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Reactions of $[Cp^{*(\wedge)}Ru(OMe)]_2$. 15.[†] Cp*Ru Complexes of Highly Fluorinated Arenes. Molecular Structure of $[Cp^{\wedge}Ru(\eta^6\text{-}C_6F_5\text{-}OH)]CF_3SO_3$ and Extremely Facile F/OH Exchange in Coordinated Fluoroarene Ligands

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Reaction of $[Cp^*Ru(OMe)]_2$ with highly fluorinated arenes gives easy access to fluoroarene Cp*Ru sandwich complexes. The reaction is demonstrated with the ligands C_6F_5OH and C_6F_6 to yield $Cp^*Ru(\eta^6\text{-}C_6F_5O)$ (**2**), $[Cp^*Ru(\eta^6\text{-}C_6F_5OH)]CF_3SO_3$ (**3**), and $[Cp^*Ru(\eta^6\text{-}C_6F_6)]CF_3SO_3$ (**4**), respectively. $[Cp^{\wedge}Ru(\eta^6\text{-}C_6F_5OH)]CF_3SO_3$ (**3b**) ($Cp^{\wedge} = \eta^5\text{-}C_5Me_4Et$) crystallizes in the space group $P\bar{1}$ (No. 2) with $a = 9.022(2)$, $b = 9.750(7)$, and $c = 13.215(3)$ Å, $\alpha = 75.04(3)$, $\beta = 76.49(1)$, and $\gamma = 80.34(3)°$, and $z = 2$. Extremely facile fluoride, for example, methoxide substitution, has been observed in the cationic fluoroarene complexes.

Highly fluorinated arenes have occupied a peculiar position as π-ligands in transition metal sandwich chemistry. The C_6F_6 ligand for example, apart from two Cr complexes ($Cr(C_6F_6)_2$ and $Cr(C_6F_6)(PF_3)_3$) prepared by the metal vapor technique,[1] has more frequently been engaged as an η^4- or an η^2- rather than a regular η^6-ligand.[2] Only recently was one of the highly fluorinated η^6-complexes structurally characterized.[3] It is shown in the following that the Cp^*Ru^+ fragment, generated from $[Cp^*Ru(OMe)]_2$ (**1**)[4] and acid, easily forms η^6-π-complexes with fluorinated arenes, a method which provides an easy and quite general access to highly fluorinated Ru sandwich complexes.

On reaction of $[Cp^*Ru(OMe)]_2$ with C_6F_5OH in ether at ambient temperature (Scheme 1), a cream-colored solid precipitated which after crystallization from acetone/pentane gave pale yellow crystals of **2** in 85% yield. Complex **2** has recently been obtained from $Cp^*Ru(NCCH_3)_3Cl$ and C_6F_5OTl and was utilized as a precursor for the preparation of $Cp^*Ru(\eta^5\text{-}C_5F_5)$.[5] The reaction is analogous to the one observed for **1** and phenol,[6] with the major difference that in this latter case a stoichiometry Ru:phenol of 1:3 was required and the product invariably was $Cp^*Ru(\eta^6\text{-}C_6H_5{=}O)\cdot 2C_6H_5OH$, where the two extra moles of phenol are strongly hydrogen bonded to the ketonic oxygen and are not easy to remove. In the present case the stronger acidity of the parent phenol and the more pronounced ketonic character of the C=O group in the pentafluorooxocyclohexadienyl ligand, as evidenced by a shift of the $\nu_{C=O}$ frequency in the IR from 1542 cm^{-1} in $Cp^*Ru(\eta^5\text{-}C_6H_5O)$[6] to 1614 cm^{-1} in **2** is the obvious reason for much weaker hydrogen bonding, leading directly to the oxocyclohexadienyl complex.

The same starting compounds in the presence of CF_3SO_3H yield a precipitate of the cationic phenol complex **3**. The pure triflate salt was obtained in 75% yield by diffusion of ether into an acetone solution. Protonation of **2** to **3** can readily be demonstrated by ^1H NMR spectroscopy, monitoring the shift of the Cp* signal from 1.88 ppm in **2** to 1.99 ppm in **3** on addition of CF_3SO_3H to a $CDCl_3$ solution of **2**.

Having demonstrated facile π-complexation of pentafluorophenol to the Cp^*Ru^+ cationic fragment, experiments were conducted with C_6F_6 as a potential 6-electron ligand. Reaction of **1** with either CF_3SO_3H or $CF_3SO_3SiMe_3$ (Scheme 1) gave a precipitate which after recrystallization from acetone had the proper analytical composition for $[Cp^*Ru(C_6F_6)]CF_3SO_3$. The ^{19}F NMR spectrum in CD_2Cl_2 showed two singlets at −74.6 and −174.4 ppm, the latter in the same region as the fluorine multiplets in derivatives **3**, **5**, and **6**, which are assigned to CF_3 and $\eta^6\text{-}C_6F_6$ groups, respectively. However, when the ^{19}F NMR spectrum was recorded in CD_3OD it revealed the presence of a pentafluorophenyl complex. Monosubstitution of one F for OMe to **5** was found to proceed by simply keeping the complex in methanol solution at ambient temperature for a short time. In the course of some days at room temperature or by refluxing the methanol solution for 10 min, further substitution to the *p*-dimethoxy complex **6** has been inferred from ^1H NMR. Complexes **5** and **6** were then prepared separately from **4** and methanol and characterized.

Nucleophilic substitution of F in fluoroaromatics and π-complexed fluorinated ligands is not without precedence and removal of fluorine from the allylic position in (fluorocyclohexadiene)tricarbonyliron has also been observed,[7] but the ease at which these occur in cationic complexes **4** and **5** is quite exceptional. Thus, fluorobenzenes frequently require prolonged heating in

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[†] For 14, see: Hörnig, A.; Englert, U.; Koelle, U. *J. Organomet. Chem.* **1993**, *453*, 255.

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[1] See: Hughes, R. P. Organotransition Metal Compounds Containing Polyfluorinated Ligands, *Adv. Organomet. Chem.* **1991**, *31*, 183.

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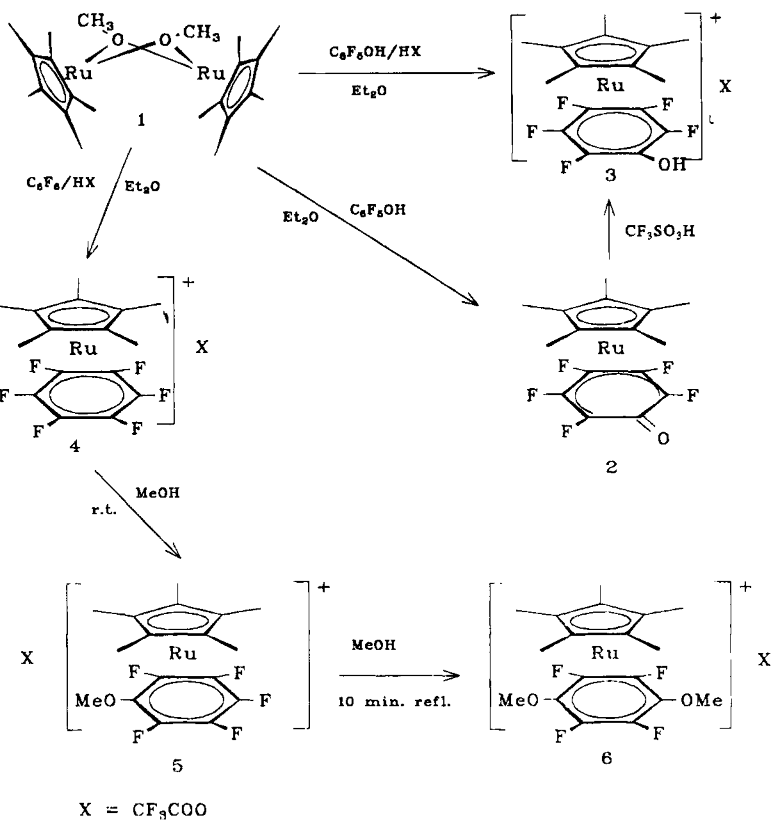
Scheme 1



alcohol in the presence of alcoholate. $Cr(C_6H_6)(C_6F_6)$ did not react with alcoholate and $Cr(C_6F_6)_2$ gave the bismethoxo complex after treatment with NaOMe in low yield.[8]

In contrast to arene congeners Cp*Ru(arene)$^+$ which resist electrochemical reduction, the more electron deficient fluoro complex **4** is electrochemically reducible with relative ease. The cyclic voltammogram[9] of **4** in propylene carbonate shows an irreversible reduction wave at -1.02 V vs SCE (E_p) assigned to a one-electron reduction followed by one of the usual follow-up reactions of the reactive neutral radical, such as dimerization or hydrogen abstraction. In more nucleophilic solvents, the cation **4** undergoes degradation. Thus, cyclic voltammetry in DMF showed an initial reduction wave with peak potential -1.00 V, assigned to the analogous process as above. This peak disappears in favor of reduction waves with peak potentials at -1.20, -1.4, and -1.63 V, appearing and disappearing successively in the course of 1 h at ambient temperature. NMR spectra taken in DMF-d_7 likewise showed the appearance of new Cp* signals and disappearance of the original one.

In an attempt to grow crystals of **4** suitable for X-ray analysis, the Cp^ (η^5-C_5Me_4Et) derivative **4b** was prepared analogously to **4a**. Crystals that separated after some time from the purified but oily material turned out to be those of [Cp^Ru(η^6-C_6F_5-OH)]CF_3SO_3 (**3b**). The presence of a pentafluorophenyl ligand was confirmed by ^{19}F NMR. In light of the above observations on facile nucleophilic exchange, the assumption that residual water in the solvent acetone had caused hydrolysis over the time required for crystallization appears very plausible.

The structure of **3b**, depicted in Figure 1, shows a sandwich molecule with a planar, π-complexed C_6F_5–OH ligand, hydrogen bonded to one oxygen of the anion. Ru–C distances to either ring are in the range frequently found for RuCp(arene) cations,[10] similar to the recent example $W(C_6F_6)_2$ where no spectacular differences from $W(C_6H_6)_2$ were found either.[3] Slippage of the metal projection from the center of the 6-membered ring away from C1–O1 is only 0.04 Å. Since C–F and C–O distances are indistinguishable in the structure, the obvious hint for the correct location of the OH group is a O1···O2 distance of 2.6 Å due to a hydrogen bond. The hydrogen atom was located in a Fourier difference synthesis and its temperature factor refined to a reasonable value.

Experimental Section

Cp*Ru(η^5-C_6F_5O) (2). To a solution of 100 mg (0.19 mmol) of [Cp*Ru(OMe)]$_2$ (**1**) was added 69 mg (0.375 mmol) of pentafluorophenol, and the solution was stirred overnight during which time the product precipitated as a cream-colored solid. The solvent was decanted, and the solid was washed with two 20 mL portions of ether and dried. Diffusion of pentane into an acetone solution of the solid gave 135 mg (85%) of yellowish crystals. ^1H NMR ($CDCl_3$): Cp* 1.88. ^{19}F NMR ($CDCl_3$): *p*-F -195.28 (t/t, ^3J = 40.3, ^4J = 13.6 Hz), *m*-F -184.69 (d/d), *o*-F -188.61 (d/d, $^3J'$ = 29.5 Hz). IR (KBr): ν_{CO} = 1614 cm^{-1}. MS (*m/z*, rel intensity): 420 (95, M$^+$), 392 (12,

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[8] McGlinchey, M. J.; Tan, T.-S. *J. Am. Chem. Soc.* **1976**, *98*, 2271.

[9] EG&G electrochemical equipment, Pt working electrode, Bu_4NPF_6 supporting electrolyte, scan rate 100 mV/s; ferrocene$^{+/0}$ vs SCE is 0.4 V in either solvent.

[10] (a) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981. (b) Fagan, P. J.; Ward, M. D.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

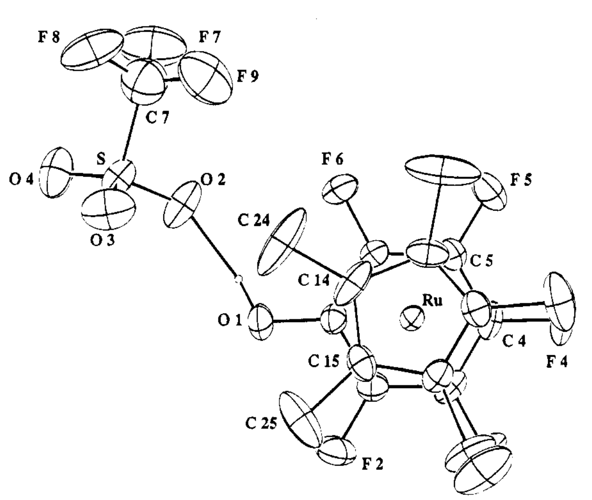

Figure 1. Structure of **3a** (ORTEP). Ellipsoids are drawn at 30% probability. Selected bond distances (Å) and angles (deg): Ru−C1 2.265(2), Ru−C2 2.198(2), Ru−C3 2.199(2), Ru−C4 2.194(2), Ru−C5 2.194(2), Ru−C6 2.223(2), Ru−C(Cp^) (av) 2.181, C1−O1 1.321(3), C2−F2 1.323(3), C3−F3 1.327(3), C4−F4 1.325(3), C5−F5 1.323(3), C6−F6 1.330(2), O1−H1 0.95, O2−H1 1.71; O1−H1−O2 155.7.

M − CO), 375 (11, $RuCp^*_2$). Anal. (M_r 419.4) Calcd: C, 45.83; H, 3.61; F, 22.65. Found: C, 45.71; H, 3.77; F, 22.76. Analytical data are in accord with those reported in ref 5. The analogous complex with a Cp^($\eta^5C_5Me_4Et$) ligand was prepared from $[Cp\text{^}Ru(OMe)]_2$ and C_6F_5OH in exactly the same way. ^1H NMR ($CDCl_3$); Cp^ 1.88 (12H), 1.04 (t, 3H), 2.26 (q, 2H). Anal. (M_r 433.4) Calcd for $C_{17}H_{17}F_5ORu$: C, 47.12; H, 3.95. Found: C, 47.44; H, 4.22.

$[Cp^{*(\wedge)}Ru(C_6F_5OH)]CF_3SO_3$ (3a(b)). Addition of a slight excess of CF_3SO_3H to the solution of 110 mg (0.206 mmol) of $[Cp^*Ru(OMe)]_2$ and 75 mg (0.412 mmol) of pentafluorophenol in 25 mL of ether caused the immediate precipitation of a white solid. After 30 min the solvent was decanted, and the precipitate was washed with ether and dried in vacuo. Slow diffusion of ether into an acetone solution gave 180 mg (75%) of white crystals. ^1H NMR ($CDCl_3$): Cp* 1.99. ^{19}F NMR ($CDCl_3$): *p*-F −179.95 (t/t, $^3J = 35.2$, $^4J = 9.8$ Hz), *m*-F −174.66 (m), *o*-F −176.95 (m), CF_3 −74.61. Anal. (M_r 579.4) Calcd for $C_{17}H_{16}F_8O_4RuS$: C, 35.86; H, 2.83; F, 26.69. Found: C, 35.88; H, 2.92; F, 26.53.

$[Cp^{*(\wedge)}Ru(C_6F_6)]CF_3SO_3$ (4a(b)). To a solution of 140 mg (0.262 mmol) of $[Cp^*Ru(OMe)]_2$ and 97 mg (0.524 mmol) of C_6F_6 in 25 mL of ether was added dropwise a slight excess of CF_3SO_3H on which **4a** slowly precipitated as a brownred solid. After stirring for two more hours at ambient temperature, the ether was decanted and the residue was washed twice with ether, dried, redissolved in the minimum quantity of acetone, and crystallized by slow diffusion of ether into the acetone solution to obtain 240 mg (80%) of yellowish crystals. ^1H NMR (CD_2Cl_2, δ): 1.73 (s, Cp*). ^{19}F NMR (CD_2Cl_2): −74.6 (s, $CF_3SO_3^-$), −174.4 (s, C_6F_6). Anal. (M_r 571.4) Calcd for $C_{17}H_{15}F_9O_3RuS$; C, 35.73; H, 2.65; F, 29.92. Found: C, 35.81; H, 2.71; F, 30.04. The analogous complex with a Cp^-ligand, **4b**, was prepared from $[Cp\text{^}Ru(OMe)]_2$ and C_6F_6 in exactly the same way. Anal. (M_r 585.4) Calcd for $C_{18}H_{17}F_9O_3RuS$: C, 36.93; H, 2.93. Found: C, 36.63; H, 3.32. Crystallization from acetone over two months, however, gave crystals of $[Cp\text{^}Ru(C_6F_5OH)]CF_3SO_3$ (**3b**).

$[Cp^*Ru(C_6F_5OMe)]CF_3SO_3$ (5). **4a** (150 mg, 0.263 mmol) was dissolved in methanol. After some hours at ambient temperature, the solvent was evaporated and the residue chromatographed over alumina (5% water) using dichloromethane/acetone 2/1 as eluent. After removal of the solvent, the solid residue was dissolved in acetone and crystallized by diffusion of pentane to give 80 mg (52%) yellowish crystals. ^1H NMR ($CDCl_3$): Cp* 1.91, OMe 4.17. ^{19}F NMR (CD_3OD): *p*-F-179.3 (t/t, $^3J = 32.7$, $^4J = 7.5$ Hz), *m*-F −177.1 (d/d, ^3J = 24.4, 31.1 Hz), *o*-F −173.2 (d/d, ^3J = 22.9, 7.5 Hz), CF_3 −74.6.

$[Cp^*Ru(p\text{-}C_6F_4(OMe)_2)]CF_3SO_3$ (6). A solution of 100 mg of $[Cp^*Ru(C_6F_6)]CF_3SO_3$ in 20 mL of methanol was refluxed for 3 h. The solution was concentrated to a small volume and the product precipitated by addition of ether. Then 70 mg (67%) of colorless, analytically pure crystals was obtained by slow diffusion of ether into an acetone solution. ^1H NMR (CD_3OD): Cp* 2.00, OMe 4.21. ^{19}F NMR (CD_3OD): −174.6 (s). Anal. Calcd: C, 38.32; H, 3.56. Found: C, 38.12; H, 3.57.

Structure solution for 3b: $C_{18}H_{18}F_8O_4SRu$, M = 583.46 g·mol^{-1}, approximate crystal dimensions 0.4 × 0.2 × 0.2 mm. ENRAF-Nonius CAD4, data collection at ambient temperature. Crystal data: triclinic space group $P\bar{1}$ (No. 2), a = 9.022(2), b = 9.750(7), and c = 13.215(3) Å, α = 75.04(3), β = 76.49(1), and γ = 80.34(3)°, V = 1085(1) Å^3, Z = 2, d_{calc} = 1.786 g/cm^3, μ(Mo Kα) = 8.89 cm^{-1}, $F(000)$ = 580. A total of 10 012 reflections were measured within $\theta < 35°$; 6967 unique reflections with $I > 3\sigma(I)$ were used in structure solution and refinement.[11] Empirical absorption correction by ψ-scans.[12] Refinement of 291 variables resulted in R = 0.044, R_w = 0.064, and $w = 1/\sigma^2(F_o)$.

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Supplementary Material Available: A list of positional parameters, displacement factors, and tables of bond lengths and bond angles (12 pages). Ordering information is given on any current masthead page.

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