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Synthesis of Silyl–Molybdenum Complexes Connected by a 1,1′-Metallocenylene Unit and Their Electrochemical Properties

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Keywords: Molybdenum / Ferrocene / Si ligands / Structure elucidation / Cyclic voltammetry

Methyl–molybdenum complexes react with hydrosilanes or hydrogermane under photo-irradiation to form the corresponding silyl– or germyl–molybdenum complexes, [(η^5-C_5Me_5)Mo(CO)$_3$(ER_3)] [ER_3 = $SiPh_3$ (**1**), $GePh_3$ (**2**), $SiMe_2Ph$ (**3**), $SiMe_2$($C_5H_4FeC_5H_5$) (**4**)]. This method can be adapted to form metallocenylene compounds that bear two dimethylsilyl groups, [{(η^5-C_5Me_5)Mo(CO)$_3$($SiMe_2C_5H_4$)}$_2$M] [M = Fe (**5**), Ru (**6**)]. All of the new complexes were fully characterized by means of ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and elemental analyses. In addition, the structures of **1**, **5**, and **6** were determined by single-crystal X-ray diffraction studies. The electrochemical measurements of the ferrocene derivatives that bear one or two {(η^5-C_5Me_5)Mo(CO)$_3$($SiMe_2$)} substituent(s) revealed that the {(η^5-C_5Me_5)Mo(CO)$_3$($SiMe_2$)} unit has an electron-donating nature.

Introduction

The transition metal complexes that have a silylferrocene moiety have been investigated as an important species for a poly(silylferrocene), which exhibits attractive conductivity, magnetic properties, and a high thermal stability.[1] When 1,1′-bis(silyl)ferrocene is the silylferrocene moiety, the complexes that have two M–Si bonds are divided into two groups. One group contains an *ansa*-type complex in which the two M–Si bonds have a direct interaction through one or two metal center(s) (Figures 1a and b) and the other group is a linear-type complex in which the two M–Si bonds are terminal (Figure 1c). However, these examples are limited, and the electrochemical properties of these complexes have not been well established.[2]

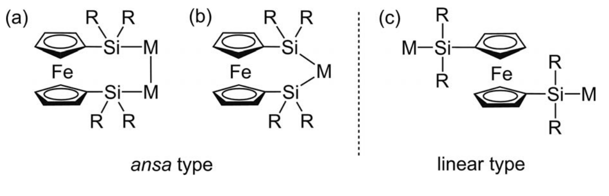
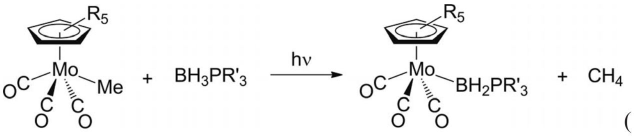


Figure 1. Two types of groups for the 1,1′-bis(silyl)ferrocenylene complex that has two M–Si bonds.

The Shimoi group[3a] and our group[3b,3c] have previously reported that Mo–B bond formation was achieved by the demethanation of an Mo–Me complex with an H–B compound [Equation (1)].

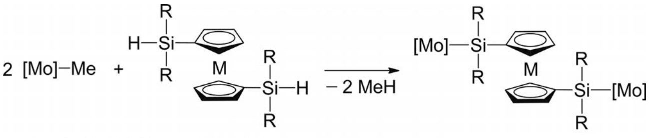


(1)

This result prompted us to examine the possibility of Mo–Si bond formation through the demethanation of an Mo–Me complex with an H–Si compound [Equation (2)].

$$\text{M–Me} + \text{H–SiR}_3 \longrightarrow \text{M–SiR}_3 + \text{CH}_4 \qquad (2)$$

There are some examples in the group 6 transition metal triads in which an M–Si bond is thought to be formed by demethanation, but few straightforward examples of demethanative M–Si bond formation have been reported.[4,5] The demethanative reactions are appealing since both of the starting compounds are easy to handle, and the methane that forms as a byproduct can be readily removed. Thus, we planned to use the demethanation reaction of a methyl–molybdenum complex with 1,1′-bis(silyl)metallocene in order to obtain linear-type complexes that have two terminal Mo–Si bonds [Equation (3)]. Herein, we report the syntheses of mononuclear Mo–Si(Ge) complexes and trinuclear



[Mo] = Cp*Mo(CO)$_3$; M = Fe, Ru

(3)

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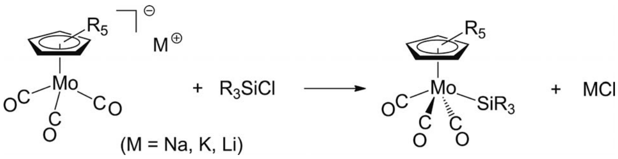
Mo–Si complexes that are connected by a 1,1′-metallocenylene unit. We also present the electrochemical properties of these complexes.

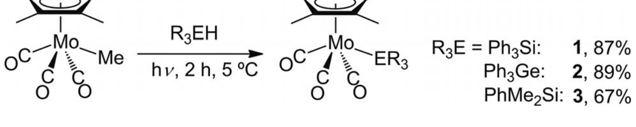
Results and Discussion

Only a few Mo–Si and Mo–Ge complexes that have a Cp ligand (Cp = η^5-C_5H_5) or its derivative have been previously synthesized.[5–7] A typical method that is used to prepare the Mo–Si complexes is the reaction of a halosilane with an alkali metal anionic species, [M{(η^5-C_5R_5)(CO)$_3$Mo}] (M = Li, Na, K; R = Me, H) [Equation (4)].[6b–6f,6j] However, this method has some shortcomings, such as the instability of the alkali metal anionic species and the inapplicability of silicon compounds that have a functional group.



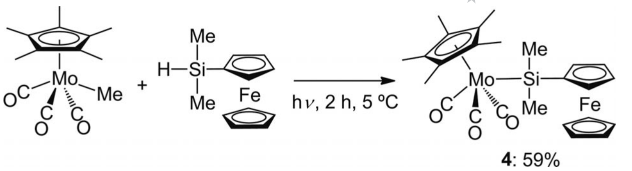
(4)

In order to overcome these shortcomings, we attempted a demethanative reaction of an Mo–Me complex with R_3SiH (R_3GeH) to form an Mo–Si(Ge) bond. The methyl–molybdenum complex, [Cp*Mo(CO)$_3$(Me)] (Cp* = η^5-C_5Me_5),[8] was treated with an equimolar amount of Ph_3EH (E = Si, Ge) in benzene at 5 °C under photo-irradiation and produced the corresponding complexes, [Cp*Mo(CO)$_3$(EPh$_3$)] [E = Si (**1**), Ge (**2**)], which contained an Mo–Si and an Mo–Ge single bond, respectively (Scheme 1). Dimethyl(phenyl)silane (Me_2PhSiH) afforded the corresponding Mo–Si complex **3** in 67% yield, whereas several complexes were formed that could not be identified when Et_3SiH and $HEt_2SiSiEt_2H$ were used. Complex **1** was stable for several weeks in air, but **3** decomposed within a few hours in solution even under nitrogen. It would seem that the Mo–Si complexes were stabilized by the electron-withdrawing substituent(s) on the Si atom. This is consistent with the stability tendency of [CpMo(CO)$_3$(SiR$_3$)] where $SiCl_3$ > $SiBr_3$ ≈ $SiCl_2H$ > $SiCl_2Me$ ≈ SiClHMe > $SiMe_3$.[6b]



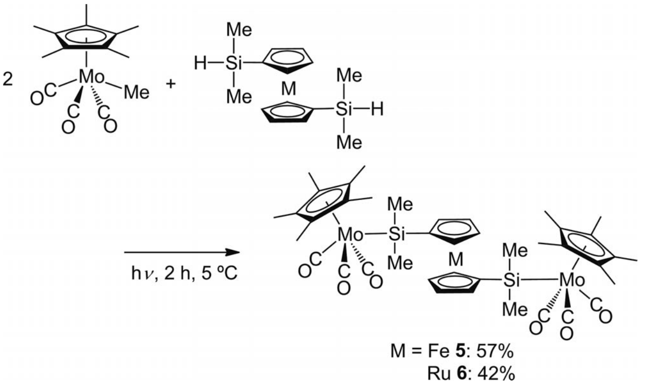
Scheme 1. Synthesis of the silyl– and germyl–molybdenum complexes.

Next, we examined the reactions of [Cp*Mo(CO)$_3$(Me)] with hydrosilanes that have a metallocene moiety as a functional group. The photoreaction of [Cp*Mo(CO)$_3$(Me)] with (dimethylsilyl)ferrocene, [(HMe$_2$SiC$_5$H$_4$)FeCp] (Cp = η^5-C_5H_5),[9] afforded the corresponding Mo–Si complex **4** (Scheme 2).



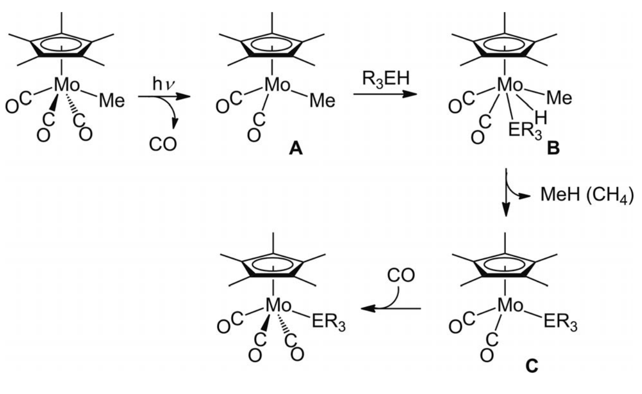
Scheme 2. Reaction of [Cp*Mo(CO)$_3$(Me)] with (dimethylsilyl)ferrocene.

A limited number of monosilylferrocenes have been reported where the silyl group is bonded to the transition metal atom.[2e,10] In addition, the reactions with 1,1′-bis(dimethylsilyl)metallocene, [(HMe$_2$SiC$_5$H$_4$)$_2$M] (M = Fe,[11] Ru[2e]), afforded the trinuclear complexes **5** and **6** that have two terminal Mo–Si bonds (Scheme 3). Although the Si atom for **4** and **5** has two Me groups, surprisingly **4** and **5** are thermally more stable than **3**, which also has two Me substituents. The ferrocenyl and metallocenylene moieties seem to have a strong electron-withdrawing property in these complexes (vide infra). In the case of the metallocenes that have one or two diphenylsilyl group(s), this method was not applicable presumably due to the steric repulsion.



Scheme 3. Reaction of [Cp*Mo(CO)$_3$(Me)] with the metallocenes that have one or two dimethylsilyl group(s).

A plausible pathway for the Mo–E (E = Si, Ge) bond formation in complexes **1**–**6** is shown in Scheme 4. One of the CO ligands in [Cp*Mo(CO)$_3$(Me)] is released by photo-irradiation to give [Cp*Mo(CO)$_2$(Me)] (**A**). The oxidative addition of an H–E bond to the 16e$^-$ Mo complex yields



Scheme 4. Proposed mechanism of demethanative Mo–E (E = Si, Ge) bond formation.

[Cp*Mo^{IV}(CO)$_2$(H)(Me)(ER$_3$)] (**B**). The subsequent reductive elimination of CH$_4$ affords [Cp*Mo^{II}(CO)$_2$(ER$_3$)] (**C**), and the recoordination of CO gives the final complex [Cp*Mo(CO)$_3$(ER$_3$)]. The evolution of CH$_4$ gas was confirmed by the ^{1}H NMR spectrum (δ = 0.15 ppm in C$_6$D$_6$). It has been reported for iron complexes[12,13] that the oxidative addition of the Si–H bond to [CpFe(CO)(SiR$_3$)] takes place and forms [CpFe(CO)(H)(SiR$_3$)$_2$], which has been isolated and characterized by X-ray analysis.[12j–12m] Therefore, the formation of the Mo^{IV} complex **B** is highly likely, although it has not been detected. An E–H agostic interaction that is followed by a σ-bond metathesis pathway cannot be ruled out in place of the E–H oxidative addition (**A** → **B**) that is followed by methane reductive elimination (**B** → **C**).

The structures of **1**, **5**, and **6** were determined by X-ray crystallography. The molecular structures of **1**, **5**, and **6** are shown in Figures 2 and 3. Selected bond lengths and angles and crystal data are listed in Tables 1 and 2, respectively. Two independent molecules of **1** crystallized in the unit cell. The molecular structure of the Mo1 molecule of **1** is depicted in Figure 2 with the atomic numbering scheme. The Mo atom has a four-legged piano-stool geometry that bears C$_5$Me$_5$ in an η^5-fashion, three terminal CO ligands, and an SiPh$_3$ ligand with an Mo–Si bond. The Mo–Si bond lengths of **1** [2.6531(7), 2.6616(7) Å] resemble those of the previously reported complexes (2.504–2.670 Å).[5,6c,6d,6g,14] For **5** and **6**, the two molybdenum units, [Cp*Mo(CO)$_3$], are connected by means of the {–(Me$_2$SiC$_5$H$_4$)M(C$_5$H$_4$SiMe$_2$)–} spacer [Figure 3a, M = Fe for **5** and Figure 3b, M = Ru for **6**]. Only two crystal structures that have the {–(R$_2$SiC$_5$H$_4$)-Fe(C$_5$H$_4$SiR$_2$)–} spacer with two M–Si (M = metal) bonds have been reported previously (Figure 4).[2a,2c] Complex **5** is the first example that has two terminal transition metal–silicon bonds. In addition, **6** is the first example of a silylated ruthenocene with metal–silicon bond(s). The Mo–Si bonds of **5** [2.6807(9), 2.6660(9) Å] and **6** [2.6675(17), 2.6752(17) Å] are slightly longer than those of **1**.

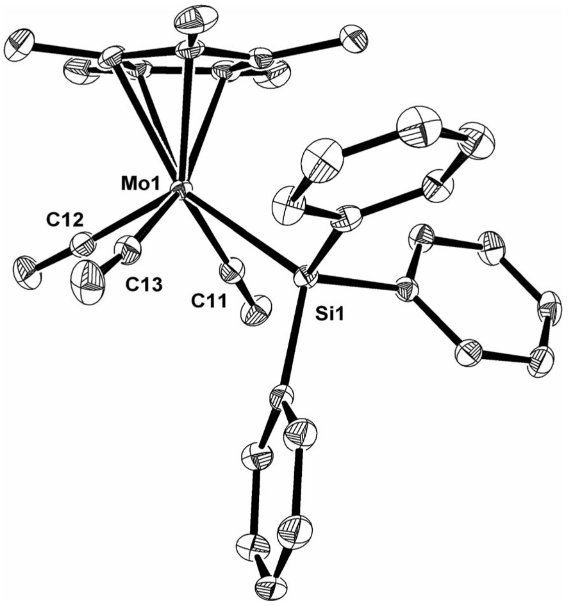


Figure 2. ORTEP drawing of the Mo1 molecule of **1** with 50% thermal ellipsoidal plots; hydrogen atoms were omitted for simplicity.

The redox behavior of **1** and **4**–**6** was examined by cyclic voltammetry (CV). The measurements were undertaken in a 0.10 M nBu$_4$NPF$_6$/CH$_2$Cl$_2$ solution at a scan rate of 0.1 V s^{-1} at room temperature. Complex **1** showed irrevers-

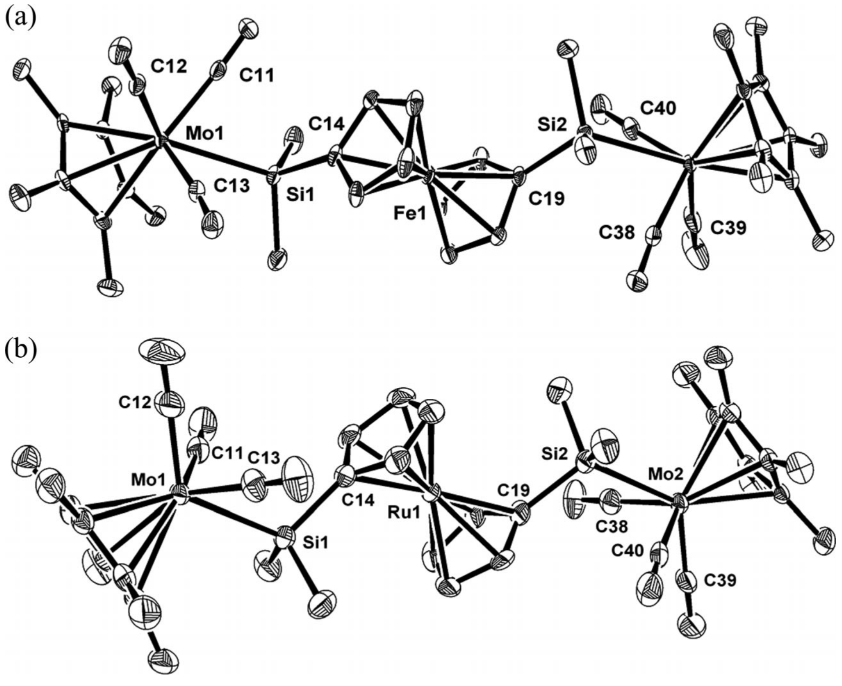


Figure 3. ORTEP drawings of **5** (a) and **6** (b) with 50% thermal ellipsoidal plots; hydrogen atoms were omitted for simplicity.

Table 1. Selected bond lengths [Å] and bond angles [°] for **1**, **5**, and **6**.

	1	**5**	**6**
Bond lengths			
Mo1–Si1	2.6531(7)	2.6803(8)	2.6675(17)
Mo1–C11	1.980(2)	1.985(3)	1.975(7)
Mo1–C12	1.968(3)	1.976(3)	1.965(7)
Mo1–C13	1.978(3)	1.972(3)	1.958(7)
Mo2–Si2	2.6616(7)	2.6658(8)	2.6752(17)
Mo2–C38 (C42 for **1**)	1.979(3)	1.967(3)	1.968(7)
Mo2–C39 (C43 for **1**)	1.987(3)	1.968(3)	1.964(6)
Mo2–C40 (C44 for **1**)	1.962(3)	1.989(3)	1.968(6)
Bond angles			
Si1–Mo1–C12	123.35(7)	126.58(9)	123.5(2)
Mo1–Si1–C14		113.30(9)	112.62(17)
Si2–Mo2–C39 (C44 for **1**)	116.38(8)	122.80(10)	126.43(17)
Mo2–Si2–C19		112.73(9)	113.82(18)

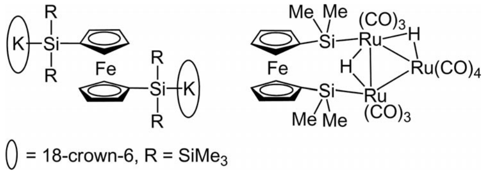


Figure 4. Two types of 1,1′-bis(silyl)ferrocene complexes with metal–silicon bonds that were previously reported.

ible redox behavior, which indicated that the Mo–Si bond is susceptible to redox reactions. In contrast, **4** and **5** underwent reversible one-electron oxidation. The cyclic voltammograms are illustrated in Figure 5 and correspond to single reversible ferrocene/ferrocenium redox behavior. Extraction of some of the effects of the two silyl substituents [–$SiMe_2H$ and –$(SiMe_2)(CO)_3MoCp^*$] on the ferrocene/ferrocenium redox behavior was attempted from the CV measurements (Figure 6). The $E_{1/2}$ value for 1,1′-bis(dimethylsilyl)ferrocene (0.30 V vs. Ag/Ag^+)[15] is higher than that for (dimethylsilyl)ferrocene (0.27 V), which in turn is higher than that of ferrocene (0.23 V). Therefore, a dimethylsilyl group on ferrocene can be considered to have an electron-withdrawing nature. This tendency is consistent with that reported by Okuda.[16] The $E_{1/2}$ value of 0.18 V for **4** is higher than the $E_{1/2}$ value of 0.12 V for **5**. The introduction of the [$Cp^*Mo(CO)_3SiMe_2$] group into the ferrocene Cp ring(s) causes the $E_{1/2}$ value to be lower cumulatively (0.23 V for ferrocene → 0.18 V for **4** → 0.12 V for **5**). Therefore, the {$Cp^*Mo(CO)_3(SiMe_2)$} moiety can be considered to be an electron-donating group. In 2008 Pannell et al. reported that the $E_{1/2}$ value of ferrocene with the {$CpFe(CO)_2(SiMe_2)$} moiety was higher than that of ferrocene. These results show that the {$CpFe(CO)_2(SiMe_2)$} moiety has an electron-withdrawing nature.[10a] The difference between the electrochemical nature of the {$Cp^*Mo(CO)_3(SiMe_2)$} and {$CpFe(CO)_2(SiMe_2)$} moieties probably stems from the stronger electron-donating ability of the pentamethylcyclopentadienyl group (Cp*) than that of the cyclopentadienyl group (Cp). It has been reported that the CV of ruthenocene shows an irreversible one-step two-electron oxidation process.[17] Complex **6**, which has a ruthenocene unit, showed the same CV behavior.

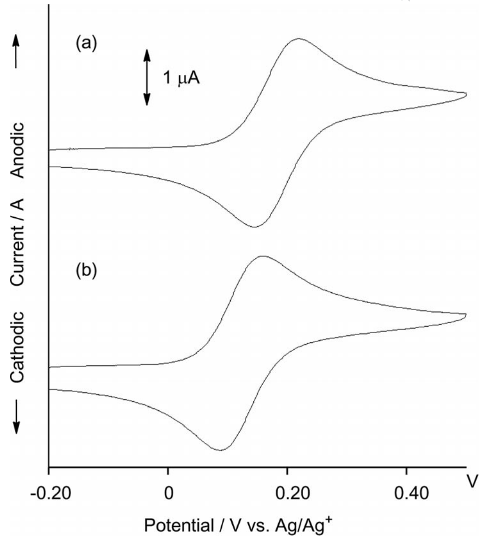


Figure 5. Cyclic voltammograms of (a) 0.5 mM of **4** at 25 °C and (b) 0.5 mM of **5** at 25 °C in a CH_2Cl_2 solution that contains nBu_4NPF_6 (0.10 M) (scan rate = 0.1 V s^{-1}); $E_{1/2}$ = 0.18 V for **4** and 0.12 V for **5**.

Conclusions

A convenient demethanative Mo–Si or Mo–Ge bond formation from an Mo–Me complex and an H–Si or H–Ge compound has been reported. The electrochemical investigations with cyclic voltammetry revealed that the $HSiMe_2$ group is electron-withdrawing and that the [$Cp^*Mo(CO)_3(SiMe_2)$] group is electron-donating.

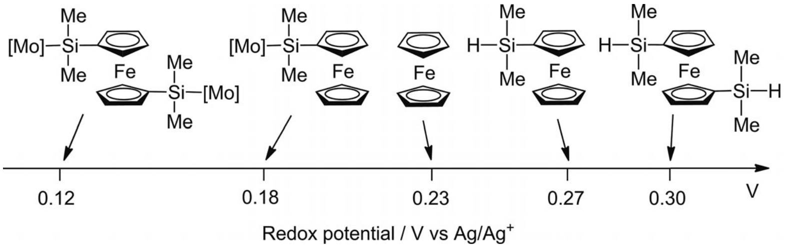


Figure 6. Redox potentials of ferrocene and the derivatives with one or two $HSiMe_2$ or {$Cp^*Mo(CO)_3(SiMe_2)$} substituent(s); [Mo] = [$Cp^*Mo(CO)_3(SiMe_2)$].

Experimental Section

General Methods: All of the manipulations were carried out by using standard Schlenk techniques under nitrogen. The methylmolybdenum complex [Cp*Mo(CO)$_3$(Me)],[8] (dimethylsilyl)ferrocene,[9] 1,1′-bis(dimethylsilyl)ferrocene,[11] and 1,1′-bis(dimethylsilyl)ruthenocene[2e] were prepared according to literature methods. The other chemicals were purchased. All of the solvents were distilled from the appropriate drying agents (sodium and benzophenone for hexane and benzene, P_2O_5 for CH_2Cl_2, and CaH_2 for MeCN) under dry nitrogen prior to use. NMR spectra (^{1}H and ^{13}C{^{1}H}) were recorded with a JEOL JNM-AL 400 spectrometer. The ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data are referenced to the residual peaks of the solvent as an internal standard. The photo-irradiation was performed with a 400 W medium-pressure mercury arc lamp at 5 °C. Cyclic voltammetric measurements were performed with an ALS-612A electrochemical analyzer by using a glassy carbon working electrode, a Pt counter electrode, and an Ag/AgPF$_6$ reference electrode in CH_2Cl_2 that contained 0.1 M nBu$_4$NPF$_6$ (MeCN) as the supporting electrolyte at a scan rate of 100 mVs^{-1}. The Fc/Fc$^+$ couple was used as an internal standard.

[Cp*Mo(CO)$_3$(SiPh$_3$)] (1): A benzene solution (8 mL) of [Cp*Mo(CO)$_3$(Me)] (1.00 mmol, 330 mg) and Ph$_3$SiH (1.00 mmol, 260 mg) was subjected to photo-irradiation at 5 °C for 2 h. The volatile materials were removed under reduced pressure and yielded an orange solid, which was washed with hexane at –70 °C, collected by filtration, and dried in vacuo to give **1** (0.87 mmol, 500 mg, 87%) as an orange powder. Yellow crystals of **1** that were suitable for an X-ray diffraction study were obtained by cooling a CH_2Cl_2/hexane solution to –20 °C for a few days. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.52 (s, 15 H, Me), 7.16–7.22 (m, 9 H, Ph), 7.79 (d, $J_{H,H}$ = 6.8 Hz, 6 H, Ph) ppm. ^{13}C{^{1}H} NMR (100.4 MHz, C$_6$D$_6$): δ = 10.79 (C*Me*), 104.76 (*C*Me), 127.77 (Ph), 128.77 (Ph), 136.70 (Ph), 141.46 (Ph-*ipso*), 229.88 (CO), 236.09 (CO) ppm. $C_{31}H_{30}MoO_3Si$ (574.60): calcd. C 64.80, H 5.26; found C 64.67, H 5.35.

[Cp*Mo(CO)$_3$(GePh$_3$)] (2): In a procedure analogous to that outlined above, [Cp*Mo(CO)$_3$(Me)] (1.00 mmol, 330 mg) and Ph$_3$GeH (1.00 mmol, 305 mg) gave **2** (0.89 mmol, 550 mg, 89%) as an orange powder. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.54 (s, 15 H, Me), 7.14–7.22 (m, 9 H, Ph), 7.77 (d, $J_{H,H}$ = 6.8 Hz, 6 H, Ph) ppm. ^{13}C{^{1}H} NMR (100.4 MHz, C$_6$D$_6$): δ = 11.02 (C*Me*), 104.69 (*C*Me), 128.08 (Ph), 128.34 (Ph), 135.89 (Ph), 143.85 (Ph-*ipso*), 229.57 (CO), 235.70 (CO) ppm. $C_{31}H_{30}GeMoO_3$ (619.11): calcd. C 60.14, H 4.88; found C 59.88, H 5.05.

[Cp*Mo(CO)$_3$(SiMe$_2$Ph)] (3): In a procedure analogous to that outlined above, [Cp*Mo(CO)$_3$(Me)] (1.00 mmol, 330 mg) and PhMe$_2$SiH (1.00 mmol, 150 µL) gave **3** (0.67 mmol, 303 mg, 67%) as an orange powder. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 0.89 (s, 6 H, SiMe), 1.53 (s, 15 H, CMe), 7.18 (d, $J_{H,H}$ = 7.6 Hz, 1 H, Ph-*p*), 7.25 (m, 2 H, Ph-*m*), 7.88 (m, 2 H, Ph-*o*) ppm. ^{13}C{^{1}H} NMR (100.4 MHz, C$_6$D$_6$): δ = 4.95 (SiMe), 10.93 (C*Me*), 104.29 (*C*Me), 127.76 (Ph), 128.61 (Ph), 134.47 (Ph), 144.45 (Ph-*ipso*), 235.71 (CO), 239.02 (CO) ppm. $C_{21}H_{26}MoO_3Si$ (450.46): calcd. C 55.99, H 5.82; found C 54.84, H 5.70.

[Cp*Mo(CO)$_3$(SiMe$_2$Fc)] (Fc = C$_5$H$_4$FeC$_5$H$_5$) (4): In a procedure analogous to that outlined above, [Cp*Mo(CO)$_3$(Me)] (1.05 mmol, 350 mg) and HSiMe$_2$Fc (0.92 mmol, 224 mg) gave **4** (0.54 mmol, 303 mg, 59%) as a yellow powder. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 0.97 (s, 6 H, SiMe), 1.55 (s, 15 H, CMe), 4.10 (s, 5 H, C$_5$H$_5$), 4.20 (d, $J_{H,H}$ = 2.0 Hz, 2 H, C$_5$H$_4$Si), 4.39 (d, $J_{H,H}$ = 2.0 Hz, 2 H, C$_5$H$_4$Si) ppm. ^{13}C{^{1}H} NMR (100.4 MHz, C$_6$D$_6$): δ = 5.19 (SiMe), 10.86 (C*Me*), 68.86 (C$_5$H$_5$), 70.61 (C$_5$H$_4$Si), 73.73 (C$_5$H$_4$Si), 79.57 (C$_5$H$_4$Si-*ipso*), 104.23 (*C*Me), 229.86 (CO), 234.46 (CO) ppm. $C_{25}H_{30}FeMoO_3Si$ (558.38): calcd. C 53.78, H 5.42; found C 53.87, H 5.45.

[Cp*Mo(CO)$_3$(SiMe$_2$Fc′Me$_2$Si)(CO)$_3$MoCp*] (Fc′ = C$_5$H$_4$FeC$_5$H$_4$) (5): In a procedure analogous to that outlined above, [Cp*Mo(CO)$_3$(Me)] (1.05 mmol, 350 mg) and HSiMe$_2$Fc′Me$_2$SiH (0.50 mmol, 224 mg) gave **5** (0.29 mmol, 226 mg, 57%) as a yellow powder. Yellow crystals of complex **5** that were suitable for an X-ray diffraction study were obtained by cooling a CH_2Cl_2/hexane solution to –20 °C for a few days. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.03 (s, 12 H, SiMe), 1.55 (s, 30 H, CMe), 4.42 (app. t, $J_{H,H}$ = 1.6 Hz, 4 H, C$_5$H$_4$Si), 4.52 (app. t, $J_{H,H}$ = 1.6 Hz, 4 H, C$_5$H$_4$Si) ppm. ^{13}C{^{1}H} NMR (100.4 MHz, C$_6$D$_6$): δ = 5.41 (SiMe), 10.97

Table 2. Crystallographic data and structural refinement details for **1**, **5**, and **6**.

	1	5	6
Empirical formula	$C_{31}H_{30}MoO_3Si$	$C_{40}H_{50}FeMo_2O_6Si_2$	$C_{40}H_{50}Mo_2O_6RuSi_2$
Formula mass	574.58	930.71	975.93
T [K]	120(2)	120(1)	200(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a [Å]	8.9900(3)	16.7453(8)	16.851(5)
b [Å]	16.2800(6)	15.7729(6)	15.842(4)
c [Å]	18.6800(8)	16.4598(7)	16.627(5)
α [°]	83.990(3)		
β [°]	89.930(5)	111.023(2)	110.158(3)
γ [°]	84.510(5)		
Unit cell volume [Å^3]	2706.35(18)	4058.0(3)	4167(2)
Number of formula units per unit cell, Z	4	4	4
$\rho_{calcd.}$ [mg m^{-3}]	1.410	1.523	1.556
μ [mm^{-1}]	0.559	1.064	1.051
F(000)	1184	1904	1976
Crystal size [mm]	0.30 × 0.20 × 0.10	0.26 × 0.24 × 0.16	0.20 × 0.10 × 0.02
Reflections collected	19755	29469	33456
R(int)	11298 (0.0168)	8746 (0.0197)	9490 (0.0611)
R_1 [$I > 2\sigma(I)$]	0.0347	0.0316	0.0718
wR_2 [$I > 2\sigma(I)$]	0.0952	0.1100	0.1241
Goodness of fit	1.178	1.183	1.186

(C*Me*), 71.76 (C$_5$H$_4$Si), 73.98 (C$_5$H$_4$Si), 79.69 (C$_5$H$_4$Si-*ipso*), 104.27 (*C*Me), 229.83 (CO), 234.20 (CO) ppm. C$_{40}$H$_{50}$FeMo$_2$O$_6$Si$_2$ (930.73): calcd. C 51.62, H 5.41; found C 51.88, H 5.41.

[Cp*Mo(CO)$_3$(SiMe$_2$Rc′Me$_2$Si)(CO)$_3$MoCp*] (Rc′ = C$_5$H$_4$RuC$_5$H$_4$) (6): In a procedure analogous to that outlined above, [Cp*(CO)$_3$Mo(Me)] (1.28 mmol, 423 mg) and HSiMe$_2$Rc′Me$_2$SiH (0.64 mmol, 221 mg) gave **6** (0.26 mmol, 260 mg, 42%) as a pale orange powder. Colorless crystals of complex **6** that were suitable for an X-ray diffraction study were obtained by cooling a CH$_2$Cl$_2$/hexane solution to –60 °C for a few days. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 0.86 (s, 12 H, SiMe), 1.62 (s, 30 H, CMe), 4.73 (app. t, $J_{\mathrm{H,H}}$ = 1.6 Hz, 4 H, C$_5$H$_4$Si), 4.92 (app. t, $J_{\mathrm{H,H}}$ = 1.6 Hz, 4 H, C$_5$H$_4$Si) ppm. ^{13}C{^{1}H} NMR (100.4 MHz, C$_6$D$_6$): δ = 5.73 (SiMe), 10.75 (C*Me*), 73.50 (br., C$_5$H$_4$Si), 75.95 (br., C$_5$H$_4$Si), 84.02 (C$_5$H$_4$Si-*ipso*), 104.23 (*C*Me), 230.03 (CO), 234.36 (CO) ppm. C$_{40}$H$_{50}$Mo$_2$O$_6$RuSi$_2$ (975.95): calcd. C 49.23, H 5.16; found C 49.02, H 5.22.

Crystal Structure Determination: Crystals of **1**, **5**, and **6** that were suitable for X-ray diffraction studies were separately mounted in a glass capillary. The data were collected at 120 K for **1** and **5** and at 200 K for **6** with a Rigaku AFC-7/Mercury CCD area-detector diffractometer that was equipped with monochromated Mo-K_α radiation (Table 2). All of the calculations were performed with the CrystalClear software package from Molecular Structure Corporation. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. The hydrogen atoms were located by assuming ideal geometry and were included in the structure calculation without further refinement of the parameters. CCDC-707638 (for **1**), -707639 (for **5**) and -755066 (for **6**) contain the supplementary crystallographic data for this paper. 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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