Chemistry of Metal Hydrides. III. Preparation of *trans*-$[PtCl(CO)(R_3P)_2]^+$ Cations and Related Compounds[1]

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Abstract: The cations *trans*-$[PtCl(CO)L_2]^+$, where L = triethyl- or triphenylphosphine, have been synthesized according to the reactions: *trans*-$[PtHCl(Et_3P)_2]$ + CO + HBF_4 → *trans*-$[PtCl(CO)(Et_3P)_2][BF_4]$ + $[H_2]$; *cis*-$[PtCl_2(Ph_3P)_2]$ + CO + $2BF_3$ → *trans*-$[PtCl(CO)(Ph_3P)_2][BF_4]$ + $[BF_2Cl]$. These platinum(II) cations are isoelectronic with $[IrCl(CO)(Ph_3P)_2]$ and its rhodium(I) analog but are much less reactive, although the carbonyl group is readily displaced by Cl^-. These syntheses allow reinterpretation of previous results[1] on the reaction of *trans*-$[PtHCl(Et_3P)_2]$ with C_2F_4 in the presence of Pyrex glass. The *trans*-$[PtCl(CO)(Et_3P)_2]^+$ cation is formed during this reaction, the counteranions being BF_4^- and the previously unknown SiF_5^- ion, in this case stabilized by the large cation. The complex reactions leading to these unexpected products are described. New, dimeric, platinum(II) cations, $[\mu\text{-}Cl_2\text{-}(PtL_2)_2]^{2+}$, are prepared by interaction of compounds, *trans*-$[PtHClL_2]$ or *cis*-$[PtCl_2L_2]$, with BF_3 or SiF_4. Reaction of $[PtH(Ph_3P)_3][BF_4]$ with C_2F_4 yields $[Pt(Ph_3P)_2(C_2F_4)]$. These compounds clarify criteria for the differentiation of *cis-trans* isomers in square-planar complexes of tertiary phosphines.

Complexes such as $[RhCl(Ph_3P)_3]$ and *trans*-$[IrCl(CO)(Ph_3P)_2]$ have been extensively studied as catalysts for the homogeneous hydrogenation of olefins since they undergo reversible addition reactions with molecular hydrogen giving $[RhH_2Cl(Ph_3P)_2]$ and $[IrH_2Cl(CO)(Ph_3P)_2]$. Many analogous addition reactions occur, for example, with HCl, O_2, or C_2H_4.[2] Iridium(I) and rhodium(I) in these complexes show a remarkable affinity for the carbonyl ligand as is evident from the preparation of $[IrCl(CO)(Ph_3P)_2]$ from Ph_3P and $IrCl_3$ in a refluxing alcohol,[3] and from the ready reaction of $[RhCl(Ph_3P)_3]$ with aldehydes to give $[RhCl(CO)(Ph_3P)_2]$.[2] $[IrCl(CO)(Ph_3P)_2]$ is also of interest for its reaction with organic azides giving the molecular nitrogen complex $[IrCl(N_2)(Ph_3P)_2]$.[4]

Previously[1] it was reported that a minor product in the reaction of *trans*-$[PtHCl(Et_3P)_2]$ with C_2F_4 was the complex $[PtHCl(Et_3P)_2(\pi\text{-}C_2F_4)]$. An X-ray diffraction study[5] of this product did not confirm this postulate but suggested the composition *trans*-$[PtCl(CO)(Et_3P)_2][BF_4]$. These results led us to a rational synthesis of this complex and to a study of the preparation and properties of platinum(II) complexes isoelectronic with the above iridium(I) and rhodium(I) complexes.

Results and Discussion

Platinum Analogs of $[IrCl(CO)(Et_3P)_2]$. We now report the synthesis and properties of two Pt(II) species which are isoelectronic with Vaska's compound,[3] $[IrCl(CO)(R_3P)_2]$, R = alkyl or aryl, and its rhodium(I) analogs.[2] The *trans*-chlorocarbonylbis(triethylphosphine)platinum(II) cation, $[PtCl(CO)(Et_3P)_2]^+$, results from the reaction of *trans*-hydridochlorobis(triethylphosphine)platinum(II) with aqueous 48% fluoroboric acid under a pressure of 5 atm of carbon monoxide in benzene.

$$trans\text{-}[PtHCl(Et_3P)_2] + CO + HBF_4 \xrightarrow[\text{benzene}]{120^\circ} trans\text{-}[PtCl(CO)(Et_3P)_2][BF_4] + [H_2]$$

The analogous reaction with *trans*-$[PtHCl(Ph_3P)_2]$ is more complex. Some *trans*-$[PtCl(CO)(Ph_3P)_2][BF_4]$ is formed, but there are other products which are difficult to separate, and the reaction has not yet been fully characterized. The *trans*-chlorocarbonylbis(triphenylphosphine)platinum(II) cation is better prepared by the reaction of *cis*-dichlorobis(triphenylphosphine)platinum(II) with gaseous boron trifluoride under a pressure of 15 atm of carbon monoxide.

$$cis\text{-}[PtCl_2(Ph_3P)_2] + CO + 2BF_3 \xrightarrow[\text{benzene}]{120^\circ} trans\text{-}[PtCl(CO)(Ph_3P)_2][BF_4] + [BF_2Cl]$$

trans-$[PtCl(CO)(Et_3P)_2][BF_4]$ and its triphenylphosphine analog are nonhygroscopic, white, crystalline solids. They are stable in air for about 1 month although after longer storage in air there is evidence of slight decomposition. Their conductivities in nitromethane solution are of the order expected for 1:1 electrolytes in this solvent[6] and the carbonyl stretching frequencies, *ca.* 2100 cm^{-1}, are similar to the reported[7] value of 2100 cm^{-1} for *cis*-$[PtCl_2(CO)(Et_2P)]$, which also has the carbonyl *trans* to chlorine. Preliminary single-crystal X-ray studies[5] show the $[PtCl(CO)(Et_3P)_2]^+$ cation to have the expected square-planar configuration about platinum and confirm the *trans* configuration for the two phosphine ligands.

The *trans*-$[PtCl(CO)(Et_3P)_2]^+$ ion is much less reactive than its iridium or rhodium analogs and does not combine with hydrogen or dry hydrogen chloride at atmospheric pressure at 25°. It has been suggested[2] that the addition of hydrogen to $[RhCl(CO)(Ph_3P)_2]$ is much more difficult than the addition to $[RhCl(Ph_3P)_3]$ because the π-accepting power of the carbonyl ligand decreases the electron density on the metal atom and hence increases the promotional energy required to form two more bonds. If the same argument holds, the positive

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[1] For parts I and II, see H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, **89**, 529, 533 (1967).

[2] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, *A*, 1711 (1966), and references therein.

[3] L. Vaska and J. W. Di Luzio, *J. Amer. Chem. Soc.*, **83**, 2784 (1961).

[4] J. P. Collman, M. Kubota, J. Y. Sun, and F. Vastine, *ibid.*, **89**, 169 (1967).

[5] H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *ibid.*, **89**, 3360 (1967).

[6] F. A. Cotton, B. F. G. Johnson, and R. M. Wing, *Inorg. Chem.*, 4, 502 (1965).

[7] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1662 (1964).

charge centered on platinum would be expected to inhibit addition of hydrogen or hydrogen chloride. The Pt—C≡O group does not react with benzoyl azide in chloroform solution, but the carbon monoxide is readily displaced by chloride ion. *trans*-$[PtCl(CO)(R_3P)_2][BF_4]$, R = Et or Ph, dissolves with effervescence in a chloroform solution of tetraethylammonium chloride, the products being Et_4NBF_4 and *cis*-$[PtCl_2(R_3P)_2]$. Since *trans*-$[PtCl_2(Et_3P)_2]$ does not isomerize under the conditions of this reaction, this implies that chloride attack occurs on the side remote from the carbonyl ligand.

The Reaction of *trans*-$[PtHCl(Et_3P)_2]$ with C_2F_4. In parts I and II of this series,[1] the reaction of *trans*-$[PtHCl(Et_3P)_2]$ with C_2F_4 was described. The major products are fluorovinyl derivatives of platinum(II), *trans*-$[PtCl(Et_3P)_2(CF{=}CF_2)]$ and *trans*-$[PtCl(Et_3P)_2(C(CF_2H){=}CF_2)]$, but it was also postulated that one of the low-yield products was a reaction intermediate, $[PtHCl(Et_3P)_2(\pi\text{-}C_2F_4)]$. As noted above, X-ray diffraction studies did not confirm this postulate and this low yield product is now known to contain the *trans*-$[PtCl(CO)(Et_3P)_2]^+$ cation. The original reactions described in parts I and II were carried out in Pyrex glass tubes, and under these conditions the anions are a mixture of BF_4^- and SiF_5^-. On the basis of analytical, conductance, and infrared spectral data reported previously, it is not possible to distinguish between the original postulate and the present formulation. However, the correctness of the latter is confirmed by (i) reaction of the complex with sodium tetraphenylborate, giving $NaBF_4$ and Na_2SiF_6 and (ii) mass spectroscopic identification of CO.

In all the salts studied here the ν_3 mode of the BF_4^- ion appears as two sharp bands at approximately 1090 (s) and 1050 (vs) cm^{-1}. In nearly all fluoroborate salts previously studied, the ν_3 mode is considerably broadened by splitting of its triplet degeneracy by site symmetry and coordination effects.[8] This broadening is often accompanied by infrared activity of the ν_1 mode which is inactive in full T_d symmetry.[9] However, in the present complexes the bands at about 1090 and 1050 cm^{-1} are relatively sharp and are presumably due simply to $\nu_3(B^{10}F_4^-)$ and $\nu_3(B^{11}F_4^-)$, respectively. This suggests that these salts are unusual in that the fluoroborate anions retain full tetrahedral symmetry in the solid state.

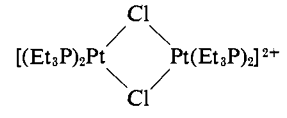
The reaction of *trans*-$[PtHCl(Et_3P)_2]$ with C_2F_4 in a silica tube leads to the pure salt *trans*-$[PtCl(CO)(Et_3P)_2][SiF_5]$. This compound represents the first reported isolation of the SiF_5^- ion. That this is an SiF_5^- salt, rather than an SiF_6^{2-} salt, is strongly suggested by analytical data, X-ray molecular weight determination[5] and preliminary structure determination, and its infrared spectrum. The molar conductivity in nitromethane solution is also consistent with that of a 1:1 electrolyte. Moreover reaction with tetraethylammonium chloride yielded a water-soluble fraction whose infrared spectrum was consistent with the formulation Et_4NSiF_5 and not $(Et_4N)_2SiF_6$. Reaction with sodium tetraphenylborate yields Na_2SiF_6, but the SiF_5^- ion would not be expected to be stabilized by the small sodium cation. A preliminary study[10] of the SiF_5^- ion has shown that it is easily prepared in the presence of large cations and under these conditions is preferred to the well-known SiF_6^{2-} ion. A detailed study is in progress to establish the exact nature of this species and to resolve such questions as the possibility of fluorine bridging in the solid state. For present purposes it is sufficient to note that the ion is easily recognized by its strong infrared absorptions at about 875 (vs, b), 775 (vs, b), 475 (s), and 440 (s) cm^{-1}, quite different from the SiF_6^{2-} ion[11] which has absorptions at about 740 (vs, b) and 480 (s) cm^{-1}.

The reaction of *trans*-$[PtHCl(Ph_3P)_2]$ with C_2F_4 is very similar to that of its triethylphosphine analog, and the fluorovinyl compounds *trans*-$[PtCl(Ph_3P)_2(CF{=}CF_2)]$ and *trans*-$[PtCl(Ph_3P)_2(C(CF_2H){=}CF_2)]$ are readily isolated. They are insufficiently soluble for characterization by ^{19}F nmr studies, but comparison of their infrared spectra in the C–F stretching region (Table II) with spectra of the analogous triethylphosphine complexes clearly establishes their identity. The *trans*-$[PtCl(CO)(Ph_3P)_2]^+$ cation is isolated from this reaction as its fluoroborate salt, but its fluorosilicate salt appears to be unstable since it could not be obtained even when reaction was carried out in a silica tube.

The formation of platinum carbonyls under such unusual conditions is an important parallel with the affinity for the carbonyl ligand exhibited by the analogous rhodium and iridium systems. It is consequently of great interest to establish the mechanism of this carbonyl formation. In summary the reactions are

$$\begin{array}{l} trans\text{-}[PtHCl(Et_3P)_2] + \text{excess } C_2F_4 \xrightarrow[\text{benzene–glass}]{120°} \\ \qquad trans\text{-}[PtCl(Et_3P)_2(CF{=}CF_2)] + \\ \qquad\quad \text{A}, \sim 20\% \\ \qquad trans\text{-}[PtCl(Et_3P)_2(C(CF_2H){=}CF_2)] + \\ \qquad\quad \text{B}, \sim 40\% \\ \qquad\qquad trans\text{-}[PtCl(CO)(Et_3P)_2]^+ \\ \qquad\qquad\quad \text{C}, \sim 30\% \end{array}$$

The carbonyl is isolated as a mixture of its BF_4^- and SiF_5^- salts, and K_2SiF_6, KBF_4, and SiF_4 are also formed at 120°. When the reaction is performed at 90°, the yields of B and C are reduced to about 15 and 8%, respectively, and no K_2SiF_6, KBF_4, or SiF_4 is detected. It was previously reported that the yield of C was higher at 90° in benzene than at 120° in cyclohexane. This was probably a solvent effect, and it is now known that in the same solvent the yield of C increases with increase of temperature. In the reaction at 90° traces of salts containing the



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cation are detected, but these result from side reactions (described below) and are almost certainly not part of the main reaction sequence.

These observations, together with some of the experiments described below, suggested that the main reactions are (i) $PtH + C_2F_4 \rightarrow PtCF_2CF_2H \rightarrow PtCF{=}CF_2 + HF$; $HF + \text{glass} \rightarrow H_2O, BF_3, SiF_4, BF_4^-$, and SiF_6^{2-}; and (ii) $2PtCF{=}CF_2 + H_2O + SiF_4 \rightarrow [Pt\text{–}C{\equiv}O]^+ + PtC(CF_2H){=}CF_2 + HF + SiF_5^-$. Gaseous BF_3 is not detected spectroscopically, but this is ex-

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(8) D. W. A. Sharp, *Advan. Fluorine Chem.*, **1**, 68 (1960).

(9) H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 1020 (1963).

(10) H. C. Clark and K. R. Dixon, *Chem. Commun.*, 717 (1967).

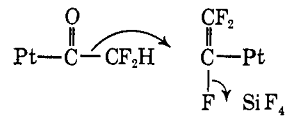
(11) D. H. Brown, K. R. Dixon, C. M. Livingston, R. H. Nuttall, and D. W. A. Sharp, *J. Chem. Soc.*, *A*, 100 (1967).

pected since, as described below, it reacts rapidly with *trans*-$[PtHCl(Et_3P)_2]$ at 70°. The water produced by reaction of HF with glass, together with that normally present in reagent grade benzene ($\sim$0.05%), is adequate to account for the oxygen in the observed yields of carbonyl. However, the quantities of gaseous SiF_4 and of fluoro anions in the solid products are too large to be produced solely by the above mechanism, and it follows that another mechanism must exist for the production of SiF_4 at 120°. Nevertheless, the main course of the reaction is as described in reactions i and ii and this is established by the following series of reactions.

(a) *trans*-$[PtCl(Et_3P)_2(CF_2CF_2H)]$ results from the addition of C_2F_4 to *trans*-$[PtHCl(Et_3P)_2]$ in a stainless-steel autoclave. Several analogous additions of metal hydrides to olefins have been reported; for example, *trans*-$[PtHCl(Et_3P)_2]$[12] or $[CoH(CO)_4]$[13] with C_2H_4, and $[MnH(CO)_5]$[14] or $[SnH_2Me_2]$[15] with C_2F_4. Heating *trans*-$[PtCl(Et_3P)_2(C_2H_5)]$ or $[Co(CO)_4(C_2H_5)]$ results in dissociation to metal hydride and ethylene, but analogous dissociation of C_2F_4 addition products is not observed. Fluoroalkyls of main group elements decompose with cleavage of the M–C bond as the first step, but it has been suggested that this is not the case with fluoroalkyls of transition metals.[14] Treatment of $[Mn(CO)_5(CF_2CF_2H)]$ with HCl at 100° in a glass vessel resulted in production of SiF_4,[14] and this may have been due to elimination of HF in a similar reaction to that observed here for *trans*-$[PtCl(Et_3P)_2(CF_2CF_2H)]$. This elimination reaction for the Pt(II) compound is very sensitive to the nature of the reaction vessel surface, and also to the presence of water and SiF_4. For example, elimination occurs readily at a glass surface at 120° or in the presence of added SiF_4 it proceeds even in a steel vessel, but in dry benzene in the absence of SiF_4 elimination is very slow at a silica surface.

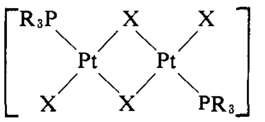
(b) When *trans*-$[PtCl(Et_3P)_2(CF_2CF_2H)]$ is heated in benzene solution in a glass tube, *trans*-$[PtCl(Et_3P)_2(CF{=}CF_2)]$ and *trans*-$[PtCl(Et_3P)_2(C(CF_2H){=}CF_2)]$ are formed, but only traces ($\sim$5%) of *trans*-$[PtCl(CO)(Et_3P)_2]^+$ salts are detected. As noted above, elimination of hydrogen fluoride from the $-C_2F_4H$ group, followed by reaction with glass or silica, is not sufficient to account for the observed quantities of fluorosilicates and fluoroborates formed in the reaction of *trans*-$[PtHCl(Et_3P)_2]$ with C_2F_4. The small yield of carbonyl in the present case is presumably due therefore to the lack of sufficient quantities of suitable anions to form stable salts.

(c) However, complete conversion of *trans*-$[PtCl(Et_3P)_2(CF_2CF_2H)]$ to approximately equimolar quantities of *trans*-$[PtCl(Et_3P)_2(C(CF_2H){=}CF_2)]$ and *trans*-$[PtCl(CO)(Et_3P)_2][SiF_5]$ is observed on heating with SiF_4 and water in benzene solution. A similar complete conversion occurs when *trans*-$[PtCl(Et_2P)_2(CF{=}CF_2)]$ is heated with SiF_4 and water in benzene solution. In both these reactions the molar yield of carbonyl is somewhat less than that of fluorovinyl compound, but this is probably due to the relative instability of the carbonyl. When *trans*-$[PtCl(Et_3P)_2(CF{=}CF_2)]$ is heated separately with either SiF_4 or water, there is very little reaction and discussion of the mechanism of this stage is therefore extremely difficult. Possibly the first stage is an SiF_4-catalyzed addition of water to the double bond to give a Pt–CF(OH)–CF_2H grouping, followed by loss of HF to give Pt–CO–CF_2H. A transition state such as



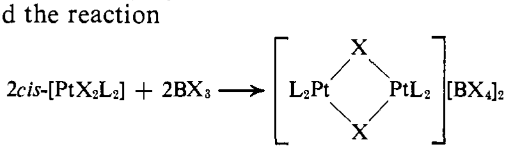
might then yield the observed products, but meaningful discussion must await further evidence.

Dimeric Platinum(II) Cations. Dimeric, halogen-bridged species of the type



R = alkyl or aryl; X = Cl, Br, or I

are well known,[7] but cationic species of this type have been mentioned only recently. Druce, *et al.*,[16] have reported the reaction



where L = $(n\text{-}Bu)_3P$ and X = Cl or Br.

As mentioned above, traces of salts of cation **1** are formed during the reaction of *trans*-$[PtHCl(Et_3P)_2]$ with C_2F_4. The reactions leading to the formation of these salts have been investigated and they may be represented by equations such as

$$2[PtHCl(Et_3P)_2] + 4SiF_4 \longrightarrow [Pt_2Cl_2(Et_3P)_4][SiF_5]_2 + 2[SiF_3H]$$

$$2[PtHCl(Et_3P)_2] + 4BF_3 \longrightarrow [Pt_2Cl_2(Et_3P)_4][BF_4]_2 + 2[BF_2H]$$

trans-$[PtHCl(Ph_3P)_2]$ reacts similarly with boron trifluoride.

The fluoroborate salt, and also its triphenylphosphine analog, may be obtained even more readily by reactions similar to those described by Druce, *et al.*, thus

$$2cis\text{-}[PtCl_2(R_3P)_2] + 4BF_3 \xrightarrow[CHCl_3]{25^\circ} [Pt_2Cl_2(R_3P)_4][BF_4]_2 + 2[BF_2Cl]$$

As suggested previously,[16] these reactions probably proceed *via* halide (or hydride) abstraction according to equations of the type

$$\begin{array}{l} \text{Pt-Cl} + BF_3 \longrightarrow Pt^+ + BF_3Cl^- \; [+ BF_3 \longrightarrow BF_4^- + BF_2Cl] \\ \qquad\qquad\qquad\quad\;\; \downarrow \\ \qquad\qquad\qquad\; \text{dimerizes} \end{array}$$

The salts of these dimeric cations are air-stable, nonhygroscopic, white, crystalline solids which have conductivities in nitromethane of the order expected for 2:1 electrolytes. The main features of their infrared spectra (Table I) require little comment except to note that the stretching absorptions of the Pt–Cl–Pt bridges (280 cm^{-1} for R = Et and 300 cm^{-1} for R = Ph) are broadened relative to the corresponding *cis*-$[PtCl_2(R_3P)_2]$ compounds (305 and 280 cm^{-1} for R = Et, and 310 and 280 cm^{-1} for R = Ph) but are not significantly lowered in frequency. It has been suggested[16] that the expected

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(12) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, *A*, 5075 (1962).

(13) R. F. Heck and D. S. Breslaw, *J. Amer. Chem. Soc.*, **83**, 4023 (1961).

(14) P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, **1**, 511 (1962).

(15) H. C. Clark, S. G. Furnival, and J. T. Kwon. *Can. J. Chem.*, **41**, 2889 (1963).

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Table I. Characteristic[a] Infrared Absorptions (cm^{-1}) of New Pt(II) Phosphine Complexes

Compd[b]	Pt–P stretch	Pt–Cl stretch	C–F stretch	Others
A	443 (m), 426 (m)	305 (m), 280 (m)		
B	415 (m)	343 (m)		
C	440 (w), 405 (m)	270 (m)		ν_{Pt-H} 2210 (s); δ_{Pt-H} 820 (m), 346 (s)
D	415 (m)	340 (m)		ν_{CO} 2110 (vs); $\nu^{13}{}_{CO}$ 2060 (vw); δ_{Pt-CO} 540 (s), 520 (w), 500 (m), 460 (m)
E	440 (m), 425 (m)	280 (w, b)		
F	410 (m)	325 (w, b)	1355 (w), 1165 (s)	640 (w), 595 (m), 545 (m), 520 (vw), 280 (m)
			1140 (m), 1080 (vs), 965 (s), 950 (s), 845 (vw), 790 (m)	
G	440 (w), 415 (w)	310 (m), 280 (m)		
H	420 (w)	335 (w)		
I	440 (w), 415 (w)	300 (w, b)		
J	425 (w)	Very weak	1240 (s), 1065 (s), 985 (vs), 970 (w, sh)	$\nu_{C=C}$ 1735 (m)
K	430 (w)	Very weak	1330 (w), 1240 (vw), 1120 (m), 1070 (m), 990 (m), 950 (m)	$\nu_{C=C}$ 1665 (s)
L	430 (w), 410 (w)		1400 (m), 1075 (s), 1040 (s)	790 (vs), 590 (w)

[a] Absorptions due to the phosphine ligands are omitted. [b] A = *cis*-$[PtCl_2(Et_3P)_2]$, B = *trans*-$[PtCl_2(Et_3P)_2]$, C = *trans*-$[PtHCl(Et_3P)_2]$, D = *trans*-$[PtCl(CO)(Et_3P)_2]^+$, E = $[Pt_2Cl_2(Et_3P)_4]^{2+}$, F = *trans*-$[PtCl(Et_3P)_2(CF_2CF_2H)]$, G = *cis*-$[PtCl_2(Ph_3P)_2]$, H = *trans*-$[PtCl(CO)(Ph_3P)_2]^+$, I = $[Pt_2Cl_2(Ph_3P)_4]^{2+}$, J = *trans*-$[PtCl(Ph_3P)_2(CF{=}CF_2)]$, K = *trans*-$[PtCl(Ph_3P)_2(C(CF_2H){=}CF_2)]$, L = $[Pt(Ph_3P)_2(C_2F_4)]$.

lowering in frequency is compensated by the positive charge on platinum.

Reaction of $[PtH(Ph_3P)_3][BF_4]$ with C_2F_4. The complexity of the reactions described above prompted us to examine the reactions with C_2F_4 of another system containing a Pt–H bond. However, the reaction of $[PtH(Ph_3P)_3][BF_4]$[17] with C_2F_4 is quite different and appears to proceed *via* a dissociative mechanism and not by interaction of the Pt–H bond with the olefin. The product $[Pt(Ph_3P)_2(C_2F_4)]$ is obtained in only about 30% yield at 95° in tetrahydrofuran solution, and the remaining 70% of the hydride is recovered unchanged. This yield is almost independent of time after the first 48 hr. The donor solvent is necessary since in acetone or benzene no reaction occurs even at 120°. These observations suggest a mechanism of the type

$$\begin{tikzcd}
{[PtH(Ph_3P)_3][BF_4]} \arrow[r, shift left, "THF"] & {[Pt(Ph_3P)_3] + HBF_4} \arrow[l, shift left] \arrow[d, shift left] \\
& {[Pt(Ph_3P)_2] + Ph_3P} \arrow[u, shift left] \arrow[d, shift left, "C_2F_4"] \\
& {[Pt(Ph_3P)_2(C_2F_4)]} \arrow[u, shift left]
\end{tikzcd}$$

This is consistent with the known dissociation[18] of $[Pt(Ph_3P)_3]$ and the previous preparation[19] of $[Pt(Ph_3P)_2(C_2F_4)]$ by reaction of C_2F_4 with $[Pt(Ph_3P)_4]$.

cis–trans **Isomerism in Square-Planar Complexes.** The configuration about platinum in the complexes of triethylphosphine reported above is established by comparison of their infrared and ^1H nmr spectra with those of compounds of known configuration.

(a) **^1H Nmr.** In part II of this series,[1] the methyl proton resonances of a series of bis(triethylphosphine)fluorovinylplatinum(II) complexes were interpreted as approximately 1:4:6:4:1 quintets arising from coupling with two methylene protons (J_{H-H} = 8 cps) and virtual coupling with two phosphorus nuclei (J_{P-H} = 7.8 cps) in a *trans* configuration. The methyl proton resonances of *trans*-$[PtCl_2(Et_3P)_2]$, *trans*-$[PtHCl(Et_3P)_2]$, *trans*-$[PtBr_2(Et_3P)_2]$, and *trans*-$[PtHBr(Et_3P)_2]$ in methylene chloride solution have now been recorded and similarly approximate to 1:4:6:4:1 quintets centered at *ca.* −1.2 ppm. The methylene proton resonances in these four compounds are broad (width at half-height, 25 cps) with complex, poorly resolved fine structure centered at *ca.* −1.9 ppm.

For two phosphorus nuclei in a *cis* configuration virtual coupling is not expected and the methyl proton resonance should be split by only one phosphorus nucleus. The coupling to this phosphorus is expected to be twice the apparent P–H coupling constant observed for the two virtually coupled phosphorus nuclei in the *trans* configuration.[20] Thus the expected methyl proton resonance for a *cis* configuration is a doublet arising from coupling with phosphorus (J_{P-H} = 16 cps) further split by coupling with two methylene protons (J_{H-H} = 8 cps) into two overlapping triplets giving a 1:2:2:2:1 quintet. In methylene chloride solution the observed spectra for *cis*-$[PtCl_2(Et_3P)_2]$ and *cis*-$[PtBr_2(Et_3P)_2]$ approximate to this description with J_{P-H} = 17 and J_{H-H} = 7.5 cps, the quintets being centered *ca.* −1.2 ppm. The methylene proton resonances for these two compounds approximate to septets centered *ca.* −2.1 ppm, but there is clearly additional unresolved fine structure within the multiplet.

The above interpretations are approximate since they omit, for example, any consideration of coupling with ^{195}Pt. However, although the observed integrated intensities deviated somewhat from the ideal ratios, the spectra of both methyl and methylene protons allowed a facile, qualitative distinction between *cis* and *trans* configurations.

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(18) R. Ugo, F. Cariati, and G. La Monica, *Chem. Commun.*, 868 (1966).

(19) M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *ibid.*, 502 (1966).

(20) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc., A*, 770 (1966).

Table II. Infrared Absorptions (cm^{-1}) due to the Vinylic Groups in Pt(II) Complexes

Compound	$\nu_{C=C}$	C–F stretching			
$[SnMe_3(CF{=}CF_2)]^a$	1712 (s)	1278 (sh)	1268 (s)	1110 (s)	998 (s)
$[PtCl(Et_3P)_2(CF{=}CF_2)]$	1724 (s)		1233 (s)	1037 (vs)	980 (vs)
$[PtCl(Ph_3P)_2(CF{=}CF_2)]$	1735 (s)		1240 (s)	1065 (s)	985 (vs), 940 (wsh)
$[PtCl(Et_3P)_2(C(CF_2H){=}CF_2)]$	1643 (s)	1344 (m)[b]	1336 (m)[b]	1114 (m)	1075 (s), [~1000],[c] 952 (m)
$[PtCl(Ph_3P)_2(C(CF_2H){=}CF_2)]$	1665 (s)	1330 (w)	1240 (vw)	1120 (m)	1070 (m), 990 (m), 950 (m)

[a] A. D. Beveridge. H. C. Clark, and J. T. Kwon, *Can. J. Chem.*, **44**, 179 (1966). [b] Previously assigned as ligand mode. [c] Obscured by ligand.

The ethyl proton resonances of $[PtCl(CO)(Et_3P)_2][SiF_5]$ and its BF_4^- analog and of $[PtCl(Et_3P)_2(C_2F_4H)]$ in deuteriochloroform solution are similar to those described above for *trans* compounds, and they are assigned this configuration. The ethyl proton resonances in $[Pt_2Cl_2(Et_3P)_4][SiF_5]_2$ and its BF_4^- analog in methanol solution are similar to those described above for *cis* compounds.

(b) **Infrared.** Some features of the spectra of the complexes studied are included in Tables I and II. *cis*- and *trans*-$[PtBr_2(Et_3P)_2]$ and *trans*-$[PtHBr(Et_3P)_2]$ are not included but have spectra very similar to the analogous chloride complexes. The spectra at 600–250 cm^{-1} for the dihalides are in good agreement with the results of Goggin and Goodfellow,[21] and *cis* and *trans* configurations can be distinguished on the basis of the Pt–P stretching modes. These workers[21] did not report a frequency for the Pt–Br antisymmetric stretching mode in *trans*-$[PtBr_2(Et_3P)_2]$ which we observe at 255 cm^{-1}. The Pt–Br stretching modes in the corresponding *cis* isomer are below 240 cm^{-1}.

For complexes of the type $[MXY(Et_3P)_2]$, Goggin and Goodfellow showed that although the symmetric P–Pt–P stretching mode is formally infrared active in both *cis* and *trans* configurations; it is of very low intensity in the *trans* case and a distinction is still possible. This appears to hold for most of the complexes studied below since those shown by ^1H nmr to have a *trans* configuration show only one absorption between 450 and 400 cm^{-1}. This is not true, however, when X = H since for *trans*-$[PtHCl(Et_3P)_2]$ and the corresponding hydrido bromide two bands are observed.

The situation for complexes of triphenylphosphine is less satisfactory. It is not possible to establish ^1H nmr criteria similar to those described above for complexes of triethylphosphine, and solubilities are too low for ^{31}P nmr studies. Triphenylphosphine has a very weak infrared absorption at 415 cm^{-1} which makes the interpretation of the Pt–P stretching region (450–400 cm^{-1}) of the spectrum difficult. However, the $[Pt_2Cl_2(Ph_3P)_4]^{2+}$ ion, $[Pt(Ph_3P)_2(C_2F_4)]$, and $[PtCl_2(Ph_3P)_2]$, all of which have *cis* configurations, show two absorptions in this region whereas $[PtCl(Ph_3P)_2(CF{=}CF_2)]$, $[PtCl(Ph_3P)_2(C(CF_2H){=}CF_2)]$, and the $[PtCl(CO)(Ph_3P)_2]^+$ ion show only one absorption. These facts, together with the analogy with the triethylphosphine system, make the *trans* configuration the most likely for the latter three complexes.

Experimental Section

Standard high-vacuum techniques were used for most reactions, which were performed in silica or thick-walled Pyrex glass tubes having volumes of about 50 ml, or in a stainless-steel autoclave having a volume of 100 ml. Infrared spectra were recorded with a Beckman IR 10 spectrophotometer and use was also made of a Beckman IR 7 spectrophotometer with cesium iodide optics. Solid samples were examined as Nujol or halocarbon oil mulls. All spectra were recorded from 4000 to 250 cm^{-1} with an accuracy of ±5 cm^{-1}, and were calibrated against polystyrene film or water vapor. ^1H and ^{19}F nmr spectra were recorded on Varian A-60 and DP 60 spectrometers. Chemical shifts are given in parts per million relative to TMS and $CFCl_3$ as external standards unless otherwise stated. Melting points were recorded by capillary methods and were corrected. Microanalyses were carried out by Dr. A. Bernhardt, Mulheim, West Germany, Dr. A. B. Gygli, Toronto, and the Schwarzkopf Microanalytical Laboratory, New York, N. Y. Conductance measurements were made with a dip-type cell of constant 0.1 cm^{-1} connected to a conductivity bridge, Model RC 18, Industrial Instruments Inc. The mass spectrum of *trans*-$[PtCl(CO)(Et_3P)_2][SiF_5]$ was obtained by Morgan Schaffer Ltd. of Montreal.

Tetrafluoroethylene was prepared and purified as previously described,[1] with SiF_4 being removed by several condensations onto moist potassium fluoride. *trans*-$[PtHCl(Et_3P)_2]$,[12] *cis*- and *trans*-$[PtCl_2(Et_3P)_2]$,[22] the corresponding hydridobromide[12] and dibromides,[22] *cis*-$[PtCl_2(Ph_3P)_2]$, and *trans*-$[PtHCl(Ph_3P)_2]$[23] were all prepared as previously described. Solvents were of reagent grade and were used as received except where dry solvents are specified below. Chloroform, SiF_4, and BF_3 were dried by vacuum distillation from suitable low-temperature baths; benzene was dried by vacuum distillation from a potassium mirror.

The infrared spectra of all products described below were recorded, and where additional characterization is not given these served to identify the products.

1. **Preparation of** *trans*-$[PtCl(CO)(Et_3P)_2][BF_4]$. *trans*-$[PtHCl(Et_3P)_2]$ (0.25 g) in 15 ml of benzene was heated with 7 drops (*ca.* 20% excess) of aqueous 48% fluoroboric acid in a stainless-steel autoclave under a pressure of 5 atm of carbon monoxide at 120° for 48 hr and then left at ambient temperature for 15 hr. The benzene was evaporated to about 5 ml, an equal volume of cyclohexane added, and the mixture filtered. *trans*-$[PtCl(CO)(Et_3P)_2][BF_4]$ (0.15 g, 73% yield relative to hydride consumed) remained as white crystals, insoluble in light petroleum, sparingly soluble in benzene, and very soluble in chloroform or methanol. The product was recrystallized from benzene or, better, from ethyl acetate containing a few drops of chloroform, mp 168–171°. *Anal.* Calcd for $C_{13}H_{30}BClF_4OP_2Pt$: C, 26.9; H, 5.2; B, 1.86; F, 13.1; P, 10.7. Found: C, 26.8; H, 5.2; B, 2.0; F, 13.3; P, 10.5. *trans*-$[PtHCl(Et_3P)_2]$ (0.08 g, 32% recovery) was recovered by evaporation of the benzene–cyclohexane filtrate.

Yields for this preparation were sometimes decreased by attack of the fluoroboric acid on the reaction vessel, particularly when the scale of reaction was increased. The resulting green material (probably iron(II) fluoroborate) was insoluble in chloroform and was thus easily separated from the product.

In addition to absorptions due to the cation (Table I), the infrared spectrum of *trans*-$[PtCl(CO)(Et_3P)_2][BF_4]$ had bands characteristic of BF_4^- at 1090 (s) and 1050 (vs, b) cm^{-1}. The ^{19}F nmr spectrum in chloroform solution was a 1:1:1:1 quartet centered at +151 ppm. The molar conductivity of a 0.6×10^{-3} *M* solution in nitromethane was 94.5 ohm^{-1} cm^2 at 25°. A sample stored in air for several months showed only slight evidence of decomposition.

2. **Preparation of** *trans*-$[PtCl(CO)(Ph_3P)_2][BF_4]$. *cis*-$[PtCl_2(Ph_3P)_2]$ (0.89 g) in 15 ml of chloroform was heated with boron trifluoride (2.4 g) under a pressure of 15 atm of CO at 110° for 36 hr in a stainless-steel autoclave. All volatile materials were removed under vacuum and the residue recrystallized from benzene as *trans*-$[PtCl(CO)(Ph_3P)_2][BF_4]$ (yield 0.6 g, 61%). The characterization of this compound is described below in reaction 6.

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[21] P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc., A.*, 1462 (1966).

[22] K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **229**, 238 (1936).

[23] J. C. Bailar, Jr., and H. Itatani, *Inorg. Chem.*, **4**, 1618 (1965).

3. **Preparation of $[Pt_2Cl_2(Et_3P)_4][BF_4]_2$.** *cis*-$[PtCl_2(Et_3P)_2]$ (0.175 g) in 5 ml of dry chloroform was shaken with dry boron trifluoride (0.3 g) at 25° in a silica tube. An almost colorless oil precipitated at once, but shaking was continued for 15 hr. The products were evaporated to dryness under vacuum and the residue extracted with methanol. Evaporation of the extract to small bulk, followed by addition of diethyl ether and light petroleum, gave 0.18 g (yield, 88%) of $[Pt_2Cl_2(Et_3P)_4][BF_4]_2$ as a white precipitate, insoluble in benzene or chloroform but soluble in methanol. The compound had no sharp melting point but decomposed about 250°. It was recrystallized by solution in the minimum volume of methanol and addition of an equal volume of diethyl ether followed by light petroleum to the cloud point; crystallization then occurred. *Anal.* Calcd for $C_{24}H_{60}B_2Cl_2F_8P_4Pt_2$: C, 26.0; H, 5.5; Cl, 6.4. Found: C, 25.8; H, 5.6; Cl, 6.2. The molar conductivity of a 0.3 × 10^{-3} *M* solution in nitromethane was 170 ohm^{-1} cm^2 at 25°.

In addition to absorptions due to the cation (see Table I), the infrared spectrum of this product had absorptions characteristic of BF_4^- at 1090 (sh), 1050 (vs, b), and 515 (m) cm^{-1}.

4. **Preparation of $[Pt_2Cl_2(Ph_3P)_4][BF_4]_2$.** *cis*-$[PtCl_2(Ph_3P)_2]$ (0.32 g) in 40 ml of chloroform was shaken with boron trifluoride (0.3 g) at 25° in a silica tube. A yellowish oil precipitated at once, but shaking was continued for 12 hr before evaporation of the products under vacuum. The residue was washed with small volumes of methanol leaving 0.3 g (yield, 85%) of $[Pt_2Cl_2(Ph_3P)_4][BF_4]_2$ as a white powder, insoluble in light petroleum and slightly soluble in chloroform or methanol. The product was recrystallized as described above for the triethylphosphine analog. *Anal.* Calcd for $C_{72}H_{60}B_2Cl_2F_8P_4Pt_2$: C, 51.3; H, 3.6; Cl, 4.2. Found: C, 50.5; H, 3.6; Cl, 3.7. The molar conductivity of a 0.5 × 10^{-3} *M* solution in nitromethane was 174 ohm^{-1} cm^2 at 25°. In addition to absorptions due to the cation (see Table I), the infrared spectrum of this product had absorptions characteristic of BF_4^- at 1080 (s, b) and 1045 (vs, b) cm^{-1}.

The same product resulted in 70% yield from reaction of *trans*-$[PtHCl(Ph_3P)_2]$ with BF_3 at 80°.

5. **Reaction of *trans*-$[PtHCl(Et_3P)_2]$ with C_2F_4. (a) In Glass.** *trans*-$[PtHCl(Et_3P)_2]$ (1.0 g) in 20 ml of benzene was heated with C_2F_4 (1.0 g) at 120° for 48 hr in a glass tube. Silicon tetrafluoride was detected in the excess C_2F_4 by infrared spectroscopy, and traces of products having absorption in the C–H and C–F stretching regions at 3000 and 1140 cm,$^{-1}$ respectively, were also observed. These products were present in very small quantity and were of similar volatility to C_2F_4 and consequently could not be identified. Some cyclo-C_4F_8 was observed but this also resulted when C_2F_4 was heated alone under similar conditions.

The benzene solution was evaporated to about 5 ml, an equal volume of cyclohexane added, and the mixture filtered. The white precipitate was washed with cyclohexane and extracted with chloroform leaving 0.01 g of a white, water-soluble residue whose infrared spectrum showed only absorptions characteristic of SiF_6^{2-} and BF_4^-, probably as potassium salts resulting from etching of the glass tube. Evaporation of the chloroform extract gave 0.29 g (yield, 23%) of a mixture of *trans*-$[PtCl(CO)(Et_3P)_2][SiF_5]$ with its BF_4^- analog as white crystals. *Anal.* Calcd for $C_{13}H_{30}Cl$ in a species of molecular wt 590: C, 26.5; H, 5.1; Cl, 6.0. Found: C, 26.5; H, 4.9; Cl, 6.0. Evaporation of the benzene–cyclohexane filtrate gave a mixture of *trans*-$[PtCl(Et_3P)_2(CF{=}CF_2)]$ with *trans*-$[PtCl(Et_3P)_2(C(CF_2H){=}CF_2)]$ in an approximately 1:2 ratio. The characterization of these fluorovinylplatinum(II) compounds has been described.[1]

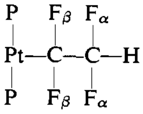
(b) **In Glass.** The previous reaction was repeated with similar quantities and work-up procedure except that heating was at 90° for 30 hr. The products were similar except that no SiF_4, K_2SiF_6, or KBF_4 was detected, the yield of *trans*-$[PtCl(CO)(Et_3P)_2]^+$ was less than 8%, the ratio of *trans*-$[PtCl(Et_3P)_2(CF{=}CF_2)]$ to *trans*-$[PtCl(Et_3P)_2(C(CF_2H){=}CF_2)]$ was approximately 3:1, and the presence of *trans*-$[PtCl(Et_3P)_2(C_2F_4H)]$ in the cyclohexane-soluble products was detected. Moreover, 0.06 g (yield 5%) of a mixture of $[Pt_2Cl_2(Et_3P)_4][SiF_5]_2$ with its BF_4^- analog was obtained as white crystals, insoluble in benzene, cyclohexane, or chloroform, but soluble in methanol.

(c) **In Silica.** *trans*-$[PtHCl(Et_3P)_2]$ (2.0 g) in 20 ml of benzene was heated with C_2F_4 (2.0 g) at 120° for 48 hr in a silica tube. A few grams of chromatographic silica gel, previously dried at 800° in a muffle furnace, was added to provide a large reactive surface. The work-up procedure and products were identical with reaction a above except that K_2SiF_6 and KBF_4 were not formed and that evaporation of the chloroform extract gave 0.76 g (yield 29%) of *trans*-$[PtCl(CO)(Et_3P)_2][SiF_5]$ as white crystals with similar solubility properties to the analogous fluoroborate described in reaction 1 above. It was recrystallized from ethyl acetate containing a few drops of chloroform, mp 147–150°. *Anal.* Calcd for $C_{13}H_{30}ClF_5OP_2PtSi$: C, 25.3; H, 4.9; Cl, 5.7; F, 15.4; P, 10.0; Pt, 31.6; Si, 4.5. Found: C, 25.2; H, 4.9; Cl, 5.8; F, 15.2; P, 9.9; Pt, 32.2; Si, 4.7.

In addition to absorptions due to the cation, the infrared spectrum of this product had absorptions characteristic of SiF_5^- at 870 (vs, b), 780 (vs, b), 475 (s), and 440 (s) cm^{-1}. The ^{19}F nmr spectrum in chloroform solution was a single line at +137.5 ppm and with width at half-height 4 cps. The molar conductivity of a 0.7 × 10^{-3} *M* solution in nitromethane was 86 ohm^{-1} cm^2 at 25°. The high-resolution mass spectrum of the pyrolysis products of this compound had a strong peak at mass 27.9950 (theoretical for $^{12}C^{16}O$ is 27.9949). A sample stored in air for several months showed only slight evidence of decomposition.

(d) **In Stainless Steel.** *trans*-$[PtHCl(Et_3P)_2]$ (0.6 g) in 10 ml of benzene was heated with C_2F_4 (1.5 g) at 120° for 48 hr in a stainless steel autoclave. After removal of excess C_2F_4 the benzene solution was evaporated and the resulting yellow oil extracted with methanol. Evaporation of the methanol extract gave an oil which slowly formed white crystals of *trans*-$[PtCl(Et_3P)_2(CF_2CF_2H)]$. These were washed with very small volumes of methanol, collected (yield 0.42 g, 58%), and recrystallized from methanol using a seed crystal to aid crystallization. The product was extremely soluble in light petroleum, benzene, or chloroform but rather less soluble in methanol, mp 78–79°. *Anal.* Calcd for $C_{14}H_{31}ClF_4P_2Pt$: C, 29.6; H, 5.5; F, 13.4. Found: C, 29.6; H, 5.6; F, 13.7.

The infrared absorptions (Table I) due to C–F vibrations are similar to those observed in other compounds containing an M–C_2F_4H grouping.[14,24–26] In addition to the expected ethyl proton resonance, the ^1H nmr spectrum in deuteriochloroform solution consisted of a 1:2:1 triplet (J = 56 cps) centered at −5.43 ppm, each component of which was split into a 1:2:1 triplet (5 cps). The integrated intensities of the triplets and the ethyl resonance were in the ratio 0.9:30. The ^{19}F nmr spectrum in $CFCl_3$ solution consisted of two multiplets of equal intensity centered at +72.3 and +126.3 ppm. The high-field resonance was a broad doublet (J = 55.5 cps; width at half-height, 11 cps) whose ^{195}Pt (33% abundance) satellites (coupling constant, 106 cps) overlapped the main peaks producing a 1:4:4:1 quartet. The low-field resonance was a 1:2:1 triplet (coupling constant, 23.2 cps) with ^{195}Pt satellites (coupling constant, 470 cps). Each component of the triplet was split into a doublet (coupling constant, 4.8 cps) and again into overlapping triplets (coupling constant, 4.5 cps) producing a 1:3:3:1 quartet. These spectra are consistent with the following interpretation



$$\begin{array}{ccccccc} P & & F_\beta & & F_\alpha & & \\ | & & | & & | & & \\ Pt & — & C & — & C & — & H \\ | & & | & & | & & \\ P & & F_\beta & & F_\alpha & & \end{array}$$

The high-field resonance is due to the α fluorine atoms and the low-field resonance to the β fluorine atoms. The coupling constants are $J_{H-F\alpha} = 55.5$, $J_{H-F_\beta} = 4.8$, $J_{F\alpha-F_\beta} = 4.5$, $J_{Pt-F\alpha} = 106$, $J_{Pt-F_\beta} = 470$, and $J_{P-F_\beta} = 23.2$ cps. J_{Pt-H} was not observed because of poor signal-to-noise ratio, but all other couplings are less than 2 cps. The magnitudes of the various coupling constants and the assignments of the spectra are in agreement with previous results on other compounds containing an M–CF_2CF_2H grouping.[14,24–26]

6. **Reaction of *trans*-$[PtHCl(Ph_3P)_2]$ with C_2F_4.** *trans*-$[PtHCl(Ph_3P)_2]$ (0.7 g) in 25 ml of benzene was heated with C_2F_4 (0.5 g) at 120° for 48 hr in a glass tube. The gaseous products were similar to those obtained in reaction 5a above except that infrared absorptions at 3000 and 1140 cm^{-1} were not observed. The benzene solution was evaporated and the residues were extracted with chloroform, leaving 0.005 g of white residue showing infrared absorptions characteristic of SiF_6^{2-} and BF_4^-. Fractional precipitation by addition of light petroleum to the chloroform extract gave 0.15 g (yield 19%) of *trans*-$[PtCl(CO)(Ph_3P)_2][BF_4]$ as the first precipitate. This product was recrystallized from benzene as white crystals, insoluble in light petroleum but soluble in chloroform or methanol, mp 278–282° dec. *Anal.* Calcd for $C_{37}H_{30}BClF_4OP_2Pt$: C, 51.2; H, 3.5; B, 1.24. Found: C, 51.2; H, 3.7; B, 1.29. In addition to ab-

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(24) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 4, 93 (1965).

(25) P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

(26) J. B. Wilford, A. Forster, and F. G. A. Stone, *ibid.*, 6519 (1965).

sorptions due to the cation (Table I), the infrared spectrum of this product had absorptions characteristic of BF$_4^-$ at 1090 (s) and 1050 (vs, b) cm^{-1}. The molar conductivity of a 1.0 × 10^{-3} *M* solution in nitromethane was 74 ohm^{-1} cm^2 at 25°.

Evaporation of the chloroform–petroleum filtrate gave 0.45 g of an approximately 3:1 mixture of *trans*-[PtCl(Ph$_3$P)$_2$(CF=CF$_2$)] with *trans*-[PtCl(Ph$_3$P)$_2$(C(CF$_2$H)=CF$_2$)]. These products were separated by chromatography on Florisil using 50% benzene in chloroform as eluent and recrystallized from an ethanol–chloroform mixture as white needles, insoluble in light petroleum, slightly soluble in benzene, and soluble in chloroform, mp 253–255 and 248–250°, respectively. *Anal.* Calcd for C$_{38}$H$_{30}$ClF$_3$P$_2$Pt: C, 54.5; H, 3.6; F, 6.8. Found: C, 55.0; H, 3.8; F, 7.6. Calcd for C$_{39}$H$_{31}$ClF$_4$P$_2$Pt: C, 54.0; H, 3.6. Found: C, 53.9; H, 3.5. The patterns of C–F absorptions (Table II) are similar to those reported previously[1] for their triethylphosphine analogs. Their solubilities were too low for ^{19}F nmr studies. The above reaction was repeated twice (a) with heating at 80° for 48 hr in a glass tube, (b) with heating at 120° for 48 hr in a silica tube to which a few grams of chromatographic silica gel (previously dried at 800° in a muffle furnace) had been added. In both cases *trans*-[PtCl(Ph$_3$P)$_2$(CF=CF$_2$)] and *trans*-[PtCl(Ph$_3$P)$_2$(C(CF$_2$H)=CF$_2$)] were formed, but no salts of *trans*-[PtCl(CO)(Ph$_3$P)$_2$]$^+$ were detected.

7. Other Reactions of ***trans*-[PtHCl(Et$_3$P)$_2$]. (a) With C$_2$F$_4$ and SiF$_4$.** *trans*-[PtHCl(Et$_3$P)$_2$] (0.5 g) in 10 ml of benzene was heated with C$_2$F$_4$ (1.0 g) and SiF$_4$ (1.0 g) at 85° for 60 hr in a stainless-steel autoclave and then left at ambient temperature for 15 hr. The gaseous products were similar to those in reaction 5a above. The benzene solution was filtered and the residue washed with chloroform leaving 0.2 g (yield 32%) of [Pt$_2$Cl$_2$(Et$_3$P)$_4$][SiF$_5$]$_2$ as whitish crystals with similar solubility properties to the BF$_4^-$ analog described above. It was recrystallized by the same method used for the BF$_4^-$ analog, mp 206–208°. *Anal.* Calcd for C$_{24}$H$_{60}$Cl$_2$F$_{10}$P$_4$Pt$_2$Si$_2$: C, 24.4; H, 5.1; F, 16.1. Found: C, 25.1; H, 5.2; F, 15.1. The molar conductivity of a 0.5 × 10^{-3} *M* solution in nitromethane was 154 ohm^{-1} cm^2 at 25°. In addition to absorptions due to the cation, the infrared spectrum of this product had absorptions characteristic of SiF$_5^-$ at 875 (vs, b), 775 (vs, b), 475 (s), and 440 (s) cm^{-1}.

The benzene–chloroform filtrate was evaporated and the residue extracted with light petroleum leaving 0.07 g (yield 11%) of *trans*-[PtCl(CO)(Et$_3$P)$_2$][SiF$_5$] as white crystals identified by infrared spectroscopy. The petroleum extract was evaporated, and the residues were separated by chromatography on Florisil, using benzene followed by chloroform as eluent. The following products were obtained: *trans*-[PtCl(Et$_3$P)$_2$(CF=CF$_2$)], *ca.* 0.04 g; *trans*-[PtCl(Et$_3$P)$_2$(C(CF$_2$H)=CF$_2$)], *ca.* 0.16 g; *trans*-[PtCl(Et$_3$P)$_2$(C$_2$F$_4$H)], *ca.* 0.02 g; and *ca.* 0.08 g of an unknown fluorocarbon–platinum complex whose infrared spectrum had C–F absorptions at 1300 (m), 1280 (w), 1175 (s), 1160 (s), 1130 (w), 1045 (s), 995 (s), 975 (m), and 915 (s) cm^{-1}. Overlap of fractions from the chromatography column prevented the isolation of sufficient material for characterization of this last product.

(b) With SiF$_4$. *trans*-[PtHCl(Et$_3$P)$_2$] (0.2 g) in 10 ml of benzene was heated with SiF$_4$ (1.0 g) at 85° for 48 hr in a stainless-steel autoclave, and then left at ambient temperature for 15 hr. After removal of excess SiF$_4$ under vacuum, the benzene solution was evaporated and the residues extracted with light petroleum and washed with chloroform leaving 0.03 g (yield 12%) of [Pt$_2$Cl$_2$(Et$_3$P)$_4$][SiF$_5$]$_2$ as white crystals. Evaporation of the petroleum extract gave 0.17 g (85% recovery) of *trans*-[PtHCl(Et$_3$P)$_2$].

(c) With BF$_3$. *trans*-[PtHCl(Et$_3$P)$_2$] (0.1 g) in 5 ml of dry benzene was heated with dry BF$_3$ (0.3 g) at 40° for 60 min in a silica tube. A brownish oil precipitated. A procedure identical with that in reaction 3 above gave 0.1 g (yield 86%) of [Pt$_2$Cl$_2$(Et$_3$P)$_4$][BF$_4$]$_2$. Very little reaction was observed when the reaction was repeated at 25° for 20 hr.

8. Reactions of ***trans*-[PtCl(CO)(Et$_3$P)$_2$]$^+$. (a).** A sample of the mixture of *trans*-[PtCl(CO)(Et$_3$P)$_2$][SiF$_5$] with its BF$_4^-$ analog obtained from reaction 5a above was dissolved in methanol with an approximately equimolar quantity of sodium tetraphenylborate. Addition of water gave a yellowish precipitate of *trans*-[PtCl(CO)(Et$_3$P)$_2$][BPh$_4$]. Evaporation of the methanol–water filtrate over NaOH in a vacuum desiccator gave an oily residue which was washed with chloroform leaving a mixture of Na$_2$SiF$_6$ and NaBF$_4$ as a white powder.

When this reaction was repeated with a sample of *trans*-[PtCl(CO)(Et$_3$P)$_2$][SiF$_5$] obtained from reaction 5c above, the only water-soluble product was Na$_2$SiF$_6$.

(b). Solid samples containing the *trans*-[PtCl(CO)(Et$_3$P)$_2$]$^+$ ion dissolved with effervescence in a chloroform solution of Et$_4$NCl. A sample of the mixture of SiF$_5^-$ and BF$_4^-$ salts obtained from reaction 5a above was dissolved in chloroform with an approximately equimolar quantity of Et$_4$NCl and the solution evaporated. The residue was extracted with water and the extract evaporated over NaOH in a vacuum desiccator leaving a mixture of Et$_4$NBF$_4$ and Et$_4$NSiF$_5$ as a white powder. In addition to absorptions characteristic of Et$_4$N$^+$ and BF$_4^-$, the infrared spectrum of this product had absorptions characteristic of SiF$_5^-$ at 870 (vs, b), 780 (vs, b), 475 (s), and 440 (s) cm^{-1}. The water-insoluble fraction was *cis*-[PtCl$_2$(Et$_3$P)$_2$]. After recrystallization from ethanol it had mp 192–194° (lit.[22] 192–193°), and a mixture with a genuine sample had mp 193–195°.

The reaction was repeated using a pure sample of *trans*-[PtCl(CO)(Et$_3$P)$_2$][BF$_4$], and *cis*-[PtCl$_2$(Et$_3$P)$_2$] was again isolated.

A sample of *trans*-[PtCl$_2$(Et$_3$P)$_2$] did not isomerize when subjected to a similar procedure of solution, evaporation, and extraction in the presence of Et$_4$NCl.

(c). A sample of *trans*-[PtCl(CO)(Et$_3$P)$_2$][BF$_4$] was stirred in chloroform solution for 20 hr under 1 atm of hydrogen. No hydrogen absorption was detected and the sample was recovered unchanged.

(d). *trans*-[PtCl(CO)(Et$_3$P)$_2$][BF$_4$] (0.05 g) in 5 ml of dry benzene was shaken with dry HCl (0.15 g) at 25°. The sample dissolved (the carbonyl is only sparingly soluble in pure benzene), but an infrared spectrum of the solution showed no evidence of interaction with the HCl. The HCl stretching absorption was shifted to 2750 cm^{-1}, but this also occurred in benzene solution in the absence of carbonyl. After shaking for 2 weeks the carbonyl was recovered unchanged except for traces of decomposition.

(e). An approximately 1:1 molar mixture of *trans*-[PtCl(CO)(Et$_3$P)$_2$][BF$_4$] with benzoyl azide was dissolved in chloroform. The infrared spectrum of the solution showed strong bands at 2135 and 2105 cm^{-1} due to azide and carbonyl, respectively. This spectrum was unchanged after 3 hr at 25° (the carbonyl absorption decayed slowly due to attack by chloride ion if the solution was kept in an NaCl cell but did not change when the solution was stored in glass) and was still unchanged after refluxing the chloroform for 5 min. After heating the solution at 55° for 18 hr in a sealed glass tube the carbonyl band was unchanged, the azide band was almost gone, and a new band had appeared at 2260 cm^{-1}. However, similar spectral changes occurred when benzoyl azide was heated alone in chloroform under the same conditions.

The reaction of [PtCl(CO)(Ph$_3$P)$_2$][BF$_4$] with benzoyl azide gave similar results.

9. Reactions of ***trans*-[PtCl(Et$_3$P)$_2$(CF$_2$CF$_2$H)].** *trans*-[PtCl(Et$_3$P)$_2$(CF$_2$CF$_2$H)] (0.043 g) was heated in 3 ml of benzene at 120° for 48 hr in a Pyrex glass tube. The solution was evaporated, a trace of SiF$_4$ being detected in the gaseous products, and the residue extracted with light petroleum followed by chloroform. Evaporation of the extracts gave 0.038 g of a mixture of *trans*-[PtCl(Et$_3$P)$_2$(CF=CF$_2$)] with *trans*-[PtCl(Et$_3$P)$_2$(C(CF$_2$H)=CF$_2$)] from the light petroleum and 0.003 g of *trans*-[PtCl(CO)(Et$_3$P)$_2$]$^+$ salts from the chloroform.

A repeat reaction, using 0.07 g of *trans*-[PtCl(Et$_3$P)$_2$(CF$_2$CF$_2$H) to which 0.3 g of SiF$_4$, a few drops of water, and 3 ml of benzene were added in a silica tube under similar conditions, gave 0.035 g of *trans*-[PtCl(Et$_3$P)$_2$(C(CF$_2$H)=CF$_2$)] and 0.025 g of *trans*-[PtCl(CO)(Et$_3$P)$_2$][SiF$_5$].

10. Reactions of ***trans*-[PtCl(Et$_3$P)$_2$(CF=CF$_2$)].** *trans*-[PtCl(Et$_3$P)$_2$(CF=CF$_2$)] from reaction 5 above was separated from *trans*-[PtCl(Et$_3$P)$_2$(C(CF$_2$H)=CF$_2$)] by chromatography on Florisil using benzene as eluent. The required compound was eluted and recrystallized from light petroleum. The other vinyl compound remained on the column but could be eluted with chloroform.

trans-[PtCl(Et$_3$P)$_2$(CF=CF$_2$)] (0.05 g) in 5 ml of benzene to which a few drops of water had been added was heated with SiF$_4$ (0.5 g) at 120° for 48 hr in a silica tube. After removal of excess SiF$_4$, the solution was evaporated and the residues were extracted with light petroleum and then with chloroform. Evaporation of the petroleum extract gave 0.025 g (yield 45%) of *trans*-[PtCl(Et$_3$P)$_2$(C(CF$_2$H)=CF$_2$)] and evaporation of the chloroform extract gave 0.02 g (yield 35%) of *trans*-[PtCl(CO)(Et$_3$P)$_2$][SiF$_5$].

When *trans*-[PtCl(Et$_3$P)$_2$(CF=CF$_2$)] in benzene solution was heated at 120° for 48 hr with SiF$_4$ or H$_2$O separately, very little reaction was observed.

11. Reaction of [PtH(Ph$_3$P)$_3$][BF$_4$] with C$_2$F$_4$. [PtH(Ph$_3$P)$_3$][BF$_4$] was prepared as previously described.[17] After recrystallization from acetone it had mp 208–211° (lit.[17] 203–205°). *Anal.* Calcd for C$_{54}$H$_{46}$BF$_4$P$_3$Pt: C, 60.6; H, 4.3. Found: C, 60.6;

H, 4.2. ν_{Pt-H} 2110 cm^{-1} (lit.[17] 2112 cm^{-1}). The ^{19}F nmr spectrum in methylene chloride solution was a 1:1:1:1 quartet (J = 1.5 cps) centered at +162 ppm.

[PtH(Ph$_3$P)$_3$][BF$_4$] (0.5 g) in 10 ml of tetrahydrofuran was heated with C_2F_4 (0.5 g) at 90° for 48 hr. The solid slowly dissolved giving a clear yellow solution. After removal of excess C_2F_4, the THF was evaporated and the residues extracted with small volumes of methanol; 0.1 g (yield 26%) of [Pt(Ph$_3$P)$_2$(C$_2$F$_4$)] remained as a white powder which was recrystallized from acetone, mp 208–209° dec (lit.[19] 218–220° dec). *Anal.* Calcd for $C_{38}H_{30}F_4P_2Pt$: C, 55.7; H, 3.7. Found: C, 55.7, H, 3.5. The ^{19}F nmr spectrum in methylene chloride solution consisted of a complex resonance centered at +130 ppm (lit.[19] +131.1 ppm). The infrared spectrum was identical with that of a sample prepared by the method of Green, *et al.*[19]

Evaporation of the methanol extract gave 0.35 g of yellow oil which was mainly [PtH(Ph$_3$P)$_3$][BF$_4$]. Further separation of products could not be achieved by solubility or chromatographic methods.

When the reaction was repeated with heating for 2 weeks at 90°, the yield was 39%. A third reaction heated at 120° for 48 hr gave a 34% yield, and some C_2F_3H was detected in the excess C_2F_4. The methanol extract in this last case probably contained other products although some [PtH(Ph$_3$P)$_3$][BF$_4$] was present. Separation of these products was not achieved.

Mechanisms of the Inner-Sphere Electron-Exchange Reactions of Chromium(II) and Aquocyano Complexes of Chromium(III)[1]

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Abstract: The kinetics of electron exchange between $Cr(H_2O)_6^{2+}$ and $(H_2O)_5CrCN^{2+}$ was studied in aqueous perchlorate solution. The exchange rate is first order in each chromium species; the second-order rate constant so defined obeys the relation $k_{ex} = k_1 + k_2/[H^+]$. The exchange rate was studied at temperatures between 5 and 35° to derive activation parameters. The reactions of Cr^{2+} with *cis*-$(H_2O)_4Cr(CN)_2^+$ and 1,2,3-$(H_2O)_3Cr(CN)_3$ both produced quantitative yields of $(H_2O)_5CrCN^{2+}$. The kinetics of each reaction was studied as a function of $[Cr^{2+}]$ and $[H^+]$. Minor spectral discrepancies at some wavelengths indicated the possible presence of a metastable reaction intermediate, but the main reaction of chromium(II) with the cyano complexes followed a mixed second-order rate law, independent of $[H^+]$. The rate constants are: $Cr(CN)_2^+$ 4.19 and $Cr(CN)_3$ 4.56 M^{-1} sec^{-1} at 25.0° and unit ionic strength. The mechanisms of the cyanide-bridged exchange reactions are discussed. The principle of microscopic reversibility was applied in considering the possible role of the isocyano complex $CrNC^{2+}$ as an unstable intermediate in the exchange reaction. A comparison is made of the exchange mechanism and linkage isomerization mechanism of cyanide and thiocyanate complexes.

Several studies have been made of Cr(II)–Cr(III) electron-exchange reactions in which ligand X^- in the Cr(III) complex $(H_2O)_5CrX^{2+}$ serves as a bridging ligand in an inner-sphere mechanism.[2–7] The electron-transfer reaction occurring between cyanocobalt(III) complexes and chromium(II)[8] afforded solutions of the previously unknown[9,10] monocyanochromium(III) ion, $(H_2O)_5CrCN^{2+}$. The role of cyanide ion as a bridging ligand in inner-sphere electron-transfer reactions has been investigated in only a few instances, and it appeared of interest to study the kinetics and mechanism of the Cr(II)–Cr(III) exchange reaction involving $CrCN^{2+}$ (eq 1).

$$(H_2O)_5CrCN^{2+} + {}^*Cr_{aq}^{2+} = Cr_{aq}^{2+} + (H_2O)_5{}^*CrCN^{2+} \quad (1)$$

The cyano complex is the stable C-bonded form, yet it is possible that the electron-exchange reaction occurs *via* the isocyano species, $CrNC^{2+}$, since CN^- is unsymmetrical and ambidentate. This complex is known[8] to be a metastable intermediate in the reaction of L_5CoCN^{2+} and Cr^{2+}. Since $CrNC^{2+}$ reacts fairly rapidly with chromium(II), it could not exist at high concentrations. It has been possible to apply the principle of microscopic reversibility to two reactions we have studied, the exchange of Cr^{2+} and $CrCN^{2+}$ and the reaction, catalyzed linkage isomerization, of Cr^{2+} and $CrNC^{2+}$. Consideration of reverse reactions has allowed us to examine the possible role of $CrNC^{2+}$ as an unstable intermediate in the exchange reaction. In addition, the same considerations allow us to learn of the inherent stability of the two bonding modes for cyanide ion by placing a limit on the equilibrium quotient for the transformation $CrNC^{2+} = CrCN^{2+}$. Similar studies of exchange[3] and isomerization[11] have been reported for the thiocyanatochromium(III) complexes, and useful comparisons of mechanism in the two cases can be made.

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[1] (a) This work was performed in the Ames Laboratory (Contribution No. 2158) under the auspices of the U. S. Atomic Energy Commission. (b) Based on the Ph.D. thesis of J. P. B., Iowa State University, May 1967.

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