

# Reaction of $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2)]^-$ with the Cumulenes 3-ClC<sub>6</sub>H<sub>4</sub>NCO, PhNCS, and CS<sub>2</sub> and with Michael Acceptors: Synthesis and Reactivity of $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{SP}_2\text{S})]$ , a Complex Containing an Unusual CSP<sub>2</sub>S Five-Membered Ring

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Deprotonation of the complex  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2\text{H})]$  (**1**) yields the anion  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2)]^-$  (**2**). Reaction of **2** with cumulenes such as 3-ClC<sub>6</sub>H<sub>4</sub>NCO and PhNCS leads, after reprotonation, to the simple addition products  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)\{\text{PPh}_2\text{C}(=\text{X})\text{NHR}\}]$  (R = 3-ClPh, X = O, **4a**; R = Ph, X = S, **4b**). Reaction of **2** with the Michael acceptors H<sub>2</sub>C=C(H)R gives the related products  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2\text{C}_2\text{H}_4\text{R})]$  (R = COOMe, **5a**; R = CN, **5b**; R = COMe, **5c**). In contrast, reaction of **2** with CS<sub>2</sub> followed by HBF<sub>4</sub> yields the complex  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{SP}_2\text{S})]$  (**3**), which has an unprecedented bridging ligand containing a CSP<sub>2</sub>S five-membered ring. Reaction of **3** with <sup>t</sup>BuLi followed by MeI yields  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)\{\text{PPh}_2\text{C}(\text{S})\text{SMe}\}]$  (**6**), in which ring scission and re-formation of the tetrahedral Mo<sub>2</sub>P<sub>2</sub> core present in complex **1** has taken place. Reaction of **3** with metal carbonyls can also lead to re-formation of the Mo<sub>2</sub>P<sub>2</sub> moiety. The crystal structures of five of the new complexes have been determined.

## Introduction

The deprotonation of a secondary phosphine within the coordination sphere of a metal complex, followed by subsequent reaction of the resulting anion with a wide variety of electrophiles, can be used to generate novel phosphine ligands, including stereogenic phosphines which are not readily obtainable by other means.<sup>1,2</sup> We recently reported in a preliminary communication that this approach leads in the case of the reaction of  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2)]^-$  (**2**) with CS<sub>2</sub> to the formation of  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{SP}_2\text{S})]$  (**3**), in which unexpected activation of the bridging diphosphorus moiety present in **2** has occurred.<sup>3</sup> This reaction is particularly interesting, as the coordinated P<sub>2</sub> unit in dimetallic complexes is generally very unreactive, previously documented reactions simply involving the donation of one or both of the uncoordinated phosphorus lone pairs of the P<sub>2</sub> unit to Lewis acids.<sup>4</sup>

In this paper we report the results of attempts to activate a P<sub>2</sub> bridging ligand via the reaction of the

anion  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2)]^-$  (**2**) with cumulenes other than CS<sub>2</sub> and with Michael acceptors. Additionally, we report reactions of the complex  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{SP}_2\text{S})]$  (**3**) with metal carbonyls and of deprotonated **3** with MeI and HBF<sub>4</sub>.

## Results and Discussion

**Reaction of the Anion  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2)]^-$  (**2**) with Electrophiles.** Deprotonation of  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2\text{H})]$  with DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) proceeds smoothly under mild conditions to yield the anion  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2)]^-$  (**2**). Stirring a solution of **2** in dichloromethane with an excess of the cumulenes 3-ClC<sub>6</sub>H<sub>4</sub>NCO and PhNCS (1.5–2 equiv) for 2 h at room temperature followed by reprotonation with HBF<sub>4</sub> gives, in addition to unreacted starting material, the simple addition products  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)\text{PPh}_2\text{C}(=\text{X})\text{NHR}]$  (R = 3-ClPh, X = O, **4a**; R = Ph, X = S, **4b**) in high yield (80–90%) (Scheme 1). Reaction of **2** with the aliphatic isothiocyanate <sup>t</sup>BuNCS, however, yielded no new products. A similar difference in the reactivities of aryl and alkyl isothiocyanates has been previously reported by Lin et al.,<sup>5</sup> who reported that the reaction of  $[\text{W}(\text{CO})_5\text{-PPh}_2]^-$  with RNCS only proceeded when R = aryl. This

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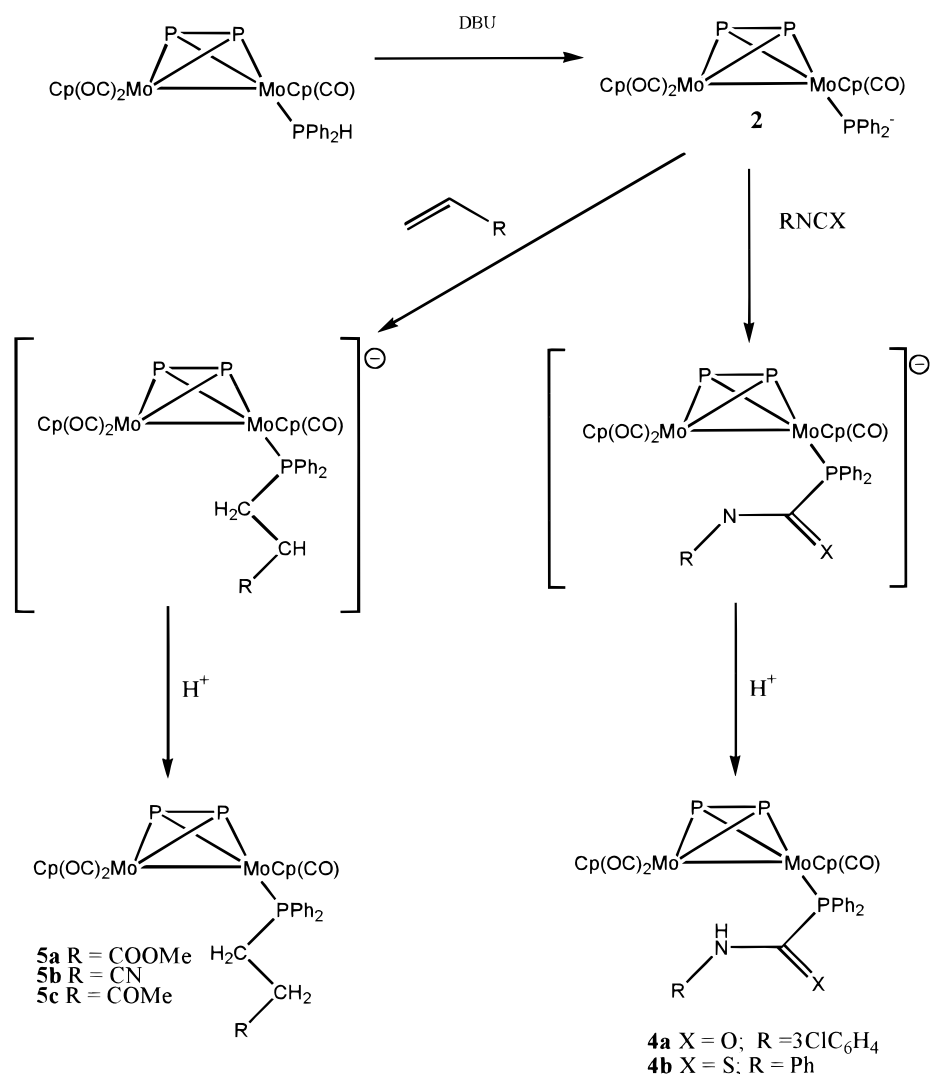
(2) See for example: (a) Weller, F.; Pertz, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1049. (b) Yih, K. H.; Cheng, M. C.; Wang, Y.; Lin, Y. C. *J. Chem. Soc., Dalton Trans.* **1995**, 1305. (c) Gal, A. W.; Gosselink, J. W.; Vollenbroek, F. A. *J. Organomet. Chem.* **1977**, 142, 357. (d) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, 94, 1375. (e) Kagan, H. B.; Sasaki, M. In *The Chemistry of Organophosphorus Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1990; Vol. 1.

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Scheme 1



difference may be due to the electron-withdrawing aryl group on the nitrogen atom increasing the partial positive charge on the carbon atom of the NCS group, hence making it more susceptible to nucleophilic attack.

In contrast to the outcome of the reactions with isocyanate and isothiocyanate, reaction of **2** with CS<sub>2</sub> does not lead to the formation of an analogue of the pendant thiolatophosphine [L<sub>n</sub>MPPH<sub>2</sub>C(S)SH], reported by Lin et al. as a product of the reaction of [W(CO)<sub>5</sub>-PPh<sub>2</sub>]<sup>-</sup> and CS<sub>2</sub>.<sup>2b</sup> Instead, the complex [Cp<sub>2</sub>(CO)<sub>3</sub>Mo<sub>2</sub>(μ-η<sup>3</sup>-Ph<sub>2</sub>PC(H)SP<sub>2</sub>S)] (**3**) is obtained. The structure of **3** has already been reported by us in a preliminary communication.<sup>3</sup>

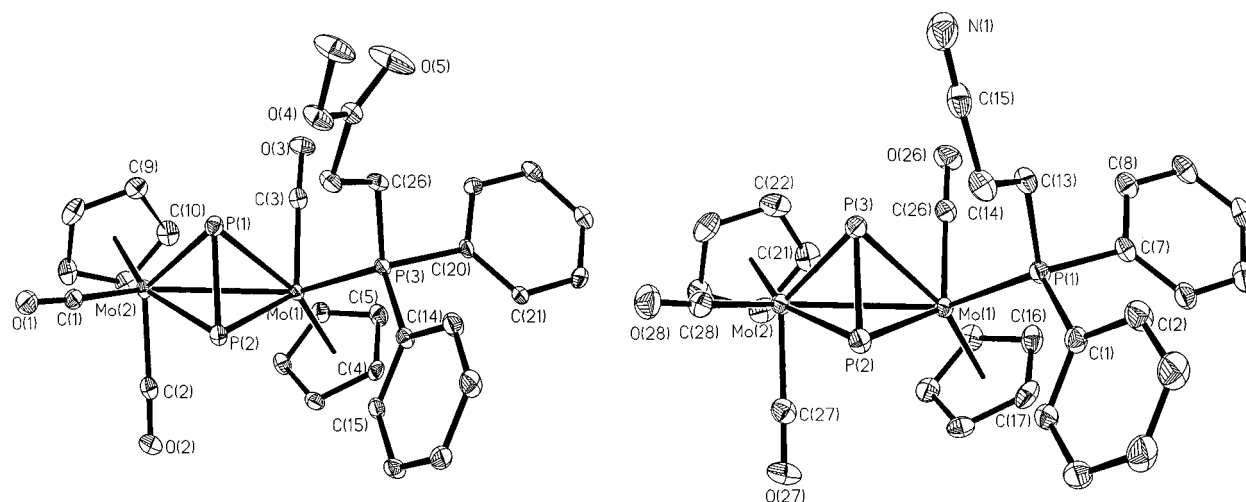
It is unclear why the reactions of **2** with isocyanate and isothiocyanate do not lead to the formation of products similar to **3**. A possible explanation is based upon the relative stabilities of the anionic adducts formed in the two cases. Reaction of **2** with either an isocyanate or isothiocyanate presumably leads initially to a coordinated phosphine of the type [Ph<sub>2</sub>PC(X)NPh]<sup>-</sup> (X = O, S), where the negative charge is formally on the amide nitrogen atom. In this coordinated phosphine the negative charge can be delocalized over both the nitrogen-bound phenyl group and the C(X) group. In contrast, in the case of reaction with CS<sub>2</sub> a less stable anionic adduct is formed in which the negative charge

is localized on the cumulene moiety, which is then a good nucleophile and attacks the μ-η<sup>2</sup>-P<sub>2</sub> unit to give the CSP<sub>2</sub>S ring.

An additional factor favoring ring formation in the reaction of **2** with CS<sub>2</sub> as compared to RNCS or RNCO may be that the CSP<sub>2</sub>S ring is more stable than the CXP<sub>2</sub>N ring, which would be formed if the RNCX adducts were to cyclize. Thus, the C-S-P bond angle of 94.7° in complex **3** suggests that a great deal of strain is present in the ring. This ring strain would be enhanced in the hypothetical CXP<sub>2</sub>N ring due to the smaller size of the N heteroatom. Hence, this ring does not form, and on reprotonation of the RNCX adducts, complexes containing a pendant phosphine of the type reported by Ambrosius et al. are obtained,<sup>6</sup> in which the Mo<sub>2</sub>P<sub>2</sub> core present in **1** and **2** remains unaltered.

Clearly, the first step in all reactions of **2** with the unsaturated species studied here is nucleophilic attack of the phosphido anion on the organic electrophile, the resulting pendant phosphine then bearing a negative charge which, in favorable cases, can attack the P<sub>2</sub> unit. To determine whether attack on the P<sub>2</sub> unit by a pendant phosphine would be facilitated if the negative

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**Figure 1.** Molecular structures of (left)  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2\text{C}_2\text{H}_4\text{COOMe})]$  (**5a**) and (right)  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2\text{C}_2\text{H}_4\text{CN})]$  (**5b**). Thermal ellipsoids are shown at the 30% probability level.

charge on the pendant ligand lay further away from the phosphine phosphorus atom than in the anions generated by reaction with RNCO and RNCS, the reactions of complex **2** with Michael acceptors such as MVK (MVK = methyl vinyl ketone) were investigated. In the presumed ionic intermediate formed on reaction of **2** with Michael acceptors (Scheme 1), the charge on the resultant pendant phosphine moiety lies either on the carbon atom  $\beta$  to the metal or on the heteroatom of the R group and is hence more distant from the phosphine phosphorus atom than in the pendant phosphines derived from reaction of **2** with RNCX. Reaction of a solution of **2** in dichloromethane with the classic Michael acceptors  $\text{H}_2\text{C}=\text{C}(\text{H})\text{R}$  ( $\text{R} = \text{COOMe}$ ,  $\text{COMe}$ ,  $\text{CN}$ ) proceeds smoothly at room temperature, but the resulting pendant phosphine ligand shows no tendency to attack the  $\eta^2\text{-P}_2$  unit, even in refluxing THF, and, after reprotonation with  $\text{HBF}_4$ , the complexes  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2\text{C}_2\text{H}_4\text{R})]$  ( $\text{R} = \text{COOMe}$ , **5a**;  $\text{R} = \text{CN}$ , **5b**;  $\text{R} = \text{COMe}$ , **5c**) were obtained in near-quantitative yield (Scheme 1).

**Characterization of 4 and 5.** The complexes **4** and **5** have been characterized spectroscopically (see Experimental Section), and the molecular structures of **5a,b** have, in addition, been determined by single-crystal X-ray diffraction studies (Figure 1). Table 1 gives selected bond lengths and angles for complexes **5a,b**. The P–P bond lengths in the  $\text{P}_2$  units in **5a** (2.077(2) Å) and **5b** (2.085(1) Å) are typical of those in other such complexes, the bond length in the unsubstituted complex  $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)]$  being 2.079(2) Å<sup>7</sup> and that in the parent complex **1** being 2.085(3) Å. The Mo–Mo bond lengths of 3.0240(9) and 3.0334(7) Å for **5a,b**, respectively, are both considerably shorter than that in the parent complex **2**. However, both values fall within the range of Mo–Mo single-bond lengths reported in related complexes, which vary from 2.954(1) Å in  $[\text{Cp}_2(\text{CO})_2\text{Mo}_2\{\mu\text{-}\eta^3\text{-CH}=\text{CHC}(\text{O})\text{Ph}\}(\mu\text{-PPh}_2)]$ <sup>8</sup> to 3.349(2) Å in **3**.<sup>3</sup> One long and one short Mo–P bond to each Mo atom are observed within the  $\text{Mo}_2\text{P}_2$  core of both **5a** and **5b**. Similarly distinct pairs of Mo–P bond distances

**Table 1.** Selected Bond Lengths (Å) and Angles (deg) for  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2\text{C}_2\text{H}_4\text{COOMe})]$  (**5a**) and  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2\text{C}_2\text{H}_4\text{CN})]$  (**5b**)

	<b>5a</b>		<b>5b</b>
Mo(1)–Mo(2)	3.0240(9)	Mo(1)–Mo(2)	3.0334(7)
Mo(1)–P(1)	2.527(2)	Mo(1)–P(1)	2.464(1)
Mo(1)–P(2)	2.463(2)	Mo(1)–P(2)	2.529(1)
Mo(1)–P(3)	2.465(2)	Mo(1)–P(3)	2.462(1)
Mo(2)–P(1)	2.455(2)	Mo(2)–P(1)	2.567(1)
Mo(2)–P(2)	2.575(2)	Mo(2)–P(2)	2.451(1)
P(1)–P(2)	2.077(2)	P(1)–P(2)	2.085(1)
P(1)–Mo(1)–P(2)	48.17(6)	P(1)–Mo(1)–P(2)	49.33(3)
P(2)–Mo(1)–P(3)	86.08(6)	P(2)–Mo(1)–P(3)	85.33(4)
P(3)–Mo(1)–P(1)	83.20(6)	P(3)–Mo(1)–P(1)	87.11(4)
P(2)–Mo(1)–Mo(2)	54.83(4)	P(2)–Mo(1)–Mo(2)	51.30(3)
P(1)–Mo(1)–Mo(2)	51.56(4)	P(1)–Mo(1)–Mo(2)	54.50(3)
P(1)–Mo(2)–P(2)	48.70(6)	P(1)–Mo(2)–P(2)	49.33(3)
P(1)–Mo(2)–Mo(1)	53.73(4)	P(1)–Mo(2)–Mo(1)	51.38(3)
P(2)–P(1)–Mo(2)	68.66(7)	P(2)–P(1)–Mo(2)	62.56(4)
Mo(2)–P(1)–Mo(1)	74.71(5)	Mo(2)–P(1)–Mo(1)	74.12(3)
P(1)–P(2)–Mo(2)	62.64(6)	P(1)–P(2)–Mo(2)	68.42(4)
P(3)–Mo(1)–Mo(2)	132.40(4)	P(3)–Mo(1)–Mo(2)	133.92(3)
P(2)–Mo(2)–Mo(1)	51.44(4)	P(2)–Mo(2)–Mo(1)	53.66(3)
P(2)–P(1)–Mo(1)	63.80(6)	P(2)–P(1)–Mo(1)	66.97(4)

are found in the  $\text{Mo}_2\text{P}_2$  core of the unsubstituted complex  $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)]$ , reported by Scherer et al.<sup>7</sup>

The  $^1\text{H}$  NMR spectra of **4a,b** show broad peaks at 9.3 and 8.8 ppm, respectively, which are assigned to the N–H proton. This is in good agreement with data recorded by Kramolowsky et al. for the related complex  $[(\text{CO})_4\text{Mn}(\text{PPh}_2\text{C}(\text{S})\text{NHPh})]$ .<sup>9</sup>

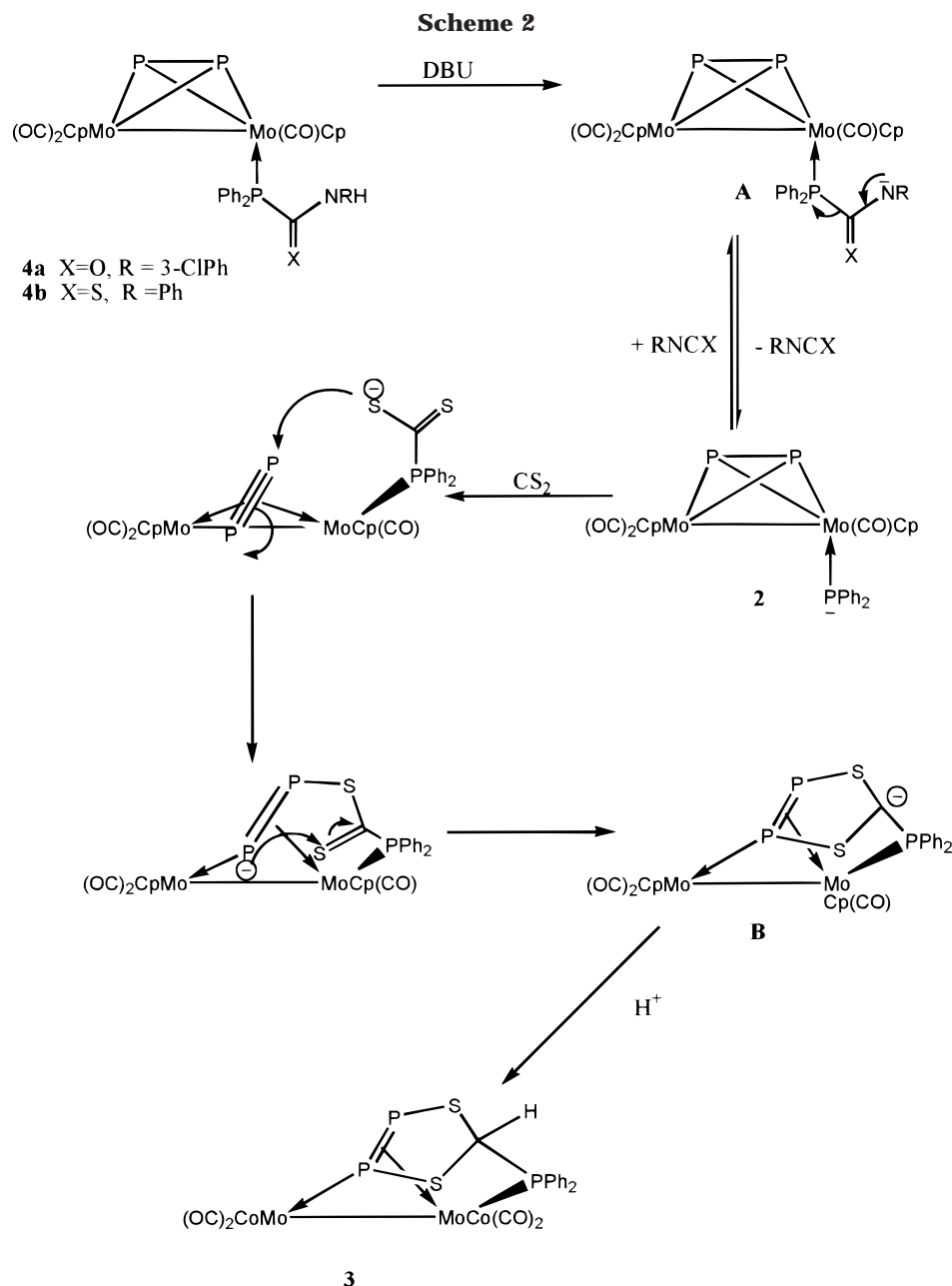
Complexes **5a–c** all show rather complicated  $^1\text{H}$  NMR spectra, due to the inequivalence of the two protons on each of the  $\alpha$ - and  $\beta$ -carbon atoms of the  $\text{PPh}_2\text{C}_\alpha\text{H}_2\text{C}_\beta\text{H}_2\text{R}$  ligand. This is presumably due to the phosphine ligand being bound to an asymmetric molybdenum center, causing the protons to become diastereomeric.

**Reaction of 4 and 5 with  $\text{CS}_2$ .** Complexes **4** and **5** both contain acidic protons and were deprotonated with DBU in order to investigate possible nucleophilic reaction of the resulting anions with  $\text{CS}_2$ . Addition of a slight excess of DBU (1.15 equiv) to a stirred solution of **4** in dichloromethane followed by addition of excess  $\text{CS}_2$

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caused an immediate color change from orange to dark brown. Filtration of the solution through silica yielded the green-brown complex **3** as the sole product in good yield (80–90%). In contrast, similar treatment of complexes **5a–c** led only to decomposition. A possible reaction pathway for the formation of **3** from **4a,b** is shown in Scheme 2. It is suggested that deprotonation yields the intermediate anion **A**, which is in equilibrium with **2** and the free isocyanate; reaction of **2** with CS<sub>2</sub> then yields **B**, the precursor anion of **3**. It is presumably the driving force of the reaction of **2** with CS<sub>2</sub> which pushes the equilibrium between intermediate **A** and **2** toward **2**, thus giving **3** as the sole product (Scheme 2). The reprotonation of the precursor anion **B** necessary for the formation of **3** presumably takes place on the silica during workup.

**Reaction of [Cp<sub>2</sub>(CO)<sub>3</sub>Mo<sub>2</sub>(μ-η<sup>3</sup>-Ph<sub>2</sub>PC(H)SP<sub>2</sub>S)] (**3**) with Organic Electrophiles.** The cyclic ligand μ-η<sup>3</sup>-PPh<sub>2</sub>C(H)SP<sub>2</sub>S possesses several possible sites for further reaction. In particular, it contains an acidic

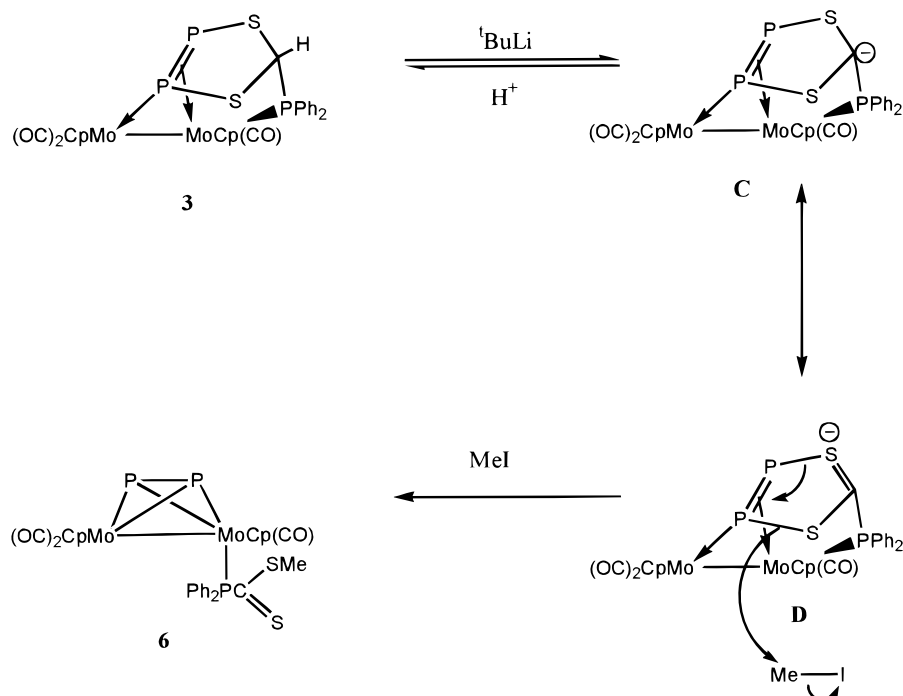
proton together with free lone pairs on each sulfur atom and on one of the phosphorus atoms of the diphosphene P<sub>2</sub> unit. It was therefore of interest to investigate the susceptibility of **3** toward electrophilic attack.

It seemed possible that deprotonation of the CSP<sub>2</sub>S ring at the carbon atom would have a 2-fold effect: it would increase the nucleophilic character of the lone pairs on phosphorus and sulfur and would also allow electrophilic attack at the carbanion. To explore this possibility, **3** was deprotonated with <sup>t</sup>BuLi and the generated anion reacted with methyl iodide. Reaction of **3** with <sup>t</sup>BuLi at −78 °C gave an orange solution; addition of a slight excess of MeI (1.1 equiv) to this solution and continued stirring at −78 °C for 1 h led to the formation of [Cp<sub>2</sub>(CO)<sub>3</sub>Mo<sub>2</sub>(μ-η<sup>2</sup>-P<sub>2</sub>)(Ph<sub>2</sub>PC(S)SMe)] (**6**) in near-quantitative yield.

The infrared spectrum of **6** shows three absorptions in the terminal carbonyl region. The pattern of these absorptions is very similar to those of complexes **4** and **5** and is in marked contrast to that for complex **3**. The



Scheme 3



$^{31}\text{P}$  NMR spectrum of **6** shows a double doublet at  $\delta$  100.4 ( $^2J_{\text{P-P}} = 18$  Hz;  $^2J_{\text{P-P}} = 5$  Hz), which is assigned as the phosphine phosphorus atom coupled to the *cis* and *trans* phosphorus atoms of the diphosphene  $\text{P}_2$  unit. A doublet of doublets at  $\delta$  -7.23 ( $^1J_{\text{P-P}} = 484$  Hz;  $^2J_{\text{P-P}} = 18$  Hz) and a doublet of doublets at  $\delta$  -17 ( $^1J_{\text{P-P}} = 484$  Hz,  $^2J_{\text{P-P}} = 5$  Hz) are assigned to the *transoid* and *cisoid* phosphorus atoms of the  $\text{P}_2$  unit, respectively.

To investigate whether the ring scission which occurs during the formation of **6** occurs on deprotonation of **3** with  $t\text{BuLi}$  or is promoted by subsequent addition of  $\text{MeI}$ ,  $\text{HBF}_4$  was added immediately after the deprotonation of **3**. This led to re-formation of **3** in near-quantitative yield, suggesting that it is the addition of  $\text{MeI}$  which causes scission.

In situ  $^{31}\text{P}$  NMR spectroscopic studies have shown that the characteristic resonances of the ring-bound phosphorus atoms are present before reprotonation of the reaction mixture of **2** +  $\text{CS}_2$  and are also the sole signals present after the addition of  $t\text{BuLi}$  to complex **3**. This leads us to propose that deprotonated **3** can exist in two resonance forms, either with the negative charge residing on the ring carbon (**C**) or on one of the ring sulfur atoms (**D**) (Scheme 3). This latter form may be regarded as a sulfur ylide. Subsequent reaction can then be rationalized in terms of HSAB theory. Clearly, resonance form **C** represents the harder of the two and would therefore be expected to react with hard electrophiles such as  $\text{H}^+$  to yield **3**, whereas resonance form **D** would react with softer electrophiles such as  $\text{MeI}$  to yield **6** (Scheme 3).

**Reaction of 3 with Metal Carbonyl Reagents.** Reaction of complex **3** with  $\text{Fe}_2(\text{CO})_9$  at room temperature for 24 h results in the formation of  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{PPh}_2\text{C(H)S}_2\text{Fe}_2(\text{CO})_5)]$  (**7**) in low yield (15–20%). The mechanism of formation of **7** has not been fully elucidated. There is a wealth of documented reactions in which lone pairs on naked phosphorus

atoms coordinate to a metal carbonyl fragment,<sup>10</sup> and this is proposed to be the first step in the formation of **7** (Scheme 4). Once the iron fragment has coordinated to the  $\text{CSP}_2\text{S}$  ring by a phosphorus lone pair, it is proposed that further interaction with the sulfur lone pairs of the  $\text{CSP}_2\text{S}$  ring occurs, leading to subsequent ring cleavage.

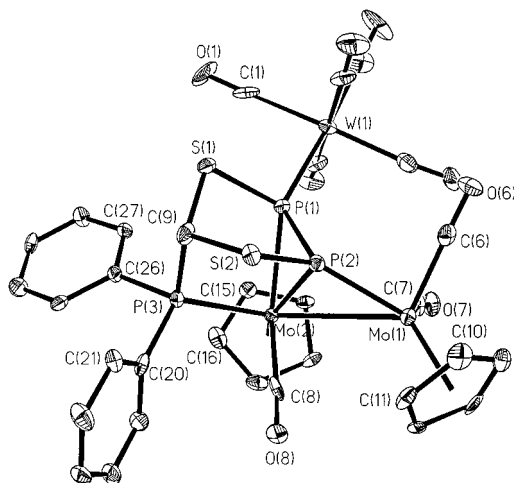
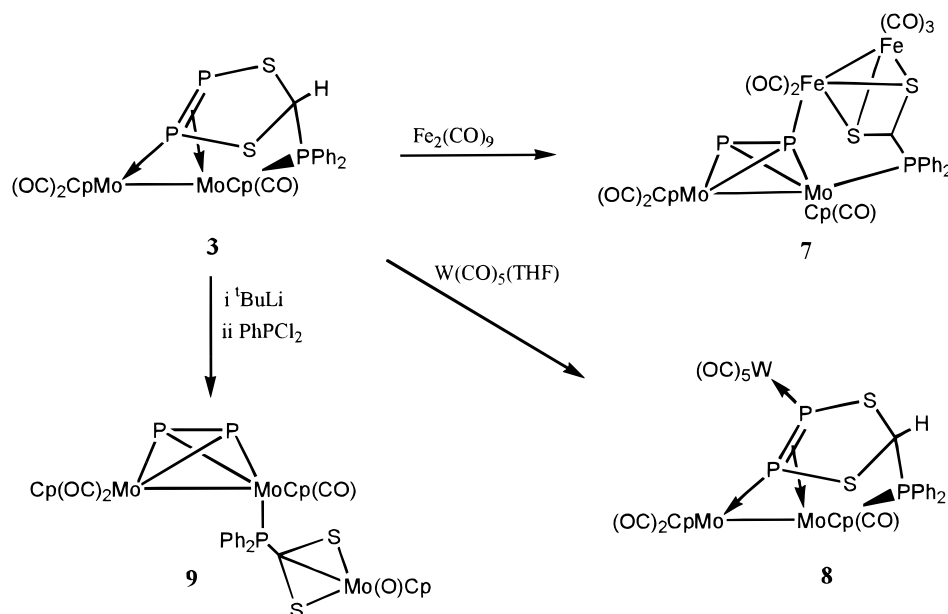
To test the first part of the above hypothesis, it was decided to react **3** with a mononuclear carbonyl complex having a labile ligand to demonstrate that the initial step is coordination to a phosphorus, rather than to a sulfur atom. Reaction of **3** with  $\text{W}(\text{CO})_5(\text{THF})$  did indeed yield  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^3\text{-Ph}_2\text{PC(H)SPP}\{\text{W}(\text{CO})_5\text{S}\})]$  (**8**) as the only isolable product in good yield (60–70%), supporting the proposal that the first step in the formation of **7** involves coordination of iron by phosphorus rather than sulfur. The molecular structure of **8** is shown in Figure 2.

A solution of **3** in dichloromethane was stirred with DBU and an excess of  $\text{PhPCl}_2$  at room temperature for 48 h, giving  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{Ph}_2\text{P}\{\eta^3\text{-CS}_2\text{Mo}(\text{O})\text{-Cp}\})]$  (**9**) as moderately air-stable brown crystals in low yield (10%). As in the reaction of **3** with  $\text{Fe}_2(\text{CO})_9$ , the  $\text{Mo}_2\text{P}_2$  tetrahedrane core has been re-formed, the molecular structure of **9** being shown in Figure 3. Complex **9** exhibits the added unusual feature of a 16-electron molybdenum atom coordinated in an allylic fashion by the dithiolato group. Although there are several examples of  $\text{RCS}_2$  acting as a three-electron donor<sup>11</sup> to a

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Scheme 4



**Figure 2.** Molecular structure of [Cp<sub>2</sub>(CO)<sub>3</sub>Mo<sub>2</sub>(μ-η<sup>3</sup>-Ph<sub>2</sub>PC(H)SPP{W(CO)<sub>5</sub>}S)] (8). Hydrogen atoms removed for clarity. Thermal ellipsoids are shown at the 30% probability level.

metal, it is rare to find this ligand bonding in an allylic η<sup>3</sup> manner; normally the carbon atom is not involved in bonding to the metal. The presence of adventitious oxygen is assumed to lead to the formation of the oxo group. The allylic CS<sub>2</sub> bound molybdenum atom in **9** is coordinated by several π donor ligands and is formally in a +5 oxidation state, which helps to explain why it departs from an 18-electron configuration.

The formation of **9** may be rationalized if it is assumed that the strongly oxidizing PhPCl<sub>2</sub> causes some metal–metal bond cleavage in **3** to give a mononuclear molybdenum complex. This could then react with a further molecule of **3** to yield **9**. This proposal is given credence by the isolation from the reaction mixture of small amounts of Cp(CO)<sub>3</sub>MoCl, which was identified by comparison of its IR spectrum with literature values.<sup>12</sup>

**Characterization of Complexes 6–9.** Complexes **6–9** have been characterized spectroscopically. In ad-

dition, complexes **7–9** have been the subject of single-crystal X-ray diffraction studies; Tables 2 and 3 show selected bond lengths and angles for **7–9**.

The Mo–Mo and P–P bond distances of, respectively, 3.079(1) and 2.080(3) Å in complex **7** are both typical of corresponding bond distances in other complexes containing a Mo<sub>2</sub>P<sub>2</sub> core.<sup>3,7,8</sup> However, unlike the other complexes containing a Mo<sub>2</sub>P<sub>2</sub> unit which have been previously described, the pattern of two long Mo–P and two short Mo–P bond lengths is not observed. Rather, there is one short bond length (Mo(2)–P(2) = 2.415(2) Å) and one long bond length (Mo(2)–P(1) = 2.608(2) Å), with the bonds to Mo(1) both being intermediate in length. The Fe–Fe bond length of 2.490(2) Å is typical of an Fe–Fe single bond, being very similar to the 2.485(1) Å observed for this bond in [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-SCH<sub>2</sub>S)].<sup>13</sup>

The structural features of the Mo<sub>2</sub>P<sub>2</sub> core of **9** are typical of those of related complexes described previously, showing a pair of long Mo–P bonds (Mo(2)–P(2) = 2.547(5) Å, Mo(1)–P(1) = 2.578(5) Å) and a pair of short Mo–P bonds (Mo(2)–P(1) = 2.464(6) Å, Mo(1)–P(2) = 2.479(5) Å). The Mo–Mo bond length of 3.045(2) Å and the P(1)–P(2) bond length of 2.087(7) Å are again typical of such complexes. The S–C bond lengths of the thiolato group are equivalent within experimental error (S(2)–C(26) = 1.70(2) Å and S(1)–C(26) = 1.74(2) Å), while the C(26)–Mo(3) bond distance of 2.20(2) Å is similar to that reported by Zubieta et al.<sup>14</sup> and Dubois et al.<sup>15</sup> for related complexes, thus confirming that the thiolato group in **9** acts as a η<sup>3</sup>-allylic donor.

Coordination of a W(CO)<sub>5</sub> unit to one of the diphosphine phosphorus atoms of **3** leads to a slight lengthening of the P–P bond from 2.111(3) Å in **3** to 2.124(3) Å in **8**, although both still fall between the values found for free diphosphines<sup>16</sup> and for P–P single bonds. The

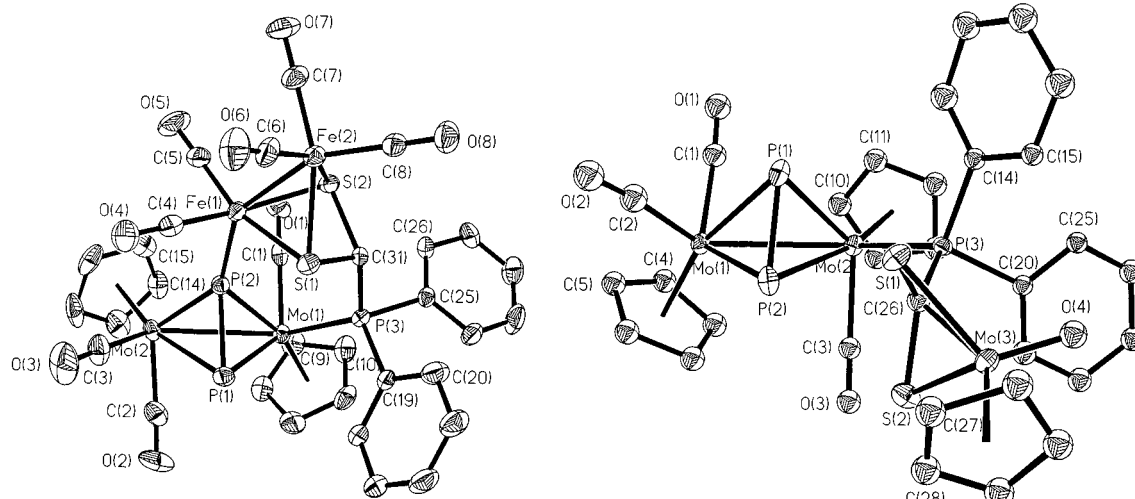
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**Figure 3.** Molecular structures of (left)  $[\text{Mo}_2\text{Cp}_2(\text{CO})_3\text{Fe}_2(\text{CO})_5(\mu_3\text{-}\eta^2\text{-P}_2)(\mu\text{-}\eta\text{-PPh}_2\text{C(H)S}_2)]$  (**7**) and (right)  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{Ph}_2\text{P}\{\eta^3\text{-CS}_2\text{Mo(O)Cp}\})]$  (**9**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

**Table 2. Bond Lengths (Å) and Angles (deg) for  $[\text{Mo}_2\text{Cp}_2(\text{CO})_3\text{Fe}_2(\text{CO})_5(\mu_3\text{-}\eta^2\text{-P}_2)(\mu\text{-}\eta\text{-PPh}_2\text{C(H)S}_2)]$  (**7**) and  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{Ph}_2\text{P}\{\eta^3\text{-CS}_2\text{Mo(O)Cp}\})]$  (**9**)**

<b>7</b>		<b>9</b>	
Mo(1)–Mo(2)	3.079(1)	Mo(1)–Mo(2)	3.045(2)
Mo(1)–P(1)	2.495(2)	Mo(1)–P(1)	2.578(5)
Mo(1)–P(2)	2.475(2)	Mo(1)–P(2)	2.479(5)
Mo(1)–P(3)	2.468(2)	Mo(2)–P(1)	2.464(6)
Mo(2)–P(1)	2.608(2)	Mo(2)–P(2)	2.547(5)
Mo(2)–P(2)	2.415(2)	Mo(2)–P(3)	2.479(4)
Fe(1)–P(2)	2.209(2)	Mo(3)–S(1)	2.353(5)
Fe(1)–S(1)	2.279(2)	Mo(3)–S(2)	2.344(5)
Fe(1)–S(2)	2.275(2)	Mo(3)–C(26)	2.20(1)
Fe(1)–Fe(2)	2.490(2)	Mo(3)–O(4)	1.67(1)
S(1)–C(31)	1.837(6)	P(1)–P(2)	2.087(7)
S(2)–C(31)	1.837(6)	S(1)–C(26)	1.70(2)
P(3)–C(31)	1.863(7)	S(2)–C(26)	1.74(2)
P(1)–P(2)	2.080(3)	P(3)–C(26)	2.89(2)
P(1)–Mo(1)–Mo(2)	54.49(5)	P(1)–Mo(1)–Mo(2)	51.2(1)
P(1)–Mo(2)–Mo(1)	51.24(5)	P(1)–Mo(2)–Mo(1)	54.6(1)
P(1)–P(2)–Mo(1)	65.77(8)	P(1)–P(2)–Mo(1)	68.1(2)
P(1)–P(2)–Mo(2)	70.49(9)	P(1)–P(2)–Mo(2)	63.3(2)
P(1)–P(2)–Fe(1)	129.7(1)	P(1)–Mo(2)–P(2)	49.2(2)
P(2)–Mo(1)–P(1)	49.48(7)	P(1)–Mo(2)–P(3)	87.8(2)
P(2)–Fe(1)–S(2)	99.59(8)	P(2)–Mo(1)–Mo(2)	53.8(1)
P(2)–Fe(1)–S(1)	95.17(9)	P(2)–Mo(2)–Mo(1)	51.7(1)
P(2)–Fe(1)–Fe(2)	146.68(7)	P(2)–P(1)–Mo(1)	63.2(2)
S(1)–Fe(1)–Fe(2)	57.08(7)	P(2)–P(1)–Mo(2)	67.5(2)
S(1)–Fe(2)–Fe(1)	56.81(6)	S(1)–C(26)–S(2)	119.7(1)
S(1)–C(31)–S(2)	94.1(3)	S(1)–C(26)–Mo(3)	73.0(6)
S(1)–C(31)–P(3)	118.1(3)	S(1)–C(26)–P(3)	121.8(1)
S(2)–Fe(1)–Fe(2)	57.11(6)	S(2)–C(26)–Mo(3)	72.0(6)
S(2)–Fe(2)–Fe(1)	56.71(6)	S(2)–C(26)–P(3)	118.0(1)
S(2)–Fe(1)–S(1)	72.37(3)	C(26)–Mo(3)–S(1)	43.8(5)
S(2)–Fe(2)–S(1)	72.05(8)	C(26)–Mo(3)–S(2)	45.0(5)
Fe(1)–P(2)–Mo(1)	132.94(9)	C(26)–S(2)–Mo(3)	63.1(6)

$^{31}\text{P}$  NMR spectrum of **8** shows that the diphosphene phosphorus atoms are coupled. A  $^1J_{\text{P-P}}$  coupling constant of 394 Hz in **8**, as compared to 446 Hz for the corresponding coupling in **3**, probably reflects a slight decrease in the P–P bond order in **8**. It is still, however, indicative of a large degree of multiple bonding, as suggested also by the X-ray analysis. The P–W bond length of 2.541(3) Å is typical for such a bond.<sup>10</sup> The Mo–Mo separation in **8** remains the same as in **3** within experimental error. Because of the breadth of the peaks

**Table 3. Selected Bond Lengths (Å), and Angles (deg) for  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)(\text{Ph}_2\text{P}\{\eta^3\text{-CS}_2\text{Mo(O)Cp}\})]$  (**8**)**

Mo(1)–Mo(2)	3.389(2)	P(1)–P(2)	2.124(4)
Mo(1)–P(2)	2.317(3)	S(1)–C(9)	1.82(1)
Mo(2)–P(1)	2.492(3)	S(1)–P(1)	2.162(4)
Mo(2)–P(2)	2.443(3)	S(2)–C(9)	1.823(1)
Mo(2)–P(3)	2.434(3)	S(2)–P(2)	2.127(4)
W(1)–P(1)	2.541(3)		
P(2)–Mo(1)–Mo(2)	46.12(7)	P(1)–P(2)–Mo(2)	65.7(1)
P(2)–Mo(2)–Mo(1)	43.13(7)	S(1)–P(1)–Mo(2)	113.05
P(2)–Mo(2)–P(1)	50.98(9)	S(1)–P(1)–W(1)	107.08
P(2)–P(1)–S(1)	98.08(1)	S(1)–C(9)–S(2)	109.9(6)
P(2)–P(1)–Mo(2)	63.31(10)	S(2)–P(2)–Mo(1)	133.6(2)
P(2)–P(1)–W(1)	131.9(1)	S(2)–P(2)–Mo(2)	111.3(1)
P(1)–P(2)–S(2)	105.1(2)	Mo(2)–P(1)–W(1)	134.0(1)
P(1)–Mo(2)–Mo(1)	80.82(7)	C(9)–S(2)–P(2)	95.0(4)
P(1)–P(2)–Mo(1)	121.3(1)	C(9)–S(1)–P(1)	96.5(3)

in the  $^{31}\text{P}$  NMR spectrum, no  $^{183}\text{W}$  coupling could be resolved.

## Experimental Section

**General Procedure.** Unless otherwise stated, all experiments were carried out under an atmosphere of dry, oxygen-free nitrogen, using conventional Schlenk line techniques, and solvents were freshly distilled from the appropriate drying agent. NMR spectra were recorded in  $\text{CDCl}_3$  using a Bruker DRX 250 spectrometer, with TMS as an external standard for  $^1\text{H}$  and  $^{13}\text{C}$  spectra and 85% aqueous  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  spectra. Infrared spectra were, unless otherwise stated, recorded in dichloromethane solution in 0.5 mm NaCl solution cells, using a Perkin-Elmer 1710 Fourier transform spectrometer. FAB mass spectra were obtained with a Kratos MS 890 instrument, using 3-nitrobenzyl alcohol as a matrix.

Preparative TLC was carried out on 1 mm silica plates prepared at the University of Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 mesh ASTM).

Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification.  $[\text{Cp}_2(\text{CO})_4\text{Mo}_2(\mu\text{-}\eta^2\text{-P}_2)]^7$  was prepared by the literature method.

**Crystal Structure Determinations:** Data were collected by the  $\omega/2\theta$  scan method on a Rigaku AFC7R four-circle diffractometer for the complexes **5a,b** and on a Rigaku AFC5R four-circle diffractometer for complex **7**. In each case, cell parameters were obtained by least-squares refinement on diffractometer angles from 25 centered reflections ( $15 < \theta <$



Table 4. Crystallographic Data for Complexes 5a,b and 7–9<sup>a</sup>

	5a	5b	7	8	9
formula	C <sub>29</sub> H <sub>27</sub> Mo <sub>2</sub> O <sub>5</sub> P <sub>3</sub>	C <sub>28</sub> H <sub>24</sub> Mo <sub>2</sub> NO <sub>3</sub> P <sub>3</sub>	C <sub>31</sub> H <sub>21</sub> Fe <sub>2</sub> Mo <sub>2</sub> O <sub>8</sub> P <sub>3</sub> S <sub>2</sub> ·CH <sub>2</sub> Cl <sub>2</sub>	C <sub>31</sub> H <sub>21</sub> Mo <sub>2</sub> O <sub>8</sub> P <sub>3</sub> S <sub>2</sub> W	C <sub>30</sub> H <sub>25</sub> Mo <sub>3</sub> O <sub>4</sub> P <sub>3</sub> S <sub>2</sub> · 3/2CH <sub>2</sub> Cl <sub>2</sub>
<i>M<sub>r</sub></i>	740.3	707.27	1067.01	1054.24	1030.24
temp/K	180(2)	180(2)	293(2)	180(2)	180(2)
instrument used	AFC7R	AFC7R	AFC5R	RAXIS	RAXIS
cryst size (mm)	0.30 × 0.20 × 0.18	0.30 × 0.25 × 0.30	0.30 × 0.20 × 0.20	0.18 × 0.15 × 0.02	0.2 × 0.06 × 0.05
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>C</i> 2
<i>a</i> /Å, α/deg	11.713(3), 90	11.804(3), 90	13.068(4), 107.07(2)	10.393(5), 90	22.306(6), 90
<i>b</i> /Å, β/deg	13.983(3), 100.27(2)	13.162(3), 93.08(2)	14.483(3), 94.93(3)	30.476(4), 102.13(4)	9.444(5), 116.51(4)
<i>c</i> /Å, γ/deg	17.662(4), 90	17.795(4), 90	10.847(4), 84.09(2)	10.931(5), 90	19.455(5), 90
<i>V</i> /Å <sup>3</sup>	2846.4(11)	2760.7(11)	1948.7(10)	3385(2)	3667(2)
<i>Z</i>	4	4	2	4	4
<i>D<sub>c</sub></i> /Mg m <sup>−3</sup>	1.728	1.702	1.818	2.069	1.866
abs coeff/mm <sup>−1</sup>	1.088	1.113	1.773	4.434	1.510
<i>F</i> (000)	1480	1408	1052	2024	2028
θ range/deg	2.67–27.5	3.55–27.51	1.57–22.5	3.63–25.22	1.84–25.17
index ranges	0 ≤ <i>h</i> ≤ 15, 0 ≤ <i>k</i> ≤ 18, −22 ≤ <i>l</i> ≤ 20	0 ≤ <i>h</i> ≤ 15, 0 ≤ <i>k</i> ≤ 17, −23 ≤ <i>l</i> ≤ 23	0 ≤ <i>h</i> ≤ 14, −15 ≤ <i>k</i> ≤ 15, −11 ≤ <i>l</i> ≤ 11	0 ≤ <i>h</i> ≤ 12, 0 ≤ <i>k</i> ≤ 36, −13 ≤ <i>l</i> ≤ 12	0 ≤ <i>h</i> ≤ 26, 0 ≤ <i>k</i> ≤ 11, −23 ≤ <i>l</i> ≤ 20
no. of rflns measd	6808	6618	5354	10 325	6400
no. of indep rflns	6507	6318	5084	5786	3443
<i>R</i> <sub>int</sub>	0.0526	0.0484	0.0400	0.0583	0.0548
max, min transmissn	0.994, 0.924	1.000, 0.950	0.999, 0.909	0.9166, 0.5024	0.9283, 0.7251
goodness of fit on <i>F</i> <sup>2</sup>	1.018	1.017	1.027	0.902	0.991
final <i>R</i> indices ( <i>I</i> > 2σ( <i>I</i> ))					
<i>R</i> 1	0.0542	0.037	0.0407	0.05	0.0619
w <i>R</i> 2	0.1078	0.0825	0.0779	0.0819	0.1532
<i>R</i> indices (all data)					
<i>R</i> 1	0.1009	0.0449	0.1007	0.0933	0.0869
w <i>R</i> 2	0.1281	0.0908	0.2905	0.0934	0.1660
largest peak, hole/e Å <sup>−3</sup>	0.855, −0.675	0.496, −0.872	0.744, −0.757	1.001, −1.386	2.008, −1.053

<sup>a</sup> For all complexes, graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å, was used.

20°). Semiempirical absorption corrections based on ψ-scan data were applied.<sup>17,18</sup>

Data for the complexes **8** and **9** were collected on a Rigaku RAXIS IIC image plate. Data processing and reduction, including refinement of the cell dimensions, was performed using the "Process" software written by Higashi.<sup>19</sup>

For the determination of complexes **5a,b**, **8**, and **9** the crystal was cooled to 180(2) K using an Oxford Cryostream cooling apparatus.

The structures were solved by direct methods (SIR 92)<sup>20</sup> and subsequent Fourier difference syntheses. For **5a,b**, **7**, and **8** structures were refined anisotropically on all non-hydrogen atoms by full-matrix least squares on *F*<sup>2</sup> (SHELXL 93).<sup>21</sup> Hydrogen atoms were placed in idealized positions and refined using a riding model. In the final cycles of refinement a weighting scheme was introduced which produced a flat analysis of variance.

For **9**, the crystal quality and parameter/data ratio were poor: heavy atoms only were refined anisotropically. Common isotropic temperature factors were used for the Cp rings. The unit cell contains two CH<sub>2</sub>Cl<sub>2</sub> molecules, one of which is disordered around a diad axis.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for

this material should quote the full literature citation. Table 4 gives crystallographic data for complexes **5a,b** and **7–9**.

**Reaction of [Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>(μ-η<sup>2</sup>-P<sub>2</sub>)] with PPh<sub>2</sub>H.** To a solution of [Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>(μ-η<sup>2</sup>-P<sub>2</sub>)] (400 mg, 0.806 mmol) in toluene (80 mL) was added diphenylphosphine (160 mg, 0.85 mmol), and the resulting mixture was heated to reflux for 7 days, after which time spot TLC analysis did not reveal the presence of any starting material. The solvent was removed under reduced pressure; the residue was redissolved in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub>, absorbed onto silica, pumped dry, and applied to the top of a chromatography column. Elution with 2:1 CH<sub>2</sub>Cl<sub>2</sub>–hexane gave orange crystalline [Cp<sub>2</sub>(CO)<sub>3</sub>Mo<sub>2</sub>(μ-η<sup>2</sup>-P<sub>2</sub>)(PPh<sub>2</sub>H)] (**1**) in 94% yield. IR: ν(CO) 1957 cm<sup>−1</sup> (s), 1894 cm<sup>−1</sup> (vs). <sup>1</sup>H NMR: δ 7.2–7.6 (m, 10H, Ph), 6.59 (d, <sup>1</sup>*J*<sub>P–H</sub> = 368 Hz, 1H, PPh<sub>2</sub>H), 5.07 (s, 5H, Cp), 4.77 (d, <sup>3</sup>*J*<sub>P–H</sub> = 2.4 Hz, 5H, Cp). <sup>31</sup>P{<sup>1</sup>H} NMR: δ 40.05 (d, <sup>2</sup>*J*<sub>P–P</sub> = 45 Hz, PPh<sub>2</sub>H), −31.05 (dd, <sup>1</sup>*J*<sub>P–P</sub> = 472 Hz, <sup>2</sup>*J*<sub>P–P</sub> = 45 Hz, μ-η<sup>2</sup>-P<sub>2</sub>), −77.25 (d, 472 Hz, μ-η<sup>2</sup>-P<sub>2</sub>). Anal. Calcd for C<sub>25</sub>H<sub>21</sub>Mo<sub>2</sub>O<sub>3</sub>P<sub>3</sub>: C, 45.87; H, 3.21; P, 14.22. Found: C, 45.53; H, 3.08; P, 14.10. FAB-MS: *m/z* 654 (M<sup>+</sup>), 600 (M<sup>+</sup> − 2CO).

**Reaction of [Cp<sub>2</sub>(CO)<sub>3</sub>Mo<sub>2</sub>(μ-η<sup>2</sup>-P<sub>2</sub>)(PPh<sub>2</sub>H)] (**1**) with DBU.** To a solution of **1** (400 mg, 0.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added DBU (0.1 g, 1.1 equiv), and the mixture was stirred for 1 h, during which time the solution turned dark orange due to the formation of [Cp<sub>2</sub>(CO)<sub>3</sub>Mo<sub>2</sub>(μ-η<sup>2</sup>-P<sub>2</sub>)(PPh<sub>2</sub>H)]<sup>−</sup> (**2**). The solution was used for further reactions without the isolation of **2**.

**Reaction of [Cp<sub>2</sub>(CO)<sub>3</sub>Mo<sub>2</sub>(μ-η<sup>2</sup>-P<sub>2</sub>)(PPh<sub>2</sub>H)]<sup>−</sup> (**2**) with CS<sub>2</sub>.** To a solution of **2** (250 mg, 0.38 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added CS<sub>2</sub> (0.5 mL, large excess), and the solution was stirred for 2 h, during which time the solution turned a deeper brown. A slight deficiency of 85% HBF<sub>4</sub>·OEt<sub>2</sub> (62 mg, 0.85 equiv) was added, the solution filtered through a silica pad, and the solvent removed under reduced pressure to yield green-brown [Cp<sub>2</sub>(CO)<sub>3</sub>Mo<sub>2</sub>(μ-η<sup>3</sup>-Ph<sub>2</sub>PC(H)SP<sub>2</sub>S)] (**3**) as the sole product (220

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mg, 80% yield). For smaller scale reactions it was not necessary to add a proton source to the reaction mixture in order to isolate the neutral product. Instead the mixture was filtered through silica and repeatedly washed with  $\text{CH}_2\text{Cl}_2$  to yield **3**. Slow diffusion of hexane into a  $\text{CH}_2\text{Cl}_2$  solution of **3** yielded green-brown crystals suitable for X-ray diffraction. IR:  $\nu(\text{CO})$  1958 (vs), 1910 (m), 1851  $\text{cm}^{-1}$  (m).  $^1\text{H}$  NMR:  $\delta$  7.6–7.0 (m, 10H, Ph), 5.52 (ddd, 1H,  $^2J_{\text{P-H}} = 24, 4, 4$  Hz,  $\text{S}_2\text{CH}$ ), 5.24 (s, 4H, Cp), 5.16 (s, 5H, Cp).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  205.45 (d,  $^1J_{\text{P-P}} = 446$  Hz,  $\text{Mo-P=PS}_2\text{CH}$ ), 145.65 (s,  $\text{PPh}_2$ ),  $-0.25$  (d,  $^1J_{\text{P-P}} = 446$  Hz,  $\text{Mo-P=PS}_2\text{C}$ ).  $^{13}\text{C}$  NMR:  $\delta$  242.3 (s, CO), 134–127 (m, Ph), 89.8 (s, Cp), 84.2 (s, Cp), 63.9 (d,  $^1J_{\text{P-C}} = 41$  Hz,  $\text{Ph}_2\text{PC(H)-S}_2$ ). Anal. Calcd for  $\text{C}_{26}\text{H}_{21}\text{Mo}_2\text{O}_3\text{P}_3\text{S}_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ : C, 41.18; H, 2.87; P, 12.02. Found: C, 40.43; H, 2.82; P, 11.37. FAB-MS:  $m/z$  730 ( $\text{M}^+$ ).

**Reaction of  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu-\eta^2\text{-P}_2)(\text{PPh}_2)]^-$  (**2**) with 3- $\text{ClC}_6\text{H}_4\text{NCO}$ .** To a solution of **2** (250 mg, 38 mmol) was added 3- $\text{ClC}_6\text{H}_4\text{NCO}$  (11.67 mg, 2 equiv), and the solution was stirred overnight. The solution was then filtered through a silica pad and the solvent removed under reduced pressure, after which the residue was redissolved in the minimum amount of  $\text{CH}_2\text{Cl}_2$  and applied to the base of TLC plates. Elution with a 3:2  $\text{CH}_2\text{Cl}_2$ –hexane mixture yielded the starting material **1** (22 mg, 9%) and orange crystalline  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu-\eta^2\text{-P}_2)(\text{PPh}_2\text{C}(\text{O})\text{NH}_3\text{-ClC}_6\text{H}_4)]$  (**4a**; 240 mg, 80%). IR:  $\nu(\text{CO})$  1961 (vs), 1897  $\text{cm}^{-1}$  (s).  $^1\text{H}$  NMR:  $\delta$  9.3 (s, 1H,  $\text{NH}$ ), 7.88–7.09 (m, 14H, Ph), 5.11 (s, 5H, Cp), 4.69 (d,  $^3J_{\text{P-H}} = 1.9$  Hz, 5H, Cp).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  66.98 (dd,  $^2J_{\text{P-P}} = 30.8$  Hz,  $^2J_{\text{P-P}} = 7.6$  Hz,  $\text{PPh}_2\text{C}(\text{O})\text{NH}_3\text{-ClPh}$ ),  $-30.27$  (dd,  $^1J_{\text{P-P}} = 473.4$  Hz,  $^2J_{\text{P-P}} = 30.8$  Hz,  $\text{trans-}\mu\text{-}\eta^2\text{-P}_2$ ),  $-46.40$  (dd,  $^1J_{\text{P-P}} = 473.4$  Hz,  $^2J_{\text{P-P}} = 7.6$  Hz,  $\text{cis-}\mu\text{-}\eta^2\text{-P}_2$ ).  $^{13}\text{C}$  NMR:  $\delta$  229 (CO), 205 (CO), 189 ( $\text{Ph}_2\text{PC}(\text{O})\text{NH}$ ), 136–122 (m, Ph), 88.3 (s, 5H, Cp), 87.1 (s, 5H, Cp). Anal. Calcd for  $\text{C}_{32}\text{ClH}_{25}\text{Mo}_2\text{NO}_4\text{P}_3$ : C, 47.58; H, 3.12; P, 11.5; N, 1.73. Found: C, 46.8; H, 3.19; P, 11.57; N, 1.59. FAB-MS:  $m/z$  807 ( $\text{M}^+$ ).

**Reaction of  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu-\eta^2\text{-P}_2)(\text{PPh}_2)]^-$  (**2**) with PhNCS.** The same procedure as in the previous paragraph was applied using a 2-fold excess of PhNCS to yield, after elution with 3:2 hexane– $\text{CH}_2\text{Cl}_2$ , orange crystalline  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu-\eta^2\text{-P}_2)(\text{PPh}_2\text{C}(\text{S})\text{NHPh})]$  (**4b**; 256 mg, 85% yield) as the sole product. IR:  $\nu(\text{CO})$  1961 (vs), 1897 (s), 1874.5  $\text{cm}^{-1}$  (s, sh).  $^1\text{H}$  NMR:  $\delta$  8.80 (s, 1H,  $\text{NH}$ ), 7.92–7.2 (m, 15H, Ph), 5.12 (s, 5H, Cp), 4.68 (d,  $^3J_{\text{P-H}} = 1.7$  Hz, 5H, Cp).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  88.94 (dd,  $^2J_{\text{P-P}} = 23.6, 7.4$  Hz,  $\text{PPh}_2\text{PhC}(\text{S})\text{NH}$ ),  $-19.69$  (dd,  $^1J_{\text{P-P}} = 476$  Hz,  $^2J_{\text{P-P}} = 23.6$  Hz,  $\text{trans-}\mu\text{-}\eta^2\text{-P}_2$ ),  $-40.63$  (dd,  $^1J_{\text{P-P}} = 467$  Hz,  $^2J_{\text{P-P}} = 7.4$  Hz,  $\text{cis-}\mu\text{-}\eta^2\text{-P}_2$ ). Anal. Calcd for  $\text{C}_{32}\text{H}_{26}\text{Mo}_2\text{NO}_3\text{P}_3\text{S}$ : C, 48.69; H, 3.32; P, 11.77; N, 1.85. Found: C, 47.96; H, 3.13; P, 11.12; N, 1.85. FAB-MS:  $m/z$  792.9 ( $\text{M}^+$ ).

**Reaction of  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu-\eta^2\text{-P}_2)(\text{PPh}_2)]^-$  (**2**) with Michael Acceptors. Methyl Acrylate.** To a solution of **2** (150 mg, 0.22 mmol) was added methyl acrylate (0.25 mL, 0.27 mmol), and the mixture was stirred for 2 h, during which time the solution color changed from orange-brown to deep orange, after which a slight deficiency of 85%  $\text{HBF}_4 \cdot \text{OEt}_2$  (37 mg, 0.85 equiv) was added. The solvent was removed in vacuo, redissolved in the minimum amount of  $\text{CH}_2\text{Cl}_2$ , and applied to the base of TLC plates. Elution with 3:2 hexane– $\text{CH}_2\text{Cl}_2$  yielded, in addition to a trace of starting material **1**, orange crystalline  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu-\eta^2\text{-P}_2)(\text{PPh}_2\text{C}_2\text{H}_4\text{COOMe})]$  (**5a**), in 70% yield. Slow evaporation of a  $\text{CH}_2\text{Cl}_2$ –hexane solution yielded orange crystals of suitable quality for X-ray diffraction analysis. IR:  $\nu(\text{CO})$  1956.8 (vs), 1891.6 (s), 1862.3  $\text{cm}^{-1}$  (s, sh).  $^1\text{H}$  NMR:  $\delta$  7.64–7.37 (m, 10H, Ph), 5.09 (s, 5H, Cp), 4.65 (d,  $^3J_{\text{P-H}} = 2$  Hz, 5H, Cp), 3.59 (s, 3H,  $\text{OCH}_3$ ), 2.86–2.44 (m, 2H,  $\text{PCH}_2\text{CH}_2$ ), 2.17–2.06 (m, 2H,  $\text{PCH}_2\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  49.87 (s, P,  $\text{MoPPh}_2$ ),  $-32.05$  (d,  $^1J_{\text{P-P}} = 477$  Hz,  $\mu\text{-}\eta^2\text{-P}_2$ ),  $-40.72$  (d,  $^1J_{\text{P-P}} = 477$  Hz,  $\mu\text{-}\eta^2\text{-P}_2$ ).  $^{13}\text{C}$  NMR:  $\delta$  232.29 (CO), 223.81 (CO), 216.54 (CO), 172.74 (d,  $^3J_{\text{P-C}} = 1.3$  Hz,  $\text{C}(\text{=O})\text{OMe}$ ), 135–127.80 (m, Ph), 87.93 (s, Cp), 83.98 (s, Cp), 60.42 (s,  $\text{OCH}_3$ ), 31.02 (d,  $^1J_{\text{P-C}} = 30$  Hz,  $\text{Ph}_2\text{PCH}_2\text{CH}_2$ ), 15.05 (d,  $^2J_{\text{P-C}} = 9$

Hz,  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{COOMe}$ ). Anal. Calcd for  $\text{C}_{29}\text{H}_{27}\text{Mo}_2\text{O}_5\text{P}_3$ : C, 47.05; H, 3.68; P, 12.55. Found: C, 47.59; H, 3.73; P, 11.95. FAB-MS:  $m/z$   $\text{M}^+ 739$ .

**(b) Acrylonitrile.** The same procedure was followed for the reaction of **2** with acrylonitrile; a 10% excess of acrylonitrile was added to a solution of **2**, to yield after 3:2  $\text{CH}_2\text{Cl}_2$ –hexane elution on TLC plates **1** (12 mg, 8%) and orange crystalline  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu-\eta^2\text{-P}_2)(\text{PPh}_2\text{C}_2\text{H}_4\text{CN})]$  (**5b**; 146 mg, 85%). Slow evaporation of a hexane/ $\text{CH}_2\text{Cl}_2$  solution yielded orange crystals suitable for X-ray diffraction. IR:  $\nu(\text{CO})$  1957 (s), 1902 (vs), 1868 (s, sh).  $^1\text{H}$  NMR:  $\delta$  7.75–7.21 (m, 10H, Ph), 5.12 (s, 5H, Cp), 4.63 (d,  $^3J_{\text{P-H}} = 1.9$  Hz, 5H, Cp), 2.93–2.64 (m, 2H,  $\text{PCH}_2$ ), 2.38–2.03 (m, 2H,  $\text{PCH}_2\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  50.88 (s (b),  $\text{Ph}_2\text{PC}_2\text{H}_4\text{CN}$ ),  $-36.60$  (d,  $^1J_{\text{P-P}} = 476.5$  Hz,  $\text{cis-}\mu\text{-}\eta^2\text{-P}_2$ ),  $-42.62$  (d,  $^1J_{\text{P-P}} = 476.5$  Hz,  $\text{trans-}\mu\text{-}\eta^2\text{-P}_2$ ).  $^{13}\text{C}$  NMR:  $\delta$  243.84 (s, CO), 231.75 (s, CO), 223.24 (s, CO), 138.924–125.737 (m, Ph), 86.485 (s, Cp), 85.39 (s, Cp), 32.38 (d,  $^1J_{\text{P-C}} = 45.5$ ,  $\text{Ph}_2\text{PCH}_2\text{R}$ ), 14.44 (d,  $^2J_{\text{P-C}} = 16$  Hz,  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CN}$ ). Anal. Calcd for  $\text{C}_{28}\text{H}_{24}\text{Mo}_2\text{NO}_3\text{P}_3$ : C, 47.55; H, 3.42; N, 1.98; P, 13.14. Found: C, 47.44; H, 3.34; N, 1.94; P, 13.27. FAB-MS:  $m/z$  709.7 ( $\text{M}^+$ ), 656.5 ( $\text{M}^+ - 2\text{CO}$ ).

**(c) MVK.** The same reaction was repeated using a 10% excess of MVK as the Michael acceptor, to yield, after elution with 3:2  $\text{CH}_2\text{Cl}_2$ –hexane on TLC plates, trace **1** and orange crystalline  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu-\eta^2\text{-P}_2)(\text{PPh}_2\text{C}_2\text{H}_4\text{C}(\text{=O})\text{Me})]$  (**5c**; 116 mg, 68%). IR:  $\nu(\text{CO})$  1958 (s), 1891 (vs), 1864  $\text{cm}^{-1}$  (s, sh).  $^1\text{H}$  NMR:  $\delta$  7.82–7.18 (m, 10H, Ph), 5.08 (s, 5H, Cp), 4.57 (d,  $^3J_{\text{P-H}} = 1.7$  Hz, 5H, Cp), 3.65–3.40 (m, 2H,  $\text{PCH}_2$ ), 2.92–2.48 (m, 2H,  $\text{PCH}_2\text{CH}_2$ ), 2.0 (s, 3H,  $\text{COCH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  50.12 (s,  $\text{Ph}_2\text{PC}_2\text{H}_4\text{COMe}$ ),  $-34.39$  (d,  $^1J_{\text{P-P}} = 479$  Hz,  $\text{trans-}\mu\text{-}\eta^2\text{-P}_2$ ),  $-41.81$  (d,  $^1J_{\text{P-P}} = 479$  Hz,  $\text{cis-}\mu\text{-}\eta^2\text{-P}_2$ ).  $^{13}\text{C}$  NMR:  $\delta$  243.1 (s, CO), 223.14 (s, CO), 223.841 (s, CO), 206.56 (d,  $^3J_{\text{P-C}} = 10.7$  Hz,  $\text{Ph}_2\text{C}_2\text{H}_4\text{C}(\text{O})\text{Me}$ ), 140.3–128.15 (m, Ph), 86.53 (s, Cp), 85.27 (s, Cp), 30.03 (s,  $\text{COCH}_3$ ), 29.45 (d,  $^1J_{\text{P-C}} = 28$  Hz,  $\text{Ph}_2\text{PCH}_2$ ), 29.08 (d,  $^2J_{\text{P-C}} = 18.5$  Hz). Anal. Calcd for  $\text{C}_{29}\text{H}_{27}\text{Mo}_2\text{O}_4\text{P}_3$ : C, 48.09; H, 3.76; P, 12.83. Found: C, 47.71; H, 3.63; P, 12.53. FAB-MS:  $m/z$  726.8 ( $\text{M}^+$ ).

**Reaction of  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu-\eta^3\text{-Ph}_2\text{PC(H)SP}_2\text{S})]$  (**3**) with  $^t\text{BuLi}$  and MeI.** A solution of **3** (250 mg, 0.34 mmol) in THF (50 mL) was cooled to  $-78^\circ\text{C}$ , and a 1.7 M solution of  $^t\text{BuLi}$  (0.2 mL, 1.1 equiv) was added over 10 min, during which time the color changed to deep orange. To the resulting mixture MeI was added (53 mg, 1.1 equiv), and the solution was stirred for  $\frac{1}{2}$  h at  $-78^\circ\text{C}$ , during which time the color changed from orange to purple. The resulting solution was filtered through a pad of silica and solvent removed in vacuo to yield purple-brown  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu-\eta^2\text{-P}_2)(\text{Ph}_2\text{PC}(\text{S})\text{SMe})]$  (**6**) as the sole product (182 mg, 72%). IR:  $\nu(\text{CO})$  1957 (s), 1892 (vs), 1863 (m, sh)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  7.85–7.38 (m, 10H, Ph), 5.07 (s, 5H, Cp), 4.6 (d,  $^3J_{\text{P-H}} = 1.8$  Hz, 5H, Cp), 2.30 (s, 3H,  $\text{SCH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  100.43 (dd,  $^2J_{\text{P-P}} = 18.2$  Hz,  $^2J_{\text{P-P}} = 5.2$  Hz,  $\text{Ph}_2\text{PCS}_2\text{Me}$ ),  $-7.32$  (dd,  $^1J_{\text{P-P}} = 484.6$  Hz,  $^2J_{\text{P-P}} = 18.2$ ,  $\text{trans-}\mu\text{-}\eta^2\text{-P}_2$ ),  $-20.32$  (dd,  $^1J_{\text{P-P}} = 484.6$  Hz,  $^2J_{\text{P-P}} = 5.2$ ,  $\text{cis-}\mu\text{-}\eta^2\text{-P}_2$ ). Anal. Calcd for  $\text{C}_{27}\text{H}_{23}\text{Mo}_2\text{O}_3\text{P}_3\text{S}_2$ : C, 43.57; H, 3.11; P, 12.48. Found: C, 43.04; H, 3.46; P, 11.99. FAB-MS:  $m/z$  743 ( $\text{M}^+$ ).

**Reaction of  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu-\eta^3\text{-Ph}_2\text{PC(H)SP}_2\text{S})]$  (**3**) with  $^t\text{BuLi}$  and  $\text{HBF}_4$ .** A solution of **3** (250 mg, 0.34 mmol) in THF (50 mL) was cooled to  $-78^\circ\text{C}$ , and a 1.7 M solution of  $^t\text{BuLi}$  (0.2 mL, 1.1 equiv) was added over 10 min, during which time the color changed to deep orange. To the resulting mixture was added a slight deficiency of 85%  $\text{HBF}_4 \cdot \text{OEt}_2$  (55 mg, 0.85 equiv), and the solution was stirred for  $\frac{1}{2}$  h at  $-78^\circ\text{C}$ , during which time the color changed from orange to green. The resulting solution was filtered through a pad of silica and solvent removed in vacuo to yield green-brown  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu-\eta^3\text{-Ph}_2\text{PC(H)SP}_2\text{S})]$  (**3**) as the sole product (208 mg, 83%).

**Reaction of  $[\text{Cp}_2(\text{CO})_3\text{Mo}_2(\mu-\eta^3\text{-Ph}_2\text{PC(H)SP}_2\text{S})]$  (**3**) with  $\text{Fe}_2(\text{CO})_9$ .** To a solution of **3** (208 mg, 0.285 mmol) in THF (50 mL) was added  $\text{Fe}_2(\text{CO})_9$  (excess), and the mixture was stirred at room temperature for 16 h. The solvent was removed under

reduced pressure and the residue redissolved in the minimum quantity of CH<sub>2</sub>Cl<sub>2</sub> and applied to the base of TLC plates. Elution with 1:1 CH<sub>2</sub>Cl<sub>2</sub>–hexane gave brown crystalline [Mo<sub>2</sub>–Cp<sub>2</sub>(CO)<sub>3</sub>Fe<sub>2</sub>(CO)<sub>5</sub>(μ<sub>3</sub>-η<sup>2</sup>-P<sub>2</sub>)(μ-η-PPH<sub>2</sub>C(H)S<sub>2</sub>)] (**7**; 41 mg, 15%). IR: ν(CO) 2045 (vs), 1991 (vs), 1978 (s), 1962 (sh), 1937 (w), 1912 (m), 1894 (sh) cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.7–7.0 (m, 10H, Ph), 5.48 (s, 5H, Cp), ~5.46 (observed, S<sub>2</sub>CH), 4.61 (s, 5H, Cp). <sup>31</sup>P{<sup>1</sup>H} NMR: 74.25 (s, Ph<sub>2</sub>P), 21.05 (br d, <sup>1</sup>J<sub>P–P</sub> = 480 Hz, *trans*-μ-η<sup>2</sup>-P<sub>2</sub>), –107.15 (v br, d, <sup>1</sup>J<sub>P–P</sub> = 480 Hz). Anal. Calcd for C<sub>31</sub>Fe<sub>2</sub>H<sub>21</sub>Mo<sub>2</sub>O<sub>8</sub>P<sub>3</sub>S<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 35.99; H, 2.16; P, 8.72. Found: C, 34.99; H, 2.11; P, 8.35. FAB-MS: *m/z* 983 (M<sup>+</sup>), M<sup>+</sup> – *n*CO (*n* = 3–8).

**Reaction of [Cp<sub>2</sub>(CO)<sub>3</sub>Mo<sub>2</sub>(μ-η<sup>3</sup>-Ph<sub>2</sub>PC(H)SP<sub>2</sub>S)] (**3**) with W(CO)<sub>5</sub>(THF).** To a freshly prepared solution of W(CO)<sub>5</sub>(THF) (200 mg, 2 equiv) in THF (80 mL) was added **3** (200 mg, 0.27 mmol), and the resulting solution was stirred for 16 h. Solvent was removed under reduced pressure and the residue redissolved in the minimum quantity of CH<sub>2</sub>Cl<sub>2</sub>, applied to the base of TLC plates, and eluted with 3:2 CH<sub>2</sub>Cl<sub>2</sub>–hexane to yield [Cp<sub>2</sub>(CO)<sub>3</sub>Mo<sub>2</sub>(μ-η<sup>3</sup>-Ph<sub>2</sub>PC(H)SPP{W(CO)<sub>5</sub>S})] (**8**; 173 mg, 60%) and unreacted starting material **3** (20 mg, 10%). Brown crystals of **8** suitable for X-ray diffraction were grown from slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>–hexane solution. IR: ν(CO) 2070 (m), 1973.2 (w, sh), 1955.1 (m), 1936.6 (vs), 1866 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.46–7.1 (m, 10H, Ph), 5.44 (s, 5H, Cp), 5.33 (s, 5H, Cp), 5.25 (t, <sup>2</sup>J<sub>P–H</sub> = 25.2 Hz, <sup>2</sup>J<sub>P–H</sub> = 25.2 Hz, 1H, S<sub>2</sub>CH). <sup>31</sup>P{<sup>1</sup>H} NMR: δ 156.32 (br d, <sup>1</sup>J<sub>P–P</sub> = 394 Hz, (CO)<sub>5</sub>W–P=P), 146.28 (s, Ph<sub>2</sub>PC), –10.465 (br d, <sup>1</sup>J<sub>P–P</sub> = 394 Hz, (CO)<sub>5</sub>W–P=P). Anal. Calcd for C<sub>31</sub>H<sub>21</sub>Mo<sub>2</sub>O<sub>8</sub>P<sub>3</sub>S<sub>2</sub>W: C, 35.32; H, 2.01; P, 8.81. Found: C, 36.03; H, 2.39; P, 8.52. FAB-MS: *m/z* 1054.4 (M<sup>+</sup>), M<sup>+</sup> – *n*CO (*n* = 3–5).

**Reaction of [Cp<sub>2</sub>(CO)<sub>3</sub>Mo<sub>2</sub>(μ-η<sup>3</sup>-Ph<sub>2</sub>PC(H)SP<sub>2</sub>S)] (**3**) with <sup>t</sup>BuLi and PhPCl<sub>2</sub>.** To a solution of **3** (200 mg, 0.27 mmol) in

THF (50 mL), cooled to –78 °C, was added a 1.7 M solution of <sup>t</sup>BuLi (0.18 mL, 1.1 equiv) over 10 min, during which time the color changed to deep orange. To the resulting mixture was added PhPCl<sub>2</sub> (100 mg, 2 equiv), and the resulting solution was warmed to room temperature and stirred for 48 h. The solvent was removed under reduced pressure and the residue redissolved in the minimum quantity of CH<sub>2</sub>Cl<sub>2</sub> and applied to the base of TLC plates. Elution with 2:1 CH<sub>2</sub>Cl<sub>2</sub>–hexane yielded, in addition to a trace of starting material and decomposition products, [Cp<sub>2</sub>(CO)<sub>3</sub>Mo<sub>2</sub>(μ-η<sup>2</sup>-P<sub>2</sub>)(Ph<sub>2</sub>P{η<sup>3</sup>-CS<sub>2</sub>-Mo(O)Cp})] (**9**) as moderately air-stable brown crystals in low yield (22 mg, 10%). IR: ν(CO) 1959 (s), 1896 (vs), 1860 (s, sh) cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.5–7.14 (m, 10H, Ph), 5.91 (s, 5H, Mo(O)-Cp), 5.11 (s, 5H, Cp), 4.81 (d, <sup>3</sup>J<sub>P–P</sub> = 1.8 Hz, 5H, Cp). <sup>31</sup>P{<sup>1</sup>H} NMR: δ 95.69 (dd, <sup>2</sup>J<sub>P–P</sub> = 20.2 Hz, <sup>2</sup>J<sub>P–P</sub> = 6.7 Hz, Ph<sub>2</sub>PCS<sub>2</sub>), –12.34 (dd, <sup>1</sup>J<sub>P–P</sub> = 483.9 Hz, <sup>2</sup>J<sub>P–P</sub> = 20.2 Hz, *trans*-μ-η<sup>2</sup>-P<sub>2</sub>), –34.9 (dd, <sup>1</sup>J<sub>P–P</sub> = 483.9 Hz, <sup>2</sup>J<sub>P–P</sub> = 6.7, *cis*-μ-η<sup>2</sup>-P<sub>2</sub>). Anal. Calcd for C<sub>31</sub>H<sub>20</sub>Mo<sub>3</sub>O<sub>4</sub>P<sub>2</sub>S<sub>2</sub>·<sup>3</sup>/<sub>2</sub>CH<sub>2</sub>Cl<sub>2</sub>: C, 37.6; H, 2.69; P, 9.02. Found: C, 38.01; H, 2.93; P, 9.01. FAB-MS: *m/z* 912.8 (M<sup>+</sup>).

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**Supporting Information Available:** Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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