Synthesis and Some Oxidative-addition Reactions of Bis(tricyclohexylphosphine)platinum

By **Juan Fornies, Michael Green, John L. Spencer, and F. Gordon A. Stone,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Treatment of bis(cyclo-octa-1,5-diene)platinum with 2 molar equivalents of tricyclohexylphosphine affords two-co-ordinate bis(tricyclohexylphosphine)platinum. The complex $[Pt(PMeBu^t_2)_2]$ may be obtained in the same manner but is markedly less stable. Bis(tricyclohexylphosphine)platinum reacts with hydrogen to give *trans*-$[PtH_2\{P(C_6H_{11})_3\}_2]$ and with a series of compounds RH, containing active hydrogen, to afford hydrides *trans*-$[PtH(R)\{P(C_6H_{11})_3\}_2]$ (R = C_6F_5, 1,3,5-$C_6F_3H_2$, 1,3-$C_6F_2H_3$, C_6F_5O, PhO, C_6F_5NH, and C_4H_4N). Tris(triethylphosphine)platinum is less reactive towards some of these substrates but with pentafluorobenzene yields *trans*-$[PtH(C_6F_5)(PEt_3)_2]$. Chlorobenzene and $[Pt\{P(C_6H_{11})_3\}_2]$ afford *trans*-$[PtCl(Ph)\{P(C_6H_{11})_3\}_2]$.

FOLLOWING Malatesta's [1] discovery of tetrakis- and tris(triphenylphosphine)platinum, there has been considerable interest in the oxidative-elimination chemistry of these and related species.[2] Although the tetrakis- and

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tris-phosphine complexes dissociate in solution thus affording vacant sites for reaction, the released phosphine ligands compete with substrate molecules for these sites, thereby reducing the reactivity of platinum(0) in these complexes. In this context, two-co-ordinate 14-electron complexes $[Pt(PR_3)_2]$ are of considerable interest as sources of Pt^0. The synthesis [3] of bis(cyclo-octa-1,5-diene)platinum provides a convenient route to these complexes by treatment with 2 molar equivalents of tertiary phosphine. Herein we describe the synthesis of bis(tricyclohexylphosphine)- and bis(methyldi-t-butylphosphine)-platinum and some reactions of the former.[4] The complex $[Pt\{P(C_6H_{11})_3\}_2]$ has been prepared independently by treating $[Pt(\eta\text{-}C_3H_5)\{P(C_6H_{11})_3\}_2][PF_6]$ with potassium t-butoxide in tetrahydrofuran. A single-crystal *X*-ray diffraction study demonstrated the monomeric character of the complex, and established a P–Pt–P bond angle of 160.5°.[5a] The compounds $[PtL_2]$ $[L = PBu^t_2Ph, P(C_6H_{11})_3, \text{ and } PPr^i_3]$ have recently been prepared [5b] by reduction of *trans*-$[PtCl_2L_2]$ with sodium amalgam, but $[Pt(PBu^t_3)_2]$ could only be obtained from $[Pt(cod)_2]$ [3] *via* the method described herein.

Analytical [a] and physical data for the hydrides *trans*-$[PtH(R)\{P(C_6H_{11})_3\}_2]$

Complex [b]	M.p. (θ_c/°C)	$\tilde{\nu}$(PtH) [c] cm^{-1}	^{1}H N.m.r.[d]	Analysis (%) C	H
$[PtH(C_6F_5)\{P(C_6H_{11})_3\}_2]$	225 (decomp.)	2 030, 2 028	18.52 (t, 12.2)	55.0 (54.6)	7.6 (7.3)
$[PtH(1,3,5\text{-}C_6F_3H_2)\{P(C_6H_{11})_3\}_2]$	253 (decomp.)	2 105, 2 090	25.02	56.6 (56.8)	8.1 (7.8)
$[PtH(1,3\text{-}C_6F_2H_3)\{P(C_6H_{11})_3\}_2]$	130 (decomp.)	2 080, 2 060		57.3 (58.0)	8.4 (8.1)
$[PtH(OC_6F_5)\{P(C_6H_{11})_3\}_2]$	195—200	2 291	34.86 (t, 14.0)	54.1 (53.7)	6.6 (7.2)
$[PtH(OPh)\{P(C_6H_{11})_3\}_2]$	140—145	2 263, 2 235	26.7 (t, 14.6)	60.4 (59.3)	8.5 (8.5)
$[PtH(NHC_6F_5)\{P(C_6H_{11})_3\}_2]$ [e]	189—192	2 198	27.50 (t, 14.6)	54.1 (53.9)	7.6 (7.4)
$[PtH(C_4H_4N)\{P(C_6H_{11})_3\}_2]$	198—205	2 134	26.54 (t, 13.4)	58.2 (58.4)	8.9 (8.7)

[a] Calculated values are given in parentheses. [b] White crystals. [c] In Nujol. [d] Chemical shift (τ) for PtH; J_{PH} in Hz is given in parentheses. [e] N, 1.6 (1.5%). [f] N, 1.6 (1.7%).

RESULTS AND DISCUSSION

The cyclo-octa-1,5-diene ligands in $[Pt(cod)_2]$ (cod = 1 5-C_8H_{12}) are labile, being readily displaced by ethylene,[3] diphenylacetylene,[6] and tertiary phosphines.[4] Treatment of $[Pt(cod)_2]$ with 2 molar equivalents of tricyclohexylphosphine or methyldi-t-butylphosphine at room temperature afforded the air-sensitive complexes $[Pt(PR_3)_2]$ $[R_3 = (C_6H_{11})_3 \text{ or } (MeBu^t_2)_3]$. These complexes are soluble in organic solvents but the $PMeBu^t_2$ derivative decomposes in the course of a few days even when stored as a solid under nitrogen. In their ^{31}P n.m.r. spectra they show substantially larger platinum–phosphorus couplings (*ca.* 4 000 Hz) than those found [7] with the $[Pt(PR_3)_4]$ complexes (*ca.* 3 000 Hz) as would be expected since the Pt–P bond in the two-co-ordinate complexes would have more *s* character.

Several oxidative-addition reactions of $[Pt\{P(C_6H_{11})_3\}_2]$ which afford hydridoplatinum species were examined. Dihydrogen reacted at atmospheric pressure and room temperature to give *trans*-$[PtH_2\{P(C_6H_{11})_3\}_2]$, previously obtained by other routes.[8,9] Carbon–hydrogen bonds of the fluorobenzenes C_6F_5H, 1,3,5-$C_6F_3H_3$, and 1,3-$C_6F_2H_4$ were cleaved at ambient temperatures to give the corresponding *trans*-hydrido-complexes (Table), but $[Pt\{P(C_6H_{11})_3\}_2]$ did not undergo oxidative-addition with 1,2-$C_6F_2H_4$, 1,4-$C_6F_2H_4$, or C_6H_5F. No reaction occurred with benzene, toluene, or naphthalene even under reflux.

The pronounced enhancement of C–H acidities in aromatic rings by fluorine substituents is well known.[10] Moreover, in metallation reactions C–H bonds with two *ortho*-fluorine substituents are the most reactive,[11] indicating greater protonic character of these hydrogens. This probably accounts for the formation of hydrides from $[Pt\{P(C_6H_{11})_3\}_2]$ and 1,3,5-$C_6F_3H_3$ or 1,3-$C_6F_2H_4$, but not from 1,2-$C_6F_2H_4$, 1,4-$C_6F_2H_4$, or C_6H_5F.

In reactions with fluorobenzenes, tris(triethylphosphine)platinum [12-14] is less reactive than bis(tricyclohexylphosphine)platinum since the former does not form a hydride on treatment with 1,3,5-$C_6F_3H_3$ or 1,3-$C_6F_2H_4$. However, with the more protonic C–H of C_6F_5H the complex *trans*-$[PtH(C_6F_5)(PEt_3)_2]$ was formed.

In view of the results with the fluorobenzenes, not surprisingly $[Pt\{P(C_6H_{11})_3\}_2]$ reacted with phenol and

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with pentafluorophenol to afford complexes *trans*-$[PtH(OR)\{P(C_6H_{11})_3\}_2]$ (R = Ph or C_6F_5). Of more interest, $[Pt\{P(C_6H_{11})_3\}_2]$ readily underwent oxidative-addition reactions with the N–H bonds of pyrrole and pentafluoroaniline to give stable hydrido-species (Table). Examples of the cleavage of N–H linkages in this manner are rare, although bis(tricyclohexylphosphine)nickel reacts with pyrrole to yield a nickel hydride.[15]

In contrast to the behaviour of $[Pt\{P(C_6H_{11})_3\}_2]$, tris(triethylphosphine)platinum did not react with pentafluoroaniline. Moreover, the N–H bonds of aniline, 1-amino-2,6-difluorobenzene, ammonia, and morpholine were not cleaved by $[Pt\{P(C_6H_{11})_3\}_2]$. Evidently the highly electronegative C_6F_5 group activates N–H in $C_6F_5NH_2$ for reaction with the tricyclohexylphosphine-platinum complex. The electron-withdrawal properties of C_6F_5 would render the N–H bond more polar thereby increasing the protonic character of the hydrogen.

Chlorobenzene reacted with $[Pt\{P(C_6H_{11})_3\}_2]$ to give *trans*-$[PtCl(Ph)\{P(C_6H_{11})_3\}_2]$, but no C–C bond cleavage occurred on treatment of PhCN with the platinum complex even when the reactants were heated. This is surprising in view of the formation of *trans*-$[Pt(CN)Ph(PEt_3)_2]$ from the reaction of tris(triethylphosphine)platinum and benzonitrile.[12] Thus, based on the studies reported herein, $[Pt\{P(C_6H_{11})_3\}_2]$ is more reactive towards C–H, O–H, and N–H bonds than is $[Pt(PEt_3)_3]$, but is less reactive towards C_6H_5–CN.

Although the complex $[Pt\{P(C_6H_{11})_3\}(C_2H_4)_2]$ [4] is also co-ordinatively unsaturated and has readily displaceable ethylene ligands, it is less reactive in oxidative-addition reactions than $[Pt\{P(C_6H_{11})_3\}_2]$ towards the substrates mentioned above. Thus no products were isolated after treatment of $[Pt\{P(C_6H_{11})_3\}(C_2H_4)_2]$ with C_6F_5OH, $C_6F_5NH_2$, or C_6F_5H. Evidently a second tricyclohexylphosphine ligand is required to increase the nucleophilicity of the platinum. Interestingly, $[Pt\{P(C_6H_{11})_3\}(C_2H_4)_2]$ does cleave the H–H bond of dihydrogen and Si–H bonds.[16]

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on Varian Associates HA100 and JEOL JNM-PFT-100 spectrometers. Phosphorus-31 and ^{19}F spectra were obtained (in C_6D_6 unless otherwise stated) on the JEOL instrument with shifts relative to CCl_3F (^{19}F) and external H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer. Experiments were carried out under a dry oxygen-free nitrogen atmosphere, using solvents dried and distilled under nitrogen prior to use. Light petroleum had b.p. 40—60 °C. Analytical and other data are given in the Table.

Syntheses.—Bis(tricyclohexylphosphine)platinum. Bis(cyclo-octa-1,5-diene)platinum (0.41 g, 1 mmol) was suspended in light petroleum (10 cm^3) and a solution of tricyclohexylphosphine (0.56 g, 2 mmol) in the same solvent (10 cm^3) was added. Solvent was removed at reduced pressure to a volume of *ca.* 5 cm^3, and the supernatant liquid was decanted from the white solid. The latter was washed twice with light petroleum (3 cm^3) and recrystallised from this solvent to give off-white *crystals* of bis(tricyclohexylphosphine)platinum (0.5 g, 66%), m.p. 217—219 °C (*in vacuo*) (Found: C, 56.9; H, 8.9. $C_{36}H_{66}P_2Pt$ requires C, 57.2; H, 8.8%). The ^{31}P n.m.r. spectrum (^1H decoupled) showed a singlet at −62.1 p.p.m. with ^{195}Pt satellites (J_{PPt} 4 159 Hz). Infrared spectrum: $\nu_{max.}$ (Nujol) at 1 341w, 1 306w, 1 296w, 1 273w, 1 210w, 1 182m, 1 115m, 1 067w, 1 008m, 923w, 899m, 862s, 828m, 761m, 745m, 718m, 524s, 484m, 471w, 424m, and 401w cm^{-1}.

Bis(methyldi-t-butylphosphine)platinum. Bis(cyclo-octa-1,5-diene)platinum (0.56 g, 1.36 mmol) in toluene (10 cm^3) was treated with methyldi-t-butylphosphine (0.43 g, 2.7 mmol) for 30 min. Solvent was removed and the residue was dissolved in hexane. Concentration to 10 cm^3 and cooling (−30 °C) afforded a white solid which was dried *in vacuo*. *Crystals* (0.45 g, 64%), m.p. 130 °C (decomp.), were obtained by dissolving the solid in toluene and adding hexane with cooling (Found: C, 40.9; H, 8.0. $C_{18}H_{42}P_2Pt$ requires C, 41.9; H, 8.2%). The ^{31}P n.m.r. spectrum (^1H decoupled) showed a singlet at −36.5 p.p.m. with ^{195}Pt satellites (J_{PPt} 4 015 Hz). Hydrogen-1 n.m.r. in C_6D_6: τ 8.77 and 8.95 (multiplets). Infrared spectrum: $\nu_{max.}$ (Nujol) at 1 390s, 1 382s, 1 375s, 1 360m, 1 307s, 1 300w, 1 292w, 1 190m, 1 032m, 1 017w, 945m, 885s, 830s, 825s, 750s, 600m, 590m, 549m, 468s, 454w, and 440w cm^{-1}.

Reactions of Bis(tricyclohexylphosphine)platinum.—(*a*) *With dihydrogen.* A slow stream of dihydrogen was passed through a solution of the complex (0.15 g, 0.2 mmol) in toluene. The initial yellow colour was rapidly discharged and after 20 min the colourless solution was evaporated to dryness at reduced pressure. Recrystallisation from light petroleum gave white crystals of *trans*-dihydridobis(tricyclohexylphosphine)platinum (0.1 g, 66%), m.p. 210 °C (Found: C, 57.5; H, 9.2. Calc. for $C_{36}H_{68}P_2Pt$: C, 57.0; H, 9.0%), $\nu_{max.}$ (Nujol) at 1 712 cm^{-1} (lit.,[8,9] 1 710 cm^{-1}). Hydrogen-1 n.m.r. spectrum in C_6H_6: τ *ca.* 8.3 (m, 66 H, C_6H_{11}) and 13.10 (t with ^{195}Pt satellites, 2 H, Pt–*H*, J_{PH} 17, J_{PPt} 796 Hz), in good agreement with the literature.[8,9] Phosphorus-31 n.m.r. in C_6H_6 (^1H decoupled): −52.8 p.p.m. (s with ^{195}Pt satellites, J_{PPt} 2 872 Hz). Partial irradiation of the ^1H spectrum at the frequency of cyclohexyl protons converted the central line of the ^{31}P spectrum into a triplet.

(*b*) *With pentafluorobenzene.* To the complex (0.67 g, 0.88 mol) in toluene (10 cm^3) was added C_6F_5H (1.5 g, 9.9 mmol). The mixture was stirred (64 h, room temperature), a white precipitate appearing. Solvent was removed *in vacuo*, and the solid was washed with light petroleum and crystallised from benzene to give white *crystals* (0.53 g, 65%) of $[PtH(C_6F_5)\{P(C_6H_{11})_3\}_2]$. Infrared spectrum: $\nu_{max.}$ (Nujol) at 2 030m, 2 028m, 1 498s, 1 433s, 1 300w, 1 285w, 1 253w, 1 236w, 1 208w, 1 190w, 1 184m, 1 168w, 1 138w, 1 126w, 1 080w, 1 070m, 1 050s, 1 016m, 958vs, 928w, 903m, 863m, 832w, 818w, 782m, 755m, 550w, 530m, 508w, and 465w cm^{-1}. N.m.r. spectra: ^{19}F, 111.1 (m, 2 F, J_{PtF} 296.8, J_{PF} 14.65 Hz) and 164.1 p.p.m. (m, 3 F); ^{31}P, −37.53 p.p.m. (d, J_{PH} 12.2, J_{PtP} 2 760 Hz).

(*c*) *With 1,3,5-trifluorobenzene.* Bis(tricyclohexylphosphine)platinum (0.7 g, 0.92 mmol) in toluene (20 cm^3) was treated with $C_6F_3H_3$ (1.3 g, 9.8 mmol) with stirring for 72 h. Solvent was removed, diethyl ether (60 cm^3) was added, and the mixture was filtered. The brown solution

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was reduced in volume to 5 cm³, a similar volume of light petroleum was added, and the mixture was cooled to −50 °C to give off-white *crystals* (0.62 g, 75%) of $[\mathrm{PtH(C_6F_3H_2)\{P(C_6H_{11})_3\}_2}]$. Infrared spectrum: $\nu_{max.}$ (Nujol) at 2 105m, 2 090m, 1 620m, 1 590s, 1 403m, 1 355w, 1 303m, 1 290m, 1 275w, 1 240w, 1 225w, 1 210m,w, 1 198w, 1 188m, 1 185w, 1 155m, 1 142w, 1 123w, 1 106s, 1 083w, 1 060w, 1 020m, 1 002s, 998s, 930m, 912m, 905m, 870m, 839s, 753m, 618w, 590w, 565w, 553w, 535s, 513m, 500m, 483w, 471w, and 441s cm⁻¹. N.m.r. spectra: ^{19}F, 80.2 (m, 2 F, J_{PtF} 272 Hz) and 120.6 p.p.m. (m, 1 F); ^{31}P, −37.32 p.p.m. (d, J_{PH} 15.9, J_{PtP} 2 795 Hz).

(*d*) *With* 1,3-*difluorobenzene*. Bis(tricyclohexylphosphine)platinum (0.7 g, 1 mmol) in toluene (10 cm³) was treated with 1,3-$\mathrm{C_6F_2H_4}$ (1 g, 8 mmol) with stirring for 66 h. Solvent was removed and the residue was dissolved in diethyl ether (80 cm³). Partial evaporation followed by addition of hexane and cooling (−20 °C) gave white *crystals* (0.4 g, 46%) of $[\mathrm{PtH(1,3\text{-}C_6F_2H_3)\{P(C_6H_{11})_3\}_2}]$. Infrared spectrum: $\nu_{max.}$ (Nujol) at 2 080m, 2 060m, 1 475s, 1 436s, 1 305w, 1 299w, 1 275w, 1 238w, 1 223m, 1 200ms, 1 184m, 1 140w, 1 120w, 1 080w, 1 055w, 1 037w, 1 015m, 961s, 928w, 910m, 900m, 861ms, 832m, 777s, 750m, 700m, 550w, 530m, and 506m cm⁻¹. N.m.r. spectra: ^{19}F, 82.6 p.p.m. (m, J_{PtF} 275 Hz); ^{31}P, −37.49 p.p.m. (d, J_{PH} 14.6, J_{PtP} 2 810 Hz).

(*e*) *With pentafluorophenol*. Bis(tricyclohexylphosphine)platinum (0.4 g, 0.6 mmol) in toluene (8 cm³) and $\mathrm{C_6F_5OH}$ (0.6 g, 3 mmol) in toluene (5 cm³) were mixed and stirred for 72 h. Solvent was evaporated and the residue was dissolved in hexane (5 cm³) and cooled to give a mixture of product and pentafluorophenol. Repeated (five times) recrystallisation (hexane) gave white *crystals* (0.3 g, 57%) of $[\mathrm{PtH(OC_6F_5)\{P(C_6H_{11})_3\}_2}]$. Infrared spectrum: $\nu_{max.}$ (Nujol) at 2 291m, 1 534s, 1 521s, 1 515s, 1 499s, 1 473s, 1 382m, 1 308w, 1 298w, 1 273w, 1 253w, 1 203w, 1 183m, 1 173m, 1 163s, 1 134w, 1 123w, 1 082w, 1 058w, 1 015s, 988s, 924w, 908m, 898m, 872w, 862m, 859m, 834w, 828w, 752m, 745m, 731w, 723w, 571w, 542m, 533m, 523m, 501m, 475w, 463m, and 428m cm⁻¹. Phosphorus-31 n.m.r. spectrum: −40.48 p.p.m. (J_{PH} 14.0, J_{PtP} 2 897 Hz).

(*f*) *With phenol*. Bis(tricyclohexylphosphine)platinum (0.6 g, 0.8 mmol) in toluene (5 cm³) with $\mathrm{C_6H_5OH}$ (0.25 g, 2.65 mmol) in toluene (3 cm³) gave after 40 h, and washing with diethyl ether, *crystals* (0.35 g, 52%) of $[\mathrm{PtH(OPh)\{P(C_6H_{11})_3\}_2}]$. Infrared spectrum: $\nu_{max.}$ (Nujol) at 3 057w, 2 263m, 2 235m, 1 613m, 1 591s, 1 573w, 1 508w, 1 492s, 1 485s, 1 476s, 1 353w, 1 342w, 1 335w, 1 325w, 1 306w, 1 287s, 1 278s, 1 271s, 1 255s, 1 203w, 1 183m, 1 178m, 1 173m, 1 168w, 1 158w, 1 138w, 1 123w, 1 078m, 1 071w, 1 043w, 1 016m, 1 002m, 930w, 912w, 901m, 895m, 888w, 883w, 868m, 864m, 862m, 854w, 848w, 843m, 838m, 833m, 828w, 821w, 806w, 774s, 763s, 760m, 753m, 711s, 633w, 585m, 552m, 542m, 531s, 508w, 498w, 482w, 468w, 438m, and 413m cm⁻¹. Phosphorus-31 n.m.r. spectrum: −39.9 p.p.m. (d, J_{PH} 14.6, J_{PtH} 2 866 Hz).

(*g*) *With pentafluoroaniline*. Bis(tricyclohexylphosphine)platinum (0.68 g, 9 mmol) in toluene (10 cm³) treated (72 h) with $\mathrm{C_6F_5NH_2}$ (0.66 g, 3.6 mmol) in toluene (5 cm³) gave, after removal of solvent and pumping *in vacuo*, a residue. The latter was dissolved in diethyl ether, concentrated, and cooled (refrigerator) to give white *crystals* (0.66 g, 72%) of $[\mathrm{PtH(NHC_6F_5)\{P(C_6H_{11})_3\}_2}]$. Infrared spectrum: $\nu_{max.}$ (Nujol) at 3 364w, 2 198m, 1 648m, 1 517s, 1 503s, 1 473s, 1 306m, 1 260m, 1 247w, 1 208w, 1 193w, 1 183m, 1 179w, 1 137m, 1 120m, 1 112m, 1 083w, 1 058w, 1 038w, 1 010s, 973s, 930w, 920w, 903m, 878w, 863m, 858m, 833w, 816w, 756m, 586w, 568w, 549w, 538w, 530m, 506w, and 468w cm⁻¹. Phosphorus-31 n.m.r. spectrum: −36.1 p.p.m. (d, J_{PH} 14.6, J_{PPt} 2 845 Hz).

(*h*) *With pyrrole*. In a similar manner, $[\mathrm{Pt\{P(C_6H_{11})_3\}_2}]$ (0.61 g, 0.8 mmol) in toluene (10 cm³) with $\mathrm{C_4H_4NH}$ (0.27 g, 4 mmol) in toluene (5 cm³) gave, after 40 h, white *crystals* (washed with light petroleum and diethyl ether) (0.54 g, 68%) of $[\mathrm{PtH(C_4H_4N)\{P(C_6H_{11})_3\}_2}]$. Infrared spectrum: $\nu_{max.}$ (Nujol) at 3 087w, 2 134s, 1 304w, 1 247w, 1 238w, 1 216w, 1 204w, 1 191w, 1 181m, 1 176w, 1 137w, 1 118w, 1 094m, 1 086w, 1 057w, 1 044m, 1 016m, 926w, 914w, 912w, 901w, 863m, 856w, 836w, 811w, 756m, 716s, 528m, and 506w cm⁻¹. Phosphorus-31 n.m.r. spectrum: −36.71 p.p.m. (d, J_{PH} 13.4, J_{PtP} 2 813 Hz).

Reaction of Bis(*tricyclohexylphosphine*)*platinum with Chlorobenzene*.—A mixture of chlorobenzene (10 cm³) and $[\mathrm{Pt\{P(C_6H_{11})_3\}_2}]$ (0.76 g, 1 mmol) was stirred at room temperature for 4 d. Solvent was removed *in vacuo* and the residue was recrystallised from diethyl ether giving white *crystals* (0.73 g, 85%) of $[\mathrm{PtCl(Ph)\{P(C_6H_{11})_3\}_2}]$, m.p. 242—245 °C (decomp.) (Found: C, 58.3; H, 8.6. $\mathrm{C_{14}H_{71}ClP_2Pt}$ requires C, 58.1; H, 8.2%). Infrared spectrum: $\nu_{max.}$ (Nujol) at 3 040w, 1 565m, 1 450s, 1 328w, 1 309w, 1 290w, 1 282m, 1 278w, 1 250m, 1 215m, 1 190w, 1 182m, 1 165w, 1 159m, 1 152w, 1 114w, 1 100m, 1 060w, 1 052m, 1 047w, 1 035w, 1 010m, 992s, 900m, 885m, 875m, 838s, 810m, 729s, 698s, 649w, 525m, 512m, 503m, 479m, 442w, and 418w cm⁻¹. N.m.r. spectra: ^{1}H, τ 2.58 (m) and 3.27 (m); ^{31}P, −17.24 p.p.m. (J_{PtP} 2 793 Hz).

Reaction of Tris(*triethylphosphine*)*platinum with Pentafluorobenzene*.—Tris(triethylphosphine)platinum (0.55 g, 1 mmol) in toluene (10 cm³) was treated with $\mathrm{C_6F_5H}$ (0.9 g, 6 mmol) with stirring for 3 d. The mixture was evaporated giving an oil which was dissolved in ethanol. On cooling (−40 °C) white *crystals* (0.19 g, 35%) of $[\mathrm{PtH(C_6F_5)(PEt_3)_2}]$, recrystallised from methanol, were obtained, m.p. 110 °C (Found: C, 36.3; H, 5.5. $\mathrm{C_{18}H_{31}F_5P_2Pt}$ requires C, 36.1; H, 5.2%). Infrared spectrum: $\nu_{max.}$ (Nujol) at 2 040s, 1 635w, 1 605w, 1 530w, 1 500s, 1 470s, 1 425s, 1 372m, 1 345m, 1 288m, 1 268m, 1 252m, 1 190w, 1 162w, 1 090w, 1 070s, 1 058s, 1 048s, 1 024m, 960s, 952s, 900w, 830w, 782s, 758s, 728w, 715m, and 645m cm⁻¹. N.m.r. spectra: ^{1}H, τ 17.68 (t, Pt*H*, J_{PH} 16.4 Hz); ^{31}P, −18.48 p.p.m. (J_{PtP} 2 684 Hz); ^{19}F, 114.2 (m) and 163.1 (m) p.p.m.

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