Multimetallic Activation of Molecular Hydrogen, Leading to Hydrogenation of the Coordinated Azulenes in Di-, Tri-, and Tetranuclear Ruthenium Carbonyl Complexes

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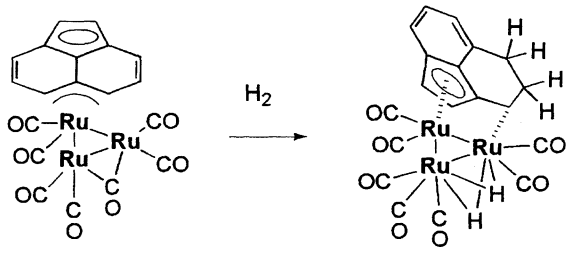
Hydrogenation of di-, tri-, and tetranuclear ruthenium carbonyl complexes bearing guaiazulene or 4,6,8-trimethylazulene as the bridging ligand to bind the multimetallic framework was studied: [μ_2 : η-guaiazulene)$Ru_2(CO)_5$ (**1a**)], [μ_2 : η-4,6,8-trimethylazulene)$Ru_2(CO)_5$ (**1b**)], [(μ_3 : η-guaiazulene)$Ru_3(CO)_7$ (**2a**)], [(μ_3 : η-4,6,8-trimethylazulene)$Ru_3(CO)_7$ (**2b**)], [(μ_3 : η-guaiazulene)$Ru_4(CO)_9$ (**3a**)], and [(μ_3 : η-4,6,8-trimethylazulene)$Ru_4(CO)_9$ (**3b**)]. Reactions of these di-, tri-, and tetraruthenium complexes with dihydrogen (P_{H_2} = 5—10 atm) at 100 °C resulted in cluster fragmentation and addition of five hydrogen atoms to the azulene ligands to form mononuclear ruthenium carbonyl hydride compounds, [(η^5-pentahydroguaiazulenyl)$RuH(CO)_2$ (**4a**)] or [(η^5-pentahydrotrimethylazulenyl)$RuH(CO)_2$ (**4b**)]. Despite potential formation of several stereoisomers dependent on the addition modes of hydrogen atoms, only one isomer of **4a** or **4b** was obtained in the hydrogenation. The crystal structure of a derivative of **4a** revealed that the addition of hydrogen atoms occurred from the face of the azulene ligand originally bonded with the ruthenium species. Hydrogenation of the di-, tri-, and tetranuclear ruthenium complexes below 100 °C revealed that only the triruthenium compounds reacted with H_2 at 50 °C via triruthenium dihydride intermediates: [(μ_2 : η-tetrahydroguaiazulene)$Ru_3H_2(CO)_7$ (**6a**)] or [(μ_2 : η-tetrahydrotrimethylazulene)$Ru_3H_2(CO)_7$ (**6b**)]; this indicates that there exists a reaction pathway to achieve facile activation of dihydrogen by the triruthenium clusters.

Hydrogenation of organic substrates on the organometallic clusters has suggested that multimetallic species may play an important role, and has attracted the attention of organometallic chemists in terms of development of cluster catalyzed reactions and model studies for heterogeneous catalysis.[1—3] Reactions of H_2 with metal clusters under mild conditions used to be difficult even with coordinatively unsaturated clusters.[1,3—6] The ruthenium carbonyl clusters usually reacted with H_2 around 100 °C, and these reactions were often accompanied by cluster fragmentation and subsequent reassembly into the stable clusters.[3,4] Recent studies revealed that compounds in which certain ligands reinforce the cluster framework underwent oxidative addition of H_2 without alteration of the nuclearity under mild conditions.[5] However, only a few examples were given in which the activated hydrogen atoms contributed to hydrogenation of organic compounds bonded with the clusters.[6] In our previous papers, we reported that a triruthenium carbonyl cluster bearing acenaphthylene as the face-capping ligand easily reacted with molecular hydrogen leading to selective hydrogenation of a carbon-carbon double bond in a six-membered ring of the acenaphthylene ligand (Scheme 1).[7] Of importance in this hydrogenation was the facile activation of the triruthenium carbonyl cluster with H_2 under mild conditions (r.t., 1—8 atm of H_2) without decomposition of the cluster framework, leading to reduction of the carbon–carbon double bond in the acenaphthylene ligand by the activated hydrogen atoms. This provided us an idea that activation of molecular hydrogen may generally be easy in multinulear ruthenium compounds analogous to the acenaphthylene complex described above, leading to the hydrogenation of the coordinated π-ligands.



Scheme 1. Hydrogenation of [(μ_3 : η^2 : η^3 : η^5-acenaphthylene)$Ru_3(CO)_7$] to [(μ_2 : η^1 : η^5-4,5-dihydroacenaphthylene)$Ru_3H_2(CO)_7$].

We report here hydrogenation of triruthenium carbonyl clusters bound to guaiazulene or 4,6,8-trimethylazulene with the face-capping bonding mode (**2a** or **2b**) and their di- and tetranuclear homologues as shown in Fig. 1. Two novel find-

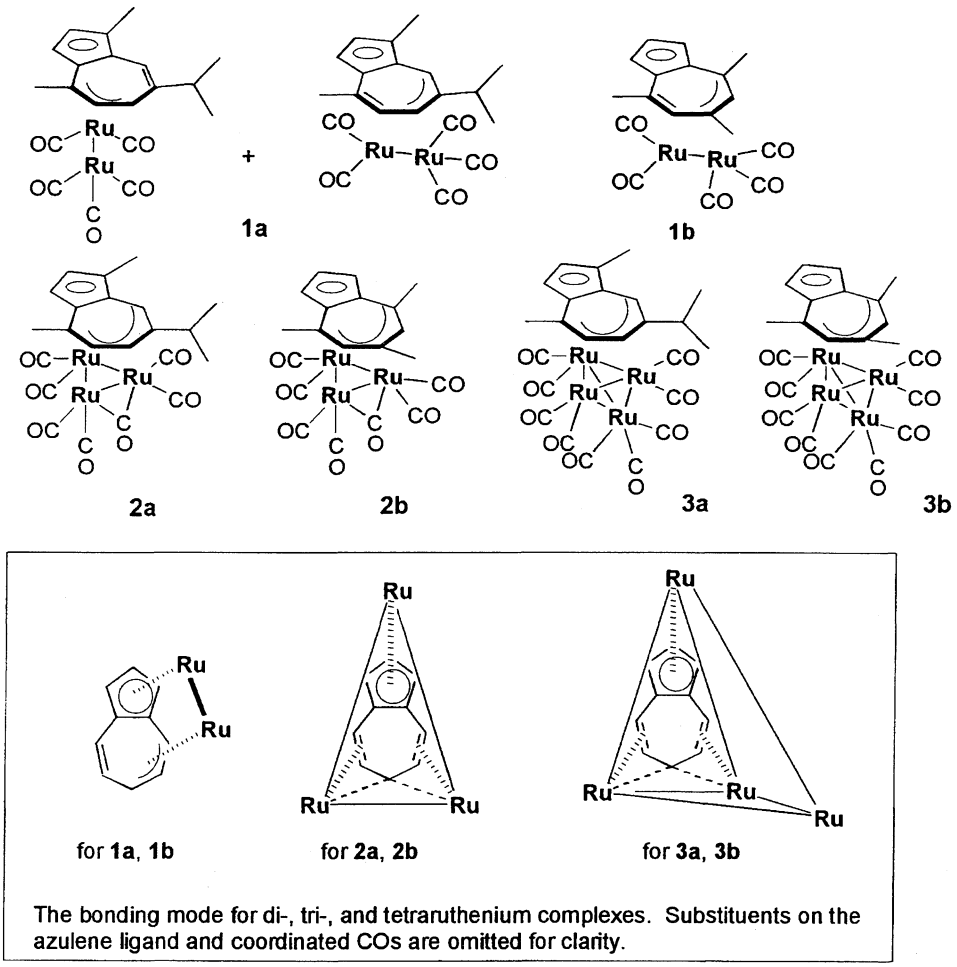


Fig. 1. Multinuclear ruthenium carbonyl complexes bound to azulenes.

ings were available: One is from the comparison in reactivity of the hydrogenation of these trinuclear clusters with di- or tetranuclear homologues; the trinuclear complexes reacted with H_2 at lower temperatures than the di- or tetranuclear homologues did. NMR studies showed that there was a reaction pathway in which activation of H_2 with the trinuclear clusters took place without decomposition of the cluster, which can explain the distinguished reactivity of the trinuclear complexes compared with that of the others. The other discovery was obtained from the stereochemical analysis of the final product of the hydrogenation. All of the multinuclear complexes described above reacted with H_2 at 100 °C to result in hydrogenation of the coordinated azulene ligands and cluster fragmentation to form a mononuclear ruthenium hydride complex. The stereochemistry of the substituents on the azulene ligand in a derivative of the final product revealed that attack of the dihydrogen occurred from the face of the azulene ligand *cis* to the ruthenium species. We think that activation of molecular hydrogen by the ruthenium clusters occurred, and the activated hydrogen atoms were transferred from the ruthenium species to the azulene ligand. These results showed that multinuclear ruthenium species are responsible for the hydrogenation of the coordinated azulenes regardless of the nuclearity of the cluster, and trinuclear ruthenium carbonyl species can activate molecular hydrogen more easily than the others can. These results contribute to better understanding of the reaction chemistry of organometallic clusters from fresh insights.

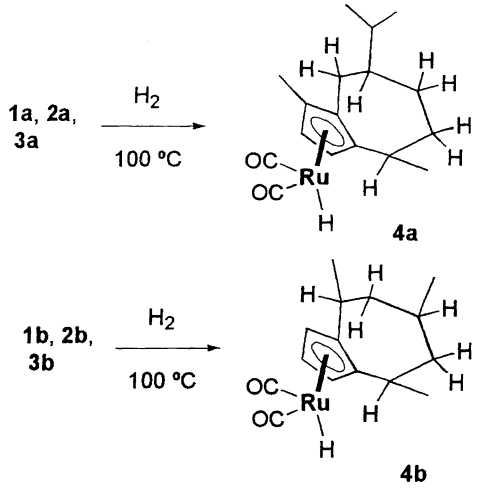
Results and Discussion

A mixture of the di-, tri-, and tetranuclear complexes **1a**, **2a**, and **3a** or **1b**, **2b**, and **3b** was synthesized by the reaction of guaiazulene or 4,6,8-trimethylazulene with $[Ru_3(CO)_{12}]$. They were easily separated by chromatography.[8,9] The formed ratios among **1a**, **2a**, and **3a** or those among **1b**, **2b**, and **3b**, were dependent on charged ratios of the azulene to $[Ru_3(CO)_{12}]$; use of excess ruthenium precursor resulted in formation of the products with high nuclearity in higher ratios. Structural assignments of **1a**[8] and **1b** were carried out by spectroscopy. The complex **1a** was obtained as a mixture of two haptotropic isomers.[8] Two multinuclear metal carbonyl complexes bearing azulene ligands, [(η-azulene)$Ru_3(CO)_7$][9a] and [(η-4,6,8-trimethylazulene)$Ru_4(CO)_9$ (**3b**)],[9b] were synthesized and crystallographically identified by Churchill and co-workers.[9] The former is a homologue of **2a** and **2b**, whereas the latter is one of **3a**. In fact, close analogies in structure between **2a** and [(η-azulene)-$Ru_3(CO)_7$] and between **3a** and **3b** were recently proved by crystallography.[10] The trinuclear ruthenium arrangement in these trinuclear complexes with a triangular geometry was

Table 1. Hydrogenation of Di-, Tri-, and Tetraruthenium Complexes

Entry	Compounds	Temp	Time	Conversion	Product; Yield
		°C	h	%	%[a]
1	**1a**	100	3	100	**4a**; 96
2	**1b**	100	3	100	**4b**; 96
3	**2a**	100	3	100	**4a**; 95
4	**2b**	100	3	100	**4b**; 99
5	**3a**	100	3	64	**4a**; 82[b]
6	**3b**	100	3	100	**4b**; 67
7	**2a**	50	3	16	**4a**; 42 **6a**; 42
8	**2b**	50	3	100	**4b**; 61 **6a**; 19
9	**2b**	R.T.	3	59	**4b**; 34 **6b**; 50

a) Yields are calculated based on amounts of the starting materials consumed. b) A small amount of an unidentified green product showing a Ru–H peak at $\delta = -10.84$ ppm in ^{1}H NMR was also formed.



Scheme 2. Hydrogenation of the azulene complexes at 100 °C.

Table 2. Crystallographic Data of **5a**

Formula	$C_{17}H_{23}ClO_2Ru$
Fw	395.9
Habit	Yellow plate
Cryst dimens/mm	$0.50 \times 0.30 \times 0.10$
Space group	$P\bar{1}$
Z	2
a/Å	9.023(1)
b/Å	14.624(3)
c/Å	7.153(3)
α/deg	93.96(3)
β/deg	104.48(2)
γ/deg	72.08(2)
V/Å^3	867.9(5)
D_{calc}/g cm^{-3}	1.51
Radiation	Mo $K\alpha$ ($\lambda = 0.71069$ Å)
Monochromator	Graphite
Transmission factors	0.92—1.12[a]
μ_{calc}/cm^{-1}	10.42
Scan type	ω–2θ
Scan rate/deg min^{-1}	32
2θ range/deg	$3.0 < 2\theta < 50.0$
No. of data collcd	4330
No. of unique data	4236
Unique data	4029 [$F_o > 3\sigma(F_o)$]
No. of variables	259
R	0.031
R_w ($w = 1$)	0.033
GOF	0.71
$(\Delta/\sigma)_{max}$	0.1
$\Delta\rho_{max}$ (e Å^{-3})	0.63

a) Scan method, normalized to an average of unity.

stabilized by six terminal CO groups, two ligands in each ruthenium atom, and one bridging CO ligand. In contrast, four ruthenium atoms define a distorted tetrahedron in the tetranuclear complexes; three of the four ruthenium atoms associated with the azulene ligand are each bonded to two terminal carbonyl ligands, whereas the fourth is linked to three terminal carbonyl atoms. In both of the complexes, the azulene ligand is arched across the face of the cluster, in which carbons in the five-membered ring are bound to one ruthenium atom with the conventional π-cyclopentadienyl-metal coordination mode, whereas the remaining five carbons in the seven-membered ring are bound to the other two ruthenium atoms with the μ_2-pentadienyl coordination mode. The center carbon of the pentadienyl group is bonded with two ruthenium atoms.

The compounds **1a**, **1b**, **2a**, **2b**, **3a**, and **3b** were hydrogenated at 100 °C under 8 atm of H_2 for 3 h (Table 1, Entries 1—6). The reactions were accompanied by the cluster fragmentation to form a mononuclear ruthenium hydride complex **4a** or **4b** as yellow air-sensitive oil. A ruthenium cluster $[Ru_4H_4(CO)_{12}]$ was also isolated from the reaction mixture, the formation of which quantitatively explained the fate of the ruthenium atoms in the charged starting materials. A singlet assignable to a proton bonded with the ruthenium atom appeared around $\delta = -11$ ppm in ^{1}H NMR of **4a** or **4b**. In ^{13}C NMR spectra of **4a** or **4b**, significant upfield shifts of five carbons in the five-membered ring of the ligand were indicative of their bonding with the metallic species. In contrast, the remaining five carbons in the seven-membered ring were assigned to methines or methylenes; this indicates that addition of one hydrogen atom to each carbon took place during the hydrogenation. These spectroscopic data suggest that structures of **4a** and **4b** could be assigned as the mononuclear ruthenium hydride complexes shown in Scheme 2. The molecular structure of a derivative of **4a** described below supported these assignments.

There are methyl and isopropyl groups bonding to the seven-membered ring in **4a** and three methyl groups in **4b**. If the addition of hydrogen atoms did not occur stereoselectively, the stereochemistry of these substitutents could afford four isomers for **4a** and six stereoisomers for **4b**. ^{1}H and ^{13}C NMR evidence suggested the formation of only one stereoisomer *regardless of the nuclearity or azulene group of the starting material.* To determine the stereochemistry, we prepared a derivative of **4a** and performed its X-ray analysis. Reaction of **4a** with CCl_4 resulted in formation of a chlororuthenium carbonyl complex **5a** as yellow microcrystals in

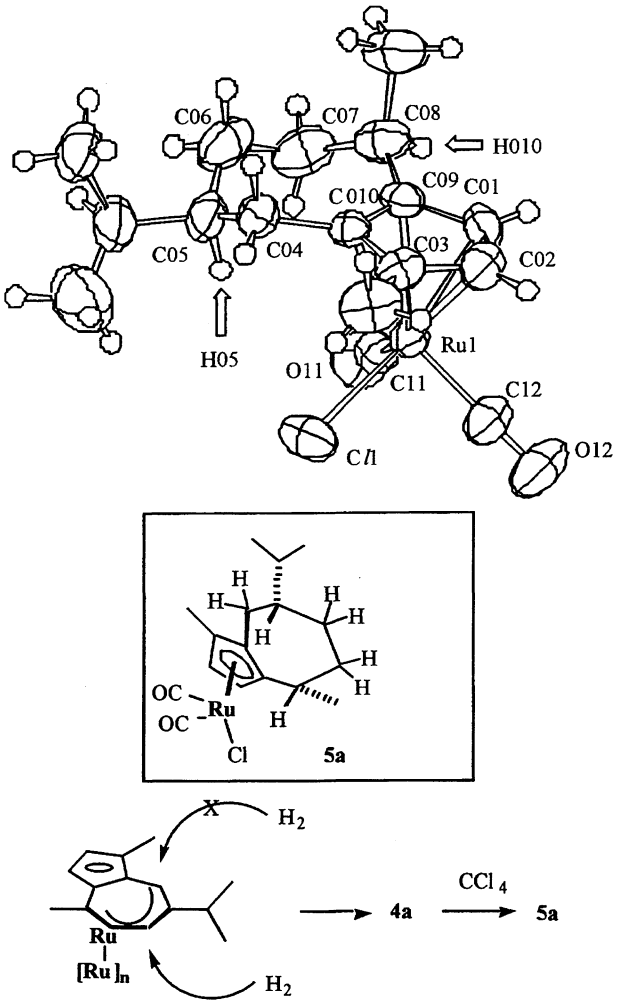


Fig. 2. Molecular structure of **5a**.

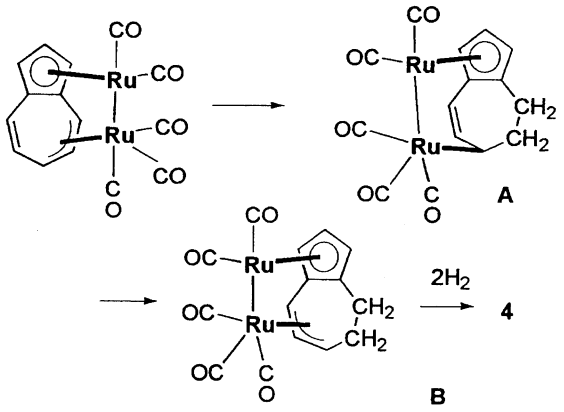
Table 3. Selected bond Angles and Distances for **5a**

Ru1–C11	2.044 (1)	C11–Ru1–C11	91.1 (1)
Ru1–C11	1.889 (4)	C11–Ru1–C12	92.2 (1)
Ru1–C12	1.892 (3)	C11–Ru1–C12	89.0 (2)
Ru1–C01	2.187 (3)	C01–Ru1–C01	37.2 (2)
Ru1–C02	2.243 (4)	C02–Ru1–C03	36.2 (2)
Ru1–C03	2.272 (3)	C03–Ru1–C010	37.3 (1)
Ru1–C09	2.258 (3)	C010–Ru1–C09	36.8 (1)
Ru1–C010	2.259 (2)	C09–Ru1–C010	37.4 (1)
C01–C02	1.41 (1)		
C02–C03	1.40 (1)		
C03–C010	1.45 (1)		
C010–C09	1.42 (1)		
C09–C01	1.43 (1)		
C04–C05	1.53 (1)		
C04–C010	1.50 (1)		
C05–C06	1.52 (1)		
C06–C07	1.53 (1)		
C07–C08	1.51 (1)		
C08–C09	1.49 (1)		

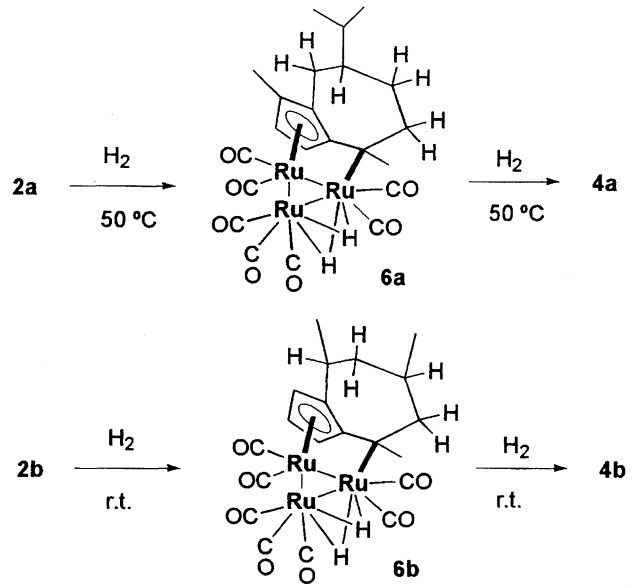
quantitative yields (Table 2). The molecular structure of **5a** was determined by crystallography, and its ORTEP drawing is shown in Fig. 2. The selected bond distances and angles are summarized in Table 3. As indicated from the NMR spectra of **4a**, the ruthenium atom was bonded with the five-membered ring of the pentahydroazulenyl ligand by the π-cyclopentadienyl coordination mode, and the remaining five carbons (two methines and three methylenes) in the seven-membered ring were uncoordinated.

It is noteworthy that *the stereochemistry of protons adjacent to the isopropyl and the methyl substituents in the seven-membered ring (H05 and H010 in Fig. 2) was exclusively cis to the $RuCl(CO)_2$ moiety*. This means that the addition of five hydrogen atoms to the azulene ligand occurred from the direction of the ruthenium moiety. A reasonable interpretation of this stereochemical outcome is that activation of H_2 took place on the multimetallic species and the activated hydrogen atoms were transferred from the metal onto the azulene ligand; the hydrogenation resulted in loss of π-ligands which contributed to stabilization of the multimetallic framework in the starting materials, leading to cluster fragmentation to form the mononuclear ruthenium hydride complex and $[Ru_4H_4(CO)_{12}]$. As an alternative possibility, one may consider the hydrogenation of the coordinated azulene ligands catalyzed by metallic species produced by decomposition of the multiruthenium species.[11] Although coordination of carbon–carbon double bonds by a transition metal usually renders the olefin unreactive toward catalytic hydrogenation, it is worthwhile to discuss the possibility because such metallic catalysts could be formed in the reaction medium by facile fission of metal–metal bonds in the organometallic clusters.[1–3] If that happened, however, the attack of the hydrogen atoms would be more apt to occur on the less hindered face of the azulene ligand of the diruthenium complexes to afford compounds with orientation of the methyl or isopropoxy substituents trans to the $RuH(CO)_2$ group. Thus, the crystallographic evidence described above rules out this possibility.

It is curious that an uncoordinated carbon–carbon double bond in the dinuclear carbonyl complex, **1a** or **1b**, underwent



Scheme 3. A possible mechanism for the hydrogenation of the dinuclear complexes. (Substitutents on the azulene ring were omitted for clarity.)



Scheme 4. Hydrogenation of trinuclear compounds at lower temperatures.

the hydrogenation; this cannot be explained by simple application of the above mechanism. In contrast to the fact that coordinated olefins are unreactive towards catalytic hydrogenation, it is known that an uncoordinated carbon–carbon double bond in the coordination compounds can be hydrogenated in the presence of heterogeneous catalysts.[11] Since **1a** and **1b** contains an uncoordinated carbon–carbon double bond, hydrogenation catalyzed by decomposition products of the multiruthenium species may be involved in the formation of **4a** and **4b**. The molecular structure of **5a** showing that the stereochemistry of added hydrogen atoms is *cis* to the $RuCl(CO)_2$ moiety is good proof ruling out the involvement of metal fragment-catalyzed hydrogenation; the diruthenium species is responsible for the formation of **4a** from **1a**. Hydrogenation of the uncoordinated carbon–carbon double bond in **1a** or **1b** is reasonably explained by the involvement of the haptotropic rearrangement as shown in Scheme 3. Activation of H_2 by diruthenium species is followed by partial reduction of the π-allyl ligand in **1a** or **1b** to form the intermediate **A**. The uncoordinated carbon–carbon double bond could contribute to formation of a new π-allyl compound **B** from **A**, and further hydrogenation of **B** gives rise to formation of **4a** or **4b**.

When the hydrogenation conditions were investigated in detail, we were aware that the hydrogenation of the trinuclear cluster **2a** and **2b** proceeded even below 50 °C. This is in sharp contrast to the fact that the di- or tetranuclear cluster did not react with H_2 at this temperature. The hydrogenation of **2a** at 50 °C for 3 h under 8 atm of H_2 resulted in conversion of 16% of **2a** to afford **4a** in 42% yield (Table 1, Entry 7). A new species **6a** was also observed in the reaction mixture. The hydrogenation of **2b** proceeded more readily at both 50 °C and room temperature to give a mixture of **4b** and **6b** (Table 1, Entries 8 and 9). The new species **6a** or **6b** is likely to be an intermediate of the hydrogenation; the reaction profiles for the hydrogenation showed that **6a** or **6b** was formed at the initial stage and then diminished. In fact, all of **6a** or **6b** disappeared after prolonged reaction time (30 h), and **4a** or **4b** was formed in quantitative yields based on the charged **2a** or **2b**, respectively. The hydrogenation of the isolated **6a** or **6b** at 50 °C under 8 atm of H_2 afforded **4a** or **4b**, respectively.

Although this new species was not very thermally stable, isolation by chromatography was possible; its ^1H NMR spectrum showed two Ru–H signals at $\delta = -9.33$ and -12.17 ppm as doublets ($J = 4.7$ Hz) with equal intensity. Appearance of two doublets in this region is very similar to the known complex [($\mu_2 : \eta^1 : \eta^5$-4,5-dihydroacenaphthylene)$Ru_3H_2(CO)_7$], which is formed by hydrogenation of [($\mu_3 : \eta^2 : \eta^3 : \eta^5$-acenaphthylene)$Ru_3(CO)_7$] as shown in Scheme 1. This and other ^1H resonances as well as similarity of IR spectra to that of [($\mu_2 : \eta^1 : \eta^5$-4,5-dihydroacenaphthylene)$Ru_3H_2(CO)_7$] suggest that the new species could be assigned as a triruthenium carbonyl cluster [($\mu_2 : \eta^1 : \eta^5$-tetrahydroazulene)$Ru_3H_2(CO)_7$], **6a** or **6b**, (Scheme 4). Seven CO peaks observed in ^{13}C NMR of **6a** or **6b** also supported such assignments. These results indicate that the facile hydrogenation of the triruthenium cluster **2a** or **2b** compared with the di- or tetranuclear analogue of either of them could be attributed to the existence of a reaction pathway through the triruthenium dihydride carbonyl cluster **6a** or **6b**.

Hydrogenation of many ruthenium carbonyl clusters occurs around 100 °C, which is accompanied by hydrogenolysis of the ruthenium–ruthenium bonds and cluster fragmentation.[3] In a typical example, treatment of $[Ru_3(CO)_{12}]$ with H_2 in refluxing octane gives $[Ru_2H_2(CO)_{12}]$.[5a] The hydrogenation of di- and tetranuclear complexes, **1a**, **1b**, **3a**, and **3b** is rather similar to the reaction of $[Ru_3(CO)_{12}]$ with H_2; of importance is the fact that the reaction of the azulene complexes is accompanied by hydrogenation of the coordinated pentadienyl ligands in addition to the hydrogenolysis of the ruthenium–ruthenium bonds and cluster fragmentation. Stereochemistry of **5a** unequivocally showed that the hydrogen atoms were added from the face of the azulene ligands which originally bonded with the multinuclear ruthenium species; this indicates that the cluster fragmentation is preceded by the activation of H_2 and the reduction of the azulene ligand. In other words, the multimetallic species in these complexes is responsible for the hydrogenation of the π-ligands.

The high reactivity of triruthenium clusters is attributed to the existence of a pathway to react with H_2 while retaining their cluster framework. Stereochemistry of **4a** and **4b** obtained by further hydrogenation of **6a** and **6b**, respectively, was the same as that obtained by direct hydrogenation of di-, tri-, and tetranuclear ruthenium complexes described above at 100 °C, showing that the hydrogen atoms activated by **6a** or **6b** contribute to the hydrogenation of the azulene ligand. Facile generation of trinuclear coordinatively unsaturated species from **2a** or **2b** may be involved in the process; Taube and Ford proposed that conversion of the bridging CO to η^2-μ^3 mode could assist dissociation of a CO or a π-ligand

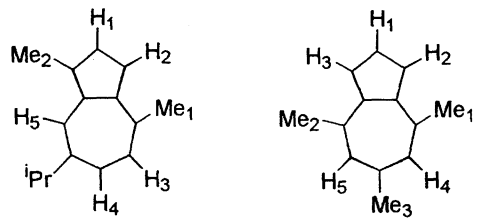
to open the coordination site for H_2 in ligand substitution of $[Ru_3H(CO)_{11}]^-$.[12]

Conclusion

Our results demonstrate that hydrogenation of the coordinated π-ligands occurred on the di-, tri-, and tetraruthenium carbonyl clusters. Regardless of the nuclearity, the multimetallic species reacted with molecular hydrogen and the activated hydrogen atoms were transferred from the metallic species to the coordinated π-ligands; these were unequivocally evidenced by the stereochemistry of **5a**, in which hydrogen atoms were introduced at the *cis*-positions with the $RuH(CO)_2$ moiety. Interestingly, the cluster can react with H_2 under milder conditions than usual if we can achieve appropriate selection of the cluster species; the azulene complexes with $Ru_3(CO)_7$ species can react with H_2 at lower temperatures than those with $Ru_2(CO)_5$ or $Ru_4(CO)_9$. There is a reaction pathway where the triruthenium complexes activate H_2 without alteration of the nuclearity. These results showed that multimetallic species play an essential role in the hydrogenation of the coordinated azulenes, though they involve different mechanisms dependent on the nuclearity of the complex. The findings described above contribute to understanding the hydrogenation of organic substrates on the cluster species from the stereochemistry of the product and the reactivity dependent on the nuclearity; these points had not earlier been fully used in the reaction chemistry of organometallic clusters, to our knowledge. It should be pointed out that there also exist similarities in bonding modes between [($\mu_3 : \eta^2 : \eta^3 : \eta^5$-acenaphthylene)-$Ru_3(CO)_7$] and the triruthenium clusters bound to azulenes, **2a** or **2b**; the only marked difference is that the μ_2-pentadienyl coordination of the azulene ligands to two ruthenium atoms in **2a** or **2b** corresponds to one π and one π-allyl interaction with each ruthenium atom in the acenaphthylene complex. Thus, hydrogenation studies of a series of the above azulene complexes could assist better understanding of the hydrogenation of the acenaphthylene complex.

Experimental

General Methods. All manipulations were carried out under an inert-gas atmosphere using standard Schlenck techniques. All of the solvents were distilled in the presence of standard drying reagents just before use. 4,6,8-Trimethylazulene was synthesized according to a procedure in the literature.[12] NMR spectra were taken with a JEOL GX-270 or a Varian Unity plus (400 MHz) spectrometer, and recorded by δ-values (ppm) and coupling constants (*J*; Hz). The solvent for NMR measurement was $CDCl_3$, unless otherwise noted. ^{13}C NMR was measured in the presence of $Cr(acac)_3$ (0.07 M) (1 M = 1 mol dm^{-3}). IR spectra were recorded on a JASCO FT/IR-230 spectrometer and measured in cm^{-1}. Elemental analysis was carried out with a Yanaco CHN corder. Silica-gels used for thin-layer chromatography (TLC) and column chromatography were purchased from Merck (7715 and 7734, respectively). Spectral data for **1a** were reported earlier.[8b]



for **2a** and **3a** for **1b**, **2b**, and **3b**

Fig. 3. Numbering of the protons on the azulene ligands for the assignment of ^1H NMR.

General Procedure for Preparation of the Azulene Complexes. A mixture of **1a**, **2a**, and **3a** was obtained by reaction of $[Ru_3(CO)_{12}]$ with guaiazulene. In a typical example, guaiazulene (164 mg, 0.83 mmol) and $[Ru_3(CO)_{12}]$ (530 mg, 0.83 mmol) were dissolved in xylene (21 mL) and the mixture was heated under reflux for 1 h. After concentration, the residue was adsorbed to celite (3 g), and placed on the top of a silica-gel column (3 cm $\Phi \times 19$ cm). Elution with hexane afforded unreacted guaiazulene and $[Ru_3(CO)_{12}]$. Using a mixture of hexane and CH_2Cl_2, in which the content of CH_2Cl_2 was gradually increased, three bands containing **1a**, **3a**, and **2a**, respectively, were available in this order. The solvents were removed from each eluent to give **1a** (91 mg, 20%), **2a** (275 mg, 48%), and **3a** (193 mg, 27%). By decreasing the ratio of guaiazulene to $[Ru_3(CO)_{12}]$, **2a** and **3a** were formed in higher yields (Fig. 3). The 4,6,8-trimethylazulene complexes were prepared by an analogous procedure using heptane as the solvent instead of xylene.

2a: Red microcrystals. TLC: R_f = 0.24 (hexane : CH_2Cl_2 = 1 : 1). Mp 176—177 °C (decomp). ^1H NMR δ = 5.75 (d, *J* = 3.2 Hz, H2), 5.36 (d, *J* = 8.5 Hz, H3), 4.80 (d, *J* = 1.7 Hz, H5), 4.60 (d, *J* = 3.2 Hz, H1), 2.35 (sep, *J* = 6.5 Hz, CH of ^{i}Pr), 2.20 (dd, *J* = 1.7, 8.5 Hz, H4), 1.51 and 1.88 (s, Me1 and Me2), 1.23 and 1.47 (d, *J* = 6.4 Hz, Me of ^{i}Pr). ^{13}C NMR (CD_2Cl_2) δ = 11.0 (CH_3), 16.9 (CH_3), 21.8 (CH_3), 27.5 (CH_3), 29.7 (CH), 38.5(CH), 60.8 (CH), 67.5 (CH), 71.4 (C), 77.1 (C), 81.6 (CH), 82.4 (CH), 90.8 (C), 93.3 (C), 101.3 (C); carbonyl region (−80 °C) 191.4, 191.6, 202.6, 203.7, 263.8.[14] IR (KBr) 2034 (s), 1988 (vs), 1948 (s), 1771 cm^{-1} (w). Anal. Calcd for $C_{22}H_{18}O_7Ru_3$: C; 37.88; H, 2.60%. Found: C, 37.92; H, 2.57%.

3a: Red microcrystals. TLC: R_f = 0.58 (hexane : CH_2Cl_2 = 1 : 1). Mp 155—157 °C (decomp). ^1H NMR δ = 5.95 (d, *J* = 3.7 Hz, H2), 5.10 (d, *J* = 8.8 Hz, H3), 4.20 (d, *J* = 3.7 Hz, H1), 4.00 (d, *J* = 1.8 Hz, H5), 2.49 (sep, *J* = 7.4 Hz, CH of ^{i}Pr), 1.68 (dd, *J* = 1.8, 8.8 Hz, H4), 1.18 and 1.75 (s, Me1 and Me2), 1.24 and 1.52 (d, *J* = 7.4 Hz, Me of ^{i}Pr). ^{13}C NMR (CD_2Cl_2) δ = 10.8 (CH_3), 18.9 (CH_3), 22.1 (CH_3), 26.5 (CH_3), 28.9 (CH), 37.2 (CH), 55.7 (CH), 60.9 (C), 68.4 (CH), 68.7 (C), 76.1 (C), 78.1 (CH), 80.5 (CH), 97.2 (C), 102.9 (C); carbonyl region (−80 °C) 193.6, 194.1, 195.8, 196.2, 199.0, 203.8.[14] IR (KBr) 2041 (s), 1986 (vs), 1953 (sh), 1919 cm^{-1} (sh). Anal. Calcd for $C_{24}H_{18}O_9Ru_4$: C; 33.72; H, 2.12%. Found: C, 33.74; H, 2.09%.

1b: Yellow oil. TLC: R_f = 0.74 (hexane : CH_2Cl_2 = 1 : 1). ^1H NMR δ = 5.70 (dd, *J* = 2.0, 2.9 Hz, H2 or H3), 5.60 (t, *J* = 2.3 Hz, H1), 5.21 (s, H4 or H5), 4.78 (s, H4 or H5), 3.91 (dd, *J* = 2.0, 2.9 Hz, H2 or H3), 2.08, 1.84, and 1.51 (s, s, d, *J* = 1.0 Hz, respectively, 3H each, Me), 1.84 (s), 2.08 (s). ^{13}C NMR δ = 20.4 (CH_3), 24.7 (CH_3), 31.7, (CH_3), 63.0 (C), 65.3 (C), 77.9 (CH), 82.5 (CH), 83.6 (CH), 86.2 (C), 86.4 (CH), 88.5 (C), 122.6 (C), 128.8 (CH); carbonyl region (−80 °C) 192.4 (2C), 202.8, 208.2, 210.9.[14] IR (KBr) 2045 (s), 1989 (vs), 1971 (sh), 1914 cm^{-1} (s). Anal. Calcd for $C_{18}H_{14}O_5Ru_2$: C, 42.18; H, 2.75%. Found: C, 42.19; H, 2.76%.

2b: Red microcrystals. TLC: R_f = 0.26 (hexane : CH_2Cl_2 = 1 : 1). Mp 135 °C (decomp). ^1H NMR δ = 5.75 (t, *J* = 2.9 Hz,

H1), 5.00 (s, 2H, H4 and H5), 4.55 (d, 2H, J = 2.9 Hz, H2 and H3), 1.95 (s, 6H, Me1 and Me2), 1.69 (s, 3H, Me3). ^{13}C NMR δ = 23.0 (CH_3), 35.5 (CH_3), 45.4 (C), 73.7 (CH), 77.0 (C), 80.4 (C), 81.5 (CH), 84.5 (CH), 205.6.[14] IR (KBr) 2036 (s), 1991 (vs), 1948 (m), 1754 cm^{-1} (s). Anal. Calcd for $C_{20}H_{14}O_7Ru_3$: C, 35.87; H, 2.11%. Found: C, 35.89; H, 2.11%.

3b: Red microcrystals. TLC: R_f = 0.56 (hexane : CH_2Cl_2 = 1 : 1). Mp 129 °C (decomp). ^{1}H NMR δ = 6.01 (t, J = 3.0 Hz, H1),4.95 (s, 2H, H4 and H5), 4.19 (d, 2H, J = 3.0 Hz, H2 and H3), 1.89 (s, 6H, Me1 and Me2), 1.46 (s, 3H, Me3). ^{13}C NMR δ = 22.7 (CH_3), 31.3 (CH_3), 44.2 (C), 67.1 (CH), 70.8 (C), 76.1 (C), 79.0 (CH), 82.2 (CH), 197.0.[14] IR (KBr) 2049 (s), 1986 (vs), 1918 cm^{-1} (sh). Anal. Calcd for $C_{22}H_{14}O_9Ru_4$: C, 31.96; H, 1.71%. Found: C, 31.95; H, 1.69%.

General Procedure for the Hydrogenation. A mixture of the complex (10—100 mg) and toluene or benzene (5—50 mL) was placed in a glass tube, and the atmosphere was replaced by H_2. The tube was moved to a stainless steel autoclave and 8 atm of H_2 was applied. The mixture was heated at 100 °C for 3 h. After removal of the solvents, the residue was passed through a short silica gel column by elution with hexane to afford the mononuclear ruthenium hydride complex, **4a** or **4b**. The conversion and the yields of the hydrogenation are summarized in Table 1.

4a: Yellow air sensitive oil. TLC: R_f = 0.57 (hexane). ^{1}H NMR δ = −10.79 (s, 1H, Ru-H), 0.88 and 0.94 (d, 3H each, J = 6.6 Hz, Me of ^{i}Pr), 1.16 (d, 3H, J = 7.4 Hz, Me in the seven-membered ring), 2.00 (s, 3H, Me in the five-membered ring), 1.60—1.85, 1.91—2.17, 2.33—2.43, and 2.54—2.63 (m, 5H, 2H, 1H, 1H each, a CH of ^{i}Pr and protons in the seven-membered ring), 4.76 and 5.05 (d, 1H each, J = 2.5 Hz, protons in the five-membered ring). ^{13}C NMR (C_6D_6) δ = 13.3 (CH_3), 19.8 (CH_3), 20.3 (CH_3), 21.0 (CH_3), 28.9 (CH_2), 29.8 (CH_2), 33.5 (CH), 34.0 (CH), 37.4 (CH_2), 49.9 (CH), 78.9 (CH), 82.9 (CH), 102.7 (C), 109.5 (C), 117.4 (C), 203.5 (CO), 203.6 (CO). IR (KBr) 2017 (s), 1949 cm^{-1} (s).

4b: Yellow air sensitive oil. TLC: R_f = 0.67 (hexane). ^{1}H NMR δ = −10.94 (s, 1H, Ru-H), 0.88 (d, 3H, J = 6.9 Hz, Me), 1.21 (d, 6H, J = 6.9 Hz, Me), 1.62—1.88, and 2.70—2.89 (m, 5H and 2H, respectively, protons in the seven-membered ring), 4.91 (t, 1H, J = 2.0 Hz, a proton in the five-membered ring), 5.15 (d, J = 2.0 Hz, 2H, protons in the five-membered ring). ^{13}C NMR (C_6D_6) δ = 19.9 (CH_3), 24.9 (CH_3), 32.8 (CH), 37.7 (CH), 45.8 (CH_2), 81.6 (CH), 86.8 (CH), 115.1 (C), 203.2 (CO). IR (KBr) 2017 (s), 1953 cm^{-1} (s).

Chlorination of the Mononuclear Hydride Complexes. In a typical example, the hydride complex **4a** prepared from **1a** (40 mg, 0.07 mmol) was dissolved in CCl_4 (3 mL), and the solution was stirred at room temperature for 10 h. After removal of the solvent, the residue was purified by silica-gel column (hexane/CH_2Cl_2) to afford **5a** as yellow microcrystals (21 mg, 79%). The 2,4,6-trimethylazulene homologue **5b** was synthesized from **4b** by using a similar procedure as a brown oil (61%).

5a: Yellow microcrystals. TLC: R_f = 0.33 (hexane/CH_2Cl_2 = 1/5). Mp 67—68 °C (decomp). ^{1}H NMR δ = 0.89 and 0.91 (d, 3H each, J = 8.0 Hz, Me of ^{i}Pr), 1.12 (d, 3H, J = 7.2 Hz, Me in the seven-membered ring), 1.92 (s, 3H, Me in the five-membered ring), 1.44—1.77, 2.23—2.32, 2.40—2.46, and 2.54—2.63 (m, 6H, 1H, 1H, and 1H, a CH proton of ^{i}Pr and protons in the seven-membered ring), 4.82 and 4.95 (d, 1H each, J = 2.7 Hz, protons in the five-membered ring). ^{13}C NMR (C_6D_6) δ = 11.8 (CH_3), 20.0 (three carbons are overlapped, CH_3), 27.4 (CH_2), 30.6 (CH_2), 30.9 (CH), 32.1 (CH), 33.4 (CH_2), 43.7 (CH_2), 76.1 (CH), 81.0 (CH), 107.3 (C), 107.7 (C), 119.5 (C), 198.9 (CO), 199.1 (CO). IR (KBr) 2031 (s), 1971 cm^{-1} (s). Anal. Calcd for $C_{16}H_{23}ClO_2Ru$: C, 51.58; H, 5.86%. Found: C, 51.64; H, 5.96%.

5b: Brown oil. TLC: R_f = 0.32 (hexane/CH_2Cl_2 = 1/5). ^{1}H NMR δ = 0.92 (d, 3H, J = 6.9 Hz, Me), 1.16 (d, 6H, J = 6.9 Hz, Me), 0.98—1.13, 1.68—1.79, 1.80—1.95, and 2.55—2.69 (m, 2H, 2H, 2H, 1H, and 2H, protons in the seven-membered ring), 4.72 (t, 1H, J = 2.0 Hz, a proton in the five-membered ring), 5.25 (d, 2H, J = 2.0 Hz, protons in the five-membered ring). ^{13}C NMR δ = 19.0 (CH_3), 24.0 (CH_3), 30.2 (CH), 36.7 (CH), 44.3 (CH_2), 74.4 (CH), 82.7 (CH), 117.3 (C), 196.9 (CO). IR (KBr) 2041 (s), 1985 cm^{-1} (s). Anal. Calcd for $C_{15}H_{19}ClO_2Ru$: C, 48.79; H, 5.21%. Found: C, 49.07; H, 5.10%.

Hydrogenation of 2a and 2b at Lower Temperatures. Hydrogenation was carried out at ambient temperature or 50 °C by a similar procedure to that described above. Trinuclear intermediates **6a** and **6b** were isolated as thermally unstable oil by purification with a silica-gel column (eluent = hexane). Further purification was unsuccessful because of the instability.

6a: Yellow oil. TLC: R_f = 0.48 (hexane). ^{1}H NMR δ = −12.17 and −9.33 (d, 1H each, J = 4.7 Hz, Ru–H), 0.81 and 0.86 (d, 3H each, J = 5.9 Hz, Me of ^{i}Pr), 0.89—2.21 (m, 8H, CH of ^{i}Pr and protons in the seven-membered ring), 1.87 and 2.08 (s, 3H each, Me), 4.51 and 5.53 (d, 1H each, J = 3.0 Hz, protons in the five-membered ring). ^{13}C NMR (CD_2Cl_2; −50 °C) δ azulene region; 12.2, 19.6, 21.3, 25.4, 26.6, 30.9, 34.4, 40.4, 44.1, 47.9, 77.7, 78.4, 91.5, 93.1, 111.7. δ carbonyl region; 186.2, 192.3, 196.0, 196.1 (2C), 200.8, 207.7. IR (KBr) 2082 (s), 2010 (vs), 1984 (sh), 1939 cm^{-1} (s).

6b: Orange oil. R_f = 0.45 (hexane). ^{1}H NMR δ = −11.89 and −9.29 (d, 1H each, J = 4.9, Ru–H), 0.77—2.14 (m, 6H, protons in the seven-membered ring), 0.95 and 1.16 (d, 3H each, J = 7.9 Hz, Me), 1.45 (s, 3H, Me), 3.71 and 5.71 (dd, 1H each, J = 1.9, 2.9 Hz, protons in the five-membered ring), 5.21 (t, 1H, J = 2.9 Hz, a proton in the five-membered ring). ^{13}C NMR (CD_2Cl_2; −50 °C) δ azulene region; 13.7, 19.2, 22.3, 24.3, 31.2, 33.5, 35.3, 44.0, 78.8, 80.6, 86.8, 90.5, 109.2. δ carbonyl region; 186.5, 192.6, 195.9, 197.0, 198.4, 201.3, 206.2. IR (KBr) 2082 (s), 2016 (vs), 1986 (s), 1962 (m), 1934 cm^{-1} (m).

X-Ray Data Collection, Solution, and Refinement of Structures. Crystals of **5a** were grown from a mixture of CH_2Cl_2 and hexane and mounted on glass fibers. X-ray data were collected with a Rigaku AFC 7R diffractometer equipped with a graphite monochromator. Calculations were carried our using the Unics-III program system.[15] Neutral atomic scattering factors and anomalous dispersion effects were taken from "International Tables for X-Ray Crystallogrphy".[16] All of the data were corrected for absorption based on empirical azimuthal scans.[17] The positions of the heavy atoms were determined from the Patterson map and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms in **2a** or **3a** were included but not refined. Hydrogen atoms of the isopropyl group in **5a** were introduced in idealized positions (HYCO80 program), which were fixed during the refinement. Other hydrogen atoms of **5a** were located in successive difference Fourier syntheses, and their atomic coordinates were refined. Crystallographic data as well as the selected bond distances and angles are summarized in Tables 2 and 3.

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