Chemistry of Metal Hydrides. I. Reactions of Some Platinum(II) Hydrides

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Abstract: The reactions of bis(triethylphosphine)chlorohydridoplatinum(II) with a number of unsaturated fluorocarbons are described. In all cases, new fluorovinyl derivatives of platinum(II) are formed, accompanied by the loss of hydrogen fluoride. In addition, a π-olefinic complex, $[(C_2H_5)_3P]_2PtHCl(\pi\text{-}C_2F_4)$, is isolated from the reaction with C_2F_4. Evidence is discussed which shows that this is the reaction intermediate, thus correlating these reactions with the catalytic behavior of many metal hydrides. The influence on the course of such reactions by the substituents on the central metal atom is also briefly considered.

The rapid development of metal hydride chemistry has been recently reviewed,[1,2] thus helping to emphasize the many areas where our understanding of the behavior of the metal–hydrogen bond is very limited. This is surprising in view of the major role which transition metal hydrides play in catalytic processes, such as the isomerization of olefins, homogeneous hydrogenations, and polymerization reactions. Clearly, the interaction of the metal hydride with the olefinic C=C system is a key step in many such processes, yet in very few instances have the addition products been characterized. It is well known[3] that ethylene and other olefins add reversibly across the Co–H bond of tetracarbonylcobalt hydride, and similarly ethylene undergoes a reversible addition[4] with $[(C_2H_5)_3P]_2PtHCl$. It is generally considered[2] that such reversible additions may well proceed *via* an unstable π-olefinic complex as intermediate, although such derivatives are now unknown.

In contrast to these reversible reactions of hydrocarbons, fluoroolefins do not add reversibly to metal hydrides. For example, tetrafluoroethylene has been shown[5–10] to add under very mild conditions to a variety of metal hydrides to give tetrafluoroethyl derivatives; thermal treatment causes decomposition and not regeneration of the hydride and olefin. Such reactions with unsaturated fluorocarbons have several advantages, among these being the considerable stability of transition metal–fluorocarbon derivatives which allows ready manipulation and easy characterization of the products. The latter is also simplified since both proton and ^{19}F nmr spectroscopy can be utilized. We have therefore examined the reactions of some platinum(II) hydrides, principally $[(C_2H_5)_3P]_2PtHCl$, with unsaturated fluorocarbons, with the joint purpose of examining new metal–fluorocarbon compounds and of gaining a better understanding of the chemical behavior of the Pt–H bond. The work is related to our previous studies of tin hydrides,[11] with which useful comparisons can be made.

Experimental Section

Standard high-vacuum techniques were used for most reactions, which were generally performed in thick-walled Pyrex glass tubes. Infrared spectra were recorded with a Beckman IR-10 double-beam spectrophotometer, while nmr spectra (^1H and ^{19}F) were obtained with Varian A-60 and DP-60 spectrometers. Melting points were taken by capillary methods and were not corrected. Molecular weights were measured by Regnault's method for volatile compounds and with a Mechrolab Model 301A vapor pressure osmometer for solids, usually in benzene solution. Micro analyses were carried out by Dr. A. Bernhardt, Mulheim, West Germany, and by the Schwarzkopf Microanalytical Laboratory, New York. Conductance measurements were made with a dipping-type cell of constant 0.66 cm^{-1} connected to a conductivity bridge, Model RC 16 B2, Industrial Instrument Inc.

Triethylphosphine, prepared by the method of Hibbert,[12] was used to obtain *cis*-dichlorobis(triethylphosphine)platinum(II), according to the method of Jensen.[13] The reduction of the latter compound to give *trans*-hydridochlorobis(triethylphosphine)platinum(II) was best achieved with potassium hydroxide in ethanol solution,[14] giving an 86% yield. Alternatively, *trans*-dichlorobis(triethylphosphine)platinum(II) could be reduced[4] to the same hydride, using $LiAlH_4$, although the best yield was then only 43%, mp 81°, lit.[14] mp 81–82°. *Anal.* Calcd for $C_{12}H_{31}ClP_2Pt$: C, 30.8; H, 6.7. Found: C, 30.98; H, 6.95.

Reactions of *trans*-$[(C_2H_5)_3P]_2PtHCl$. (a) With Tetrafluoroethylene. Tetrafluoroethylene was prepared by heating Teflon chips in a silica tube under vacuum at about 500° and was purified by vacuum fractionation through traps at −125 and −196°. The −196° fraction, which was spectroscopically free of perfluoropropene, was used in these reactions.

(i) *trans*-$[(C_2H_5)_3P]_2PtHCl$ (1.08 g, 2.32 mmoles) in 60 ml of cyclohexane was heated with tetrafluoroethylene (1.3 g, 13 mmoles) at 120° for 50 hr. Vacuum fractionation gave unreacted C_2F_4 and some silicon tetrafluoride at −196°, these being identified by their infrared spectra, and cyclohexane at −78 and −46°. The remaining solid was extracted with warm cyclohexane and filtered, and the residue was then extracted with chloroform.

The cyclohexane extract on evaporation gave a white solid whose infrared spectrum showed two peaks in the C=C stretching region at 1724 and 1643 cm^{-1}. Chromatography on Florisil with *n*-pentane–chloroform in a 1:2 ratio as eluent gave as the first product perfluorovinylchlorobis(triethylphosphine)platinum(II), ClPt[P-

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$(C_2H_5)_3]_2(CF{=}CF_2)$: mp 61°; 0.341 g, 29% yield; $\nu_{C=C}$ 1724 cm^{-1}. *Anal.* Calcd for $C_{14}H_{30}ClF_3P_2Pt$: C, 30.6; H, 5.48; F, 10.4. Found: C, 30.75; H, 5.67; F, 10.06. The second product was (1-difluoromethyl-2,2-difluorovinyl)chlorobis(triethylphosphine)platinum(II), $ClPt[P(C_2H_5)_3]_2[C(CF_2H){=}CF_2]$: mp 59°; 0.25 g, 20% yield; $\nu_{C=C}$ 1643 cm^{-1}. *Anal.* Calcd for $C_{15}H_{31}F_2ClP_2Pt$: C, 31.1; H, 5.35; F, 13.1. Found: C, 31.23; H, 5.52; F, 13.3.

The chloroform extract was filtered and cyclohexane was added. White crystals formed, which were separated and recrystallized from 2-methoxylethanol. This product was $PtHCl[P(C_2H_5)_3]_2(C_2F_4)$: 0.1 g, 8.2% yield; ν_{Pt-H} 2100 cm^{-1}. *Anal.* Calcd for $C_{14}H_{31}ClF_4P_2Pt$: F, 13.4; P, 10.9; Pt, 34.4. Found: F, 12.7; P, 10.72; Pt, 34.4. Conductivity data for this compound in nitrobenzene are given in Table I.

Table I. Conductivity Data for $[(C_2H_5)_3P]_2PtHCl(C_2F_4)$ in Nitrobenzene at 24°

$\sqrt{C}$, (mole/l.)$^{1/2}$	Λ, molar conductance, ohm^{-1} cm^2	$\sqrt{C}$, (mole/l.)$^{1/2}$	Λ, molar conductance, ohm^{-1} cm^2
0.0915	28.99	0.0364	32.28
0.0772	29.5	0.0294	32.9
0.0634	30.33	0.0271	33.6
0.0535	31.13	0.0238	34.0
0.0425	31.96	0.0212	34.4

(ii) *trans*-$[(C_2H_5)_3P]_2PtHCl$ (0.91 g, 1.95 mmoles) and C_2F_4 (1.0 g, 10 mmoles) were heated in benzene at 90° for 27 hr. Silicon tetrafluoride was observed spectroscopically in the excess unreacted tetrafluoroethylene, and the involatile solids were treated as in (i) above to give a mixture (0.41 g) of the two vinyl derivatives and $[(C_2H_5)_3P]_2PtHCl(C_2F_4)$, 0.15 g, 13.6% yield.

(b) **With Perfluoropropene.** The material supplied by Columbia Organic Chemical Co. was purified by vacuum fractionation to give at −126° a spectroscopically pure sample.

trans-$[(C_2H_5)_3P]_2PtHCl$ (0.884 g, 1.89 mmoles), in 55 ml of cyclohexane, and perfluoropropene (1.7 g, 11.3 mmoles) were heated in a sealed tube at 120° for 50 hr. After vacuum fractionation of the volatile products, appreciable amounts of silicon tetrafluoride were detected spectroscopically in the unreacted perfluoropropene. The involatile product was purified chromatographically on Florisil with chloroform as eluent and identified as (perfluoropropenyl)chlorobis(triethylphosphine)platinum(II), a pale yellow, involatile liquid, 0.474 g, 42% yield. *Anal.* Calcd for $C_{15}H_{30}F_5ClP_2Pt$: C, 30.15: H, 5.02; F, 15.9. Found: C, 30.22; H, 5.20; F, 15.67.

(c) **With Perfluorocyclobutene.** The compound (Peninsular ChemResearch Inc.) was spectroscopically pure and was used without further treatment.

trans-$[(C_2H_5)_3P]_2PtHCl$ (1.0 g, 2.14 mmoles), in 40 ml of cyclohexane, and perfluorocyclobutene (2.71 g, 16.75 mmoles) were heated in a sealed tube at 105° for 21 hr. On vacuum fractionation, silicon tetrafluoride was detected spectroscopically in the unreacted perfluorocyclobutene, and an involatile, pale yellow solid remained. This was purified by passage over a Florisil column with a 1:1 mixture of chloroform and petroleum ether to give white, crystalline (perfluorocyclobut-1-ene)chlorobis(triethylphosphine)platinum(II), $ClPt[P(C_2H_5)_3]_2C_4F_5$: 0.5 g, 39% yield; mp 67–68°. *Anal.* Calcd for $C_{16}H_{30}ClF_5P_2Pt$: C, 31.52; H, 4.93; F, 15.6. Found: C, 31.49; H, 4.52; F, 15.9.

(d) **With Trifluoroethylene.** Vacuum fractionation of the material supplied by Columbia Organic Chemical Co. gave a fraction condensing at −150° which was spectroscopically pure.

trans-$[(C_2H_5)_3P]_2PtHCl$ (1.26 g, 2.70 mmoles), in 60 ml of cyclohexane, and trifluoroethylene (13.1 mmoles) were heated in a sealed tube at 120° for 48 hr. The recovered olefin contained silicon tetrafluoride, observed spectroscopically, and the residue was extracted first with warm cyclohexane and then with acetone. Evaporation of the cyclohexane extract, followed by recrystallization from petroleum ether, gave a white crystalline product showing peaks at 1680 and 1635 cm^{-1} in the C=C stretching region. The proton nmr spectrum showed, in addition to the peaks expected for the ethyl protons of the phosphine, two quartets of equal intensity centered at −5.54 and −7.58 ppm relative to external tetramethylsilane. This suggested an approximately equimolar mixture (0.57 g) of the *cis*-and *trans*-olefinic isomers of (1,2-difluorovinyl)chlorobis(triethylphosphine)platinum(II), $[(C_2H_5)_3P]_2PtCl(CF{=}CFH)$. *Anal.* Calcd for $C_{14}H_{31}ClF_2P_2Pt$: C, 31.75; H, 5.85; mol wt, 529. Found: C, 31.74; H, 5.82; mol wt, 520. This mixture was eluted on a Florisil column with benzene, the first fraction being identified as the *cis* isomer by its proton nmr spectrum, and had $\nu_{C=C}$ 1635 cm^{-1}, mp 69–71°. Owing to tailing on the column, the *trans* isomer could not be obtained free of the *cis* form, although by difference $\nu_{C=C}$ of the *trans* form must be at 1680 cm^{-1}.

The acetone extract from the original reaction was filtered and deposited a white solid when carbon tetrachloride was added. This solid was further purified by passage over Florisil in chloroform to give white $[(C_2H_5)_3P]_2PtClF$ (0.02 g). *Anal.* Calcd for $C_{12}H_{30}ClFP_2Pt$: C, 29.7; H, 6.2; F, 2.55. Found: C, 29.1; H, 6.14; F, 2.88.

(e) **With Perfluorobut-2-yne.** *trans*-$[(C_2H_5)_3P]_2PtHCl$ (1.0 g, 2.14 mmoles) in 40 ml of cyclohexane and perfluorobut-2-yne (2.08 g, 12.9 mmoles) were heated at 90° for 25 hr. After the volatile products had been removed, the remaining solid was purified chromatographically on Florisil with 1:1 toluene–petroleum ether to give a white crystalline solid, [1,2-bis(trifluoromethyl)vinyl]chlorobis(triethylphosphine)platinum(II), $[(C_2H_5)_3P]_2PtCl[C(CF_3){=}C(CF_3)H]$: 0.55 g, 41% yield; mp 90–91°. *Anal.* Calcd for $C_{16}H_{31}ClF_6P_2Pt$: C, 30.5; H, 4.92; F, 18.1. Found: C, 30.8; H, 4.72; F, 18.0. Spectroscopic data discussed in the following paper showed it to be the *trans* isomer with respect to the vinylic group.

(f) **With Bromotrifluoroethylene.** *trans*-$[(C_2H_5)_3P]_2PtHCl$ (1.925 g, 4.12 mmoles) in 45 ml of cyclohexane and bromotrifluoroethylene (2.65 g, 16.5 mmoles) were heated at 100° for 18 hr and then at 115° for a further 24 hr. Following vacuum fractionation, appreciable amounts of trifluoroethylene were detected in the −196° fraction. The remaining solid was extracted with hot ethanol and then recrystallized from ethanol to give crystalline *trans*-$[(C_2H_5)_3P]_2PtBrCl$: 0.78 g, 35% yield; mp 132–133°. *Anal.* Calcd for $C_{12}H_{30}ClBrP_2Pt$: C, 26.35; H, 5.49. Found: C, 26.23; H, 5.60.

(g) **With Tetrachloroethylene.** *trans*-$[(C_2H_5)_3P]_2PtHCl$ (1.0 g, 2.14 mmoles), in 45 ml of *n*-pentane, and C_2Cl_4 (1.07 g, 6.42 mmoles) were heated at 105° for 24 hr and at 115° for a further 24 hr. The volatile products were fractionated and the −46° fraction showed, in addition to the peaks of C_2Cl_4, bands at 2960 (w), 1693 (w), 906 (vs), 793 (m), and 776 (s), attributable to $CCl_2{=}CClH$.[15] Extraction of the remaining solid with *n*-pentane, followed by chromatography on Florisil with a chloroform–pentane mixture (1:1) as eluent, and recrystallization from ethanol gave *trans*-$[(C_2H_5)_3P]_2PtCl_2$, mp[13] 142–143°. *Anal.* Calcd for $C_{12}H_{30}Cl_2P_2Pt$: C, 28.7; H, 5.97; Cl, 14.15. Found: C, 29.0; H, 5.86; Cl, 14.1. Unreacted hydride (0.38 g), mp[3] 81–82°, was also recovered.

Reaction of *trans*-$[(C_2H_5)_3P]_2PtH(SnCl_3)$. *trans*-$[(C_2H_5)_3P)_2PtHCl$ (6.45 g, 13.8 mmoles) and tin(II) chloride (3.11 g, 13.8 mmoles) were dissolved in the minimum amount of methanol at room temperature. On standing, white crystals were deposited, which were collected and recrystallized from cyclohexane: 4.0 g, 44% yield; ν_{Pt-H} 2105 cm^{-1}.[16] *Anal.* Calcd for $C_{12}H_{31}Cl_3P_2SnPt$: C, 21.9; H, 4.75. Found: C, 21.8; H, 4.71.

trans-$[(C_2H_5)_3P]_2PtH(SnCl_3)$ (1.0 g, 1.5 mmoles), in 10 ml of benzene (previously dried over sodium wire), and C_2F_4 (1.24 g, 12.4 mmoles) were heated at 85° for 24 hr and at 95° for a further 24 hr. Upon vacuum fractionation, appreciable amounts of silicon tetrafluoride were detected spectroscopically in the excess C_2F_4. The remaining viscous liquid contained at least two components, since its spectrum showed two C=C stretching absorptions at 1720 and 1645 cm^{-1}. Chromatographic separation on Florisil with a chloroform–pentane mixture (7:3) gave two products; one of these was identified by its infrared and proton nmr spectra as $[(C_2H_5)_3P]_2PtCl[C(CF_3H){=}CF_2]$ (0.09 g) described previously. Chlorine analysis also confirmed that the $-SnCl_3$ group was not present. *Anal.* Calcd for $C_{15}H_{31}ClF_4P_2Pt$: Cl, 6.13. Found: Cl, 6.59. The other product (0.03 g) was tentatively assigned the formula $[(C_2H_5)_3P]_2Pt(SnCl_3)(CF{=}CF_2)$, since its infrared spectrum was identical with that of $[(C_2H_5)_3P]_2PtCl(CF{=}CF_2)$ in the 4000–350-cm^{-1} range, and additionally showed a strong Sn–Cl stretching mode at 330 cm^{-1}. Satisfactory carbon and hydrogen analyses were not obtained, but a chlorine determination was in moderate agreement. *Anal.* Calcd for $C_{14}H_{30}Cl_3F_3P_2Pt$: Cl, 14.44. Found: Cl, 13.54.

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Results and Discussion

The first stable hydrido complex of platinum(II), *trans*-$[(C_2H_5)_3P)_2PtHCl$ was prepared by Chatt, *et al.*,[14] in 1957. It is a white crystalline solid, mp 81–82°, and is volatile, distilling at 130° (0.01 mm) and subliming at 75° (0.01 mm), in both cases with negligible decomposition. The structure is square planar as is the analogous bromide,[17] and it behaves as a mild reducing agent.

With tetrafluoroethylene at 120° in cyclohexane, this hydride gave three solid products as well as silicon tetrafluoride. Since the reactions were performed in glass Carius tubes, the latter clearly arose from the elimination of hydrogen fluoride which attacked the silica. The solid products were $[(C_2H_5)_3P]_2PtCl(CF{=}CF_2)$ and $[(C_2H_5)_3P]_2PtCl[C(CF_2H){=}CF_2]$, formed in approximately equal molar yield, and smaller amounts of the complex $[(C_2H_5)_3P]_2PtHCl(C_2F_4)$. The spectroscopic data leading to the characterization of these two and other vinyl products are discussed fully in the accompanying paper; only the data for the last compound will be considered here. The route by which $[(C_2H_5)_3P]_2PtCl[C(CF_2H){=}CF_2]$ was formed is not clear, since the tetrafluoroethylene was spectroscopically free of perfluoropropene. However, tetrafluoroethylene is known to polymerize readily under pressure, and even traces of oxygen are efficient polymerization catalysts, so that some C_3F_6 may have been present since the reactions occurred at an estimated pressure of 30–40 atm. Since the direct reaction of the hydride with pure perfluoropropene did *not* give $[(C_2H_5)_3P]_2PtCl[C(CF_2H){=}CF_2]$, this does not seem a likely route, although clearly some type of C_3 fragment is formed from the C_2F_4.

The most significant reaction apparently follows the equation

$$[(C_2H_5)_3P]_2PtHCl + C_2F_4 \longrightarrow [\text{intermediate complex}] \longrightarrow [(C_2H_5)_3P]_2PtCl(CF{=}CF_2) + HF$$

the particularly interesting features being the ease of elimination of hydrogen fluoride to give the previously unknown transition metal–perfluorovinyl compounds, and the mechanism by which this occurs. The latter is established through characterization of the compound $[(C_2H_5)_3P]_2PtHCl(C_2F_4)$. That this is a π complex of tetrafluoroethylene is established by the following data: (a) analytical data and (b) its infrared spectrum. The latter showed a Pt–H stretching absorption at 2100 cm^{-1}, quite different from the 2220-cm^{-1} frequency of the original hydride. In addition, C–F stretching vibrations were observed at 1094 (s), 1060 (vs), 1040 (s), and 881 (s) with weak shoulders at 1015 and 985 cm^{-1}. These are in general agreement with those reported[10,18] for other π-C_2F_4 complexes, particularly $(acac)Rh(C_2F_4)(C_5H_5N)_2$ (*cis*) (where acac = acetylacetone), although in no case can full assignments be made. The ^{19}F nmr spectrum of this new π-C_2F_4 complex showed a single resonance at +72.2 ppm relative to external trifluoroacetic acid, so that there is no evidence of coupling with phosphorus or ^{195}Pt. This apparent equivalence of the four fluorine atoms is consistent with data on other fluoroolefin complexes,[10] as is the fact that we do not observe any band attributable to the C=C stretching frequency in the 2000–1500-cm^{-1} region. One very surprising feature is that the proton spectrum of $[(C_2H_5)_3P]_2PtHCl(C_2F_4)$ shows no high-field resonance attributable to the hydridic proton, even though the same solution used in the nmr study shows the Pt–H stretching band at 2100 cm^{-1} in the infrared spectrum.[19]

The compound $[(C_2H_5)_3P]_2PtHCl(C_2F_4)$ is soluble in methanol, chloroform, and nitrobenzene, but insoluble in carbon tetrachloride, cyclohexane, and benzene. The nitrobenzene solution is conducting and the data (Table I) show that the compound is a strong electrolyte. On extrapolation to infinite dilution, the limiting molar conductance in nitrobenzene was found to be approximately 38 cm^2 mole^{-1} ohm^{-1}. Two ionization schemes are possible.

$$[(C_2H_5)_3P]_2PtHCl(C_2F_4) \rightleftharpoons H^+ + [(C_2H_5)_3P]_2PtCl(C_2F_4)^- \quad (1)$$

or

$$[(C_2H_5)_3P]_2PtHCl(C_2F_4) \rightleftharpoons [(C_2H_5)_3P]_2PtH(C_2F_4)^+ + Cl^- \quad (2)$$

The former is certainly consistent with the lack of a high-field signal in the proton spectrum, but since the nitrobenzene solution at concentrations 0.027, 0.009, and 0.0045 *M* still showed the Pt–H vibration at 2100 cm^{-1} in the infrared spectrum, eq 2 seems more probable. This would then require, regardless of the degree of ionization, that both the neutral complex and the hydridic cation show the same Pt–H stretching frequency. However, there are numerous instances[2] where the frequency difference between two such closely related species is found to be very small. If ionization occurs according to eq 2 above, then, allowing for the chloride ion having an ionic conductance at infinite dilution in nitrobenzene[20] of 22.2 cm^2 mole^{-1} ohm^{-1}, the complex cation $[(C_2H_5)_3P]_2PtH(C_2F_4)]^+$ has an ionic conductance of 16 cm^2 mole^{-1} ohm^{-1}, a not unreasonable value.

The stereochemistry of $[(C_2H_5)_3P]_2PtHCl(C_2F_4)$ is uncertain. The solid compound may have a five-coordinate structure, either trigonal bipyramidal or square pyramidal, or alternatively it may be an ionic complex, $[(C_2H_5)_3P]_2PtH(C_2F_4)^+Cl^-$. Certainly it is not possible to determine at this stage whether the olefin is more correctly regarded as π-bonded to platinum, or whether both carbon atoms are bound to platinum by essentially σ bonds in a three-membered ring. The most significant point is that this compound contains both an olefin–metal linkage and a metal–hydrogen bond, and therefore represents the type of intermediate postulated as occurring in many catalytic processes. That this particular complex is sufficiently stable to allow full characterization, and even prolonged storage, is due to the considerable stability of the parent hydride, perhaps combined with the known stability of transition metal–fluorocarbon derivatives. That this compound is the precursor to the perfluorovinylplatinum compound is apparent from the fact that, when the reaction is performed at lower temperatures, there is an in-

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(18) G. W. Parshall and F. N. Jones, *J. Am. Chem. Soc.*, **87**, 5356 (1965).

(19) M. J. Mays (private communication) has also prepared this π complex and has obtained nmr and conductivity data in essential agreement with those reported here.

(20) C. R. Witschonke and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 2472 (1947).

creased yield of the olefinic complex and less of the vinyl product. The ready elimination of hydrogen fluoride, perhaps aided by the presence of silica but nevertheless occurring remarkably easily, can be attributed to the proximity of the hydridic proton to a fluorine atom in the olefinic complex.

The extension of this reaction to other fluoroolefins gave results consistent with the above reaction sequence. Vinyl-type products were formed in nearly all cases accompanied by the formation of silicon tetrafluoride, although with no other olefin was a stable olefinic complex isolated. The parent Pt(II) hydride reacted with perfluoropropene to give *trans*-bis(triethylphosphine)(perfluoropropenyl)chloroplatinum(II), $[(C_2H_5)_3P]_2PtCl(CF{=}CFCF_3)$; the final product contained the olefinic *cis* and *trans* isomers in a 2:3 ratio (see accompanying paper). Silicon tetrafluoride was also formed, and it is believed that reaction occurred through the formation of an unstable olefinic complex from which HF was readily eliminated to give the perfluoropropenyl derivative. The ease of this reaction, together with the nature of the products, contrasts with the lack of addition of perfluoropropene to metal carbonyl hydrides,[5-9] again suggesting that direct addition across the M–H bond is not involved here.

With perfluorocyclobutene, *trans*-$[(C_2H_5)_3P]_2PtHCl$ gave bis(triethylphosphine)perfluorocyclobut-1-enechloroplatinum(II), $[(C_2H_5)_3P]_2PtCl(C_4F_5)$, again accompanied by the formation of silicon tetrafluoride. The elimination of hydrogen fluoride has therefore again occurred readily, presumably through formation of an olefinic complex as intermediate. It is interesting that while this work was in progress, Stone, *et al.*,[21] reported the formation of other metal–perfluorocyclobut-1-enyl compounds through the reaction of carbonyl metal anions with perfluorocyclobutene, and Cullen and Styan[22] described the addition of arsenes and other main group element hydrides to perfluorocyclobutene to give hexafluorocyclobutyl derivatives. Only in the case of trimethyltin hydride did fluorine elimination occur due to the formation of trimethyltin fluoride and 1-H-pentafluorocyclobutene.

The reaction of trifluoroethylene with *trans*-$[(C_2H_5)_3P]_2PtHCl$ gave a 40% yield of a mixture of the *cis*- and *trans*-olefinic isomers of *trans*-bis(triethylphosphine)-1,2-difluorovinylchloroplatinum(II), $[(C_2H_5)_3P]_2PtCl(CF{=}CFH)$, with SiF_4 as the secondary product. Even from experiments conducted at temperatures as low as 55°, no product corresponding to the olefinic complex could be isolated, nor was any trifluoroethyl derivative found. In all reactions, a very small yield was obtained of a product thought to be $[(C_2H_5)_3P]_2PtClF$, presumably formed by reduction of the olefin. There is no evidence to indicate the mechanism of such a process.

$$trans\text{-}[(C_2H_5)_3P]_2PtHCl + CF_2{=}CFH \longrightarrow trans\text{-}[(C_2H_5)_3P]_2PtClF + C_2F_2H$$

With perfluorobut-2-yne, the hydridochloroplatinum(II) complex gave the *cis*-olefinic isomers of *trans*-$[(C_2H_5)_3P]_2PtCl[CF_3C{=}CF_3H]$, and as expected silicon tetrafluoride was not formed. That the *cis* isomer was isolated is in direct contrast to the work of Stone, *et al.*,[5-8] on the carbonyl hydrides of manganese and rhenium, which gave *trans*-olefinic products. On the other hand, $HCo(CO)_4$ reduces the butyne[9] to *trans*-1,2-bis(trifluoromethyl)ethylene. Moreover, Cullen, *et al.*,[23] have shown that the *cis* isomer of $(CH_3)_2AsC(CF_3){=}C(CF_3)H$ isomerizes at 140° or higher to the *trans* form. The formation of just the *cis* isomer in the present case may then be a consequence just of the lower reaction temperature (90°), or alternatively may be due to a quite different reaction mechanism.

The reactions described so far involved fully or partially fluorinated olefins. When olefins containing other halogens were used, only a hydrogen–halogen exchange occurred. Thus, trifluorobromoethylene and *trans*-$[(C_2H_5)_3P]_2PtHCl$ gave *trans*-$[(C_2H_5)_3P]_2PtClBr$ and CF_2–CFH. This contrasts with the additions[5,8] of CF_2CFCl and CF_2CCl_2 across the Mn–H and Re–H bonds to give relatively stable alkyl derivatives. The only cases at all similar are those involving $HCo(CO)_4$ reacting with CF_2CFCl and other chloroolefins.[9] However, here the C–C bonds were saturated to give ethanes. While the present reaction possibly involved the formation and thermal decomposition of an alkylplatinum compound, we are inclined to favor the alternative route whereby formation of an olefinic complex of the hydride facilitates the exchange of hydrogen and bromine atoms. A similar exchange occurred in the reaction of the hydride with tetrachloroethylene to give $[(C_2H_5)_3P]_2PtCl_2$ and CCl_2CClH.

In view of the behavior of platinum–tin chloride complexes as homogeneous catalysts,[24] and the ability of the $-SnCl_3$ ligand to stabilize five-coordinate platinum derivatives,[16] it was worthwhile examining the reaction of the hydride *trans*-$[(C_2H_5)_3P]_2PtH(SnCl_3)$ with tetrafluoroethylene. In view of the strongly *trans*-activating properties[16] of $-SnCl_3$, a more ready reaction with C_2F_4 might be expected than for the chlorohydride. Surprisingly, the reaction gave only very small amounts of $[(C_2H_5)_3P]_2Pt(SnCl_3)(CF{=}CF_2)$ and $[(C_2H_5)_3P]_2Pt(SnCl_3)[C(CF_2H){=}CF_2]$, and there was no evidence that an olefinic complex could be isolated. It is not at all clear why this reaction should become more difficult when the $-SnCl_3$ ligand replaces Cl on platinum. Finally, we were interested to know whether the *trans* configuration of the initial hydride was an important factor in these reactions. The only reasonably stable *cis* platinum hydride so far reported[25] is *cis*-bis(triphenylphosphine)chloroplatinum(II) hydride, *cis*-$(PPh_3)_2PtHCl$. The reaction of this hydride with trifluoroethylene was attempted at 115°, but no silicon tetrafluoride or fluorocarbon–platinum products were produced. Instead extensive isomerization to the *trans* form took place, and we have so far been unable to find conditions under which reaction with a fluoroolefin can occur, without at the same time causing conversion to the *trans* isomer which may itself react with the olefin.

It is clear that these reactions are of considerable importance in that they not only lead to the previously unknown transition metal–fluorovinyl derivatives, but also provide valuable information concerning the interaction of olefins with hydrides. One of the major questions so far raised by this study is why the platinum

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hydride should react with fluoroolefins to give vinyl compounds through the intermediacy of a π complex, whereas the metal carbonyl hydrides give only fluoroalkyl derivatives. The explanation that can be offered at present is that the platinum(II) hydride has a square-planar geometry and so can readily form a π-olefinic complex which functions as the reaction intermediate. The carbonyl hydrides are generally five- or six-coordinate and can less readily increase their coordination shell. The latter hydrides, therefore, are more likely to react with olefins *via* a four-center- or free-radical-type mechanism.

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Chemistry of Metal Hydrides. II. Spectroscopic Studies of Fluorovinylplatinum(II) Derivatives

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Abstract: Infrared and nuclear magnetic resonance (^{1}H and ^{19}F) spectroscopic data are presented for some new fluorovinyl derivatives of platinum(II). Some features of the infrared spectra are examined in the light of current evidence of π bonding between fluorocarbon groups and transition metals. These are the first organoplatinum(II) compounds in which spin–spin coupling is observed between ^{19}F and ^{195}Pt, and also between ^{19}F and the ^{31}P nuclei of the tertiary phosphine ligands. The stereochemistries of the products are established, and results pertinent to the concept of "through-space coupling " are described.

In the previous paper[1] the reactions of some platinum(II) hydrides, principally $[(C_2H_5)_3P]_2PtHCl$, with a number of unsaturated fluorocarbons were described, the principal products being fluorovinyl derivatives. These are among the first of a new class of organometallic compounds, although others were reported while our work was in progress,[2] obtained from reactions between metal carbonyl anions and fluoroolefins. The spectroscopic properties of these new Pt(II) compounds not only enabled detailed characterizations to be made, but also provide valuable information concerning the bonding of fluorocarbon groups to transition metals. This has considerable interest at present, since recent studies[3–6] provide clear evidence of π-type interactions between fluorocarbon groups and transition metal atoms. In fluorovinyl derivatives, the presence of the C=C π system may enhance such interaction, and the data described in this paper have been examined with this in mind.

Experimental Section

The preparation of all the compounds has been described in the previous paper, together with the analytical data. Infrared spectra were recorded with a Beckman IR-10 double-beam spectrophotommeter, using Nujol or halocarbon oil mulls; spectra were calibrated against polystyrene. Nmr spectra were obtained with Varian A-60 (proton spectra) and DP-60 (^{19}F spectra) spectrometers. Proton chemical shifts are reported in ppm with respect to tetramethylsilane as external standard, and ^{19}F spectra with respect to trifluoroacetic acid as external standard; unless otherwise stated, deuteriochloroform was used as solvent.

Discussion

Infrared Spectra. The observed infrared absorption frequencies of the new fluorovinylplatinum(II) compounds are listed in Table I. Many of these bands arise from vibrations of the triethylphosphine groups, and assignments have been made by comparison with those given for the free phosphine.[7] No detailed consideration will be given to vibrations other than the P–C stretching and Pt–P stretching modes, since absorptions due to the hydrocarbon portions of the molecules are fairly standard and show no unique features. The suggested range[8] for P–C stretching vibrations in a series of phosphonium compounds is 650–750 cm^{-1}, and it has also been pointed out[8] that the presence of a $P-C_2H_5$ group in a molecule is characterized by two bands in the 1227–1282-cm^{-1} region. Chatt, *et al.*,[9] have studied the infrared spectra of a series of alkylplatinum(II) complexes stabilized by tertiary phosphines. For trimethylphosphine complexes, they assigned bands in the 669–689- and 720–743-cm^{-1} regions to the symmetrical and asymmetrical P–C stretching vibrations, respectively. Triethylphosphine complexes gave more complicated spectra, but it was possible to assign bands in the 625–643-cm^{-1} region to the P–C symmetrical stretching mode. In the spectra of the present investigation, generally only one band was found in the region 625–643 cm^{-1}, and this is therefore attributed to the same vibration. Moreover, usually

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