C–C and C–N Couplings in Reactions of the Benzylidyne-Bridged Complex $[Mo_2Cp_2(\mu\text{-CPh})(\mu\text{-PCy}_2)(CO)_2]$ with Small Unsaturated Organics.

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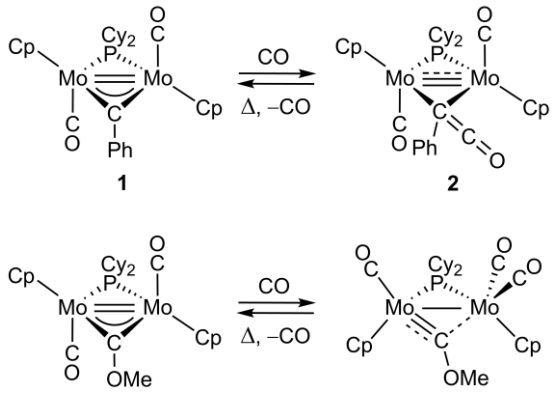
Supporting Information Placeholder

ABSTRACT: The ability of the title compound to promote C–C coupling processes has been analyzed by examining its reactions with diazoalkanes, alkynes and other unsaturated organic molecules. The title compound reacted with N_2CPh_2 at room temperature to give a mixture of the ketenyl complex $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-C(Ph)CO}\}(\mu\text{-PCy}_2)(CO)(\kappa^1\text{-}N_2CPh_2)]$ and the carbyne complex $[Mo_2Cp_2(\mu\text{-CPh})(\mu\text{-PCy}_2)(CO)(\kappa^1\text{-}N_2CPh_2)]$, products which can be converted into each other by addition/removal of CO, respectively. In contrast, denitrogenation took place rapidly in analogous reactions with diazomethane and benzylazide at room temperature, to yield respectively the corresponding alkenyl $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-C(Ph)CH}_2\}(\mu\text{-PCy}_2)(CO)_2]$ and iminoacyl $[Mo_2Cp_2\{\mu\text{-C(Ph)NCH}_2\text{Ph}\}(\mu\text{-PCy}_2)(CO)_2]$ derivatives, following from selective C–C and C–N couplings. The title compound reacted at 333 K with methyl propiolate to give the corresponding propenylylidene derivative $[Mo_2Cp_2\{\mu\text{-}\kappa^2\text{:}\eta^3\text{-CPhCHC(CO}_2\text{Me)}\}(\mu\text{-PCy}_2)(CO)_2]$, as a result of selective coupling of the carbyne ligand to the terminal carbon of the alkyne. A related complex could be obtained when using the internal alkyne dimethyl acetylenedicarboxylate.

INTRODUCTION

Carbyne complexes constitute a vast family of organometallic molecules with a rich chemistry much derived from the multiple character of the metal–carbyne bond, of highest order for terminal ligands.[1] Multiplicity in the M–C bond is significantly reduced in carbyne-bridged binuclear complexes, and hence the corresponding reactivity, but the latter can be increased in the presence of metal–metal multiple bonds, this promoting fast coordination of external molecules and allowing for possible cooperative effects between M–M and M–C multiple bonds.[2] For instance, we have shown previously that 30-electron complex cations of the type $[Mo_2Cp_2(\mu\text{-CX})(\mu\text{-COR})(\mu\text{-PCy}_2)]^+$ (X = OMe, Ph; R = H, Me), having metal–metal triple bonds, add readily simple ligands such as CO and isocyanides, thus promoting C–C coupling processes between carbyne ligands which can be reversed,[3,4] and a similarly reversible P–C coupling between phosphanyl and benzylidyne ligands can be induced at the triply-bonded thiolate-bridged complex $[Mo_2Cp_2(\mu\text{-CPh})(\mu\text{-PCy}_2)(\mu\text{-SPh})]^+$ upon carbonylation, to give the corresponding phosphinocarbene derivative.[5] Nucleophilic attack of simple ligands on bridging carbyne groups to give carbene or related derivatives, however, can also occur at electron-precise complexes provided they are electrophilic enough, a circumstance particularly well met for cationic complexes.[6] For instance, the methylidyne-bridged diiron cation $[Fe_2Cp_2(\mu\text{-CH})(\mu\text{-CO})(CO)_2]^+$ has been shown to react under mild conditions with CO and CN^tBu to give the corresponding ketenyl- and iminoketenyl-bridged derivatives.[7]

Scheme 1



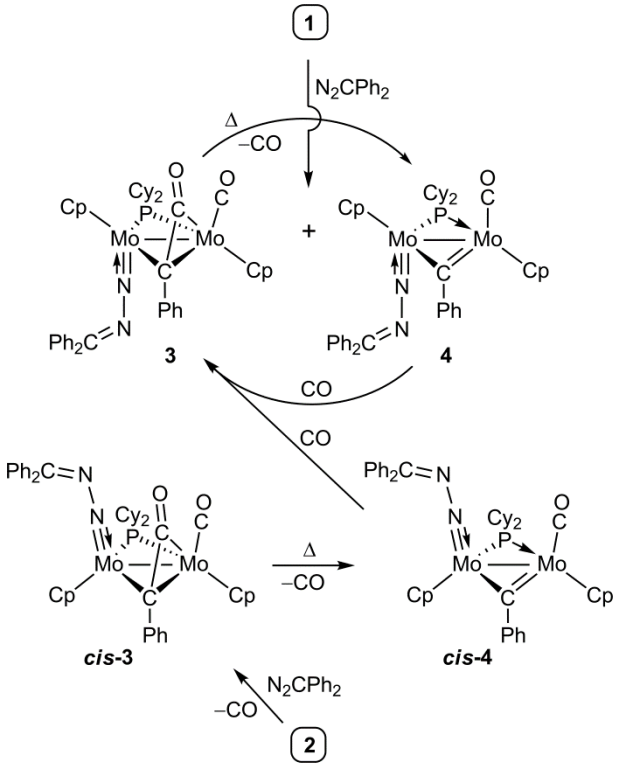
Some time ago we reported the preparation of the 32-electron benzylidyne complex $[Mo_2Cp_2(\mu\text{-CPh})(\mu\text{-PCy}_2)(CO)_2]$ (**1**), an unsaturated compound readily reacting with CO to give the ketenyl-bridged derivative $[Mo_2Cp_2\{\mu\text{-C(Ph)CO}\}(\mu\text{-PCy}_2)(CO)_2]$ (**2**), a molecule still retaining substantial unsaturation at the dimetal site (Scheme 1).[4a,8] This result was somewhat unexpected by recalling that the related methoxycarbyne-bridged complex would react under analogous conditions to just give the corresponding electron-precise tricarbonyl derivative, this being accompanied by a *trans* to *cis* rearrangement of the Mo_2Cp_2 platform.[9] This difference pointed to some particular preference of complex **1** for C–C coupling processes involving the carbyne ligand, a sort of reactions of general interest in the context of Fischer-Tropsh chemistry, which involves C–C couplings between different hydrogenation products of carbon monoxide, notably methyne

and methylene ligands.[10] We here analyze the ability of **1** for promoting this sort of C–C couplings by exploring its reactions with diazoalkanes, alkynes and some other small unsaturated organic molecules. A preliminary account of some of these reactions has appeared.[11]

RESULTS AND DISCUSSION

Reactions with diphenyldiazomethane. Compound **1** reacts with N_2CPh_2 at room temperature, but only at very high concentrations of reagents, to give a mixture of two products having in each case a metal-bound diazoalkane molecule: the ketenyl complex $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(Ph)CO\}(\mu\text{-}PCy_2)(CO)(\kappa^1\text{-}N_2CPh_2)]$ (**3**) and the carbyne complex $[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(CO)(\kappa^1\text{-}N_2CPh_2)]$ (**4**). Separate experiments revealed that these products are related by carbonylation/decarbonylation processes, therefore allowing for their selective preparation (Scheme 2). Thus, the above mixture can be transformed into pure **3** upon reaction with CO (ca. 3 atm) in dichloromethane solution at room temperature. In contrast, heating at 353 K a toluene solution of this mixture for 30 min yields pure compound **4** (see the Experimental Section). We note that no denitrogenation of the diazoalkane molecule is observed in the above reactions, a circumstance also observed in reactions of this reagent with the triply-bonded $[Mo_2Cp_2(CO)_4]$,[12] and more recently in reactions with the 30-electron ditungsten hydride $[W_2Cp_2H(\mu\text{-}PCy_2)(CO)_2]$.[13]

Scheme 2



The formation of **3** gives experimental support to our previous hypothesis that carbonylation of **1** to yield the ketenyl complex **2** would likely imply initial coordination of CO to the unsaturated dimetal center of **1** followed by reorganization, rather than direct attack of CO to the electron-rich carbyne ligand.[8] In line with this hypothesis, a ^{31}P NMR monitoring of the carbonylation reaction of **4** revealed the transient formation of two new species **A** and **B** (identified by ^{31}P NMR resonances at 201.5 and 197.4 ppm) which were also detected as intermediate species in the reaction of **1** with N_2CPh_2. These transient species seem to be the actual precursors of the ketenyl complex **3** and presumably are two isomers of the electron-precise species of formula $[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(CO)_2(\kappa^1\text{-}N_2CPh_2)]$ that would follow either from coordination of a diazoalkane molecule to complex **1**, or from coordination of a CO molecule to complex **4**, thus being structurally related to the tricarbonyl complex $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(CO)_3]$ depicted in Scheme 1.

The presence of a ketenyl ligand in **3** suggests that this complex could possibly be obtained also through reaction of diphenyldiazomethane with the ketenyl complex **2**. Indeed such reaction takes place rapidly at room temperature, but the product is an isomer of the sought complex, now with the terminal carbonyl and diazoalkane ligands in a cisoid arrangement (***cis*-3**, Scheme 2). This complex can be decarbonylated under the same conditions used for its transoid isomer (toluene solution, 353 K, 30 min), which now gives the corresponding carbyne derivative ***cis*-4**, along with a small amount of the transoid isomer **4** (ratio ca. 5/1), thus indicating a good retention of the stereochemistry at the Mo_2Cp_2 platform. The formation of ***cis*-4**, however, is now an irreversible process, since carbonylation of the latter does not regenerate the cisoid isomer but the transoid one **3** (Scheme 2).

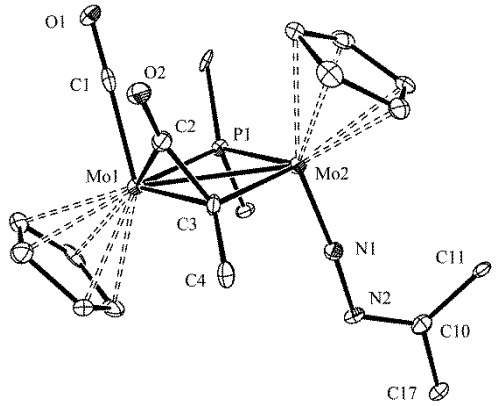


Figure 1. ORTEP drawing (30% probability) of compound **3**, with H atoms, cyclohexyl and phenyl rings (except the C^1 atoms) omitted for clarity.[11] Selected bond lengths (Å) and angles (deg): Mo1–Mo2 = 2.8935(9), Mo1–P1 = 2.364(2), Mo1–C1 = 1.932(8), Mo1–C2 = 2.163(7), Mo1–C3 = 2.203(7), Mo2–P1 = 2.432(2), Mo2–C3 = 2.148(7), Mo2–N1 = 1.748(5), N1–N2 = 1.338(7), N2–C10 = 1.306(8), C3–C2 = 1.398(9), C2–O2 = 1.215(8); Mo2–Mo1–C1 = 96.4(2), Mo1–Mo2–N1 = 103.6(2). Mo2–N1–N2 = 174.6(5), N1–N2–C10 = 120.0(6), C3–C2–O2 = 142.3(7), Mo1–C2–O2 = 144.2(5).

Structural Characterization of Ketenyl Complexes 3. The structure of the transoid isomer **3** was determined by an X-ray study during our preliminary analysis of the chemistry of **1** (Figure 1),[11] and will be only briefly discussed here. The terminal diazoalkane ligand displays an imido-like coordination mode,[14] with almost triple Mo–N (1.748(5) Å) and single N–N (1.338(7) Å) bonds, and therefore acts as a four-electron donor to the dimetal center, as previously found in the related complexes $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)(\kappa^1\text{-}N_2CPh_2)]$,[15a] $[Mo_2Cp_2(CO)_3(CPh_2)(\kappa^1\text{-}N_2CPh_2)]$,[15b] and $[W_2Cp_2H(\mu\text{-}$

$PCy_2)(CO)_2\{\kappa^1\text{-}N_2CH(SiMe_3)\}]$.[13] The superior donor ability of the diazoalkane ligand (compared to CO) is balanced by an alkenyl-like asymmetric coordination ($\mu\text{-}\kappa^1\text{:}\eta^2$ mode) of the three-electron donor ketenyl ligand, η^2-bound to the carbonyl-bearing Mo atom, and by a stronger coordination of the PCy_2 ligand to that atom. Overall, the molecule formally is electron-precise, and this is in agreement with the relatively large intermetallic length of ca. 2.90 Å. We finally note that the asymmetric coordination mode of the ketenyl ligand found in **3** has been previously characterized in a few, usually heterometallic substrates,[16] the only homometallic precedent being the ditungsten complex $[W_2(\mu\text{-}Br)Br_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(4\text{-}Me\text{-}C_6H_4)CO\}(CO)\{\mu\text{-}F_2PN(Me)PF_2\}_2]$.[17]

Table 1. Selected IR and NMR Data for New Compounds

Compound	ν(CO)[a]	δ(P)[b]	$\delta(\mu$-C)[b]
$[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(CO)_2]$ (**1**)[c]	1905 (w, sh), 1880 (vs)	117.6	428.4 [5]
$[Mo_2Cp_2\{\mu\text{-}C(Ph)CO\}(\mu\text{-}PCy_2)(CO)_2]$ (**2**)[c]	1993 (s), 1895 (s), 1838 (vs)	132.6	15.8 [1]
$[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(Ph)CO\}(\mu\text{-}PCy_2)(CO)(\kappa^1\text{-}N_2CPh_2)]$ (**3**)	1864 (s)	216.4	134.4
cis-$[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(Ph)CO\}(\mu\text{-}PCy_2)(CO)(\kappa^1\text{-}N_2CPh_2)]$ (***cis*-3**)	1877 (s)	202.7	132.7
$[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(CO)(\kappa^1\text{-}N_2CPh_2)]$ (**4**)	1872 (s)	188.7	373.5 [6]
cis-$[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(CO)(\kappa^1\text{-}N_2CPh_2)]$ (***cis*-4**)	1895 (s)	185.1	
$[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(Ph)CH_2\}(\mu\text{-}PCy_2)(CO)_2]$ (**5**)	1884 (s), 1790 (m)	143.6	182.0
$[Mo_2Cp_2\{\mu\text{-}C(Ph)NCH_2Ph\}(\mu\text{-}PCy_2)(CO)_2]$ (**6**)	1885 (w, sh), 1859 (vs)	155.5[d]	189.9 [23][d]
$[Mo_2Cp_2\{\mu\text{-}\kappa^2\text{:}\eta^3\text{-}CPhCHC(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (**7a**)	1916 (s), 1886 (vs), 1676 (w),[e] 1658 (w)[e]	140.3	137.7 78.4 [28]
$[Mo_2Cp_2\{\mu\text{-}\kappa^2\text{:}\eta^3\text{-}CPhC(CO_2Me)C(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (**7b**)	1926 (m, sh), 1910 (vs), 1676 (m)[e]	154.7	101.0 80.0 [24]
cis-$[Mo_2Cp_2\{\mu\text{-}\kappa^2\text{:}\eta^3\text{-}CPhC(CO_2Me)C(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (***cis*-7b**)	1964 (vs), 1909 (w, sh), 1670 (w)[e]	135.7	99.5 63.7 [30]

[a] Recorded in dichloromethane solution, ν in cm^{-1}. [b] Recorded in CD_2Cl_2 solutions at 290 K and 300.13 (^{1}H), 121.50 (^{31}P) or 75.47 (^{13}C) MHz, δ in ppm relative to internal TMS (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P); Coupling constants to ^{31}P are shown in square brackets and are given in Hz. [c] Data taken from reference 8. [d] Recorded at 253 K. [e] Stretch of CO_2Me groups.

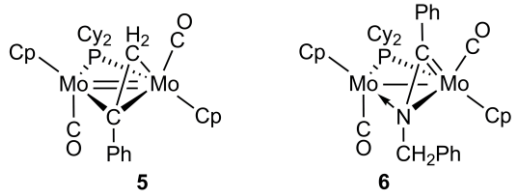
Spectroscopic data for **3** are consistent with retention in solution of the structure found in the crystal. In particular, we note that its ^{31}P NMR resonance is considerably more deshielded than that of the 32-electron precursor **1** (Table 1), and has a chemical shift rather approaching the values found for related electron-precise complexes (*cf.* 218.8 ppm for $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$).[18] This requires the retention of the 3-electron donor $\mu\text{-}\kappa^1\text{:}\eta^2$ coordination of the ketenyl ligand in solution, rather than adopting the more symmetrical $\mu\text{-}\kappa^1\text{:}\kappa^1$ mode found in complex **2**, which is consistent with the large difference in the ^{13}C chemical shifts of the corresponding bridgehead carbon atoms of these two compounds (134.4 *vs.* 15.8 ppm). Spectroscopic data for the cisoid isomer ***cis*-3** are similar to those of **3** as expected. Interestingly, its C–O stretching frequency is a bit higher, as usually found when comparing related pairs of *cis* and *trans* isomers of the oxo carbonyl complexes $[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(O)(CO)]$,[19] and $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(O)(CO)]$,[20] which are isoelectronic with our diazoalkane complexes. The conformation assumed for this cisoid isomer is consistent with the observation of a positive NOE enhancement between the hydrogen atoms of the Cp rings and those of the phenyl ring of the carbyne ligand.

Solution Structure of Carbyne Complexes 4. Compound **4** and its *cis* isomer are assumed to display terminal, imido-like diazoalkane ligands, as found for **3**. This renders electron-precise molecules which are isoelectronic with the carbyne-bridged oxo complexes *trans*- and *cis*-$[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(O)(CO)]$ structurally characterized recently by us.[19] Indeed, spectroscopic data for **4** and ***cis*-4** are comparable to those of the mentioned oxo complexes as concerning their considerably deshielded ^{31}P (ca. 190 ppm) and ^{13}C(carbyne) NMR resonances; as expected, the *cis* isomer displays a C–O stretching frequency significantly higher than that of the *trans* isomer **4** (Table 1). The structural data of the oxo complexes mentioned above indicate that, in order to balance the much stronger donor ability of the oxo ligand (compared to CO), both the carbyne and the bridging PCy_2 groups bind more tightly the carbonyl-bearing Mo atom, and the same structural effect is assumed to occur for our diazoalkane complexes, which are thus depicted in Scheme 2 with a very asymmetric coordination of the bridging ligands.

Reaction of 1 with Diazomethane. In contrast to the reaction with diphenyldiazomethane discussed above, denitrogenation takes place rapidly in the reaction of **1** with diazomethane at room temperature. This incorporates a methylene group to the dimetal centre of **1**, eventually coupled with the carbyne ligand to yield the 32-electron alkenyl-bridged derivative $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(Ph)CH_2\}(\mu\text{-}PCy_2)(CO)_2]$ (**5**) (Chart 1). This sort of reaction is well documented in the chemistry of heterometallic carbyne-bridged complexes,[1b] and has been also observed previously for the cationic methoxycarbyne complex $[W_2Cp_2(\mu\text{-}COMe)(CO)_2(\mu\text{-}Ph_2CH_2PPh_2)]^+$, a molecule isoelectronic to **1**.[21]

We have previously reported the preparation of complexes very similar to **5** through the reaction of the unsaturated hydrides $[M_2Cp_2(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_2]$ with HCC(*p*-tol) (M = Mo, W; *p*-tol = 4-C_6H_4Me).[22] Spectroscopic data for **5** (Table 1 and Experimental Section) are indeed very similar to those of the mentioned *p*-tol-substituted compounds and will not be discussed in detail. We just note that these complexes are thermally unstable and evolve at room temperature to yield the corresponding β-substituted alkenyl isomers, a transformation also observed for **5** but not investigated in detail.

Chart 1

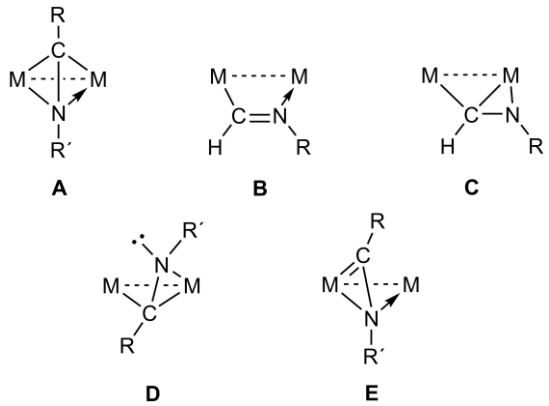


Reaction of 1 with Benzylazide. As found in the reactions with diphenyldiazomethane, reaction of **1** with benzylazide occurs at room temperature, but only at high concentration of reagents, and proceeds with denitrogenation along with carbyne to nitrene coupling, to eventually give the iminoacyl-bridged derivative $[Mo_2Cp_2\{\mu\text{-C(Ph)NCH}_2\text{Ph}\}(\mu\text{-PCy}_2)(CO)_2]$ (**6**) in good yield (Chart 1). Related heterocumulenes such as ^{t}BuNCO and (*p*-tol)NCS failed to react with **1** under the same conditions. Compound **6** was thermally unstable, and decomposed slowly at room temperature to give a mixture of uncharacterized species. Unfortunately, all attempts to grow single crystals of this product were unsuccessful, and the precise definition of the coordination mode of the iminoacyl ligand in **6** remains somewhat uncertain even after consideration of the corresponding spectroscopic data and the results of theoretical calculations discussed below.

The IR spectrum of **6** in solution displays two C–O stretches with a pattern (weak and strong, in order of decreasing frequency) characteristic of transoid $M_2(CO)_2$ oscillators having essentially antiparallel CO ligands,[23] as found in the parent complex **1** (Table 1). The MoCp fragments of the molecule, however, are inequivalent, as revealed by the observation of distinct NMR resonances for the pairs of CO and Cp ligands (see the Experimental Section), and the chemical shifts of the bridgehead atoms of the phosphanyl (δ_P 155.5 ppm) and iminoacyl (δ_C 189.9 ppm) ligands are comparable to those of the corresponding atoms in the alkenyl complex **5**. The resonances for the bridgehead carbon atom in these two compounds, however, differ substantially in their two-bond coupling to the P atom, being negligible in the alkenyl complex **5** but relatively high for **6** (J_{PC} = 23 Hz), and this indicates that the P–Mo–C angles involving the bridgehead carbon in both compounds probably differ substantially from each other.[24]

We have previously prepared formimidoyl- and iminoacyl-bridged complexes related to compound **6** through insertion of isocyanides into unsaturated hydride- and alkyl-bridged complexes of the type $[M_2Cp_2(\mu\text{-X})(\mu\text{-PCy}_2)(CO)_2]$ (M = Mo, W; X = H, Me).[25,26] In most cases, the coordination of the *C*,*N*-donor ligand in these compounds corresponds to the 5-electron donor $\mu\text{-}\eta^2\text{:}\eta^2$ mode (**A** in Chart 2), which in these cases allows the dimetal centre to reach electronic saturation. The bridgehead carbon atom in this coordination mode is characterized by a relatively shielded ^{13}C NMR resonance around 60 ppm which displays a substantial P–C coupling of ca. 30 Hz, with the latter feature being related to the acute value of the P–M–C angle in this arrangement for the mentioned complexes (N atom close to the M_2P plane). Only in the case of complex $[W_2Cp_2(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-HCNXyl})(\mu\text{-PCy}_2)(CO)_2]$ we found that the preferred coordination of the *C*,*N*-donor ligand was the 3-electron donor $\mu\text{-}\kappa^1\text{:}\kappa^1$ mode (**B** in Chart 2), which was attributed to steric effects,[26] and the formimidoyl carbon atom in this complex expectedly gives rise to a quite deshielded ^{13}C NMR resonance (215.0 ppm) with negligible P–C coupling (the computed P–W–C angle in this arrangement is ca. 125°). Thus the carbon atom of the formimidoyl ligand in **6** seems to have a chemical shift not far from that expected for mode **B**, but a P–C coupling indicative of a P–Mo–C angle substantially different. In search for possible structural alternatives we noticed that an analysis of the crystallographic databases revealed that, in the case of formimidoyl-bridged complexes, there were a few examples displaying a third possible coordination geometry for this sort of bridging ligand, the planar $\mu\text{-}\kappa^1\text{:}\eta^2$ mode (**C** in Chart 2),[27] this implying a less obvious formal contribution to the dimetal centre, somewhere between 3 and 5 electrons depending on the degree of π(N to M) bonding contribution to the M–N interaction. Still non-planar, $\mu\text{-}\kappa^1\text{:}\eta^2$ coordination modes can be also conceived for this sort of *C*,*N*-donor ligands (**D** and **E** in Chart 2), although no examples of them seem to have been identified crystallographically so far.

Chart 2



The NMR spectroscopic properties of the iminoacyl carbon atom in **6** (high chemical shift and high P–C coupling) might be consistent with a non-planar coordination of type **E** for the iminoacyl ligand in this compound. To test such hypothesis we resorted to density functional theory (DFT) calculations in search for likely energy minima of this compound (see Experimental Section and the Supporting Information for details). We explored for **6** possible geometries for all coordination modes **A** to **E**, but no energy minima with iminoacyl coordination of types **C** and **E** were found. The most stable isomer was found to be the one of type **B**, this being followed by two isomers of type **A** (**6A1** and **6A2** in Figure 2). Incidentally, we recall here that the same relative ordering was computed for the formimidoyl complex $[W_2Cp_2(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-HCNXyl})(\mu\text{-PCy}_2)(CO)_2]$.[26] We also note that two isomers of type **D** were found, but these were too energetic (some 80 kJ/mol above **6B**) to be considered as likely structures for compound **6**. Interestingly, the computed ^{13}C NMR parameters for the most

stable isomers **6B** and **6A1** (see the SI) reproduced reasonably well the experimental values, already discussed, measured for compounds actually displaying such structures,[25,26] and thus gives credibility to our hypothesis that the actual structure of **6** in solution does not correspond to any of the types **A** to **D**. We still consider a structure of type **E**, which can be viewed as intermediate between structures **6A1** and **6B**, as the more likely structure for compound **6** in solution. Perhaps our failure to find such a minimum in the corresponding potential energy surface is related to the low thermal stability of this compound, possibly a kinetic product which decomposes rapidly to products different from its more stable iminoacyl isomer **6B**.

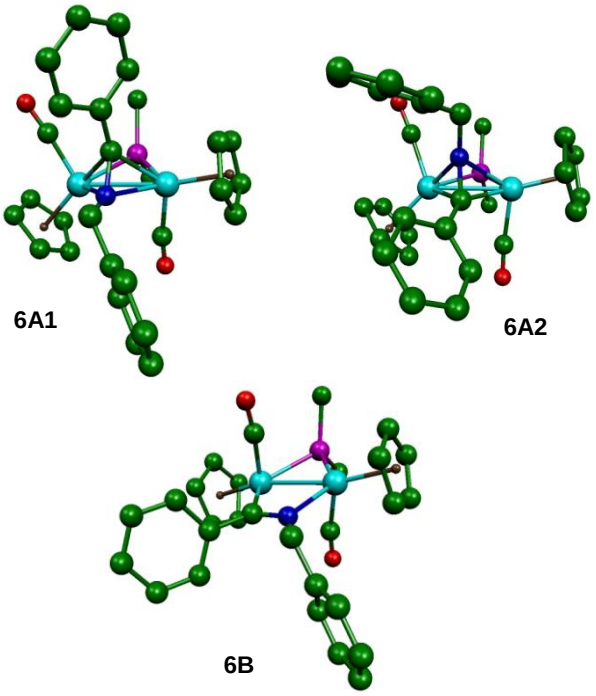
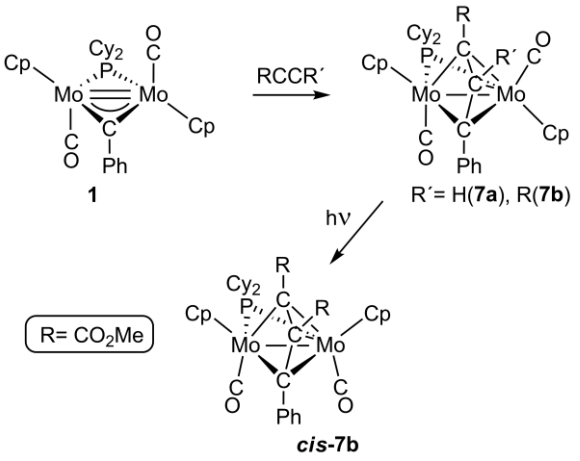


Figure 2. DFT-optimized structures of different isomers of compound **6** with the iminoacyl ligand in coordination modes **A** and **B**, with H atoms omitted. Relative Gibbs free energies were 15.9 (**6A1**), 38.5 (**6A2**) and 0.0 kJ/mol (**6B**).

Reaction of 1 with Alkynes. Compound **1** reacts at 333 K in toluene solution with an activated terminal alkyne such as methyl propiolate to give the corresponding propenylylidene derivative $[Mo_2Cp_2\{\mu\text{-}\kappa^2\text{:}\eta^3\text{-}CPhCHC(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (**7a**), a species following from selective coupling of the carbyne ligand to the terminal carbon of the alkyne (Scheme 3). A related complex $[Mo_2Cp_2\{\mu\text{-}\kappa^2\text{:}\eta^3\text{-}CPhC(CO_2Me)C(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (**7b**) could be obtained when using the internal alkyne dimethyl acetylenedicarboxylate, although in that case the reaction had to be carried out at 393 K to overcome the higher steric barrier involved in the corresponding C–C coupling. In any case, we note that this behavior is comparable to the one previously found for related carbyne-bridged complexes such as the dimolybdenum complex $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(CO)_2]$,[28] or the heterometallic $[FeMoCp\{\mu\text{-}C(p\text{-}tol)\}(CO)_5]$.[29]

In an attempt to test the reversibility of the C–C coupling process leading to complexes **7** we irradiated tetrahydrofuran solutions of **7b** with visible-UV light in the hope that an hypothetical decarbonylation could in turn trigger a C–C cleavage process. Instead, a full *trans* to *cis* isomerization of the Mo_2Cp_2 platform of **7b** takes place under these conditions, to give the *cis*-dicarbonyl isomer *cis*-$[Mo_2Cp_2\{\mu\text{-}\kappa^2\text{:}\eta^3\text{-}CPhC(CO_2Me)C(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (***cis*-7b**) in a selective way (Scheme 3).

Scheme 3



Structural Characterization of Propenylylidene Derivatives 7. The structure of compound **7a** was determined by an X-ray study during our preliminary exploration on the chemistry of **1** (Figure 3),[11] and turned to be very similar to that of *trans*-$[Mo_2Cp_2\{\mu\text{-}\kappa^2\text{:}\eta^3\text{-}C(OMe)CHC(p\text{-}tol)\}(\mu\text{-}PCy_2)(CO)_2]$, a molecule which we have discussed in detail previously,[28] therefore no further discussion on the structural aspects of compounds **7** is needed.

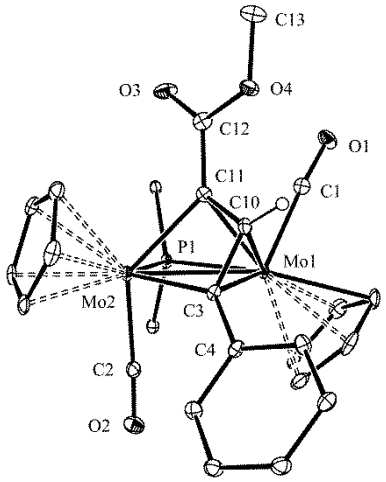


Figure 3. ORTEP drawing (30% probability) of compound **7a**, with H atoms (except H10) and cyclohexyl rings (except the C^1 atoms) omitted for clarity.[11] Selected bond lengths (Å) and angles (deg): Mo1–Mo2 = 2.8349(5), Mo1–P1 = 2.475(1), Mo1–C1 = 1.971(5), Mo1–C3 = 2.399(4), Mo1–C10 = 2.279(5), Mo1–C11 = 2.198(5), Mo2–P1 = 2.416(1), Mo2–C2 = 1.991(5), Mo2–C3 = 2.184(4), Mo2–C11 = 2.193(5), C3–C10 = 1.402(6), C10–C11 = 1.446(6), C11–C12 = 1.458(7), C12–O3 = 1.210(6), C12–O4 = 1.350(6); Mo2–Mo1–C1 = 117.9(1), Mo1–Mo2–C2 = 84.0(1).

Spectroscopic data in solution for **7a** and **7b** (Table 1 and Experimental section) are similar to each other and consistent with the solid-state structure of the former, thus indicating

retention of this structure in solution. These data are also comparable to those previously reported for related propenylylidene complexes of the type [$Mo_2Cp_2\{\mu$-κ^2:η^3-C(OMe)CRCR´}(μ-PCy_2)$(CO)_2$] and will not be discussed in detail. We just note that the symmetric C–O stretch for **7a** is now of strong (instead of weak) intensity, in agreement with the angle of ca. 150° defined by the carbonyl ligands in its quite distorted transoid $Mo_2(CO)_2$ oscillator. However, the symmetric stretch for **7b** is weaker, indicative of the presence of a less distorted transoid $Mo_2(CO)_2$ oscillator in that case. We also note for both compounds the quite different coupling to P of the bridging C atoms of the hydrocarbon chain, negligible for the C(Ph) atom and of ca. 25 Hz for the C(CO_2Me) atom, in agreement with the much more acute P–Mo–C angle in the latter case (average values in the solid-state structure of **7a** are ca. 105 and 78° respectively).[24]

Spectroscopic data for the cisoid isomer ***cis*-7b** are comparable to those of its transoid isomer **7b**, but there are two significant differences. First, the symmetric C–O stretch is now much stronger than the asymmetric one, as expected for a $M_2(CO)_2$ oscillator having almost parallel CO ligands.[23] The second spectroscopic difference is unexpected: the ^{1}H and ^{13}C NMR spectra indicates that both MoCp(CO) fragments of the molecule are apparently equivalent, which is inconsistent with the asymmetric coordination of the propenylylidene ligand in this complex, and this situation remained the same on cooling the solution down to 183 K. We have previously encountered the same situation in the related methoxy-substituted complex *cis*-[$Mo_2Cp_2\{\mu$-κ^2:η^3-C(OMe)CRCR}(μ-PCy_2)$(CO)_2$] (R = CO_2Me),[28] and have interpreted it as resulting from a fluxional process whereby the central C atom of the hydrocarbon chain (C10 in Figure 3) binds alternatively each of the Mo atoms, a rearrangement which yields, on the fast exchange limit, equivalent environments for the pairs of CO and Cp ligands.

CONCLUDING REMARKS

The electronic and coordinative unsaturation of dicarbonyl complex **1** facilitates the coordination to its dimetal center of small unsaturated organic molecules such as diazoalkanes, azides and activated alkynes under mild conditions, whereby new molecules of low thermal stability can be prepared, as it is the case of the alkenyl complex **5**, the iminocyl complex **6** or even the ketenyl complex **3**. Coupling of the carbyne ligand to the incoming molecule is strongly favored in the case of activated alkynes, but for diazoalkanes and azides such a process seems to be linked to denitrogenation, otherwise no reaction (azides) or carbyne-carbonyl coupling (diazoalkanes) takes place instead.

EXPERIMENTAL SECTION

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures, and distilled prior to use.[30] Compounds **1** and **2**,[8] N_2CPh_2,[31] and Et_2O solutions of CH_2N_2,[32] were prepared as described previously, and all other reagents were obtained from the usual commercial suppliers and used as received, unless otherwise stated. Petroleum ether refers to that fraction distilling in the range 338-343 K. Photochemical experiments were performed using jacketed Pyrex Schlenk tubes cooled by tap water (ca. 288 K). A 400 W medium-pressure mercury lamp placed ca. 1 cm away from the Schlenk tube was used for these experiments. Filtrations were carried out through diatomaceous earth unless otherwise indicated. Chromatographic separations were carried out using jacketed columns refrigerated by tap water (ca. 288 K) or by a closed 2-propanol circuit kept at the desired temperature with a cryostat. Commercial aluminum oxide (activity I, 70-290 mesh) was degassed under vacuum prior to use. The latter was mixed afterwards under nitrogen with the appropriate amount of water to reach activity IV. IR stretching frequencies of CO ligands were measured in solution using CaF_2 windows. NMR spectra were routinely recorded at 300.13 (^{1}H), 121.50 (^{31}P{^{1}H}) and 75.47 MHz (^{13}C{^{1}H}) at 295 K in CD_2Cl_2 solution unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (*J*) are given in Hertz.

Preparation of [$Mo_2Cp_2\{\mu$-κ^1:η^2-C(Ph)CO}(μ-PCy_2)(CO)(κ^1-N_2CPh_2)] (3). A Et_2O solution of N_2CPh_2 (3 mL of a 0.08 M solution, 0.24 mmol) was added to a solution of compound **1** (0.050 g, 0.075 mmol) in dichloromethane (5 mL) and the mixture was stirred for 5 min. Solvents were then removed under vacuum, the residue was dissolved in dichloromethane, the tube was cooled at 77 K, evacuated under vacuum, and then refilled with CO and closed. The mixture was then stirred while allowing it to reach room temperature slowly for 2 h, to give a green solution which was concentrated under vacuum and then chromatographed through alumina at 288 K. Elution with dichloromethane/petroleum ether (1/4) gave a green fraction yielding, after removal of solvents, compound **3** as a green microcrystalline solid (0.058 g, 90%). Anal. Calcd for $C_{44}H_{47}Mo_2N_2O_2P$: C, 61.54; H, 5.52; N, 3.26. Found: C, 61.78; H, 5.32; N, 3.11. ^{1}H NMR: δ 7.49-7.36 (m, 8H, Ph), 7.32-7.22 (m, 4H, Ph), 7.04 [t, J_{HH} = 7, 1H, H^4(Ph)], 6.80 [false d, J_{HH} = 7, 2H, H^2(Ph)], 5.09, 4.72 (2s, 2 x 5H, Cp), 2.60-1.20 (m, 21H, Cy), 0.82 (m, 1H, Cy). ^{13}C{^{1}H} NMR: δ 234.4 (d, J_{CP} = 12, MoCO), 226.0 [s, μ-CPh(*C*O)], 166.7 [s, C^1(Ph)], 149.9 [s, 2C^1(Ph)], 136.5 (s, N$_2$*C*Ph$_2$), 134.4 (s, μ-*C*Ph), 131.4, 130.2, 130.0, 129.5, 128.9, 128.6, 128.3, 128.3, 124.7 (9s, Ph), 99.0, 91.1 (2s, Cp), 56.0 [d, J_{CP} = 11, C^1(Cy)], 51.8 [d, J_{CP} = 17, C^1(Cy)], 37.3 [s, C^2(Cy)], 37.0 [d, J_{CP} = 5, C^2(Cy)], 35.2 [d, J_{CP} = 3, C^2(Cy)], 35.1 [d, J_{CP} = 6, C^2(Cy)], 29.3 [d, J_{CP} = 10, C^3(Cy)], 29.0 [d, J_{CP} = 9, C^3(Cy)], 28.9 [d, J_{CP} = 13, C^3(Cy)], 28.6 [d, J_{CP} = 9, C^3(Cy)], 26.9 [s, 2C^4(Cy)].

Preparation of *cis*-[$Mo_2Cp_2\{\mu$-κ^1:η^2-C(Ph)CO}(μ-PCy_2)(CO)(κ^1-N_2CPh_2)] (*cis*-3). A Et_2O solution of N_2CPh_2 (3 mL of a 0.08 M solution, 0.24 mmol) was added to a solution of compound **2** (0.050 g, 0.072 mmol) in dichloromethane (2 mL) and the mixture was stirred for 5 min at room temperature to give a black-greenish solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/10) and the extracts were chromatographed on alumina at 288 K. Elution with dichloromethane/petroleum ether (1/1) gave a dark green fraction yielding, after removal of solvents, compound ***cis*-3** as a green-black microcrystalline solid (0.055 g, 89%). Anal. Calcd for $C_{44}H_{47}Mo_2N_2O_2P$: C, 61.54; H, 5.52; N, 3.26. Found: C, 61.25; H, 5.35; N, 3.02. ^{1}H NMR: δ 7.58-7.56 (m, 2H, Ph), 7.42-7.25 (m, 10H, Ph), 7.06-7.02 (m, 3H, Ph), 5.10, 4.93 (2s, 2 x 5H, Cp), 2.60-2.59 (m, 2H, Cy), 2.36-2.27 (m, 2H, Cy), 2.00-1.20 (m, 18H, Cy). ^{13}C{^{1}H} NMR (100.61 MHz): δ 232.1 (d, J_{CP} = 12, MoCO), 216.4 [s, μ-CPh(*C*O)], 151.6 (s, N$_2$*C*Ph$_2$), 150.2, 137.0 [2s, 3C^1(Ph)], 132.7 (s, μ-*C*Ph), 130.4, 130.1, 129.6, 128.9, 128.7, 128.4, 128.1, 128.1, 124.6 (9s, Ph), 100.1, 89.9 (2s, Cp), 52.2 [d, J_{CP} = 22, C^1(Cy)], 46.6 [d, J_{CP} = 10, C^1(Cy)], 35.1, 34.8 [2s, 2C^2(Cy)], 33.6 [d, J_{CP} = 5, C^2(Cy)], 33.1 [s, C^2(Cy)], 28.7 [d, J_{CP} = 10, C^3(Cy)], 28.5 [d, J_{CP} = 11, C^3(Cy)], 28.3 [d, J_{CP} = 12, C^3(Cy)], 28.1 [d, J_{CP} = 12, C^3(Cy)] 27.0, 26.9 [2s, 2C^4(Cy)].

Preparation of [$Mo_2Cp_2(\mu$-CPh)(μ-PCy_2)(CO)(κ^1-N_2CPh_2)] (4). A Et_2O solution of N_2CPh_2 (3 mL of a 0.08 M solution, 0.24 mmol) was added to a solution of compound **1** (0.050 g, 0.075 mmol) in dichloromethane (5 mL). Solvents were then removed under vacuum, the oily residue was dissolved in toluene, and the mixture was stirred at 353 K for 30 min to give a dark brown solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane and the extract was chromatographed through alumina at 288 K. Elution with dichloromethane/petroleum ether (1/9) gave a brown fraction yielding, after removal of solvents, compound

4 as a brown powder (0.058 g, 93%). Anal. Calcd for $C_{43}H_{47}Mo_2N_2OP$: C, 62.17; H, 5.70; N, 3.37. Found: C, 61.85; H, 5.57; N, 3.45. ^{1}H NMR (400.13 MHz): δ 7.53 [m, 1H, H^4(Ph)], 7.40 [false t, J_{HH} = 7, 2H, H^3(Ph)], 7.35-7.32 (m, 3H, Ph), 7.26-7.24 (m, 6H, Ph), 7.09 [t, J_{HH} = 7, 1H, H^4(Ph)], 6.76 [false d, J_{HH} = 7, 2H, H^2(Ph)], 5.39, 5.05 (2s, 2 x 5H, Cp), 2.74 (d, br, J_{HP} = 12, 1H, Cy), 2.20-1.20 (m, 21H, Cy). ^{13}C{^{1}H} NMR (100.61 MHz): δ 373.5 (d, J_{CP} = 6, μ-*C*Ph), 248.5 (d, J_{CP} = 10, MoCO), 165.4, 148.2, 137.9 [3s, C^1(Ph)], 133.9 (s, N$_2$*C*Ph$_2$), 129.6, 129.3, 124.2 [3s, C^4(Ph)], 129.5, 128.8, 128.6, 127.7, 127.6, 123.1 [6s, C^{2,3}(Ph)], 98.9, 91.6 (2s, Cp), 50.0 [d, J_{CP} = 18, C^1(Cy)], 48.0 [s, br, C^1(Cy)], 37.4 [s, C^2(Cy)], 34.7 [d, J_{CP} = 2, C^2(Cy)], 34.6, 33.4 [2s, C^2(Cy)], 29.1 [d, J_{CP} = 12, C^3(Cy)], 28.7 [d, J_{CP} = 11, C^3(Cy)], 28.5 [d, J_{CP} = 10, C^3(Cy)], 28.4 [d, J_{CP} = 11, C^3(Cy)], 26.8, 26.7 [2s, C^4(Cy)].

Preparation of *cis*-[Mo$_2$Cp$_2$(μ-CPh)(μ-PCy$_2$)(CO)(κ^1-N$_2$CPh$_2$)] (*cis*-4). A Et$_2$O solution of N_2CPh_2 (3 mL of a 0.08 M solution, 0.24 mmol) was added to a solution of compound **2** (0.050 g, 0.072 mmol) in dichloromethane (2 mL) and the mixture was stirred at room temperature for 5 min to give a dark green solution. Solvent was then removed under vacuum, the residue was dissolved in toluene, and the mixture was stirred at 353 K for 30 min to give a dark brown solution containing a mixture of isomers **4** and ***cis*-4** (ca. 1/5). The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/10) and the extracts were chromatographed through alumina at 253 K. Elution with dichloromethane/petroleum ether (1/9) gave a brown fraction yielding, after removal of solvents, compound **4** as a brown powder (0.008 g, 13%). Elution with dichloromethane/petroleum ether (1/8) gave a yellow-brown fraction yielding analogously compound ***cis*-4** as a yellow-brown powder (0.045 g, 75%). Anal. Calcd for $C_{43}H_{47}Mo_2N_2OP$: C, 62.17; H, 5.70; N, 3.37. Found: C, 61.80; H, 5.43; N, 3.13. ^{1}H NMR: δ 7.79 [m, 1H, H^4(Ph)], 7.59 [t, J_{HH} = 7, 1H, H^4(Ph)], 7.47 [false t, J_{HH} = 7, 2H, H^3(Ph)], 7.46-7.15 (m, 8H, Ph), 6.99 [t, J_{HH} = 7, 1H, H^4(Ph)], 6.43 [false d, J_{HH} = 7, 2H, H^2(Ph)], 5.40, 4.90 (2s, 2 x 5H, Cp), 2.60-0.90 (m, 22H, Cy).

Preparation of [Mo$_2$Cp$_2${μ-κ^1:η^2-C(Ph)CH$_2$}(μ-PCy$_2$)(CO)$_2$] (5). A Et$_2$O solution of N_2CH_2 (2 mL of a 0.07 M solution, 0.14 mmol) was added to a solution of compound **1** (0.050 g, 0.075 mmol) in dichloromethane (5 mL) and the mixture was stirred at room temperature for 5 min. Solvents were then removed under vacuum, the brown residue was extracted with dichloromethane/petroleum ether (1/10) and the extracts were chromatographed through alumina at 288 K. Elution with dichloromethane/petroleum ether (1/8) gave a greenish brown fraction yielding, after removal of solvents, compound **5** as a brown solid (0.045 g, 88%). Attempts to grow single crystals of this complex were unsuccessful due to its progressive transformation in solution into a mixture of two isomers, not characterized (see text). Anal. Calcd for $C_{32}H_{39}Mo_2O_2P$: C, 56.65; H, 5.79. Found: C, 56.30; H, 5.45. ^{1}H NMR: δ 7.16 [false t, J_{HH} = 7, 2H, H^3(Ph)], 7.05 [t, J_{HH} = 7, 1H, H^4(Ph)], 6.88 [false d, J_{HH} = 7, 2H, H^2(Ph)], 5.29 (s, 5H, Cp), 5.13 (d, J_{HH} = 2.2, 1H, CH$_2$), 5.09 (s, 5H, Cp), 5.09 (d, J_{HH} = 2.2, 1H, CH$_2$), 2.47-2.43 (m, 2H, Cy), 2.35 (m, 1H, Cy), 1.92-1.12 (m, 19H, Cy). ^{13}C{^{1}H} NMR: δ 246.6 (d, J_{CP} = 14, MoCO), 246.5 (d, J_{CP} = 10, MoCO), 182.0 (s, μ-CPh), 152.0 [s, C^1(Ph)], 128.9 [s, C^4(Ph)], 128.1, 127.3 [2s, C^{2,3}(Ph)], 90.8, 89.6 (2s, Cp), 68.3 (s, CH$_2$), 49.8 [d, J_{CP} = 22, C^1(Cy)], 41.5 [d, J_{CP} = 16, C^1(Cy)], 34.8 [d, J_{CP} = 4, C^2(Cy)], 34.6 [d, J_{CP} = 2, C^2(Cy)], 34.3 [d, J_{CP} = 1, C^2(Cy)], 34.0 [d, J_{CP} = 5, C^2(Cy)], 28.8 [d, J_{CP} = 12, C^3(Cy)], 28.3 [d, J_{CP} = 14, C^3(Cy)], 28.2 [d, J_{CP} = 10, 2C^3(Cy)], 26.7, 26.5 [2s, C^4(Cy)].

Preparation of [Mo$_2$Cp$_2${μ-C(Ph)NCH$_2$Ph}(μ-PCy$_2$)(CO)$_2$] (6). Neat N_3CH_2Ph (15 μL, 0.12 mmol) was added to a solution of compound **1** (0.050 g, 0.075 mmol) in dichloromethane (5 mL), and the mixture was stirred at room temperature for 5 min (Caution: benzyl azide is a flammable liquid and forms explosive vapour/air mixtures). The solvent was then removed under vacuum, the residue was kept under vacuum for 1 h and then extracted with dichloromethane/petroleum ether (1/10), and the extracts were chromatographed through alumina at 263 K. Elution with dichloromethane/tetrahydrofuran (9/1) gave a brown fraction yielding, after removal of solvents, compound **6** as a brown microcrystalline solid (0.050 g, 86%). Attempts to grow single crystals of this complex were unsuccessful due to its progressive transformation in solution into a mixture of different products, not characterized. Anal. Calcd for $C_{39}H_{46}Cl_2Mo_2NO_2P$ (**6**·CH_2Cl_2): C, 54.82; H, 5.43; N, 1.64. Found: C, 54.44; H, 5.53; N, 1.81. ^{1}H NMR (400.13 MHz, 253 K): δ 7.39-7.35 (m, 3H, Ph), 7.30-7.24 (m, 6H, Ph), 7.02 [tt, J_{HH} = 7, 1.5, 1H, H^4(Ph)], 5.10, 5.04 (2s, 2 x 5H, Cp), 4.92, 4.81 (2d, J_{HH} = 13, 2 x 1H, NCH$_2$), 2.18-1.05 (m, 22H, Cy). ^{13}C{^{1}H} NMR (100.61 MHz, 253 K): δ 257.9 (d, J_{CP} = 11, MoCO), 244.7 (d, J_{CP} = 7, MoCO), 189.9 (d, J_{CP} = 23, μ-CPh), 158.5, 136.4 [2s, 2C^1(Ph)], 129.4, 129.0, 128.4, 127.3, 126.7, 124.6 (6s, Ph), 92.7, 91.8 (2s, Cp), 70.0 (s, NCH$_2$), 54.4 [d, J_{CP} = 12, C^1(Cy)], 50.0 [s, C^1(Cy)], 36.9 [d, J_{CP} = 6, C^2(Cy)], 35.4, 35.1 [2d, J_{CP} = 4, C^2(Cy)], 34.7 [d, J_{CP} = 6, C^2(Cy)], 29.3 [d, J_{CP} = 11, C^3(Cy)], 29.1, 28.6, 28.5 [3d, J_{CP} = 10, C^3(Cy)], 26.9, 26.6 [2s, C^4(Cy)].

Preparation of [Mo$_2$Cp$_2${μ-κ^2:η^3-CPhCHC(CO$_2$Me)}(μ-PCy$_2$)(CO)$_2$] (7a). Neat methyl propiolate (40 μL, 0.45 mmol) was added to a solution of compound **1** (0.050 g, 0.075 mmol) in toluene (10 mL), and the mixture was stirred at 333 K for 2 h to give an orange solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/10) and the extracts were chromatographed through alumina at 288 K. Elution with dichloromethane/petroleum ether (1/4) gave an orange fraction yielding, after removal of the solvents, compound **7a** as an orange microcrystalline solid (0.041 g, 73%). Anal. Calcd for $C_{35}H_{41}Mo_2O_4P$: C, 56.16; H, 5.52. Found: C, 56.46; H, 5.71. ^{1}H NMR: δ 7.34-7.25 [m, 4H, H^{2,3}(Ph)], 7.12 [t, J_{HH} = 7, 1H, H^4(Ph)], 6.79 (d, J_{HP} = 2, 1H, CH), 5.11, 4.65 (2s, 2 x 5H, Cp), 3.54 (s, 3H, OMe), 2.30-0.90 (m, 22H, Cy). ^{13}C{^{1}H} NMR: δ 251.6 (d, J_{CP} = 12, MoCO), 233.3 (d, J_{CP} = 6, MoCO), 177.2 (s, *C*O$_2$Me), 145.9 [s, C^1(Ph)], 137.7 (s, μ-*C*Ph), 128.3, 127.0 [2s, C^{2,3}(Ph)], 126.8 [s, C^4(Ph)], 92.1 (d, J_{CP} = 5, MoCH), 91.2, 88.1 (2s, Cp), 78.4 (d, J_{CP} = 28, μ-*C*CO$_2$Me), 51.4 (s, OMe), 51.3 [d, J_{CP} = 14, C^1(Cy)], 47.0 [d, J_{CP} = 5, C^1(Cy)], 37.8 [s, C^2(Cy)], 36.5 [d, J_{CP} = 6, C^2(Cy)], 35.5 [d, J_{CP} = 3, C^2(Cy)], 35.2 [d, J_{CP} = 6, C^2(Cy)], 29.6, 29.1 [2d, J_{CP} = 12, C^3(Cy)], 28.8 [d, J_{CP} = 8, C^3(Cy)], 28.6 [d, J_{CP} = 12, C^3(Cy)], 27.1, 26.9 [2s, C^4(Cy)].

Preparation of [Mo$_2$Cp$_2${μ-κ^2:η^3-CPhC(CO$_2$Me)C(CO$_2$Me)}(μ-PCy$_2$)(CO)$_2$] (7b). Neat $C_2(CO_2Me)_2$ (50 μL, 0.407 mmol) was added to a solution of compound **1** (0.050 g, 0.075 mmol) in toluene (10 mL), and the mixture was stirred at 393 K for 7 h to give a brown- orange solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/10) and the extracts were chromatographed through alumina at 288 K. Elution with dichloromethane/petroleum ether (1/1) gave an orange fraction yielding, after removal of solvents, compound **7b** as an orange microcrystalline solid (0.040 g, 66%). Anal. Calcd for $C_{37}H_{43}Mo_2O_6P$: C, 55.10; H, 5.37. Found: C, 55.42; H, 5.36. ^{1}H NMR: δ 7.20-7.14 (m, 2H, Ph), 7.12-7.06 (m, 3H, Ph), 5.12, 5.07 (2s, 2 x 5H, Cp), 3.61, 3.37 (2s, 2 x 3H, OMe), 2.37 (m, 1H, Cy), 2.40-0.60 (m, 21H, Cy). ^{13}C{^{1}H} NMR (100.61 MHz): δ 248.0 (d, J_{CP} = 11, MoCO), 232.5 (d, J_{CP} = 7, CO), 175.4 (s, 2CO$_2$Me), 140.4 [s, C^1(Ph)], 128.7, 127.5 [2s, C^{2,3}(Ph)], 126.3 [s, C^4(Ph)], 112.1 [d, J_{CP} = 4, *C*(CO$_2$Me)], 101.0 (s, μ-*C*Ph), 91.2, 89.0 (2s, Cp), 80.0 [d, J_{CP} = 24, μ-*C*(CO$_2$Me)], 53.3 [d, J_{CP} = 16, C^1(Cy)], 51.7, 51.0 (2s, OMe), 46.7 [d, J_{CP} = 2, C^1(Cy)], 38.0 [s, C^2(Cy)], 36.3 [d, J_{CP} = 7, C^2(Cy)], 35.3, 35.0 [2s, C^2(Cy)], 29.5 [d, J_{CP} = 11, C^3(Cy)], 28.9 [d, J_{CP} = 10, C^3(Cy)], 28.8 [d, J_{CP} = 12, 2C^3(Cy)], 27.0, 26.8 [2s, C^4(Cy)].

Preparation of *cis*-[Mo$_2$Cp$_2${μ-κ^2:η^3-CPhC(CO$_2$Me)C(CO$_2$Me)}(μ-PCy$_2$)(CO)$_2$] (*cis*-7b). A solution of compound **7b** (0.050 g, 0.062 mmol) in tetrahydrofuran (5 mL) was irradiated with visible-UV light for 20 min at 288 K, to give a yellow solution. Work-up as described for **7b** yielded compound ***cis*-7b** as an orange microcrystalline solid (0.042 g, 84%). Anal. Calcd for $C_{37}H_{43}Mo_2O_6P$: C, 55.10; H, 5.37. Found: C, 49.82; H, 5.12. ^{1}H NMR: δ 7.26-7.15 [m, 3H, H^{3,4}(Ph)], 6.85 [false d, J_{HH} = 8, 2H, H^2(Ph)], 5.15 (s, 10H, Cp), 3.45, 3.42 (2s, 2 x 3H, OMe), 1.90-1.10 (m, 22H, Cy). ^{13}C{^{1}H} NMR (100.61 MHz): δ 236.1 (d, J_{CP} = 10, 2MoCO), 177.8 (d, J_{CP} = 3, *C*O$_2$Me), 177.5 (s, *C*O$_2$Me), 137.9 [s,

C^1(Ph)], 128.3, 127.9 [2s, $C^{2,3}$(Ph)], 127.4 [s, C^4(Ph)], 126.0 [d, J_{CP} = 4, *C*(CO_2Me)], 99.5 (s, μ-*C*Ph), 89.3 (s, 2Cp), 63.7 [d, J_{CP} = 30, μ-*C*(CO_2Me)], 51.6, 51.5 (2s, OMe), 49.3 [d, J_{CP} = 16, C^1(Cy)], 45.0 [d, J_{CP} = 8, C^1(Cy)], 35.5 [d, J_{CP} = 3, C^2(Cy)], 34.8 [d, J_{CP} = 4, C^2(Cy)], 28.8, 28.5 [2d, J_{CP} = 10, C^3(Cy)], 26.6 [s, $2C^4$(Cy)].

Computational Details. All DFT computations were carried out using the GAUSSIAN09 package,[33] in which the hybrid method B3LYP was used with the Becke three-parameter exchange functional[34] and the Lee−Yang−Parr correlation functional.[35] An accurate numerical integration grid (99,590) was used for all the calculations via the keyword Int=Ultrafine. Effective core potentials and their associated double-ζ LANL2DZ basis set were used for the metal atoms.[36] The light elements (P, O, C and H) were described with the 6-31G* basis.[37] Geometry optimizations were performed under no symmetry restrictions, and frequency analyses were performed for all the stationary points to ensure that minimum structures with no imaginary frequencies were achieved. NMR shielding contributions and coupling constants were calculated using the gauge-including atomic orbitals (GIAO) method,[38] in combination with the LANL2DZ basis set for the Mo atoms and the 6-311+G(2d,p) basis set for the remaining atoms.[39]

ASSOCIATED CONTENT

Supporting Information

A PDF file containing the complete reference 33, and results of DFT calculations (drawings, atomic coordinates, energies and NMR parameters for different isomers of compound **6**). The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interest.

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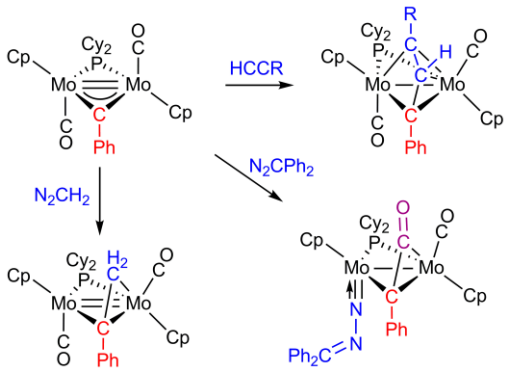

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