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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 $SiMe_4$ (^1H), 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^+). ^1H 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^+). ^1H 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^+). ^1H 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^+). ^1H 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^+). ^1H 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^+). ^1H 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),