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Synthesis of Carbene Complexes by Reaction of Platinum Thiocarbamoyl and Thio Ester Complexes with Electrophiles

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Carbene complexes of the type $\{Pt(Cl)[C(SR)Y]L_2\}\{A\}$, where R = CH_3 or C_2H_5, Y = OCH_3, SC_2H_5, or $N(CH_3)_2$, L = $P(C_6H_5)_3$ or $P(CH_3)(C_6H_5)_2$, were prepared by alkylation of the sulfur of the parent thio ester, $Pt(Cl)[C(S)OCH_3]L_2$ or $Pt(Cl)[C(S)SC_2H_5]L_2$, or thiocarbamoyl complex $Pt(Cl)[C(S)N(CH_3)_2]L_2$ with $(C_2H_5)_3O^+$ or CH_3OSO_2F. The thiocarbamoyl complex also reacts with benzyl bromide, allyl bromide, CH_3HgCl, and CF_3SO_3H to give the sulfur addition products $\{Pt(Cl)[C(SR')N(CH_3)_2][P(C_6H_5)_3]_2\}\{A\}$, where R' = $C_6H_5CH_2$, $CH_2{=}CHCH_2$, CH_3Hg, or H and A^- = BF_4^- or $CF_3SO_3^-$. The chloride ligand is removed from $Pt(Cl)[C(S)N(CH_3)_2]L_2$ on reaction with $SnCl_4$ to give $\{Pt[C(S)N(CH_3)_2][P(C_6H_5)_3]_2\}_2(SnCl_5)_2$, containing the known, thiocarbamoyl-bridged, dimeric cation. The structures of the carbene ligands in the complexes are discussed on the basis of their infrared and proton NMR spectra. Also a few dealkylation reactions of the carbene complexes are described.

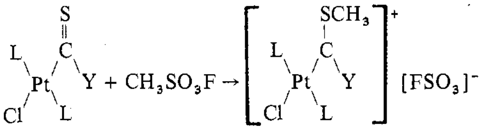
Introduction

There has been much recent interest in transition metal complexes with carbene ligands,[1,2] and there is currently considerable emphasis on developing general preparative methods for these complexes. Carbene complexes of platinum(II) and palladium(II) are generally prepared either by addition of nucleophiles such as alcohols or amines to coordinated isonitrile ligands[3] or via ligand displacement by carbene fragments derived from electron-rich olefins.[4] We report here a new method for the preparation of cationic carbene complexes of platinum(II) involving electrophilic addition of various cations to the thiocarbonyl sulfur atom of complexes containing thiomethoxycarbonyl ($-CSOCH_3$), dithioethoxycarbonyl ($-CS_2C_2H_5$), and *N,N*-dimethylthiocarbamoyl [$-CSN(CH_3)_2$] ligands.

Previously, Dean and Treichel[5] reported the preparation of the $Mn(CO)_4[CSN(CH_3)_2]$ and $(C_5H_5)Mo(CO)_2[CSN(CH_3)_2]$ complexes which contained the thiocarbamoyl ligand, but it was believed that *both* the carbon and sulfur atoms were coordinated to the metal. The sulfur atom in these complexes could be methylated to give products in which the C and S atoms apparently remained bound to the metal. In the complexes reported herein, only the carbon atom is coordinated to the metal.

Results and Discussion

Reactions of $Pt(Cl)[C(S)OCH_3]L_2$ and $Pt(Cl)[C(S)SC_2H_5]L_2$, Where L = $P(C_6H_5)_3$ or $P(CH_3)(C_6H_5)_2$, with Electrophiles. The trans complexes $Pt(Cl)[C(S)OCH_3][P(C_6H_5)_3]_2$[6] and $Pt(Cl)[C(S)SC_2H_5][P(C_6H_5)_3]_2$[7] react readily at 0° in CH_2Cl_2 with alkylating agents such as CH_3SO_3F and $[(C_2H_5)_3O][BF_4]$ to form cationic carbene complexes (eq 1), where L = $P(C_6H_5)_3$ or $P(CH_3)(C_6H_5)_2$



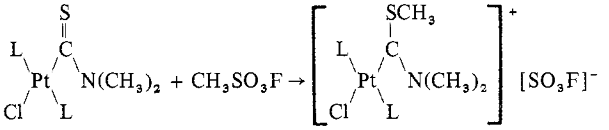
(1)

and Y = OCH_3 or SC_2H_5. This behavior contrasts with that of the oxygen analog, $Pt(Cl)[C(O)OCH_3][P(C_6H_5)_3]_2$, which yields $\{Pt(Cl)(CO)[P(C_6H_5)_3]_2\}\{BF_4\}$ and methyl ethyl ether on reaction with $[(C_2H_5)_3O][BF_4]$.

The carbene complex $\{Pt(Cl)[C(SCH_3)OCH_3][P(C_6H_5)_3]_2\}\{FSO_3\}$, undergoes complete decomposition within 3 hr in CD_2Cl_2 or $CDCl_3$ solution at 25°. This decomposition proceeds in part with the formation of CH_3Cl as determined by NMR. Addition of excess Cl^- or $HN(CH_3)_2$ to solutions of this complex causes rapid decomposition with formation of CH_3Cl or $HN(CH_3)_3^+$. In addition, relatively small amounts of $(CH_3)_2S$ and $\{PtCl(CO)[P(C_6H_5)_3]_2\}^+$ are formed in what appears to be a minor decomposition pathway. The $\{Pt(Cl)[C(SCH_3)(OCH_3)][P(CH_3)(C_6H_5)_2]_2\}\{FSO_3\}$ derivative showed no sign of decomposition in solution after several hours at 25°. This increase in stability is presumably due to the higher electron-donating ability of $P(CH_3)(C_6H_5)_2$, which provides more electron density at the sulfur and/or oxygen atom thus enhancing the binding of the CH_3 groups at those sites. These are the first examples of carbene complexes in which both oxygen and sulfur are present as the carbene heteroatoms. The carbene complexes in which both heteroatoms are sulfur are very stable in solution and do not react with either Cl^- or $HN(CH_3)_2$.

Both $Pt(Cl)[C(S)OCH_3][P(C_6H_5)_3]_2$ and $Pt(Cl)[C(S)SC_2H_5][P(C_6H_5)_3]_2$ react with dry HCl gas in CH_2Cl_2 solution at 25° to form methanol or ethanethiol and a complex believed to be $\{Pt(Cl)(CS)[P(C_6H_5)_3]_2\}\{Cl\}$. This complex has been prepared by an independent method which will be reported elsewhere.

Reactions of $Pt(Cl)[C(S)N(CH_3)_2][P(C_6H_5)_3]_2$[8] with Electrophiles. Like the thio ester complexes, the thiocarbamoyl complex $Pt(Cl)[C(S)N(CH_3)_2][P(C_6H_5)_3]_2$, **1**, reacts with $(C_2H_5)_3O^+$ and CH_3SO_3F to give the S-alkylated product, where L = $P(C_6H_5)_3$. The analogous carbamoyl complex



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(2)

$Pt(Cl)[C(O)N(CH_3)_2][P(C_2H_5)_3]_2$, however, reacts[9] with $(C_2H_5)_3O^+$ to yield $Pt(Cl)(CO)[P(C_2H_5)_3]_2^+$ and $N(CH_3)_2(C_2H_5)$. Unlike the carbene complexes derived from the thio esters, these are very stable in solution and do not react with either Cl^- or $HN(CH_3)_2$ at 25°.

Complex **1** reacts (eq 3) slowly with the milder alkylating

$$1 + (CH_3O)_2SO_2 \xrightarrow{CH_2Cl_2,\ 25°} \{Pt(Cl)[C(SCH_3)N(CH_3)_2][P(C_6H_5)_3]_2\}^+\{CH_3SO_4^-\} \qquad (3)$$

agent dimethyl sulfate to form the same carbene cation obtained from reaction 2. The NMR spectrum of the product revealed absorptions characteristic of the carbene cation as well as an additional singlet (τ 6.38 in $CDCl_3$) assigned to the anion $\{CH_3SO_4\}^-$. A conductivity measurement showed the complex to be a 1:1 electrolyte in CH_2Cl_2.

Reaction of **1** with benzyl bromide or allyl bromide occurs slowly over a period of about 1 hr at 25°. Treatment of the reaction solution with $AgBF_4$ causes precipitation of AgBr allowing the carbene cations to be isolated as the $\{BF_4\}^-$ salts (eq 4).

From the reaction of **1** with allyl bromide a mixed-

$$\mathbf{1} + C_6H_5CH_2Br \xrightarrow{AgBF_4} \{Pt(Cl)[C(SCH_2C_6H_5)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\} + AgBr \tag{4}$$

halide–carbene product (with both chloride and bromide ligands present) was obtained. The halide mixture most likely results from replacement (eq 5) of chloride by free bromide

$$\{Pt(Cl)[C(SCH_2CHCH_2)N(CH_3)_2][P(C_6H_5)_3]_2\}^+ + Br^- \rightleftharpoons \{Pt(Br)[C(SCH_2CHCH_2)N(CH_3)_2][P(C_6H_5)_3]_2\}^+ + Cl^- \tag{5}$$

ion produced in the alkylation reaction. The mixed-halide carbene is converted entirely to the chloro carbene over a period of 25 hr in the presence of an excess of bis(triphenylphosphine)iminium chloride, $[(C_6H_5)_3P]_2NCl$, in acetonitrile at 25°. The pure bromo–carbene complex was obtained more conveniently by allowing the bromo analog of **1** to react with allyl bromide followed by treatment with $AgBF_4$.

It is interesting that we do not observe this halide exchange in the reaction of **1** with benzyl bromide under the same conditions as used with allyl bromide. Also the $P(CH_3)(C_6H_5)_2$ analog of **1** reacts with allyl bromide to give the carbene cation with no halide exchange. The ease of halide exchange in $\{Pt(Cl)[C(SCH_2CHCH_2)N(CH_3)_2][P(C_6H_5)_3]_2\}^+$ but not in $\{Pt(Cl)[C(SCH_2CHCH_2)N(CH_3)_2][P(CH_3)(C_6H_5)_2]_2\}^+$ or $\{Pt(Cl)[(SCH_2C_6H_5)N(CH_3)_2][P(C_6H_5)_3]_2\}^+$ suggests that coordination of the allyl olefin bond to the metal may promote the exchange in the $P(C_6H_5)_3$ derivative; this will be discussed further in the next section.

Reactions of **1** with Lewis acids other than carbonium ions were also investigated. It was found that **1** reacts with CH_3HgCl at 25° when $AgBF_4$ is added to the solution. The product $\{Pt(Cl)[C(SHgCH_3)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$ does not form, however, when $AgBF_4$ is not present to assist with the removal of Cl^- from CH_3HgCl. Coordination of CH_3Hg^+ to the thiocarbamoyl sulfur atom is related to the previously noted thiocarbamoyl sulfur coordination to metals in the dimeric complexes $\{Pd(Cl)[C(S)N(CH_3)_2][P(OCH_3)_3]\}_2$[10] and $\{M[C(S)N(CH_3)_2][P(C_6H_5)_3]_2\}_2{}^{2+}$, where M = Pd or Pt.[8]

The mercury-containing carbene complex is stable both in the solid state and in solution. However, on adding $[(C_6H_5)_3P]_2NCl$ to a CD_3CN solution of the complex at 25° the mercury–sulfur bond is rapidly cleaved giving CH_3HgCl and the original thiocarbamoyl complex. The products were easily identified from the NMR spectrum of the solution.

The reaction of **1** with the Lewis acid $SnCl_4$ (eq 6) does not

$$\mathbf{1} + 2SnCl_4 \rightarrow \{Pt[C(S)N(CH_3)][P(C_6H_5)_3]_2\}_2(SnCl_5)_2 \tag{6}$$

proceed in the same manner as the above reactions. Instead, $SnCl_4$ removes a chloride ion from the complex forming $SnCl_5{}^-$ and the known thiocarbamoyl-bridged dimer[8] $\{Pt[C(S)N(CH_3)_2][P(C_6H_5)_3]_2\}_2{}^{2+}$. This dimer was isolated as a pale yellow crystalline solid and identified by its NMR spectrum[8] and its characteristic reaction[8] with excess Cl^- to regenerate **1**. The presence of $SnCl_5{}^-$ 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.

A methylene chloride solution of **1** reacts with dry HCl gas (eq 7) to give a clear, colorless solution, which on purging with

$$\mathbf{1} + HCl \rightleftharpoons \{Pt(Cl)[C(SH)N(CH_3)_2][P(C_6H_5)_3]_2\}\{Cl\} \tag{7}$$

N_2 gives reversible regeneration of **1** and the yellow color. The colorless solution contains the carbene cation which results from protonation of the thiocarbonyl sulfur atom. The protonated complex could be isolated as the $BF_4{}^-$ salt after treating the acidic reaction solution with $AgBF_4$. In the NMR spectrum of this complex, the presence of two separate *N*-methyl resonances and the absence of a high-field (τ 10–30) proton resonance rule out the possibility of protonation of the nitrogen or the metal atom. A shift in the nitrogen methyl resonances (relative to **1**) is observed which is identical with the shift observed for the other carbene cations derived from **1**. However, we do not observe a resonance in the NMR spectrum which can be assigned to the sulfur proton, but it is possible that this resonance is very broad or obscured by the broad phenyl absorptions (τ 2–3) of the phosphine ligands. This white crystalline complex turns to a pale yellow color on standing at room temperature for several hours indicating slow decomposition, and satisfactory elemental analyses could not be obtained. However, the protonated carbene complex was isolated as a stable white crystalline solid of the composition $\{Pt(Cl)[C(SH)N(CH_3)_2][P(C_6H_5)_3]_2\}\{CF_3SO_3\}\cdot 0.5CH_2Cl_2$ when **1** was treated with CF_3SO_3H instead of HCl.

Table I. Ir Spectra[a] (cm^{-1}) of Carbene Complexes Derived from $Pt(Cl)[CSN(CH_3)_2][P(C_6H_5)_3]_2$

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

[a] All spectra were recorded on 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 ref 8. [c] Derived from $PtBr(CSNMe_2)(PPh_3)_2$. This complex also shows a very weak band at 1637 cm^{-1} for ν(C=C) of the allyl group (see text).

Spectra and Structures. Bands corresponding to the predominantly C=S stretching mode ν(CS) in the infrared spectra of the complexes $Pt(Cl)[C(S)OCH_3]L_2$, $Pt(Cl)[C(S)SC_2H_5]L_2$, and $Pt(Cl)[C(S)N(CH_3)_2]L_2$, where L = $P(C_6H_5)_3$, are observed at 1200, 1058, and 964 cm^{-1}, respectively. The reported assignments for the dithioethoxycarbonyl[7] and thiocarbamoyl[8] complexes are based on values for similar organic compounds. The band at 1200 cm^{-1} for the thiomethoxycarbonyl complex is reasonably assigned to the ν(CS) mode since compounds of the type $(RO)_2CS$ have relatively high CS stretching frequencies (1212–1234 cm^{-1}).[11]

While it is difficult to make an unambiguous assignment of a C=S stretching frequency when the CS group is attached to nitrogen, it has been observed[12] that *N,N*-dialkylthioformamides show a characteristic band in the region 950–1000 cm^{-1} (e.g., 975 cm^{-1} for $HCSN(CH_3)_2$). Although coupled with other vibrations, this band has been assigned[12] to a predominantly single-bond CS stretching vibration. The origin of the 964-cm^{-1} band in **1** is believed to be the same.

It has been shown[12] that S-methylation of $HCSN(CH_3)_2$ causes a shift of this band from 975 to 860 cm^{-1}. We observe that the 964-cm^{-1} band of **1** is shifted to 910–920 cm^{-1} (see Table I) on forming the carbene complexes described here. All organic thioamides also exhibit a strong characteristic band between 1500 and 1600 cm^{-1} which is believed to have the CN stretching vibration as its major component; a shift to higher frequencies for this band is observed on S-alkylation.[12] For **1** this band is observed at 1510 cm^{-1} and is shifted to 1530–1570 cm^{-1} (see Table I) on formation of the carbene ligand. This shift can be accounted for by an increase in double-bond character of the C–N bond expected on alkylation of the sulfur atom. For the thiomethoxycarbonyl and dithioethoxycarbonyl complexes, the ν(CS) band is likely to be shifted to considerably lower frequencies on formation of the carbene ligand, but no assignments are made for this shifted

Table II. ^{1}H NMR Spectra of Platinum–Carbene Complexes[a]

	τ(SR)[b]	τ(XR$'_n$)[b]	*J*(PtCS-SCH), Hz	*J*(PtCX-CH),[c] Hz	Solvent
$\mathrm{PtCl(CSOMe)(PPh_3)_2}$		7.01 s		9.0	$\mathrm{CDCl_3}$
$\mathrm{PtCl(CSOMe)(PMePh_2)_2}$[d]		6.91 s		9.0	$\mathrm{CDCl_3}$
$\mathrm{PtCl(CS_2Et)(PPh_3)_2}$[e]	7.8 m, 9.4 t				$\mathrm{CDCl_3}$
$\mathrm{PtCl(CSNMe_2)(PPh_3)_2}$[f]		7.35 s, 7.76 s		7.5	$\mathrm{CDCl_3}$
$\mathrm{\{PtCl[C(SMe)OMe](PPh_3)_2\}\{FSO_3\}}$	8.39 s	5.61 s		6.5	$\mathrm{CD_2Cl_2}$
$\mathrm{\{PtCl[C(SEt)OMe](PPh_3)_2\}\{BF_4\}}$	7.86 m, 9.28 t	5.54 s		6.8	$\mathrm{CD_2Cl_2}$
$\mathrm{\{PtCl[C(SMe)OMe](PMePh_2)_2\}\{FSO_3\}}$[g]	8.33 s	5.66 s	7.0	6.5	$\mathrm{CD_2Cl_2}$
$\mathrm{\{PtCl[C(SEt)_2](PPh_3)_2\}\{BF_4\}}$	9.07 t, 6.40 m 8.78 t, 7.72 m				$\mathrm{CD_3CN}$
$\mathrm{\{PtCl[C(SEt)SMe](PPh_3)_2\}\{BF_4\}}$	9.09 t, 6.45 m 8.79 t, 7.72 m 8.05 s, 6.95 s		 7.5[h]		$\mathrm{CD_3CN}$
$\mathrm{\{PtCl[C(SMe)NMe_2](PPh_3)_2\}\{FSO_3\}}$	7.27 s	6.70 s, 7.69 s	6.0	9.7	$\mathrm{CDCl_3}$
$\mathrm{\{PtCl[C(SEt)NMe_2](PPh_3)_2\}\{BF_4\}}$	9.05 t, 6.45 m	6.76 s, 7.68 s		9.0	$\mathrm{CDCl_3}$
$\mathrm{\{PtCl[C(SH)NMe_2](PPh_3)_2\}\{CF_3SO_3\}}$		6.77 s, 7.73 s		9.8	$\mathrm{CD_3CN}$
$\mathrm{\{PtCl[C(SCH_2Ph)NMe_2](PPh_3)_2\}\{BF_4\}}$	5.34 s[i]	6.75 s, 7.77 s	8.0	9.5	$\mathrm{CD_3CN}$
$\mathrm{\{PtBr[C(SCH_2CHCH_2)NMe_2](PPh_3)_2\}\{BF_4\}}$	4.9 m, 5.7 m	6.72 s, 7.78 s		9.5	$\mathrm{CD_3CN}$
$\mathrm{\{PtCl[C(SHgMe)NMe_2](PPh_3)_2\}\{BF_4\}}$	9.00 s[j]	7.15 s, 7.73 s	183[k]	9.0	$\mathrm{CD_3CN}$

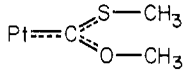
[a] All spectra were recorded at room temperature with tetramethylsilane as an internal standard. Abbreviations: s, singlet; t, triplet; m, multiplet. [b] R = Me, Et, H, $\mathrm{CH_2Ph}$, $\mathrm{CH_2CHCH_2}$, or $\mathrm{HgCH_3}$; X = O or N; R$'$ = Me; *n* = 1 or 2. When X = N, then *n* = 2, and 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*-$\mathrm{CH_3}$ protons: τ 7.83 t with satellites, *J*(PCH) = 3.7 Hz, and *J*(PtPCH) = 32.5 Hz. [e] See ref 7. [f] See ref 8. [g] For *P*-$\mathrm{CH_3}$ protons: τ 7.62 t with satellites, *J*(PCH) = 4.1 Hz, and *J*(PtPCH) = 28.5 Hz. [h] This *J* value is for the methyl resonance at τ 6.95 s. Platinum satellites are not resolved for the methyl resonance at τ 8.05 s. [i] For the $\mathrm{CH_2}$ protons of the benzyl group. [j] For the *Hg*-$\mathrm{CH_3}$ protons. [k] This coupling constant is for *J*(^{199}HgCH). The protons in $\mathrm{HgCH_3}$ show no coupling to ^{195}Pt.

ν(CS) band due to the complexity of the lower region in these spectra.

The proton NMR spectra (Table II) of $\mathrm{Pt(Cl)[C(S)OCH_3][P(C_6H_5)_2(CH_3)]_2}$ and its carbene derivative, $\mathrm{\{Pt(Cl)[C(SCH_3)(OCH_3)][P(C_6H_5)_2(CH_3)]_2\}\{FSO_3\}}$, exhibit a 1:2:1 triplet for the *P*-$\mathrm{CH_3}$ protons, which is characteristic[13] of a geometry in which the $\mathrm{P(C_6H_5)_2(CH_3)}$ groups are trans to each other. It is believed that all of the other complexes described in this paper also have the trans stereochemistry. As has been found in other carbene complexes,[1,2] the plane of the planar carbene ligands described herein is probably perpendicular to the square plane around the Pt.

The ^{1}H NMR spectra show that the methyl or ethyl protons in the starting neutral complexes undergo the expected downfield shift on forming the carbene cations (see Table II). Long-range coupling *J*(^{195}Pt–C–X–C–^{1}H) of 6–10 Hz (X = O, S, or N) is observed for the carbene complexes as well as for the neutral precursor complexes (see Table II). Carbene complexes of the type $\mathrm{\{Pt(CH_3)[C(OCH_3)R]L_2\}\{PF_6\}}$ show a similar long-range coupling of ~7 Hz.[14]

Evidence[1,2] indicates that there is considerable double-bond character in the C(carbene)–heteroatom bonds of the planar carbene ligands thus causing restricted rotation about these bonds; this gives rise to the possibility of finding different isomers of the carbene ligand. In the complex *trans*-$\mathrm{\{Pt(Cl)[C(SCH_3)(OCH_3)]L_2\}\{FSO_3\}}$, where L = $\mathrm{P(C_6H_5)_3}$ or $\mathrm{P(CH_3)(C_6H_5)_2}$, the configurations **2**–**4** can be considered.



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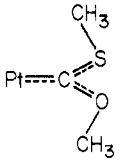

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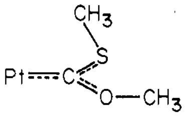
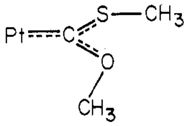


4a

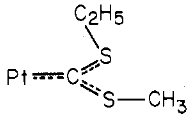


4b

A study of models[1,2] of these different configurations indicates that structures **2** and **3** are unfavorable because of steric hindrance and that structures of type **4a** or **4b** should be sterically favored. The NMR spectrum of $\mathrm{\{Pt(Cl)[C(SCH_3)(OCH_3)][P(C_6H_5)_3]_2\}^+}$ shows only two methyl proton resonances. This could mean that structures **4a** and **4b** are rapidly interconverting at room temperature on the NMR time scale. It could also mean that one methyl group is restricted to a cis or trans position while the other methyl is rotating rapidly. For the complex $\mathrm{(CO)_5Cr[C(OCH_3)CH_3]}$ it has been shown[15] that rotation about the C(carbene)–O bond is rapid at room temperature and cis–trans isomers are observed only at −40°. A less likely possibility is that only one isomer (either **4a** or **4b**) is present in solution; further studies will be required to distinguish among these possibilities.

The NMR spectrum of $\mathrm{\{Pt(Cl)[C(SC_2H_5)_2][P(C_6H_5)_3]_2\}\{BF_4\}}$ in $\mathrm{CD_3CN}$ at room temperature shows two distinct ethyl resonances of equal intensity (Table II). This definitely rules out a configuration of type **2** or type **3** only but is consistent with a configuration of type **4** with one ethyl in the cis position and the other in the trans position. It thus appears that there is restricted rotation around the C(carbene)–S bonds in this complex.

The NMR spectrum of the similar complex $\mathrm{\{Pt(Cl)[C(SC_2H_5)(SCH_3)][P(C_6H_5)_3]_2\}\{FSO_3\}}$ shows two methyl resonances and two ethyl resonances. This too is consistent with the presence of one alkyl group in the carbene ligand cis to the Pt atom while the other is in the trans position. The



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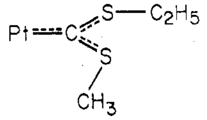

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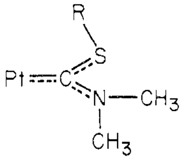
isomers **5** and **6** appear to be present in approximately equal amounts in solution ($\mathrm{CDCl_3}$ or $\mathrm{CD_3CN}$) at room temperature. Both methyl resonances show long-range coupling with ^{195}Pt although the satellite peaks are not fully resolved for the higher field methyl resonance. The higher field position for this $\mathrm{CH_3}$ group indicates that it is in a position cis (i.e., structure **6**) to the Pt where there is greater shielding from the phosphine phenyl groups.[8] The lower field methyl group may then be assigned to structure **5** in which the $\mathrm{CH_3}$ group is trans to the Pt. The larger observed *J*(^{195}PtCSCH) coupling constant for this trans CH_3 group is also consistent with this assignment. Methyl groups trans to Pt in carbamoyl[8] and carbene[16] complexes have previously been observed to exhibit larger coupling constants than cis CH_3 groups.

The carbene cations **7**–**9**, formed by alkylation of **1**, still show nonequivalent CH_3 groups on the nitrogen atom due to restricted rotation around the C(carbene)–N bond. As for **1**,[8] the methyl proton resonance (Table II) with the larger $J(^{195}PtCNCH)$ coupling constant and at lower field may be assigned to the CH_3 group trans to the Pt, while the resonance at higher field corresponds to that of the cis CH_3 group. It is not clear whether or not there is restricted rotation around the C(carbene)–S bond in these compounds and if so whether the R group is cis or trans to the Pt. In structure **7**, it is shown in the cis position as was found in an X-ray structural investigation[17] of $\{trans\text{-}Pt(CNCH_3)_2[C(NHCH_3)(SC_2H_5)]_2\}\{PF_6\}_2$.

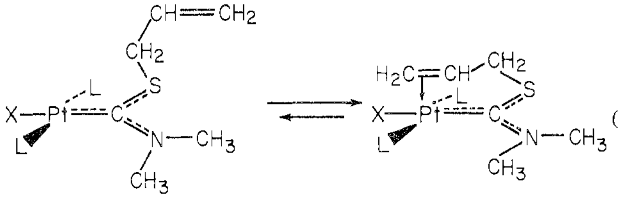


7, R = CH_3 or C_2H_5
8, R = $CH_2C_6H_5$
9, R = $CH_2CH{=}CH_2$
10, R = $HgCH_3$

It may be noted that the trans CH_3 group of **1** is shifted downfield in the carbene derivatives more so than is the cis CH_3 group. This is perhaps due to the overriding importance of shielding of the cis CH_3 group by the phosphine phenyl groups, thus making these protons less sensitive to the electronic effects caused by alkylation of the S atom.

The NMR spectrum of **9** shows two complex multiplets for the allyl protons at τ 4.9 and 5.7 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 τ 5.7 by comparison with the spectrum of free allyl bromide (doublet at τ 6.02 for *Br*-CH_2). The downfield shift of ~0.3 ppm observed for these protons as well as for the methylene protons of **8** can be ascribed to the deshielding effect of the positive charge. The *S*-methylene protons of **9** are coupled to the ^{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 (τ 4.9) observed for the three olefinic protons indicates ^{195}Pt coupling to these protons, which further suggests the olefinic group is coordinating to the Pt. The ir spectra (in CH_2Cl_2) of both the mixed-halide complex $\{Pt(X)[C(SCH_2CHCH_2)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$ (X = Cl and Br), and the pure bromo complex show an extremely weak band at 1637 cm^{-1}. This band, although still weak, is considerably stronger in the $P(CH_3)(C_6H_5)_2$ analog. This band is not present in any of the other carbene complexes and can be assigned to $\nu(C{=}C)$ of an uncoordinated olefin bond ($\nu(C{=}C)$ 1637 cm^{-1} for CH_2CHCH_2Br in CH_2Cl_2 solution). Since the NMR spectrum suggests that the olefin bond is coordinated and since the 1637-cm^{-1} band is extremely weak, there may be an equilibrium in solution between the four- and five-coordinate forms with the five-coordinate form predominating (eq 8). The observed ^{195}Pt coupling would imply that the interconversion of these two forms is slow on the NMR time scale.



(8)

The NMR spectrum of **10** (in CD_3CN) shows a sharp singlet for the *Hg*-CH_3 protons (τ 9.00) which is essentially unshifted from the singlet observed for CH_3HgCl (τ 9.02) in the same solvent. However, the $(^{199}HgCH)$ coupling constants are appreciably different with $J(^{199}HgCH)$ = 183 Hz for the carbene complex and $J(^{199}HgCH)$ = 217 Hz for CH_3HgCl.

Experimental Section

The ^1H 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 with an Industrial Instruments Inc. Model RC16B2 conductivity bridge. Microanalyses were performed by Chemalytics Inc. and Schwarzkopf Microanalytical Laboratory.

Materials. The complexes $Pt(Cl)(CS_2C_2H_5)[P(C_6H_5)_3]_2$[7] and $PtCl[C(S)N(CH_3)_2]L_2$[8] (where L = $P(C_6H_5)_3$ or $P(CH_3)(C_6H_5)_2$) were prepared according to methods described in the literature. The bromide derivative $Pt(Br)[C(S)N(CH_3)_2][P(C_6H_5)_3]_2$ was prepared by stirring 0.53 g (0.63 mmol) of $Pt(Cl)[C(S)N(CH_3)_2][P(C_6H_5)_3]_2$ with an excess of $[(C_2H_5)_4N]Br$ in a mixture of 15 ml of acetone and 4 ml of water for 20 hr at 25°. The suspension was then filtered; the solid was washed with water, ethanol, and finally ethyl ether and then recrystallized from $CHCl_3$–hexane to give 0.50 g (91%) of the yellow-green crystalline product. The PtL_4 compounds (L = $P(C_6H_5)_3$ or $P(CH_3)(C_6H_5)_2$) were prepared by the standard method.[18] Methyl thiochloroformate[19] ($ClCSOCH_3$) was prepared as described in the literature and purified by distillation under nitrogen. All reactions described were carried out under nitrogen atmosphere.

$PtCl[C(S)OCH_3]L_2$ (Where L = $P(C_6H_5)_3$ or $P(CH_3)(C_6H_5)_2$). 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 $ClC(S)OCH_3$. After stirring for 10 min at 25°, the benzene was removed under vacuum and the residue was 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, mp 150–152° dec. Anal. Calcd for $Pt(Cl)[C(S)OCH_3][P(C_6H_5)_3]_2$: C, 54.93; H, 4.01; S, 3.87. Found: C, 54.75; H, 4.12; S, 4.43.

The $P(CH_3)(C_6H_5)_2$ analog, $Pt(Cl)[C(S)OCH_3][P(CH_3)(C_6H_5)_2]_2$, 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.

$\{Pt(Cl)[C(SR)OCH_3]L_2\}\{A\}$ (Where R = CH_3 or C_2H_5, L = $P(C_6H_5)_3$ or $P(CH_3)(C_6H_5)_2$, A^- = FSO_3^- or BF_4^-). The complexes (a) $\{Pt(Cl)[C(SC_2H_5)OCH_3][P(C_6H_5)_3]_2\}\{BF_4\}$ and (b) $\{Pt(Cl)[C(SCH_3)OCH_3]L_2\}\{FSO_3\}$ (where L = $P(C_6H_5)_3$ or $P(CH_3)(C_6H_5)_2$) were prepared similarly. As an example, 0.21 g (0.30 mmol) of $Pt(Cl)[C(S)OCH_3][P(CH_3)(C_6H_5)_2]_2$ in 10 ml of CH_2Cl_2 was treated with 0.07 g (0.61 mmol) of CH_3SO_3F 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 hr, 0.18 g (72%) of the product was obtained as white crystals, mp 125°. Anal. Calcd for $\{Pt(Cl)[C(SCH_3)OCH_3][P(CH_3)(C_6H_5)_2]_2\}\{FSO_3\}$: C, 42.43; H, 3.94; S, 7.83. Found: C, 42.63; H, 4.08; S, 7.26. In the preparation of complex a, $[(C_2H_5)_3O][BF_4]$ was substituted for CH_3SO_3F.

$\{Pt(Cl)[C(SR)SC_2H_5][P(C_6H_5)_3]_2\}\{A\}$ (Where R = CH_3 or C_2H_5, A^- = FSO_3^- or BF_4^-). The complexes (a) $\{Pt(Cl)[C(SCH_3)SC_2H_5][P(C_6H_5)_3]_2\}\{FSO_3\}$ and (b) $\{Pt(Cl)[C(SC_2H_5)_2][P(C_6H_5)_3]_2\}\{BF_4\}$ were prepared similarly. For complex a, 0.39 g (0.45 mmol) of $Pt(Cl)(CS_2C_2H_5)[P(C_6H_5)_3]_2$ 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 separate as a yellow oil. Recrystallization from CH_2Cl_2–hexane at 0° gave 0.32 g (64%) of complex a as pale yellow crystals. After drying under vacuum at 25° for 7 hr, the complex was obtained as a CH_2Cl_2 solvate. Anal. Calcd for $\{Pt(Cl)[C(SCH_3)SC_2H_5][P(C_6H_5)_3]_2\}\{FSO_3\}\cdot 1.4CH_2Cl_2$: 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 also as the CH_2Cl_2 solvate was prepared using $[(C_2H_5)_3O][BF_4]$ in place of CH_3SO_3F. Attempts to remove chlorinated hydrocarbon solvents from solvates of many complexes, by drying under vacuum, were generally unsuccessful. For this reason the complexes were analyzed as the solvates and the presence of the solvent was confirmed by their proton NMR spectra.

$\{Pt(Cl)[C(SR)N(CH_3)_2][P(C_6H_5)_3]_2\}\{A\}$ (Where R = CH_3 or C_2H_5, A^- = FSO_3^-, BF_4^-, or $CH_3OSO_3^-$). The complexes (a) $\{Pt(Cl)[C(SCH_3)N(CH_3)_2][P(C_6H_5)_3]_2\}\{FSO_3\}$ and (b) $\{Pt(Cl)[C(SC_2H_5)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$ were prepared similarly. For complex b, 0.33 g (0.39 mmol) of $Pt(Cl)[CSN(CH_3)_2][P(C_6H_5)_3]_2$ 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 $\sim$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, mp 287°. After drying under vacuum at 25° for 10 hr, the complex was obtained as the CH_2Cl_2 solvate. Anal. Calcd for $\{Pt(Cl)[(SC_2H_5)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}\cdot CH_2Cl_2$: 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%), mp 265°, and also contained solvent of crystallization when recrystallized from CH_2Cl_2 or $CHCl_3$.

The complex $\{Pt(Cl)[C(SCH_3)N(CH_3)_2][P(C_6H_5)_3]_2\}\{CH_3OSO_3\}$ was obtained from the reaction of the thiocarbamoyl complex with dimethyl sulfate. To 0.19 g (0.23 mmol) of $Pt(Cl)[CSN(CH_3)_2][P(C_6H_5)_3]_2$ in 7 ml of CH_2Cl_2 was added 0.15 g (1.19 mmol) of $(CH_3O)_2SO_2$. After stirring for 4 hr at 25°, the solution was filtered and concentrated to $\sim$3-ml total volume under an N_2 stream. Addition of hexane gave the product as white crystals (50%), mp 235°. This complex was also obtained as a solvate when recrystallized from CH_2Cl_2 or $CHCl_3$. The $CHCl_3$ solvate of this complex gave a value of $\Lambda_M = 48\ ohm^{-1}\ cm^2\ mol^{-1}$ 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.[20]

$\{Pt(Cl)[C(SH)N(CH_3)_2][P(C_6H_5)_3]_2\}\{CF_3SO_3\}$. 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 $Pt(Cl)[CSN(CH_3)_2][P(C_6H_5)_3]_2$ in 6 ml of CH_2Cl_2 at 25° was treated with 3 drops of pure CF_3SO_3H causing the solution to turn instantly from yellow to colorless. The solution was then concentrated to $\sim$3-ml total volume under an N_2 stream, followed by addition of hexane ($\sim$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 hr gave 0.23 g (81%) of the CH_2Cl_2-solvated complex as white crystals, mp 165–168°. Anal. Calcd for $\{Pt(Cl)[C(SH)N(CH_3)_2][P(C_6H_5)_3]_2\}\{CF_3SO_3\}\cdot 0.5CH_2Cl_2$: 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; it is insoluble in 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 to give $Pt(Cl)[CSN(CH_3)_2][P(C_6H_5)_3]_2$ as the product. The $CHCl_3$ phase turns from colorless to yellow accompanied by vigorous effervescence (CO_2) indicating deprotonation of the carbene cation by CO_3^{2-}.

$\{Pt(Cl)[C(SCH_2C_6H_5)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$. To 0.20 g (0.24 mmol) of $Pt(Cl)[CSN(CH_3)_2][P(C_6H_5)_3]_2$ 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 hr, 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 hr gave 0.17 g (69%) of the product as white crystals, mp 272°. Anal. Calcd for $\{Pt(Cl)[C(SCH_2C_6H_5)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$: C, 54.06; H, 4.25; Cl, 3.47. Found: C, 54.28; H, 4.51; Cl, 3.99. This complex is very stable both in the solid state and in solution and is considerably more soluble in CH_2Cl_2 or $CHCl_3$ than any of the other carbene complexes in this series.

$\{Pt(Br)[C(SCH_2CH{=}CH_2)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$. To 0.26 g (0.29 mmol) of $Pt(Br)[CSN(CH_3)_2][P(C_6H_5)_3]_2$ 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 hr 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 $\sim$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 hr gave 0.20 g (70%) of the product as white crystals, mp 267° dec. Anal. Calcd for $\{Pt(Br)[C(SCH_2CH{=}CH_2)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$: 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 $Pt(Cl)[CSN(CH_3)_2][P(C_6H_5)_3]_2$, the product obtained was $\{Pt(X)[C(SCH_2CH{=}CH_2)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$, where X was present as both Cl and Br. The product consisted of approximately two-thirds chloride and one-third bromide after a 3-hr reaction time and an equimolar mixture of chloride and bromide when the reaction solution was left stirring for 20 hr. The presence of both Cl and Br was indicated by halide analyses. The relative amounts of the two derivatives present could be estimated from the NMR spectrum in which the chemical shift of the trans *N*-CH_3 resonance was slightly different for the different halide complexes. When a large excess of $[(C_6H_5)_3P]_2NCl$ was added to these NMR samples, it was found that the bromide derivative in the mixture was converted to the chloride complex.

$\{Pt(Cl)[C(SHgCH_3)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$. To 0.23 g (0.27 mmol) of $Pt(Cl)[CSN(CH_3)_2][P(C_6H_5)_3]_2$ 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 hr, 0.23 g (73%) of white needles, mp 160–165°, were obtained. Anal. Calcd for $\{Pt(Cl)[C(SHgCH_3)N(CH_3)_2][P(C_6H_5)_3]_2\}\{BF_4\}$: 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 $[(C_6H_5)_3P]_2NCl$ at 25° a yellow color immediately results, and yellow crystals of $Pt(Cl)[CSN(CH_3)_2][P(C_6H_5)_3]_2$ begin to precipitate. The NMR spectrum of this solution indicated the formation of CH_3HgCl (τ 9.02, $J(^{199}Hg-^{1}H) = 217$ Hz), and the yellow crystals were identified as the thiocarbamoyl complex from their NMR spectrum in $CDCl_3$.

Reaction of $Pt(Cl)[CSN(CH_3)_2][P(C_6H_5)_3]_2$ with $SnCl_4$. To 0.33 g (0.39 mmol) of $Pt(Cl)[CSN(CH_3)_2][P(C_6H_5)_3]_2$ 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 solution. Concentration of the solution to $\sim$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 $\{Pt[CSN(CH_3)_2][P(C_6H_5)_3]_2\}_2\{SnCl_5\}_2$. This dimeric cation was previously reported[8] 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*[21] solution of the complex gave a molar conductance $\Lambda_M = 97\ ohm^{-1}\ cm^2\ mol^{-1}$ at 25° in CH_2Cl_2 solution. This value for Λ_M corresponds to a 2:1 electrolyte in CH_2Cl_2.[20] Anal. Calcd for the preceding formula: Cl, 16.08. Found: Cl, 15.87.

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Registry No. $PtCl(CSOMe)(PPh_3)_2$, 54823-03-9; $PtCl(CSOMe)(PMePh_2)_2$, 54823-01-7; $PtCl(CS_2Et)(PPh_3)_2$, 54868-45-0; $PtCl(CSNMe_2)(PPh_3)_2$, 38682-71-2; $\{PtCl[C(SMe)OMe](PPh_3)_2\}\{FSO_3\}$, 54823-06-2; $\{PtCl[C(SEt)OMe](PPh_3)_2\}\{BF_4\}$, 54823-08-4; $\{PtCl[C(SMe)OMe](PMePh_2)_2\}\{FSO_3\}$, 54822-99-0; $\{PtCl[C(SEt)_2](PPh_3)_2\}\{BF_4\}$, 54823-10-8; $\{PtCl[C(SEt)SMe](PPh_3)_2\}\{BF_4\}$, 54823-12-0; $\{PtCl[C(SMe)NMe_2](PPh_3)_2\}\{FSO_3\}$, 54823-14-2; $\{PtCl[C(SEt)NMe_2](PPh_3)_2\}\{BF_4\}$, 54823-16-4; $\{PtCl[C(SH)NMe_2](PPh_3)_2\}\{CF_3SO_3\}$, 54823-04-0; $\{PtCl[C(SCH_2Ph)NMe_2](PPh_3)_2\}\{BF_4\}$, 54823-18-6; $\{PtBr[C(SCH_2CHCH_2)NMe_2](PPh_3)_2\}\{BF_4\}$, 54844-41-6; $\{PtCl[C(SHgMe)NMe_2](PPh_3)_2\}\{BF_4\}$, 54844-43-8; $\{PtCl[C(SMe)NMe_2](PPh_3)_2\}\{CH_3OSO_3\}$, 54823-19-7; $PtBr(CSNMe_2)(PPh_3)_2$, 54823-00-6; $\{Pt[CSN(CH_3)_2][P(C_6H_5)_3]_2\}_2\{SnCl_5\}_2$, 54823-02-8; $Pt[P(C_6H_5)_3]_4$, 14221-02-4; $Pt[PCH_3(C_6H_5)_2]_4$, 27121-53-5; $ClC(S)OCH_3$, 2812-72-8; CH_3SO_3F, 558-25-8; $[(C_2H_5)_3O][BF_4]$, 368-39-8; $(CH_3O)_2SO_2$, 77-78-1; benzyl bromide, 100-39-0; allyl bromide, 106-95-6; CH_3HgCl, 115-09-3; $SnCl_4$, 7646-78-8.

References and Notes

(1) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972); D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, **2**, 99 (1973).
(2) F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16**, 487 (1972).
(3) P. M. Treichel, *Adv. Organomet. Chem.*, **11**, 21 (1973).
(4) D. J. Cardin, B. Cetinkaya, E. Cetinkaya, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 514 (1973).
(5) W. K. Dean and P. M. Treichel, *J. Organomet. Chem.*, **66**, 87 (1974).
(6) See Experimental Section for the preparation of this complex.
(7) D. Commereuc, I. Douek, and G. Wilkinson, *J. Chem. Soc. A*, 1771 (1970).
(8) C. R. Green and R. J. Angelici, *Inorg. Chem.*, **11**, 2095 (1972).
(9) T. Sawai and R. J. Angelici, unpublished results.
(10) S. K. Porter, H. White, C. R. Green, R. J. Angelici, and J. Clardy, *J. Chem. Soc., Chem. Commun.*, 493 (1973).
(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Wiley, New York, N.Y., 1958, p 356.
(12) K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, **20**, 597 (1966).
(13) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).
(14) M. H. Chisholm and H. C. Clark, *Chem. Commun.*, 763 (1970); *Inorg. Chem.*, **10**, 1711 (1971).
(15) C. G. Kreiter and E. O. Fischer, *Angew. Chem., Int. Ed. Engl.*, **8**, 761 (1969).
(16) B. Crociani and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 693 (1974).
(17) W. M. Butler and J. H. Enemark, *Inorg. Chem.*, **12**, 540 (1973).
(18) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958).
(19) M. M. Delepine, *Bull. Soc. Chim. Fr.*, [4] **9**, 901 (1911).
(20) P. M. Treichel, W. J. Knebel, and R. W. Hess, *J. Am. Chem. Soc.*, **93**, 5424 (1971).
(21) This value for the concentration is based on mol wt 2206 for the formula given.

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Ligand-Induced Fluxionality in Some η^3-Allylplatinum(II) Complexes Containing Chelating Ligands. Isolation of Dynamic 1:1 Adducts

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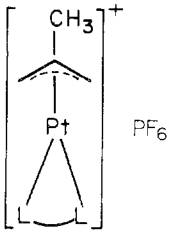
Several static, symmetrically bonded η^3-allyl complexes of the form $(\widehat{LL})Pt(2\text{-}Me(all))^+$ have been prepared (all = allyl). Reaction with neutral bases leads to syn–anti interchange but the effectiveness of conversion to a dynamic system is a function of nucleophilicity toward Pt(II). Good nucleophiles such as PPh_2Me give stable 1:1 adducts which are dynamic in solution at room temperature and appear to have a η^1-allyl (σ-allyl) structure at low temperature. A mechanism is proposed to account for the base-induced fluxionality.

Platinum(II) lacks the overwhelming preference of palladium(II) to form η^3-allyl complexes.[1] Although several η^3-allyl complexes of Pt(II) have been prepared,[2-7] little is known concerning their reactivity[8-10] or the nature and occurrence of the fluxional processes which are characteristic of η^3-allyl complexes in general and of Pd(II) in particular.

It is well-known that many static η^3-allyl complexes of Pd(II) become dynamic in the presence of added base.[11] The suggestion has been made[11,12a] that the major intermediates involved in these dynamic systems are four-coordinate η^1-allyl rather than five-coordinate η^3-allyl complexes implying a concerted reaction with base. Preliminary evidence relating to the observation of such four-coordinate η^1-allyl compounds of Pd(II) has recently been reported.[12b] η^1-Allyl complexes of Ir(I) have also been isolated.[12c]

Both the increasing number of five-coordinate complexes of Pt(II) reported in the recent literature[13] and the compelling nature of the evidence[12a] proposed to eliminate five-coordinate η^3-allylic species as important intermediates for Pd(II) make extrapolation of this concerted mechanism to Pt(II) systems somewhat tenuous. Hence we have prepared several chelated allyl complexes of Pt(II) with the expectation that they should be less labile than their Pd(II) analogs in the presence of a greater variety of nucleophilic bases.[12a] The direct observation of four-coordinate η^1-allyl complexes of Pt(II) might then be a real possibility. In addition, the presence of a chelating ligand, LL, should preclude the rapid ligand exchange which has complicated many of the previous studies of Pd(II) systems. We therefore report the preparation and properties of several cationic 2-methylallyl complexes, I, where LL is a chelating diphosphine or diarsine ligand.[14,15]



I

Results and Discussion

Preparation of the Allylic Complexes. (a) $\widehat{LL}$ = 1,2-Bis(diphenylphosphino)ethane (diphos). (diphos)$PtMe_2$,[16] II, was readily prepared by reaction of dimethyl(π-1,5-cyclooctadiene)platinum(II),[17] III, with diphos

$$\underset{III}{(1,5\text{-}C_8H_{10})PtMe_2} + diphos \xrightarrow{CH_2Cl_2} \underset{II}{(diphos)PtMe_2} \xrightarrow[HCl]{1\ equiv} \underset{IV}{(diphos)PtMeCl}$$

Reaction of II with 1 equiv of hydrogen chloride prepared in situ from 1 equiv of acetyl chloride and excess methanol gave the methylchloro derivative IV via an oxidative addition–