PERGAMON

Polyhedron 18 (1999) 2913–2917

POLYHEDRON

www.elsevier.nl/locate/poly

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

Eric G. Hope*, Ray D.W. Kemmitt, Danny R. Paige, Alison M. Stuart, Dan R.W. Wood

Department of Chemistry, University of Leicester, Leicester, LE1 7RH UK

Received 17 May 1999; accepted 7 July 1999

Abstract

The synthesis and coordination chemistry of the $PPh_x(C_6H_4\text{-}3\text{-}C_6F_{13})_{3-x}$ ($x=0$, 1, 2) ligands containing perfluoroalkyl ponytails have been investigated. A comparison of the spectroscopic data for coordination complexes containing these ligands with those for complexes containing PPh_3 or the related *para*-derivatised triarylphosphines indicates that these *meta*-derivatised ligands are slightly poorer σ-donors and that steric crowding in the $[PtCl_2L_2]$ complexes results in the formation of the normally thermodynamically less-favourable *trans*-isomers.

Keywords: Fluorous biphase; Phosphine; Platinum group metals

1. Introduction

Following the introduction of the fluorous biphase approach to the heterogenisation of homogeneous catalysis [1,2], a range of ligand systems and metal complexes have been derivatised with long perfluoroalkyl 'ponytails' and their solubilities and reactivities under fluorous biphasic conditions have been described [2–16]. Throughout this work, phosphorus(III) ligands, in particular phosphines, have been pre-eminent [2–12]. We have described a general route to the synthesis of *para*-derivatised triaryl phosphine ligands [8] and have recently established the criteria for preferential perfluorocarbon solubility as well as the electronic influence of the perfluoroalkyl substituents on the coordination chemistry of these ligands [11]. Here, we extend this work to an analogous series of *meta*-substituted ligands to establish the steric and electronic implications of introducing the perfluoroalkyl substituents in this position.

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 on a Bruker DRX 400 spectrometer at 400.13, 376.50 and 161.98 MHz. All chemical shifts are quoted in ppm using the high-frequency positive convention; ^1H NMR spectra were referenced to external $SiMe_4$, ^{19}F NMR spectra to external $CFCl_3$ and ^{31}P NMR spectra to external 85% H_3PO_4. Assignments of the ^{19}F NMR resonances were made using correlation experiments and follow the order outlined previously [8]. The IR spectra were recorded on a Digilab FTS40 Fourier-transform spectrometer at 4 cm^{-1} resolution for the complexes as Nujol mulls held between KBr discs. Elemental analyses were performed by Butterworth Laboratories Ltd. Mass spectra were recorded on a Kratos Concept 1H mass spectrometer.

The complexes, $[Cp^*RhCl_2]_2$ and $[RhCl(CO)_2]_2$, were commercial samples (Aldrich) and were used as supplied whilst *cis*-$[PtCl_2(MeCN)_2]$ was prepared as previously described [17]. Dichloromethane, chloroform and perfluoro-1,3-dimethylcyclohexane (PP3) were each dried by refluxing over calcium hydride under dinitrogen, distilled under nitrogen and stored in closed ampoules over molecular sieves. PP3 was also freezed/pumped/thawed three times to remove all dissolved gases. Hexane was dried by refluxing over potassium metal under nitrogen, distilled and was stored similarly. Toluene and diethyl ether were dried by refluxing over sodium metal under nitrogen, distilled and stored similarly.

*Corresponding author. Tel.: +44-116-252-2108; fax: +44-116-252-3789.

E-mail address: egh1@le.ac.uk (E.G. Hope)

0277-5387/99/$ – see front matter
PII: S0277-5387(99)00202-8

2.1. 3-(Tridecafluorohexyl)bromobenzene **1**

A solution of $C_6F_{13}I$ (18.78 g, 0.042 mol) in hexafluorobenzene (40 cm^3) was added dropwise over 3 h to a stirred mixture of 3-bromoiodobenzene (11.91 g, 0.042 mol), copper powder (5.88 g, 0.092 mol), 2,2′-bipyridine (0.46 g, 2.95 mmol), DMSO (40 cm^3) and C_6F_6 (60 cm^3) at 70°C. The mixture was subsequently stirred at 70°C for 72 h. After cooling, it was poured into a beaker containing dichloromethane (100 cm^3) and water (100 cm^3). After filtering, the organic layer was separated, washed with water (3×50 cm^3) and dried over $CaCl_2$ and $MgSO_4$. After concentration in vacuo to ca. 30 cm^3, the crude product was extracted into PP3 (3×20 cm^3) and the solvent was removed in vacuo. Distillation in vacuo using a Kugelröhr apparatus gave the product as a colourless liquid (bp 80–90°C, 0.02 mmHg) (8.6 g, 0.018 mol, 45%) (Found: C, 29.5; H, 0.8; $C_{12}H_4BrF_{13}$ requires C, 30.3; H, 0.8%); *m*/*z* (EI) 474/6 ($[M]^+$, 27%), 455/7 (6), 205/7 (100), 126 (37) and 69 (15): δ_H ($CDCl_3$) 7.67 (1H, s, 2-C_6H_4), 7.65 (1H, d, $^3J_{HH}$ 7.9, 6-C_6H_4), 7.45 (1H, d, $^3J_{HH}$ 7.9, 4-C_6H_4), 7.31 (1H, t, $^3J_{HH}$ 7.9, 5-C_6H_4); δ_F ($CDCl_3$) −81.3 (3F, t, $^3J_{FF}$ 10, CF_3), −111.2 (2F, t, $^3J_{FF}$14, $C^{\alpha}F_2$), −122.0 (2F, m, $C^{\beta}F_2$), −122.2 (2F, m, $C^{\delta}F_2$), −123.2 (2F, m, $C^{\epsilon}F_2$), −126.6 (2F, m, $C^{\gamma}F_2$).

2.2. $PPh_2(C_6H_4\text{-}3\text{-}C_6F_{13})$ **2**

n-Butyl-lithium (8.63 cm^3, 1.6 M solution in hexane) in diethyl ether (25 cm^3) was added dropwise over 1 h to BrC_6H_4-3-C_6F_{13} (6.57 g, 0.014 mol) with stirring under nitrogen in diethyl ether (75 cm^3) at −78°C and the reaction mixture was stirred at this temperature for a further 1 h. Diphenylchlorophosphine (3.04 g, 0.014 mol) in diethyl ether (25 cm^3) was then added dropwise, at −78°C, to the reaction mixture over a further hour before the reaction mixture was allowed to warm slowly to room temperature with continuous stirring over a 12 h period. The mixture was hydrolysed with 10% aqueous NH_4Cl (50 cm^3), the organic layer was collected, washed with water (2×30 cm^3) and dried over $MgSO_4$. The organic layer was concentrated in vacuo to ca. 15 cm^3 and passed quickly through a separating funnel half-filled with alumina using light petroleum (bp 40–60°C) as eluent. After the solvent was removed, the white solid was heated in a Kugelröhr apparatus (180°C, 0.05 mmHg) to remove any remaining starting material, yielding the product as a white solid (5.1 g, 62%) (Found: C, 49.3; H, 2.3; $C_{24}H_{14}F_{13}P$ requires C, 49.7; H, 2.4); *m*/*z* (FAB) 580 ($[M]^+$, 100%), 503 (21); δ_P ($CDCl_3$) −4.8 (s); δ_H ($CDCl_3$) 7.2–7.6 (14H, m, C_6H_5 and C_6H_4); δ_F ($CDCl_3$) −81.1 (3F, t, $^3J_{FF}$ 10, CF_3), −111.1 (2F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −122.0 (2F, m, $C^{\beta}F_2$), −122.2 (2F, m, $C^{\delta}F_2$), −123.2 (2F, m, $C^{\epsilon}F_2$), −126.7 (2F, m, $C^{\gamma}F_2$).

2.3. $PPh(C_6H_4\text{-}3\text{-}C_6F_{13})_2$ **3**

This was prepared similarly using phenyldichlorophosphine (1.16 g, 6.50 mmol) affording the product as a white solid (3.4 g, 54%) (Found: C, 40.4; H, 1.5; P, 4.6; $C_{30}H_{13}F_{26}P$ requires C, 40.1; H, 1.4; P, 3.5%); *m*/*z* (FAB) 898 ($[M]^+$, 56%), 821 (6) and 503 (18); δ_P ($CDCl_3$) −5.0 (s); δ_H ($CDCl_3$) 7.2–7.6 (13H, m, C_6H_5 and C_6H_4); δ_F ($CDCl_3$) −81.2 (6F, t, $^3J_{FF}$ 10, CF_3), −111.2 (4F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −122.0 (4F, m, $C^{\beta}F_2$), −122.2 (4F, m, $C^{\delta}F_2$), −123.2 (4F, m, $C^{\epsilon}F_2$), −126.7 (4F, m, $C^{\gamma}F_2$).

2.4. $P(C_6H_4\text{-}3\text{-}C_6F_{13})_3$ **4**

This was prepared similarly using phosphorus trichloride (0.57 g, 4.20 mmol), affording the product as a white solid (4.1 g, 71%) (Found: C, 35.4; H, 1.0; P, 4.4; $C_{36}H_{12}F_{39}P$ requires C, 35.5; H, 1.0; P, 2.5%); *m*/*z* (FAB) 1216 ($[M]^+$, 97%), 821 (51) 169 (21) and 69 (100); δ_P ($CDCl_3$) −6.0 (s); δ_H ($CDCl_3$) 7.2–7.8 (12H, m, C_6H_4); δ_F ($CDCl_3$) −81.5 (9F, t, $^3J_{FF}$ 10, CF_3), −111.7 (6F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −122.0 (6F, m, $C^{\beta}F_2$), −122.5 (6F, m, $C^{\delta}F_2$), −123.4 (6F, m, $C^{\epsilon}F_2$), −126.8 (6F, m, $C^{\gamma}F_2$).

2.5. $[RhCl_2(\eta^5\text{-}C_5Me_5)\{PPh_2(C_6H_4\text{-}3\text{-}C_6F_{13})\}]$ **5**

The ligand (0.145 g, 0.25 mmol) and $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ (0.77 g, 0.12 mmol) were stirred in refluxing ethanol (60 cm^3) under nitrogen for 1 h. The solvent was removed in vacuo and the resulting reddish solid was washed with hexane (10 cm^3), yielding a fine, red/orange powder (0.14 g, 0.16 mmol, 67%) (Found: C, 45.7; H, 3.1; $C_{34}H_{29}F_{13}PCl_2Rh$ requires C, 45.9; H, 3.3%); *m*/*z* (FAB) 853 ($[M-Cl]^+$) and 818 ($[M-2Cl]^+$); δ_P ($CDCl_3$) 30.6 (d, $^1J_{RhP}$ 144); δ_H ($CDCl_3$) 7.3–8.0 (14H, m, C_6H_5 and C_6H_4), 1.4 (15H, d, J_{HP} 4, Cp*); δ_F ($CDCl_3$) −81.7 (3F, t, $^3J_{FF}$ 10, CF_3), −111.3 (2F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −122.0 (2F, m, $C^{\beta}F_2$), −122.4 (2F, m, $C^{\delta}F_2$), −123.3 (2F, m, $C^{\epsilon}F_2$), −126.7 (2F, m, $C^{\gamma}F_2$).

2.6. $[RhCl_2(\eta^5\text{-}C_5Me_5)\{PPh(C_6H_4\text{-}3\text{-}C_6F_{13})_2\}]$ **6**

This was prepared similarly using $PPh(C_6H_4\text{-}3\text{-}C_6F_{13})_2$ **3** (0.225 g, 0.25 mmol) and the resulting red solid was recrystallized from dichloromethane–hexane, affording a fine, red/orange powder (0.23 g, 0.18 mmol, 78%) (Found: C, 40.2; H, 2.4; P, 2.2; $C_{40}H_{28}F_{26}PCl_2Rh$ requires C, 39.8; H, 2.3; P, 2.6%); *m*/*z* (FAB) 1206 ($[M]^+$), 1171 ($[M-Cl]^+$) and 1136 ($[M-2Cl]^+$); δ_P ($CDCl_3$) 30.8 (d, $^1J_{RhP}$ 147); δ_H ($CDCl_3$) 7.2–8.0 (13H, m, C_6H_5 and C_6H_4), 1.4 (15H, d, J_{HP} 4, Cp*); δ_F ($CDCl_3$) −81.3 (6F, t, $^3J_{FF}$ 10, CF_3), −111.6 (4F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −121.9 (4F, m, $C^{\beta}F_2$), −122.1 (4F, m, $C^{\delta}F_2$), −123.4 (4F, m, $C^{\epsilon}F_2$), −126.7 (4F, m, $C^{\gamma}F_2$).

*2.7. [$RhCl_2(\eta^5$-$C_5Me_5)\{P(C_6H_4$-3-$C_6F_{13})_3\}$] **7***

This was prepared similarly using $P(C_6H_4$-3-$C_6F_{13})_3$ **4** (0.304 g, 0.25 mmol) and the resulting red solid was recrystallized from dichloromethane–hexane, affording a fine, red/orange powder (0.30 g, 0.20 mmol, 83%) (Found: C, 36.4; H, 1.8; P, 3.3; $C_{46}H_{27}F_{39}PCl_2Rh$ requires C, 36.2; H, 1.8; P, 2.0%); *m/z* (FAB) 1489 ($[M-Cl]^+$) and 1454 ($[M-2Cl]^+$); δ_P ($CDCl_3$) 30.6 (d, $^1J_{RhP}$ 147); δ_H ($CDCl_3$) 7.4–7.9 (12H, m, C_6H_4), 1.4 (15H, d, J_{HP} 4, Cp*); δ_F ($CDCl_3$) −81.5 (9F, t, $^3J_{FF}$ 10, CF_3), −111.5 (6F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −122.1 (6F, m, $C^{\beta}F_2$), −122.3 (6F, m, $C^{\delta}F_2$), −123.5 (6F, m, $C^{\epsilon}F_2$), −126.8 (6F, m, $C^{\gamma}F_2$).

*2.8. trans-[$RhCl(CO)\{PPh_2(C_6H_4$-3-$C_6F_{13})\}_2$] **8***

The ligand (0.273 g, 0.47 mmol) and $[RhCl(CO)_2]_2$ (0.044 g, 0.11 mmol) were stirred for 2 h in refluxing dry dichloromethane (60 cm^3) under nitrogen. The solvent was removed in vacuo and the resulting yellow solid was washed with light petroleum (bp 40–60°C) (10 cm^3), yielding a fine yellow powder (0.42 g, 0.16 mmol, 73%) (Found: C, 45.0; H, 2.1; P, 5.6; $C_{49}H_{28}F_{26}P_2ClORh$ requires C, 44.3; H, 2.1; P, 4.7%); *m/z* (FAB) 1298 ($[M-CO]^+$) and 1263 ($[M-CO-Cl]^+$); δ_P ($CDCl_3$)(233K) 29.7 (d, $^1J_{RhP}$ 128); δ_H ($CDCl_3$) 7.2–7.9 (28H, m, C_6H_5 and C_6H_4); δ_F ($CDCl_3$) −81.3 (6F, t, $^3J_{FF}$ 10, CF_3), −111.4 (4F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −121.8 (4F, m, $C^{\beta}F_2$), −122.4 (4F, m, $C^{\delta}F_2$), −123.2 (4F, m, $C^{\epsilon}F_2$), −126.6 (4F, m, $C^{\gamma}F_2$).

*2.9. trans-[$RhCl(CO)\{PPh(C_6H_4$-3-$C_6F_{13})_2\}_2$] **9***

This was prepared similarly using $PPh(C_6H_4$-3-$C_6F_{13})_2$ **3** (0.422 g, 0.47 mmol), yielding the product as a yellow powder (0.30 g, 0.15 mmol, 69%) (Found: C, 37.6; H, 1.4; P, 3.6; $C_{61}H_{26}F_{52}P_2ClORh$ requires C, 37.3; H, 1.3; P, 3.2%); *m/z* (FAB) 1934 ($[M-CO]^+$) and 1899 ($[M-CO-Cl]^+$); δ_P ($CDCl_3$) 29.9 (d, $^1J_{RhP}$ 129); δ_H ($CDCl_3$) 7.3–7.8 (26H, m, C_6H_5 and C_6H_4); δ_F ($CDCl_3$) −81.3 (12F, t, $^3J_{FF}$ 11, CF_3), −111.5 (8F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −121.9 (8F, m, $C^{\beta}F_2$), −122.2 (8F, m, $C^{\delta}F_2$), −123.3 (8F, m, $C^{\epsilon}F_2$), −126.7 (8F, m, $C^{\gamma}F_2$).

*2.10. trans-[$RhCl(CO)\{P(C_6H_4$-3-$C_6F_{13})_3\}_2$] **10***

This was prepared similarly using $P(C_6H_4$-3-$C_6F_{13})_3$ **4** (0.571 g, 0.47 mmol), yielding the product as a yellow powder (0.45 g, 0.17 mmol, 78%) (Found: C, 33.8; H, 1.0; P, 2.5; $C_{73}H_{24}F_{78}P_2ClORh$ requires C, 33.7; H, 0.9; P, 2.4%); *m/z* (FAB) 2570 ($[M-CO]^+$) and 2535 ($[M-CO-Cl]^+$); δ_P (d^6-acetone) 31.8 (d, $^1J_{RhP}$ 132); δ_H (d^6-acetone) 7.7–8.2 (24H, m, C_6H_4); δ_F (d^6-acetone) −81.2 (18F, t, $^3J_{FF}$ 10, CF_3), −111.8 (12F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −121.2 (12F, m, $C^{\beta}F_2$), −121.8 (12F, m, $C^{\delta}F_2$), −122.8 (12F, m, $C^{\epsilon}F_2$), −126.1 (12F, m, $C^{\gamma}F_2$).

*2.11. cis- and trans-[$PtCl_2\{PPh_2(C_6H_4$-3-$C_6F_{13})\}_2$] **11***

The ligand (0.377 g, 0.65 mmol) and *cis*-$[PtCl_2(MeCN)_2]$ (0.105 g, 0.30 mmol) were stirred for 2 h in refluxing, dry, dichloromethane (60 cm^3) under nitrogen. The solvent was removed in vacuo and the resulting off-white solid was washed with light petroleum (bp 40–60°C) (10 cm^3). Recrystallization from dichloromethane–hexane resulted in a fine, white powder (0.31 g, 0.22 mmol, 73%) (Found: C, 39.1; H, 2.0; $C_{48}H_{28}F_{26}P_2ClPt$ requires C, 40.4; H, 2.0%); *m/z* (FAB) 1391 ($[M-Cl]^+$) and 1356 ($[M-2Cl]^+$); δ_P ($CDCl_3$) 21.2 (s, $^1J_{PtP}$ 2646, *trans*), 15.3 (s, $^1J_{PtP}$3633, *cis*); δ_H ($CDCl_3$) 7.2–7.8 (28H, m, C_6H_5 and C_6H_4); δ_F ($CDCl_3$) −81.4 (6F, t, $^3J_{FF}$ 10, CF_3), −111.8 (4F, t, $^3J_{FF}$ 14, C_2^{α}), −121.8 (4F, m, $C^{\beta}F_2$), −122.3 (4F, m, $C^{\delta}F_2$), −123.2 (4F, m, $C^{\epsilon}F_2$), −126.6 (4F, m, $C^{\gamma}F_2$); IR (Nujol) υ(M−Cl) 350(*trans*), 303, 328 (*cis*).

*2.12. cis- and trans-[$PtCl_2\{PPh(C_6H_4$-3-$C_6F_{13})_2\}_2$] **12***

This was prepared similarly using $PPh(C_6H_4$-3-$C_6F_{13})_2$ **3** (0.583 g, 0.65 mmol), yielding the product as a white powder (0.33 g, 0.16 mmol, 53%) (Found: C, 34.2; H, 1.3; $C_{60}H_{26}F_{52}P_2ClPt$ requires C, 35.0; H, 1.3%); *m/z* (FAB) 2062 ($[M]^+$) and 2027 ($[M-Cl]^+$); δ_P ($CDCl_3$) 21.8 (s, $^1J_{PtP}$ 2696, *trans*), 15.8 (s, $^1J_{PtP}$3602, *cis*); δ_H ($CDCl_3$) 7.2–7.8 (26H, m, C_6H_5 and C_6H_4); δ_F ($CDCl_3$) −81.4 (12F, t, $^3J_{FF}$ 10, CF_3), −111.8 (8F, t, $^3J_{FF}$ 14, $C^{\alpha}F_2$), −121.8 (8F, m, $C^{\beta}F_2$), −122.3 (8F, m, $C^{\delta}F_2$), −123.2 (8F, m, $C^{\epsilon}F_2$), −126.6 (8F, m, $C^{\gamma}F_2$); IR (Nujol) υ(M−Cl) 351(*trans*), 303, 323 (*cis*).

*2.13. trans-[$PtCl_2\{P(C_6H_4$-3-$C_6F_{13})_3\}_2$] **13***

This was prepared similarly using $P(C_6H_4$-3-$C_6F_{13})_3$ **4** (0.790 g, 0.65 mmol), yielding the product as a white powder (0.62 g, 0.23 mmol, 78%) (Found: C, 31.8; H, 1.0; $C_{72}H_{24}F_{78}P_2ClPt$ requires C, 32.0; H, 0.9%); *m/z* (FAB) 2663 ($[M-Cl]^+$); δ_P ($C_6H_5CF_3$) 21.8 (s, $^1J_{PtP}$ 2723, *trans*); IR (Nujol) υ(M−Cl) 351.

*2.14. [$RhCl\{P(C_6H_4$-3-$C_6F_{13})_3\}_3$] **14***

To the ligand (0.16 mmol), dissolved in dry, degassed, perfluoro-1,3-dimethylcyclohexane (1 cm^3) in a Schlenk flask, was added, by syringe, $[RhCl(C_2H_4)_2]_2$ (0.010 g, 0.027 mmol) dissolved in dry, degassed, CH_2Cl_2 (1 cm^3) under nitrogen. The resulting mixture was stirred vigorously for 2 min, after which time, all of the colour associated

with the rhodium had transferred to the lower, fluorous, phase. A sample was removed by syringe and the NMR spectrum was recorded in PP3 in a Young's NMR tube. δ_P 37.5 (2P, dd, $^1J_{RhP}$ 142, $^2J_{PP}$ 38, $P_{trans\text{-}P}$), 49.0 (1P, dt, $^1J_{RhP}$ 189, $^2J_{PP}$ 38, $P_{trans\text{-}Cl}$).

2.15. [RhCl{P(C$_6$H$_4$-3-CF$_3$)$_3$}$_3$] **15**

This was prepared similarly using dry, degassed, $CDCl_3$ as the solvent throughout. δ_P 37.3 (2P, dd, $^1J_{RhP}$ 142, $^2J_{PP}$ 38, $P_{trans\text{-}P}$), 50.5 (1P, dt, $^1J_{RhP}$ 188, $^2J_{PP}$ 38, $P_{trans\text{-}Cl}$).

3. Results and discussion

The syntheses of the *meta*-derivatised triaryl phosphines **2–4** with one, two and three perfluoroalkyl substituents respectively, via 3-bromo-perfluorohexylbenzene, (Scheme 1) is essentially the same as the route used to prepare the analogous *para*-derivatised compounds. The ligands were formed in 54–70% yields as air-stable, white solids. The spectroscopic data (Experimental) are entirely consistent with the formulations, in particular, each gave a single resonance in the $^{31}P\{^1H\}$ NMR spectrum (at ca. δ −5) typical for triarylphosphines. Only the tris-derivatised phosphine is preferentially soluble in perfluorocarbon solvents.

We have previously shown [11], for the *para*-derivatised triarylphosphine ligands, that the introduction of the perfluoroalkyl group does not restrict the type of reactivity shown by these ligands, and we observe comparable effects for the *meta*-derivatised ligands, i.e. facile displacement of weakly coordinated ligands and cleavage of halide-bridged dinuclear metal complexes. On reaction with $[Cp^*RhCl_2]_2$, the mononuclear $[Cp^*RhCl_2L]$ (**5–7**) are formed as air-stable orange solids, which are not soluble in perfluorocarbon solvents. For these complexes, $^1J_{RhP}$ is insensitive to both the number of perfluoroalkyl substituents and the position of the perfluoroalkyl groups on the aryl rings.

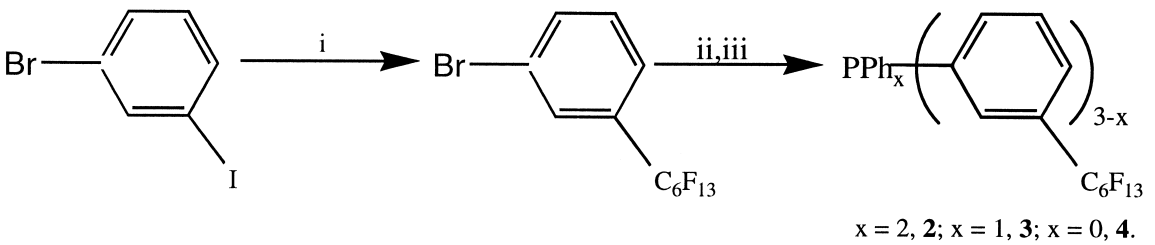
For the air-stable, yellow *trans*-$[RhCl(CO)L_2]$ (**8–10**), prepared from $[RhCl(CO)_2]_2$ and the free ligands, the ^{31}P NMR spectroscopic data are also insensitive to the number of perfluoroalkyl substituents and their positions on the aryl rings. Interestingly, as seen for *trans*-[RhCl(CO){PPh$_2$(C$_6$H$_4$-4-C$_6$F$_{13}$)}$_2$], the ^{31}P NMR spectrum for *trans*-[RhCl(CO){PPh$_2$(C$_6$H$_4$-3-C$_6$F$_{13}$)}$_2$] **8** is a broad singlet at room temperature, which only resolves into the expected rhodium coupled doublet at 233 K, suggesting that both of these complexes are fluxional at room temperature. In marked contrast to the NMR spectroscopic data, ν(CO) shows a variation with the number of perfluoroalkyl substituents, but is insensitive to the position of the perfluoroalkyl group on the aryl rings (Table 1), indicating that, in this series, *meta*- and *para*-substitution reduce the σ-donor properties of these phosphine ligands by a similar amount. Only *trans*-[RhCl(CO){P(C$_6$H$_4$-3-C$_6$F$_{13}$)$_3$}$_2$] **10** is preferentially soluble in perfluorocarbon solvents.

Table 1
Variation of ν(CO)[a] in *trans*-$[RhCl(CO)L_2]$ with the number and position of perfluoroalkyl groups

L	*meta*-substitution ($x=3$)	*para*-substitution ($x=4$)
PPh$_3$[b]	1965	1965
PPh$_2$(C$_6$H$_4$-*x*-C$_6$F$_{13}$)	1980	1982
PPh(C$_6$H$_4$-*x*-C$_6$F$_{13}$)$_2$	1984	1983
P(C$_6$H$_4$-*x*-C$_6$F$_{13}$)$_3$	1992	1993

[a] ν(CO)/cm^{-1}. Recorded as Nujol mulls unless otherwise stated.
[b] In CH_2Cl_2 solution. Data taken from ref. [21].

The reactions of the free phosphines with *cis*-$[PtCl_2(MeCN)_2]$ (affording **11–13**) offered the first indication of the steric influence of the *meta*-substituents in these ligands. Previously, we have shown that, although exclusively *cis*-$[PtCl_2L_2]$ complexes are obtained from the reaction of the mono- and bis-derivatised *para*-substituted ligands {PPh$_2$(C$_6$H$_4$-4-C$_6$F$_{13}$) and PPh(C$_6$H$_4$-4-C$_6$F$_{13}$)$_2$} with $[PtCl_2(MeCN)_2]$, an inseparable mixture of *cis*- and *trans*-isomers was obtained in the same reaction with P(C$_6$H$_4$-4-C$_6$F$_{13}$)$_3$ [11]. In this work, complexes [PtCl$_2${PPh$_2$(C$_6$H$_4$-3-C$_6$F$_{13}$)$_2$}] **11** and [PtCl$_2${PPh(C$_6$H$_4$-3-C$_6$F$_{13}$)$_2$}$_2$] **12** were obtained as mixtures of *cis*- and *trans*-isomers, whilst complex **13** is exclusively *trans*-



x = 2, **2**; x = 1, **3**; x = 0, **4**.

(i) $C_6F_{13}I$, Cu, bipy, C_6F_6, dmso; (ii) nBuLi, Et_2O, -78 °C; (iii) PPh_xCl_{3-x}, Et_2O

Scheme 1.

$[PtCl_2\{P(C_6H_4\text{-}3\text{-}C_6F_{13})_3\}_2]$, as revealed by IR and ^{31}P NMR spectroscopic data (Experimental). The observed thermodynamic preference, which is opposite to that usually seen for $[PtCl_2(phosphine)_2]$ complexes, can only arise from steric congestion around the metal centres for the *cis*-isomers, which increases progressively with the number of perfluoroalkyl substituents. We note that, although integration in ^{31}P NMR is a poor quantitative tool [18], the *cis*:*trans* ratios in $[PtCl_2\{PPh_2(C_6H_4\text{-}3\text{-}C_6F_{13})_2]$ **11** and $[PtCl_2\{PPh(C_6H_4\text{-}3\text{-}C_6F_{13})_2\}_2]$ **12** are approximately 3:2 and 1:3, respectively. Table 2 summarises the $^1J_{PtP}$ coupling constant data for these and related platinum(II) complexes. In line with the υ(CO) data for *trans*-$[RhCl(CO)L_2]$, $^1J_{PtP}$ for the *cis*-isomers decreases with the number of perfluoroalkyl substituents, reflecting the reduction in σ-donor power of the phosphorus atoms [19]. For the *trans*-isomers, $^1J_{PtP}$ *increases* with the number of perfluoroalkyl groups, an effect that is mirrored in the variation of $^1J_{PtP}$ for *trans*-$[PtCl_2L_2]$ ($PBu_3 < PPr_3 < PEt_3$) [20], which can be ascribed to the increased π-acceptor ability of the phosphorus atoms on the introduction of the electron-withdrawing perfluoroalkyl substituents. This data, for the first time in our work, also suggests a subtle variation in the influence of the perfluoroalkyl groups with ring position where $^1J_{PtP}$ for *cis*-$[PtCl_2\{PPh_2(C_6H_4\text{-}3\text{-}C_6F_{13})_2]$ **11** and *cis*-$[PtCl_2\{PPh(C_6H_4\text{-}3\text{-}C_6F_{13})_2\}_2]$ **12** are less than those for the analogous *para*-substituted metal complexes, indicating a slightly greater electron-withdrawing effect for the *meta*-derivatised ligands than their *para*-derivatised congeners. None of the $[PtCl_2L_2]$ complexes are preferentially soluble in perfluorocarbon solvents.

Steric congestion at the metal centre does not preclude formation of the preferentially perfluorocarbon solvent-soluble $[RhCl\{P(C_6H_4\text{-}3\text{-}C_6F_{13})_3\}_3]$ (**14**) for which the NMR spectroscopic data are almost identical to those for the analogous tris-*para*-substituted ligand [11] and for the tris-*meta*-CF_3 ligand (**15**) complexes.

Table 2
$^{31}P\{^1H\}$ NMR data for $[PtCl_2Cl_2]$[a]

Ligand	*cis*-$[PtCl_2L_2]$		*trans*-$[PtCl_2L_2]$	
	$\Delta(^{31}P)$	$^1J_{PtP}$	$\Delta(^{31}P)$	$^1J_{PtP}$
PPh_3[b]	18.9	3676	25.4	2635
$PPh_2(C_6H_4\text{-}3\text{-}C_6F_{13})$	20.1	3633	26.0	2646
$PPh(C_6H_4\text{-}3\text{-}C_6F_{13})_2$	20.8	3602	26.8	2696
$P(C_6H_4\text{-}3\text{-}C_6F_{13})_3$	–	–	27.8	2723
$PPh_2(C_6H_4\text{-}4\text{-}C_6F_{13})$	19.6	3653	–	–
$PPh(C_6H_4\text{-}4\text{-}C_6F_{13})_2$	20.0	3635	–	–
$P(C_6H_4\text{-}4\text{-}C_6F_{13})_3$	21.5	3631	28.8	2719

[a] $\Delta(^{31}P) = \delta_{metal\ complex} - \delta_{free\ ligand}$/ppm, $^1J_{PtP}$/Hz.
[b] Data taken from Ref. [22].

4. Conclusions

The introduction of perfluoroalkyl ponytails into the *meta*-positions of triarylphosphine ligands is straightforward. These ligands readily coordinate to a series of platinum group metals wherein the *meta*-substitution induces little or no greater electronic influence than the related *para*-substitution, although there is some evidence for a greater steric influence. Only the free tris-derivatised ligand and the complexes *trans*-$[RhCl(CO)L_2]$ and $[RhClL_3]$ $\{L = P(C_6H_4\text{-}4\text{-}C_6F_{13})_3\}$ are preferentially soluble in perfluorocarbon solvents.

Acknowledgements

We thank the EPSRC (D.R.P. and A.M.S.), BP Chemicals Ltd. (D.R.P.) and the Royal Society (E.G.H.) for financial support.

References

[1] I.T. Horváth, J. Rábai, Science 260 (1994) 72.
[2] I.T. Horváth, Acc. Chem. Res. 31 (1998) 641.
[3] J. Fawcett, E.G. Hope, R.D.W. Kemmitt, D.R. Paige, D.R. Russell, A.M. Stuart, D.J. Cole-Hamilton, M.J. Payne, Chem. Commun. (1997) 1127.
[4] M.-A. Guillevic, A.M. Arif, I.T. Horváth, J.A. Gladysz, Angew. Chem., Int. Ed. Engl. 36 (1997) 1612.
[5] M.-A. Guillevic, C. Rocaboy, A.M. Arif, I.T. Horváth, J.A. Gladysz, Organometallics 17 (1998) 707.
[6] J.J.J. Juliette, I.T. Horváth, J.A. Gladysz, Angew. Chem., Int. Ed. Engl. 36 (1997) 1610.
[7] B. Betzmeier, P. Knochel, Angew. Chem., Int. Ed. Engl. 36 (1997) 2623.
[8] P. Bhattacharyya, D. Gudmunsen, E.G. Hope, R.D.W. Kemmitt, D.R. Paige, A.M. Stuart, J. Chem. Soc., Perkin Trans. 1 (1997) 3609.
[9] V. Herrera, P.J.F. de Rege, I.T. Horváth, T. Le Husebo, R.P. Hughes, Inorg. Chem. Commun. 1 (1998) 197.
[10] L.J. Alvey, D. Rutherford, J.J.J. Juliette, J.A. Gladysz, J. Org. Chem. 63 (1998) 6302.
[11] J. Fawcett, E.G. Hope, R.D.W. Kemmitt, D.R. Paige, D.R. Russell, A.M. Stuart, J. Chem. Soc., Dalton Trans. (1998) 3751.
[12] C.M. Haar, J. Huang, S.P. Nolan, J.L. Petersen, Organometallics 17 (1998) 5018.
[13] G. Pozzi, S. Banfi, A. Manfredi, F. Montanari, S. Quici, Tetrahedron 52 (1996) 11879.
[14] G. Pozzi, F. Montanari, S. Quici, Chem. Commun. (1997) 69.
[15] G. Pozzi, I. Colombani, M. Miglioli, F. Montanari, S. Quici, Tetrahedron 53 (1997) 6145.
[16] G. Pozzi, F. Cinato, F. Montanari, S. Quici, Chem. Commun. (1998) 877.
[17] G. Pacchioni, P.S. Bagus, Inorg. Chem. 31 (1992) 4391.
[18] S.R. Davies, M.C. Mitchell, C.P. Cain, P.G. Devitt, R.J. Taylor, T.P. Kee, J. Organomet. Chem. 550 (1998) 29.
[19] C.J. Cobley, P.G. Pringle, Inorg. Chim. Acta 265 (1997) 107.
[20] R.F. Gould, in: Platinum Group Metals and Complexes, ACS, Washington, DC, 1971, p. 102.
[21] K.G. Moloy, J.L. Peterson, J. Am. Chem. Soc. 117 (1995) 7696.
[22] R.G. Goel, Inorg. Nucl. Chem. Lett. 15 (1979) 437.