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Synthesis and characterisation of trisarylphosphine selenides: Further insight into the effect of fluoroalkylation on the electronic properties of trisarylphosphines

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Abstract

Variations in the magnitude of the $^1J_{SeP}$ coupling constants for a range of phosphorus(V) selenides allow the efficiency of different spacer groups at insulating the phosphorus centre in triarylphosphines from highly electron-withdrawing perfluoroalkyl groups to be established.

Keywords: Phosphine; Fluorous; NMR; Selenide

1. Introduction

Since the introduction of the fluorous biphase approach to catalyst/product separation in homogeneous catalysis by Horváth and Rábai, [1] phosphines, as modifying ligands for metal catalysts, have received substantially more interest than any other ligand class, with applications including hydrogenation, [2] hydrosilylation [3] and palladium-catalysed cross-coupling reactions [4]. Throughout, preferential solubility of the ligand in the perfluorocarbon (or fluorous) solvent is achieved by derivatising the catalyst with so-called perfluorocarbon ‘ponytails’, such that the catalyst in the fluorous solvent can be recycled by a simple phase separation following the reaction. To-date, work has focussed on two key ligand properties: Firstly, since preferential solubility in the perfluorocarbon solvents is critical, the solubilising power of different groups has been evaluated, [5] and there have been a number of attempts at maximising the number of ponytails present [6]. Secondly, the high electron-withdrawing ability of the perfluorocarbon groups has led many to attempt to minimise this effect on the phosphorus centre of the triarylphosphine by the introduction of so-called ‘spacer groups’, including the aromatic ring itself, [7] as well as additional alkyl groups such as CH_2CH_2 [8] and the incorporation of a heteroatom such as oxygen [9] or silicon [10]. In this regard, theoretical calculations, on trialkylphosphines, suggest that five methylene spacer units are necessary to completely eliminate the electronic influence of the perfluoroalkyl units [11]. The effect of the perfluoroalkyl groups on the electronic properties of the donor phosphine has been probed experimentally, but work is limited to variations in ν_{CO} in a few analogues of Vaska’s complex [12] and $^1J_{PtP}$ coupling constants for some *cis*-[$PtCl_2L_2$] complexes [13,14]. Systematic comparisons have not been possible for a variety of reasons, including variations in approach/procedure by different groups, the absence of specific complexes or questions over the significance of steric/electronic factors, particularly for bulky ligands. An alternative, valuable, method for probing the effect of substitution on the aryl rings of triarylphosphines is the $|^1J_{SeP}|$ coupling

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constant [15] of the corresponding phosphorus(V) selenide, [16,17] prepared by the oxidation of the phosphine with elemental selenium, where phosphorus(V) selenides incorporating electron-withdrawing groups exhibit larger coupling constants that those for phosphorus(V) selenides incorporating electron-donating groups. Here, we report data for a comprehensive series of phosphorus(V) selenides, which offer a clearer insight into the effect of perfluoroalkyl groups on the electronic properties of phosphines used in fluorous catalysis.

2. Experimental

Proton, ^{19}F and ^{31}P NMR spectroscopies were carried out on a Bruker ARX250 spectrometer at 250.13, 235.34 and 101.26 MHz or a Bruker DPX300 spectrometer at 300.14, 282.41 and 121.50 MHz, respectively, and were referenced to external $SiMe_4$ (^{1}H), external $CFCl_3$ (^{19}F) and to external H_3PO_4 (^{31}P) using the high frequency positive convention. Abbreviations for NMR spectral multiplicities are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Elemental analyses were performed by the Elemental Analysis Service at the University of North London. Mass spectra were recorded on a Kratos Concept 1H mass spectrometer.

$P(4\text{-}C_6H_4R)_3$ (R = H, F, Cl, Me, OMe and NMe_2) and BINAP were commercial samples and used as received, whilst *cis*-$[PtCl_2(MeCN)_2]$ was prepared by the literature route [18].

2.1. General procedure for the preparation of phosphines

n-BuLi (2.0 mmol, 1.6 M solution in hexane) was added dropwise over 1 h to a solution of the required bromobenzene (2.0 mmol) in diethyl ether at −78 °C. This solution was then stirred at −78 °C for 3 h. The requisite chlorophosphine (2.0 mmol for diphenylchlorophosphines, 1.0 mmol for dichlorophenylphosphines or 0.66 mmol for PCl_3) was then added dropwise in a solution of diethyl ether over 1 h and the solution allowed to warm to room temperature overnight. The solution was then washed well with water, the organic layer separated, dried and the solvent removed in vacuo. The resulting phosphine was purified by column chromatography using petroleum ether as the eluent. Uniquely, **1f** was prepared by a modification of the literature route for **3f**, [6b] by the reaction of the chlorosilane with the lithiate formed from the reaction of $Ph_2P(C_6H_4\text{-}4\text{-}Br)$ with BuLi at low temperature in diethylether. Many of the phosphines prepared in this work have been described previously (**1b**, [7]; **2b**, [7]; **3a**, [15]; **3b**, [7]; **3d**, [8b]; **3e**, [11]; **3f**, [6b]; **3g**, [9a]; **3h**, [9b]; **3j**, [19]; **3k**, [20]; **3l**, [21]; **4b**, [14]; **5b**, [14]; **6b**, [22]; **7a**, [23]; **7b**, [24]; **7c**, [24]; **8a**, [24]; **8b**, [24]; **9a**, [22,23]; **10a**, [24]; **10b**, [24]; **11b**, [25]; **11d**, [25]), and here we just report data for new ligands and additional data for established species where appropriate.

2.1.1. 4-(Trifluoromethylphenyl)diphenylphosphine (*1a*)

M.p. = 53–54 °C (Lit. 51–53 °C) [26]. *m*/*z* (FAB) 330 (M^+). ^{1}H NMR ($CDCl_3$) 7.50 (2H, d, $^3J_{HH}$ 10.0, ArH), 7.30 (2H, d, $^3J_{HH}$ 10.0, ArH), 7.28 (10H, m, ArH). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −63.20 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$) −5.4 (s).

2.1.2. 4-(Heptadecafluoro-n-octylphenyl)diphenylphosphine (*1c*)

M.p. = 89–91 °C. *Anal.* Calc. for $C_{26}H_{14}F_{17}P$: C, 45.88; H, 2.06. Found: C, 45.89; H, 1.95%. *m*/*z* (FAB) 680 (M^+). ^{1}H NMR ($CDCl_3$) 7.45 (2H, d, $^3J_{HH}$ 8.0, ArH), 7.31 (12H, m, ArH). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −80.76 (3F, t, $^4J_{FF}$ 10.0, CF_3), −110.78 (2F, t, $^4J_{FF}$ 14.4, α-CF_2), −121.21 (2F, m, CF_2), −121.84 (6F, m, 3 × CF_2), −122.68 (2F, m, CF_2), −126.12 (2F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) −5.4 (s).

2.1.3. 4-(1H,1H,2H,2H-tridecafluoro-n-octyldimethylsilylphenyl)diphenylphosphine (*1f*)

M.p. = 186 °C dec. *Anal.* Calc. for $C_{28}H_{24}F_{13}PSi$: C, 50.37; H, 3.60. Found: C, 50.51; H, 3.58%. *m*/*z* (FAB) 667 (MH^+). ^{1}H NMR ($CDCl_3$) 7.31 (2H, dd, $^3J_{PH}$ 10.9, $^3J_{HH}$ 8.0, ArH-2,6), 7.20 (12H, m, ArH), 1.87 (2H, m, CH_2), 0.85 (2H, m, CH_2Si), 0.18 (6H, s, CH_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.30 (3F, t, $^4J_{FF}$ 10.1, CF_3), −116.45 (2F, t, $^4J_{FF}$ 14.0, α-CF_2), −122.48 (2F, m, CF_2), −123.40 (2F, m, CF_2), −123.66 (2F, m, CF_2), −126.67 (2F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) −5.7 (s).

2.1.4. Tris-(4-heptadecafluoro-n-octylphenyl)phosphine (*3c*)

M.p. = 92 °C (Lit. 92–95 °C) [27]. *m*/*z* (FAB) 1516 (M^+). ^{1}H NMR ($CDCl_3$) 7.53 (6H, d, $^3J_{HH}$ 7.9, ArH-3,5), 7.35 (6H, t, $^3J_{HH}$ 7.7, $^3J_{PH}$ 7.7, ArH-2,6). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −80.76 (9F, t, $^4J_{FF}$ 8.9, CF_3), −110.99 (6F, t, $^4J_{FF}$ 14.0, α-CF_2), −121.17 (6F, m, CF_2), −121.72 (18F, m, 3 × CF_2), −122.67 (6F, m, CF_2), −126.08 (6F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) −6.2 (s).

2.1.5. 3-(Heptadecafluoro-n-octylphenyl)diphenylphosphine (*4c*)

Oil. *Anal.* Calc. for $C_{26}H_{14}F_{17}P$: C, 45.88; H, 2.06. Found: C, 45.72; H, 2.00%. *m*/*z* (FAB) 680 (M^+). ^{1}H NMR ($CDCl_3$) 7.46 (2H, m, ArH), 7.37 (2H, m, ArH), 7.22 (10H, m, ArH). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −80.78 (3F, t, $^4J_{FF}$ 10.0, CF_3), −110.89 (2F, t, $^4J_{FF}$ 14.2, α-CF_2), −121.31 (2F, m, CF_2), −122.04 (6F, m, 3 × CF_2), −122.78 (2F, m, CF_2), −126.20 (2F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) −5.1 (s).

2.1.6. Tris-(3-heptadecafluoro-n-octylphenyl)phosphine (*5c*)

M.p. = 77–78 °C (Lit. 84–86 °C) [27]. *m*/*z* (FAB) 1516 (M^+). ^{1}H NMR ($CDCl_3$) 7.59–7.46 (9H, m, ArH), 7.35 (3H, d, $^3J_{HH}$ 6.3, ArH). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −80.92 (9F, t, $^4J_{FF}$ 9.4, CF_3), −111.47 (6F, t, $^4J_{FF}$ 14.0, α-CF_2), −121.45 (6F, m, CF_2), −122.10 (18F, m, 3 × CF_2),

Table 1
NMR spectral data for phosphorus(V) selenides[a]

Phosphine	M.p. (°C)	Elemental analysis[b]	*m*/*z*[c]	^{1}H	$^{19}F\{^{1}H\}$	$^{31}P\{^{1}H\}$
1a	88–91	C, 55.63 (55.88); H, 3.36 (3.43)	409 (M^+)	7.76 (2H, dd, $^{3}J_{PH}$ 12.4, $^{3}J_{HH}$ 8.4, ArH-2,6), 7.61 (6H, m, ArH), 7.40 (6H, m, ArH)	−63.09 (3F, s, CF_3)	35.1 (s, $^{1}J_{SeP}$ 741), 35.5 (s, $^{1}J_{SeP}$ 774)[d]
1b	39–40	C, 43.64 (43.77); H, 1.97 (2.13)	661 (MH^+)	7.79 (2H, dd, $^{3}J_{PH}$ 12.9, $^{3}J_{HH}$ 8.5, ArH-2,6), 7.65 (6H, m, ArH), 7.42 (6H, m, ArH)	−81.32 (3F, t, $^{4}J_{FF}$ 9.9, CF_3), −111.55 (2F, t, $^{4}J_{FF}$ 13.7, α-CF_2), −121.93 (4F, m, 2 × CF_2), −123.25 (2F, m, CF_2), −126.62 (2F, m, CF_2)	34.9 (s, $^{1}J_{SeP}$ 743), 34.7 (s,$^{1}J_{SeP}$ 774)[d]
1c	88–89	C, 41.38 (41.11); H, 1.92 (1.84)	759 (M^+)	7.78 (2H, dd, $^{3}J_{PH}$ 12.8, $^{3}J_{HH}$ 8.3, H-2,6), 7.67 (6H, m, ArH), 7.46 (6H, m, ArH)	−80.75 (3F, t, $^{4}J_{FF}$ 10.0, CF_3), −111.05 (2F, t, $^{4}J_{FF}$ 14.2, α-CF_2), −121.15 (2F, m, CF_2), −121.47 (2F, m, CF_2), −121.82 (4F, m, 2 × CF_2), −122.66 (2F, m, CF_2), −126.10 (2F, m, CF_2)	35.1 (s, $^{1}J_{SeP}$ 742), 35.5 (s, $^{1}J_{SeP}$ 775)[d]
1f	99–101	C, 45.10 (45.16); H, 3.13 (3.23)	747 (MH^+)	7.64–7.54 (6H, m, ArH), 7.45–7.31 (8H, m, ArH), 1.88 (2H, m, CH_2CF_2), 0.87 (2H, m, CH_2Si), 0.20 (6H, s, CH_3)	−81.27 (3F, t, $^{4}J_{FF}$ 9.0, CF_3), −116.71 (2F, t, $^{4}J_{FF}$ 12.0, α-CF_2), −122.49 (2F, m, CF_2), −123.66 (2F, m, CF_2), −124.04 (2F, m, CF_2), −126.68 (2F, m, CF_2)	35.0 (s, $^{1}J_{SeP}$ 730), 36.8 (s, $^{1}J_{SeP}$ 766)[d]
2b	Oil	C, 37.08 (36.89); H, 1.25 (1.33)	979 (MH^+)	7.78 (4H, dd, $^{3}J_{PH}$ 12.9, $^{3}J_{HH}$ 8.5, ArH-2,6), 7.64 (5H, m, ArH), 7.44 (4H, m, ArH)	−81.38 (6F, t, $^{4}J_{FF}$ 9.6, CF_3), −111.72 (4F, t, $^{4}J_{FF}$ 13.58, α-CF_2), −121.95 (8F, m, 2 × CF_2), −123.28 (4F, m, CF_2), −126.64 (4F, m, CF_2)	34.5 (s, $^{1}J_{SeP}$ 756), 34.7 (s, $^{1}J_{SeP}$ 782)[d]
3b	76–77	C, 33.48 (33.38); H 0.71 (0.93)	1297 (MH^+)	7.79 (6H, dd, $^{3}J_{PH}$ 13.0, $^{3}J_{HH}$ 8.3, ArH-2,6), 7.64 (6H, dd, $^{3}J_{HH}$ 8.3, $^{4}J_{PH}$ 2.9, ArH-3,5)	−81.40 (9F, t, $^{4}J_{FF}$ 9.8, CF_3), −111.74 (6F, t, $^{4}J_{FF}$ 13.6, α-CF_2), −121.99 (12F, m, 2 × CF_2), −123.29 (6F, m, CF_2), −126.67 (6F, m, CF_2)	34.0 (s, $^{1}J_{SeP}$ 769), 33.9 (s, $^{1}J_{SeP}$ 792)[d]
3c	126–127	C, 31.67 (31.62); H, 0.78 (0.75)	1596 (MH^+)	7.80 (6H, dd, $^{3}J_{PH}$ 13.2, $^{3}J_{HH}$ 8.5, ArH-2,6), 7.62 (6H, dd, $^{3}J_{HH}$ 8.5, $^{4}J_{PH}$ 2.1, ArH-3,5)	−81.19 (9F, t, $^{4}J_{FF}$ 9.8, CF_3), −111.56 (6F, t, $^{4}J_{FF}$ 13.3, α-CF_2), −121.57 (6F, m, CF_2), −121.92 (6F, m, CF_2), −122.24 (12F, m, 2 × CF_2), −123.07 (6F, m, CF_2), −126.50 (6F, m, CF_2)	35.8 (s, $^{1}J_{SeP}$ 793)[d]
3d	71–72	C, 36.60 (36.57); H, 1.89 (1.74)	1380 (MH^+)	7.59 (6H, dd, $^{3}J_{PH}$ 13.3, $^{3}J_{HH}$ 8.2, ArH-2,6), 7.22 (6H, dd, $^{3}J_{HH}$ 8.2, $^{4}J_{PH}$ 2.5, ArH-3,5), 2.88 (6H, m, CH_2), 2.32 (6H, m, CH_2)	−80.82 (9F, t, $^{4}J_{FF}$ 9.8, CF_3), −114.51 (6F, t, $^{4}J_{FF}$ 14.5, α-CF_2), −121.86 (6F, m, CF_2), −123.42 (6F, m, CF_2), −123.47 (6F, m, CF_2), −126.12 (6F, m, CF_2)	33.8 (s, $^{1}J_{SeP}$ 733), 34.2 (s, $^{1}J_{SeP}$ 767)[d]
3e	118–120	C, 38.14 (38.03); H, 2.03 (2.11)	1423 (MH^+)	7.58 (6H, dd, $^{3}J_{PH}$ 13.3, $^{3}J_{HH}$ 8.2, ArH-2,6), 7.19 (6H, m, ArH-3,5), 2.67 (6H, m, CH_2), 1.97 (12H, m, 2 × CH_2)	−80.77 (9F, t, $^{4}J_{FF}$ 10.0, CF_3), −114.10 (6F, t, $^{4}J_{FF}$ 14.8, α-CF_2), −121.89 (6F, m, CF_2), −122.85 (6F, m, CF_2), −123.35 (6F, m, CF_2), −126.08 (6F, m, CF_2)	33.8 (s, $^{1}J_{SeP}$ 725), 34.2 (s, $^{1}J_{SeP}$ 764)[d]
3g	112–114	C, 32.84 (32.73); H, 1.00 (1.17)	1537 (MH^+)	7.59 (6H, dd, $^{3}J_{PH}$ 12.9, $^{3}J_{HH}$ 9.1, ArH-2,6), 6.92 (6H, dd, $^{3}J_{HH}$ 9.1 $^{4}J_{PH}$ 2.1 ArH-3,5), 4.42 (6H, t, $^{3}J_{HF}$ 12.60, OCH_2)	−81.36 (9F, t, $^{4}J_{FF}$ 10.1, CF_3), −119.84 (6F, m, α-CF_2), −122.53 (12F, m, 2 × CF_2), −122.79 (6F, m, CF_2), −123.58 (6F, m, CF_2), −126.73 (6F, m, CF_2)	31.1 (s, $^{1}J_{SeP}$ 729), 33.3 (s, $^{1}J_{SeP}$ 759)[d]
3h	80–81 (dec)		1770 (MH^+)	7.56 (6H, dd, $^{3}J_{PH}$ 12.9, $^{3}J_{HH}$ 8.8, ArH-2,6), 6.85 (6H, dd, $^{3}J_{HH}$ 8.8, $^{4}J_{PH}$ 2.0, ArH-3,5), 4.00 (6H, m, OCH_2), 2.18 (6H, m, CH_2), 2.09 (6H, m, CH_2)	−81.25 (9F, t, $^{4}J_{FF}$ 9.0, CF_3), −114.83 (6F, t, $^{4}J_{FF}$ 15.0, α-CF_2), −122.69 (18F, m, 3 × CF_2), −123.58 (6F, m, CF_2), −124.46 (6F, m, CF_2), −126.58 (6F, m, CF_2)	31.4 (s, $^{1}J_{SeP}$ 715), 33.2 (s, $^{1}J_{SeP}$ 754)[d]
3l	121–123	C, 37.25 (37.44); H, 1.98 (2.08)	579 (MH^+)	7.52–7.43 (12H, m, ArH)		33.7 (s, $^{1}J_{SeP}$ 748), 35.4 (s, $^{1}J_{SeP}$ 778)[d]
4a	Oil	C, 55.69 (55.75); H, 3.50 (3.42)	411 (MH^+)	7.94 (1H, d, $^{3}J_{PH}$ 13.4, ArH-2), 7.81 (1H, dd, $^{3}J_{PH}$ 12.9 $^{3}J_{HH}$ 7.6, ArH-6), 7.64 (5H, m, ArH), 7.39 (7H, m, ArH)	−62.75 (s, CF_3)	35.3 (s, $^{1}J_{SeP}$ 742)
4b	Oil		661 (MH^+)	7.92 (1H, dd, $^{3}J_{PH}$ 13.0, $^{3}J_{HH}$ 7.6, ArH-6), 7.82 (1H, d, $^{3}J_{PH}$ 13.5, ArH-2), 7.67–7.42 (12H, m, ArH)	−80.86 (3F, t, $^{4}J_{FF}$ 9.5, CF_3), −111.01 (2F, t, $^{4}J_{FF}$ 14.1, α-CF_2), −121.38 (2F, m, CF_2), −121.91 (2F, m, CF_2), −122.80 (2F, m, CF_2), −126.15 (2F, m, CF_2)	35.3 (s, $^{1}J_{SeP}$ 744), 35.7 (s, $^{1}J_{SeP}$ 774)[d]

(*continued on next page*)

Table 1 (*continued*)

Phosphine	M.p. (°C)	Elemental analysis[b]	m/z[c]	^{1}H	^{19}F{^{1}H}	^{31}P{^{1}H}
4c	0Oil		760 (MH$^+$)	7.93 (1H, dd, $^3J_{PH}$ 12.9, $^3J_{HH}$ 7.5, ArH-6), 7.83 (1H, d, $^3J_{PH}$ 13.8, ArH-2), 7.70–7.35 (12H, m, ArH)	−80.83 (3F, t, $^4J_{FF}$ 9.1, CF$_3$), −111.28 (2F, t, $^4J_{FF}$ 14.0, α-CF$_2$), −121.20 (2F, m, CF$_2$), −121.73 (2F, m, CF$_2$), −121.89 (2F, m, CF$_2$), −122.54 (2F, m, CF$_2$), −122.68 (2F, m, CF$_2$), −126.14 (2F, m, CF$_2$)	35.3 (s, $^1J_{SeP}$ 744)
5b	157–158	C, 33.14 (33.38); H, 0.98 (0.93)	1297 (MH$^+$)	8.09 (3H, dd, $^3J_{PH}$ 13.7, $^3J_{HH}$ 7.6, ArH-2), 7.69 (9H, m, ArH)	−81.45 (9F, t, $^4J_{FF}$ 9.3, CF$_3$), −112.07 (6F, t, $^4J_{FF}$ 14.0, α-CF$_2$), −122.13 (6F, m, CF$_2$), −122.48 (6F, m, CF$_2$), −123.57 (6F, m, CF$_2$), −126.86 (6F, m, CF$_2$)	34.7 (s, $^1J_{SeP}$ 772), 35.8 (s, $^1J_{SeP}$ 796)[d]
5c	126–127	C, 31.82 (31.62); H, 0.67 (0.75)	1596 (M$^+$)	8.16 (3H, dd, $^3J_{PH}$ 13.8, $^3J_{HH}$ 7.2, ArH-2), 7.61 (9H, m, ArH)	−80.75 (9F, t, $^4J_{FF}$ 8.5, CF$_3$), −111.08 (6F, t, $^4J_{FF}$ 14.1, α-CF$_2$), −121.15 (6F, m, CF$_2$), −122.00 (18F, m, 3 × CF$_2$), −122.68 (6F, m, CF$_2$) −126.10 (6F, m, CF$_2$)	34.6 (s, $^1J_{SeP}$ 773)
6a	97–100	C, 55.86 (55.75); H, 3.51 (3.42)	411 (MH$^+$)[e]	7.75 (4H, m, ArH), 7.55 (2H, m, ArH), 7.40 (8H, m, ArH)	−53.52 (d, $^4J_{PF}$ 3, CF$_3$)	38.0 (q, $^4J_{PF}$ 3, $^1J_{SeP}$ 752)
6b	108–109	C, 43.59 (43.77); H, 2.13 (2.13)		7.70 (4H, m, ArH), 7.55 (2H, m, ArH), 7.38 (8H, m, ArH)	−80.81 (3F, t, $^4J_{FF}$ 11.3, CF$_3$), −99.69 (2F, dt, $^4J_{PF}$ 10.0, $^4J_{FF}$ 15.3, α-CF$_2$), −117.62 (2F, m, CF$_2$), −121.41 (2F, m, CF$_2$), −122.88 (2F, m, CF$_2$), −126.17 (2F, m, CF$_2$)	40.4 (t, $^4J_{PF}$ 10, $^1J_{SeP}$ 757), 39.9 (t, $^4J_{PF}$ 10, $^1J_{SeP}$ 791)
7a	Oil	C, 50.69 (50.42); H, 2.60 (2.73)	477 (M$^+$)	8.09 (2H, d, $^3J_{PH}$ 12.6, ArH-2,6), 7.91 (1H, s, ArH-4), 7.63 (4H, m, ArH), 7.44 (6H, m, ArH)	−62.84 (s, CF$_3$)	35.0 (s, $^1J_{SeP}$ 755), 35.8 (s, $^1J_{SeP}$ 784)[d]
7b	Oil	C, 36.72 (36.89); H, 1.30 (1.33)	977 (M$^+$)	8.08 (2H, d, $^3J_{PH}$ 12.7, ArH-2,6), 7.82 (1H, s, ArH-4), 7.63 (4H, m, ArH), 7.59 (6H, m, ArH)	−80.82 (6F, t, $^4J_{FF}$ 9.7, CF$_3$), −111.08 (4F, t, $^4J_{FF}$ 14.0, α-CF$_2$), −121.30 (4F, m, CF$_2$), −121.89 (4F, m, CF$_2$), −122.73 (4F, m, CF$_2$), −126.11 (4F, m, CF$_2$)	35.2 (s, $^1J_{SeP}$ 758), 35.8 (s, $^1J_{SeP}$ 785)[d]
7c	Oil	C, 34.44 (34.66); H, 1.00 (1.10)		8.08 (2H, d, $^3J_{PH}$ 12.9, ArH-2,6), 7.83 (1H, s, ArH-4), 7.53 (10H, m, ArH)	−81.78 (6F, t, $^4J_{FF}$ 10.4, CF$_3$), −111.21 (4F, t, $^4J_{FF}$ 14.2, α-CF$_2$), −121.11 (8F, m, 2 × CF$_2$), −121.90 (8F, m, 2 × CF$_2$), −122.67 (4F, m, CF$_2$), −126.06 (4F, m, CF$_2$)	35.2 (s, $^1J_{SeP}$ 758)
8a	Oil	C, 43.15 (43.14); H, 1.82 (1.80)	613 (M$^+$)	8.09 (4H, d, $^3J_{PH}$ 13.0, ArH-2,6), 7.99 (2H, s, ArH-4), 7.54 (5H, m, ArH)	−63.04 (s, CF$_3$)	34.6 (s, $^1J_{SeP}$ 779), 35.2 (s, $^1J_{SeP}$ 801)[d]
8b	Oil	C, 31.54 (31.27); H, 0.59 (0.68)	1613 (M$^+$)	8.03 (4H, d, $^3J_{PH}$ 12.8, ArH-2,6), 7.89 (2H, s, ArH-4), 7.49 (5H, m, ArH)	−81.09 (12F, t, $^4J_{FF}$ 9.8, CF$_3$), −111.74 (8F, t, $^4J_{FF}$ 14.2, α-CF$_2$), −121.50 (8F, m, CF$_2$), −122.12 (8F, m, CF$_2$), −122.96 (8F, m, CF$_2$), −126.40 (8F, m, CF$_2$),	34.7 (s, $^1J_{SeP}$ 785), 35.3 (s, $^1J_{SeP}$ 806)[d]
9a[16]				8.11 (6H, d, $^3J_{PH}$ 13.1 ArH-2,6), 8.09 (3H, s, ArH-4),	−63.50 (s, CF$_3$)	34.3 (s, $^1J_{SeP}$ 803), 34.3 (s, $^1J_{SeP}$ 817)[d]
10a	Oil	C, 34.59 (34.53); H, 0.90 (0.99)		8.08 (2H, d, $^3J_{PH}$ 13.0, ArH-2′,6′), 7.99 (1H, s, ArH-4’), 7.80 (4H, m, C$_6$H$_4$), 7.70 (4H, m, C$_6$H$_4$)	−62.93 (6F, s, CF$_3$), −80.78 (6F, t, $^4J_{FF}$ 9.8, CF$_3$), −111.29 (4F, t, $^4J_{FF}$ 14.3, α-CF$_2$), −121.33 (4F, m, CF$_2$), −121.70 (4F, m, CF$_2$), −122.82 (4F, m, CF$_2$), −126.08 (4F, m, CF$_2$)	34.2 (s, $^1J_{SeP}$ 780), 34.8 (s, $^1J_{SeP}$ 801)[d]
10b	Oil	C, 31.48 (31.27); H, 0.55 (0.68)	1613 (M$^+$)	8.01 (2H, d, $^3J_{PH}$ 13.0, ArH-2′,6′), 7.87 (1H, s, ArH-4’), 7.78 (4H, dd, $^3J_{PH}$ 13.2, $^3J_{HH}$ 8.3, ArH-2,6), 7.66 (4H, dd, $^3J_{HH}$ 8.3, $^4J_{PH}$ 2.2, ArH-3,5)	−81.21 (12F, t, $^4J_{FF}$ 10.7, CF$_3$), −111.45 (4F, t, $^4J_{FF}$ 14.2, α-CF$_2$), −111.72 (4F, t, $^4J_{FF}$ 14.2, α-CF$_2$), −121.56 (8F, m, CF$_2$), −122.14 (8F, m, CF$_2$), −123.0 (8F, m, CF$_2$), −126.42 (8F, m, CF$_2$)	34.0 (s, $^1J_{SeP}$ 785), 34.3 (s, $^1J_{SeP}$ 803)[d]

11b[f]	125–127		1417 $[MH]^{+}$[e]	7.96 (2H, s, ArH), 7.89 (2H, dd, $^3J_{HH}$ 10.0, $^4J_{HH}$ 2.5, ArH), 7.66–7.54 (8H, m, PhH), 7.52 (2H, d, $^3J_{HH}$ 7.5, ArH), 7.35–7.21 (12H, m, PhH), 6.64 (2H, d, $^3J_{HH}$ 10.0, ArH), 6.59 (2H, d, $^3J_{HH}$ 10.0, ArH)	−81.18 (6F, t, $^4J_{FF}$ 9.8, CF_3), −110.77 (4F, m, α-CF_2), −121.48 (4F, m, CF_2), −121.80 (4F, m, CF_2), −123.16 (4F, m, CF_2), −126.48 (4F, m, CF_2)	32.7 (s, $^1J_{SeP}$ 749)
11d[g]	127–131	C, 49.14 (48.91); H, 2.48 (2.58)	1473 $[MH]^{+}$[e]	7.69 (6H, m, PhH), 7.56 (4H, m, PhH), 7.50 (2H, s, ArH), 7.40 (2H, dd, J_{HH} 12.2, J_{HH} 8.8, ArH), 7.34–7.13 (12H, m, ArH and PhH), 6.58 (2H, d, $^3J_{HH}$ 8.7, ArH), 6.33 (2H, dd, $^3J_{HH}$ 8.8, $^4J_{HH}$ 1.5, ArH), 2.84 (4H, m, CH_2), 2.25 (4H, m, CH_2)	−80.75 (6F, t, $^4J_{FF}$ 10.4, CF_3), −114.52 (4F, m, α-CF_2), −121.79 (4F, m, CF_2), −122.80 (4F, m, CF_2), −123.38 (4F, m, CF_2), −126.08 (4F, m, CF_2)	32.8 (s, $^1J_{SeP}$ 743)
11i[h]	> 300		781 $[MH]^{+}$[e]	7.71–7.53 (12H, m, ArH and PhH), 7.43 (2H, m, ArH), 7.29–7.09 (14H, m, ArH and PhH), 6.69 (2H, d, $^3J_{HH}$ 8.4, ArH), 6.63 (2H, m, ArH)		33.7 (s, $^1J_{SeP}$ 739)

[a] Spectra recorded in $CDCl_3$ unless otherwise stated. Data given as δ (intensity, multiplicity, J (Hz), assignment).

[b] Calculated values in parentheses.

[c] FAB spectra unless otherwise stated.

[d] Spectra recorded in diethyl ether.

[e] ES^{+} spectra.

[f] $[\alpha]_D$ ($CHCl_3$) 20.7° ($c = 1.2$).

[g] $[\alpha]_D$ ($CHCl_3$) 17.72° ($c = 0.9$).

[h] $[\alpha]_D$ ($CHCl_3$) 19.0° ($c = 1.6$).

−122.90 (6F, m, CF_2) −126.29 (6F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) −6.9 (s).

2.2. General procedure for the preparation of phosphorus(V) selenides

The phosphine (0.20 g) was dissolved in chloroform (10 ml) and selenium powder added (0.30 g, 3.8 mmol). The mixture was heated to 70 °C overnight. After cooling, the excess selenium was removed by filtration through a cotton wool plug and the solvent removed in vacuo to give the phosphorus(V) selenide in a 64–89% yield. A few of the phosphorus(V) selenides used in this study have been reported previously; tris(4-*N*,*N*-dimethylaminophenyl) phosphine selenide, [28] tris(4-methoxyphenyl)phosphine selenide, tris(4-methylphenyl)phosphine selenide, triphenylphosphine selenide, tris(4-fluorophenyl)phosphine selenide, tris(4-trifluoromethylphenyl)phosphine selenide, tris (3-trifluoromethylphenyl)phosphine selenide and tris(3,5-trifluoromethylphenyl)phosphine selenide, [15] and tris(4-chlorophenyl)phosphine [29]. Table 1 summarises all the analytical and NMR spectroscopic data for the new phosphorus(V) selenides prepared in this work.

2.3. General procedure for the preparation of $[PtCl_2L_2]$ complexes

The phosphine (0.1 mmol) and $[PtCl_2(CH_3CN)_2]$ (0.05 mmol) were dissolved in dichloromethane (10 ml) and heated to reflux for 2 h. After cooling, the solvent was removed and the resulting solid washed well with petroleum ether to give a pale yellow solid in 84–91% yield.

2.3.1. cis- and trans-$[PtCl_2\{Ph_2P(C_6H_4\text{-}4\text{-}CF_3)\}_2]$

Anal. Calc. for $C_{38}H_{28}Cl_2F_6P_2Pt$: C, 49.30; H, 3.03. Found: C, 49.15; H, 3.03%. *m*/*z* (FAB) 891 $(M-Cl)^{+}$. ^1H NMR ($CDCl_3$) 7.96 (8H, m, ArH), 7.36 (12H, m, ArH), 7.19 (8H, m, ArH). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −63.00 (s, *trans*), −63.10 (s, *cis*). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 20.5 (s, $^1J_{PtP}$ 2656, *trans*), 14.7 (s, $^1J_{PtP}$ 3653, *cis*).

2.3.2. cis- and trans-$[PtCl_2\{Ph_2P(C_6H_4\text{-}4\text{-}C_8F_{17})\}_2]$

m/*z* (FAB) 1591 $(M-Cl)^{+}$. ^1H NMR ($CDCl_3$) 7.70 (4H, d, $^3J_{HH}$ 7.8, ArH-3,5), 7.53 (4H, t, $^3J_{HH} = {}^3J_{PH}$ 7.8, ArH-2,6), 7.34 (16H, m, PhH), 7.19 (4H, m, PhH). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −80.73 (6F, t, $^4J_{FF}$ 9.8, CF_3), −111.09 (4F, t, $^4J_{FF}$ 13.7, α-CF_2), −121.17 (4F, m, CF_2), −121.54 (4F, m, CF_2), −121.84 (8F, m, 2 × CF_2), −122.64 (4F, m, CF_2), −126.06 (2F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 20.5 (s, $^1J_{PtP}$ 2664, *trans*), 14.5 (s, $^1J_{PtP}$ 3653, *cis*).

2.3.3. cis- and trans-$[PtCl_2\{Ph_2P(C_6H_4\text{-}4\text{-}SiMe_2C_2H_4C_6F_{13})\}_2]$

Anal. Calc. for $C_{56}H_{48}Cl_2F_{26}P_2Pt$: C, 42.08; H, 3.01. Found: C, 42.06; H, 2.89%. *m*/*z* (FAB) 1563 $(M-Cl)^{+}$. ^1H NMR ($CDCl_3$) 7.63–7.08 (28H, m, ArH), 1.89 (4H, m, CH_2CF_2), 0.88 (4H, m, CH_2Si), 0.23 (12H, s, CH_3).

$^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.30 (6F, t, $^4J_{FF}$ 9.9, CF_3), −116.68 (4F, t, $^4J_{FF}$ 14.1, α-CF_2), −123.06 (4F, m, CF_2), −123.63 (4F, m, CF_2), −124.02 (4F, m, CF_2), −126.67 (4F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 19.9 (s, $^1J_{PtP}$ 2632, *trans*), 13.8 (s, $^1J_{PtP}$ 3673, *cis*).

2.3.4. *cis- and trans-*$[PtCl_2\{P(C_6H_4\text{-}4\text{-}CH_2CH_2CH_2C_6F_{13})_3\}_2]$

Anal. Calc. for $C_{90}H_{60}Cl_2F_{78}P_2Pt$: C, 36.61; H, 2.03. Found: C, 36.70; H, 1.96%. *m/z* (FAB) 2915 $(M-Cl)^+$. ^1H NMR ($CDCl_3$) 7.34 (12H, dd, $^3J_{PH}$ 11.2, $^3J_{HH}$ 8.2, ArH-2,6), 6.90 (12H, m, ArH-3,5), 2.60 (12H, m, CH_2), 1.87 (24H, m, CH_2). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.10 (18F, t, $^4J_{FF}$ 9.9, CF_3), −114.31 (12F, t, $^4J_{FF}$ 12.3, α-CF_2), −122.09 (12F, m, CF_2), −122.68 (12F, m, CF_2), −123.06 (12F, m, CF_2), −126.42 (12F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 18.6 (s, $^1J_{PtP}$ 2614, *trans*), 12.8 (s, $^1J_{PtP}$ 3679, *cis*).

2.3.5. *cis-*$[PtCl_2\{Ph_2P(C_6H_4\text{-}3\text{-}CF_3)\}_2]$

Anal. Calc. for $C_{38}H_{28}Cl_2F_6P_2Pt$: C, 49.24; H, 3.02. Found: C, 49.18; H, 2.96%. *m/z* (FAB) ^1H NMR ($CDCl_3$) 7.46 (14H, m, ArH), 7.27 (4H, m, ArH), 7.18 (10H, m, ArH). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −62.69 (s, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 15.1 (s, $^1J_{PtP}$ 3653).

2.3.6. *cis- and trans-*$[PtCl_2\{Ph_2P(C_6H_4\text{-}3\text{-}C_8F_{17})\}_2]$

Anal. Calc. for $C_{52}H_{28}Cl_2F_{34}P_2Pt$: C, 35.35; H, 1.72. Found: C, 34.15; H, 1.73%. *m/z* (FAB) 1591 $(M-Cl)^+$. ^1H NMR ($CDCl_3$) 8.00–7.20 (28H, m, ArH). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −80.91 (6F, m, CF_3), −111.01 (4F, m, α-CF_2), −121.19 (4F, m, CF_2), −121.81 (12F, m, 3 × CF_2), −122.67 (4F, m, CF_2), −126.08 (4F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 21.2 (s, $^1J_{PtP}$ 2663, *trans*), 16.1 (s, $^1J_{PtP}$ 3650, *cis*).

2.3.7. *cis- and trans-*$[PtCl_2\{P(C_6H_4\text{-}4\text{-}C_8F_{17})_3\}_2]$

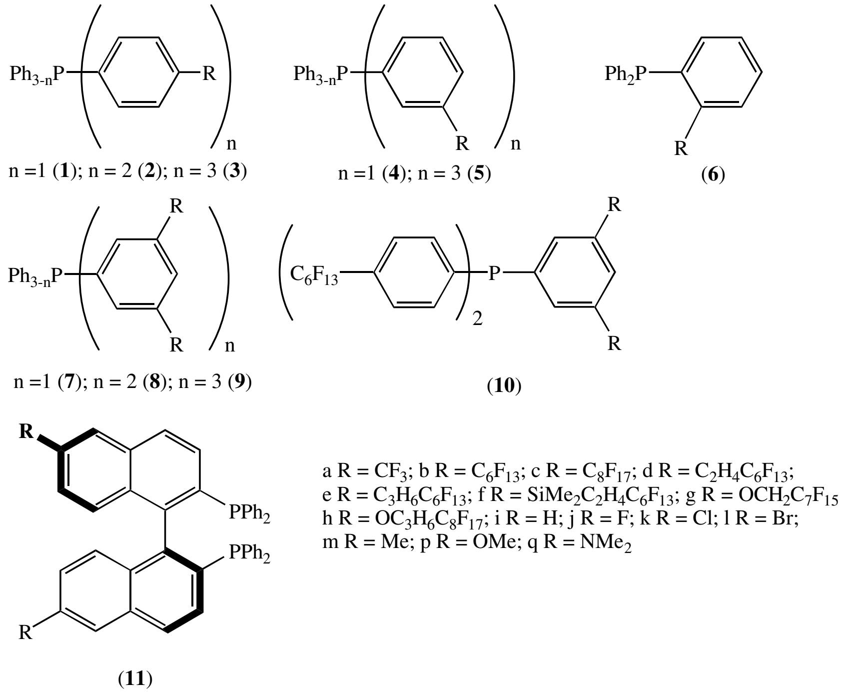
Anal. Calc. for $C_{84}H_{24}Cl_2F_{102}P_2Pt$: C, 30.58; H, 0.73. Found: C, 30.50; H, 0.64%. *m/z* (MALDI-TOF) 3227 $(M-2Cl)^+$. ^1H NMR (C_6D_6/C_6F_6) 7.98 (6H, dd, $^3J_{HH}$ 8.2, $^3J_{PH}$ 5.5, ArH-2,6), 7.79 (6H, dd, $^3J_{HH}$ 8.2, $^3J_{PH}$ 8.5, ArH-2,6), 7.72 (12H, d, $^3J_{HH}$ 8.2, ArH-3,5). $^{19}F\{^1H\}$ NMR (C_6D_6/C_6F_6) −83.48 (18F, t, $^4J_{FF}$ 10.0, CF_3), −113.30 (6F, t, $^4J_{FF}$ 14.6, α-CF_2), −113.43 (6F, t, $^4J_{FF}$ 15.5, α-CF_2), −122.92 (12F, m, CF_2), −123.33 (24F, m, 2 × CF_2), −123.49 (12F, m, CF_2), −124.34 (12F, m, CF_2), −128.04 (12F, m, CF_2). $^{31}P\{^1H\}$ NMR (C_6D_6/C_6F_6) 20.5 (s, $^1J_{PtP}$ 2741, *trans*), 15.2 (s, $^1J_{PtP}$ 3570, *cis*).

2.3.8. *cis- and trans-*$[PtCl_2\{Ph_2P(C_6H_3\text{-}3,5\text{-}[CF_3]_2)\}_2]$

Anal. Calc. for $C_{40}H_{26}Cl_2F_{12}P_2Pt$: C, 45.24; H, 2.45. Found: C, 45.03; H, 2.38%. *m/z* (FAB) 1027 $(M-Cl)^+$. ^1H NMR ($CDCl_3$) 7.66 (2H, s, ArH-4), 7.60 (2H, d, $^3J_{PH}$ 11.6, ArH-2,6), 7.58 (2H, d, $^3J_{PH}$ 11.1, ArH-2,6), 7.42 (12H, m, PhH), 7.25 (8H, m, PhH). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −62.96 (s, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 22.1 (s, $^1J_{PtP}$ 2685, *trans*), 15.9 (s, $^1J_{PtP}$ 3630, *cis*).

3. Results and discussion

Measuring $^1J_{PtP}$ for *cis*-$[PtCl_2L_2]$ (L = triarylphosphine) is a very useful tool for the characterisation of platinum complexes, with the magnitude of the coupling constant being a predictive function of the triarylphosphine ligand, and Pringle et al. have shown that these values correlate very well with the Hammett σ_p parameter of the substituent



n =1 (**1**); n = 2 (**2**); n = 3 (**3**)

n =1 (**4**); n = 3 (**5**)

(**6**)

n =1 (**7**); n = 2 (**8**); n = 3 (**9**)

(**10**)

(**11**)

a R = CF_3; b R = C_6F_{13}; c R = C_8F_{17}; d R = $C_2H_4C_6F_{13}$;
e R = $C_3H_6C_6F_{13}$; f R = $SiMe_2C_2H_4C_6F_{13}$; g R = $OCH_2C_7F_{15}$
h R = $OC_3H_6C_8F_{17}$; i R = H; j R = F; k R = Cl; l R = Br;
m R = Me; p R = OMe; q R = NMe_2

Fig. 1. Phosphines used in this study.

on the aryl ring [30]. We have previously used this technique to probe the effect of perfluoroalkylation on the donor properties of triarylphosphines [13]. However, systematic comparison of the electronic impact of the perfluoroalkyl-substituent is not always possible since, as a consequence of steric constraints, some *cis*-$[PtCl_2L_2]$ complexes are not available. Furthermore, even where the complexes can be formed, it is difficult to be certain that the effect being probed is entirely electronic. For example, the $^1J_{PtP}$ values for the *cis*-$[PtCl_2L_2]$ complexes derived from $Ph_2P(C_6H_4\text{-}4\text{-}C_6F_{13})$ and $Ph_2P(C_6H_4\text{-}3\text{-}C_6F_{13})$ are 3653 Hz [13] and 3635 Hz [14], respectively, although it

Table 2
Coupling constant data for phosphorus(V) selenides and *cis*-/*trans*-$[PtCl_2L_2]$ complexes[a]

Phosphine	Substituent	$\lvert ^1J_{SeP}\rvert$	ΔJ_{SeP}[b]	$\lvert ^1J_{SeP}\rvert$[c]	$\lvert ^1J_{PtP}\rvert$[d]	$\lvert ^1J_{PtP}\rvert$[e]
3q	NMe_2	683[f]	−53		3747[g]	
3p	OMe	710[h]	−20	746	3707[g]	
3m	Me	715[h]	−15		3691[g]	
3h	$OC_3H_6C_8F_{17}$	715	−15	754		
3e	$C_3H_6C_6F_{13}$	725	−5	764	3679	2614
3g	$OCH_2C_7F_{15}$	729	−1	759	3680[i]	
3i	H	730	0	767	3675[g]	2635[j]
1f	$SiMe_2C_2H_4C_6F_{13}$	730	0	766	3673	2632
3d	$C_2H_4C_6F_{13}$	733	3	767	3679[k]	
3j	F	741[h]	11	772	3666[l]	
3k	Cl	748	18	775	3648[g]	
3l	Br	748	18	778	3646	
1a	CF_3	741	11	774	3653	2656
1b	C_6F_{13}	743	13	774	3653[m]	
1c	C_8F_{17}	742	12	775	3653	2664
4a	CF_3	742	12		3653	
4b	C_6F_{13}	744	14	774	3633[n]	2646[n]
4c	C_8F_{17}	744	14		3650	2663
6a	CF_3	752	22			2805[o]
6b	C_6F_{13}	757	27	791		2826[o]
2b	C_6F_{13}	756	26	782	3635[m]	
7a	CF_3	755	25	784	3630	2685
7b	C_6F_{13}	758	28	785	3630[p]	2692[p]
7c	C_8F_{17}	758	28		3622[p]	2695[p]
3a	CF_3	765[h]	35		3611[g]	
3b	C_6F_{13}	769	39	792	3615[m]	2712[m]
3c	C_8F_{17}	insol.		793	3570	2741
5a	CF_3	766[h]	36		3608[l]	2720[l]
5b	C_6F_{13}	772	42	796		2723[n]
5c	C_8F_{17}	773	43			
8a	CF_3	779	49	801		2739[p]
8b	C_6F_{13}	785	55	806		2741[p]
10a	CF_3/C_6F_{13}	780	50	801	3591[p]	2741[p]
10b	C_6F_{13}	785	55	803	3576[p]	2744[p]
9a	CF_3	803	73	817	3621[l]	2786[l]
11i	H	739	0[q]		3665[r]	
11d	$C_2H_4C_6F_{13}$	743	4[q]		3665[r]	
11b	C_6F_{13}	749	10[q]		3636[r]	

[a] Data (Hz) recorded for compounds dissolved in $CDCl_3$ unless otherwise stated.
[b] $\Delta J_{SeP} = \lvert ^1J_{SeP}\rvert(L) - \lvert ^1J_{SeP}\rvert(PPh_3)$ unless otherwise stated.
[c] Diethyl ether.
[d] *cis*-$[PtCl_2L_2]$.
[e] *trans*-$[PtCl_2L_2]$.
[f] Data from Ref. 28.
[g] Data from Ref. 30.
[h] Data from Ref. 16.
[i] Data from Ref. 31.
[j] Data from Ref. 32.
[k] Data from Ref. 33.
[l] Data from Ref. 22.
[m] Data from Ref. 13.
[n] Data from Ref. 14.
[o] Data from Ref. 34.
[p] Data taken from Ref. 22.
[q] $\Delta J_{SeP} = \lvert ^1J_{SeP}\rvert(L) - \lvert ^1J_{SeP}\rvert$ (**11i**).
[r] Data taken from Ref. 25.

would be anticipated that placing the perfluoroalkyl group in the *para*- or *meta*-position would have little effect on the electronic properties of the phosphine and, indeed, Howell et al. report that the electron-withdrawing effect of the purely inductive CF_3 is felt almost equally at the *ortho*-, *meta*- and *para*-positions [16].

In order to fully understand the electronic influence of perfluoroalkyl substituents on the donor properties of triarylphosphines, we have prepared a comprehensive series of phosphorus(V) selenides from a range of triaryl phosphines (Fig. 1). NMR spectroscopic data for these compounds, alongside those for the *cis*-$[PtCl_2L_2]$ complexes and selected values from the literature, are presented in Table 2. The NMR data, in particular the $|^1J_{SeP}|$ coupling constants, [15] are solvent dependent and this must be borne in mind in any comparison. Unfortunately, not all the phosphorus(V) selenides are soluble in either $CDCl_3$ or diethyl ether so, in order to offer a comprehensive analysis, data for many of the compounds are reported for both solvents; the correlations discussed below apply equally well to both sets of data.

These data reveal a number of significant facts. Firstly, as reported previously for the CF_3-derivatised aryl phosphines, [16] the $|^1J_{SeP}|$ values for the C_6F_{13} derivatised phosphorus(V) selenides are cumulative. So, ΔJ_{PSe} (relative to Se = PPh_3) for the selenide derived from $P(C_6H_4\text{-}4\text{-}C_6F_{13})_3$, **3b**, is three times that for the selenide derived from $Ph_2P(C_6H_4\text{-}4\text{-}C_6F_{13})$, **1b**. Similarly, that from **8b** gives a value four times greater than that from **1b**. Secondly, despite various anecdotal, spectroscopic and catalytic evidence to the contrary, the lengths of the perfluoroalkyl substituents have no impact upon the electronic environment at phosphorus since ΔJ_{SeP} for related series (phosphines = **1a**, **1b** and **1c**; **3a**, **3b** and **3c**; **4a**, **4b** and **4c**; **5a**, **5b** and **5c**; **6a** and **6b**; **7a**, **7b** and **7c**) are virtually identical. Finally, since the values from the *meta*- and *para*-substituted phosphines (**1a**, **1b** and **1c**; **4a**, **4b** and **4c**) are very similar and those from **10b** and **8b** give identical results, the electron-withdrawing effect of the perfluoroalkyl groups on the phosphorus centre is independent of their position in these phosphines. As indicated above, this effect is not apparent from the $^1J_{PtP}$ values for pairs of *cis*-$[PtCl_2L_2]$ complexes, particularly since all attempts at forming *cis*-$[PtCl_2L_2]$ for phosphine **8b** failed, presumably due to steric congestion. However, in direct contrast to the observations of Howell et al., [16] this cannot be extended to the *ortho*-substituted phosphines, **6a** and **6b**, where $|^1J_{SeP}|$ for their selenides are substantially different to those for the selenides of **1a**, **4a**, **1b** and **4b**. This type of effect has, for the *ortho*-methylated triarylphosphine selenides, been attributed to the steric impact of the substituents, [17] and this could equally apply to our fluoroalkylated phosphine selenides. An alternative explanation arises from through space interactions between the phosphorus and fluorine atoms [34]. This is clearly evident in the free phosphines ($R = C_6F_{13}$, $^4J_{PF} = 99$ Hz; $R = CF_3$, $^4J_{PF} = 53$ Hz) and, although the magnitude of the interaction is reduced in the phosphine selenides ($R = C_6F_{13}$, $^4J_{PF} = 10$ Hz; $R = CF_3$, $^4J_{PF} = 3$ Hz), its presence is likely to seriously alter the electronic properties of the phosphorus atoms and hence the P–Se interaction.

As expected, since both parameters are affected by the electronic environment of the phosphine, there is a linear relationship between $|^1J_{SeP}|$ and $|^1J_{PtP}|$ for both the *cis*-, Fig. 2, and *trans*-$[PtCl_2L_2]$ complexes, Fig. 3. The only data point which does not show the linear correlation in Fig. 2 is that for the *cis*-$[PtCl_2(\mathbf{9a})_2]$ quoted by Alt et al. [22]. However, although ΔJ_{SeP} for the selenide of **9a** is entirely consistent with the presence of six CF_3 groups, we were unable to prepare the *cis*-platinum metal complex to confirm the magnitude of this $^1J_{PtP}$ coupling constant. In contrast, in Fig. 3, the data for *trans*-$[PtCl_2(\mathbf{9a})_2]$ is consistent with the linear correlation. In Fig. 3, the data points associated with phosphines **6a** and **6b** do not follow the linear correlation, which is accounted for by the additional steric and electronic interactions in both their selenides and platinum metal complexes [34].

Many attempts have been made to minimise the electronic effect of fluoroalkyl groups on the donor properties of the

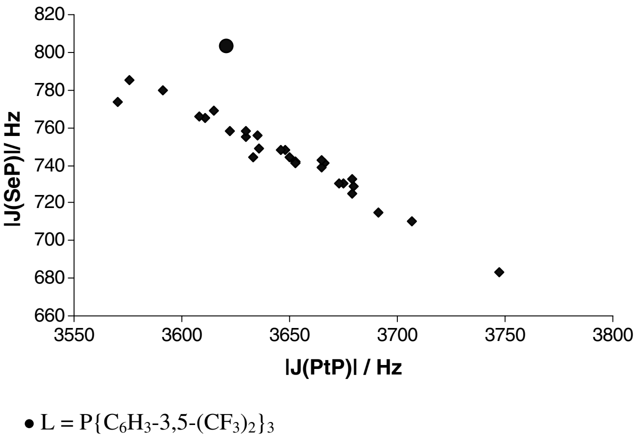


Fig. 2. Correlation between $|^1J_{SeP}|$ for trisarylphosphine selenides and $|^1J_{PtP}|$ for *cis*-$[PtCl_2L_2]$.

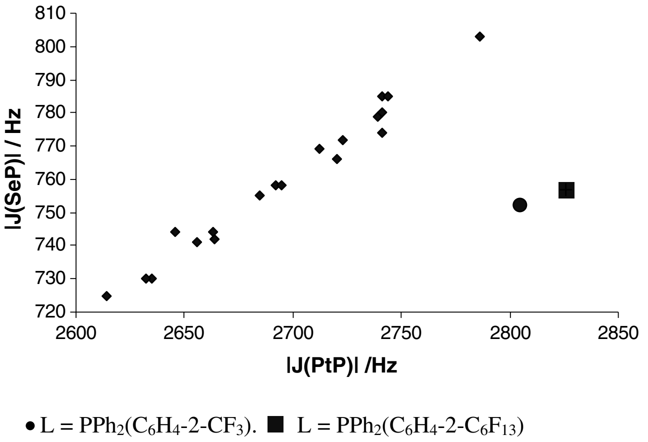


Fig. 3. Correlation between $|^1J_{SeP}|$ for Se = PR_3 and $|^1J_{PtP}|$ for *trans*-$[PtCl_2(PR_3)_2]$.

Table 3
Influence of electronic spacer units on $|^1J_{SeP}|$ coupling constants for $Se=P(4\text{-}C_6H_4R)_3$

R	Label	$\|^1J_{SeP}\|$ ($CDCl_3$) (Hz)	ΔJ_{SeP} (Hz)[a]
OMe	**3p**	710	−20
Me	**3m**	715	−15
$OCH_2CH_2CH_2C_8F_{17}$	**3h**	715	−15
$CH_2CH_2CH_2C_6F_{13}$	**3e**	725	−5
$OCH_2C_7F_{15}$	**3g**	729	−1
H	**3i**	730	0
$CH_2CH_2C_6F_{13}$	**3d**	733	3
CF_3	**3a**	765	35
C_6F_{13}	**3b**	769	39

[a] $\Delta J_{SeP}=|^1J_{SeP}|(L)-|^1J_{SeP}|(PPh_3)$.

phosphines, which has been achieved by the introduction of spacer groups between the perfluoroalkyl group and the aromatic ring. By examining the $^1J_{SeP}$ data it is possible to determine the efficiency of these groups at insulating the phosphorus centre from the perfluoroalkyl groups and illustrative data are collected in Table 3. It can be seen that, using these different perfluoroalkyl groups, it is possible to generate a range of different electronic environments at the phosphorus atoms. For these triarylphosphines, additional CH_2 spacer units can provide insulation of the phosphorus atom from the perfluoroalkyl groups, but at least two are required for complete insulation. Finally, by using spacer groups incorporating an oxygen atom, it is possible to generate phosphines for use in a perfluorocarbon solvent that are actually electron rich, as illustrated by the data for the $OCH_2CH_2CH_2$ (**3h**) spacer group substituted phosphine that gives the same $^1J_{SeP}$ as tris(4-tolyl)phosphine selenide (**3m**).

4. Conclusions

The $^1J_{SeP}$ coupling constants of a series of trisarylphosphines derivatised with a variety of different perfluoroalkyl groups have been measured, which allow the direct comparison between phosphine ligands that is not possible via other spectroscopic probes. The values have been used to compare a range of different fluorinated groups and to determine the efficiency of a variety of spacer groups at insulating the phosphorus centre from the electron-withdrawing effect of the perfluoroalkyl group. This data illustrates that it is possible to generate phosphines for use in fluorous catalysis that are either electron rich, electron neutral or electron poor with respect to triphenylphosphine.

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