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Reactivity of the α-Agostic Methyl Bridge in the Unsaturated Complex [$Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^1:\eta^2\text{-}CH_3)(\mu\text{-}PCy_2)(CO)_2$]: Migratory Behavior and Methylidyne Derivatives

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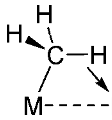
Summary: The bridging methyl ligand present in the title compound can migrate up to the cyclopentadienyl (Cp) site upon reaction with CO to achieve an overall exchange between the methyl and hydrogen (Cp) positions. In the presence of different metal−carbonyl complexes, easy dehydrogenation of the methyl group takes place under photochemical conditions to give methylidyne-bridged heterometallic clusters.

Methyl- and other alkyl-bridged complexes are species of interest for several reasons, including the fact that they serve as models both for intermediates in alkyl-transfer processes and for adsorbates in several heterogeneously catalyzed reactions such as the Fischer−Tropsch synthesis and also because they are implied as catalysts or precursors of the homogeneous catalysts used in the polymerization of olefins.[1,2] Although a large number of such binuclear complexes have been reported so far, only some of them display metal−metal bonds, these generally exhibiting an asymmetric coordination of the methyl (or alkyl) bridge in which a C−H bond is involved in an α-agostic interaction with one of the metal atoms, the ligand then behaving formally as a three-electron donor (Chart 1). The reactivity reported so far for the methyl bridges in the latter complexes includes the oxidative addition of the agostic C−H bond at trimetal centers,[3] rearrangement of the ligand to a terminal coordination mode,[4] deprotonation,[5] reductive elimination with other ligands,[6] and insertion of CO.[4b,c,7] Among all the alkyl-bridged complexes described so far, however, only a few of them display multiple intermetallic bonding,[8] and their reactivity has not been explored. In this context, our recent preparation of the unsaturated methyl complex [$Mo_2Cp_2(\mu\text{-}\eta^1:\eta^2\text{-}CH_3)(\mu\text{-}PCy_2)(CO)_2$] (**1**;[9] Cp = η^5-C_5H_5) gave us the opportunity to study the chemical behavior of an α-agostic methyl ligand bridging a multiple metal−metal bond. In this paper we report our preliminary results on the reactivity of compound **1**, which reveal several unusual features such as the facile migration of the methyl ligand up to the coordinated cyclopentadienyl groups and its easy dehydrogenation in the presence of metal−carbonyl fragments, then providing a rational synthetic route to novel heterometallic clusters having methylidyne bridges (Scheme 1).

Chart 1



According to recent DFT calculations,[9a] the agostic interaction in **1** is rather weak; therefore, the view of the methyl ligand as a 3-electron donor to yield a 32-electron species is somewhat exaggerated yet is a useful formalism to interpret its reactivity. In any case, the presence of this weak agostic interaction along with the multiple intermetallic bond makes this compound quite reactive toward simple donors such as carbon monoxide, isocyanides, and diphosphines at room temperature, to give a variety of products, many of which involve the migration of the methyl ligand. The most remarkable migratory behavior is that observed in the reaction with CO, this giving as major products the acetyl-bridged complex [$Mo_2Cp_2\{\mu\text{-}\eta^1:\kappa^1\text{-}C(Me)O\}(\mu\text{-}PCy_2)(CO)_3$] (**2**) and the hydrides [$Mo_2Cp(\eta^5\text{-}C_5H_4Me)(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4$] (**3**) and [$Mo_2Cp\{\eta^5\text{-}C_5H_4C(O)Me\}(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4$] (**4**), the last two complexes having methyl- and acetyl-substituted cyclopentadienyl ligands, respectively. The relative amounts of these products are dependent on the experimental conditions, and separate experiments indicate that toluene solutions of the acetyl complex **2** decompose progressively at room temperature to give mainly the methylcyclopentadienyl hydride complex **3**, along with small amounts of **4** and other products.

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[2] For some recent work on alkyl-bridged complexes see, for example: (a) Bolton, P. D.; Clot, E.; Cowley, A. R.; Mountford, P. *J. Am. Chem. Soc.* **2006**, *128*, 15005. (b) Dietrich, H. M.; Grove, H.; Törnroos, K. W.; Anwander, R. *J. Am. Chem. Soc.* **2006**, *128*, 1458. (c) Weng, Z.; Teo, S.; Koh, L. L.; Hor, T. S. A. *Chem. Commun.* **2006**, 1319.

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[6] (a) Carlucci, L.; Proserpio, D. M.; D'Alfonso, G. *Organometallics* **1999**, *18*, 2091. (b) Noh, S. K.; Sendlinger, S. C.; Janiak, C.; Theopold, K. H. *J. Am. Chem. Soc.* **1989**, *111*, 9127.

[7] Gao, Y.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2001**, *20*, 1882.

[8] Apparently only a few complexes (all dichromium ones) have been reported to have alkyl bridges across multiple metal−metal bonds: (a) Heintz, R. A.; Ostrander, R. L.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1994**, *116*, 11387. (b) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646. (c) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446.

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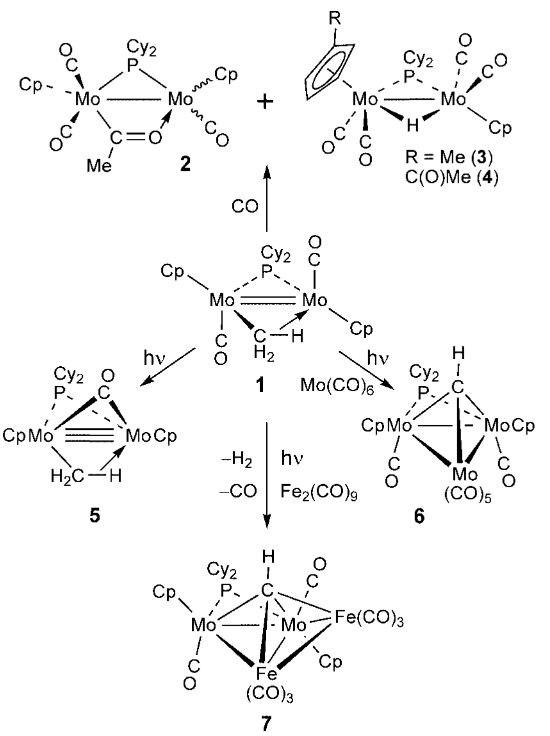
Scheme 1



The acetyl complex **2** is structurally related to its methoxycarbyne isomer $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(CO)_3]$ recently prepared by us[10] but has a more complex structure in solution, this involving cis/trans isomerism.[11,12] The presence of the acyl ligand is denoted by the appearance of a C−O stretching band at 1583 cm^{-1} in the IR spectrum. On the other hand, the spectroscopic data for the hydride complexes **3**[13] and **4**[14] clearly establish that they have the same structure as the bis(cyclopentadienyl) complex $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$,[15] except for the presence of a methyl and acetyl substituent, respectively, in one of the Cp rings. The formation of compounds **3** and **4** requires a complex sequence of steps resulting in the exchange of positions between a metal-bound methyl or acetyl ligand and the H atom of a cyclopentadienyl ligand and is itself unprecedented. To our knowledge, the closest migratory transformations reported previously are the thermal decompositions above 373 K of the complexes $[MCpR(CO)_3]$ (M = Mo, W, R = Et, Ph, CH_2Ph) to give hexacarbonyl dimers of the type $[M_2Cp_2(CO)_6]$ having one or two $\eta^5\text{-}C_5H_4R$ ligands.[16] Further studies to better understand these singular reactions, including those of the benzyl analogue of **1**,[9a] are now in progress.

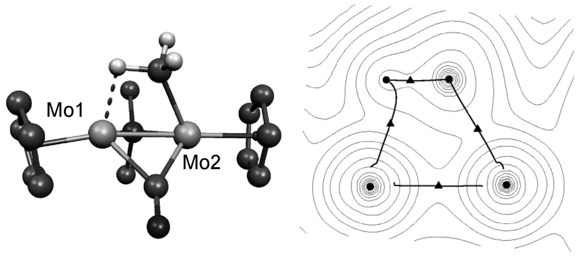


Figure 1. DFT optimized structure of compound **5**, with H atoms (except those of the methyl group) and Cy rings (except the C^1 atoms) removed for clarity, and the corresponding electron density map in the Mo_2C(methyl) plane, with nuclear positions (●), bond critical points (▲), and bond critical paths (−) indicated. Selected bond lengths (Å): Mo1−Mo2 = 2.485; Mo1−*C*O = 2.181; Mo2−*C*O = 2.032; Mo1−*C*H$_3$= 2.434; Mo2−*C*H$_3$ = 2.195; Mo1−*H*CH$_2$ = 1.982; Mo1−*P* = 2.408; Mo2−*P* = 2.431.

Even when the removal of a ligand from a complex having an α-agostic methyl bridge might force the oxidative addition of the agostic C−H bond to yield a less unsaturated methylene hydride derivative, this turned out to be a difficult process in the case of **1**. Indeed, a carbonyl ligand can be cleanly removed from **1** upon irradiation with visible−UV light in toluene solution, but this gives the extremely air-sensitive monocarbonyl derivative $[Mo_2Cp_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CH_3)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (**5**), still retaining the α-agostic interaction. The averaged ^1H NMR methyl resonance for this fluxional complex (δ_H −1.60 ppm, J_{CH} = 116 Hz)[17] is comparable to that observed for **1** (δ_H −0.77 ppm, J_{CH} = 124 Hz),[9] but its C−H coupling is significantly lower, thus suggesting a stronger C−H−Mo agostic interaction. To better define the hapticity of this metal−methyl interaction, we carried out a DFT calculation on **5**, and this yielded a minimized structure with a quite asymmetric α-agostic bridging methyl group (Mo1−H = 1.982 Å, Mo1−C = 2.434 Å, Mo2−C = 2.195 Å; see Figure 1 and the Supporting Information).[18] This suggests that the agostic interaction in **5** is much stronger than that in **1**,[9a] thus effectively yielding a 30-electron complex with a triple intermetallic bond (Mo−Mo = 2.485 Å). In agreement with this, an AIM analysis of the topology of the electron density in **5** revealed the presence of a bond path (and the corresponding bond critical point) connecting the Mo1 and H (but not C) atoms (Figure 1 and the Supporting Information), as previously observed for strong β-agostic interactions in mononuclear complexes[19] but not for the weak interaction in **1**.[9a] We note that this is the first time that such a topology has been reported for a bridging α-agostic alkyl ligand.

Having established the photochemical stability of the methyl bridge in **1**, we turned to study its photochemical reactions with metal−carbonyl complexes of the type $[M(CO)_x]$ or $[MCp(CO)_y]$ (M = Cr, Mo, W, Mn, Fe, Ru; *x*, *y* = 3−6) to examine the synthetic potential of **1** in the preparation of heterometallic clusters. To our surprise, compound **1** underwent dehydroge-

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(10) García, M. E.; García-Vivó, D.; Ruiz, M. A.; Aullón, G.; Alvarez, S. *Organometallics* **2007**, *26*, 5912.

(11) Selected data for **2**: ν(CO) (CH_2Cl_2) 1919 (s), 1849 (vs), 1816 (m), 1583 (w, C=O) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.52 MHz, 290 K, $CDCl_3$) δ 264.5 (s, br, isomer cis), 217.6 (s, isomer trans).

(12) Cis/trans isomerism in alkenyl-bridged dimolybdenum complexes isoelectronic with compound **2** has been recently discussed by us; see: Alvarez, M. A.; García, M. E.; Ramos, A.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **2007**, *26*, 5454.

(13) Selected data for **3**: ν(CO) (CH_2Cl_2) 1953 (m, sh), 1924 (vs), 1852 (s), 1819 (w, sh) cm^{-1}; ^1H NMR (300.13 MHz, 290 K, $CDCl_3$) δ 5.37, 5.17, 5.04, 4.93 (4 × m, 4 × 1H, C_5H_4), 5.32 (s, 5H, Cp), 2.27 (s, 3H, Me), −13.18 (d, 1H, J_{PH} = 35 Hz, μ-H).

(14) Selected data for **4**: ν(CO) (CH_2Cl_2) 1950 (m, sh), 1933 (vs), 1864 (s), 1678 (w, C=O) cm^{-1}; ^1H NMR (300.13 MHz, 290 K, $CDCl_3$) δ 6.03, 5.81, 5.37, 5.08 (4 × m, 4 × 1H, C_5H_4), 5.32 (s, 5H, Cp), 2.50 (s, 3H, Me), −13.31 (d, 1H, J_{PH} = 35 Hz, μ-H); $^{13}C\{^1H\}$ NMR (100.63 MHz, 213 K) δ 243.0, 242.3 (2 × d, J_{CP} = 27 Hz, MoCO), 236.0, 233.8 (2 × s, MoCO), 195.8 (s, C(O)Me).

(15) García; M. E.; Riera, V.; Ruiz, M. A.; Rueda, M. T.; Sáez, D. *Organometallics* **2002**, *21*, 5515.

(16) Pittman, C. U., Jr.; Felis, R. F. *J. Organomet. Chem.* **1974**, *72*, 399.

(17) Selected data for **5**: ν(CO) (toluene) 1697 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.52 MHz, 290 K, toluene-d_8) δ 231.9 (s); ^1H NMR (300.13 MHz, 290 K, toluene-d_8) δ 5.54 (s, 10H, Cp), −1.60 (s, 3H, J_{HC} = 116 Hz, $\mu\text{-}\eta^1\text{:}\eta^2\text{-}CH_3$).

(18) Density functional calculations were performed with the GAUSSIAN03 program package using the hybrid method B3LYP, together with a standard 6-311G* basis set on all atoms except Mo, for which a valence double-ζ-quality basis set and LANL2DZ effective core potentials were used. See the Supporting Information for further details.

(19) Popelier, P. L. A.; Logothetis, G. *J. Organomet. Chem.* **1998**, *555*, 101.

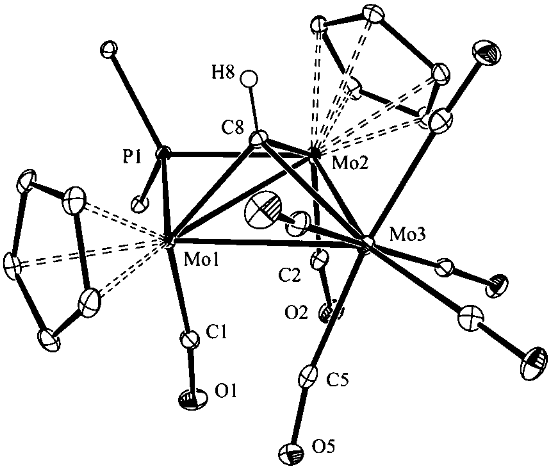

Figure 2. ORTEP drawing (30% probability) of compound **6**, with H atoms (except that on C8) and cyclohexyl rings (except the C^1 atoms) omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1−Mo2 = 2.9283(3), Mo1−Mo3 = 3.1245(3), Mo2−Mo3 = 3.0938(3), Mo1−C8 = 2.040(3), Mo2−C8 = 2.053(3), Mo3−C8 = 2.316(3), Mo1−P1 = 2.410(1), Mo2−P1 = 2.425(1); C1−Mo1−Mo2 = 86.8(1), C2−Mo2−Mo1 = 87.0(1).

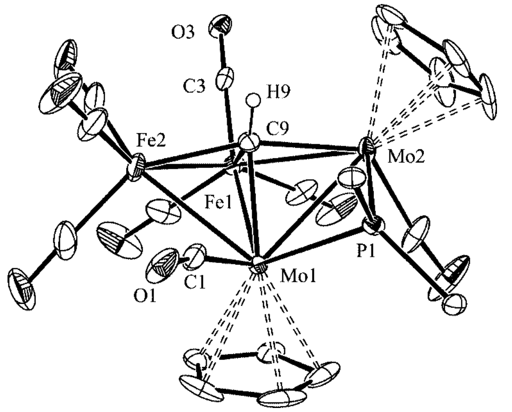

Figure 3. ORTEP drawing (30% probability) of compound **7**, with H atoms (except that on C9) and cyclohexyl rings (except the C^1 atoms) omitted for clarity. Selected bond lengths (Å): Mo1−Mo2 = 2.835(1), Mo1−Fe1 = 2.725(1), Mo1−Fe2 = 2.707(1), Mo2−Fe1 = 2.770(1), Fe1−Fe2 = 2.537(1), Mo1−C9 = 2.144(6), Mo2−C9 = 2.113(6), Fe1−C9 = 1.906(6), Fe2−C9 = 2.001(6), Mo1−P(1) = 2.476(2), Mo2−P1 = 2.392(1).

nation in many of these reactions to give methylidyne-bridged clusters. For instance, the reaction of **1** and $[Mo(CO)_6]$ under visible−UV irradiation gives the trimetallic cluster $[Mo_3Cp_2(\mu_3\text{-}CH)(\mu\text{-}PCy_2)(CO)_7]$ (**6**) in high yield.[20] The structure of **6** results from the addition of a $Mo(CO)_5$ fragment to the unsaturated Mo_2 center of **1**, this being accompanied by dehydrogenation of the methyl ligand and trans to cis isomerization of the original $Mo_2(CO)_2$ moiety (Figure 2).[21] The methylidyne ligand in this electron-precise (48-electron) cluster (δ_C 244.7 ppm, J_{CH} = 162 Hz) exhibits a quite asymmetric coordination, it being strongly bound to the MoCp centers (Mo−C = ca. 2.06 Å) and more weakly to the $Mo(CO)_5$ fragment (Mo−C = ca. 2.32 Å). We note here that only one other methylidyne-bridged Mo_3 cluster appears to have been described previously.[22] The most remarkable reaction, however, occurs upon irradiation of toluene solutions of **1** and $[Fe_2(CO)_9]$, since this allows the incorporation of two $Fe(CO)_3$ moieties to the unsaturated Mo_2 center and dehydrogenation of the methyl ligand to give the methylidyne cluster $[Fe_2Mo_2Cp_2(\mu_4\text{-}CH)(\mu\text{-}PCy_2)(CO)_8]$ (**7**) in high yield.[23] Unexpectedly, this 60-electron cluster does not display a tetrahedral structure but a "butterfly" one with the CH ligand (δ_C 243.8 ppm, J_{CH} = 143 Hz) bridging the four metal atoms (Figure 3),[24] and therefore the molecule must be considered as unsaturated. In agreement with this, the intermetallic lengths are 0.1−0.2 Å shorter than the corresponding single-bond lengths of reference, this indicating a delocalization of such an unsaturation. It is interesting to note that only a few similar "butterfly" methylidyne clusters, $[Fe_4(\mu\text{-}CH)(\mu\text{-}H)(CO)_{12}]$ and $[MFe_3(\mu\text{-}CH)(CO)_x]^n$ (M = Cr, W, Mn, Rh; x = 12, 13; n = 0, 1−),[25] have been reported previously. These, however, display CH ligands involved in agostic C−H−M interactions, therefore yielding electron-precise (62-electron) "butterfly" structures. Methylidyne clusters are relatively scarce molecules related to the surface species following methane activation by metal atoms and surfaces, and to those involved in relevant heterogeneously catalyzed industrial processes such as the Fischer−Tropsch synthesis,[26] and further work on the synthesis and chemical behavior of these heterometallic methylidyne derivatives of **1** is currently in progress.

In summary, we have shown that the unsaturated α-agostic methyl complex **1** displays reactivity patterns not observed in related electron-precise binuclear complexes, such as an unprecedented migratory behavior under mild conditions, yielding an overall exchange between methyl and H(cyclopentadienyl) positions, and easy dehydrogenation in the presence of metal−carbonyl fragments, thus providing a new and rational route to novel heterometallic clusters having methylidyne bridges.

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Supporting Information Available: Text, tables, and figures giving experimental procedures and spectroscopic data for new compounds and details of DFT calculations on compound **5** and CIF files giving crystallographic data for compounds **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Selected data for **6**: ν(CO) (CH_2Cl_2) 2042 (s), 1949 (s, sh), 1935 (vs), 1825 (w) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.52 MHz, 290 K, CD_2Cl_2) δ 172.8 (s); ^1H NMR (300.13 MHz, 290 K, CD_2Cl_2) δ 12.26 (d, J_{PH} = 5, J_{CH} = 162 Hz, 1H, μ-CH), 5.25 (d, J_{PH} = 1 Hz, 10H, Cp); $^{13}C\{^1H\}$ NMR (75.48 MHz, 290 K, CD_2Cl_2) δ 244.7 (d, J_{CP} = 21 Hz, μ-CH).

(21) X-ray data for **6**: brown crystals, monoclinic ($P2_1/c$), a = 10.0881(2) Å, b = 15.5800(3) Å, c = 19.2306(4) Å, β = 95.895(1)°, V = 3006.5(1) $Å^3$, T = 100 K, Z = 4, R = 0.0342 (observed data with $I > 2\sigma(I)$), GOF = 1.04.

(22) Akita, M.; Noda, K.; Moro-oka, Y. *Organometallics* **1994**, *13*, 4145.

(23) Selected data for **7**: ν(CO) (CH_2Cl_2) 2022 (s), 1984 (m, sh), 1972 (vs), 1944 (s), 1911 (m), 1870 (w) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.52 MHz, 290 K, CD_2Cl_2) δ 164.2 (s); ^1H NMR (400.13 MHz, 290 K, CD_2Cl_2) δ 5.46, 5.00 (2 × s, 2 × 5H, Cp), 4.24 (d, 1H, J_{PH} = 2 Hz, μ-CH); $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2) δ 234.3 (d, J_{CP} = 11 Hz, μ-CH).

(24) X-ray data for **7**: black crystals, monoclinic ($P2_1/c$), a = 13.3752(2) Å, b = 11.7509(2) Å, c = 25.3894(4) Å, β = 119.262(1)°, V = 3481.3(1) $Å^3$, T = 100 K, Z = 2, R = 0.0476 (observed data with $I > 2\sigma(I)$), GOF = 1.19.

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(26) (a) Cho, H.-G.; Lester, A. *J. Phys. Chem. A* **2006**, *110*, 3886. (b) Marsh, A. L.; Becraft, K. A.; Somorjai, G. A. *J. Phys. Chem. B* **2005**, *109*, 13619. (c) Maitlis, P. M. *J. Organomet. Chem.* **2004**, *689*, 4366. (d) Maitlis, P. M. *J. Mol. Catal. A* **2003**, *204−205*, 55. (e) Dry, M. E. *Catal. Today* **2002**, *71*, 227.