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Multiple coupling of silanes with imido complexes of Mo [†]

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The bis(imido) complexes ($^tBuN=)_2Mo(PMe_3)(L)$ (L= PMe_3, C_2H_4) reacts with up to three equivalents of silane $PhSiH_3$ to give the imido-bridged disilyl silyl Mo(VI) complex ($^tBuN=)\{\mu\text{-}^tBuN(SiHPh)_2\}Mo(PMe_3)(H)(SiH_2Ph)$ (**3**) studied by NMR, IR and X-ray diffraction. NMR data supported by DFT calculations show that complex **3** is an unusual example of a silyl hydride of Mo(VI),
10 without significant Si···H interaction. Mechanistic NMR studies revealed that silane addition proceeds in a stepwise manner via a series of Si-H···M agostic and silanimine complexes whose structures were further elucidated by DFT calculations.

Introduction

Metal mediated transformations of silanes are important in the
15 context of hydrosilylation reactions,[1] silane aminolysis and alcoholysis,[2] and C-C coupling reactions of silicates.[3] In most cases metal complexes can add only one equivalent of silane to give the silyl or silane products and intermediates, but addition of two equivalents of silane is also well documented.[4] In contrast,
20 only very few examples of multiple silane addition are known.[5-9] These include the preparation of tris(silyl) complexes of Pt[5,6] and Ni,[7] a bis(silyl) bis(disilane) σ-complex of Pd,[8] and a tetra(silane) complex of Ti.[9]

We have previously reported couplings of silanes with imido
25 complexes of Mo to give β-agostic silylamido complexes[10] and more recently reported a double silane addition to the bis(arylimido) complex ($ArN=)_2Mo(PMe_3)_3$ to give the agostic silylamido silyl complex ($ArN=)(\eta^3\text{-}ArNSiPhH\text{-}H)Mo(PMe_3)(SiH_2Ph)$.[11] Reactions of the latter compound with
30 unsaturated substrates showed the possibility of multicomponent silane additions to organic molecules,[12] however, making such interesting transformations in a catalytic fashion requires the detachment of the transformed imido moiety from the metal at some step. Here we report a triple silane addition to the
35 bis(alkylimido) complex ($^tBuN=)_2Mo(PMe_3)_2$ which results in the ultimate disconnection of one of the imido ligands from the metal. Mechanistic studies further revealed the intermediacy of rare γ-Si-H agostic[13,14] and silanimine[12,15] complexes.

Results and discussion

40 Room temperature reactions of the bis(imido) complexes ($^tBuN=)_2Mo(L)(PMe_3)$ (L = PMe_3 (**1**), $\eta^2\text{-}CH_2=CH_2$ (**2**)) with 3 equivalents of $PhSiH_3$ afford the compound ($^tBuN)\{\mu\text{-}^tBuN(SiHPh)_2\}Mo(H)(SiH_2Ph)(PMe_3)_2$ (**3**) in 82 % isolated yield after crystallization at – 30 ºC (Scheme 1). Complex **3** was
45 characterized by IR, multinuclear NMR, and X-Ray diffraction

study (Figure 1). The ^{1}H-NMR spectrum of **3** at –28 ºC shows four Si*H* signals of equal intensity: at 5.13 ppm (bd, $^2J_{H\text{-}P}$ = 19.6 Hz) and 5.60 ppm (dd, $^3J_{H\text{-}P}$ = 14.9 Hz, $^2J_{H\text{-}H}$ = 7.5 Hz) for the SiH$_2$Ph group and at 6.03 ppm (dd, $^3J_{H\text{-}P}$ = 9.6, 3.7 Hz) and 6.67
50 ppm (ddd, $^2J_{H\text{-}H}$ = 5.9 Hz, $^3J_{H\text{-}P}$ = 11.6, 17.2 Hz) for the $\{(SiHPh)_2(\mu\text{-}N^tBu)\}$ ligand. The Mo-bound hydride gives rise to a ^{31}P-coupled signal at 1.54 ppm (d, $^2J_{H\text{-}P}$ = 21.0 Hz). The formulation of complex **3** as a classical tris(silyl) hydride species is supported by the observation of large values of the $^1J_{Si\text{-}H}$
55 coupling constants (154.5, 186.0, and 166.9 Hz) for all three silicon signals in the ^{29}Si INEPT+ NMR spectrum at -14.3, -5.0, and 1.4 ppm, respectively, and the absence of any significant Si-H coupling to the Mo-bound hydride.[16] Furthermore, the ^{29}Si INEPT experiment at – 18 ºC shows the presence of only one Si-
60 bound proton on each silicon centre of the $\{(SiHPh)_2(\mu\text{-}N^tBu)\}$
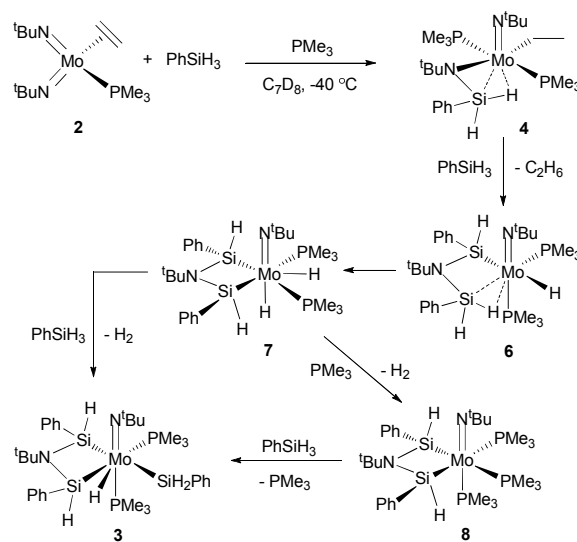
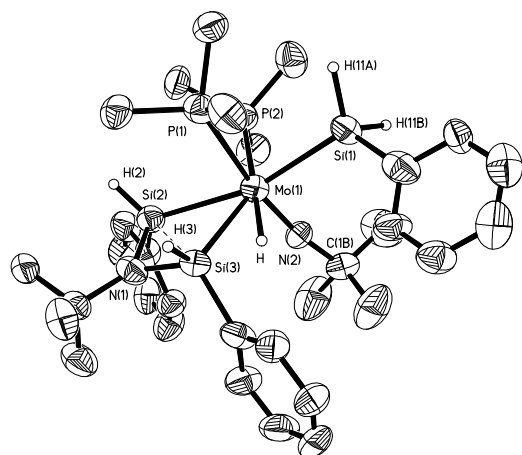**Scheme 1** Intermediates observed *en route* to complex **3**.

Fig. 1 Molecular structure of complex **3**. Thermal ellipsoids are plotted at 50% probability. Hydrogen atoms, apart from hydrides, are omitted for clarity. Selected bonds (Å) and angles (°): Mo1-N2 1.723(8), Mo1-P1 2.685(3), Mo1-P2 2.522(4), Mo1-Si1 2.571(3), Mo1-Si2 2.615(3), Mo1-Si3 2.560(3), N2-Mo1-Si1 90.6(3), N2-Mo1-Si2 104.3(3), N2-Mo1-Si3 100.2(3), N2-Mo1-P1 167.8(3), N2-Mo1-P2 98.6(3), P2-Mo1-Si1 88.85(11), P2-Mo1-Si2 83.49(10), Si1-Mo1-Si2 164.09(11), Si3-Mo1-Si1 122.63(11), Si3-Mo1-Si2 60.85(10), P2-Mo1-P1 87.43(11), Si3-Mo1-P1 80.81(10), Si1-Mo1-P1 78.77(10), Si2-Mo1-P1 86.94(10), Si3-N1-Si2 98.1(4).

ligand, whereas large values of the $^2J_{Si-P}$ coupling constants (25.0 and 20.3 Hz) for the {(SiHPh)$_2$(μ-N^{t}Bu)} fragment suggest the presence of direct bonding between the silicon atoms and Mo. Altogether these spectroscopic features provide evidence for the presence of a tris(silyl) hydride complex in the unusually high oxidation state Mo(VI). The only other precedents for Mo(VI) silylhydrides are the observation of transient species Cp(ArN=)Mo(SiH$_2$Ph)$_2$H[17] and (ArN=)Mo(PMe$_3$)$_2$(SiH$_2$Ph)$_2$H$_2$.[18]

The molecular structure of **3** (Figure 1) can be described as an edge-capped octahedron. The hydride atom is located *trans* to the phosphine P(2) whereas the other phosphine P(1) is *trans* to the imido group. The Si(2) atom of the imido-bis(silyl) ligand {μ-^{t}BuN(SiHPh)$_2$} occupies the coordination site *trans* to the silyl SiH$_2$Ph (the Si(2)-Mo-Si(1) angle is 164.1°), whereas the Si(3) atom sits on the Si(2)-hydride edge 2.14 Å away from the molybdenum-bound hydride, suggesting the absence of any significant Si-H bonding and indicating that the molybdenum atom is in the oxidation state Mo(VI). This conclusion agrees well with the spectroscopic data in solution and is further supported by other structural data.[19] Thus, the Mo-Si(3) distance of 2.560(3) Å is much shorter than the Mo-Si(2) bond of 2.615(3) Å and is actually very close the single Mo-SiH$_2$Ph bond of 2.571(3) Å. In contrast, in silane σ-complexes and Si-H agostic compounds elongated M-Si bonds are observed.[4,14] The Mo-silyl bonds in **3** compare well with the Mo-Si distance of 2.569(3) Å in the silyl hydride (ArN=)Mo(PMe$_3$)$_2$(SiH$_2$Ph)(H)[18] and with the Mo-Si bonds (2.550(2)-2.566(2) Å) in related complex Cp$_2$Mo(SiMe$_2$)$_2$(μ-S).[20] The Si(2)-Si(3) distance of 2.621(5) in **3** is relatively short and is actually close to the upper end of Si-Si σ-bonds (2.33–2.70 Å), which may suggest the occurrence of some Si···Si interaction.[21] A similar feature is observed in other complexes with the {μ-R'N(SiR$_2$-)$_2$} ligand.[20,22]

The reaction of **2** with two equivs of PhSiH$_3$ in the presence of 1 equiv. PMe$_3$ was followed by low temperature NMR. After 2h

at -40 °C, 80% of **2** converts to a 1:1 mixture of (^{t}BuN)Mo(η^3-N^{t}Bu-SiHPh-H)(PMe$_3$)$_2$(Et) (**4**) and (^{t}BuN)Mo(η^3-N^{t}Bu-SiHPh-H)(PMe$_3$)$_2$(SiH$_2$Ph) (**5**). Complex **4** is likely formed upon Si-H bond addition across the Mo=N bond of **2**[10-12,23] and then undergoes Et/SiH$_2$Ph metathesis with PhSiH$_3$ to give **5**.[24] In the ^{1}H NMR spectrum complex **4** gives rise to broad signals at 5.62 ppm ($^1J_{Si-H}$ = 212.0 Hz) and -0.85 ppm ($^1J_{Si-H}$ = 125.1 Hz) for the classical and agostic SiH, respectively. The latter coupling constant is comparable with the range of $^1J_{Si-H}$ found for other agostic d^2 silylamide complexes.[14] Both Si-H resonances are coupled in ^{1}H-^{29}Si HSQC to the Si signal at -74.5 ppm. The diastereotopic CH$_2$ protons of the Et group give rise to multiplets at 2.61 and 2.49 ppm coupled to a triplet at 1.96 ppm ($^3J_{H-H}$ = 7.53 Hz). Two nonequivalent phosphines in **4** are in the *trans* arrangement indicated by the large $^2J_{P-P}$ of 291.8 Hz. The other product, complex **5** is highly fluxional at -40 °C, but lowering the temperature to -80 °C reveals two singlets at 5.78 and 5.83 ppm for the SiH$_2$Ph group coupled in ^{1}H-^{29}Si HSQC to a resonance at -8.4 ppm. The protons from the agostic silyl group are coupled to an upfield ^{29}Si resonance -81.1 ppm with $^1J_{Si-H}$ = 226.1 Hz and 110.3 Hz. The latter coupling constant corresponds to the agostic Si-H···Mo bond. Similarly to complex **4**, the ^{31}P NMR spectrum of **5** shows two doublets with a large $^2J_{P-P}$ of 268 Hz indicating two *trans* phosphines. A 1D EXSY experiment revealed an exchange at -80 °C between the Si-H protons of the silylamido ligand of **5**, but no exchange with the Mo-SiH$_2$Ph group or with free PhSiH$_3$. An equivalent of free ethane is seen in the ^{1}H-NMR (δ = 0.92 ppm), suggesting that complex **5** may be formed *via* a metathesis between the ethyl group of **4** and free PhSiH$_3$ to generate the silyl ligand.

Warming a mixture of **4** and **5** to 0 °C results in complete conversion into the γ-agostic complex (^{t}BuN=)Mo(H)(η^3-PhHSi-N(^{t}Bu)-SiHPh-H)(PMe$_3$)$_2$ (**6**, Scheme 1) and production of a noticeable amount of free H$_2$ (δ = 4.57 ppm). The formation of **6** presents the first case of a double silane addition to a metal-imido bond and a rare example of a γ-agostic SiH complex.[13,14] Compound **6** forms as a mixture of two isomers. At –30 °C the major isomer exhibits the Mo-H signal at -4.40 ppm (dd, $^2J_{H-P}$ = 15.8 Hz and 48.4 Hz) and the Si-H resonance for the classical NSiH(Ph)Mo fragment at 6.91 ppm, coupled in the ^{1}H-^{29}Si HSQC to the ^{29}Si signal at 5.2 ppm (d, $^1J_{Si-H}$ = 172.3 Hz). The terminal proton of the NSiH$_2$Ph moiety gives rise to a broad doublet at 6.82 ppm ($^2J_{H-H}$ = 5.3 Hz), coupled in the ^{1}H-^{29}Si HSQC to the ^{29}Si-NMR signal at -16.2 ppm, whereas the agostic proton gives rise to a broad multiplet at 0.37 ppm (ddd, $^2J_{H-P}$ = 45.5 Hz, $^2J_{P-H}$ = 4.5 Hz, $^2J_{H-H}$ = 4.4 Hz) coupled to the same ^{29}Si-NMR signal. In ^{29}Si INEPT+ NMR the agostic silyl signal at -16.2 ppm comes as a doublet of doublets (dd, $^1J_{H-Si}$ = 34.9 Hz, $^1J_{H-Si}$ = 195.6 Hz). The significantly reduced coupling (34.9 Hz) establishes the presence of a γ-agostic SiH···Mo bond. A NOESY experiment further agrees with the relative disposition of substituents shown in Scheme 1. In particular, the bridging ^{t}BuN group "sees" only the terminal SiH and *o*-Ph protons, but neither the ^{t}BuN=Mo nor the phosphine groups, indicating its detachment from the Mo centre.

Addition of another equivalent of PhSiH$_3$ to a freshly generated sample of **6** and warming to 0 °C leads to formation of the final product **3**. This may happen either via oxidative addition

of the agostic Si-H bond to metal affording a Mo(VI) dihydride species, which after elimination of H_2 adds $PhSiH_3$ (pathway A, Scheme 2), or via a Mo-H/Si-H metathesis with the added silane (pathway B). To differentiate between these two possibilities, a labeling experiment was attempted. Addition of an equivalent of $PhSiD_3$ to **6** led to deuterium scrambling into the MoH and all SiH positions. The same result happens upon addition of $PhSiD_3$ to **3**. These experiment indicates reversible behaviour which can be interpreted as reversible addition of silane to a silanimine intermediate and exchange of the agostic Si-H bond between both sides of the PhHSi-N(^{t}Bu)-SiHPh unit of **6**. The latter exchange can happen by reversible Si-H bond oxidative addition/reductive elimination. D-scrambling in **3** can be also explained by reversible Si-H bond formation and cleavage between the silicon atoms of the disilacyclobutane ring and the Mo-bound hydride.
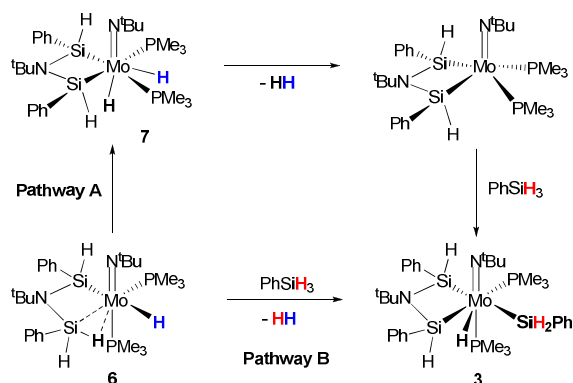
Scheme 2 Possible pathways for the reaction of **6** with $PhSiH_3$.

Although the labeling studies do not allow us to distinguish between the pathways A and B of Scheme 2, the following experiments suggest that the pathway A (oxidative addition of agostic Si-H) is realized. When $(^tBuN)_2Mo(PMe_3)(\eta^2$-$C_2H_4)$ reacts with 2 equivalents of $PhSiH_3$ in the presence of PMe_3 for 3 hours at -20 °C, a mixture of **6** (80%), **3** (2%), and a new dihydride complex $(^tBuN)Mo\{(SiHPh)_2(\mu$-$N^tBu)\}(PMe_3)_2H_2$ (**7**, 18%) is formed. At 0 °C, **7** exhibits two Si-H resonances in the ^{1}H-NMR at 5.92 ($^3J_{H-P}$ = 3.8 Hz, $^3J_{H-P}$ = 5.9 Hz, $^3J_{H-H}$ = 11.6 Hz) and 6.51 ppm ($^3J_{H-H}$ = 6.1 Hz, $^2J_{H-P}$ = 6.1 Hz, $^2J_{H-P}$ = 12.2 Hz) correlated to two different ^{29}Si signals in ^{1}H-^{29}Si HSQC NMR at 4.1 ppm ($^1J_{Si-H}$ = 170.0 Hz) and -2.2 ppm ($^1J_{Si-H}$ = 185.3 Hz), respectively. Each Si-H signal is coupled to each PMe_3 ligand and to a distinct Mo-H hydride, confirmed by a ^{1}H$\{^{31}$P$\}$ experiment. Although the hydride resonances are obscured and could not be observed directly by ^{1}H-NMR, a combination of ^{1}H-^{1}H COSY, ^{1}H-^{29}Si HSQC and ^{1}H-^{31}P HSQC allowed us to establish their positions at 1.48 ppm (coupled to both ^{29}Si signals at -2.2 ppm and 4.1 ppm and to the ^{31}P signal at -9.65 ppm) and at 1.25 ppm (coupled only to the ^{29}Si resonance at 4.1 ppm and to both ^{31}P signals). These data, however, do not allow us to distinguish between a dihydride vs. stretched dihydrogen description of **7**.[25]

In another experiment, keeping a solution of **6** at -30 °C for three days produces significant amounts of the imido-bridged bis(silyl) complex $(^tBuN=)Mo\{\eta^2$-$N^tBu(SiHPh)_2\}(PMe_3)_3$ (**8**, Scheme 1), which most likely forms via oxidative addition of the agostic SiH bond to Mo in **6**, dihydrogen elimination and addition of PMe_3, which provides further support towards the pathway A. The structure of **8** was established by multinuclear NMR and NOESY experiments. At 0 °C, complex **8** exhibits two Si-H resonances at 5.36 ppm (ddd, $^2J_{H-P}$ = 3.0 Hz, $^2J_{H-P}$ = 5.0 Hz, $^2J_{H-P}$ = 7.8 Hz) and 7.05 (bd, $^3J_{H-P}$ = 9 Hz) in the ^{1}H NMR, corresponding to two nonequivalent silyl groups stemming from the different orientation of the Ph and H substituents. The signal at 5.36 ppm shows a $^3J_{H-P}$ coupling to three nonequivalent PMe_3 groups. In ^{31}P NMR these phosphines give rise to a triplet at 5.66 (t, $^2J_{P-P}$ = 22.6 Hz, 1P), coming from the PMe_3 located *trans* to the imido group, and two doublet of doublets ($^2J_{P-P}$ =18.2 Hz and $^2J_{P-P}$ = 91.2 Hz) for two mutually *trans* phosphines at -7.48 and -13.54 ppm. The ^{29}Si INEPT+ NMR spectrum revealed two ^{29}Si resonances: a broad doublet at 41.7 ppm ($^1J_{Si-H}$ = 169.3 Hz) and a doublet of ^{31}P-coupled multiplets at -10.42 ppm (dddd, Mo-*Si*HPh, $^1J_{Si-H}$ = 152.0 Hz, $^2J_{Si-P}$ = 19.3 Hz, $^2J_{Si-P}$ = 19.3 Hz, $^2J_{Si-P}$ = 38.3 Hz). Altogether these spectroscopic observations provide evidence of a pseudo-octahedral structure having *transoid* orientation of the Ph and H substituents at the silicon centres.

A similar low temperature NMR study for the reaction of complex $(^tBuN)_2Mo(PMe_3)_2$ (**1**) with $PhSiH_3$ also revealed the intermediate **6** and its conversion to **3**.

The structure and interconversion of various species formed *en route* to compound **3** were further investigated by DFT calculations of the real system $(^tBuN=)_2Mo(PMe_3)_2/H_3SiPh$. Solvent effects were taken into account by the polarizable continuum model (PCM).[26] The data are given in Table 1. Addition of silane to the Mo=N bond of $(^tBuN=)_2Mo(PMe_3)_2$ (**1**) proceeds via the **TS$_{14}$** ($\Delta G^{\neq}$ = 34.1 kcal/mol) and affords the silylamido complex **4H**, a hydride analogue of the ethyl complex **4**. We found two isomers of this species. The most stable isomer **4Ha** (ΔG_f =12.5 kcal/mol) has a trigonal bipyramidal structure with two trans phosphines and a nonagostic silylamido ligand (the SiH···Mo distance is 2.586 Å, Figure 2). The higher energy isomer **4Hb** (ΔG_f = 17.2 kcal/mol) has a pseudo-octahedral structure, with the hydride lying trans to the imido ligand and one of the vertices being occupied by a silicon-bond hydride to form the SiH···Mo distance of 1.913 Å. The latter isomer can be classified as a β-SiH agostic complex. In the next step elimination of dihydrogen from **4H** takes place via the transition state **TS$_{49}$**, lying 31.9 kcal/mol above the starting complex **1**, to give the

Table 1 DFT calculated energies (in kcal/mol) for the reaction between **1** and silane $PhSiH_3$ to give complex **3** in gas phase and benzene solution. The energy of the pair **1** + H_3SiPh is taken as 0.

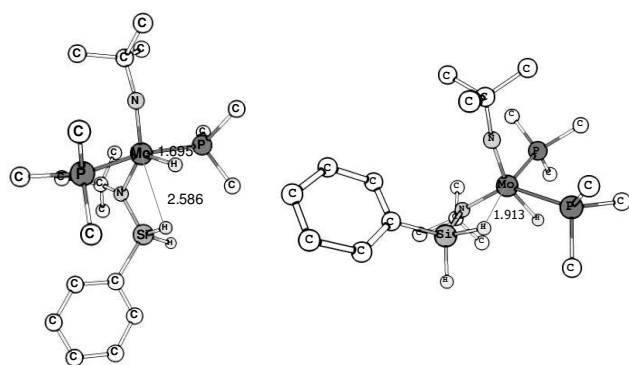| Structure	Gas phase	Solution
1	0	0
3	–25.3	–24.0
TS$_{4H}$	19.7	19.5
4Ha	–2.2	–1.4
4Hb	–0.1	0.5
TS$_{49}$	15.9	16.4
9	–0.5	–0.2
6	–21.2	–20.1
TS$_{67}$	–9.1	–8.3
7	–18.9	–18.4
TS$_{710}$	–17.9	–17.3
10	–18.9	–18.1
11	–12.4	–12.6

Fig. 2 Calculated isomers of intermediate **4H: 4Ha** – left, **4Hb** – right)

silanimine intermediate **9** (Figure 3). Formation of **4H** is strongly endergonic, whereas **9** is only marginally (by 1.2 kcal/mol, which is within the error of our calculation) more stable than **1**, which explains why both species could not be observed experimentally. Considering the fact that the real complexes **4** and **6** form reasonably fast even at low themperature (-40 °C), the calculated barriers for the two first steps appear to be too high. This may be in part due to the overestimation the entropy contribution by our calculations or, more likely, indicate the presence of an alternative but yet unknown reaction pathway.

Silane addition to **9** across the Mo-N bond of the silanimine ligand affords the γ-agostic complex **6**, the first intermediate observed by low temperature NMR for the mixture of ('BuN=)$_2$Mo(PMe$_3$)$_2$ and H$_3$SiPh. Compound **6** is stabilized

relative to the starting compound **1** by 7.4 kcal/mol. The agostic SiH hydride in **6** is located 2.045 Å away from Mo, *trans* to the imido ligand and *cis* to the Mo-H bond. Oxidative addition of the Si-H bond to Mo generates the dihydride species **7** by overcoming a modest barrier of 12.8 kcal/mol (**TS$_{67}$**). In **7** the distance between the Mo-bound hydrides is 1.628 Å, which allows us to classify this species as a *cis* dihydride complex.[25] Compound **7** is connected via the transition state **TS$_{710}$** with the dihydrogen complex **10** characterized by the short H⋯H distance of 0.908 Å.[25,27] The potential surface around **7** and **10** is very shallow, so that both species must be in fast equilibrium. **7** and **10** are ~ 4.0 kcal/mol more stable than **1** and together they account for the second observable intermediate. Elimination of dihydrogen affords the imido-bridged bis(silyl) complex **11**. The experimentally observed compound **8** can be regarded as an adduct of **11** with PMe$_3$. Finally addition of silane to **11** to furnish complex **3** completes this reaction sequence.

Conclusion

We have demonstrated an unusual triple silane addition to the bis(imido) complexes of Mo **1** and **2** which proceeds via a series of Si-H agostic and silanimine intermediates and results in complete detachment of one of the imido ligands from Mo. Studies are underway to probe the relevance of these species to catalytic coupling of PhSiH$_3$ with unsaturated organic molecules.

Experimental

All manipulations were carried out using conventional inert atmosphere glove-box and Schlenk techniques. Dry diethyl ether,
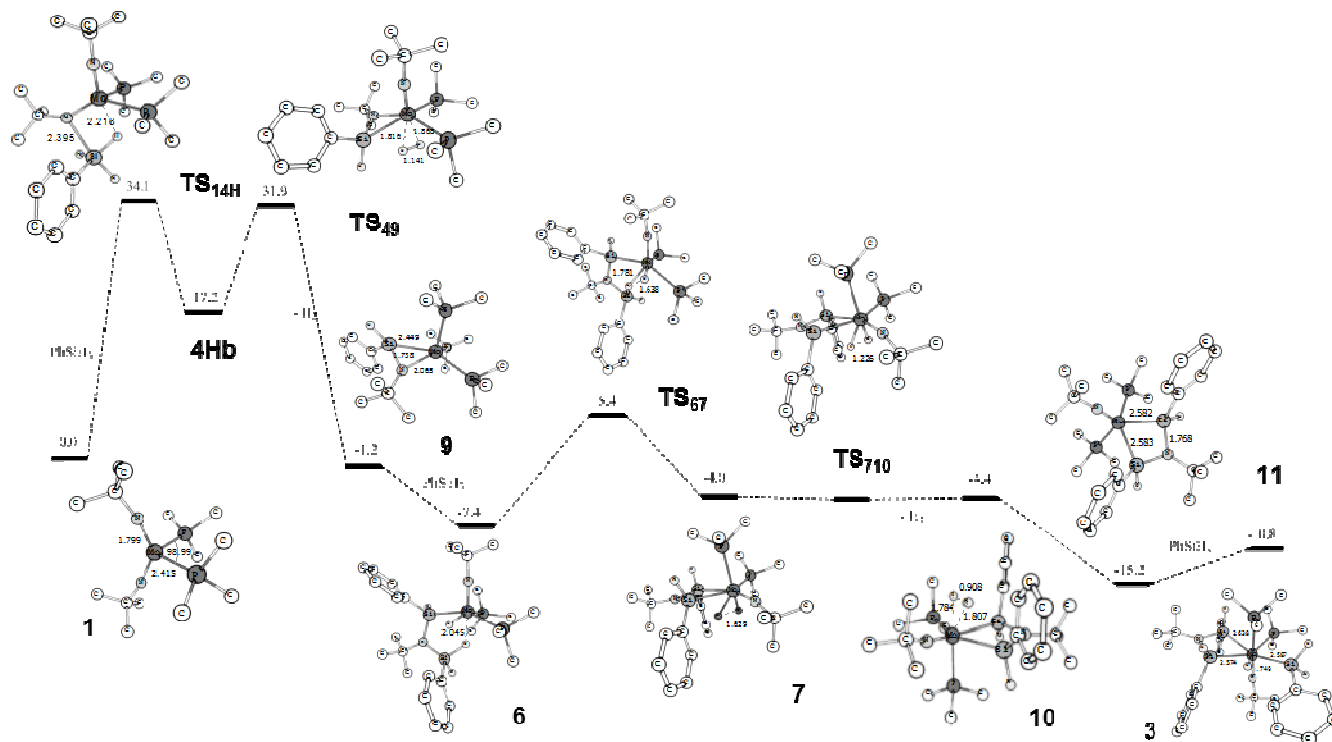

Fig. 3 Mechanism of formation of complex **3**. Hydrogen atoms, apart from hydrides on Si and Mo are omitted for clarity. Gibbs free energy is given in kcal·mol^{-1}. The **TS$_{710}$** is just 0.6 kcal/mol above **7** on the electronic energy surface but is 1 kcal/mol lower on the Gibbs free energy surface.

toluene, hexanes, and acetonitrile were obtained, using Grubbs-type purification columns, other solvents were dried by distillation from appropriate drying agents. NMR spectra were obtained with a Bruker DPX-300 and Bruker DPX-600 instruments (^{1}H: 300 and 600 MHz; ^{13}C: 75.5 and 151 M Hz; ^{29}Si: 59.6 and 119.2 MHz; ^{31}P: 121.5 and 243 MHz). NMR spectra were taken at room temperature unless specified. IR spectra were measured on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses were performed in "ANALEST" laboratories (University of Toronto). Preparation of (^{t}BuN=)$_2$Mo(PMe$_3$)$_2$ (**1**)^{10a,28} and (^{t}BuN=)$_2$Mo(PMe$_3$)(η^2-C$_2$H$_4$) (**2**)^{29} was reported previously. PhSiH$_3$ and PhSiD$_3$ were prepared from PhSiCl$_3$ by treatment with LiAlH$_4$ or LiAlD$_4$, respectively. Mechanistic studies were carried out under nitrogen atmosphere, using NMR tubes equipped with Teflon valves.

Synthesis of (^{t}BuN){μ-^{t}BuN(SiHPh)$_2$}Mo(H)(SiH$_2$Ph)(PMe$_3$)$_2$ (3).
A solution of **1** (300.0 mg, 0.769 mmol) in hexanes (12 mL) was precooled to -30 °C using an acetone/CO$_2$ bath. PhSiH$_3$ (0.19 mL, 1.54) was added in one portion and the mixture stirred for 1 h 20 min at -30 °C. After this time the solution was warmed to -5 °C and all volatiles removed in vacuum to give a light brown powder (0.38 g, 82%). Alternatively, a similar procedure using complex **2** with one equivalent of PMe$_3$ in a hexane/toluene (5:1) mixture can be employed resulting in similar yields and purity. ^{1}H-NMR (600 MHz; toluene-d_8; -28 °C; δ, ppm): 0.62 (s, 9H, ^{t}BuN), 0.99 (d, $^2J_{P-H}$ = 6.0 Hz, 9H, PMe_3), 1.04 (d, $^2J_{P-H}$ = 7.5 Hz, 9H, PMe_3), 1.47 (s, 9H, ^{t}BuN), 1.54 (bd, 1H, $^2J_{P-H}$ = 21.0 Hz, MoH), 5.13 (bd, 1H, $^2J_{P-H}$ = 19.6 Hz, SiH_2Ph), 5.60 (dd, 1H, $^3J_{P-H}$ = 14.9 Hz, $^2J_{H-H}$ = 7.5 Hz, SiH_2Ph), 6.03 (dd, 1H, $^3J_{P-H}$ = 9.6 Hz, $^3J_{P-H}$ = 3.7 Hz, {(SiHPh)$_2$(μ-N^{t}Bu)}), 6.67 (ddd, 1H, $^2J_{H-H}$ = 5.9 Hz, $^3J_{P-H}$ = 11.6 Hz, $^3J_{P-H}$ = 17.2 Hz, {(SiHPh)$_2$(μ-N^{t}Bu)}), 7.26 (m, 2H, *p*-H, SiPh), 7.32 (t, 1H, $^3J_{H-H}$ = 7.5 Hz, *p*-H, SiPh), 7.40 (t, 2H, $^3J_{H-H}$ = 7.5 Hz, *m*-H, SiPh), 7.46 (t, 2H, $^3J_{H-H}$ = 7.5 Hz, *m*-H, SiPh), 7.49 (t, 2H, $^3J_{H-H}$ = 7.5 Hz, *m*-H, SiPh), 8.32 (bs, 2H, *o*-H, SiPh), 8.48 (d, 2H, $^3J_{H-H}$ = 6.6 Hz, *o*-H, SiPh), 8.54 (d, 2H, $^3J_{H-H}$ = 6.7 Hz, *o*-H, SiPh). ^{1}H-NMR (600 MHz; toluene-d_8; 22 °C; δ, ppm): 0.61 (s, 9H, ^{t}BuN), 1.05 (d, $^2J_{P-H}$ = 6.4 Hz, PMe_3), 1.14 (d, 9H, $^2J_{P-H}$ = 7.7 Hz, PMe_3), 1.39 (s, 9H, ^{t}BuN), 1.50 (bd, 1H, $^2J_{P-H}$ = 21.0 Hz, MoH), 5.05 (d, 1H, $^3J_{P-H}$ = 19.4 Hz, SiH_2Ph), 5.50 (bddd, 1H, $^3J_{P-H}$ = 15.9 Hz, $^2J_{H-H}$ = 7.4 Hz, SiH_2Ph), 6.04 (dd, 1H, $^3J_{P-H}$ = 3.7 Hz, $^3J_{P-H}$ = 9.2 Hz, {(SiHPh)$_2$(μ-N^{t}Bu)}), 6.59 (ddd, 1H, $^2J_{H-H}$ = 5.8 Hz, $^3J_{P-H}$ = 11.6 Hz, $^3J_{P-H}$ = 17.5 Hz, {(SiHPh)$_2$(μ-N^{t}Bu)}), 7.23 (m, 3H, *p*-H, SiPh), 7.36 (t, 2H, $^3J_{H-H}$ = 7.3 Hz, *m*-H, SiPh), 7.40 (t, 4H, $^3J_{H-H}$ = 7.0 Hz, *m*-H, SiPh), 8.25 (d, 2H, $^3J_{H-H}$ = 7.0 Hz, *o*-H, SiPh), 8.37 (d, 2H, $^3J_{H-H}$ = 7.3 Hz, *o*-H, SiPh), 8.39 (d, 2H, $^3J_{H-H}$ = 7.3 Hz, *o*-H, SiPh). ^{1}H{^{31}P}-NMR (600 MHz, toluene-d_8, 22 °C, δ, ppm, selected resonances): 6.59 (d, 1H, $^2J_{H-H}$ = 5.9 Hz, {(SiHPh)$_2$(μ-N^{t}Bu)}), 6.04 (s, 1H, {(SiHPh)$_2$(μ-N^{t}Bu)}), 5.49 (s, 1H, SiH_2Ph), 5.05 (s, 1H, SiH_2Ph), 1.55 (d, 1H, $^2J_{H-H}$ = 5.9 Hz, MoH). ^{31}P{^{1}H}-NMR (243.0 MHz, toluene-d_8, -28 °C, δ, ppm): -40.2 (d, $^2J_{P-P}$ = 34.5 Hz, PMe_3), -16.3 (d, $^2J_{P-P}$ = 34.5 Hz, PMe_3). ^{31}P{^{1}H}-NMR (121.5 MHz, toluene-d_8, 22 °C, δ, ppm): -41.5 (d, $^2J_{P-P}$ = 32.0 Hz, PMe_3), -17.2 (d, $^2J_{P-P}$ = 34.5 Hz, PMe_3). ^{29}Si INEPT+ NMR (119.2 MHz, toluene-d_8, -28 °C, J = 180 Hz, δ, ppm): -14.3 (tdd, $^1J_{Si-H}$ = 154.4 Hz, $^2J_{Si-P}$ = 25.0 Hz, $^2J_{Si-P}$ = 28.6 Hz, SiH_2Ph), -5.0 (d, $^1J_{Si-H}$ = 186.0 Hz, {(SiHPh)$_2$(μ-N^{t}Bu)}), 1.4 (ddd, $^1J_{Si-H}$ = 166.9 Hz, $^2J_{Si-P}$ = 25.0 Hz, $^2J_{Si-P}$ = 20.3 Hz,

{(SiHPh)$_2$(μ-N^{t}Bu)}). ^{29}Si RF INEPT NMR (119.2 MHz, toluene-d_8, -18 °C, J = 180 Hz, δ, ppm): 1.4 (dd, $^2J_{Si-P}$ = 16.7 Hz, $^2J_{Si-P}$ = 28.6 Hz, {(SiHPh)$_2$(μ-N^{t}Bu)}, "up"), -5.1 (d, $^2J_{Si-P}$ = 10.7 Hz, {(SiHPh)$_2$(μ-N^{t}Bu)}, "up"), -14.7 (t, $^2J_{Si-P}$ = 23.8 Hz, SiH_2Ph, "down"). ^{1}H-^{31}P HSQC JC NMR (243.0 Hz, toluene-d_8; -20 °C; J = 15 Hz; ^{1}H proj.; δ, ppm): 1.6 (d, $^2J_{H-P}$ = 30.0 Hz, {(SiHPh)$_2$(*u*-N^{t}Bu)}). ^{13}C{^{1}H]-NMR (151 MHz; toluene-d_8; - 28 °C; δ, ppm): 14.9 (d, $^1J_{C-P}$ = 18.1 Hz, PMe_3), 19.1 (d, $^1J_{C-P}$ = 24.1 Hz, PMe_3), 30.3 (s, CH_3, ^{t}BuN), 31.7 (s, CH_3, ^{t}BuN), 34.8 (s, CH_3, ^{t}BuN=Mo), 54.7 (s, C(CH$_3$)$_3$, ^{t}BuN), 127.3 (s, *m*-C, SiPh), 127.5 (s, *m*-C, SiPh), 128.1 (s, *m*-C, SiPh), 128.2 (s, *p*-C, SiPh), 128.4 (s, *p*-C, SiPh), 133.9 (s, *o*-C, SiPh), 137.1 (s, *o*-C, SiPh), 137.8 (s, *o*-C, SiPh), 143.2 (s, *i*-C, SiPh), 147.8 (s, *i*-C, SiPh), 148.8 (s, *i*-C, SiPh). IR (nujol, cm^{-1}): 1825 (m, Mo-H), 1890 (s, Si-H), 2037 (s, Si-H), 2142 (s, Si-H). Elem. Anal. (%): calc. for C$_{32}$H$_{56}$MoN$_2$P$_2$Si$_3$ (710.945) C 54.06, H 7.94, N 3.94; found C 53.99 H 7.87, N 4.22.

General Procedure for Addition of PhSiH$_3$ on NMR scale
To a solution of (^{t}BuN)Mo(PMe$_3$)(L) (L = PMe$_3$ (**1**), η^2-C$_2$H$_4$ (**2**)) in toluene-d_8, PMe$_3$ was added in one portion at room temperature. The sample was cooled to -196 °C using liquid nitrogen on a Schlenk line and PhSiH$_3$ was directly added. The sample was quickly removed from the liquid nitrogen and inverted once, then immediately placed back. The sample was then placed into a pre-cooled NMR machine at the appropriate temperature and monitored at various temperatures. In some cases, the sample was allowed to react for 2-4 hours at -40 °C, then monitored by NMR at the appropriate temperature.

(^{t}BuN)Mo(η^3-N^{t}Bu-SiHPh-H)(PMe$_3$)$_2$(Et) (**4**): ^{1}H-NMR (600 MHz, toluene-d_8, -53 °C, δ, ppm): -0.82 (s, 1H, Si-H_{ag}, $^1J_{Si-H}$ = 125.1 Hz, found by ^{1}H-^{29}Si HSQC 1D JC), 1.03 (s, 9H, 3 CH$_3$, ^{t}BuN=Mo), 1.10 (s, 9H, 3 CH$_3$, Mo-N^{t}Bu-SiH$_2$Ph), 1.32 (d, 9H, PMe_3, $^2J_{H-P}$ = 5.22 Hz), 1.43 (d, 9H, PMe_3, $^2J_{H-P}$ = 5.28 Hz), 1.96 (t, 3H, CH$_3$, Mo-CH$_2$-CH_3, $^3J_{H-H}$ = 7.53 Hz), 2.50 (m, 1H, Mo-CH_2-CH$_3$), 2.61 (m, 1H, Mo-CH_2-CH$_3$), 5.66 (s, 1H, Si-H_{class}, $^1J_{Si-H}$ = 212.0 Hz, found by ^{1}H-^{29}Si HSQC 1D JC), 7.27 (m, 2H, *m*-Ph), 7.96 (d, 2H, *o*-Ph, $^3J_{H-H}$ = 6.9 Hz).^{31}P{^{1}H}-NMR (243.0 MHz, toluene-d_8, -53 °C, δ, ppm): -7.78 (d, 1P, PMe_3, $^2J_{P-P}$ = 291.7 Hz), -10.12 (d, 1P, PMe_3, $^2J_{P-P}$ = 291.8 Hz).^{1}H-^{29}Si HSQC NMR (119.0 MHZ, toluene-d_8; -53 °C; J = 150 Hz; ^{29}Si projection, δ, ppm): -75.4 (Mo-N^{t}Bu-SiH$_2$Ph).

(^{t}BuN)Mo(η^3-N^{t}Bu-SiHPh-H)(PMe$_3$)$_2$(SiH$_2$Ph) (**5**): ^{1}H-NMR (600 MHz, toluene-d_8, -78 °C, δ, ppm): 0.17 (s, 1H, Si-H_{ag}, $^1J_{Si-H}$ = 110.3 Hz, found by ^{1}H-^{29}Si HSQC 1D JC), 1.00 (s, 9H, 3 CH$_3$, ^{t}BuN=Mo), 1.35 (bs, 18H, 2 PMe_3), 1.37 (s, 9H, 3 CH$_3$, Mo-N^{t}Bu-SiH$_2$Ph), 5.43 (s, 1H, Si-H_{class}, $^1J_{Si-H}$ = 226.1 Hz, found by ^{1}H-^{29}Si HSQC 1D JC), 5.76 (s, 1H, Mo-SiH_2Ph), 5.81 (s, 1H, Mo-SiH_2Ph), 7.23 (t, 2H, *m*-Ph, Mo-N^{t}BuSiHPh,$^3J_{H-H}$ = 7.26 Hz), 7.37 (t, 2H, *m*-Ph, Mo-SiH$_2$$Ph$,$^3J_{H-H}$ = 7.23 Hz), 7.84 (d, 2H, *o*-Ph, Mo-N^{t}BuSiHPh, $^3J_{H-H}$ = 6.84 Hz), 8.22 (d, 2H, *o*-Ph, Mo-SiH$_2$$Ph$, $^3J_{H-H}$ = 6.98 Hz).^{31}P{^{1}H}-NMR (243.0 MHz, toluene-d_8, -72 °C, δ, ppm): -10.9 (d, 1P, PMe_3, $^2J_{P-P}$ = 268.2 Hz), -13.0 (d, 1P, PMe_3, $^2J_{P-P}$ = 266.8 Hz).^{1}H-^{29}Si HSQC NMR (119.0 MHZ, toluene-d_8; -53 °C; J = 150 Hz; ^{29}Si proj., δ, ppm): -8.4 (Mo-SiH$_2$Ph), -81.1 (Mo-N^{t}Bu-SiH$_2$Ph).

($^tBuN)Mo(H)(\eta^3$-$PhHSi$-$N(^tBu)$-$SiHPh$-$H)(PMe_3)_2$ (**6**): ^{1}H-NMR (600 MHz, toluene-d$_8$, -41 °C, δ, ppm): -4.63 (dd, 1H, $^2J_{H-P}$ = 54.9 Hz,$^2J_{H-P}$ = 19.5 Hz, Mo*H*, minor isomer), -4.43 (ddd, 1H, $^2J_{H-P}$ = 46.1 Hz,$^2J_{H-P}$ = 16.7 Hz,$^2J_{H-H}$ = 4.4 Hz, Mo*H*, major isomer), 0.37 (dt, 1H, $^2J_{H-P}$ = 45.5 Hz,$^2J_{H-H}$ = 4.4 Hz, Si*H*$_{ag}$, major isomer), 0.81(d, 9H, $^2J_{H-P}$ = 7.3 Hz, P*Me*$_3$, major isomer), 0.88 (d, 9H, $^2J_{H-P}$ = 7.3 Hz, P*Me*$_3$, major isomer), 1.36 (s, 9H, ^tBuN=Mo, major isomer),1.44 (s, 9H, μ-N^tBu, major isomer), 6.84 (bd, 1H, $^2J_{H-H}$ = 5.3 Hz, Si*H*$_{class}$, major isomer), 6.92 (bs, 1H, Mo-Si*H*Ph, major isomer), 7.22 (bs, 1H, Mo-Si*H*Ph, minor isomer), 7.23 (t, 1H, $^3J_{H-H}$ = 7.4 Hz, *p*-H, Mo-Si*H*P*h*, major isomer), 7.27 (t, 1H, *p*-H, $^3J_{H-H}$ = 7.4 Hz, SiH$_2$P*h*, major isomer), 7.36 (t, 1H, *m*-H, Mo-Si*H*P*h*, major isomer),7.43 (t, 2H, *m*-H, SiH$_2$P*h*, $^3J_{H-H}$ = 7.3 Hz, major isomer), 7.47 (t, 1H, *m*-H, Mo-Si*H*P*h*, $^3J_{H-H}$ = 6.9 Hz, major isomer), 8.25 (bd, 1H, *o*-H, Mo-Si*H*P*h*, $^3J_{H-H}$ = 6.2 Hz, major isomer), 8.39 (bs, 2H, *o*-H, SiH$_2$P*h*, $^3J_{H-H}$ = 7.3 Hz, major isomer), 8.56 (bd, 1H, *o*-H, Mo-Si*H*P*h*, $^3J_{H-H}$ = 6.3 Hz, major isomer).^{31}P{^{1}H}-NMR (243.0 MHz, toluene-d$_8$, -25 °C, δ, ppm): 2.4 (d, $^2J_{P-P}$ = 43.7 Hz, P*Me*$_3$, minor isomer), -0.8 (d, $^2J_{P-P}$ = 43.7 Hz, P*Me*$_3$, major isomer), -5.1 (d, $^2J_{P-P}$ = 43.7 Hz, P*Me*$_3$, minor isomer), -7.0 (d, $^2J_{P-P}$ = 43.7 Hz, P*Me*$_3$, major isomer). ^{29}Si INEPT+ NMR (119 MHz, toluene-d$_8$, -40 °C, *J* = 200 Hz, δ, ppm): -19.5 (dd, $^1J_{H-Si}$ = 37.3 Hz, $^1J_{H-Si}$ = 199.8 Hz, *Si*H$_2$Ph, minor isomer), -16.2 (dd, $^1J_{H-Si}$ = 34.9 Hz, $^1J_{H-Si}$ = 195.6 Hz, *Si*H$_2$Ph, major isomer), 5.2 (d, $^1J_{H-Si}$ = 172.3 Hz, *Si*HPh, major isomer), 7.5 (d, $^1J_{H-Si}$ = 182.7 Hz, *Si*HPh, minor isomer).^{13}C{^{1}H}-NMR (151 MHz; toluene-d$_8$; - 40 °C; δ, ppm): 19.89 (d, P*Me*$_3$, $^1J_{C-P}$ = 23.8 Hz), 22.65 (d, P*Me*$_3$, $^1J_{C-P}$ = 24.8 Hz), 31.35 (s, *C*H$_3$, ^tBuN), 31.97 (s, *C*H$_3$, ^tBuN), 54.54 (s, *C*(CH$_3$)$_3$, ^tBuN), 65.70 (s, *C*(CH$_3$)$_3$, ^tBuN), 127-130 (*p*-Ph, *m*-Ph, overlapped with solvent signals, found by ^{1}H-^{13}C HSQC), 134.0 (*o*-Ph, MoSiH*Ph*), 137.1 (*o*-Ph, Si*Ph*), 149.2 (*i*-Ph, Si*Ph*), 151.0 (*i*-Ph, Si*Ph*).

($^tBuN)Mo\{(SiHPh)_2(\mu-N^tBu)\}(PMe_3)_2H_2$ (**7**): ^{1}H-NMR (600 MHz, toluene-d$_8$, 0 °C, δ, ppm): 0.80 (s, 9H, 3 CH$_3$, Mo=N^tBu), 1.05 (d, 9H, P*Me*$_3$, $^2J_{H-P}$ = 7.7 Hz), 1.10 (d, 9H, P*Me*$_3$, $^2J_{H-P}$ = 6.7 Hz), 1.25 (Mo*H*, found by ^{1}H-^{1}H COSY and ^{1}H-^{29}Si HSQC (*J* = 7 Hz), partially obscured by complex **3**) 1.39 (s, 9H, 3 CH$_3$, Si-N^tBu-Si), 1.48 (Mo-H, found by ^{1}H-^{1}H COSY and ^{1}H-^{29}Si HSQC (*J* = 7 Hz), partially obscured by complex **3**), 5.92 (ddd, 1H, Si*H*, $^3J_{H-H}$ = 3.8 Hz, $^3J_{H-P}$ = 5.93 Hz, $^2J_{H-P}$ = 11.57 Hz, $^1J_{Si-H}$ = 169.2 Hz {found by ^{1}H-^{29}Si HSQC 1D JC}), 6.51 (dt, 1H, Si*H*, $^3J_{H-H}$ = 6.1 Hz, $^2J_{H-P}$ = 6.1 Hz, $^2J_{H-P}$ = 12.2 Hz, $^1J_{Si-H}$ = 187.1 Hz {found by ^{1}H-^{29}Si HSQC 1D JC}), 8.33 (d, 2H, *o*-Ph, $^3J_{H-H}$ = 6.9 Hz). ^{1}H{^{31}P}-NMR (600 MHz, toluene-d$_8$, 0 °C, δ, ppm, selected resonances): 6.51 (d, 1H, Si*H*, $^3J_{H-H}$ = 6.12 Hz), 5.92 (bd, 1H, Si*H*, $^3J_{H-H}$ = 3.7 Hz), 1.10 (s, P*Me*$_3$), 1.05 (s, P*Me*$_3$).^{31}P{^{1}H}-NMR (243.0 MHz, toluene-d$_8$, 0 °C, δ, ppm): -9.65 (d, 1P, P*Me*$_3$, $^2J_{P-P}$ = 31.3 Hz), -34.60 (d, 1P, P*Me*$_3$, $^2J_{P-P}$ = 31.1 Hz).^{31}P{^{1}H}-NMR (selectively decoupled from Me groups at 1.10 ppm in ^{1}H-NMR, 243.0 MHz, toluene-d$_8$, 0 °C, δ, ppm): -9.63 (bt, 1P, P*Me*$_3$, $^2J_{P-P}$ = 33.4 Hz), -34.49 (m, 1P, P*Me*$_3$, $^3J_{P-H}$ = 13.0 Hz, $^2J_{P-P}$ = 27.6 Hz, $^2J_{P-H}$ = 51.7 Hz).^{31}P{^{1}H}-NMR (selectively decoupled from Me groups at 1.05 ppm in ^{1}H-NMR, 243.0 MHz, toluene-d$_8$, 0 °C, δ, ppm): -9.63 (dd, 1P, P*Me*$_3$, $^2J_{P-P}$ = 33.4 Hz, $^2J_{P-H}$ = 33.4 Hz), -34.70 (m, 1P, P*Me*$_3$).^{31}P{^{1}H}-NMR (selectively decoupled from hydride at 1.25 ppm in ^{1}H-NMR, 243.0 MHz, toluene-d$_8$, 0 °C, δ, ppm): -9.63 (d, 1P, P*Me*$_3$, $^2J_{P-P}$ = 33.4 Hz), -34.60 (m, 1P,

P*Me*$_3$).^{29}Si INEPT+ NMR (119 MHz, toluene-d$_8$, 0 °C, *J* = 150 Hz, δ, ppm): 4.05 (d, $^1J_{Si-H}$ = 170.0 Hz), -2.17 (d, $^1J_{Si-H}$ = 185.3 Hz).

($^tBuN)\{\mu-^tBuN(SiHPh)_2\}Mo(PMe_3)_3$ (**8**): ^{1}H-NMR (600 MHz, toluene-d$_8$, 0 °C, δ, ppm): 0.90 (d, 9H, P*Me*$_3$, $^2J_{H-P}$ = 6.78 Hz), 1.06 (s, 9H, 3 CH$_3$, ^tBuN=Mo), 1.26 (d, 9H, P*Me*$_3$, $^2J_{H-P}$ = 6.12 Hz), 1.45 (s, 9H, 3 CH$_3$, μ-N^tBu), 1.74 (d, 9H, P*Me*$_3$, $^2J_{H-P}$ = 6.90 Hz), 5.36 (ddd, 1H, MoSi*H*Ph, $^1J_{Si-H}$ = 226.1 Hz, found by ^{1}H-^{29}Si HSQC 1D JC, $^2J_{H-P}$ = 3.00 Hz, $^2J_{H-P}$ = 4.98 Hz, $^2J_{H-P}$ = 7.80 Hz), 7.05 (bd, 1H, MoSi*H*Ph, $^1J_{Si-H}$ = 226.1 Hz, found by ^{1}H-^{29}Si HSQC 1D JC, partially obscured by solvent signals), 7.29 (t, 2H, *m*-Ph,$^3J_{H-H}$ = 7.56 Hz), 7.47 (t, 2H, *m*-Ph, $^3J_{H-H}$ = 7.47 Hz), 7.96 (d, 2H, *o*-Ph, $^3J_{H-H}$ = 7.08Hz), 8.27 (d, 2H, *o*-Ph, $^3J_{H-H}$ = 6.96 Hz). ^{1}H{^{31}P}-NMR (600 MHz, toluene-d$_8$, 0 °C, δ, ppm; selected resonances): 0.90 (s, 9H, P*Me*$_3$), 1.26 (s, 9H, P*Me*$_3$), 1.74 (s, 9H, P*Me*$_3$), 5.36 (s, 1H, MoSi*H*Ph), 7.05 (s, 1H, MoSi*H*Ph). ^{31}P{^{1}H}-NMR (243.0 MHz, toluene-d$_8$, 0 °C, δ, ppm): 5.66 (t, 1P, P*Me*$_3$, $^2J_{P-P}$ = 22.6 Hz), -7.48 (dd, 1P, P*Me*$_3$, $^2J_{P-Pcis}$ = 18.2 Hz, $^2J_{P-Ptrans}$ = 91.1 Hz), -13.54 (dd, 1P, P*Me*$_3$, $^2J_{P-Pcis}$ = 27.4 Hz, $^2J_{P-Ptrans}$ = 91.2 Hz). ^{29}Si INEPT+ NMR (119 MHz, toluene-d$_8$, 0 °C, *J* = 150 Hz, δ, ppm): 41.70 (bd, $^1J_{Si-H}$ = 169.3 Hz), -10.42 (dddd, Mo-*Si*HPh, $^1J_{Si-H}$ = 152.0 Hz, $^2J_{Si-P}$ = 19.3 Hz, $^2J_{Si-P}$ = 19.3 Hz, $^2J_{Si-P}$ = 38.3 Hz).

DFT calculations

The unconstrained geometry optimization was carried out for all the considered structures with the Gaussian03 program package[30] using DFT and applying Becke three parameter hybrid exchange functional in conjunction with gradient-corrected nonlocal correlation functional of Perdew and Wang (B3PW91).[31] The 6-31G(d,p) basis set was used for the H, C, N, O, Si, P and Cl atoms. The Hay-Wadt effective core potentials (ECP) and the corresponding VDZ basis sets were used for the Mo atoms.[32] The same level of theory was used in the frequency calculations performed at all the located stationary points. The thermodynamic parameters were calculated in the rigid rotor-harmonic oscillator approximation. For all the located transition state structures, the minimum energy reaction paths were investigated using the Gonzales-Schlegel method.[33] The solvent effect was assessed using the polarizable continuum model (PCM).[26] The standard solvent parameters for benzene were used as implemented in the Gaussian program along with the same theory level and basis sets used in the gas phase calculations.

Crystal structure determination

The single crystals of complex **3**, suitable for X-ray diffraction analysis, were grown from Et$_2$O solution at -80 °C. The crystals were mounted in a film of perfluoropolyether oil on a glass fibre and transferred to a Siemens three-circle diffractometer with a CCD detector (SMART-1K system). The crystals represented nonsystematic twins and thus were of a rather poor quality. Nevertheless, we have managed to carry out indexing reflections although the data file contained many odd reflections. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[34] and refined by full-matrix least squares procedures.[35] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms except the hydrides were placed in calculated positions and refined in the "riding" model.

The Mo-bound hydride was and positionally refined isotropically. The hydrogen atoms bound to silicon atoms were also located from Fourier difference synthesis but their positions were not refined. One of the methyl group of the ^{t}Bu fragment at the N2 atom is disordered over two positions with the ratio of occupancies 0.6:0.4.The crystallographic data and the characteristics of structure solution and refinement are given in Table 2. Although geometric positions of light atoms were obtained with not too high accuracy, the total image of molecular structure is certainly correct and the distances between heavy atoms are accurate enough to discuss them in the article.

Table 2 Crystal and structure refinement data for **3**.

	3
Empirical formula	$C_{32}H_{55}MoN_2P_2Si_3$
Formula weight	710.94
Crystal size, mm^3	$0.22 \times 0.10 \times 0.08$
Crystal system	monoclinic
Space group	P2$_1$/n
Unit cell dimensions:	
a, Å	10.893(3)
b, Å	22.133(7)
c, Å	15.524(5)
β, deg.	100.687(14)
Volume, Å^3	3678(2)
Z	4
Density (calculated), g/cm^3	1.284
Absorption coefficient, mm^{-1}	0.565
F(000)	1504
Diffractometer	Bruker SMART-1K
Temperature, K	123(2)
Radiation, (lambda, Å) ,	(0.71073) Mo K$_\alpha$
Scan mode	ω
Time per step, sec.	15
Theta range for data collection, deg	1.62 – 27.50
Index ranges	$-14 \le h \le 14$, $-28 \le k \le 28$, $-20 \le l \le 20$
Reflections collected	24037
Independent reflections	8295
Absorption correction	multi-scan
Max. transmission	0.9562
Min. transmission	0.8858
Refinement method	Full-matrix least-square on F^2
Data / restraints / parameters	8295/0/362
Goodness-of-fit on F^2	0.742
Final R indices [I>2sigma(I)]	0.0960 (0.2055)
R indices (all data)	0.3144 (0.2650)
Largest diff. peak and hole, e.Å^{-3}	0.919 and -0.887

Notes and references

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Graphical abstract
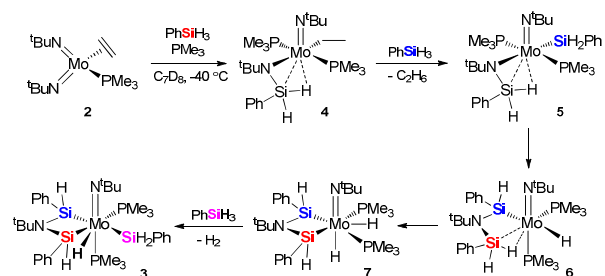
Coupling of the Mo=NR moiety of the Mo(IV) bis(imido) precursors (^{t}BuN)$_2$Mo(PMe$_3$)(L) (L= PMe$_3$, C$_2$H$_4$) with PhSiH$_3$ results in the product of triple silane addition, (^{t}BuN){μ-^{t}BuN(SiHPh)$_2$}Mo(PMe$_3$)(H)(SiH$_2$Ph) (**3**). Formation of **3** proceeds via a series of silanimine and Si-H$^{...}$Mo agostic species observed by NMR and studied by DFT calculations