

Multisite Reactivity of the Unsaturated Methoxycarbyne Complex [Mo₂(η⁵-C₅H₅)₂(μ-COMe)(μ-PCy₂)(μ-CO)]

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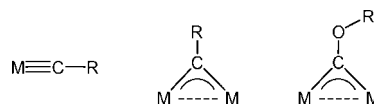
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Summary: The methoxycarbyne-bridged complex [Mo₂Cp₂(μ-COMe)(μ-PCy₂)(μ-CO)] (**1**) has a reactive Mo₂C center, as illustrated through the addition reactions taking place with [MnCp(CO)₂(THF)] or gray selenium to give the cluster [MnMo₂Cp₃(μ₃-COMe)(μ-PCy₂)(CO)₄] and the diselenide complex [Mo₂Cp₂(μ-PCy₂)(μ-κ¹,η¹:κ¹,η¹-SeC(O)C(OMe))(μ-κ¹:κ¹-Se₂)], respectively. In contrast, the reactions with molecules having active E–H bonds (E = p-block element) involve the cleavage of one of the two C–O bonds in the methoxycarbyne ligand, as observed in the reaction of **1** with HSiPh₃ to give the arylcarbyne compound [Mo₂Cp₂(μ-C(2-C₆H₄SiPh₂OMe))(μ-PCy₂)(μ-CO)], this requiring the occurrence of a complex sequence of elemental steps including the cleavage of C–O, C–H, and Si–H bonds, as well as the formation of new C–C and O–Si bonds.

The chemistry of carbyne complexes is a mature field within the organometallic science. These complexes display a high reactivity derived from the multiple nature of their metal–carbon bonds in either the terminal or edge-bridging coordination modes, which can be further increased in the latter case by the presence of multiple metal–metal bonds (Chart 1),¹ and they are also involved in several industrial processes such as CO hydrogenation² and alkyne metathesis.³ In comparison to this

Chart 1



state of knowledge, the chemistry of alkoxy-carbyne compounds is considerably less developed. Most of the complexes described so far contain the COR ligand acting as a μ₂ or μ₃ group on electron-precise di- or trinuclear complexes,⁴ and therefore the behavior of the alkoxy-carbyne ligand in the presence of multiple metal–metal bonds is almost unknown. We thus initiated a systematic study of the reactivity of such unsaturated species, focused so far on cationic binuclear complexes with 32- and 30-electron counts,^{5,6} where electrophilicity is the dominant property. In this paper we report our preliminary results on the reactivity of a more electron rich species, the neutral 30-electron complex [Mo₂Cp₂(μ-COMe)(μ-PCy₂)(μ-CO)] (**1**,⁷ Cp = η⁵-C₅H₅; Scheme 1). Although recent DFT calculations reveal that the frontier orbitals in this molecule mainly involve the multiple Mo–Mo bond and the π-component of the Mo–C bonds,⁸ our experimental results indicate that compound **1** actually displays a remarkable multisite reactivity involving not only these multiple Mo–Mo and Mo–C bonds but also the C–O or O–Me bonds of the methoxycarbyne ligand, depending on the reagent used, thus providing this molecule with a high synthetic potential.

Compound **1** reacts readily with several carbonyl complexes of Mn, Fe, Ru, or Co to give heterometallic clusters containing a μ₃-methoxycarbyne ligand. For example, the reaction of **1** with [MnCp(CO)₂(THF)] rapidly gives the electron-precise cluster [MnMo₂Cp₃(μ₃-COMe)(μ-PCy₂)(CO)₄] (**2**),⁹ which follows from the addition of the 16-electron fragment MnCp(CO)₂ to the unsaturated Mo₂C center of **1** and further spontaneous carbonylation of the electron-deficient (46-electron) cluster thus generated. The structure of **2** displays a Mo₂Mn triangle bridged

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(9) Selected data for **2**: ν(CO) (CH₂Cl₂) 1928 (vs), 1862 (w), 1800 (w), 1749 (w) cm⁻¹; ³¹P{¹H} NMR (121.52 MHz, 290 K, CD₂Cl₂) δ 143.7 (s); ¹H NMR (300.13 MHz, 290 K, CD₂Cl₂) δ 5.15 (s, MoCp, 10H), 4.61 (s, MnCp, 5H), 3.85 (s, OMe, 3H).

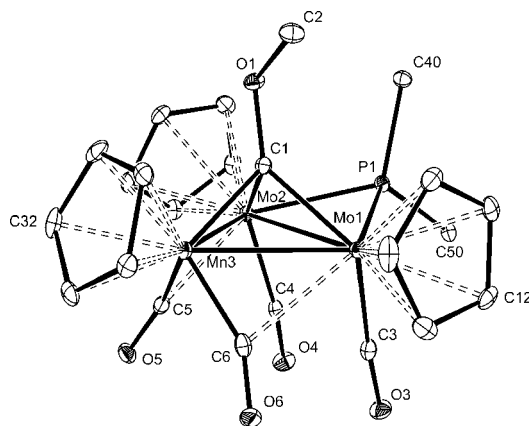
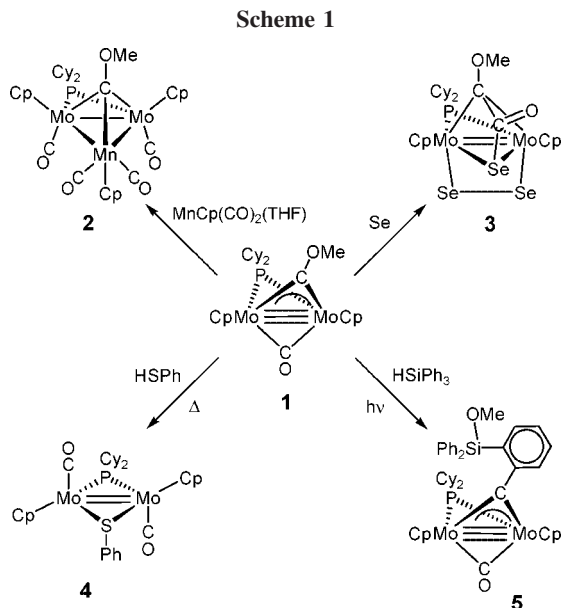


Figure 1. Structure of compound **2**, with H atoms and cyclohexyl rings (except the C¹ atoms) omitted for clarity. Selected bond lengths (Å): Mo(1)–Mo(2) = 2.986(1), Mo(1)–Mn(3) = 2.824(1), Mo(2)–Mn(3) = 2.830(1), Mo(1)–C(1) = 2.085(3), Mo(2)–C(1) = 2.136(2), Mn(3)–C(1) = 1.989(3), Mo(1)–P(1) = 2.438(1), Mo(2)–P(1) = 2.453(1), Mo(1)–C(3) = 1.968(3), Mo(2)–C(4) = 1.959(3), Mn(3)–C(5) = 1.819(3), Mo(2)–C(5) = 2.391(3), Mn(3)–C(6) = 1.811(3), Mo(1)–C(6) = 2.472(3), C(1)–O(1) = 1.383(3).

by the COMe ligand in an essentially symmetrical way, if we allow for the ca. 0.1 Å difference in the covalent radii of Mo and Mn (Figure 1),¹⁰ and the molecule is completed with one cyclopentadienyl ligand on each metal atom (defining a cisoid conformation) and with one (Mo) or two (Mn) terminal CO ligands. The latter are involved in semibringing interactions with the Mo atoms, thus balancing the electron densities at the Mo and Mn atoms (the local electron counts would be 17.5 and 19 electrons, respectively, for an all-terminal CO structure). The Mo–Mo length of 2.986(1) Å in **2** is substantially longer than that recently measured in the 46-electron cluster [MnMo₂Cp₂-Cp'(μ₃-H)(μ-PCy₂)(CO)₄], (Cp' = η⁵-C₅H₄Me, Mo–Mo = 2.6448(8) Å),¹¹ as expected now for an electron-precise (48-electron) cluster. We note that, apart from the above compounds, only one other complex having a triangular Mo₂Mn skeleton appears to have been reported previously.¹²

The relatively high electron density at the dimetal center in **1** makes this complex also very reactive toward the electrophilic group 16 elements. The most remarkable reaction occurs between **1** and gray selenium, this leading at room temperature to the polyaddition derivative [Mo₂Cp₂(μ-PCy₂){μ-κ¹,η¹:κ¹,η¹-SeC(O)C(OMe)}(μ-κ¹:κ¹-Se₂)] (**3**) in good yield.¹³ The formation of **3** requires the coupling of the methoxycarbonyne and carbonyl ligands to a selenium atom to give a carbene–selenolate ligand, thus resembling the behavior of heterodinuclear aryl-carbyne-bridged complexes toward elemental oxygen and sulfur.¹⁴ There is also a κ¹:κ¹-diselenido ligand bridging the molybdenum atoms in **3**, its formation being obviously facilitated by the high unsaturation of the metal center in **1**. The intermetallic length in **3** is quite short, considering the size of

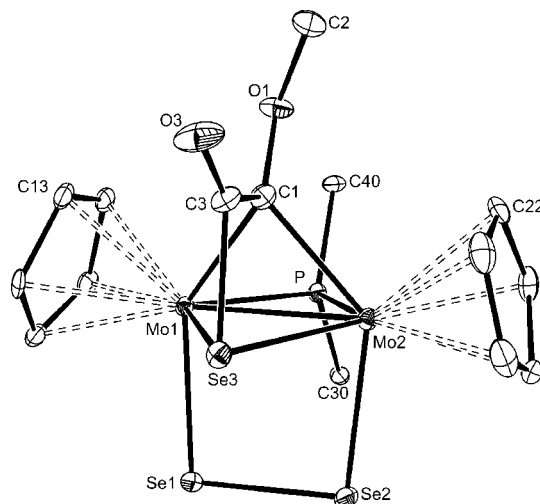


Figure 2. Structure of compound **3**, with H atoms and cyclohexyl rings (except the C¹ atoms) omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)–Mo(2) = 2.709(1), Mo(1)–P = 2.414(1), Mo(2)–P = 2.431(1), Mo(1)–C(1) = 2.194(5), Mo(2)–C(1) = 2.223(5), Mo(1)–Se(3) = 2.596(1), Mo(2)–Se(3) = 2.591(1), Mo(1)–Se(1) = 2.541(1), Mo(2)–Se(2) = 2.539(1), Se(1)–Se(2) = 2.309(1), Se(3)–C(3) = 2.009(5), C(3)–O(3) = 1.198(6), C(3)–C(1) = 1.433(7); Mo(1)–Se(1)–Se(2) = 93.7(1).

the bridging atoms (2.709(1) Å, Figure 2),¹⁵ this being consistent with the formulation of a double Mo–Mo bond for this molecule under the EAN formalism, if single Mo–Se bonds are assumed for the diselenide ligand. However, the Mo–Se lengths for this ligand in **3** (ca. 2.54 Å) are ca. 0.05 Å shorter than those involving the bridging selenolate atom Se(3) and ca. 0.1 Å shorter than the single-bond W–Se lengths in the triselenide-bridged complex [W₂Cp₂(μ-κ¹:κ¹-Se₃)(CO)₆].¹⁶ All of this points to the presence of some multiplicity in the corresponding

(10) X-ray data for **2**: orange-brown crystals, triclinic (*P*1̄), *a* = 9.1962(17) Å, *b* = 12.467(2) Å, *c* = 15.803(3) Å, α = 101.450(3)°, β = 91.795(3)°, γ = 90.698(3)°, *V* = 1774.6(6) Å³, *T* = 100 K, *Z* = 1, *R* = 0.0300 (observed data with *I* > 2σ(*I*)), GOF = 1.094.

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(13) Selected data for **3**: ν(CO) (CH₂Cl₂) 1646 (m) cm⁻¹; ³¹P{¹H} NMR (121.52 MHz, 290 K, CD₂Cl₂) δ 181.3 (s); ¹H NMR (300.13 MHz, 290 K, CD₂Cl₂) δ 5.89 (s, Cp, 10H), 3.43 (s, OMe, 3H); ¹³C{¹H} NMR (75.48 MHz, 290 K, CD₂Cl₂) δ 177.7 (s, C=O), 134.8 (d, *J*_{CP} = 17 Hz, COMe).

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(15) X-ray data for **3**: green crystals, trigonal (*P*3̄), *a* = *b* = 23.367(2) Å, *c* = 9.183(2) Å, α = β = 90°, γ = 120°, *V* = 4342.3(11) Å³, *T* = 100 K, *Z* = 6, *R* = 0.0384 (observed data with *I* > 2σ(*I*)), GOF = 1.002.

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Se–Mo bonds in **3** ($p\pi$ – $d\pi$ donation), which would somewhat reduce the strength of the intermetallic interaction. We should note that no other dimolybdenum complex having a $\kappa^1:\kappa^1$ -diselenido bridging ligand appears to have been reported previously. These ligands are more often found in the $\kappa^2:\kappa^2$ bridging mode,¹² but in the case of **3** this mode must be disfavored, since it would lead to an electronic and coordinative oversaturation of the dimetal center.

In the above reactions of complex **1** the methoxycarbonyl ligand keeps its C–O–C skeleton unperturbed, but this changes dramatically in the presence of reagents having active E–H bonds (E = *p*-block element), since these molecules induce the cleavage of one of the two C–O bonds of the methoxycarbonyl ligand. The reaction of compound **1** with thiols, primary phosphines, or tin hydrides all result in the destruction of the methoxycarbonyl ligand, presumably by the elimination of methane (O–Me bond cleavage) and formation of the corresponding dicarbonyl complex, which incorporates the dehydrogenated “E” residue as a bridging group. Thus, **1** reacts with HSPH in toluene at 353 K to give the known complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-SPh})(\mu\text{-PCy}_2)(\text{CO})_2]$ (**4**) (Scheme 1).¹⁷ In a similar way, the reaction of **1** with HSnPh_3 gives the Mo_2Sn cluster $[\text{Mo}_2\text{Cp}_2(\mu\text{-SnPh}_3)(\mu\text{-PCy}_2)(\text{CO})_2]$.¹⁸ In contrast, silanes react photochemically with **1** by inducing the cleavage of the C–OMe bond of the methoxycarbonyl ligand. Thus, the photolysis of toluene solutions of **1** and HSiPh_3 with UV–visible light gives the arylcarbyne complex $[\text{Mo}_2\text{Cp}_2\{\mu\text{-C}(2\text{-C}_6\text{H}_4\text{SiPh}_2\text{OMe})\}(\mu\text{-PCy}_2)(\mu\text{-CO})]$ (**5**) in medium yield.¹⁹ The structure of **5** (Figure 3)²⁰ is quite similar to that of **1**, with the methoxyl group being here replaced by an aryl ring which bears a $\text{SiPh}_2(\text{OMe})$ group in an ortho position. The formation of **5** thus requires a complex sequence of reactions involving dehydrogenation and the cleavage of Si–H, C–H, and C–O bonds, as well as the

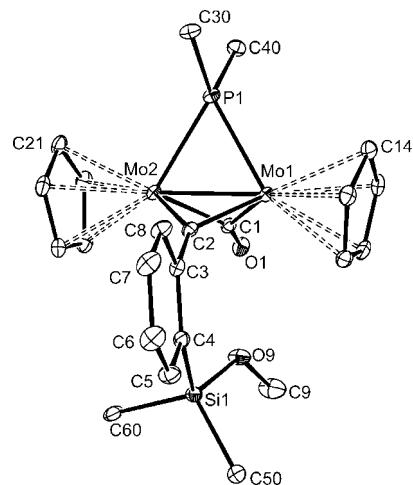


Figure 3. Structure of compound **5**, with H atoms and cyclohexyl rings (except the C¹ atoms) omitted for clarity. Selected bond lengths (Å): Mo(1)–Mo(2) = 2.469(1), Mo(1)–P(1) = 2.393(1), Mo(2)–P(1) = 2.396(1), Mo(1)–C(1) = 2.119(2), Mo(2)–C(1) = 2.081(2), Mo(1)–C(2) = 1.980(2), Mo(2)–C(2) = 2.002(2).

formation of new C–C and Si–O bonds, and further work will be needed to better understand these unusual transformations.

In summary, we have shown that the neutral methoxycarbonyl complex **1** has a remarkably wide reactivity involving not only its multiple Mo–Mo and Mo–C bonds but also the activation of both C–O bonds of the carbonyl ligand, the latter leading to overall demethylation or methoxyl migration processes. Novel structures that would be otherwise difficult to obtain are formed in these reactions, and further work to expand the synthetic potential of compound **1** is now in progress.

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Supporting Information Available: Text giving experimental procedures and spectroscopic data for new compounds and CIF files giving crystallographic data for compounds **2**, **3**, and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>

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(19) Selected data for **5**: $\nu(\text{CO})$ (CH_2Cl_2) 1683 (s) cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.52 MHz, 290 K, CD_2Cl_2) δ 223.6 (s); ^1H NMR (300.13 MHz, 290 K, CD_2Cl_2) δ 7.12 (m, C_6H_4 , 2H), 6.83 (m, C_6H_4 , 1H), 6.69 (m, C_6H_4 , 1H), 5.60 (s, Cp, 10H), 3.14 (s, OMe, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, 290 K, CD_2Cl_2) δ 386.2 (s, br, $\mu\text{-CC}_6\text{H}_4$), 300.8 (d, $J_{\text{CP}} = 6$ Hz, $\mu\text{-CO}$).

(20) X-ray data for **5**: orange crystals, triclinic ($P\bar{1}$), $a = 11.313(3)$ Å, $b = 12.471(3)$ Å, $c = 17.090(4)$ Å, $\alpha = 68.836(4)^\circ$, $\beta = 84.285(4)^\circ$, $\gamma = 81.815(4)^\circ$, $V = 2222.6(10)$ Å³, $T = 100$ K, $Z = 2$, $R = 0.0260$ (observed data with $I > 2\sigma(I)$), $\text{GOF} = 1.023$.