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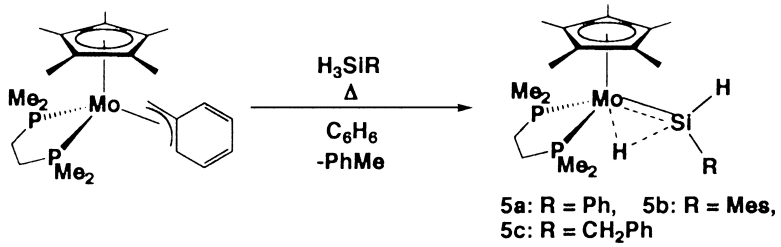


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# Silylene Hydride Complexes of Molybdenum with Silicon−Hydrogen Interactions: Neutron Structure of ($\eta^5$-$C_5Me_5$)($Me_2PCH_2CH_2PMe_2$)Mo(H)($SiEt_2$)

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***Abstract:*** Reduction of Cp*$MoCl_4$ with 3.1 equiv of Na/Hg amalgam (1.0% w/w) in the presence of 1 equiv of dmpe and 1 equiv of trimethylphosphine afforded the molybdenum(II) chloride complex Cp*(dmpe)-($PMe_3$)MoCl (**1**) (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl, dmpe = 1,2-bis(dimethylphosphino)ethane). Alkylation of **1** with $PhCH_2MgCl$ proceeded in high yield to liberate $PMe_3$ and give the 18-electron $\pi$-benzyl complex Cp*(dmpe)Mo($\eta^3$-$CH_2Ph$) (**2**). Variable temperature NMR experiments provided evidence that **2** is in equilibrium with its 16-electron $\eta^1$-benzyl isomer [Cp*(dmpe)Mo($\eta^1$-$CH_2Ph$)]. This was further supported by reaction of **2** with CO to yield the carbonyl benzyl complex Cp*(dmpe)(CO)Mo($\eta^1$-$CH_2Ph$) (**3**). Complex **2** was found to react with disubstituted silanes $H_2SiRR'$ (RR' = $Me_2$, $Et_2$, MePh, and $Ph_2$) to form toluene and the silylene complexes Cp*(dmpe)Mo(H)(SiRR') (**4a**: RR' = $Me_2$; **4b**: RR' = $Et_2$; **4c**: RR' = MePh; **4d**: RR' = $Ph_2$). Reactions of **2** with monosubstituted silanes $H_3SiR$ (R = Ph, Mes, Mes = 2,4,6-trimethylphenyl) produced rare examples of hydrosilylene complexes Cp*(dmpe)Mo(H)Si(H)R (**5a**: R = Ph; **5b**: R = Mes; **5c**: R = $CH_2Ph$). Reactivity of complexes **4a**−**c** and **5a**−**d** is dominated by 1,2-hydride migration from metal to silicon, and these complexes possess H···Si bonding interactions, as supported by spectroscopic and structural data. For example, the $J_{HSi}$ coupling constants in these species range in value from 30 to 48 Hz and are larger than would be expected in the absence of H···Si bonding. A neutron diffraction study on a single crystal of diethylsilylene complex **4b** unequivocally determined the hydride ligand to be in a bridging position across the molybdenum−silicon bond (Mo−H 1.85(1) Å, Si−H 1.68(1) Å). The synthesis and reactivity properties of these complexes are described in detail.

## Introduction

Metal silylene complexes have attracted much attention as silicon analogues of metal carbenes and as potential intermediates in metal-catalyzed syntheses and transformations of organosilanes.[1] To date, more than 20 examples of base-free metal silylene complexes are known,[2,3] and these include a variety of transition metals, ancillary ligand sets, and substituents at silicon.[4] The chemistry of metal carbene complexes is much more extensively developed,[5] and these complexes exhibit great utility in organic and organometallic chemistry (e.g., in olefin metathesis reactions).[6] Thus, silylene complexes are expected to be of use in stoichiometric and catalytic reactions involving

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[‡] Argonne National Laboratory.

(1) (a) Tilley, T. D. In *The Silicon Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; p 245. (b) Okazaki, M.; Tobita, H.; Ogino, H. *J. Chem. Soc., Dalton Trans.* **2003**, 493. (c) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *Organometallics* **2002**, *21*, 4648. (d) Eisen, M. S. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds., Wiley: New York, 1998; Vol. 2, Chapter 35. (e) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (f) Tamao, K.; Sun, G. R.; Kawachi, A. *J. Am. Chem. Soc.* **1995**, *117*, 8043. (g) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37. (h) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley-Interscience: New York, 2000.

(2) For the purposes of this discussion, the term "base-free silylene complexes" refers to those complexes that feature three-coordinate silicon centers and no stabilization by Lewis bases. This excludes those complexes that have coordinated Lewis bases and those that have $\pi$-donating substituents at silicon.

(3) For some examples of base-stabilized molybdenum silylene complexes, see: (a) Ueno, K.; Masuko, A.; Ogino, H. *Organometallics* **1999**, *18*, 2694. (b) Clendenning, S. B.; Gehrhus, B.; Hitchcock, P. B.; Moser, D. F.; Nixon, J. F.; West, R. *J. Chem. Soc., Dalton Trans.* **2002**, *2002*, 484. (c) Petri, S. H. A.; Eikenberg, D.; Neumann, B.; Stammler, H.-G.; Jutzi, P. *Organometallics* **1999**, *18*, 2615.

(4) (a) Grumbine, S. K.; Mitchell, G. P.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Organometallics* **1998**, *17*, 5607. (b) Wanandi, P. W.; Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 972. (c) Gusev, D. G.; Fontaine, F.-G.; Lough, A. J.; Zargarian, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 216. (d) Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871. (e) Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 9702. (f) Mitchell, G. P.; Tilley, T. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2524. (g) Ueno, K.; Asami, S.; Watanabe, N.; Ogino, H. *Organometallics* **2002**, *21*, 1326. (h) Feldman, J. D.; Mitchell, G. P.; Nolte, J. O.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 11184. (i) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816. (j) Simons, R. S.; Gallucci, J. C.; Tessier, C. A.; Yougs, W. J. *J. Organomet. Chem.* **2002**, *654*, 224.

(5) (a) Dötz, K. H.; Fischer, H.; Hoffman, P.; Kreissel, R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983. (b) Schrock, R. R. *J. Chem. Soc., Dalton Trans.* **2001**, 2451. (c) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley-Interscience: New York, 1994. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987. (e) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. (f) Elschenbroich, Ch.; Salzer, A. *Organometallics, A Concise Introduction*, 2nd ed.; VCH: New York, 1992.

(6) (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (b) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.


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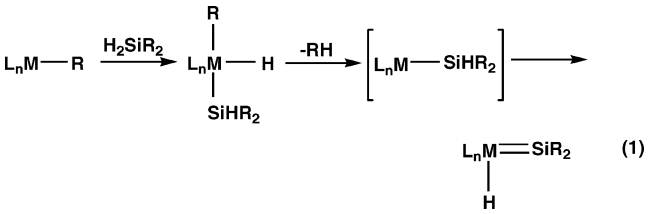
silicon, but such applications may require the availability of a larger and more diverse family of compounds of the type $L_nM{=}SiR_2$ (R = H, alkyl, or aryl). Toward this end, a number of research efforts have been directed toward the synthesis and study of new silylene complexes.[1−4,7]

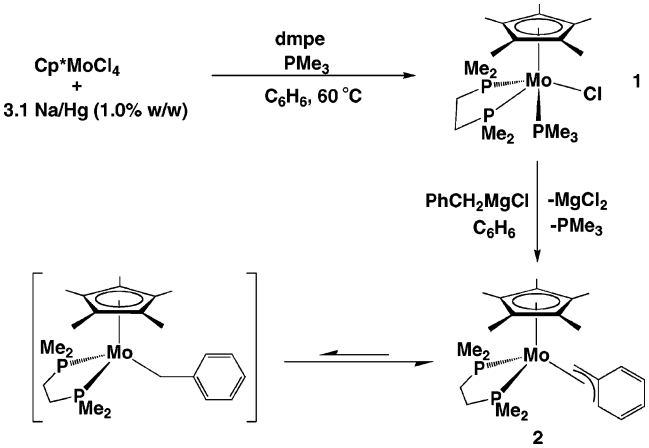
Many of the known base-free silylene complexes are cationic, since their preparations involve anion abstraction steps.[4] A significant challenge is therefore the synthesis of neutral silylene complexes, as these species should be compatible with a wide range of solvents and should exhibit reactivity that is not influenced by the participation of counteranions. Few examples of neutral silylene complexes have been published, and these include $(Cy_3P)_2Pt{=}SiMes_2$,[4h] $Cp(CO)_2(SiMe_3)W{=}SiMes_2$,[4g] $OsH_3(SiClPh)\{2,6\text{-}(CH_2P^tBu_2)_2C_6H_3\}$,[4c] and the zwitterionic complexes $[\kappa^3\text{-}PhB(CH_2PPh_2)_3](H)_2Ir{=}SiR_2$ ($R_2$ = $Mes_2$, $Me_2$, $Et_2$, and $Ph_2$).[4d] Neutral silylene complexes have also been synthesized from cyclic diamido silylenes, which are stable as free species and act as primarily $\sigma$-donors.[7] The chemical and spectroscopic properties of these silylene complexes appear to be distinctly different from the former type,[4] which involves silylene groups that are not stable as free species and feature alkyl, aryl, silyl, or hydride substituents at silicon.

Recently, we have developed routes to silylene complexes that employ reactive transition-metal fragments and double Si−H bond activations of a hydrosilane.[4d,e,8] This typically involves an oxidative addition of one Si−H bond, followed by α-elimination of the second Si−H in an electronically unsaturated hydrosilyl intermediate. If the starting metal complex features a $\sigma$-bonded organic ligand, then liberation of a hydrocarbon via C−H bond reductive elimination may provide a driving force for the formation of a silylene complex (eq 1). Coordinatively and electronically unsaturated metal alkyl complexes therefore represent promising precursors to silylene complexes.




For these reasons, we have synthesized the molybdenum benzyl complex Cp*(dmpe)Mo($\eta^3$-$CH_2Ph$) (Cp* = $\eta^5$-$C_5Me_5$, dmpe = 1,2-bis(dimethylphosphino)ethane), which reacts with hydrosilanes $H_2SiRR'$ (RR' = $Me_2$, $Et_2$, MePh, $Ph_2$, (H)Ph, (H)Mes, and (H)$CH_2Ph$) to eliminate toluene and form the molybdenum(II) silylene complexes Cp*(dmpe)Mo(H)(SiRR'). These are neutral, early transition-metal silylene complexes, and three of these compounds feature rare incorporation of hydrogen as a substituent at a silylene center. Structural and spectroscopic data support the presence of H···Si bonding interactions in this series of compounds, and their reactivities indicate that they are in equilibria with reactive 16-electron silyl complexes of the type Cp*(dmpe)MoSiHRR'. The molybdenum benzyl complex and the silylene complex Cp*(dmpe)Mo(H)SiClMes were communicated previously as precursors to the first complex with silylyne character, [Cp*(dmpe)Mo(H)(SiMes)][$B(C_6F_5)_4$].[8]

***Scheme 1***




## Results and Discussion

**Synthesis and Characterization of a Molybdenum Benzyl Complex.** The initial goal of this work was the synthesis of a 16-electron alkyl complex that could be used in the synthesis of a silylene complex (eq 1). Baker and co-workers have reported the 16-electron chloride complex Cp*$(PMe_3)_2$MoCl, which undergoes oxidative addition of $H_2$ to give the 18-electron complex Cp*$(PMe_3)_2MoH_2Cl$.[9] Unfortunately, analogous 16-electron alkyl complexes are not known. The allyl complex Cp*-$(PMe_3)_2$Mo($\eta^3$-$C_3H_5$)[10] may be envisioned as a source of the 16-electron species Cp*$(PMe_3)_2$Mo($\eta^1$-$C_3H_5$), via $\eta^1/\eta^3$ interconversion of the allyl ligand. However, elimination of propene in reactions of an allyl complex with silanes may result in secondary processes such as hydrosilylation.

For application of the synthetic procedure outlined in eq 1, benzyl derivatives were targeted as starting compounds. Benzyl ligands are known to participate in $\eta^1/\eta^3$ interconversions, and toluene should be a generally unreactive elimination product. The synthesis of an appropriate $\eta^3$-benzyl complex required access to the corresponding Cp*$L_n$MoCl ($n$ = 2 or 3) precursor. The chelating diphosphine dmpe was employed to impart stability to the complexes and provide a relatively metalation-resistant ancillary ligand framework. Reduction of Cp*$MoCl_4$[11] in the presence of 1 equiv of dmpe and 1 equiv of $PMe_3$ proceeded at 60 °C in benzene over 16 h to give Cp*(dmpe)-$(PMe_3)$MoCl (**1**) in 89% yield as a red-purple microcrystalline solid (Scheme 1). Compound **1** is analogous to Poli's Cp*-$(PMe_3)_3$MoCl, and its preparation was derived from the published procedure for the latter compound.[10]

The spectroscopic properties of **1** are consistent with the structure shown in Scheme 1. For example, the $^1$H NMR spectrum of **1** exhibits four separate doublet resonances for the symmetry-inequivalent dmpe methyl groups at $\delta$ 1.47, 1.35, 1.15, and 0.94 ($J_{HP}$ = 8, 8, 7, and 7 Hz, respectively). The

(7) For some examples of metal complexes of stable silylenes, see: (a) Haaf, M.; Schmedake, T. A.; West. R. *Acc. Chem. Res.* **2000**, *33*, 704. (b) Gehrus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *Organometallics* **1998**, *17*, 5599. (c) Evans, W. T.; Perotti, J. M.; Moser, D. F.; West, R. *Organometallics* **2003**, *22*, 1160. (d) Dysard, J. M.; Tilley, T. D. *Organometallics* **2000**, *19*, 4726. (e) Amoroso, D.; Haaf, M.; Yap, G. P.; West, R.; Fogg, D. E. *Organometallics* **2002**, *21*, 534.

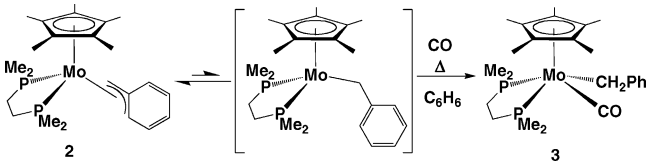
(8) Mork, B. V.; Tilley, T. D. *Angew Chem., Int. Ed.* **2003**, *42*, 357.

(9) Baker, R. T.; Calabrese, J. C.; Harlow, R. L.; Williams, I. D. *Organometallics* **1993**, *12*, 830.

(10) Abugideiri, F.; Kelland, M. A.; Poli, R.; Rheingold, A. L. *Organometallics* **1992**, *11*, 1303.

(11) Murray, R. C.; Blum, L.; Liu, A. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 954.

*Scheme 2*



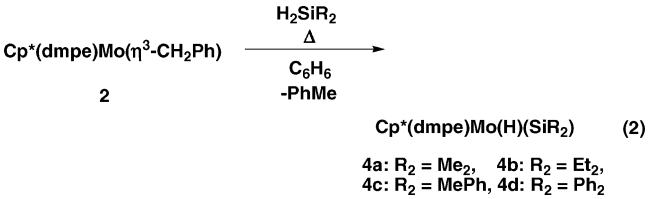

resonance due to the $PMe_3$ methyl groups is observed at $\delta$ 1.29 ($J_{HP}$ = 7 Hz). The $^{31}P\{^1H\}$ NMR spectrum of **1** also agrees with the low-symmetry structure, and it exhibits three separate resonances at $\delta$ 66.0 (dd, $J_{PP}$ = 30 Hz, $J_{PP'}$ = 22 Hz), 61.2 (dd, $J_{PP'}$ = 59 Hz, $J_{PP''}$ = 30 Hz), and 13.3 (dd, $J_{PP'}$ = 59 Hz, $J_{PP''}$ = 22 Hz).

Alkylation of **1** with $PhCH_2MgCl$ in benzene at room temperature occurred immediately upon mixing the reagents. The color of the solution changed from red-purple to orange-red, and a precipitate was observed. The new product, Cp*-(dmpe)Mo($\eta^3$-$CH_2Ph$) (**2**, Scheme 1), was isolated in 85% yield as an orange-brown solid by recrystallization from toluene.

Spectroscopic data support the description of **2** as an $\eta^3$-benzyl complex. For example, the $^1H$ NMR spectrum of **2** in benzene-$d_6$ exhibits four inequivalent resonances for the dmpe methyl groups at $\delta$ 1.48, 1.10, 0.98, and 0.62. The methylene protons of the benzyl group are inequivalent and are observed at $\delta$ 2.76 and −0.50. The ligand peaks in this spectrum, with the exception of a sharp singlet for the Cp* ligand, are slightly broadened, and this is likely due to a dynamic $\eta^1/\eta^3$ equilibrium involving the benzyl ligand (Scheme 1). The $^1H$ NMR spectrum of **2** at 50 °C displays a sharp Cp* resonance, while the dmpe and benzyl ligand resonances are nearly broadened into the baseline at this temperature. Attempts to obtain spectra at temperatures above 80 °C were unsuccessful because of decomposition of the benzyl complex to a mixture of unidentified products. At −20 °C in toluene-$d_8$, the $^1H$ NMR spectrum of **2** displays sharp resonances for all of the ligand protons, indicating the slow exchange limit for this dynamic process. For example, inequivalent resonances are observed for the aryl hydrogens at $\delta$ 7.09, 6.98, 6.56, 6.24, and 2.60. The latter resonance is shifted upfield because of binding of the aryl carbon to the molybdenum center.

The reaction of complex **2** with carbon monoxide provided evidence for the equilibrium in Scheme 1, as it results in trapping of the putative 16-electron benzyl complex as a CO adduct. A dark orange-red solution of **2** was placed under 1 atm of CO at room temperature, and the flask was sealed. Heating the mixture at 60 °C for 1 h resulted in a light orange solution of Cp*-(dmpe)(CO)Mo($CH_2Ph$) (**3**, Scheme 2). The carbonyl complex **3** was recrystallized from diethyl ether, but because of its high solubility in hydrocarbon solvents it was isolated in only 21% yield. The infrared spectrum of **3** indicates that the molybdenum center of the [Cp*(dmpe)Mo($CH_2Ph$)] fragment is quite electron-rich and strongly $\pi$-back-donating; **3** exhibits an absorbance for the CO stretch at $\nu_{CO}$ = 1779 cm$^{-1}$.

**Silylene Complexes via Double Si−H Bond Activation Reactions.** The apparent $\eta^1/\eta^3$ equilibrium of **2** was exploited in the synthesis of silylene complexes. For example, the reaction of **2** with an excess (approximately 5 equiv) of $H_2SiMe_2$ at 50 °C for 15 min resulted in a color change of the solution from orange-red to dark red. Isolation of the new product by recrystallization from pentane gave the dimethylsilylene complex Cp*(dmpe)Mo(H)($SiMe_2$) (**4a**, eq 2) as dark red crystals in 83% yield.




The spectroscopic characterization of **4a** is in agreement with its description as a silylene hydride complex. The $^1H$ NMR spectrum of **4a** in benzene-$d_6$ exhibits a $C_s$ symmetric structure at room temperature. Two doublet resonances are observed at $\delta$ 1.35 and 1.06 for the two pairs of dmpe methyl groups, and the molybdenum hydride is observed as a triplet with $^{29}Si$ satellites at $\delta$ −14.06 ($J_{HP}$ = 17 Hz, $J_{HSi}$ = 30 Hz). The silicon−methyl groups are observed as a singlet resonance at $\delta$ 0.67. Symmetry equivalent phosphorus nuclei are observed by $^{31}P\{^1H\}$ NMR spectroscopy as a singlet resonance at $\delta$ 70.2. A common indication of $sp^2$ hybridization at silicon is a significantly downfield-shifted $^{29}Si\{^1H\}$ NMR resonance.[1h] The $^{29}Si\{^1H\}$ NMR spectrum of **4a** implies silylene character for the silicon-based ligand in this compound, which exhibits a resonance at $\delta$ 263.

Reactions of **2** with secondary silanes provide a general route to silylene hydride complexes via the liberation of toluene. Reactions of the silanes $H_2SiEt_2$, $H_2SiMePh$, and $H_2SiPh_2$ were complete after 15 min at 50 °C, and the color of the product silylene complexes depends somewhat on the substituents at silicon. Table 1 provides $^{29}Si$ NMR chemical shifts as well as the $J_{HSi}$ values and colors of these silylene hydride complexes. Generally, the $^{29}Si$ NMR chemical shifts of the resonances for Cp*(dmpe)Mo(H)Si(RR') complexes (**4a**−**d**: RR' = $Me_2$, $Et_2$, MePh, and $Ph_2$, respectively; eq 2) are downfield-shifted and support their identification as silylene complexes. However, it is noteworthy that the observed $J_{HSi}$ values are in the range of 30−48 Hz. These hydrogen−silicon coupling constants are larger than those observed in the cationic tungsten silylene complexes [Cp*(dmpe)$(H)_2$W=SiRR'][B($C_6F_5$)$_4$] (RR' = $Me_2$, PhMe, $Ph_2$), which are in the range of 7−17 Hz.[4e] It is often accepted that $J_{HSi}$ values of ≤20 Hz indicate little or no bonding interaction between H and Si centers in the coordination sphere of a metal center.[12] The $J_{HSi}$ values observed in complexes **4a**−**d** are therefore indicative of the presence of weak H···Si bonding interactions in these compounds. No absorbances assigned to molybdenum hydride stretching frequencies were observed by IR spectroscopy of complexes **4a**−**d**. Comparison of the IR spectra for Cp*(dmpe)Mo(H)($SiPh_2$) (**4d**) and Cp*(dmpe)Mo-(D)($SiPh_2$) (**4d**-$d_1$, synthesized by reaction of **2** with $Ph_2SiD_2$) resulted in no detectable differences, indicating that any absorbances due to vibrational modes involving the metal hydride or deuteride in these compounds are very weak.

**Structural Studies of Dialkylsilylene Complexes.** Further characterization of the molecular structures of these silylene complexes involved analysis by single-crystal X-ray diffraction. Details of the data collection are listed in Table 2, and an ORTEP diagram of **4a** is shown in Figure 1. Selected bond

(12) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

***Table 1.*** Selected NMR Data and Colors of Silylene Complexes **4a**−**d** and **5a**−**c**

| silylene complex | $\delta$, $^{29}Si\{^1H\}$ NMR | $J_{HSi}$ ($^1H$ NMR) | color |
|---|---|---|---|
| Cp*(dmpe)Mo(H)($SiMe_2$), **4a** | 263 | 30 Hz | red |
| Cp*(dmpe)Mo(H)($SiEt_2$), **4b** | 273 | 44 Hz | red |
| Cp*(dmpe)Mo(H)(SiMePh), **4c** | 214 | 46 Hz | purple |
| Cp*(dmpe)Mo(H)($SiPh_2$), **4d** | 242 | 37 Hz | red-purple |
| Cp*(dmpe)Mo(H)(SiHPh), **5a** | 250 | 30 Hz | yellow-black |
| Cp*(dmpe)Mo(H)(SiHMes), **5b** | 214 | 48 Hz | purple |
| Cp*(dmpe)Mo(H)($SiHCH_2Ph$), **5c** | 239 | 42 Hz | purple |

***Table 2.*** Details of Crystallographic Data Collection

| compound | **4a** | **4b** (X-ray) | **4b** (neutron) | **5a** | **7** | **8** |
|---|---|---|---|---|---|---|
| empirical formula | $C_{18}H_{38}MoP_2Si$ | $C_{20}H_{42}MoP_2Si$ | $C_{20}H_{42}MoP_2Si$ | $C_{22}H_{38}MoP_2Si$ | $C_{28}H_{46}MoP_2Si_2$ | $C_{23}H_{48}MoP_2Si_2$ |
| fw | 440.47 | 468.53 | 468.53 | 488.52 | 596.73 | 538.69 |
| cryst size ($mm^3$) | 0.20 × 0.17 × 0.11 | 0.28 × 0.25 × 0.18 | 2 × 1 × 1 | 0.22 × 0.16 × 0.15 | 0.14 × 0.10 × 0.02 | 0.20 × 0.18 × 0.10 |
| color | red | red | red | yellow-black | yellow | orange |
| cryst syst | monoclinic | monoclinic | monoclinic | orthorhombic | monoclinic | monoclinic |
| space group | $P2_1/m$ (No. 11) | $P2_1/n$ (No. 14) | $P2_1/n$ (No. 14) | *Pnma* (No. 62) | $P2_1/c$ (No. 14) | $P2_1/n$ (No. 14) |
| $a$ (Å) | 8.7648(9) | 8.700(1) | 8.615(3) | 14.111(1) | 15.894(1) | 9.0505(5) |
| $b$ (Å) | 13.714(1) | 17.233(1) | 17.087(5) | 12.242(1) | 10.642(1) | 14.5815(8) |
| $c$ (Å) | 9.811(1) | 16.333(1) | 16.187(6) | 14.001(1) | 17.582(1) | 21.9795(12) |
| α (deg) | 90 | 90 | 90 | 90 | 90 | 90 |
| $\beta$ (deg) | 109.383(1) | 102.332(1) | 102.49(3) | 90 | 95.083(3) | 96.229(1) |
| $\gamma$ (deg) | 90 | 90 | 90 | 90 | 90 | 90 |
| $V$ ($Å^3$) | 1112.5(2) | 2392.2(3) | 2326.6(14) | 2418.54(7) | 2962.2(2) | 2883.5(3) |
| $Z$ | 2 | 4 | 4 | 4 | 4 | 4 |
| temp (K) | 171(1) | 144(1) | 20(1) | 143(1) | 116(1) | 128(1) |
| radiation | X-ray | X-ray | neutron | X-ray | X-ray | X-ray |
| $R$ | 0.048 | 0.032 | 0.085 | 0.030 | 0.072 | 0.043 |
| wR2 | 0.124 | 0.088 | 0.135 | 0.076 | 0.168 | 0.100 |
| $R_{all}$ | 0.130 | 0.037 | − | 0.041 | 0.151 | 0.112 |
| GOF | 1.12 | 1.15 | 1.44 | 0.91 | 0.99 | 1.05 |

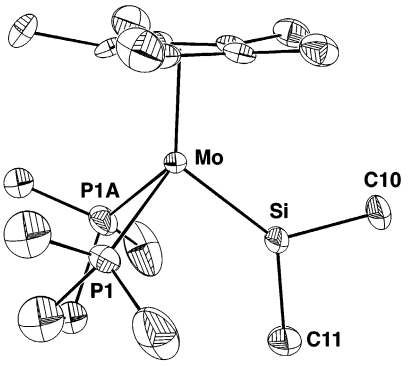


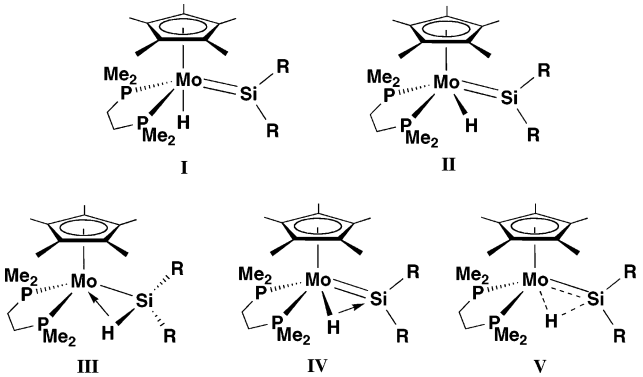

***Figure 1.*** ORTEP diagram of dimethylsilylene complex **4a**.

***Table 3.*** Selected Bond Distances (Angstroms) and Angles (deg) for **4a**

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Mo−Si | 2.315(2) | Mo−C3 | 2.362(4) |
| Mo−P1 | 2.377(1) | Si−C10 | 1.896(7) |
| Mo−Cl | 2.326(5) | Si−C11 | 1.892(7) |
| Mo−C2 | 2.321(4) | | |
| Bond Angles | | | |
| P1−Mo−P1A | 76.87(6) | Mo−Si−C10 | 127.3(2) |
| P1−Mo−Si | 93.98(5) | Mo−Si−C11 | 133.2(3) |
| C10−Si−C11 | 99.5(3) | | |

distances and angles from the structure are given in Table 3. A crystallographic mirror plane bisects the molecule, and two Cp* carbon atoms, the molybdenum, silicon, and silicon−methyl carbon atoms reside on the mirror plane. The molybdenum−silicon bond distance of 2.315(2) Å is considerably shorter than other reported Mo−Si distances, which fall into the range of 2.412(1)−2.670(2) Å (Cambridge Structural Database).

***Chart 1***




The crystallographic mirror plane for crystals of **4a** results in a disorder of the dmpe ligand, which cannot adopt a conformation that is consistent with this mirror symmetry. Thus, the zigzag conformation of the dmpe ligand backbone is disordered over two possible orientations. This disorder was modeled by refining the dmpe backbone carbon at 50% occupancy over two positions. In addition, one of the phosphorus methyl groups is disordered. It was refined over two positions at 50% occupancy. For clarity, only one conformation of the dmpe ligand is shown in Figure 1.

Crucial ambiguities that arise in the analysis of the structure of **4a** are the location of the hydride ligand and its proximity to the silicon center. The hydride ligand was not located in the Fourier difference electron density map, and therefore its absolute location is unknown. Five possible representations of the structure for this complex are shown in Chart 1. Structure type **I** features a hydride ligand positioned approximately trans to the centroid of the Cp* ligand. This structure would conform

to the observed mirror symmetry in the solid state, but is inconsistent with a hydrogen−silicon bonding interaction, as implied by the $J_{HSi}$ coupling constant. The silylene ligand is oriented such that its p orbital is directed away from the vicinity of the metal hydride in structure **I**, and this geometry would not likely produce a $J_{HSi}$ value as high as 30 Hz. In structure **II**, the hydride ligand is one of the four "legs" of a four-legged piano stool-type structure. Structure type **II** would also appear to be a poor description of **4a**, since it does not feature an Si−H bonding interaction. Structure **III** describes an α-agostic hydrosilyl complex, which features a formal Si−H bond. However, the planarity at the silicon center in the solid-state structure and the low-field shift of its $^{29}$Si NMR resonance in solution imply more silylene character and therefore argue against this depiction of the structure. Another relevant structure may be described as a silylene hydride complex in which the hydride ligand donates electron density to the electrophilic silicon center (structure **IV**). Related interactions have been proposed to describe short hydrogen−silicon contacts in silyl hydride complexes.[13] The planarity at silicon in the solid state, the short molybdenum−silicon bond distance, the significantly downfield-shifted $^{29}$Si NMR resonance, and a relatively weak H···Si bonding interaction for **4a** favor the latter two descriptions, with structure type **IV** being perhaps most important. This view may be simply described by structure **V**, which represents a hybrid of the two structures possessing a silicon−hydrogen interaction (**III** and **IV**). However, the proposed structure **V** would not have mirror symmetry. A reasonable hypothesis is that the hydride ligand is disordered over bridging positions on both sides of the Mo−Si bond, and that the heavier atoms (carbon, phosphorus, molybdenum, and silicon) conform to the crystallographically imposed mirror symmetry.

It is, of course, possible that two or more of these structures are quite close in energy and in fast exchange with one another in solution. Variable temperature NMR spectroscopy reveals a low-symmetry structure for **4a** at −50 °C in toluene-$d_8$. For example, two separate resonances are observed by $^{31}$P{$^1$H} NMR spectroscopy at $\delta$ 76.2 and 74.1 ($J_{PP}$ = 28 Hz). Although the dmpe methyl groups are nonequivalent by $^1$H NMR spectroscopy at this temperature, the silicon−methyl groups remain symmetry-equivalent. The $J_{HSi}$ value does not change over the temperature range of −75 to 50 °C, and it is difficult to ascertain the nature of this exchange process. This behavior could be simply explained by a "freezing out" of the conformational exchange of the dmpe molybdenum ring. The same behavior is observed for diethylsilylene complex **4b**. Even at −80 °C, the $^{13}$C {$^1$H} NMR spectrum of **4b** exhibits a symmetry-equivalent set of ethyl groups.

X-ray diffraction data were also collected for a dark red crystal of the diethylsilylene complex **4b**. An ORTEP diagram of **4b** (Figure 2) reveals a structural model that is distinctly different from that of **4a**. The hydride ligand of **4b** was located as the largest peak in the residual electron density map, and its coordinates were refined. The hydride was located in a bridging position across the molybdenum−silicon bond and resides in the wedge between Si and P2. The P−Mo−Si angles of 101.44(3)° and 86.88(3)° reveal that this complex is far from mirror-symmetric and that it has a structure of type **V** in Chart 1. The

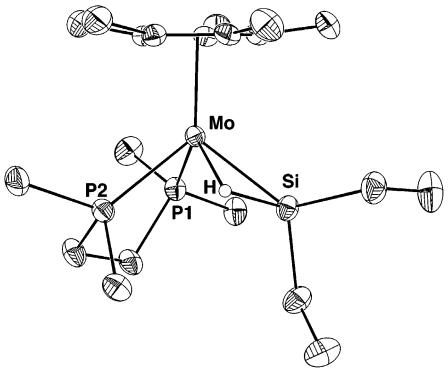



***Figure 2.*** ORTEP diagram of diethylsilylene complex **4b**.

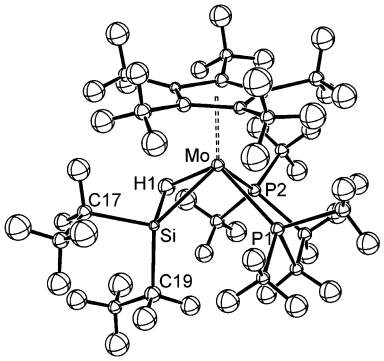



***Figure 3.*** ORTEP diagram from the neutron structure of diethylsilylene complex **4b**.

***Table 4.*** Selected Bond Distances (Angstroms) and Angles (deg) for **4b** from Neutron Diffraction Data at 20 K

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Mo−Si | 2.343(10) | Si−C19 | 1.899(11) |
| Mo−H | 1.847(12) | Mo−P1 | 2.399(9) |
| Si−H1 | 1.683(13) | Mo−P2 | 2.395(9) |
| Si−C17 | 1.873(10) | | |
| Bond Angles | | | |
| Mo−H−Si | 83.0(6) | C17−Si−H1 | 102.0(6) |
| H−Mo−Si | 45.5(4) | C19−Si−H1 | 114.5(6) |
| Mo−Si−H1 | 51.5(4) | Si−Mo−P1 | 87.1(3) |
| Mo−Si−C17 | 125.3(5) | Si−Mo−P2 | 101.9(4) |
| Mo−Si−C19 | 131.5(5) | P1−Mo−P2 | 77.4(3) |
| C17−Si−C19 | 102.1(5) | | |

Mo−Si bond distance in **4b** (2.348(7) Å) is similar to the short Mo−Si separation observed in the structure of **4a**.

Single-crystal neutron diffraction is a useful tool for accurately determining locations of hydrogen atoms in molecular structures. Therefore, neutron data were collected for a large (2 mm$^3$) dark red crystal of **4b**. The sample was later determined to contain a second crystallite. The two components were indexed separately with their respective orientation matrixes. In general, observed peaks were indexed for one or the other crystallite, but not for both. Attempts to refine the 42 hydrogen atoms with anisotropic thermal ellipsoids led to nonpositive definite ellipsoids for two of the hydrogen atoms. Therefore, in the final refinement all the atoms were refined isotropically. An ORTEP diagram of the structure of **4b**, as determined by neutron diffraction, is shown in Figure 3, and bond distances and angles are given in Table 4.

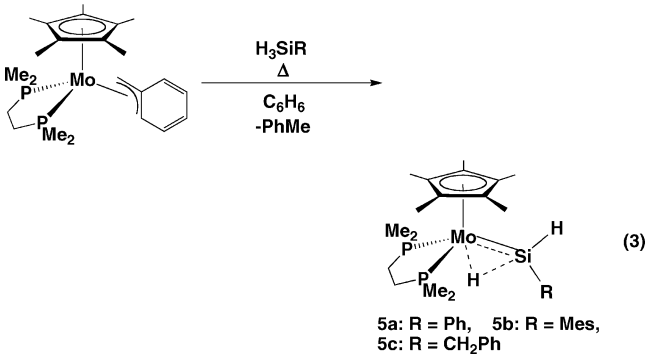
The structure derived from the neutron data unequivocally determines the location of the hydride ligand of **4b** to be in a bridging position associated with the molybdenum−silicon

(13) Nikonov, G. I. *Organometallics* **2003**, *22*, 1597 and references therein.

bond. The molybdenum−hydrogen separation of 1.85(1) Å is approximately 15 pm longer than those observed in the structures of $Cp_2MoH_2$ (Mo−H = 1.685(3) Å)[14] and (2,6-$Me_2C_6H_3$($^i$Pr)N)$_2$($\eta^2$-2,6-$Me_2C_6H_3$N═$CMe_2$)MoH[15] (Mo−H = 1.69(5) Å). The silicon−hydrogen separation of 1.68(1) Å is approximately 20 pm longer than 1.48 Å, the average value observed in hydrosilanes.[12]

For comparison, the only other complex characterized by neutron diffraction that features a metal−hydrogen−silicon three-center bonding interaction is the compound ($\eta^5$-$C_5H_4$Me)-(CO)$_2$(H)Mn(SiFPh$_2$), which was reported by Schubert and coworkers.[16] This complex features a long silicon−hydrogen distance of 1.802(5) Å and a manganese−hydrogen bond length of 1.569(4) Å. The structure of this species has been described as representing an "arrested" stage of oxidative addition of the silicon−hydrogen bond to the Mn center.

**Reactions of Complex 2 with Monosubstituted Silanes.** Silylene complexes featuring hydride substituents at silicon are rare, and very little is known about the chemistry of the Si−H bonds at sp$^2$ hybridized silicon centers. Hydrosilylene complexes have been generated and studied in situ, but none have been isolated and structurally characterized.[4d,j] It is therefore noteworthy that reactions of **2** with the monosubstituted silanes $PhSiH_3$, $MesSiH_3$, and $PhCH_2SiH_3$ resulted in formation of the hydrosilylene complexes Cp*(dmpe)Mo(H)Si(H)R (**5a**: R = Ph, **5b**: R = Mes, **5c**: R = $CH_2$Ph), as shown in eq 3.




Spectroscopic data for complexes **5a**−**c** are consistent with their descriptions as silylene hydride complexes with significant hydrogen−silicon bonding interactions. For example, the phenylsilylene complex **5a** exhibits a downfield-shifted triplet resonance in its $^{29}$Si{$^1$H} NMR spectrum at $\delta$ 250 ($J_{SiP}$ = 26 Hz). Silylene character at the silicon centers of **5b** and **5c** is also implied by downfield-shifted $^{29}$Si NMR resonances at $\delta$ 214 and 239, respectively. Significant features of the $^1$H NMR spectrum of **5a** are the Si−H and bridging Mo−H resonances at $\delta$ 9.45 and −9.96, respectively. The Si−H resonance is a multiplet coupled to the molybdenum-bound hydride ligand ($J_{HH}$ = 3 Hz) and the phosphorus nuclei ($J_{HP}$ = 3 Hz). This resonance exhibits $^{29}$Si satellites with a $J_{HSi}$ value of 130 Hz. The molybdenum hydride resonance is observed as a doublet of triplets with silicon satellites ($J_{HP}$ = 19 Hz, $J_{HH}$ = 3 Hz, $J_{HSi}$ = 30 Hz). Selected data for these complexes are also included in Table 1. Infrared spectroscopy of complexes **5a** and **5b** revealed Si−H stretching absorbances at 1896 and 1948 cm$^{-1}$, respectively. The metal hydride stretching absorbances were not detected for complexes **5a** and **5b**. Compounds **5a** and **5b** were isolated by recrystallization from pentane in 69 and 60% yields, respectively. Benzylsilylene complex **5c** was isolated as a purple sticky solid and could not be obtained as an analytically pure material. Reactions of **2** with the hydrosilanes $C_6F_5SiH_3$ and $SiH_4$ resulted in decomposition to mixtures of unidentified products.

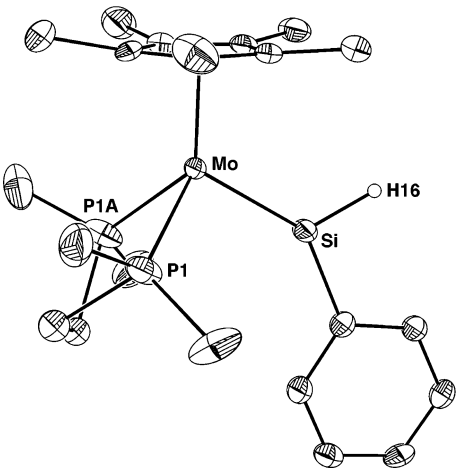


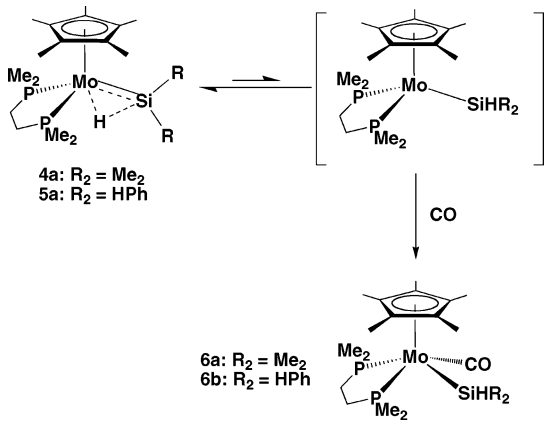

***Figure 4.*** ORTEP diagram of phenylsilylene complex **5a**.

Phenylsilylene complex **5a** was isolated as black-yellow crystals by recrystallization from pentane, and its structure was determined by an X-ray diffraction study. An ORTEP diagram of the structure is shown in Figure 4. A crystallographically imposed mirror plane bisects the molecule, as in the structure of **4a**. This results in the same disorder in the dmpe ligand conformation, and this disorder was modeled accordingly. For clarity, only one orientation of the dmpe ligand is shown in Figure 4. The molybdenum hydride ligand was not located in the final Fourier difference electron density map, although it probably interacts with the silicon center in a three-center two-electron fashion, as is clearly the case in the structure of **4b**. A peak for the terminal silicon hydride was located in the electron density map, and its position was refined to a location on the mirror plane 1.43(4) Å from the silicon center. This is in the expected range of Si−H bond distances for organosilanes and metal−hydrosilyl complexes (the average Si−H distance in hydrosilanes is approximately 1.48 Å).[12] The Mo−Si distance of 2.317(1) Å is quite short and is in keeping with the descriptions of these species as having significant silylene character.

**Reactions of Molybdenum Silylene Complexes with CO.** As further characterization of these new silylene complexes, their reactions with carbon monoxide were examined. An excess (approximately 5 equiv at 1 atm) of carbon monoxide was introduced to a red benzene solution of Cp*(dmpe)Mo(H)-($SiMe_2$). After 5 min, the solution changed color to yellow-orange, and a new product had formed by $^{31}$P{$^1$H} NMR spectroscopy ($\delta$ 60.5, 54.4; $J_{PP}$ = 20 Hz). The new compound, isolated by recrystallization from toluene, was characterized as the silyl carbonyl complex Cp*(dmpe)(CO)MoSiHMe$_2$ (**6a**, Scheme 3). This species is a CO adduct of the putative 16-electron silyl intermediate [Cp*(dmpe)MoSiHMe$_2$], and its

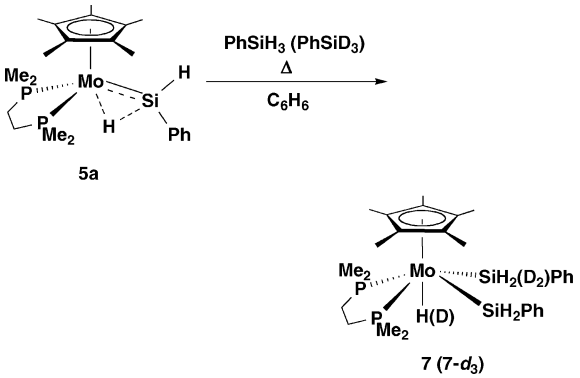
(14) Schultz, A. J.; Stearley, K. L.; Williams, J. M.; Mink, R.; Stucky, G. D. *Inorg. Chem.* **1977**, *12*, 3303.
(15) Tsai, Y.-C.; Johnson, M. J. A.; Mindiola, D. J.; Cummins, C. C. *J. Am. Chem. Soc.* **1999**, *121*, 10426.
(16) (a) Schubert, U.; Ackermann, K.; Wörle, B. *J. Am. Chem. Soc.* **1982**, *104*, 7378. (b) Schubert, U.; Scholz, G.; Müller, J.; Ackermann, K.; Wörle, B.; Stansfield, R. F. D. *J. Organomet. Chem.* **1986**, *306*, 303.

*Scheme 3*




formation suggests the possibility of reversible hydride migration from silicon to molybdenum, as shown in Scheme 3. The same result was observed in the reaction of phenylsilylene complex **5a** with CO to give the phenylsilyl compound **6b** (Scheme 3). Characteristic data for complexes **6a** and **6b** include their $^{29}$Si{$^1$H} NMR shifts at $\delta$ 21 and 16, respectively. In addition, the complexes exhibit CO stretching frequencies at 1781 and 1788 cm$^{-1}$, respectively. Carbon−oxygen stretching frequencies of such low energy indicate that the molybdenum centers are quite electron-rich and strongly $\pi$-back-donating.

**Reaction of 5a with PhSiH$_3$.** Phenylsilylene complex **5a** was found to react with 1 equiv of PhSiH$_3$ at 60 °C over 14 h in benzene solution. As the reaction progressed, the solution changed from the black-yellow color of **5a** to the light yellow color of the new product. Isolation and spectroscopic characterization of this product identified it as the bis(silyl) hydride complex Cp*(dmpe)(H)Mo(SiH$_2$Ph)$_2$ (**7**, eq 4). Compound **7** possesses $C_s$ symmetry by $^{31}$P{$^1$H} NMR spectroscopy, and its proton NMR spectrum features resonances for a single Mo−H and four Si−H hydrogens. The hydride ligand resonance ($\delta$ −7.27, $J_{HP}$ = 40 Hz) does not feature observable silicon satellites, and therefore $J_{HSi} \leq 10$ Hz. This suggests that there is little or no bonding interaction between the hydride and the two silicon centers in **7**. A single resonance at $\delta$ 10.1 is observed for the symmetry-equivalent silicon centers in the $^{29}$Si{$^1$H} NMR spectrum of **7**, implying silyl character for the silicon-based ligands.




(4)

A deuterium-labeling study was performed by reaction of **5a** with PhSiD$_3$ over 14 h at 60 °C in benzene. The product of this reaction was the deuterated species Cp*(dmpe)(D)Mo(SiD$_2$Ph)(SiH$_2$Ph) (**7**-$d_3$). The $^2$H{$^1$H} NMR spectrum of **7**-$d_3$ exhibits a triplet resonance for the molybdenum deuteride at $\delta$ −7.30 ($J_{DP}$ = 6 Hz), as well as a broad resonance for the −SiD$_2$Ph group at $\delta$ 4.97. The isotopomer that is formed in this reaction appears to result from Si−D bond activation of PhSiD$_3$ by an intermediate 16-electron molybdenum silyl complex. Thus, this reaction also proceeds via the initial migration of hydrogen from molybdenum to silicon.

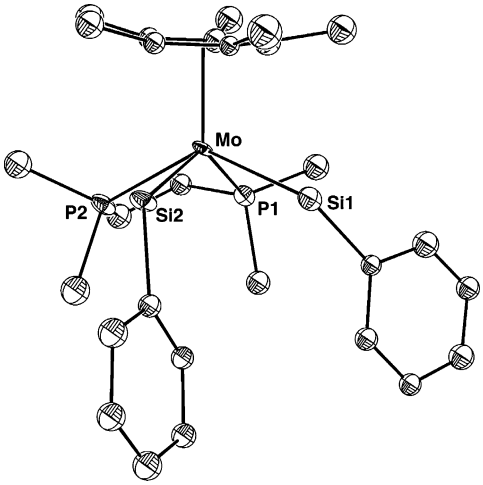



***Figure 5.*** ORTEP diagram of bis(silyl) complex **7**.

***Table 5.*** Selected Bond Distances (Angstroms) and Angles (deg) for **7**[a]

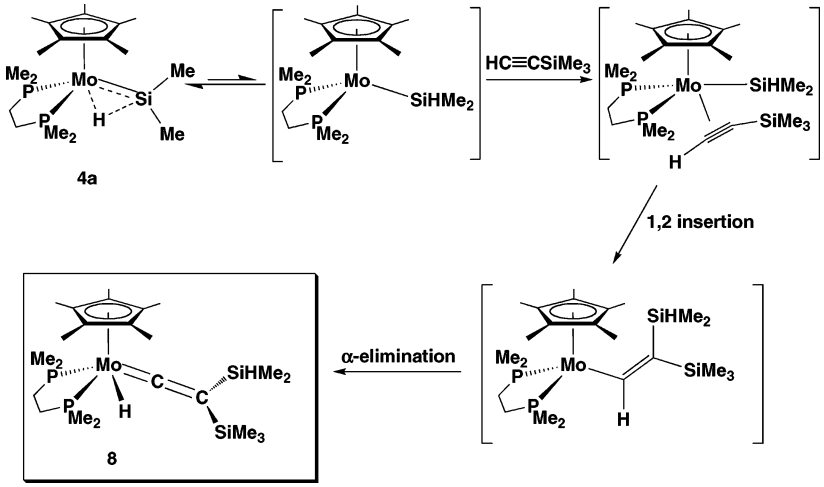
| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Mo−Si1 | 2.504(3) | Mo−Si2 | 2.531(3) |
| Mo−P1 | 2.447(3) | Mo−P2 | 2.480(3) |
| Bond Angles | | | |
| P1−Mo−P2 | 75.7(1) | Si1−Mo1−Si2 | 78.1(1) |
| P1−Mo−Si1 | 89.5(1) | P1−Mo−Si2 | 134.6(1) |
| P2−Mo−Si1 | 131.4(1) | P2−Mo−Si2 | 80.5(1) |
| CNT−Mo−P1 | 116.5(3) | CNT−Mo−P2 | 118.4(3) |
| CNT−Mo−Si1 | 109.7(3) | CNT−Mo−Si2 | 108.8(3) |

[a] The abbreviation CNT represents the centroid of the C$_5$Me$_5$ ligand.

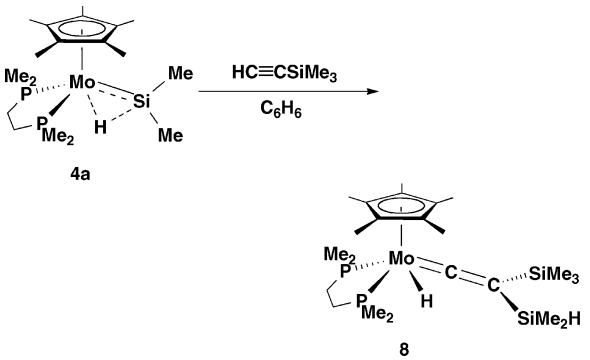
Yellow, X-ray quality crystals of the bis(silyl) hydride complex **7** were obtained by recrystallization from toluene, and the structure of **7** was determined by X-ray diffraction techniques. An ORTEP diagram of complex **7** is shown in Figure 5, and selected bond distances and angles are listed in Table 5. Although the molybdenum hydride ligand was not located in the electron density map, it might be located in the open coordination site trans to the Cp* ligand. This five-legged piano stool geometry has precedent in complexes such as Cp*WMe$_5$[17] and [WCl$_4$(PMe$_3$)]$_2$($\eta^5$,$\eta^5$-C$_5$Et$_4$CH$_2$CH$_2$C$_5$Et$_4$).[18] Unfortunately, determination of the silicon−hydrogen bond distances of interest was not possible by neutron diffraction, since crystals of complex **7** were too small and thin. The X-ray diffraction data collected for this complex were somewhat weak, and this resulted in a low data-to-parameter ratio for the model refinement. The final model included anisotropically refined Mo, Si, and P atoms, while the carbon atoms were refined isotropically. Although accurate metric parameters could not be obtained for the structure of **7**, the data unambiguously determine the connectivity of the complex and its identity as a bis(silyl) species.

(17) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282.
(18) MacLaughlin, S. A.; Murray, R. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1985**, *4*, 796.

***Scheme 4***




**Reactions of Silylene Complexes with Unsaturated Organic Compounds.** It was of interest to define the reactivity of these new silylene complexes toward unsaturated organic substrates. In reactions of complexes **4a** and **5a** with benzaldehyde and benzophenone, decomposition to unidentified mixtures of products was observed. No clean compounds could be isolated from these mixtures by crystallization from pentane or toluene at −30 °C over 12 h. Complexes **4a** and **5a** were found to be unreactive toward stoichiometric or excess amounts of bis(trimethylsilyl)acetylene, diphenylacetylene, ethylene, and 1-hexene at room temperature. In each reaction, heating the mixture to 100 °C resulted in decomposition to a complex mixture of products. However, a clean transformation *was* observed in the reaction of complex **4a** with the terminal alkyne $Me_3SiC{\equiv}CH$ in benzene solution. Recrystallization of the new product from diethyl ether resulted in orange crystals of the vinylidene complex Cp*(dmpe)(H)Mo=C=C($SiMe_3$)($SiMe_2H$) (**8**, eq 5). Interestingly, this is the first observation of a reaction that transforms a silylene complex into a carbene-like complex.




(5)

Spectroscopic data for **8** are in agreement with its description as a vinylidene hydride complex. The $^1$H NMR spectrum of **8** features a triplet resonance for the molybdenum hydride ligand at $\delta$ −7.34 ($J_{HP}$ = 34 Hz). Compound **8**, like the silylene complexes reported here, exhibits $C_s$ symmetry by NMR spectroscopy at room temperature. The $^{13}C\{^1H\}$ NMR spectrum of **8** exhibits characteristic resonances for the $C_\alpha$ and $C_\beta$ carbons of the vinylidene ligand at $\delta$ 317.9 (triplet, $J_{CP}$ = 12 Hz) and 92.5 (singlet), respectively.

Given the observed structures for the molybdenum silylene hydride complexes described above, it was of interest to determine whether the vinylidene complex **8** possesses a hydrogen-α-carbon interaction. This issue was addressed by acquiring a proton-coupled $^{13}$C NMR spectrum and observing the resonance for $C_\alpha$. The $^{13}$C NMR spectrum of complex **8** displays a multiplet resonance for $C_\alpha$ ($J_{CP}$ = 13 Hz, $J_{CH}$ = 13 Hz). A $J_{CH}$ coupling constant of 13 Hz is much lower than would be expected for a significant bonding interaction between $C_\alpha$ and the hydride ligand.[19]

The mechanism of the reaction that forms **8** would seem to involve multiple steps, though no intermediates were observed when the reaction was monitored by $^1$H and $^{31}P\{^1H\}$ NMR spectroscopy at room temperature. A plausible mechanism for this transformation is shown in Scheme 4 and involves coordination of the alkyne to the intermediate 16-electron silyl complex as a first step. Insertion of the alkyne into the metal−silicon bond and subsequent α-elimination of the vinyl hydrogen would result in the observed product **8**. The closely related vinylidene complex Cp[P($OMe_3$)]$_2$BrMo=C=C(H)Ph was reported by Green et al. and was formed by a mechanism involving nucleophilic attack of a hydride on coordinated 1-bromo-2-phenylacetylene in the cation {Cp[P(OMe)$_3$]$_2$Mo-($\eta^2$-PhC≡CBr)}$^+$.[20]

The structure of vinylidene complex **8** was verified by an X-ray diffraction study, and an ORTEP diagram of the complex is shown in Figure 6. Table 6 lists selected bond distances and angles for the structure. The short Mo−C17 bond distance (C17 = $C_\alpha$) of 1.920(4) Å and the Mo−C17−C18 angle of 171.5(3)° support the formulation of **8** as a vinylidene complex. The hydride ligand was located as a peak in the Fourier difference electron density map, and its coordinates were refined to a location 1.52(8) Å from the molybdenum center. The H−C17 distance of 1.723 Å is much longer than that of a typical C−H bond (approximately 1.0 Å), and this also indicates the absence of an Mo−H···$C_\alpha$ interaction.

**Reactions of Complex 4a with Lewis Bases.** Most of the reported base-free silylene complexes are electrophilic at silicon and bind Lewis bases at their silicon centers.[4] In fact, many silylene complexes have only been isolated in their base-

(19) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.
(20) (a) Beevor, R. G.; Greem, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1983**, *673*. (b) Beevor, R. G.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1319.

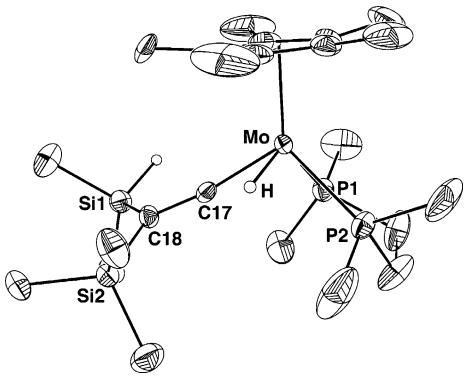



***Figure 6.*** ORTEP diagram of vinylidene complex **8**.

***Table 6.*** Selected Bond Distances (Angstroms) and Angles (deg) for **8**

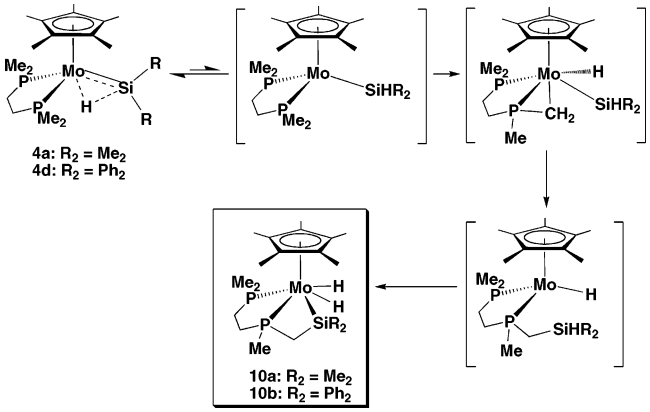
| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Mo−C17 | 1.920(4) | C17−C18 | 1.345(5) |
| Mo−P1 | 2.408(1) | C18−Si1 | 1.840(4) |
| Mo−P2 | 2.407(1) | C18−Si2 | 1.865(4) |
| Mo−H | 1.52(8) | | |
| Bond Angles | | | |
| P1−Mo−P12 | 76.23(4) | P1−Mo−H | 121(3) |
| P1−Mo−C17 | 86.2(1) | P2−Mo−H | 71(3) |
| P2−Mo−C17 | 105.0(1) | C17−Mo−H | 59(3) |

stabilized forms.[1,21] To explore the electronic properties of the silylene complexes reported here, the interactions of silylene complex **4a** with the Lewis bases THF and DMAP were examined (DMAP = 4-(dimethylamino)pyridine). When 1 equiv of THF was added to a solution of dimethylsilylene complex **4a** in benzene-$d_6$, there was no apparent change in color of the red solution. Analysis of NMR spectra of this mixture revealed that the THF does not bind to **4a** under these conditions. The chemical shift of the $^{29}$Si NMR resonance for the mixture is exactly the same as for **4a** in the absence of THF ($\delta$ 263).

Addition of 1 equiv of DMAP to a benzene-$d_6$ solution of **4a** resulted in an immediate color change to a darker red. The spectral data of this solution are consistent with the formation of the base-stabilized silylene complex Cp*(dmpe)Mo(H)-($SiMe_2$·DMAP) (**9**). The $^1$H NMR spectrum of compound **9** features a resonance for its hydride ligand at −12.92 (triplet, $J_{HP}$ = 20 Hz). The $^1$H, $^{29}$Si HMBC NMR spectrum of **9** exhibits a cross-peak for the hydride ligand resonance at $\delta$ 179 ($J_{SiH}$ = 17 Hz). In comparison with the attempted reaction of **4a** with THF, it seems that the stronger donor DMAP coordinates to the dimethylsilylene silicon center. However, the $^{29}$Si NMR resonance is significantly downfield-shifted, indicating significant silylene character for complex **9**. It seems that the DMAP ligand is only weakly bound to the silicon center, and **9** appears to be in rapid equilibrium with **4a** and free DMAP.

**Thermal Rearrangements of 4a and 4d.** Thermal decompositions proceeded cleanly for **4a** and **4d**. Heating a benzene solution of **4a** at 100 °C for 4 h quantitatively produced a new product. This species exhibits two doublet resonances in the $^{31}$P{$^1$H} NMR spectrum, at $\delta$ 59.5 and 39.6 ($J_{PP'}$ = 18 Hz). Careful analysis of the $^1$H NMR spectrum of the new product revealed resonances for three inequivalent PMe groups, as well as two inequivalent silicon−methyl groups. The NMR data therefore suggest that the new product resulted from a reaction involving one of the dmpe methyl groups. The chemical shift of the $^{29}$Si{$^1$H} NMR resonance ($\delta$ 9.0) is consistent with a molybdenum silyl complex. Taken together, the spectroscopic data are in keeping with the structure Cp*($\kappa^3$-$Me_2PCH_2$-$CH_2P(Me)CH_2SiMe_2$)$MoH_2$ (**10a**, Scheme 5), in which the silylene and dmpe fragments have been coupled to form a tridentate bis(phosphine)silyl ligand. A plausible mechanism for this rearrangement involves initial C−H activation of a dmpe methyl group. Subsequent C−Si bond reductive elimination followed by Si−H bond oxidative addition would give the observed product (Scheme 5).

***Scheme 5***




The structure of complex **10a** was confirmed by an X-ray diffraction study. Although the solution verifies the connectivity proposed for **10a**, the structure contains a significant amount of positional disorder in the Cp* and $Me_2PCH_2CH_2P(Me)CH_2$-$SiMe_2$ ligands. The data are not of sufficient quality to obtain a good model for this disorder, and therefore accurate metric parameters for **10a** could not be derived from the analysis. Stobart and co-workers have published related examples of transition-metal complexes containing bis(phosphine)silyl ligands.[22]

A thermal rearrangement was also observed for diphenylsilylene complex **4d** at 100 °C in benzene, and the new complex exhibits a $^{29}$Si NMR resonance at $\delta$ −3.4. The product exhibited $^1$H, $^{13}$C{$^1$H}, $^{31}$P{$^1$H}, and NMR spectra very similar to those of **10a** and was therefore characterized as the diphenyl analogue of **10a**, Cp*($\kappa^3$−$Me_2PCH_2CH_2P(Me)CH_2SiPh_2$)$MoH_2$ (**10b**). For comparison, the hydrosilylene complexes **5a** and **5b** do not decompose cleanly at 110 °C over a few hours.

## Concluding Remarks

These investigations highlight the utility of a coordinatively unsaturated transition-metal alkyl complex as a starting point for the synthesis of molybdenum silylene complexes. Benzyl complex **2** reacts with a series of hydrosilanes to give a new class of neutral, base-free silylene complexes. These species are remarkably stable, and their thermal decompositions are observed only at temperatures above 100 °C.

The compounds **4a**−**d** and **5a**−**c** are best described as silylene hydride complexes that feature weak H···Si bonding interactions

(21) See, for example: (a) Leis, C.; Wilkinson, D. L.; Handwerker, H. Zybill, C. *Organometallics* **1992**, *11*, 514. (b) Sakaba, H.; Tsukamoto, M.; Hirata, T.; Kabuto, C.; Horino, H. *J. Am. Chem. Soc.* **2000**, *122*, 11511. (c) Ueno, K.; Sakai, M.; Ogino, H. *Organometallics* **1998**, *17*, 2138.

(22) See, for example: (a) Zhou, X.; Stobart, S. R. *Organometallics* **2001**, *20*, 1898. (b) Bushnell, G. W.; Casado, M. A.; Stobart, S. R. *Organometallics* **2001**, *20*, 601.

in their ground-state structures. The $^{29}$Si NMR resonances for these complexes fall in the range of $\delta$ 213−273. These chemical shifts, taken with the planar geometries observed for the $MoSiR_2$ fragments in their solid-state structures, provide support for their formulation as silylene complexes. However, the combination of high $J_{HSi}$ coupling constants (in the range of 30−48 Hz) and the bridging hydride ligand in the solid-state neutron structure of **4b** provides good evidence for the presence of weak hydrogen−silicon bonding interactions in this class of compounds. Therefore, it is suitable to describe these silylene compounds with the structural model depicted by structure **V** in Chart 1. This structure is intermediate between a silylene hydride complex with a hydride silicon donor interaction and one with entirely α-agostic hydrosilyl character (structures **IV** and **III** in Chart 1, respectively). These compounds are the first examples of base-free molybdenum silylene complexes and represent an important step in expanding silylene chemistry to the early transition elements. These complexes may be considered as possessing molybdenum(II), $d^4$ metal centers. Alternatively, in the extreme case of complete scission of the Si−H bond and very strong $\pi$-back-bonding to the silylene ligand they could be classified as having molybdenum(IV), $d^2$ metal centers. As most of the known examples of silylene complexes feature late transition elements with six or more d-electrons, these molybdenum silylenes are rare in that they have a relatively low $d^n$ electron configuration.

The observed reactions of silylene complexes of the type Cp*-(dmpe)Mo(H)(SiRR') are dominated by initial α-hydrogen migrations to form 16-electron silyl species, Cp*(dmpe)-MoSiHRR'. This suggests that the silylene hydride and 16-electron silyl complexes are in rapid equilibrium, with the latter species being more reactive. This reactivity mode is also consistent with the observation of significant hydrogen−silicon interactions in the ground-state structures of the silylene complexes. Thus, these complexes act as resting states for reactive, coordinatively unsaturated silyl compounds. Future studies will involve use of the synthetic methodology described here in the synthesis of early metal silylene complexes without hydride ligands. Such complexes should allow further characterization of the chemistry of silylene complexes with low $d^n$ configurations.

## Experimental Section

**General.** All experiments were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or in a drybox. Pentane and ether were distilled from sodium/benzophenone, and benzene was distilled from potassium. Toluene was pretreated with $H_2SO_4$, $NaHCO_3$, and $MgSO_4$ to remove trace thiophene impurities and then distilled from sodium. To remove olefin impurities, pentane was pretreated with concentrated $H_2SO_4$, 0.5 N $KMnO_4$ in 3M $H_2SO_4$, $NaHCO_3$, and then anhydrous $MgSO_4$. Benzene-$d_6$ and toluene-$d_8$ were distilled from Na/K alloy. The reagents $Cp^*MoCl_4$,[11] 1,2-bis(dimethylphosphino)ethane,[23] $MesSiH_3$,[24] $PhSiH_3$,[25] and $Ph_2CH_2SiH_3$[25] were synthesized according to published procedures. Other chemicals were obtained from commercial suppliers and used as received. Elemental analyses were performed by the Microanalytical Laboratory in the College of Chemistry at the University of California, Berkeley. FT-infrared spectra were recorded as KBr pellets on a Mattson FTIR 3000 instrument.

**NMR Measurements.** Routine $^1$H, $^{13}$C{$^1$H}, $^{31}$P{$^1$H}, and $^{29}$Si{$^1$H} NMR spectra were recorded at 298 K on either a Bruker DRX-500 instrument equipped with a 5 mm broad band probe and operating at 500.1 MHz ($^1$H), 125.8 MHz ($^{13}$C), 202.5 MHz ($^{31}$P), and 99.4 MHz ($^{29}$Si), or a Bruker AMX-400 instrument operating at 400.1 MHz ($^1$H) or 100.6 MHz ($^{13}$C). Chemical shifts are reported in ppm downfield from internal $SiMe_4$ ($^1$H, $^{13}$C, $^{29}$Si), and external 85% $H_3PO_4$ ($^{31}$P); coupling constants are given in Hz. Bruker XWINNMR software (ver. 2.1) was used for all data processing.

**X-ray Crystallography.** All single-crystal X-ray analyses were carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements were made on a Bruker SMART CCD area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Data were integrated by the program SAINT and analyzed for agreement using XPREP. Empirical absorption corrections were made using SADABS. Structures were solved by direct methods and expanded using Fourier techniques. Calculations for all structures were performed using the SHELX-TL software package. Details of data collections and refinements are given in Table 2 and in the supporting CIF files.

**Neutron Crystallography.** Neutron diffraction data were obtained at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory using the time-of-flight Laue single-crystal diffractometer (SCD).[26] A crystal of compound **4b** with approximate dimensions of 2 × 1 × 1 mm$^3$ was covered in a fluorocarbon grease in a glovebag, wrapped in aluminum foil, and glued to an aluminum pin, which was mounted on the cold stage of a closed-cycle helium refrigerator operating at 20 ± 0.1 K for data collection. The GSAS software package was used for structural analysis.[27] Data collection and refinement parameters are summarized in Table 2, with details provided in the supporting CIF files.

**$Cp^*(dmpe)(PMe_3)MoCl$ (1).** A slurry of $Cp^*MoCl_4$ (5.00 g, 13.4 mmol) in 100 mL of benzene was added to a rapidly stirring mixture of $PMe_3$ (1.39 mL, 13.4 mmol), dmpe (2.24 mL, 13.4 mmol), and 94 g Na/Hg (1.0% w/w) in 100 mL of benzene. Stirring was continued for 16 h at 60 °C, and then the mixture was allowed to cool to room temperature. The purple-red solution was filtered to remove salts, and the benzene was removed under reduced pressure to give 5.85 g of **1** as a purple solid in 89% yield. The crude product was pure by $^1$H NMR spectroscopy and was of sufficient purity for further use. Analytically pure **1** can be obtained by recrystallization from pentane. $^1$H NMR (benzene-$d_6$): $\delta$ 1.64 (s, 15 H, $C_5Me_5$), 1.47 (d, 3 H, P*Me*, $J_{HP}$ = 8 Hz), 1.35 (d, 3 H, P*Me*, $J_{HP}$ = 8 Hz), 1.29 (d, 9 H, P$Me_3$, $J_{HP}$ = 7 Hz), 1.15 (d, 3 H, P*Me*, $J_{HP}$ = 7 Hz), 0.94 (d, 3 H, P*Me*, $J_{HP}$ = 7 Hz). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 98.7 (s, $C_5Me_5$), 36.9 (m, P*Me*), 27.2 (dd, P$CH_2$, $J_{CP}$ =23 Hz, $J_{CP'}$ = 7 Hz), 25.1 (dd, P$CH_2$, $J_{CP}$ = 23 Hz, $J_{CP'}$ = 17 Hz), 24.5 (m, P*Me*), 21.4 (m, P*Me*), 21.2 (d, P$Me_3$, $J_{CP}$ = 20 Hz), 19.4 (m, P*Me*), 12.7 (s, $C_5Me_5$). $^{31}$P{$^1$H} NMR (benzene-$d_6$): $\delta$ 66.0 (dd, $J_{PP'}$ = 30 Hz, $J_{PP''}$ = 22 Hz), 61.2 (dd, $J_{PP'}$ = 59 Hz, $J_{PP''}$ = 30 Hz), 13.3 (dd, $J_{PP'}$ = 59 Hz, $J_{PP''}$ = 22 Hz). IR (KBr, cm$^{-1}$) 2972 m, 2946 w, 2902 s, 1462 w, 1415 m, 1371 m, 1296 w, 1263 m, 1076 w, 1024 m, 933 s, 912, s, 897 s, 833 m, 802 w, 690 m, 659 w, 631 m, 453 w. Anal. Calcd for $C_{19}H_{40}ClMoP_3$: C, 46.31; H, 8.18. Found: C, 46.14; H, 8.37.

**$Cp^*(dmpe)Mo(\eta^3\text{-}CH_2Ph)$ (2).** A solution of 9.74 mmol of $PhCH_2$-MgCl (1.0 M in $Et_2O$) was added dropwise over 10 min to a stirred solution of 4.80 g (9.74 mmol) of **1** in 200 mL of benzene. Upon addition, the mixture changed color from red-purple to red-orange. Stirring was continued for 1 h, and a precipitate was observed. The mixture was then allowed to settle, and the supernatant was filtered into another flask. The remaining salts were washed with benzene (2

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(24) (a) Malisch, W.; Hindahl, K.; Käb, H.; Reising, J.; Adam, W.; Prechtl, F. *Chem. Ber.* **1995**, *128*, 9632. (b) Söldner, M.; Sandor, M.; Schier, A.; Schmidbaur, H. *Chem. Ber.* **1997**, *130*, 1671.
(25) Sakurai, H.; Shoji, M.; Yajima, M.; Hosomi, A. *Synthesis* **1984**, *7*, 598.
(26) Schultz, A. J.; Srinivasan, K.; Teller, R. G.; Williams, J. M.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 999−1003.
(27) Larson, A. C.; Von Dreele, R. B. *General Structure Analysis System--GSAS*. Los Alamos National Laboratory: Report LAUR 86-748, 2000.

× 10 mL), and the filtrates were combined. Removal of the solvent under reduced pressure gave crude **2** as an orange-brown solid. Recrystallization from 40 mL of toluene at −80 °C over 14 h gave 3.91 g of **2** (85% yield). $^1$H NMR (benzene-$d_6$, 23 °C): $\delta$ 7.13 (s br, 1 H, Ar-*H*), 7.03 (s br, 1 H, Ar-*H*), 6.58 (t, 1 H, Ar-*H*, $J_{HH}$ = 7 Hz), 6.25 (s br, 1 H, Ar-*H*), 2.80 (m br, 1 H, PhC$H_2$), 2.70 (s br, 1 H, Ar-*H*), 1.70 (s, 15 H, $C_5Me_5$), 1.48 (s br, 3 H, P*Me*), 1.3 (br, 2 H, PC$H_2$), 1.10 (s br, 3 H, P*Me*), 0.98 (s br, 3 H, P*Me*), 0.8 (br, 2 H, PC$H_2$), 0.62 (s br, 3 H, P*Me*), −0.54 (s br, 1 H, PhC$H_2$). $^1$H NMR (toluene-$d_8$, −20 °C): 7.09 (m, 1 H, Ar-*H*), 6.98 (m, 1 H, Ar-*H*), 6.56 (m, 1 H, Ar-*H*), 6.24 (m, 1 H, Ar-*H*), 2.76 (dd, 1 H, PhC$H_2$, $J_{HP}$ = 13 Hz, $J_{HH}$ = 3 Hz), 2.60 (d, 1 H, Ar-*H*, $J_{HH}$ = 6 Hz), 1.69 (s, 15 H, $C_5Me_5$), 1.47 (d, 3 H, P*Me*, $J_{HP}$ = 6 Hz), 1.3 (m br, 1 H, PC$H_2$), 1.09 (d, 3 H, P*Me*, $J_{HP}$ = 5 Hz), 1.0 (m br, 1 H, PC$H_2$), 0.99 (d, 3 H, P*Me*, $J_{HP}$ = 7 Hz), 0.82 (m, 1 H, PC$H_2$), 0.75 (m, 1 H, PC$H_2$), 0.58 (d, 3 H, P*Me*, $J_{HP}$ = 6 Hz), −0.62 (m, 1 H, PhC$H_2$). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 23 °C): $\delta$ 139.1, 135.5, 122.4, 120.6, 98.2 (s, *Ar*), 95.9 (s, $C_5$Me$_5$), 66.2 (s, *Ar*, Mo-bound), 36.9 (s, Ar$CH_2$), 29.8 (s br, P$CH_2$), 28.0 (s br, P$CH_2$), 25.2, 23.2, 21.0, 14.4 (s, P*Me*), 12.7 (s, $C_5Me_5$). $^{31}$P {$^1$H} NMR (benzene-$d_6$, 23 ° C): $\delta$ 63.8 (s), 61.2 (s). IR (KBr, cm$^{-1}$): 3027 w, 2979 m, 2964 m, 2905 s, 2854 m, 1587 w, 1508 w, 1463 w, 1410 m, 1371 m, 1354 w, 1286 m, 1269 m, 1082 m, 1022 m, 926 s, 897 m, 825 w, 764 w, 727 s, 701 m, 683 m, 623 w, 604 w. Anal. Calcd for $C_{23}H_{38}MoP_2$: C, 58.47; H, 8.11. Found: C, 58.39; H, 8.22.

**Cp*(dmpe)(CO)MoCH$_2$Ph (3).** A solution of 0.170 g (0.360 mmol) of **2** in 5 mL of benzene was placed under an excess (approximately 5 equiv) of CO at 1 atm. The mixture was heated at 60 °C for 1 h, and this resulted in a light orange solution. The volatile materials were removed under reduced pressure, and the product was redissolved in 5 mL of diethyl ether. The ether solution was concentrated to approximately 1 mL and placed in the freezer at −30 °C for 3 d. Orange crystals of **3** were isolated in 21% yield (0.038 g) by decanting the supernatant and drying the product under vacuum. The yield of **3** is low because of its high solubility. $^1$H NMR (benzene-$d_6$): $\delta$ 7.13 (m, 2 H, Ar-*H*), 7.06 (m, 2 H, Ar-*H*), 6.94 (m, 1 H, Ar-*H*), 2.37 (s, 2 H, PhC$H_2$), 1.68 (s, 15 H, $C_5Me_5$), 1.54 (d, 3 H, P*Me*, $J_{HP}$ = 10 Hz), 1.4 (m br, 1 H, PC$H_2$), 1.3 (m br, 1 H, PC$H_2$), 1.15 (d, 3 H, P*Me*, $J_{HP}$ = 8 Hz), 1.0 (m, 1 H, PC$H_2$), 0.89 (d, 3 H, P*Me*, $J_{HP}$ = 8 Hz), 0.8 (m, 1 H, PC$H_2$), 0.38 (d, 3 H, P*Me*, $J_{HP}$ = 9 Hz). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 253.2 (m, *C*O), 165.8, 147.4, 146.2, 143.3 (*Ar*), 100.4 (s, $C_5$-Me$_5$), 34.4 (dd, P$CH_2$, $J_{CP}$ = 31 Hz, $J_{CP'}$ = 19 Hz), 30.4 (m, P$CH_2$), 21.5 m, Ph$CH_2$), 21.2 (m, P*Me*), 19.8 (m, P*Me*), 17.0 (m, P*Me*), 15.3 (m, P*Me*), 12.2 (s, $C_5Me_5$). $^{31}$P{$^1$H} NMR (benzene-$d_6$): $\delta$ 54.1 (d, $J_{PP}$ = 26 Hz), 42.9 (d, $J_{PP}$ = 26 Hz). IR (KBr, cm$^{-1}$): 3046 w, 2963 w, 2901 m, 2861 w, 1779 s ($\nu_{CO}$), 1572 w, 1553 w, 1478 m, 1421 m, 1374 m, 1278 m, 1024 w, 932 m, 893 m, 835 w, 798 m, 766 w, 712 w, 689 m, 653 m, 577 w, 516 w. Anal. Calcd for $C_{24}H_{38}MoOP_2$: C, 57.60; H, 7.65. Found: C, 57.65; H, 7.73.

**Cp*(dmpe)Mo(H)(SiMe$_2$) (4a).** A 50-mL Schlenk flask was charged with 0.350 g (0.741 mmol) of **2** and 10 mL of benzene. The headspace above the solution was evacuated briefly and then backfilled with 1 atm of $Me_2SiH_2$. The reaction mixture was agitated for a few seconds to draw $Me_2SiH_2$ into solution. The flask was then sealed and heated to 50 °C for 15 min. The benzene was removed in vacuo, and the resulting solid was extracted into 20 mL of pentane. The red solution was filtered into another Schlenk flask and concentrated to 3 mL under reduced pressure. Cooling the concentrated solution at −30 °C for 20 h gave 0.165 g (51% yield) of **4a** as dark red crystals. A second crop of crystals raised the total yield to 0.271 g (83% yield). $^1$H NMR (benzene-$d_6$): $\delta$ 2.02 (s, 15 H, $C_5Me_5$), 1.5 (m, 4 H, 2 PC$H_2$), 1.35 (m, 6 H, 2 P*Me*), 1.06 (m, 6 H, 2 P*Me*), 0.67 (d, 6 H, Si*Me*$_2$, $J_{HH}$ = 2 Hz), −14.06 (t, 1 H, Mo-*H*, $J_{HP}$ = 17 Hz, $J_{HSi}$ = 30 Hz). $^1$H NMR (toluene-$d_8$, 223 K): $\delta$ 2.06 (s, 15 H, $C_5Me_5$), 1.65 (m, 1 H, PC$H_2$), 1.55 (m, 1 H, PC$H_2$), 1.48 (d, 3 H, P*Me*, $J_{HP}$ = 7 Hz), 1.38 (m, 1 H, PC$H_2$), 1.22 (m, 3 H, P*Me*, $J_{HP}$ = 6 Hz), 1.19 (d, 3 H, P*Me*, $J_{HP}$ = 5 Hz), 1.08 (m, 1 H, PC$H_2$), 0.93 (d, 3 H, P*Me*, $J_{HP}$ = 5 Hz), −14.04 (m, 1 H, Mo*H*, $J_{HSi}$ = 30 Hz). $^{13}$C {$^1$H} NMR (benzene-$d_6$): $\delta$ 98.3 (s, $C_5$Me$_5$), 34.8 (m br, 2 P*Me*), 33.9 (m br, 2 P*Me*), 23.2 (m, br 2 P$CH_2$), 19.8 (s, Si*Me*$_2$), 14.1 (s, $C_5Me_5$). $^{31}$P {$^1$H} NMR (benzene-$d_6$): $\delta$ 70.2 (s). $^{31}$P {$^1$H} NMR (toluene-$d_8$, 223 K): $\delta$ 76.2 (d, $J_{PP}$ = 28 Hz), 74.1 (d, $J_{PP}$ = 28 Hz). $^{29}$Si {$^1$H} NMR (benzene-$d_6$): $\delta$ 263 (m). IR (KBr, cm$^{-1}$): 2955 s, 2898 s br, 2803 m, 1548 m br, 1480 w, 1453 w, 1416 m, 1370 m, 1268 m, 1219 m, 1063 w, 1025 m, 924 s br, 826 s, 731 m, 686 m, 654 s, 624 m, 457 w. Anal. Calcd for $C_{18}H_{38}MoP_2Si$: C, 49.08; H, 8.70. Found: C, 49.09; H, 8.56.

**Cp*(dmpe)Mo(H)(SiEt$_2$) (4b).** Diethylsilane (0.045 g, 0.508 mmol) and 0.200 g (0.423 mmol) of **2** were dissolved in 5 mL of benzene. The mixture was heated at 50 °C for 15 min, and the solution changed color to red. The product was isolated by the same method as for **4a**, which gave 0.133 g of red crystals of **4b** in 67% yield. $^1$H NMR (benzene-$d_6$): $\delta$ 2.02 (s, 15 H, $C_5Me_5$), 1.5 (m br, 4 H, 2 PC$H_2$), 1.38 (m, 6 H, 2 P*Me*), 1.11 (s, 6 H, 2 SiCH$_2$C$H_3$), 1.1 (br, 4 H, 2 SiC$H_2$-CH$_3$), 1.06 (m, 6 H, 2 P*Me*), −13.91 (t, 1 H, Mo-*H*, $J_{HP}$ = 17 Hz, $J_{HSi}$ = 44 Hz). $^1$H NMR (toluene-$d_8$, −80 °C): $\delta$ 2.00 (s, 15 H, $C_5Me_5$), 1.8 (m, 1 H, PC$H_2$), 1.5 (m, 1 H, PC$H_2$), 1.45 (d, 3 H, P*Me*, $J_{HP}$ = 7 Hz), 1.31 (m, 1 H, PC$H_2$), 1.2 (m br, 4 H, 2 SiC$H_2$), 1.18 (d, 3 H, P*Me*, $J_{HP}$ = 6 Hz), 1.17 (m, 6 H, 2 SiCH$_2$C$H_3$), 1.09 (d, 3 H, P*Me*, $J_{HP}$ = 6 Hz), 0.9 (m, 1 H, PC$H_2$), 0.84 (d, 3 H, P*Me*, $J_{HP}$ = 5 Hz), −13.9 (dd, Mo-*H*, $J_{HP}$ = 25 Hz, $J_{HP'}$ = 5 Hz). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 23 °C): $\delta$ 98.5 (s, $C_5$Me$_5$), 35.1 (m, 2 P*Me*), 35 (br, 2 P$CH_2$), 23.6 (s, 2 Si$CH_2$), 23.4 (m, 2 P*Me*), 14.1 (s, $C_5Me_5$), 8.5 (s, 2 SiCH$_2$CH$_3$). $^{13}$C-{$^1$H} NMR (toluene-$d_8$, −80 °C): $\delta$ 97.9 (s, $C_5$Me$_5$), 35.5 (m, P$CH_2$), 35.3 (m, P*Me*), 32.9 (m, P$CH_2$), 32.6 (P*Me*), 23.3 (m, P*Me*), 23.2 (br, 2 Si$CH_2$), 21.8 (m, P*Me*), 14.1 (s, $C_5Me_5$), 8.7 (s, 2 SiCH$_2$CH$_3$). $^{31}$P-{$^1$H} NMR (benzene-$d_6$, 23 °C): $\delta$ 71.3 (s). $^{31}$P{$^1$H} NMR (toluene-$d_8$, −80 °C): $\delta$ 72.0 (d, $J_{PP}$ = 28 Hz), 69.9 (d, $J_{PP}$ = 28 Hz). $^{29}$Si{$^1$H} NMR (benzene-$d_6$, 23 °C): $\delta$ 273 (m). IR (KBr, cm$^{-1}$): 2944 s, 2897 s, 2865 s, 1482 w, 1454 w, 1415 m, 1370 m, 1284 w, 1268 m, 1220 w, 1025 m, 927 s, 882 m, 826 m, 703 m, 675 m, 621 m, 590 w, 454 w. Anal. Calcd for $C_{20}H_{42}MoP_2Si$: C, 51.27; H, 9.04. Found: C, 51.41; H, 9.04.

**Cp*(dmpe)Mo(H)(SiMePh) (4c).** Phenylmethylsilane (0.052 g, 0.423 mmol) and 0.200 g (0.423 mmol) of **2** were dissolved in 5 mL of benzene. The mixture was heated at 50 °C for 15 min, and the solution changed color to burgundy. The product was isolated by the same method as for **4a**, which gave 0.132 g of purple microcrystalline **4c** in 62% yield. $^1$H NMR (benzene-$d_6$): $\delta$ 7.44 (m, 2H, *o-Ph*), 7.25 (t, 2 H, *m-Ph*, $J_{HH}$ = 7 Hz), 7.12 (m, 1 H, *p-Ph*), 1.91 (s, 15 H, $C_5Me_5$), 1.49 (m, 4 H, 2 PC$H_2$), 1.45 (m, 6 H, 2 P*Me*), 1.04 (m, 6 H, 2 P*Me*), 0.78 (d, Si*Me*, $J_{HH}$ = 2 Hz), −13.10 (t, 1 H, Mo-*H*, $J_{HP}$ = 17 Hz, $J_{HSi}$ = 46 Hz). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 156.5, 130.5, 127.5, 127.0 (s, *Ph*), 98.6 (s, $C_5$Me$_5$), 34.5 (m, 2 P$CH_2$), 33.8 (m, 2 P*Me*), 23.3 (m, 2 P*Me*), 21.2 (s, Si*Me*), 13.9 (s, $C_5Me_5$). $^{31}$P{$^1$H} NMR (benzene-$d_6$): $\delta$ 69.9 (s). $^{29}$Si{$^1$H} NMR (benzene-$d_6$): $\delta$ 214 (t, $J_{SiP}$ = 25 Hz). IR (cm$^{-1}$): 3059 w, 3043 w, 2959 m, 2898 s, 1480 w, 1422 m, 1372 m, 1284 w, 1270 m, 1225 w, 1092 m, 1062 w, 1025 m, 932 s, 901 m, 830 w, 781 m, 728 w, 701 s, 666 m, 479 m, 434 m. Anal. Calcd for $C_{23}H_{40}$-$MoP_2Si$: C, 54.79; H, 8.03. Found: C, 54.98; H, 8.18.

**Cp*(dmpe)Mo(H)(SiPh$_2$) (4d).** Diphenylsilane (0.078 g, 0.423 mmol) and 0.200 g (0.423 mmol) of **2** were dissolved in 5 mL of benzene. The mixture was heated at 50 °C for 15 min, and the solution changed color to burgundy. The product was isolated by the same method as for **4a**, which gave 0.138 g of purple microcrystalline **4d** in 58% yield. $^1$H NMR (benzene-$d_6$): $\delta$ 7.54 (m, 4 H, *o-Ph*), 7.18 (m, 4 H, *m-Ph*), 7.07 (m, 2 H, *p-Ph*), 1.88 (s, 15 H, $C_5Me_5$), 1.52 (m, 6 H, 2 P*Me*), 1.49 (m, 2 H, 2 PC$H_2$), 1.35 (m, 2 H, 2 PC$H_2$), 1.00 (m, 6 H, 2 P*Me*), −11.36 (t, 1 H, Mo*H*, $J_{HP}$ = 18 Hz, $J_{HSi}$ = 37 Hz). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 154.7, 131.9, 127.5, 127.2 (s, *Ph*), 98.6 (s, $C_5$-Me$_5$), 34.3 (m, 2 P*Me*), 33.3 (m, 2 P$CH_2$), 23.3 (m, 2 P*Me*), 13.8 (s, $C_5Me_5$). $^{31}$P{$^1$H} NMR (benzene-$d_6$): $\delta$ 70.0 (s). $^{29}$Si{$^1$H} NMR (benzene-$d_6$): $\delta$ 242 (t, $J_{SiP}$ = 24 Hz). IR (cm$^{-1}$): 3056 w, 3041 w, 2980 m, 2961 m, 2945 m, 2899 s, 1476 w, 1421 m, 1372 w, 1269 m,

1091 m, 1026 w, 927 s, 896 w, 740 w, 726 w, 701 s, 681 m, 628 w, 513 s, 464 m. Anal. Calcd for $C_{28}H_{42}MoP_2Si$: C, 59.56; H, 7.50. Found: C, 59.81; H, 7.70.

**Cp*(dmpe)Mo(D)(SiPh$_2$) (4d-*d*$_1$).** Complex **2** (0.020 g, 0.042 mmol) and $Ph_2SiD_2$ (0.0078 g, 0.042 mmol) were combined in 0.4 mL of benzene-$d_6$, and the tube was heated at 50 °C for 20 min. The $^1$H NMR spectrum of **4-*d*$_1$** is identical to that of **4** except for the absence of a resonance for the hydride ligand. The reaction is quantitative by $^1$H and $^{31}$P NMR spectroscopy. $^2$H{$^1$H} NMR (benzene-$d_6$): $\delta$ −11.45 (t, $J_{DP}$ = 3 Hz). $^{31}$P{$^1$H} NMR (benzene-$d_6$): $\delta$ 69.5 (s). The $J_{PD}$ coupling is not resolved in the $^{31}$P{$^1$H} NMR spectrum of **4d-*d*$_1$**.

**Cp*(dmpe)Mo(H)Si(H)Ph (5a).** Phenylsilane (0.058 g, 0.54 mmol) and **2** (0.250 g, 0.529 mmol) were dissolved in 6 mL of benzene, and the solution was heated at 50 °C for 15 min, resulting in a brown solution. The benzene was removed under reduced pressure, and the resulting solid was extracted into 10 mL of pentane. Filtration of the pentane solution removed a small amount of insoluble impurities. The solution was then concentrated in vacuo to 2 mL and placed in the freezer at −30 °C for 14 h, and this resulted in crystallization of 0.179 g of dark green crystals of complex **5a** (69% yield). $^1$H NMR (benzene-$d_6$): $\delta$ 9.45 (m, 1 H, Si*H*, $J_{Hsi}$ = 130 Hz, $J_{HH}$ = 3 Hz, $J_{HP}$ = 3 Hz), 8.09 (d, 2 H, *o-Ph*, $J_{HH}$ = 7 Hz), 7.32 (t, 2 H, *m-Ph*, $J_{HH}$ = 7 Hz), 7.19 (m, 1 H, *p-Ph*), 2.01 (s, 15 H, $C_5$*Me*$_5$), 1.47 (m, 4 H, 2 PC*H*$_2$), 1.44 (m, 6 H, 2 P*Me*), 1.02 (m, 6 H, 2 P*Me*), −9.96 (td, 1 H, Mo-*H*, $J_{HP}$ = 19 Hz, $J_{HH}$ = 3 Hz, $J_{HSi}$ = 30 Hz). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 151.8, 135.2, 128.6, 127.9 (s, *Ph*), 98.0 (s, *C*$_5$Me$_5$), 34.8 (m, 2 P*C*H$_2$), 30.8 (m, 2 P*Me*), 22.1 (m, 2 P*Me*), 13.8 (s, $C_5$*Me*$_5$). $^{31}$P{$^1$H} NMR (benzene-$d_6$): $\delta$ 63.5 (s). $^{29}$Si{$^1$H} NMR (benzene-$d_6$): $\delta$ 250 (t, $J_{SiP}$ = 26 Hz). IR (cm$^{-1}$): 3056 w, 2960 m, 2891 s, 1896 s ($\nu_{SiH}$), 1475 w, 1413 m, 1375 m, 1286 w, 1273 m, 1088 m, 1062 w, 1026 w, 931 s, 885 s, 831 w, 735 m, 700 m, 683 m, 636 m, 474 w. Anal. Calcd for $C_{22}H_{38}MoP_2Si$: C, 54.10; H, 7.84. Found: C, 54.11; H, 7.87.

**Cp*(dmpe)Mo(H)Si(H)Mes (5b).** Mesitylsilane (0.064 g, 0.426 mmol) and 0.200 g (0.423 mmol) of **2** were dissolved in 5 mL of benzene. The mixture was heated at 50 °C for 15 min, and the solution changed color to purple. The product was isolated by the same method as for **5a**, which gave 0.134 g of purple crystals of **5b** in 60% yield. $^1$H NMR (benzene-$d_6$): $\delta$ 9.36 (s, 1 H, Si*H*, $J_{HSi}$ = 139 Hz), 6.82 (s, 2 H, Ar-*H*), 2.54 (s, 6 H, *o-Me*), 2.21 (s, 3 H, *p-Me*), 1.84 (s, 15 H, $C_5$*Me*$_5$), 1.65 (m, 4 H, 2 PC*H*$_2$), 1.45 (m, 6 H, 2 P*Me*), 1.04 (m, 6 H, 2 P*Me*), −13.08 (t, 1 H, Mo*H*, $J_{HP}$ = 17 Hz, $J_{HSi}$ = 48 Hz). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 146.3, 139.1, 137.0, 128.1 (s, *Ar*), 98.7 (s, *C*$_5$Me$_5$), 33.9 (m, 2 P*C*H$_2$), 32.5 (m, 2 P*Me*), 22.8 (m, 2 P*Me*), 22.6 (s, *o-Me*), 21.3 (s, *p-Me*), 13.3 (s, $C_5$*Me*$_5$). $^{31}$P{$^1$H} NMR (benzene-$d_6$): $\delta$ 66.5 (s). $^{29}$Si{$^1$H} NMR (benzene-$d_6$): $\delta$ 214 (t, $J_{SiP}$ = 26 Hz). IR (cm$^{-1}$): 2964 s, 2892 s, 2848 m, 1948 s ($\nu_{SiH}$), 1601 m, 1460 m, 1411 s, 1373 m, 1284 w, 1269 m, 1116 w, 1065 m, 1024 m, 929 s, 852 m, 838 s, 705 m, 682 m, 605 m, 457 m. Anal. Calcd for $C_{25}H_{45}MoP_2Si$: C, 56.49; H, 8.53. Found: C, 56.14; H, 8.36.

**Cp*(dmpe)Mo(H)Si(H)CH$_2$Ph (5c).** Benzylsilane (0.020 g, 0.164 mmol) and 0.075 g (0.159 mmol) of **2** were dissolved in 2 mL of benzene. The mixture was heated at 50 °C for 15 min, and the solution changed color to purple. The volatile materials were removed in vacuo, and the residue was redissolved in 3 mL of pentane. The resulting solution was filtered and then concentrated to approximately 0.3 mL under reduced pressure. The solution was cooled to −30 °C for 12 h, and complex **5c** was isolated as 0.41 g of a sticky solid (51% yield). The high solubility of the product made it difficult to separate from trace impurities. $^1$H NMR (benzene-$d_6$): $\delta$ 8.51 (t, 1 H, Si*H*, $J_{HH}$ = 3 Hz, $J_{HSi}$ = 138 Hz), 7.22 (m, 2 H, Ar-*H*), 7.11 (m, 2 H, Ar-*H*), 7.00 (m, 1 H, Ar-*H*), 2.59 (br, 2 H, C*H*$_2$Ph), 1.97 (s, 15 H, $C_5$*Me*$_5$), 1.5 (m br, 4 H, 2 PC*H*$_2$), 1.32 (m, 6 H, 2 P*Me*), 0.97 (m, 6 H, 2 P*Me*), −13.29 (t, 1 H, Mo*H*, $J_{HP}$ = 17 Hz, $J_{HSi}$ = 42 Hz). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 141.6, 128.7, 128.4, 123.9 (s, *Ar*), 98.9 (s, *C*$_5$Me$_5$), 42.9 (s, *C*H$_2$-Ph), 34.5 (t, 2 P*C*H$_2$, $J_{CP}$ = 23 Hz), 33.8 (dd, 2 P*Me*, $J_{CP}$ = 16 Hz, $J_{CP'}$ = 12 Hz), 22.4 (dd, 2 P*Me*, $J_{CP}$ = 8 Hz, $J_{CP'}$ = 5 Hz), 13.8 (s, C$_5$Me$_5$). $^{31}$P{$^1$H} NMR (benzene-$d_6$): $\delta$ 66.3 (s). $^{29}$Si{$^1$H} NMR (benzene-$d_6$): $\delta$ 239 (m). IR (KBr, cm$^{-1}$): 2961 m, 2898 s, 2857 m, 1979 m ($\nu_{SiH}$), 1597 w, 1490 m, 1418 m, 1373 w, 1271 w, 1202 w, 1113 m, 1027 m, 932 s, 859 s, 801 m, 754 m, 697 s, 630 w, 479 w.

**Cp*(dmpe)(CO)MoSiHMe$_2$ (6a).** The dimethylsilylene complex **4a** (0.100 g, 0.227 mmol) was dissolved in 4 mL of benzene in a 25 mL sealable flask, and the headspace was evacuated briefly. The flask was then backfilled with CO, and the mixture was agitated to dissolve the gas. The reaction vessel was sealed under 1 atm of CO, and the mixture was stirred at room temperature. After 5 min, the solution had changed color from dark red to orange-yellow. The volatiles were removed in vacuo, and the yellow product was extracted into 3 mL of toluene. Recrystallization from 1 mL of a concentrated toluene solution at −30 °C gave the silyl complex **6a** in 58% yield (0.062 g). $^1$H NMR (benzene-$d_6$): 4.87 (m, 1 H, Si*H*, $J_{HSi}$ = 162 Hz), 1.79 (s, 15 H, $C_5$*Me*$_5$), 1.51 (d, 3 H, P*Me*, $J_{HP}$ = 8 Hz), 1.25 (d, 3 H, P*Me*, $J_{HP}$ = 7 Hz), 1.2 (m, 2 H, 2 PC*H*$_2$), 1.0 (m, 2 H, 2 PC*H*$_2$), 0.98 (d, 3 H, P*Me*, $J_{HP}$ = 7 Hz), 0.92 (d, 3 H, Si*Me*, $J_{HH}$ = 3 Hz), 0.89 (d, 3 H, P*Me*, $J_{HP}$ = 6 Hz), 0.65 (d, 3 H, Si*Me*, $J_{HH}$ = 3 Hz). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 243.0 (m, *C*O), 98.5 (s, *C*$_5$Me$_5$), 31.9 (dd, P*C*H$_2$, $J_{CP}$ = 24 Hz, $J_{CP'}$ = 17 Hz), 31.4 (dd, P*C*H$_2$, $J_{CP}$ = 27 Hz, $J_{CP'}$ = 20 Hz), 23.5 (d, P*Me*, $J_{CP}$ = 20 Hz), 20.1 (d, P*Me*, $J_{CP}$ = 12 Hz), 19.3 (dd, P*Me*, $J_{CP}$ = 35 Hz, $J_{CP'}$ = 4 Hz), 17.3 (dd, P*Me*, $J_{CP}$ = 24 Hz, $J_{CP'}$ = 7 Hz), 12.0 (s, $C_5$*Me*$_5$), 5.4 (d, Si*Me*, $J_{CP}$ = 5 Hz), 3.6 (d, Si*Me*, $J_{CP}$ = 3 Hz). $^{31}$P{$^1$H} NMR (benzene-$d_6$): $\delta$ 60.5 (d, $J_{PP}$ = 20 Hz), 54.4 (d, $J_{PP}$ = 20 Hz). $^{29}$Si{$^1$H} NMR (benzene-$d_6$): $\delta$ 21 (dd, $J_{SiP}$ = 39 Hz, $J_{SiP'}$ = 8 Hz). IR (cm$^{-1}$): 2962 w, 2947 w, 2904 m, 1987 m ($\nu_{SiH}$), 1781 s ($\nu_{CO}$), 1478 w, 1421 w, 1374 w, 1228 w, 1089 w, 1025 w, 936 m, 904 m, 864 m, 823 w, 695 w, 627 w. Anal. Calcd for $C_{19}H_{38}MoOP_2Si$: C, 48.71, H, 8.18. Found: C, 48.90; H, 8.16.

**Cp*(dmpe)(CO)MoSiH$_2$Ph (6b).** This complex was prepared in the same manner as that used for **6a**. Recrystallization of the product from 1 mL of toluene at −30 °C gave 0.069 g of the molybdenum silyl **6b** (65% yield). $^1$H NMR (benzene-$d_6$): $\delta$ 8.16 (d, 2 H, *o-Ph*, $J_{HH}$ = 7 Hz), 7.26 (t, 2 H, *m-Ph*, $J_{HH}$ = 7 Hz), 7.16 (m, 1 H, *p-Ph*), 5.04 (m, 1 H, Si*H*, $J_{HSi}$ = 167 Hz), 5.00 (m, 1 H, Si*H*, $J_{HSi}$ = 159 Hz), 1.75 (s, 15 H, $C_5$*Me*$_5$), 1.55 (d, 3 H, $J_{HP}$ = 8 Hz), 1.18 (m, 1 H, PC*H*$_2$), 1.13 (m, 1 H, PC*H*$_2$), 1.06 (d, 3 H, P*Me*, $J_{HP}$ = 7 Hz), 1.04 (m, 1 H, PC*H*$_2$), 1.01 (d, 3 H, P*Me*, $J_{HP}$ = 8 Hz), 0.89 (d, 3 H, P*Me*, $J_{HP}$ = 7 Hz), 0.85 (m, 1 H, PC*H*$_2$). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 244.7 (m, *C*O), 145.3 (m, *i-Ph*), 137.1 s, *o-Ph*), 127.5 (s, *m-Ph*), 127.4 (s, *p-Ph*), 97.8 (s, *C*$_5$Me$_5$), 32.2 (dd, P*C*H$_2$, $J_{CP}$ = 25 Hz, $J_{CP'}$ = 19 Hz), 29.8 (dd, P*C*H$_2$, $J_{CP}$ = 25 Hz, $J_{CP'}$ = 19 Hz), 21.3 (dd, P*Me*, $J_{CP}$ = 11 Hz, $J_{CP'}$ = 3 Hz), 21.0 (dd, P*Me*, $J_{CP}$ = 34 Hz, $J_{CP'}$ = 3 Hz), 20.2 (dd, P*Me*, $J_{CP}$ = 14 Hz, $J_{CP'}$ = 1 Hz), 17.4 (dd, P*Me*, $J_{CP}$ = 26 Hz, $J_{CP'}$ = 5 Hz), 11.3 (s, $C_5$*Me*$_5$). $^{31}$P{$^1$H} NMR (benzene-$d_6$): $\delta$ 60.0 (d, $J_{PP}$ = 24 Hz), 50.9 (d, $J_{PP}$ = 24 Hz). $^{29}$Si{$^1$H} NMR (benzene-$d_6$): $\delta$ 16. IR (cm$^{-1}$): 2971 w, 2951 w, 2907 m, 2855 w, 2023 m ($\nu_{SiH}$), 1997 m ($\nu_{SiH}$), 1788 s ($\nu_{CO}$), 1478 w, 1424 w, 1374 w, 1294 w, 1281 w, 1094 w, 1027 w, 936 m, 830 s, 729 w, 703 w, 630 w, 544 w. Anal. Calcd for $C_{23}H_{38}MoOP_2Si$: C, 53.48, H, 7.42. Found: C, 53.86; H, 7.77.

**Cp*(dmpe)(H)Mo(SiH$_2$Ph)$_2$ (7).** A sealable flask was charged with 0.100 g (0.205 mmol) of **5a**, 0.024 g (0.225 mmol) of $PhSiH_3$, and 0.4 mL of benzene. The flask was heated in an oil bath at 60 °C for 14 h, and this produced a yellow-brown solution. The volatile materials were removed under reduced pressure, and the orange-red solid residue was washed twice with 3 mL of pentane to remove dark-colored impurities. The off-white solid was then dissolved in 10 mL of toluene. Concentration of this solution to 3 mL under vacuum and storage in the freezer at −30 °C for 18 h gave yellow crystals of **7**. Decanting the supernatant and drying the sample under vacuum gave 0.075 g of the product (61% yield). $^1$H NMR (benzene-$d_6$): $\delta$ 8.10 (d, 4 H, *o-Ph*, $J_{HH}$ = 8 Hz), 7.27 (t, 4 H, *m-Ph*, $J_{HH}$ = 8 Hz), 7.10 (m, 2 H, *p-Ph*), 5.00 (d, 2 H, Si*H*, $J_{HP}$ = 7 Hz, $J_{HSi}$ = 165 Hz), 4.97 (d, 2 H, Si*H*, $J_{HP}$ = 9 Hz, $J_{HSi}$ = 158 Hz), 1.59 (s, 15 H, $C_5$*Me*$_5$), 1.05 (m, 12 H, 4 P*Me*), 0.97 (m, 2 H, 2 PC*H*$_2$), 0.74 (m, 2 H, 2 PC*H*$_2$), −7.27 (t, 1 H, Mo*H*, $J_{HP}$ = 40

Hz). $^{13}C\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 150.0 (s, *i-Ph*), 137.4 (s, *o-Ph*), 127.3 (s, *m-Ph*), 127.1 (s, *p-Ph*), 93.5 (s, $C_5Me_5$), 31.1 (m, 2 P*C*H$_2$), 23.1 (m, 2 P*Me*), 16.8 (m, 2 P*Me*), 10.6 (s, $C_5$*Me*$_5$). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 47.5 (s). $^1H$, $^{29}Si$ HMQC NMR (benzene-$d_6$): $\delta$ ($^1H$, $^{29}Si$) 5.0 (m), 10.1. IR (cm$^{-1}$): 3054 w, 2997 w, 2955 w, 2095 m, 2043 m ($\nu_{SiH}$), 2020 s ($\nu_{SiH}$), 1989 m ($\nu_{SiH}$), 1478 w, 1424 w, 1375 w, 1088 w, 1025 w, 954 m, 939 m, 856 s, 832 s, 722 m, 699 m, 632 m, 531 w. Anal. Calcd for $C_{28}H_{46}MoP_2Si_2$: C, 56.36; H, 7.77. Found: C, 56.12; H, 7.88.

**Cp*(dmpe)(D)Mo(SiH$_2$Ph)(SiD$_2$Ph) (7-*d*$_3$).** A sealable flask was charged with 0.100 g (0.205 mmol) of **5a**, 0.025 g (0.225 mmol) of PhSiD$_3$, and 0.4 mL of benzene. The flask was heated in an oil bath at 60 °C for 14 h, and this gave a yellow-brown solution. The volatile materials were removed under reduced pressure, and the orange-red solid residue was washed twice with 3 mL of pentane to remove dark-colored impurities. The off-white solid was then dissolved in 10 mL of toluene. Concentration of this solution to 4 mL under vacuum and storage in the freezer at −30 °C for 12 h gave yellow crystals of **7-*d*$_3$**. Decanting the supernatant and drying the sample under vacuum gave 0.68 g of the product (55% yield). This complex's NMR spectra were analogous to those of the **7** with the predicted exceptions. For example, the $^1H$ NMR spectrum exhibited the two doublets for the Si*H*$_2$ group integrating to just one hydrogen atom each, and no Mo−H resonance was observed. In addition, the $^{31}P\{^1H\}$ NMR spectrum exhibits coupling to the deuterium nuclei. $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 47.5 (m). IR (cm$^{-1}$): 2043 w ($\nu_{SiH}$), 2018 m ($\nu_{SiH}$), 1992 w ($\nu_{SiH}$), 1486 w ($\nu_{SiD}$), 1466 m ($\nu_{SiD}$), 1450 w ($\nu_{SiD}$). $^2H\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 4.97 (br, Si*D*$_2$Ph), −7.30 (t br, Mo*D*, $J_{DP}$ = 6 Hz).

**Cp*(dmpe)(H)Mo=C=C(SiHMe$_2$)(SiMe$_3$) (8).** Dimethylsilylene complex **4a** (0.085 g, 0.193 mmol) was dissolved in 3 mL of benzene, and 0.095 g (0.97 mmol) of trimethylsilylacetylene was added to the solution. The red solution was stirred for 16 h, and the color changed to orange. The volatile material was removed under reduced pressure, and the product was dissolved in diethyl ether (2 mL). Crystallization from this concentrated solution at −30 °C for 14 h gave 0.060 g of **8** as orange crystals (58% yield). $^1H$ NMR (benzene-$d_6$): $\delta$ 4.69 (septet, 1 H, Si*H*, $J_{HH}$ = 3 Hz), 1.93 (s, 15 H, $C_5$*Me*$_5$), 1.39 (m, 6 H, 2 P*Me*), 1.22 (m, 2 H, 2 PC*H*$_2$), 1.09 (m, 2 H, 2 PC*H*$_2$), 1.08 (m, 6 H, 2 P*Me*), 6.27 (d, 6 H, Si*Me*$_2$H, $J_{HH}$ = 3 Hz), 0.37 (s, 9 H, Si*Me*$_3$), −7.34 (t, 1 H, Mo*H*, $J_{HP}$ = 34 Hz). $^{13}C\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 317.9 (t, Mo=*C*=C, $J_{CP}$ = 12 Hz), 100.4 (s, *C*$_5$Me$_5$), 92.5 (s, Mo=C=*C*), 32.2 (t, 2 P*C*H$_2$, $J_{CP}$ = 23 Hz), 23.9 (m, 2 P*Me*), 20.4 (m, 2 P*Me*), 12.8 (s, $C_5$*Me*$_5$), 2.2 (s, Si*Me*$_2$H, $J_{CSi}$ = 51 Hz), 0.4 (s, $J_{CSi}$ = 49 Hz). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 57.2. $^{29}Si\{^1H\}$ NMR (benzene-$d_6$): $\delta$ −9.9 (s, *Si*Me$_2$H), −18.2 (s, *Si*Me$_3$). IR (cm$^{-1}$): 2948 m, 2900 s, 2085 m ($\nu_{SiH}$), 1815 w ($\nu_{MoH}$), 1476 s, 1422 s, 1376 m, 1286 w, 1274 w, 1239 m, 1064 w, 1024 m, 929 s, 879 s, 828 s, 759 w, 718 w, 688 m, 642 m, 605 w. Anal. Calcd for $C_{23}H_{47}MoP_2Si_2$: C, 51.28; H, 8.98. Found: C, 51.35; H, 8.92.

**Cp*(dmpe)Mo(H)(SiMe$_2$·DMAP) (9).** To 0.015 g (0.0341 mmol) of complex **4a** in 0.5 mL of benzene-$d_6$ was added 0.0042 g (0.341 mmol) of DMAP. The mixture immediately became darker red in color, and the reaction was complete by $^1H$ NMR spectroscopy. The product was lyophilized from the benzene-$d_6$ under reduced pressure to give **9** as 0.018 g of an orange powder in 94% yield. $^1H$ NMR (benzene-$d_6$): $\delta$ 8.69 (m, 2 H, *o*-DMAP), 5.98 (m, 2 H, *m*-DMAP), 2.15 (s, 15 H, $C_5$*Me*$_5$), 2.10 (s, 6 H, N*Me*$_2$), 1.55 (m, 4 H, 2 PC*H*$_2$), 1.40 (d, 6 H, 2 P*Me*), 1.28 (d, 6 H, *2 PMe*), 0.72 (s, 6 H, Si*Me*$_2$), −12.93 (t, 1 H, Mo*H*, $J_{HP}$ = 20 Hz, $J_{HSi}$ = 17 Hz). $^{13}C\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 154.5 (s, *p*-DMAP), 149.1 (s, *o*-DMAP), 106.0 (s, *m*-DMAP), 96.3 (s, *C*$_5$Me$_5$), 38.2 (s, N*Me*$_2$), 35.1 (m br, 2 P*C*H$_2$), 32.0 (m br, 2 P*Me*), 24.5 (m br, 2 P*Me*), 18.5 (s, Si*Me*$_2$), 14.3 (s, $C_5$*Me*$_5$). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 70.3 (s br). $^1H$, $^{29}Si$ HMQC (benzene-$d_6$): $\delta$ ($^1H$, $^{29}Si$) −12.93, 179 ($J_{HSi}$ = 17 Hz). IR (KBr, cm$^{-1}$): 2955 m, 2896 s, 1836 w ($\nu_{MoH}$), 1621 m, 1603 s, 1537 m, 1524 m, 1445 w, 1418 w, 1376 m, 1273 w, 1224 s, 1065 w, 1014 m, 988 m, 919 s, 810 s, 778 m, 637 m, 623 m, 534 w, 504 w. Anal. Calcd for $C_{25}H_{48}N_2P_2MoSi$: C, 53.36; H, 8.60; N, 4.98. Found: C, 53.43; H, 8.47; N, 4.59.

**Cp*($\kappa^3$-Me$_2$PCH$_2$CH$_2$P(Me)CH$_2$SiMe$_2$)MoH$_2$ (10a).** Heating 0.100 g of dimethylsilylene complex **4a** at 100 °C in 3 mL of benzene resulted in a green-yellow solution. Removal of the solvent under reduced pressure and scraping the product from the flask gave 0.069 g of **10a** as a sticky green solid (69% yield). The yield is less than quantitative because of difficulty removing the product from the reaction flask. $^1H$ NMR (benzene-$d_6$): 2.22 (m, 1 H, PC*H*$_2$Si), 1.99 (m, 1 H, PC*H*$_2$Si) 1.98 (s, 15 H, $C_5$*Me*$_5$), 1.6 (m br, 1 H, PC*H*$_2$), 1.50 (m br, 1H, PC*H*$_2$), 1.41 (d, 3 H, P*Me*, $J_{HP}$ = 8 Hz), 1.4 (m br, 1 H, PC*H*$_2$), 1.37 (d, 3 H, P*Me*, $J_{HP}$ = 8 Hz), 1.03 (d, 3 H, P*Me*, $J_{HP}$ = 6 Hz), 0.87 (m br, 1 H, PC*H*$_2$), 0.85 (s, 3 H, Si*Me*), 0.53 (s, 3 H, Si*Me*), −8.57 (m, 2 H, Mo*H*$_2$). $^{13}C\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 96.2 (s, *C*$_5$Me$_5$), 45.4 (br, P*C*H$_2$Si), 33.6 (dd, P*C*H$_2$ $J_{CP}$ = 22 Hz, $J_{CP'}$ = 17 Hz), 31.9 (dd, P*C*H$_2$, $J_{CP}$ = 28 Hz, $J_{CP'}$ = 15 Hz), 24.7 (dd, P*Me*, $J_{CP}$ = 20 Hz, $J_{CP'}$ = 5 Hz), 21.9 (d, P*Me*, $J_{CP}$ = 16 Hz), 20.7 (s, P*Me*), 15.8 (s, Si*Me*), 13.8 (s, $C_5$*Me*$_5$), 12.9 (s, Si*Me*). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): 59.5 (d, $J_{PP}$ = 18 Hz), 39.6 (d, $J_{PP}$ = 18 Hz). $^{29}Si\{^1H\}$ NMR (benzene-$d_6$): $\delta$ −9.0 (m). IR (KBr, cm$^{-1}$): 3044 w, 2985 m, 2936 w, 2829 m, 1829 w ($\nu_{MoH}$), 1735 m ($\nu_{MoH}$), 1474 w, 1457 w, 1416 s, 1374 s, 1273 m, 1228 m, 1091 m, 1067 m, 933 m, 875 m, 830 w, 795 w, 752 w, 687 w, 667 w. Anal. Calcd for $C_{18}H_{38}MoP_2Si$: C, 49.08; H, 8.70. Found: C, 50.21; H, 8.60. Compound **10a** is very soluble in hydrocarbon solvents, and this prevented isolation of analytically pure material. Small amounts (<5% yield) of crystalline **10a** were obtained by storing a 0.5-mL toluene solution containing 0.100 g of **10a** in the freezer at −30 °C for 14 h.

**Cp*($\kappa^3$-Me$_2$PCH$_2$CH$_2$P(Me)CH$_2$SiPh$_2$)MoH$_2$ (10b).** Heating 0.100 g of diphenylsilylene complex **4d** at 100 °C in 3 mL of benzene resulted in an orange solution. Removal of the solvent in vacuo and recrystallization from 2 mL of diethyl ether at −30 °C over 12 h gave 0.073 g of **10b** as orange crystals (73% yield). $^1H$ NMR (benzene-$d_6$): $\delta$ 7.89 (m, 4 H, *o-Ph*), 7.82 (m, 4 H, *m-Ph*), 7.27 (m, 1 H, *p-Ph*), 7.21 (m, 1 H, *p-Ph*), 2.76 (m, 1 H, PC*H*$_2$Si), 2.52 (m, 1 H, PC*H*$_2$Si), 1.94 (s, $C_5$*Me*$_5$), 1.75 (m br, 1 H, PC*H*$_2$), 1.39 (m, br, 1 H, PC*H*$_2$), 1.37 (d, 3 H, P*Me*, $J_{HP}$ = 8 Hz), 1.10 (m br, PC*H*$_2$), 0.94 (d, 3 H, P*Me*, $J_{HP}$ = 8 Hz), 0.90 (m br, 1 H, PC*H*$_2$), 0.89 (d, 3 H, P*Me*, $J_{HP}$ = 7 Hz), −8.06 (m, 2 H, Mo*H*$_2$). $^{13}C\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 152.0 (s, *i-Ph*), 148.8 (s, *i-Ph*), 135.1 (s, *o-Ph*), 135.0 (s, *o-Ph*), 134.1 (s, *m-Ph*), 134.0 (s, *m-Ph*), 127.2 (s, *p-Ph*), 127.0 (s, *p-Ph*), 96.2 (s, *C*$_5$Me$_5$), 43.5 (d, P*C*H$_2$-Si, $J_{CP}$ = 13 Hz), 32.8 (dd, P*C*H$_2$, $J_{CP}$ = 23 Hz, $J_{CP'}$ = 16 Hz), 31.3 (dd, P*C*H$_2$, $J_{CP}$ = 29 Hz, $J_{CP'}$ = 14 Hz), 22.2 (d, P*Me*, $J_{CP}$ = 16 Hz), 20.7 (dd, P*Me*, $J_{CP}$ = 20 Hz, $J_{CP'}$ = 5 Hz), 20.0 (m, P*Me*), 13.7 (s, $C_5$*Me*$_5$). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 56.1 (d, $J_{PP}$ = 18 Hz), 39.9 (d, $J_{PP}$ = 18 Hz). $^1H$,$^{29}Si$ HMQC NMR (benzene-$d_6$): $\delta$ −3.4. IR (cm$^{-1}$): 3058 w, 2973 m, 2950 w, 2897 s, 2855 w, 1819 w ($\nu_{MoH}$), 1763 w ($\nu_{MoH}$), 1479 w, 1423 m, 1372 w, 1092 m, 1066 w, 1017 m, 934 m, 917 w, 878 m, 842 w, 743 m, 703 s, 685 w, 497 m, 434 w. Anal. Calcd for $C_{28}H_{42}MoP_2Si$: C, 59.56; H, 7.50. Found: C, 59.53; H, 7.72.

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**Supporting Information Available:** Structures of **4a**, **4b**, **5a**, **7**, and **8** (CIF). Neutron data collection, refinement, and description of structure I (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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