Novel η^3-Cyclopentenoyl Complexes of Ruthenium(IV): X-Ray Structures of $Ru(\eta^5-C_5H_5)(\eta^3-C_5H_4OBr)Br_2$ and $Ru(\eta^5-C_5H_5)(\eta^3-C_5H_5O)Br_2$

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$Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)Br$ **1** reacts with Br_2 to yield the novel η^3-allyl complex $Ru(\eta^5-C_5H_5)(\eta^3-C_5H_4OBr)Br_2$ **3**; treatment of $Ru(\eta^5-C_5H_5)(\eta^4-C_8H_{12})Br$ **5** with 3-bromo-4-cyclopentene-1-one gives the parent cyclopentenoyl complex $Ru(\eta^5-C_5H_5)(\eta^3-C_5H_5O)Br_2$ **6**, which in the presence of NEt_3 is readily converted to the cyclopentadienone complex **1**; X-ray structures of **3** and **6** are presented.

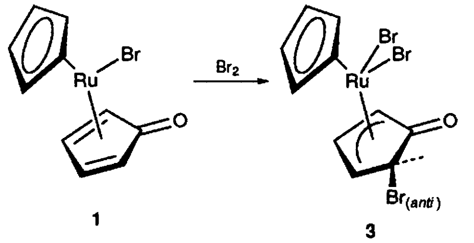
Transition-metal complexes featuring η^4-cylopentadienone as a ligand display novel and interesting reactivity.[1,2] Here, we report the synthesis and characterization of η^3-cyclopentenoyl Ru^{IV} complexes, formed by reaction of the neutral cyclopentadienone complexes $Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)Br$ **1**[3] and $Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)Cl$ **2**[3] with Br_2 and Cl_2, respectively. η^3-Cyclopentenoyl Ru^{IV} complexes are shown to be potential precursors for cyclopentadienone Ru^{II} complexes.

A suspension of **1** in $MeNO_2$ is treated with 1 equiv. of Br_2 at 70 °C for 2 h. The red complex obtained is identified as the η^3-allyl complex $Ru(\eta^5-C_5H_5)(\eta^3-C_5H_4OBr)Br_2$ **3** by means of ^1H, $^{13}C\{^1H\}$ NMR and IR spectroscopy, and elemental analysis (Scheme 1).† The recovered yield is 90%. Complex **3** is only sparingly soluble in most common organic solvents ($MeNO_2$ and Me_2SO have proved to be the best) and is air stable as a solid and in solution. The characteristic spectroscopic features comprise a marked down-field shift of the ^1H and ^{13}C resonances, indicative of the higher oxidation state of the ruthenium ion. The ^{13}C resonance of the carbonyl carbon atom is observed at δ 198.0 (*cf.* the respective ^{13}C resonances of η^4-cyclopentadienones, which are found at *ca.* δ 180).[1,4] The ketonic $\nu_{C=O}$ is shifted from 1685 cm^{-1} in **1**[3] to 1718 cm^{-1} in **3**, owing to an increase in bond order.

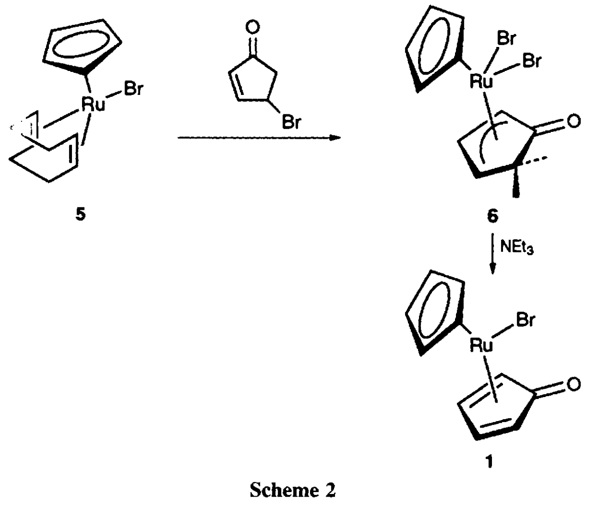
A structural view of **3**, determined by X-ray diffraction and depicted in Fig. 1,‡ clearly demonstrates that bromine addition on the cyclopentadienone has occurred *anti* to the coordinated ruthenium and exclusively α to the ketone functional group. The enyl function of the cyclopentenoyl ligand is bonded nearly symmetrically to the metal with the Ru–C bond to the central enyl carbon atom C(9) [2.116(7) Å] being distinctly shorter than those to the outer carbon atoms C(8) and C(10) [2.219(7) and 2.232(8) Å, respectively]. This bonding pattern is similar to that found for the η^3-cyclobutenyl ligand in $Ru(\eta^5-C_5H_5)(\eta^3-C_4H_4OMe)Cl_2$.[5] The Ru–Br(1) and Ru–Br(2) bond distances are nearly identical, being 2.537(1) and 2.533(1) Å, respectively.

Reaction of **2** with Cl_2 in CH_2Cl_2 at ambient temperature gives the analogous chloro complex $Ru(\eta^5-C_5H_5)(\eta^3-C_5H_4OCl)Cl_2$ **4**, albeit in a lower yield (45%).†

Ru^{IV} η^3-allyl complexes are typically prepared by oxidative addition of allylic halides to suitable Ru^{II} precursors, such as $Ru(\eta^5-C_5H_5)(\eta^4-C_8H_{12})Br$ **5**[6] (C_8H_{12} = cycloocta-1,5-diene) or $Ru(\eta^5-C_5H_5)(CO)_2Br$.[7] Following this procedure, treatment of 3-bromo-4-cyclopentene-1-one[8] with **5** in ethanol gives a red precipitate of the parent η^3-cyclopentenoyl complex $Ru(\eta^5-C_5H_5)(\eta^3-C_5H_5O)Br_2$ **6** in 86% yield (Scheme 2). Complex **6** is characterized by ^1H, $^{13}C\{^1H\}$ NMR and IR



Scheme 1



Scheme 2

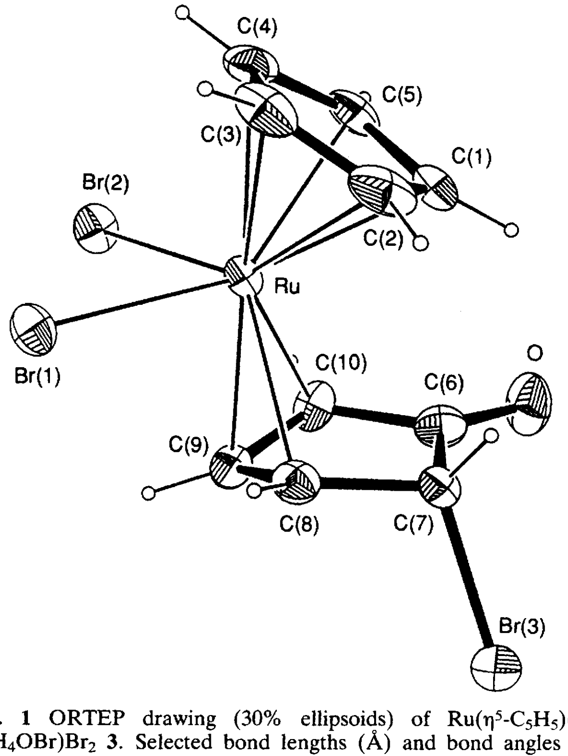


Fig. 1 ORTEP drawing (30% ellipsoids) of $Ru(\eta^5-C_5H_5)(\eta^3-C_5H_4OBr)Br_2$ **3**. Selected bond lengths (Å) and bond angles (°): Ru–Br(1) 2.537(1), Ru–Br(2) 2.533(1), Ru–C(1–5)$_{av}$ 2.215(8), Ru–C(8) 2.219(7), Ru–C(9) 2.116(7), Ru–C(10) 2.232(8), C(6)–C(7), 1.528(11), C(7)–C(8) 1.495(11), C(8)–C(9) 1.418(11), C(9)–C(10) 1.413(11), C(10)–C(6) 1.459(11), C(6)–O 1.206(10), C(7)–Br(3) 1.981(7); Br(1)–Ru–Br(2) 85.03(3), C(7)–C(8)–C(9) 109.3(6), C(8)–C(9)–C(10) 105.7(6), C(9)–C(10)–C(6) 109.5(7).

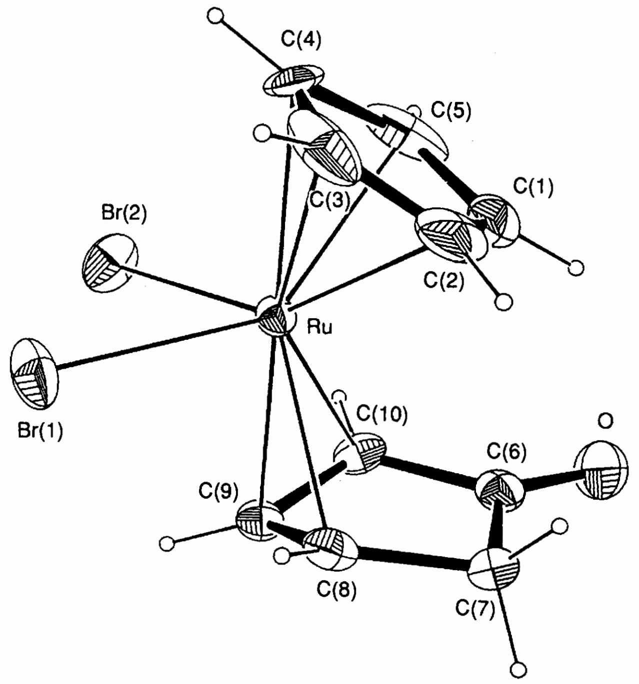


Fig. 2 ORTEP drawing (30% ellipsoids) of Ru(η^5-C_5H_5)(η^3-C_5H_5O)Br_2 **6**. Selected bond lengths (Å) and bond angles (°): Ru–Br(1) 2.530(1), Ru–Br(2) 2.544(1), Ru–C(1–5)$_{av}$ 2.194(9), Ru–C(8) 2.251(7), Ru–C(9) 2.107(7), Ru–C(10) 2.224(7), C(6)–C(7) 1.509(11), C(7)–C(8) 1.507(12), C(8)–C(9) 1.427(11), C(9)–C(10) 1.413(10), C(10)–C(6) 1.467(11), C(6)–O 1.208(10); Br(1)–Ru–Br(2) 84.06(4), C(7)–C(8)–C(9) 109.0(7), C(8)–C(9)–C(10) 104.6(6), C(9)–C(10)–C(6) 109.2(6).

spectroscopy, and by elemental analysis.[§] The spectroscopic properties of this complex are similar to that of **3**; the geminal methylene protons of the η^3-C_5H_5O-ring give rise to two characteristic doublets in the ^1H NMR spectrum at δ 3.39 (d, 1 H, $^2J_{HH}$ 19.5 Hz) and 2.43 (d, 1 H, $^2J_{HH}$ 19.5 Hz). The ^{13}C resonance of the carbonyl carbon atom is observed at δ 204.6 and the $\nu_{C=O}$ stretching frequency occurs at 1717 cm^{-1}. X-Ray diffraction analysis of crystals of **6** establishes the structure given in Fig. 2.[‡] The overall stereochemistry of **6** is remarkably similar to that of **3** and is not discussed here.

The reactivities of **3** and **6**, however, are different. Preliminary investigations reveal that on treatment of **6** with 1 equiv. of NEt_3 in DMF solution, the neutral cyclopentadienone complex **1** is formed in 70% isolated yield (Scheme 2) while the same treatment of **3** does not give the corresponding 5-bromo-2,4-cyclopentadiene-1-one Ru^{II} complex. Reaction of **6** with Me_2SO at 80 °C for 3 h results in the liberation of 3-bromo-4-cyclopentene-1-one whereupon a new, not yet identified complex is formed, presumably a cyclopentadienyl Ru^{II} complex (as inferred from ^1H NMR spectroscopy).

Oxidative additions in octahedral d^6-systems, by implication, involve ligand displacement. For **1** and **2**, however, no ligand substitution takes place—the oxidative addition of halogens being accompanied by both a hapticity change and nucleophilic addition of halide on the cyclopentadienone ring, adjacent to the ketonic group. These reactions have no precedent in ruthenium chemistry. Complexes **3** and **4** appear to be the first Ru^{IV} complexes having substituted η^3-cyclopentenoyl ligands.

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Footnotes

[†] *Selected data* for **3**: Satisfactory elemental analysis for C, H, Br; ^1H NMR [250.13 MHz, $(CD_3)_2SO$] δ 6.41 (m, 1 H), 6.08 (s, 5 H), 5.73 (m, 1 H), 5.17 (t, 1 H), 5.11 (t, 1 H); $^{13}C\{^1H\}$ NMR (62.68 MHz, $(CD_3)_2SO$ δ 198.0 (C=O), 105.4, 99.0 (C_5H_5), 74.1, 69.6, 50.0; IR ν/cm^{-1} (KBr pellet) 1718s (C=O).

For **4**: Satisfactory elemental analysis for C, H, Cl; ^1H NMR (250.13 MHz, CD_3CN) δ 6.16 (m, 1 H), 5.83 (s, 5 H), 5.61 (m, 1 H), 5.07 (t, 1 H), 4.39 (m, 1 H); IR ν/cm^{-1} [poly(chlorotrifluoroethylene)] 1722s (C=O).

[‡] *Crystal data* for **3**: $C_{10}H_9OBr_3Ru$, M = 485.96, red crystals, monoclinic, space group $P2_1/n$, a = 22.235(3), b = 6.937(1), c = 7.853(1) Å, β = 91.00(1)°, V = 1211.1(3) Å^3, Z = 4, D_c = 2.665 g cm^{-3}, μ = 110.5 cm^{-1}, F(000) = 904, T = 24 °C. A plate-like crystal fragment (0.018 × 0.07 × 0.37 mm) was used for data collection (Philips PW 1100 diffractometer, Mo-Kα radiation). Of 2590 reflections collected ($2\theta_{max}$ = 25°, correction for Lorentz and polarization effects, and absorption applied), 2136 were independent, and 1468 with $F_0 > 6\sigma(F_0)$ 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 = 0.029 and R_w = 0.031, and the final difference electron-density synthesis showed minimum and maximum values of −0.53 and +0.82 e Å^{-3}.

Crystal data for **6**: $C_{10}H_{10}OBr_2Ru$, M = 407.07, red crystals, orthorhombic, space group $P2_12_12_1$, a = 13.085(3), b = 12.107(3), c = 6.937(2) Å, V = 1099.0(5) Å^3, Z = 4, D_c = 2.460 g cm^{-3}, μ = 85.7 cm^{-1}, F(000) = 768, T = 24 °C. A crystal plate (0.044 × 0.20 × 0.23 mm) was used for data collection (Philips PW1100 diffractometer, Mo-Kα radiation). Of 2331 reflections collected ($2\theta_{max}$ = 25°, correction for Lorentz and polarization effects, and absorption applied), 1945 were independent, and 1720 with $F_o > 6\sigma(F_o)$ 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 = 0.030 and R_w = 0.035 and the final difference electron-density synthesis showed minimum and maximum values of −0.79 and +0.61 e Å^{-3}.

For both structures, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

[§] *Selected NMR and IR data* for **6**: ^1H NMR (250.13 MHz, CD_3NO_2) δ 6.27 (m, 1 H), 5.82 (m, 1 H), 5.69 (s, 5 H), 5.13 (t, 1 H), 3.43–3.36 (d, 1 H, J 19.5 Hz), 2.47–2.39 (d, 1 H, J 19.5 Hz); $^{13}C\{^1H\}$ NMR (62.68 MHz, $(CD_3)_2SO$ δ 204.6 (C=O), 106.8, 97.8 (C_5H_5), 77.6, 74.4, 42.0; IR ν/cm^{-1} [poly(chlorotrifluoroethylene)] 1717s (C=O).

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