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Dehydrogenative Formation and Reactivity of the Unsaturated Benzylidyne-Bridged Complex [$Mo_2Cp_2(\mu$-CPh)(μ-PCy_2)(μ-CO)]: C−C and C−P Coupling Reactions

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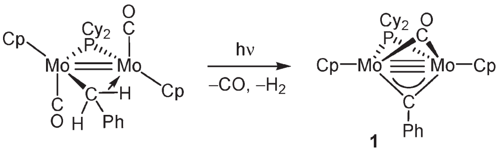
Summary: The title complex is formed through the photochemical treatment of the benzyl complex [$Mo_2Cp_2(\mu$-$CH_2Ph)(\mu$-$PCy_2)(CO)_2$] (Cp = η^5-C_5H_5). It reacts reversibly with CO to give the ketenyl complex [$Mo_2Cp_2\{\mu$-C(Ph)CO$\}(\mu$-$PCy_2)(CO)_2$] and with methyl triflate to give the mixed-carbyne derivative [$Mo_2Cp_2(\mu$-COMe)(μ-CPh)(μ-PCy_2)](CF_3SO_3), which in turn yields reversibly the C−C coupled products [$Mo_2Cp_2\{\mu$-η^2:η^2-C(OMe)-CPh$\}(\mu$-$PCy_2)L_2$](CF_3SO_3) (L = CO, CN^{t}Bu) upon addition of L. In the presence of [$FeCp_2$](BF_4), the title complex adds three $PHEt_2$ molecules to give the phosphinocarbene derivative [$Mo_2Cp_2\{\mu$-η^1:η^1,κ^1-C(Ph)$PEt_2\}(\mu$-PEt_2)(CO)($PHEt_2$)](BF_4).

Recently we reported the preparation, structure, and bonding of the unsaturated alkyl-bridged complexes [$Mo_2Cp_2(\mu$-R)(μ-$PCy_2)(CO)_2$] (Cp = η^5-C_5H_5; R = CH_3, CH_2Ph), this revealing that the alkyl ligand in each case is involved in a very weak α-agostic interaction with the dimetal center both in the solid state and in solution.[1] In a preliminary study on the chemical behavior of the methyl-bridged complex we found that, while a molecule of CO could be removed photochemically to yield the carbonyl derivative [$Mo_2Cp_2(\mu$-η^1:η^2-$CH_3)(\mu$-PCy_2)(μ-CO)] having a strengthened agostic interaction, its photochemical treatment in the presence of [$Mo(CO)_6$] or [$Fe_2(CO)_9$] would gave methylidyne-bridged heterometallic clusters, thus revealing the occurrence of easy dehydrogenation steps after cluster formation.[2] This is an unusual evolution of a bridging agostic alkyl ligand. Actually, we can quote only a couple of precedents of related μ-CH_3/μ-CH transformations involving agostic ligands, these reported to occur at room temperature at Ru_2 (through dehydrogenation)[3a] and Fe_3 (through double oxidative addition of C−H bonds) metal centers.[3b] In addition, related μ-CH_2R/μ-CH/μ-CR transformations (R = CH_2Ph) were described recently to occur at 120 °C in a Ru_3 cluster.[4] We here report that the photochemical treatment of the benzyl complex [$Mo_2Cp_2(\mu$-$CH_2Ph)(\mu$-$PCy_2)(CO)_2$] promotes the full dehydrogenation of this ligand without the need of a third metal center, to give the benzylidyne-bridged derivative [$Mo_2Cp_2(\mu$-CPh)-(μ-PCy_2)(μ-CO)] (**1**) in good yield (Scheme 1). This unsaturated compound is isoelectronic with the methoxycarbyne complex [$Mo_2Cp_2(\mu$-COMe)(μ-PCy_2)(μ-CO)], a molecule exhibiting a remarkable multisite reactivity involving both the Mo−Mo and Mo−C multiple bonds,[5] and therefore provides an excellent opportunity to examine the reactivity of an arylcarbyne ligand at a highly unsaturated dimetal center while comparing it to that of the mentioned methoxycarbyne complex. The chemistry of a carbyne ligand at an unsaturated dimetal center can be considered as the simplest (if crude) model of the chemical behavior of related surface species formed in different heterogeneously catalyzed reactions, notably the Fischer−Tropsch (FT) synthesis of hydrocarbons from syngas (CO + H_2),[6] a process of increasing significance in a scene of high prices and short stocks for crude oil. Indeed there is increasing evidence that surface methylidyne groups are important not only in the initial C−C coupling steps of the FT reaction but also as the propagating species causing the growth of the hydrocarbon chain.[6a] As shown below, our initial studies on the behavior of compound **1** show that the chemistry of this 30-electron carbyne complex involves different C−C and C−P coupling processes, some of them being reversible.

Scheme 1



Compound **1** is easily prepared in good yield through the irradiation with visible−UV light of toluene solutions of the benzyl complex [$Mo_2Cp_2(\mu$-$CH_2Ph)(\mu$-$PCy_2)(CO)_2$], the transformation being complete in ca. 2 h at 288 K.[7] Although the formation of **1** is obviously a multistep process involving the eventual elimination of H_2 and a molecule of CO, no intermediates could be detected in this reaction through IR and ^{31}P NMR

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[1] García, M. E.; Ramos, A.; Ruiz, M. A.; Lanfranchi, M.; Marchiò, L. *Organometallics* **2007**, *26*, 6197.

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[3] (a) Connelly, N. G.; Forrow, N. J.; Gracey, B. P.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 14. (b) Dutta, T. K.; Vites, J. C.; Jacobsen, G. B.; Fehlner, T. P. *Organometallics* **1987**, *6*, 842.

[4] Temjimbayashi, R.; Murotani, E.; Takemori, T.; Takao, T.; Suzuki, H. *J. Organomet. Chem.* **2007**, *692*, 442.

[5] (a) Alvarez, C. M.; Alvarez, M. A.; García, M. E.; García-Vivó, D.; Ruiz, M. A. *Organometallics* **2005**, *24*, 4122. (b) García, M. E.; García-Vivó, D.; Ruiz, M. A.; Alvarez, S.; Aullón, G. *Organometallics* **2007**, *26*, 4930. (c) García, M. E.; García-Vivó, D.; Ruiz, M. A.; Alvarez, S.; Aullón, G. *Organometallics* **2007**, *26*, 5912. (d) García, M. E.; García-Vivó, D.; Ruiz, M. A. *Organometallics* **2008**, *27*, 169. (e) García, M. E.; García-Vivó, D.; Ruiz, M. A. *Organometallics* **2009**, *28*, 4385.

[6] (a) Maitlis, P. M.; Zanotti, V. *Chem. Commun.* **2009**, 1619. (b) Cho, H.-G.; Lester, A. *J. Phys. Chem. A* **2006**, *110*, 3886. (c) Marsh, A. L.; Becraft, K. A.; Somorjai, G. A. *J. Phys. Chem. B* **2005**, *109*, 13619. (d) Maitlis, P. M. *J. Organomet. Chem.* **2004**, *689*, 4366. (e) Maitlis, P. M. *J. Mol. Catal. A* **2003**, *204−205*, 55. (f) Dry, M. E. *Catal. Today* **2002**, *71*, 227.

[7] Selected data for **1**: ν(CO) (CH_2Cl_2) 1686 (s) cm^{-1}; ^{31}P{^{1}H} NMR (121.52 MHz, CD_2Cl_2) δ 228.5 (s); ^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2) δ 385.2 (d, J_{CP} = 15 Hz, μ-CPh), 300.8 (d, J_{CP} = 9 Hz, μ-CO).

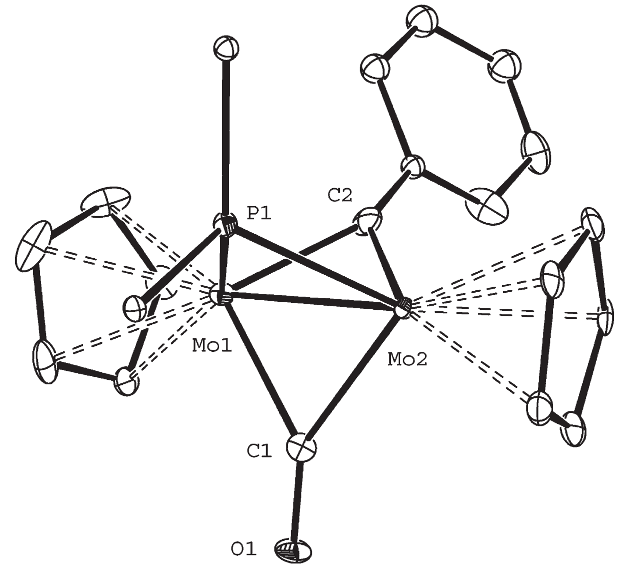


Figure 1. ORTEP drawing (30% probability) of compound **1**, with H atoms and cyclohexyl rings (except the C^1 atoms) omitted for clarity. Only one of the two disordered positions of the phenyl ring is shown. Selected bond lengths (Å): Mo(1)−Mo(2) = 2.464(1), Mo(1)−C(1) = 2.11(1), Mo(2)−C(1) = 2.09(1), Mo(1)−C(2) = 1.97(1), Mo(2)−C(2) = 1.99(1), Mo(1)−P(1) = 2.403(2), Mo(2)−P(1) = 2.402(2).

monitoring of the corresponding solutions. Moreover, we have found that the dehydrogenation leading to **1** is irreversible, since this product does not react with H_2 even under pressure (60 bar). The structure of **1** (Figure 1)[8] is quite similar to that determined previously for the isoelectronic ethoxycarbyne complex $[Mo_2Cp_2(\mu\text{-COEt})(\mu\text{-PCy}_2)(\mu\text{-CO})]$[9] and also displays a very short intermetallic length of 2.464(1) Å, consistent with the triple bond to be proposed for these molecules on the basis of the EAN formalism and DFT calculations,[5b] and quite short Mo−CPh lengths of ca. 1.98 Å, consistent with the expected formal bond order (1.5) in a symmetrically bridging carbyne ligand. The benzylidyne ligand (δ_C 385.2 ppm), however, seems to behave as an acceptor group stronger than an alkoxycarbyne ligand, since the C−O stretching frequency of the bridging carbonyl in **1** is some 12 cm^{-1} higher than that in the mentioned alkoxycarbyne complex. This might be the origin of substantial differences in the acid−base reactivity of these molecules at their most active positions, located at the dimetal site, C(carbyne) and O(carbonyl) atoms, as seems to be the case.

The reactivity of **1** is illustrated through the reactions collected in Scheme 2. As expected for an unsaturated molecule, compound **1** readily adds CO (ca. 4 bar) at room temperature, but the reaction involves not just the addition of CO to the dimetal center (as observed for the methoxycarbyne analogue)[5c] but also to the carbyne ligand, to give the ketenyl derivative $[Mo_2Cp_2\{\mu\text{-C(Ph)CO}\}(\mu\text{-PCy}_2)(CO)_2]$ (**2**) almost quantitatively.[10] This process is fully reversed by irradiation of toluene solutions of **2** with visible−UV light at room temperature. Again, although several steps must be involved in both the forward and back reactions, no intermediates have been detected by IR monitoring of these processes. The molecule of **2** (Figure 2)[11] features a ketenyl ligand symmetrically bridging the dimetal center through its C atom. The intermetallic distance (2.6101(2) Å) is intermediate between that measured for the doubly bonded carbyne complex $[Mo_2Cp_2\{\mu\text{-C(CO}_2\text{Me)}\}(\mu\text{-PCy}_2)(CO)_2]$ (2.656(1) Å)[12] and that for the almost triply bonded phenyl complex $[Mo_2Cp_2(\mu\text{-Ph})(\mu\text{-PCy}_2)(CO)_2]$ (2.557(2) Å)[1] and therefore suggests that the

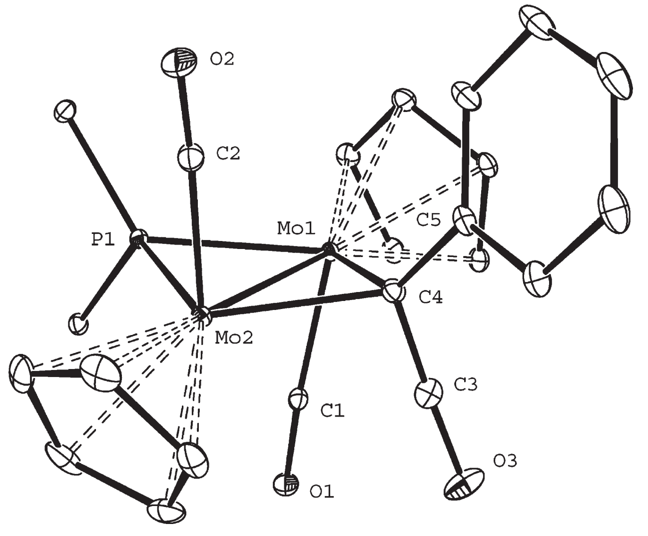
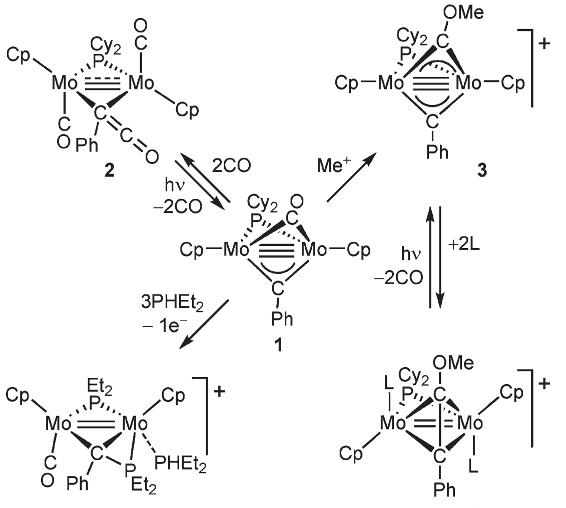


Figure 2. ORTEP drawing (30% probability) of compound **2**, with H atoms and cyclohexyl rings (except the C^1 atoms) omitted for clarity. Only one of the two independent molecules in the crystal lattice is shown. Selected bond lengths (Å) and angles (deg): Mo(1)−Mo(2) = 2.6101(2), Mo(1)−C(1) = 1.939(2), Mo(2)−C(2) = 1.957(2), Mo(1)−C(4) = 2.238(2), Mo(2)−C(4) = 2.255(2), Mo(1)−P(1) = 2.3984(4), Mo(2)−P(1) = 2.3857(4), C(4)−C(3) = 1.324(2), C(3)−O(3) = 1.177(2); C(1)−Mo(1)−Mo(2) = 75.2(1), C(2)−Mo(2)−Mo(1) = 92.3(1).

Scheme 2



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(8) X-ray data for **1**: red crystals, monoclinic ($C2/c$), $a = 25.741(4)$ Å, $b = 12.375(2)$ Å, $c = 19.531(3)$ Å, $\beta = 112.156(2)°$, $V = 5762(2)$ Å^3, $T = 120$ K, $Z = 8$, $R = 0.0793$ (observed data with $I > 2\sigma(I)$), GOF = 1.347.

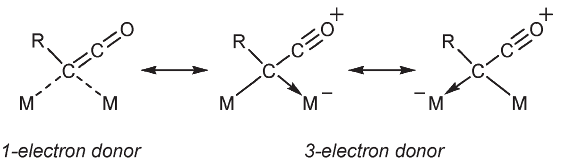
(9) García, M. E.; Melón, S.; Ramos, A.; Riera, V.; Ruiz, M. A.; Belletti, D.; Graiff, C.; Tiripicchio, A. *Organometallics* **2003**, *22*, 1983.

(10) Selected data for **2**: ν(CO) (CH_2Cl_2) 1993 (s), 1895 (s), 1838 (vs) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.52 MHz, CD_2Cl_2) δ 132.6 (s); $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2) δ 249.4 (d, $J_{CP} = 13$ Hz, MoCO), 242.0 (d, $J_{CP} = 16$ Hz, MoCO), 145.0 (s, μ-CCO), 15.8 (d, $J_{CP} = 1$ Hz, μ-CCO).

(11) X-ray data for **2**: brown-green crystals, triclinic ($P\bar{1}$), $a = 10.4310(1)$ Å, $b = 18.4643(3)$ Å, $c = 19.0331(2)$ Å, $\alpha = 108.999(1)°$, $\beta = 104.246(1)°$, $\gamma = 102.762(1)°$, $V = 3173.12(7)$ Å^3, $T = 100$ K, $Z = 4$, $R = 0.0314$ (observed data with $I > 2\sigma(I)$), GOF = 1.10.

(12) García, M. E.; García-Vivó, D.; Ruiz, M. A. *Organometallics* **2008**, *27*, 543.

Chart 1



ketenyl ligand in **2** is effectively providing the dimetal center with more than one electron. This effect has been previously found in other ketenyl complexes, such as the heterometallic complex $[FeWCp\{\mu\text{-}C(SiPh_3)CO\}(CO)_5]$, and can be rationalized by assuming the contribution of ketenyl (one-electron donor) and acylium (three-electron donor) resonant forms to the electronic structure of the bridging ligand (Chart 1).[13] Accordingly, the Mo−C bond distances in **2** (ca. 2.24 Å) are significantly shorter than those measured for the aforementioned phenyl complex (ca. 2.35 Å),[1] taken here as a rough model for a one-electron C(sp^2)-donor ligand, while the C−CO distance (1.324(2) Å) is slightly longer than that expected for a C(sp^2)−C(sp) double bond (ca. 1.31 Å). We should note that the presence of the phenyl substituent in the carbyne ligand is critical for the stability of this ketenyl complex. For instance, the analogous (unknown) methoxyl-substituted complex $[Mo_2Cp_2\{\mu\text{-}C(OMe)CO\}(\mu\text{-}PCy_2)(CO)_2]$ has been predicted by DFT calculations to spontaneously undergo a 1,2-shift of the methoxyl substituent to afford the (stable) carboxycarbyne isomer $[Mo_2Cp_2\{\mu\text{-}C(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$.[12]

Compound **1** undergoes easy O-alkylation at its bridging carbonyl with a variety of reagents to give the corresponding mixed alkoxycarbyne/phenylcarbyne derivatives. Thus, its reaction with excess CF_3SO_3Me at room temperature gives $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}CPh)(\mu\text{-}PCy_2)](CF_3SO_3)$ (**3**) in good yield,[14] along with small and variable amounts of a side product yet uncharacterized (δ_P 236.6 ppm). Spectroscopic data for **3** are comparable to those of the bis(methoxycarbyne) cation $[Mo_2Cp_2(\mu\text{-}COMe)_2(\mu\text{-}PCy_2)]^+$.[5a] Of particular interest is the presence of different carbyne ligands in **3**, denoted by the corresponding ^{13}C NMR resonances at 422.0 (μ-*C*Ph) and 365.6 ppm (μ-*C*OMe). We have previously shown that the mentioned bis(methoxycarbyne) complex undergoes an unusually reversible C−C coupling between its carbyne ligands.[5a,12] Analogously, compound **3** reacts with CO (290 K, 40 bar) or ^{t}BuCN (223 K) to give the corresponding alkyne complexes $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(OMe)CPh\}(\mu\text{-}PCy_2)L_2](CF_3SO_3)$ (L = CO (**4a**), CN^{t}Bu (**4b**)) resulting from the addition of two molecules of the ligand and C−C coupling between the carbyne ligands to yield a bridging phenylmethoxylacetylene molecule, a process that can be fully reversed in the case of the dicarbonyl compound **4a** upon photolysis in tetrahydrofuran solution.[15,16] We should note that only a few other reversible couplings between carbyne ligands have been reported to date, these taking place invariably at polynuclear (Fe_3 and Fe_4) iron clusters.[17,18] In fact, the transformations **3**/**4a** prove for the first time that two metal centers are enough to accomplish the reversible coupling between alkylidyne and alkoxycarbyne ligands, the process being triggered by the uptake and release of CO.

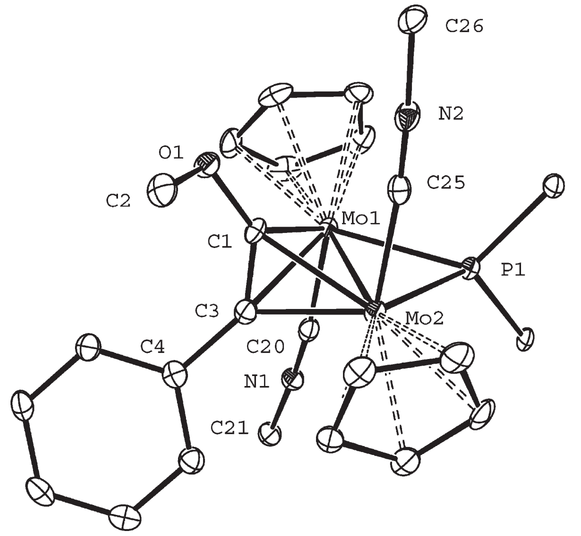


Figure 3. ORTEP drawing (30% probability) of compound **4b**, with H atoms, cyclohexyl rings, and ^{t}Bu groups (except the C^1 atoms) omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)−Mo(2) = 2.6377(6), Mo(1)−C(1) = 2.115(6), Mo(2)−C(1) = 2.227(5), Mo(1)−C(3) = 2.269(6), Mo(2)−C(3) = 2.149(6), C(1)−C(3) = 1.328(8), Mo(1)−C(20) = 2.075(6), Mo(2)−C(25) = 2.038(6), Mo(1)−P(1) = 2.379(1), Mo(2)−P(1) = 2.380(2); C(20)−Mo(1)−Mo(2) = 98.0(2), C(25)−Mo(2)−Mo(1) = 87.7(2).

The complexes **4** are formed in the above reactions mainly as the corresponding trans isomers, along with smaller amounts of the corresponding cis isomers (two cis isomers for the less crowded dicarbonyl complex; see the Supporting Information). An X-ray diffraction study on the major isomer in **4b** confirmed the trans arrangement of the isocyanide ligands and the coupling of the carbyne ligands to yield an alkyne molecule bound almost perpendicularly to the intermetallic bond (twist angle ca. 8°, Figure 3).[19] The structure is thus very similar to that of the dimetoxylacetylene complex $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2(OMe)_2\}(\mu\text{-}PCy_2)(CN^tBu)_2]^+$ [5a,12] and displays an analogously short intermetallic length (2.6377(6) Å), just below the separation measured for the mentioned 32-electron carbyne complex $[Mo_2Cp_2\{\mu\text{-}C(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (2.656(1) Å).[12] This suggests the presence of a double intermetallic bond and therefore indicates that the alkyne molecule can be viewed as a four-electron donor in this cation. The coupling of the carbyne ligands is retained in solution, as indicated by the considerable ^{13}C NMR shielding (relative to those in **3**) of the resonances for the corresponding metal-bound carbon atoms, now located at ca. 140 (μ-*C*OMe) and 125 (μ-*C*Ph) ppm.

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[13] Jeffery, J. C.; Ruiz, M. A.; Stone, F. G. A. *J. Organomet. Chem.* **1988**, *355*, 231.

[14] Selected data for **3**: $^{31}P\{^1H\}$ NMR (121.52 MHz, CD_2Cl_2) δ 265.6 (s); $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2) δ 422.0 (s, μ-*C*Ph), 365.6 (d, J_{CP} = 14 Hz, μ-*C*OMe).

[15] Selected data for *trans*-**4a**: ν(CO) (CH_2Cl_2) 1986 (m, sh), 1962 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.52 MHz, CD_2Cl_2) δ 155.3 (s); $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2) δ 218.0 (d, J_{CP} = 12 Hz, MoCO), 217.5 (d, J_{CP} = 11 Hz, MoCO), 138.0 (s, μ-*C*OMe), 125.6 (s, μ-*C*Ph).

[16] Selected data for *trans*-**4b**: ν(CN) (CH_2Cl_2) 2137 (s), 2118 (m, sh) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.52 MHz, CD_2Cl_2) δ 170.9 (s); $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2) δ 184.0, 172.5 (2d, J_{CP} = 4 Hz, MoCN),143.6 (s, μ-*C*OMe), 126.0 (s, μ-*C*Ph).

[17] Nuel, D.; Daham, F.; Mathieu, R. *Organometallics* **1985**, *4*, 1436.

[18] (a) Okazaki, M.; Takano, M.; Ozawa, F. *J. Am. Chem. Soc.* **2009**, *131*, 1684. (b) Okazaki, M.; Ohtani, T.; Ogino, H. *J. Am. Chem. Soc.* **2004**, *126*, 4104.

[19] X-ray data for **4b**: red crystals, monoclinic ($P2_1/c$), $a = 9.6041(2)$ Å, $b = 15.6382(5)$ Å, $c = 28.7158(7)$ Å, $\beta = 93.126(2)°$, $V = 4306.4(2)$ Å^3, $T = 100$ K, $Z = 4$, $R = 0.060$ (observed data with $I > 2\sigma(I)$), GOF = 1.099.

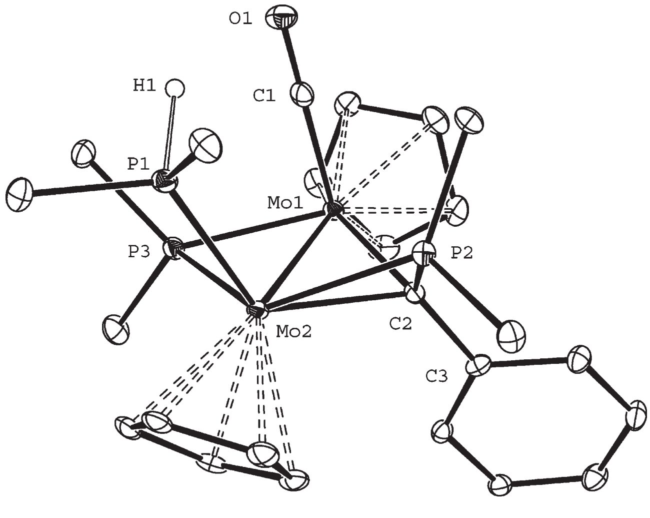

Figure 4. ORTEP drawing (30% probability) of compound **5**, with H atoms (except H(1)) and ethyl groups (except the C^1 atoms) omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)−Mo(2) = 2.7817(5), Mo(1)−C(1) = 1.930(4), Mo(2)−P(1) = 2.469(1), Mo(1)−P(3) = 2.344(1), Mo(2)−P(3) = 2.431(1), Mo(1)−C(2) = 2.104(4), Mo(2)−C(2) = 2.286(4), Mo(2)−P(2) = 2.446(1), C(2)−P(2) = 1.737(4); C(1)−Mo(1)−Mo(2) = 84.6(1), P(1)−Mo(2)−Mo(1) = 106.6(1), P(1)−Mo(2)−P(2) = 90.4(1), P(1)−Mo(2)−P(3) = 89.1(1), P(2)−Mo(2)−P(3) = 128.0(1).

The reactivity of the carbyne complex **1** can be much increased through one-electron oxidation. For instance, although **1** does not react with donor molecules such as secondary phosphines (HPR_2) or thiols (HSR) at room temperature, it does it instantaneously in the presence of stoichiometric amounts of the ferrocenium salt $[FeCp_2]BF_4$. The most impressive result is achieved in the reaction with $PHEt_2$, this leading almost instantaneously to the phosphinocarbene derivative $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^1,\kappa^1\text{-}C(Ph)PEt_2\}(\mu\text{-}PEt_2)(CO)(PHEt_2)](BF_4)$ (**5**) in high yield.[20] We have been able to grow good-quality crystals of the $(BAr'_4)^-$ salt of this cation (**5′**, Ar′ = 3,5-$C_6H_3(CF_3)_2$; Figure 4).[21] The coordination of the phosphinocarbene ligand in **5′** strongly resembles that usually observed for μ-η^1:η^2-alkenyl ligands, with the bridgehead C atom asymmetrically bound to the metal centers (Mo−C lengths ca. 2.10 and 2.29 Å) and the phosphorus atom strongly bound to both the C (ca. 1.74 Å) and Mo atoms (ca. 2.45 Å). The intermetallic distance (2.7817(5) Å) is significantly longer than expected for a double metal−metal bond (cf. 2.6377(6) Å in **4b**), perhaps as a result of the large number of P-donors in the cation. We finally note that only three other complexes having a similarly bridging phosphinocarbene ligand appear to have been previously reported, these being also formed through the coupling between coordinated phosphide and carbyne ligands.[22] The formation of **5** is likely to be initiated by an electron transfer to give the extremely reactive 29-electron radical $[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(\mu\text{-}CO)]^+$ (not detected) rapidly adding up to three $PHEt_2$ molecules, one of them replacing the dicyclohexylphosphide bridge (itself a very unusual reaction), another one being coupled to the carbyne ligand (and being dehydrogenated), and a third one just being bound in a terminal fashion to alleviate the coordinative unsaturation of the cation so generated. Further work is now in progress to examine the mechanistic aspects and synthetic potential of this oxidatively induced reactivity of the carbyne complex **1**.

In summary, we have discovered an efficient synthetic route to a novel and highly unsaturated benzylidyne-bridged complex. Our initial research suggests that its reactivity may involve unusual C−C and C−P coupling processes, with the first ones being reversibly induced by the addition of simple two-electron-donor ligands. Further studies are being carried out now to explore in more detail the chemical behavior of this electron-deficient carbyne complex.

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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 **1**, **2**, **4b**, and **5′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Selected data for **5**: ν(CO) (CH_2Cl_2) 1850 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR (162.09 MHz, CD_2Cl_2) δ 154.2 (d, J_{PP} = 18 Hz, μ-P), 41.8 (dd, J_{PP} = 54, 18 Hz, PCPh), −48.9 (d, J_{PP} = 54 Hz, PH); $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2): δ 250.6 (d, J_{CP} = 10 Hz, MoCO), 129.6 (d, J_{CP} = 20 Hz, μ-CP).

(21) X-ray data for **5′**: brown crystals, triclinic ($P\bar{1}$), a = 12.9909(6) Å, b = 13.0073(6) Å, c = 19.9051(9) Å, α = 82.299(3)°, β = 74.667(3)°, γ = 86.240(3)°, V = 3212.9(3) $Å^3$, T = 100 K, Z = 2, R = 0.0489 (observed data with $I > 2\sigma(I)$), GOF = 1.06.

(22) (a) Davies, S. J.; Howard, J. A. K.; Pilotti, M. U.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1989**, 190. (b) El Amin, E. A. E.; Jeffery, J. C.; Walters, T. M. *J. Chem. Soc., Chem. Commun.* **1990**, 170.