

Trinuclear Ruthenium Complex with a Face-Capping Benzene Ligand. Hapticity Change Induced by Two-Electron Redox Reaction

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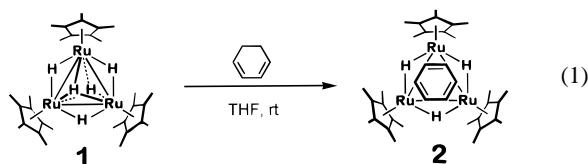
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Transition metal complexes with facial arene ligands have been of great interest, since these compounds may be reasonable models of arenes chemisorbed at a 3-fold site on the surface of a close-packed metal lattice.¹ Thus far, several trinuclear clusters containing facial arene ligands have been reported since the trismium cluster $\text{Os}_3(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}\text{C}_6\text{H}_6)$ was reported in 1985.² We recently synthesized a novel facial benzene complex $\{(\text{C}_5\text{Me}_5)\text{Ru}\}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}\text{C}_6\text{H}_6)$ (**2**) through the reaction of $\{(\text{C}_5\text{Me}_5)\text{Ru}\}_3(\mu\text{-H})_3(\mu_3\text{-H})_2$ (**1**) with 1,3-cyclohexadiene during studies of substrates activation on di- and trinuclear

polyhydride complexes of ruthenium.³ We describe herein a new synthetic method of facial benzene complex and a hapticity change in **2** caused by a redox reaction.

The reaction of **1** with 5 equiv of 1,3-cyclohexadiene in tetrahydrofuran for 12 h at ambient temperature led to the quantitative formation of **2** as a result of C–H bond cleavage at the allylic carbon atoms (eq 1).



Notable features of the ^1H and ^{13}C NMR spectra of **2** are the upfield shifts of the resonances for the coordinated benzene. The shifts of δ 2.43 and 35.8 for the ^1H and ^{13}C NMR resonances, respectively, are much higher than those observed in $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}\text{C}_6\text{H}_6)$ (δ_{H} 4.56)⁴ and $\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}\text{C}_6\text{H}_6)$ (δ_{H} 4.42, δ_{C} 38.2).⁵ The $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2$ coordination of the benzene ring was unequivocally confirmed by X-ray diffraction (Figure 1). Average “coordinated” and “uncoordinated” C–C distances of C_6H_6 ligand in **2** are almost equal within the experimental error.

In an attempt to observe intermediates by NMR spectroscopy, the reaction was performed in an NMR tube using tetrahydrofuran- d_8 at 0 °C. Although no signal, except for those attributable to **1**, **2**, and H_2 (δ 4.46) was observed, the reaction most likely proceed *via* an intermediary $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2$ -cyclohexadiene complex. Recently, we have confirmed the formation of such a $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2$ -*s-cis*-diene complex with an agostic C–H–Ru interaction in the reaction of **1** with an acyclic 1,3-diene such as butadiene or isoprene.⁶ In the present reaction, two of the three metal centers in **1** act as coordination sites and the third metal plays a role of an activation site to cleave an allylic C–H bond.

The reaction between **1** and 1,3-cyclohexadiene to give **2** is first-order in both cyclohexadiene and **1** ($k_{\text{obsd}} = 2.7(1) \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ at 66 °C) with $\Delta H^\ddagger = 13.5(8) \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -30.6(3) \text{ cal mol}^{-1} \text{ deg}^{-1}$. The negative large value of ΔS^\ddagger and the relatively small value of ΔH^\ddagger indicate that fitting into the size and shape between the substrate and the reaction site surrounded by three C_5Me_5 groups is substantial for the progress of the reaction. 1,3-Dienes having *s-cis* conformation favorable to coordination to the triangular Ru_3 site are, therefore, allowed to react with **1** even at low temperature. For example, the reaction of **1** with cyclopentadiene, butadiene, or isoprene smoothly proceeds at room temperature.^{3,6} The reaction with 1,4-cyclohexadiene, however, requires heating at 60 °C for 26 h to be completed because the orientation of two carbon–carbon double bonds may not be suitable for coordination to the Ru_3 site.

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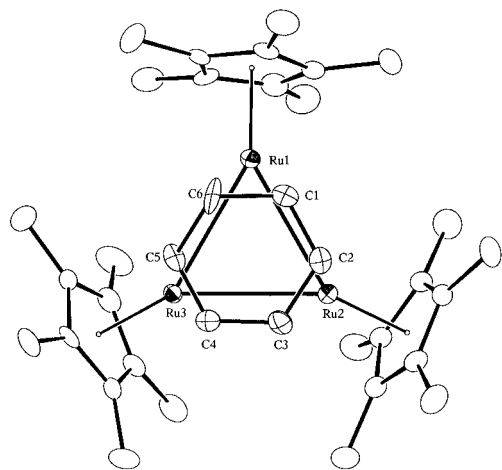
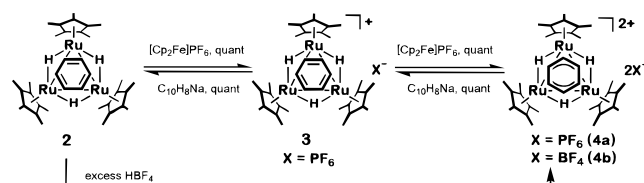


Figure 1. Molecular structure of $\{(\text{C}_5\text{Me}_5)\text{Ru}\}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ (**2**) with thermal ellipsoids at the 30% probability level. Selected bond length (Å) and angles (deg) are as follows: Ru(1)–Ru(2) 3.0493(8), Ru(1)–Ru(3) 3.0468(9), Ru(2)–Ru(3) 3.0537(8), Ru(1)–C(6) 2.221(8), Ru(1)–C(1) 2.192(7), Ru(2)–C(2) 2.173(7), Ru(2)–C(3) 2.240(7), Ru(3)–C(4) 2.176(7), Ru(3)–C(5) 2.180(7), C(1)–C(2) 1.436(10), C(2)–C(3) 1.45(1), C(3)–C(4) 1.43(1), C(4)–C(5) 1.40(1), C(5)–C(6) 1.42(1), C(6)–C(1) 1.43(1); Ru(2)–Ru(1)–Ru(3) 60.10(3), Ru(1)–Ru(2)–Ru(3) 59.91(2), Ru(1)–Ru(3)–Ru(2), 59.98(3), C(6)–C(1)–C(2) 118.7(6), C(1)–C(2)–C(3) 118.4(6), C(2)–C(3)–C(4) 121.4(6), C(3)–C(4)–C(5) 119.7(6), C(4)–C(5)–C(6) 119.7(7), C(5)–C(6)–C(1) 121.9(7).

Scheme 1



In the cyclic voltammogram recorded in tetrahydrofuran, two reversible one-electron oxidations were observed at -490 and -224 mV vs Ag/AgCl. These anodic waves correspond to $2^{0/+1}$ and $2^{+1/+2}$, respectively. In view of the interest in the correlation between oxidation state and structure of the face-capping benzene complex, oxidation of **2** with ferricinium salt was examined (Scheme 1).

Treatment of **2** with 1 equiv of $[(\text{C}_5\text{H}_5)_2\text{Fe}]\text{PF}_6$ in toluene at ambient temperature for 12 h quantitatively yielded the monocationic complex $\{[(\text{C}_5\text{Me}_5)\text{Ru}]_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]\text{PF}_6$ (**3**) which was isolated as a brown crystalline solid. Complex **3** is paramagnetic, and the ^1H signals for coordinated benzene and the C_5Me_5 group shift downfield, observed at δ 15.53 ($w_{1/2} = 60.2$ Hz) and 30.64 ($w_{1/2} = 67.7$ Hz), respectively. The resonance signal for hydrides could not be observed. The X-ray diffraction study using a single crystal obtained from cold (-33 °C) acetonitrile established the $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ coordination of benzene ligand in **3**.⁷

As was anticipated from the electrochemical study, the diamagnetic complex $\{[(\text{C}_5\text{Me}_5)\text{Ru}]_3(\mu\text{-H})_3(\mu_3\text{-}\eta^3\text{:}\eta^3\text{-C}_6\text{H}_6)](\text{PF}_6)_2$ (**4a**) was obtained *via* two-electron oxidation of **2**. The reaction of **2** with 2 equiv of $[(\text{C}_5\text{H}_5)_2\text{Fe}]\text{PF}_6$ in toluene proceeded at ambient temperature to result in the formation of **4a**. Treatment of paramagnetic **3** with 1 equiv of ferricinium salt afford, of course, the dication **4a** in a quantitative yield. The dicationic complex was alternatively prepared by treatment of **2** with HBF_4 in diethyl ether. Protonation of **2** and successive reductive elimination of molecular hydrogen led to the formation of $\{[(\text{C}_5\text{Me}_5)\text{Ru}]_3(\mu\text{-H})_3(\mu_3\text{-}\eta^3\text{:}\eta^3\text{-C}_6\text{H}_6)](\text{BF}_4)_2$ (**4b**). The struc-

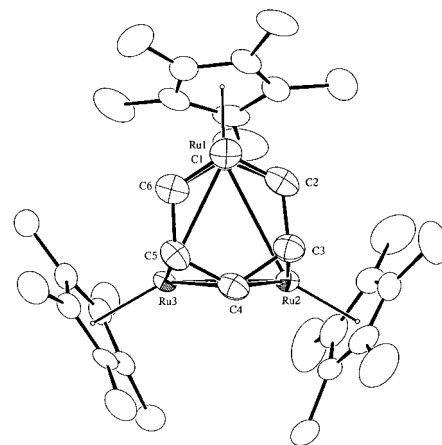


Figure 2. Molecular structure of $\{[(\text{C}_5\text{Me}_5)\text{Ru}]_3(\mu\text{-H})_3(\mu_3\text{-}\eta^3\text{:}\eta^3\text{-C}_6\text{H}_6)](\text{BPh}_4)_2$ (**4c**) with thermal ellipsoids at the 30% probability level. Selected bond length (Å) and angles (deg) are as follows: Ru(1)–Ru(2) 2.972(1), Ru(1)–Ru(3) 2.972(1), Ru(2)–Ru(3) 2.731(1), Ru(1)–C(6) 2.376(8), Ru(1)–C(1) 2.165(8), Ru(1)–C(2) 2.34(1), Ru(2)–C(3) 2.151(8), Ru(2)–C(4) 2.329(7), Ru(3)–C(4) 2.43(1), Ru(3)–C(5) 2.126(8), C(1)–C(2) 1.42(1), C(2)–C(3) 1.47(1), C(3)–C(4) 1.50(1), C(4)–C(5) 1.48(1), C(5)–C(6) 1.46(1), C(6)–C(1) 1.44(1); Ru(2)–Ru(1)–Ru(3) 54.35(2), Ru(1)–Ru(2)–Ru(3) 62.18(2), Ru(1)–Ru(3)–Ru(2), 63.48(2), C(6)–C(1)–C(2) 117.7(7), C(1)–C(2)–C(3) 122.2(7), C(2)–C(3)–C(4) 117.7(7), C(3)–C(4)–C(5) 117.5(7), C(4)–C(5)–C(6) 120.0(6), C(5)–C(6)–C(1) 120.0(8). The BPh_4 anions are omitted for clarity.

ture was determined by X-ray crystallography of a single crystal of $\{[(\text{C}_5\text{Me}_5)\text{Ru}]_3(\mu\text{-H})_3(\mu_3\text{-}\eta^3\text{:}\eta^3\text{-C}_6\text{H}_6)](\text{BPh}_4)_2$ (**4c**), which was quantitatively obtained upon treatment of **4b** with excess NaBPh_4 in methanol (Figure 2).⁸

The most striking structural feature is the $\mu_3\text{-}\eta^3\text{:}\eta^3$ coordination of the C_6 ring. An allyl moiety is coordinated to one of three ruthenium centers, and another allyl moiety bridges two ruthenium centers. Thus far, there have been a few precedents of trinuclear $\mu_3\text{-}\eta^3\text{:}\eta^3\text{-C}_6\text{H}_6$ complex.⁹ Complex **4** is, however, the first example of the hapticity change in face-capping benzene ligand induced by a redox process.

Although the C_6H_6 ligand in **4a** has four inequivalent sets of hydrogens in the solid state, the hydrogens are in time-averaged environments in solution and both ^1H and ^{13}C NMR resonances for the C_6 ring in **4a** appear as singlet peaks at δ_{H} 4.56 and δ_{C} 71.5, respectively, in temperatures ranging from 25 to -100 °C. The exact mechanism to account for this time-averaged spectrum has not been elucidated yet.

The dication **4** is reduced stepwise to form **2** quantitatively *via* the monocation **3** by treatment with sodium naphthalide.

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Supporting Information Available: A table of ^1H and ^{13}C NMR spectral assignments of **2**, **3**, and **4a–c** and ORTEP diagrams, texts describing X-ray procedures, and tables of X-ray data, positional and thermal parameters, and distances and angles for **2** and **4c** (44 pages). See any current masthead page for ordering and Internet access instructions.

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(8) Two acetone molecules were contained in a unit cell as solvents of crystallization.

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