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Catalytic and Stoichiometric Reactivity of β-Silylamido Agostic Complex of Mo: Intermediacy of a Silanimine Complex and Applications to Multicomponent Coupling

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Supporting Information

ABSTRACT: The reaction of complex $(ArN{=})_2Mo(PMe_3)_3$ (Ar = 2,6-diisopropylphenyl) with $PhSiH_3$ gives the β-agostic NSi-H···M silyamido complex $(ArN{=})Mo(SiH_2Ph)(PMe_3)$-$(\eta^3$-ArN-SiHPh-H) (**3**) as the first product. **3** decomposes in the mother liquor to a mixture of hydride compounds, including complex $\{\eta^3$-SiH(Ph)-N(Ar)-SiHPh-H···$\}MoH_3(PMe_3)_3$ characterized by NMR. Compound **3** was obtained on preparative scale by reacting $(ArN{=})_2Mo(PMe_3)_3$ with 2 equiv of $PhSiH_3$ under N_2 purging and characterized by multinuclear NMR, IR, and X-ray diffraction. Analogous reaction of $(Ar'N{=})_2Mo(PMe_3)_3$ (Ar′ = 2,6-dimethylphenyl) with $PhSiH_3$ affords the nonagostic silylamido derivative $(Ar'N{=})Mo(SiH_2Ph)(PMe_3)_2(NAr'\{SiH_2Ph\})$ (**5**) as the first product. **5** decomposes in the mother liquor to a mixture of $\{\eta^3$-PhHSi-N(Ar′)-SiHPh-H···$\}MoH_3(PMe_3)_3$, $(Ar'N{=})Mo(H)_2(PMe_3)_2(\eta^2$-Ar′N=SiHPh), and other hydride species. Catalytic and stoichiometric reactivity of **3** was studied. Complex **3** undergoes exchange with its minor diastereomer **3**′ by an agostic bond-opening/closing mechanism. It also exchanges the classical silyl group with free silane by an associative mechanism which most likely includes dissociation of the Si−H agostic bond followed by the rate-determining silane σ-bond metathesis. However, labeling experiments suggest the possibility of an alternative (minor) pathway in this exchange including a silanimine intermediate. **3** was found to catalyze dehydrogenative coupling of silane, hydrosilylation of carbonyls and nitriles, and dehydrogenative silylation of alcohols and amines. Stoichiometric reactions of **3** with nitriles proceed via intermediate formation of η^2-adducts $(ArN{=})Mo(PMe_3)(\eta^2$-ArN=SiHPh)$(\eta^2$-N≡CR), followed by an unusual Si−N coupling to give $(ArN{=})Mo(PMe_3)(\kappa^2$-NAr-SiHPh-C(R)=N−). Reactions of **3** with carbonyls lead to η^2-carbonyl adducts $(ArN{=})_2Mo(O{=}CRR')(PMe_3)$ which were independently prepared by reactions of $(ArN{=})_2Mo(PMe_3)_3$ with the corresponding carbonyl O=CRR′. In the case of reaction with benzaldehyde, the silanimine adduct $(ArN{=})Mo(PMe_3)(\eta^2$-ArN=SiHPh)-$(\eta^2$-O=CHPh) was observed by NMR. Reactions of complex **3** with olefins lead to products of Si_{ag}−C coupling, $(ArN{=})Mo(Et)(PMe_3)(\eta^3$-NAr-SiHPh-CH=$CH_2$) (**17**) and $(ArN{=})Mo(H)(PMe_3)(\eta^3$-NAr-SiHPh-CH=CHPh), for ethylene and styrene, respectively. The hydride complex $(ArN{=})Mo(H)(PMe_3)(\eta^3$-NAr-SiHPh-CH=$CH_2$) was obtained from **17** by hydrogenation and reaction with $PhSiH_3$. Mechanistic studies of the latter process revealed an unusual dependence of the rate constant on phosphine concentration, which was explained by competition of two reaction pathways. Reaction of **17** with $PhSiH_3$ in the presence of BPh_3 leads to agostic complex $(ArN{=})Mo(SiH_2Ph)(\eta^3$-NAr-Si(Et)Ph-H$)(\eta^2$-$CH_2$=$CH_2$) (**24**) having the Et substituent at the agostic silicon. Mechanistic studies show that the Et group stems from hydrogenation of the vinyl substituent by silane. Reaction of **24** with PMe_3 gives the agostic complex $(ArN{=})Mo(SiH_2Ph)(PMe_3)(\eta^3$-NAr-Si(Et)Ph-H), which slowly reacts with $PhSiH_3$ to furnish silylamide **3** and the hydrosilylation product $PhEtSiH_2$. A mechanism involving silane attack on the imido ligand was proposed to explain this transformation.

INTRODUCTION

Hydrosilylation of unsaturated organic substrates is an important industrial and laboratory reaction widely used for preparation of silane monomers and polymers, crafting of surfaces, and production of specialty silicon chemicals.[1] In transition-metal-catalyzed hydrosilylation, these useful products are produced via interaction of a transition metal silyl complex with an unsaturated organic substrate followed by reductive elimination.[2] Several groups have recently reported an alternative mechanism in which unsaturated substrates (olefin or carbonyl) add to a metal silylene complex formed upon double Si−H activation in the silane H_2SiRX (X = H or R).[3−5] These findings bring about two general questions: Can an organosilicon ligand other than silyl or silylene bind unsaturated molecules? and What is the possible synthetic application of such reactivity? In this regard, a reaction which would include the generation of a reactive organosilicon moiety

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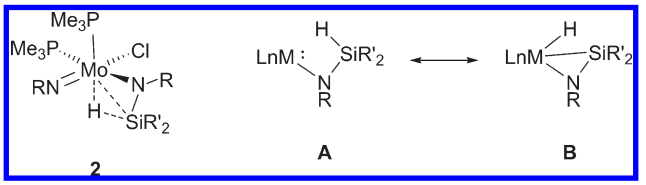
Scheme 1. Possible Tricomponent Coupling of a Silane, an Amine, and an Unsaturated Substrate(X,Y = C, N, O, S, ...)

Chart 1. Valence Bond Description of Bonding in Agostic Complexes 2



in the coordination sphere of metal prior to its reaction with an unsaturated substrate (alkene, alkyne, carbonyl, nitrile, etc.) would be of particular interest. The ideal goal will be to achieve a tricomponent (or more) coupling of silanes with organic molecules to generate functionalized silane products, for instance, as shown in Scheme 1, and to do this transformation catalytically.

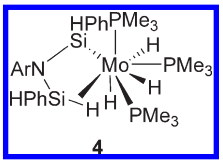
Very recently, stoichiometric reactions of nitriles,[6] ketones,[7] α,β-unsaturated carbonyls,[8] oxiranes,[9] isocyanates,[10] and amides[7a] with metal silylene complexes have been disclosed. Sakaba et al. reported the addition of methanol to η^3-1-silaallyl and η^3-1-silapropargyl complexes[11] and the addition of ketones to an η^1,η^2-alkynyl-bridged W—Si complex derived from a silylacetylene.[12] Also, Kira et al. described nitrile addition to a bridging μ,η^2,η^2-silane complex to generate a μ-iminosilyl complex, along with several hydrosilylation reactions catalyzed by the same μ,η^2,η^2-silane complex.[13] Most relevant to the present research is the report by Berry et al. on stoichiometric reactions of alkenes, alkynes, carbonyls, and CO_2 with the silanimine complex $Cp_2Zr(^tBuN{=}SiMe_2)(PMe_3)$ (**1**) to give products of addition across the Zr—Si bond.[14]

We have previously discovered a silane/imido coupling reaction leading to β-SiH agostic silylamido complexes $(RN{=})Mo(Cl)(PMe_3)_2(\eta^3\text{-RN-SiR'}_2\text{-H})$ (**2**), which can be a first step in a possible tricomponent coupling reaction between a silane, an amine, and an unsaturated substrate (Scheme 1).[15] Moreover, the d^2 electronic configuration of **2** allows for its description as a masked form of a silanimine complex (see **B** in Chart 1), suggesting the possibility of coupling reactions with alkenes, alkynes, carbonyls, etc., akin to the silanimine complex **1**. This hypothesis was further substantiated by the observation of a transient silanimine complex and the products of silanimine dimerization in the reactions of $(RN{=})_2M(PMe_3)_3$ (M = Mo, W) with $HSiCl_3$.[15b] Here we report the preparation of a new β-SiH agostic silyamido complex of molybdenum $(ArN{=})Mo(SiH_2Ph)(PMe_3)(\eta^3\text{-ArN-SiHPh-H})$ (**3**, Ar = 2,6-diisopropylphenyl), the investigation of its stoichiometric reactivity toward unsaturated substrates, and the first application to catalytic hydrosilylation. We garnered evidence that these reactions occur via coupling of a silanimine intermediates with unsaturated substrates, which is a possible second step in the multicomponent coupling shown in Scheme 1. A preliminary communication has been published.[16]

RESULTS AND DISCUSSION

Preparation of Agostic Complex $(ArN{=})(PhH_2Si)(PMe_3)Mo(\eta^3\text{-N(Ar)-SiHPh-H})$ (3). We have previously found that bis(imido) compounds $(RN{=})_2Mo(PMe_3)_3$ react with chlorohydrosilanes $HClSiR'_2$ to give the products of Si—N coupling and Si—Cl activation, the agostic species $(RN{=})Mo(Cl)(PMe_3)_2(\eta^3\text{-RN-SiR'}_2\text{-H})$ (**2**). In this study, our initial goal was to investigate the reactions of bis(imides) $(RN{=})_2Mo(PMe_3)_3$ with chlorine-free primary and secondary silanes H_2SiRX (X = R, H) with the hope to achieve double Si—H activation and to prepare the putative hydride compound $(RN{=})Mo(H)(PMe_3)_2(\eta^3\text{-RN-SiR'}_2\text{-H})$, analogous to **2** and, presumably, more reactive than **2**.

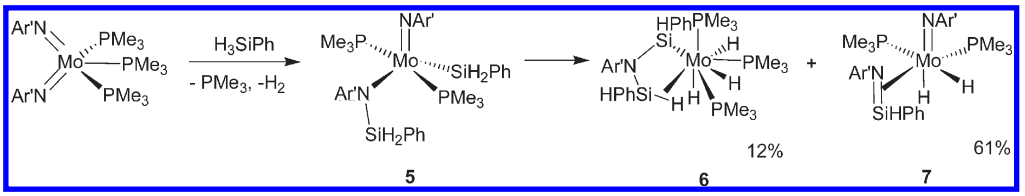
Attempted reaction of $(ArN{=})_2Mo(PMe_3)_3$ with 1 equiv of $PhSiH_3$ at room temperature led to a 1:1 mixture of the starting complex and a product of double silane addition, the β-agostic NSi-H···M complex $(ArN{=})Mo(SiH_2Ph)(PMe_3)(\eta^3\text{-N(Ar)-SiHPh-H})$ (**3**). The latter compound decomposes in the mother liquor to a mixture of hydride complexes, one of which is tentatively assigned (by NMR) the structure $\{\eta^3\text{-SiH(Ph)-N(Ar)-SiHPh-H}\cdots\}MoH_3(PMe_3)_3$ (**4**).



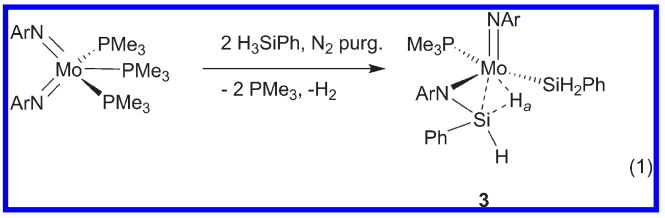
Complex **4** is highly fluxional at room temperature, but cooling the sample to −45 °C allows for the observation in ^1H NMR of three nonequivalent hydride resonances of equal intensity, at −8.82 (d, $^2J_{H-P}$ = 19.2 Hz), −6.58 (t, $^2J_{H-P}$ = 36.0 Hz), and −5.61 ppm (d, $^2J_{H-P}$ = 53.4 Hz). The presence of one NAr moiety was suggested on the basis of integration of the ^1H NMR spectrum. The Si-bound protons give rise to broad singlets at 5.22 and 5.63 ppm coupled in $^1H-^{29}Si$ HSQC to the ^{29}Si signals at −14.2 and 51.3 ppm, respectively. Also, the presence of two nonequivalent SiHPh groups is confirmed by the observation of two doublets for the *ortho*-protons at 8.90 and 8.47 ppm in ^1H NMR. At −45 °C, the ^{31}P NMR spectrum of **4** shows three nonequivalent resonances at −8.8 (t, $^2J_{P-P}$ = 40.0 Hz), −6.6 (dd, $^2J_{P-P}$ = 21.9 and 40.0 Hz), and 3.7 ppm (dd, $^2J_{P-P}$ = 21.9, 40.0 Hz), which merge into a broad singlet at −7.7 ppm at room temperature. Unfortunately, we failed to assign a signal due to the agostic Si—H···Mo hydride, presumably because it was obscured by other signals. However, the formulation of **4** as a Mo(IV) agostic species is a more reasonable alternative to the formation of a Mo(V) bis(silyl) derivative $\{\eta^2\text{-SiH(Ph)-N(Ar)-SiHPh}\}MoH_3(PMe_3)_3$ which should be paramagnetic. The observation of **4** is of interest as it suggests the possibility of detaching the functionalized silicon product from the metal after the proposed Si—N coupling step.

The reaction of $(ArN{=})_2Mo(PMe_3)_3$ with 1 equiv of $PhSiH_3$ at low temperature was followed by NMR spectroscopy. At −30 °C, 50% conversion of the starting complex to **3** was achieved, without observation of any intermediates. Upon warming this sample to room temperature, decomposition starts to give the same reaction mixture as observed in the room-temperature experiment. To eliminate phosphine as a

Scheme 2. Formation of 5 and Its Decomposition to 6



possible reason for decomposition, the reaction was repeated in the presence of 2 equiv of BPh_3. This allows for the preparation of impure **3** at room temperature, but a scale-up was complicated by the separation from $Me_3P{\cdot}BPh_3$ and other byproducts. The preparative-scale synthesis of **3**, in 77% isolated yield, was eventually achieved by reacting $(ArN{=})_2Mo(PMe_3)_3$ with 2 equiv of $PhSiH_3$ under N_2 purging (eq 1):



The silylamide **3** was fully characterized by multinuclear NMR, IR, and X-ray diffraction. Complex **3** is fluxional at room temperature (*vide infra*), but at −50 °C the ^1H NMR spectrum shows the presence of two silicon centers: a silyl group with two diastereotopic Si*H* signals at 5.97 and 5.68 ppm coupled to the ^{29}Si signal at 1.2 ppm (t, $^1J_{Si-H}$ = 153.5 Hz[17]) and an agostic ArN-SiH_2Ph ligand, in which the agostic SiH_a hydride gives rise to an upfield resonance at 4.35 ppm (bm) coupled to the terminal Si*H* hydride at 6.03 ppm (bd, $^2J_{H_a-H}$ = 5.4 Hz). Both these signals are coupled in $^1H-^{29}Si$ HSQC to the silicon signal at −72.9 ppm (dd, $^1J_{Si-H_a}$ = 113.0 Hz, $^1J_{Si-H}$ = 245.3 Hz[17]). These spectroscopic features, and in particular the upfield SiH_a shift in ^1H NMR, the upfield shifted ^{29}Si signal,[15] and the small value of the $^1J_{Si-H_a}$, suggest the coordination of the Si−H bond to molybdenum.[18] In d^0 silylamido agostic complexes, the SiH coupling constants are usually found in the range of 125−155 Hz,[19] although coupling as low as 113.2 Hz has been also observed.[19b] In the related d^2 systems, the J_{Si-H} is further reduced to 96−129 Hz due to back-bonding from the metal.[15,20,21] Additional support for agostic bonding in **3** was provided by the observation of a red-shifted band at 1694 cm^{-1} for the agostic Si−H_a bond in the IR spectrum, whereas three other classical Si−H stretches are found at 2014, 2041, and 2165 cm^{-1}.[18] At −30 °C, the proton-coupled ^{31}P NMR spectrum of **3** with selective decoupling from the Me groups shows a doublet at 10.6 ppm ($^2J_{P-H}$ = 9.3 Hz) due to the coupling to the agostic SiH_a. The formulation of complex **3** as an agostic species was further supported by X-ray diffraction analysis described previously in a preliminary communication.[16]

Reaction of $(Ar'N{=})_2Mo(PMe_3)_3$ with $PhSiH_3$. In order to understand the effect of the imido unit on the course of silane/imido coupling, the reactivity of the bis(imido)complex $(Ar'N{=})_2Mo(PMe_3)_3$ (Ar′ = 2,6-dimethylphenyl) was studied. The treatment of $(Ar'N{=})_2Mo(PMe_3)_3$ with $PhSiH_3$ at room temperature affords after 10 min the silylamido derivative $(Ar'N{=})Mo(SiH_2Ph)(PMe_3)_2(NAr'\{SiH_2Ph\})$ (**5**, Scheme 2) as the initial product. When a stoichiometric reaction between $(Ar'N{=})_2Mo(PMe_3)_3$ and 1 equiv of $PhSiH_3$ was carried out at low temperature, no intermediates were observed and only complex **5** was detected after 15 min at −5 °C (50% conversion of the starting material). The compound **5** is highly fluxional, giving rise to broad, featureless resonances in the aliphatic and aromatic regions in the room-temperature ^1H NMR spectrum. Nevertheless, ^1H NMR at −71 °C reveals two pairs of diastereotopic Si*H* signals, for the Mo-bound silyl group at 5.80 and 5.96 ppm and for the silylamide ligand at 5.71 and 6.02 ppm. These signals are coupled in $^1H-^{29}Si$ HSQC to two ^{29}Si resonances at 1.3 and −32.1 ppm, corresponding to the Mo-bound silyl and the silylamide group, respectively. In contrast to its agostic analogue **3**, no coupling of the hydrides of the Ar′N-SiH_2Ph ligand to phosphines can be seen in ^1H and $^1H-^{31}P$ HSQC NMR spectra, suggesting the absence of any Si−H bond coordination to molybdenum. In the ^{31}P NMR spectrum of **5**, two nonequivalent PMe_3 ligands give rise to two mutually coupled doublets at −9.3 and −13.6 ppm, whose large $^2J_{P-P}$ of 199.2 Hz indicates the *trans*-arrangement. Similarly to the agostic compound **3**, complex **5** is not stable in solution in the presence of PMe_3 and H_2 and decomposes overnight at room temperature into a difficult-to-separate mixture of $\{\eta^3$-PhHSi-N(Ar′)-SiHPh-H···$\}MoH_3(PMe_3)_3$ (**6**) and other hydride species, whose spectroscopic features are analogous to the related Ar chemistry.

Unlike the thermal decomposition of **3**, the decay of **5** is also accompanied by the formation of a large amount (61%) of a complex with a trapped silanimine ligand, $(Ar'N{=})Mo(H)_2(PMe_3)_2(\eta^2$-Ar′N=SiHPh) (**7**, Scheme 2), whose structure was revealed by NMR analysis. Thus, the room-temperature ^1H NMR showed upfield resonances for two nonequivalent Mo-bound hydrides at −4.76 (ddd, $^2J_{H-P}$ = 45.3, 55.3 Hz, $^2J_{H-H}$ = 8.5 Hz) and −2.46 ppm (ddd, $^2J_{H-P}$ = 15.3, 31.6 Hz, $^2J_{H-H}$ = 8.5 Hz), coupled in the $^1H-^{31}P$ HSQC to two phosphorus signals at 4.2 and 8.4 ppm. The small value of the $^2J_{P-P}$ (15.8 Hz) in the ^{31}P NMR spectrum indicates the *cis*-arrangement of the PMe_3 ligands. The Si-bound proton of the silanimine ligand gives rise to a downfield resonance at 6.36 ppm (dd, $^3J_{H-P}$ = 2.3, 15.0 Hz), which according to the $^1H-^{31}P$ HSQC spectrum is coupled to the same ^{31}P signals. In $^1H-^{29}Si$ HSQC, the Si-bound hydride correlates with the ^{29}Si resonance at −12.1 ppm, which in the ^{29}Si NMR spectrum shows large coupling to a terminal hydride ($^1J_{H-Si}$ = 218.8 Hz), consistent with the Si−H bond being uncoordinated to the metal. The formulation of **7** as a silanimine complex, in particular, the direct bonding between the Mo and Si atoms, is supported by the observation of a reasonably large $^2J_{Si-P}$ constant of 15.0 Hz. For comparison, in the related complex $(ArN{=})Mo(Cl)_2(PMe_3)_2(\eta^2$-ArN=SiHCl), the silanimine ligand gives rise to a ^{29}Si signal at −42.4 ppm, also showing large coupling to

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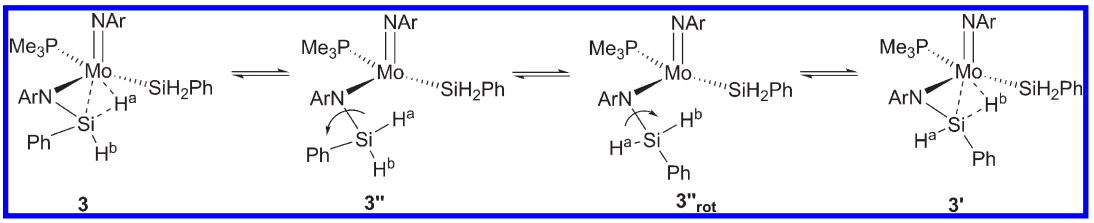
Scheme 3. Suggested Dynamic Process in Complex 3



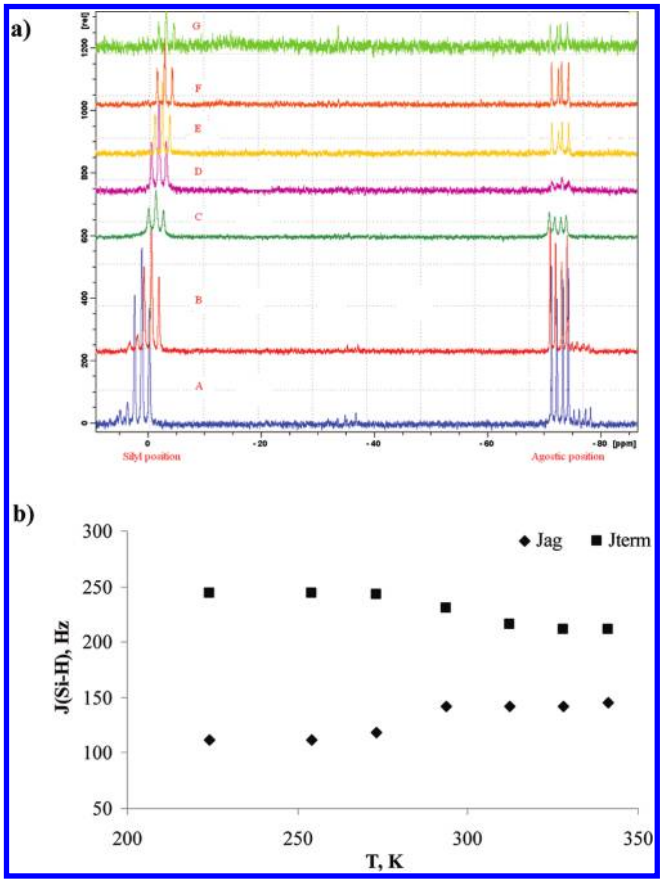


Figure 1. (a) ^{29}Si INEPT+ NMR spectra of **3** at −49 (A), −19 (B), 0 (C), 21 (D), 39 (E), 55 (F), and 68 °C (G). (b) Effect of temperature on the $^{1}J_{Si-H}$ values for the agostic silyl center in **3**.

the phosphine and hydride ligands.[15b] For the isolated silanimine $Cp_2Zr(CO)(\eta^2$-$^{t}BuN{=}SiMe_2)$, the ^{29}Si signal is found at −69.9 ppm.[14a]

Attempts at isolation of complexes **5** and **7** were hampered by their instability and the formation of byproducts of comparable solubility, one of which was assigned the structure **6** (Scheme 2) by analogy with the related Ar complex **4**.

Fluxional Behavior of 3. As the fluxional behavior of complex **3** could be pertinent to its reactivity, a variable-temperatue (VT) NMR study was performed. The room-temperature ^{1}H NMR spectrum shows slightly broadened resonances for the terminal SiH_2Ph group but significantly broad signals for the agostic silyl, suggesting that the fluxionality is related to the change in agostic bonding. This could happen by opening the Si−H···Mo bond, rotating around the N−Si bond, and closing a new Si−H···Mo

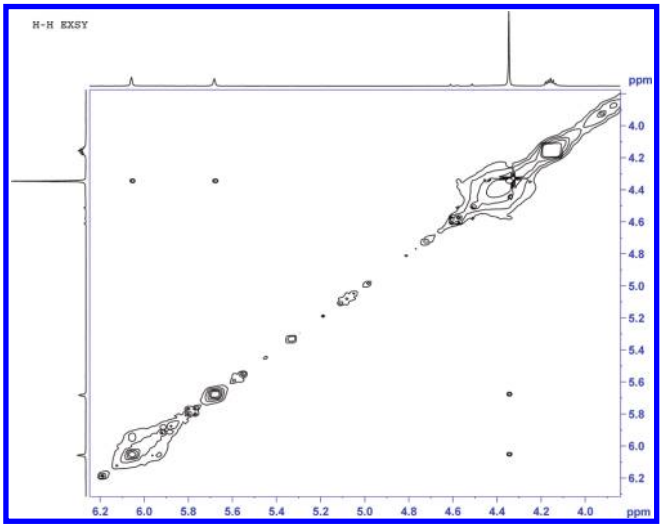


Figure 2. ^{1}H−^{1}H EXSY NMR spectrum (22 °C) of a mixture of **3** and $PhSiH_3$. Signals at ∼4.35, 5.67, and 6.05 ppm correspond to SiH protons of $PhSiH_3$ and Mo-SiH_2Ph of **3**, respectively.

bond to what used to be the terminal hydride on silicon (Scheme 3). Given the chirality of the agostic silicon and molybdenum centers in **3**, this process would convert **3** into its diastereomer **3′**. Indeed, we did observe **3′** in small amount (∼5%) by ^{1}H NMR at −50 °C (in toluene-d_8) and observed its exchange with **3** by EXSY NMR. Signals of **3′** were also observed by ^{29}Si INEPT+ very close to the corresponding signals of **3** (Figure 1a).

To understand better the nature of fluxionality in **3**, variable temperature (−49 to 68 °C) ^{29}Si NMR studies were performed. The increase of temperature leads to the merging of the ^{29}Si resonances of **3** and **3′** (Figure 1a). Furthermore, it brings the $^{1}J^{ag}_{Si-H}$ and $^{1}J^{term}_{Si-H}$ for the η^3-NAr-SiHPh-H ligand closer to each other (Figure 1b), whereas the $^{1}J_{Si-H}$ for the SiH_2Ph ligand remains virtually the same. These observations can be accounted for by the increased contribution of an open form of **3** (complex **3″** in Scheme 3).

Reactions of Complex 3 with Hydrosilanes. Addition of excess $PhSiH_3$ (10 equiv) to a solution of **3** in C_6D_6 results in a slow silane coupling and redistribution process, indicating the possibility of Si−H bond activation.[22] The reaction proceeds at room temperature and gives overnight 70% conversion of $PhSiH_3$ to a mixture of Ph_2SiH_2 (34%), SiH_4 (34%), and PhH_2Si-SiH_2Ph (2%). Full conversion of the phenylsilane was observed upon heating the mixture overnight at 50 °C, affording Ph_2SiH_2, SiH_4, and PhH_2Si-SiH_2Ph in 47, 47, and 6% yield (by ^{1}H NMR), respectively. In attempt to understand the catalytic silane activation mediated by **3**, NMR studies of its reactions with hydrosilanes were performed.

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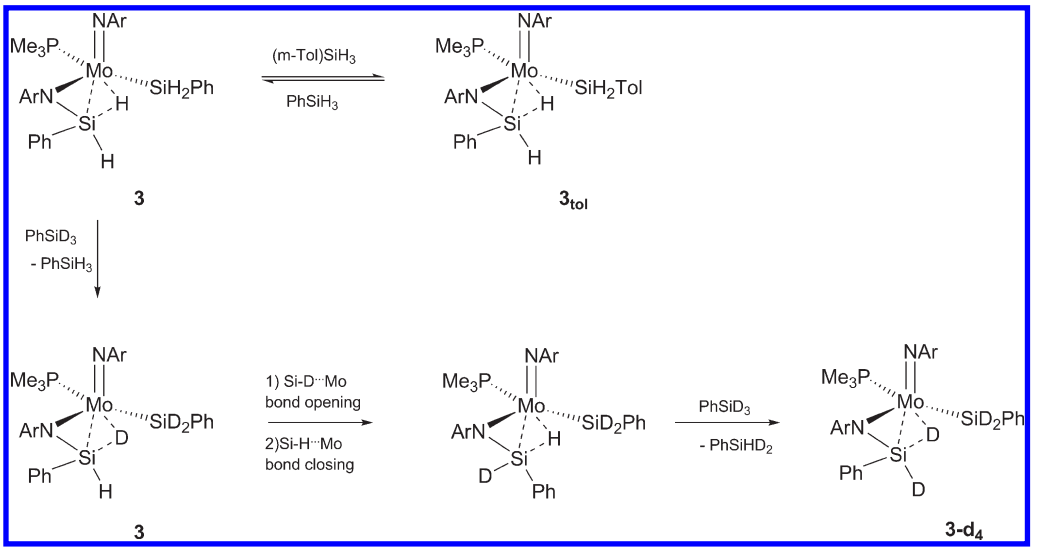
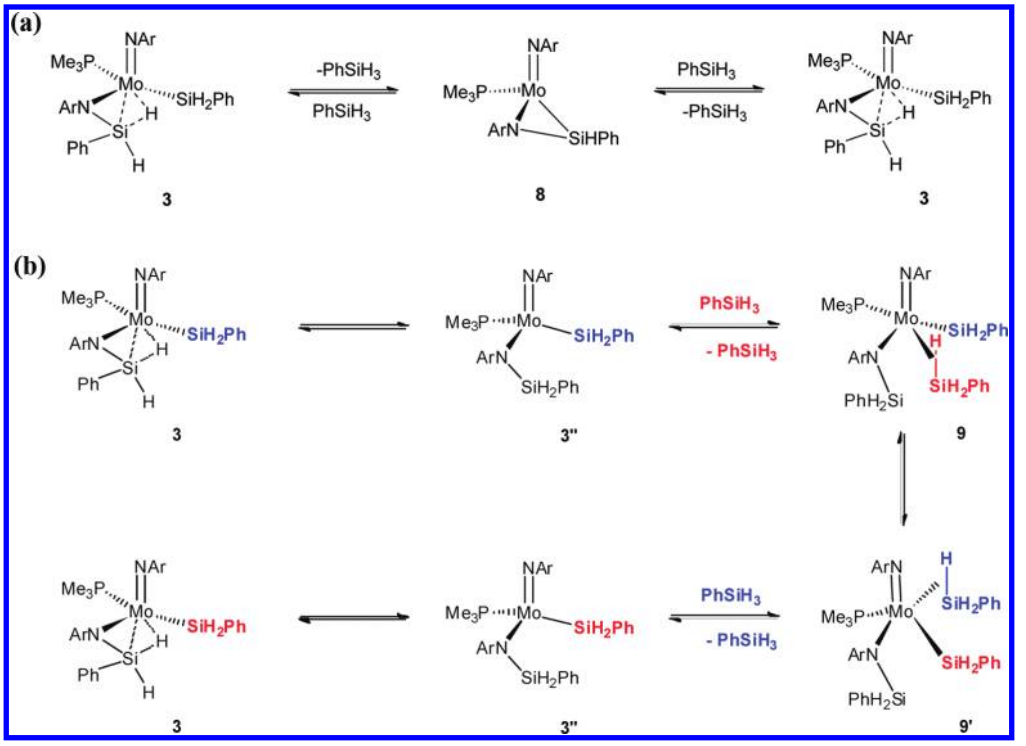
Scheme 4. Exchange of 3 with (*m*-Tol)SiH_3 and $PhSiD_3$



Scheme 5. Silane/Silyl Exchange in 3 via (a) Silanimine Intermediate 8 (Dissociative Mechanism) and (b) an Associative Mechanism



Variable-temperature (−4 to 22 °C) $^1H-^1H$ EXSY experiments of a stoichiometric mixture of **3** and $PhSiH_3$ showed an exchange process between the free silane and the classical SiH_2Ph ligand, but not with the agostic silylamide fragment (Figure 2).[23] On the other hand, an NMR experiment with a labeled silane $PhSiD_3$ revealed after 5 min at room temperature a nearly statistical redistribution of deuterium on all silicon centers in (ArN═)Mo(SiD_2Ph)(PMe_3)(η^3-NAr-SiDPh-D) (**3d$_4$**), suggesting a fast exchange between the Si-bound protons of both silyl groups and the free silane (Scheme 4).

Hypothetically, such a substitution of hydrides for deuterium could proceed without the exchange of silicon centers of the silane and the silyl groups of **3**. This suggestion was examined by using the labeled silane (*m*-Tol)SiH_3. Thus, the treatment of **3** with (*m*-Tol)SiH_3 leads after 10 min at room temperature to the replacement of the classical SiH_2Ph ligand with the tolylsilyl group,

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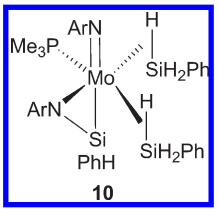
forming $\mathbf{3}_{tol}$ (43% conversion; Scheme 4). The agostic SiH_2Ph group remains unreacted according to the $^1H-^{13}C$ HMBC-GP experiment, which shows a long-range correlation between the Si-bound protons and the *ipso*- and *ortho*-carbons of the Ph group. Assuming that the Si−C bond is not cleaved in these experiments, the aryl group can serve as a label for the silicon center. Furthermore, analogous treatment of the silylamide **3** with excess $PhMeSiH_2$ leads to partial displacement of the classical SiH_2Ph ligand with SiHMePh.

Our initial interpretation of these exchange reactions, supported by the reactivity studies (*vide infra*), was that they proceed via $PhSiH_3$ elimination and formation of a reactive 16-electron (assuming that the nitrogen of the [ArNSiHPh] ligand donates up to 4e) silanimine intermediate (ArN═)Mo(PMe_3)(η^2-ArN═SiHPh) (**8**, Scheme 5a).[16] Alternatively, the exchange could proceed via an associative mechanism, for example, via the easy dissociation of the agostic Si−H···Mo bond to give **3″** (*vide supra*) followed by rate-limiting silane coordination to form the silane σ-complex **9** (Scheme 5b).[18,24] Dissociation of the σ-bond-coordinated silane derived from the classical SiH_2Ph ligand would result in selective exchange between the free silane and the silyl ligand.

To distinguish between the associative and dissociative pathways, a variable-temperature kinetic study was performed. The activation parameters of exchange were determined using 1D ^1H EXSY NMR[25] for a mixture of **3** and phenylsilane in the range 12−42 °C. The large negative entropy of activation $\Delta S^{\ddagger} = -36.7 \pm 2.2$ cal·mol^{-1}·K^{-1} was measured from the Eyring plot (Figure 3),[26] which suggests a dominant associative mechanism of the silyl/silane exchange.[27] It should be noted, however, that the associative mechanism offered in Scheme 5b cannot account for the deuterium scrambling into the agostic position, leaving room for speculations that either there is a minor pathway via the silanimine **8** shown in Scheme 5a or the associative mechanism involves the crowded silanimine **10** with two σ-coordinated silane ligands. Furthermore, coupling reactions of the compound **3** with unsaturated organic substrates strongly suggest the intermediacy of a silanimine complex (*vide infra*).



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Catalytic Reactivity of Complex 3. The observation of catalytic dehydrogenative coupling and redistribution of $PhSiH_3$ mediated by the agostic complex **3** suggested the possibility of its catalytic activity in the hydrosilylation of unsaturated organic molecules. Although β-agostic silylamide complexes have been known for almost two decades, their reactivity has not been studied yet.[19,20] We found that compound **3** catalyzes a variety of hydrosilylation processes, details of which are given in the Supporting Information. In summary, these include the catalytic hydrosilylation of aldehydes and ketones and one of the first examples of chemoselective catalytic mono-hydrosilylation of nitriles,[6a,13,28−32] as well as alcoholysis and aminolysis of silanes.[1d,33−35] For alkenes, however, we primarily observed reduction to corresponding alkanes (Table SI2), albeit ethylene could be hydrosilylated by

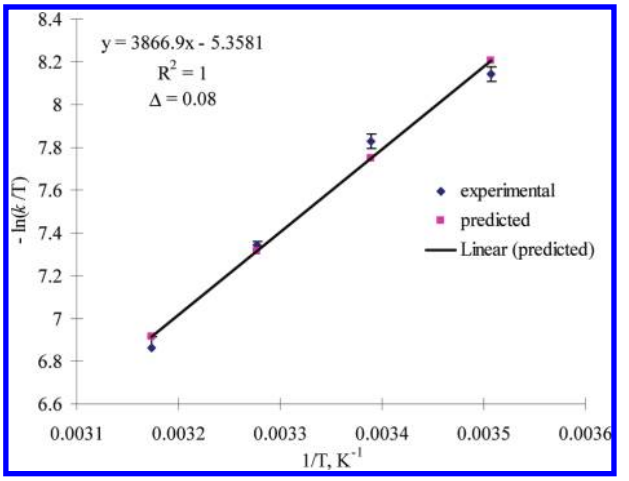

Figure 3. Eyring plot for the exchange between **3** and $PhSiH_3$ (standard error: 0.08).

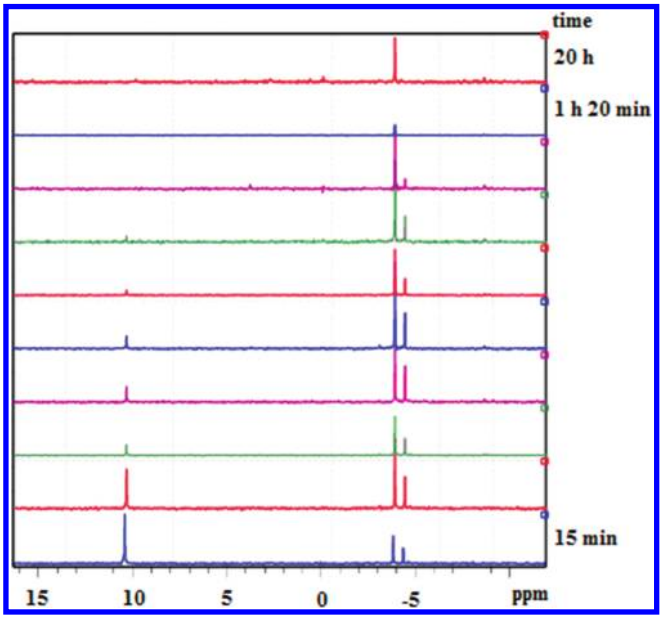

Figure 4. $^{31}P\{^1H\}$-NMR spectra of the reaction mixture of **3** and ^{i}PrCN (the signals at 10.5, −3.8, and −4.4 ppm correspond to **3**, **12d**, and **11d**, respectively).

$PhSiH_3$ to a mixture of $PhEtSiH_2$ (19%), $PhEt_2SiH$, and $PhEt_3Si$ (estimated combined yield 30%).

Reactions of Complex 3 with Nitriles. To shed light on the possible mechanism(s) of hydrosilylation reactions, the stoichiometric reactivity of complex **3** was studied. All reactions with unsaturated organic molecules (nitriles, carbonyls, alkenes, alkynes) are accompanied by the release of 1 equiv of silane, suggesting that a silanimine intermediate may be involved.

Treatment of **3** at room temperature with equimolar amounts of nitriles (CH_3CN, PhCN, ^{i}PrCN, and ^{t}BuCN) gives initially the η^2-adducts (ArN═)Mo(PMe_3)(η^2-ArN═SiHPh)(η^2-N≡CR) (R = Me (**11a**), Ph (**11b**), ^{i}Pr (**11c**), and ^{t}Bu (**11d**); Scheme 6), evidenced by the diagnostic ^{13}C NMR signals at 187−204 ppm for the C≡N carbon.[36] The reaction rate depends on the steric demand of the R group and varies from 10 min for R = Me to a couple of hours for R = ^{t}Bu.

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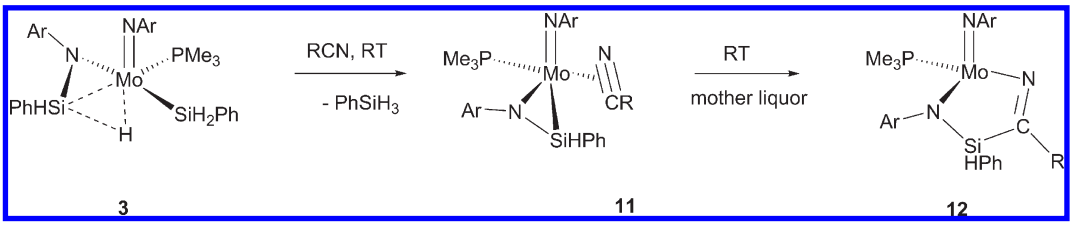
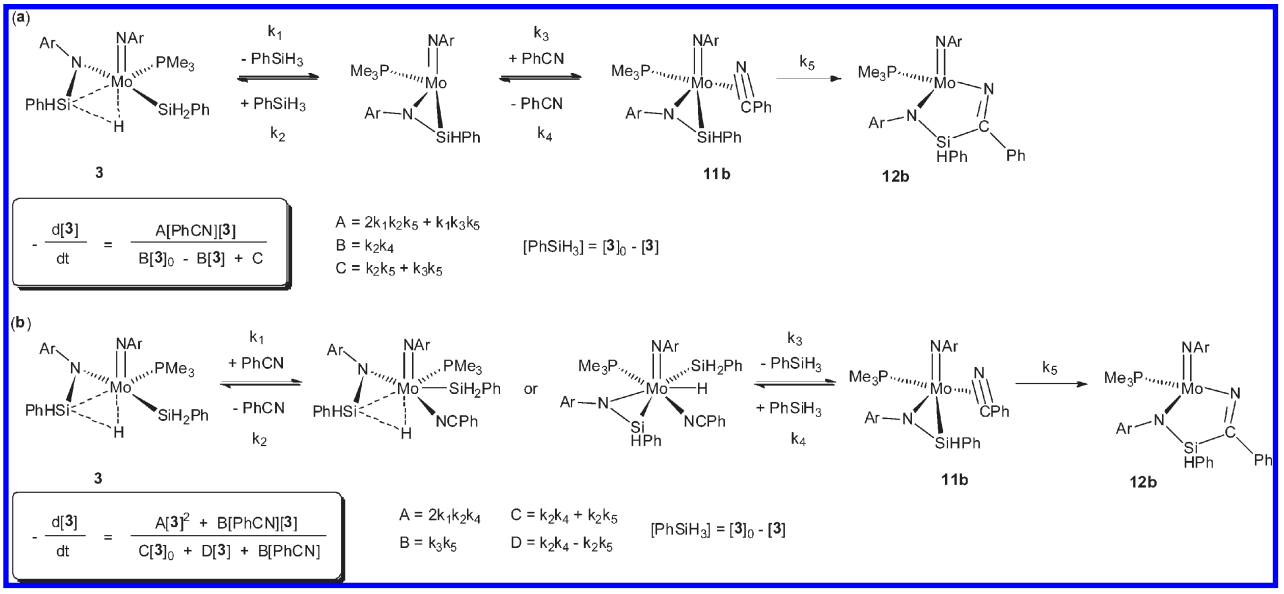
Scheme 6. Reactions of 3 with Nitriles



Scheme 7. Possible Mechanisms, Dissociative (a) and Associative (b), for the Reaction of 3 with PhCN



Kinetics of the reaction of **3** with PhCN (1−7 equiv) was studied by NMR spectroscopy. The data obtained from the NMR experiments could be linearized in both $-\ln[\mathbf{3}]/t$ and $(1/[\mathbf{3}])/t$ coordinates, resulting in the effective rate constant being proportional to the concentration of nitrile (see the Supporting Information). We considered two pathways for this reaction, dissociative (a) and associative (b) (Scheme 7). Both kinetic equations in Scheme 7 (see the Supporting Information for details) at certain ratios of coefficients $A-D$ qualitatively agree with the observed kinetics, which does not allow us to distinguish between the proposed mechanisms. However, the release of $PhSiH_3$ in the reaction of **3** with benzonitrile suggests that the process most likely does not proceed through dissociation of the agostic Si−H bond and formation of silylamides (ArN═)Mo(PMe_3)(NArSiH_2Ph)(SiH_2Ph) (**3″**) and (ArN═)Mo(PMe_3)(NArSiH_2Ph)(SiH_2Ph)(N≡CPh).

Complexes **11a**−**d** are unstable in solution and undergo slow rearrangement through the insertion of the C≡N moiety into the Mo−Si bond of the silanimine ligand to give compounds (ArN═)Mo(PMe_3)(κ^2-NAr-SiHPh-C(R)═N) (R = Me (**12a**), Ph (**12b**) ^{i}Pr (**12c**), and ^{t}Bu (**12d**); Scheme 6 and Figure 4).

The rate of rearrangement depends strongly on the bulkiness of the nitrile substituent. As expected, the slowest reaction was observed for the *tret*-butyl complex **11d**. The rearrangement of the methyl derivative **11a** is complicated because of additional activation of the C−H bond of the CH_3CN ligand.[37] NMR study of the final products **12a**−**d** showed unexpectedly the formation of the [PhHSi-C(R)═N] fragment rather than a product of Si−N bond coupling.[6a,13] In particular, the ^{1}H−^{13}C HMBC spectrum of **12c** shows correlation of the Si*H*, C*H*, and CH_3 protons with the RN═C carbon, thus establishing the presence of a direct bond between the silicon atom and the imine carbon atom (Figure 5). Such a selective *N*-addition of the RC≡N ligand to molybdenum can be accounted for by the highly electron deficient nature of compounds **12a**−**d**, in which the direct bonding between the molybdenum and methylenamido centers[38] allows for additional lone pair donation from the latter to the former, stabilizing the 16-electron valence shell. Despite the electron deficiency of the Mo center the downfield shifts of the Si*H* signals (5.31 - 6.56 ppm) in ^{1}H NMR, the large values of the $^1J_{Si-H}$ coupling constants (218.3 - 225.4 Hz) in ^{29}Si INEPT+ NMR spectra, as well as the observation of normal Si−H stretches at 2103-2118 cm^{-1} in IR evidence the absence of Si−H bond coordination to molybdenum.[18]

Treatment of the nitrile coupling product (ArN═)Mo(PMe_3)(η^2-NAr-SiHPh-C(^{i}Pr)═N) (**12c**) with excess $PhSiH_3$ at room temperature leads to a slow (4 days) conversion into the agostic complex (ArN═)Mo(SiH_2Ph)(PMe_3)(η^3-NAr-SiHPh-H) (**3**, 65%), accompanied by the formation of a

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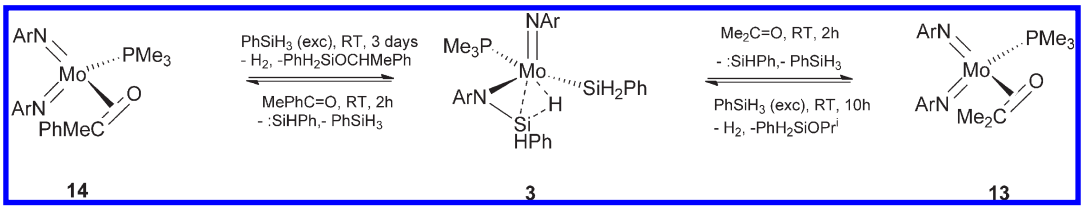
Scheme 8. Reactions of 3 with Ketones To Give Compounds 13 and 14



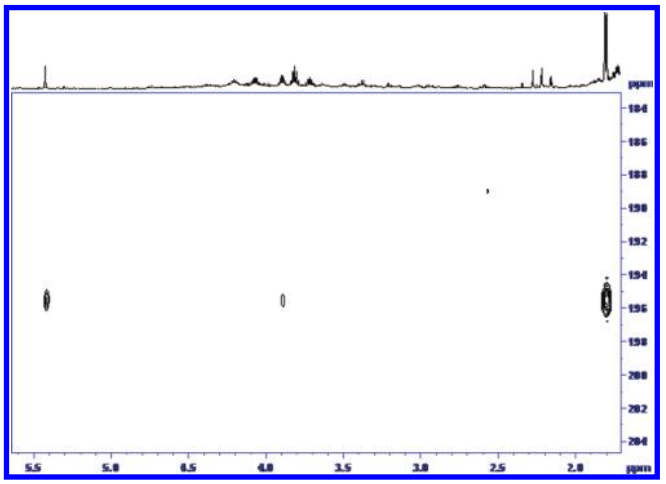


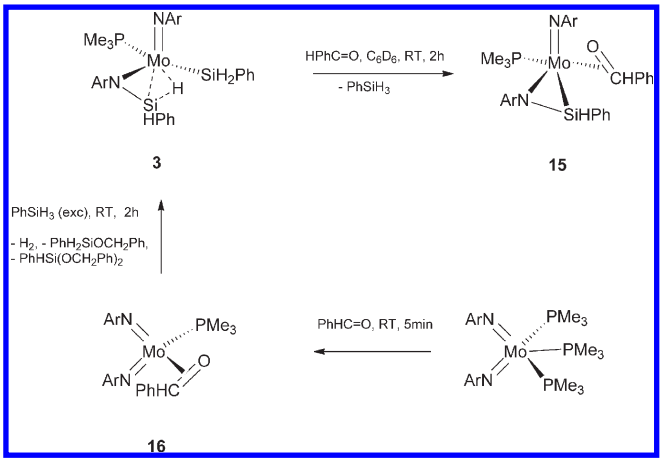
Figure 5. $^{1}H-^{13}C$ HMBC NMR spectrum of **12c** taken directly from the reaction mixture . Signals at 5.4, 3.9, and 1.8 ppm correspond to the Si*H*, C*H*, and CH_3 protons, respectively.

difficult-to-characterize mixture of silicon-containing products. At the moment, it remains unclear whether a structure akin to **12c** is related to the catalytic hydrosilylation of nitriles mediated by **3** or is a dormant state of the catalyst.

Reactions of Complex 3 with Carbonyls. Unlike the nitrile chemistry, reaction of the agostic silylamide **3** with acetone does not afford a product of insertion into the Mo−Si_{ag} bond. Instead, the formation of bis(imido) carbonyl adducts (ArN═)$_2$Mo(η^2-O═CMe_2)(PMe_3) (**13**)[39] and (ArN═)$_2$Mo(η^2-O═CMePh)(PMe_3) (**14**)[40] was observed (Scheme 8). The reactions are accompanied by elimination of 1 equiv of $PhSiH_3$ and give a difficult-to-characterize mixture of silicon-containing compounds. All attempts to trace the fate of the extruded silylene fragment:SiHPh were unsuccessful.[41] Carbonyl adducts **13** and **14** were also independently synthesized by the reaction of (ArN═)$_2$Mo(PMe_3)$_3$ with the corresponding ketone. The treatment of **13** and **14** with excess $PhSiH_3$ results in elimination of ketone and selective regeneration of the agostic complex **3** (Scheme 8).

In contrast to ketones, the reaction of **3** with benzaldehyde gives a highly fluxional product whose ^{1}H NMR spectrum exhibits a doublet at 13.28 ppm (J_{H-P} = 7.2 Hz) coupled to the phosphine and assigned to the O═C*H* proton. Although the downfield shift of the O═C*H* signal may suggest the η^1-coordination of benzaldehyde, the large value of J_{H-P} is more consistent with the η^2-coordination.[42] The observation of a downfield Si*H* signal at 6.83 ppm (1 H) coupled to phosphorus in $^{1}H-^{31}P$ HSQC suggests the formation of a silanimine complex bearing a coordinated benzaldehyde, (ArN═)Mo(PMe_3)(η^2-ArN═SiHPh)(η^2-O═CHPh)

Scheme 9. Reaction of 3 with Benzaldehyde and Formation of Complex 16



(**15**, Scheme 9), which is also in accord with the observation of large Si−H coupling (241.4 Hz) indicative of the increased silicon s-character in the Si−H bond.

As for the acetone adduct **13**, the reaction of (ArN═)$_2$-Mo(PMe_3)$_3$ with benzaldehyde gives the η^2-carbonyl adduct (ArN═)$_2$Mo(η^2-O═CHPh)(PMe_3) (**16**) characterized by the typical upfield O═C*H* signal at 5.69 ppm in its ^{1}H NMR spectrum.[39]

Treatment of complex **16** with excess $PhSiH_3$ regenerates the silylamide **3** (Scheme 9), accompanied by the release of hydrosilylation products $PhH_2Si(OBn)$ and $PhHSi(OBn)_2$. However, the formation of the silanimine/aldehyde adduct **15** in the reaction of **3** with benzaldehyde suggests that the active catalyst in hydrosilylation of carbonyls can be formed after silane elimination from **3** but before the silylene extrusion from (ArN═)Mo(η^2-ArN═SiHPh)(PMe_3) (**8**). In order to verify this assumption, the acetophenone adduct **14** was tested in catalytic hydrosilylation of acetophenone with $PhSiH_3$. A much slower conversion (35% after 20 days, TON = 38) than in the case of **3** (100% after 20 days, TON = 107) was observed when the same conditions were applied (room temperature and catalyst load 1.0 mol %). This observation shows that bis(imido)/carbonyl adducts akin to **13**, **14**, and **16** are not involved in the actual catalytic cycle of carbonyl hydrosilylation mediated by the silylamide **3**.

Reactions of 3 with Alkenes. Reactions of complex **3** with olefins lead to products of Si_{ag}−C coupling, containing only one classical Si−H group. Thus, a reaction of **3** with excess ethylene cleanly affords the ethyl/vinylsilyl derivative (ArN═)Mo(Et)-(PMe_3)(η^3-NAr-SiHPh-CH═CH_2) (**17**, Scheme 10) characterized by spectroscopic methods (IR and multinuclear NMR) and by X-ray diffraction.[16] The ^{1}H NMR spectrum of **17** exhibits a

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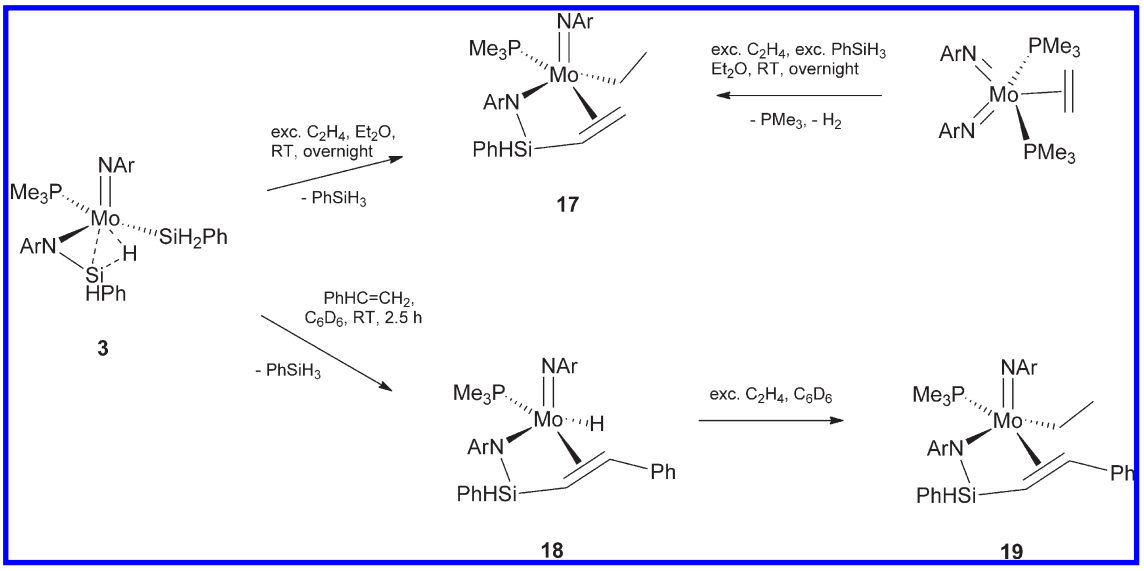
Scheme 10. Reactions of Complex 3 with Ethylene and Styrene



downfield singlet for the Si*H* proton at 6.48 ppm coupled in ^{1}H−^{29}Si HSQC to the ^{29}Si signal at −28.2 ppm. The observation of a doublet for the silicon signal in the ^{29}Si INEPT+ NMR spectrum and the large $^{1}J_{\mathrm{Si-H}}$ of 207.8 Hz evidence the presence of only a classical Si*H* proton, which is further supported by the characteristic Si−H stretch at 2105 cm^{-1} in IR. Also, the absence of a Si*H*/^{31}P correlation in ^{1}H−^{31}P HSQC speaks against the agostic bonding NSi−H···Mo. The coordination of the vinyl moiety to Mo results in the appearance of three C*H* signals of equal intensity at 2.95 (dd, $^{3}J_{\mathrm{H-H}}$ = 13.0, 15.6 Hz), 4.09 (m, obscured by a signal from the ^{i}Pr group of NAr), and 4.30 ppm (dd, $^{3}J_{\mathrm{H-H}}$ = 3.9, 13.0 Hz) in the ^{1}H NMR spectrum. The upfield shift of these C*H* resonances in ^{1}H NMR and the presence of a cross-peak in ^{1}H−^{31}P HSQC, as well as significant upfield shift of vinyl resonances in the ^{13}C NMR spectrum (49.9 and 75.4 ppm, coupled to ^{31}P with $^{2}J_{\mathrm{C-P}}$ = 4.7 and 13.2 Hz, respectively), point to the formation of an η^2-olefin adduct. The structure of complex **17** was also confirmed by X-ray diffraction analysis described previously in a preliminary communication.[16]

Compound **17** is also produced when the ethylene complex (ArN=)$_2$Mo(η^2-CH$_2$=CH$_2$)(PMe$_3$)$_2$[43] reacts with excess PhSiH$_3$ under the atmosphere of ethylene. This reaction is of interest as it presents an example of two tandem steps in the possible multicomponent coupling shown in Scheme 1. In the absence of olefin, complex (ArN=)$_2$Mo(η^2-CH$_2$=CH$_2$)-(PMe$_3$)$_2$ reacts with PhSiH$_3$ (2 equiv) in the presence of BPh$_3$ to give the agostic complex **3** and 1 equiv of ethylene, suggesting that the Si−C coupling follows the initial Si−N coupling.

In contrast to ethylene, the reaction of **3** with styrene stops at the hydrido vinylsilyl complex (ArN=)Mo(H)(PMe$_3$)(η^3-NAr-SiHPh-CH=CHPh) (**18**, Scheme 10). No styrene insertion into the Mo−H bond occurs even when excess styrene is used. In the IR spectrum of **18**, the Mo−H and Si−H hydrides give rise to bands at 1812 and 2098 cm^{-1}, respectively. Their presence is further supported by the observation of a downfield ^{1}H NMR signal at 3.05 ppm (d, $^{2}J_{\mathrm{H-P}}$ = 43.2 Hz) for Mo*H* and a downfield Si*H* signal at 6.15 ppm (d, $J_{\mathrm{H-P}}$ = 6.6 Hz). The latter signal correlates in ^{1}H−^{29}Si HSQC with the ^{29}Si resonance at −8.2 ppm. ^{29}Si INEPT+ shows a large value of $^{1}J_{\mathrm{S-H}}$ = 197.9 Hz, suggesting that the Si−H bond is not coordinated to molybdenum. This conclusion is, however, compromised by the coupling of the Si*H* signal to phosphine ($J_{\mathrm{H-P}}$ = 6.6 Hz) in ^{1}H NMR which is too large for a four-bond separation. We tentatively assign this coupling to the through-space coupling. Similarly to **17**, the ^{1}H NMR data support the η^2-coordination of the vinyl ligand [CH=CHPh]. The bonding between the silicon atom and the vinyl carbon in **18** was established by ^{1}H−^{13}C HMBC, which revealed coupling between the Si*H* proton and the vinyl carbon. The ^{1}H−^{13}C HMBC also established the positioning of the phenyl substituent of the vinyl group at the β-carbon relative to silicon, which is likely caused by the steric repulsions from the Ph substituent in the silyl group.

The reaction of **3** with 1-hexene goes via the same Si$_{ag}$−C coupling route; however, the formation of a mixture of isomers for the vinylsilyl derivative as well as the concurrent isomerization of 1-hexene to 2-hexene and its subsequent reaction with **3** hampered the isolation and in-depth characterization of the products.

Analogous coupling with alkenes has been previously observed by Berry et al. for the silanimine complex Cp$_2$Zr-(η^2-^{t}BuN=SiMe$_2$)(PMe$_3$) (**1**).[14a,b] Taking into account that the reaction of **3** with olefins is accompanied by the release of 1 equiv of PhSiH$_3$, the formation of a silanimine intermediate (ArN=)Mo(η^2-ArN=SiHPh)(PMe$_3$) (**8**) in this process is a reasonable mechanistic suggestion (Scheme 11). Coupling of this electron-deficient intermediate with olefins followed by β-C−H bond activation in the formed CH$_2$CHR moiety would give a hydrido vinylsilylamido derivative, which is the final product in the case of substituted olefins (styrene and hexane). However, for ethylene the hydride complex reacts further to give the ethyl derivative **17** (Scheme 11). A similar insertion of ethylene into the Mo−H bond of **18** to give the ethyl derivative (ArN=)Mo(Et)(PMe$_3$)(η^3-NAr-SiHPh-CH=CHPh) (**19**, Scheme 10) is observed when a C$_6$D$_6$ solution of compound **18** is treated with ethylene in an NMR tube at room temperature. The ethylene insertion

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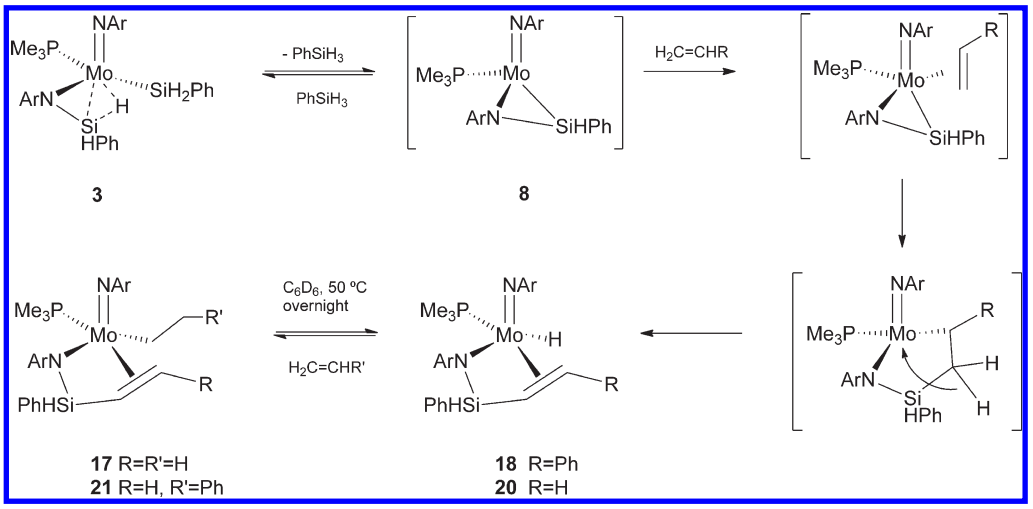
Scheme 11. Suggested Mechanism of the Reaction of Complex 3 with Olefins



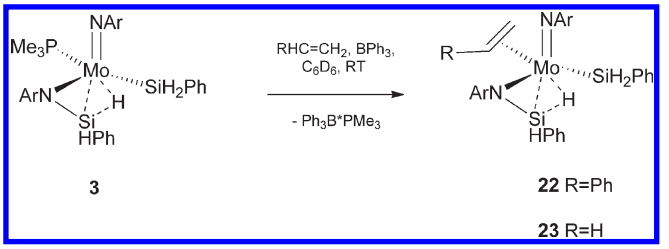
is reversible because heating the C_6D_6 solution of **17** at 50 °C overnight results in slow evolution of ethylene and production of the hydride derivative (ArN═)(H)(PMe_3)Mo-(η^3-NAr-SiHPh-CH═CH_2) (**20**) in 40% yield (by integration of the ^{31}P NMR spectrum), which is similar to compound **18**. The olefin insertion reaction is very sensitive to sterics: while the styrene derivative **18** does not add a second equivalent of styrene, the ethylene hydride derivative **20** inserts styrene to give the 2-phenylethyl complex (ArN═)Mo-(CH_2CH_2Ph)(PMe_3)(η^3-NAr-SiHPh-CH═CH_2) (**21**).

The hydride derivative **20** was independently synthesized in 66% yield by a preparative-scale reaction between the ethyl complex **17** and $PhSiH_3$ (*vide infra*) in the presence of a stoichiometric amount of PMe_3. The ^{1}H NMR spectrum of **20** is similar to that of its ethyl analogue **17**, except for the replacement of the ethyl signals with the hydride signal at 2.69 ppm (d, $^2J_{H-P}$ = 41.7 Hz). The IR spectrum shows two characteristic bands at 2098 and 1796 cm^{-1}, assigned to the Si−H and Mo−H stretches, respectively.

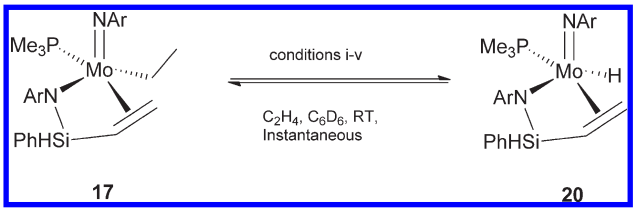
The Si_{ag}−C coupling in reactions of **3** with olefins (styrene and ethylene) can be suppressed by the addition of 1 equiv of BPh_3. In this case, the process goes via the abstraction of the PMe_3 ligand and formation of labile η^2-alkene silylamido agostic complexes, (ArN═)Mo(SiH_2Ph)(η^3-NAr-SiHPh-H)-(η^2-CH_2═CHR) (R = Ph (**22**), H (**23**); Scheme 12). Unfortunately, all attempts at isolation of compounds **22** and **23** were unsuccessful because of their instability. Nevertheless, the connectivity of **22** and **23** was reliably established by NMR and IR spectroscopy, which indicate the presence of classical and agostic silyl groups as well as the η^2-coordination of the alkene ligand (see Experimental Section). The position of the olefin ligand *trans* to the Si−H···Mo unit is suggested by analogy with the structure of the related phosphine derivative (ArN═)Mo-(SiH_2Ph)(PMe_3)(η^3-NAr-SiHPh-H) (**3**). Furthermore, addition of 1 equiv of phosphine to **22** selectively recovers the starting compound **3** with the release of a molecule of olefin, which then reacts further to give (ArN═)Mo(H)(PMe_3)(η^3-NAr-SiHPh-CH═CHPh) (**18**).

Reactions of 17 with Hydrosilanes and H_2. Reaction of complex **17** with a 20-fold excess of $PhSiH_3$ at room temperature for 2 days results in 17% conversion into the hydride **20**,

Scheme 12. Reactions of 3 with Olefins in the Presence of BPh_3



Scheme 13. Thermal Stability of 17 and Its Reactions with Hydrosilanes and H_2[a]



[a] Conditions: (i)C_6D_6, 50 °C, 40% yield by NMR; (ii) 20 $PhSiH_3$, C_6D_6, RT, 2 days, 17% yield by NMR; (iii) 1.2 $PhSiH_3$, PMe_3, toluene, 50 °C, overnight, 66%; (iv) $PhMe_2SiH$, PMe_3, C_6D_6, 50 °C, overnight, 50%; (v) 1.5 atm H_2, C_6D_6, 50 °C, 36 h, 50% yield by NMR.

accompanied by the evolution of $PhEtSiH_2$.[44] Complete conversion with selective production of **20** can be achieved upon the treatment of **17** with $PhSiH_3$, H_2, or $PhMeSiH_2$ at 50 °C overnight, accompanied by the release of $PhEtSiH_2$, ethane, or PhMeEtSiH, respectively (Scheme 13).

The mechanism of the reaction of **17** with hydrosilanes was investigated by means of D-labeling and kinetic NMR studies. Treatment of **17** with $PhSiD_3$ at 50 °C affords exclusively (ArN═)Mo(D)(PMe_3)(η^3-NAr-SiHPh-CH═CH_2) (**20$_D$**) and $PhEtSiD_2$, indicating that the hydride in **20** comes from the silane, not from the β-C−H activation of the ethyl ligand in **17**. Our initial mechanistic rationalization of these reactions was that

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they proceed via phosphine dissociation followed by a σ-bond metathesis or oxidative addition of the E−H bond (E = Si or H). To our surprise, the addition of 1 equiv of PMe_3 to a mixture of **17** and silane significantly increases the rate of the reaction. This fact suggests that the transformation of complex **17** into **20** does not necessarily involve phosphine dissociation in the first step. Instead, the reactivity of **17** could be related to the dissociation of the vinyl fragment.

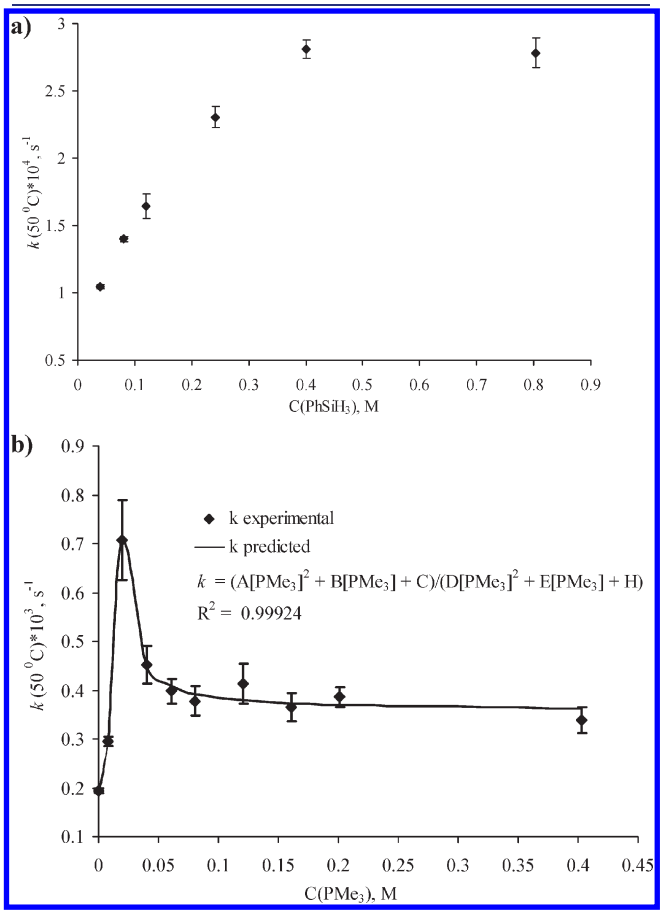


Figure 6. Dependence of the rate constant of the reaction of **17** with $PhSiH_3$ (10 equiv of $PhSiH_3$) at 50 °C on (a) the concentration of $PhSiH_3$ and (b) the concentration of PMe_3.

To get more insight into the mechanism of formation of hydride **20**, kinetic studies of the reaction of **17** with $PhSiH_3$ at 50 °C were performed. At large silane concentrations, the reaction obeys pseudo-first-order kinetics (k_{eff}(50 °C) = (2.8 ± 0.1) × 10^{-4} s^{-1}, Figure 6a), consistent with the rate-limiting dissociation of either the PMe_3 or the vinyl part of η^3-NArSiHPhCH=CH_2, followed by fast addition of $PhSiH_3$. At the same time, the dependence of the reaction rate in the pseudo-first-order regime (10-fold excess $PhSiH_3$) on the concentration of phosphine proved to be more complicated (Figure 6b), suggesting the occurrence of several pathways.

A possible mechanism consistent with the dependence of k_{eff} on the PMe_3 concentration is shown in Scheme 14. This mechanism includes two competing rate-determining steps. Route A starts with PMe_3-assisted vinyl dissociation. The competing route B involves the dissociation of PMe_3. In both cases, the hydride complex **20** is furnished after a σ-bond metathesis between $PhSiH_3$ and the ethyl group. The alternative oxidative addition of silane cannot be excluded but is less likely, as it would require a Mo(VI) intermediate.[45] Assuming steady-state conditions for reactive intermediates of Scheme 14, the rate of consumption of compound **17** can be expressed as

$$-\frac{d[17]}{dt} = \frac{k_1k_3k_5k_7[PhSiH_3][PMe_3]^2 + (k_1k_3k_5k_8[PhSiH_3] + k_2k_4k_6k_8)[PhSiH_3][PMe_3] + (k_2k_5k_6k_8 + k_3k_5k_6k_8)[PhSiH_3]^2}{k_2k_4k_7[PMe_3]^2 + (k_2k_5k_7 + k_3k_5k_7 + k_3k_4k_8)[PhSiH_3][PMe_3] + (k_2k_5k_8 + k_3k_5k_8)[PhSiH_3]^2} \quad [17]$$

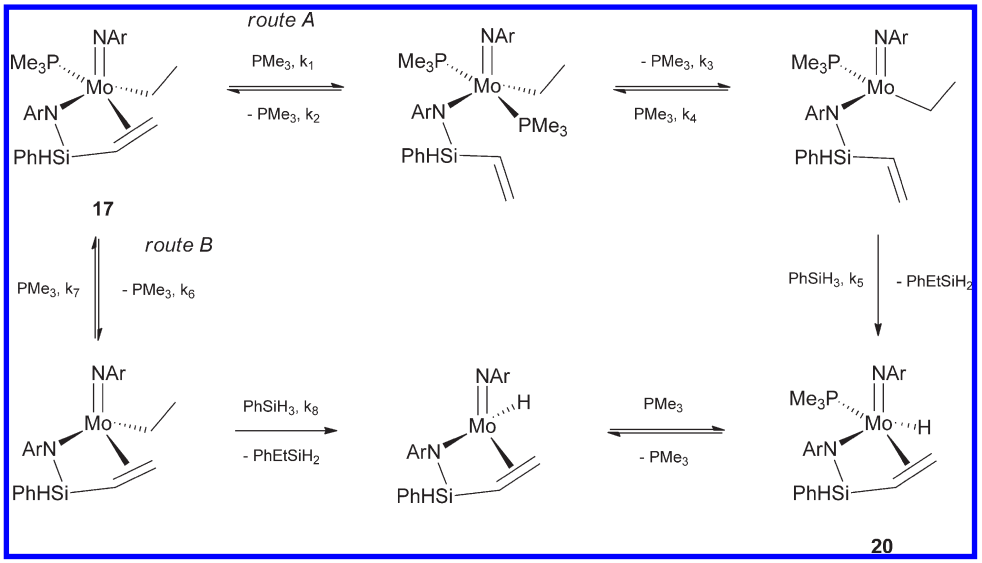
$k_1k_3k_5k_7[PhSiH_3] = \mathbf{A}$
$(k_1k_3k_5k_8[PhSiH_3] + k_2k_4k_6k_8)[PhSiH_3] = \mathbf{B}$
$(k_2k_5k_6k_8 + k_3k_5k_6k_8)[PhSiH_3]^2 = \mathbf{C}$
$k_2k_4k_7 = \mathbf{D}$
$(k_2k_5k_7 + k_3k_5k_7 + k_2k_4k_8)[PhSiH_3] = \mathbf{E}$
$(k_2k_5k_8 + k_3k_5k_8)[PhSiH_3]^2 = \mathbf{H}$

$$-\frac{d[17]}{dt} = \frac{\mathbf{A}[PMe_3]^2 + \mathbf{B}[PMe_3] + \mathbf{C}}{\mathbf{D}[PMe_3]^2 + \mathbf{E}[PMe_3] + \mathbf{H}} \quad [17]$$

$$k_{eff} = \frac{\mathbf{A}[PMe_3]^2 + \mathbf{B}[PMe_3] + \mathbf{C}}{\mathbf{D}[PMe_3]^2 + \mathbf{E}[PMe_3] + \mathbf{H}}$$

At large $PhSiH_3$ concentrations (the pseudo-first-order regime), when the members A, B, C, E, and H can be considered constant,

Scheme 14. Proposed Mechanism of the Reaction of 17 with $PhSiH_3$ in the Presence of PMe_3



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the function $k_{eff}([PMe_3])$ fits perfectly the experimental data (Figure 6b).

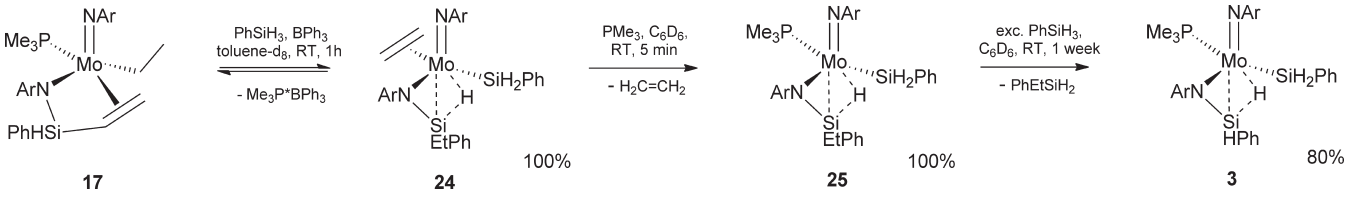
Abstraction of phosphine from **17** with BPh_3 in the presence of $PhSiH_3$ results in the formation of an agostic silylamide (ArN═)Mo(SiH_2Ph)(η^3-NAr-Si(Et)Ph-H)(η^2-CH_2═CH_2) (**24**, Scheme 15) having an ethyl substituent at silicon. A similar reaction (in NMR tube) with the labeled silane $PhSiD_3$ affords complex (ArN═)Mo(SiD_2Ph)(η^3-NAr-Si(Et_D)Ph-H)(η^2-CH_2═CH_2) (**24$_D$**), showing exclusive deuterium scrambling in the ethyl but not the agostic Si*H* position. This proves that the SiEtPhH fragment in **24** stems from hydrogenation of the (vinyl)silyl fragment in **17** rather than from coupling of $PhSiH_3$ with the ethyl ligand and subsequent reaction of $PhEtSiH_2$ with the imido ligand. Like for the related olefin adducts **22** and **23**, complex **24** eluded isolation, presumably because of dissociation of the loosely coordinated ethylene under vacuum.

The connectivity of **24** was established by NMR and IR spectroscopy. At −53 °C, ^{1}H NMR reveals the presence of three nonequivalent Si*H* signals at 6.07 and 5.75 ppm for the two diastereotopic protons of the SiH_2Ph ligand and at 4.99 ppm for the agostic Si*H* proton. The coordination of ethylene to Mo results in four broad upfield resonances at 3.42, 3.24, 3.13, and 1.84 ppm, coupled in ^{1}H−^{13}C HSQC to the upfield ^{13}C signals at 44.0 and 51.2 ppm. The presence of the NSi−H···Mo agostic bonding is supported by the ^{29}Si INEPT+ spectrum showing two silicon resonances, at 0.9 ppm (dd, $^1J_{Si-H}$ = 173.0, 163.4 Hz) for the classical SiH_2Ph ligand and at −64.4 ppm (d, $^1J_{Si-H}$ = 107.3 Hz) for the agostic Si(Et)PhH group. Such a coordination of the Si−H bond to Mo results in a red-shift of the Si−H_{ag} band to 1772 cm^{-1} in the IR specrum,[18] which also shows a normal Si−H stretch (2077 cm^{-1}) for the classical SiH_2Ph ligand. The lower $^1J_{Si-H_{ag}}$ in **24** than in **3** (107.3 vs 113.0 Hz) indicates more advanced Si−H activation in the former. Unlike **3**, no exchange of **24** with $PhSiH_3$ was observed by ^{1}H−^{1}H EXSY at room temperature, which can be attributed to a stronger NSiH···Mo bond in **24**.

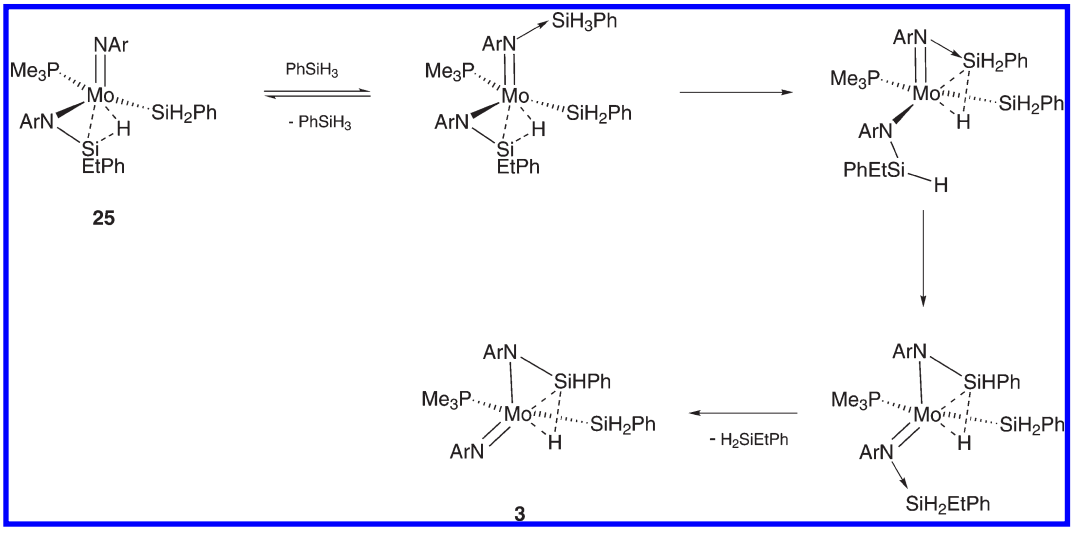
Addition of 1 equiv of PMe_3 to the compound **24** results in an almost instantaneous release of 1 equiv of ethylene and formation of agostic complex (ArN═)Mo(SiH_2Ph)(PMe_3)(η^3-NAr-Si(Et)Ph-H) (**25**). **25** is formed as a mixture of two diastereomers (2:1, according to ^{31}P{^{1}H} NMR) due to the chirality of the agostic silicon and molybdenum centers (Scheme 15). The NMR and IR features of **25** are similar to those for the related agostic complexes **3** and **24**. Like **24**, the $^1J_{Si-H_{ag}}$ for both diastereomers of **25** (105.4 and 107.1 Hz) is slightly reduced in comparison with that for **3** ($^1J_{Si-H_{ag}}$ = 113.0 Hz).

Analogously to the ethylene adduct **24**, the ^{1}H−^{1}H EXSY did not reveal any exchange between **25** and excess $PhSiH_3$ (*vide infra*). Given the fact that the Si−H bond in **24** and **25** is a bit more activated than in **3** (see the $^1J_{Si-H_{ag}}$ values discussed above), this fact supports further our conclusion that the main exchange pathway involves the opening of the agostic Mo···HSi bond rather than oxidative addition of this Si−H agostic bond to metal (see pathway a versus b in Scheme 5). However, we cannot exclude entirely that the difference between complex **3** and

Scheme 15. Formation and Reactivity of Complexes 24 and 25



Scheme 16. Suggested Mechanism for the Reaction of 25 with Excess $PhSiH_3$



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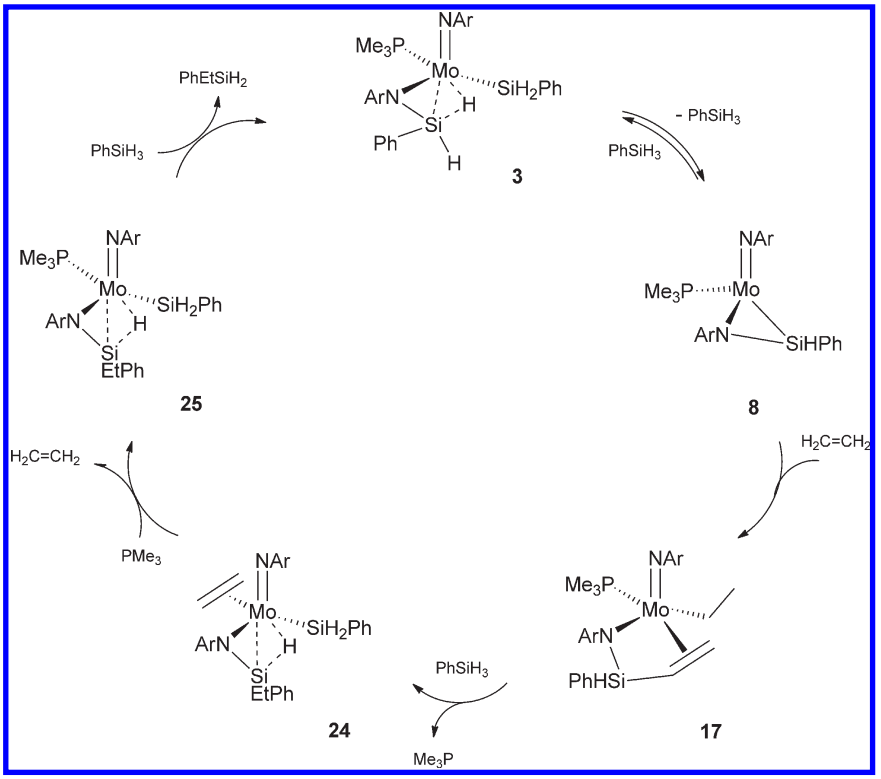
complexes **24** and **25** toward the exchange with free silane is caused by steric factors.

Leaving a mixture of **25** and $PhSiH_3$ for 1 week at room temperature leads to slow conversion of **25** into the silylamide **3**, accompanied by the release of $PhEtSiH_2$ (Scheme 15). A similar observation has been made for the reaction of the hydride derivative **20** with an excess of $PhSiH_3$. For both processes, the evolution of ethylphenylsilane suggests a pathway involving the cleavage of the N−Si bond of the silylamide ligand η^3-NAr-Si(R)Ph-H, which was also supported by a labeling experiment. When compound **25** was reacted with (*m*-Tol)SiH_3, the first process observed was an exchange between (*m*-Tol)SiH_3 and the SiH_2Ph group, followed by a slow release of $PhEtSiH_2$ and formation of complex $\mathbf{3_{tol}}$, in which the tolyl group is scrambled over two possible silicon positions (established by a $^1H-^{13}C$ HMBC experiment). Furthermore, the treatment of **25** with $PhSiD_3$ gives selectively PhEtSiHD and $\mathbf{3d_4}$. These observations suggest a plausible mechanism for the reaction of **25** with phenylsilane (Scheme 16) based on coordination of the external silane to the imido group of **25** to give a "new" silylamido ligand and elimination of $PhEtSiH_2$ from the "old" silylamide. A similar pathway has been previously suggested by Tilley et al. for the silyl/silane exchange in a silylamido/imido complex of tantalum.[46] Taking into account the stoichiometric coupling of the agostic compound **3** with alkenes and nitriles (*vide supra*), such a noninnocent behavior of the imido ligand toward hydrosilanes[15,46] may be pertinent to the catalytic cycle of hydrosilylation reactions mediated by complex **3**.

CONCLUSIONS

This study shows that SiH···M agostic complexes are not merely a laboratory curiosity but can be precursors and/or intermediates in metal-mediated transformation of organic substrates. We are interested in developing metal-catalyzed multicomponent coupling of silanes with unsaturated molecules. In this work, we accomplished several steps of such a multicomponent coupling, including one case of tandem Si−N and Si−C couplings. The reaction is believed to start with silane addition to the imido ligand, exemplified by the formation of silyl amides **3** and **5**. The observation of hydride decomposition products $\{\eta^3$-SiH(Ph)-N(Ar)-SiHPh-H···$\}MoH_3(PMe_3)_3$ (**4**) and $\{\eta^3$-SiH(Ph)-N(Ar′)-SiHPh-H···$\}MoH_3(PMe_3)_3$ (**6**) in reactions of $(R'N{=})_2Mo(PMe_3)_3$ with $PhSiH_3$ proves our notion that the silylamide moiety can be, in principle, detached from the metal, which will be the final, but yet unachieved, step of the proposed multicomponent coupling. Investigation of stoichiometric reactions of **3** with nitriles and olefins led to the discovery of unusual Si−C couplings. Mechanistic studies suggest that these reactions involve silanimine intermediates, and indeed we managed to observe some of these species by NMR. The Si−C bond formation could be the second step in the proposed multicomponent coupling, but also it could be a step in the hydrosilylation reactions catalyzed by **3**. The latter can be particularly pertinent to the hydrosilylation of olefins, for which the whole catalytic cycle was modeled by stoichiometric reactions. The mechanistic picture that emerged is unusual because it does not involve the commonly invoked steps of olefin coordination to metal and migratory insertions into the M−H or M−Si bonds.[2a,47] Rather, the vinylsilyl derivatives (ArN=)Mo(X)(PMe_3)

Scheme 17. Possible Catalytic Cycle for the Hydrosilylation of Ethylene by $PhSiH_3$ Mediated by 3



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(η^3-NAr-SiHPh-CH=CH_2) (X = H, Alk; **17**−**21**) are formed which undergo hydrogenation of the vinyl moiety by silane to give agostic species, exemplified by the formation of agostic complexes (ArN=)Mo(SiH_2Ph)(η^3-NAr-Si(Et)Ph-H)(L) (L = η^2-CH_2=CH_2 or PMe_3). The final step in the possible catalytic hydrosilylation cycle is the detachment of the silyl product which occurs by means of silyl group exchange (Scheme 17). Although detailed mechanistic evidence on the latter reaction is still missing, we believe that it happens via the attack by $PhSiH_3$ on the imido group to give a bis(silylamido) intermediate, followed by hydride shift and elimination of silane. Agostic interactions play the major role in stabilizing the unsaturated intermediates throughout the cycle. The detachment of vinylsilylamido groups from metal in species like **17**−**21** will be the culminating point of multicomponent coupling, which we continue to pursue.

EXPERIMENTAL SECTION

All manipulations were carried out using conventional inert atmosphere glovebox and Schlenk techniques. Dry diethyl ether, toluene, hexanes, and acetonitrile were obtained using Innovative Technology solvent purification columns; other solvents were dried by distillation over appropriate drying agents. C_6D_6 and PhMe-d_8 were dried by distillation over the K/Na alloy. NMR spectra were obtained with a Bruker DPX-300 and Bruker DPX-600 instruments (^{1}H, 300 and 600 MHz; ^{2}D, 92.1 MHz; ^{13}C, 75.5 and 151 MHz; ^{29}Si, 59.6 and 119.2 MHz; ^{31}P, 121.5 and 243 MHz; ^{11}B, 96.3 and 192.6 MHz). IR spectra were measured on an ATI Mattson FTIR spectrometer. Elemental analyses were performed by the ANALEST laboratory (University of Toronto). $PhSiCl_3$, $(EtO)_3SiH$, $SiMe_4$, $SiCl_4$, $PhMeSiCl_2$, PMe_3, BPh_3, and (*m*-Tol)MgCl were purchased from Aldrich. $PhSiH_3$ and $PhSiD_3$ were prepared by the reduction of $PhSiCl_3$ with $LiAlH_4$ and $LiAlD_4$, respectively. (*m*-Tol)SiH_3 was prepared by the reaction of $SiCl_4$ with *m*-TolMgCl, followed by reduction with $LiAlH_4$.[48] Organic substrates (benzaldehyde, acetophenone, acetone, 1-hexene, cyclohexene, ethylene, styrene, benzonitrile, acetonitrile, ^{i}PrCN, ^{t}BuCN, 1-octyne, phenylacetylene, 3-hexyne, ethanol, and propanol-2) were purchased from Sigma-Aldrich and used without further purification. Preparation of the triphosphine complexes (RN=)$_2$Mo(PMe_3)$_3$ (R = Ar, Ar′) was reported previously.[15b] (ArN=)$_2$Mo(η^2-C_2H_4)(PMe_3)$_2$ was synthesized using a literature procedure.[43] All catalytic and NMR-scale reactions, as well as kinetic experiments, were done under nitrogen atmosphere using NMR tubes equipped with Teflon valves. The structures and yields of all hydrosilylated and hydrogenated products were determined by NMR analysis using tetramethylsilane as an internal standard. NMR analysis was performed at room temperature unless stated otherwise.

NMR-Scale Reaction of (ArN=)$_2$Mo(PMe_3)$_3$ with $PhSiH_3$. *A. Ambient-Temperature Reaction.* $PhSiH_3$ (8.0 μL, 0.063 mmol) was added to a solution of (ArN=)$_2$Mo(PMe_3)$_3$ (42.5 mg, 0.063 mmol) in 0.6 mL of C_6D_6 in an NMR tube. NMR analysis revealed immediate formation of a 1:1 mixture of the starting material and a highly fluxional silyl complex (assigned to (ArN=)Mo(SiH_2Ph)(PMe_3)(η^3-N(Ar)-SiHPh-H) (**3**) on the basis of low-temperature NMR-scale reaction (see below)). The reaction mixture was left at room temperature for 6 days. NMR spectra showed the formation of a difficult-to-separate mixture of the starting material and polyhydride products: {η^3-SiH-(Ph)-N(Ar)-SiHPh-H···}MoH_3(PMe_3)$_3$ (**4**, 48%) and unidentified hydride species (21%). The ^{1}H NMR analysis also revealed the presence of Ph_2SiH_2, Ph_3SiH, and SiH_4. Further addition of excess $PhSiH_3$ (10.0 μL, 0.081 mmol) overnight at room temperature leads to increased amounts of Ph_2SiH_2, Ph_3SiH, and SiH_4.

4. ^{1}H NMR (600 MHz; toluene-d_8; −46 °C; δ, ppm): 8.90 (bs, 2H, *o-H*, Si*Ph*), 8.47 (bs, 2H, *o-H*, Si*Ph*), 6.84−7.35 (m, 9H, *m-H* and *p-H* of Si*Ph* and *m-H* and *p-H* of *Ar*N), 5.63 (bs, 1H, Si*H*Ph), 5.22 (bs, 1H, Si*H*Ph), 3.92 (bs, 2H, 2 *CH*, *Ar*N), 1.73 (bs, 12H, 4 CH_3, *Ar*N), 1.32 (bs, 9H, PMe_3), 1.08 (bs, 9H, PMe_3), 0.73 (bs, 9H, PMe_3), −5.61 (d, $^2J_{H-P}$ = 53.4 Hz, 1H, Mo-*H*), −6.58 (t, $^2J_{H-P}$ = 36.0 Hz, 1H, Mo-*H*), −8.82 (d, $^2J_{H-P}$ = 19.2 Hz, 1H, Mo-*H*); agostic Si*H* signal was not observed. ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): −7.7 (s, 3 PMe_3). ^{31}P{^{1}H} NMR (243 MHz; toluene-d_8; −45 °C; δ, ppm): −8.8 (t, $^2J_{P-P}$ = 40.0 Hz, PMe_3), −6.6 (dd, $^2J_{P-P}$ = 21.9 Hz, $^2J_{P-P}$ = 40.0 Hz, PMe_3), 3.7 (dd, $^2J_{P-P}$ = 21.9 Hz, $^2J_{P-P}$ = 40.0 Hz, PMe_3). ^{29}Si{^{1}H} NMR (119.2 MHz; toluene-d_8; δ, ppm): −14.2 (s, *Si*HPh), 51.3 (s, *Si*HPh).

B. Low-Temperature Reaction. $PhSiH_3$ (8.0 μL, 0.063 mmol) was added to a solution of (ArN=)$_2$Mo(PMe_3)$_3$ (42.5 mg, 0.063 mmol) in 0.6 mL of toluene-d_8 frozen in liquid N_2 in an NMR tube. The sample was immediately placed in an NMR instrument precooled to −30 °C. The temperature was dropped to −60 °C and then gradually increased with monitoring of the reaction by ^{1}H and ^{31}P{^{1}H} NMR. At −30 °C, the release of 2 equiv of PMe_3 and selective formation of **3** at 50% conversion of the starting material was observed. Increasing temperature leads to decomposition of **3** to a mixture of **4** and unidentified polyhydride species, the same as observed in the room-temperature experiment described above. See the preparation and full characterization of complex **3** below.

Preparation of (ArN=)Mo(SiH_2Ph)(PMe_3)(η^3-N(Ar)-SiHPh-H) (3). $PhSiH_3$ (0.37 mL, 3.0 mmol) was added to a solution of (ArN=)$_2$Mo(PMe_3)$_3$ (1.01 g, 1.5 mmol) in 100 mL of hexane at room temperature. The color of the reaction mixture turned from dark-green to brown, and the formation of a brown precipitate was observed. The mixture was stirred vigorously under N_2 purging at room temperature for 30 min, concentrated, and left at −30 °C overnight. More crystalline brown precipitate formed. The precipitate was filtered off, washed with cold hexanes (10 mL), and dried under vacuum to give a fine brown powder of **3** as a mixture of two diastereomers (>95/5). Yield: 0.7 g, 77%. The product is fluxional at room temperature. Due to the low content of the minor isomer, only spectroscopic data for the major isomer are presented. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 0.36 (bs, 3H, CH_3, ArN), 1.04 (d, $^2J_{H-P}$ = 8.4 Hz, 9H, PMe_3), 1.14 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, ArN), 1.18 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, 2CH_3, ArN), 1.23 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, ArN), 1.27 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, 2CH_3, ArN), 1.34 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, ArN), 2.71 (sept, $^3J_{H-H}$ = 6.6 Hz, 1H, *CH*, ArN), 3.46 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, *CH*, ArN), 4.04 (sept, $^3J_{H-H}$ = 6.6 Hz, 2H, 2*CH*, ArN), 4.30 (bs, 1H, ArN-Si-H_{ag}), 5.57 (s, 1H, Mo-Si-*H*), 5.78 (bs, 1H, ArN-Si-H_{term}), 5.94 (s, 1H, Mo-Si-*H*), 6.91−6.94 and 6.99−7.24 (m, 8H, *m-H* and *p-H* of NAr, and *p-H* of Si-Ph), 6.96 (t, $^3J_{H-H}$ = 7.1 Hz, 2H, *m-H*, Si-Ph), 7.32 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *m-H*, Si-Ph), 7.43 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o-H*, Si-Ph), 8.31 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o-H*, Si-Ph). ^{1}H NMR (600 MHz; toluene-d_8; δ, ppm): 0.30 (bs, 3H, CH_3, ArN), 1.05 (d, $^2J_{H-P}$ = 8.4 Hz, 9H, PMe_3), 1.12 (bs, 3H, CH_3, ArN), 1.17 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, 2CH_3, ArN), 1.20 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, ArN), 1.27 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, 2CH_3, ArN), 1.35 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, ArN), 2.68 (sept, $^3J_{H-H}$ = 6.6 Hz, 1H, *CH*, ArN), 3.47 (bs, 1H, *CH*, ArN), 4.01 (sept, $^3J_{H-H}$ = 6.6 Hz, 2H, 2*CH*, ArN), 4.25 (bs, 1H, ArN-Si-*H*, agostic), 5.46 (s, 1H, Mo-Si-*H*), 5.75 (bs, 1H, ArN-Si-*H*, terminal), 5.84 (s, 1H, Mo-Si-*H*), 6.86−6.95 and 6.96−7.03 and 7.13 (m, 6H, *m-H* and *p-H*, NAr), 6.95 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *m-H*, Si-Ph), 7.06 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p-H*, Si-Ph), 7.22 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p-H*, Si-Ph), 7.29 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *m-H*, Si-Ph), 7.40 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o-H*, Si-Ph), 8.22 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o-H*, Si-Ph). ^{1}H NMR (600 MHz; toluene-d_8; −50 °C; δ, ppm): 0.15 (bs, 3H, CH_3, ArN), 0.962 (d, $^2J_{H-P}$ = 8.4 Hz, 9H, PMe_3), 1.02 (bs, 3H, CH_3, ArN), 1.16 (bs, 3H, CH_3, ArN), 1.19 (bs, 6H, 2CH_3, ArN), 1.28 (bs, 6H, 2CH_3, ArN), 1.41 (bs, 3H, CH_3, ArN), 2.75 (bs, 1H, *CH*, ArN), 3.52 (bs, 1H, *CH*, ArN), 3.97 (bs, 2H, 2*CH*, ArN), 4.35 (bm, $^2J_{H-H}$ = 5.4 Hz, 1H, ArN-Si-H_{ag}), 5.68 (s, 1H, Mo-Si-*H*), 5.97 (s, 1H, Mo-Si-*H*), 6.03 (bd, $^2J_{H-H}$ = 5.4 Hz, ArN-Si-H_{term}),

6.80−7.02 and 7.06−7.16 (m, 9H, *m-H* and *p-H*, NAr′, and 1 *o-H* and 1 *p-H*, SiPh), 7.28 (bt, $^3J_{H-H}$ = 7.2 Hz, 1H, *p-H*, Si-Ph), 7.37 (bt, $^3J_{H-H}$ = 7.2 Hz, 2H, *o-H*, Si-Ph), 7.40 (bd, $^3J_{H-H}$ = 7.2 Hz, 2H, *m-H*, Si-Ph), 8.49 (bd, $^3J_{H-H}$ = 7.2 Hz, 2H, *m-H*, Si-Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz; C_6D_6; δ, ppm): 10.4 (s, PMe_3). $^{31}P\{^1H\}$ NMR (121.5 MHz; toluene-d_8; δ, ppm): 10.6 (s, PMe_3). ^{31}P NMR (selectively decoupled from methyl groups; 243 MHz; toluene-d_8; δ, ppm): 10.6 (d, $^2J_{H-P}$ = 9.3 Hz, PMe_3). $^{13}C\{^1H\}$ NMR (150.9 MHz; toluene-d_8; δ, ppm): 17.8 (d, $^1J_{C-P}$ = 25.7 Hz, P*Me*$_3$), 22.5 (s, *CH*$_3$, ArN), 23.4 (s, *2CH*$_3$, ArN), 23.5 (s, *CH*$_3$, ArN), 24.1 (s, *2CH*$_3$, ArN), 26.3 (s, *CH*$_3$, ArN), 26.6 (s, *CH*$_3$, ArN), 26.9 (s, *CH*, ArN), 27.8 (s, *CH*, ArN), 28.9 (s, *2CH*, ArN), 122.2 (s, ArN), 122.9 (s, ArN), 123.0 (s, ArN), 123.1 (s, ArN), 125.0 (s, *o-C*, ArN), 126.1 (s, *p-C*, SiPh), 127.4 (s, *p-C*, SiPh), 127.6 (s, *m-C*, SiPh), 127.9 (s, *o-C*, ArN), 128.0 (s, *m-C*, SiPh), 128.2 (s, *o-C*, NAr), 128.8 (s, NAr), 130.6 (s, NAr), 136.0 (s, *o-C*, SiPh), 136.3 (s, *o-C*, SiPh), 136.9 (s, *o-C*, NAr), 140.2 (s, *i-C*, SiPh), 141.4 (s, *i-C*, SiPh), 144.5 (s, *i-C*, NAr), 153.6 (s, *i-C*, NAr). $^{29}Si\{^1H\}$ NMR (119.2 MHz; toluene-d_8; −50 °C; δ, ppm): −72.9 (dd, $^1J_{Si-H}$ = 113.0 Hz, $^1J_{Si-H}$ = 245.3 Hz, ArN-*Si*H$_2$Ph), 1.2 (t, $^1J_{Si-H}$ = 153.5 Hz, Mo-*Si*H$_2$Ph). IR (Nujol): 1694, 2014, 2041, and 2165 cm^{-1}. Elemental analysis (%): calcd for $C_{39}H_{57}MoN_2PSi_2$ (736.968), C 63.56, H 7.80, N 3.80; found, C 62.76, H 7.48, N 3.86.

NMR-Scale Reaction of (Ar′N═)$_2$Mo(PMe$_3$)$_3$ with PhSiH$_3$. *Method A.* $PhSiH_3$ (8.6 μL, 0.07 mmol) was added to a solution of (Ar′N═)$_2$Mo(PMe$_3$)$_3$ (39 mg, 0.07 mmol) in 0.6 mL of C_6D_6 in an NMR tube. NMR analysis of the mixture after 10 min at room temperature established the formation of (Ar′N═)Mo(SiH$_2$Ph)-(PMe$_3$)$_2$(NAr′{SiH$_2$Ph}) (**5**). The mixture was left at room temperature overnight. All volatiles were pumped off; the residue was dried under vacuum and redissolved in fresh C_6D_6. NMR spectra showed the formation of a difficult-to-separate mixture of products: (Ar′N═)Mo(H)$_2$(PMe$_3$)$_2$(η^2-Ar′N═SiHPh) (**7**, 61%), {η^3-PhHSi-N-(Ar′)-SiHPh-H···}MoH$_3$(PMe$_3$)$_3$ (**6**, 12%), and unidentified hydride species (27%). $PhSiH_3$ (5.6 μL, 0.05 mmol) was added to the NMR tube. The mixture was left overnight, showing no further reaction with the silane. Heating the mixture at 100 °C for 1 h leads to decomposition of **7**, disappearance of $PhSiH_3$, and formation of Ph_2SiH_2, Ph_3SiH, and SiH_4. Complex **6** remained unreacted.

Method B. A solution of $PhSiH_3$ (19.6 μL, 0.16 mmol) and BPh_3 (7.7 mg, 0.032 mmol) in 0.6 mL of C_6D_6 was added to (Ar′N═)$_2$-Mo(PMe$_3$)$_3$ (17.9 mg, 0.032 mmol). The reaction mixture was immediately transferred to an NMR tube, and the reaction was monitored by NMR spectroscopy for 24 h, showing the full conversion of the starting material and formation of a difficult-to-separate mixture of complexes **6** (75%), **7** (14%), and unidentified hydride species (11%).

5. ^1H NMR (600 MHz; toluene-d_8; −2 °C; δ, ppm): 8.16 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o-H*, Si*Ph*), 7.46 (d, $^3J_{H-H}$ = 7.4 Hz, 2H, *o-H*, Si*Ph*), 6.83−7.22 (m, 12H, Si*Ph* and *Ar*′N, obscured by toluene signals), 5.93 (s, 2H, Si*H*$_2$Ph), 5.72 (s, 2H, Si*H*$_2$Ph), 2.66 (s, 3H, *CH*$_3$, *Ar*′N), 2.48 (s, 3H, *CH*$_3$, *Ar*′N), 2.38 (s, 3H, *CH*$_3$, *Ar*′N), 2.22 (s, 3H, *CH*$_3$, *Ar*′N), 1.31 (d, $^2J_{H-P}$ = 7.7 Hz, 18H, 2 P*Me*$_3$). ^1H NMR (600 MHz; toluene-d_8; −71 °C; δ, ppm): 8.21 (bs, 2H, *o-H*, Si*Ph*), 7.44 (bm, 8H, *o-H*, *m-H*, and *p-H*, Si*Ph*), 6.98 (bm, 3H, *m-H* and *p-H*, *Ar*′N), 6.02 (bs, 1H, Si*H*$_2$Ph), 5.96 (bs, 1H, Si*H*$_2$Ph), 5.80 (bs, 1H, Si*H*$_2$Ph), 5.71 (bs, 1H, Si*H*$_2$Ph), 2.66 (bs, 3H, *CH*$_3$, *Ar*′N), 2.52 (bs, 3H, *CH*$_3$, *Ar*′N), 2.40 (bs, 3H, *CH*$_3$, *Ar*′N), 2.21 (bs, 3H, *CH*$_3$, *Ar*′N), 1.36 (bs, 9H, P*Me*$_3$), 0.78 (bs, 9H, P*Me*$_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz; C_6D_6; δ, ppm): −13.2 (bs, 2 *P*Me$_3$). $^{31}P\{^1H\}$ NMR (243 MHz; toluene-d_8; 0 °C; δ, ppm): −12.8 (s, 2 *P*Me$_3$). $^{31}P\{^1H\}$ NMR (243 MHz; toluene-d_8; −71 °C; δ, ppm): −9.3 (d, $^2J_{P-P}$ = 199.2 Hz, *P*Me$_3$), −13.6 (d, $^2J_{P-P}$ = 199.2 Hz, *P*Me$_3$). $^1H-^{29}Si$ HSQC NMR (119.2 MHz; toluene-d_8; −71 °C; *J* = 150 Hz; ^{29}Si projection; δ, ppm): 1.3 (Mo-*Si*H$_2$Ph), −32.1 (Ar′N-*Si*H$_2$Ph). $^1H-^{29}Si$ HSQC NMR (119.2 MHz; toluene-d_8; −42 °C; *J* = 150 Hz; ^{29}Si projection; δ, ppm): 1.1 (Mo-*Si*H$_2$Ph), −31.7 (Ar′N-*Si*H$_2$Ph).

6. ^1H NMR (600 MHz; C_6D_6; δ, ppm; selected resonances): −7.08 (bs, Mo*H*$_3$), 0.80 (bs, 18H, 3 P*Me*$_3$), 2.50 (bs, 6H, 2 *CH*$_3$, *Ar*′N), 5.55 (bs, 2H, 2 Si*H*Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz; C_6D_6; δ, ppm): −9.0 (bs, 3 *P*Me$_3$).

7. ^1H NMR (600 MHz; C_6D_6; δ, ppm): −4.76 (ddd, $^2J_{H-P}$ = 45.3 Hz, $^2J_{H-P}$ = 55.3 Hz, $^2J_{H-H}$ = 8.5 Hz, 1H, Mo*H*$_2$), −2.46 (ddd, $^2J_{H-P}$ = 15.3 Hz, $^2J_{H-P}$ = 31.6 Hz, $^2J_{H-H}$ = 8.5 Hz, 1H, Mo*H*$_2$), 0.85 (d, $^2J_{H-P}$ = 7.8 Hz, 9H, P*Me*$_3$), 1.35 (d, $^2J_{H-P}$ = 8.0 Hz, 9H, P*Me*$_3$), 1.80 (s, 3H, *CH*$_3$, *Ar*′N), 2.73 (s, 3H, *CH*$_3$, *Ar*′N), 2.83 (s, 3H, *CH*$_3$, *Ar*′N), 3.13 (s, 3H, *CH*$_3$, *Ar*′N), 6.36 (dd, $^3J_{H-P}$ = 2.3 Hz, $^3J_{H-P}$ = 15.0 Hz, 1H, Si*H*Ph), 7.08 (m, 3H, *m-H* and *p-H*, *Ar*′N), 7.34 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p-H*, Si*Ph*) 7.42 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *m-H*, Si*Ph*), 8.25 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o-H*, Si*Ph*). $^{31}P\{^1H\}$ NMR (121.5 MHz; C_6D_6; δ, ppm): 4.2 (d, $^2J_{P-P}$ = 15.8 Hz, *P*Me$_3$), 8.4 (d, $^2J_{P-P}$ = 15.8 Hz, *P*Me$_3$). ^{29}Si NMR (119.2 MHz; C_6D_6; δ, ppm): −12.1 (d, $^1J_{H-Si}$ = 218.8 Hz, *Si*HPh).

Kinetic NMR Studies of the Exchange between Complex 3 and PhSiH$_3$. A solution of **3** (15.0 mg, 0.02 mmol) and $PhSiH_3$ (2.5 μL, 0.02 mmol) in 0.6 mL of C_6D_6 in NMR tubes was immediately frozen after preparation. The sample was placed into a Bruker DPX-600 instrument at the appropriate temperature (12, 22, 32, or 42 °C). A series of 1D ^1H EXSY NMR experiments (irradiation was applied for the resonance of one of the Si-bound protons of the classical Mo-bound SiH_2Ph group) with different mixing times (t_m = 0−0.6 s) were performed. Rate constants of the exchange process at different temperatures were calculated using the initial rate approximation method.[25,49]

NMR-Scale Reaction of Complex 3 with Acetonitrile. Acetonitrile (6.5 μL, 0.12 mmol) was added to a solution of **3** (30.4 mg, 0.04 mmol) frozen in 0.6 mL of toluene-d_8 in liquid N_2 in an NMR tube. The sample was placed into a precooled (−30 °C) NMR instrument, and the reaction was monitored by low-temperature VT NMR. At −30 °C, the evolution of 1 equiv of $PhSiH_3$ and the formation of (ArN═)Mo(PMe$_3$)(η^2-ArN═SiHPh)(η^2-N≡CMe) (**11a**) were observed. Warming the sample to room temperature gave (ArN═)Mo(PMe$_3$)(η^2-NAr-SiHPh-C(Me)═N) (**12a**) in a mixture with unidentified decomposition products.

11a. ^1H NMR (600 MHz; toluene-d_8; −23 °C; δ, ppm): 7.95 (bs, 2H, *o*-H, Si*Ph*), 6.97−7.17 (m, 9H, *m*-H and *p*-H of 2 N*Ar* and Si*Ph*, overlapping with residual toluene-d_8 signals), 5.23 (s, 1H, Si*H*), 4.02 (bs, 1H, *CH*, N*Ar*), 3.76 (broad sept, $^3J_{H-H}$ = 5.4 Hz, 2H, 2 *CH*, N*Ar*), 3.64 (bs, 1H, *CH*, N*Ar*), 3.32 (s, 3H, NC*Me*), 1.42 (bd, $^3J_{H-H}$ = 6.0 Hz, 3H, *CH*$_3$, N*Ar*), 1.31 (bs, 3H, *CH*$_3$, N*Ar*), 1.24 (bs, 3H, *CH*$_3$, N*Ar*), 1.21 (bd, $^3J_{H-H}$ = 5.4 Hz, 6H, 2 *CH*$_3$, N*Ar*), 1.16 (bd, $^3J_{H-H}$ = 5.4 Hz, 6H, 2 *CH*$_3$, N*Ar*), 1.07 (bd, $^2J_{H-P}$ = 8.4 Hz, 9H, P*Me*$_3$), 0.54 (bs, 3H, *CH*$_3$, N*Ar*). $^{31}P\{^1H\}$ NMR (243 MHz; toluene-d_8; −22 °C; δ, ppm): −1.8 (s, *P*Me$_3$). $^{13}C\{^1H\}$ NMR (151 MHz; toluene-d_8; −20 °C; δ, ppm): 186.5 (s, NCMe), 155.32, 155.26, 153.5, 136.7, 122.3; other aromatic carbons are overlapping with the signals of toluene-d_8, 28.0 (s, CH), 27.89 (s, CH), 27, 85 (s, CH), 26.8 (s, *CH*$_3$, N*Ar*), 23.9 (s, *CH*$_3$, N*Ar*), 23.5(s, *CH*$_3$, N*Ar*), 23.1 (s, *CH*$_3$, N*Ar*), 22.8 (s, NC*Me*), 22.2 (s, *CH*$_3$, N*Ar*), 21.5 (s, *CH*$_3$, N*Ar*), 13.5 (d, $^1J_{C-P}$ = 22.6 Hz, P*Me*$_3$). ^{29}Si INEPT + NMR (119.2 MHz; toluene-d_8; *J* = 200 Hz; −20 °C; δ, ppm): −45.2 (d, $^1J_{Si-H}$ = 219.4 Hz, η^2-ArN═*Si*HPh).

12a. ^1H NMR (600 MHz; toluene-d_8; −23 °C; selected resonances; δ, ppm): 7.45 (bd, $^3J_{H-H}$ = 6.0 Hz, 2H, *o*-H, Si*Ph*), 5.76 (bs, 1H, Si*H*), 3.03 (s, 3H, C(*Me*)═N), 1.12 (bs, 9H, P*Me*$_3$). $^{31}P\{^1H\}$ NMR (243 MHz; toluene-d_8; −22 °C; δ, ppm): −1.7 (s, *P*Me$_3$). ^{29}Si INEPT + NMR (119.2 MHz; toluene-d_8; *J* = 200 Hz; −20 °C; δ, ppm): −47.6 (d, $^1J_{Si-H}$ = 228.9 Hz, N*Si*HPh).

Preparation of (ArN═)Mo(PMe$_3$)(η^2-NAr-SiHPh-C(^{i}Pr)═N) (12c). ^{i}PrCN (37.7 μL, 0.42 mmol) was added to a solution of **3** (281.3 mg, 0.38 mmol) in 15 mL of toluene. The reaction mixture was stirred at room temperature for 2 h. All volatiles were then pumped off; the residue was dried under vacuum, redissolved in fresh toluene, and allowed to stir at room temperature overnight. All volatiles were removed under reduced

pressure, and the residue was extracted with hexanes. The solvent was pumped off to leave an oily substance, which was dissolved in 5 mL of Et_2O. The solution was left with stirring for 2 h, and then ether was removed under vacuum to give a brown foam of **12c**. Yield: 193.3 mg, 73%. All attempts to recrystallize the product gave an oily substance. The product is not stable at room temperature in solution, and after 4 days NMR analysis showed slow decomposition to a mixture of unidentified compounds.

NMR-Scale Reaction of Complex 3 with Acetone. Acetone (1.6 μL, 0.022 mmol) was added to a solution of **3** (16.0 mg, 0.022 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The reaction mixture was left at room temperature for 2 h. During this time the reaction was monitored by NMR analysis, which showed 100% conversion of **3** and the formation of $(ArN{=})_2Mo(\eta^2\text{-}O{=}CMe_2)(PMe_3)$ (**13**), accompanied by the evolution of 1 equiv of $PhSiH_3$. Other silicon-containing products were not detected. All attempts to isolate complex **13** in analytically pure form by recrystallization were unsuccessful. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.07−6.96 (m, 6H, *p*-H and *m*-H, N*Ar*), 3.98 (sept, $^3J_{H-H}$ = 6.9 Hz, 4H, *CH*, N*Ar*), 2.30 (s, 6H, η^2-O=C*Me*$_2$), 1.19 (m, 33H, *CH*$_3$ of N*Ar* and 9H of P*Me*$_3$). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): 7.3 (s, *P*Me$_3$). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; δ, ppm): 13.3 (d, $^1J_{C-P}$ = 27.8 Hz, P*Me*$_3$), 24.0 (s, *CH*$_3$, N*Ar*), 24.1 (s, *CH*$_3$, N*Ar*), 28.0 (s, *CH*, N*Ar*), 32.3 (s, *CH*$_3$, η^2-O=C*Me*$_2$), 85.8 (s, η^2-O=C*Me*$_2$), 122.7 (s, *m*-C, N*Ar*), 123.9 (s, *p*-C, N*Ar*), 141.6 (s, *o*-C, N*Ar*), 153.9 (s, *i*-C, N*Ar*). IR (Nujol): 1621 cm^{-1} (strong, O=C).

NMR-Scale Reaction of Complex 3 with Benzaldehyde. PhC(O)H (3.0 μL, 0.029 mmol) was added in one portion at −30 °C to a solution of **3** (21.0 mg, 0.029 mmol) in 0.6 mL of toluene-d_8 in an NMR tube. The sample was immediately frozen in liquid N_2 and placed into the NMR instrument precooled to −30 °C. The reaction was monitored by low-temperature VT NMR spectroscopy, showing at −10 °C the formation of a difficult-to-characterize mixture of products, one of which was assigned the structure $(ArN{=})Mo(PMe_3)(\eta^2\text{-}ArN{=}SiHPh)(\eta^2\text{-}O{=}CHPh)$ (**15**). Warming the sample to room temperature led to decomposition to a mixture of unidentified products.

15. ^{1}H NMR (600 MHz; toluene-d_8; −7 °C; selected resonances; δ, ppm): 13.28 (d, J_{H-P} = 6.9 Hz, 1H, C(O)*H*), 6.83 (bs, 1H, η^2-ArN=Si*H*Ph). ^{31}P{^{1}H} NMR (243 MHz; toluene-d_8; −50 °C; δ, ppm): 2.9 (s, *P*Me$_3$). ^{29}Si INEPT+ NMR (119.2 MHz; J = 200 Hz; toluene-d_8; −50 °C; δ, ppm): −49.9 (d, $^1J_{Si-H}$ = 241.4 Hz, η^2-ArN=*Si*HPh).

Preparation of $(ArN{=})Mo(Et)(PMe_3)(\eta^3$-NAr-SiHPh-CH=CH$_2)$ (17). *Method A.* Ethylene gas was added via vacuum transfer to a solution of **3** (502.6 mg, 0.682 mmol) in 100 mL of Et_2O at −80 °C. The reaction mixture was warmed to ambient temperature and allowed to stir for 12 h. All volatiles were pumped off, and the residue was dried and extracted with 100 mL of hexanes. The solution was concentrated to 10 mL and left at −30 °C overnight to form a brown precipitate, which was filtered off, washed with 5 mL of cold hexanes, and dried under vacuum. Yield: 362.7 mg, 84%.

Method B. $PhSiH_3$ (0.3 mL, 2.431 mmol) was added to a solution of $(ArN{=})_2Mo(\eta^2\text{-}C_2H_4)(PMe_3)_2$ (267 mg, 0.425 mmol) in 30 mL of Et_2O at −80 °C. The mixture was immediately frozen in liquid N_2, and excess ethylene was added via vacuum transfer. The reaction mixture was slowly warmed to room temperature and allowed to stir for 3 days. During this time the color of the mixture changed from purple to brown. All volatiles were pumped off, and the residue was extracted with 50 mL of hexanes. Hexanes solution was concentrated to 10 mL and left at −30 °C for 2 days to form a brown precipitate of **17**, which was filtered off and dried under vacuum. Yield: 139.7 mg, 48%. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.67 (m, 2H, *o*-H, Si*Ph*), 6.85−7.10 (m, 9H, *m*-H and *p*-H of N*Ar* and Si*Ph*), 6.48 (s, 1H, Si*H*), 4.30 (dd, J_{H-H} = 3.9 Hz, 13.0 Hz, 1H, *H*$_2$*C*=CH), 4.09 (m, 2H, *H*$_2$*C*=CH and *CH* of N*Ar*), 3.83 (sept, $^3J_{H-H}$ = 6.6 Hz, 1H, *CH*, N*Ar*), 3.71 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, *CH*, N*Ar*), 2.95 (dd, $^3J_{H-H}$ = 13.0 Hz, 15.6 Hz, 1H, H$_2$*C*=*CH*), 2.70 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, *CH*, N*Ar*), 2.54 (m, 1H, *CH*$_2$, Mo*Et*), 2.04 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, *CH*$_3$, Mo*Et*), 1.54 (m, 6H, 2*CH*$_3$, N*Ar*), 1.47 (m, 1H, *CH*$_2$, Mo*Et*), 1.40 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, 2*CH*$_3$, N*Ar*), 1.15 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, *CH*$_3$, N*Ar*), 1.10 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, 2*CH*$_3$, N*Ar*), 0.70 (d, $^2J_{P-H}$ = 7.5 Hz, 9H, P*Me*$_3$), 0.31 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, *CH*$_3$, N*Ar*). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): −17.2 (s, *P*Me$_3$). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; δ, ppm): 14.0 (d, $^1J_{C-P}$ = 19.6 Hz, P*Me*$_3$), 15.5 (s, *CH*$_3$, N*Ar*), 19.6 (d, $^3J_{C-P}$ = 5.9 Hz, *CH*$_3$, Mo*Et*), 22.1 (s, *CH*$_3$, N*Ar*), 24.2 (s, *CH*$_3$, N*Ar*), 24.3 (s, *CH*$_3$, N*Ar*), 25.5 (s, *CH*$_3$, N*Ar*), 27.2 (s, *CH*, N*Ar*), 27.6 (s, *CH*$_3$, N*Ar*), 27.9 (s, *CH*, N*Ar*), 29.7 (s, *CH*$_3$, N*Ar*), 30.2 (s, *CH*, N*Ar*), 31.6 (d, $^2J_{C-P}$ = 6.3 Hz, *CH*$_2$, Mo*Et*), 49.9 (d, J_{C-P} = 4.7 Hz, *CH*=CH$_2$), 75.4 (d, J_{C-P} = 13.2 Hz, CH=*CH*$_2$), 123.0 (s, *p*-C, Si*Ph*), 123.1 (s, *m*-C, N*Ar*), 123.7 (s, *p*-C, N*Ar*), 124.0 (s, *m*-C, N*Ar*), 127.0 (s, *m*-C, N*Ar*), 129.5 (s, *m*-C, Si*Ph*), 134.3 (s, *o*-C, Si*Ph*), 140.4 (s, *o*-C, N*Ar*), 141.3 (s, *o*-C, N*Ar*), 143.7 (s, *o*-C, N*Ar*), 144.2 (s, *o*-C, N*Ar*), 147.8 (s, *i*-C, Si*Ph*), 150.4 (s, *i*-C, N*Ar*), 152.0 (s, *i*-C, N*Ar*). ^{29}Si INEPT+ NMR (59.6 MHz; C_6D_6; J = 200 Hz; δ, ppm): −28.2 (d, $^1J_{Si-H}$ = 207.8 Hz, *Si*H). IR (Nujol): 2105 cm^{-1} (Si−H). Elemental analysis (%): calcd for $C_{37}H_{57}MoN_2PSi$ (684.861), C 64.89, H 8.39, N 4.09; found, C 64.48, H 8.30, N 3.74.

NMR-Scale Generation of $(ArN{=})Mo(H)(PMe_3)(\eta^2$-NAr-SiHPh-CH=CHPh) (18). Styrene (3.5 μL, 0.031 mmol) was added to a solution of **3** (22.5 mg, 0.031 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The reaction mixture was left at room temperature for 2.5 h. NMR analysis showed full conversion of the starting material and formation of **18**. All attempts to isolate **18** in analytically pure form were unsuccessful due to its decomposition. ^{1}H NMR (600 MHz; C_6D_6; δ, ppm): 8.00 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, *o*-H, C*Ph*), 7.41 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, *o*-H, Si*Ph*), 7.27 (m, 2H, *m*-H, C*Ph*), 7.06−6.88 (m, 10H, *p*-H of C*Ph*, *m*-H and *p*-H of Si*Ph*, *m*-H and *p*-H of N*Ar*), 6.22 (d, $^3J_{H-H}$ = 15.0 Hz, 1H, CH=CH), 6.15 (d, $^4J_{H-P}$ = 6.6 Hz, 1H, Si*H*), 3.56 (sept, $^3J_{H-H}$ = 6.6 Hz, 1H, *CH*, N*Ar*), 3.36 (sept, $^3J_{H-H}$ = 7.2 Hz, 1H, *CH*, N*Ar*), 3.30 (d, $^3J_{H-H}$ = 15.0 Hz, 1H, CH=*CH*), 3.05 (d, $^2J_{H-P}$ = 43.2 Hz, 1H, Mo*H*), 2.63 (sept, $^3J_{H-H}$ = 7.2 Hz, 1H, *CH*, N*Ar*), 1.78 (sept, $^3J_{H-H}$ = 7.2 Hz, 1H, *CH*, N*Ar*), 1.39 (d, $^3J_{H-H}$ = 7.2 Hz, 3H, *CH*$_3$, N*Ar*), 1.30 (d, $^3J_{H-H}$ = 7.2 Hz, 3H, *CH*$_3$, N*Ar*), 1.14 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, 2*CH*$_3$, N*Ar*), 1.12 (d, $^3J_{H-H}$ = 7.2 Hz, 3H, *CH*$_3$, N*Ar*), 1.10 (d, $^3J_{H-H}$ = 7.2 Hz, 3H, *CH*$_3$, N*Ar*), 0.95 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, *CH*$_3$, N*Ar*), 0.75 (d, $^2J_{H-P}$ = 7.8 Hz, 9H, P*Me*$_3$), 0.47 (d, $^3J_{H-H}$ = 7.2 Hz, 3H, *CH*$_3$, N*Ar*). ^{31}P{^{1}H} NMR (243 MHz; C_6D_6; δ, ppm): −19.2 (s, *P*Me$_3$). ^{31}P NMR (selectively decoupled from methyl groups; 243 MHz; C_6D_6; δ, ppm): −19.2 (dd, $^2J_{H-P}$ = 43.7 Hz, $^4J_{H-P}$ = 7.3 Hz *P*Me$_3$). ^{29}Si INEPT+ NMR (119.2 MHz; C_6D_6; 200 Hz; δ, ppm): −8.2 (d, $^1J_{Si-H}$ = 197.9 Hz, *Si*H). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; δ, ppm): 17.4 (d, $^1J_{C-P}$ = 21.1 Hz, P*Me*$_3$), 18.4 (s, *CH*$_3$, N*Ar*), 24.0 (s, *CH*$_3$, N*Ar*), 24.7 (s, *CH*$_3$, N*Ar*), 25.2 (s, *CH*$_3$, N*Ar*), 25.3 (s, *CH*$_3$, N*Ar*), 26.4 (s, *CH*$_3$, N*Ar*), 27.7 (s, *CH*$_3$, N*Ar*), 28.2 (s, *CH*, N*Ar*), 28.3 (s, *CH*, N*Ar*), 28.5 (s, *CH*, N*Ar*), 28.7 (s, *CH*, N*Ar*), 37.5 (d, $^4J_{C-P}$ = 6.8 Hz, *CH*=CHPh), 83.4 (d, $^5J_{C-P}$ = 3.4 Hz, CH=*CH*Ph), 123.1, 123.2, 123.4, 123.8, 125.0, 126.6, 126.8, 127.1, 127.8, 128.1 (s, *p*-C of C*Ph*, *p*-C and *m*-C of Si*Ph* and N*Ar*), 128.2 (s, *m*-C, C*Ph*), 130.2 (s, *m*-C, C*Ph*), 135.5 (s, *o*-C, C*Ph*), 136.0, 136.1, 136.4, 136.8 (s, *o*-C, Si*Ph*), 138.5, 141.1, 141.4, 147.4, 147.6, 150.6, 150.7, 151.3 (s, aromatic quaternary carbons). IR (Nujol): 1812 (Mo−H), 2098 cm^{-1} (Si−H).

NMR-Scale Generation of $(ArN{=})Mo(SiH_2Ph)(\eta^3$-N(Ar)-SiHPh-H)$(\eta^2$-CH$_2$=CHPh) (22). A solution of BPh_3 (6.0 mg, 0.025 mmol) and styrene (2.9 μL, 0.025 mmol) in 0.6 mL of C_6D_6 was added to **3** (18.3 mg, 0.025 mmol). The mixture was immediately transferred to an NMR tube, and the reaction was monitored by NMR analysis, showing full conversion of **3** after 1.4 h to form selectively $Ph_3B\cdot PMe_3$ and fluxional complex **22**. All volatiles were pumped off; the oily residue was dried under vacuum and redissolved in C_6D_6. The product was thermally unstable in solution and fully decomposed overnight at room temperature. After all NMR experiments, PMe_3 (2.6 μL, 0.025 mmol)

was added to the sample. NMR analysis showed immediate substitution of the PhCH=CH_2 ligand with PMe_3, regeneration of **3**, and slow reaction of the latter with styrene to give complex **18**.

22. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 8.05 (d, $^3J_{H-H}$ = 6.3 Hz, 2H, *o*-H, SiH_2Ph), 6.75−7.29 (m, 19H, *m*-H and *p*-H of SiH_2Ph, *m*-H and *p*-H of N*Ar*, *m*-H, *p*-H, and *o*-H of NAr-SiH*Ph*-H and η^2-CH_2=CH*Ph*), 6.10 (s, 1H, SiH_2Ph), 5.70 (s, 1H, SiH_2Ph), 5.33 (bs, 1H, NAr-Si*H*Ph-H, found by ^{1}H−^{29}Si HSQC with *J* = 200 and 7 Hz), 4.56 (bs, 1H, NAr-SiHPh-*H*, ^{1}H−^{29}Si HSQC with *J* = 7 Hz), 3.78 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, 2*CH*, N*Ar*), 3.64 (m, 2H, *CH* of N*Ar* and PhCH=CH_2, found by ^{1}H−^{1}H COSY and ^{1}H−^{13}C HSQC), 3.54 (m, 1H, PhCH=CH_2), 3.39 (d, $^3J_{H-H}$ = 12.0 Hz, 1H, Ph*CH*=CH_2), 2.15 (bm, 1H, *CH*, NAr), 1.47 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*), 1.22 (d, $^3J_{H-H}$ = 6.9 Hz, 9H, 3CH_3, N*Ar*), 1.11 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*), 0.96 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, 2CH_3, N*Ar*), 0.48 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; δ, ppm): 152.9, 147.2, 146.5, 146.2 145.6, 142.2, 142.1 141.3, 136.6 (s, *o*-C, SiH_2Ph), 136.0 (s, *o*-C, NAr-SiH*Ph*-H), 128.1, 127.8, 125.4, 125.0, 124.9, 124.2, 123.8, 123.4, 122.6, 67.5 (bs, CH_2=*CH*Ph), 53.0 (s, CH_2=CHPh), 29.4 (s, *CH*, N*Ar*), 29.3 (s, *CH*, N*Ar*), 28.3 (s, *CH*, N*Ar*), 28.1 (s, *CH*, N*Ar*), 25.6 (s, CH_3, N*Ar*), 24.7 (s, CH_3, N*Ar*), 24.1 (s, CH_3, N*Ar*), 24.0 (s, CH_3, N*Ar*), 22.8 (s, CH_3, N*Ar*), 20.8 (s, CH_3, N*Ar*), 18.9 (s, CH_3, N*Ar*), 11.6 (s, CH_3, N*Ar*). ^{1}H−^{29}Si HSQC NMR (f1, 600 MHz; f2, 119.2 MHz; *J* = 200 Hz; toluene-d_8; ^{29}Si projection; δ, ppm): −82.4 (NAr-*Si*HPh-H), 1.9 (*Si*H_2Ph). ^{1}H−^{29}Si HSQC 1D JC NMR (f1, 600 MHz; f2, 119.2 Hz; *J* = 100 Hz; toluene-d_8; −50 °C; ^{1}H projection; δ, ppm): 4.68 (d, $^1J_{H-Si}$ = 112.4 Hz, 1H, NAr-SiHPh-*H*). ^{1}H−^{29}Si HSQC 1D JC NMR (f1, 600 MHz; f2, 119.2 Hz; *J* = 200 Hz; toluene-d_8; −50 °C; ^{1}H projection; δ, ppm): 5.65 (d, $^1J_{H-Si}$ = 255.3 Hz, 1H, NAr-Si*H*Ph-H). ^{1}H−^{29}Si HSQC 1D JC NMR (f1, 600 MHz; f2, 119.2 Hz; *J* = 200 Hz; toluene-d_8; 22 °C; ^{1}H projection; δ, ppm): 6.05 (d, $^1J_{H-Si}$ = 186.1 Hz, 1H, SiH_2Ph); 5.65 (d, $^1J_{H-Si}$ = 168.1 Hz, 1H, SiH_2Ph). IR (Nujol): 1571 (weak), 1589 (medium), 1771 (weak, broad, NAr-SiHPh-*H*), 2080 (strong, broad, SiH_2Ph), 2160 cm^{-1} (medium, broad, NAr-Si*H*Ph-H).

NMR-Scale Generation of (ArN)Mo(SiH_2Ph)(η^3-N(Ar)-SiHPh-H)(η^2-C_2H_4) (23). A solution of BPh_3 (5.6 mg, 0.023 mmol) in 0.3 mL of C_6D_6 was added at −30 °C to a solution of complex **3** (17.1 mg, 0.023 mmol) in 0.3 mL of C_6D_6 in an NMR tube. The mixture was immediately frozen in liquid N_2, and ethylene was added via vacuum transfer. The reaction mixture was slowly warmed to room temperature and left for an additional 5 min. NMR analysis showed quantitative formation of **23**, accompanied by the production of $Ph_3B\cdot PMe_3$. Compound **23** was unstable in solution at room temperature and fully decomposed after 30 min to give a difficult-to-characterize mixture of unidentified compounds. The instability of **23** also hampered its full spectroscopic characterization. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.79 (m, 2H, *o*-H, SiH_2Ph), 6.83−7.30 (m, overlapping with the residual C_6D_6 signal, 14H, *p*-H and *m*-H of SiH_2Ph, *o*-H, *m*-H, and *p*-H of NAr-SiH*Ph*-H, *m*-H and *p*-H of N*Ar*), 5.89 (d, $^2J_{H-H}$ = 3.3 Hz, 1H, SiH_2Ph), 5.80 (d, $^2J_{H-H}$ = 3.3 Hz, 1H, SiH_2Ph), 4.83 (d, $^2J_{H-H}$ = 5.1 Hz, 1H, NAr-Si*H*Ph-H), 3.60 (bs, 1H, NAr-SiHPh-*H*), 3.47 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, *CH*, N*Ar*), 3.32 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, 2*CH*, N*Ar*), 3.23 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, *CH*, N*Ar*), 3.03 (m, J_{H-H} = 5.7 and 12.3 Hz, 1H, C_2H_4), 2.82 (m, J_{H-H} = 6.3 and 13.5 Hz, 1H, C_2H_4), 2.61 (m, J_{H-H} = 6.3 and 12.3 Hz, 1H, C_2H_4), 1.37 (m, 1H, C_2H_4, found by ^{1}H−^{1}H COSY), 1.25 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*), 1.19 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*), 1.12 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, 2CH_3, N*Ar*), 0.98 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, 2CH_3, N*Ar*), 0.94 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*), 0.76 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*).

Preparation of (ArN=)Mo(H)(PMe_3)(η^3-NAr-SiHPh-CH=CH_2) (20). *Method A.* $PhSiH_3$ (39.6 μL, 0.321 mmol) was added to a solution of **17** (11.0 mg, 0.016 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The reaction mixture was left at room temperature for 2 days. NMR analysis showed 17% conversion of the starting material to complex **20**.

Method B. $PhSiH_3$ (3.5 μL, 0.028 mmol) and PMe_3 (2.8 μL, 0.027 mmol) were added to a solution of **17** (18.4 mg, 0.027 mmol) in 0.6 mL of C_6D_6 in an NMR tube. After 10 min at room temperature, NMR analysis showed no reaction, and the mixture was heated overnight at 50 °C. During this time, the color turned to another tint of brown, and NMR spectra showed the selective formation of **20** and $PhEtSiH_2$.[44] Redistribution of $PhSiH_3$ to give Ph_2SiH_2 and SiH_4 was also observed.[22]

Method C. The reaction was done on NMR scale analogously to method B using 4.8 μL (0.035 mmol) of $PhMeSiH_2$, 3.6 μL (0.035 mmol) of PMe_3, and 24.0 mg (0.035 mmol) of **17**. Selective formation of **20** and PhMeEtSiH was also observed by NMR.

Method D. Hydrogen gas was added via vacuum transfer solution of **17** (16.1 mg, 0.024 mmol) in 0.6 mL of C_6D_6 to a frozen in liquid N_2 in an NMR tube. The mixture was warmed to room temperature and left for 30 min, showing no reaction. The reaction mixture was heated at 50 °C for 36 h. NMR analysis showed full conversion of **17** to form **20** (67% yield, according to ^{31}P{^{1}H} NMR), ethane, and unidentified decomposition products. Traces of $ArNH_2$ were also observed by NMR spectroscopy.

Method E. PMe_3 (6.7 μL, 0.064 mmol) and $PhSiH_3$ (8.0 μL, 0.064 mmol) were added to a solution of **17** (44.1 mg, 0.064 mmol) in 10 mL of toluene. The reaction mixture was left overnight at 50 °C. All volatiles were pumped off; the residue was dried and extracted with 15 mL of hexanes. The solvent was removed under vacuum to give an oily brown residue of **20** (28.0 mg, 66%). All attempts to obtain **20** in analytically pure form by recrystallization were unsuccessful. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.60 (m, 2H, *o*-H, Si*Ph*), 6.87−7.10 (m, 9H, *m*-H and *p*-H of N*Ar* and Si*Ph*), 6.62 (s, 1H, Si*H*), 4.53 (dd, $^3J_{H-H}$ = 5.1 Hz, 12.6 Hz, 1H, H_2C=CH), 4.43 (dd, $^3J_{H-H}$ = 5.1 Hz, 15.3 Hz, 1H, H_2C=CH), 4.08 (sept, $^3J_{H-H}$ = 6.6 Hz, 1H, *CH*, N*Ar*), 3.82 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, 2*CH*, N*Ar*), 2.69 (d, $^2J_{H-P}$ = 41.7 Hz, 1H, Mo-*H*), 2.50 (m, 1H, *CH*, N*Ar*), 2.49 (dd, $^3J_{H-H}$ = 12.6 Hz, 15.3 Hz, 1H, H_2C=*CH*), 1.57 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, N*Ar*), 1.43 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*), 1.31 (d, $^3J_{H-H}$ = 6.6 Hz, 12H, 4CH_3, N*Ar*), 0.98 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*), 0.80 (d, $^2J_{P-H}$ = 7.8 Hz, 9H, PMe_3), 0.41 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): −15.6 (s, PMe_3). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; δ, ppm): 17.8 (d, $^1J_{C-P}$ = 21.9 Hz, PMe_3), 23.7 (s, CH_3, N*Ar*), 24.2 (s, CH_3, N*Ar*), 25.5 (s, CH_3, N*Ar*), 26.2 (s, CH_3, N*Ar*), 27.3 (s, *CH*, N*Ar*), 27.6 (s, *CH*, N*Ar*), 28.2 (s, *CH*, N*Ar*), 28.8 (s, CH_3, N*Ar*), 39.7 (d, J_{C-P} = 6.8 Hz, *CH*=CH_2), 63.0 (d, J_{C-P} = 5.3 Hz, CH=CH_2), 123.2 (s, *p*-C, Si*Ph*), 123.3, 123.7, 123.6 (s, *m*-C and *p*-C, N*Ar*), 127.4 (s, *m*-C, N*Ar*), 129.7 (s, *m*-C, Si*Ph*), 140.65 (s, *o*-C, N*Ar*), 140.7 (s, *o*-C, N*Ar*), 140.9 (s, *o*-C, N*Ar*), 141.0 (s, *o*-C, Si*Ph*), 142.5 (s, *o*-C, N*Ar*), 151.0 (s, *i*-C, Si*Ph*), 151.8 (s, *i*-C, N*Ar*), 156.1 (s, *i*-C, N*Ar*). ^{29}Si INEPT+ NMR (59.6 MHz; C_6D_6; *J* = 200 Hz; δ, ppm): −27.7 (d, $^1J_{Si-H}$ = 204.9 Hz, *Si*H). IR (Nujol): 2098 (Si−H); 1796 cm^{-1} (Mo−H).

NMR-Scale Reaction of Complex 17 with $PhSiD_3$. The reaction was done on NMR scale analogously to the preparation of **19** (method A) using 3.4 μL (0.028 mmol) of $PhSiD_3$ and 18.8 mg (0.028 mmol) of **17**. After overnight at 50 °C, NMR analysis showed the formation of only (ArN=)Mo(D)(PMe_3)(η^3-NAr-SiHPh-CH=CH_2) (**20_D**). The spectral data of **20_D** are similar to those for **20** except for the Mo*H* resonance, which was not observed in the ^{1}H NMR spectrum of **20_D** due to substitution with deuterium.

NMR-Scale Reaction of Complex 20 with $PhSiH_3$. $PhSiH_3$ (39.6 μL, 0.032 mmol) was added to a solution of **20** (10.5 mg, 0.016 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The reaction mixture was left at room temperature for 1 week, showing 63% conversion of **20** and the formation of complex **3**, accompanied by the release of $PhEtSiH_2$.[44]

NMR-Scale Reaction of Complex 20 with Ethylene. Ethylene was added via vacuum transfer to a solution of **20** (19.0 mg, 0.029 mmol)

in 0.6 mL of C_6D_6 frozen in liquid N_2 in an NMR tube. The mixture was warmed to room temperature and left for 15 min. NMR analysis showed the selective formation of complex **17**.

Preparation of (ArN═)Mo(CH_2CH_2Ph)(PMe_3)(η^3-NAr-SiHPh-CH═CH_2) (21). Styrene (3.6 μL, 0.032 mmol) was added to a solution of **20** (21.1 mg, 0.032 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The reaction mixture was left at room temperature for 3 days until all the starting material was consumed. All volatiles were pumped off; the residue was extracted with 2 mL of hexanes to give a dark-brown oil of **21** (20.0 mg, 83%). All attempts to obtain **21** in analytically pure form by recrystallization were unsuccessful. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.67 (m, 2H, *o*-H, Si*Ph*), 7.48 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o*-H, CH_2CH_2*Ph*), 7.32 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *m*-H, CH_2CH_2*Ph*), 6.81−7.11 (m, 10H, *p*-H of CH_2CH_2*Ph*, *m*-H and *p*-H of Si*Ph*, and *m*-H and *p*-H or N*Ar*), 6.49 (s, 1H, Si*H*), 4.35 (dd, $^2J_{H-H}$ = 3.9 Hz, $^3J_{H-H}$ = 12.9 Hz, 1H, H_2C═CH), 4.17 (dd, $^2J_{H-H}$ = 3.9 Hz, $^3J_{H-H}$ = 15.6 Hz, 1H, H_2C═CH), 4.09 (sept, $^3J_{H-H}$ = 6.6 Hz 1H, *CH*, N*Ar*), 3.82 (sept, $^3J_{H-H}$ = 6.6 Hz, 2H, 2*CH*, N*Ar*), 3.66 (ddd, $^2J_{H-H}$ = 4.5 Hz, $^3J_{H-H}$ = 13.2 Hz, $^3J_{H-H}$ = 18.0 Hz, 1H, $MoCH_2CH_2$Ph), 3.24 (ddd, $^2J_{H-H}$ = 3.6 Hz, $^3J_{H-H}$ = 13.2 Hz, $^3J_{H-H}$ = 18.0 Hz, 1H, $MoCH_2CH_2$Ph), 2.98 (dd, $^3J_{H-H}$ = 12.9 and 15.6 Hz, 1H, H_2C═*CH*), 2.72 (m, 2H, $MoCH_2CH_2$Ph and *CH* from N*Ar*), 1.69 (m, 1H, $MoCH_2CH_2$Ph), 1.55 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, N*Ar*), 1.54 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, N*Ar*), 1.39 (m, 6H, 2CH_3, N*Ar*), 1.22 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, N*Ar*), 1.13 (m, 6H, 2CH_3, N*Ar*), 0.65 (d, $^2J_{H-P}$ = 7.5 Hz, 9H, PMe_3), 0.35 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, N*Ar*). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): −17.1 (s, PMe_3). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; δ, ppm): 13.9 (d, $^1J_{C-P}$ = 19.6 Hz, PMe_3), 22.3 (s, CH_3, N*Ar*), 24.1 (s, CH_3, N*Ar*), 24.2 (s, CH_3, N*Ar*), 24.6 (s, CH_3, N*Ar*), 25.5 (s, CH_3, N*Ar*), 25.7 (s, CH_3, N*Ar*), 27.3 (s, *CH*, N*Ar*), 27.8 (s, CH_3, N*Ar*), 28.3 (s, *CH*, N*Ar*), 28.4 (s, *CH*, N*Ar*), 29.5 (s, CH_3, N*Ar*), 30.1 (s, *CH*, N*Ar*), 41.0 (d, $^2J_{C-P}$ = 6.8 Hz, $MoCH_2CH_2$Ph), 41.7 (d, $^3J_{C-P}$ = 5.3 Hz, $MoCH_2CH_2$Ph), 50.2 (d, J_{C-P} = 4.5 Hz, *CH*═CH_2), 75.1 (d, J_{C-P} = 12.8 Hz, CH═CH_2), 123.0 (s, N*Ar*), 123.2 (s, *p*-C, Si*Ph*), 123.9 (s, *p*-C, $MoCH_2CH_2$*Ph*), 125.4 (s, N*Ar*), 128.5 (s, *o*-C, $MoCH_2CH_2$*Ph*), 128.6 (s, *m*-C, Si*Ph*), 128.7 (s, *m*-C, $MoCH_2CH_2$*Ph*), 129.5 (s, N*Ar*), 134.2 (s, *o*-C, Si*Ph*), 141.1 (s, *o*-C, N*Ar*), 143.5 (s, *o*-C, N*Ar*), 147.7, 149.2, 150.2, 151.9 (s, *i*-C of N*Ar*, Si*Ph*, and $MoCH_2CH_2$*Ph*). ^{29}Si INEPT+ NMR (59.6 MHz; C_6D_6; J = 200 Hz; δ, ppm): −28.1 (d, $^1J_{Si-H}$ = 206.0 Hz, *Si*HPh).

NMR-Scale Reaction of Complex 18 with Ethylene. Excess ethylene was added via vacuum transfer to a solution of **18** (17.0 mg, 0.023 mmol) in 0.6 mL of C_6D_6 frozen in liquid N_2 in an NMR tube. The mixture was warmed to room temperature and left for an additional 1.5 h. All volatiles were pumped off; the residue was dried under vacuum and redissolved in 0.6 mL of C_6D_6. NMR analysis showed the formation of (ArN═)Mo(Et)(PMe_3)(η^3-NAr-SiHPh-CH═CHPh) (**19**; 36% by ^{31}P{^{1}H} NMR) in a mixture with unidentified decomposition products. All attempts to purify complex **19** by recrystallization from different solvents were unsuccessful. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.67 (d, $^3J_{H-H}$ = 6.3 Hz, *o*-H, Si*Ph*), 6.77−7.55 (m, 14H, aromatic protons of 2 N*Ar*, Si*Ph*, and C*Ph*), 5.97 (bs, 1H, Si*H*), 4.25 (m, 2H, CH═CHPh and *CH* from N*Ar*), 3.72 (m, 2H, CH═CHPh and *CH* from N*Ar*), 3.33 (sept, $^3J_{H-H}$ = 6.6 Hz, 1H, *CH*, N*Ar*), 2.64 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, *CH*, N*Ar*), 0.7−1.59 (broad agglomerate of signals of CH_3 groups of *Ar*N, Mo*Et*, and PMe_3 overlapping with each other and with signals of decomposition products), 0.40 (bs, 3H, CH_3, N*Ar*). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): −19.5 (s, PMe_3). ^{29}Si INEPT+ NMR (59.6 MHz; C_6D_6; J = 200 Hz; δ, ppm): −18.8 (d, $^1J_{Si-H}$ = 187.9 Hz, *Si*HPh).

NMR-Scale Reaction of 19 with $PhSiH_3$ and PMe_3. $PhSiH_3$ (2.7 μL, 0.022 mmol) and PMe_3 (1.9 μL, 0.018 mmol) were added to a solution of **19** (generated *in situ* using 17.0 mg (0.023 mmol) of **18** and excess ethylene) in 0.6 mL of C_6D_6 in an NMR tube. No reaction was observed at room temperature, and the mixture was left at 50 °C overnight. NMR analysis showed the formation of $PhEtSiH_2$,[44] complex **18**, and unidentified decomposition products. No formation of ($PhCH_2CH_2$)SiH_2Ph was observed by NMR spectroscopy.

NMR-Scale Reaction of Complex 17 with $PhSiH_3$ and BPh_3. A solution of complex **17** (20.8 mg, 0.030 mmol) and $PhSiH_3$ (3.8 μL, 0.030 mmol) in 0.6 mL of toluene-d_8 was added to BPh_3 (7.4 mg, 0.030 mmol). The mixture was immediately transferred to an NMR tube, and the reaction was monitored by NMR spectroscopy at room temperature for 1 h until all the starting material was consumed. NMR spectra showed the formation of $Ph_3B\cdot PMe_3$ and the highly fluxional complex (ArN═)Mo(SiH_2Ph)(η^3-NAr-Si(Et)Ph-H)(η^2-C_2H_4) (**24**). All attempts to isolate the product led to decomposition, presumably due to the instability of the compound under vacuum. In solution, the product is stable at ambient temperature under an inert gas atmosphere for 1 week. ^{1}H NMR (300 MHz; toluene-d_8; δ, ppm): 7.82 (d, $^3J_{H-H}$ = 7.5 Hz, 2H, *o*-H, SiH_2*Ph*), 7.38 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, *o*-H, NAr-Si(Et)*Ph*-H), 6.89−7.32 (m, overlapping with the residual toulene-d_8 signals, 12H, *m*-H and *p*-H of N*Ar*, SiH_2*Ph* and NAr-Si(Et)*Ph*-H), 6.00 (s, 2H, SiH_2Ph, found by ^{1}H−^{29}Si HSQC with J = 200 Hz), 4.32 (bs, 1H, NAr-Si(Et)Ph-*H*, found by ^{1}H−^{29}Si HSQC with J = 7 Hz), 3.80 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, 2*CH*, N*Ar*), 3.16 (m, 1H, C_2H_4, found by ^{1}H−^{13}C HSQC), 3.05 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, *CH*, N*Ar*), 2.79 (m, 3H, 2H of C_2H_4, found by ^{1}H−^{13}C HSQC, and 1*CH* of N*Ar*), 1.57 (m, 1H, C_2H_4, found by ^{1}H−^{13}C HSQC), 1.23 (m, 3H, CH_3, Si*Et*), 1.20 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, 2CH_3, N*Ar*), 1.14 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*), 1.11 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*), 1.04 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, 1CH_3, N*Ar*), 1.01 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, 2CH_3, N*Ar*), 0.86 (m, 2H, CH_2, Si*Et*), 0.39 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*). ^{1}H NMR (600 MHz; −53 °C; toluene-d_8; δ, ppm): 8.09 (bs, 2H, *o*-H, SiH_2*Ph*), 7.46 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o*-H, NAr-Si(Et)*Ph*-H), 6.83−7.39 (m, overlapping with the residual toulene-d_8 signals, 10H, *m*-H and *p*-H of N*Ar* and SiH_2*Ph*, *p*-H of NAr-Si(Et)*Ph*-H), 7.34 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *m*-H, NAr-Si(Et)*Ph*-H), 6.07 (s, 1H, SiH_2Ph), 5.75 (s, 1H, SiH_2Ph), 4.99 (s, 1H, SiH_2Ph), 4.21 (bs, 2H, 2*CH*, N*Ar*), 3.42 (bm, 1H, C_2H_4), 3.24 (m, 2H, 1H of C_2H_4 and *CH* of N*Ar*), 3.13 (bm, 1H, C_2H_4), 3.38 (bm, 1H, *CH*, N*Ar*), 1.84 (bm 1H, C_2H_4), 1.29 (bm, 8H, CH_2 of Si*Et* and 2CH_3 or N*Ar*), 1.20 (bs, 3H, CH_3, N*Ar*), 1.13 (bs, 3H, CH_3, N*Ar*), 1.07 (bs, 6H, 2CH_3, N*Ar*), 0.97 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, CH_3, Si*Et*), 0.93 (bm, 3H, CH_3, N*Ar*), 0.35 (bd, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; δ, ppm): 153.6 (s, *i*-C, N*Ar*), 144.6 (s, *o*-C, N*Ar*), 143.3 (s, *i*-C, N*Ar*), 142.0 and 141.7 (singlets, *i*-C of SiH_2*Ph* and NAr-Si(Et)*Ph*-H), 138.6 (s, *o*-C, N*Ar*), 135.6 (s, *o*-C, SiH_2*Ph*), 135.4 (s, *o*-C, NAr-Si(Et)*Ph*-H), 131.1 (s, *m*-C, NAr-Si(Et)*Ph*-H), 130.7 (s, *m*-C, SiH_2*Ph*), 127.5, 126.4, 123.8, 123.7, 122.8 (all s, *p*-C of SiH_2*Ph* and NAr-Si(Et)*Ph*-H, *m*-C and *p*-C of N*Ar*), 51.2 (s, C_2H_4), 44.0 (s, C_2H_4), 28.33 (bs, 2*CH*, N*Ar*), 28.28 (s, *CH*, N*Ar*), 27.5 (s, *CH*, N*Ar*), 25.0 (s, CH_3, N*Ar*), 24.8 (s, CH_3, N*Ar*), 24.6 (s, CH_3, N*Ar*), 24.1 (s, 2CH_3, N*Ar*), 23.5 (s, 2CH_3, N*Ar*), 22.7 (s, CH_3, N*Ar*), 14.0 (s, CH_3, Si*Et*), 7.4 (s, CH_2, Si*Et*). ^{1}H−^{29}Si HSQC JC (600 MHz; −56 °C; toluene-d_8; ^{1}H projection; δ, ppm): 6.11 (d, $^1J_{Si-H}$ = 201.8 Hz, 1H, SiH_2Ph), 5.82 (d, $^1J_{Si-H}$ = 194.5 Hz, 1H, SiH_2Ph), 5.03 (d, $^1J_{Si-H}$ = 104.7 Hz, 1H, NAr-Si(Et)Ph-*H*). ^{29}Si INEPT+ NMR (119.2 MHz; −56 °C; toluene-d_8; J = 100 Hz; δ, ppm): −0.9 (t, $^1J_{Si-H}$ = 173.0 Hz, 163.4 Hz, *Si*H_2Ph), −64.4 (d, $^1J_{Si-H}$ = 107.3 Hz, NAr-*Si*(Et)Ph-H). IR (Nujol): 2077 (broad, intensive, Si−H of SiH_2Ph), 1772 cm^{-1} (broad, weak, Si−H of NAr-Si(Et)Ph-H).

NMR-Scale Reaction of Complex 17 with $PhSiD_3$ and BPh_3. This reaction was done analogously to the reaction of **17** with $PhSiH_3$. Treatment of complex **17** (16.2 mg, 0.024 mmol) with $PhSiD_3$ (2.9 μL, 0.024 mmol) and 1 equiv of BPh_3 (5.7 mg, 0.024 mmol) gave the deuterated derivative (ArN═)Mo(SiD_2Ph)(η^3-NAr-Si(Et_d)Ph-H)(η^2-C_2H_4) (**24$_D$**). The presence of proton in the agostic position was confirmed by ^{1}H NMR at −50 °C in toluene-d_8. ^{1}H NMR analysis also

showed ~30% of H for both Si*H* signals in the SiH_2Ph substituent (the ratio H/D was found by the integration of the ^1H NMR spectrum). Apart from the Si*D* signal of the silyl SiD_2Ph ligand, the ^2D NMR spectrum registered at room temperature in toluene-h_8 showed the presence of deuterium also in the methylene and methyl positions of the ethyl substituent at the agostic silicon center. ^2D NMR (92.1 MHz; toluene-h_8; δ, ppm): 5.74 (bs, SiD_2Ph), 1.04 (bs, methyl of Si*Et*), 0.79 (bs, methylene of Si*Et*).

NMR-Scale Reaction of Complex 24 with PMe_3. PMe_3 (3.1 μL, 0.03 mmol) was added to a solution of **23** (prepared *in situ* by the treatment of **17** (20.8 mg, 0.030 mmol) with $PhSiH_3$ (3.8 μL, 0.030 mmol) and BPh_3 (7.4 mg, 0.030 mmol)) in 0.6 mL of C_6D_6 in an NMR tube. The mixture was left at room temperature for 5 min. NMR analysis showed the release of ethylene and formation of (ArN═)Mo(SiH_2Ph)(PMe_3)(η^3-NAr-Si(Et)Ph-H) (**25**, 2:1 mixture of diastereomers according to $^{31}P\{^1H\}$ NMR). Attempts to purify **25** by recrystallization were unsuccessful. IR (Nujol): 2114 (broad, strong), 2033 (broad, strong), 1652 cm^{-1} (broad, weak). $^{13}C\{^1H\}$ NMR (150.9 MHz; toluene-d_8; −12 °C; δ, ppm; signals for both isomers): 153.5, 149.2, 144.9, 144.2, 143.8, 142.9, 141.7, 141.1, 141.0, 140.4 (s, aromatic quaternary carbons for both isomers), 137.0 (s, *o*-C, SiH_2*Ph*, major isomer), 136.0 (s, *o*-C, SiH_2*Ph*, minor isomer), 135.9 (s, *o*-C, NAr-Si(Et)*Ph*-H, major isomer), 135.8 (s, *o*-C, NAr-Si(Et)*Ph*-H, major isomer), 130.3 (s, *m*-H, SiH_2*Ph*, minor isomer), 129.9 (s, *m*-H, SiH_2*Ph*, major isomer), 129.0 (s, *m*-H, N*Ar*, major isomer), 128.3 (s, *m*-H, NAr-Si(Et)*Ph*-H, major isomer), 128.14, 128.11, 128.0, 127.4, 126.1 125.2, 124.5, 123.5, 123.2, 123.1, 122.9 (s, aromatic for both isomers), 28.5, 28.1, 27.9, 27.8, 27.7, 26.9 (s, *CH*, N*Ar*, both isomers), 26.3, 25.4, 24.4, 24.0, 23.9, 23.8, 23.6 (s, CH_3, N*Ar*, both isomers), 18.2 (d, $^1J_{C-P}$ = 25.7 Hz, PMe_3, minor isomer), 17.8 (d, $^1J_{C-P}$ = 27.2 Hz, PMe_3, major isomer), 8.8, 7.9, 7.11, 10.9 (s, Si*Et*, both isomers).

Major Isomer. ^1H NMR (300 MHz; C_6D_6; δ, ppm): 8.39 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o*-H, SiH_2*Ph*), 6.89−7.54 (m, overlapping with the residual C_6D_6 signal and signals for minor isomer, 14H, *m*-H and *p*-H of N*Ar*, *m*-H and *p*-H of SiH_2*Ph*, and *o*-H, *m*-H, *p*-H of NAr-Si(Et)*Ph*-H), 5.92 (bs, 1H, SiH_2Ph), 5.62 (bs, 1H, SiH_2Ph), 4.11 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, 2*CH*, N*Ar*), 3.97 (broad dd, $^3J_{H-H}$ = 4.8 Hz, $^2J_{H-P}$ = 12.9 Hz, 1H, NAr-Si(Et)Ph-*H*, found by $^1H-^{31}P$ HSQC with J = 5 Hz and $^1H-^{29}Si$ HSQC with J = 100 Hz), 2.58 (sept, $^3J_{H-H}$ = 6.6 Hz, 1H, *CH*, N*Ar*), 1.39 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*), 1.26 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, 2CH_3, N*Ar*), 1.50 (m, overlapping with signal for minor isomer, 12H (4CH_3) of N*Ar* and 5H of Si*Et*, found by $^1H-^1H$ COSY), 1.05 (d, $^3J_{H-H}$ = 8.7 Hz, 9H, PMe_3), 0.08 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, N*Ar*). $^1H\{^{31}P\}$ NMR (300 MHz; C_6D_6; δ, ppm; selected resonances): 5.92 (d, $^2J_{H-H}$ = 2.7 Hz, 1H, SiH_2Ph), 5.62 (d, $^2J_{H-H}$ = 2.7 Hz, 1H, SiH_2Ph), 3.97 (d, $^3J_{H-H}$ = 4.8 Hz, 1H, NAr-Si(Et)Ph-*H*), 1.03 (s, 9H, PMe_3). $^{31}P\{^1H\}$ NMR (121.5 MHz; C_6D_6; δ, ppm): 7.4 (s, PMe_3). $^1H-^{29}Si$ HSQC NMR (f1, 600 MHz; f2, 119.2 MHz; J = 200 Hz; toluene-d_8; −50 °C; ^{29}Si projection; δ, ppm): 4.0 (SiH_2Ph). $^1H-^{29}Si$ HSQC NMR (f1, 600 MHz; f2, 119.2 MHz; J = 100 Hz; toluene-d_8; −50 °C; ^{29}Si projection; δ, ppm): −53.3 (NAr-*Si*(Et)Ph-H). $^1H-^{29}Si$ HSQC JC NMR (600 MHz; J = 100 Hz; toluene-d_8; −14 °C; ^1H projection; δ, ppm): 4.10 (dd, 1H, $^1J_{H-Si}$ = 105.4 Hz, $^2J_{H-P}$ = 11.6 Hz, NAr-Si(Et)Ph-*H*), 5.66 (d, $^1J_{H-Si}$ = 150.1 Hz, 1H, SiH_2Ph), 5.92 (d, $^1J_{H-Si}$ = 168.1 Hz, 1H, SiH_2Ph).

Minor Isomer. ^1H NMR (300 MHz; C_6D_6; δ, ppm): 8.24 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, *o*-H, SiH_2*Ph*), 6.89−7.54 (m, overlapping with the residual C_6D_6 signal and signals for major isomer, 14H, *m*-H and *p*-H of N*Ar*, *m*-H and *p*-H of SiH_2*Ph*, and *o*-H, *m*-H, *p*-H of NAr-Si(Et)*Ph*-H), 5.88 (bs, 1H, SiH_2Ph), 5.49 (bs, 1H, SiH_2Ph), 4.20 (m, 2H, 2*CH*, N*Ar*), 3.59 (m, NAr-Si(Et)Ph-*H* overlapping with *CH* of N*Ar* of major isomer, found by $^1H-^{31}P$ HSQC with J = 5 Hz and $^1H-^{29}Si$ HSQC NMR with J = 100 Hz), 3.00 (m, 2H, 2*CH*, N*Ar*), 1.34 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*), 1.22 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, 2CH_3, N*Ar*), 1.50 (m, 3H (CH_3) of N*Ar* and 5H of Si*Et* (found by $^1H-^1H$ COSY) overlapping with 12H (4CH_3) of N*Ar* of major isomer), 1.11 (d, $^3J_{H-H}$ = 8.4 Hz, 9H, PMe_3), 1.01 (m, 3H, CH_3, N*Ar*), 0.30 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3, N*Ar*). $^1H\{^{31}P\}$ NMR (300 MHz; C_6D_6; δ, ppm; selected resonances): 5.88 (d, $^2J_{H-H}$ = 1.8 Hz, 1H, SiH_2Ph), 5.49 (d, $^2J_{H-H}$ = 1.8 Hz, 1H, SiH_2Ph), 1.12 (s, 9H, PMe_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, δ, ppm): 8.4 (s, PMe_3). $^1H-^{29}Si$ HSQC NMR (f1, 600 MHz; f2, 119.2 MHz; J = 200 Hz; toluene-d_8; −50 °C; ^{29}Si projection; δ, ppm): 3.1 (SiH_2Ph). $^1H-^{29}Si$ HSQC NMR (f1, 600 MHz; f2, 119.2 MHz; J = 100 Hz; toluene-d_8; −50 °C; ^{29}Si projection; δ, ppm): −55.0 (NAr-*Si*(Et)Ph-H). $^1H-^{29}Si$ HSQC JC NMR (600 MHz; J = 100 Hz; toluene-d_8; −14 °C; ^1H projection; δ, ppm): 3.68 (dd, 1H, $^1J_{H-Si}$ = 107.1 Hz, $^2J_{H-P}$ = 10.7 Hz, NAr-Si(Et)Ph-*H*), 5.48 (d, $^1J_{H-Si}$ = 156.1 Hz, 1H, SiH_2Ph), 5.89 (d, $^1J_{H-Si}$ = 168.1 Hz, 1H, SiH_2Ph).

NMR-Scale Reaction of Complex 25 with $PhSiH_3$. $PhSiH_3$ (18.5 μL, 0.15 mmol) was added to a solution of **25** (generated *in situ* by the reaction of **17** (20.5 mg, 0.03 mmol) with $PhSiH_3$ (3.7 μL, 0.03 mmol) and BPh_3 (7.2 mg, 0.03 mmol), followed by the addition of 3.1 μL (0.03 mmol) of PMe_3) in 0.6 mL of C_6H_6 in an NMR tube. The mixture was left at room temperature for 1 week. NMR analysis showed selective formation of $PhEtSiH_2$[44] and **3**.

General Procedure for Kinetic NMR Studies of the Reaction of Complex 17 with $PhSiH_3$. Reagents, either $PhSiH_3$ (variable concentration) or mixtures of 10 equiv of $PhSiH_3$ and a variable concentration of PMe_3, were added to a solution of **17** (16.5 mg, 0.024 mmol) and either 5.0 mol % of tetramethylsilane (for reactions with $PhSiH_3$) or 5.0 mol % of P(*o*-Tol)$_3$ (for reactions with $PhSiH_3$ and PMe_3) in 0.6 mL of C_6D_6 in an NMR tube. No reaction was observed at room temperature. The sample was placed into the NMR instrument, the temperature was raised to 50 °C, and the reaction was monitored by either ^1H (for reactions with $PhSiH_3$) or $^{31}P\{^1H\}$ NMR (for reactions with $PhSiH_3$ and PMe_3) overnight. The rate constants for each concentration of $PhSiH_3$ or PMe_3 were obtained by integration of the Si*H* (^1H NMR) or the *P*Me_3 ($^{31}P\{^1H\}$ NMR) resonance, respectively (integrals were normalized to the integral of the standard: tetramethylsilane or P(*o*-Tol)$_3$). Data obtained from NMR analysis and corresponding concentrations were linearized in the −ln[**17**]/time coordinates.

Experimental Details of EXSY NMR Studies. The EXSY NMR spectra were acquired on a Bruker Avance AV600 spectrometer equipped with a BBO-Z grad probe and VT accessory. ^{31}P and ^1H 2D EXSY NMR spectra were recorded at different temperatures with a pulse sequence "noesygpph" (2D homonuclear correlation via dipolar coupling; dipolar coupling may be due to NOE or chemical exchange; phase sensitive, with gradient pulses in mixing time)[50] from the Bruker pulse program library. A total of 2 scans per FID for ^1H and 4 scans for ^{31}P of 2K data points were used per time increment. A total of 256 time increments were collected for both ^1H and ^{31}P. The FIDs were Fourier transformed to generate a 1024 × 1024 data matrix. Two EXSY spectra were recorded at each temperature, one EXSY spectrum with a mixing time (t_m) between 100 and 500 ms, which contains the exchange cross peaks, and a reference EXSY spectrum with a mixing time 0 ms, which shows no exchange cross peaks. All spectra were processed and analyzed by using Bruker Topspin 2.1 Pl4 software running on Windows XP. The peak volumes of the 2D spectra were determined by direct integration. The exchange rates were calculated using the Mestre Lab EXSY Calc 1.0 software (www.mestrelab.com).[51] The series of ^1H 1D EXSY NMR spectra were recorded at different temperatures using the "selnogp" (1D NOESY using selective refocusing with a shaped pulse; dipolar coupling may be due to NOE or chemical exchange)[52] pulse sequence from the Bruker library. Each spectrum was acquired using 16 scans and 32K data points with a spectral width of 20 kHz. The offset frequency was always adjusted on resonance with the analyzed signal. The acquired FIDs were processed using a line broadening of 0.3 Hz and zero-filled to 65K points. At each temperature a series of 5−8 1D EXSY spectra were

recorded with a mixing time ranging from 25 to 2000 ms, optimized for each exchange rate, and a ^{1}H 1D spectrum was used as a reference. The slopes of the buildup curves at 0 ms mixing time were determined by the initial rate approximation.[49] More accurate measurements of the rates were also performed by employing the CIFIT2.0 software courtesy to Prof. Alex D. Bain from McMaster University (www.chemistry.mcmaster.ca/bain).[53] T1 relaxation times were measured by inversion recovery method using the Bruker "t1ir" pulse program.

■ ASSOCIATED CONTENT

Supporting Information. Description of kinetic experiments, selected experimental procedures and product characterization, kinetic plots, and deduction of kinetic equations. This material is available free of charge via the Internet at http://pubs.acs.org.

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