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Reactions of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ with Phosphanylalkynes: Rearrangement of Phosphanylalkynes into Phosphido-Substituted Vinylidenyl Ligands by Cleavage of the P–C(alkyne) Bond and Formation of a P–C(alkene) Bond

Bin Li,[a] Shansheng Xu,[a] Haibin Song,[a] and Baiquan Wang*[a,b]

Keywords: Molybdenum / Phosphorus / Alkynes / Rearrangement / Bridging ligands / X-ray diffraction

This article deals with the thermal reactions of the doubly bridged bis(cyclopentadienyl) dinuclear molybdenum complex $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (**1**) with a series of phosphanylalkynes $Ph_nP(C{\equiv}CR)_{3-n}$ (n = 2, 1, 0; R = Ph, Fc). In addition to the complex $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}\eta^2(\perp)\text{-}R^1C{\equiv}CR^2)]$ [R^1 = Ph, R^2 = Ph_2P, **2**; R^1 = Ph, R^2 = $Ph_2P(O)$, **4**; R^1 = Ph, R^2 = PhP(C≡CPh), **6**; R^1 = Fc, R^2 = PhP(C≡CFc), **8**; and R^1 = Fc, R^2 = PhP(O)(C≡CFc), **10**], in which the phosphanylalkynes acted as disubstituted acetylenes, the P–C(alkyne) bond cleavage and phosphanylalkyne rearrangement products $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4\{\mu\text{-}\eta^1\text{-}\eta^2\text{-}C{=}C(R^1)R^2\}]$ [R^1 = Ph, R^2 = Ph_2P, **3**; R^1 = Fc, R^2 = Ph_2P, **5**; R^1 = Ph, R^2 = PhP(C≡CPh), **7**; and R^1 = Fc, R^2 = PhP(C≡CPh), **9**] were also isolated when mono- and bis-(ethynyl)-functionalized phosphanes reacted with **1**. Reactions of tris(ethynyl)-functionalized phosphanes with **1** afforded the phosphanylalkyne-bridged complexes (or/and their oxide) $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}\eta^2(\perp)\text{-}R^1C{\equiv}CR^2)]$ [R^1 = Ph, R^2 = $P(C{\equiv}CPh)_2$, **11a** and **11b**; R^1 = Ph, R^2 = $P(O)(C{\equiv}CPh)_2$, **12**; and R^1 = Fc, R^2 = $P(C{\equiv}CFc)_2$, **13**]. All the new complexes were fully characterized. X-ray characterization of **3**, **5**, **6**, **7**, **11a**, **11b**, **13**, and $P(C{\equiv}CFc)_3$ are also provided.

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Introduction

Phosphanylalkynes are a source of rich chemistry, and these compounds have been used widely in organometallic and coordination chemistry. Phosphanylalkynes of the $PPh_2C{\equiv}CR$ type are potentially bifunctional ligands, and they have been shown to react with mononuclear and polynuclear complexes in various ways. Although these ligands act mostly as P-donor phosphanes and/or the C≡C moiety towards most transition-metal center(s),[1] there are also many cases in which they undergo cleavage of the P–C(alkyne) bond, which can be induced by thermolysis, photolysis, and chemical activation, to generate separate phosphido (PPh_2) and acetylide (C≡CR) fragments.[2] In some cases, the subsequent formation of a P–C bond has even been observed.[3,4] Furthermore, the $PPh_2C{\equiv}CR$ ligands can insert into reactive M–H and M–C bonds.[2g,5]

Due to the rigidity of the doubly bridged bis(cyclopentadienyl) ligands, the corresponding metal complexes exhibit unique properties in terms of structure, reactivity, and catalysis in comparison to the properties exhibited by their nonbridged and singly bridged analogues.[6] We recently reported that the Me_2C and Me_2Si doubly bridged bis(cyclopentadienyl) dinuclear molybdenum carbonyl complex $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (**1**) contained an unusually long Mo–Mo bond length,[7] which is a good precursor for the synthesis of other new dinuclear molybdenum complexes, and led to a number of interesting but not always predictable reactions. More recently, our research has focused on the reactions of complex **1** with a series of unsaturated organic molecules. Reactions of **1** with nitrile mainly afforded the η^2-η^2-perpendicularly coordinated nitrile complex, and the resulting nitrile complex underwent C≡N bond cleavage of acetonitrile to form μ_4- and μ_5-N MoRu clusters.[8] The reaction of complex **1** with the allene $H_2C{=}C{=}CHCO_2Me$ produced two allene-isomerization products and two allene-coupling products, which is significantly different from the reactivity of allene with nonbridged and singly bridged dinuclear molybdenum carbonyl complexes.[9] The N–N bond cleavage of diazoalkane Ar_2CN_2 following orthometalation of the aryl and disproportionation of CS_2 were observed in thermal reactions with **1**.[10] In this contribution, we report the reactions of complex **1** with a series of phosphanylalkynes $Ph_nP(C{\equiv}CR)_{3-n}$ [n = 2, 1, 0; R = Ph, Fc (ferrocenyl, $C_{10}H_9$)], in which the phosphanylalkynes behaved as disubstituted

[a] State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University,
Tianjin 300071, People's Republic of China
Fax: +86-22-23504781
E-mail: bqwang@nankai.edu.cn
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

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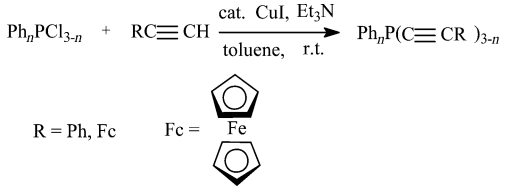
acetylenes, and/or the cleavage of P–C(alkyne) bond and rearrangement of phosphanylalkynes into phosphido-substituted vinylidenyl ligand were observed.

Results and Discussion

Synthesis and Characterization of Phosphanylalkyne Ligands $Ph_nP(C{\equiv}CR)_{3-n}$ (R = Ph, Fc; *n* = 2, 1, 0)

Beletskaya and coworkers demonstrated the synthesis of phosphanylalkyne ligands by means of cross-coupling reaction of chlorophosphanes Ph_nPCl_{3-n} with terminal alkynes catalyzed by cuprous salts.[11] This method also proceeds smoothly in the synthesis of (ferrocenylethynyl)phosphanes (Scheme 1). The ^1H and ^{31}P NMR spectra of the phosphanylalkyne complexes were in good agreement with the data previously reported.[11,12] Furthermore, tris(ferrocenylethynyl)phosphane $P(C{\equiv}CFc)_3$ was confirmed by X-ray diffraction analysis (Figure 1).



Scheme 1.

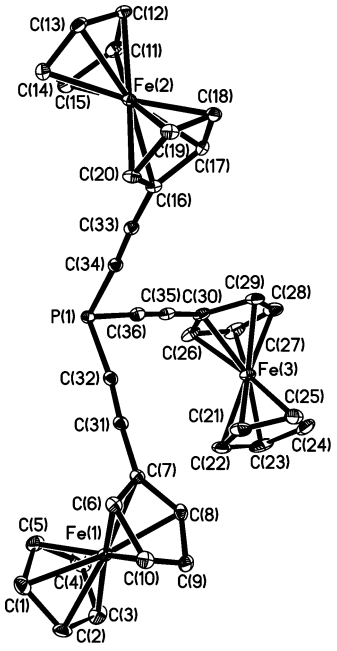


Figure 1. ORTEP diagram of $P(C{\equiv}CFc)_3$. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(31)–C(32) 1.197(4), C(33)–C(34) 1.206(4), C(35)–C(36) 1.203(4), C(36)–P(1)–C(34) 99.08(13), C(36)–P(1)–C(32) 99.30(13), C(34)–P(1)–C(32) 99.80(12).

Reaction of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (1) with Phosphanylalkynes $Ph_nP(C{\equiv}CR)_{3-n}$ (*n* = 2, 1, 0; R = Ph, Fc)

When complex **1** reacted with $Ph_2PC{\equiv}CPh$ in refluxing toluene, the P–C(alkyne) bond cleavage and phosphanylalkyne rearrangement product $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4\{\mu\text{–}\eta^1\text{-}\eta^2\text{-}C{=}C(Ph)PPh_2\}]$ (**3**) was obtained in 40% yield, along with two alkyne-bridged complexes $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}\eta^2(\perp)\text{-}RC{\equiv}CPh)]$ [R = Ph_2P (**2**), 10%; $Ph_2P(O)$ (**4**), 5%] (Scheme 2). Although P–C(alkyne) bond cleavage of phosphanylalkynes is well established,[2] its rearrangement is not.[3] To the best of our knowledge, the rearrangement of phosphanylalkynes into phosphido-substituted vinylidenyl ligands by cleavage of the P–C(alkyne) bond and formation of a P–C(alkene) bond has not been reported. In the reaction of $Ph_2PC{\equiv}CFc$ with complex **1**, only the phosphanylalkyne rearrangement product **5** was isolated in 41% yield.

Both complexes **2** and **4** are deep-brown, air-stable crystals. Complex **2** displays four absorption signals in the IR spectrum that can be assigned to the terminal carbonyl ligands, it also displays three resonances in the ^1H NMR spectrum, which can be assigned to equivalent Cp rings. Complex **4** has IR and ^1H NMR spectra similar to those of **2**, but their $^{31}P\{^1H\}$ NMR spectra differ greatly. Signals appear at δ = 19.95 ppm for **2** and δ = 27.71 ppm for **4**, which are both significantly downfield shifted in comparison to the signal of $Ph_2PC{\equiv}CPh$ (δ = –33.50 ppm).[13] It was reported that phosphanylalkyne itself[14] and phosphanylalkyne-bridged metal complexes such as $Co_2(CO)_6(\mu\text{-}Ph_2PC{\equiv}Ct\text{-}Bu)$[15] and $(\mu\text{-}Ph_2PCH_2PPh_2)Co_2(CO)_4(\mu\text{-}Ph_2PC{\equiv}CR)$ (R = Ph, *t*-Bu, and Ph_2P)[16] could be oxidized to their oxide partly during chromatography. The signal in the $^{31}P\{^1H\}$ NMR spectrum of the phosphanylalkyne-bridged metal complex is also shifted upfield relative to that of its oxide, for instance, δ = 6.8 ppm for $(\mu\text{-}Ph_2PCH_2PPh_2)Co_2(CO)_4(\mu\text{-}Ph_2PC{\equiv}CPh)$ versus δ = 28.4 ppm for its oxide.[16b] So, complex **4** can be presumed to be the oxide of **2**. To confirm this, the reaction of **1** with $Ph_2P(O)C{\equiv}CPh$ was examined and complex **4** was obtained as expected. The P=O bond was reflected by the absorption at 1174 cm^{-1} in the IR spectrum.

Complex **3** is a deep-orange air-stable crystalline solid. Four terminal carbonyl absorptions are observed in its IR spectrum. Its ^1H NMR spectrum comprises six resonances for six Cp protons, revealing that the two Cp ligands are inequivalent. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ = –78.0 ppm, which is significantly upfield shifted from that found for $Ph_2PC{\equiv}CPh$ (δ = –33.5 ppm).[13] In addition, the $^{13}C\{^1H\}$ NMR spectrum exhibits two significantly low-field doublets at δ = 273.1 and 241.4 ppm, which are even more downfield than the signals for the carbonyl groups (δ = 238.7–232.9 ppm). All these data suggest that complex **3** has an unusual structure, which was confirmed by the single-crystal X-ray diffraction analysis. Complex **5** has IR and ^1H and $^{31}P\{^1H\}$ NMR spectra that are similar to those of **3**, and their structures are very similar as well.

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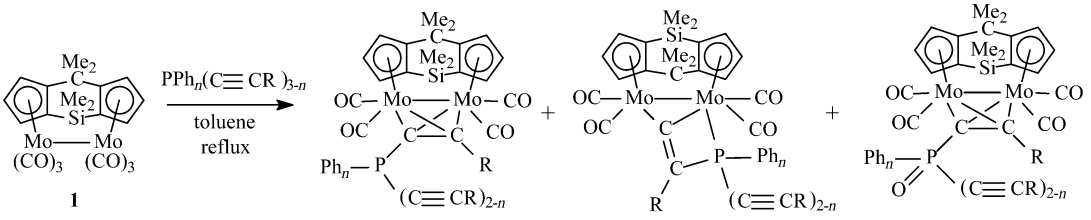

$n = 2$	R = Ph	**2** (10%)	**3** (40%)	**4** (5%)
	R = Fc	—	**5** (41%)	—
$n = 1$	R = Ph	**6** (36%)	**7** (9%)	—
	R = Fc	**8** (8%)	**9** (17%)	**10** (16%)
$n = 0$	R = Ph	**11**a (32%) + **11b** (9%)	—	**12** (17%)
	R = Fc	**13** (23%)	—	—

Scheme 2.

As shown in Scheme 2, the reaction of **1** with bis(ethynyl)-functionalized phosphanes gave similar products: alkyne-bridged complex **6** (36%) and phosphanylalkyne rearrangement complex **7** (9%) for $PhP(C{\equiv}CPh)_2$, alkyne-bridged complex **8** (8%), alkyne-bridged oxide **10** (16%) and phosphanylalkyne rearrangement complex **9** (17%) for $PhP(C{\equiv}CFc)_2$. In the reaction of **1** with tris(ethynyl)-functionalized phosphanes, the alkyne-bridged complexes (or and alkyne-bridged oxide) were isolated without the phosphanylalkyne rearrangement complex: alkyne-bridged complexes **11a** (32%) and **11b** (9%) and alkyne-bridged oxide **12** (17%) for $P(C{\equiv}CPh)_3$, alkyne-bridged complex **13** (23%) for $P(C{\equiv}CFc)_3$. All these compounds were characterized by multinuclear NMR spectroscopy, IR spectroscopy, and elemental analysis, and the molecular structures of complexes **6**, **7**, **11a**, **11b**, and **13** were also determined by single-crystal X-ray diffraction analysis.

Except for the four stretching vibrations for the terminal carbonyl ligands, complexes **6**–**13** exhibit stretching signals in their IR spectra in the range 2173–2144 cm^{-1}, and this is in good agreement with the retention of the uncoordinated $\nu(C{\equiv}C)$ frequency. In the ^1H NMR spectra, complexes **6**–**9** show six (and five for complex **10**) resonances for the Cp protons, indicating the nonequivalence of the two Cp ligands, whereas complexes **11**–**13** show three peaks for the equivalent Cp rings as expected for symmetrical structures. In contrast, the $^{31}P\{^1H\}$ NMR chemical shifts of these complexes are quite different. The phosphanylalkyne rearrangement complexes **7** and **9** have $^{31}P\{^1H\}$ NMR resonance signals that are significantly upfield shifted in comparison to those of phosphanylalkyne. However, alkyne-bridged complexes **6**, **8**, **11a**, **11b**, and **13** (including alkyne-bridged oxides **10** and **12**) show $^{31}P\{^1H\}$ NMR signals that are evidently downfield shifted in comparison to those in the spectrum of phosphanylalkyne.

It is interesting to note that complexes **11a** and **11b** are two isomers of the alkyne $[P(C{\equiv}CPh)_3]$-bridged complexes. The difference between the isomeric pairs is the location of the CMe_2 and $SiMe_2$ bridging groups, which is confirmed by single-crystal X-ray diffraction analysis. The $^{31}P\{^1H\}$ NMR spectra of the two isomers are greatly different from each other [δ = –41.1 (**11a**) and –28.3 ppm (**11b**)]. The chemical shifts in the ^1H NMR spectra of the two isomers are also very distinct: for example, four sets of resonance signals of the phenyl protons with a ratio of 1:1:12:1 are shown for **11a**, whereas eight sets with a ratio of 1:3:2:1:3:2:2:1 are shown for **11b** (see Experimental Section for details). In addition, the signal for the CMe_2 equatorial methyl protons (δ = 0.72 ppm) of isomer **11b** are approximately 0.7 ppm upfield from the typical one, which might be attributable to a pronounced shielding of the equatorial methyl group by the nearby conjugated phenyl group. Such a phenomenon was also observed in complexes **2**, **4**, and **6**. The X-ray structure of **11b**, which will be discussed in more detail below (Figure 7b), confirms the close nonbonding interaction between the CMe_2 equatorial methyl group and the π system of the phenyl group.

Molecular Structures

Single-crystal X-ray analysis revealed the final structure assignment of complex **3**. In its unit cell, there are two independent molecules that are an enantiomeric pair, and they differ only slightly in their bond lengths and angles (Figure 2). The most salient feature is the presence of the $C{=}C(Ph)PPh_2$ phosphido-substituted vinylidenyl ligand, which bridges the Mo–Mo bond through the C(20) atom in an unsymmetrical fashion [Mo(1)–C(20) 2.325(4) Å, Mo(2)–C(20) 1.998(5) Å] and coordinates to Mo(1) through the P(1) atom [Mo(1)–P(1) 2.4357(15) Å] as a four-electron donor. The shorter Mo–Mo distance in **3** [3.1578(6) Å] versus that found in **1** [3.4328(12) Å][7] is probably a consequence of the additional bridge. The C(20)–C(21) bond length of 1.345(6) Å indicates that it changes from a triple bond to a double bond, but the torsion angles Mo(2)–C(20)–C(21)–P(1) of 173.0° and Mo(2)–C(20)–C(21)–P(1) of 167.5° show that the six atoms of the alkene are not

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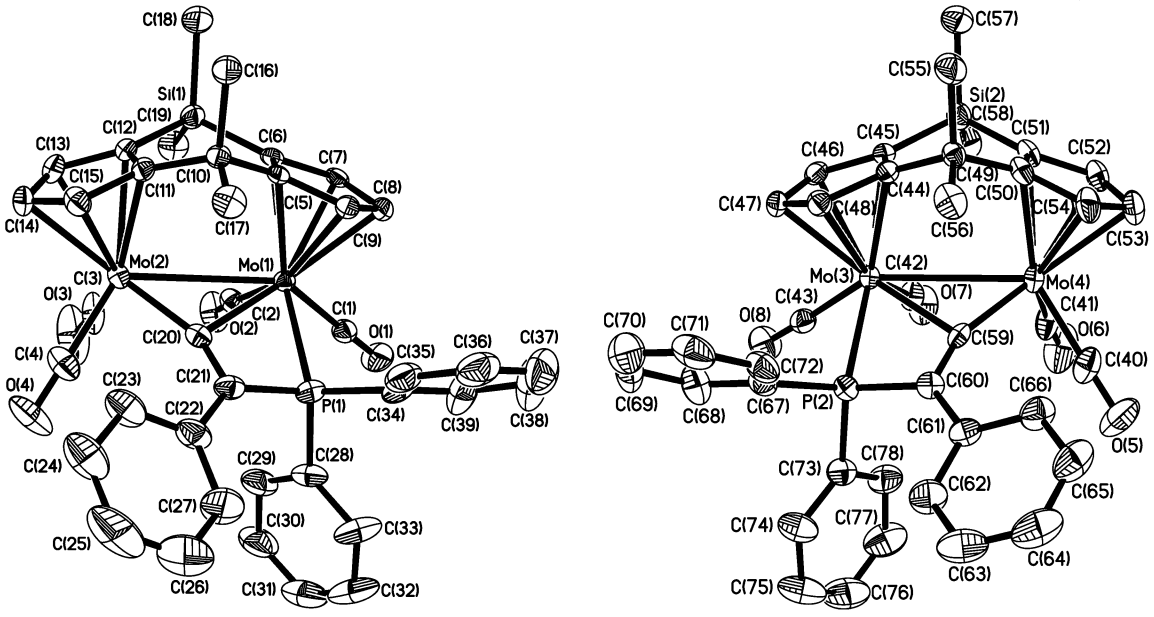

Figure 2. ORTEP diagram of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}C(Ph)PPh_2\}]$ (**3**), showing the two crystallographically independent molecules in the unit cell. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity.

well settled in an ideal alkenyl plane. This contributes to minimizing the steric interactions between the phenyl group and the C(4)–O(4) carbonyl group. Similarly, the phosphorus P(1) atom lies 0.4703 Å below the ethenyl plane mentioned above. In the absence of a metal–metal bond, Mo(2) formally has 16 valence electrons and Mo(1) has 18 valence electrons. Thus, a dative Mo(1)→Mo(2) bond achieves the 36-electron bimetallic complex. In addition, one of the four carbonyl ligands, C(2)–O(2), adopts a weak semibridging coordination to the Mo–Mo bond [∠Mo(1)–C(2)–O(2) 167.7(4)°].[17]

Complexes **5** and **7** have structures similar to that of **3** and their molecular structures are depicted in Figures 3 and 4, respectively. Selected bond lengths and angles are listed in Table 1. The bond lengths and angles of the $Mo_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}CP\}$ core structure in complexes **5** and **7** vary little compared to those of **3**.

Single-crystal X-ray analysis of **6** (Figure 5), **11a** (Figure 6), **11b** (Figure 7), and **13** (Figure 8) confirms that these compounds are crosswise-substituted alkyne-bridged complexes. The dimensions of the Mo_2C_2 core are similar to those found in the $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}\eta^2\text{-}HC{\equiv}CCH_2CO_2Me)]$[9] complex and the unbridged $Cp_2Mo_2(CO)_4(\mu\text{-}RC{\equiv}CR)$ analogue.[18] The alkyne ligands

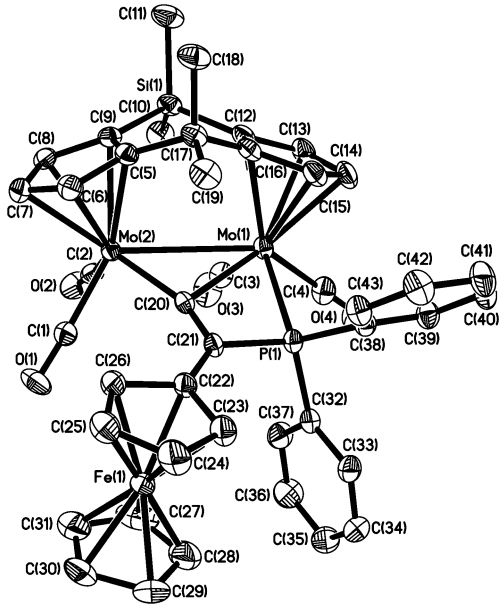

Figure 3. ORTEP diagram of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}C(Fc)PPh_2\}]$ (**5**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity.

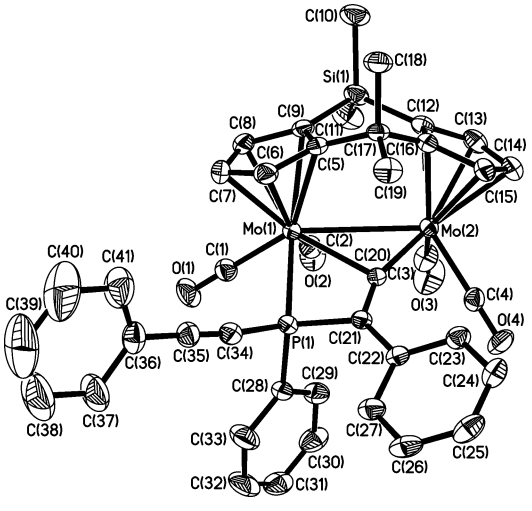

Figure 4. ORTEP diagram of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}C(Ph)PPh(C{\equiv}CPh)\}]$ (**7**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms and solvent molecules are omitted for clarity.

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Table 1. Selected bond lengths [Å] and angles [°] for **3**, **5**, and **7**.

	3	**5**	**7**
Mo(1)–Mo(2)	3.1577(7)	3.1785(4)	3.1786(7)
Mo(1)–C(20)	2.324(5)	2.353(2)	2.351(5)
Mo(2)–C(20)	1.999(5)	2.021(2)	1.989(5)
C(20)–C(21)	1.347(7)	1.352(3)	1.380(7)
C(21)–P(1)	1.742(6)	1.761(2)	1.746(5)
Mo(1)–P(1)	2.4357(15)	2.4477(7)	2.4230(14)
Mo(2)–C(20)–Mo(1)	93.54(19)	92.91(9)	93.81(19)
Mo(2)–C(20)–C(21)	155.4(4)	155.68(18)	156.8(4)
Mo(1)–C(20)–C(21)	111.0(4)	110.68(16)	109.3(3)
C(20)–C(21)–P(1)	94.9(4)	95.63(16)	93.5(3)
Mo(1)–P(1)–C(21)	93.28(18)	93.45(8)	94.41(16)

in these complexes are all tipped over to the CMe_2 bridge side of the doubly bridged ligand, possibly owing to the smaller steric effect of the CMe_2 bridge than that of the $SiMe_2$ bridge.

The spectroscopic data of these complexes are consistent with their structures, except for **11b** and **13** (Figures 7 and 8). Both of these compounds show no symmetry in the solid state, but in the ^{1}H NMR spectra, **11b** and **13** exhibit three resonances for the Cp protons, which is suggestive of C_s symmetry. Therefore, a rotation process about the C(18)–P(1) bond of complex **11b**, which creates a mirror plane that cuts the whole molecule into two equivalent halves, occurs in solution. A similar fluxional process is also apparent in the C(21)–C(22) bond of complex **13** in solution. In complexes **6** and **11b**, the phenyl group lies close to the CMe_2 bridging group, which accounts for the migration of the proton peaks of CMe_2 to a higher field, as mentioned above.

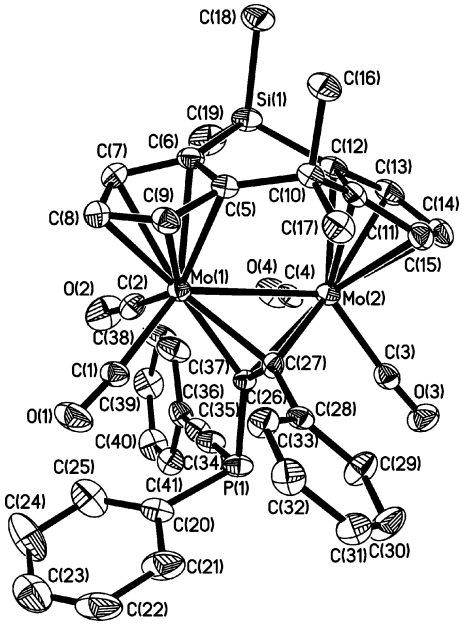

Figure 5. ORTEP diagram of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}PhC{\equiv}CPPh(C{\equiv}CPh)\}]$ (**6**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo(1)–Mo(2) 2.9293(9), Mo(1)–C(26) 2.211(6), Mo(1)–C(27) 2.162(6), Mo(2)–C(26) 2.206(6), Mo(2)–C(27) 2.187(5), C(34)–C(35) 1.197(9), Mo(2)–C(26)–Mo(1) 83.09(19), Mo(1)–C(27)–Mo(2) 84.7(2), C(26)–C(27)–C(28) 131.1(5), C(27)–C(26)–P(1) 128.4(4), C(35)–C(34)–P(1) 174.0(6), C(34)–C(35)–C(36) 176.0(8).

After the structures of all the products were determined clearly, we were then interested in the stereochemistry of these complexes. Due to the difference in the CMe_2 and

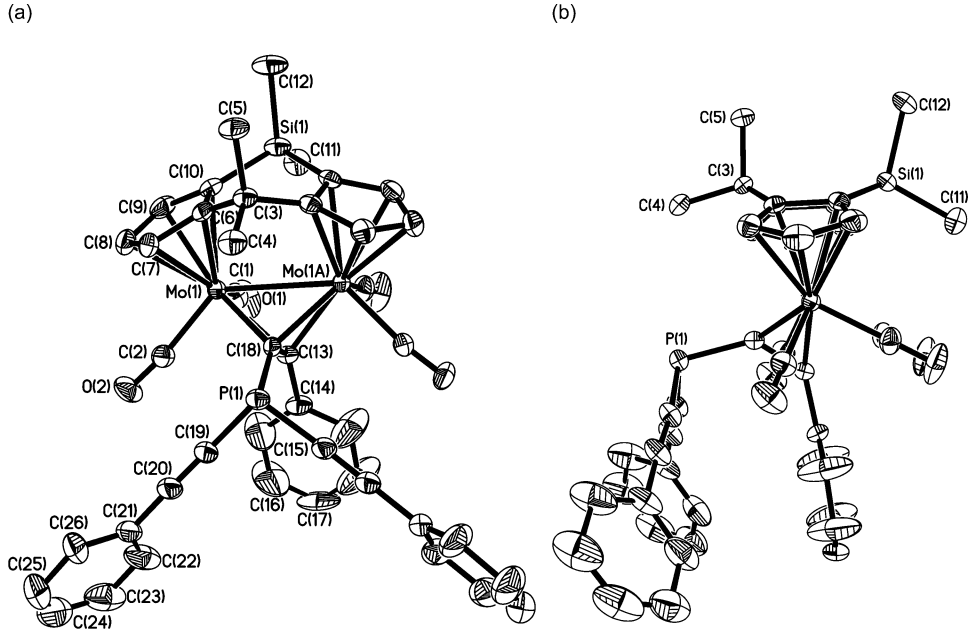

Figure 6. ORTEP diagram of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}PhC{\equiv}CP(C{\equiv}CPh)_2\}]$ (**11a**): (a) viewed perpendicular to the Mo–Mo bond and (b) viewed down the Mo–Mo axis. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo(1)–Mo(1A) 2.9267(7), Mo(1)–C(13) 2.208(4), Mo(1)–C(18) 2.165(4), C(13)–C(18) 1.361(7), C(19)–C(20) 1.194(6), Mo(1)–C(13)–Mo(1A) 83.02(18), Mo(1)–C(18)–Mo(1A) 85.05(19).

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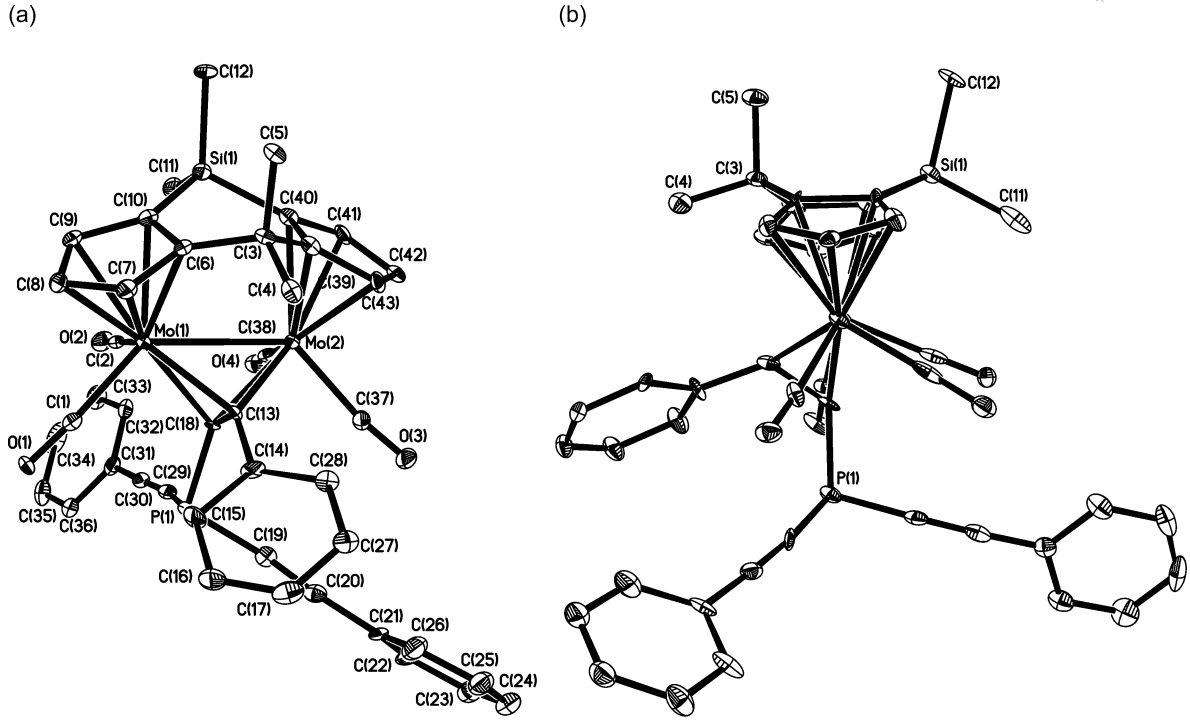

Figure 7. ORTEP diagram of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}PhC{\equiv}CP(C{\equiv}CPh)_2\}]$ (**11b**), showing one of the two crystallographically independent molecules in the unit cell: (a) viewed perpendicular to the Mo–Mo bond and (b) viewed down the Mo–Mo axis. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo(1)–Mo(2) 2.9403(11), Mo(1)–C(18) 2.220(8), Mo(2)–C(18) 2.201(7), Mo(1)–C(13) 2.197(8), Mo(2)–C(13) 2.181(8), C(13)–C(18) 1.399(14), C(19)–C(20) 1.189(11), C(29)–C(30) 1.266(14), Mo(2)–C(18)–Mo(1) 83.4(3), Mo(2)–C(13)–Mo(1) 84.4(3), C(18)–C(13)–C(14) 125.8(7), C(13)–C(18)–P(1) 124.5(6), C(20)–C(19)–P(1) 169.7(8), C(30)–C(29)–P(1) 167.1(8).

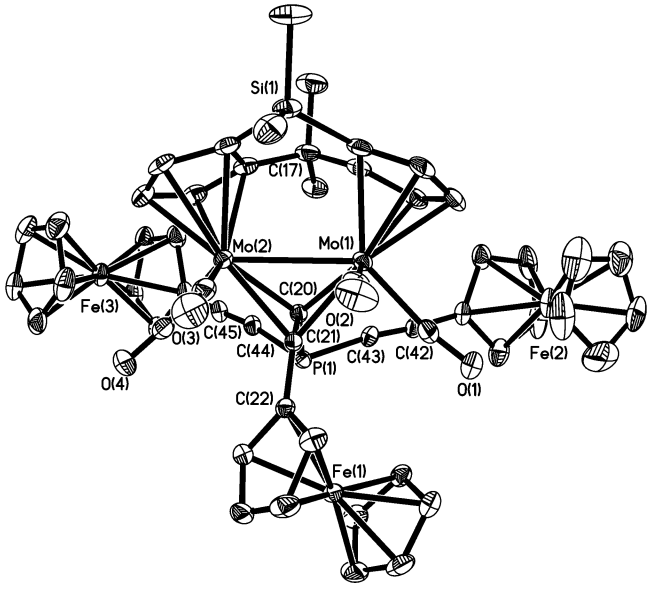

Figure 8. ORTEP diagram of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}FcC{\equiv}CP(C{\equiv}CFc)_2\}]$ (**13**), showing one of the two crystallographically independent molecules in the unit cell. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo(1)–Mo(2) 2.956(2), Mo(1)–C(20) 2.216(4), Mo(1)–C(21) 2.219(5), Mo(2)–C(20) 2.205(4), Mo(2)–C(21) 2.291(4), C(20)–C(21) 1.390(6), C(42)–C(43) 1.210(7), C(44)–C(45) 1.206(7), Mo(2)–C(20)–Mo(1) 83.93(16), Mo(1)–C(21)–Mo(2) 81.90(15), C(20)–C(21)–C(22) 135.7(4), C(21)–C(20)–P(1) 121.6(3), C(42)–C(43)–P(1) 172.7(4), C(43)–C(42)–C(41) 174.8(5), C(45)–C(44)–P(1) 170.3(5), C(44)–C(45)–C(46) 175.8(5).

$SiMe_2$ bridging groups of precursor **1** and to the fact that the introduced phosphanylalkyne ligand is inclined to lie to one side of the doubly bridged ligand, every compound is chiral. For instance, there are four isomers in theory for products **2**–**5** and **11**–**13** in the reactions of **1** with mono- or tris(ethynyl)-functionalized phosphanes and even more isomeric possibilities for products **6**–**10** of the reactions of **1** with bis(ethynyl)-functionalized phosphanes, as the phosphanes in these compounds are also chiral. However, in the crystal unit cells, an enantiomeric pair was found for **3**, whereas only one isomer was found for **5**, **6**, 7, and **13**. It is surprising that **11a** and **11b** are the only isomeric pairs to be observed. The reason was not very clear, but the steric distinction between the CMe_2 and $SiMe_2$ bridging groups of precursor **1** is essential for the site of the ligand addition to the title complex and to the structures of the products.

Conclusions

To conclude, reactions of the doubly bridged bis(cyclopentadienyl) dinuclear molybdenum complex $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (**1**) with a series of phosphanylalkynes $Ph_nP(C{\equiv}CR)_{3-n}$ (n = 0, 1, 2; R = Ph, Fc) afforded not only the normal alkyne-bridged complexes (or and alkyne-bridged oxide) but also phosphanylalkyne P–C(alkyne) bond cleavage and phosphanylalkyne rearrangement complexes. It should also be noted that a phosphanylalkyne rearrangement complex is prominent in the reaction of **1**

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with monoethynyl-functionalized phosphanes, but tris(ethynyl)-functionalized phosphanes behave as disubstituted acetylenes when treated with complex **1**. The mechanism of the rearrangement of phosphanylalkynes into phosphido-substituted vinylidenyl ligands is still under study.

Experimental Section

General Procedures: Schlenk and vacuum-line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under an atmosphere of argon prior to use. Melting points are uncorrected. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded with a Bruker AV300 instrument [^{1}H at 300 MHz and ^{31}P{^{1}H} at 121.5 MHz]. ^{13}C{^{1}H} NMR experiments were carried out with a Varian Mercury VX300 or a Bruker AV400 instrument [^{13}C{^{1}H} at 75.5 or 100 MHz]. All spectra were referenced to the residual signals of the deuterated solvents. IR spectra were recorded as KBr disks with a Nicolet 380 FTIR spectrometer. Elemental analyses were performed with a Perkin–Elmer 240C analyzer. $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (**1**),[7] $Ph_nP(C{\equiv}CPh)_{3-n}$ (n = 0, 1, 2),[12] $Ph_2P(O)C{\equiv}CPh$,[19] and $FcC{\equiv}CH$[20] were prepared by literature methods.

Reaction of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (1) with $Ph_2PC{\equiv}CPh$: A solution of **1** (117 mg, 0.20 mmol) and $Ph_2PC{\equiv}CPh$ (60 mg, 0.21 mmol) in toluene (30 mL) was heated at reflux for 6 h. During this time the solution turned from deep green to dark brown. After removal of the solvent, the residue was chromatographed on an alumina column. Elution with petroleum ether/CH_2Cl_2 gave a brown band and an orange band, which afforded **2** (16 mg, 10% yield) and **3** (65 mg, 40% yield) as brown and deep-orange crystals, respectively. Elution with CH_2Cl_2/acetone developed a brown band, which afforded **4** (8 mg, 5% yield) as brown crystals.

Complex 2: M.p. 166 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 7.58 (t, 5 H, Ph-H), 7.37–7.20 (m, 10 H, Ph-H), 5.46 (br. s, 2 H, Cp-H), 5.28 (br. s, 2 H, Cp-H), 4.98 (br. s, 2 H, Cp-H), 1.57 (s, 3 H, CMe), 0.65 (s, 3 H, CMe), 0.64 (s, 3 H, SiMe), 0.42 (s, 3 H, SiMe) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 19.9 (s) ppm. IR: $\tilde{\nu}$ = 1985 (s) (ν_{CO}), 1946 (s) (ν_{CO}), 1914 (s) (ν_{CO}), 1893 (s) (ν_{CO}) cm^{-1}. $C_{39}H_{33}Mo_2O_4PSi$ (820.00): calcd. C 57.36, H 4.07; found C 57.57, H 4.35.

Complex: 3: M.p. 178–9 °C. ^{1}H NMR ($CDCl_3$): δ = 7.67 (m, 2 H, Ph-H), 7.50 (m, 3 H, Ph-H), 7.31–7.14 (m, 9 H, Ph-H), 7.05 (t, 1 H, Ph-H), 5.93 (m, 1 H, Cp-H), 5.75 (t, 1 H, Cp-H), 5.12 (t, 1 H, Cp-H), 5.09 (m, 1 H, Cp-H), 4.94 (t, 1 H, Cp-H), 3.85 (m, 1 H, Cp-H), 1.38 (s, 3 H, CMe), 1.28 (s, 3 H, CMe), 0.73 (s, 3 H, SiMe), 0.58 (s, 3 H, SiMe) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 273.1 [d, J = 31.3 Hz, $Ph_2P(Ph)C{=}CMo_2$], 241.4 [d, $J_{C,P}$ = 35.7 Hz, $Ph_2P(Ph)C{=}CMo_2$], 238.7, 235.6, 233.0, 232.9 (CO), 147.2 (d, $J_{C,P}$ = 46.6 Hz, Ph), 144.7, 137.2 (Cp), 134.8 (d, J = 30.8 Hz), 132.9 (d, $J_{C,P}$ = 45.1 Hz), 131.7, 131.6, 131.2, 131.1, 130.4, 130.0, 129.0, 128.9, 128.8, 128.6, 128.1, 125.4, 123.6, 123.5 (Ph), 105.5 (d, J = 5.2 Hz), 99.2, 98.9 (d, $J_{C,P}$ = 4.2 Hz), 92.1, 89.1, 86.3 (d, J = 15.1 Hz), 85.7 (d, J = 13.7 Hz), 85.0 (d, J = 16.0 Hz, Cp), 37.7 (d, J = 7.8 Hz, CMe_2), 35.8 (*C*Me$_2$), 23.8 (d, J = 7.3 Hz, CMe_2), 4.1, 0.2 (SiMe_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –78.0 (s) ppm. IR: $\tilde{\nu}$ = 1955 (s) (ν_{CO}), 1921 (s) (ν_{CO}), 1871 (s) (ν_{CO}), 1843 (m) (ν_{CO}) cm^{-1}. $C_{39}H_{33}Mo_2O_4PSi$ (820.00): calcd. C 57.36, H 4.07; found C 57.22, H 4.18.

Complex 4: M.p. 214 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 7.62 (m, 5 H, Ph-H), 7.34–7.18 (m, 10 H, Ph-H), 5.33 (t, 2 H, Cp-H), 5.21 (m, 2 H, Cp-H), 4.87 (t, 2 H, Cp-H), 1.55 (s, 3 H, CMe), 0.63 (s, 3 H, CMe), 0.56 (s, 3 H, SiMe), 0.49 (s, 3 H, SiMe) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 27.7 (s) ppm. IR: $\tilde{\nu}$ = 1994 (s) (ν_{CO}), 1953 (s) (ν_{CO}), 1907 (s) (ν_{CO}), 1893 (m) (ν_{CO}), 1174 (w) ($\nu_{P=O}$) cm^{-1}. $C_{39}H_{33}Mo_2O_5PSi$ (835.99): calcd. C 56.26, H 3.99; found C 55.98, H 4.06.

Reaction of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (1) with $Ph_2P(O)C{\equiv}CPh$: A solution of **1** (117 mg, 0.20 mmol) and $Ph_2P(O)C{\equiv}CPh$ (90 mg, 0.30 mmol) in toluene (30 mL) was heated at reflux for 10 h. During this time the solution turned from deep green to dark brown. After removal of the solvent, the residue was chromatographed on an alumina column. Elution with CH_2Cl_2/acetone developed a brown band, which afforded **3** (75 mg, 45% yield) as brown crystals.

Reaction of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (1) with $PhP(C{\equiv}CPh)_2$: A solution of **1** (117 mg, 0.20 mmol) and $PhP(C{\equiv}CPh)_2$ (70 mg, 0.22 mmol) in toluene (30 mL) was heated at reflux for 6 h. During this time the solution turned from deep green to dark brown. After removal of the solvent, the residue was chromatographed on an alumina column by using petroleum ether/CH_2Cl_2 as the eluent. The first band (brown) gave **6** (60 mg, 36% yield) as deep-brown crystals. The second band (purple) gave **7** (15 mg, 9% yield) as brown crystals.

Complex 6: M.p. 172–3 °C. ^{1}H NMR ($CDCl_3$): δ = 7.39 (m, 4 H, Ph-H), 7.34 (d, J = 1.48 Hz, 1 H, Ph-H), 7.25 (m, 5 H, Ph-H), 7.21 (m, 1 H, Ph-H), 7.18–7.10 (m, 4 H, Ph-H), 5.53 (t, 1 H, Cp-H), 5.40 (t, 1 H, Cp-H), 5.23 (br. s, 1 H, Cp-H), 5.21 (br. s, 1 H, Cp-H), 4.97 (m, 1 H, Cp-H), 4.93 (m, 1 H, Cp-H), 1.56 (s, 3 H, CMe), 0.69 (s, 3 H, CMe), 0.62 (s, 3 H, SiMe), 0.39 (s, 3 H, SiMe) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –4.3 (s) ppm. IR: $\tilde{\nu}$ = 2156 (w) ($\nu_{C\equiv C}$), 1989 (s) (ν_{CO}), 1949 (s) (ν_{CO}), 1920 (s) (ν_{CO}), 1893 (m) (ν_{CO}) cm^{-1}. $C_{41}H_{33}Mo_2O_4PSi$ (844.00): calcd. C 58.58, H 3.96; found C 58.86, H 3.96.

Complex 7: M.p. 167 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 7.59 (t, 1 H, Ph-H), 7.56 (d, J = 1.68 Hz, 2 H, Ph-H), 7.43 (m, 2 H, Ph-H), 7.40 (br. s, 2 H, Ph-H), 7.39–7.33 (m, 5 H, Ph-H), 7.27 (m, 2 H, Ph-H), 7.08 (t, 1 H, Ph-H), 5.95 (m, 1 H, Cp-H), 5.76 (t, 1 H, Cp-H), 5.47 (t, 1 H, Cp-H), 5.30 (br. s, 1 H, Cp-H), 5.15 (m, 1 H, Cp-H), 5.11 (t, 1 H, Cp-H), 1.50 (s, 3 H, CMe), 1.38 (s, 3 H, CMe), 0.70 (s, 3 H, SiMe), 0.63 (s, 3 H, SiMe) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 273.7 [d, J = 33.2 Hz, $Ph(C{\equiv}CPh)P(Ph)C{=}CMo_2$], 239.6 [d, $J_{C,P}$ = 36.4 Hz, $Ph(C{\equiv}CPh)P(Ph)C{=}CMo_2$], 238.0, 235.7, 232.7, 232.6 (CO), 148.5 (d, $J_{C,P}$ = 52.1 Hz, Ph), 145.3, 136.2 (Cp), 132.6, 131.8, 131.4, 130.7, 130.6, 130.5, 130.4, 129.2, 129.0, 128.9, 128.4, 125.7, 123.6, 123.4, 121.3 (Ph), 106.3 (d, J = 6.3 Hz), 105.9 (d, J = 4.7 Hz), 100.4 (Cp), 100.1 (d, J = 10.4 Hz, $PC{\equiv}CPh$), 92.8, 89.0, 86.8 (d, J = 13.6 Hz), 85.9 (d, J = 13.6 Hz), 85.0 (d, J = 5.9 Hz, Cp), 81.9 (d, $J_{C,P}$ = 50.9 Hz, P*C*≡CPh), 38.3 (d, J = 7.1 Hz, CMe_2), 36.3 (*C*Me$_2$), 24.2 (d, J = 6.6 Hz, CMe_2), 4.4, 0.6 (SiMe_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –102.9 (s) ppm. IR: $\tilde{\nu}$ = 2159 (m) ($\nu_{C\equiv C}$), 1958 (s) (ν_{CO}), 1925 (s) (ν_{CO}), 1981 (s) (ν_{CO}), 1848 (m) (ν_{CO}) cm^{-1}. $C_{41}H_{33}Mo_2O_4PSi$ (844.00): calcd. C 58.58, H 3.96; found C 58.53, H 3.87.

Reaction of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (1) with $P(C{\equiv}CPh)_3$: A solution of **1** (117 mg, 0.20 mmol) and $P(C{\equiv}CPh)_3$ (103 mg, 0.31 mmol) in toluene (30 mL) was heated at reflux for 5 h. During this time the solution turned from deep green to dark brown. After removal of the solvent, the residue was chromatographed on an alumina column by using petroleum ether/CH_2Cl_2 as the eluent. The first band (brown) gave **11a** (56 mg, 32% yield) as deep-brown crystals. The second band (brown) gave **11b** (16 mg, 9% yield) as brown crystals. Elution with CH_2Cl_2/acetone devel-

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oped a brown band, which afforded **12** (30 mg, 17% yield) as green crystals.

Complex 11a: M.p. 195 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 7.93 (m, 1 H, Ph-H), 7.90 (m, 1 H, Ph-H), 7.36–7.24 (m, 12 H, Ph-H), 7.14 (t, 1 H, Ph-H), 5.45 (t, 2 H, Cp-H), 5.41 (m, 2 H, Cp-H), 5.28 (m, 2 H, Cp-H), 1.69 (s, 3 H, CMe), 1.62 (s, 3 H, CMe), 0.66 (s, 3 H, SiMe), 0.47 (s, 3 H, SiMe) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –41.1 (s) ppm. IR: $\tilde{\nu}$ = 2154 (w) ($\nu_{C\equiv C}$), 1993 (s) (ν_{CO}), 1944 (s) (ν_{CO}), 1921 (s) (ν_{CO}), 1893 (s) (ν_{CO}) cm^{-1}. $C_{43}H_{33}Mo_2O_4PSi$ (868.00): calcd. C 59.73, H 3.85; found C 59.51, H 4.05.

Complex 11b: M.p. 218 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 7.37 (m, 1 H, Ph-H), 7.34 (m, 3 H, Ph-H), 7.33 (t, 2 H, Ph-H), 7.32 (s, 1 H, Ph-H), 7.25 (m, 3 H, Ph-H), 7.23 (m, 2 H, Ph-H), 7.08 (t, 2 H, Ph-H), 6.98 (t, 1 H, Ph-H), 5.56 (t, 2 H, Cp-H), 5.27 (m, 2 H, Cp-H), 5.03 (m, 2 H, Cp-H), 1.59 (s, 3 H, CMe), 0.72 (s, 3 H, CMe), 0.64 (s, 3 H, SiMe), 0.44 (s, 3 H, SiMe) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –28.3 (s) ppm. IR: $\tilde{\nu}$ = 2158 (w) ($\nu_{C\equiv C}$), 1994 (s) (ν_{CO}), 1959 (s) (ν_{CO}), 1925 (s) (ν_{CO}), 1897 (s) (ν_{CO}) cm^{-1}. $C_{43}H_{33}Mo_2O_4PSi$ (868.00): calcd. C 59.73, H 3.85; found C 59.41, H 4.07.

Complex 12: M.p. 248 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 7.75 (s, 1 H, Ph-H), 7.72 (s, 1 H, Ph-H), 7.36–7.20 (m, 15 H, Ph-H), 7.06 (t, 1 H, Ph-H), 5.70 (br. s, 2 H, Cp-H), 5.55 (t, 2 H, Cp-H), 5.28 (m, 2 H, Cp-H), 1.67 (s, 3 H, CMe), 1.65 (s, 3 H, CMe), 0.69 (s, 3 H, SiMe), 0.49 (s, 3 H, SiMe) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –1.3 (s) ppm. IR: $\tilde{\nu}$ = 2173 (m) ($\nu_{C\equiv C}$), 1998 (s) (ν_{CO}), 1952 (s) (ν_{CO}), 1924 (s) (ν_{CO}), 1897 (m) (ν_{CO}), 1199 (m) ($\nu_{P=O}$) cm^{-1}. $C_{43}H_{33}Mo_2O_5PSi$ (883.99): calcd. C 58.65, H 3.78; found C 58.50, H 3.82.

Preparation of the $Ph_{2-n}P(C\equiv CFc)_n$ (Fc = ferrocenyl, n = 0, 1, 2) Ligand: Ligands $Ph_{2-n}P(C\equiv CFc)_n$ (n = 0, 1, 2) were synthesized by using the method for the preparation of $Ph_{2-n}P(C\equiv CPh)_n$ (n = 0, 1, 2).[12] A solution of Ph_2PCl (1.10 g, 5.00 mmol), Et_3N (3.10 g, 15 mmol), FcC≡CH (1.05 g, 5.00 mmol), and CuI (10 mg, 0.05 mmol) in toluene (30 mL) was mixed in a Schlenk flask and stirred at room temperature overnight. Then, the resulting ammonium salt was removed by filtration, and the solvent was evaporated under reduced pressure. The crude product was then chromatographed on an alumina column by using petroleum ether/CH_2Cl_2 as the eluent. The resulting orange band gave $Ph_2PC\equiv CFc$ (1.15 g, 60% yield) as orange solids. Data for $Ph_2PC\equiv CFc$:[11] M.p. 96–7 °C. ^{1}H NMR ($CDCl_3$): δ = 7.66 (m, 4H, Ph-H), 7.35 (m, 6H, Ph-H), 4.54 (t, 2H, Cp-H), 4.25 (t, 2H, Cp-H), 4.23 (m, 2H, Cp-H) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –32.8 (s) ppm.

A solution of $PhPCl_2$ (0.45 g, 2.50 mmol), Et_3N (3.10 g, 15 mmol), FcC≡CH (1.05 g, 5.00 mmol), and CuI (10 mg, 0.05 mmol) in toluene (30 mL) was mixed in a Schlenk flask and stirred at room temperature for 16 h. Then, the resulting ammonium salt was removed by filtration, and the solvent was evaporated under reduced pressure. The crude product was then chromatographed on an alumina column by using petroleum ether/CH_2Cl_2 as the eluent. The first band (yellow) afforded unreacted FcC≡CH (0.20 g). The second band (orange) gave $PhP(C\equiv CFc)_2$ (0.78 g, 72% yield with respect to consuming FcC≡CH) as orange crystals. Data for $PhP(C\equiv CFc)_2$:[11] M.p. 142–3 °C. ^{1}H NMR ($CDCl_3$): δ = 7.84 (m, 2H, Ph-H), 7.44 (m, 3H, Ph-H), 4.53 (br. s, 4H, Cp-H), 4.24 (br. s, 14H, Cp-H) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –59.4 (s) ppm.

A solution of PCl_3 (0.22 g, 1.60 mmol), Et_3N (3.00 g, 14.4 mmol), FcC≡CH (1.01 g, 4.81 mmol), and CuI (10 mg, 0.05 mmol) in toluene (30 mL) was mixed in a Schlenk flask and stirred at room temperature for 15 h. Then, the resulting ammonium salt was removed by filtration, and the solvent was evaporated under reduced pressure. The crude product was then chromatographed on an alumina column by using petroleum ether/CH_2Cl_2 as the eluent. The first band (yellow) afforded unreacted FcC≡CH (0.12 g). The second band (orange) gave $P(C\equiv CFc)_3$ (0.61 g, 66% yield with respect to consuming FcC≡CH) as orange crystals. Data for $P(C\equiv CFc)_3$:[11] M.p. 205 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 4.55 (m, 6H, Cp-H), 4.26 (m, 21H, Cp-H) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –87.8 (s) ppm.

Reaction of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (1) with $Ph_2P(C\equiv CFc)$ (Fc = ferrocenyl, $C_{10}H_9Fe$): A solution of **1** (117 mg, 0.20 mmol) and $Ph_2PC\equiv CFc$ (87 mg, 0.22 mmol) in toluene (30 mL) was heated at reflux for 6 h. During this time the solution turned from deep green to dark brown. After removal of the solvent, the residue was chromatographed on an alumina column. Elution with petroleum ether/CH_2Cl_2 gave an orange band, which afforded **5** (75 mg, 41% yield) as brown crystals.

Complex 5: M.p. 226 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 7.75 (m, 2 H, Ph-H), 7.50 (br. s, 3 H, Ph-H), 7.39 (br. s, 3 H, Ph-H), 7.29 (m, 2 H, Ph-H), 5.82 (m, 1 H, Cp-H), 5.58 (br. s, 1 H, Cp-H), 5.07 (t, 1 H, Cp-H), 5.02 (br. s, 1 H, Cp-H), 4.82 (t, 1 H, Cp-H), 4.71 (s, 1 H, Fc-H), 4.24 (s, 1 H, Fc-H), 4.08 (s, 1 H, Fc-H), 3.91 (s, 1 H, Fc-H),3.73 (br. s, 1 H, Cp-H), 3.53 (s, 5 H, Fc-H), 1.31 (s, 3 H, CMe), 1.18 (s, 3 H, CMe), 0.73 (s, 3 H, SiMe), 0.55 (s, 3 H, SiMe) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 270.5 [br. s, $Ph_2P(Fc)C=\mathit{C}Mo_2$], 242.5 [d, $J_{C,P}$ = 34.9 Hz, $Ph_2P(Fc)\mathit{C}{=}CMo_2$], 239.3, 238.2, 233.9, 233.8 (CO), 143.1 (Cp), 136.8, 136.4, 133.7, 132.9, 132.8, 131.6, 131.4, 131.3, 130.5, 130.2, 128.8, 128.7, 128.6 (Ph), 104.9.1, 100.2 (d, J = 8.0 Hz), 97.1, 91.9, 88.0, 86.2 (d, J = 15.8 Hz), 86.0 (d, J = 17.1 Hz), 85.2 (d, J = 17.1 Hz, Cp), 69.7, 69.6, 68.0, 66.7, 65.0, 64.1 (br. s, Fc), 38.64 (d, J = 7.4 Hz, CMe_2), 35.7 ($\mathit{C}Me_2$), 24.1 (d, J = 6.4 Hz, CMe_2), 4.2, 0.4 (SiMe_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –77.2 (s) ppm. IR: $\tilde{\nu}$ = 1948 (s) (ν_{CO}), 1909 (s) (ν_{CO}), 1869 (s) (ν_{CO}), 18430 (s) (ν_{CO}) cm^{-1}. $C_{43}H_{37}FeMo_2O_4PSi$ (927.97): calcd. C 55.61, H 4.02; found C 55.52, H 4.29.

Reaction of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (1) with $PhP(C\equiv CFc)_2$ (Fc = ferrocenyl, $C_{10}H_9Fe$): A solution of **1** (117 mg, 0.20 mmol) and $PhP(C\equiv CFc)_2$ (130 mg, 0.25 mmol) in toluene (30 mL) was heated at reflux for 6 h. During this time the solution turned from deep green to dark brown. After removal of the solvent, the residue was chromatographed on an alumina column. Elution with petroleum ether/CH_2Cl_2 gave a brown band and an orange band, which afforded **8** (18 mg, 8% yield) and **9** (38 mg, 17% yield) as brown crystals, respectively. Elution with CH_2Cl_2/acetone developed a brown band, which afforded **10** (35 mg, 16% yield) as brown crystals.

Complex 8: M.p. 182 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 7.90 (t, 2 H, Ph-H), 7.38 (m, 3 H, Ph-H), 5.53 (br. s, 1 H, Cp-H), 5.46 (t, 1 H, Cp-H), 5.26 (t, 1 H, Cp-H), 5.22 (m, 1 H, Cp-H), 5.08 (m, 1 H, Cp-H), 4.69 (m, 1 H, Cp-H), 4.55 (m, 3 H, Fc-H), 4.33 (m, 6 H, Fc-H), 4.29 (m, 9 H, Fc-H), 1.46 (s, 3 H, CMe), 0.97 (s, 3 H, CMe), 0.55 (s, 3 H, SiMe), 0.37 (s, 3 H, SiMe) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –11.2 (s) ppm. IR: $\tilde{\nu}$ = 2154 (m) ($\nu_{C\equiv C}$), 1976 (s) (ν_{CO}), 1892 (s) (ν_{CO}), 1831 (m) (ν_{CO}) cm^{-1}. $C_{49}H_{41}Fe_2Mo_2O_4PSi$ (1059.93): calcd. C 55.71, H 3.91; found C 55.80, H 4.39.

Complex 9: M.p. 193–194 °C. ^{1}H NMR ($CDCl_3$): δ = 7.51 (m, 2 H, Ph-H), 7.40 (m, 3 H, Ph-H), 5.91 (m, 1 H, Cp-H), 5.63 (br. s, 1 H, Cp-H), 5.44 (t, 1 H, Cp-H), 5.30 (br. s, 1 H, Cp-H), 5.13 (m, 1 H, Cp-H), 5.00 (t, 1 H, Cp-H), 4.67 (m, 2 H, Fc-H), 4.46 (s, 1 H, Fc-H), 4.38 (br. s, 2 H, Fc-H), 4.31 (s, 4 H, Fc-H), 4.27 (s, 1 H, Fc-

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H), 4.14 (s, 1 H, Fc-H), 4.10 (s, 1 H, Fc-H), 4.07 (br. s, 1 H, Fc-H), 3.92 (s, 5 H, Fc-H), 1.51 (s, 3 H, CMe), 1.48 (s, 3 H, CMe), 0.70 (s, 3 H, SiMe), 0.62 (s, 3 H, SiMe) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 270.0 [br. s, PhP(FcC≡C)C=*C*Mo$_2$], 240.1 [d, $J_{C,P}$ = 36.5 Hz, Ph_2P(FcC≡C)*C*=CMo$_2$], 239.4, 236.8, 233.6, 233.5 (CO), 144.7 (Cp), 130.9, 130.4, 128.8, 128.6 (Ph), 107.7 (d, J = 7.1 Hz, Fc*C*≡CP), 107.6, 105.5, 100.7, 99.4, 92.7, 88.1, 86.6, 85.3, 84.8 (Cp),78.5 (d, $J_{C,P}$ = 52.0 Hz, FcC≡*C*P), 72.4, 70.3, 70.0, 69.2, 69.1, 67.6 (d, J = 8.5 Hz), 66.9 (d, J = 9.0 Hz), 64.9 (br. s), 63.9 (br., s), 62.2, 62.1 (Fc), 38.3 (d, J = 4.9 Hz, C*Me*$_2$), 35.9 (*C*Me$_2$), 24.3 (d, J = 4.8 Hz, C*Me*$_2$), 4.2, 0.4 (Si*Me*$_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –101.6 (s) ppm. IR: $\tilde{\nu}$ = 2146 (m) ($\nu_{C\equiv C}$), 1957 (s) (ν_{CO}), 1924 (s) (ν_{CO}), 1878 (s) (ν_{CO}), 1844 (m) (ν_{CO}) cm^{-1}. $C_{49}H_{41}Fe_2Mo_2O_4PSi$ (1059.93): calcd. C 55.71, H 3.91; found C 55.07, H 4.25.

Table 2. Crystal data and summary of X-ray data collection for **3**, **5**, **6**, and **7**.

	3	**5**	**6**·CH_2Cl_2	**7**·0.5CH_2Cl_2
Empirical formula	$C_{39}H_{33}Mo_2O_4PSi$	$C_{43}H_{37}FeMo_2O_4PSi$	$C_{42}H_{35}Cl_2Mo_2O_4PSi$	$C_{41.50}H_{34}ClMo_2O_4PSi$
Fw	816.59	924.52	925.54	883.08
T [K]	294(2)	294(2)	294(2)	294(2)
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$	$P2(1)/n$
a [Å]	13.542(2)	12.2776(15)	12.251(3)	11.3110(12)
b [Å]	14.150(2)	16.5610(19)	12.690(3)	21.936(3)
c [Å]	19.359(4)	19.052(2)	14.223(3)	16.8453(18)
α [°]	102.949(8)	90	111.546(3)	90
β [°]	98.072(7)	98.600(2)	96.514(4)	103.255(2)
γ [°]	90.435(7)	90	103.295(4)	90
V [Å^3]	3576.4(11)	3830.2(8)	1953.1(7)	4068.3(8)
Z	4	4	2	4
$D_{calcd.}$ [g cm^{-3}]	1.517	1.603	1.574	1.442
μ [mm^{-1}]	0.819	1.134	0.892	0.789
F(000)	1648	1864	932	1780
Crystal size [mm]	0.26 × 0.20 × 0.12	0.22 × 0.16 × 0.12	0.26 × 0.20 × 0.18	0.22 × 0.20 × 0.16
Max. 2θ [°]	52.36	52.78	52.80	52.88
Reflections collected	19701	21856	11005	22869
Independent reflns/R_{int}	13878/0.0329	7830/0.0218	7854/0.0334	8338/0.0385
No. of parameters	855	469	483	497
GOF on F^2	0.853	1.064	1.033	1.074
R_1, wR_2 [$I > 2\sigma(I)$]	0.0424, 0.0982	0.0254, 0.0582	0.0539, 0.1322	0.0445, 0.1321
R_1, wR_2 (all data)	0.0857, 0.1239	0.0365, 0.0649	0.1013, 0.1623	0.0792, 0.1524
Largest peak in final diff. map [e Å^{-3}]	0.621	0.811	1.597	1.014

Table 3. Crystal data and summary of X-ray data collection for **11a**, **11b**, **13**, and P(C≡CFc)$_3$.

	11a	**11b**	**13**·0.5CH_2Cl_2	P(C≡CFc)$_3$
Empirical formula	$C_{43}H_{33}Mo_2O_4PSi$	$C_{43}H_{33}Mo_2O_4PSi$	$C_{55.50}H_{46}ClFe_3Mo_2O_4PSi$	$C_{36}H_{27}Fe_3P$
Fw	864.63	864.63	1230.86	658.10
T [K]	294(2)	113(2)	294(2)	113(2)
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic
Space group	*Pnma*	$P2(1)/c$	$P\bar{1}$	$P2(1)/a$
a [Å]	12.6571(15)	19.278(3)	10.428(7)	13.2787(7)
b [Å]	16.744(2)	25.060(6)	15.217(10)	11.0982(5)
c [Å]	18.014(2)	15.893(4)	18.545(12)	19.1156(11)
α [°]	90	90	102.600(10)	90
β [°]	90	90.341(9)	103.423(10)	92.081(3)
γ [°]	90	90	107.828(10)	90
V [Å^3]	3817.8(8)	7678(3)	2589(3)	2815.2(3)
Z	4	8	2	4
$D_{calcd.}$ [g cm^{-3}]	1.504	1.496	1.579	1.553
μ [mm^{-1}]	0.772	0.767	1.442	1.607
F(000)	1744	3488	1238	1344
Crystal size [mm]	0.24 × 0.22 × 0.16	0.24 × 0.20 × 0.18	0.22 × 0.20 × 0.14	0.14 × 0.12 × 0.12
Max. 2θ [°]	52.76	55.70	50.04	55.76
Reflections collected	20809	43835	12927	25862
Independent reflns/R_{int}	4042/0.0408	16295/0.0854	8938/0.0227	6710/0.0525
No. of parameters	251	930	622	362
GOF on F^2	1.008	1.091	1.064	1.105
R_1, wR_2 [$I > 2\sigma(I)$]	0.0314, 0.0699	0.0717, 0.1794	0.0375, 0.1059	0.0461, 0.0957
R_1, wR_2 (all data)	0.0666, 0.0877	0.0868, 0.2096	0.0557, 0.1205	0.0561, 0.1028
Largest peak in final diff. map [e Å^{-3}]	0.647	1.807	1.083	0.464

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Complex 10: M.p. 179–180 °C. ^{1}H NMR ($CDCl_3$): δ = 7.59 (m, 2 H, Ph-H), 7.34 (t, 1 H, Ph-H), 7.26 (m, 2 H, Ph-H), 5.60 (t, 1 H, Cp-H), 5.54 (br. s, 1 H, Cp-H), 5.50 (br. s, 1 H, Cp-H), 5.49 (br. s, 1 H, Cp-H), 5.30 (s, 1 H, Cp-H), 5.25 (t, 1 H, Cp-H), 4.47 (br. s, 2 H, Fc-H), 4.26 (m, 2 H, Fc-H), 4.24 (s, 1 H, Fc-H), 4.19 (s, 5 H, Fc-H), 4.17 (s, 5 H, Fc-H), 3.97 (br. s, 1 H, Fc-H), 3.84 (br. s, 2 H, Fc-H), 1.64 (s, 3 H, CMe), 1.51 (s, 3 H, CMe), 0.67 (s, 3 H, SiMe), 0.50 (s, 3 H, SiMe) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 24.4 (s) ppm. IR: $\tilde{\nu}$ = 2160 (m) ($\nu_{C\equiv C}$), 2000 (m) (ν_{CO}), 1949 (s) (ν_{CO}), 1920 (s) (ν_{CO}), 1888 (m) (ν_{CO}), 1191 (w) ($\nu_{P=O}$) cm^{-1}. $C_{49}H_{41}Fe_2Mo_2O_5PSi$ (1075.93): calcd. C 54.65, H 3.84; found C 54.86, H 3.92.

Reaction of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (1) with $P(C\equiv CFc)_3$ (Fc = ferrocenyl, $C_{10}H_9Fe$): A solution of **1** (117 mg, 0.20 mmol) and $P(C\equiv CFc)_3$ (145 mg, 0.22 mmol) in toluene (30 mL) was heated at reflux for 6 h. During this time the solution turned from deep green to dark brown. After removal of the solvent, the residue was chromatographed on an alumina column. Elution with petroleum ether/CH_2Cl_2 gave a brown band, which afforded **13** (55 mg, 23% yield) as brown crystals.

Complex 13: M.p. 205 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 5.64 (br. s, 2 H, Cp-H), 5.48 (t, 2 H, Cp-H), 5.23 (br. s, 2 H, Cp-H), 4.52 (br. s, 6 H, Fc-H), 4.32 (s, 4 H, Fc-H), 4.28 (br. s, 17 H, Fc-H), 1.66 (s, 6 H, CMe), 0.62 (s, 3 H, SiMe), 0.37 (s, 3 H, SiMe) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –37.4 (s) ppm. IR: $\tilde{\nu}$ = 2144 (m) ($\nu_{C\equiv C}$), 1976 (s) (ν_{CO}), 1946 (s) (ν_{CO}), 1909 (s) (ν_{CO}) cm^{-1}. $C_{55}H_{45}Fe_3Mo_2O_4PSi$ (1191.90): calcd. C 55.37, H 3.81; found C 55.19, H 4.01.

Crystallographic Studies: Single crystals of all complexes suitable for X-ray diffraction were obtained from hexane/CH_2Cl_2. Data collection of complexes **3**, **5**, **6**, **7**, **11a**, and **13** were performed with a Bruker SMART 1000 at 294(2) K, whereas those of **11b** and $P(C\equiv CFc)_3$ were performed with a Rigaku Saturn 70 equipped with a rotating anode system at 113(2) K by using graphite-monochromated Mo-K_α radiation (ω-2θ scans, λ = 0.71073 Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were performed with the SHELXL-97 program system. The molecular structures of **6**, **7**, and **13** contained CH_2Cl_2 molecules of solvation. The crystal data and summary of X-ray data collection are presented in Tables 2 and 3. CCDC-636554 (for **3**), -689564 (for **5**), -689565 (for **6**), -689566 (for **7**), -689567 (for **11a**), -689568 (for **11b**), -689831 (for **13**), and -689569 [for $P(C\equiv CFc)_3$] contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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