starting material had passed through. The residue from evaporation of the eluate was sublimed at 80° (0.05 torr) for 36 hr to yield 0.28 g (26%) of the orange solid product, mp 125–127°.

Anal. Calcd for $C_{15}H_{14}WO_2$: C, 43.92; H, 3.45. Found. C, 44.1; H, 3.50.

The infrared spectrum (cyclohexane) had strong bands at 1945 and 1868 cm^{-1} (± 5 cm^{-1}). This compound is very similar to its molybdenum analog except that it reacts more readily with chlorinated solvents and is, in general, less soluble in organic media.

Spectroscopic Measurements. Infrared spectra were recorded on Perkin-Elmer 237 and 337 spectrometers.

Nmr spectra were measured with a Varian Associates A-60 spectrometer. Temperature calibration was achieved by measuring the peak separation in methanol and ethylene glycol samples. The spectra were calibrated at the lowest temperature with a Krohn-Hite Model 450 oscillator and a Hewlett-Packard Model 524 electronic counter.

To assure rigorous exclusion of oxygen from nmr samples, solvents and tetramethylsilane were degassed and distilled under high vacuum directly onto the solids which had been previously placed in standard-size nmr tubes using a nitrogen-filled glove box.

Treatment of Nmr Data. The rate of rearrangement at a given temperature was estimated by comparison of experimental spectra with those calculated by the method of Kubo[21] and Sack[22] in a manner previously described[23,24] using a computer program written by Professor G. M. Whitesides of this department for the IBM 360 computer. The computer output consisted of line shapes drawn by a Calcomp plotter and these were visually compared with experimental spectra.

To achieve maximum accuracy in kinetic measurements, spectra were recorded at minimum sweep width and maximum spectrum amplitude. In instances where spectral features were difficult to discern (*e.g.*, near coalescence points) several scans were made of the spectrum. In cases where the separate resonances for each of two exchanging protons were discernible at all times during their collapse, computed spectra were fitted to give the best agreement with both signals. Where one resonance was obscured by other peaks in the spectrum during its collapse, computed spectra were fitted only to the completely visible resonance. In the case of the high-field ring protons in (h^3-$CH_3C_6H_4CH_2$)(h^5-C_5H_5)$Mo(CO)_2$, each exchanging component was simulated as a doublet (due to *ortho* coupling) with the most intense component again split into a doublet (due to what was apparently long-range coupling). Furthermore, since the high-field resonance was partially obscured by the cyclopentadienyl peak, the line width and intensity of the smaller component of the doublet were estimated from the spectrum in the fast exchange limit.

A computer program written by Mr. W. K. Bratton was used to fit Arrhenius plots by the method of least squares and to compute activation parameters.

Acknowledgment. We thank Professor George M. Whitesides for several helpful and stimulating discussions, and particularly for persuading us that the effort required to synthesize the 3,5-diisopropylbenzyl compound would probably be rewarded by useful results. We thank Professor Dietmar Seyferth for the use of some glpc equipment.

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Chemistry of Metal Hydrides.[1] V. Preparation of Platinum Hydrides from $[PtX(CO)(R_3P)_2]^+$ and $[PtX(COOR)(Ph_3P)_2]$

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Abstract: The synthesis of $[Pt_2X_2(R_3P)_4][BF_4]_2$ for X = Br or I with R = phenyl, and for X = Br with R = ethyl, is described. The rates of cleavage of these dihalo-bridged diplatinum cations with carbon monoxide to give the carbonyls, *trans*-$[PtX(CO)(R_3P)_2][BF_4]$, have been studied qualitatively. *trans*-$[PtCl(CO)(Et_3P)_2][BF_4]$ reacts with water giving *trans*-$[PtHCl(Et_3P)_2]$ and carbon dioxide. The triphenylphosphine analog, *trans*-$[PtX(CO)(Ph_3P)_2][BF_4]$, where X = Cl, Br, or I, reacts readily with methanol or ethanol giving the alkoxycarbonyl $[PtX(COOR)(Ph_3P)_2]$ where R = CH_3 or C_2H_5. These alkoxycarbonyls react with water in the presence of salt catalyst giving *trans*-$[PtHX(Ph_3P)_2]$. Possible mechanisms for these conversions are discussed.

The ability of $[RhCl(Ph_3P)_2]$ and *trans*-$[IrCl(CO)(Ph_3P)_2]$ to act as catalysts for the homogeneous hydrogenation of olefins and to undergo oxidative additions is well known.[2] This reactivity led us to examine the isoelectronic cation $[PtX(CO)(R_3P)_2]^+$ for similar activity. Although such catalytic character has not as yet been observed for these platinum(II) complexes, we have found that their reactions with water and alcohols are of considerable interest. This paper describes the facile production of the hydridoplatinum(II) compounds, *trans*-$[PtHX(R_3P)_2]$, with X = halide and R = ethyl or phenyl, directly from the platinum(II) carbonyl cation by reaction with water, and indirectly *via* an alkoxycarbonyl compound.

Results and Discussion

The compounds *trans*-$[PtX(CO)(R_3P)_2][BF_4]$, where X = Cl, Br, or I with R = phenyl, and where X = Cl or Br with R = ethyl, can be synthesized by various routes.[1,3,4] It was of interest, however, to prepare these

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Table I. Properties of Halocarbonylplatinum(II) Salts

Compound	% yield from carbonylation reaction[a]	Mp, °C	Recrystn solvents	CO stretching freq,[b] cm^{-1}	Analysis Calcd %C	Analysis Calcd %H	Analysis Found %C	Analysis Found %H	Time for complete carbonylation, min In CHCl$_3$	Time for complete carbonylation, min In CH$_3$NO$_2$
[PtCl(CO)(Ph$_3$P)$_2$][BF$_4$]	85	Slow decomp above 200° with liquefaction near 270°	Benzene	2120	51.2	3.5	51.2	3.7	20	. . .[c]
[PtBr(CO)(Ph$_3$P)$_2$][BF$_4$]	80		Benzene	2111	48.6	3.3	49.0	3.5	8	25
[PtI(CO)(Ph$_3$P)$_2$][BF$_4$]	50		. . .	2120	46.2	3.2	45.4	3.4	7	6
[PtCl(CO)(Et$_3$P)$_2$][BF$_4$]	89	168–171° dec	Ethyl acetate	2098	26.0	5.5	25.8	5.6	2.5	. . .[c]
[PtBr(CO)(Et$_3$P)$_2$][BF$_4$]	85	158–160° dec	Ethyl acetate	2112	24.9	4.8	25.0	4.6	2.5	20

[a] Yields represent first crop of crystals except for [PtI(CO)(Ph$_3$P)$_2$][BF$_4$]. [b] As chloroform solution. [c] No reaction was observed.

carbonyls in two steps. Initially the appropriate dihalobisphosphine complex was allowed to react with boron trifluoride as previously described[3,5] to give the dihalo-bridged diplatinum cation, $[Pt_2X_2(R_3P)_4]^{2+}$.

$$2cis\text{-}[PtX_2(R_3P)_2] + 4BF_3 \xrightarrow{CHCl_3} [Pt_2X_2(R_3P)_4][BF_4]_2 + 2[BF_2X]$$

These reactions have now been extended for X = Cl, Br, or I with R = phenyl and X = Cl or Br for R = ethyl, with the yield of the halo-bridged dimeric species increasing markedly in the order I < Br < Cl. Both compounds $[Pt_2Cl_2(R_3P)_4][BF_4]_2$ with R = ethyl or phenyl are formed quantitatively at room temperature, while even at elevated temperatures lower yields of the bromo and iodo analogs are obtained. The reaction of *cis*-$[PtI_2(Et_3P)_2]$ with boron trifluoride gives entirely different products. Low yields of the previously described[6] uncharged iodo-bridged dimer$[Pt_2I_4(Et_3P)_2]$ and of the new compound iodotris(triethylphosphine)platinum(II) tetrafluoroborate, $[PtI(Et_3P)_3][BF_4]$, are obtained.

$$3cis\text{-}[PtI_2(Et_3P)_2] + 3BF_3 \xrightarrow[70^\circ]{CHCl_3} Pt_2I_4(Et_3P)_2 + [PtI(Et_3P)_3][BF_4] + [Et_3P\cdot BF_3] + [BF_2Cl]$$

The ability of carbon monoxide to cleave a halo-bridged diplatinum(II) compound is well known[6] for the series $[Pt_2X_4(R_3P)_2]$. Hence, the analogous facile reaction of carbon monoxide with the cationic dimeric species, $[Pt_2X_2(R_3P)_4][BF_4]_2$, is not surprising. In a suspension in chloroform, the dimeric cations react in minutes with carbon monoxide at 1 atm.

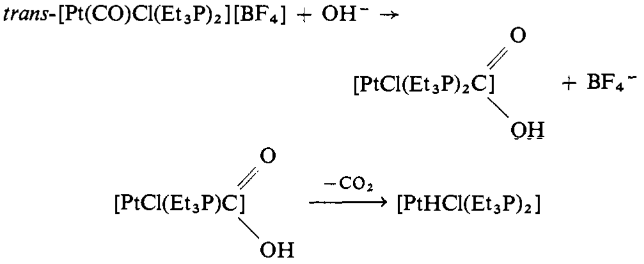
$$[Pt_2X_2(R_3P)_4][BF_4]_2 + 2CO \rightleftarrows 2[PtX(CO)(R_3P)_2][BF_4]$$

For X = Cl or Br and R = ethyl or phenyl, the equilibrium lies well to the right, and the carbonyl can be isolated as an air-insensitive crystalline solid. For X = I and R = phenyl, the equilibrium lies to the right for carbon monoxide saturated solutions and for the crystalline solid. However, in solutions devoid of carbon monoxide, the dimeric salt rapidly precipitates. The rates of reaction (see Table I) are functions of halogen type, phosphine type, and reaction solvent. With chloroform as solvent, the reaction rate increases in the order X = Cl < Br < I and R_3P = Ph_3P < Et_3P, with the phosphine type being the more important factor in determining reaction rate. However, in nitromethane the halogen has the more marked effect. For X = Cl and R = ethyl or phenyl, the equilibrium clearly lies to the left, and while the bromo analog requires over 20 min for complete reaction, the iodo dimer cleavage is complete within 6 min.

Although these carbonyl platinum cations do not appear to show the same catalytic reactivity as the isoelectronic iridium and rhodium compounds, they do undergo two unexpected reactions. The first is that of chlorocarbonylbis(triethylphosphine)platinum(II) fluoroborate with water.[7] Under reflux for 30 min, quantitative yields of carbon dioxide and *trans*-$[PtHCl(Et_3P)_2]$ are obtained. This reaction is analogous to that of the hexacarbonylmanganese(I) cation with water[8]

$$[Mn(CO)_6]^+ + H_2O \rightarrow HMn(CO)_5 + CO_2$$

Hieber and Kruck[8] suggested that this reaction proceeds through the attack of a hydroxyl group to form a short-lived carboxylic acid. Further attack by hydroxide gives the manganese pentacarbonyl anion which then could abstract a proton from water. We feel that the formation of a short-lived carboxylic acid group is indeed feasible. However, decarboxylation seems to offer a direct and likely subsequent step to produce hydridoplatinum(II).



$$trans\text{-}[Pt(CO)Cl(Et_3P)_2][BF_4] + OH^- \rightarrow [PtCl(Et_3P)_2C(=O)OH] + BF_4^-$$

$$[PtCl(Et_3P)C(=O)OH] \xrightarrow{-CO_2} [PtHCl(Et_3P)_2]$$

trans-$[Pt(CO)Cl(Ph_3P)_2][BF_4]$ is not so readily converted to the hydride, due perhaps to the lower solubility of the carbonyl or to the greater electron-withdrawing ability of the triphenylphosphine ligands.

The remarkable reaction of the alkoxide ion in attacking the C≡O bond of cationic metal carbonyls has been

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Table II. Alkoxycarbonylplatinum(II) Compounds

Compound	Mp, °C[a]	ν(C=O), cm^{-1} CHCl$_3$ sol	Nujol mull	Approx time, min[b]	Analysis Calcd % C	% H	Found % C	% H
$PtCl(COOMe)(Ph_3P)_2$	222–227	1637	1664	2	56.1	4.1	55.8	4.2
$PtBr(COOMe)(Ph_3P)_2$	226–231	1637	1665	2	53.2	3.9	53.0	4.0
$PtI(COOMe)(Ph_3P)_2$	226–229	1648	1655	2	50.4	3.7	50.3	3.9
$PtCl(COOEt)(Ph_3P)_2$	215–217	1638		40	56.6	4.3	56.5	4.2
$PtBr(COOEt)(Ph_3P)_2$	226–231	1638		10	53.7	4.0	53.8	4.0
$PtI(COOEt)(Ph_3P)_2$	221–229	1638		5	51.0	3.8	51.1	3.8

[a] All compounds softened and discolored above 180°. [b] For complete reaction of carbonyl with appropriate alcohol.

described for iridium,[9] manganese,[10] and rhodium[11] central metals with a number of different surrounding ligands. We previously gave a preliminary report[7] of the reactions of *trans*-$[PtCl(CO)(Ph_3P)_2][BF_4]$ with methanol and ethanol, and we now give full details as well as describing the extension to the other halo analogs. Unlike the above reactions,[9-11] where a basic medium must be provided by ammonia or alkali metal hydroxide, these platinum carbonyls are capable of reaction in neat methanol or ethanol. The reaction is rapid (see Table II) but reversible in acidic solutions. Reaction of *trans*-$[PtCl(CO)(Et_3P)_2][BF_4]$ with dried methanol appears to give the alkoxycarbonyl although the product is very unstable and as yet not fully characterized. In the light of these results, it appears that the reaction of transition metal carbonyl cations with alcohols to give alkoxycarbonyls is quite general when such π-accepting ligands as carbon monoxide or triphenylphosphine are bonded to the central metal.

The platinum alkoxycarbonyl compounds undergo a reaction with water which is also novel.

$$[PtX(COOR)(Ph_3P)_2] + H_2O \xrightarrow[\text{or KX}]{NH_4X} trans\text{-}[PtHX(Ph_3P)_2] + CO_2 + ROH$$

For X = Cl the reaction is quantitative, but for X = Br the yields are lower, and for X = I only trace amounts of the hydride are isolated. Such a reaction can be understood when two other facts are also considered: (1) the alkoxy group exchanges with other alkoxy groups

$$[PtX(COOR)(Ph_3P)_2] + R'OH \rightarrow [PtX(COOR')(Ph_3P)_2] + ROH$$

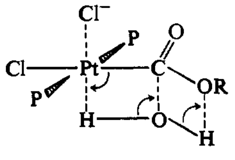
(2) *trans*-$[PtCl(CO)(Et_3P)_2][BF_4]$ reacts directly with water to give the hydride, possibly *via* a short-lived carboxylic acid.

The lability of the alkoxy group toward exchange with other alcohols suggests that a similar exchange with hydroxide could result in the formation of a carboxylic acid. The instability of such an acid and its ready decarboxylation would give the platinum hydride.

$$[PtCl(Ph_3P)_2(COOMe)] + OH^- \rightarrow [PtCl(Ph_3P)_2COOH] + OMe^-$$

$$[PtCl(Ph_3P)_2COOH] \xrightarrow{-CO_2} trans\text{-}[PtHCl(Ph_3P)_2]$$

The reaction proceeds readily only in the presence of a salt such as NH_4X, NMe_4X, or KX (X = halide). While catalysis may be due to the cation fulfilling a role similar to that of the proton in the acid-catalyzed hydrolysis of esters, the fact that X$^-$ is the common species strongly favors *anionic* catalysis. Coordination of X$^-$ to the platinum of the alkoxycarbonyl may well facilitate both decarboxylation and hydride formation through a transition state such as I. The kinetics of this system and its unusual catalysis apparently by halide ion are currently under investigation in the hope of elucidating this mechanism. We are also currently studying the reactivity of alkoxycarbonyls of other transition metals.



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The remarkably facile conversion under relatively mild conditions of *trans*-$[PtX(CO)(Et_3P)_2][BF_4]$ and $[PtX(COOR)(Ph_3P)_2]$ to give the corresponding hydrido compounds is of great interest. Not only do these reactions present a new preparative method for metal hydrides involving the extraction of a hydridic hydrogen from water, but they also act as model systems for the formation, under biological conditions, of transition metal hydrides believed to be of importance[12] in bacterial nitrogen fixing in legume plants.

Experimental Section

The general techniques and instrumentation employed have been described previously.[3] The preparation of platinum(II) dihalide complexes used as starting materials was achieved by described procedures.[13]

1. Preparation of $[Pt_2X_2(R_3P)_4][BF_4]_2$. The procedure described[3] for the preparation of $[PtCl_2(Et_3P)_4][BF_4]_2$ was used in the following cases, the only modification being that the reaction mixture was extracted with nitromethane rather than methanol.

(a) *cis*-$[PtBr_2(Ph_3P)_2]$ (0.34 g) and boron trifluoride (0.4 g), heated at 70° in a Pyrex Carius tube for 12 hr, gave pale yellow crystals of $[PtBr_2(Ph_3P)_4][BF_4]_2$ (0.29 g). Recrystallization was from nitromethane-petroleum ether (bp 30-60°)-diethyl ether mixture. *Anal.* Calcd for $C_{72}H_{60}B_2Br_2F_8P_4Pt_2$: C, 48.8; H, 3.4. Found: C, 49.4; H, 3.7.

(b) *cis*-$[PtI_2(Ph_3P)_2]$ (2.30 g) and boron trifluoride (0.5 g) after 48 hr at 130° in chloroform-benzene solution gave $[Pt_2I_2(Ph_3P)_4]$-

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Table III. Proton Nmr of Alkoxycarbonyls

Compound	Solvent	Chemical shifts (τ) of alkoxy protons CH_3[a]	CH_2	Coupling constants, cps J_{Pt-H}	J_{H-H}
$PtCl(COOMe)(Ph_3P)_2$	CH_2Cl_2	7.6 (t)[b]	. . .	15	. . .
$PtBr(COOMe)(Ph_3P)_2$	CH_2Cl_2	7.6 (t)	. . .	15	. . .
$PtCl(COOEt)(Ph_3P)_2$	CH_2Cl_2		7.3 (m)[c]	15	15
		9.5 (t)		<1	15
$PtCl(COOMe)(Et_3P)_2$[d]	C_6H_6	7.1 (t)	. . .	15	. . .

[a] (t) = triplet. [b] The methyl protons are split by ^{195}Pt (34% abundance) with $I = {}^1/_2$ into a 1:4:1 triplet. [c] The multiplet results from splitting by CH_3 protons and ^{195}Pt. [d] This compound is not fully characterized.

$[BF_4]_2$ (0.77 g, 35%). *Anal.* Calcd for $C_{72}H_{60}B_2F_8I_2P_4Pt_2$: C, 46.3; H, 3.2. Found: C, 46.0; H, 3.1.

(c) *cis*-$[PtBr_2(Et_3P)_2]$ (0.29 g) and boron trifluoride (0.25 g) heated at 50° for 12 hr in chloroform gave white crystalline $[Pt_2Br_2(Et_3P)_4][BF_4]_2$ (0.19 g, 75%). *Anal.* Calcd for $C_{24}H_{60}B_2Br_2F_8P_4Pt_2$: C, 24.1; H, 5.1. Found: C, 24.7; H, 5.2. The residue insoluble in methanol–diethyl ether was identified spectroscopically as *trans*-$[PtBr_2(Et_3P)_2]$ (0.10 g).

2. Reaction of *cis*-$[PtI_2(Et_3P)_2]$ with BF_3. *cis*-$[PtI_2(Et_3P)_2]$ (1.0 g) was heated at 70° for 28 hr in a sealed tube with boron trifluoride (0.3 g) and chloroform (3 ml). After removal of the volatiles under vacuum, extraction with methanol, followed by recrystallization at 25° from a chloroform–diethyl ether mixture, gave yellow plates of $[PtI(Et_3P)_3]BF_4$ (0.20 g), mp 148–150°. *Anal.* Calcd for $C_{18}H_{45}BF_4IP_3Pt$: C, 28.3; H, 6.1. Found: C, 28.3; H, 6.0. Further extraction of the residue with chloroform gave *trans*-$[PtI_2(Et_3P)_2]$ (0.52 g) identified spectroscopically, and recrystallization of the remaining residue from acetone–methylene chloride gave orange crystals of $Pt_2I_4(Et_3P)_2$ (0.23 g). *Anal.* Calcd for $C_{12}H_{30}I_4P_2Pt_2$: C, 12.7; H, 2.7. Found: C, 13.7; H, 2.6. The new compound $[PtI(Et_3P)_3]BF_4$ can also be identified by characteristic infrared absorptions due to ν(Pt–P) at 425 (m) with weak shoulders at 410 and 440 cm^{-1}.

3. Reaction of $[Pt_2X_2(R_3P)_4][BF_4]_2$ with CO. The compound $[PtX_2(R_3P)_4][BF_4]_2$ was stirred in a closed system at 23° in degassed chloroform (20 ml) under carbon monoxide (1 atm). The course of reaction was followed by measuring the CO uptake. For X = Cl or Br, and R = Et or Ph, the chloroform was then removed under vacuum and the residue recrystallized, as shown in Table I. For X = I and R = Ph, work-up was carried out in a carbon monoxide atmosphere by the addition of the chloroform solution to a carbon monoxide-saturated diethyl ether–petroleum ether mixture. The resulting yellow solid was not recrystallized. When the above reaction was carried out in nitromethane for X = Cl and R = Et or Ph, no carbon monoxide uptake was observed. Details of these reactions are given in Table I.

4. Preparation of $[PtX(COOR)(Ph_3P)_2]$ (X = Cl, Br, I; R = CH_3, C_2H_5). Typically, for R = CH_3, $[PtX(CO)(Ph_3P)_2][BF_4]$ (X = Cl, Br, I) was stirred in methanol at 25° for 1 hr. The fine precipitate was filtered, washed with water and a small volume of methanol, and dried under vacuum. Evaporation of the methanol mother liquor gave a further crop of the product and an oil which had absorptions in the infrared region characteristic of the fluoroborate anion. For R = ethyl, the same procedure was followed except ethanol replaced methanol as both reactant and wash solvent, and the reaction was carried out for 12 hr. Both sets of compounds were slouble in chloroform and methylene chloride and only slightly soluble in alcohols and benzene. Yields were essentially quantitative. These white or pale yellow crystalline compounds (Table II) were characterized by infrared spectroscopy, proton nmr spectroscopy, and chemical reactions (see reactions 6 and 9). Infrared absorptions for the methoxycarbonyl compounds at 1660 cm^{-1} (Nujol mull) were assigned to the C═O stretching vibration, and strong broad peaks centered at 1060 cm^{-1} were assigned to OMe. Similar absorptions appeared at about 1635 and 1080 cm^{-1} for the ethoxy analogs.

5. Reaction of $[PtCl(CO)(Et_3P)_2][BF_4]$ with Dried Methanol. $[PtCl(CO)(Et_3P)_2][BF_4]$ (0.10 g) was heated with 2 ml of dried methanol for 18 hr at 60° in a dried evacuated Pyrex tube. The volatiles were removed under vacuum leaving a white oily solid. Characterization of this residue was incomplete because of its instability. However, infrared and proton nmr spectroscopy indicate a compound analogous to the products of reaction 4, *i.e.*, $[PtCl(COOMe)(Et_3P)_2]$: infrared absorptions (cm^{-1}), ν(C═O) 1600, ν(Pt–P) 410 (br), ν(Pt–Cl) 270 cm^{-1} (w); nmr methyl absorptions, triplet at δ 2.9 ppm, J_{Pt-H} = 15 cps.

6. Reaction of $[PtCl(COOR)(Ph_3P)_2]$ with Fluoroboric Acid. $[PtCl(COOMe)(Ph_3P)_2]$ (0.12 g, 0.15 mmole) was shaken at 25° for 1 hr with methylene chloride (5 ml) and 48% aqueous fluoroboric acid (1 ml). After separation of the two layers, absorptions of the water layer showed a singlet at 3.4 ppm assigned to the methyl protons of methanol. Petroleum ether (bp 30–60°) was added to the methylene chloride solution affording $[PtCl(CO)(Ph_3P)_2][BF_4]$ (0.12 g, 0.14 mmole) identified by infrared spectroscopy.

A similar reaction with $[PtCl(COOEt)(Ph_3P)_2]$ gave *trans*-$[PtCl(CO)(Ph_3P)_2][BF_4]$ in good yield. Proton nmr spectroscopy indicated ethanol as the other hydrolysis product.

Hydrochloric acid could also be used in place of fluoroboric acid for the above hydrolysis. However, the product was the dichloride *cis*-$[PtCl_2(Ph_3P)_2]$.

7. Reactions of *trans*-$[PtCl(CO)(Et_3P)_2][BF_4]$ with Water. (i) *trans*-$[PtCl(CO)(Et_3P)_2][BF_4]$ (0.155 g, 0.27 mmole) was heated at 110° for 18 hr in degassed 1:1 methanol–water solution (2 ml) in an evacuated Pyrex tube. A white crystalline solid formed on cooling. The volatile products were fractionated under vacuum through −78, −120, and −196° traps. Carbon dioxide (0.011 g, 0.25 mmole) was collected and identified by infrared spectroscopy. The residue was extracted with water affording a white solid (0.030 g) with infrared absorptions characteristic of SiF_6^{2-} and BF_4^- anions. The residual solid was *trans*-$[PtHCl(Et_3P)_2]$ (0.122 g, 0.26 mmole), characterized by its melting point (80–82°), proton nmr spectroscopy, and infrared spectroscopy.

(ii) The above reaction was repeated with water alone as solvent. Although the reaction was not homogeneous and some reduction to metallic platinum occurred, the yields of CO_2 and $[PtHCl(Et_3P)_2]$ were nearly quantitative after 1-hr refluxing in a nitrogen atmosphere.

(iii) The above reaction was repeated using D_2O (98% pure) in place of water. The reaction was complete within 1 hr giving CO_2 and *trans*-$[PtDCl(PEt_3)_2]$. The latter product was identified by infrared spectroscopy[14] [ν(Pt–D) 1595, δ(Pt–D) 580 cm^{-1}]. A study of the rate of exchange of D_2O with *trans*-$PtHCl(Et_3P)_2$ under conditions identical with those of the above reactions indicated that the formation of *trans*-$[PtDCl(Et_3P)_2]$ cannot be attributed to initial formation of *trans*-$[PtHCl(Et_3P)_2]$ and subsequent exchange with D_2O.

8. Reaction of *trans*-$[PtCl(CO)(Ph_3P)_2][BF_4]$ with Water. *trans*-$[PtCl(CO)(Ph_3P)_2][BF_4]$ (0.10 g) was shaken at 110° for 12 hr with water (2 ml). The volatile products were removed under vacuum, and carbon dioxide and carbon monoxide were identified spectroscopically. The residue was extracted with methylene chloride which on slow evaporation afforded *trans*-$[PtHCl(Ph_3P)_2]$ (0.01 g) identified by infrared spectroscopy.[15] Further evaporation of the methylene chloride solution afforded an oil which remained uncharacterized.

9. Reactions of $[PtX(COOCH_3)(Ph_3P)_2]$ with Water (X = Cl, Br, I). (i) *trans*-$[PtCl(COOMe)(Ph_3P)_2]$ (0.17 g, 0.21 mmole) was heated at 105° for 18 hr in an evacuated Pyrex tube containing degassed saturated water–potassium chloride solution (3.0 ml). The

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(14) J. Chatt, *Proc. Chem. Soc.*, 318 (1962).

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

volatile products were fractionated under vacuum through −78, −120, and −196° traps. Carbon dioxide (0.0073 g, 0.17 mmole) was collected and identified by infrared spectroscopy. The −120° trap contained methanol identified by infrared spectroscopy and proton nmr spectroscopy. The residue was extracted with water, dried, then extracted with methylene chloride affording *trans*-[PtHCl($Ph_3P)_2$] (0.15 g, 0.20 mmole) identified by melting point (216–221°) and infrared spectroscopy.[15] An uncharacterized insoluble compound (0.015 g) was left as residue.

The above reaction was repeated with D_2O (98% pure) instead of water. Carbon dioxide and *trans*-[PtDCl($Ph_3P)_2$] were formed, both identified by infrared spectroscopy [ν(Pt–D) 1585 cm^{-1}].

trans-[PtHCl($Ph_3P)_2$] was heated in a sealed tube at 110° for 12 hr in D_2O (98% pure). The starting material was obtained quantitatively and no exchange had occurred.

(ii) Reactions under conditions identical with the chloro analog were carried out with [PtX($COOCH_3$)($Ph_3P)_2$] in concentrated H_2O–KX solution (X = Br or I). For X = Br, *trans*-[PtHBr($Ph_3P)_2$] was isolated in 65% yield and the remainder of the product was starting material. For X = I, only a trace of *trans*-[PtHI($Ph_3P)_2$] was obtained.

10. Reactions of [PtX($COOC_2H_5$)($Ph_3P)_2$] with Water. (i) [PtCl($COOC_2H_5$)($Ph_3P)_2$] (0.16 g, 0.19 mmole) was heated for 18 hr at 110° in an evacuated Carius tube containing a degassed concentrated water-potassium chloride solution (2 ml). The volatile products were fractionated through −78, −120, and −196° traps. Carbon dioxide (0.0075 g, 0.17 mmole) was collected and identified by infrared spectroscopy. Ethanol was also identified as a volatile product by proton nmr spectroscopy. The solid residue was extracted with methylene chloride affording *trans*-[PtHCl($Ph_3P)_2$] (0.14 g, 0.19 mmole) characterized by melting point (217–220°) and infrared spectroscopy. Further extraction of the residue afforded 0.004 g of unidentified solid. The water-soluble, white residue which remained was assumed to be potassium chloride.

(ii) Similar reactions were carried out with [PtX($COOC_2H_5$)($Ph_3P)_2$]–KX–H_2O systems for X = Br or I. For [PtBr($COOC_2H_5$)($Ph_3P)_2$] as starting material, *trans*-[PtHBr($Ph_3P)_2$] was obtained in 90% yield. For the iodo analog only trace reaction was observed.

11. Reactions of [PtX(COOR)($Ph_3P)_2$] with Water and No Salt Catalyst. In all cases it was found that reaction to give the platinum hydrido compound from the ester species did not occur in the absence of a salt. However, NH_4Cl and NMe_4Cl could replace KCl as the salt catalyst.

12. Reaction of [PtCl($COOC_2H_5$)($Ph_3P)_2$] with Methanol. [PtCl($COOC_2H_5$)($Ph_3P)_2$] (0.01 g) was heated with methanol at 63° for 12 hr in an evacuated sealed tube. The solid product was filtered and identified from infrared spectroscopy as [PtCl(COOMe)($Ph_3P)_2$] (0.008 g): for [PtCl($COOC_2H_5$)($Ph_3P)_2$], ν(C=O) 1638 cm^{-1} (Nujol mull); for [PtCl($COOCH_3$)($Ph_3P)_2$], ν(C=O) 1665 cm^{-1} (Nujol mull).

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