Monatshefte für Chemie 131, 1225–1239 (2000)

Monatshefte für Chemie
Chemical Monthly

Invited Review

Facile Hydrogenation of Acenapthylenes and Azulenes on the Face of a Triruthenium Carbonyl Moiety: Discovery of Specific Reactions on the Cluster Framework Providing Unique Insight for Cluster Catalysis

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Summary. Activation of molecular hydrogen by triruthenium carbonyl clusters bearing acenaphthylene or aceanthrylene as the face-capping ligand results in partial hydrogenation of these polyaromatic ligands, giving the corresponding hydride carbonyl clusters bound to hydrogenated acenaphthylene or aceanthrylene. The first isolation of 4,5-dihydroacenaphthylene or 4,5-dihydroaceanthrylene was achieved by treatment of the resulting hydride carbonyl clusters with CO. Similarly, triruthenium carbonyl species bearing substituted azulenes as the face-capping moiety gives the corresponding hydride carbonyl cluster bearing partially hydrogenated azulenes at room temperature; the corresponding partial hydrogenation of azulenes does not occur with di- or tetraruthenium homologues. Hydrogenation of di-, tri-, and tetraruthenium carbonyl clusters bearing substituted azulenes at elevated temperatures furnishes hydrogenative cluster fragmentation to mononuclear ruthenium hydrides; the stereochemistry of these complexes suggests that the reaction takes place through the activation of H_2 by the multinuclear species. The roles of the acenaphthylene or azulene ligands as hemilabile μ_3-ligands for triruthenium carbonyl clusters are discussed.

Keywords. Ruthenium; Cluster; Hydrogenation; Arene; Face capping mode.

Introduction

Catalysis of organometallic clusters has long received much attention from chemists, proposing unique molecular models for better a understanding of heterogeneous catalysis [1–3]. In recent years, it has become increasingly important that certain clusters provide a novel class of homogeneous catalysts enabling reactions unavailable by conventional mononuclear transition metal catalysts [1, 4]. According to *Laine*, cluster catalysis is defined as "the reaction mediated by catalysts containing at least two metal atoms (and at least one metal-metal bond) that both participate in the transformation of the substrates (multisite activation)" [1a]. Research of synthesis, structure, and elementary reactions of transition metal clusters is one way to develop cluster catalysis, and a number of reports with a variety of clusters has been published contributing to the knowledge in this field [1–4]. An important problem of the reaction of clusters is the possibility of facile cluster fragmentation, which sometimes results in the formation of highly reactive species with lower nuclearity [4]. Introduction of certain bridging ligands which effectively reinforce the cluster framework has been examined to solve this problem and attained some success [3a,b, 5].

Polyaromatic or polyene ligands are of potential utility as bridging ligands for organometallic clusters [6]. As observed with well-investigated mononuclear organometallic complexes bearing arene ligands [7], conjugated π-ligands are bound to the metal center *via* a variety of bonding modes, and each bonding mode can easily interconvert each other by way of hapticity change [7, 8]. This flexibility in coordination modes sometimes produces a coordination site for organic substrate by ring slippage [8]. In other words, if we can introduce bridging polyaromatic or polyene ligands in transition metal clusters, which contribute to the stability of the cluster framework, these ligands might act as hemilabile ligands which easily open coordination sites by hapticity change. Diiron carbonyl complexes bearing bridging polycyclic conjugated π-ligands, acenaphthylene and azulenes, have been synthesized and subjected to studies on structures and CO exchange processes [9–11], whereas fluxional behavior suggesting facile hapticity change has been evidenced in the haptotropic rearrangement of dinuclear systems [12, 13]. However, little was known on the further reactivity of these compounds when we started to investigate their reactions.

Another important aspect for clusters bearing polyaromatic or polyene ligands is related to the activation of arenes by coordination to transition metal species. The well-investigated chemistry of mononuclear arene transition metal complexes reveals that coordination of arenes to transition metals results in their facile reaction with nucleophiles, C–H bond activation, and other phenomena occurring in coordination sphere of transition metals [7]. A cluster version of the arene transition metal chemistry has been explored by *Johnson* and *Wadepohl* who reported interesting structures and fluxional behavior of trinuclear clusters bearing triply bridging monocyclic arene ligands which cover the face of the trimetallic triangle [6]. One can expect a cluster effect with respect to the reactivity of the coordinated arene ligands on the face of the cluster in comparison with those of the corresponding mononuclear compounds; however, the μ_3-arene ligand is generally robust, and only little work has been done on the reactivity of the arene ligand [14].

In recent years we have been working on the synthesis and reactions of di-, tri-, or tetraruthenium carbonyl clusters bearing acenaphthylene, aceanthrylene, or substituted azulene ligands. As to the reaction studies, we have focused on the reactions with H_2 because of the following two reasons: (*i*): The reaction with H_2 ranks among the best studied processes related to reactions and catalysis of organometallic clusters [15]. Through the studies on the hydrogenation of the triruthenium clusters described above, we may see how the polyaromatic or polyene ligands affect the reactivity of the clusters towards hydrogenation. (*ii*): The hydrogenation of coordinated arenes is important for a better understanding of catalytic hydrogenation of arenes, which is more easily achieved with heterogeneous catalysis than with homogeneous procedures [16]. The aim of this review is

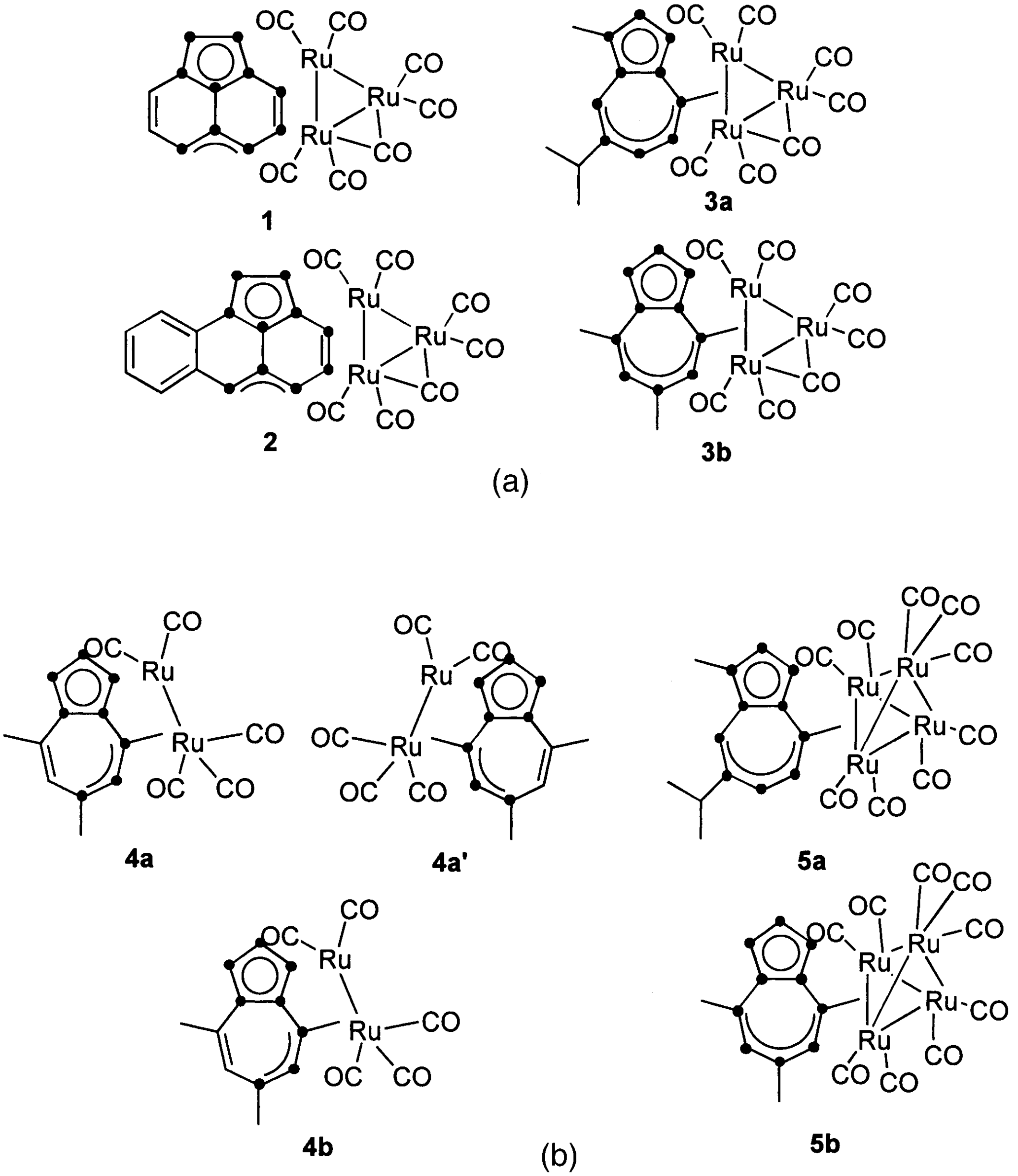


Fig. 1. (a) Triruthenium carbonyl clusters bearing μ-acenaphthylene (**1**), μ-aceanthrylene (**2**), μ-guaiazulene (**3**), and μ-4,6,8-trimethylazulene (**4**) ligands; (b) di- and tetraruthenium carbonyl clusters bearing μ-guaizulene (**4a**, **5a**) and μ-4,6,8-trimethylazulene (**4b**, **5b**) ligands; ●: carbon atoms bonded to Ru

to help to understand these two points, namely the role of bridging conjugated π-ligands in the reactivity of clusters and the hydrogenation behaviour of the coordinated arenes in the coordination sphere of multimetallic species, by summarizing our recent studies on the synthesis and hydrogenation of a series of di-, tri-, and tetranuclear clusters bearing acenaphthylene, aceanthrylene, or azulene ligands [17–21].

Synthesis and Structures of (μ-*L*)$Ru_3(CO)_7$

Triruthenium or osmium carbonyl clusters of the general formula ($\mu_3:\eta^2:\eta^2:\eta^2$-arene)$M_3(CO)_9$ in which arenes are coordinated in the facial bonding mode have been reported by *Johnson* and coworkers [6a–c]. Although ($\mu_3:\eta^2:\eta^2:\eta^2$-arene)$Ru_3(CO)_9$ cannot be directly synthesized by simple substitution of CO ligands of $Ru_3(CO)_{12}$ by arene [22], thermal displacement of five CO ligands of $Ru_3(CO)_{12}$ by acenaphthylene or aceanthrylene took place easily to give ($\mu_3:\eta^2:\eta^3:\eta^5$-acenaphthylene)$Ru_3(CO)_7$ (**I**) or ($\mu_3:\eta^2:\eta^3:\eta^5$-aceanthrylene)$Ru_3(CO)_7$ (**2**) [15, 16]. A similar reaction of $Ru_3(CO)_{12}$ with azulenes afforded **3** in moderate yield and was accompanied by the corresponding Ru_2 and Ru_4 analogues [9a, 11, 18]; the coordination mode of the azulene ligand in (μ-guaiazulene)$Ru_3(CO)_7$ (**3a**) or (μ-4,6,8-trimethylazulene)$Ru_3(CO)_7$ (**3b**) is partly different from that of **1** and **2** (Scheme 1, Fig. 1). Thus, the triruthenium arrangement in **1**–**3** with a triangular geometry is stabilized by six terminal CO groups, two ligands at each ruthenium atom, and one bridging CO ligand. The conjugated π-ligands are bound to the face of the triruthenium moiety. The carbon atoms in the five-membered ring of the π-ligand are coordinated to one ruthenium atom with the conventional π-cyclopentadienyl mode. In **1** and **2**, other two ruthenium atoms are bound to two and three carbons with η^2- and η^3-coordination modes, respectively. In contrast, five carbons in the seven membered ring in **3a** or **3b** are bound to two ruthenium atoms

$$\mathrm{Ru_3(CO)_{12}} + \text{acenaphthylene} \rightarrow (\mu_3:\eta^2:\eta^3:\eta^5\text{-acenaphthylene})\mathrm{Ru_3(CO)_7}\ (\mathbf{1})$$

$$\mathrm{Ru_3(CO)_{12}} + \text{aceanthrylene} \rightarrow (\mu_3:\eta^2:\eta^3:\eta^5\text{-aceanthrylene})\mathrm{Ru_3(CO)_7}\ (\mathbf{2})$$

$$\mathrm{Ru_3(CO)_{12}} + \text{guaiazulene} \rightarrow \left\{ \begin{array}{c} (\mu_2:\eta^3:\eta^5\text{-guaiazulene})\mathrm{Ru_2(CO)_5}\ (\mathbf{4a}) \\ + \\ (\mu\text{-guaiazulene})\mathrm{Ru_3(CO)_7}\ (\mathbf{3a}) \\ + \\ (\mu\text{-guaiazulene})\mathrm{Ru_4(CO)_9}\ (\mathbf{5a}) \end{array} \right.$$

$$\mathrm{Ru_3(CO)_{12}} + 4,6,8\text{-}\mathit{TMA} \rightarrow \left\{ \begin{array}{c} (\mu_2:\eta^3:\eta^5\text{-}4,6,8\text{-}\mathit{TMA})\mathrm{Ru_2(CO)_5}\ (\mathbf{4b}) \\ + \\ (\mu\text{-}4,6,8\text{-}\mathit{TMA})\mathrm{Ru_3(CO)_7}\ (\mathbf{3b}) \\ + \\ (\mu\text{-}4,6,8\text{-}\mathit{TMA})\mathrm{Ru_4(CO)_9}\ (\mathbf{5b}) \end{array} \right.$$

$$\mathit{TMA} = 4,6,8\text{-trimethylazulene}$$

Scheme 1

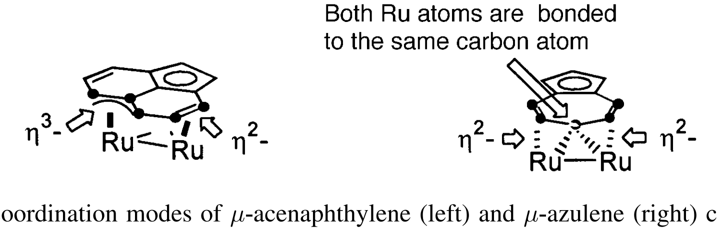


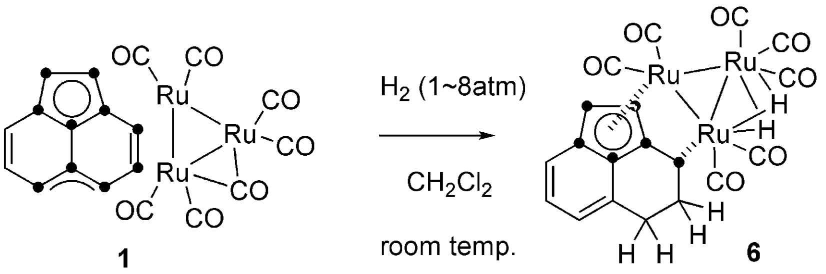
Fig. 2. Coordination modes of μ-acenaphthylene (left) and μ-azulene (right) complexes

in the μ_2-pentadienyl fashion, in which the central carbon is located within bonding distances of both ruthenium atoms. According to coordination to the face of the cluster, the acenaphthylene or aceanthrylene ligand slightly deviates from the planar structure, whereas the azulene ligands are significantly distorted like an arch. Synthesis of the azulene complexes also produces the diruthenium (**4a**,**b**) and tetraruthenium (**5a**,**b**) analogues. In **4a**,**b**, carbons in the five-membered ring are bound to one ruthenium atom in the π-cyclopentadienyl mode, whereas three carbons in the seven membered ring are bonded with the other ruthenium atom in the η^3-allyl mode. In contrast, the azulene ligand is located on a face of the tetraruthenium core in the tetraruthenium analogues **5a**,**b**; their coordination mode is similar to that observed in **3a**,**b**.

Hydrogenation of (μ-*L*)$Ru_3(CO)_7$

Activation of molecular hydrogen is one of the fundamental reactions with respect to catalysis, and studies towards this goal have been performed from the early days of the cluster chemistry [15, 16]. Activation of H_2 generally takes place around 100°C, accompanied by cleavage of the metal-metal bond and subsequent cluster fragmentation and recombination; for example, $Ru_3(CO)_{12}$ reacted with H_2 at 100°C to form $Ru_4H_4(CO)_{12}$ [23]. In other words, two problems arising from this result are how to suppress the cluster fragmentation and how to activate H_2 at lower temperature. We expected that introduction of acenaphthylene, aceanthrylene, or azulenes as the μ_3-ligand would contribute to a prevention of cluster fragmentation, whereas the potential capability of ring slippage of these ligands, *i.e.* hapticity change of π-ligand, might take part in facile opening of a coordination site for H_2. Two important results emerged from hydrogenation studies on **1**–**3** [17]; one of them was as expected, whereas the other one was unprecedented. Hydrogenation of **1** was usually complete within several hours at ambient temperature, and the triruthenium framework was maintained during the hydrogenation. A $Ru_3H_2(CO)_7$ moiety was produced by oxidative addition of H_2 to the Ru_3 species. Interestingly, the hydrogenation did not stop when one molecule of H_2 was consumed. Two molecules of H_2 reacted with **1** to take part in the formation of dihydride species and partial hydrogenation of the acenaphthylene ligand. The molecular structure of the product, ($\mu_2:\eta^1:\eta^5$-4,5-dihydroacenaphthylene)$Ru_3H_2(CO)_7$ (**6**), revealed that the Ru_3 moiety contained seven terminal CO groups and two bridging hydride ligands. A carbon-carbon double bond in the acenapthylene ligand in **1** was selectively hydrogenated; this is unusual in the chemistry of acenapthylene as will be descussed later. The resulting 4,5-dihydroacenaphthylene is bound to the Ru_3 core in the μ_2-fulvene coordination mode; the Ru-C bond distances suggest that the five carbons in the five-membered ring are coordinated to one ruthenium atom with a η^5-cyclopentadienyl coordination mode, whereas there is a σ-bond between the *exo*-carbon of the cyclopentadienyl ring and the other ruthenium atom. The planar dihydroacenaphthylene ligand adopts an angle of 42.5° with respect to the Ru_3 plane.

Hydrogenation of **2** also proceeded in a similar fashion at ambient temperature to form the corresponding dihydride complex **7** which was characterized by spectroscopy and crystallography. Hydrogenation products of the azulene



Scheme 2

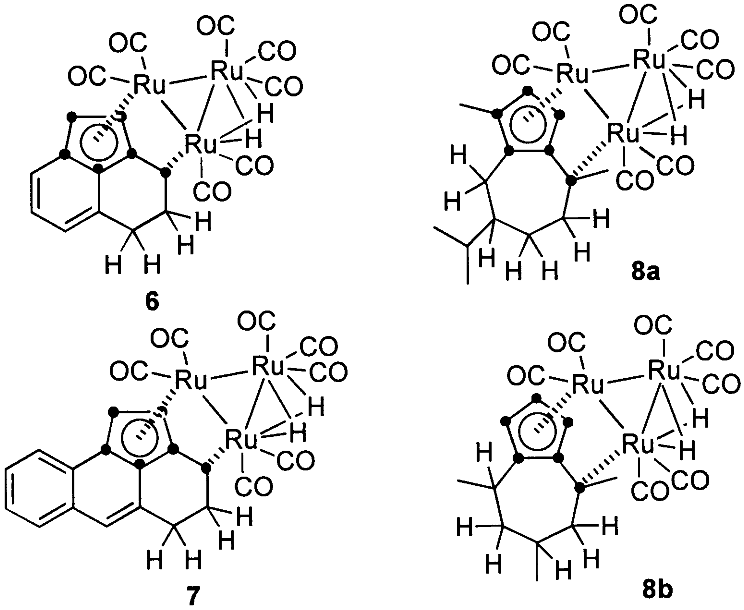


Fig. 3. Triruthenium dihydride carbonyl clusters bearing μ_2-acenaphthylene (**6**), μ_2-aceanthrylene (**7**), μ_2-guaiazulene (**8a**), and μ_2-4,6,8-trimethylazulene (**8b**) ligands; ●: carbon atoms bonded to Ru

complexes are unstable and result in a further hydrogenation described below; however, spectroscopic evidence showed that **3a**,**b** reacted with H_2 to form the corresponding dihydride complexes **8a**,**b**, respectively, at room temperature under conservation of the Ru_3 framework. Two of the carbon-carbon double bonds in the seven-membered ring of the azulene ligand were selectively hydrogenated.

$$\mathbf{2} \rightarrow (\mu_2\!:\!\eta^1\!:\!\eta^5\text{-4,5-dihydroaceanthylene})\mathrm{Ru_2H_2(CO)_7}\ (\mathbf{7})$$

$$\mathbf{3a} \rightarrow (\mu_2\!:\!\eta^1\!:\!\eta^5\text{-4,5,6,7-tetrahydroguaiazulene})\mathrm{Ru_2H_2(CO)_7}\ (\mathbf{8a})$$

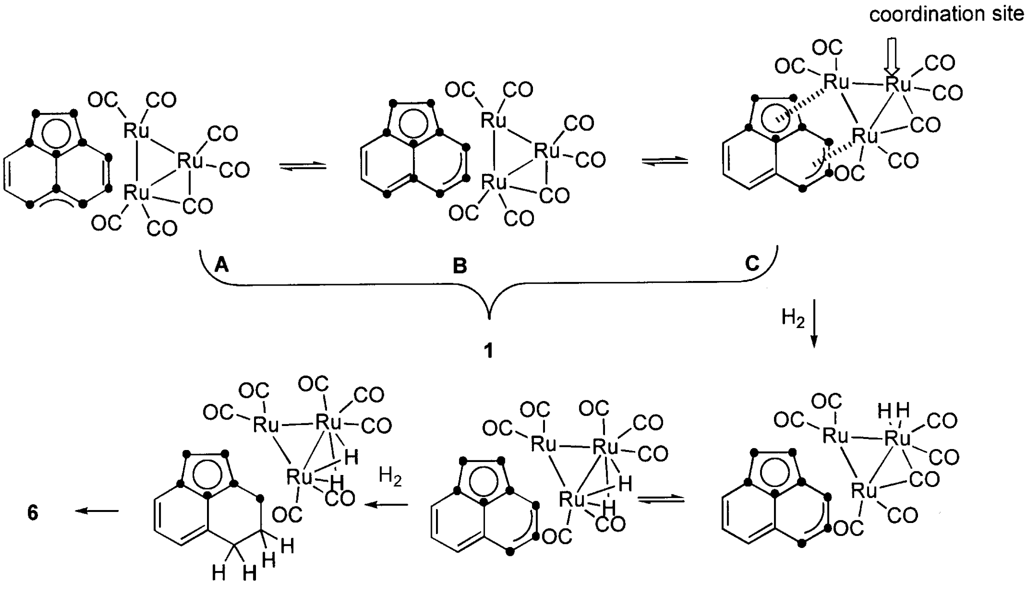
$$\mathbf{3b} \rightarrow (\mu_2\!:\!\eta^1\!:\!\eta^5\text{-4,5,6,7-tetrahydro-}\mathit{TMA})\mathrm{Ru_2H_2(CO)_7}\ (\mathbf{8b})$$

$$\mathit{TMA} = \text{4,6,8-trimethylazulene}$$

Scheme 3

It is important to note that these reactions with H_2 proceed at lower temperatures than those of $Ru_3(CO)_{12}$ and other triruthenium clusters, though the clusters **1**–**3** are coordinatively saturated. This suggests hemilability of the acenaphthylene, aceanthrylene, and azulene ligands, which effectively stabilize the triruthenium cluster but readily open the coordination site for activation of H_2 as soon as the solution of these clusters is exposed to hydrogen. The fact that the hydrogenation induces the dynamic change of the coordination mode of the conjugated π-ligands, *e.g.* $\mu_3{:}\eta^2{:}\eta^3{:}\eta^5$-acenaphthylene to $\mu_2{:}\eta^1{:}\eta^5$-dihydroacenaphthylene, is a clue to understand their hemilability in the hydrogenation. As noted above, a hapticity change of conjugated π-ligands occurs in these clusters, which, for example, is involved in the haptotropic interconversion between two isomers of $(\mu_2{:}\eta^3{:}\eta^5$-acenaphthylene$)Fe_2(CO)_5$ [12, 13]. Thus, one possible mechanism for the formation of **6** from **1** may be that illustrated in Scheme 4. A small movement of the Ru_3 moiety on the acenapthylene ligand accomplishes the change of the coordination mode from **A** to **B**. Dissociation of the η^2-carbon-carbon double bond in **B** from the ruthenium atom results in a conversion of the $\mu_3{:}\eta^2{:}\eta^3{:}\eta^5$-coordination mode in **1** to the $\mu_2{:}\eta^3{:}\eta^5$-fashion in **C**. This reaction produces a coordination site for oxidative addition of H_2. A facile CO scrambling process leads to the formation of a bridging dihydride, which takes part in hydrogenating the η^3-allyl moiety in **C** accompanied by oxidative addition of another molecule of H_2. These processes involve facile hapticity change of the coordination modes, oxidative addition of H_2, and interconversion of terminal dihydride to bridging accompanied by conversion of the bridging CO group to the terminal one.

An interesting feature of the activation of H_2 by these triruthenium clusters is that the reaction furnishes the addition of H_2 to carbon-carbon double bonds in the π-ligand. Of particular importance is the selective hydrogenation of a carbon-carbon double bond in the six membered ring of the acenaphthylene or acenthrylene

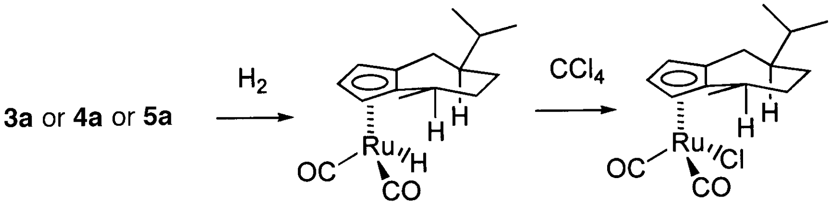


Scheme 4

ligands on the face of the Ru_3 framework. Acenaphthylene or aceanthrylene feature both a reactive carbon-carbon double bond in the five-membered ring and a naphthalene or anthracene part [24]. The former is generally active towards hydrogenation, whereas the latter is robust. Coordination of these compounds to the Ru_3 moiety results in a decrease of the reactivity of the carbon-carbon double bond in the five-membered ring and an increase of the reactivity of a carbon-carbon bond in the six-membered ring, thus leading to preferential hydrogenation of the carbon-carbon double bond in the six-membered ring. A clue to understand this result is the coordination mode of the acenapthylene or aceanthrylene ligand. The π-cyclopentadienyl coordination of carbons in the five-membered ring decreases the reactivity of the carbon-carbon double bond, whereas coordination of carbons in the six-membered ring diminishes the aromaticity of the naphthalene or anthracene part and increases its reactivity towards hydrogenation. The π-cyclopentadienyl coordination of carbons in the five-membered ring of the azulene ligands prevents the addition of H_2 to these carbons. In other words, the Ru_3 cluster effectively blocks the carbon-carbon double bond in the five-membered ring by π-cyclopentadienyl coordination, a feature first achieved by coordination of the discussed ligands to the multiruthenium system.

As mentioned above, the triruthenium hydride clusters **8** are unstable and easily undergo further reaction with H_2. Formation of two products, a mononuclear ruthenium hydride (**9**) and $RuH_4(CO)_{12}$ (**10**), was observed in the ^1H NMR spectrum of the reaction mixture. When the hydrogenation was carried out at 100°C, all starting material **3** was quantitatively converted to a mixture of **9** and **10**. Four hydrogen molecules reacted with **3** of which five hydrogen atoms contribute to formation of a pentahydroazulenyl ligand, one hydrogen atom generates the Ru-H in **9**, and the remaining two hydrogen atoms lead to the formation of two molecules of $HRu(CO)_3$, tetramerization of which forms the stable cluster $Ru_4H_4(CO)_{12}$. Similar hydrogenative cluster fragmentation to form a monoruthenium hydride complex and **10** was also observed in a reaction of **1** or **2** with H_2 at elevated temperatures [25].

The mononuclear ruthenium hydride complexes **9** formed by hydrogenation of **3** were expected to consist of a mixture of diastereomers as a result of the two asymmetric carbon atoms present in **9**. However, the ^1H NMR spectrum of **9** indicates the formation of only one diastereomer. Although **9** itself is an oil and its stereochemistry cannot be determined by crystallography, replacement of the ruthenium hydride by a chlorine atom gave crystals of **11** suitable for X-ray structure determination. The molecular structure of **11** unequivocally showed that



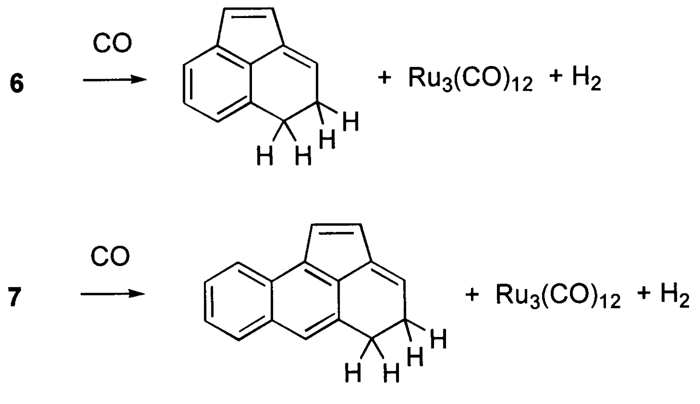
Scheme 5

all of hydrogen atoms introduced by the hydrogenation are *cis* to the ruthenium atom. This result suggests that the activation of H_2 takes place by the Ru_n moiety in the starting cluster and the activated hydrogen atoms readily induce hydrogenolysis of the Ru-C bonds to give **9**.

As described above, compounds **4** and **5**, di- and tetranuclear analogues of **3**, are isolated as by-products in the synthesis of **3**. Hydrogenation of **4** and **5** provides interesting aspects in considering the effect of nuclearity in the hydrogenation of clusters. Reactions of **4** or **5** with H_2 did not occur below 100°C. At 100°C, **4** and **5** were quantitatively converted to a mixture of **9** and **10**. No intermediates such as homologues of **8** were observed in these hydrogenations. The ruthenium hydride **9** obtained this way is a single stereoisomer, the stereochemistry of which is similar to that of **9** obtained by hydrogenation of **3**. The fact that the reaction requires a temperature above 100°C shows that only the triruthenium cluster **3** offers a reaction pathway activating H_2 at lower temperatures in keeping the triruthenium framework. We consider that the activation of H_2 by **4** or **5** is slow and accompanied by hydrogenolysis of the Ru-C bonds, thus leading to partial hydrogenation of the coordinated azulene ligands and hydrogenolysis of the Ru-Ru bond, in turn giving rise to formation of ruthenium hydrides and cluster fragmentation. As described above, we propose that facile hapticity change leads to the high reactivity of triruthenium clusters **1**–**3**. Although the di- or tetraruthenium homologues might also be prone to hapticity change, they did not react with H_2 at low temperature. This indicates that the nuclearity of the cluster apparently affects the hydrogenation activity that may be ascribed to the reactivity of the coordinatively unsaturated species produced by the hapticity change.

Removal of *L* from $(\mu\text{-}L)Ru_3H_2(CO)_7$ and Related Reactions

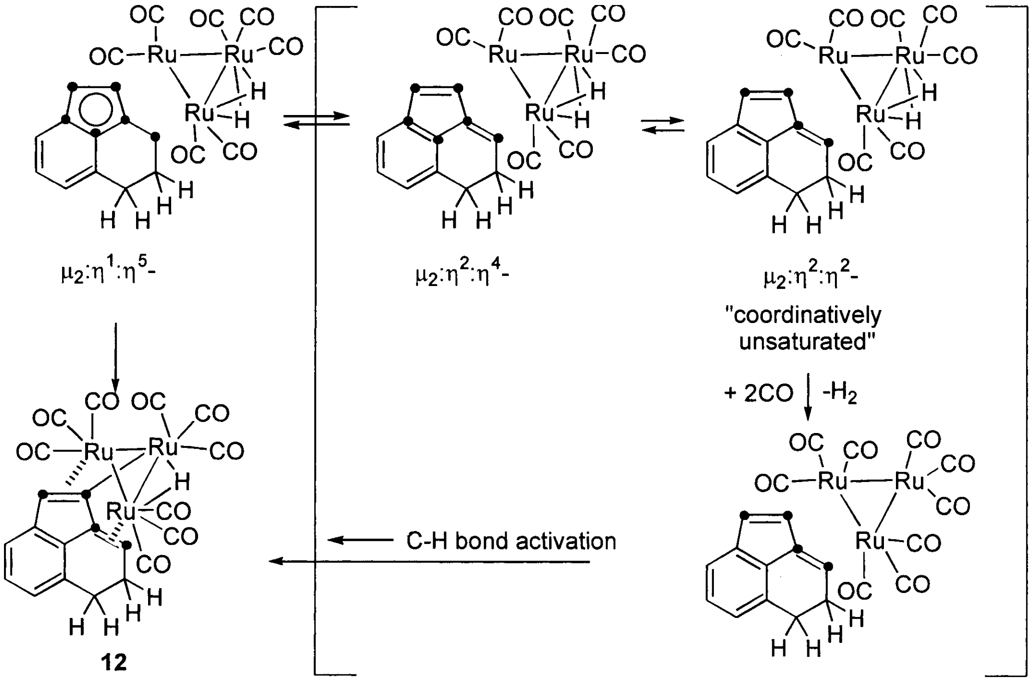
Hydrogenation of the coordinated acenaphthylene or azulenes at room temperature takes place at a carbon-carbon double bond in the six membered ring. This is unusual in the hydrogenation of these aromatic compounds in which selective hydrogenation of a carbon-carbon double bond in the five membered ring generally occurs. The resulting dihydride cluster has either 4,5-dihydroacenaphthylene or 4,5-dihydroaceanthrylene as the bridging ligand. In other words, removal of the hydrogenated aromatic compound from the cluster framework is a method to synthesize 4,5-dihydroacenaphthylene or 4,5-dihydroaceanthrylene. It is known that hydrogenation of acenapthylene or aceanthrylene generally gives acenapthylene or aceanthrene, respectively, whereas alkali metal reduction affords 1,5-dihydroacenaphthylene or 1,7-dihydroaceanthrylene [24]. However, 4,5-dihydroacenapthylene and 4,5-dihydroaceanthrylene were unknown compounds when we started this research. After some elaboration, we found that treatment of the dihydride clusters **4** or **5** with CO in hexane resulted in successful isolation of 4,5-dihydroacenaphthylene or 4,5-dihydroaceanthrylene as shown in Scheme 6. The ruthenium atoms are completely recovered as $Ru_3(CO)_{12}$. The resulting new isomers of acenaphthene and aceanthrene were characterized by their NMR and mass spectra. Attempts to isolate them failed, mainly because of the readily polymerizing 1,3-diene conjugated to benzene or the naphthalene ring; accordingly, these compounds are stable only in dilute solution. Although we anticipated a similar removal of



Scheme 6

tetrahydroazulenes from **3**, attempted carbonylation of **3** only produced a mixture of intractable products.

Crystal structures of the Ru$_3$-dihydride clusters **6** and **7** reveal that the dihydroacenaphthylene or aceanthrylene ligand is bonded to two ruthenium atoms in the $\mu_2:\eta^1:\eta^5$-coordination mode. Facile elimination of 4,5-dihydroacenapthylene or 4,5-aceanthrylene from **6** or **7** is attributed to facile change of the coordination mode from $\mu_2:\eta^1:\eta^5$ to $\mu_2:\eta^2:\eta^4$. In the latter mode, three carbon-carbon double bonds which can easily be replaced by CO are bonded to two ruthenium atoms. Supporting evidence for this change of the coordination mode is available from a structure of a by-product in the reaction of CO with **6** in CH$_2$Cl$_2$. As shown in Scheme 7, this product (**12**) is considered to be formed by a scheme involving



Scheme 7

hapticity change from a $\mu_2:\eta^2:\eta^4$-fulvene structure to a $\mu_2:\eta^2:\eta^2$-diene moiety. These results again demonstrate the flexible change of the coordination modes of conjugated π-ligands in the cluster; this flexibility is likely to produce a high reactivity towards CO.

Comparison with Other Clusters

The results described above provide the following interesting aspects:

(*i*) Triruthenium clusters bearing acenapthylene, aceanthrylene, and azulenes in the facial capping mode easily activate molecular hydrogen at ambient temperature. The activated H_2 contributes to the formation of ruthenium hydrides and partial hydrogenation of the π-ligand. The high reactivity of these trinuclear clusters may be ascribed to facile hapticity change of the coordinated π-ligand on the cluster, which produces coordinatively unsaturated species capable of activating H_2.

(*ii*) The selective hydrogenation takes place at the aromatic part of coordinated acenaphthylene or aceanthrylene or at the seven-membered ring of azulenes. Carbons in the five-membered ring of these π-ligands are tightly bound to the ruthenium atom and inactive towards hydrogenation.

(*iii*) Hydrogenation results in a change of the coordination mode from μ_3 to μ_2. The μ_2-coordination mode is not effective in keeping the trinuclear framework, and hydrogenative cluster fragmentation gradually takes place to form mononuclear ruthenium hydrides.

(*iv*) The stereochemistry of mononuclear ruthenium hydride formed by hydrogenative cluster fragmentation shows that the Ru_3 species activates H_2 and that the activated hydrides are transferred to the π-ligand to furnish the partial hydrogenation.

(*v*) Comparison in reactivity towards hydrogenation with Ru_2- or Ru_4-homologues reveals the particularly high reactivity of triruthenium clusters.

As noted above, hydrogenation of ruthenium carbonyl clusters generally induces hydrogenative cluster fragmentation and recombination of the metal fragments [15]. Introduction of μ_3-ligands has been examined to suppress cluster fragmentation, and the results have been well summarized in a recent review by *Lavigne* [3a]. Representative examples are illustrated in Fig. 4. Facile activation of H_2 by these clusters is the next problem, and hemilability of μ_3-ligands, which effectively stabilizes the cluster framework but easily open the coordination site in the reaction, is recognized as an important point to solve this problem. In particular, extensive work has been done on a series of aminopyridyl (*ampy*) ligands as an ancillary hemilabile 5-electron donor ligands of triruthenium carbonyl clusters by *Lavigne*, *Caveza*, and others [3a, 5]. In these complexes, the pyridine is coordinated to one ruthenium atom, whereas the amino ligand is bonded to two ruthenium atoms as a doubly bridging three-electron donor. The ruthenium atoms stabilized by the doubly-bridging amino ligand are reactive towards ligand substitution; this is considered to proceed *via* a bridge-opening reaction of the amino group, namely interconversion between the bridging amino group and the terminal one. *Cabeza* and coworkers have reported that reaction of certain triruthenium carbonyl clusters

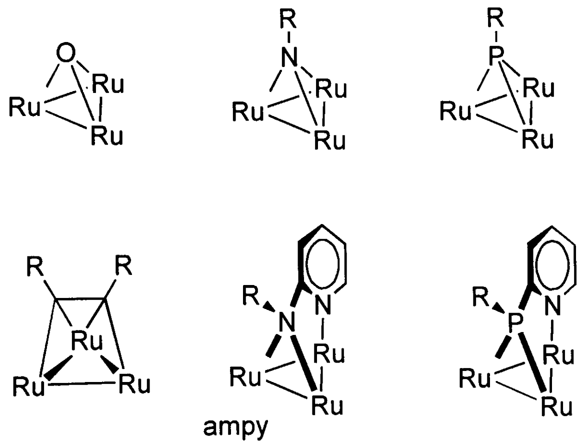
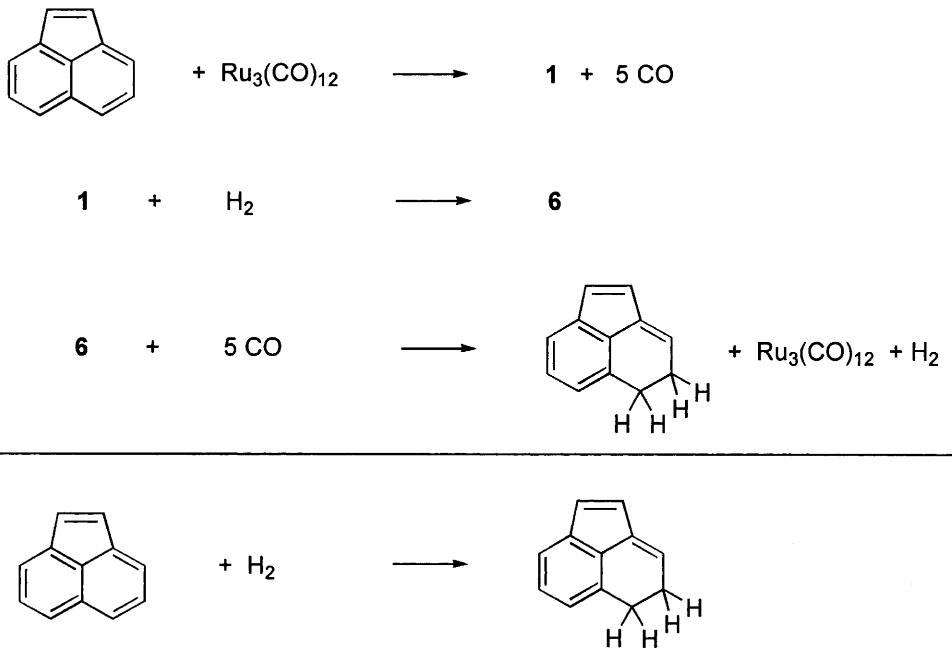


Fig. 4. Representative examples of Ru_3 clusters bearing μ_3-ligands

bearing μ_3-*ampy* ligands with H_2 leads to the formation of ruthenium hydride clusters [26]; no cluster fragmentation has been observed. The *ampy* ligand is similar to the μ_3-acenapthylene, aceanthrylene, or azulene ligands with respect to hemilability. We consider that our results are the first examples to prove the effect of conjugated π-ligands as hemilabile μ_3-ligands.

Hydrogenation of a series of azulene complexes reveals the difference in their reactivity towards hydrogenation among the Ru_2, Ru_3, and Ru_4 clusters. The reason of this reactivity difference should be investigated in further experiments; however, we suggest that the combination of properly designed hemilabile μ-ligands with



Scheme 8

appropriate multimetallic species capable of activation of H_2 is essential to synthesize active cluster compounds.

The results presented in this review also provide an important aspect from the viewpoint of hydrogenation of arenes by clusters [16]. The novel isomer of acenaphthene or aceanthrene can be synthesized by partial hydrogenation of acenapthylene or aceanthrylene on the face of the Ru_3 moiety followed by liberation of the hydrogenated products from the Ru_3H_2 species by treatment with CO. As shown in Scheme 8, a formal catalytic cycle can be designed by synthesis of **1** (or **2**) from $Ru_3(CO)_{12}$, hydrogenation of **1** (or **7**), and carbonylation of **3** (or **4**). This catalytic cycle does not operate in the attempted hydrogenation of acenapthylene in the presence of a catalytic amount of $Ru_3(CO)_{12}$, because there is a fast reaction pathway to hydrogenate acenapthylene to acenaphthene, presumably *via* a ruthenium species produced by decomposition of $Ru_3(CO)_{12}$. However, it is important that this is a rare organometallic evidence that hydrogenation of arenes actually takes place on the face of the cluster.

Conclusions

In this account, recent results of the role of acenapthylene, aceanthrylene, and azulenes as μ_3-hemilabile π-ligands in triruthenium clusters are summarized and discussed. It is also important that selective partial hydrogenation of acenapthylene and aceanthrylene can be achieved on the face of the Ru_3 cluster, which had never been accomplished by other methods. Proper design of reactive organometallic clusters might be a means to develop a novel class of catalysts for chemical transformation of organic molecules. The results are interesting in relation to the rational design of active multimetallic species in cluster catalysis as well as to those which exist on the surface of heterogeneous catalysts [27]. However, the results obtained so far are only a small introductory part to the profound reaction chemistry of clusters bearing π-ligands. A number of questions, *e.g.* details of active species, remain unsolved. Currently, detailed studies on hapticity change in the clusters which would provide a rational design of hemilabile π-ligands for the clusters or access to reactions other than hydrogenation are in progress. Also, the effect of hemilabile μ_3-π-ligands might be extendable to cluster catalysis [28]. The design of clusters which activate both arenes, including substituted benzenes, and H_2 may provide novel catalysts for full or partial hydrogenation of arenes.

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Received April 28, 2000. Accepted May 9, 2000