Reversible Transformation between Methylene and Methylidyne-Hydride Moieties on the $Ru_{10}C_2$ Framework

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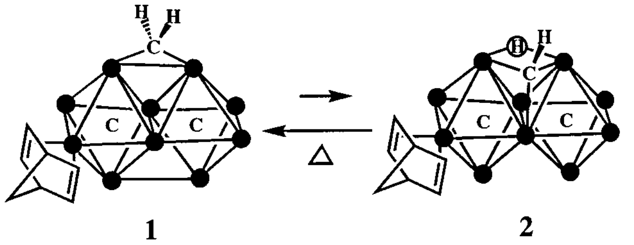
Summary: Oxidative substitution of $[Ru_{10}C_2(CO)_{22}(NBD)]^{2-}$ *with ferrocenium ion and diazomethane forms a methylene compound,* $Ru_{10}C_2(CO)_{22}(NBD)(\mu\text{-}CH_2)$*, in which the methylene ligand symmetrically bridges two adjacent apical ruthenium centers in the edge-fused bioctahedral* $Ru_{10}C_2$ *framework. A methylidyne tautomer,* $Ru_{10}C_2(CO)_{22}(NBD)(CH)(H)$*, is formed reversibly at 80 °C.*

Scheme 1



Introduction

Organometallic cluster complexes are often viewed as molecular models for hydrocarbon fragments chemisorbed on metal surfaces.[1] Reversible transformations among the simplest C_1 fragments, CH, CH_2, and CH_3, are of particular interest as probes of hydrogen atom transfer between carbon and metal centers.[2,3] Higher nuclearity clusters incorporating these simple ligands are relatively rare,[4] although the structural and electronic flexibility of such cluster frameworks may more closely approach the surface properties of catalytically active metal particles.[5] In previous work we have shown that the higher nuclearity cluster system based on $[Ru_{10}C_2(CO)_{24}]^{2-}$ [6] is especially robust, undergoing direct thermal substitution with such four-electron hydrocarbon ligands as diphenylacetylene, allene, and norbornadiene to form $[Ru_{10}C_2(CO)_{22}(C_2Ph_2)]^{2-}$,[7a] $[Ru_{10}C_2(CO)_{22}(C_3H_4)]^{2-}$,[8a,b] and $[Ru_{10}C_2(CO)_{22}(NBD)]^{2-}$,[8a,c] respectively. These anionic clusters also undergo oxidative substitution with a ferrocenium/ligand combination to form further derivatives.[7b,8a] We now report the synthesis of the methylene derivative $Ru_{10}C_2(CO)_{22}(NBD)(CH_2)$ and demonstrate its reversible interconversion with a methylidyne-hydride tautomer (see Scheme 1).

Experimental Section

Materials and Methods. All reactions were carried out under a nitrogen atmosphere by using standard inert atmosphere techniques.[9] Diglyme (Aldrich) and toluene (Fisher Scientific) were dried over molten sodium and distilled immediately before use; other solvents used were reagent grade. The reagents norbornadiene (Aldrich), Diazald (Aldrich), ^{13}C-enriched Diazald (Aldrich), and carbon monoxide (MG Industries) were used as received. $[PPN]_2[Ru_{10}C_2(CO)_{24}]$[6] and $[Cp_2Fe][BF_4]$[10] were prepared according to the literature. Infrared spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer. NMR spectra were recorded on a Varian Unity 400 spectrometer (^1H@400 MHz and ^{13}C@100 MHz). FAB(−) mass spectra and elemental analyses were provided by the staffs of the Mass Spectrometry Center and the Microanalytical Laboratory of the School of Chemical Sciences, respectively.

Preparation of $Ru_{10}C_2(CO)_{22}(NBD)(CH_2)$ (1). A diglyme (20 mL) solution of $[PPN]_2[Ru_{10}C_2(CO)_{24}]$ (116.8 mg, 0.0420 mmol) was prepared in a 100 mL three-necked flask equipped with a reflux condenser. The ligand NBD (3 mL, 28 mmol) was introduced via syringe, and the solution was heated to 140 °C. After ca. 2 h, the IR peak pattern (2039w, 2016m, 1997vs) showed the complete formation of $[PPN]_2[Ru_{10}C_2(CO)_{22}(NBD)]$.[8c] The solvent was removed under vacuum. Dry dichloromethane (20 mL) was introduced, and then diazomethane/ether (ca. 5 molar excess) was added. A quantity of $[Cp_2Fe][BF_4]$ (30.0 mg, 0.1100 mmol) was added as a solid, and vigorous gas evolution was observed. After 5 min, the solvent was removed under vacuum, and the resulting dark residue was separated on a silica gel TLC plate with dichloromethane/hexane (1/1). The purple major band was extracted

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with dichloromethane, and dark crystals (24.5 mg, 0.0139 mmol, 33%) were formed from diffusion of hexane at room temperature. Anal. Calcd for $C_{32}H_{10}O_{22}Ru_{10}\cdot CH_2Cl_2$: C, 21.52; H, 0.66. Found: C, 21.35; H, 0.59. FAB(−) mass spectrum (^{102}Ru): *m/z* 1765 ([$Ru_{10}C_2(CO)_{22}(NBD)(CH_2)]^-$) as well as 1765 − 28*x*, *x* = 1−15. IR (CH_2Cl_2): ν_{CO}, 2088(vw), 2068(m), 2042(s), 2011(w, br), 1992(vw, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.52 (d, 1H$_a$, μ-CH$_a$H$_b$, J(H$_a$H$_b$) = 5.4 Hz), 7.19 (d, 1H$_b$), 4.38 (m, 1H, =CH), 4.17 (m, 1H, −CH), 4.09 (m, 1H, =CH), 4.05 (m, 1H, −CH), 3.79 (m, 1H, =CH), 3.52 (m, 1H, =CH), 1.62 (d, 1H$_c$, CH$_c$H$_d$, J(H$_c$H$_d$) = 10.8 Hz), 1.56 (d, 1H$_d$). ^{13}C NMR of $Ru_{10}C_2(CO)_{22}(NBD)(^{13}CH_2)$ (CD_2Cl_2, 20 °C): δ 85.2 (t, J(CH) = 147 Hz).

Preparation of $Ru_{10}C_2(CO)_{22}(NBD)(CH)(H)$ (2). A toluene (20 mL) solution of **1** (24.5 mg, 0.0139 mmol) in a 100 mL three-necked flask equipped with a reflux condenser was heated at 80 °C for 30 min. The solvent was removed under vacuum, and the resulting dark residue was separated by TLC with dichloromethane/hexane (1/1). A brown band of **2** (3.0 mg, 0.0017 mmol, 12%) and a red-purple band of **1** (18.3 mg, 0.0104 mmol, 75% recovery) were obtained in order of elution. Data for **2**: FAB(−) mass spectrum (^{102}Ru): *m/z* 1765 ([$Ru_{10}C_2(CO)_{22}(NBD)(CH)(H)]^-$) as well as 1765 − 28*x*, *x* = 1−15. IR (CH_2Cl_2): ν_{CO}, 2095(m), 2065(m, sh), 2058(s), 2048(vs), 2013(m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 12.54 (d, 1H, μ_3-CH$_a$, J(H$_a$H$_d$) = 1.5 Hz), 4.25 (m, 1H, −CH), 4.06 (m, 1H, −CH), 3.90 (m, 1H, =CH), 3.82 (m, 1H, =CH), 3.78 (m, 1H, =CH), 3.70 (m, 1H, =CH), 1.70 (d, 1H$_b$, CH$_b$H$_c$, J(H$_b$H$_c$) = 10.0 Hz), 1.66 (d, 1H$_c$), −16.99 (d, 1H$_d$). ^{13}C NMR of $Ru_{10}C_2(CO)_{22}(NBD)(^{13}CH)(H)$ ($CDCl_3$, 20 °C): δ 229.4 (dd, J(CH$_a$) = 166 Hz, J(CH$_d$) = 3 Hz).

Thermolysis of Compound 2. A toluene solution (10 mL) of **2** (5.2 mg, 0.0030 mmol) in a 50 mL flask was heated at 80 °C for 20 min. The solvent was removed under vacuum, and the resulting dark residue was separated by TLC with dichloromethane/hexane (1/1). A brown band of **2** (0.7 mg, 0.0004 mmol, 13% recovery) and a red-purple band of **1** (4.0 mg, 0.0023 mmol, 77%) were obtained in order of elution.

X-ray Crystallographic Study of 1. Crystals of **1** were obtained from the slow diffusion of hexane into dichloromethane solution at room temperature. The data crystal (dimensions 0.14 × 0.30 × 0.46 mm^3) was mounted with oil to a thin glass fiber. Data collection was carried out at 198(2) K on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods (SHELXS-90); positions for the ruthenium atoms were deduced from an E map.[11] One cycle of isotropic least-squares refinement followed by an unweighted difference Fourier synthesis revealed positions for the ruthenium and remaining non-hydrogen atoms. Hydrogen atoms were not included in the final structure factor calculations. All non-hydrogen atoms were refined with anisotropic thermal coefficients. Successful convergence of full-matrix least-squares refinement on F^2 (SHELXTL) was indicated by the maximum shift/error for the final cycle.[12] The final difference Fourier map had no important features. A summary of crystallographic information is presented in Table 1. Metal−metal distances for the cluster core are listed in Table 2.

Table 1. Summary of Crystallographic Data for $Ru_{10}C_2(CO)_{22}(NBD)(CH_2)\cdot CH_2Cl_2$

formula	$C_{33}H_{12}Cl_2O_{22}Ru_{10}$
fw	1842.03
cryst syst	monoclinic
space group	*C*2/*c*
a (Å)	21.108(4)
b (Å)	11.551(2)
c (Å)	36.393(7)
β (deg)	99.58(3)
V (Å^3)	8750(3)
Z	8
λ(Mo Kα) (Å)	0.710 69
ρ_{calc} (g·cm$^{-3)}$	2.797
μ (mm^{-1})	3.553
trans coeffs, max/min	0.618/0.303
absorp correction	integration
no. reflns collected	6147
no. indep reflns	5964
R_{int}	0.0229
R1 [$I > 2\sigma(I)$][a]	0.0319
wR2[b]	0.0770

[a] $R1 = \sum|F_o - F_c|/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]\}^{1/2}$.

Table 2. Ru−Ru Distances (Å) in $Ru_{10}C_2(CO)_{22}(NBD)(CH_2)$

	Apical−Equatorial (CO Bridged)		
Ru1−Ru3	2.839(1)	Ru7−Ru8	2.829(1)
	Apical−Equatorial (Nonbridged)		
Ru1−Ru2	2.934(1)	Ru6−Ru8	2.888(1)
Ru2−Ru4	2.935(1)	Ru3−Ru4	3.061(1)
Ru5−Ru6	2.989(1)	Ru5−Ru7	2.864(1)
	Apical−Hinge		
Ru1−Ru9	3.025(1)	Ru5−Ru9	2.949(1)
Ru4−Ru9	2.857(1)	Ru8−Ru9	2.876(1)
Ru1−Ru10	2.851(1)	Ru5−Ru10	2.794(1)
Ru4−Ru10	2.931(1)	Ru8··Ru10	3.412(1)
	Hinge−Hinge		
Ru9−Ru10	2.862(1)		
	Equatorial−Hinge		
Ru2−Ru9	2.840(1)	Ru3−Ru10	2.943(1)
Ru6−Ru10	2.873(1)	Ru7−Ru9	2.903(1)
	Equatorial−Equatorial		
Ru2−Ru3	3.000(1)	Ru6−Ru7	2.993(1)
	Apical−Apical		
Ru4−Ru5	3.071(1)	Ru1−Ru8	3.106(1)

Results and Discussion

Synthesis and Spectroscopic Characterization of $Ru_{10}C_2(CO)_{22}(NBD)(CH_2)$ (1). Treatment of $[PPN]_2[Ru_{10}C_2(CO)_{22}(NBD)]$[8a,c] in dichloromethane with 2 equiv of $[Cp_2Fe][BF_4]$ and excess diazomethane in ether formed a dark brown solution within 5 min, and a completely new set of peaks were observed in the IR (ν_{CO}) spectrum. Subsequent purification by TLC and crystallization afforded **1** as a purple-brown solid in 33% yield. The negative ion FAB mass spectrum of this compound showed the molecular ion multiplet corresponding to $[Ru_{10}C_2(CO)_{22}(NBD)(CH_2)]^-$ as well as a long sequence of multiplets separated by the mass of one carbonyl ligand. The ^{1}H NMR spectrum of **1** exhibits eight separate signals for the hydrogens of the NBD ligand, consistent with a total lack of symmetry in the molecule. The ^{1}H NMR parameters (δ 7.52, 7.19; J_{HH} = 5.4 Hz) for the inequivalent methylene hydrogens and the ^{13}C NMR parameters (δ 85.2; J_{CH} = 147 Hz) for the methylene carbon in **1** are comparable to those reported for various compounds shown to have a methylene ligand bridging two metal atoms.[2a,3a,4a,13−15]

Solid-State Structure of 1. Structural diagrams of **1** are shown in Figure 1. The overall geometry of the 10 ruthenium atoms is derived from the edge-shared bioctahedral framework displayed by the parent compound,[6] and the methylene ligand symmetrically bridges apical ruthenium atoms Ru4 and Ru5. The NBD ligand chelates in the η^2, η^2 mode to equatorial ruthenium Ru3

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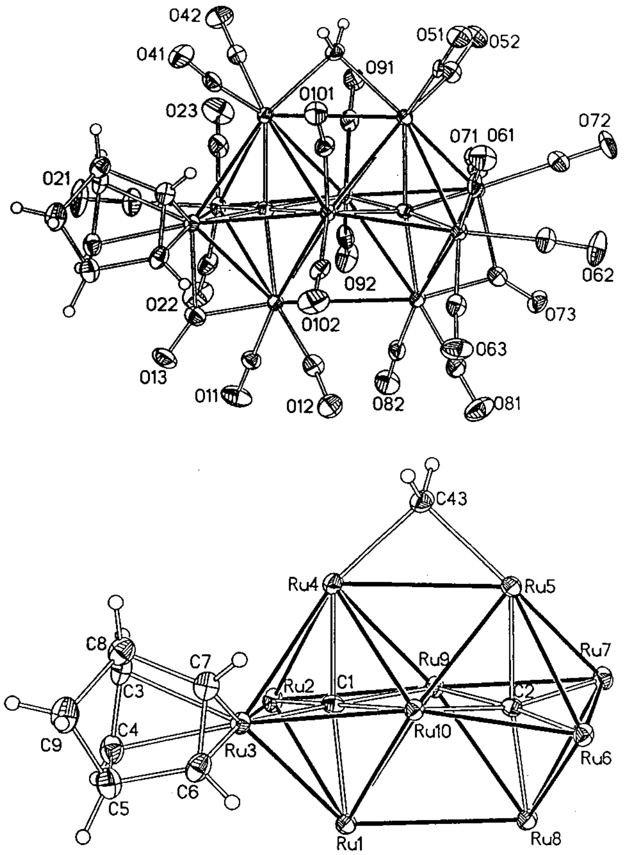

Figure 1. Structural diagrams for $\mathrm{Ru_{10}C_2(CO)_{22}(NBD)(CH_2)}$ (35% thermal ellipsoids). Entire molecule with carbonyl oxygen atoms labeled (top). Cluster framework with ruthenium and carbon atom labeling (bottom).

with distances to C3 and C4 (2.17(1) and 2.17(1) Å) that are marginally shorter than those to C6 and C7 (2.19(1) and 2.20(1) Å). All carbonyl ligands are terminal, except two bridging carbonyls along the Ru1−Ru3 and Ru7−Ru8 edges. If the NBD ligand were replaced by two terminal carbonyls, the molecule would exhibit approximate C_2 symmetry, with the rotation axis passing through the methylene ligand. The methylene-bridged Ru4−Ru5 distance (3.071(1) Å) is significantly longer than those for known triruthenium compounds,[15] and consequently the angle defined by Ru4−C43−Ru5 (93.4(3)°) is among the largest seen for M−C−M systems.[13] However, the Ru−C distances to the methylene ligand (Ru4−C43 = 2.12(1) and Ru5−C43 = 2.10(1) Å) are quite comparable to the triruthenium μ-$\mathrm{CH_2}$ complexes.[15]

In compound **1**, the apical Ru4−Ru5 distance (3.071(1) Å) bridged by the methylene ligand is only slightly shorter than the apical Ru−Ru distances (3.122(2) and 3.138(2) Å) considered nonbonding in $[\mathrm{Ru_{10}C_2(CO)_{24}}]^{2-}$,[6] and the opposite apical Ru1−Ru8 distance (3.106(1) Å) falls in between. This situation contrasts with that displayed in the structure of $\mathrm{Ru_{10}C_2(CO)_{23}(C_2Ph_2)}$,[7b] in which there is one very short apical−apical distance (2.738(2) Å) involving the bridging alkyne ligand and one very long apical−apical distance (3.892(2) Å). However, in both of these neutral clusters containing nominally 25 donor ligands, there is in addition one apical−hinge distance that is markedly lengthened, viz., 3.292(2) Å in the alkyne complex[7b] and Ru8−Ru10 = 3.412(1) Å in **1**. These variations in Ru−Ru distances clearly show the flexibility of the $\mathrm{Ru_{10}C_2}$ framework in adapting to the specific steric and electronic requirements of different hydrocarbon ligands.

Reversible Formation and Spectroscopic Characterization of $\mathbf{Ru_{10}C_2(CO)_{22}(NBD)(CH)(H)}$ (2). When compound **1** was heated in toluene at 80 °C, the growth of a new IR peak at 2095 $\mathrm{cm^{-1}}$ was observed. The IR band pattern stopped changing after 30 min of heating. Subsequent separation by TLC afforded a new minor brown band of **2** followed by the major band of **1**. The negative ion FAB mass spectrum of **2** showed the same pattern of ion multiplets as observed for **1**. The ^{1}H NMR spectrum of **2** exhibited two sharp doublets of 1:1 relative intensity at δ 12.54 and −16.99 ($J_{\mathrm{HH}} = 1.5$ Hz), thus indicating the presence of a methylidyne hydrogen and a hydride, as well as eight signals due to the hydrogens of the NBD ligand. In the ^{13}C NMR spectrum of **2**, a doublet ($J_{\mathrm{CH}} = 166$ Hz) for the methylidyne carbon appeared at δ 229.4 and displayed a small additional coupling ($J_{\mathrm{CH'}} = 3$ Hz) due to the hydride ligand. The latter small coupling constant is too small to be due to an agostic interaction.[16] The ^{1}H and ^{13}C NMR parameters for the methylidyne ligand in **2** are comparable to those reported for the compounds $(\mu\text{-H})_3\mathrm{Ru_3(CO)_9}(\mu_3\text{-CH})$,[2b] $(\mu\text{-H})_3\mathrm{Fe_3(CO)_9}(\mu_3\text{-CH})$,[3b] and $\mathrm{Cp^*Ir(CpCo)_2}(\mu\text{-H})(\mathrm{CO})(\mu_3\text{-CH})$.[3a] Thus, it is highly likely that the methylidyne unit in **2** also adopts a face-capping μ_3-CH bonding mode. The ^{1}H and ^{13}C NMR parameters of **2** did not change upon lowering the temperature to −55 °C, which suggests that **2** exists in only one isomeric form. Therefore, this brown complex **2** is formulated as $\mathrm{Ru_{10}C_2(CO)_{22}(NBD)}(\mu\text{-H})(\mu_3\text{-CH})$.

Heating isolated **2** in toluene at 80 °C for 20 min formed a mixture of **1** and **2** in the same ratio that was observed from the thermolysis of **1**. Prolonged heating starting from either **1** or **2** simply caused decomposition without changing the product ratio.

The facile interconversion between compounds **1** and **2** suggests that the methylidyne and the hydride units in **2** are located near the apical ruthenium centers, which have been shown in several $\mathrm{Ru_{10}C_2}$ derivatives to be the most responsive toward the specific ligand bonding requirements.[7,8] Also, the significant spin−spin couplings between the μ_3-CH and μ-H ligands suggest that they are in close proximity. Because the methylidyne-hydride ligand combination provides two more electrons than the methylene ligand, the framework of **2** has to "reconstruct" from that of **1** in a fashion that can accommodate the two extra electrons. This reconstruction very likely takes the form of significant lengthening of one of the Ru−Ru distances in the methylidyne-hydride compound, possibly the opposite apical Ru−Ru distance as depicted in Scheme 1.

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Supporting Information Available: Tables of positional parameters, bond distances, bond angles, and anisotropic thermal parameters for the structural analysis of $Ru_{10}C_2(CO)_{22}(NBD)(CH_2)\cdot CH_2Cl_2$ (17 pages). See any current masthead page for ordering and Internet access instructions.

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