Synthesis and Reactivity of $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-cyclopentadienone})$ Complexes. X-ray Structures of $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$, $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Br)Br$, and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_2O\text{-}2\text{-}Me,5\text{-}PCy_3)Br]CF_3SO_3$

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$Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$ (**1a**) and $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Me)Br$ (**1b**) are synthesized via the synthetic intermediates $Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_5H_5O)Br_2$ and $Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_5H_4O\text{-}2\text{-}Me)Br_2$. Complex **1a** crystallizes in the space group *Pnma* (No. 62), with $a = 11.080(2)$ Å, $b = 10.557(2)$ Å, $c = 12.225(2)$ Å, $V = 1430.0(5)$ Å^3, and $Z = 4$. The structure was refined to $R = 0.021$ and $R_w = 0.023$. Complexes **1a** and **1b** react with Br_2 to afford the bromo substituted η^3-cyclopentenoyl Ru(IV) complexes **2a** and **2b**. Bromine attack occurs exclusively α to the ketonic functional group and anti to the coordinated ruthenium. On addition of excess triflic acid, **2a** is shown to undergo facile conversion to $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}Br)Br]CF_3SO_3$ (**4**). Deprotonation of **4** with excess H_2O gives $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Br)Br$ (**5**) in 98% yield. Complex **5** has been found to crystallize in space group $P2_1/c$ (No. 14), with $a = 9.606(2)$ Å, $b = 13.421(4)$ Å, $c = 12.946(4)$ Å, $\beta = 111.46(1)°$, $V = 1553.3(7)$ Å^3, and $Z = 4$. The structure was refined to $R = 0.027$ and $R_w = 0.026$. Cationic complexes $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)(CH_3CN)]^+$ (**7a**), $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Me)(CH_3CN)]^+$ (**7b**), and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}PCy_3)(CH_3CN)]^{2+}$ (**10**) are prepared by the action of $AgCF_3SO_3$ on **1a**, **1b**, and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}PCy_3)Br]^+$ (**9a**$_1$), respectively. Complex **7a** reacts readily with nucleophiles (Nuc = PCy_3 and $PPhMe_2$) to form regioselectively $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}Nuc)]^+$ (**8a**$_1$, **8a**$_2$). PPh_3 did not react with **7a**. Complexes **8a**$_1$ and **8a**$_2$ undergo facile oxidation with Br_2 to give **9a**$_1$ and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}PPhMe_2)Br]^+$ (**9a**$_2$), respectively. In analogous fashion, $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_2O\text{-}2\text{-}Me,\ 5\text{-}PCy_3)Br]^+$ (**9b**) is obtained on treatment of **7b** with PCy_3 and subsequent oxidation with Br_2. A single crystal structural study has been carried out for this complex. The space group is $P2_1/c$ (No. 14), with $a = 12.226(2)$ Å, $b = 16.304(3)$ Å, $c = 18.803(3)$ Å, $\beta = 93.75(1)°$, $V = 3740(1)$ Å^3, and $Z = 4$. The structure was refined to $R = 0.036$ and $R_w = 0.037$.

Introduction

Recent interest in the chemistry of transition metal complexes with cyclopentadienones as ligands stems from the paucity of examples and what appears to be an inherently rich reaction chemistry.[2] We previously reported the synthesis and reactivity of various neutral and cationic $Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-cyclopentadienone})$ complexes.[3,4] The multifunctionality of the cyclopentadienone ligands accounts for much of the unusual chemistry discovered (i) being able to react at the terminus of a coordinated 1,3-diene[5] and (ii), in contrast to simple 1,3-diene ligands, being able to act both as a $2e^-$ oxidizing agent and as a H^+ acceptor.

Here we report on the synthesis and reactivity of $Ru(C_5Me_5)(\eta^4\text{-cyclopentadienone})$ complexes. When the parent C_5H_5 ion is replaced by its more electron-donating and more bulky permethylated derivative C_5Me_5, the chemistry of the $Ru(\eta^4\text{-cyclopentadienone})$ moiety might change significantly. A preliminary account has already been published showing that the presence of methyl groups makes the ketonic oxygen of the cyclopentadienone ligand more basic such that adducts with Lewis acids are formed readily.[6] Another aspect of the change in reactivity in going to more electron-rich complexes is an increased stabilization of higher oxidation states.

Experimental Section

General Information. Manipulations were performed under an inert atmosphere of purified nitrogen by using

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standard Schlenk techniques and/or a glovebox unless otherwise noted. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[7] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. IR spectra were obtained on a Mattson RS1 FTIR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC 250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to $SiMe_4$. Microanalyses were done by the Microanalytical Laboratories, University of Vienna. $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$ (**1a**) has been synthesized according to the literature.[6]

Synthesis. $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Me)Br$ (1b). This compound was prepared according to a literature method.[6] Yield: 57%. Anal. Calcd for $C_{16}H_{21}BrORu$: C, 46.84; H, 5.16; Br, 19.47. Found: C, 46.52; H, 5.12; Br, 19.66. ^1H NMR (δ, CD_2Cl_2, 20 °C): 4.74 (m, 1H), 4.64 (t, 1H), 3.73 (m, 1H), 1.81 (s, 15H), 1.38 (s, 3H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 181.8 (C=O), 97.4 (C_5Me_5), 86.9, 84.8, 83.4, 65.6, 11.1 ($C_5\mathit{Me}_5$), 9.7 (Me). IR (poly(chlorotrifluoroethylene), cm^{-1}): 1668 (s, $\nu_{C=O}$).

$Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_5H_4O\text{-}5\text{-}Br)Br_2$ (2a). At −50 °C, Br_2 (43 μL, 0.840 mmol) dissolved in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of **1a** (317 mg, 0.800 mmol) in CH_2Cl_2 (10 mL) within a period of 1 h. The solution was then warmed to room temperature, and the volatiles were removed under vacuum. The remaining solid was redissolved in CH_2Cl_2 (2 mL), and undissolved materials were removed by filtration. On addition of anhydrous diethyl ether, a red precipitate was formed which was collected on a glass frit and dried under vacuum. Yield: 367 mg (83%). Anal. Calcd for $C_{15}H_{19}Br_3ORu$: C, 32.40; H, 3.44; Br, 43.11. Found: C, 32.37; H, 3.35; Br, 42.93. ^1H NMR (δ, $CDCl_3$, 20 °C): 6.74 (m, 1H), 5.36 (m, 1H), 4.79 (m, 1H), 4.19 (m, 1H), 1.79 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 196.6 (C=O), 109.1 (C_5Me_5), 106.2, 71.5, 68.3, 49.9 (*C*HBr), 10.4 ($C_5\mathit{Me}_5$).

$Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_5H_3O\text{-}2\text{-}Me,5\text{-}Br)Br_2$ (2b). This complex was synthesized analogously to **2a** with **1b** as starting material. Yield: 77%. Anal. Calcd for $C_{16}H_{21}Br_3ORu$: C, 33.71; H, 3.71; Br, 42.05. Found: C, 33.48; H, 3.66; Br, 42.21. ^1H NMR (δ, $CDCl_3$, 20 °C): 6.54 (m, 1H), 5.47 (m, 1H), 4.26 (s, 1H), 1.68 (s, 15H), 1.53 (s, 3H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 197.1 (C=O), 108.5 (C_5Me_5), 107.7, 71.1, 69.1, 49.5 (*C*HBr), 11.1 ($C_5\mathit{Me}_5$), 9.9 (Me).

Attempted Reaction of 2a with Pyridine. This reaction was performed on a scale suitable for a NMR experiment. **2a** (50 mg, 0.090 mmol) was dissolved in 0.5 mL of CD_2Cl_2 and treated with pyridine (7.3 μL, 0.090 mmol). The reaction mixture were loaded into a NMR tube, and a ^1H NMR spectrum was recorded after 1 h showing complete decomposition of **2a** to several as yet not identified products.

$[Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_5H_3O\text{-}2\text{-}Me,5\text{-}py)Br_2]Br$ (3). A solution of **2b** (215 mg, 0.377 mmol) in CH_2Cl_2 (5mL) and pyridine (31 μL, 0.377 mmol) was stirred for 1 h. Addition of diethyl ether afforded 235 mg (96%) of analytically pure **3**. Anal. Calcd for $C_{21}H_{26}Br_3NORu$: C, 38.85; H, 4.04; Br, 36.92. Found: C, 38.87; H, 3.95; Br, 36.82. ^1H NMR (δ, CD_3NO_2, 20 °C): 9.32 (m, 2H), 8.68 (m, 1H), 8.20 (m, 2H), 6.92 (m, 1H), 5.47 (m, 1H), 5.06 (m, 1H), 1.87 (s, 15H), 1.61 (s, 3H).

$[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}Br)Br]CF_3SO_3$ (4). A solution of **2a** (204 mg, 0.367 mmol) in CH_2Cl_2 (10 mL) was treated with neat triflic acid (2.5 equiv) at 0 °C, whereupon the red solution rapidly turned olive-green. On addition of anhydrous diethyl ether, a microcrystalline green solid was slowly formed. Filtration, followed by washing with diethyl ether, gave 222 mg (97%) of **4**. Anal. Calcd for $C_{16}H_{19}Br_2F_3O_4RuS$: C, 30.74; H, 3.06; Br, 25.56; S, 5.13. Found: C, 30.71; H, 3.12; Br, 25.36; S, 5.25. ^1H NMR (δ, CD_3NO_2, 20 °C): 5.36 (m, 1H), 5.23 (m, 1H), 4.89 (m, 1H), 2.06 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, 20 °C): 166.4 (C-O), 106.5 (C_5Me_5), 89.3, 87.1, 69.3, 69.1, 12.0 ($C_5\mathit{Me}_5$).

$Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Br)Br$ (5). Treatment of **4** (220 mg, 0.352 mmol) with excess water (ca. 50 mL) resulted in an immediate color change from olive-green to dark red. Extraction with CH_2Cl_2 (50 mL) yielded, on removal of the solvent, 164 mg (98%) of **5**. Anal. Calcd for $C_{15}H_{18}Br_2ORu$: C, 37.91; H, 3.82; Br, 33.63. Found: C, 37.31; H, 3.86; Br, 34.01. ^1H NMR (δ, CD_2Cl_2, 20 °C): 4.93 (dd, J = 3.3 Hz, J = 1.6 Hz, 1H), 4.78 (dd, J = 4.0 Hz, J = 3.3 Hz, 1H), 3.95 (dd, J, = 4.0 Hz, J = 1.6 Hz, 1H), 1.84 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 176.0 (C=O), 99.3 (C_5Me_5), 85.4, 84.7, 72.1, 68.4, 11.1 ($C_5\mathit{Me}_5$).

$Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_5H_3O\text{-}2,5\text{-}Br_2)Br_2$ (6). A 5 mm NMR tube was charged with **5** (30 mg, 0.063 mmol) in CD_2Cl_2 (0.5 mL) and was capped with a septum. Br_2 (ca. 3.3 μL, 0.063 mmol) was added by syringe, and the sample was transferred to a NMR probe. ^1H and $^{13}C\{^1H\}$NMR spectra were immediately recorded and showed essentially quantitative formation of **6**. Attempts to isolate this complex, however, were unsuccessful. ^1H NMR (δ, CD_2Cl_2, 20 °C): 6.71 (dd, J = 4.2 Hz, J = 1.9 Hz, 1H), 5.55 (dd, J = 4.2 Hz, J = 1.1 Hz, 1H), 4.37 (dd, J = 1.9 Hz, J = 1.1 Hz, 1H), 1.73 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 190.7 (C=O), 110.0 (C_5Me_5), 104.6, 76.1, 66.6, 47.2 (*C*HBr), 10.4 ($C_5\mathit{Me}_5$).

$[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)(CH_3CN)]CF_3SO_3$ (7a). **1a** (1.05 g, 2.65 mmol) was dissolved in 10 mL of CH_3CN. $AgCF_3SO_3$ (0.8 g, 2.65 mmol) was added, and the mixture was stirred for 2 h. The resulting precipitate of AgBr was removed by filtration, and the volatiles were removed under vacuum. The crude product was chromatographed with CH_3CN on an alumina column. Reduction of the volume of the solution, under vacuum, to about 5 mL and addition of diethyl ether gave bright yellow microcrystals. Yield: 0.84 g (63%). Anal. Calcd for $C_{18}H_{22}F_3NO_4RuS$: C, 42.68; H, 4.38; N, 2.77; S, 6.33. Found: C, 42.65; H, 4.32; N, 2.81; S, 6.50. ^1H NMR (δ, CD_3NO_2, 20 °C): 5.46 (m, $2H_\beta$), 4.31 (m, $2H_\alpha$), 2.66 (s, 3H), 1.93 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 182.9 (C=O), 124.9 (CN), 102.1 (C_5Me_5), 92.8 (C_β), 73.1 (C_α), 11.1 ($C_5\mathit{Me}_5$), 5.0 (Me).

$[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Me)(CH_3CN)]CF_3SO_3$ (7b). This complex was synthesized analogously to **7a** with **1b** as starting material. Yield: 59%. Anal. Calcd for $C_{19}H_{24}F_3NO_4RuS$: C, 43.84; H, 4.65; N, 2.69; S, 6.16. Found: C, 43.54; H, 4.56; N, 2.71; S, 6.05. ^1H NMR (δ, CD_2Cl_2, 20 °C): 5.48 (m, 1H), 5.31 (t, 2H), 4.40 (m, 1H), 2.83 (s, 3H), 2.03 (s, 15H), 1.67 (s, 3H). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 185.8 (C=O), 124.1 (CN), 100.9 (C_5Me_5), 93.0, 90.1, 89.7, 70.2, 11.2 ($C_5\mathit{Me}_5$), 9.5 (Me), 6.1 (Me).

$[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}PCy_3)]CF_3SO_3$ (8a₁). A solution of **7a** (231 mg, 0.456 mmol) in CH_3CN (5 mL) was treated with PCy_3 (134 mg, 0.456 mmol), and the mixture was stirred for 2 h. The solution was then evaporated to dryness, and in order to remove unreacted PCy_3, the solid residue was washed three times with anhydrous diethyl ether (10 mL). The crude product was redissolved in CH_2Cl_2 (5 mL), and undissolved materials were removed by filtration. Solvent removal under vacuum, followed by washing with diethyl ether, gave 316 mg (93%) of analytically pure **8a**. Anal. Calcd for $C_{34}H_{52}F_3O_4PRuS$: C, 54.75; H, 7.03; P, 4.15. Found: C, 54.80; H, 6.98; P, 4.23. ^1H NMR (δ, CD_2Cl_2, 20 °C): 7.82 (br, 1H), 4.67 (m, 1H), 4.10 (m, 1H), 3.95 (m, 1H), 2.63−1.30 (m, 33H), 1.81 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 125.8 (d, J_{CP} = 7.0 Hz, C−O), 87.3 (C_5Me_5), 73.7 (d, J_{CP} = 8.6 Hz), 69.1 (d, J_{CP} = 8.3 Hz), 68.7 (d, J_{CP} = 9.2 Hz), 47.9 (d, J_{CP} = 85.0 Hz), 31.3 (d, J_{CP} = 44.2 Hz, PCy_3), 27.6−25.8 (PCy_3), 11.1 ($C_5\mathit{Me}_5$).

$[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}PPhMe_2)]CF_3SO_3$ (8a₂). This complex was synthesized analogously to **8a₁** with **7a** and $PPhMe_2$ as starting material. Yield: 91%. Anal. Calcd for $C_{24}H_{30}F_3O_4PRuS$: C, 47.76; H, 5.01; P, 5.13. Found: C, 47.52; H, 5.11; P, 5.01. ^1H NMR (δ, CD_3NO_2, 20 °C): 7.70−7.30 (m,

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5H), 4.58 (m, 1H), 4.26 (m, 2H), 2.42 (d, J_{HP} = 14.6 Hz, 3H), 2.26 (d, J_{HP} = 14.0 Hz, 3H), 1.95 (s, 15H).

Attempted Reaction of 7a with PPh_3. This reaction was performed on a scale suitable for a NMR experiment. **7a** (20 mg, 0.059 mmol) was dissolved in 0.5 mL of CD_3NO_2 and treated with PPh_3 (30 mg, 0.118 mmol). The reaction mixture were loaded into a NMR tube, and a ^1H NMR spectrum was recorded. After 3 days, no reaction had occurred, and ≥97% of **7a** remained.

[Ru(η^5-C_5Me_5)(η^4-C_5H_3O-2-PCy_3)Br]CF_3SO_3 ($9a_1$). To a solution of $8a_1$ (350 mg, 0.469 mmol) in CH_2Cl_2 (5 mL) was added Br_2 (25 μL, 0.493 mmol) by syringe, and the mixture was stirred for 1 h at room temperature. Upon addition of diethyl ether, a red precipitate was immediately formed, which was collected on a glass frit, washed with diethyl ether, and air-dried. The crude product was then redissolved in CH_2Cl_2 (2 mL), and solid materials were removed by filtration. Addition of diethyl ether resulted in the precipitation of $9a_1$ as a microcrystaline red powder. Yield: 321 mg (83%). Anal. Calcd for $C_{34}H_{51}BrF_3O_4PRuS$: C, 49.51; H, 6.23; P, 3.76; Br, 9.69. Found: C, 49.48; H, 6.20; P, 3.81; Br, 9.82. ^1H NMR (δ, $CDCl_3$, 20 °C): 5.80 (m, 1H), 5.65 (m, 1H), 4.14 (m, 1H), 2.50–1.30 (m, 33H), 1.96 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 180.5 (C=O), 101.3 (C_5Me_5), 91.3 (d, J_{CP} = 7.8 Hz), 89.8 (d, J_{CP} = 7.4 Hz), 74.3 (d, J_{CP} = 10.7 Hz), 55.1 (d, J_{CP} = 120.4 Hz), 32.3 (d, J_{CP} = 40.8 Hz, PCy_3), 27.5–25.9 (PCy_3), 12.3 (C_5Me_5).

[Ru(η^5-C_5Me_5)(η^4-C_5H_3O-2-$PPhMe_2$)Br]CF_3SO_3 ($9a_2$). This complex was synthesized analogously to $9a_1$ with $8a_2$ as starting material. Yield: 76%. Anal. Calcd for $C_{24}H_{29}BrF_3O_4PRuS$: C, 42.24; H, 4.28; P, 4.54; Br, 11.71. Found: C, 42.20; H, 4.32; P, 4.44; Br, 11.69. ^1H NMR (δ, CD_3CN, 20 °C): 7.87–7.64 (m, 5H), 5.65 (m, 1H), 5.41 (m, 1H), 4.14 (m, 1H), 2.22 (d, J_{HP} = 14.8 Hz), 2.14 (d, J_{HP} = 15.0 Hz, 3H), 1.78 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, CD_3CN, 20 °C): 180.7 (d, J_{CP} = 7.3 Hz, C=O), 135.6 (d, J_{CP} = 9.3 Hz, Ph), 132.4 (d, J_{CP} = 10.6 Hz, Ph), 130.8 (d, J_{CP} = 12.5 Hz, Ph), 123.4 (d, J_{CP} = 103.0 Hz, Ph), 102.2 (C_5Me_5), 90.4 (d, J_{CP} = 10.7 Hz), 86.8 (d, J_{CP} = 10.6 Hz), 73.9 (d, J_{CP} =10.3 Hz), 59.8 (d, J_{CP} = 83.8 Hz), 11.4 (C_5Me_5), 9.9 (d, J_{CP} = 57.7 Hz, Me), 9.0 (d, J_{CP} = 60.1 Hz, Me).

[Ru(η^5-C_5Me_5)(η^4-C_5H_2O-2-Me,5-PCy_3)Br]CF_3SO_3 (9b). A solution of **7b** (256 mg, 0.492 mmol) in CH_3CN (5 mL) was treated with PCy_3 (138 mg, 0.492 mmol), and the reaction mixture was stirred for 2 h at room temperature. After removal of the solvent, the solid residue was washed three times with anhydrous diethyl ether (10 mL). The crude product was redissolved in CH_2Cl_2 (5 mL), possible undissolved materials were removed by filtration, Br_2 (26 μL, 0.516 mmol) was added by syringe, and the reaction mixture was stirred for 1 h. Upon addition of diethyl ether a red precipitate was formed which was collected on a glass frit, washed with diethyl ether, and air-dried. Yield: 322 mg (78%). Anal. Calcd for $C_{35}H_{53}BrF_3O_4PRuS$: C, 50.12; H, 6.73; P, 3.69; Br, 9.53. Found: C, 50.21; H, 6.69; P, 3.58; S, 9.78. ^1H NMR (δ, CD_2Cl_2, 20 °C): 5.46 (d, 1H), 5.21 (t, 1H), 2.36 (m, 3H), 2.10–1.10 (m, 30H), 1.96 (s, 15H), 1.44 (s, 3H).

[Ru(η^5-C_5Me_5)(η^4-C_5H_3O-2-PCy_3)(CH_3CN)]$(CF_3SO_3)_2$ (10). $AgCF_3SO_3$ (50 mg, 0.204 mmol) was added to a flask containing a solution of $9a_1$ (168 mg, 0.204 mmol) in acetonitrile (3 mL). After the reaction mixture was stirred for 1 h, the precipitate of AgBr formed in this reaction was removed by filtration and the crude product was precipitated with diethyl ether as an orange-brown solid. In order to remove AgBr completely, the complex was redissolved in CH_2Cl_2 (3ml) and solid materials were removed by filtration. Analytically pure product was obtained upon precipitation with diethyl ether. Yield: 93 mg (45%). Anal. Calcd for $C_{37}H_{54}F_6NO_7PRuS_2$: C, 43.79; H, 5.36; N, 1.38; S, 6.32. Found: C, 43.67; H, 5.32; N, 1.42; S, 6.40. ^1H NMR (δ, CD_2Cl_2, 20 °C): 6.38 (m, 1H), 5.85 (m, 1H), 4.78 (m, 1H), 2.50 (m, 3H), 2.10–1.10 (m, 30H), 2.00 (s, 15H).

Table 1. Crystal Data for 1a, 5, and 9b

	1a	5	9b
formula	$C_{15}H_{19}BrORu$	$C_{15}H_{18}Br_2ORu$	$C_{35}H_{53}BrF_3O_4PRuS$
fw	396.29	475.18	838.80
space group	*Pnma* (No. 62)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	11.080 (2)	9.606(2)	12.226(2)
b, Å	10.557(2)	13.421(4)	16.304(3)
c, Å	12.225(2)	12.946(4)	18.803(3)
β, deg		111.46(1)	93.75(1)
V, Å^3	1430.0(5)	1553.3(7)	3740(1)
Z	4	4	4
ϱ_{calc}, g cm^{-3}	1.841	2.032	1.490
T, K	297	296	296
μ, cm^{-1}	40.7 (Mo Kα)	60.8 (Mo Kα)	16.1 (Mo Kα)
no. of data refined	1346	2079	4696
no. of LS params	99	189	436
R^a	0.021	0.027	0.036
R_w^b	0.023	0.026	0.037
GOF	1.33	1.32	1.85

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

Table 2. Atomic Positional and Isotropic Displacement Parameters (Å^2) for Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br (1a)

	x/a	*y/b*	*z/c*	U_{eq}^a
Ru	0.36573(2)	1/4	0.47842(2)	0.0268(1)
Br	0.57650(4)	1/4	0.39525(4)	0.0543(2)
C(1)	0.1708(3)	1/4	0.4462(3)	0.036(1)
C(2)	0.2202(2)	0.1393(2)	0.3943(2)	0.035(1)
C(3)	0.3028(2)	0.1812(2)	0.3149(2)	0.032(1)
C(6)	0.0668(4)	1/4	0.5261(3)	0.055(2)
C(7)	0.1835(3)	0.0046(3)	0.4154(3)	0.051(1)
C(8)	0.3678(2)	0.1014(3)	0.2325(2)	0.048(1)
C(11)	0.5268(4)	1/4	0.6359(3)	0.046(1)
C(12)	0.4455(3)	0.1418(3)	0.6185(2)	0.053(1)
C(13)	0.3287(3)	0.1837(3)	0.6398(2)	0.065(1)
O	0.6334(3)	1/4	0.6595(3)	0.064(1)

^{a} $U_{eq} = 1/3\sum_i\sum_j U_{ij}a_ia_j(\mathbf{a_i}\mathbf{a_j})$.

Crystallography. Crystal data and experimental details are given in Table 1. X-ray data were collected on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo Kα (λ = 0.710 69 Å) radiation and the θ - 2θ scan technique. Three representative reference reflections were measured every 120 min and used to correct for crystal decay and system instability. Data reduction included corrections for Lorentz, polarization, and absorption effects. The program SHELX76[8] was used for structure solution and refinement; the XTAL3.2[9] suite of programs was used to produce molecular diagrams and tabular matter.

Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br (1a). A red prismatic crystal fragment with dimensions of 0.16 × 0.17 × 0.44 mm was used to measure the intensities of 3448 reflections with θ < 27°, 0 ≤ *h* ≤ 14, 0 ≤ *k* ≤ 13, −15 ≤ *l* ≤ 15. Merging gave 1654 unique data (R_{merge} = 0.017 on F). The positions of Ru and Br were found via direct methods, the remaining atoms from difference Fourier maps. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were initially calculated from the C-atom positions and then refined as parts of rigid groups (CH_3) or riding with the atoms to which they were bonded (C_5H_4O; for all H-atoms, C−H = 0.96 Å). The final full-matrix least-squares [$F_o \geq 6\sigma(F_o)$], minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$, yielded the positional parameters given in Table 2.

Ru(η^5-C_5Me_5)(η^4-C_5H_3O-2-Br)Br (5). A red prismatic crystal fragment with dimensions of 0.09 × 0.13 × 0.30 mm was used to measure the intensities of 3049 reflections with θ < 25°, 0 ≤ *h* ≤ 11, 0 ≤ *k* ≤ 15, −15 ≤ *l* ≤ 14; 2747 of these

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Table 3. Atomic Positional and Isotropic Displacement Parameters (Å²) for Ru(η^5-C_5Me_5)(η^4-C_5H_3O-2-Br)Br (5)

	x/a	y/b	z/c	U_{eq}[a]
Ru	0.38173(4)	0.44844(3)	0.25857(3)	0.0271(1)
Br(1)	0.45764(6)	0.29907(4)	0.38867(4)	0.0431(2)
Br(2)	0.64534(6)	0.34501(4)	0.14568(4)	0.0505(2)
C(1)	0.1918(5)	0.5327(3)	0.1427(3)	0.033(2)
C(2)	0.1579(5)	0.5153(3)	0.2400(3)	0.035(2)
C(3)	0.1486(5)	0.4118(3)	0.2522(4)	0.035(2)
C(4)	0.1780(5)	0.3625(3)	0.1619(3)	0.034(2)
C(5)	0.2010(5)	0.4374(3)	0.0935(3)	0.033(2)
C(6)	0.1921(6)	0.6329(3)	0.0909(4)	0.044(2)
C(7)	0.1250(6)	0.5940(4)	0.3099(4)	0.051(2)
C(8)	0.0977(6)	0.3609(4)	0.3357(4)	0.052(2)
C(9)	0.1686(6)	0.2534(4)	0.1380(5)	0.051(2)
C(10)	0.2250(6)	0.4221(4)	−0.0142(4)	0.046(2)
C(11)	0.6761(5)	0.4440(4)	0.3575(4)	0.042(2)
C(12)	0.5965(5)	0.4376(3)	0.2358(4)	0.035(2)
C(13)	0.5250(5)	0.5299(3)	0.1974(4)	0.038(2)
C(14)	0.5188(5)	0.5816(3)	0.2920(5)	0.047(2)
C(15)	0.5874(5)	0.5220(4)	0.3865(4)	0.045(2)
O	0.7816(4)	0.3955(3)	0.4150(3)	0.060(2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_ia_j(\mathbf{a}_i\mathbf{a}_j)$.

reflections were independent. The positions of Ru and Br were found via direct methods, the remaining atoms from difference Fourier maps. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were found from a difference Fourier map and were refined either as parts of rigid CH_3 groups or riding with the carbon atoms to which they were bonded (C_5H_3OBr; all C−H distances idealized at 0.96 Å). A single variable multiplied with U_{eq} values of the carrier carbon atoms was used for the isotropic temperature factors of the hydrogen atoms. The final refinement by full-matrix least-squares [$F_o \geq 6\sigma(F_o)$] minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$, and gave the parameters presented in Table 3.

[Ru(η^5-C_5Me_5)(η^4-C_5H_2O-2-Me, 5-PCy_3)Br]CF_3SO_3 (9b). A red prismatic crystal with dimensions of 0.18 × 0.25 × 0.60 mm was used to measure the intensities of 7204 reflections with $\theta < 25°$, $-22 \leq h \leq 22$, $0 \leq k \leq 19$, $0 \leq l \leq 14$; 6621 of these reflections were independent. The positions of Ru and Br were found via direct methods, the remaining atoms from difference Fourier maps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in calculated positions (C−H = 0.96 Å) and were refined either as parts of rigid CH_3 groups or riding with the carbon atoms to which they were bonded (CH and CH_2). The isotropic temperature factors of the H-atoms were refined with two variables (one for CH and CH_2, one for CH_3) that were multiplied with the U_{eq} values of the carrier carbon atoms. The final large block matrix least-squares [$F_o \geq 6\sigma(F_o)$] minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$, and gave the parameters shown in Table 4.

Table 4. Atomic Positional and Isotropic Displacement Parameters (Å²) for [Ru(η^5-C_5Me_5)(η^4-C_5H_3O-2-Me, 5-PCy_3)Br]CF_3SO_3 (9b)

	x/a	y/b	z/c	U_{eq}[a]
Ru	0.14402(3)	0.08742(2)	0.23151(2)	0.0333(1)
Br	0.24989(4)	0.13645(3)	0.34438(2)	0.0562(2)
C(1)	0.1941(3)	−0.0385(2)	0.2725(2)	0.049(2)
C(2)	0.0882(4)	−0.0162(3)	0.2948(2)	0.049(2)
C(3)	0.0168(3)	−0.0079(2)	0.2334(2)	0.045(1)
C(4)	0.0798(3)	−0.0212(2)	0.1722(2)	0.042(1)
C(5)	0.1896(3)	−0.0407(2)	0.1973(2)	0.044(1)
C(6)	0.2917(4)	−0.0640(3)	0.3210(3)	0.073(2)
C(7)	0.0557(5)	−0.0138(3)	0.3706(2)	0.077(2)
C(8)	−0.1050(3)	0.0049(3)	0.2316(3)	0.060(2)
C(9)	0.0353(4)	−0.0283(3)	0.0966(2)	0.059(2)
C(10)	0.2780(4)	−0.0693(3)	0.1518(3)	0.064(2)
C(11)	0.1715(3)	0.2480(2)	0.2218(2)	0.042(1)
C(12)	0.0625(3)	0.2132(2)	0.2352(2)	0.046(1)
C(13)	0.0272(3)	0.1680(3)	0.1760(2)	0.047(1)
C(14)	0.1182(3)	0.1526(2)	0.1337(2)	0.038(1)
C(15)	0.2124(3)	0.1920(2)	0.1662(2)	0.034(1)
C(16)	−0.0063(4)	0.2454(3)	0.2926(3)	0.076(2)
O(1)	0.2163(2)	0.3070(2)	0.2501(2)	0.052(1)
P	0.33457(8)	0.21304(6)	0.12230(5)	0.0335(3)
C(17)	0.3355(3)	0.3232(2)	0.1068(2)	0.037(1)
C(18)	0.2287(3)	0.3595(2)	0.0707(2)	0.044(1)
C(19)	0.2342(4)	0.4529(3)	0.0733(2)	0.052(2)
C(20)	0.3352(3)	0.4851(3)	0.0401(2)	0.051(2)
C(21)	0.4386(3)	0.4473(3)	0.0747(2)	0.052(2)
C(22)	0.4358(3)	0.3541(3)	0.0709(2)	0.046(1)
C(23)	0.4599(3)	0.1896(2)	0.1767(2)	0.037(1)
C(24)	0.4785(3)	0.2447(3)	0.2427(2)	0.050(2)
C(25)	0.5876(4)	0.2240(3)	0.2825(3)	0.066(2)
C(26)	0.5954(4)	0.1335(3)	0.3023(3)	0.069(2)
C(27)	0.5773(4)	0.0800(3)	0.2372(2)	0.061(2)
C(28)	0.4674(3)	0.0988(2)	0.1974(2)	0.045(1)
C(29)	0.3317(3)	0.1508(2)	0.0408(2)	0.038(1)
C(30)	0.4446(3)	0.1394(3)	0.0113(2)	0.049(2)
C(31)	0.4370(4)	0.0808(3)	−0.0521(2)	0.062(2)
C(32)	0.3540(4)	0.1099(3)	−0.1096(2)	0.066(2)
C(33)	0.2432(4)	0.1221(3)	−0.0808(2)	0.054(2)
C(34)	0.2504(3)	0.1829(3)	−0.0184(2)	0.043(1)
S	0.7698(2)	0.1903(2)	0.0471(1)	0.116(1)
O(2)	0.8304(7)	0.1230(3)	0.0507(3)	0.205(4)
O(3)	0.7522(7)	0.2225(5)	0.1091(4)	0.247(5)
O(4)	0.6829(5)	0.190(1)	−0.0040(5)	0.409(9)
C(35)	0.8504(8)	0.2677(6)	0.0067(5)	0.130(4)
F(1)	0.8173(6)	0.3374(3)	−0.0009(4)	0.229(4)
F(2)	0.8539(8)	0.2454(4)	−0.0607(4)	0.269(5)
F(3)	0.9413(6)	0.2743(5)	0.0402(6)	0.329(6)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_ia_j(\mathbf{a}_i\mathbf{a}_j)$.

Results and Discussion

Synthesis and Reactivity of Neutral Ru(η^5-C_5Me_5)(η^4-cyclopentadienone) Complexes. As we previously reported,[6] the η^3-cyclopentenoyl Ru(IV) complex Ru(η^5-C_5Me_5)(η^3-C_5H_5O)Br_2, prepared by the action of [Ru(η^5-C_5Me_5)Br]$_4$[10] on 4-bromo-2-cyclopenten-1-one,[11] is a convenient precursor for the synthesis of Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br (**1a**). The methyl-substituted derivative, Ru(η^5-C_5Me_5)(η^4-C_5H_3O-2-Me)Br (**1b**), was prepared in analogous fashion by utilizing 4-bromo-2-methylcyclopenten-1-one[11] as starting material. **1a** and **1b** are fully characterized by a combination of elemental analysis, IR, and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

In the IR spectra of **1a** and **1b**, the carbonyl stretching frequencies are observed at 1678 and 1668 cm^{-1}, respectively, consistent with other cyclopentadienone complexes.[2a,3a-c,4,12] These values are slightly lower than are the frequencies for the free ligand observed at 1727 and 1724 cm^{-1}.[13] Thus, as expected, coordination leads to a decrease of the C=O bond strength. In the ^1H NMR spectrum of **1a**, the cyclopentadienone ligand displays an AA'XX' splitting pattern of two apparent multiplets at 4.80 (2H) and 3.82 ppm (2H) assignable to the β and α protons, respectively. The cyclopentadienone ligand of **1b** exhibits three multiplets centered at 4.74 ($1H_\beta$), 4.64 ($1H_\beta$), and 3.73 ppm ($1H_\alpha$) and a singlet resonance of the methyl group at 1.38 ppm (3H). The $^{13}C\{^1H\}$ NMR spectra of **1a** and **1b** exhibit a characteristic

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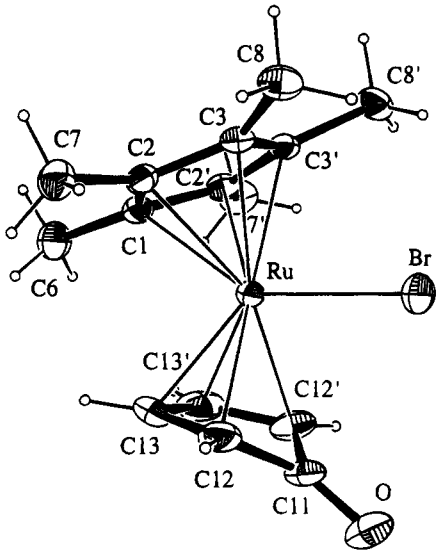
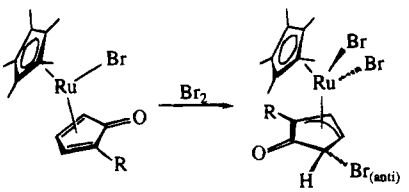


Figure 1. Structural view of $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)$ (**1a**).

Scheme 1



1a R = H
1b R = Me
5 R = Br

2a, 2b, 6

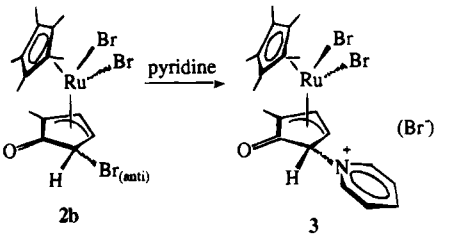
singlet assigned to the resonances of the "carbonyl" carbon at 182.2 and 181.8 ppm, respectively. A structural view of **1a** as determined by X-ray diffraction is depicted in Figure 1.

On treatment of **1a** and **1b** with 1 equiv of Br_2 at −50 °C, η^3-cyclopentenoyl Ru(IV) complexes **2a** and **2b** are obtained in 83 and 77% yields, respectively (Scheme 1). Both complexes are characterized by means of ^1H and $^{13}C\{^1H\}$ NMR and elemental analysis.

The allyl protons of the cyclopentenoyl ligand in **2a** resonate at 6.74 (central allyl proton, H^3), 5.36 (H^4), and 5.79 ppm (H^2), while the aliphatic proton gives rise to a multiplet at 4.19 (H_{syn}, with respect to Ru). Complex **2b** exhibits a spectrum similar to that of **2a**, but with important differences resulting from the presence of the methyl substituent (see Experimental Section). The ^{13}C NMR spectra of **2a** and **2b** bear no unusual features, with the characteristic resonance of the "carbonyl" carbon observed at 196.6 and 197.1 ppm, respectively.

Bromine addition to the η^4-cyclopentadienone ligand occurs exclusively α to the ketone functional group and anti to the coordinated ruthenium. Formation of **2a** and **2b** is, thus, most likely to proceed through a cationic $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-cyclopentadienone})Br_2]^+$ intermediate followed by nucleophilic attack of the remaining bromide counterion from an antifacial direction. The enhanced reactivity of cyclopentadienone is a consequence of the strong electron-withdrawing effect of the Ru(IV) metal center. Removal of charge typically dominates at the α-carbon atoms and is, thus, the preferred site of a nucleophilic attack.[5] Confirmation of the regioselectivity of this process was readily apparent from the

Scheme 2



2b **3**

spectroscopic characterization of the products. Proof of the stereospecific anti addition was obtained through a 2-D NOE experiment, performed on **2a** and **2b** in CD_2Cl_2 as a solvent, showing a strong interaction between the protons of the C_5Me_5 ligand and the aliphatic proton of the cyclopentenoyl moiety. This latter proton is, therefore, unequivocally syn with respect to the metal center. The experiment also demonstrates that **2a** and **2b** adopt the endo conformation with respect to the orientation of the allyl moiety (as drawn in Scheme 1). Moreover, temperature-dependent ^1H NMR spectroscopy (−63 °C to +25 °C in CD_2Cl_2, 25−70 °C in CD_3NO_2) shows that, in solution, **2a** and **2b** are not dynamic and the endo conformation is retained over a large temperature range. In fact, the endo conformation, both in the solid state and in solution, is adopted by most of the $Ru(\eta^5\text{-}C_5R_5)(\eta^3\text{-allyl})X_2$ complexes (R = H, Me; X = Cl, Br) reported in the literature,[14-16] and it would, thus, appear to be a general trend.

In an attempt to obtain complexes with bromo-substituted cyclopentadienone ligands, complexes **2a** and **2b** were subjected to the action of the base pyridine. While the reaction of **2a** with pyridine yields only intractable material, **2b** is cleanly converted to a new complex readily identified as a cationic pyridinium-substituted η^3-cyclopentenoyl complex (Scheme 2), rather than a η^4-cyclopentadienone complex. Abstraction of a syn proton by a base is presumably not possible for steric reasons.

Complex **3** is characterized by elemental analysis and ^1H NMR spectroscopy. Unfortunately, the poor solubility of complex **3** precluded the recording of a $^{13}C\{^1H\}$ NMR spectrum. Therefore, the formulation of **3** is rather tentative. An alternative isomer, as suggested by a reviewer, with the pyridinium and the methyl group bound to the same carbon atom seems less reasonable for reasons to be presented in detail in a following paper.

Following the strategy applied for the synthesis of complexes **1a** and **1b**,[6] complex **2a** was readily converted on addition of triflic acid and subsequent dehydrobromination with H_2O to the desired η^4-cyclopentadienone complex **5** (Scheme 3). **2a** reacts with triflic acid in CH_2Cl_2 at 0 °C to yield the novel high valent hydroxyruthenocene complex $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}Br)Br]\text{-}CF_3SO_3$ (**4**). This reaction is essentially quantitative from ^1H NMR spectroscopic data of the product solution (CD_2Cl_2); the recovered yield is 97%. **4** is characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and elemental

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(15) Masuda, K.; Saitoh. M.; Aoki, K.; Itoh, K. *J. Organomet. Chem.* **1994**, *473*, 285.
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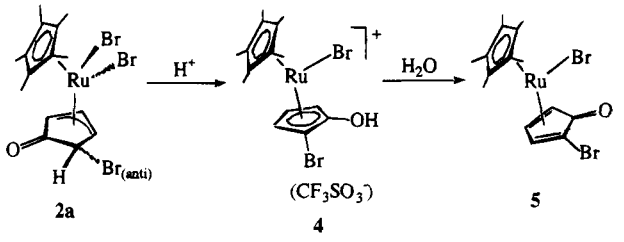
Scheme 3



analysis. The ketonic oxygen of the η^3-cyclopentenoyl ligand is a potential nucleophilic site and protonation gives rise to conversion of the η^3-cyclopentenoyl ligand to the aromatic alcohol η^5-C_5H_3OH-2-Br. In the course of this reaction the formal oxidation state of the metal center does not change. It is worth mentioning, however, that oxygen-centered protonation reactions of analogous cyclopentadienyl complexes $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-cyclopentenoyl})Br_2$ have not been observed.[4] On addition of excess water, complex **4** is readily deprotonated to afford, on workup, $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Br)Br$ (**5**) in 98% isolated yield (Scheme 3).

Complex **5** is characterized by means of ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and elemental analysis. Both ^1H and $^{13}C\{^1H\}$ NMR spectra of **5** show the expected singlet resonances for the C_5Me_5 ligand at 1.84 ppm (15H) and 99.3 (C_5Me_5) and 11.1 ppm ($C_5\mathit{Me}_5$), respectively. Also, the resonances for the η^4-2-bromocyclopentadienone moiety are observed in the expected range (see Experimental Section). The $^{13}C\{^1H\}$ NMR resonance of the "carbonyl" carbon appears at 176.0 ppm. An X-ray structure of **5** was determined. The molecular structure of **5** is shown in Figure 2.

Treatment of **5** with Br_2 results in the formation of complex **6**, the C_5H_3O-2-Br ring being converted quantitatively to the corresponding η^3-cyclopentenoyl C_5H_3O-2, 5-Br_2 (Scheme 1). Though **6** could not be isolated as a solid, its structure was determined by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Indicative of the formation of **6** was the resonance of the "carbonyl" carbon observed at 190.7 ppm and the bromine-bearing aliphatic carbon atom resonating at 47.2 ppm.

Synthesis and Reactivity of Cationic $Ru(\eta^5\text{-}C_5Me_5)(\eta^4$-cyclopentadienone) Complexes. Cationic complexes **7a**, **7b**, and **10** are obtained on addition of $AgCF_3SO_3$ (1 equiv) to CH_3CN solutions of **1a**, **1b**, and **9a$_1$**, respectively, in reasonable yields. These complexes are characterized by elemental analysis and ^1H NMR spectroscopy. In addition, complexes **7a** and **7b** are characterized by $^{13}C\{^1H\}$ NMR spectroscopy. The data bear no remarkable new features and will not be considered further.

When a CH_2Cl_2 solution of **7a** is treated with PCy_3 and $PPhMe_2$, respectively, the bright yellow solution rapidly turns pale yellow. In either case, nucleophilic substitution takes place exclusively on the cyclopentadienone ring, being reduced to the alcohols, η^5-C_5H_3OH-2-PCy_3 and η^5-C_5H_3OH-2-$PPhMe_2$, respectively (Scheme 4). By use of ^1H NMR spectroscopy on the product solutions (CD_2Cl_2), the reactions are found to be essentially quantitative; the recovered yields are about 90%. Interestingly, the weaker nucleophile PPh_3 attacks neither the cyclopentadienone ring nor the metal center of compound **7a**. This is in sharp contrast to the reaction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CH_3CN)]^+$ with PPh_3

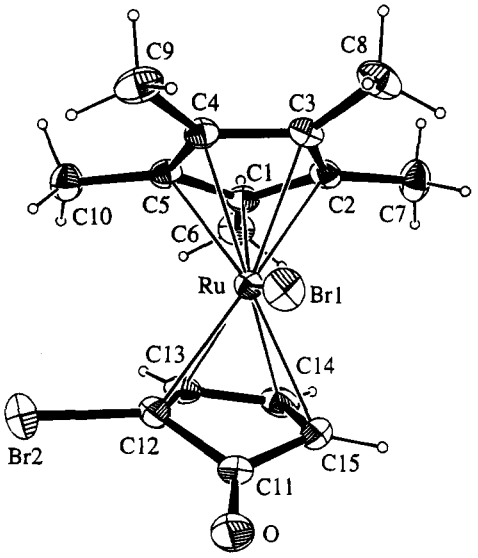
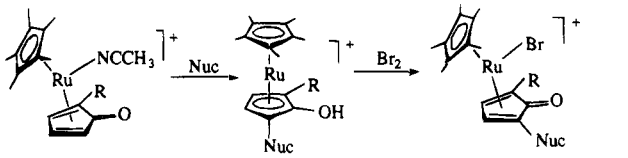


Figure 2. Structural view of $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Br)$ (**5**).

Scheme 4



described recently, which has been shown to quantitatively form the 1,2-disubstituted ruthenocene complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}PPh_3)]^+$.[3a,c] The ^1H and $^{13}C\{^1H\}$ NMR spectra of **8a$_1$** and **8a$_2$** reveal the same overall resonance pattern diagnostic for a 1,2-disubstituted cyclopentadienyl ring. The ^1H NMR spectrum of **8a$_1$** recorded in CD_2Cl_2 consists of five signals: a broad singlet at 7.82 ppm (1H), three multiplets centered at 4.67 (1H), 4.10 (1H), and 3.95 ppm (1H), and a multiplet between 2.63 and 1.30 ppm (30H), which is superimposed by a singlet at 1.81 ppm (15H).

Due to the coupling with ^{31}P of the phosphine moiety, the ^{13}C resonances of the disubstituted ring are split into doublets, including the resonance of the "hydroxy" carbon observed at 125.8 ppm (J_{CP} = 7.0 Hz). The singlet at 87.3 ppm is assigned to the ring carbons of the C_5Me_5 ring.

Cationic η^4-diene complexes are considered to be among the substrates most receptive to nucleophilic attack, this being favored at the terminal carbons, i.e., in the case of η^4-C_5H_4O in the position α to the ketonic group.[5,17] This has indeed been demonstrated very recently by the reactions of $[Mo(CO)_2(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)]^+$ with various carbanions, which yield substituted η^3-cyclopentenoyl complexes[2a] and by the reactions of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CH_3CN)]^+$ with PPh_3, PPh_2Me, and $P(p\text{-}PhOMe)_3$, respectively, which yield substituted η^5-hydroxycyclopentadienyl complexes.[3a,c,d] A molecular orbital analysis carried out recently[4b] suggested that coordinated η^4-cyclopentadienone should be at-

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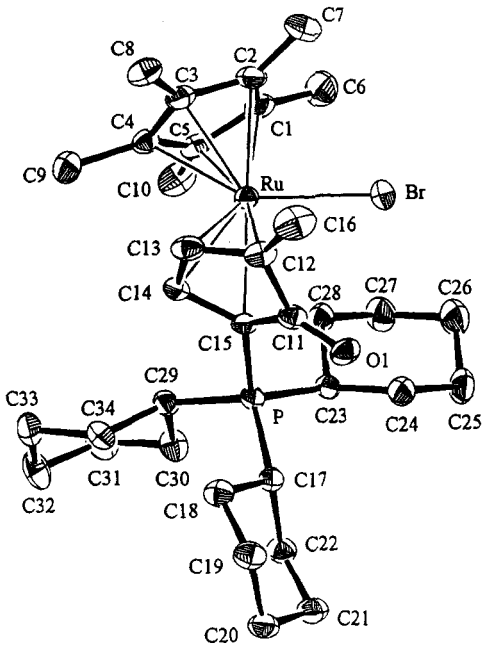

Figure 3. Structural view of [Ru(η^5-C_5Me_5)(η^4-C_5H_2O-2-Me, 5-PCy_3)Br]CF_3SO_3 (**9b**).

tacked in the α-position since the p_z-orbitals of the α-carbons contribute much more strongly to the LUMO than the β-carbon orbitals. Therefore, it is assumed that the observed regioselectivity of the reaction of [Ru(η^5-C_5Me_5)(η^4-cyclopentadienone)(CH_3CN)]$^+$ with tertiary phosphines may also be rationalized in terms of frontier orbital control.

Complexes **9a$_1$** and **9a$_2$** are obtained in good yields through oxidation of **8a$_1$** and **8a$_2$** with Br_2 in CH_2Cl_2 at ambient temperature (Scheme 4). Interestingly, not the Ru metal center but the ligand η^5-C_5H_3OH-2-Nuc (Nuc = PCy_3, $PPhMe_2$) is cleanly oxidized to give the corresponding η^4-cyclopentadienone. This two-electron oxidation is accompanied by a change in the coordination mode. There is no evidence of the formation of the Ru(IV) complex [Ru(η^5-C_5Me_5)(η^5-C_5H_3OH-2-Nuc)Br]$^{2+}$.

In analogous fashion, complex **7b** was converted to the cationic complex [Ru(η^5-C_5Me_5)(η^5-C_5H_2O-2-Me, 5-PCy_3)Br]$^+$ (**9b**) by the above procedure and is characterized by ^{1}H NMR spectroscopy and elemental analysis. Single crystals of the $CF_3SO_3^-$ salt of **9b** have been obtained, and the X-ray analysis has established the structure given in Figure 3. Thereby also the regioselective attack of PCy_3 in the position α to the ketonic group in **7b** is established.

Crystal Structures of Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br (1a), Ru(η^5-C_5Me_5)(η^4-C_5H_3O-2-Br) (5), and [Ru(η^5-C_5Me_5)(η^4-C_5H_2O-2-Me, 5-PCy_3)Br]CF_3SO_3 (9b). Structural views of complexes **1a**, **5**, and **9b** are shown in Figures 1–3, respectively. Selected bond lengths are given in Table 5. In all three complexes the C_5Me_5 ring is staggered with respect to the Ru–Br bond and with respect to the cyclopentadienone ring, which is exo-oriented. The latter feature is common to all ruthenium cyclopentadienone complexes investigated thus far.[4b] Noteworthily, the cyclopentadienone ligand of the structurally related complex [Mo(η^5-C_5H_5)(η^4-C_5H_4O)$(CO)_2$]$^+$ adopts the endo orientation.[3a] Bond lengths and angles of **1a**, **5**, and **9b** agree essentially with previous findings on Ru(η^5-C_5H_5)(η^4-cyclopentadienone) complexes.[4b] A

Table 5. Selected Bond Lengths (Å) for 1a, 5, and 9b

	1a[a]	5	9b
Ru–Br	2.547(1)	2.547(1)	2.542(1)
Ru–C(1)	2.196(3)	2.203(4)	2.263(4)
Ru–C(2)	2.242(2)	2.260(5)	2.201(4)
Ru–C(3)	2.239(2)	2.265(5)	2.201(4)
Ru–C(4)		2.222(4)	2.210(4)
Ru–C(5)		2.211(4)	2.265(4)
Ru–C(12)	2.241(3)	2.193(5)	2.283(4)
Ru–C(13)	2.133(3)	2.125(5)	2.159(4)
Ru–C(14)		2.167(5)	2.130(4)
Ru–C(15)		2.286(4)	2.291(4)
C(11)–C(12)	1.470(4)	1.481(6)	1.485(6)
C(11)–C(15)		1.482(8)	1.499(5)
C(12)–C(13)	1.392(4)	1.414(6)	1.380(6)
C(13)–C(14)	1.400(7)	1.429(8)	1.433(6)
C(14)–C(15)		1.407(7)	1.422(5)
C(11)–O	1.216(5)	1.205(6)	1.211(5)
Br(2)–C(12)		1.878(5)	
C(15)–P			1.786(4)
P–C(17)			1.819(4)
P–C(23)			1.826(4)
P–C(29)			1.837(4)

[a] For **1a** the atom designations C(4), C(5), C(14), and C(15) used in this table correspond to mirror symmetric equivalents of C(3), C(2), C(13), and C(12) of Table 1.

main feature comprises the envelope conformation of the cyclopentadienone ring, which can be subdivided into two planes, one defined by C(12), C(13), C(14), and C(15) (butadiene fragment) and the other defined by C(12), C(11), O(1), and C(15). The angles between these planes are 24.9(2), 24.4(3), and 21.4(2)° for **1a**, **5**, and **9b**, respectively. The angles between the butadiene fragments and the C_5Me_5 rings are 35.8(2), 35.6(2), and 38.6(2)°. The dienone character of the cyclopentadienones is still apparent as indicated by the short–long–short pattern of the C–C distances (Table 5) although the standard deviations are comparatively high. The Ru–C bond lengths of the cyclopentadienone moieties are systematically shorter by about 0.1 Å for C(13) and C(14) than for C(11) and C(15). The C–O bond lengths are on average 1.21 Å. The Ru–C mean bond distances of the C_5Me_5 rings, 2.232(3), 2.232(5), and 2.228(4) Å for **1a**, **5**, and **9b**, respectively, are very uniform and similar to the bis(water) adduct of complex **1a** reported previously.[6] It is interesting to note that these metal carbon distances are systematically larger by 0.03 Å than in the analogous Ru(η^5-C_5H_5)(η^4-cyclopentadienone) complexes.[4b] Complex **1a** has crystallographic mirror symmetry with the mirror plane bisecting the cyclopentadienone ligand and the Ru and Br atoms. Complexes **5** and **9b** are significantly distorted due to the substituents of the cyclopentadienone ring. As depicted in Figure 2, the five-membered rings adopt a "skew" orientation relative to one another with the effect that Ru–C bond lengths in the left half of Figure 2 are systematically shorter than in the right half. A related distortion is also present in compound **9b**. However, not the asymmetrically substituted cyclopentadienone ligand but the C_5Me_5 ring is subject to some "side slipping" as apparent in the Ru–C bond distances, which are short for C(2) and C(3), and long for C(1) and C(5).

Conclusion

The work reported here bears some similarity to the related Ru(η^5-C_5H_5)(η^4-cyclopentadienone) and Ru-

(η^5-C_5H_5)(η^3-cyclopentenoyl) systems.[3,4] However, due to the electron-releasing methyl substituents of the C_5Me_5 ligand, the basicity of the ketonic oxygen atoms of both the η^4-cyclopentadienone and the η^3-cyclopentenoyl ligands is significantly increased. Thus, facile oxygen-centered protonation reactions become feasible, leading to η^5-hydroxycyclopentadienyl Ru(IV) compounds which are useful synthetic precursors for substituted cyclopentadienone ruthenium complexes. Furthermore, in the case of cyclopentadienone complexes, even adduct formation with H_2O has been observed.[6]

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Supplementary Material Available: Crystal structure data and listings of anisotropic temperature factors, hydrogen positional and isotropic displacement parameters, bond distances, complete bond angles, and least-squares planes for complexes **1a**, **5**, and **9b** (29 pages). Ordering information is given on any current masthead page.

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