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# Carbon–Hydrogen Bond Activation by Triruthenium Carbonyl Species during Carbon Monoxide Promoted Elimination of 4,5-Dihydroacenaphthylene from $[(\mu_2:\eta^1:\eta^5\text{-}C_{12}H_{10})Ru_3H_2(CO)_7]$: Implication of Reaction Intermediates

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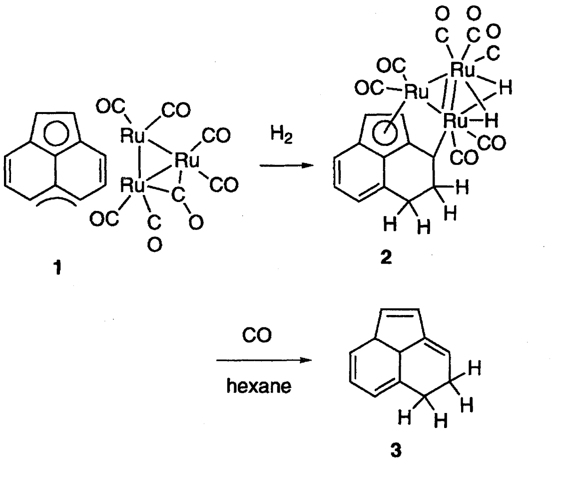
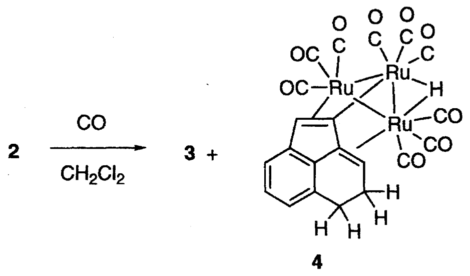
Oxidative addition of a vinylic C–H bond occurred during the CO-promoted elimination of 4,5-dihydroacenaphthylene (**3**) from $[(\mu_2:\eta^1:\eta^5\text{-}C_{12}H_{10})Ru_3H_2(CO)_7]$ (**2**) in $CH_2Cl_2$. The product, $[(\mu_3:\eta^1:\eta^2:\eta^2\text{-}C_{12}H_9)Ru_3H(CO)_9]$ (**4**), was isolated and characterized by spectroscopy and crystallography. The carbonylation of a deuterium-labelled complex, $[(\mu_2:\eta^1:\eta^5\text{-}C_{12}H_8D_2)Ru_3D_2(CO)_7]$ (**2-d₄**), under the same conditions as that from **2** to **3** in $CH_2Cl_2$ afforded 4,5-dideuterioacenaphthylene (**3-d₂**) and $[(\mu_3:\eta^1:\eta^2:\eta^2\text{-}C_{12}H_7D_2)Ru_3H(CO)_9]$ (**4-d₂**). The lack of incorporation of deuterium atoms into the ruthenium hydride in **4-d₂** suggested that dissociation of $D_2$ from the triruthenium moiety in **2-d₄** induced the oxidative addition of the vinylic C–H bond. Further carbonylation of **4** did not occur under the same conditions as the reaction from **2** to **4**, but gave **3** in moderate yields under higher CO pressure (8 atm) at 50—100 °C. These results suggest that **4** was not directly involved in the CO promoted elimination of **3** from **2**, but was closely related to the actual intermediates. Possible reaction mechanisms are discussed.

Reactions of organometallic clusters are an intriguing starting point for development of cluster catalysts[1,2] or model studies on heterogeneous catalysis.[1,3] In contrast to the diverse chemistry of mononuclear arene complexes,[4] little of the chemistry of multimetallic complexes bound to arene ligands had been investigated until Johnson,[5] Morokuma,[6] Wadepohl,[7] Suzuki,[8] and our group[9] have actively explored this field. In particular, our recent discovery that hydrogenation of acenaphthylene was mediated by a triruthenium carbonyl cluster to form a novel isomer of acenaphthene, 4,5-dihydroacenaphthylene (**3**), brought about novel chemical transformation of aromatic compounds which had never been achieved by conventional organic or organometallic methodology.[9] As shown in Scheme 1, the hydrogenation involves coordination of acenaphthylene to a triruthenium species with the face-capping mode to form $[(\mu_3:\eta^2:\eta^3:\eta^5\text{-}C_{12}H_8)Ru_3(CO)_7]$ (**1**), hydrogenation from **1** to $[(\mu_2:\eta^1:\eta^5\text{-}C_{12}H_{10})Ru_3H_2(CO)_7]$ (**2**), and removal of **3** from the metallic species. The cluster species apparently play important roles in each step of the hydrogenation, e.g. facile activation of $H_2$ by the triruthenium species,[10] high chemoselectivity in the addition of hydrogen, and CO promoted generation of **3**, but mechanisms of these reactions have not been fully investigated.

In this paper we wish to report new findings which aid in our understanding of the mechanisms of generation of **3** from **2** under a CO atmosphere. As reported earlier, the carbonylation of **2** efficiently proceeded in hexane to give **3** in high yields.[9b)] When the reaction was carried out using $CH_2Cl_2$ instead of hexane as the solvent, we obtained **3** in moderate yields. It is noteworthy that a novel ruthenium cluster $[(\mu_3:\eta^1:\eta^2:\eta^2\text{-}C_{12}H_9)Ru_3H(CO)_9]$ (**4**) shown in Scheme 2 was formed concomitantly. Compound **4** was formed from **2** via addition of two CO ligands, reductive elimination of $H_2$, and oxidative addition of a C–H bond in the dihydroacenaphthylene ligand to a ruthenium atom in the cluster. Since **4** did not react with CO under the same conditions as



Scheme 1.



Scheme 2.

those in which **3** was efficiently produced from **2**, it is not a net intermediate in the reaction from **2** to **3**. However, the actual intermediates could be deduced from the structure of **4**, because there was a reaction pathway from **4** to **3** at elevated temperatures under CO pressure. Possible reaction pathways are discussed from the structure of **4** and other supporting data.

## Results and Discussion

As described,[9b)] a hexane solution of **2** was treated with CO (1 atm, 1 atm = 101325 Pa) at room temperature for several hours to result in precipitation of $Ru_3(CO)_{12}$. From a yellow supernatant, **3** was obtained in 91% yield. When the same reaction was carried out in $CH_2Cl_2$, the reaction mixture retained homogeneity until the end of the reaction, and the resulting solution contained a mixture of **3**, $Ru_3(CO)_{12}$, and a new complex **4**; the isolated yields were 43, 20, and 53%, respectively. IR spectrum of **4** showed four absorption bands derived from terminal metal carbonyls. $^1$H NMR spectra of **4** revealed that only one Ru–H signal was seen at $\delta = -19.08$ as a singlet in the $^1$H NMR spectrum of **4**; this is in contrast to the appearance of two Ru–H peaks at $\delta = -9.01$ and $-12.96$ as doublets in that of **2**. The peak area of the Ru–H signal in **4** was half of that in **2**. Although there were ten $^1$H resonances assignable to the dihydroacenaphthylene ligand in **2**, only nine were observed in **4**, and a proton bonded with the carbon–carbon double bond in the five-membered ring was missing. This is consistent with the coupled $^{13}$C NMR spectrum of **4**, and suggests the existence of two methylenes, five methines, and five quaternary carbons. These NMR data indicated that the carbonylation of **2** resulted in the C–H bond cleavage of the dihydroacenaphthylene ligand by metallic species.

The molecular structure of **4** was confirmed by a single-crystal X-ray diffraction study (Table 1). The ORTEP drawing is illustrated in Fig. 1, and relevant bond distances and angles are summarized in Table 2. The cluster framework is nearly an isosceles triangle of which the metal–metal distances are 2.721(1), 2.920(1), and 2.987(1) Å, in which a hydrogen atom bridges the longest edge (Ru2–Ru3). Each ruthenium atom bears a tricarbonyl unit consisting of two equatorial ligands and one axial ligand similar to that seen in $[(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)M_3(CO)_9]$ (M = Ru, Os) and its derivatives.[5)] The dihydroacenaphthylene ligand acts as a $\mu_3$-dienyl ligand, namely a triply bridging five-electron donor. Two carbon–carbon double bonds, one inside the five-membered ring and the other at its *exo*-position, are bound to the Ru(1) and Ru(3) atoms, respectively, with the $\eta^2$-fashion. There is a $\sigma$-bond between the Ru(2) atom and a carbon in the five-membered ring [C02] with a metal–carbon bond of 2.06(1) Å. Several examples of triply bridging five-electron donor ligands were reported; however, the $\mu_3$-dienyl ligand similar to that seen in **4** is rare.[1d)] The closest example was reported by Carty and co-workers,[13,14)] who carried out structure determination of $Ru_3(\mu_3:\eta^1:\eta^2:\eta^2\text{-}CH_2{=}C^iPrC{=}CH_2)(PPh_2)(CO)_7(PPh_3)$ including the $\mu_3$-butadienyl moiety. Comparison in typical Ru–C and C–C bond distances between **4** and Carty's complex is depicted in Fig. 2.

Table 1. Crystallographic Data for **4**

| | **4** |
|---|---|
| Formula | $Ru_3C_{21}O_9H_{10}$ |
| Formula weight | 709 |
| Mp °C | 135 (decomp) |
| Space group | $P2_1/n$ |
| Crystal size/mm | 0.10 × 0.20 × 0.30 |
| Crystal shape | Plate |
| Crystal color | Orange |
| Unit cell demensions | |
| $a$/Å | 9.300(2) |
| $b$/Å | 8.496(2) |
| $c$/Å | 27.926(3) |
| $\beta$/deg | 96.46(2) |
| $V$/Å$^3$ | 2192.5(6) |
| $Z$ | 4 |
| $D_{calcd}$/g cm$^{-1}$ | 2.15 |
| $\mu$/cm$^{-1}$ | 20.51 |
| Absorption correction | |
| $T_{min}$ | 0.92 |
| $T_{max}$ | 1.10 |
| Diffractometer | Rigaku AFC 7R |
| Radiation ($\lambda$/Å) | Mo $K\alpha$ (0.71069) |
| Temperature/K | 296 |
| $2\theta$ range measured/° | $3.0 < 2\theta < 55.0$ |
| Scan mode | $\omega$–$2\theta$ |
| Scan range | $(0.997 + 0.30 \tan\theta)$° |
| Scan speed | 32° min$^{-1}$ |
| No. of data collected | 4544 |
| No. of unique data | 4502 |
| No. of data used | 4487 $\|F_o\| > 3\sigma(F_o)$ |
| No. of variables | 328 |
| Weighting scheme $w$ | $w$=1 |
| $R_F$ | 0.035 |
| $R_{wF}$ | 0.050 |
| $S$ | 3.04 |
| $(\Delta/\sigma)_{max}$ | 0.1 |
| $\Delta\rho_{max}$/e Å$^{-3}$ | 0.57 |

It is apparent from the above structure that the overall reaction of **2** to **4** involves addition of two CO molecules to the metallic moiety, loss of two coordinated hydrogen atoms, and formation of a new carbon–ruthenium bond. A possible reaction pathway for the cleavage of the C–H bond is the oxidative addition shown in path A of Scheme 3. Facile intramolecular activation of vinylic C–H bonds is often seen in cluster chemistry;[1d,15a)] for example, $Os_3(\eta^2\text{-}CH_2{=}CH_2)$-

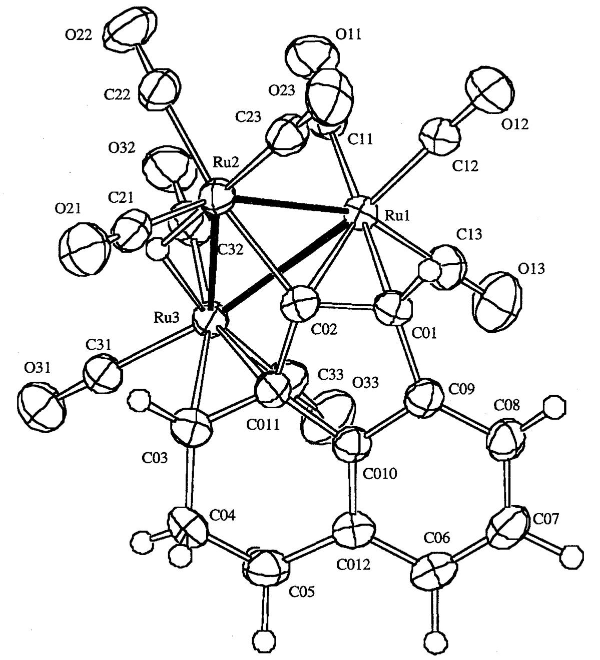
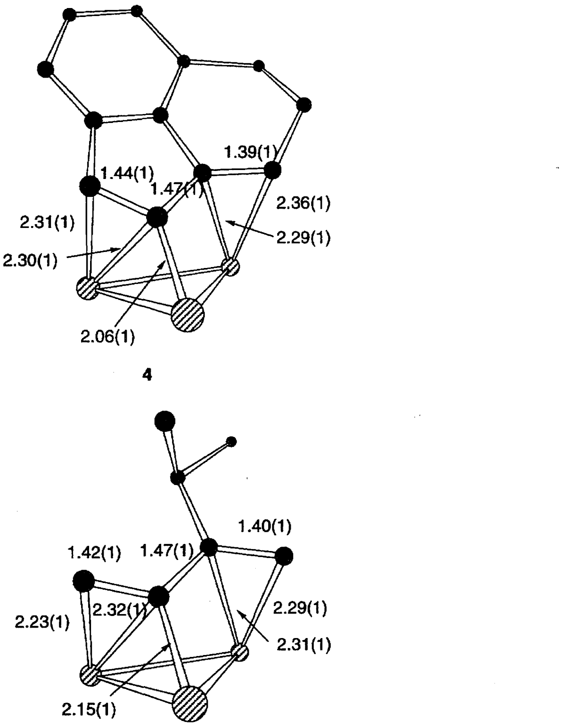


Fig. 1. The ORTEP drawing of **4**. Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **4**

Figures in parenthesis are estimated standard deviations.

| | | | |
|---|---|---|---|
| (a) Bond lengths | | | |
| Ru1–Ru2 | 2.721(1) | Ru2–Ru3 | 2.987(1) |
| Ru1–Ru3 | 2.920(1) | Ru1–C01 | 2.31(1) |
| Ru1–C02 | 2.30(1) | Ru2–C02 | 2.06(1) |
| Ru3–C03 | 2.36(1) | Ru3–C011 | 2.29(1) |
| Ru1–C11 | 1.89(1) | Ru1–C12 | 1.93(1) |
| Ru1–C13 | 1.90(1) | Ru2–C21 | 1.94(1) |
| Ru2–C22 | 1.96(1) | Ru2–C23 | 1.89(1) |
| Ru3–C31 | 1.93(1) | Ru3–C32 | 1.90(1) |
| Ru3–C33 | 1.94(1) | C01–C02 | 1.44(1) |
| C02–C011 | 1.47(1) | C03–C011 | 1.39(1) |
| (b) Bond angles | | | |
| C01–Ru1–C02 | 36.3(2) | C11–Ru1–C12 | 99.2(3) |
| C11–Ru1–C13 | 87.7(3) | C12–Ru1–C13 | 95.7(3) |
| Ru1–Ru2–C02 | 55.3(2) | Ru3–Ru2–C02 | 62.5(2) |
| C21–Ru2–C22 | 99.6(3) | C21–Ru2–C23 | 94.4(3) |
| C22–Ru2–C23 | 94.0(3) | C03–Ru3–C011 | 34.8(2) |
| C31–Ru3–C32 | 90.4(3) | C31–Ru3–C33 | 95.8(3) |
| C32–Ru3–C33 | 93.5(3) | Ru1–Ru2–Ru3 | 61.33(2) |
| Ru2–Ru1–Ru3 | 63.83(2) | Ru1–Ru3–Ru2 | 54.84(2) |

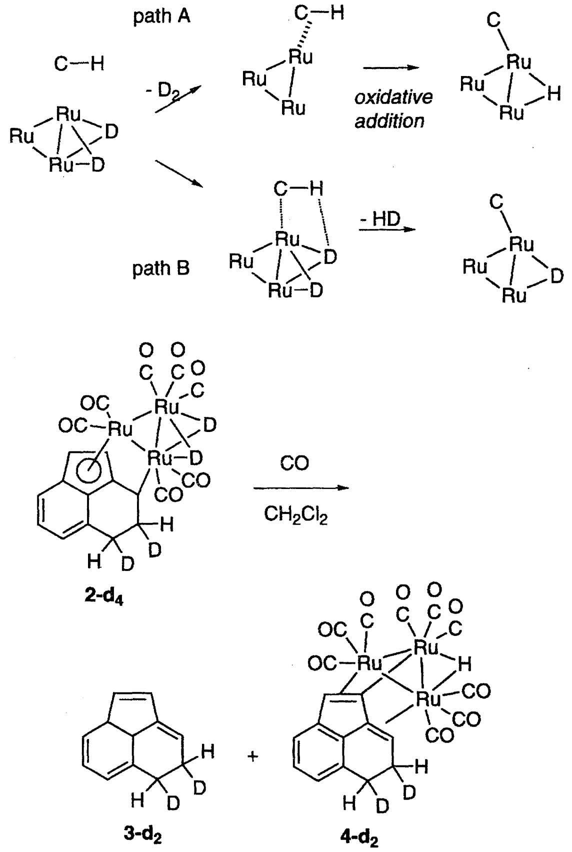


$Ru_3(CO)_6(\mu\text{-}CO)(PPh_3)(\mu_3\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}CH_2{=}C(^iPr)C{=}CH_2)(\mu\text{-}PPh_2)$ (ref. 13)

Fig. 2. Comparison of selected bond lengths between two triruthenium clusters.

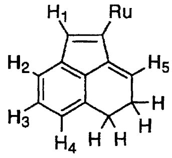
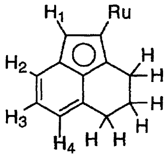
$(CO)_{11}$ is readily converted to $Os_3H_2(CO)_9(\mu\text{-}C{=}CH_2)$.[15b)] This vinylidene cluster was also formed by the reaction of $Os_3H_2(CO)_{10}$ with ethylene; reaction mechanisms were studied by the reaction of $Os_3D_2(CO)_{10}$ with ethylene, which afforded a product having no deuterium atoms.[15c)] This deuterium experiment suggests that dissociation of $D_2$ (and presumably agostic C–H interaction to the metal, too) was preceded by the oxidative addition of the C–H bond.[16)] Similar experiments using a labelled compound $[(\mu_2:\eta^1:\eta^5\text{-}C_{12}H_8D_2)Ru_3D_2(CO)_7]$ (**2-d₄**) were carried out by us, and gave $[(\mu_3:\eta^1:\eta^2:\eta^2\text{-}C_{12}H_7D_2)Ru_3H(CO)_9]$ (**4-d₂**) exclusively. $^1H$ and $^2H$ NMR spectra revealed that two deuterium atoms in the six-membered ring remained in the product, but no deuterium was incorporated in the Ru–H moiety (Table 3). This result supports path A; two deuterium ligands were eliminated from **2** as $D_2$, and the oxidative addition of the C–H bond on the five-membered ring of the dihydroacenaphthylene ligand to the ruthenium atom afforded **4-d₂**. As an alternative pathway, direct elimination of molecular hydrogen from the complex as shown in path B may be proposed, but the deuterium experiment ruled this out.

As described above, the carbonylation of **2** in $CH_2Cl_2$ afforded a mixture of **3** and **4**. If the C–H bond activation is reversible, there should be a reaction pathway from **4** and **3**. Attempted carbonylation of **4** in $CH_2Cl_2$ at room temperature or 50 °C under a CO atmosphere resulted in complete recovery of **4**. Under forced conditions ($P_{CO} = 8$ atm, 50 °C for 8 h or 110 °C for 1 h), the formation of **3** was detected; the yield determined by $^1H$ NMR was 40%. Two non-volatile products obtained by chromatography were $Ru_3(CO)_{12}$ and a new complex **5** in 68 and 32% yields, respectively. $^1H$ NMR spectrum of **5** showed no Ru–H signal, and three methylene groups were observed in the hydrocarbon ligand. The existence of the three methylenes was supported by the coupled $^{13}C$ NMR spectrum. $^{13}C$ NMR spectra revealed characteristic upfield shifts of four quaternary carbons, indicating that the carbons in the five-membered ring of **5** were bound to a ruthenium atom in the η-cyclopentadienyl coordination mode. The structure shown in Scheme 4 resulting from migration of the Ru–H species in **4** from the ruthenium atom



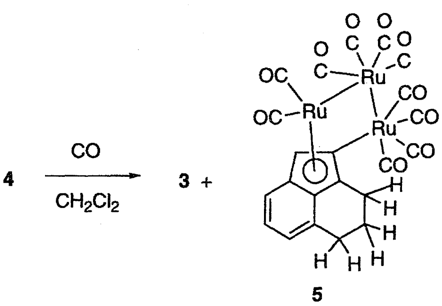
Scheme 3.

Table 3. $^1$H NMR Data ($\delta$, ppm) for **4** and **5**

| | **4** in $CD_2Cl_2$ | **5** in $CDCl_3$ |
|---|---|---|
| |  |  |
| $H_1$ | 5.80 (s) | 4.83 (s) |
| $H_2$ or $H_4$ | 6.70 (d, $J=7.4$ Hz) | 6.82 (d, $J=6.3$ Hz) |
| $H_2$ or $H_4$ | 7.24 (d, $J=8.0$ Hz) | 7.13 (d, $J=8.5$ Hz) |
| $H_3$ | 7.07 (dd, $J=7.4$, 8.0 Hz) | 7.03 (dd, $J=6.3$, 8.5 Hz) |
| $H_5$ | 4.36 (broad s) | — |
| $CH_2$ | 2.30—2.45 (m, 1H) | 1.92—2.04 (m, 1H) |
| | 2.70—2.80 (m, 1H) | 2.20—2.23 (m, 1H) |
| | 3.05—3.30 (m, 2H) | 2.46—2.51 (m, 1H) |
| | | 2.78—2.89 (m, 3H) |
| Ru-H | −19.08 (s, 1H) | — |

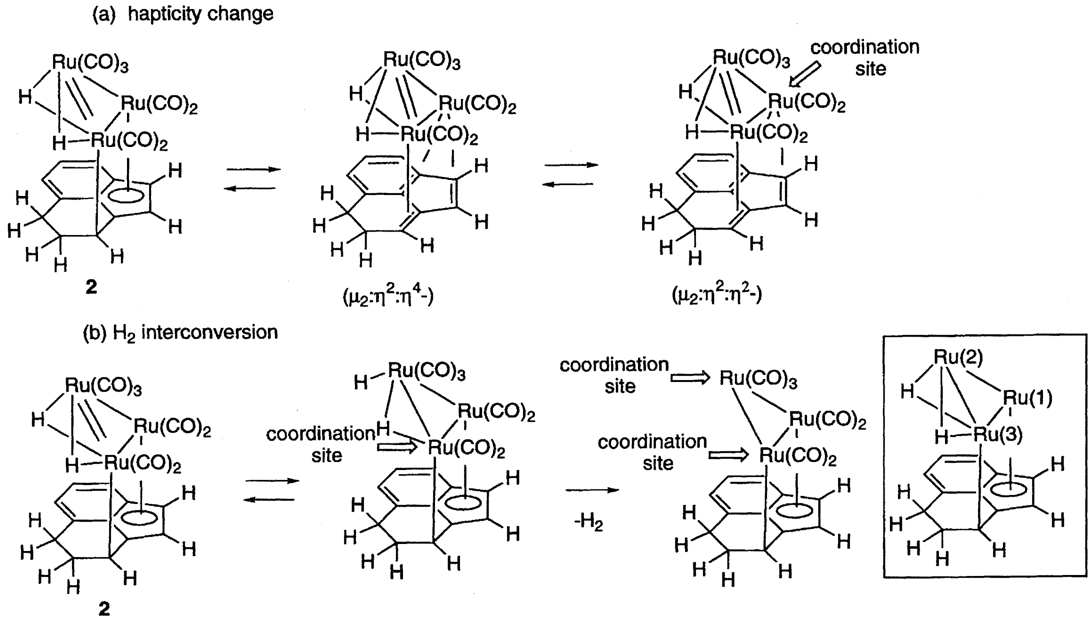
to the *exo*-carbon–carbon double bond in the dihydroacenaphthylene ligand during the carbonylation could explain these spectral data; this was supported by preliminary X-ray analysis.[17)]

The carbonylation from **2** to **4** involves addition of two CO ligands and oxidative addition of one C–H bond. In order to achieve these two elementary reactions, coordinatively unsaturated species should be generated on the ruthenium atoms from **2**. It was pointed out by Deeming that **2** including doubly bridged hydride ligands may be a model for the unknown compound $Ru_3(\mu\text{-}H)_2(CO)_{10}$.[1d)] It is well known that $Os_3(\mu_2\text{-}H)_2(CO)_{10}$, the osmium analogue of $Ru_3(\mu_2\text{-}H_2)(CO)_{10}$, can react with CO to form $Os_3(CO)_{12}$ and $H_2$.[18)] Detailed kinetic studies for this process performed by Poë and coworkers[19)] revealed that equilibrium exists between $Os_3(\mu_2\text{-}H)_2(CO)_{10}+CO$ and $Os_3(\mu_2\text{-}H)(H)(CO)_{11}$, and reductive elimination of $H_2$ from $Os_3(\mu_2\text{-}H)(H)(CO)_{11}$ leads to formation of $Os_3(CO)_{11}$. These facts indicate that both the interconversion between $[(\mu_2:\eta^1:\eta^5\text{-}C_{12}H_{10})Ru_3(\mu_2\text{-}H)_2(CO)_7]$ and $[(\mu_2:\eta^1:\eta^5\text{-}C_{12}H_{10})Ru_3(\mu_2\text{-}H)(H)(CO)_7]$ and the subsequent $H_2$ elimination from the latter species can produce a coordination site for the CO addition or the C–H bond activation (Scheme 5). An alternative process to open the coordination site in **2** is the hapticity change of the dihydroacenaphthylene ligand.[20)] Crystal structure of **2** revealed that this ligand is coordinated to the two ruthenium atoms with $\mu_2:\eta^1:\eta^5$-mode in solid states;[9a,21)] however, this bonding mode can be interconverted with $\mu_2:\eta^2:\eta^4$-fashion in solution. Thus, ring slippage, i.e. dissociation of a coordinated carbon–carbon double bond, could produce another coordinatively unsaturated site (Scheme 5). A possible mechanism for production of **4** from **2** is shown in Scheme 6. The reaction from **2** to **4** involves addition of two CO ligands to the cluster, one CO ligand to Ru(1) and the other bonded with Ru(3). The CO addition to Ru(1) could be promoted by the ring slippage, whereas that to Ru(3) could be done by the ($\mu_2$-H)/($\mu_2$-H)(H) interconversion; these form intermediate **A**. Coordinatively unsaturated species **B** generated by elimination of $H_2$ from **A** reacts with the C–H bond to form **4** through the intermediate **D** or with CO molecules to procedure **3** via the intermediate **C**. The reverse reaction from **3** and $Ru_3(CO)_{12}$ to **C** is not involved in the process; it was confirmed that their $CD_2Cl_2$ solution did not change at all at room temperature under a CO or argon atmosphere.

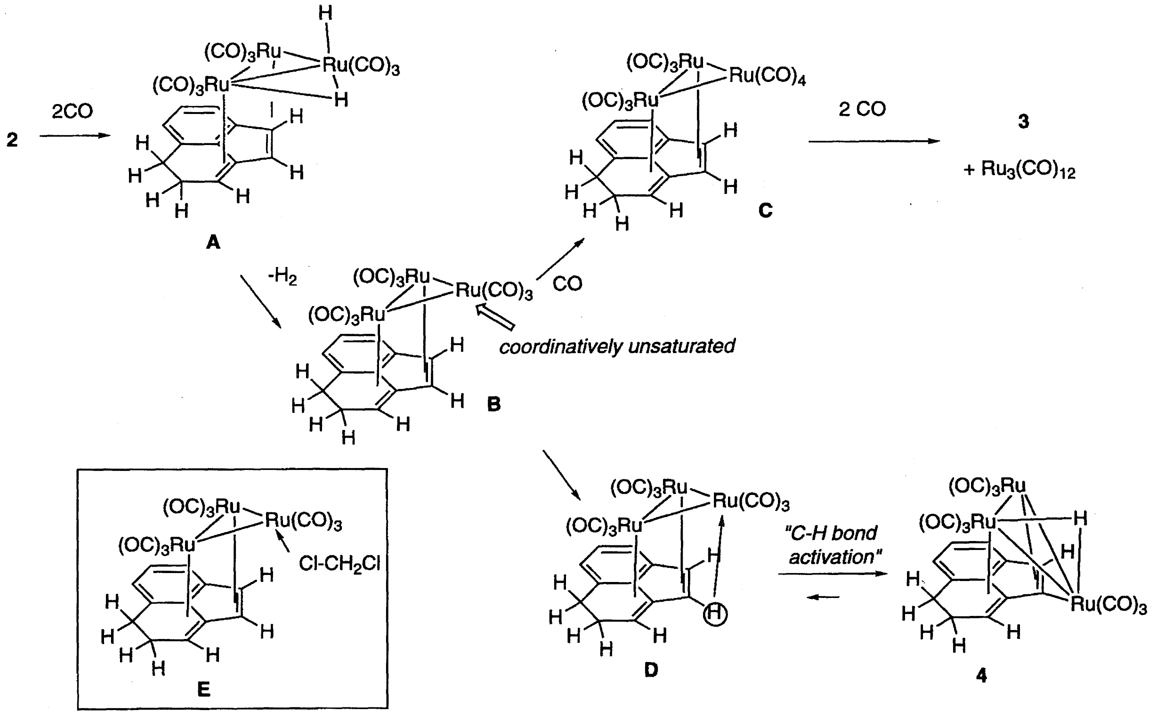


Scheme 4.

This mechanism is informative in considering a reaction pathway from **2** to **3** in hexane. Since **3** was also formed from **2** in $CH_2Cl_2$, there should be close similarity in mechanisms between the reaction in hexane and that in $CH_2Cl_2$. The fact that reductive elimination of the C–H bond in **4** did not occur at room temperature under a CO atmosphere where the reaction from **2** to **3** took place suggests that the carbonylation in hexane does not involve **4** as the intermediate. However, the intermediate **B** could be involved in the reaction in hexane. The reaction from **4** to **3** proceeding over 80 °C under CO



Scheme 5.



Scheme 6.

pressure supports existence of the reaction pathway from **D** to **3** through **B** and **C**; this indicates that **D** may also be involved in the reaction in hexane. In hexane, the intermediate **B** (or **D**, too) smoothly reacts with CO molecules to form **3** via the intermediate **C**. In $CH_2Cl_2$, the carbonylation leading to **3** is competitive with the C–H bond activation to form **4**. It is not very clear at present why such a difference in the reaction pathway occurs dependent on the solvent; solvation of $CH_2Cl_2$ to the coordinatively unsaturated species (the intermediate **E**) may play a role to facilitate the C–H bond activation from **D**[22] or to suppress the CO addition to **B**.

## Conclusion

There is great room for discussion on the reaction mechanisms of the hydrogenation of acenaphthylene to 4,5-dihydroacenaphthylene on the triruthenium carbonyl cluster. As briefly noted in our communication,[9b] formation of **3** from **2** by CO requires some explanation, because the molecular structure of **2** revealed that the dihydroacenaphthylene ligand is bonded by two ruthenium atoms with the $\mu_2:\eta^1:\eta^5$-coordination mode. From this bonding mode, one can consider the possibility of CO insertion between the carbon–ruthenium $\sigma$-bond, but not the dissociation of **3**. There should be a hapticity change from the $\mu_2:\eta^1:\eta^5$-coordination mode to the $\mu_2:\eta^2:\eta^4$-mode containing three carbon–carbon double bonds by CO. Formation of **4** as the by-product in the carbonylation of **2** in $CH_2Cl_2$ was fascinating for elucidation of the reaction mechanism as discussed above; the molecular structure of **4** indicates that the reaction of **2** with CO involves the hapticity change from the $\mu_2:\eta^1:\eta^5$-coordination mode to the $\mu_2:\eta^2:\eta^4$-mode, which could be converted to the $\mu_2:\eta^2:\eta^2$-bonding mode by the ring slippage, leading to addition of a CO molecule. The labelled experiment showed that the dissociation of $H_2$ from **2** occurred during the carbonylation, which produced the coordinatively unsaturated species in the cluster. Both the C–H bond activation affording **4** and the addition of CO leading to the formation of **3** can be accomplished by generation of these coordinatively unsaturated species, and weakly bound $CH_2Cl_2$ is likely to bring about the favorable C–H bond activation. The present results not only contribute to our understanding of the reaction mechanism for the elimination of a hydrocarbon ligand in the particular compound **2**, but also provide knowledge of some important aspects in the reaction chemistry of organometallic clusters such as involvement of facile hapticity change, interconversion of bridging hydrides, and reversible vinylic C–H bond activation.

## Experimental

**General Procedures.** Reactions were carried out in an argon atmosphere by conventional Schlenk techniques. Dichloromethane was distilled from $P_2O_5$ just before use. NMR spectra were recorded on a Varian Unity plus ($^{13}C$ 100 MHz) or a JEOL GX-270 ($^1H$, 270 MHz) spectrometer. $^1H$ and $^{13}C\{^1H\}$ spectra were referenced to tetramethylsilane by residual protons or carbons of NMR solvents. $^1H$NMR data of **4** and **5** are listed in Table 3. $^{13}C\{^1H\}$ spectra were measured in the presence of $Cr(acac)_3$ (0.07 M, $1\ M = 1\ mol\,dm^{-3}$). IR spectra were recorded in $CH_2Cl_2$ on a JASCO IR 3A spectrometer. Elemental analysis was performed on a Yanaco CHN corder. Preparative procedures for **1** and **2** were reported elsewhere.[9]

**Carbonylation of 2 in $CH_2Cl_2$ Leading to Formation of 4 or 4-$d_2$.** A solution of **2** (50 mg, 0.076 mmol) in $CH_2Cl_2$ (7 mL) was stirred in a CO atmosphere for 1.5 h. The initial red color of the solution gradually faded. The reaction mixture was cooled at −40 °C in order to remove a part of $Ru_3(CO)_{12}$ (14.9 mg, 0.023 mmol) by precipitation. The resulting supernatant was separated by decantation. The solid was repeatedly extracted by hexane. Concentration of the supernatant and the extracts combined gave **3** in 43% yield (5.1 mg, 0.033 mmol). The residue was purified by column chromatography (silica gel); the first orange band obtained by eluting with hexane contained $Ru_3(CO)_{12}$ (9.3 mg, 20%), whereas **4** (28.5 mg, 53%) was available from the second yellow band by eluting with $CH_2Cl_2$. Mp 135—136 °C (decomp). IR 2084 (m), 2060 (s), 2032 (s), 1985 (w) $cm^{-1}$. $^{13}C$NMR ($CD_2Cl_2$) $\delta = 25.05$ ($CH_2$), 30.61 ($CH_2$), 69.55 (CH), 79.18 (CH), 86.80 (C), 119.60 (CH), 123.86 (CH), 130.96 (CH), 133.02 (C), 140.14 (C), 150.89 (C), 156.38 (C), 199.39 (CO), 197.58 (CO), 192.06 (CO). Found: C, 35.27; H, 1.49%. Calcd for $C_{21}H_{10}Ru_3O_9$: C, 35.55; H, 1.42%. Following a similar procedure, **4-$d_2$** was synthesized from **2-$d_4$**.

**Carbonylation of 4.** In a glass autoclave, **4** was dissolved in $CH_2Cl_2$ (2 mL), and CO (8 atm) was applied. The reaction mixture was heated at 50 °C for 8 h. Removal of solvents from the resulting yellow solution afforded a mixture of **3**, $Ru_3(CO)_{12}$, and **5**. $^1H$NMR of the reaction mixture showed that the yield of **3** was approximately 40%. Purification of the mixture with a silica gel column led to isolation of two non-volatile compounds; elution with hexane gave $Ru_3(CO)_{12}$ (12.4 mg, 68%), whereas that with a 10 : 1 mixture of hexane and $CH_2Cl_2$ afforded **5** (6.8 mg, 32%) as yellow microcrystals; mp 133—135 °C (decomp). IR 2110 (w), 2062 (s), 2023 (vs), 1990 (s), 1968 (m), 1924 (w) $cm^{-1}$. $^{13}C$NMR ($CDCl_3$) $\delta = 24.13$ ($CH_2$), 25.81 ($CH_2$), 27.08 ($CH_2$), 78.91 (CH), 99.31 (C), 99.56 (C), 106.14 (C), 104.82 (C), 118.37 (CH), 120.47 (CH), 126.82 (CH), 133.73 (C). Carbon resonances derived from the CO ligand were not visible at room temperature due to rapid scrambling on the NMR time scale. Found: C, 35.46; H, 1.30%. Calcd for $C_{22}H_{10}Ru_3O_{10}$: C, 35.82; H, 1.35%.

**X-Ray Data Collection, Solution, and Refinement of Structures.**[23] Crystals of **4** were grown from a mixture of $CH_2Cl_2$ and hexane, and mounted on a glass fiber. X-Ray data were collected with a Rigaku AFC 7R diffractometer equipped with a graphite monochromator. Calculations were carried out using the Unics-III program.[24] Neutral atomic scattering factors and anomalous dispersion effects were taken from the standard source.[25] Data were corrected by empirical absorption correction based on azimuthal scans.[26] The positions of the heavy atoms were determined from the Patterson map. The remaining atoms including the hydrogen atoms were located in successive difference Fourier syntheses. All of the non-hydrogen atoms were refined anisotropically by using full-matrix least-squares techniques on *F*. The hydrogen atoms were fixed during the refinement.

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