DERIVATIVES OF *CIS*-TETRACARBONYL *BIS* (TRICHLOROSILYL) RUTHENIUM

by

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ABSTRACT

The compound *cis*-$Ru(CO)_4(SiCl_3)_2$ is unusual in metal carbonyl chemistry in that the carbonyl groups *trans* to the $SiCl_3$ substituents undergo facile substitution at room temperature. This has been illustrated with the preparation of a series of new compounds in which these carbonyl groups have been substituted by a variety of monodentate (L) and bidentate (L-L) ligands.

The bidentate ligands used included dienes and sulfur, phosphorus, arsenic chelates. Besides complexes of the type $(L\text{-}L)Ru(CO)_2(SiCl_3)_2$ it was possible with the bidentate ligands $Ph_2E(CH_2)_2EPh_2$ (E = P, As) to isolate the bridged complexes of the type $(Cl_3Si)_2(OC)_3Ru(L\text{-}L)Ru(CO)_3(SiCl_3)_2$.

With monodentate ligands of the type ER_3 (E = P, As, Sb; R = alkyl, aryl and F), both monosubstituted $(R_3E)Ru(CO)_3(SiCl_3)_2$ and disubstituted $(R_3E)_2Ru(CO)_2(SiCl_3)_2$ complexes were obtained. The complexes were characterized by elemental analysis, i.r., n.m.r. (including ^{31}P) and mass spectroscopy. The *bis* substituted molecules could only be prepared when the cone angle of ER_3 was small. (The cone angle is the solid angle subtended by the ligand as viewed from the metal atom.)

It was also possible to isolate the mono and disubstituted derivatives, $LRu(CO)_3(SiCl_3)_2$ and $L_2Ru(CO)_2(SiCl_3)_2$, where L = TeR_2 and Te_2R_2. The ditellurides Te_2R_2 also formed the bridged complexes $(Cl_3Si)_2(OC)_3Ru(Te_2R_2)Ru(CO)_3(SiCl_3)_2$.

Tellurium derivatives of transition metals are rare, especially those containing Te-Te bonds. Tellurium n.m.r. and Mössbauer spectral data of the tellurium derivatives are also discussed.

The compounds described here provide examples of ***trans*** substitution, which is unusual in metal carbonyl chemistry.

To

My husband

and

my mother

for

their

understanding and encouragement

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LIST OF ABBREVIATIONS

bipy - bipyridine

Cy - cyclohexyl

DiArs - o-phenylene*bis*(dimethylarsine)

Diphos - tetraphenyldiphosphinoethane

ER_3 - triorgano or trihalo group Vb ligand

ETPB - 4-ethyl-2,6,7,trioxa-1-phosphabicyclo[2.2.2]octane

Et - ethyl, C_2H_5

L - 2 electron donor ligand

L-L - bidentate ligand

M - metal

Me - methyl, CH_3

OEt - ethoxy, OC_2H_5

OMe - methoxy, OCH_3

Ph - phenyl, C_6H_5

R - alkyl

X - halide, F^-, Cl^-, Br^-, I^-

CHAPTER 1

SILICON DERIVATIVES OF TRANSITION METALS: INTRODUCTION AND LITERATURE REVIEW

1.1 GENERAL SURVEY

Many organometallic complexes are known to contain transition metals covalently linked to Group IV b metals (silicon, germanium, tin and lead). The first compound with a silicon-transition metal bond to be synthesized was $Me_3SiFe(CO)_2(\eta-C_5H_5)$[1], in 1956. Since then numerous such complexes have been made. In this chapter, the preparative routes and some features of interest of selected compounds in this class will be outlined.

1.1.1 SYNTHESIS OF TRANSITION METAL-SILICON BONDED COMPLEXES

The reaction of a transition metal carbonyl anion with the appropriate silicon halide has been used to synthesize several compounds, such as $H_3SiCo(CO)_4$ [2], $(H_3Si)_2Fe(CO)_4$ [3] and $Me_3SiFe(CO)_2(\eta-C_5H_5)$[1], i.e.,

$$H_3SiI + Co(CO)_4^- \longrightarrow H_3SiCo(CO)_4 + I^-$$

$$2H_3SiI + Fe(CO)_4^{2-} \longrightarrow (H_3Si)_2Fe(CO)_4 + 2I^-$$

$$Me_3SiCl + (\eta-C_5H_5)Fe(CO)_2^- \longrightarrow Me_3SiFe(CO)_2(\eta-C_5H_5) + Cl^-$$

In the same way, a transition metal halide complex may be reacted with the lithium or sodium derivative of an alkyl or aryl silicon compound to obtain the required product[4,5]:

$$Ph_3SiLi + (\eta\text{-}C_5H_5)_2ZrCl_2 \longrightarrow (Ph_3Si)Zr(Cl)(\eta\text{-}C_5H_5)_2 + LiCl$$

$$2Ph_2MeSiLi + (PhMe_2P)_2PtCl_2 \longrightarrow (Ph_2MeSi)_2Pt(PMe_2Ph)_2 + 2LiCl$$

The reaction involving the oxidative addition of a silane to a transition metal complex has been a major route to the synthesis of complexes containing silicon-transition metal bonds. These include complexes such as $[(EtO)_3Si]Ir(H)(Cl)(CO)(PPh_3)_2$ [6], $(Cl_3Si)_2Pt(PPh_3)_2$ [7], $(Ph_2HSi)_2Pt(diphos)$ [7], $(p\text{-}FC_6H_4)_3SiPt(H)(PPh_3)_2$ [7], $(MeCl_2Si)Rh(H)(Cl)(PPh_3)_2$ [8] and $Cl_3SiRh(H)(Br)(AsPh_3)_2$ [9].

$$(EtO)_3SiH + (Ph_3P)_2Ir(CO)Cl \longrightarrow (EtO)_3SiIr(H)(Cl)(CO)(PPh_3)_2$$

$$2Cl_3SiH + (Ph_3P)_4Pt \longrightarrow (Cl_3Si)_2Pt(PPh_3)_2 + H_2 + 2Ph_3P$$

$$2Ph_2SiH_2 + (diphos)_2Pt \longrightarrow (Ph_2HSi)_2Pt(diphos) + H_2 + diphos$$

$$(p\text{-}FC_6H_4)_3SiH + (Ph_3P)_4Pt \longrightarrow (p\text{-}FC_6H_4)_3SiPt(H)(PPh_3)_2 + 2Ph_3P$$

$$MeCl_2SiH + (Ph_3P)_3RhCl \longrightarrow (MeCl_2Si)Rh(H)(Cl)(PPh_3)_2 + Ph_3P$$

$$Cl_3SiH + (Ph_3As)_3RhBr \longrightarrow (Cl_3Si)Rh(H)(Br)(AsPh_3)_2 + Ph_3As$$

Silyl derivatives of transition metal complexes, in addition to being an important new class of organometallic compounds, were found to be intermediates in catalytic hydrosilation. In fact, the similarities of the reactions of a silane and hydrogen with transition metal complexes, coupled with the ability of octacarbonyldicobalt to catalyze the hydroformylation of olefins, originally suggested an investigation of the silicon/octacarbonyldicobalt system for potential catalytic hydrosilation of olefins. The catalytic effect observed[10] was consistent with a two step reaction of the silane with $Co_2(CO)_8$ giving $R_3SiCo(CO)_4$ and H_2, as shown below.

$$R_3SiH + Co_2(CO)_8 \longrightarrow R_3SiCo(CO)_4 + HCo(CO)_4$$

$$R_3SiH + HCo(CO)_4 \longrightarrow R_3SiCo(CO)_4 + H_2$$

A similar type of reaction has been observed with $Fe_3(CO)_{12}$[11] and $Mn_2(CO)_{10}$[12]. The major product with $Fe_3(CO)_{12}$ was found to be $(R_3Si)_2Fe(CO)_4$.

$$6Et_3SiH + Fe_3(CO)_{12} \longrightarrow 3(Et_3Si)_2Fe(CO)_4 + 3H_2$$

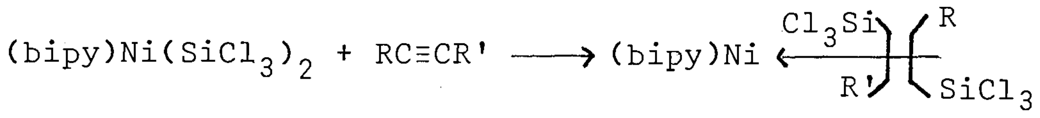
$$2\,Ph_3SiH + Mn_2(CO)_{10} \longrightarrow 2(Ph_3Si)Mn(CO)_5 + H_2$$

The hydridosilyl complexes *cis*-$(R_3Si)Pt(H)(PMe_2Ph)_2$, (R = Ph or *p*-FC_6H_4) have been synthesized[13] by the reactions of Ph_3SiH or $(p\text{-}FC_6H_4)_3SiH$ with *cis*-$PtMe_2(PMe_2Ph)_2$. The *bis*-(silyl) complexes *cis*-$(Ph_2MeSi)_2Pt(PMe_2Ph)_2$ and $(Ph_2HSi)_2Pt(PMe_2Ph)_2$ have been synthesized in a similar manner. The reaction between $PtL_2(C_2H_4)$ ($L = PPh_3$) and a variety of organosilicon hydrides, R_3SiH, has given[14] the complexes $R_3SiPt(H)L_2$ where $R_3Si = Ph_3Si$, Ph_2MeSi, Ph_2HSi, $PhMe(CH_2{=}CH)Si$, Et_3Si, $(EtO)_3Si$ and $(Me_3SiO)_2MeSi$. The hydride $MeCl_2SiH$, however, gives the *bis*-(silyl) complex $(ClMe_2Si)_2PtL_2$.

The hydrosilation reaction has also been used[15] for the synthesis of silicon heterocyclic compounds. The chloroplatinic acid used as the catalyst in this process is thought to form a cyclic intermediate, by reacting with alkyl silane and the unsaturated hydrocarbon (olefin or diene) according to the scheme given in Fig. 1. It is interesting to note that most of the compounds discussed so far have been observed as intermediates in the catalytic hydrosilation of olefins.

The possibility that hydrosilation of acetylenes may involve the insertion of an acetylene into a metal-silicon bond was suggested by the work of Kiso, Tamao and Kumada[16]. They prepared the complex $(bipy)Ni(SiCl_3)_2$ from $HSiCl_3$ and $(bipy)_2Ni$ and reacted it with an acetylene to give an olefinic product:

$$Ni(bipy)_2 + 2HSiCl_3 \longrightarrow (bipy)Ni(SiCl_3)_2 + H_2$$

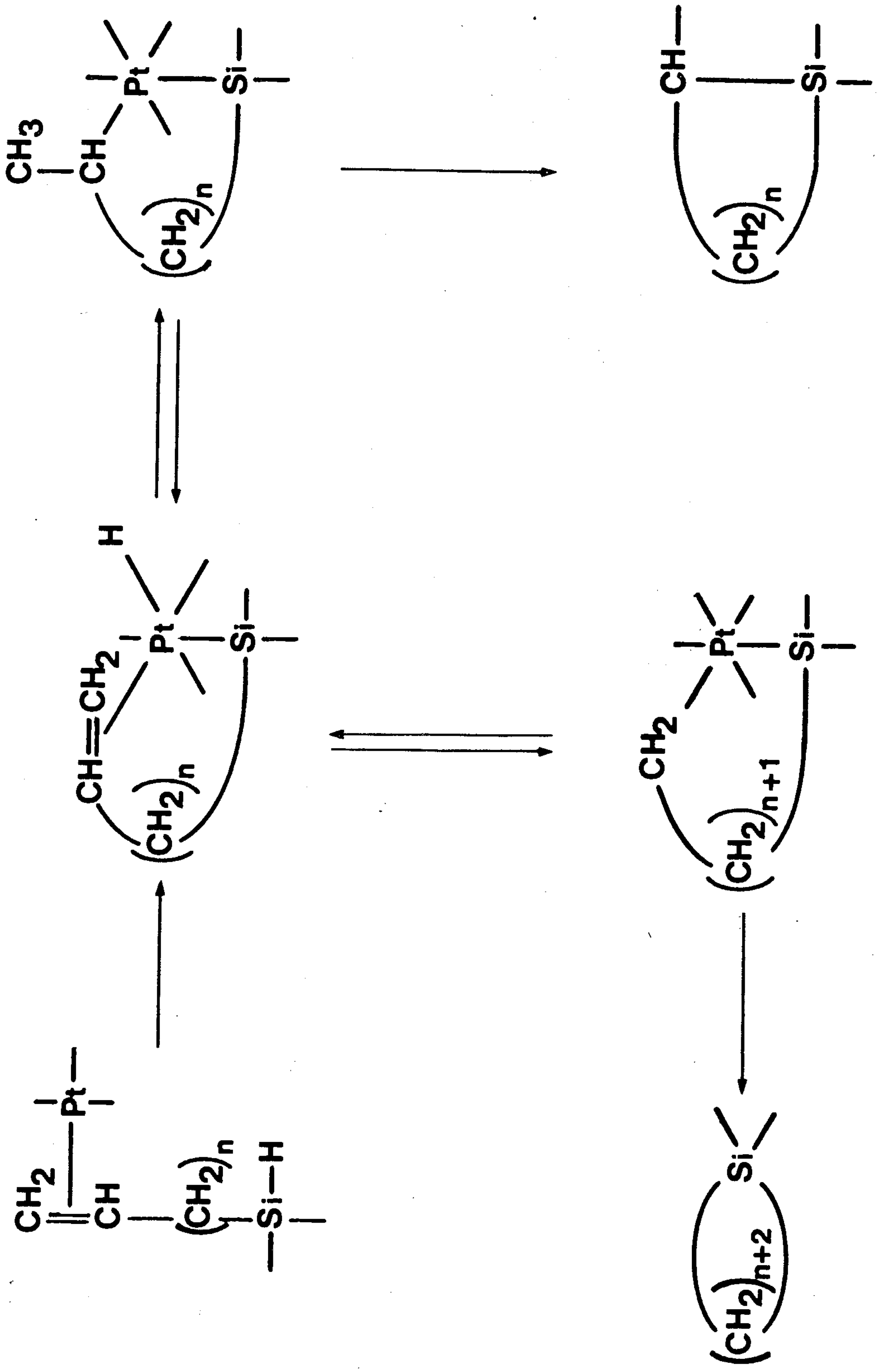


$$(bipy)Ni(SiCl_3)_2 + RC\equiv CR' \longrightarrow (bipy)Ni \leftarrow \begin{matrix} Cl_3Si & & R \\ & C{=}C & \\ R' & & SiCl_3 \end{matrix}$$

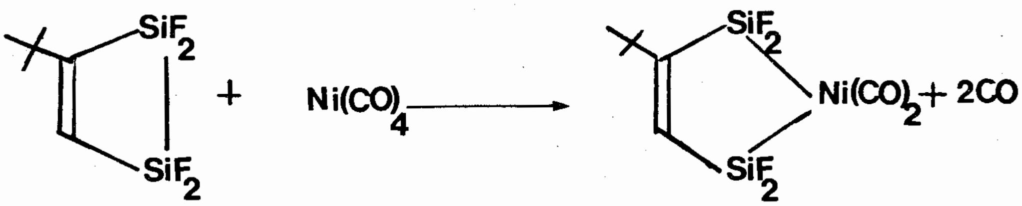
A closely related di-silylation of an acetylene has been achieved by an oxidative addition of an Si-Si bond to Ni(0):

Figure 1

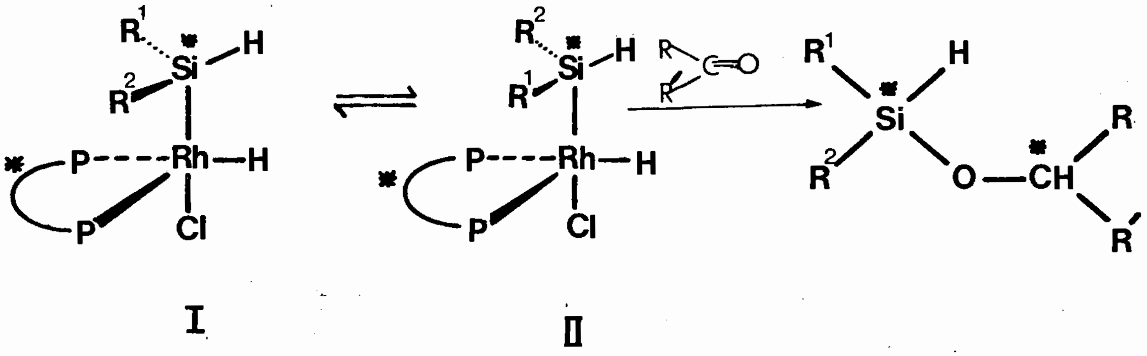
The Proposed Mechanism for the Formation Of Silicon Heterocyclic Compounds Via Platinum-Silyl Intermediates



CH2=CH
(CH2)n
Si—H
Pt
H
CH=CH2
CH3
CH
CH2
(CH2)n+1
Si
(CH2)n+2



Optically active alkoxysilanes have been synthesized by asymmetric hydrosilation of ketones in the presence of a chiral phosphine-rhodium complex. The oxidative addition of the silane to the chiral rhodium complex leads to two complexes, I and II, which can react at the two faces (α and β) of the ketone, producing a mixture of optically active alkoxy silanes.



1.1.2 PHYSICAL PROPERTIES

The M-Si bond lengths [M = transition metal] as determined by X-ray crystallography, in most of the cases are found to be shorter than the sum of the covalent radii of the component atoms, illustrating the multiple nature of the bonds. For example, a Si-Co bond length of 2.254 Å has been determined[19] from an X-ray crystallographic study of $Cl_3SiCo(CO)_4$ which is

0.12 Å less than the minimum calculated distance for a single covalent Si-Co bond of 2.37 Å. Similarly, a Si-Mn bond length of 2.50 Å has been found in $Me_3SiMn(CO)_5$, which is 0.13 Å less than the amount calculated on the basis of covalent radii.

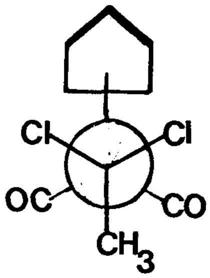
The π-acceptor properties of the $SiCl_3$ group, when bonded to a transition metal, is believed[20,21] to be comparable with that of strong π-acceptor $SnCl_3$[22] and this, presumably, applies to $GeCl_3$[23] as well. The greater stability of these Group IV b compounds, compared with their carbon analogues, has been attributed to the presence of double bond character in the Group IV b-transition metal bond.

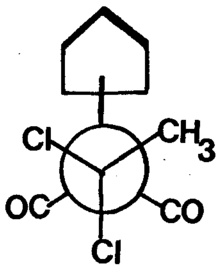
Such dπ-dπ bonding between a transition metal and a Group IV b element might be expected to affect the extent of π-bonding between the transition metal and the other associated ligands. Infrared studies of complexes containing carbonyl groups have provided supporting evidence[24,25] for partial dπ-dπ bonding in the Group IV b-transition metal bond.

On examining the structure of the silicon-transition metal bonded compounds, it becomes apparent that, in most cases, the "transition metal portion" is derived from the corresponding metal carbonyl or a derivative thereof. As such, these compounds contain carbonyl groups and their infrared spectra become useful in assigning a particular configuration for the molecules. For example, the compounds $(H_3Si)_2Fe(CO)_4$ and $(Et_3Si)_2Fe(CO)_4$ show four infrared bands in the carbonyl region which suggest octahedral sturctures, with the R_3Si groups ($R = H$ or alkyl) in the *cis* configuration. On the other hand,

$(Cl_3Si)_2Ru(CO)_4$ has been isolated in both the *cis* and the *trans* forms, with the latter having only a single strong band in the carbonyl region. It could be easily distinguished from the *cis* isomer, which shows a four band infrared spectrum.

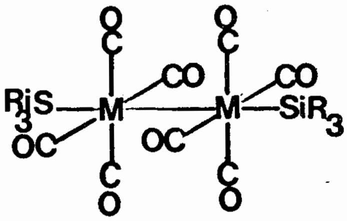
Infrared spectroscopy can also be useful in detecting the existence of conformational isomers. The compounds $Me_3SiFe(CO)_2(\eta\text{-}C_5H_5)$ and $Cl_3SiFe(CO)_2(\eta\text{-}C_5H_5)$ show two carbonyl bands, as expected, whereas $(MeCl_2Si)Fe(CO)_2(\eta\text{-}C_5H_5)$ exhibits four bands. To explain this, the existence of two conformational isomers (shown below) has been suggested.



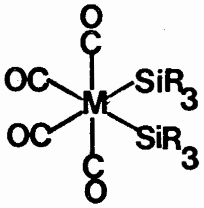


1.2 REACTIONS INVOLVING ORGANOSILANES AND THE IRON TRIAD CARBONYLS

A number of silicon derivatives of the iron-triad carbonyls have been reported[26,27]. Triorganosilanes [e.g., Me_3SiH, Et_3SiH] react with the dodecacarbonyls of ruthenium and osmium, giving a wide variety of products depending on the conditions. The main product at temperatures around 80° C is $[M(CO)_4SiR_3]_2$ [M = Ru or Os, R = alkyl] (I). Ultraviolet irradiation of the same reactants gives I as the major product, but, in addition, the mononuclear complex $M(CO)_4(SiR_3)_2$ (II) is also produced in very low yield (10%). Both I and II are



I

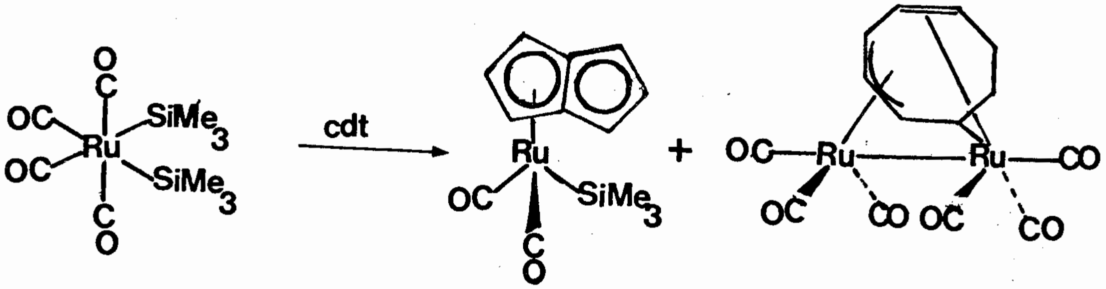


II

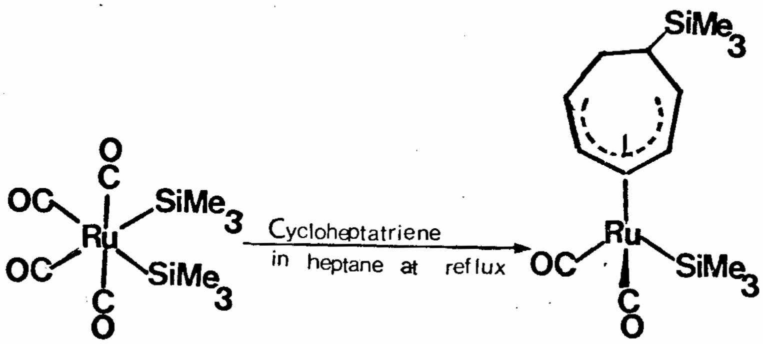
found to be relatively stable in air. When either of them contains chlorine the stability in air is considerably reduced[28], as is the solubility in hydrocarbon solvents.

Treatment of $Os_3(CO)_{12}$ with R_3SiH in hexane, either at 140° C or under prolonged u.v. irradiation, has been shown to produce[29,30] $Os(CO)_4(H)SiR_3$ in addition to products of the types I and II mentioned above. The analogous ruthenium derivative, $Ru(CO)_4(H)(SiR_3)$, has not been isolated, although it has been postulated as an intermediate in the formation of $Ru(CO)_4(SiR_3)_2$ and $[Ru(CO)_4SiMe_3]_2$. Mixed derivatives such as $Me_3SiRu(CO)_4GeBu_3$ and $Me_3SiRu(CO)_4SnMe_3$ have been prepared by the reaction of the anion $[Me_3SiRu(CO)_4]^-$ with the organometal halides Bu_3GeCl and Me_3SnCl respectively.

Reactions of cyclic polyolefins with organosilyl and germyl-(carbonyl)ruthenium compounds, at reflux temperatures in inert solvents, have been found to produce hydrocarbon complexes of various structural types, many of which were fluxional. Cyclododecatriene (cdt) has been shown[31] to undergo a ring contraction on reaction with $Ru(CO)_4(SiMe_3)_2$ forming the tetrahydropentalenyl complex $(C_8H_9)Ru(CO)_2(SiMe_3)$ and the fluxional complex $[Ru_2(CO)_6(C_8H_{10})]$.



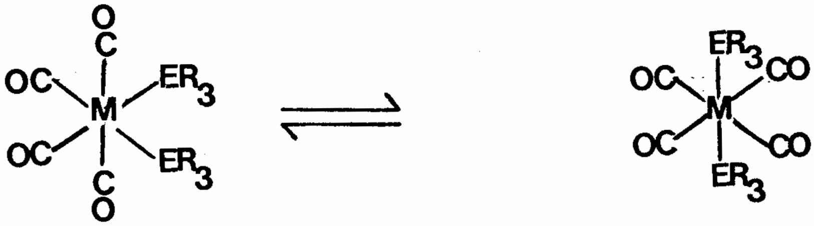
The same products have been obtained in low yields on treatment of $[Ru(CO)_4SiMe_3]_2$ with cyclooctadiene or cyclooctatriene. With the latter, however, the major product was $Ru_3(CO)_9(C_{12}H_{15})H$ (60%). Reaction of II with cyclopentadiene has been shown[32] to give the cyclopentadienyl complex $(\eta\text{-}C_5H_5)Ru(CO)_2(SiMe_3)$. The same complex has been obtained by the 'classic' metathetical reaction of the $[Ru(CO)_2(\eta\text{-}C_5H_5)]^-$ anion with Me_3SiX [X = halide]. Treatment of II with cyclohepta-1,3-diene has been shown to proceed in an analogous manner, affording cycloheptadienyl complexes, $[(1\text{-}5\text{-}\eta\text{-}C_7H_9)Ru(CO)(SiMe_3)]$, in high yield (70-75%). Reaction of II with cycloheptatriene produced[33] the cycloheptadienyl complex $(1\text{-}5\text{-}\eta\text{-}C_7H_8SiMe_3\text{-}6)Ru(CO)_2(SiMe_3)$, in which migration of $SiMe_3$ group to the organic ring has occurred.



Reaction of the binuclear species [$Ru(CO)_4SiMe_3]_2$ with cycloheptatriene has been found to produce (1-5-η-C_7H_8-$SiMe_3$-6)$Ru(CO)_2(SiMe_3)$ and $Ru_3(CO)_6(C_7H_7)(C_7H_6)$ in low yields, with bridging cycloheptatrienyl complexes [1-2,3-4-η:5-7-η-(C_7H_9)]$Ru_2(CO)_5(SiMe_3)$ as the major product. N.m.r. spectroscopy (both ^{13}C and ^{1}H) has played an important role in identifying the different products.

1.3 Tetracarbonyl*bis*(trichlorosilyl)ruthenium [$Ru(CO)_4(SiCl_3)_2$]

Cis-$Ru(CO)_4(SiCl_3)_2$ is a member of the series of molecules of the type $M(CO)_4(ER_3)_2$[34] [M = Fe, Ru, Os; E = Si, Ge, Sn, Pb; R = alkyl, Cl, phenyl, etc.]. Many of these molecules are non-rigid on the n.m.r. time scale. The mechanism of rearrangement is believed to be intramolecular involving *cis* to *trans* isomerizations.



In some cases (e.g., the Fe compounds) the *trans* isomer is not observed, although averaging of the ^{13}C n.m.r. signals of the axial and equatorial carbonyl groups is observed at temperatures below 0° C.

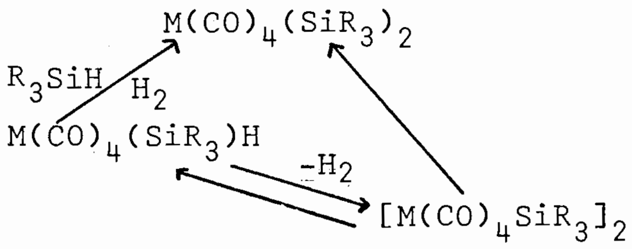
CIS-$Ru(CO)_4(SiCl_3)_2$ isomerizes[34] to the *trans* form at observable rates above 70° C to give an equilibrium mixture of *cis* and *trans* compounds in the ratio of approximately 1:2. The synthesis of this compound involves two methods[35].

Method 1. $Ru_3(CO)_{12} + Cl_3SiH \xrightarrow[70\ \text{atm. CO}]{180°}$ *cis/trans*-$Ru(CO)_4(SiCl_3)_2$

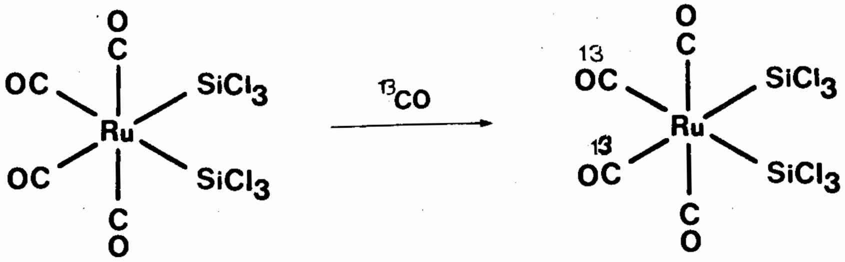
The pure *trans* compound separates out on cooling since it is less soluble in hexane. The *cis/trans* mixtures can also be separated by fractional sublimation.

Method 2. $Ru_3(CO)_{12} + Cl_3SiH \xrightarrow[CO]{h\nu/3\ \text{days}}$ *cis*-$Ru(CO)_4(SiCl_3)_2$

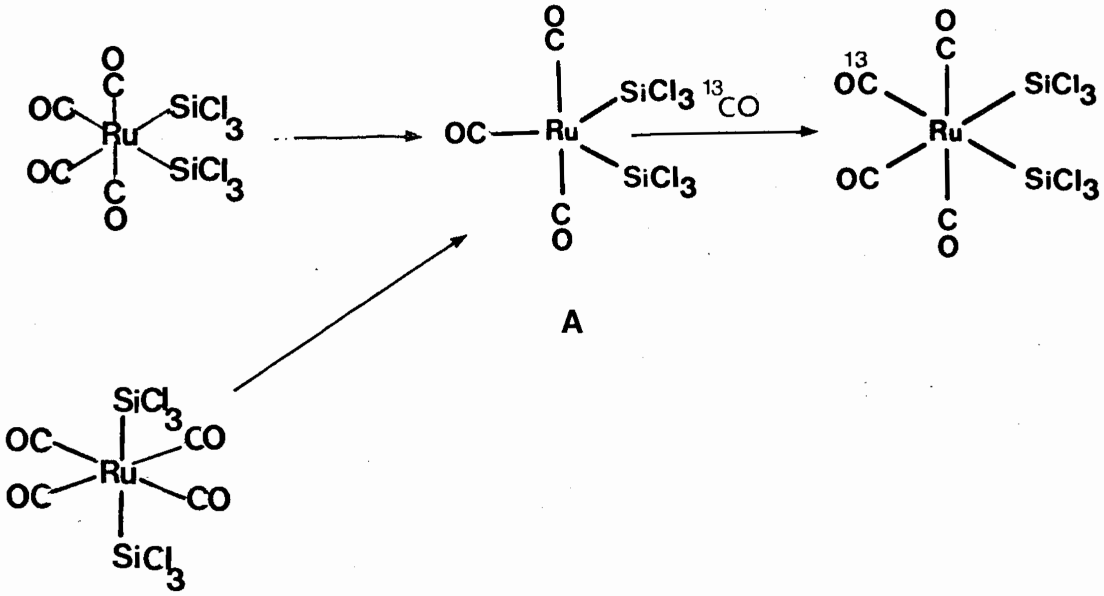
This method gives pure *cis*-$Ru(CO)_4(SiCl_3)_2$ in almost quantitative yield. However, if the reaction is stopped after a few hours, a mixture of $Ru(CO)_4(SiCl_3)H$, $[Ru(CO)_4SiCl_3]_2$ and *cis*-$Ru(CO)_4(SiCl_3)_2$ is obtained. The following reaction scheme, established for triorganosilanes[30] probably applies for trichlorosilane as well.



cis-$Ru(CO)_4(SiCl_3)_2$, unlike the other members of the series, exchanges ^{13}CO when solutions are stirred under a ^{13}CO atmosphere at room temperature[36]. Furthermore, the exchange is completely stereospecific in that only those CO groups *trans* to the $SiCl_3$ groups undergo exchange:



The *trans* isomer does not exchange with ^{13}CO under the same conditions. However, upon u.v. irradiation under ^{13}CO, it also gives the stereospecific *cis* compound. To explain these results, a common intermediate A (shown below) has been invoked.



It appears that in *cis*-$Ru(CO)_4(SiCl_3)_2$ the $SiCl_3$ group has a greater *trans* effect than the CO group. Although little work has been done on the *trans* effect of the $SiCl_3$ ligand, some studies have been carried out with trichlorotin compounds. It was found to be a strong π-acceptor ligand and a weak σ donor in square planar platinum complexes. Platinum complexes containing the $SnCl_3$ group have been found to catalyze[37] the hydrogenation of olefins under mild conditions. They also facilitate the carbonylation of olefins to esters in an alcoholic medium. Presumably, the $SnCl_3$ ligands activate the complexes, by creating a labile site *trans* to itself.

Such properties of metal complexes with $SnCl_3$ ligands have given stimulation for the synthesis and investigation of the properties of the derivatives of *cis*-$Ru(CO)_4(SiCl_3)_2$. It was also expected that such data might help in the understanding of the catalytic uses of such complexes.

The reaction of *cis*-$Ru(CO)_4(SiCl_3)_2$ and *cis*-$Ru(CO)_4(SiCl_3)H$ with PPh_3 has illustrated[38] the large *trans* effect of the $SiCl_3$ group when bonded to ruthenium. In contrast, the iron and osmium analogues do not undergo ready substitution by ligands[38].

It was also of interest to study the effect of the ligand L on the substitution of the remaining equatorial CO group in derivatives of the type $LRu(CO)_3(SiCl_3)_2$. Recent investigations have indicated[39] that *cis* effects are important in the substitution of metal carbonyl derivatives.

CHAPTER 2

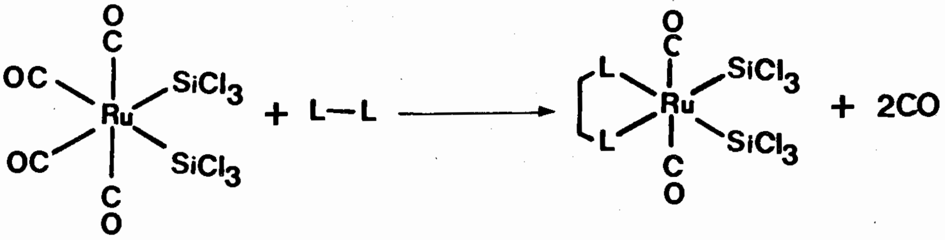
THE REACTION OF *cis*-$Ru(CO)_4(SiCl_3)_2$ WITH BIDENTATE LIGANDS

2.1 RESULTS AND DISCUSSION

The substitution of the equatorial carbonyl groups in *cis*-$Ru(CO)_4(SiCl_3)_2$ by a variety of bidentate ligands L-L produced compounds of the type $(L\text{-}L)Ru(CO)_2(SiCl_3)_2$. Except for dienes the rate of substitution was comparable to that of ^{13}CO exchange. Table I lists the bidentate ligands studied, together with the melting points and analytical data of the derivatives.

2.1.1 SULFUR DERIVATIVES

The reaction of *cis*-$Ru(CO)_4(SiCl_3)_2$ with the sulfur chelates $CH_3S(CH_2)_2SCH_3$, $R_2P(S)P(S)R_2$ [$R = CH_3$, C_2H_5] proceeds smoothly in solution at room temperature to give $(L\text{-}L)Ru(CO)_2(SiCl_3)_2$ derivatives (L-L = chelate ligand). These compounds, and the other $(L\text{-}L)Ru(CO)_2(SiCl_3)_2$ derivatives (except the bipyridine derivative $(bipy)Ru(CO)_2(SiCl_3)_2$) reported here are white, moderately air-stable, crystalline solids which exhibit one absorption in the infrared carbonyl stretching region (Fig. 2). The single carbonyl absorption is consistent with a *trans* arrangement of the carbonyl groups. This in turn agrees with the ^{13}CO exchange studies which indicated that only the carbonyl groups *trans* to the $SiCl_3$ ligands are labile[36]. The synthesis of these derivatives may therefore be summarized in the following equation:



The infrared spectra taken during the course of the reaction showed no evidence for the monosubstituted derivative (L-L) $Ru(CO)_3(SiCl_3)_2$. This suggests that the rate of conversion of the monosubstituted derivative to the chelate derivative is much faster than the reaction of the five coordinate intermediate $Ru(CO)_3(SiCl_3)_2$ with the chelating ligand L-L.

<u>i</u>.<u>e</u>. $k_3 >> k_1 + k_2$

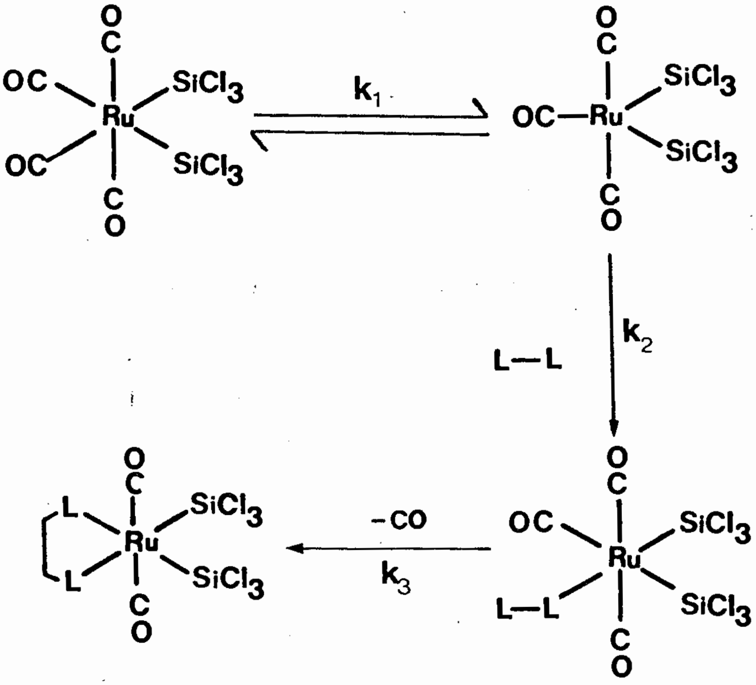


TABLE I

Analytical Data for (L-L)Ru(CO)$_2$(SiCl$_3$)$_2$ Complexes

L - L	melting point (°C)	%C		%H	
		Calcd	Found	Calcd	Found
$(CH_3)_2P(S)P(S)(CH_3)_2$	183	11.77	12.06	1.97	2.04
$(C_2H_5)_2P(S)P(S)(C_2H_5)_2$	165	17.97	18.17	3.02	2.98
$CH_3S(CH_2)_2SCH_3$	204	13.14	13.45	1.84	1.86
$(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$	245	40.80	40.62	2.93	3.13
$(C_6H_5)_2PCH_2P(C_6H_5)_2$	243	40.02	38.70	2.74	3.01
o-$C_6H_4[As(CH_3)_2]_2$	dec.>200	20.24	20.61	2.26	2.23
$(C_6H_5)_2As(CH_2)_2As(C_6H_5)_2$	dec.>240	36.86	36.95	2.65	2.60
C_7H_8[a]	160	20.86	21.30	1.57	1.61
C_8H_{12}[a]	182	22.49	22.90	2.26	2.29
C_8H_8[a]	150 dec.	22.66	23.20	1.52	1.50
$C_{10}H_8N_2$[b]	205	24.75	25.30	1.39	1.39

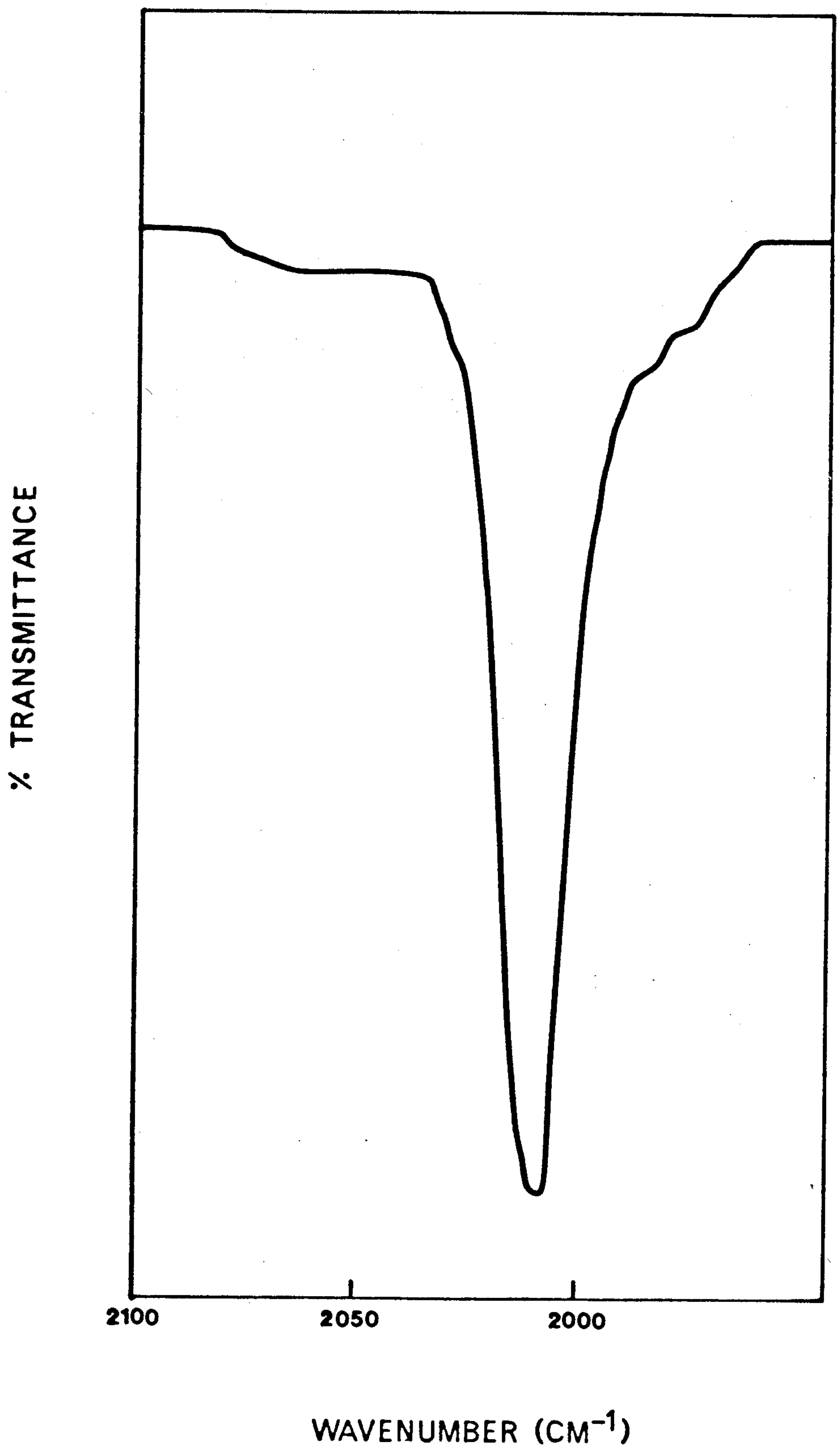
a = parent ion observed in mass spectrum

b = %N calcd. = 4.81, found = 4.85

Figure 2

Infrared Spectrum Of $[(CH_3)_2P(S)P(S)(CH_3)_2]Ru(CO)_2(SiCl_3)_2$
In the Carbonyl Stretching Region

Solvent -CH_2Cl_2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Previously it has been shown that ligands which are weaker π-acceptors than CO, upon substitution for CO, labilize the complex towards dissociative CO loss preferentially from *cis* positions. It is possible that the *cis* labilizing effect of sulfur donors on the remaining equatorial carbonyl group of the monosubstituted derivative $(L\text{-}L)Ru(CO)_3(SiCl_3)_2$ [X] is so large that the conversion of X to the chelate derivative takes place immediately after the attack of the five coordinate intermediate by the ligand.

2.1.2 PHOSPHORUS DERIVATIVES

The compounds $[Ph_2P(CH_2)_nPPh_2]Ru(CO)_2(SiCl_3)_2$ (n = 1,2) were prepared in a similar manner to the sulfur chelates. However, unlike the sulfur compounds there was infrared evidence for the monodentate intermediates $(L\text{-}L)Ru(CO)_3(SiCl_3)_2$. These compounds could not be isolated due to their rapid conversion to the chelate derivatives, $(L\text{-}L)Ru(CO)_2(SiCl_3)_2$. The intermediates (not unexpectedly) had identical stretching frequencies as the corresponding bridged compounds $(L\text{-}L)[Ru(CO)_3(SiCl_3)_2]_2$ (*vide infra*). However, unlike the monodentate derivatives, the bridged derivatives do not give chelate complexes under the same conditions. For example, when the reaction was carried out in hexane solution, a mixture of chelate and the bridged complex were formed, (identified from infrared and ^{31}P n.m.r. spectroscopy) and there was no visible change in the infrared spectrum on stirring this mixture with a large excess of the ligand in a solution of methylene chloride for two days. When a solution of this mixture and the ligand in benzene was heated to 50° C, pure chelate derivative was formed. Subsequently, after the isolation of the bridged complex, it was confirmed that the conversion of the bridged to the chelate complex requires higher temperatures.

$$\begin{tikzcd}
\textit{cis}\text{-}Ru(CO)_4(SiCl_3)_2 \arrow[rr, "L\text{-}L", "k_1"'] \arrow[dr, "L\text{-}L", "k_2"'] & & (L\text{-}L)Ru(CO)_2(SiCl_3)_2 \\
& (L\text{-}L)[Ru(CO)_3(SiCl_3)_2]_2 \arrow[ur, "k_3\ 50^\circ", "L\text{-}L"'] &
\end{tikzcd}$$

$$k_1 \sim k_2 > k_3$$

Other workers have found [41] that similar products are obtained by the reaction of metal carbonyls $M(CO)_6$ [M = Mo,Cr] with diphosphines. Kinetic studies have shown[41] that the rate of conversion of the dinuclear complex to the chelate derivative is dependent on the concentration of the dinuclear complex and independent of that of the diphosphine. Therefore, the splitting of the metal phosphorus bond was considered as the rate determining step of these conversions, i.e.,

$$PP[M(CO)_5]_2 \rightleftarrows PPM(CO)_5 + M(CO)_5$$

$$M(CO)_5 + PP \rightarrow PPM(CO)_5$$

$$PPM(CO)_5 \rightarrow PPM(CO)_4 + CO$$

It is probable that the present system follows a similar path. Although the compound $(Ph_2PCH_2PPh_2)Ru(CO)_2(SiCl_3)_2$ was prepared in a similar manner to that of the $Ph_2P(CH_2)_2PPh_2$ analogue, the product could not be obtained in the analytically pure form even after several recrystallizations in different solvent systems. It has previously been reported[42] that the coordinating ability of chelating diphosphines decreases in the order: $Ph_2P(CH_2)_3PPh_2 \sim Ph_2P(CH_2)_2PPh_2 > Ph_2P(CH_2)_4PPh_2 > Ph_2PCH_2PPh_2$. The last was thought to have an inadequate bite to form a stable chelate complex[42] and perhaps the same applies in these complexes.

For the case of (L-L) = $Ph_2P(CH_2)_2PPh_2$ it was shown that the same (L-L)$Ru(CO)_2(SiCl_3)_2$ derivative could be prepared by heating *trans*-$Ru(CO)_4(SiCl_3)_2$ with L-L in solution at 80° C. The requirement of higher temperatures (as compared with the reaction of the *cis* isomer) as well as the formation of the same product are in accordance with the following observations:

(a) the *trans* isomer does not exchange ^{13}CO at room temperature

and (b) *trans*-$Ru(CO)_4(SiCl_3)_2$ isomerizes to the *cis* isomer (to give an equilibrium mixture of the two forms) at 80° C[43].

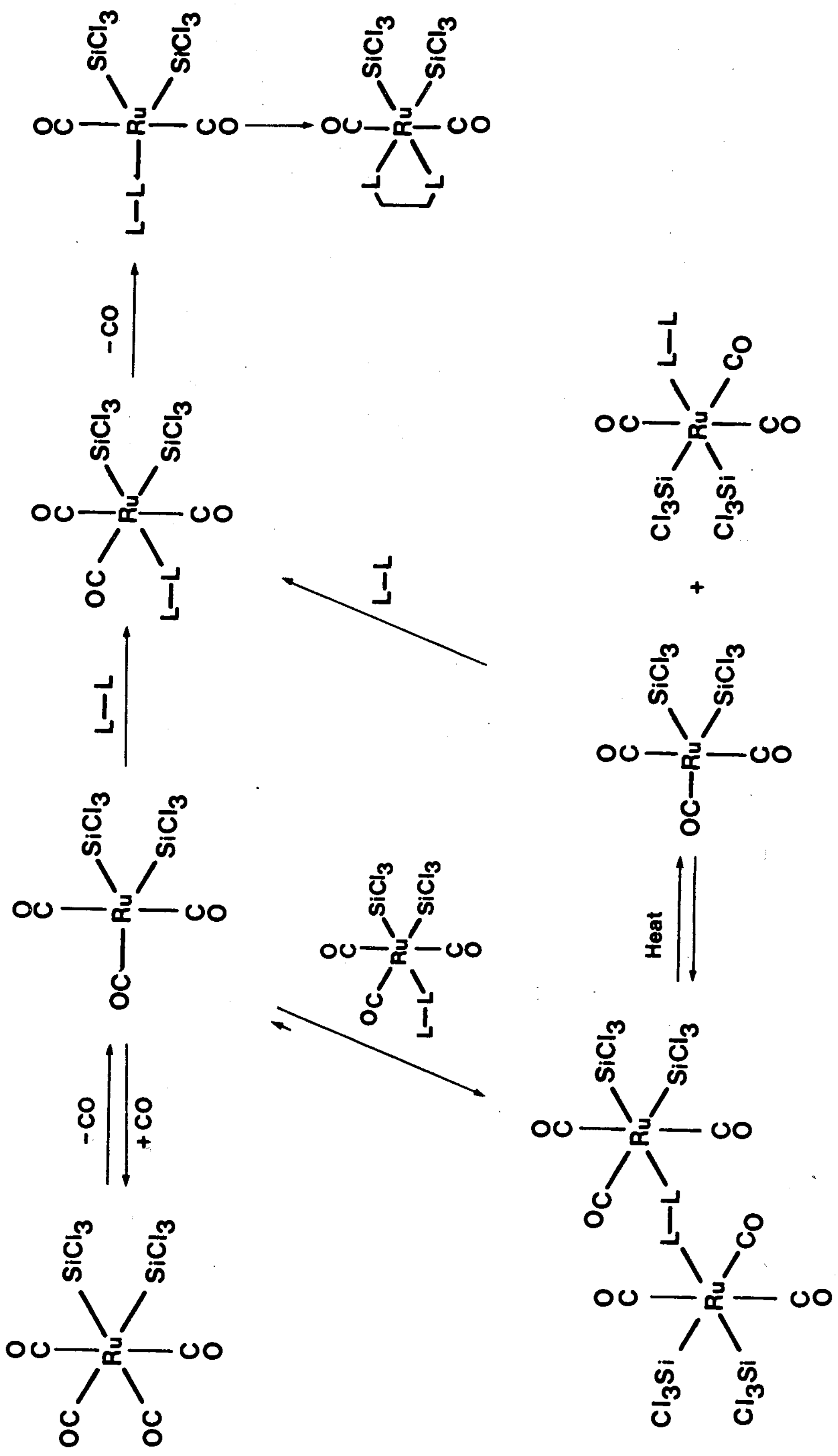
The dinuclear derivatives $(Cl_3Si)_2(OC)_3RuPh_2P(CH_2)_nPPh_2Ru(CO)_3(SiCl_3)_2$ (n = 1,2) were prepared by slowly adding a solution of the ligand to a solution containing excess *cis*-$Ru(CO)_4(SiCl_3)_2$. The identity of these compounds was established by infrared spectroscopy, which was typical of the compounds of the type $LRu(CO)_3(SiCl_3)_2$ (see Chapter 3), carbon and hydrogen analysis (Table II) and by the fact that they exhibit only one ^{31}P n.m.r. resonance. The other reasonable possibility, (L-L)$Ru(CO)_3(SiCl_3)_2$, can be

Table II Analytical and Infrared Data for $(L\text{-}L)[Ru(CO)_3(SiCl_3)_2]_2$

L-L	%C		%H		$\nu(CO)cm^{-1}$, CH_2Cl_2 soln.
	Calcd.	Found	Calcd.	Found	
$(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$	29.42	29.90	1.85	1.93	2117m, 2075s, 2049vs
$(C_6H_5)_2PCH_2P(C_6H_5)_2$	28.81	29.13	1.72	2.25	2116m, 2075m, 2049vs
$(C_6H_5)_2As(CH_2)_2As(C_6H_5)_2$	27.56	28.22	1.74	1.68	2117m, 2072m, 2049m

Figure 3

The Reaction Scheme for $Ph_2E(CH_2)_2EPh_2$ [E = P, As] With *cis*-$Ru(CO)_4(SiCl_3)_2$


SiCl3
OC
Ru
CO
-CO
+CO
L—L
Heat
Cl3Si
+

rejected from the analytical data and by the fact that such compounds would be expected to exhibit two ^{31}P n.m.r. resonances.

It is surprising that the reaction to form the chelate derivative: $(L\text{-}L)Ru(CO)_3(SiCl_3)_2 \rightarrow (L\text{-}L)Ru(CO)_2(SiCl_3)_2$ does not occur, even though this process is known to be reasonably fast in CH_2Cl_2 solution. The formation of the bridged complex is presumed to involve combination of $(L\text{-}L)Ru(CO)_3(SiCl_3)_2$ with the five coordinate intermediate $Ru(CO)_3(SiCl_3)_2$:

$$Ru(CO)_3(SiCl_3)_2 + (L\text{-}L)Ru(CO)_3(SiCl_3)_2 \rightarrow (L\text{-}L)[Ru(CO)_3(SiCl_3)_2]_2$$

A second order reaction between $(L\text{-}L)Ru(CO)_3(SiCl_3)_2$ and $Ru(CO)_4(SiCl_3)_2$ is thought unlikely since it would involve a seven coordinate, 20-electron, transition species. It may be that in hexane the intermediate $(L\text{-}L)Ru(CO)_3(SiCl_3)_2$ initially precipitates from solution such that its effective concentration is less than that of $Ru(CO)_3(SiCl_3)_2$, which is relatively high due to the large excess of $Ru(CO)_4(SiCl_3)_2$ employed. Under these conditions the formation of the bridged derivative would be the preferred reaction. Some support for this explanation is the observation that the bridged compound could not be prepared in CH_2Cl_2 solution.

2.1.3 ARSENIC DERIVATIVES

The preparation (in excellent yield) of

$\{C_6H_4[As(CH_3)_2]_2\}Ru(CO)_2(SiCl_3)_2$ was similar to the preparation of the sulfur chelate derivatives. There was infrared evidence for the intermediate $\{C_6H_4[As(CH_3)_2]_2\}Ru(CO)_3(SiCl_3)_2$, but it could not be isolated.

However, the reaction at room temperature (in CH_2Cl_2) of $Ph_2As(CH_2)_2AsPh_2$(As-As) with *cis*-$Ru(CO)_4(SiCl_3)_2$, in a 1:1 mole ratio, gave approximately a 1:1 mixture of (As-As)$Ru(CO)_2(SiCl_3)_2$ and the bridged derivative $(Cl_3Si)_2(OC)_3Ru$(As-As)$Ru(CO)_3(SiCl_3)_2$. This is illustrated in Figure 4. This mixture remained almost unchanged on stirring for a further four days. There was no significant change in the infrared spectrum on passing N_2 over the solution for two days.

The pure mononuclear compound could be obtained at 80° C, whereas the pure dinuclear compound could be prepared by reacting the arsine ligand with a large excess of *cis*-$Ru(CO)_4(SiCl_3)_2$ in solution at room temperature.

2.1.4 DIENE DERIVATIVES

The reaction of the dienes, norbornadiene and cyclooctadiene, with *cis*-$Ru(CO)_4(SiCl_3)_2$ to give (diene)$Ru(CO)_2(SiCl_3)_2$ takes up to four days to go to completion even when the diene is used as the solvent. This is considerably longer than the preparation of the other derivatives reported here. There is no evidence for a monosubstituted derivative during the reaction, which suggests that it is the initial attack on the presumed intermediate, $Ru(CO)_3(SiCl_3)_2$, which is the rate determining

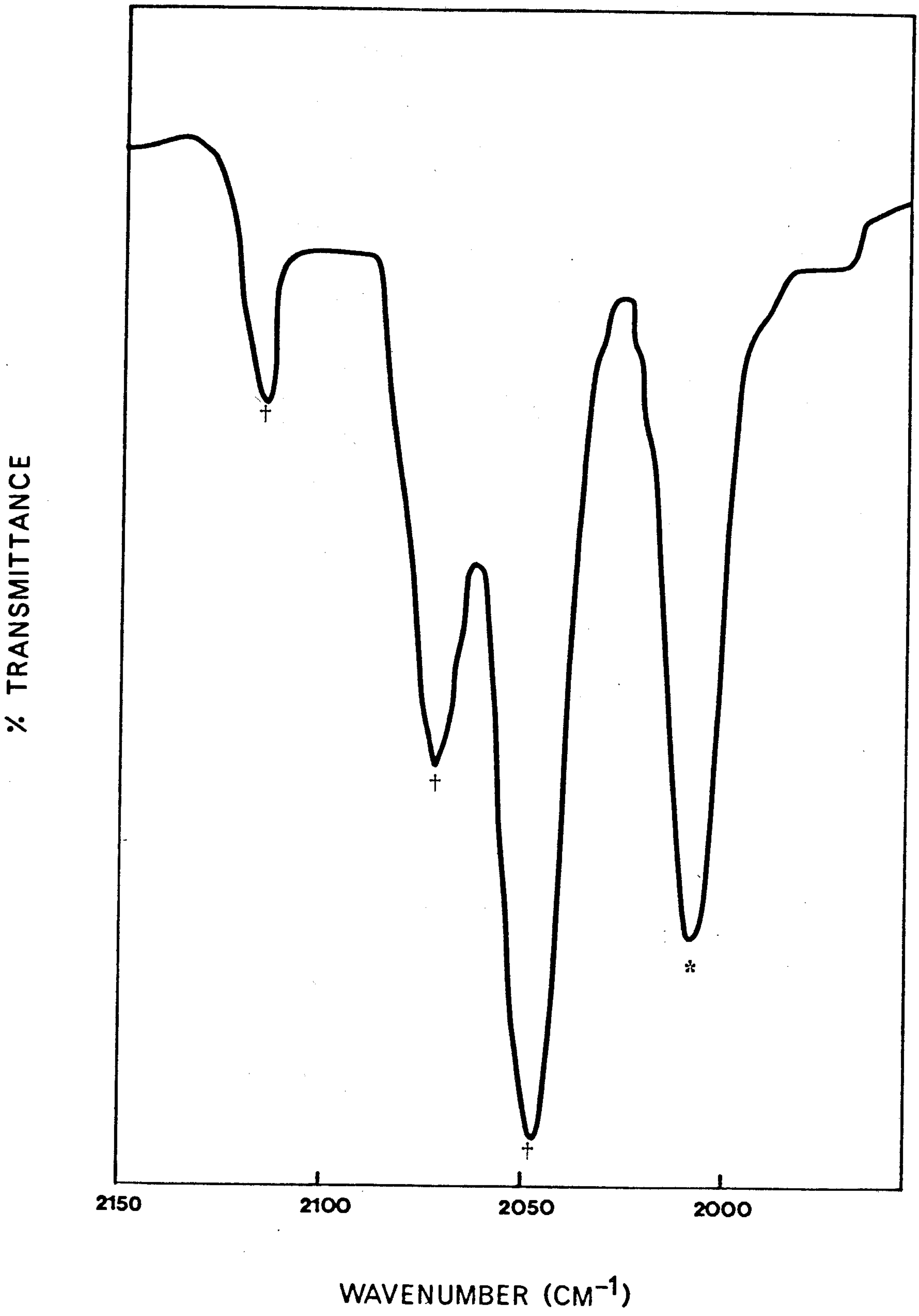
Figure 4

Infrared Spectrum of a Mixture of $(As\text{-}As)Ru(CO)_2(SiCl_3)_2$ and $(SiCl_3)_2(OC)_3Ru(As\text{-}As)Ru(CO)_3(SiCl_3)_2$ In the Carbonyl Stretching Region

Solvent -CH_2Cl_2

*band due to $(As\text{-}As)Ru(CO)_2(SiCl_3)_2$

†bands due to $(As\text{-}As)[Ru(CO)_3(SiCl_3)_2]_2$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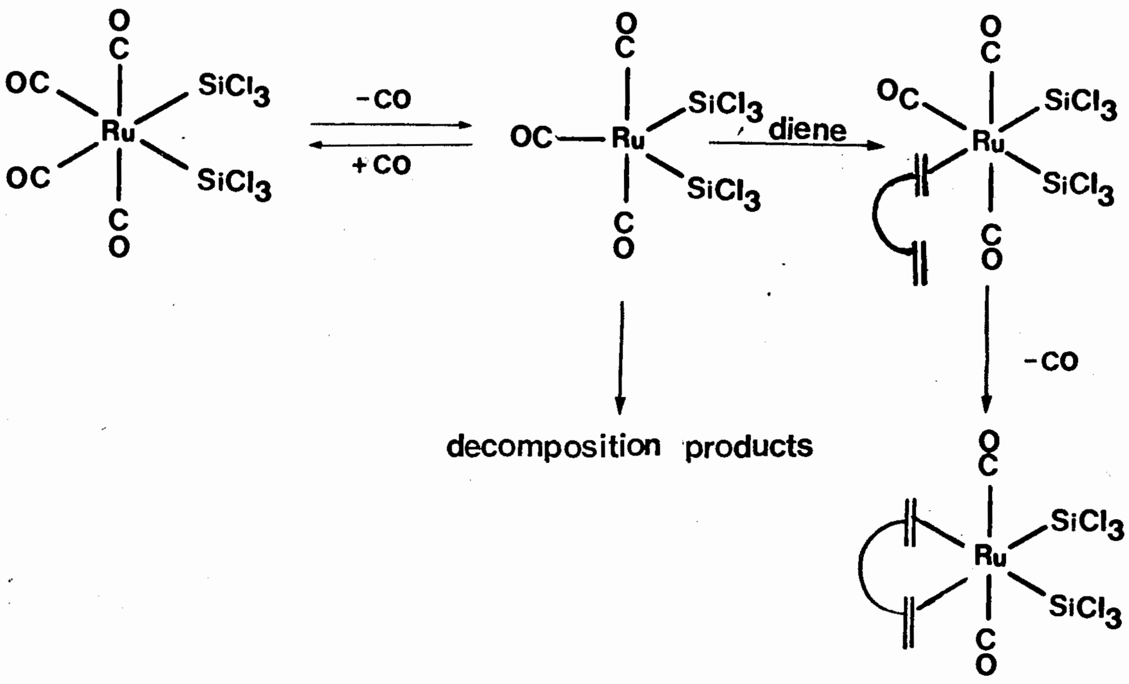
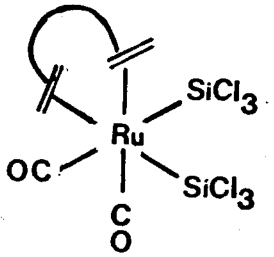
WAVENUMBER (CM^{-1})

step. It is probable that there is competition for the intermediate by the diene and the carbon monoxide produced from the reaction. In support of this suggestion is the fact that the reaction proceeds at the normal rate when the carbon monoxide is removed by continuously passing a slow stream of nitrogen over the stirred reaction solution.

Diene could not be displaced from (diene)Ru(CO)$_2$(SiCl$_3$)$_2$ by passing carbon monoxide through a solution of the appropriate compound. In contrast cyclooctatetraene (COT) was displaced from (COT)Ru(CO)$_2$(SiCl$_3$)$_2$ on treatment (in solution) with carbon monoxide. The much lower yield of the cyclooctatetraene derivative suggests that it is less stable than the diene derivatives. The low affinity of the diene for the five coordinate intermediate allows decomposition of the intermediate to occur.



In the solid state the compounds are reasonably air stable crystals which can be sublimed under vacuum at elevated temperatures. The mass spectra of these molecules exhibit a weak parent ion and a stronger set of peaks due to $[P\text{-}Cl]^+$. This behavior is frequently observed in this type of compound[44]. Similar to other molecules reported here, the diene derivatives exhibit one strong carbonyl stretch in the infrared spectrum (Figure 5). However, (norbornadiene)$Ru(CO)_2(SiCl_3)_2$ did show (in hexane solution) two additional, very weak adsorptions to higher frequency of the main CO stretching peak. These bands remained unchanged on recrystallization and sublimation. It is possible that these minor peaks are due to trace amounts of the isomer having one of the alkene linkages coordinated in the axial position, i.e.,

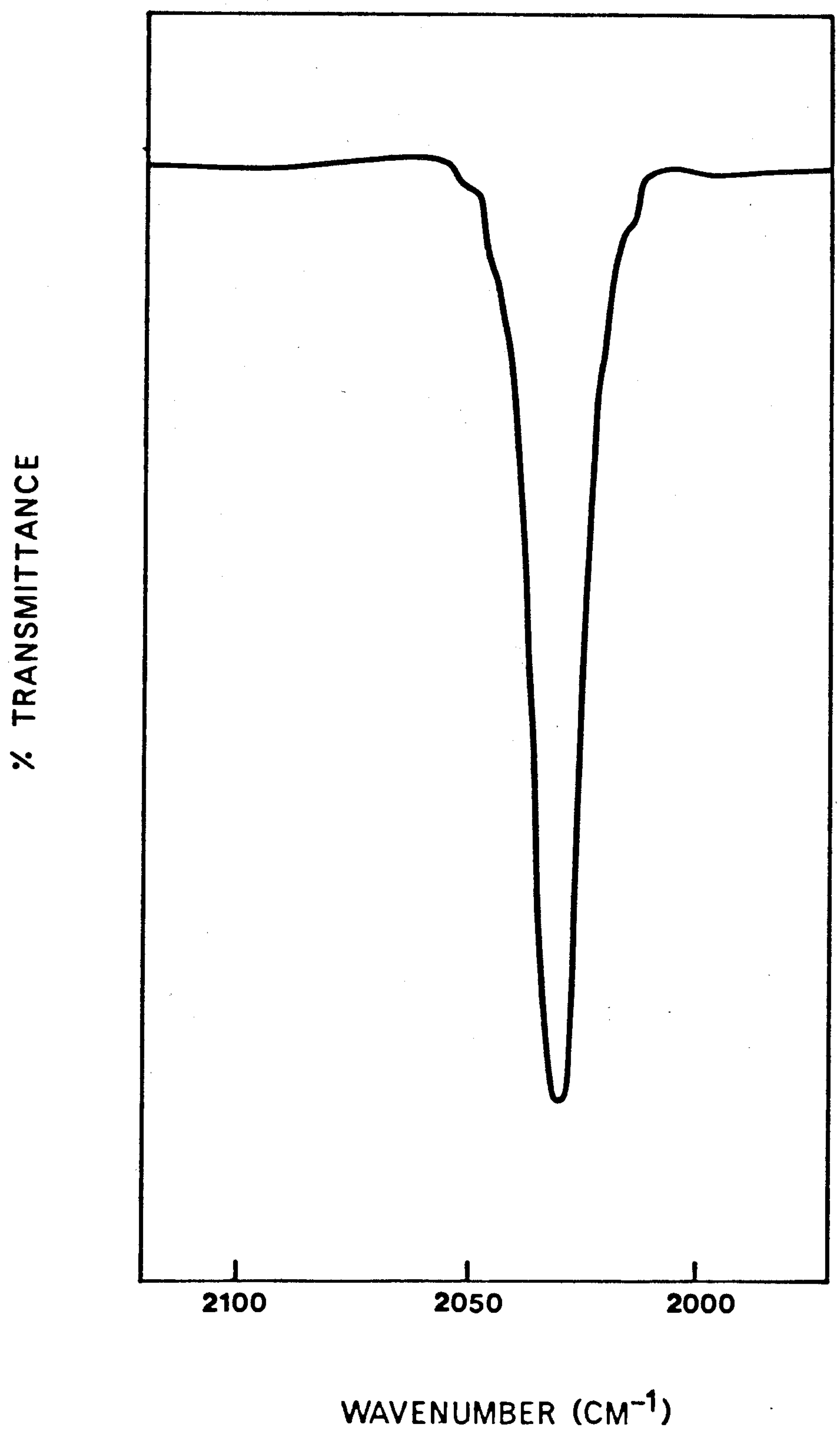


The higher carbonyl stretching frequencies of diene derivatives, when compared to the other derivatives (Table III), could be explained in terms of the π-acceptor properties of the ligands. Sulfur, phosphorus and arsenic ligands, which are thought to be good σ-donors, increase the electron density at the metal and hence enhance the back bonding from metal to CO.

Figure 5

Infrared Spectrum of $(C_8H_{12})Ru(CO)_2(SiCl_3)_2$
In the Carbonyl Stretching Region

Solvent - CH_2Cl_2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2000
WAVENUMBER (CM^{-1})

Table III. Infrared CO Stretching Frequencies of $(L\text{-}L)Ru(CO)_2(SiCl_3)_2$ in CH_2Cl_2

L - L	$\nu CO(cm^{-1})$
$(CH_3)_2P(S)P(S)(CH_3)_2$	2008
$(C_2H_5)_2P(S)P(S)(C_2H_5)_2$	2005
$CH_3S(CH_2)_2SCH_3$	2019
$(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$	2012
$(C_6H_5)_2PCH_2P(C_6H_5)_2$	2008
$o\text{-}C_6H_4[As(CH_3)_2]_2$	2015
$(C_6H_5)_2As(CH_2)_2As(C_6H_5)_2$	2008
C_7H_8	2039
C_8H_{12}	2030
C_8H_8	2042
$C_{10}H_8N_2$	2017

This in turn decreases the bond order of C-O and hence the stretching frequency. The high carbonyl stretching frequencies observed in diene complexes could be accounted for as involving weaker σ-bonding of diene to metal, and stronger metal to ligand π-interaction involving the filled d orbitals of the metal and the empty antibonding (π^*) orbitals of the ligand. The cyclooctatetraene derivative exhibits a higher carbonyl stretching frequency when compared to cyclooctadiene and norbornadiene analogues. This is not surprising since there is an extended conjugation of the double bonds of the ligand which enhances the metal to ligand (π^*) interaction by lowering the energy of the latter orbitals.

The bipyridine derivative (bipy)Ru$(CO)_2(SiCl_3)_2$ was prepared in a manner similar to that described for the sulfur chelates. There was no infrared evidence for the intermediate (bipy)Ru$(CO)_3(SiCl_3)_2$. The rigid nature of the carbon skeleton connecting the two donor atoms may be one of the reasons for it. Unlike other chlelate derivatives, (bipy)Ru$(CO)_2(SiCl_3)_2$, was extremely air sensitive both in solution and in the solid state. It is not clear why the bipyridine complex should be so unstable.

2.1.5 PHOSPHORUS N.M.R.

^{31}P n.m.r. data of the phosphorus containing derivatives are given in Table IV. It has been observed previously that there is a large downfield shift of the ^{31}P signal on forming

Table IV. Phosphorus n.m.r. Data (in CH_2Cl_2)

Compound	δ(ppm)	Δ_{CS}(ppm)[a]
$[Ph_2P(CH_2)_2PPh_2]Ru(CO)_2(SiCl_3)_2$	-48.1	-60.95
$(Ph_2PCH_2PPh_2)Ru(CO)_2(SiCl_3)_2$	-48.4	-61.5
$Ph_2P(CH_2)_2PPh_2[Ru(CO)_3(SiCl_3)_2]_2$	-15.3	-28.15
$Ph_2PCH_2PPh_2[Ru(CO)_3(SiCl_3)_2]_2$	-15.4	-28.7
$(C_2H_5)_2P(S)P(S)(C_2H_5)_2Ru(CO)_2(SiCl_3)_2$[b]	-67.2	-16.3

[a] Δ_{CS} is the coodination chemical shift defined as $\delta_{complex} - \delta_{ligand}$, where δ complex and δ ligand are the chemical shifts of the complexed and the free ligand, respectively

[b] coordination of the ligand is through sulfur

a four or five membered chelate ring[45]. This effect was observed in this study as well. The large chelation shift has been attributed principally to those constraints in the chelate ring which lead to an increase in the bond angles at phosphorus in complexes $Ph_2P(CH_2)_nPPh_2Ru(CO)_2(SiCl_3)_2$ ($n = 1,2$). From a comparison of the bridged with the chelate derivatives, it is possible to say that, in these compounds, approximately half the downfield shift may be accounted for by the coordination of the phosphorus to the transition metal, the other half of the shift being due to the formation of the chelate ring.

The tetraethyl *bis*-phosphine disulfide derivative $[(C_2H_5)_2P(S)P(S)(C_2H_5)_2]Ru(CO)_2(SiCl_3)_2$ in which the two sulfur atoms are bonded to the metal, show a smaller ^{31}P coordination chemical shift when compared to the other phosphorus containing compounds. This is not surprising since there is no direct interaction of the two phosphorus atoms with the metal.

2.2 EXPERIMENTAL SECTION

Unless otherwise stated, reactions were carried out under a nitrogen atmosphere using Schlenk apparatus. All the air sensitive materials were handled in a dry box. As a further precaution some of the reactions were carried out in the dry box. A standard high vacuum system was used in most of the preparations described in this work. Melting points were measured in sealed capillaries using a Gallenkamp apparatus; they are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237 spectrometer fitted with an external recorder, using 0.5 mm cells. The spectra were calibrated using carbon monoxide in a 10 cm gas cell (approximately 1 atmosphere). Proton nuclear magnetic resonance spectra were obtained on a Varian A 56/60 or XL 100 spectrometer using $CDCl_3$ as solvent and TMS as internal standard ($\delta = 0$) unless otherwise stated. Phosphorus n.m.r. spectra were obtained on the latter instrument (operating in the Fourier Transform mode) using CH_2Cl_2 as solvent and H_3PO_4 (85%) as an external reference ($\delta = 0$, downfield negative). Mass spectra were obtained on a Hitachi - Perkin Elmer RMU-6E double focusing mass spectrometer using an ionization voltage of 80 eV. Microanalyses were performed by Mr. M. K. Yang of the Simon Fraser University microanalytical laboratory.

All the hydrocarbon solvents were refluxed (under nitrogen) over freshly cut potassium for several hours before being distilled and stored over molecular sieves under nitrogen.

Dichloromethane was distilled from phosphorus pentoxide and stored over molecular sieves under nitrogen. Ethoxyethanol was dried and distilled from anhydrous $MgSO_4$ overnight before being fractionated, and stored over molecular sieves. Ethanol was dried and distilled from magnesium ribbons.

2.2.1 THE PREPARATION OF STARTING MATERIALS

$Ru_3(CO)_{12}$

$Ru_3(CO)_{12}$ was synthesized as described[46], from $RuCl_3 \cdot 3H_2O$ (obtained from Engelhardt Industries) in two steps according to the equations given below.

$$1.\quad RuCl_3 \cdot 3H_2O \xrightarrow[135^\circ\ C]{CO\ (1\ atm)} Ru(CO)_nCl_m$$

$$2.\quad Ru(CO)_nCl_m \xrightarrow[CO\ (1\ atm)]{Zn,\ 80^\circ} Ru_3(CO)_{12} + ZnCl_2$$

The yields varied between 60-80%.

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

A solution of $Ru_3(CO)_{12}$ (1.0 g) and $HSiCl_3$ (6 mL) in hexane (20 mL) was placed in a quartz Carius tube (fitted with a teflon valve). The tube was sealed and placed in liquid nitrogen and, when the solution was frozen, evacuated. The solution was then degassed with one freeze/thaw cycle and finally pressurized with 2 atomospheres of carbon monoxide. It was then irradiated with ultraviolet light (200 watt, Hanovia Lamp) for 72 hours. The solution was stirred rapidly throughout this period. After this time, the resulting colourless solution was transferred into a Schlenk tube and cooled to -78° C (using dry ice) for at least 2 hours. The supernatant liquid was then decanted from the white crystals which were then dried under vacuum. Further purification was carried out by subliming the solid under vacuum (0.02 mm) at 40° C on to a probe cooled to -78° C. It is essential that the water jacket for the u.v. lamp is clean, otherwise the reaction does not go to completion and the very air sensitive *cis*-$Ru(CO)_4(SiCl_3)(H)$ contaminates the product. When u.v. apparatus and the Carius tube containing the solution were enclosed in aluminum foil, the reaction was complete in two days. The yield of the product obtained was almost quantitative (2.26 g).

2.2.2 LIGANDS

The ligands were commercially available and most of them were used without further purification. Cyclooctadiene was, however, purified by distilling and drying over $MgSO_4$ before use.

2.2.3 PREPARATION OF $[CH_3S(CH_2)_2SCH_3]Ru(CO)_2(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.24 g, 0.5 mmol) and dithiahexane (0.07 g, 0.6 mmol) in n-hexane (15 mL) was stirred at room temperature for 6 hours. The infrared spectrum taken after this time showed only the product (single carbonyl stretching mode at 2019 cm^{-1}). The solvent was then removed from the white solid, washed with four 10 mL portions of n-hexane and dried under vacuum. The product $(CH_3SCH_2CH_2SCH_3)Ru(CO)_2(SiCl_3)_2$ (0.22g, 80%) was analytically pure as obtained. The proton n.m.r. spectrum of the product showed two singlets at $\delta = 2.6$ and 2.9 (ratio 3:2) corresponding to CH_3 and CH_2 protons respectively. The corresponding $R_2P(S)P(S)R_2$ ($R = CH_3$, C_2H_5) derivatives were similarly prepared (85% and 90% yields respectively). There was no spectroscopic evidence for the monocoordinated intermediate during these reactions.

2.2.4 PREPARATION OF $(Ph_2PCH_2CH_2PPh_2)Ru(CO)_2(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.273 g, 0.566 mmol) and $Ph_2PCH_2CH_2PPh_2$ (0.225 g, 0.565 mmol) in benzene (15 mL) was stirred overnight at 50° C. n-Hexane was then added and the solution was placed in the refrigerator to complete precipitation. Solvent was removed from the white product which was further washed with n-hexane and dried on the vacuum line. The yield of $(Ph_2PCH_2CH_2PPh_2)Ru(CO)_2(SiCl_3)_2$ (0.460 g) was essentially quantitative. The analytical sample was obtained as fine white needles by recrystallization from benzene.

The compound $(Ph_2PCH_2PPh_2)Ru(CO)_2(SiCl_3)_2$ was similarly prepared. The yield of the product was essentially quantitative. The product could not be obtained in the analytically pure form even after several recrystallizations with different solvent systems (CH_2Cl_2/hexane; benzene/hexane). ^{31}P n.m.r. showed a single resonance at -48.4 ppm.

It was subsequently found that these reactions could be conveniently carried out at room temperature with reaction times of approximately 18 hours. In these reactions there was infrared evidence for the monosubstituted derivatives $(L\text{-}L)Ru(CO)_3(SiCl_3)_2$ but the bands thought to be due to these compounds were never very intense and, as the reaction progressed, they weakened with a corresponding increase in the intensity of the band due to the dicarbonyl derivative. It was also found that $[Ph_2P(CH_2)_2PPh_2]Ru(CO)_2(SiCl_3)_2$ could be prepared by heating at 80° solutions of $Ph_2P(CH_2)_2PPh_2$ and *trans*-$Ru(CO)_4(SiCl_3)_2$. The reaction was complete after 6 hours and was essentially quantitative.

2.2.5 PREPARATION OF $Ph_2P(CH_2)_2PPh_2[Ru(CO)_3(SiCl_3)_2]_2$

To a stirred solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.70 g, 1.45 mmol) in n-hexane (30 mL), was added dropwise over 8 h, $Ph_2P(CH_2)_2PPh_2$ (0.259 g, 0.63 mmol) in n-hexane (200 mL), using a pressure equilizing dropping funnel. After the addition was complete, the solution was stirred for a further two hours. The supernatant liquid was then removed from the white solid of product, $Ph_2P(CH_2)_2PPh_2[Ru(CO)_3(SiCl_3)_2]_2$, which was further washed with four 10 mL portions of n-hexane and dried under vacuum. The yield was essentially quantitative (based on $Ph_2P(CH_2)_2PPh_2$). The product showed three infrared bands in the carbonyl region (2117m, 2075s, 2049vs cm^{-1}), and was analytically pure.

^{31}P n.m.r.: singlet at $\delta = -15.3$ ppm. The $Ph_2PCH_2PPh_2$ analogue was prepared similarly. The analytical sample was recrysallized from CH_2Cl_2 and n-hexane. The resulting white solid showed three infrared bands at 2116m, 2075m, 2049vs cm^{-1}.

^{31}P n.m.r.: singlet at $\delta = -15.4$ ppm.

2.2.6 PREPARATION OF $[(CH_3)_2AsC_6H_4As(CH_3)_2]Ru(CO)_2(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.24 g, 0.5 mmol) and *ortho*-$(CH_3)_2AsC_6H_4As(CH_3)_2$ (0.14 g, 0.7 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 24 hours. The solution was then filtered, n-hexane added (15 mL) and cooled at -78° for a few hours. The solvent was removed from the product, $(CH_3)_2AsC_6H_4As(CH_3)_2Ru(CO)_2(SiCl_3)_2$, washed with four 5 mL portions of n-hexane and dried under vacuum. The white crystals so obtained were found to be pure by infrared examination and elemental analysis. The ^1H n.m.r. spectrum showed a singlet at $\delta = 2.5$ ppm due to CH_3 protons and a multiplet at $\delta = 7.2$-8.2 corresponding to aromatic (CH) protons.

2.2.7 PREPARATION OF $(Ph_2AsCH_2CH_2AsPh_2)Ru(CO)_2(SiCl_3)_2$.

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.482 g, 1.0 mmol) was heated at 75-80° C in an evacuated sealed tube (fitted with a teflon valve). Approximately every 12 hours, the tube was cooled and reevacuated. The infrared spectrum taken after four days showed only the product (single band in the carbonyl region at 2008 cm^{-1}). The reaction mixture was then transferred into a Schlenk tube, an equal volume of n-hexane added to the solution, and stored in the refrigerator for complete precipitation of the product. The supernatant liquid was then removed from the white product $(Ph_2AsCH_2CH_2AsPh_2)Ru(CO)_2(SiCl_3)_2$ which was washed and dried as before. The yield was essentially quantitative.

When the reaction was carried out in CH_2Cl_2 at room temperature, an infrared spectrum after 18 h showed approximately equal amounts of $(Ph_2AsCH_2CH_2AsPh_2)Ru(CO)_2(SiCl_3)_2$ and $(Ph_2AsCH_2CH_2AsPh_2)[Ru(CO)_3(SiCl_3)_2]_2$. A spectrum of the solution after it had been stirred for a further three days was virtually unchanged.

2.2.8 PREPARATION OF $Ph_2As(CH_2)_2AsPh_2[Ru(CO)_3(SiCl_3)_2]_2$

A solution containing *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.150 g, 0.31 mmol) and $Ph_2As(CH_2)_2AsPh_2$ (0.05 g, 0.10 mmol) in n-hexane (15 mL) was stirred overnight. The white precipitate of $Ph_2As(CH_2)_2AsPh_2[Ru(CO)_3(SiCl_3)_2]_2$ (0.12 g, 85%) was separated from the mother liquor, washed with n-hexane (five 10 mL portions) and dried on the vacuum line. The product showed three infrared bands in the carbonyl region at 2117m, 2072m, 2049vs, as expected. The analytical sample was recrystallized from CH_2Cl_2 and n-hexane, and the results obtained for C% and H% were consistent with the dinuclear (bridged) complex.

2.2.9 PREPARATION OF $(C_8H_{12})Ru(CO)_2(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.482 g, 1.0 mmol) in cyclooctadiene (5 mL) was stirred at room temperature for four days. After this time, n-hexane (10 mL) was added and the resulting solution stored in the refrigerator to complete precipitation. Excess diene and n-hexane was removed from the white crystalline product, which was washed with n-hexane and dried on the vacuum line. The yield of $(C_8H_{12})Ru(CO)_2(SiCl_3)_2$ was 80% and appeared pure by infrared spectrum. The analytical sample was obtained by recrystallization from CH_2Cl_2-n-hexane. ^1H n.m.r. of the product showed two broad resonances at $\delta = 2.55$ and 5.35 ppm (ratio 2:1). The norbornadiene analogue was prepared similarly (75% yield) as was the cyclooctatetraene derivative $(C_8H_8)Ru(CO)_2(SiCl_3)_2$. However, in the latter case, the crude product appeared brown in colour due to decomposition products, and was purified by stirring a solution of CH_2Cl_2 with decolourizing charcoal. The resulting solution was evaporated after filtration to half the volume (using vacuum line), n-hexane added, and cooled to -78° C. The solvent was removed from the white needles of the product, which was dried as before. The solid so obtained was analytically pure and showed a single infrared band (2042 cm^{-1}) as expected. The ^1H n.m.r. spectrum of the product consisted of two singlets at 6.05 and 6.50 ppm (ratio 1:1). The COT derivative and the other diene derivatives appeared stable in air for short periods, the norbornadiene derivative sublimes at 110° C (0.02 mm). When carbon monoxide was bubbled through a solution of $(C_8H_8)Ru(CO)_2(SiCl_3)_2$ in CH_2Cl_2, it reverted to *cis*-$Ru(CO)_4(SiCl_3)_2$ over 18 h.

2.2.10 PREPARATION OF $[2,2'-(C_5H_4N)_2]Ru(CO)_2(SiCl_3)_2$

The method of preparation of this compound was essentially that given for the dithiahexane derivative (section 2.2.3). The compound was very air sensitive and decomposed rapidly in solution, preventing adequate study. An analytically pure sample was obtained by carrying out the entire reaction inside the dry box.

CHAPTER 3

THE REACTION OF *cis*-$Ru(CO)_4(SiCl_3)_2$ WITH MONODENTATE LIGANDS

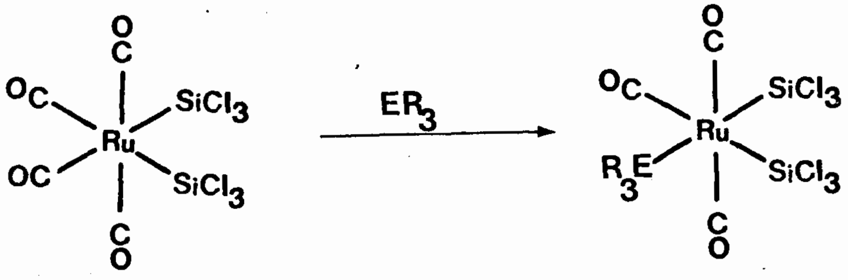
3.1 RESULTS AND DISCUSSION

The large *trans* effect of the $SiCl_3$ group when bonded to ruthenium is illustrated in Chapter II of this thesis and in some of the preliminary investigations carreid out with *cis*-$Ru(CO)_4(SiCl_3)H$ and *cis*-$Ru(CO)_4(SiCl_3)_2$.[38] Studies of the latter compound with a variety of monodentate ligands of the type ER_3 (E = Group V b element) further establishing this effect are reported in this chapter.

cis-$Ru(CO)_4(SiCl_3)_2$ reacts with monodentate ligands ER_3 to produce compounds of the type $(R_3E)Ru(CO)_3(SiCl_3)_2$ and $(R_3E)_2Ru(CO)_2(SiCl_3)_2$. Whether *bis* substitution occurs depends on the nature of the ligand, the reaction conditions employed and the quantities of each reagent used.

3.1.1 MONOSUBSTITUTED DERIVATIVES-$R_3ERu(CO)_3(SiCl_3)_2$

The synthesis of the monosubstituted derivatives $R_3ERu(CO)_3(SiCl_3)_2$ may be represented by the following equation:



The rate of formation of $R_3ERu(CO)_3(SiCl_3)_2$ is comparable to the rate of ^{13}CO exchange of the parent molecule. The analytical results for the series of complexes of this type are reported in Table V. All the compounds are white crystalline solids which decompose on exposure to air. There appears to be a rough correlation of air stability with the lability of groups *trans* to the $SiCl_3$ groups in these derivatives. Thus, *cis*-$Ru(CO)_4(SiCl_3)_2$ is very air sensitive, yet $L_2Ru(CO)_2(SiCl_3)_2$ compounds appear quite stable. $LRu(CO)_3(SiCl_3)_2$ derivatives are of intermediate stability, depending on how easily the remaining CO is replaced. For example, $(o\text{-tolyl})_3PRu(CO)_3(SiCl_3)_2$ is very air sensitive yet $(MeO)_3PRu(CO)_3(SiCl_3)_2$ is moderately stable. A similar pattern exists for *cis*-$Ru(CO)_4(SiCl_3)(H)$ (very air sensitive), $Ph_3PRu(CO)_3(SiCl_3)H$ (air stable) and $Os(CO)_4(SiCl_3)_2$ (which is much more air stable than the ruthenium analogue). A further example of this instability is that satisfactory analyses could not be obtained for those $LRu(CO)_3(SiCl_3)_2$ derivatives with a labile equatorial CO group (at room temperature) unless they were recrystallized under carbon monoxide.

It was also of interest to note that the unstable complexes contain ligands which have large cone angles, e.g. PPh_3 and $P(o\text{-tolyl})_3$ derivatives decomposed rapidly when compared to those with smaller ligands. The greater steric labilization of the remaining equatorial carbonyl group by these ligands could account for the instability of complexes

TABLE V

Analytical Data for $LRu(CO)_3(SiCl_3)_2$ Complexes

L	%C		%H	
	Calcd.	Found	Calcd.	Found
PF_3	6.65	6.42	0.00	0.00
ETPB	17.52	16.47	1.78	2.00
$P(OPh)_3$	33.00	33.01	1.98	2.05
$P(OMe)_3$	12.47	12.88	1.57	1.59
$P(OEt)_3$	17.43	17.72	2.44	2.49
PPh_3	35.23	35.74	2.11	2.19
$AsPh_3$	33.18	33.46	1.99	2.03
$SbPh_3$	31.25	31.08	1.87	1.90
PPh_2Me	29.40	30.62	2.01	2.21
$P(o\text{-}C_6H_4CH_3)_3$	38.0	37.13	2.70	2.88
$PPhMe_2$	22.31	22.75	1.87	1.97
$P(n\text{-}C_4H_9)_3$	27.45	27.30	4.15	4.04
$P(C_6H_{11})_3$	34.34	34.48	4.53	4.48

with larger ligands. The greater *cis* labilizing effect of large ligands on carbonyl dissociation of metal complexes has previously been described.[47]

INFRARED DATA

The infrared spectra of all the compounds of the type mer-$R_3ERu(CO)_3(SiCl_3)_2$ exhibit three bands in the carbonyl region (Fig. 6 and Fig. 7), consistent with the suggested arrangement of the carbonyl groups. Often solubility requirements necessitated the use of a polar solvent (CH_2Cl_2) for infrared studies. The carbonyl stretching frequencies for a series of complexes of the type $R_3ERu(CO)_3(SiCl_3)_2$ are given in Table VI.

These results show that the replacement of a carbonyl group by a Group V b ligand causes the stretching frequencies (νCO) of the remaining carbonyls to decrease by an amount depending on the nature of the ligand. Similar results have been observed[48] in most of the known metal carbonyl complexes. It is also apparent that the increasing order of carbonyl stretching frequencies follows the increasing order of π-acceptor properties of the ligands.[49] The extent to which back donation occurs (M to ligand) will depend on the nature of the donor atom of the ligand and the electronegativities of the substituents.[50] This is well illustrated in the series given. For example, PF_3, which is the strongest π-accepting ligand in the series, causes the smallest decrease in νCO of the remaining carbonyls, on coordinating to the metal. Tricyclohexyl phosphine, which is the poorest π-accepting ligand

Figure 6

Infrared Spectrum of $(n\text{-}C_4H_9)_3PRu(CO)_3(SiCl_3)_2$
In the Carbonyl Stretching Region

Solvent - *n*-Hexane

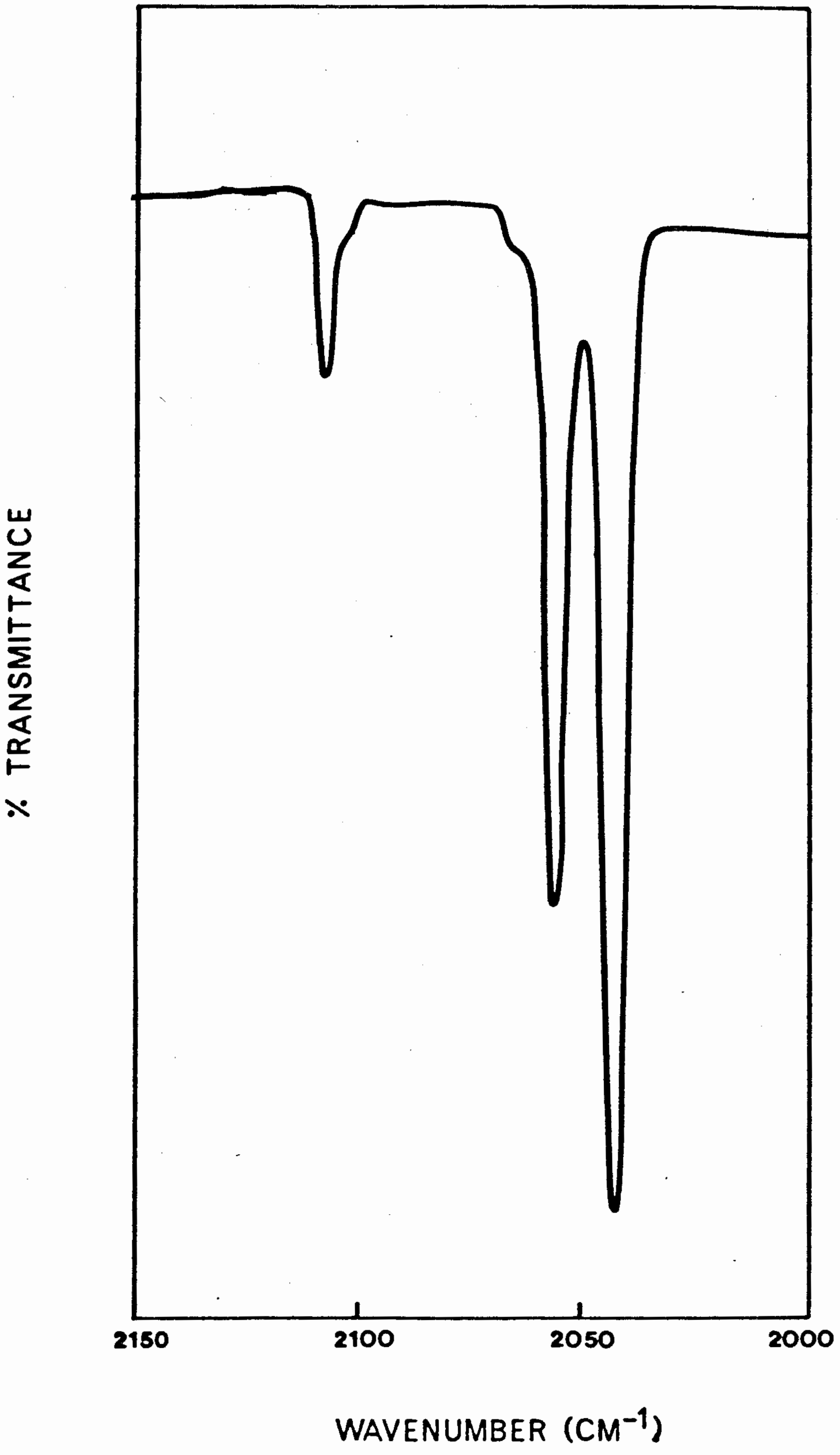

% TRANSMITTANCE
2150
2100
2050
2000
WAVENUMBER (CM^{-1})

Figure 7

Infrared Spectrum of $(F_3P)Ru(CO)_3(SiCl_3)_2$
In the Carbonyl Stretching Region

Solvent- *n*-Hexane

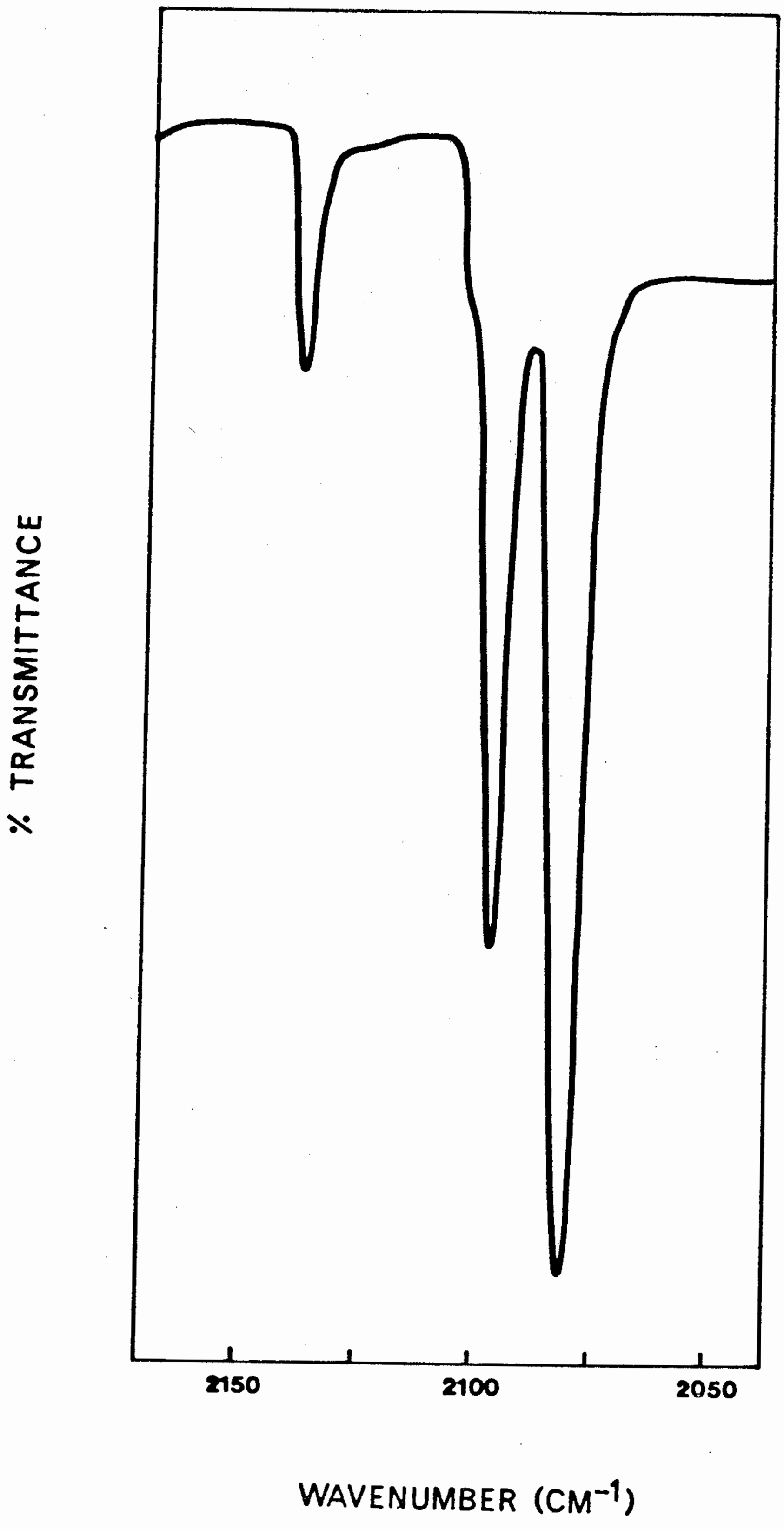

% TRANSMITTANCE
2150
2100
2050
WAVENUMBER (CM^{-1})

TABLE VI

Infrared Data for $LRu(CO)_3(SiCl_3)_2$ Complexes

L	$\nu(CO)cm^{-1}$ CH_2Cl_2 soln.
PF_3[a]	2138w, 2096m, 2081s
ETPB	2133w, 2089m, 2068s
$P(OPh)_3$	2124w, 2077m, 2064s
$P(OMe)_3$	2123w, 2082m, 2055s
$P(OEt)_3$	2122w, 2081m, 2054s
PPh_3	2117w, 2075m, 2050s
$AsPh_3$	2118w, 2072m, 2049s
$SbPh_3$	2114w, 2070m, 2047s
PPh_2Me	2115w, 2072m, 2046s
$PPhMe_2$	2117w, 2075m, 2049s
$P(o-C_6H_4CH_3)_3$	2111w, 2066m, 2041s
$P(n-C_4H_9)_3$	2112w, 2062m, 2044s
$P(C_6H_{11})_3$	2106w, 2056m, 2037s

a = in hexane solution

in the series causes the largest decrease. A similar trend has been observed[48] in complexes of the type $Ni(CO)_3[P(X_1X_2X_3)]$ (X_1, X_2, X_3 being alkyl, aryl, or halide).

Another striking feature observed in this series is that the insertion of an oxygen between an organic group R and phosphorus increases the carbonyl stretching frequencies. For example, the triphenyl phosphine derivative $Ph_3PRu(CO)_3(SiCl_3)_2$ shows three bands in the carbonyl region, at 2117, 2075, and 2050 cm^{-1}, whereas the corresponding $P(OPh)_3$ derivative shows bands at 2124, 2077 and 2064 cm^{-1}. It is also interesting to note that the strained cyclic phosphite derivative, $(ETPB)Ru(CO)_3(SiCl_3)_2$, shows very high carbonyl stretching frequencies (2133, 2089, and 2068 cm^{-1}). It has previously been reported[51] that increasing constraints in the ligand cause a decrease in electron density at the metal and an increase in the carbonyl stretching frequency. On examining Table VI, it becomes apparent that the carbonyl stretching frequencies in $Ph_3ERu(CO)_3(SiCl_3)_2$ (E = P, As, Sb) are nearly independent of the nature of E. But it has previously been reported[42] that the M-E bond strengths can be very different and generally fall rapidly in the order of P>As>Sb>Bi. Attempts to prepare $BiPh_3$ derivative were unsuccesful due to thermal instability of the compound.

^{31}P N.M.R. DATA

The ^{31}P chemical shifts of the complexes $R_3ERu(CO)_3(SiCl_3)_2$ (E = P) and free ligands are given in

Table VII. The spectra of all the complexes (except the PF_3 derivative) consisted of a single resonance as expected. It can be seen that there is no general correlation between the ^{31}P chemical shift of the free ligand with its π-acceptor character. This is true for the coordination chemical shifts Δ_{CS} ($\delta_{complex}-\delta_{ligand}$), as well. All the phosphines listed in the table show a downfield shift on coordinating to the metal, wereas phosphites (except ETPB) show an upfield shift.

Previous work with $[Ni(CO)_2(PR_3)_2]$ (R = alkyl, aryl) has shown[52] that, for systems where rehybridization effects are approximately constant and steric effects are unimportant, the coordination shifts (Δ_{CS}) are approximately constant. For such systems, it has been suggested that the downfield shift on coordination is mainly due to the strong σ bond from phosphorus to metal with dπ-dπ contributions being either small or constant.[52] The lowfield chemical shift is thought to be a function of the opening of the angles between the substituents, on forming the σ bond. Similar results are observed for the present molecules of the type $R_3PRu(CO)_3(SiCl_3)_2$. However, the o-tolyl complex (o-tolyl)$_3PRu(CO)_3(SiCl_3)_2$ shows a smaller coordination shift when compared to all the other derivatives of this type. This is not surprising since it has previously been shown that, for ligands with larger cone angles, the angle opening on coordination is smaller when compared to small ligands.

Tolman[48] has used a method based on infrared spectroscopic measurements to determine the donor-acceptor properties

TABLE VII

Phosphorus n.m.r. Data for $R_3PRu(CO)_3(SiCl_3)_2$ Complexes (in CH_2Cl_2)

Ligand	δ_{ligand}(ppm)	$\delta_{complex}$(ppm)	Δ_{CS}(ppm)[a]
$P(OEt)_3$	-137.8	-116.6	+21.2
$P(OMe)_3$	-140.3	-123.4	+16.9
$P(OPh)_3$	-127.4	-119.2	+ 8.2
ETPB	- 92.5	-119.7	-27.2
PPh_3	+ 6.1	- 22.9	-29
PPh_2Me	+ 27.8	- 2.2	-30
PMe_2Ph	+ 46.4	+ 14.2	-32.2
$(o\text{-}C_6H_4CH_3)_3P$	+ 30.8	+ 13.5	-17.3
$(C_6H_{11})_3P$	- 10.2	- 37.9	-27.7
PF_3	- 97*	-126.9[b]	-29.9
$(n\text{-}C_4H_9)_3P$	+ 31.8	+ 5.2	-26.6

* Reported in literature

[a] Δ_{CS} is the coordination chemical shift, defined as $\delta_{complex} - \delta_{ligand}$, where $\delta_{complex}$ and δ_{ligand} are the chemical shifts of the complexed and free ligand, respectively

[b] In $CDCl_3$ solution

of 70 phosphorus containing ligands. $P(cyclohexyl)_3$ was second in order on this scale of donor-acceptor strength, whereas PF_3 was the seventieth (i.e. the highest). However, the results given in Table VII show that the downfield shift Δ_{CS} of the ^{31}P resonance is almost exactly the same for both $P(C_6H_{11})_3$ or PF_3 complexes. Phosphites, which are from 40-60 on Tolman's scale, show an upfield shift of the ^{31}P resonance on coordinating to the ruthenium atom. From these observations, it may be concluded that any interpretation of ^{31}P Δ_{CS} values based upon increase or decrease of the σ-π properties of the phosphorus ligand is very tenuous. The fact that ETPB (4 - ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane) shows a downfield shift on coordination further shows that secondary effects are responsible for the chemical shifts observed. The change in hybridization, with its increase in the phosphorus-non-metal substituents angles, could be responsible for the behavior of chemical shifts.

^{31}P n.m.r. of the PF_3 derivative $F_3PRu(CO)_3(SiCl_3)_2$ (without fluorine decoupling) showed a simple quartet due to P-F coupling with a J_{P-F} value of 1380 Hz. The ^{19}F decoupled spectrum of the same compound gave a singlet at -126.9 ppm (Figure 8).

3.1.2 BIS (PHOSPHINE/PHOSPHITE) DERIVATIVES

The reaction of *cis*-$Ru(CO)_4(SiCl_3)_2$ with an excess of

Figure 8

^{31}P Nuclear Magnetic Resonance Spectrum of $(F_3P)Ru(CO)_3(SiCl_3)_2$.

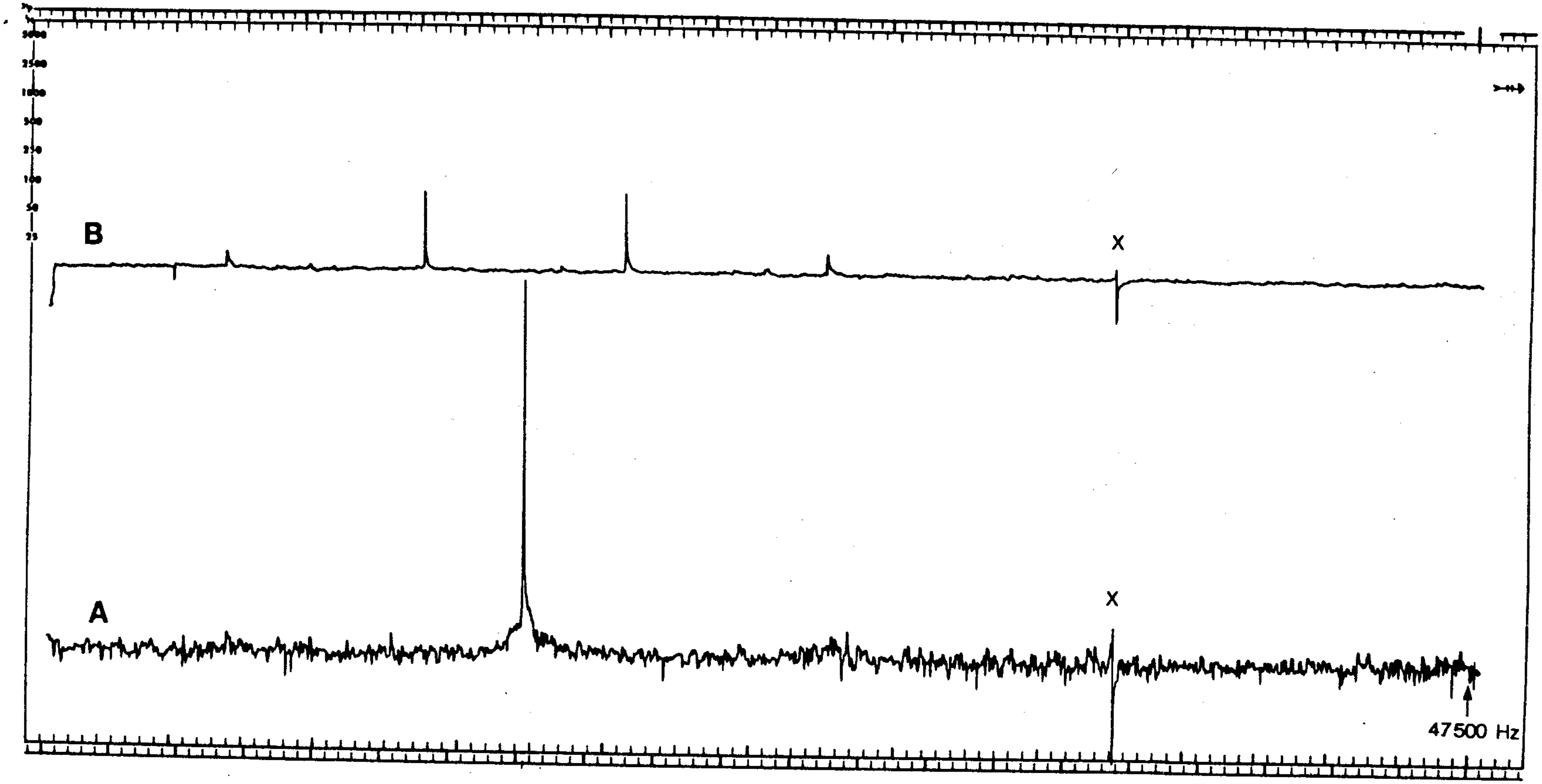
A. With ^{19}F Decoupling

B. Without ^{19}F Decoupling

Sweep Width: 10000 Hz

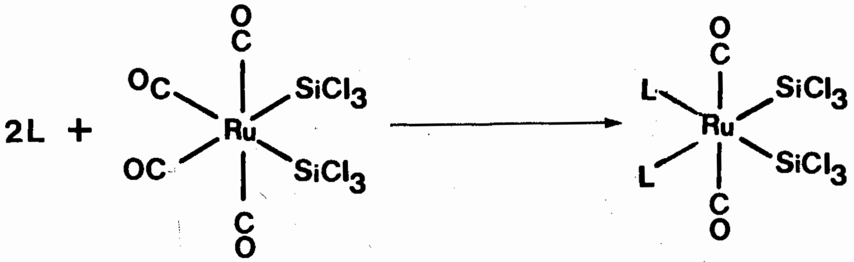
Solvent : $CDCl_3$

External Standard: H_3PO_4

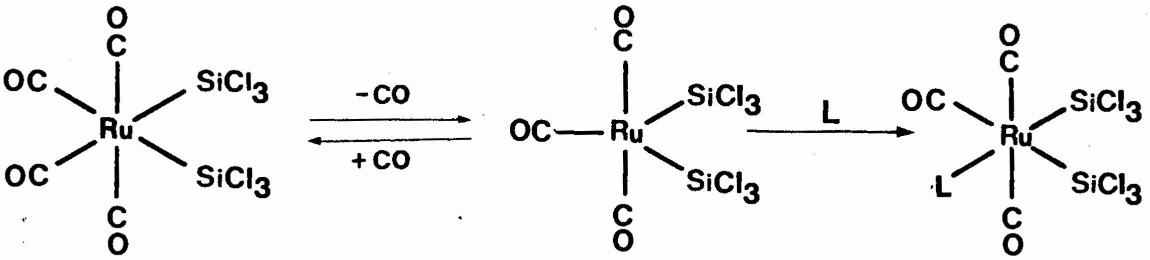


X - GLITCH

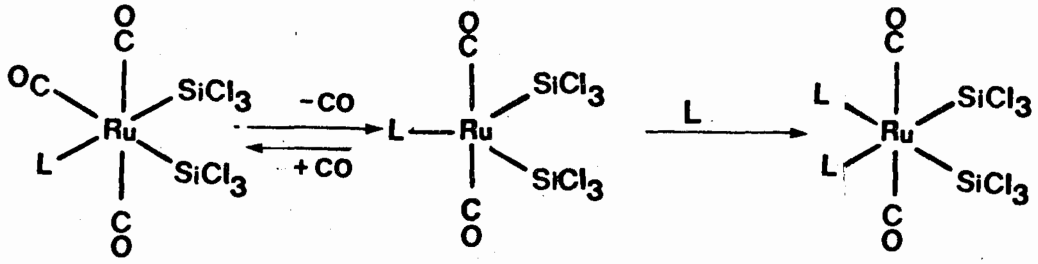
the ligands PR_3 or $P(OR)_3$ produced compounds of the type $L_2Ru(CO)_2(SiCl_3)_2$ ($L = P(OR)_3$ or PR_3)



The phosphines $P(n\text{-}C_4H_9)_3$, PMe_2Ph, $PMePh_2$ and the phosphites $P(OMe)_3$, $P(OEt)_3$, ETPB reacted with *cis*-$Ru(CO)_4(SiCl_3)_2$ when the solutions were heated at 50° C overnight. The reactions of tri-cyclohexyl phosphine and triphenyl phosphite with *cis*-$Ru(CO)_4(SiCl_3)_2$ were very slow even at 80° C, although larger ligands are expected to labilize the remaining equatorial carbonyl group in $LRu(CO)_3(SiCl_3)_2$ to a greater extent. It may be that CO evolved during the reaction competes with the ligand for the five coordinate intermediate $LRu(CO)_2(SiCl_3)_2$.



continued



Subsequent work has shown[a] that the remaining carbonyl group in $(PhO)_3PRu(CO)_3(SiCl_3)_2$ undergoes substitution with $P(OMe)_3$ at room temperature. This suggests that, with $P(OPh)_3$, the *bis* derivative should be formed under mild conditions if carbon monoxide is removed. In both of these cases ($P(OPh)_3$ and PCy_3), the reaction went to completion only in the presence of a large excess of the ligand. Triphenyl phosphine and tri o-tolyl phosphine did not give the *bis* substituted derivatives even at higher temperatures, indicating that the bonding ability of a ligand depends on the other groups present. Although PPh_3 did not form the *bis* derivative $(Ph_3P)_2Ru(CO)_2(SiCl_3)_2$, the monosubstituted derivative $Ph_3PRu(CO)_3(SiCl_3)_2$ reacted readily with $P(OMe)_3$ when a solution in CH_2Cl_2 was stirred at room temperature, giving the mixed phosphine derivative $(MeO)_3P(Ph_3P)Ru(CO)_2(SiCl_3)_2$. This illustrates the large *cis* labilizing effect[39,40] of the PPh_3 group on the remaining CO group. However, when a solution of $Ph_3PRu(CO)_3(SiCl_3)_2$ was heated to 50° C, with an exess of $P(OMe)_3$, the pure *bis* trimethylphosphite derivative was formed, i.e. $[(MeO)_3P]_2Ru(CO)_2(SiCl_3)_2$.

All the compounds described here are white, moderately

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[a] Personal communication, Ms. Karen Egan, Department of Chemistry, S.F.U.

air stable (except the PCy_3 derivative), crystalline solids. The analytical results are given in Table VIII.

INFRARED SPECTROSCOPIC DATA

Infrared data for the series of complexes of the type $L_2Ru(CO)_2(SiCl_3)_2$ are given in Table IX. All the compounds show a single band (Fig. 9) in the carbonyl region [1900-2200 cm^{-1}], consistent with the *trans* arrangement of the carbonyl groups. Although the carbonyl stretching frequencies of the monosubstituted derivatives were explained purely in terms of the electronic parameters, the results obtained for certain *bis* complexes could not be explained in this manner. For example, the complexes of the ligands with large cone angles [$P(OPh)_3$,$P(C_6H_{11})_3$] showed lower carbonyl stretching frequencies than expected.

The expected order of $\nu(CO)^S$ on the basis of electronic parameter is:

PF_3>ETPB>$P(OPh)_3$>$P(OMe)_3$>$P(OEt)_3$>PPh_2Me>$PPhMe_2$>$P(n\text{-}C_4H_9)_3$>PCy_3.

The observed order was:

PF_3>ETPB>$P(OMe)_3$>$P(OEt)_3$>$PPhMe_2$>PPh_2Me>$P(n\text{-}C_4H_9)_3$>$PCy_3 \sim P(OPh)_3$.

The extremely low carbonyl stretching frequency of the triphenyl phosphite derivative may be due to the distortion of the octahedron caused by the large $P(OPh)_3$ groups. This may cause the bending of the two axial carbonyl groups away from the bulky phosphite groups.

TABLE VIII

Analytical Data for $L_2Ru(CO)_2(SiCl_3)_2$ Complexes

Ligand (L)	%C		%H	
	Calcd.	Found	Calcd.	Found
PF_3	4.00	4.16	0.00	0.00
ETPB	22.41	21.22	2.96	2.91
$P(OPh)_3$	43.61	43.64	2.98	2.93
$P(OMe)_3$	14.35	14.56	2.69	2.57
$P(OEt)_3$	22.18	22.39	3.99	3.91
PPh_2Me	40.66	39.17	3.17	3.17
$PPhMe_2$	30.78	31.68	3.16	3.52
$P(n-C_4H_9)_3$	37.60	37.78	6.55	6.53

TABLE IX

Infrared Data for $L_2Ru(CO)_2(SiCl_3)_2$ Complexes

Ligand (L)	$\nu(CO)$ cm^{-1} CH_2Cl_2 soln.
PF_3	2078[x]
ETPB	2046
$P(OPh)_3$	1986
$P(OMe)_3$	2026
$P(OEt)_3$	2023
PPh_2Me	2000
$PPhMe_2$	2002
$P(n\text{-}C_4H_9)_3$	1999
$P(C_6H_{11})_3$	1986

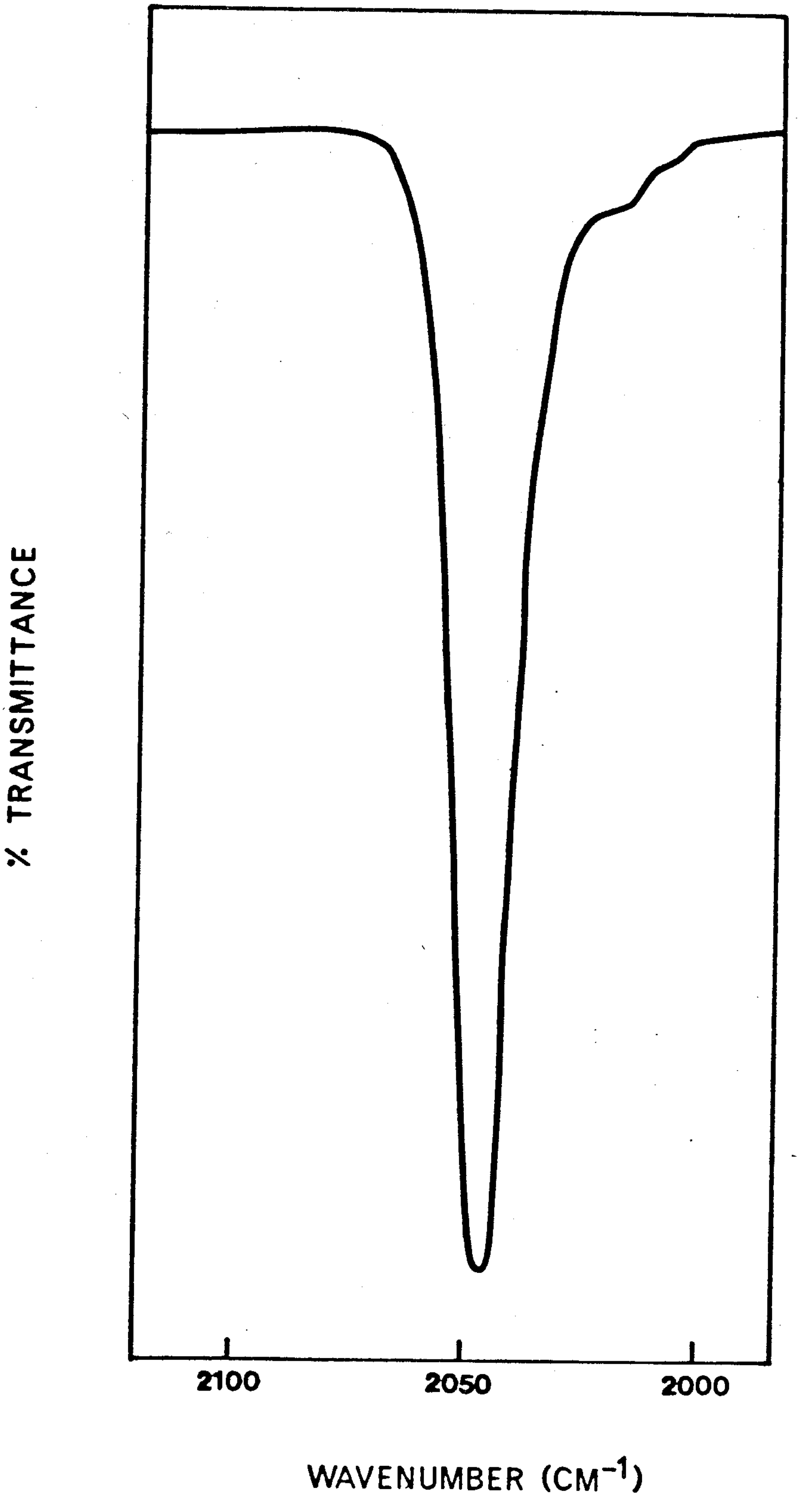
[x] In hexane solution

Figure 9

Infrared Spectrum of $(ETPB)_2Ru(CO)_2(SiCl_3)_2$

In the Carbonyl Stretching Region

Solvent - CH_2Cl_2


% TRANSMITTANCE
2100
2050
2000
WAVENUMBER (CM^{-1})

^{31}P N.M.R. SPECTROSCOPIC DATA OF $L_2Ru(CO)_2(SiCl_3)_2$

The phosphorus n.m.r. spectra of these complexes (taken at ambient temperatures) consists of a single resonance, establishing that in each case the two phosphorus donor atoms are equivalent. This is consistent with the *cis* arrangement of the ligands in an equatorial plane, as indicated by the infrared spectroscopic data (single stretching mode in the carbonyl region).

The coordination chemical shifts of all the complexes (Table X) exhibit the same trend shown by the monosubstituted derivatives. The phosphites $P(OEt)_3$, $P(OMe)_3$ show upfield shifts which are smaller in magnitude when compared to the corresponding monosubstituted derivatives. This may be due to the lower flexibility of the phosphites in *bis* complexes. Triphenyl phosphite shows an upfield shift comparable to the shift observed for the monosubstituted derivatives.

The downfield shift observed for *bis* phosphine complexes [except the cyclohexyl phosphine derivative] show a constancy, resembling the monosubstituted derivatives. The extremely small coordination shifts (-16.9 ppm) of the tri-cyclohexyl phosphine derivative when compared to others could be explained in terms of the steric parameters of the ligand, i.e. the larger ligands are thought to show less rehybridization effects, and hence exhibit smaller coordination shifts on coordinating to the metal.

The ^{31}P n.m.r. spectrum of the PF_3 derivative

TABLE X

Phosphorus N.M.R. Data for $(R_3P)_2Ru(CO)_2(SiCl_3)_2$ Complexes in CH_2Cl_2 (relative to H_3PO_4)

Ligand	δ_{ligand}(ppm)	$\delta_{complex}$(ppm)	Δ_{CS}[a]
$P(OEt)_3$	-137.8	-123.6	+ 14.2
$P(OMe)_3$	-140.3	-130.2	+ 10.1
$P(OPh)_3$	-127.4	-117.4	+ 10.0
ETPB	- 92.5	-125.3	- 32.8
PPh_2Me	+ 27.8	- 2.9	- 30.7
PMe_2Ph	+ 46.4	+ 9.4	- 37.0
$(C_6H_{11})_3P$	- 10.2	- 27.1	- 16.9
F_3P	- 97*	-129.6 [b]	- 32.6
$(n\text{-}C_4H_9)_3P$	+ 31.87	0.0	- 31.87

* reported in literature

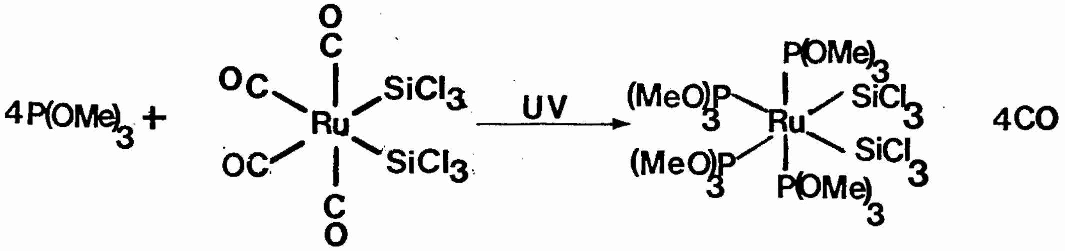
[a] $\Delta_{CS} = \delta_{complex} - \delta_{ligand}$

[b] In $CDCl_3$ solution

$(F_3P)_2Ru(CO)_2(SiCl_3)_2$ [Fig. 10] was essentially similar to that of the monosubstituted derivative, with the phosphorus-fluorine coupling constant being 1360 Hz. Unlike the monosubstituted derivative, each component of the quartet showed hyperfine splitting due to long range couplings (J_{PMPF} and J_{PP}). The values of these coupling constants could not be measured due to poor resolution. The fluorine decoupled spectrum of the same compound showed a broad signal (due to incomplete decoupling) at -129.6 ppm, confirming the *cis* arrangement of the two PF_3 groups. The ^{19}F n.m.r. spectrum of this complex (Fig. 11) consisted of a doublet, each component showing hyperfine splitting due to long range couplings.

3.1.3 $Ru[P(OMe)_3]_4(SiCl_3)_2$

Ultraviolet irradiation of a solution containing *cis*-$Ru(CO)_4(SiCl_3)_2$ and a large excess of $P(OMe)_3$ (in a quartz Carius tube) produced the tetrasubstituted derivative $Ru[P(OMe)_3]_4(SiCl_3)_2$.



The product showed no infrared absorptions in the carbonyl region as expected. The identity of the product was based on elemental analysis. Further study could not be carried out due to the very poor yield of the product.

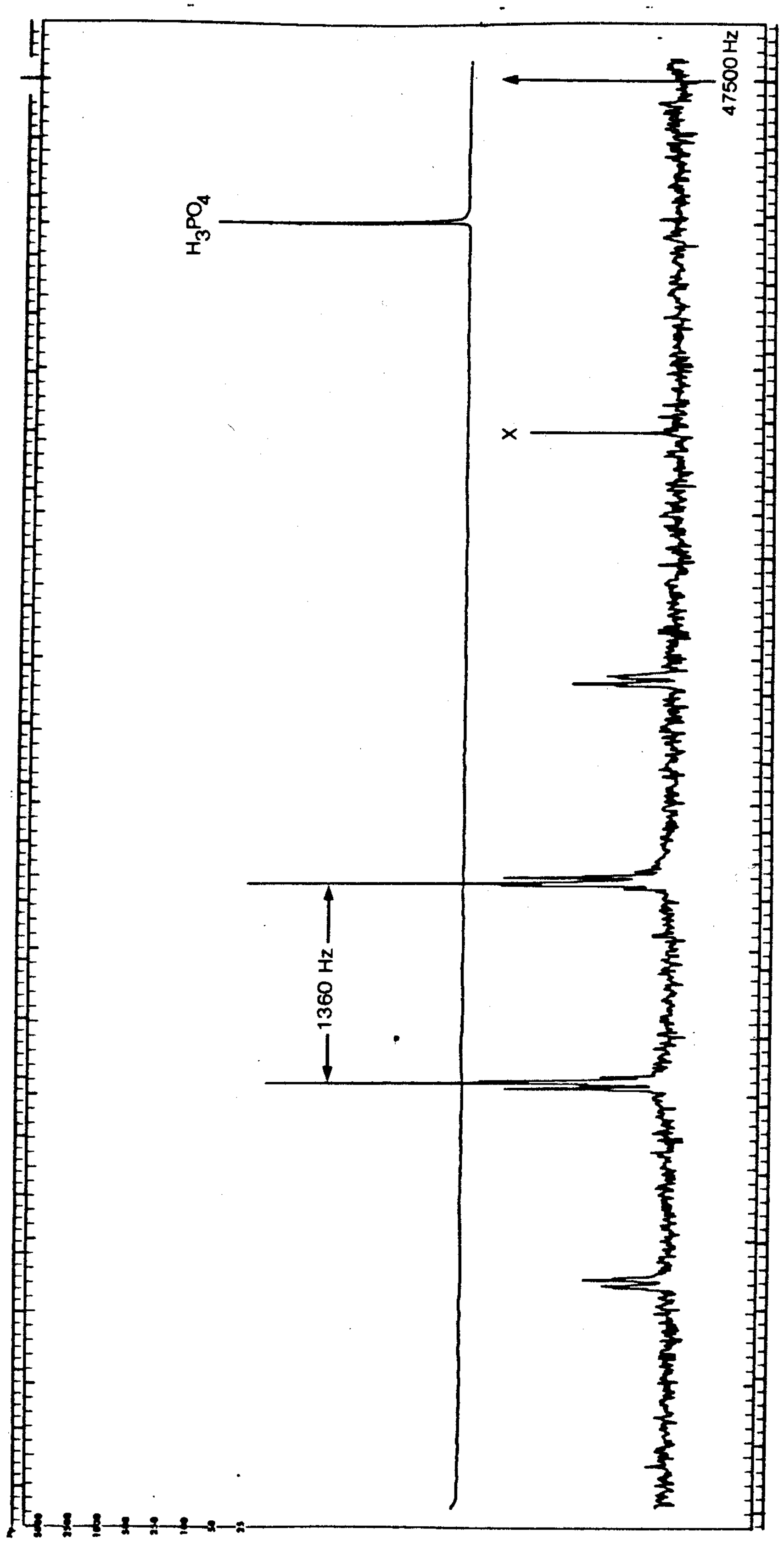
Figure 10

^{31}P Nuclear Magnetic Resonance Spectrum of $(F_3P)_2Ru(CO)_2(SiCl_3)_2$.

Sweep Width: 10000 Hz

Solvent: $CDCl_3$

External Standard: H_3PO_4



X - GLITCH

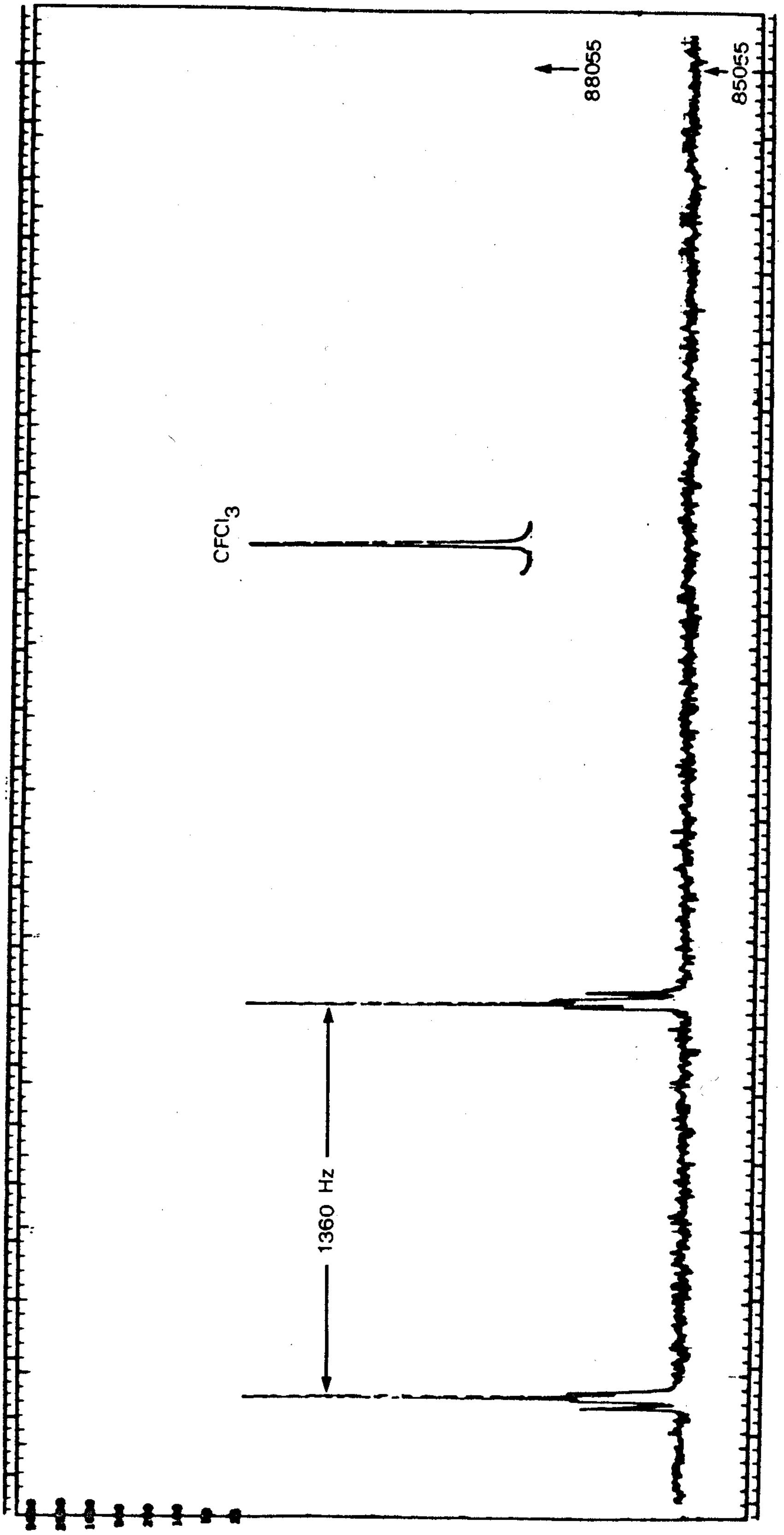
Figure 11

^{19}F Nuclear Magnetic Resonance Spectrum of $(F_3P)_2Ru(CO)_2(SiCl_3)_2$.

Sweep Width: 5000 Hz

Solvent: $CDCl_3$

External Standard: $CFCl_3$


CFCl$_3$
1360 Hz
88055
85055

3.2 EXPERIMENTAL SECTION

The physico-chemical measurements are described in Chapter II of this thesis. Unless otherwise stated, the reactions for the synthesis of the monosubstituted derivatives were carried out under a carbon monoxide atmosphere and those for the *bis* derivatives under a nitrogen atmosphere. (Some of the monosubstituted derivatives were first prepared by Dr. R.K. Pomeroy.)

3.2.1 PREPARATION of (o-tolyl)$_3$PRu(CO)$_3$(SiCl$_3$)$_2$

A solution of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ (0.297 g, 0.616 mmol) and tri-o-tolyl phosphine (0.19 g, 0.624 mmol) in hexane (20 mL) was stirred at room temperature in a schlenk tube for 8 h. The infrared spectrum taken after this time showed only the product (three infrared bands at 2111, 2066 and 2041 cm^{-1}). The white solid (o-tolyl)$_3$PRu(CO)$_3$(SiCl$_3$)$_2$ (0.416 g, 89.4%) was separated from the mother liquor, washed with two 10 mL portions of n-hexane and dried on the vacuum line. The analytical sample was recrystallized from dichloromethane and n-hexane under a carbon monoxide atmosphere. The purity of the product was checked by elemental analysis. (^{31}P n.m.r. of the product showed a singlet at +13.5 ppm.)

3.2.2 PREPARATION OF (n-C$_4$H$_9$)$_3$PRu(CO)$_3$(SiCl$_3$)$_2$

A solution of n-butyl phosphine (0.1 g, 0.495 mmol) and *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ (0.20 g, 0.42 mmol) in hexane (20 mL) was stirred at room temperature for 8 h. as in the previous experiment. The reaction mixture was then stored in the refrigerator for the complete precipitation of the product. The supernatant liquid was removed from the white solid $(n\text{-}C_4H_9)_3PRu(CO)_3(SiCl_3)_2$ (0.23 g, 83%), which was further washed with two 5 mL portions of cold n-hexane and dried on the vacuum line. The analytical sample was obtained by recrystallizing the product with CH_2Cl_2-n-hexane under a carbon monoxide atmosphere. The infrared spectrum of the product showed three bands (2112w, 2062m, 2044s) as expected.

The ^{31}P n.m.r. spectrum exhibited a singlet at +5.24 ppm.

3.2.3 PREPARATION OF $(C_6H_{11})_3PRu(CO)_3(SiCl_3)_2$

A solution containing *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.26 g, 0.53 mmol) and $(C_6H_{11})_3P$ (0.15 g, 0.536 mmol) was stirred at room temperature for 8 h. and worked up in a manner simlar to that described in the section 3.2.1. The yield of the crude product was almost quantitative. The analytical sample was recrystallized from CH_2Cl_2-n-hexane.

The ^{31}P n.m.r. spectrum of the product showed a single resonance at -37.9 ppm.

3.2.4 PREPARATION OF $(ETPB)Ru(CO)_3(SiCl_3)_2$

The synthetic procedure was essentially that given for other derivatives. The analytical sample was recrystallized from CH_2Cl_2-n-hexane. The product showed three infrared bands in the carbonyl region (2133w, 2089m, 2068s) and a single resonance at -119.7 ppm in the ^{31}P n.m.r. spectrum.

3.2.5 PREPARATION OF $F_3PRu(CO)_3(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.199g, 0.412 mmol) in hexane in a sealed Carius tube (fitted with a teflon valve) was cooled in liquid N_2 and evacuated. The solution was then pressurized with 2 atmosphere of PF_3 and stirred at room temperature for 7 h. During this period the tube was chilled (in liquid N_2 until all the PF_3 was frozen) and evacuated every hour to remove any carbon monoxide evolved during the reaction. The reaction was monitored by taking infrared spectra at regular intervals. The infrared spectrum taken after 7 h. showed three bands corresponding to the pure product. The solution was filtered into a Schlenk tube under carbon monoxide and stored in dry ice for several hours. The solution was then removed from the white crystalline solid $F_3PRu(CO)_3(SiCl_3)_2$ [yield = 0.200 g, 89.4%], which was dried on the vacuum line. The analytical sample was obtained by subliming the solid under vacuum (0.02 mm) onto a probe cooled to 78° C. The purity of the product was checked by elemental analysis, ^{31}P n.m.r. and infrared spectroscopy.

3.2.6. PREPARATION OF $[(MeO)_3P]_2Ru(CO)_2(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ [0.32 g, 0.664 mmol] and trimethylphosphite [0.2 g, 1.6 mmol] in benzene was heated at 50° C for 18 h. The infrared spectrum taken after this time showed only a single band (2026 cm^{-1}) in the carbonyl region, indicating the completion of the reaction. The solution was filtered, an equal volume of hexane added, and stored in the refrigerator to complete precipitation. The mother liquor was removed from the product $[(MeO)_3P]_2Ru(CO)_2(SiCl_3)_2$ [0.40 g, 90%], which was dried on the vacuum line for several hours.

The ^{31}P n.m.r. spectrum of the solid showed a singlet at δ = -130.2 ppm.

3.2.7 PREPARATION OF $[(EtO)_3P]_2Ru(CO)_2(SiCl_3)_2$

The reaction of *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.302 g, 0.626 mmol) with $P(OEt)_3$ (0.21 g, 1.265 mmol) was carried out according to the procedure employed in the previous experiment. The product $[(EtO)_3P]_2Ru(CO)_2(SiCl_3)_2$ (0.33 g, 70%) was recrystallized from CH_2Cl_2-n-hexane. The infrared spectrum of the solid taken in the range of 2200-1900 cm^{-1} showed a single band at 2023 cm^{-1}. ^{31}P n.m.r. - singlet at -123.6 ppm.

3.2.8 PREPARATION OF $(ETPB)_2Ru(CO)_2(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.52 g, 1.08 mmol) and ETPB (0.35 g, 2.16 mmol) in benzene (20 mL) was heated at 50° C for 18 h. and worked up as in the previous experiments. The yield of the product $(ETPB)_2Ru(CO)_2(SiCl_3)_2$ was 74.5% and appeared pure from its infrared spectrum (single band at

2046 cm^{-1}). The analytical sample was recrystallized from CH_2Cl_2-n-hexane. ^{31}P n.m.r. spectrum of the product showed a singlet at -125.3 ppm.

3.2.9 PREPARATION OF $[(n\text{-}C_4H_9)_3P]_2Ru(CO)_2(SiCl_3)_2$

$(n\text{-}C_4H_9)_3P$ [0.4 g, 1.98 mmol] and *cis*-$Ru(CO)_4(SiCl_3)_2$ [0.465 g, 0.096 mmol] in heptane were heated at 50° for 18 h. Dichloromethane was then added dropwise to the reaction mixture until the precipitate was dissolved. The solution was then filtered and stored in the refrigerator to complete precipitation. The mother liquor was decanted from the colorless crystalline solid $[(n\text{-}C_4H_9)_3P]_2Ru(CO)_2(SiCl_3)_2$ (0.537 g, 88.6%) which was washed with two 5 mL portions of cold n-hexane and dried as before. The product was analytically pure and showed a single infrared band in the carbonyl region at 1999 cm^{-1} (CH_2Cl_2 soln.).

^{31}P n.m.r. - singlet at 0.0 ppm.

3.2.10 PREPARATION OF $[Ph_2MeP]_2Ru(CO)_2(SiCl_3)_2$

This compound was prepared in a manner similar to that employed in the previous experiments. The product $(Ph_2MeP)_2Ru(CO)_2(SiCl_3)_2$ (0.591 g, 91.4%) exhibited a single infrared band in the carbonyl region at 2000 cm^{-1}.
^{31}P n.m.r. spectrum showed a single resonance at -2.9 ppm.

3.2.11 PREPARATION OF $[PhMe_2P]_2Ru(CO)_2(SiCl_3)_2]_2$

The reaction of $PhMe_2P$ (0.264 g, 1.91 mmol) with *cis*-$Ru(CO)_4(SiCl_3)_2$ [0.336 g, 0.697 mmol] was carried out as before. The infrared spectrum of the product $[Ph_2MeP]_2Ru(CO)_2(SiCl_3)_2$ [0.402 g, 82.14%] taken in the carbonyl region showed a single band at 2002 cm^{-1}. A ^{31}P n.m.r. spectrum showed a singlet at +9.4 ppm.

3.2.12 PREPARATION OF $[(PhO)_3P]_2Ru(CO)_2(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ [0.253 g, 0.525 mmol] and $P(OPh)_3$ (0.60 g, 1.935 mmol] in benzene (20 mL) was heated in an evacuated sealed tube (fitted with a teflon valve) at 75-80° C for four days. Approximately every twelve hours during this period, the tube was cooled and reevacuated. The reaction was followed by infrared spectrscopy. After four days the reaction mixture was transferred into a Schlenk tube and an equal volume of n-hexane added. It was then placed in the refrigerator overnight for complete precipitation of the product. The supernatant liquid was then removed from the white solid, which was further washed with n-hexane and dried under vacuum. The product $[(PhO)_3P]_2Ru(CO)_2(SiCl_3)_2$ (0.405 g, 74%) showed a single infrared band in the carbonyl region at 1986 cm^{-1}. The analytical sample was recrystallized from CH_2Cl_2-n-hexane.

^{31}P n.m.r. spectrum showed a singlet at -117.4 ppm.

3.2.13 PREPARATION OF $[(C_6H_{11})_3P]_2Ru(CO)_2(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.20 g, 0.415 mmol) and a large excess of tricyclohexylphosphine (0.80 g, 2.8 mmol) in benzene (20 mL) was heated in an evacuated sealed tube at 75-80° C for four days. After this time the tube was cooled and worked up in a manner simlar to that employed for the $P(OPh)_3$ analogue. The yield was very poor due to the decomposition of the product in solution. The product showed a single infrared band in the carbonyl region at 1986 cm^{-1}. Analytically pure sample could not be obtained even after repeated recrystallization.

3.2.14 PREPARATION OF $(F_3P)_2Ru(CO)_2(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.328 g, 0.680 mmol) was placed in an evacuated sealed tube, pressurized with two atmospheres of PF_3, and stirred at room temperature for four days. The tube was cooled in liquid nitrogen and evacuated approximately every 8 h. during this period in order to remove the carbon monoxide released during the reaction. After four days the solution was filtered into a Schlenk tube and cooled to -78° C. The supernatant liquid was removed from the colorless crystalline product $(F_3P)_2Ru(CO)_2(SiCl_3)_2$, which was dried under vacuum. The yield was almost quantitative. The product was purified by subliming under vacuum onto a probe cooled to -78° C.

^{31}P n.m.r. spectrum of the product showed a quartet centered at -129.6 ppm. J_{P-F} = 1360 Hz.

^{19}F n.m.r. spectrum showed a doublet with a J_{P-F} value of 1360.

Attempts to prepare *bis* PPh_3 and $P(o\text{-tolyl})_3$ derivatives were unsuccessful.

3.2.15 PREPARATION OF $[(MeO)_3P]_4Ru(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ and a large excess of $P(OMe)_3$ [1 mL] in an evacuated quartz Carius tube was irradiated for 12 h. The solution was degassed every 2 h. during this period. The infrared spectrum of the solution taken after this time showed no carbonyl bands. The reaction mixture was transferred into a Schlenk tube, added an equal volume of n-hexane, and stored in the refrigerator to complete precipitation. The solid so obtained was recrystallized from dichloromethane and n-hexane.

Elemental analysis: % C Calc. 16.64, Found 16.32
% H Calc. 4.18, Found 3.93

CHAPTER 4

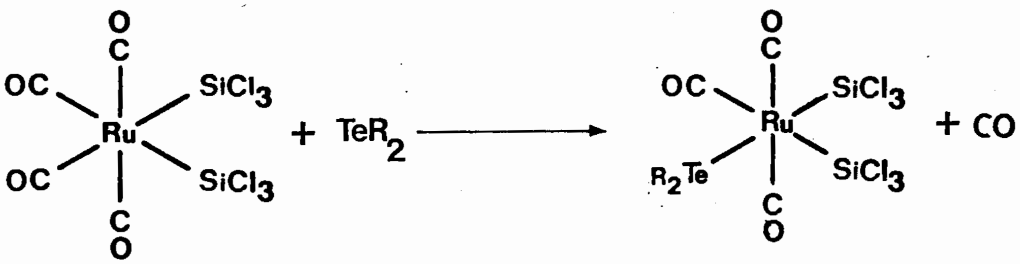
REACTION OF *cis*-$Ru(CO)_4(SiCl_3)_2$ WITH DIORGANO TELLURIDES AND DIORGANO DITELLURIDES

4.1 RESULTS AND DISCUSSION

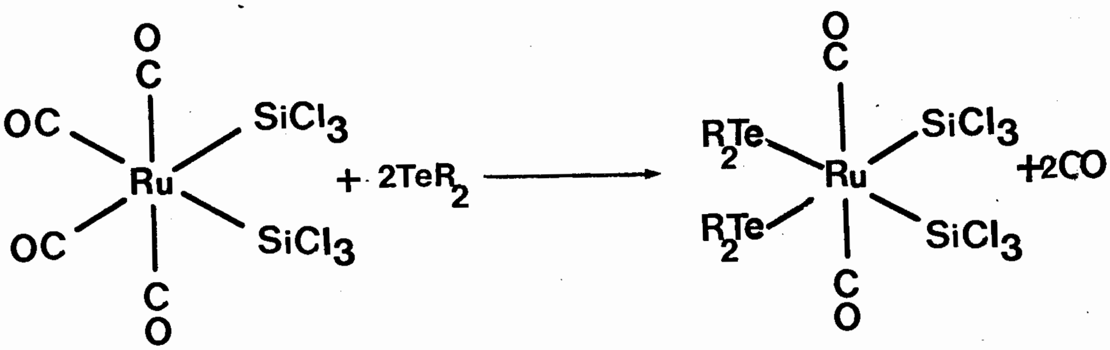
The chemistry governing the interaction of organotellurium donor ligands such as diorganotellurides (TeR_2) and diorganoditellurides (Te_2R_2) with ruthenium has not been well investigated, although the existence of complexes with Ru-Te bonds has been reported previously by Schermer and Baddley.[53] They have shown that the reactions of $Ru_3(CO)_{12}$ with diphenyl diselenide and diphenyl ditelluride produce dinuclear complexes of the type $[Ru(CO)_3EPh]_2$ and the polymeric species $[Ru(CO)_2(EPh)_2]_n$ [E = Se, Te]. In both these types of complexes, the Te-Te bond is broken. Therefore, in addition to investigating the reactivity of the ligands TeR_2 and Te_2R_2 [R = *p*-$OEtC_6H_4$, C_6H_5], it was of interest to study the mode of binding of these ligands to Ru in *cis*-$Ru(CO)_4(SiCl_3)_2$.

4.1.1 Te (p-$OEtC_6H_4$)$_2$ Derivatives

As with other ligands, the reaction of *cis*-$Ru(CO)_4(SiCl_3)_2$ with the diorganotelluride Te(p-$OEtC_6H_4$)$_2$ proceeds smoothly in solution at room temperature to produce $R_2TeRu(CO)_3(SiCl_3)_2$ [R = p-$OEtC_6H_4$].



The product was identified by the characteristic three band infrared spectrum (Figure 12) in the carbonyl region. The resulting white crystalline solid was found to be fairly unstable in solution in the absence of carbon monoxide, resembling other monosubstituted derivatives of the type $LRu(CO)_3(SiCl_3)_2$. However, in the solid state the compound was moderately stable. When the *cis*-$Ru(CO)_4(SiCl_3)_2$ was reacted with a large excess of TeR_2 at higher temperatures (80° C) the *bis* derivative was formed.

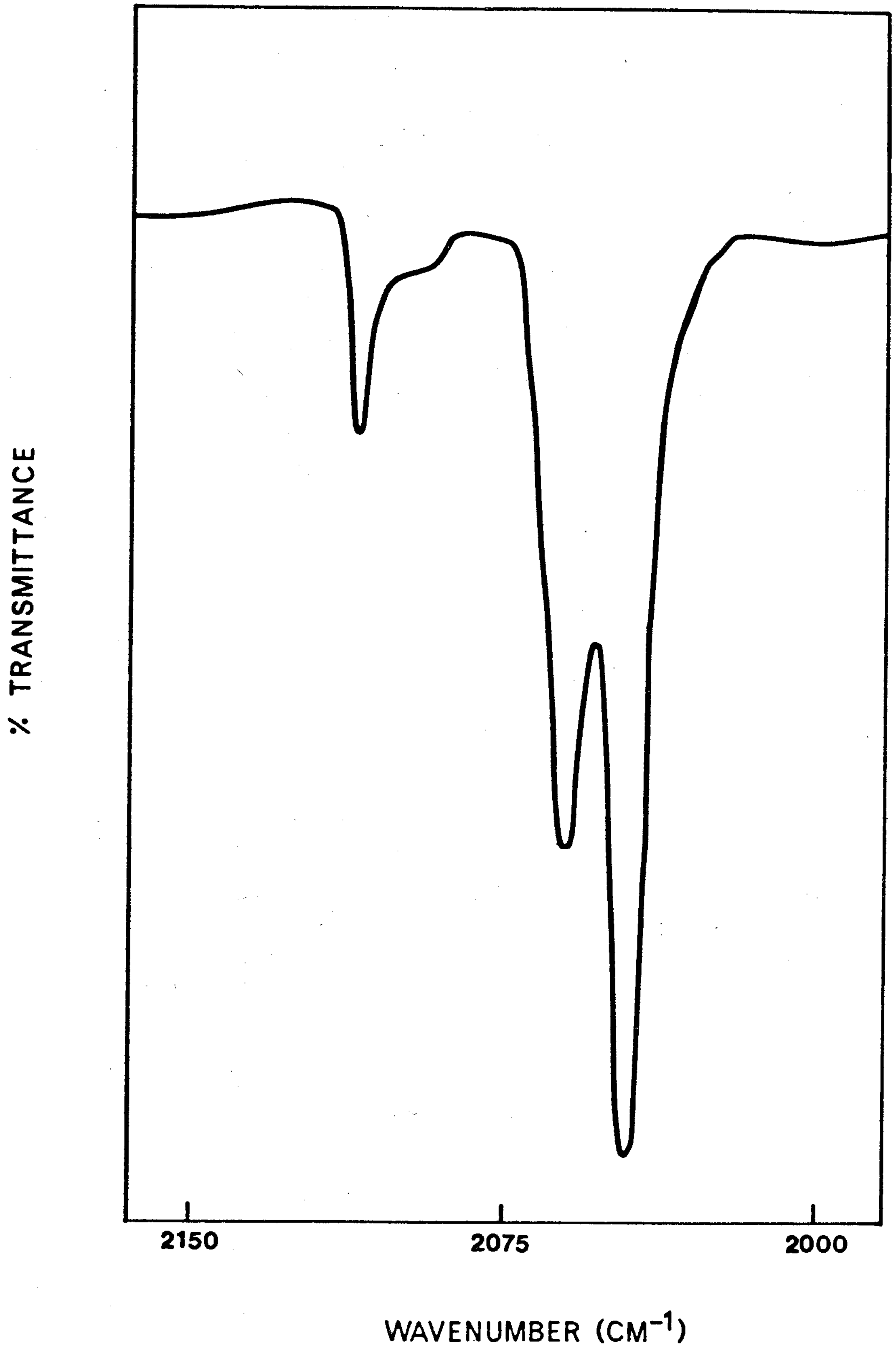


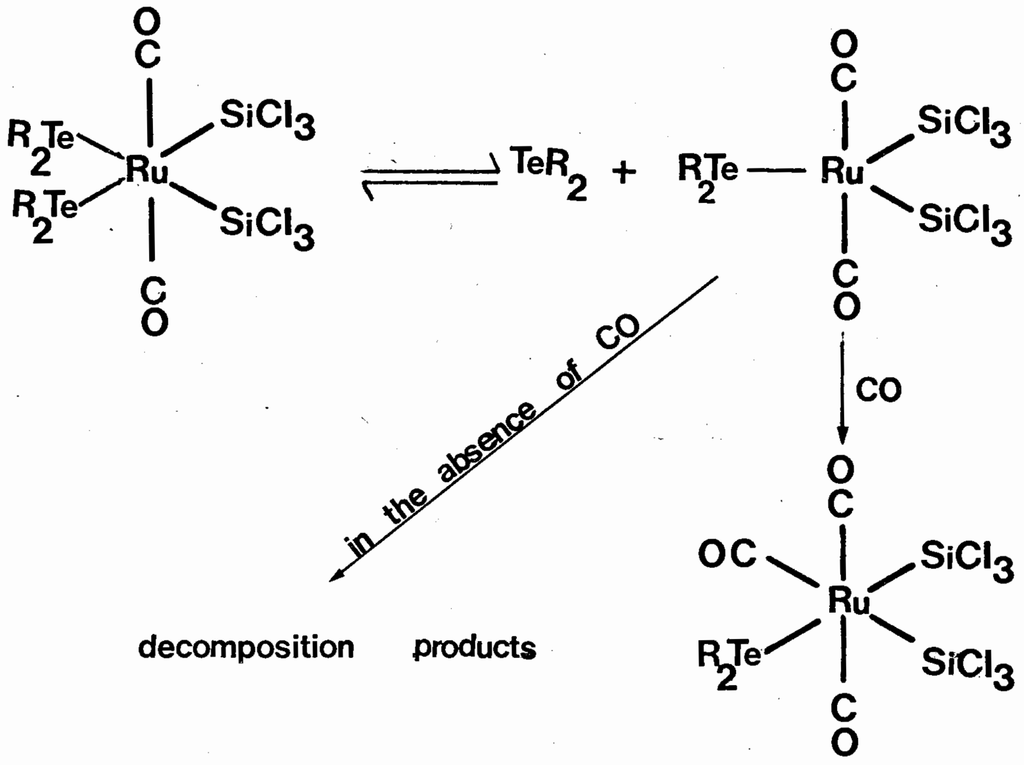
The reaction did not go to completion when the ligand and *cis*-$Ru(CO)_4(SiCl_3)_2$ were used in the ratio of 2:1. In the absence of excess ligand, the product decomposed rapidly in solution. It was also found to undergo substitution with carbon monoxide at room temperature, giving the monosubstituted derivative $R_2TeRu(CO)_3(SiCl_3)_2$.

Figure 12

Infrared Spectrum of $(R_2Te)Ru(CO)_3(SiCl_3)_2$
In the Carbonyl Stretching
Region

Solvent: CH_2Cl_2


% TRANSMITTANCE
2150
2075
2000
WAVENUMBER (CM^{-1})



Like other *bis* derivatives $(R_2Te)_2Ru(CO)_2(SiCl_3)_2$ also showed a single band infrared spectrum (2000 cm $^{-1}$) in the carbonyl region. Both mono and *bis* TeR_2 derivatives were white crystalline solids. The analytical results for these complexes are given in Table XI.

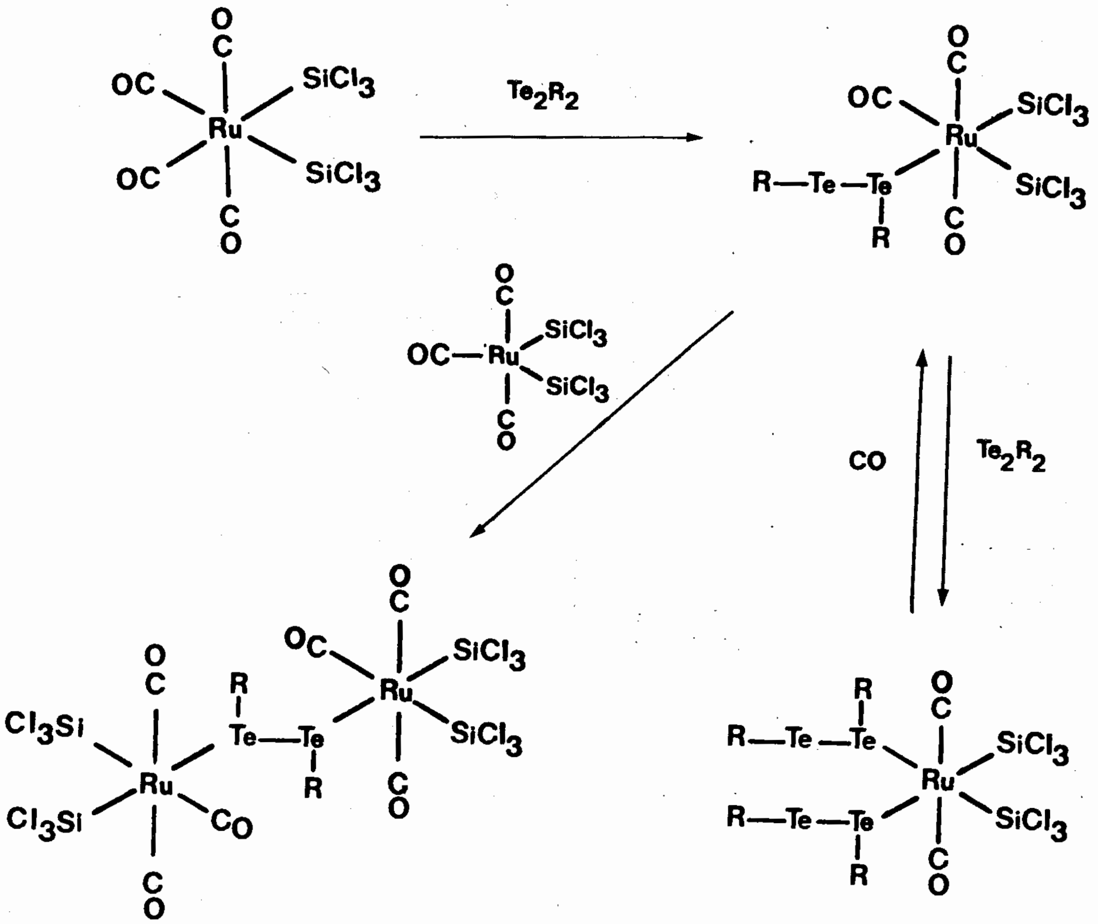
4.1.2 DIORGANO DITELLURIDE DERIVATIVES

The reactions of ditellurides Te_2R_2 [R = p-OEtC_6H_4, C_6H_5] with *cis*-$Ru(CO)_4(SiCl_3)_2$ gave three types of products: $R_2Te_2Ru(CO)_3(SiCl_3)_2$, $(R_2Te_2)_2Ru(CO)_2(SiCl_3)_2$ and $R_2Te_2[Ru(CO)_3(SiCl_3)_2]_2$.

TABLE XI. Analytical Data for Tellurium Derivatives

COMPOUND	%C		%H	
	Calcd.	Found	Calcd.	Found
$(p\text{-}OEtC_6H_4)_2Te_2Ru(CO)_3(SiCl_3)_2$	23.99	24.33	1.91	1.84
*$(p\text{-}OEtC_6H_4)_2Te_2[Ru(CO)_3(SiCl_3)_2]_2$	18.80	18.80	1.30	1.30
$(C_6H_5)_2Te_2[Ru(CO)_3(SiCl_3)_2]_2$	16.41	16.63	0.77	0.77
$(p\text{-}OEtC_6H_4)_2TeRu(CO)_3(SiCl_3)_2$	27.70	27.07	2.20	2.13
$[(p\text{-}OEtC_6H_4)_2Te_2]_2Ru(CO)_2(SiCl_3)_2$	28.74	28.93	2.55	2.50
$[(C_6H_5)_2Te_2]_2Ru(CO)_2(SiCl_3)_2$	25.09	25.63	1.62	1.65
$[(p\text{-}OEtC_6H_4)_2Te_2]_2Ru(CO)_2(SiCl_3)_2$	35.03	35.50	3.11	3.18

* Calcd. % Te = 18.15 Found % Te = 16.7



The extent to which substitution occurs depends on the reaction conditions employed and the quantities of the reagents used.

When a large excess of *cis*-$Ru(CO)_4(SiCl_3)_2$ was reacted with Te_2R_2 (in hexane), the bridged ligand complex $R_2Te_2[Ru(CO)_3(SiCl_3)_2]_2$ was formed. The identity of the product was based on stoichiometry, elemental analysis and infrared spectroscopy. When equimolar proportions of the same reactants were stirred in a solution of CH_2Cl_2, the mononuclear species $R_2Te_2Ru(CO)_3(SiCl_3)_2$ was formed. When a large excess of the ditelluride was used in the above reaction, the *bis* ditelluride derivative $(R_2Te_2)_2Ru(CO)_2(SiCl_3)_2$ was formed.

Unlike the TeR_2 derivatives, all the ditelluride derivatives are colored, intensity being dependent on the degree to which substitution has taken place. Both the dinuclear derivatives $R_2Te_2[Ru(CO)_3(SiCl_3)_2]_2$ [R = p-OEtC$_6$H$_4$ and C_6H_5] were pale yellow in color, whereas the mononuclear species $R_2Te_2Ru(CO)_3(SiCl_3)_2$ was orange-red. The *bis* ditelluride derivatives $(R_2Te_2)_2Ru(CO)_2(SiCl_3)_2$ were deep purple in color. These three types of complexes were distinguished and characterized by infrared spectroscopy (CO stretching frequencies given in Table XII) and elemental analysis (Table XI). The dinuclear complex was found to be relatively stable both in solution and in the solid state compared to the other two types of tellurium derivatives reported here. The *bis* ditelluride derivative was moderately stable in the solid state, but decomposed rapidly in solution. However, in the presence of a large excess of the ligand, it was found to be reasonably stable, resembling the TeR_2 analogue. It also undergoes substitution with carbon monoxide, giving the mono substituted derivative, i.e.

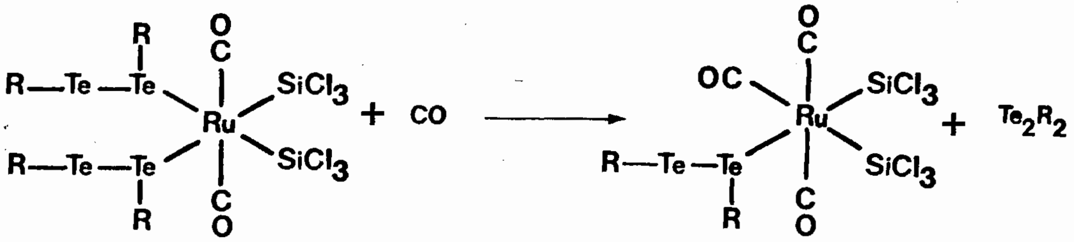
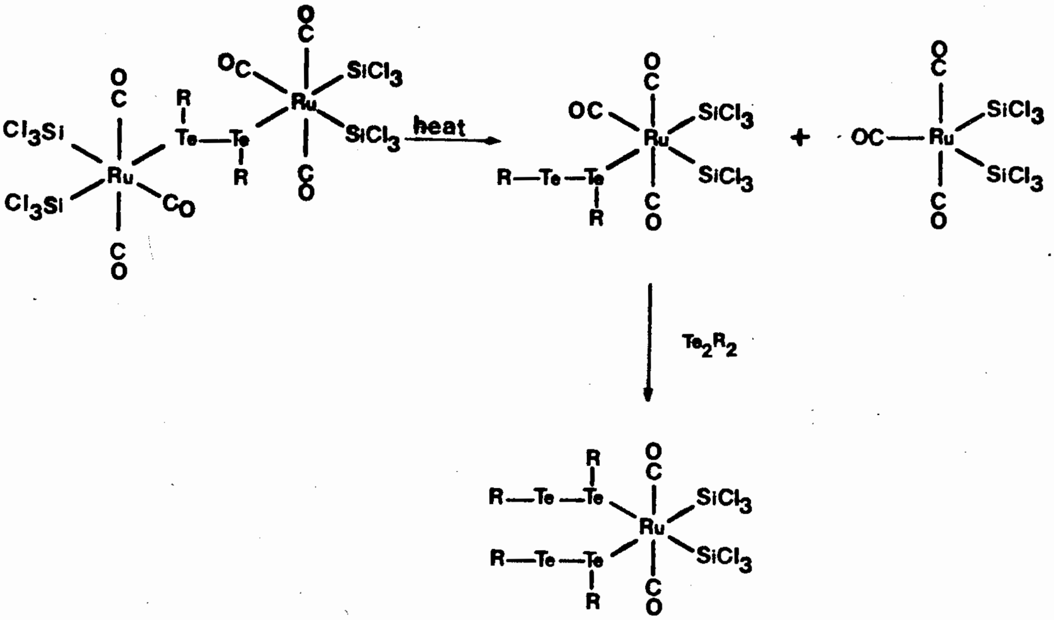


TABLE XII. Infrared Data for Tellurium Derivatives

COMPOUND	ν(CO) cm^{-1} CH_2Cl_2 soln.
$(p\text{-}OEtC_6H_4)_2Te_2Ru(CO)_3(SiCl_3)_2$	2114w, 2065m, 2048s
$(p\text{-}OEtC_6H_4)_2Te_2[Ru(CO)_3(SiCl_3)_2]_2$	2117w, 2066m, 2051s*
$(C_6H_5)_2Te_2[Ru(CO)_3(SiCl_3)_2]_2$	2116w, 2065m, 2050s*
$(p\text{-}OEtC_6H_4)_2TeRu(CO)_3(SiCl_3)_2$	2114w, 2066m, 2046s
$[(p\text{-}OEtC_6H_4)_2Te_2]_2Ru(CO)_2(SiCl_3)_2$	2016
$[(C_6H_5)_2Te_2]_2Ru(CO)_2(SiCl_3)_2$	2014
$[(p\text{-}OEtC_6H_4)_2Te]_2Ru(CO)_2(SiCl_3)_2$	2000

* Medium and strong bands in the lower frequency region were not very well resolved

When a solution of the *bis* ditelluride derivative and a large excess of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ in CH$_2$Cl$_2$ was stirred in a sealed flask, the dinuclear complex R$_2$Te$_2$[Ru(CO)$_3$(SiCl$_3$)$_2$]$_2$ was formed [identified from infrared spectrum and elemental analysis]. The above experimental results are summarized in the scheme given in Figure 13. When the bridged complex was heated with a large excess of the ditelluride over a period of 4 days, the pure *bis* derivative [R$_2$Te$_2$]$_2$Ru(CO)$_2$(SiCl$_3$)$_2$ was formed. The Te-Te bond did not break even under these conditions.

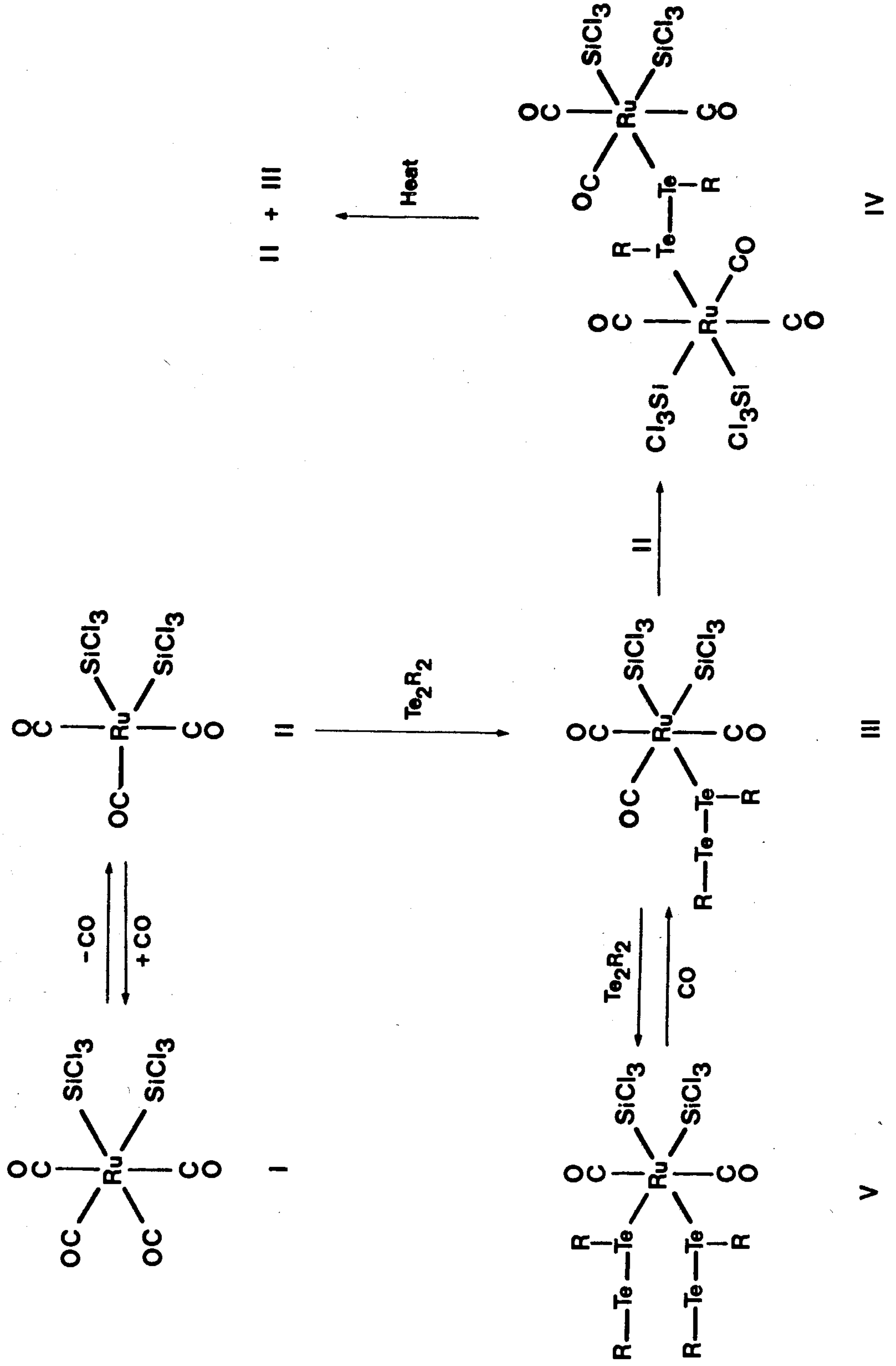


The dinuclear complex [R$_2$Te$_2$][Ru(CO)$_3$(SiCl$_3$)$_2$]$_2$ and the mono-substituted derivative R$_2$Te$_2$Ru(CO)$_3$(SiCl$_3$)$_2$ gave similar infrared spectra in the carbonyl region; they were distinguished

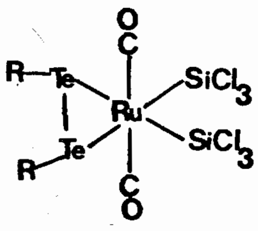
Figure 13

The Reaction Scheme for Ditellurides

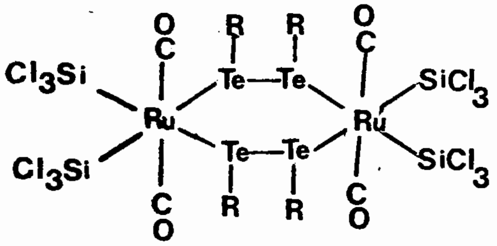
With *cis*-$Ru(CO)_4(SiCl_3)_2$


I
-CO
+CO
II
Te2R2
III
Te2R2
CO
V
II
IV
Heat
II + III

from each other by the elemental analysis and from their yields calculated on the basis of their stoichiometries. In both these types of complexes, the medium and strong carbonyl bands at lower frequencies were not very well resolved. The carbonyl stretching frequencies were similar to that observed for $R_2TeRu(CO)_3(SiCl_3)_2$. The *bis* ditelluride derivatives $(R_2Te_2)_2Ru(CO)_2(SiCl_3)_2$ showed the typical single carbonyl band in the infrared spectrum consistent with a *trans* (axial) arrangement of the carbonyl groups. Although compounds A and B given below would also fit the infrared data, they could be ruled out on the basis of elemental analysis and tellurium n.m.r. data (see below).



A



B

The carbonyl stretching frequencies observed for the ditelluride *bis* derivatives [Ph = 2014, p-OEtC_6H_4= 2016 cm^{-1}] were some 15 cm^{-1} higher than that observed for $Te(p\text{-}OEtC_6H_4)_2$ analogue. It may be that the axial carbonyl groups of the TeR_2 derivatives bend away from the bulky TeR_2 groups causing a decrease in carbonyl stretching frequency.

The proton n.m.r. spectra of the ditelluride derivatives $R_2Te_2Ru(CO)_3(SiCl_3)_2$ [Fig. 14] and $(R_2Te_2)_2Ru(CO)_2(SiCl_3)_2$

[R = p-OEtC_6H_4] support the proposed structures (i.e., III, V).

^{1}H n.m.r. data for (p-OEtC_6H_4)$_2$$Te_2Ru(CO)_3(SiCl_3)_2$

Chemical Shift	Description	Assignment
* 1.41, 1.44	2 triplets J = 7 Hz	CH_3
* 4.0, 4.08	2 quartets J = 7 Hz	CH_2
6.5-8.1	multiplet	aromatic protons

* The chemical shifts given are the centres of each of the two sets of triplets and quartets.

The ^{1}H n.m.r. data given above suggests that the two ethoxy groups of the ditelluride are in slightly different chemical environments and thus agrees with the proposed structure.

The ^{1}H n.m.r. of [(*p*-OEtC_6H_4)$_2$$Te_2$]$_2$$Ru(CO)_2(SiCl_3)_2$ showed a similar pattern, but unlike the monosubstituted derivative, the intensities of the two sets were not the same. The decomposition of some of the *bis* derivative in solution to its free ligand could account for this since the ethoxy groups of the free ligand and the ethoxy group bound to the uncoordinated Te would be expected to have similar chemical environments and similar chemical shifts.

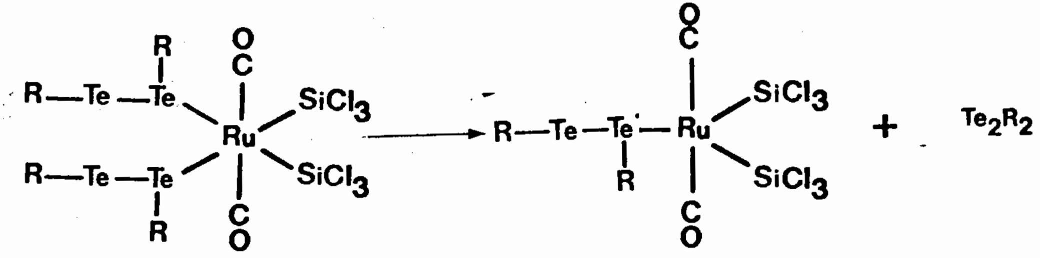


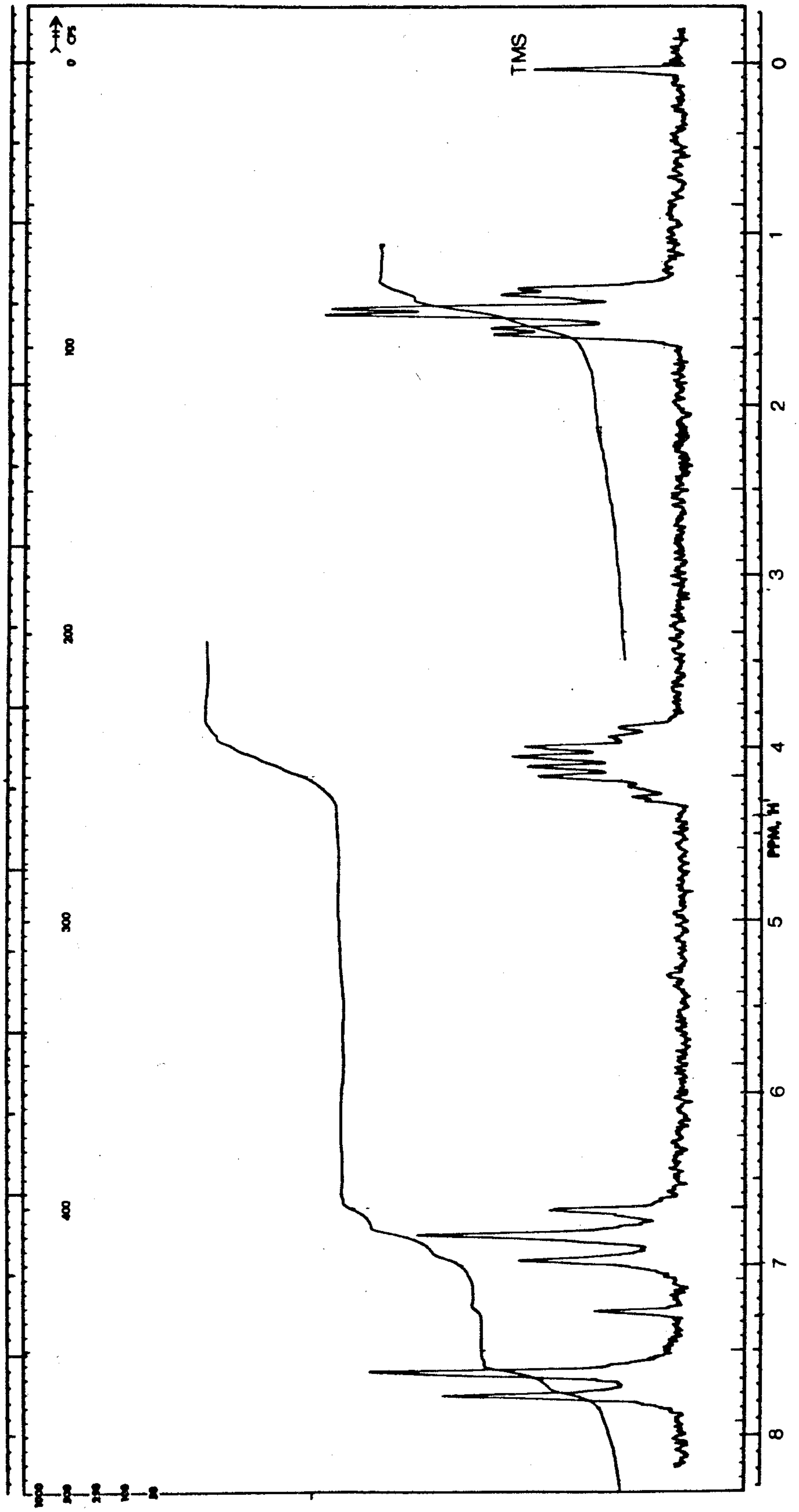
Figure 14

60 MHz Proton Magnetic Resonance
Spectrum of $(p\text{-}OEtC_6H_4)_2Te_2Ru(CO)_3(SiCl_3)_2$

Sweep Width: 500 Hz

Solvent: $CDCl_3$

Internal Standard: TMS

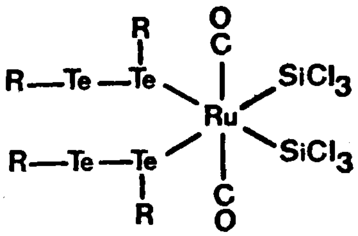


X= CHCl$_3$: ⁚.

This is further supported by the fact that addition of a minute amount of the free ligand increased the intensity of the more intense triplet.

4.1.3 ^{125}Te N.M.R. DATA FOR TELLURIUM DERIVATIVES

The tellurium n.m.r. spectral data for the ditelluride complexes $R_2Te_2Ru(CO)_3(SiCl_3)_2$ and $(R_2Te_2)_2Ru(CO)_2(SiCl_3)_2$ are given in Table XIII. Both of these types of complexes show two telluirum signals, supporting the proposed structures. For example, the *bis* ditelluride derivative $[(p\text{-}OEtC_6H_4)_2Te_2]_2Ru(CO)_2(SiCl_3)_2$ showed two Te signals at -455 and -144 ppm (δ for $TeMe_2 = 0$). Since the free ligand gives a signal at -452.5 ppm, the signal at -455 ppm may be assigned to unbound Te atom and the resonance at -144 ppm to that bound to the Ru.



The monosubstituted derivative $(p\text{-}OEtC_6H_4)_2Te_2Ru(CO)_3(SiCl_3)_2$ showed two signals at -346 ppm and -735 ppm. The signal at -346 may be assigned to the Te bound to the metal and the one at -735 ppm to the free Te. The extremely lowfield chemical

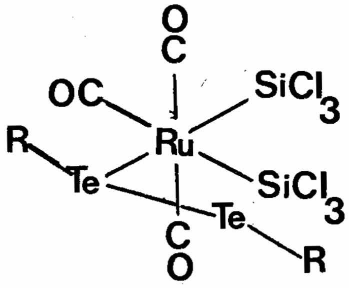
TABLE XIII. ^{125}Te n.m.r. spectroscopic Data of Tellurium Ligands and their Derivatives

COMPOUND	Chemical Shift (δ)* ppm
$Te(p\text{-}OEtC_6H_4)_2$	-644.7
$(p\text{-}OEtC_6H_4)_2TeRu(CO)_3(SiCl_3)_2$	-507.0
$[(p\text{-}OEtC_6H_4)_2Te]_2Ru(CO)_2(SiCl_3)_2$	-556.0
$Te_2(p\text{-}OEtC_6H_4)_2$	-452.5
$[Te_2(p\text{-}OEtC_6H_4)_2]_2Ru(CO)_2(SiCl_3)_2$	-455, -144
$Te_2(p\text{-}OEtC_6H_4)_2Ru(CO)_3(SiCl_3)_2$	-346, -735
$Te_2(C_6H_5)_2$	-434
$[Te_2(C_6H_5)_2]_2Ru(CO)_2(SiCl_3)_2$	-420, -540

* $TeMe_2$ was used as the external standard

$\delta TeMe_2 = 0$

shift observed for the free Te is quite unusual in that the value observed for the free Te in the *bis* derivative was very close to that of the free ligand. It may be that, in the monosubstituted derivative, due to the flexibility of the ligand, the molecule attains a configuration where the uncoordinated tellurium is in fairly close proximity to the chlorine atoms of one of the $SiCl_3$ groups (see below).

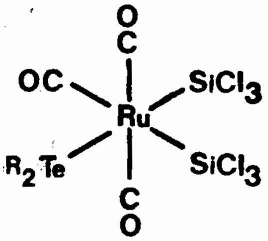


The ^{125}Tellurium n.m.r. spectra of both the TeR_2 derivatives consisted of a broad signal, consistent with the structures predicted. In both the compounds, ^{125}Te shows an upfield shift on coordination to the metal (relative to the free ligand). The shift observed for the monosubstituted derivative was greater than that obsreved for the disubstituted derivative.

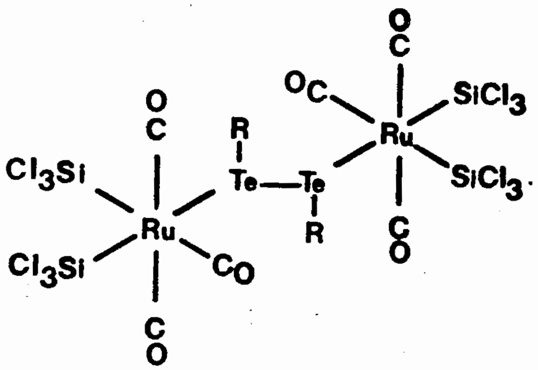
^{125}Te n.m.r. has not been studied very much and the chemical shifts are not fully understood. Due to low abundance of ^{125}Te and solubility problems, the signals observed were very weak. On leaving for longer periods, the compounds decomposed.

4.1.4 MÖSSBAUER SPECTRA OF ORGANO TELLURIUM DERIVATIVES

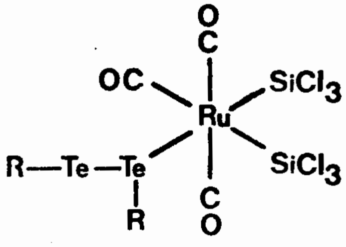
The Mössbauer spectral data of some selected Tellurium derivatives are given in Table XIV. The chemical isomer shifts (δ) of the TeR_2 and Te_2R_2 derivatives are not very informative in understanding the mode of binding of these molecules to ruthenium. However, the quadrupole splittings (Δ) of the TeR_2 derivative $R_2TeRu(CO)_3(SiCl_3)_2$ (I) and the dinuclear complex $R_2Te_2[Ru(CO)_3(SiCl_3)_2]$ (II) suggest that the tellurium atoms in these two complexes are in similar environments. The ditelluride complexes $R_2Te_2Ru(CO)_3(SiCl_3)_2$ (III) and $(R_2Te_2)_2Ru(CO)_2(SiCl_3)_2$ (IV) show approximately similar Δ values and are greater than those observed for previous compounds I and II shown below.



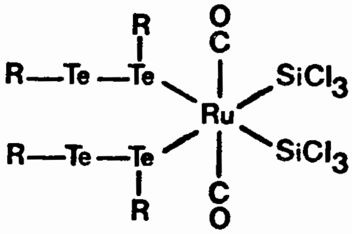
I



II



III



IV

TABLE XIV. Mössbauer Parameters for Tellurium Derivatives

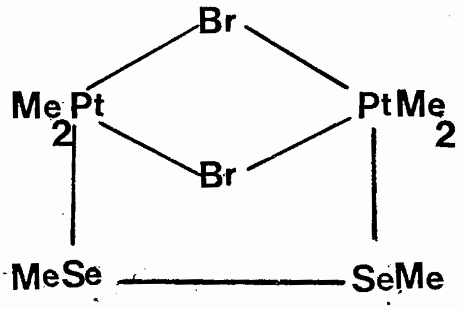
Compound	δ mm s^{-1^x} ±0.08	Δ mm s^{-1} ±0.1	Γ exp mm s^{-1}	
$R_2TeRu(CO)_3(SiCl_3)_2$	0.31	7.2	6.2	
$R_2Te_2[Ru(CO)_3(SiCl_3)_2]_2$	0.22	7.4	5.4	
$(R_2Te_2)Ru(CO)_3(SiCl_3)_2$	0.23	8.6	7.8	
$(R_2Te_2)_2Ru(CO)_2(SiCl_3)_2$	0.34	8.9	7.6	*
	0.39	8.9	6.6	

R = p-OEtC$_6$H$_4$, Γ exp = experimental line width, x = relative to TeR_2

* 2 measurements on independent samples

The reaction of ditelluirdes with transition metal complexes usually gives derivatives in which the Te-Te bond has cleaved. The available data indicates that this has not occurred in the present case. This may be due to the relatively mild conditions employed in the synthesis.

Recent work has shown[54] that the tetrameric bromomethylplatinum $[(Me_3PtBr)_4]$ reacts with dimethyl diselenide (Me_2Se_2) to give a dinuclear species $(PtBrMe_2)_2MeSeSeMe$ in which the Se-Se bond is intact.

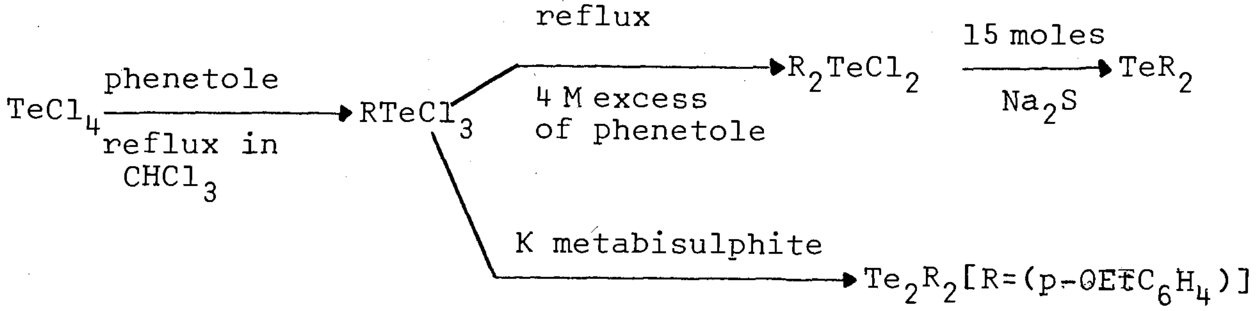


This is the first example of a diselenide in a bridging role.

4.2 EXPERIMENTAL SECTION

4.2.1. PREPARATION OF LIGANDS

The ligands TeR_2 and Te_2R_2 [R = p-OEtC_6H_4] were synthesized[55] from tellurium tetrachloride according to the scheme given below.



PREPARATION OF (p-OEtC_6H_4)$TeCl_3$

$TeCl_4$ (12 g, 0.45 mmol) and phenetole (17 g, .139 mmol) in $CHCl_3$ were refluxed for 2 h. and cooled for several minutes. The resulting pale yellow crystalline solid (quantitative yield) was filtered by suction, washed with $CHCl_3$ and dried under vacuum.

PREPARATION OF Te_2(p-OEtC_6H_4)$_2$

A suspension of (p-OEtC_6H_4)$_2TeCl_3$ (6 g), potassium meta bisulphite (11.3 g) in distilled water (50 mL) was stirred for 3 h at 0° C. A brown red solid formed which was filtered under vacuum, washed with water and recrystallized from hot petroleum ether.

PREPARATION OF $Te(p\text{-}OEtC_6H_4)_2$

$(p\text{-}OEtC_6H_4)_2TeCl_2$ (1.1 g) and hydrated Na_2S (9.0 g) and water (5 mL) were heated on a water bath (~75° C) with stirring until all the R_2TeCl_2 had reacted (15 minutes) leaving a yellow oil. The oil was extracted with two 25 mL portions of ethyl ether and dried over $MgSO_4$. The filtered ether extract was evaporated to dryness and the crude material obtained was recrystallized from hot ethanol to give white crystals of product.

Te n.m.r. -644.7 ppm (relative to $TeMe_2$).

PREPARATION OF R_2TeCl_2(R = $p\text{-}OEtC_6H_4$)

$RTeCl_3$ (2 g) was refluxed with phenetole (8 g) under a nitrogen atmosphere for 6 h. and cooled. Phenetole was removed on the vacuum line and the resulting white solid recrystallized from methanol to give white needles of the product.

PREPARATION OF Te_2Ph_2

Diphenyl ditelluride was prepared according to the method given by Haller and Irgolic.[56] The one step reaction of PhMgBr with elemental tellurium followed by hydrolysis and oxidation of the reaction mixture (with O_2) produced Te_2Ph_2

$$PhMgBr + Te \rightarrow PhTeMgBr$$

$$2PhTeMgBr \xrightarrow{O_2} Ph_2Te_2 + MgBr_2 + MgO$$

4.2.2 PREPARATION OF $(p\text{-}OEtC_6H_4)_2TeRu(CO)_3(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ [0.184 g, 0.381 mmol] and $Te(p\text{-}OEtC_6H_4)_2$ (0.141 g, 0.381 mmol) in hexane was stirred at room temperature for 4 h. The infrared spectrum taken after this time showed only the product (3 carbonyl bands at 2114w, 2066m, 2046s cm^{-1}). Dichloromethane was added dropwise to the reaction mixture until the precipitate dissolved. The solution was then filtered under carbon monoxide and stored in the refrigerator overnight. The solvent was removed from the white, crystalline solid, washed with two 5 mL portions of hexane and dried under vacuum. The product $[(p\text{-}OEtC_6H_4)_2TeRu(CO)_3(SiCl_3)_2$ (yield: 0.196 g, 62.4%) was analytically pure.

The ^{125}Te n.m. r. showed a singlet at -507 ppm (relative to $TeMe_2$).

4.2.3 PREPARATION OF $[(p\text{-}OEtC_6H_4)_2Te]_2Ru(CO)_2(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.283 g, .587 mmol) and $Te(p\text{-}OEtC_6H_4)_2$ (0.55 g, 1.49 mmol) in heptane (20 mL) was heated at 80° C in an evacuated sealed tube for 3 days. The tube was cooled and reevacuated approximately every 8 h. during this period. The infrared spectrum taken after 3 days showed a single band (2000 cm^{-1}) in the carbonyl region corresponding to the pure *bis* derivative. The reaction mixture was transferred to a Schlenk tube under N_2, the mother liquor was removed from the white solid which was washed and dried as before. The analytical sample was obtained as white crystals on recrystallizing from CH_2Cl_2-n-hexane.

^{125}Te n.m.r. showed a singlet at -556 ppm (relative to $TeMe_2$).

4.2.4 PREPARATION OF $[(p\text{-}OEtC_6H_4)_2Te_2]Ru(CO)_3(SiCl_3)_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.35 g, 0.726 mmol) and $Te_2(p\text{-}OEtC_6H_4)_2$ (0.37 g, 0.743 mmol) in dichloromethane (20 mL) was stirred at room temperature for two days under a carbon monoxide atmosphere. The reaction was very slow in the presence of CO but, in the absence of CO, a mixture of mono and *bis* ditelluride derivatives were formed. The solution was filtered under CO, evaporated to half the original volume (using the vacuum line), and an equal volume of n-hexane added. It was then cooled to -78° C overnight. The solution was removed from the orange-red crystals of product which were washed and dried as before. The product $(p\text{-}OEtC_6H_4)_2Te_2Ru(CO)_3(SiCl_3)_2$ (yield 0.445 g, 63%) appeared pure from its infrared spectrum and elemental analysis.

The ^{125}Te n.m.r. showed two signals at -346 and -735 ppm (relative to $TeMe_2$).

4.2.5 PREPARATION OF $[(p\text{-}OEtC_6H_4)_2Te_2]_2Ru(CO)_2(SiCl_3)_2$

A solution containing *cis*-$Ru(CO)_4(SiCl_3)_2$ (0.115 g, 0.239 mmol) and $Te_2(p\text{-}OEtC_6H_4)_2$ (0.334 g, 0.672 mmol) in benzene (20 mL) was heated in an evacuated sealed tube (fitted with a teflon valve) for two days. The tube was cooled and reevacuated every 12 h. during this period. The infrared spectrum taken after this time showed only the product (single carbonyl band at 2016 cm^{-1}). The solution was then removed from the deep purple microcrystalline solid $[(p\text{-}OEtC_6H_4)_2Te_2]_2Ru(CO)_2(SiCl_3)_2$, washed with five 10 mL portions of n-hexane to remove the excess of the ligand and dried under vacuum. The yield of the product (based on the amount of *cis*-$Ru(CO)_4(SiCl_3)_2$ used was 90.9%) and was analytically pure.

^{125}Te n.m.r. showed two singlets at -455 and -144 ppm (relative to $TeMe_2$).

The corresponding diphenyl ditelluride derivative was similarly prepared [yield: 80.9%].

4.2.6 PREPARATION OF $(p\text{-}OEtC_6H_4)_2Te_2[Ru(CO)_3(SiCl_3)_2]_2$

A solution of *cis*-$Ru(CO)_4(SiCl_3)_2$ [0.37 g, 0.76 mmol] and $(p\text{-}OEtC_6H_4)_2Te_2$ [0.135 g, .027 mmol] was heated in an evacuated sealed tube for 4 h at 70° C. The reaction mixture was transferred into a Schlenk tube and worked up in a manner similar to that employed for the $(R_2Te_2)_2Ru(CO)_2(SiCl_3)_2$ derivatives.

The corresponding Ph_2Te_2 derivative was prepared similarly.

The compounds were identified from infrared spectroscopy and elemental analysis. The yields calculated (on the basis of the amount of the ditellurides used) were almost quantitative.

^{125}Te n.m.r. spectroscopic studies were carried out by Dr. C. Lassigne.

The FT n.m.r. high resolution spectra were obtained on a home built, crossed-coil pulse spectrometer operating at 15.06 MHz and equipped with a Nicolet 1082 system. Non-spinning sample tubes 912 min) were used.

Mössbauer spectral measurements were taken by Mr. Marik Dombsky.

The spectra were recorded using Harwell Instrument's constant acceleration drive and liquid helium dewar. The source was ^{125}Sb/Cu.

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