

Platinum group metal complexes of a bis(diphenylphosphino)ethane ligand containing perfluoroalkyl ponytails

Eric G. Hope,* Raymond D. W. Kemmitt and Alison M. Stuart

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

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The perfluoroalkyl-derivatised bidentate phosphine (4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)₂ reacted with [PtCl₂(MeCN)₂], [PdCl₂(MeCN)₂] or [{RhCl(COD)}₂] to yield the complexes [PtCl₂(L-L)] **1**, [PdCl₂(L-L)] **2** and [Pd(L-L)₂]²⁺2Cl⁻ **3** or [{RhCl(L-L)}₂] **5** respectively. Complex **3** was reduced with NaBH₄ to [Pd(L-L)₂] **4** and the chloride bridges in **5** were cleaved with triphenylphosphine to yield [RhCl(L-L)(PPh₃)] **6**. The reaction of the ligand with [{RhCl₂(η⁵-C₅Me₅)₂] in a 1:1 or a 2:1 ratio yielded either [{RhCl₂(η⁵-C₅Me₅)₂(L-L)] **7** or, after metathesis with NH₄BF₄ in acetone, [RhCl(η⁵-C₅Me₅)(L-L)]⁺BF₄⁻ **8** respectively. Throughout, spectroscopic studies indicated that the ligand co-ordinates in a similar fashion to bis(diphenylphosphino)ethane (dppe). Complex **7** and the analogous dppe complex are fluxional at room temperature. At the low temperature limit, all the nuclei within these molecules are chemically inequivalent for which simulation suggests a *gauche*-eclipsed conformation around the PCH₂-CH₂P bond. Solubility studies indicated that only **4** and **5** are preferentially soluble in perfluorocarbon solvents.

Following the proposal of the fluorous biphasic concept as a solution to the problem of catalyst/product separation in homogeneous catalysis,¹ a number of ligands derivatised with long perfluoroalkyl sidechains have been prepared and their application in this field tested.¹⁻⁶ Many of these systems involve monodentate phosphine ligands but, in view of the additional catalyst stability offered by chelating ligands and their widespread application in homogeneous catalysis, we have recently prepared a perfluoroalkyl-derivatised analogue of bis(diphenylphosphino)ethane (dppe).⁷ Here, we illustrate the influence of the fluorous ponytails on the donor properties of this ligand by the synthesis and characterisation of a series of platinum metal group complexes.

Experimental

Proton, ¹⁹F and ³¹P NMR spectroscopies were carried out on a Bruker ARX250 spectrometer at 250.13, 235.34 and 101.26 MHz or a Bruker DRX 400 spectrometer at 400.13, 376.50 and 161.98 MHz and were referenced to external SiMe₄ (¹H), to external CFCl₃ (¹⁹F) and to external 85% H₃PO₄ (³¹P) using the high-frequency positive convention. Elemental analyses were performed by Butterworth Laboratories Ltd. Mass spectra were recorded on a Kratos Concept 1H mass spectrometer.

The ligand,⁷ [{RhCl(COD)}₂],⁸ [PdCl₂(MeCN)₂] and [PtCl₂(MeCN)₂]⁹ were prepared by the literature routes. Toluene and diethyl ether were dried by refluxing over sodium, dichloromethane by refluxing over calcium hydride and perfluoro-1,3-dimethylcyclohexane (PP3) by refluxing over calcium hydride and then freeze/thaw/degassed. Each solvent was stored in a closed glass ampoule over molecular sieves.

Preparations

[PtCl₂{(4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)₂}] **1**. A mixture of [PtCl₂(MeCN)₂] (0.139 g, 0.4 mmol), the ligand (0.67 g, 0.4 mmol) and dichloromethane (50 cm³) was refluxed under nitrogen for 5 h. After cooling to room temperature the solvent was removed on a rotary evaporator and the white solid (0.68 g, 88%) washed with hexane (Found: C, 32.0; H, 1.0. C₅₀H₂₀Cl₂F₅₂P₂Pt requires C, 31.0; H, 1.0%). MS (FAB): *m/z* 1901 (M - Cl)⁺. ¹⁹F NMR [(CD₃)₂CO]: δ -80.8 (12F, t,

³J_{FF} 10, CF₃), -110.5 [8F, unresolved(u)m, C^αF₂], -121.1 (16F, um, C^βF₂ and C^δF₂), -122.4 (8F, um, C^εF₂) and -125.8 (8F, um, C^γF₂).

[PdCl₂{(4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)₂}] **2**. A mixture of [PdCl₂(MeCN)₂] (0.078 g, 0.3 mmol), the ligand (0.52 g, 0.3 mmol) and dichloromethane (50 cm³) was refluxed under nitrogen for 4 h. After cooling to room temperature the solvent was removed on a rotary evaporator and the products were washed with light petroleum (bp 40–60 °C) to give a pale yellow solid (0.50 g, 90%) (Found: C, 32.8; H, 0.8. C₅₀H₂₀Cl₂F₅₂P₂Pd requires C, 32.5; H, 1.1%). MS (EI): *m/z* 1811 (M - Cl)⁺ and 1776 (M - HCl)⁺. ¹⁹F NMR (CDCl₃): δ -81.2 (12F, t, ³J_{FF} 10, CF₃), -111.9 (8F, um, C^αF₂), -121.8 (16F, um, C^βF₂ and C^δF₂), -123.2 (8F, um, C^εF₂) and -126.6 (8F, um, C^γF₂).

[Pd{(4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)₂}]²⁺2Cl⁻ **3**. A mixture of [PdCl₂(MeCN)₂] (0.039 g, 0.15 mmol), the ligand (0.530 g, 0.32 mmol) and dichloromethane (100 cm³) was refluxed under nitrogen for 19 h. After cooling to room temperature the volume of solvent was reduced to 20 cm³ on a rotary evaporator and the product filtered off. It was washed with light petroleum and dichloromethane to give an insoluble white solid (0.435 g, 82%) (Found: C, 34.0; H, 1.1; F, 50.1; P, 4.0. C₁₀₀H₄₀Cl₂F₁₀₄P₄Pd requires C, 34.1; H, 1.15; F, 56.2; P, 3.5%). MS (FAB): *m/z* 3483 (M - Cl)⁺ and 3447 (M - Cl₂)⁺.

[Pd{(4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)₂}] **4**. A solution of NaBH₄ (0.11 g, 2.9 mmol) in water (10 cm³) was added dropwise over 15 min to a suspension of complex **3** (0.34 g, 0.1 mmol) in water (15 cm³) and acetone (15 cm³) under nitrogen. An exotherm (50 °C) was observed during the addition. The reaction mixture was stirred at room temperature under nitrogen for 2 h. The product was extracted into ether and washed with water. After drying the ether layer over MgSO₄ the ether was removed. The product was washed twice with dichloromethane and then dried under vacuum to give an orange solid (0.19 g, 57%) which decomposed slowly in solution and was light sensitive (Found: C, 34.3; H, 1.2. C₁₀₀H₄₀F₁₀₄P₄Pd requires C, 34.8; H, 1.2%). MS (FAB): *m/z* 3448 (M)⁺. ¹⁹F

NMR (CD₂Cl₂): δ -81.8 (24F, t, $^3J_{\text{FF}}$ 10, CF₃), -111.7 (16F, um, C ^{α} F₂), -122.3 (32F, um, C ^{β} F₂ and C ^{δ} F₂), -123.6 (16F, um, C ^{ϵ} F₂) and -126.9 (16F, um, C ^{ν} F₂).

[{RhCl}[(4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)₂]}]₂}]⁺BF₄⁻ **5. A solution of the ligand (1.0 g, 0.6 mmol) in perfluoro-1,3-dimethylcyclohexane (PP3) (20 cm³) was added to a solution of [{RhCl(COD)}]₂ (0.15 g, 0.3 mmol) in toluene (15 cm³) with stirring at 60 °C under nitrogen. The reaction mixture was heated to 90 °C for 4 h and the bottom layer changed from cloudy white to yellow to an orange-red clear solution. After cooling the bottom layer was transferred under nitrogen to another Schlenk flask and the solvent removed *in vacuo* to leave an orange-red solid (0.89 g, 82%) (Found: C, 33.6; H, 0.9; F, 51.2. C₁₀₀H₄₀Cl₂F₁₀₄P₄Rh requires C, 33.2; H, 1.1; F, 54.6%). ¹⁹F NMR ([²H₈]toluene): δ -81.6 (24F, t, $^3J_{\text{FF}}$ 9, CF₃), -111.4 (16F, t, $^3J_{\text{FF}}$ 14, C ^{α} F₂), -121.8 (16F, um, C ^{β} F₂), -121.9 (16F, um, C ^{δ} F₂), -123.3 (16F, um, C ^{ϵ} F₂) and -126.7 (16F, um, C ^{ν} F₂).**

[RhCl{(4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)}](PPh₃) **6. A solution of the ligand (0.70 g, 0.4 mmol) in PP3 (30 cm³) was added to [{RhCl(COD)}]₂ (0.098 g, 0.2 mmol) with stirring in toluene (20 cm³) at 50 °C under nitrogen. The reaction mixture was then heated at 80 °C for 3 h. The bottom, fluorous, layer was then transferred, under nitrogen, on to triphenylphosphine (0.11 g, 0.42 mmol) with stirring in toluene (15 cm³) and stirred at 50 °C for 2 h under nitrogen. After cooling the solvents were removed *in vacuo* to leave a yellow solid. The product was finally washed with toluene to remove traces of any excess of triphenylphosphine (0.56 g, 68%) (Found: C, 39.8; H, 1.4; F, 42.4; P, 4.0. C₆₈H₃₅ClF₅₂P₃Rh requires C, 39.4; H, 1.7; F, 47.7; P, 4.5%). MS (FAB): *m/z* 1773 (M - Cl - PPh₃)⁺. ¹⁹F NMR (diethyl ether): δ -81.9 (12F, um, CF₃), -111.4 (8F, um, C ^{α} F₂), -122.0 (16F, um, C ^{β} F₂ and C ^{δ} F₂), -123.4 (8F, um, C ^{ϵ} F₂) and -126.9 (8F, um, C ^{ν} F₂).**

[{RhCl₂(η^5 -C₅Me₅)₂}(4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)}]₂}]⁺BF₄⁻ **7. A solution of [{RhCl₂(η^5 -C₅Me₅)₂}] (Aldrich) (0.105 g, 0.17 mmol) and the ligand (0.29 g, 0.17 mmol) in dichloromethane (50 cm³) was stirred at room temperature under nitrogen for 2.5 h. After removing the solvent on the rotary evaporator, the product was washed with hexane to give a red solid (0.23 g, 59%) (Found: C, 37.1; H, 2.1; P, 3.6. C₇₀H₅₀Cl₄F₅₂P₂Rh₂ requires C, 36.7; H, 2.2; P, 2.7%). MS (FAB): *m/z* 2253 (M - Cl)⁺, 2118 (M - Cp*Cl)⁺, 2081 (M - Cl₂Cp*)⁺, 1978 (M - RhCp*Cl₂)⁺, 1943 (M - RhCp*Cl₃)⁺, 1908 (M - RhCp*Cl₄)⁺ and 1808 (M - RhCp*₂Cl₃)⁺. ¹⁹F NMR ([²H₈]toluene): 363 K, δ -81.5 (12F, t, $^3J_{\text{FF}}$ 10, CF₃), -110.8 (8F, t, $^3J_{\text{FF}}$ 14, C ^{α} F₂), -121.2 (16F, um, C ^{β} F₂ and C ^{δ} F₂), -122.6 (8F, um, C ^{ϵ} F₂) and -126.0 (8F, um, C ^{ν} F₂); 233 K, δ -81.2 (3F, t, $^3J_{\text{FF}}$ 9, CF₃), -81.3 (3F, t, $^3J_{\text{FF}}$ 9, CF₃), -81.4 (3F, t, $^3J_{\text{FF}}$ 9, CF₃), -81.5 (3F, t, $^3J_{\text{FF}}$ 9, CF₃), -111.5 (2F, um, C ^{α} F₂), -111.7 (2F, t, $^3J_{\text{FF}}$ 14, C ^{α} F₂), -111.9 (2F, t, $^3J_{\text{FF}}$ 14, C ^{α} F₂), -112.2 (2F, t, $^3J_{\text{FF}}$ 14, C ^{α} F₂), -122.2 (16F, br m, C ^{β} F₂ and C ^{δ} F₂), -123.6 (8F, br m, C ^{ϵ} F₂), -126.8 (4F, br m, C ^{ν} F₂) and -127.1 (4F, br m, C ^{ν} F₂).**

[RhCl(η^5 -C₅Me₅)(4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)}]₂}]⁺BF₄⁻ **8. A solution of [{RhCl₂(η^5 -C₅Me₅)₂}] (Aldrich) (0.049 g, 0.079 mmol) and the ligand (0.271 g, 0.16 mmol) in toluene (50 cm³) was stirred at room temperature under nitrogen for 6 h. After filtering the solution the toluene was removed on the rotary evaporator to give a red solid which was a mixture of products, [{RhCl₂(η^5 -C₅Me₅)₂}(4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)₂}] and [RhCl₂(η^5 -C₅Me₅)(4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)] and unchanged ligand. This mixture (0.241 g) was dissolved in acetone (50 cm³) and an excess of NH₄BF₄ (1 g) added. The suspension was stirred under nitrogen at room temperature for 20 h and changed from**

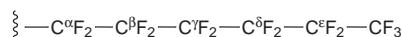
orange-red to lemon yellow. The acetone was removed on the rotary evaporator and the product washed with water and light petroleum to give the yellow product (0.161 g, 50%). The [RhCl(η^5 -C₅Me₅)(4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)₂}]⁺BF₄⁻ was finally recrystallised from dichloromethane (Found: C, 35.8; H, 1.5; P, 3.0. C₆₀H₃₅BClF₅₆P₂Rh requires C, 35.5; H, 1.7; P, 3.1%). MS (FAB): *m/z* 1943/5 (M - BF₄)⁺ and 1909 (M - Cl - BF₄)⁺. ¹⁹F NMR [(CD₂)₂CO]: δ -82.1 (12F, m, CF₃), -111.8 (4F, t, $^3J_{\text{FF}}$ 14, C ^{α} F₂), -112.0 (4F, br m, C ^{α} F₂), -122.4 (6F, um, C ^{β} F₂ and C ^{δ} F₂), -122.5 (2F, um, C ^{β} F₂), -123.8 (8F, um, C ^{ϵ} F₂) and -127.1 (8F, um, C ^{ν} F₂).

Results and discussion

The reactions between the new fluorous-ponytail-derivatised analogue of bis(diphenylphosphino)ethane and some conventional platinum-group metal starting materials yields analogues of well established co-ordination and organometallic complexes either by cleavage of chloride-bridged dimers or by the displacement of weakly co-ordinating ligands. The products were all obtained as solids in 50–90% yield and were characterised by mass spectrometry, ¹H, ¹⁹F and ³¹P NMR spectroscopies. In the mass spectra most of the complexes showed either the parent ion or [M - Cl]⁺, in line with mass spectral data for the analogous DPPE complexes.

NMR spectroscopic studies

Fluorine-19 NMR data (Experimental section) for all the complexes show, principally, five or six highly consistent multiplet resonances which are similar to those for the 'free' ligand⁷ and for metal complexes of related perfluoroalkyl-derivatised triarylphosphines.¹⁰ The highest frequency resonances are assigned to the terminal CF₃ groups and the remaining, CF₂, resonances are assigned according to Scheme 1 from ¹⁹F-¹⁹F COSY experiments.



Scheme 1

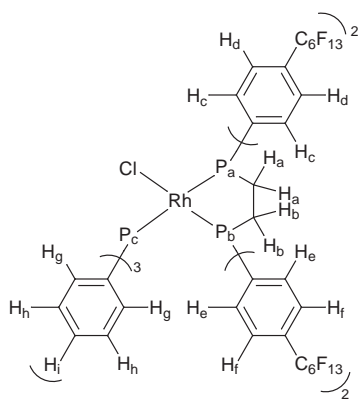
For the platinum and palladium complexes **1**, **2** and **4**, the ¹H and ¹H-³¹P NMR data (Table 1) are similar to those for the 'free' ligand⁷ and to those for the analogous dppe complexes prepared by the literature routes.^{12,13} Complex **3** is insoluble in all solvents and, hence, NMR data are unavailable. For **1**, **2** and **4** a doublet/multiplet resonance is observed for the C₂H₄ protons for which $^3J_{\text{HP}}$ is comparable to that for the analogous DPPE complexes, whilst the aryl protons are shifted to higher frequency than those for the dppe complexes, due to the electron withdrawing perfluoroalkyl chain, and show well resolved $^3J_{\text{HH}}$ and $^3J_{\text{HP}}$ couplings. The ³¹P-¹H NMR spectra (Table 1) exhibit a single resonance (Pd) or a single resonance with satellites (Pt) where δ_{p} is virtually identical to that for the analogous dppe complexes. For **1**, $^1J_{\text{PtP}}$, which is normally a fair indicator of electronic effects, is smaller than the value for [PtCl₂(dppe)] (3568 *cf.* 3594 Hz). From data for a series of related [PtCl₂(PR₃)₂] (R = aryl) complexes it has been concluded that a reduction in $^1J_{\text{PtP}}$ can be correlated with the Hammett function for the ligand which can be accounted for by a reduction in the P→Pt σ donation of the ligand and a weaker Pt–P bond.¹⁴ Therefore, for **1**, these NMR data suggest that the aryl spacer groups do not completely insulate the metal from the electronic effects of the perfluoroalkyl substituents. However, we have noted¹⁰ a comparable reduction in $^1J_{\text{PtP}}$ (3676 to 3631 Hz) for *cis*-[PtCl₂L₂] [L = PPh_{3-x}(C₆H₄C₆F₁₃-4)_x; x = 0, 1, 2 or 3] but structural data for the platinum complexes when x = 0 and 3 indicate that the metal–phosphorus bond lengths are unaffected by the introduction of the perfluoroalkyl units.

For the chloride-bridged dimer **5** the NMR data are also very similar to those for the analogous dppe complex.¹¹ In

Table 1 Proton, ^1H - $\{^{31}\text{P}\}$ and ^{31}P - $\{^1\text{H}\}$ NMR data (δ , J/Hz) for some DPPE complexes and their analogues with perfluoroalkyl substituents^a

Compound	^1H NMR Data	^1H - $\{^{31}\text{P}\}$ NMR Data	^{31}P - $\{^1\text{H}\}$ NMR Data
1 [PtCl ₂ (L-L)] ^{b,c}	2.88 (4 H, br d, $^3J_{\text{HP}}$ 19.0, PCH ₂), 7.77 (8 H, d, $^3J_{\text{HH}}$ 8.3, <i>m</i> -H of C ₆ H ₄ P), 8.14 (8 H, dd, $^3J_{\text{HH}}$ 8.4, $^3J_{\text{HP}}$ 11.9, <i>o</i> -H of C ₆ H ₄ P)	2.88 (4 H, s, PCH ₂), 7.77 (8 H, d, $^3J_{\text{HH}}$ 8.3, <i>m</i> -H of C ₆ H ₄ P), 8.14 (8 H, d, $^3J_{\text{HH}}$ 8.3, <i>o</i> -H of C ₆ H ₄ P)	43.4 (s, $^1J_{\text{PP}}$ 3568)
[PtCl ₂ (dppe)] ^c	2.49 (4 H, d, $^3J_{\text{HP}}$ 18.9, PCH ₂), 7.40 (8 H, tm, $^3J_{\text{HH}}$ 7.5 and 7.0, <i>m</i> -H of C ₆ H ₅ P), 7.46 (4 H, m, <i>p</i> -H of C ₆ H ₅ P), 7.82 (8 H, m, <i>o</i> -H of C ₆ H ₅ P)	2.49 (4 H, s, PCH ₂), 7.40 (8 H, t, $^3J_{\text{HH}}$ 7.5 and 7.0, <i>m</i> -H of C ₆ H ₅ P), 7.46 (4 H, m, <i>p</i> -H of C ₆ H ₅ P), 7.82 (8 H, d, $^3J_{\text{HH}}$ 6.7, <i>o</i> -H of C ₆ H ₅ P)	42.8 (s, $^1J_{\text{PP}}$ 3594)
2 [PdCl ₂ (L-L)] ^{b,d}	2.60 (4 H, d, $^3J_{\text{HP}}$ 23.2, PCH ₂), 7.68 (8 H, d, $^3J_{\text{HH}}$ 8.3, <i>m</i> -H of C ₆ H ₄ P), 7.98 (8 H, dd, $^3J_{\text{HH}}$ 8.2, $^3J_{\text{HP}}$ 11.7, <i>o</i> -H of C ₆ H ₄ P)	2.59 (4 H, s, PCH ₂), 7.68 (8 H, d, $^3J_{\text{HH}}$ 8.3, <i>m</i> -H of C ₆ H ₄ P), 7.98 (8 H, d, $^3J_{\text{HH}}$ 8.2, <i>o</i> -H of C ₆ H ₄ P)	62.7 (s)
[PdCl ₂ (dppe)] ^d	2.38 (4 H, d, $^3J_{\text{HP}}$ 22.9, PCH ₂), 7.42 (8 H, td, $^3J_{\text{HH}}$ 7.3, $^4J_{\text{HP}}$ 2.5, <i>m</i> -H of C ₆ H ₅ P), 7.48 (4 H, m, <i>p</i> -H of C ₆ H ₅ P), 7.81 (8 H, m, <i>o</i> -H of C ₆ H ₅ P)	2.38 (4 H, s, PCH ₂), 7.42 (8 H, t, $^3J_{\text{HH}}$ 7.3, <i>m</i> -H of C ₆ H ₅ P), 7.49 (4 H, m, <i>p</i> -H of C ₆ H ₅ P), 7.81 (8 H, dm, $^3J_{\text{HH}}$ 7.0, <i>o</i> -H of C ₆ H ₅ P)	64.2 (s)
4 [Pd(L-L)] ₂ ^{b,e}	2.18 (4 H, m, PCH ₂), 7.24 (8 H, d, $^3J_{\text{HH}}$ 7.9, <i>m</i> -H of C ₆ H ₄ P), 7.34 (8 H, m, <i>o</i> -H of C ₆ H ₄ P)	2.18 (4 H, s, PCH ₂), 7.24 (8 H, d, $^3J_{\text{HH}}$ 8.3, <i>m</i> -H of C ₆ H ₄ P), 7.34 (8 H, d, $^3J_{\text{HH}}$ 8.2, <i>o</i> -H of C ₆ H ₄ P)	29.6 (s)
[Pd(dppe)] ₂ ^e	2.00 (8 H, m, PCH ₂), 6.95 (16 H, t, $^3J_{\text{HH}}$ 7.0, <i>m</i> -H of C ₆ H ₅ P), 7.06 (8 H, t, $^3J_{\text{HH}}$ 7.0, <i>p</i> -H of C ₆ H ₅ P), 7.28 (16 H, m, <i>o</i> -H of C ₆ H ₅ P)	Not recorded	31.4 (s)
5 [{RhCl(L-L)}] ₂ ^b	1.56 (8 H, br d, $^3J_{\text{HP}}$ 18.5, PCH ₂), 7.31 (16 H, d, $^3J_{\text{HH}}$ 8.2, <i>m</i> -H of C ₆ H ₄ P), 7.77 (16 H, t, $^3J_{\text{HH}}$ 8.2, $^3J_{\text{HP}}$ 8.8, <i>o</i> -H of C ₆ H ₄ P)	Not recorded	74.9 (d, $^1J_{\text{RHP}}$ 198)
6 [RhCl(L-L)(PPh ₃)] ^{b,e}	2.07 (8 H, br d, $^3J_{\text{HP}}$ 20, PCH ₂), 7.20–7.85 (40 H, br m, aryl protons)	Not reported	74.2 (d, $^1J_{\text{RHP}}$ 198)
7 [RhCl(L-L)(PPh ₃)] ^{b,e}	2.03 (2 H, dm, $^3J_{\text{HP}}$ 32, H _a), 2.11 (2 H, dm, $^3J_{\text{HP}}$ 31, H _b), 7.15 (6 H, td, $^3J_{\text{HH}}$ 7.7, $^4J_{\text{HP}}$ 1.6, H _c), 7.31 (3 H, tm, $^3J_{\text{HH}}$ 7.5, H _i), 7.40 (6 H, t, $^3J_{\text{HP}}$ 9.8, $^3J_{\text{HH}}$ 7.6, H _g), 7.46 (4 H, d, $^3J_{\text{HH}}$ 8.2, H _f), 7.70 (4 H, t, $^3J_{\text{HP}}$ 10.7, $^3J_{\text{HH}}$ 7.9, H _e), 7.73 (4 H, d, $^3J_{\text{HH}}$ 7.3, H _d), 8.14 (4 H, t, $^3J_{\text{HP}}$ 10.7, $^3J_{\text{HH}}$ 7.3, H _j)	7.13 (6 H, t, $^3J_{\text{HH}}$ 7.6, 7.1, H _b), 7.27 (3 H, t, $^3J_{\text{HH}}$ 7.1, H _i), 7.47 (6 H, d, $^3J_{\text{HH}}$ 7.6, H _g), 7.53 (4 H, d, $^3J_{\text{HH}}$ 7.9, H _f), 7.73 (4 H, d, $^3J_{\text{HH}}$ 7.9, H _d), 7.80 (4 H, d, $^3J_{\text{HH}}$ 7.6, H _e), 8.29 (4 H, d, $^3J_{\text{HH}}$ 7.9, H _c) ^g	30.6 (1 P, ddd, $^2J_{\text{PCPa}}$ 358, $^1J_{\text{RHP}}$ 131, $^2J_{\text{PCPb}}$ 36, P _c), 61.0 (1 P, ddd, $^2J_{\text{PAPc}}$ 358, $^1J_{\text{RHP}}$ 142, $^2J_{\text{PAPb}}$ 33, P _a), 75.5 (1 P, dt, $^1J_{\text{RHP}}$ 187, $^2J_{\text{PCPb}}$ 36, $^2J_{\text{PAPb}}$ 33, P _b)
8 [RhCl ₂ (η ⁵ -C ₅ Me ₅) ₂ (L-L)] ^b (373 K)	1.11 (30 H, d, J_{HP} 3.4, CH ₃), 3.10 (4 H, d, $^3J_{\text{HP}}$ 2.4, PCH ₂), 7.45 (8 H, d, $^3J_{\text{HH}}$ 8.1, <i>m</i> -H of C ₆ H ₄ P), 8.02 (8 H, t, $^3J_{\text{HP}}$ 9.3, $^3J_{\text{HH}}$ 8.1, <i>o</i> -H of C ₆ H ₄ P)	1.11 (30 H, s, CH ₃), 3.10 (4 H, s, PCH ₂), 7.45 (8 H, d, $^3J_{\text{HH}}$ 8.1, <i>m</i> -H of C ₆ H ₄ P), 8.02 (8 H, d, $^3J_{\text{HH}}$ 8.1, <i>o</i> -H of C ₆ H ₄ P)	29.3 (AA'XX' spectrum, $^1J_{\text{RHP}}$ 145, $^3J_{\text{PP}}$ 36, $^4J_{\text{RHP}}$ 0)
(233 K)	0.94 (15 H, d, J_{HP} 3.1, CH ₃), 1.11 (15 H, d, J_{HP} 3.1, CH ₃), 2.52 (1 H, m, PCH ₂), 2.68 (1 H, m, PCH ₂), 3.45 (1 H, m, PCH ₂), 3.75 (1 H, m, PCH ₂), 6.77 (2 H, d, $^3J_{\text{HH}}$ 7.7, <i>m</i> -H of C ₆ H ₄ P), 7.39 (2 H, d, $^3J_{\text{HH}}$ 8.6, <i>m</i> -H of C ₆ H ₄ P), 7.52 (2 H, d, $^3J_{\text{HH}}$ 7.8, <i>m</i> -H of C ₆ H ₄ P), 7.66 (2 H, t, $^3J_{\text{HP}}$ 8.1, $^3J_{\text{HH}}$ 7.3, <i>o</i> -H of C ₆ H ₄ P), 8.28 (3 H, br s, C ₆ H ₄), 8.93 (1 H, br s, C ₆ H ₄) ^h	0.95 (15 H, s, CH ₃), 1.11 (15 H, s, CH ₃), 2.52 (1 H, t, $^2J_{\text{HaHc}}$ 4.6, $^3J_{\text{HaHb}}$ -14.6, $^3J_{\text{HaHd}}$ 11.9, H _d), 2.68 (1 H, t, $^2J_{\text{HaHc}}$ 4.6, $^3J_{\text{HbHc}}$ 11.9, $^3J_{\text{HcHd}}$ -14.6, H _c), 3.44 (1 H, t, $^2J_{\text{HbHd}}$ 4.6, $^3J_{\text{HaHb}}$ -14.6, $^3J_{\text{HbHc}}$ 11.9, H _b), 3.75 (1 H, t, $^2J_{\text{HbHd}}$ 4.6, $^3J_{\text{HcHd}}$ -14.6, $^3J_{\text{HaHd}}$ 11.9, H _d), 6.79 (2 H, d, $^3J_{\text{HH}}$ 7.7, <i>m</i> -H of C ₆ H ₄ P), 7.40 (2 H, d, $^3J_{\text{HH}}$ 7.9, <i>m</i> -H of C ₆ H ₄ P), 7.52 (2 H, d, $^3J_{\text{HH}}$ 8.0, <i>m</i> -H of C ₆ H ₄ P), 7.67 (2 H, d, $^3J_{\text{HH}}$ 7.3, <i>o</i> -H of C ₆ H ₄ P), 8.28 (3 H, br s, C ₆ H ₄), 8.91 (1 H, br s, C ₆ H ₄) ^h	28.8 (1 P, $^1J_{\text{RHP}}$ 144, $^3J_{\text{PP}}$ 35, $^4J_{\text{RHP}}$ 0, P _a), 29.4 (1 P, $^1J_{\text{RHP}}$ 144, $^3J_{\text{PP}}$ 35, $^4J_{\text{RHP}}$ 0, P _b) (ABXY spectrum)
9 [RhCl ₂ (η ⁵ -C ₅ Me ₅) ₂ (dppe)] (343 K)	1.27 (30 H, m, J_{HP} 3.2, CH ₃), 3.27 (4 H, d, $^3J_{\text{HP}}$ 2.3, PCH ₂), 7.17 (12 H, m, <i>m</i> - and <i>p</i> -H of C ₆ H ₅), 8.09 (8 H, br t, <i>o</i> -H of C ₆ H ₅)	1.27 (30 H, s, CH ₃), 3.27 (4 H, s, PCH ₂), 7.17 (12 H, m, <i>m</i> - and <i>p</i> -H of C ₆ H ₅), 8.09 (8 H, d, $^3J_{\text{HH}}$ 7.0, <i>o</i> -H of C ₆ H ₅)	30.3 (AA'XX' spectrum, $^1J_{\text{RHP}}$ 143, $^3J_{\text{PP}}$ 33, $^4J_{\text{RHP}}$ 0)
(243 K)	1.16 (15 H, d, J_{HP} 3.1, CH ₃), 1.45 (15 H, d, J_{HP} 3.2, CH ₃), 2.96 (1 H, br m, PCH ₂), 3.21 (1 H, br m, PCH ₂), 3.46 (1 H, br m, PCH ₂), 3.81 (1 H, br m, PCH ₂), 6.94 (4 H, br s, aryl), 7.07 (4 H, br s, aryl), 7.44 (4 H, br s, aryl), 7.73 (4 H, t, $^3J_{\text{HH}}$ 7.0, $^3J_{\text{HP}}$ 9.0, <i>o</i> -H of C ₆ H ₅), 7.81 (2 H, br s, aryl), 8.44 (2 H, br s, aryl)	1.18 (15 H, s, CH ₃), 1.47 (15 H, s, CH ₃), 2.97 (1 H, br t, PCH ₂), 3.23 (1 H, br t, PCH ₂), 3.48 (1 H, br t, PCH ₂), 3.83 (1 H, br t, PCH ₂), 6.96 (4 H, br s, aryl), 7.09 (4 H, br m, aryl), 7.46 (4 H, br s, aryl), 7.75 (4 H, d, $^3J_{\text{HH}}$ 7.0, <i>o</i> -H of C ₆ H ₅), 7.84 (2 H, br s, aryl), 8.26 (2 H, br s, aryl)	28.1 (1 P, dd, $^1J_{\text{RHP}}$ 143, $^3J_{\text{PP}}$ 36, $^4J_{\text{RHP}}$ 1, P _a), 30.5 (1 P, dd, $^1J_{\text{RHP}}$ 143, $^3J_{\text{PP}}$ 36, $^4J_{\text{RHP}}$ 1, P _b) (ABXY spectrum)
10 [RhCl(η ⁵ -C ₅ Me ₅)(L-L)] ₂ [BF ₄] ^{b,c}	1.54 (15 H, t, J_{HP} 3.5, CH ₃), 3.01 (2 H, m, PCH ₂), 3.32 (2 H, m, PCH ₂), 7.55 (4 H, t, $^3J_{\text{HP}}$ 11.1, $^3J_{\text{HH}}$ 7.9, <i>o</i> -H of C ₆ H ₄ P), 7.86 (8 H, d, $^3J_{\text{HH}}$ 7.9, <i>m</i> -H of C ₆ H ₄ P), 7.96 (4 H, t, $^3J_{\text{HP}}$ 11.5, $^3J_{\text{HH}}$ 7.9, <i>o</i> -H of C ₆ H ₄ P)	1.54 (15 H, s, CH ₃), 3.01 (2 H, m, PCH ₂), 3.32 (2 H, m, PCH ₂), 7.55 (4 H, d, $^3J_{\text{HH}}$ 8.1, <i>o</i> -H of C ₆ H ₄ P), 7.85 (8 H, d, $^3J_{\text{HH}}$ 7.9, <i>m</i> -H of C ₆ H ₄ P), 7.96 (4 H, d, $^3J_{\text{HH}}$ 8.3, <i>o</i> -H of C ₆ H ₄ P)	66.7 (d, $^1J_{\text{RHP}}$ 133)
11 [RhCl(η ⁵ -C ₅ Me ₅)(dppe)] ₂ [BF ₄] ^c	1.45 (15 H, t, J_{HP} 3.4, CH ₃), 2.62 (2 H, m, PCH ₂), 3.16 (2 H, m, PCH ₂), 7.19 (4 H, m, <i>o</i> -H of C ₆ H ₅ P), 7.54 (16 H, m, aryl)	1.45 (15 H, s, CH ₃), 2.61 (2 H, m, PCH ₂), 3.10 (2 H, m, PCH ₂), 7.19 (4 H, d, $^3J_{\text{HH}}$ 7.3, <i>o</i> -H of C ₆ H ₅ P), 7.54 (16 H, m, aryl)	66.2 (d, $^1J_{\text{RHP}}$ 132)

^a Spectra recorded in [D₂H₆]toluene unless otherwise stated. ^b L-L = (4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)₂. ^c Spectra recorded in (CD₃)₂CO. ^d Spectra recorded in CDCl₃. ^e Spectra recorded in CD₂Cl₂. ^f Data taken from ref. 11. ^g Data recorded in Et₂O using D₂O as lock substance. Backbone protons hidden under solvent signals. ^h Other aryl peaks hidden under solvent peaks.



Scheme 2

particular, δ_P , $^1J_{\text{RhP}}$ and $^3J_{\text{HP}}$ (PCH_2) are virtually identical implying that the perfluoroalkyl groups do not have a significant effect on the co-ordination properties of the ligand in this system. Cleavage of the dimer with triphenylphosphine gives an analogue of Wilkinson's complex, **6**. Here, the NMR spectral data are complicated and the data in Table 1 have been assigned according to the labels in Scheme 2. The ^{31}P - $\{^1\text{H}\}$ NMR data confirm that the two ends of the bidentate ligand are inequivalent. Consequently, the spectra show two well resolved mutually coupled doublets of doublets of doublets and a doublet of apparent triplets in contrast to the highly second-order spectrum for the structurally characterised $[\text{RhCl}(\text{PPh}_3)(\text{dfppe})]$ [$\text{dfppe} = (\text{F}_5\text{C}_6)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2$].¹⁵ There are few compounds with which to compare these spectroscopic data. The $^1J_{\text{RhP}}$ couplings for $\text{P}_{\text{trans-P}}$ are smaller than that for $\text{P}_{\text{trans-Cl}}$ as expected from the relative *trans* influence of phosphorus and chlorine and as seen for Wilkinson's complex;¹⁶ the *cis*- $^2J_{\text{PP}}$ couplings are also similar to those for Wilkinson's complex. The *trans*- $^2J_{\text{PP}}$ coupling constant is an order of magnitude larger than these *cis*- $^2J_{\text{PP}}$ values as seen for the comparable couplings in *cis*- and *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ ($\text{L} = \text{monodentate phosphine}$).¹⁷ The inequivalent phosphorus atoms create asymmetry in the bidentate ligand. The backbone protons are inequivalent and give two unresolved multiplets, in the ^1H NMR spectrum, both showing resolvable coupling to phosphorus. Similarly, the protons on the aryl rings are now inequivalent and the assignments, including those for the triphenylphosphine protons, have been made using ^1H - ^{31}P

COSY and HMQC (heteronuclear multiple quantum correlation) (selected for $J_{\text{HP}} = 10$ and 30 Hz) and then ^1H homonuclear decoupling experiments. We note that the resonances in the ^{19}F NMR spectrum for this complex are unusually broad and no resolvable couplings could be identified. It is likely that this occurs due to the inequivalence of the aryl rings on P_a and P_b which would render the perfluoroalkyl chains inequivalent and so each peak in the ^{19}F NMR spectrum arises from the overlap of at least two sets of fluorine resonances.

In the reactions of $[\{\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)_2\}]$ with bidentate phosphine ligands (L-L) three types of product can be obtained, a ligand-bridged dinuclear complex, $[(\text{RhCl}_2\text{Cp}^*)_2(\text{L-L})]$, a neutral mononuclear complex $[\text{RhCl}_2\text{Cp}^*(\text{L-L})]$ or a cationic $[\text{RhClCp}^*(\text{L-L})]^+$ species.¹⁸⁻²¹ We have observed, by NMR spectroscopy, all three types of complex in the reaction of $(4\text{-F}_{13}\text{C}_6\text{H}_4)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_4\text{C}_6\text{F}_{13-4})_2$ with $[\{\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)_2\}]$, but have only obtained the first (**7**) and the last (**8**) complexes analytically pure. As a part of this study we have also prepared the analogous complexes with *dpe* (**9** and **10**), to allow a direct comparison between the NMR spectral data for complexes with our ligand and with *dpe*. The ^{31}P NMR spectrum of the cationic complex **8** is a simple doublet in which $^1J_{\text{RhP}}$ is comparable to that for related complexes. In the ^1H NMR spectrum the protons on the pentamethylcyclopentadienyl ring show equivalent couplings to both phosphorus atoms, confirming that this ligand is undergoing unrestricted rotation. Although there is a single doublet for the aryl protons *meta* to P, the resonances for the *ortho*-aryl and backbone protons are split into two multiplets. This arises from chelation of the ligand and asymmetry at the metal centre, *i.e.* two of the backbone protons are on the same side of the chelate ring as the Cp^* ligand, whilst the other two protons are on the opposite side. Similarly, although there is unhindered rotation about the P-C (aryl) bonds, one aryl ring is *cis*- Cp^* whilst the other is *trans*- Cp^* . This effect is mirrored in the ^1H NMR spectrum of **10** and in the ^{19}F NMR spectra of the fluorinated *dpe* analogues $[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{L-L})]^+$ ($\text{L-L} = \text{dfppe}^{21}$ or ddfpe {1,2-bis[bis(2,6-difluorophenyl)phosphino]ethane}²²). Interestingly, this asymmetry is also seen in the ^{19}F NMR spectrum of **8** (Experimental section) where two sets of multiplets can be assigned to the $\text{C}^{\alpha}\text{F}_2$ and $\text{C}^{\beta}\text{F}_2$ fluorine atoms. The fluorine atoms further along the perfluoroalkyl chains cannot be distinguished but the resonances for these fluorine atoms are significantly broader than those for the 'free' ligand⁷ or for **1-4**.

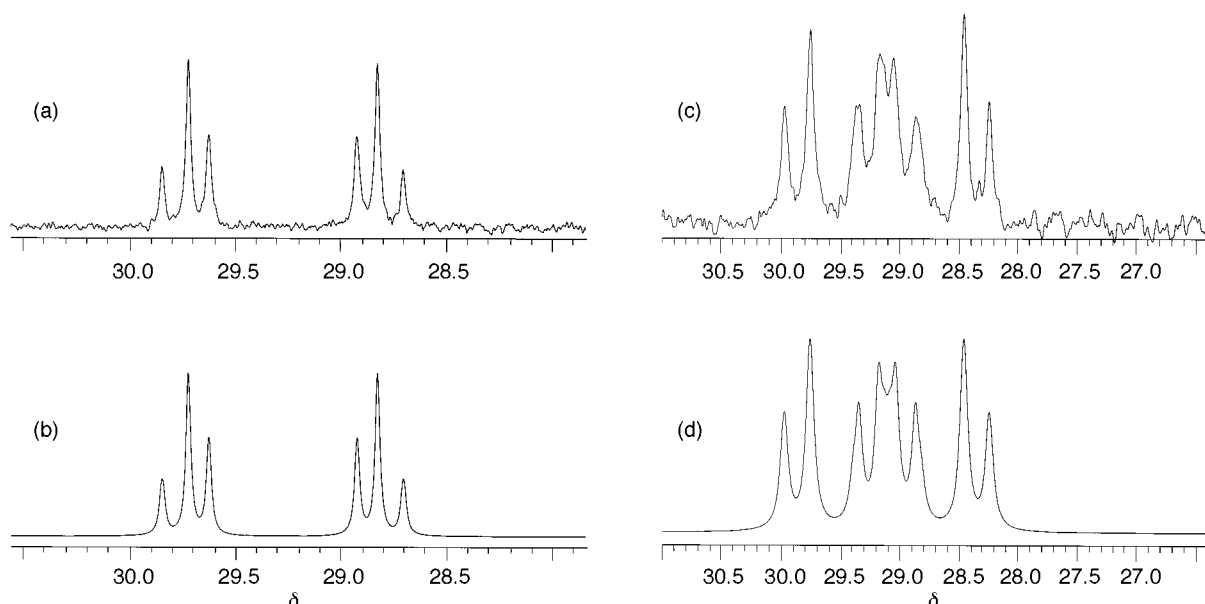


Fig. 1 Experimental [at 363 (a) and 233 K (c)] and simulated (b and d) ^{31}P - $\{^1\text{H}\}$ NMR spectra of $[\{\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)_2\}_2\{(4\text{-F}_{13}\text{C}_6\text{H}_4)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_4\text{C}_6\text{F}_{13-4})_2\}]$ **7**.

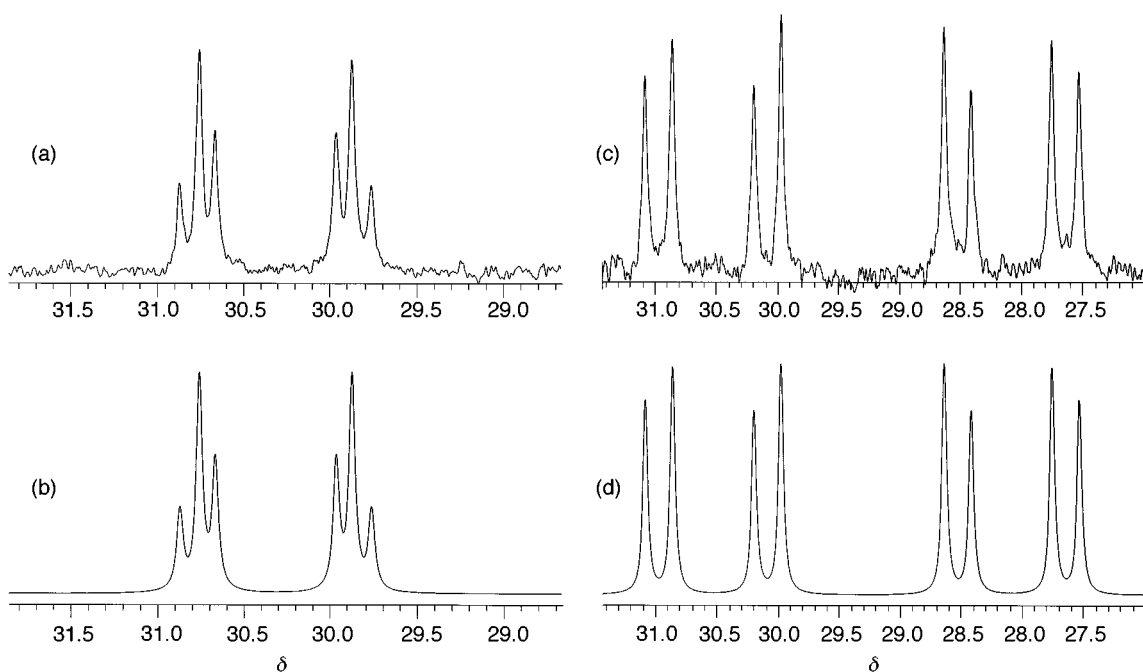


Fig. 2 Experimental [at 373 (a) and 243 K (c)] and simulated (b and d) $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of $[\{\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{dppe})\}_2]$ **9**.

The NMR spectra for complexes **7** and **9** are not simple and variable temperature experiments and simulation were required for assignment. As identified in the earliest preparation of **9**,¹⁸ the Cp* protons show an unusual pattern in the ^1H NMR spectrum which was thought to be a result of the magnetic inequivalence of the phosphorus atoms. Subsequently, the related complex $[\{\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)_2\}_2\{\text{Ph}_2\text{PCH}_2\text{CH}(\text{CH}_3)\text{-PPh}_2\}]$,¹⁹ in which the phosphorus atoms are chemically inequivalent, was shown to be fluxional at room temperature, although no mention of fluxionality or magnetic inequivalence was made in a paper on a comprehensive series of diphosphine-bridged dirhodium complexes.²⁰ For **7** (at 363 K) and **9** (at 373 K), in $[\text{D}_6]\text{toluene}$, the high temperature limit reveals classical AA'XX' second order $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra [Figs. 1(a,b) and 2(a,b)] which can be simulated²³ using the values listed in Table 1. The similarity between the values for **7** and **9** illustrates, again, that the aryl rings are very good insulators of the electronic influence of the perfluoroalkyl groups. Similarly, at this high temperature limit, the ^{19}F NMR spectrum for **7** (Experimental section) reveals the five resonances typical for equivalent perfluoroalkyl groups. Apart from the unusual three-line pattern assigned to the Cp* protons for **9**, the magnetic inequivalence of the phosphorus atoms is not obvious from the ^1H NMR spectra. In particular, the simpler doublet pattern for the Cp* protons for **7** suggests that the longer range phosphorus-proton coupling in this molecule is too small to affect the appearance of this resonance.

On cooling the NMR spectra look very different to those at the high temperature limit and the spectra are well resolved at 233 K [**7**, Figs. 1(c,d) and 3] and at 243 K [**9**, Fig. 2(c,d)]. The low temperature spectra for complexes **7** and **9** are similar and can be simulated (Table 1) and interpreted in the same way. For **7**, two resonances in the ^{31}P NMR spectrum (Fig. 1) indicate that the phosphorus atoms are now inequivalent. This is confirmed from the ^1H NMR spectrum in which two low-frequency doublets, assigned to the Cp* protons, indicate that the two ends of the molecule are inequivalent and, from the $^1\text{H}\{-^{31}\text{P}\}$ NMR spectrum (Fig. 3), four mutually coupled resonances can be assigned to the backbone protons indicating that there is restricted rotation about the C-C (backbone) bond. Furthermore, in the ^{19}F NMR spectrum in the high frequency region associated with the terminal CF_3 fluorine atoms, four well

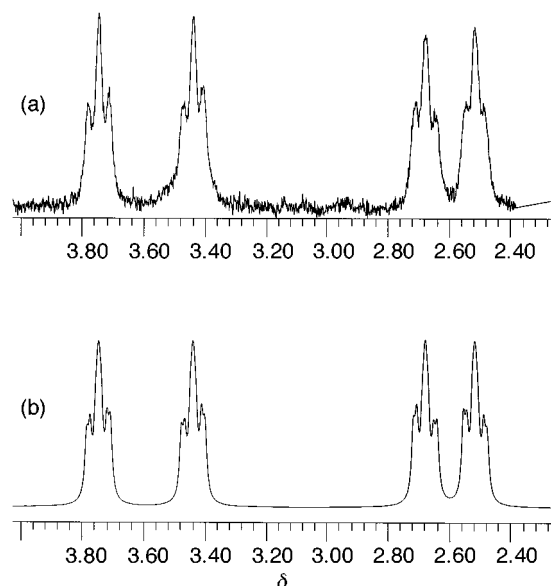


Fig. 3 Experimental at 233 K (a) and simulated (b) $^1\text{H}\{-^{31}\text{P}\}$ NMR spectra of complex **7** in the region δ 2.3 to 4.0.

resolved triplet resonances (Experimental section) indicate that all four perfluoroalkyl chains are inequivalent. The ^{31}P NMR spectrum can be simulated in terms of a second order ABXY spin system in which $\delta(\text{P}_\text{A})$ and $\delta(\text{P}_\text{B})$ have only slightly different values (Table 1; Fig. 1). The backbone region of the $^1\text{H}\{-^{31}\text{P}\}$ NMR spectrum can be simulated as an ABCD spin system (Table 1; Fig. 3) for which the $^3J_{\text{HH}}$ and $^2J_{\text{HH}}$ coupling constants suggest that the Karplus angle²⁴ for the backbone at the low temperature limit is 6° (Fig. 4), a *gauche*-eclipsed conformation. Hence, the molecule has no symmetry and all the nuclei are chemically inequivalent. The similarity in the spectral parameters for **7** and **9** indicates, again, that the aryl groups are good insulators of the electronic influence of the perfluoroalkyl ponytails.

Solubility studies

Part of the rationale behind this study was to prepare potential

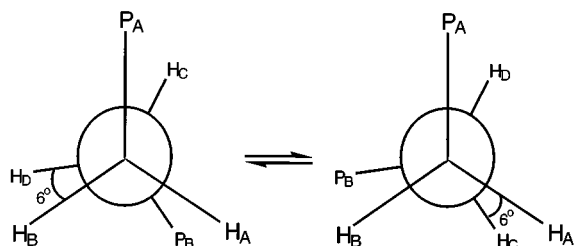


Fig. 4 Newman projection of complex 7 along the CH₂-CH₂ axis at the low-temperature limit.

catalysts with a bidentate ligand for catalysis in a fluorous biphasic system. However, although the 'free' ligand is preferentially soluble in perfluorocarbon solvents, as shown by qualitative ³¹P-{¹H} NMR studies (see preceding paper), only complexes 4 and 5, which contain two substituted ligands, are similarly soluble. Consequently, to make appropriate catalysts for catalysis in a fluorous biphasic system, longer and/or more perfluoroalkyl substituents need to be introduced in this system.

Conclusion

Co-ordination complexes of the perfluoroalkyl-derivatised analogue of dppe, (4-F₁₃C₆H₄)₂PCH₂CH₂P(C₆H₄C₆F₁₃-4)₂, have very similar spectroscopic properties to those containing dppe indicating that the aryl rings are good insulators of the electron withdrawing effects of the perfluoroalkyl groups. However, only those complexes with two of these ligands are preferentially soluble in perfluorocarbon solvents, restricting their applicability for fluorous biphasic catalysis.

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