Preliminary communication

Interconversion between methylene and methylidyne–hydride species on a tetraruthenium system

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Abstract

Hydrogenation of the labile diruthenium di-μ-methylene complex, $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(MeCN)$, produces a tetranuclear μ_3-methylidyne–μ_3-hydride complex, $Cp_4Ru_4(\mu_3\text{-}CH)(\mu_3\text{-}H)(\mu_3\text{-}CO)_2$, through methane-elimination and C–H oxidative addition. Treatment of the tetranuclear μ_3-methylidyne–μ_3-hydride complex with CO reverses the latter process to give a mixture of a mono-μ-methylene complex, $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2$, and a carbonyl complex, $Cp_2Ru_2(\mu\text{-}CO)_2(CO)_2$. © 1997 Elsevier Science S.A.

Interconversion of C1 species (CH_x) via formation and cleavage of a C–H bond is involved as elementary steps of surface-catalyzed transformation of hydrocarbons and carbon monoxide [1]. For example, in the Fischer–Tropsch mechanism of catalytic CO hydrogenation, it is proposed that repeated couplings of surface carbide and hydride species lead to the formation of CH_x intermediates ($x = 1$–3), subsequent C–C coupling of which results in carbon chain propagation. Such processes can be reproduced on discrete polynuclear transition metal species as originally reported by Shapley [2] (for a system related to the present study see Ref. [3]). In a previous paper, we reported reversible $CH_3 \rightleftarrows CH_2$–H interconversion on the diruthenium μ-methylene species, $Cp_2Ru_2(\mu\text{-}CH_2)(H)(SiR_3)$ [4]. Herein we disclose analogous $CH_2 \rightleftarrows CH$–H interconversion on a tetranuclear system.

When a benzene solution of the labile MeCN adduct of the diruthenium di-μ-methylene species, $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(MeCN)$ **1** [5], was stirred under hydrogen atmosphere (1 atm) overnight at room temperature, black solid **2** which was precipitated out from the reaction mixture was isolated as a sole organometallic product in 85% yield (Eq. (1)). [The starting compound **1** was prepared by photolysis of $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)_2$ [6] in

MeCN in a manner analogous to the synthesis of the mono-μ-methylene derivative [7].]

$$ (1) $$

2 (85 %: $Ru = RuCp$)
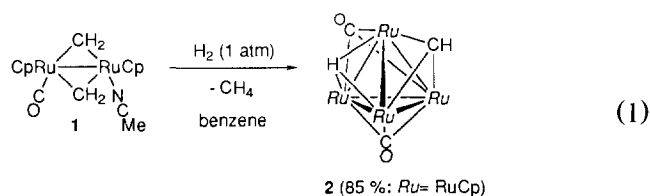
A ^{1}H NMR spectrum of **2** containing a pair of highly shielded and deshielded singlet signals [δ_H −12.63 (1H), 14.97 (1H)] in addition to Cp_4 resonances in a 5:10:5 ratio suggests a tetranuclear methylidyne–hydride structure, but satisfactory ^{13}C NMR data was not obtained because of the poor solubility in organic solvents. Spectral data for **2**: δ_H (in $CDCl_3$) 14.97 (1H, s, μ_3-CH), 5.31 (5H, s, Cp), 5.00 (10H, s, Cp_2), 4.78 (5H, s, Cp), −12.63 (1H, s, μ_3-H); δ_C (in $CDCl_3$) 91.8, 88.2, 85.3 (d × 3, $J = 177$ Hz, Cp_4); ν(CO) (KBr pellet) 1617 cm^{-1}. The structure of **2** has been determined by X-ray crystallography, as shown in Fig. 1. Crystal data for **2**: $C_{23}H_{22}O_2Ru_4 \cdot (CH_2Cl_2)_{0.25} \cdot (H_2O)_{0.25}$, $M = 759.9$, monoclinic, space group $C2/c$, $a = 36.12(1)$, $b = 9.537(2)$, $c = 30.04(1)$ Å, $\beta = 118.56(2)°$, $V = 9089(5)$ Å^3, $Z = 16$, $D_c = 2.22$, $R(R_w) = 0.045(0.041)$ for 6360 unique data with $I > 3\sigma(I)$ and 555 variables. During the course of the refinement it was found that the μ_3-CX ligands were disordered. As for one of the two independent molecules (shown in
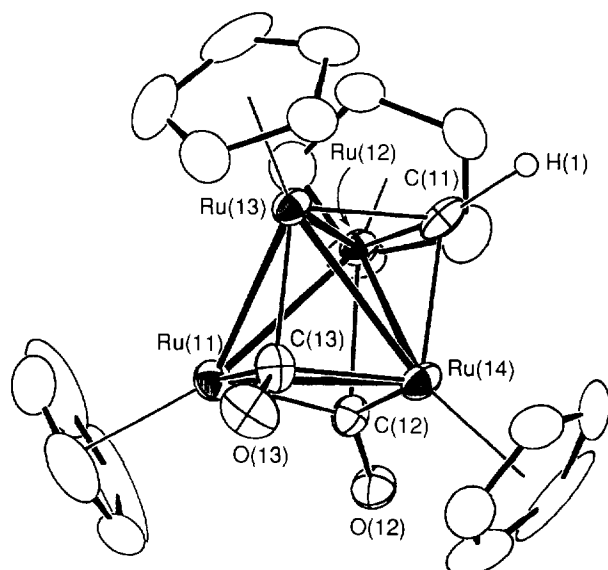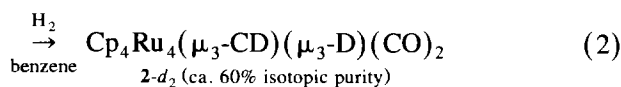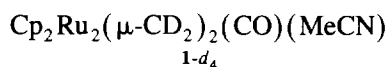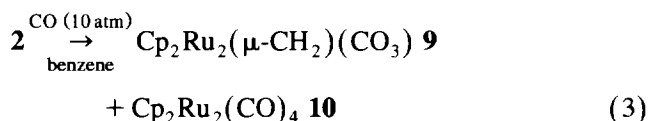
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Fig. 1. Molecular structure of 2 (one of the two independent molecules). Selected bond lengths (Å): Ru(11)–Ru(12) 2.717(2), Ru(11)–Ru(13) 2.716(1), Ru(11)–Ru(14) 2.708(2), Ru(12)–Ru(13) 2.720(1), Ru(12)–Ru(14) 2.702(3), Ru(13)–Ru(14) 2.706(3), Ru(11)–C(12) 2.06(1), Ru(11)–C(13) 2.04(1), Ru(12)–C(11) 2.04(1), Ru(12)–C(12) 2.06(1), Ru(13)–O(13) C(11) 2.04(1), Ru(13)–C(13) 2.05(1), Ru(14)–C(11) 2.03(1), Ru(14)–C(12) 2.15(1), Ru(14)–C(13) 2.09(1), C(12)–O(12) 1.22(1), C(13)–O(13) 1.25(1).

Fig. 1), the negligible minor component was not included in the refinement. In the other molecule, the occupancy of the oxygen atom in the three μ_3-CX positions was refined to be 0.757, 0.724, and 0.519. The four ruthenium atoms are arranged in a tetrahedral array with Ru–Ru distances of ca. 2.7 Å. Three of the four equilateral metal triangles are capped by either of the μ_3-CX ligands (X = H, O) in a symmetrical manner (Ru–C distances: 2.01–2.15 Å), and the remaining Ru11–Ru12–Ru13 face should be capped by the hydride ligand which cannot be located crystallographically. The apparent mirror-symmetrical structure with respect to the plane defined by the C11, Ru11, and Ru14 atoms is consistent with the ^{1}H NMR data, and a CO stretching vibration appears in the lower energy region (1617 cm^{-1}), characteristic of a μ_3-CO ligand. The tetraruthenium μ_3-methylidyne–μ_3-hydride cluster compound 2 is an electron precise species with 60 cluster valence electrons (CVE), and the origin of the μ_3-CH and μ_3-H ligands in 2 has been confirmed to be the bridging methylene ligand in 1 by the labeling experiment using Cp$_2$Ru$_2$(μ-CD$_2$)$_2$(CO)(MeCN) 1-d_4 (Eq. (2)), though considerable H–D exchange is evident.

$$Cp_2Ru_2(\mu\text{-}CD_2)_2(CO)(MeCN)$$
$$1\text{-}d_4$$

$$\xrightarrow[\text{benzene}]{H_2} Cp_4Ru_4(\mu_3\text{-}CD)(\mu_3\text{-}D)(CO)_2 \qquad (2)$$

2-d_2 (ca. 60% isotopic purity)

Comparison of the structure of 2 with that of the starting compound 1 suggests occurrence of elimination of methane as well as dimerization of the dinuclear structure during the formation process of 2. Actually, methane (104% based on 1: Eq. (1)) was detected by GLC analysis of the gas phase of a reaction mixture. On the basis of the results obtained, a plausible formation mechanism of 2 can be delineated as summarized in Scheme 1. Treatment of 1 with H$_2$ produces methane by way of the sequential oxidative addition (3), intramolecular rearrangement (5), reductive elimination (6). A similar process is observed for the related mono-μ-methylene species Cp$_2$Ru$_2$(μ-CH$_2$)(μ-CO)(CO)(MeCN) as reported by us [4], and the lower isotopic purity in the labeling experiment (Eq. (2)) may be attributed to the H–D scrambling via the CH$_2$–H (3) ↔ CH$_3$ (4) interconversion. The triply bonded species 6 may further interact with either of the labile starting complex 1 or the highly coordinatively unsaturated species 7 arising from hydrogenolysis of 6 to form the tetrahedral μ-methylene intermediate 8 with 58 CVE. Finally, the resulting coordinatively unsaturated species 8 is converted into the electron precise 60 CVE species 2 via the C–H oxidative addition. Because the selectivity is excellent, 6 should be captured by 1 or 7 as soon as 6 is formed.

The conversion of the methylene species 8 into the methylidyne–hydride species 2 has been found to be reversible. Treatment of 2 with CO (10 atm) at 80 °C afforded a mixture of the mono-μ-methylene complex 9 and the carbonyl complex 10 (Eq. (3)).

$$2 \xrightarrow[\text{benzene}]{CO\,(10\,atm)} Cp_2Ru_2(\mu\text{-}CH_2)(CO_3)\ 9$$

$$+ Cp_2Ru_2(CO)_4\ 10 \qquad (3)$$

Their formation is interpreted in terms of C–H reductive elimination from 2 regenerating the μ-methylene functional group (8) followed by fragmentation of the tetranuclear structure through CO addition (Scheme 1).
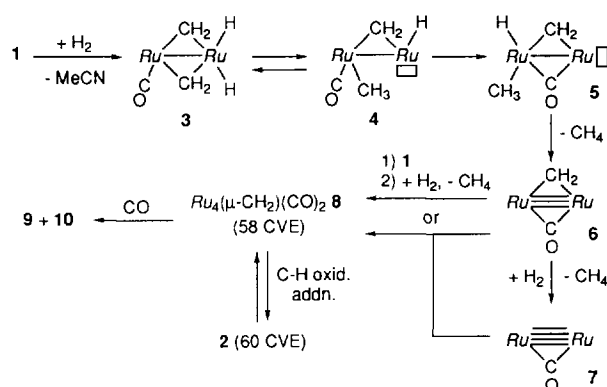
Scheme 1. (Ru: RuCp; □: coordinatively unsaturated site).
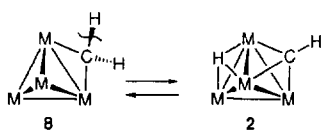
Scheme 2.

In summary, hydrogenolysis of the labile di-μ-methylene species **1** results in the formation of methane together with the coordinatively unsaturated species (**6** or **7**), which couples with another dinuclear species in an efficient manner to give the tetranuclear μ-methylene species **8**. Subsequent intramolecular C–H scission on the cluster system gives rise to the μ₃-methylidyne–μ₃-hydride complex **2**, and the reverse process can be realized by treatment with CO. The present interconversion can be viewed as a model system for the similar $CH_2 \leftrightarrow CH-H$ interconversion on a heterogeneous catalyst surface [1] (Scheme 2).

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