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Formation of a Trinuclear μ_3-Methylidyne Complex, (μ_3-CH)[MoCp(CO)$_2$]$_3$, through Reduction of a CO Ligand in $Cp_2Mo_2(CO)_4$ by a Hydrosilane

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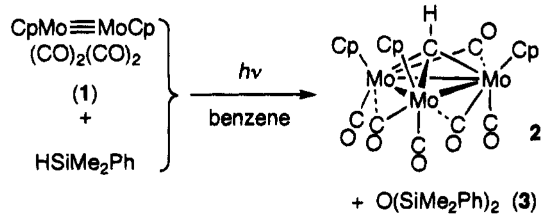
Summary: Irradiation of a benzene solution of $Cp_2Mo_2(CO)_4$ (1) and $HSiMe_2Ph$ results in reduction of CO to give an isomeric mixture of the trimolybdenum μ_3-methylidyne complex (μ_3-CH)[MoCp(CO)$_2$]$_3$ (2) with semibridging CO ligands. Crystallographic and spectroscopic analyses of 2 reveal complicated dynamic behavior by way of gearlike rotation and local rotation of the CpMo(CO)$_2$ unit(s) accompanying switching of the semibridging CO ligands.

Reductive transformation of CO into CH_x species has been recognized as a key step of the Fischer−Tropsch mechanism proposed for catalytic CO hydrogenation.[1] In order to realize efficient reduction of CO ligands in model transition-metal carbonyl complexes, we have employed hydrosilanes ($HSiR_3$) as equivalents for dihydrogen.[2] It has been established that the H−Si bond exhibits reactivities similar to those of the H−H bond (e.g. oxidative addition to low-valent metal centers and catalyzed addition reactions to unsaturated organic substrates),[3,4] and furthermore, it is expected that highly electrophilic silyl−metal species (M−SiR_3) resulting from the oxidative addition, like the acidic site on a catalyst surface, can activate such O-containing functional groups[5] as CO so as to promote subsequent hydride transfer and deoxygenation leading to CH_x species. As we described previously, thermal reaction of the diruthenium carbonyl complex $Cp_2Ru_2(CO)_4$ with hydrosilanes produced μ-methylene complexes $Cp_2Ru_2(\mu\text{-}CH_2)_n(CO)_{4-n}$ ($n = 1, 2$; $x = 2$) successfully.[2c] Herein we wish to report formation of a trinuclear μ_3-methylidyne complex, another member of the CH_x family ($x = 1$), by reduction of the dimolybdenum carbonyl complex $Cp_2Mo_2(CO)_4$ (**1**). While a number of trinuclear μ_3-alkylidyne complexes[6] have been prepared and studied as models for surface-bound species so far, examples of the parent methylidyne complexes (μ_3-CH)M_3L_n[7] are rather limited. Typical preparative methods involve (i) incorporation of a C1 organic reagent (e.g. $CHCl_3$) into a cluster system,[7a,b] (ii) a combination of electrophilic or nucleophilic activation of CO and addition of hydride or proton,[7c−g] (iii) transformation of μ-methylene complexes,[7h,i] (iv) reduction of μ_3-C−X complexes,[7j] and (v) metal exchange of preformed μ_3-CH complexes.[7k] To our knowledge, the present system is the first example of a direct one-step transformation of a coordinated CO into a μ_3-CH ligand.

When a mixture of the dimolybdenum tetracarbonyl complex **1** and excess $HSiMe_2Ph$ dissolved in benzene was irradiated by a high-pressure mercury lamp, the deep purple complex **2** was isolated in 26% yield (based on CO)[8] together with siloxane $O(SiMe_2Ph)_2$ (**3**) after chromatographic separation (eq 1).[9] Although complex **2** showed complicated dynamic behavior as described below, it was readily assigned to the trinuclear μ_3-



(1)

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(8) Yields of **2** and **3** determined by ^{1}H NMR were 38% (based on CO) and 115% (based on **1**), respectively.

(9) A benzene solution (300 mL) of **1** (3.3 g, 7.7 mmol) and $HSiMe_2Ph$ (4.0 mL, 26 mmol) was irradiated by a high-pressure mercury lamp for 43 h. The reaction was monitored by TLC (silica gel). After evaporation of the volatiles the residue was subjected to column chromatography (silica gel eluted with CH_2Cl_2−hexanes). The complex **2** was isolated as deep purple crystals (770 mg, 1.16 mmol, 26% yield based on total CO) after recrystalization from CH_2Cl_2−hexanes. Anal. Calcd for $C_{22}H_{16}O_6Mo_3$: C, 39.78; H, 2.43. Found: C, 39.76; H, 2.33. ^{1}H NMR (CD_2Cl_2) (at 27 °C): **2A** δ 13.37 (1H, s, μ_3-CH), 5.23 (15H, s, Cp_3); **2B**, δ 11.85 (1H, s, μ_3-CH), 5.16 (15H, s, Cp_3). ^{1}H NMR (CD_2Cl_2) (at −80 °C): **2A**, δ 13.37 (1H, s, μ_3-CH), 5.30 (15H, s, Cp_3); **2B**, δ 11.73 (1H, s, μ_3-CH), 5.24 (10H, s, Cp_2), 5.12 (5H, s, Cp). ^{13}C NMR (CD_2Cl_2) (at 27 °C): **2A**, δ 262.3 (d, $J = 156$ Hz, μ_3-CH), 231.2, 227.4 (s, CO), 92.5 (d, $J = 177$ Hz, Cp); **2B**, δ 245.6 (d, $J = 162$ Hz, μ_3-CH) (the other signals overlap with those of **2A**). ^{13}C NMR (CD_2Cl_2) (at −80 °C) **2B**, 260.5 (μ_3-CH), 231.2, 228.2 (CO), 92.5 (Cp); **2B**, δ 242.5 (μ_3-CH), 234.6 (br, CO). IR (CH_2Cl_2): 1989, 1939, 1927, 1871, 1852, 1810 cm^{-1}. FDMS: 670 (M^+ for the ^{98}Mo isotopomer). The reaction also proceeded under thermal conditions (120 °C) with poor reproducibility.

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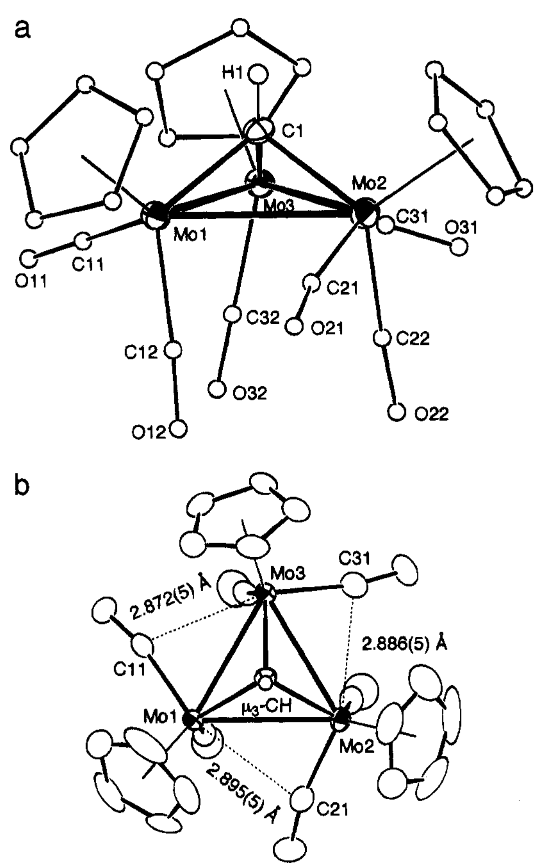
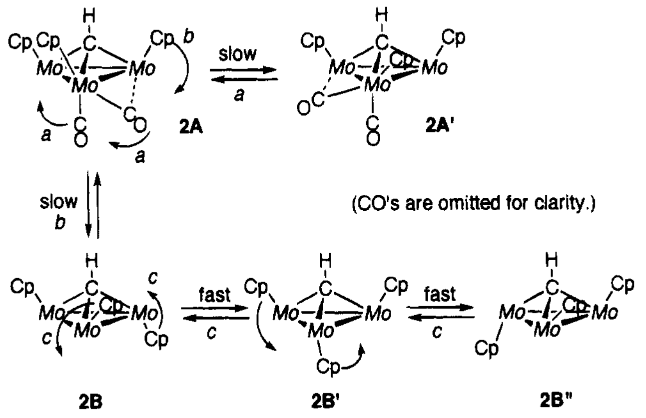


Figure 1. Molecular structure of **2**: (a) side view; (b) top view. Selected bond lengths (Å): Mo1–Mo2 = 3.0624(9), Mo1–Mo3 = 3.046(1), Mo2–Mo3 = 3.053(1), C1–Mo1 = 2.063(5), C1–Mo2 = 2.081(4), C1–Mo3 = 2.079(4), Mo1–C11 = 1.978(5), Mo1–C12 = 1.973(5), Mo2–C21 = 1.970(5), Mo2–C22 = 1.966(5), Mo3–C31 = 1.960(5), Mo3–C32 = 1.971(5), C11–O11 = 1.157(5), C12–O12 = 1.140(5), C21–O21 = 1.167(5), C22–O22 = 1.150(5), C31–O31 = 1.158(5), C32–O32 = 1.150(5).

methylidyne complex (μ_3-CH)[MoCp(CO)$_2$]$_3$ on the basis of the ^{1}H NMR data[9] ((1) the highly deshielded singlet signals characteristic of a μ_3-CH ligand (**2A**, δ 13.37; **2B**, δ 11.85);[7] (2) the intensity ratio of the C*H* and C$_5$*H*$_5$ signals (1 : 15)). The methylidyne carbon signals are also located at low field (**2A**, δ 262.3 (d, J = 156 Hz); **2B**, δ 245.6 (d, J = 162 Hz)), as reported for (μ_3-CH)M$_3$ cluster compounds.[7] The molecular structure of **2** determined by X-ray crystallography (Figure 1a)[10] contains a typical tetrahedral CMo$_3$ core of virtual C_3 symmetry[6b,c] and as is anticipated from the ^{13}C NMR and IR data,[9] one of the two CO ligands attached to each Mo center weakly interacts with the adjacent Mo atom (Mo1–C11–O11 = 168.5(4)°, Mo2–C21–O21 = 168.9(4)°, Mo3–C31–O31 = 169.6(5)°, C11···Mo3 = 2.872(5) Å, C21···Mo1 = 2.895(5) Å, C31···Mo2 = 2.886(5) Å; for the linear CO ligands, Mo1–C12-O12 = 176.4(4)°, Mo2–C22–O22 = 175.5(5)°, Mo3–C32–O32 = 174.8(5)°, C12···Mo2 = 3.441(5) Å, C22···Mo3 = 3.433(5) Å, C32···Mo1 = 3.447(5) Å (Figure 1b)) in a manner similar to that for the semibridging CO ligands in the sterically congested polynuclear molybdenum carbonyl complexes.[11]

Scheme 1



(CO's are omitted for clarity.)

The NMR analyses[9] reveal that the μ_3-methylidyne complex **2** exists as an equilibrated mixture of the two isomers **2A** and **2B**, the ratio of which depends on the solvent and temperature. The proportion of **2B** appears to be correlated with the dielectric constant of the solvents. Typically, the ^{1}H NMR spectrum recorded in CD$_2$Cl$_2$ contains two sets of the μ_3-CH and Cp signals in a ca. 1:1 ratio, whereas in less polar solvents the set of the more shielded signals (**2B**) is observed as the major component (**2A**:**2B** = 1:3 (CDCl$_3$), 1:6 (toluene-d_8)). When the CD$_2$Cl$_2$ solution is cooled to −80 °C, the isomer ratio changes to 1.5:1 and, at the same time, the Cp signal of **2B** separates into two signals of the 2:1 intensity ratio. On the basis of the simple NMR features indicating a symmetrical structure and the ^{13}C CP MAS NMR data of single crystals, the isomer **2A** is assigned to the structure that was characterized by X-ray crystallography. The C_3-symmetrical structure of **2A** is retained in solution in the temperature range of −80 to +27 °C, and the terminal and semibridging CO ligands are observed separately even at room temperature.[12] On the other hand, the decoalescence of the Cp and CO signals of **2B** at lower temperatures leads to the assignment to a stereoisomer where one of the CpMo(CO)$_2$ parts is inverted (Scheme 1). Such unsymmetrical orientation of the metal components is found in (μ_3-CF)[MoCp(CO)$_2$]$_3$,[13] the only structurally characterized analogue of **2**. The similar local geometries around the CH moieties in **2A** and **2B** are anticipated from the similar J_{C-H} values for the μ_3-CH parts.[9] As judged from the coalescence temperatures, the switching of the terminal and semibridging CO ligands in **2A** (path a in Scheme 2) and the intercon-

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[10] Crystal data: **2**·CH$_3$CN, C$_{22}$H$_{16}$O$_6$Mo$_3$·CH$_3$CN, M_r = 705.24, orthorhombic, space group *Pbca*, a = 18.205(6) Å, b = 16.684(4) Å, c = 15.818(5) Å, V = 4804(4) Å^3, Z = 8, d_{calc} = 1.95 g cm^{-3}, μ = 15.8 cm^{-1}, R (R_w) = 0.027 (0.021) for 3235 data with $I > 3\sigma(I)$. The structure was solved by the teXsan structure solving system. All of the non-hydrogen atoms were refined anisotropically. The position of H1 was confirmed by using the isotropic thermal parameter, and the remaining Cp and solvent H atoms were fixed at the calculated positions and not refined. The complex **2**·(toluene), characterized by X-ray crystallography, also adopted the same conformation.

[11] See, for example, the dimolybdenum μ-η^2:η^2-alkyne complexes. Baily, W. I., Jr., Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.

[12] The μ_3-CC$_6$H$_4$-*p*-Me derivative of **2** contained only one CO signal (^{13}C NMR), although some dynamic behavior was observed for a mixed-metal complex (M$_3$ = Mo$_2$W): Green, M.; Porter, S. J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 513. Local rotation was proposed for a mixed-metal alkylidyne complex (M$_3$ = MoCo$_2$): Sutin, K. A.; Kolis, J. W.; Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Quilliam, M. A.; Faggiani, R.; Lock, C. J. L.; McGlinchey, M. J.; Jaouen, G. *Organometallics* **1987**, *6*, 439.

[13] Schulze, W.; Hartl, H.; Seppelt, K. *J. Organomet. Chem.* **1987**, *319*, 77. Dynamic behavior in solution was not mentioned at all for the μ_3-CF complex.

version between **2A** and **2B** (path b)[14] are estimated to be slower than the NMR time scale at ambient temperature. More importantly the isomerization of **2B** to **2B′** and **2B″** proceeds via very fast gearlike rotation of the three $CpMo(CO)_2$ moieties (path c), and the local rotational process (path b)[12] proves to be a rather high energy process compared to path c, presumably owing to a steric problem. The rates have been estimated to be in the order c > b > a.

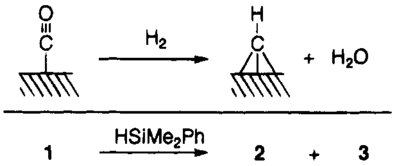
The H and C atoms in the μ_3-CH ligand in **2** originate from *C*O and *H*SiMe$_2$Ph, respectively, as verified by the labeling experiments affording the deuteriomethylidyne complex **2**-*d* (eq 2) and the μ_3-^{13}CH(D) isotopomers (eq 3). Except for the labeling experiments, little information on the reaction mechanism has been obtained. No substantial amount of Cp-containing intermediate or byproduct can be detected by ^{1}H NMR monitoring of a reaction mixture, although formation of insoluble materials is evident. Taking into account the related studies on photochemical hydrogenation of $(\eta^5\text{-}C_5Me_5)_2Mo_2(CO)_4$ (the C_5Me_5 analogue of **1**) giving $(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}H)_2(CO)_4$[15] and formation of tricobalt siloxymethylidyne complexes $(\mu_3\text{-}COSiR_3)Co_3(CO)_9$ from interaction of $Co_2(CO)_8$ with hydrosilane,[16] the formation mechanism of **2** may involve a combination of (i) generation of an Si—Mo species and its electrophilic attack at Mo—CO, (ii) H transfer from $HSiMe_2Ph$, (iii) deoxygenation as the siloxane (**3**), and (iv) addition of a Mo fragment to give a trinuclear skeleton.

$$\mathbf{1} + DSiMe_2Ph \xrightarrow{h\nu} \underset{\mathbf{2}\text{-}d}{(\mu_3\text{-}CD)[MoCp(CO)_2]_3} \quad (2)$$

$$\underset{(30\%\ ^{13}CO)}{\mathbf{1}} + H(D)SiMe_2Ph \xrightarrow{h\nu} \underset{\substack{\mathbf{2}\text{-}^{13}CH(D) \\ (30\%\ ^{13}C\ \text{enriched})}}{[\mu_3\text{-}^{13}CH(D)][MoCp(CO)_2]_3} \quad (3)$$

In conclusion, the present reaction can be viewed as a good model system for formation of a CH species via the Fischer–Tropsch mechanism (Scheme 2); that is, a CO ligand in **1** is converted to the methylidyne functional group through reduction with the hydrogen equivalent ($HSiMe_2Ph$) accompanying elimination of the siloxane (**3**: silylated water).

Scheme 2



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Supplementary Material Available: Text giving the experimental procedures for X-ray crystallography, tables of crystallographic data, positional parameters and B_{eq} values, anisotropic thermal parameters, and bond distances and angles, and a figure giving the numbering scheme for **2**·CH$_3$CN (8 pages). Ordering information is given on any current masthead page.

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[14] The interconversion was confirmed by means of the ^{1}H NMR saturation transfer experiment.

[15] Alt, H.; Mahmoud, K. A.; Rest, A. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 544.

[16] Kim, M. W.; Uh, D. S.; Kim, S.; Do, Y. *Inorg. Chem.* **1993**, *32*, 5883 and references cited therein.