Alkenyl Derivatives of the Unsaturated Dimolybdenum Hydride Complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$

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The 30-electron hydride complex $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ reacts at room temperature with *p*-tolylacetylene to give the unsaturated $\sigma{:}\pi$-bonded alkenyl derivatives *trans*-$[Mo_2Cp_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CRCH_2)(\mu\text{-}PCy_2)(CO)_2]$ and *trans*-$[Mo_2Cp_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CHCHR)(\mu\text{-}PCy_2)(CO)_2]$ (R = *p*tol; Cp = η^5-C_5H_5), with the α-substituted alkenyl complex being transformed completely into its β-substituted isomer slowly at room temperature. In solution, both compounds exhibit an isomeric equilibrium (rapid on the NMR time scale) involving the alternate π-binding of the alkenyl ligand to each of the metal centers. In addition, the presence of CO allows the partial conversion of the α-substituted complex into its *cis*-dicarbonyl isomer *cis*-$[Mo_2Cp_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CRCH_2)(\mu\text{-}PCy_2)(CO)_2]$, so as to reach a roughly equimolar equilibrium ratio. In contrast, the β-substituted alkenyl complex experiences full carbonylation under the same conditions to give the tricarbonyl complex $[Mo_2Cp_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}CHCHR\}(\mu\text{-}PCy_2)(CO)_3]$, but similarly displaying a *cisoid* arrangement of the Cp ligands. The title hydride complex also reacts at room temperature with methyl propiolate, to afford the α-alkenyl complexes *cis*- and *trans*-$[Mo_2Cp_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(CO_2Me)CH_2\}(\mu\text{-}PCy_2)(CO)_2]$, which are in a solvent-dependent equilibrium and are also involved in further dynamic processes derived from the flipping of the alkenyl ligand, but do not undergo α−β alkenyl isomerization. This reaction also gives smaller amounts of the 30-electron alkenylphosphine complex $[Mo_2Cp_2\{\mu\text{-}\kappa^1{:}\eta^2\text{-}Cy_2PCHCH(CO_2Me)\}(CO)_2]$ (Mo−Mo = 2.526(2) Å), formed through a reductive elimination between the alkenyl and dicyclohexylphosphide ligands. The title hydride complex also reacts at room temperature with an internal alkyne such as dimethylacetylenedicarboxylate to give alkenyl derivatives, but now the unsaturation of the metal center induces the coordination of one of the oxygen atoms of the carboxylate group in the β-position to give three different C,C,O-bonded isomers of the electron-precise $[Mo_2Cp_2\{\mu\text{-}\eta^1,\kappa{:}^2\text{-}C(CO_2Me)CH(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$, all of them characterized through single-crystal X-ray diffraction studies. Two of these isomers, which are in a slow equilibrium in solution, display a similar *transoid* arrangement of the CO and Cp ligands, but have different relative arrangements of the alkenyl and phosphide bridges, implying *transoid* or *cisoid* positions of the metal-bound P and O atoms, respectively. The third isomer displays a *cisoid* arrangement of the Cp and CO ligands, but a *transoid* position of the metal-bound P and O atoms. All three isomers exhibit relatively large intermetallic separations (ca. 2.88−2.96 Å), as expected for molecules having single Mo−Mo bonds.

Introduction

During our previous studies on the reactivity of the triply bonded hydride $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ (**1**) we found that this 30-electron complex was able to react under mild conditions toward small unsaturated organic molecules containing nitrogen such as isonitriles or azides to afford products mainly derived from the insertion of the incoming molecule into the Mo−H bond.[1] These results prompted us to study the reactions of compound **1** with different alkynes. The latter are well known to give insertion reactions into M−H, M−C, or even M−X (X = halogen) bonds, and these reactions have attracted much interest during the last decades not only from a stoichiometric and mechanistic point of view but also in terms of their potential applications, in both industry and academe, as models of fundamental steps operating in different catalytic processes such as hydrogenation, oligomerization (linear or cyclic), or polymerization of alkynes.[2,3]

The reactions of unsaturated di- or trinuclear hydride complexes toward alkynes have been previously studied by several authors. Thus, the 32-electron cation $[Ir_2Cp^*_2(\mu\text{-}H)_2(\mu\text{-}dmpm)]^{2+}$ has been found to react smoothly with ethyne and other

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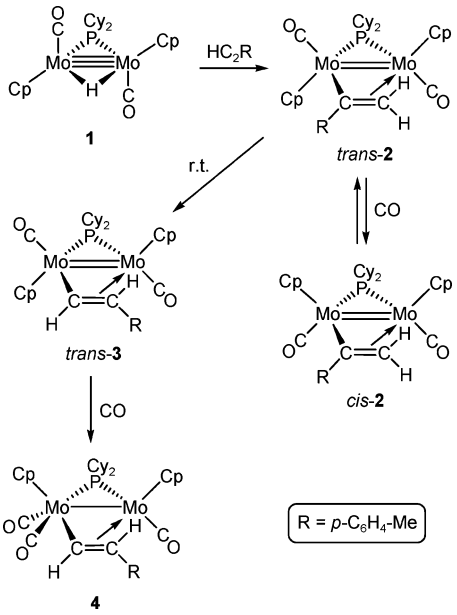
1-alkynes to give $\sigma:\pi$-alkenyl derivatives,[4] whereas the isoelectronic diruthenium complex $[Ru_2(\mu\text{-H})(\mu\text{-CO})(CO)_3(\mu\text{-dppm})]^+$ gives either $\sigma:\pi$- or just σ-bonded alkenyl derivatives.[5] The 30-electron polyhydrides $[Ru_2Cp^*_2(\mu\text{-H})_4]$ and $[IrRuCp^*_2(\mu\text{-H})_3]$ are also reactive toward alkynes,[6] with the diruthenium complex reacting with C_2Ph_2 to give a $\mu\text{-}\eta^2\text{:}\eta^2$-alkyne derivative as the major product,[6a,b] while the iridium−ruthenium complex gives initially the expected $\sigma:\pi$-alkenyl derivatives when using PhCCR (R = Me, Ph), which then experience subsequent orthometalation of a phenyl group.[6a,c] The reactivity of neutral compounds having an unsaturated "$M_2(\mu\text{-H})_2$" core with a formal double metal−metal bond toward alkynes has also been widely explored. Thus, the 32-electron dihydride $[Mn_2(\mu\text{-H})_2(CO)_6(\mu\text{-dppm})]$ was found to react with several 1-alkynes (RCCH) at room temperature to give different products depending on the substituent of the alkyne, ranging from the expected alkenyl derivatives $[Mn_2(\mu\text{-H})(\mu\text{-}\eta^1\text{:}\eta^2\text{-CR=CH}_2)(CO)_6(\mu\text{-dppm})]$ to the alkenylidene complexes $[Mn_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-C=CRH})(CO)_6(\mu\text{-dppm})]$, which in turn isomerize to give the hydride-alkynyl derivatives $[Mn_2(\mu\text{-H})(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CR})(CO)_6(\mu\text{-dppm})]$.[7] On the other hand, the isoelectronic complex $[Mn_2(\mu\text{-H})_2(CO)_4(\mu\text{-dppm})_2]$ was also reported to react easily with alkynes, but the products were not be characterized at the time,[8] whereas the also isoelectronic dirhenium complex $[Re_2(\mu\text{-H})_2(CO)_6(\mu\text{-L−L})]$ (L−L = dppm or tedip) surprisingly failed to react with acetylene.[9] Finally, detailed studies on the reactivity of the triosmium cluster $[Os_3(\mu\text{-H})_2(CO)_{10}]$ toward alkynes have also been carried out, this being the main route to obtain the corresponding $\mu\text{-}\eta^1\text{:}\eta^2$-alkenyl derivatives, usually under mild conditions, although different products can be obtained after subsequent rearrangements of the latter ligand, ranging from C−H activations, to coupling reactions with additional molecules of alkyne, to alkyne cyclotrimerization, etc.[10]

The examples mentioned above prove the ability of those complexes having a hydride-bridged unsaturated dimetal center of the type $M_2(\mu\text{-H})_x$ to react, usually under mild conditions (at room temperature or below, and without the need for photochemical activation), toward all kinds of alkynes to give not only the expected insertion products ($\sigma:\pi$-bonded alkenyl complexes) but also other types of compounds derived from further reactions or reorganizations in the initial products, which are possible and/or favored by the electronic and coordinative unsaturation of the respective dimetal centers. In this respect, the study of the reactions of compound **1** with alkynes was of particular interest because this complex is unique in combining the presence of a formal triple Mo−Mo bond and just a single bridging hydride ligand. As a result, the expected alkenyl complexes derived from the initial insertion of the alkyne into the Mo−H bond would still be an unsaturated 32-electron species, a circumstance that should favor further reactions or reorganizations of these initial products. In this paper we report our studies on the reactivity of **1** toward terminal alkynes, HC≡CR (R = ^{t}Bu, *p*-tol, CO_2Me), and one activated internal alkyne such as dimethylacetylenedicarboxylate, as well as some carbonylation reactions of the corresponding products designed to check their unsaturated nature. As will be discussed, the alkenyl complexes initially formed in the reactions of **1** with terminal alkynes are indeed unsaturated and rather unstable species, but although exhibiting a relatively complex dynamic behavior in solution, they fail to add further alkyne molecules easily. However, the alkenyl ligands in these products were found to experience several reorganizations at room temperature, the observed processes being $\alpha-\beta$ alkenyl isomerization and reductive P−C coupling between the alkenyl and dicyclohexylphosphide ligands.

Scheme 1 . Reactions of Compound 1 with HC≡C(*p*tol)



Results and Discussion

Reactivity of Compound 1 toward 1-Alkynes. Although complex **1** does react slowly with HC≡C^{t}Bu at room temperature, a complex mixture of air-sensitive products was formed, and they could not be properly separated or characterized. Fortunately, alkynes having more acidic substituents (*p*tol, CO_2Me) on the alkyne led to more stable products. The reaction of **1** with HC≡C(*p*tol) leads mainly to the 32-electron alkenyl derivatives $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(ptol)CH}_2\}(\mu\text{-PCy}_2)(CO)_2]$ (*trans*-**2**) and $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-CHCH(ptol)}\}(\mu\text{-PCy}_2)(CO)_2]$ (*trans*-**3**) in a ca. 3:1 ratio after 4 h in toluene at room temperature (Scheme 1). This ratio turned out to be dependent on time and temperature. In fact, a separate experiment proved that the α-substituted alkenyl *trans*-**2** transforms completely into its β-substituted isomer *trans*-**3** after 24 h at room temperature, or just in 1 h at 60 °C, a matter to be discussed later on. The room-temperature reaction also gives small amounts of the α-substituted alkenyl, *cis*-dicarbonyl complex *cis*-$[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(ptol)CH}_2\}(\mu\text{-PCy}_2)(CO)_2]$ (*cis*-**2**) and the β-substituted tricarbonyl $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-CHCH(ptol)}\}(\mu\text{-PCy}_2)(CO)_3]$ (**4**), the formation of which requires the presence of extra CO molecules, probably generated by the decomposition of other products in the reaction mixture. The ^{31}P NMR spectrum of the reaction mixture revealed the presence of a small amount of yet another compound, characterized by an unusually shielded

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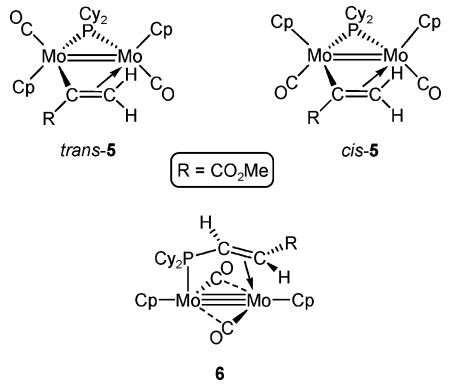
Chart 1



resonance at ca. 20 ppm, which was tentatively identified as the alkenylphosphine derivative $[Mo_2Cp_2\{\mu\text{-}\kappa\text{:}\eta^2\text{-}PCy_2CHCH(ptol)\}(CO)_2]$ by analogy with compound **6** (see below). However, the characterization of this very minor product could not be completed since we were not able to isolate it using chromatographic techniques. On the other hand, separate experiments showed that the reaction of *trans*-**2** with CO (1 atm) caused its partial isomerization into *cis*-**2**, so as to reach an equimolar equilibrium mixture after 1 h at room temperature, whereas *trans*-**3** was fully carbonylated under the same conditions to give the tricarbonyl **4** after 24 h (Scheme 1).

Compound **1** also reacts readily with an excess of HC≡C(CO_2Me) in toluene at room temperature, to give after 3 h a mixture of the α-substituted alkenyls $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CO_2Me)CH_2\}(\mu\text{-}PCy_2)(CO)_2]$ (*cis*-**5** and *trans*-**5**), which are in a solvent-dependent equilibrium always favoring the *cis* isomer (see Experimental Section), and the alkenylphosphine derivative $[Mo_2Cp_2\{\mu\text{-}\kappa\text{:}\eta^2\text{-}PCy_2CHCH(CO_2Me)\}(CO)_2]$ (**6**) (ratio **5**/**6** ca. 4 based on the ^{31}P NMR spectra), as well as small amounts of other uncharacterized products (Chart 1). This reaction can be completed in only 20 min at 60 °C, but although the ratio **5**/**6** remains similar, higher proportions of other products are then obtained. Two of them were shown (by ^{1}H NMR) to incorporate two molecules of alkyne, but unfortunately we could not isolate nor fully characterize them. Our attempts to increase their proportion in the reaction mixture were also unsuccessful; for instance, no significant change in the product distribution was observed when replacing toluene by tetrahydrofuran as reaction solvent.

Solution Structure of the *trans*-Dicarbonyl Complexes 2 to 5. Although we could not grow X-ray quality crystals for any of the complexes **2** to **5**, due in part to their relatively high sensitivity to air, the spectroscopic data recorded for these compounds, added to the structural data available in the literature for other σ:π-bonded alkenyl complexes, allow for a satisfactory characterization of these species in solution, which turned out to be relatively complex.

Unexpectedly for a dicarbonyl complex, the IR spectrum in petroleum ether of either *trans*-**2** or *trans*-**3** displays three C−O stretching bands in the 1900−1800 cm^{-1} region, with strong, medium, and strong intensities (Table 1). The same pattern was already observed for the related alkenyl complex $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CH_3)CH_2\}(\mu\text{-}PCy_2)(CO)_2]$, previously synthesized by us through the reaction of the unsaturated anion $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$ with allyl chloride.[11] At the time we proposed a rapid interconversion between *cis*- and *trans*-dicarbonyl isomers to explain such an unexpected pattern. However, with the data now available for compounds **2** to **5**, and particularly after the identification of the authentic isomer *cis*-**2** (to be discussed later on), we must now rule out our former explanation. In fact, the isomer *cis*-**2** displays two C−O stretching bands at 1940 (vs) and 1868 (m) cm^{-1}, which are wavenumbers substantially higher than those of the isomer *trans*-**2** or *trans*-**3** and close to the values measured for the only two complexes of the type *cis*-$[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]$ (R = R′ = Ph; R = Ph, R′ = ^{t}Bu) previously reported in the literature.[12]

To explain the anomalous pattern of the C−O stretching bands of compounds *trans*-**2** and *trans*-**3**, we must assume the presence in solution of two further isomers (**A** and **B** in Scheme 2) in each case, which must be interconverting rapidly on the NMR time scale since only a single species is apparent in the NMR spectra of these complexes even at low temperatures (see below). The structure of isomer **A** is based on that determined crystallographically for the isoelectronic alkenyl complex $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CH_3)CHCH_3\}(\mu\text{-}SPh)(CO)_2]$[13] and would exhibit a quite antiparallel arrangement of the CO ligands (relative angle close to 180°), similar to that found in most of the complexes of the type *trans*-$[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}X)(CO)_2]$ (X = PR′$_2$,[12,14] H,[1a] or other three-electron-donor groups).[1b,11,12b] For all these complexes, two close C−O stretching bands around 1850 cm^{-1}, with the expected weak and strong relative intensities (in order of decreasing frequency),[15] are usually observed in their IR spectra. Therefore we assign the intermediate band in the spectra of *trans*-**2** (1865 cm^{-1}) and *trans*-**3** (1838 cm^{-1}) to the asymmetric stretch (strong band) of the corresponding isomers of type **A**, while the weak symmetric stretch must be obviously masked by the stronger band of the isomer **B**. Note that, out of the two isomers of type **A** possible in the case of compound *trans*-**3** (differing in the relative positions of H and R at the β-carbon), only one of them is present in solution, as proven by the NMR data to be discussed later on, this being presumably the one with the R group pointing away from the dimetal center (more favored on steric grounds). As for the isomer **B**, we propose it to be derived from a flip of the alkenyl ligand so as to coordinate the β-carbon to the other Mo atom. This is a common dynamic process in alkenyl-bridged complexes (the windshield wiper movement first proposed by Shapley et al.),[16] but in our case it is an isomerization driving the CHR group closer to a carbonyl ligand, thus increasing the steric repulsions. In order to relieve this steric pressure, the MoCp(CO) moieties would rotate in opposite directions, this causing the angle defined by the CO ligands to deviate strongly from 180°, approaching the value of 90°, for which two C−O stretches of similar intensity are expected.[15] Indeed, this is a structural effect found previously by us in several complexes having two MoCp(CO) moieties connected by two or three bridging ligands[17] and is reflected in the appearance of two C−O stretching bands of similar intensity and strongly separated (by as much as 100 cm^{-1}). Thus we identify the two strong bands in the spectra of either *trans*-**2** or *trans*-**3** as arising from the isomers of type **B**.

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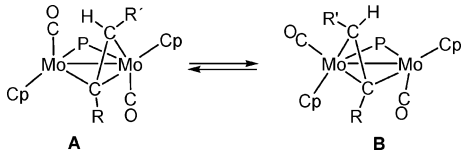
Table 1. Selected Spectroscopic Data (IR[a] and NMR[b]) for New Compounds

compound	ν_{CO}	δ_P	δ_H $H_\alpha[J_{HH}]$ $H_\beta[J_{HH}]$	δ_C $C_\alpha[J_{CP}]$ C_β
$[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(}p\text{tol)CH}_2\}(\mu\text{-PCy}_2)(CO)_2]$ (*trans*-**2**)	1903 (s), 1865 (m) 1805 (s)[c]	142.7	5.14 [2.5] 5.13 [2.5]	182.2 68.7[d]
$[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(}p\text{tol)CH}_2\}(\mu\text{-PCy}_2)(CO)_2]$ (*cis*-**2**)	1940 (vs), 1868 (m)[c]	175.2	4.78 [1.4] 4.35 [1.4]	
$[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-CHCH(}p\text{tol)}\}(\mu\text{-PCy}_2)(CO)_2]$ (*trans*-**3**)	1885 (s), 1838 (m) 1811 (s)[c]	136.7	8.86 [12] 6.76 [12]	149.7 [2.5] 100.9
$[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-CHCH(}p\text{tol)}(\mu\text{-PCy}_2)(CO)_3]$ (**4**)	1938 (vs), 1866 (s) 1839 (m)	251.2	9.27 [9] masked	143.1 [10] 65.4
$[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(CO}_2\text{Me)CH}_2\}(\mu\text{-PCy}_2)(CO)_2]$ (*trans*-**5**)	1897 (br, s), 1800 (br, s) 1669 (m)	152.5	5.30 [3] 4.93 [3][e]	155.2 72.9[e]
$[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(CO}_2\text{Me)CH}_2\}(\mu\text{-PCy}_2)(CO)_2]$ (*cis*-**5**)	1933 (vs), 1854 (m) 1669 (m)	186.4[e,f]	4.63 [1.2] 3.78 [1.2][e]	152.7 49.2[e]
$[Mo_2Cp_2\{\mu\text{-}\kappa\text{:}\eta^2\text{-PCy}_2\text{CHCH(CO}_2\text{Me)}\}(CO)_2]$ (**6**)	1793(m, sh), 1762 (vs) 1690 (m)	23.5[g]	4.15 [10] 2.46 [10][g]	3.4 [38] 41.1
$[Mo_2Cp_2\{\eta^1,\kappa\text{:}\eta^2\text{-C(CO}_2\text{Me)CH(CO}_2\text{Me)}\}(\mu\text{-PCy}_2)(CO)_2]$ (*trans*-**7**)	1910 (w, sh), 1863 (vs) 1667 (w), 1650 (vw, sh)	165.4	3.24	
$[Mo_2Cp_2\{\eta^1,\kappa\text{:}\eta^2\text{-C(CO}_2\text{Me)CH(CO}_2\text{Me)}\}(\mu\text{-PCy}_2)(CO)_2]$ (*cis*-**7**)	1943 (vs), 1832 (m) 1650 (m), 1631 (w, sh)	193.4	2.84	119.3 [20] 33.4[e]
$[Mo_2Cp_2\{\eta^1,\kappa\text{:}\eta^2\text{-C(CO}_2\text{Me)CH(CO}_2\text{Me)}\}(\mu\text{-PCy}_2)(CO)_2]$ (*trans*-**8**)	1912 (w), 1866 (vs) 1668 (w), 1653 (vw, sh)	180.9	4.25	

[a] Recorded in dichloromethane solution, unless otherwise stated, ν in cm^{-1}; bands in the range 2000−1800 cm^{-1} correspond to the C−O stretches of the carbonyl ligands; those in the range 1700−1600 cm^{-1} to the C−O stretches of the CO_2Me groups. [b] Recorded at 300.13 (^1H), 121.50 ($^{31}P\{^1H\}$), or 75.47 MHz ($^{13}C\{^1H\}$) at 290 K in $CDCl_3$ solutions unless otherwise stated, δ in ppm relative to TMS (^1H, $^{13}C\{^1H\}$) or external 85% aqueous H_3PO_4 ($^{31}P\{^1H\}$), J in Hz; the bridgehead carbon of the alkenyl ligand is referred to as α-carbon. [c] In petroleum ether. [d] In CD_2Cl_2 at 100.63 MHz and 243 K. [e] In CD_2Cl_2 at 100.63 MHz. [f] δ 189.5 (isomer **C**) and 184.0 (isomer **D**) when recorded in CD_2Cl_2 at 100.63 MHz and 183 K. [g] In C_6D_6 solution.

Scheme 2. Isomerization Equilibrium Proposed for Compounds *trans*-2 (R = *p*tol, R′ = H), *trans*-3 (R = H, R′ = *p*tol), and *trans*-5 (R = CO_2Me, R′ = H)



Apparently, this sort of isomerism has not been previously identified in related binuclear alkenyl complexes.

At this point, we should note that the IR spectra of the isoelectronic thiolate derivatives $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(CH}_3)\text{-CHCH}_3\}(\mu\text{-SR})(CO)_2]$ (R = Me, Ph) in dichloromethane solution also display in each case two strongly separated bands of similar intensities (at ca. 1900 and 1800 cm^{-1}).[13] This is inconsistent with the structure of type **A** found in the X-ray study of the butenyl complex and suggests the predominance of an isomer of type **B** in the solutions of these thiolate complexes, although apparently such a circumstance was not recognized at the time.[13]

The IR spectrum of the equilibrium mixture of the *cis* and *trans* isomers of compound **5** in CH_2Cl_2 exhibits four different bands in the C−O stretching region, excluding those arising from the CO_2Me groups. The two strongest ones (1933 (vs), 1854 (m) cm^{-1}) have a pattern and frequency similar to those observed for *cis*-**2** and are therefore assigned to the major isomer *cis*-**5**. The two other bands, appearing as weaker and broad bands, have a position (1897 and 1800 cm^{-1}) and relative intensity similar to those of *trans*-**2** and are therefore identified as the two strong bands expected for the isomer **B** of *trans*-**5** (the band of the hypothetical isomer of type **A** in *trans*-**5** would not be detected because of the low *trans*/*cis* ratio in this compound).

The ^1H and ^{13}C NMR spectra of compounds **2** to **5** exhibit resonances from the corresponding σ:π-bonded alkenyl ligands with chemical shifts and coupling constants within the range found for other related di- or trinuclear derivatives bearing Cp and/or CO ligands coordinated to Mo or W,[11,13,17d,18,19] Mn,[7,20] Re,[21] Fe,[22] Ru,[22i,23] Os,[24] and Ir[4] centers. The *trans*-dicarbonyl derivatives *trans*-**2**, *trans*-**3**, and *trans*-**5** exhibit a ^{31}P NMR resonance for the PCy_2 ligand in the range 155−135 ppm at room temperature, slightly downfield from that found for the propenyl derivative mentioned above (131.2 ppm),[11] with the

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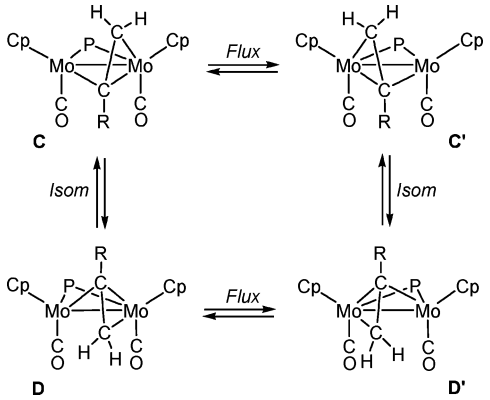
carboxylate compound *trans*-**5** giving the most deshielded resonance. This resonance remained essentially unchanged down to 183 K for all three compounds, thus meaning that the interconversion between isomers **A** and **B** in each case is rapid on the NMR time scale, so only averaged NMR parameters are being observed at all temperatures. In spite of this, the ^{1}H NMR spectra define unambiguously the stereochemistry of the alkenyl ligand in each case. Thus, the α-substituted alkenyls *trans*-**2** and *trans*-**5** exhibit in each case two doublets for the H_β nuclei in the range 6−4 ppm, with a small mutual coupling (ca. 3 Hz), which is a characteristic of geminal hydrogens. In contrast, the *β*-substituted *trans*-**3** displays strongly coupled alkenyl resonances (J_{HH} = 12), thus indicating a *transoid* arrangement (*E*-conformation) of the corresponding H nuclei (note that this arrangement also gives the less crowded isomer of type **A**). The resonances due to the C_α and C_β nuclei in the ^{13}C NMR spectra of these *trans*-dicarbonyl derivatives are also close to those observed for the propenyl complex mentioned above,[11] falling in the range 185−145 ppm (C_α) and 65−100 ppm (C_β), respectively, with small or negligible P−C_α couplings. The rest of the resonances in the ^{1}H and ^{13}C NMR spectra denote the lack of symmetry elements in these compounds, rendering two distinct resonances for the inequivalent Cp or the CO ligands, as well as 12 ^{13}C resonances for the Cy groups.

Solution Structure of the *cis*-Dicarbonyl Complexes 2 and 5. At room temperature, these isomers display a ^{31}P NMR resonance at ca. 180 ppm, some 30 ppm more deshielded than the resonances in the corresponding *trans*-dicarbonyl isomers. This effect on the ^{31}P shielding has been previously detected in the isoelectronic bis(phosphide) pairs *cis*- and *trans*-[Mo_2Cp_2-(μ-PR_2)(μ-PR'_2)$(CO)_2$] (R = R′ = Ph; R = Ph, R′ = ^{t}Bu),[12] with the resonances corresponding to the *cis* isomers appearing some 45 ppm above those of the *trans* isomers. As for the ^{1}H NMR spectra at room temperature, both compounds display independent resonances for the geminal H nuclei in the usual range, with small H−H couplings as expected (<2 Hz), but the inequivalent Cp ligands give rise to two broad signals. In line with this, the ^{13}C NMR spectrum of *cis*-**5** at room temperature displays two broad signals for the Cp groups and also exhibits one broad resonance for the four inequivalent $C^{2,6}$ atoms of the Cy groups and a broad multiplet for the $C^{3,5}$ nuclei. All this is indicative of dynamic behavior in solution for these complexes, which we have studied in detail only for *cis*-**5**. Apart from this, the inequivalent CO ligands give rise to two distinct resonances as expected (260.3 and 239.2 ppm), but the strong deshielding of one of them suggests that one of these ligands has some semibridging character, derived from its bending over the metal−metal vector. For example, the semibridging carbonyl ligand in the unsaturated hydride [Mo_2Cp_2(μ-PCy_2)$_2$(H)(CO)]-BF_4 (Mo−Mo−C = 63.5(4)°) has an almost identical ^{13}C chemical shift (δ_C 260.6 ppm).[12b]

The low-temperature ^{1}H, ^{31}P, and ^{13}C NMR spectra of *cis*-**5** (recall that it is in equilibrium with *trans*-**5**) were carried out in CD_2Cl_2. At 263 K both Cp resonances are already sharp in the ^{1}H spectrum, whereas there are no significant changes in the rest of the resonances. In a similar way, the ^{13}C NMR spectrum at 223 K displayed already two sharp resonances for both Cp ligands and one resonance for each of the four inequivalent $C^{2,6}$ atoms of the Cy groups, itself in agreement with a static structure, thus indicating that the dynamic process causing the broadening in the room-temperature ^{1}H and ^{13}C NMR spectra is slow enough by then. However, an additional process can be detected through the ^{31}P NMR spectrum on further cooling, since the resonance at ca. 186 ppm experiences a progressive broadening, to reach its biggest width at 203 K (coalescence), then splitting into two different resonances at 189.5 and 184.0 ppm (183 K) corresponding to two different isomers, denoted as **C** and **D** (**C**/**D** ratio = 2:3). From the coalescence temperature and ignoring the small population difference between isomers, we can estimate an average activation energy ($\Delta G^{\#}$) for this process of 36 ± 1 kJ mol^{-1}.[25] On the other hand, in order to estimate the energy of the process responsible for the broadening of ^{1}H and ^{13}C NMR lines at room temperature, we carried out high-temperature NMR measurements in C_6D_6 solutions. In this way, the broad Cp resonances were found to coalesce into a single one at 315 K (^{1}H spectrum) or 310 K (^{13}C spectrum). Both measurements yield the same $\Delta G^{\#}$ value of 60 ± 1 kJ mol^{-1} for the corresponding fluxional process, a barrier much higher than that found for the isomerization process detected at low temperature.

Scheme 3. Isomerism and Fluxionality Proposed for Compound *cis*-5 in Solution (P = PCy_2)



There are two possible isomers for a *cis*-dicarbonyl alkenyl complex, depending on the relative position of the alkenyl and cyclopentadienyl (or carbonyl) ligands (**C** and **D** in Scheme 3). We note, however, that our identification of isomer **C** as that with the most deshielded ^{31}P resonance (189.5 ppm at 183 K) is arbitrary. In any case, the low-energy process would consist in a rapid exchange between isomers **C** and **D** through a rotation of the CH_2 group from above to below the Mo_2P plane and vice versa. Perhaps this movement does not require complete cleavage of the Mo−C_β binding, thus explaining the low activation barrier of the process. Unfortunately, we have found no evidence in the literature for this type of isomerization process in a binuclear alkenyl species, although similar *cis* isomers were already postulated (but only one found) by Knox et al.[22i] for geometrically related (but electron-precise) Fe and Ru complexes. To account for the high-energy process, we suggest a windshield wiper movement analogous to that proposed above for the isomerization **A**/**B** in *trans*-**2**, *trans*-**3**, and *trans*-**5**. Such a process now implies the mutual exchange between the pairs of Cp or CO ligands and the chemical equivalence of diastereotopic pairs of cyclohexyl carbon atoms, in agreement with the high-temperature NMR data (see Experimental Section). Since this fluxional process requires detachment of the π C−C bond in the transition state, it is reasonable that the corresponding barrier (60 kJ mol^{-1}) is higher than the one for the nondissociative isomerization **C**/**D**. In any case, the above barrier falls within the range of values measured for related systems bearing fluxional alkenyl ligands (34 to 68 kJmol^{-1}).[22c]

(25) Calculated using the modified Eyring equation $\Delta G^{\#} = 19.14T_c[9.97 + \log(T_c/\Delta\nu)]$ (in J mol^{-1}). See: Günther, H. *NMR Spectroscopy*; John Wiley: Chichester, U.K., 1980; p 243.

Solution Structure of the Tricarbonyl Complex 4. In solution, this compound displays three C−O stretching bands with a pattern similar to that found for the closely related complexes $[Mo_2Cp_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CRCHR}')(\mu\text{-}PPh_2)(CO)_3]$ (R, R′ = H, Me, Et), previously synthesized through the photochemical reaction of $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-}PPh_2)(CO)_4]$ with RCCR′.[18] Among the latter compounds, the structure of the 2-butyne derivative was shown by a diffraction study to display Cp ligands in a *cisoid* arrangement with respect to the Mo_2P plane, as we propose for compound **4** on the basis of its similar IR spectrum (Scheme 1). In order to balance the different number of terminal carbonyls at the metal centers, the alkenyl ligand must be specifically π-bonded to the monocarbonylic metal fragment, and therefore is not expected to be fluxional.

The ^{31}P NMR spectrum of compound **4**, which is now an electron-precise complex, exhibits a strongly deshielded resonance (δ_P 251.2 ppm), ca. 115 ppm above that of its unsaturated precursor *trans*-**3**. This large difference is similar to that found for the related pair $[Mo_2Cp_2(\mu\text{-}PEt_2)_2(CO)_3]$/*trans*-$[Mo_2Cp_2(\mu\text{-}PEt_2)_2(CO)_2]$ and seems to be a general trend when comparing PR_2 ligands bridging over single and double M−M bonds (M = Mo, W) in these binuclear cyclopentadienyl complexes.[12a] The ^{13}C NMR spectrum of **4** reveals the absence of any symmetry elements in the molecule, thus displaying separate resonances for each of the CO and Cp ligands and for each of the Cy carbon atoms (see Experimental Section). It is to be noted that some of the Cy resonances display anomalous shifts, when compared to those generally observed for PCy_2 bridging ligands in our dimolybdenum complexes. In particular, one of the C^1 nuclei appears unusually deshielded (δ_C 59.4 ppm), whereas one of the $C^{2,6}$ nuclei is rather shielded (δ_C 28.6 ppm), actually appearing in the region characteristic of the $C^{3,5}$ resonances. At the same time one of the Cy multiplets in the ^1H NMR spectrum appears anomalously shielded (δ_H 0.0 ppm). All these effects might be related to the spatial proximity of one of the Cy rings to the alkenyl bridge in a structure having a *cisoid* arrangement of the MoCp fragments. On the other hand, the alkenyl ligand gives rise to two ^{13}C resonances at 143.1 and 65.4 ppm, in the usual regions, and the H_α atom gives rise to a highly deshielded resonance (9.27 ppm) as expected, but its coupling to the H_β nucleus is somewhat low (9 Hz). We interpret this as accidental rather than indicative of a change in the relative positions of the alkenylic H atoms (from *E*- to *Z*-conformation). In fact, the *E*-alkenyl ligand $(Cy_2P)HC{=}CH(CO_2Me)$ in compound **6** exhibits an H−H coupling of just 10 Hz (see below). However, we note that *Z*/*E* or *E*/*Z* isomerizations in bridging alkenyl complexes can occur at room temperature.[21,22d]

Structure of the Alkenylphosphine Complex 6. The structure of compound **6** was determined through a single-crystal X-ray diffraction study (Figure 1 and Table 2). The molecule is made up of two MoCp(CO) fragments bridged by an alkenylphosphine ligand, which binds the metal atoms through its P atom and double C=C bond. The intermetallic distance of 2.526(2) Å is consistent with the Mo−Mo triple bond that is proposed for this molecule according to the EAN formalism; it is almost identical to that measured for the hydride **1**[1a] and even 0.07 Å shorter than that found for the isoelectronic alkenylphosphine complex $[Mo_2Cp_2(\mu\text{-}PPh_2)\{\mu\text{-}Ph_2PC(Me){=}CHMe\}(\mu\text{-}CO)]^+$.[14b] The carbonyl ligand attached to Mo(1) has a very weak semibridging character (Mo−C distances 1.95(1) and 2.60(1) Å), but the parameters for the CO ligand bound to Mo(2) are indicative of a stronger semibridging interaction (Mo−C distances 1.97(1) and 2.30(1) Å; M−C−O and M−M−C angles 159(1)° and 60.1(4)°). All these values are not far from those found for related complexes bearing semibridging CO ligands over triple W−W bonds such as $[W_2Cp_2(CO)_4]$,[26] $[W_2Cp_2(\mu\text{-}CO)_2(\mu\text{-dppm})]$,[27] $[W_2Cp_2(\mu\text{-CO})(CO)\{P(OMe)_3\}(\mu\text{-dppm})]^+$,[28] and the previously mentioned dimolybdenum cations $[Mo_2Cp_2(\mu\text{-}PCy_2)_2(H)(CO)]^+$ [12b] and $[Mo_2Cp_2(\mu\text{-}PPh_2)\{\mu\text{-}Ph_2PC(Me){=}CHMe\}(\mu\text{-CO})]^+$.[14b] All these CO ligands can be identified as type II linear semibridging carbonyls, according to the classification of Crabtree and Lavin.[29] This type of semibridging interaction is usually found for carbonyl complexes with multiple metal−metal bonds and seems to imply some donation of electron density from the dimetal center to carbonyl π*-acceptor orbitals.[30] According to this, we should expect the stronger semibridging interaction to be established with the metal center having a higher electron density, which in our case is Mo(1) (since it bears a phosphine instead of an alkene ligand), in agreement with the experimental findings.

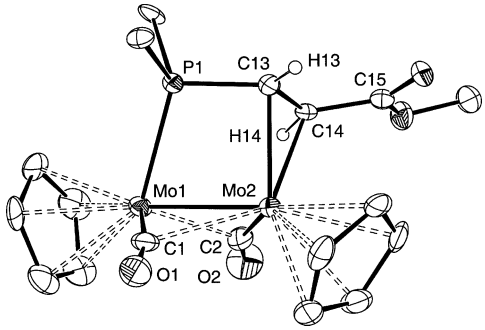


Figure 1. ORTEP diagram (30% probability) of compound **6**, with H atoms (except H13 and H14) and Cy rings (except their C^1 atoms) omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 6

Mo(1)−Mo(2)	2.525(2)	O(1)−C(1)−Mo(1)	168(1)
Mo(1)−C(1)	1.95(1)	O(1)−C(1)−Mo(2)	125.6(9)
Mo(2)−C(1)	2.60(1)	O(2)−C(2)−Mo(2)	159(1)
Mo(2)−C(2)	1.97(1)	O(2)−C(2)−Mo(1)	129(1)
Mo(1)−C(2)	2.30(1)	C(14)−C(13)−P(1)	119.3(8)
Mo(1)−P(1)	2.459(3)	C(13)−C(14)−C(15)	117(1)
Mo(2)−C(13)	2.26(1)	P(1)−Mo(1)−Mo(2)	71.8(1)
Mo(2)−C(14)	2.29(1)	C(1)−Mo(1)−Mo(2)	69.7(3)
C(13)−C(14)	1.45(2)	C(2)−Mo(2)−Mo(1)	60.1(4)
C(14)−C(15)	1.49(2)		

As for the alkenylphosphine ligand, the C(13)−C(14) distance of 1.45(2) Å is slightly longer than those found for similar ligands η^2-bound to dimolybdenum centers such as the mentioned $[Mo_2Cp_2(\mu\text{-}PPh_2)\{\mu\text{-}Ph_2PC(Me){=}CHMe\}(\mu\text{-CO})]^+$ (1.42(2) Å)[14b] and $[Mo_2Cp_2\{\mu\text{-}Ph_2PCH{=}CH_2\}(CO)_4]$ (1.409(4) Å).[31] The latter distances fall in the middle of typical single C−C and double C=C bond lengths, this being consistent with the π-coordination of the olefin to one Mo center. However, the P(1)−C(13)−C(14) and C(13)−C(14)−C(15) angles in **6** are still very close to the theoretical 120° corresponding to an sp^2 hybridization in the alkenylic carbons.

Spectroscopic data in solution for compound **6** are fully consistent with its solid-state structure. Thus, the IR spectrum

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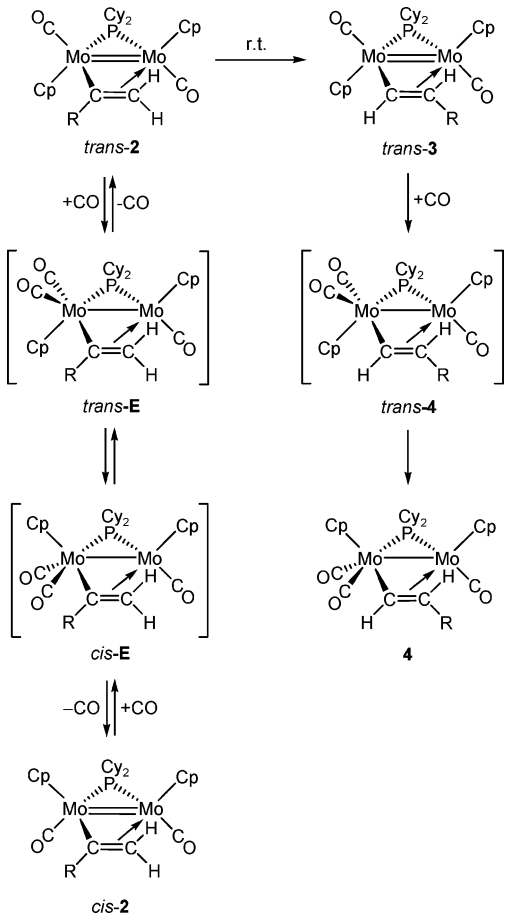
(31) Davies, J. E.; Mays, M. J.; Raithby, P. R.; Woods, A. D. *Chem. Commun.* **1999**, 2455.

in CH_2Cl_2 exhibits a typical pattern for two CO ligands in a *transoid* arrangement,[15] with bands at 1793 and 1762 cm^{-1}. An additional band is observed at 1690 cm^{-1}, due to the C−O stretch in the carboxylate group. The ^{31}P NMR spectrum now exhibits a considerably shielded resonance (δ_P 23.5 ppm), consistent with the presence of a Mo-bound tertiary phosphine ligand, the position being similar to those found for the mentioned dimolybdenum alkenylphosphine complexes.[14b,31] As expected, the ^1H NMR spectrum exhibits separated Cp resonances, whereas the alkenylic protons give rise to multiplets at 3.65 (H_α, $J_{HH} = 10$, $J_{PH} = 14$) and 2.11 (H_β, $J_{HH} = 10$, $J_{PH} = 5$) ppm, in the range found for other alkenylphosphine ligands in related di-[14b,22b,31−33] and polynuclear[34,35] compounds. As anticipated for a fully asymmetric molecule, the ^{13}C NMR spectrum of **6** displays separate resonances for each of the 12 carbon nuclei of the Cy groups and the inequivalent Cp and CO ligands. The quite different shielding of the latter resonances, located at 272.9 and 257.7 ppm, reveals the persistency in solution of semibridging interactions of distinct intensity for the CO ligands, as found in the crystal. These chemical shifts are comparable to that found for the cationic $[Mo_2Cp_2(\mu\text{-}PPh_2)\{\mu\text{-}Ph_2PC(Me)=CHMe\}(\mu\text{-}CO)]^+$ (268.9 ppm).[14b] As for the alkenyl group, two upfield signals can be assigned to the C_α (3.4 ppm, $J_{PC} = 38$) and C_β nuclei (41.1 ppm), in the range expected for this type of ligand when coordinated.

Pathways for the Reaction of 1 with HC≡C(*p*tol). As discussed above, the 30-electron hydride **1** reacts with *p*-tolylacetylene at room temperature to give different mixtures of the α-substituted alkenyl complex *trans*-**2** and the *β*-substituted isomer *trans*-**3**, depending on time and temperature, with *trans*-**3** being clearly favored at longer reaction times and higher temperatures, due to the thermal conversion of the former into the latter, as revealed by independent experiments (Scheme 1). Thus, the kinetic product appears to be *trans*-**2**, which results from the Markovnikov-type addition of the Mo−H bond (with polarity Mo^--H^+) to the unsaturated organic substrate, usually favored for these additions.[22] We note, however, that in the absence of a detailed kinetic study we cannot exclude that a small amount of the *β*-substituted isomer *trans*-**3** could be actually formed directly from **1**. The α−*β* isomerization converting the initially formed *trans*-**2** into the thermodynamic product *trans*-**3** requires formally an overall [2,1] H shift, a rarely observed process, of which we have found only two clear precedents. In the first one, Hogarth et al. found that compounds $[Fe_2(\mu\text{-}CRCH_2)(\mu\text{-}PPh_2)(CO)_6]$ rearranged to give the *β*-substituted alkenyl complexes in refluxing toluene, the process possibly involving a C−H bond cleavage to give an alkyne-hydride intermediate, according to the experimental data available.[22a] The second precedent involves a similar α−*β* isomerization in the cationic $[Ir_2Cp^*_2(\mu\text{-}CRCH_2)(\mu\text{-}dmpm)]^{2+}$, also under energetic conditions (120 °C).[4] In contrast, *trans*-**2** isomerizes to the *β*-alkenyl complex *trans*-**3** under much milder conditions (24 h at room temperature or just 1 h at 60 °C). This substantial difference must be attributed to the electronic and coordinative unsaturation of the dimetal center in the dicarbonyl complexes **2** and **3**, thus providing the empty orbitals and room facilitating the oxidative addition of the C−H bond to the metal center, as required in the hydride mechanism for the α−*β* isomerization.

Scheme 4. Proposed Reaction Pathways in the Reaction of 1 with HC≡C(*p*tol)



The carbonylation of the 32-electron complex *trans*-**3** gives a saturated tricarbonyl **4** displaying a *cisoid* arrangement of the Cp (or carbonyl) ligands with respect to the Mo_2P plane. This requires a 180° rotation of either the $MoCp(CO)_2$ or the MoCp(CO) moieties around the Mo−Mo vector in the *transoid* tricarbonyl derivative (*trans*-**4** in Scheme 4) expectedly formed (but not detected) after the initial coordination of the CO ligand. There are just a few examples in the literature of binuclear tricarbonyl complexes of the group 6 metals such as **4**, since usually the corresponding di- or tetracarbonyl derivatives ($[M_2Cp_2(\mu\text{-}X)(\mu\text{-}Y)(CO)_n]$, $n = 2, 4$) are more stable. This is the case of the bis(phosphide) complex *cis*-$[Mo_2Cp_2(\mu\text{-}PEt_2)_2(CO)_3]$, detected at low temperatures in the carbonylation reaction of $[Mo_2Cp_2(\mu\text{-}PEt_2)_2(\mu\text{-}CO)]$, which rapidly evolves to a *trans*-dicarbonyl derivative at room temperature.[12a] In a similar way, the stannyl compound $[Mo_2Cp_2(\mu\text{-}PCy_2)(SnPh_3)(CO)_3]$ decomposes progressively in solution to give a mixture of the corresponding di- and tetracarbonyl derivatives in the absence of CO.[36] The low stability of these tricarbonyl derivatives explains perhaps our inability to detect similar species in the carbonylation reaction of the α-substituted alkenyl *trans*-**2**, which instead yields an equilibrium mixture of this complex with its *cis*-dicarbonyl isomer. Yet, we propose that this isomerization requires CO capture at a transient stage in order to proceed. Thus, the carbonylation of *trans*-**2** would give a *transoid* tricarbonyl derivative (*trans*-**E** in Scheme 4, undetected), which would rearrange to give the corresponding *cisoid*

(32) Henrick, K.; McPartlin, M.; Iggo, J. A.; Kemball, A. C.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1987**, 2669.
(33) Hogarth, G. *J. Organomet. Chem.* **1991**, *407*, 91.
(34) Acum, G. A.; Mays, M. J.; Raithby, P. R.; Solan, G. A. *J. Organomet. Chem.* **1996**, *508*, 137.
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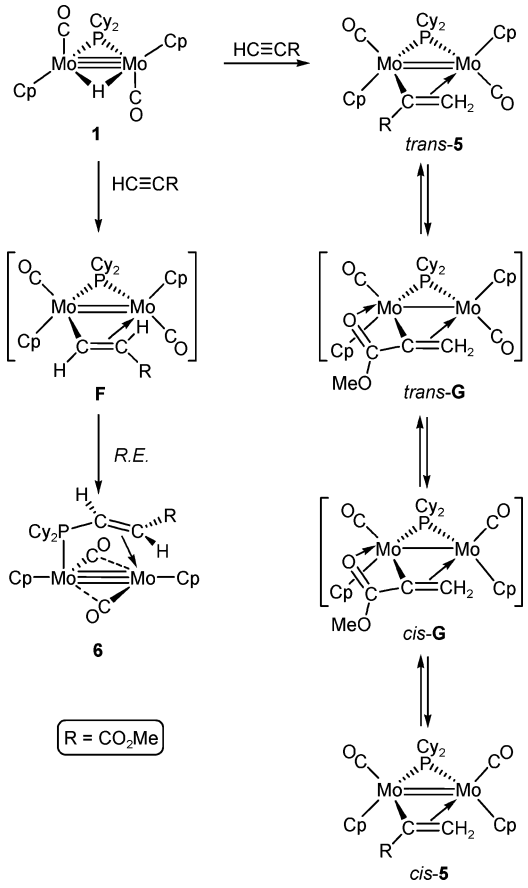
(36) Alvarez, M. A.; García, M. E.; Ramos, A.; Ruiz, M. A. *Organometallics* **2006**, *25*, 5374.

Scheme 5. Proposed Reaction Pathways in the Reaction of 1 with HC≡CCO$_2$Me (R.E. = Reductive Elimination)



tricarbonyl (*cis*-**E**). This intermediate, also undetected and comparable to compound **4**, would be much more unstable toward decarbonylation and then would yield the dicarbonyl *cis*-**2** spontaneously. Finally, in order to explain that an equilibrium mixture (rather than full isomerization) of these dicarbonyl complexes is attained, it must be assumed that all these transformations are reversible. We have previously shown that the few known *cis*-dicarbonyl complexes of type *cis*-[$Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2$] experience full transformation into their *trans*-dicarbonyl isomers either spontaneously at room temperature (M = Mo, W; R = R′ = Ph)[12b] or in the presence of CO (M = Mo; R = Ph; R′ = ^{t}Bu),[12a] but to our knowledge the reverse process (i.e., *cis*- to *trans*-dicarbonyl rearrangement) has not been observed previously in phosphide-bridged complexes of the group 6 metals.

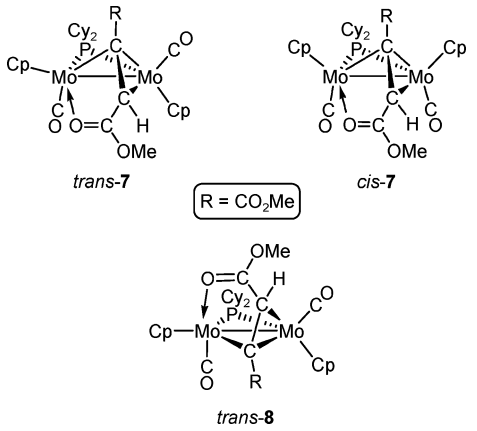
Pathways for the Reaction of 1 with HC≡CCO$_2$Me. There are a few differences between this reaction and the one with *p*-tolylacetylene just discussed. First of all, no β-substituted alkenyl complexes are detected in this case; instead, the β-substituted alkenyl group is specifically found as a constituent of the alkenylphosphine complex **6**. Moreover, separate experiments indicated that the α-substituted alkenyl complexes **5** did not rearrange by heating into either β-alkenyl complexes or into compound **6**. Then we propose that an undetected β-alkenyl complex (**F** in Scheme 5) must be formed directly from **1**, then experiencing fast P−C bond reductive elimination to yield compound **6**. There are only a few precedents of similar P−C bond formation reactions in the literature, most of them requiring energetic conditions and the addition of external ligands. For example, the alkenylphosphine compounds [$Mn_2\{PPh_2C(R)$═$CHR\}(CO)_9$] could be made by heating the corresponding alkenyl complexes [$Mn_2(\mu\text{-}CRCRH)(\mu\text{-}PPh_2)(CO)_7$] (R = H, Ph) under a CO atmosphere.[32] Likewise, the iron complex [$Fe_2(\mu\text{-}CPhCH_2)(\mu\text{-}PPh_2)(CO)_6$] reacts under thermal conditions with the diphosphine dppm to give the alkenylphosphine derivative [$Fe_2(\mu\text{-}PPh_2CPhCH_2)(CO)_5(\mu\text{-dppm})$] as a byproduct.[22b] Interestingly, the opposite reaction, i.e., a P−C bond cleavage to re-form an alkenyl phosphide derivative, takes place for the diiron complex upon decarbonylation in refluxing toluene.[22b] However, the reaction of the anionic [$Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4$]$^-$ with acryloyl chloride leads to the vinylphosphine derivative [$Mo_2Cp_2(\mu\text{-}PPh_2CHCH_2)(CO)_4$] at room temperature, presumably after CO elimination and subsequent reductive elimination in an undetected alkenyl intermediate.[31]

The major products of the reaction of compound **1** with methyl propiolate are the α-substituted alkenyl complexes *cis*-**5** and *trans*-**5**. In contrast to the behavior of compounds **2**, the presence of CO is not required now to reach an equilibrium between *cis* and *trans* isomers. Actually, no significant changes in the ratio were observed for **5** either under a CO atmosphere or after exposure to vis−UV light. However, the *cis*/*trans* equilibrium ratio was found to be solvent-dependent, although little sensitive to temperature changes, as shown by the ^{1}H NMR spectra recorded in different solvents (see Experimental Section). In any case, this proves that *cis*/*trans* interconversion occurs spontaneously in solution. Interestingly, no α−β alkenyl isomerization was observed for **5**, which also denotes a different behavior when compared to compounds **2**. To account for the above differences derived from the replacement of a *p*-tolyl by a methyl carboxylate substituent at the α position of the alkenyl ligand, we postulate that O-coordination of the carbonyl group of the latter substituent takes place in a transient step to give an electron-precise intermediate *trans*-**G** (Scheme 5), analogous to the tricarbonyl intermediate *trans*-**E** mentioned earlier. *Trans* to *cis* isomerization would take place analogously at this step to give *cis*-**G**, with the right geometry to yield *cis*-**5** after detachment of the carboxylate group. As we will discuss later on, metal coordination of carboxylate substituents of alkynes is well documented and is identified in stable derivatives of **1** when this substituent is placed at the β-position of the alkenyl ligand. The lack of any detectable α−β alkenyl isomerizaton in compound **5** is more difficult to explain, considering how easy this transformation occurs in the *p*-tolyl compound *trans*-**2**. A possible explanation is that, having a more electron-withdrawing substituent on the alkenyl ligand, the dimetal center in **5** has a lower electron density (reflected in higher C−O stretching frequencies; see Table 1), thus making the required oxidative addition of the C−H bond of the alkenyl group less likely.

Finally, we should note that the reaction of the 30-electron hydride **1** with 1-alkynes seems to be a good synthetic route to obtain alkenyl derivatives with a formal double Mo═Mo bond under mild conditions. Actually, related dicarbonyl derivatives have been obtained previously only under photolytic conditions starting from the saturated thiolate complexes [$Mo_2Cp_2(\mu\text{-H})(\mu\text{-SR})(CO)_4$].[13] Under analogous photolytic conditions, only electron-precise tricarbonyl complexes were obtained using the related phosphide-bridged complex [$Mo_2Cp_2(\mu\text{-H})(\mu\text{-PMe}_2)(CO)_4$].[18]

Reactivity of Compound 1 toward Dimethylacetylenedicarboxylate. The unsaturated hydride **1** reacts with an excess of $C_2(CO_2Me)_2$ in toluene at room temperature to yield after 4 h a mixture of three isomers of the complex [$Mo_2Cp_2\{\mu\text{-}\eta^1,\kappa\text{:}\eta^2\text{-}C(CO_2Me)CH(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2$] (*cis*-**7**, *trans*-**7**, and *trans*-**8**), all of them having a σ:π-bonded alkenyl bridge of *E*-conformation with an additional Mo−O(carbonyl) bonding

Chart 2



interaction from the carboxylate group attached to C_β. Compounds **7** have the coordinated O atom placed in a *transoid* position with respect to the dicyclohexylphosphide bridge and differ in the relative arrangement (*trans* or *cis*) of their carbonyl ligands. In contrast, *trans*-**8** exhibits a *cisoid* arrangement of the coordinated O and P atoms and displays a *transoid* arrangement of its carbonyl ligands (Chart 2). There is no evidence of the formation of a *cisoid* isomer of the latter (*cis*-**8**) in this reaction. In solution, compounds *trans*-**7** and *trans*-**8** slowly transform into each other to yield a roughly equimolar equilibrium ratio, although separated crystals of both isomers could be obtained from these solutions. However, upon dissolution of single crystals of any of these isomers, the equilibrium mixture is attained after several hours. In contrast, the isomer *cis*-**7**, which is the minor product of the reaction, does not transform into the other isomers. In fact, we did not observe any interconversion between *cis* and *trans* isomers, at least at room temperature.

Solid-State Structures of Isomers 7 and 8. Suitable crystals for an X-ray diffraction study could be grown for all three isomers *cis*-**7**, *trans*-**7**, and *trans*-**8** (Figures 2 to 4 and Tables 3 to 5). All compounds display two Mo(CO)Cp moieties bridged by a symmetrically bonded dicyclohexylphosphide group and by a five-electron-donor alkenyl ligand, π-bonded to one of the metal atoms through its double $C_\alpha{=}C_\beta$bond and σ-bonded to the second metal atom through the C_α atom and the O(carbonyl) atom of the carboxylate group attached to C_β, this completing an almost flat five-membered MoC_3O ring. The relative positioning of the bridging ligands is identical in *cis*-**7** and *trans*-**7**, these exhibiting a *transoid* coordination of the O- and P-donor atoms (P−Mo−O ca. 133°), while in *trans*-**8** these atoms are arranged *cis* (P−Mo−O ca. 85°). The other difference concerns the relative arrangement (*cis* or *trans*) of the Mo(CO)Cp moieties with respect to the Mo_2P plane. In *cis*-**7** this results in carbonyl ligands almost parallel to each other and placed at right angles with respect to the intermetallic vector. In *trans*-**7** and *trans*-**8**, the carbonyl ligand on the Mo atom bound to oxygen is slightly bent over the intermetallic vector (C−Mo−Mo angles ca. 82° and 76°, respectively), while the second carbonyl ligand opens away from the dinuclear center (C−Mo−Mo angles ca. 118° and 107°, respectively). To our knowledge, three comparable C,C,O-bonded alkenyl dimolybdenum complexes have

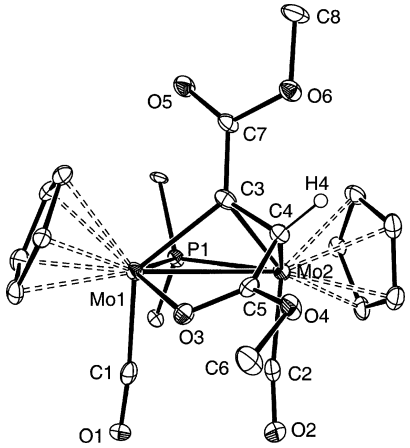


Figure 2. ORTEP diagram (30% probability) of compound *cis*-**7**, with H atoms (except H4) and Cy rings (except their C^1 atoms) omitted for clarity.

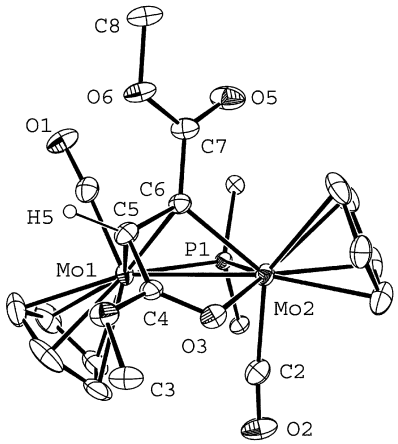


Figure 3. ORTEP diagram (30% probability) of compound *trans*-**7**, with H atoms (except H5) and Cy rings (except their C^1 atoms) omitted for clarity.

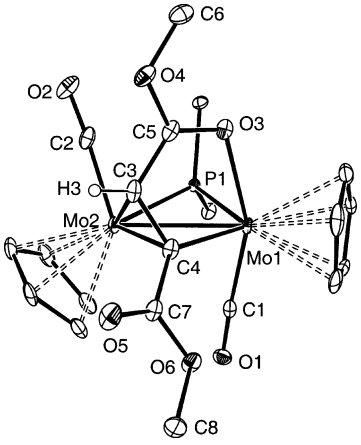


Figure 4. ORTEP diagram (30% probability) of compound *trans*-**8**, with H atoms (except H3) and Cy rings (except their C^1 atoms) omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound *cis*-7

Mo(1)−Mo(2)	2.961(1)	O(1)−C(1)−Mo(1)	174.8(8)
Mo(1)−C(1)	1.98(1)	O(2)−C(2)−Mo(2)	172.3(8)
Mo(2)−C(2)	1.93(1)	Mo(1)−P(1)−Mo(2)	74.78(7)
Mo(1)−O(3)	2.197(6)	C(1)−Mo(1)−Mo(2)	89.2(3)
Mo(1)−C(3)	2.174(9)	C(2)−Mo(2)−Mo(1)	80.4(3)
Mo(2)−C(3)	2.14(1)	O(3)−Mo(1)−P(1)	134.4(2)
Mo(2)−C(4)	2.24(1)	C(4)−C(3)−Mo(1)	108.5(6)
Mo(1)−P(1)	2.427(3)	Mo(2)−C(3)−Mo(1)	86.7(3)
Mo(2)−P(1)	2.449(2)	C(5)−C(4)−C(3)	114.0(8)
C(3)−C(4)	1.45(1)	C(5)−C(4)−H(4)	115(6)
C(4)−C(5)	1.41(1)	C(3)−C(4)−H(4)	117(6)
O(3)−C(5)	1.26(1)		
O(5)−C(7)	1.22(1)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound *trans*-7

Mo(1)−Mo(2)	2.9278(8)	O(1)−C(1)−Mo(1)	177.2(7)
Mo(1)−C(1)	1.949(9)	O(2)−C(2)−Mo(2)	174.1(7)
Mo(2)−C(2)	1.982(8)	Mo(1)−P(1)−Mo(2)	73.2(1)
Mo(2)−O(3)	2.264(5)	C(1)−Mo(1)−Mo(2)	117.5(2)
Mo(1)−C(5)	2.244(7)	C(2)−Mo(2)−Mo(1)	82.2(2)
Mo(1)−C(6)	2.154(7)	O(3)−Mo(2)−P(1)	132.5(1)
Mo(2)−C(6)	2.174(7)	C(5)−C(6)−Mo(1)	74.1(4)
Mo(1)−P(1)	2.453(2)	Mo(2)−C(6)−Mo(1)	85.1(2)
Mo(2)−P(1)	2.456(2)	C(4)−C(5)−C(6)	114.3(6)
C(4)−C(5)	1.42(1)	C(4)−C(5)−H(5)	109(3)
C(5)−C(6)	1.46(1)	C(6)−C(5)−H(5)	133(3)
O(3)−C(4)	1.250(8)		
O(5)−C(7)	1.24(1)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound *trans*-8

Mo(1)−Mo(2)	2.8755(4)	O(1)−C(1)−Mo(1)	176.1(3)
Mo(1)−C(1)	1.988(3)	O(2)−C(2)−Mo(2)	176.2(3)
Mo(2)−C(2)	1.946(4)	Mo(1)−P(1)−Mo(2)	73.4(1)
Mo(1)−O(3)	2.264(2)	C(1)−Mo(1)−Mo(2)	76.4(1)
Mo(2)−C(3)	2.294(3)	C(2)−Mo(2)−Mo(1)	107.4(1)
Mo(1)−C(4)	2.123(3)	O(3)−Mo(1)−P(1)	84.6(1)
Mo(2)−C(4)	2.212(3)	C(3)−C(4)−Mo(1)	111.2(2)
Mo(1)−P(1)	2.401(1)	Mo(2)−C(4)−Mo(1)	83.1(1)
Mo(2)−P(1)	2.409(1)	C(5)−C(3)−C(4)	114.4(3)
C(3)−C(4)	1.439(5)	C(5)−C(3)−H(3)	118(2)
C(3)−C(5)	1.434(5)	C(4)−C(3)−H(3)	125(2)
O(3)−C(5)	1.258(4)		
O(5)−C(7)	1.213(4)		

been previously characterized through X-ray diffraction, these being *trans*-[$Mo_2Cp_2\{\mu$-η^1,κ:η^2-C(CO_2Me)CH(CO_2Me)}(μ-X)($CO)_2$] (X = PPh_2, S^{i}Pr)[37] and *trans*-[$Mo_2Cp_2\{\mu$-η^1,κ:η^2-CHCH(COPh)}(μ-PPh_2)($CO)_2$],[38] all of them with a conformation identical to that of *trans*-**7**.

The conformational differences between our C,C,O-bonded complexes have little or very modest influence upon the metal−ligand binding and result in internuclear separations comparable to those measured in the above-mentioned complexes[37,38] or in other alkenyl-bridged dimolybdenum complexes.[17d] The isomers **7** display almost identical Mo−C lengths for the alkenyl ligand, these revealing strong σ- (Mo−C_α ca. 2.17 Å) and π-binding (Mo−C_α ca. 2.15 Å; Mo−C_β ca. 2.24 Å) of this group. In agreement with this, the C_α−C_β length is quite large (ca. 1.45 Å), even slightly longer than the single-bond C−CO_2Me length. The most significant difference is found in the Mo−O separations, with that in *trans*-**7** (2.264(5) Å) being ca. 0.07 Å longer than that in *cis*-**7**, suggesting a weaker O−Mo binding in the first case. As a result of this, the dimetal center is electron poorer, hence the slightly shorter (by ca. 0.03 Å) intermetallic separation in *trans*-**7**. As for *trans*-**8**, the Mo−O separation is identical to that in *trans*-**7**, but the alkenyl ligand becomes more asymmetrically bound, so that its σ-binding becomes stronger (Mo−C_α ca. 2.12 Å) and its π-binding weaker (Mo−C_α ca. 2.21 Å, Mo−C_β ca. 2.29 Å). Overall, the alkenyl ligand in *trans*-**8** seems to behave as a less efficient donor, since the intermetallic separation is now 2.8755(4) Å, some 0.05 Å shorter than that in *trans*-**7**.

Solution Structures of Isomers 7 and 8. Spectroscopic data in solution for the latter three isomers are fully consistent with the structures found in the crystal. The IR spectra in solution for compounds *trans*-**7** and *trans*-**8** could not be measured with full precision, since these isomers are in slow equilibrium in solution and could not be satisfactorily separated by chromatographic techniques, so all we could obtain were mixtures temporary enriched in one or the other isomer (before thermal equilibrium was reached). The mixtures where *trans*-**7** is dominant display an IR spectrum with a typical pattern of *transoid* $M_2(CO)_2$ oscillators,[15] with the strongest C−O stretching band at 1863 cm^{-1} and a weak shoulder at 1910 cm^{-1}. In contrast, when *trans*-**8** is more abundant in the mixture, the strongest band increases its frequency somewhat (1866 cm^{-1}) and the weak symmetric stretch becomes a better defined weak band at 1912 cm^{-1}. As for *cis*-**7**, it displays a typical pattern of *cisoid* $M_2(CO)_2$ oscillators [1943 (vs), 1832 (m) cm^{-1}], with bands comparable to those measured for compound *cis*-**2** or *cis*-**5** (Table 1).

The ^{31}P NMR resonances for the electron-precise compounds **7** and **8** appear at higher chemical shifts than those of the unsaturated alkenyl complexes **2** to **5**, which seems to be a general trend when comparing 34-electron and 32-electron dimolybdenum complexes with PR_2 bridges.[12a] The figures also follow the expected trends with respect to the *cis*/*trans* isomerism of dicarbonyl compounds,[12] so that *cis*-**7** exhibits a resonance some 30 ppm above that of *trans*-**7**.

The slow equilibrium involving the isomers *trans*-**7** and *trans*-**8** could be followed using ^{1}H NMR spectroscopy of the solutions obtained from crystalline samples of these compounds, which could be separated thanks to the different color of their crystals. The ^{1}H NMR spectra of $CDCl_3$ solutions obtained from either dark brown crystals of *trans*-**8** or pale red ones of *trans*-**7** behaved similarly: after a few minutes, small quantities of the other isomer were already present in both samples, and the same equilibrium ratio was reached in ca. 12 h at room temperature. Other features of the ^{1}H and ^{13}C NMR spectra of compounds **7** and **8** are comparable to those in compounds **2** to **5** or related alkenyl complexes and need not to be further discussed. We note here that Morris et al. also observed a slow equilibrium between two dicarbonyl isomers of [$Mo_2Cp_2\{\mu$-η,κ:η^2-C(CO_2Me)CH(CO_2Me)}(μ-X)($CO)_2$] (X = PPh_2, SEt, S^{i}Pr).[37,39] At the time, the authors proposed a *cis*/*trans* dicarbonyl isomerism for their complexes. However, in view of our data we tend to think that the isomers actually present for the above diphenylphosphide complex are rather two *trans* isomers similar to *trans*-**7** and *trans*-**8**, a proposal that would better account for their similar IR patterns and ^{31}P chemical shifts ($\Delta\delta_P$ ca. 10 ppm, to be compared to ca. 15 ppm in our complexes).

Finally, we should note that previous examples available of dimolybdenum compounds having C,C,O-bonded alkenyl ligands could be synthesized only under drastic thermal conditions and prolonged reaction times, starting from the saturated alkyne derivatives [$Mo_2Cp_2(\mu$-η^2:η^2-RCCR)($CO)_3$L] (L = CO, PPh_3).[14b,37−39] In contrast, compounds **7** and **8** can be obtained under mild conditions (room temperature) and short times (4 h), which is of course only possible due to the unsaturated nature of hydride **1**. As a result, new isomers can be prepared that otherwise just would not be even detected.

Concluding Remarks

The 30-electron hydride **1** reacts under mild conditions with the 1-alkynes RC≡CH (R = *p*tol, CO_2Me) to mainly give unsaturated alkenyl derivatives with a formal Mo═Mo double bond, as a result of the alkyne insertion into the Mo−H bond of **1**. When R = *p*tol, this insertion occurs selectively to give

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(38) Doel, G. R.; Feasey, N. D.; Knox, S. A. R.; Orpen, A. G.; Webster, J. *J. Chem. Soc., Chem. Commun.* **1986**, 542.
(39) Adams, H.; Bailey, N. A.; Gay, S. R.; Hamilton, T.; Morris, M. J. *J. Organomet. Chem.* **1995**, *493*, C25.

the α-substituted alkenyl derivative, with retention of the *transoid* arrangement of the Mo(CO)Cp moieties (*trans*-**2**), which then rearranges thermally to its *β*-substituted alkenyl isomer (*trans*-**3**). The unsaturated nature of these products is revealed by their reactions with CO, causing full carbonylation in the latter case but only partial *trans*- to *cis*-dicarbonyl isomerization in the α-substituted isomer. Replacement of the *p*tol substituent in the alkyne by the small and electron-withdrawing methylcarboxylate group has several effects: First, the insertion takes place in the two possible ways to give α- and *β*-substituted alkenyl derivatives, which, however, evolve very differently. Second, the presence of the carboxylate group at the α-carbon of the alkenyl ligand allows for the transient O-coordination of its carbonyl group, thus facilitating the *trans* to *cis* arrangement of the Mo(CO)Cp fragments (*trans*-**5**/*cis*-**5** equilibrium) via an electron-precise intermediate. Third, for reasons not clear at the moment, the presence of the carboxylate group at the *β*-carbon of the alkenyl ligand induces the reductive elimination between this ligand and the dicyclohexylphosphide bridge, rendering a four-electron-donor alkenylphosphine ligand (compound **6**). A carboxylate group at the *β*-carbon may, however, lead to the stable coordination of its carbonyl group to the unsaturated metal center to give an electron-precise complex, this being the dominant feature in the reaction of **1** with the disubstituted alkyne $(MeO_2C)C{\equiv}C(CO_2Me)$, which occurs analogously at room temperature to give three isomers of the 34-electron complex $[Mo_2Cp_2\{\mu\text{-}\eta,\kappa\text{:}\eta^2\text{-}C(CO_2Me)CH(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$. The mild conditions under which this reaction occurs allow for the isolation of isomers previously undetected in comparable products obtained through more energetic routes, as usually required when using electron-precise binuclear precursors.

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.[40] Compound $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ (**1**) was prepared as described previously,[11] 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 338−345 K. Photochemical experiments were performed using jacketed Pyrex Schlenk tubes, cooled by tap water (ca. 288 K). A 400 W mercury lamp (as source of visible−UV light) placed ca. 1 cm away from the Schlenk tube was used for these experiments. Low-temperature chromatographic separations were carried out using jacketed columns refrigerated by a closed 2-propanol circuit kept at the desired temperature with a cryostat, or by tap water. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity desired. IR stretching frequencies of CO ligands were measured either in solution (using CaF_2 windows) or in Nujol mulls (using NaCl windows) and are referred to as ν(CO). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (^{1}H), 121.50 (^{31}P{^{1}H}), or 75.47 MHz (^{13}C{^{1}H}) at 290 K in CD_2Cl_2 solutions 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 solutions (^{31}P). Coupling constants (J) are given in hertz. The metal-bound carbon atoms of the alkenyl ligands are referred to as C_α and C_β, with C_α corresponding to the bridgehead carbon atom.

(40) Armarego, W. L. F.; Chai, C. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: Oxford, UK, 2003.

Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(ptol)CH_2\}(\mu\text{-}PCy_2)(CO)_2]$ (*trans*-2). Compound **1** (0.050 g, 0.087 mmol) and $HC_2(ptol)$ (50 μL, 0.382 mmol) were stirred in toluene (10 mL) for 4 h to obtain a greenish-brown solution. Solvent was then removed under vacuum, and the residue was extracted with dichloromethane−petroleum ether (1:8) and chromatographed on an alumina column (activity II) at 248 K. Elution with the latter mixture gave two green fractions, which, after removal of solvents, yielded $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}CHCH(p\text{-}tol)\}(\mu\text{-}PCy_2)(CO)_2]$ (*trans*-**3**, 0.009 g, 15%) and *trans*-**2** (0.036 g, 46%), both as brownish-red solids contaminated with small amounts of *cis*-$[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(p\text{-}tol)CH_2\}(\mu\text{-}PCy_2)(CO)_2]$ (*cis*-**2**) and $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}CHCH(p\text{-}tol)\}(\mu\text{-}PCy_2)(CO)_3]$ (**4**). Spectroscopic data for compounds *trans*-**3**, *cis*-**2**, and **4** are given later on. *Data for trans*-**2**: ^{1}H NMR ($CDCl_3$): δ 7.00, 6.80 (2 × d, J_{HH} = 8, C_6H_4, 2 × 2H), 5.29 (s, Cp, 5H), 5.14, 5.13 (AB, J_{HH} = 2.5, CH_2, 2 × 1H), 5.11 (s, Cp, 5H), 2.60−1.00 (m, Cy, 22H), 2.28 (s, CH_3, 3H). ^{13}C{^{1}H} NMR (100.63 MHz, 243 K): δ 246.7 (d, J_{CP} = 14, CO), 246.5 (d, br, J_{CP} = 10, CO), 182.1 (s, C_α), 152.5 (s, C^1-*p*tol), 135.8 (s, C^4-*p*tol), 128.0, 127.7 (2 × s, C^2,C^3-*p*tol), 91.0, 89.8 (2 × s, 2 × Cp), 68.7 (s, C_β), 49.6 (d, J_{CP} = 24, C^1-Cy), 38.7 (d, J_{CP} = 16, C^1-Cy), 37.8 (d, J_{CP} = 3.5, $C^{2,6}$-Cy), 33.9 (d, J_{CP} = 1, $C^{2,6}$-Cy), 33.4 (d, J_{CP} = 5, $C^{2,6}$-Cy), 31.2 (d, J_{CP} = 3.5, $C^{2,6}$-Cy), 28.4 (d, J_{CP} = 13, $C^{3,5}$-Cy), 28.1 (d, J_{CP} = 15, $C^{3,5}$-Cy), 28.0 (d, J_{CP} = 10, $C^{3,5}$-Cy), 27.9 (d, J_{CP} = 10, $C^{3,5}$-Cy), 26.5, 26.2 (2 × s, C^4-Cy), 21.2 (s, CH_3).

Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(ptol)CH_2\}(\mu\text{-}PCy_2)(CO)_2]$ (*cis*-2). Compound *trans*-**2** (0.036 g, 0.052 mmol) was stirred in toluene (10 mL) under a CO atmosphere (1 atm) for 1 h to yield a greenish-orange solution containing a 1:1 mixture (measured by NMR) of compounds *trans*-**2** and *cis*-**2**, as well as small amounts of compounds *trans*-**3** and **4**. Compound *cis*-**2** could not be properly separated from the other components of the reaction mixture by chromatographic techniques or fractional crystallization. ^{1}H NMR ($CDCl_3$): δ 5.40, 4.30 (2 × s, br, Cp, 2 × 5H), 4.78, 4.35 (2 × d, J_{HH} = 1.4, CH_2, 2 × 1H). The rest of the signals due to compound *cis*-**2** were masked or overlapped by those of compound *trans*-**2**.

Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}CHCH(ptol)\}(\mu\text{-}PCy_2)(CO)_2]$ (*trans*-3). Compound **1** (0.060 g, 0.104 mmol) and $HC_2(p\text{-tol})$ (50 μL, 0.394 mmol) were heated in toluene (10 mL) at 60 °C for 1 h to yield a greenish-brown solution. Solvent was then removed under vacuum, and the residue was extracted with dichloromethane−petroleum ether (1:8) and chromatographed on an alumina column (activity IV) at 288 K. Elution with the latter mixture gave, after removal of solvents under vacuum, compound *trans*-**3** (0.060 g, 83%) as a brownish-red solid. Anal. Calcd for $C_{33}H_{41}Mo_2O_2P$: C, 57.23; H, 5.97. Found: C, 56.85; H, 5.75. ^{1}H NMR ($CDCl_3$): δ 8.86 (dd, J_{HH} = 12, J_{PH} = 1, $C_\alpha H$, 1H), 7.17, 7.13 (2 × d, J_{HH} = 9, C_6H_4, 2 × 2H), 6.76 (d, J_{HH} = 12, $C_\beta H$, 1H), 5.39, 4.97 (2 × s, 2 × Cp, 2 × 5H), 2.50−1.00 (m, Cy, 22H), 2.37 (s, CH_3, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 249.9 (d, J_{CP} = 14, CO), 237.7 (d, J_{CP} = 13, CO), 149.7 (d, J_{CP} = 3, C_α), 141.1 (s, C^1-*p*tol), 136.3 (s, C^4-*p*tol), 129.5 (s, C^2-*p*tol), 127.2 (s, C^3-*p*tol), 100.9 (s, C_β), 90.6, 90.0 (2 × s, Cp), 46.6 (d, J_{CP} = 21, C^1-Cy), 44.1 (d, J_{CP} = 17, C^1-Cy), 34.6 (d, J_{PC} = 3, $C^{2,6}$-Cy), 34.1 (d, J_{CP} = 4, $C^{2,6}$-Cy), 33.4, 32.6 (2 × s, $C^{2,6}$-Cy), 28.4 (d, J_{CP} = 13, $C^{3,5}$-Cy), 28.3 (d, J_{CP} = 13, $C^{3,5}$-Cy), 28.3 (d, J_{CP} = 11, $C^{3,5}$-Cy), 28.1 (d, J_{CP} = 11, $C^{3,5}$-Cy), 26.5 (s, 2 × C^4-Cy), 21.2 (s, CH_3).

Preparation of $[Mo_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}CHCH(p\text{-}tol)\}(\mu\text{-}PCy_2)(CO)_3]$ (4). Compound *trans*-**3** was stirred in toluene (10 mL) under a CO atmosphere (1 atm) for 24 h to give an orange solution. Solvent was then removed under vacuum, the residue was extracted with dichloromethane−petroleum ether (1:9), and the extracts were chromatographed on an alumina column (activity IV) at 253 K. Elution with the latter mixture gave an orange fraction, which yielded, after removal of solvents, compound **4** (0.050 g, 80%) as an orange solid. Anal. Calcd for $C_{34}H_{41}Mo_2O_3P$ (**4**): C, 56.67; H, 5.74. Found: C, 56.35; H, 5.98. ^{1}H NMR (400.54 MHz, $CDCl_3$):

δ 9.27 (dd, $J_{HH} = 9$, $J_{PH} = 3$, $C_\alpha H$, 1H), 7.09, 7.01 (AB, $J_{HH} = 8$, C_6H_4, 4H), 5.23, 5.04 (2 × s, 2 × Cp, 2 × 5H), 2.60−1.10 (m, Cy and $C_\beta H$, 21H), 2.28 (s, CH_3, 3H), 0.70, 0.01(2 × m, Cy, 2 × 1H); the resonance due to the H atom bonded to C_β is somewhere masked by the signals due to the cyclohexyl groups. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 242.2 (d, $J_{CP} = 20$, CO), 242.0 (d, $J_{CP} = 23$, CO), 236.8 (s, CO), 144.4 (s, C^1- *p*tol), 143.1 (d, $J_{CP} = 10$, C_α), 134.4 (s, C^4- *p*tol), 128.6 (s, C^2- *p*tol), 124.7 (s, C^3-*p*tol), 92.9, 92.1 (2 × s, 2 × Cp), 65.4 (s, C_β), 59.4 (d, $J_{CP} = 11$, C^1-Cy), 42.7 (d, $J_{CP} = 16$, C^1-Cy), 36.8 (s, $C^{2,6}$-Cy), 33.2 (d, $J_{CP} = 6$, $C^{2,6}$-Cy), 32.8 (s, $C^{2,6}$-Cy), 29.1 (d, $J_{CP} = 11$, $C^{3,5}$-Cy), 28.6 (s, $C^{2,6}$-Cy), 28.4 (d, $J_{CP} = 7$, $C^{3,5}$-Cy), 28.0 (d, $J_{CP} = 11$, $C^{3,5}$-Cy), 27.5 (d, $J_{CP} = 13$, $C^{3,5}$-Cy), 26.5, 26.0 (2 × s, 2 × C^4-Cy), 21.1 (s, CH_3).

Reaction of Compound 1 with Methyl Propiolate. Compound **1** (0.090 g, 0.156 mmol) and $HC_2(CO_2Me)$ (50 μL, 0.556 mmol) were stirred in toluene (12 mL) for 3 h at room temperature to give a brownish-orange solution. Solvent was then removed under vacuum, and the residue was extracted with dichloromethane−petroleum ether (1:4) and chromatographed on an alumina column (activity IV) at 288 K. Elution with dichloromethane−petroleum ether (1:3) gave a pale brown fraction, which, after removal of solvents, yielded $[Mo_2Cp_2\{\mu$-κ:η^2-$PCy_2CHCH(CO_2Me)\}(CO)_2]$ (**6**) as a brownish-orange solid (0.015 g, 15%). Elution with dichloromethane−petroleum ether (1:1) gave an orange fraction, which yielded, after removal of solvents, a mixture of compounds *cis*- and *trans*-$[Mo_2Cp_2(\mu$-$PCy_2)\{\mu$-η^1:η^2-$C(CO_2Me)CH_2\}(CO)_2]$ (*cis*-**5** and *trans*-**5**) as an orange solid (0.057 g, 55% overall yield). In solution, these isomers are in a solvent-dependent equilibrium, with their ratio (measured by ^1H NMR) being *cis*-**5**/*trans*-**5** = 2.7 (CD_2Cl_2), 3.8 [$(CD_3)_2CO$], and 1.9 (C_6D_6). The crystals of compound **6** used in the X-ray diffraction study were grown by the slow diffusion of a layer of petroleum ether into a concentrated solution of **6** in toluene at 253 K. Anal. Calcd for $C_{28}H_{37}Mo_2O_4P$ (*trans*-**5** and *cis*-**5**): C, 50.92; H, 5.65. Found: C, 50.83; H, 5.49. Anal. Calcd for $C_{28}H_{37}Mo_2O_4P$ (**6**): C, 50.92; H, 5.65. Found: C, 50.71; H, 5.82. *Spectroscopic data for compound trans-5*: $^{31}P\{^1H\}$ NMR (162.01 MHz, 263 K): δ 153.1 (s, μ-PCy_2). $^{31}P\{^1H\}$ NMR (162.01 MHz, 183 K): δ 156.0 (s, μ-PCy_2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 149.6 (s, μ-PCy_2). ^1H NMR (400.13 MHz): δ 5.32 (s, Cp, 10H), 5.30 (dd, $J_{HH} = 3$, $J_{PH} = 1$, CH_2, 1H), 4.85 (d, $J_{HH} = 3$, CH_2, 1H), 3.50 (s, OCH_3, 3H). ^1H NMR (400.13 MHz, 263 K): δ 5.37, 5.35 (2 × s, 2 × Cp, 2 × 5H), 5.30 (dd, $J_{HH} = 3$, $J_{PH} = 1$, CH_2, 1H), 4.93 (d, $J_{HH} = 3$, CH_2, 1H), 3.50 (s, OCH_3, 3H). ^1H NMR (400.13 MHz, 183 K): δ 5.49, 5.43 (2 × s, 2 × Cp, 2 × 5H), 5.30, 5.07 (2 × br, CH_2, 2 × 1H), 3.49 (s, OCH_3, 3H). ^1H NMR (C_6D_6): δ 5.65 (d, $J_{HH} = 3$, CH_2, 1H), 5.24 (s, Cp, 5H), 5.19 (d, $J_{HH} = 3$, CH_2, 1H), 4.91 (s, Cp, 5H), 3.50 (s, OCH_3, 3H); signals due to the Cy protons are masked by those of the major isomer *cis*-**5** in all ^1H NMR spectra. $^{13}C\{^1H\}$ NMR (100.63 MHz): δ 246.6 (d, $J_{CP} = 14$, CO), 244.4 (d, $J_{CP} = 11$, CO), 178.5 (s, *C*O_2Me), 155.2 (s, C_α), 90.6, 89.1 (2 × s, 2 × Cp), 72.9 (s, C_β), 51.2 (s, OCH_3), 48.8 (d, $J_{CP} = 22$, C^1-Cy), 43.3 (d, $J_{CP} = 16$, C^1-Cy), 34.4 (d, $J_{CP} = 3$, $C^{2,6}$-Cy), 33.9 (d, $J_{CP} = 4$, $C^{2,6}$-Cy), 32.0, 31.8 (2 × s, 2 × $C^{2,6}$-Cy), 26.6, 26.4 (2 × s, 2 × C^4-Cy); signals due to the $C^{3,5}$-Cy nuclei are masked by those of compound *cis*-**5** in the range 28.5−27.5. *Spectroscopic data for compound cis-5*: $^{31}P\{^1H\}$ NMR (162.01 MHz): δ 186.4 (s, μ-PCy_2, **C** and **D**). $^{31}P\{^1H\}$ NMR (162.01 MHz, 203 K): δ 186.3 (s, br, μ-PCy_2, **C** and **D**). $^{31}P\{^1H\}$ NMR (162.01 MHz, 183 K): δ 189.5 (s, μ-PCy_2, **C**), 184.0 (s, μ-PCy_2, **D**); **C**/**D** = 2/3. ^1H NMR (400.13 MHz, **C** and **D**): δ 5.36 (s, br, Cp, 5H), 4.64 (t, $J_{HH} = J_{PH} = 1.2$, CH_2, 1H), 4.62 (s, br, Cp, 5H), 3.78 (d, $J_{HH} = 1.2$, CH_2, 1H), 3.27 (s, OCH_3, 3H), 2.50−0.40 (m, Cy, 22H). ^1H NMR (400.13 MHz, 263 K, **C** and **D**): δ 5.38 (s, Cp, 5H), 4.63 (t, $J_{HH} = J_{PH} = 1.2$, CH_2, 1H), 4.62 (s, Cp, 5H), 3.78 (d, $J_{HH} = 1.2$, CH_2, 1H), 3.27 (s, OCH_3, 3H), 2.50−0.40 (m, Cy, 22H). ^1H NMR (400.13 MHz, 183 K, **C** and **D**): δ 5.38, 4.62 (2 × s, 2 × Cp, 2 × 5H), 3.26 (s, OCH_3, 3H), 2.50−0.20 (m, Cy, 22H); signals due to geminal hydrogens from the alkenyl ligand could not be unambiguously assigned due to broadening and/or overlapping with those of the Cp ligands. $^{13}C\{^1H\}$ NMR (100.63 MHz, **C** and **D**): δ 260.3 (br, CO), 239.2 (br, CO), 179.7 (s, *C*O_2Me), 152.7 (s, C_α), 89.3, 86.8 (2 × s, br, 2 × Cp), 50.5 (s, OCH_3), 49.6 (d, $J_{CP} = 25$, C^1-Cy), 49.2 (s, C_β), 43.0 (d, $J_{CP} = 16$, C^1-Cy), 33.4 (m, br, $C^{2,6}$-Cy), 28.7−28.0 (m, $C^{3,5}$-Cy), 27.0, 26.7 (2 × s, 2 × C^4-Cy). $^{13}C\{^1H\}$ NMR (100.63 MHz, 223 K, **C** and **D**): δ 260.4 (d, $J_{CP} = 6$, CO), 240.0 (d, $J_{CP} = 11$, CO), 179.9 (s, *C*O_2Me), 151.0 (s, C_α), 89.2, 87.0 (2 × s, 2 × Cp), 51.2 (s, OCH_3), 48.3 (br, C^1-Cy), 41.6 (d, $J_{CP} = 11$, C^1-Cy), 34.1, 33.2, 32.3, 31.9 (4 × s, 4 × $C^{2,6}$-Cy), 28.5−27.5 (m, $C^{3,5}$-Cy), 26.7, 26.3 (2 × s, C^4-Cy). $^{13}C\{^1H\}$ NMR (100.63 MHz, 310 K, only C−H resonances, **C** and **D**): δ 88.0 (br, Cp), 50.6 (s, OCH_3), 49.8 (s, C_β), 49.7 (d, $J_{CP} = 28$, C^1-Cy), 42.9 (d, $J_{CP} = 11$, C^1-Cy), 33.4 (s, br, C^2-Cy), 28.5, 28.1 (2 × d, $J_{CP} = 12$, 2 × C^3-Cy), 27.0, 26.8 (2 × s, 2 × C^4-Cy). *Spectroscopic data for compound 6*: ^1H NMR (C_6D_6): δ 4.96 (s, Cp, 5H), 4.90 (d, $J_{PH} = 2.5$, Cp, 5H), 4.15 (dd, $J_{HH} = 10$, $J_{PH} = 14$, P-CH, 1H), 3.37 (s, OCH_3, 3H), 2.46 (dd, $J_{HH} = 10$, $J_{PH} = 5$, CH=C*H*), 2.50−0.80 (m, Cy, 22H). $^{13}C\{^1H\}$ NMR: δ 272.9 (s, CO), 257.7 (s, CO), 176.7 (d, $J_{CP} = 13$, *C*O_2Me), 95.9, 92.1 (2 × s, Cp), 51.5 (s, OCH_3), 41.1 (s, *C*HCO_2Me), 40.3 (d, $J_{CP} = 11$, C^1-Cy), 37.5 (d, $J_{CP} = 31$, C^1-Cy), 30.1 (d, $J_{CP} = 2$, $C^{2,6}$-Cy), 29.7 (s, $C^{2,6}$-Cy), 29.4 (d, $J_{CP} = 3$, $C^{2,6}$-Cy), 28.5 (s, $C^{2,6}$-Cy), 28.2 (d, $J_{CP} = 11$, $C^{3,5}$-Cy), 27.9 (d, $J_{CP} = 9$, $C^{3,5}$-Cy), 27.6 (d, $J_{CP} = 9$, $C^{3,5}$-Cy), 27.5 (d, $J_{CP} = 11$, $C^{3,5}$-Cy), 26.8 (d, $J_{CP} = 1.6$, C^4-Cy), 26.6 (d, $J_{CP} = 1.6$, C^4-Cy), 3.4 (d, $J_{CP} = 38$, *C*$HPCy_2$).

Reaction of Compound 1 with Dimethylacetylenedicarboxylate. Compound **1** (0.045 g, 0.078 mmol) and $C_2(CO_2Me)_2$ (40 μL, 0.322 mmol) were stirred in toluene (10 mL) for 4 h to obtain a brown solution. Solvent was then removed under vacuum, and the residue was extracted with dichloromethane−petroleum ether (1:8) and chromatographed on an alumina column (activity IV) at 253 K. Elution with dichloromethane−petroleum ether (1:3) gave an orange-brown fraction, which gave, after removal of solvents, a mixture of the isomers $[Mo_2Cp_2\{\mu$-η,κ:η^2-$C(CO_2Me)CH(CO_2Me)\}$-$(\mu$-$PCy_2)(CO)_2]$ (*trans*-**7** and *trans*-**8**) in a 1:1 ratio, as a brown solid (0.038 g, 68%). Elution with dichloromethane−petroleum ether (1:1) gave an orange fraction, giving analogously compound *cis*-$[Mo_2Cp_2\{\mu$-η,κ:η^2-$C(CO_2Me)CH(CO_2Me)\}(\mu$-$PCy_2)(CO)_2]$ (*cis*-**7**) as an orange solid (0.010 g, 18%). The crystals used in the X-ray study of compounds *trans*-**7** and *trans*-**8** were grown by cooling at 253 K a concentrated solution of the isomeric mixture in petroleum ether. After several days, dark brown crystals of *trans*-**8** as well as red crystals of *trans*-**7** were formed, and they were separated by their color. The crystals used in the X-ray study of *cis*-**7** were grown by slow diffusion of a petroleum ether layer into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{30}H_{39}Mo_2O_6P$ (*cis*-**7**): C, 50.15; H, 5.47. Found: C, 50.06; H, 5.39. Anal. Calcd for $C_{30}H_{39}Mo_2O_6P$ (*trans*-**8**): C, 50.15; H, 5.47. Found: C, 50.03; H, 5.31. *Spectroscopic data for isomer trans-7*: ^1H NMR (400.13 MHz, $CDCl_3$): δ 5.28 (d, $J_{PH} = 3$, Cp, 5H), 4.97 (s, Cp, 5H), 3.71, 3.45 (2 × s, OMe, 2 × 3H), 3.24 (s, CH, 1H), 2.50−0.70 (m, Cy, 22H). *Spectroscopic data for compound cis-7*: ^1H NMR (400.13 MHz, $CDCl_3$): δ 5.20 (d, $J_{PH} = 1.5$, Cp, 5H), 5.03 (d, $J_{PH} = 1$, Cp, 5H), 3.58, 3.54 (2 × s, OMe, 2 × 3H), 2.84 (s, CH, 1H), 2.72, 2.08 (2 × m, 2 × H^1-Cy, 2 × 1H), 1.80−1.10 (m, Cy, 20H). $^{13}C\{^1H\}$ NMR (100.63 MHz): δ 252.7 (d, $J_{CP} = 11$, CO), 245.8 (d, $J_{CP} = 7$, CO), 195.7 (s, *C*O−Mo), 181.2 (d, $J_{CP} = 4$, *C*O_2Me), 119.3 (d, $J_{CP} = 20$, C_α), 91.1, 87.9 (2 × s, 2 × Cp), 53.5 (s, OCH_3), 52.4 (d, $J_{CP} = 15$, C^1-Cy), 50.3 (s, OCH_3), 48.6 (d, $J_{CP} = 6$, C^1-Cy), 35.1 (d, $J_{CP} = 3$, $C^{2,6}$-Cy), 34.6 (d, $J_{CP} = 5$, $C^{2,6}$-Cy), 34.5 (d, $J_{CP} = 5$, $C^{2,6}$-Cy), 33.8 (d, $J_{CP} = 6$, $C^{2,6}$-Cy), 33.4 (s, C_β), 28.8 (d, $J_{CP} = 10$, $C^{3,5}$-Cy), 28.7 (d, $J_{CP} = 11$, 2 × $C^{3,5}$-Cy), 28.6 (d, $J_{CP} = 9$, $C^{3,5}$-Cy), 26.7 (d, $J_{CP} = 1.5$, C^4-Cy), 26.7 (d, $J_{CP} = 1.5$, C^4-Cy). *Spectroscopic data for isomer trans-8*: ^1H NMR (400.13 MHz, $CDCl_3$): δ 5.28, 4.93 (2

Table 6. Crystal Data for Compounds 6, 7, and 8

	6	*cis*-**7**	*trans*-**7**	*trans*-**8**
mol formula	$C_{28}H_{37}Mo_2O_4P$	$C_{30}H_{39}Mo_2O_6P$	$C_{30}H_{39}Mo_2O_6P$	$C_{30}H_{39}Mo_2O_6P$
mol wt	660.43	718.46	718.46	718.46
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$
radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073
a, Å	10.128(5)	10.021(2)	11.1386(2)	9.7517(4)
b, Å	10.219(5)	14.848(3)	14.9749(3)	16.2182(6)
c, Å	14.175(8)	19.166(4)	19.9107(5)	18.3839(6)
α, deg	84.40(2)	90	90	90
β, deg	72.77(2)	94.815(4)	117.7950(10)	91.547(2)
γ, deg	77.58(2)	90	90	90
V, Å^3	1367.6(12)	2841.7(10)	2937.91(11)	2906.45(19)
Z	2	4	4	4
calcd density, g cm^{-1}	1.604	1.679	1.624	1.642
absorp coeff, mm^{-1}	1.007	0.982	0.95	0.960
temperature, K	293(2)	100(2)	100(2)	100(2)
θ range, deg	3.01 to 24.00	1.74 to 25.35	2.07 to 25.24	1.67 to 26.73
index ranges (h, k, l)	−10, 11; −11, 11; 0, 16	−12, 12; 0, 17; 0, 23	−13, 13; −17, 0; −23, 12	−12, 12; 0, 20; 0, 23
no. of reflns collected	4183	26 195	28 384	28 943
no. of indep reflns (R_{int})	4183 (0)	5420 (0.1403)	4966 (0.0411)	6396 (0.0523)
no. of reflns with $I > 2\sigma(I)$	2565	3070	3822	4532
R indexes (data with $I > 2\sigma(I)$)[a]	$R_1 = 0.0651$	$R_1 = 0.0729$	$R_1 = 0.0527$	$R_1 = 0.0360$
	$wR_2 = 0.1647$[b]	$wR_2 = 0.1773$[c]	$wR_2 = 0.1451$[d]	$wR_2 = 0.0678$[e]
R indexes (all data)[a]	$R_1 = 0.1118$	$R_1 = 0.1181$	$R_1 = 0.0795$	$R_1 = 0.0598$
	$wR_2 = 0.1875$[b]	$wR_2 = 0.2008$[c]	$wR_2 = 0.1843$[d]	$wR_2 = 0.0728$[e]
GOF	0.958	0.939	1.164	1.042
no. of restraints/params	0/317	0/358	0/358	0/358
$\Delta\rho$(max., min.), e Å^{-3}	1.002, −1.127	1.624, −2.194	0.904, −2.05	0.999, −0.442

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] $a = 0.1012$, $b = 0.0000$. [c] $a = 0.1190$, $b = 0.0000$. [d] $a = 0.0947$, $b = 12.6366$. [e] $a = 0.0312$, $b = 0.2262$.

× s, Cp, 2 × 5H), 4.25 (s, CH, 1H), 3.77, 3.31 (2 × s, OMe, 2 × 3H), 2.50−0.70 (m, Cy, 22H).

X-ray Structure Determination of Compound 6. The X-ray intensity data were collected on a Philips PW diffractometer using graphite-monochromated Mo Kα radiation at 273 K. Cell constants were obtained from a least-square refinement of the setting angles of 24 randomly distributed and carefully centered reflections (6.00° < 2θ < 16.00°). No crystal decay was observed during the data collection. The structure was solved by direct methods (SIR97)[41] and refined with full-matrix least-squares (SHELXL97),[42] using the WinGX software package.[43] The non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were placed at their calculated positions. Further experimental details are collected in Table 6.

X-ray Structure Determination of Compound *cis*-7. The X-ray intensity data were collected on a Smart-CCD-1000 Bruker diffractometer using graphite-monochromated Mo Kα radiation at 100 K. The software SMART[44] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The collected frames were then processed for integration by the software SAINT,[44] and a multiscan absorption correction was applied with SADABS.[45] Using the program suite WinGX,[43] the structure was solved by Patterson interpretation and phase expansion and refined with full-matrix least-squares on F^2 with SHELXL97.[42] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed at calculated positions except H(4), which was located in the Fourier map, and all of them were given an overall isotropic thermal parameter. Further experimental details are collected in Table 6.

X-ray Structure Determination of Compound *trans*-7. The X-ray data collection was performed at 100 K on a Nonius KappaCCD single-crystal diffractometer, using graphite-monochromated Mo Kα radiation. Images were collected at a 30 mm fixed crystal−detector distance, using the oscillation method, with 1° oscillation and 60 s exposure time for each image. Data collection strategy was calculated with the program Collect.[46] Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack,[47] and a semiempirical absorption correction was applied using the program SORTAV.[48] Using the program suite WinGX,[43] the structure was solved by Patterson interpretation and phase expansion and refined with full-matrix least-squares on F^2 with SHELXL97.[42] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed at calculated positions except H(5), which was located in the Fourier map, and all of them were given an overall isotropic thermal parameter. Further experimental details are collected in Table 6.

X-ray Structure Determination of Compound *trans*-8. The X-ray intensity data for *trans*-**8** were collected on a Kappa-Appex-II Bruker diffractometer using graphite-monochromated Mo Kα radiation at 100 K. The software APEX[49] was used for collecting frames with the omega/phi scans measurement method. The Bruker SAINT[44] software was used for the data reduction, and a multiscan absorption correction was applied with SADABS.[45] Using the program suite WinGX,[43] the structure was solved by Patterson interpretation and phase expansion and refined with full-matrix least-squares on F^2 with SHELXL97.[42] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed at calculated positions except H(3), which was located in the Fourier

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map, and all of them were given an overall isotropic thermal parameter. Further experimental details are collected in Table 6.

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Supporting Information Available: Crystallographic data for the structural analysis of compounds **6**, *cis*-**7**, *trans*-**7**, and *trans*-**8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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