Fluorous-phase soluble rhodium complexes: X-ray structure of [RhCl(CO)(P($C_2H_4C_6F_{13}$)$_3$)$_2$]

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Rhodium(I) complexes of the ligands P($CH_2CH_2C_6F_{13}$)$_3$ and P($C_6H_4C_6F_{13}$-4)$_3$, which can be compared to their perprotio analogues, maintain their structures in fluorous solvents.

Following the first report of the alternative approach to two-phase catalysis called the 'fluorous biphase system' (FBS)[1] this methodology has been employed in a number of organic reactions,[2] and catalytically in the epoxidation of alkenes.[3] In short, the FBS approach involves derivatising inorganic or organic reagents with long perfluorinated aliphatic 'ponytails' which renders these reagents soluble in a perfluorocarbon phase allowing the facile separation of these reagents, after catalysis, from the substrate/product dissolved in an organic solvent. The approach is attracting significant interest since it should allow the facile separation of catalyst from reactants and products using simple liquid/liquid separation techniques and benign, non-toxic, reusable perfluorocarbon solvents for industrial scale homogeneous catalysis. However, although it has been shown that catalyst separation is readily achieved under FBS regimes,[1–3] the exact nature and the influence of the highly electron-withdrawing fluorous ponytails on these fluorous-soluble catalysts has not been established. Since (*i*) phosphorus(III) ligands have found wide application in homogeneous catalysis, (*ii*) the first FBS report outlined the use of an uncharacterised rhodium–phosphine catalyst[1] and (*iii*) we have a long-standing interest in fluorinated phosphorus(III) ligands,[4] we have been investigating the coordination chemistry of a series of derivatised phosphine ligands and here report the synthesis and characterisation of some rhodium(I) complexes and the first structural characterisation of a fluorous-phase soluble metal complex.

The reaction of either of the tris-derivatised fluorous-phase soluble ligands P($CH_2CH_2C_6F_{13}$)$_3$ or P($C_6H_4C_6F_{13}$-4)$_3$[5] with [{RhCl(CO)$_2$}$_2$] yields the complexes [RhCl(CO)L$_2$], in high yields, as slightly air-sensitive yellow solids. Despite the unusually high molecular masses of these complexes, they have been characterised by standard techniques.† The influence of the C_6F_{13} units can be probed by a comparison of the ν(CO) and ^1J(RhP) data with that for the analogous triethyl- and triphenyl-phosphine complexes {ν(CO): [RhCl(CO)(PEt$_3$)$_2$] 1953 cm^{②1}, [RhCl(CO)(PPh$_3$)$_2$] 1961 cm^{②1}; ^1J(RhP): [RhCl(CO)(PEt$_3$)$_2$] 116 Hz, [RhCl(CO)(PPh$_3$)$_2$] 124 Hz}.[6] In both cases, although the ^1J(RhP) values are very similar, ν(CO) is significantly higher as a result of introducing the fluorous ponytails, suggesting that the electron-withdrawing capacity of the ponytails is removing electron density from the metal centres.

Crystals of [RhCl(CO){P($CH_2CH_2C_6F_{13}$)$_3$}$_2$], suitable for crystallographic characterisation, have been obtained by slow evaporation from perfluoro-1,3-dimethylcyclohexane solution (Fig. 1).‡ The ^{1}H, ^{19}F and ^{31}P{^{1}H} NMR, IR and mass spectra of **1a** and **1b** are entirely consistent with this structure.† The metal coordination geometry is very similar to that obtained for a range of *trans*-square-planar complexes, [RhCl(CO)L$_2$] (L = monodentate phosphine) Rh–P$_{\text{mean}}$ 2.328 Å, Rh–Cl$_{\text{mean}}$ 2.386 Å, Rh–C$_{\text{mean}}$ 1.803 Å.[7] For **1a**, the Rh–P and Rh–Cl bond distances are shorter than these calculated mean values, but are not the shortest metal–ligand distances seen for this class of complex and are very similar to those reported for trisalkyl phosphine ligands, *e.g.* [RhCl(CO)(PMe$_3$)$_2$] (Rh–P 2.307, 2.310 Å; Rh–Cl 2.354 Å).[8] Although there are no unusual angles at phosphorus, there are two types of fluorinated tails. Two pairs on each phosphorus spiral, in a similar fashion to that observed for fully fluorinated hydrocarbons, above and below the Cl–Rh–CO axis in nearly planar 'rugby-post' arrangements. These sets of rugby-posts stack on top of each other in adjacent unit cells. The third, unique, ponytail on each phosphorus does not spiral but kinks, in the same direction, either above or below the Cl–Rh–CO axis into the space in the unit cell between adjacent sets of rugby-posts pointing, generally, away from any other fluorous part of the molecule.

We were interested to establish whether these complexes dissolve, without reaction, in fluorous solvents and have investigated the first coordination sphere at the metal centre in the solid-state and in fluorous solution by rhodium K-edge

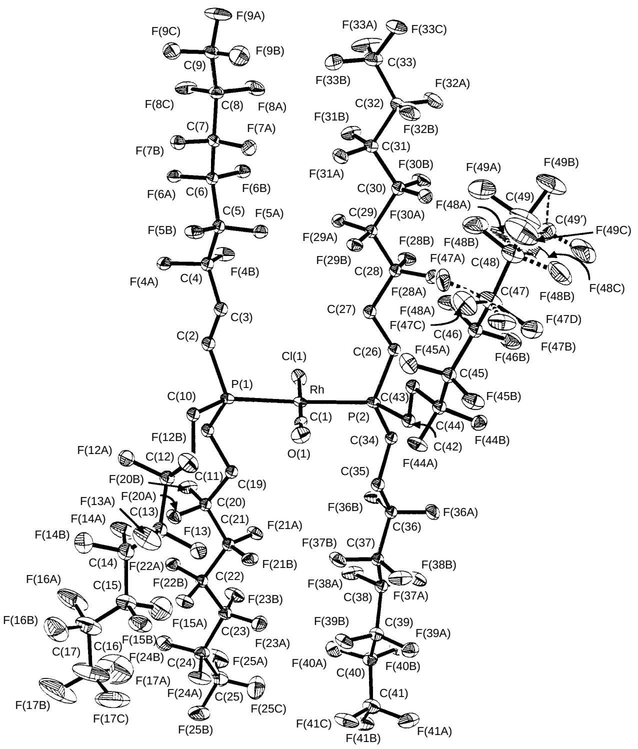

Fig. 1 Molecular structure of **1a**. Selected interatomic distances (Å) and angles (°): Rh–P(1) 2.300(2), Rh–P(2) 2.304(2), Rh–Cl 2.356(2), Rh–C(1) 1.807(5), C(1)–O(1) 1.152(6), P(1)–C(2) 1.835(6), P(1)–C(10) 1.833(5), P(1)–C(18) 1.830(5), P(2)–C(26) 1.829(5), P(2)–C(34) 1.834(6), P(2)–C(42) 1.844(5), av. C–C 1.523(8), av. C–F 1.341(6), P(2)–Rh–P(1) 172.12(10), C(1)–Rh–Cl 179.4(5), av. C–P–Rh 115.3(2).

Table 1 Metal-centred interatomic distances for **1a**[a]

	X-Ray	Solid-state EXAFS[b]		Solution EXAFS[c]	
	d/Å	d/Å	$2\sigma^2$/Å[d]	d/Å	$2\sigma^2$/Å[d]
Rh–P	2.300(2), 2.304(2)	2.300(1)	0.005(1)	2.301(2)	0.010(1)
Rh–Cl	2.356(2)	2.360(9)	0.016(1)	—	—
Rh–C	1.807(5)	1.787(4)	0.004(1)	1.792(6)	0.008(1)
Rh···O	2.959	2.929(6)	0.016(1)	2.912(5)	0.013(1)
C–O	1.152(6)	1.142	—	1.120	—

[a] Standard deviation in parentheses. [b] Transmission EXAFS data collected on station 9:2 using a Si(220) monochromator for **1a** diluted with boron nitride and held between Sellotape strips. Note that the systematic errors in bond distances arising from the data collection and analysis procedures are *ca.* ±0.02 Å for the first coordination shells and *ca.* ±0.04 Å for subsequent shells. Fit index = $\Sigma_i[\chi^{T}$ ② $\chi^{E})k_i^{3}]^2$ = 0.380. R = $[\int(\chi^{T}$ ② $\chi^{E})k^3\mathrm{d}k/\int\chi^{E}k^3\mathrm{d}k]$ = 23.0% [c] Transmission EXAFS data for a *ca.* 0.013 mol dm^{②3} solution of **1a** in perfluoro-1,3-dimethylcyclohexane in a flattened FEP (perfluoroethylene–propylene copolymer) tube.[10] The poorer data quality did not allow for the distinction between the Rh–P and Rh–Cl shells. The fit given here is for a single shell of 3 P atoms. Fit index = $\Sigma_i[(\chi^{T}$ ② $\chi^{E})k_i^{3}]^2$ = 0.580. R = $[\int(\chi^{T}$ ② $\chi^{E})k^3\mathrm{d}k/\int\chi^{E}k^3\mathrm{d}k]$ = 22.6%. [d] Debye–Waller factor.

EXAFS (Table 1). The data, analysed by standard procedures,[9,10] clearly indicate that these complexes dissolve without reaction in fluorous solvents and that the active sites of fluorous soluble metal catalysts could be probed in this way; the active sites of hydrocarbon soluble metal catalysts have been probed, under catalytic conditions, by EXAFS.[9] Further work on the coordination chemistry of these, and related, ligands and the catalytic activity of these metal complexes under the FBS regime is underway.

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Footnotes

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† *Data* for **1a**, Anal. Calc. for $C_{49}H_{24}ClF_{78}OP_2Rh$: C 25.5, H 1.0, F 64.1. Found: C 25.4, H 1.0, F 63.1%. MS(FAB): *m/z* 2311(M$^+$). IR 1990 cm^{②1} [ν(CO)]. NMR: δ_H [250.13 MHz, $(CD_3)_2CO$], 2.62 (2 H, m, CH_2) 3.22 (2 H, t, J 12 Hz, CH_2): δ_P [101.26 MHz, $(CD_3)_2CO$] 22.9 [d, ^1J(RhP) 121 Hz]: δ_F [235.34 MHz, $(CD_3)_2CO$] ② 80.36 (3F, t, J 11 Hz, CF_3), ② 114.39 (2F, m), ② 121.69 (2F, m) ② 122.70 (2F, m), ② 122.96 (2F, m), ② 126.07 (2F, m).

For **1b**, Anal. Calc. for $C_{73}H_{24}ClF_{78}OP_2Rh$: C, 33.7, H, 0.9, P, 2.4; Found: C, 33.5, H, 0.9, P, 2.5%. MS(FAB): *m/z* 2535 ([M ② Cl ② CO]$^+$). IR 1992 [ν(CO)]. NMR: ν_H (250.13 MHz, $CDCl_3$) 7.65 (2 H, m), 7.80 (2 H, m): δ_P (101.26 MHz, $CDCl_3$) 30.0 [d, ^1J(RhP) 131 Hz]; δ_F (235.34, $CDCl_3$) ② 81.40 (3F, t, J 11.5 Hz, CF_3), ② 111.73 (2F, m), ② 121.89 (2F, m), ② 122.05 (2F, m), ② 123.29 (2F, m), ② 126.69 (2F, m).

‡ *Crystal data* for **1a**: $C_{49}H_{24}ClF_{78}OP_2Rh$, M = 2310.98, triclinic, space group $P\bar{1}$, a = 11.205(9), b = 15.062(4), c = 22.506(5) Å, α = 84.70(2), β = 86.23(4), γ = 79.93(2)°, U = 3719(3) Å^3, Z = 2, D_c = 2.064 Mg m^{②3}, $F(000)$ = 2240, μ(Mo-Kα) = 0.815 mm^{②1}, crystal dimensions 0.71 ③ 0.40 ③ 0.12 mm. Accurate unit-cell dimensions were determined by least-squares refinement of 37 centred reflections with 2.53 < θ < 12.5°. Data were measured on a Siemens P4 diffractometer at 150 K with Mo-Kα radiation using ω-scans. 15 371 reflections were measured with θ < 25° and ② 1 ☚ h ☚ 12, ② 17 ☚ k ☚ 17, ② 26 ☚ l ☚ 26. The reflections were corrected for Lorentz and polarisation effects and merged to give 11 855 independent reflections (R_{int} = 0.0188). An analytical absorption correction was applied to the data (T_{max}, T_{min} = 0.88, 0.65, respectively). The structure was solved by direct methods using the program SHELXTL-PC. The terminal atoms of one of the chains were found to be disordered with the atoms having 60:40 occupancy over two sites. All hydrogen atoms were included in calculated positions (C–H 0.96 Å) with isotropic displacement parameters set to 1.2 U_{eq} of the bonded C atom. The first six carbon atoms of each chain were refined with isotropic displacement parameters and all other atoms were refined with anisotropic thermal parameters. Final cycles of refinement with full-matrix least squares on F^2 gave R_1 = 0.0560, wR_2 = 0.1287. The maximum and minimum residual electron densities in the final ΔF map were 1.686 and ② 0.571 e Å^{②3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/459.

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