# ORGANOMETALLICS

# Binuclear Carbyne and Ketenyl Derivatives of the Alkyl-Bridged Complexes $[Mo_2(\eta^5-C_5H_5)_2(\mu-CH_2R)(\mu-PCy_2)(CO)_2]$ (R = H, Ph)

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Supporting Information

**ABSTRACT:** The 30-electron benzylidyne complex  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)(\mu-CO)]$  (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) could be conveniently prepared upon photolysis of the benzyl-bridged complex  $[Mo_2Cp_2(\mu-CH_2Ph)(\mu-PCy_2)(CO)_2]$ . It reacted with CO to give the ketenyl complex  $[Mo_2Cp_2\{\mu-C(Ph)CO\}(\mu-$ 



 $PCy_2(CO)_2$  (2.6101(2) Å), which in turn could be selectively decarbonylated at 353 K to give the 32-electron benzylidyne derivative  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)(CO)_2]$  (Mo-Mo = 2.666(1) Å). Related methylidyne complexes could be obtained from the methyl-bridged complex  $[Mo_2Cp_2(\mu-CH_3)(\mu-PCy_2)(CO)_2]$  via its trinuclear derivative  $[Mo_3Cp_2(\mu_3-CH)(\mu-PCy_2)(CO)_7]$ . Thus, the carbonylation of the latter cluster gave the ketenyl complex  $[Mo_2Cp_2\{\mu-C(H)CO\}(\mu-PCy_2)(CO)_2]$ , whereas its reaction with  $P(OMe)_3$  gave the substituted cluster  $[Mo_3Cp_2(\mu_3-CH)(\mu-PCy_2)(CO)_6\{P(OMe)_3\}]$ , which in turn could be thermally degraded to give selectively the 30-electron methylidyne derivative  $[Mo_2Cp_2(\mu-CH)(\mu-PCy_2)(\mu-CO)]$  (Mo-Mo = 2.467(1) Å). DFT calculations on the phenylketenyl complex revealed that the metal-ligand interaction is intermediate between the extreme descriptions represented by the acylium (3-electron donor) and ketenyl (1-electron donor) canonical forms of this ligand.

# INTRODUCTION

Recently, we reported that the photochemical treatment of the agostic benzyl complex  $[Mo_2Cp_2(\mu-CH_2Ph)(\mu-PCy_2)(CO)_2]$ (1a) (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) promotes its partial decarbonylation and full dehydrogenation of the alkyl ligand to give with good yield the benzylidyne-bridged derivative  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2) (\mu$ -CO)] (2), a reactive 30-electron carbyne complex undergoing unusual C-C and C-P coupling processes under mild conditions.<sup>1</sup> In contrast, the photolysis of the related methylbridged complex  $[Mo_2Cp_2(\mu-CH_3)(\mu-PCy_2)(CO)_2]$  (1b) caused the ejection of just a CO molecule to yield a carbonyl derivative  $[Mo_2Cp_2(\mu-CH_3)(\mu-PCy_2)(\mu-CO)]$  having a strengthened agostic interaction (Scheme 1). However, the photolysis of 1b in the presence of several carbonyl complexes gave different methylidyne-bridged heterometallic clusters, thus revealing the occurrence of easy dehydrogenation steps after cluster formation.<sup>2</sup> The above dehydrogenation reactions are rare events for agostic alkyl-bridged complexes. Actually, we can quote only a couple of precedents of related  $\mu$ -CH<sub>3</sub>/ $\mu$ -CH transformations involving agostic ligands, those reported to occur at room temperature at Ru<sub>2</sub> (through dehydrogenation)<sup>3a</sup> and Fe<sub>3</sub> (through double oxidative addition of C-H bonds) metal centers.<sup>3b</sup> In addition, related  $\mu$ -CH<sub>2</sub>R/ $\mu$ -CH/ $\mu$ -CR transformations (R = CH<sub>2</sub>Ph) were described recently to occur at 393 K in a Ru<sub>3</sub> cluster.<sup>4</sup> Yet this sort of dehydrogenation reaction could provide a useful synthetic entry to unsaturated binuclear complexes bridged by arylcarbyne or methylidyne ligands, a type of relatively scarce molecules that might be considered as the simplest (if crude) models of related surface species formed in different heterogeneously catalyzed reactions, notably the Fischer-Tropsch (FT) synthesis of hydrocarbons from syngas  $(CO + H_2)^{.5}$  In

this Article, we give full details of the preparation and structural characterization of compound 2 as well as some unsaturated benzylidyne and phenylketenyl derivatives, including a DFT analysis of the latter species, aimed to better understand the metal-ligand interactions in these electron-deficient molecules. We also report that related unsaturated methylidyne- and ketenyl-bridged complexes can be obtained from the methylbridged complex 1b via its trinuclear derivative  $[Mo_3Cp_2(\mu_3 CH)(\mu - PCy_2)(CO)_7].$ 

# RESULTS AND DISCUSSION

Derivatives of the Benzyl Complex 1a. The photolysis of toluene solutions of 1a can be carried out easily at 288 K using visible-UV light to give with good yield the benzylidyne-bridged derivative  $[Mo_2Cp_2(\mu$ -CPh)( $\mu$ -PCy\_2)( $\mu$ -CO)] (2), the transformation being complete in ca. 2 h. Although the formation of 2 is obviously a multistep process involving the eventual elimination of  $H_2$  and a molecule of CO (Scheme 1), no intermediates could be detected in this reaction through IR and <sup>31</sup>P NMR monitoring of the corresponding solutions. The dehydrogenation step leading to 2 is irreversible, because this product does not react with H<sub>2</sub> even under pressure (60 bar) at room temperature, but the decarbonylation step is not, as expected for a 30-electron molecule. Indeed the reaction of **2** with CO (ca. 4 bar) proceeds smoothly at room temperature (ca. 2 d for completion), to give the ketenyl derivative  $[Mo_2Cp_2\{\mu$ -C(Ph)-CO { $(\mu$ -PCy<sub>2</sub>)(CO)<sub>2</sub>] (3) almost quantitatively (Scheme 2). As

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#### Scheme 1



Scheme 2



discussed later, the metal—ketenyl interaction in this molecule is intermediate between those expected for 1- and 3-electron donors, so we have depicted it with an intermetallic bond order between three and two. The formation of this complex does not involve just the addition of CO to the unsaturated dimetal center, but also to the carbyne ligand, and it can be fully reversed by irradiation of toluene solutions of **3** with visible-UV light at room temperature. Again, although several steps must be involved both in the forward and in the back reactions, no intermediates were detected by IR monitoring of these reactions.

We should note the significant influence that the substituent at the carbyne ligand has on the overall course of the reactions under discussion. Thus, we have recently shown that the methoxycarbyne complex [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -COMe)( $\mu$ -PCy<sub>2</sub>)( $\mu$ -CO)], a molecule isoelectronic with **2**, reacts with CO to give the electron-precise tricarbonyl [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -COMe)( $\mu$ -PCy<sub>2</sub>)(CO)<sub>3</sub>], rather than a ketenyl complex.<sup>6</sup> Actually, the hypothetical methoxylketenyl complex [Mo<sub>2</sub>Cp<sub>2</sub>{ $\mu$ -C(OMe)CO}( $\mu$ -PCy<sub>2</sub>)(CO)<sub>2</sub>] was predicted by DFT calculations to spontaneously undergo a 1,2-shift of the methoxyl substituent to yield the stable carboxycarbyne isomer [Mo<sub>2</sub>Cp<sub>2</sub>{ $\mu$ -C(CO<sub>2</sub>Me)}( $\mu$ -PCy<sub>2</sub>)(CO)<sub>2</sub>].<sup>7</sup>

The decarbonylation of the phenylketenyl complex **3** can be controlled thermally. Actually, it is possible to remove selectively a CO molecule from this compound by heating its toluene solutions at 353 K for 2 h, to give the dicarbonyl benzylidyne complex  $[Mo_2Cp_2(\mu$ -CPh) $(\mu$ -PCy<sub>2</sub>)(CO)<sub>2</sub>] (4) in good yield. Further decarbonylation of 4 to give the starting compound **2** is very slow under these conditions (in fact, only 50% conversion is reached after 7 h in refluxing toluene), although it can be performed rapidly (5 min) under visible-UV irradiation, as expected

Scheme 3



(Scheme 2). On the other hand, the reaction of 4 with CO (ca. 4 bar) to give back the ketenyl complex 3 takes place readily at room temperature in ca. 4 h, that is, faster than the carbonylation of **2**. Thus, there would be no chance to grow significant amounts of **4** by direct carbonylation of the starting carbyne complex **2**, in agreement with our experimental results.

It might be questioned whether the carbonylation of 4 to give the ketenyl complex 3 proceeds by direct attack of CO to the carbyne ligand, or rather would yield initially an isomeric tricarbonyl complex  $[Mo_2Cp_2(\mu$ -CPh)( $\mu$ -PCy\_2)(CO)\_3] (as observed in the carbonylation of  $[Mo_2Cp_2(\mu$ -COMe)( $\mu$ -PCy<sub>2</sub>)( $\mu$ -CO)] mentioned above), then rearranging into its ketenyl isomer 3. Indeed, direct attack of Lewis bases on bridging carbyne complexes is a well-established reaction for electron-precise carbyne-bridged cations such as  $[Fe_2Cp_2(\mu$ -CPh)( $\mu$ -CO)(CO)<sub>2</sub>]<sup>+</sup> and  $[Fe_2Cp_2$ - $(\mu$ -CH) $(\mu$ -CO) $(CO)_2^{-1}^{+.89}$  On the basis of the DFT study of the isoelectronic complex  $[Mo_2Cp_2{\mu-C(CO_2Me)}(\mu-PCy_2)(CO)_2]^6$ we could anticipate that both events are likely results of the reaction of 4 with CO from an orbital point of view. This would be so because the LUMO in the dicarbonyl complex has a large  $\pi^*$ -(Mo-Mo) character (thus expectedly favoring the formation of the tricarbonyl derivative) while the LUMO+1 orbital (0.96 eV higher in energy) has a large  $\pi^*(Mo-C)$  character (then favoring the direct attack of CO at the C atom to give 3). However, the atomic charge at the carbyne atom is 0.2-0.3e more negative than those at the Mo atoms (close to 0), and this should disfavor the direct attack of CO at the carbyne ligand. Thus, we rather trust that the carbonylation of 4 follows the two-step pathway outlined above.

As for the carbonylation of the carbyne complex **2**, this is likely to follow initially a reaction pathway analogous to that of the isoelectronic diphosphide-bridged complexes of the type  $[M_2Cp_2(\mu-PR_2)(\mu-PR_2')(\mu-CO)]$  previously studied by us (M = Mo, W).<sup>10</sup> Under that scheme, complex **2** might yield the mentioned species  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)(CO)_3]$  stepwise via a cis isomer of the dicarbonyl **4**, with the tricarbonyl intermediate then finally rearranging into **3** as proposed above.

**Derivatives of the Methyl Complex 1b.** As stated in the Introduction, no dehydrogenation could be induced directly on the methyl ligand of complex **1b**, but this took place easily upon photolysis of the complex in the presence of different metal carbonyls, to give heterometallic clusters bridged by methylidyne ligands. Of particular interest was the trimolybdenum cluster  $[Mo_3Cp_2(\mu_3-CH)(\mu-PCy_2)(CO)_7]$  (**5**) (Scheme 3), a compound



**Figure 1.** ORTEP diagram (30% probability) of compound 8, with Cy rings (except the  $C^1$  atoms) and H atoms (except that at the carbyne ligand) omitted for clarity.

obtained in good yield upon photolysis of **1b** in the presence of  $[Mo(CO)_6]$ .<sup>2</sup> According to an X-ray study, the methylidyne ligand in this unsaturated cluster bridges the metal atoms quite asymmetrically, with the HC-Mo(CO)<sub>5</sub> distance of 2.316(3) Å being substantially longer than the other HC-Mo lengths (ca. 2.05 Å). Thus, we wondered if compound **5** might be used as a precursor of binuclear methylidyne complexes related to compounds **2**–**4**, provided that the Mo(CO)<sub>5</sub> fragment could be removed from the cluster in some convenient way.

Heating a toluene solution of compound **5** at 388 K produced no significant changes in a few hours. In contrast, this cluster reacted slowly with CO (ca. 4 atm) at 333 K to cleanly give the ketenyl complex  $[Mo_2Cp_2\{\mu-C(H)CO\}(\mu-PCy_2)(CO)_2]$  (6) and  $[Mo(CO)_6]$  as major products, the latter being identified by its characteristic C–O stretching band. Compound **6** could be thus isolated in a conventional way and displays the same structure as compound **3** (see below). However, our attempts to selectively decarbonylate the ketenyl complex **6**, so as to obtain dicarbonyl or monocarbonyl analogues of the benzylidyne complexes **2** and **4**, were unsuccessful by either thermolytic or photolytic procedures.

To avoid the formation of the ketenyl ligand upon degradation of **5** with CO, we also examined some reactions of **5** with simple P-donors. The best results were obtained with  $P(OMe)_3$ . This reaction takes place smoothly at room temperature, but no cleavage of the cluster occurs. Instead, the substituted cluster  $[Mo_3Cp_2(\mu_3-CH)(\mu-PCy_2)(CO)_6\{P(OMe)_3\}]$  (7) is obtained in good yield. Fortunately, this cluster degrades completely in refluxing toluene to give the 30-electron methylidyne complex  $[Mo_2Cp_2(\mu-CH)(\mu-PCy_2)(\mu-CO)]$  (8) and  $[Mo(CO)_5 \{P(OMe)_3\}]$ , the latter being identified in the reaction mixture by the presence in the corresponding IR spectrum of characteristic C–O stretching bands at 2079 (w) and 1950 (vs) cm<sup>-1.11</sup> Compound 8 could be thus isolated in a conventional way and was shown to display the same structure as compound 2, as discussed below.

Structural Characterization of the Triply Bonded Carbyne Complexes 2 and 8. The structure of the methylidyne complex 8 (Figure 1 and Table 1) is very similar to that determined for the benzylidyne complex 2 in our preliminary report,<sup>1</sup> and to that of the isoelectronic ethoxycarbyne complex  $[Mo_2Cp_2(\mu$ -COEt)( $\mu$ -PCy<sub>2</sub>)( $\mu$ -CO)].<sup>12</sup> The molecule is built up from two MoCp units symmetrically bridged by dicyclohexylphosphide, carbonyl and methylidyne ligands. The intermetallic distance is very short (2.467(1) Å) and consistent with the triple intermetallic bond to be proposed for these molecules on the basis of the EAN

Table 1. Selected Bond Lengths and Angles for Compounds 2and 8

	$2^1$	8
Mo(1)-Mo(2)	2.464(1)	2.467(1)
Mo(1) - C(1)	2.09(1)	2.16(2)
Mo(2) - C(1)	2.11(1)	2.07(2)
Mo(1) - C(2)	1.99(1)	1.92(1)
Mo(2) - C(2)	1.97(1)	1.89(2)
Mo(1)-P	2.402(2)	2.407(1)
Mo(2)-P	2.403(2)	2.407(1)
C(2)-H(2)		0.98(2)
Mo(1)-C(1)-Mo(2)	71.9(3)	71.5(6)
Mo(1)-C(2)-Mo(2)	77.2(3)	80.7(7)
Mo(1)-P-Mo(2)	61.7(1)	61.7(1)

formalism and DFT calculations on the related methoxycarbyne complex,<sup>13</sup> while the Mo–C(carbyne) lengths of ca. 1.91 Å are shorter than the Mo–C(carbonyl) ones (ca. 2.12 Å), as expected from the different bond orders (1.5 vs 1) of the corresponding Mo–C interactions. We note that the Mo–C lengths in 8 are ca. 0.1 Å shorter than the corresponding distances in 2 or in the mentioned ethoxycarbyne complex (ca. 1.99 Å), thus pointing to an especially strong M–C bond in this case, perhaps resulting from the minimum steric requirements of the methylidyne ligand, as compared to the CPh or COEt groups.

Spectroscopic data in solution for 2 and 8 are comparable to each other and fully consistent with their solid-state structures (Table 2). The most characteristic spectroscopic features are the presence of a band at 1686  $\text{cm}^{-1}$  in the corresponding IR spectra, due to the C-O stretch of the bridging carbonyl, and a strongly deshielded <sup>13</sup>C NMR resonance at ca. 385 ppm corresponding to the bridgehead carbon atom of the carbyne ligand. The phosphide ligand in 2 gives rise to a quite deshielded <sup>31</sup>P NMR resonance at 228.5 ppm, a value comparable to those measured for the alkoxycarbyne complexes  $[Mo_2Cp_2(\mu-COR)(\mu-PCy_2)(\mu-PCy_2)]$ CO)].<sup>12</sup> In contrast, the methylidyne complex 8 gives rise to a much more deshielded <sup>31</sup>P resonance (288.2 ppm) with no obvious structural reason for it. We note, however, that the isoelectronic hydroxycarbyne-bridged cation [Mo<sub>2</sub>Cp<sub>2</sub>(µ-COH)- $(\mu$ -PCy<sub>2</sub>)<sub>2</sub>]<sup>+</sup> gives also a comparably deshielded resonance (278.3 ppm).<sup>14</sup> Another salient spectroscopic feature of the methylidyne ligand in 8 is the strong deshielding of its H nucleus, with a chemical shift ( $\delta$  16.74 ppm) ca. 5 ppm above that in the triply bridged methylidyne cluster 5 and the Mo<sub>2</sub>W and Mo<sub>2</sub>Cr analogues (ca. 12 ppm). This can be attributed to the strong anisotropy associated with the  $\pi$   $_{
m Mo-C}$  electron density in 8 (absent in any  $\mu_3$ -CH ligand), this expectedly imposing a deshielding influence on the CH proton comparable to that of the double and aromatic C-C bonds in hydrocarbons.<sup>15</sup>

Strutural Characterization of the Doubly Bonded Carbyne Complex 4. The structure of this dicarbonyl complex (Figure 2 and Table 3) is very similar to that of the isoelectronic carboxycarbyne complex  $[Mo_2Cp_2{\mu-C(CO_2Me)}(\mu-PCy_2)(CO)_2]$ previously determined by us.<sup>7</sup> The molecule displays two symmetry-related MoCp(CO) fragments in a transoid arrangement bridged symmetrically by dicyclohexylphosphide and phenylcarbyne ligands, with the carbonyl ligands slightly bent over the intermetallic vector (C-Mo-Mo 83.8(4)°). The latter is a

compound	$\nu(\mathrm{CO})^a$	$\delta(\mathrm{P})^b$	$\delta(\mu$ -C) <sup>b</sup>	$\delta(\mu$ -CH) <sup>b</sup>
$[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (2)	1686 (s)	228.5	385.2 [15]	
$[Mo_2Cp_2{\mu-C(Ph)CO}(\mu-PCy_2)(CO)_2]$ (3)	1993 (s), 1895 (s), 1838 (vs)	132.6	15.8[1]	
$[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)(CO)_2]$ (4)	1913 (w, sh), 1895 (vs) <sup>c</sup>	117.6	428.4 [5]	
$[Mo_2Cp_2{\mu-C(H)CO}(\mu-PCy_2)(CO)_2]$ (6)	1954 (s), 1878 (s), 1838 (vs) <sup>d</sup>	133.0	-13.9	3.31
$[Mo_3Cp_2(\mu_3-CH)(\mu-PCy_2)(CO)_6{P(OMe)_3}]$ (7)	2006 (m), 1946 (w, sh), 1919 (vs), 1886 (m)	163.9 [2], 163.0 (br)		11.42 [6,6]
$[Mo_2Cp_2(\mu-CH)(\mu-PCy_2)(\mu-CO)]$ (8)	1686 (s)	288.2	382.7 [14]	16.74

<sup>*a*</sup> Recorded in dichloromethane solution,  $\nu$  in cm<sup>-1</sup>. <sup>*b*</sup> Recorded in CD<sub>2</sub>Cl<sub>2</sub> solutions at 290 K and 400.13 (<sup>1</sup>H), 162.17 (<sup>31</sup>P), or 100.63 (<sup>13</sup>C) MHz,  $\delta$  in ppm relative to internal TMS (<sup>1</sup>H, <sup>13</sup>C) or external 85% aqueous H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Coupling constants to <sup>31</sup>P are shown in square brackets and are given in Hz. <sup>*c*</sup> Recorded in petroleum ether solution. <sup>*d*</sup> Recorded in toluene solution.



**Figure 2.** ORTEP diagram (30% probability) of compound 4, with Cy rings (except the  $C^1$  atoms) and H atoms omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) forCompound 4

Mo(1)-Mo(1)'	2.666(1)	Mo(1)-P-Mo(1)'	67.2(1)
Mo(1) - C(1)	1.974(7)	Mo(1)-C(7)-Mo(1)'	83.8(4)
Mo(1) - C(7)	1.995(8)	C(1)-Mo(1)-Mo(1)'	83.6(2)
Mo(1)-P	2.408(2)	C(1)-Mo(1)-P	87.7(2)
C(1) - O(1)	1.17(1)	C(1)-Mo(1)-C(7)	84.6(2)
C(7) - C(8)	1.46(2)	C(7)-Mo(1)-P	104.5(2)

characteristic feature of electron-deficient molecules of the type  $[Mo_2Cp_2(\mu-PR_2)(\mu-X)(CO)_2]$  (X = 1–3-electron donor group).<sup>16,17</sup> The Mo–Mo distance is quite short, 2.666(1) Å, consistent with the double metal–metal bond to be proposed for this molecule on the basis of the EAN rule and DFT calculations on the mentioned carboxycarbyne complex.<sup>6</sup> Finally, the Mo–C-(carbyne) distances (ca. 1.98 Å) are also quite short, as expected from the formal bond order of the Mo–C interactions (1.5); in fact, these lengths are almost identical to those in the mono-carbonyl complex 2 (Table 1).

The spectroscopic data in solution for compound 4 (Table 2 and Experimental Section) are fully consistent with its solid-state structure. Its IR spectrum displays two C–O stretching bands with the typical pattern of *trans*-dicarbonyl complexes (weak and strong, in order of decreasing frequency) defining angles between CO groups close to  $180^{\circ}$ .<sup>11</sup> We note, however, that the average C–O stretching frequency (1904 cm<sup>-1</sup>) is 26 cm<sup>-1</sup> higher than the corresponding figure in the isostructural methoxycarbyne complex [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -COMe)( $\mu$ -PCy<sub>2</sub>)(CO)<sub>2</sub>] (1878 cm<sup>-1</sup>).<sup>2</sup> The same qualitative trend is observed for the



**Figure 3.** ORTEP diagram (30% probability) of compound 7, with Cy rings (except the  $C^1$  atoms) and H atoms (except that at the carbyne ligand) omitted for clarity.

monocarbonyl complex 2 ( $12 \text{ cm}^{-1}$  higher than its isoelectronic methoxycarbyne complex). All of this suggests a better electronacceptor character of the phenylcarbyne ligand (relative to the COMe ligand), as far as the metal centers are concerned, and this is in agreement with the higher electronic charge at the carbyne C atom computed for the carboxycarbyne complex  $[Mo_2Cp_2{\mu-C(CO_2Me)}(\mu-PCy_2)(CO)_2]$  (as compared to its methoxycarbyne analogue).<sup>6</sup> This also suggests that compound 4 might display a significant donor ability toward different electron acceptors, a matter under current study.

Other spectroscopic features of 4 are as expected and deserve no detailed comments. For instance, the <sup>31</sup>P chemical shift of the PCy<sub>2</sub> group (117.6 ppm) falls in the range found for related 32electron compounds of the type *trans*-[Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -PCy<sub>2</sub>)( $\mu$ -X)(CO)<sub>2</sub>] (X = 3e-donor ligand),<sup>10,14,16</sup> while the presence of the bridging carbyne is denoted by the appearance of a strongly deshielded resonance in the <sup>13</sup>C NMR spectrum (428.4 ppm), with a shift some 25 ppm higher than those of the isoelectronic methoxycarbyne or carboxycarbyne complexes already mentioned (ca. 405 ppm). Note that these chemical shifts are in turn some 40–50 ppm higher than those of the corresponding 30electron complexes of the type [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -PCy<sub>2</sub>)( $\mu$ -CX)( $\mu$ -CO)] despite the very similar Mo–C distances in all of these complexes, an effect possibly derived from the different intermetallic bonding interactions in these two families of compounds.

Solid-State and Solution Structure of the Methylidyne-Bridged Cluster 7. The structure of the trimolybdenum compound 7 (Figure 3) is very similar to that of its unsubstituted precursor 5,<sup>2</sup> as it can be appreciated from the metric data collected in the Table 4, and therefore needs not to be discussed

	<b>5</b> <sup>2</sup>	7
Mo(1)-Mo(2)	2.9283(3)	2.927(3)
Mo(1)-Mo(3)	3.0938(3)	3.086(3)
Mo(2)-Mo(3)	3.1245(3)	3.078(3)
Mo(1) - C(10)	2.053(3)	2.02(3)
Mo(2) - C(10)	2.040(3)	2.07(3)
Mo(3) - C(10)	2.316(3)	2.31(2)
Mo(1) - P(1)	2.425(1)	2.422(7)
Mo(2) - P(1)	2.410(1)	2.418(6)
Mo(3) - P(2)		2.421(7)
С(10)-Н	0.99(3)	1.10(2)
Mo(1) - Mo(3) - Mo(2)	56.2(1)	56.7(1)
Mo(1)-Mo(2)-C(2)	86.7(1)	89(1)
Mo(2)-Mo(1)-C(1)	87.0(1)	86(1)
Mo(2)-P-Mo(1)	74.5(1)	74.4(2)
Mo(1)-C(1)-O(1)	170.5(2)	172(2)
Mo(2)-C(2)-O(2)	170.9(2)	171(2)
Mo(1)-C(10)-Mo(2)	91.4(1)	91(1)
Mo(1) - C(10) - H	126(2)	114(10)
Mo(2) - C(10) - H	129(2)	131(10)
P(1)-Mo(1)-C(10)	78.4(1)	79(1)
P(1)-Mo(2)-C(10)	79.0(1)	79(1)
P(2)-Mo(3)-C(10)		163(1)

Table 4.Selected Bond Lengths and Angles for Compounds 5and 7

in detail. Although the quality of the diffraction data was very poor, it is quite apparent that the Mo–Mo, Mo–P, and Mo–C-(carbyne) lengths in these two clusters are very similar to each other. Noticeably, the phosphite ligand bound to the Mo(3) atom is positioned trans to the carbyne ligand (P–Mo–C ca. 163°), but this seems to change not much the bonding of the carbyne ligand to that metal atom, it remaining weaker than the other two Mo–C bonds (Mo(3)–C = 2.31(2) Å vs Mo–C ca. 2.05 Å).

Spectroscopic data for 7 (Table 2 and Experimental Section) suggest that the solid-state structure is retained in solution. In particular, the chemical equivalence of the Cp ligands indicates the retention of the cis arrangement of the MoCp(CO) fragments, while the relative intensities of the bands above 1900 cm<sup>-1</sup> suggest the presence of a *trans*-[Mo(CO)<sub>4</sub>XY] oscillator in the molecule.<sup>11</sup> The methylidyne ligand gives rise to a <sup>1</sup>H NMR resonance at 11.47 ppm, a position comparable to that of its precursor **5** (12.26 ppm), with a coupling of 6 Hz to both P atoms. The latter in turn gives rise to very close and weakly coupled <sup>31</sup>P NMR resonances at 163.9 and 163.0 ppm that could be equally well assigned to either dicyclohexylphosphide (e.g., 172.8 ppm for **5**) or Mo-bound trimethylphosphite ligands.

Structural Characterization of the Ketenyl Complexes 3 and 6. The structure of the phenylketenyl complex 3 was reported in our preliminary work (Figure 4)<sup>1</sup> and is not very different from that of the carbyne complex 4. The molecule features two transoid MoCp(CO) fragments symmetrically bridged by dicyclohexylphosphide and phenylketenyl ligands, with the O–C– C–C(Ph) chain of the latter essentially contained in the same plane and positioned roughly perpendicular to the intermetallic vector. The CO ligands, however, are not longer antiparallel, as



**Figure 4.** ORTEP diagram (30% probability) of compound 3, with Cy rings (except the  $C^1$  atoms) and H atoms omitted for clarity (taken from ref 1).

Chart 1



denoted by the distinct bending of the CO ligands over the intermetallic vector (C–Mo–Mo angles ca. 75 and 92°) and the puckering of the PMoCMo ring (ca. 166°). This geometrical distortion is not unusual for dicarbonyl complexes of the type  $[Mo_2Cp_2(\mu$ -PCy<sub>2</sub>)( $\mu$ -X)(CO)<sub>2</sub>],<sup>16a,18</sup> and it seems to relieve the pressure induced by the presence of sterically demanding X groups (in this case,  $\mu$ -C(Ph)CO >  $\mu$ -CPh). The Mo–Mo distance in 3 (2.6101(2) Å) is intermediate between those measured for the doubly bonded carbyne complexes 4 or [Mo<sub>2</sub>Cp<sub>2</sub>- $\{\mu$ -C(CO<sub>2</sub>Me) $\}(\mu$ -PCy<sub>2</sub>)(CO)<sub>2</sub>] (ca. 2.66 Å), and that for the almost triply bonded phenyl complex  $[Mo_2Cp_2(\mu-\kappa^1-Ph)(\mu-\mu)]$  $PCy_2)(CO)_2$  (2.557(2) Å),<sup>16b</sup> and therefore would suggest that the ketenyl ligand in 3 is effectively providing the dimetal center with more than one electron. This can be rationalized by assuming the contribution of ketenyl (1-electron donor) and acylium (3-electron donor) resonant forms to the electronic structure of the bridging ligand (Chart 1), as proposed previously for other ketenyl-bridged complexes, such as the neutral complexes  $[FeWCp{\mu-C(SiPh_3)CO}(CO)_5]^{19}$  and  $[Mn_2Cp_2{\mu-C(p-C_6H_4-Me)CO}(CO)_4]^{20}$  or the cation  $[Fe_2Cp_2(\mu-C(H)CO)_5]^{1+9a}$  (Complexes the Merice Complexes) and distances in 2  $(\mu$ -CO)(CO)<sub>2</sub>]<sup>+.9a</sup> Accordingly, the Mo–C bond distances in 3 (ca. 2.24 Å) are significantly shorter than those measured for the mentioned phenyl complex (ca. 2.35 Å),16b taken here as an imperfect model (because of the presence of some additional  $\pi$ interaction) for a 1-electron  $C(sp^2)$ -donor ligand. In contrast, the C-CO distance (1.324(2) Å) is only slightly longer than that expected for a  $C(sp^2)-C(sp)$  double bond (ca. 1.31 Å),<sup>21</sup> this being somewhat contradictory with the other data. We will further discuss the bonding within the ketenyl ligand in 3 in the light of DFT calculations.

Spectroscopic data in solution for **3** and **6** (Table 2 and Experimental Section) are similar to each other, thus indicating that they share the same basic structure, consistent with the solid-state structure found for **3**. For instance, they both give a  $^{31}$ P NMR resonance at ca. 133 ppm, a chemical shift similar to that of **2** and also comparable to those usually found for other PCy<sub>2</sub>-

bridged dimolybdenum complexes with 32-electron counts,<sup>14,16</sup> thus suggesting an important contribution of the acylium form to the actual bonding in our ketenyl complexes. In the same line, the bridgehead carbon atom of the ketenyl ligand in compounds **3** and **6** gives rise to quite shielded <sup>13</sup>C NMR resonances (15.8 and -13.9 ppm, respectively), an effect observable also for the proton resonance of the ketenyl ligand in **6** (3.31 ppm). The comparison of the latter figures with those of the mentioned ketenyl complex [Fe<sub>2</sub>Cp<sub>2</sub>( $\mu$ -C(H)CO}( $\mu$ -CO)(CO)<sub>2</sub>]<sup>+</sup> ( $\delta$ <sub>C</sub> 27.5 ppm,  $\delta$ <sub>H</sub> 6.94 ppm)<sup>9a</sup> suggests a still greater contribution of the acylium form in the case of our compounds.

The IR spectra of compounds 3 and 6 display three C-Ostretching bands in each case. The two less energetic bands have similar frequencies and are thus assigned to the C-O stretches of the carbonyl ligands, as verified by a DFT calculation on 3 (see below). Therefore, the more energetic band mainly arises from the C-O stretch of the ketenyl ligand in each case, and it is substantially more energetic for 3 (1993  $\text{cm}^{-1}$ ) than for 6  $(1954 \text{ cm}^{-1})$ , with both figures falling in any case within the range usually observed for bridging ketenyl ligands (1850- $2100 \text{ cm}^{-1}$ ).<sup>22</sup> This suggests that the exact contributions of the acylium and ketenyl forms to the bonding in these two complexes might not be exactly the same. Finally, we must note that the relative intensities of the two carbonyl bands (strong and very strong, in order of decreasing frequencies, Table 2) are somewhat unexpected considering that the angle defined by the CO ligands in 3 is close to 165°, then leading to the prediction that the symmetrical C–O stretch (the band at ca.  $1890 \text{ cm}^{-1}$ ) should be rather weak.<sup>11</sup> These relative intensities were not modified when recording the IR spectrum in the solid state, thus excluding a significant modification of the geometry of the  $Mo_2(CO)_2$ oscillator upon dissolution of the solid. Instead, the unexpected intensities of the C–O stretches in 3 can be attributed to the mixing of the carbonyl and ketenyl vibrations, as shown by DFT calculations to be discussed next.

DFT Calculations on the Phenylketenyl Complex 3. The electronic structure of the ketenyl cation [Fe<sub>2</sub>Cp<sub>2</sub>( $\mu$ -C(H)CO}- $(\mu$ -CO)(CO)<sub>2</sub>]<sup>+</sup> was analyzed some years ago using Fenske-Hall MO calculations, and some evidence was then found for both the acylium and the ketenyl contributions to the metalligand bonding in this compound, although no single orbital having a large  $\pi$  [C–C(O)] bonding character was found.<sup>9a</sup> We then judged of interest to analyze the bonding in the phenylketenyl complex 3 using modern Density Functional Theory (DFT) methods (see the Experimental Section for details).<sup>23</sup> Following the methodology previously used by us in the study of unsaturated carbyne complexes related to compounds 2 and 4,<sup>6,13</sup> we have analyzed the electronic structure and bonding in compound 3 through the properties of the relevant Kohn-Sham molecular orbitals, and also by inspection of the topological properties of the electron density, as managed in the Atoms in Molecules (AIM) theory.<sup>2</sup>

The most relevant parameters derived from the geometry optimization of **3** (Figure 5) can be found in Table 5, along with the corresponding experimental values. The optimized bond lengths for **3** are in good agreement with the data measured using X-ray diffraction,<sup>1</sup> although the computed values for lengths involving the metal atoms tend to be slightly longer (less than 0.05 Å) than the corresponding experimental data. This is a common trend with the functionals currently used in the DFT computations of transition metal compounds.<sup>23a,25</sup> The computed C–O stretches were 2109, 1979, and 1944 cm<sup>-1</sup>, with



Figure 5. DFT-optimized structure of compound 3, with H atoms omitted for clarity.

Table 5. Selected Data for the DFT-Optimized Geometry of Complex  $3^a$  and the Topological Properties of Its Electron Density<sup>b</sup>

bond	calc $d/\alpha$	$\exp d/\alpha$	ρ	$\nabla^2  ho$
Mo1-Mo2	2.638	2.6101(2)	0.487	1.34
Mo1-P	2.452	2.3984(4)	0.523	3.05
Mo2-P	2.440	2.3857(4)	0.531	3.10
Mo1-C1	1.945	1.939(2)	0.946	10.20
Mo2-C2	1.962	1.957(2)	0.900	10.58
Mo1-C3	2.259	2.238(2)	0.527	4.63
Mo2-C3	2.308	2.255(2)	0.459	4.86
C3-C5	1.493	1.486(2)	1.720	-14.27
$C-C(Ph)^{c}$	1.399	1.393(2)	2.097	-20.46
C3-C4	1.335	1.324(2)	2.158	-16.65
C1-O	1.173	1.1642	2.919	22.01
C2-O	1.167	1.157(2)	2.957	23.84
C4-0	1.178	1.177(2)	2.910	17.06
C1-Mo1-Mo2	76.9	75.2(1)		
C2-Mo2-Mo1	92.8	92.3(1)		
X-C3-C4	119.4	119.6(2)		
$ \begin{array}{c}                                     $				

<sup>*a*</sup> Bond lengths (*d*, Å) and angles ( $\alpha$ , deg) according to the labeling shown in the figure, with experimental values taken from ref 1. <sup>*b*</sup> Values of the electron density at the bond critical points ( $\rho$ ) are given in e Å<sup>-3</sup>; values of the laplacian of  $\rho$  at these points ( $\nabla^2 \rho$ ) are given in e Å<sup>-5</sup>; see the Experimental Section for details of the DFT calculations. <sup>*c*</sup> Average values within the Ph ring.

relative intensities 94:60:100, corresponding mainly to the ketenyl and carbonyl (symmetric and asymmetric vibrations) ligands, respectively. These values overestimate the experimental frequencies (Table 2) by 5-10%, which seems to be a normal bias for DFT-derived IR data,<sup>6,13,26</sup> while the relative intensities are in reasonable agreement with those observed in the solution spectra.

The frontier molecular orbitals for **3** (those accounting for the metal-metal bonding), as well as those involving the most



Figure 6. Selected molecular orbitals of compound 3, with their energies (in eV) and main bonding character indicated below.

significant part of the  $\pi$  interactions in the ketenyl ligand, are shown in Figure 6. The intermetallic bonding for ideal edgesharing bioctahedral complexes should follow from the occupation of one  $\sigma$ , one  $\pi$ , and one  $\delta$  bonding MO's, with the corresponding antibonding orbitals being next in energy.<sup>27</sup> We might therefore expect a configuration of the type  $\sigma^2 \pi^2 \delta^2 (\delta^*)^2$ for 3, although orbital mixing with the  $\pi$  acceptor ligands usually modifies this simple picture. Indeed, the frontier orbitals for 3 display considerable mixing. The HOMO is a recognizable metal-metal  $\delta^*$  orbital (with significant contributions of the  $\pi^*_{\mathrm{C-O}}$  orbitals of the terminal carbonyls), but the  $\delta$  and  $\pi$ bonding orbitals are mixed and distributed among the three orbitals below, these being followed by the  $\sigma$  component of the intermetallic bonding (MO144). Noticeably, both the MO146 and the MO145 orbitals have significant  $\sigma$  bonding M-C-(ketenyl) character, with orbital interactions comparable to those usually found for  $\mu$ -PR<sub>2</sub> ligands, and this points to the 3-electron donor behavior derived from the acylium form of the ketenyl ligand (Chart 1). We note, however, a small  $\pi(C-C)$  overlap in

MO145 (and also in MO92) that might be identified with the interaction expected for the ketenyl form.

The dominant  $\pi$  overlaps within the ketenyl ligand, however, are located between the C and O atoms and are mostly concentrated in the orbitals MO110 and MO90 (for the overlap perpendicular to the intermetallic vector) and in the MO92 (overlap parallel to the M–M vector), thus pointing to a dominant triple-bond picture of the C–O interaction. Thus, we conclude that, from the point of view of the MO analysis, the electronic structure of the ketenyl ligand in 3 is closer to the acylium form. However, some  $\pi_{C-C}$  overlap can be appreciated in the ketenyl ligand (orbitals MO145 and MO92).

The electron density ( $\rho$ ) and its laplacian ( $\nabla^2 \rho$ ) at the most relevant bond critical points (bcp) of compound 3 are also collected in Table 5. First, we note that the electron density at the intermetallic bcp (0.487 e  $Å^{-3}$ ) is somewhat closer to that computed for the 32-electron carboxycarbyne complex  $[Mo_2Cp_2{\mu-C(CO_2Me)}(\mu-PCy_2)(CO)_2] (0.444 \text{ e} \text{ Å}^{-3})^6 \text{ than}$ to the one computed for the 30-electron hydride  $[Mo_2Cp_2(\mu H)(\mu - PCy_2)(CO)_2]$  (0.582 e Å<sup>-3</sup>),<sup>16b</sup> again in favor of a somewhat higher contribution of the acylium form. However, the electron density at the Mo–C (ketenyl) bonds (ca. 0.49 e Å<sup>-3</sup>) is much lower than that in the carbyne complex (ca. 0.93 e  $Å^{-3}$ ), and indeed lower than the reference values for a single bond (e.g., ca. 0.71 e  $Å^{-3}$  for the bridging carbonyls in methoxycarbyne complex  $[Mo_2Cp_2(\mu$ -COMe)( $\mu$ -PCy<sub>2</sub>)( $\mu$ -CO)]),<sup>13</sup> as expected if the ketenyl form were to be dominant. Thus, we have to conclude that both forms should be taken into account to describe the actual bonding in 3. In fact, the parameters within the ketenyl C-C-O chain have values intermediate between those implied by each of the canonical forms. Thus, the density at the C–CO bond (2.158 e Å<sup>-3</sup>) is higher than expected for a single C–C bond (e.g., 1.927 e Å<sup>-3</sup> in the mentioned carboxycarbyne complex), and comparable to the average density in the aromatic ring of the complex (2.097 e  $Å^{-3}$ ), while the values of  $\rho$  and its laplacian at the CC–O bond (2.910 e Å<sup>-3</sup> and 17.06 e  $\text{\AA}^{-5}$ ) are almost as high as the ones computed for the carbonyl ligands. Thus, from the point of view of the AIM analysis, it can be said that both the ketenyl and the acylium forms are of comparable relevance to describe the metal-ketenyl bonding in 3, this being in reasonable agreement with the structural data.

### CONCLUDING REMARKS

The photochemically induced dehydrogenation of the benzyl complex  $[Mo_2Cp_2(\mu-CH_2Ph)(\mu-PCy_2)(CO)_2]$ , followed by suitable carbonylation/decarbonylation steps, allows the synthesis of the unsaturated benzylidyne complexes  $[Mo_2Cp_2(\mu-CPh)(\mu PCy_2(\mu-CO)$  and  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)(CO)_2]$ , and that of the phenylketenyl complex  $[Mo_2Cp_2-{\mu-C(Ph)CO}(\mu PCy_2)(CO)_2$  (3). Related methylidyne complexes can be prepared from the methyl complex  $[Mo_2Cp_2(\mu-CH_3)(\mu-PCy_2) (CO)_2$  via degradation of its trimolybdenum methylidyne-bridged derivatives  $[Mo_3Cp_2(\mu_3-CH)(\mu-PCy_2)(CO)_7]$  and  $[Mo_3Cp_2(\mu_3-CH)(\mu-PCy_2)(CO)_7]$ CH)( $\mu$ -PCy<sub>2</sub>)(CO)<sub>6</sub>{P(OMe)<sub>3</sub>}]. As compared to their related methoxycarbyne-bridged complexes, the carbyne compounds here reported display the following differences: (a) higher stability of the ketenyl derivatives  $[Mo_2Cp_2\{\mu-C(X)CO\}(\mu-C(X)CO)]$  $PCy_2(CO)_2$  as compared to the corresponding isomeric and electron-precise tricarbonyls  $[Mo_2Cp_2(\mu-CX)(\mu-PCy_2)(CO)_3]$ , and (b) a stronger  $\pi$  acceptor character, this leading to reduced electron density at the metal site and increased electron density at the bridgehead carbon atom. On the other hand, the bonding in the phenylketenyl ligand is intermediate between the extreme descriptions represented by the acylium and the ketenyl canonical forms, according to the AIM analysis on compound **3**, although the analysis of the orbital interactions in this molecule suggests that the acylium form would be somewhat more dominant.

## 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.<sup>28</sup> Petroleum ether refers to that fraction distilling in the range 338-343 K. The compounds  $[Mo_2Cp_2(\mu-CH_2Ph)(\mu-PCy_2)(CO)_2]$  (1a),  $[Mo_2Cp_2(\mu-CH_2Ph)(\mu-PCy_2)(CO)_2]$  (1a),  $[Mo_2Cp_2(\mu-CH_2Ph)(\mu-PCy_2)(CO)_2]$ CH<sub>3</sub>)( $\mu$ -PCy<sub>2</sub>)(CO)<sub>2</sub>] (1b), and [Mo<sub>3</sub>Cp<sub>2</sub>( $\mu_3$ -CH)( $\mu$ -PCy<sub>2</sub>)(CO)<sub>7</sub>] (5) were prepared as described previously.<sup>2b,16b</sup> All other reagents were obtained from the usual commercial suppliers and used as received. Photochemical experiments were performed using jacketed quartz or Pyrex Schlenk tubes, cooled by tap water (ca. 288 K). A 400 W mercury lamp placed ca. 1 cm away from the Schlenk tube was used for all the experiments. Chromatographic separations were carried out using jacketed columns cooled by tap water. Commercial aluminum oxide (Aldrich, 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 ( $\nu$ ) were measured in solution or Nujol mulls and are given in cm<sup>-1</sup>. Nuclear magnetic resonance (NMR) spectra were routinely recorded at 400.13  $({}^{1}H)$ , 162.17  $({}^{31}P{}^{1}H{})$ , or 100.63 MHz  $({}^{13}C{}^{1}H{})$  at 290 K in CD<sub>2</sub>Cl<sub>2</sub> solutions unless otherwise is stated. Chemical shifts  $(\delta)$  are given in ppm, relative to internal tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C) or external 85% aqueous  $H_3PO_4$  (<sup>31</sup>P). Coupling constants (J) are given in Hz.

Preparation of  $[Mo_2Cp_2(\mu-CPh)(\mu-PCy_2)(\mu-CO)]$  (2). A toluene solution (20 mL) of complex 1b (0.500 g, 0.750 mmol) was irradiated with visible-UV light in a quartz Schlenk flask at 288 K for 2 h with a gentle N<sub>2</sub> purge to give a red-brown solution. The solvent was then removed under vacuum, and the residue was extracted with dichloromethane-petroleum ether (1:10), and the extracts were chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane-petroleum ether (1:1) gave a red fraction yielding, after removal of the solvents under vacuum, compound 2 as a red solid (0.300 g, 63%). Anal. Calcd for C<sub>30</sub>H<sub>37</sub>Mo<sub>2</sub>OP: C, 56.61; H, 5.86. Found: C, 56.91; H, 5.96. <sup>1</sup>H NMR:  $\delta$  7.11 [false t,  $J_{\rm HH}$  = 8, 2H,  $H^{3}(Ph)$ ], 6.98 [t,  $J_{HH}$  = 7, 1H,  $H^{4}(Ph)$ ], 6.58 [false d,  $J_{HH}$  = 7, 2H,  $H^{2}(Ph)$ ], 5.79 (s, 10H, Cp), 1.82–0.55 (m, 22H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$ 385.2 (d,  $J_{CP} = 15, \mu$ -CPh), 300.8 (d,  $J_{CP} = 9, \mu$ -CO), 163.0 [s, C<sup>1</sup>(Ph)], 127.7 [s,  $C^{3}(Ph)$ ], 124.4 [s,  $C^{4}(Ph)$ ], 121.2 [s,  $C^{2}(Ph)$ ], 95.6 (s, Cp), 42.6 [d,  $J_{CP} = 15$ ,  $C^{1}(Cy)$ ], 42.1 [d,  $J_{CP} = 13$ ,  $C^{1}(Cy)$ ], 33.6, 33.5 [2s,  $C^{2}(Cy)$ ], 27.6, 27.4 [2d,  $J_{CP} = 6$ ,  $C^{3}(Cy)$ ], 26.3, 26.2 [2s,  $C^{4}(Cy)$ ].

**Preparation of [Mo<sub>2</sub>Cp<sub>2</sub>{μ-C(Ph)CO}(μ-PCy<sub>2</sub>)(CO)<sub>2</sub>] (3).** A toluene solution (10 mL) of compound 2 (0.160 g, 0.252 mmol) was placed in a bulb equipped with a Young's valve. The bulb was cooled at 77 K, evacuated under vacuum, and then refilled with CO. The valve was then closed, and the solution was allowed to reach room temperature and was further stirred for 40 h to give a green solution. The solvent was then removed under vacuum, and the residue was chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane–petroleum ether (1:6) gave a green fraction yielding, after removal of the solvents under vacuum, compound 3 as a green microcrystalline solid (0.140 g, 80%). Anal. Calcd for  $C_{32}H_{37}Mo_2O_3P$ : C, 55.50; H, 5.39. Found: C, 55.67; H, 5.13. <sup>1</sup>H NMR: δ 7.30–7.03 (m, Ph, SH), 5.30, 5.06 (2s, 2 × 5H, Cp), 2.38–1.10 (m, 22H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 249.4 (d, *J*<sub>CP</sub> = 13, MoCO), 242.0 (d, *J*<sub>CP</sub> = 16, MoCO), 158.7 [s, C<sup>1</sup>(Ph)], 145.0 (s, μ-CCO), 128.3 [s, C<sup>2.3</sup>(Ph)], 125.6 [s, C<sup>4</sup>(Ph)],

90.6, 90.3 (2s, Cp), 50.2 [d,  $J_{CP} = 22$ ,  $C^1(Cy)$ ], 42.7 [d,  $J_{CP} = 17$ ,  $C^1(Cy)$ ], 35.0 [d,  $J_{CP} = 3$ ,  $C^2(Cy)$ ], 34.1 [d,  $J_{CP} = 4$ ,  $C^2(Cy)$ ], 33.8 [d,  $J_{CP} = 3$ ,  $C^2(Cy)$ ], 32.5 [s,  $C^2(Cy)$ ], 28.5–28.1 [m,  $C^3(Cy)$ ], 26.6, 26.3 [2s,  $C^4(Cy)$ ], 15.8 (d,  $J_{CP} = 1$ ,  $\mu$ -CCO).

Preparation of [Mo<sub>2</sub>Cp<sub>2</sub>(µ-CPh)(µ-PCy<sub>2</sub>)(CO)<sub>2</sub>] (4). A toluene solution (5 mL) of compound 3 (0.150 g, 0.216 mmol) was stirred at 353 K for 2 h to give an orange solution. The solvent was then removed under vacuum, and the residue was chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane-petroleum ether (1:10) gave a rose fraction yielding, after removal of the solvents under vacuum, compound 4 as an orange microcrystalline solid (0.119 g, 83%). The crystals used in the X-ray study were grown by slow diffusion of petroleum ether into a dichloromethane solution of the complex at 253 K. Anal. Calcd for C<sub>31</sub>H<sub>37</sub>Mo<sub>2</sub>O<sub>2</sub>P: C, 56.03; H, 5.61. Found: C, 55.97; H, 5.75. <sup>1</sup>H NMR:  $\delta$  7.47 [false t, J<sub>HH</sub> = 8, 2H,  $H^{3}(Ph)$ ], 7.19 [false dd,  $J_{HH}$  = 8, 1, 2H,  $H^{2}(Ph)$ ], 7.12 [tt,  $J_{HH}$  = 8, 1, 1H, H<sup>4</sup>(Ph)], 5.39 (s, 10H, Cp), 2.50 (m, 2H, Cy), 2.06–1.11 (m, 20H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  428.4 (d,  $J_{CP}$  = 5,  $\mu$ -CPh), 221.5 (d,  $J_{CP}$  = 12, MoCO), 167.3 [s, C<sup>1</sup>(Ph)], 127.7 [s, C<sup>3</sup>(Ph)], 125.0 [s, C<sup>4</sup>(Ph)], 119.6 [s,  $C^{2}(Ph)$ ], 91.8 (s, Cp), 44.8 [d,  $J_{CP}$  = 18,  $C^{1}(Cy)$ ], 36.5 [s,  $C^{2,6}(Cy)$ ], 34.4 [s,  $C^{6,2}(Cy)$ ], 28.5 [d,  $J_{CP}$  = 12,  $C^{3,5}(Cy)$ ], 28.4 [d,  $J_{CP}$  = 9,  $C^{5,3}(Cy)$ ], 26.6 [s,  $C^{4}(Cy)$ ].

Preparation of  $[Mo_2Cp_2{\mu-C(H)CO}(\mu-PCy_2)(CO)_2]$  (6). A toluene solution (5 mL) of compound 5 (0.075 g, 0.091 mmol) was placed in a bulb equipped with a Young's valve. The bulb was cooled at 77 K, evacuated under vacuum, and then refilled with CO. The valve was then closed, and the solution was allowed to reach room temperature and further stirred at 333 K for 2.5 days to give a yellow-green solution. The solvent was then removed under vacuum, and the residue was washed with petroleum ether  $(4 \times 4 \text{ mL})$  to give compound 6 as a green microcrystalline solid (0.042 g, 75%). Anal. Calcd for C<sub>26</sub>H<sub>33</sub>Mo<sub>2</sub>O<sub>3</sub>P: C, 50.66; H, 5.40; Found: C, 50.57; H, 5.33. <sup>1</sup>H NMR: δ 5.28, 5.16 (2s, 2  $\times$  5H, Cp), 3.31 [s, 1H,  $\mu\text{-C(H)CO]}$ , 2.22–1.22 (m, 22H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  247.7 (d,  $J_{CP}$  = 14, MoCO), 245.0 (d,  $J_{CP}$  = 15, MoCO), 159.9 [s, μ-C(H)CO], 88.7, 88.3 (2s, Cp), 47.5 [d, J<sub>CP</sub> = 20,  $C^{1}(Cy)$ ], 43.6 [d,  $J_{CP}$  = 17,  $C^{1}(Cy)$ ], 33.8 [d,  $J_{CP}$  = 2,  $C^{2}(Cy)$ ], 32.9 [d,  $J_{\rm CP} = 3, C^2({\rm Cy})], 32.5, 32.45 [2s, C^2({\rm Cy})], 27.3 [d, J_{\rm CP} = 12, 2C^2({\rm Cy})],$ 27.1, 27.0 [2d,  $J_{CP}$  = 11, C<sup>2</sup>(Cy)], 25.4, 25.3 [2s, C<sup>4</sup>(Cy)], -13.9 [s,  $\mu$ -C(H)CO].

**Preparation of [Mo<sub>3</sub>Cp<sub>2</sub>(\mu\_3-CH)(\mu-PCy<sub>2</sub>)(CO)<sub>6</sub>{P(OMe)<sub>3</sub>}] (7).** Neat P(OMe)<sub>3</sub> (12 μL, 0.102 mmol) was added to a toluene solution (10 mL) of compound 5 (0.056 g, 0.068 mmol), and the mixture was stirred at room temperature for 1.5 h to give an orange solution. The solvent was then removed under vacuum, and the residue was chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane—petroleum ether (1:4) gave an orange fraction yielding, after removal of the solvents under vacuum, compound 7 as an orange microcrystalline solid (0.052 g, 84%). The crystals used in the X-ray study were grown by slow diffusion of petroleum ether into a toluene solution of the complex at 273 K. Anal. Calcd for C<sub>32</sub>H<sub>42</sub>-Mo<sub>3</sub>O<sub>9</sub>P<sub>2</sub>: C, 41.76; H, 4.60. Found: C, 41.87; H, 4.66. <sup>1</sup>H NMR: δ 11.42 (t, *J*<sub>PH</sub> = 6, 1H, *μ*-CH), 5.15 (s, 10H, Cp), 3.70 (d, *J*<sub>PH</sub> = 11, 9H, OMe), 2.08–1.13 (m, 22H, Cy).

**Preparation of [Mo<sub>2</sub>Cp<sub>2</sub>(μ-CH)(μ-PCy<sub>2</sub>)(μ-CO)] (8).** A toluene solution (10 mL) of compound 7 (0.050 g, 0.054 mmol) was refluxed for 15 min to give a rose solution. The solvent was then removed under vacuum, and the residue was chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane petroleum ether (1:3) gave a rose fraction yielding, after removal of solvents under vacuum, compound 8 as a rose solid (0.022 g, 73%). The crystals used in the X-ray study were grown by slow diffusion of petroleum ether into a dichloromethane solution of the complex at 253 K. Anal. Calcd for C<sub>24</sub>H<sub>33</sub>Mo<sub>2</sub>OP: C, 51.44; H, 5.94. Found: C, 51.22; H, 5.73. <sup>1</sup>H NMR: δ 16.74 (s, 1H, μ-CH), 5.82 (s, 10H, Cp),

Table 6. Crystal Data for New Compounds

	4	7	8
mol formula	C <sub>31</sub> H <sub>37</sub> Mo <sub>2</sub> O <sub>2</sub> P	$C_{32}H_{42}Mo_{3}O_{9}P_{2}$	C24H33Mo2OP
mol wt	664.46	920.42	560.35
cryst syst	tetragonal	monoclinic	monoclinic
space group	P4 <sub>1</sub> 2 <sub>1</sub> 2	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
radiation $(\lambda, \text{\AA})$	0.71073	1.54184	1.54184
<i>a,</i> Å	9.9779(3)	23.7133(10)	8.09170(10)
<i>b,</i> Å	9.9779(3)	10.2228(3)	12.0945(2)
<i>c,</i> Å	28.4996(6)	31.4145(4)	23.2847(2)
α, deg	90	90	90
eta, deg	90	113.877(3)	100.078(2)
γ, deg	90	90	90
<i>V</i> , Å <sup>3</sup>	2837.38(13)	6963.6(4)	2243.60(5)
Z	4	8	4
calcd density, g cm $^{-3}$	1.555	1.756	1.659
absorp coeff, mm <sup>-1</sup>	0.966	10.018	9.906
temperature, K	100(2)	100(2)	100(2)
$\theta$ range (deg)	2.16-25.22	2.94-74.89	3.86-73.57
index ranges ( <i>h, k, l</i> )	0, 11; 0, 11; -34, 34	-28, 28; -7, 11; -38, 38	-8, 9; -10, 14; -28, 28
no. of reflns collected	32 596	36 111	11 425
no. of indep reflns	2554	12 655	4073
$(R_{\rm int})$	(0.0388)	(0.1065)	(0.0318)
reflns with $I > 2\sigma(I)$	2426	8637	3985
R indexes	$R_1 = 0.048$	$R_1 = 0.1342$	$R_1 = 0.0432$
$[\text{data with } I > 2\sigma(I)]^a$	$wR_2 = 0.1177^b$	$wR_2 = 0.3307^c$	$wR_2 = 0.1276^d$
R indexes	$R_1 = 0.0558$	$R_1 = 0.1767$	$R_1 = 0.0463$
(all data) <sup>a</sup>	$wR_2 = 0.1302^b$	$wR_2 = 0.3499^c$	$wR_2 = 0.148^d$
GOF	1.145	1.097	1.171
no. of restraints/params	0/219	2/731	0/255
$\Delta ho({ m max,min})$ , e Å $^{-3}$	1.078, -0.918	5.148, -2.14	0.914, -1.293
$R = \Sigma   F_{o}  -  F_{c}   / \Sigma  F_{o} $ . wR = $[\Sigma w$	$[ F_{o} ^{2} -  F_{c} ^{2})^{2}/\Sigma w  F_{o} ^{2}]^{1/2}$ . $w = 1/2$	$[\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP]$ , where $P = (F_{o}^{2} + 2P)^{2}$	$2F_{\rm c}^2)/3$ . <sup>b</sup> $a = 0.0777$ , $b = 0.6356$ . <sup>c</sup> $a$

 $= 0.0072, b = 1077.0286.^{d} a = 0.0896, b = 7.1456.$ 

1.81–0.37 (m, 22H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR (233 K):  $\delta$  382.7 (d,  $J_{CP}$  = 14,  $\mu$ -CH), 304.9 (d,  $J_{CP}$  = 10,  $\mu$ -CO), 94.4 (s, Cp), 40.3, 38.0 [2d,  $J_{CP}$  = 18, C<sup>1</sup>(Cy)], 33.4, 33.0 [2s, C<sup>2</sup>(Cy)], 27.2 [d,  $J_{CP}$  = 12, 2C<sup>3</sup>(Cy)], 26.1, 26.0 [2s, C<sup>4</sup>(Cy)].

X-ray Structure Determination of Compound 4. Data collection was performed on a Nonius Kappa CCD single diffractometer, using graphite-monochromated  $MoK_{\alpha}$  radiation. Images were collected at 45 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and 80 s exposure time per image. Data collection strategy was calculated with the program Collect.<sup>29</sup> Data reduction and cell refinements were performed with the programs HKL Denzo and Scalepack.<sup>30</sup> Semiempirical absorption corrections were applied using the program SORTAV.<sup>31</sup> Using the program suite WinGX,<sup>32</sup> the structure was solved by Patterson interpretation and phase expansion and was refined with full-matrix least-squares on  $F^2$  with SHELXL97.<sup>33</sup> During the solution process, the compound was found to be placed on the symmetry operation y, x, -z, and displayed a disorder on a cyclohexyl group, which was modeled introducing 12 instead of 6 carbon atoms with occupancy factors of 0.5. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were geometrically placed and refined using a riding model. Further details of the data collection and refinements are given in Table 6.

X-ray Structure Determination of Compound 7. Data collection was performed on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu K<sub> $\alpha$ </sub> radiation. Images were collected at 65 mm fixed crystal-detector distance, using the oscillation method, with  $1^{\circ}$  oscillation and variable exposure time per image (15-40 s). Data collection strategy was calculated with the program CrysAlis Pro CCD.<sup>34</sup> Data reduction and cell refinement were performed with the program CrysAlis Pro RED.<sup>34</sup> An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.<sup>34</sup> Using the program suite WinGX,<sup>32</sup> the structure was solved by Patterson interpretation and phase expansion and was refined with full-matrix least-squares on  $F^2$  using SHELXL97.<sup>33</sup> During the solution process, two independent molecules of the compound were found to be present in the asymmetric unit. Most of the non-hydrogen atoms were refined anisotropically, but due to the poor quality of the diffraction data a dozen C atoms in each independent molecule had to be refined isotropically to prevent their temperature factors from becoming nonpositive definite. Therefore, the final R factors were quite high, all above 10%. Hydrogen atoms were geometrically placed riding on their parent atoms, except for H(10B), which was located in the Fourier map and refined isotropically. The atom H(10) was found in the Fourier map, but some restraints were necessary to obtain a correct convergence. Further details of the data collection and refinements are given in Table 6.

X-ray Structure Determination of Compound 8. Data collection, data reduction, and absorption correction were performed as described for 7 (5–20 s exposure time). Using the program suite WinGX,<sup>32</sup> the structure was solved by direct methods and was refined

with full-matrix least-squares on  $F^2$  with SHELXL97.<sup>33</sup> During the final stages of the refinement, one of the cyclopentadienyl ligands, the carbyne, and the bridging carbonyl ligands were found to be disordered in two positions, which were satisfactorily solved by assigning occupancy factors of 0.5 in all cases. All of the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined anisotropically, except for the atoms involved in the disorder, which were refined isotropically. All hydrogen atoms were geometrically placed and refined using a riding model, except for H(2), which was positioned at fixed coordinates, obtaining satisfactory convergence. Further details of the data collection and refinements are given in Table 6.

**Computational Details.** The computations for compound 3 were carried out using the Gaussian 03 package, <sup>35</sup> in which the hybrid method B3LYP was applied with the Becke three parameters exchange functional<sup>36</sup> and the Lee–Yang–Parr correlation functional.<sup>37</sup> Effective core potentials (ECP) and their associated double- $\zeta$  LANL2DZ basis set were used for the metal atoms.<sup>38</sup> The addition of an f-polarization function to the basis set of the Mo atoms<sup>39</sup> caused no significant modifications in the computed geometry and electron distribution for this molecule. The light elements (P, O, C, and H) were described with the 6-31G\* basis.<sup>40</sup> Geometry optimizations were performed under no symmetry restrictions, using initial coordinates derived from X-ray data of the complex, and frequency analysis was performed to ensure that a minimum structure with no imaginary frequencies was achieved. Molecular orbitals and vibrational modes were visualized using the Molekel program.<sup>41</sup> The topological analysis of  $\rho$  was carried out with the Xaim routine.<sup>42</sup>

# ASSOCIATED CONTENT

**Supporting Information.** CIF file giving the crystallographic data for the structural analysis of compounds 4, 7, and 8. This material is available free of charge via the Internet at http:// pubs.acs.org.

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