Organometallics **1997,** *16,* 4746−4754

Synthesis and Reactivity of d^0 Bis(imido) Silyl and Germyl Complexes of Molybdenum and Tungsten

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Received June 23, 1997[⊗]

The syntheses and reactivities of d^0 bis(imido) molybdenum/tungsten silyl chloride complexes $(2,6\text{-}^i\mathrm{Pr_2C_6H_3N})_2\mathrm{M[Si(SiMe_3)_3]Cl}$ (**1**, M = Mo; **2**, M = W) and the corresponding germyl complexes $(2,6\text{-}^i\mathrm{Pr_2C_6H_3N})_2\mathrm{M[Ge(SiMe_3)_3]Cl}$ (**3**, M = Mo; **4**, M = W) are described. The complex $(2,6\text{-}^i\mathrm{Pr_2C_6H_3N})_2\mathrm{Mo[Si(SiMe_3)_3]Cl}$ (**1**), prepared by the reaction of $(2,6\text{-}^i\mathrm{Pr_2C_6H_3N})_2\mathrm{MoCl_2(dme)}$ with $\mathrm{(THF)_3LiSi(SiMe_3)_3}$, has been structurally characterized. In general, these complexes are rather stable and do not react with CO, H_2, or CH_3CN. Complex **1** reacts with $2,6\text{-}\mathrm{Me_2C_6H_3NC}$ to provide the insertion product $(2,6\text{-}^i\mathrm{Pr_2C_6H_3N})_2\mathrm{Mo}[\eta^2\text{-C(N-}2,6\text{-}\mathrm{Me_2C_6H_3)Si(SiMe_3)_3](Cl)}$ (**5**) and with AgOTf to give the silyl triflate complex $(2,6\text{-}^i\mathrm{Pr_2C_6H_3N})_2\mathrm{Mo[Si(SiMe_3)_3]OSO_2CF_3}$ (**6**) in high yield. Complexes **1**−**6** react with neopentylmagnesium chloride to produce the silyl neopentyl complexes $(2,6\text{-}^i\mathrm{Pr_2C_6H_3N})_2\mathrm{M[E(SiMe_3)_3](CH_2CMe_3)}$ (**7**, M = Mo, E = Si; **8**, M = W, E = Si; **9**, M = Mo, E = Ge; **10**, M = W, E = Ge). Complex **7**, which was characterized by X-ray crystallography, contains an agostic interaction involving the α hydrogen of the neopentyl ligand (d(Mo−H) 2.55(4)Å). The neopentyl complexes **7**−**10** readily react with hydrogen (1 atm) to generate free neopentane and $\mathrm{HSiMe_3}$, probably via hydrogenation of the Mo−C bond to generate a highly unstable silyl hydride intermediate. The mechanism of $\mathrm{HSiMe_3}$ formation is unknown but may involve decomposition of the silyl hydride species via a four-membered transition state to generate a highly reactive silylene species. The corresponding tungsten analog **8** undergoes a similar reaction, but at a much slower rate. Attempts to trap the possible silylene intermediates $(2,6\text{-}^i\mathrm{Pr_2C_6H_3N})_2\mathrm{M{=}Si(SiMe_3)_2}$ (M = Mo, W) were unsuccessful.

Introduction

Early transition-metal silicon chemistry is an emerging field of increasing importance in organometallic chemistry.[1−15] Our interest in this area has recently focused on use of group 4 d^0 metallocene complexes as catalysts for silane dehydropolymerizations.[16] Mechanistic studies have suggested that this dehydropolymerization occurs by a purely σ-bond metathesis mechanism mediated by a metal hydride catalyst and involving

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

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S0276-7333(97)00527-X CCC: $14.00

only two steps. Studies directed toward optimization of catalyst structures for production of high molecular weight polysilanes have indicated that the activities are dramatically influenced by subtle changes in the structures of zirconocene-type catalyst precursors. On the basis of these studies, however, we predicted that the next generation of catalysts with substantially superior properties “will be monomer-stabilized d^0 hydride derivatives (or direct precursors thereof) featuring ancillary ligands other than cyclopentadienyl groups”.[16b] In this paper, we describe attempts to develop the silyl chemistry of d^0 metal centers with ancillary imido ligands. On the basis of the “isolobal” relationship between bent metallocenes of the group 4 elements and bis(imido) complexes of group 6,[17] it seemed that complexes of the latter type might represent interesting candidates for investigation.

In this report, we describe synthetic routes to silyl and germyl derivatives of the $(2,6\text{-}{}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{N})_2\mathrm{M}$ (M = Mo, W) fragment. Initial investigations into this chemistry have concentrated on reactions with hydrosilanes and attempts to generate coordinatively unsaturated, d^0 silyl hydride complexes. Complexes of the latter type are of interest as potential intermediates in the dehydropolymerization of silanes, and they appear to be highly reactive based on the fact that they have proven difficult to isolate. We have recently reported the first 16-electron d^0 silyl hydride complexes $\mathrm{CpCp^*Hf[Si(SiMe_3)_3]H}$ and $\mathrm{CpCp^*Hf[SiH(SiMe_3)_2]H}$, which are reactive toward hydrosilanes and unsaturated molecules.[18] As described herein, attempts to produce silyl hydride complexes of molybdenum and tungsten appear to generate highly reactive intermediates which degrade via a novel σ-bond metathesis process.

Experimental Section

General Considerations. All manipulations were performed under an inert atmosphere of nitrogen or argon using either standard Schlenk techniques or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. To remove olefin impurities, pentane and benzene were pretreated with concentrated H_2SO_4, then 0.5 N $KMnO_4$ in 3 M H_2SO_4, followed by $NaHCO_3$, and finally $MgSO_4$. Benzene-d_6 and toluene-d_8 were purified by vacuum distillation from Na/K alloy. Yields determined by ^{1}H NMR spectroscopy were measured by relative integration against ferrocene as an internal standard, using a long delay time and a short pulse width. The compounds $(2,6\text{-}{}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{N})_2\mathrm{MoCl}_2(\mathrm{dme})$,[19] $(2,6\text{-}{}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{N})_2\mathrm{WCl}_2(\mathrm{dme})$,[20] $\mathrm{(THF)_3LiSi(SiMe_3)_3}$,[21] and $\mathrm{(THF)_3LiGe(SiMe_3)_3}$[22] were prepared according to literature procedures. Elemental analyses were performed by the Microanalytical Laboratory in the College of Chemistry at the University of California, Berkeley. NMR spectra were recorded on AMX-300 and VBAMX-400 spectrometers, and infrared spectra were recorded on a Mattson FTIR 3000 instrument.

$(2,6\text{-}{}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{N})_2\mathrm{Mo[Si(SiMe_3)_3]Cl}$ (1). $(2,6\text{-}{}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3\mathrm{N})_2\mathrm{MoCl}_2(\mathrm{dme})$ (4.80 g, 7.91 mmol) and $\mathrm{(THF)_3LiSi(SiMe_3)_3}$ (3.71 g, 7.90 mmol) were combined in a round bottom Schlenk flask equipped with a stir bar, and this mixture was then cooled to −80 °C. Cold (−80 °C) diethyl ether (50 mL) was added, the resulting solution was allowed to warm to room temperature, and stirring was continued for 10 h. The volatile material was removed by vacuum transfer, and the resulting residue was extracted with hexanes (50 mL). The hexane extract was filtered, and then the solvent was removed by vacuum transfer. The resulting deep red foam was dissolved in hexamethyldisiloxane (2 × 20 mL). This solution was filtered, concentrated, and cooled to 0 °C to afford deep red crystals of complex **1** (1.55 g, 1.97 mmol, 27%). Efforts to isolate more of complex **1** via crystallization afforded only a red oil. IR (Nujol, NaCl, $\mathrm{cm^{-1}}$): 3052 (w), 2951 (s), 2922 (s), 2854 (s), 2358 (m), 2341 (m), 1460 (s), 1379 (m), 1321 (m), 1257 (m), 1242 (m), 1176 (m), 1105 (m), 1043 (m), 1018 (m), 813 (s), 750 (m). ^{1}H NMR (dichloromethane-d_2, 300 MHz, 24 °C): δ 7.15−6.95 (m, 6 H, $\mathrm{NC_6}H_3{}^i\mathrm{Pr_2}$), 3.54 (sept, $J = 6.8$ Hz, 4 H, $\mathrm{NC_6H_3C}H\mathrm{Me_2}$), 1.05 (d, $J = 6.8$ Hz, 12 H, $\mathrm{NC_6H_3CH}Me_2$), 0.99 (d, $J = 6.8$ Hz, 12 H, $\mathrm{NC_6H_3CH}Me_2$), 0.41 (s, $\mathrm{Si(Si}Me_3)_3$, 27 H). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (dichloromethane-d_2, 75 MHz, 24 °C): δ 153.8, 143.1, 127.6,

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123.4 ($NC_6H_3{}^iPr_2$), 28.8 ($NC_6H_3CHMe_2$), 24.2, 24.1 ($NC_6H_3CHMe_2$), 3.25 ($Si(SiMe_3)_3$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 24 °C): δ −4.5 ($Si(SiMe_3)_3$), −9.3 ($Si(SiMe_3)_3$). Anal. Calcd for $C_{33}H_{61}ClN_2MoSi_4$: C, 54.33; H, 8.43; N, 3.84. Found: C, 53.70; H, 8.54; N, 3.73.

$(2,6\text{-}{}^iPr_2C_6H_3N)_2W[Si(SiMe_3)_3]Cl$ (2). To a cold (−80 °C) diethyl ether (30 mL) solution of $(2,6\text{-}{}^iPr_2C_6H_3N)_2WCl_2(dme)$ (5.00 g, 7.20 mmol) was added a diethyl ether (30 mL) solution of $(THF)_3LiSi(SiMe_3)_3$ (3.38 g, 7.20 mmol). The reaction mixture was allowed to slowly warm to room temperature with stirring over a 12 h period. The volatile material was removed under vacuum, and the resulting residue was extracted with hexanes (50 mL). Filtration and concentration of the hexanes solution followed by cooling to −80 °C afforded an orange powder that was impure by ^1H NMR spectroscopy and contained numerous organosilicon species, as indicated by the presence of peaks near δ 0.00. In an effort to obtain an analytically pure sample, this material was extracted into hexamethyldisiloxane (2 × 20 mL) to afford a dark orange solution, which was filtered, concentrated, and cooled to 0 °C. Unfortunately, crystallization attempts at both 0 and −35 °C were unsuccessful. Structural assignment for **2** follows from analysis of spectroscopic data for the crude material and by its conversion to the completely characterized neopentyl derivative **8**. ^1H NMR (benzene-d_6, 300 MHz, 24 °C): δ 7.10−6.85 (m, 6 H, $NC_6H_3{}^iPr_2$), 3.68 (sept, $J = 6.8$ Hz, 4 H, $NC_6H_3CHMe_2$), 1.11 (d, $J = 6.8$ Hz, 12 H, $NC_6H_3CHMe_2$), 1.07 (d, $J = 6.8$ Hz, 12 H, $NC_6H_3CHMe_2$), 0.44 (s, $Si(SiMe_3)_3$, 27 H). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75 MHz, 24 °C): δ 151.9, 143.2, 127.1, 122.9 ($NC_6H_3{}^iPr_2$), 28.6 ($NC_6H_3CHMe_2$), 24.3, 24.2 ($NC_6H_3CHMe_2$), 3.60 ($Si(SiMe_3)_3$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 24 °C): δ −2.0 ($Si(SiMe_3)_3$), −22.9 ($Si(SiMe_3)_3$).

$(2,6\text{-}{}^iPr_2C_6H_3N)_2Mo[Ge(SiMe_3)_3]Cl$ (3). The method for **1** was followed, utilizing $(2,6\text{-}{}^iPr_2C_6H_3N)_2MoCl_2(dme)$ (5.00 g, 8.24 mmol) and $(THF)_3LiGe(SiMe_3)_3$ (4.24 g, 8.23 mmol). Complex **3** was isolated as red crystals in 29% yield (1.81 g, 2.34 mmol) after four successive crops from hexamethyldisiloxane at −35 °C. Efforts to crystallize more material afforded a dark red oil containing the desired material. IR (toluene, NaCl, cm^{-1}): 3058 (m), 2969 (m), 2889 (m), 2279 (s), 1328 (m), 1244 (s), 854 (s), 827 (s), 619 (m). ^1H NMR (benzene-d_6, 400 MHz, 24 °C): δ 6.93 (s, 6 H, $NC_6H_3{}^iPr_2$), 3.76 (sept, $J = 7.0$ Hz, 4 H, $NC_6H_3CHMe_2$), 1.12 (d, $J = 6.9$ Hz, 12 H, $NC_6H_3CHMe_2$), 1.08 (d, $J = 6.9$ Hz, 12 H, $NC_6H_3CHMe_2$), 0.51 (s, 27 H, $Ge(SiMe_3)_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100 MHz, 24 °C): δ 153.8, 143.0, 127.7, 123.2 ($NC_6H_3{}^iPr_2$), 28.7 ($NC_6H_3CHMe_2$), 24.1 ($NC_6H_3CHMe_2$), 3.90 ($Ge(SiMe_3)_3$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 24 °C): δ 2.23 ($Ge(SiMe_3)_3$). Anal. Calcd for $C_{33}H_{61}ClGeMoN_2Si_3$: C, 51.20; H, 7.94; N, 3.62. Found: C, 51.42; H, 8.30; N, 3.46.

$(2,6\text{-}{}^iPr_2C_6H_3N)_2W[Ge(SiMe_3)_3]Cl$ (4). The method for complex **2** was followed, utilizing $(2,6\text{-}{}^iPr_2C_6H_3N)_2WCl_2(dme)$ (5.00 g, 7.20 mmol) and $(THF)_3LiGe(SiMe_3)_3$ (3.71 g, 7.20 mmol). The volatile materials were removed by vacuum transfer, and the resulting orange foam was extracted with hexanes (50 mL). The hexanes solution was filtered, concentrated, and cooled to −80 °C to afford an orange solid which was contaminated by organogermanium compounds, as determined by the presence of several singlets near δ 0.00 in the ^1H NMR spectrum. In an effort to obtain an analytically pure sample, this material was extracted into hexamethyldisiloxane (2 × 20 mL) to afford a dark orange solution, which was filtered, concentrated, and cooled to 0 °C. Unfortunately, crystallization attempts at both 0 and −35 °C were unsuccessful. Structural assignment for **4** follows from analysis of spectroscopic data for the crude material and by its conversion to the completely characterized neopentyl derivative **10**. ^1H NMR (benzene-d_6, 400 MHz, 24 °C): δ 7.10−6.85 (m, 6 H, $NC_6H_3{}^iPr_2$), 3.78 (sept, $J = 7.0$ Hz, 4 H, $NC_6H_3CHMe_2$), 1.18 (d, $J = 7.0$ Hz, 12 H, $NC_6H_3CHMe_2$), 1.14 (d, $J = 7.0$ Hz, 12 H, $NC_6H_3CHMe_2$), 0.52 (s, $Ge(SiMe_3)_3$, 27 H). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75 MHz, 24 °C): δ 151.9, 143.2, 127.0, 122.9 ($NC_6H_3{}^iPr_2$), 28.6 ($NC_6H_3CHMe_2$), 24.3, 24.1 ($NC_6H_3CHMe_2$), 4.23 ($Si(SiMe_3)_3$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 24 °C): δ 4.43 ($Ge(SiMe_3)_3$).

$(2,6\text{-}{}^iPr_2C_6H_3N)_2Mo[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3](Cl)$ (5). In a Schlenk tube, $(2,6\text{-}{}^iPr_2C_6H_3N)_2Mo[Si(SiMe_3)_3]Cl$ (0.400 g, 0.549 mmol) and 2,6-dimethylphenyl isocyanide (0.075 g, 0.58 mmol) were combined. Benzene (15 mL) was added at room temperature, and the solution was stirred for 6 h. The volatile material was removed, and the resulting residue was extracted into pentane (2 × 10 mL). The combined extracts were filtered, concentrated, and cooled to −80 °C to afford complex **5** (0.388 g, 0.451 mmol, 82%) as light orange crystals. IR (neat, NaCl, cm^{-1}): 3874 (w), 3709 (w), 3425 (w), 3055 (w), 3026 (w), 2960 (m), 2916 (m), 2906 (m), 2864 (m), 1608 (br, $\upsilon_{C=N}$), 1460 (m), 1423 (m), 1381 (m), 1360 (m), 1323 (m), 1286 (m), 1263 (m), 1248 (m), 1223 (m), 1113 (m), 1093 (m), 1059 (m), 1045 (m), 976 (m), 835 (s), 795 (m), 773 (m), 750 (m), 690 (m). ^1H NMR (benzene-d_6, 300 MHz, 24 °C): δ 7.10−6.85 (m, 9 H, $NC_6H_3{}^iPr_2$, $C_6H_3Me_2$), 4.02 (sept, $J = 6.7$ Hz, 4 H, $NC_6H_3CHMe_2$), 2.13 (s, 6 H, $CNC_6H_3Me_2$), 1.27 (d, $J = 6.7$ Hz, 12 H, $NC_6H_3CHMe_2$), 1.26 (d, $J = 6.7$ Hz, 12 H, $NC_6H_3CHMe_2$), 0.13 (s, 27 H, $Si(SiMe_3)_3$). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2, 100 MHz, 24 °C): δ 232.8 ($C(NAr)Si(SiMe_3)_3$), 153.7, 143.4, 128.8, 122.7 ($NC_6H_3{}^iPr_2$), 142.3, 130.0, 127.8, 125.7 ($NC_6H_3Me_2$), 28.5 ($NC_6H_3CHMe_2$), 24.5, 24.3 ($NC_6H_3CHMe_2$), 19.3 ($NC_6H_3Me_2$), 2.21 ($Si(SiMe_3)_3$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 24 °C): δ −9.7 ($Si(SiMe_3)_3$), −75.2 ($Si(SiMe_3)_3$). Anal. Calcd for $C_{42}H_{70}ClMoN_3Si_4$: C, 58.61; H, 8.20; N, 4.88. Found: C, 58.91; H, 8.34; N, 4.74.

$(2,6\text{-}{}^iPr_2C_6H_3N)_2Mo[Si(SiMe_3)_3](OSO_2CF_3)$ (6). In a Schlenk tube, $(2,6\text{-}{}^iPr_2C_6H_3N)_2Mo[Si(SiMe_3)_3]Cl$ (0.200 g, 0.274 mmol) and silver trifluoromethanesulfonate (0.074 g, 0.288 mmol) were combined. Benzene (20 mL) was added, and the solution was allowed to stir overnight at room temperature. The volatile material was removed, leaving a foamy residue to which hexanes (∼40 mL) was added. The resulting slurry was filtered to remove the solids, and the filtrate was concentrated and cooled to −35 °C to afford complex **6** (0.207 g, 0.245 mmol, 89%) as purple crystals. IR (neat, NaCl, cm^{-1}): 2960 (m), 2929 (m), 2914 (m), 2883 (m), 1527 (w), 1458 (m), 1259 (m), 1244 (m), 1093 (m), 1030 (m), 837 (s), 795 (m), 752 (m), 634 (m). ^1H NMR (benzene-d_6, 300 MHz, 24 °C): δ 6.90 (s, 6 H, $NC_6H_3{}^iPr_2$), 3.61 (sept, $J = 6.9$ Hz, 4 H, $NC_6H_3CHMe_2$), 1.11 (d, $J = 6.9$ Hz, 12 H, $NC_6H_3CHMe_2$), 1.08 (d, $J = 6.9$ Hz, 12 H, $NC_6H_3CHMe_2$), 0.43 (s, 27 H, $Si(SiMe_3)_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75 MHz, 24 °C): δ 153.7, 143.9, 128.9, 123.6 ($NC_6H_3{}^iPr_2$), 29.1 ($NC_6H_3CHMe_2$), 24.6, 24.2 ($NC_6H_3CHMe_2$), 3.48 ($Si(SiMe_3)_3$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 24 °C): δ 4.7 ($Si(SiMe_3)_3$), −2.9 ($Si(SiMe_3)_3$). Anal. Calcd for $C_{34}H_{61}F_3MoN_2O_3SSi_4$: C, 48.43; H, 7.29; N, 3.32. Found: C, 48.39; H, 7.43; N, 3.30.

$(2,6\text{-}{}^iPr_2C_6H_3N)_2Mo[Si(SiMe_3)_3](CH_2CMe_3)$ (7). Procedure A: Compound **6** (0.200 g, 0.237 mmol) and $(Me_3CCH_2)_2Mg$ (0.021 g, 0.125 mmol) were combined in a Schlenk tube. Toluene (∼25 mL) was added, and the solution was stirred overnight at room temperature. The volatile material was removed under reduced pressure, and the resulting residue was extracted into pentane (2 × 10 mL). The combined pentane extracts were filtered, concentrated (∼5 mL), and cooled to −35 °C to afford complex **7** (0.136 g, 0.178 mmol, 75%) as deep red crystals. IR (neat, NaCl, cm^{-1}): 2960 (m), 2883 (w), 2353 (w), 1261 (m), 1242 (m), 1093 (m), 1016 (m), 978 (m), 814 (s), 750 (m), 679 (m), 619 (m). ^1H NMR (benzene-d_6, 400 MHz, 24 °C): δ 7.05−6.90 (m, 6 H, $NC_6H_3{}^iPr_2$), 3.85 (sept, $J = 6.8$ Hz, 4 H, $NC_6H_3CHMe_2$), 2.08 (br s, 2 H, CH_2CMe_3), 1.21 (s, 9 H, CH_2CMe_3), 1.15 (d, $J = 6.8$ Hz, 12 H, $NC_6H_3CHMe_2$), 1.12 (d, $J = 6.8$ Hz, 12 H, $NC_6H_3CHMe_2$), 0.44 (s, 27 H, $Si(SiMe_3)_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100 MHz, 24 °C): δ 153.3, 143.0, 126.6, 123.3 ($NC_6H_3{}^iPr_2$), 124.7 (CH_2CMe_3), 40.1 (CH_2CMe_3), 33.1 (CH_2CMe_3), 28.3 ($NC_6H_3CHMe_2$), 24.7, 24.1 ($NC_6H_3CHMe_2$), 3.80 ($Si(SiMe_3)_3$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 24 °C): δ −5.3 ($Si(SiMe_3)_3$), −65.0 ($Si(SiMe_3)_3$).

Anal. Calcd for $C_{38}H_{72}MoN_2Si_4$: C, 59.64; H, 9.48; N, 3.66. Found: C, 59.69; H, 9.72; N, 3.65.

Procedure B: To a diethyl ether (20 mL) solution of (2,6-$^iPr_2C_6H_3N)_2Mo[Si(SiMe_3)_3]Cl$ (1.00 g, 1.37 mmol) was added an ether solution of $ClMgCH_2CMe_3$ (0.78 M, 1.80 mL, 1.40 mmol) at room temperature. Immediately the color of the solution changed from dark red to light red, and the solution was stirred overnight at room temperature. The volatile material was evacuated, and the resulting residue was extracted into pentane (3 × 5 mL). The combined extracts were filtered, concentrated, and cooled to −35 °C to afford complex **7** (0.590 g, 0.771 mmol, 55%) as deep red crystals.

(2,6-$^iPr_2C_6H_3N)_2Mo[Ge(SiMe_3)_3](CH_2CMe_3)$ (8). This complex was prepared as described for **7** (procedure B), from **3** (0.280 g, 0.362 mmol) and a dilute ether solution (5 mL) of $ClMgCH_2CMe_3$ (0.78 M, 1.80 mL, 1.40 mmol). Complex **8** was isolated as dark red crystals in 30% yield (0.072 g). IR (toluene, NaCl, cm^{-1}): 3068 (m), 3039 (m), 2989 (m), 2870 (m), 2698 (w), 1361 (w), 1323 (m), 1263 (m), 1242 (s), 860 (s), 823 (s), 619 (s). ^{1}H NMR (benzene-d_6, 300 MHz, 24 °C): δ 7.10−6.90 (m, 6 H, $NC_6H_3{}^iPr_2$), 3.85 (sept, J = 6.8 Hz, 4 H, $NC_6H_3CHMe_2$), 2.03 (br s, 2 H, CH_2CMe_3), 1.21 (s, 9H, CH_2CMe_3), 1.15 (d, J = 7.2 Hz, 12 H, $NC_6H_3CHMe_2$), 1.13 (d, J = 7.2 Hz, 12 H, $NC_6H_3CHMe_2$), 0.47 (s, 27 H, $Ge(SiMe_3)_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100 MHz, 24 °C): δ 153.3, 142.9, 126.5, 123.2 ($NC_6H_3{}^iPr_2$), 121.6 (CH_2CMe_3), 39.7 (CH_2CMe_3), 33.1 (CH_2CMe_3), 28.3 ($NC_6H_3CHMe_2$), 24.7 ($NC_6H_3CHMe_2$), 24.0 ($NC_6H_3CHMe_2$), 4.38 ($Ge(SiMe_3)_3$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 24 °C): δ 0.20 ($Ge(SiMe_3)_3$). Anal. Calcd for $C_{38}H_{72}GeMoN_2Si_3$: C, 56.36; H, 8.96; N, 3.46. Found: C, 56.63; H, 9.16; N, 3.36.

(2,6-$^iPr_2C_6H_3N)_2W[Si(SiMe_3)_3](CH_2CMe_3)$ (9). In a round bottom flask, a diethyl ether solution (20 mL) of crude (2,6-$^iPr_2C_6H_3N)_2W[Si(SiMe_3)_3]Cl$ (0.500 g) was stirred at room temperature. To this mixture was added a diethyl ether solution (diluted to ∼5 mL) of $ClMgCH_2CMe_3$ (0.78 M; 1.5 equiv). The color of the solution immediately changed from dark orange to light orange, and the solution was stirred overnight. The volatile materials were removed under vacuum, and the resulting residue was extracted with pentane (2 × 5 mL). The combined extracts were filtered, concentrated, and cooled to −35 °C to afford complex **9** (0.11 g, ca. 20%; unoptimized) as orange crystals. IR (neat, NaCl, cm^{-1}): 2960 (m), 2931 (m), 2902 (m), 2862 (m), 2353 (w), 2337 (w), 1454 (m), 1425 (m), 1327 (m), 1279 (m), 1259 (m), 1242 (m), 1109 (m), 1088 (m), 1024 (m), 804 (s), 750 (m), 680 (m). ^{1}H NMR (benzene-d_6, 400 MHz, 24 °C): δ 7.10−6.85 (m, 6 H, $NC_6H_3{}^iPr_2$), 3.80 (sept, J = 6.8 Hz, 4 H, $NC_6H_3CHMe_2$), 1.62 (br s, 2 H, CH_2CMe_3), 1.19 (s, 12 H, CH_2CMe_3), 1.17 (d, J = 6.8 Hz, 12 H, $NC_6H_3CHMe_2$), 1.14 (d, J = 6.8 Hz, 12 H, $NC_6H_3CHMe_2$), 0.43 (s, 27 H, $Si(SiMe_3)_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100 MHz, 24 °C): δ 152.4, 143.0, 135.3, 123.0 ($NC_6H_3{}^iPr_2$), 126.0 (CH_2CMe_3), 41.0 (CH_2CMe_3), 33.5 (CH_2CMe_3), 28.3 ($NC_6H_3CHMe_2$), 24.7, 24.1 ($NC_6H_3CHMe_2$), 4.00 ($Si(SiMe_3)_3$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 24 °C): δ −2.1 ($Si(SiMe_3)_3$), −59.4 ($Si(SiMe_3)_3$). Anal. Calcd for $C_{38}H_{72}MoN_2Si_4$: C, 53.50; H, 8.51; N, 3.28. Found: C, 52.95; H, 8.57; N, 3.29.

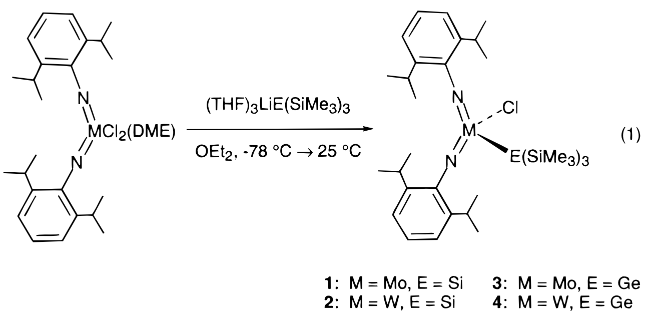
(2,6-$^iPr_2C_6H_3N)_2W[Ge(SiMe_3)_3](CH_2CMe_3)$ (10). To a stirred diethyl ether solution (∼15 mL) of crude (2,6-$^iPr_2C_6H_3N)_2W[Ge(SiMe_3)_3]Cl$ (2.00 g, 2.32 mmol) was added an excess of $ClMgCH_2CMe_3$ (∼3 equiv) as a diethyl ether solution at room temperature. The solution was stirred for an additional 8 h. The volatile materials were removed, and the residue was extracted with pentane (2 × 10 mL). The combined extracts were filtered, concentrated, and cooled to −35 °C to afford **10** (1.50 g, 72%) as orange crystals. IR (toluene, NaCl, cm^{-1}): 3068 (m), 3026 (m), 3001 (m), 2960 (m), 2916 (m), 2887 (m), 2873 (w), 2802 (w), 1604 (w), 1468 (w), 1346 (m), 1327 (m), 1284 (m), 1242 (m), 849 (s), 831 (s), 748 (m), 619 (m). ^{1}H NMR (benzene-d_6, 400 MHz, 24 °C): δ 7.08−6.90 (m, 6 H, $NC_6H_3{}^iPr_2$), 3.80 (sept, J = 6.8 Hz, 4 H, $NC_6H_3CHMe_2$), 1.57 (br s, 2 H, CH_2CMe_3), 1.19 (s, 9H, CH_2CMe_3), 1.17 (d, J = 8.7 Hz, 12 H, $NC_6H_3CHMe_2$), 1.15 (d, J = 8.7 Hz, 12 H, $NC_6H_3CHMe_2$), 0.47 (s, 27 H, $Si(SiMe_3)_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100 MHz, 24 °C): δ 152.4, 142.9, 125.9, 122.9 ($NC_6H_3{}^iPr_2$), 132.1 (CH_2CMe_3), 40.6 (CH_2CMe_3), 33.6 (CH_2CMe_3), 28.3 ($NC_6H_3CHMe_2$), 24.7, 24.1 ($NC_6H_3CHMe_2$), 4.60 ($Si(SiMe_3)_3$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 24 °C): δ 3.41 ($Ge(SiMe_3)_3$). Anal. Calcd for $C_{38}H_{72}MoN_2Si_4$: C, 50.84; H, 8.08; N, 3.12. Found: C, 50.52; H, 8.18; N, 3.02.

(2,6-$^iPr_2C_6H_3N)_2Mo[\eta^2$-C(N-2,6-$Me_2C_6H_3)Si(SiMe_3)_3](CH_2CMe_3)$ (11). The compounds **7** (0.200 g, 0.261 mmol) and 2,6-dimethylphenyl isocyanide (0.035 g, 0.267 mmol) were combined in a Schlenk flask. Benzene (∼10 mL) was added at room temperature, and the solution was stirred for an additional 3 h. The volatile materials were removed, and the residue was extracted with pentane (10 mL). The combined extracts were filtered, concentrated, and cooled to −35 °C to afford complex **11** as small yellow crystals (0.092 g, 39%). NMR-tube experiments indicate that the reaction proceeds in greater than 80% yield. IR (neat, NaCl, cm^{-1}): 3058 (w), 3048 (m), 2925 (m), 2897 (m), 2865 (m), 2781 (w), 1594 (br, $\upsilon_{C=N}$), 1460 (m), 1423 (m), 1319 (m), 1250 (m), 1246 (m), 1101 (m), 1020 (m), 830 (s), 827 (s), 750 (m). ^{1}H NMR (benzene-d_6, 300 MHz, 24 °C): δ 7.15−6.80 (m, 9 H, $NC_6H_3{}^iPr_2$, $CNC_6H_3Me_2$), 3.94 (sept, J = 7.0 Hz, 4 H, $NC_6H_3CHMe_2$), 2.68 (s, 2 H, CH_2CMe_3), 2.04 (s, 6 H, $CNC_6H_3Me_2$), 1.28 (d, J = 7.0 Hz, 12 H, $NC_6H_3CHMe_2$), 1.26 (d, J = 7.0 Hz, 12 H, $NC_6H_3CHMe_2$), 1.00 (s, 9H, CH_2CMe_3), 0.18 (s, 27 H, $Si(SiMe_3)_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100 MHz, 24 °C): δ 244.8 ($C(NAr)Si(SiMe_3)_3$), 153.7, 143.1, 129.2, 123.2 ($NC_6H_3{}^iPr_2$), 142.3, 129.2, 127.0, 124.5 ($NC_6H_3Me_2$), 53.6 (CH_2CMe_3), 35.6 (CH_2CMe_3), 34.7 (CH_2CMe_3), 27.9 ($NC_6H_3CHMe_2$), 25.1, 24.8 ($NC_6H_3CHMe_2$), 19.1 ($NC_6H_3Me_2$), 2.70 ($Si(SiMe_3)_3$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 24 °C): δ −10.2 ($Si(SiMe_3)_3$), −78.5 ($Si(SiMe_3)_3$). Anal. Calcd for $C_{47}H_{81}MoN_3Si_4$: C, 62.97; H, 9.11; N, 4.69. Found: C, 62.68; H, 9.09; N, 4.64.

X-ray Crystallography. Crystallographic data for complexes **1** and **7** are collected in Table 1. For **1** the space group was uniquely determined by systematic absences, and for **7** the centrosymmetric alternative was initially assumed and was found to be computationally stable. Empirical corrections for absorption were applied to the data. Solutions were by direct methods, and all non-hydrogen atoms were anisotropically refined. Hydrogen atoms were idealized, except for H(1) in **7** which was located and refined with a fixed thermal parameter. In **7**, the $SiMe_3$ groups are disordered over two sites in an 80/20 ratio. For the minority site, only the Si atom positions were resolved as Si(2′), Si(3′), and Si(4′). SHELXTL-(5.1) software was used for all computations (G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

Bis(imido) Silyl and Germyl Complexes. The silyl chloride complexes (2,6-$^iPr_2C_6H_3N)_2M[Si(SiMe_3)_3]$-Cl (**1**, M = Mo; **2**, M = W) were prepared by reaction of $(THF)_3LiSi(SiMe_3)_3$ with the corresponding dichlorides (2,6-$^iPr_2C_6H_3N)_2MCl_2(dme)$ (M = Mo,[19] W[20]) in diethyl ether (eq 1). To our knowledge, compound **1** represents



1: M = Mo, E = Si **3**: M = Mo, E = Ge
2: M = W, E = Si **4**: M = W, E = Ge

Table 1. Crystallographic Data for Compounds 1 and 7

	1	**7**
	(a) Crystal Parameters	
formula	$C_{33}H_{61}ClMoN_2Si_4$	$C_{38}H_{72}MoN_2Si_4$
fw	729.59	764.27
cryst color, habit	red block	red plate
cryst size, mm	0.14 × 0.10 × 0.08	0.40 × 0.40 × 0.20
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	9.3039(3)	11.2900(9)
b, Å	20.5308(5)	12.895(1)
c, Å	21.7343(5)	16.756(5)
α, deg		96.378(9)
β, deg	97.360(10)	94.183(9)
γ, deg		109.141(7)
volume, Å^3	4117.4(2)	2274.6(4)
Z	4	2
ρ (calcd), g cm^{-3}	1.177	1.116
μ (Mo Kα), cm^{-1}	5.22	4.19
temp, K	193(2)	233(2)
	(b) Data Collection	
diffractometer	Siemens SMART	Siemens SMART
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
θ range for data collection, deg	1.37−26.38	2.09−30.00
no. of rflns collected	16 610	14 801
no. of unique rflns	8012 (R_{int} = 0.0546)	13 082 (R_{int} = 0.0344)
	(c) Refinement	
rfln/param ratio	21.6	30.0
$R(F)$, %	7.43	5.88
$R(wF^2)$, %	17.11	11.01
GOF	1.481	1.203
max/min peak in final diff map, e Å^{-3}	0.643, −0.574	0.674, −0.478

the first example of a d^0 silyl complex of molybdenum, however, the d^0 tungsten complex $(Me_3CCH_2)_2W{\equiv}CMe_3[Si(SiMe_3)_3]$ is known.[7a] An analytically pure sample of **1** was obtained from hexamethyldisiloxane at 0 °C as dark red, platelike crystals in 27% yield. Complex **2**, however, was obtained as a bright orange powder that was contaminated by a number of organosilicon byproducts, as determined by ^{1}H NMR spectroscopy. Spectroscopic data for **1** and **2** are consistent with the proposed structures. The ^{1}H NMR spectra contain singlets for the silyl ligands, at 0.41 ppm for **1** and 0.44 ppm for **2**, and two doublets (δ 0.99 and 1.05 for **1**; δ 1.07 and 1.11 for **2**) for the inequivalent methyl groups of the imido ligands reflecting an unsymmetrical substitution pattern at the metal. As expected, only one septet for the methine protons of the isopropyl groups is observed (**1**, δ 3.54; **2**, δ 3.68). The ^{29}Si NMR spectra for complexes **1** and **2** are quite unusual in that the metal-bound silicon atoms are remarkably downfield-shifted (**1**, δ −9.3; **2**, δ −22.9) relative to similar silicon atoms in other early metal $-Si(SiMe_3)_3$ derivatives. For comparison, the ^{29}Si shifts for the metal-bound silicon atoms in $CpCp^*Zr[\mathit{Si}(SiMe_3)_3]Cl$,[3k] $CpCp^*Hf[\mathit{Si}(SiMe_3)_3]Cl$,[23] and $Cp^*(2,6\text{-}^iPr_2C_6H_3N)Ta[\mathit{Si}(SiMe_3)_3]Cl$[24] are −87.3, −77.9, and −48.3 ppm, respectively. Further support for the structural assignments for complexes **1** and **2** is based on their conversions to silyl−neopentyl derivatives (*vide infra*). Finally, the molecular structure of complex **1** was confirmed by X-ray crystallography.

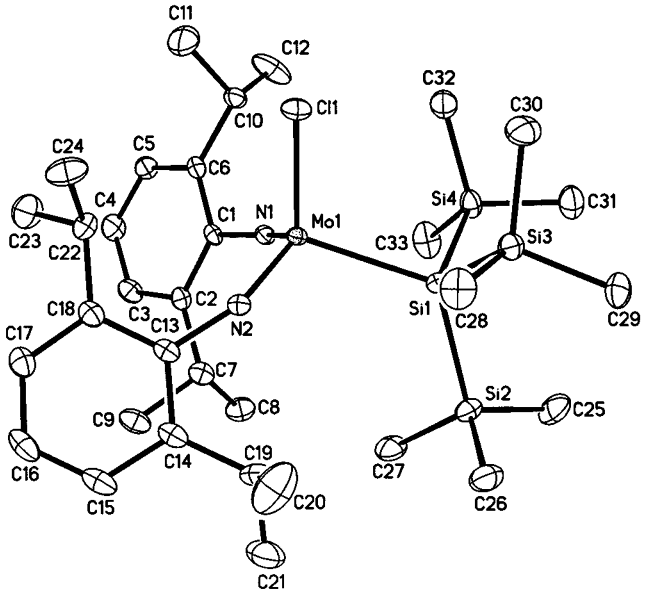


Figure 1. ORTEP view of the molecular structure of $(2,6\text{-}^iPr_2C_6H_3N)_2MoCl[Si(SiMe_3)_3]$ (**1**).

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $(2,6\text{-}^iPr_2C_6H_3N)_2Mo[Si(SiMe_3)_3](Cl)$ (1)

	(a) Bond Distances		
Mo(1)−N(1)	1.748(4)	Mo(1)−N(2)	1.753(4)
Mo(1)−Si(1)	2.562(2)	Mo(1)−Cl(1)	2.3093(14)
Si(1)−Si(2)	2.355(2)	Si(1)−Si(3)	2.363(2)
Si(1)−Si(4)	2.365(2)	Si(2)−C(25)	1.857(8)
N(1)−C(1)	1.394(6)	N(2)−C(13)	1.408(7)
	(b) Bond Angles		
N(1)−Mo(1)−N(2)	109.3(2)	Cl(1)−Mo(1)−Si(1)	109.24(5)
N(1)−Mo(1)−Cl(1)	112.83(14)	C(13)−N(2)−Mo(1)	151.3(4)
N(1)−Mo(1)−Si(1)	103.19(14)	C(1)−N(1)−Mo(1)	155.5(4)

The structure of complex **1** is shown in Figure 1, and selected bond distances and angles are summarized in Table 2. The Mo−N bond distances of 1.748(4) and 1.753(4) Å are consistent with related values in other molybdenum imido complexes.[25] The Mo−Si bond distance of 2.562(2) Å is similar to the corresponding distance in the d^2 molybdocene silyl complex $Cp_2Mo(SiMe_2Cl)H$, 2.513(1) Å[26] but is slightly shorter than the Mo−Si bond length of 2.670(2) Å in $Mo_2[Si(SiMe_3)_3]_2(NMe_2)_4$.[27] The M−N−C angles of 155.5(4)° (Mo−N(1)−C(1)) and 151.3(4)° (Mo−N(2)−C(13)) are consistent with the corresponding angles in $[(2,6\text{-}^iPr_2C_6H_3N)(^tBuN)Mo(CH_2CMe_3)_2]$ (156.2(1)° and 157.9(1)°).[25]

The analogous germyl complexes $(2,6\text{-}^iPr_2C_6H_3N)_2M[Ge(SiMe_3)_3]Cl$ (**3**, M = Mo; **4**, M = W) have been prepared by reaction of $(THF)_3LiGe(SiMe_3)_3$ with the corresponding dichlorides $(2,6\text{-}^iPr_2C_6H_3N)_2MCl_2(DME)$ (M = Mo, W; eq 1). As for the silyl derivatives, only the molybdenum analog was obtained in analytically pure form. Complex **3** was isolated from hexamethyldisiloxane at 0 °C as dark red crystals in 29% yield. Spectroscopic data for the germyl complexes are, as expected, very similar to those for the corresponding silyl derivatives.

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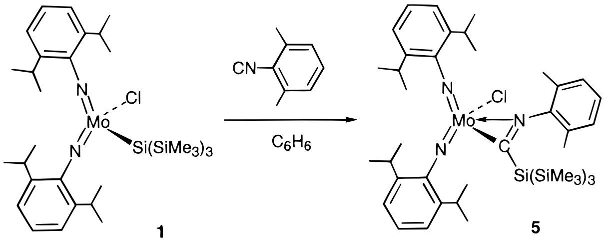
Reactions of Bis(imido) Silyl and Germyl Complexes. Complex **1** does not react with H_2, CO, or C_2H_4 (benzene-d_6, 1 atm, 24 h) or with CH_3CN (1.5 equiv, benzene-d_6, 24 h). Also, there is no reaction between **1** and $PhSiH_3$ (1.0 equiv) in benzene-d_6 at room temperature over 12 h. After the latter mixture was heated to 62 °C for 1 day, mostly starting material remained (94%) but trace amounts of the products $HSi(SiMe_3)_3$ (7%), Ph_2SiH_2 (5%), and $HSiMe_3$ (3%) were also detected. Heating to 80 °C for a second day produced a mixture containing 65% of the starting material **1** as well as $HSi(SiMe_3)_3$ (18%), $HSiMe_3$ (4%), and the redistribution product Ph_2SiH_2 (8%). Similarly, a benzene-d_6 solution of complex **1** did not react with Ph_2SiH_2 (1.0 equiv) at room temperature, but heating for 4 days at 62 °C produced trace amounts of $HSi(SiMe_3)_3$ (8%), $HSiMe_3$ (2%), and Ph_3SiH (2%). The generation of $HSi(SiMe_3)_3$ in these reactions suggests a σ-bond metathesis mechanism,[16,23] but the molybdenum-containing product(s) could not be characterized. Particularly interesting is the production of $HSiMe_3$, which results from Si−Si bond cleavage. As discussed below, this product may result from decomposition of $(2,6\text{-}^iPr_2C_6H_3N)_2Mo[Si(SiMe_3)_3](H)$, which could form in the above reactions of the silanes via an Si−H/Mo−Cl exchange.

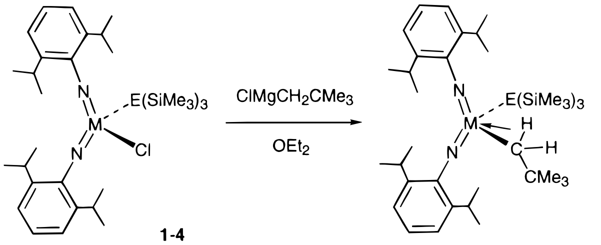
Complex **1** reacted rapidly with 2,6-dimethylphenylisocyanide in benzene at room temperature to afford the corresponding insertion product **5** (eq 2). An analytically pure sample of **5** was obtained in 82% yield from pentane as light orange needles. The ^1H NMR spectrum of complex **5** contains two doublets (δ 1.26 and 1.27) for the inequivalent methyl groups of the imido ligands and a singlet at δ 2.13 for the methyl groups of the isocyanide group. The ^{13}C NMR spectrum contains a resonance for the deshielded isonitrile carbon at δ 232.8, and the infrared stretch for the iminosilaacyl ligand at 1608 cm^{-1} is characteristic for complexes of this type.[3d,k,n,28]



1   5   (2)

To examine potential electronic effects on reactions of Mo−Si bonds in this system, we prepared the silyl triflate complex $(2,6\text{-}^iPr_2C_6H_3N)_2Mo[Si(SiMe_3)_3](OTf)$ (**6**) from **1** and silver triflate in benzene solution. The complex was obtained in 89% yield as purple needles from hexanes. The ^1H NMR spectrum of complex **6** contains two doublets (δ 1.08 and 1.11) for the inequivalent methyl groups of the imido ligand and a new singlet at δ 0.43 for the silyl ligand. Also, the ^{29}Si NMR spectrum reveals that the chemical shift for the coordinated silicon atom, at δ 4.73, is dramatically downfield-shifted relative to silicon atoms in similar early-metal complexes (*vide supra*). The infrared spectrum contains a band at 1458 cm^{-1} which may be assigned as the $\nu(SO_3)$ stretching frequency for an inner-sphere triflate complex.[29] Complex **6** did not react with $PhSiH_3$ (1 equiv) in benzene-d_6 at room temperature after 6 h, but when this reaction mixture was heated to 62 °C for 12 h, complete consumption of $PhSiH_3$ occurred and 35% of **6** remained unreacted. Also produced in this reaction was $HSi(SiMe_3)_3$ (0.19 equiv), $HSiMe_3$ (0.11 equiv), Ph_2SiH_2 (0.12 equiv), and Me_3SiOTf (0.19 equiv).

Silyl−Neopentyl and Germyl−Neopentyl Complexes of Mo(VI) and W(VI). Complexes **1**−**4** and **6** react with neopentylmagnesium chloride or bis(neopentyl)magnesium to afford the corresponding neopentyl complexes **7**−**10** (eq 3). Analytically pure samples of **7**−**10** were obtained from pentane at −35 °C as red (**7** and **9**) or orange (**8** and **10**) crystals, typically in greater than 70% yield. These complexes contain α-agostic M−C−H interactions, as determined by NMR spectroscopy and X-ray crystallography. Complexes containing α-agostic interactions are often highly fluxional and undergo rapid exchange of the agostic hydrogen with other hydrogens bound to the same carbon atom.[30] In the ^1H NMR spectrum of **7**, the methylene hydrogens of the neopentyl ligand appear at δ 2.08 as a broad singlet, suggesting a dynamic process involving exchange of the two methylene hydrogen atoms. This resonance only broadened further as a dichloromethane-d_2 solution of **7** was cooled to −80 °C, suggesting a barrier to interconversion of <7−8 kcal mol^{-1}. This situation, therefore, differs somewhat from the recently characterized complexes $[Cp(2,6\text{-}^iPr_2C_6H_3N)Nb(CH_2CMe_3)Cl]$,[31] $(2,6\text{-}^iPr_2C_6H_3N)(^tBuN)Mo(CH_2CMe_3)_2]$,[25] and $[Cp(2,6\text{-}^iPr_2C_6H_3N)Nb(CH_2CMe_3)Cl]$,[31] which exhibit sharp doublet resonances for the methylene protons ($^2J_{HH} \approx 12$ Hz).



1-4   (3)

7: M = Mo, E = Si   **9**: M = Mo, E = Ge
8: M = W, E = Si   **10**: M = W, E = Ge

The ^{13}C NMR spectrum of **7** contains a resonance at δ 124.7 attributed to the highly deshielded α carbon of the neopentyl ligand. For comparison, the ^{13}C shifts for the α-carbon atoms of the neopentyl ligands in $[(2,6\text{-}^iPr_2C_6H_3N)(^tBuN)Mo(CH_2CMe_3)_2]$,[25] $[Cp(2,6\text{-}^iPr_2C_6H_3N)Nb(CH_2CMe_3)Cl]$,[31] and $[Cp(2,6\text{-}^iPr_2C_6H_3N)Nb(CH_2CMe_3)_2]$[31] are 77.9, 86.3, and 85.7 ppm, respectively. The IR spectra for complexes containing an α-agostic interaction typically contain a C−H stretch in the range 2700−2300 cm^{-1},[30,31] but no such assignment for an α-agostic C−H stretch could be made for complexes **7**−**10**.

The structure of **7** is shown in Figure 2, and selected bond distances and angles are summarized in Table 3.

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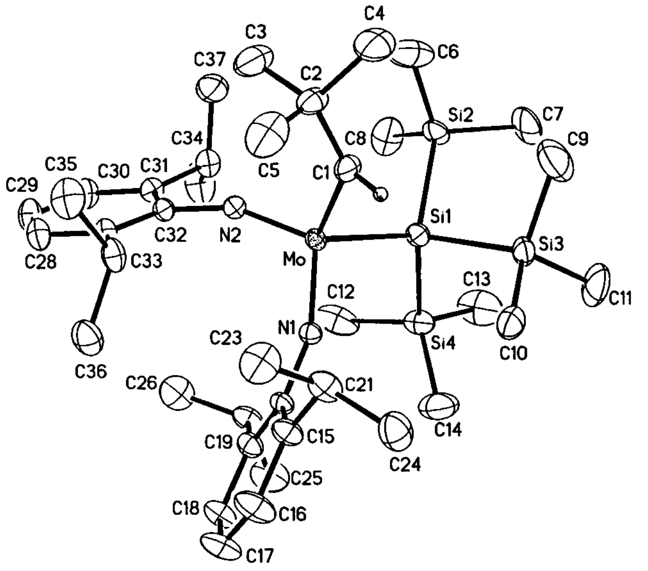


Figure 2. ORTEP view of the molecular structure of (2,6-$^iPr_2C_6H_3N)_2Mo[Si(SiMe_3)_3](CH_2CMe_3)$ (**7**).

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for (2,6-$^iPr_2C_6H_3N)_2Mo(CH_2CMe_3)[Si(SiMe_3)_3]$ (7)

(a) Bond Distances			
Mo(1)–N(1)	1.754(2)	Mo(1)–N(2)	1.752(2)
Mo(1)–Si(1)	2.6048(9)	Mo(1)–C(1)	2.083(3)
N(1)–C(20)	1.404(3)	N(2)–C(32)	1.399(4)
Mo(1)–H(1)	2.55(4)	Si(1)–Si(3)	2.416(2)
Si(1)–Si(4)	2.321(2)	Si(1)–Si(2)	2.3431(14)
C(2)–C(3)	1.503(5)	C(1)–C(2)	1.502(4)
(b) Bond Angles			
N(1)–Mo(1)–N(2)	112.68(11)	C(1)–Mo(1)–Si(1)	106.39(10)
N(1)–Mo(1)–C(1)	110.66(10)	C(20)–N(1)–Mo	161.6(2)
N(1)–Mo(1)–Si(1)	104.87(7)	C(32)–N(2)–Mo	157.4(2)
C(2)–C(1)–Mo	136.6(2)	Si(2)–Si(1)–Mo	118.13(5)

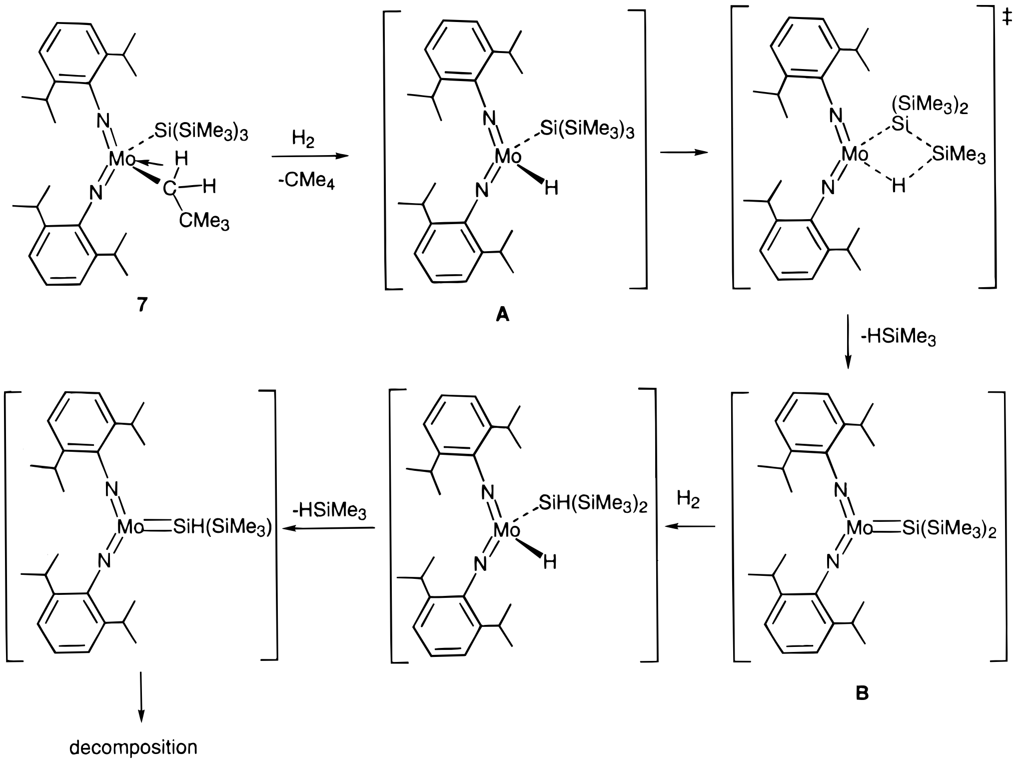
The interesting feature of this structure is the presence of an α-agostic interaction involving a hydrogen of the neopentyl ligand. The hydrogen atom involved in this interaction was located and refined with a fixed thermal parameter. The Mo–H(agostic) distance of 2.55(4) Å is comparable to related distances in molybdenum neopentyl complexes. For example, α-agostic interactions for the two neopentyl ligands in (2,6-$Pr^i_2C_6H_3N)(^tBuN)Mo(CH_2CMe_3)_2$ result in Mo–H distances of 2.35 and 2.44 Å.[25] The Mo–Si bond distance of 2.608(9) Å in **7** is close to the related distance in **1** of 2.562(2) Å. Furthermore, the Mo–N bond distances of 1.754(2) and 1.752(2) Å are consistent with alkyl and aryl imido ligands bonded to molybdenum. The M–N–C angles of 157.4(2)° (Mo–N(2)–C(32)) and 161.6(2)° (Mo–N(1)–C(20)) are consistent with the corresponding angles of 156.2(1)° and 157.9(1)° in [(2,6-$Pr^i_2C_6H_3N)(Bu^tN)Mo(CH_2CMe_3)_2$].[25]

Reactions of the Silyl–Neopentyl and Germyl–Neopentyl Complexes. Complex **7** reacted rapidly with 2,6-dimethylphenyl isocyanide to afford the insertion product (2,6-$^iPr_2C_6H_3N)_2Mo[CH_2CMe_3][\eta^2$-C(N-2,6-$Me_2C_6H_3)Si(SiMe_3)_3]$ (**11**), isolated from pentane in 39% yield. Exclusive insertion of the isocyanide into the Mo–Si bond is revealed by characteristic ^{13}C NMR and infrared data.[3d,k,n,28] The iminosilaacyl carbon resonates at δ 244.8 in the ^{13}C NMR spectrum, and the ν(C=N) stretch was observed at 1594 cm^{-1}.

The reaction of complex **7** with excess $PhSiH_3$ (3 equiv) resulted in complete consumption of both starting materials after 12 h and production of neopentane (1 equiv), trimethylsilane (1.08 equiv), and minor amounts of tris(trimethylsilyl)silane (0.12 equiv) and Ph_2SiH_2 (0.05 equiv). The remaining molybdenum-containing material could not be identified, and the ^1H NMR spectrum of the crude reaction mixture reveals a plethora of broad, featureless peaks in the imido, aryl, and silyl regions. In the absence of a precipitate, this suggests that at least some of the molybdenum-containing product(s) are paramagnetic. The formation of 1 equiv of neopentane suggests that the initial product of reaction is the bis(silyl) complex (2,6-$^iPr_2C_6H_3N)_2Mo[Si(SiMe_3)_3](SiH_2Ph)$. However, this species could not be observed in solution, and based on the chemistry described below, it is tempting to speculate that the trimethylsilane results from decomposition of the silyl hydride (2,6-$^iPr_2C_6H_3N)_2Mo[Si(SiMe_3)_3](H)$ (**A**), which could arise from reaction of the bis(silyl) complex with a second equivalent of $PhSiH_3$. Interestingly, however, PhH_2SiSiH_2Ph is not observed as a product in the reaction mixture. Of course, PhH_2SiSiH_2Ph may be consumed as it is formed and converted to other, unidentified organosilicon compounds. If 1 equiv of $PhSiH_3$ is employed in the reaction, only ca. 40% of **7** is consumed and the observed products (by ^1H NMR spectroscopy) are neopentane (0.42 equiv), $HSiMe_3$ (0.60 equiv), $HSi(SiMe_3)_3$ (0.08 equiv), and Ph_2SiH_2 (0.01 equiv).

To further probe the possibility of silyl hydride intermediates in the above reaction involving phenylsilane, we investigated the reactions of **7–10** with hydrogen. When a benzene-d_6 solution of **7** was placed under an atmosphere of H_2 at room temperature, the color of the solution changed from red to brown and free neopentane (0.94 equiv) and $HSiMe_3$ (1.8 equiv) were produced within 3 h. When the reaction was complete (6 h), the only observable products (by ^1H NMR spectroscopy) were neopentane and trimethylsilane. The absence of any well-defined ^1H NMR resonances attributable to 2,6-$^iPr_2C_6H_3N$ ligands and the lack of a precipitate suggest that the Mo-containing products are paramagnetic. In addition, the silanes $HSi(SiMe_3)_3$ and $H_2Si(SiMe_3)_2$ were not detected as products. The initial step in this reaction appears to involve hydrogenolysis of the Mo–C bond of **7** to produce neopentane, and further evidence for this was found in the reaction of **7** with deuterium, which gave neopentane-d_1 and $DSiMe_3$ (by ^2H NMR spectroscopy). Thus, the initial Mo-containing product is probably the silyl hydride species (2,6-$^iPr_2C_6H_3N)_2Mo[Si(SiMe_3)_3](H)$ (**A**), which is apparently too reactive to be detected as an intermediate during the course of the reaction. It therefore appears that the $HSiMe_3$ product in this reaction results from an interesting elimination from **A**. Further support for this was observed in the reaction of **1** (in benzene-d_6) with a THF solution of $LiBEt_3H$ (1.5 equiv), which produced trimethylsilane as the major product (by ^1H NMR spectroscopy). On the basis of our very limited knowledge of d^0 silyl hydride complexes, it is difficult at this time to speculate on the mechanism of such an elimination. However, an intriguing possibility involves decomposition of **A** via a 4-centered transition state to generate a silylene complex (Scheme 1). The observed

Scheme 1



formation of ca. 2 equiv of $HSiMe_3$ requires that such a process be repeated, and this could occur via hydrogenation of the proposed silylene complex with a second equivalent of hydrogen, as shown in Scheme 1. Hengge and co-workers have suggested a similar elimination involving Si−Si bond cleavage for a polymerization catalyzed by titanocene derivatives.[8b]

We also considered the possibility that the $HSiMe_3$ product arises via a metal-catalyzed redistribution reaction of $HSi(SiMe_3)_3$, which is the typical silicon-containing decomposition product of $M-Si(SiMe)_3$ derivatives. To test this, complex **7** was allowed to react with hydrogen in the presence of 10 equiv of $HSi(SiMe_3)_3$. In this reaction, the conversion of **7** occurred without enhanced production of $HSiMe_3$. It therefore seems that free $HSi(SiMe_3)_3$ is not an intermediate in the decomposition of **A** to $HSiMe_3$.

Numerous attempts to trap a potential silylene intermediate with excess amounts of various silylene trapping reagents failed. Interestingly, when a benzene-d_6 solution of complex **7** was allowed to react with excess PMe_3, 2-butyne, or 1,3-butadiene under 1 atm of hydrogen for 24 h, the major products were free neopentane and $HSi(SiMe_3)_3$ and only a minor amount of $HSiMe_3$ was detected (by NMR spectroscopy). However, hydrogenations in the presence of diphenylacetylene, methyl iodide, or trimethylsilyl bromide produced neopentane and $HSiMe_3$ as the major products, and only a minor amount of $HSi(SiMe_3)_3$ was observed. In all but one case, the remaining molybdenum-containing material could not be isolated. In the presence of excess PMe_3, the hydrogenation of **7** produced $(2,6\text{-}^iPr_2C_6H_3N)_2Mo(PMe_3)_2$.[17d] These observations seem to indicate that better ligands for molybdenum (L = PMe_3, 2-butyne, or 1,3-butadiene) transiently trap the proposed silyl hydride intermediate to give species of the type $(2,6\text{-}^iPr_2C_6H_3N)_2Mo[Si(SiMe_3)_3](H)(L)$, which then decompose via reductive elimination of silane. Alternatively, with less coordinating reagents (MeI, diphenylacetylene, Me_3SiBr), the silyl hydride intermediate is not intercepted and decomposition via Si−Si bond cleavage occurs.

With the hope of stabilizing intermediates such as **B**, we examined the reactions of **8**−**10** with hydrogen. The tungsten complex **8** undergoes the same reaction with hydrogen (1 atm, room temperature) but at a much slower rate (complete conversion after ca. 7 days). No intermediates were observed in this reaction, and only broad, featureless peaks were observed for the imido ligands (by ^1H NMR spectroscopy). The reactions of **9** and **10** with hydrogen were also examined, which according to Scheme 1 would generate the potentially more stable germylene complexes $(2,6\text{-}^iPr_2C_6H_3N)_2M{=}Ge(SiMe_3)_2$ (M = Mo, W). However, attempts to trap these possible germylene intermediates with 2-butyne and diphenyl acetylene were unsuccessful.

Conclusions

In summary, we have prepared and investigated the reactivity of several d^0, bis(imido) silyl complexes. In some respects, these silyl complexes are less reactive than the corresponding group 4 metallocene complexes. The bis(imido) silyl complexes do not polymerize hydrosilanes, but instead mediate interesting reactions involving Si−Si bond cleavage. Complexes **1**−**4** are readily alkylated to the corresponding neopentyl complexes **7**−**10** in good to high yield. Complexes **7**−**10** react with hydrogen or hydrosilanes to generate the probable hydride intermediates $(2,6\text{-}^iPr_2C_6H_3N)_2M[E(SiMe_3)_3](H)$ (**A**), which rapidly decompose via elimination of trimethylsilane. In contrast, the group 4 hydrido silyl complex $CpCp^*Hf[Si(SiMe_3)_3]H$ decomposes by elimination of $HSi(SiMe_3)_3$, and no $HSiMe_3$ is observed.[18] This chemistry raises some interesting questions concerning possible reactivity patterns for early transition-metal silyl complexes. It suggests operation of a σ-bond metathesis mechanism for Si−Si bond cleavage, but this remains quite speculative at the moment given the lack of direct experimental evidence. The observed elimination chemistry also suggests the possible formation of heretofore unknown early transition-metal silylene complexes and the possible intermediacy of such complexes in catalytic chemistry. Efforts in this area continue to focus on isolating or trapping such silylene species.

Acknowledgment is made to the National Science Foundation for their generous support of this work. Dr. Charles Campana is acknowledged for his assistance with the structure determinations.

Supporting Information Available: Tables of crystal data, collection, and refinement parameters, positional and anisotropic displacement parameters, bond distances and angles, and hydrogen coordinates for **1** and **7** (13 pages). Ordering information is given on any current masthead page.

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