

# Chemistry of Unsaturated Group 6 Metal Complexes with Bridging Hydroxy and Methoxycarbyne Ligands. 6. C–E Bond Formation and C–O Bond Cleavage Processes in the Reactions of $[Mo_2(\eta^5-C_5H_5)_2(\mu$ -COMe)( $\mu$ -PCy<sub>2</sub>)( $\mu$ -CO)] with Several *p*-Block Elements (E) and Their Hydride Derivatives

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The unsaturated complex  $[Mo_2Cp_2(\mu$ -COMe)( $\mu$ -PCy<sub>2</sub>)( $\mu$ -CO)](1) reacts with several HER<sub>n</sub> molecules  $(\text{HER}_n = \text{HSPh}, \text{HPHPh}, \text{HSnPh}_3)$  in toluene at 263–288 K to give the corresponding derivatives  $[Mo_2Cp_2(\mu-ER_n)(\mu-PCy_2)(CO)_2]$ . A related reaction takes place in toluene at 263 K with the diphosphite  $(EtO)_2POP(OEt)_2$  to give a mixture of the diethoxyphosphide derivatives  $[Mo_2Cp_2(\mu-PCy_2)\{\mu-P(OEt)_2\}$ - $(CO)_2$  and  $[Mo_2Cp(\eta^5-C_5H_4CH_2Ph)(\mu-PCy_2){\mu-P(OEt)_2}(CO)_2]$ , the latter incorporating a benzyl group from the solvent, and with iodine (in dichloromethane at room temperature) to give first the iodide complex  $[Mo_2Cp_2(\mu-I)(\mu-PCy_2)(CO)_2]$  and then the triiodide derivative  $[Mo_2Cp_2(\mu-I)I_2(\mu-PCy_2)(CO)_2]$ . In all of the above reactions, neat demethylation of the methoxycarbyne ligand takes place. In contrast, the silanes HSiPh<sub>3</sub> and H<sub>2</sub>SiPh<sub>2</sub> (unreactive toward 1 in refluxing toluene) react slowly under visible-UV irradiation at room temperature to give in good yields the novel complexes  $[Mo_2Cp_2\{u-C(2-C_6H_4SiPh_2OMe)\}$  $(\mu$ -PCy<sub>2</sub>) $(\mu$ -CO)] and [Mo<sub>2</sub>Cp<sub>2</sub> $(\mu$ -CSiPh<sub>2</sub>OMe) $(\mu$ -PCy<sub>2</sub>) $(\mu$ -CO)], having any learby ne and silvlear by ne ligands, respectively, the latter resulting from the overall elimination of  $H_2$  and insertion of  $Ph_2SiC_6H_4$  and SiPh<sub>2</sub> fragments, respectively, into the strong C–OMe bond of the carbyne ligand. The reactions of 1 with elemental selenium and sulfur involve the incorporation of three to four chalcogen atoms to the dimetal center under mild conditions, to give respectively the carbene-seleniolate derivative  $[Mo_2Cp_2\{\mu$ -C(OMe)- $C(O)Se_{(\mu-PCy_2)(\mu-Se_2)]}$  and the O-methyldithiocarbonate  $[Mo_2Cp_2(\mu-PCy_2)\{\mu-S_2C(OMe)\}(S)_2]$ , the latter derived from an unexpected coupling of two sulfur atoms to the carbyne ligand.

# Introduction

The chemistry of carbyne complexes is a well-developed field within organometallic science. These complexes usually display a high reactivity derived from the multiple nature of their metal-carbon bonds in either the terminal or the  $\mu_2$ -bridging coordination modes, which can be further increased in the latter case by the presence of multiple metal-metal bonds (Chart 1),<sup>1</sup> and they are also involved in several industrial processes of interest such as the Fischer-Tropsch synthesis of hydrocarbons from syngas (CO + H<sub>2</sub>)<sup>2</sup> and

alkyne metathesis.<sup>3</sup> In contrast, the chemistry of alkoxycarbyne complexes is considerably less developed,<sup>4</sup> especially in the case of binuclear compounds having multiple metalmetal bonds. We thus initiated a systematic study of the reactivity of such unsaturated species using group 6 metal substrates, focused first on cationic binuclear complexes

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Scheme 1. Reactivity of the Methoxycarbyne Complex 1



with 32- and 30-electron counts<sup>5,6</sup> and then on an electronricher species, the neutral 30-electron complex  $[Mo_2Cp_2(\mu -$ COMe)( $\mu$ -PCy<sub>2</sub>)( $\mu$ -CO)] (1) (Cp =  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>).<sup>7</sup> In line with the increased electron density of the latter, we have found that 1 can be easily protonated or alkylated at the oxygen atom of its bridging carbonyl ligand in a charge-controlled process, to give the corresponding cations having new hydroxy- or alkoxycarbyne groups, respectively,<sup>8</sup> while the electron density accumulated at the Mo<sub>2</sub>C triangle, having  $\pi$  (metal-carbyne)-bonding character, seems well-suited for the complex to act as a base under conditions of orbital control, with this enabling compound 1 to act as a useful building block for the rational synthesis of heterometallic clusters upon the addition of different coordinatively unsaturated metal fragments (Scheme 1).9 On the other hand, compound 1 can also behave as an acceptor molecule, as expected for an unsaturated (30-electron) complex, and thus reacts readily with CO to give the electron-precise derivative  $[Mo_2Cp_2(\mu$ -COMe)( $\mu$ -PCy<sub>2</sub>)(CO)<sub>3</sub>].<sup>10</sup> In all these reactions, the methoxycarbyne ligand remains unperturbed, except for changes in its coordination mode (e.g., from  $\mu_2$  to  $\mu_3$ ), and behaves much in the same way as an alkyl- or arylcarbyne ligand would. However, our preliminary experiments on the

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reactivity of 1, reported as a communication,<sup>11</sup> revealed that there are also reactions in which either C–O bond cleavage or other substantial modifications in the methoxycarbyne ligand of compound 1 might take place, which are not possible for alkyl- or arylcarbyne complexes. In this paper we report full details of these reactions, ranging from those taking place between 1 and several *p*-block elements (chalcogens, iodine) to those with some hydride derivatives of the former elements (HER<sub>n</sub>), such as thiols, primary phosphines, or silanes. As will be discussed below, these reactions may involve *inter alia* several processes modifying the methoxycarbyne ligand extensively, such as overall demethylation, C–E and C–C bond formation at the bridgehead C atom, and insertion into the C–OMe bond, with some of these reactions being almost unprecedented in the chemistry of carbyne complexes.

## **Results and Discussion**

Reactions with Small Molecules Having E-H Bonds (E =O, S, N, P, Si, Sn). Compound 1 was found to be unreactive at room temperature or even under forcing thermal conditions (several hours in refluxing toluene solution) toward simple alcohols (PhOH), amines (PhNH<sub>2</sub>), and silanes (Ph<sub>3</sub>SiH, Ph<sub>2</sub>SiH<sub>2</sub>). A very slow reaction (ca. 20% conversion after 4 h) was observed with the stannane Ph<sub>3</sub>SnH in refluxing toluene to give the known stannyl-bridged complex  $[Mo_2Cp_2(\mu-SnPh_3)(\mu-PCy_2)(CO)_2]$ <sup>12</sup> with this obviously having no practical use. In contrast, the thiol PhSH reacts with 1 at a reasonable rate (completion after ca. 6 h at 353 K) to give with good yield the known thiolate-bridged derivative  $[Mo_2Cp_2(\mu-PCy_2)(\mu-SPh)(CO)_2](2)$ ,<sup>13</sup> whereas the primary phosphine PhPH<sub>2</sub> reacts analogously (but more slowly) to give the novel phenylphosphide-bridged derivative [Mo2- $Cp_2(\mu$ -PCy<sub>2</sub>)( $\mu$ -PHPh)(CO)<sub>2</sub>] (3) (Chart 2). In all of the above reactions the methoxycarbyne ligand of 1 has been demethylated, presumably by formation of methane with the hydrogen atom of the incoming reagent. Obviously, the strength of the corresponding E-H bond being cleaved is a critical factor determining the feasibility of these reactions. Since the corresponding order of bond energy (in kJ mol<sup>-1</sup>) is  $O(459) \gg N(386) > S(363) > P(322) \cong Si(318) \gg Sn$ (<214),<sup>14</sup> the failure of **1** to react with amines and alcohols can be thus easily explained. However, the slow (Sn) or negligible (Si) thermal reactivity of stannanes and silanes, respectively, in spite of their low E-H bond strengths, suggests that the presence of electron pairs on E might be relevant for the reaction to proceed at a significant rate, a matter to be discussed later on.

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Table 1. Selected IR <sup>4</sup> and NMR <sup>4</sup>	" Data for New Complexes
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compound	ν(CO)	$\delta(\mathbf{P})$	$\delta(\mu$ - $C) [J_{CP}]$
$\frac{[Mo_2Cp_2(\mu-COMe)(\mu-PCy_2)(\mu-CO)](1)^c}{[Mo_2Cp_2(\mu-PCy_2)(\mu-PHPh)(CO)_2](3)}$ $\frac{[Mo_2Cp_2(\mu-PCy_2)\{\mu-P(OEt)_2\}(CO)_2](4a)}{[Mo_2Cp(n^5-C+H_2CH_2Ph)(\mu-PCy_2)\{\mu-P(OEt)_2\}(CO)_2](4b)}$	1674 (s) 1868 (m, sh), 1836 (vs) 1876 (m, sh), 1848 (vs) 1873 (w, sh), 1845 (vs)	228.5 113.6, 28.5 <sup>d</sup> 352.1, 119.5 <sup>e</sup> 349.5 117.3 <sup>e</sup>	352.0 [15], 305 [9]
$ \begin{split} & [\text{Mo}_2\text{Cp}_2\{\mu\text{-C}(2\text{-}C_6\text{H}_4\text{SiPh}_2\text{-}O\text{Me})](\mu\text{-PCy}_2)(\mu\text{-CO})](\textbf{5}) \\ & [\text{Mo}_2\text{Cp}_2(\mu\text{-CSiPh}_2\text{-}O\text{Me})](\mu\text{-PCy}_2)(\mu\text{-CO})](\textbf{5}) \\ & [\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)\{\mu\text{-S}_2\text{C}(\text{OMe})\}(\text{S})_2](\textbf{7}) \\ & [\text{Mo}_2\text{Cp}_2\{\mu\text{-C}(\text{OMe})\text{C}(\text{O})\text{Se}\}(\mu\text{-PCy}_2)(\mu\text{-Se}_2)](\textbf{8}) \\ & [\text{Mo}_2\text{Cp}_2(\mu\text{-P}\text{Cy}_2)(\mu\text{-PCy}_2)(\text{CO})_2](\textbf{10}) \end{split}{}$	1683 (s) 1687 (s) 1646 (m) 1932 (vs), 1909 (m) <sup>g</sup>	223.6 230.7 84.2 <sup>f</sup> 181.3 159.9 <sup>h</sup>	386.2, 300.8 [6] 417.9 [13], 302.3 [8] 225.9 <sup>7</sup> 134.8 [17]

<sup>*a*</sup> Recorded in dichloromethane solution,  $\nu$ (CO) in cm<sup>-1</sup> for carbonyl groups. <sup>*b*</sup> Recorded in CD<sub>2</sub>Cl<sub>2</sub> solutions at 290 K and 121.50 (<sup>31</sup>P) or 75.48 (<sup>13</sup>C) MHz, unless otherwise stated;  $\delta$  in ppm relative to internal TMS (<sup>13</sup>C) or external 85% aqueous H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P), *J* in Hz. <sup>*c*</sup> Data taken from ref 7. <sup>*d*</sup> In CDCl<sub>3</sub> solution, with the more deshielded resonance arising from the PCy<sub>2</sub> ligand;  $J_{PP} = 8$ . <sup>*e*</sup> The more shielded resonance arises from the PCy<sub>2</sub> ligand;  $J_{PP} = 19$ . <sup>*f*</sup> Averaged resonances at 290 K in CDCl<sub>3</sub> solution (see text). <sup>*g*</sup> In THF solution. <sup>*h*</sup> In C<sub>6</sub>D<sub>6</sub> solution.

The spectroscopic data for **3** (Table 1) are comparable to those of **2** and to those of different bis(phosphide) complexes *trans*-[M<sub>2</sub>Cp<sub>2</sub>( $\mu$ -PR<sub>2</sub>)( $\mu$ -PR'<sub>2</sub>)(CO)<sub>2</sub>] (M = Mo, W; R, R' = Ph, Cy, Et, H, etc.) previously described by us and others.<sup>15,16</sup> The latter are characterized by displaying relatively shielded <sup>31</sup>P NMR resonances and C–O stretching bands of weak and strong intensities (in order of decreasing frequency), as expected for transoid M<sub>2</sub>(CO)<sub>2</sub> oscillators.<sup>17</sup> In addition, we note that the presence of the PPhH bridge in **3** now makes the two cyclopentadienyl groups inequivalent, as observed in the corresponding <sup>1</sup>H NMR spectrum, with the latter also displaying a characteristic (strongly coupled to phosphorus) P–H resonance at 6.25 ppm (<sup>1</sup>J<sub>PH</sub> = 367 Hz; see Experimental Section).

Reactions with Other P-Donors. Since two CO molecules are easily added to compound 1 (Scheme 1), it might have been anticipated that 1 should add easily different phosphine or diphosphine ligands. In fact, it is somewhat surprising that the reaction with PPhH<sub>2</sub> would proceed very slowly, as noted above. Actually, the presence of a P-H bond (thus providing a path for demethylation) seems to be of relevance since no reaction took place at all between complex 1 and several good P-donors such as P(OMe)<sub>3</sub> or Me<sub>2</sub>PCH<sub>2</sub>PMe<sub>2</sub> after several hours in refluxing toluene. A slow reaction, however, was observed with the diphosphite (EtO)<sub>2</sub>POP(OEt)<sub>2</sub> (24 h at 363 K for completion), to give not the simple addition product but unexpectedly a mixture of two diethoxyphosphide-bridged derivatives,  $[Mo_2Cp_2(\mu - PCy_2){\mu - P(OEt)_2}(CO)_2](4a)$  and  $[Mo_2Cp(\eta^3-C_5H_4CH_2Ph)(\mu-PCy_2)\{\mu-P(OEt)_2\}(CO)_2]$  (4b) in a ca. 2:5 ratio (Chart 3).

Compound **4a** has been recently reported by us to be the main product in the reaction of the anion  $[Mo_2Cp_2(\mu-PCy_2)(\mu-CO)_2]^-$  with ClP(OEt)<sub>2</sub>.<sup>12b</sup> As for the major product **4b**, the corresponding spectroscopic data are indeed very similar to those of **4a** (Table 1 and Experimental Section) except for the cyclopentadienyl resonances. In fact, both the <sup>1</sup>H and the <sup>13</sup>C NMR spectra reveal that compound **4b** has one benzyl-substituted cyclopentadienyl ligand, clearly denoted by the appearance of five inequivalent <sup>13</sup>C resonances for the corresponding protons, all of this in agreement with the lack of symmetry introduced by the presence of two different bridging phosphide ligands.



The formation of compounds **4a**,**b** implies once more a demethylation of the methoxycarbyne ligand, perhaps involving the formation of  $P(OEt)_2(OMe)$  and/or  $P(O)Me(OEt)_2$ . Although we have not investigated this in detail, we note that the <sup>31</sup>P NMR spectra of the crude reaction mixtures exhibit several resonances at ca. 140 ppm and at ca. 0 ppm that might correspond to species of the type  $P(OEt)_2(OR)$  and  $P(O)(OEt)_2R$ , respectively, according to their chemical shifts.<sup>18</sup>

**Reaction Pathways in the Demethylation of the Carbyne Ligand in Compound 1.** In general terms, the C–O bond of the alkyl group of a bridging alkoxycarbyne ligand in a neutral complex is strong enough to remain unperturbed under most reaction conditions and is not expected to be cleaved easily. Actually, there are only a limited number of precedents involving the rupture of that bond. These include the migration of the alkyl group to the carbon atom under thermal or photochemical activation to give the corresponding acyl-bridged isomers,<sup>4d,f,h</sup> and to the metal atom, also under thermal activation, to give alkyl complexes.<sup>4a,19</sup> The demethylation reactions observed for compound **1** thus represent a different way (eventual methane elimination) for inducing the cleavage of the Me–O bond of a methoxycarbyne ligand.

As noted above, the reactions of 1 with  $HER_n$  molecules resulting in the loss of the Me group are rather slow. Yet, we have detected no intermediate species by IR or <sup>31</sup>P NMR monitoring of the corresponding reactions, which are necessarily complex and multistep in nature. As also noted, the presence of an electron pair on E seems to have a beneficial effect on the reaction rate. We thus propose, in agreement with the unsaturated nature of 1, that the first step would be just the coordination (even if weak) of the H–ER<sub>n</sub> molecule

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Scheme 2. Proposed Pathways for the Reactions of 1 with  $H-ER_n$  Molecules<sup>*a*</sup>



<sup>*a*</sup> Mo-Mo = Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -PCy<sub>2</sub>); ER<sub>n</sub> = SPh, PHPh, SnPh<sub>3</sub>.

to the metal center through the electron pair of E or, when this is not possible (Si, Sn), through the E-H bond, to give 32-electron intermediates (A or A', respectively, Scheme 2). The reduced donor ability of an E-H bond (compared with a nonbonding electron pair on E) would explain the very slow rate of the HSnPh<sub>3</sub> reaction in spite of the very weak H-Sn bond to be eventually cleaved. The strength of the E-H bond would actually be a determinant factor for the next step, the oxidative addition of this bond to the unsaturated intermediates A (or A') to give a hydride intermediate B. This would occur less easily for the stronger E-H bonds, thus justifying the failure of 1 to react with phenol and phenylamine, while the failure of silanes to react with 1 would follow from the combined effect of the low coordination ability and relatively high strength of the Si-H bond. In any case, we note that these oxidative addition reactions are not uncommon at unsaturated dimetal centers. For instance, the reaction of primary and secondary phosphines has been used extensively to synthesize phosphide-bridged dimolybdenum and ditungsten cyclopentadienyl complexes,<sup>15,20</sup> and we have reported recently that HSnPh<sub>3</sub> undergoes a fast Sn-H cleavage at room temperature when reacting with the unsaturated hydride [Mo<sub>2</sub>Cp<sub>2</sub>(µ-H)(µ-PCy<sub>2</sub>)(CO)<sub>2</sub>].<sup>12a</sup> Intermediates **B** now would evolve through Me migration to the metal to give methyl-hydride derivatives C, then undergo the reductive elimination of methane to yield the corresponding ER<sub>n</sub>-bridged derivatives finally isolated. As noted above, there are precedents of methyl migrations to the metal in alkoxycarbyne complexes. In our case, however, the eventual CH<sub>4</sub> elimination seems to be critical for this migration to

proceed because, in the absence of added reagents, compound 1 does not undergo any methyl migration process (to give its isomer  $[Mo_2Cp_2(\mu-CH_3)(\mu-PCy_2)(CO)_2])$  either in refluxing toluene or under photochemical activation.<sup>7a</sup>

The reaction of **1** with the diphosphite  $(EtO)_2POP(OEt)_2$ to give **4a** can be understood along the same lines just discussed, if we allow the backbone P–O bond of this ligand to play the role of the E–H bond in the reactions with HER<sub>n</sub> molecules. This requires the oxidative addition of the backbone P–O bond of the diphosphite to the metal center (to yield diethoxyphosphide and diethylphosphonate groups) after coordination, a process possible at unsaturated dimolybdenum and ditungsten complexes, as shown by previous work from our laboratory.<sup>21</sup> The final step (**C** to **4a**) now would involve the reductive elimination of the methyl and phosphonate groups in the form of either P(OEt)<sub>2</sub>(OMe) or P(O)Me(OEt)<sub>2</sub>, two molecules possibly present in the crude reaction mixtures, as noted above.

The formation of 4b, having the same structure as 4a but with a benzyl-substituted cyclopentadienyl ligand, is much more difficult to explain, and we will not dare to give any hypothetical sequence of elemental steps. We must note, however, that recent work from our laboratory has shown that the unsaturated benzyl-bridged complex [Mo<sub>2</sub>Cp<sub>2</sub>(µ-CH<sub>2</sub>Ph)(µ-PCy<sub>2</sub>)(CO)<sub>2</sub>] reacts with CO to give the hydride  $[Mo_2Cp(\eta^2-C_5H_4CH_2Ph) (\mu$ -H) $(\mu$ -PCy<sub>2</sub>)(CO)<sub>4</sub>], having a benzyl-substituted cyclopentadienyl ligand, thus accomplishing an overall H/CH<sub>2</sub>Ph exchange at one of the cyclopentadienyl rings of the complex.<sup>22</sup> Therefore, we can conceive that a toluene molecule might become coordinated at some intermediate step of the reaction of 1 with the diphosphite and then converted into benzyl and hydride ligands after oxidative addition, thus initiating a sequence yielding a  $(\eta^{5}-C_{5}H_{4}CH_{2}Ph)$  group, as observed for the mentioned benzyl complex. A separate experiment showed that no detectable (by <sup>1</sup>H and <sup>31</sup>P NMR) modification of compound 1 took place after heating a toluene solution of this complex at 373 K for 24 h, thus confirming that the presence of the diphosphite is compulsory for the incorporation of the benzyl group at the Cp ring in these substrates.

Photochemical Reactions with Silanes. Although Ph<sub>3</sub>SiH and Ph<sub>2</sub>SiH<sub>2</sub> fail to react with compound 1 in refluxing toluene, they do it slowly under visible-UV irradiation at room temperature to give in good yields the novel complexes  $[Mo_2Cp_2\{\mu-C(2-C_6H_4SiPh_2OMe)\}(\mu-PCy_2)(\mu-CO)]$  (5) and  $[Mo_2Cp_2(\mu$ -CSiPh<sub>2</sub>OMe)( $\mu$ -PCy<sub>2</sub>)( $\mu$ -CO)] (6), having arylcarbyne and silylcarbyne ligands, respectively (Chart 4). Some other minor products are formed in the above reactions, but they could not be purified nor properly characterized. Moreover, even when the extensive rearrangement needed to give the above products requires several elemental steps to take place, no clear intermediates could be identified in these reactions through IR or <sup>31</sup>P NMR monitoring of the corresponding mixtures. Compound 1 also reacted with the primary silane (n-Hex)SiH<sub>3</sub> under comparable conditions, but the reaction was much less selective and no pure products could be isolated nor properly characterized in that case.

The structure of the arylcarbyne complex 5 was confirmed through a single-crystal X-ray study and is shown in Figure 1.<sup>11</sup> The coordination environment of the dimetal

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**Figure 1.** ORTEP drawing of compound **5**, with H atoms and cyclohexyl rings (except the C<sup>1</sup> atoms) omitted for clarity (reproduced from ref 11). Selected bond lengths (Å): Mo(1)-Mo(2) = 2.469(1), Mo(1)-P(1)=2.393(1), Mo(2)-P(1)=2.396(1), Mo(1)-C(1)=2.119(2), Mo(2)-C(1)=2.081(2), Mo(1)-C(2)=1.980(2), Mo(2)-C(2) = 2.002(2).



center is very similar to that of the isoelectronic ethoxycarbyne complex  $[Mo_2Cp_2(\mu\text{-COEt})(\mu\text{-PCy}_2)(\mu\text{-CO})]^{7a}$  and almost identical to that of the benzylidyne complex  $[Mo_2-Cp_2(\mu\text{-CPh})(\mu\text{-PCy}_2)(\mu\text{-CO})]$  recently reported by us,<sup>23</sup> and therefore does not need to be discussed in detail. We just note the very short intermetallic separation of 2.469(1) Å, consistent with the triple bond proposed for all these molecules on the basis of the EAN formalism and DFT calculations,<sup>8</sup> and the quite short Mo–C(carbyne) lengths of ca. 1.99 Å, consistent with the formal bond order (1.5) in a carbyne ligand symmetrically bridging two metal atoms. The SiPh<sub>2</sub>-(OMe) group placed at the *ortho* position of the phenyl substituent of the carbyne ligand introduces no significant distortions in the molecule and displays unnoticeable interatomic distances.

Spectroscopic data for **5** and **6** in solution are similar to each other except for the resonances corresponding to the respective substituents at the carbyne ligand and are consistent with the structure found in the crystal for **5**. Moreover they are not very different from those of the methoxycarbyne precursor **1** (Table 1). All these complexes are characterized by a relatively deshielded <sup>31</sup>P NMR resonance and by a lowfrequency C–O stretching band corresponding to the bridging carbonyl, as also found for the isoelectronic phosphide complexes of the type  $[M_2Cp_2(\mu-PR_2)(\mu-PR'_2)(\mu-CO)]$ .<sup>15,16</sup> The carbyne ligand is identified by a strongly deshielded <sup>13</sup>C Scheme 3. Proposed Pathways for the Reactions of 1 with Silanes<sup>*a*</sup>



<sup>*a*</sup> Mo-Mo = Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -PCy<sub>2</sub>).

NMR resonance at 386.2 ppm (**5**) and 417.9 ppm (**6**), as expected. Note the progressive deshielding of the carbyne <sup>13</sup>C nucleus as we move from alkoxycarbyne to arylcarbyne and then to silylcarbyne ligands. This trend is also found for mononuclear complexes<sup>24</sup> and can be related to the increased electron density at the bridgehead carbon atom in that sequence, also reflected in the concomitant reduction of electronic charge at the dimetal center, as indicated by the relative C–O stretching frequencies of the bridging carbonyl in these complexes (1 < 5 < 6, Table 1). The nature of the substituent of the carbyne ligand in compounds **5** and **6** is readily apparent from the corresponding <sup>1</sup>H and NMR data (see Experimental Section) and deserves no specific comments.

Pathways in the Photochemical Reactions of Silanes with Compound 1. As noted above, no intermediates could be identified in the necessarily complex rearrangements connecting the methoxycarbyne complex 1 with their aryl- or silylcarbyne derivatives 5 and 6. Yet we can outline sensible steps to justify the formation of these products (Scheme 3). For this we propose that, under photochemical activation,

<sup>(24)</sup> Mann, B. E.; Taylor, B. F. <sup>13</sup>C NMR Data for Organometallic Compounds; Academic Press: London, U.K., 1981.

the weak initial adduct of type A' proposed for the thermal reactions would now undergo a double oxidative addition, first of H-Si bonds (to give the corresponding intermediates of type **B**) and then of an H-C(Ph) bond (reaction with HSiPh<sub>3</sub>) or a second H-Si bond (reaction with H<sub>2</sub>SiPh<sub>2</sub>), thus providing an irreversible path for H<sub>2</sub> elimination, eventually introducing SiPh<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>) and SiPh<sub>2</sub> fragments in the molecule, respectively. In the latter case, the silylene intermediate E thus generated might undergo a Si-C coupling analogous to the methylene-carbyne coupling reactions previously observed for other arylcarbyne- and methoxycarbyne-bridged complexes.<sup>25,5a</sup> This leads to an intermediate F that would yield the final product 6 through a 1,2-shift of the OMe group from C to Si atoms, thermodynamically favored by the much higher strength of the Si–O over the Si–C bond.<sup>14</sup> We have shown recently that a related 1,2-shift (from C to C) takes place instantaneously at the ketenyl intermediate [Mo<sub>2</sub>Cp<sub>2</sub>{µ-C- $(OMe)CO{(\mu-PCy_2)(CO)_2}$  to give the carboxycarbyne derivative  $[Mo_2Cp_2\{\mu$ -CC(O)OMe $\}(\mu$ -PCy<sub>2</sub>)(CO)<sub>2</sub>].<sup>6b</sup>

In the reaction with HSiPh<sub>3</sub>, the *ortho*-metalated silyl intermediate H generated after H<sub>2</sub> elimination might evolve through C–C coupling to the carbyne ligand (preferred over Si–C coupling due to the higher strength of the C–C bond) to give a silyl-carbene intermediate I, which might rearrange into the silylcarbyne product 5 through migration of the methoxyl group from C to Si via the dimetal center, something facilitated by the electronic and coordinative unsaturation of the latter. Once again, the formation of a very strong Si–O bond would provide a significant driving force for this rearrangement.

Irrespectively of the actual sequence of elemental steps connecting the methoxycarbyne compound 1 with the aryl and silylcarbyne derivatives 5 and 6, it should be remarked that it is the quite strong MeO-C(carbyne) bond (the one having some degree of  $\pi$ -bonding component)<sup>8,10</sup> that is the bond to be cleaved in these reactions. This is a very unusual process for an alkoxycarbyne ligand, only observed previously in a few instances, upon reaction either with a strong reducing agent such as Na (to give a carbide ligand)<sup>4b</sup> or with molecules able to remove in some way the methoxyl group such us  $BH_3^{5b,c}$  or  $H_2^{4e}$  (to give a methylidyne ligand). Interestingly, the removal of a methoxyl group from a bridging methoxycarbene ligand using strong acids such as  $Me_3O^+$  or BBr<sub>3</sub> has been successfully used previously for the synthesis of several carbyne-bridged binuclear complexes.<sup>26</sup> Clearly, silicon plays in our reactions the role of an "intramolecular extractor" of the methoxyl group by virtue of the strong Si-O bond thus formed. Besides all this, we should note that the formation of compounds 5 and 6 implies the overall insertion of ylidene- or diyl-type fragments into the strong C-OMe bond of an alkoxycarbyne ligand, a process having, to our knowledge, no precedent in the literature.

**Reactions with Group 16 Elements.** We have noted previously that compound **1** is oxygen-sensitive, giving the oxo derivative *cis*-[Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -COMe)( $\mu$ -PCy<sub>2</sub>)(O)(CO)] upon brief exposure to air.<sup>7a</sup> Thus it was not surprising that this complex would react with elemental sulfur and selenium under mild conditions. These reactions, however, unexpectedly involve the incorporation of three to four chalcogen atoms to the dimetal center, to give respectively the



**Figure 2.** ORTEP drawing of compound **8**, with H atoms and cyclohexyl rings (except the C<sup>1</sup> atoms) omitted for clarity (reproduced from ref 11). Selected bond lengths (Å) and angles (deg): Mo(1)-Mo(2) = 2.709(1), Mo(1)-P = 2.414(1), Mo(2)-P = 2.431(1), Mo(1)-C(1) = 2.194(5), Mo(2)-C(1) = 2.223(5), Mo(1)-Se(3) = 2.596(1), Mo(2)-Se(3) = 2.591(1), Mo(1)-Se(1) = 2.541(1), Mo(2)-Se(2) = 2.539(1), Se(1)-Se(2) = 2.309(1), Se(3)-C(3) = 2.009(5), C(3)-O(3) = 1.198(6), C(3)-C(1) = 1.433(7); Mo(1)-Se(1)-Se(2) = 93.7(1).



*O*-methyldithiocarbonate  $[Mo_2Cp_2(\mu-PCy_2)\{\mu-S_2C(OMe)\}$ -(S)<sub>2</sub>] (7) and the carbene-seleniolate derivative  $[Mo_2Cp_2-\{\mu-C(OMe)C(O)Se\}(\mu-PCy_2)(\mu-Se_2)]$  (8) with good yields (Chart 5). Attempts to obtain products derived from the incorporation of just one or two chalcogen atoms to the unsaturated dimetal center of complex **1** were unsuccessful.

The structure of the selenium derivative **8** was confirmed through a single-crystal X-ray study and is shown in Figure 2.<sup>11</sup> The molecule displays two cyclopentadienylmolybdenum fragments symmetrically bridged by dicyclohexylphosphide,  $\kappa^1:\kappa^1$ -diselenide, and carbene-seleniolate ligands, the latter derived from the coupling of the methoxycarbyne and carbonyl ligands to a selenium atom, thus resembling the behavior of heterodinuclear arylcarbyne-bridged complexes toward elemental oxygen and sulfur.<sup>27</sup> The intermetallic length in **8** is quite short considering the size of the bridging atoms (2.709(1) Å), this being consistent with the formulation of a double Mo–Mo bond for this molecule under the

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EAN formalism, if single Mo-Se bonds are assumed for the diselenide ligand, and the Se–Se length of 2.309(1) A is very similar to the values found for comparable diselenide complexes (e.g., 2.307(1) Å for  $[V_2Cp_2^*(\mu-S)_2(\mu-\kappa^1:\kappa^1-Se_2)]$ .<sup>28</sup> However, the Mo-Se lengths for this ligand in 8 (ca. 2.54 Å) are ca. 0.05 Å shorter than those involving the bridging seleniolate atom Se(3) and ca. 0.1 Å shorter than the singlebond W-Se lengths in the triselenide-bridged complex  $[W_2Cp_2(\mu - \kappa^1 : \kappa^1 - Se_3)(CO)_6]$ .<sup>29</sup> All of this points to the presence of some multiplicity in the corresponding Se-Mo bonds in 8  $(p\pi - d\pi \text{ donation})$ , which would somewhat reduce the strength of the intermetallic interaction. We should note that no other dimolybdenum complex having a  $\kappa^1$ : $\kappa^1$ -diselenido bridging ligand appears to have been reported previously. These ligands are more often found in the  $\kappa^2 \kappa^2$ -bridging mode,<sup>30</sup> but in the case of 8 this mode must be disfavored because it would lead to an electronic and coordinative oversaturation of the dimetal center. Finally we note that the Mo-C(1) lengths of ca. 2.20 Å can be considered normal for a single bond in bridging carbene and related hydrocarbyl ligands (e.g., ca. 2.22 Å in  $[W_2Cp_2\{\mu$ -C(p-tol)C(O)C(p-tol)\}- $(CO)_4$ <sup>31</sup> and ca. 2.20 Å in the cation  $[W_2Cp_2(\mu-CH_2)-$ { $\mu$ -C(OMe)CH<sub>2</sub>}(CO)<sub>2</sub>( $\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)]<sup>+</sup>).<sup>5a</sup>

The spectroscopic data in solution for 8 (Table 1 and Experimental Section) are consistent with the structure found in the crystal, effectively implying the chemical equivalence of both metal fragments in solution. The former carbyne atom gives rise now to a much more shielded <sup>13</sup>C NMR resonance (124.8 ppm), as expected for a bridging carbene-like ligand, while the coupling of the former carbonyl ligand to the C(OMe) group is denoted by the substantial shielding (compared to a Mo-bound ligand) of its <sup>13</sup>C resonance ( $\delta_{\rm C}$  177.7 ppm) and decreased C–O stretching frequency (1646  $\text{cm}^{-1}$ ).

The structure of the sulfur derivative 7 is substantially different from that of the selenium compound just discussed. Although all attempts to obtain suitable crystals for an X-ray analysis of this complex were unsuccessful, the essential structural details can be obtained unambiguously from the spectrometric and spectroscopic data available (Table 1 and Experimental Section). In the first place, the presence of four S atoms in the molecule is firmly established by the microanalytical data and the mass spectrum of the complex, the latter displaying the corresponding molecular ion as well as those derived from the loss of COMeS and COMeS<sub>2</sub> fragments from the latter. This is suggestive of the presence of an *O*-methyldithiocarbonate (or xanthate) ligand ( $\mu$ -S<sub>2</sub>COMe), in turn consistent with the appearance of a resonance at 225.9 ppm in the corresponding <sup>13</sup>C NMR spectrum when recorded at room temperature. Indeed, that chemical shift is comparable to those of different molybdenum complexes having unidentated or chelating alkyldithiocarbonate ligands (in the range ca. 190-240 ppm).<sup>32</sup> This spectrum, however, displays anomalously broad resonances for the  $C^1$  ( $\delta_C$ 41.3 ppm) and C<sup>2</sup> ( $\delta_{\rm C}$  27.7 and 25.5 ppm) carbons of two apparently equivalent cyclohexyl rings, which suggests the operation of dynamic effects. This was confirmed by variable-temperature <sup>1</sup>H and <sup>31</sup>P NMR measurements revealing that, on lowering the temperature, the single phosphorus or cyclopentadienyl resonances of 7 eventually split into two resonances with ca. 2:1 relative intensities in each case (see Experimental Section). Thus it is clear that compound 7 exists in solution as an equilibrium mixture of two isomers. Both of them have similar spectroscopic properties (equivalent Cp and Cy rings, related by a  $C_2$  rotation) and therefore are proposed to have the remaining sulfur atoms as terminal ligands placed in a transoid arrangement (Chart 5). The difference between both isomers would just lie in the coordination mode of the dithiocarbonate ligand, bridging the dimetal center through one (7A) or both (7B) sulfur atoms, although we do not know which of them is the major isomer in solution (arbitrarily chosen as A). In any case, these isomers are formally 32-electron complexes, isostructural with the dicarbonyls of the type trans- $[Mo_2Cp_2(\mu-PR_2)(\mu-PR'_2)-$ (CO)<sub>2</sub>], and accordingly they exhibit comparatively shielded <sup>31</sup>P NMR resonances at ca. 84.2 ppm (cf. 95.4 ppm for the complex with R = R' = Cy).<sup>15</sup>

The isomerism proposed for compound 7 in solution is well established for carboxylate complexes, and we have previously reported a comparable equilibrium for formate-bridged complexes at dimanganese centers.<sup>33</sup> In the case of the alkyldithiocarbonate and related ligands, the bridging coordination modes proposed for compound 7 are comparatively rare, and we can quote just one example of such isomerism for metalmetal bonded complexes, this being reported for the trinuclear cluster  $[Os_3(\mu-H){\mu-S_2C(OEt)}(CO)_{10}]$ . In that case, however, no interconversion takes place in solution and the isomers could be separated from each other using conventional chromatographic techniques.34

The formation of 7 implies the coupling of two sulfur atoms and a bridging carbyne ligand to give a dithiocarboxylate-type ligand. As far as we know, such a process has been observed previously only for terminal alkyl- or arylcarbyne ligands.<sup>35</sup> We can quote, however, examples of the addition of a single sulfur atom to several heterometallic arylcarbyne-bridged complexes, to give the corresponding thioacyl-bridged derivatives.<sup>27,36</sup> Finally we note that the formation of 7 also requires the elimination of a CO ligand and the addition of two more sulfur atoms as terminal ligands. This is not unexpected for the reaction of a triply bonded dimolybdenum complex with elemental sulfur and is reminiscent of the behavior of some isoelectronic  $[M_2L_2(CO)_4]$  complexes (L = Cp or related ligand;  $M = Mo, W).^{37}$ 

Reactions with Iodine. Compound 1 reacts rapidly with iodine in dichloromethane at room temperature. When one equivalent of iodine is added, a mixture of the known iodide complex  $[Mo_2Cp_2(\mu-I)(\mu-PCy_2)(CO)_2]$  (9)<sup>7a</sup> and the new triiodide complex  $[Mo_2Cp_2(\mu-I)I_2(\mu-PCy_2)(CO)_2]$  (10) is

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Chart 6

obtained (Chart 6), with the former being an intermediate for the latter. Thus, the addition of a second equivalent of iodine to the above mixture completes the formation of the triiodide complex **10**, which could be isolated in the conventional way and characterized by spectroscopic methods.

The IR spectrum of 10 displays two C-O stretching bands of strong and medium relative intensities in order of decreasing frequency (Table 1), this indicating a relative arrangement of the two CO ligands of the molecule defining an angle smaller than 90°.<sup>17</sup> This is only compatible with a cisoid arrangement of the CpMo(CO)I fragments of the molecule. On the other hand, the <sup>1</sup>H and <sup>13</sup>C NMR data reveal the chemical inequivalence of these metal fragments, with the carbonyl resonances exhibiting very different coupling to the phosphorus atoms. By recalling that for complexes of type [MoCpXYL<sub>2</sub>] it is well established that  ${}^{2}J_{XY}$  coupling constants increase algebraically with the X-Mo-Y angle, and being usually negative at acute angles,<sup>38</sup> we can safely assign the more strongly coupled resonance ( $\delta$  241.7 ppm,  $J_{CP}$  = 11 Hz) to a carbonyl ligand *cis* to the phosphide bridge, whereas the other resonance ( $\delta$  236.7 ppm,  $J_{CP}$  ca. 0 Hz) is assigned to a carbonyl *trans* to that bridge (Chart 6).

The formation of the triiodide complex 10 in the reaction of 1 with iodine can be understood in similar terms to those discussed for the reactions with  $H-ER_n$  molecules (Scheme 2) if we let the I–I bond here play a role comparable to that of the H–E bonds there, with the difference that now the nucleophile would be the carbyne complex. The reaction would thus be initiated by the nucleophilic attack of the latter complex to the iodine molecule, this eventually resulting in the formation of the iodide-bridged complex 9 and methyl iodide, thus accomplishing once more the neat demethylation of the carbyne ligand. However, compound 9 is still a cordinatively and electronically unsaturated species. Then it is not unexpected that this complex in turn reacts rapidly with a second molecule of iodine to give complex 10, the product of the oxidative addition of iodine across a double metal bond to give an electron-precise derivative.

### **Concluding Remarks**

The electronic and coordinative unsaturation of the methoxycarbyne complex 1 facilitates the approach of different  $H-ER_n$ molecules to the dimetal center, eventually accomplishing a full demethylation of the carbyne ligand (presumably through formation of methane) and formation of the corresponding derivative [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -ER<sub>n</sub>)( $\mu$ -PCy<sub>2</sub>)(CO)<sub>2</sub>]. The reactions with iodine and the diphosphite (EtO)<sub>2</sub>POP(OEt)<sub>2</sub> to yield [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -I)( $\mu$ -PCy<sub>2</sub>)(CO)<sub>2</sub>] and [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -PCy<sub>2</sub>){ $\mu$ -P(OEt)<sub>2</sub>}(CO)<sub>2</sub>] can be interpreted analogously, with the I–I and backbone P–O bonds in the latter reactions playing a role analogous to the H–E bonds in the former ones. In contrast, the photochemical reactions of the silanes HSiPh<sub>3</sub> and H<sub>2</sub>SiPh<sub>2</sub> with 1 do not involve demethylation, but dehydrogenation and insertion of the fragments Ph<sub>2</sub>SiC<sub>6</sub>H<sub>4</sub> and SiPh<sub>2</sub>, respectively, into the strong C–OMe bond of the carbyne ligand, with silicon playing here the role of "intramolecular extractor" of the methoxyl group by virtue of the strong Si–O bond thus formed. All the above reactions involve the cleavage of C–O bonds and are therefore exclusive of alkoxycarbyne ligands. The reactions of **1** with selenium and sulfur still reveal other unusual transformations of the methoxycarbyne ligand. Thus, along with the expected incorporation of chalcogenide or dichalcogenide ligands to the unsaturated dimetal center, additional chalcogen atoms can couple to the methoxycarbyne ligand (formation of the *O*-methyldithiocarbonate ligand  $\mu$ -S<sub>2</sub>C(OMe)) or induce the coupling of a CO ligand (formation of the carbene-seleniolate ligand  $\mu$ -C(OMe)C(O)Se).

#### **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 their use.<sup>39</sup> Petroleum ether refers to that fraction distilling in the range 338-343 K. Compound 1 was prepared as described previously. 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) or by a closed 2-propanol circuit, kept at the desired temperature with a cryostat. A 400 W mercury lamp placed ca. 1 cm away from the Schlenk tube was used for all these experiments. Chromatographic separations were carried out using jacketed columns. 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. Filtrations were carried out using diatomaceous earth. IR C-O stretching frequencies were measured in solution, are referred to as  $\nu$ (CO), and are given in wavenumber units (cm<sup>-1</sup>). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (<sup>1</sup>H), 121.50 (<sup>31</sup>P{<sup>1</sup>H}), or 75.47 MHz  $(^{13}C{^{1}H})$  at 290 K in CD<sub>2</sub>Cl<sub>2</sub> solutions unless otherwise 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**  $[Mo_2Cp_2(\mu$ -PCy<sub>2</sub>)( $\mu$ -SPh)(CO)<sub>2</sub>] (2). Compound 1 (0.050 g, 0.085 mmol) and PhSH (30  $\mu$ L, 0.292 mmol) were heated in toluene (10 mL) at 353 K for 6 h to give a green solution, which was filtered. Removal of the solvent from the filtrate under vacuum gave a residue, which was crystallized by slow diffusion of a layer of petroleum ether into a dichloromethane solution of the product to yield compound 2 as a dark green microcrystalline solid (0.046 g, 83%). Microanalytical and spectroscopic data for this product were identical to those previously reported by us for complex 2 using a different synthetic route.<sup>13</sup>

**Preparation of** [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -PCy<sub>2</sub>)( $\mu$ -PHPh)(CO)<sub>2</sub>] (3). Compound 1 (0.050 g, 0.085 mmol) and PH<sub>2</sub>Ph (20 $\mu$ L, 0.182 mmol) were refluxed in toluene (10 mL) for 12 h to give a green solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane–petroleum ether (1:9), and the extracts were chromatographed on alumina (activity IV) at 288 K. Elution with dichloromethane–petroleum ether (1:2) gave a green fraction, which yielded, after removal of solvents under vacuum, compound **3** as a dark green solid (0.044 g, 75%). Anal. Calcd for C<sub>30</sub>H<sub>38</sub>Mo<sub>2</sub>O<sub>2</sub>P<sub>2</sub>: C, 52.64; H, 5.60. Found: C, 52.35; H, 5.20. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.59 (m, Ph, 2H), 7.35–7.22 (m, Ph, 3H), 6.25 (dd, *J*<sub>HH</sub> = 367, 2, P–H, 1H), 5.35, 5.33 (2d, Cp, 2 × 5H), 2.40–1.10 (m, Cy, 22H).

**Reaction of Compound 1 with (EtO)<sub>2</sub>POP(OEt)<sub>2</sub>.** A toluene solution (20 mL) of compound **1** (0.100 g, 0.169 mmol) and (EtO)<sub>2</sub>POP(OEt)<sub>2</sub> (120  $\mu$ L, 0.491 mmol) was placed into a

<sup>(38) (</sup>a) Jameson, C. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G.; Quin, L. D., Eds.; VCH: New York, 1987; Chapter 6. (b) Wrackmeyer, B.; Alt, H. G.; Maisel, H. E. *J. Organomet. Chem.* **1990**, *399*, 125.

<sup>(39)</sup> Armarego, W. L. F.; Chai, C. Purification of Laboratory Chemicals, 5th ed.; Butterworth-Heinemann: Oxford, U.K., 2003.

Schlenk tube equipped with a Young's valve, and the mixture was heated at 363 K for 24 h to give a brown solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane-petroleum ether (1:5), and the extracts were chromatographed on alumina (activity II) at 243 K. Elution with dichloromethane-petroleum ether (1:4) gave first a yellowish-green fraction and then an orange fraction. Removal of solvents from the first fraction gave complex  $[Mo_2Cp_2(\mu-PCy_2){\mu-P(OEt)_2}(CO)_2]$ (4a) as a yellowish-green solid (0.024 g, 20%). Spectroscopic data for this product were identical to those previously reported by us for complex 4a using a different synthetic route.<sup>12b</sup> Removal of solvents from the second fraction gave an orange solid shown (by NMR) to contain the complex  $[Mo_2Cp(\eta^5-C_5H_4CH_2Ph)(\mu-PCy_2){\mu-P-}$  $(OEt)_2$  (CO)<sub>2</sub> (4b) contaminated with small and variable amounts of an uncharacterized species (0.065 g, ca. 50%). All attempts to further separate or purify this solid were unsuccessful and resulted in its progressive decomposition. Spectroscopic data for compound 4b: <sup>1</sup>H NMR (400.13 MHz): δ 7.30–7.15 (m, Ph, 5H), 5.89, 5.82 (2 m, br,  $C_5H_4, 2\times 1H),$  5.43 (s, Cp, 5H), 5.16, 4.77 (2 m,  $C_5H_4, 2\times 1H),$ 4.27, 4.03 (2 m, OCH<sub>2</sub>, 2 × 2H), 3.21, 3.10 (AB,  $J_{HH} = 15$ , CH<sub>2</sub>Ph,  $2 \times 1$ H), 1.38 (t,  $J_{\text{HH}} = 7$ , Me, 6H), 2.40–1.10 (m, Cy, 22H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz): δ 236.2, 232.9 (2s, br, MoCO), 141.7 [s, C<sup>1</sup>(Ph)], 128.8 [s, C<sup>2</sup> and C<sup>3</sup>(Ph)], 126.5 [s, C<sup>4</sup>(Ph)], 110.7 [s, C<sup>1</sup>(C<sub>5</sub>H<sub>4</sub>)], 90.6, 89.4, 85.2, 85.0 [4s, C<sup>2-5</sup>(C<sub>5</sub>H<sub>4</sub>)], 88.3 (s, Cp), 65.72  $C^{1}(Cy)]$ , 44.0 [d,  $J_{CP} = 17$ ,  $C^{1}(Cy)]$ , 35.9, 35.0, 34.4 [3s, br,  $C^{2}(Cy)]$ , 34.7, 33.4 [2s,  $C^{2}(Cy)$  and  $CH_{2}Ph$ ], 28.5 [d,  $J_{CP} = 12$ ,  $2C^{3}(Cy)]$ , 28.4 [d,  $J_{CP} = 10$ ,  $C^{3}(Cy)]$ , 28.3 [d,  $J_{CP} = 11$ ,  $C^{3}(Cy)]$ , 26.7, 26.6 [2s,  $C^{4}(Cy)]$ , 17.4 (s, Me), 17.3 [d,  $J_{CP} = 3$ , Me].

Preparation of  $[Mo_2Cp_2{\mu-C(2-C_6H_4SiPh_2OMe)}(\mu-PCy_2) (\mu$ -CO)] (5). Neat SiHPh<sub>3</sub> (0.090 g, 0.346 mmol) was added to a toluene solution (15 mL) of compound 1 (0.040 g, 0.068 mmol), and the mixture was exposed to visible-UV radiation in a quartz Schlenk tube at 288 K for 3.5 h to give a brown mixture. The solvent was then removed under vacuum, the residue was extracted with dichloromethane-petroleum ether (1:4), and the extracts were chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane-petroleum ether (1:3) gave a brown fraction containing an uncharacterized mixture of silane derivatives and then an orange fraction. Removal of solvents from the latter fraction gave compound 5 as an orange powder (0.030 g,52%). Anal. Calcd for C<sub>43</sub>H<sub>49</sub>Mo<sub>2</sub>O<sub>2</sub>PSi: C, 60.85; H, 5.82. Found: C, 60.63; H, 5.65. <sup>1</sup>H NMR: δ 7.50-7.30 (m, Ph, 10H), 7.12 (m, C<sub>6</sub>H<sub>4</sub>, 2H), 6.83 (m, C<sub>6</sub>H<sub>4</sub>, 1H), 6.69 (m, C<sub>6</sub>H<sub>4</sub>, 1H), 5.60 (s, Cp, 10H), 3.14 (s, OMe, 3H), 1.60–0.30 (m, Cy, 22H).  $^{13}C{^{1}H}$  NMR: δ 386.2 (s, br,  $\mu$ -CC<sub>6</sub>H<sub>4</sub>), 300.8 (d,  $J_{CP} = 6$ ,  $\mu$ -CO), 173.4 [s, C<sup>1</sup>(C<sub>6</sub>H<sub>4</sub>)], 136.5 [s, C<sup>2</sup>(C<sub>6</sub>H<sub>4</sub>)], 135.9 [s, C<sup>1</sup>(Ph)], 135.8 [s, C<sup>2</sup>(Ph)], 130.1 [s, C<sup>4</sup>(Ph)], 128.2 [s, C<sup>3</sup>(Ph)], 128.7, 121.6, 121.3, 120.5 [4s,  $C^{3-6}(C_6H_4)$ ], 95.8 (s, Cp), 52.1 (s, OMe), 46.5 [d,  $J_{CP} = 18, C^1(Cy)$ ], 42.3 [d,  $J_{CP} = 19$ ,  $C^{1}(Cy)$ ], 33.4, 32.5 [2s,  $C^{2}(Cy)$ ], 27.7 [d,  $J_{CP} = 12$ ,  $C^{3}(Cy)$ ], 27.4 [d,  $J_{CP} = 11$ ,  $C^{3}(Cy)$ ], 26.2, 23.0 [2s,  $C^{4}(Cy)$ ].

Preparation of [Mo<sub>2</sub>Cp<sub>2</sub>(µ-CSiPh<sub>2</sub>OMe)(µ-PCy<sub>2</sub>)(µ-CO)] (6). Neat SiH<sub>2</sub>Ph<sub>2</sub> (70  $\mu$ L, 0.380 mmol) was added to a toluene solution (15 mL) of compound 1 (0.040 g, 0.068 mmol), and the mixture was exposed to visible-UV radiation in a quartz Schlenk tube at 288 K for 2.5 h to give a brown mixture. The solvent was then removed under vacuum, the residue was extracted with dichloromethane-petroleum ether (1:5), and the extracts were chromatographed through an alumina column (activity IV) at 253 K. Elution with dichloromethane-petroleum ether (1:1) gave a orange fraction, which yielded, after removal of solvents under vacuum, compound 6 as an orange powder (0.030 g, 57%). Anal. Calcd for C37H45M02O2PSi: C, 57.51; H, 5.87. Found: C, 57.64; H, 5.98. <sup>1</sup>H NMR:  $\delta$  7.40–7.10 (m, Ph, 10H), 5.71 (s, Cp, 10H), 3.41 (s, OMe, 3H), 1.90–0.30 (m, Cy, 22H). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 417.9 (d,  $J_{CP} = 13$ ,  $\mu$ -CSi), 302.3 (d,  $J_{CP} = 8$ ,  $\mu$ -CO), 136.6 [s, C<sup>1</sup>(Ph)], 135.5 [s, C<sup>2</sup>(Ph)], 129.6 [s, C<sup>4</sup>(Ph)], 127.9 [s, C<sup>3</sup>(Ph)], 95.6 (s, Cp), 51.7 (s, OMe), 42.3 [d,  $J_{CP} = 17$ , C<sup>1</sup>(Cy)], 42.2 [d,  $J_{\rm CP} = 18, \, {\rm C}^1({\rm Cy})], \, 33.5, \, 33.0 \, [2s, \, {\rm C}^2({\rm Cy})], \, 27.5, \, 27.4 \, [2d, \, J_{\rm CP} = 100, \, {\rm C}^2({\rm Cy})], \, 27.5, \, 27.4 \, [2d, \, J_{\rm CP} = 100, \, {\rm C}^2({\rm Cy})], \, 37.5, \, {\rm C}^2({\rm Cy})], \, {\rm C}^2({\rm Cy})],$  $12, C^{3}(Cy)], 26.2 [s, 2C^{4}(Cy)].$ 

Preparation of  $[Mo_2Cp_2(\mu - PCy_2){\mu - S_2C(OMe)}(S)_2]$  (7). Solid sulfur (0.022 g, 0.086 mmol of S<sub>8</sub>) was added to a dichloromethane solution (10 mL) of compound 1 (0.050 g, 0.085 mmol), and the mixture was refluxed for 2 h to give a purple solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane-petroleum ether (1:5), and the extracts were chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane-petroleum ether (1:3) gave a deep-rose fraction, which gave, after removal of solvents, compound 7 as a deep-rose powder (0.048 g, 82%). Anal. Calcd for C<sub>24</sub>H<sub>35</sub>Mo<sub>2</sub>OPS<sub>4</sub>: C, 41.74; H, 5.11; S, 18.57. Found: C, 42.04; H, 5.40; S, 17.80. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.37 (s, Cp, 10H), 3.82 (s, OMe, 3H), 1.60–0.90 (m, Cy, 22H).  ${}^{13}C{}^{1}H{}$  NMR (CDCl<sub>3</sub>):  $\delta$ 225.9 (s,  $\mu$ -S<sub>2</sub>C), 96.5 (s, Cp), 66.3 (s, OMe), 41.3 [d, br,  $J_{CP} = 15$ , C<sup>1</sup>(Cy)], 34.0, 33.1 [2s, br, C<sup>2</sup>(Cy)], 27.7, 25.5 [2d,  $J_{CP} = 8$ , C<sup>3</sup>(Cy)], 25.5 [s, 2C<sup>4</sup>(Cy)]. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 223 K): δ 6.41 (s, Cp, 10H, isomer A), 6.40 (s, Cp, 10H, isomer B), 3.81 (s, OMe, 3H, isomer A), 3.80 (s, OMe, 3H, isomer B), 1.60-0.80 (m, Cy, 22H, isomers A and B). Ratio A/B = 2.  ${}^{31}P{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 223 K): δ 83.9 (s, μ-P, isomer A), 83.7 (s, μ-P, isomer B). SI-MS (m/z): 689.8 (M<sup>+</sup>), 614.9 (M<sup>+</sup> - COMeS), 582.9 (M<sup>+</sup> - COMeS<sub>2</sub>), 417.7  $(M^+ - COMeS - PCy_2).$ 

Preparation of  $[Mo_2Cp_2\{\mu$ -C(OMe)C(O)Se $\}(\mu$ -PCy<sub>2</sub>)( $\mu$ -Se<sub>2</sub>)] (8). Gray selenium (0.055 g, 0.696 mmol) was added to a dichloromethane solution (10 mL) of compound 1 (0.050 g, 0.085 mmol), and the mixture was stirred for 2.5 h to give a greenish-blue solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethanepetroleum ether (1:5), and the extracts were chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane-petroleum ether (1:4) gave a blue fraction containing a small amount of an uncharacterized compound. Elution with a 1:2 mixture gave a dark green fraction, yielding, after removal of solvents, compound 8 as a green powder (0.040 g, 57%). Anal. Calcd for C<sub>27.33</sub>H<sub>37.66</sub>Mo<sub>2</sub>-O<sub>2</sub>PSe<sub>3</sub> (3·1/3C<sub>7</sub>H<sub>8</sub>): C, 38.26; H, 4.42. Found: C, 38.18; H, 4.34. <sup>1</sup>H NMR:  $\delta$  5.89 (s, Cp, 10H), 3.43 (s, OMe, 3H), 2.30–0.90 (m, Cy, 22H). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  177.7 (s, C=O), 134.8 (d, J<sub>CP</sub> = 17, COMe), 94.8 (s, Cp), 58.9 (s, OMe), 48.3 [d, 134.8 (d,  $J_{CP} = 1/$ , COIVIE), 94.8 (S, CP), 56.7 (S, OHC), 16.5 [a,  $J_{CP} = 18$ ,  $C^{1}(Cy)$ ], 40.4 [d,  $J_{CP} = 13$ ,  $C^{1}(Cy)$ ], 34.6 [d,  $J_{CP} = 3$ ,  $C^{2}(Cy)$ ], 34.2 [d,  $J_{CP} = 4$ ,  $C^{2}(Cy)$ ], 29.0 [d,  $J_{CP} = 11$ ,  $C^{3}(Cy)$ ], 27.7 [d,  $J_{CP} = 9$ ,  $C^{3}(Cy)$ ], 26.7, 26.6 [2s,  $C^{4}(Cy)$ ]. SI-MS (m/z): 828.6 (M<sup>+</sup>), 799.6 (M<sup>+</sup> - CO), 756.6 (M<sup>+</sup> -CO - COMe).

**Preparation of** [Mo<sub>2</sub>Cp<sub>2</sub>(*μ*-I)I<sub>2</sub>(*μ*-PCy<sub>2</sub>)(CO)<sub>2</sub>] (10). Solid iodine (0.043 g, 0.167 mmol) was added to a tetrahydrofuran solution of compound 1 (0.050 g, 0.085 mmol), and the mixture was stirred for 15 min to give an orange solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane–petroleum ether (1:5), and the extracts were filtered. Removal of the solvents from the filtrate under vacuum gave compound 10 as an orange powder (0.074 g, 91%). Anal. Calcd for C<sub>24</sub>H<sub>32</sub>I<sub>3</sub>Mo<sub>2</sub>O<sub>2</sub>P: C, 30.15; H, 3.37. Found: C, 30.26; H, 3.46. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 5.41, 5.12 (2s, Cp, 2 × 5H), 2.95, 2.53 (2 m, Cy, 2 × 1H), 1.80–0.70 (m, Cy, 20H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 241.7 (d, *J*<sub>CP</sub> = 11, MoCO), 236.7 (s, MoCO), 98.1, 91.6 (2s, Cp), 48.7 [d, *J*<sub>CP</sub> = 5, C<sup>2</sup>(Cy)], 32.9, 32.2 [2s, C<sup>2</sup>(Cy)], 28.0, 26.5 [2d, *J*<sub>CP</sub> = 9, C<sup>3</sup>(Cy)], 27.6 [d, *J*<sub>CP</sub> = 8, C<sup>3</sup>(Cy)], 27.4 [d, *J*<sub>CP</sub> = 12, C<sup>3</sup>(Cy)], 25.6, 26.1 [2s, C<sup>4</sup>(Cy)].

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Supporting Information Available: A CIF file giving the crystallographic data for the structural analysis of compounds 5 and 8. This material is available free of charge via the Internet at http://pubs.acs.org.