

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

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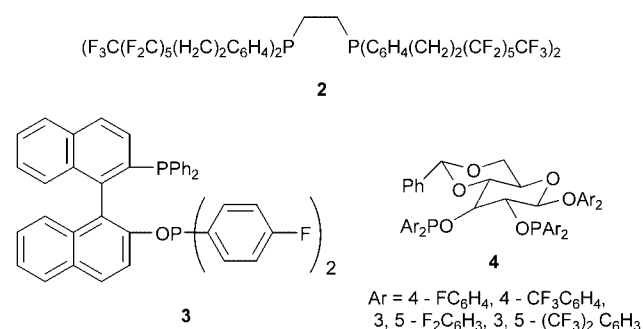
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A series of 2-, 3- or 4-trifluoromethyl substituted triarylphosphines and their oxide, chalcogenide and Fe(CO)₄ derivatives have been prepared and characterised spectroscopically and crystallographically. Electronic effects of CF₃ substitution are 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(CH₂CH₂-(CF₂)₅CF₃)₃, **1** and **2** for application in catalysis using fluororous media or supercritical CO₂ 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.

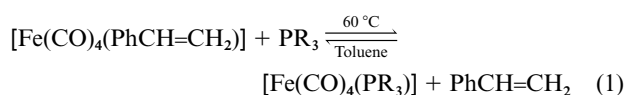
We report here our results on the effect of fluoro and trifluoromethyl substitution on the complexing properties of triarylphosphines towards Fe(CO)₄, together with studies on the stereodynamics of the *ortho*-substituted derivatives which have also yielded valuable information regarding the energetics 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 PCl₃. The mixed derivatives **11a** and **12a** were prepared similarly by reaction of 2-CF₃-C₆H₄Li with (2-CH₃C₆H₄)PCl₂ **5** and (2-CH₃C₆H₄)₂PCl **6** respectively.

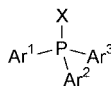
Stable oxides **7b**, **11b**, **12b** and **13b** are formed by all phosphines in the P(2-CH₃C₆H₄)_n(2-CF₃C₆H₄)_{3-n} (*n* = 0–3) series. In contrast, reaction with sulfur and selenium is restricted to the higher alkylated members **12a** and **13a**. While reactions of **13a** with S and Se under standard conditions⁵ 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 ³¹P 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 Fe₂(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 reaction⁶ (1). No substitution is observed with **7a**,



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 ₃ C ₆ H ₄	2-CF ₃ C ₆ H ₄	2-CF ₃ C ₆ H ₄
8a – c	X = lp, Se, Fe(CO) ₄	3-CF ₃ C ₆ H ₄	3-CF ₃ C ₆ H ₄	3-CF ₃ C ₆ H ₄
9a – c	X = lp, Se, Fe(CO) ₄	4-CF ₃ C ₆ H ₄	4-CF ₃ C ₆ H ₄	4-CF ₃ C ₆ H ₄
10a – c	X = lp, Se, Fe(CO) ₄	3, 5-(CF ₃) ₂ C ₆ H ₃	3, 5-(CF ₃) ₂ C ₆ H ₃	3, 5-(CF ₃) ₂ C ₆ H ₃
11a – c	X = lp, O, Fe(CO) ₄	2-CH ₃ C ₆ H ₄	2-CF ₃ C ₆ H ₄	2-CF ₃ C ₆ H ₄
12a – c	X = lp, O, S, Se, Fe(CO) ₄	2-CH ₃ C ₆ H ₄	2-CH ₃ C ₆ H ₄	2-CF ₃ C ₆ H ₄
13a – c	X = lp, O, S, Se, Fe(CO) ₄	2-CH ₃ C ₆ H ₄	2-CH ₃ C ₆ H ₄	2-CH ₃ C ₆ H ₄
14a – c	X = lp, Se, Fe(CO) ₄	4-FC ₆ H ₄	4-FC ₆ H ₄	4-FC ₆ H ₄
15	X = Fe(CO) ₄	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅
16	X = Fe(CO) ₄	OC ₆ H ₅	OC ₆ H ₅	OC ₆ H 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(PPh₃)] **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-CH₃C₆H₄)₃PSe adopts an *exo*₁ configuration, those of **8b** and **10b** are *exo*₂, in keeping with the reduced tendency of CF₃ to occupy an *endo* position (see below), though energy differences between *exolendo* 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 CH₃ by electron withdrawing CF₃, 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 δ(¹³CO) 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(OC₆H₅)₃ and P[3,5-(CF₃)₂C₆H₃]₃ are similar in their overall electronic interactions with Fe(CO)₄. DFT Calculations¹⁸ 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(C₆H₂(CH₃)₃-2,4,6)₃ does not.¹⁹

Selenium satellites generated by the ³¹P⁷⁷Se isotopomers (7.6% natural abundance) are readily observed in the ³¹P 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 CF₃ derivatives examined, J(PSe) values appear cumulative. Thus ΔJ (PSe) (relative to SePPh₃) for SeP(3,5-(CF₃)₂C₆H₃)₃ is twice that of SeP(3-CF₃C₆H₄)₃. For 4 substitution, the electron-withdrawing power of F is approximately one half to one third that of CF₃. 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 CH₃ increases in the order *m* < *p* < *o* while the electron withdrawing effect of the almost purely inductive CF₃ 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-(MeO)₃C₆H₂]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-CF₃C₆H₄)₃}]₂ **17a** as a minor component ($\tilde{\nu}_{\text{CO}}$ = 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(PPh₃)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} ≤ 6°) with opposite chirality of the triaryl helices, that of **17a** is staggered (C_{ipso}–P–P'–C'_{ipso} ≤ 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

† 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.

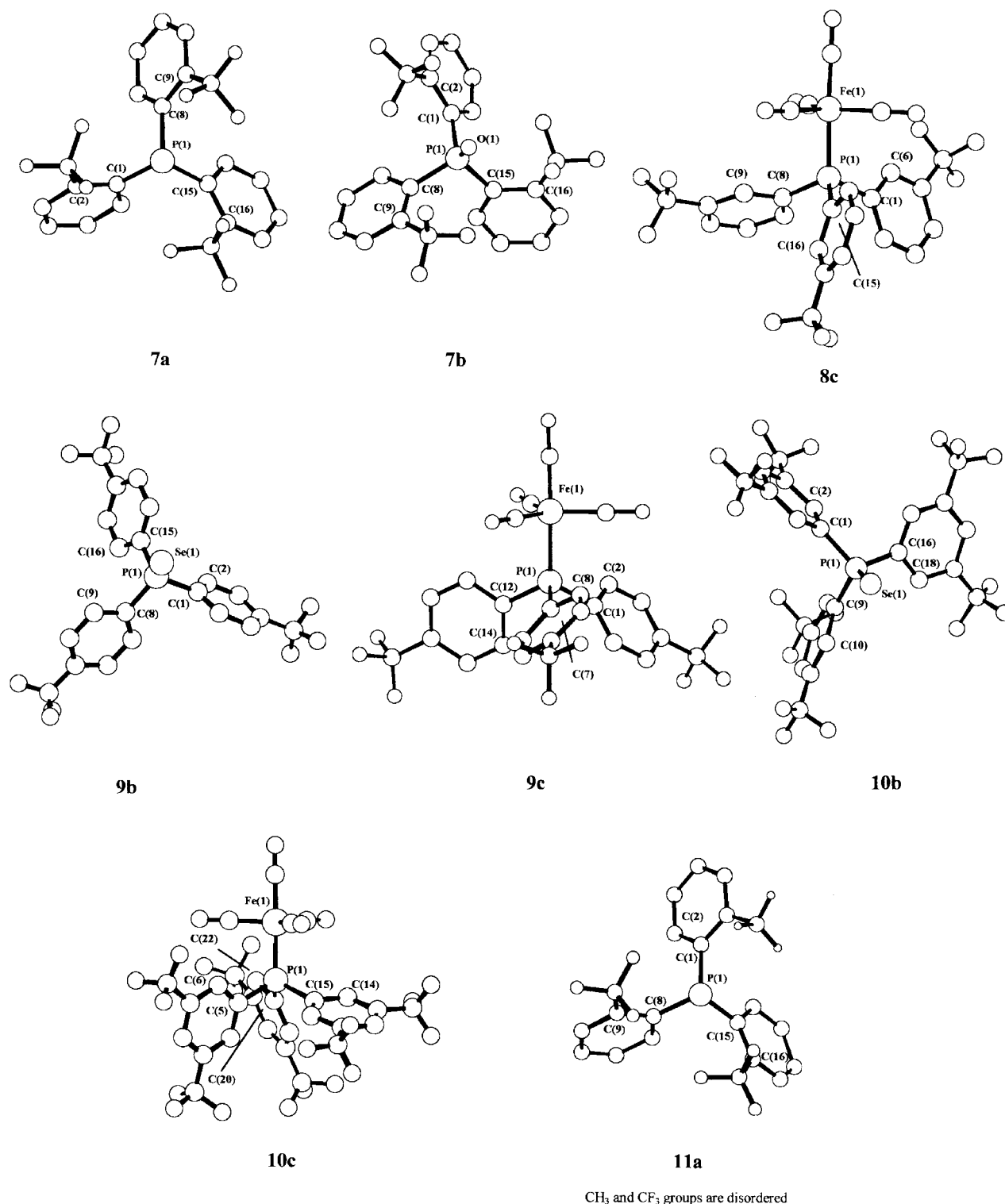


Fig. 1 Molecular structures of compounds 7a, 7b, 8c, 9b, 9c, 10b, 10c and 11a.

perpendicular T-shaped type, those in **17a** are almost exclusively of a parallel face-to-face arrangement. It may be noted that whereas $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ is conformationally identical to **17b**,^{12d} $[\text{Os}(\text{CO})_3(\text{PPh}_3)_2]$ has a staggered conformation similar to that of **17a** ($C_{\text{ipso}}\text{--P--P'}\text{--C'}_{\text{ipso}} = 48^\circ$) 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 $\text{Fe}(\text{CO})_4\text{L}$ 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 *exolendo* ring exchange

which has been previously observed for the 2- CH_3 substituted derivatives⁵ and in general for molecular propellers of the types Ar_3Z and Ar_3ZX .²²

Crystal structure determinations of various $\text{P}(2\text{-CH}_3\text{C}_6\text{H}_4)_3$ derivatives, including those reported herein, exhibit either *exo*₃²³ or *exo*₂²⁴ conformations. On the assumption that only these two isomers are populated, P–C rotational isomerism for an $\text{Ar}_2\text{Ar}'\text{PX}$ 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-

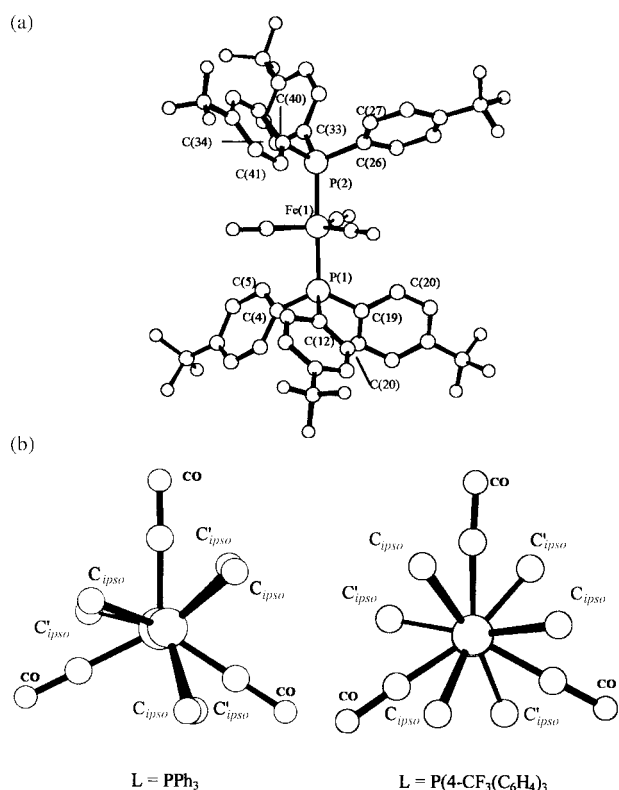
Table 1 Important structural parameters for **7a**, **7d**, **8c**, **9b**, **10b**, **10c**, **11a** and related compounds

Compound	$d(\text{P-X})/\text{\AA}$	$d(\text{P-C})/\text{\AA}$	$\text{C-P-C}/^\circ$	$\text{X-P-C}_{\text{ipso}}/^\circ$	$d(\text{Fe-C}_{\text{ax}})/\text{\AA}$	$d(\text{Fe-C}_{\text{eq}})/\text{\AA}$	$\text{P-Fe-C}_{\text{ax}}(\text{P})/^\circ$	$\text{P-Fe-C}_{\text{eq}}/^\circ$	$\text{C}_{\text{eq}}\text{-Fe-C}_{\text{eq}}/^\circ$	$\text{CO}_{\text{ax}}\text{-Fe-CO}_{\text{eq}}/^\circ$	Cone angle/ $^\circ$
$\text{P}(\text{2-CF}_3\text{C}_6\text{H}_4)_3$		1.84 ± 0.01	101.5 ± 0.4	35 ± 2							205
$\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)(\text{2-CF}_3\text{C}_6\text{H}_4)_2$		1.83 ± 0.02	101.9 ± 0.9	36 ± 2							203
$\text{OP}(\text{2-CF}_3\text{C}_6\text{H}_4)_3$	$1.471(1)$	1.831 ± 0.001	104.5 ± 2.2	42 ± 7							
$\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_3$ ⁷		1.835 ± 0.002	102.8 ± 0.8	42 ± 2							
$\text{OP}(\text{2-CH}_3\text{C}_6\text{H}_4)_3$ ⁷	$1.473(4)$	1.82 ± 0.01	105.4 ± 1.7	45 ± 7							
$\text{SeP}(\text{3-CF}_3\text{C}_6\text{H}_4)_3$ ⁸	$2.094(2)$	1.82 ± 0.02	105.6 ± 0.8	80 (<i>endo</i>)							
				22 (<i>exo</i>)							
				-6 (<i>exo</i>)							
$\text{SeP}(\text{3-CH}_3\text{C}_6\text{H}_4)_3$ ⁹	$2.1091(5)$	1.82 ± 0.05	106.5 ± 1.5	62 (<i>endo</i>)							
				28 (<i>endo</i>)							
				14 (<i>exo</i>)							
$\text{SeP}(\text{3,5-(CF}_3)_2\text{C}_6\text{H}_4)_3$	$2.085(1)$	1.821 ± 0.002	104.5 ± 0.6	85							
				18							
				-6							
$\text{SeP}(\text{4-CF}_3\text{C}_6\text{H}_4)_3$	$2.100(1)$	1.814 ± 0.004	105.3 ± 1.2	38 ± 5							
$[\text{Fe}(\text{CO})_4\{\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_3\}]^{10}$	$2.306(1)$	1.849 ± 0.009	103.3 ± 1.4	53 ± 4	$1.776(2)$		$178.9(2)$	120.0 ± 1.1	89.4 ± 0.8		165
$[\text{Fe}(\text{CO})_4\{\text{P}(\text{C}_6\text{H}_5)_3\}]^{11}$	$2.244(1)$	1.831 ± 0.001	103.9 ± 0.3	44 ± 3	$1.795(2)$						155
$[\text{Fe}(\text{CO})_4\{\text{P}(\text{3-CF}_3\text{C}_6\text{H}_4)_3\}]$	$2.234(1)$	1.835 ± 0.009	103.2 ± 0.1	64 (<i>exo</i>)	$1.786(5)$		$175.4(2)$	120.0 ± 5.3	90.3 ± 1.7		164
				25 (<i>endo</i>)							
				23 (<i>exo</i>)							
$[\text{Fe}(\text{CO})_4\{\text{P}(\text{4-CF}_3\text{C}_6\text{H}_4)_3\}]$	$2.245(1)$	1.835 ± 0.002	103.7 ± 0.8	35 ± 16	$1.772(7)$		$175.5(1)$	120.0 ± 2.8	89.8 ± 0.8		164
$[\text{Fe}(\text{CO})_4\{\text{P}(\text{3,5-(CF}_3)_2\text{C}_6\text{H}_4)_3\}]$	$2.210(1)$	1.828 ± 0.004	102.7 ± 0.8	69	$1.802(6)$		$178.7(2)$	120.0 ± 1.6	89.7 ± 1.5		160
				32							
				19							
$[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]^{12}$	$2.218(9)$	1.832 ± 0.008	102.5 ± 1.4	39 ± 19							
				-47 ± 15							
$[\text{Fe}(\text{CO})_3\{\text{P}(\text{4-CF}_3\text{C}_6\text{H}_4)_3\}_2]$	$2.204(4)$	1.831 ± 0.02	102.4 ± 1.4	43 ± 14	1.770 ± 0.006		$175.6(1)$	120.0 ± 3.5			162
				45 ± 12	1.773 ± 0.029		$178.7(1)$	120.0 ± 3.4			154

^a Number represents the average \pm one standard deviation of chemically equivalent bonds or angles.

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

Compound	$d(\text{P}=\text{Se})/\text{\AA}$	$d(\text{P}-\text{Fe})/\text{\AA}$	$J(\text{P}-\text{Se})/\text{Hz}$	$\nu(\text{CO})/\text{cm}^{-1}$	$\delta(^{13}\text{CO})$	σ_{m} or σ_{p}
$\text{P}(\text{2-CH}_3\text{OC}_6\text{H}_4)_3$ ¹⁴			720			
$\text{P}[\text{2,6-(CH}_3\text{O)}_2\text{C}_6\text{H}_3]_3$ ^{14,15}	2.135(3)		717			
$\text{P}(\text{4-CH}_3\text{OC}_6\text{H}_4)_3$ ¹⁴			710			−0.12
$\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_3$ ^{7,14}	2.116(5)	2.306(1)	703	2047	214.6	
$\text{P}(\text{3-CH}_3\text{C}_6\text{H}_4)_3$ ^{9,14}	2.109(5)		726			−0.06
$\text{P}(\text{4-CH}_3\text{C}_6\text{H}_4)_3$ ¹⁴			715			−0.14
$\text{P}(\text{C}_6\text{H}_5)_3$ ^{14,16}	2.112	2.244(1)	733	2050	213.6	0
$\text{P}(\text{4-FC}_6\text{H}_5)_3$ ¹⁷			741	2052	213.5	0.15
$\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)(\text{2-CF}_3\text{C}_6\text{H}_4)_2$				2052		
$\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_2(\text{2-CF}_3\text{C}_6\text{H}_4)$			727	2050		
$\text{P}(\text{3-CF}_3\text{C}_6\text{H}_4)_3$ ⁸	2.094(2)	2.234(1)	766	2057	212.7	0.46
$\text{P}(\text{4-CF}_3\text{C}_6\text{H}_4)_3$	2.100(1)	2.245(1)	765	2056	212.8	0.53
$\text{P}(\text{3,5-(CF}_3)_2\text{C}_6\text{H}_4)_3$	2.085(1)	2.210(1)	802	2065	210.7	
$\text{P}(\text{OC}_6\text{H}_5)_3$				2065	211.4	

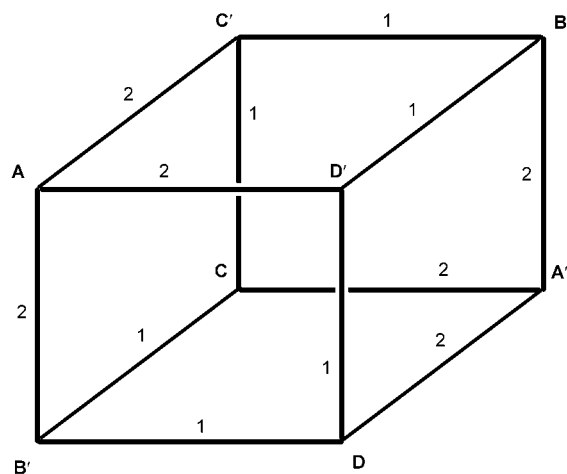
**Fig. 2** (a) Molecular structure of $[\text{Fe}(\text{CO})_3\{\text{P}(\text{4-CF}_3\text{C}_6\text{H}_4)_3\}_2]$. (b) View down P–P axis of $[\text{Fe}(\text{CO})_3\text{L}_2]$ [$\text{L} = \text{PPh}_3$ or $\text{P}(\text{4-CF}_3\text{C}_6\text{H}_4)_3$] (only *ipso* carbon of aryl ring shown).

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 CF₃ substitution. For the mixed derivatives, conformers with *endo* 2-CF₃C₆H₄ rings are less stable than those with *endo* 2-CH₃C₆H₄. 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.

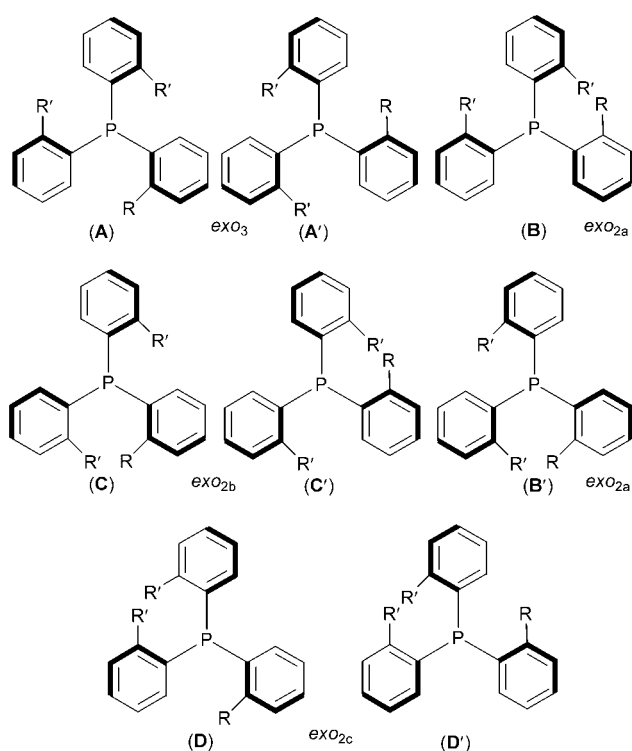
The ³¹P NMR spectra of all the phosphines exhibit a single ³¹P resonance down to −100 °C, indicative of either an exclusive population of *exo*₃ or an *exo*₂/*exo*₃ mixture in which interconversion remains fast on the NMR timescale. The essentially identical chemical shift of H6 for the 2-CH₃C₆H₄ (δ 6.56–6.73) and 2-CF₃C₆H₄ (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 PAr₃, it is required for exchange of chemically equivalent rings in PAr₂Ar' and can be observed experimentally in the broadening and resolution into two of the CF₃ (¹⁹F) and CH₃ (¹H) resonances of **11a** and **12a** respectively (Table 5, Fig. 3). The presence of long range P–F coupling in the 2-CF₃C₆H₄ 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 ³¹P 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 ¹⁹F spectrum of **7b** exhibits a single large resonance assignable to equivalent CF₃ groups of *exo*₃ together with three minor resonances due to the non-equivalent CF₃ 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 CF₃/CH₃ oxides **11b** and **12b**, line shape analysis of the higher temperature ¹⁹F and ¹H 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 CF₃-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 CF₃ substitution. In particular, the large linewidths in the ³¹P 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 CF₃ substitution. The influence of increasing CF₃ substitution on the increasing barrier to 3-ring flip in the oxides is much more substantial (*ca.* 12%), consistent with a more demanding oxygen–CF₃ as opposed to lone pair–CF₃ interaction in the presumed intermediate (**IV**).

In contrast to compounds **11b** and **12b**, the single room temperature ¹⁹F 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



$R = R' = \text{CF}_3$; $\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_3$ $R = \text{CF}_3$, $R' = \text{CH}_3$; $\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)(\text{2-CH}_3\text{C}_6\text{H}_4)_2$

$R = R' = \text{CH}_3$; $\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_3$ $R = \text{CH}_3$, $R' = \text{CF}_3$; $\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)(\text{2-CH}_3\text{C}_6\text{H}_4)_2$

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 $\text{OP}(\text{2-CH}_3\text{C}_6\text{H}_4)_3$ and $\text{SeP}(\text{2-CH}_3\text{C}_6\text{H}_4)_3$ ($\Delta\Delta G^\ddagger \approx 9 \text{ kcal mol}^{-1}$).⁵

The barrier for the higher temperature ring averaging process in compound **12d** may be determined from line shape analysis of the CH_3 (^1H) 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 \ll 1-ring, for the sulfide or selenide the ordering changes to 2-ring < 1-ring < 3-ring, and that $\text{C} \longleftrightarrow \text{C}'$ 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 $\text{XP}(\text{aryl})_3$ 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 ($\text{X} = \text{lp}$ or O) to 1-ring flip for larger substituents ($\text{X} = \text{Se}$).

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 $[\text{Fe}_2(\text{CO})_9]$ generate toxic, volatile $\text{Fe}(\text{CO})_5$ as a by-product. Care should be taken to trap this material when evaporating solutions.

The NMR spectra were recorded using either JEOL GSX270 (^1H , 270; ^{13}C , 68; ^{31}P , 109 MHz) or Bruker DPX300 (^1H , 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 (^1H , ^{13}C), 85% H_3PO_4 (^{31}P) and CFCl_3 (^{19}F); numbers in parentheses after ^{13}C chemical shifts represent $J(\text{P}–\text{C})$ 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 Sutherland²⁷ 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.

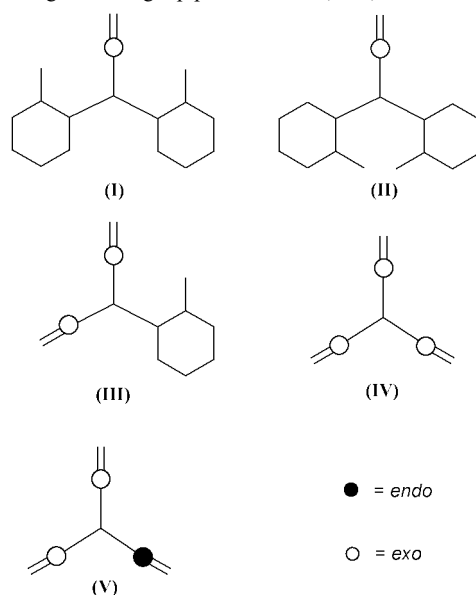
Diethyl ether and tetrahydrofuran were distilled from LiAlH_4 . Reactions involving lithium and magnesium reagents were conducted under argon. Excepting the preparation of phosphine oxides, other reactions were conducted under nitrogen. The phosphines 2-, 3- and 4- $\text{CF}_3\text{C}_6\text{H}_4)_3\text{P}$ ²⁸ and $[\text{3,5}-(\text{CF}_3)_2\text{C}_6\text{H}_3]_3\text{P}$ ²⁹ were prepared as described. The $[\text{Fe}(\text{CO})_4\text{L}]$ complexes of $(4\text{-FC}_6\text{H}_5)_3\text{P}$,³⁰ $(\text{2-CH}_3\text{C}_6\text{H}_4)_3\text{P}$,¹⁰ PPh_3 and $\text{P}(\text{OPh})_3$ ³¹ have previously been reported. Syntheses of **5**³² and **6**³³ were adapted from literature procedures.

Syntheses

(a) (2-CH₃C₆H₄)PCl₂ 5. A solution of the Grignard reagent $\text{2-CH}_3\text{C}_6\text{H}_4\text{MgBr}$ 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 $(\text{Et}_2\text{N})_2\text{PCl}$ (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 $(\text{Et}_2\text{N})_2\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)$ (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	$d(\text{P}-\text{C})/\text{\AA}$	$\text{C}-\text{P}-\text{C}/^\circ$	$\text{X}-\text{P}-\text{C}_{\text{ipso}}-\text{C}_{\text{a}}/^\circ$
$\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_2$	<i>exo</i> ₃	0	1.841	102.5	43
	<i>exo</i> ₂	2.3	1.842	103.4	20 (<i>endo</i>), 48, 55
$\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_2(\text{2-CF}_3\text{C}_6\text{H}_4)$	<i>exo</i> ₃	0	1.841	102.6	42
	<i>exo</i> _{2a}	4.3	1.842	104.0	21 (<i>endo</i>), 48, 56
	<i>exo</i> _{2b}	2.7	1.842	103.5	21 (<i>endo</i>), 48, 53
	<i>exo</i> _{2c}	2.7	1.841	103.5	26 (<i>endo</i>), 38, 57
	<i>exo</i> ₃	0	1.840	102.7	41
$\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)(\text{2-CF}_3\text{C}_6\text{H}_4)_2$	<i>exo</i> ₃	0	1.841	103.7	26 (<i>endo</i>), 40, 53
	<i>exo</i> _{2a}	3.1	1.841	103.7	26 (<i>endo</i>), 40, 53
	<i>exo</i> _{2b}	4.9	1.841	104.1	24 (<i>endo</i>), 44, 56
	<i>exo</i> _{2c}	4.3	1.842	104.1	21 (<i>endo</i>), 50, 53
	<i>exo</i> ₃	0	1.840	102.9	38
$\text{P}(\text{2-CF}_3\text{C}_6\text{H}_4)_3$	<i>exo</i> ₃	0	1.840	102.9	38
	<i>exo</i> ₂	4.7	1.841	104.3	25 (<i>endo</i>), 45, 53

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

Compound	Flip mechanism	Interconversion	Intermediate type	Energy/kcal
$\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_3$	2-ring	$\text{A} \longleftrightarrow \text{B}'$	III	3.0
	3-ring	$\text{A} \longleftrightarrow \text{A}'$	IV	8.1
	3-ring	$\text{B} \longleftrightarrow \text{B}'$	V	19.3
	1-ring	$\text{B} \longleftrightarrow \text{B}'$	I	12.1
	1-ring	$\text{B} \longleftrightarrow \text{B}'$	II	29.6
$\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_2(\text{2-CF}_3\text{C}_6\text{H}_4)$	2-ring	$\text{A} \longleftrightarrow \text{B}'$	III	4.2
	2-ring	$\text{A} \longleftrightarrow \text{C}'$	III	3.5
	2-ring	$\text{A} \longleftrightarrow \text{D}'$	III	3.5
	3-ring	$\text{A} \longleftrightarrow \text{A}'$	IV	8.8
	3-ring	$\text{B} \longleftrightarrow \text{B}'$	V	25.1
	3-ring	$\text{C/D} \longleftrightarrow \text{D'/C'}$	V	19.6
	1-ring	$\text{B} \longleftrightarrow \text{C}'$	II	35.4
	1-ring	$\text{C} \longleftrightarrow \text{C}'$	I	13.0
	1-ring	$\text{D} \longleftrightarrow \text{D}'$	II	30.4
	1-ring	$\text{B} \longleftrightarrow \text{D}'$	I	13.7
	2-ring	$\text{A} \longleftrightarrow \text{B}'$	III	4.9
	2-ring	$\text{A} \longleftrightarrow \text{C}'$	III	4.7
	2-ring	$\text{A} \longleftrightarrow \text{D}'$	III	5.0
$\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)(\text{2-CF}_3\text{C}_6\text{H}_4)_2$	3-ring	$\text{A} \longleftrightarrow \text{A}'$	IV	10.6
	3-ring	$\text{B} \longleftrightarrow \text{B}'$	V	20.7
	3-ring	$\text{C/D} \longleftrightarrow \text{C'/D'}$	V	25.1
	1-ring	$\text{B} \longleftrightarrow \text{C}'$	II	35.4
	1-ring	$\text{C} \longleftrightarrow \text{C}'$	I	16.4
	1-ring	$\text{D} \longleftrightarrow \text{D}'$	II	39.0
	1-ring	$\text{B} \longleftrightarrow \text{D}'$	I	14.5
	2-ring	$\text{A} \longleftrightarrow \text{B}'$	III	6.1
	3-ring	$\text{A} \longleftrightarrow \text{A}'$	IV	13.4
	3-ring	$\text{B} \longleftrightarrow \text{B}'$	V	25.4
	1-ring	$\text{B} \longleftrightarrow \text{B}'$	I	16.9
	1-ring	$\text{B} \longleftrightarrow \text{B}'$	II	38.2
$\text{P}(\text{2-CF}_3\text{C}_6\text{H}_4)_3$	2-ring	$\text{A} \longleftrightarrow \text{B}'$	III	6.1
	3-ring	$\text{A} \longleftrightarrow \text{A}'$	IV	13.4
	3-ring	$\text{B} \longleftrightarrow \text{B}'$	V	25.4
	1-ring	$\text{B} \longleftrightarrow \text{B}'$	I	16.9
	1-ring	$\text{B} \longleftrightarrow \text{B}'$	II	38.2

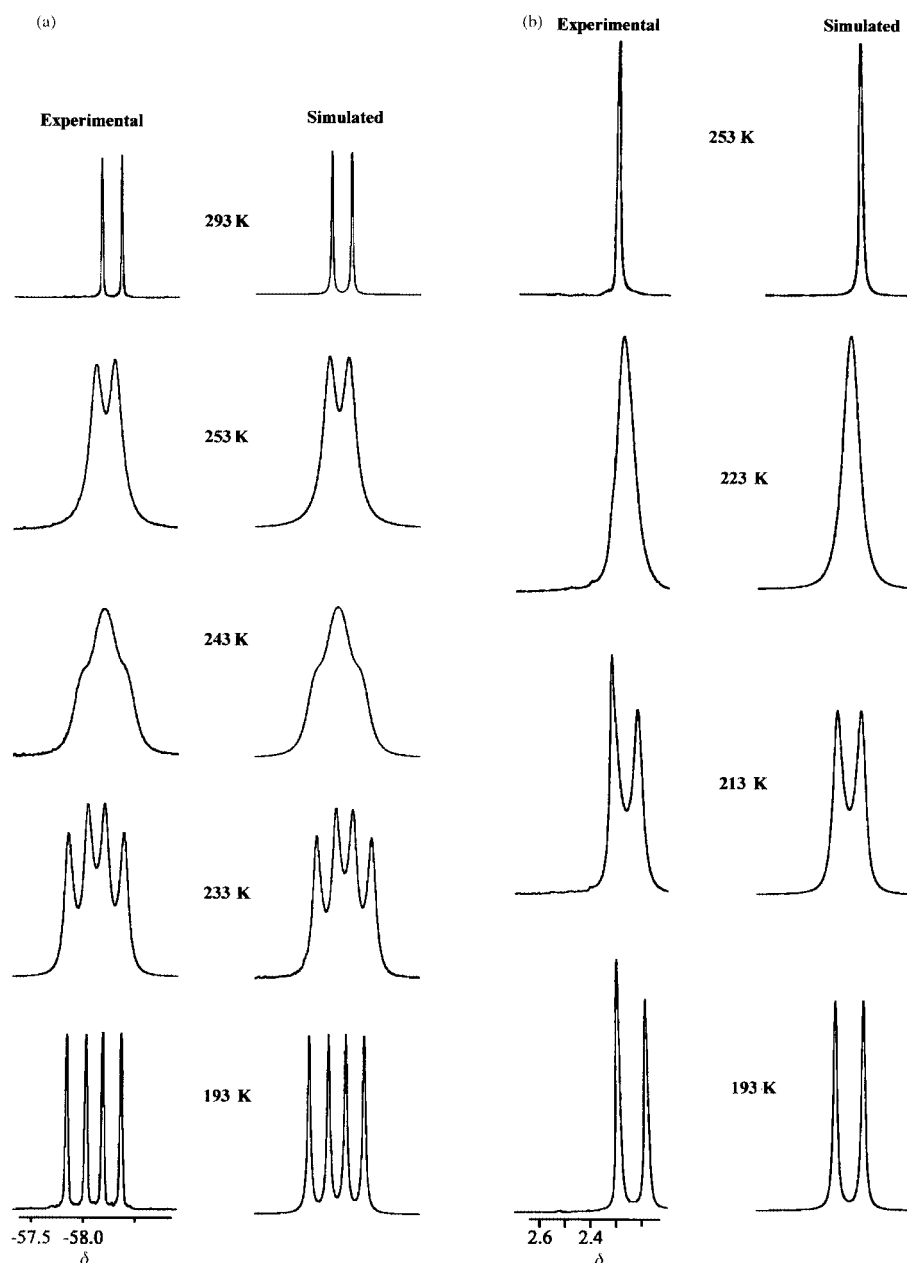


Fig. 3 Representative experimental and simulated variable temperature NMR spectra: (a) ^{19}F of compound **11a**; (b) ^1H of **12a**.

was bubbled through the solution for 3 h. After filtration of the copious precipitate of $[\text{Et}_2\text{NH}_2]\text{Cl}$ 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, $J(\text{PH})$ 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) $(2\text{-CH}_3\text{C}_6\text{H}_4)_2\text{PCl}$ **6.** A solution of the Grignard reagent $2\text{-CH}_3\text{C}_6\text{H}_4\text{MgCl}$ 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 $(2\text{-CH}_3\text{C}_6\text{H}_4)_2\text{PBr}$.] 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, $J(\text{PH})$ 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) $(2\text{-CH}_3\text{C}_6\text{H}_4)(2\text{-CF}_3\text{C}_6\text{H}_4)_2\text{P}$ **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*- $\text{BrC}_6\text{H}_4\text{CF}_3$ (3.6 g, 60.4 mmol) in diethyl ether (25 ml) at -10°C . After stirring for 30 min, $(2\text{-CH}_3\text{C}_6\text{H}_4)_2\text{PCl}_2$ (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 $(2\text{-CH}_3\text{C}_6\text{H}_4)_2\text{PCl}$.

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

Compound	$exo_2 \longrightarrow exo_3$ (minor \longrightarrow major)				Ring exchange (1- or 3-ring flip)			
	<i>T</i> /K	<i>K</i>	<i>k</i> /s ^{−1}	ΔG^\ddagger /kJ mol ^{−1}	<i>T</i> /K	<i>k</i> /s ^{−1}	ΔG^\ddagger /kJ mol ^{−1}	ΔH^\ddagger /kJ mol ^{−1} ΔS^\ddagger /J K ^{−1} mol ^{−1}
OP(2-CH ₃ C ₆ H ₄) ₃	163	3.0	600	30.4 ± 0.3	223	32	47.7 ± 0.8	
	173	2.7	2600	30.3 ± 0.3	233	75	48.1 ± 0.4	
	183	2.5	9300	30.3 ± 0.3	243	190	48.5 ± 0.4	
	193	2.3	25000	30.3 ± 0.3	253	500	48.5 ± 0.4	
	213	1.9	120000	30.8 ± 0.8	273	32000	48.5 ± 0.8	
OP(2-CF ₃ C ₆ H 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-CH ₃ C ₆ H ₄)(2-CF ₃ C ₆ H 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-CH ₃ C ₆ H ₄)(2-CF ₃ C ₆ H ₄) ₂	163	15	180	32.2 ± 0.4	273	20	59.8 ± 0.8	59 ± 4
	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	
P(2-CH ₃ C ₆ H ₄) ₂ (2-CF ₃ C ₆ H 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	
					213	25	46.0 ± 0.4	
					223	85	46.0 ± 0.4	
					233	250	46.0 ± 0.4	
					253	2800	44.7 ± 1.3	
	163	20	318	31.4 ± 0.8	223	1.7	53.1 ± 0.8	62 ± 5
	173	17	1500	31.0 ± 1.3	233	9.3	52.3 ± 0.4	
OP(2-CH ₃ C ₆ H ₄) ₂ (2-CF ₃ C ₆ H ₄)	193	13	20000	30.5 ± 1.3	243	33	51.9 ± 0.4	
					253	100	51.9 ± 1.3	
	193	85 (A)	450 (C \longrightarrow A)	36.8	183	11	40.5 ± 0.8	29 ± 8
		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	
SeP(2-CH ₃ C ₆ H ₄) ₂ (2-CF ₃ C ₆ H ₄)		2.6 (C)			233	370	45.2 ± 0.4	
	213	81	7100	36.0	253	2000	45.6 ± 0.8	
		10.3	2100	38.1	273	9000	46.0 ± 1.7	
		4.7	3000	37.2	293	27000	46.8 ± 1.7	
		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				

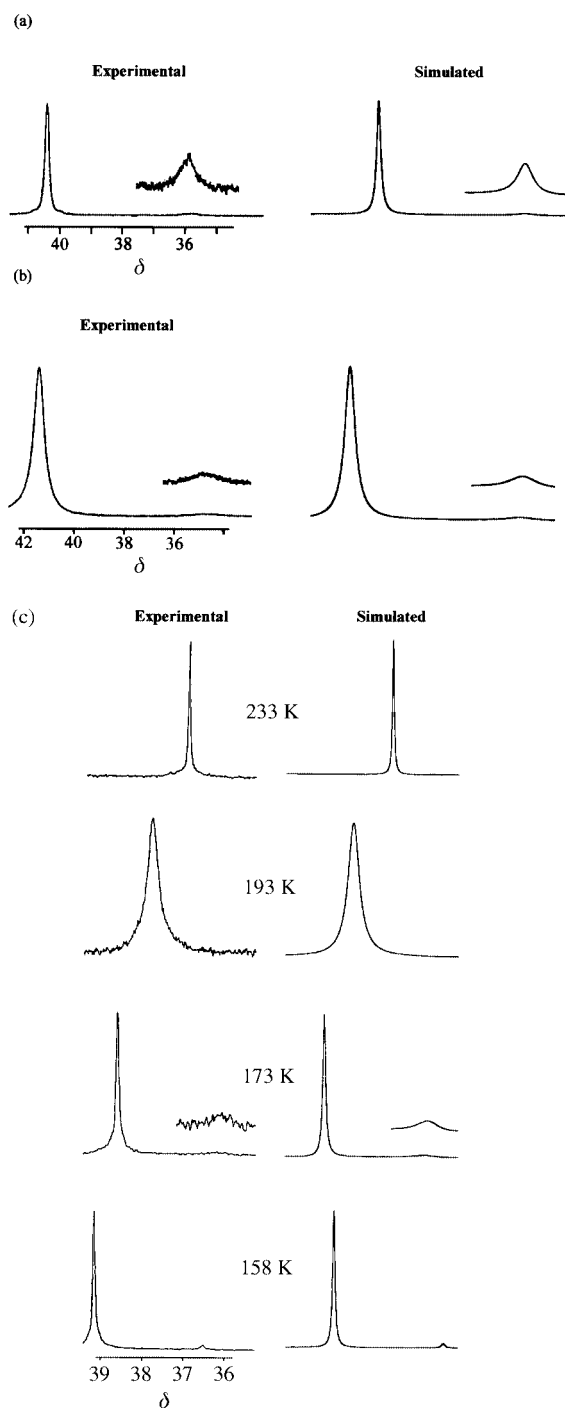


Fig. 4 Representative experimental and simulated ^{31}P NMR spectra: (a) compound **11b** at 164 K, (b) **12b** at 163 K and (c) **7b**.

spectra of **13a**, **13b** were assigned unambiguously by COSY and HeteroCOSY techniques; assignments of 2- $\text{CH}_3\text{C}_6\text{H}_4$ 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, $J(\text{PF})$ 55 Hz]; δ_{F} (CDCl_3) –57.9 (d); δ_{C} (CDCl_3) 134.8 (31) [dq, $J(\text{CF})$ 2, C1], 134.3 (27) [m, $J(\text{CF})$ 31, C2], 127.0 (6) [m, $J(\text{CF})$ 6, C3], 129.3 (s, C4), 131.6 (s, C5), 136.0 (s, C6) and 124.1 [q, $J(\text{CF})$ 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, $J(\text{CF})$ 4, C2], 131.3 (8) [qd, $J(\text{CF})$ 33, C3], 126.2 [q, $J(\text{CF})$ 4, C4], 129.4

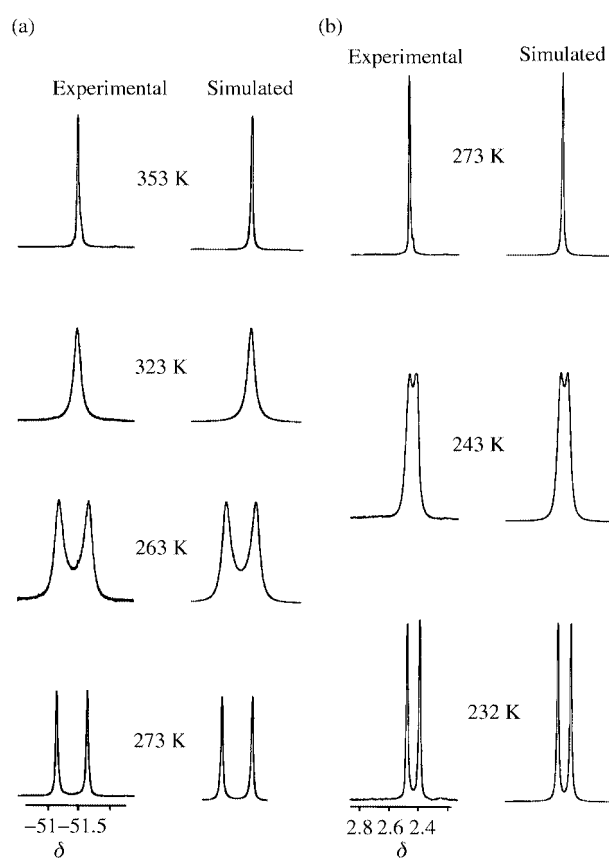


Fig. 5 Representative experimental and simulated NMR spectra: (a) ^{19}F of **11b**, (b) ^1H of **12b**.

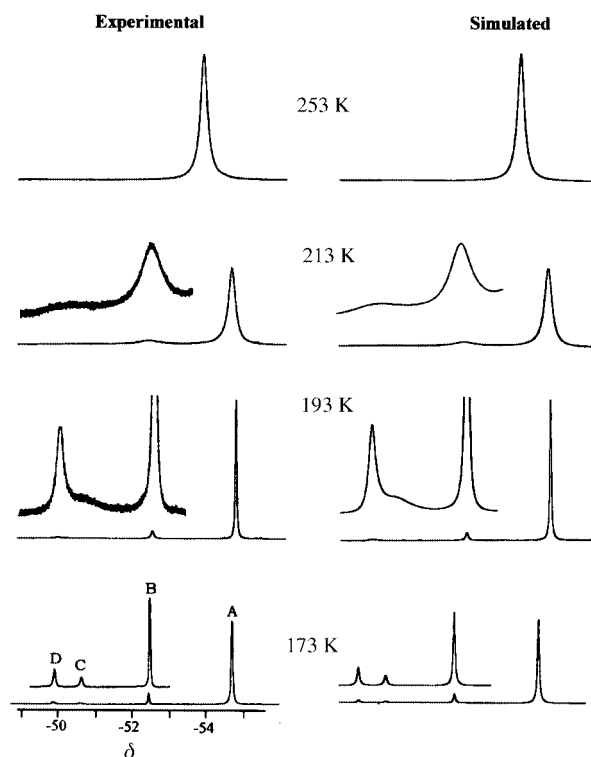


Fig. 6 Representative experimental and simulated variable temperature ^{19}F NMR spectra of compound **12b**.

(5) (d, C5), 136.7 (16) [dq, $J(\text{CF})$ 2, C6] and 123.8 [q, $J(\text{CF})$ 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)

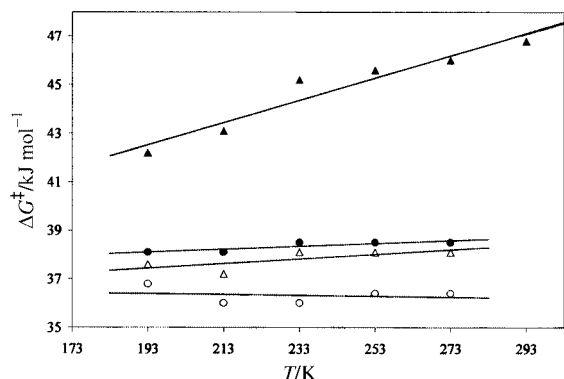


Fig. 7 Plots of ΔG^\ddagger against temperature for compound **12d**: ▲ complete aryl exchange process, ○ ($C \rightarrow A$) interconversion, ● ($C \rightarrow B$) interconversion and △ ($C \rightarrow D$) interconversion.

140.2 (14) (d, C1), 134.0 (20) (d, C2), 125.7 (8) [m, $J(\text{CF})$ 3, C3], 131.6 [q, $J(\text{CF})$ 33, C4] and 123.8 [q, $J(\text{CF})$ 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, $J(\text{CF})$ 34, C3], 124.3 (m, C4) and 122.7 [q, $J(\text{CF})$ 273 Hz, CF_3].

Compound **11a**: mp 132–134 °C (Found: C, 62.0; H, 3.65. $\text{C}_{21}\text{H}_{15}\text{F}_6\text{P}$ 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, $J(\text{PH})$ 1.1 Hz, CH_3]; δ_{P} (CDCl_3) –21.3 [sept, $J(\text{PF})$ 54 Hz]; δ_{F} (CDCl_3) –58.0 (d); δ_{C} (CDCl_3) (2- $\text{CH}_3\text{C}_6\text{H}_4$) 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- $\text{CF}_3\text{C}_6\text{H}_4$) 135.1 (30) (d, C1), 134.6 (27) [m, $J(\text{CF})$ 31, C2], 126.7 (6) [m, $J(\text{CF})$ 6, C3], 129.1 (s, C4), 131.6 (s, C5), 136.0 (s, C6) and 124.2 [q, $J(\text{CF})$ 275 Hz, CF_3].

Compound **12a**: mp 95–96 °C (Found: C, 70.2; H, 4.99. $\text{C}_{21}\text{H}_{18}\text{F}_3\text{P}$ 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, $J(\text{PH})$ 0.9 Hz, Me]; δ_{P} (CDCl_3) –24.5 [q, $J(\text{PF})$ 53 Hz]; δ_{F} (CDCl_3) –58.1 (d); δ_{C} (CDCl_3) (2- $\text{CH}_3\text{C}_6\text{H}_4$) 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- $\text{CF}_3\text{C}_6\text{H}_4$) 135.6 (28) (d, C1), 135.1 (26) [m, $J(\text{CF})$ 30, C2], 126.4 (6) [m, $J(\text{CF})$ 6, C3], 128.9 (s, C4), 131.7 (s, C5), 136.4 (2) (d, C6) and 124.3 [q, $J(\text{CF})$ 275 Hz, CF_3].

Compound **13a**: δ_{H} (CDCl_3) 6.73 [H6, $J(\text{PH})$ 4.3], 7.05 [H5, $J(\text{PH})$ 1.5], 7.24 [H4, $J(\text{PH})$ 1.5], 7.21 [H3, $J(\text{PH})$ 1.5] and 2.39 [$J(\text{PH})$ 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, $J(\text{CF})$ 3, C1], 135.3 (21) [dd, $J(\text{CF})$ 8, C2], 115.9 (8) [dd, $J(\text{CF})$ 21, C3] and 163.4 [d, $J(\text{CF})$ 250 Hz, C4].

(d) (2- $\text{CH}_3\text{C}_6\text{H}_4$)(2- $\text{CF}_3\text{C}_6\text{H}_4$)**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- $\text{CH}_3\text{C}_6\text{H}_4$)-(2- $\text{CF}_3\text{C}_6\text{H}_4$)**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, $J(\text{CF})$ 2, C1], 133.6 (5) [qd, $J(\text{CF})$ 33, C2], 128.3 (9) [m, $J(\text{CF})$ 6, C3], 132.3

(3) (d, C4), 131.0 (13) (d, C5), 135.1 (11) (d, C6) and 123.4 (3) [qd, $J(\text{CF})$ 275 Hz, CF_3].

Compound **11b**: mp 192–195 °C (Found: C, 59.0; H, 3.37. $\text{C}_{21}\text{H}_{15}\text{F}_6\text{OP}$ 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- $\text{CH}_3\text{C}_6\text{H}_4$) 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- $\text{CF}_3\text{C}_6\text{H}_4$) 128.3 (8) [m, $J(\text{CF})$ 6, C3], 131.9 (3) (d, C4), 131.1 (br, C5), 134.9 (10) (d, C6) and 123.4 (3) [qd, $J(\text{CF})$ 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. $\text{C}_{21}\text{H}_{18}\text{F}_3\text{OP}$ 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- $\text{CH}_3\text{C}_6\text{H}_4$) 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- $\text{CF}_3\text{C}_6\text{H}_4$) 131.9 (92) (d, C1), 133.8 (5) [qd, $J(\text{CF})$ 33, C2], 128.0 (8) [m, $J(\text{CF})$ 6, C3], 131.8 (3) (d, C4), 131.3 (12) (d, C5), 135.0 (11) (d, C6) and 123.4 (3) [qd, $J(\text{CF})$ 276 Hz, CF_3].

Compound **13b**: δ_{H} (CDCl_3) 7.10 [H6, $J(\text{PH})$ 14.3], 7.15 [H5, $J(\text{PH})$ 2.5], 7.42 [H4, $J(\text{PH})$ 1.6], 7.31 [H2, $J(\text{PH})$ 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- $\text{CH}_3\text{C}_6\text{H}_4$)(2- $\text{CF}_3\text{C}_6\text{H}_4$)**PSe 12d**. A solution of (2- $\text{CH}_3\text{C}_6\text{H}_4$)(2- $\text{CF}_3\text{C}_6\text{H}_4$)**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. $\text{C}_{21}\text{H}_{12}\text{F}_9\text{PSe}$ requires C, 46.3; H, 2.22%); δ_{H} (CDCl_3) 7.6–7.9 (m); δ_{P} (CDCl_3) 34.9 [$J(^{77}\text{SeP})$ 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, $J(\text{CF})$ 4, C3], 134.0 (3) [qd, $J(\text{CF})$ 34, C4] and 123.3 [q, $J(\text{CF})$ 273 Hz, CF_3].

Compound **10b**: mp 147–149 °C (decomp.) (Found: C, 38.1; H, 1.08. $\text{C}_{24}\text{H}_9\text{F}_{18}\text{PSe}$ 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 [$J(^{77}\text{SeP})$ 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, $J(\text{CF})$ 31, C3], 120.3 (m, C4) and 122.3 [q, $J(\text{CF})$ 274 Hz, CF_3].

Compound **12d**: mp 150–165 °C (decomp.) (Found: C, 56.7; H, 4.01. $\text{C}_{21}\text{H}_{18}\text{F}_3\text{PSe}$ 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 [$J(^{77}\text{SeP})$ 727 Hz]; δ_{F} (CD_2Cl_2) –53.4; δ_{C} (CDCl_3) (2- $\text{CH}_3\text{C}_6\text{H}_4$) 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- $\text{CF}_3\text{C}_6\text{H}_4$) 128.3 (60) [dq, $J(\text{CF})$ 2, C1], 134.2 (13) [qd, $J(\text{CF})$ 43, C2], 128.2 (6) [m, $J(\text{CF})$ 6, C3], 132.0 (3) (d, C4), 132.1 (13) (d, C5), 139.7 (14) (d, C6) and 123.0 (2) [qd, $J(\text{CF})$ 275 Hz, CF_3].

(f) $[\text{Fe}(\text{CO})_4\{\text{P}(\text{3-}\text{CF}_3\text{C}_6\text{H}_4)_3\}]$ **8c**. To a solution of (3- $\text{CF}_3\text{C}_6\text{H}_4$)**P** (0.4 g, 0.86 mmol) in diethyl ether (25 ml) was added $[\text{Fe}_2(\text{CO})_9]$ (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 ₉ P	C ₂₁ H ₁₂ F ₉ OP	C ₂₅ H ₁₂ F ₉ FeO ₄ P	C ₂₁ H ₁₂ F ₉ PSe	C ₂₅ H ₁₂ F ₉ FeO ₄ P	C ₃₄ H ₉ F ₁₈ PSe	C ₂₈ H ₉ F ₁₈ FeO ₄ P	C ₂₁ H ₁₅ F ₉ P	C ₄₅ H ₂₄ F ₁₈ FeO ₃ P ₂
<i>M</i>	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	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /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)
<i>b</i> /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)
<i>c</i> /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)
<i>a</i> / <i>b</i>							90.250(10)		
<i>β</i> /°		99.14(1)	103.87(2)	104.70(2)	94.904(3)	90.965(8)	114.980(10)	108.12(2)	111.50(5)
<i>V</i> /Å ³		1990.2(3)	2544.6(7)	2175.4(9)	2486.9(2)	2805.1(5)	89.810(10)	1969.6(14)	4907.8(2)
<i>T</i> /K	293(2)	293(2)	293(2)	294(2)	150(2)	293(2)	293(2)	293(2)	293(2)
<i>Z</i>	4	4	4	4	4	4	2	4	4
<i>d</i> /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
<i>R</i>	0.0683	0.0543	0.0450	0.0769	0.0558	0.0767	0.0803	0.0919	0.0992
<i>wR</i>	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 $\text{Fe}(\text{CO})_4$ 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. $\text{C}_{25}\text{H}_{12}\text{F}_9\text{FeO}_4\text{P}$ requires C, 47.3; H, 1.91%); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (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_2Cl_2) 134.5 (48) (d, C1), 129.9 (9) [dq, $J(\text{CF})$ 4, C2], 131.8 (12) [qd, $J(\text{CF})$ 33, C3], 128.8 (6) [m, $J(\text{CF})$ 6, C4], 130.3 (10) (d, C5), 136.8 (10) [dq, $J(\text{CF})$ 1.5, C6], 123.9 [q, $J(\text{CF})$ 273 Hz, CF_3] and 212.7 (19) (d, CO).

Compound **9c**: mp 159–161 °C (Found: C, 47.2; H, 1.83. $\text{C}_{25}\text{H}_{12}\text{F}_9\text{FeO}_4\text{P}$ requires C, 47.3; H, 1.91%); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (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_2Cl_2) 137.5 (46) (d, C1), 134.0 (11) (d, C2), 126.3 (11) [m, $J(\text{CF})$ 5, C3], 133.6 (2) [qd, $J(\text{CF})$ 34, C4], 123.5 [q, $J(\text{CF})$ 273 Hz, CF_3] and 212.8 (19) (d, CO).

Compound **10c**: mp 118–120 °C (Found: C, 40.1; H, 1.03. $\text{C}_{28}\text{H}_9\text{F}_{18}\text{FeO}_4\text{P}$ requires C, 40.1; H, 1.08%); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (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_2Cl_2) 134.7 (46) (d, C1), 132.5 (12) (br d, C2), 132.9 (11) [qd, $J(\text{CF})$ 34, C3], 126.3 (m, C4), 122.3 [q, $J(\text{CF})$ 274 Hz, CF_3] and 210.7 (18) (d, CO).

Compound **13c**: $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (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_2Cl_2) 53.0; δ_{C} (CD_2Cl_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; $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (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_2Cl_2) 129.9 (52) [dd, $J(\text{CF})$ 3, C1], 135.8 (12) [dd, $J(\text{CF})$ 9, C2], 116.5 (8) [dd, $J(\text{CF})$ 21, C3], 164.8 [d, $J(\text{CF})$ 256 Hz, C4] and 213.5 (19) (d, CO).

Compound **15**: mp 202–204 °C; $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (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_2Cl_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; $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (CO) 2063, 1993 and 1953 (hexane); δ_{H} (CDCl_3) 7.1–7.5 (m); δ_{P} (CDCl_3) 175.7; δ_{C} (CD_2Cl_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 $[\text{Fe}(\text{CO})_4(\text{PhCH}=\text{CH}_2)]^{36}$ 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 $[\text{Fe}(\text{CO})_4\text{L}]$ and $[\text{Fe}(\text{CO})_4(\text{PhCH}=\text{CH}_2)]$ (2083 cm^{-1}).

Crystallographic studies

Crystallographic data are summarised in Table 6. Structures were solved by direct methods³⁷ and refined by full matrix least squares.^{38a,b} SHELX operations were rendered paperless using ORTEP.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 $[\text{Fe}(\text{CO})_4\text{L}]$ 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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