DALTON
FULL PAPER

Synthesis and coordination chemistry of *ortho*-perfluoroalkyl-derivatised triarylphosphines

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Received 15th August 2001, Accepted 16th November 2001
First published as an Advance Article on the web 28th January 2002

In order to establish the steric and electronic effects of fluorous ponytails in the *ortho*-positions of triarylphosphines the two novel phosphines, $PPh_2(2\text{-}C_6H_4C_6F_{13})$ **II** and $P(4\text{-}C_6H_4C_6F_{13})_2(2\text{-}C_6H_4C_6F_{13})$ **V**, have been synthesised and their coordination chemistry investigated and compared with that of the *ortho*-trifluoromethyl-derivatised ligand, $PPh_2(2\text{-}C_6H_4CF_3)$ **VI**. The single crystal X-ray structures of $Ph_2P(O)(2\text{-}C_6H_4C_6F_{13})$ and $Ph_2P(O)(2\text{-}C_6H_4CF_3)$, along with that of $PPh_2(2\text{-}C_6H_4CF_3)$, are reported and compared with each other. The large steric influence of the *ortho*-trifluoromethyl and -perfluorohexyl substituents results in the formation of the, normally, less-thermodynamically favoured *trans*-$[PtCl_2L_2]$ complexes. Analysis of the single crystal X-ray structures of *trans*-$[PtCl_2\{PPh_2(2\text{-}C_6H_4\text{-}CF_3)\}_2]$ **1**, *trans*-$[PtCl_2\{PPh_2(2\text{-}C_6H_4C_6F_{13})\}_2]$ **2** and *trans*-$[RhCl(CO)\{PPh_2(2\text{-}C_6H_4CF_3)\}_2]$ **4** reveals a larger cone angle for $PPh_2(2\text{-}C_6H_4CF_3)$ (169°) than for $PPh_2(2\text{-}C_6H_4C_6F_{13})$. An average cone angle of 166° was calculated for the latter phosphine with values ranging from 164 to 168°.

Introduction

It is becoming increasingly important that expensive metal catalysts in selective homogeneous catalytic processes can be recovered and recycled efficiently. Since fluorous biphase catalysis[1] offers the benefits of both homogeneous catalysis and heterogeneous separation of the catalyst from the product, it has been receiving considerable attention recently and work in this area has been extensively reviewed.[2] This new strategy has now been applied to a wide range of catalytic processes such as hydroformylation,[1,3] hydrogenation,[4,5] hydroboration,[6] oxidation[7] and carbon–carbon bond forming reactions.[8]

We have recently described a two step synthesis to perfluoroalkyl-derivatised triarylphosphine ligands[9,10] and examined the coordination of these ligands to transition metals.[10,11] As well as establishing the criteria for preferential solubility in perfluorocarbon solvents, we have investigated the electronic and steric influence of the perfluorohexyl groups in the *meta*- and *para*-derivatised ligands using spectroscopic methods[10,11] and used the fluorous biphase hydrogenation of styrene as a model system to establish the influence of the fluorous substituents on the rates of a catalytic reaction.[5]

Preliminary work has also shown that it is not possible to form the tris-derivatised *ortho*-substituted phosphine, $P(2\text{-}C_6H_4C_6F_{13})_3$. Although 2-(tridecafluorohexyl)bromobenzene **I** undergoes lithium/bromine exchange with *n*-butyllithium, when it subsequently reacts with phosphorus trichloride it does not undergo complete substitution and the main product is $ClP(2\text{-}C_6H_4C_6F_{13})_2$ (Fig. 1).[12] Presumably, this occurs because of the steric congestion around the phosphorus atom caused by the two *ortho*-C_6F_{13} ponytails. The X-ray crystal structure of $ClP(2\text{-}C_6H_4C_6F_{13})_2$ has shown that there are short intramolecular interactions between phosphorus and fluorine atoms on the perfluoroalkyl substituents and consequently this compound is both air- and moisture-stable. Here, we have extended this work and synthesised the two new ligands, $PPh_2(2\text{-}C_6H_4C_6F_{13})$ **II** and $P(4\text{-}C_6H_4C_6F_{13})_2(2\text{-}C_6H_4C_6F_{13})$ **V**, and investigated their coordination chemistry in order to study both the steric and electronic influences of the fluorous ponytails in the *ortho*-positions.

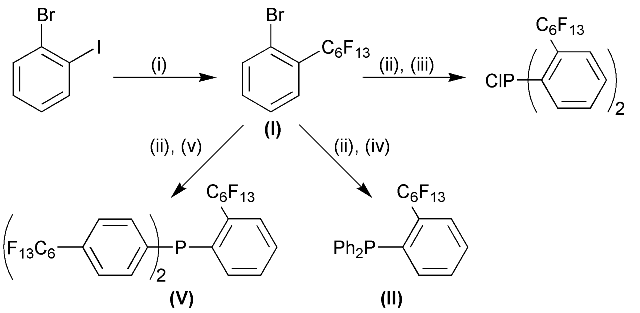


Fig. 1 (i) $F_{13}C_6I$, Cu, 2,2′-bipyridine, DMSO, fluorobenzene, 70 °C, 72 h; (ii) *n*-BuLi, Et_2O, −78 °C; (iii) PCl_3, Et_2O; (iv) Ph_2PCl, Et_2O; (v) $ClP(4\text{-}C_6H_4C_6F_{13})_2$ **IV**, Et_2O.

Results and discussion

Synthesis and characterisation of phosphines (II) and (V)

The selective copper coupling reaction of 2-bromoiodobenzene with perfluorohexyl iodide was used to prepare 2-(tridecafluorohexyl)bromobenzene **I** (Fig. 1). The reaction of **I** with *n*-butyllithium in ether at −78 °C proceeded smoothly and the aryllithiate was subsequently reacted with chlorodiphenylphosphine to give the new *ortho*-derivatised phosphine, $PPh_2(2\text{-}C_6H_4C_6F_{13})$ **II**, in 42% yield.

Since we have already shown that the tris-derivatised *ortho*-substituted phosphine, $P(2\text{-}C_6H_4C_6F_{13})_3$, could not be prepared[12] and that three perfluoroalkyl groups are normally required for preferential perfluorocarbon solubility,[9] we have synthesised the novel tris-derivatised triarylphosphine **V** with perfluoroalkyl groups in the *ortho*- and *para*-positions. The first step in this synthesis was the preparation of an analogue of chlorodiphenylphosphine, $ClP(4\text{-}C_6H_4C_6F_{13})_2$ **IV**, using established methodologies. After lithiating 4-(tridecafluorohexyl)bromobenzene, two equivalents were reacted with diethylphosphoramidous dichloride, Et_2NPCl_2, to give the intermediate, $Et_2NP(4\text{-}C_6H_4C_6F_{13})_2$ **III**. Hydrogen chloride was then passed over a stirred solution of $Et_2NP(4\text{-}C_6H_4C_6F_{13})_2$ to form $ClP(4\text{-}C_6H_4C_6F_{13})_2$ **IV** as a white crystalline solid in an

DOI: 10.1039/b107390g

Table 1 $^{31}P\{^1H\}$ NMR data of triarylphosphine ligands

Ligand	δ_P (CDCl$_3$)
PPh_3	−5.0 (s)
$PPh_2(2\text{-}C_6H_4CF_3)$	−10.9 (q, $^4J_{PF}$ 53 Hz)
$PPh_2(2\text{-}C_6H_4C_6F_{13})$ **II**	−6.7 (ttt, $^4J_{PF}$ 99, $^5J_{PF}$ 49, $^6J_{PF}$ 4 Hz)
$PPh_2(3\text{-}C_6H_4C_6F_{13})$[a]	−4.8 (s)
$PPh_2(4\text{-}C_6H_4C_6F_{13})$[b]	−5.0 (s)
$P(4\text{-}C_6H_4C_6F_{13})_2(2\text{-}C_6H_4C_6F_{13})$ **V**	−6.3 (tt, $^4J_{PF}$ 98, $^5J_{PF}$ 49 Hz)
$P(4\text{-}C_6H_4C_6F_{13})_3$[b]	−6.0 (s)

[a] Data taken from ref. 10. [b] Data taken from ref. 9.

overall yield of 41%. 2-(Tridecafluorohexyl)bromobenzene **I** was then lithiated with *n*-butyllithium before being reacted with $ClP(4\text{-}C_6H_4C_6F_{13})_2$ to give the new ligand, $P(4\text{-}C_6H_4C_6F_{13})_2(2\text{-}C_6H_4C_6F_{13})$ **V**.

Both ligands **II** and **V**, which are air-stable in the solid-state but oxidise in solution, have been fully characterised by elemental analysis, mass spectrometry and multinuclear NMR spectroscopies (see Experimental). The $^{31}P\{^1H\}$ NMR spectra of both compounds showed a 7 line pattern corresponding to an overlapping triplet of triplets which arose from "through-space" P–F spin–spin couplings (Table 1). This phenomenon has been observed previously[13] in the series of *ortho*-derivatised triarylphosphines with one, two and three trifluoromethyl groups. For example, the $^{31}P\{^1H\}$ spectrum of $PPh_2(2\text{-}C_6H_4CF_3)$ **VI** is a quartet at −10.9 ppm with a $^4J_{PF}$ coupling constant of 53 Hz. With both phosphines **II** and **V** there are much larger $^4J_{PF}$ coupling constants of approximately 99 Hz presumably due to shorter intramolecular P–F distances. These phosphines also contain an additional $^5J_{PF}$ coupling constant which is approximately half of the $^4J_{PF}$ coupling constant and this explains why the overlapping triplet of triplets appears as a 7 line pattern. Furthermore, **II** also contained a $^6J_{PF}$ coupling to the γ-CF$_2$'s. Surprisingly, both of these multiplets are centred around −6 ppm and although this is fairly typical for triarylphosphines, an upfield chemical shift similar to that observed for $PPh_2(2\text{-}C_6H_4CF_3)$ had been expected for **II** and **V** due to the steric influence of the *ortho* substituents.[14] These slightly anomalous chemical shifts together with the large $^4J_{PF}$ coupling constants possibly indicate that **II** and **V** have different configurations at phosphorus than that for **VI**, which is supported by the crystallographic studies (*vide infra*). The "through-space" P–F spin–spin coupling was also observed in the $^{19}F\{^1H\}$ NMR spectra of both compounds giving a doublet of triplets at −100 ppm for the α-CF$_2$ ($^4J_{PF}$ = 99 Hz) and a doublet of multiplets at −119.5 ppm for the β-CF$_2$ ($^5J_{PF}$ = 47 Hz). In addition, for the mixed ligand **V** it was possible to distinguish between the α-CF$_2$'s in the *ortho*- and *para*-substituted aromatic rings at −100.1 and −111.5 ppm respectively in a 1:2 ratio in the $^{19}F\{^1H\}$ NMR spectrum. It was also possible to distinguish between the protons on the *ortho*- and *para*-substituted aromatic rings in the proton NMR spectrum. Only the tris-substituted ligand **V** was preferentially soluble in perfluorocarbon solvents.

Structural studies of IIb, VIb and VI

Although we were unable to structurally characterise either **II** or **V**, we did obtain single crystals of $Ph_2P(O)(2\text{-}C_6H_4C_6F_{13})$ **IIb** from an ether–hexane solution of the free ligand left to stand for several weeks. In addition, single crystals of both $PPh_2(2\text{-}C_6H_4CF_3)$ **VI** and $Ph_2P(O)(2\text{-}C_6H_4CF_3)$ **VIb** were obtained from an ether–hexane solution of $PPh_2(2\text{-}C_6H_4CF_3)$ **VI**. Selected bond lengths and bond angles for **IIb**, **VIb** and $P(O)Ph_3$ are directly compared in Table 2. Previous work has shown that for $P(O)Ph_3$ the mean O–P–C angle (112.4°) is greater than the mean C–P–C angle (106.4°) as a result of the repulsive effect of the short electron-rich P=O double bond.[15] A similar effect is also observed for $Ph_2P(O)(2\text{-}C_6H_4CF_3)$ **VIb**, but is slightly more pronounced (mean O–P–C = 113.3° > mean C–P–C = 105.4°) because the *ortho*-trifluoromethyl group points in the same direction as the P=O bond (Fig. 2). In fact, there seems to be an attractive interaction between two of the fluorines and the oxygen that causes the trifluoromethyl group to point in this direction since there are two short non-bonded O ··· F distances of 2.858 and 2.899 Å. In contrast, the *ortho*-perfluorohexyl group in $Ph_2P(O)(2\text{-}C_6H_4C_6F_{13})$ **IIb** radiates linearly away from the P=O bond in the opposite direction (Fig. 3). To accommodate the steric bulk of the perfluorohexyl

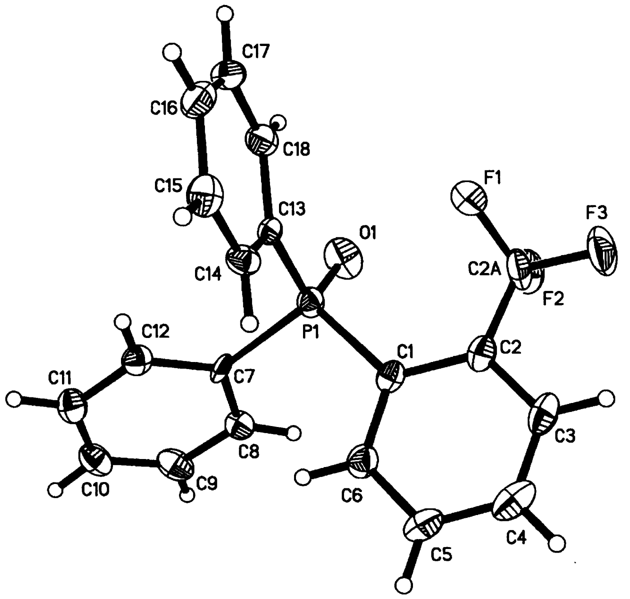


Fig. 2 Molecular structure of $Ph_2P(O)(2\text{-}C_6H_4CF_3)$ **VIb**. Displacement ellipsoids are shown at the 30% probability level. The H atoms are omitted for clarity.

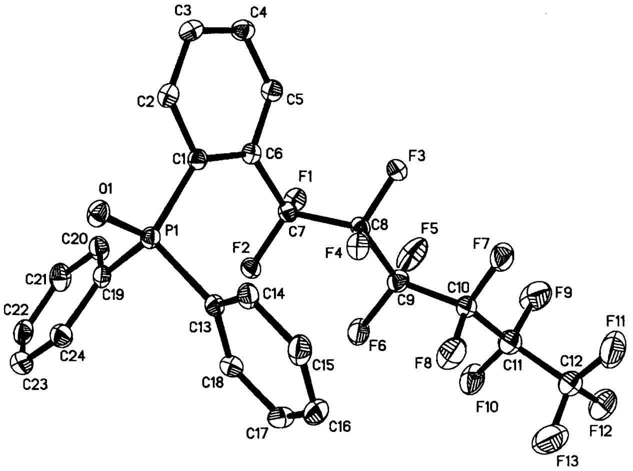


Fig. 3 Molecular structure of $Ph_2P(O)(2\text{-}C_6H_4C_6F_{13})$ **IIb**. Details as in Fig. 2.

Table 2 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $P(O)Ph_3$, $Ph_2P(O)(2\text{-}C_6H_4CF_3)$ **VIb** and $Ph_2P(O)(2\text{-}C_6H_4C_6F_{13})$ **IIb**

	$P(O)Ph_3$ [a]	**VIb**	**IIb**
P=O	1.487(3)	1.454(4)	1.4908(17)
P–C	1.804(5)	1.787(6)	1.808(2)
P–C	1.799(5)	1.805(6)	1.809(2)
P–C	1.795(5)	1.826(6) [b]	1.848(2) [b]
O–P–C	111.8(2)	114.3(3)	110.32(10)
O–P–C	113.3(2)	110.6(3)	110.90(10)
O–P–C	112.0(2)	114.9(3) [b]	107.92(10) [b]
Av. O–P–C	112.4	113.3	109.7
C–P–C	106.4(2)	106.0(2)	107.11(11)
C–P–C	106.4(2)	104.8(2) [b]	111.35(10) [b]
C–P–C	106.4(2)	105.4(2) [b]	109.26(10) [b]
Av. C–P–C	106.4	105.4	109.2

[a] Data taken from ref. 15. [b] Denotes C1 for both **VIb** and **IIb**.

group the C–P–C angles increase, especially those of the phenyl ring which contains the C_6F_{13} group, and consequently the O–P–C angles decrease with the most dramatic effect observed in the O–P–C1 angle (107.92°). As a result the mean C–P–C angle (109.2°) is now very similar to the mean O–P–C angle (109.7°). Although it is not certain that the different arrangements of the *ortho*-CF_3 and *ortho*-C_6F_{13} units would exist in solution for the parent phosphines, these arrangements could be responsible for the differences in both δ(P) and $^4J_{PF}$ coupling constants.

In previous structural determinations, we have concluded that the perfluoroalkyl groups control the solid-state packing and the preference for the fluorous ponytails to align results in fluorous domains within the structure.[11,12] A similar conclusion can also be drawn from the crystal packing diagram of $Ph_2P(O)(2\text{-}C_6H_4C_6F_{13})$ **IIb** and consequently, there are three short F ··· F contacts (2.732, 2.936 and 2.993 Å) between adjacent molecules.

In the crystal structure of $PPh_2(2\text{-}C_6H_4CF_3)$ **VI** there are two unique molecules in the asymmetric unit (Fig. 4). Selected bond lengths and bond angles for both of these molecules are shown in Table 3 and the P–C bond lengths are virtually the same in both molecules. However, there is a much greater variation in the C–P–C bond angles in the second molecule even though the mean value is very similar for both. The structural characterisation of PPh_3, like that for $P(O)Ph_3$, has shown that the mean C–P–C angle (102.8°) is substantially smaller than 109.5° because of repulsion from the lone-pair site.[16] A similar effect is also observed for $PPh_2(2\text{-}C_6H_4CF_3)$ but the mean C–P–C angles are slightly smaller (101.5 and 101.3°) due to the steric bulk of the *ortho*-trifluoromethyl group which points in the same direction as the lone-pair site.

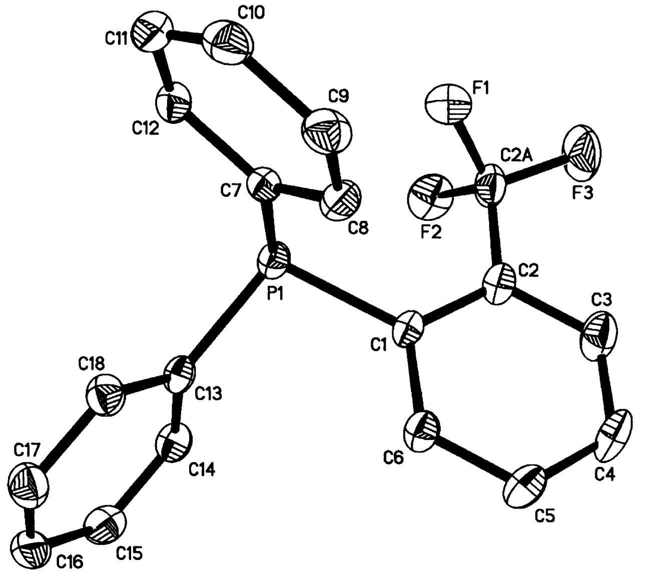


Fig. 4 Molecular structure of one of the unique molecules of $PPh_2(2\text{-}C_6H_4CF_3)$ **VI**. Details as in Fig. 2.

Table 3 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for PPh_3 and $PPh_2(2\text{-}C_6H_4CF_3)$ **VI**

	PPh_3 [a]	**VI**	**VI**
P–C	1.834(2)	1.829(2)	1.829(2)
P–C	1.832(2)	1.829(2)	1.831(2)
P–C	1.828(2)	1.848(2) [b]	1.852(2) [b]
C–P–C	103.3(1)	101.82(9)	103.32(9)
C–P–C	103.3(1)	101.92(10) [b]	100.52(10) [b]
C–P–C	101.7(1)	100.72(10) [b]	99.98(8) [b]
Av. C–P–C	102.8	101.5	101.3

[a] Data taken from ref. 16. [b] Denotes the carbon of the aryl ring which contains the trifluoromethyl moiety.

Coordination chemistry of phosphines II, V and VI

The reactions of the phosphines, $PPh_2(2\text{-}C_6H_4CF_3)$ **VI**, $PPh_2(2\text{-}C_6H_4C_6F_{13})$ **II** and $P(4\text{-}C_6H_4C_6F_{13})_2(2\text{-}C_6H_4C_6F_{13})$ **V**, with *cis*-$[PtCl_2(CH_3CN)_2]$ gave the platinum complexes $[PtCl_2L_2]$ {L = $PPh_2(2\text{-}C_6H_4CF_3)$ **1**, $PPh_2(2\text{-}C_6H_4C_6F_{13})$ **2** and $P(4\text{-}C_6H_4C_6F_{13})_2(2\text{-}C_6H_4C_6F_{13})$ **3**} exclusively as the *trans*-isomers indicating the large steric influence of the trifluoromethyl and perfluorohexyl substituents in the *ortho*-positions. Normally, with conventional arylphosphine ligands, the thermodynamically favoured products are the *cis*-isomers[17] and with the series of *para*-derivatised phosphines, $PPh_2(4\text{-}C_6H_4C_6F_{13})$, $PPh(4\text{-}C_6H_4C_6F_{13})_2$ and $P(4\text{-}C_6H_4C_6F_{13})_3$, only the *cis*-isomers were obtained with the first two ligands, whereas a mixture of the *cis*- and *trans*-isomers was formed with the tris-substituted ligand.[11] In contrast, a mixture of the *cis*- and *trans*-isomers was obtained with the mono- and bis-*meta*-substituted ligands and only the *trans*-isomer was obtained with $P(3\text{-}C_6H_4C_6F_{13})_3$ demonstrating the larger steric influence of the *meta*-substituents over the *para*-C_6F_{13} group.[10] It is, therefore, not surprising that the *ortho*-derivatised phosphines gave the *trans*-isomers, especially since the cone angle of $PPh_2(2\text{-}C_6H_4CF_3)$ has been calculated to be 175°.[18]

The *trans* geometries of the complexes **1**–**3** were established from the $^{31}P\{^1H\}$ NMR data. The $^{31}P\{^1H\}$ NMR spectrum of **1** appears as a virtual septet with satellites, arising from the powerful coupling between the *trans* phosphorus atoms leading to the apparent equivalent coupling to both sets of CF_3's *i.e.* it is the A part of an $AA'M_3M'_3X$ spectrum. Consequently, the $^{19}F\{^1H\}$ NMR spectrum is a virtual triplet. Similarly, for complexes **2** and **3** the $^{31}P\{^1H\}$ NMR spectra give virtual quintets with satellites, for the A part of an $AA'M_2M'_2X$ spectrum but the α-CF_2 resonance in both complexes is only a broad singlet in their $^{19}F\{^1H\}$ NMR spectra. In the latter two complexes no coupling is observed between the phosphorus and the β-CF_2's even though this coupling was observed in the free ligands.

For the series of *trans*-$[PtCl_2L_2]$ complexes shown in Table 4 it can be seen that $^1J_{PtP}$ increases as the number of perfluoroalkyl groups increases and this trend has been observed before with the series of *meta*-derivatised phosphines[10] where the electron-withdrawing fluorous ponytails increase the π-acceptor ability of the phosphorus atoms. Similarly, in the series of *trans*-$[PtClMeL_2]$ complexes where the ligands are all *para*-substituted triarylphosphines, $P(4\text{-}C_6H_4X)_3$, the $^1J_{PtP}$ coupling constants increased in the order $X = NMe_2 < OMe < Me < H < Cl < CF_3$.[20] The trifluoromethyl and perfluorohexyl substituents

Table 4 $^{31}P\{^1H\}$ NMR data for *trans*-$[PtCl_2L_2]$ and *trans*-$[RhCl(CO)L_2]$ and $\nu(CO)$ for *trans*-$[RhCl(CO)L_2]$

	trans-$[PtCl_2L_2]$		*trans*-$[RhCl(CO)L_2]$		
Ligand	$\Delta(^{31}P)^a$	$^1J_{PtP}$/Hz	$\Delta(^{31}P)^a$	$^1J_{RhP}$/Hz	$\nu(CO)/cm^{-1}$
PPh_3	25.4^b	2635^b	31.9	127	1964
$PPh_2(4\text{-}C_6H_4C_6F_{13})$	—	—	35.0	127	1982
$PPh_2(3\text{-}C_6H_4C_6F_{13})$	26.0	2646	34.5	128	1980
$P(4\text{-}C_6H_4C_6F_{13})_3$	28.8	2719	36.0	131	1993
$P(3\text{-}C_6H_4C_6F_{13})_3$	27.8	2723	37.8	132	1992
$PPh_2(2\text{-}C_6H_4CF_3)$	32.6^c	2805	47.5^d	134	1957
$PPh_2(2\text{-}C_6H_4C_6F_{13})$	30.6^e	2826	46.4^f	136	1965
$P(4\text{-}C_6H_4C_6F_{13})_2(2\text{-}C_6H_4C_6F_{13})$	29.9^g	2873	46.4^h	139	1960/1984

[a] $\Delta(^{31}P) = \delta_{metal\ complex} - \delta_{free\ ligand}$. [b] Data taken from ref. 19. [c] $\frac{1}{2}|^4J_{PF} + {}^6J_{PF}|$ 9. [d] $\frac{1}{2}|^4J_{PF} + {}^6J_{PF}|$ 11. [e] $\frac{1}{2}|^4J_{PF} + {}^6J_{PF}|$ 18. [f] $\frac{1}{2}|^4J_{PF} + {}^6J_{PF}|$ 21. [g] $\frac{1}{2}|^4J_{PF} + {}^6J_{PF}|$ 20. [h] $\frac{1}{2}|^4J_{PF} + {}^6J_{PF}|$ 22.

in the *ortho*-positions have a very similar effect on the $^1J_{PtP}$ coupling constants but the $^1J_{PtP}$ for the C_6F_{13} moiety is slightly bigger because it is slightly more electron-withdrawing. However, there is a dramatic increase in $^1J_{PtP}$ when the perfluorohexyl group is moved from the *meta*- to the *ortho*-position in the ligand. In fact, $^1J_{PtP}$ is much bigger for $PPh_2(2\text{-}C_6H_4C_6F_{13})$ (2826 Hz) than for $P(3\text{-}C_6H_4C_6F_{13})_3$ (2723 Hz). Although the inductive electron-withdrawing effect is expected to be greater at the *ortho* position than at the *meta* position, it is difficult to believe that this is the only reason that the $^1J_{PtP}$ increased so dramatically and it is postulated that the bigger cone angle of the *ortho*-substituted ligands will decrease the s character of the P–Pt bond and hence affect the $^1J_{PtP}$ coupling constant.

The series of *trans*-$[RhCl(CO)L_2]$ {L = $PPh_2(2\text{-}C_6H_4CF_3)$ **4**, $PPh_2(2\text{-}C_6H_4C_6F_{13})$ **5** and $P(4\text{-}C_6H_4C_6F_{13})_2(2\text{-}C_6H_4C_6F_{13})$ **6**} complexes were prepared by the reaction of $[RhCl(CO)_2]_2$ with the free ligands. Virtual coupling in the $^{31}P\{^1H\}$ NMR spectra was again observed because of the *trans* geometries giving rise to doublets of virtual septets for **4** and doublets of virtual quintets for both **5** and **6**. The resonances in the $^{19}F\{^1H\}$ NMR spectra mirrored this effect with that for **4** appearing as a virtual triplet but only a broad singlet was observed for the α-CF_2 resonance in both **5** and **6**. In the spectra of both **3** and **6** it is possible to distinguish between the *ortho*- and *para*-CF_3 resonances as well as the *ortho* α-CF_2 resonance at −99 ppm and the *para* α-CF_2 at −112 ppm. The four proton signals for the *ortho*-substituted aromatic ring can also be distinguished from the signals for the *para*-substituted ring. As seen for the series of *trans*-$[PtCl_2L_2]$ complexes, there is an increase in both $\Delta(^{31}P)$ and $^1J_{RhP}$ within the *trans*-$[RhCl(CO)L_2]$ complexes shown in Table 4 giving an indication of both the electronic and steric properties of the phosphines. Since the $^1J_{RhP}$ coupling constant for $PPh_2(2\text{-}C_6H_4C_6F_{13})$ (136 Hz) is much bigger than that for either $PPh_2(3\text{-}C_6H_4C_6F_{13})$ (128 Hz) or $P(3\text{-}C_6H_4C_6F_{13})_3$ (132 Hz) there is obviously a large steric effect as well as an electronic effect.

Previously, we have shown that as the number of perfluoroalkyl groups is increased in both the *meta*- and *para*-substituted series of phosphines then $\nu(CO)$ is increased (Table 4) and this demonstrates that there is an increase in the π-acceptor ability of the phosphines.[10,11] However, it is known that although $\nu(CO)$ increases with decreasing basicity of the phosphine, it also decreases with increasing cone angle.[21] Hence, for *trans*-$[RhCl(CO)\{PPh_2(2\text{-}C_6H_4C_6F_{13})\}_2]$ **5** the increase in cone angle is cancelled out by the decrease in basicity making the value of $\nu(CO)$ very similar to that for *trans*-$[RhCl(CO)(PPh_3)_2]$. In compound **4**, however, the effect of the cone angle predominates slightly because $PPh_2(2\text{-}C_6H_4CF_3)$ is slightly more basic than $PPh_2(2\text{-}C_6H_4C_6F_{13})$. However, the situation is not straightforward for compound **6** which, surprisingly, exhibits two carbonyl stretches in its IR spectrum at 1960 and 1984 cm^{-1}. Since compound **6** is analytically pure and has been fully characterised as a single species in solution by NMR spectroscopies, our only explanation for this curious observation is the presence of two geometric isomers in the solid-state giving rise to the two different carbonyl stretches. The only way that this could be possible is if in one of the two structures the two *ortho*-perfluorohexyl groups are arranged on opposite sides of the Cl–Rh–CO axis in a similar way to that of the trifluoromethyl groups in the molecular structure of **4** (Fig. 8, *vide infra*), whilst in the other the *ortho*-perfluorohexyl groups are lined up on the same side of the Cl–Rh–CO axis in a similar fashion to that observed in the molecular structure of the platinum complex **2** (Fig. 6, *vide infra*).

Structural studies of 1, 2 and 4

The platinum complexes, *trans*-$[PtCl_2\{PPh_2(2\text{-}C_6H_4CF_3)\}_2]$ **1** and *trans*-$[PtCl_2\{PPh_2(2\text{-}C_6H_4C_6F_{13})\}_2]$ **2**, have both been structurally characterised. The molecular structure of **1** is shown in Fig. 5. The platinum atom lies on a crystallographic centre of symmetry and the trifluoromethyl groups are held on opposite sides of the P–Pt–P axis in a *trans*-configuration. Consequently, the geometry around the metal centre is very similar to both *trans*-$[PtCl_2(PPh_3)_2]$[22] and *trans*-$[PtCl_2\{P(4\text{-}C_6H_4C_6F_{13})_3\}_2]$[11] (Table 5). Although there are actually two unique molecules in the asymmetric unit of **2**, rather surprisingly, both perfluorohexyl groups in these unique molecules are held on the same side of the P–Pt–P axis occupying a *cis*-configuration (Fig. 6). Presumably, this is to maximise the number of attractive F ··· F interactions and hence set up large fluorous domains which appear to control the packing in these fluorous-derivatised compounds (Fig. 7). Consequently there are eight unique intermolecular F ··· F interactions that are less than

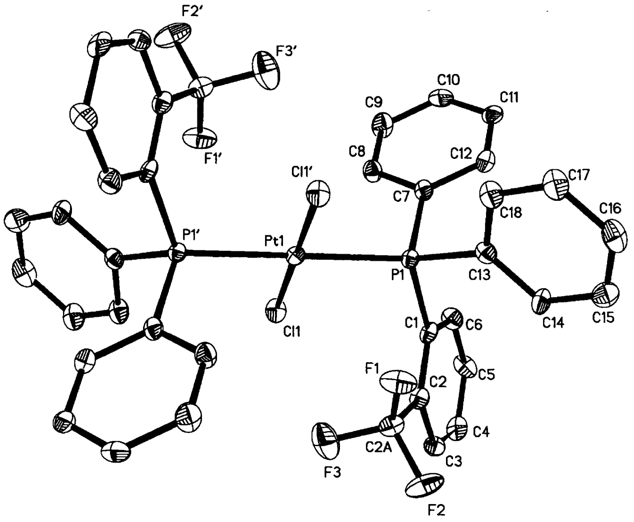


Fig. 5 Molecular structure of *trans*-$[PtCl_2\{PPh_2(2\text{-}C_6H_4CF_3)\}_2]$ **1**. Primed atoms are generated by symmetry (1 − *x*, −*y*, 1 − *z*). Details as in Fig. 2.

Table 5 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for *trans*-[$PtCl_2L_2$] where L = PPh_3, $P(4\text{-}C_6H_4C_6F_{13})_3$, $PPh_2(2\text{-}C_6H_4CF_3)$ **1** and $PPh_2(2\text{-}C_6H_4C_6F_{13})$ **2**

	PPh_3[a]	$P(4\text{-}C_6H_4C_6F_{13})_3$[b]	**1**	**2**		**2**	
Pt–Cl	2.2997(11)	2.331(2)	2.307(2)	2.3106(15)	2.3017(16)	2.3208(15)	2.2969(15)
Pt–P	2.3163(11)	2.330(3)	2.312(2)	2.3175(16)	2.3231(16)	2.3201(17)	2.3053(17)
P–C	1.819(3)	—	1.835(4)	1.826(3)	1.837(3)	1.836(3)	1.829(3)
P–C	1.819(3)	—	1.846(4)	1.835(3)	1.840(3)	1.842(4)	1.832(3)
P–C	1.820(3)	—	1.874(4)[c]	1.900(3)[c]	1.893(3)[c]	1.877(3)[c]	1.886(3)[c]
Cl–Pt–Cl	180.0	180.0	180.0	170.24(6)		174.53(6)	
Cl–Pt–P	92.12(4)	93.34	92.93(8)	91.04(6)	91.78(6)	90.36(6)	92.05(6)
Cl–Pt–P	87.88(4)	86.66(9)	87.07(8)	87.93(5)	89.55(5)	88.69(6)	88.60(6)
P–Pt–P	180.0	180.0	180.0	176.80(6)		175.93(6)	
C–P–Pt	111.97(10)	108.9(3)	108.52(19)	118.38(15)	121.08(14)	121.08(15)	119.66(15)
C–P–Pt	111.83(11)	116.2(3)	122.6(2)	106.88(15)	108.82(15)	109.70(16)	102.64(15)
C–P–Pt	117.60(11)	115.3(3)	112.6(2)[c]	118.60(14)[c]	114.78(14)[c]	111.60(14)[c]	118.49(14)[c]
C–P–C	106.49(14)	105.8(5)	102.5(3)	106.63(19)	106.4(2)	100.6(2)	108.6(2)
C–P–C	103.77(15)	101.5(5)	104.8(3)[c]	101.54(19)[c]	100.72(19)[c]	105.78(19)[c]	102.3(2)[c]
C–P–C	104.23(15)	108.7(5)	104.0(3)[c]	103.36(19)[c]	103.29(19)[c]	106.80(19)[c]	103.88(19)[c]

[a] Data taken from ref. 22. [b] Data taken from ref. 11. [c] Denotes the carbon of the aryl ring which contains the trifluoromethyl or the perfluorohexyl moiety.

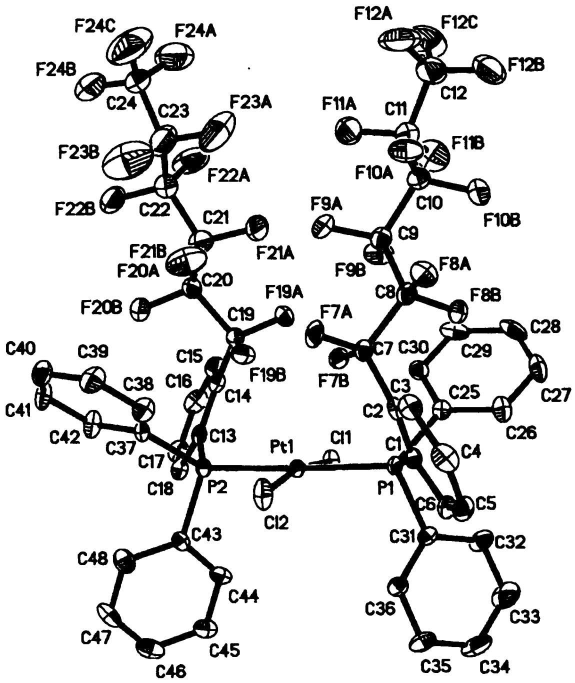
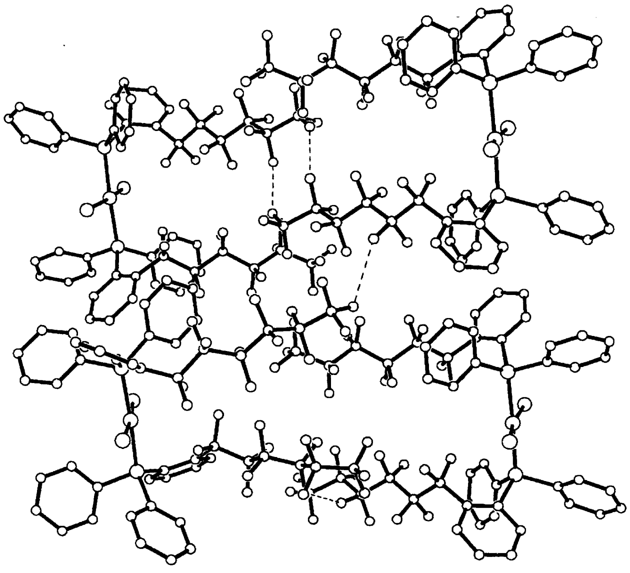


Fig. 6 Molecular structure of one of the unique molecules of *trans*-[$PtCl_2\{PPh_2(2\text{-}C_6H_4C_6F_{13})\}_2$] **2**. Details as in Fig. 2.

3 Å in the extended structure of **2**. The Cl–Pt–Cl bond angle is now significantly distorted to 170.24° in one of the molecules because the chloride ligands bend away from the steric bulk associated with the two perfluorohexyl groups held on the same side of the molecule. In the other unique molecule the distortion is not as dramatic but is still significant with a Cl–Pt–Cl bond angle of 174.53° and a P–Pt–P bond angle of 175.93°.

The structure of *trans*-[$RhCl(CO)\{PPh_2(2\text{-}C_6H_4CF_3)\}_2$] **4** was also determined by single crystal X-ray diffraction (Fig. 8). The rhodium atom lies on a crystallographic centre of symmetry such that the carbonyl and chloride ligands are disordered which is not uncommon in these types of metal complexes. Similar to the structure of *trans*-[$PtCl_2\{PPh_2(2\text{-}C_6H_4CF_3)\}_2$] **1**, the *ortho*-trifluoromethyl groups in **4** are held on opposite sides of the P–Rh–P axis and consequently they do not interfere with the coordination geometry around the metal centre with all of the bond lengths and bond angles being very similar to those found in the structure of *trans*-[$RhCl(CO)(PPh_3)_2$] (Table 6).[23]

The cone angles of the two phosphines, $PPh_2(2\text{-}C_6H_4CF_3)$ and $PPh_2(2\text{-}C_6H_4C_6F_{13})$, were calculated from the crystal structures, *trans*-[$PtCl_2\{PPh_2(2\text{-}C_6H_4CF_3)\}_2$] **1**, *trans*-[$PtCl_2\{PPh_2(2\text{-}C_6H_4C_6F_{13})\}_2$] **2** and *trans*-[$RhCl(CO)\{PPh_2(2\text{-}C_6H_4CF_3)\}_2$] **4**.[24] The same value was obtained for $PPh_2(2\text{-}C_6H_4CF_3)$ from the structures **1** and **4** giving cone angles of 169°, but this value is much smaller than the previously reported value of 175°.[18] Four different cone angles were measured for $PPh_2(2\text{-}C_6H_4C_6F_{13})$ from **2** because there are two unique molecules which contain two different phosphines in each case. These values were calculated to be 164, 166, 166 and 168°, giving an average value of 166°.



F12B..F24B	2.952	F22A..F58A	2.874
F9A..F24C	2.975	F20A..F72A	2.969
F24A..F56B	2.938	F20A..F72C	2.870
F24C..F23A	2.872	F59A..F9A	2.913

Fig. 7 Extended structure of *trans*-[$PtCl_2\{PPh_2(2\text{-}C_6H_4C_6F_{13})\}_2$] **2**. Short intermolecular F ··· F interactions are shown with dashed lines.

Conclusions

The two novel phosphines, $PPh_2(2\text{-}C_6H_4C_6F_{13})$ **II** and $P(4\text{-}C_6H_4C_6F_{13})_2(2\text{-}C_6H_4C_6F_{13})$ **V**, were synthesised using established methodologies. The *ortho*-fluorous ponytails significantly increase the steric bulk of these triaryl ligands compared to the

Table 6 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for *trans*-[RhCl(CO)L_2] where L = PPh_3 and $PPh_2(2\text{-}C_6H_4CF_3)$ **4**

	PPh_3[a]		**4**
Rh–Cl	2.395(1)		2.401(2)
Rh–P	2.333(1)	2.327(1)	2.3279(6)
Rh–C	1.821(5)		1.736(6)
C–O	1.141(6)		1.153(7)
P–C	1.828(3)	1.820(3)	1.827(2)
P–C	1.839(3)	1.839(3)	1.8282(19)
P–C	1.848(4)	1.842(3)	1.8496(19)[b]
Cl–Rh–P	87.5(1)		86.91(7)
Cl–Rh–P	89.1(1)		93.09(7)
P–Rh–P	176.1(1)		180.0
P–Rh–C	92.1(2)		92.6(2)
P–Rh–C	91.4(2)		87.4(2)
Rh–P–C	116.4(1)	117.0(1)	109.13(7)
Rh–P–C	114.2(1)	109.8(1)	123.23(6)
Rh–P–C	112.7(1)	117.1(1)	113.10(6)[b]
C–P–C	—	—	102.01(9)
C–P–C	—	—	103.99(9)[b]
C–P–C	—	—	103.35(9)[b]

[a] Data taken from ref. 23. [b] Denotes the carbon of the aryl ring which contains the trifluoromethyl moiety.

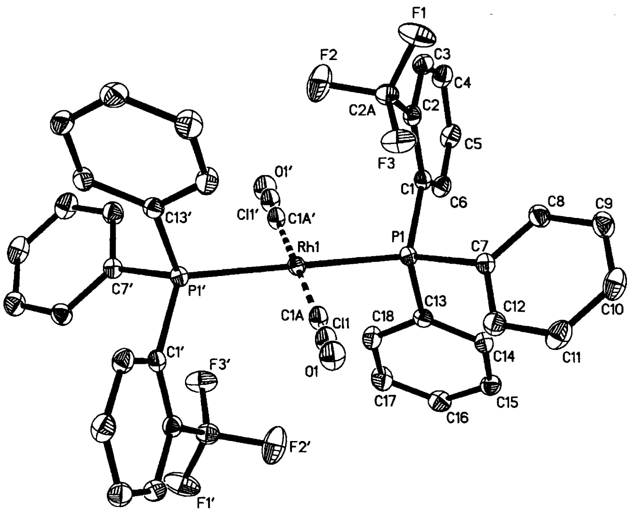


Fig. 8 Molecular structure of *trans*-[RhCl(CO){$PPh_2(2\text{-}C_6H_4CF_3)$}$_2$] **4**. Primed atoms are generated by symmetry ($1 - x$, $1 - y$, $- z$). Dashed bonds indicate disorder of Cl and CO groups. Details as in Fig. 2.

meta- and *para*-isomers and this large steric influence was illustrated by the exclusive formation of the *trans*-[$PtCl_2L_2$] complexes and in the carbonyl stretching frequencies of the *trans*-[RhCl(CO)L_2] complexes. Surprisingly, a slightly larger cone angle was measured for $PPh_2(2\text{-}C_6H_4CF_3)$ (169°) from the crystal structures, *trans*-[$PtCl_2${$PPh_2(2\text{-}C_6H_4CF_3)$}$_2$] **1** and *trans*-[RhCl(CO){$PPh_2(2\text{-}C_6H_4CF_3)$}$_2$] **4**, than for $PPh_2(2\text{-}C_6H_4\text{-}C_6F_{13})$ (166°) from the crystal structure of *trans*-[$PtCl_2${$PPh_2\text{-}(2\text{-}C_6H_4C_6F_{13})$}$_2$] **2**.

Experimental

Proton, ^{19}F and ^{31}P NMR spectroscopies were carried out on a Bruker ARX 250 spectrometer at 250.13, 235.34 and 101.26 MHz or on a Bruker DRX 400 spectrometer at 400.13, 376.50 and 161.98 MHz. All chemical shifts are quoted in ppm using the high-frequency positive convention; ^1H NMR spectra were referenced to external $SiMe_4$, ^{19}F NMR spectra to external $CFCl_3$ and ^{31}P NMR spectra to external 85% H_3PO_4. The IR spectra were recorded on a Digilab FTS40 Fourier-transform spectrometer at 4 cm^{-1} resolution for the complexes as Nujol mulls held between KBr discs. Elemental analyses were performed by either Butterworth Laboratories Ltd. or the Elemental Analysis Service at the University of North London. Mass spectra were recorded on a Kratos Concept 1H mass spectrometer.

The compound 4-(tridecafluorohexyl)bromobenzene,[9] the ligand $PPh_2(2\text{-}C_6H_4CF_3)$[25] and the complex *cis*-[$PtCl_2$(Me-CN)$_2$][26] were prepared as described previously and the complex [RhCl(CO)$_2$]$_2$ (Aldrich) was used as supplied. Dichloromethane and perfluoro-1,3-dimethylcyclohexane (PP3) were each dried by refluxing over calcium hydride under nitrogen, distilled under nitrogen and stored in closed ampoules over molecular sieves. PP3 was also freezed/pumped/thawed three times to remove all dissolved gases. Hexane was dried by refluxing over potassium metal under nitrogen, distilled and was stored similarly. Diethyl ether was dried by refluxing over sodium metal under nitrogen, distilled and stored similarly.

Preparations

2-(Tridecafluorohexyl)bromobenzene I. A solution of $C_6F_{13}I$ (39.42 g, 0.088 mol) in fluorobenzene (40 cm^3) was added dropwise over 36 h to a stirred mixture of 2-bromoiodobenzene (25.00 g, 0.088 mol), copper powder (12.36 g, 0.194 mol), 2,2′-bipyridine (0.99 g, 6.3 mmol), DMSO (100 cm^3), and fluorobenzene (75 cm^3) at 70 °C. The reaction mixture was subsequently stirred for a further 72 h at this temperature. After cooling to room temperature, it was poured into a beaker containing ether (200 cm^3) and water (200 cm^3). After filtering, the organic layer was separated, washed with water (3 × 100 cm^3) and dried over $MgSO_4$. Distillation *in vacuo* gave the product **I** as a colourless, slightly viscous liquid (19.23 g, 46%) (bp 42–45 °C, 0.01 mmHg). δ_H ($CDCl_3$) 7.34 (2H, um, 4H- and 5H-ArRf), 7.54 (1H, dd, $^3J_{HH}$ 8, $^4J_{HH}$ 2, 3H-ArRf), 7.67 (1H, dd, $^3J_{HH}$ 8, $^4J_{HH}$ 1, 6H-ArRf); δ_F −81.25 (3F, t, $^4J_{FF}$ 10, CF_3), −107.02 (2F, t, $^4J_{FF}$ 15, α-CF_2), −120.07 (2F, m, CF_2), −122.08 (2F, m, CF_2), −123.14 (2F, m, CF_2), −126.52 (2F, m, CF_2); accurate *m*/*z*: Found 473.9285; Calcd. 473.9288; *m*/*z* (EI) 474/476 (M^+, 48%), 205/207 (100), 126 (33), 69 (11).

$PPh_2(2\text{-}C_6H_4C_6F_{13})$ II. *n*-Butyllithium (8.0 cm^3, 1.6 M in hexane, 0.013 mol) in diethyl ether (25 cm^3) was added dropwise over 1 h to 2-(tridecafluorohexyl)bromobenzene (6.17 g, 0.013 mol) stirring under nitrogen in diethyl ether (75 cm^3) at −60 °C and the reaction mixture was stirred at this temperature for 1 h. A solution of chlorodiphenylphosphine (2.35 cm^3, 0.013 mol) in diethyl ether (25 cm^3) was then added dropwise over 1 h to the reaction mixture stirring at −60 °C before being allowed to warm slowly to room temperature over 12 h. The yellow solution was then hydrolysed with a 10% ammonium chloride solution (100 cm^3), the organic layer was collected, washed with water (2 × 100 cm^3) and finally dried over $MgSO_4$. The solvent was removed *in vacuo* and the dense, viscous liquid obtained was then dissolved in the minimum volume of light petroleum (bp 40–60 °C), before being passed through an alumina column using light petroleum (bp 40–60 °C) as the eluent. After the solvent was removed, the colourless viscous liquid was distilled in a Kugelröhr oven (120–124 °C, 0.04 mmHg) to give the product as a white solid (3.19 g, 42%). (Found: C, 49.4; H, 2.4; P, 5.4. $C_{24}H_{14}F_{13}P$ requires C, 49.7; H, 2.4; P, 5.3%); δ_P ($CDCl_3$) −6.7 (ttt, $^4J_{PF}$ 99, $^5J_{PF}$ 49, $^6J_{PF}$ 4); δ_H 7.13 (5H, um, ArH's), 7.25 (5H, um, ArH's), 7.37 (3H, um, ArH's), 7.58 (1H, um, 6H-ArRf); $^1H\{^{31}P\}$ 7.13 (5H, um, ArH's), 7.25 (5H, um, ArH's), 7.37 (3H, um, ArH's), 7.59 (1H, br d, $^3J_{HH}$ 7, 6H-ArRf); δ_F −81.22 (3F, t, $^4J_{FF}$ 10, CF_3), −99.95 (2F, dt, $^4J_{PF}$ 99, $^4J_{FF}$ 15, α-CF_2), −119.53 (2F, dm, $^5J_{PF}$ 47, β-CF_2), −121.82 (2F, m, CF_2), −123.05 (2F, m, CF_2), −126.44 (2F, m, CF_2); *m*/*z* (EI) 581 (M^+, 55%).

$Ph_2P(O)(2\text{-}C_6H_4C_6F_{13})$ IIb. Crystals of $Ph_2P(O)(2\text{-}C_6H_4\text{-}C_6F_{13})$ **IIb** suitable for X-ray diffraction were grown from an ether–hexane solution of $PPh_2(2\text{-}C_6H_4C_6F_{13})$ left to stand for several weeks.

$Et_2NP(4\text{-}C_6H_4C_6F_{13})_2$ III. *n*-Butyllithium (18.9 cm^3, 1.6 M solution in hexane, 0.030 mol) in diethyl ether (50 cm^3) was added dropwise over 1 h to a stirred solution of 4-(tridecafluorohexyl)bromobenzene (14.40 g, 0.030 mol) in ether (50 cm^3) at −78 °C and the reaction mixture was stirred at this temperature for a further 1 h. Diethylphosphoramidous dichloride, Et_2NPCl_2, (2.64 g, 0.015 mol) in ether (20 cm^3), was then added dropwise to the reaction mixture over 1 h at −78 °C before allowing the reaction mixture to warm slowly to room temperature over a 12 h period. The cream coloured solution was filtered and the solvent removed *in vacuo* to isolate the $Et_2NP(4\text{-}C_6H_4C_6F_{13})_2$ intermediate. (Found: C, 37.1; H, 2.0; N, 1.9; P, 3.9. $C_{28}H_{18}F_{26}NP$ requires C, 37.6; H, 2.0; N, 1.9; P, 3.5%); δ_P ($CDCl_3$) 60.2 (s); δ_H 0.57 (6H, t, $^3J_{HH}$ 7, CH_3), 2.65 (4H, m, CH_2), 7.05 (4H, dd, $^3J_{HH}$ 8, $^3J_{HP}$ 7, 2-ArH), 7.15 (4H, d, $^3J_{HH}$ 8, 3-ArH); $^1H\{^{31}P\}$ 0.57 (6H, t, $^3J_{HH}$ 7, CH_3), 2.65 (4H, q, $^3J_{HH}$ 7, CH_2), 7.05 (4H, d, $^3J_{HH}$ 8, 2-ArH), 7.15 (4H, d, $^3J_{HH}$ 8, 3-ArH); δ_F −81.64 (3F, t, $^4J_{FF}$ 10, CF_3), −111.07 (2F, t, $^4J_{FF}$ 14, α-CF_2), −121.90 (2F, m, CF_2), −122.18 (2F, m, CF_2), −123.33 (2F, m, CF_2), −126.75 (2F, m, CF_2); *m*/*z* (EI) 894 (MH^+, 36%), 837 (45).

$ClP(4\text{-}C_6H_4C_6F_{13})_2$ IV. Hydrogen chloride was passed over a stirred solution of $Et_2NP(4\text{-}C_6H_4C_6F_{13})_2$ **III** in hexane (120 cm^3) and diethyl ether (120 cm^3) for 25 min. The solution turned from golden yellow to white indicating the formation of the amine salt, $Et_2NH_2^+Cl^-$. The reaction mixture was then filtered through celite under an atmosphere of nitrogen and the solvent was removed *in vacuo* to produce a creamy white solid. The chlorophosphine was purified by distillation in a Kugelröhr oven (160–175 °C, 0.04 mmHg) and the product was isolated as a pure white crystalline solid (5.28 g, 41%). (Found: C, 33.8; H, 1.0; P, 3.9. $C_{24}H_8ClF_{26}P$ requires C, 33.6; H, 0.9; P, 3.6%); δ_P ($CDCl_3$) 75.3 (s); δ_H 7.58 (4H, d, $^3J_{HH}$ 8, 3H-ArRf), 7.63 (4H, m, 2H-ArRf); $^1H\{^{31}P\}$ 7.58 (4H, d, $^3J_{HH}$ 8, 3H-ArRf), 7.63 (4H, d, $^3J_{HH}$ 8, 2H-ArRf); δ_F −81.25 (3F, t, $^4J_{FF}$ 10, CF_3), −111.51 (2F, t, $^4J_{FF}$ 14, α-CF_2), −122.05 (2F, m, CF_2), −122.16 (2F, m, CF_2), −123.23 (2F, m, CF_2), −126.55 (2F, m, CF_2); *m*/*z* (EI) 856/858 (M^+, 30%), 695 (22), 445 (100).

$P(4\text{-}C_6H_4C_6F_{13})_2(2\text{-}C_6H_4C_6F_{13})$ V. This was synthesised using the method that was used to prepare $PPh_2(2\text{-}C_6H_4C_6F_{13})$ **II** using *n*-butyllithium (3.6 cm^3, 1.6 M in hexane, 5.7 mmol), 2-(tridecafluorohexyl)bromobenzene (2.71 g, 5.7 mmol) and a suspension of $ClP(4\text{-}C_6H_4C_6F_{13})_2$ (4.9 g, 5.7 mmol) in diethyl ether (100 cm^3). The product was obtained as a white solid (2.39 g, 34%) (198–200 °C, 0.04 mmHg). (Found: C, 35.9; H, 1.0; P, 2.6. $C_{36}H_{12}F_{39}P$ requires C, 35.55; H, 1.0; P, 2.55%); δ_P ($CDCl_3$) −6.3 (tt, $^4J_{PF}$ 98, $^5J_{PF}$ 49); δ_H 7.15 (1H, dd, $^3J_{HH}$ 7, $^4J_{HH}$ 3, 3-ArH in *o*-ArRf), 7.35 (4H, dd, $^3J_{HH}$ 8, $^3J_{HP}$ 7, 2-ArH in *p*-ArRf), 7.50 (1H, m, ArH in *o*-ArRf), 7.57 (4H, d, $^3J_{HH}$ 8, 3-ArH in *p*-ArRf), 7.57 (1H, m, ArH in *o*-ArRf), 7.74 (1H, m, ArH in *o*-ArRf); δ_F −81.25 (9F, t, $^4J_{FF}$ 10, *o*- and *p*-CF_3), −100.14 (2F, dt, $^4J_{PF}$ 100, $^4J_{FF}$ 13, *o*-α-CF_2), −111.46 (4F, t, $^4J_{FF}$ 15, *p*-α-CF_2), −119.54 (2F, d of m, $^5J_{PF}$ 47, *o*-β-CF_2), −121.95 (6F, m, *o*- and *p*-CF_2's), −122.25 (4F, m, *p*-CF_2's), −123.25 (6F, m, *o*- and *p*-CF_2's), −126.60 (6F, m, *o*- and *p*-CF_2's); *m*/*z* (EI) 1216 (M^+, 100%), 1197 (18), 998 (34), 339 (10).

$PPh_2(2\text{-}C_6H_4CF_3)$ VI and $Ph_2P(O)(2\text{-}C_6H_4CF_3)$ VIb. Crystals of $PPh_2(2\text{-}C_6H_4CF_3)$ **VI** and $Ph_2P(O)(2\text{-}C_6H_4CF_3)$ **VIb** suitable for X-ray diffraction were grown from an ether–hexane solution of $PPh_2(2\text{-}C_6H_4CF_3)$ **VI** left to stand for several weeks.

***trans*-$[PtCl_2\{PPh_2(2\text{-}C_6H_4CF_3)\}_2]$ 1.** The ligand (0.300 g, 0.91 mmol) and $[PtCl_2(MeCN)_2]$ (0.150 g, 0.43 mmol) were refluxed for 4 h in dichloromethane (40 cm^3). After cooling to room temperature the volume of dichloromethane was reduced to approximately 15 cm^3 and hexane was added to precipitate out the product. The pale yellow solid was filtered off and washed with hexane. Yield 0.27 g, 68%. Crystals suitable for X-ray diffraction were grown from dichloromethane. (Found: C, 47.6; H, 2.7; P, 6.3. $C_{38}H_{28}Cl_2F_6P_2Pt\cdot\frac{1}{2}CH_2Cl_2$ requires C, 47.7; H, 3.0; P, 6.4%); δ_P(CD_2Cl_2) 21.9 (A part of an $AA'M_3M'_3X$ spectrum, $^1J_{PtP}$ 2805, ½ $|^4J_{PF} + {}^6J_{PF}|$ 9); δ_H 7.00 (1H, AB pattern, 6H-$ArCF_3$), 7.40 (8H, um, ArH's), 7.66 (1H, dd, $^3J_{HH}$ 8, $^4J_{HP}$ 1, 3H-$ArCF_3$), 7.82 (4H, AB pattern, 2,6-ArH's); $^1H\{^{31}P\}$ 7.00 (1H, d, $^3J_{HH}$ 8, 6H-$ArCF_3$), 7.40 (8H, um, ArH's), 7.66 (1H, d, $^3J_{HH}$ 8, 3H-$ArCF_3$), 7.82 (4H, d, $^3J_{HH}$ 7, 2,6-ArH's); δ_F −53.59 (vt, ½ $|^4J_{PF} + {}^6J_{PF}|$ 9); *m*/*z* (FAB) 925 (M^+), 890 (M − Cl), 853 (M − 2Cl).

***trans*-$[PtCl_2\{PPh_2(2\text{-}C_6H_4C_6F_{13})\}_2]$ 2.** Complex **2** was prepared similarly to **1** from the ligand (0.300 g, 0.52 mmol) and $[PtCl_2(MeCN)_2]$ (0.086 g, 0.25 mmol). Yield 0.26 g, 73%. Crystals suitable for X-ray diffraction were grown from acetone. (Found: C, 40.3; H, 1.95; P, 4.3. $C_{48}H_{28}Cl_2F_{26}P_2Pt$ requires C, 40.4; H, 2.0; P, 4.3%); δ_P (CD_2Cl_2) 23.9 (A part of an $AA'M_2M'_2X$ spectrum, $^1J_{PtP}$ 2826, ½ $|^4J_{PF} + {}^6J_{PF}|$ 18); δ_H 7.15 (1H, AB pattern, 6H-$ArCF_3$), 7.40 (8H, um, ArH's), 7.60 (1H, br dd, $^3J_{HH}$ 8, $^4J_{HP}$ 1, 3H-ArRf), 7.86 (4H, AB pattern, 2,6-ArH's); $^1H\{^{31}P\}$ 7.16 (1H, d, $^3J_{HH}$ 8, 6H-ArRf), 7.39 (8H, um, ArH's), 7.60 (1H, d, $^3J_{HH}$ 8, 3H-ArRf), 7.86 (4H, d, $^3J_{HH}$ 7, 2,6-ArH's); δ_F −81.23 (3F, t, $^4J_{FF}$ 10, CF_3), −99.40 (2F, br s, α-CF_2), −119.07 (2F, m, CF_2), −121.73 (2F, m, CF_2), −123.08 (2F, m, CF_2), −126.47 (2F, m, CF_2); *m*/*z* (FAB) 1426 (MH^+), 1390 (M − Cl), 1353 (M − 2Cl).

***trans*-$[PtCl_2\{P(4\text{-}C_6H_4C_6F_{13})_2(2\text{-}C_6H_4C_6F_{13})\}_2]$ 3.** Complex **3** was prepared similarly to **1** from the ligand (0.300 g, 0.25 mmol) and $[PtCl_2(MeCN)_2]$ (0.043 g, 0.12 mmol). Yield 0.26 g, 77%. (Found: C, 31.3; H, 0.9. $C_{72}H_{24}F_{78}P_2Cl_2Pt$ requires C, 32.0; H, 0.9%); δ_P (THF, d^6-benzene insert) 23.6 (A part of an $AA'M_2M'_2X$ spectrum, $^1J_{PtP}$ 2873, ½ $|^4J_{PF} + {}^6J_{PF}|$ 20); δ_H (d^6-acetone) 7.48 (1H, m, 6-ArH in *o*-ArRf), 7.71(1H, t, $^3J_{HH}$ 8, ArH in *o*-ArRf), 7.81 (1H, t, $^3J_{HH}$ 8, ArH in *o*-ArRf), 7.85 (1H, m, 3-ArH in *o*-ArRf), 7.88 (4H, d, $^3J_{HH}$ 8, 3-ArH in *p*-ArRf), 8.28 (4H, m, 2-ArH in *p*-ArRf); δ_F (d^6-acetone) −82.20 (6F, t, $^4J_{FF}$ 10, *p*-CF_3), −82.49 (3F, t, $^4J_{FF}$ 10, *o*-CF_3), −100.07 (2F, br m, *o*-α-CF_2), −112.03 (4F, um, *p*-α-CF_2), −120.24 (2F, m, *o*-CF_2), −122.51 (10F m, *o*- and *p*-CF_2's), −123.8 (4F, m, *p*-CF_2), −124.04 (2F, m, *o*-CF_2), −127.26 (4F, m, *p*-CF_2), −127.46 (2F, m, *o*-CF_2); *m*/*z* (FAB) 2627 (M − 2Cl).

***trans*-$[RhCl(CO)\{PPh_2(2\text{-}C_6H_4CF_3)\}_2]$ 4.** The ligand (0.349 g, 1.06 mmol) and $[RhCl(CO)_2]_2$ (0.100 g, 0.257 mmol) were stirred under an atmosphere of nitrogen for 1.5 h in dichloromethane (50 cm^3). The solvent was removed *in vacuo* and the resulting product was washed with light petroleum (bp 40–60 °C) to give a yellow powder (0.195 g, 46%). Crystals suitable for X-ray diffraction were grown from a dichloromethane–hexane solution. (Found: C, 56.6; H, 3.3; P, 6.9. $C_{39}H_{28}ClF_6OP_2Rh$ requires C, 56.6; H, 3.4; P, 7.5%); ν_{max}/cm^{-1} (CO) 1957 (Nujol); δ_P ($CDCl_3$) 36.8 (A part of $AA'M_3M'_3X$ spectrum, $^1J_{RhP}$ 134, ½ $|^4J_{PF} + {}^6J_{PF}|$ 10); δ_H 7.04 (1H, AB pattern, 6H-$ArCF_3$), 7.36 (8H, um, ArH's), 7.72 (5H, um, ArH's); $^1H\{^{31}P\}$ 7.04 (1H, d, $^3J_{HH}$ 8, 6H-$ArCF_3$), 7.36 (8H, um, ArH's), 7.72 (5H, um, ArH's); δ_F −53.3 (vt, ½ $|^4J_{PF} + {}^6J_{PF}|$ 11); *m*/*z* (FAB) 825/827 (M^+), 797/799 (M − CO), 790 (M − Cl), 762 (M − COCl).

***trans*-$[RhCl(CO)\{PPh_2(2\text{-}C_6H_4C_6F_{13})\}_2]$ 5.** Complex **5** was prepared similarly to complex **4** using the ligand (0.176 g, 0.3 mmol) and $[RhCl(CO)_2]_2$ (0.025 g, 0.065 mmol). Yield 0.118 g, 68%. (Found: C, 44.2; H, 2.05; P, 4.8. $C_{49}H_{28}ClF_{26}OP_2Rh$ requires C, 44.3; H, 2.1; P, 4.7%); ν_{max}/cm^{-1} (CO) 1965 (Nujol); δ_P ($CDCl_3$) 39.7 (A part of $AA'M_2M'_2X$ spectrum, $^1J_{RhP}$ 136, ½ $|^4J_{PF} + {}^6J_{PF}|$ 21); δ_H 7.27–7.45 (8H, um, ArH's),

Table 7 Crystallographic data for $Ph_2P(O)(2\text{-}C_6H_4C_6F_{13})$ **IIb**, $PPh_2(2\text{-}C_6H_4CF_3)$ **VI**, $Ph_2P(O)(2\text{-}C_6H_4CF_3)$ **VIb**, *trans*-$[PtCl_2\{PPh_2(2\text{-}C_6H_4CF_3)\}_2]$ **1**, *trans*-$[PtCl_2\{PPh_2(2\text{-}C_6H_4C_6F_{13})\}_2]$ **2** and *trans*-$[RhCl(CO)\{PPh_2(2\text{-}C_6H_4CF_3)\}_2]$ **4**

	IIb	**VI**	**VIb**	**1**	**2**	**4**
Formula	$C_{24}H_{14}F_{13}OP$	$C_{19}H_{14}F_3P$	$C_{19}H_{14}F_3OP$	$C_{38}H_{28}Cl_2F_6P_2Pt$	$C_{48}H_{28}Cl_2F_{26}P_2Pt$	$C_{39}H_{28}ClF_6OP_2Rh$
M	596.32	330.27	346.27	926.53	1426.63	826.91
System	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$Pbca$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/Å	10.942(1)	17.478(2)	8.488(11)	11.415(5)	12.280(2)	11.469(1)
b/Å	10.023(1)	10.490(1)	10.057(12)	11.238(8)	18.509(2)	11.185(1)
c/Å	42.863(4)	18.570(2)	11.032(14)	13.819(7)	23.735(4)	13.837(1)
α/°	90	90	63.97(3)	90	78.74(1)	90
β/°	90	107.22(1)	76.31(2)	101.91(4)	77.80(1)	101.00(1)
γ/°	90	90	72.82(3)	90	88.85(1)	90
V/Å^3	4701.0(8)	3251.9(6)	802.1(17)	1734.6(17)	5170.1(13)	1742.4(3)
T/K	160	180	180	190	190	180
Z	8	8^a	2	2^b	4^a	2^b
μ(Mo-Kα)/mm^{-1}	0.238	0.195	0.206	4.351	3.008	0.723
refln. measured	35823	17858	4588	3474	20707	9685
refln. independent	4877	6377	3095	2997	20219	3402
Rint	0.023	0.042	0.196	0.048	0.020	0.051
refln. $\{I > 2\sigma(I)\}$	4065	3733	1293	2148	13740	3045
θ_{max}, % complete	27, 99.7	26, 99.8	26, 98.3	25, 97.6	26, 99.5	26, 99.7
$R1$ $\{I > 2\sigma(I)\}$	0.051	0.042	0.083	0.048	0.048	0.030
$wR2$ (F^2) all data	0.157	0.083	0.221	0.128	0.094	0.0736

[a] There are two unique molecules in the asymmetric unit. [b] The metal atom is located on a centre of symmetry with half a molecule in the asymmetric unit.

7.48 (1H, t, $^3J_{HH}$ 8, ArH in ArRf), 7.71 (1H, d, $^3J_{HH}$ 8, 3H-ArRf), 7.83 (4H, AB pattern, 2,6-ArH's); $^1H\{^{31}P\}$ 7.27–7.45 (8H, um, ArH's), 7.48 (1H, t, $^3J_{HH}$ 8, ArH in ArRf), 7.71 (1H, d, $^3J_{HH}$ 8, 3H-ArRf), 7.83 (4H, d, $^3J_{HH}$ 8, 2,6-ArH's); δ_F −81.36 (3F, t, $^4J_{FF}$ 10, CF_3), −99.03 (2F, br s, α-CF_2), −118.68 (2F, m, CF_2), −122.12 (2F, m, CF_2), −123.28 (2F, m, CF_2), −126.72 (2F, m, CF_2); m/z (FAB) 1300 (M − CO), 1292 (M − Cl), 1264 (M − COCl).

***trans*-$[RhCl(CO)\{P(4\text{-}C_6H_4C_6F_{13})_2(2\text{-}C_6H_4C_6F_{13})\}_2]$ 6.** Complex **6** was prepared similarly to complex **4** using the ligand (0.375 g, 0.31 mmol) and $[RhCl(CO)_2]_2$ (0.029 g, 0.073 mmol). Yield 0.31 g, 77%. (Found: C, 33.3; H, 0.7; P, 2.7. $C_{73}H_{24}F_{78}P_2ClORh$ requires C, 33.7; H, 0.9; P, 2.4%); ν_{max}/cm^{-1} (CO) 1960 and 1984 (Nujol); δ_P (PP3, d^6-benzene insert) 40.1 (A part of AA′M$_2$M′$_2$X spectrum, $^1J_{RhP}$ 139, ½ $|^4J_{PF} + {}^6J_{PF}|$ 22); δ_H (d^6-acetone) 7.37 (1H, m, 6-ArH in o-ArRf), 7.56 (1H, t, $^3J_{HH}$ 8, ArH in o-ArRf), 7.65 (1H, m, ArH in o-ArRf), 7.69 (4H, d, $^3J_{HH}$ 8, 3-ArH in p-ArRf), 7.77 (1H, br m, 3-ArH in o-ArRf), 8.05 (4H, m, 2-ArH in p-ArRf); $^1H\{^{31}P\}$ NMR (d^6-acetone) 7.37 (1H, d, $^3J_{HH}$ 8, 6-ArH in o-ArRf), 7.56 (1H, t, $^3J_{HH}$ 8, ArH in o-ArRf), 7.65 (1H, m, ArH in o-ArRf), 7.69 (4H, d, $^3J_{HH}$ 8, 3-ArH in p-ArRf), 7.77 (1H, d, $^3J_{HH}$ 7, 3-ArH in o-ArRf), 8.05 (4H, d, $^3J_{HH}$ 8, 2-ArH in p-ArRf); δ_F (diethyl ether, d^6-benzene insert) −81.74 (6F, t, $^4J_{FF}$ 10, p-CF_3), −81.93 (3F, t, $^4J_{FF}$ 10, o-CF_3), −98.42 (2F, um, o-α-CF_2), −111.60 (4F, t, $^4J_{FF}$ 14, p-α-CF_2), −118.69 (2F, m, o-CF_2), −121.88 (10F, m, CF_2's), −123.03 (6F, m, CF_2), −126.72 (6F m, CF_2); m/z (FAB) 2563 (M − Cl).

Crystal structure determinations

Table 7 summarises the crystallographic data for compounds **IIb**, **VI** and **VIb** and complexes **1**, **2** and **4**. Data for **IIb**, **VI**, **VIb** and **4** were measured on a Bruker SMART diffractometer with a 2K CCD area detector. Data for **1** and **2** were measured on a Bruker P4 diffractometer. All data were collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Semi-empirical absorption corrections, based on comparison of Laue equivalents, were applied to the data sets. The structures were solved by direct methods and refined by full-matrix least squares cycles on F^2 for all data, using SHELXTL.[27] All non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in refinement cycles riding on bonded atoms. Compound **VI** and complex **2** both crystallised with two independent molecules in the asymmetric unit.

CCDC reference numbers 168966–168971.

See http://www.rsc.org/suppdata/dt/b1/b107390g/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Royal Society (E. G. H. and A. M. S.) for financial support.

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