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FULL PAPER

Effect of fluorine and trifluoromethyl substitution on the donor properties and stereodynamical behaviour of triarylphosphines

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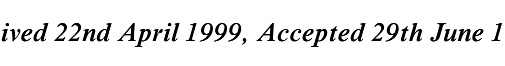
A series of 2-, 3- or 4-trifluoromethyl substituted triarylphosphines and their oxide, chalcogenide and $Fe(CO)_4$ derivatives have been prepared and characterised spectroscopically and crystallographically. Electronic effects of CF_3 substitution are cumulative and felt equally in the 2, 3 or 4 position. Substitution in the 2 position substantially hinders the complexing ability for steric reasons. Correlated P–C rotation in the 2-substituted derivatives has been analysed by variable temperature NMR and molecular mechanics calculations.

Introduction

The synthesis and study of fluorinated analogues of organic molecules continues to be an area of intense activity. In organometallic chemistry a related interest has been manifest in the design of fluorinated phosphorus donor ligands. Two particular areas are worthy of recent note, namely the development of long chain fluorinated phosphines such as $P(CH_2CH_2(CF_2)_5CF_3)_3$ **1** and **2** for application in catalysis using fluorous media or supercritical CO_2 as solvent,[1,2] and the fine tuning of enantioselectivity in the use of diarylphosphinite ligands such as **3** and **4** through fluoro or trifluoromethyl substitution of the aryl ring.[3] Of particular interest for **4** is the observation that such electron withdrawing groups enhance enantioselectivity in the hydrocyanation of alkenes where reductive elimination is viewed as the key mechanistic step, whereas for hydrogenation, where oxidative addition is rate determining, enantioselectivity is enhanced by electron donor substituents on the aryl ring.[3a] An understanding of the consequences of fluorine for hydrogen substitution on the donor properties and structure and stereodynamics of such ligands and their metal complexes is thus desirable.



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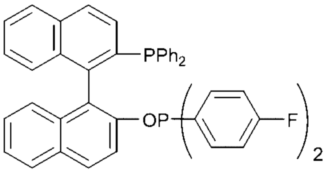

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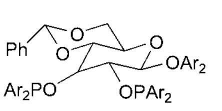

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Ar = 4 - FC_6H_4, 4 - $CF_3C_6H_4$,
3, 5 - $F_2C_6H_3$, 3, 5 - $(CF_3)_2C_6H_3$

We report here our results on the effect of fluoro and trifluoromethyl substitution on the complexing properties of triarylphosphines towards $Fe(CO)_4$, together with studies on the stereodynamics of the *ortho*-substituted derivatives which have also yielded valuable information regarding the energetics of correlated P–C rotation in both the free phosphines and their oxide and chalcogenide derivatives.[4]

Results and discussion

The fluorinated phosphines **7a**–**10a** were prepared by reaction of the appropriate aryllithium with PCl_3. The mixed derivatives **11a** and **12a** were prepared similarly by reaction of 2-CF_3-C_6H_4Li with $(2\text{-}CH_3C_6H_4)PCl_2$ **5** and $(2\text{-}CH_3C_6H_4)_2PCl$ **6** respectively.

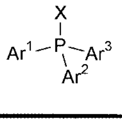
Stable oxides **7b**, **11b**, **12b** and **13b** are formed by all phosphines in the $P(2\text{-}CH_3C_6H_4)_n(2\text{-}CF_3C_6H_4)_{3-n}$ ($n = 0$–3) series. In contrast, reaction with sulfur and selenium is restricted to the higher alkylated members **12a** and **13a**. While reactions of **13a** with S and Se under standard conditions[5] proceed to completion to give **13c** and **13d**, treatment of **12a** under the same conditions provides only mixtures of **12a** with **12c** and **12d** [**12a** : **12c** = 5.3 : 1; **12a** : **12d** = 1 : 1.5, identified by integration of ^{31}P resonances]. Only the selenide **12d** has been isolated preparatively, and on heating in benzene is reconverted through selenium extrusion into the same ratio of **12a** : **12d**. The results surprisingly imply a greater thermodynamic stability for the selenide compared to the sulfide. No adduct formation is observed on reaction of **7a** or **11a** with S or Se, whereas reactions of **8a**, **9a** and **10a** proceed to completion to give the selenides **8b**, **9b** and **10b**.

Complexation to $Fe(CO)_4$ tends to mirror the selenide chemistry. Stable $Fe(CO)_4$ adducts **8c**, **9c**, **10c**, **13c** and **14c** are isolated from the reaction of $Fe_2(CO)_9$ with compounds **8a**, **9a**, **10a**, **13a** and **14a**. Reaction of **7a** provides only recovered starting material, while reactions using **11a** and **12a** are incomplete and are best investigated under equilibrium conditions using the exchange reaction[6] (1). No substitution is observed with **7a**,

$$[Fe(CO)_4(PhCH{=}CH_2)] + PR_3 \xrightleftharpoons[\text{Toluene}]{60\ ^\circ\text{C}} [Fe(CO)_4(PR_3)] + PhCH{=}CH_2 \quad (1)$$

whereas reactions using **11a** and **12a** proceed to equilibrium with equilibrium constants of 0.06 and 0.6 respectively.

The crystal and molecular structures of the phosphines **7a** and **11a**, the oxide **7b**, the selenides **9b** and **10b** and $Fe(CO)_4$ complexes **8c**, **9c** and **10c** have been determined by X-ray diffraction as part of this work (Fig. 1). Important structural and geometric parameters are listed in Table 1, together with relevant literature data. All $Fe(CO)_4$ compounds exhibit structures



Compound		Ar^1	Ar^2	Ar^3
7a, b	X = lp, O	2-$CF_3C_6H_4$	2-$CF_3C_6H_4$	2-$CF_3C_6H_4$
8a – c	X = lp, Se, $Fe(CO)_4$	3-$CF_3C_6H_4$	3-$CF_3C_6H_4$	3-$CF_3C_6H_4$
9a – c	X = lp, Se, $Fe(CO)_4$	4-$CF_3C_6H_4$	4-$CF_3C_6H_4$	4-$CF_3C_6H_4$
10a – c	X = lp, Se, $Fe(CO)_4$	3, 5-$(CF_3)_2C_6H_3$	3, 5-$(CF_3)_2C_6H_3$	3, 5-$(CF_3)_2C_6H_3$
11a – c	X = lp, O, $Fe(CO)_4$	2-$CH_3C_6H_4$	2-$CF_3C_6H_4$	2-$CF_3C_6H_4$
12a – e	X = lp, O, S, Se, $Fe(CO)_4$	2-$CH_3C_6H_4$	2-$CH_3C_6H_4$	2-$CF_3C_6H_4$
13a – e	X = lp, O, S, Se, $Fe(CO)_4$	2-$CH_3C_6H_4$	2-$CH_3C_6H_4$	2-$CH_3C_6H_4$
14a – c	X = lp, Se, $Fe(CO)_4$	4-FC_6H_4	4-FC_6H_4	4-FC_6H_4
15	X = $Fe(CO)_4$	C_6H_5	C_6H_5	C_6H_5
16	X = $Fe(CO)_4$	OC_6H_5	OC_6H_5	OC_6H_5

which depart little from trigonal bipyramidal, with phosphines in the axial position. Compounds **7a**, **11a** and **7b** exhibit an *exo*$_3$† conformation of the triaryl moiety. Examination of the X–P–C_{ipso}–C_α torsion angles shows that almost all 2- and 4-substituted derivatives and $[Fe(CO)_4(PPh_3)]$ **15** exhibit a regular helical array of the triaryl propeller which is slightly flattened by the introduction of O, Se or $Fe(CO)_4$ into the fourth co-ordination position. In contrast, the aryl conformations in the 3-substituted derivatives deviate considerably from regular helicity, containing one ring whose plane is collinear with the P–X axis (X–P–C_{ipso}–C_α −6 to 23°), one ring perpendicular to the P–X axis (62–85°) and one ring at an intermediate value (18–32°). Whilst $(3\text{-}CH_3C_6H_4)_3PSe$ adopts an *exo*$_1$ configuration, those of **8b** and **10b** are *exo*$_2$, in keeping with the reduced tendency of CF_3 to occupy an *endo* position (see below), though energy differences between *exo*/*endo* conformations for 3-substituted compounds are clearly less than those for the 2-substituted analogues. Though the P=O distance in **7b** and **13b** is not responsive to substitution of CH_3 by electron withdrawing CF_3, both P=Se and P–Fe bond lengths respond to the electron withdrawing nature of the aryl substituent. These bond lengths, and other appropriate spectroscopic measures of donor/acceptor character, are collected in Table 2 together with relevant literature data. Generally, both P=Se and P–Fe bond lengths decrease with increasing electron withdrawing character of the aryl substituent. Increasing $\delta(^{13}CO)$ and J(P–CO) values are also consistent with decreasing σ-donor/π-acceptor character of the phosphine, with consequent diminution in back donation to carbon monoxide. The data indicate that $P(OC_6H_5)_3$ and $P[3,5\text{-}(CF_3)_2C_6H_3]_3$ are similar in their overall electronic interactions with $Fe(CO)_4$. DFT Calculations[18] indicate that this is due to a decreased σ donation for the phosphine, but an increased π-acceptor character for the phosphite. The lack of reactivity of **7a** thus appears purely steric in origin. Though **13a** forms a stable selenide, $P(C_6H_2(CH_3)_3\text{-}2,4,6)_3$ does not.[19]

Selenium satellites generated by the $^{31}P^{77}Se$ isotopomers (7.6% natural abundance) are readily observed in the ^{31}P NMR spectra. Covering a range of appropriately 100 Hz in Table 2, these J(PSe) values provide probably the most sensitive probe, increasing with increasing electron withdrawing character of the aryl substituent. Though this is said to reflect increasing s-orbital participation on the phosphorus, there is no systematic variation in the C–P–C angles from structural data (Table 1). Values of J(PSe) correlate well with other data, and with the Hammett σ_m and σ_p parameters.[13] For the CF_3 derivatives examined, J(PSe) values appear cumulative. Thus ΔJ (PSe) (relative to $SePPh_3$) for $SeP(3,5\text{-}(CF_3)_2C_6H_3)_3$ is twice that of $SeP(3\text{-}CF_3C_6H_4)_3$. For 4 substitution, the electron-withdrawing power of F is approximately one half to one third that of CF_3. It is tempting to speculate that J(PSe) values may provide an estimate of the *electronic* effect only of 2 substitution. On this basis, donation by CH_3 increases in the order $m < p < o$ while the electron withdrawing effect of the almost purely inductive CF_3 is felt almost equally at the *o*, *m* and *p* positions.

It may be noted that J(PSe) values for 2-methoxy derivatives are perhaps not as low as expected. Crystal structures of the oxide, sulfide and selenide of $[2,4,6\text{-}(MeO)_3C_6H_2]_3P$[15,20] have demonstrated a possible interaction between the methoxy lone pair and phosphorus which reduces its ability to enter into resonance with the aromatic ring. Crystal structures of several metal complexes of 2-methoxy substituted triarylphosphines also demonstrate metal co-ordination of the methoxy lone pair.[21]

During slow recrystallisation of compound **9c**, a small amount of disproportionation resulted in deposition of $[Fe(CO)_3\{P(4\text{-}CF_3C_6H_4)_3\}_2]$ **17a** as a minor component ($\tilde{\nu}_{CO}$ = 1901, 1914 (sh) cm^{-1}) which was also structurally characterised (Fig. 2, Table 1). The phosphine ligands occupy *trans* positions in a trigonal bipyramidal structure and in common with $[Fe(CO)_3(PPh_3)_2]$ **17b**,[12a,b] the Fe–P bond length is substantially shortened relative to the $[Fe(CO)_4L]$ analogue. Compounds **17a**, **17b** exhibit an interesting conformational difference in that while **17b** has an almost eclipsed array of phenyl rings (C_{ipso}–P–P′–$C'_{ipso} \leq 6°$) with opposite chirality of the triaryl helices, that of **17a** is staggered (C_{ipso}–P–P′–$C'_{ipso} \leq 76°$) with the same chirality of the helices (Fig. 2). It has been suggested[12c] that intermolecular arene–arene interactions may be important in determining conformation in the solid state. Examination of the solid state packing shows that whereas shorter range arene–arene interactions in **17b** are of a

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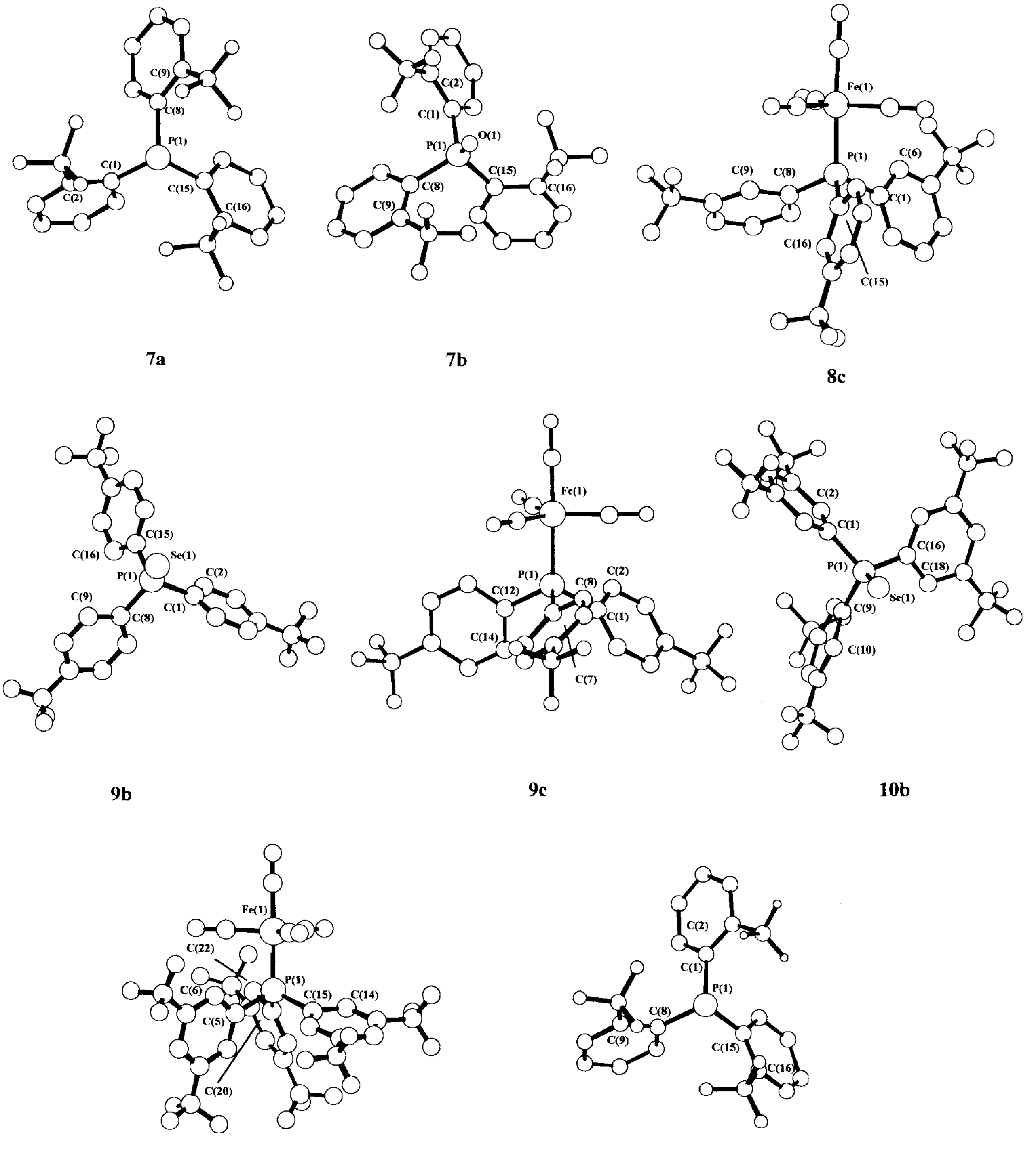
† If a regular pyramid is constructed from the lone pair (lp), O, Se or $Fe(CO)_4$ as the apex and the three *para* ring carbons as the base, an *exo* substituent will point away from the base, while an *endo* substituent will point towards the base.



7a **7b** **8c**

9b **9c** **10b**

10c **11a**

CH_3 and CF_3 groups are disordered

Fig. 1 Molecular structures of compounds **7a**, **7b**, **8c**, **9b**, **9c**, **10b**, **10c** and **11a**.

perpendicular T-shaped type, those in **17a** are almost exclusively of a parallel face-to-face arrangement. It may be noted that whereas $[Ru(CO)_3(PPh_3)_2]$ is conformationally identical to **17b**,[12d] $[Os(CO)_3(PPh_3)_2]$ has a staggered conformation similar to that of **17a** (C_{ipso}–P–P′–C'_{ipso} = 48°) with the same sign of helicity.[12e]

NMR Spectra of all 3- and 4-CF_3 substituted derivatives are temperature invariant down to −100 °C, implying that P–C and P–Fe rotation and pseudorotation of the $Fe(CO)_4L$ trigonal bipyramid remain fast on the NMR timescale. In contrast, several of the 2-CF_3 substituted complexes exhibit temperature dependent ^1H, ^{19}F and ^{31}P spectra which are consistent with correlated P–C rotation and consequent *exo*/*endo* ring exchange which has been previously observed for the 2-CH_3 substituted derivatives[5] and in general for molecular propellers of the types Ar_3Z and Ar_3ZX.[22]

Crystal structure determinations of various $P(2\text{-}CH_3C_6H_4)_3$ derivatives, including those reported herein, exhibit either exo_3[23] or exo_2[24] conformations. On the assumption that only these two isomers are populated, P–C rotational isomerism for an $Ar_2Ar'PX$ compound *via* 1-, 2- and 3-ring flip mechanisms may be represented as in Scheme 1. Eight conformers [(**A**)–(**D**) and their enantiomeric equivalents (**A′**)–(**D′**)] are possible. For Ar_3PX derivatives, (**B**)–(**D**) and (**B′**)–(**D′**) are equivalent and the number of conformers is reduced to four.

Molecular mechanics calculations on the phosphines repro-

Table 1 Important structural parameters for **7a**, **7d**, **8c**, **9b**, **10b**, **10c**, **11a** and related compounds

Compound	d(P–X)/Å	d(P–C)[a]/Å	C–P–C[a]/°	X–P–C_{ipso}–C_α[a]/°	$d(Fe–C_{ax})$/Å	$d(Fe–C_{eq})$[a]/Å	P–Fe–C_{ax}(P)/°	P–Fe–C_{eq}[a]/°	C_{eq}–Fe–C_{eq}[a]/°	CO_{ax}–Fe–CO_{eq}[a]/°	Cone angle/°
$P(2-CF_3C_6H_4)_3$		1.84 ± 0.01	101.5 ± 0.4	35 ± 2							205
$P(2-CH_3C_6H_4)(2-CF_3C_6H_4)_2$		1.83 ± 0.02	101.9 ± 0.9	36 ± 2							203
$OP(2-CF_3C_6H_4)_3$	1.471(1)	1.831 ± 0.001	104.5 ± 2.2	42 ± 7							
$P(2-CH_3C_6H_4)_3$[7]		1.835 ± 0.002	102.8 ± 0.8	42 ± 2							
$OP(2-CH_3C_6H_4)_3$[7]	1.473(4)	1.82 ± 0.01	105.4 ± 1.7	45 ± 7							
$SeP(3-CF_3C_6H_4)_3$[8]	2.094(2)	1.82 ± 0.02	105.6 ± 0.8	80 (*endo*)							
				22 (*exo*)							
				−6 (*exo*)							
$SeP(3-CH_3C_6H_4)_3$[9]	2.1091(5)	1.82 ± 0.05	106.5 ± 1.5	62 (*endo*)							
				28 (*endo*)							
				14 (*exo*)							
$SeP(3,5-(CF_3)_2C_6H_4)_3$	2.085(1)	1.821 ± 0.002	104.5 ± 0.6	85							
				18							
				−6							
$SeP(4-CF_3C_6H_4)_3$	2.100(1)	1.814 ± 0.004	105.3 ± 1.2	38 ± 5							
$[Fe(CO)_4\{P(2-CH_3C_6H_4)_3\}]$[10]	2.306(1)	1.849 ± 0.009	103.3 ± 1.4	53 ± 4	1.776(2)	1.773 ± 0.006	178.9(2)	90.6 ± 0.6	120.0 ± 1.1	89.4 ± 0.8	165
$[Fe(CO)_4\{P(C_6H_5)_3\}]$[11]	2.244(1)	1.831 ± 0.001	103.9 ± 0.3	44 ± 3	1.795(2)						155
$[Fe(CO)_4\{P(3-CF_3C_6H_4)_3\}]$	2.234(1)	1.835 ± 0.009	103.2 ± 0.1	64 (*exo*)	1.786(5)	1.784 ± 0.007	175.4(2)	89.9 ± 2.2	120.0 ± 5.3	90.3 ± 1.7	164
				25 (*endo*)							
				23 (*exo*)							
$[Fe(CO)_4\{P(4-CF_3C_6H_4)_3\}]$	2.245(1)	1.835 ± 0.002	103.7 ± 0.8	35 ± 16	1.772(7)	1.780 ± 0.006	175.5(1)	90.2 ± 3.3	120.0 ± 2.8	89.8 ± 0.8	164
$[Fe(CO)_4\{P(3,5-(CF_3)_2C_6H_4)_3\}]$	2.210(1)	1.828 ± 0.004	102.7 ± 0.8	69	1.802(6)	1.790 ± 0.007	178.7(2)	90.3 ± 0.4	120.0 ± 1.6	89.7 ± 1.5	160
				32							
				19							
$[Fe(CO)_3(PPh_3)_2]$[12]	2.218(9)	1.832 ± 0.008	102.5 ± 1.4	39 ± 19							
				−47 ± 15		1.770 ± 0.006	175.6(1)	90.1 ± 2.9	120.0 ± 3.5		162
$[Fe(CO)_3\{P(4-CF_3C_6H_4)_3\}_2]$	2.204(4)	1.831 ± 0.02	102.4 ± 1.4	43 ± 14							
				45 ± 12		1.773 ± 0.029	178.7(1)	90.0 ± 0.7	120.0 ± 3.4		154

[a] Number represents the average ± one standard deviation of chemically equivalent bonds or angles.

Table 2 Structural and spectroscopic data relevant to donor/acceptor character

Compound	d(P=Se)/Å	d(P–Fe)/Å	J(P–Se)/Hz	$\tilde{\nu}$(CO)/cm^{-1}	δ (^{13}CO)	σ_m or σ_p
$P(2\text{-}CH_3OC_6H_4)_3$[14]			720			
$P[2,6\text{-}(CH_3O)_2C_6H_3]_3$[14,15]	2.135(3)		717			
$P(4\text{-}CH_3OC_6H_4)_3$[14]			710			−0.12
$P(2\text{-}CH_3C_6H_4)_3$[7,14]	2.116(5)	2.306(1)	703	2047	214.6	
$P(3\text{-}CH_3C_6H_4)_3$[9,14]	2.109(5)		726			−0.06
$P(4\text{-}CH_3C_6H_4)_3$[14]			715			−0.14
$P(C_6H_5)_3$[14,16]	2.112	2.244(1)	733	2050	213.6	0
$P(4\text{-}FC_6H_5)_3$[17]			741	2052	213.5	0.15
$P(2\text{-}CH_3C_6H_4)(2\text{-}CF_3C_6H_4)_2$				2052		
$P(2\text{-}CH_3C_6H_4)_2(2\text{-}CF_3C_6H_4)$			727	2050		
$P(3\text{-}CF_3C_6H_4)_3$[8]	2.094(2)	2.234(1)	766	2057	212.7	0.46
$P(4\text{-}CF_3C_6H_4)_3$	2.100(1)	2.245(1)	765	2056	212.8	0.53
$P(3,5\text{-}(CF_3)_2C_6H_4)_3$	2.085(1)	2.210(1)	802	2065	210.7	
$P(OC_6H_5)_3$				2065	211.4	

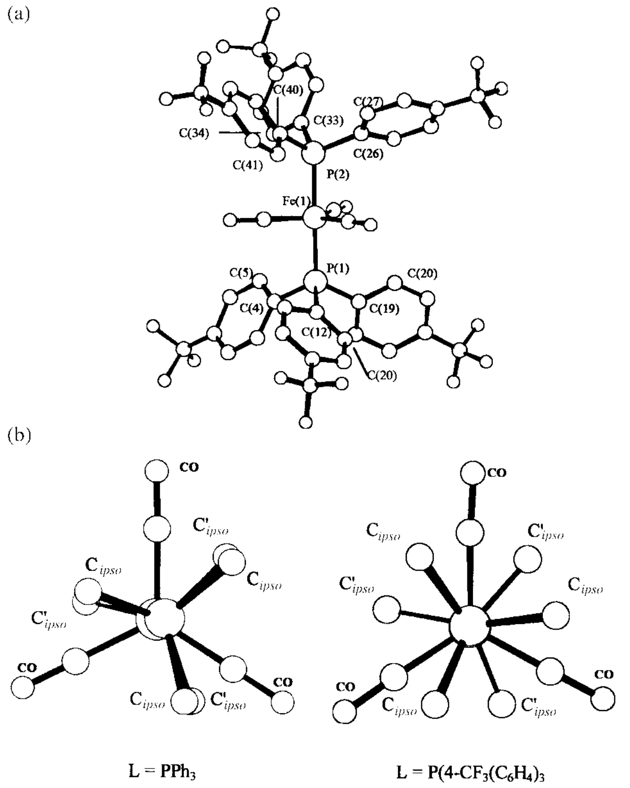


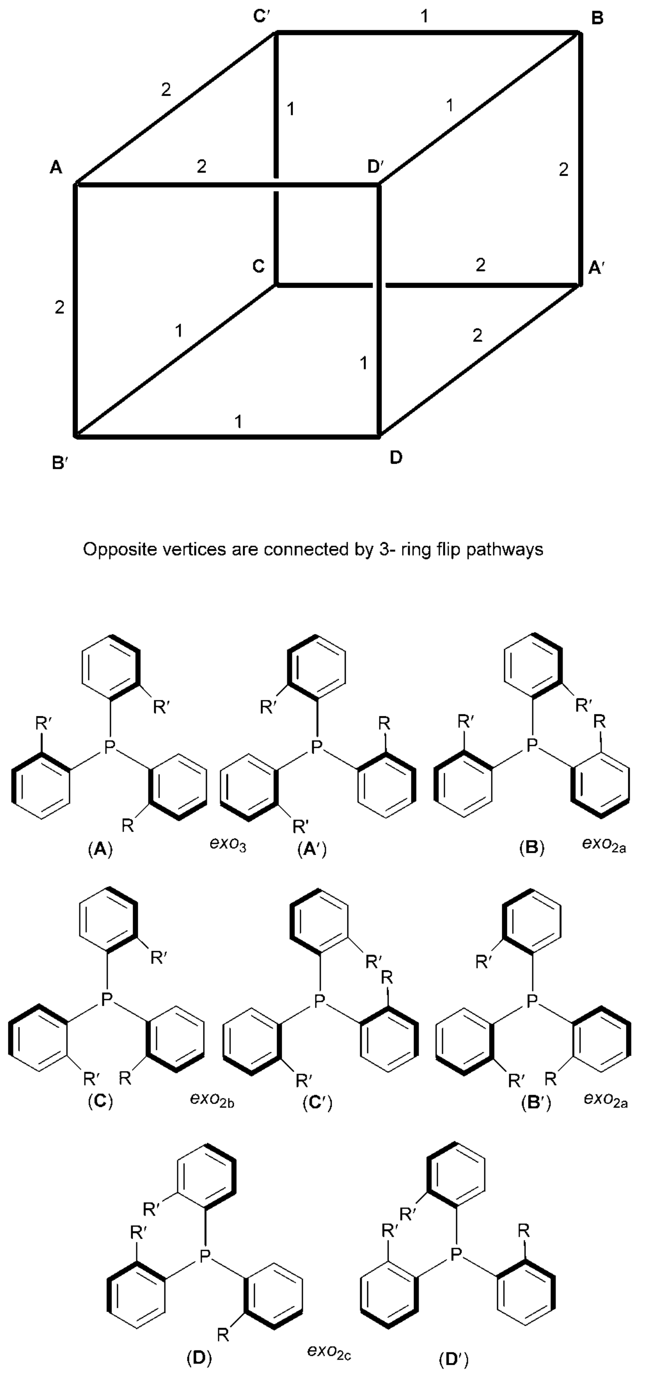
Fig. 2 (a) Molecular structure of $[Fe(CO)_3\{P(4\text{-}CF_3(C_6H_4)_3\}_2]$. (b) View down P–P axis of $[Fe(CO)_3L_2]$ [L = PPh_3 or $P(4\text{-}CF_3C_6H_4)_3$] (only *ipso* carbon of aryl ring shown).

duce well the observed *exo*$_3$ geometry as the energy minimum in all cases. The minimised geometries of the *exo*$_2$ conformers are also consistent with observed *exo*$_2$ structures, particularly the approximate collinearity of the plane of the *endo* ring with the lp–P axis. The *exo*$_2$ isomers lie between 2.0 and 4.3 kcal higher in energy than *exo*$_3$ (Table 3), with the energy difference becoming more pronounced with increasing CF_3 substitution. For the mixed derivatives, conformers with *endo* $2\text{-}CF_3C_6H_4$ rings are less stable than those with *endo* $2\text{-}CH_3C_6H_4$. Relative barriers for the various ring flip processes may be screened by molecular mechanics calculations of the energies of idealised transition states for the 1-ring (**I**, **II**), 2-ring (**III**) and 3-ring (**IV**, **V**) flip processes (Table 4). For the phosphines, the calculations show clearly that the 2-ring flip (interconverting *exo*$_2$ and *exo*$_3$) is the process of lowest energy, followed by the 3-ring flip (helix interconversion in the *exo*$_3$). Intermediates **I**, **II** and **V** lie at much higher energies, and indeed are not required to rationalise the variable temperature NMR spectra of the phosphines or phosphine oxides.

The ^{31}P NMR spectra of all the phosphines exhibit a single ^{31}P resonance down to −100 °C, indicative of either an exclusive population of *exo*$_3$ or an *exo*$_2$/*exo*$_3$ mixture in which interconversion remains fast on the NMR timescale. The essentially identical chemical shift of H6 for the $2\text{-}CH_3C_6H_4$ (δ 6.56–6.73) and $2\text{-}CF_3C_6H_4$ (δ 6.89–7.06) rings, which may be used as a measure of *exo*$_2$ content,[5] indicates that the former explanation is correct. While helix inversion (3-ring flip) of the *exo*$_3$ conformer represents a hidden process for PAr_3, it is required for exchange of chemically equivalent rings in PAr_2Ar' and can be observed experimentally in the broadening and resolution into two of the CF_3 (^{19}F) and CH_3 (^{1}H) resonances of **11a** and **12a** respectively (Table 5, Fig. 3). The presence of long range P–F coupling in the $2\text{-}CF_3C_6H_4$ phosphines **7a**, **11a**, **12a** may be noted, but is absent in the oxides **7b**, **11b** and **12b**, the selenide **12d** and the 3- and 4-substituted phosphines.

The ^{31}P spectra of the oxides **7b**, **11b** and **12b** are all resolved into two unequally populated resonances at low temperature (Fig. 4). The major and minor resonances are assigned to *exo*$_3$ and *exo*$_2$ respectively. In agreement, for example, the ^{19}F spectrum of **7b** exhibits a single large resonance assignable to equivalent CF_3 groups of *exo*$_3$ together with three minor resonances due to the non-equivalent CF_3 groups of the *exo*$_2$ isomer. For the mixed derivatives **11b** and **12b**, a population of only one of the three possible *exo*$_2$ conformers is observed. Line shape analyses, shown only for **7b**, provide barriers for the 2-ring flip *exo*$_2$/*exo*$_3$ exchange process. For the mixed CF_3/CH_3 oxides **11b** and **12b**, line shape analysis of the higher temperature ^{19}F and ^{1}H spectra respectively (Fig. 5) also provides barriers for the higher energy 3-ring flip process. Two points of interest may be noted. (i) Relative to **13b**, all CF_3-substituted oxides exhibit a reduced population of the *exo*$_2$ isomer. In all cases, however, the *exo*$_2$ population increases substantially with increasing temperature, with the sensitivity to temperature becoming more pronounced with increasing degree of CF_3 substitution. In particular, the large linewidths in the ^{31}P spectra of **7b** in the 193–213 K range are impossible to simulate without the approximate five- to ten-fold decrease in K_{eq}. (ii) Barriers for the 2-ring flip process in the oxides and 3-ring flip process in the phosphines increase slightly (*ca.* 5%) with increasing degree of CF_3 substitution. The influence of increasing CF_3 substitution on the increasing barrier to 3-ring flip in the oxides is much more substantial (*ca.* 12%), consistent with a more demanding oxygen–CF_3 as opposed to lone pair–CF_3 interaction in the presumed intermediate (**IV**).

In contrast to compounds **11b** and **12b**, the single room temperature ^{19}F resonance of the selenide **12d** is resolved into four unequal resonances at low temperatures, consistent with population of the four possible conformers *exo*$_3$ and *exo*$_{2a–c}$. Satisfactory simulation of the spectrum (Fig. 6) can be accomplished only by assigning the least abundant resonance **C** to *exo*$_3$ and assuming that this represents a unique pivot for



Opposite vertices are connected by 3- ring flip pathways

R = R′ = CF$_3$; P(2-CF$_3$C$_6$H$_4$)$_3$ R = CF$_3$, R′ = CH$_3$; P(2-CF$_3$C$_6$H$_4$)(2-CH$_3$C$_6$H$_4$)$_2$

R = R′ = CH$_3$; P(2-CH$_3$C$_6$H$_4$)$_3$ R = CH$_3$, R′ = CF$_3$; P(2-CF$_3$C$_6$H$_4$)$_2$(2-CH$_3$C$_6$H$_4$)

Scheme 1

exchange between *exo*$_2$ conformers. The implication, confirmed by preliminary molecular mechanics calculations on the phosphines, is that direct interconversion between *exo*$_2$ isomers *via* 1-ring flip processes does not contribute to the exchange process in this temperature range. Barriers for the three independent 2-ring flip processes differ only slightly and the increase in barriers for the 2-ring flip process between **12b** and **12d** is comparable to that observed between OP(2-CH$_3$C$_6$H$_4$)$_3$ and SeP(2-CH$_3$C$_6$H$_4$)$_3$ ($\Delta\Delta G^\ddagger \approx 9$ kcal mol^{-1}).[5]

The barrier for the higher temperature ring averaging process in compound **12d** may be determined from line shape analysis of the CH$_3$ (^{1}H) subspectra, which in appearance are similar to those of Fig. 5. Though, as expected, it is higher than the barrier for 2-ring flip, it is surprisingly lower than the measured 3-ring flip barrier for oxides **11b** and **12b** and characterised by a strongly negative rather than neutral entropy of activation (Fig. 7). The results imply a different mechanism for the higher energy ring exchange process in **12d**. Indeed, preliminary molecular mechanics calculations show that, whereas for the phosphine **12a** and phosphine oxide **12b** relative magnitudes of the barriers are in the order 2-ring < 3-ring ⩽ 1-ring, for the sulfide or selenide the ordering changes to 2-ring < 1-ring < 3-ring, and that **C** $\longleftrightarrow$ **C′** exchange *via* a 1-ring flip mechanism provides the pathway of lowest energy for helix inversion (and thus exchange of chemically equivalent aryl rings).

Conclusion

The electronic effect of CF$_3$ substitution on complexation properties of triarylphosphines is cumulative and essentially independent of position; sterically, 2-CF$_3$ substitution dramatically reduces complexing ability towards transition metal fragments. Rotational mobility about phosphorus–aryl bonds in XP(aryl)$_3$ compounds is substantially reduced in the 2-substituted derivatives. While *exo*$_2$/*exo*$_3$ exchange invariably occurs by a 2-ring flip mechanism, the mechanism for helix inversion changes from 3-ring flip for small substituents (X = lp or O) to 1-ring flip for larger substituents (X = Se).

Experimental

CAUTION: explosions have been reported in the preparation of Grignard and lithium reagents from fluoro- and trifluoromethyl-arenes, probably associated with elimination of LiF from solid reagents formed by solvent evaporation.[25,26] Reactions using [Fe$_2$(CO)$_9$] generate toxic, volatile Fe(CO)$_5$ as a by-product. Care should be taken to trap this material when evaporating solutions.

The NMR spectra were recorded using either JEOL GSX270 (^{1}H, 270; ^{13}C, 68; ^{31}P, 109 MHz) or Bruker DPX300 (^{1}H, 300; ^{13}C, 75; ^{31}P, 121; ^{19}F, 282 MHz) spectrometers. Temperatures were measured using the built in copper–constantan thermocouple previously calibrated with a platinum resistance thermometer. Chemical shifts were measured relative to SiMe$_4$ (^{1}H, ^{13}C), 85% H$_3$PO$_4$ (^{31}P) and CFCl$_3$ (^{19}F); numbers in parentheses after ^{13}C chemical shifts represent *J*(P–C) values. Infrared spectra were recorded on Perkin-Elmer 257 or Paragon 1000 spectrometers and calibrated with polystyrene. Line shape analyses of NMR spectra were performed by computer simulation. For the case of two exchanging nuclei, an in-house program based on the equation of Sutherland[27] was used. For greater numbers of nuclei a program written by R. E. D. McClung, Department of Chemistry, University of Alberta, Canada was adapted for use.

Diethyl ether and tetrahydrofuran were distilled from LiAlH$_4$. Reactions involving lithium and magnesium reagents were conducted under argon. Excepting the preparation of phosphine oxides, other reactions were conducted under nitrogen. The phosphines (2-, (3- and (4-CF$_3$C$_6$H$_4$)$_3$P[28] and [3,5-(CF$_3$)$_2$C$_6$H$_3$]$_3$P[29] were prepared as described. The [Fe(CO)$_4$L] complexes of (4-FC$_6$H$_5$)$_3$P,[30] (2-CH$_3$C$_6$H$_4$)$_3$P,[10] PPh$_3$ and P(OPh)$_3$[31] have previously been reported. Syntheses of **5**[32] and **6**[33] were adapted from literature procedures.

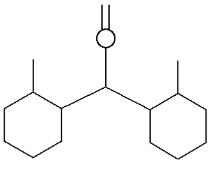
Syntheses

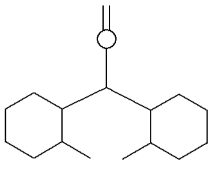
(a) (2-CH$_3$C$_6$H$_4$)PCl$_2$ 5. A solution of the Grignard reagent 2-CH$_3$C$_6$H$_4$MgBr was prepared by addition of *o*-bromotoluene (47.1 g, 280 mmol) in diethyl ether (200 ml) to magnesium turnings (6.81 g, 280 mmol) using 1,2-dibromoethane as initiator. After refluxing for 1 h the solution was cooled to −60 °C and (Et$_2$N)$_2$PCl (48.8 g, 232 mmol, δ_P (CDCl$_3$) 160.6)[34] in diethyl ether (70 ml) added with stirring. After warming to room temperature and stirring for a further hour, the solvent was evaporated and the crude (Et$_2$N)$_2$P(2-CH$_3$C$_6$H$_4$) (δ_P (CDCl$_3$) 92.3) was redissolved in diethyl ether (150 ml). With stirring, HCl gas

Table 3 Molecular mechanics energies and geometries of **7a**, **11a**, **12a** and **13a**

Compound	Conformer	Energy/kcal	*d*(P–C)/Å	C–P–C/°	X–P–C_{ipso}–C_{α}/°
$P(2\text{-}CH_3C_6H_4)_2$	*exo*$_3$	0	1.841	102.5	43
	exo$_2$	2.3	1.842	103.4	20 (*endo*), 48, 55
$P(2\text{-}CH_3C_6H_4)_2(2\text{-}CF_3C_6H_4)$	*exo*$_3$	0	1.841	102.6	42
	exo$_{2a}$	4.3	1.842	104.0	21 (*endo*), 48, 56
	exo$_{2b}$	2.7	1.842	103.5	21 (*endo*), 48, 53
	exo$_{2c}$	2.7	1.841	103.5	26 (*endo*), 38, 57
$P(2\text{-}CH_3C_6H_4)(2\text{-}CF_3C_6H_4)_2$	*exo*$_3$	0	1.840	102.7	41
	exo$_{2a}$	3.1	1.841	103.7	26 (*endo*), 40, 53
	exo$_{2b}$	4.9	1.841	104.1	24 (*endo*), 44, 56
	exo$_{2c}$	4.3	1.842	104.1	21 (*endo*), 50, 53
$P(2\text{-}CF_3C_6H_4)_3$	*exo*$_3$	0	1.840	102.9	38
	exo$_2$	4.7	1.841	104.3	25 (*endo*), 45, 53

Table 4 Molecular mechanics transition state energies for ring flip processes in **7a**, **11a**, **12a** and **13a**


(I)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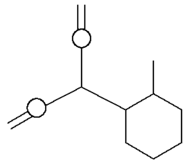
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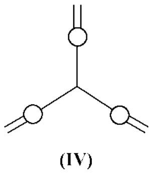
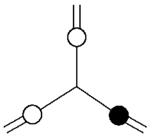

(IV)


(V)

● = *endo*

○ = *exo*

Compound	Flip mechanism	Interconversion	Intermediate type	Energy/kcal
$P(2\text{-}CH_3C_6H_4)_3$	2-ring	**A** ⟷ **B′**	**III**	3.0
	3-ring	**A** ⟷ **A′**	**IV**	8.1
	3-ring	**B** ⟷ **B′**	**V**	19.3
	1-ring	**B** ⟷ **B′**	**I**	12.1
	1-ring	**B** ⟷ **B′**	**II**	29.6
$P(2\text{-}CH_3C_6H_4)_2(2\text{-}CF_3C_6H_4)$	2-ring	**A** ⟷ **B′**	**III**	4.2
	2-ring	**A** ⟷ **C′**	**III**	3.5
	2-ring	**A** ⟷ **D′**	**III**	3.5
	3-ring	**A** ⟷ **A′**	**IV**	8.8
	3-ring	**B** ⟷ **B′**	**V**	25.1
	3-ring	**C/D** ⟷ **D′/C′**	**V**	19.6
	1-ring	**B** ⟷ **C′**	**II**	35.4
	1-ring	**C** ⟷ **C′**	**I**	13.0
	1-ring	**D** ⟷ **D′**	**II**	30.4
	1-ring	**B** ⟷ **D′**	**I**	13.7
$P(2\text{-}CH_3C_6H_4)(2\text{-}CF_3C_6H_4)_2$	2-ring	**A** ⟷ **B′**	**III**	4.9
	2-ring	**A** ⟷ **C′**	**III**	4.7
	2-ring	**A** ⟷ **D′**	**III**	5.0
	3-ring	**A** ⟷ **A′**	**IV**	10.6
	3-ring	**B** ⟷ **B′**	**V**	20.7
	3-ring	**C/D** ⟷ **C′/D′**	**V**	25.1
	1-ring	**B** ⟷ **C′**	**II**	35.4
	1-ring	**C** ⟷ **C′**	**I**	16.4
	1-ring	**D** ⟷ **D′**	**II**	39.0
	1-ring	**B** ⟷ **D′**	**I**	14.5
$P(2\text{-}CF_3C_6H_4)_3$	2-ring	**A** ⟷ **B′**	**III**	6.1
	3-ring	**A** ⟷ **A′**	**IV**	13.4
	3-ring	**B** ⟷ **B′**	**V**	25.4
	1-ring	**B** ⟷ **B′**	**I**	16.9
	1-ring	**B** ⟷ **B′**	**II**	38.2

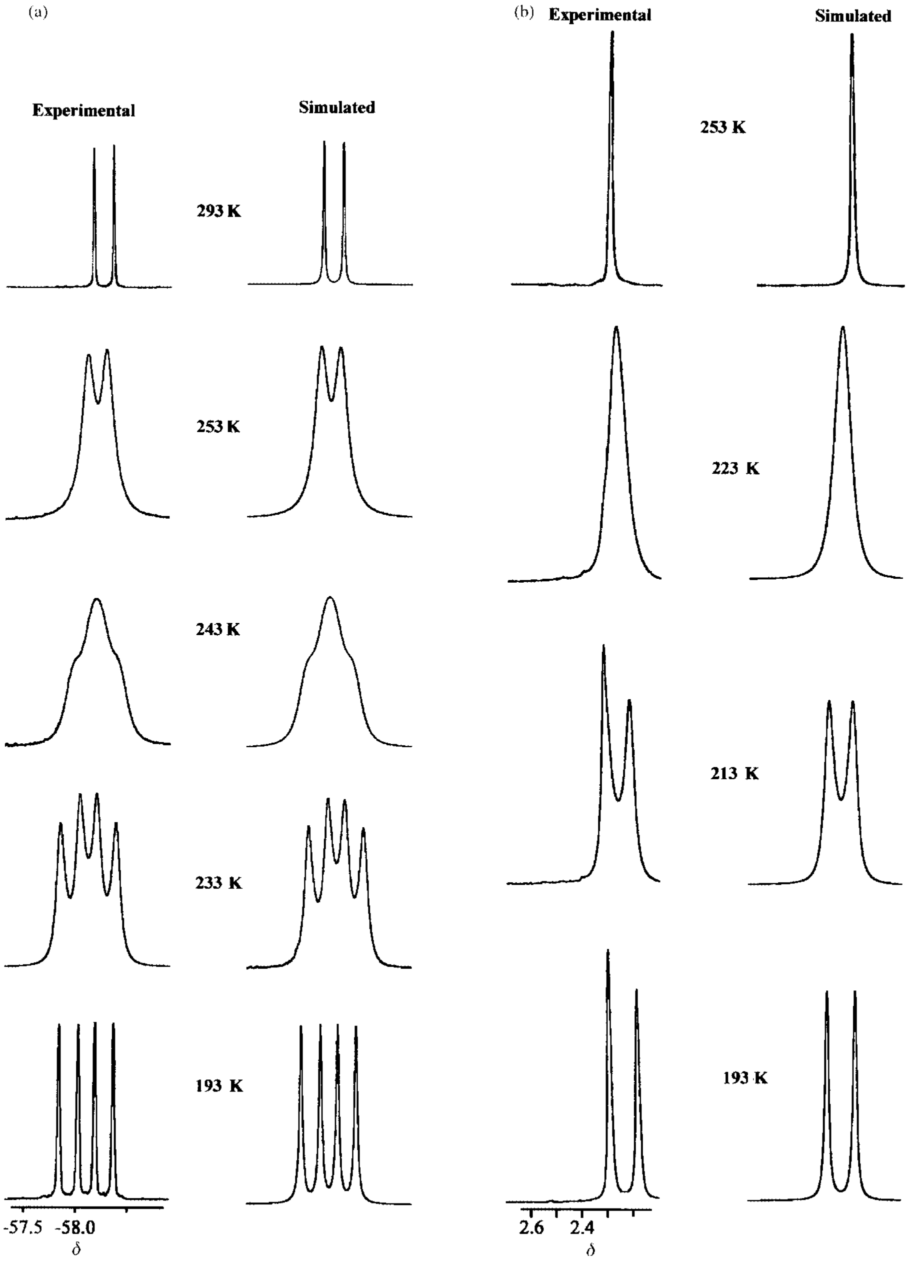


Fig. 3 Representative experimental and simulated variable temperature NMR spectra: (a) ^{19}F of compound **11a**; (b) ^{1}H of **12a**.

was bubbled through the solution for 3 h. After filtration of the copious precipitate of $[Et_2NH_2]Cl$ and removal of solvent, the residue was distilled (60–76 °C, 0.5 mmHg) to provide compound **5** as a clear liquid (26.5 g, 64%). δ_P ($CDCl_3$) 163.9. δ_H ($CDCl_3$) 7.20 (1 H, t, Ph), 7.3–7.5 (2 H, m, Ph), 8.01 (1 H, t, Ph) and 2.62 [3 H, d, *J*(PH) 3.4 Hz, Me]. δ_C ($CDCl_3$) 126.9 (2), 130.2 (11), 130.7 (3), 132.5, 137.7 (57), 140.5 (35), 19.8 (26 Hz).

(b) $(2\text{-}CH_3C_6H_4)_2PCl$ 6. A solution of the Grignard reagent $2\text{-}CH_3C_6H_4MgCl$ was prepared by the slow addition of *o*-chlorotoluene (17.8 g, 140 mmol) in tetrahydrofuran (15 ml) to magnesium turnings (3.6 g, 150 mmol) suspended in tetrahydrofuran (10 ml). After initiation, the reaction was controlled by further addition of tetrahydrofuran (20–30 ml). [The use of 1,2-dibromoethane as initiator results in contamination of the product with $(2\text{-}CH_3C_6H_4)_2PBr$.] After refluxing for 6 h the solution was cooled, transferred under argon to a pressure equalised dropping funnel and added to a solution of PCl_3 (8.2 g, 60 mmol) in tetrahydrofuran (12 ml) cooled to −78 °C. After warming to room temperature the reaction was stirred overnight and then refluxed for 1 h. After removal of solvent under vacuum, toluene (100 ml) was added and the solution filtered. After removal of solvent, the residue was distilled (120–130 °C, 0.01 mmHg) to yield compound **6** as a colourless liquid which solidified to a white solid (8.1 g, 54%). δ_P ($CDCl_3$) 74.3. δ_H ($CDCl_3$) 7.1–7.5 (4 H, m, Ph) and 2.45 [3 H, d, *J*(PH) 2.4 Hz, Me]. δ_C ($CDCl_3$) 126.4, 130.3 (4), 130.4, 131.5 (4), 135.6 (35), 141.5 (31), 20.6 (24 Hz).

(c) $(2\text{-}CH_3C_6H_4)(2\text{-}CF_3C_6H_4)_2P$ 11a. Butyllithium (23.1 ml of a 1.6 M solution in hexane, 64.6 mmol) was added dropwise over 30 min to a stirred solution of *o*-$BrC_6H_4CF_3$ (3.6 g, 60.4 mmol) in diethyl ether (25 ml) at −10 °C. After stirring for 30 min, $(2\text{-}CH_3C_6H_4)_2PCl_2$ (5.0 g, 25.9 mmol) dissolved in diethyl ether (15 ml) was added slowly over 1 h. After warming to room temperature and stirring for 6 h the reaction was hydrolysed with degassed saturated NH_4Cl solution (5 ml). The organic layer was separated, washed with water and dried over $MgSO_4$. Removal of solvent followed by recrystallisation from ethanol gave compound **11a** as white crystals (4.1 g, 38%); **12a** was prepared similarly using $(2\text{-}CH_3C_6H_4)_2PCl$.

Spectroscopic data for phosphines are given below, together with analytical data for new compounds. The ^{13}C NMR

Table 5 Kinetic and thermodynamic data from NMR line shape analysis

	$exo_2 \longrightarrow exo_3$ (minor $\longrightarrow$ major)				Ring exchange (1- or 3-ring flip)				
Compound	T/K	K	k/s^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}	T/K	k/s^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
$OP(2\text{-}CH_3C_6H_4)_3$	163	3.0	600	30.4 ± 0.3					
	173	2.7	2600	30.3 ± 0.3					
	183	2.5	9300	30.3 ± 0.3					
	193	2.3	25000	30.3 ± 0.3					
	213	1.9	120000	30.8 ± 0.8					
$OP(2\text{-}CF_3C_6H_4)_3$	158	21	13	34.3 ± 0.8					
	173	10	200	33.9 ± 0.8					
	193	4.5	2800	33.9 ± 0.8					
	213	2.7	9000	35.6 ± 0.8					
$P(2\text{-}CH_3C_6H_4)(2\text{-}CF_3C_6H_4)_2$					223	32	47.7 ± 0.8		
					233	75	48.1 ± 0.4		
					243	190	48.5 ± 0.4		
					253	500	48.5 ± 0.4		
					273	32000	48.5 ± 0.8		
$OP(2\text{-}CH_3C_6H_4)(2\text{-}CF_3C_6H_4)_2$	163	15	180	32.2 ± 0.4	273	20	59.8 ± 0.8	59 ± 4	−8 ± 12
	173	10	900	31.7 ± 0.4	283	47	60.2 ± 0.4		
	193	5.0	13200	31.4 ± 0.8	293	127	59.8 ± 0.4		
	213	2.9	100000	31.4 ± 1.3	303	295	59.8 ± 0.4		
					313	610	60.2 ± 0.4		
					323	1150	60.2 ± 0.4		
					333	2100	60.7 ± 0.8		
					343	3900	60.7 ± 0.8		
					353	8250	60.7 ± 0.8		
$P(2\text{-}CH_3C_6H_4)_2(2\text{-}CF_3C_6H_4)$					213	25	46.0 ± 0.4		
					223	85	46.0 ± 0.4		
					233	250	46.0 ± 0.4		
					253	2800	44.7 ± 1.3		
$OP(2\text{-}CH_3C_6H_4)_2(2\text{-}CF_3C_6H_4)$	163	20	318	31.4 ± 0.8	223	1.7	53.1 ± 0.8	62 ± 5	38 ± 25
	173	17	1500	31.0 ± 1.3	233	9.3	52.3 ± 0.4		
	193	13	20000	30.5 ± 1.3	243	33	51.9 ± 0.4		
					253	100	51.9 ± 1.3		
$SeP(2\text{-}CH_3C_6H_4)_2(2\text{-}CF_3C_6H_4)$	193	85 (A)	450 (**C** $\longrightarrow$ **A**)	36.8	183	11	40.5 ± 0.8	29 ± 8	−51 ± 13
		8.9 (B)	180 (**C** $\longrightarrow$ **B**)	38.1	193	16	42.2 ± 0.4		
		3.5 (D)	270 (**C** $\longrightarrow$ **D**)	37.6	213	110	43.1 ± 0.4		
		2.6 (C)			233	370	45.2 ± 0.4		
					253	2000	45.6 ± 0.8		
	213	81	7100	36.0	273	9000	46.0 ± 1.7		
		10.3	2100	38.1	293	27000	46.8 ± 1.7		
		4.7	3000	37.2					
		4.0							
	233		44400	36.0					
			14400	38.5					
			18300	38.1					
	253		208000	36.4					
			74000	38.5					
			92000	38.1					
	273		783000	36.4					
			300000	38.5					
			36800	38.1					

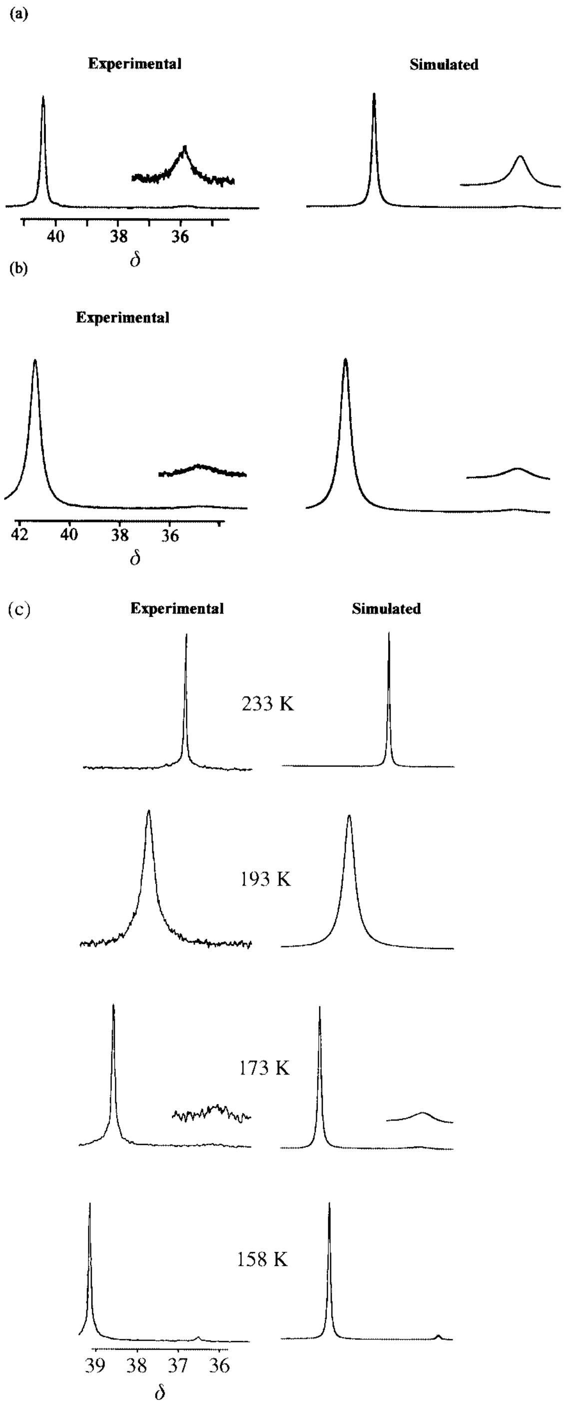


Fig. 4 Representative experimental and simulated ^{31}P NMR spectra: (a) compound **11b** at 164 K, (b) **12b** at 163 K and (c) **7b**.

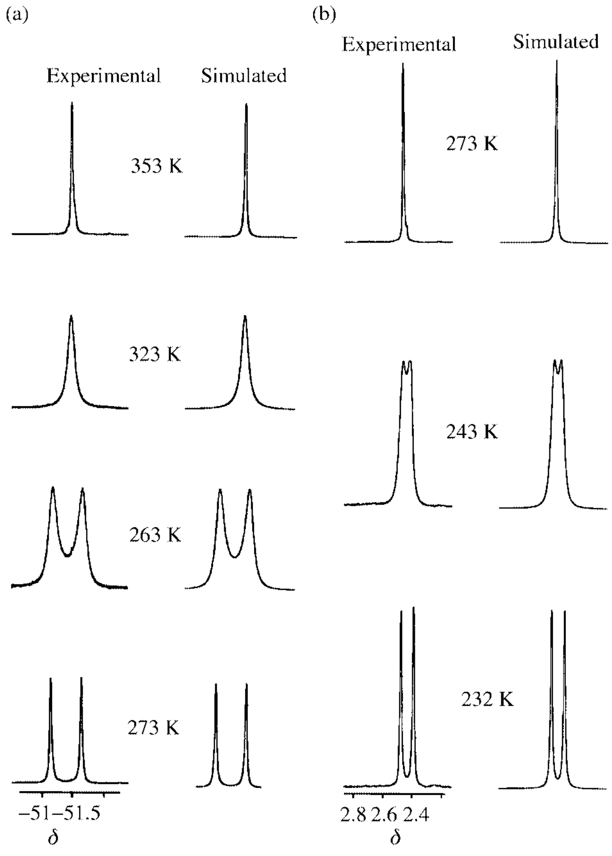


Fig. 5 Representative experimental and simulated NMR spectra: (a) ^{19}F of **11b**, (b) ^1H of **12b**.

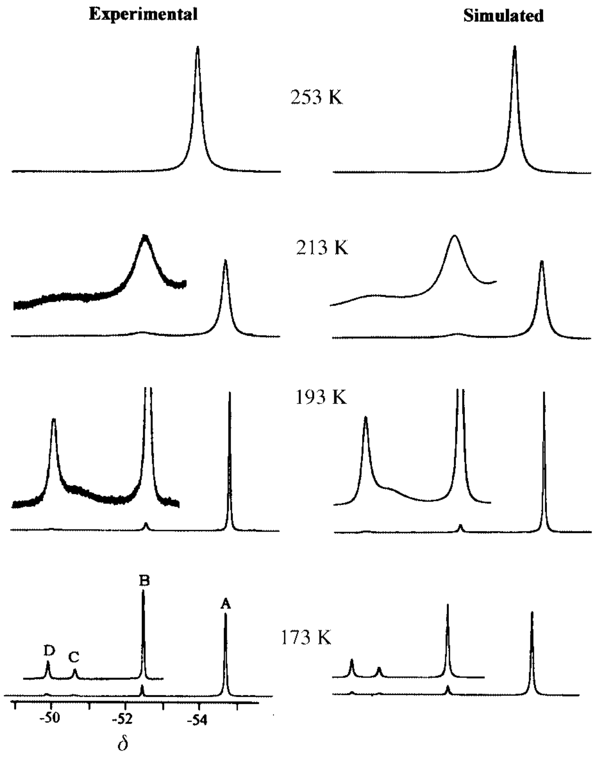


Fig. 6 Representative experimental and simulated variable temperature ^{19}F NMR spectra of compound **12b**.

spectra of **13a**, **13b** were assigned unambiguously by COSY and HeteroCOSY techniques; assignments of 2-$CH_3C_6H_4$ resonances for the mixed derivatives are based on this. Assignments for fluoro and trifluoromethyl rings are based on ^{13}C–^{19}F coupling constants and published substituent effects for PPh_2, CF_3 and F.[35]

Compound **7a**: mp 172–174 °C; δ_H ($CDCl_3$) 6.89 (1 H, m), 7.35–7.55 (2 H, m) and 7.75 (1 H, m); δ_P ($CDCl_3$) −17.6 [decet, *J*(PF) 55 Hz]; δ_F ($CDCl_3$) −57.9 (d); δ_C ($CDCl_3$) 134.8 (31) [dq, *J*(CF) 2, C1], 134.3 (27) [m, *J*(CF) 31, C2], 127.0 (6) [m, *J*(CF) 6, C3], 129.3 (s, C4), 131.6 (s, C5), 136.0 (s, C6) and 124.1 [q, *J*(CF) 275 Hz, CF_3].

Compound **8a**: oil; δ_H ($CDCl_3$) 7.39 (1 H, t), 7.48 (1 H, t), 7.56 (1 H, d) and 7.63 (1 H, d); δ_P ($CDCl_3$) −4.30; δ_F ($CDCl_3$) −63.3; δ_C ($CDCl_3$) 137.0 (14) (d, C1), 130.3 (25) [dq, *J*(CF) 4, C2], 131.3 (8) [qd, *J*(CF) 33, C3], 126.2 [q, *J*(CF) 4, C4], 129.4 (5) (d, C5), 136.7 (16) [dq, *J*(CF) 2, C6] and 123.8 [q, *J*(CF) 273 Hz, CF_3].

Compound **9a**: mp 72–74 °C; δ_H ($CDCl_3$) 7.39 (2H, t) and 7.60 (2H, d); δ_P ($CDCl_3$) −5.30; δ_F ($CDCl_3$) −63.4; δ_C ($CDCl_3$)

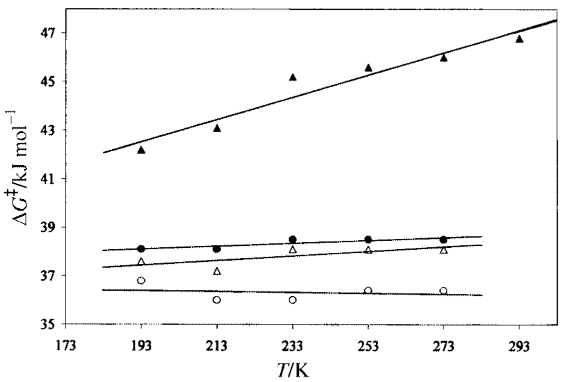


Fig. 7 Plots of $\Delta G^{\ddagger}$ against temperature for compound **12d**: ▲ complete aryl exchange process, ○ ($\mathbf{C} \longrightarrow \mathbf{A}$) interconversion, ● ($\mathbf{C} \longrightarrow \mathbf{B}$) interconversion and △ ($\mathbf{C} \longrightarrow \mathbf{D}$) interconversion.

140.2 (14) (d, C1), 134.0 (20) (d, C2), 125.7 (8) [m, J(CF) 3, C3], 131.6 [q, J(CF) 33, C4] and 123.8 [q, J(CF) 272 Hz, CF_3].

Compound **10a**: mp 98–100 °C; δ_H ($CDCl_3$) 7.71 (2 H, d) and 8.50 (1 H, s); δ_P ($CDCl_3$) −3.40; δ_F ($CDCl_3$) −63.6; δ_C ($CDCl_3$) 137.3 (18) (d, C1), 133.2 (21) (br d, C2), 132.8 (7) [qd, J(CF) 34, C3], 124.3 (m, C4) and 122.7 [q, J(CF) 273 Hz, CF_3].

Compound **11a**: mp 132–134 °C (Found: C, 62.0; H, 3.65. $C_{21}H_{15}F_6P$ requires C, 61.2; H, 3.67%); δ_H ($CDCl_3$) 6.56 (1 H, dd), 6.99 (2 H, dd), 7.05 (1 H, t), 7.15–7.50 (6 H, m), 7.75 (2 H, m) and 2.25 [3 H, d, J(PH) 1.1 Hz, CH_3]; δ_P ($CDCl_3$) −21.3 [sept, J(PF) 54 Hz]; δ_F ($CDCl_3$) −58.0 (d); δ_C ($CDCl_3$) (2-$CH_3C_6H_4$) 134.5 (13) (d, C1), 142.0 (28) (d, C2), 130.3 (5) (d, C3), 129.0 (s, C4), 126.2 (s, C5), 133.2 (s, C6) and 21.0 (23) (d, CH_3); (2-$CF_3C_6H_4$) 135.1 (30) (d, C1), 134.6 (27) [m, J(CF) 31, C2], 126.7 (6) [m, J(CF) 6, C3], 129.1 (s, C4), 131.6 (s, C5), 136.0 (s, C6) and 124.2 [q, J(CF) 275 Hz, CF_3].

Compound **12a**: mp 95–96 °C (Found: C, 70.2; H, 4.99. $C_{21}H_{18}F_3P$ requires C, 70.4; H, 5.07%); δ_H ($CDCl_3$) 6.63 (2 H, dd), 7.06 (1 H, t), 7.15–7.30 (5 H, m), 7.40 (1 H, m), 7.76 (1 H, dd) and 2.32 [6 H, d, J(PH) 0.9 Hz, Me]; δ_P ($CDCl_3$) −24.5 [q, J(PF) 53 Hz]; δ_F ($CDCl_3$) −58.1 (d); δ_C ($CDCl_3$) (2-$CH_3C_6H_4$) 134.5 (12) (d, C1), 142.3 (27) (d, C2), 130.2 (5) (d, C3), 128.8 (s, C4), 126.1 (s, C5), 133.0 (s, C6) and 21.1 (22) (d, CH_3); (2-$CF_3C_6H_4$) 135.6 (28) (d, C1), 135.1 (26) [m, J(CF) 30, C2], 126.4 (6) [m, J(CF) 6, C3], 128.9 (s, C4), 131.7 (s, C5), 136.4 (2) (d, C6) and 124.3 [q, J(CF) 275 Hz, CF_3].

Compound **13a**: δ_H ($CDCl_3$) 6.73 [H6, J(PH) 4.3], 7.05 [H5, J(PH) 1.5], 7.24 [H4, J(PH) 1.5], 7.21 [H3, J(PH) 1.5] and 2.39 [J(PH) 1.2 Hz, Me]; δ_P ($CDCl_3$) −29.1; δ_C ($CDCl_3$) 134.3 (10) (d, C1), 142.8 (26) (d, C2), 130.2 (5) (d, C3), 128.9 (s, C4), 126.3 (s, C5), 133.2 (s, C6) and 21.3 (22) (d, CH_3).

Compound **14a**: δ_H ($CDCl_3$) 7.03 (2 H, t) and 7.18–7.28 (2 H, m); δ_P ($CDCl_3$) −8.8; δ_F ($CDCl_3$) −112.4; δ_C ($CDCl_3$) 132.4 (6) [dd, J(CF) 3, C1], 135.3 (21) [dd, J(CF) 8, C2], 115.9 (8) [dd, J(CF) 21, C3] and 163.4 [d, J(CF) 250 Hz, C4].

(d) (2-$CH_3C_6H_4$)(2-$CF_3C_6H_4$)$_2$PO 11b. A solution of *m*-chloroperbenzoic acid (0.16 g, 0.92 mmol) in toluene (15 ml) was added dropwise to a stirred solution of (2-$CH_3C_6H_4$)-(2-$CF_3C_6H_4$)$_2$P (0.3 g, 0.73 mmol) in toluene (10 ml). After monitoring to completion by TLC (12 h), the solution was washed with 10% Na_2CO_3 solution (30 ml) and dried over $MgSO_4$. After removal of solvent, recrystallisation from ethanol–light petroleum (bp 60–80 °C) gave compound **11b** as white crystals (0.25 g, 80%). Spectroscopic data on **11b** and other oxides, together with analytical data for new compounds, are given below.

Compound **7b**: mp 252–255 °C; δ_H ($CDCl_3$) 7.28 (1 H, dd), 7.50 (1 H, t), 7.66 (1 H, t) and 7.90 (1 H, dd); δ_P ($CDCl_3$) 35.5; δ_F ($CDCl_3$) −57.0; δ_C ($CDCl_3$) 131.7 (102) [dq, J(CF) 2, C1], 133.6 (5) [qd, J(CF) 33, C2], 128.3 (9) [m, J(CF) 6, C3], 132.3 (3) (d, C4), 131.0 (13) (d, C5), 135.1 (11) (d, C6) and 123.4 (3) [qd, J(CF) 275 Hz, CF_3].

Compound **11b**: mp 192–195 °C (Found: C, 59.0; H, 3.37. $C_{21}H_{15}F_6OP$ requires C, 58.9; H, 3.53%); δ_H ($CDCl_3$) 6.79 (1 H, dd), 7.10–7.65 (7 H, m), 7.73 (2 H, t) and 7.93 (2 H, dd); δ_P ($CDCl_3$) 35.8; δ_F ($CDCl_3$) −57.1 and −57.3 (br); δ_C ($CDCl_3$) (2-$CH_3C_6H_4$) 130.6 (110) (d, C1), 143.7 (8) (d, C2), 133.3 (13) (d, C3), 132.2 (s, C4), 125.1 (14) (d, C5), 132.1 (10) (d, C6) and 22.0 (4) (d, CH_3); (2-$CF_3C_6H_4$) 128.3 (8) [m, J(CF) 6, C3], 131.9 (3) (d, C4), 131.1 (br, C5), 134.9 (10) (d, C6) and 123.4 (3) [qd, J(CF) 277 Hz, CF_3] (C1 and C2 are not seen and presumably broadened in the baseline).

Compound **12b**: mp 186–188 °C (Found: C, 67.6; H, 4.91. $C_{21}H_{18}F_3OP$ requires C, 67.4; H, 4.85%); δ_H ($CDCl_3$) 6.89 (2 H, dd), 7.13 (2 H, t), 7.3–7.6 (6 H, m), 7.70 (1 H, t) and 7.93 (1 H, dd); δ_P ($CDCl_3$) 37.9; δ_F ($CDCl_3$) −57.1; δ_C ($CDCl_3$) (2-$CH_3C_6H_4$) 130.7 (106) (d, C1), 143.6 (8) (d, C2), 132.9 (13) (d, C3), 132.0 (s, C4), 125.2 (13) (d, C5), 132.0 (13) (d, C6) and 21.9 (5) (d, CH_3); (2-$CF_3C_6H_4$) 131.9 (92) (d, C1), 133.8 (5) [qd, J(CF) 33, C2], 128.0 (8) [m, J(CF) 6, C3], 131.8 (3) (d, C4), 131.3 (12) (d, C5), 135.0 (11) (d, C6) and 123.4 (3) [qd, J(CF) 276 Hz, CF_3].

Compound **13b**: δ_H ($CDCl_3$) 7.10 [H6, J(PH) 14.3], 7.15 [H5, J(PH) 2.5], 7.42 [H4, J(PH) 1.6], 7.31 [H2, J(PH) 4.0 Hz] and 2.44 (CH_3); δ_P ($CDCl_3$) 37.5; δ_C ($CDCl_3$) 130.5 (102) (d, C1), 143.5 (8) (d, C2), 132.0 (11) (d, C3), 131.4 (3) (d, C4), 125.5 (13) (d, C5), 132.9 (13) (d, C6) and 22.0 (5) (d, CH_3).

(e) (2-$CH_3C_6H_4$)$_2$(2-$CF_3C_6H_4$)PSe 12d. A solution of (2-$CH_3C_6H_4$)(2-$CF_3C_6H_4$)$_2$P (0.3 g, 0.85 mmol) in $CHCl_3$ (10 ml) was refluxed with selenium powder (0.2 g, 2.56 mmol) for 3 d, after which time ^{31}P NMR analysis indicated an unchanging **12a**:**12d** ratio of 2:3. The suspension was filtered through Celite and the solvent removed. Purification by preparative TLC (1:9 ethyl acetate–light petroleum (bp 40–60 °C)) followed by recrystallisation from ethanol–light petroleum (bp 60–80 °C) gave off-white crystals of compound **12d** containing a 4% impurity of **12a**. Other selenides were prepared similarly. Spectroscopic data are given below, together with analytical data for new compounds.

Compound **9b**: mp 196–198 °C (decomp.) (Found: C, 46.7; H, 2.19. $C_{21}H_{12}F_9PSe$ requires C, 46.3; H, 2.22%); δ_H ($CDCl_3$) 7.6–7.9 (m); δ_P ($CDCl_3$) 34.9 [J(^{77}SeP) 765 Hz]; δ_F ($CDCl_3$) −63.7; δ_C ($CDCl_3$) 134.9 (92) (d, C1), 133.0 (12) (d, C2), 125.8 (14) [dq, J(CF) 4, C3], 134.0 (3) [qd, J(CF) 34, C4] and 123.3 [q, J(CF) 273 Hz, CF_3].

Compound **10b**: mp 147–149 °C (decomp.) (Found: C, 38.1; H, 1.08. $C_{24}H_9F_{18}PSe$ requires C, 38.5; H, 1.21%); δ_H ($CDCl_3$) 8.10 (2 H, s) and 8.15 (1 H, s); δ_P ($CDCl_3$) 33.9 [J(^{77}SeP) 802 Hz]; δ_F ($CDCl_3$) −63.5; δ_C ($CDCl_3$) 133.5 (80) (d, C1), 132.2 (13) (br d, C2), 132.6 (13) [qd, J(CF) 31, C3], 120.3 (m, C4) and 122.3 [q, J(CF) 274 Hz, CF_3].

Compound **12d**: mp 150–165 °C (decomp.) (Found: C, 56.7; H, 4.01. $C_{21}H_{18}F_3PSe$ requires C, 57.7; H, 4.15%); δ_H (CD_2Cl_2) 6.90–7.75 (10 H, m), 8.96 (2 H, dd) and 2.38 (s, CH_3); δ_P (CD_2Cl_2) 37.2 [J(^{77}SeP) 727 Hz]; δ_F (CD_2Cl_2) −53.4; δ_C ($CDCl_3$) (2-$CH_3C_6H_4$) 128.4 (78) (d, C1), 142.9 (11) (d, C2), 133.1 (12) (d, C3), 131.7 (3) (d, C4), 125.2 (13) (d, C5), 132.8 (12) (d, C6) and 23.0 (5) (d, CH_3); (2-$CF_3C_6H_4$) 128.3 (60) [dq, J(CF) 2, C1], 134.2 (13) [qd, J(CF) 43, C2], 128.2 (6) [m, J(CF) 6, C3], 132.0 (3) (d, C4), 132.1 (13) (d, C5), 139.7 (14) (d, C6) and 123.0 (2) [qd, J(CF) 275 Hz, CF_3].

(f) [Fe(CO)$_4${P(3-$CF_3C_6H_4$)$_3$}] 8c. To a solution of (3-CF_3-C_6H_4)$_3$P (0.4 g, 0.86 mmol) in diethyl ether (25 ml) was added [$Fe_2(CO)_9$] (0.63 g, 1.72 mmol). After stirring for 6 h the solution was filtered through Celite and the solvent removed under vacuum. After purification by column chromatography [Grade IV alumina, light petroleum (bp 40–60 °C)], recrystallisation from light petroleum (bp 60–80 °C) gave compound **8c**

Table 6 Crystallographic data

	7a	**7b**	**8c**	**9b**	**9c**	**10b**	**10c**	**11a**	**17a**
Formula	$C_{21}H_{12}F_9P$	$C_{21}H_{12}F_9OP$	$C_{25}H_{12}F_9FeO_4P$	$C_{21}H_{12}F_9PSe$	$C_{25}H_{12}F_9FeO_4P$	$C_{24}H_9F_{18}PSe$	$C_{28}H_9F_{18}FeO_4P$	$C_{21}H_{15}F_6P$	$C_{45}H_{24}F_{18}FeO_3P_2$
M	466.28	482.28	634.17	545.24	634.17	749.24	838.17	412.30	1072.4
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	15.962(3)	10.935(1)	12.738(2)	10.695(2)	9.3214(5)	12.4920(8)	11.7970(10)	15.721(5)	15.529(3)
b/Å	7.800(1)	12.1856(7)	9.2250(10)	15.799(4)	13.2317(7)	10.3510(12)	12.1030(10)	7.721(4)	18.720(4)
c/Å	17.328(4)	15.128(1)	22.305(4)	13.310(4)	20.2370(7)	21.697(3)	12.700(2)	17.073(6)	18.145(4)
α/°							90.250(10)		
β/°	107.600(10)	99.14(1)	103.87(2)	104.70(2)	94.904(3)	90.965(8)	114.980(10)	108.12(2)	111.50(5)
γ/°							89.810(10)		
U/Å^3	2056.4(7)	1990.2(3)	2544.6(7)	2175.4(9)	2486.9(2)	2805.1(5)	1643.7(3)	1969.6(14)	4907.8(2)
T/K	293(2)	293(2)	293(2)	294(2)	150(2)	293(2)	293(2)	293(2)	293(2)
Z	4	4	4	4	4	4	2	4	4
μ/mm^{-1}	0.218	0.232	0.753	1.882	0.770	1.530	0.643	0.197	0.478
Measured reflections	5251	5216	3373	4176	23859	4226	6151	3625	9769
Independent reflections	4957	4795	3114	3825	3544	3891	5762	3454	4971
*R*1	0.0683	0.0543	0.0450	0.0769	0.0558	0.0767	0.0803	0.0919	0.0992
*wR*2	0.1908	0.1526	0.1618	0.2050	0.1104	0.1101	0.2433	0.2551	0.2642

as yellow crystals (0.35 g, 64%). Other Fe(CO)$_4$ complexes were prepared similarly. Spectroscopic data are given below, together with analytical data for new compounds.

Compound **8c**: mp 79–80 °C (Found: C, 47.6; H, 1.84. $C_{25}H_{12}F_9FeO_4P$ requires C, 47.3; H, 1.91%); $\tilde{\nu}_{max}$/cm^{-1} (CO) 2051, 1983 and 1947 (hexane); δ_H (CDCl$_3$) 7.6–7.9 (4 H, m); δ_P (CDCl$_3$) 79.9; δ_F (CDCl$_3$) −63.5; δ_C (CD$_2$Cl$_2$) 134.5 (48) (d, C1), 129.9 (9) [dq, *J*(CF) 4, C2], 131.8 (12) [qd, *J*(CF) 33, C3], 128.8 (6) [m, *J*(CF) 6, C4], 130.3 (10) (d, C5), 136.8 (10) [dq, *J*(CF) 1.5, C6], 123.9 [q, *J*(CF) 273 Hz, CF$_3$] and 212.7 (19) (d, CO).

Compound **9c**: mp 159–161 °C (Found: C, 47.2; H, 1.83. $C_{25}H_{12}F_9FeO_4P$ requires C, 47.3; H, 1.91%); $\tilde{\nu}_{max}$/cm^{-1} (CO) 2051, 1985 and 1949 (hexane); δ_H (CDCl$_3$) 7.65 (2 H, t) and 7.77 (2H, d); δ_P (CDCl$_3$) 78.8; δ_F (CDCl$_3$) −62.1; δ_C (CD$_2$Cl$_2$) 137.5 (46) (d, C1), 134.0 (11) (d, C2), 126.3 (11) [m, *J*(CF) 5, C3], 133.6 (2) [qd, *J*(CF) 34, C4], 123.5 [q, *J*(CF) 273 Hz, CF$_3$] and 212.8 (19) (d, CO).

Compound **10c**: mp 118–120 °C (Found: C, 40.1; H, 1.03. $C_{28}H_9F_{18}FeO_4P$ requires C, 40.1; H, 1.08%); $\tilde{\nu}_{max}$/cm^{-1} (CO) 2063, 1995 and 1955 (hexane); δ_H (CDCl$_3$) 7.92 (2 H, d) and 8.11 (1 H, s); δ_P (CDCl$_3$) 84.9; δ_F (CDCl$_3$) −63.8; δ_C (CD$_2$Cl$_2$) 134.7 (46) (d, C1), 132.5 (12) (br d, C2), 132.9 (11) [qd, *J*(CF) 34, C3], 126.3 (m, C4), 122.3 [q, *J*(CF) 274 Hz, CF$_3$] and 210.7 (18) (d, CO).

Compound **13e**: $\tilde{\nu}_{max}$/cm^{-1} (CO) 2047, 1971 and 1943 (hexane); δ_H (CDCl$_3$) 7.05 (1 H, t), 7.16 (1 H, t), 7.35–7.50 (2 H, m); δ_P (CD$_2$Cl$_2$) 53.0; δ_C (CD$_2$Cl$_2$) 129.8 (43) (d, C1), 143.2 (11) (d, C2), 132.0 (s, C3, C6), 131.1 (s, C4), 125.9 (9) (d, C5), 23.9 (s, CH$_3$) and 214.6 (18) (d, CO).

Compound **14c**: mp 167–170 °C; $\tilde{\nu}_{max}$/cm^{-1} (CO) 2047, 1979 and 1947 (hexane); δ_H (CDCl$_3$) 7.11 (2 H, m) and 7.46 (2 H, m); δ_P (CDCl$_3$) 71.9; δ_F (CDCl$_3$) −108.3; δ_C (CD$_2$Cl$_2$) 129.9 (52) [dd, *J*(CF) 3, C1], 135.8 (12) [dd, *J*(CF) 9, C2], 116.5 (8) [dd, *J*(CF) 21, C3], 164.8 [d, *J*(CF) 256 Hz, C4] and 213.5 (19) (d, CO).

Compound **15**: mp 202–204 °C; $\tilde{\nu}_{max}$/cm^{-1} (CO) 2043, 1971 and 1937 (hexane); δ_H (CDCl$_3$) 7.38–7.50 (5 H, m); δ_P (CDCl$_3$) 71.9; δ_C (CD$_2$Cl$_2$) 133.9 (50) (d, C1), 133.1 (11) (d, C2), 128.6 (6) (d, C3), 130.9 (3) (d, C4) and 213.6 (19) (d, CO).

Compound **16**: mp 69–70 °C; $\tilde{\nu}_{max}$/cm^{-1} (CO) 2063, 1993 and 1953 (hexane); δ_H (CDCl$_3$) 7.1–7.5 (m); δ_P (CDCl$_3$) 175.7; δ_C (CD$_2$Cl$_2$) 150.4 (8) (d, C1), 121.3 (4) (d, C2), 129.7 (2) (d, C3), 125.6 (2) (d, C4) and 211.4 (22) (d, CO).

In situ infrared studies of complexation

To a solution of [Fe(CO)$_4$(PhCH=CH$_2$)][36] in toluene (15.8 mg in 25 ml, 2×10^{-3} M) under argon was added sufficient ligand to produce a concentration of 6×10^{-3} M. The solution was heated at 60 °C and aliquots removed periodically for analysis by FTIR. The extent of reaction was measured using the relative intensities of the a$_1$ vibration of [Fe(CO)$_4$L] and [Fe(CO)$_4$(PhCH=CH$_2$)] (2083 cm^{-1}).

Crystallographic studies

Crystallographic data are summarised in Table 6. Structures were solved by direct methods[37] and refined by full matrix least squares;[38a,b] SHELX operations were rendered paperless using ORTEX.[39] Data were corrected for Lorentz-polarisation effects, but not for absorption. For compound **10c** two of the unit cell angles are close to 90°, though the system is not monoclinic and all attempts to solve the structure in possible monoclinic space groups failed. For **11a** the CF$_3$ groups are disordered with the CH$_3$ group and were refined using C(7) 50% CF$_3$, C(14) 75% CF$_3$ and C(21) 75% CF$_3$. For **10b**, **10c** thermal parameters for the fluorine atoms were large, though attempts to use a disordered model for the CF$_3$ groups were not successful.

Cone angles in Table 2 were calculated from crystal structures after adjustment of the P–Fe distance to 2.28 Å or addition of an Fe atom to the free phosphine in cases where the crystal structure of the [Fe(CO)$_4$L] complex was not available. Van der Waals radii of 2.10 and 2.46 Å were used for CH$_3$ and CF$_3$ respectively.[40]

CCDC reference number 186/1546.

Molecular mechanics studies

Molecular mechanics calculations were performed using HYPERCHEM with a parameter set designed specifically for triarylphosphines. Full details will be published elsewhere.

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