SYNTHESIS OF RHODIUM COMPLEXES WITH NOVEL PERFLUOROALKYL SUBSTITUTED CYCLOPENTADIENYL LIGANDS

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Mixtures of isomers of (perfluoroalkyl)tetramethylcyclopenta-1,3-dienes $(CH_3)_4C_5H(CF_2)_nCF_3$ (n = 3, 5, 7, 9) were synthesized as precursors of new cyclopentadienyl ligands for organo-transition metal catalysis in fluorous biphase media and characterized by combination of GC-MS and ^{13}C NMR spectroscopy. Rhodium(III) chloro complexes $[Rh\{(CH_3)_4C_5(CF_2)_nCF_3\}Cl_2]_2$ and rhodium(I) carbonyl complexes $[Rh\{(CH_3)_4C_5(CF_2)_nCF_3\}(CO)_2]$ were prepared from the cyclopentadienes and molecular structure of $[Rh\{(CH_3)_4C_5(CF_2)_5CF_3\}Cl_2]_2$ was determined by X-ray diffraction. The ligands are electronically close to the unsubstituted cyclopentadienyl as shown by values of carbonyl stretching frequencies in the carbonyl complexes. Neither carbonyl frequencies nor NMR chemical shifts of the complexes are substantially affected by the length of the perfluoroalkyl chain.

Keywords: Fluorous biphasic catalysis; Carbonyl complexes; Cyclopentadienes; Fluorinated compounds; Rhodium; Sandwich complexes; Fluorophilic ligands.

Catalysis in fluorous biphase systems (FBS), a method of catalyst separation alternative to catalyst heterogenization[1,2] or other biphase systems[3,4], has gained considerable attention since the first report by Horváth and Rábai[5] in 1994. The interest in the topic, recently reviewed[6–8], continues to grow. Although the majority of work still concentrates on solubilization of phosphine ligands, including the pioneering work of Horváth and Rábai, the range of available fluorophilic ligands broadens. It is somewhat surprising that research on solubilization of cyclopentadienyl ligands laggs behind

since about 80% of all organometallic complexes contain cyclopentadienyl ligands[9].

To our best knowledge, there are only two reports on cyclopentadienes containing perfluoroalkyl chain (the term "ponytail" has been coined[5]). The first synthesis[10] of $C_5H_5[(CH_2)_n(CF_2)_mF]$ (n, m = 0, 8; 0, 10; 0, 12; 2, 6; 2, 8; 2, 10) used the reaction of the corresponding fluoroalkyl iodides with nickelocene and triphenylphosphine. A series of (polyfluoroalkyl)cyclopentadienes (n = 2) was prepared by the reaction of sodium cyclopentadienide with the corresponding fluoroalkyl iodides in THF but the yields were low. Use of phase transfer catalysis improved the yields; nevertheless, a 2.5 molar excess of the iodide (the more expensive of the two reagents) was necessary.

(Perfluoroalkyl)cyclopentadienes (n = 0) were available only *via* nickelocene. Other complications in the work with those compounds were their facile dimerization and instability of perfluoroalkylated cyclopentadienide anions (n = 0) even at low temperatures.

Recently $C_5H_5[(CH_2)_2(CF_2)_{10}F]$ (a mixture of isomers as in all the previous examples) was used to solubilize fullerene C_{60} by Diels–Alder reaction[11], nothing new, however, was reported regarding the methodology of synthesis of the fluorophilic cyclopentadiene which was prepared by a slight modification of a known procedure[10].

From the above mentioned ligand precursors, carbonyl complexes of Mn, Re, Co, and also a ferrocene derivative were prepared[10], as well as some rhodium complexes[12]. (Trifluoromethyl)tetramethylcyclopentadienyl[13] can be considered to be the first member of a new series of (perfluoroalkyl)-tetramethylcyclopentadienyl ligands. Synthesis of a rhodium complex with this ligand $[Rh_2(\eta^5\text{-}C_5Me_4CF_3)_2Cl_2(\mu\text{-}Cl)_2]$ was reported[14] and the structure determined by X-ray diffraction.

We now report[15] on synthesis and characterization of a series of new (perfluoroalkyl)tetramethylcyclopenta-1,3-dienes, which do not dimerize spontaneously by Diels–Alder reaction. Rhodium(III) chloro complexes and rhodium(I) carbonyl complexes were prepared from these precursors; the former complexes by the reaction of the cyclopentadienes with rhodium trichloride trihydrate in the presence of cyclohexa-1,3-diene, the latter ones by the reduction of the chloro complexes with zinc in the presence of carbon monoxide.

EXPERIMENTAL

General

Syntheses of rhodium complexes and all operations with Grignard reagents were carried out under argon atmosphere. ^{1}H, ^{13}C, and ^{19}F NMR spectra were taken on a Varian UNITY 200 spectrometer at 200.1, 50.3, and 188.2 MHz, respectively, unless stated otherwise. Hexamethyldisilane was used as internal standard for ^{1}H and ^{13}C, trifluoromethylbenzene was used for ^{19}F NMR spectra. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. Mass spectra were measured by GC-MS method on a capillary gas chromatograph (Varian, model 3500) equipped with a mass detector (Finnigan MAT, model ITD 800). Fourier-transform infrared spectra in the range 400–4 000 cm^{-1} were measured on a Nicolet Magna 760 instrument in Nujol with resolution of 4 cm^{-1} using 64 scans for each sample.

Chemicals

Solvents were dried by usual procedures[16] then distilled and kept under nitrogen or argon. Perfluoroalkyl iodides, $POCl_3$, cyclohexa-1,3-diene (all Aldrich), rhodium trichloride trihydrate (Safina Vestec), carbon monoxide (Linde), and zinc powder (Merck) were commercially available, 2,3,4,5-tetramethylcyclopent-2-en-1-one (mixture of *cis*- and *trans*-isomers) was prepared according to literature[17].

(Perfluoroalkyl)tetramethylcyclopenta-1,3-dienes. General Procedure

Perfluoroalkyl iodide (44.8 mmol) was dissolved in 200 ml of diethyl ether in a Schlenk flask and the mixture was cooled to –70°C. Phenylmagnesium bromide (32 ml of 1.4 M solution; 44.8 mmol) was slowly added with stirring followed by 2,3,4,5-tetramethylcyclopent-2-en-1-one (44.9 mmol). The mixture was left to warm to room temperature and stirred for 1 h. The reaction mixture was poured onto ice, concentrated HCl was added (0.28 mol) and stirring was continued for 1 h. The layers were separated and the water phase was extracted three times with ether. The combined extracts were washed four times with 10% $NaHCO_3$ solution, then twice with saturated NaCl solution, and finally dried with anhydrous $MgSO_4$. Removal of solvent at atmospheric pressure and distillation of the residue *in vacuo* gave a liquid mixture of alcohols.

A mixture of (perfluoroalkyl)tetramethylcyclopentenols (31.9 mmol) was dissolved in pyridine and slowly dropped with stirring into a solution of $POCl_3$ (171 mmol) in pyridine at 0 °C. The mixture was left to warm to room temperature (1 h), subsequently stirred at 90 °C for 4 h, then left to stand overnight. The mixture was poured onto mixture of ice and concentrated hydrochloric acid and left to warm to room temperature while stirring. The same workup as for the alcohols gave the products after vacuum distillation.

*(Perfluorobutyl)tetramethylcyclopenta-1,3-dienes (**1a**–**1c**)*

The fraction boiling at 52 °C/3 Torr afforded 68% yield of alcohols. GC-MS, *m/z*: 341 ($M^{+\bullet}$ – H_2O + 1), 139 ($M^{+\bullet}$ – C_4F_9).

The fraction boiling at 66 °C/5 Torr afforded 63% yield of cyclopentadienes. GC-MS, *m/z*: 340 ($M^{+\bullet}$), 171 ($M^{+\bullet}$ – C_3F_7). ^{13}C NMR ($CDCl_3$): 10.86 s (CH_3); 12.38 s (CH_3); 60.12 t, $^{2}J_{C\text{-}F}$ = 18.8 (C-CF_2); 127.94 s (>C=); 140.07 s (>C=); 108–126 m (CF) (isomer **1a**); 10.24 s (CH_3);

11.56 s (CH_3); 12.64 bs (CH_3); 13.92 bs (CH_3); 50.02 s (CH); 127.85 t, $^2J_{C-F}$ = 24.3 (=C-CF_2); 134.23 d, $^3J_{C-F}$ = 2.0 (>C=); 146.42 s (>C=); 150.76 bs (>C=); 108–126 m (CF) (isomer **1b**); 11.26 s (CH_3); 20.43 s (CH_3); 20.54 s (CH_3); 45.72 s (CH); 47.35 s (CH); 106.34 s (=CH_2); 145.55 bs (>C=); 159.00 s (>C=); 108–126 m (CF) (isomer **1c**).

*(Perfluorohexyl)tetramethylcyclopenta-1,3-dienes (**2a**–**2c**)*

The fraction boiling at 97 °C/5 Torr afforded 71% yield of alcohols. GC-MS, *m/z*: 441 ($M^{+\bullet}$ – H_2O + 1), 139 ($M^{+\bullet}$ – C_6F_{13}).

The fraction boiling at 80–81 °C/4 Torr afforded 53% yield of cyclopentadienes. GC-MS, *m/z*: 440 ($M^{+\bullet}$), 171 ($M^{+\bullet}$ – C_5F_{11}). ^{13}C NMR ($CDCl_3$, 125.7 MHz): 10.94 s (CH_3); 12.48 s (CH_3); 60.27 t, $^2J_{C-F}$ = 17.5 (C-CF_2); 128.01 s (>C=); 140.07 s (>C=); 108–121 m (CF) (isomer **2a**); 10.36 s (CH_3); 11.67 s (CH_3); 12.74 bs (CH_3); 14.00 bs (CH_3); 50.06 s (CH); 127.49 t, $^2J_{C-F}$ = 23.4 (=C-CF_2); 134.28 d, $^3J_{C-F}$ = 1.8 (>C=); 146.49 s (>C=); 150.83 bs (>C=); 108–121 m (CF) (isomer **2b**); 11.11 s (CH_3); 20.39 s (CH_3); 20.49 s (CH_3); 45.73 s (CH); 47.38 s (CH); 106.31 s (=CH_2); 145.54 bs (>C=); 159.04 s (>C=); 108–121 m (CF) (isomer **2c**).

*(Perfluorooctyl)tetramethylcyclopenta-1,3-dienes (**3a**–**3c**)*

The fraction boiling at 105 °C/5 Torr afforded 74% yield of alcohols. GC-MS, *m/z*: 140 ($M^{+\bullet}$ – C_8F_{17} + 1).

The fraction boiling at 100 °C/3 Torr afforded 50% yield of cyclopentadienes. GC-MS, *m/z*: 540 ($M^{+\bullet}$), 171 ($M^{+\bullet}$ – C_7F_{15}), 121 ($M^{+\bullet}$ – C_8F_{17}). ^{13}C NMR ($CDCl_3$, 125.7 MHz): 11.03 s (CH_3); 12.51 s (CH_3); 60.24 t, $^2J_{C-F}$ = 19.2 (C-CF_2); 128.00 s (>C=); 140.03 s (>C=); 108–121 m (CF) (isomer **3a**); 10.42 s (CH_3); 11.74 s (CH_3); 12.77 bs (CH_3); 14.01 bs (CH_3); 50.01 s (CH); 127.44 t, $^2J_{C-F}$ = 23.8 (=C-CF_2); 134.24 d, $^3J_{C-F}$ = 1.8 (>C=); 146.46 s (>C=); 150.79 bs (>C=); 108–121 m (CF) (isomer **3b**); 11.15 s (CH_3); 20.40 s (CH_3); 20.51 s (CH_3); 45.68 s (CH); 47.33 s (CH); 106.30 s (=CH_2); 145.48 bs (>C=); 159.02 s (>C=); 108–121 m (CF) (isomer **3c**).

*(Perfluorodecyl)tetramethylcyclopenta-1,3-dienes (**4a**–**4c**)*

As the alcohols uncontrollably decomposed on distillation, a crude product mixture (GC-MS, *m/z*: 139 ($M^{+\bullet}$ – $C_{10}F_{21}$)) was dehydrated.

The fraction boiling at 95 °C/2 Torr afforded 24% yield of cyclopentadienes (based on the starting iodide). GC-MS, *m/z*: 171 ($M^{+\bullet}$ – C_9F_{19}), 121 ($M^{+\bullet}$ – $C_{10}F_{21}$). ^{13}C NMR ($CDCl_3$): 11.02 s (CH_3); 12.49 s (CH_3); 60.17 t, $^2J_{C-F}$ = 19.0 (C-CF_2); 127.93 s (>C=); 139.96 s (>C=); 104–120 m (CF) (isomer **4a**); 10.42 s (CH_3); 11.74 s (CH_3); 12.77 bs (CH_3); 13.98 bs (CH_3); 49.97 s (CH); 127.25 b, *J* not resolved (=C-CF_2); 134.20 bs (>C=); 146.40 s (>C=); 150.71 bs (>C=); 104–120 m (CF) (isomer **4b**); 11.10 s (CH_3); 20.37 s (CH_3); 20.48 s (CH_3); 45.61 s (CH); 47.25 s (CH); 106.27 s (=CH_2); 145.37 bs (>C=); 158.85 s (>C=); 104–120 m (CF) (isomer **4c**).

Rhodium(III) Complexes. General Procedure

Rhodium(III) trichloride hydrate (4.5 mmol) was dissolved in methanol in a Schlenk flask, a mixture of (perfluoroalkyl)tetramethylcyclopentadienes (4.6 mmol) and cyclohexa-1,3-diene (4.6 mmol) was added by syringe. The mixture was refluxed for 3 h, then left to stand overnight. The orange-red precipitate was filtered off by cannula and dried in vacuum.

Di-μ-chloro-dichloro-bis[η^5-(perfluorobutyl)tetramethylcyclopentadienyl]dirhodium(III) (**5**). Yield 88%. ^{1}H NMR ($CDCl_3$): 1.76 s, 1 H (CH_3); 1.89 s, 1 H (CH_3). ^{13}C NMR ($CDCl_3$): 9.53 s (CH_3); 10.43 bs (CH_3); 72.50 dt, $^2J_{C-F}$ = 23.7, $^1J_{C-Rh}$ = 12.0 (Rh-C-CF_2); 98.00 d, $^1J_{C-Rh}$ = 8.5 (Rh-C); 102.63 d, $^1J_{C-Rh}$ = 8.5 (Rh-C); 102–120 m (CF). ^{19}F NMR ($CDCl_3$): –18.5 m, 3 F; –43.87 t, $^3J_{F-F}$ = 12.5, 2 F; –59.82 m, 2 F; –63.50 m, 2 F.

Di-μ-chloro-dichloro-bis[η^5-(perfluorohexyl)tetramethylcyclopentadienyl]dirhodium(III) (**6**). Yield 75%. ^{1}H NMR ($CDCl_3$): 1.76 s, 1 H (CH_3); 1.90 s, 1 H (CH_3). ^{13}C NMR ($CDCl_3$): 9.51 s (CH_3); 10.39 bs (CH_3); 73.01 dt, $^2J_{C-F}$ = 23.6, $^1J_{C-Rh}$ = 11.9 (Rh-C-CF_2); 98.02 d, $^1J_{C-Rh}$ = 8.3 (Rh-C); 102.62 d, $^1J_{C-Rh}$ = 8.0 (Rh-C); 102–122 m (CF). ^{19}F NMR ($CDCl_3$): –18.5 m, 3 F; –43.7 m, 2 F; –58.89 m, 2 F; –59.47 bs, 2 F; –60.41 bs, 2 F; –63.8 m, 2 F.

Di-μ-chloro-dichloro-bis[η^5-(perfluorooctyl)tetramethylcyclopentadienyl]dirhodium(III) (**7**). Yield 85%. ^{1}H NMR ($CDCl_3$): 1.76 s, 1 H (CH_3); 1.90 s, 1 H (CH_3). ^{13}C NMR ($CDCl_3$): 9.52 s (CH_3); 10.41 bs (CH_3); 73.01 dt, $^2J_{C-F}$ = 23.6, $^1J_{C-Rh}$ = 12.2 (Rh-C-CF_2); 98.05 d, $^1J_{C-Rh}$ = 6.8 (Rh-C); 102.62 d, $^1J_{C-Rh}$ = 6.8 (Rh-C); 104–122 m (CF). ^{19}F NMR ($CDCl_3$): –18.4 m, 3 F; –43.6 m, 2 F; –58.7 m, 2 F; –59.5 b, 6 F; –60.4 b, 2 F; –63.8 b, 2 F.

Di-μ-chloro-dichloro-bis[η^5-(perfluorodecyl)tetramethylcyclopentadienyl]dirhodium(III) (**8**). Yield 71%. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.76 s, 1 H (CH_3); 1.89 s, 1 H (CH_3). ^{13}C NMR ($CDCl_3$, 125.7 MHz): 9.55 s (CH_3); 10.47 bs (CH_3); 73.05 dt, $^2J_{C-F}$ = 23.6, $^1J_{C-Rh}$ = 12.0 (Rh-C-CF_2); 98.02 d, $^1J_{C-Rh}$ = 7.3 (Rh-C); 102.62 d, $^1J_{C-Rh}$ = 7.5 (Rh-C); 106–122 m (CF). ^{19}F NMR ($CDCl_3$): –18.4 m, 3 F; –43.6 m, 2 F; –58.7 m, 2 F; –59.3 b, 10 F; –60.3 b, 2 F; –63.7 b, 2 F.

Rhodium(I) Complexes. General Procedure

Di-μ-chloro-dichloro-bis[η^5-(perfluoroalkyl)tetramethylcyclopentadienyl]dirhodium(III) (0.73 mmol) was suspended in dry methanol in a Schlenk flask and zinc dust (2.1 mmol) was added. Carbon monoxide was bubbled through the stirred mixture at 70 °C for 3 h. The mixture was left to cool to room temperature, then the solid was filtered off by cannula. The filtrate was concentrated in vacuum to about one half. When a solid started to crystallize, the flask was put into a freezer (–30 °C) for a few days. The orange-brown needle-like crystals were then filtered off by cannula and dried in vacuum.

Dicarbonyl-[η^5-(perfluorobutyl)tetramethylcyclopentadienyl]rhodium(I) (**9**). Yield 90%. ^{1}H NMR ($CDCl_3$): 2.09 s, 1 H (CH_3); 2.10 s, 1 H (CH_3). ^{13}C NMR ($CDCl_3$): 10.72 s (CH_3); 11.23 bs (CH_3); 93.03 dt, $^2J_{C-F}$ = 22.7, $^1J_{C-Rh}$ = 5.8 (Rh-C-CF_2); 100.53 d, $^1J_{C-Rh}$ = 2.9 (Rh-C); 106.34 d, $^1J_{C-Rh}$ = 3.6 (Rh-C); 108–122 m (CF); 191.20 d, $^1J_{Rh-C}$ = 84.7 (CO). ^{19}F NMR ($CDCl_3$): –18.8 m, 3 F; –36.47 t, 2 F; –59.95 q, 2 F; –63.70 m, 2 F.

Dicarbonyl-[η^5-(perfluorohexyl)tetramethylcyclopentadienyl]rhodium(I) (**10**). Yield 88%. ^{1}H NMR ($CDCl_3$): 2.09 s, 1 H (CH_3); 2.10 s, 1 H (CH_3). ^{13}C NMR ($CDCl_3$): 10.80 s (CH_3); 11.28 bs (CH_3); 93.22 dt, $^2J_{C-F}$ = 24.6, $^1J_{C-Rh}$ = 5.0 (Rh-C-CF_2); 100.51 d, $^1J_{C-Rh}$ = 2.7 (Rh-C); 106.28 d, $^1J_{C-Rh}$ = 3.6 (Rh-C); 108–122 m (CF); 191.20 d, $^1J_{Rh-C}$ = 84.7 (CO). ^{19}F NMR ($CDCl_3$): –18.5 m, 3 F; –36.2 m, $^3J_{F-F}$ = 15.6, 2 F; –58.9 m, 2 F; –59.4 m, 2 F; –60.4 m, 2 F; –63.8 m, 2 F.

Dicarbonyl-[h^5-(perfluorooctyl)tetramethylcyclopentadienyl]rhodium(I) (**11**). Yield 69%. ^{1}H NMR ($CDCl_3$): 2.10 s, 1 H (CH_3). ^{13}C NMR ($CDCl_3$): 10.76 s (CH_3); 11.23 bs (CH_3); 93.20 dt, $^2J_{C-F}$ = 22.9, $^1J_{C-Rh}$ = 5.8 (Rh-C-CF_2); 100.51 d, $^1J_{C-Rh}$ = 3.0 (Rh-C); 106.29 d, $^1J_{C-Rh}$ = 3.6 (Rh-C); 104–122 m (CF); 191.20 d, $^1J_{Rh-C}$ = 84.5 (CO). ^{19}F NMR ($CDCl_3$): –18.4 t, 3 F; –36.2 m, 2 F; –58.8 m, 2 F; –59.4 bm, 6 F; –60.3 m, 2 F; –63.7 m, 2 F.

Dicarbonyl-[η^5-(perfluorodecyl)tetramethylcyclopentadienyl]rhodium(I) (**12**). Yield 72%. ^{1}H NMR ($CDCl_3$): 2.09 s, 1 H (CH_3); 2.10 s, 1 H (CH_3). ^{13}C NMR ($CDCl_3$): 10.81 s (CH_3); 11.28 bs

(CH_3); 93.22 dt, $^2J_{C\text{-}F}$ = 24.3, $^1J_{C\text{-}Rh}$ = 5.9 (Rh-C-CF_2); 100.56 d, $^1J_{C\text{-}Rh}$ = 2.7 (Rh-C); 106.27 d, $^1J_{C\text{-}Rh}$ = 3.6 (Rh-C); 106–122 m (CF); 191.20 d, $^1J_{Rh\text{-}C}$ = 84.7 (CO). ^{19}F NMR ($CDCl_3$): –18.4 t, 3 F; –36.2 m, 2 F; –58.9 m, 2 F; –59.4 bm, 10 F; –60.3 m, 2 F; –63.8 m, 2 F.

X-Ray Structure of Complex **6**

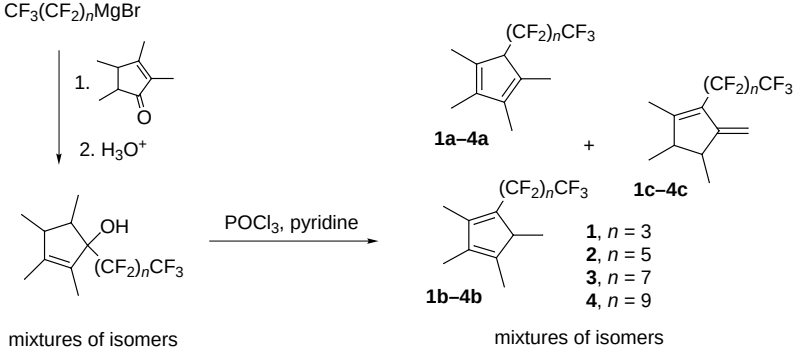
The diffraction-quality crystals of compound **6** were grown from its $CHCl_3$ solution by slow evaporation in an NMR tube. The crystals were mounted on glass fibres in random orientation with epoxy glue. Diffraction data were collected on a Nonius KappaCCD diffractometer at 293(1) K using graphite monochromated MoKα radiation (λ = 0.71073 Å) and analyzed using an HKL program package[18]. The cell parameters of studied compounds were determined from all measured data[18].

The structure was solved by direct methods (SIR92)[19] and refined by full-matrix least-squares techniques on F^2 (SHELXL97)[20]. Scattering factors for neutral atoms used were included in the SHELXL97 program. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were not found in this structure due to two kinds of disorder ($CHCl_3$ solvate molecules and $CF_3(CF_2)_n$ chains). They were included in calculated positions (SHELXL97)[20]. Table I gives pertinent crystallographic data; selected bond distances and angles are listed in Table II. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-154411. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

RESULTS AND DISCUSSION

Synthesis and Characterization of Ligands

(Perfluoroalkyl)tetramethylcyclopentadienes $(CH_3)_4C_5H(CF_2)_nCF_3$ (**1**, n = 3; **2**, n = 5; **3**, n = 7; **4**, n = 9) were prepared by the addition of (perfluoroalkyl)-magnesium bromides to 2,3,4,5-tetramethylcyclopent-2-en-1-one, followed by dehydration of the resulting tertiary alcohols with $POCl_3$ in pyridine (Scheme 1).



SCHEME 1

TABLE I
Exprimental data for the X-ray diffraction study of **6**

Formula	$C_{30}H_{24}Cl_4Rh_{32} \cdot CHCl_3$
M	1 345.48
T, K	293(1)
Shape and colour	irregular, deep orange
Crystal system	orthorhombic
Space group	*Pbca* (No. 61)
a, Å	12.1010(10)
b, Å	22.3840(3)
c, Å	33.1980(5)
α, °	90
β, °	90
γ, °	90
U, Å^3	8 992.3(2)
Z	8
D_c, g cm^{-3}	1.986
λ, Å	0.71073
μ, mm^{-1}	1.284
F(000)	5 224
Scan mode	ω-scans
θ range of data collection, °	2.08; 25.04
Index ranges	0,14; 0.26; 0.39
Number of reflections measured	7 632
R_σ	0.0453
Number of reflections observed [$I > 2\sigma(I)$]	5 730
Number of independent reflections	7 625
R_{int}	–
Coefficients in weighting scheme[a]	0.0774; 91.9633
Data, restrains, parameters	7 625; 42; 628
Goodness-of-fit on F^2	1.074 (42 restraints)
Final *R*, *R*′ indices [$I \geq 2\sigma(I)$][b]	0.0636; 0.1777
Mean shift, e.s.d.	0.000
Maximum shift, e.s.d.	0.001
Largest difference peak and hole, e Å^3	1.81; –1.16

[a] $w = 1/[\sigma^2(F_o^2) + (A * P)^2 + B * P]$, where $P = (F_o^2 + 2F_c^2)/3$ (SHELXL97, ref.[20]); [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_c|$, $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (SHELXL97, ref.[20]).

The perfluorinated Grignard reagents were prepared *in situ* from the corresponding perfluoroalkyl iodides and phenylmagnesium bromide at low temperature[21]. The mixtures of intermediary alcohols were isolated except in the case of perfluorodecyl compounds and analyzed by GC-MS (*e.g.* Fig. 1). Three isomers were identified in all cases. Mass spectra of the alcohols did not exhibit a molecular ion, only a very small $M^{+\bullet} - H_2O$ ion was visible. The characteristic base peak in the spectra was found at *m/z* 139, indicating a loss of the perfluorinated chain.

The cyclopentadienes isolated after dehydration were always mixtures of isomers as it is usual in the reaction sequence: nucleophile addition to tetramethylcyclopentenone carbonyl-dehydration[22,23]. Six isomers were identified by GC-MS (Fig. 2), three of them in quantities over 10%. The ratios of these isomers varied along the series without any trend and even

TABLE II
Selected bond lengths (in Å) and angles (in °) for **6** with e.s.d. in parentheses

Atoms	Bond lengths	Atoms	Bond lengths	Atoms	Angles
Rh1–Rh2	3.593(1)	Rh2–C24	2.161(8)	Rh1–Cl3–Rh2	95.74(7)
Rh1–Cl1	2.360(2)	Rh2–C25	2.162(8)	Rh1–Cl4–Rh2	95.30(7)
Rh1–Cl3	2.423(2)	C14–C1A	1.493(11)	Cl3–Rh1–Cl4	84.20(7)
Rh1–Cl4	2.441(2)	C1A–C2A	1.529(10)	Cl3–Rh2–Cl4	84.67(7)
Rh2–Cl2	2.369(2)	C2A–C3A	1.550(12)	Cl1–Rh1–Cl3	89.12(8)
Rh2–Cl3	2.422(2)	C3A–C4A	1.418(16)	Cl1–Rh1–Cl4	88.90(7)
Rh2–Cl4	2.421(2)	C4A–C5A	1.638(17)	Cl2–Rh2–Cl3	90.38(8)
Rh1–C11	2.167(8)	C5A–C6A	1.432(17)	Cl2–Rh2–Cl4	88.79(7)
Rh1–C12	2.152(8)	C21–C1B	1.497(12)		
Rh1–C13	2.164(8)	C1B–C2B	1.540(11)		
Rh1–C14	2.091(8)	C2B–C3B	1.511(13)		
Rh1–C15	2.153(8)	C3B–C4B	1.623(15)		
Rh2–C21	2.095(8)	C4B–C5B	1.468(16)		
Rh2–C22	2.149(8)	C5B–C6B	1.438(15)		
Rh2–C23	2.155(8)				

reproducibility of the ratios was poor; nevertheless all the isomers were always present. A characteristic feature of the mass spectra of the isomers was the presence of a strong molecular ion (in some cases even the base peak), the main fragmentation path being the cleavage of the C_α–C_β bond of the perfluorinated chain. Signals in 1D ^{1}H NMR spectra even at 500 MHz were

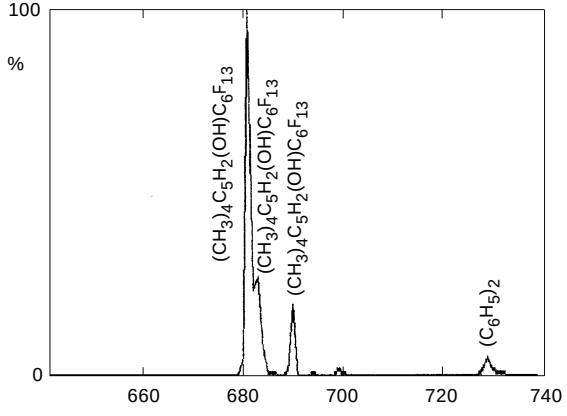


FIG. 1
Total ion current chromatogram of a mixture of (perfluorohexyl)tetramethylcyclopentadienols, retention time in s

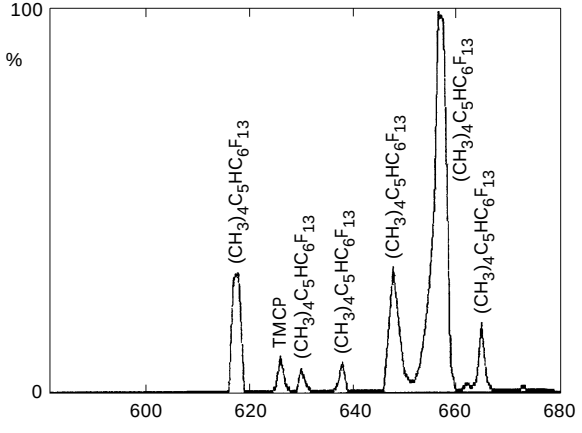
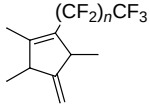
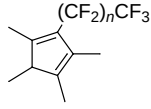


FIG. 2
Total ion current chromatogram of a mixture of (perfluorohexyl)tetramethylcyclopentadienes (**2a**–**2c** plus other isomers), TMCP = 2,3,4,5-tetramethylcyclopent-2-en-1-one, retention time in s

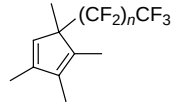
not sufficiently resolved to allow unambiguous identification and structure determination of all three major isomers. However, resolution of signals in ^{13}C NMR spectra was sufficient and structures **a**–**c** were assigned to the three major isomeric products. The assignment was facilitated by analyzing mixtures with different ratios of the isomers. The characteristic signal of the symmetric isomer **a** is the triplet around 60 ppm assigned to perfluoroalkyl substituted ring methine carbon. A similar characteristic of isomer **c** is terminal carbon of an exocyclic double bond found at about 106 ppm; the alternative structure **d** for the latter isomer was excluded since the signal of quarternary carbon of exocyclic double bond in isomer **d** would not likely be broadened by long-range coupling with fluorines of the perfluorinated chain. Similar arguments, *i.e.* the presence of long-range coupling between fluorines and carbons α to the ponytail substituted carbon (triplets or broadening of the signals), helped in favouring the structure **b** over alternative structure **e**.



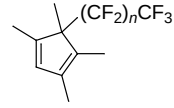
d



e



f



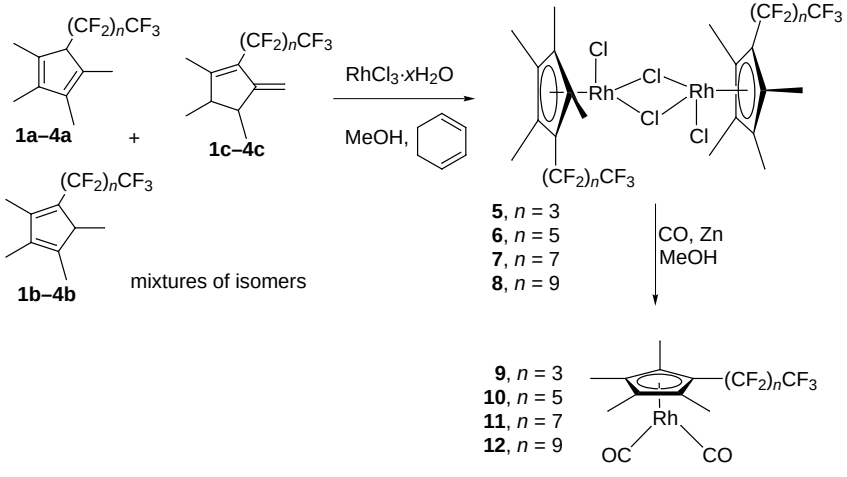
g

Owing to the expected close chemical behaviour, no attempt was made to separate the isomers. Furthermore, for the purpose of synthesis of transition metal complexes, the sufficient prerequisite is an allylic position of the remaining ring proton in the isomers. Deprotonation of all the isomers would then give the same cyclopentadienyl anion. The isomers with ring proton in vinyl position (**f**, **g**) observed in similar isomer mixtures[22,23] would be characterized by the triplet (coupled to the CF_2 group) signals of aliphatic quarternary carbons accompanied by aromatic methine signals; however, such signals were never observed in our isomer mixtures.

Rhodium(III) Complexes

Attempts to prepare anions stable enough for further reactions from cyclopentadienes **1**–**4** were not successful using various reagents even at low temperatures (thallium salts[24] were not attempted). Stable cyclopentadienyl complexes were obtained by modification of a known procedure[25] for the Maitlis complex[26] $[Cp^*RhCl_2]_2$. The reaction of $RhCl_3 \cdot xH_2O$ with cyclopentadienes in methanol at first yielded no crystalline products. Addi-

tion of cyclohexa-1,3-diene as a proton acceptor[10], however, resulted in isolation of Rh(III) dimer complexes **5**–**8** (Scheme 2) in yields ranging from 71 to 88%. The calculated yields were always based on a mixture of isomers; since the major isomer content in the mixture was 50% at the maximum, this is circumstantial evidence that other isomers afforded the complexes as well. The η^5-coordination of the substituted cyclopentadienyl ligands found in the solid state (see below) was also confirmed in solution by the observation of coupling to rhodium of all the ring carbons including the perfluoroalkyl substituted one. The differences in chemical shifts between complexes with different ponytail lengths were very small, indicating only small changes of electronic properties of the ligands when lengthening the chain.



SCHEME 2

Single-crystal structure of complex **6** was determined by X-ray diffraction (Fig. 3). The coordination geometry around the Rh(III) atom was essentially the same as that in the pentamethylcyclopentadienyl analogue[27], *i.e.* "three-legged piano stool", and bond lengths and angles were similar; for instance, distances of rhodium atoms from least-squares planes of the rings were 1.762(4) and 1.760(4) Å as compared to 1.7558(3) Å in the Cp* analogue. Exceptions include perfluoroalkyl substituted ring carbons C14 and C21 lying about 0.05 Å closer to the metal than the other ring carbons, which resulted in a very slight envelope-like distortion of the η^5-coordinated rings, and nonbonding Rh–Rh distance of 3.5933(9) Å which was by 0.126 Å shorter than that in the Cp* analogue (see also ref.[14]).

Two kinds of disorder were observed. The first one is caused by the molecule of solvent $CHCl_3$, which was located in two positions (the ratio of occupancies 49 : 51) with the common C–H bond. The position of hydrogen atom in the disordered solvent molecule was not established.

The other is connected with conformations of perfluoroalkyl chains. The two chains in the molecule of the complex had different conformations on the bonds C5–C4 and C3–C2. The chain B adopted the conformation all-*anti* (straight chain); the chain A the conformation *gauche-anti-gauche-anti* (bent chain; see Table II). Such behaviour was observed previously[28–30] as a means to maximize fluorophilic interactions of molecules which do not lie in the same parallel-stack layer. The main reason for the observed disorder is probably the fact that some fraction of molecules with both straight chains occurred in positions of the more abundant molecules with one straight and one bent chain. The observed high thermal motion of terminal CF_2CF_3 units was also noted previously[29]. Our attempts to determine the structure at low temperature has failed so far due to high increase of mosaicity of crystals.

It should be noted here that compound **6** ranks among only a few transition metal complexes with polyfluoroalkyl substituted ligands, the structures of which are known[28–31]. With one exception[31], all of them contain

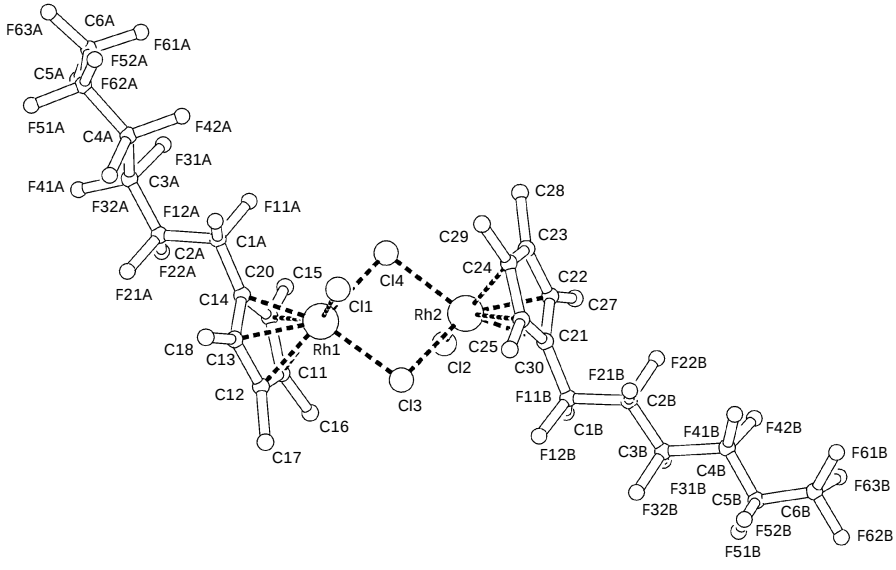


FIG. 3
PLUTON view of the molecular structure of **6**. Hydrogen atoms are omitted for clarity

phosphine ligands; the fluorinated chain is always linked to the parent ligand with a two-methylene spacer. To our best knowledge, no X-ray structure of a cyclopentadienyl complex with the ligand substituted with per- or polyfluoroalkyl chain has been published so far.

Rhodium(I) Complexes

Reduction of rhodium(III) chloro complexes with zinc in the presence of carbon monoxide led to the formation of rhodium(I) carbonyl complexes **9**–**12**, isolated in 69–90% yields. The NMR chemical shifts of corresponding signals of all the complexes lie in a very narrow range and did not differ much from the shifts of rhodium(III) chloro complexes. The carbonyl stretching frequencies in complexes **9**–**12** were used as a probe of the change of electronic properties of tetramethylcyclopentadienyl ligands caused by attachment of perfluoroalkyl chains of various lengths to the ring. The frequencies are summarized in Table III, together with some literature data, showing that electronically (perfluoroalkyl)tetramethylcyclopentadienyl ligands lie close to unsubstituted cyclopentadienyl. The balancing of the electronic effect of trifluoromethyl group by four methyl groups on the Cp ring has been observed by Gassman[13]; our results show that lengthening of the chain does not substantially affect this balance.

In conclusion, four new perfluoroalkyl substituted cyclopentadienes (in mixtures of isomers) were synthesized as ligand precursors for transition

TABLE III
Carbonyl stretching frequencies of polyfluoroalkyl substituted rhodium cyclopentadienyl complexes

Complex	ν(CO), cm^{-1}
$[Rh(C_5Me_5)(CO)_2]$	2 000, 1 950[a]
$[Rh(C_5Me_4C_4F_9)(CO)_2]$ (**9**)	2 042, 1 982[b]
$[Rh(C_5Me_4C_6F_{13})(CO)_2]$ (**10**)	2 043, 1 982[b]
$[Rh(C_5Me_4C_8F_{17})(CO)_2]$ (**11**)	2 043, 1 982[b]
$[Rh\{C_5H_4(CH_2)_2(CF_2)_9CF_3)\}(CO)_2]$	2 049, 1 987[c]
$[Rh(C_5H_5)(CO)_2]$	2 051, 1 978[d]

[a] KBr, ref.[32]; [b] Nujol, this work; [c] hexane solution, ref.[12]; [d] Nujol, ref.[32]

metal complexes. The cyclopentadienes are easy to handle due to the absence of self-dimerization. Cyclopentadienyl ligands obtained from them exhibit electronic properties of unsubstituted cyclopentadienyl while retaining steric properties of pentamethylcyclopentadienyl similarly to the Gassman ligand[13] $[(CH_3)_4C_5CF_3]^-$. Furthermore, the electronic properties do not change with the length of perfluoroalkyl chain and the ligands and complexes are soluble in fluorous phases[33]. While the isolated cyclopentadienide anions could not be prepared (see also Gassman[13]), stable rhodium(III) and rhodium(I) complexes were synthesized and characterized in solution, and molecular structure of one Rh(III) complex was determined by X-ray diffraction. The use of the complexes in homogeneous catalysis of various reactions including C–H activation[34,35] may be expected (*e.g.*, the Gassman ligand was recently shown to change substantially the course of a reaction[36] as compared to Cp*, including improvement of the C–H activation of aldehydes[34]). Research is currently being carried out in this direction.

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