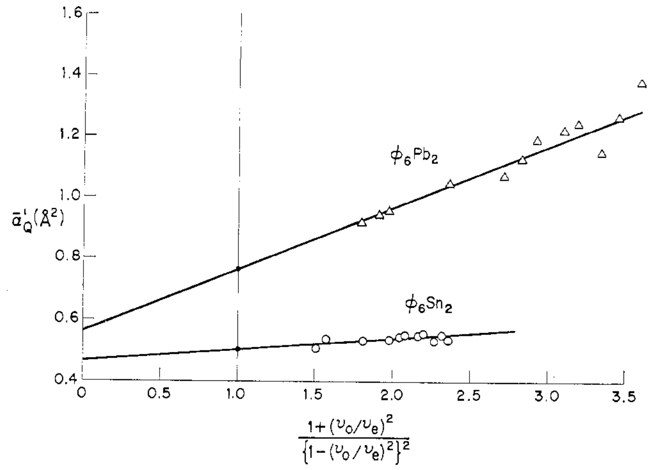

Figure 2.—Apparent molecular polarizability derivatives for the 112-cm$^{-1}$ line of $(C_6H_5)_6Pb_2$ and the 138-cm$^{-1}$ line of $(C_6H_5)_6Sn_2$ *vs.* $[1 + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2]^2$. $\nu_0$ is the laser exciting frequency; $\nu_e$ is the effective absorption frequency. $\nu_e((C_6H_5)_6Sn_2)$ = 40,468 cm$^{-1}$ (247 m$\mu$); $\nu_e((C_6H_5)_6Pb_2)$ = 34,014 cm$^{-1}$ (294m$\mu$).

uncertainties, but the metal–metal force constants found appear to be largely independent of the assumptions made. Comparison of these force constants with the corresponding quantities for hexamethylditin and -dilead indicates that the metal–metal bonding is very similar for both ligands. For the tin compounds this interpretation is borne out by the intensity analyses.

For $(C_6H_5)_6Sn_2$, the value of $n/2$(M–M) falls in the "normal range,[2b] 0.3–0.4, for single homonuclear metal–metal bonds. The value for $(C_6H_5)_6Pb_2$, however, is well above this range. This is the second exceptional case, along with $(CO)_{10}Mn_2$ ($n/2$ = 0.66),[2a] out of eight metal–metal bonds for which $n/2$ values have been determined.[2b] The only obvious characteristic that $(C_6H_5)_6Pb_2$ and $(CO)_{10}Mn_2$ have in common[23–25] is significant intensity enhancement through the resonance Raman effect. The possibility arises, therefore, that the extrapolation procedure (Figure 2) used to compensate for this effect does not in fact do so adequately. Further exploration of this question is needed.

## Experimental Section

Hexaphenylditin and -dilead were purchased from Alfa Inorganics, Inc., and used without purification. Tetrakis(triphenyltin)tin, $[(C_6H_5)_3Sn]_4Sn$, was prepared by the method given by Willemsens and Van der Kerk.[26] The crude product was purified by extracting hexaphenylditin, the major impurity, with small, rapid washings of chloroform. The extraction procedure was monitored *via* uv spectra (Beckman DB-G) using the spectral information given in the literature.[18] The product was then recrystallized from toluene, yielding large opaque crystals.

The Raman instrument used has been described.[2a] Preliminary spectra were excited with the 6328-Å line of a Spectra Physics Model 125 He–Ne laser. The studies of Raman intensity as a function of exciting frequency were performed with a Coherent Radiation Model 52 Ar–Kr ion laser producing lines of usable power throughout the region from 6764 to 4765 Å.

Spectra were obtained from the microcrystalline solids and from saturated solutions in $CHCl_3$ or $CS_2$. Absolute Raman intensities were measured as described in the earlier report.[2a]

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(23) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, Chapter 3.

(24) A referee has pointed out that if Allred's[25] modification of Pauling's[23] electronegativity value for lead is used ($X$ = 2.33 instead of 1.8), then $(n/2)$(Pb–Pb) is reduced to 0.68, a value even closer to $(n/2)$(Mn–Mn).

(25) A. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).

(26) L. C. Willemsens and G. J. Van der Kerk, *J. Organometal. Chem.*, **2**, 260 (1964).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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# Insertion Reactions into the Methyl–Platinum Bond. II.[1] Intermediate $\pi$ Complexes

BY H. C. CLARK* AND R. J. PUDDEPHATT

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$\pi$ complexes of tetrafluoroethylene and hexafluorobut-2-yne with *trans*-$PtXCH_3L_2$ (X = halogen, L = tertiary phosphine, arsine, or stibine) have been prepared, and their structures and stabilities investigated. In some cases, the complexes may rearrange to give the products of insertion of the olefin or acetylene into the methyl–platinum bond. Reactions of tetrafluoroethylene and hexafluorobut-2-yne with *cis*-$Pt(CH_3)_2L_2$ and *trans*-$PtHClL_2$ are also described.

## Introduction

The current interest in the use of transition metal complexes for the homogeneous catalysis of polymerization or hydrogenation of unsaturated compounds has led to several attempts to isolate the types of intermediates involved in these processes.[2–7] Thus, Bailar[2] isolated a hydridoplatinum(II) cyclooctadiene complex which was believed to be an intermediate in the catalytic hydrogenation of the diene, and, more recently, Baddley reported[3] that similar

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* To whom correspondence should be addressed.

(1) Part I: H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, **9**, 2670 (1970).

(2) H. A. Tayim and J. C. Bailar, *J. Amer. Chem. Soc.*, **89**, 4330 (1967).

(3) W. H. Baddley and M. S. Frazer, *ibid.*, **91**, 3661 (1969).

(4) P. Uguagliatti and W. H. Baddley, *ibid.*, **90**, 5446 (1968); G. W. Parshall and F. N. Jones, *ibid.*, **87**, 5356 (1965).

(5) D. R. Coulson, *ibid.*, **91**, 200 (1969).

(6) H. C. Clark and W. S. Tsang, *ibid.*, **89**, 529 (1967).

(7) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *ibid.*, **90**, 2259 (1968).

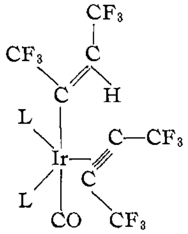
TABLE I

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF COMPLEXES $PtXCH_3L_2 \cdot C_4F_6$

| Compound | | Analysis, % C | | H | | F | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| X | L | Calcd | Found | Calcd | Found | Calcd | Found | Dec pt,[a] °C | Mp, °C | Yield, % |
| Cl | $P(CH_3)_3$ | 23.6 | 23.4 | 3.8 | 4.0 | 20.4 | 15.0 | [b] | 171–173 | 39 |
| Cl | $As(CH_3)_3$ | 20.4 | 20.9 | 3.3 | 3.4 | 17.6 | 16.5 | 85–115 | 148–153 | 53 |
| Br | $As(CH_3)_3$ | 19.1 | 19.2 | 3.1 | 3.4 | 16.5 | 16.3 | 100–110 | 149–155 | 56 |
| Cl | $As(CH_3)_2C_6H_5$ | 32.7 | 32.3 | 3.3 | 4.0 | 14.8 | 14.5 | 70–80 | 110–115 | 43 |
| Cl | $Sb(CH_3)_3$ | 17.8 | 18.7 | 2.8 | 2.6 | 15.4 | 14.9 | 80–90 | 110 | 17 |

[a] Products of decomposition were *trans*-$PtXCH_3L_2$ and $C_4F_6$. [b] Compound decomposed during several days at room temperature. We are unable to obtain a satisfactory fluorine analysis.

intermediates were formed in the reactions of $IrHCO[P(C_6H_5)_3]_3$ with unsaturated compounds. In particular, hexafluorobut-2-yne ($C_4F_6$) gave complex I, $L = P(C_6H_5)_3$, which is the type of intermediate believed to be involved in the transition metal catalyzed polymerization of acetylenes.



I

In neither case, however, was the reaction of the intermediate to give the product of insertion of the olefin or acetylene into the metal–hydrogen or metal–carbon bond followed.

We recently described[1] some insertion reactions of tetrafluoroethylene ($C_2F_4$) and hexafluorobut-2-yne ($C_4F_6$) into the methyl–platinum bond of compounds of the types *trans*-$PtXCH_3L_2$ and *cis*-$Pt(CH_3)_2L_2$ (X = halogen, L = tertiary phosphine or arsine). It was deduced that the reactivity of the methylplatinum compounds toward insertion was dependent on the stability of the intermediate platinum–olefin or –acetylene $\pi$ complex, which, in turn, was determined by the nature of the ligand L. In this paper, the isolation[8] of the intermediate complexes, $PtXCH_3L_2 \cdot C_2F_4$ and $PtXCH_3L_2 \cdot C_4F_6$, is fully described and a study of their structures and stabilities is reported.

## Results

**Isolation and Stability of the Complexes $PtXCH_3L_2 \cdot C_2F_4$ and $PtXCH_3L_2 \cdot C_4F_6$.**—At room temperature, *trans*-$PtXCH_3L_2$ (X = halogen, L = tertiary phosphine, arsine, or stibine) reacted with $C_2F_4$ or $C_4F_6$ to give the 1:1 complex $PtXCH_3L_2 \cdot C_2F_4$ or $PtXCH_3L_2 \cdot C_4F_6$ (III), respectively. Thus, the complex $PtClCH_3[As(CH_3)_3]_2 \cdot C_2F_4$ (II) could be crystallized from a concentrated solution of *trans*-$PtClCH_3[As(CH_3)_3]_2$ in benzene containing excess tetrafluoroethylene. Attempts to prepare the corresponding trimethylphosphine or dimethylphenylarsine complexes were unsuccessful. A wider range of hexafluorobut-2-yne complexes, III, was prepared (Table I). Thus, complexes III with X = Cl, L = $P(CH_3)_3$, $As(CH_3)_3$, $Sb(CH_3)_3$, or $As(CH_3)_2C_6H_5$ and X = Br, L = $As(CH_3)_3$ could be isolated. The complexes III when X = Cl, L = $P(C_2H_5)_3$ or $P(CH_3)_2C_6H_5$ were not formed in sufficient concentration, and when X = I, L = $P(CH_3)_3$, $As(CH_3)_3$, or $As(CH_3)_2C_6H_5$, the products were too soluble for isolation. Chlorotrifluoroethylene and hexafluoropropene failed to give isolable complexes with *trans*-$PtClCH_3[As(CH_3)_3]_2$.

The solid complex II was stable in air at room temperature but decomposed to $C_2F_4$ and the Pt(II) complex on heating to 90° or on dissolution in benzene. The thermal stability of the hexafluorobut-2-yne complexes varied with the nature of the ligand. Thus, while the complex III, X = Cl and L = $As(CH_3)_3$, was indefinitely stable at room temperature, the corresponding complex with X = Cl and L = $P(CH_3)_3$ decomposed appreciably during 1 week giving *trans*-$PtClCH_3[P(CH_3)_3]_2$ and, presumably, hexafluorobut-2-yne.

The temperatures at which the complexes III decompose to $C_4F_6$ and *trans*-$PtClCH_3L_2$ are given in Table I. The decomposition temperatures are generally higher for those complexes which possessed greater stability at room temperature. In all cases, hexafluorobut-2-yne was evolved below the melting point, the complex then melting a few degrees lower than pure *trans*-$PtXCH_3L_2$.

A more detailed study of the stability of the hexafluorobut-2-yne complexes (III) was made by nmr spectroscopy. Thus, when *trans*-$PtClCH_3L_2$ in a variety of solvents was treated with hexafluorobut-2-yne in a sealed nmr tube, the $^1H$ and $^{19}F$ nmr spectra (Table II) generally indicated an equilibrium between complex III and the starting materials. In favorable cases, integration of both $^1H$ and $^{19}F$ nmr spectra allowed the determination of the concentrations of all species present and hence of the equilibrium constant for complex formation (Table II). The order of stability of III is then given by the series L = $As(CH_3)_3 \sim As(CH_3)_2C_6H_5 \gg Sb(CH_3)_3 > P(CH_3)_3 > P(C_2H_5)_3 \sim P(CH_3)_2C_6H_5$. Thus, when *trans*-$PtClCH_3L_2$ was treated with excess $C_4F_6$, the arsine complexes gave III almost quantitatively, while the stibine and phosphine complexes gave little or no III, most remaining as unchanged starting materials. The equilibrium constant for formation of III, X = Cl, L = $As(CH_3)_3$, was 2 $M^{-1}$ in chloroform and 21 $M^{-1}$ in dichloromethane, while for III, X = I, L = $As(CH_3)_3$, the corresponding value in chloroform was 3 $M^{-1}$.

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(8) H. C. Clark and R. J. Puddephatt, *Chem. Commun.*, 92 (1970).

TABLE II

NMR SPECTRA OF SYSTEM *trans*-$PtXCH_3L_2 + C_4F_6$[a]

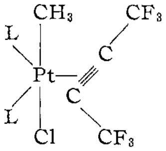
| Compound | | | *trans*-$PtXCH_3L_2$ | | | | | | $C_4F_6$ | $PtXCH_3L_2 \cdot C_4F_6$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| X | L | Solvent | $\delta(CH_3Pt)$ | $^2J(PtH)$ | $^3J(PH)$ | $\delta(CH_3Y)^b$ | $^3J(PtH)$ | $^2J(PH)^c$ | $\delta(F)$ | $\delta(CH_3Pt)$ | $^2J(PtH)$ | $\delta(CH_3Y)^b$ | $^3J(PtH)$ | $\delta(F)$ | $^3J(PtF)$ |
| Cl | $P(CH_3)_3$ | $CHCl_3$ | −0.42 | 81.4 | 6.9 | −1.49 | 27.9 | 7.3 | 53.8 | *d* | | *d* | | 54.1[e] | 34 |
| Cl | $P(CH_3)_3$ | $C_6H_6$ | −0.82 | | 7.0 | −1.36 | 27.9 | 6.7 | 53.7 | *d* | | *d* | | 54.1[e] | 33.9 |
| Cl | $As(CH_3)_3$ | $CHCl_3$ | −0.43 | 81.7 | ... | −1.43 | 21.3 | ... | 53.6 | −0.46 | 68.5 | −1.56 | 14.8 | 55.7 | 40.1 |
| Cl | $As(CH_3)_3$ | $CH_2Cl_2$ | −0.38 | 81 | ... | −1.37 | 21.3 | ... | 53.4 | −0.41 | 67.2 | −1.49 | 15.4 | 55.3 | 40.0 |
| Cl | $As(CH_3)_3$ | $(CD_3)_2CO$ | | | | | | | 53.7 | −0.43 | 67.3 | −1.54 | 14.2 | 55.1 | 39.9 |
| I | $As(CH_3)_3$ | $CHCl_3$ | −0.70 | 77 | ... | −1.62 | 20.0 | ... | 53.7 | −0.85 | 65.8 | −1.74 | 14.8 | 55.6 | 39.5 |
| Cl | $Sb(CH_3)_3$ | $CHCl_3$ | −1.29 | 67.0 | ... | −1.15 | | ... | 53.8 | *d* | | *d* | | 53.8[f] | 28.0 |
| Cl | $As(CH_3)_2C_6H_5$ | $CHCl_3$ | | | | | | | 53.9 | −0.45 | 68.0 | −1.78,<br>−1.83 | 14.0 | 55.3 | 41.0 |
| Cl | $As(CH_3)_2C_6H_5$ | $(CD_3)_2CO$ | | | | | | | 53.7 | −0.50 | 67.2 | −1.87,<br>−1.92 | 13 | 55.4 | 40.6 |
| I | $As(CH_3)_2C_6H_5$ | $CHCl_3$ | −0.52 | 78 | ... | −1.95 | ... | ... | 53.8 | | | | | 55.5 | 40.5 |
| Cl | $P(CH_3)_2C_6H_5$ | $CHCl_3$ | −0.24 | 81 | 7.0 | −1.86 | 29.5 | 7.0 | 53.7 | *d* | | *d* | | | |
| I | $P(CH_3)_2C_6H_5$ | $CHCl_3$ | −0.35 | 79.0 | 7.1 | −2.05 | 29.4 | 6.6 | 53.8 | *d* | | *d* | | | |

[a] As solutions in sealed nmr tubes containing excess $C_4F_6$. [b] Y = P, As, or Sb. [c] $J(PH) = {}^2J(PH) + {}^4J(P'H)$. [d] Concentration too low to allow measurement. [e] Separation of chief doublet (Figure 1) = $^4J(PF) + {}^4J(P'F)$ = 15.5 Hz. [f] Central peak obscured; deduced from satellite positions.

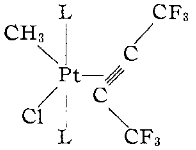
Some confirmation of the above stability series was obtained by infrared spectroscopy. Thus, when a benzene solution of *trans*-$PtICH_3L_2$ was treated with $C_4F_6$, the infrared spectrum of the solution showed bands at 1868 (s) and 1815 cm$^{-1}$ (m) due to the C≡C stretching mode in III when L = $As(CH_3)_2C_6H_5$ but no such bands when L = $P(CH_3)_2C_6H_5$.

## Structure of the Complexes

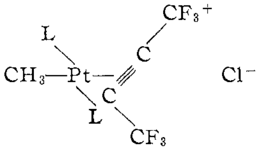
The structure of the complexes III of hexafluorobut-2-yne may be deduced from spectroscopic evidence. The most likely structures, on the basis of known structures,[4,9,10] are



IIIa



IV



V

Structure IIIa is favored on the following grounds. (1) The nmr spectra of dimethylphenylarsine complexes in which the ligands are identically situated normally contain a single peak for the methylarsine protons. However, if there is a lack of symmetry in the molecule, the methylarsine groups become nonequivalent and two such peaks may be observed. The $^1H$ nmr spectrum of the complex with L = $As(CH_3)_2C_6H_5$ showed *two* peaks due to methylarsine protons, proving that there is no plane of symmetry containing the $PtAs_2$ unit[1] and so eliminating structure V. The complex with L = $As(CH_3)_3$ showed a single peak for the methylarsine protons. (2) The $^{19}F$ nmr spectra of all complexes showed a single peak due to coordinated $C_4F_6$. Complex IV would show two such peaks due to nonequivalent $CF_3$ groups, unless the $C_4F_6$ was rotating rapidly. (3) Finally, the $^{19}F$ nmr spectrum of the trimethylphosphine complex (Figure 1) shows the typical[11] X pattern of an $AA'X_3X'_3$ spin system, due to $^{31}P-^{19}F$ coupling, with partially resolved satellites due to coupling with $^{195}Pt$ ($I = {}^1/_2$, natural

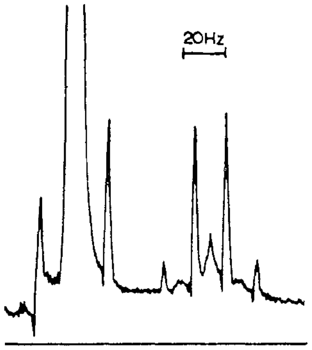


Figure 1.—The $^{19}F$ nmr spectrum of $PtClCH_3[P(CH_3)_3]_2 \cdot C_4F_6$ in a solution containing excess $C_4F_6$.

TABLE III

INFRARED SPECTRA (2500–1500, 1300–750 CM$^{-1}$) OF COMPLEXES $PtXCH_3[Y(CH_3)_3]_2 \cdot C_4F_6$ (I) AND *trans*-$PtCl[C(CF_3)=C(CF_3)CH_3][As(CH_3)_3]_2$ (II)

| | I | | | | |
|---|---|---|---|---|---|
| Assignment | X = Cl, Y = P | X = Cl, Y = As | X = Br, Y = As | X = Cl, Y = Sb | II |
| ν(C≡C) | 1840 vs | 1855 vs | 1855 s | 1865 s | 1610 m |
| | 1815 m | 1822 m | 1825 m | | |
| $\delta_s(CH_3Y)$ | 1314 w | 1287 m | 1287 m | | |
| | 1294 m | | | | |
| $\delta_s(CH_3Pt)$ | 1252 s | 1250 ms | 1249 ms | 1254 sh | |
| $\nu(CF_3)$ | 1265 s | 1267 vs | 1268 s | 1265 s | 1289 s |
| | 1225 vs | 1227 vs | 1227 s | 1224 s | 1242 s |
| | | | | | 1156 vs |
| | 1115 vs | 1120 vs | 1119 vs | 1122 s | 1123 vs |
| $\rho(CH_3)Y$ | 957 vs | 912 vs | 912 s | 839 ms | 904 vs |
| | | 904 sh | | | |
| | 865 m | 838 m | 838 m | 772 w | 839 mw |
| ν(C—C) | 803 m | 800 s | 801 m | 795 w | 802 w |
| Other bands | 1205 sh | 1205 sh | 1203 sh | | |
| | 1186 m | 1154 ms | 1153 sh | 1153 m | |
| | 1146 sh | 1136 sh | | 1135 sh | 1015 ms |
| | 908 w | 970 w | | 903 w | |

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(9) K. W. Muir and J. A. Ibers, *J. Organometal. Chem.*, **18**, 175 (1969), and references therein.

(10) T. Theophanides and P. C. Kong, *Can. J. Chem.*, **48**, 1084 (1970), and references therein.

(11) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

TABLE IV

INFRARED (750–140 CM$^{-1}$) AND RAMAN (700–70 CM$^{-1}$) SPECTRA OF $PtXCH_3[Y(CH_3)_3]_2 \cdot C_4F_6$ (I) AND *trans*-$PtCl[C(CF_3){=}C(CF_3)CH_3][As(CH_3)_3]_2$ (II)

| | I | | | | | | II | |
|---|---|---|---|---|---|---|---|---|
| | X = Cl, Y = P | | X = Cl, Y = As | | X = Br, Y = As | | | |
| Assignment | Ir | R | Ir | R | Ir | R | Ir | R |
| $\nu(YC_3)$ | 749 ms | | 624 s | 624 m | 623 s | 619 s | 624 ms | 621 s |
| | | 690 ms | | | | | | |
| | 676 ms | 678 ms | 600 m | 601 s | 601 m | 586 vs | 599 m | 593 vs |
| $\nu(PtCH_3)$ | 539 w? | 552 vs | 539 w? | 552 ms | 540 w | 542 s | | |
| $\nu(PtY)$ | 369 w | 370 w, br | 273 m | | 270 m | | 273 m | |
| | 354 mw | 323 m | | | | | 266 m | 265 m |
| $\nu(PtX)$ | 237 s | 248 sh | 243 s | 246 sh | 162 s | 158 s | 302 vs | 301 m |
| $\delta(YC_3)$ | | 282 m | | 224 ms | | 221 s | 218 w | 219 ms |
| Other bands | | | 730 m, br | 729 mw | 731 m | | 727 ms | |
| | | | 679 s | 674 w | 679 s | | 660 m | |
| | | | 650 w | | 651 w | | 539 w | |
| | 503 w | 504 w | 501 w | | 502 w | | 459 mw | 453 w |
| | | | | | | | 239 w | |
| | | 255 vs | 255 sh | 256 s | 241 ms | 250 s | | |
| | 215 ms | 219 s | | | | | | |
| | | 207 ms | | | | | | |
| | | 182 sh | 182 ms | 185 ms | 183 m | 185 s | 187 w | |
| | | 160 w | | 161 ms | | 145 sh | | |
| | | 128 s | | 112 m | | 104 m | | |
| | | 114 m | | 90 ms | | 94 sh | | |
| | | 109 sh | | | | | | |

abundance 34%). Unfortunately the complex was present only as a very low equilibrium concentration and the spectrum obtained did not permit a detailed analysis. However, both structure IV and structure IIIa with a rapidly rotating $C_4F_6$ group should show $A_2X_6$-type spectra. Hence the complexes have structure IIIa in which the acetylene is probably rigidly bonded and approximately coplanar with the $PtL_2$ unit. Such a structure may be regarded as a trigonal bipyramid, although it may also be described as a distorted square pyramid with the two ligands L bent below the basal plane.

The infrared and Raman spectra of the hexafluorobut-2-yne complexes are given in Tables III and IV. Assignments have been made on the basis of previous work on trimethylphosphine, -arsine, and -stibine complexes of platinum[12–14] and on methylplatinum compounds.[15–17] The spectra show the presence of both methyl–platinum and platinum–halogen bonds and thus are consistent with structure IIIa. The platinum–halogen stretching frequencies are rather low, as expected for IIIa in which the halogen is trans to the methyl group, which has a high trans influence.[16,17] The values for III with L = $As(CH_3)_3$ are 243 and 169 cm$^{-1}$ for X = Cl and Br, respectively; the former may be compared with a Pt–Cl stretching frequency of 302 cm$^{-1}$ in the insertion product *trans*-$PtCl[C(CF_3){=}C(CF_3)CH_3][As(CH_3)_3]_2$. Complexes III gave strong Raman absorption bands at *ca.* 259 cm$^{-1}$, which may have some platinum–acetylene stretching character. This assignment is very tentative since a bending mode of hexafluorobut-2-yne is also expected in this region.[18]

The spectra of the tetrafluoroethylene complex II and of the insertion product[1] *trans*-$PtCl(CF_2CF_2CH_3)[As(CH_3)_3]_2$ are given in Table V. Structure II for the tetrafluoroethylene complex follows from the similarity of its spectra to those of III in the skeletal stretching region. The Pt–Cl stretching frequency for *trans*-$PtCl(CF_2CF_2CH_3)[As(CH_3)_3]_2$ (291 cm$^{-1}$) is higher than for *trans*-$PtClCH_3[As(CH_3)_3]_2$ (277 cm$^{-1}$). Thus, as expected from its higher electronegativity,[19,20] the fluoroalkyl group has a lower trans influence than the methyl group. The Pt—$C_2F_4$ and C=C stretching frequencies could not be assigned with confidence. The difference in the carbon–carbon stretching frequency between tetrafluoroethylene (1872 cm$^{-1}$)[21] and hexafluoroethane (349 cm$^{-1}$)[22] is much greater than between ethylene (1623 cm$^{-1}$)[21] and ethane (993 cm$^{-1}$).[23] Since the bond order decreases on coordination of the olefin, a much larger decrease for the C=C stretching frequency is expected for tetrafluoroethylene complexes than for ethylene complexes. The only unassigned band in the Raman spectrum of II above 599 cm$^{-1}$ is a strong band at 771 cm$^{-1}$. While a C—F deformation mode is expected in this region,[21] the band could also have some C=C stretching character.

## Bonding in the Complexes

There is much current interest in the nature of

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[12] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc. A*, 545 (1970).

[13] P. J. D. Park and P. J. Hendra, *Spectrochim. Acta, Part A*, **25**, 227 (1969).

[14] J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc. A*, 2972 (1969).

[15] D. M. Adams, J. Chatt, and B. L. Shaw, *ibid.*, 2047 (1960).

[16] J. D. Ruddick and B. L. Shaw, *ibid.*, *A*, 2801 (1969).

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TABLE V

INFRARED (2000–140 CM$^{-1}$) AND RAMAN (1700–70 CM$^{-1}$) SPECTRA OF $PtClCH_3[As(CH_3)_3]_2 \cdot C_2F_4$ (I) AND $PtCl(CF_2CF_2CH_3)[As(CH_3)_3]_2$ (II)

| | | I | | II |
|---|---|---|---|---|
| Assignment | Ir | R | Ir | R |
| $\delta_a(CH_3As)$ | 1415 s | 1416 mw | | 1418 m |
| $\delta_s(CH_3As)$ | 1267 sh | 1263 mw | 1264 m | |
| | 1258 s | 1253 w | | 1257 w |
| $\nu(CF)$ | 1132 vs | 1135 w | 1159 ms | 1148 w |
| | 1070 vs | 1066 mw | 1042 sh | |
| | | | 1026 s | |
| | | | 1011 ms | |
| | | | 975 ms | |
| | | | 943 sh | |
| | | | 923 sh | 921 w, br |
| $\rho(CH_3As)$ | 915 vs | | 911 vs | |
| | 906 s, sh | | 862 m | |
| | 838 m | | 843 w | |
| $\nu(AsC_3)$ | 626 ms | 628 ms | 623 s | 619 ms |
| | 604 m | 598 s | 599 m | 598 s |
| $\nu(PtCH_3)$ | 563 w | 557 ms | | |
| $\nu(PtAs_2)$ | 276 sh | 277 m | 274 sh | 270 sh |
| | 270 sh | | | 260 m |
| $\nu(PtCl)$ | 262 vs | 261 m | 291 s | 291 m |
| $\delta(YC_3)$ | 222 s | 222 ms | | 219 mw |
| Other bands | 1380 m | | | 1385 w |
| | 1288 w | 1286 mw | | 1330 w |
| | | | | 1280 m |
| | 1144 sh | | 1204 m | 1206 w |
| | 816 m | | 884 w | |
| | 793 vs | | | |
| | 778 sh | 771 s | | |
| | 736 m | . . . | 729 m | |
| | 615 m | | 658 w | |
| | | | 590 ms | |
| | | | 529 m | |
| | | 359 m | | |
| | | 316 m | | 325 w |
| | | | 239 w | 235 mw |
| | 188 w | 178 s | 182 w | 177 s |
| | 164 w | 158 m | | |
| | | 124 ms | | 126 m |
| | | 102 m | | |
| | | 85 ms | | |

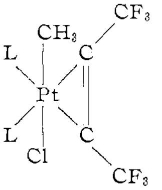
TABLE VI

INFRARED AND NMR SPECTROSCOPIC DATA FOR SOME HEXAFLUOROBUT-2-YNE COMPLEXES

| Compound | $\nu$ ($C\equiv C$),[a] cm$^{-1}$ | $\Delta\nu$ ($C\equiv C$), cm$^{-1}$ | $^3J$ (Pt—F), Hz | $J$(P—F), Hz | Ref |
|---|---|---|---|---|---|
| $CF_3C\equiv CCF_3$ | 2300 | . . . | . . . | . . . | 18 |
| $RhCl[P(C_6H_5)_3]_2 \cdot C_4F_6$ | 1917 | 383 | . . . | <1 | 26 |
| $Pt[P(C_6H_5)_3]_2 \cdot C_4F_6$ | 1775 | 525 | 65.1 | 10.3[b] | 27 |
| $Pt[As(C_6H_5)_3]_2 \cdot C_4F_6$ | 1775 | 525 | 80 | . . . | 27 |
| $PtClCH_3[P(CH_3)_3]_2 \cdot C_4F_6$ | 1827 | 473 | 34 | 15.5 | [c] |
| $PtClCH_3[As(CH_3)_3]_2 \cdot C_4F_6$ | 1838 | 462 | 40 | . . . | [c] |
| $PtClCH_3[Sb(CH_3)_3]_2 \cdot C_4F_6$ | 1865 | 435 | 28? | . . . | [c] |

[a] Mean value given when two bands are present. [b] Doublet due to coupling only with trans P. [c] This work.

metal–acetylene bonding.[24–27] The hexafluorobut-2-yne complexes may be considered as five-coordinate platinum(II) complexes IIIa or as six-coordinate platinum(IV) complexes IIIb or, more realistically,[24] as the intermediate IIIc between these limiting cases.


IIIb

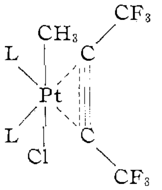

IIIc

Table VI contains values for the mean $C\equiv C$ stretching frequencies and coupling constants $^3J$(PtF) for some hexafluorobut-2-yne complexes. The type of bonding in such complexes has often been assigned[24–27] by consideration of the reduction [$\Delta\nu(C\equiv C)$] of the $C\equiv C$ stretching frequency of the acetylene on coordination, this being least for type IIIa [$\Delta\nu(C\equiv C)$ = 200–400 cm$^{-1}$] and greatest for type IIIb [$\Delta\nu(C\equiv C) >$ 500 cm$^{-1}$] complexes. On this basis the complexes are best assigned the intermediate structure IIIc. This structure accounts for the fact that the $C_4F_6$ is rigidly bound without invoking a platinum(IV) species IIIb. Curiously, $\Delta\nu(C\equiv C)$ is greatest for the phosphine complex indicating the strongest platinum–acetylene bonding in this case, while all other evidence shows that this bonding is strongest for the arsine complex. Thus small differences in $\Delta\nu(C\equiv C)$ are probably not a good criterion for deciding relative bond types.[28] The greater coupling constant $^3J$(Pt—F) (40 Hz) for the arsine complex over that for the phosphine complex (34 Hz) is probably a better criterion. A similar trend was observed[27] for the complexes $PtL_2 \cdot C_4F_6$ [L = $As(C_6H_5)_3$ and $P(C_6H_5)_3$]. The relatively high values of the coupling constants $^4J$(PF) in both $Pt[P(C_6H_5)_3]_2 \cdot C_4F_6$ and $PtClCH_3[P(CH_3)_3]_2 \cdot C_4F_6$ may indicate delocalization of electrons over the planar diphosphine–platinum–acetylene unit in each case.[29] In the compounds $RhCl[P(C_6H_5)_3]_2 \cdot C_4F_6$ and VI, L = $P(CH_3)_2$-$C_6H_5$, which do not have this planar moiety the coupling $^4J$(PF) is too low to be observed. High values of $^4J$(PF) are observed in some trifluoropropynylplatinum complexes with phosphine ligands, in which delocalization of $\pi$ electrons may also be important.[30]

The coupling constants $^2J$(Pt–C–H) and $^3J$(Pt–As–C–H), due to coupling of $^{195}Pt$ with the methylplatinum and methylarsine protons, respectively, in III, L = $As(CH_3)_3$ or $As(CH_3)_2C_6H_5$, are close to the values expected for platinum(IV) complexes[16,17,31] and are considerably lower than those observed for square-planar platinum(II) complexes.[16,17,32,33] However, the lower coupling constants could be due to the change in stereochemistry and hybridization at platinum, so that this cannot be considered as evidence for structure IIIb for these complexes.

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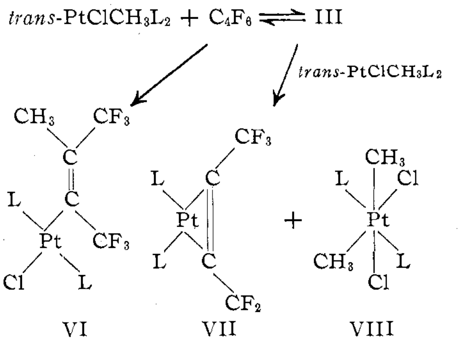
## Further Reactions of the Complexes

Equation 1 below shows the products formed when *trans*-PtClCH$_3$L$_2$ in chloroform was treated with excess C$_4$F$_6$ in a sealed nmr tube and the solution was allowed to stand for several weeks.



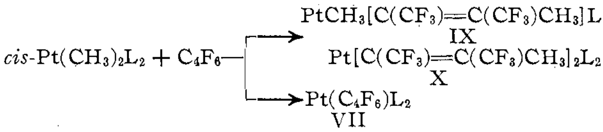
(1)

When L = As(CH$_3$)$_2$C$_6$H$_5$, the peaks in the nmr spectra due to the initial equilibrium mixture were slowly replaced by peaks due to the product of insertion of hexafluorobut-2-yne into the methyl–platinum bond (VI). After 3 weeks at room temperature the reaction was complete and the product, which had previously been prepared from the same reaction at high temperature,[1] was isolated. It is perhaps surprising that insertion into the stable methyl–platinum bond occurs under such mild conditions. It has been suggested that the kinetic stability of transition metal alkyls is greatest when the energy between the highest filled and the lowest unfilled metal orbital is greatest[34] and also that this separation for d$^8$ complexes is higher for square-planar than for trigonal-bipyramidal complexes.[10] Thus the methyl–platinum bond should be more readily cleaved in the acetylene complex than in the square-planar compound. A similar effect is believed to supply the driving force for polymerization of olefins by organotitanium compounds.[35] It should also be noted that the platinum–methyl stretching frequency is somewhat lower in III, X = Cl, L = As(CH$_3$)$_3$ (552 cm$^{-1}$), than in *trans*-PtClCH$_3$[As(CH$_3$)$_3$]$_2$ (564 cm$^{-1}$).[30]

When L = P(CH$_3$)$_2$C$_6$H$_5$, however, the reaction was complete in 2 weeks at room temperature and gave equimolar proportions of complexes VII and VIII. The same products were formed in the presence of excess methyl chloride. In independent experiments, methyl chloride was found to react only very slowly with *trans*-PtClCH$_3$L$_2$ to give VIII, L = P(CH$_3$)$_2$C$_6$H$_5$, and did not react at all with VII, L = P(CH$_3$)$_2$C$_6$H$_5$. Thus the mechanism of this novel disproportionation reaction may proceed by nucleophilic attack of *trans*-PtClCH$_3$L$_2$ at the platinum-bonded methyl group in complex III, which is present in very low equilibrium concentration. This is the type of mechanism which may operate in many oxidative addition reactions.[36] Curiously, the same reaction at higher temperature gave the insertion product VI, L = P(CH$_3$)$_2$C$_6$H$_5$.[1]

**Reactions with *cis*-Pt(CH$_3$)$_2$L$_2$.**—The reactions of C$_2$F$_4$ with *cis*-Pt(CH$_3$)$_2$L$_2$ at higher temperatures have been described[1] and lead to the products of insertion of C$_2$F$_4$ into one or both of the methyl–platinum bonds. At room temperature, however, as determined by nmr spectroscopy, there was generally no detectable interaction. The only exception was with *cis*-Pt(CH$_3$)$_2$[As(CH$_3$)$_3$]$_2$; the $^{19}$F nmr spectrum of a solution containing excess C$_2$F$_4$ showed a peak at 127.4 ppm, with satellites due to coupling with $^{195}$Pt, $^2J$(PtF) = 212 Hz, which may be due to a complex Pt(CH$_3$)$_2$[As(CH$_3$)$_3$]$_2\cdot$C$_2$F$_4$. In the complex Pt(C$_2$F$_4$)[P(C$_6$H$_5$)$_3$]$_2$ the coupling constant $^2J$(PtF) is 288 Hz.[37] Unfortunately, we were unable to characterize this product further.

In contrast to the above behavior, C$_4$F$_6$ reacted very rapidly with *cis*-Pt(CH$_3$)$_2$L$_2$ giving the products shown in eq 2, so that no intermediate complexes could be observed.



$$cis\text{-Pt(CH}_3)_2\text{L}_2 + \text{C}_4\text{F}_6 \longrightarrow \begin{cases} \underset{\text{IX}}{\text{PtCH}_3[\text{C(CF}_3)\text{=C(CF}_3)\text{CH}_3]\text{L}_2} + \underset{\text{X}}{\text{Pt[C(CF}_3)\text{=C(CF}_3)\text{CH}_3]_2\text{L}_2} \\ \underset{\text{VII}}{\text{Pt(C}_4\text{F}_6)\text{L}_2} \end{cases} \quad (2)$$

For L = As(CH$_3$)$_2$C$_6$H$_5$, insertion of C$_4$F$_6$ into one of the methyl–platinum bonds occurred giving mostly IX, L = As(CH$_3$)$_2$C$_6$H$_5$, probably as a mixture of the cis and trans isomers, along with a little X, L = As(CH$_3$)$_2$C$_6$H$_5$. The compounds were oils which were characterized by analysis and by spectroscopy, by comparison with the known insertion products *trans*-PtX[C(CF$_3$)=C(CF$_3$)CH$_3$]L$_2$.[1]

However, when L = P(CH$_3$)$_2$C$_6$H$_5$ the same reaction gave either X, L = P(CH$_3$)$_2$C$_6$H$_5$, due to insertion into both methyl–platinum bonds, or VII, L = P(CH$_3$)$_2$C$_6$H$_5$, formed by elimination of the elements of ethane from an intermediate complex, depending on the experimental conditions. It appears that the concentration of C$_4$F$_6$ may be the determining factor, rather than the nature of the solvent,[8] high concentrations tending to give the elimination reaction. Formation of VII was always accompanied by formation of some polymer of C$_4$F$_6$, and the methyl groups eliminated may be incorporated into this polymer. Certainly no ethane was observed in the reaction products.

The reaction of *cis*-Pt(CH$_3$)$_2$[P(CH$_3$)$_3$]$_2$ with C$_4$F$_6$ apparently gave a mixture of the insertion products IX and X and the elimination product VII, L = P(CH$_3$)$_3$, while reactions of C$_4$F$_6$ and C$_2$F$_4$ with *trans*-PtHClL$_2$, L = P(CH$_3$)$_3$ or As(CH$_3$)$_3$, led only to the formation of previously described[6,7] insertion and subsequent reaction products.

## Discussion

The formation of complexes III may be considered[37] as a "partial oxidative addition" and the factors which

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promote oxidative addition reactions might be expected to stabilize the complexes. Thus, stable complexes are formed only by those olefins and acetylenes which contain highly electronegative substituents. Also, metal–arsine complexes are known to undergo oxidative additions more readily than the corresponding metal–phosphine complexes,[38–40] accounting for the greater stability of III containing arsine ligands. However, stibines may promote oxidative addition reactions more than arsines,[38] and iodides more than chlorides,[40,41] but we find that arsines stabilize III more than stibines while substitution of iodide for chloride has little effect.

In complexes IIIb the hexafluorobut-2-yne may be considered to be trans to the ligands L, and the stability might be determined by the trans influence of L. In the complexes *cis*-$PtCl_2L_2$ the trans influence of L follows the order $PR_3 > SbR_3 > AsR_3$ (R = alkyl),[13,20] so that, if this order is the same in III, this effect can account for the relative stabilities observed. It seems reasonable that the trans influence of L as well as its ability to promote oxidative addition reactions may influence the stability of complexes III.

Finally, the influence of the ligand in stabilizing III parallels the influence, determined previously,[1] in promoting insertion into the methyl–platinum bond. This supports our view that the reactivity of methyl–platinum compounds toward insertion reactions depends on the stability of the intermediate complex.

## Experimental Section

General methods have been described previously.[1] Far-infrared spectra (350–140 $cm^{-1}$) were recorded on a Beckman IR-11 spectrometer. Samples were prepared as Nujol mulls between propathene plates. Raman spectra of crystalline materials were recorded on a Spex Model 1400 spectrometer using the 6328-Å line of a helium–neon laser as source. Band frequencies are believed to be accurate within $\pm 5$ $cm^{-1}$.

*trans*-**$PtHCl[As(CH_3)_3]_2$** was prepared by the method of Chatt and Shaw;[42] yield 25%; mp 154–156° dec; $\nu(PtH)$ 2190 $cm^{-1}$. *Anal.* Calcd for $C_6H_{19}ClAs_2Pt$: C, 15.3; H, 4.1. Found: C, 15.4; H, 4.0.

**Preparation of $\pi$ Complexes.**—Representative examples are given below. Analytical and physical data are in Table I.

**$PtClCH_3[As(CH_3)_3]_2 \cdot C_4F_6$.**—A solution of *trans*-$PtClCH_3[As(CH_3)_3]_2$ (0.115 g, 0.24 mmol) in benzene (2 ml) was treated with $C_4F_6$ (1.0 mmol) in a sealed tube (5 ml). The solution was heated to redissolve the white precipitate formed. On cooling, white needles of the product were formed. The tube was opened, the solvent decanted off, and the product washed rapidly with benzene and pentane and dried under vacuum; yield 0.082 g (53%).

Similar attempts to prepare $C_4F_6$ complexes of *trans*-$PtXCH_3L_2$, where X = Cl, L = $P(C_2H_5)_3$, $P(CH_3)_2C_6H_5$ or X = I, L = $As(CH_3)_3$, $As(CH_3)_2C_6H_5$, $P(CH_3)_2C_6H_5$, were unsuccessful.

$PtClCH_3[As(CH_3)_3]_2 \cdot C_4F_6$ was heated *in vacuo*. A gas was evolved at 85–115°. The gas was weighed by condensing into a molecular weight bulb and then identified as pure $C_4F_6$ (70% yield) by its infrared spectrum. Decomposition temperatures of other complexes are given in Table I.

**$PtClCH_3[As(CH_3)_3]_2 \cdot C_2F_4$** was prepared in a similar way from *trans*-$PtClCH_3[As(CH_3)_3]_2$ (0.126 g, 0.26 mmol) and $C_2F_4$ (1.0 mmol) in benzene (1.5 ml); yield 0.076 g (50%). The compound decrepitated at 90–100° as $C_2F_4$ was evolved and melted at 147–151°. *Anal.* Calcd for $C_9H_{21}ClAs_2Pt$: C, 18.5; H, 3.6; F, 13.0. Found: C, 19.0; H, 3.4; F, 13.6.

Attempts to prepare $C_2F_4$ complexes of *trans*-$PtXCH_3L_2$, where X = Cl, L = $As(CH_3)_2C_6H_5$, X = Cl, L = $P(CH_3)_3$, or X = I, L = $As(CH_3)_3$, were unsuccessful.

*trans*-**$PtClCH_3[As(CH_3)_3]_2$ with $C_2F_3Cl$.**—A solution of *trans*-$PtClCH_3[As(CH_3)_3]_2$ (0.080 g) in benzene (0.5 ml) was treated with $C_2F_3Cl$ (2.0 mmol) in a sealed tube (5 ml). No precipitate appeared. The mixture was cooled to 0° for 1 week. The precipitate formed was filtered off and identified (melting point, in spectrum) as *cis*-$PtCl_2[As(CH_3)_3]_2$ (0.008 g). The solvent was evaporated from the filtrate giving unreacted *trans*-$PtClCH_3[As(CH_3)_3]_2$ (0.062 g).

**Study of $\pi$ Complexes by Nmr.**—The nmr spectra of $\pi$ complexes $PtXCH_3L_2 \cdot C_4F_6$ are given in Table II. A representative example is given.

*trans*-**$PtClCH_3[As(CH_3)_3]_2$ with $C_4F_6$ in $CH_2Cl_2$.**—A solution of *trans*-$PtClCH_3[As(CH_3)_3]_2$ (0.0615 g, 0.126 mmol) in $CH_2Cl_2$ (0.53 g) was treated with $C_4F_6$ ($\sim$0.03 g, 0.18 mmol) in a sealed nmr tube. The $^1H$ and $^{19}F$ nmr spectra showed peaks due to a mixture of *trans*-$PtClCH_3[As(CH_3)_3]_2$, $PtClCH_3[As(CH_3)_3]_2 \cdot C_4F_6$, and $C_4F_6$ (Table II). Integration of both $^1H$ and $^{19}F$ spectra enabled calculation of all concentrations.

*cis*-**$Pt(CH_3)_2[As(CH_3)_3]_2$ with $C_2F_4$.**—A solution of *cis*-$Pt(CH_3)_2[As(CH_3)_3]_2$ (0.105 g) in benzene (0.5 ml) was treated with $C_2F_4$ (0.4 mmol) in a sealed nmr tube. The $^1H$ nmr showed complex, unresolved peaks. The $^{19}F$ nmr spectrum contained peaks due to free $C_2F_4$ ($\delta$ 134.1 ppm) and complexed $C_2F_4$ ($\delta$ 127.4 ppm, $^2J(PtF)$ = 211.6 Hz). No pure compounds could be isolated from the mixture.

*trans*-**$PtClCH_3[As(CH_3)_3]_2$ with $C_2F_4$.**—A solution of *trans*-$PtClCH_3[As(CH_3)_3]_2$ (0.042 g) in $CHCl_3$ (0.3 ml) was treated with $C_2F_4$ (0.2 mmol) in a sealed nmr tube. The $^1H$ and $^{19}F$ nmr spectra showed the presence of *trans*-$PtClCH_3[As(CH_3)_3]_2$ and free $C_2F_4$ only.

Similar experiments showed that there was no interaction between $C_2F_4$ and *cis*-$Pt(CH_3)_2[P(CH_3)_3]_2$ or *trans*-$PtClCH_3[P(CH_3)_3]_2$ at room temperature.

**Study of $\pi$ Complexes by Infrared Spectroscopy.** *trans*-**$PtICH_3[As(CH_3)_2C_6H_5]_2$ with $C_4F_6$.**—A solution of *trans*-$PtICH_3[As(CH_3)_2C_6H_5]_2$ (0.15 g) in benzene (0.4 ml) was treated with $C_4F_6$ ($\sim$1 mmol). The infrared spectrum of the solution showed bands at 1868 (s), 1815 $cm^{-1}$ (m) due to the $\pi$ complex.

Similar reactions of $C_4F_6$ with *trans*-$PtClCH_3[P(C_2H_5)_3]_2$ and *trans*-$PtXCH_3[P(CH_3)_2C_6H_5]$, X = Cl, I, showed *no* infrared bands in the region 1700–2000 $cm^{-1}$.

**Further Reactions of $\pi$ Complexes.** *trans*-**$PtClCH_3[As(CH_3)_2C_6H_5]_2$ with $C_4F_6$.**—A solution of *trans*-$PtClCH_3[As(CH_3)_2C_6H_5]_2$ (0.065 g, 0.11 mmol) in $CHCl_3$ (0.3 ml) was treated with $C_4F_6$ (0.3 mmol) in a sealed nmr tube. The peaks in the $^1H$ and $^{19}F$ spectra due to the mixture of *trans*-$PtClCH_3[As(CH_3)_2C_6H_5]_2$ and $PtClCH_3[As(CH_3)_2C_6H_5]_2 \cdot C_4F_6$ (see Table II) were slowly replaced by peaks due to the insertion product, *trans*-$PtCl[C(CF_3){=}C(CF_3)CH_3][As(CH_3)_2C_6H_5]_2$.[1] The reaction was complete after 3 weeks at room temperature. The tube was opened, the solvent evaporated, and the product recrystallized from methanol. It was identical (ir spectrum, melting point, mixture melting point) with an authentic sample;[1] yield 0.035 g (42%).

The reaction of *trans*-$PtClCH_3[As(CH_3)_3]_2$ with $C_4F_6$ in $CHCl_3$ or $CH_2Cl_2$ was very similar.

*trans*-**$PtClCH_3[P(CH_3)_2C_6H_5]_2$ with $C_4F_6$.**—A solution of *trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ (0.10 g) in $CHCl_3$ (0.3 ml) was treated with $C_4F_6$ (0.3 mmol) in a sealed nmr tube. The nmr spectra showed that there was no interaction. However after 2 weeks the nmr spectra indicated that equimolar proportions of $Pt(C_4F_6)[P(CH_3)_2C_6H_5]_2$ [$\delta$ (F) 55.1 ppm (doublet + satellites), $^4J(PF)$ = 11.2 Hz, $^3J(PtF)$ = 67.6 Hz; $\delta(CH_3P)$ $-1.75$ ppm (doublet + satellites), $^2J(PH)$ = 8.7 Hz, $^3J(PtH)$ = 31.5 Hz] and $PtCl_2(CH_3)_2[P(CH_3)_2C_6H_5]_2$ [$\delta(CH_3Pt)$ $-0.58$ ppm (triplet + satellites), $^3J(PH)$ = 5.6 Hz, $^2J(PtH)$ = 68.5 Hz; $\delta(CH_3P)$ $-2.15$ ppm (triplet + satellites), $^2J + {}^4J(PH)$ = 8.3 Hz, $^3J$

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$(PtH) = 17.2$ Hz] had been formed. The tube was opened and the solvent evaporated giving a yellow oil. The oil was extracted with ether and the ether evaporated, giving a yellow solid (0.03 g) identical (ir, nmr, melting point) with $Pt(C_4F_6)[P(CH_3)_2C_6H_5]_2$.[24] The ether-insoluble fraction was recrystallized twice from $CH_2Cl_2$–petroleum ether giving white crystals of $PtCl_2(CH_3)_2[P(CH_3)_2C_6H_5]_2$ (0.02 g) identical (melting point, mixture melting point, ir) with an authentic sample;[16] mp 189–190° dec. *Anal.* Calcd for $C_{18}H_{28}Cl_2P_2Pt$: Cl, 12.4. Found: Cl, 12.25.

Similar reactions in benzene and ether gave the same products. Analogous products were formed in the reaction of *trans*-$PtClCH_3[P(CH_3)_3]_2$ or *trans*-$PtBrCH_3[P(CH_3)_2C_6H_5]_2$ with $C_4F_6$ in a sealed nmr tube.

***trans*-$\mathbf{PtClCH_3[P(CH_3)_2C_6H_5]_2}$ with $\mathbf{CH_3Cl}$.**—A mixture of *trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ (0.100 g, 0.191 mmol) and $CH_3Cl$ (0.7 mmol) in $CHCl_3$ (0.40 ml) was sealed in an nmr tube. Reaction to give $PtCl_2(CH_3)_2[P(CH_3)_2C_6H_5]_2$, as determined by integration of the nmr spectrum, was 13% complete after 130 hr at room temperature.

A similar reaction of *trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ (0.19 mmol) with $C_4F_6$ (0.3 mmol) and $CH_3Cl$ (0.7 mmol) in $CHCl_3$ (0.4 ml) giving a mixture of $Pt(C_4F_6)[P(CH_3)_2C_6H_5]_2$ and $PtCl_2(CH_3)_2[P(CH_3)_2C_6H_5]_2$ was 50% complete in 130 hr at room temperature. In the absence of $CH_3Cl$, this reaction was 65% complete after 130 hr.

$Pt(C_4F_6)[P(CH_3)_2C_6H_5]_2$ gave no reaction with $CH_3Cl$ in $CHCl_3$ after 130 hr at room temperature.

**Reactions of $\mathbf{C_4F_6}$ with *cis*-$\mathbf{Pt(CH_3)_2L_2}$.**—1. ***cis*-$\mathbf{Pt(CH_3)_2[As(CH_3)_2C_6H_5]_2}$.**—A solution of *cis*-$Pt(CH_3)_2[As(CH_3)_2C_6H_5]_2$ (0.121 g) in ether (3 ml) was stirred under $C_4F_6$ (1 atm) for 1 hr. The solvent was evaporated giving a colorless, viscous oil, probably a mixture of *cis*- and *trans*-$PtCH_3[C(CF^1{}_3)=C(CF^2{}_3)CH^1{}_3][As(CH_3)_2C_6H_5]_2$. $\nu(C=C)$ 1610 (m), $\nu(CF)$ 1275 (s), 1239 (s), 1145 (vs), 1120 cm$^{-1}$ (vs). Nmr in benzene: $\delta(CH_3Pt)$ $-1.25$ ppm, $^2J(PtH) = 73$ Hz; $\delta(CH_3As)$ $-1.51$, $-1.47$, $-1.37$, $-1.32$, $-1.28$ ppm; $\delta(CH^1{}_3)$ $-2.71$ ppm (quartet), $^5J(H^1F^1) = 2.0$ Hz, $-2.59$ ppm (unresolved quartet); $\delta(F^1)$ 48.6 ppm (quartet + satellites), $^5J(F^1F^2) = 14.9$ Hz, $^3J(PtF^1) = 123.6$ Hz, 49.6 ppm (quartet + satellites), $^5J(F^1F^2) = 14.9$ Hz, $^3J(PtF^1) = 153.6$ Hz; $\delta(F^2)$ 60.3 ppm (quartet), 59.1 ppm (quartet). *Anal.* Calcd for $C_{22}H_{28}F_6As_2Pt$: C, 35.2; H, 3.8; F, 14.9; mol wt 751. Found: C, 34.4; H, 3.3; F, 17.0; mol wt 744.

A similar reaction in benzene solution in a sealed nmr tube gave the same product mixture within 15 min at room temperature.

**2. *cis*-$\mathbf{Pt(CH_3)_2[P(CH_3)_2C_6H_5]_2}$.**—a. A solution of *cis*-$Pt(CH_3)_2[P(CH_3)_2C_6H_5]_2$ (0.158 g, 0.31 mmol) in ether (1.5 ml) was treated with $C_4F_6$ (1.0 mmol) in a sealed tube (5 ml). On warming to room temperature the solution became yellow and some insoluble polymer formed. After 2 hr the solution was filtered, the solvent evaporated, and the product crystallized from petroleum ether (bp 60–80°), giving $Pt(C_4F_6)[P(CH_3)_2C_6H_5]_2$ (0.062 g, 31%); mp 143–144° (lit.[24] mp 141–142); $\nu(C\equiv C)$ 1760 cm$^{-1}$. Nmr in benzene: $\delta(CH_3P)$ $-1.58$ ppm (doublet + satellites) $^2J(PH) = 8.4$ Hz, $^3J(PtH) = 31.2$ Hz; $\delta(F)$ 54.9 ppm (doublet + satellites), $^4J(PF) = 11.2$ Hz, $^3J(PtF) = 68.5$ Hz.

b. A solution of *cis*-$Pt(CH_3)_2[P(CH_3)_2C_6H_5]_2$ (0.16 g, 0.31 mmol) in ether (3 ml) was stirred under $C_4F_6$ (1 atm) for 2 hr. The solvent was evaporated leaving a pale yellow oil, identified as $Pt[C(CF_3)=C(CF_3)CH_3]_2[P(CH_3)_2C_6H_5]_2$; $\nu(C=C)$ 1610 cm$^{-1}$ (m). Nmr in benzene: $\delta(CH_3P)$ $-1.39$ ppm (triplet + satellites), $^2J + {}^4J(PH) = 19.3$ Hz, $^3J(Pt\text{–}H) = 37.3$ Hz; $\delta$ $-1.45$ ppm (triplet + satellites), $^2J + {}^4J(PH) = 19.3$ Hz, $^3J(PtH) = 37$ Hz; $\delta(CH_3\text{–}C)$ $-2.46$, $-2.81$ ppm (unresolved peaks). *Anal.* Calcd for $C_{26}H_{28}F_{12}P_2Pt$: C, 37.8; H, 3.4; F, 27.6. Found: C, 37.5; H, 3.7; F, 26.5.

A reaction in benzene solution under similar conditions gave the same product.

**3. *cis*-$\mathbf{Pt(CH_3)_2[P(CH_3)_3]_2}$.**—A solution of *cis*-$Pt(CH_3)_2[P(CH_3)_2]_2$ (0.23 g) in benzene (2 ml) was treated with $C_4F_6$ (1.0 mmol) in a sealed tube (10 ml). The solution became brown. After 3 hr, the solvent was evaporated giving a yellow-brown oil, identified as a mixture of $Pt(C_4F_6)[P(CH_3)_3]_2$ [$\nu(C=C)$ 1760 cm$^{-1}$; $\delta(F)$ 54.4 ppm (doublet + satellites), $^4J(PF) = 11.5$ Hz, $^3J(PtF) = 66.8$ Hz] and insertion product $PtCH_3[C(CF^1{}_3)=C(CF^2{}_3)CH_3][P(CH_3)_3]_2$ [$\nu(C=C)$ 1605 cm$^{-1}$; $\delta(F^1)$ 49.0 ppm (quartet + satellites), $^5J(F^1F^2) = 15.0$ Hz, $^3J(PtF) = 126$ Hz; 51.2 ppm (quartet), $^5J(F^1F^2) = 15.0$ Hz; $\delta(F^2)$ 63.0 (quartet), 59.7 ppm (quartet). No pure products could be isolated from the mixture.

**Reactions with *trans*-$\mathbf{PtHClL_2}$.** 1. ***trans*-$\mathbf{PtHCl[As(CH_3)_3]_2}$ with $\mathbf{C_4F_6}$.**—A solution of *trans*-$PtHCl[As(CH_3)_3]_2$ (0.070 g, 0.15 mmol) in benzene (0.5 ml) was treated with $C_4F_6$ (0.3 mmol) in a sealed tube (5 ml). After 15 min, the solvent was evaporated and the product crystallized from methanol, giving *trans*-$PtCl[C(CF^1{}_3)=C(CF^2{}_3)H][As(CH_3)_3]_2$ (0.056 g, 59%), mp 148–150°; $\nu(C=C)$ 1609 cm$^{-1}$ (s). Nmr in $CHCl_3$: $\delta(CH_3As)$ $-1.44$ ppm, $^3J(PtH) = 22.6$ Hz; $\delta(H\text{—}C)$ $-6.04$ ppm (quartet of quartets), $^4J(HF^1) = 1.1$ Hz, $^3J(HF^2) = 9.7$ Hz. *Anal.* Calcd for $C_{10}H_{19}F_6ClAs_2Pt$: C, 19.0; H, 3.0; F, 18.0. Found: C, 18.9; H, 2.8; F, 17.9.

$C_4F_6$ reacted rapidly with *trans*-$PtHCl[P(CH_3)_3]_2$ to give *trans*-$PtCl[C(CF_3)=C(CF_3)H][P(CH_3)_3]_2$, $\nu(C=C)$ 1614 cm$^{-1}$. In the case, the product was not isolated.

**2. *trans*-$\mathbf{PtHCl[P(CH_3)_3]_2}$ with $\mathbf{C_2F_4}$.**—A solution of *trans*-$PtHCl[P(CH_3)_3]_2$ (0.090 g) in benzene (1.0 ml) was treated with $C_2F_4$ (1.0 mmol) in a sealed tube (5 ml). A precipitate formed after 1 hr at room temperature. After 24 hr the solution was filtered. The solvent was evaporated from the filtrate giving a mixture of *trans*-$PtCl(CF=CF_2)[P(CH_3)_3]_2$, $\nu(C=C)$ 1724 cm$^{-1}$, and *trans*-$PtCl[C(CF_2H)=CF_2][P(CH_3)_3]_2$, $\nu(C=C)$ 1634 cm$^{-1}$. The precipitate showed the characteristic ir spectrum[6] of the *trans*-$PtCl(CO)[P(CH_3)_3]_2{}^+$ cation, $\nu(CO)$ 2114 cm$^{-1}$, and the anions $BF_4{}^-$ and $SiF_5{}^-$.

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