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Tetramethyl(perfluoroalkyl)cyclopentadienyl rhodium(III) complexes containing phosphorus and nitrogen monodentate donors. Crystal structure of $[(\eta^5\text{-}C_5Me_4C_4F_9)Rh(PPr^i_3)Cl_2]$

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Abstract

Cleavage of a double μ-halo bridge in complexes $[(C_5Me_4C_nF_{2n+1})RhX_2]_2$ ($n = 4$, 6; X = Cl, Br) with two-electron monodentate P-donors like phosphines or phosphites or monodenate N-donors like pyridine-derived heterocyclic amines gave mononuclear Rh(III) complexes of piano-stool type $[(C_5Me_4C_nF_{2n+1})RhX_2L]$ (L = two-electron donor). Crystal structure of $[(\eta^5\text{-}C_5Me_4C_4F_9)Rh(PPr^i_3)Cl_2]$ was determined by X-ray diffraction. The compound had a pseudo-tetrahedral ligand arrangement around the Rh atom. The perfluoroalkyl chain was averted from the phosphine ligand but not completely; after projection to the ring plane the P– (ring centroid) – CF_2 angle was around 166°. In contrast to their Cp^* analogs, the pyridine complexes were stable in solution at room temperature. Free rotation of triarylphosphine ligands around Rh–P bond and 2-substituted pyridine ligands around Rh–N bond was hindered, giving the values of $\Delta G^{\ddagger} = 14.8 \pm 0.1$ kcal mol^{-1} at 27 °C and $\Delta G^{\ddagger} = 14.9 \pm 0.1$ kcal mol^{-1} at 52 °C for tri(*m*-tolyl)phosphine and quinoline complexes, respectively, as followed from the analysis of variable temperature NMR spectra. In the 2-methylpyridine complex, the hindered rotation was accompanied by a reversible decoordination of the ligand at higher temperatures.

Keywords: Fluorous cyclopentadienes; Rhodium complexes; Hindered ligand rotation

1. Introduction

Being devised to modify both electronic (more electron donating) and steric (more bulky) properties of η^5-cyclopentadienyl ligand, pentamethylcyclopentadienyl, Cp^*, is now ubiquitous in organometallic chemistry [1]. Further developments led to even much bulkier or supracyclopentadienyl ligands [2], the changes in size being usually accompanied by the changes of electronic properties compared to unsubstituted Cp. A cyclopentadienyl ligand that would modify steric properties only was reported by Gassman et al. [3a] who prepared tetramethyl(trifluoromethyl)cyclopentadiene as a precursor providing the ligand with steric properties comparable to Cp^* but electronic properties close to Cp. Several complexes with tetramethyl(trifluoromethyl)cyclopentadienyl ligand were reported [3] including measurements documenting the above mentioned properties of the ligand. Recently, as a part of our ongoing effort to synthesize fluorophilic cyclopentadienes [4], we developed an easy and practical synthesis of analogs of the Gassman ligand containing longer perfluorinated chains (“ponytails”) and prepared some of their Rh(III) and Rh(I) complexes [5] with an additional feature – solubility in fluorous media [6] and in supercritical CO_2. We now report the synthesis and properties of monodentate P and N donor complexes with sterically demanding $[(C_5Me_4C_nF_{2n+1})Rh]$ fragment and their comparison with

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known [Cp*Rh] analogs to find out the influence of higher π-acidity of the perfluoroalkylated ligand on the properties of the complexes.

2. Experimental

2.1. General

Syntheses of rhodium complexes were carried out under argon or dry nitrogen atmosphere. Most of the compounds described in this paper, however, are stable to air at least in the solid state.

Starting phosphines and heterocyclic amines were commercial products (Aldrich) used without further purification, except tri(*m*-tolyl)phosphine, triethylphosphite, tris(2-biphenylyl)phosphite, 2-bromopyridine, 2-methylpyridine, 4-methylpyridine and 4-methylaniline (*p*-toluidine) which were from laboratory stock; their purity was checked by NMR. Acetone was dried over $CaCl_2$. Di-μ-chloro-dichloro-bis[η^5-(perfluoroalkyl)tetramethylcyclopentadienyl]-dirhodium(III) complexes were prepared according to a literature method [5]. ^1H, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$, and $^{13}C\{^1H\}$ Infrared spectra were recorded on a Nicolet Impact 400 instrument in the range of 4000–400 cm^{-1}. Samples were measured in thin films by reflexion technique and by transmission technique after evaporation from dichloromethane solutions. NMR spectra were measured on a Varian Mercury 300 spectrometer at 299.98, 80.98, 282.23, and 75.44 MHz, respectively, in $CDCl_3$ solution unless stated otherwise. Chemical shifts (δ) are reported in ppm relative to TMS, referenced to hexamethyldisilane or the solvent peak (^1H, ^{13}C), external H_3PO_4 (^{31}P), and external $CFCl_3$ (^{19}F). Methanol and ethylene glycol were used for temperature calibration in variable temperature experiments. The Gibbs activation energy of rotation was determined by the method of peak separation at coalescence temperature. The values for peak separation at coalescence temperature were extrapolated from slow exchange region using linear regression.

2.2. Syntheses of the complexes

2.2.1. Di-μ-bromo-dibromo-bis[η^5-(perfluorobutyl)-tetramethylcyclopentadienyl]-dirhodium(III), **2**

Twenty equivalents of NaBr (503 mg, 4.89 mmol) were added to a solution of dichloro dimer **1** (251 mg, 0.245 mmol) in acetone (25 ml). The reaction mixture was refluxed with stirring for 2 h, after cooling down the solvent was evaporated in vacuum. The residue was exctracted with dichloromethane (50 ml), filtered, and hexane (7 ml) added. Partial evaporation of solvents gave red powder, the solvent mixture was decanted and the product (230 mg, 78%) dried in vacuum.

Elem. Anal. Calc. for $C_{26}H_{24}Br_4F_{18}Rh_2$: C, 25.94; H, 2.01. Found: C, 24.63; H, 2.01%. IR (cm^{-1}): 489 (m), 532 (m), 556 (w), 573 (m), 638 (m), 701 (w), 733 (s), 749 (m), 799 (s), 817 (s), 854 (m), 1008 (m), 1134 (s), 1173 (vs), 1191 (vs), 1210 (vs), 1229 (vs), 1260 (m), 1347 (s), 1395 (s), 1477 (s), 2911 (w), 2962 (w).

^1H NMR (299.98 MHz, $CDCl_3$): δ 1.86 (s, CH_3); 2.05 (s, CH_3).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 9.94 (s, CH_3); 11.37 (bs, CH_3); 73.41 (m, F_2C–*C*–Rh); 98.66 (m, C–Rh); 102.49 (m, C–Rh); 102–121 (m, C_4F_9).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.24 (m, CF_2); −122.41 (m, CF_2); −105.92 (m, CF_2); −81.29 (m, CF_3).

2.2.2. Dichloro-(perfluorobutyl)tetramethylcyclopentadienyltrimethylphosphine-rhodium(III) (**3**)

A solution of trimethylphosphine in THF (396 μl of 1.0 M soln., 0.396 mmol) was added to a solution of **1** (203 mg, 0.198 mmol) in THF (50 ml). The reaction mixture was magnetically stirred for 1.5 h, then the solvent was evaporated leaving red viscous material as a product (200 mg, 86%). Complex **17** was prepared in the same way.

Elem. Anal. Calc. for $C_{16}H_{21}Cl_2F_9PRh$: C, 32.62; H, 3.59. Found: C, 32.08; H, 4.26%. IR (cm^{-1}): 678 (w), 733 (s), 799 (vs), 822 (vs), 859 (s), 955 (vs), 1022 (s), 1093 (s), 1134 (vs), 1199 (vs), 1216 (vs), 1233 (vs), 1259 (vs), 1284 (m), 1348 (m), 1408 (m), 2912 (m), 2960 (m).

^1H NMR (299.98 MHz, $CDCl_3$): δ 1.72 (d, $^2J_{PH} = 11.7$ Hz, CH_3); 1.78 (d, $^4J_{PH} = 3.1$ Hz, CH_3); 1.91 (d, $^4J_{PH} = 4.0$ Hz, CH_3).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 9.02 (d, $^3J_{PC} = 1.7$ Hz, CH_3); 10.26 (bs, CH_3); 15.78 (d, $^1J_{PC} = 35.0$ Hz); 77.87 (m, F_2C–*C*–Rh); 103.47 (bs, C–Rh); 104.22 (m, C–Rh); 108–120 (m, C_4F_9).

^{31}P NMR (121.44 MHz, $CDCl_3$): δ 14.11 (d, $^1J_{PRh} = 129.8$ Hz).

2.2.3. Dichloro-(perfluorobutyl)tetramethylcyclopentadienyl-triethylphosphine-rhodium(III) (**4**)

Triethylphosphine (58 μl, 46 mg, 0.39 mmol) was added to a solution of **1** (200 mg, 0.195 mmol) in chloroform (15–20 ml). The reaction mixture was magnetically stirred for 2–4 h, then the solvent was evaporated leaving red viscous material as a product (200 mg, 81%). Tributylphosphine, triisopropylphosphine, tricyclohexylphosphine, triphenylphosphine, tri(*m*-tolyl)phosphine, triethylphosphite, tris(2-biphenylyl)phosphite, diphenyl-*p*-tolylphosphine, and tri(*p*-tolyl)phosphine (from both Cl and Br dimer) complexes **5**–**14** were prepared in an analogous way.

^1H NMR (299.98 MHz, $CDCl_3$): δ 1.18 (dt, $^3J_{HH} = 7.5$ Hz, $^3J_{PH} = 15.8$ Hz, CH_3); 1.77 (d, $^4J_{PH} = 2.6$ Hz, CH_3); 1.88 (d, $^4J_{PH} = 3.1$ Hz, CH_3); 2.18 (dq, $^3J_{HH} = 7.5$ Hz, $^2J_{PH} = 11.0$ Hz, CH_2).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 7.98 (d, $^2J_{PC} = 5.1$ Hz, CH_3); 9.12 (s, CH_3); 10.33 (bs, CH_3); 17.83 (d, $^1J_{PC} = 28.7$ Hz, CH_2); 84.03 (m, F_2C–*C*–Rh); 103.65 (m, C–Rh); 104.77 (m, C–Rh); 109–121 (m, C_4F_9).

^{31}P NMR (121.44 MHz, $CDCl_3$): δ 34.37 (d, $^1J_{PRh} = 130.7$ Hz).

*2.2.4. Dichloro-(perfluorobutyl)tetramethylcyclopentadienyl-tri(n-butyl)phosphine-rhodium(III) (**5**)*

Yield 94%.

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 0.93 (t, $^3J_{HH}$ = 7.0 Hz, CH_3); 1.38 (m, CH_2); 1.48–1.60 (m, CH_2); 1.75 (d, $^4J_{PH}$ = 3.1 Hz, CH_3); 1.86 (d, $^4J_{PH}$ = 3.1 Hz, CH_3); 2.07–2.16 (m, CH_2).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 9.09 (d, $^3J_{PC}$ = 1.4 Hz, CH_3); 10.37 (bs, CH_3); 13.63 (s, CH_3); 24.34 (d, $^2J_{PC}$ = 13.2 Hz, CH_2); 25.24 (d, $^1J_{PC}$ = 27.6 Hz, CH_2); 25.75 (d, $^3J_{PC}$ = 4.3 Hz, CH_2); 83.84 (m, F_2C–*C*–Rh); 103.73 (m, C–Rh); 104.60 (m, C–Rh); 107–126 (m, C_4F_9).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.26 (m, CF_2); −122.02 (m, CF_2); −106.35 (m, CF_2); −81.36 (m, CF_3).

^{31}P NMR (121.44 MHz, $CDCl_3$): δ 28.37 (d, $^1J_{PRh}$ = 130.6 Hz).

*2.2.5. Dichloro-(perfluorobutyl)tetramethylcyclopentadienyl-triisopropylphosphine-rhodium(III) (**6**)*

Yield 85%.

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.41 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 14.1 Hz, CH_3); 1.70 (d, $^4J_{PH}$ = 2.6 Hz, CH_3); 1.83 (bs, CH_3); 2.78–2.94 (m, CH).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 9.28 (d, $^3J_{PC}$ = 1.4 Hz, CH_3); 11.22 (bs, CH_3); 20.42 (d, $^2J_{PC}$ = 2.4 Hz); 27.59 (d, $^1J_{PC}$ = 27.6 Hz, CH); 82.84 (m, F_2C–*C*–Rh); 103.70 (m, C–Rh); 105.60 (m, C–Rh); 107.5–118.0 (m, C_4F_9).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.26 (m, CF_2); −121.57 (m, CF_2); −106.96 (m, CF_2); −81.35 (m, CF_3).

^{31}P NMR (121.44 MHz, $CDCl_3$): δ 50.26 (d, $^1J_{PRh}$ = 129.6 Hz).

2.2.6. Dichloro-(perfluorobutyl)tetramethylcyclopentadienyl-tricyclohexylphosphine-rhodium(III) (7)

Yield 98%.

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.68 (d, $^4J_{PH}$ = 2.9 Hz, CH_3); 1.82 (bs, CH_3); 1.23–2.58 (m, C_6H_{11}); (C_6D_6): δ 1.39 (d, $^4J_{PH}$ = 2.6 Hz, CH_3); 1.67 (bs, CH_3); 1.00–2.65 (m, C_6H_{11}).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 9.26 (d, $^3J_{PC}$ = 1.4 Hz, CH_3); 11.18 (bs, CH_3); 26.08 (s, CH_2); 27.42 (d, $^2J_{PC}$ = 10.1 Hz, CH_2); 30.07 (s, CH_2); 38.05 (d, $^1J_{PC}$ = 17.9 Hz, CH); ca. 77.4 (m, F_2C–*C*–Rh, obscured by $CDCl_3$), 103.65 (m, C–Rh); 104.4 (m, C–Rh); 110–120 (m, C_4F_9); (C_6D_6): δ 9.69 (s, CH_3); 11.78 (bs, CH_3); 26.98 (s, CH_2); 28.26 (d, $^2J_{PC}$ = 10.1 Hz, CH_2); 30.98 (s, CH_2); 38.80 (d, $^1J_{PC}$ = 17.9 Hz, CH); 77.52 (m, F_2C–*C*–Rh), 104.21 (m, C–Rh); 105.35 (m, C–Rh); 110–120 (m, C_4F_9).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.23 (m, CF_2); −121.67 (m, CF_2); −106.37 (m, CF_2); −81.38 (t, $^3J_{FF}$ = 9.9 Hz, CF_3).

^{31}P NMR (121.44 MHz, $CDCl_3$): δ 41.97 (d, $^1J_{PRh}$ = 128.9 Hz); (C_6D_6): δ 41.14 (d, $^1J_{PRh}$ = 129.9 Hz).

*2.2.7. Dichloro-(perfluorobutyl)tetramethylcyclopentadienyl-triphenylphosphine-rhodium(III) (**8**)*

Yield 96%. Elem. Anal. Calc. for $C_{31}H_{27}Cl_2F_9PRh$: C, 48.02; H, 3.51. Found: C, 47.17; H, 3.29%. IR (cm^{-1}): 455 (m), 500 (vs), 513 (vs), 526 (vs), 699 (vs), 732 (vs), 823 (s), 860 (s), 1000 (m), 1095 (s), 1134 (vs), 1194 (vs), 1218 (vs), 1235 (vs), 1348 (s), 1404 (m), 1435 (vs), 1483 (s), 2915 (w), 2982 (w), 3055 (m).

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.46 (d, $^4J_{PH}$ = 3.5 Hz, CH_3); 1.48 (bs, CH_3); 7.32 (m, 9CH_{Ar}); 7.79–7.85 (m, 6CH_{Ar}).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 8.63 (d, $^3J_{PC}$ = 1.7 Hz, CH_3); 9.66 (bs, CH_3); 78.8 (m, F_2C–*C*–Rh), 102.24 (m, C–Rh); 107.00 (m, C–Rh); 115–119 (m, C_4F_9), 127.86 (bs, C-arom.); 130.65 (bs, C-arom.); 134.87 (bs, C-arom.).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.24 (m, CF_2); −122.04 (m, CF_2); −106.63 (bs, CF_2); −81.35 (m, CF_3).

^{31}P NMR (121.44 MHz, $CDCl_3$): δ 31.3 (d, $^1J_{PRh}$ = 137.3 Hz).

*2.2.8. Dichloro-(perfluorobutyl)tetramethylcyclopentadienyl-tri(m-tolyl)phosphine-rhodium(III) (**9**)*

Yield 95%. Elem. Anal. Calc. for $C_{34}H_{33}Cl_2F_9PRh$: C, 49.96; H, 4.07. Found: C, 48.48; H, 3.80%. IR (cm^{-1}): 452 (m), 464 (m), 479 (m), 556 (s), 695 (s), 732 (s), 781 (m), 822 (s), 860 (m), 998 (m), 1108 (s), 1134 (vs), 1197 (vs), 1217 (vs), 1234 (vs), 1346 (s), 1403 (s), 1449 (m), 1478 (m), 1592 (m), 2856 (w), 2920 (m), 2974 (w), 3013–3053 (w, mp).

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.46 (d, $^4J_{PH}$ = 3.5 Hz, CH_3); 1.48 (d, $^4J_{PH}$ = 3.7 Hz, CH_3); 2.32 (bs, CH_3(*m*-tol)); 7.47–7.77 (m, CH_{Ar}).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 8.57 (s, CH_3); 9.58 (s, CH_3); 21.31 (s, CH_3(*m*-tol)); 78.8–79.6 (m, F_2C–*C*–Rh); 102.20 (m, C–Rh); 106.96 (m, C–Rh); 110–120 (m, C_4F_9); 127.52 (bs, C-arom.); 131.76 (bs, C-arom.); 135.79 (bs, C-arom.); 137.47 (bs, C-arom.).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.23 (m, CF_2); −121.97 (m, CF_2); −106.72 (m, CF_2); −81.36 (m, CF_3).

^{31}P NMR (121.44 MHz, $CDCl_3$): δ 31.7 (d, $^1J_{PRh}$ = 136.4 Hz).

*2.2.9. Dichloro-(perfluorobutyl)tetramethylcyclopentadienyl-triethylphosphite-rhodium(III) (**10**)*

Yield 82%.

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.31 (t, $^3J_{HH}$ = 7.0 Hz, CH_3); 1.72 (d, $^4J_{PH}$ = 4.4 Hz, CH_3); 1.89 (bs, CH_3); 4.30 (dq, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 7.0 Hz, CH_2).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 8.76 (d, $^3J_{PC}$ = 2.6 Hz, CH_3); 10.04 (d, $^3J_{PC}$ = 2.6 Hz, CH_3); 15.97 (d, $^3J_{PC}$ = 6.0 Hz, CH_3); 64.46 (d, $^2J_{PC}$ = 7.5 Hz, CH_2); 79.45 (m, F_2C–*C*–Rh), 103.98 (m, C–Rh); 107.22 (m, C–Rh); 108–120 (m, C_4F_9).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.29 (m, CF_2); −122.4 (m, CF_2); −106.68 (bs, CF_2); −81.36 (m, CF_3).

^{31}P NMR (121.44 MHz, $CDCl_3$): δ 104.13 (d, $^1J_{PRh}$ = 203.1 Hz).

*2.2.10. Dichloro-(perfluorobutyl)tetramethylcyclopentadienyl-tris(2-biphenylyl)phosphite-rhodium(III) (**11**)*

Yield 95%. Elem. Anal. Calc. for $C_{49}H_{39}Cl_2F_9O_3PRh$: C, 55.96; H, 3.74. Found: C, 54.23; H, 3.51%. IR (cm^{-1}): 697 (s), 730 (s), 753 (s), 821 (m), 861 (m), 927 (vs, br), 1053 (s), 1116 (s), 1135 (vs), 1175 (vs), 1202 (vs), 1216 (vs), 1233 (vs), 1347 (m), 1433 (vs), 1480 (vs), 1503 (s), 1581 (m), 1603 (m), 2921 (w), 2978 (w), 3027 (m), 3058 (m).

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.17 (d, $^4J_{PH}$ = 5.9 Hz, CH_3); 1.48 (d, $^4J_{PH}$ = 5.0 Hz, CH_3); 6.9–7.6 (m, CH_{Ar}).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 8.4 (d, $^3J_{PC}$ = 2.3 Hz, CH_3); δ 9.93 (d, $^3J_{PC}$ = 1.4 Hz, CH_3); 80.7–81.8 (m, F_2C–*C*–Rh); 103.28 (m, C–Rh); 108.86 (m, C–Rh); 110–120 (m, C_4F_9); 120.83 (d, J_{PC} = 4.0 Hz, CH_{Ar}); 124.49 (s, CH_{Ar}); 126.99 (s, CH_{Ar}); 127.96 (s, CH_{Ar}); 128.26 (s, CH_{Ar}); 129.60 (s, CH_{Ar}); 131.28 (s, CH_{Ar}); 132.27 (d, J_{PC} = 6.0 Hz, C_{Ar}); 137.35 (s, C_{Ar}); 148.35 (d, J_{PC} = 13.0 Hz, C_{Ar}).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.35 (m, CF_2); −122.43 (m, CF_2); −107.02 (m, CF_2); −81.37 (m, CF_3).

^{31}P NMR (121.44 MHz, $CDCl_3$): δ 95.6 (d, $^1J_{PRh}$ = 236.5 Hz).

*2.2.11. Dichloro-(perfluorobutyl)tetramethylcyclopentadienyl-diphenyl(p-tolyl)phosphine-rhodium(III) (**12**)*

Yield 96%.

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.44 (d, $^4J_{PH}$ = 3.5 Hz, CH_3); 1.49 (bs, CH_3); 2.35 (bs, CH_3 (*p*-tol)); 7.10–7.23 (m, $2CH_{Ar}$ (*p*-tol)); 7.28–7.58 (m, $5CH_{Ar}$ (Ph)); 7.64–7.74 (m, $2CH_{Ar}$ (*p*-tol)); 7.76–7.88 (m, $5CH_{Ar}$ (Ph)).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 8.61 (d, $^3J_{PC}$ = 1.4 Hz, CH_3); 9.69 (bs, CH_3); 21.31 (s, CH_3 (*p*-tol)); 80.0 (m, F_2C–*C*–Rh); 101.99 (m, C–Rh); 106.97 (m, C–Rh); 113–121 (m, C_4F_9); 127.77 (m, C-arom. (Ph)); 128.65 (m, C-arom. (*p*-tol)); 130.52 (m, C-arom. (Ph)); 134.86 (m, C-arom. (Ph)); 141.13 (m, C-arom. (*p*-tol)).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.25 (m, CF_2); −122.06 (m, CF_2); −106.96 (m, CF_2); −81.36 (m, CF_3).

^{31}P NMR (121.44 MHz, $CDCl_3$): δ 30.97 (d, $^1J_{PRh}$ = 136.8 Hz).

*2.2.12. Dichloro-(perfluorobutyl)tetramethylcyclopentadienyl-tri(p-tolyl)phosphine-rhodium(III) (**13**)*

Yield 96%.

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.41 (d, $^4J_{PH}$ = 3.1 Hz, CH_3); 1.51 (bs, CH_3); 2.34 (bs, CH_3 (*p*-tol)); 7.15 (m, CH_{Ar}); 7.69 (m, CH_{Ar}).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 8.55 (d, $^3J_{PC}$ = 1.2 Hz, CH_3); 9.70 (bs, CH_3); 21.25 (bs, CH_3 (*p*-tol)); 80.11 (m, F_2C–*C*–Rh); 101.54 (m, C–Rh); 106.88 (m, C–Rh); 108.8–120.8 (m, C_4F_9); 128.51 (m, C-arom.); 134.72 (m, C-arom.); 140.77 (m, C-arom.).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.25 (m, CF_2); −122.08 (m, CF_2); −106.80 (m, CF_2); −81.38 (m, CF_3).

^{31}P NMR (121.44 MHz, $CDCl_3$): δ 30.25 (d, $^1J_{PRh}$ = 135.9 Hz).

*2.2.13. Dibromo-(perfluorobutyl)tetramethylcyclopentadienyl-tri(p-tolyl)phosphine-rhodium(III) (**14**)*

Yield 93%.

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.55 (d, $^4J_{PH}$ = 3.5 Hz, CH_3); 1.68 (bs, CH_3); 2.38 (bs, CH_3 (*p*-tol)); 6.70–7.45 (m, CH_{Ar}); 7.67 (m, CH_{Ar}).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 9.30 (s, CH_3); 10.56 (bs, CH_3); 21.33 (bs, CH_3 (*p*-tol)); 82.01 (m, F_2C–*C*–Rh); 102.00 (m, C–Rh); 106.57 (m, C–Rh); 108.3–122.9 (m, C_4F_9); 126.43–129.21 (m, C-arom.); 129.71 (d, $^1J_{PC}$ = 13.3 Hz, C-arom.); 132.58 (d, $^1J_{PC}$ = 11.3 Hz, C-arom.); 133.6–136.2 (m, C-arom.); 139.5–142.0 (m, C-arom.); 144.25 (s, C-arom.).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.24 (m, CF_2); −121.93 (m, CF_2); −106.33 (m, CF_2); −81.36 (m, CF_3).

^{31}P NMR (121.44 MHz, $CDCl_3$): δ 27.34 (d, $^1J_{PRh}$ = 138.5 Hz).

*2.2.14. Dichloro-(perfluorobutyl)tetramethylcyclopentadienyl-pyridine-rhodium(III) (**15**)*

Pyridine (33.5 mg, 0.42 mmol) was added to a solution of **1** (200 mg, 0.195 mmol) in chloroform (5 ml) and the mixture was stirred for 2 h at room temperature. Then the solvent was evaporated and the residue was dried in vacuum. The product was obtained as a red-orange solid (178 mg, 77%). Complex **18** was prepared in the same way.

Elem. Anal. Calc. for $C_{18}H_{17}Cl_2F_9NRh$: C, 36.51; H, 2.89; N, 2.37. Found: C, 36.46; H, 2.75; N, 2.37%. IR (cm^{-1}): 427 (w), 449 (w), 482 (w), 535 (w), 574 (w), 641 (m), 695 (s), 735 (vs), 761 (s), 822 (vs), 858 (s), 1000 (m), 1015 (m), 1070 (s), 1134 (vs), 1196 (vs), 1217 (vs), 1234 (vs), 1348 (s), 1405 (s), 1448 (vs), 1484 (s), 1602 (s), 2923 (w), 2979 (w), 2999–3104 (w, mp).

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.67 (s, CH_3); 1.84 (s, CH_3); 7.41 (m, CH_{meta}); 7.84 (m, CH_{para}); 9.03 (d, $^3J_{HH}$ = 5.3 Hz, CH_{ortho}).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 9.05 (s, CH_3); 9.61 (s, CH_3); 75.06 (dt, $^1J_{CRh}$ = 10.6 Hz, $^3J_{CF}$ not resolved, F_2C–*C*–Rh); 97.03 (d, $^1J_{CRh}$ = 7.2 Hz, C–Rh); 102.26 (d, $^1J_{CRh}$ = 7.5 Hz, C–Rh); 106–122 (m, C_4F_9); 125.29 (s, CH_{meta}); 138.38 (s, CH_{para}); 154.39 (s, CH_{ortho}).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.3 (m, CF_2); −122.5 (m, CF_2); −106.2 (m, CF_2); −81.4 (m, CF_3).

*2.2.15. Dichloro-(perfluorobutyl)tetramethylcyclopentadienyl-quinoline-rhodium(III) (**16**)*

Quinoline (49.4 mg, 0.38 mmol) was added to a solution of **1** (200 mg, 0.195 mmol) in chloroform (5 ml) and the mixture was stirred for 2 h at room temperature. The solvent was then evaporated and the residue was dried in vacuum. The product was obtained as a red-brown solid (250 mg, 100%).

At −20 °C signals of two equally populated conformers are visible in NMR spectra. Signals in ^{1}H spectra were assigned on the basis of gCOSY experiment at −20 °C.

^{1}H NMR (299.98 MHz, $CDCl_2CDCl_2$, −20 °C): δ 1.04 (s, CH_3); 1.80 (s, CH_3); 1.89 (s, CH_3); 1.99 (s, CH_3); 7.40 (dd, $^3J_{HH} = 8.2$ Hz, $^3J_{HH} = 5.6$ Hz, CH^3_{Ar}); 7.44 (dd, $^3J_{HH} = 8.5$ Hz, $^3J_{HH} = 4.7$ Hz, CH^3_{Ar}); 7.59 (m, CH^6_{Ar}); 7.61 (m, CH^6_{Ar}); 7.76 (m, CH^7_{Ar}); 7.85 (m, $CH^{5,7}_{Ar}$); 8.13 (d, $^3J_{HH} = 8.5$ Hz, CH^8_{Ar}); 8.23 (d, $^3J_{HH} = 8.5$ Hz, CH^4_{Ar}); 8.25 (d, $^3J_{HH} = 8.2$ Hz, CH^4_{Ar}); 8.90 (d, $^3J_{HH} = 4.7$ Hz, CH^2_{Ar}); 8.90 (d, $^3J_{HH} = 8.5$ Hz, CH^8_{Ar}); 9.77 (d, $^3J_{HH} = 5.6$ Hz, CH^2_{Ar}); (80 °C): δ 1.50 (s, CH_3); 1.81 (s, CH_3); 7.36 (dd, $^3J_{HH} = 8.2$ Hz, $^3J_{HH} = 4.7$ Hz, CH^3_{Ar}); 7.52 (m, CH^6_{Ar}); 7.70 (m, CH^7_{Ar}); 7.79 (d, $^3J_{HH} = 8.2$ Hz, CH^5_{Ar}); 8.16 (d, $^3J_{HH} = 8.2$ Hz, CH^4_{Ar}); 8.50 (bs, CH^8_{Ar}); 9.30 (bs, CH^2_{Ar}).

^{13}C NMR (75.44 MHz, $CDCl_2CDCl_2$, −20 °C): δ 9.14 (s, CH_3); 9.36 (s, CH_3); 9.62 (bs, CH_3); 10.63 (bs, CH_3); 72.84 (m, partially overlapping with solvent peak, F_2C–*C*–Rh); 95.18 (m, C–Rh); 98.87 (m, C–Rh); 102.05 (m, C–Rh); 106.02 (m, C–Rh); 106–119 (m, C_4F_9); 121.22 (s, CH_{Ar}); 126.70 (s, CH_{Ar}); 127.40 (s, CH_{Ar}); 127.96 (s, CH_{Ar}); 128.00 (s, C_{Ar}); 128.66 (s, CH_{Ar}); 129.02 (s, CH_{Ar}); 129.43 (s, CH_{Ar}); 129.72 (s, CH_{Ar}); 130.00 (s, C_{Ar}); 130.38 (s, CH_{Ar}); 136.61 (s, CH^8_{Ar}); 139.95 (s, CH^8_{Ar}); 146.63 (s, C^9_{Ar}); 147.32 (s, C^9_{Ar}); 150.23 (s, CH^2_{Ar}); 158.71 (s, CH^2_{Ar}); (80 °C): δ 9.13 (s, CH_3); 10.06 (bs, CH_3); F_2C–*C*–Rh is overlapping with solvent peak; 97.04 (bs, C–Rh); 103.00 (bs, C–Rh); 106–120 (m, C_4F_9); 121.10 (s, CH_{Ar}); 126.91 (s, CH_{Ar}); 128.17 (s, CH_{Ar}); 129.12 (s, C_{Ar}); 129.74 (s, $2CH_{Ar}$); 137.64 (bs, CH^8_{Ar}); 147.82 (C^9_{Ar}); 154.04 (bs, CH^2_{Ar}).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.33 (m, CF_2); −122.35 (m, CF_2); −106.33 (m, CF_2); −81.35 (t, $^3J_{FF} = 9.9$ Hz, CF_3).

*2.2.16. Dichloro-(perfluorohexyl)tetramethylcyclopentadienyl-trimethylphosphine-rhodium(III) (**17**)*

Yield 77%.

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.72 (d, $^2J_{PH} = 11.7$ Hz, CH_3); 1.78 (d, $^4J_{PH} = 3.1$ Hz, CH_3); 1.91 (d, $^4J_{PH} = 2.0$ Hz, CH_3).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 9.09 (bs, CH_3); 10.31 (bs, CH_3); 15.91 (d, $^1J_{PC} = 34.9$ Hz); 78.02 (m, F_2C–*C*–Rh); 103.26 (bs, C–Rh); 104.45 (m, C–Rh); 106–121 (m, C_4F_9).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.53 (m, CF_2); −123.14 (m, CF_2); −122.17 (m, CF_2); −121.15 (m, CF_2); −105.38 (m, CF_2); −81.21 (m, CF_3).

^{31}P NMR (121.44 MHz, $CDCl_3$): δ 14.11 (d, $^1J_{PRh} = 130.5$ Hz).

*2.2.17. Dichloro-(perfluorohexyl)tetramethylcyclopentadienyl-pyridine-rhodium(III) (**18**)*

Yield 90%.

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.67 (s, CH_3); 1.85 (s, CH_3); 7.41 (m, CH_{meta}); 7.84 (m, CH_{para}); 9.04 (d, $^3J_{HH} = 5.3$ Hz, CH_{ortho}).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 9.08 (s, CH_3); 9.64 (s, CH_3); 75.32 (dt, $^1J_{CRh} = 10.7$ Hz, $^3J_{CF} = 23.6$ Hz, F_2C–*C*–Rh); 97.09 (d, $^1J_{CRh} = 7.2$ Hz, C–Rh); 102.26 (d, $^1J_{CRh} = 7.5$ Hz, C–Rh); 125.31 (s, CH_{meta}); 138.39 (s, CH_{para}); 154.47 (s, CH_{ortho}).

^{19}F NMR (282.24 MHz, $CDCl_3$) δ: −126.6 (m, CF_2); −123.2 (m, CF_2); −122.4 (m, CF_2); −121.4 (m, CF_2); −106.0 (m, CF_2); −81.2 (m, CF_3).

*2.2.18. Dichloro-(perfluorohexyl)tetramethylcyclopentadienyl-(2-methylpyridine)-rhodium(III) (**19**)*

2-Methylpyridine (29.6 μl, 0.30 mmol) was added to a solution of **1** (184 mg, 0.15 mmol) in chloroform (5 ml) and the mixture was stirred for 2 h at room temperature. Then the solvent was evaporated and the residue was dried in vacuum. The product was obtained as a red-orange solid (212 mg, 100%).

^{1}H NMR (299.98 MHz, $CDCl_3$, −30 °C): δ 1.53 (s, CH_3); 1.82 (s, CH_3); 1.89 (s, CH_3); 1.95 (s, CH_3); 3.00 (s, CH_3Ar); 7.22 (m, CH^5_{Ar}); 7.38 (d, $^3J_{HH} = 7.6$ Hz, CH^3_{Ar}); 7.73 (m, CH^4_{Ar}); 9.44 (d, $^3J_{HH} = 5.6$ Hz, CH^6_{Ar}).

^{19}F NMR (282.24 MHz, $CDCl_3$, −30 °C): δ −126.96 (m, CF_2); −123.55 (m, CF_2); −122.57 (m, CF_2); −121.80 (m, CF_2); −106.72 (m, CF_2); −81.12 (t, $^3J_{FF} = 9.9$ Hz, CF_3).

Dynamic processes did not allow the recording of useful ^{13}C spectrum.

*2.2.19. Dichloro-(perfluorohexyl)tetramethylcyclopentadienyl-(3-methylpyridine)-rhodium(III) (**20**)*

3-Methylpyridine (29.2 μl, 0.30 mmol) was added to a solution of **1** (184 mg, 0.15 mmol) in chloroform (5 ml) and the mixture was stirred for 2 h at room temperature. Then the solvent was evaporated and the residue was dried in vacuum. The product was obtained as a red-orange solid (212 mg, 100%).

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.66 (s, CH_3); 1.84 (s, CH_3); 2.37 (s, CH_3Ar); 7.29 (dd, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 5.6$ Hz, CH^5_{Ar}); 7.63 (d, $^3J_{HH} = 7.6$ Hz, CH^4_{Ar}); 8.83 (d, $^3J_{HH} = 5.6$ Hz, CH^6_{Ar}); 8.86 (s, CH^2_{Ar}).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 9.03 (s, CH_3); 9.59 (s, CH_3); 18.35 (s, CH_3Ar); 75.10 (dt, $^1J_{CRh} = 10.1$ Hz, $^2J_{CF} = 23.6$ Hz, F_2C–*C*–Rh); 96.94 (d, $^1J_{CRh} = 7.2$ Hz, C–Rh); 102.17 (d, $^1J_{CRh} = 7.5$ Hz, C–Rh);

105–121 (m, C_6H_{13}); 124.72 (s, CH^5_{Ar}); 135.32 (s, C_{Ar}); 138.92 (s, CH^4_{Ar}); 151.59 (s, CH^6_{Ar}); 154.41 (s, CH^2_{Ar}).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.60 (m, CF_2); −123.22 (m, CF_2); −122.21 (m, CF_2); −121.55 (m, CF_2); −106.16 (t, $^3J_{FF} = 11.9$ Hz, CF_2); −81.28 (t, $^3J_{FF} = 9.9$ Hz, CF_3).

2.2.20. Dichloro-(perfluorohexyl)tetramethylcyclopentadienyl-(4-methylpyridine)-rhodium(III) (21)

4-Methylpyridine (29.2 μl, 0.30 mmol) was added to a solution of **1** (184 mg, 0.15 mmol) in chloroform (5 ml) and the mixture was stirred for 2 h at room temperature. Then the solvent was evaporated and the residue was dried in vacuum. The product was obtained as an orange solid (212 mg, 100%).

Elem. Anal. Calc. for $C_{21}H_{19}Cl_2F_{13}NRh$: C, 35.72; H, 2.71; N, 1.98. Found: C, 35.87; H, 2.54; N, 1.85%. IR (cm^{-1}): 504 (m), 666 (m), 717 (s), 733 (s), 772 (m), 806 (s), 872 (w), 889 (w), 1073 (s), 1146 (vs), 1201 (vs), 1237 (vs), 1360 (s), 1383 (w), 1404 (s), 1447 (m), 1621 (s), 2927 (w), 2980 (w), 3012-3074 (w, mp).

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.67 (s, CH_3); 1.85 (s, CH_3); 2.43 (s, CH_3Ar); 7.21 (d, $^3J_{HH} = 6.2$ Hz, $CH^{3,5}_{Ar}$); 8.86 (d, $^3J_{HH} = 6.2$ Hz, $CH^{2,6}_{Ar}$).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 9.13 (s, CH_3); 9.70 (s, CH_3); 20.97 (s, CH_3Ar); 75.24 (dt, $^1J_{CRh} = 10.4$ Hz, $^2J_{CF} = 23.3$ Hz, F_2C–*C*–Rh); 96.99 (d, $^1J_{CRh} = 7.5$ Hz, C–Rh); 102.13 (d, $^1J_{C–Rh} = 7.5$ Hz, C–Rh); 105–121 (m, C_6H_{13}); 126.24 (s, $CH^{3,5}_{Ar}$); 150.48 (s, C_{Ar}); 153.84 (s, $CH^{2,6}_{Ar}$).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.54 (m, CF_2); −123.18 (m, CF_2); −122.17 (m, CF_2); −121.55 (m, CF_2); −106.01 (m, CF_2); −81.17 (t, $^3J_{FF} = 9.9$ Hz, CF_3).

2.2.21. Dichloro-(perfluorohexyl)tetramethylcyclopentadienyl-(3-bromopyridine)-rhodium(III) (22)

3-Bromopyridine (28.9 μl, 0.30 mmol) was added to a solution of **1** (184 mg, 0.15 mmol) in chloroform (5 ml) and the mixture was stirred for 2 h at room temperature. Then the solvent was evaporated and the residue was dried in vacuum. The product was obtained as an orange solid (231 mg, 100%).

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.70 (s, CH_3); 1.86 (s, CH_3); 7.33 (m, CH^5_{Ar}); 7.98 (m, CH^4_{Ar}); 9.02 (d, $^3J_{HH} = 4.4$ Hz, CH^6_{Ar}); 9.13 (s, CH^2_{Ar}).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 9.21 (s, CH_3); 9.75 (s, CH_3); 75.83 (dt, $^1J_{CRh} = 10.1$ Hz, $^2J_{CF} = 23.9$ Hz, F_2C–*C*–Rh); 97.24 (d, $^1J_{CRh} = 7.5$ Hz, C–Rh); 102.30 (d, $^1J_{CRh} = 7.5$ Hz, C–Rh); 105–121 (m, C_6H_{13}); 121.07 (s, C_{Ar}); 125.92 (s, CH^5_{Ar}); 141.25 (s, CH^4_{Ar}); 152.90 (s, CH^6_{Ar}); 155.13 (s, CH^2_{Ar}).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.51 (m, CF_2); −123.13 (m, CF_2); −122.12 (m, CF_2); −121.45 (m, CF_2); −105.98 (t, $^3J_{FF} = 11.9$ Hz, CF_2); −81.18 (t, $^3J_{FF} = 9.9$ Hz, CF_3).

2.2.22. Dichloro-(perfluorohexyl)tetramethylcyclopentadienyl-(p-toluidine)-rhodium(III) (23)

A solution of *p*-toluidine (32 mg, 0.30 mmol) in chloroform (1 ml) was added to a solution of **1** (184 mg, 0.15 mmol) in chloroform (5 ml) and the mixture was stirred for 2 h at room temperature. Then the solvent was evaporated and the residue was dried in vacuum. The product was obtained as a brick red solid (216 mg, 100%).

Elem. Anal. Calc. for $C_{22}H_{21}Cl_2F_{13}NRh$: C, 36.69; H, 2.94; N, 1.94. Found: C, 37.13; H, 2.89; N, 1.80%. IR (cm^{-1}): 444 (s), 484 (s), 534 (s), 545 (s), 662 (s), 717 (s), 732 (vs), 771 (s), 817 (vs), 1009 (vs), 1116 (vs), 1142 (vs), 1192 (vs), 1234 (vs), 1362 (s), 1401 (s), 1455 (s), 1513 (vs), 1580 (s), 2871 (w), 2930 (m), 3034-3289 (m, mp).

^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.41 (s, CH_3); 1.65 (s, CH_3); 2.32 (s, CH_3Ar); 5.18 (bs, NH_2); 7.13 (m, CH_{Ar}); 7.28 (m, CH_{Ar}).

^{13}C NMR (75.44 MHz, $CDCl_3$): δ 9.05 (s, CH_3); 9.10 (s, CH_3); 20.84 (s, CH_3Ar); 74.03 (dt, $^1J_{CRh} = 10.9$ Hz, $^2J_{CF} = 23.9$ Hz, F_2C–*C*–Rh); 96.08 (d, $^1J_{CRh} = 7.7$ Hz, C–Rh); 103.35 (d, $^1J_{CRh} = 7.8$ Hz, C–Rh); 106–119 (m, C_6H_{13}); 121.10 (s, CH_{Ar}); 129.86 (s, CH_{Ar}); 135.76 (s, C_{Ar}); 138.22 (s, C_{Ar}).

^{19}F NMR (282.24 MHz, $CDCl_3$): δ −126.50 (m, CF_2); −123.12 (m, CF_2); −122.11 (m, CF_2); −121.44 (m, CF_2); −105.37 (m, CF_2Cp); −81.16 (t, $^3J_{FF} = 9.9$ Hz, CF_3).

X-ray data for **6**: $C_{22}H_{33}F_9P_1Cl_2Rh_1$, $M = 673.27$ g/mol, monoclinic system, space group $P2_1/c$, $a = 22.9050(2)$, $b = 8.5100(1)$, $c = 13.6090(3)$ Å, $\beta = 92.169(8)$, $Z = 4$, $V = 2650.8(1)$ Å^3, $D_c = 1.69$ g cm^{-3}, μ(Mo Kα) = 0.98 mm^{-1}, crystal dimensions of $0.4 \times 0.3 \times 0.1$ mm. Data were collected at 150 K on a Nonius KappaCCD diffractometer with graphite monochromated Mo Kα radiation. The structure was solved by direct methods [7]. The whole structure was refined by full matrix least-squares on *F* values [8]. All heavy atoms were refined anisotropically. Hydrogen atoms were located from expected geometry and were refined isotropically. This model converged to final $R = 0.0222$ and $R_w = 0.0249$ using 5116 independent reflections ($\theta_{max} = 27.5°$).

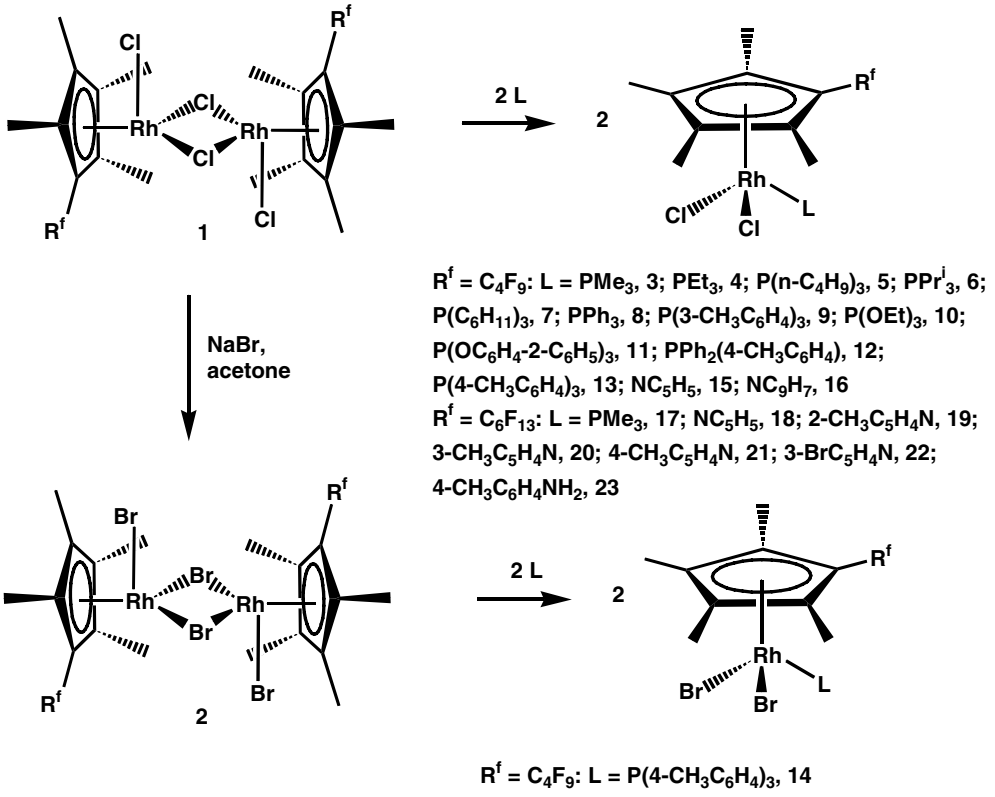
3. Results and discussion

Cleavage of double μ-halo bridge of $[Cp^*RhX_2]_2$ complex is known to take place with many monodentate two-electron donors, e.g. phosphines [9] or amines including heterocyclic ones [9a,10]. Reaction of complexes **1** and **2** with selected phosphines, phosphites and N-donors (Scheme 1) gave in direct analogy mononuclear piano-stool-type complexes **3**–**23** which were characterized by their ^{1}H, ^{19}F, ^{31}P{^{1}H} and ^{13}C{^{1}H}NMR spectra. Fluorine-19 spectra were the simplest showing in most cases the presence of only one fluorous ponytail of C_4 or C_6 length, even if different rotamers (see below) were present. The signals of CF_2 groups appeared at a given field as broad singlets no coupling being resolvable. ^{1}H spectra showed

two inequivalent groups of methyl protons, in addition to signals coming from the P- or N-donor ligands. The four-bond coupling constants between phosphorus and ring methyl protons in the case of P donor complexes are of the same magnitude as those found in the Cp^* analogs [9a]. Although the integral intensities of the two groups were equal, one of the peaks was considerably broader as observed previously [5] also with the parent dimer **1**. The broadening was tentatively ascribed to higher through-space relaxation of methyl groups next to the perfluorinated substituent on the Cp ring. Similar broadening was observed also in $^{13}C\{^1H\}$ spectra which showed in case of N-donor complexes a pair of doublets of methyl-substituted ring carbons due to ^{103}Rh splitting and a characteristic doublet of triplets of the ponytail-substituted ring carbon atom. Signals of P-donor complexes were more complex due to the additional splitting of ring carbon signals by ^{31}P, appearing thus approximately as triplets in case of methyl-substituted carbons or multiplets in case of CF_2-substituted carbon. In $^{31}P\{^1H\}$ spectra the P-donor complexes showed doublets with the usual values of $^1J_{PRh}$ coupling constants.

The fragment [Cp^*Rh] is known to be sterically very demanding, therefore it limits the free movement of coordinated ligands in some cases [9b] and stabilizes coordinative unsaturation. Creation of such highly coordinatively unsaturated moiety (14 valence electrons for Rh^I) was sought [9c,11] in attempts to activate strong, most frequently C–H, bonds.

As expected, steric hindrance exerted by our perfluoroalkyl-substituted ligands manifested itself in the preparation of their complexes, too. Whereas pyridine cleaved the dimer **1** easily, mononuclear complexes with 2-bromopyridine and 2,6-dimethylpyridine could not be obtained and unreacted dimer was isolated from reaction mixtures. 4-Methylaniline, all methylpyridines, and 3-bromopyridine gave also N-donor complexes. At variance with the properties of their Cp^* analog [9a], the pyridine complexes **15** and **18** were stable in chloroform solution at room temperature (as were also the other N-donor complexes) even upon complete removal of the solvent, probably due to a higher π-acidity of ($C_5Me_4C_nF_{2n+1}$) compared to Cp^*. Quinoline also reacted with **1**, the product **16** was found to be approximately 1:1 mixture of two rotamers at room temperature (see variable temperature experiments below). Somewhat surprisingly, with ligands traditionally classified as bulky like tricyclohexylphosphine or triisopropylphosphine the rotation around phosphorus–metal bond was unhindered. However, triaryl ligands did show hindered rotation at room temperature. Sharp aromatic carbon signals were identified in the ^{13}C NMR spectrum of triphenylphosphine complex **8** at 80 °C, they broadened on cooling giving rise to carbon signals of individual phenyls at −30 °C. Owing to their overlap the signals could not be inequivocably assigned, however. Tri(*p*-tolyl)phosphine dichloro complex **13** was therefore prepared as well as a dibromo complex **14** to enable the direct comparison of its barrier of rotation



$R^f = C_4F_9$: L = PMe_3, 3; PEt_3, 4; $P(n\text{-}C_4H_9)_3$, 5; PPr^i_3, 6; $P(C_6H_{11})_3$, 7; PPh_3, 8; $P(3\text{-}CH_3C_6H_4)_3$, 9; $P(OEt)_3$, 10; $P(OC_6H_4\text{-}2\text{-}C_6H_5)_3$, 11; $PPh_2(4\text{-}CH_3C_6H_4)$, 12; $P(4\text{-}CH_3C_6H_4)_3$, 13; NC_5H_5, 15; NC_9H_7, 16

$R^f = C_6F_{13}$: L = PMe_3, 17; NC_5H_5, 18; $2\text{-}CH_3C_5H_4N$, 19; $3\text{-}CH_3C_5H_4N$, 20; $4\text{-}CH_3C_5H_4N$, 21; $3\text{-}BrC_5H_4N$, 22; $4\text{-}CH_3C_6H_4NH_2$, 23

$R^f = C_4F_9$: L = $P(4\text{-}CH_3C_6H_4)_3$, 14

Scheme 1.

with a known value for Cp* analog [9b]. Variable temperature measurements of the compound **14** were carried out in the temperature range −40 °C to 31 °C. In the region of *p*-tolylphosphine methyl resonances (Fig. 1) the broadening of initially sharp signals of two inequivalent groups of protons in the ratio of 2:1 with temperature was observed, leading finally to coalescence of the signals. Coalescence temperature 27 °C was determined both from the halfwidth and symmetry of the coalesced signal. The low-temperature limit −19.9 °C was obtained as a temperature at which the separation of the two groups of protons (at 2.24 ppm and 2.40 ppm) started to be constant. The values were then used for the calculation of the first order rate constant of rotation at the coalescence temperature according to a simple Eq. (1)

$$k = \pi\delta\nu/\sqrt{2} \quad (1)$$

This method, based on peak separation, although being far from accurate is still widely popular and used in cases of two exchanging sites with moderate difference in site population [12]. The obtained value of the rate constant 106 s^{-1} was then used in the Eyring equation to calculate $\Delta G^{\ddagger}$ and errors in $\Delta G^{\ddagger}$ were calculated [9b], using the values of 10 s^{-1} and 2 K as the errors in k and T_C, respectively. The value of $\Delta G^{\ddagger}$ thus obtained, 14.8 ± 0.1 kcal mol^{-1}, is exactly the same as the value determined for the Cp* analog [9b]. This result was somewhat surprising, showing our ligand to be sterically exactly equivalent to Cp* despite the presence of one perfluorinated chain in place of a methyl. One possible explanation is the fixation of the mutual positions of the chain and the two chloride ligands close to each other in conformation(s) not far from that found in the crystal structure also in solution, i.e. the limited rotation of cyclopentadienyl ring with respect to the legs of the piano stool, which could cause the phosphine ligand to experience the same steric environment (two methyl groups in proximity) as in the Cp* complex.

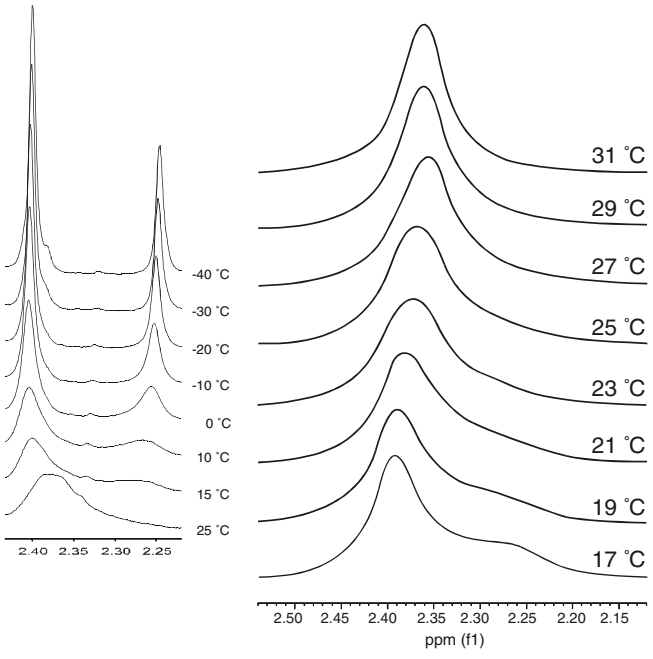


Fig. 1. Variable temperature ^{1}H spectra of **14** in the region of methyl protons of the tri(*p*-tolyl)phosphine ligand.

Steric crowding at metal center was even more obvious in case of complexes with nitrogen heterocyclic ligands, which is consistent with shorter Rh-donor atom bond and with rigid structure of substituted pyridines. In case of pyridines bearing bulky substituents at α-position(s) the steric effects even precluded the formation of expected complexes.

Pyridines with less bulky groups at α-position (2-methylpyridine, quinoline) did react with rhodium dimer but the NMR spectra of products were more complex than expected. While the spectra of other synthesized complexes showed expected number, multiplicity, and chemical shifts of signals (the signals of nitrogen ligands shifted slightly downfield compared to signals of free bases and the signals of methyl groups on cyclopentadienyl ring shifted slightly upfield compared to parent dimer), spectra of both **16** and **19** contained more peaks than expected when measured at 25 °C, some of them being quite broad. Spectra of both complexes were highly temperature dependent which suggested that some kind of dynamic behavior on the NMR timescale was present.

In the case of the quinoline complex **16** there are two complete sets of well resolved narrow signals in both proton and carbon spectra at −20 °C. ^{1}H spectrum shows two signals for each group with the expected splitting pattern and in the ratio approx. 1:1 which does not change with the temperature until the coalescence of the signals is reached. Only one set of signals remains at 72 °C in both spectra, though some of them are still very broad (Fig. 2). The ^{19}F spectrum is not affected by temperature and displays only one set of signals. This behavior can be explained by hindered rotation of quinoline ligand about the rhodium–nitrogen bond with two equally populated frozen conformers at low temperatures. Similar behavior was already described, e.g. for square planar Pd(II) and Pt(II) quinoline complexes [13,14].

We assume that the Cp ring is oriented in such a way that the carbon bearing the fluorous ponytail is closest to both chloro ligands and farthest from quinoline in analogy with the situation in the related tri(isopropyl)phosphine complex **6** the crystal structure of which was determined in this work, too. The two chloro ligands and two methyl groups closer to quinoline then divide the space around nitrogen into four quadrants (Fig. 3) which means four possible conformers, two of them (with quinoline in segments **II** and **IV**) being a pair of enantiomers. On the basis of the NMR spectra at variable temperatures we suppose that two of them are present, namely the conformer with homoaromatic quinoline ring stuck between the two Cp methyl groups (segment **I**) and the opposite one with the same quinoline ring between both chloride ligands (segment **III**) which corresponds with the conformer ratio

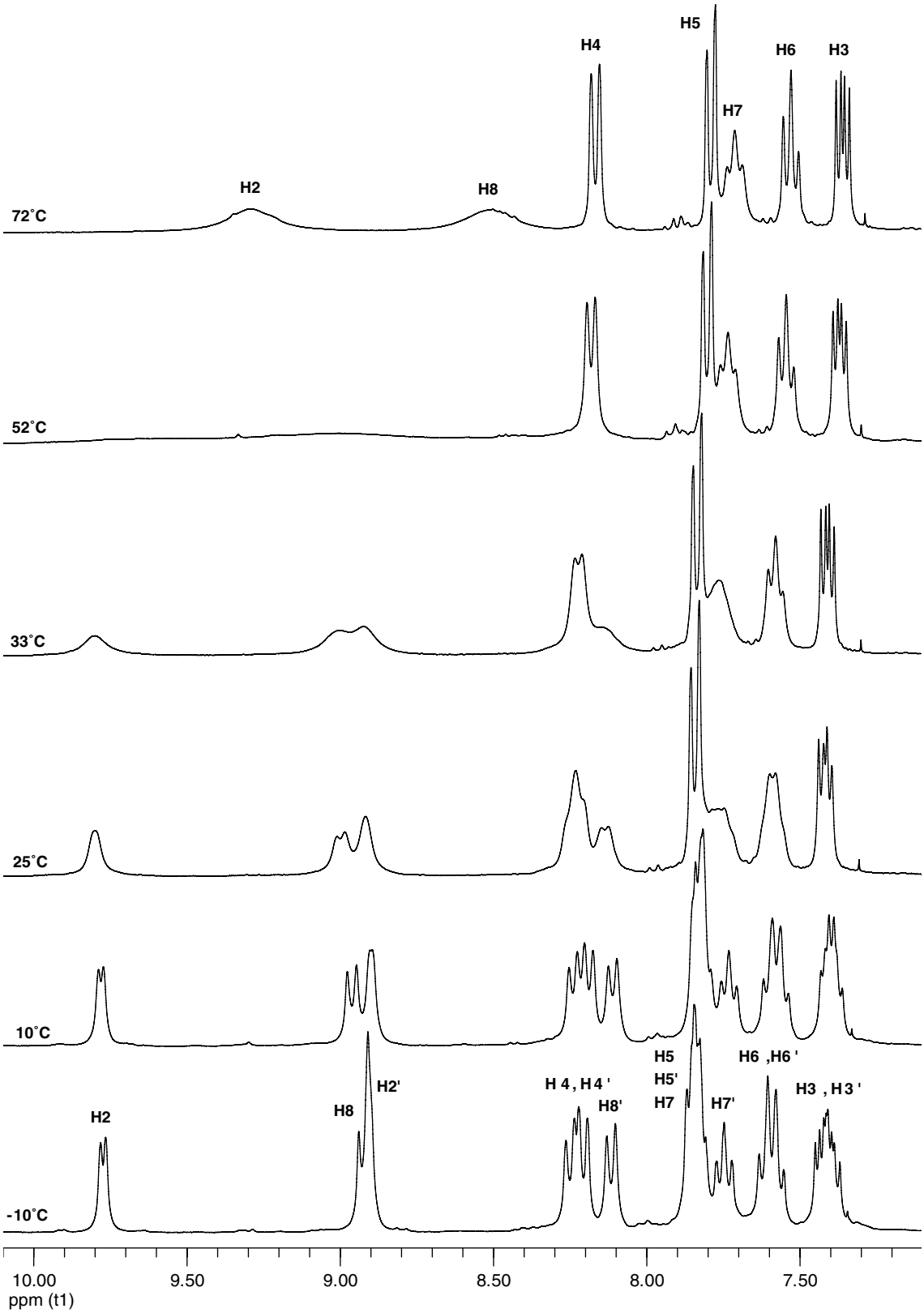


Fig. 2. Aromatic protons region of variable temperature ^{1}H spectra of quinoline complex **16**. Labels refer to the position on the quinoline system, the two conformers at low temperature being discriminated by an apostrophe.

1:1. The second possibility is the presence of conformer in segment **I** together with the other one rotating freely in segments **II** to **IV** which is more consistent with the results obtained for the 2-methylpyridine complex **19** (see below). Other combinations of conformers would give different number of signals in the NMR spectra.

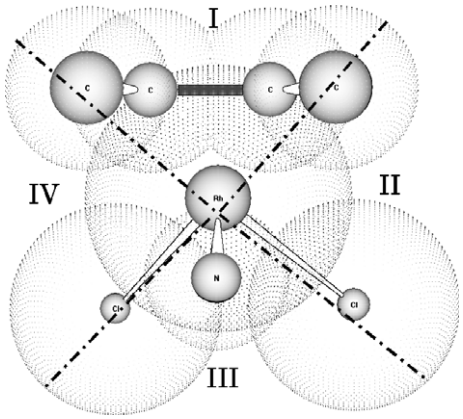


Fig. 3. Quadrants on $[Rh(C_5Me_4C_nF_{2n+1})Cl_2N]$ fragment.

Not all quinoline atoms are influenced to the same extent by rotation. The signals of protons in the position 2 and 8 of quinoline ligand show the largest peak separation (more than 250 Hz, see Fig. 2) which allowed to determine the barrier to rotation at coalescence temperature as above. Both signals coalesce at the same temperature (52 °C) and give the same value of $\Delta G^{\ddagger}$ (14.9 ± 0.1 kcal mol^{-1}).

The behavior of 2-methylpyridine complex **19** is markedly different although the steric demands of both ligands are similar due to similar substitution in the α-position of the heterocyclic ring. In both proton (Fig. 4) and fluorine (Fig. 5) spectra two sets of signals are detectable. The intensity ratio between the two sets depends on temperature, but to a lesser extent also on solvent and concentration. As for the *ortho* proton of the heterocycle, at −30 °C the ratio of deshielded to shielded signal is as high as 11:1 in $CDCl_3$, gradually decreasing with increasing temperature and reaching 1:1 ratio at ca. 35 °C. From 44 °C only one signal is visible, which shifts further upfield with increasing temperature. Similar behavior of two CF_2 groups closest to the Cp ring can be seen in ^{19}F spectra (Fig. 5), except that no coalescence can be seen in the temperature region studied. Instead, after reaching 1:1 ratio at ca. 20 °C the more shielded signal begins to increase and dominates in the high temperature spectra.

We suppose that there is an exchange between free and coordinated base in the solution, the rate and equilibrium of which depends on temperature and also on other conditions (solvent, concentration). In low temperature region the exchange is slow and the product of the cleavage prevails in the mixture, whereas at high temperatures there is a rapid exchange and the rhodium dimer dominates in solution. The process is reversible, after cooling the sample again the same spectra are obtained at lower temperatures.

Besides the ligand exchange also the hindered rotation is evident from the proton spectra of complex **19**. Below −20 °C six signals originating from Cp methyl groups are visible in the spectra, while only one set of signals belonging to coordinated ligand and one set of free base signals are present. At ca. 0 °C two pairs of methyl signals coalesce and only four signals are visible at higher temperatures. Using the same concept of four segments as for the quinoline complex **16**, this behavior corresponds to the presence of two enantiomeric frozen conformers in segments **II** and **IV** at low temperature and to free rotation of ligand in segments **II** to **IV** at higher temperature. The segment **I** remains probably unoccupied because of slightly larger steric demands of 2-methylpyridine compared to quinoline.

The crystal structure of complex **6** is shown in Fig. 6. The compound had a pseudo-tetrahedral ligand arrangement around the Rh atom. The distance between Rh and the centroid of the Cp ring was 1.84 Å. The bulkiest substituent on the ring, the fluoroalkyl chain, was averted from the phosphine ligand, but not completely. After projection to the ring plane (Fig. 7) the P– (ring centroid) –CF_2 angle was around 166°. Simultaneously, the chlorine atoms also corrupted the potentional C_S symmetry of the molecule (as was again apparent from the projection to the Cp ring plane). This resulted in unsymmetric intramolecular CH–Cl interaction. Cl1 was found to be in a stronger interaction with methyl hydrogen atoms of both Pr^i and Cp methyl groups than Cl2. On the contrary, Cl2 created slightly stronger intermolecular interaction with Pr^i groups in neighboring molecules in the crystal packing (2.96 Å vs. 3.02 Å for Cl1).

Additionally, a typical tilting of the Cp ring substituents to the opposite side from the coordinated metal atom was identified in this structure. The tilting was characterized by the value of (ring centroid)–(ring carbon)–(substituent carbon) angle and for the five ring substituents CF_2, C10, C11, C12, C13 amounted to about 3.0°, 1.4°, 4.9°, 3.9°, 1.3°, respectively.

In the molecular packing we could find a characteristic pattern for the fluoroalkyl chain containing molecules. The fluoroalkyl chains in neighboring molecules were perfectly interlocking. The whole structure was thus created by separated domains that contained either fluoroalkyl chains or phosphine ligands.

4. Conclusions

Twenty two new rhodium(III) complexes containing tetramethylperfluorobutylcyclopentadienyl or tetramethylperfluorohexylcyclopentadienyl ligand and monodentate phosphines, phosphites or aromatic heterocyclic N-donors as other ligands were prepared. The compounds were characterized by NMR and structure of one complex was confirmed by X-ray diffraction. The higher π-acidity of the fluorinated cyclopentadienyl ligands compared to Cp^* was manifested by the higher stability of their aromatic N-donor complexes. Sterically demanding $[(C_5Me_4C_n\text{-}F_{2n+1})Rh]$ fragment, similarly to Cp^*Rh, caused hindered rotation of aromatic phosphines

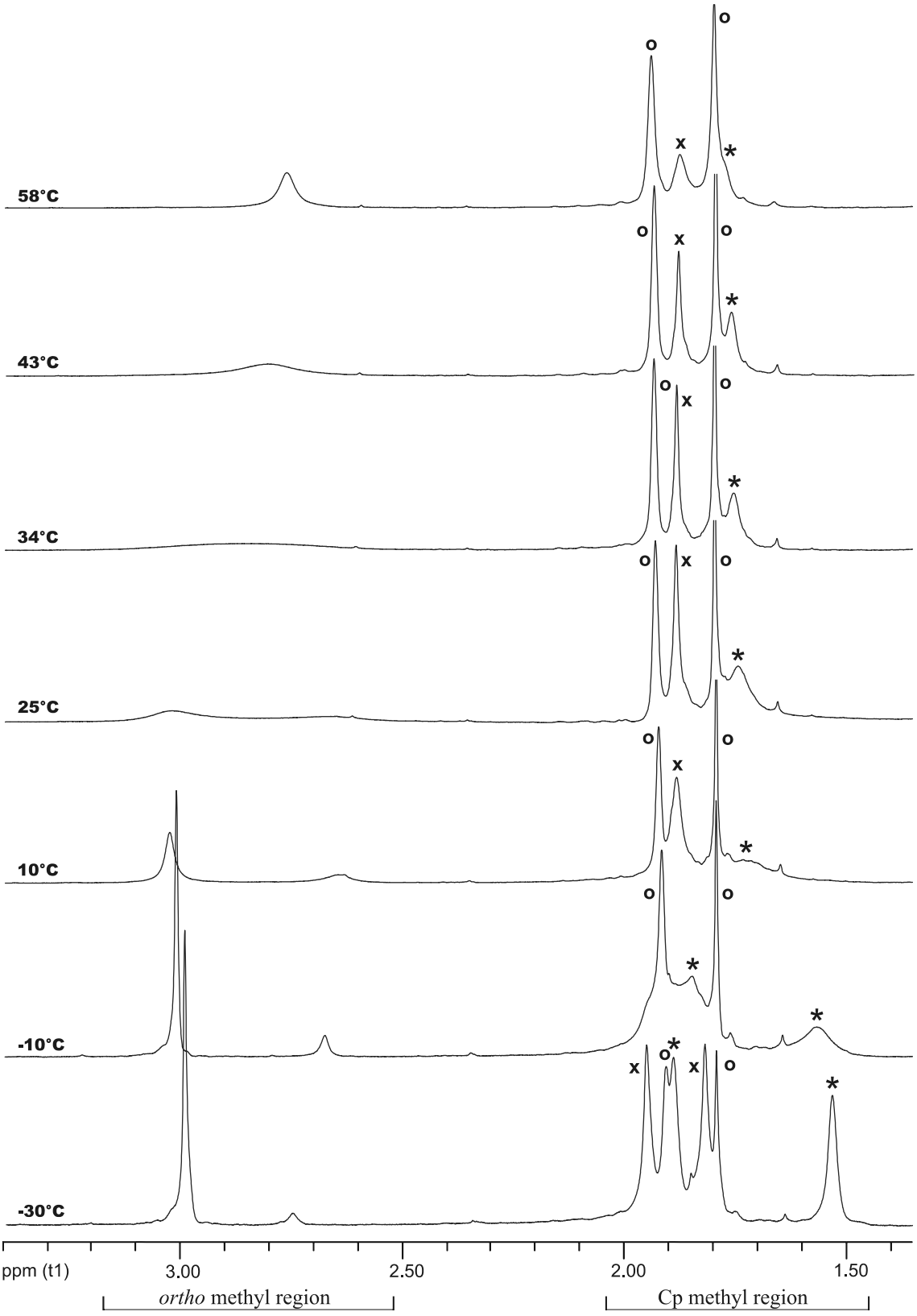


Fig. 4. High field region of variable temperature ^{1}H spectra of 2-methylpyridine complex **19**. Labels: (○) denotes the peaks of the starting dimer, (×) and (∗) the peaks of the 2-methylpyridine complex which both split into two peaks at low temperature.

and 2-substituted pyridines around Rh–P and Rh–N bonds, respectively. This rotation was analyzed by variable temperature NMR to reveal somewhat surprisingly the same steric hindrance as that caused by $Cp^{*}Rh$ frag-

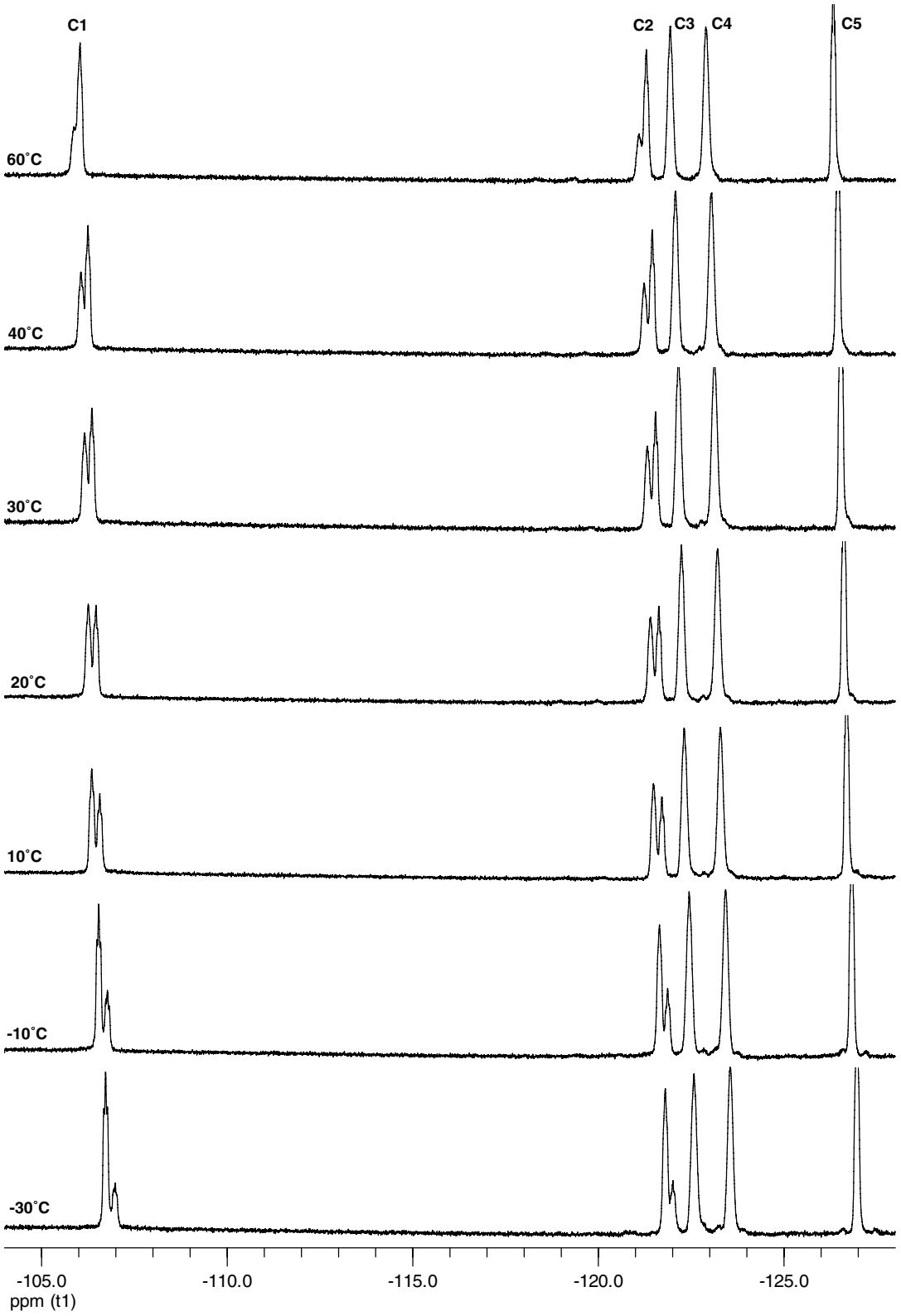


Fig. 5. Variable temperature ^{19}F spectra of 2-methylpyridine complex **19**. Only signals of the CF_2 groups of the perfluorohexyl chain are shown.

ment. A possible explanation could be the tendency of perfluoroalkyl substituted cyclopentadienyl ring to stay in solution in conformation or conformations that do not allow the perfluoro substituent to get close to the monodenate donor, securing the latter the same steric environment as in the Cp^*Rh complex.

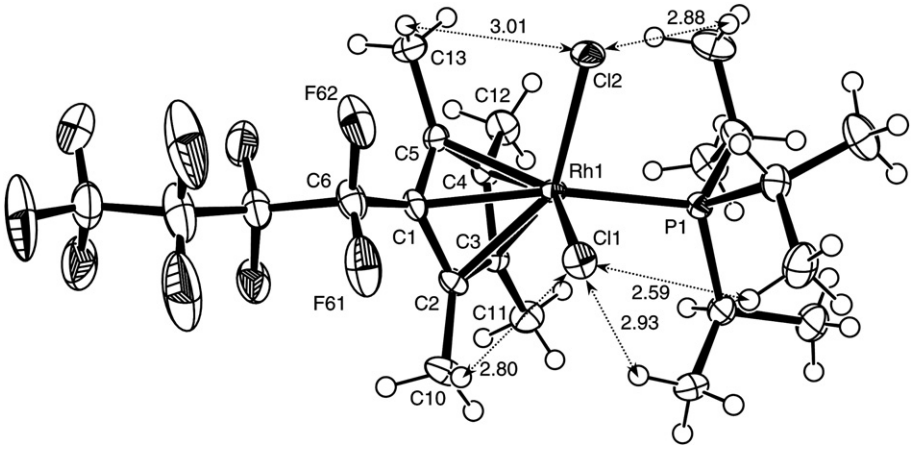


Fig. 6. X-ray structure of **6**. Some interatomic distances are indicated.

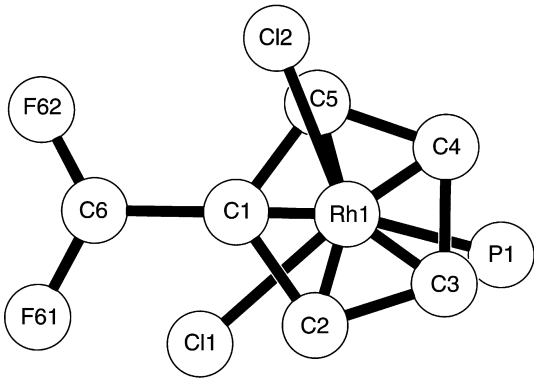


Fig. 7. Projection to the ring plane in structure of **6**.

Acknowledgements

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Appendix A. Supplementary data

CCDC 614541 contains the supplementary crystallographic data for **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.12.004.

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