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Synthesis and Molecular Structure of $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5F_5)]$. Intramolecular Structural Comparison of the Cyclopentadienyl Ligand with Its Perfluorinated Analogue

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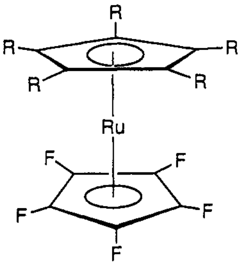
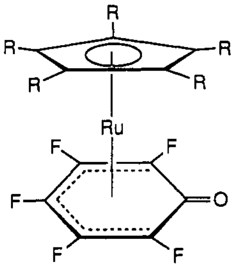
Summary: Reaction of $[RuCp(\eta^4\text{-butadiene})Cl]$ *(Cp =* $\eta^5\text{-}C_5H_5$*) with* $[Tl(OC_6F_5)]$ *in refluxing THF yields* $[RuCp((2\text{–}6\text{-}\eta^5)\text{-}C_6F_5O)]$ *(**2b**), characterized by its* ^1H *and* ^{19}F *NMR, and infrared spectra. Flash vacuum pyrolysis of **2b** (640 °C;* 10^{-4} *Torr) gives* $[RuCp(\eta^5\text{-}C_5F_5)]$ *(**1b**) in 84% yield. Compound **1b** contains only the second example of an* η^5*-pentafluorocyclopentadienyl ligand and was characterized by its* ^1H *NMR,* ^{19}F *NMR,* $^{13}C\{^1H\}$ *NMR, and mass spectra. The structure was confirmed by a single-crystal X-ray diffraction study. The two rings are eclipsed, with the pentafluorocyclopentadienyl ligand being significantly closer to the metal than its hydrocarbon analogue.*

Recently we described the first successful synthesis of the complex **1a**, containing the perfluorocyclopentadienyl ligand, by flash vacuum pyrolytic decarbonylation of the η^5-oxocyclohexadienyl precursor **2a**.[2] Although **1a** was thoroughly characterized by spectroscopy and microanalysis, analysis of the intimate structural features of the new perfluorocyclopentadienyl ligand and its ligation to ruthenium by X-ray diffraction was thwarted by disorder problems in the crystals. Here we report the synthesis and X-ray structural determination of the analogue $[Ru(C_5H_5)(C_5F_5)]$ (**1b**) containing the perfluorocyclopentadienyl ligand and its cyclopentadienyl parent, allowing for the first time a direct intramolecular comparison of the structural features of these two ligands.



1 a. R = Me
b. R = H



2 a. R = Me
b. R = H

The η^5-oxocyclohexadienyl complex **2b** is most cleanly prepared (70%) by the reaction of the known compound $[RuCp(\eta^4\text{-butadiene})Cl]$[3] (Cp = $\eta^5\text{-}C_5H_5$) with $[Tl(OC_6F_5)]$[2] in refluxing THF. Use of other precursors such as $[RuCp(\eta^4\text{-cyclooctadiene})Cl]$[3] or $[RuCp(CH_3CN)_3]PF_6$[4] gives much lower yields along with uncharacterized side products. The ^{19}F NMR spectrum of **2b** contains three multiplet resonances for the F substituents of the η^5-pentafluorooxocyclohexadienyl ligand,[5] shifted downfield by 5–9 ppm from those of **2a**.[2] The IR spectrum of **2b** shows $\nu_{C=O}$ at 1634 cm^{-1}, a frequency significantly higher than that observed (1620 cm^{-1}) for the pentamethylcyclopentadienyl analogue **2a**.[2]

Flash vacuum pyrolysis (FVP) of **2b** at 640 °C (130 mg scale; 10^{-4} Torr) results in CO extrusion and formation of the pure pentafluorocyclopentadienyl complex **1b** in 84% yield.[6] The ^1H and ^{19}F NMR spectra of **1b** show singlets[7] at δ 4.35 and −206.0 ppm, respectively. Further structural confirmation is provided by the $^{13}C\{^1H\}$ NMR spectrum, which shows a singlet for the C_5H_5 ligand and a somewhat broader doublet ($^1J_{CF}$ = 298 Hz) for the carbons of the C_5F_5 ligand.[6] The mass spectra of the two pentafluorocyclopentadienyl complexes show significant differences; in contrast to the spectrum of **1a**, in which no peak due to loss of C_5F_5 was observed and in which the peak corresponding to $[Ru(C_5F_5)]^+$ (28.6%) is prominent,[2] the base peak in that of **1b** is $[Ru(C_5H_5)]^+$, corresponding to loss of the fluorinated ligand, and only a small peak due to $[Ru(C_5F_5)]^+$ is observed.[6]

A single crystal of **1b** was subjected to an X-ray diffraction analysis.[10] The ORTEP diagram is shown in Figure 1, along with some key bond distances. As with other ruthenocenes, the two rings are eclipsed and parallel; the angle subtended by vectors from the two ring centroids to ruthenium is 178.3(2)°. The fluorines are bent back from the plane of the C_5F_5 ring by 5–6°. Table 1 shows

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(1) (a) Dartmouth College. (b) University of Delaware.

(2) Curnow, O. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1992,** *114,* 5895.

(3) Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1986,** *5,* 2199.

(4) Mann, K. R.; Gill, T. P. *Organometallics* **1982,** *1,* 485.

(5) **2b**: ^1H NMR (C_6D_6) δ 4.10 (s, Cp); ^{19}F NMR (C_6D_6) δ −178.1 (m, 2F, *m*-C_6F_5O), −181.4 (m, 2F, *o*-C_6F_5O), −190.8 (tt, 1F, *p*-C_6F_5O); IR (KBr) $\nu_{C=O}$ 1634 cm^{-1}. Anal. Calcd for $C_{10}H_5F_5ORu$: C, 37.83; H, 1.44. Found: C, 37.59; H, 1.75.

(6) **1b**: ^1H NMR (C_6D_6) δ 4.35 (s, Cp); ^{19}F NMR (C_6D_6) δ −206.9 (s, C_5F_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 78.88 (s, C_5H_5), 109.10 (d, $^1J_{CF}$ = 298 Hz, C_5F_5); EI (70 eV) mass spectrum (*m/e* using ^{102}Ru (relative intensity)) 322 (76%) P^+, 282 (7%) $P^+ - HF$, 257 (3%) $Ru(C_5F_5)^+$, 167 (100%) $Ru(C_5H_5)^+$, 155 (14%) $(C_5F_5)^+$, 141 (26%) $Ru(C_3H_3)^+$, 114 (23%) RuC^+, 102 (15%) Ru^+.

(7) Unlike the mixed-sandwhich complexes $[M(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6F_6)]$ (M = Cr,[8] Mo,[9] W[9]), no inter-ring ^1H–^{19}F coupling is observed. The ^{19}F resonance in **1b** is at lower field than that in **1a**, consistent with the trend reported for $[M(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6F_6)]$ and $[M(\eta^6\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6F_6)]$ (M = Mo, W).[9]

(8) (a) Faggiani, R.; Hao, N.; Lock, C. J. L.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1983,** *2,* 96. (b) McGlinchey, M. J.; Tan. T.-S. *Can. J. Chem.* **1974,** *52,* 2439. (c) McGlinchey, M. J.; Tan, T.-S. *J. Am. Chem. Soc.* **1976,** *98,* 2271. (d) Middleton, R.; Hull, J. R.; Simpson, S. R.; Tomlinson, C. H.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1973,** 120.

(9) Barker, J. J.; Orpen, A. G.; Seeley, A. J.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1993,** 3097.

0276-7333/94/2313-1567$04.50/0

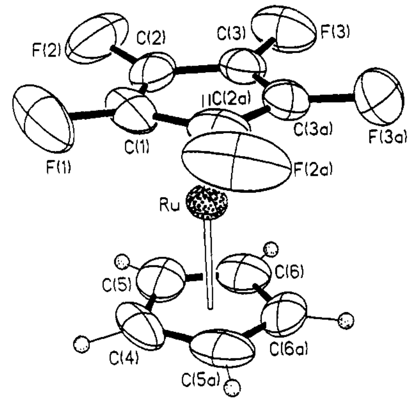

Figure 1. Molecular structure of [Ru(C_5H_5)(C_5F_5)] (**1b**). Selected bond lengths (Å): Ru–C(1), 2.104(6); Ru–C(2), 2.125(6); Ru–C(3), 2.136(6); Ru–C(4), 2.181(10); Ru–C(5), 2.186(8); Ru–C(6), 2.196(5); C(1)–C(2), 1.424(9); C(2)–C(3), 1.374(9); C(3)–C(3a), 1.399(12); C(4)–C(5), 1.410(10); C(5)–C(6), 1.340(11); C(6)–C(6a), 1.399(15); Ru–CNT(C_5F_5), 1.716(6); Ru–CNT(C_5H_5), 1.847(5).

Table 1. Average Ru–C and C–C Distances in Ruthenocenes [Ru(C_5H_5)(C_5X_5)] (X = H, Me, F (1b))[13]

	av distance (Å)		
	[Ru(C_5H_5)$_2$][11]	[Ru(C_5H_5)-(C_5Me_5)][12]	[Ru(C_5H_5)-(C_5F_5)]
Ru–C (C_5H_5)	2.191(7)	2.190(5)	2.189(6)
Ru–C (C_5Me_5)		2.165(5)	
Ru–C (C_5F_5)			2.125(10)
C–C (C_5H_5)	1.441(9)	1.416(5)	1.380(10)
C–C (C_5Me_5)		1.427(6)	
C–C (C_5F_5)			1.399(10)

a comparison of average Ru–C and C–C distances for the series of three ruthenocenes [Ru(C_5H_5)(C_5X_5)] (X = H,[11] Me,[12] F (**1b**)).[13] In **1b** the C_5F_5 ring is significantly closer to the metal than the C_5H_5 ring, but the mean C–C distances within each ring are identical. Curiously, the mean Ru–C distances to the C_5H_5 rings in the three compounds are independent of the substituent X on the opposite ring, whereas the average C–C distances in the C_5H_5 ring are significantly different, decreasing as X changes from H > Me > F. With a constant C_5H_5 ligand in the three complexes, the opposite ring is bound more closely to the metal as X changes from H > Me > F. The closer interaction of the C_5F_5 ring with the metal compared with hydrocarbon analogues is consistent with trends observed for olefinic and other unsaturated ligands.[14]

Further studies of the chemistry, physical properties, and electronic structures of (pentafluorocyclopentadienyl)-metal complexes are in progress.

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Supplementary Material Available: Tables giving a structure determination summary, atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, ansiotropic displacement coefficients, and H-atom coordinates and isotropic displacement coefficients for **1b** (8 pages). Ordering information is given on any current masthead page.

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[10] Crystal data for **1b**: monoclinic, $P2_1/m$, a = 6.703(1) Å, b = 11.179(2) Å, c = 7.004(1) Å, β = 108.01(1)°, V = 499.09(17) Å^3, Z = 2, $R(F)$ = 4.03%, $R(wF)$ = 5.82%. The molecule is situated on a mirror plane containing Ru and the two ring centroids. Of 1645 data collected ($2\theta_{max}$ = 60°, Mo Kα), 1539 were independent and 1158 were observed ($4\sigma F$). The alternative space group $P2_1$ was rejected on the basis of refinement stability. All computations used SHELXTL (4.2) software (G. Sheldrick, Siemens XRD, Madison, WI).

[11] Seiler, P.; Dunitz, J. *Acta Crystallogr.* **1980**, *B36*, 2946.

[12] Zanin, I. E.; Antipin, M. Yu.; Struchkov, Yu. T. *Kristallografiya* **1991**, *36*, 420.

[13] The structures of [Ru(C_5H_5)(C_5X_5)] (X = H, Me) were determined both at 293 K and at low temperature. The data at 293 K are used to compare with data for **1b**.

[14] Hughes, R. P. *Adv. Organomet. Chem.* **1990**, *31*, 183 and references therein.