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FULL PAPER

Structural and electronic impact of fluorine in the *ortho* positions of triphenylphosphine and 1,2-bis(diphenylphosphino)ethane; a comparison of 2,6-difluorophenyl- with pentafluorophenylphosphines

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The new fluorine-containing phosphines $PPh_2(C_6H_3F_2\text{-}2,6)$ **I** and $PPh(C_6H_3F_2\text{-}2,6)_2$ **II** were synthesized in high yield from $C_6H_3BrF_2\text{-}2,6$ and PPh_2Cl or $PPhCl_2$. Phosphines **I**, **II** and the previously reported $P(C_6H_3F_2\text{-}2,6)_3$ **III** have been structurally characterized by single-crystal X-ray diffraction. A range of transition metal complexes of **I**–**III** and the diphosphine $(C_6H_3F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2$ have been prepared and their spectroscopic properties compared with those of the analogous complexes of the pentafluorophenylphosphines $PPh_x(C_6F_5)_{3-x}$ ($x = 0$–2) and the diphosphine $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$. The structures of *trans*-$[PtCl_2(PEt_3)\{PPh_x(C_6H_3F_2\text{-}2,6)_{3-x}\}]$ ($x = 2$, 1 or 0), *trans*-$[MCl(CO)\{PPh(C_6H_3F_2\text{-}2,6)_2\}_2]$ (M = Rh or Ir), *trans*-$[IrCl(CO)\{P(C_6H_3F_2\text{-}2,6)_3\}_2]$ and *trans*-$[PtCl_2\{PPh(C_6H_3F_2\text{-}2,6)_2\}_2]$ have been determined by single-crystal X-ray diffraction. The spectroscopic and structural data indicate that the 2,6-difluorophenylphosphines are more basic than the analogous pentafluorophenylphosphines and exert a similar or slightly smaller steric influence.

The σ-withdrawing property of fluorine and its larger size compared with hydrogen (van der Waals radius 1.47 *cf.* 1.20 Å)[1] are expected to exert a profound influence on phosphorus(III) ligands and their transition metal complexes when fluorine is incorporated at strategic sites in the ligands. As part of our project into studying and exploiting these effects we have investigated complexes of the polyfluorinated phenylphosphines $P(C_6F_5)_3$,[2–5] $PPh(C_6F_5)_2$,[2,4,5] $PPh_2(C_6F_5)$[2,4,5] and $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe).[2,5,6] We, and others,[7–23] have found that these ligands are more bulky and less basic than their perprotio analogues and that complexes of these ligands can possess chemical, structural and spectroscopic properties which are significantly different to those of complexes of the analogous phosphines PPh_3 and dppe. We were interested in extending our study to phosphines containing the 2,6-difluorophenyl group, $PPh_x(C_6H_3F_2\text{-}2,6)_{3-x}$ ($x = 2$ **I**, 1 **II**, or 0 **III**) and $(C_6H_3F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2$, **IV**. It is envisaged that these phosphines would exhibit similar steric effects to the pentafluorophenyl analogues, but would be more basic by virtue of comprising only two fluorine atoms per phenyl group. It is clear that perfluorination of only one phenyl ring of PPh_3 leads to steric and electronic effects which cause significant structural and chemical changes in the complexes. Also, complexes and reactions of the perfluorinated phosphine $P(C_6F_5)_3$ can be different to those of both PPh_3 and $PPh_2(C_6F_5)$. Complexes and reactions of $PPh(C_6F_5)_2$, depending on the metal and ancillary ligands, resemble those of either $PPh_2(C_6F_5)$, as in the complexes $[RhCl(CO)\{PPh_x(C_6F_5)_{3-x}\}_2]$,[2] or $P(C_6F_5)_3$, as in the lack of reaction with $[\{RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$.[5] Recent studies have shown that, in reactions with $[\{MCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$ (M = Rh or Ir), **IV** displays differences to dfppe which were ascribed to both electronic and small steric differences between the diphosphine ligands.[24] Here we report our study of the new phosphines **I** and **II**, together with **III**, which has been reported previously,[9] but for which very few complexes are known, and the recently synthesized diphosphine **IV**.[24]

Results and discussion

Synthesis, characterization and structures of phosphines I, II and III

Addition of PPh_2Cl to $[C_6H_3F_2\text{-}2,6]^-Li^+$, formed by treatment of $C_6H_3BrF_2\text{-}2,6$ with Bu^nLi at −78 °C, afforded (2,6-difluorophenyl)diphenylphosphine, **I**, in 70% yield. Bis(2,6-difluorophenyl)phenylphosphine, **II**, and tris(2,6-difluorophenyl)phosphine, **III**, were prepared similarly from $PPhCl_2$ and PCl_3 in 49 and 87% yields respectively. Phosphines **I**–**III** were characterized by elemental analysis, high resolution mass spectrometry and multinuclear NMR spectroscopies (Table 1). Their $^{19}F\text{-}\{^1H\}$ NMR spectra exhibit doublets at *ca.* δ −100, consistent with that of **IV** (δ −101.39).[24] The $^{31}P\text{-}\{^1H\}$ NMR spectra exhibit a triplet at δ −27.7, a quintet at δ −50.6 and a septet at δ −78.2 respectively, comparable with those of $PPh_2(C_6F_5)$ at δ −24.7, $PPh(C_6F_5)_2$ at δ −45.1 and $P(C_6F_5)_3$ at δ −74.0. The values of $|^3J(PF)|$ for **I**, **II** and **III** are 3–6 Hz larger than those for the respective pentafluorophenylphosphines[25] and also larger than 30.1 Hz for **IV**.[24]

The structures of the phosphines **I** (Fig. 1), **II** (Fig. 2) and **III** (Fig. 3) have been determined by single-crystal X-ray diffraction. The structure of **IV** has been reported.[24] Bond lengths and selected angles are given in Table 2. There are no significant intermolecular interactions in the structures with the closest contacts being greater than the sums of the van der Waals radii. The structure of phosphine **I** is similar to that of $PPh_2(C_6F_5)$.[20] In particular, the P–C (phenyl), P–C (fluorophenyl), PC–C and C–F distances and the C–P–C, C–C(P)–C and P–C–CF angles are the same within experimental error for the two compounds. For one phenyl ring of **I** the P–C–C angles are identical to those of the phenyl rings of $PPh_2(C_6F_5)$, which have one smaller angle of *ca.* 116° and one of *ca.* 125°. The other phenyl ring of **I** has both P–C–C angles close to 120°. The mean PC–C–F angle of **I** [117.9(2)°] is slightly more acute than that of $PPh_2(C_6F_5)$ [119.7(2)°].[20] The structure of phosphine **II** is similar to that of

Table 1 Analytical, mass spectral and NMR data for ligands **I**–**III** and complexes **1**–**12**, **14** and **15**

Analysis (%)[a] and *m*/*z* Compound	NMR[b]
I C, 72.6 (72.5); H, 4.1 (4.4) *m*/*z* 298 (M^+), 220 ($[M - C_6H_5 - H]^+$), 201 ($[M - C_6H_5 - F - H]^+$) (Found for M^+ 298.07233. $C_{18}H_{13}F_2P$ requires 298.07230)[c]	^{1}H: 7.37 (11 H, m, Ph and H$_p$ of $C_6H_3F_2$), 6.91 (2 H, m, H$_m$ of $C_6H_3F_2$)[d] ^{13}C-{^{1}H}: 165.6 [d, ^1J(CF) 250, C$_o$ of $C_6H_3F_2$], 135.6 (m), 133.2 (m), 128.9 (m), 112.4 [d, ^2J(CF) 23, C$_m$ of $C_6H_3F_2$][d] ^{19}F-{^{1}H}: −98.18 [d, ^3J(PF) 42.2][d] ^{31}P-{^{1}H}: −27.7 [t, ^3J(PF) 42.2][d]
II C, 64.6 (64.7); H, 3.1 (3.3) *m*/*z* 334 (M^+), 201 ($[M - C_6H_3F_2 - F - H]^+$) (Found for M^+ 334.05336. $C_{18}H_{11}F_4P$ requires 334.05345)[c]	^{1}H: 7.54 (2 H, m, H$_m$ of C_6H_5), 7.33 (5 H, m, H$_o$ and H$_p$ of C_6H_5 and H$_p$ of $C_6H_3F_2$), 6.85 [4 H, ddd, ^3J(H$_m$H$_p$) ≈ ^3J(H$_m$F) 8.2, ^4J(H$_m$P) 2.2, H$_m$ of $C_6H_3F_2$][d] ^{13}C-{^{1}H}: 163.3 [dm, ^1J(CF) 249, C$_o$ of $C_6H_3F_2$], 132.3 [dm, ^1J(CP) 9, C$_{ipso}$ of C_6H_5], 131.7 [d, ^2J(CP) 23, C$_o$ of C_6H_5], 130.8 [tm, ^3J(CF) 11, C$_p$ of $C_6H_3F_2$], 128.0 (s, C$_p$ of C_6H_5), 127.2 [d, ^3J(CP) 9, C$_m$ of C_6H_5], 110.6 [dm, ^2J(CF) 28, C$_m$ of $C_6H_3F_2$][d] ^{19}F-{^{1}H}: −99.74 [d, ^3J(PF) 36.2][d] ^{31}P-{^{1}H}: −50.6 [quin, ^3J(PF) 36.2][d]
III C, 58.5 (58.4); H, 2.3 (2.5) *m*/*z* 370 (M^+), 351 ($[M - F]^+$), 257 ($[M - C_6H_3F_2]^+$) (Found for M^+ 370.03460. $C_{18}H_9F_6P$ requires 370.03461)[c]	^{1}H: 7.25 (3 H, m, H$_p$), 6.80 (6 H, m, H$_m$)[d] ^{13}C-{^{1}H}: 163.3 [dm, ^1J(C$_o$F) 250, C$_o$], 130.8 [tm, ^3J(C$_p$F) 11, C$_p$], 111.6 [dm, ^2J(C$_m$F) 28, C$_m$][d] ^{19}F-{^{1}H}: −101.43 [d, ^3J(PF) 39.2][d] ^{31}P-{^{1}H}: −78.2 [sept, ^3J(PF) 39.2][d]
1 C, 55.1 (55.4); H, 4.4 (4.7); Cl, 11.6 (11.7) *m*/*z* 571 ($[M - Cl]^+$), 536 ($[M - 2Cl]^+$)[e]	^{1}H: 7.85 (4 H, m, H$_o$ of C_6H_5), 7.26 (7 H, m, H$_p$ of $C_6H_3F_2$ and H$_m$ and H$_p$ of C_6H_5), 6.94 [2 H, dd, ^3J(H$_m$H$_p$) ≈ ^3J(H$_m$F) 8.5, H$_m$ of $C_6H_3F_2$], 1.43 [15 H, d, ^1J(PH) 3.5, CH$_3$][d] ^{19}F-{^{1}H}: −90.19 (s)[d] ^{31}P-{^{1}H}: 15.8 [d, ^1J(RhP) 148][d]
2 C, 42.5 (42.3); H, 4.0 (4.1); Cl, 9.9 (10.4) *m*/*z* 682 (M^+), 647 ($[M - Cl]^+$), 611 ($[M - 2Cl]^+$)[e]	^{1}H: 7.84 [4 H, dd, ^3J(PH) 8.9, ^3J(H$_o$H$_m$) 7.2, H$_o$ of C_6H_5], 7.36 (7 H, m, H$_p$ of $C_6H_3F_2$ and H$_m$ and H$_p$ of C_6H_5], 6.79 [2 H, ddd, ^3J(H$_m$H$_p$) ≈ ^3J(H$_m$F) 8.5, ^4J(PH) 3.4, H$_m$ of $C_6H_3F_2$], 1.88 (6 H, m, CH$_2$), 1.16 [9 H, dtd, ^3J(PH) 15.5, ^3J(HH) 7.6, ^5J(PH) 1.6, CH$_3$][f] ^{19}F-{^{1}H}: −90.95 [dd, ^3J(PF) 5.8, ^5J(PF) 1.4][f] ^{31}P-{^{1}H}: 14.6 [d, ^2J(PP) 486, ^1J(PtP) 2625, PEt$_3$], 9.1 [dt, ^2J(PP) 486, ^3J(PF) 5.8, ^1J(PtP) 2444, PPh$_2$($C_6H_3F_2$)][f]
3 C, 40.8 (40.1); H, 3.7 (3.65) *m*/*z* 718 (M^+), 683 ($[M - Cl]^+$)[e]	^{1}H: 7.75 [2 H, dd, ^3J(PH) 12.2, ^3J(H$_o$H$_m$) 7.6, H$_o$ of C_6H_5], 7.34 (5 H, m, H$_p$ of $C_6H_3F_2$ and H$_m$ and H$_p$ of C_6H_5], 6.85 [4 H, ddd, ^3J(H$_m$H$_p$) ≈ ^3J(H$_m$F) 8.4, ^4J(PH) 3.1, H$_m$ of $C_6H_3F_2$], 1.83 (6 H, m, CH$_2$), 1.09 [9 H, dt, ^3J(PH) 16.8, ^3J(HH) 7.7, CH$_3$][f] ^{19}F-{^{1}H}: −95.58 [d, ^3J(PF) 7.4][f] ^{31}P-{^{1}H}: 10.5 [d, ^2J(PP) 504, ^1J(PtP) 2756, PEt$_3$], −5.8 [dquin, ^2J(PP) 504, ^3J(PF) 7.3, ^1J(PtP) 2374, PPh($C_6H_3F_2$)$_2$][f]
4 C, 38.3 (38.2); H, 2.8 (3.2) *m*/*z* 754 (M^+), 719 ($[M - Cl]^+$), 683 ($[M - 2Cl]^+$)[e]	^{1}H: 7.50 [3 H, tt, ^3J(H$_p$H$_m$) 8.4, ^4J(H$_p$F) 6.2, H$_p$], 6.79 [6 H, ddd, ^3J(H$_m$H$_p$) ≈ ^3J(H$_m$F) 8.6, ^4J(PH$_m$) 3.4, H$_m$], 1.93 (6 H, m, CH$_2$), 1.19 [9 H, dt, ^3J(PH) 17.1, ^3J(HH) 7.6, CH$_3$][f] ^{19}F-{^{1}H}: (293 K) −96.69 (br s);[f] (223 K) −93.78 [d, ^3J(PF) 30.0], −98.79 (s), −101.31 (s)[f] ^{31}P-{^{1}H}: 16.3 [d, ^2J(PP) 526, ^1J(PtP) 2847, PEt$_3$], −22.2 [dsept, ^2J(PP) 526, ^3J(PF) 9, ^1J(PtP) 2352, P($C_6H_3F_2$)$_3$][f]
5 C, 59.6 (58.3); H, 4.5 (4.3); Cl, 3.7 (4.7) *m*/*z* 734 ($[M - CO - H]^+$), 728 ($[M - Cl]^+$), 699 ($[M - CO - Cl - H]^+$)[e]	^{1}H: 7.89 [8 H, dd, ^3J(H$_o$H$_m$) 6.3, ^3J(PH) 6.0, H$_o$ of C_6H_5], 7.39 [14 H, m, H$_p$ of $C_6H_3F_2$ and H$_m$ and H$_p$ of C_6H_5], 6.84 [4 H, dd, ^3J(H$_m$H$_p$) ≈ ^3J(H$_m$F) 8.5, H$_m$ of $C_6H_3F_2$][d] ^{13}C-{^{1}H}: 187.7 [dm, ^1J(RhC) 80, CO][d] ^{19}F-{^{1}H}: −94.96 [vt, $\frac{1}{2}\lvert{}^3J(\mathrm{PF}) + {}^5J(\mathrm{PF})\rvert$ 5.6][d] ^{31}P-{^{1}H}: 18.7 [A part of AA′M$_2$M′$_2$X spectrum, ^1J(RhP) 133][d]
6 C, 52.7 (53.3); H, 2.4 (2.7) *m*/*z* 834 ($[M - H]^+$), 799 ($[M - H - Cl]^+$), 771 ($[M - CO - H - Cl]^+$)[e]	^{1}H: 7.79 [4 H, dd, ^3J(H$_o$H$_m$) ≈ ^3J(HP) 6.8, H$_o$ of C_6H_5], 7.31 (10 H, m, H$_m$ and H$_p$ of C_6H_5 and H$_p$ of $C_6H_3F_2$), 6.80 [8 H, dd, ^3J(H$_m$H$_p$) ≈ ^3J(H$_m$F) 8.8, H$_m$ of $C_6H_3F_2$][f] ^{19}F-{^{1}H}: −95.96 [vt, $\frac{1}{2}\lvert{}^3J(\mathrm{PF}) + {}^5J(\mathrm{PF})\rvert$ 6.3][f] ^{31}P-{^{1}H}: 0.4 [A part of AA′M$_4$M′$_4$X spectrum, ^1J(RhP) 137][f]
7 C, 49.6 (49.0); H, 2.0 (2.0) *m*/*z* 906 (M^+), 878 ($[M - CO]^+$), 871 ($[M - Cl]^+$), 843 ($[M - CO - Cl]^+$)[e]	^{1}H: 7.32 (6 H, m, H$_p$), 6.97 [12 H, dd, ^3J(H$_m$H$_p$) ≈ ^3J(H$_m$F) 9.1, H$_m$][d] ^{19}F-{^{1}H}: −96.76 (br s);[d] (373 K) −95.39 [vt, $\frac{1}{2}\lvert{}^3J(\mathrm{PF}) + {}^5J(\mathrm{PF})\rvert$ 8.2][g] ^{31}P-{^{1}H}: −28.2 [A part of AA′M$_6$M′$_6$X spectrum, ^1J(RhP) 144][d]
8 C, 51.4 (52.15); H, 3.1 (3.1) *m*/*z* 852 (M^+), 817 ($[M - Cl]^+$), 787 ($[M - CO - Cl - 2H]^+$)[e]	^{1}H: 7.89 [8 H, dd, ^3J(H$_o$H$_m$) ≈ ^3J(PH$_o$) 6.2, H$_o$ of C_6H_5], 7.39 [14 H, m, H$_p$ of $C_6H_3F_2$ and H$_m$ and H$_p$ of C_6H_5], 6.81 [4 H, ddm, ^3J(H$_m$H$_p$) ≈ ^3J(HF) 8.5, H$_m$ of $C_6H_3F_2$][f] ^{19}F-{^{1}H}: −95.01[vt, $\frac{1}{2}\lvert{}^3J(\mathrm{PF}) + {}^5J(\mathrm{PF})\rvert$ 2.5][f] ^{31}P-{^{1}H}: 18.0 [A part of AA′M$_2$M′$_2$ spectrum][f]
9 C, 47.15 (48.1); H, 2.2 (2.4) *m*/*z* 924 (M^+), 889 ($[M - Cl]^+$), 859 ($[M - CO - Cl - 2H]^+$)[e]	^{1}H: 7.82 [4 H, dd, ^3J(H$_o$H$_m$) ≈ ^3J(HP) 6.8, H$_o$ of C_6H_5], 7.31 (10 H, m, H$_m$ and H$_p$ of C_6H_5 and H$_p$ of $C_6H_3F_2$), 6.81 [8 H, dd, ^3J(H$_m$H$_p$) ≈ ^3J(H$_m$F) 8.6, H$_m$ of $C_6H_3F_2$][f] ^{19}F-{^{1}H}: −95.73 [vt, $\frac{1}{2}\lvert{}^3J(\mathrm{PF}) + {}^5J(\mathrm{PF})\rvert$ 3.3][f] ^{31}P-{^{1}H}: −5.3 [A part of AA′M$_4$M′$_4$ spectrum][f]
10 C, 43.9 (44.6); H, 1.7 (1.8) *m*/*z* 995 ($[M - H]^+$), 967 ($[M - H - CO]^+$), 960 ($[M - Cl]^+$), 932 ($[M - CO - Cl]^+$)[e]	^{1}H: 7.32 [6 H, tt, ^3J(H$_m$H$_p$) 8.3, ^4J(HF) 6.1, H$_p$], 6.79 [12 H, ddm, ^3J(H$_m$H$_p$) ≈ ^3J(H$_m$F) 8.7, H$_m$][f] ^{19}F-{^{1}H}: (293 K) −97.01 (br s);[f] (373 K) −97.01 [vt, $\frac{1}{2}\lvert{}^3J(\mathrm{PF}) + {}^5J(\mathrm{PF})\rvert$ 5.0][g] ^{31}P-{^{1}H}: −33.4 [A part of AA′M$_6$M′$_6$ spectrum][f]
11 C, 50.1 (50.05); H, 2.8 (3.0) *m*/*z* 862 (M^+), 827 ($[M - Cl]^+$), 791 ($[M - 2Cl]^+$)	^{1}H: 7.88 [8 H, dd, ^3J(H$_o$H$_m$) ≈ ^3J(PH) 6.4, H$_o$ of C_6H_5], 7.38 [14 H, m, H$_p$ of $C_6H_3F_2$ and H$_m$ and H$_p$ of C_6H_5], 6.80 [4 H, dd, ^3J(H$_m$H$_p$) ≈ ^3J(H$_m$F) 8.5, H$_m$ of $C_6H_3F_2$][d] ^{19}F-{^{1}H}: −95.19 [vt, $\frac{1}{2}\lvert{}^3J(\mathrm{PF}) + {}^5J(\mathrm{PF})\rvert$ 3.9][d] ^{31}P-{^{1}H}: 8.5 [A part of AA′M$_2$M′$_2$ spectrum, ^1J(PtP) 2754][d]
12 C, 45.6 (46.3); H, 1.9 (2.4) *m*/*z* 934 (M^+), 899 ($[M - Cl]^+$), 862 ($[M - 2Cl]^+$)	^{1}H: 7.79 (4 H, m, H$_o$ of C_6H_5), 7.38 (10 H, m, H$_m$ and H$_p$ of C_6H_5 and H$_p$ of $C_6H_3F_2$), 6.84 [8 H, dd, ^3J(H$_m$H$_p$) ≈ ^3J(H$_m$F) 8.4, H$_m$ of $C_6H_3F_2$][d] ^{19}F-{^{1}H}: −95.25 [vt, $\frac{1}{2}\lvert{}^3J(\mathrm{PF}) + {}^5J(\mathrm{PF})\rvert$ 4.2][d] ^{31}P-{^{1}H}: −8.9 [A part of AA′M$_4$M′$_4$ spectrum, ^1J(PtP) 2862][d]
14 C, 48.2 (48.0); H, 1.9 (2.2) *m*/*z* 751 (M^+), 723 ($[M - CO]^+$), 695 ($[M - 2CO]^+$), 667 ($[M - 3CO]^+$), 640 ($[M - 4CO + H]^+$)[e]	^{1}H: 7.26 (4 H, m, H$_p$), 6.80 [8 H, ddm, ^3J(H$_m$H$_p$) ≈ ^3J(H$_m$F) 8.5, H$_m$], 2.91 [4 H, d, ^2J(PH) 19.2, CH$_2$][d] ^{19}F-{^{1}H}: −100.23 (X part of an AA′X$_4$X′$_4$ spectrum)[d] ^{31}P-{^{1}H}: 28.6 (A part of an AA′X$_4$X′$_4$ spectrum)[d]
15[h] C, 38.5 (38.6); H, 1.8 (2.0); Cl, 8.3 (8.8) *m*/*z* 807 (M^+, *n* = 1), 772 ($[M - Cl]^+$, *n* = 1), 737 ($[M - 2Cl]^+$, *n* = 1)[e]	

[a] Required values are given in parentheses. [b] Recorded at 298 K, unless stated otherwise. Data given as chemical shift (δ) [relative intensity, multiplicity, *J*/Hz, assignment], s = singlet, d = doublet, t = triplet, quin = quintet, vt = virtual triplet, sept = septet, m = multiplet, br denotes a signal broadened due to a fluxional process. [c] EI. [d] Recorded in $CDCl_3$. [e] Positive ion fast-atom bombardment with *m*-nitrobenzyl alcohol as matrix. [f] Recorded in CD_2Cl_2. [g] Recorded in CD_3CD_5. [h] Insufficiently soluble for NMR study.

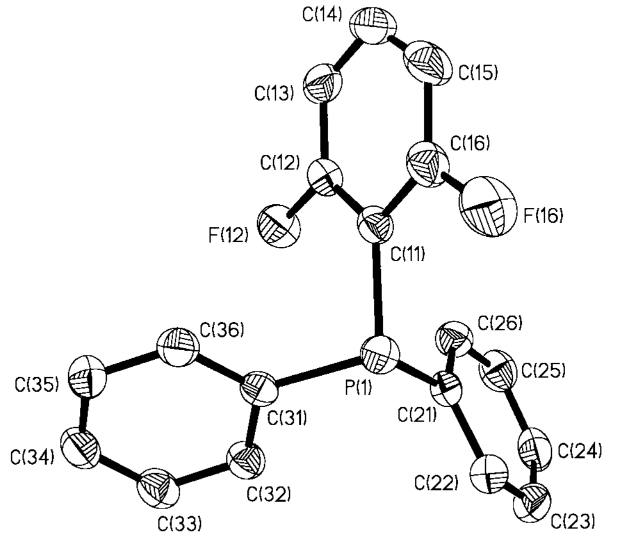


Fig. 1 Structure of $PPh_2(C_6H_3F_2\text{-}2,6)$ **I**. Thermal ellipsoids are shown at the 30% probability level.

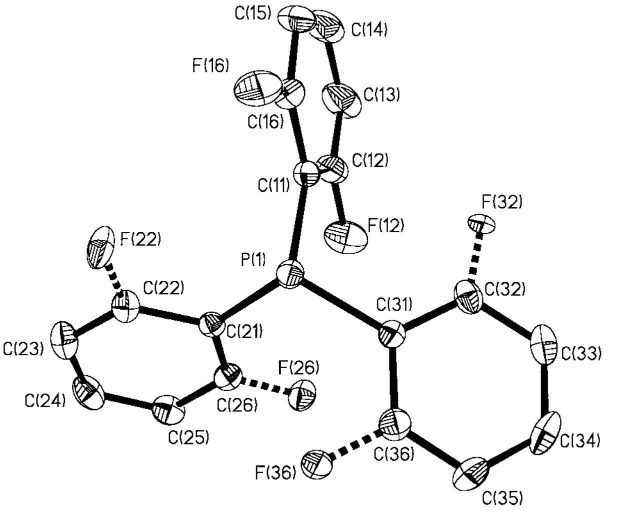


Fig. 2 Structure of $PPh(C_6H_3F_2\text{-}2,6)_2$ **II**. Thermal ellipsoids are shown at the 30% probability level. Bonds to disordered sites shown as dashed lines.

Table 2 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $PPh_2(C_6H_3F_2\text{-}2,6)$ **I**, $PPh(C_6H_3F_2\text{-}2,6)_2$ **II** and $P(C_6H_3F_2\text{-}2,6)_3$ **III**

	I	**II**	**III**
P–C(11)	1.836(2)	1.832(3)	1.841(4)
P–C(21)	1.832(3)	1.838(3)	1.837(4)
P–C(31)	1.832(2)	1.823(3)	1.851(4)
C(11)–C(12)	1.392(3)	1.383(5)	1.392(5)
C(11)–C(16)	1.382(3)	1.384(5)	1.389(5)
C(21)–C(22)	1.390(3)	1.390(4)	1.399(6)
C(21)–C(26)	1.383(3)	1.389(4)	1.386(5)
C(31)–C(32)	1.381(3)	1.388(4)	1.392(5)
C(31)–C(36)	1.384(3)	1.401(4)	1.400(5)
C(12)–F(12)	1.352(3)	1.356(4)	1.357(4)
C(16)–F(16)	1.358(3)	1.363(4)	1.368(5)
C(22)–F(22)	—	1.334(4)	1.358(5)
C(26)–F(26)	—	1.313(4)	1.368(5)
C(32)–F(32)	—	1.194(5)	1.362(4)
C(36)–F(36)	—	1.345(5)	1.359(4)
C(11)–P–C(21)	103.42(10)	100.73(13)	105.8(2)
C(11)–P–C(31)	102.53(10)	104.71(13)	104.3(2)
C(21)–P–C(31)	102.84(10)	105.41(12)	99.6(2)
P–C(11)–C(12)	128.0(2)	126.5(2)	129.9(3)
P–C(11)–C(16)	118.7(2)	119.3(3)	116.1(3)
P–C(21)–C(22)	116.1(2)	115.6(2)	126.5(3)
P–C(21)–C(26)	126.0(2)	128.8(2)	119.0(3)
P–C(31)–C(32)	121.8(2)	124.8(2)	117.3(3)
P–C(31)–C(36)	119.9(2)	117.7(2)	130.0(3)
C(12)–C(11)–C(16)	113.3(2)	114.2(3)	113.7(4)
C(22)–C(21)–C(26)	117.9(2)	115.6(3)	114.4(4)
C(32)–C(31)–C(36)	117.9(2)	116.9(3)	112.6(3)
C(11)–C(12)–F(12)	118.0(2)	117.9(3)	119.2(3)
C(11)–C(16)–F(16)	117.9(2)	118.0(3)	116.8(3)
C(21)–C(22)–F(22)	—	119.0(3)	117.9(4)
C(21)–C(26)–F(26)	—	120.8(3)	118.2(4)
C(31)–C(32)–F(32)	—	127.8(4)	116.0(3)
C(31)–C(32)–F(36)	—	117.1(3)	118.8(3)

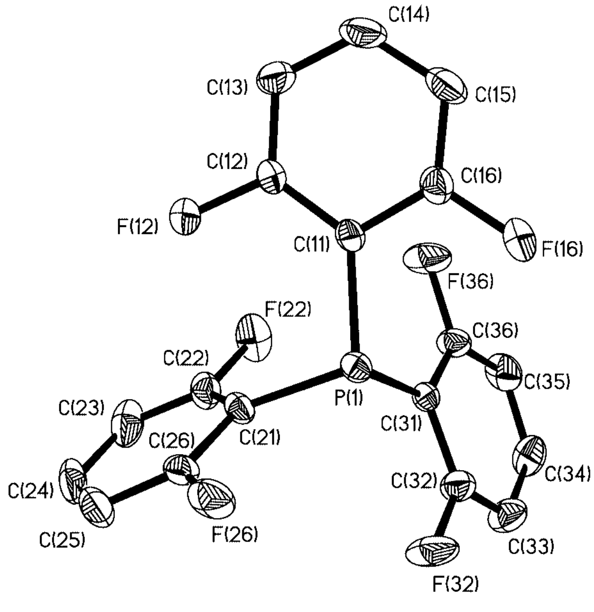
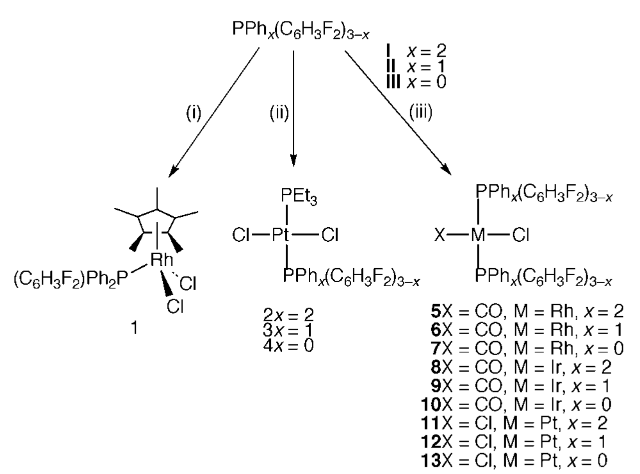


Fig. 3 Structure of $P(C_6H_3F_2\text{-}2,6)_3$ **III**. Details as for Fig. 1.

I, but shows disorder of the phenyl ring and one of the difluorophenyl rings, such that the fluorine atom sites F(22), F(26), F(32) and F(36) were modelled with $\frac{2}{3}$, $\frac{2}{3}$, $\frac{1}{3}$ and $\frac{1}{3}$ occupancies respectively. The P–C distances are identical within experimental error, similar to the case of **I**, but, unlike **I**, there are two C–P–C angles of *ca.* 105° and one more acute angle of 100.73(13)°. Each phenyl ring exhibits a larger P–C–C angle of >124° and a smaller P–C–C angle of <120°. The C–C(P)–C angles are all considerably less than 120°, consistent with the structures of **I**, **III** and **IV**. Four C–F distances are in the range 1.333(4) to 1.363(5) Å, consistent with those of other polyfluorophenylphosphines, but C(26)–F(26) and especially C(32)–F(32) are anomalously short. This is probably as a result of the disorder rather than a real effect. Similarly, four PC–C–F angles lie in the range 117.1(3) to 119.0(3), whereas C(21)–C(26)–F(26) and C(31)–C(32)–F(32) are anomalously large. The structure of phosphine **III** is similar to that of $P(C_6F_5)_3$.[17] The P–C, PC–C and C–F bond lengths and C–P–C angles are identical within experimental error for the two compounds and the three sets of P–C–C and C–C(P)–C angles are similar. The PC–C–F angles of **III** lie in the range 116.0(3) to 119.2(3)° with a mean of 117.8(3)° and are more acute than those of $P(C_6F_5)_3$, which have a mean of 119.5(3)°.[17] The more acute PC–C–F angles for the difluorophenylphosphines **I** and **III** compared with the pentafluorophenyl analogues are consistent with the more acute PC–C–F angles of **IV**[24] in comparison to those of dfppe.[2] It may be presumed that the mean PC–C–F angle of all $P(C_6H_3F_2\text{-}2,6)$ moieties is smaller than that of the analogous $P(C_6F_5)$ moieties.

Transition metal complexes of phosphines I, II and III

Treatment of the dimer $[\{RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$ with **I** in refluxing benzene afforded $[RhCl_2\{PPh_2(C_6H_3F_2\text{-}2,6)\}(\eta^5\text{-}C_5Me_5)]$ **1** in high yield (Scheme 1). The values of δ_P and $|^1J(RhP)|$



Scheme 1 (*i*) [{RhCl(μ-Cl)(η^5-C$_5$Me$_5$)}$_2$], C$_6$H$_6$, heat; (*ii*) [{PtCl(μ-Cl)(PEt$_3$)}$_2$], acetone, heat; (*iii*) M = Rh, [{Rh(μ-Cl)(CO)$_2$}$_2$], CH$_2$Cl$_2$, or M = Ir, [{Ir(μ-Cl)(η^2,η'^{2}-C$_8$H$_{12}$)}$_2$], CH$_2$Cl$_2$, 1 atm CO, or M = Pt, X = Cl, [PtCl$_2$(NCMe)$_2$], CH$_2$Cl$_2$, heat.

(Table 1) are similar to those of δ_P 18.8 and 149 Hz for the analogous complex [RhCl$_2${PPh$_2$(C$_6$F$_5$)}(η^5-C$_5$Me$_5$)],[5] and δ_P 7.9 and 144 Hz for [RhCl$_2$(PPh$_3$)(η^5-C$_5$Me$_5$)].[26] Phosphines **II** and **III** failed to react with [{RhCl(μ-Cl)(η^5-C$_5$Me$_5$)}$_2$], consistent with observations for PPh(C$_6$F$_5$)$_2$ and P(C$_6$F$_5$)$_3$.[5] Presumably this is due to the greater bulk of these phosphines compared to **I** and PPh$_2$(C$_6$F$_5$).

Treatment of the dimer [{PtCl(μ-Cl)(PEt$_3$)}$_2$] with **I**, **II** or **III** in acetone afforded the complexes *trans*-[PtCl$_2$(PEt$_3$){PPh$_x$(C$_6$H$_3$F$_2$-2,6)$_{3-x}$}] (x = 2 **2**, 1 **3** or 0 **4**) in moderate yields (Scheme 1). The *trans* geometries of these complexes are confirmed by the magnitudes of the phosphorus–phosphorus and platinum–phosphorus couplings, |^2J(PP)| and |^1J(PtP)| (Table 1), which are similar to the respective values for the analogous pentafluorophenylphosphine complexes *trans*-[PtCl$_2$(PEt$_3$){PPh$_x$(C$_6$F$_5$)$_{3-x}$}] (x = 0–2).[4] The values of |^1J(PtPPh$_x$(C$_6$H$_3$F$_2$)$_{3-x}$)| decrease and those of |^1J(PtPEt$_3$)| and |^2J(PP)| increase regularly as phenyl is substituted by difluorophenyl. In addition, the phosphorus–fluorine coupling is resolved, and at 298 K the phosphorus resonance assigned to the PPh$_x$(C$_6$H$_3$F$_2$-2,6)$_{3-x}$ ligand appears as a doublet of triplets for **2**, a doublet of quintets for **3** and a doublet of septets for **4**. Further, the ^{19}F-{^{1}H} NMR spectrum of **2** exhibits a doublet of doublets indicating that the fluorine atoms are coupled to both phosphorus atoms, but |^5J(PF)| cannot be resolved in the ^{19}F-{^{1}H} NMR spectrum of **3**. In contrast, the ^{19}F-{^{1}H} NMR spectrum of **4**, recorded at 376.50 MHz and 298 K, exhibits a broad signal suggestive of a fluxional process. On cooling to 223 K three sharp signals of equal intensity are observed. These data are consistent with restricted rotation about the P–C bonds, as has been observed in *trans*-[PtCl$_2$(PEt$_3$){P(C$_6$F$_5$)$_3$}].[4] The three signals occur as two singlets and a doublet with a phosphorus–fluorine coupling, |^3J(PF)|, of 30.0 Hz. The coupling is confirmed by the ^{31}P-{^{1}H} NMR spectrum at 223 K, which exhibits a doublet of triplets for the P(C$_6$H$_3$F$_2$-2,6)$_3$ resonance. The low temperature data are consistent with the conformation of the P(C$_6$H$_3$F$_2$-2,6)$_3$ ligand depicted in Fig. 4(a). There is a unique phenyl ring which lies perpendicular to the plane defined by the Pt–P bond and respective P–C bond such that the fluorine atoms are equivalent (F$_a$). The other two rings lie twisted to the planes defined by the Pt–P bond and respective P–C bonds such that there is a mirror plane through the phosphorus atom relating the two rings. The two fluorine atoms of each of these rings are non-equivalent, but are equivalent to the fluorine atoms of the other ring (F$_b$ and F$_c$). This conformation is similar to that adopted by the P(C$_6$F$_5$)$_3$ ligand of *trans*-[PtCl$_2$(PEt$_3$){P(C$_6$F$_5$)$_3$}] at low temperature in solution.[4] Since all the P–C–C–F torsion angles must be *ca.* 0°, it is not clear as to why only one pair of fluorine atoms shows coupling to the phosphorus atoms, or as to which pair of fluorine atoms it is.

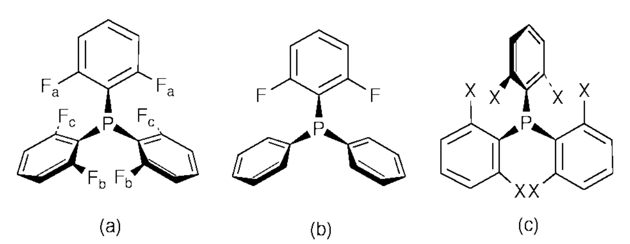


Fig. 4 Diagrammatic representations of the arrangements of the phenyl rings of the PPh$_x$(C$_6$H$_3$F$_2$-2,6)$_{3-x}$ ligands of (*a*) complex **4** in solution at the low temperature limit, (*b*) **2** and (*c*) **3** and **4** (X = H or F) in the solid state structures viewed along the Pt–P bond.

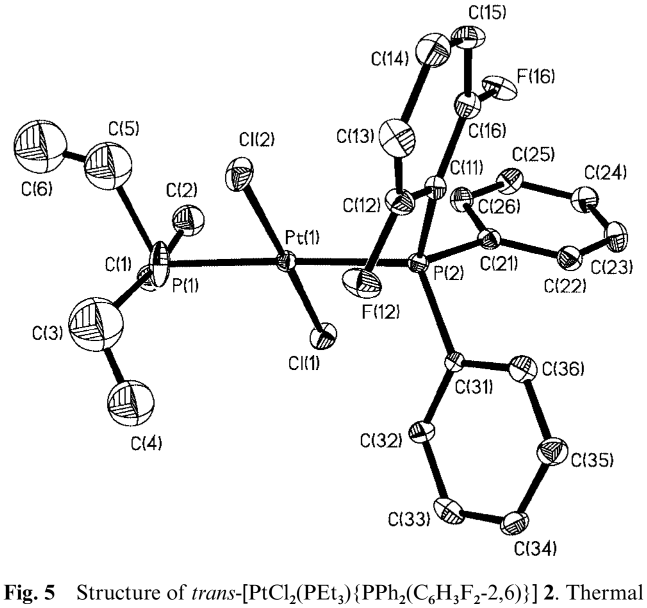


Fig. 5 Structure of *trans*-[PtCl$_2$(PEt$_3$){PPh$_2$(C$_6$H$_3$F$_2$-2,6)}] **2**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

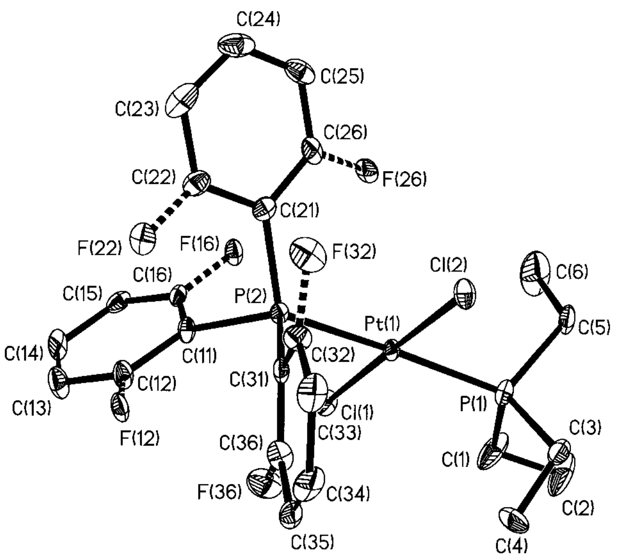


Fig. 6 Structure of *trans*-[PtCl$_2$(PEt$_3$){PPh(C$_6$H$_3$F$_2$-2,6)$_2$}] **3**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Bonds to disordered sites shown as dashed lines.

The structures of complexes **2** (Fig. 5), **3** (Fig. 6) and **4** (Fig. 7) were determined by single-crystal X-ray diffraction. The structure of **3** shows disorder of the phenyl and both difluorophenyl rings, which was modelled with $\frac{2}{3}$ occupancy of all the fluorine atom sites. Selected bond lengths and angles for **2**–**4** are given in Table 3. The structures of **2** and **4** possess no inter-

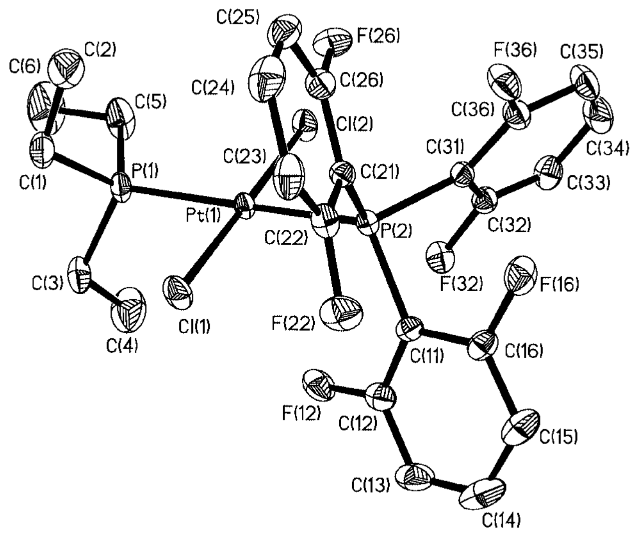


Fig. 7 Structure of *trans*-[PtCl$_2$(PEt$_3$){P(C$_6$H$_3$F$_2$-2,6)$_3$}] **4**. Details as for Fig. 5.

molecular contacts less than the sums of the van der Waals radii, but that of **3** contains one H···F distance of 2.367 Å. The structural determinations confirm the *trans* square-planar geometry of the complexes. For **2**–**4** and *trans*-[PtCl$_2$(PEt$_3$){PPh$_2$(C$_6$F$_5$)}][4] the Pt–PPh$_x$(C$_6$H$_3$F$_2$-2,6)$_{3-x}$ distances are the same within experimental error, as are the Pt–PEt$_3$ distances, which are *ca.* 0.04 Å shorter. The Pt–Cl bond lengths of **3** and **4** are the same within experimental error, whereas those of **2** differ by *ca.* 0.03 Å, but with a mean value [2.304(3) Å] similar to those for **3** [2.310(3) Å], **4** [2.305(2) Å] and *trans*-[PtCl$_2$(PEt$_3$){PPh$_2$(C$_6$F$_5$)}] [2.309(2) Å].[4] The P–C$_6$H$_3$F$_2$ and P–C$_6$H$_5$ bond lengths of **2**, **3** and **4** are the same within experimental error. This is consistent with the P–C$_6$F$_5$ and P–C$_6$H$_5$ bond lengths of the pentafluorophenylphosphine ligand in *trans*-[PtCl$_2$(PEt$_3$){PPh$_2$(C$_6$F$_5$)}],[4] but in contrast to those of *trans*-[PtMe(PEt$_3$){PPh$_2$(C$_6$F$_5$)}(OC$_6$F$_4$PPh$_2$-2)] in which the P–C$_6$F$_5$ distance is significantly longer than the P–C$_6$H$_5$ distances.[19] The complexes differ in the angles about the phosphorus atoms of the triarylphosphine ligands. The Pt–P–C$_6$H$_5$ angles of **2** are the same within experimental error and the Pt–P–C$_6$H$_3$F$_2$ angle is *ca.* 2.5° smaller. In contrast, the Pt–P–C angles of **3** and **4** show a great variation with two of *ca.* 120° and one of *ca.* 103°. The conformation of the PPh$_2$(C$_6$H$_3$F$_2$-2,6) ligand in **2** is similar to that of PPh$_2$(C$_6$F$_5$) in *trans*-[PtCl$_2$(PEt$_3$){PPh$_2$(C$_6$F$_5$)}].[4] The difluorinated phenyl ring of complex **2** lies perpendicular to the plane defined by the Pt–P bond and respective P–C$_6$H$_3$F$_2$ bonds [*i.e.* the absolute Pt–P(2)–C(11)–C torsion angles are close to 90°] and the two phenyl rings lie twisted by *ca.* 25° from coplanar with the planes defined by the respective Pt–P and P–C bonds [*i.e.* the absolute Pt–P–C–C torsion angles are close to 25 and 155° for each ring] (Fig. 4b). This conformation resembles that of the P(C$_6$H$_3$F$_2$-2,6)$_3$ ligand of **4** in solution. In contrast to the PPh$_2$(C$_6$H$_3$F$_2$-2,6) ligand of **2**, one aryl ring of the PPh(C$_6$H$_3$F$_2$-2,6)$_2$ ligand of **3** lies almost coplanar to the plane defined by the respective Pt–P and P–C bonds [*i.e.* the absolute Pt–P(2)–C(21)–C torsion angles are close to 180 and 0°] and the other two aryl rings lie twisted by *ca.* 30° from the perpendicular to the plane defined by the respective Pt–P and P–C bonds [*i.e.* the absolute Pt–P(2)–C(11)–C and Pt–P(2)–C(31)–C torsion angles are close to 120 and 60°] (Fig. 4c). The conformation of the P(C$_6$H$_3$F$_2$-2,6)$_3$ ligand of **4** in the solid state is similar to that of the PPh(C$_6$H$_3$F$_2$-2,6)$_2$ ligand of **3** and is similar to those adopted by the P(C$_6$F$_5$)$_3$ ligands in the solid state structures of the square-planar complexes *trans*-[IrBr(CO){P(C$_6$F$_5$)$_3$}$_2$],[3] *trans*-[PtX$_2${P(C$_6$F$_5$)$_3$}$_2$] (X = Cl[13] or I[12]) and *trans*-[PdCl$_2${P(C$_6$F$_5$)$_3$}$_2$].[14] This conformation is inconsistent with the low temperature ^{19}F-{^{1}H} NMR spectrum of **4** and indicates that the conformations adopted by the P(C$_6$H$_3$F$_2$-2,6)$_3$ ligand of **4** in the solid state and at low temperature in solution are different. This supports the same conclusion drawn for the conformations of P(C$_6$F$_5$)$_3$ in square-planar complexes.[4] The mean PC–C–F angle of **2** is 117.7(8)°, which may be compared with that of the pentafluorophenylphosphine analogue *trans*-[PtCl$_2$(PEt$_3$){PPh$_2$(C$_6$F$_5$)}] [120.3(8)°].[4] The PC–C–F angles of **2** and **4** [mean 118.5(6)°] are similar to those of **I** and **III** respectively. The PC–C–F angles of **3** and **II** are also similar, but both contain an anomalously large angle of greater than 125°, which may be a consequence of the disorder exhibited in both structures.

Table 3 Selected bond lengths (Å) and bond and torsion angles (°) with e.s.d.s in parentheses for *trans*-[PtCl$_2$(PEt$_3$){PPh$_2$(C$_6$H$_3$F$_2$-2,6)}] **2**, *trans*-[PtCl$_2$(PEt$_3$){PPh(C$_6$H$_3$F$_2$-2,6)$_2$}] **3** and *trans*-[PtCl$_2$(PEt$_3$){P(C$_6$H$_3$F$_2$-2,6)$_3$}] **4**

	2	**3**	**4**
Pt–P(1)	2.293(2)	2.293(3)	2.288(2)
Pt–P(2)	2.330(2)	2.320(3)	2.328(2)
Pt–Cl(1)	2.320(2)	2.308(3)	2.308(2)
Pt–Cl(2)	2.287(3)	2.312(3)	2.303(2)
P(2)–C(11)	1.822(10)	1.832(11)	1.821(6)
P(2)–C(21)	1.815(9)	1.829(13)	1.834(6)
P(2)–C(31)	1.829(9)	1.832(11)	1.828(6)
C(12)–F(12)	1.355(11)	1.36(2)	1.344(8)
C(16)–F(16)	1.352(11)	1.369(14)	1.348(8)
C(22)–F(22)	—	1.35(2)	1.346(8)
C(26)–F(26)	—	1.35(2)	1.348(8)
C(32)–F(32)	—	1.32(2)	1.363(7)
C(36)–F(36)	—	1.34(2)	1.364(8)
P(1)–Pt–P(2)	175.80(10)	169.79(11)	169.97(6)
P(1)–Pt–Cl(1)	90.57(11)	93.34(12)	86.91(7)
P(1)–Pt–Cl(2)	86.57(11)	86.41(12)	93.29(7)
P(2)–Pt–Cl(1)	91.10(9)	93.41(11)	86.01(6)
P(2)–Pt–Cl(2)	91.88(9)	86.66(11)	93.66(6)
Cl(1)–Pt–Cl(2)	176.62(10)	178.66(11)	178.91(7)
Pt–P(2)–C(11)	111.5(3)	120.0(4)	120.1(2)
Pt–P(2)–C(21)	114.1(3)	119.6(4)	103.0(2)
Pt–P(2)–C(31)	115.8(3)	103.2(4)	119.5(2)
P(2)–C(11)–C(12)	119.9(7)	127.6(9)	123.9(5)
P(2)–C(11)–C(16)	126.5(7)	117.8(8)	120.8(5)
P(2)–C(21)–C(22)	122.8(7)	120.0(9)	126.2(5)
P(2)–C(21)–C(26)	118.1(7)	123.7(10)	117.5(5)
P(2)–C(31)–C(32)	119.1(7)	124.7(9)	117.2(5)
P(2)–C(31)–C(36)	121.4(7)	117.7(9)	129.0(5)
C(11)–C(12)–F(12)	116.9(8)	118.6(10)	119.4(6)
C(11)–C(16)–F(16)	118.4(8)	117.9(10)	117.8(6)
C(21)–C(22)–F(22)	—	120.5(12)	120.4(6)
C(21)–C(26)–F(26)	—	119.3(12)	117.5(6)
C(31)–C(32)–F(32)	—	125.2(12)	117.0(6)
C(31)–C(36)–F(36)	—	117.6(11)	119.0(6)
Cl(2)–Pt–P(2)–C(11)	−7.3(3)	176.2(4)	−124.7(2)
Cl(2)–Pt–P(2)–C(21)	−128.0(3)	55.5(4)	116.5(2)
Cl(2)–Pt–P(2)–C(31)	111.1(3)	−62.8(4)	−3.4(2)
Pt–P(2)–C(11)–C(12)	71.0(8)	119.2(1.1)	14.2(6)
Pt–P(2)–C(11)–C(16)	96.8(8)	−61.2(1.1)	−170.8(4)
Pt–P(2)–C(21)–C(22)	160.7(7)	−171.7(8)	105.2(6)
Pt–P(2)–C(21)–C(26)	20.7(9)	11.5(1.1)	−62.1(5)
Pt–P(2)–C(31)–C(32)	31.0(8)	106.3(1.0)	−61.9(6)
Pt–P(2)–C(31)–C(36)	152.6(7)	−62.4(9)	120.1(6)

Phosphines **I**, **II** and **III** reacted with [{Rh(μ-Cl)(CO)$_2$}$_2$] to form the yellow complexes *trans*-[RhCl(CO){PPh$_x$(C$_6$H$_3$F$_2$-2,6)$_{3-x}$}$_2$] (x = 2 **5**, 1 **6** or 0 **7**) in high yield (Scheme 1). The compounds were characterized by elemental analysis, mass spectrometry and multinuclear NMR spectroscopies (Table 1). The *trans* geometry of the complexes was established by ^{31}P NMR spectroscopy, which showed a single resonance for each. The ^{31}P-{^{1}H} and ^{19}F-{^{1}H} NMR spectra are those of AA′M$_n$M′$_n$X (n = 2 **5**, 4 **6** or 6 **7**) spin systems. The ^{31}P-{^{1}H} NMR spectra exhibit resonances centred at δ 18.7, 0.4 and −28.2 respectively similar to those of the respective pentafluorophenyl

Table 4 $\nu(C{\equiv}O)$ for *trans*-$[MCl(CO)(PR_3)_2]$ complexes

Phosphine	$\tilde{\nu}(C{\equiv}O)/cm^{-1}$ M = Rh	M = Ir
PPh_3	1961[a]	1951[b]
$P(C_6H_4F\text{-}4)_3$	1984[c]	1960
$PPh_2(C_6H_3F_2\text{-}2,6)$ **I**	1967 (**5**)[d]	1953 (**8**)[d]
$PPh_2(C_6F_5)$	1982[e]	—
$PPh(C_6H_3F_2\text{-}2,6)_2$ **II**	1961 (**6**)[d]	1952 (**9**)[d]
$PPh(C_6F_5)_2$	2002[e]	—
$P(C_6H_3F_2\text{-}2,6)_3$ **III**	1965 (**7**)[d]	1952 (**10**)[d]
$P(C_6F_5)_3$	2008[e]	1996[f]

[a] Ref. 27. [b] Ref. 28. [c] Ref. 29. [d] Resolution ±4 cm^{-1}. [e] Ref. 2. [f] Ref. 3.

analogues (δ 24.0, 3.4 and -25.8).[2] The magnitudes of the rhodium–phosphorus couplings, $|{}^1J(\mathrm{RhP})|$, were calculated to be 133, 137 and 144 Hz respectively, which can be compared to the values of 133, 136 and 155 for the respective pentafluorophenyl analogues.[2] It is noted that the values of $|{}^1J(\mathrm{RhP})|$ for **5**–**7** increase slightly with the number of difluorophenyl groups, whereas $|{}^1J(\mathrm{RhP})|$ for *trans*-$[RhCl(CO)\{P(C_6F_5)_3\}_2]$ is significantly larger than for *trans*-$[RhCl(CO)\{PPh_x(C_6F_5)_{3-x}\}_2]$ (x = 1 or 2). The $^{19}F\text{-}\{^1H\}$ NMR resonances of **5** and **6** appear as virtual triplets. The $^{19}F\text{-}\{^1H\}$ NMR spectrum of **7**, recorded in CD_2Cl_2 at a spectrometer frequency of 376.50 MHz, exhibits a broad resonance indicative of a fluxional process. On cooling the resonance broadens and at 213 K the spectrum exhibits a triplet at δ_F -94.45 with a coupling, $|{}^3J(\mathrm{PF})|$, of 27.6 Hz, and a singlet at δ_F -103.59. On further cooling to 188 K the spectrum exhibits four broad resonances at *ca.* δ_F -93.3, -95.4, -98.5 and -103.2 in addition to the triplet and singlet resonances. This is consistent with the observation of six resonances, assigned to *ortho* fluorine atoms, in the low temperature ^{19}F NMR spectrum of the bis{tris(pentafluorophenyl)phosphine} complex *trans*-$[PtCl_2\{P(C_6F_5)_3\}_2]$.[11] The ^{19}F NMR behaviour of **7** was also investigated at higher temperature in $C_6D_5CD_3$. On warming, the broad resonance sharpens and two doublet resonances arise and grow in intensity. At 373 K the original broad resonance appears as a virtual triplet at δ_F -95.39 with an apparent coupling, $\frac{1}{2}|{}^3J(\mathrm{PF}) + {}^5J(\mathrm{PF})|$, of 8.2 Hz. This resonance is consistent with those of **5** and **6** at ambient temperature. The two doublet resonances are centred at δ_F -95.89 and -101.04 with couplings, $|{}^3J(\mathrm{PF})|$, of 15.6 and 40.3 Hz respectively with a ratio of integration of *ca.* 2 : 1. The latter resonance is assigned to **III** by comparison of the data with those obtained for the phosphine in $CDCl_3$ at 298 K (Table 1). The identity of the compound giving rise to the former resonance is unknown, but may arise due to the loss of **III** from **7**. Unfortunately complex **7** is not sufficiently soluble in toluene to allow the ^{31}P NMR spectrum to be recorded at 373 K.

The values of $\nu(C{\equiv}O)$ for complexes **5** to **7** and, for comparison, those for other *trans*-$[RhCl(CO)(PR_3)_2]$ complexes are presented in Table 4. The structure of **6** (Fig. 8) has been determined by single-crystal X-ray diffraction. Selected bond distances and angles are given in Table 5. There are two short intermolecular contacts in the structure F(32) ··· Cl(1′) (3.038 Å) and F(32) ··· F(36′) (2.561 Å). The rhodium atom lies on a crystallographic centre of symmetry such that the carbonyl and chloride ligands are disordered. The $PPh(C_6H_3F_2\text{-}2,6)_2$ ligands are identical and show disorder of the phenyl ring and one difluorophenyl ring, which was modelled with 80% occupancy of the fluorine atom sites F(22) and F(26) and 20% occupancy of F(32) and F(36). The conformation of the $PPh(C_6H_3F_2\text{-}2,6)_2$ ligands relative to the P–Rh–P axis is similar to that of $PPh(C_6H_3F_2\text{-}2,6)_2$ in **3** (*i.e.* absolute Cl–Rh–P–C torsion angles of *ca.* 180, 60 and 60°, and absolute Rh–P–C–C torsion angles of *ca.* 180, 0, 120, 60, 120 and 60°). The structure of **6** may be compared to that of *trans*-$[RhCl(CO)(PPh_3)_2]$, which possesses no centre of symmetry.[30] The Rh–Cl distance is longer and the Rh–P distances shorter for **6** than for *trans*-$[RhCl(CO)(PPh_3)_2]$, but the Rh–C and C≡O distances for the two compounds are identical within experimental error, consistent with the IR spectral data. Compound **6** possesses two Rh–P–C angles of 117–120° and one of *ca.* 104°. In contrast, the Rh–P–C angles of *trans*-$[RhCl(CO)(PPh_3)_2]$ lie in the range 109.8(1) to 117.1(1)°. The PC–C–F angles of **6** are similar to those of phosphine **II**, including one anomalously large angle of 125.1(6)°.

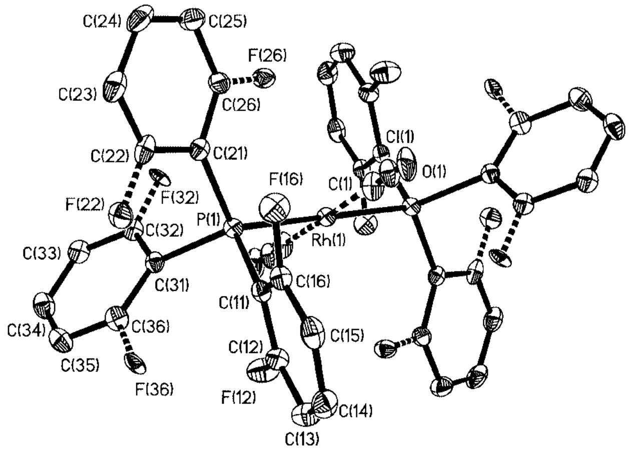


Fig. 8 Structure of *trans*-$[RhCl(CO)\{PPh(C_6H_3F_2\text{-}2,6)_2\}_2]$, **6**. Details as for Fig. 6.

The iridium complexes *trans*-$[IrCl(CO)\{PPh_x(C_6H_3F_2\text{-}2,6)_{3-x}\}_2]$ (x = 2 **8**, 1 **9** or 0 **10**) were prepared in high yield by treatment of $[\{Ir(\mu\text{-}Cl)(\eta^2,\eta^{2\prime}\text{-}C_8H_{12})\}_2]$ with four equivalents of **I**, **II** or **III** respectively under an atmosphere of CO and isolated as yellow crystalline solids. Complex **10** was also prepared in low yield by treatment of $IrCl_3{\cdot}xH_2O$ with **III** in refluxing 2-methoxyethanol. The compounds were characterized by elemental analysis, mass spectrometry and multinuclear NMR spectroscopies (Table 1). The *trans* geometry of the complexes was established by ^{31}P NMR spectroscopy, which showed a single resonance for each. Similarly to **5**–**7**, the complexes **8**–**10** exhibit second order $^{31}P\text{-}\{^1H\}$ and $^{19}F\text{-}\{^1H\}$ NMR spectra consistent with $AA'X_nX'_n$ (n = 2 **8**, 4 **9** or 6 **10**) spin systems. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **10** exhibits a resonance at δ -33.4 consistent with that of *trans*-$[IrCl(CO)\{P(C_6F_5)_3\}_2]$ (δ -31.3).[3] The $^{19}F\text{-}\{^1H\}$ NMR resonances of **8** and **9** appear as virtual triplets, whereas that of **10** is a broad indicative of a fluxional process, presumably hindered rotation about the P–C bonds as for **4** and **7**. On cooling a solution of **10** in CD_2Cl_2 to 213 K the $^{19}F\text{-}\{^1H\}$ NMR spectrum exhibits an unresolved triplet resonance at δ_F -94.45 and a singlet at δ_F -103.51. This is consistent with the spectrum observed for **7** at 203 K. At the high temperature limit the $^{19}F\text{-}\{^1H\}$ NMR spectrum of **10** appears as a virtual triplet with $\frac{1}{2}|{}^3J(\mathrm{PF}) + {}^5J(\mathrm{PF})| = 5.0$ Hz. The values of $\nu(C{\equiv}O)$ for complexes **8** to **10** and, for comparison, those for other *trans*-$[IrCl(CO)(PR_3)_2]$ complexes are presented in Table 4. It is apparent that $\nu(C{\equiv}O)$ for the *trans*-$[MCl(CO)(PAr_3)_2]$ (M = Rh or Ir) complexes of the difluorophenylphosphines are more comparable with those of $[MCl(CO)(PPh_3)_2]$ than with those of the pentafluorophenylphosphine complexes.

The structures of complexes **9** (Fig. 9) and **10** (Fig. 10) have been determined by single-crystal X-ray diffraction. Selected bond distances and angles are given in Table 5. Neither structure possesses significant intermolecular interactions. The iridium atoms of both **9** and **10** lie on crystallographic centres of symmetry giving rise to disorder between the carbonyl and chloride ligands and P–Ir–P and Cl–Ir–C angles of 180°. This is in contrast to the structures of *trans*-$[IrX(CO)\{P(C_6F_5)_3\}_2]$ (X = Cl[31] or Br[3]) in which there is no centre of symmetry and no disorder, and the P–Ir–P and X–Ir–C angles are *ca.* 169.8 and 175.5° respectively. The $PPh(C_6H_3F_2\text{-}2,6)_2$ ligands of **9** also

Table 5 Selected bond lengths (Å) and bond and torsion angles (°) with e.s.d.s in parentheses for *trans*-[RhCl(CO){PPh($C_6H_3F_2$-2,6)$_2$}$_2$] **6**, *trans*-[IrCl(CO){PPh($C_6H_3F_2$-2,6)$_2$}$_2$] **9** and *trans*-[IrCl(CO){P($C_6H_3F_2$-2,6)$_3$}$_2$] **10**

	6	**9**	**10**
M–P	2.3100(13)	2.3045(13)	2.3025(12)
M–Cl	2.419(5)	2.375(5)	2.408(4)
M–C	1.759(14)	1.84(3)	1.783(12)
C–O	1.14(2)	1.07(3)	1.152(12)
P–C	1.831(4)	1.825(5)	1.827(5)
	1.835(4)	1.826(5)	1.832(5)
	1.836(4)	1.837(5)	1.835(5)
C–F	1.379(5), 1.337(5)	1.353(6), 1.344(7)	1.354(5), 1.370(5)
	1.335(6), 1.340(5)	1.27, 1.37	1.360(6), 1.359(5)
	1.261(11), 1.337(12)	1.42, 1.29	1.359(5), 1.350(5)
P–M–P	180.0	180.0	180.0
P–M–Cl	85.57(13), 94.43(13)	91.4(2), 88.6(2)	94.07(9), 85.93(9)
P–M–C	93.3(5), 86.7(5)	91.1(8), 88.9(8)	86.5(4), 93.5(4)
Cl–M–C	180.0	180.0	180.0
M–C–O	178.3(20)	171.7(28)	177(2)
M–P–C	119.58(14)	119.7(2)	119.3(2)
	117.91(15)	118.7(2)	118.83(14)
	104.26(14)	106.4(2)	103.4(2)
P–C–CF	127.4(3), 117.7(3)	124.0(4), 121.0(4)	118.4(3), 127.2(4)
	122.3(3), 122.6(4)	123.1(3), 119.5(4)	124.0(4), 121.7(4)
	125.8(3), 116.2(3)	117.9(3), 125.7(4)	118.3(3), 128.0(3)
C(P)–C–F	116.6(4), 120.1(4)	118.6(4), 118.4(5)	119.2(4), 116.5(4)
	117.5(4), 120.5(4)	119.9(5), 120.4(5)	117.3(4), 119.4(4)
	118.8(6), 125.1(6)	118.7(5), 116.2(5)	116.8(4), 118.8(4)
Cl–M–P–C	−60.58(22)	−93.89 (28)	−64.64(20)
	58.12(22)	145.65(28)	55.06(21)
	−178.67(24)	26.21(27)	177.34(21)
M–P–C–C	−65.01(36), 104.31(40)	−88.94(44), 82.52(42)	104.92(42), −65.16(39)
	−168.54(31), 16.73(41)	155.73(37), −31.33(49)	−167.28(31), 15.14(46)
	−54.95(38), 125.14(37)	−148.25(38), 38.58 (45)	−55.41(38), 124.92(37)

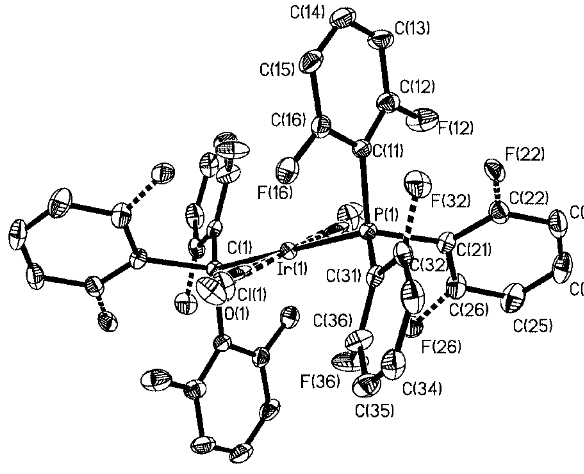


Fig. 9 Structure of *trans*-[IrCl(CO){PPh($C_6H_3F_2$-2,6)$_2$}$_2$], **9**. Details as for Fig. 6.

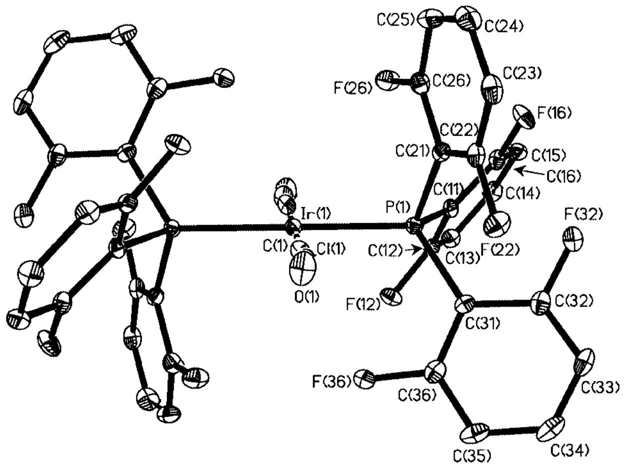


Fig. 10 Structure of *trans*-[IrCl(CO){P($C_6H_3F_2$-2,6)$_3$}$_2$], **10**. Details as for Fig. 5.

show disorder between the phenyl ring and one difluorophenyl ring which was modelled by $\frac{1}{2}$ occupancy of the fluorine atom sites F(22), F(26), F(32) and F(36). These ligands adopt a conformation similar to that in complex **3**, with one aryl ring perpendicular to the plane defined by the Ir–P and respective P–C bonds (*i.e.* Ir–P–C–C torsion angles of *ca.* 90 and −90°) and the other two aryl rings twisted by *ca.* 30° from parallel with the plane defined by the Ir–P and respective P–C bonds (*i.e.* absolute Ir–P–C–C torsion angles of *ca.* 150 and 30°). The P($C_6H_3F_2$-2,6)$_3$ ligands of **10** adopt the same conformation as in **4**. The Ir–P distances of **9** and **10** are identical within experimental error, consistent with the similarity of the M–P distances of the platinum complexes **2**, **3** and **4**. The Ir–Cl distance of **10** is *ca.* 0.02 Å longer than those of **9**, *trans*-[IrCl(CO){P(C_6F_5)$_3$}$_2$] (2.369 Å) and *trans*-[IrCl(CO)(PPh_3)$_2$] [2.382(3) Å].[32] The Ir–C bond length of **10** is similar to that of *trans*-[IrCl(CO)(PPh_3)$_2$], but significantly shorter than those of *trans*-[IrX(CO){P(C_6F_5)$_3$}$_2$] (X = Cl or Br, *ca.* 1.85 Å). The C≡O bond distance is similar to that of *trans*-[IrCl(CO)(PPh_3)$_2$] and *ca.* 0.1 Å longer than that of *trans*-[IrBr(CO){P(C_6F_5)$_3$}$_2$]. These observations are consistent with the values of ν(C≡O) for **10** and *trans*-[IrCl(CO)(PPh_3)$_2$] being similar and that for *trans*-[IrBr(CO){P(C_6F_5)$_3$}$_2$] being *ca.* 40 cm^{-1} higher (Table 4). The estimated standard deviations of the Ir–C and C≡O bond distances of **9** are too large to permit comparison with those of other *trans*-[IrCl(CO)(PR_3)$_2$] complexes. As for **6** and *trans*-[IrX(CO){P(C_6F_5)$_3$}$_2$], the structures of **9** and **10** possess two M–P–C angles of *ca.* 118° and one of *ca.* 105°. The more acute nature of the PC–C–F angles of **III** compared to P(C_6F_5)$_3$ is manifested in complex **10**, which has a mean PC–C–F angle of

Table 6 Selected bond lengths (Å) and bond and torsion angles (°) with e.s.d.s in parentheses for *trans*-$[PtCl_2\{PPh(C_6H_3F_2\text{-}2,6)_2\}_2]$ **12**

Pt–P	2.303(2)	Pt–Cl	2.302(2)
P–C	1.808(10)	C–F	1.28(3), 1.25(4)
	1.819(10)		1.362(10), 1.349(11)
	1.828(10)		1.336(12), 1.346(12)
P–Pt–P	180.0	Cl–Pt–Cl	180.0
P(1)–Pt–Cl(1)	85.60(8)	P(1)–Pt–Cl(1′)	94.40(8)
Pt–P–C	116.5(3)	P–C–CF	126.5(9), 117.2(7)
	105.0(3)		117.0(8), 128.1(9)
	119.5(3)		122.3(8), 123.5(8)
C(P)–C–F	116(2), 123(2)		
	117.9(9), 118.3(10)		
	120.5(10), 117.4(10)		
Cl(1)–Pt–P(1)–C	178.61(40)	Pt–P–C–C	55.98(77), −123.14 (87)
	59.80(36)		63.62(86), −105.86 (95)
	−60.36(34)		−16.06(94), 169.69 (68)

118.0(4)° compared to 120.3° for *trans*-$[IrCl(CO)\{P(C_6F_5)_3\}_2]$. The PC–C–F angles of **9** have a mean of 118.7(5)°, and in contrast to the structures of **II**, **3** and **6** there is no anomalously large angle in spite of the disorder.

Treatment of *cis*-$[PtCl_2(NCMe)_2]$ with two equivalents of **I**, **II** or **III** afforded the platinum complexes *trans*-$[PtCl_2\{PPh_x(C_6H_3F_2\text{-}2,6)_{3-x}\}_2]$ ($x = 2$ **11**, 1 **12** or 0 **13**) as pale yellow crystalline solids in high yield. Complex **13** and its bromide analogue have been reported previously.[9] Complexes **11** and **12** were characterized by elemental analysis, mass spectrometry and multinuclear NMR spectroscopies (Table 1). Complex **13** was found to be insufficiently soluble for an NMR study. The *trans* geometry was established by comparison of the values of ^1J(PtP) with those for a range of *cis* and *trans* bis(phosphine)-dichloroplatinum complexes.[33] The values are intermediate between those of non-fluorinated trialkyl- and triaryl-phosphines, 2300–2600 Hz,[33] and that of 3140 Hz for *trans*-$[PtCl_2\{P(C_6F_5)_3\}_2]$.[13] The *trans* geometry of **12** was further confirmed by single-crystal X-ray diffraction (Fig. 11). Selected bond distances and angles are given in Table 6. The structure possesses no significant intermolecular interactions. The platinum atom of **12** lies on a crystallographic centre of symmetry. The $PPh(C_6H_3F_2\text{-}2,6)_2$ ligands of **12** also show disorder between the phenyl ring and one difluorophenyl ring which was modelled by 20% occupancy of the fluorine atom sites F(12) and F(16) and 90% occupancy of sites F(22), F(26), F(32) and F(36). The P–Pt–Cl angles are 85.60(8) and 94.40(8)°, which are the same within experimental error as those of the tris(pentafluorophenyl)phosphine analogue *trans*-$[PtCl_2\{P(C_6F_5)_3\}_2]$.[13] The Pt–Cl distance is the same as that for *trans*-$[PtCl_2\{P(C_6F_5)_3\}_2]$.[13] The Pt–P distance is *ca.* 0.03 Å shorter than the Pt–$PPh(C_6H_3F_2\text{-}2,6)_2$ distance of **3**, but *ca.* 0.02 Å longer than that of *trans*-$[PtCl_2\{P(C_6F_5)_3\}_2]$ and the same as that of *trans*-$[PtI_2\{P(C_6F_5)_3\}_2]$.[12] The $PPh(C_6H_3F_2\text{-}2,6)_2$ ligands of **12** adopt a conformation similar to that in complex **3**, with a conformation about the Pt–P axis as depicted in Fig. 4(c). The Pt–P–C angles are similar to those found in **3**, **6** and **9**. As a result of the large e.s.d.s of the PC–C–F angles of **12**, no meaningful comparison can be made with those of **II**, **3**, **6** and **9**.

The cone angles[10] of phosphines **I**–**III** were estimated from the structures of their complexes. That of **I** was calculated to be 157° from the structure of **2**. This is comparable to the value of 158° for $PPh_2(C_6F_5)$ quoted by Tolman.[10] However, the structure of *trans*-$[PtCl_2(PEt_3)\{PPh_2(C_6F_5)\}]$[4] yields a value of 165°, and it can be concluded that **I** is slightly less sterically demanding than $PPh_2(C_6F_5)$. The cone angle of **II** was calculated to be 166° from the structure of **6** and 167° from that of **12**. These angles are slightly smaller than that of 171° for $PPh(C_6F_5)_2$ reported by Tolman,[10] but there are no structures of complexes of $PPh(C_6F_5)_2$ to confirm this value and with which to compare the structures of **6** and **12**. Cone angles were not obtained from the structures of **3** and **9** because of the high degree of disorder in the phosphine ligand. The cone angle of **III** was calculated to be 176 and 171° from the structures of **4** and **10** respectively. Tolman[10] has reported the cone angle of $P(C_6F_5)_3$ as 184°, but the value calculated from the structure of *trans*-$[IrBr(CO)\{P(C_6F_5)_3\}_2]$[3] is only 172°. Thus, it appears that there is very little difference in steric properties between difluorophenylphosphines and the pentafluorophenyl analogues.

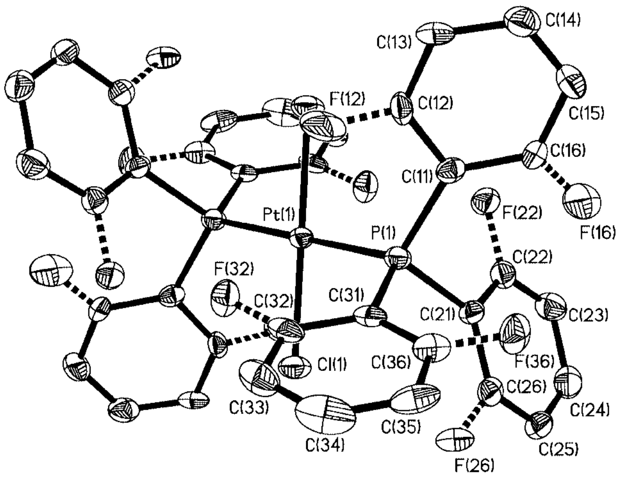


Fig. 11 Structure of *trans*-$[PtCl_2\{PPh(C_6H_3F_2\text{-}2,6)_2\}_2]$, **12**. Details as for Fig. 6.

Wilson and co-workers[34] have attempted to quantify the relationship between $\nu(C{\equiv}O)$ and the steric and electronic properties of phosphines for complexes of the form *trans*-$[IrCl(CO)(PR_3)_2]$ and have developed the empirical equation (1),

$$\nu(C{\equiv}O) = a\chi - b\theta + c \qquad (1)$$

where a, b and c are constants, χ is the electron donor capacity and is larger for weaker donors and θ is the cone angle.[10] Therefore, $\nu(C{\equiv}O)$ increases with decreasing basicity and decreasing cone angle. Presumably a similar relationship also exists for *trans*-$[RhCl(CO)(PR_3)_2]$ complexes. The values of $\nu(C{\equiv}O)$ for *trans*-$[MCl(CO)(PR_3)_2]$ (M = Rh or Ir) comprising **I**, **II** and **III** are similar to those of *trans*-$[MCl(CO)(PPh_3)_2]$, whereas $\nu(C{\equiv}O)$ for the complexes comprising pentafluorophenylphosphines are at significantly higher frequency and follow the order $PPh_3 < PPh_2(C_6F_5) < PPh(C_6F_5)_2 < P(C_6F_5)_3$ for *trans*-$[RhCl(CO)(PR_3)_2]$ (Table 4). For the pentafluorophenylphosphine ligands the decreasing basicity dominates over the increasing cone angle such that $\nu(C{\equiv}O)$ increases in the order PPh_3 ($\chi = 13.25$ cm^{-1}, $\theta = 145°$) < $PPh_2(C_6F_5)$ ($\chi = 18.7$ cm^{-1}) < $PPh(C_6F_5)_2$ < $P(C_6F_5)_3$ ($\chi = 35.6$ cm^{-1}).[10,34] However, for difluorophenylphosphines it appears that the donor and steric properties are matched such that increases of χ and θ in the series PPh_3, **I**, **II**,

Table 7 Infrared carbonyl stretching frequencies for $[Mo(CO)_4(R_2PCH_2CH_2PR_2)]$

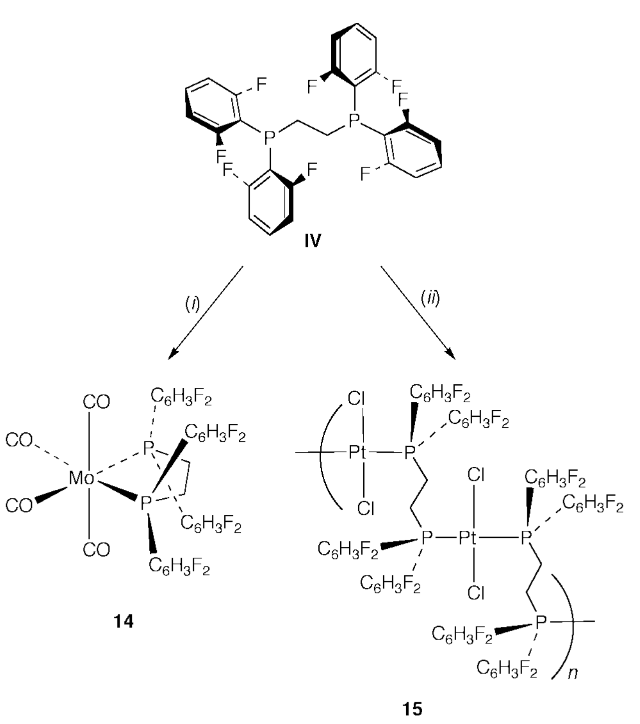
	$\tilde{\nu}(C{\equiv}O)/cm^{-1}$			
Compound	$A_1{}^1$	$A_1{}^2$	B_1	B_2
$[Mo(CO)_4\{(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2\}]$ [a]	2064	1993	1982	1955
$[Mo(CO)_4(dfppe)]$ [a]	2041	1965	1935	1935
$[Mo(CO)_4\{(MeO)_2PCH_2CH_2P(OMe)_2\}]$ [b]	2033	1965	1941	1916
14 [c]	2030	1945	1924	1885
$[Mo(CO)_4(dppe)]$ [d]	2020	1919	1907	1881
$[Mo(CO)_4(Et_2PCH_2CH_2PEt_2)]$ [d]	2012	1909	1891	1873

[a] Ref. 19. [b] Ref 35. [c] Recorded as a Nujol mull. Assignments made by comparison with the spectrum of $[Mo(CO)_4(dfppe)]$. [d] Ref. 36.

III leave $\nu(C{\equiv}O)$ constant. Since the values of θ for phosphines **I**–**III** are similar or slightly less than those for the pentafluorophenyl analogues it follows that, as expected, **I**–**III** are more basic than the respective pentafluorophenylphosphines.

Transition metal complexes of diphosphine IV

Treatment of *cis*-$[Mo(CO)_4(NHC_5H_{10})_2]$ with **IV** in dichloromethane afforded $[Mo(CO)_4\{(C_6H_3F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2\}]$ **14** as pale yellow crystals (Scheme 2). The $^{31}P\text{-}\{^1H\}$ and $^{19}F\text{-}\{^1H\}$ NMR spectra, which have been simulated, are the A and X parts respectively of an $AA'X_4X'_4$ spectrum and resemble those of **IV**.[24] The spectra have been simulated with the values of $|^3J(PP')|$ 11.0, $|^3J(PF)|$ 9.8, $|^5J(PF')|$ 2.0 and $|^8J(FF')|$ 0 Hz. The values of $|^3J(PP')|$ and $|^3J(PF)|$ are significantly smaller than those of 47.4 and 30.1 Hz respectively for **IV**. As expected the infrared spectrum of **14** exhibits four carbonyl stretching bands (Table 7), which were assigned by comparison with the spectrum of $[Mo(CO)_4(dfppe)]$.[22] The values of $\nu(C{\equiv}O)$, in particular the A_1 band, give an indication of the π-acceptor properties of the ligand,[22] and as can be seen from Table 7 the π acidity of **14** is intermediate between those of dfppe and dppe, and similar to that of the diphosphonite complex $[Mo(CO)_4\{(MeO)_2PCH_2CH_2P(OMe)_2\}]$.[35]



Scheme 2 (*i*) *cis*-$[Mo(CO)_4(NHC_5H_{10})_2]$, CH_2Cl_2, heat; (*ii*) *cis*-$[PtCl_2(NCMe)_2]$, CH_2Cl_2, heat.

Treatment of *cis*-$[PtCl_2(NCMe)_2]$ with **IV** gave a white solid of formulation $[PtCl_2\{(C_6H_3F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2\}]$, **15**, in high yield. Compound **15** was characterized by elemental analysis and FAB mass spectrometry, which showed peaks at *m*/*z* 807, 772 and 737 consistent with M^+, $[M - Cl]^+$ and $[M - Cl]^{2+}$, but was insufficiently soluble in all common solvents for an NMR spectroscopic investigation. On the basis of the very different solubilities of **15** and $[PtCl_2(dfppe)]$, and the tendency of diphosphine **IV** to bridge $[IrCl_2(\eta^5\text{-}C_5Me_5)]$ moieties rather than chelate,[24] we tentatively suggest that compound **15** is a polymeric species, as depicted in Scheme 2, rather than a mononuclear species. Although the mass spectral data suggest a mononuclear compound, this may arise from fragmentation of the polymer under the conditions required to observe a spectrum.

Conclusion

In conclusion, we have prepared the new 2,6-difluorophenylphosphines $PPh_x(C_6H_3F_2\text{-}2,6)_{3-x}$ ($x = 1$ or 2) and a range of transition metal complexes of these and the previously reported phosphines $P(C_6H_3F_2\text{-}2,6)_3$ and $(C_6H_3F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2$. The structural and spectroscopic data of the complexes indicate that, as expected, these phosphines are more basic than the analogous pentafluorophenylphosphines, but much less basic than triphenylphosphine or dppe. The difluorophenylphosphines exert a similar or slightly smaller steric effect than the analogous pentafluorophenylphosphines, and possess more acute PC–C–F angles than the latter.

Experimental

Physical measurements

Proton, ^{19}F and ^{31}P NMR spectra were recorded on Bruker DRX400, AM300 or ARX250 spectrometers: ^1H (250.13, 300.14 or 400.13 MHz) were referenced internally using the residual protio solvent resonance relative to $SiMe_4$ (δ 0), ^{13}C (62.90 MHz) internally using the deuteriated solvent resonance relative to $SiMe_4$ (δ 0), ^{19}F (235.36, 282.41 or 376.50 MHz) externally to $CFCl_3$ (δ 0) and ^{31}P (101.26, 121.50 or 161.98 MHz) externally to 85% H_3PO_4 (δ 0) using the high frequency positive convention. All chemical shifts (δ) are quoted in ppm and coupling constants in Hz. The IR spectra were recorded on a Digilab FTS40 Fourier transform spectrometer, EI and positive-ion FAB mass spectra on a Kratos Concept 1H mass spectrometer. Elemental analyses were performed by Butterworths Ltd. or by A.S.E.P., The School of Chemistry, The Queen's University of Belfast.

Materials

The compounds $C_6H_3BrF_2\text{-}2,6$ (Fluorochem), PPh_2Cl, $PPhCl_2$, $[\{RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$, $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ and $IrCl_3\cdot xH_2O$ (Aldrich) were used as supplied, $[\{PtCl(\mu\text{-}Cl)(PEt_3)\}_2]$,[37] $[\{Ir(\mu\text{-}Cl)(\eta^2,\eta^{2'}\text{-}C_8H_{12})\}_2]$,[38] **IV**,[24] *cis*-$[PtCl_2(NCMe)_2]$[39] and $[Mo(CO)_4(NHC_5H_{10})_2]$[40] were prepared as described and PCl_3 was distilled under nitrogen. Diethyl ether was dried by distillation under nitrogen from over sodium. Light petroleum (bp 40–60 °C) was used throughout.

Preparations

(2,6-Difluorophenyl)diphenylphosphine I. *n*-Butyllithium 1.6 M in hexane (32.5 cm^3, 0,052 mol) was diluted with 30 cm^3 of diethyl ether and added during 45 min to $C_6H_3BrF_2$-2,6 (10.24 g, 0.052 mol) in diethyl ether (100 cm^3) at −78 °C under nitrogen and stirred for $1\frac{1}{2}$ h. The compound PPh_2Cl (9.8 cm^3, 0.052 mol) in diethyl ether (50 cm^3) was added to the solution during 45 min. The reaction mixture was allowed to warm slowly to room temperature over 12 h. The resulting slurry was added to 10% NH_4Cl(aq) (200 cm^3) and the organic layer separated, washed with 10% NH_4Cl(aq) (100 cm^3) and water (2 × 100 cm^3) and dried over $MgSO_4$. The solution was filtered and the solvent removed by rotary evaporation to yield **I** as a white solid, which was purified by column chromatography using diethyl ether as eluent. Yield 10.68 g, 70%.

Bis(2,6-difluorophenyl)phenylphosphine II. Phosphine **II** was prepared similarly to **I** from $C_6H_3BrF_2$-2,6 (8.27 g, 0.042 mol) and $PPhCl_2$ (3.76 g, 0.021 mol). Yield 3.46 g, 49%.

Tris(2,6-difluorophenyl)phosphine III. Phosphine **III** was prepared similarly to **I** from $C_6H_3BrF_2$-2,6 (10.24 g, 0.052 mol) and PCl_3 (1.2 cm^3, 0.014 mol). Yield 4.51 g, 87%.

[RhCl$_2${PPh$_2$(C$_6$H$_3$F$_2$-2,6)}(η^5-C$_5$Me$_5$)] 1. A slurry of [{RhCl(μ-Cl)(η^5-C$_5$Me$_5$)}$_2$] (0.010 g, 0.16 mmol) and compound **I** (0.10g, 0.32 mmol) in benzene (50 cm^3) was refluxed for $4\frac{1}{2}$ h. Removal of the solvent by rotary evaporation afforded complex **1** as an orange solid, which was recrystallized from dichloromethane. Yield 0.14 g, 71%.

***trans*-[PtCl$_2$(PEt$_3$){PPh$_2$(C$_6$H$_3$F$_2$-2,6)}] 2.** A slurry of [{PtCl(μ-Cl)(PEt$_3$)}$_2$] (0.010 g, 0.13 mmol) and compound **I** (0.075 g, 0.25 mmol) in acetone (30 cm^3) was heated gently for *ca.* 5 min. The solution was filtered and light petroleum added to afford pale yellow crystals of **2**. Yield 0.15 g, 38%.

***trans*-[PtCl$_2$(PEt$_3$){PPh(C$_6$H$_3$F$_2$-2,6)$_2$}] 3.** Complex **3** was prepared similarly to **2** from [{PtCl(μ-Cl)(PEt$_3$)}$_2$] (0.153 g, 0.20 mmol) and compound **II** (0.134 g, 0.40 mmol). Yield 0.251 g, 87%.

***trans*-[PtCl$_2$(PEt$_3$){P(C$_6$H$_3$F$_2$-2,6)$_3$}] 4.** Complex **4** was prepared similarly to **2** from [{PtCl(μ-Cl)(PEt$_3$)}$_2$] (0.097 g, 0.14 mmol) and compound **III** (0.102 g, 0.28 mmol). Yield 0.116 g, 58%.

***trans*-[RhCl(CO){PPh$_2$(C$_6$H$_3$F$_2$-2,6)}$_2$] 5.** The dimer [{Rh(μ-Cl)(CO)$_2$}$_2$] (0.027 g, 0.07 mmol) in dichloromethane (20 cm^3) was added to compound **I** (0.091 g, 0.31 mmol) in dichloromethane (30 cm^3) and the mixture stirred for 30 min. Concentration by rotary evaporation and addition of light petroleum gave lemon yellow crystals of **5**. Yield *ca.* 0.09 g, 85%.

***trans*-[RhCl(CO){PPh(C$_6$H$_3$F$_2$-2,6)$_2$}$_2$] 6.** Complex **6** was prepared similarly to **5** from [{Rh(μ-Cl)(CO)$_2$}$_2$] (0.122 g, 0.31 mmol) and compound **II** (0.418 g, 1.25 mmol). Yield 0.42 g, 81%.

***trans*-[RhCl(CO){P(C$_6$H$_3$F$_2$-2,6)$_3$}$_2$] 7.** Complex **7** was prepared similarly to **5** from [{Rh(μ-Cl)(CO)$_2$}$_2$] (0.120 g, 0.30 mmol) and compound **III** (0.555 g, 1.5 mmol). Yield 0.48 g, 88%.

***trans*-[IrCl(CO){PPh$_2$(C$_6$H$_3$F$_2$-2,6)}$_2$] 8.** A mixture of [{Ir(μ-Cl)(η^2,η$^{2'}$-C$_8$H$_{12}$)}$_2$] (0.168 g, 0.25 mmol) and compound **I** (0.298 g, 1.00 mmol) in dichloromethane (35 cm^3) was stirred at 25 °C under carbon monoxide for 1 h. The solvent was removed

Table 8 Crystal data collection, solution and refinement details[a] for PPh$_2$(C$_6$H$_3$F$_2$-2,6) **I**, PPh(C$_6$H$_3$F$_2$-2,6)$_2$ **II**, P(C$_6$H$_3$F$_2$-2,6)$_3$ **III**, *trans*-[PtCl$_2$(PEt$_3$){PPh$_2$(C$_6$H$_3$F$_2$-2,6)}] **2**, *trans*-[PtCl$_2$(PEt$_3$){PPh(C$_6$H$_3$F$_2$-2,6)$_2$}] **3**, *trans*-[PtCl$_2$(PEt$_3$){P(C$_6$H$_3$F$_2$-2,6)$_3$}] **4**, *trans*-[RhCl(CO){PPh(C$_6$H$_3$F$_2$-2,6)$_2$}$_2$] **6**, *trans*-[IrCl(CO){PPh(C$_6$H$_3$F$_2$-2,6)$_2$}$_2$] **9**, *trans*-[IrCl(CO){P(C$_6$H$_3$F$_2$-2,6)$_3$}$_2$] **10** and *trans*-[PtCl$_2${PPh(C$_6$H$_3$F$_2$-2,6)$_2$}$_2$] **12**

	I	**II**	**III**	**2**	**3**	**4**	**6**	**9**	**10**	**12**
Formula	$C_{18}H_{13}F_2P$	$C_{18}H_{11}F_4P$	$C_{18}H_9F_6P$	$C_{24}H_{28}Cl_2F_2P_2Pt$	$C_{24}H_{26}Cl_2F_4P_2Pt$	$C_{24}H_{24}Cl_2F_6P_2Pt$	$C_{37}H_{22}ClF_8OP_2Rh$	$C_{37}H_{22}ClF_8IrOP_2$	$C_{37}H_{18}ClF_{12}IrOP_2$	$C_{36}H_{22}Cl_2F_8P_2Pt$
M	298.25	334.24	370.22	682.39	718.38	754.36	834.85	924.14	996.10	934.47
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	*Pbca*	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$	*Pbca*	$P2_1/n$	*Pbca*	*Pbca*
a/Å	12.382(3)	8.241(1)	9.548(2)	9.984(2)	13.152(10)	13.253(2)	16.194(7)	9.524(1)	16.159(2)	16.312(4)
b/Å	9.993(4)	14.043(3)	13.703(2)	15.583(4)	10.867(4)	10.866(1)	12.255(5)	13.309(4)	12.536(3)	12.303(4)
c/Å	11.931(4)	27.145(4)	13.222(6)	16.459(4)	19.251(4)	19.356(3)	16.621(7)	13.145(2)	16.644(3)	16.451(4)
β/°	99.45(2)	—	110.23(3)	102.05(2)	103.58(4)	103.19(1)	—	92.04(2)	—	—
U/Å^3	1456.2(8)	3141.4(9)	1623.2(8)	2504.3(10)	2674(2)	2713.9(6)	3299(2)	1665.1(6)	3371.6(11)	3301.5(17)
Z	4	8	4	4	4	4	4	2	4	4
μ/mm^{-1}	0.200	0.211	0.230	5.969	5.605	5.538	0.773	4.262	4.234	4.582
Total data	2817	2882	2590	5127	6316	7355	3636	3857	4172	3890
Unique data, R_{int}	2146, 0.0166	2177, 0.0199	1941, 0.0508	4517, 0.0208	5500, 0.0644	5892, 0.0412	3162, 0.0223	3260, 0.0313	3662, 0.0187	3396, 0.0589
*R*1, *wR*2 [$I > 2\sigma(I)$][a]	0.0365, 0.0838	0.0428, 0.0949	0.0441, 0.0905	0.0477, 0.1020	0.0653, 0.1674	0.0405, 0.0934	0.0467, 0.0942	0.0306, 0.0680	0.0314, 0.0525	0.0459, 0.0723
(all data)	0.0539, 0.0924	0.0690, 0.1026	0.0726, 0.1028	0.0726, 0.1132	0.0942, 0.1918	0.0622, 0.1059	0.0735, 0.1067	0.0416, 0.0718	0.0580, 0.0607	0.1469, 0.0990

under reduced pressure and the solid product washed with light petroleum and dried *in vacuo*. Yield 0.37 g, 87%.

***trans*-[IrCl(CO){PPh($C_6H_3F_2$-2,6)$_2$}$_2$] 9.** Complex **9** was prepared similarly to **8** from [Ir(μ-Cl)(η^2,$\eta^{2\prime}$-C_8H_{12})] (0.182 g, 0.27 mmol) and compound **II** (0.361 g, 1.08 mmol). Yield 0.35 g, 70%.

***trans*-[IrCl(CO){P($C_6H_3F_2$-2,6)$_3$}$_2$] 10.** A mixture of $IrCl_3\cdot xH_2O$ (0.12 g, *ca.* 0.35 mmol) and compound **III** (0.30 g, 7.04 mmol) in 2-methoxyethanol (50 cm^3) was refluxed under nitrogen for 4 h. The solvent was removed by rotary evaporation, and the product extracted into dichloromethane (100 cm^3). The solution was filtered and concentrated by rotary evaporation. Addition of light petroleum precipitated **10** as a yellow solid. Yield 0.09 g, *ca.* 25%.

***trans*-[PtCl$_2${PPh$_2$($C_6H_3F_2$-2,6)}$_2$] 11.** A slurry of *cis*-[PtCl$_2$(NCMe)$_2$] (0.202 g, 0.58 mmol) and compound **I** (0.346 g, 1.16 mmol) in dichloromethane (50 cm^3) was refluxed for 4 h. After cooling to room temperature the solvent was removed by rotary evaporation to yield the product as a pale yellow solid, which was washed with light petroleum. Yield 0.48 g, 96%.

***trans*-[PtCl$_2${PPh($C_6H_3F_2$-2,6)$_2$}$_2$] 12.** Complex was prepared similarly to **11** from *cis*-[PtCl$_2$(NCMe)$_2$] (0.349 g, 1.00 mmol) and compound **II** (0.674 g, 2.02 mmol). Yield 0.706 g, 76%.

[Mo(CO)$_4${($C_6H_3F_2$-2,6)$_2$PCH$_2$CH$_2$P($C_6H_3F_2$-2,6)$_2$}] 14. A mixture of [Mo(CO)$_4$(NHC$_5$H$_{10}$)$_2$] (0.1 g, 0.294 mmol) and compound **IV** (0.14 g, 0.258 mmol) in dichloromethane (30 cm^3) was refluxed for 4 h. The solution was concentrated by rotary evaporation to afford pale yellow crystals of **14**, which were washed with methanol and dried *in vacuo*. Yield 0.11 g, 58%.

[{PtCl$_2$[($C_6H_3F_2$-2,6)$_2$PCH$_2$CH$_2$P($C_6H_3F_2$-2,6)$_2$]}$_n$] 15. Phosphine **IV** (0.13 g, 0.24 mmol) was added to *cis*-[PtCl$_2$(NCMe)$_2$] (0.09 g, 0.247 mmol) in dichloromethane and stirred for $1\frac{1}{2}$ h to give a white precipitate. The solid was filtered off, washed with dichloromethane, acetone and light petroleum and dried *in vacuo*. Yield 0.16 g, 84%.

X-Ray crystallography

Crystals of compound **I** were grown from acetone–light petroleum and **II** and **III** from diethyl ether, complexes **2**, **3** and **4** from acetone, **6** from chloroform and **9**, **10** and **12** from dichloromethane. Data were collected at 293(2) K (**I**, **4** and **12**), 180(2) K (**II**), 190(2) K (**III**, **3**, **6**, **9** and **10**) and 200(2) K (**2**). Table 8 summarizes the crystallographic data. All data sets were corrected for Lorentz-polarization effects. For the metal complex structures empirical absorption corrections were applied to the data sets based on psi scan data. The structures of **I**, **II** and **III** were solved by direct methods using the program SHELXTL PC[41] and refined on F^2 with full-matrix least squares using the program SHELXL 97.[42] The remaining structures were solved by Patterson methods using the program SHELXTL PC.[41] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in calculated positions (C–H 0.96 Å) with isotropic displacement parameters set at $1.2U_{eq}$ of the bonded carbon atom or $1.5U_{eq}$ for methyl H atoms.

CCDC reference number 186/1733.

See http://www.rsc.org/suppdata/dt/a9/a907759f/ for crystallographic files in .cif format.

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References

1 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
2 M. J. Atherton, K. S. Coleman, J. Fawcett, J. H. Holloway, E. G. Hope, A. Karaçar, L. A. Peck and G. C. Saunders, *J. Chem. Soc., Dalton Trans.*, 1995, 4029.
3 J. H. Holloway, E. G. Hope, D. R. Russell, G. C. Saunders and M. J. Atherton, *Polyhedron*, 1996, **15**, 173.
4 M. J. Atherton, J. Fawcett, J. H. Holloway, E. G. Hope, D. R. Russell and G. C. Saunders, *J. Chem. Soc., Dalton Trans.*, 1997, 2217.
5 M. J. Atherton, J. Fawcett, J. H. Holloway, E. G. Hope, S. M. Martin, D. R. Russell and G. C. Saunders, *J. Organomet. Chem.*, 1998, **555**, 67.
6 M. J. Atherton, K. S. Coleman, J. Fawcett, J. H. Holloway, E. G. Hope, A. Karaçar, D. R. Russell and G. C. Saunders, *J. Chem. Soc., Dalton Trans.*, 1996, 3215.
7 M. G. Hogben, R. S. Gray and W. A. Graham, *J. Am. Chem. Soc.*, 1966, **88**, 3457; 1969, **91**, 283; S. T. Bond and N. V. Duffy, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3241; D. Rehder and J. Schmidt, *Transition Met. Chem.*, 1977, **2**, 41; G. M. Bodner, M. P. May and L. E. McKinney, *Inorg. Chem.*, 1980, **19**, 1951.
8 R. D. W. Kemmitt, D. I. Nichols and R. D. Peacock, *Chem. Commun.*, 1967, 599; *J. Chem. Soc. A*, 1968, 1898.
9 R. D. W. Kemmitt, D. I. Nichols and R. D. Peacock, *J. Chem. Soc. A*, 1968, 2149.
10 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
11 J. B. Docherty, D. S. Rycroft, D. W. A. Sharp and G. A. Webb, *J. Chem. Soc., Chem. Commun.*, 1979, 336.
12 W. N. Hunter, K. W. Muir and D. W. A. Sharp, *Acta Crystallogr., Sect. C*, 1986, **42**, 1743.
13 W. P. Schaefer, D. K. Lyon, J. A. Labinger and J. E. Bercaw, *Acta Crystallogr., Sect. C*, 1992, **48**, 1582.
14 B. Bertsch-Frank and W. Frank, *Acta Crystallogr., Sect. C*, 1996, **52**, 328.
15 I. Ojima and H. B. Kwon, *J. Am. Chem. Soc.*, 1988, **110**, 5617.
16 H. G. Ang, W. L. Kwik, W. K. Leong and J. A. Potenza, *Acta Crystallogr., Sect. C*, 1989, **45**, 1713.
17 A. Karipides and C. M. Cosio, *Acta Crystallogr., Sect. C*, 1989, **45**, 1743.
18 S. Park, M. Pointer-Johnson and D. M. Roundhill, *J. Am. Chem. Soc.*, 1989, **111**, 3101.
19 S. Park, M. Pointer-Johnson and D. M. Roundhill, *Inorg. Chem.*, 1990, **29**, 2687.
20 O. B. Shawkataly, M.-L. Chong, H.-K. Fun and K. Sivakumar, *Acta Crystallogr., Sect. C*, 1996, **52**, 1725.
21 R. L. Cook and J. G. Morse, *Inorg. Chem.*, 1982, **21**, 4103; M. F. Ernst and D. M. Roddick, *Inorg. Chem.*, 1990, **29**, 3627; A. S. C. Chan, C.-C. Pai, T.-K. Yang and S.-M. Chen, *J. Chem. Soc., Chem. Commun.*, 1995, 2031.
22 R. L. Cook and J. G. Morse, *Inorg. Chem.*, 1984, **23**, 2332; M. F. Ernst and D. M. Roddick, *Inorg. Chem.*, 1989, **28**, 1624.
23 R. K. Merwin, R. C. Schnabel, J. D. Koola and D. M. Roddick, *Organometallics*, 1992, **11**, 2972.
24 J. Fawcett, S. Friedrichs, J. H. Holloway, E. G. Hope, V. McKee, M. Nieuwenhuyzen, D. R. Russell and G. C. Saunders, *J. Chem. Soc., Dalton Trans.*, 1998, 1477.
25 D. I. Nichols, *J. Chem. Soc. A*, 1969, 1471.
26 M. J. Atherton, J. Fawcett, A. P. Hill, J. H. Holloway, E. G. Hope, D. R. Russell, G. C. Saunders and R. M. J. Stead, *J. Chem. Soc., Dalton Trans.*, 1997, 1137.
27 J. Chatt and B. L. Shaw, *J. Chem. Soc. A*, 1996, 1437.
28 R. Ugo, A. Pasini, A. Fuji and S. Cenini, *J. Am. Chem. Soc.*, 1972, **94**, 7364.
29 D. J. Evans, J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1968, **11**, 99.
30 A. L. Rheingold and S. J. Geib, *Acta Crystallogr., Sect. C*, 1987, **43**, 784.
31 M. Selke, W. L. Karney, S. I. Khan and C. S. Foote, *Inorg. Chem.*, 1995, **34**, 5715.
32 M. R. Churchill, J. C. Fettinger, L. A. Buttrey, M. D. Barkan and J. S. Thompson, *J. Organomet. Chem.*, 1988, **340**, 257.
33 R. Favez, R. Roulet, A. A. Pinkerton and D. Schwarzenbach, *Inorg. Chem.*, 1980, **19**, 1356.
34 M. R. Wilson, D. C. Woska, A. Prock and W. P. Giering, *Organometallics*, 1993, **12**, 1742; M. R. Wilson, H. Liu, A. Prock and W. P. Giering, *ibid.*, 1993, **12**, 2044.
35 R. B. King and W. M. Rhee, *Inorg. Chem.*, 1978, **17**, 2961.
36 J. Chatt and R. H. Watson, *J. Chem. Soc.*, 1961, 4980.
37 R. J. Goodfellow and L. M. Venanzi, *J. Chem. Soc.*, 1965, 7533.
38 J. L. Herde, J. C. Lambert and C. V. Senoff, *Inorg. Synth.*, 1974, **15**, 18.

39 F. R. Hartley, S. G. Murray and C. A. McAuliffe, *Inorg. Chem.*, 1979, **18**, 1394.
40 D. J. Darensbourg and R. L. Kump, *Inorg. Chem.*, 1978, **17**, 2680.
41 G. M. Sheldrick, SHELXTL PC, Release 4.2, Siemens Analytical X-Ray Instruments, Madison, WI, 1991.
42 G. M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, 1997.

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