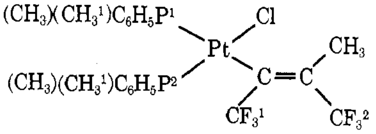
in the refrigerator gave pale yellow crystals. Recrystallization from dichloromethane–ether gave *trans*-$[PtCCF_3{=}C(CH_3)CF_3(CO)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-$ as a white crystalline solid, mp 176–178°, characterized by comparison with an authenticated sample.[5]

cis-$PtCl\{-CCF_3{=}(CH_3)CF_3\}\{P(CH_3)_2C_6H_5\}_2$.—*trans*-$PtClCH_3\{P(CH_3)_2C_6H_5\}_2$ (0.258 g, 0.5 mmol) and *trans*-$[PtCH_3(acetone)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-$ (0.014 g, 0.02 mmol) were dissolved in dichloromethane (15 ml) in a two-necked round-bottomed flask (25 ml) fitted with a magnetic stirring bar. $CF_3C{\equiv}CCF_3$ was bubbled through the solution for 2 min. The solution was then stirred for 3 hr before removing the solvent under reduced pressure. This gave a pale yellow sticky solid which was extracted with benzene and passed through a short Florisil column eluting with benzene to remove any cationic platinum and poly(fluorovinyl) derivatives. Crystallization from benzene–pentane solution gave *cis*-$PtCl(-CCF_3{=}C(CH_3)CH_3)\{P(CH_3)_2C_6H_5\}_2$ as a white crystalline compound, mp 155°. *Anal.* Calcd for $PtP_2F_6ClC_{21}H_{25}$: C, 36.90; H, 3.69; F, 16.69; Cl, 5.20. Found: C, 37.15; H, 3.76; F, 17.07; Cl, 5.66.

The nmr data recorded in dichloromethane solution at 31° and at 100 MHz are interpreted according to the stereochemistry



Chemical shifts, δ, measured from TMS or $CFCl_3$ internal reference are as follows: P¹ methyls: $\delta(CH_3)$ -1.55, -1.51 ppm, $^3J(PtH) = 14.0$ Hz, $J(PH) = 10.4$ Hz; P² methyls: $\delta(CH_3)$ -1.65, -1.60 ppm, $^3J(PtH) = 44.4$ Hz, $J(PH) = 10.4$ Hz; vinyl methyl: $\delta(CH_3)$ -2.35 ppm (b), $^4J(PtH) =$ *ca.* 13 Hz; trifluoromethyls: $\delta(CF_3{}^1)$ 48.00 ppm, $^3J(PtF^1) = 98.5$ Hz, $^4J(PF^1) = 9.1$ Hz, $J(F^1F^1) = 15.0$ Hz, $J(HF^1) = 2.2$ Hz; $\delta(CF_3{}^2)$ 61.48 ppm, $^4J(PtF^2) = 5$ Hz, $^5J(PF^2) = 2.0$ Hz, $J(F^1F^2) = 15.0$ Hz.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WESTERN ONTARIO, LONDON, ONTARIO, CANADA

Chemistry of Metal Hydrides. XII. The Role of Cationic Intermediates in Olefin Insertions into the Platinum–Hydrogen Bond

BY H. C. CLARK* AND H. KUROSAWA

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trans-$PtHX(PR_3)_2$ (X = Cl or Br) reacted with ethylene in the presence of $AgBF_4$ or $AgPF_6$ in acetone–CH_2Cl_2 solution at room temperature and atmospheric pressure for $PR_3 = PPh_3$, PPh_2Me, or PMe_2Ph and in boiling acetone solution (1 atm) for $PR_3 = PEt_3$, giving ethylplatinum compounds. Similar reactions occurred between *trans*-$PtH(NO_3)(PPh_2Me)_2$ and ethylene or *trans*-$PtHX(PPh_2Me)_2$–$AgBF_4$ and propene or butene-1. Some π-allylplatinum(II) phosphine complexes were prepared by a similar reaction of *trans*-$PtHX(PR_3)_2$ with allene or butadiene in the presence of $AgPF_6$. These facile olefin insertion reactions into the Pt–H bond are interpreted in terms of an intermediate four-coordinate cationic complex, *trans*-$[PtH(PR_3)_2(olefin)]^+$.

Introduction

The catalytic homogeneous hydrogenation, isomerization, and polymerization of olefins and acetylenes have been the subject of many studies, particularly for those cases where transition metal complexes are the most effective catalysts. It has generally been accepted that the formation of the metal–hydrido bond and its reaction with unsaturated compounds are the key steps in the overall reactions.[1] Thus, some hydridophosphine complexes of platinum(II) have been shown to undergo insertion reactions toward simple olefins such as ethylene and propene[2,3] as well as several dienes,[4] tetrafluoroethylene,[5] and phosphine-substituted styrene.[6] The first example was reported by Chatt and Shaw,[2] who observed the reversible reaction of *trans*-$PtHCl(PEt_3)_2$ with ethylene to give *trans*-$PtEtCl(PEt_3)_2$ under rather vigorous conditions (95° and 80 atm)

$$trans\text{-}PtHCl(PEt_3)_2 + C_2H_4 \rightleftharpoons trans\text{-}PtEtCl(PEt_3)_2 \quad (1)$$

Cramer and Lindsey reported[7] that the above equilibrium is established within 30 min at 25° and 1 atm in the presence of 1 mol % of tin(II) chloride ($K_{eq} = 35$ l.$^{-1}$ mol), although they did not describe the detailed experimental procedure. The suggestions have been accepted[3,8] that both forward and reverse reactions proceed *via* five-coordinate π-olefinic hydrido complexes and that the strong trans influence and good π-acceptor property of the $SnCl_3^-$ ligand[9,10] may cause both the weakening of the Pt–H bond and the greater interaction of ethylene with platinum. On the other hand, the reactivity of $RhHCl_2(PPh_3)_2$[10] or $HCo(CO)_4$[11]

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(1) See, *e.g.*, R. S. Coffey, "Aspects of Homogeneous Catalysis," Vol. 1, R. Ugo, Ed., Manfredi, Milan, 1970, p 1; F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969); see p 835.

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with olefins was explained in terms of an active species where the central metal ion is coordinatively unsaturated. We are currently investigating[12-14] the reactivity of unsaturated molecules which occupy the fourth coordination site in cationic alkylplatinum(II) complexes, and we hence expected that a similar effect to that suggested above for the cobalt or rhodium cases might be possible in the reactions of platinum hydrido complexes which contain readily displaceable ligands. A recent report[4] on the displacement of nitrate ligand in *trans*-$PtH(NO_3)(PEt_3)_2$ by ethylene or dienes prompts us to describe the facile insertion reactions of cationic hydridoplatinum(II) complexes with several simple olefins as well as dienes, all of which proceed *via* four-coordinate intermediates.[15]

Results and Discussion

In the preceding paper[16] we described an improved method for preparing *trans*-$PtHX(PR_3)_2$ (PR_3 = PPh_2Me, PMe_2Ph; X = halide). We also described an interesting preparative intermediate, *trans*-$[PtH(PPh_2Me)_2(acetone)]^+$ (I), which was formed *in situ* from *trans*-$PtHBr(PPh_2Me)_2$ and $AgPF_6$ in an acetone–methylene chloride solution. The acetone molecule in this complex is coordinated to platinum very weakly since ν(Pt–H), τ(Pt–H), and J(Pt–H) for the hydrido proton of this complex are the largest for several hydrido(diphenyl)methylphosphine complexes of Pt(II) studied[16] (Table I). We have now observed that I reacts with ethylene at −50° to give a hydridoethylene complex (II) whose structure is *trans*-$[PtH(PPh_2Me)_2(C_2H_4)]^+$, while at room temperature the same reaction gives *trans*-$[PtEt(PPh_2Me)_2(C_2H_4)]^+$ (III) very rapidly. Both II and III were characterized by their proton nmr spectra and by the preparation of the cationic derivatives, *trans*-$[PtH(PPh_2Me)_2L]^+PF_6^-$ and *trans*-$[PtEt(PPh_2Me)_2L]^+PF_6^-$, by replacement of ethylene with L = 2,4,6-trimethylpyridine for the hydrido complex and L = 2,4,6-trimethylpyridine, carbon monoxide, or a carbene[13] of the type $\overline{COCH_2CH_2CH_2}$ for the ethylplatinum(II) compounds. The proton nmr spectrum of II (Table II) exhibited in the hydridic hydrogen region features very similar to those[4] of the nmr spectrum of *trans*-$[PtH(PEt_3)_2(C_2H_4)]^+BPh_4^-$ which was precipitated as a stable crystalline solid at room temperature on addition of ethylene to a methanolic solution of *trans*-$PtH(NO_3)(PEt_3)_2$ and sodium tetraphenylborate. The chemical shift of coordinated ethylene in II is also similar to that of the triethylphosphine analog as well as to those of III and *trans*-$[PtMe(PMe_2Ph)_2(C_2H_4)]^+$, which was obtained[17,18] from *trans*-$[PtMe(PMe_2Ph)_2(acetone)]^+$ and ethylene (Table II). Therefore, we assume that complex II has an essentially planar four-coordinate geometry about platinum. The trans influence of the ethylene ligand in II seems stronger than those of pyridines but weaker than those of alkyl isocyanides as suggested from the comparison of values of τ(Pt–H) and J(Pt–H) in *trans*-$[PtH(PPh_2Me)_2L]^+$ (Table I), although the replacement of ethylene by pyridines can be accomplished as described earlier. However, this is not surprising because the trans influence is not necessarily affected by the kinetic factors which determine the trans effect of ligands.

TABLE I[a]

PROTON NMR DATA FOR SOME CATIONIC PLATINUM(II) HYDRIDES, *trans*-$[PtH(PPh_2Me)_2L]^+PF_6^-$

L[b]	τ(Pt–H)	J(Pt–H)	J(P–H)
Acetone	33.60 t	1458	14.5
A	27.20 t	1080	14.3
B	26.53 t	1073	14.0
C_2H_4	16.32 t	931	11.5
p-$CH_3C_6H_4NC$	16.10 t	872	13.5
PPh_2Me	15.39 x	840	18.0 167

[a] τ in ppm (TMS = 10.00) and J in Hz in CH_2Cl_2 solution. t = triplet, x = doublet of triplets. All compounds except those for L = C_2H_4 are from ref 16. [b] A = 2-methylpyridine, B = 2,4,6-trimethylpyridine.

$$trans\text{-}PtHBr(PPh_2Me)_2 + AgPF_6 \xrightarrow{\text{acetone-}CH_2Cl_2} \underset{\text{I}}{trans\text{-}[PtH(PPh_2Me)_2(acetone)]^+PF_6^-} + AgBr$$

$$\begin{tikzcd} & \underset{\text{II}}{trans\text{-}[PtH(PPh_2Me)_2(C_2H_4)]^+PF_6^-} \quad (2) \\ \text{I} + C_2H_4 \arrow[ur, "-50^\circ"] \arrow[dr, "\text{room temp}"'] & \\ & \underset{\text{III}}{trans\text{-}[PtEt(PPh_2Me)_2(C_2H_4)]^+PF_6^-} \quad (3) \end{tikzcd}$$

trans-$PtHCl(PR_3)_2$ (PR_3 = PMe_2Ph, PPh_3) were found to undergo similar ethylene insertion reactions in acetone in the presence of an equimolar amount of $AgPF_6$ at room temperature, while *trans*-$[PtH(PEt_3)_2(C_2H_4)]^+PF_6^-$, which was formed from *trans*-$PtHCl(PEt_3)_2$ and ethylene in an acetone–methylene chloride solution in the presence of $AgPF_6$, was stable toward further reaction with ethylene at room temperature. However if this complex was allowed to react further with ethylene in boiling acetone solution for 40 min, insertion occurred giving *trans*-$[PtEt(PEt_3)_2L]^+PF_6^-$ (L = ethylene and/or acetone), the formation of which was confirmed by conversion to the known compound *trans*-$PtEtCl(PEt_3)_2$[2] by addition of LiCl–MeOH. On the other hand, previous workers reported[4] that further treatment of *trans*-$[PtH(PEt_3)_2(C_2H_4)]^+BPh_4^-$ with ethylene resulted only in the formation of $PtPh_2(PEt_3)_2$.

These remarkable ethylene-insertion reactions of cationic hydridoacetone complexes of Pt(II) are comparable to those of $RhHCl_2(PPh_3)_2$[10] or $HCo(CO)_3$.[11] In order to confirm further the importance of coordinative unsaturation in metal hydrido complexes in determining their reactivities toward olefins, reactions of ethylene with neutral as well as other cationic hydrido complexes of Pt(II) were investigated. *trans*-$PtHBr(PPh_2Me)_2$ failed to react with ethylene at the same conditions as those for reaction 3, and the reaction of *trans*-$PtHCl(PEt_3)_2$ with ethylene was reported[2,3] to require very vigorous conditions (95° and 80 atm or more). On the other hand, *trans*-$PtH(NO_3)(PPh_2Me)_2$ was found to react with ethylene very rapidly at

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[15] For a preliminary communication see H. C. Clark and H. Kurosawa, *J. Chem. Soc. D*, 957 (1971).

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TABLE II

PROTON NMR DATA FOR SOME ETHYLENE COMPLEXES OF PLATINUM(II)[a]

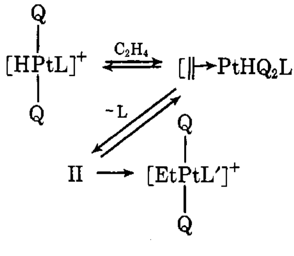
	C_2H_4		Pt–H		
Compd	$\tau(C_2H_4)$	J(Pt–H)	τ(Pt–H)	J(Pt–H)	J(P–H)
trans-$[PtH(PPh_2Me)_2(C_2H_4)]^+PF_6^-$	6.86 b		16.32 t	931	11.5
trans-$[PtH(PEt_3)_2(C_2H_4)]^+$	6.47[b] b	36[b]	17.2[c] t	908[c]	12.0[c]
trans-$[PtEt(PPh_2Me)_2(C_2H_4)]^+PF_6^-$	6.63 b				
trans-$[PtMe(PMe_2Ph)_2(C_2H_4)]^+PF_6^-$ [d]	5.88[e] t	36.8			

[a] τ in ppm (TMS = 10.00) and J in Hz in CH_2Cl_2 solution. b = broad, t = triplet. [b] PF_6^- salt. [c] BPh_4^- salt from ref 4. [d] Reference 18. [e] J(P–H) = 2.7 Hz.

room temperature and 1 atm to give good yields of *trans*-$PtEt(NO_3)(PPh_2Me)_2$

$$\mathit{trans}\text{-}PtH(NO_3)(PPh_2Me)_2 + C_2H_4 \xrightarrow{\text{acetone or } CH_2Cl_2} \mathit{trans}\text{-}PtEt(NO_3)(PPh_2Me)_2 \quad (4)$$

Several cationic hydrides *trans*-$[PtH(PPh_2Me)_2L]^+$ (L = 2,4,6-trimethylpyridine, PPh_2Me, p-$CH_3C_6H_4NC$) did not give any insertion products with ethylene under the same conditions as those for reaction 3 or 4. Thus, the ease with which ethylene insertion into the Pt–H bond occurs under very mild conditions is closely related to the ease of displacement of the ligand trans to hydrogen in *trans*-$PtH(PR_3)_2L$; acetone and NO_3^- [4] can be replaced by ethylene as shown by formation of hydridoethylene complexes, while other ligands such as halides, pyridines, phosphines, and alkyl isocyanides cannot readily be substituted by ethylene.[18] These facts may be explained in terms of the reaction profile. This profile must have two maxima, the minimum between them corresponding to the intermediate which is the cationic trans hydridoolefin complex which we have isolated. The first transition state may well have a five-coordinate geometry similar to that postulated previously[3,8] for reaction 1. Also, the magnitude of the activation energy for this transition state is determined by the ease of displacement of the ligand trans to hydridic hydrogen in the original complex. While the presently available evidence provides no information about the nature or geometry of the transition state corresponding to the second maximum, the formation of the four-coordinate trans hydridoolefin intermediate is clearly essential and provides a much lower total energy barrier for the overall insertion reaction than any other route, since the olefin is apparently activated toward insertion into the Pt–H bond once it occupies the position trans to hydridic hydrogen. This is in good agreement with the reactivities of coordinated acetylenes,[13,14] allenes,[17] and perfluoroarylnitriles[12] in the four-coordinate platinum(II) complexes *trans*-$[PtMe(PMe_2Ph)_2(\text{unsaturate})]^+$. The conversion of II into the ethylplatinum(II) complex may involve the proximity of a hydridic hydrogen to ethylene through an intramolecular rearrangement of II, which may or may not be solvent assisted. Alternatively, a bimolecular process involving II cannot be ruled out. Further work is required before the most probable mechanism can be established with certainty.



The different reactivity of the Pt–H bond toward ethylene according to the particular phosphine present is not readily explained. Perhaps the more electron-withdrawing phosphines such as triphenyl-, diphenyl(methyl)-, or dimethyl(phenyl)phosphine produce a greater positive charge on platinum resulting in a greater degree of activation of ethylene. Less electron density on platinum in these phosphine complexes may also bring about easier cleavage of the Pt–H bond.

Although it has been briefly mentioned previously[7] that the addition of 1% tin(II) chloride solution catalyzed the addition of ethylene to the Pt–H bond of *trans*-$PtHCl(PEt_3)_2$ at room temperature and atmospheric pressure, the same procedure with *trans*-$PtHCl(PPh_2Me)_2$ and ethylene in acetone gave rise to rather low yields of *trans*-$PtEtCl(PPh_2Me)_2$. On the other hand, the reaction of *trans*-$PtHBr(PPh_2Me)_2$ or *trans*-$PtHCl(PMe_2Ph)_2$ with ethylene in acetone was shown to give moderate to good yields of *trans*-$PtEtBr(PPh_2Me)_2$ or *trans*-$PtEtCl(PMe_2Ph)_2$, respectively, in the presence of only catalytic amounts of $AgPF_6$. These reactions may well proceed by the sequence

$$\begin{tikzcd}
\mathit{trans}\text{-}PtHX(PR_3)_2 \xrightarrow{AgPF_6} & \\
\mathit{trans}\text{-}[PtH(PR_3)_2L]^+ \arrow[r, "C_2H_4"] & \mathit{trans}\text{-}[PtEt(PR_3)_2L]^+ \arrow[d, shift left, "\mathit{trans}\text{-}PtHX(PR_3)_2"] \\
& \mathit{trans}\text{-}[PtH(PR_3)_2L]^+ + \mathit{trans}\text{-}PtEtX(PR_3)_2 \quad (5) \arrow[u, shift left] \arrow[ul]
\end{tikzcd}$$

where PR_3 = PPh_2Me or PMe_2Ph; L = acetone and/or C_2H_4; X = Cl or Br.

Some reactions of other olefins were also investigated using these highly reactive hydridoacetone complexes of Pt(II). Thus, propene and butene-1 underwent similar insertion reactions (eq 6) under mild conditions to give n-propyl- and n-butylplatinum(II) complexes, respectively, while *cis*-butene-2, vinyl fluoride and methyl vinyl ether did not react with *trans*-$[PtH(PPh_2Me)_2(\text{acetone})]^+$ under the reaction conditions used for (3) or (4).

$$\mathit{trans}\text{-}[PtH(PPh_2Me)_2(\text{acetone})]^+ \xrightarrow{\text{propene or butene-1}} \mathit{trans}\text{-}[Pt(C_nH_{2n+1})(PPh_2Me)_2L]^+ \quad (6)$$

(L = acetone and/or olefin; n = 3, 4)

While the above mechanistic conclusions also apply to these cases, both the electronic and steric properties of the olefins are important in determining the ease of these insertion reactions; the much weaker σ basicity of those olefins containing electron-withdrawing groups would account for the failure of the reactions with $CH_2{=}CHF$ and $CH_2{=}CHOMe$. The stability of the final insertion products must also affect the course of the reactions. Only n-alkyl derivatives of platinum(II) were formed in those reactions which were successful, as

TABLE III

PROTON NMR DATA FOR SOME ALKYLPLATINUM(II) COMPLEXES[a]

	Phosphine methyl			$Pt(-CH_2-)_n$		$Pt(CH_2)_nCH_3$			
Compd[b]	$\tau(P-CH_3)$	$J(P-CH_3)$	$J(Pt-CH_3)$	τ	$J(Pt-H)$	τ	$J(H-H)$	$J(Pt-CH_3)$	Other
trans-$[PtEt(PPh_2Me)_2L]^+PF_6^-$									
L = acetone[c]	7.88 t	6.5	34.0	~8.6 b	*d*	9.3 b		80	
L = C_2H_4	7.75 t	6.0	33.0	8.52 b, q	*d*	9.17 t	7	74	*e*
L = B	8.08 t	6.5	32.5	8.72 q	*d*	9.41 t	7	56	*f*
L = CO	7.58 t	7.0	34.5	8.70 q	*d*	9.45 t	7	42	
L = C	7.82 t	7.0	35.0	8.78 b	*d*	9.22 t	7	29	*g*
trans-$PtEtX(PPh_2Me)_2$									
X = Br	7.71 t	7.0	31.5	9.23 q	78	9.67 t	7	72	
X = NO_3	7.99 t	6.5	31.0	9.08 q	84	9.79 t	8	73	
trans-$PtEtCl(PMe_2Ph)_2$	8.20 t	7.0	30.5	9.17 x	*d*	9.23 s	8[h]	72[h]	
trans-$[Pt(n-Pr)(PPh_2Me)_2C]^+PF_6^-$	7.86 t	7.0	36.0	9.18 x	*d*	9.46 t	5	*d*	*i*
trans-$[Pt(n-Pr)(PPh_2Me)_2(C_5H_5N)]^+BF_4^-$	8.00 t	7.0	33.0	8.90 x	*d*	9.43 s, b		*d*	
trans-$[Pt(n-Bu)(PPh_2Me)_2(C_5H_5N)]^+BF_4^-$	7.98 t	6.5	34.5	8.95 x 9.15 x	*d*	9.46[j]		*d*	

[a] τ in ppm (TMS = 10.00) and J in Hz in CH_2Cl_2 solution. t = triplet, q = quartet, s = singlet, x = complex, b = broad. [b] B = 2,4,6-trimethylpyridine, C = $\overline{COCH_2CH_2CH_2}$. [c] Obtained *in situ* from *trans*-$PtEtBr(PPh_2Me)_2$, $AgPF_6$, and acetone. [d] Unresolved. [e] Table II. [f] $\tau(o-CH_3)$ 7.40, $J(Pt-H) = 5$ Hz; $\tau(p-CH_3)$ 7.97. [g] $\tau(\alpha-CH_2)$ 8.0, $\tau(\beta-CH_2)$ 8.33, $\tau(\gamma-CH_2)$ 5.95. [h] Peaks due to ^{195}Pt satellites are triplet. [i] $\tau(\alpha-CH_2)$ 8.0, $\tau(\beta-CH_2)$ 8.42, $\tau(\gamma-CH_2)$ 5.94. [j] Collapsed triplet.

well as in the reaction of Li_2PtCl_4 with a terminal olefin and formic acid to give $[(C_nH_{2n+1})Pt(CO)Cl]_2$;[19] moreover, attempts to prepare *sec*-alkylplatinum(II) compounds resulted in the formation of the platinum–hydrido bond.[2] However, *trans*-$[PtH(PR_3)_2(acetone)]^+$ readily reacted with allene or butadiene to give the corresponding π-allyl- or π-crotylplatinum(II) complexes, *e.g.*

$$trans\text{-}[PtH(PR_3)_2(acetone)]^+PF_6^- \xrightarrow{\text{allene}} [Pt(\pi\text{-allyl})(PR_3)_2]^+PF_6^- \quad (7)$$

$$(PR_3 = PPh_3,\ PPh_2Me,\ PMe_2Ph)$$

A reaction mechanism similar to that proposed for the reaction of *trans*-$PtH(NO_3)(PEt_3)_2$ and dienes[4] or of *trans*-$[PtMe(PMe_2Ph)_2(acetone)]^+$ and allene[17] may be suggested, where the formation of hydridodiene complexes or *trans*-$[PtMe(PMe_2Ph)_2(allene)]^+$ is a key step.

Proton Nmr Spectra of Insertion Products (Table III).—All the diphenyl(methyl)- and dimethyl(phenyl)-phosphineplatinum(II) complexes, except for the π-allyl derivatives, were shown to have a trans configuration from their proton nmr spectra; phosphine methyl proton signals appeared as 1:2:1 triplets accompanied by ^{195}Pt satellites due to mutually trans phosphines.[20] Straight-chain structures for the propyl- and butylplatinum(II) compounds were suggested by the appearance of only one terminal methyl resonance as reported in $[(C_nH_{2n+1})Pt(CO)Cl]_2$.[19] Both methyl and methylene protons in the ethyl group attached to platinum showed spin–spin coupling with ^{195}Pt although the coupling with ^{31}P could not be resolved well. $^3J(Pt-C-CH_3)$ values in *trans*-$[PtEt(PPh_2Me)_2L]^+$ as shown in Table III also change as the trans influence of L varies. Much the same order of increasing trans influence of L as that found from $^2J(Pt-CH_3)$ in *trans*-$[PtMe(PMe_2Ph)_2L]^+$ [13,14,18,21] is deduced from $^3J(Pt-C-CH_3)$ (acetone < C_2H_4 < 2,4,6-trimethylpyridine < CO < $\overline{COCH_2CH_2}$) although the J value for L = C_2H_4 may be somewhat larger than expected because of ligand exchange.

The proton nmr spectra of $[Pt(\pi-C_3H_5)(PR_3)_2]^+PF_6^-$ (PR_3 = PPh_2Me, PMe_2Ph) showed the existence of the frozen π-allyl ligand at room temperature. $[Pt(\pi-C_3H_5)(PPh_3)_2]^+PF_6^-$ was too insoluble to obtain a satisfactory spectrum in any suitable solvent. $Pt(C_3H_5)(PPh_3)_2Cl$ was reported[22] to contain a dynamic π-allyl system showing an AX_4 pattern in $CDCl_3$ solution at room temperature. Proton nmr spectra of $[Pt(\pi-C_4H_7)(PR_3)_2]^+PF_6^-$ (PR_3 = PPh_2Me, PMe_2Ph) showed nonequivalent phosphine methyl proton signals as well as the other peaks expected for the π-crotyl ligand. It is difficult at this time to distinguish the two isomers of this ligand, syn and anti, because the 1-methyl proton signals are partly overlapped by the phosphine methyl resonances and the other terminal proton signals appear as very broad patterns due to coupling with the 2 proton and ^{31}P and ^{195}Pt nuclei.

Experimental Section

The following chemicals were obtained commercially and were sufficiently pure for immediate use: K_2PtCl_4 from Johnson, Matthey and Mallory, $AgBF_4$ and $AgPF_6$ from Alfa Inorganic Inc., ethylene, butene-1, *cis*-butene-2, allene, butadiene, vinyl fluoride, and methyl vinyl ether from Matheson of Canada Ltd., and propene from Liquid Carbonic Co. *trans*-$PtHX(PR_3)_2$ (PR_3 = PPh_3,[2] PPh_2Me,[16] PMe_2Ph,[16] PEt_3[2]) were prepared by the reported methods. Microanalyses (Table IV) were performed by Dr. A. B. Gygli, Toronto.

Infrared spectra were recorded on Beckmann IR-10 and IR-7 spectrophotometers, with samples prepared in Nujol mulls; spectra were calibrated against the spectrum of polystyrene film. Proton nmr spectra were obtained using Varian T-60 and HA-100 spectrometers using methylene chloride as solvent as well as internal standard for ethylplatinum(II) complexes. TMS was used as internal standard for the other complexes.

Reaction of *trans*-$PtHX(PR_3)_2$ with Ethylene in the Presence of $AgPF_6$. (a) **PR_3 = PPh_2Me.**—A methylene chloride solution of *trans*-$[PtH(PPh_2Me)_2(acetone)]^+PF_6^-$ was prepared by the method described previously.[16] Ethylene was passed through this solution for 1 min at −50° in an nmr sample tube, and the proton nmr spectrum was run immediately at −50°. When this sample was allowed to warm gradually to room temperature, the evolution of excess ethylene was observed, and the proton nmr spectrum showed the presence of a platinum ethyl group. This solution, which is thought to contain *trans*-$[PtEt(PPh_2Me)(C_2H_4)]^+PF_6^-$, was treated with 2,4,6-trimethylpyridine. The solid which precipitated out on addition of *n*-pentane was purified by dissolving it in methylene chloride,

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TABLE IV

MELTING POINTS AND ANALYTICAL DATA FOR SOME ALKYLPLATINUM(II) COMPLEXES

Compd[a]	Mp, °C	% C Calcd	% C Found	% H Calcd	% H Found	% N or halogen Calcd	% N or halogen Found
trans-PtEtX(PPh$_2$Me)$_2$							
X = Br	148–149 dec	47.74	47.82	4.44	4.31	11.34	11.49
X = NO$_3$	145–146 dec	48.98	48.95	4.55	4.60	2.04	2.14
trans-PtEtCl(PMe$_2$Ph)$_2$	114–115	40.34	40.20	5.08	5.07	6.61	6.64
trans-[PtEt(PPh$_2$Me)$_2$L]$^+$PF$_6^-$							
L = B	161–163	48.54	48.66	4.75	5.02	1.57	1.43
L = CO	154–156 dec	43.67	43.58	3.92	3.88		
L = C	149–150 dec	45.77	46.05	4.44	4.43		
trans-[Pt(*n*-Pr)(PPh$_2$Me)$_2$C]$^+$PF$_6^-$	166–168 dec	46.43	46.29	4.60	4.64		
trans-[Pt(*n*-Pr)(PPh$_2$Me)$_2$(C$_5$H$_5$N)]$^+$BF$_4^-$	156–157 dec	50.76	50.80	4.76	5.01	1.74	1.85
trans-[Pt(*n*-Bu)(PPh$_2$Me)$_2$(C$_5$H$_5$N)]$^+$BF$_4^-$	143–146 dec	51.36	51.27	4.93	4.82	1.71	1.80
[Pt(C$_3$H$_5$)(PPh$_3$)$_2$]$^+$PF$_6^-$	247–250 dec	51.72	51.52	3.90	4.03		
[Pt(C$_3$H$_5$)(PPh$_2$Me)$_2$]$^+$PF$_6^-$	165–167	44.57	44.68	4.00	4.24		
[Pt(C$_3$H$_5$)(PMe$_2$Ph)$_2$]$^+$PF$_6^-$	158–160	34.71	34.76	4.14	3.74		
[Pt(C$_4$H$_7$)(PPh$_2$Me)$_2$]$^+$PF$_6^-$	87–90	45.29	45.42	4.18	3.92		
[Pt(C$_4$H$_7$)(PMe$_2$Ph)$_2$]$^+$PF$_6^-$	135–137	35.78	35.96	4.35	4.40		

[a] B = 2,4,6-trimethylpyridine, C = $\overline{\mathrm{COCH_2CH_2CH_2}}$.

passing the solution through a Florisil column, and recrystallizing by addition of *n*-pentane to give white, solid *trans*-[PtEt(PPh$_2$Me)$_2$(B)]$^+$PF$_6^-$ (B = 2,4,6-trimethylpyridine) (60%). Similarly, *trans*-[PtEt(PPh$_2$Me)$_2$(CO)]$^+$PF$_6^-$ was prepared by bubbling CO gas into a solution of *trans*-[PtEt(PPh$_2$Me)$_2$(C$_2$H$_4$)]$^+$PF$_6^-$ for 5 min (yield 60% after recrystallization twice). The infrared spectrum showed ν(C≡O) at 2088 cm^{-1}. *trans*-[PtEt(PPh$_2$Me)$_2$(C)]$^+$PF$_6^-$ (C = $\overline{\mathrm{COCH_2CH_2CH_2}}$) was obtained by treatment of *trans*-[PtEt(PPh$_2$Me)$_2$(C$_2$H$_4$)]$^+$PF$_6^-$ with an equimolar amount of 1-butyn-4-ol (yield 70%). The above complexes were also prepared in acetone solution with the time of ethylene treatment being 10 min. If a methylene chloride solution of *trans*-[PtH(PPh$_2$Me)$_2$(C$_2$H$_4$)]$^+$PF$_6^-$ was added to an equimolar amount of 2,4,6-trimethylpyridine in methylene chloride at −50°, the product obtained after evaporating the solvent was *trans*-[PtH(PPh$_2$Me)$_2$(B)]$^+$PF$_6^-$ [16] as identified by its infrared spectrum.

(b) **PR$_3$ = PEt$_3$.**—A methylene chloride solution of *trans*-[PtH(PEt$_3$)$_2$(C$_2$H$_4$)]$^+$PF$_6^-$ was obtained in a manner similar to that for the diphenylmethylphosphine analog at room temperature using *trans*-PtHCl(PEt$_3$)$_2$. Treatment of this solution with ethylene for 2 hr at room temperature caused no change in the proton nmr spectrum. Alternatively, the reaction of *trans*-[PtH(PEt$_3$)$_2$(acetone)]$^+$PF$_6^-$ with ethylene was done in boiling acetone solution for 40 min. To this solution was added an excess of a methanolic solution of LiCl, and the solvent was evaporated. The residual solid was extracted with benzene and *n*-pentane was added to give colorless crystals of *trans*-PtEtCl(PEt$_3$)$_2$ (58%), mp 49–51°; lit.[2] mp 53–55°; infrared vibrations ν(Pt–C) 530 cm^{-1} and δ(CH$_2$–Pt) 1200 cm^{-1}.

(c) **PR$_3$ = PMe$_2$Ph.**—Ethylene was bubbled into an acetone solution of *trans*-PtHCl(PMe$_2$Ph)$_2$ (0.213 g/5 ml). Silver tetrafluoroborate (0.08 g) in acetone was added dropwise at room temperature while ethylene was bubbled through the solution. Ethylene was passed for 5 min more, and AgCl was then filtered off. A methanol solution of LiCl (0.1 g/3 ml) was added, and the solvent was evaporated under vacuum. The residual mixture was extracted with benzene, and *n*-pentane was added to give white crystals of *trans*-PtEtCl(PMe$_2$Ph)$_2$ (0.16 g, 72%); ν(Pt–C) 540 cm^{-1} and δ(CH$_2$–Pt) 1210 cm^{-1}.

(d) **PR$_3$ = PPh$_3$.**—The reaction of *trans*-PtHCl(PPh$_3$)$_2$ with AgBF$_4$ was performed similarly in acetone. After filtering off AgCl, ethylene was bubbled through the filtrate for 1 hr at room temperature. Carbon monoxide was then passed through this solution for 5 min, and the solvent was evaporated. The infrared spectrum showed ν(C≡O) at 2080 cm^{-1}, but no bands due to *trans*-[PtH(PPh$_3$)$_2$(CO)]$^+$BF$_4^-$; δ(CH$_2$–Pt) 1185 cm^{-1}. The proton nmr spectrum in methylene chloride solution showed the presence of a platinum ethyl group; τ(CH$_3$) 10.2 (triplet) (J(Pt–H) = 38 Hz, J(H–H) = 7 Hz) and τ(CH$_2$) 9.0 (quartet). These data indicate that the product is *trans*-[PtEt(PPh$_3$)$_2$(CO)]$^+$BF$_4^-$.

Reaction of *trans*-PtHX(PR$_3$)$_2$ with Ethylene in the Presence of a Catalytic Amount of AgPF$_6$.—To an acetone solution (5 ml) of *trans*-PtHBr(PPh$_2$Me)$_2$ (0.15 g) was added 0.003 g of AgPF$_6$. Very small amounts of AgBr were filtered off, and ethylene was bubbled through this solution for 30 min at room temperature with stirring. After evaporating the solvent, the residual solid was recrystallized from benzene–*n*-pentane to give slightly pale yellow crystals of *trans*-PtEtBr(PPh$_2$Me)$_2$ (0.13 g, 84%); ν(Pt–C) 525 cm^{-1} and δ(CH$_2$–Pt) 1205 cm^{-1}. Similarly, *trans*-PtEtCl(PMe$_2$Ph)$_2$ was obtained from *trans*-PtHCl(PMe$_2$Ph)$_2$ and ethylene in the presence of a catalytic amount of AgPF$_6$ (yield 60%). No reaction was observed when AgPF$_6$ or AgBF$_4$ was absent in the above reactions nor when NaPF$_6$ was used in place of a silver salt.

Reaction of *trans*-PtHCl(PPh$_2$Me)$_2$ with Ethylene in the Presence of a Catalytic Amount of Tin(II) Chloride.—Ethylene was bubbled into an acetone solution (3 ml) of *trans*-PtHCl(PPh$_2$Me)$_2$ (0.075 g) and SnCl$_2$ (0.001 g) for 1 hr at room temperature. The solvent was evaporated under vacuum, and the residual mixture was extracted with benzene (10 ml). The benzene extract was evaporated to a volume of 3 ml, and *n*-pentane (15 ml) was added to give a yellow powder (0.03 g). The infrared spectrum of this product did not show bands attributable to ν(Pt–H), ν(Pt–C), nor δ(CH$_2$–Pt). Further colorless crystals (0.015 g) were obtained with slow crystallization from the mother liquor. The infrared spectrum of this product showed ν(Pt–C) at 532 cm^{-1} and δ(CH$_2$–Pt) at 1210 cm^{-1}, suggesting that the material is *trans*-PtEtCl(PPh$_2$Me)$_2$.

Reaction of *trans*-PtH(NO$_3$)(PPh$_2$Me)$_2$ with Ethylene.—The reaction was performed by treating *trans*-PtH(NO$_3$)(PPh$_2$Me)$_2$ with ethylene (bubbling) for 30 min at room temperature in either methylene chloride or acetone. Recrystallization from methylene chloride gave white crystals of *trans*-PtEt(NO$_3$)(PPh$_2$Me)$_2$ (75%); δ(CH$_2$–Pt) 1210 cm^{-1}.

Reaction of *trans*-[PtH(PPh$_2$Me)$_2$(acetone)]$^+$ with Propene or Butene-1.—*trans*-[PtH(PPh$_2$Me)$_2$(acetone)]$^+$(BF$_4^-$ or PF$_6^-$) in acetone solution was treated with propene or butene-1 for 1–3 hr at room temperature at atmospheric pressure. The procedure was then similar to that described for the preparation of *trans*-[PtEt(PPh$_2$Me)$_2$(B)]$^+$PF$_6^-$, to give *trans*-[Pt(*n*-Pr)(PPh$_2$Me)$_2$(C$_5$H$_5$N)]$^+$BF$_4^-$ (55%), *trans*-[Pt(*n*-Pr)(PPh$_2$Me)$_2$(C)]$^+$PF$_6^-$ (63%), and *trans*-[Pt(*n*-Bu)(PPh$_2$Me)$_2$(C$_5$H$_5$N)]$^+$BF$_4^-$ (70%).

Reaction of *trans*-[PtH(PR$_3$)$_2$(acetone)]$^+$ with Allene or Butadiene.—*trans*-[PtH(PPh$_2$Me)$_2$(acetone)]$^+$PF$_6^-$ in acetone was allowed to react with allene or butadiene at room temperature for 5 min. After evaporating off the solvent, the solid was recrystallized from methylene chloride–*n*-pentane to give [Pt(C$_3$H$_5$)(PPh$_2$Me)]$^+$PF$_6^-$ (75%) or [Pt(C$_4$H$_7$)(PPh$_2$Me)$_2$]$^+$PF$_6^-$ (85%). The proton nmr spectra in CD$_2$Cl$_2$ are as follows: for the former compound, τ(P–CH$_3$) 8.07 (doublet), J(P–H) = 9.5 Hz, J(Pt–H) = 37.5 Hz; τ(anti H) 7.10, J(H–H) = 13 Hz, J(P–H) = 8 Hz, J(Pt–H) = 43 Hz; τ(syn H) 6.14 (doublet), J(H–H) = 7 Hz; τ(2-H) 4.75 (multiplet); for the latter compound, τ(P–CH$_3$) 8.10 (doublet), J(P–H) = 9.5 Hz, J(Pt–H) = 37 Hz; τ(P–CH$_3$) 8.12 (doublet), J(P–H) = 10.0 Hz, J(Pt–H) = 39.5 Hz; τ(1-CH$_3$) 8.98 (broad) and 8.68 (multiplet); other resonances, τ 7.25 (quartet), 6.54 (broad multiplet), 6.25 (broad), 5.50 (broad), 4.95 (multiplet). [Pt(C$_3$H$_5$)(PPh$_3$)$_2$]$^+$PF$_6^-$ was similarly obtained (70%). [Pt(C$_3$H$_5$)(PMe$_2$Ph)$_2$]$^+$PF$_6^-$ and [Pt-

$(C_4H_7)(PMe_2Ph)_2]^+PF_6^-$ were prepared by adding an acetone solution of $AgPF_6$ to *trans*-$PtHBr(PMe_2Ph)_2$ in acetone while allene or butadiene was bubbled through the solution (yield 65 and 75%). The proton nmr spectra in CD_2Cl_2 are as follows: for the former compound, $\tau(P\text{-}CH_3)$ 8.21 (doublet), $J(P\text{-}H) = 10.0$ Hz, $J(Pt\text{-}H) = 36.5$ Hz; τ(anti H) 7.07 (doublet of doublets), $J(H\text{-}H) = 13$ Hz, $J(P\text{-}H) = 8$ Hz, $J(Pt\text{-}H) = 42$ Hz; τ(syn H) 5.70 (doublet), $J(H\text{-}H) = 7$ Hz; τ(2-H) 4.75 (multiplet); for the latter compound, $\tau(P\text{-}CH_3)$ 8.09 (doublet), $J(P\text{-}H) = 10.5$ Hz, $J(Pt\text{-}H) = 39.$ Hz; $\tau(P\text{-}CH_3)$ 8.32 (doublet), $J(P\text{-}H) = 9.5$ Hz, $J(Pt\text{-}H) = 35$ Hz; $\tau(1\text{-}CH_3)$ 8.73 (multiplet) and overlapped by the phosphine methyl; other resonances, τ 7.21 (quartet), 6.45 (multiplet), 5.95 (broad), 4.97 (multiplet).

Other Reactions.—Reactions of ethylene with *trans*-$[PtH(PPh_2Me)_2L]^+PF_6^-$ (L = 2,4,6-trimethylpyridine, *p*-$CH_3C_6H_4NC$, PPh_2Me)[16] were attempted under conditions similar to those used for the reaction of *trans*-$[PtH(PPh_2Me)_2(acetone)]^+$ (1 hr, room temperature). However, no reaction occurred in every case as shown by the unchanged infrared spectra of the reaction mixtures.

Reactions of *trans*-$[PtH(PPh_2Me)_2(acetone)]^+PF_6^-$ with *cis*-butene-2, vinyl fluoride, and methyl vinyl ether were attempted under conditions similar to those for (3) or (4) (1 hr). 2,4,6-Trimethylpyridine was added to the reaction mixture; however, the infrared spectra of the solid products obtained after evaporating the solvent were identical with that of *trans*-$[PtH(PPh_2Me)_2(B)]^+PF_6^-$[16] (B = 2,4,6-trimethylpyridine).

CONTRIBUTION FROM THE E. F. SMITH LABORATORY OF CHEMISTRY AND THE LABORATORY FOR RESEARCH ON THE STRUCTURE OF MATTER, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA 19104

Palladium(II) and Platinum(II) Alkyl Sulfoxide Complexes. Examples of Sulfur-Bonded, Mixed Sulfur- and Oxygen-Bonded, and Totally Oxygen-Bonded Complexes

BY JEROLD H. PRICE, ALEX N. WILLIAMSON, ROBERT F. SCHRAMM, AND BRADFORD B. WAYLAND*

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A series of Pd(II) and Pt(II) cationic complexes of the form $[PdL_4](BF_4)_2$ [L = dimethyl sulfoxide (DMSO), tetramethylene sulfoxide (TMSO), diethyl sulfoxide (DESO), di-*n*-propyl sulfoxide (NPSO), di-*n*-butyl sulfoxide (NBSO), and diisoamyl sulfoxide (IASO)] has been prepared and the general structural features of the complexes have been studied by ir spectrometry. Many new complexes, including $[Pt(DMSO)_4](ClO_4)_2$, which contain mixed S- and O-coordination sites, are reported. Proton nmr studies of $[Pt(DMSO)_4](ClO_4)_2$ demonstrate that two S-bonded and two O-bonded sulfoxides are retained in CH_3NO_2 solution. O-Bonded sulfoxides are found to exchange rapidly with free ligand, while the S-bonded sulfoxides are relatively kinetically stable. Steric effects are manifested in both the cationic and neutral chloride complexes of diisoamyl sulfoxide. The complex $[Pd(IASO)_4](BF_4)_2$ is the first example of a completely oxygen-bonded palladium(II) sulfoxide complex. Cationic Pd(II) and Pt(II) complexes of 2,5-dithiahexane 2,5-dioxide ($DTHO_2$) are prepared and polymeric structures with all sulfur and mixed sulfur and oxygen coordination are proposed.

Introduction

Sulfoxide ligands have two potential donor sites. The lighter or more highly charged metal ions favor oxygen coordination while a few heavier metals prefer the sulfur donor site.[1,2] We recently proposed $[Pd(DMSO)_2]X_2$ ($X^- = BF_4^-, ClO_4^-$) as the first example of a complex which contains both S- and O-bonded sulfoxide ligands. Two S-bonded and two O-bonded ligands in a cis array were inferred primarily from ir spectra.[3,4] These structural features have now been confirmed by a complete X-ray study.[5] Interest in determining the factors which govern the donor site and consequently the complex configuration prompted us to investigate a series of alkyl sulfoxide donors with Pd(II)[6] and to extend these studies to Pt(II). The ligands were selected to reveal the influence of steric effects on the donor site and examples of sulfur-bonded, mixed sulfur- and oxygen-bonded, and totally oxygen-bonded complexes are reported.

Results and Discussion

Neutral Complexes of Pd(II) and Pt(II) with Sulfoxide Donors.—A trans S-bonded structure for solid $[Pd(DMSO)_2Cl_2]$ has been proven by single-crystal X-ray studies[7] while a cis S-bonded structure for $[Pt(DMSO)_2Cl_2]$ is indicated by ir studies.[1] The proton nmr spectrum for the latter complex in CD_3NO_2 is shown in Figure 1a. A single methyl proton resonance at −1.00 ppm relative to free DMSO with ^{195}Pt satellites ($J_{^{195}Pt-^1H} = 23.1$ Hz) indicates the absence of detectable ligand dissociation and retention of the S-bonded structure in this solvent. Similar, although time-dependent, results were obtained for this complex by Kitching, *et al.*, when pyridine was used as the solvent.[8] If the cis configuration is maintained in solution, then the methyl group equivalence probably indicates rapid rotation about both the Pt–S and C–S bonds. Intermolecular exchange has been shown to be slow on the nmr time scale by addition of excess free ligand.

In the palladium complexes $[PdL_2Cl_2]$ (L = di-*n*-ethyl, di-*n*-propyl, di-*n*-butyl, diisoamyl, and tetra-

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