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Formation of Novel Trinuclear Ruthenium Alkoxo Complexes and a Tetrameric Ruthenium Hydroxo Complex. Crystal Structure of $[(\eta^5\text{-}C_5Me_5)Ru]_3(\mu_3\text{-}O)(\mu_3\text{-}O^iPr)$ and $[(\eta^5\text{-}C_5Me_5)Ru(\mu_3\text{-}OH)]_4$

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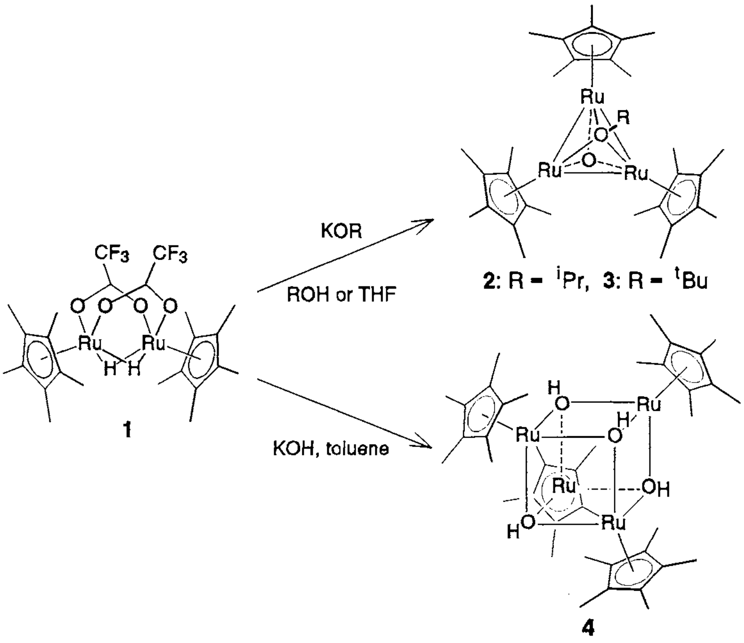
The dinuclear μ-carboxylatoruthenium complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}OCOCF_3)(\mu\text{-}H)]_2$ (**1**) reacts with alkali metal alkoxide ROM (R = ^{i}Pr, ^{t}Bu; M = Na, K) to give novel trinuclear μ_3-alkoxo-μ_3-oxoruthenium complexes $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu_3\text{-}O)(\mu_3\text{-}OR)$ (R = ^{i}Pr, ^{t}Bu). The tetrameric μ-hydroxoruthenium complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu_3\text{-}OH)]_4$ is synthesized by treating **1** with potassium hydroxide. The structures of the complexes have been determined by single crystal X-ray diffraction studies.

Recent studies have shown that $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}Cl)(Cl)]_2$ [1] and $[((\eta^5\text{-}C_5Me_5)Ru(\mu_3\text{-}Cl)]_4$ [2] are one of the most versatile starting materials for the synthesis of a variety of Ru(II) half-sandwich complexes. Tilley and co-workers[3] as well as Koelle *et al.*[4] have recently reported the preparation of methoxo- and ethoxoruthenium(II) complexes by the reaction of $[(\eta^5\text{-}C_5Me_5)Ru(\mu_3\text{-}Cl)]_4$ with MeONa or EtONa. In the preceding communication, we have shown that the coordinatively unsaturated fragment "$(\eta^5\text{-}C_5Me_5)Ru^+$", could readily be generated from $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}OCOCF_3)(\mu\text{-}H)]_2$ (**1**) and reacted with benzene to give saturated cationic π-arene complex.[5] Here we describe the preparation of novel ruthenium alkoxo- and hydroxo complexes by the reaction of **1** with the corresponding alkoxides and hydroxide. The X-ray crystal structures of the trinuclear μ_3-oxo-μ_3-*iso*-propoxo complex $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu_3\text{-}O)(\mu_3\text{-}O^iPr)$ (**2**) and tetrameric μ_3-hydroxo complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu_3\text{-}OH)]_4$ (**4**) are also reported.

Treatment of **1** with excess amounts (ca. 16 equiv) of ^{i}PrONa in the mixed (1/1) solvent of ^{i}PrOH and tetrahydrofuran at ambient temperature for 3 h affords a novel trinuclear ruthenium cluster $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu_3\text{-}O)(\mu_3\text{-}O^iPr)$ (**2**) having triply bridged *iso*-propoxo and oxo ligands in a 76% yield.

Similarly, the reaction of **1** with ^{t}BuOK in tetrahydrofuran at room temperature results in the formation of the corresponding trinuclear cluster complex $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu_3\text{-}O)(\mu_3\text{-}O^tBu)$ (**3**). These μ_3-alkoxo complexes were characterized by means of IR, ^{1}H NMR, and ^{13}C NMR spectroscopy as well as elemental analysis.[6] Notable features of the ^{1}H and ^{13}C NMR spectra of these μ_3-alkoxo complexes are the downfield shifts of the resonance signals for the triply bridging alkoxy groups in comparison with those for the corresponding alcohols (Δ = 0.2–0.4 ppm for the ^{1}H and Δ = 10–20 ppm for the ^{13}C NMR). The ^{1}H NMR spectra of **2** revealed the resonance signals for methyl and methine protons in *iso*–propyl group at δ 1.50 and 4.11 ppm, respectively. The signals for α–carbons of alkoxy groups in **2** and **3** were observed at δ 82.1 and 81.2 ppm, respectively, in the ^{13}C NMR spectra.



Scheme 1.

The molecular structure of **2** was determined on the basis of the X–ray diffraction studies.[7] The single crystals were grown from the mixed solvent of toluene and pentane stored at –20 °C. The resulting structure of **2** is displayed in Fig. 1 with some relevant bond distances and angles.

The X–ray structure determination of **2** shows the presence of an approximate equilateral triangle of rutheniums (mean Ru–Ru 2.888(2) Å) each η^5–bonded to a C_5Me_5 ligand, which is capped on one side by a *iso*–propoxo ligand (mean Ru–O 2.15(1) Å) and another side by an oxygen (mean Ru–O 2.05(1) Å). The C_5Me_5 ligand bonded to Ru(1) and *iso*–propoxo ligand were disordered in the relative proportions 56:44 and 67:33, respectively. The results of the X–ray diffraction study of *t*–butyl analogue of **2** reveal that **3** has also Ru_3–triangular structure capped by μ_3–oxo and μ_3–*t*–butoxo ligands.

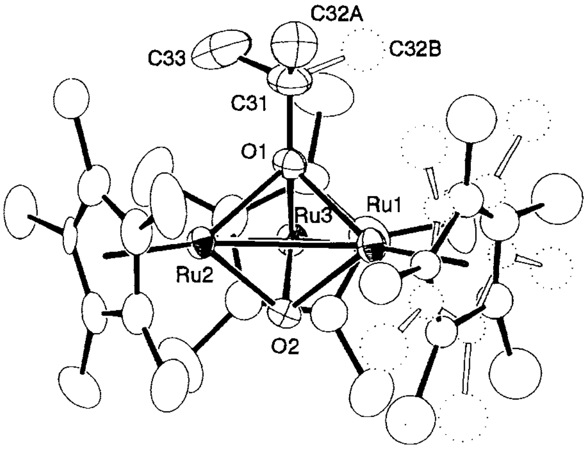


Fig. 1. Molecular structure of trinuclear μ_3–*iso*–propoxo complex **2**. Selected bond lengths (Å) and angles (°) are as follows: Ru(1)–Ru(2) 2.880(2), Ru(1)–Ru(3) 2.890(2), Ru(2)–Ru(3) 2.894(2), Ru(1)–O(1) 2.14(1), Ru(2)–O(1) 2.16(1), Ru(3)–O(1) 2.14(1), Ru(1)–O(2) 2.09(1), Ru(2)–O(2) 2.03(1), Ru(3)–O(2) 2.039(9), Ru(1)–Ru(2)–Ru(3) 60.07(5), Ru(1)–Ru(3)–Ru(2) 59.72(5), Ru(2)–Ru(1)–Ru(3) 60.21(5).

The alkoxo complexes, **2**, and **3** can be alternatively prepared by the reaction of the dimeric dichlororuthenium(III) complex $[(\eta^5\text{–}C_5Me_5)RuCl_2]_2$ with excess ^{i}PrONa or ^{t}BuOK, respectively, in toluene at ambient temperature. Whereas the reaction of **1** with bulky alkoxide such as ^{t}BuOK or ^{i}PrONa affords the trinuclear μ_3–alkoxo–μ_3–oxo complex as mentioned above, KOH reacts with **1** in the completely different fashion.

Treatment of **1** with large excess amounts (18 equiv) of aqueous KOH in toluene at room temperature for 7 h, followed by chromatographic purification on neutral alumina with toluene affords a tetrameric hydroxoruthenium(II) complex $[(\eta^5\text{–}C_5Me_5)Ru(\mu_3\text{–}OH)]_4$ (**4**) in a 74% yield as yellow micro prisms. Complex **4** was characterized on the basis of ^{1}H and ^{13}C NMR, IR, and FD-mass spectra,[8] and the structure was confirmed by X-ray diffraction studies by using a single crystal obtained from tetrahydrofuran.[9] The results is displayed in Fig. 2.

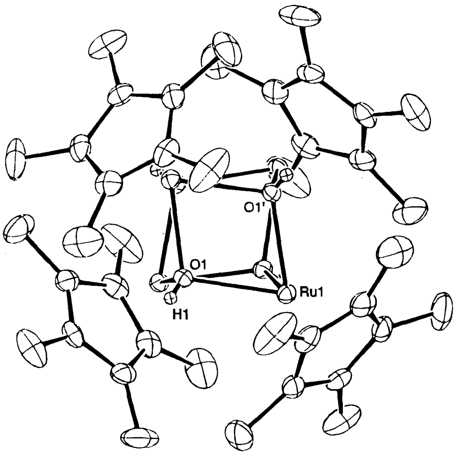


Fig. 2. Molecular structure of tetranuclear μ_3-hydroxo complex **4**. Selected bond lengths (Å) and angles (°) are as follows: Ru(1)-O(1) 2.191(2), O(1)-H(1) 0.78(3), O(1)-Ru(1)-O(1) 72.77(9), 72.89(8), 72.79(8), Ru(1)-O(1)-Ru(1) 104.91(9), 104.71(9), 104.83(8), Ru(1)-O(1)-H(1) 108(2), 113(2), 118(2).

The four Ru and four O atoms occupy the vertices of a distorted cube and array in approximate *Td* point group symmetry. A C_5Me_5 ligand is bound in a η^5 fashion to each Ru atom. This structure is closely related to the cationic hydroxo derivatives $[(\eta^6\text{-arene})Ru(\mu_3\text{-}OH)]_4^{4+}$ [10] and the tetrameric chlororuthenium complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu_3\text{-}Cl)]_4$.[2] The average Ru-O distance of 2.189(2) Å is slightly longer than that in the $[(\eta^6\text{-}C_6H_6)Ru(\mu_3\text{-}OH)]_4[SO_4]_2$ (2.12 Å). The O···O separation of 2.597(4) is comparable to that observed in $[(\eta^6\text{-}C_6H_6)Ru(\mu_3\text{-}OH)]_4[SO_4]_2$ (2.62 Å). There must be no bonding interactions between Ru atoms because the Ru···Ru distance of 3.468(1) Å is much longer than those for Ru-Ru single bonds.

Primary alkoxide such as MeONa readily reacts with **1** to form a dimeric complex having doubly bridging alkoxides. Treatment of **1** with 5 equiv of MeONa (1 **M** in MeOH) in tetrahydrofuran at room temperature for 15 min gives the dinuclear methoxoruthenium complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}OMe)]_2$ (**5**) in a 94% yield, whose dimeric structure was established by Tilley *et al.* based on X-ray structure analysis.[3]

Tetrameric hydroxoruthenium complex **4** can readily be converted to **2** or **5** in quantitative yields upon treatment with $^{i}PrOH$ or MeOH, respectively.

Further mechanistic studies pertaining the formation of the trinuclear μ_3-alkoxo complexes **2** and **3** will be reported elsewhere.

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6) **2**: ^{1}H NMR (C_6D_6, 500 MHz; δ/ppm) 4.11 (septet, J = 7.4 Hz, 1 H, $OCH(CH_3)_2$), 1.75 (s, 45 H, C_5Me_5), 1.50 (d, J = 6.1 Hz, 6 H, $OCH(CH_3)_2$); ^{13}C NMR (C_6D_6, 125 MHz; δ/ppm) 82.1 ($OCH(CH_3)_2$), 78.0 (C_5Me_5), 28.1 ($OCH(CH_3)_2$), 12.5 (C_5Me_5); IR (KBr) 2969, 2895, 1453, 1372, 1112, 1074, 1023, 940, 620, 584, 445 cm^{-1}; Anal. Found: C, 50.90; H, 6.54 %. Calcd for $C_{33}H_{52}O_2Ru_3$: C, 50.56; H, 6.69 %. **3**: ^{1}H NMR (C_6D_6, 100 MHz; δ/ppm) 1.75 (s, 45 H, C_5Me_5), 1.65 (s, 9 H, $OC(CH_3)_3$); ^{13}C NMR (C_6H_6, 67.5 MHz; δ/ppm) 81.2 ($OC(CH_3)_3$), 78.0 (C_5Me_5), 32.8 ($OC(CH_3)_3$), 12.5 (C_5Me_5); IR (KBr) 2972, 2948, 2895, 2050, 1629, 1452, 1372, 1355, 1244, 1163, 1071, 1020, 893, 779, 725, 618, 582, 445 cm^{-1}; Anal. Found: C, 51.02; H, 6.94 %. Calcd for $C_{34}H_{54}O_2Ru_3$: C, 51.17; H, 6.82 %.

7) Complex **2** crystallized from toluene-pentane in the triclinic system, space group $P\bar{1}$ (#2), with a = 11.250(4) Å, b = 17.894(5) Å, c = 8.958(6) Å, α = 90.48(4)°, β = 102.76(4)°, γ = 90.47(2)°, V = 1767(2) Å^3, Z = 2, and D_c = 1.473 g cm^{-3}. Intensity data were collected at 23 °C on a Rigaku AFC5R diffractometer with graphite-monochromated Mo$K\alpha$ radiation in the $5° < 2\theta < 55°$ range. Absorption correction was not applied. The structure was solved by direct methods. The non-hydrogen atoms were refined either anisotropically or isotropically by a full-matrix least-squares technique. The final R and Rw values are 0.075 and 0.089 for 3214 reflections with $F_o > 6\sigma(F_o)$. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.

8) **4**: ^{1}H NMR (C_6D_6, 500 MHz, δ/ppm) 1.68 (s, 60 H, C_5Me_5), 0.63 (s, 4 H, OH); ^{13}C NMR (C_6D_6, 125 MHz, δ/ppm) 96.3 (C_5Me_5), 11.6 (C_5Me_5); IR (KBr) 3400, 2945, 2900, 1455, 1425, 1375, 1070, 1027, 715, 415, 370 cm^{-1}; Anal. Found: C, 47.30; H, 6.29 %. Calcd for $C_{40}H_{64}O_4Ru_4$: C, 47.42; H, 6.37 %. Field-desorption mass spectrum was recorded on a Hitachi M-80 high-resolution mass spectrometer, and intensities of the obtained isotopic peaks for $C_{40}H_{64}O_4Ru_4$ agreed well with the calculated values.

9) Complex **4** crystallized from tetrahydrofuran in the tetragonal system, space group $I\bar{4}$ (#82), with a = 12.069(5) Å, c = 14.487(6) Å, V = 2108(3) Å^3, Z = 8, and D_c = 1.595 g cm^{-3}. Intensity data were collected at 23 °C on a Rigaku AFC5R diffractometer with graphite-monochromated Mo$K\alpha$ radiation in the $5° < 2\theta < 60°$ range. The structure was solved by direct methods and expanded by using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The position of hydrogen atom (H1) bound to oxygen atom was obtained by subsequent difference Fourier synthesis. Hydrogen atom H1 was refined isotropically, the rest were included in fixed positions. The final R and Rw values are 0.019 and 0.019 for 1808 reflections with $F_o > 3\sigma(F_o)$. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.

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