Synthesis, Characterization, and Reactivity of Ru(η^5-C_5H_5)(η^4-cyclopentadienone)Br Complexes

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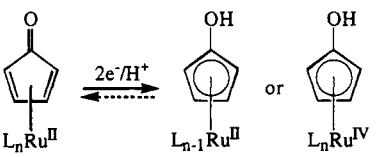
Treatment of Ru(η^5-C_5H_5)(η^4-C_8H_{12})Br (1) with 4-bromo-2-cyclopenten-1-one, 4-bromo-2-methyl-2-cyclopenten-1-one, 4-bromo-2-pentyl-2-cyclopenten-1-one, or 4-bromo-3-methyl-2-cyclopenten-1-one results in the formation of the (η^3-cyclopentenoyl)ruthenium(IV) complexes Ru(η^5-C_5H_5)(η^3-C_5H_5O)Br_2 (**4a**), Ru(η^5-C_5H_5)(η^3-C_5H_4O-2-Me)Br_2 (**4b**), Ru(η^5-C_5H_5)(η^3-C_5H_4O-2-C_5H_{11})Br_2 (**4c**), and Ru(η^5-C_5H_5)(η^3-C_5H_4O-3-Me)Br_2 (**4d**), respectively, in high yields. Addition of NEt_3 to solutions of **4a–d** leads to facile dehydrobromination, giving the corresponding (η^4-cyclopentadienone)ruthenium(II) complexes Ru(η^5-C_5H_5)(η^4-C_5H_4O)Br (**5a**), Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-Me)Br (**5b**), Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-C_5H_{11})Br (**5c**), and Ru(η^5-C_5H_5)(η^4-C_5H_3O-3-Me)Br (**5d**). As determined by X-ray diffraction techniques, Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-Me)Br (**5b**) crystallizes in the monoclinic space group $P2_1/a$ (No. 14), with a = 13.983(3) Å, b = 12.149(3) Å, c = 6.353(2) Å, β = 103.08(1)°, V = 1051.2 Å^3, Z = 4. The structure was refined to R = 0.025 and R_w = 0.024. Alternatively, (η^4-cyclopentadienone)ruthenium(II) complexes are obtained by oxidation of hydroxyruthenocene complexes. This procedure is illustrated by the reactions of Ru(η^5-C_5H_5)(η^5-C_5H_4OH) (**3a**), [Ru(η^5-C_5H_5)(η^5-C_5H_3OH-2-PPh_2Me)]$^+$ (**3b**), and [Ru(η^5-C_5H_5)(η^5-C_5H_3OH-2-P(*p*-PhOMe)$_3$)]$^+$ (**3c**) with Br_2, yielding complexes **5a**, [Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-PPh_2Me)Br]$^+$ (**6a**), and [Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-P(*p*-PhOMe)$_3$)Br]$^+$ (**6b**), respectively, in high yield. **5a** and **5b** undergo facile protonation reactions to afford the cationic hydroxyruthenocene complexes [Ru(η^5-C_5H_5)(η^5-C_5H_4OH)Br]$^+$ (**7a**) and [Ru(η^5-C_5H_5)(η^5-C_5H_3-OH-2-Me)Br]$^+$ (**7b**), respectively. **5a–c** are shown to react with Br_2 to yield the novel η^3-cyclopentenoyl complexes Ru(η^5-C_5H_5)(η^3-C_5H_4OBr)Br_2 (**8a**), Ru(η^5-C_5H_5)(η^3-C_5H_3OBr-2-Me)-Br_2 (**8b**), and Ru(η^5-C_5H_5)(η^3-C_5H_3OBr-2-C_5H_{11})Br_2 (**8c**). Bromine addition occurs anti to the coordinated ruthenium and exclusively α to the cyclopentadienone C=O moiety.

Introduction

Organometallic ruthenium complexes containing both cyclopentadienyl and cyclopentadienone ligands have recently attracted much of our attention. The reason is the exceptionally rich reaction chemistry encountered, however, not fully exploited yet. Much of the chemistry discovered with this ligand combination is directly associated with the oxidizing function of coordinated cyclopentadienone (Scheme 1). In particular, we have dealt with the cationic complexes [Ru(η^5-C_5H_5)(η^4-C_5H_4O)]$_2^{2+}$ and [Ru(η^5-C_5H_5)(η^4-C_5H_4O)(CH_3CN)]$^+$ [2,3] and the neutral complexes Ru(η^5-C_5H_5)(η^4-C_5H_4O)X (X = Cl, Br).[4] The former undergo facile and chemoselective nucleophilic substitution reactions on the C_5H_5 ring and in some cases on the C_5H_4O ligand, yielding η^5-hydroxycyclopentadienyl complexes.[5,6] The latter react with chlorine or bromine via oxidative addition to give novel (η^3-cyclopentenoyl) ruthenium(IV) complexes.[7] Apart from that, Ru(η^5-C_5H_5)-

Scheme 1



(η^4-C_5H_4O)X is readily reduced by Zn or NaHg to hydroxyruthenocene.[8]

So far only unsubstituted cyclopentadienone complexes have been utilized, prepared from the reaction of the Ru(IV) complex [Ru(η^5-C_5H_5)$_2$X]$^+$ (X = Cl, Br)[9] with H_2O or Ag_2O/CH_3CN at elevated temperatures.[2,4] From this procedure, however, the yield is moderate (*ca.* 30%) and restriction is to unsubstituted cyclopentadienone. In an attempt to extend the descriptive chemistry of [Ru(η^5-C_5H_5)(η^4-C_5H_4O)]$^+$ further, we have sought to develop a convenient and simple high-yield synthetic route to complexes featuring the above moiety, including substituted cyclopentadienones. Herein we present the first generalized synthesis for such complexes and report on their reactivity. Also included is the X-ray crystal structure of one of the products, *viz.* Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-Me)Br. Parts of this work have been the subject of a preliminary communication.[7]

Experimental Section

General Information. All chemicals were standard reagent grade and used without further purification. The solvents were

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purified according to standard procedures.[10] The deuterated solvents were purchased from Aldrich and dried over 4-Å molecular sieves. All preparations and reactions were performed in air unless otherwise noted. 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(η^5-C_5H_5)(η^4-C_8H_{12})Br (**1**),[11] Ru(η^5-C_5H_5)(η^4-C_5H_4O)Cl (**2**),[4] Ru(η^5-C_5H_5)(η^5-C_5H_4OH) (**3a**),[8] [Ru(η^5-C_5H_5)(η^5-C_5H_4OH-2-PPh_2Me)]PF_6 (**3b**),[6] and [Ru(η^5-C_5H_5)(η^5-C_5H_4OH-2-P(*p*-PhOMe)$_3$)]PF_6 (**3c**)[6] have been synthesized according to the literature. 4-Bromo-2-cyclopenten-1-one, 4-bromo-2-methyl-2-cyclopenten-1-one, 4-bromo-2-pentyl-2-cyclopenten-1-one, and 4-bromo-3-methyl-2-cyclopenten-1-one were prepared according to the method of Depuy using the corresponding 2-cyclopenten-1-ones.[12]

Synthesis. Ru(η^5-C_5H_5)(η^3-C_5H_5O)Br_2 (4a). A solution of 1 (500 mg, 1.41 mmol) in ethanol (3 mL) was treated with 4-bromo-2-cyclopenten-1-one (*ca.* 5 equiv). The mixture was stirred for 30 min at 40 °C, whereupon a red precipitate was formed which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 470 mg (82%). Anal. Calcd for $C_{10}H_{10}Br_2ORu$: C, 29.51; H, 2.48; Br, 39.26. Found: C, 29.60; H, 2.23; Br, 39.35. ^1H NMR (δ, CD_3NO_2, 20 °C): 6.27 (m, 1H), 5.82 (m, 1H), 5.69 (s, 5H), 5.13 (t, 1H, J = 2.6 Hz), 3.39 (d, 1H, $^2J_{HH}$ = 19.5 Hz), 2.43 (d, 1H, $^2J_{HH}$ = 19.5 Hz). $^{13}C\{^1H\}$ NMR (δ, dmso-d_6, 20 °C): 204.6 (C=O), 106.8, 97.8 (C_5H_5), 77.6, 74.4, 42.0. IR (poly(chlorotrifluoroethylene)): 1717 cm^{-1} (s, $\nu_{C=O}$). X-ray structural data for **4a** have been reported previously.[7]

Ru(η^5-C_5H_5)(η^3-C_5H_4O-2-Me)Br_2 (4b). To a solution of 1 (300 mg, 0.85 mmol) in boiling CH_2Cl_2 (3 mL) was added 4-bromo-2-methyl-2-cyclopenten-1-one (*ca.* 5 equiv). The mixture was stirred for 1 h, whereupon a red precipitate was formed which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 296 mg (83%). Anal. Calcd for $C_{11}H_{12}Br_2ORu$: C, 31.38; H, 2.87; Br, 37.95. Found: C, 31.24; H, 2.67; Br, 38.09. ^1H NMR (δ, CD_2Cl_2, 20 °C): 6.18 (m, 1H), 5.81 (m, 1H), 5.46 (s, 5H), 3.50 (d, 1H, $^2J_{HH}$ = 19.3 Hz), 2.31 (d, 1H, $^2J_{HH}$ = 19.3 Hz), 1.93 (s, 3H). IR (poly(chlorotrifluoroethylene)): 1704 cm^{-1} (s, $\nu_{C=O}$).

Ru(η^5-C_5H_5)(η^3-C_5H_4O-2-C_5H_{11})Br_2 (4c). 4-Bromo-2-pentyl-2-cyclopenten-1-one (0.5 mL, excess) was added to a CH_2Cl_2 solution (3 mL) of 1 (400 mg, 1.13 mmol) and the mixture was refluxed for 5 h. The red solution was treated with petroleum ether (bp 40–60 °C), whereupon a red precipitate was formed which was collected on a glass frit, washed with petroleum ether, and dried under vacuum. Yield: 409 mg (76%). Anal. Calcd for $C_{15}H_{20}Br_2ORu$: C, 37.75; H, 4.22; Br, 33.49. Found: C, 37.70; H, 4.28; Br, 33.38. ^1H NMR (δ, CD_2Cl_2, 20 °C): 6.17 (m, 1H), 5.85 (m, 1H), 5.47 (s, 5H), 3.49 (d, 1H, $^2J_{HH}$ = 19.2 Hz), 2.59 (m, 2H), 2.32 (d, 1H, $^2J_{HH}$ = 19.2 Hz), 1.53 (m, 2H), 1.33 (m, 4H), 0.89 (m, 3H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 204.2 (C=O), 107.9, 97.3 (C_5H_5), 77.9, 73.8, 45.0, 32.1, 29.1, 28.0, 27.9, 13.7. IR (poly(chlorotrifluoroethylene)): 1719 cm^{-1} (s, $\nu_{C=O}$).

Ru(η^5-C_5H_5)(η^3-C_5H_4O-3-Me)Br_2 (4d). This complex was prepared in the same manner as **4b** with 1 and 4-bromo-3-methyl-2-cyclopenten-1-one as starting material. Yield: 62%. Anal. Calcd for $C_{11}H_{12}Br_2ORu$: C, 31.38; H, 2.87; Br, 37.95. Found: C, 30.97; H, 2.71; Br, 36.89. ^1H NMR (δ, CD_2Cl_2, 20 °C): 5.65 (s, 5H), 5.36 (m, 1H), 4.89 (d, 1H, $^3J_{HH}$ = 2.5 Hz), 3.37 (dd, 1H, $^2J_{HH}$ = 19.0 Hz, J = 2.5 Hz), 2.68 (s, 3H), 2.26 (d, 1H, $^2J_{HH}$ = 19.0 Hz). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 204.0 (C=O), 121.0, 98.7 (C_5H_5), 75.2, 74.9, 46.5, 16.9 (Me). IR (poly(chlorotrifluoroethylene)): 1719 cm^{-1} (s, $\nu_{C=O}$).

Ru(η^5-C_5H_5)(η^4-C_5H_4O)Br (5a). (a) To a stirred solution of **4a** (100 mg, 0.25 mmol) in *N*,*N*-dimethylformamide (2 mL) was added NEt_3 (35 μL, 0.25 mmol). After 20 min the red precipitate was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 56 mg (70%). Anal. Calcd for $C_{10}H_9BrORu$: C, 36.83; H, 2.78; Br, 24.50. Found: C, 36.77; H, 2.73; Br, 24.64. ^1H NMR (δ, CD_3NO_2, 20 °C): 6.02 (m, 2H_β), 5.51 (s, 5H), 4.17 (m, 2H_α). IR (KBr): 1685 cm^{-1} (s, $\nu_{C=O}$). (b) Under an inert atmosphere of nitrogen **3a** (200 mg, 0.81 mmol) was dissolved in nitromethane (3 mL) and was treated with 1 equiv of Br_2, whereupon an immediate color change from yellow to red occurred. Within a few minutes **5a** precipitated nearly quantitatively as a microcrystalline red solid and was collected on a glass frit, washed with diethyl ether, and air dried. Yield: 251 mg (95%).

Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-Me)Br (5b). A suspension of **4b** (300 mg, 0.71 mmol) in CH_3CN (3 mL) was treated with NEt_3 (104 μL, 0.75 mmol) at room temperature for 2 h. The red solid was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 149 mg (62%). Anal. Calcd for $C_{11}H_{11}BrORu$: C, 38.84; H, 3.26; Br, 23.49. Found: C, 37.77; H, 3.11; Br, 23.54. ^1H NMR (δ, CD_3NO_2, 20 °C): 5.83 (m, 1H), 5.68 (t, 1H, J = 3.5 Hz), 5.41 (s, 5H), 4.15 (m, 1H), 1.56 (s, 3H). IR (poly(chlorotrifluoroethylene)): 1670, 1682 cm^{-1} (s, $\nu_{C=O}$).

Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-C_5H_{11})Br (5c). A solution of **4c** (400 mg, 0.83 mmol) in CH_3CN (3 mL) was treated with NEt_3 (124 μL, 0.89 mmol) at room temperature for 2 h. Upon addition of diethyl ether a precipitate of triethylamine hydrochloride was formed, which was removed by filtration. After addition of an additional 200 mL of diethyl ether the cloudy red solution was kept at −20 °C for 24 h, whereupon a red microcrystalline solid was formed, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 176 mg (54%). Anal. Calcd for $C_{15}H_{19}BrORu$: C, 45.46; H, 4.83; Br, 20.16. Found: C, 45.40; H, 4.92; Br, 20.24. ^1H NMR (δ, CD_2Cl_2, 20 °C): 5.54 (m, 1H), 5.49 (m, 1H), 5.30 (s, 5H), 4.15 (m, 1H), 2.00–1.70 (m, 2H), 1.28 (m, 6H), 0.87 (m, 3H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 181.7 (C=O), 95.3, 84.9 (C_5H_5), 79.3, 77.4, 67.1, 32.0, 29.0, 24.7, 22.7, 14.1. IR (poly(chlorotrifluoroethylene)): 1668 cm^{-1} (s, $\nu_{C=O}$).

Ru(η^5-C_5H_5)(η^4-C_5H_3O-3-Me)Br (5d). A suspension of **4d** (200 mg, 0.47 mmol) in CH_2Cl_2 (3 mL) was treated with NEt_3 (67 μL, 0.47 mmol) at 60 °C for 2 h. The red solid was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 25 mg (15%). Anal. Calcd for $C_{11}H_{11}BrORu$: C, 38.84; H, 3.26; Br, 23.49. Found: C, 37.97; H, 3.10; Br, 24.11. ^1H NMR (δ, CD_3NO_2, 20 °C): 5.83 (m, 1H), 5.31 (s, 5H), 4.13 (s, 1H), 4.11 (m, 1H), 2.23 (s, 3H). $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, 20 °C): 183.4 (C=O), 102.7, 88.2 (C_5H_5), 83.6, 73.6, 69.8, 17.4 (Me).

[Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-PPh_2Me)Br]PF_6 (6a). This compound was prepared by the procedure previously described for the analogous PPh_3 complex.[5] Yield: 76%. Anal. Calcd for $C_{23}H_{21}BrOP_2F_6Ru$: C, 41.21; H, 3.16; P, 9.24. Found: C, 41.30; H, 3.01; P, 9.27. ^1H NMR (δ, CD_3CN, 20 °C): 7.86 (m, 10H), 6.47 (m, 1H), 6.16 (m, 1H), 5.21 (s, 5H), 4.62 (m, 1H), 2.60 (d, J_{HP} = 14.8 Hz, 3H).

[Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-P(*p*-PhOMe)$_3$)Br]PF_6 (6b). This compound was prepared by the procedure previously described for the analogous PPh_3 complex.[5] Yield: 79%. Anal. Calcd for $C_{31}H_{29}BrO_4P_2F_6Ru$: C, 45.27; H, 3.55; P, 7.53. Found: C, 44.89; H, 3.43; P, 7.64. ^1H NMR (δ, CD_3CN, 20 °C): 7.59 (m, 6H), 7.19 (m, 6H), 6.29 (m, 1H), 5.70 (m, 1H), 5.31 (s, 5H), 4.61 (m, 1H), 3.89 (s, 9H).

[Ru(η^5-C_5H_5)(η^5-C_5H_4OH)Br]CF_3SO_3 (7a). Under an inert atmosphere of nitrogen a suspension of **5a** (200 mg, 0.61 mmol) in nitromethane was treated with triflic acid (270 μL, 3.05 mmol) and the color of the reaction mixture changed from red to green. Upon addition of diethyl ether an olive-green precipitate was formed which was collected on a glass-frit, washed with diethyl ether, and dried under vacuum. Yield: 225 mg (77%). Anal. Calcd for $C_{11}H_{10}BrF_3O_4SRu$: C, 27.74; H, 2.12; Br, 16.78. Found: C, 27.94; H, 2.09; Br, 16.79. ^1H NMR (δ, CD_3NO_2, 20

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°C): 12.47 (br, 1H), 6.00 (t, 2H), 5.85 (s, 5H), 5.00 (t, 2H). $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, 20 °C): 170.9 (C–O), 91.9 (C_5H_5), 84.2 (C_β), 72.0 (C_α).

[Ru(η^5-C_5H_5)(η^5-C_5H_3OH-2-Me)Br]CF_3SO_3 (7b). This compound was prepared in analogy to **7a**. Yield: (34%). Anal. Calcd for $C_{12}H_{12}BrF_3O_4SRu$: C, 29.40; H, 2.47; Br, 16.30. Found: C, 29.36; H, 2.52; Br, 16.44. ^1H NMR (δ, CD_3NO_2, 20 °C): 5.98 (m, 1H), 5.87 (s, 5H), 5.81 (m, 1H), 5.12 (m, 1H), 1.82 (s, 3H). $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, 20 °C): 169.7 (C–O), 91.7 (C_5H_5), 90.5, 84.8, 80.9, 68.6, 10.3 (Me).

Ru(η^5-C_5H_5)(η^3-C_5H_4OBr)Br_2 (8a). A suspension of **5a** (530 mg, 1.62 mmol) in CH_3NO_2 (3 mL) was treated with Br_2 (84 μL, 1.62 mmol) and was stirred for 2 h at 70 °C. The red precipitate formed was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 710 mg (90%). Anal. Calcd for $C_{10}H_9Br_3ORu$: C, 24.72; H, 1.87; Br, 49.33. Found: C, 25.04; H, 1.67; Br, 49.00. ^1H NMR (δ, dmso-d_6, 20 °C): 6.41 (m, 1H), 6.08 (s, 5H), 5.73 (m, 1H), 5.17 (t, 1H, J = 1.1 Hz), 5.11 (dd, 1H, J = 2.3 Hz, J = 2.6 Hz). $^{13}C\{^1H\}$ NMR (δ, dmso-d_6, 20 °C): 198.0 (C=O), 105.4, 99.0 (C_5H_5), 74.1, 69.6, 50.0. IR (KBr): 1718 cm^{-1} (s, $\nu_{C=O}$). X-ray structural data for **8a** have been reported previously.[7]

Ru(η^5-C_5H_5)(η^3-C_5H_3OBr-2-Me)Br_2 (8b). This complex was prepared in analogy to **8a** with **5b** as starting material. Yield: 73%. Anal. Calcd for $C_{11}H_{11}Br_3ORu$: C, 26.42; H, 2.22; Br, 47.94. Found: C, 26.33; H, 2.27; Br, 48.05. ^1H NMR (δ, dmso-d_6, 20 °C): 6.27 (m, 1H), 5.94 (s, 5H), 5.67 (m, 1H), 5.19 (s, 1H), 1.86 (s, 3H). $^{13}C\{^1H\}$ NMR (δ, dmso-d_6, 20 °C): 198.6 (C=O), 105.6, 98.4 (C_5H_5), 86.9, 70.9, 49.8, 14.5 (Me). IR (poly(chlorotrifluoroethylene): 1714 cm^{-1} (s, $\nu_{C=O}$).

Ru(η^5-C_5H_5)(η^3-C_5H_3OBr-2-C_5H_{11})Br_2 (8c). To a solution of **5c** (142 mg, 0.36 mmol) in CH_3NO_2 (3 mL), was added Br_2 (18 μL, 0.36 mmol), and the mixture was stirred for 1 h at room temperature. The volume of the solution was reduced to about 0.5 mL, and the red solid formed was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 114 mg (55%). Anal. Calcd for $C_{15}H_{19}Br_3ORu$: C, 32.40; H, 3.44; Br, 43.11. Found: C, 32.24; H, 3.51; Br, 43.00. ^1H NMR (δ, CD_2Cl_2, 20 °C): 6.21 (dd, 1H, J = 4.0 Hz, J = 1.5 Hz), 5.94 (dd, 1H, J = 4.0 Hz, J = 1.1 Hz), 5.62 (s, 5H), 4.46 (m, 1H), 2.62 (m, 1H), 2.22 (m, 1H), 1.60 (m, 2H), 1.50–1.30 (m, 4H), 0.90 (t, 3H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 197.2 (C=O), 106.6, 98.4 (C_5H_5), 94.5, 72.8, 48.7, 31.7, 28.9, 27.7, 22.6, 14.0. IR (poly(chlorotrifluoroethylene)): 1715 cm^{-1} (s, $\nu_{C=O}$).

Ru(η^5-C_5H_5)(η^3-C_5H_4OCl)Cl_2 (9). Cl_2 was passed through a suspension of **2** (141 mg, 0.50 mmol) in CH_2Cl_2 for 2 min, and the mixture was stirred for additional 30 min. The red precipitate was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 135 mg (77%). Anal. Calcd for $C_{10}H_9Cl_3ORu$: C, 34.06; H, 2.57; Cl, 30.16. Found: C, 34.12; H, 2.43; Cl, 29.34. ^1H NMR (δ, CD_3CN, 20 °C): 6.16 (m, 1H), 5.83 (s, 5H), 5.61 (m, 1H), 5.07 (t, 1H), 4.39 (m, 1H). IR (poly(chlorotrifluoroethylene): 1722 cm^{-1} (s, $\nu_{C=O}$).

Reactions of 7a and 7b with H_2O. A 100 mg (0.21 mmol) sample of **7a** in nitromethane (3 mL) was treated with H_2O (2 equiv), whereupon an immediate color change from green to red occurred. Within a few minutes **5a** precipitated nearly quantitatively as a red solid and was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 66 mg (96%). The analogous reaction of **7b** and H_2O gave **5b** in 95% isolated yield.

X-ray Structure Determination of 5b. Crystal data are given in Table 1. A red prism with dimensions of 0.05 × 0.05 × 0.25 mm was mounted on a glass fiber. X-ray data were collected on a Philips PW1100 four-circle diffractometer using graphite monochromated Mo Kα (λ = 0.710 69 Å) radiation. The intensities of 2614 reflections with $\theta < 27°$, $-17 \le h \le 17$, $0 \le k \le 15$, and $0 \le l \le 8$ were measured by θ–2θ scans with scan widths of 1° + 0.33° tan(θ) and a scan speed of 1.2° min^{-1}. Three representative standard reflections were measured every 120 minutes and showed insignificant fluctuations. The data were corrected for Lorentz, polarization, and absorption effects (Gaussian integration, transmission factors 0.74–0.81) and were merged to 2296 independent reflections (R_{merge} = 0.027 on F_o). 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 calculated from the C-atom positions. The hydrogen atoms were refined as parts of a rigid CH_3 group (C–H = 0.96 Å) or riding on the atoms to which they were bonded (C_5H_5 and C_5H_3O moieties, C–H = 0.96 Å). The isotropic temperature factors of the H atoms refined to 1.31(9) times the equivalent isotropic temperature factors of their host C atoms. The final least-squares refinement included 131 parameters and converged with 1713 reflections [$F_o \ge 6\sigma(F_o)$] and weights $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$ to R = 0.025 and R_w = 0.024. The maximum shift/esd was ≤0.01, and the final difference map showed residuals between –0.55 and +0.65 e $Å^{-3}$, with the most prominent feature near Br. The program SHELX76[13] was used for structure solution and refinement; the XTAL3.2 suite of programs[14] was used to produce molecular diagrams and tabular matter. Atomic positional parameters are given in Table 2.

Table 1. Crystal Data for Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-Me)Br (5b)

formula	$C_{11}H_{11}BrORu$
fw	340.18
space group	$P2_1/a$ (No. 14)
a, Å	13.983(3)
b, Å	12.149(3)
c, Å	6.353(2)
β, deg	103.08(1)
V, $Å^3$	1051.2 (5)
Z	4
ρ_{calc}, g cm^{-3}	2.149
T, K	295
μ, cm^{-1}	51.9 (Mo Kα)
no. of data refined	1713
no. of LS params	131
R^a	0.025
$R_w{}^b$	0.024
GOF	1.11

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

Table 2. Atomic Positional and Isotropic Displacement Parameters ($Å^2$) for Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-Me)Br (5b)

	x/a	y/b	z/c	$U_{eq}{}^a$
Ru	0.16156(2)	0.36021(2)	0.22214(5)	0.0268(1)
Br	0.16015(3)	0.55647(3)	0.36313(7)	0.0453(1)
C(1)	0.0790(3)	0.2061(4)	0.1732(8)	0.055(2)
C(2)	0.0179(3)	0.2901(5)	0.0630(9)	0.062(2)
C(3)	0.0037(3)	0.3658(4)	0.2109(9)	0.060(2)
C(4)	0.0532(3)	0.3294(4)	0.4191(8)	0.054(2)
C(5)	0.0986(3)	0.2308(4)	0.3972(8)	0.047(2)
C(6)	0.3172(3)	0.4621(3)	0.1618(7)	0.039(1)
C(7)	0.3279(2)	0.3750(3)	0.3318(6)	0.035(1)
C(8)	0.2971(3)	0.2754(3)	0.2216(7)	0.040(1)
C(9)	0.2465(3)	0.2999(3)	0.0052(7)	0.044(2)
C(10)	0.2453(3)	0.4154(3)	–0.0217(7)	0.041(1)
C(11)	0.3851(3)	0.3905(4)	0.5543(7)	0.047(2)
O	0.3571(2)	0.5524(2)	0.1812(5)	0.054(1)

^{a} $U_{eq} = {}^1/_3 \sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i\mathbf{a}_j)$.

Results and Discussion

Synthesis and Characterization of (η^3-Cyclopentenoyl)ruthenium (IV) Complexes. Following established procedures for the synthesis of Ru(IV) allyl complexes,[15–18] treatment of **1** with an excess of 4-bromo-

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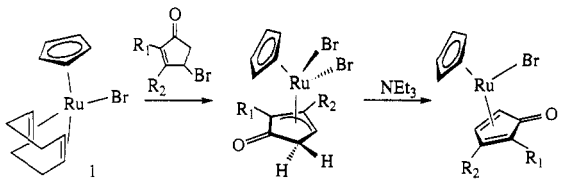
Scheme 2



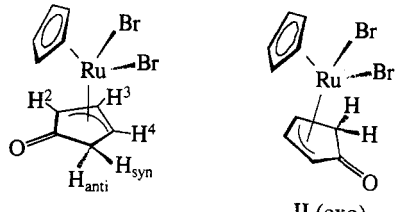
4a $R_1 = H$; $R_2 = H$
4b $R_1 = Me$; $R_2 = H$
4c $R_1 = C_5H_{11}$; $R_2 = H$
4d $R_1 = H$; $R_2 = Me$

5a $R_1 = H$; $R_2 = H$
5b $R_1 = Me$; $R_2 = H$
5c $R_1 = C_5H_{11}$; $R_2 = H$
5d $R_1 = H$; $R_2 = Me$

2-cyclopenten-1-one, 4-bromo-2-methyl-2-cyclopenten-1-one, 4-bromo-2-pentyl-2-cyclopenten-1-one, or 4-bromo-3-methyl-2-cyclopenten-1-one in hot ethanol or boiling CH_2Cl_2 gives the neutral (η^3-cyclopentenoyl)ruthenium(IV) complexes **4a–d** in 86, 83, 76, and 62% isolated yields, respectively (Scheme 2). Except for **4c**, the compounds are only sparingly soluble in most common organic solvents. All complexes are stable to air in the solid state and for extended periods in solution. **4a–d** have been characterized by ^1H NMR and IR spectroscopy and elemental analysis. Where solubility has permitted (**4a**, **4c**, **4d**), $^{13}C\{^1H\}$ NMR spectra have been recorded.

The allyl protons of the cyclopentenoyl ligand in **4a** resonate at 6.27 (H^3), 5.82 (H^4), and 5.13 ppm (H^2), while the geminal methylene protons give rise to two doublets at 3.39 (H_{anti}, with respect to Ru) and 2.43 ppm (H_{syn}, with respect to Ru) with a $^2J_{HH}$ coupling constant of 19.5 Hz. The signal for the C_5H_5 ligand appears at 5.69 ppm. Complexes **4b–d** exhibit spectra similar to that of **4a**, but with important differences resulting from the presence of alkyl substituents (see Experimental Section). As the ^{13}C NMR spectra of **4a**, **4c**, and **4d** bear no unusual features, it is sufficient to point out that the resonance of the "carbonyl" carbon is observed at 204.5, 204.2, and 204.0 ppm, respectively. The $\nu_{C=O}$ stretching frequencies of **4a–d** are found at 1717, 1704, 1719, and 1719 cm^{-1}, respectively.

In the solid state η^3-allyl complexes are found to exist either as endo or exo conformers with respect to the orientation of the allyl moiety. Thus, exo or endo isomers may also exist in (η^3-cyclopentenoyl)ruthenium(IV) complexes, as illustrated by **I** and **II**. The X-ray crystal



I (endo)

II (exo)

structures of **4a** and of the analogous bromine substituted complex **8a** reported previously[7] show that in the solid state the η^3-allyl moiety is endo oriented (conformer **I**). The same conformation is found in the crystal structures of the η^3-cyclobutenyl complex $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_4H_4OMe)Cl_2$[15] and $Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_3H_5)Br_2$,[16c] while the exo conformation has been observed for structurally related (η^3-cyclohexenyl)$Mo(\eta^5\text{-}C_5H_5)(CO)_2$ complexes.[19]

In solution, conformational equilibria between such isomeric species have been reported.[20] From ^1H NMR spectroscopy, complexes **4a–d** are not dynamic in solution (−63 to +25 °C in CD_2Cl_2, 25–80 °C in CD_3NO_2). There is, thus, one predominant isomer. In order to establish what kind of orientation is adopted, a 2-D NOE experiment has been performed on **4a** in CD_2Cl_2 as a solvent. If it were an exo conformer, a strong correlation between the central allyl proton H^3 and the protons of the C_5H_5 ring is expected.[20] The endo conformer, on the other hand, should not exhibit such a correlation but instead should reveal some NOE with the syn proton of the cyclopentenoyl ligand and the C_5H_5 ring protons. The NOESY spectrum of **4a** shows a weak correlation between the protons of the C_5H_5 ligand and the syn proton of the cyclopentenoyl moiety. Therefore, the endo conformation adopted in the crystalline state appears to be retained in solution. Incidentally, according to the NOESY spectrum of the pentamethyl derivative $Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_5H_4O)Br_2$, there is a strong correlation between the methyl protons of the C_5Me_5 ligand and the syn proton of the allyl ligand.[21] A similar behavior is exhibited by open (η^3-allyl) ruthenium(IV) complexes.[16c]

Synthesis and Characterization of (η^4-Cyclopentadienone)ruthenium(II) Complexes. Treatment of **4a–d** with NEt_3 leads to facile dehydrobromination, yielding the neutral (η^4-cyclopentadienone)ruthenium(II) complexes **5a–d** in 70, 62, 54, and 15% isolated yields, respectively (Scheme 2). These complexes are fully characterized by a combination of elemental analysis and IR and ^1H NMR spectroscopy. **5c** and **5d** have also been characterized by $^{13}C\{^1H\}$ NMR spectroscopy.

In the IR spectra of **5a–c** the carbonyl stretching frequencies are observed between 1685 and 1668 cm^{-1}, consistent with values seen for other known cyclopentadienone complexes.[2,3,20,22] This is somewhat lower than the frequency for the free ligand observed at 1727 and 1724 cm^{-1} (stabilized in an argon matrix at 10 K).[23] Thus, as expected, coordination leads to a decrease of the C=O bond strength. The ^1H NMR spectra of **5a–d** show the expected singlet resonance for the C_5H_5 ring appearing in the range 5.51–5.30 ppm. The cyclopentadienone ligand of **5a** displays an AA'XX' splitting pattern of two apparent multiplets at 6.02 (2H) and 4.17 ppm (2H) assignable to the β and α protons, respectively. This assignment was afforded by comparing the ^1H NMR spectrum of **5a** with those of both 2-methyl- and 3-methylcyclopentadienone complexes **5b** and **5d** (see Experimental Section). In order to establish the proton–carbon connectivity within the cyclopentadienone ligand, a ^1H–^{13}C chemical shift correlation experiment has been performed on the more soluble acetonitrile derivative $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CH_3CN)]^+$.[3,24] The poor solubility of **5a** precluded such as experiment. It should be emphasized that the signals of the β protons correlating with the β carbons are shifted downfield with respect to the α protons and carbons,

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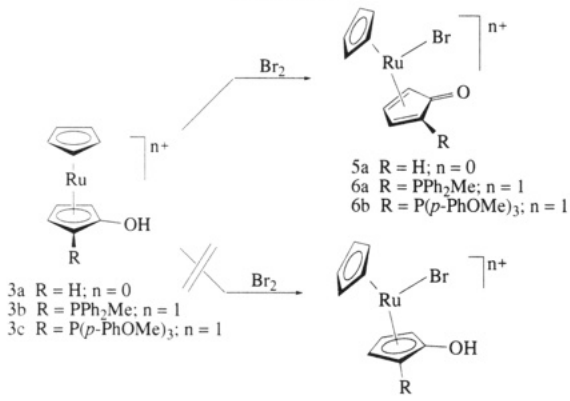
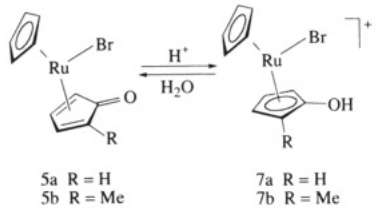
(17) Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843.
(18) Koelle, U.; Kossakowski, J. *J. Organomet. Chem.* **1989**, *362*, 383.
(19) (a) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400. (b) Pearson, A. J.; Blystone, S. L.; Nar, H.; Pinkerton, A. A.; Roden, B.; Yoon, J. *J. Am. Chem. Soc.* **1989**, *111*, 134.
(20) Liebeskind, L. S.; Bombrun, A. *J. Am. Chem. Soc.* **1991**, *113*, 8736.
(21) Unpublished results.
(22) Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* **1977**, *128*, 237.
(23) Maier, G.; Franz, L. H.; Harten, H.-G.; Lanz, K.; Reisenbauer, H. P. *Chem. Ber.* **1985**, *118*, 3196.

Figure 1. LUMO (lowest unoccupied molecular orbital) of uncomplexed cyclopentadienone (left) and of coordinated η^4-cyclopentadienone in $Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)Br$ (**5a**) (right).

Scheme 3



Scheme 4



respectively, despite the fact that nucleophilic attack occurs exclusively α to the ketonic functional group.[5,6,20] Consequently, former assignments[2-5,20] based upon intuition are proved to be erroneous except for $Fe(\eta^4\text{-}C_5H_4O)(CO)_3$ which is consistent with the present one.[22,25]

For the uncomplexed cyclopentadienone molecule no respective ^1H and ^{13}C NMR spectroscopic data are available. A conventional organic analysis, however, would suggest that the signals of both β protons and carbons are shifted downfield with respect to the α protons and carbons, respectively, as is the case for α,β-unsaturated carbonyl compounds. Accordingly, nucleophilic attack would, thus, occur either at or β to the carbonyl group.

Closer examination of the frontier orbitals relevant for nucleophilic attack using a density functional method[26] supports this view. As indicated in Figure 1 the uncomplexed cyclopentadienone molecule should be attacked in the β-position since the p_z orbitals of the β carbons contribute much more strongly to the LUMO (lowest unoccupied molecular orbital) than the α carbon orbitals. On coordination to Ru, the shape of the cyclopentadienone frontier orbital changes drastically, so that nucleophilic attack on the coordinated η^4-cyclopentadienone molecule is now preferred at the p_z orbitals of the α carbons.

(24) The $^{13}C\{^1H\}$ NMR spectrum of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CH_3CN)]^+$ (δ, CD_3NO_2, 20 °C) shows peaks at 182.8 (C=O), 133.8 (CN), 88.0 (C_5H_5), 87.9 (C_β), 74.6 (C_α), and 5.0 (Me); assignments made previously (ref 2) proved to be erroneous. The ^1H NMR spectrum of this complex (δ, CD_3NO_2, 20 °C) exhibits peaks at 6.25 (m, 2H, H_β), 5.65 (s, 5H, C_5H_5), 4.66 (m, 2H, H_α), and 2.58 ppm (s, 3H, Me). A $^1H\text{-}^{13}C\{^1H\}$ chemical shift correlation spectrum reveals that the resonances of C_α and C_β are correlated with those of H_α and H_β, respectively.

(25) Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1960**, 989.

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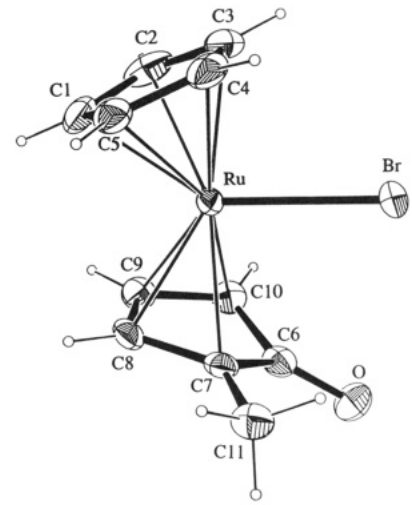


Figure 2. ORTEP drawing (30% ellipsoids) of $Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Me)Br$ (**5b**).

Scheme 5

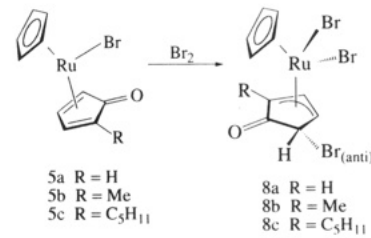


Table 3. Bond Distances (Å) and Selected Bond Angles (deg) for $Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Me)Br$ (5b)

Bond Distances			
Ru–Br	2.549(1)	C(1)–C(5)	1.419(7)
Ru–C(1)	2.185(5)	C(2)–C(3)	1.361(8)
Ru–C(2)	2.205(5)	C(3)–C(4)	1.418(7)
Ru–C(3)	2.194(4)	C(4)–C(5)	1.377(6)
Ru–C(4)	2.204(5)	C(6)–C(7)	1.496(6)
Ru–C(5)	2.220(5)	C(6)–C(10)	1.470(5)
Ru–C(7)	2.279(3)	C(6)–O	1.224(5)
Ru–C(8)	2.158(4)	C(7)–C(8)	1.415(5)
Ru–C(9)	2.142(5)	C(7)–C(11)	1.470(5)
Ru–C(10)	2.245(5)	C(8)–C(9)	1.428(6)
C(1)–C(2)	1.411(7)	C(9)–C(10)	1.413(6)
Selected Bond Angles			
C(2)–C(1)–C(5)	107.6(4)	C(10)–C(6)–O	129.8(4)
C(1)–C(2)–C(3)	108.3(4)	C(6)–C(7)–C(8)	106.1(3)
C(2)–C(3)–C(4)	108.4(4)	C(6)–C(7)–C(11)	123.2(3)
C(3)–C(4)–C(5)	108.4(4)	C(8)–C(7)–C(11)	128.6(4)
C(1)–C(5)–C(4)	107.2(4)	C(7)–C(8)–C(9)	109.1(3)
C(7)–C(6)–C(10)	103.8(3)	C(8)–C(9)–C(10)	108.2(4)
C(7)–C(6)–O	126.3(3)	C(6)–C(10)–C(9)	107.5(3)

Consequently, nucleophilic attack on the coordinated η^4-cyclopentadienone is interpretable as frontier orbital controlled rather than charge controlled (*cf.* Davies–Green–Mingos rules[27]).

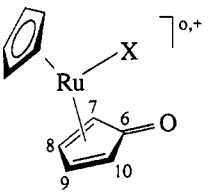
By an alternative approach, complex **5a** is obtained almost quantitatively through oxidation of **3a** with Br_2 in CH_3NO_2 at ambient temperature (Scheme 3). Though this type of reaction is of no practical use in the particular case (**3a** is actually synthesized by reduction of **5a**), this procedure is, nevertheless, of more general importance. For instance, substituted hydroxyruthenocenes **3b** and **3c**, readily obtained by the reaction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CH_3CN)]^+$ and PPh_2Me or $P(p\text{-}PhOMe)_3$, re-

(27) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047.

Table 4. Comparison of Bond Distances (Å) and Ring Dihedral Angles (deg) in Some $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)X]^{0,+}$ Complexes

X	Ru–C_{av} η^5-C_5H_5	Ru–$C_{7,10}$	Ru–$C_{8,9}$	C=C $C_{7,9}$–$C_{8,10}$	C–C C_8–C_9	C=O	dihedral angle[a]	dihedral angle[b]	ref
Br^-	2.212	2.263	2.165	1.419	1.457	1.216	20.4	36.2	4
$AsMe_3$	2.203	2.245	2.143	1.395	1.431	1.210	21.5	34.5	30
$AsPh_3$	2.203	2.267	2.161	1.395	1.429	1.219	23.1	36.3	30
$P(OPh)_3$	2.214	2.269	2.174	1.392	1.436	1.212	23.7	36.5	5
CH_3CN	2.193	2.264	2.160	1.391	1.431	1.221	18.0	36.0	3
Br^- **(5b)**[c]	2.202	2.262	2.150	1.414	1.428	1.240	20.9	34.4	this work
CH_3CN[d]	2.188	2.254	2.162	1.376	1.428	1.208	16.3	35.5	5

[a] Angle formed between the planes defined by C_7, C_8, C_9, C_{10}, and C_7, C_6, O, C_{10}. [b] Angle formed between the planes defined by C_7, C_8, C_9, C_{10}, and the η^5-C_5H_5 ring. [c] η^4-Cyclopentadienone = η^4-C_5H_3O-2-Me. [d] η^4-Cyclopentadienone = η^4-C_5H_3O-2-PPh_3.



spectively,[5,6] are oxidized by Br_2 to give **6a** and **6b** in 76 and 79% isolated yield (Scheme 3).

Halogens readily oxidize the parent ruthenocene and its derivatives to the corresponding halo–Ru(IV) metallocenes, e.g., Br_2 converts ruthenocene nearly quantitatively to the cationic complex $[Ru(\eta^5\text{-}C_5H_5)_2Br]^+$.[9] In the case of hydroxyruthenocenes **3a–c**, however, not the Ru metal center but the ligand η^5-C_5H_3OH-2-R (R = H, PPh_2-Me, P(*p*-PhOMe)$_3$) is cleanly oxidized to give the corresponding η^4-cyclopentadienone. This is a two electron oxidation accompanied by a change in the coordination mode. There is no evidence that $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3\text{-}OH\text{-}2\text{-}R)Br]^{n+}$ is formed (Scheme 3).

Protonation of 5a and 5b. However, complexes of the type $Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}R)Br$ (R = H, Me) are available through protonation of η^4-cyclopentadienone complexes. Scheme 4 depicts the reaction of **5** with triflic acid in CH_2Cl_2, producing the high valent hydroxyruthenocene complexes **7**. Thus, the ketonic oxygen of the η^4-cyclopentadienone ligand is a potential nucleophilic site. Protonation of the oxygen atom gives rise to reduction of the η^4-cyclopentadienone ligands to the alcohols η^5-C_5H_4-OH and η^5-C_5H_3OH-2-Me, respectively, while the oxidation state of the metal center formally changes from +2 to +4. These reactions are essentially quantitative from ^1H NMR spectroscopic data of the product solutions (CD_3NO_2) but the recovered yields were only 77 and 34%, respectively. **7a** and **7b** have been characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and elemental analysis. The NMR spectra of **7a** and **7b** contain no unusual features, except perhaps the marked downfield chemical shifts indicative of the high oxidation state of the ruthenium center. Upon protonation, the ^1H NMR absorption of the C_5H_5 rings of **5a** and **5b** are shifted downfield by about 0.4 ppm. On addition of water both **7a** and **7b** are quantitatively deprotonated to **5a** and **5b** (Scheme 4).

Protonation/deprotonation reactions are reported for η^5-oxocyclohexadienyl/η^6-phenol $Ru(C_5Me_5)$ systems.[28] Similar reactions are also known for hydroxycobalticenium and hydroxyrhodicenium salts which are in protolytic equilibria with their corresponding stable η^4-cyclopentadienone complexes.[29]

Oxidative Addition Reactions. Novel (η^3-cyclopentenoyl)ruthenium(IV) complexes **8a–c** are obtained by oxidative addition of Br_2 to **5a–c** in CH_3NO_2 with 90, 73, and 55% isolated yields, respectively (Scheme 5). All complexes are characterized by means of ^1H, $^{13}C\{^1H\}$ NMR, and IR spectroscopy and elemental analysis. Both ^1H and $^{13}C\{^1H\}$ NMR spectra of **8a–c** show the expected singlet resonance for the C_5H_5 ligand in the range 6.1–5.4 ppm and 99.0–94.5 ppm, respectively. Likewise, the resonances for the η^3-cyclopentenoyl moiety are observed in the expected ranges (see Experimental Section). The ^{13}C resonance of the "carbonyl" carbon appears at about 198.0 ppm (*cf.* the respective ^{13}C resonances of η^4-cyclopentadienone complexes are found at about 180 ppm).[2-5,20]

Bromine addition to the η^4-cyclopentadienone ligand occurs anti to the coordinated ruthenium and exclusively α to the ketone functional group, as established by X-ray crystallography.[7] The overall stereochemistry of **8a** is remarkably similar to that of **4a**, adopting also the endo conformation in the solid state. Reaction of $Ru(\eta^5\text{-}C_5H_5)$-$(\eta^4\text{-}C_5H_4O)Cl$ (**2**) with Cl_2 in CH_2Cl_2 at ambient temperature gives the chloro complex $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_4OCl)Cl_2$ (**9**) in 77% yield.

Scheme 5 is worth emphasizing since oxidative additions in octahedral d^6 systems are necessarily accompanied by ligand displacement. In the formation of complexes **8a–c** and **9**, however, no ligand substitution takes place. Whereas one halogen atom is attached to the ruthenium center, the other one is nucleophilically added on the cyclopentadienone ring adjacent to the ketonic group, resulting in a hapticity change from η^4 to η^3. These reactions have no precedent in ruthenium chemistry; complexes **8a–c** and **9** are the first Ru(IV) complexes with halo-η^3-cyclopentenoyl ligands.

Crystal Structure of $Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Me)Br$ (5b). A representation of the molecular structure of **5b** is depicted in Figure 2. Listings of bond lengths and selected bond angles are given in Table 3. The cyclopentadienone ligand is exo oriented. Noteworthily, the cyclopentadienone ligand of the structurally related complex $[Mo(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CO)_2]^+$ adopts the endo orientation in the solid state.[20] The C_5H_5 and C_5H_3O-2-Me rings are approximately staggered with respect to one another. The C_5H_3O-2-Me ligand is distinctly bent and can be subdivided into two planes, one defined by C(7),

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C(8), C(9), and C(10) (butadiene fragment) and the other defined by C(7), C(6), O(1), and C(10). The angle between these planes is 20.9(2)°. The methyl group is approximately coplanar with the plane formed by the butadiene fragment. The deviation of C(11) from that plane is bent 0.044(8) Å away from the metal. The diene C–C bonds exhibit a short–long–short pattern (1.414(5) *vs* 1.428(6) Å). The angle between the C_5H_5 plane and the butadiene fragment of C_5H_4O is 34.4(3)°. The average Ru–C(C_5H_5) distance is 2.202(5) Å. The bond distances between Ru and the butadiene fragment are short for C(8) and C(9), 2.158(4) and 2.142(5) Å, respectively, and long for C(7) and C(10), 2.279(3) and 2.245(5) Å, respectively, a feature that is characteristic of η^4-cyclopentadienone complexes in general. The length of the C(6)–O(1) bond is 1.224(5) Å. For comparison, structural data of related η^4-cyclopentadienone complexes are given in Table 4. In all these complexes the cyclopentadienone moieties adopt the exo conformation, which means that the dihedral angle X–Ru–C(6)–O (*cf.* structure diagram in Table 4) is close to 0°. The overall structural features of these complexes are very similar except for the internal tilt of the cyclopentadienone ligand. This angle appears to be controlled by the space requirements of the X ligand and is small for X = CH_3CN, intermediate for X = Br^- and $AsMe_3$, and large for the bulky ligands X = $AsPh_3$ and $P(OPh)_3$.

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Supplementary Material Available: A packing diagram of **5b** and listings of anisotropic temperature factors, hydrogen positional and isotropic displacement parameters, complete bond distances and angles, and least-squares planes (5 pages). Ordering information is given on any current masthead page.

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