Synthesis of $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$: Formation of an Unprecedented Bis(water) Adduct Exhibiting a Two-Dimensional Hydrogen-Bonded Water Network

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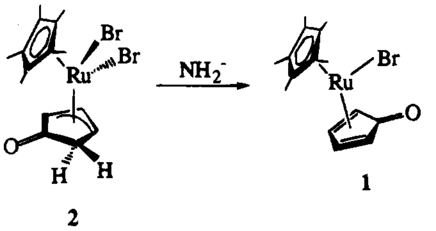
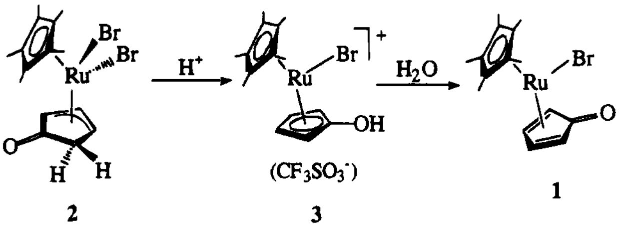
*Summary: $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$ (**1**) is formed from $Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_5H_5O)Br_2$ (**2**) by reaction with $LiNH_2$. More conveniently, **1** was synthesized in 97% yield via conversion of **2** to $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_4OH)Br]CF_3SO_3$ (**3**) on addition of triflic acid and subsequent dehydrobromination with H_2O. From aqueous acetone (≤5% H_2O), **1** crystallized within a few days to give the unexpected bis(water) adduct $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br\cdot 2H_2O$ (**4**) interlinked by a hydrogen-bonded water network. In contrast, crystallization from a water-rich solution (≤5% acetone) yielded a water-free product. The molecular structure of **4** has been determined by X-ray diffraction techniques.*

Complexes containing the $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)]^+$ moiety have been shown to undergo a variety of reactions, including nucleophilic substitutions on $C_5H_5^-$ and/or C_5H_4O,[2-4] reduction of C_5H_4O,[5] and oxidative addition of halogens.[6] We considered it worthwhile to study the change in reactivity when the cyclopentadienyl ligand is replaced by its more electron-donating permethylated derivative $C_5Me_5^-$. As a main result of the methyl groups introduced the ketonic oxygen of the coligand becomes more basic so as to form molecular adducts with Lewis acids. Here we report on the synthesis of $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$ (**1**) via the Ru(IV) η^3-cyclopentenoyl complex $Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_5H_5O)Br_2$ (**2**).[7,8] In addition, the formation of the bis(water) adduct $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br\cdot 2H_2O$ (**4**) is described.

Scheme 1



Scheme 2



In an attempt to obtain complex **1** containing η^4-cyclopentadienone, **2** was subjected to the action of the base NH_2^-. **2** reacted with $LiNH_2$ (1 equiv) in CH_3NO_2 at room temperature to give **1** in 74% yield (Scheme 1).[9]

More conveniently, **1** has been synthesized via the cationic Ru(IV) intermediate $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_4OH)Br]CF_3SO_3$ (**3**), as depicted in Scheme 2. When a CH_2Cl_2 solution of **2** was treated with neat triflic acid (2.5 equiv) at room temperature, the red solution rapidly turned olive green and, on addition of anhydrous diethyl ether, **3** was precipitated in essentially quantitative yield.[10] The unexpected hapticity change from η^3 to η^5, not possible for simple η^3-allyl systems, is obviously made feasible by the ketonic oxygen of the η^3-cyclopentenoyl ligand. Complex **3** reacted with H_2O to give, on workup, complex **1** in 97% yield.[9] Complex **1** is only

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(7) **2** has been prepared according to the literature (Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843). Yield: 95%. Anal. Calcd for $C_{15}H_{20}Br_2ORu$: C, 37.75; H, 4.22; Br, 33.49. Found: C, 37.34; H, 4.28; Br, 33.37. ^1H NMR (δ, CD_2Cl_2, 20 °C): 6.60 (m, 1H), 5.15 (m, 1H), 4.72 (m, 1H), 3.10 (d, 1 H, $^2J_{HH} = 18.6$ Hz), 2.11 (d, 1 H, $^2J_{HH} = 18.6$ Hz), 1.69 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 203.5 (C=O), 107.9, 107.3 (C_5Me_5), 73.6, 72.7, 41.4, 10.1 (C_5Me_5). IR(poly(chlorotrifluoroethylene), cm^{-1}): 1709 (s, $\nu_{C=O}$).

(8) Ru(IV)—allyl complexes have also been prepared by reaction of allyl halides with $[Ru(\eta^5\text{-}C_5Me_5)X_2]_n$ (X = Cl, Br) in ethanol (Nagashima, H.; Mukai, K.; Shiota, Y.; Yamaguchi, K.; Ara, K.; Fukahori, T.; Suzuki, H.; Akita, M.; Moro-oka, Y.; Itoh, K. *Organometallics* **1990**, *9*, 799). This method, however, failed for the synthesis of complex **2**.

(9) The syntheses of **1** were carried out as follows. (a) **2** (0.223 g, 0.47 mmol) was treated with $LiNH_2$ (1 equiv) in CH_3NO_2 (10 mL) at room temperature for 2 h. After filtration, diethyl ether was added, whereupon a red precipitate was formed, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 0.137 g (74%). (b) Treatment of **3** (8.67 g, 15.86 mmol) with excess water (ca. 100 mL) resulted in an immediate color change from olive green to dark red. Extraction with CH_2Cl_2 (150 mL) yielded, on removal of solvent, 6.1 g (97%) of **1**. Anal. Calcd for $C_{15}H_{19}BrORu$: C, 37.75; H, 4.22; Br, 33.49. Found: C, 37.66; H, 4.29; Br, 33.58. ^1H NMR (δ, CD_2Cl_2, 20 °C): 4.80 (m, $2H_\beta$), 3.82 (m, $2H_\alpha$), 1.83 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 182.2 (C=O), 98.1 (C_5Me_5), 86.0 (C_β), 68.9 (C_α), 11.1 (C_5Me_5). IR (poly(chlorotrifluoroethylene), cm^{-1}): 1678 (s, $\nu_{C=O}$).

(10) Characterization data for **3** are as follows. Anal. Calcd for $C_{16}H_{20}BrF_3O_4SRu$: C, 35.17; H, 3.69; Br, 14.62. Found: C, 35.20; H, 3.63; Br, 15.01. ^1H NMR (δ, CD_3NO_2, 20 °C): 5.17 (t, $1H_\beta$), 4.77 (t, $1H_\alpha$), 2.06 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, 20 °C): 169.7 (C—O), 105.8 (C_5Me_5), 89.0 (C_β), 70.1 (C_α), 12.2 (C_5Me_5). IR (poly(chlorotrifluoroethylene), cm^{-1}): 1538 (s, ν_{C-O}).

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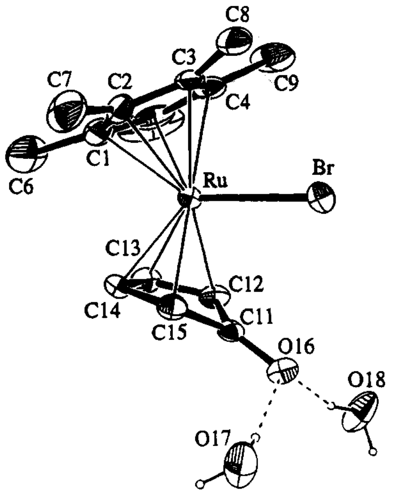

Figure 1. ORTEP drawing (30% ellipsoids) of Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br·2H_2O (4). Dotted lines are hydrogen bonds. Selected bond lengths (Å): Ru–Br, 2.535(1); Ru–C(1–5)$_{av}$, 2.221(8); Ru–C(12), 2.258(7); Ru–C(13), 2.126(8); Ru–C(14), 2.125(7); Ru–C(15), 2.239(7); C(11)–O(16), 1.240(8); C(11)–C(12), 1.450(10); C(11)–C(15), 1.465(10); C(12)–C(13), 1.389(10); C(13)–C(14), 1.420(11); C(14)–C(15), 1.378(11). Hydrogen bonds (Å): O(16)···O(17), 2.886(8); O(16)···O(18), 2.821(8); O(17)···O(18), 2.733(10); O(17)···O(18′), 2.792(10).

sparingly soluble in neat H_2O but very soluble in common organic solvents.

The unexpected bis(water) adduct Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br·2H_2O (4) crystallized within a few days from an acetone solution of 1 containing a slight excess of H_2O (≤5%), as shown in Figure 1. The ^1H and $^{13}C\{^1H\}$ NMR solution spectra of 4 are composed of the resonances of 1 together with those of free H_2O. Thus, the adduct is largely dissociated in solution. Though 4 has been isolated several times, the recovery of this product is quite erratic and the yields are variable, ranging from about 30 to 60%. It came as a surprise to find that from an aqueous solution containing ca. 5% acetone 1 crystallizes without any H_2O coordinated. An ad hoc interpretation of this observation is difficult because of the potentially complicated balance between a range of kinetic and thermodynamic effects. Perhaps the protic environment of the nearly pure water favors the hydrophobic preorganization of solute molecules during the crystallization process.

The solid-state structures of 1 and 4 have been established by IR spectroscopy and X-ray crystallography.[11,12] In the solid-state IR spectra of 1 and 4, the carbonyl stretching frequencies were observed at 1678 and 1640 cm^{-1}, respectively. Coordination of H_2O to the ketonic oxygen atom of the cyclopentadienyl ligand of 4, thus, leads to a significant increase of the C=O bond polarity.

The molecular arrangement of 4 consists of a Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br moiety with the ketonic oxygen atom of the C_5H_4O ligand connected via hydrogen bonds to a pair of H_2O molecules (Figure 1). The H_2O molecules are mutually linked via hydrogen bonds to form chains parallel to the *z* axis. By additional hydrogen bonds to the ketonic oxygen O(16) an unusual two-dimensional network of hydrogen bonds with 6- and 10-membered rings of oxygen atoms is formed parallel to (100) (Figure 2). The C(11)–O(16) bond in the dihydrate (1.240(8) Å) is slightly longer than the respective bond in the anhydrate 1 (1.216(5) Å).[11] The hydrogen bond distances between the ketonic oxygen O(16) and the two water molecules O(17) and O(18) are 2.886(8) and 2.821(8) Å, respectively, whereas the water–water hydrogen-bond distances with values of 2.733(10) and 2.792(10) Å, respectively, are slightly shorter.

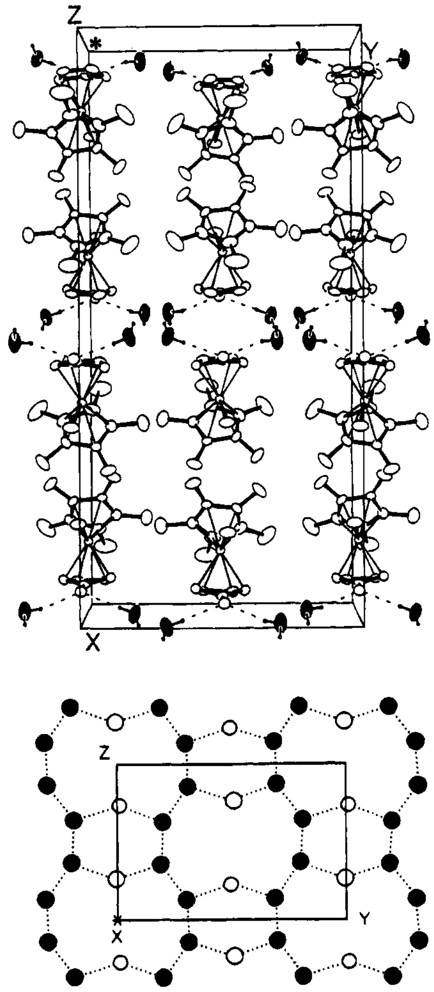

Figure 2. Unit cell of Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br·2H_2O (4) with water molecules as filled ellipsoids and hydrogen bonds as dotted lines (upper part). The water molecules form layerlike hydrophilic zones parallel to (100) alternating with hydrophobic zones of the metal complexes. A projection of the H-bonded network is shown in the lower part.

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[11] The X-ray crystal structure of complex 1 will be published separately.

[12] Crystal data for 4: $C_{15}H_{23}BrO_3Ru$, M_r = 432.3, red crystals, orthorhombic, space group *Pccn* (No. 56), *a* = 28.055(3) Å, *b* = 13.272(2) Å, *c* = 8.990(1) Å, *V* = 3347.4(7) Å^3, *Z* = 8, D_c = 1.716 g cm^{-3}, μ = 32.9 cm^{-1}, *F*(000) = 1728, *T* = 295 K. A plate (0.046 × 0.18 × 0.33 mm) was used for data collection (Philips PW1100 diffractometer, Mo Kα). Of 3372 reflections collected (θ_{max} = 25°, correction for Lorentz and polarization effects, and for absorption applied), 2950 were independent, and 1701 with $F_o \geq 4\sigma(F_o)$ were used for the least-squares refinement after solving the structure with direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions. At final convergence, *R* = 0.039 and R_w = 0.038 and the final difference electron-density synthesis showed minimum and maximum values of −0.45 and +0.41 e Å^{-3}.

To our knowledge, the formation of a hydrogen-bonded network involving water molecules and a carbonyl group leading to a crystal structure which consists of alternating hydrophilic and hydrophobic layers has no precedent in organometallic chemistry. Hydrogen bonding to ketonic functional groups like that in the cyclopentadienone ligand is well-known for organic acids such as phenol and hydroquinone.[13]

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Supplementary Material Available: Results of the crystal structure study of **4**, including tables of crystal data, positional and thermal parameters, bond distances and angles, dihedral angles, and least-squares planes and deviations therefrom (9 pages). Ordering information is given on any current masthead page.

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