

Partial Hydrogenation of Acenaphthylene on the Face of a Triruthenium Cluster: Formation of $(\mu_3\eta^1\eta^5\text{-C}_{12}\text{H}_{10})\text{Ru}_3\text{H}_2(\text{CO})_7$ from $(\mu_3\eta^2\eta^3\eta^5\text{-C}_{12}\text{H}_8)\text{Ru}_3(\text{CO})_7$

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A face-capping bonding mode for aromatic ligands in organometallic clusters has received considerable attention from organometallic chemists as a molecular model for adsorbed aromatic hydrocarbons on the surface.^{1–3} Recently, detailed studies on $(\mu_3\eta^2\eta^2\eta^2\text{-benzene})\text{M}_3(\text{CO})_9$ [M = Ru, Os]^{2a–d} and $[\mu_3\eta^2\eta^2\eta^2\text{-substituted benzene}][\text{Co}(\eta^5\text{-C}_5\text{H}_5)]_3$ ³ were reported, revealing the unique structures, electronic properties, and dynamic behavior of the coordinated arene ligands on the face of a trimetallic triangle. Of particular interest for this class of compounds are the potential reactivities of the arene ligands on the cluster framework, which may prove to be a novel aspect of the reactions and catalysis of organometallic clusters. However, the face-capping arene ligands so far reported are generally stable, and harsh reaction conditions are required for their transformation.^{1c,2a,e,f} We report here the preparation of a triruthenium cluster with acenaphthylene as the face-capping ligand and its high reactivity toward the reaction with H₂. The reaction of Ru₃(CO)₁₂ with acenaphthylene gave $(\mu_3\eta^2\eta^3\eta^5\text{-acenaphthylene})\text{-Ru}_3(\text{CO})_7$ (**1**), the hydrogenation of which produced a novel hydride complex having a μ_2 -fulvene structure, $(\mu_2\eta^1\eta^5\text{-4,5-dihydroacenaphthylene})\text{Ru}_3\text{H}_2(\text{CO})_7$ (**2**) (Scheme I). Molecular structures of **1** and **2** unequivocally show that this first hydrogenation of the face-capping arene ligand on a cluster framework results in partial hydrogenation of the acenaphthylene ligand in **1**, involving slippage of the acenaphthylene framework from the face of the Ru₃ triangle to an edge position.

Preparation of **1** was done by the reaction of Ru₃(CO)₁₂ with acenaphthylene in heptane under reflux for 24 h. The formed precipitates were purified on a silica gel column (CH₂Cl₂) to give **1** as dark brown crystals in 92% yield.⁴ The X-ray structure of **1** shows that the asymmetric unit contains two crystallographically distinct and independent molecules which are chemically equivalent. One of the molecules is shown in Figure 1. The Ru₃(CO)₇

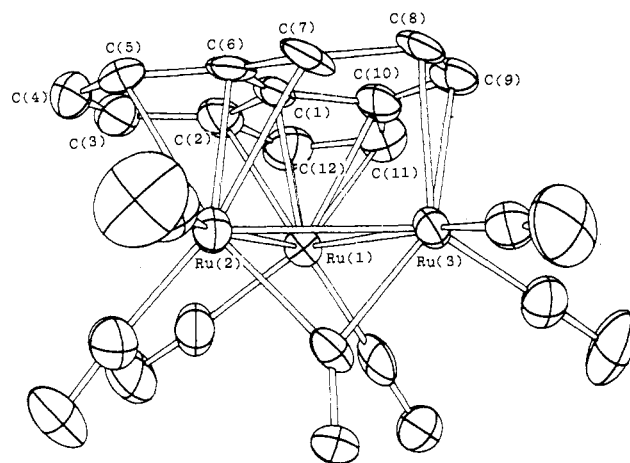
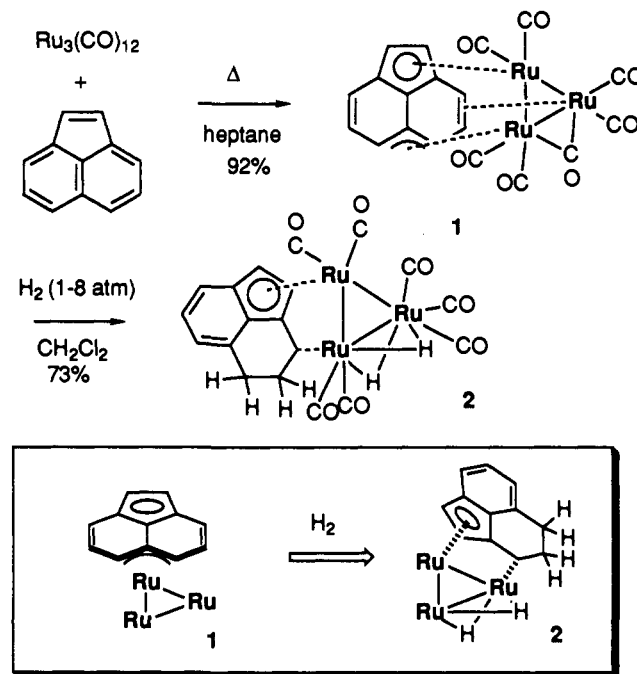


Figure 1. ORTEP view of **1**. Important bond distances (Å) and bond angles (deg): Ru(1)–Ru(2) = 2.876(2), Ru(2)–Ru(3) = 2.748(2), Ru(1)–Ru(3) = 2.939(2), Ru(1)–C(1) = 2.21(2), Ru(1)–C(2) = 2.27(2), Ru(1)–C(10) = 2.25(2), Ru(1)–C(11) = 2.28(2), Ru(1)–C(12) = 2.27(2), Ru(2)–C(5) = 2.45(2), Ru(2)–C(6) = 2.29(1), Ru(2)–C(7) = 2.46(1), Ru(3)–C(8) = 2.28(2), Ru(3)–C(9) = 2.36(2); Ru(2)–Ru(1)–Ru(3) = 52.39(4), Ru(1)–Ru(2)–Ru(3) = 62.96(5), Ru(1)–Ru(3)–Ru(2) = 60.65(5).

Scheme I



(1) For reviews, see: (a) Silverthorn, W. E. *Adv. Organomet. Chem.* **1975**, *13*, 47. (b) Muettterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. *Chem. Rev.* **1982**, *82*, 499. (c) Wade, P. L. *Chem. Rev.* **1982**, *82*, 499. (d) Wade, P. L. *Chem. Rev.* **1992**, *31*, 247.

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(3) Wade, P. L.; Büchner, K.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1259. Wade, P. L.; Büchner, K.; Pritzkow, H. *Organometallics* **1989**, *8*, 2745. Wade, P. L.; Zhu, L. *J. Organomet. Chem.* **1989**, *376*, 115.

(4) Crystallographic and spectral data for **1**: C_{38.50}H₁₇O₁₄ClRu₆, space group P2₁/n, a = 20.3092(7), b = 9.347(2), and c = 20.4772(8) Å, β = 93.028(3)°, Z = 4, R_F and R_wF of 0.070 and 0.076, respectively, for 4527 reflections with F_o > 5σ(F_o); ¹H NMR (CDCl₃) δ 6.47 (d, J = 6.35 Hz), 6.24 (dd, J = 5.86, 9.28 Hz), 6.00 (d, J = 2.44 Hz), 5.80 (d, J = 9.28 Hz), 5.57 (t, J = 6.35 Hz), 5.47 (d, J = 5.86 Hz), 4.89 (d, J = 2.44 Hz), 2.51 (d, J = 6.35 Hz); ¹³C NMR (acenaphthylene region; CDCl₃) δ 38.0, 66.0, 68.9, 79.0, 79.9, 82.3, 84.8, 88.4, 99.0, 116.4, 125.6, 130.4; (CO region; THF-d₆; –60 °C) δ 188.6, 192.0, 195.4, 203.6, 204.4, 207.0, 264.6; IR (KBr) 2024, 2030, 2010, 1996, 1986, 1953, and 1770 cm⁻¹.

moiety contains two terminal CO ligands to each Ru atom and one bridging CO ligand across the Ru(2)–Ru(3) bond. The acenaphthylene ligand is bonded over the face of the Ru₃ triangle. The face-capping coordination causes distortion of the acenaphthylene ligand from the planarity with mean deviation of 0.07 Å for each molecule. The ruthenium–acenaphthylene distances indicate that the acenaphthylene ligand is bonded to each Ru atom in η²-olefin, η³-allyl, and η⁵-cyclopentadienyl modes, and the carbon–carbon double bond within the six-membered ring remains uncoordinated. The π-cyclopentadienyl → metal coordination is often observed as a partial structure of di- or polynuclear compounds of azulenes⁵ and diiron complexes of

(5) (a) For a review, see: Churchill, M. R. *Prog. Inorg. Chem.* **1970**, *11*, 53. (b) Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1973**, *12*, 191.

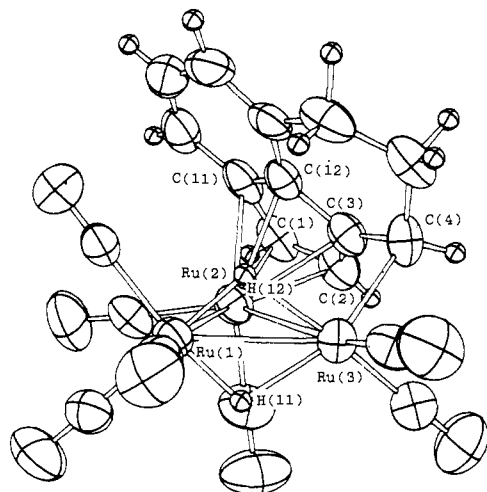


Figure 2. ORTEP view of **2**. Important bond distances (Å) and bond angles (deg): Ru(1)–Ru(2) = 2.833(1), Ru(2)–Ru(3) = 2.858(1), Ru(1)–Ru(3) = 2.666(1), Ru(2)–C(1) = 2.229(8), Ru(2)–C(2) = 2.211(6), Ru(2)–C(3) = 2.297(5), Ru(2)–C(11) = 2.352(8), Ru(2)–C(12) = 2.360(6), Ru(3)–C(4) = 2.150(7), Ru(1)–H(11) = 1.49(4), Ru(1)–H(12) = 1.55(4), Ru(3)–H(11) = 1.86(4), Ru(3)–H(12) = 1.96(4); Ru(2)–Ru(1)–Ru(3) = 62.55(3), Ru(1)–Ru(2)–Ru(3) = 55.86(2), Ru(1)–Ru(3)–Ru(2) = 61.60(3), Ru(2)–Ru(3)–C(4) = 83.0(2), C(3)–C(4)–Ru(3) = 91.1(4).

acenaphthylene.⁶ The closest structure analogous to **1** would be μ_3 -(azulene)Ru₃(CO)₇,^{5b} which has the π -cyclopentadienyl \rightarrow Ru coordination and a rather unusual π -dienyl ligand bound to two Ru atoms bridged by a CO ligand with two metal–olefin bonds and a three center Ru–C–Ru bond. In contrast, interatomic distances of **1** indicate that three ruthenium atoms coordinate to acenaphthylene with normal olefin–metal, π -allyl–metal, and π -cyclopentadienyl–metal bonds.

Hydrogenation of **1** occurred in CH₂Cl₂ at room temperature for 9 h under 1–8 atm of H₂ to give a novel triruthenium hydride cluster (**2**) in 73% yield as yellow crystals.⁷ The X-ray structure of **2** revealed that the complex consists of a 4,5-dihydroacenaphthylene ligand and a Ru₃H₂(CO)₇ moiety, as shown in Figure 2. The Ru₃H₂(CO)₇ moiety, having seven terminal CO ligands, contains two bridging Ru–H bonds between Ru(1) and Ru(3). The dihydroacenaphthylene ligand is bonded to two Ru atoms in the cluster framework in the μ_2 -fulvene coordination mode, similar to the bonding observed in several dinuclear metal carbonyl complexes with bridging fulvene ligands.⁸ The fulvene plane in the dihydroacenaphthylene ligand makes an angle of 48.5° with the Ru₃ plane.

(6) Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1970**, *9*, 2239. Nagashima, H.; Fukahori, K.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1991**, 786.

(7) Crystallographic and spectral data for **2**, C₁₉H₁₂O₇Ru₃, space group C2/c, *a* = 20.355(6), *b* = 14.625(2), and *c* = 16.559(4) Å, β = 124.29(1)°, *Z* = 8, *R_F* and *R_{wF}* of 0.0398 and 0.0227, respectively, for 3295 reflections with *F_o* > 3 σ (*F_o*); ¹H NMR (CD₂Cl₂) δ 7.26 (d, 1H, *J* = 7.3 Hz), 7.11 (t, 1H, *J* = 7.3 Hz), 6.75 (d, 1H, *J* = 7.3 Hz), 6.24 (d, 1H, *J* = 2.9 Hz), 4.58 (d, 1H, *J* = 2.9 Hz), 4.27 (br s, 1H), 2.52–2.77 (m, 2H), 2.06–2.30 (m, 2H), –9.01 (d, 1H, *J* = 4.4 Hz), –12.96 (d, 1H, *J* = 4.4 Hz); ¹³C NMR (CD₂Cl₂) δ 23.2, 23.9 (CH₂), 30.1 (CH₂), 69.9, 76.9, 78.6, 105.7, 111.5, 118.7, 123.3, 130.7, 136.7, 185.8, 189.0, 194.8 (two C), 196.1, 200.0, 203.5; IR (KBr) 2082, 2017, 1987, 1955, and 1940 cm^{–1}.

The formation of **2** from **1** revealed the following. First, 2 mol of H₂ react with **1** to form two bridging Ru–H moieties and contribute to partial hydrogenation of the acenaphthylene ligand. This is the first example of successful hydrogenation of arenes on the face of the trimetallic cluster. Second, the hydrogenation takes place at a C–C double bond within the six-membered ring of the acenaphthylene ligand to give the 4,5-dihydroacenaphthylene ligand. Hydrogenation of acenaphthylene usually takes place at the C–C double bond within the five-membered ring to give acenaphthene.⁹ Furthermore, 4,5-dihydroacenaphthylene itself is unstable and, to our knowledge, has never been isolated. Coordination to the Ru₃ cluster with the μ_2 : η^1 : η^5 mode contributes to the special stabilization of this unstable species. Third, the position of the acenaphthylene plane is shifted from the face of the Ru₃ triangle to the edge position during the hydrogenation. Dramatic alternation of the coordination mode from the μ_3 : η^2 : η^3 : η^5 -face-capping to the μ_2 : η^1 : η^5 -fulvene occurs concomitantly, explainable by a process involving a dynamic hapticity change of the acenaphthylene ligand during the hydrogenation.¹⁰

In sharp contrast to the general robustness of the face-capping μ_3 : η^2 : η^2 -arene ligands,^{2,3} high reactivity of the face-capping acenaphthylene ligand for the hydrogenation on the cluster framework is observed here. The face-capping acenaphthylene ligands are also sensitive to CO, and facile decapping of the acenaphthylene ligand instantly takes place at room temperature under a CO atmosphere to regenerate acenaphthylene and Ru₃(CO)₁₂ in quantitative yields. These features suggest that clusters with face-capping arene ligands are no longer a simple static model for surface chemisorbed species but are an intriguing starting point for exploring new reactions on the transition-metal clusters.¹¹

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Supplementary Material Available: Synthetic procedures and spectral data for **1** and **2**, detailed data for X-ray analyses of **1** and **2** (experimental, crystallographic data, atomic coordinates, temperature factors, bond distances, bond angles, and ORTEP drawings (23 pages); listing of observed and calculated structure factors (33 pages). Ordering information is given on any masthead page.

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(9) Bradley, J. S.; Hill, E.; Leonowicz, M. E.; Witzke, H. *J. Mol. Catal.* **1987**, *41*, 59.

(10) Variable-temperature ¹H NMR studies of **1** from –60 to 100 °C revealed no fluxional behavior of the acenaphthylene signals, indicating that the hapticity change does not occur in the absence of H₂.

(11) The present results may stimulate mechanistic discussion of the transformation of organic molecules on the heterogeneous catalysts. Recently, Saito and co-workers claimed the importance of the coordination of organic substrates on the face of the Ru₃ triangle in the heterogeneous dehydrogenation of cyclic alkenes with an immobilized Ru₃(CO)₁₂ catalyst on carbon. Yukawa, K.; Kanaboshi, H.; Saito, Y. *Chem. Lett.* **1992**, 1177.