ELSEVIER

Journal of Organometallic Chemistry 580 (1999) 239–244

Journal of Organo metallic Chemistry

A tetraruthenium carbonyl cluster bearing indenyl-type ligand as the facial bonding mode

Hideo Nagashima [a,]*, Akihiro Suzuki [b], Hideo Kondo [b], Mitsuharu Nobata [b], Katsuyuki Aoki [b], Kenji Itoh [c]

[a] *Institute of Advanced Material Study and CREST, Japan Science and Technology Coorporation (JST), Kyushu University, Kasuga, Fukuoka 816-8580, Japan*

[b] *Department of Materials Science, Toyohashi University of Technology, Toyohashi, Aichi 441-8580, Japan*

[c] *Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya, Aichi 464-8601, Japan*

Received 11 September 1998; received in revised form 23 November 1998

Abstract

A tetraruthenium carbonyl cluster, (μ_3:η^1:η^3:η^5-3,4,5-trihydroacenaphthylenyl)$Ru_4H(CO)_9$ (**3**), was synthesized from (μ_3:η^1:η^5-dihydroacenaphthylene)$Ru_3H_2(CO)_{12}$ (**2**) in chloroform. The molecular structure showed the trihydroacenaphthylenyl ligand to be a rare example of triply bridging nine electron donor ligands, being bound to three ruthenium atoms by the face-capping mode. One ruthenium atom was bonded by the π-cyclopentadienyl coordination mode, whereas the latter two were bound to four carbons in the six-membered ring by the η^1:η^3-bonding mode.

Keywords: Tetranuclear cluster; Ruthenium; Face-capping ligand; Indeyl

1. Introduction

Coordination of aromatic compounds to transition metals has attracted the attention of organometallic chemists both experimentally and theoretically [1,2]. Transition metal clusters bound to arenes with the facial coordination mode have been investigated particularly actively in the last decade as a discrete molecular model of chemisorbed aromatic compounds on the surface [3]. A series of work on osmium and ruthenium carbonyl clusters attached to substituted benzene ligands by the μ_3:η^2:η^2:η^2-bonding mode by Lewis, Johnson, and Braga has provided information on many intriguing aspects of coordination modes, structural isomerism, and the relationship between molecular shapes and organization in a solid [3].

In contrast to the well-investigated chemistry of clusters with μ_3:η^2:η^2:η^2-benzenes, little study has been made of clusters in which the metal triangle is capped by μ_3-polyaromatic hydrocarbon ligands [4], though some of the complexes were synthesized and structurally analyzed as early as the late 1960s [5]. It is a most interesting feature of the polyaromatic compounds as a face-capping ligand that they contribute to stabilization of the cluster framework as triply-bridging more than seven electron donor ligands which have not yet been fully researched in cluster chemistry [4]. For example, we reported (μ_3:η^2:η^3:η^5-$C_{12}H_8$)$Ru_3(CO)_{12}$ (**1**), in which the acenaphthylene ligand was bonded with three ruthenium atoms, donating 10 electrons to the cluster moiety [6]. Azulene derivatives take part in stabilizing $Ru_3(CO)_7$ and $Ru_3(CO)_9$ moieties as triply bridging 10 electron donor ligands [5,7]. Coordination of these polyaromatic hydrocarbon ligands not only results in successful preparation of clusters having significant difference in structures and bonding modes from those bonded with μ_3:η^2:η^2:η^2-monocyclic arene ligands, but also provides particularly high reactivity

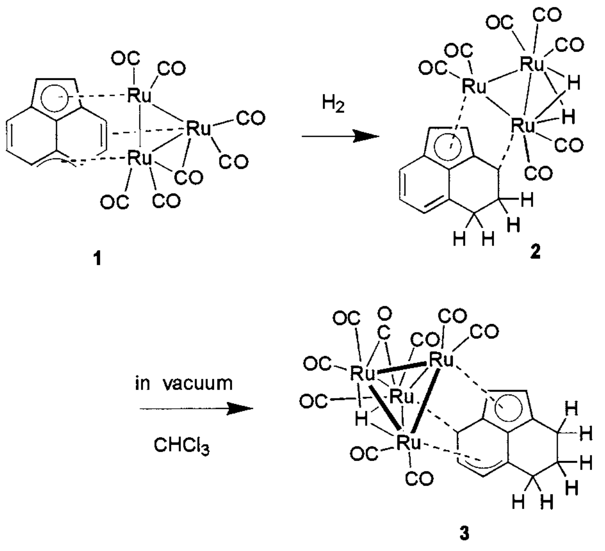
---

* Corresponding author. Fax: + 8192-583-7819.

0022-328X/99/$ - see front matter
PII: S0022-328X(98)01155-3

towards activation of H_2 by the cluster species [6]. In contrast to the fact that arene ligands in (μ_3:η^2:η^2:η^2-benzene)$Ru_3(CO)_9$ and its derivatives are robust with respect to hydrogenation [3], **1** easily reacted with H_2 at room temperature to result in partial reduction of the acenaphthylene ligand (Scheme 1). Furthermore, monocylic arene ligands on the face of the Ru_3 triangle easily undergo nucleophilic addition reaction [8], while reactions of **1** with nucleophiles resulted in decomposition of the cluster [9].

These significant differences in structures and chemical reactivity of clusters bound to polyaromatic hydrocarbon ligands from those bearing μ_3:η^2:η^2:η^2-arene ligands strongly prompted us to explore organometallic clusters bearing μ_3-π-ligands other than those acting as 10-electron donors. We report here a tetraruthenium complex **3** in which a 3,4,5-trihydroacenaphthyl group was bound to the face of a tetrahedral Ru_4 core, donating nine electrons to the cluster moiety. Three of the ruthenium atoms were bonded by the trihydroacenaphthylenyl ligand with η^1:η^3:η^5-bonding mode as shown in Scheme 1. Among a number of arene clusters structurally elucidated, none having μ_3-indenyl-like compound as a triply bridging nine electron donors has been isolated to our knowledge. Furthermore, the μ_3:η^2:η^2:η^2-monocyclic arene ligand has been found in clusters of three, five, and six nuclearity, but not in tetranuclear clusters; only tetranuclear clusters bearing apical (η^6) arene ligands have been investigated [3]. Recent reports by Johnson and Braga stated that several Ru_4 clusters bearing isopropenylbenzene and its analogues were successfully synthesized [10]. The isopropenyl groups contribute to stabilizing the tetraruthenium core by η^2-coordination. The cluster presented in this paper is another example that the substituents in monocyclic arenes effectively stabilize the Ru_4 core, although the coordination mode is different from the isopropenylbenzene derivatives.



Scheme 1.

2. Results and discussion

The dihydride complex **2** was stable in solution under an inert gas atmosphere. However, it was gradually converted to a mixture of compounds including **3**, when the solution was allowed to stand in vacuum (0.1 Torr). In chloroform (or chloroform-d_1), the reaction at room temperature for 20 h afforded four products, **3**–**6**. The yields of **3**, **4**, **5**, and **6** based on the ruthenium atoms were 54, 10, 14, and 7%, respectively. In the ^{1}H-NMR spectrum of the major product **3**, a Ru–H signal appeared at $\delta-16.14$ ppm as a singlet. The organic ligand afforded five protons assignable to aromatic protons, which were significantly shifted upfield due to their coordination to the metal, and six protons at the hydrocarbon region (δ 0.73–0 2.86 ppm). Twelve ^{13}C resonances composed of three CH_2, five CH, and four quaternary carbons appeared, in which two CH_2 peaks were closely overlapped at δ 28.12 ppm. All of the carbon signals derived from the CH and quaternary carbons appeared at significantly higher fields than usual, suggesting that they are bonded to the metallic species. Assignments of the ^{1}H and ^{13}C-NMR spectra of the aromatic ligand were made with the aid of 'C–H' COSY experiments and the results are summarized in the experimental section. Five 'terminal' CO signals were observed at 189–215 ppm, whereas one 'bridging' CO peak was seen at 230.34 ppm. The relative peak intensities were 1:1:2:1:3:1. Existence of plural 'terminal' and one 'bridging' CO ligand were also consistent with the IR spectrum of **3** showing absorptions at 2050, 2010, 1977, 1957, and 1820 cm^{-1}.

These spectroscopic data are consistent with the crystal structure. A single crystal suitable for X-ray structure determination was available from a solution of dichloromethane and hexane. The crystallographic data and representative bond lengths and angles are summarized in Tables 1 and 2, and the ORTEP drawing is shown in Fig. 1.

The trihydroacenaphthyl ligand is arched across the largest face of an irregular tetrahedron of ruthenium atoms, in which Ru–Ru distances vary from 2.760(1) to 3.034 Å. Two terminal CO ligands are bonded with each ruthenium atom, and two of the ruthenium atoms, Ru(2) and Ru(4), are linked by a bridging CO ligand. Carbons in the five-membered ring are bound to Ru(3) by the common metal-π-cyclopentadienyl coordination mode (Ru–C distances; 2.24–2.27 Å). There exists a Ru–C σ-bond between Ru(2) and C(13) with a Ru–C distance of 2.27 Å. The partial structure consisting of Ru(2), Ru(3), C(10), C(11), C(12), C(13), C(20), and C(21) is similar to the μ_2:η^1:η^5-bonding mode seen in

Table 1
Crystallographic data of **3**[a]

	3
Formula	$C_{21}H_{12}O_9Ru_4$
Formula weight	812.6
Habit	Red plate
Crystal dimension (mm)	$0.25 \times 0.07 \times 0.10$
Space group	$P2_1/c$
Z	4
a (Å)	12.916 (2)
b (Å)	9.664 (3)
c (Å)	17.958 (2)
β (deg)	93.08 (1)
V (Å^3)	2238.2 (7)
D_{calc} (g cm^{-3})	2.41
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)
Monochrometer	Graphite
Transmission factors	$0.96 \sim 1.03$
μ_{calc} (cm^{-1})	26.49
Scan type	ω–2θ
Scan rate (° min^{-1})	32
2θ range	$3.0 < 2\theta < 55.0$
No. of data collected	5812
No. of used data	3787 ($F_o > 3\sigma(F_o)$)
R	0.053
R_w	0.040 ($\omega = [\sigma^2(F_o)]^{-1}$)
GOF	2.0
(Δ/σ)max	0.2
$\Delta\rho$ max (e Å^{-3})	1.18

[a] Scan method, normalized to an average of unity.

the dihydroacenaphthylene cluster **2**. The three carbons in the six-membered ring, C(14), C(15), and C(16), are bound to Ru(1) with Ru–C distances of 2.47, 2.21, and 2.21 Å, respectively. These three carbons can be regarded as a distorted η^3-allyl ligand in which the Ru–C(14) bond is significantly longer than the others. The long Ru–C distance is attributable to the steric demands of the trihydroacenaphthyl ligand. Molecular modeling study of **3** revealed that it is difficult to keep the Ru–C distances in this π-allyl moiety within a reasonable range. As noted above, to our knowledge the indenyl ligand and its analogues have rarely been used as a bridging ligand of multimetallic compounds. A dinuclear complex, pentacarbonyl-7H-indenediiron (μ_2:η^3:η^5-C_9H_8)$Fe_2(CO)_5$, bearing an indenyl skeleton was reported by Cotton [11]; bond distances between carbons in the indene ligand and iron atoms are 2.06–2.17 Å, and the distorted π-allyl coordination seen in **3** is not observed in this diiron compound. The hydrogen atom bonded with ruthenium atoms was seen in the difference Fourier map on the face of the Ru_4 core consisting of Ru(1), Ru(2), and Ru(3), which may act as a rare example of triply bridging one electron donor ligand.

As noted above, a face-capped six-membered ring of a tetranuclear cluster had not been found until a discovery of several Ru_4-clusters bearing isopropenyl benzene as the facial ligand. This suggests that the bonding mode of benzene itself does not fit the face of the Ru_4 tetrahedral, and that coordination of carbon–carbon double bonds on the side chain besides three olefinic bonds in the benzene ring is essential for the formation of tetranuclear clusters. The role of the five-membered ring in cluster **3** is similar to that of the isopropenyl groups in the above clusters. An important feature of the bonding mode of **3** is that carbons in the five-membered ring act like a cyclopentadienyl group, and hence, the π-ligand in **3** donates odd (9) electrons to the metals. In the isopropenyl benzene derivatives, the μ_3-π-ligands donate even (8 or 10) electrons to the cluster core.

Compounds **4**, **5**, and **6** were also available as byproducts of the formation of **3**. Combined yields of **3**, **4**, **5**, and **6** can explain the fate of 81% of ruthenium atoms in the starting material. Spectral data of **4** are quite similar to those of **2**, suggesting that the structure of **4** would be close to that of **2**. Elemental analysis was consistent with the formula $C_{19}H_{11}O_7ClRu_3$. These indicate that one of the Ru–H moieties was replaced by a chlorine atom; this is supported by the results of preliminary X-ray structure determination. The dinuclear ruthenium complex **5** was obtained as a 1:1 mixture of *cis* and *trans* isomers. The formation of **5** was supported by the fact that oxidative cleavage of the ruthenium–ruthenium bond in **5** by I_2 gave mononuclear ruthenium iodide **7** in quantitative yield (Scheme 2). The known tetranuclear cluster **6** was assigned from its ^{1}H-NMR and IR data [12].

The mechanism in the formation of **3** from **2** is not clear at present. It is important to allow the $CHCl_3$ solution of **2** to stand in vacuum; no reaction took place under an inert gas or hydrogen atmosphere. To keep the solution in vacuum may induce dissociation of either H_2 or CO from **2**, which triggers the formation of **3**. Since facile replacement of a hydrogen atom of the Ru–H moiety by a chlorine atom is known to be promoted by polyhalogenated solvents [13], the chlorine atom of **4** could be derived from chloroform. The chlorination of **2** took place more rapidly in CCl_4 to give **4** and $CHCl_3$. The formation of **3** from **2** easily occurred in chloroform and dichloromethane but not in solvents which did not contain chlorine atoms such as THF and benzene. Furthermore, the reaction profile of **4** in $CDCl_3$ showed that the amount of **4** was initially increased, and then gradually diminished. Although this result may suggest that **4** is an intermediate for the formation of **3**, this can be ruled out by the fact that a $CDCl_3$ solution of **4** in vacuum gave a complicated mixture of products, which did not include **3**.

Table 2
Selected bond distances and angles of **3**

Bond distances (Å)					
Ru1–Ru2	2.944(1)	Ru1–Ru3	3.033(1)	Ru1–Ru4	2.784(1)
Ru2–Ru3	2.886(1)	Ru2–Ru4	2.760(1)	Ru3–Ru4	2.961(1)
Ru1–C1	1.92(1)	Ru1–C2	1.86(1)	Ru1–C14	2.47(1)
Ru1–C15	2.21(1)	Ru1–C16	2.21(1)	Ru2–C3	1.88(1)
Ru2–C4	1.87(1)	Ru2–C9	2.21(1)	Ru2–C13	2.26(1)
Ru3–C5	1.88(1)	Ru3–C6	1.92(1)	Ru3–C10	2.25(1)
Ru3–C11	2.24(1)	Ru3–C12	2.27(1)	Ru3–C20	2.26(1)
Ru3–C21	2.26(1)	Ru4–C7	1.86(1)	Ru4–C8	1.87(1)
Ru4–C9	2.01(1)	Ru1–H12	1.7(1)	Ru2–H12	1.8(1)
Ru4–H12	2.1(1)	C10–C11	1.45(1)	C10–C20	1.43(1)
C11–C12	1.44(1)	C12–C13	1.50(1)	C12–C21	1.46(1)
C13–C14	1.43(1)	C14–C15	1.40(1)	C15–C16	1.47(1)
C16–C17	1.50(1)	C16–C2	1.45(1)	C20–C21	1.43(1)
Bond angles (°)					
Ru2–Ru1–Ru3	57.72(2)	Ru2–Ru1–Ru4	57.52(3)		
Ru3–Ru1–Ru4	61.00(3)	Ru1–Ru2–Ru3	62.69(3)		
Ru1–Ru2–Ru4	58.32(3)	Ru1–Ru3–Ru2	59.59(3)		
Ru1–Ru3–Ru4	55.34(2)	Ru1–Ru4–Ru2	64.16(3)		
Ru1–Ru4–Ru3	63.66(3)	Ru2–C9–Ru4	81.50(4)		
Ru2–C9–O9	134.4(8)	Ru4–C9–O9	144.0(8)		

3. Conclusion

We have found a preparative route of **3**, which is a novel ruthenium cluster bearing μ_3-indenyl type ligand. To our knowledge, the 3,4,5-trihydroacenaphthyl ligand in **3** is a rare example of a triply bridging 9-electron donor, which takes part in stabilizing the complex by capping the face of the tetrahedral Ru_4 core. Further investigation focusing on the reactions of this new complex with hydrogen and other reagents is underway.

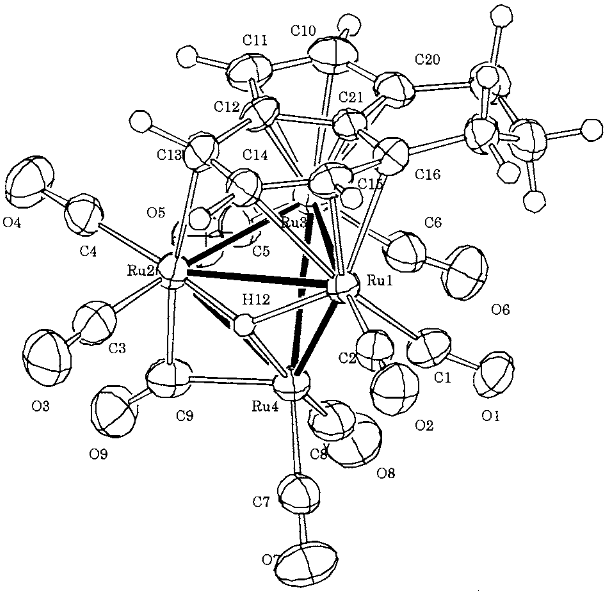


Fig. 1. Molecular structure of **3**.

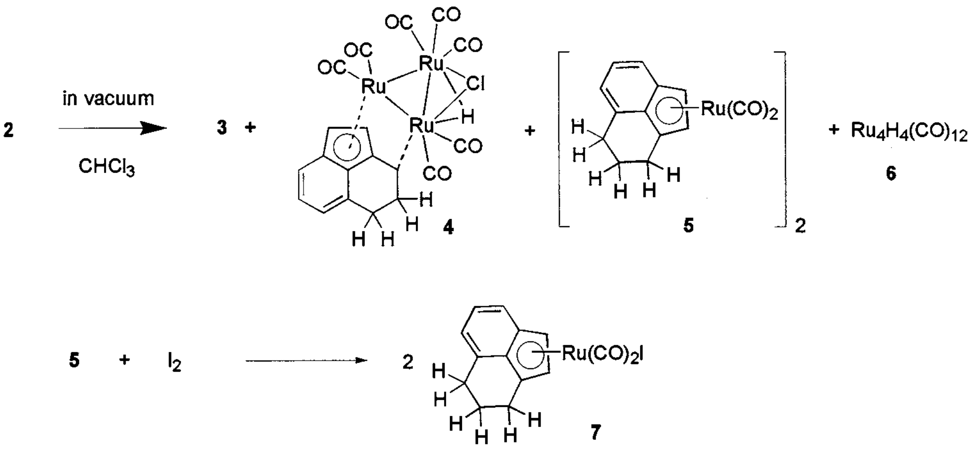
4. Experimental

4.1. General methods

All manipulations were carried out under an argon atmosphere by the standard Schlenk technique. All solvents were distilled just before use over standard drying reagents. ^1H- and ^{13}C-NMR spectra were recorded on a JEOL GX270, JNM-LA400, or Varian Unity plus (400 MHz) spectrometer. IR spectra were taken on a JASCO FT/IR-230 spectrometer. Elemental analysis was performed with a YANACO CHN recorder.

4.2. Preparation of 3

In a sealed tube **2** (40 mg, 0.061 mmol) was dissolved in $CHCl_3$ (or $CDCl_3$) (0.6 ml). The solution was cooled to −78°C and degassed several times, then the tube was sealed by flame. The solution was kept in the dark at room temperature for 20 h, and then concentrated. The residue was purified with a silica-gel column (1.2∅ × 13 cm; Merck 7734). By elution with hexane two yellow bands were obtained; the first contained **6** (2.5 mg) whereas **4** was available from the second band (4.4 mg). From the yellow band obtained by eluting with hexane/ether (10:1), **5** (8.1 mg) was isolated. The desired product **3** (20 mg) was obtained from the orange band obtained by elution with ether.

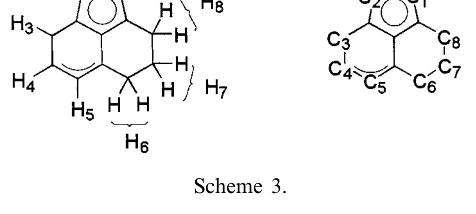


Scheme 2.

3: TLC: $R_f=0.26$ (ether). M.p. 171–172°C (dec). ^{1}H-NMR (CD_2Cl_2) δ 6.40 (d, $J=5.6$ Hz, 1H, H3), 6.01 (d, $J=6.1$ Hz, 1H, H5), 5.40 (d, $J=3.0$ Hz, 1H, H1), 3.72 (dd, $J=5.6$, 6.1 Hz, 1H, H4), 3.60 (d, $J=3.0$ Hz, 1H, H2), 2.26 ∼ 2.71 (m, 2H, H6), 2.18 ∼ 2.28(m, 1H, H8), 1.92 ∼ 1.97 (m, 1H, H7), 1.75 ∼ 1.80 (m, 1H, H8), 0.73 ∼ 0.77(m, 1H, H7), −16.14 (s, 1H, Ru–H). ^{13}C-NMR (CD_2Cl_2) δ 6.94 (C3), 22.15 (two carbons are overlapped, C7 and C8), 28.12 (C6), 64.78 (C4), 65.64 (C), 69.16 (C), 69.92 (C5), 78.13 (C2), 78.37 (C1), 79.77 (C), 104.18 (C), 189.04 (CO), 194.76 (CO), 194.89 (CO), 198.69 (CO), 214.64 (CO), 230.34 (CO). H–H COSY, C–H COSY, and differential NOE techniques unequivocally determined assignment of ^{1}H and ^{13}C resonances. IR (CH_2Cl_2) 2050 (s), 2010 (vs), 1977 (s), 1957 (sh), 1820 (w) cm^{-1}. Anal. Found: C, 30.87; H, 1.44. $C_{21}H_{12}O_9Ru_4$ Calc.: C, 31.03; H, 1.48 (Scheme 3).

4: TLC: $R_f=0.51$ (hexane). M.p. 128–134°C (dec) ^{1}H-NMR($CDCl_3$) δ 7.54 (d, $J=8.4$ Hz, 1H, H4 or H6), 7.15 (dd, $J=6.6$, 8.4 Hz, 1H, H5), 6.97 (d, $J=6.6$ Hz, 1H, H4 or H6), 6.15 (d, $J=2.9$ Hz, 1H, H1 or H2), 5.00 (br–s, 1H, H3), 3.85 (d, $J=2.9$ Hz, H1 or H2), 2.68 ∼ 2.84 (m, 3H, CH_2), 2.49 ∼ 2.57 (m, 1H, CH_2), −11.00 (s, 1H, Ru–H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 24.21 (CH), 24.77 (CH_2), 32.28 (CH_2), 69.99 (C), 80.99 (CH), 84.62 (CH), 101.69 (C), 108.95 (C), 121.19 (C), 124.64 (CH), 127.73 (CH), 130.92 (C), 180.49 (CO), 188.65 (CO), 196.32 (CO), 197.18 (CO), 197.84 (CO), 200.61 (CO), 200.91 (CO). IR (CH_2Cl_2): 2020 (m), 2005 (vs), 1960 (m), 1940 (m) cm^{-1}. The atom-connectivity was confirmed by preliminary X-ray structure determination [$C_{19}H_{11}O_7Cl_1Ru_3$, space group $P\bar{1}$, $a=10.798$ (2), $b=11.549$ (2), $c=8.487$ (4) Å, $\alpha=90.39$ (2)°, $\beta=94.69$ (2)°, $\gamma=93.09$ (1)°, $Z=2$, R_F and $R_{wF}=0.062$, GOF = 9.9, for 4665 reflections with $F_o > 3\sigma(F_c)$]. Although the high GOF value indicates that this result contains some crystallographic problems, the results are good enough to prove the atom connectivity of **4**.

5: A 1:1 mixture of *cis* and *trans* isomers was obtained [TLC: $R_f=0.31$(hexane)]. Two isomers were separated by careful purification by column chromatography. Isomer 1: ^{1}H-NMR($CDCl_3$) δ 7.20 (dd, $J=6.9$, 8.9 Hz, 1H, H4), 6.95 (d, $J=6.9$ Hz, 1H, H3 or H5), 6.65 (d, $J=8.9$ Hz, 1H, H3 or H5), 5.49 (d, $J=3.0$ Hz, 1H, H1 or H2), 4.66 (d, $J=3.0$ Hz, H1 or H2), 2.77 ∼ 3.08 (m, 4H, CH_2), 2.11 ∼ 2.33 (m, 2H, CH_2). IR (KBr): 1981 (m), 1943 (s), 1783 (s) cm^{-1}. Isomer 2: ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.22 (dd, $J=6.9$, 8.9 Hz, 1H, H4), 6.94 (d, $J=6.9$ Hz, 1H, H3 or H5), 6.72 (d, $J=8.9$ Hz, 1H, H3 or H5), 5.46 (d, $J=3.0$ Hz, 1H, H1 or H2), 4.77 (d, $J=3.0$ Hz, H1 or H2), 2.77 ∼ 3.08 (m, 4H, CH_2), 2.11 ∼ 2.33 (m, 2H, CH_2). IR (KBr): 1943(s), 1789(s) cm^{-1}. Unequivocal identification of this compound was carried out by oxidative cleavage of the Ru–Ru bond by iodine. A solution of **5** (9.4 mg, 0.015 mmol) in CCl_4 (12 ml) was treated with I_2 (2.1 mg, 0.017 mmol) in CCl_4 (3 ml) at room temperature for 1 h. Removal of the solvent in vacuo was followed by purification of the residue with a silica-gel column (1∅ × 5 cm, −20°C, elution by hexane and CH_2Cl_2). The mononuclear complex **7** was obtained in 69% yield (9 mg). TLC: $R_f=0.34$ (hexane: CH_2Cl_2 = 1: 1). m.p. 138–142°C. ^{1}H-NMR ($CDCl_3$) δ 7.28 (dd, $J=0.9$, 8.6 Hz, 1H, H3 or H5), 7.21 (dd, $J=6.8$, 8.6 Hz, 1H, H4), 7.03 (dd, $J=0.9$, 6.8 Hz, 1H, H3 or H5), 5.54 (d, $J=2.4$ Hz, 1H, H1 or H2), 5.47 (d, $J=2.4$ Hz, H1 or H2), 3.04 ∼ 3.18 (m, 2H, CH_2), 2.77 ∼ 2.90 (m, 2H, CH_2), 2.28 ∼ 2.38 (m, 1H, CH_2),



Scheme 3.

1.98 ~ 2.08 (m, 1H, CH_2). ^{13}C-NMR ($CDCl_3$) δ 22.66 (CH_2), 23.39 (CH_2), 26.84 (CH_2), 68.06 (CH), 87.64 (CH), 93.89 (C), 108.14 (C), 110.65 (C), 121.18 (CH), 124.16 (CH), 130.27 (CH), 136.33 (C), 196.35 (CO), 196.45 (CO). IR (KBr) 2026 (s), 1969 (vs) cm^{-1}. Anal. Found: C, 38.26; H, 2.49. $C_{14}H_{11}O_2RuI$. Calc.: C, 38.28; H, 2.53.

4.3. X-ray structure determination

A single crystal of **3** grown from a solution of hexane and CH_2Cl_2 was mounted on a glass fiber. Reflections were recorded on a Rigaku AFC 7R diffractometer. Crystallograpic data are summarized in Table 1. The structure was solved by a Windows version of the Unics III program system [14]. Neutral atomic scattering factors and anomalous dispersion effects were taken from the International Tables for X-ray Crystallography [15]. All of the data were corrected for absorption based on empirical azimuthal scans [16]. The positions of the heavy atoms were determined from the Patterson map and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located in successive difference Fourier synthesis, and their atomic coordinates were refined. Crystallographic data as well as the selected bond distances and angles are summarized in Tables 1 and 2.

Acknowledgements

The authors are grateful to Dr Makoto Sakuta for his kind donation of a Windows version of the Unics-III program system. Experimental assistance by Takafumi Iura is also acknowledged.

References

[1] For recent reviews on metal cluster chemistry: (a) G. Gonzárez-Moraga, Cluster Chemistry, Springer-Verlag, Berlin (1993). (b) D.F. Shriver, H.D. Kaesz, R.D. Adams (Eds.), The Chemistry of Metal Cluster Complexes, VCH, NY (1990). (c) L.N. Lewis, Chem. Rev. 93 (1993) 2693. (d) G. Süss-Fink, G. Meister, Adv. Organometal. Chem. 35 (1993) 41. (e) R.M. Laine, J. Mol. Catal. 14 (1982) 137.

[2] For representative reviews: (a) E.L. Muetterties, J.R. Bleeke, E.J. Wucherer, T.A. Albright, Chem. Rev. 82 (1982) 499. (b) H. Wadepohl, Angew. Chem. Int. Ed. Eng. 31 (1992) 247.

[3] (a) D. Braga, P.J. Dyson, F. Grepioni, B.F.G. Johnson, Chem. Rev. 94 (1994) 1585. (b) P.J. Dyson, B.F.G. Johnson, C.M. Martin, Coord. Chem. Rev. 155 (1996) 69; (c) J. Chem. Soc. Dalton Trans. (1996) 2395; (d) Coord. Chem. Rev. 155 (1996) 69.

[4] A.K. Smith, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Chapter 13, vol. 7, Pergamon Press, Oxford, UK, 1995.

[5] (a) M.R. Churchill, J. Wormald, Inorg. Chem. 12 (1973) 191. (b) M.R. Churchill, P.H. Bird, J. Am. Chem. Soc. 90 (1968) 800. (c) M.R. Churchill, Prog. Inorg. Chem. 11 (1970) 53.

[6] (a) H. Nagashima, T. Fukahori, K. Aoki, K. Itoh, J. Am. Chem. Soc. 115 (1993) 10430. (b) H. Nagashima, A. Suzuki, M. Nobata, K. Itoh, J. Am. Chem. Soc. 118 (1996) 687.

[7] (a) B.F.G. Johnson, D.S. Shephard, A.J. Edwards, D. Braga, E. Parisini, P.R. Raithby, J. Chem. Soc. Dalton Trans. (1995) 3307. (b) H. Nagashima, A. Suzuki, M. Nobata, K. Aoki, K. Itoh, Bull. Chem. Soc. Jpn. 71 (1998) 2441.

[8] M.A. Gallop, B.F.. G. Johnson, J. Lewis, A.H. Wright, J. Chem. Soc. Dalton Trans. (1989) 481.

[9] H. Nagashima, A. Suzuki, unpublished.

[10] (a) D. Braga, J.J. Byrne, F. Grepioni, E. Parisini, P.J. Dyson, P.E. Gaede, B.F.G. Johnson, D. Reed, Organometallics 14 (1995) 4892. (b) P.E. Gaede, S. Parsons, B.F.G. Johnson, J. Chem. Soc. Dalton Trans. (1996) 3833. (c) P.E. Gaede, B.F.G. Johnson, M. McPartlin, M-A, Pearsall, J. Chem. Soc. Dalton Trans. (1996) 4621.

[11] F.A. Cotton, B.E. Hanson, Inorg. Chem. 16 (1977) 1861.

[12] S.A.R. Knox, J.W. Koepke, M.A. Andrews, H.D. Kaesz, J. Am. Chem. Soc. 97 (1975) 3942.

[13] S. Bhaduri, N.Y. Sapre, K.R. Sharma, P.G. Jones, J. Organometal. Chem. 364 (1989) C8.

[14] T. Sakurai, K. Kobayashi, Rep. Int. Phys. Chem. Res. 55 (1979) 69.

[15] International Tables for X-ray Crystallography, vol. C, Kluwer Academic Publishers, Boston, 1992.

[16] A.T.C. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr. A 24 (1968) 351.