.05	2.98	37.58
$(CH_3C_6H_5)Ru(CO)(GeCl_3)_2$[b]	16.59	1.39	2.76	36.73	10.93	1.38	3.16	35.66
$[o\text{-}(CH_3)_2C_6H_4]Ru(CO)(GeCl_3)_2$	18.22	1.70	2.70	35.86	18.53	1.70	-	-
$[m\text{-}(CH_3)_2C_6H_4]Ru(CO)(GeCl_3)_2$	18.22	1.70	2.70	35.86	18.75	1.84	-	-
$[p\text{-}(CH_3)_2C_6H_4]Ru(CO)(GeCl_3)_2$	18.22	1.70	2.70	35.86	18.54	1.91	-	-
$[(CH_3)_3C_6H_3]Ru(CO)(GeCl_3)_2$[c]	19.78	1.99	2.64	35.03	20.32	2.19	2.81	35.21
$(C_6H_6)Ru(CO)(SiCl_3)_2$	17.66	1.27	3.36	44.68	18.06	1.37	3.47	45.00
$[(CH_3)_3C_6H_3]Ru(CO)(GeBr_3)_2$	13.74	1.38	1.83	54.86	14.04	1.30	2.14	55.98

---

a = Mol. wt. calcd. 565; found, 566. b = mol. wt. calcd. 579; found, 581. c = mol. wt. calcd. 607; found 607.

(Molecular weights as found by mass spectroscopy).

CHAPTER 7

SOLID STATE INFRARED AND RAMAN SPECTRA OF *trans*-M'$(CO)_4(MX_3)_2$ Compounds

INTRODUCTION

Commercial instruments are now available which make the far infrared region (ca. 30 - 400 cm^{-1}) an accessible area of study. Furthermore, the use of laser sources has spectacularly increased the application of Raman spectroscopy to this region.

With the exception of the CO stretching vibrations, the fundamental modes of *trans*-M'$(CO)_4(MX_3)_2$ compounds come below 800 cm^{-1}.

These compounds are almost ideally suited for study in this area. A structural determination [126] of *trans*-$Ru(CO)_4(GeCl_3)_2$ has established a relative simple and symmetric geometry. For this reason the Raman and infrared spectra of these derivatives is not expected to be too complicated.

The assignment of these modes is facilitated by having a series of compounds in which one atom (or set of atoms) is changed.

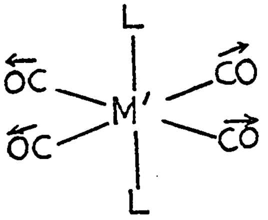
In most cases these compounds are stable, white, crystalline solids and hence excellent for Raman spectra.

No attempt at a completely rigorous assignment of modes is given. However, even the qualitative features are valuable as a structural tool.

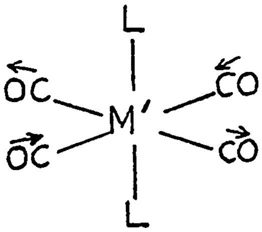
RESULTS AND DISCUSSION

The Carbonyl Stretching Region

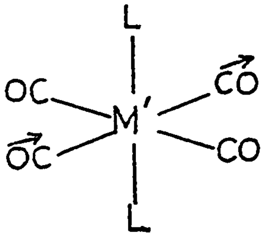
The three modes of carbonyl stretching vibration of *trans*-$\text{M}'(\text{CO})_4\text{L}_2$ (of symmetry D_{4h}) are shown below with their appropriate symmetry designations.[178] The order of energy of the frequencies must be $A_{1g} > B_{1g} > E_u$.[150]



A_{1g}



B_{1g}



E_u

In strict D_{4h} symmetry the A_{1g} and B_{1g} modes are infrared inactive but Raman active, whereas the E_u mode is infrared active but not active in the Raman. However, when L is MX_3 the molecule no longer has D_{4h} symmetry since the MX_3 group does not possess a four-fold axis of symmetry. Due to this lowering of symmetry the A_1 and B_1 modes may gain some infrared intensity.

In some cases where L is PR_3 (e.g., $\text{Cr(CO)}_4(\text{PPh}_3)_2$[201]) very weak high frequency satellites have been observed and assigned[150] to the A_1 and B_1 modes. Similar weak bands are observed in the present compounds (Table 7.1, Fig. 7.1-

TABLE 7.1

Infrared Spectra (2200-2000 cm^{-1}) for M'(CO)$_4$(MX$_3$)$_2$ Compounds

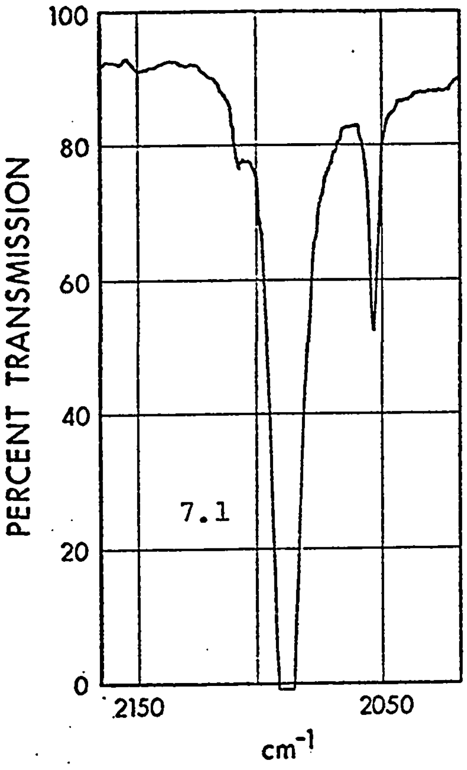
Compound	Medium	Infrared Spectrum (2200-2000 cm^{-1})
Ru(CO)$_4$(SiCl$_3$)$_2$	heptane	2109wsh, 2089.5vs, 2054.5
Ru(CO)$_4$(SiCl$_3$)$_2$	CH$_2$Cl$_2$	2156vw, 2111sh? 2062m 2092vs
Ru(CO)$_4$(SiCl$_3$)$_2$	nujol	2156w, 2149w, 2118sh, 2101vs, 2096vs, 2092vs, 2089vs, 2058m
Ru(CO)$_4$(GeCl$_3$)$_2$	CH$_2$Cl$_2$	2168vvw, 2131msh, 2111vvs, 2076m
Ru(CO)$_4$(GeCl$_3$)$_2$	nujol	2172w, 2138w, 2115vs, 2112vs, 2082m, 2079m
Ru(CO)$_4$(GeBr$_3$)$_2$	hexane	2172w, 2120 (2103vs) 2071m
Ru(CO)$_4$(GeBr$_3$)$_2$	CH$_2$Cl$_2$	2165(?), 2128, (2108vs), 2074m
Ru(CO)$_4$(SnCl$_3$)$_2$	CH$_2$Cl$_2$	2161(?), 2026wsh, 2106vvs, 2073m
Ru(CO)$_4$(SnCl$_3$)$_2$	nujol	2172vvw, 2166vvw, 2133w 2112s, 2109s, 2077m
Fe(CO)$_4$(GeCl$_3$)$_2$	CH$_2$Cl$_2$	2148w, 2089vs, 2058m
Os(CO)$_4$(SiMeCl$_2$)$_2$	heptane	2145vvw, 2094w, 2059vs (asymmetric)

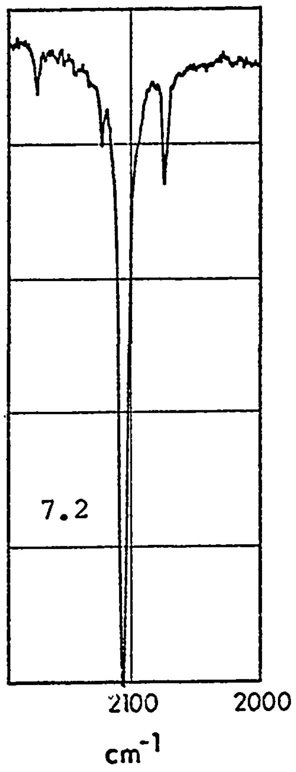
FIGURE 7.1 Infrared spectrum of *trans*-$Ru(CO)_4(SiCl_3)_2$ (heptane solution)

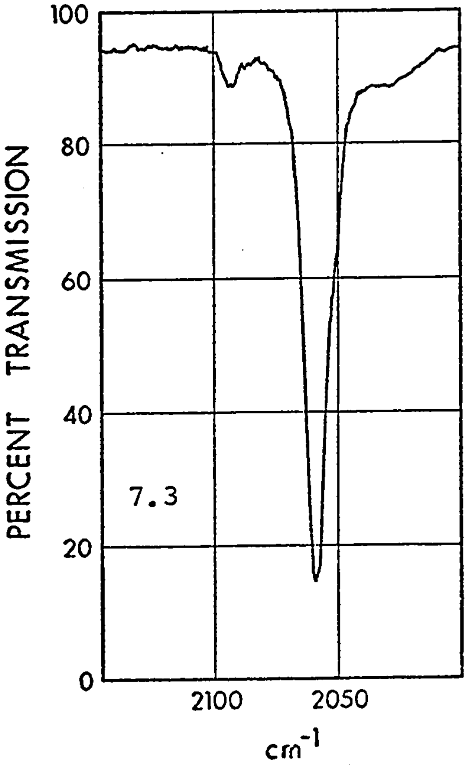
FIGURE 7.2 Infrared spectrum of *trans*-$Ru(CO)_4(GeBr_3)_2$ (heptane solution)

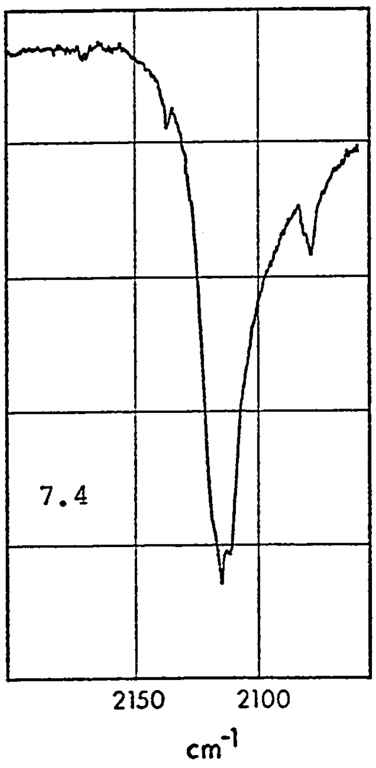
FIGURE 7.3 Infrared spectrum of *trans*-$Os(CO)_4(SiMeCl_2)_2$ (heptane solution)

FIGURE 7.4 Infrared spectrum of *trans*-$Ru(CO)_4(GeCl_3)_2$ (nujol mull).

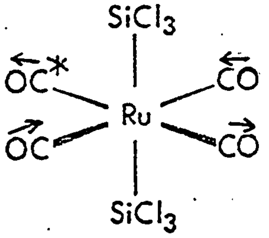

100
80
60
40
20
0
PERCENT TRANSMISSION
7.1
2150
2050
cm^{-1}


7.2
2100
2000
cm^{-1}


100
80
60
40
20
0
PERCENT TRANSMISSION
7.3
2100
2050
cm^{-1}


7.4
2150
2100
cm^{-1}

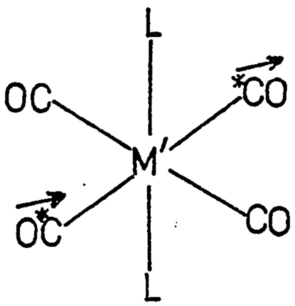
7.3). However, from the calculations outlined in Chapter 5 it appears that an alternative assignment is possible. The weak band originally assigned to the B_1 mode of unsubstituted *trans*-$Ru(CO)_4(SiCl_3)_2$ could be better fitted with the calculated data if this band was assigned to an A_1 mode of the monosubstituted molecule (7.1). Note since ^{13}CO is distinct from ^{12}CO, the molecule has even lower symmetry than the unsubstituted molecule and thus could quite easily be far more intense than the B_1 mode of the unsubstituted molecule. Molecules such as 7.1 are present to the extent of 4% in normal products.



(Normal Mode Shown)
7.1

This is not to say that this band in other spectra should be assigned to a B_1 mode of the monosubstituted compound. It is probable in most cases the assignment of this band to the B_1 mode of the unsubstituted molecule is correct. This is especially true when the non-carbonyl groups are bulky or asymmetric - consider the spectrum of *trans*-$Os(CO)_4(SiMeCl_2)_2$ (Fig. 7.3); in this case even the main E_u band has an asymmetric appearance due to the lowering of the symmetry.

The assignment of the band under discussion to the B_1 mode of the unsubstituted molecule can be confidently made if this absorption is more intense than the ^{13}CO mode of the main peak (i.e., due to the mode shown in 7.2). It is not expected that a mode such as shown in 7.1 will be

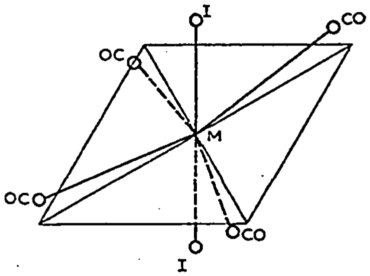


7.2

more intense than that shown in 7.2.

When the 'B_1 mode' is less intense than the ^{13}CO vibration to lower frequency of the main E_u band caution should be made in the assignment e.g., *trans*-$Ru(CO)_4(GeBr_3)_2$ (Fig. 7.2).

Pańkowski and Bigorgne [129] have interpreted the appearance of the 'B_1 mode' in *trans*-$M(CO)_4I_2$ species as due to a distortion of the ideal D_{4h} symmetry in a manner shown in 7.3. However, the assignment of this band to an A_1 mode of the monosubstituted molecule is not inconsistent with the available data. There was no distortion of the type shown

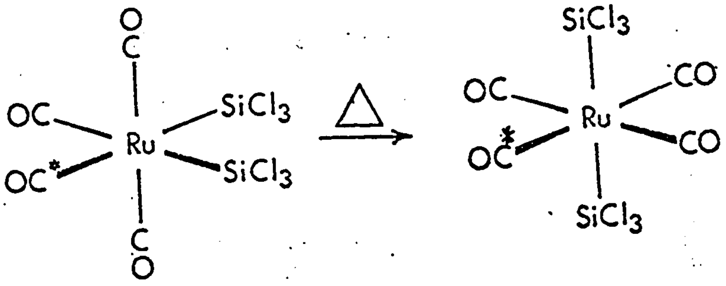


7.3

in 7.3 in the structure of *trans*-Ru(CO)$_4$(GeCl$_3$)$_2$.

That this band was due to an A$_1$ mode of the monosubstituted molecule could have been confirmed by showing that the Raman active B$_1$ mode of the unsubstituted molecule came at a different frequency. Unfortunately the compound was not soluble enough in heptane to see any absorption in the Raman. Since the differences in the two assignments is so small, the solid state Raman spectrum was of little use in this problem because in the solid state the bands shift relative to those in solution in an unpredictable manner.

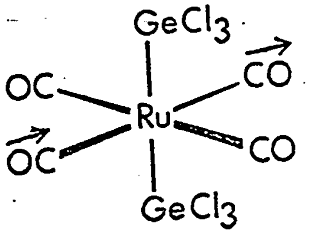
The assignment might be confirmed by studying the infrared spectrum of *trans*-Ru(CO)$_3$(^{13}CO)(SiCl$_3$)$_2$ which could be prepared by VII.1



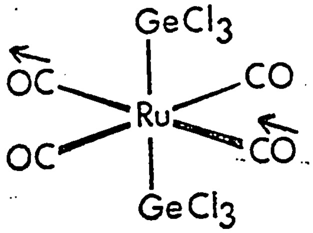
VII.1

In the ensuing discussion of solid state spectra in the carbonyl region, *trans*-$Ru(CO)_4(GeCl_3)_2$ will be taken as the specific example because its structure in the solid has been determined.[126]

The symmetry of *trans*-$Ru(CO)_4(GeCl_3)_2$ may be lower in the solid state than in solution because of the environment of the molecule in the crystal. In such a situation the two components (7.4, 7.5) of the E_u mode may not be



7.4



7.5

degenerate and hence the signal will be split. The crystal structure revealed that the only requirement of the crystal symmetry is that the molecule have a center of inversion.

Such a splitting is indeed seen (Fig. 7.4). This may be due to non-degeneracy of the components of the E_u mode or it may be due to the fact that there are two distinct molecules per unit cell (see below).

In the solid state Raman spectrum we expect to see two absorptions (A_1 and B_1) in the carbonyl stretching region. As can be observed (Fig. 7.5 and 7.6) the lower energy B_1 mode is split. This cannot arise from a single molecule since the B_1 mode is non-degenerate. The reason for this splitting is almost certainly due to the fact that there are two distinct molecules per unit cell[126] and the B_1 modes of each molecule come at a different frequency. Although the A_1 mode is not similarly split it does, in some cases, appear to have a shoulder.

That all the molecules of the type *trans*-$M'(CO)_4(MCl_3)_2$ synthesized here (an example is shown in Fig 7.6) may indicate that they have the same solid state structure.

In solution we would, of course, expect only a single B_1 absorption in the Raman, however, due to the insolubility of these compounds, such spectra could not be obtained.

Unfortunately insufficient *cis*-$Ru(CO)_4(GeCl_3)_2$ was available for comparable studies to be carried out. It would have been of interest to relate its solid state spectra with its known crystal structure, which also revealed two

TABLE 7.2

Raman Spectra for *trans*-M'$(CO)_4(MX_3)_2$ in 2200-2000 cm^{-1} Region

Compound	A_1	B_1
$Fe(CO)_4(GeCl_3)_2$	2132m	2108m, 2004m
$Ru(CO)_4(SiCl_3)_2$	2163s	2129m, 2121s
$Ru(CO)_4(GeCl_3)_2$	2176s	2148m, 2142s
$Ru(CO)_4(GeBr_3)_2$	2170s	2139m, 2130m
$Ru(CO)_4(SnCl_3)_2$	2173s	2143m, 2137s
$Os(CO)_4(SiCl_3)_2$	2169s	2129m, 2119s
$Os(CO)_4(GeCl_3)_2$	2181s	2145m, 2138s
$Os(CO)_4(SnCl_3)_2$	2175s	2140m, 2134s

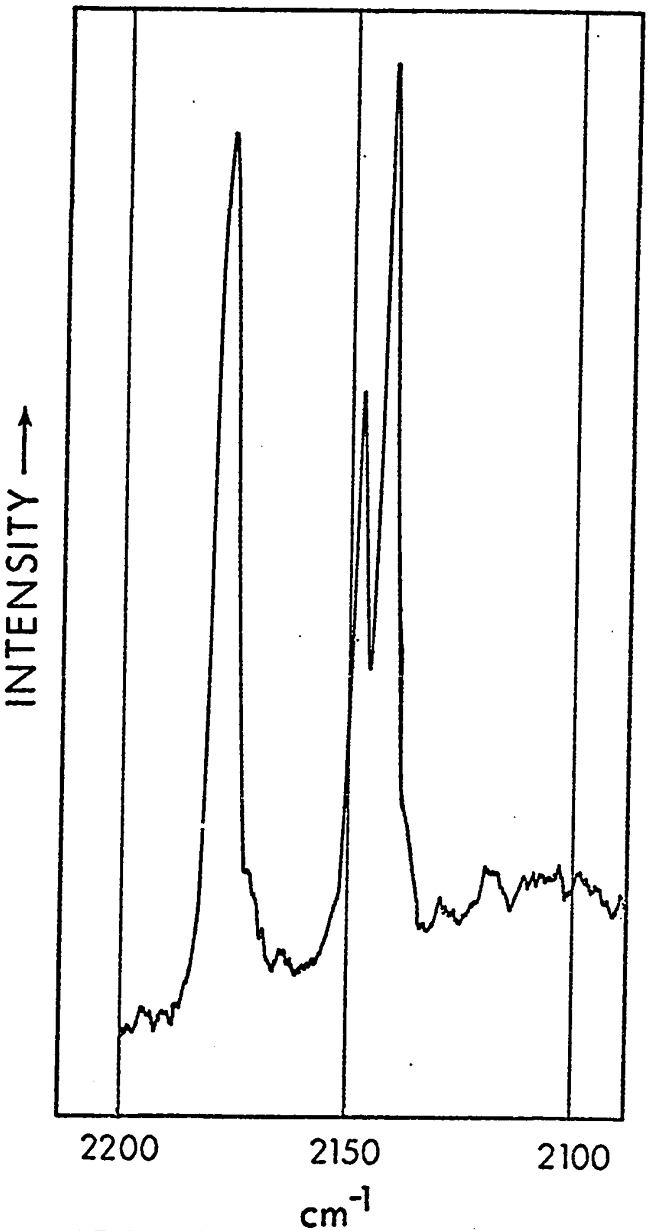


FIGURE 7.5 Raman Spectrum of *trans*-Ru(CO)$_4$(GeCl$_3$)$_2$

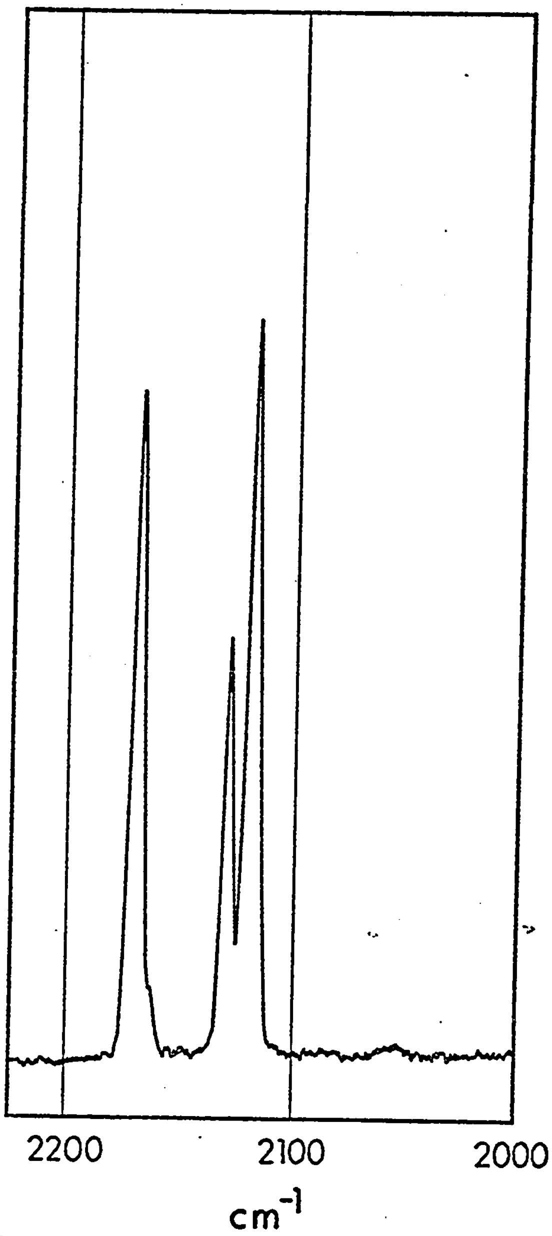


FIGURE 7.6 Raman Spectrum of *trans*-Os(CO)$_4$(SiCl$_3$)$_2$

distinct molecules per unit cell.

The solid state spectra of the *cis*-derivatives investigated did not show (Fig. 7.7 and 7.8) any extra bands that could be attributed to splitting. In fact it was found that one of the four Raman active CO stretches was very weak or not observed.

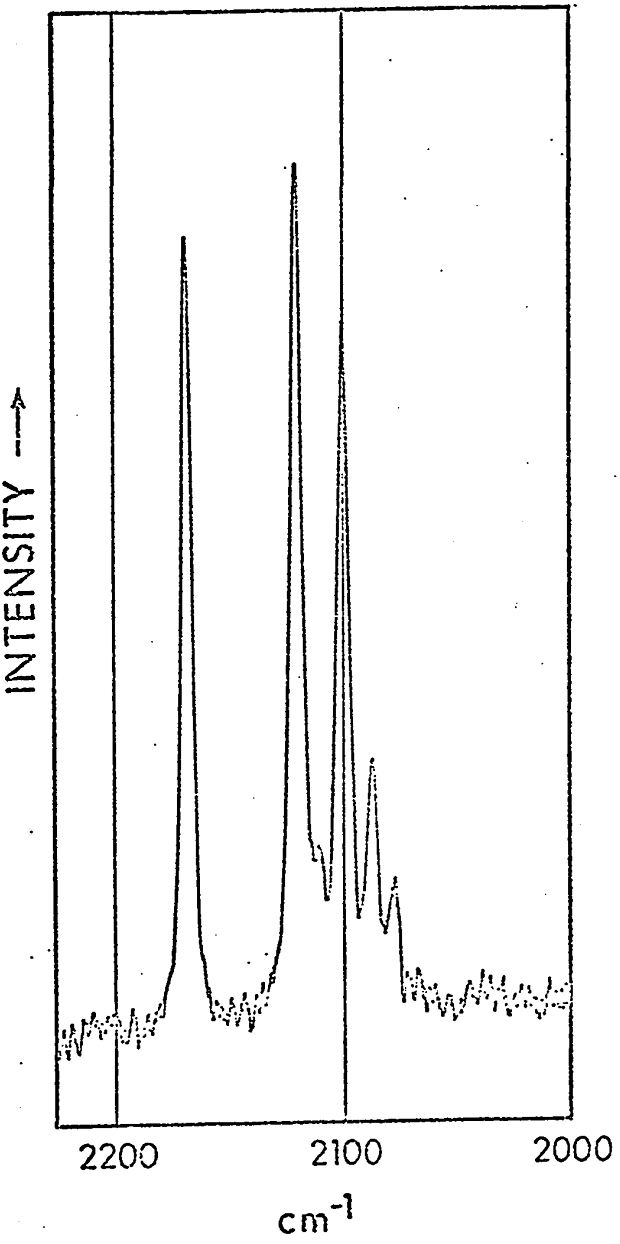


FIGURE 7.7 Raman Spectrum of *cis*-$Os(CO)_4(SiF_3)_2$

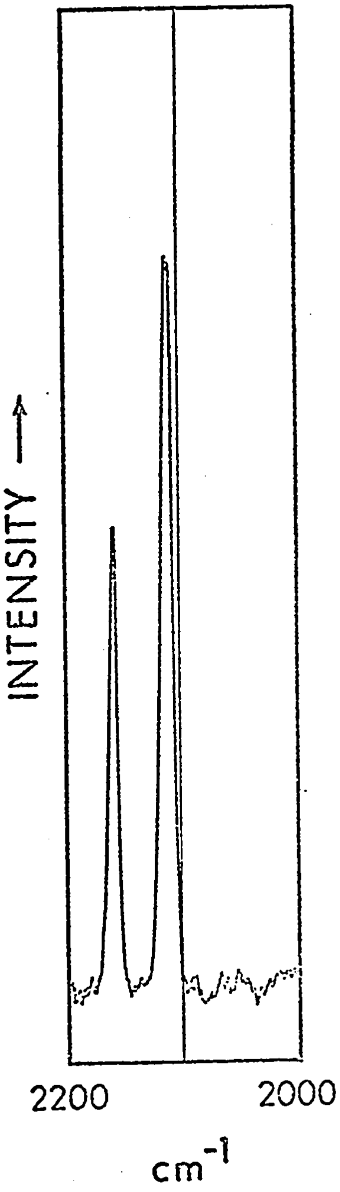


FIGURE 7.8 Raman Spectrum of *cis*-$Ru(CO)_4(SiCl_3)_2$

The Far Infrared Region

The M-X Modes

In this discussion we will consider the *trans*-$M'(CO)_4(MX_3)_2$ as either $L'MX_3$ or $M'(CO)_4L_2$.

Despite mixing of internal coordinates (bond lengths and interbond angles) which may occur in a normal mode of vibration several features of simple compounds - relative atomic masses, bond force constants and molecular symmetry - usually permit one to assign a band as due to mainly one mode of vibration.

The M-X modes of vibration may easily be assigned without any previous knowledge of where these modes usually occur. In the ir spectrum of *trans*-$Ru(CO)_4(GeCl_3)_2$ there is a broad band at 396 cm^{-1} which in the tin analogue is, (Fig 7.9), shifted to 354 cm^{-1} in the tin compound, all the other bands remain approximately constant. On going to *trans*-$Ru(CO)_4(SnBr_3)_2$ this band is further shifted to 253 cm^{-1}. These observations are qualitatively exactly what we should expect for a stretch involving M-X.

Although no resort to the literature is needed in the qualitative assignment of these modes they are quite consistent with reported valid assignments for MX_4, MX_3^-, M_2X_6 and $X_3M-M'(CO)_n$.[70,178,201-206]

Actually two modes of vibration (A_1 and E_1) are expected in this region for the MX_3 entity. However in

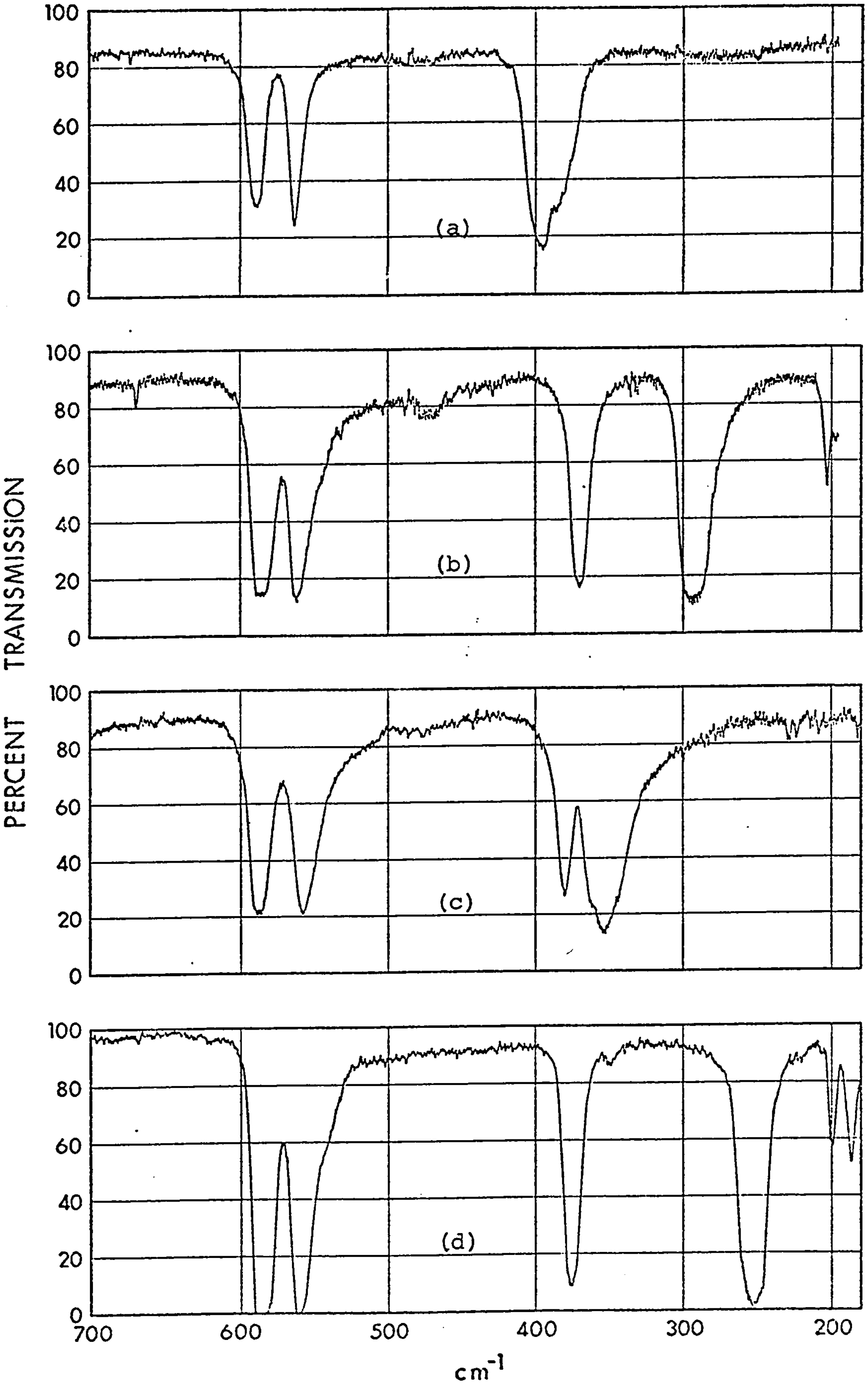
FIGURE 7.9 Far infrared spectra (700-200 cm^{-1})

(a) *trans*-$Ru(CO)_4(GeCl_3)_2$

(b) *trans*-$Ru(CO)_4(GeBr_3)_2$

(c) *trans*-$Ru(CO)_4(SnCl_3)_2$

(d) *trans*-$Ru(CO)_4(SnBr_3)_2$

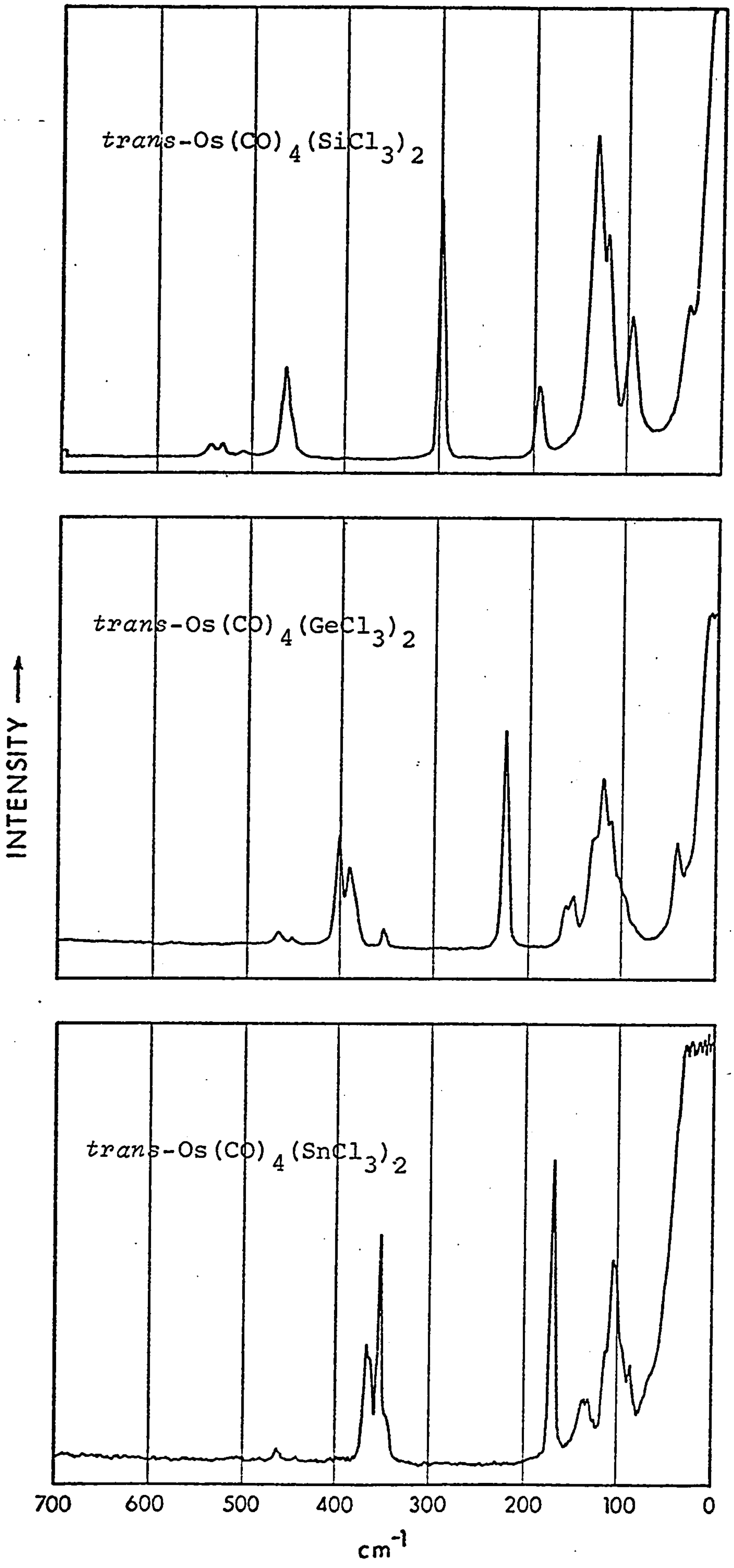

100
80
60
40
20
0
(a)
(b)
(c)
(d)
PERCENT TRANSMISSION
700
600
500
400
300
200
cm^{-1}

other reported cases the bands are close together and often not resolved. In some of the present compounds the band has two components, in others only a single band is observed although it is broad.

These modes are also active in the Raman and as seen (Fig. 7.10) two bands are observed in the same region (see also Table 7.3). The symmetric stretch (A_1) is expected at higher energy.

In some of the Raman spectra the two bands are asymmetric and in some cases split e.g., *trans*-$Os(CO)_4(SnCl_3)_2$. Some of these bands could be M-C stretches that have gained intensity by mixing with the M-X modes or it could be due to the fact that there are two different molecules within the crystal as already discussed. It is probable that only modes involving the peripheral ligands will show this effect since the difference in the two molecules is in their environment.

We also expect [70,178] two MX_3 bands (δMX_3) at much lower frequencies (less than 200 cm^{-1}). In this region skeletal vibrations involving C-M'-C and M-M'-M occur, and these may couple with δ(MCO). This results in many bands in the Raman in this segment of spectra. Infrared spectra in this range, using the IR 11, were very noisy, so that it was impossible to distinguish bands from the background absorption. As this was only a preliminary study no



<u>FIGURE 7.10</u> Solid state Raman spectra

TABLE 7.3

Solid-State IR and Raman Data Below 700 cm^{-1} on Compounds of the Type *trans*-$\mathrm{M'(CO)_4(MCl_3)_2}$

Compound	δ(MCO)		ν(MC)		ν(MX)		ν(M'M)		Other Modes	
	IR	R	IR	R	IR	R	IR	R	IR	RAMAN
trans-$\mathrm{M'(CO)_4(MX_3)_2}$	A_{2u}, E_u	A_{2g}, B_{2g}, E_g	E_u	A_1, B_1			(as) A_{2u}	(sym) A_{1g}		
$\mathrm{Fe(CO)_4(GeCl_3)_2}$	625s 612s	454w	455s		400s 383s	383m 369s		205vs		146m, 141m, 118m, 96vs, 75w, 79w,
$\mathrm{Ru(CO)_4(SiCl_3)_2}$	603s 576s	432m	390m		533s	541w 527w	488s 479s 294w	293vs	208w(δMX)	191m(δMX) 131vs, 119s, 95m, 38w
$\mathrm{Ru(CO)_4(GeCl_3)_2}$	589s 563s	440w, 430w	386s,br		396s	397m 386m 380sh	248vw,	220vs	168m 130w 108w 75v br	158w, 150w, 117s, 108m, 99w, 92w, 39w
$\mathrm{Ru(CO)_4(GoBr_3)_2}$	585s 562s	420w	370s		294s,br	291m 233m	203m	173vvs		116w, 103m, 87m, 74s, 69s, 64m, 33m,
$\mathrm{Ru(CO)_4(SnCl_3)_2}$	588s 558s	424w	380s		361sh 354s,br	361m 349m	229vw	164vs	144m 120m 103m 91w 55v br	144w, 139w, 101s, 82w, 65w, 28m
$\mathrm{Ru(CO)_4(SnBr_3)_2}$	588s 562s		376s		253s	242(?)	200m(as) 188m	133vs		24? 62?
$\mathrm{Os(CO)_4(SiCl_3)_2}$	608s 582s	463w	387m		538s	544 532	488(as) 291m(sym)	298vs	210w(δMX)	195m(δMX) 134vs, 122s, 95m, 35w
$\mathrm{Os(CO)_4(GeCl_3)_2}$	598s 567s	467w 450w	378s	353w	403sh 397s 390sh	400m 390m	235w	225vs		160w, 152w, 130m, 121s 112m, 105sh, 42m
$\mathrm{Os(CO)_4(SnCl_3)_2}$	602s 568s	462vw	385s		362sh 355s 348sh	366m 362m 355s 347sh	203w	170vs		139m, 132m, 113m 103s 87w, 30w

attempt was made to assign this lower region.

A band observed in the Raman spectra of *trans*-$Ru(CO)_4(SiCl_3)_2$ and *trans*-$Os(CO)_4(SiCl_3)_2$ at approximately 190 cm^{-1} is assigned to the symmetric $\delta(SiCl_3)$ deformation. This is in agreement with the assignment of a band at 200 cm^{-1} found in $Cl_3SiCo(CO)_4$.[202]

If we neglect the symmetry of the MX_3 (L) group the expected modes of vibration of *trans*-$M'(CO)_4L_2$ are given in Table 7. along with whether they are expected to be active in the Raman or infrared.

The MCO Bends and M-C Stretches

Assignment of ν(M-C) (metal carbon stretch) and δ(MCO) (MCO bend) in substituted octahedral carbonyls have been made mainly by analogy with binary carbonyls,[207] and the operative ranges are

ν(M-C)	428 - 366 cm^{-1}
δ(MCO)	787 - 468 cm^{-1}

The above ranges may be applied to the present compounds. Caution must be employed, however, because of the nature of these compounds. The fact that these compounds have a CO stretch in the neighbourhood of 2180 cm^{-1} would suggest [178] that the corresponding M-C stretches would be very low - possibly lower than 366 cm^{-1}.

What is more important is that the MCO bends come at higher energy than the M-C stretches. This is in agreement with the far infrared spectra of the *trans*-$M'(CO)_4(MX_3)_2$ derivatives, two strong bands are observed in the region 550-625 cm^{-1} and one at approximately 380 cm^{-1}. These results agree with the predictions made by group theory (Table 7.4).

The assignment of ν(M-C) to the 455 cm^{-1} absorption in *trans*-$Fe(CO)_4(GeCl_3)_2$ is consistent with the lower CO stretches observed for this compound (Table 7.2).

If the assignment of the M-C mode is correct an interesting point arises. Normally it is found that the highest ν(M-C) frequencies are associated with the lowest ν(CO) values and this is taken as one of the best pieces of evidence for the generally accepted dπ-pπ bonding scheme.

However, in *trans*- $Ru(CO)_4(GeCl_3)_2$ (ν(CO) = 2111 cm^{-1}, CH_2Cl_2 solution) the M-C stretch comes at 386 cm^{-1} whereas in *trans*-$Ru(CO)_4(SnCl_3)_2$ (ν(CO) = 2105 cm^{-1}, CH_2Cl_2 solution) this mode is at 380 cm^{-1}. These observations imply that in these compounds the higher the CO stretching frequency the stronger the M-C bond. Although this is contrary to what is found for most carbonyl compounds it is consistent with the results of Chapter 4 which showed that the CO group with the lowest stretching force constant was the most labile.

For the corresponding osmium compounds the situation

TABLE 7.4

Number and Species of Expected C-O, M-C, M-C-O and M-L Bands for *trans*-M'$(CO)_4L_2$ (D_{4h} Symmetry)

Type of Mode	Symmetry Label	Raman or Infrared Activity
M-C (C-O) stretching	A_{1g}	R
M-C (C-O) stretching	B_{1g}	R
M-C (C-O) stretching	E_u	IR
M-C-O bending	A_{2g}	R
M-C-O bending	B_{2g}	R
M-C-O bending	E_g	R
M-C-O bending	A_{2u}	IR
M-C-O bending	B_{2u}	-
M-C-O bending	E_u	IR
M-L stretching	A_{1g}	R
M-L stretching	A_{2u}	IR

is reversed, the ν(CO) of the germanium compound is some 5 cm^{-1} higher than in the tin compound yet the ν(M-C) of *trans*-$Os(CO)_4(GeCl_3)_2$ is 7 cm^{-1} lower than the corresponding stretch in the tin derivative.

These results illustrate that there are two opposing effects (σ- and π-effects) determining the CO stretching frequency. It is only in the present compounds where the π-contribution is small that the σ effect is noticeable.

In the Raman δ(MCO) and δ(MC) are very weak and only seem to appear when they can couple with M-X vibrations.

The Metal-Metal Bond Stretches

For *trans*-$M'(CO)_4(MX_3)_2$ we expect the symmetric M'-M stretch to be Raman active and the asymmetric stretch to be infrared active. Previous studies [206,208] have shown that the metal-metal stretch is often the most intense band in the spectrum. Indeed, high Raman intensity appears to be a characteristic of ν(M'-M), owing to the large change in polarizability when a covalent bond between two atoms of high atomic number is deformed.[208]

In contrast it is found that ν(M'-M) proves difficult to detect by far infrared spectroscopy, and is frequently so weak as to escape observation unless coupling with other frequencies such as metal halogen is extensive.[208]

This agrees with what is observed in the present spectra. The most intense band in the Raman spectra shows the expected shift on changing the group IV atom (Fig. 7. 10); it is found in the same region found for other metal-metal stretches.[201,202,206,208] Further in the case of *trans*-$Ru(CO)_4(GeCl_3)_2$ the band at 220 cm^{-1} was of sufficient intensity to observe it in solution where it was found to be polarized, in agreement with this being a totally symmetric mode.[142]

In the infrared the asymmetric stretch is expected at higher frequencies than the symmetric stretch.[202,206] In agreement with other work it is very weak in most cases (this is illustrated in Fig. 7.11 for *trans*-$Ru(CO)_4(GeCl_3)_2$ where only in a concentrated mull spectrum is the mode detected. However, in the cases where the M-X vibrations are close to the M'-M stretch they can couple and the metal-metal bond gains some intensity e.g., *trans*-$Ru(CO)_4(MBr_3)_2$, M = Ge or Sn (Fig. 7.9).

In some cases the infrared forbidden symmetric metal-metal stretch is also observed. This is probably because the true symmetry of the molecule is not D_{4h} but only C_{2v} and it might be expected that the M'-M bond would be most sensitive to this.

Splitting of the symmetric stretch is also observed in some of the derivatives, this again may result from the fact that there are two distinct molecules in the unit cell.

On going from Fe-Ge to Ru-Ge to Os-Ge we would

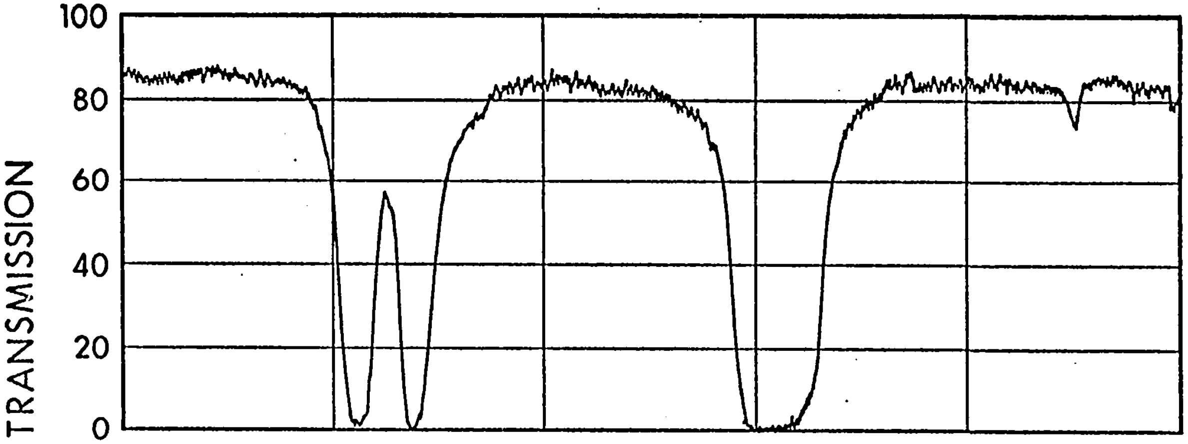


FIGURE 7.11 Far Infrared Spectrum of *trans*-$Ru(CO)_4(GeCl_3)_2$

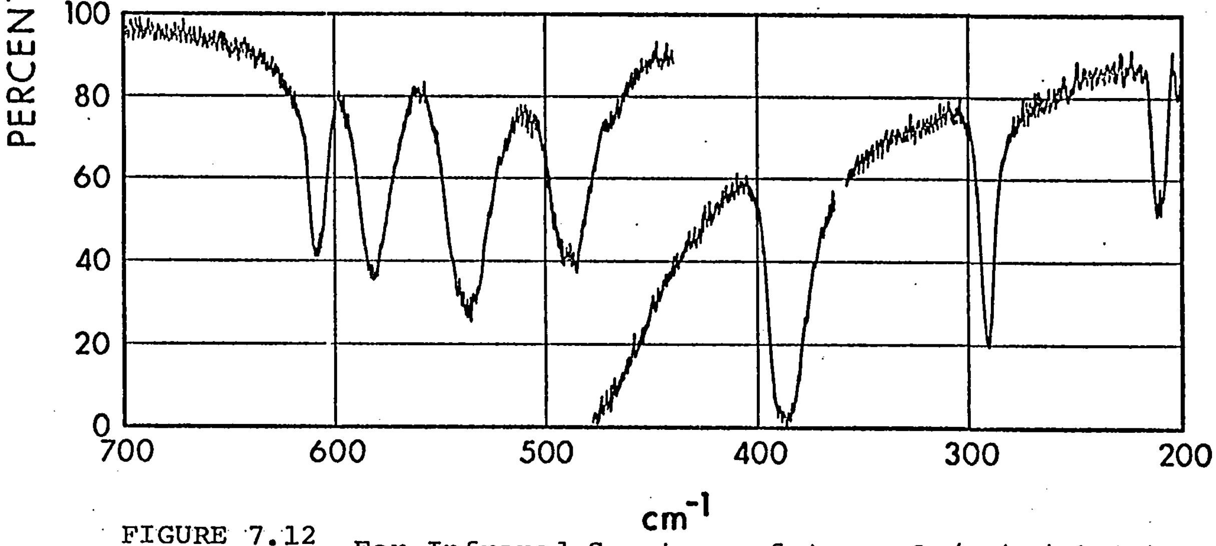


FIGURE 7.12 Far Infrared Spectrum of *trans*-$Os(CO)_4(SiCl_3)_2$

expect a progressive decrease in the stretching frequency due to the increase in mass of the transition metal; consider for example Os-M and M-Cl (M = Si, Ge and Sn). However, as can be seen in Fig. 7.13 the reverse is true. This may be explained by the fact that on going down the periodic table the M'—M bond becomes stronger. This agrees with the ideas put forward in Chapter 3 that there is more π-bonding in the metal-metal bond on going from Fe to Ru to Os.

That the difference between the asymmetric and symmetric stretches is small may mean considerable π-bonding in these M-M'-M systems.

Assignment of the Modes in the Infrared Spectrum of *trans*-$Os(CO)_4(SiCl_3)_2$

As an illustration of the assignment of the infrared spectra, the case of *trans*-$Os(CO)_4(SiCl_3)_2$ is given here (Fig. 7.12).

From the CO stretches in this compound the δ(MCO) and ν(M-C) modes are not expected to be too different from other members of the series. Note ν(M-C) is rather insensitive to the nature of MX_3 group. For this region the absorptions at 608 and 582 cm^{-1} are assigned to δ(MCO) and that at 378 cm^{-1} to ν(M-C).

The absorption at 538 cm^{-1} is assigned to ν(M-X) since it has its counterpart in the Raman, as expected, and since it is in the region found for $\nu(SiCl_3)$.[202]

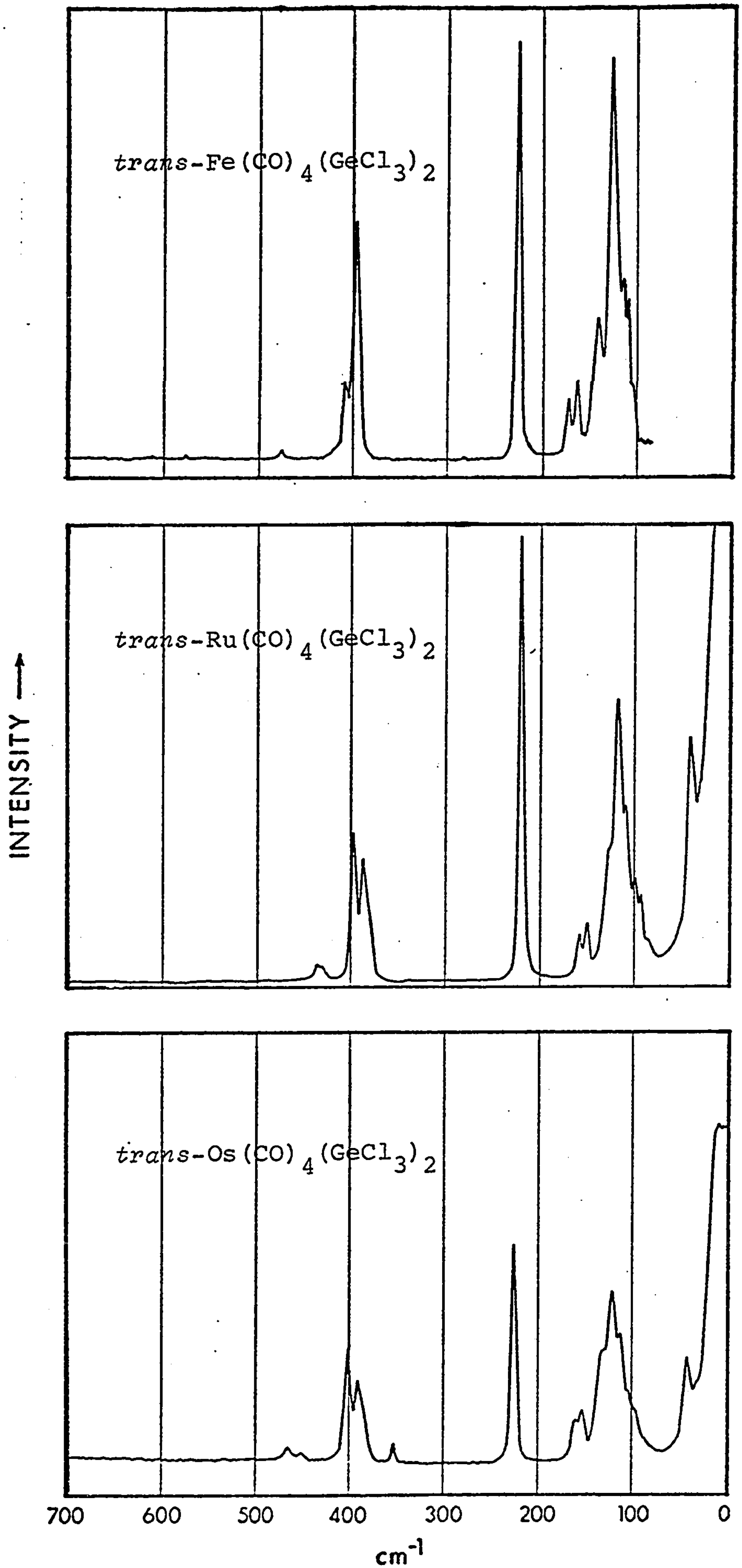


FIGURE 7.13 Solid State Raman Spectra

The band at 291 cm^{-1} is attributed to symmetric ν(Os-Si) since there is an intense band at this value in the Raman. The remaining band above 250 cm^{-1} is reasonably assigned to the asymmetric stretch since it is the expected region and occurs at higher energy than the band at 291 cm^{-1}.

The remaining mode at 210 cm^{-1} is assigned to $SiCl_3$ deformation.[202]

Raman Spectra for Other Compounds Containing a M'-M Bond

As seen from Table 7.5 the metal-metal stretch appears as a strong band in other types of derivatives synthesized in this work.

In the case of $Ru_3(CO)_{12}SnCl_4$ and $Os_3(CO)_{12}SnCl_4$ only bands at 339 and 365 cm^{-1} can be assigned to ν(M-M): there are no bands in the region 150-300 cm^{-1} where normal M'-Sn bonds occur. The bonds below 150 cm^{-1} can be assigned to M'-M' stretches (M' = Ru or Os).[209]

The region in the neighbourhood of 350 cm^{-1} is also the area where ν(Sn-Cl) modes occur, however, these bands are usually weak.

If $M'_3(CO)_{12}SnCl_4$ had a linear structure with a terminal M'-Sn bond we might have expected an absorption in the region 150-225 cm^{-1}. It is difficult to say where ν(M'-Sn) would come if it had the adduct structure. It is possible that the effective mass of $M'_3(CO)_{12}$ would be lower than a direct bond to M' thus causing a rise in frequency.

TABLE 7. 5

Raman Spectra of Some Compounds Containing a M'-M Bond

Compound	Raman Spectrum			
cis-$Ru(CO)_4(SiF_3)_2$	2167s,	2128s,	2112s,	2093w[b]
	467s,	357m,	330m,	318m
cis-$Ru(CO)_4(SiCl_3)_2$	2158m,	2109s,	2112s	
	550w,	425m,	360m,	298vvs[a]
	205m,	168vvs,		
cis-$Os(CO)_4(SiF_3)_2$	2168s,	2120s,	2100s,	2088m,
	2077w			
	478s,	395w,	352s[a],	333w,
	227m,	220m,	196m,	110vs
$(C_6H_6)Ru(CO)(GeCl_3)_2$	2046w,			
	395m,	375w,	331w,	293vs[a]
	175m,	150s,	135m	
$Ru_2(CO)_5SnCl_6$	2149w,	2095w,	2077vw,	2027w
	470w,	439w,	343m,	332w
	313w,	277w,	200vs[a]	147w,
	128w,			
$Ru_3(CO)_{12}SnCl_4$	2171w,	2124m,	2081w,	2052w,
	2036w			
	598w,	546s,	440m,	434m,
	339s,	305vw,	140m,	122m
$Os_3(CO)_{12}SnCl_4$	578w,	495w,	485w,	365vvs,
	130s,	85sh		

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a = assigned to ν(M-M)

b = poor spectrum (decomposition in beam?)

Conclusions

Even the superficial study reported here of the far infrared and Raman spectra of these metal-metal bonded systems have revealed several interesting features. It would therefore appear that this area of research warrants a more detailed investigation.

EXPERIMENTAL

The syntheses of the compounds studied here have been described in Chapters 2 and 3.

Infrared spectra in the region 800-180 cm^{-1} were run as nujol mulls using CsI optics on a Beckman IR 11 instrument.

Raman spectra were run on solid samples which had been packed into capillary tubes. The spectra were calibrated using the band of carbon tetrachloride at 461.5 cm^{-1}. The instrument used was a Spex Laser Raman.

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