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A Versatile and Unprecedented Triply Bonded Dimolybdenum Carbonyl Anion

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Summary: Chemical reduction of $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}PA_2)(CO)_2]$ *(A = Cy, Ph, OEt) gives the corresponding alkaline metal salts of the triply bonded anions* $[Mo_2Cp_2(\mu\text{-}PA_2)(\mu\text{-}CO)_2]^-$*, which exhibit both molybdenum and oxygen nucleophilic sites. The* PCy_2 *anion reacts easily with* NH_4^+, $[AuCl(PR_3)]$*, or MeI to give unsaturated dicarbonyls* $[Mo_2Cp_2(\mu\text{-}X)(\mu\text{-}PA_2)(CO)_2]$ *(X = H,* $AuPR_3$*, Me), while* $[Me_3O]BF_4$ *gives the methoxycarbyne* $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ *and allyl chloride rearranges to give the unsaturated alkenyl complex* $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CMeCH_2)(CO)_2]$*.*

Transition-metal carbonyl anions are very useful reagents in organometallic synthesis. This is mainly due to their nucleophilicity, which allows these molecules to react with a great variety of electrophiles, thus forming new M−E bonds (E = H, C, p-element, d-element, etc.).[1] Although a large number of mononuclear and polynuclear species are known, the number of metal−metal bonded binuclear anions is comparatively low, and only a few of them exhibit M−M bond orders (BO) higher than one. In fact, examples of the latter are restricted to the paramagnetic $[Fe_2(\mu\text{-}P^tBu_2)_2(CO)_5]^-$ (BO = 1.5),[2] dihydrides $[M_2(\mu\text{-}H)_2(CO)_8]^{2-}$ (BO = 2; M = Cr, Mo, W),[3] the phosphido complex $[Fe_2(\mu\text{-}PPh_2)(CO)_6]^-$ (BO = 2),[4] and the diphosphine-bridged $[Mn_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)]^{2-}$ (BO = 2).[5] The unusual combination of a negative charge and a double M−M bond in these substrates provides these anions with a remarkably wide synthetic potential.[4,5] We here report the synthesis of the very reactive dimolybdenum anions $[Mo_2Cp_2(\mu\text{-}PA_2)(\mu\text{-}CO)_2]^-$ (**2a**−**c**) [A = Cy (**a**), Ph (**b**), OEt (**c**)]. To our knowledge, these 30 e^- species are the first examples of transition-metal carbonyl anions displaying a triple intermetallic bond. Moreover, their high reactivity gives a unique opportunity to explore the chemistry of binuclear anions under a highly unsaturated metal environment. As shown below, these anions allow the synthesis of unsaturated derivatives that cannot be prepared through other routes, and they also promote unusual coordination modes or rearrangements in the incoming electrophile, always under mild conditions.

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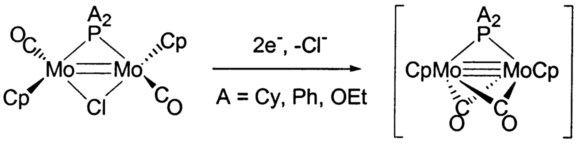
Tetrahydrofuran solutions of anions **2a**−**c** are easily generated in a two-step reaction. First, the new chloro complexes [$Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}PA_2)(CO)_2$] (**1a**−**c**) are synthesized through the oxidative addition of the corresponding $ClPA_2$ on [$Mo_2Cp_2(CO)_6$] in refluxing toluene (Cy, Ph) or diglyme (OEt) (eq 1).[6]

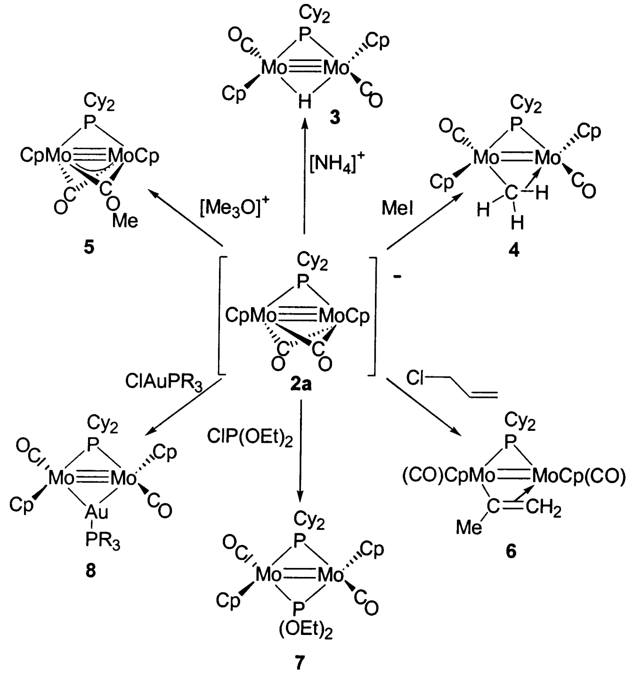


1a-c **2a-c**

Complexes **1** are structurally related to the mixed-phosphido compounds [$M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'R'')(CO)_2$],[7] but they are much more unstable and could not be isolated. In a second step, tetrahydrofuran solutions of the crude compounds **1** are reacted with several reducing agents such as Li[$BHEt_3$], Na(Hg), or K[$BH(s\text{Bu})_3$] to give the corresponding alkaline metal salts of anions **2a**−**c**. Although these complexes could not be isolated, IR and ^{31}P NMR data of the corresponding reaction mixtures indicated the presence of single major species in each case,[8] so these crude solutions could be used for further studies. The IR spectra of anions **2** clearly reveal the presence of two bridging carbonyls. These spectra are sensitive to the nature of the alkaline counterion, an indication of ion-pair effects,[9] yet to be studied.

The high synthetic potential of the unsaturated anions **2** is illustrated through the reactions of **2a** (Li^+ salt) shown in Scheme 1. As expected, this anion is easily protonated by [NH_4]PF_6 to give the corresponding hydride [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2$] (**3**).[10] Compound **3** is a rare example of a metal carbonyl displaying a bridging H ligand across a triple M−M bond. Precedents for this 30 e^- compound are restricted to the monocarbonyls [$M_2Cp^*_2(\mu\text{-}H)(\mu\text{-}CO)$] (M = Ru,[11a,b] Os[11c]) and the cations [$W_2Cp_2(\mu\text{-}H)(CO)_2(\mu\text{-}R_2PCH_2PR_2)$]$^+$ (R = Me, Ph).[12] More importantly, our initial studies indicate that hydride **3** is very reactive toward a great variety of small molecules.

Scheme 1



The reactions of **2a** with other electrophiles reveal that not only the metal atoms but also the O (carbonyl) atoms are nucleophilic sites of the anion. For example, reaction of **2a** with MeI gives the methyl complex [$Mo_2Cp_2(\mu\text{-}Me)(\mu\text{-}PCy_2)(CO)_2$] (**4**),[13] whereas reaction of **2a** with [Me_3O]BF_4 gives the methoxycarbyne [$Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)$] (**5**).[14] Although NMR data for **4** down to 193 K indicate the presence of a symmetric methyl group, we propose for this compound a fluxional monohapto agostic ligand instead. This is supported by the ^{31}P chemical shift of **4**, with a value characteristic of doubly bonded complexes of the type [$M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}X)(CO)_2$] (M = Mo, W; X = three-electron ligand).[7] A number of related agostic complexes have been described, but none of them seem to involve a bridging methyl across a double M−M bond. It is to be seen whether this will enhance the reactivity of the methyl ligand, for example with respect to C−C coupling reactions.

Compound **5** retains the most significant structural features present in the parent anion **2**, that is, the triple Mo−Mo bond and the bridging carbonyls. This has been confirmed through an X-ray study on the ethoxycarbyne **5′**, which can be conveniently prepared from **2a** and Et_2SO_4 (Figure 1).[15,16] Indeed, compound **5′** displays a Mo−Mo distance (2.4793(15) and 2.4772(11) Å in the two crystallographically independent molecules) com-

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(6) Selected spectroscopic data for compounds **1**: ν(CO) (toluene): 1844(vs) cm^{-1} (**1a**); 1859(vs) cm^{-1} (**1b**). ν(CO) (diglyme): 1890(m, sh), 1867(vs) cm^{-1} (**1c**). $^{31}P\{^1H\}$ NMR (81.03 MHz): δ 155.6 ppm (**1a**, C_6D_6); 135.3 ppm (**1b**, CD_2Cl_2), 329.2 ppm (**1c**, CD_2Cl_2).

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

(8) Selected spectroscopic data for compounds **2**: ν(CO) (THF): 1588(m), 1562(vs) cm^{-1} (**2a**, Li^+ salt); 1644(m), 1604(vs), 1593(s, sh) cm^{-1} (**2b**, Na^+ salt); 1605(m), 1570(vs) cm^{-1} (**2c**, Li^+ salt). $^{31}P\{^1H\}$ NMR (121.50 MHz, THF): δ 209.8 ppm(**2a**); 334.8 ppm(**2c**).

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(10) Selected data for **3**: ν(CO) (THF): 1871(w, sh), 1837(s) cm^{-1}. ^1H NMR (300.13 MHz, CD_2Cl_2): δ 5.09 (s, 10H, Cp), −6.94 (d, J_{HP} = 11, 1H, μ-H) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ 232.3 (s, μ-P) ppm.

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(13) Selected data for **4**: ν(CO) (CH_2Cl_2): 1854(w, sh), 1815(s) cm^{-1}. ^1H NMR (300.13 MHz, CD_2Cl_2): δ 5.16 (s, 10H, Cp), −0.77 (d, J_{HP} = 2.5, J_{HC} = 124, 3H, μ-Me) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ 153.3 (s, μ-P) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2): δ 249.6 (d, J_{CP} = 15, CO), 89.4 (s, Cp), −44.3 (d, J_{CP} = 2.5, μ-Me) ppm.

(14) Selected data for **5**: ν(CO) (CH_2Cl_2): 1674(s) cm^{-1}. ^1H NMR (300.13 MHz, CD_2Cl_2): δ 5.75 (s, 10H, Cp), 3.74 (s, 3H, OMe) ppm. $^{31}P\{^1H\}$ NMR (121.52 MHz, CD_2Cl_2): δ 228.5 (s, μ-P) ppm. $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 213 K): δ 352.0 (d, J_{CP} = 15, μ-COMe), 305.0 (d, J_{CP} = 9, μ-CO), 93.5 (s, Cp), 66.4 (s, OMe) ppm.

(15) Selected data for **5′**: ν(CO) (CH_2Cl_2) 1672(s) cm^{-1}. ^1H NMR (200.13 MHz, CD_2Cl_2): δ 5.72 (s, 10H, Cp), 3.92 (q, J_{HH} = 7, 2H, OCH_2), 1.28 (t, J_{HH} = 7, 3H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (81.04 MHz, CD_2Cl_2): δ 227.8 (s, μ-P) ppm. $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2): δ 351.0 (d, J_{CP} = 15, μ-COEt), 303.5 (d, J_{CP} = 9, μ-CO), 93.6 (s, Cp), 76.3 (s, OCH_2) ppm.

(16) X-ray data for **5′**: red crystals, $Mo_2PO_2C_{26}H_{37}$, fw 604.41, triclinic, ($P\bar{1}$), a = 17.489(5) Å, b = 15.118(5) Å, c = 10.254(5) Å, α = 91.75(5)°, β = 92.51(5)°, γ = 72.57(5)°, V = 2583.7(17) Å^3, Z = 4, T = 293 K, R1 = 0.0551 [for $I > 2\sigma(I)$], wR2 = 0.1481 (all data), GOF = 0.851.

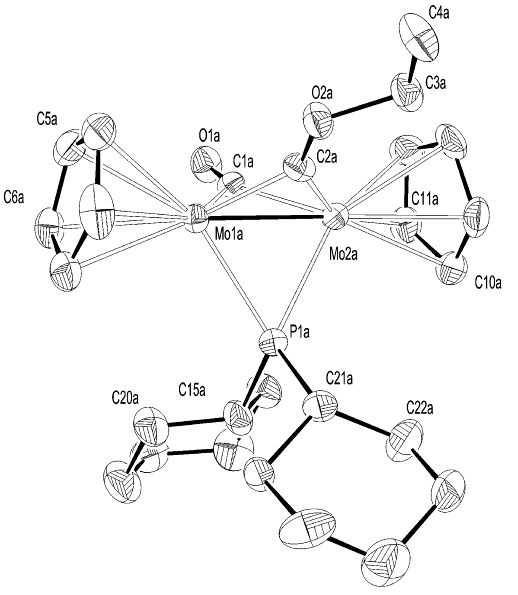

Figure 1. View of the molecular structure of compound **5′**.

parable to those found for related triply bonded neutral complexes such as $[Mo_2Cp_2(CO)_4]$[17a] or $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$.[17b] Interatomic distances within the ethoxycarbyne ligand are similar to those in the cation $[W_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PPh_2)_2]^+$.[18] These two complexes are the only known examples of COR ligands across triple M−M bonds to be structurally characterized and have a considerable synthetic potential derived from the simultaneous presence of M−M and M−C multiple bonds.

The unsaturated nature of the dimetal center in **2a** might promote some unusual rearrangements in the incoming electrophile. For example, **2a** reacts readily at room temperature with allyl chloride to give the alkenyl derivative $[Mo_2Cp_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}PCy_2)(CO)_2]$ (**6**) as sole product.[19] This requires a 2,1-H atom shift in the original allyl group at some stage of the reaction. Noticeably, this unexpected rearrangement is opposite the 1,2-shift (alkenyl to allyl) proposed to occur during the photolysis of alkynes at Mn_2 or MnMo centers.[20] Compound **6** exists in solution as a mixture of *cis*- and *trans*-dicarbonyl isomers,[7] as deduced from its IR spectrum. Interestingly, these isomers interconvert rapidly on the NMR time scale, a process not detected previously in the related alkenyl complexes $[Mo_2Cp_2(\mu\text{-}CMeCHMe)(\mu\text{-}SR)(CO)_2]$.[21]

Other synthetic uses of anion **2a** are illustrated through the reactions with $ClP(OEt)_2$ and $[AuCl\{P(p\text{-}tol)_3\}]$, which lead to the unsaturated mixed-phosphido complex $[Mo_2Cp_2(\mu\text{-}PCy_2)\{\mu\text{-}P(OEt)_2\}(CO)_2]$ (**7**)[22] and the unstable heterometallic cluster $[Mo_2AuCp_2(\mu\text{-}PCy_2)(CO)_2\{P(p\text{-}tol)_3\}]$ (**8**), respectively.[23]

In summary, we have shown that the triply bonded anion **2a** is quite reactive toward a great variety of electrophiles under mild conditions, thus leading to unsaturated molecules that are not accessible through conventional preparative routes. Anion **2a** displays both *Mo* and *O* nucleophilic sites, and the presence of the triple Mo−Mo bond might have a critical influence on the coordination mode or rearrangements in the incoming electrophile. We are further exploring the synthetic potential of anions **2** and some of their unsaturated derivatives.

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Supporting Information Available: Experimental procedures for new complexes and crystallographic data for **5′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] García, M. E.; Riera, V.; Rueda, M. T.; Ruiz, M. A.; Halut, S. *J. Am. Chem. Soc.* **1999**, *121*, 1960.

[19] Selected data for **6**: ν(CO) (petroleum ether) 1888(vs), 1838(s), 1808(vs) cm^{-1}. ^1H NMR (300.13 MHz, CD_2Cl_2): δ 5.36, 5.31 (2 × s, 2 × 5H, Cp), 5.07, 4.68 (2 x d, $J_{HH} = 2.6$, 2 × 1H, CH_2), 2.27 (s, 3H, Me) ppm. $^{31}P\{^1H\}$ NMR (121.52 MHz, CD_2Cl_2): δ 131.2 (s, μ-P) ppm. $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 213 K): δ 250.0 (d, $J_{CP} = 14$, CO), 237.9 (d, $J_{CP} = 13$, CO), 174.6 (s, $C{=}CH_2$), 90.0, 89.0 (2 × s, Cp), 79.3 (s, $C{=}CH_2$), 38.7 (s, Me) ppm.

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[22] Selected data for **7**: ν(CO) (CH_2Cl_2) 1875(w, sh), 1848(s) cm^{-1}. ^1H NMR (300.13 MHz, CD_2Cl_2): δ 5.40 (s, 10H, Cp), 4.28, 3.98 (2 × m, 2 × 2H, OCH_2), 1.37 (t, $J_{HH} = 7$, 6H, CH_3). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ 351.1 [d, $J_{PP} = 19$, μ-P(OEt)$_2$], 119.5 (d, $J_{PP} = 19$, μ-PCy$_2$) ppm.

[23] Selected data for **8**: ν(CO) (CH_2Cl_2): 1765 cm^{-1}. ^1H NMR (200.13 MHz, CD_2Cl_2): δ 7.60−7.10 (m, 12H, $p\text{-}C_6H_4CH_3$), 4.89 (s, 10H, Cp), 2.33 (s, 9H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (81.04 MHz, CD_2Cl_2): δ 213.9 (s, μ-PCy$_2$), 63.3 [s, AuP(p-tol)$_3$] ppm.