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Formation and Cleavage of C−C, C−O, and O−H Bonds Involving Methoxycarbyne and Hydroxycarbyne Ligands at Unsaturated Dimolybdenum Complexes

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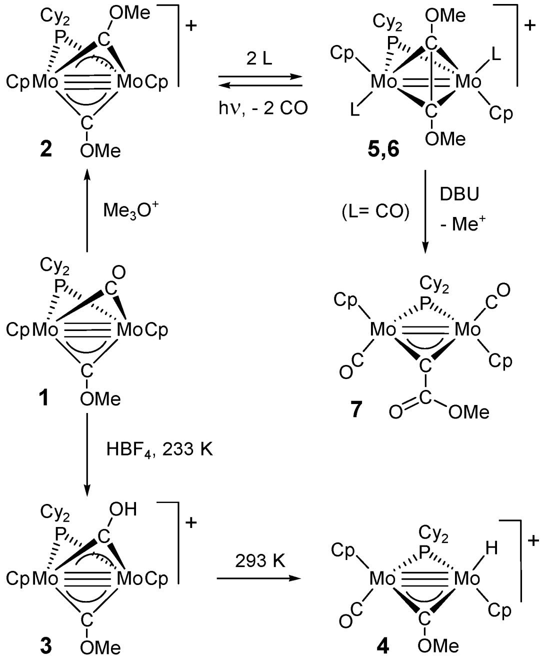
Summary: Reversible carbyne−carbyne coupling occurs upon addition of simple ligands L (CO, ^{t}BuNC) to the bis(methoxycarbyne) complex $[\mathrm{Mo_2Cp_2(\mu\text{-}COMe)_2(\mu\text{-}PCy_2)]BF_4}$ to give the dimethoxyacetylene-bridged derivatives $[\mathrm{Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}C_2(OMe)_2\}(\mu\text{-}PCy_2)L_2]BF_4}$. Upon demethylation, the dicarbonyl cation experiences a 1,2-methoxyl shift to give the carboxycarbyne derivative $[\mathrm{Mo_2Cp_2\{\mu\text{-}C(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2}]$.

Recently we reported the synthesis of the unsaturated complex $[\mathrm{Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)}]$ (**1**), which contains a methoxycarbyne ligand bridging a triple intermetallic bond.[1] The presence of a bridging carbonyl in this relatively electron-rich molecule makes the corresponding oxygen atom a nucleophilic site, and this prompted us to examine the reactions of **1** with some electrophiles as a rational route to compounds containing two alkoxycarbyne ligands bridging a multiple metal−metal bond, no examples of which appear to have been described previously. In the context of the widely accepted analogy between metal surfaces and metal clusters,[2] a binuclear complex having a multiple metal−metal bond can be considered the simplest (if crude) model for a metal surface, as the former shares some of the principal features of the latter: that is, coordinative and electronic unsaturation at the metal centers. The study of the reactivity of such complexes, therefore, can yield results of interest not only from the point of view of the stoichiometric and homogeneous reactions but also as models for elemental steps possibly occurring during chemical reactions heterogeneously catalyzed by metal surfaces or nanoparticles.

Scheme 1



In this paper we report the synthesis of the bis(methoxycarbyne) compound $[\mathrm{Mo_2Cp_2(\mu\text{-}COMe)_2(\mu\text{-}PCy_2)]BF_4}$ (**2**) and the hydroxy- and methoxycarbyne analogue $[\mathrm{Mo_2Cp_2(\mu\text{-}COH)(\mu\text{-}COMe)(\mu\text{-}PCy_2)]BF_4}$ (**3**), as well as some unusual transformations experienced by these highly unsaturated cations, which involve the formation and cleavage of C−C, C−O, or O−H bonds under very mild conditions (Scheme 1). Among the latter transformations we should note the observation of a reversible coupling between methoxycarbyne ligands induced on **2** by carbonylation. While there are several reports of carbyne−carbyne coupling yielding coordinated alkynes or the reverse,[3] rarely have these processes been found as involving alkoxycarbyne ligands[4] or being reversible. In fact, we can quote only two previous examples of reversible coupling between carbyne ligands of any type, these occurring at Fe$_3$ or Fe$_4$ clusters.[5] Our results thus show for the first time that two metal centers are enough to sustain a reversible coupling between carbyne ligands. This finding might be of interest in the context of the metal-catalyzed hydrogenation of CO under either homogeneous or heterogeneous conditions, a subject of substantial academic and industrial interest, especially in the current (and future) scene of high prices for crude oil.[6] As for the heterogeneous processes (Fischer−

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[6] For some recent reviews on the subject see, for example: (a) Maitlis, P. M. *J. Organomet. Chem.* **2004**, *689*, 4366. (b) Maitlis, P. M. *J. Mol. Catal. A* **2003**, *204−205*, 55. (c) Dry, M. E. *Catal. Today* **2002**, *71*, 227.

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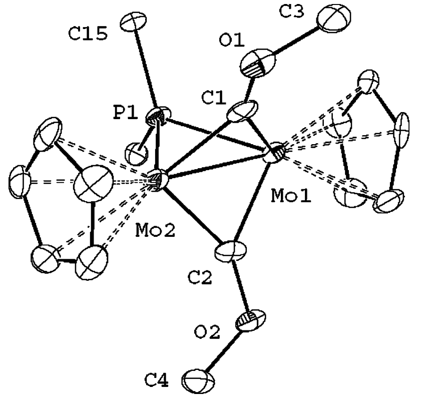

Figure 1. ORTEP diagram for the cation in compound **2**. Cyclohexyl groups (except the C^1 atoms) and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)−Mo(2) = 2.4742(14), Mo(1)−C(1) = 2.00(1), Mo(1)−C(2) = 1.99(1), Mo(1)−P(1) = 2.405(3), Mo(2)−C(1) = 2.00(1), Mo(2)−C(2) = 2.01(1), Mo(2)−P(1) = 2.409(3), C(1)−O(1) = 1.31(1), O(1)−C(3) = 1.47(2), C(2)−O(2) = 1.33(1), O(2)−C(4) = 1.48(1); Mo(1)−P(1)−Mo(2) = 61.9(1), Mo(1)−C(1)−Mo(2) = 76.4(4), Mo(1)−C(2)−Mo(2) = 76.6(4), C(1)−O(1)−C(3) = 115.8(10), C(2)−O(2)−C(4) = 116.6(9).

Tropsch synthesis), our results suggest that C−C coupling in FT reactions might also occur (even if as a side pathway) through hydroxycarbyne intermediates, without involvement of fully hydrogenated (CH_x) surface species. As for the homogeneous hydrogenations, our results suggest that a hypothetical binuclear catalyst for the formation of C_2 oxygenates might not require extensive hydrogenation up to hydroxymethyl intermediates prior to C−C coupling but might promote this coupling through hydroxycarbyne intermediates as well. We note that hydroxycarbyne ligands have been suggested previously as possible intermediates in carbon monoxide hydrogenation,[7] and we have even accomplished a model COH to CH reduction at the unsaturated ditungsten cation $[W_2Cp_2(\mu\text{-COH})(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]^+$.[8] However, no experimental evidence for the involvement of hydroxycarbyne species in real catalytic systems has yet been found.

Compound **1** experiences easy O-alkylation with $(Me_3O)BF_4$ to give the bis(methoxycarbyne) derivative **2**.[9] The symmetrical cation in this product (Figure 1)[10] displays a very short intermetallic length of 2.4742(14) Å, this being almost identical with that measured at the neutral precursor **1** and consistent with the triple Mo−Mo bond formulated for these 30-electron molecules.[1] The bridging carbyne atoms define a $Mo_2(\mu\text{-}C)_2$ dihedral angle of ca. 130° and are not far away from each other (C(1)⋯C(2) = 2.836 Å), a circumstance that surely facilitates their easy coupling (see below).

Compound **1** can be also protonated at the oxygen position by using $HBF_4{\cdot}OEt_2$ in dichloromethane at 233 K, thus giving the hydroxycarbyne derivative **3**.[11] Spectroscopic data for **3** are similar to those for **2**, and thus both cations are assumed to have the same structure. Hydroxycarbyne complexes are extremely rare, generally unstable species,[12] and this is also the case for **3**, as it rearranges above 253 K in dichloromethane solution to give the corresponding hydride−carbonyl isomer $[Mo_2Cp_2(\mu\text{-COMe})(H)(\mu\text{-}PCy_2)(CO)]BF_4$ (**4**).[13] The latter complex is unique in having its hydride ligand terminally bonded to a metal engaged in a triple intermetallic bond (bridging hydrides are usually found for this type of organometallic molecule),[14] but this leaves the dimetal center relatively unprotected, and further reactions occur at room temperature, currently under study.

In contrast to the hydroxycarbyne **3**, the bis(methoxycarbyne) complex **2** is quite stable thermally, and it can be heated in refluxing 1,2-dichloroethane or acetonitrile for several hours without significant change. However, compound **2** reacts readily with simple electron donors such as CO (293 K, 60 bar) and CN^tBu (above 243 K) to give the corresponding alkyne-bridged derivatives $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}C_2(OMe)_2\}(\mu\text{-}PCy_2)L_2]BF_4$ (L = CO (**5**), CN^tBu (**6**)),[15,16] as a result of a carbyne−carbyne coupling forced by the incorporation of two new ligands to the dimetal site. No intermediates were detected in these reactions. The cation in **6** contains a dimethoxyacetylene molecule almost perpendicularly bridging (twist angle ca. 10°) the dimolybdenum center (Figure 2),[17] and the terminal isocyanide groups are arranged in a trans disposition. Incidentally, we note that compound **6** is the first complex containing the unstable dimethoxyacetylene molecule to be structurally characterized. The C(1)−C(2) distance, 1.325(3) Å, is quite short, perhaps indicative of some multiplicity in that bond, which would imply that the alkyne ligand in **6** could be acting as a donor of less than 4 electrons, thus yielding a total electron count for the complex below 32. As a result, the formal order for the intermetallic bond should be somewhat higher than 2, in agreement with the Mo(1)−Mo(2) distance of 2.6550(5) Å, a figure shorter than that expected for a double bond (cf. 2.71 Å for the 32-electron complex $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$).[18]

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[9] Selected spectroscopic data for **2**: ^1H NMR (CD_2Cl_2) δ 6.22 (s, 10H, Cp), 4.00 (s, 6H, OMe) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2); δ 264.2 ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 366.0 (d, J_{CP} = 13 Hz, μ-COMe) ppm.

[10] X-ray data for $\mathbf{2}{\cdot}CH_2Cl_2$: brown crystals, monoclinic ($C2/c$), a = 33.404(6) Å, b = 13.912(2) Å, c = 13.422(2) Å, β = 95.131(3)°, V = 6212.4(17) Å^3, T = 293 K, Z = 8, R = 7.37 (observed data with $I > 2\sigma(I)$), GOF = 1.028.

[11] Selected spectroscopic data for **3**: ^1H NMR (CD_2Cl_2, 233 K) δ 13.16 (br, 1H, COH), 6.18 (s, 10H, Cp), 3.94 (s, 3H, OMe) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 233 K) δ 261.5 ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 233 K) δ 365.8 (d, br, J_{CP} = 13 Hz, μ-COH), 363.0 (d, J_{CP} = 13 Hz, μ-COMe) ppm.

[12] (a) García, M. E.; Riera, V.; Rueda, M. T.; Ruiz, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 1960. (b) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **1999**, *18*, 634 and references therein.

[13] Selected spectroscopic data for **4**: ν_{CO} (CH_2Cl_2) 1873 cm^{-1}; ^1H NMR (CD_2Cl_2, 243 K) δ 6.00, 5.91 (2 × s, 2 × 5H, Cp), 4.16 (s, 3H, OMe), −1.40 (d, J_{HP} = 32 Hz, Mo−H) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 243 K) δ 294.5 ppm.

[14] Alvarez, C. M.; Alvarez, M. A.; García, M. E.; Ramos, A.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **2005**, *24*, 7 and references therein.

[15] Selected spectroscopic data for **5**: ν_{CO} (CH_2Cl_2) 1954 (vs) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 5.93 (s, 10H, Cp), 3.95 (s, 6H, OMe) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 156.7 ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 217.1 (d, J_{CP} = 12 Hz, CO), 151.3 (d, J_{CP} = 3 Hz, μ-CC) ppm.

[16] Selected spectroscopic data for **6**: ν_{CN} (CH_2Cl_2) 2113 (vs) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 5.35 (s, 10H, Cp), 3.92 (s, 6H, OMe), 1.16 (s, 18H, ^{t}Bu) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 167.0 ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 160.3 (d, J_{CP} = 10 Hz, Mo−CN), 147.4 (s, μ-CC) ppm.

[17] X-ray data for $\mathbf{6}{\cdot}CH_2Cl_2$: red crystals, monoclinic ($P2_1/n$), a = 9.2905(19) Å, b = 17.630(4) Å, c = 25.898(5) Å, β = 94.555(4)°, V = 4228.5(15) Å^3, T = 293 K, Z = 4, R = 3.04 (observed data with $I > 2\sigma(I)$), GOF = 1.054.

[18] Adatia, T.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1555.

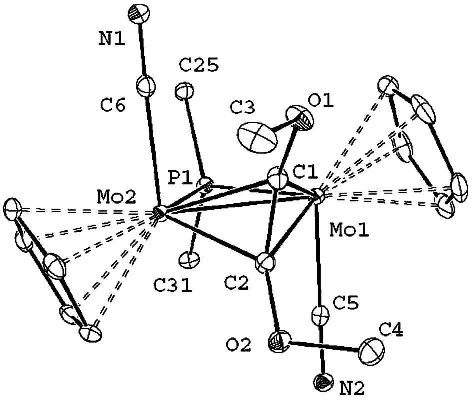

Figure 2. ORTEP diagram for the cation in compound **6**. Cy (except the C^1 atoms) and ^{t}Bu groups and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)−Mo(2) = 2.6550(5), Mo(1)−C(1) = 2.103(2), Mo(1)−C(2) = 2.262(2), Mo(1)−P(1) = 2.3796(8), Mo(2)−C(1) = 2.275(2), Mo(2)−C(2) = 2.107(2), Mo(2)−P(1) = 2.3801(7), Mo(1)−C(5) = 2.055(2), Mo(2)−C(6) = 2.058(2), C(1)−O(1) = 1.374(3), O(1)−C(3) = 1.427(3), C(2)−O(2) = 1.371(3), O(2)−C(4) = 1.435(3); C(5)−Mo(1)−Mo(2) = 90.2(1), C(6)−Mo(2)−Mo(1) = 92.8(1), Mo(1)−P(1)−Mo(2) = 67.81(2), Mo(1)−C(1)−Mo(2) = 74.6(1), Mo(1)−C(2)−Mo(2) = 74.7(1), C(1)−O(1)−C(3) = 112.7(2), C(2)−O(2)−C(4) = 112.6(2).

The coupling reaction leading to compound **5** is fully reversible, and the starting carbyne complex **2** can be rapidly (ca. 5 min) and quantitatively (by NMR) regenerated through photochemical decarbonylation of tetrahydrofuran solutions of **5** at 285 K. No intermediates were detected in this double-decarbonylation process. As stated above, only two precedents for reversible coupling between carbyne ligands have been reported previously,[5] and the closest precedent involving binuclear complexes is found in the (irreversible) cleavage of alkynes by triply bonded ditungsten alkoxide or silyloxide complexes.[19]

The dimethoxyacetylene ligand in the cation **5** is activated not only toward C−C bond cleavage but also toward C−O cleavage. Demethylation is cleanly accomplished by treatment of **5** with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) but gives unexpectedly the neutral carboxycarbyne complex $[Mo_2Cp_2\{\mu\text{-}C(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (**7**).[20] This seems to result from a 1,2-shift of the methoxyl group remaining at the ketenyl intermediate (not detected), which is presumably formed after initial demethylation in **5**, a rearrangement for which we have found no precedent in the literature.

In summary, we have shown that the presence of multiple bonds at dimolybdenum centers induces or allows several unusual transformations involving methoxycarbyne or hydroxycarbyne bridging ligands, these including hydroxycarbyne/hydride−carbonyl isomerization, reversible coupling between methoxycarbyne ligands, and 1,2-methoxyl shifts at ketenyl intermediates. Apart from their novelty, these transformations might be used as models for some of the complex reactions taking place during metal-catalyzed reductions of carbon monoxide, under either homogeneous or heterogeneous conditions. Further work is now under way to extend the scope of the above transformations.

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Supporting Information Available: Text giving experimental procedures and spectroscopic data for new compounds and a CIF file giving crystallographic data for compounds **2** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Selected spectroscopic data for **7**: ν_{CO} (CH_2Cl_2) 1900 (vs, Mo−CO), 1652 (w, C=O) cm^{-1}; ^1H NMR (C_6D_6) δ 5.27 (s, 10H, Cp), 4.02 (s, 3H, OMe) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 128.2 ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 402.8 (s, μ-C), 221.4 (d, J_{CP} = 11 Hz, Mo−CO), 191.8 (s, C=O) ppm.