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Synthesis, Characterization, and Crystal Structure of Hydroxyruthenocene

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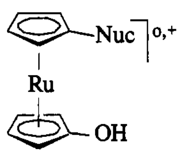
Introduction

We recently reported that the moiety $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)]^+$, introduced as either $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CH_3CN)](PF_6)$[1] or $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)]_2(PF_6)_2$,[1] reacts readily with nucleophiles (Nuc) such as phosphines, thiolates, and CN^- to give hydroxyruthenocenes of types I or II.[2] Here we describe the synthesis and the structural characterization of the parent hydroxyruthenocene, $Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4OH)$, which is obtained by the reaction of $Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)Br$ with Zn in tetrahydrofuran as a solvent. The corresponding sodium salt, $Na[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4O)]$, was synthesized in high yield by using NaHg instead of Zn as a reductant.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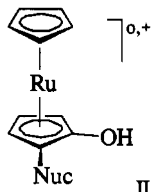
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Of possible analogous complexes that could be formed by the Fe–Ru–Os triad, only hydroxyferrocene is known. It was synthesized by Nesmeyanov and co-workers in 1959 by the action of ferroceneboronic acid on copper acetate and subsequent hydrolysis with KOH.[3,4] This procedure, however, does not work in the case of the analogous ruthenium compound, which, to the best of our knowledge, has hitherto not been reported.

Experimental Section

Materials and Measurements. The synthesis of $Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)Br$ (**1**) is described elsewhere.[5] All chemicals used were standard reagent grade and were used without further purification. The solvents were purified according to standard procedures.[6] The deuterated solvents were purchased from Aldrich and dried over 4-Å molecular sieves. All experiments were performed under an inert atmosphere in an argon-filled Vacuum Atmospheres Dri-Lab glovebox. Infrared spectra were recorded on an IBM 98 FTIR with samples prepared as KBr pellets. ^1H NMR spectra were obtained on a Nicolet NT-300WB operating at 300 MHz and were referenced to $SiMe_4$. Microanalyses were done by Desert Analytics, Tucson, AZ.

Synthesis of $Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4OH)$ (Hydroxyruthenocene) (2). A 300-mg sample of **1** was dispersed in 25 mL of anhydrous tetrahydrofuran, and 20 g of granular zinc (2–14 mesh) was added. The mixture was stirred until the color of the solution changed from orange-red to yellow (8–16 h). Prior to filtration, ca. 25 mL of anhydrous diethyl ether was added and the solvent was evaporated to dryness. The residue was redissolved in diethyl ether (30 mL), and possible nonsoluble products were removed by filtration. The filtrate was concentrated under vacuum to a volume of ca. 5 mL, and was placed in a closed vial with carbon tetrachloride. After 2 days, orange-brown crystals were collected by filtration, washed with diethyl ether, and dried under vacuum. Yield: 88 mg (22%). Anal. Calc for $C_{10}H_{10}ORu$; C, 48.57; H, 4.07. Found: C, 48.16; H, 4.03. ^1H NMR (δ, acetone-d_6, 20 °C): 4.53 (t, 2H), 4.47 (s, 5H), 4.12 (t, 2H). IR (KBr): 1498 cm^{-1} (s, C–O).

Synthesis of $Na[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4O)]$ (3). A 300-mg quantity of **1** was dispersed in 50 mL of anhydrous tetrahydrofuran, and 5 g of sodium amalgam (3% Na) was added. The mixture was stirred until the solution developed a yellow color and all the starting material was consumed (3–6 h). Then, the solution was filtered and about two-thirds of the solvent was distilled off, leaving a pale yellow precipitate. The solid was filtered off, washed with anhydrous diethyl ether, and dried for 12 h under vacuum. Yield: 150 mg (51%). By treatment of the filtrate with diethyl ether (10 mL), an additional 50 mg of the product could be recovered. Total yield: 68%. Anal. Calc for $C_{10}H_9ORuNa$: C, 47.52; H, 3.37; Na, 7.58. Found: C, 46.59; H, 3.97; Na, 7.24. ^1H NMR (δ, acetone-d_6, 20 °C): 4.28 (s, 5H), 4.07 (t, 2H), 3.97 (t, 2H). IR (KBr): 1478 cm^{-1} (s, C–O).

X-ray Crystallography. A crystal of **2** with dimensions of 0.11 × 0.23 × 0.40 mm was mounted on a thin glass fiber. The data collection was carried out on a Syntex P2$_1$ diffractometer upgraded to Nicolet R3m specifications.[7] Graphite monochromated Mo Kα (λ = 0.710 69 Å) radiation was used. The orientation matrix and lattice parameters were optimized from a least-squares calculation on 25 carefully centered reflections with high Bragg angles. Two standard reflections monitored every 96 reflections showed no significant fluctuations. The intensities of 1441 reflections were measured using a Wyckoff scan (1.0° scan range) with scan speeds varying from 4 to 29.3° min^{-1} out to a $2\Theta(max)$ of 60°. The *hkl* ranges were $0 \leq h \leq 19$, $0 \leq k \leq 14$, $0 \leq l \leq 7$. Following the data reduction, 1270 unique reflections remained, with 986 having $|F_o| > 3\sigma(F_o)$. Systematic absences were consistent with space groups *Pnma* and $Pn2_1a$. Assuming a cell content of 4 formula units and the acentric space group $Pn2_1a$, the position of the Ru atom was found via direct methods and the remaining atoms were located from a subsequent electron difference Fourier synthesis. An examination of the results obtained so far showed that the structure did not deviate significantly from a centrosymmetric one with space group *Pnma*. In this space group, the $Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4OH)$ complex is located on a mirror plane and has its OH group statistically distributed over a half-occupied site with two alternately occupied positions at both sides of the mirror plane. This latter structure model was finally favored on the basis of the *R* values, and hydrogen atoms were added in calculated but unrefined positions. All non-hydrogen atoms were refined anisotropically. After the omission of 7 unreliable data, the final refinement converged with 979 reflections, weights $w = 1/(\sigma^2(F_o) + 0.0006F_o^2)$, and 65 varied parameters to R = 0.036 and R_w = 0.051. The goodness of fit was 1.52, and the final difference map showed a residual density of 0.95 e $Å^{-3}$ near Ru, attributable to the neglect of an absorption correction (μ = 17.8 cm^{-1}). The program SHELX76 was used for structure solution and refinement.[8] The XTAL3.1 suite of programs was used to produce the molecular diagram.[9] Crystallographic data are given in Table I, atomic positional parameters in Table II, and bond distances in Table III.

Results and Discussion

The reduction of **1** by Zn in tetrahydrofuran as a solvent gives **2** in about 22% yield. The reaction time was strongly dependent on the surface area of the reductant varying from 8 to 16 h. It turned out that Zn (2–4 mesh) worked best for this synthesis. Attempts to use Zn powder as a reductant proved to be unsuccessful.

The C=O peak in the IR spectrum shifted from 1674 cm^{-1} for **1** to 1498 cm^{-1} for **2**, indicating loss of π-electron density from this group to the ring and metal. Similar observations were made for other related systems; e.g., upon protonation of $Co(\eta^5\text{-}$

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Table I. Crystallographic Data for Ru(η^5-C_5H_5)(η^5-C_5H_4OH)

empirical formula	$C_{10}H_{10}ORu$
fw	247.3
space group	*Pnma* (No. 62)
a, Å	13.748(3)
b, Å	10.704(3)
c, Å	5.679(1)
V, Å^3	835.7(3)
Z	4
T, °C	22
λ, Å	0.710 69
ρ_{calc}, g cm^{-3}	1.97
μ, cm^{-1}	17.8
R^a	0.036
$R_w{}^b$	0.051

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for Ru(η^5-C_5H_5)(η^5-C_5H_4OH)

	x/a	y/b	z/c	$U_{eq}{}^a$
Ru	0.07203(2)	$^1/_4$	–0.00384(5)	0.0406(1)
C(1)	–0.0267(3)	$^1/_4$	0.3010(8)	0.065(2)
C(2)	–0.0457(3)	0.1434(4)	0.1620(7)	0.059(1)
C(3)	–0.0763(2)	0.1856(5)	–0.0629(8)	0.056(1)
C(4)	0.2269(3)	$^1/_4$	0.081(1)	0.069(2)
C(5)	0.2051(3)	0.1408(5)	–0.0578(7)	0.061(1)
C(6)	0.1711(2)	0.1836(3)	–0.2800(5)	0.050(1)
O^b	0.1531(7)	0.1065(8)	–0.4720(9)	0.077(3)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Statistically half-occupied.

Table III. Bond Lengths (Å) for Ru(η^5-C_5H_5)(η^5-C_5H_4OH)[a]

Ru–C(1)	2.200(5)	C(2)–C(3)	1.418(6)
Ru–C(2)	2.192(4)	C(3)–C(3′)	1.379(11)
Ru–C(3)	2.178(3)	C(4)–C(5)	1.442(6)
Ru–C(4)	2.182(5)	C(5)–C(6)	1.421(5)
Ru–C(5)	2.192(4)	C(6)–C(6′)	1.422(7)
Ru–C(6)	2.196(3)	C(6)–O	1.390(7)
C(1)–C(2)	1.412(5)		

[a] Atoms generated by the symmetry operation x, $^1/_2-y$, z are marked with a prime.

C_5H_5)(η^4-C_5Me_4O), the C=O stretching frequency is lowered from 1570 to 1485 cm^{-1}.[10] The ^{1}H NMR spectrum of **2** exhibits two apparent triplets centered at 4.53 ppm (2H) and 4.12 ppm (2H), respectively, and a singlet at 4.47 ppm (5H). The downfield triplet is assigned to the α protons, the upfield triplet to the β protons of C_5H_4OH, and the singlet to the C_5H_5 protons. The signal of the OH proton was not observed.

By use of the stronger reductant NaHg (3% Na), **3** was obtained in form of pale-yellow crystals in almost 70% yield which is readily converted to **2** upon addition of triflic acid. The carbonyl stretching frequency for **3** is observed at 1478 cm^{-1}, compound **3** thus suffering an even stronger decrease in bond order than complex **2**. The ^{1}H NMR spectrum of **3** shows a pattern similar to that of **2**, revealing two apparent triplets centered at 4.07 ppm (2H) and 3.97 ppm (2H), respectively, and a singlet at 4.28 ppm (5H). In comparison to the ^{1}H NMR spectrum of **2**, all signals are shifted somewhat upfield.

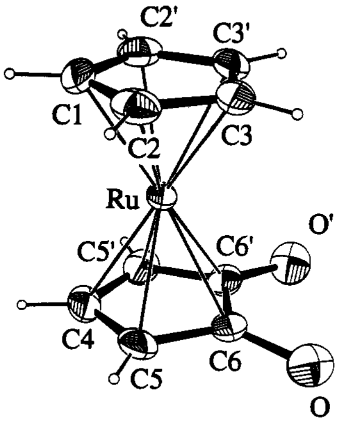

Figure 1. ORTEP plot (30% ellipsoids) of Ru(η^5-C_5H_5)(η^5-C_5H_4OH). Note that, due to disorder, only one of the two crystallographically equivalent oxygen positions is occupied.

The analysis of the X-ray diffraction data confirmed the structure of the new complex, and a structural view of **2** is shown in Figure 1. The cyclopentadienyl rings adopt an eclipsed conformation and are almost parallel to one another, the least-squares planes of the two rings having a dihedral angle of 2.2(2)°. The OH group deviates from the cyclopentadienyl plane in that it is located 0.15(1) Å out of the C_5 plane bent away from the metal, corresponding to a respective tilt of 6.0(5)°. The average C–C length in C_5H_5 is 1.408 Å, and the average metal–carbon bond length is 2.190 Å. The corresponding average distances for ruthenocene are 1.441 and 2.191 Å, respectively.[11] It should be mentioned that the crystal structure of **2** shows some resemblance to that of ruthenocene. The latter also crystallizes in space group *Pnma* (a = 7.119 Å, b = 8.985 Å, c = 12.794 Å, Z = 4), and the molecule is also located on a mirror plane. However, the spatial arrangement of ruthenocene differs from that of **2**. The proton attached to O was not located in the X-ray analysis, but its presence is inferred from the long C(6)–O bond length of 1.390(7) Å, corresponding to a single bond (*cf.* the C–O distances of the η^5-bound C_5Ph_4OH ligand in [$Ru_2(CO)_5${μ-σ^2:η^5-OC_4Ph_3-η^6-C_6H_4Ru(η^5-C_5Ph_4OH)}][12] and [$Mo_2(CO)_3$(μ-PPh_2)(μ-σ:η^5-C_5Ph_4O)(η^5-C_5Ph_4OH)],[13] which are 1.378(9) and 1.412(12) Å, respectively).

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Supplementary Material Available: Listings of hydrogen atom coordinates, anisotropic temperature factors, complete bond angles, and least-squares planes (3 pages). Ordering information is given on any current masthead page.

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