Some Reactions of Phosphine Complexes of Platinum(0) and Palladium(0) with Acidic Solvents; a Phosphorus-31 Nuclear Magnetic Resonance Study

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The complexes $[Pt(PPh_3)_4]$ and $[Pt(PPh_3)_3]$ react quantitatively with anhydrous hydrogen chloride and bromide to give *cis*-dihalogenobis(triphenylphosphine)platinum(II) complexes and hydrogen. $[Pd(PPh_3)_4]$ In liquid hydrogen chloride reacts to give *trans*-dichlorobis(triphenylphosphine)palladium(II) and hydrogen but the reaction proceeds with further replacement of triphenylphosphine at the metal, since *trans*-$[PdCl_2(PPh_3)_2]$ itself reacts in liquid hydrogen chloride to give triphenylphosphonium tetrachlorodi-μ-chloro-dipalladate(II), $[Ph_3PH]_2[Pd_2Cl_6]$. $[NiCl_2(PPh_3)_2]$ Reacts with liquid hydrogen chloride to give $NiCl_2$ and $Ph_3PH^+HCl_2^-$. The reactions of $[Pt(PPh_3)_4]$ with sulphuric and trifluoroacetic acids have also been studied.

THE reactions of acids with complexes of transition metals in formally low oxidation states are of considerable interest, since various courses are possible. Protonation may occur at one of the ligands, without change of oxidation state. Alternatively, oxidation of the metal may take place, together with reduction of the acid, giving either a metal–hydrido-complex (oxidative addition), or liberating hydrogen.[1-4] Various weak acids HX have been shown to react with tris- or tetrakis-triphenylphosphine complexes of platinum(0) and palladium(0), forming hydrido-complexes of the type $[M(PPh_3)_2HX]$.[5-12] The reaction products with stronger acids appear to depend on the conditions, however.[13-16] Cariati *et al.* reported that hydrogen chloride in benzene solution produces the covalent hydride $[Pt(PPh_3)_2HCl]$ from tris- or tetrakis-triphenylphosphineplatinum(0), while in alcoholic solution it gives the ionic compound $[(PPh_3)_3PtH]^+Cl^-$.[13] Kudo *et al.* prepared *trans*-$[PdHCl(PPh_3)_2]$ by the action of hydrogen chloride on $[Pd(PPh_3)_4]$ or $[Pd(PPh_3)_3(CO)]$ in ether at 223 K, but found that excess of acid led to the formation of *trans*-$[PdCl_2(PPh_3)_2]$.[14] The action of liquid hydrogen fluoride on $[Pt(PPh_3)_4]$ has been used to prepare difluorobis(triphenylphosphine)platinum(II),[15] but more recently both this reaction and that of tris(triphenylphosphine)platinum(0) with hydrogen fluoride have been reported to produce a compound $[PtF_3(PPh_3)_3H]$, tentatively formulated as $[PtF(PPh_3)_3]HF_2$.[16] The products have generally been characterised after their isolation as solids, however, and few investigations of solution reactions have been carried out. As part of a series of studies of the liquid hydrogen chloride solvent system,[17] we have investigated the reactions of $[Pt(PPh_3)_4]$, $[Pt(PPh_3)_3]$, $[Pd(PPh_3)_4]$, *cis*-$[Pt(PPh_3)_2Cl_2]$, *trans*-$[Pd(PPh_3)_2Cl_2]$, and $[Ni(PPh_3)_2Cl_2]$ with liquid HCl *in situ* by means of ^{31}P n.m.r. spectroscopy. Results are also reported for the reaction of $[Pt(PPh_3)_4]$ with liquid DCl, HBr, CF_3CO_2H, and 100% H_2SO_4.

EXPERIMENTAL

Manipulations were carried out either *in vacuo*, or in an inert atmosphere box under dry nitrogen. Commercial chemicals were of the best available grade, and were used without further purification, except as described below. Hydrogen chloride and hydrogen bromide were purified as described in previous papers.[17,18] Triphenylphosphine was recrystallised from acetone. Boron trichloride was treated with mercury to remove any traces of chlorine. Deuterium chloride was kindly donated by Dr. C. J. Ludman, and tetrakis(triphenylphosphine)palladium(0) by Dr. T. Inglis. Tetrakis- and tris-triphenylphosphineplatinum(0),[19] and dichlorobis(triphenylphosphine)nickel(II),[20] were prepared by standard methods.

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Triphenylphosphonium Hydrogendichloride, $Ph_3PH^+HCl_2^-$.—Triphenylphosphine (1 mmol) was dissolved in hydrogen chloride (2 ml) at 178 K. The solution was allowed to equilibrate and excess of HCl was pumped off until a sticky white solid remained. Further pumping at room temperature resulted in the evolution of more gas, identified as HCl from its i.r. spectrum, and left a white powder (Found: C, 64·4; H, 4·45. $Ph_3PH^+HCl_2^-$ requires C, 64·49; H, 5·08%). The i.r. spectrum contained a sharp, weak absorption at 2406 cm^{-1} not found in the spectrum of triphenylphosphine, and assigned to ν_{P-H} in the cation.[21,22] The presence of HCl_2^- was shown by a strong broad absorption with a maximum at *ca.* 750 cm^{-1}, tailing off towards 1300 cm^{-1}.[23]

Reaction between $[Pt(PPh_3)_4]$ *and* HCl.—HCl (200 mmol) Was condensed at 77 K into a 13 mm-o.d. quartz ampoule containing $[Pt(PPh_3)_4]$ (0·716 mmol). The ampoule was sealed and allowed to warm to room temperature, to give a pale yellow solution. After 12 h at 293 K, the ampoule was cooled to 77 K and opened *via* the vacuum line to a spiral gauge. A permanent gas was detected of molecular weight 1 ± 1, and was assumed to be hydrogen. The sample was warmed to 178 K and HCl pumped off to leave a white solid. The last trace of HCl was removed by pumping for 2 h at room temperature. The solid analysed as a 2 : 1 mixture of $Ph_3PH^+HCl_2^-$ and *cis*-$[Pt(PPh_3)_2Cl_2]$ (Found: C, 60·1; H, 5·0; Cl, 11·6; P, 8·95. The 2 : 1 mixture requires C, 59·2; H, 4·35; Cl, 14·6; P, 8·49%). The low value for chlorine is probably due to loss of hydrogen chloride from triphenylphosphonium hydrogendichloride. The i.r. spectrum of the solid showed all the bands found for *cis*-$[Pt(PPh_3)_2Cl_2]$,[24] but the weak band at *ca.* 2400 cm^{-1} and broad underlying absorption at 750 cm^{-1} expected for Ph_3PH^+ [21,22] and HCl_2^- [23] respectively were not readily apparent. The i.r. spectrum of a 2 : 1 molar ratio of authentic samples of $Ph_3PH^+HCl_2^-$ and *cis*-$[Pt(PPh_3)_2Cl_2]$ was recorded, however, and the P–H absorption at 2408 cm^{-1} was barely detectable, being of the same order as machine noise, while the hydrogendichloride absorption was apparently absent.

Reaction between $[Pt(PPh_3)_4]$ *and* BCl_3 *in Liquid* HCl.—HCl (200 mmol) Was condensed at 77 K into a 13 mm-o.d. quartz tube containing $[Pt(PPh_3)_4]$ (0·8 mmol), followed by BCl_3 (11·4 mmol). A clear, pale yellow, solution was obtained on warming to room temperature. After 24 h at 293 K, the ampoule was cooled to 178 K and opened to the vacuum line. HCl Was pumped off, and further pumping for 12 h at room temperature removed excess of BCl_3. The white solid analysed as a 2 : 1 mixture of $Ph_3PH^+BCl_4^-$ and $[Pt(PPh_3)_2Cl_2]$ (Found: C, 51·6; H, 3·90; Cl, 23·2; P, 8·20. The mixture requires C, 53·3; H, 3·95; Cl, 21·9; P, 7·65%). The i.r. spectrum contained absorptions characteristic of *cis*-$[(Ph_3P)_2PtCl_2]$,[24] together with a broad absorption with maxima at 690 and 664 cm^{-1}, assigned to the tetrachloroborate ion.[25,26]

Triphenylphosphonium Tetrachlorodi-μ-chloro-dipalladate(II), $[Ph_3PH]_2[Pd_2Cl_6]$.—This compound was deposited as red crystals from solutions of *trans*-$[Pd(PPh_3)_2Cl_2]$ in liquid HCl (Found: C, 45·3; H, 3·55; Cl, 22·4; P, 6·6; Pd, 24·1. $[Ph_3PH]_2[Pd_2Cl_6]$ requires C, 45·4; H, 3·36; Cl, 22·4; P, 6·51; Pd, 22·3%). The i.r. spectrum contained bands at 357s, 305m, and 267ms cm^{-1}, similar to those reported by Adams *et al.* for other salts of the $[Pd_2Cl_6]^{2-}$ ion.[27] The weak P–H absorption expected for Ph_3PH^+ around 2400 cm^{-1} was not detected, but this band is not apparent in the spectra of other triphenylphosphonium salts of high molecular weight, as mentioned above.

N.m.r. samples in liquid HCl, DCl, or HBr were prepared by condensing the appropriate solvent at 77 K onto the complex (*ca.* 0·1 mmol) or mixture (see Discussion section) in an 8 mm-o.d. quartz tube connected to a vacuum line. A non-condensible gas was evolved from Pt^0 and Pd^0 complexes, identified as hydrogen from a separate experiment. The tubes were sealed, and tested to 313 K to make sure that they could withstand the pressure. (The operating temperature of the n.m.r. spectrometer was 307·2 K.) Trifluoroacetic and 100% sulphuric acids were added by syringe to samples of $[Pt(PPh_3)_4]$ (0·20 and 0·17 mmol respectively) contained in 8 mm-o.d. Pyrex ampoules. The ampoules were cooled to 77 K, evacuated to remove any non-condensible gas, and sealed. They were then allowed to warm to room temperature. ^{31}P N.m.r. spectra were recorded on a Perkin-Elmer R10 spectrometer operating at 24·29 MHz, with a Digiac signal-averaging accessory. Chemical shifts were measured relative to external P_4O_6, but are quoted relative to 85% phosphoric acid.

I.r. spectra were recorded on a Perkin-Elmer 457 instrument in the range 4000—250 cm^{-1}. Carbon, hydrogen, and nitrogen microanalyses were obtained by combustion using a Perkin-Elmer 240 Elemental Analyser. Phosphorus was determined colorimetrically as the phosphomolybdovanado-complex after decomposition of the compound by heating with sodium peroxide in a nickel Parr bomb. Chloride was determined by potentiometric titration against silver nitrate, and palladium by atomic absorptiometry using a Perkin-Elmer 403 atomic absorption spectrophotometer.

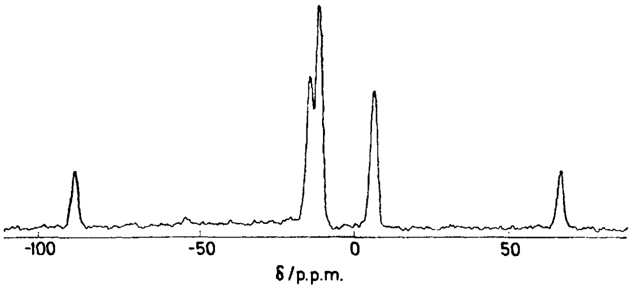

FIGURE 1 The ^{31}P n.m.r. spectrum of $[Pt(PPh_3)_4]$ in liquid HCl

RESULTS AND DISCUSSION

The ^{31}P n.m.r. spectrum of tetrakis(triphenylphosphine)platinum(0) in liquid HCl is shown in Figure 1. There are clearly two phosphorus-containing species present. The triplet resonance is assigned to triphenylphosphine groups bound to platinum; the outer peaks arise from coupling with the ^{195}Pt isotope present in

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33·7% abundance[28] ($\delta^{31}P$ = −11·4 p.p.m.; $^1J_{^{31}P-^{195}Pt}$ = 3875 ± 10 Hz). The magnitude of the coupling constant indicates that the ligands are in a *cis*-configuration.[29-31] The coupling constant of the remaining doublet is as expected for P–H coupling[28,32] ($\delta^{31}P$ = −4·0 p.p.m.; $^1J_{^{31}P-^{1}H}$ = 510 ± 5 Hz). The signal is therefore ascribed to the triphenylphosphonium ion, Ph_3PH^+, which has been isolated previously from HCl solution as the tetrachloroborate.[33] The two resonances are present in a 1 : 1 intensity ratio, showing that two phosphine ligands have been displaced in the reaction. A chemical shift of 0·0 has been reported for triphenylphosphonium chloride,[32] but the difference between that value and our observations is not surprising in view of differences in both diamagnetic susceptibility and counter-ion.

The results for $[Pt(PPh_3)_4]$ in liquid deuterium chloride support the above conclusions (Figure 2). The triplet is again present ($\delta^{31}P$ — 13·5 p.p.m.; $^1J_{^{31}P-^{195}Pt}$ 3873 ± 10 Hz) but the doublet is replaced by a 1 : 1 : 1 triplet, as expected for phosphorus–deuterium coupling ($\delta^{31}P$ — 5·7 p.p.m.; $^1J_{^{31}P-^{2}H}$ 77·5 ± 1 Hz). The ratio of the coupling constants $^1J_{^{31}P-^{1}H} : {}^1J_{^{31}P-^{2}H}$ is 6·58, in good agreement with the theoretical value of 6·51[34] and with values from previous determinations of P–^{2}H coupling constants.[35-38]

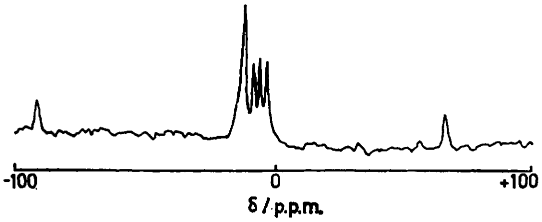


FIGURE 2 The ^{31}P n.m.r. spectrum of $[Pt(PPh_3)_4]$ in liquid DCl

The assignment of the doublet to Ph_3PH^+ and of the 1 : 1 : 1 triplet to Ph_3PD^+ has been confirmed by recording the spectrum of triphenylphosphine in liquid HCl and DCl. Values of $\delta^{31}P$ = −6·0 p.p.m., $^1J_{^{31}P-^{1}H}$ = 512 ± 5 Hz (HCl) and $\delta^{31}P$ = −5·5 p.p.m., $^1J_{^{31}P-^{2}H}$ = 77·5 ± 1 Hz (DCl) were obtained, in excellent agreement with those found for the platinum-containing solutions. Triphenylphosphonium hydrogendichloride, $Ph_3PH^+HCl_2^-$, was isolated from HCl solution and identified by elemental analysis and i.r. spectroscopy.[21-23]

The evolution of hydrogen shows that oxidation of platinum(0) takes place, and the most probable product to accord with the n.m.r. data is *cis*-dichlorobis(triphenylphosphine)platinum(II), as shown by the equation.

$$[Pt(PPh_3)_4] + 6HCl \longrightarrow [Pt(PPh_3)_2Cl_2] + 2[Ph_3PH]^+[HCl_2]^- + H_2$$

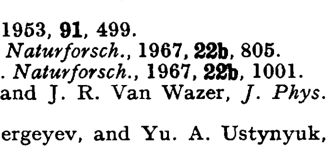
The i.r. spectrum and elemental analysis of the residual solid isolated by pumping off the solvent were entirely compatible with this equation (Experimental section). The identity of the platinum-containing component has been confirmed by a series of experiments. The ^{31}P n.m.r. spectrum of a sample of *cis*-$[Pt(PPh_3)_2Cl_2]$ in liquid HCl consisted of a triplet at −12·1 p.p.m., with $^1J_{^{31}P-^{195}Pt}$ 3873 ± 10 Hz. No signals due to Ph_3PH^+ were found, and in an independent experiment it was shown that the starting material could be recovered unchanged. The ^{31}P n.m.r. spectrum of a 2 : 1 mixture of triphenylphosphine and *cis*-$[Pt(PPh_3)_2Cl_2]$ in liquid HCl contained a triplet at −10 p.p.m. ($^1J_{^{31}P-^{195}Pt}$ 3876 ± 10 Hz) and a 1 : 1 doublet at −4·5 p.p.m. ($^1J_{^{31}P-^{1}H}$ 512 ± 5 Hz), in an overall 1 : 1 intensity ratio. Finally, a 1 : 1 mixture of $[Pt(PPh_3)_4]$ and *cis*-$[Pt(PPh_3)_2Cl_2]$ in liquid HCl showed only one triplet in the ^{31}P spectrum for phosphines bound to platinum at −12·1 p.p.m. ($^1J_{^{31}P-^{195}Pt}$ 3873 ± 10 Hz), together with a doublet at −4·5 p.p.m. ($^1J_{^{31}P-^{1}H}$ 510 ± 5 Hz), in a 2 : 1 intensity ratio.

Further evidence in favour of the postulated course of reaction is provided by the results of the addition of boron trichloride to a solution of $[Pt(PPh_3)_4]$ in HCl. The i.r. spectrum and elemental analysis of the white solid obtained after removal of the excess of HCl and BCl_3 were as expected for a 2 : 1 molar ratio of triphenylphosphonium tetrachloroborate to *cis*-$[Pt(PPh_3)_2Cl_2]$, formed according to:

$$[Pt(PPh_3)_4] + 4HCl + 2BCl_3 \longrightarrow 2Ph_3PH^+BCl_4^- + [Pt(PPh_3)_2Cl_2] + H_2$$

Druce, Lappert, and Riley have reported recently that *cis*-dihalogenobis(tri-n-butylphosphine)platinum(II) complexes react with an excess of boron trichloride to give halogen-bridged binuclear cationic platinum(II) complexes,[39] as shown by the equation:

$$2\ cis\text{-}[L_2PtX_2] + 2BX_3 \longrightarrow$$



No evidence for such a reaction was found here, however. Presumably boron trichloride, a powerful Lewis acid, reacts with the tri-n-butylphosphine complex by

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abstracting chloride ions. Liquid hydrogen chloride is also a good chloride ion acceptor, but *cis*-$[Pt(PPh_3)_2Cl_2]$ may be recovered unchanged from this solvent, as indicated above, so that its lack of reactivity towards boron trichloride is not unexpected.

Tetrakis(triphenylphosphine)platinum(0) reacts with liquid hydrogen bromide in an analogous manner to its reaction with HCl. The ^{31}P n.m.r. spectrum contains a triplet at −11·5 p.p.m. with $^{1}J_{^{31}P-^{195}Pt}$ 3790 ± 10 Hz, and a triphenylphosphonium doublet, one peak of which partially overlaps the central peak of the triplet, at −1·9 p.p.m. with $^{1}J_{^{31}P-^{1}H}$ 510 ± 5 Hz, in a 1 : 1 intensity ratio. The product is thus again a *cis*-dihalogenobis(triphenylphosphine)platinum(II) complex, according to:

$$[Pt(PPh_3)_4] + 2HBr \longrightarrow cis\text{-}[Pt(PPh_3)_2Br_2] + 2Ph_3PH^+ + 2Br^-(\text{solvated}) + H_2$$

The products from the reaction of tris(triphenylphosphine)platinum(0) with liquid HCl are identical with those from the tetrakis-compound, but in a 1 : 1 molar ratio of *cis*-$[Pt(PPh_3)_2Cl_2]$ to $[Ph_3PH]^+[HCl_2]^-$, thus giving a 2 : 1 intensity ratio of triplet to doublet in the ^{31}P spectrum ($\delta^{31}P$ P–Pt −12·5 p.p.m.; $^{1}J_{^{31}P-^{195}Pt}$ 3876 ± 10 Hz; $\delta^{31}P$ Ph_3PH^+ −4·5 p.p.m.; $^{1}J_{^{31}P-^{1}H}$ 510 ± 5 Hz). The results show clearly that one triphenylphosphine ligand only is displaced. We therefore conclude that triphenylphosphine complexes of platinum(0) react quantitatively with liquid HCl, DCl, and HBr to yield *cis*-dihalogenobis(triphenylphosphine)platinum(II). The products are different from those reported by Cariati *et al.*[13] for the reaction of hydrogen chloride with $[Pt(PPh_3)_4]$ and $[Pt(PPh_3)_3]$ in benzene or ethanol solutions, but the conditions here are by no means comparable, since even a change of solvent may produce profound effects. The reaction appears to be similar to that with liquid hydrogen fluoride reported by Sharp and his co-workers,[15] and may also be compared with the observation of Kudo *et al.* that an excess of hydrogen chloride led to the formation of *trans*-dichlorobis(triphenylphosphine)palladium(II) from $[Pd(PPh_3)_4]$ instead of a hydrido-complex.[14]

The reaction of tetrakis(triphenylphosphine)palladium(0) with liquid HCl is more complicated than those of the platinum(0) complexes. The ^{31}P n.m.r. spectrum shows three resonances, two apparent singlets at −35·0 and −31·0 p.p.m., probably due to triphenylphosphine–palladium complexes, and a triphenylphosphonium doublet at −3·6 p.p.m., with $^{1}J_{^{31}P-^{1}H}$ 510 ± 5 Hz. The approximate intensity ratios are 1 : 10 : 60 respectively. (No satellite peaks for coupling between phosphorus and the ^{105}Pd isotope, which is present in 22·3% abundance and has a spin of 5/2,[28] were observed.) Extensive displacement of triphenylphosphine ligands has evidently occurred, beyond the stage reached in the platinum(0) systems. A yellow solid obtained on removal of the solvent showed the i.r. bands expected for *trans*-$[Pd(PPh_3)_2Cl_2]$, and a very weak band at 2400 cm^{-1} assignable to Ph_3PH^+.[21,22] The behaviour of *trans*-$[Pd(PPh_3)_2Cl_2]$ in liquid HCl was therefore investigated. The complex dissolved slowly in the solvent, but then began to deposit red crystals. The ^{31}P spectrum of the yellow solution above the crystals showed only a 1 : 1 doublet at −2·7 p.p.m., with $^{1}J_{^{31}P-^{1}H}$ 504 ± 5 Hz, characteristic of Ph_3PH^+. Displacement of phosphine ligands from the palladium(II) complex thus takes place. The red air-stable solid was identified as $[Ph_3PH]_2^+$ $[Pd_2Cl_6]^-$ from a complete elemental analysis and its i.r. spectrum. The non-formation of this complex from the palladium(0) compound appears surprising at first sight, but displacement of further triphenylphosphine groups may well be difficult in the presence of a high concentration of Ph_3PH^+ ions, which would be produced in this reaction.

The reaction of the tetrahedral nickel complex dichlorobis(triphenylphosphine)nickel(II) with liquid HCl was also studied. A buff precipitate was produced at room temperature, and the ^{31}P n.m.r. spectrum showed only a weak doublet at −3·5 p.p.m., with $^{1}J_{^{31}P-^{1}H}$ 510 Hz, assigned to Ph_3PH^+. The analysis and i.r. spectrum of the solid, which was pale pink after separation from HCl, were as expected for a mixture of nickel(II) chloride and triphenylphosphonium hydrogendichloride. Complete displacement of triphenylphosphine ligands thus appears to occur, and the contrast in the behaviour of the dichlorobis(triphenylphosphine)platinum(II), -palladium(II), and -nickel(II) complexes is noteworthy.

The reactions of $[Pt(PPh_3)_4]$ with the strong acids 100% H_2SO_4 and CF_3CO_2H have also been investigated by ^{31}P n.m.r. The spectrum of the complex in 100% H_2SO_4 contains a triplet for triphenylphosphine groups bound to platinum at −27 p.p.m., with $^{1}J_{^{31}P-^{195}Pt}$ 2805 ± 10 Hz, and a triphenylphosphonium doublet at −5·5 p.p.m. with $^{1}J_{^{31}P-^{1}H}$ 510 ± 5 Hz, in an approximately 1 : 2 intensity ratio, together with a small unidentified peak at −47 p.p.m. The magnitude of the phosphorus–platinum coupling constant suggests that the initial product is a *trans*-bis(triphenylphosphine)platinum(II) complex[29–31] but the relative intensities indicate that this compound also reacts with the solvent to produce more triphenylphosphonium ion. Three signals are present in the spectrum of the trifluoroacetic acid solution, a triplet at −20 p.p.m. with $^{1}J_{^{31}P-^{195}Pt}$ 2850 ± 5 Hz, a doublet at −5·0 p.p.m. with $^{1}J_{^{31}P-^{1}H}$ 514 ± 5 Hz, and a weak singlet at −23·6 p.p.m. These signals are assigned to a *trans*-bis(triphenylphosphine)platinum(II) complex, the Ph_3PH^+ ion, and possibly a second phosphorus–platinum species respectively. The intensity of the doublet relative to that of the triplet increased over a period of several months from *ca.* 0·33 : 1 to *ca.* 0·5 : 1, showing that reaction was still proceeding. Roundhill and his co-workers[12] have recently reported the preparation of the ionic hydride $[(Ph_3P)_3PtH]^+$-$H(CF_3COO)_2^-$ from the reaction of $[Pt(PPh_3)_4]$ and trifluoroacetic acid in benzene. The ^{1}H n.m.r. of their complex showed a ^{31}P–^{1}H coupling of 160 Hz arising from the phosphine group *trans* to hydrogen, but the

^{31}P spectrum contained a single peak only, at +26·6 p.p.m., ascribed to the two phosphine groups *trans* to each other, and the additional signal expected was not detected. In the present work, we observed no signal at +26·6 p.p.m., and found no evidence from the ^{31}P n.m.r. spectrum for formation of a protonated species. As in the liquid HCl work, the reaction medium is completely different from that used by Roundhill, so that the difference in products is not surprising.

It appears, therefore, that platinum(0)- and palladium(0)-triphenylphosphine complexes are oxidised to the +2 oxidation state in the acidic solvents. Tetrakis(triphenylphosphine)platinum(0) reacts quantitatively with HCl, DCl, and HBr to produce the corresponding *cis*-dihalogenobis(triphenylphosphine)platinum(II) complex which is then stable in the solvent, together with triphenylphosphonium ion and hydrogen (or deuterium). Tris(triphenylphosphine)platinum(0) behaves in a similar way with HCl. The action of HCl on tetrakis(triphenylphosphine)palladium(0) produces a palladium(II) complex, probably *trans*-dichlorobis(triphenylphosphine)palladium(II), but this is further attacked by the solvent. *trans*-[Pd(PPh$_3$)$_2$Cl$_2$] Itself reacts comparatively slowly with liquid HCl to yield triphenylphosphonium tetrachloro-di-μ-chloro-dipalladate(II), and the nickel(II) complex [Ni(PPh$_3$)$_2$Cl$_2$] produces nickel(II) chloride and triphenylphosphonium hydrogendichloride. [Pt(PPh$_3$)$_4$] Also reacts with 100% H_2SO_4 and CF_3CO_2H to give *trans*-bis(triphenylphosphine)platinum(II) complexes, which are then subject to further attack with the formation of more triphenylphosphonium ion.

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