Tetramethyl(perfluoroalkyl)cyclopentadienyl rhodium(I) complexes with ethylene or diene ligands. Crystal structure of [(η5-C5Me4C6F13)Rh(CO)2]

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ABSTRACT

Tetramethyl(perfluoroalkyl)cyclopentadienyl rhodium(I) complexes with ethylene or diene (norbornadiene, cyclooocta-1,5-diene, 2,3-dimethylbuta-1,3-diene, cyclohexa-1,3-diene) ligands were obtained by reduction of tetramethyl(perfluoroalkyl)rhodium(III) dichloro dimers by zinc in THF or by propan-2-ol/sodium carbonate in the presence of the ligands. Reduction in the presence of cyclooocta-1,3-diene gave a different product, an η3-cycloooctenyl complex, which was not reduced further. During the reduction in the presence of ethylene, a new tetramethyl(perfluoroalkyl)-η4-cyclopentadiene complex was observed by NMR. This compound, formed by hydrogen transfer from the metal to the ligand, is probably in an equilibrium with the parent hydridocyclopentadienyl complex. Crystal and molecular structure of dicarbonyltetramethyl(perfluorohexyl)cyclopentadienylrhodium(I) complex was determined by X-ray diffraction. The structure shows a moderate ring slippage of the rhodium atom which was not observed in the only other known structure of a complex with the same ligand, the rhodium(III) dichloro dimer.

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1. Introduction

Complexes with pentamethylcyclopentadienylrhodium fragment were studied thoroughly [1] since the pentamethylcyclopentadienyl ligand (Cp*) had been reported for the first time and the interest in them continues [2]. Special attention was devoted to studies on photochemical activation of [Cp*Rh(CO)2] to generate an unsaturated species capable of activation of C–H bonds [3] but there were also other applications in catalysis [4]. Complexes with alkene and diene ligands have for a long time represented an important subtype of complexes having Cp*Rh[I] fragment [5].

Recently, we have prepared higher homologs of the Gassman tetramethyl(trifluoromethyl)cyclopentadienyl ligand [6]. These ligands, having the formula $C_5(CH_3)_4C_nF_{2n+1}$ (Cp+Rfn) [7], were found to be, similarly to the original Gassman ligand, electronically close to unsubstituted cyclopentadienyl ligand (Cp) inde-

pendently of the length of perfluorinated chain (n = 4, 6, 8, 10). Steric properties were estimated by comparison of the barrier to rotation of triarylphosphine ligands caused by Cp+Rf4Rh fragment with the known barrier to rotation caused by Cp*Rh fragment [8]. Somewhat surprisingly, the former ligands were found to be within experimental error exactly of the same size as Cp* [9].

No rhodium(I) complexes with Cp+Rfn ligands are known with the exception of a series of [Cp+RfnRh(CO)2] complexes (n = 4, 6, 8, 10) [7]; we report here the synthesis and properties of new ethylene and diene complexes with these ligands. The first X-ray structure determination of a rhodium(I) carbonyl complex with the Cp+Rfn ligand is also reported.

2. Experimental

2.1. General

Syntheses of rhodium complexes were carried out under dry argon or nitrogen atmosphere using standard Schlenk techniques.

Starting dienes were commercial products (Aldrich) used without further purification, ethylene (purity 3.0) was obtained from Linde and used as supplied, zinc powder (Aldrich) was used as supplied. Di-μ-chloro-dichloro-bis[η^5-tetramethyl(perfluoroalkyl) cyclopentadienyl]dirhodium(III) complexes **1a–c**
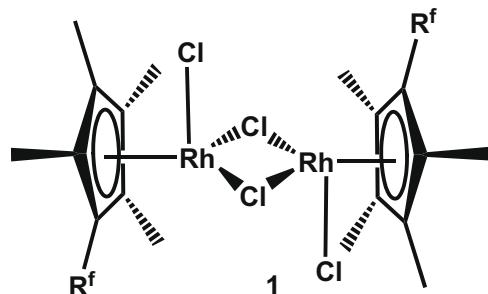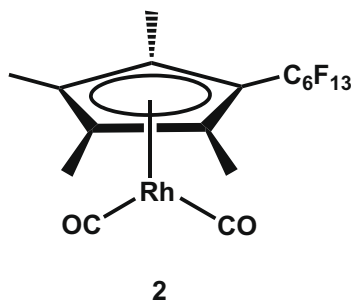

R^f = C$_4$F$_9$, **1a**
R^f = C$_6$F$_{13}$, **1b**
R^f = C$_8$F$_{17}$, **1c**

and dicarbonyl[η^5-tetramethyl(perfluorohexyl)cyclopentadienyl]-rhodium(I) complex **2**

were prepared as previously reported [7]. ^{1}H, ^{19}F{1H}, and ^{13}C{1H} NMR spectra were measured on a Varian Mercury 300 spectrometer at 299.98, 282.23, and 75.44 MHz, respectively, in C$_6$D$_6$ or CDCl$_3$ solutions at 25 °C. Chemical shifts (δ) are reported in ppm relative to TMS, referenced to hexamethyldisilane or the solvent peak (^{1}H, ^{13}C), and external CFCl$_3$ (^{19}F).

2.2. Bis(ethylene)tetramethyl(perfluorooctyl)cyclopentadienylrhodium(I) complex, 3c

Rhodium(III) dimer **1c** (285 mg, 0.2 mmol) and Na$_2$CO$_3$ (64 mg, 0.6 mmol) were dispersed in 20 ml of propan-2-ol and the suspension was heated to 70 °C. Ethylene was bubbled through the heated reaction mixture for 3 h with simultaneous stirring. After cooling to room temperature the volatiles were removed under reduced pressure and the residue was extracted with 6 ml of pentane. The solids were filtered off and the solvent was removed under reduced pressure to give rhodium(I) complex [RhCp^{+Rf8}(C$_2$H$_4$)$_2$] (262 mg, 94%) as a light brown highly viscous oil. ^{1}H NMR (C$_6$D$_6$): δ 1.41 (s, 6H, CH$_3$–Cp′), 1.47 (s, 6H, CH$_3$–Cp′), 1.5 (b, 4H, H–CH=), 2.1 (b, 4H, H–CH=). ^{13}C{1H} NMR (C$_6$D$_6$): δ 8.79 (s, CH$_3$–Cp′), 9.86 (s, CH$_3$–Cp′), 47.09 (d, $^1J_{C-Rh}$ = 13.5 Hz, CH$_2$=), 88.94 (dt, $^1J_{C-Rh}$ = 6.3 Hz, $^2J_{C-F}$ = 23.2 Hz, C$_{Cp′}$-R$_F$), 96.76 (td, coupling

not resolved, C$_{Cp′}$-CH$_3$), 103.78 (d, $^1J_{C-Rh}$ = 3.5 Hz, C$_{Cp′}$-CH$_3$), 107–121 (m, R$_F$). ^{19}F NMR (C$_6$D$_6$) δ: −126.7 (m, CF$_2$), −123.2 (m, CF$_2$), −122.2 (m, 3xCF$_2$), −121.7 (m, CF$_2$), −99.1 (m, CF$_2$), −81.6 (t, $^3J_{F-F}$ = 9.9 Hz, CF$_3$).

2.3. Bis(ethylene)tetramethyl(perfluorohexyl)cyclopentadienylrhodium(I) complex, 3b

Complex [RhCp^{+Rf6}(C$_2$H$_4$)$_2$], **3b**, was obtained by the same procedure as **3c** from the corresponding Rh(III) chloro dimer in 85% yield. ^{1}H NMR (C$_6$D$_6$): δ 1.39 (s, 6H, CH$_3$–Cp′), 1.46 (s, 6H, CH$_3$–Cp′), 1.5 (b, 4H, H-CH=), 2.1 (b, 4H, H-CH=). ^{13}C{1H} NMR (C$_6$D$_6$): δ 8.80 (s, CH$_3$–Cp′), 9.87 (s, CH$_3$–Cp′), 47.10 (d, $^1J_{C-Rh}$ = 13.5 Hz, CH$_2$=), 88.89 (dt, $^1J_{C-Rh}$ = 6.2 Hz, $^2J_{C-F}$ = 23.2 Hz, C$_{Cp′}$-R$_F$), 96.73 (td, coupling not resolved, C$_{Cp′}$-CH$_3$), 103.79 (d, $^1J_{C-Rh}$ = 3.7 Hz, C$_{Cp′}$-CH$_3$), 107–121 (m, R$_F$). ^{19}F NMR (C$_6$D$_6$): δ −126.6 (m, CF$_2$), −123.1 (m, CF$_2$), −122.1 (m, CF$_2$), −121.7 (m, CF$_2$), −99.1 (t, $^3J_{F-F}$ = 13.9 Hz, CF$_2$), −81.5 (t, $^3J_{F-F}$ = 9.9 Hz, CF$_3$).

2.4. (2,3-Dimethylbuta-1,3-diene)tetramethyl(perfluorooctyl)cyclopentadienylrhodium(I) complex, 4c

Rhodium(III) dimer **1c** (285 mg, 0.2 mmol) and Na$_2$CO$_3$ (64 mg, 0.6 mmol) were suspended in 20 ml of propan-2-ol, 2,3-dimethylbuta-1,3-diene (164 mg, 2.0 mmol) was added and the mixture was stirred for 18 h at room temperature. The resulting yellow suspension was filtered, volatiles were removed from the filtrate under reduced pressure and the residue was extracted with 3 ml of pentane. The solids were filtered off and the solvent was removed under reduced pressure to give rhodium(I) complex [RhCp^{+Rf8}(C$_6$H$_{10}$)] (283 mg, 98%) as a light orange viscous oil. ^{1}H NMR (CDCl$_3$): δ 0.50 (s, 2H, H-CH=), 1.80 (s, 2H, H-CH=), 1.83 (s, 6H, CH$_3$–Cp′), 1.86 (s, 6H, CH$_3$-C=), 1.97 (bs, 6H, CH$_3$–Cp′). ^{13}C{1H} NMR (CDCl$_3$): δ 9.76 (s, CH$_3$–Cp′), 11.09 (s, CH$_3$–Cp′), 17.89 (s, CH$_3$-C=), 41.75 (d, $^1J_{C-Rh}$ = 17.0 Hz, CH$_2$=), 84.95 (dt, $^1J_{C-Rh}$ = 8.0 Hz, $^2J_{C-F}$ = 23.1 Hz, C$_{Cp′}$-R$_F$), 90.02 (d, $^1J_{C-Rh}$ = 7.5 Hz, =C-CH$_3$), 95.94 (td, $^3J_{C-F}$ = 2.6 Hz, $^1J_{C-Rh}$ = 5.2 Hz, C$_{Cp′}$-CH$_3$), 98.25 (d, $^1J_{C-Rh}$ = 4.9 Hz, C$_{Cp′}$-CH$_3$), 106–120 (m, R$_F$).

Complex **4c** was also prepared by reduction with zinc as follows.

Zinc powder (0.26 g, 4.0 mmol) was added to a stirred mixture of rhodium(III) dimer **1c** (0.4 g, 0.15 mmol) and 2,3-dimethylbuta-1,3-diene (0.23 g, 2.8 mmol) in 20 ml of THF in small portions during 30 min, then the mixture was stirred for 6 h at room temperature. The resulting green brown suspension was filtered, volatiles were removed from the filtrate under reduced pressure and the residue was extracted with 25 ml of pentane. The solids were filtered off and the solvent was removed under reduced pressure to give rhodium(I) complex [RhCp^{+Rf8}(C$_6$H$_{10}$)] (0.3 g, 74%).

2.5. (2,3-Dimethylbuta-1,3-diene)tetramethyl(perfluorobutyl) cyclopentadienylrhodium(I) complex, 4a

Complex [RhCp^{+Rf4}(C$_6$H$_{10}$)], **4a**, was obtained by the reduction with propan-2-ol/Na$_2$CO$_3$ as described for **4c** from the corresponding Rh(III) chloro dimer in 97% yield. ^{1}H NMR (C$_6$D$_6$): δ 0.62 (s, 2H, H-CH=), 1.50 (s, 6H, CH$_3$–Cp′), 1.64 (s, 6H, CH$_3$–Cp′), 1.80 (s, 2H, H-CH=), 1.90 (s, 6H, CH$_3$-C=). ^{13}C{1H} NMR (C$_6$D$_6$): δ 10.04 (s, CH$_3$–Cp′), 11.54 (s, CH$_3$–Cp′), 18.52 (s, CH$_3$-C=), 42.68 (d, $^1J_{C-Rh}$ = 17.0 Hz, CH$_2$=), 90.86 (d, $^1J_{C-Rh}$ = 7.5 Hz, =C-CH$_3$), 96.69 (td, coupling not resolved, C$_{Cp′}$-CH$_3$), 98.90 (d, $^1J_{C-Rh}$ = 4.9 Hz, C$_{Cp′}$-CH$_3$), 106–120 (m,

R_F). ^{19}F NMR (C_6D_6): δ −126.2 (m, CF_2), −122.6 (m, CF_2), −99.9 (m, CF_2), −81.5 (t, $^3J_{F-F}$ = 9.9 Hz, CF_3).

2.6. (Cyclohexa-1,3-diene)tetramethyl(perfluorohexyl) cyclopentadienylrhodium(I) complex, 5b

To a stirred suspension of rhodium(III) dimer 1b (245 mg, 0.2 mmol) and Na_2CO_3 (64 mg, 0.6 mmol) in 20 ml of propan-2-ol was added cyclohexa-1,3-diene (160 mg, 2 mmol) and the mixture was stirred for 21 h at room temperature. The resulting brown suspension was filtered and the volatiles were removed from the filtrate under reduced pressure to give rhodium(I) complex [RhCp^{+Rf6}(C_6H_8)] (179 mg, 94%) as a brown viscous oil. ^{1}H NMR (C_6D_6): δ 1.28 (m, 2H, H–CH), 1.63 (m, 2H, H–CH), 1.66 (s, 6H, CH_3–Cp′), 2.02 (s, 6H, CH_3–Cp′), 3.00 (m, 2H, HC=), 4.56 (m, 2H, HC=). ^{13}C{1H} NMR (C_6D_6): δ 10.70 (s, CH_3–Cp′), 11.82 (m, CH_3–Cp′), 26.83 (d, $^1J_{C-Rh}$ = 1.7 Hz, CH_2), 61.77 (d, $^1J_{C-Rh}$ = 16.0 Hz, CH=), 78.52 (d, $^1J_{C-Rh}$ = 7.1 Hz, CH=), 85.84 (dt, $^1J_{C-Rh}$ = 8.5 Hz, $^2J_{C-F}$ = 22.9 Hz, $C_{Cp'}$-R_F), 96.68 (td, $^3J_{C-F}$ = 2.4 Hz, $^1J_{C-Rh}$ = 5.2 Hz, $C_{Cp'}$-CH_3), 99.89 (d, $^1J_{C-Rh}$ = 4.7 Hz, $C_{Cp'}$-CH_3), 104–121 (m, R_F). ^{19}F NMR (C_6D_6): δ −126.5 (m, CF_2), −123.1 (m, CF_2), −122.1 (m, CF_2), −121.6 (m, CF_2), −99.2 (t, $^3J_{F-F}$ = 15.3 Hz, CF_2), −81.5 (t, $^3J_{F-F}$ = 10.2 Hz, CF_3).

2.7. (η^4-Bicyclo[2.2.1]hepta-2,5-diene)tetramethyl(perfluorobutyl) cyclopentadienylrhodium(I) complex, 6a

Rhodium(III) dimer 1a (204 mg, 0.2 mmol) and Na_2CO_3 (64 mg, 0.6 mmol) were suspended in 20 ml of propan-2-ol and norbornadiene (184 mg, 2.0 mmol) was added, then the mixture was stirred for 21 h at room temperature. The resulting brown suspension was filtered and the volatiles were removed from the filtrate under reduced pressure to give rhodium(I) complex [RhCp^{+Rf4}(C_7H_8)] (213 mg, 100%) as a brown viscous oil. ^{1}H NMR (C_6D_6): δ 0.88 (m, 2H, CH_2), 1.67 (s, 6H, CH_3–Cp′), 1.70 (s, 6H, CH_3–Cp′), 2.73 (m, 4H, HC=), 3.26 (bs, 2H, CH). ^{13}C{1H} NMR (C_6D_6): δ 10.51 (t, $^4J_{C-F}$ = 1.7 Hz, CH_3–Cp′), 10.74 (s, CH_3–Cp′), 36.05 (d, $^1J_{C-Rh}$ = 10.4 Hz, CH=), 47.74 (d, $^2J_{C-Rh}$ = 2.6 Hz, CH), 56.81 (d, $^3J_{C-Rh}$ = 6.6 Hz, CH_2), 88.40 (dt, $^1J_{C-Rh}$ = 6.6 Hz, $^2J_{C-F}$ = 22.7 Hz, $C_{Cp'}$-R_F), 95.47 (td, coupling not resolved, $C_{Cp'}$-CH_3), 101.41 (d, $^1J_{C-Rh}$ = 4.3 Hz, $C_{Cp'}$-CH_3), 106–120 (m, R_F). ^{19}F NMR (C_6D_6): δ −126.2 (m, CF_2), −122.6 (m, CF_2), −98.1 (m, CF_2), −81.6 (t, $^3J_{F-F}$ = 9.9 Hz, CF_3).

2.8. (Cyclooocta-1,5-diene)tetramethyl(perfluorooctyl) cyclopentadienylrhodium(I) complex, 7c

Zinc powder (0.25 g, 3.8 mmol) was added to a stirred mixture of rhodium(III) dimer 1c (0.4 g, 0.15 mmol) and cycloocta-1,5-diene (0.3 g, 2.7 mmol) in 20 ml of THF in small portions during 30 min, then the mixture was stirred for 6 h at room temperature. The resulting green brown suspension was filtered, volatiles were removed from the filtrate under reduced pressure and the residue was extracted with 25 ml of pentane. The solids were filtered off and the solvent was removed under reduced pressure to give rhodium(I) complex [RhCp^{+Rf8}(C_8H_{12})] (0.2 g, 49%) as a yellow viscous oil. ^{1}H NMR (C_6D_6): δ 1.55 (s, 6H, CH_3–Cp′), 1.60 (s, 6H, CH_3–Cp′), 1.93 (m, 4H, H–CH), 2.18 (m, 4H, H–CH), 3.24 (m, 4H, HC=). ^{13}C{1H} NMR (C_6D_6): δ 9.57 (s, CH_3–Cp′), 9.90 (s, CH_3–Cp′), 33.17 (s, H_2), 72.71 (d, $^1J_{C-Rh}$ = 13.9 Hz, CH=), 96.49 (td, coupling not resolved, $C_{Cp'}$-CH_3), 103.28 (d, $^1J_{C-Rh}$ = 3.7 Hz, $C_{Cp'}$-CH_3), 106–120 (m, R_F).

Table 1
Experimental data for the X-ray diffraction study of 2.

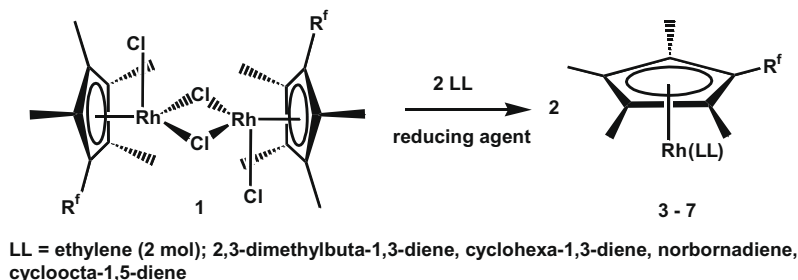|	2
Formula	$C_{17}H_{12}F_{13}O_2Rh$
M	598.18
T (K)	150
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimension	
a (Å)	7.2560(1)
b (Å)	25.8730(4)
c (Å)	10.9040(1)
α (°)	90
β (°)	90.5320(8)
γ (°)	90
V (Å^3)	2046.97(5)
Z	4
D_{calc} (g cm^{-3})	1.941
Absorption coefficient μ (mm^{-1})	0.963
$F(0\,0\,0)$	1168
Crystal size/mm^3	0.23 × 0.30 × 0.38
θ Range of data collection (°)	1.57–27.47
Index ranges	
h	−9.9
k	−33.33
l	−14.14
Reflections collected [R_σ]	9194 [0.0188]
Independent reflections [R_{int}]	4683 [0.0123]
Number of reflections observed [$I > 2\sigma(I)$]	4314
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restrains/parameters	4683/9/303
Goodness-of-fit on F^2	1.089
Final R, R' indices [$I > 2\sigma(I)$][b]	0.0564; 0.1592
Maximum shift/e.s.d.	0.000
Coefficients in weighting scheme[a]	0.0764; 11.3403
Largest difference in peak and hole (e Å^3)	2.731; −0.898

[a] $w = 1/[\sigma^2(F_o^2) + (A*P)^2 + B*P]$ where $P = (F_o^2 + 2F_c^2)/3$ (SHELXL97, [12]).
[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, [12]).

2.9. Chloro(cyclooct-2-en-1-yl)tetramethyl(perfluorobutyl) cyclopentadienylrhodium(III) complex, 8a

Rhodium(III) dimer 1a (202 mg, 0.196 mmol) and Na_2CO_3 (68 mg, 0.64 mmol) were suspended in 10 ml of propan-2-ol and cycloocta-1,3-diene (218 mg, 2.01 mmol) in propan-2-ol (10 ml) was added, then the mixture was stirred for 22 h at room temperature. The resulting red brown suspension was filtered and the volatiles were removed from the filtrate under reduced pressure to give product (194 mg, 90%) as a red brown viscous oil. ^{1}H NMR (C_6D_6): δ 1.30 (m, 1H, H–CH), 1.33 (s, 6H, CH_3–Cp′), 1.40 (m, 4H, CH_2), 1.42 (s, 6H, CH_3–Cp′), 1.74 (m, 1H, H–CH), 2.01 (m, 2H, H–CH–CH=), 2.47 (m, 2H, H–CH–CH=), 3.66 (m, 1H, HC=), 4.30 (m, 2H, HC=). ^{13}C{1H} NMR (C_6D_6): δ 9.21 (s, CH_3–Cp′), 10.12 (s, CH_3–Cp′), 25.00 (s, CH_2), 27.85 (s, CH_2), 29.32 (s, CH_2–CH=), 73.98 (d, $^1J_{C-Rh}$ = 10.1 Hz, CH=), 88.21 (dt, $^1J_{C-Rh}$ = 6.9 Hz, $^2J_{C-F}$ = 22.5 Hz, $C_{Cp'}$-R_F), 88.41 (d, $^1J_{C-Rh}$ = 6.6 Hz, CH=), 100.49 (td, coupling not resolved, $C_{Cp'}$-CH_3), 103.08 (d, $^1J_{C-Rh}$ = 4.9 Hz, $C_{Cp'}$-CH_3), 108–121 (m, R_F). ^{19}F NMR (C_6D_6): δ −126.3 (m, CF_2), −122.6 (m, CF_2), −101.7 (m, CF_2), −81.5 (t, $^3J_{F-F}$ = 9.9 Hz, CF_3).

The diffraction-quality crystals of complex [(η^5-$C_5Me_4C_6F_{13}$)Rh(CO)$_2$] (2) were grown by very slow sublimation of the compound in a sealed ampoule. Selected crystals were quickly transferred to perfluoropolyalkylether oil (F06206R, ABCR Karlsruhe), mounted on glass fibres in random orientation and cooled to 150(1) K. Diffraction data were collected using Nonius Kappa CCD diffractometer (Enraf-Nonius) at 150(1) K (Cryo-

LL = ethylene (2 mol); 2,3-dimethylbuta-1,3-diene, cyclohexa-1,3-diene, norbornadiene, cycloocta-1,5-diene

Scheme 1.

stream Cooler Oxford Cryosystem) and analyzed using the HKL program package [10]. The structure was solved by direct, and refined by full-matrix least-squares techniques (SIR92 [11], SHELXL97 [12]). Scattering factors for neutral atoms used were included in the program SHELXL97. Final geometric calculations were carried out with SHELXL97 and a recent version of the PLATON program [13]. Table 1 gives pertinent crystallographic data.

3. Results and discussion

Rhodium(III) complexes **1a–1c** were reduced in the presence of ethylene or dienes to rhodium(I) complexes **3–7** with two coordinated double bonds (Scheme 1), no influence of the length of perfluorinated chain on the course of the reaction was observed in cases where compounds differed in chain length. Careful choice of the reducing agent is necessary if reduction is to leave the perfluoroalkyl substituent of the cyclopentadienyl ligand intact. For example, use of sodium amalgam (5%) caused defluorination in the α-position and after prolonged reaction also in the more distant positions of the perfluoroalkyl substituent even under mild reaction conditions (stirring at room temperature) giving unseparable mixtures of products (see also [14], p. 5).

Two different reduction methods were used. Zinc powder in THF was employed to prepare complexes with 2,3-dimethylbuta-1,3-diene (**4c**) and cycloocta-1,5-diene (**7c**). The other reduction method for cyclopentadienyl chloro rhodium(III) complexes, developed by Maitlis et al., is a mild reduction by isopropylalcohol in the presence of a base and in our hands it gave superior yields with other ligands used. Products were yellow to brown oily to semisolid compounds as is common with compounds having polyfluorinated substituents. Structures of the complexes were assigned on the basis of ^{1}H, ^{13}C, and ^{19}F NMR data. The latter data while not very informative for purposes of structural analysis are nevertheless useful to check whether the fluorous ponytails are still intact. This was the case with all the prepared complexes confirming thus the absence of α-carbon defluorination. More information was obtained from ^{1}H and especially ^{13}C NMR data since all the spectra of Cp* analogs are described in the literature except for the carbon spectrum of Cp* analog of **6a**.

As expected, the ethylene ligand was fluxional at room temperature in complexes **3b,c** showing a symmetric pattern of two broad multiplets in ^{1}H spectra. The chemical shifts of the multiplets were independent on the ponytail length and somewhat surprisingly also on the NMR solvent used. Signals of protons on double bonds in other complexes both with conjugated and non-conjugated dienes were generally much sharper suggesting

Table 2
Comparison of ^{13}C NMR chemical shifts of double bond carbons in the synthesized complexes with their Cp* analogs.

Compound	δ (C=) [ppm]	Cp* analog: δ (C=) [ppm]
3b	47.10[a]	43.8[b] Ref [16]; 42.9[c] Ref. [17]
3c	47.09[a]	43.8[b] Ref. [16]; 42.9[c] Ref. [17]
4a	42.68, 90.86[a]	40.8, 87.6[a] Ref. [18]
4c	41.75, 90.02[b]	40.8, 87.6[a] Ref. [18]
5b	61.77, 78.52[a]	58.5, 76.1[a] Ref. [18]
7c	72.71[a]	70.43[a] Ref. [19]

Solvent: [a]C_6D_6, [b]$CDCl_3$, [c]toluene-d_8, −70 °C.

the rotation around Rh-cyclopentadienyl bond as the sole dynamic process. Chemical shifts of those protons could not be correlated with differences between Cp* and Cp^{+Rfn} ligands. The comparison of chemical shifts of ethylene protons of bis(ethylene)rhodium(I) complexes with variably substituted cyclopentadienyl ligands from the literature [5a,15] also shows no apparent trend. Probably, in these flexible ethylene complexes where double bond positions are not mutually fixed, the chemical shift is influenced mainly by steric properties of the substituted cyclopentadienyl ligand.

More information about the electronic influence of the perfluorinated chain on chemical shift was provided by the chemical shifts of double bond carbons. In all cases where literature data were available the chemical shift of double bond carbons of the perfluoroalkylated cyclopentadienyl complex was higher than the corresponding chemical shift in its Cp* analog (Table 2) documenting the long-range influence of the electron-attracting perfluorinated chain.

Reaction conditions leading with ethylene and some dienes to rhodium(I) complexes gave in the case of cycloocta-1,3-diene a rhodium(III) complex **8a** with the ligand coordinated as an η^3-allyl. The structure was solved by NMR with the aid of gCOSY and gHSQC experiments. The formation of such complexes was first reported by Maitlis et al. as a side reaction to the Rh(I) diene complex formation, taking place when the first double bond is inserted into Rh–H bond faster than the reaction with the base in the presence of the second double bond gives Rh(I) diene product. Indeed, as is shown in Scheme 2, if k_3 is higher than k_4, complex **V** is formed from **IV** instead of Rh(I) diene product **VI**. The interconversion **IV–V** obviously should be considered reversible. Maitlis [5a] observed that the analogous reaction of Cp* complexes led finally to complexes of type **VI** through this equilibrium since the interconversion **IV–VI** was irreversible under the reaction conditions. Under our reaction conditions, however, the apparently kinetic product **8a** could be isolated in high yield.

$R^f = C_6F_{13}$, 3b;
$R^f = C_8F_{17}$, 3c

$R^f = C_4F_9$, 4a;
$R^f = C_8F_{17}$, 4c

5b

6a

7c

8a

Scheme 2.
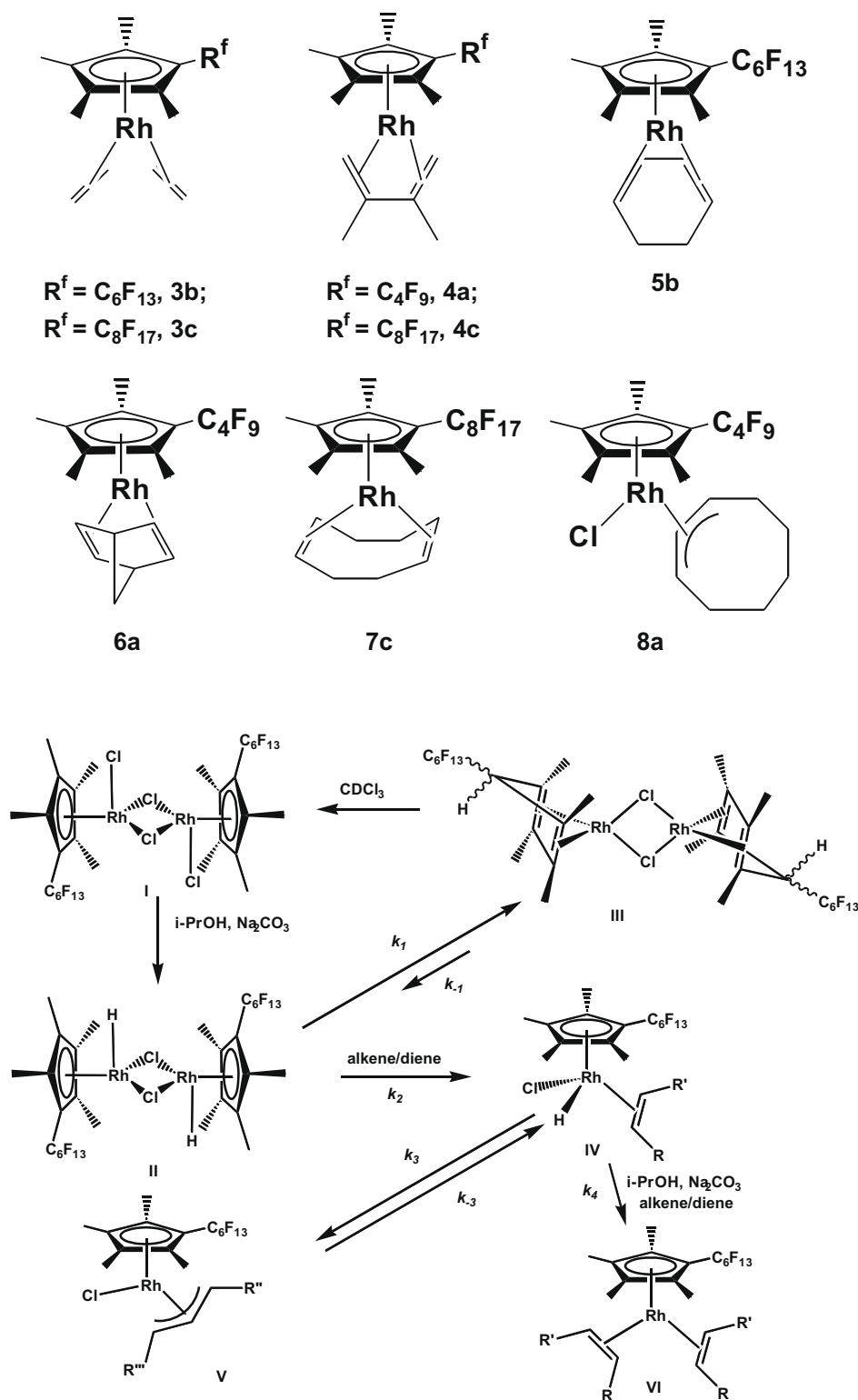
Another byproduct was observed in the early stages of the reduction of **1b** in the presence of ethylene. Cyclopentadienyl chloro rhodium(III) hydride **II**, Cp* analog of which Maitlis [5a] describes as too reactive to be isolated (but which we formulate as a bridging dimer instead of a monomer [5a]), can stabilize itself by intramolecular transfer of the hydride to cyclopentadienyl ligand forming thereby an η⁴-cyclopentadiene dimer **III**. Signals of this compound were observed both in ¹H and ¹³C NMR spectra but the compound was not isolated. The most characteristic signals are those of the ring carbon with pefluoroalkyl substituent and a hydrogen attached to it which were found at δ 60.48 ppm and 3.31 ppm, respectively. Ring methyls resonate as singlets at 1.05 and 1.88 ppm in ¹H and 10.23 and 15.00 ppm in ¹³C NMR spectra, only one of the two expected signals for ring quarternary carbons
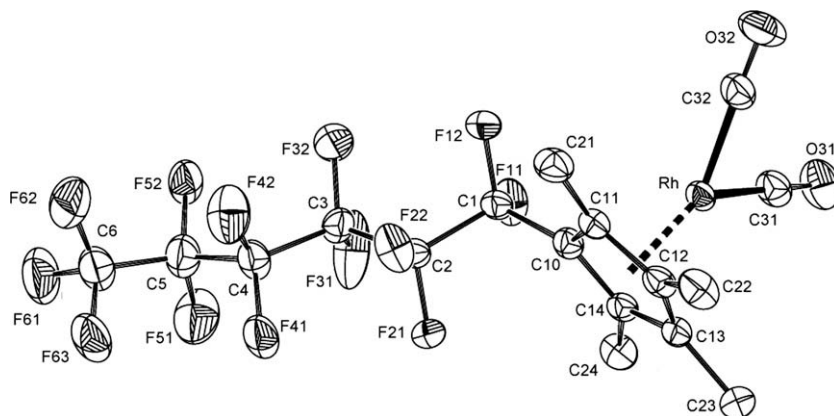
Fig. 1. ORTEP view of **2**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Rh–Cp ring centroid (QC) 1.9118(3), Rh–C31 1.858(5), Rh–C32 1.877(6), C31–O31 1.148(7), C32–O32 1.132(7), C1–C10 1.499(6), C10–C11 1.429(6), C10–C14 1.434(7), C11–C12 1.446(7), C13–C14 1.441(6), C12–C13 1.403(7), C1–C10-QC 177.12(42).

was detected at 92.58 ppm. On increasing the reaction time from 3 to 6 h, the amount of **III** in the product mixture decreased approximately from 30% to 10% with concomitant decrease of the total yield from 85% to 79% and appearance of dark (probably metallic) precipitate in the reaction mixture. While it is possible that certain amount of **III** decomposes after longer reaction time this result suggests that **III** can be transformed under the reaction conditions back to **II** and further on in the mechanism. The complex **III** also reacts with chloroform forming the starting dimer **I** in a reaction similar to the reaction of [Ir(C₅Me₅)(PPh₃)HCl] in chloroform leading to [Ir(C₅Me₅)(PPh₃)Cl₂] [5a]. Complexes with η^4-cyclopentadiene ligands were previously observed not only with rhodium [6e–6g,20] and it seems that their formation may be favoured with cyclopentadienyls substituted by strongly electronaccepting groups. In the absence of further evidence it is not clear whether the fluorous ponytail is in *exo* or *endo* position with respect to the metal since both possibilities were speculated in analogous trifluoromethyl iron complex [6e] while trifluoromethyl platinum analog is claimed to be *exo* [6g] but similar cobalt compound is described as an *endo* isomer [20].

Despite considerable effort, no diffraction-quality crystals of compounds **3**–**8** were obtained. Fortunate spontaneous crystallization on long-time standing of one of the dicarbonyl complexes prepared earlier [7], however, gave us the opportunity to study the molecular structure of that compound (**2**, Fig. 1), which is believed to be structurally very close to rhodium(I) alkene complexes. Therefore this first determined structure of a rhodium(I) complex with Cp⁺ᴿᶠⁿ ligand is presented in this article. Its main features are similar to those in the other two-legged piano stool complexes. As expected the perfluorinated chain is slightly helically twisted [21] and bent away a little from the rhodium atom, the angle on C10 between the bond to the ring centroid and C10–C1 bond being about 177°. The least-squares plane of the ring positions C11 and C14 closer to and the other ring carbons farther from the central atom. Rhodium is closer to carbons C11, C10, and C14 than to C12 and C13, showing thus a ring slippage. The distance between perpendicular projection of rhodium atom on ring least-squares plane and ring centroid is 0.085 Å. Bond distance C12–C13 (1.403 Å) is considerably smaller than other bond distances in the ring, which shows partial electron localization in this bond and further supports ring slippage. Interestingly, such a shift of rhodium position was not observed in the crystal structure of Rh(III) complex **1b** [7], neither was the contraction of the ring bond opposite to the carbon substituted with fluorous ponytail recorded.

4. Conclusions

The reduction of tetramethyl(pefluoroalkyl)cyclopentadienyl rhodium(III) dichloro dimers in the presence of ethylene and dienes to new tetramethyl(pefluoroalkyl)cyclopentadienyl rhodium(I) complexes with two double bonds coordinated requires careful choice of the reductant. The exceptional course of the reaction was observed with cycloocta-1,3-diene but formation of the product, an η^3-coordinated complex, in this case may be explained on the basis of modified Maitlis mechanism [5a] of reduction of Cp* analogue. It is suggested that an η^4-cyclopentadiene complex which was identified by NMR in the reaction mixture during the reduction in the presence of ethylene is formed by a reversible transfer of hydrogen from the metal to the cyclopentadienyl ligand. Molecular structure of the rhodium(I) dicarbonyl complex with tetramethyl(pefluorohexyl)cyclopentadienyl ligand shows moderate ring slippage of the cyclopentadienyl. The fact that such a slippage was not observed previously in the structure of the similar Rh(III) dichloro dimer may be ascribed to generally higher electron density in the cyclopentadienyl ring of the Rh(I) complex.

Acknowledgements

Appendix A. Supplementary material

CCDC 740183 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.037.

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