Selective Hydrogenation of Aromatic Hydrocarbons Using a Triruthenium Carbonyl Cluster as a Template to Control the Hydrogenation Site: First Successful Isolation of 4,5-Dihydroacenaphthylene and 4,5-Dihydroaceanthrylene

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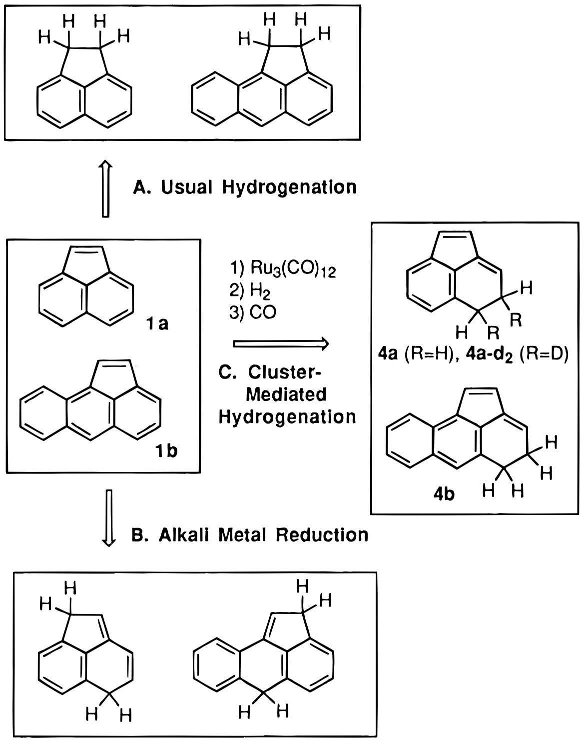
It is well-known that η^6-coordination of arenes to organotransition metal species dramatically changes the chemical nature of the benzene ring, giving rise to the discovery of many fascinating new synthetic reactions of aromatic compounds.[1,2] Typically, the complexation reduces the electron density of the π-electrons, leading to unusual nucleophilic substitution of arenes by a three-step process consisting of the complexation, the reaction with nucleophiles, and oxidative removal of the metallic species. Several organometallic clusters in which arene ligands are bonded to dual metal atoms were recently synthesized and characterized by several groups including us.[3−5] Since coordination to multimetallic centers could affect the arene reactivity by affording an electronic nature and steric factors that are different from those observed in monometallic arene complexes, it is of keen interest that novel transformation of aromatic compounds may be possible via complexation to clusters.[4] In this paper, we report the first clear example of multimetallic coordination of aromatic compounds resulting in the successful synthesis of new aromatic compounds which had never been achieved by other methods.

The two aromatic compounds 4,5-dihydroacenaphthylene (**4a**) and 4,5-dihydroaceanthrylene (**4b**) have not yet been reported. The simplest possible synthetic route to these compounds is selective hydrogenation of a carbon−carbon double bond in the six-membered ring in acenaphthylene (**1a**) or aceanthrylene (**1b**). However, either catalytic hydrogenation[6] or treatment with stoichiometric amounts of reducing reagents[7] exclusively afforded acenaphthene or aceanthrene as shown in Scheme 1, route A, because the carbon−carbon double bond at the peri position of **1a** or **1b** is the most reactive toward hydrogenation. The only way to access different isomers of acenaphthylene or aceanthrylene is alkali-metal reduction of **1a** or **1b**, which affords 1,5-dihydroacenaphthylene or 2,6-dihydroaceanthrylene (Scheme 1, route B).[8] We discovered a clue to synthesizing **4a** in our previous study,[5] in which hydrogenation of a triruthenium carbonyl cluster (**2a**) having acenaphthylene as a face-capping ligand resulted in the formation of **3a**. The molecular structure of **3a** showed that the dihydroacenaphthylene ligand is bonded to two ruthenium atoms with σ- and π-cyclopentadienyl (μ_2:η^1:η^5) coordination modes; however, it is formally considered that 4,5-dihydroacenaphthylene is bonded to two ruthenium atoms. Thus, if we find a method to remove the metal species from **3a**, **4a** could be isolable. After trial and error, we discovered that isolation of **4a** or **4b** was easily accomplished by treatment of **3a** or **3b** with CO.

Scheme 1



A hexane solution of **3a** (50 mg, 0.076 mmol in 5 mL of hexane) was stirred under a CO atmosphere at room temperature for 4 h, resulting in formation of an orange suspension. The yellow supernatant was separated by decantation and passed through a short alumina column by elution with hexane. From the resulting pale yellow solution, **4a** was isolated in 91% yield (10.6 mg).[9] The solid material in the orange suspension is $Ru_3(CO)_{12}$, which was obtained in over 90% yield by purification with an alumina column following elution with dichloromethane. The reaction can be drawn as follows: **3a** + 5CO → **4a** + $Ru_3(CO)_{12}$ + H_2 (Scheme 2). A deuterated compound, 4,5-dideuterioacenaphthylene, was obtained using D_2; treatment of **2a** with D_2 (8 atm) at room temperature for 12 h afforded **3a**−d_4 in 62% yield, and subsequent carbonylation gave 4,5-dideuterioacenaphthylene (**4a**−d_2)[9] in 63% yield.

A similar three-step process can be adopted to synthesize **4b**; reaction of aceanthrylene with $Ru_3(CO)_{12}$ afforded a triruthenium cluster **2b** in 90% yield. Hydrogenation (P_{H2} = 4 atm) of **2b** in CH_2Cl_2 at 50 °C for 18 h gave **3b** in 38% yield with

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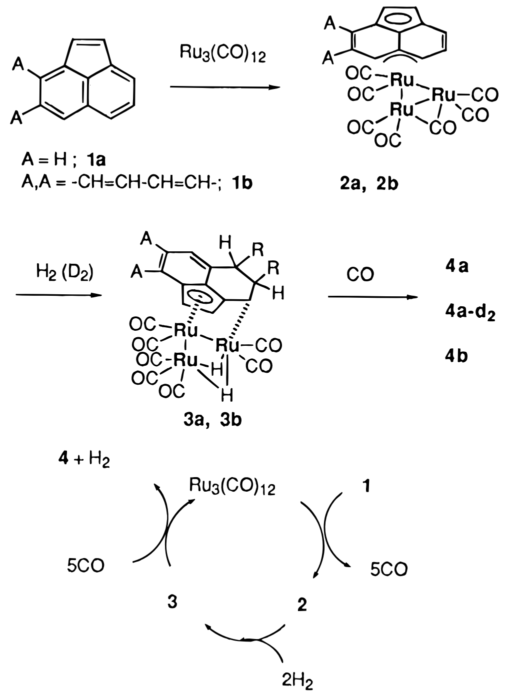
Scheme 2



a recovery of **2b** (12%).[10] Since **3b** is not very stable under these conditions, raising the conversion close to 100% caused a decrease in the yield of **3b**. Treatment of **3b** with CO(P_{CO} = 20 atm, −20 °C) gave **4b**[9] in 55% yield.

The selective hydrogenation of a carbon−carbon double bond in the six-membered ring of **1a** or **1b** can be attributed to the effective blocking of the most reactive carbon−carbon double bond at the peri position by π-cyclopentadienyl coordination to the ruthenium atom in **2a** or **2b**. Although the resulting μ_2:η^1:η^5-coordination mode in **3a** or **3b** is resistant to further hydrogenation, it readily reacts with CO, presumably through interconversion to the μ_2:η^2:^{4}-mode consisting of three π-bonds bound to the metals, which are easily replaced by CO to form **4a** or **4b**. Semiempirical molecular orbital calculations (PM3) suggested that hydrogenation of acenaphthylene was slightly endothermic (−0.1 kcal/mol), whereas that of aceanthrylene is exothermic by 3.0 kcal/mol. Thus, thermodynamically not very favorable hydrogenation from **1a** or **1b** to **4a** or **4b** was achieved in the coordination sphere of the cluster. The thermodynamic stability among the isomers was increased in the order **4a** < 1,5-dihydroacenaphthylene < acenaphthene, and **4b** < 2,6-dihydroaceanthrylene < aceanthrene. There is a great energy difference between **4a** and acenaphthene (21.1 kcal/mol) or **4b** and aceanthrene (17.5 kcal/mol). These calculations are consistent with facile dehydrogenation (DDQ, room temperature, 1 h) from **4a** or **4b** to **1a** or **1b**, respectively, and base-catalyzed isomerization (alcoholic KOH, room temperature, 24 h) of **4a** or **4b** to acenaphthene or aceanthrene, respectively.

Besides the sensitivity toward dehydrogenating reagents or bases, the diene moiety conjugated to the benzene ring is thought to be reactive with radicals. In fact, **4a** and **4b** are metastable yellow solid and gave a yellow intractable product within a few hours, probably derived from radical polymerization, upon storage in a solid state. In dilute solutions where the collision of molecules is rare, these compounds are stable for several days. High reactivity of **4a** and **4b** leading to their instability would be the primary reason why these compounds have not yet been synthesized, and the success of isolation by the cluster method described above is attributed to the mild reaction conditions (room temperature under neutral conditions) at the formation of **4a** and **4b**.

Consequently, the discovery that the metallic species can easily be removed from the arene−ruthenium cluster **3a** or **3b** made possible the three-step hydrogenation method of **1a** or **1b**, which selectively afforded **4a** and **4b** as a novel isomer of acenaphthene or aceanthrene. The triruthenium moiety was used as a template to activate H_2 and to control the hydrogenation site effectively, and it was recovered as recyclable $Ru_3(CO)_{12}$ at the final step of the reaction. The mild reaction conditions at the final step make possible the successful isolation of metastable **4a** or **4b**. We believe that this is an interesting entry to a cluster-assisted organic reaction, and that many new reactions using the cluster species as a template of the reaction, which cannot be achieved with mononuclear organometallic compounds, will appear in further investigations.[5]

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Supporting Information Available: Experimental details and characterization data for all new compounds including NMR (^{1}H, ^{13}C, ^{2}H) and mass spectra of **4a**, **4b**, and **4a**−d_2, crystallographic data and the ORTEP drawings of **2b** and **3b**, and summary of PM3 calculations (38 pages). This material is contained in many libraries on microfice, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[9] Spectral data for **4a**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.79−2.84 (m, 2H), 2.92−2.97 (m, 2H), 6.43 (t, J = 3.9 Hz, 1H), 6.53 (d, J = 5.4 Hz, 1H), 6.90 (d, J = 5.4 Hz, 1H), 6.95, 7.11, 7.12 (ABC pattern, J_{AB} = 0.6 Hz, J_{AC} = 7.0 Hz, J_{BC} = 8.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.50, 25.97, 117.85, 123.00, 125.35, 127.41, 128.76, 132.61, 129.96, 133.28, 138.28, 138.79; IR (CH_2Cl_2, cm^{-1}) 3221 (w), 2938 (s), 2838 (sh); UV (hexane; λ_{max} (nm), ϵ_{max}) 202.0 [7197], 256.0 [5462], 327.0 [1391]; M$^+$ 154. **4b**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.89−2.93 (m, 2H), 3.09−3.14 (m, 2H), 6.61 (d, J = 5.4 Hz, 1H), 6.69 (t, J = 4.1 Hz, 1H), 7.31−7.45 (m, 4H), 7.78 (dd, J = 7.7, 1.3 Hz, 1H), 7.99 (dd, J = 7.7, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 24.22, 26.58, 121.83, 123.39, 123.99, 124.50, 124.76, 128.25, 130.55, 133.06, 126.56, 129.63, 130.81, 134.26, 134.67, 140.06; IR (KBr, cm^{-1}) 3044 (w), 2930 (s), 2857 (sh); UV (hexane; λ_{max} (nm), ϵ_{max}) 219.0 [3496], 256.0 [8129], 293.0 [1363], 343.0 [495], 347.0 [513], 358.0 [551], 369.0 [480], 391.0 [374]; M$^+$ 204. **4a**-d_2: ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.76−2.85 (m, 1H), 2.90−2.98 (m, 1H), 6.43 (d, J = 3.9 Hz, 1H), 6.53 (d, J = 5.4 Hz, 1H), 6.91 (d, J = 5.4 Hz, 1H), 6.96, 7.12, 7.13 (ABC pattern, J_{AB} = 0.6 Hz, J_{AC} = 7.0 Hz, J_{BC} = 8.2 Hz, 3H); ^{2}H NMR (47 MHz, $CHCl_3$) δ 2.71−3.05 (m, 2D); IR (CH_2Cl_2, cm^{-1}) 2935 (s), 2863 (s), 2030 (vs); M$^+$ 156.

[10] The X-ray structures of **2b** and **3b** are analogous to those of **2a** and **3a**, respectively. See details in the supporting information.