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Synthesis and reactions of organometallic complexes of platinum and palladium

Edward David Dobrzynski
Iowa State University

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Synthesis and reactions of organometallic complexes of platinum and palladium

by

Edward David Dobrzynski

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TABLE OF CONTENTS

ALKOXYCARBONYL AND ALKOXALYL COMPLEXES

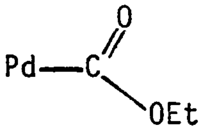
Introduction

Organic reactions which are catalyzed by platinum and palladium are numerous[1], and many of these reactions such as olefin oxidation and oligomerization, carbonylation, vinylation, and specific isomerizations are of industrial importance. The catalyst is usually in the form of the pure metal, the dihalide, e.g. $PdCl_2$, or complexes of M(0) or M(II), where M = Pt or Pd. Although there is little known about the exact mechanisms of these catalyzed processes, it is believed that such fundamental reactions as oxidative-addition[2], CO insertion[1,3], and electrophilic or nucleophilic attack at coordinated organic ligands[4] are often key steps within the catalytic cycle. In this work both the formation and reactivity of specific organometallic complexes of platinum and palladium were studied within the framework of these three basic modes of reaction.

It has been shown that ethanol will react with CO and a base in the presence of $PdCl_2$ to form diethyl carbonate and palladium metal.[5]

$$2EtOH + CO + 2Na_2CO_3 + PdCl_2 \rightarrow (EtO)_2CO + Pd + 2NaCl + 2NaHCO_3 \qquad (1)$$

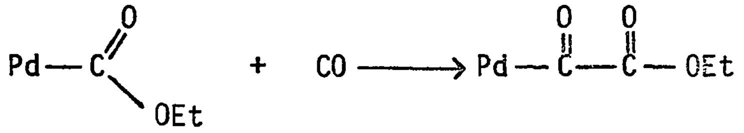
It has been postulated[5] that this reaction proceeds through an unstable ethoxycarbonyl intermediate,



which undergoes nucleophilic attack by ethoxide at the carbonyl carbon atom to yield the product. Recently Fenton and Steinwand[6] have found that $PdCl_2$, together with $CuCl_2$ as a cocatalyst, catalyzes the reaction of ethanol with CO and O_2 to give diethyl oxalate.

$$OH + 2CO + \tfrac{1}{2}O_2 \xrightarrow{PdCl_2,CuCl_2} EtOCOCO_2Et + H_2O \qquad (2)$$

These workers have also postulated that this reaction proceeds through an intermediate ethoxycarbonyl complex, Pd-CO_2Et. Under the high CO pressures employed, this intermediate complex could undergo CO insertion into the metal-carbon bond to form an ethoxalyl ligand.



(3)

The product, diethyl oxlate, could then result from ethoxide attack at the carbonyl group adjacent to the metal.

It is obvious that a study of the formation and reactivity of stable complexes of the type $MCl(CO_2R)L_2$ and $MCl(COCO_2R)L_2$, where M = Pt or Pd and L = a phosphine, could give some insight into the mechanisms of the metal-promoted reactions just described. Stable alkoxycarbonyl complexes of the type $PdCl(CO_2R)L_2$ have been prepared[7,8,9], and this supports the proposed ethoxycarbonyl complex, Pd-CO_2Et, intermediate for the above reactions. The main purpose of our work was to prepare stable Pt(II) and Pd(II) complexes containing alkoxalyl, -$COCO_2$R, ligands and to investigate the reactivity of the alkoxalyl ligand within these complexes. The possible preparation of such complexes according to equation 3 is of considerable interest and importance, and this reaction was also investigated.

Results and Discussion

Syntheses

Preparative methods for alkoxycarbonyl complexes of the type $MCl(CO_2R)L_2$[10], where M = Pt or Pd, R = Me or Et and L = PPh_3 were investigated at the outset of this work. At this time the methoxycarbonyl and ethoxycarbonyl complexes of platinum had been reported.[11] The preparative method used involved the reaction of the known cationic carbonyl complex with the appropriate alcohol.

$$[PtCl(CO)L_2][BF_4] + ROH \xrightarrow{25°} PtCl(CO_2R)L_2 + HBF_4 \qquad (4)$$

This method is inconvenient since it requires the prior preparation of $[PtCl(CO)L_2][BF_4]$.

The preparation of $PdCl(CO_2Et)(PPh_3)_2$ by the oxidative-addition of ethylchloroformate to $Pd(PPh_3)_4$ was reported by Fitton[7] and coworkers in 1968. We employed this type of reaction as a general method for the preparation of alkoxycarbonyl complexes of platinum and palladium.

$$ML_4 + ClCO_2R \longrightarrow MCl(CO_2R)L_2 + 2L \qquad (5)$$

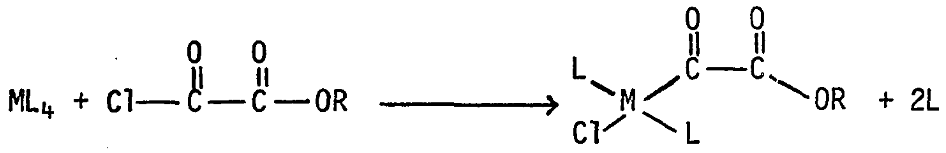
The ethoxycarbonyl complex of palladium[7] is readily formed at room temperature when $ClCO_2Et$ is added to a benzene solution of $Pd(PPh_3)_4$. We've found that the corresponding methoxycarbonyl complex could also be prepared under mild conditions by this method. It was also discovered that these reactions do not proceed readily at room temperature with $Pt(PPh_3)_4$. However, the preparation of alkoxycarbonyl complexes of platinum was achieved by refluxing benzene or toluene solutions of $Pt(PPh_3)_4$ with an excess of the alkylchloroformate. This demonstrates the greater susceptibility toward oxidative-addition of Pd(0) as compared to Pt(0).[12]

The synthesis of carbamoyl complexes, $MCl(CONR_2)L_2$, of platinum and palladium was previously carried out in this laboratory[13] by reacting the bis-phosphine dichlorides with CO and a secondary amine. By substituting sodium methoxide and methanol for the amine, we've employed this method for preparing alkoxycarbonyl complexes.

$$MCl_2L_2 + CO + NaOCH_3 \xrightarrow[\text{5 hrs.}]{CH_3OH, 25°} MCl(CO_2CH_3)L_2 + NaCl \qquad (6)$$

This is the most desirable method for the preparation of alkoxycarbonyl complexes since the bis-phosphine dichlorides are convenient starting materials, the reaction proceeds under mild conditions for both Pt and Pd, and the products are obtained in high yield (90%). This same reaction has been reported for MX_2L_2 complexes where X is an easily displaced anion such as: acetate[14], trifluoroacetate[14], azide[15] or cyanate.[8] More recently the preparation of $PdCl(CO_2CH_3)(PPh_3)_2$ by the same method has been reported.[9]

The synthesis of alkoxalyl complexes of Pt(II) and Pd(II) was conveniently carried out by the oxidative-addition reaction of alkyloxalyl chlorides to the zero-valent metal phosphine complexes,



$$ML_4 + Cl{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OR \longrightarrow L(Cl)M(L){-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OR + 2L \qquad (7)$$

where M = Pt or Pd, R = Me or Et and L = a phosphine. Unlike chloroformates, oxalyl chlorides react rapidly with $Pt(PPh_3)_4$ in benzene at room temperature. Reaction of oxalyl chlorides with $Pd(PPh_3)_4$ occurs readily in toluene at 0°. The products are stable, yellow solids and are obtained in high yield.

In the reaction of $ClCOCO_2Et$ with $Pt(PPh_3)_4$ a small amount of the hydride trans-$PtCl(H)(PPh_3)_2$[16] is formed along with the ethoxalyl complex. The hydride was easily identified in the product mixture by its characteristic infrared (ν(Pt-H) = 2210 cm^{-1}) and high-field proton NMR (τ 26 for Pt-H) spectra. Formation of the hydride complex is suspected to arise from the reaction of $Pt(PPh_3)_4$ with HCl present in $ClCOCO_2Et$ as a hydrolysis product.

Structures

Two structural aspects of the alkoxalyl complexes which are of interest are the configuration of the ligands about the metal atom and the exact conformation of the alkoxalyl ligand. These structural features for the complexes in solution were elucidated by IR and NMR measurements. A more detailed structural analysis was carried out for $PdCl(COCO_2Me)(PPh_3)_2$ in the solid state by means of an X-ray diffraction structure determination.[17]

Proton NMR spectra (Table 1) show that the methyl proton resonance in the methoxycarbonyl and methoxalyl ligands is shifted upfield relative to the starting chlorides $ClCO_2CH_3$ and $ClCOCO_2CH_3$. This indicates the greater shielding effect of L_2ClPt- as compared to Cl, and this may to some extent be due to the lower electron-withdrawing ability of the metal as compared to Cl. However, diamagnetic shielding by the phenyl groups of the PPh_3 ligands is most likely responsible for this observed upfield shift. This is particularly noticeable for the methoxycarbonyl complexes, $PdCl(CO_2Me)L_2$, where L is PPh_3(τ 7.60) or PEt_3(τ 6.51). Thus, substituting PEt_3 for PPh_3 causes a downfield shift of the OCH_3 resonance even though PEt_3 is considerably less electron-withdrawing than PPh_3. The same

Table 1. Infrared and proton NMR data

	$\nu(CO)^a$, cm^{-1}	τ^b for -OR group
$PtCl(CO_2Me)(PPh_3)_2$[c]	1644	7.65 (s with satellites)[d]
$PtCl(CO_2Et)(PPh_3)_2$[c]	1636	7.35 (m), 9.55 (t)
$PtCl(COCO_2Me)(PPh_3)_2$	1735m,sh, 1715s 1665m,sh, 1645s	6.98 (s)
$PtCl(COCO_2Et)(PPh_3)_2$	1650, 1710[e]	6.55 (q), 9.12 (t)
$PtCl(COCO_2Me)(PMePh_2)_2$	1645, 1720	6.90 (s)[f]
$PdCl(CO_2Me)(PPh_3)_2$	1655	7.60 (s)
$PdCl(CO_2Et)(PPh_3)_2$[g]	1650	7.30 (q), 9.53 (t)
$PdCl(COCO_2Me)(PPh_3)_2$	1674, 1722	6.93 (s)
$PdCl(COCO_2Et)(PPh_3)_2$	1670, 1720	6.55 (q), 9.12 (t)
$PdCl(COCO_2Me)(PMePh_2)_2$	1665, 1720	6.92 (s)[h]
$PdCl(CO_2Me)(PEt_3)_2$	1650	6.51 (s)
$PdCl(COCO_2Me)(PEt_3)_2$	1660, 1720	6.26 (s)
$ClCOCO_2Me$	1761 (broad)	6.01 (s)
$ClCOCO_2Et$	1754, 1786	5.60 (q), 8.60 (t)

[a] In $CHCl_3$ solution.

[b] In $CDCl_3$ solution with tetramethylsilane (τ10.0) as an internal standard. Abbreviations: s, singlet; t, triplet; q, quartet; m, multiplet.

[c] See reference 11.

[d] J(PtCOCH) = 7 Hz.

[e] 1725s,sh, 1710s, 1665m,sh, 1652s in CH_2CL_2.

[f] For $P-CH_3$ protons, τ7.85(t) with satellites and J(PCH) = 4 Hz and J(PtPCH) = 33 Hz.

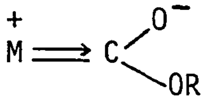
[g] See reference 7.

[h] For $P-CH_3$ protons, τ7.93(t) with J(PCH) = 3.5 Hz.

trend is observed for the methoxalyl complexes though the effect is smaller here due to the increased distance between the methyl group and the phosphine ligands.

The methyl group in the methoxycarbonyl complex of platinum appears as a singlet with satellites due to splitting by ^{195}Pt (33% abundant) with J(PtCOCH) = 7 Hz. Platinum alkoxalyl complexes show no splitting of the ligand protons by ^{195}Pt due to the increased distance between these protons and the metal atom as a result of the additional carbonyl group. In the NMR spectra of the complexes $MCl(COCO_2Me)(PMePh_2)_2$ the phosphine CH_3 group is observed as a 1:2:1 triplet with 1:2:1 triplet satellites when M is Pt. This splitting pattern arises from virtual coupling of both ^{31}P nuclei and indicates[18] that the phosphine ligands are trans to each other.

The alkoxycarbonyl complexes of platinum show a strong infrared absorption at 1640 cm^{-1} which is assigned to the carbonyl stretching mode of the $-CO_2R$ ligand (Table 1). For the analogous palladium complexes this band is at a slightly higher frequency (1650 cm^{-1}). This band is 60 to 100 cm^{-1} lower than the ν(C=O) frequency observed for saturated aliphatic esters, and this lowering can be attributed to some degree of back bonding from a d orbital of the metal atom to the π-system of the carbonyl group[19], and can be represented by the following contributing resonance structure:



The ν(C=O) band of the similar acyl complexes, M-COR, is in the range of 1628 to 1636 cm^{-1} for M = Pt and 1661 to 1675 cm^{-1} for M = Pd. This was interpreted[19] to mean that there is less metal to ligand back bonding for palladium, and this also appears to be the case for the alkoxycarbonyl and alkoxalyl complexes described here (see Table 1).

The infrared spectra of the alkoxalyl complexes of both platinum and palladium show two strong well-separated bands in the C = 0 carbonyl region (Table 1). The lower frequency absorption occurs in the range of 1640 - 1670 cm^{-1} and is assigned to the carbonyl group adjacent to the metal. This assignment is in accord with the low carbonyl frequencies observed for the alkoxycarbonyl complexes. The higher frequency band occurs in the range of 1710 - 1725 cm^{-1}. This region is common for the ν(C=O) frequency of organic esters and this band is therefore assigned to the ν(C=O) mode of the ester carbonyl group in the alkoxalyl ligand.

The X-ray structure determination* of $PdCl(COCO_2Me)(PPh_3)_2$ (Fig. 1) was carried out for the purpose of elucidating the structural details of the methoxalyl ligand.[17] The Pd-C(1) bond distance 1.97(2)Å is very similar to that observed for other Pd-C(sp^2) bonds.[20] The methoxalyl ligand has an s-trans (see Fig. 4) planar conformation in the solid state (Fig. 1) as do the similar organic compounds dimethyl oxalate[21] and oxalyl chloride.[22] The largest deviation from the least squares plane of the methoxalyl ligand is 0.12Å for carbon atom C(3), and this plane makes an angle of 93(2)° with the plane formed by Pd, Cl, P(1), and P(2). Other salient features of the structure are the unexpectedly large C(1)-C(2)-O(2) angle, 135(4)°, and small O(2)-C(2)-O(3) angle, 103(3)°, which appear

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*The X-ray structure determination was carried out by Dr. Jose Fayos under the supervision of Dr. Jon Clardy of this department.

Figure 1. Computer generated drawing of *trans*-$PdCl(COCO_2Me)(PPh_3)_2$.

Bond distances (Å)

Pd-C(1), 1.97(2)

C(1)-O(1), 1.19(2)

C(1)-C(2), 1.41(4)

C(2)-O(2), 1.23(2)

C(2)-O(3), 1.46(3)

O(3)-C(3), 1.32(3)

Pd-O(2), 3.22(2)

Pd-Cl, 2.433(6)

Pd-P(1), 2.320(7)

Pd-P(2), 2.329(6)

Bond angles

Pd-C(1)-O(1), 128(2)°

Pd-C(1)-C(2), 113(2)°

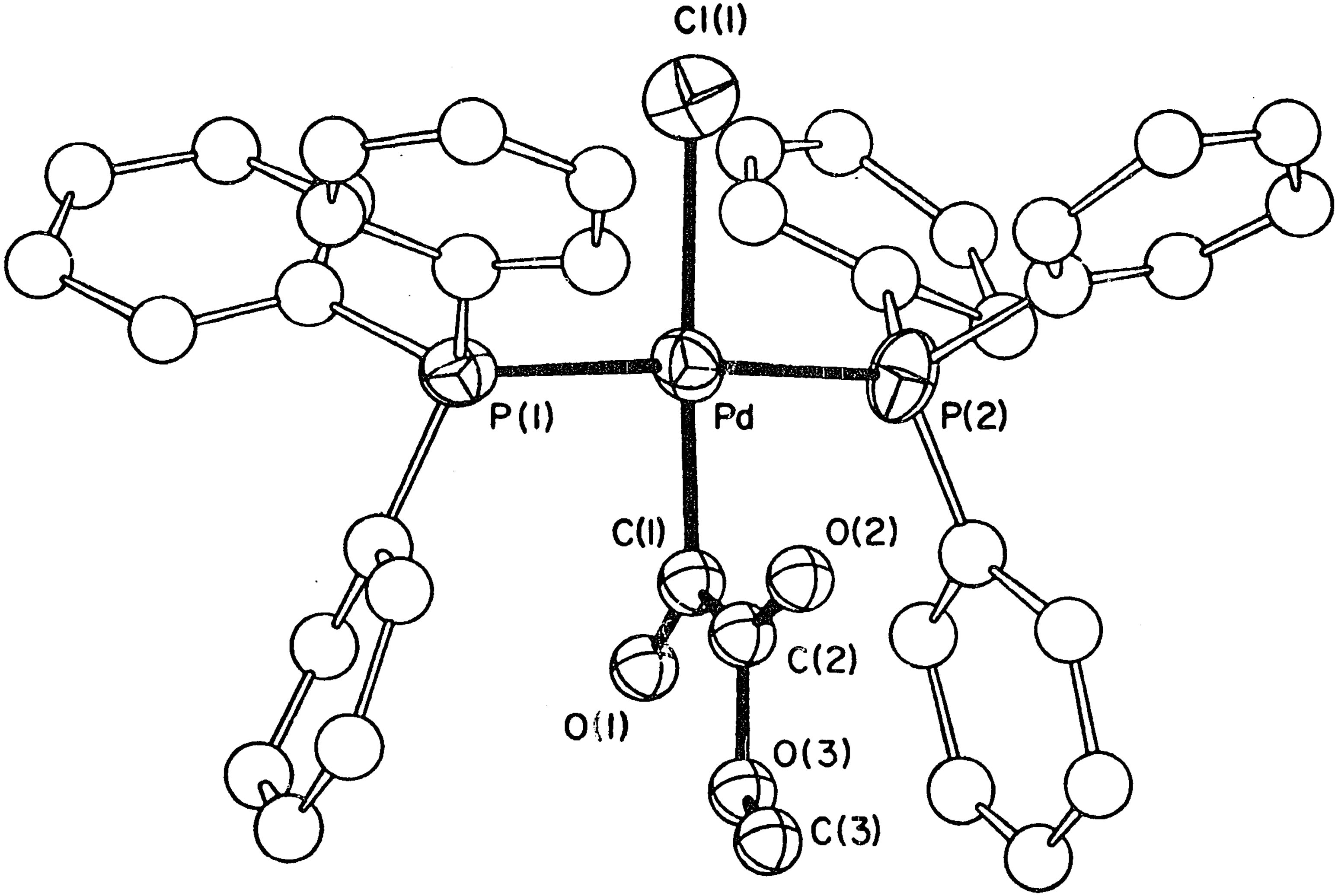
O(1)-C(1)-C(2), 118(3)°

C(1)-C(2)-O(2), 135(4)°

C(1)-C(2)-O(3), 121(3)°

O(2)-C(2)-O(3), 103(3)°

C(2)-O(3)-C(3), 122(3)°


Cl(1)
P(1)
Pd
P(2)
C(1)
O(2)
C(2)
O(1)
O(3)
C(3)

to result from repulsion between the Pd and O(2), and the short C(1)-C(2) bond distance, 1.41(4)Å, which indicates that there is some double bond character in this bond.

The solid state infrared spectrum of $PdCl(COCO_2Me)(PPh_3)_2$ shows two carbonyl bands (Fig. 2) at 1675 and 1720 cm^{-1}, and it is known from the X-ray structure determination[17] that the methoxalyl ligand in this complex has the s-trans conformation in the solid. The spectrum in $CHCl_3$ is essentially the same with only two bands present at 1674 and 1722 cm^{-1}. Thus it appears that only the s-trans isomer is present in solution also.

The solid state infrared spectrum of $PtCl(COCO_2Me)(PPh_3)_2$ shows two carbonyl bands (Fig. 2) at 1670 and 1710 cm^{-1}, and by comparison with the spectrum of the analogous palladium complex it appears that the methoxalyl ligand in this complex also has the s-trans conformation in the solid. The origin of the shoulder on the low frequency band is uncertain but could possibly be due to the presence of another conformational isomer. However, in solution this complex shows two pairs of carbonyl bands with the lower frequency pair being only partially resolved (Fig. 3). This indicates the presence of isomers resulting from different conformations of the methoxalyl ligand. As previously mentioned for the complex $PdCl(COCO_2Me)(PPh_3)_2$, the planarity of the methoxalyl ligand and the short C-C bond distance (1.41Å) indicate the partial double bond character of this bond. Assuming this to also be the case for the platinum analog, one would expect restricted rotation about this C-C bond in solution and this could give rise to s-trans and s-cis isomers (Fig. 4) provided the planar geometry of the methoxalyl ligand is maintained.

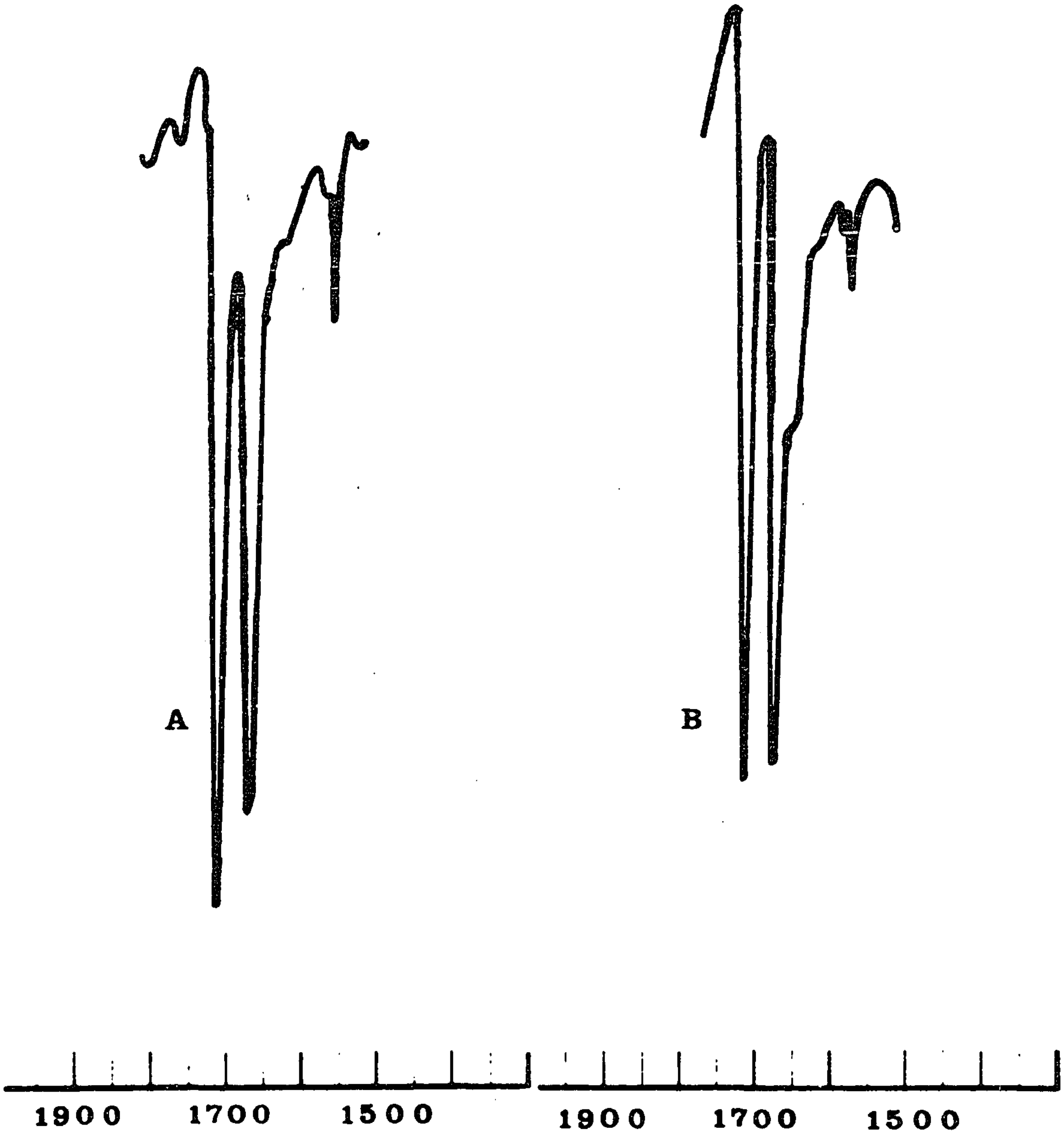


Figure 2. Infrared spectra of $PdCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ (A) and $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ (B) as nujol mulls.

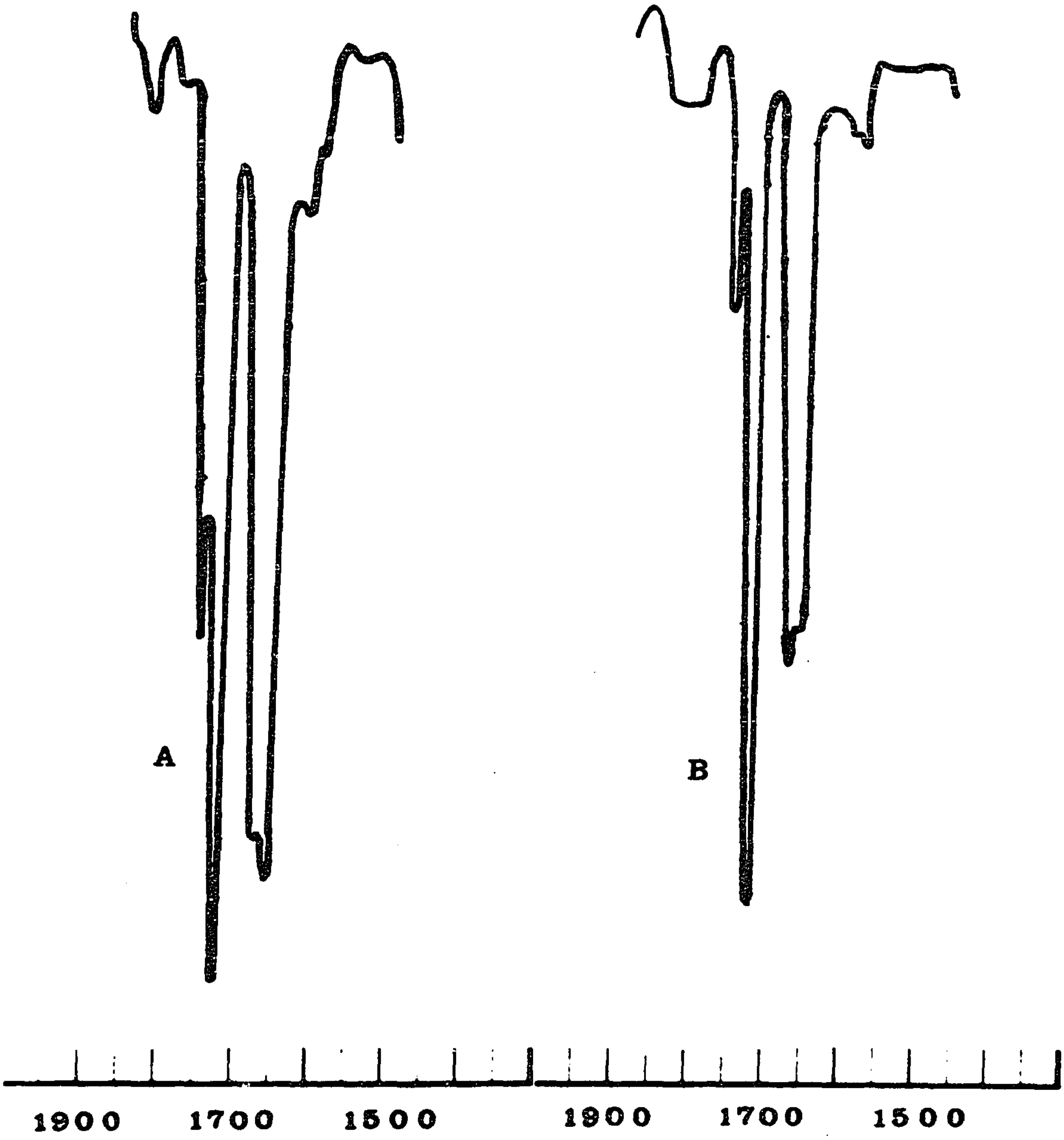


Figure 3. Infrared spectra of $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ in CH_2Cl_2 solution (A) and in C_6H_6 solution (B).

The presence of both the s-cis and s-trans conformers for the platinum methoxalyl complex in solution accounts for the two sets of carbonyl bands observed (Fig. 3). The 1660 and 1715 cm^{-1} bands are assigned to the s-trans isomer, based on a comparison of these band positions with those of the carbonyl bands present in the solid state and solution spectra of $PdCl(COCO_2Me)(PPh_3)_2$ and the solid state spectrum of $PtCl(COCO_2Me)(PPh_3)_2$. The remaining two absorptions at 1640 and 1735 cm^{-1} are assigned to the s-cis isomer.

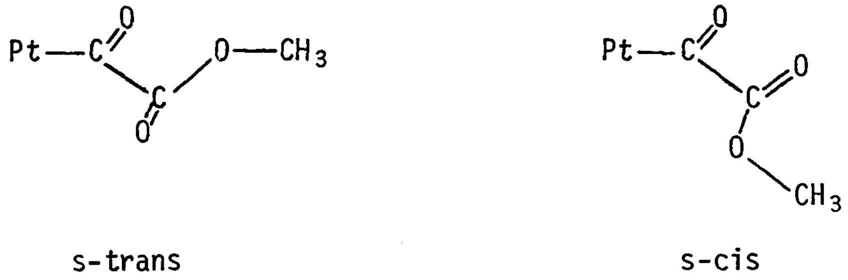


Figure 4. Structures of the s-trans and s-cis conformations of the methoxalyl ligand.

A change in the relative amounts of s-cis and s-trans isomers in solution is indicated by a change in the relative intensities of the appropriate carbonyl bands. The ratio of the 1735 cm^{-1} band intensity to the 1715 cm^{-1} band intensity was used to measure changes in the s-cis/s-trans isomer ratio. When measured in different solvents this ratio increases as the dielectric constant of the solvent increases (Table 2). This means that the amount of s-cis isomer increases relative to the amount of s-trans isomer as the solvent polarity increases. This is reasonable since the s-cis isomer, having both carbonyl dipoles aligned in the same general direction, would be more polar than the s-trans isomer where the carbonyl dipoles are aligned in opposite directions. The same general trend was observed for $PtCl(COCO_2Me)(PMePh_2)_2$ (intensity ratio values in parentheses). The slightly higher ratios for this complex in all solvents may result from the methoxy group encountering less steric hindrance from $PMePh_2$ as compared to PPh_3 when the ligand is in the s-cis conformation.

Table 2. Effect of solvent polarity on the s-cis/s-trans isomer ratio of $PtCl(COCO_2Me)(PPh_3)_2$

Solvent	Dielectric constant	Ratio[a]
C_6H_6	2.27	0.16 (0.19)[b]
CS_2	2.63	0.17
$CHCl_3$	4.73	0.27 (0.34)
CH_2Cl_2	8.93	0.41 (0.45)
CH_3NO_2	35.9	0.59
CH_3CN	38.8	0.48

[a] Ratio of absorbances of the 1735 to 1715 cm^{-1} bands.

[b] Values in parentheses are for $PtCl(COCO_2Me)(PMePh_2)_2$.

For $PtCl(COCO_2Me)(PPh_3)_2$, the amount of s-cis isomer increases relative to the amount of s-trans isomer as the temperature of the solution increases, and there is a sharp decrease in the s-cis/s-trans ratio when the temperature is lowered to -75° (Table 3). From this data it is concluded that the s-trans to s-cis isomerization is endothermic.

In contrast to the alkoxalyl complexes, organic oxalyl derivatives can exist in either planar or nonplanar conformations. Dimethyl oxalate was shown to have a nonplanar structure in solution*[23] with the dihedral angle between the carbonyl groups varying from 0 to 180°, and from electron diffraction studies[24] it was concluded that oxalyl halides exist as a mixture of gauche and trans conformers in the gaseous state. These results indicate a low barrier to rotation about the C-C bond and this is consistent with the normal C-C single bond distances (1.53Å) observed for these organic compounds.[21,22] The organic oxalyl derivatives assume the s-trans conformation in the solid state, and this is believed to be due to steric interaction and not restricted rotation about the C-C bond.

Table 3. Effect of temperature on the s-cis/s-trans isomer ratio of $PtCl(COCO_2Me)(PPh_3)_2$

Solvent	-75°	25°	40°	60°
C_6H_6		0.16	0.17	0.18
$CHCl_3$		0.23	0.26	
CH_2Cl_2	0.32	0.41		

Reactions

Complexes such as $PtCl(CO_2Me)(PPh_3)_2$ and $PtCl(CONMe_2)(PPh_3)_2$ readily react with protonic acids to yield the carbonyl cation, $[PtCl(CO)(PPh_3)_2]^+$, and either the alcohol or the amine.[10] Although the reaction is reversi-

$$PtCl(CO_2Me)(PPh_3)_2 + HX \rightleftharpoons [PtCl(CO)(PPh_3)_2]\ [X] + CH_3OH \qquad (8)$$

ble, complete coversion to the carbonyl cation occurs rapidly in the presence of excess acid. It was conceivable that the alkoxalyl complexes could also react with acids to form the same products along with the loss of CO. However, treatment of $MCl(COCO_2Me)(PPh_3)_2$, where M is Pt or Pd, with aqueous HBF_4 or with Cl_3CCO_2H in $CHCl_3$ showed the complexes to be remarkably inert to these acids.

Transesterification of the methoxalyl ligand can be achieved under mild conditions. A catalytic amount of NaOEt was used. Reaction occurs

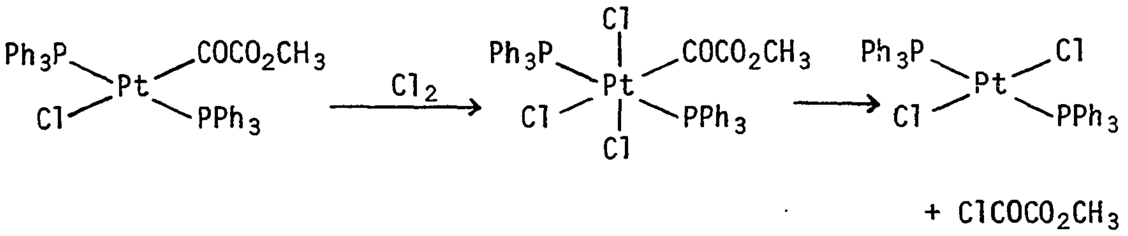
$$PtCl(COCO_2Me)(PPh_3)_2 + EtOH \xrightarrow[NaOEt]{THF, 25°, 2\ hrs.} PtCl(COCO_2Et)(PPh_3)_2 \qquad (9)$$

readily in THF in which the starting complex and product are soluble. This reaction was initially attempted in ethanol in which the alkoxalyl complexes are not soluble, and it was found that no reaction takes place on stirring a suspension of the methoxalyl complex in ethanol either with or without added NaOEt.

When chlorine was bubbled into a $CHCl_3$ solution of $PtCl(COCO_2Me)(PPh_3)_2$ reaction occurred immediately to produce a bright-yellow solid precipitate which was identified as <u>trans</u>-$PtCl_2(PPh_3)_2$ by its far infrared spectrum[25], ν(Pt-Cl) = 343 cm^{-1}. The other product was easily identified as $ClCOCO_2CH_3$ from its characteristic infrared and NMR spectra.

$$PtCl(COCO_2Me)(PPh_3)_2 + Cl_2 \xrightarrow[25°]{CHCl_3} \underline{trans}\text{-}PtCl_2(PPh_3)_2 + ClCOCO_2CH_3 \qquad (10)$$

Thus, chlorine causes facile cleavage of the Pt-C bond in the methoxalyl complex, and the dichloride is obtained in near quantitative yield. When this reaction is carried out using equimolar amounts of Cl_2 and methoxalyl complex, the products are $ClCOCO_2CH_3$ and the white solid <u>cis</u>-$PtCl_2(PPh_3)_2$ which was identified by its far infrared spectrum[25], ν(Pt-Cl) = 295 and 320 cm^{-1}. It is not clear why different isomers of $PtCl_2(PPh_3)_2$ are produced when different amounts of Cl_2 are used. A plausible mechanism for this reaction could be the oxidative-addition of chlorine to the Pt(II) methoxalyl complex to form a six-coordinate Pt(IV) intermediate which could then undergo a reductive elimination reaction to give the observed products.



(11)

The palladium alkoxalyl complexes are not stable in solution at room temperature and undergo rapid decarbonylation to give the corresponding alkoxalyl complexes.

$$PdCl(COCO_2R)L_2 \xrightarrow[CHCl_3, CH_2Cl_2 \text{ or } C_6H_6]{25°} PdCl(CO_2R)L_2 + CO \qquad (12)$$

When the complexes are dissolved in CH_2Cl_2,$CHCl_3$ or benzene the evolution of gas bubbles ensues immediately and the decarbonylation can be followed in the infrared spectrum. For $PdCl(COCO_2Me)(PPh_3)_2$ in $CHCl_3$ at 25° the decarbonylation was complete in 20 minutes. Solutions of this complex stored at -20° showed no decarbonylation after 2 days. It was found that the decarbonylation could be retarded at room temperature by adding PPh_3 to the solutions (Table 4). The reason for this stabilizing effect is presently unknown, but it is possible that the excess phosphine suppresses phosphine dissociation of the complex thereby stabilizing the alkoxalyl ligand. This would imply that the decarbonylation mechanism involves PPh_3 dissociation followed by $-CO_2R$ migration and loss of the resulting CO ligand. This stabilization by excess PPh_3 made it possible to record NMR

Table 4. Conditions for decarbonylation of $PdCl(COCO_2Me)(PPh_3)_2$(I) and $PtCl(COCO_2Me)(PPh_3)_2$(II)

Complex	Solvent	Temperature	Excess PPh_3[a]	Results
I	$CHCl_3$	25°	0	Rapid decarbonylation, complete after 20 min.
I	$CHCl_3$	25	0.2	Small amount of decarbonylation after 10 hrs., complete after 2 days
I	$CHCl_3$	25°	2.0	No decarbonylation[b]
I	$CHCl_3$	-20°	0	No decarbonylation[b]
II	$CHCl_3$	25°	0	No decarbonylation[c]
II	$CHCl_3$	50°	0	No decarbonylation[d]
II	C_6H_6	80°	0	Complete decarbonylation in 2 hrs.
II	solid[e]	175°	0	75% decarbonylation[f] after 30 hrs.

[a] Moles of PPh_3 per mole of complex.

[b] Checked after 2 days.

[c] Checked after several weeks.

[d] Checked after several hours.

[e] The solid complex was heated under vacuum.

[f] The alkoxycarbonyl complex is the only product formed.

spectra and carry out recrystallizations without degradation of the alkoxalyl ligand. It appears that the isolation of palladium alkoxalyl complexes from the oxidative-addition reaction of $Pd(PPh_3)_4$ with alkoxalyl halides was possible because the complexes were stabilized in solution by the free PPh_3 concomitantly produced (eq. 7).

The platinum alkoxalyl complexes are stable in solution at 25° (Table 4). For $PtCl(COCO_2Me)(PPh_3)_2$ decarbonylation occurs when the complex is refluxed in benzene or heated to 175° for several hours in the solid state. In both cases the decarbonylation gives the alkoxalyl complex and CO as the only products. At temperatures above 200° the platinum alkoxalyl complexes melt to clear yellow liquids with the emission of gas bubbles indicating decarbonylation. The palladium analogs simply decompose to black solids when heated.

Attempts were made to prepare alkoxalyl complexes by the insertion of CO into the M-C bond of the alkoxycarbonyl complexes (eq. 3). Only decomposition was observed for alkoxycarbonyl complexes with PPh_3 ligands. This is similar to results obtained by Booth and Chatt[26] in their studies of the carbonyl insertion reaction of $MX(CH_3)L_2$ to give $MX(COCH_3)L_2$, where M = Pt or Pd, X = halide, L = PPh_3 or PEt_3. These workers observed CO insertion to take place most readily for the palladium complex with PEt_3 ligands. Therefore, most of our attempts at carbonylation were carried out using $PdCl(CO_2Me)(PEt_3)_2$. The reaction could be monitored by the infrared spectrum of the solution since the alkoxalyl complexes have a distinctive carbonyl pattern. It appears that CO insertion occurs to produce the alkoxalyl complex, but the extent of carbonylation as well as the extent of decomposition are very sensitive to reaction conditions (eq. CO pressure, temperature, presence of excess phosphine, length of reaction time, and purity of the starting complex).

$$PdCl(CO_2Me)(PEt_3)_2 + CO \longrightarrow PdCl(COCO_2Me)(PEt_3)_2 \qquad (13)$$

Complete carbonylation was observed in one particular run (see experimental section for conditions). However, formation of the methoxalyl complex by CO insertion under these or other conditions was not reproducible.

Experimental

Methods and materials

Infrared spectra were recorded on a Perkin-Elmer 337 or Beckman IR-12 spectrophotometer as nujol mulls or in $CHCl_3$ solution. NMR spectra were obtained on a Perkin-Elmer Hitachi R-20B spectrometer in $CDCl_3$ solution. High temperature infrared spectra were obtained using a jacketed cell through which water from a constant temperature bath could be circulated. The low temperature infrared spectrum was obtained using a jacketed cell which was connected to a dewar flask filled with a dry ice-acetone mixture. The cell was enclosed in a sealed chamber with NaCl windows which was evacuated to prevent moisture from condensing on the cell. Melting points were determined on a Thomas model 40 micro hot stage and are uncorrected. Analyses were performed by Meade microanalytical laboratories, Amherst, Mass. All reactions were carried out in schlenk tubes under a nitrogen atmosphere. All solvents were reagent grade. Benzene was deoxygenated by purging with nitrogen and THF was refluxed over $LiAlH_4$ before use.

Platinum black was used as the basic starting material for all platinum complexes. The metal was converted to K_2PtCl_4 by the procedure described in the literature.[27] The compounds PtL_4 (L = $P(C_6H_5)_3$ or $P(CH_3)(C_6H_5)_2$) were prepared as described in the literature.[28] The analogous PdL_4 complexes were prepared by adding L to a pentane solution of $(\pi\text{-}C_5H_5)Pd(\pi\text{-}C_3H_5)$.[29] Solutions of $Pd[P(C_2H_5)_3]_4$ were prepared by slowly adding $P(C_2H_5)_3$ to a pentane solution of $(\pi\text{-}C_5H_5)Pd(\pi\text{-}C_3H_5)$ until the color turned from red to yellow. This solution was used directly for subsequent oxidative-addition reactions. The $(\pi\text{-}C_5H_5)Pd(\pi\text{-}C_3H_5)$ was prepared either by the literature method[30] or by a more convenient modification using TlC_5H_5 instead of NaC_5H_5. This was done by stirring a solution of 1.94 g (5.3 mmol) of $[(\pi\text{-}C_3H_5)PdCl]_2$[31] and 2.87 g (10.7 mmol) of TlC_5H_5 in 25 ml of tetrahydrofuran (THF) under a nitrogen atmosphere at 25° for 5 min. After evaporating the solvent under vacuum, the residue was extracted with 50 ml of pentane. After filtering, the pentane was removed under vacuum leaving 1.89 g (85%) of the red crystalline product.

Alkoxycarbonyl complexes by oxidative-addition reactions

$PdCl(CO_2CH_3)[P(C_6H_5)_3]_2$ To a solution of 0.67 g (0.58 mmol) of $Pd[P(C_6H_5)_3]_4$ in 20 ml of benzene under N_2 was added 0.054 g (0.58 mmol) of $ClCO_2CH_3$. After stirring for 5 hrs at 25°, the solvent was removed under vacuum and the remaining residue was washed with diethyl ether. Recrystallization from CH_2Cl_2-hexane gave the pale-yellow crystalline product (0.34 g, 80% yield).

Anal. Calcd for $PdCl(CO_2CH_3)[P(C_6H_5)_3]_2$: C, 63.0; H, 4.56; Cl, 4.84. Found: C, 63.4; H, 4.83; Cl, 5.01.

$PtCl(CO_2CH_3)[P(C_6H_5)_3]_2$ Methyl chloroformate ($ClCO_2CH_3$) was added to a refluxing solution of 1.16 g (0.94 mmol) of $Pt[P(C_6H_5)_3]_4$ in 50 ml of benzene under an N_2 atmosphere until the yellow solution became pale yellow. Removal of benzene under vacuum yielded a white solid which was washed with ether and recrystallized from CH_2Cl_2-hexane to give 0.57 g (75%) of the product. Its IR and proton NMR spectra (Table 1) were virtually identical to those reported for this compound prepared by a different method.[11] The analogous $Pt(Cl)(CO_2C_2H_5)[P(C_6H_5)_3]_2$ was prepared by refluxing a 20 ml toluene solution of 0.91 g (8.4 mmol) of $ClCO_2C_2H_5$ and 0.46 g (0.47 mmol) of $Pt[P(C_6H_5)_3]_3$[32] for 12 hrs. Isolation as described above gave 0.21 g (54%) of the white product.[11]

Alkoxycarbonyl complexes by carbonylation of MCl_2L_2 complexes

$PdCl(CO_2CH_3)[P(C_6H_5)_3]_2$ A suspension of 0.74 g (1.0 mmol) of trans-$PdCl_2[P(C_6H_5)_3]_2$ and 0.057 g (1.0 mmol) of $NaOCH_3$ in 50 ml of CH_3OH was stirred under CO (1 atm) for 5 hrs at 25°. The resulting pale-pink solid was collected by filtration and washed with H_2O, C_2H_5OH, and finally ether to give 0.67 g (88%) of $PdCl(CO_2CH_3)[P(C_6H_5)_3]_2$, whose spectra (Table 1) were identical to those of this complex prepared by the oxidative-addition route. The platinum analog was prepared similarly from cis-$PtCl_2[P(C_6H_5)_3]_2$.

$PdCl(CO_2CH_3)[P(C_2H_5)_3]_2$ A suspension of 0.39 g (0.95 mmol) of trans-$PdCl_2[P(C_2H_5)_3]_2$ and 0.20 g (1.90 mmol) of Na_2CO_3 in 25 ml of CH_3OH was stirred under CO (1 atm) for 15 min. After vacuum removal of the CH_3OH, the orange-brown residue was extracted with 40 ml of pentane. After treatment with activated charcoal and filtration, the pale-yellow solution was concentrated under vacuum to about 15 ml. Cooling to -20° gave white needles of the product (0.13 g, 32%), which was identified by its spectra (Table 1).

Preparation of alkoxalyl complexes

$PtCl(COCO_2R)L_2$, where $R = CH_3$ or C_2H_5 and $L = P(C_6H_5)_3$ or $P(CH_3)(C_6H_5)_2$ These complexes were all prepared similarly. As an example, 0.23 g (1.92 mmol) of methyl oxalyl chloride ($ClCOCO_2CH_3$) was added to a solution of 2.39 g (1.93 mmol) of $Pt[P(C_6H_5)_3]_4$ in 50 ml of benzene under an N_2 atmosphere. Stirring for 5 min at 25° gave a pale-yellow solution. Benzene was removed under vacuum leaving a yellow solid. The solid was triturated with ether and recrystallized from CH_2Cl_2-hexane to give yellow crystals of $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ (1.30 g, 81%; mp 215-220° with loss of CO).

Anal. Calcd for $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$: C, 55.6; H, 3.95; Cl, 4.22. Found: C, 55.7; H, 4.04; Cl, 4.98.

The alkoxalyl complexes in the platinum series are all bright-yellow crystalline solids which are stable in both solution and in the solid state at room temperature and are not decomposed by air or water.

$PdCl(COCO_2R)L_2$, where $R = CH_3$ or C_2H_5 and $L = P(C_6H_5)_3$ or $P(CH_3)(C_6H_5)_2$ Like their platinum analogs, the palladium alkoxalyl complexes were also prepared by the oxidative-addition method. As a typical example, 0.313 g (2.30 mmol) of $ClCOCO_2C_2H_5$ was added to a solution of 2.66 g (2.30 mmol) of $Pd[P(C_6H_5)_3]_4$ in 40 ml of toluene at 0°. After stirring the solution for 15 min at 0°, 80 ml of ether was added to precipitate the yellow solid product. After filtration, the solid was washed several times with ether and then dried under vacuum to give $PdCl(COCO_2C_2H_5)[P(C_6H_5)_3]_2$ (1.47 g, 84%) as a bright-yellow powder.

Anal. Calcd for $PdCl(COCO_2C_2H_5)[P(C_6H_5)_3]_2$: C, 62.5; H, 4.61; Cl, 4.62. Found: C, 62.0; H, 4.54; Cl, 4.54.

The $PdCl(COCO_2CH_3)[P(C_2H_5)_3]_2$ complex was prepared by reacting equimolar (1.97 mmol) $Pd[P(C_2H_5)_3]_4$ and $ClCOCO_2CH_3$ in 10 ml of pentane at 25°. After filtering, the solution was concentrated under vacuum and cooled to -20° giving yellow crystals (~15%) of the product.

The complexes in this series are all bright-yellow solids which are stable in the solid state and do not react with air or water. Unlike their platinum analogs, however, they do undergo noticeable decomposition when stored at room temperature for several months. In CH_2Cl_2, $CHCl_3$ or benzene solution, they are not stable and readily lose CO to give the corresponding alkoxycarbonyl complexes. Addition of $P(C_6H_5)_3$ to these solutions greatly retards this decarbonylation thus allowing the complexes to be recrystallized from CH_2Cl_2-hexane.

Reactions of alkoxalyl complexes

Transesterification of $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ To a solution of 0.22 g (0.26 mmol) of $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ in 15 ml of dry THF was added 5 ml of C_2H_5OH containing a trace of $NaOC_2H_5$. After stirring for 2 hrs at 25°, an additional 10 ml of C_2H_5OH was added causing the precipitation of a light yellow solid (0.20 g), which was washed with C_2H_5OH and dried under a stream of N_2. A proton NMR spectrum of the precipitate in $CDCl_3$ indicated, by comparison with spectra of authentic samples (Table 1), that 88% of it was $PtCl(COCO_2C_2H_5)[P(C_6H_5)_3]_2$ while the remaining 12% was unreacted starting material.

Reaction of $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ with Cl_2 An excess of Cl_2 was condensed onto a solution of 0.12 g (0.14 mmol) of $PtCl(COCO_2CH_3)[P(C_6H_5)_3]_2$ in $CDCl_3$ at -196° under vacuum. On warming to room temperature, a yellow solid precipitated and was separated by filtration. The proton NMR spectrum of the $CDCl_3$ solution showed only the characteristic singlet (τ 6.01) of $ClCOCO_2CH_3$; the infrared spectrum of this solution indicated the presence of $ClCOCO_2CH_3$ by the ν(C=O) band at 1760 cm^{-1}. The yellow solid was identified as trans-$PtCl_2[P(C_6H_5)_3]_2$ (0.11 g, 96%) by its strong ν(Pt-Cl) band at 343 cm^{-1}.[25] When the reaction was carried out with equimolar amounts (0.23 mmol) of complex and Cl_2 under the same conditions as above, $ClCOCO_2CH_3$ was again observed but the tan solid precipitate was identified as cis-$PtCl_2[P(C_6H_5)_3]_2$ by characteristic ν(Pt-Cl) bands at 295 and 320 cm^{-1}.[25] When Cl_2 is simply bubbled into a $CHCl_3$ solution of the complex at 25°, the dichloride is obtained as the trans isomer.

Attempted carbonylation of $PdCl(CO_2CH_3)[P(C_2H_5)_3]_2$ A solution of 0.02 g of $PdCl(CO_2CH_3)[P(C_2H_5)_3]_2$ in 3 ml of pentane was allowed to stand under 17 atm of CO in a stainless steel pressure bomb at 25°. The bomb also contained a pentane solution of $P(C_2H_5)_3$ in a separate glass vessel (Fig. 5) which was specially designed to transfer this solution to the reaction flask upon release of the CO pressure within the bomb. After 21 hrs the CO pressure was released and the phosphine solution was automatically transferred to the reaction flask. The infrared spectrum of the reaction solution showed strong bands at 1725 cm^{-1} and 1650 cm^{-1} which were identical to the ν(C=O) bands observed for $PdCl(COCO_2CH_3)[P(C_2H_5)_3]_2$ prepared by the oxidative-addition method. It appears that the methoxalyl

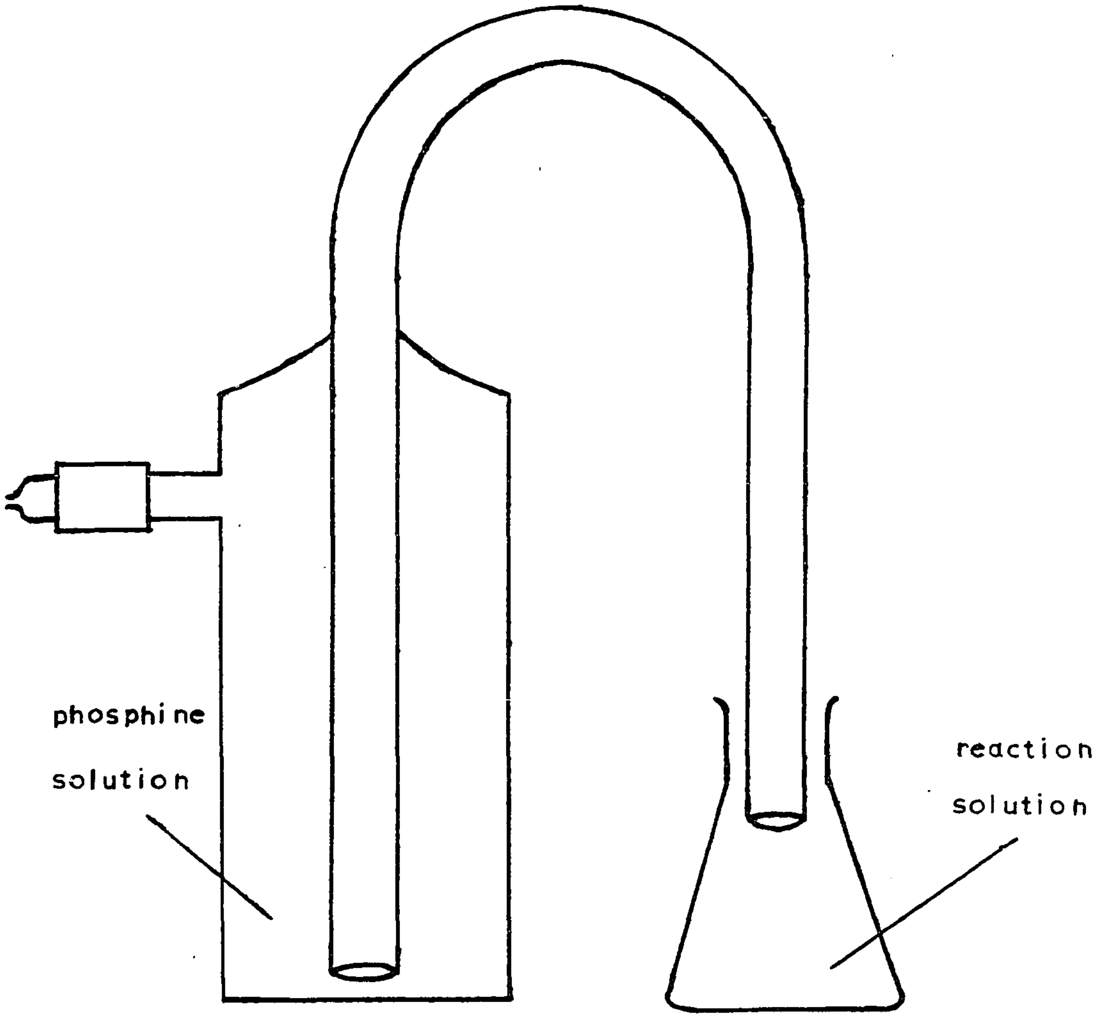


Figure 5. Apparatus used to transfer phosphine solution to reaction solution upon release of CO pressure within the high-pressure bomb.

complex is formed by CO insertion, however, this result was not reproducible. In other attempts different CO pressures, temperatures, reaction times and solvents were examined and smaller amounts of carbonylation were indicated by a strong band at 1650 cm^{-1} and a relatively weak band at 1725 cm^{-1}. The results again were irreproducible.

X-ray structure determination of $PdCl(COCO_2CH_3)[P(C_6H_5)_3]_2$*

Yellow crystals of $PdCl(COCO_2CH_3)[P(C_6H_5)_3]_2 \cdot 0.6\ CH_2Cl_2$ were obtained by slow evaporation of a CH_2Cl_2-hexane solution containing the complex and twice as many moles of $P(C_6H_5)_3$. Diffractometer measured cell constants for the monoclinic unit cell are: a = 14.932(9)Å, b = 15.723(5)Å, c = 17.813(15)Å and β = 65.2(3)°. There are four molecules per unit cell which belongs to the common space group $P2_{1/c}$. Data were collected on a fully-automated Hilger-Watts four-circle diffractometer using Zr-filtered Mo radiation (0.7107Å). A total of 1669 reflections were judged observed after correction for Lorentz, polarization and background effects. All 49 nonhydrogen atoms in the asymmetric unit were easily located using the heavy atom method. Full-matrix, least-squares refinements varying positional and anisotropic thermal parameters for the heavy atoms of the complex, positional and isotropic parameters for the light atoms of the complex and positional and occupancy parameters for the solvent molecule converged to the present minimum discrepancy index of 0.091.

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*The X-ray structure determination was carried out by Dr. Jose Fayos under the supervision of Dr. Jon Clardy of this department.

NOVEL COMPLEXES WITH SULFUR-CONTAINING LIGANDS

Introduction

Thiocarbonyl complexes

The first transition metal complex containing a terminal CS ligand, $RhCl(CS)(PPh_3)_2$, was reported in 1966.[33] In the 7 years which followed a variety of CS containing complexes have been reported, and at present thiocarbonyl complexes are known for the metals: manganese[34], iron[35], ruthenium[36,37], cobalt[38], rhodium[39,40], iridum[41-44], and the group VI metals[45] chromium, molybdenum, and tungsten. In all the complexes CS is present with other ligands, and the complexes $CpMn(CO)(CS)_2$[34] and $CpMn(CS)_3$[34] are presently the only known examples in which more than one CS group is attached to the same metal atom. Although no stable binary thiocarbonyl complexes, M(CS)n, have been isolated, the species $Ni(CS)_4$ has been detected[46] in a low temperature matrix. X-ray structure determinations of $RhCl(CS)(PPh_3)_2$[47] and $[Ir(CO)_2(CS)(PPh_3)_2][PF_6]\cdot Me_2CO$[48] show a linear M-C-S, completely analogous to that found in metal carbonyls.

The known thiocarbonyl complexes are found to be very stable and theoretical calculations[49] indicate that CS ligands should be even more strongly bound to transition metals than are CO ligands. The fact that thiocarbonyl complexes are still scarce compared to the well known carbonyl complexes is due to the lack of suitable preparative methods for the former. Synthesis of the common transition metal carbonyl complexes is achieved by direct carbonylation with CO. This method is not possible for thiocarbonyl complexes since CS does not exist under ordinary conditions. The first successful preparative method was the reaction of suitable metal complexes with CS_2 and triphenylphosphine in methanol[36,41] (eq. 14). Another method involves the reaction of anionic metal carbonyl complexes

$$RhCl(PPh_3)_3 + CS_2 \xrightarrow{PPh_3,MeOH} RhCl(CS)(PPh_3)_2 + SPPh_3 \qquad (14)$$

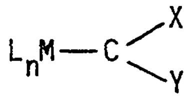
with alkyl thiochloroformates[35] (eq. 15) or thiophosgene.[45]

$$CpFe(CO)_2^- \xrightarrow{EtOCSCl} CpFe(CO)_2CSOEt \xrightarrow[-EtOH]{HCl} CpFe(CO)_2CS^+ \qquad (15)$$

No platinum or palladium complexes containing a CS ligand have been reported, and the synthesis of the complex $[PtCl(CS)(PPh_3)_2][BF_4]$, for which the carbonyl analog does exist[50], was attempted in this work. A review of transition metal complexes with CS ligands has recently been published.[51]

Carbene complexes

The synthesis and structural study of transition metal carbene complexes has received much attention over the last few years and the important results in this area have been summarized in recent review articles.[52,53] Carbene complexes are those of the general structural type

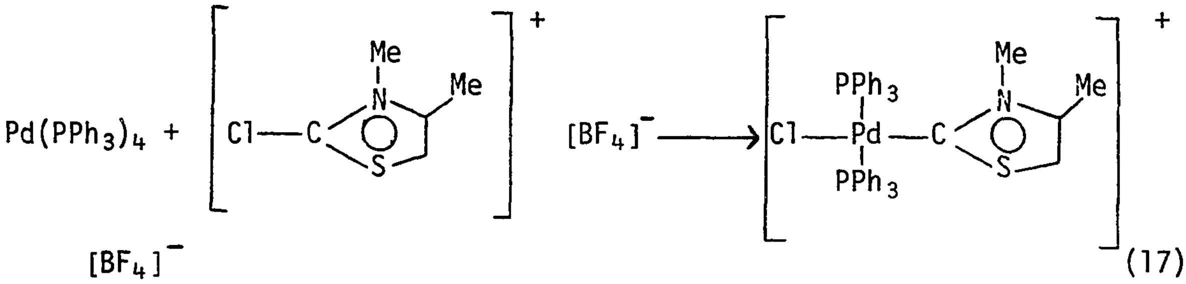


where M is a metal and L represents various other ligands. In most known carbene complexes X and Y are O, S, or N. The uncoordinated ligand, :CXY, is regarded as a neutral nucleophilic carbene species. The carbene appears to be a "soft" ligand since it is usually coordinated to metals in low oxidation states.

The first carbene complexes were prepared in 1915[54], although not characterized as such until 1970.[55] However, interest in this area was initiated in 1964 when Fischer prepared $(CO)_5WC(OMe)Ph$ and formulated it as a carbene complex.[56] Some of the more general preparative methods so far developed include: 1) modification of a coordinated ligand; 2) oxidative-addition; 3) nucleophilic substitution by metal carbonyl anions; and 4) ligand displacement by carbene fragments. Method 1 has been employed extensively by Fischer[57] in the synthesis of group VI metal carbene complexes (eq. 16). This general method is also demonstrated

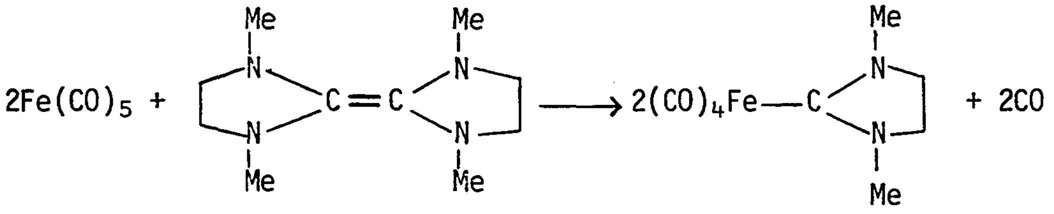
$$\mathrm{Cr(CO)_6} \xrightarrow{\mathrm{MeLi}} \mathrm{[(CO)_5CrCOMe]^-\ Li^+} \xrightarrow{\mathrm{[Me_3O][BF_4]}} \mathrm{(CO)_5CrC(OMe)Me + LiBF_4 + Me_2O} \qquad (16)$$

in the preparation of several platinum and palladium carbene complexes by the addition of nucleophiles, such as alcohols and amines, to coordinated isocyanide ligands.[58] The oxidative-addition route (method 2) has been used to prepare cyclic carbene complexes of Ir(III), Ni(II), Pd(II), and Pt(II) by the reaction of N-methyl-2-chloro-4-methylthiazolium tetrafluoroborate with Ir(I), Ni(0), Pd(0), and Pt(0) complexes[59] (eq. 17). Method 3 simply involves the



(17)

nucleophilic displacement of chloride in the N-methyl-2-chloro-4-methylthiazolium cation by metal carbonyl anions and has been used[60] to prepare carbene complexes of Ir(I), Rh(I), Mn(I), Cr(0), and Fe(0). Method 4 is a very general method based on displacement of CO, olefin, phosphine, or halide from metal complexes by a nucleophilic carbene fragment derived from an electron-rich olefin[61,62] (eq. 18). This method has been used to prepare



(18)

carbene complexes of Cr(0), Fe(0), Ir(I), Pd(II), Pt(II), and Au(I).

Structural data[52,53] for transition metal carbene complexes show that the metal, carbene carbon, and heteroatoms are coplanar indicating sp^2 hybridization for the carbene carbon atom. There is believed to be little double bond character in the M-C (carbene) bond and appreciable π-bonding in the C (carbene)-heteroatom bonds.

We discovered that platinum complexes containing a metal-bonded, nonterminal thiocarbonyl function $(\mathrm{Pt}\text{-}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\text{-})$ undergo attack by carbonium ions and other cations at the sulfur atom to form the carbene type ligands described above. This method was then used to prepare a variety of cationic platinum carbene complexes.

Oxidative-addition as a preparative method

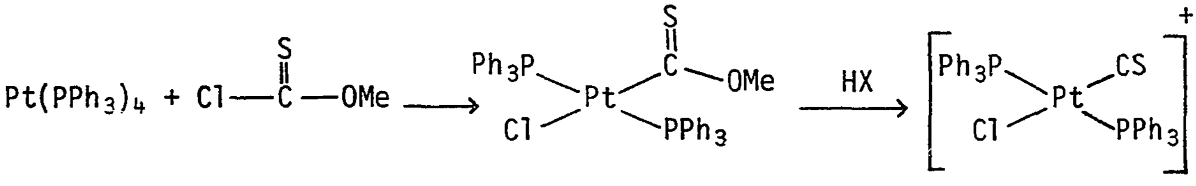
In section I it was mentioned that oxidative-addition reactions (eq. 5) are believed to be important steps in catalytic reactions involving platinum and palladium. The oxidative-addition reaction has also proven to be a very useful method of preparing many new and novel organometallic complexes of platinum group metals. The most general type of oxidative-addition reaction with organic compounds involves the cleavage of carbon-halogen bonds in alkyl halides, acyl halides, and other organic halogen compounds. This type of reaction has been a reliable method for preparing complexes with specific organic ligands where the ligand is coordinated via a metal-carbon bond. An example is the synthesis of alkoxalyl complexes described previously.

The reactivity of cyclic trithiocarbonates toward PtL_4, where L = PPh_3 or $PMePh_2$, was investigated in this work, and it was found that oxidative-addition occurs readily with carbon-sulfur bond cleavage in the trithiocarbonate. Carbon-sulfur bond cleavage has not been shown to be a general mode of reaction of organosulfur compounds with low-valent metal complexes. Further investigation of this reaction was carried out to determine if carbon-sulfur bond cleavage by Pt(0) is general for organic compounds containing a trithiocarbonate group.

Results and Discussion

Thiocarbonyl and related complexes

The preparation of the thiocarbonyl cation $[PtCl(CS)(PPh_3)_2]^+$ was initially attempted by the following route.



$+ X^- + MeOH$ (19)

The complex $PtCl(CSOMe)(PPh_3)_2$ has not been previously reported and was prepared here by the indicated oxidative-addition reaction.[63] It is a stable complex and was easily isolated and characterized by infrared and proton NMR spectra as well as elemental analyses. The second reaction in the sequence was attempted using acids such as aqueous HBF_4 or trichloroacetic acid, and the IR spectra of the resulting solutions did not show the presence of a terminal CS ligand. When powerful alkylating agents such as $[Et_3O][BF_4]$ or $MeSO_3F$ ("magic methyl") were used in place of protonic acids reaction occurred rapidly but the IR spectra again did not show the presence of a terminal CS ligand. Although the attempted reactions with protonic acids did not produce the desired product, it still seemed reasonable that a "hard" Lewis acid would preferentially attack the O atom in the methoxythiocarbonyl ligand and thus abstract methoxide to give the thiocarbonyl cation. When this reaction was carried out using BF_3 the IR spectrum of the reaction solution did show a strong new band at 1400 cm^{-1}, a strong broad absorption at 1050 cm^{-1}, and a disappearance of the original $\nu(C{=}S)$ band at 1200 cm^{-1}. The band at 1400 cm^{-1} is assigned to $\nu(C{\equiv}S)$ of the product. This is higher than the CS band observed in other thiocarbonyl complexes and this is not surprising since the carbonyl analog of this complex has an exceptionally high CO stretching frequency (2120 cm^{-1}). The broad absorption at 1050 cm^{-1} is typical of the BF_4^- ion. From the IR spectrum alone it appears that reaction occurs with BF_3 (eq. 20) to give the thiocarbonyl complex. When solvent was removed the product remained as

$$PtCl(CSOMe)(PPh_3)_2 + 2BF_3 \xrightarrow[25°,20\ hrs]{CH_2Cl_2} [PtCl(CS)(PPh_3)_2][BF_4] + BF_2(OCH_3) \qquad (20)$$

a yellow oil. Attempted recrystallization from CH_2Cl_2-hexane also gave an oil. This oil could be solidified by warming under vacuum to give a noncrystalline, impure form of theproduct. This solid reacts with nucleophiles to give products which indicate the presence of a terminal CS ligand in the reactant (Fig. 6). The products were easily identified from their characteristic IR and NMR spectra. The products from the reactions

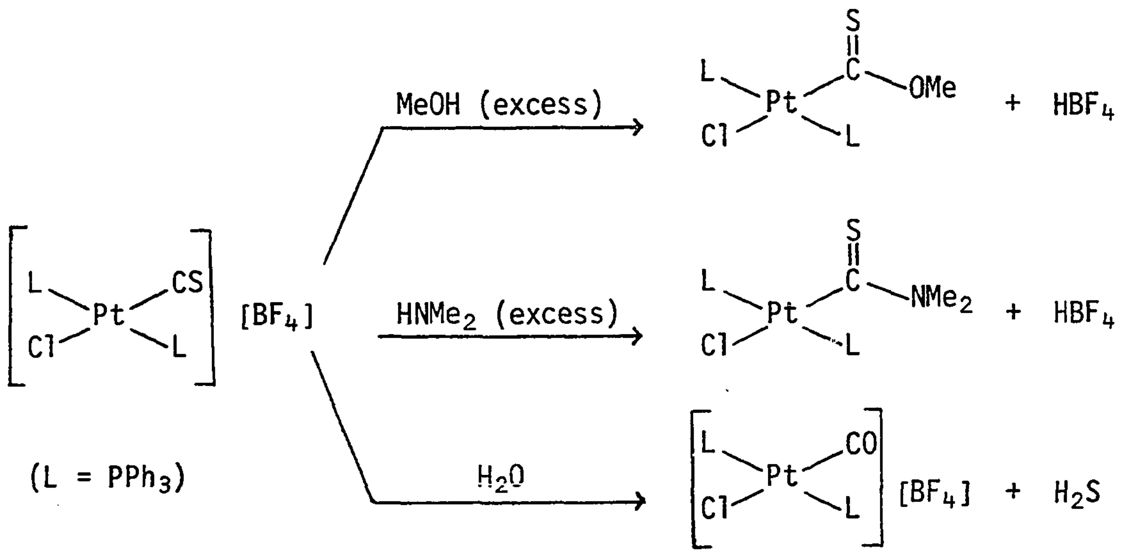


Figure 6. Some reactions of $[PtCl(CS)(PPh_3)_2][BF_4]$

with MeOH and $HNMe_2$, after isolation and recrystallization, were obtained in 60-70% yield. A known amount of the impure solid thiocarbonyl product was allowed to react with an excess of MeOH and the amount of thiomethoxycarbonyl complex formed was measured from the intensity of the $\nu(C=S)$ band at 1200 cm^{-1} ($\varepsilon=3.24 \times 10^{-2}$). Assuming that the reaction between the thiocarbonyl cation and MeOH is quantitative, the amount of thiomethoxycarbonyl complex formed indicates that the impure solid from the BF_3 reaction is ~66% $[PtCl(CS)(PPh_3)_2][BF_4]$. When this complex in CH_2Cl_2 solution is shaken with a small amount of water the IR spectrum of the CH_2Cl_2 solution shows a disappearance of the terminal thiocarbonyl band at 1400 cm^{-1} and the appearance of a new band at 2115 cm^{-1}. The presence of H_2S

in this reaction is detected by its odor. The solid thiocarbonyl complex also undergoes slow hydrolysis when exposed to the atmosphere for several hours.

It was mentioned that attempted recrystallization from CH_2Cl_2-hexane caused the impure thiocarbonyl complex to separate as an oil. However, when a small quantity of hexane was carefully added to a CH_2Cl_2 solution of the oil, and the clear solution allowed to stand at 25° for several days, well-defined yellow crystals gradually formed. This yellow solid is not the thiocarbonyl complex originally present in solution since it shows no $\nu(C{\equiv}S)$ band in the IR spectrum, however an elemental analysis does show the presence of sulfur. The complex is very stable and does not react with MeOH. It is a 1:1 electrolyte in CH_2Cl_2 and contains the BF_4^- anion (broad band at 1050 cm^{-1}). The proton NMR spectrum showed the presence of phenyl protons only and the IR spectrum gave no information as to the structure of the cation. A crystal structure determination* of the complex was carried out in order to elucidate the structure of the cation. It was found that the cation is dimeric (Fig. 7). There is one BF_4^- per dimer indicating a unit positive charge for the dimeric cation and this is consistent with the conductivity measurement. The structure (Fig. 7) shows a square-planar geometry about each platinum atom with the two planes being perpendicular to each other. The atoms Pt(2), P(3), P(4), S(1), and S(2) lie in one plane and this plane makes an angle of 89.97° with the plane defined by Pt(1), Cl(1), P(1), P(2) and C(1). The Pt(1)-C(1) bond

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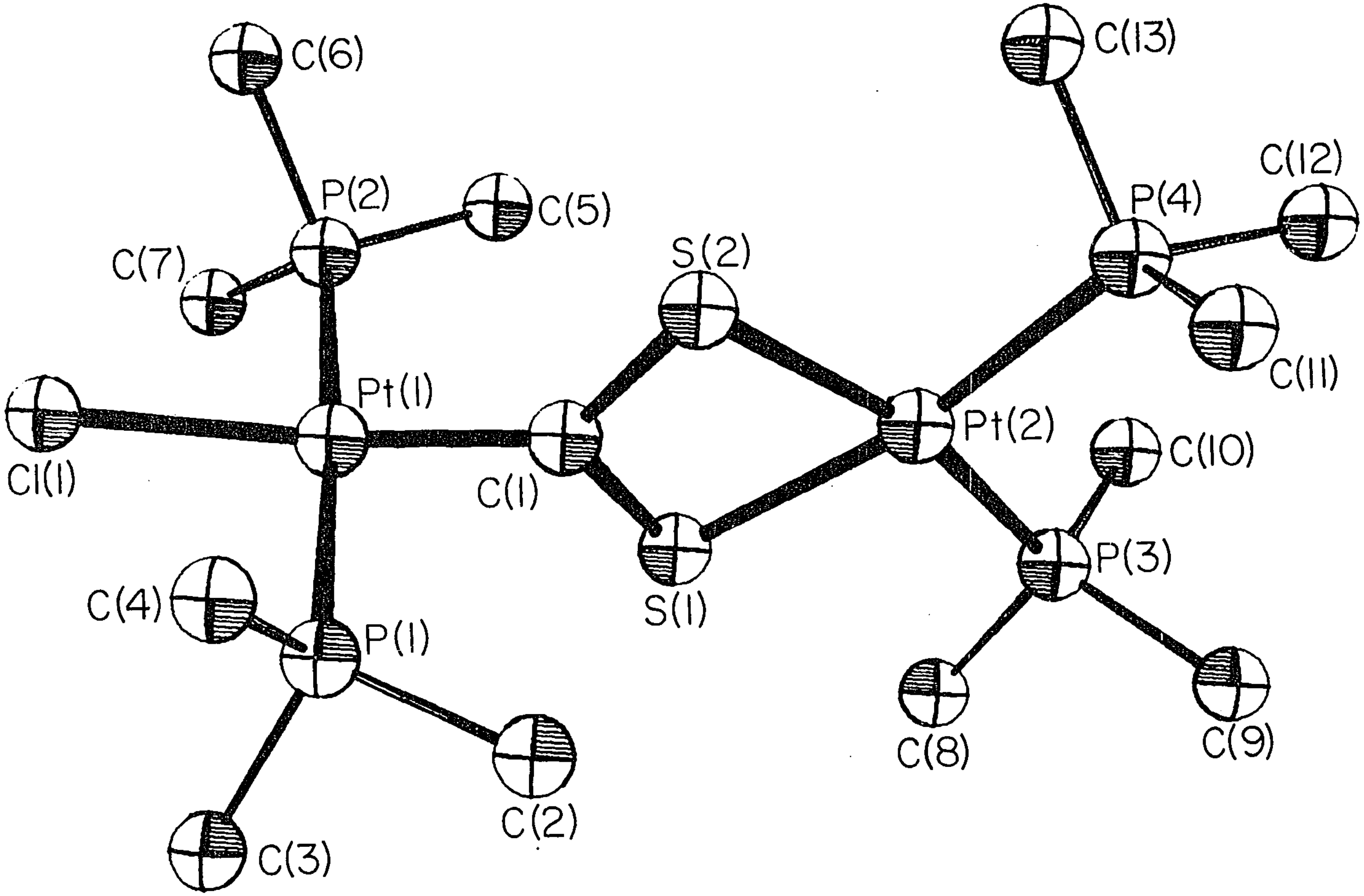
*The X-ray structure determination was carried out by Jim Lisy under the supervision of Dr. Jon Clardy of this department.

Figure 7. Computer generated drawing of $[Cl(PPh_3)_2Pt(CS_2)Pt(PPh_3)_2][BF_4]$.

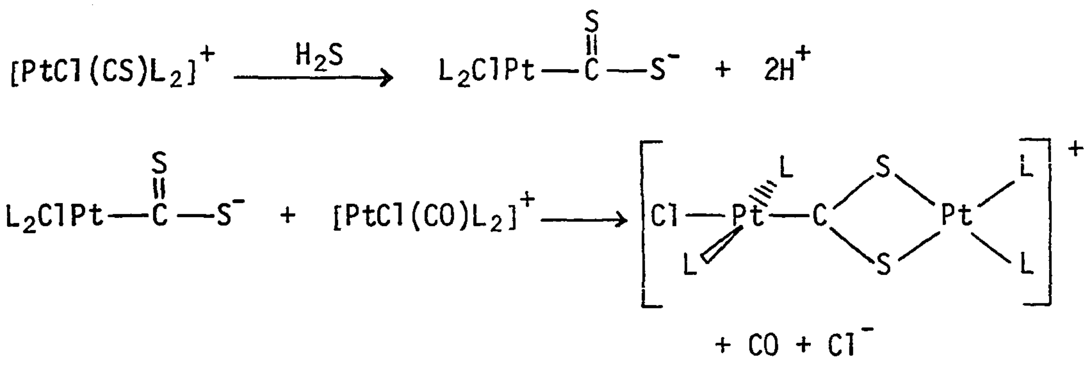
Bond distances (Å)	Bond angles
Pt(1)-C(1), 1.950(15)	Pt(1)-C(1)-S(1), 122.6(1.1)
Pt(1)-Cl(1), 2.382(5)	Pt(1)-C(1)-S(2), 127.5(1.2)
C(1)-S(1), 1.709(21)	S(1)-C(1)-S(2), 109.9(9)
C(1)-S(2), 1.692(20)	C(1)-S(1)-Pt(2), 88.8(6)
Pt(2)-S(1), 2.353(5)	C(1)-S(2)-Pt(2), 88.9(7)
Pt(2)-S(2), 2.361(5)	S(1)-Pt(2)-S(2), 72.4(2)
Pt(1)-P(1), 2.331(6)	S(2)-Pt(2)-P(4), 92.7(2)
Pt(1)-P(2), 2.339(6)	P(4)-Pt(2)-P(3), 101.6(2)
Pt(2)-P(3), 2.310(6)	P(3)-Pt(2)-S(1), 93.3(2)
Pt(2)-P(4), 2.287(6)	


C(6)
C(13)
C(12)
P(2)
C(5)
P(4)
S(2)
C(7)
C(11)
Pt(1)
Cl(1)
Pt(2)
C(10)
C(1)
P(3)
S(1)
C(4)
P(1)
C(8)
C(9)
C(2)
C(3)

distance is slightly shorter than typical Pt-C(sp^2) bond distances and this may be due to a small amount of π-bonding. The Pt(2)-S(1) and Pt(2)-S(2) bond distances are similar to Pt-S bond distances (2.32Å ave.) observed in the dithiocarbamate complex $(Et_2NCS_2)_2Pt$.[64] The S(1)-Pt(2)-S(2) bond angle is 72.4(2)° while the S-Pt-S angle of the mentioned dithiocarbamate complex[64] is 75.5°. The C(1)-S(1) and C(1)-S(2) bond distances are also very similar to the C-S distances observed in both dithiocarbamate and xanthate complexes.[65]

The formation of this complex from the starting thiocarbonyl complex is currently under investigation. Since the solid thiocarbonyl complex is sensitive to atmospheric moisture, it is possible that solutions of this complex absorb H_2O from the atmosphere and form the dimeric cation by the following route.

$$[PtCl(CS)L_2]^+ \xrightarrow{H_2O} [PtCl(CO)L_2]^+ + H_2S$$



$$[PtCl(CS)L_2]^+ \xrightarrow{H_2S} L_2ClPt-\overset{\overset{S}{\|}}{C}-S^- + 2H^+$$

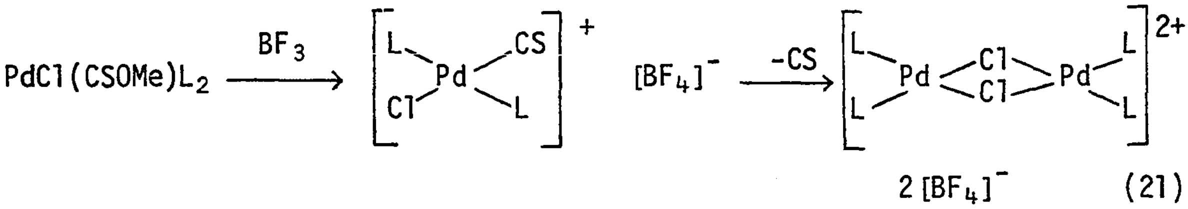
$$L_2ClPt-\overset{\overset{S}{\|}}{C}-S^- + [PtCl(CO)L_2]^+ \longrightarrow [\ldots]^+ + CO + Cl^-$$

It was later found that dry HCl gas could be used in place of BF_3 to generate the thiocarbonyl cation in solution (eq. 21). When this reaction solution was treated with $AgBF_4$ and the AgCl precipitate removed, a yellow

$$PtCl(CSOMe)(PPh_3)_2 \xrightarrow{HCl} [PtCl(CS)(PPh_3)_2]^+ + Cl^- + MeOH \qquad (21)$$

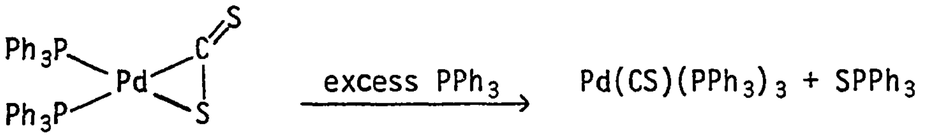
crystalline solid could be isolated. This yellow complex showed no ν(C≡S) band in the IR spectrum and appeared to be the dimeric complex previously described.

The analogous palladium methoxythiocarbonyl complex PdCl(CSOMe) $(PPh_3)_2$ was prepared and reacted with BF_3 in an attempt to prepare $[PdCl(CS)(PPh_3)_2][BF_4]$ for which the carbonyl analog is unknown. A stable, bright yellow solid was isolated from this reaction and identified as the dimeric complex $[PdCl(PPh_3)_2]_2 2[BF_4]$.[66] It is possible that $[PdCl(CS)(PPh_3)_2]^+$ is initially formed but is unstable and loses CS (eq. 21).



(21)

An attempt was made to prepare a Pd(0) thiocarbonyl complex by reacting the known carbon disulfide adduct $Pd(CS_2)(PPh_3)_2$[67] with excess PPh_3 (eq. 22). This would be similar to the reaction used (eq. 14) to prepare thiocarbonyl complexes of Rh and Ir.[41] On refluxing



(22)

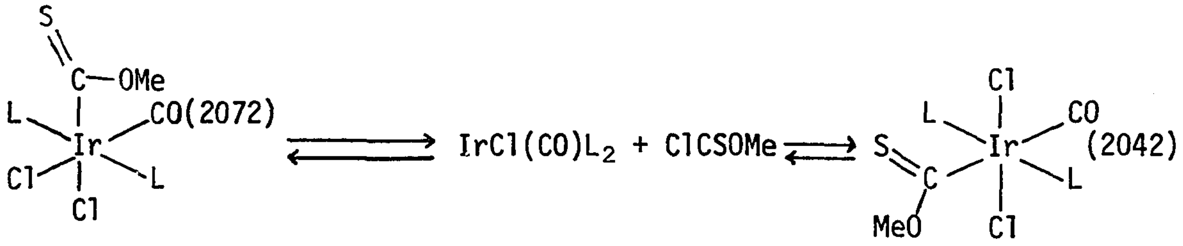
in CS_2 or $CHCl_3$ solution for several hours a new band appeared at 1260 cm^{-1} and the original ν(C=S) band at 1190 cm^{-1} gradually diminished. The band at 1260 cm^{-1} can reasonably be attributed to the CS stretching frequency of a Pd(0) thiocarbonyl complex. However, all attempts to isolate this product by careful recrystallization gave only $Pd(PPh_3)_4$.

The susceptibility of the sulfur atoms in the complexes $M(CS_2)(PPh_3)_2$[67], where M = Pt or Pd, toward methylation by $MeSO_3F$ was examined as a possible route to dithioester complexes $M\text{-}CS_2Me$. Both CS_2 complexes gave dark brown solutions when treated with $MeSO_3F$ under mild conditions. Only dark colored oils could be isolated from these solutions and their NMR spectra clearly indicated that the desired product was not present.

The synthesis of a cationic iridium thiocarbonyl complex by a route similar to 19 was considered. The Ir(I) complex $IrCl(CO)(PPh_3)_2$ was treated with an excess of ClCSOMe in benzene to give the Ir(III) oxidative-addition product $IrCl_2(CO)(CSOMe)(PPh_3)_2$ which gradually precipitated from the reaction solution as a pale yellow solid when hexane was added. The IR spectrum of this Ir(III) complex in $CHCl_3$ solution initially shows a strong ν(CO) band at 2072 cm^{-1} and relatively weak ν(CO) bands at 2042 cm^{-1} and 1964 cm^{-1}. The spectrum changes rapidly with time as the 2072 cm^{-1} band grows weaker while the 2042 and 1964 cm^{-1} bands grow stronger. The band at 1964 cm^{-1} is due to ν(CO) of $IrCl(CO)(PPh_3)_2$, and an increase in the intensity of this band indicates that reductive-elimination of ClCSOMe from the Ir(III) complex occurs in $CHCl_3$ solution.

The CO bands at 2072 and 2042 cm^{-1} were tentatively assigned to the isomers I and II respectively (Fig. 8) in order to construct a model which could explain the observed changes taking place in solution.

The spectrum of the solid product (nujol mull) shows a strong CO band at 2066 cm^{-1} for I with a weak shoulder at 2040 cm^{-1} representing a relatively small amount of II. In the lower region of the spectrum there is a strong band at 1230 cm^{-1} which can be assigned to ν(C=S) of I. In the



I II

Figure 8. Products of the oxidative-addition reaction of IrCl(CO)$(PPh_3)_2$ with ClCSOMe.

far IR spectrum ν(Ir-Cl) bands are observed at 270 and 321 cm^{-1} for the solid. These values are very similar to the Ir-Cl stretching frequencies observed[68] for $IrCl_2(CO)(CO_2Me)(PMe_2Ph)_2$ which is known to have the configuration shown for I, and this supports the assignment of configuration I to the major product isolated from the oxidative-addition reaction.

When the solid Ir(III) product is dissolved in $CHCl_3$ containing an excess of ClCSOMe the 2072 cm^{-1} band again decreases while the 2042 cm^{-1} band increases, but no band is observed at 1964 cm^{-1}. This is reasonable since a high concentration of ClCSOMe would permit only a very low concentration of $IrCl(CO)(PPh_3)_2$ in solution. These results indicate that configuration I is not stable relative to configuration II in $CHCl_3$ solution and that conversion of I to II takes place by reductive-elimination followed by oxidative-addition. The IR spectrum of the solid complex in benzene shows a strong band at 2076 cm^{-1} and a weak band at 2040 cm^{-1} and the spectrum does not change with time. Therefore in benzene solution configuration I is stable with respect to isomerization to II.

When ClCSOMe was added to a solution of $IrCl(CO)(PPh_3)_2$ in $CHCl_3$ and the IR spectrum immediately scanned, a strong band was observed at 2042 cm^{-1} and an extremely weak band was also present at 2072 cm^{-1}. The same experiment in benzene solution gives a strong band at 2042 cm^{-1} and a relatively weak band at 2076 cm^{-1}. These spectra did not change with time. Thus II is preferentially formed from the oxidative-addition reaction in either $CHCl_3$ or benzene. The fact that the solid product isolated from the original oxidative-addition reaction in benzene is predominantly I may be due to a much lower solubility for I.

After observing the oxidative-addition reaction in benzene to give predominantly II as the product in solution (above experiment), hexane was carefully added to this benzene reaction solution causing a solid to precipitate slowly. This solid was isolated and redissolved in benzene. The IR spectrum of this solution had only one CO band at 2076 cm^{-1} indicating the solid to be I. Thus it appears that I precipitates from an equilibrium mixture thereby causing the conversion of II to I in solution. Of the two configurations (Fig. 8) I would most likely be the more polar because of the arrangement of the chloride ligands and this isomer would therefore have a lower solubility in nonpolar solvents such as benzene and hexane. After isolation the solid product is only moderately soluble in benzene.

The NMR spectrum of the solid complex in $CDCl_3$ initially shows an intense singlet at τ 7.07 and a weak singlet at τ 7.22. The intensity of the τ 7.07 peak decreases with time while the τ 7.22 peak gradually increases in intensity. After 8 hours only one strong peak at τ 7.22 was present. This change in the NMR spectrum in $CDCl_3$ solution corresponds to the change in the IR spectrum in $CHCl_3$ solution, and the singlet at τ 7.07 can be assigned to the $-OCH_3$ protons of I while the singlet at τ 7.22 is assigned to the $-OCH_3$ protons of II.

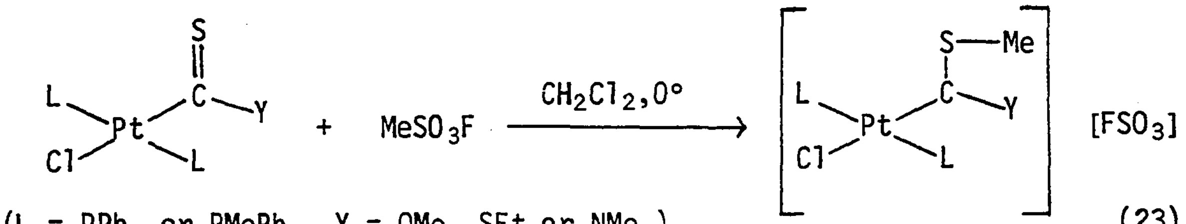
A reaction occurs between $IrCl_2(CO)(CSOMe)(PPh_3)_2$ and BF_3, but a $\nu(CO)$ band above 2100 cm^{-1}, which would be expected for $IrCl_2(CO)(CS)(PPh_3)_2^+$, is not present in the reaction solution. There is also no band corresponding to a terminal CS ligand. This complex obviously reacts differently with BF_3 than does the methoxythiocarbonyl complex of platinum.

Cationic carbene complexes of Pt(II)

A brief account of the preparations and properties of the complexes will be presented first followed by a discussion of the important spectral and structural features of the carbene ligands.

In the section on thiocarbonyl complexes it was mentioned that $PtCl(CSOMe)(PPh_3)_2$[69] readily reacts with alkylating agents to give a product other than the thiocarbonyl complex. This reaction was later reinvestigated and the product isolated and characterized as a cationic carbene complex. It was also found that other complexes containing a Pt-CS- group such as $PtCl(CS_2Et)(PPh_3)_2$[70] and $PtCl(CSNMe_2)(PPh_3)_2$[13] undergo the same reaction (eq. 23) to give carbene complexes. The above three complexes all react rapidly with either $MeSO_3F$ ("magic methyl") or $[Et_3O][BF_4]$ in CH_2Cl_2 at 0°.

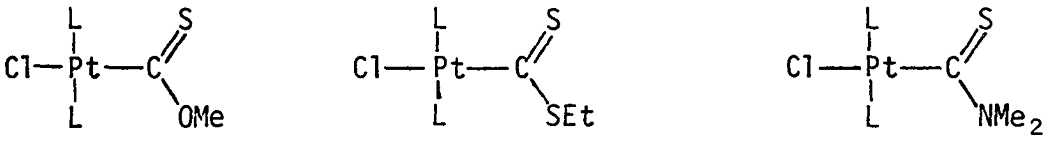
The carbene complex $\{PtCl[C(SMe)OMe](PPh_3)_2\}\{FSO_3\}$ decomposes within a few hours in solution at room temperature. The identification of relatively small amounts of Me_2S and $[PtCl(CO)(PPh_3)_2]^+$ as products indicate



(L = PPh_3 or $PMePh_2$, Y = OMe, SEt or NMe_2) (23)

that a minor mode of decomposition involves the transfer of a methyl group from O to S in the carbene ligand. The major mode of decomposition gives a relatively large amount of CH_3Cl, the other products being unidentified. Addition of excess Cl^- or $HNMe_2$ to solutions of this complex cause rapid decomposition with formation of CH_3Cl or $HNMe_3^+$. When $PMePh_2$ was substituted for PPh_3 the stability of the complex was greatly increased, and showed no sign of decomposition in solution after several hours at 25°. This increase in stability is presumably due to the fact that $PMePh_2$ being less electron-withdrawing than PPh_3, provides more electron density at the sulfur atom thus enhancing the binding of a carbonium ion at this site.

The carbene cations derived from 2 and 3 (Fig. 9) are very stable in solution and do not react with either Cl^- or $HNMe_2$. The increased



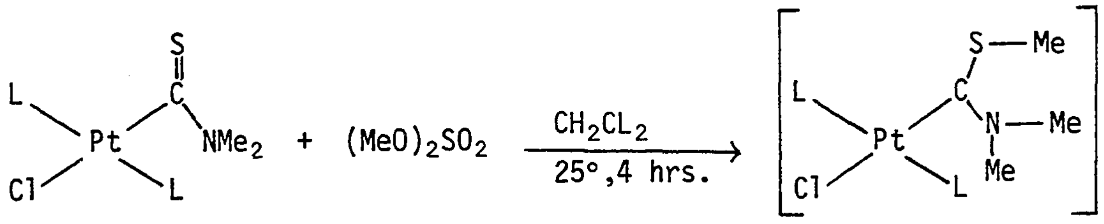
1 2 3

Figure 9. The neutral complexes from which the carbene cations are derived.

stability of these carbene complexes is reasonable since there should be more electron density at the sulfur atom of the CS group in 2 and 3 than in 1. Thus the tendency for these neutral complexes to undergo electrophilic attack at the thiocarbonyl sulfur atom as well as the stability of the resultant carbene cations should increase in the order $1<2<3$.

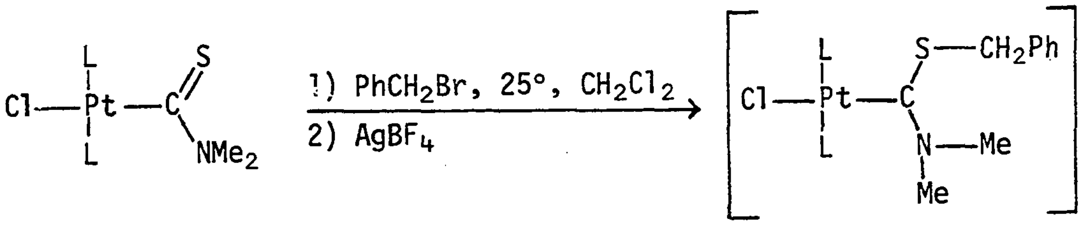
Although the carbene complexes derived from 2 and 3 appear to be equally stable, their reactivity toward HCl does indicate a difference in the relative tendency of these two complexes to form carbene cations. Both 1 and 2 react readily with dry HCl gas in CH_2Cl_2 solution to give methanol or ethanethiol and the thiocarbonyl complex previously described, $[PtCl(CS)(PPh_3)_2]^+$. In these reactions the original yellow solutions turn to a deeper yellow color characteristic of the thiocarbonyl cation. Under the same conditions a yellow solution of 3 reacts with HCl to give a clear, colorless solution. This reaction is reversible and purging the solution with nitrogen causes regeneration of 3 and the yellow color. The product of this reaction is the carbene cation which results from protonation of the thiocarbonyl sulfur atom. This complex can be isolated as a stable, white crystalline solid, $\{PtCl[C(SH)NMe_2](PPh_3)_2\}\{CF_3SO_3\}$, when CF_3SO_3H is used instead of HCl. The complex is stable in solution and does not react with water. However, reaction occurs readily when aqueous Na_2CO_3 is shaken with a $CHCl_3$ solution of the complex. The $CHCl_3$ phase turns yellow and there is a vigorous effervescence. The neutral thiocarbamoyl complex was isolated from the $CHCl_3$ phase indicating deprotonation of the carbene cation by the carbonate.

The reactivity of 3 with milder alkylating agents was investigated. Reaction takes place slowly with dimethyl sulfate (eq. 24) to give the same carbene cation obtained from reaction with $MeSO_3F$. Reaction of 3 with benzyl bromide or allyl bromide occurs slowly at 25° when an excess



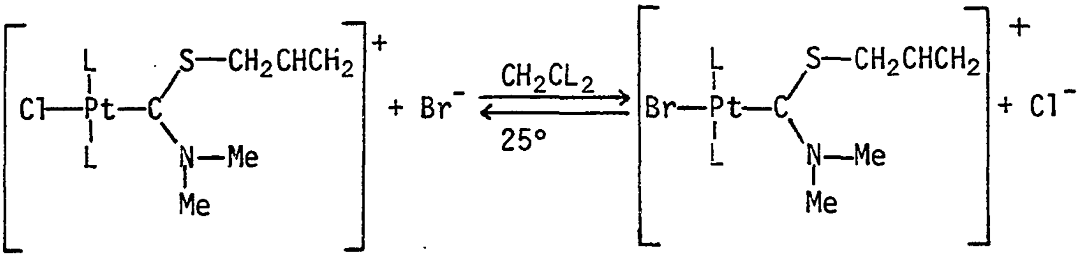
[$MeSO_4$] (24)

of the organic halide is present. When these reaction solutions are treated with a solution of $AgBF_4$ the solid AgBr separates and the carbene cations can be isolated as the BF_4^- salts. From the reaction with allyl



[BF_4] + AgBr (25)

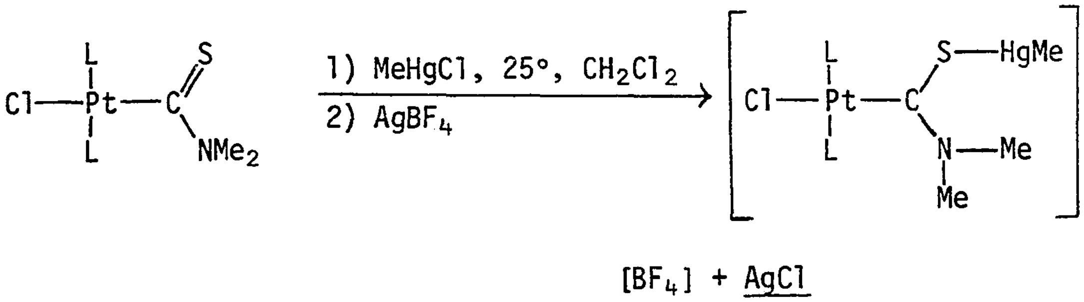
bromide a mixed-halide carbene cation (both Cl and Br ligands present) was obtained. This halide mixture most likely results from replacement of chloride by free bromide in solution (eq. 26) prior to the addition of $AgBF_4$. It is interesting that this type of halide exchange is not ob-



(26)

served in the reaction of 3 witn benzyl bromide. It was also found that the $PMePh_2$ derivative of 3 reacts with allyl bromide to give the carbene cation with no halide exchange. The mixed-halide carbene complex could be completely converted to the chloride complex in the presence of an excess of bis-(triphenylphosphine) imminium chloride, $[N(PPh_3)_2]Cl$. The mono-halide carbene complex was obtained more conveniently by reacting the bromo analog of 3 with allyl bromide.

A few reactions of 3 with Lewis acids other than carbonium ions were investigated. The methylmercury cation, CH_3Hg^+, adds to 3 by forming an Hg-S bond and giving the stable carbene cation (eq. 27). There appears to be no reaction between 3 itself and CH_3HgCl in CH_2Cl_2 solution at 25°



(27)

since the original yellow color of the reaction solution did not change after 1 hour. Addition of $AgBF_4$ to this yellow solution immediately produced a white suspension of AgCl. The added Ag^+ apparently abstracts Cl^- from CH_3HgCl and the resultant CH_3Hg^+ cation binds to the sulfur atom of the thiocarbamoyl complex to form the carbene cation. This mercury-containing carbene complex is stable in the solid state and in solution. However, in solution excess Cl^- readily cleaves the Hg-S bond giving CH_3HgCl and the neutral thiocarbamoyl complex. This reaction occurs rapidly on adding $[N(PPh_3)_2]Cl$ to a solution of the carbene complex in CD_3CN, and the products were easily identified from the NMR spectrum of the solution.

The reaction of 3 with the Lewis acid $SnCl_4$ does not proceed in the same manner as the above reactions. Instead, $SnCl_4$ removes a chloride ion from the thiocarbamoyl complex forming $SnCl_5^-$ and the known[13] dimeric dication $[Pt(CSNMe_2)(PPh_3)_2]_2^{2+}$. The dimeric complex was isolated as a pale yellow crystalline solid, identified by its NMR spectrum and its characteristic reaction[13] with excess Cl^- to regenerate 3. The presence of the $SnCl_5^-$ anion was confirmed by a chloride analysis and a conductivity measurement in CH_2Cl_2 which showed the complex to be a 2:1 electrolyte.

The IR spectra of the carbene complexes show strong bands characteristic of the anions FSO_3^- (1070 and 1275 cm^{-1}) and BF_4^- (1050 cm^{-1}, broad). Bands corresponding to $\nu(C{=}S)$ in the complexes 1, 2, and 3 are observed at 1200 cm^{-1}, 1058 cm^{-1} and 964 cm^{-1} respectively. The IR spectra of the carbene cations derived from these complexes show no bands at these positions. For 1 and 2 the $\nu(C{=}S)$ band is likely to be shifted to considerably lower frequencies on formation of the carbene ligand, but no assignments are made for this shifted band due to the complexity of the lower region of these spectra. The band at 964 cm^{-1} for 3 likely results from interaction of various vibrations within the -$CSNMe_2$ ligand, and it is known that an unambiguous assignment of a C=S stretching frequency is possible only when the CS group is attached to atoms other than nitrogen.[71] However, an extensive study of the infrared spectra of organic thioamides[72] has shown that a characteristic band is observed in this region for N,N-dialkylthioformamides (eq. 975 cm^{-1} for $HCSNMe_2$) and, although coupled with other vibrations, is due to a predominantly single bond CS stretching vibration. The origin of the 964 cm^{-1} band in 3 is believed to be the same. It was shown[72] that S-methylation of $HCSNMe_2$ causes a shift of this band from 975 to 860 cm^{-1}. It was observed here that the 964 cm^{-1} band of 3 is shifted to 910-920 cm^{-1} (see Table 5) on forming the carbene complexes. All thioamides exhibit a strong characteristic band between 1500 and 1600 cm^{-1} which arises from vibrational interactions, but is believed to have the C-N stretching vibration as its major component.[72] This band is shifted to higher frequencies on S-alkylation. For 3 this band is observed at 1510 cm^{-1} and is shifted to 1530-1570 cm^{-1} (see Table 5) on formation of the carbene ligand. This shift can be accounted for by the increase in double bond character of the C-N bond expected on alkylation of the sulfur atom.

Proton NMR spectra of the carbene complexes and their neutral precursors show that the methyl or ethyl protons in 1, 2 and 3 undergo a downfield shift on forming the carbene cations (see Table 6). This

Table 5. IR spectra[a] of carbene complexes derived from $PtCl[CSN(CH_3)_2][P(C_6H_5)_3]$

	$\nu(CN)$ cm^{-1}	$\nu(CS)$ cm^{-1}	Anion absorptions, cm^{-1}
$PtCl(CSNMe_2)(PPh_3)_2$[b]	1510	964	
$\{PtCl[C(SMe)NMe_2](PPh_3)_2\}\{FSO_3\}$	1535	912	1075, 1275 (broad)
$\{PtCl[C(SEt)NMe_2](PPh_3)_2\}\{BF_4\}$	1534	916	1050 (broad)
$\{PtCl[C(SCH_2Ph)NMe_2](PPh_3)_2\}\{BF_4\}$	1539	916	1050 (broad)
$\{PtBr[C(SCH_2CHCH_2)NMe_2](PPh_3)_2\}\{BF_4\}$[c]	1535	937	1050 (broad)
$\{PtCl[C(SHgMe)NMe_2](PPh_3)_2\}\{BF_4\}$	1543	916	1050 (broad)
$\{PtCl[C(SH)NMe_2](PPh_3)_2\}\{CF_3SO_3\}$	1564		1030, 1155, 1223

[a] All spectra recorded for CH_2Cl_2 solutions at room temperature. Absorption bands were calibrated with polystyrene using an expansion recorder and are believed to be accurate to ±1 cm^{-1}.

[b] See reference 13.

[c] Derived from $PtBr(CSNMe_2)(PPh_3)_2$. This complex also shows a very weak band at 1637 cm^{-1} for $\nu(C{=}C)$ of the allyl group (see text).

desielding effect is expected for attaching a carbonium ion to the thiocarbonyl sulfur atom of the neutral complexes. The carbene complexes show a long-range coupling $J(^{195}Pt\text{-}C\text{-}X\text{-}C\text{-}{}^{1}H)$ of 6-10 Hz (X=O, S or N) which is also observed for the complexes 1, 2 and 3 (Table 6).

The NMR spectra of carbene complexes derived from $PtCl(CSOMe)L_2$, where L = PPh_3 or $PMePh_2$, show that the $-OCH_3$ protons undergo a very large

Table 6. H' NMR spectra of platinum carbene complexes[a]

	τ(SR)[b]	τ(XR'n)[b]	J(PtCSCH),Hz	J(PtCXCH),Hz[c]	Solvent
$PtCl(CSOMe)(PPh_3)_2$		7.01(s)		9.0	$CDCl_3$
$PtCl(CSOMe)(PMePh_2)_2$[d]		6.91(s)		9.0	$CDCl_3$
$PtCl(CS_2Et)(PPh_3)_2$[e]	7.8 (m), 9.4 (t)				$CDCl_3$
$PtCl(CSNMe_2)(PPh_3)_2$[f]		7.35(s), 7.76(s)		7.5	$CDCl_3$
$\{PtCl[C(SMe)OMe](PPh_3)_2\}\{FSO_3\}$	8.39(s)	5.61(s)		6.5	CD_2Cl_2
$\{PtCl[C(SEt)OMe](PPh_3)_2\}\{BF_4\}$	7.86(m), 9.28(t)	5.54(s)		6.8	CD_2Cl_2

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[a] All spectra were recorded at room temperature with tetramethylsilane as an internal standard. Abbreviations: s, singlet; t, triplet; m, multiplet.

[b] R = Me, Et, H, $-CH_2Ph$, $-CH_2CHCH_2$ or $-HgCH_3$; X = O or N; R' = Me; n = 1 or 2. When X = N then n = 2, and the trans-Me group is listed first followed by the cis-Me group.

[c] For X = N, these J values are for the trans-Me only since the platinum satellites are not resolved for the cis-Me.

[d] For $P-CH_3$ protons, τ7.83(t) with satellites, J(PCH) = 3.7 Hz and J(PtPCH) = 32.5 Hz.

[e] See reference 70.

[f] See reference 13.

Table 6. (Continued)

	τ(SR)5	τ(XR'n)7	J(PtCSCH),Hz	J(PtCXCH),Hz	Solvent
$\{PtCl[C(SMe)OMe](PMePh_2)_2\}\{FSO_3\}$[g]	8.33(s)	5.66(s)	7.0	6.5	CD_2Cl_2
$\{PtCl[C(SEt)_2](PPh_3)_2\}\{BF_4\}$	9.07(t), 6.40(m) 8.78(t), 7.72(m)				CD_3CN
$\{PtCl[C(SEt)SMe](PPh_3)_2\}\{BF_4\}$	9.09(t), 6.45(m) 8.79(t), 7.72(m) 8.05(s), 6.95(s)		7.5[h]		CD_3CN
$\{PtCl[C(SMe)NMe_2](PPh_3)_2\}\{FSO_3\}$	7.27(s)	6.70(s), 7.69(s)	6.0	9.7	$CDCl_3$
$\{PtCl[C(SEt)NMe_2](PPh_3)_2\}\{BF_4\}$	9.05(t), 6.45(m)	6.76(s), 7.68(s)		9.0	$CDCl_3$
$\{PtCl[C(SH)NMe_2](PPh_3)_2\}\{CF_3SO_3\}$		6.77(s), 7.73(s)		9.8	CD_3CN

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[g] For P-CH_3 protons, τ7.62(t) with satellites, J(PCH) = 4.1 Hz and J(PtPCH) = 28.5 Hz.

[h] This J value is for the methyl resonance at τ6.95(s). Platinum satellites are not resolved for the methyl resonance at 8.05(s).

Table 6. (Continued)

	τ(SR)5	τ(XR'n)7	J(PtCSCH),Hz	J(PtCXCH),Hz	Solvent
$\{PtCl[C(SCH_2Ph)NMe_2](PPh_3)_2\}\{BF_4\}$	5.34(s)[i]	6.75(s), 7.77(s)	8.0	9.5	CD_3CN
$\{PtBr[C(SCH_2CHCH_2)NMe_2](PPh_3)_2\}\{BF_4\}$	4.9 (m) 5.7 (m)	6.72(s), 7.78(s)		9.5	CD_3CN
$\{PtCl[C(SHgMe)NMe_2](PPh_3)_2\}\{BF_4\}$	9.00(s)[j]	7.15(s), 7.73(s)	183[k]	9.0	CD_3CN

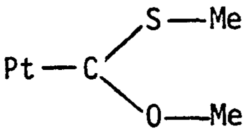
[i] For the $-CH_2-$ protons of the benzyl group.

[j] For the $-HgCH_3$ protons.

[k] This coupling constant is for J(^{199}Hg-C-'H). The protons in $-HgCH_3$ show no coupling to ^{195}Pt.

downfield shift on forming the carbene cations (Fig. 10). The assignment of this signal to the -OCH$_3$ group in these carbene complexes is obvious from the spectrum of $\{PtCl[C(SEt)OMe](PPh_3)_2\}\{BF_4\}$ (Fig. 10b). On forming carbene cations from 3 the protons of the N-methyl group which has been assigned[13] the trans position* are appreciably shifted downfield while the cis-N-methyl protons are only slightly shifted downfield (Fig. 11). For the trans-N-methyl J(^{195}Pt-'H) = 9-10 Hz while for the cis-N-methyl J(^{195}Pt-'H) is considerably smaller and the satellite peaks are not resolved. The assignment of the low field resonance shown in Figs. 11a and 11b to the trans-N-methyl group and the middle resonance in Fig. 11a to the S-methyl group is straight-forward since the N-methyl resonances would not be appreciably shifted on going from the S-methyl carbene to the S-ethyl carbene. This N-methyl pattern is similar for all carbene complexes derived from 3.

It is known that there is considerable double bond character in the C (carbene) - heteroatom bonds of carbene complexes thus causing restricted rotation about these bonds and giving rise to the possibility of different configurations for the carbene ligand.[53] In the complex $\{PtCl[C(SMe)OMe]L_2\}\{FSO_3\}$, the following configurations can be considered for the carbene ligand.



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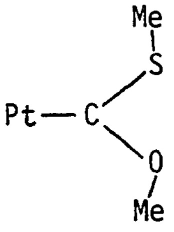

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*Here the cis and trans positions are in reference to the C (carbene)-heteroatom bond with respect to the metal atom.

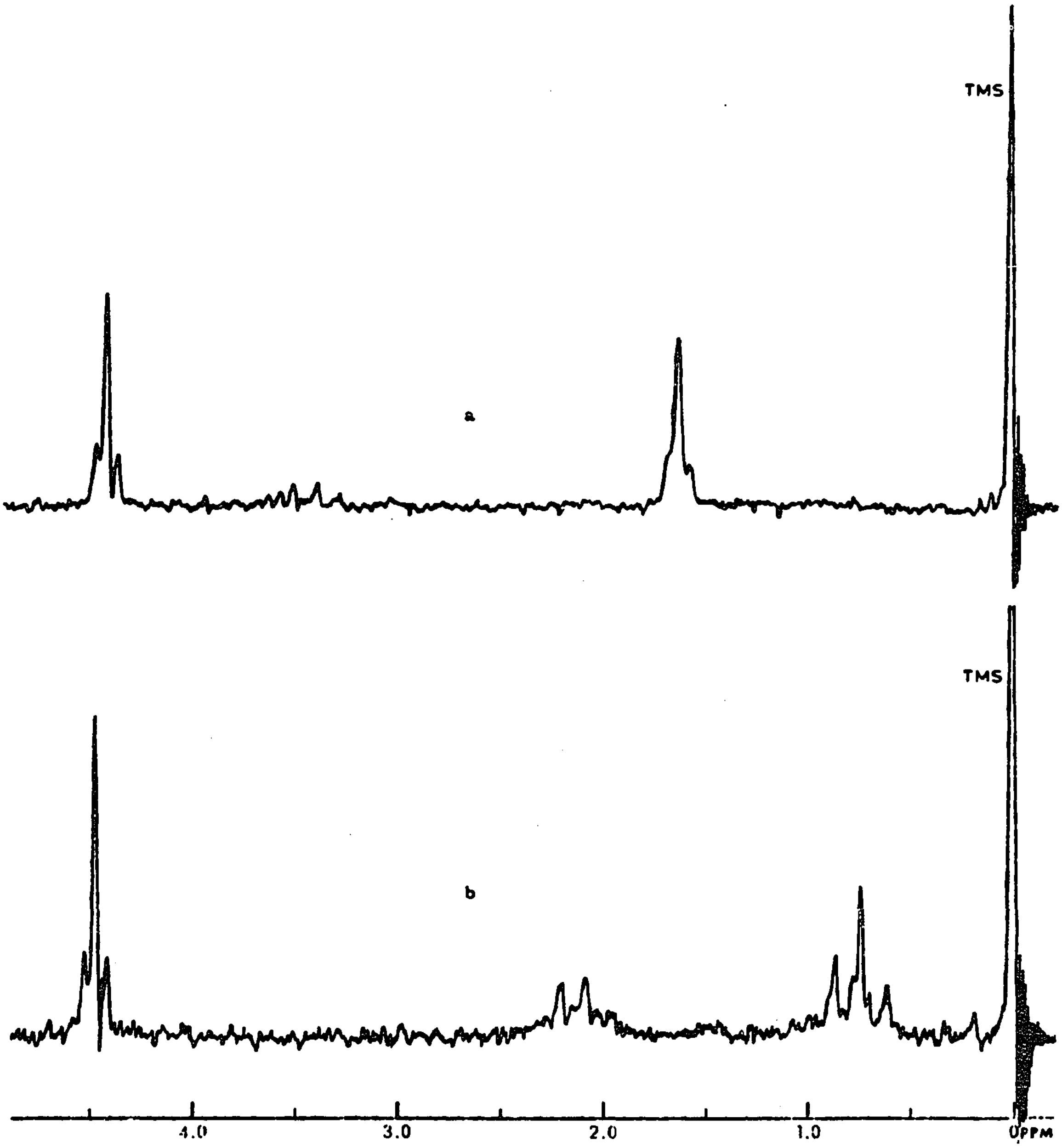


Figure 10. NMR spectra of $\{PtCl[C(SCH_3)OCH_3][P(C_6H_5)_3]_2\}\{FSO_3\}$ (a) and $\{PtCl[C(SC_2H_5)OCH_3][P(C_6H_5)_3]_2\}\{BF_4\}$ (b).

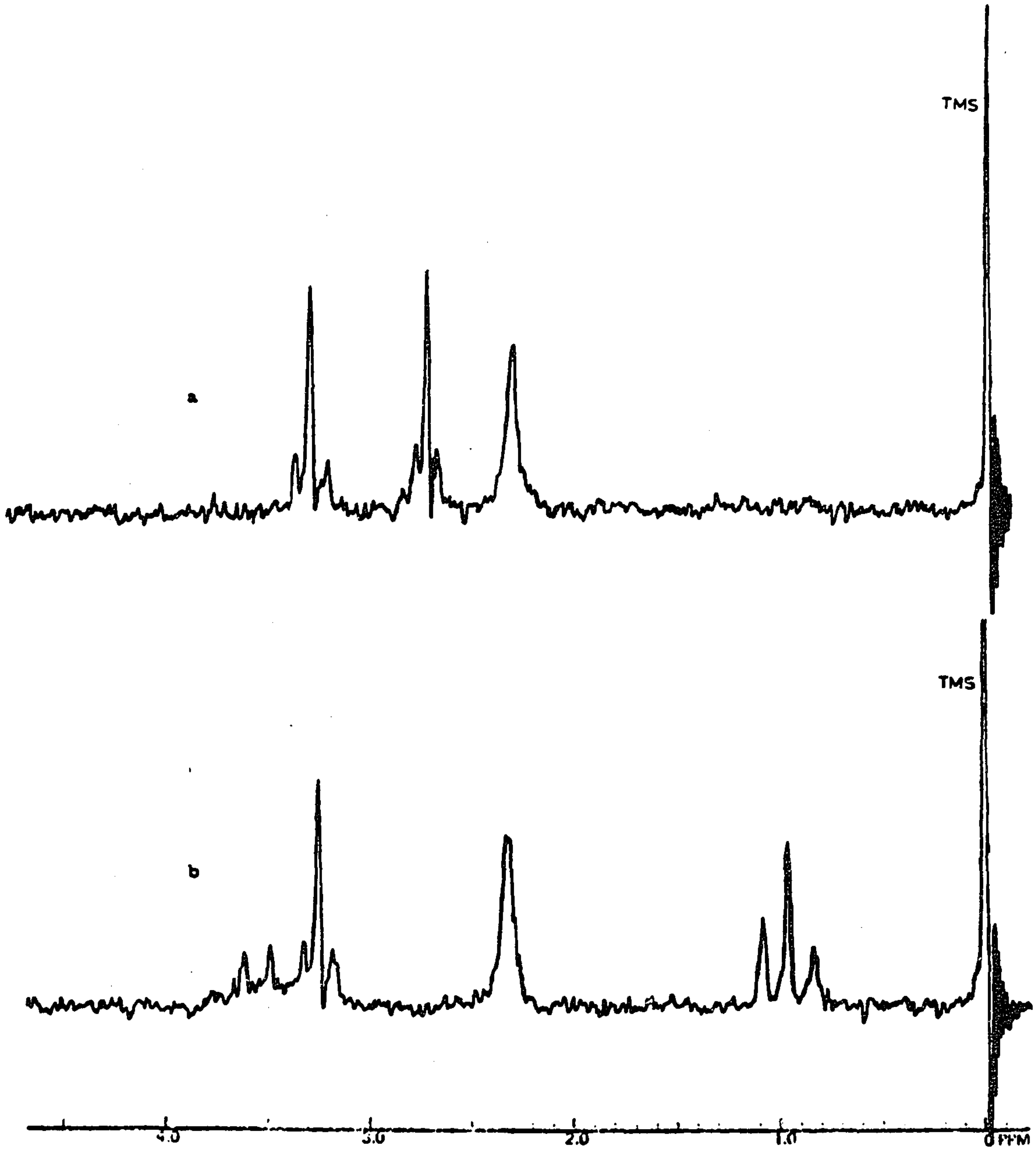
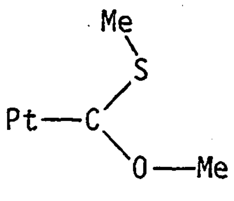
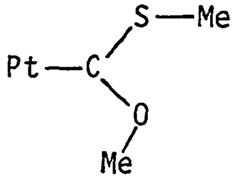


Figure 11. NMR spectra of $\{PtCl[C(SCH_3)N(CH_3)_2][P(C_6H_5)_3]_2\}\{FSO_3\}$ (a) and $\{PtCl[C(SC_2H_5)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$ (b).



6a

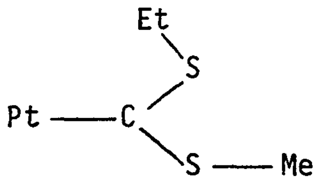


6b

A study of models of these different configurations indicates that 4 is very unfavorable because of severe steric hindrance between the two methyl groups. Structure 5 would be expected to have some steric repulsion between the methyl groups and the bulky PPh_3 ligands, and it seems that a structure of type 6 would be sterically favored. The NMR spectrum (Fig. 10a) shows two distinct methyl resonances of equal intensity and is consistent with the presence of either 6a or 6b. If the barrier to rotation about the C (carbene) - heteroatom bonds is low[73] then it is possible that the configurations 6a and 6b are interconverting rapidly (compared to the NMR time scale) at room temperature. It is also possible that rotation about only one of the C (carbene) - heteroatom bonds is rapid thus giving one averaged methyl resonance and one resonance corresponding to a methyl in the cis position. Either of these last two possibilities would also be consistent with the observed spectrum.

The NMR spectrum of $\{PtCl[C(SEt)_2]L_2\}\{BF_4\}$ shows two distinct ethyl resonances of equal intensity (Fig. 12a). This definitely rules out a configuration of type 4 or 5, and it is highly unlikely that the two chemically different ethyl groups would be due to an equimolar mixture of these two structural types. It is also unreasonable to consider rapid (compared to the NMR time scale) rotation about only one of the two C (carbene) - heteroatom bonds since these two bonds are identical. It can therefore be concluded that in solution at room temperature this carbene cation exists in a configuration of type 6 with one ethyl in the cis position and the other in the trans position.

The NMR spectrum of the similar carbene complex $\{PtCl[C(SMe)SEt]L_2\}$ $\{FSO_3\}$ shows two methyl resonances and two ethyl resonances (Fig. 12b). By the same reasoning as above it can be concluded that one alkyl group is in the cis position while the other is in the trans position. For this complex two different isomers (7 and 8) exist in solution while only one configuration is possible for the analogous diethyl carbene cation previously discussed. The isomers 7 and 8 appear to be present in approximately equal amount in solution ($CDCl_3$ or CD_3CN) at room temperature. Both methyl resonances show long-range coupling with ^{195}Pt although the satellite peaks are not fully resolved for one of these. The chemical shifts and splitting patterns of the two ethyl resonances are virtually identical to those observed for the analogous diethyl carbene complex.



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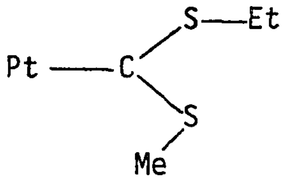

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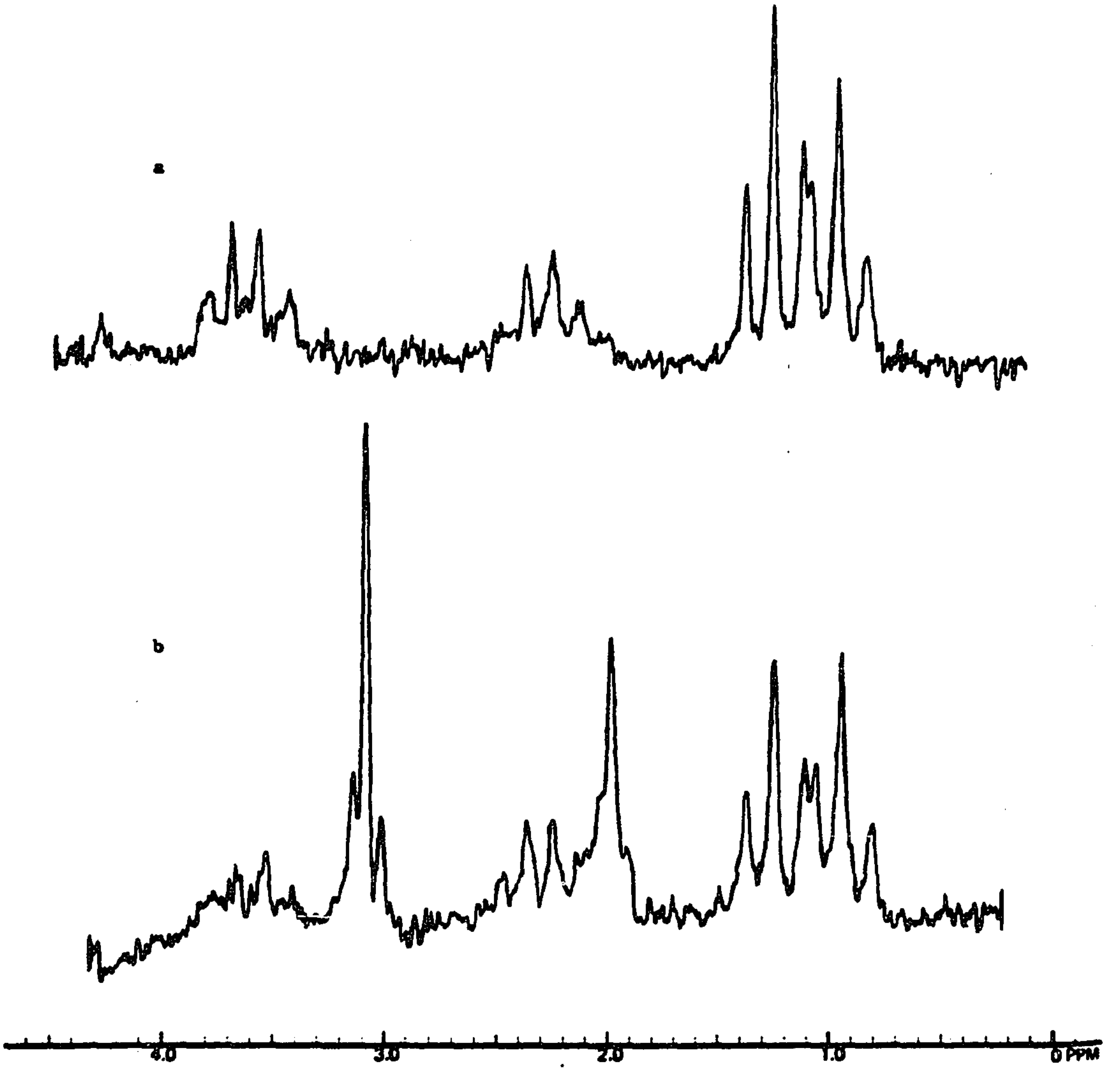
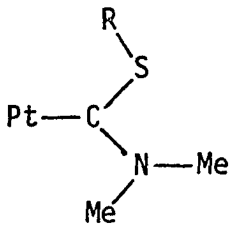


Figure 12. NMR spectra of $\{PtCl[C(SC_2H_5)_2][P(C_6H_5)_3]_2\}\{BF_4\}$ (a) and $\{PtCl[C(SCH_3)SC_2H_5][P(C_6H_5)_3]_2\}\{FSO_3\}$ (b).

The complex $\{PtCl[C(SMe)SEt]L_2\}\{FSO_3\}$ melts over the broad range 125-145°. When heated further the yellow liquid remains unchanged up to 160° at which temperature a solid begins to form. Complete crystallization of the sample to a pale yellow solid occurs over the range 160-165°. On continued heating the solid undergoes partial melting at 170°, and the resulting mixture of liquid and solid remained unchanged on further heating until complete melting of the remaining solid occurred at 203°. This behavior may be due to a separation of the isomers 7 and 8 in the solid state when the sample resolidifies at 160-165° followed by individual melting of the separate isomers at 170° and 203°. It is also possible that this behavior may be due to some other type of phase change. The different melting points do not appear to be the result of decomposition products since there is no obvious sign of decomposition below 203°. The analogous diethyl carbene complex simply melts with decomposition at 263°.

On considering the configuration of the carbene ligand in carbene complexes derived from $PtCl(CSNMe_2)L_2$, it is obvious that both the cis and trans positions will be occupied by the N-methyl groups. Therefore, based on the previous structural considerations, these carbene complexes would be expected to have the configuration shown for 9. The similar cationic carbene complexes $\{PtCl[C(NHR)OR']L_2\}\{ClO_4\}$, where R = Ph or $p\text{-}C_6H_4CH_3$, R' = Me or Et and L = PMe_2Ph or PEt_3, have been assigned the same configuration, with the H and R' occupying cis positions, based on NMR studies.[74]



9

10 R = $-CH_2Ph$

11 R = $-CH_2CHCH_2$

12 R = $-HgCH_3$

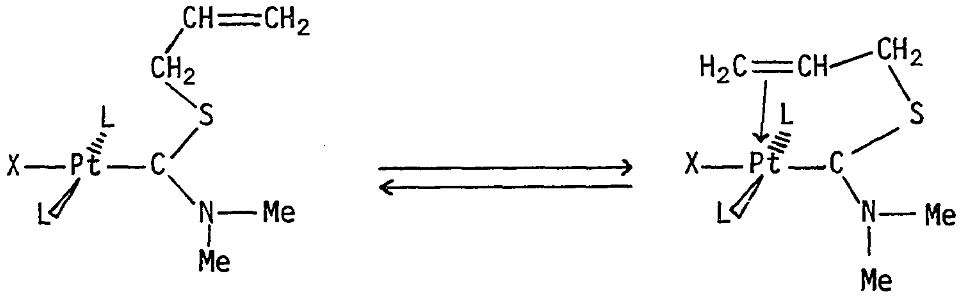
The carbene complex $\{PtCl[C(SH)NMe_2](PPh_3)_2\}\{CF_3SO_3\}$was previously described. In the NMR spectrum of this complex, the presence of two separate N-methyl resonances and the absence of a high field (τ10 to τ30) proton signal rule out the possibility of protonation of the nitrogen or the metal atom. A shift in the N-methyl resonances (relative to 3) is observed which is identical to that of the other carbene cations derived from 3. A signal which can be assigned to the sulfur proton is not observed, but it is possible that this signal may be buried under the broad phenyl absorptions (τ2-3).

In the NMR spectrum of 10 the methylene protons in the carbene ligand appear as a singlet at τ5.32 with ^{195}Pt satellite peaks. For benzyl bromide this resonance occurs as a sharp singlet at τ5.59. In addition the typically shifted N-methyl resonances are observed (Table 6).

The NMR spectrum of 11 shows two complex multiplets for the allyl protons at τ4.9 and τ5.7 with intensity ratios corresponding to 3 and 2 protons respectively. It is believed that the $S-CH_2-$ protons give rise to the multiplet at τ5.7 by comparison with the spectrum of free allyl bromide (doublet at τ6.02 for $Br-CH_2-$). The downfield shift of 0.3 ppm observed for these protons as well as the methylene protons of 10 can be ascribed to the deshielding effect of the positive charge in the complexes.

The methylene protons of 11 are coupled to ^{195}Pt and the adjacent proton to give a poorly resolved multiplet.

A study of models of this complex indicates that the olefin bond of the allyl group can easily be within close proximity of the metal atom, and coordination of this olefin bond to give a five-coordinate complex offers a reasonable explanation for some of the observed spectral properties. The complex multiplet at τ4.9 for the three olefinic protons seems to suggest bonding interaction between the C=C bond and the metal atom since for free allyl bromide these protons give two well-separated signals with less complicated splitting patterns. The IR spectra (in CH_2Cl_2) of the mixed-halide complex $\{PtX[C(SCH_2CHCH_2)NMe_2](PPh_3)_2\}\{BF_4\}$, (X = Cl and Br) and the monohalide complex, (X = Br), both show an extremely weak band at 1637 cm^{-1}. This band, although still weak, is considerably stronger in the $PMePh_2$ analog. This band is not present in any of the other carbene complexes and can be assigned to ν(C=C) of an uncoordinated olefin bond (ν(C=C) = 1637 cm^{-1} for allyl bromide in CH_2Cl_2 solution). Since the NMR spectrum suggests that the olefin bond is coordinated and since the band at 1637 cm^{-1} is extremely weak, there may be an equilibrium between the four- and five-coordinate forms in solution with the five-coordinate form predominating. This would also imply that the interconversion of these two forms is slow compared to the NMR time scale.



The NMR spectrum of 12 (in CD_3CN) shows a sharp singlet for the Hg - CH_3 protons at τ9.00 which is essentially unshifted from the singlet observed for CH_3HgCl(τ9.02) in the same solvent. However, the (^{199}Hg-C-'H) coupling constants are appreciably different with J(^{199}Hg-'H) = 183 Hz for the carbene complex and J(^{199}Hg-'H) = 217 Hz for CH_3HgCl (all spectra in CD_3CN soln.). The trans N-methyl (τ7.15) in this carbene complex shows a smaller deshielding effect than is observed for all other carbene complexes derived from $PtCl(CSNMe_2)(PPh_3)_2$ (see Table 6).

A study correlating the (^{199}Hg-'H) spin-spin coupling constants of methylmercury salts of organic acids CH_3HgX, where X = OR^-, SR^- or $RCOO^-$, with the pK's of the monobasic parent acids has recently been reported.[75] Using the data obtained for X = SR^- we can estimate the pK of the protonated complex $\{PtCl[C(SH)NMe_2](PPh_3)_2\}^+$ to be ~5.*

Oxidative-addition across a carbon-sulfur bond with Pt(0)

The reactivity of ethylene trithiocarbonate, $C_2H_4CS_3$, toward M(0) complexes is not immediately obvious, but oxidative-addition with cleavage of one of the carbon-sulfur bonds was considered as a possibility. It was found that $C_2H_4CS_3$ reacts readily with $Pt(PPh_3)_4$ in benzene solution at 25° with cleavage of a carbon-sulfur bond and formation of a Pt(II) complex with a cyclic structure. The NMR spectrum of cis-$\overline{PtCS_2CH_2CH_2S}(PPh_3)_2$ (in $CDCl_3$) shows complex multiplets at τ7.5 and τ6.9 indicating nonequivalence of the ethylene protons in the bound ligand. The shielding effect of

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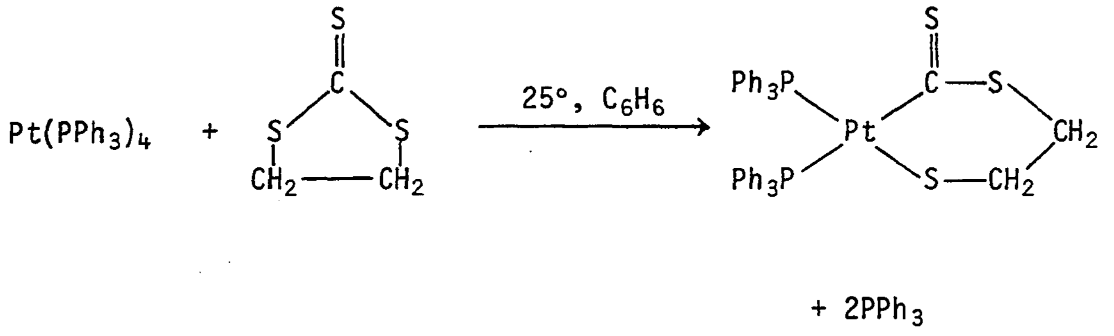
*The complex 12 has a J(^{199}Hg-'H) value of 193 Hz in pyridine solution while dithizone (diphenylthiocarbazone), pK = 4.82, has a J(^{199}Hg-'H) value of 190 Hz in pyridine (see ref. 75).



(28)

the PPh_3 ligands is shown by the relatively high field position of these multiplets compared to the singlet observed for free $C_2H_4CS_3$ at τ6.02.

The $PMePh_2$ analog, cis-$\overline{PtCS_2CH_2CH_2S}(PMePh_3)_2$, was prepared similarly. The NMR spectrum of this derivative (Fig. 13) clearly shows that the phosphine ligands are cis to each other and that they are nonequivalent as a result of the mode of bonding of the trithioester ligand. The spectrum (Fig. 13) reveals two doublets, each of which has doublet satellites, and there is slight overlapping between the inner sets of satellite peaks. The separate doublets of equal intensity are due to phosphine-methyl groups and indicate the presence of two nonequivalent phosphine ligands. Each of these methyl resonances (τ8.43 and 7.89) occurs as a doublet due to coupling of the methyl protons with ^{31}P with $J(^{31}P-{}^{1}H)$ values of 8 Hz and 10 Hz respectively, and the doublet satellites are due to splitting by ^{195}Pt with $J(^{195}Pt-{}^{1}H)$ values of 26 Hz and 37 Hz respectively. The fact that the phosphine-methyl protons are only coupled to the phosphorous to which that methyl group is attached indicates that the two ^{31}P nuclei are not vitually coupled and are therefore in the cis configuration.[18]

The solid state (nujol mull) IR spectrum of cis-$\overline{PtCS_2CH_2CH_2S}(PPh_3)_2$ shows sharp bands at 1089 cm^{-1} and 1100 cm^{-1}, one of which is probably due

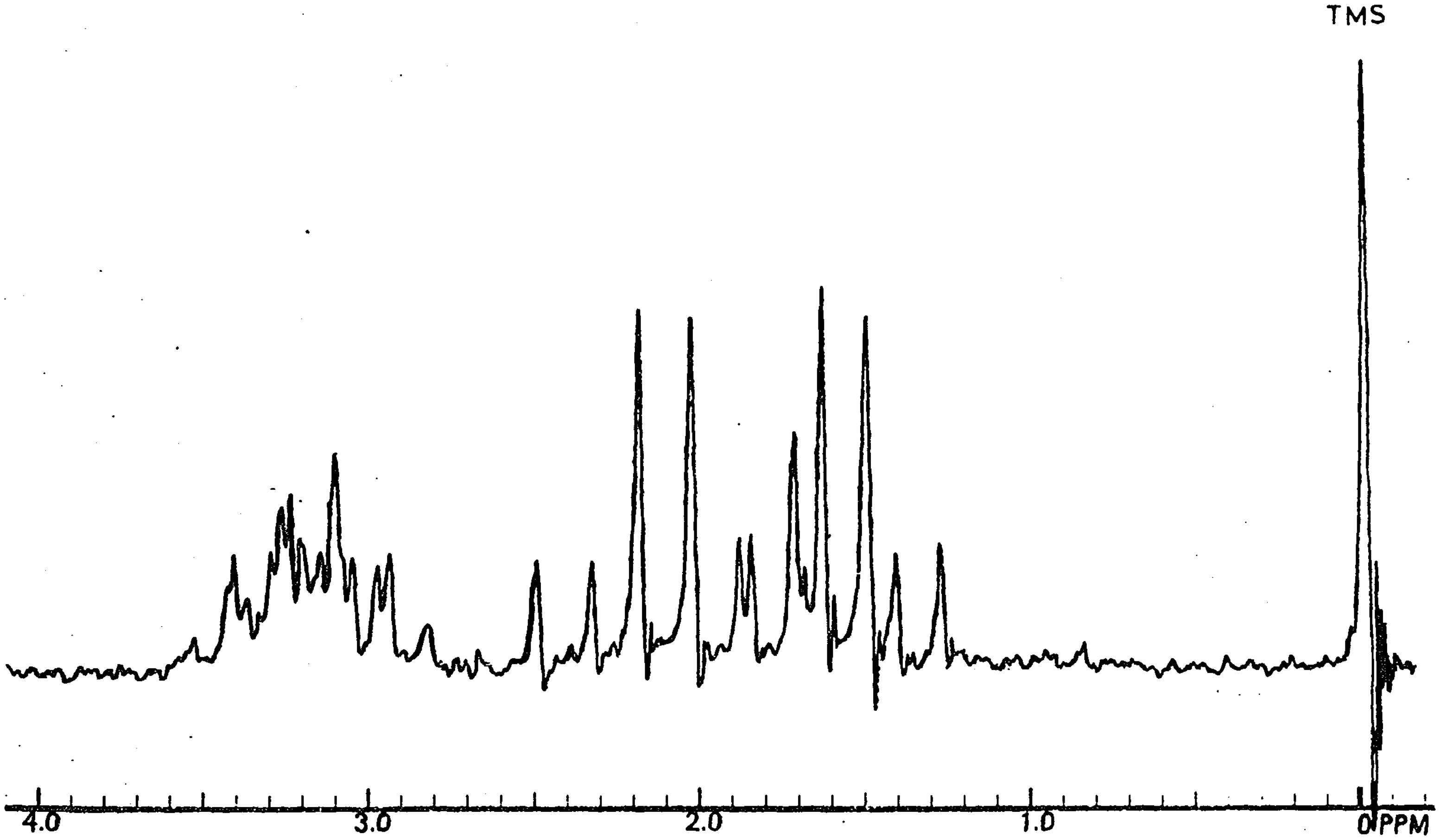
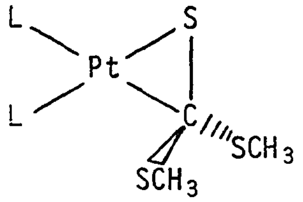


Figure 13. NMR spectrum of *cis*-Pt$\overline{\text{CS}_2\text{CH}_2\text{CH}_2\text{S}}$(PMePh$_2$)$_2$ in CDCl$_3$.

to ν(C=S). The IR spectrum of the complex in $CHCl_3$ shows only a single, strong absorption at 1095 cm^{-1}. However, a strong band at this position is commonly observed in Pt(II) complexes with PPh_3 ligands due to the in-plane C-H bending mode of the phenyl groups, and it is believed that the ν(C=S) mode is not resolved from this band in the solution spectrum. The free ligand, $C_2H_4CS_3$, shows a strong ν(C=S) band at 1076 cm^{-1}.

When $Pt(PPh_3)_4$ was treated with dimethyl trithiocarbonate, $(CH_3S)_2CS$[76], in benzene at 25°, a reaction occurs as indicated by the color change from yellow to orange. An orange colored solid was isolated from this reaction, but this product decomposed rapidly when redissolved and was not characterized. When this reaction was followed by NMR (in C_6D_6) only a sharp singlet at τ7.54 was observed for the product ($(CH_3S)_2CS$ shows a singlet at τ7.78 in C_6D_6). This clearly indicates that cleavage of a carbon-sulfur bond in $(CH_3S)_2CS$ to give $Pt(SCH_3)(CS_2CH_3)(PPh_3)_2$ does not occur, and that the specific reaction of $C_2H_4CS_3$ with Pt(0), described above, is not a general reaction of trithioesters. The product formed in the reaction of $(CH_3S)_2CS$ with $Pt(PPh_3)_4$ may arise from either oxidative-addition 13 or ligand substitution 14. Either of these products would be



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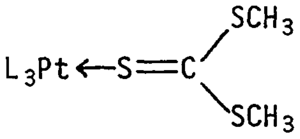
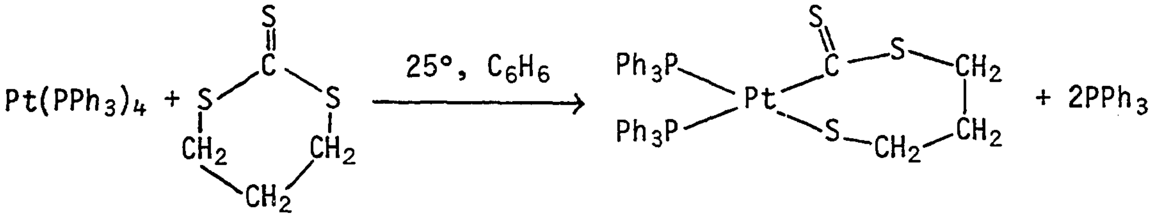


14

consistent with the appearance of only a singlet in the NMR spectrum of the reaction solution. The reaction of $Pt(PPh_3)_4$ with perfluorothioacetone has been reported[67] to give a product with the same structure as *13*.

In order to determine if carbon-sulfur bond cleavage in $C_2H_4CS_3$ is a result of ring strain in the 5-membered ring structure, the reactivity of the 6-membered ring compound, $(CH_2)_3CS_3$[77], with $Pt(PPh_3)_4$ was examined. It was found that reaction occurred readily with carbon-sulfur bond cleavage to give the analogous complex. The NMR spectrum (in $CDCl_3$) of the



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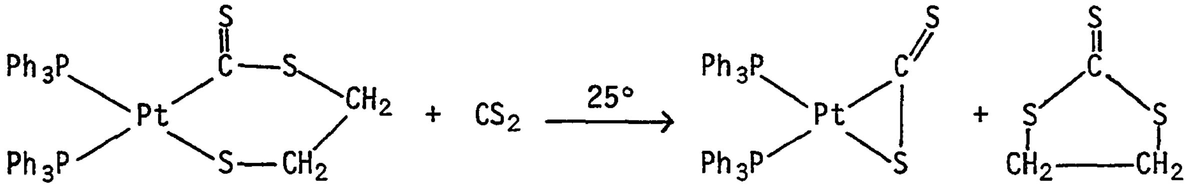
product *cis*-$\overline{PtCS_2CH_2CH_2CH_2S}(PPh_3)_2$ shows three complex multiplets for the methylene protons at $\tau 8.1$, $\tau 7.4$, and $\tau 6.7$. Therefore, it appears that ring strain is not the controlling factor in the reaction of cyclic trithiocarbonates with Pt(0). The specific reactivity observed may be due to the stability of the chelate ring formed in the products. The cyclic oxygen analog, ethylene carbonate, $C_2H_4CO_3$, does not react with $Pt(PPh_3)_4$ in benzene at 25°.

The complex *cis*-$\overline{PtCS_2CH_2CH_2S}(PPh_3)_2$ reacts with CS_2 to form the known adduct $Pt(CS_2)(PPh_3)_2$[67] and free $C_2H_4CS_3$. These products were easily identified in solution by the strong bands in the IR spectrum at 1157 cm^{-1}



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and 1076 cm^{-1} corresponding to $\nu(C{=}S)$ of $Pt(CS_2)(PPh_3)_2$ and free $C_2H_4CS_3$ respectively, and by the singlet in the NMR spectrum at $\tau 6.02$ for free $C_2H_4CS_3$. Complete ligand displacement occurs within 20 minutes at 25° when the complex is dissolved in CS_2, and over a period of about 10 hours when CS_2 is added to a solution of the complex in either C_6H_6 or $CHCl_3$. The analogous *cis*-$\overline{PtCS_2CH_2CH_2CH_2S}(PPh_3)_2$ reacts similarly with CS_2 to give $Pt(CS_2)(PPh_3)_2$ and free $(CH_2)_3CS_3$.

Experimental

Methods and materials

The 'H NMR spectra were obtained on a Perkin-Elmer Hitachi R-20B spectrometer, and infrared measurements were made with a Perkin-Elmer 337 spectrophotometer. Conductivity measurements were carried out in CH_2Cl_2 solution using an Industrial Instruments Inc. model RC16B2 conductivity bridge. Melting points were determined using either a Mel-Temp apparatus or a Thomas hot-stage. Microanalyses were performed by Chemalytics Inc. and Schwarzkopf microanalytical laboratory. All solvents were reagent grade and all reactions were carried out under a nitrogen atmosphere.

Methyl thiochloroformate, $ClCSOCH_3$, was prepared from methanol and thiophosgene. Thiophosgene (17.0 g) was cooled to 0° in an ice bath under an N_2 atmosphere and twice as many moles of absolute methanol (9.5 g) was added very slowly. The orange-yellow solution was allowed to stand for 20 hours in a stoppered schlenk tube at 10-15° (running tap water). The reaction solution was kept in the dark during this time to prevent photodecomposition. The solution was then cooled in an ice bath and 30 ml of deoxygenated ether was added followed by 20 ml of deoxygenated water. The yellow ether phase was then separated and dried over $CaCl_2$ for 3 hours. After this initial drying the ether solution was transferred to a fresh portion of $CaCl_2$ and allowed to stand overnight. The product was isolated by distillation under nitrogen at atmospheric pressure. A fraction containing the desired product and a relatively small amount of an unknown impurity distilled at 80° while most of the product in pure form distilled at 105°. The product, an air-sensitive yellow liquid, was stored under nitrogen in the dark at room temperature. Ethyl dithiochloroformate, $ClCS_2C_2H_5$, was prepared from thiophosgene and ethanethiol. Thiophosgene (19.2 g) was dissolved in 20 ml of CS_2 and an equimolar amount of EtSH (10.4 g), dissolved in 20 ml of CS_2, was slowly added at 0° under nitrogen. The orange solution was then stirred at 0° for 1 hour and at 25° for 1 hour. Solvent was then removed under vacuum leaving the product as a yellow oil. Ethylene trithiocarbonate, $C_2H_4CS_3$, was obtained from Aldrich Chemical Co. and trimethylene trithiocarbonate, $(CH_2)_3CS_3$, was prepared as described in the literature.[77]

Preparative methods for the Pt(0) and Pd(0) phosphine complexes are described previously. The complexes $PtCl(CS_2Et)(PPh_3)_2$[70], $M(CS_2)(PPh_3)_2$[67], where M = Pt or Pd, and $PtCl(CSNMe_2)(PPh_3)_2$[13] were prepared according to methods described in the literature, and $IrCl(CO)(PPh_3)_2$ was obtained from

Pressure Chemical Co. The bromide derivative $PtBr(CSNMe_2)(PPh_3)_2$ was prepared by stirring 0.53 g (0.63 mmol) of $PtCl(CSNMe_2)(PPh_3)_2$ with an excess of $[NEt_4]Br$ in a mixture of 15 ml of acetone and 4 ml of water for 20 hours at 25°. The suspension was then filtered and the solid washed with water, ethanol, and finally ether, and then recrystallized from $CHCl_3$-hexane to give 0.50 g (91%) of the yellow-green crystalline product.

Preparation of methoxythiocarbonyl complexes

$PtCl(CSOCH_3)L_2$, where $L = P(C_6H_5)_3$ or $PCH_3(C_6H_5)_2$ To 1.21 g (0.97 mmol) of $Pt[P(C_6H_5)_3]_4$ in 30 ml of degassed benzene was added 0.21 g (1.91 mmol) of $ClCSOCH_3$. After stirring for 10 min. at 25°, the benzene was removed under vacuum and the residue triturated with ether and collected by filtration. Recrystallization from CH_2Cl_2-hexane at 0° gave 0.76 g (94%) of the product as pale yellow needles, m.p. 150-152°(d).

Anal. Calcd for $PtCl(CSOCH_3)[P(C_6H_5)_3]_2$: C, 54.9; H, 4.01; S, 3.87. Found: C, 54.8; H, 4.12; S, 4.43. The complex $PtCl(CSOCH_3)[PCH_3(C_6H_5)_2]_2$ was prepared by the same procedure using $Pt[PCH_3(C_6H_5)_2]_4$. This complex was obtained as a pale yellow crystalline solid (70% yield) and identified by its IR and NMR spectra.

$PdCl(CSOCH_3)[P(C_6H_5)_3]_2$ This complex was prepared and isolated using the same procedure as described above for the platinum analog. It is a bright yellow crystalline solid, m.p. 100-105°(d), and was obtained in 80% yield.

Anal. Calcd for $PdCl(CSOCH_3)[P(C_6H_5)_3]_2$: C, 61.5; H, 4.50; S, 4.34. Found: C, 61.1; H, 4.33; S, 4.41.

$IrCl_2(CO)(CSOCH_3)[P(C_6H_5)_3]_2$ To a solution of 0.24 g (0.28 mmol) of $IrCl(CO)(PPh_3)_2$ in 20 ml of degassed benzene was added a large excess of $ClCSOCH_3$. The solution was stirred under nitrogen for 2 days at 25°. Hexane was then added to give a pale yellow solid precipitate of the product which also contained a relatively small amount of unreacted $IrCl(CO)[P(C_6H_5)_3]_2$. A total of 0.22 g (~81%) was obtained after drying under vacuum.

Preparation and reactions of $\{PtCl(CS)[P(C_6H_5)_3]_2\}\{BF_4\}$

$\{PtCl(CS)[P(C_6H_5)_3]_2\}\{BF_4\}$ A solution of 0.46 g of $PtCl(CSOCH_3)$-$[P(C_6H_5)_3]_2$ in 15 ml of CH_2Cl_2 was stirred under 1 atm of BF_3 for 18 hours at 25°. During this time the solution changed from pale yellow to deep yellow in color. The BF_3 was then flushed from the system with nitrogen and the solvent evaporated under a stream of nitrogen to leave the product as a yellow oil. The oil is highly impure and could not be recrystallized, but could be solidified by gently warming under vacuum. The product was characterized by a strong band in the IR spectrum for $\nu(C\equiv S)$ at 1400 cm^{-1} and by its reactions with CH_3OH and $HN(CH_3)_2$. The crude solid product is approximately 70% $\{PtCl(CS)[P(C_6H_5)_3]_2\}\{BF_4\}$.

Reaction of $\{PtCl(CS)[P(C_6H_5)_3]_2\}\{BF_4\}$ with CH_3OH Approximately 10 ml of dry methanol was distilled onto 0.10 g of impure solid $\{PtCl(CS)[P(C_6H_5)_3]_2\}\{BF_4\}$ under vacuum. The resulting suspension was stirred for 5 minutes at 25°. The pale yellow, solid precipitate (0.07 g) was collected, washed with methanol and dried under nitrogen. This solid product was easily identified as $PtCl(CSOCH_3)[P(C_6H_5)_3]_2$ by its characteristic IR and NMR spectra.

Reaction of $\{PtCl(CS)[P(C_6H_5)_3]_2\}\{BF_4\}$ with $HN(CH_3)_2$ A solution of 0.13 g of impure solid $\{PtCl(CS)[P(C_6H_5)_3]_2\}\{BF_4\}$ in 15 ml of CH_2Cl_2 was stirred at 25° under nitrogen and anhydrous dimethyl amine was bubbled through the solution at a slow rate for 5 minutes. The solvent was then removed under a nitrogen stream to leave a yellow residue. The residue was extracted with benzene and filtered to remove $[H_2N(CH_3)_2][BF_4]$. Benzene was then removed under vacuum and the remaining yellow oil recrystallized from CH_2Cl_2-ether to give 0.10 g of a yellow solid product. This solid was identified as $PtCl[CSN(CH_3)_2][P(C_6H_5)_3]_2$ by its characteristic NMR spectrum.

Preparation of carbene complexes

$\{PtCl[C(SR)OCH_3]L_2\}\{A\}$, (where $R = CH_3$ or C_2H_5, $L = P(C_6H_5)_3$ or $PCH_3(C_6H_5)_3$, $A = FSO_3^-$ or BF_4^-) The complexes (a) $\{PtCl[C(SC_2H_5)OCH_3]$-$[P(C_6H_5)_3]_2\}\{BF_4\}$ and (b) $\{PtCl[C(SCH_3)OCH_3]L_2\}\{FSO_3\}$, (where $L = P(C_6H_5)_3$ or $PCH_3(C_6H_5)_2$), were prepared similarly. As an example, 0.21 g (0.30 mmol) of $PtCl(CSOCH_3)[PCH_3(C_6H_5)_2]_2$ in 10 ml of CH_2Cl_2 was treated with 0.07 g (0.61 mmol) of CH_3SO_3F ("magic methyl") at 0°. The solution was then concentrated to 3 ml total volume under an N_2 stream and hexane added to precipitate the product as a white crystalline solid. After recrystallizing from CH_2Cl_2-hexane at -20° and drying under vacuum at 25° for 10 hrs., 0.18 g (72%) of $\{PtCl[C(SCH_3)OCH_3][PCH_3(C_6H_5)_2]_2\}\{FSO_3\}$ was obtained as white crystals, m.p. 120-125°.

Anal. Calcd for $\{PtCl[C(SCH_3)OCH_3][PCH_3(C_6H_5)_2]_2\}\{FSO_3\}$: C, 42.43; H, 3.94; S, 7.83. Found: C, 42.63; H, 4.08; S, 7.26. For complex (a) $[(C_2H_5)_3O][BF_4]$ was substituted for CH_3SO_3F. This complex was obtained as a white crystalline solid (40%), m.p. 166-168°.

$\{PtCl[C(SR)SC_2H_5][P(C_6H_5)_3]_2\}\{A\}$, (where R = CH_3 or C_2H_5, A = FSO_3^- or BF_4^- The complexes (a) $\{PtCl[C(SCH_3)SC_2H_5][P(C_6H_5)_3]_2\}\{FSO_3\}$ and (b) $\{PtCl[C(SC_2H_5)_2][P(C_6H_5)_3]_2\}\{BF_4\}$ were prepared similarly. For complex (a) 0.39 g (0.45 mmol) of $PtCl(CS_2C_2H_5)[P(C_6H_5)_3]_2$ in 6 ml of CH_2Cl_2 was treated with 0.06 g (0.53 mmol) of CH_3SO_3F at 0°. Addition of hexane to this solution caused the product to precipitate as a yellow oil. Recrystallization from CH_2Cl_2-hexane at 0° gave 0.32 g (64%) of complex (a) as pale yellow crystals, m.p. 125-145°. After drying under vacuum at 25° for 7 hrs. the complex was obtained as a solvate containing CH_2Cl_2.

Anal. Calcd for $\{PtCl[C(SCH_3)SC_2H_5][P(C_6H_5)_3]_2\}\{FSO_3\} \cdot 1.4\ CH_2Cl_2$: C, 45.11; H, 3.76; Cl, 12.33; S, 8.80. Found: C, 45.00; H, 3.68; Cl, 12.40; S, 9.36. Complex (b) was prepared using $[(C_2H_5)_3O][BF_4]$ in place of CH_3SO_3F. This complex was obtained as a pale yellow, crystalline solid (62%), m.p. 263° (d).

$\{PtCl[C(SR)N(CH_3)_2][P(C_6H_5)_3]_2\}\{A\}$, (where R = CH_3 or C_2H_5, A = FSO_3^-, BF_4^- or $CH_3OSO_3^-$) The complexes (a) $\{PtCl[C(SCH_3)N(CH_3)_2][P(C_6H_5)_3]_2\}\{FSO_3\}$ and (b) $\{PtCl[C(SC_2H_5)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$ were prepared similarly. For complex (b) 0.33 g (0.39 mmol) of $PtCl[CSN(CH_3)_2]$-$[P(C_6H_5)_3]_2$ in 10 ml of CH_2Cl_2 was treated with 0.08 g (0.42 mmol) of $[(C_2H_5)_3O][BF_4]$ at 0°. The solution was concentrated to 4 ml total volume under an N_2 stream. Addition of hexane followed by cooling to -20° gave the product, 0.35 g (87%), as a white crystalline solid, m.p. 287°. After drying under vacuum at 25° for 10 hours the complex was obtained as a solvate containing CH_2Cl_2 in equimolar amount.

Anal. Calcd for $\{PtCl[C(SC_2H_5)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\} \cdot CH_2Cl_2$: C, 48.28; H, 4.15; N, 1.34; Cl, 10.20. Found: C, 48.19; H, 4.13; N, 1.53; Cl, 10.19. Complex (a) was prepared using CH_3SO_3F in place of $[(C_2H_5)_3O][BF_4]$. This complex was obtained as a white crystalline solid (80%), m.p. 265°, and also contained solvent of crystallization when recrystallized from CH_2Cl_2 or $CHCl_3$ (1.7 $CHCl_3$ per complex). The complex $\{PtCl[C(SCH_3)N(CH_3)_2][P(C_6H_5)_3]_2\}\{CH_3OSO_3\}$ was obtained from the reaction of the thiocarbamoyl complex with dimethyl sulfate. To 0.19 g (0.23 mmol) of $PtCl[CSN(CH_3)_2][P(C_6H_5)_3]_2$ in 7 ml of CH_2Cl_2 was added 0.15 g (1.19 mmol) of $(CH_3O)_2SO_2$. After stirring for 4 hrs. at 25° the solution was filtered and concentrated to 3 ml total volume under an N_2 stream. Addition of hexane gave the product as white crystals (50%), m.p. 235°. This complex was also obtained as a solvate when recrystallized from CH_2Cl_2 or $CHCl_3$ (2.12 $CHCl_3$ per complex). The $CHCl_3$ solvate of this complex gave a value of $\Lambda_M = 48$ for the molar conductance of a 7.4×10^{-4} M solution in CH_2Cl_2 at 25°. This value for Λ_M indicates a 1:1 electrolyte when compared with conductivity data obtained for other complexes in CH_2Cl_2.[78]

$\underline{\{PtCl[C(SH)N(CH_3)_2][P(C_6H_5)_3]_2\}\{CF_3SO_3\}}$ The thiocarbamoyl complex in CH_2Cl_2 solution is readily protonated by HCl (g), CH_3SO_3H or CF_3SO_3H, however, the solid product was most easily isolated as the $CF_3SO_3^-$ salt. A solution of 0.23 g (0.27 mmol) of $PtCl[CSN(CH_3)_2][P(C_6H_5)_3]_2$ in 6 ml of CH_2Cl_2 at 25° was treated with 3 drops of pure CF_3SO_3H causing the solution to instantly turn from yellow to colorless. The solution was then concentrated to 3 ml total volume under an N_2 stream, followed by addition of hexane (2 ml), giving the product as a white crystalline solid. Recrystallization from CH_2Cl_2-ether followed by drying under vacuum at 25° for 24 hrs. gave 0.23 g (81%) of the solvated complex (containing CH_2Cl_2) as white crystals, m.p. 165-168°.

Anal. Calcd for $\{PtCl[C(SH)N(CH_3)_2][P(C_6H_5)_3]_2\}\{CF_3SO_3\}\cdot 0.5\ CH_2Cl_2$: C, 46.92; H, 3.70; Cl, 6.85. Found: C, 46.82; H, 3.64; Cl, 6.86. This complex is stable in the solid state and in solution.

$\{PtCl[C(SCH_2C_6H_5)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$ To 0.20 g (0.24 mmol) of $PtCl[CSN(CH_3)_2][P(C_6H_5)_3]_2$ in 8 ml of CH_2Cl_2 was added 0.41 g (2.40 mmol) of benzyl bromide. After stirring for 30 min. at 25° the original yellow solution was almost completely colorless. After stirring for 3 hrs. a solution of 0.05 g (0.25 mmol) of $AgBF_4$ in 0.5 ml of acetone was added producing a white suspension of AgBr which was then filtered to give a clear colorless filtrate. Concentration of the filtrate to half-volume under an N_2 stream followed by addition of hexane caused the product to precipitate as a white crystalline solid. A second recrystallization from CH_2Cl_2-hexane at 25° followed by drying under vacuum at 25° for 24 hrs. gave 0.17 g (69%) of the product as white crystals, m.p. 272°.

Anal. Calcd for $\{PtCl[C(SCH_2C_6H_5)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$: C, 54.06; H, 4.25; Cl, 3.47. Found: C, 54.28; H, 4.51; Cl, 3.99. This complex is very stable in both the solid state and in solution and is considerably more soluble in CH_2Cl_2 or $CHCl_3$ than the other carbene complexes in this series.

$\{PtBr[C(SCH_2CH{=}CH_2)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$ To 0.26 g (0.29 mmol) of $PtBr[CSN(CH_3)_2][P(C_6H_5)_3]_2$ in 10 ml of CH_2Cl_2 was added 0.36 g (2.97 mmol) of allyl bromide. After stirring for 1 hr. at 25° the original yellow solution was almost completely colorless. After stirring for 3 hrs. a solution of 0.06 g (0.30 mmol) of $AgBF_4$ in 0.9 ml of acetone was added producing a white suspension of AgBr which was then filtered to give a clear colorless filtrate. Concentration of the filtrate to 5 ml total volume under an N_2 stream followed by addition of hexane caused the product to precipitate as a white crystalline solid. Recrystallization from acetonitrile-ether at -20° followed by drying under vacuum at 80° for 8 hrs. gave 0.20 g (70%) of the product as white crystals, m.p. 267°(d).

Anal. Calcd for $\{PtBr[C(SCH_2CH{=}CH_2)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$: C, 49.64; H, 4.07; Br, 7.86. Found: C, 49.69; H, 3.95; Br, 7.85. When the above reaction was carried out using $PtCl[CSN(CH_3)_2][P(C_6H_5)_3]_2$ the product obtained was $\{PtX[C(SCH_2CH{=}CH_2)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$, where X was present as both Cl and Br. The product consisted of approximately 2/3 chloride and 1/3 bromide after a 3 hr. reaction time, and an equimolar mixture of chloride and bromide when the reaction solution was left stirring for 20 hrs. The presence of both Cl and Br was indicated by halide analyses, and the relative amounts of the two derivatives present could be estimated from the NMR spectrum in which the trans $N{-}CH_3$ resonance has a slightly different chemical shift for each halide. When a large excess of $N[P(C_6H_5)_3]_2Cl$ was added to these NMR samples it was found that the bromide derivative in the mixture was converted to the corresponding chloride complex.

$\{PtCl[C(SHgCH_3)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$ To 0.23 g (0.27 mmol) of $PtCl[CSN(CH_3)_2][P(C_6H_5)_3]_2$ in 8 ml of CH_2Cl_2 was added 0.12 g (0.48 mmol) of CH_3HgCl. After stirring for 1 hr. at 25° there was no color change in the original yellow solution. Addition of 0.06 g (0.30 mmol) of $AgBF_4$ in 2.1 ml of acetone at this time immediately gave a white suspension of AgCl which was filtered leaving a clear colorless filtrate. Concentration of the filtrate to half volume followed by addition of hexane and cooling to -20° caused colorless crystals to precipitate along with a small amount of black solid. The product was redissolved in CH_2Cl_2, filtered, and recrystallized by adding hexane and cooling to -20°. After drying under vacuum at 25° for 12 hrs., 0.23 g (73%) of white needles, m.p. 160-165°, were obtained.

Anal. Calcd for $\{PtCl[C(SHgCH_3)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$: C, 41.89; H, 3.43; Hg, 17.51. Found: C, 42.19; H, 3.50; Hg, 17.06. When a colorless solution of this complex in CD_3CN is treated with an equimolar amount of $N[P(C_6H_5)_3]_2Cl$ at 25° a yellow color immediately results and yellow crystals of $PtCl[CSN(CH_3)_2][P(C_6H_5)_3]_2$ begin to precipitate. The NMR spectrum of this solution indicated the presence of CH_3HgCl (τ9.02, $J(^{199}Hg-^{1}H)$ = 217 Hz), and the yellow crystals were identified as the thiocarbamoyl complex from the NMR spectrum after redissolving in $CDCl_3$.

Reaction of $PtCl[CSN(CH_3)_2][P(C_6H_5)_3]_2$ with $SnCl_4$ To 0.33 g (0.39 mmol) of $PtCl[CSN(CH_3)_2][P(C_6H_5)_3]_2$ in 10 ml of CH_2Cl_2 was added 0.30 g (1.15 mmol) of anhydrous $SnCl_4$ at 25° to produce an orange colored solution. Concentration of the solution to 4 ml total volume under an N_2 stream followed by addition of ether and cooling to -20° caused a pale-yellow crystalline solid to precipitate. Recrystallization from CH_2Cl_2-hexane at -20° followed by drying under N_2 gave 0.40 g (92%) of the pale-yellow crystalline solid identified as $\{Pt[CSN(CH_3)][P(C_6H_5)_3]_2\}_2$ $2\{SnCl_5\}$. This dimeric cation was previously reported[13] and was easily identified here from its NMR spectrum and characteristic reaction with excess Cl^- in solution to regenerate the neutral thiocarbamoyl complex. A 3.7×10^{-4} M solution[*] of the complex gave a molar conductance Λ_M = 97

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[*] This concentration is based on a mol. wt. of 2206 corresponding to the formula given.

at 25° in CH_2Cl_2 solution. This value for Λ_M corresponds to a 2:1 electrolyte in CH_2Cl_2.

Anal. Calcd for above formula: Cl, 16.08. Found: Cl, 15.87.

Preparation of complexes from cyclic trithiocarbonates

cis-$\overline{PtCS_2CH_2CH_2S}[P(C_6H_5)_3]_2$ To a solution of 1.41 g (1.13 mmol) of $Pt[P(C_6H_5)_3]_4$ in 30 ml of benzene was added 0.16 g (1.20 mmol) of ethylene trithiocarbonate. The solution turned from a deep yellow to a pale yellow color on adding the ethylene trithiocarbonate. After stirring for 10 min. at 25° the benzene was removed under vacuum and the remaining white solid triturated with ether and collected by filtration. Recrystallization from $CHCl_3$-hexane at 0° gave 0.93 g (96%) of a cream-white crystalline solid, m.p. 182°(d).

Anal. Calcd for $Pt(C_2H_4CS_3)[P(C_6H_5)_3]_2$: C, 54.7; H, 4.0; S, 11.3. Found: C, 54.9; H, 4.1; S, 11.3. Mol. wt. osmometrically in benzene, Found: 860; Calcd: 856. The product is air-stable and is soluble in CH_2Cl_2, $CHCl_3$ and benzene, and insoluble in ether and hexane. The complex *cis*-$\overline{PtCS_2CH_2CH_2S}[PCH_3(C_6H_5)_2]_2$ was prepared by the same procedure using $Pt[PCH_3(C_6H_5)_2]_4$. This complex is a stable, white crystalline solid and was obtained in 92% yield.

cis-$\overline{PtCS_2CH_2CH_2CH_2S}[P(C_6H_5)_3]_2$ To a solution of 1.04 g (0.84 mmol) of $Pt[P(C_6H_5)_3]_4$ in 30 ml of benzene was added 0.14 g (0.95 mmol) of trimethylene trithiocarbonate. There was only a very slight color change in the original deep yellow solution on adding the $(CH_2)_3CS_3$, and the color remained unchanged after stirring for 1 hour at 25°. Benzene was then removed under vacuum and the remaining yellow solid was triturated with ether and collected by filtration. Recrystallization from $CHCl_3$-hexane at 0° gave 0.53 g (73%) of the yellow, crystalline product, m.p. 200°(d). This complex is air-stable, soluble in CH_2Cl_2, $CHCl_3$ and benzene, and insoluble in ether and hexane. After recrystallizing from $CHCl_3$-hexane and drying under vacuum at 55° for 15 hours, the complex was obtained as a solvate containing 1 molecule of $CHCl_3$ per 10 molecules of complex.

Anal. Calcd for $Pt(CH_2)_3CS_3[P(C_6H_5)_3]_2 \cdot 0.1\ CHCl_3$: C, 54.6; H, 4.13; S, 10.9; Cl, 1.20. Found: C, 54.3; H, 4.18; S, 10.1; Cl, 1.02.

X-ray structure determination of $[Cl(PPh_3)_2Pt(CS_2)Pt(PPh_3)_2][BF_4]$*

Yellow crystals of $[Cl(PPh_3)_2Pt(CS_2)Pt(PPh_3)_2][BF_4] \cdot nCH_2Cl_2$ were obtained when a solution of the impure thiocarbonyl complex $[PtCl(CS)(PPh_3)_2][BF_4]$ in a mixture of CH_2Cl_2 and hexane was allowed to stand for over 24 hours at room temperature. The crystal used for the structure determination contained 0.2 moles of CH_2Cl_2 per mole of complex although analytical samples of the material indicated the presence of a larger amount of solvent. It was found that the complex could be isolated free of solvent when the recrystallization was carried out in acetonitrile-ether and the crystals so obtained gave satisfactory elemental analyses for the above formula. Data were collected on a fully automated Syntex $P2_1$ four-circle diffractometer using monochromatic CuKα(1.5418Å) radia-

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*The X-ray structure determination was carried out by Jim Lisy under the supervision of Dr. Jon Clardy of this department.

tion. There are four molecules of complex in the unit cell which belongs to the common space group $P2_1/c$. Diffractometer measured cell constants for the monoclinic unit cell are a = 15.577(1), b = 16.539(3) and c = 27.190(2)Å and β = 95.061(7)°. A total of 5351 reflections were judged observed after correction for Lorentz, polarization and background effects. All 90 nonhydrogen atoms were located using heavy atom methods. Full-matrix least squares refinement varying positional and anisotropic thermal parameters for the atoms of the complex and positional and occupancy parameters for the solvent converged to the present discrepancy index of 0.07.

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