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β-Agostic Silylamido and Silyl-Hydrido Compounds of Molybdenum and Tungsten[†]

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Reactions of bis(imido) compounds $(RN)_2Mo(PMe_3)_n$ (n = 2, R = ^{t}Bu; n = 3, R =2,6-dimethylphenyl (Ar′) and 2,6-diisopropylphenyl (Ar)) and $(RN)_2W(PMe_3)_3$ (R = 2,6-dimethylphenyl and 2,6-diisopropylphenyl) with silanes afford four types of products: the β-agostic silylamido compounds $(RN)(\eta^3\text{-}RN{-}SiR'_2{-}H\cdots)MCl(PMe_3)_2$ (M = Mo and W), mono(imides) $(RN)MCl_2(PMe_3)_3$ (M = Mo and W), silyl hydride bis(imido) derivative $(ArN)_2W(PMe_3)(H)(SiMeCl_2)$, and $Si{-}Cl\cdots W$ bridged product $(ArN)(\eta^2\text{-}ArN{-}SiHMeCl{-}Cl\cdots)WCl(PMe_3)_2$. Reactions of molybdenum compounds $(RN)_2Mo(PMe_3)_m$ (m = 2 or 3) with mono- and dichlorosilanes $HSiCl_nR'_{3-n}$ (R′ = Me, Ph; n = 1,2) afford mainly the agostic compounds $(RN)(\eta^3\text{-}RN{-}SiR'_2{-}H\cdots)MoCl(PMe_3)_2$, accompanied by small amounts of mono(imido) derivatives $(RN)MoCl_2(PMe_3)_3$. In contrast, the latter compounds are the only transition metal products in reactions with $HSiCl_3$, the silicon co-product being the silanimine dimer $(RNSiHCl)_2$. The reaction of $(ArN)_2W(PMe_3)_3$ with $HSiCl_2Me$ under continuous removal of PMe_3 affords the silyl hydride species $(ArN)_2W(PMe_3)(SiMeCl_2)H$, characterized by NMR and X-ray diffraction. This product is stable in the absence of phosphine, but addition of catalytic amounts of PMe_3 causes a fast rearrangement into the $Si{-}Cl\cdots W$ bridged product $(ArN)(\eta^2\text{-}ArN{-}SiHMeCl{-}Cl\cdots)WCl(PMe_3)_2$. The mechanism of silane addition to complexes $(RN)_2Mo(PMe_3)_n$ has been elucidated by means of density functional theory calculations of model complexes $(MeN)_2Mo(PMe_3)_n$ (n = 1−3). Complex $(MeN)_2Mo(PMe_3)_2$ is found to be the most stable form. It undergoes facile silane-to-imido addition reactions that afford silylamido hydride complexes stabilized by additional $Si\cdots H$ interactions. The ease of this addition increases from $HSiMe_2Cl$ to $HSiCl_3$, consistent with experimental observations. The most stable final products of silane addition are the agostic complexes $(MeN)(\eta^3\text{-}MeN{-}SiR_2{-}H\cdots)MoCl(PMe_3)_2$ (R_2 = Me_2, MeCl, Cl_2) and Cl-bridged silylamido complexes $(MeN)(\eta^2\text{-}MeN{-}SiRH{-}Cl\cdots)MoCl(PMe_3)_2$ (R = Me or Cl). In the case of $HSiMeCl_2$ addition the former is the most stable, but for $HSiCl_3$ addition the latter is the preferred product. In all cases, the isomeric silyl hydride species $(MeN)_2Mo(PMe_3)(H)(SiClR_2)$ are less stable by about 6 kcal mol^{-1}. Silane additions to the imido ligand of the tris(phosphine) $(MeN)_2Mo(PMe_3)_3$ afford octahedral silylamido hydride derivatives. The different isomers of these addition products are destabilized relative to $(MeN)_2Mo(PMe_3)_3$ only by 7−24 kcal mol^{-1} (for the $HSiMe_2Cl$ additions), but since the starting tris(phosphine) is 14.8 kcal mol^{-1} less stable than $(MeN)_2Mo(PMe_3)_2$, silane addition to the latter is a more preferred pathway. A double phosphine dissociation pathway via the species $(MeN)_2Mo(PMe_3)$ was ruled out because this complex is by 24.7 kcal mol^{-1} less stable than $(MeN)_2Mo(PMe_3)_2$.

Introduction

Transition metal compounds with agostic $Si{-}H\cdots M$ interactions[1] (**1**) have attracted significant recent attention, in part because of their relevance to a wide range of metal-mediated transformations of organosilicon compounds, such as hydrosilylation, dehydrogenative polymerization of silanes, silane alcoholysis, and so forth.[1a] Among different types of "arms" linking the agostic Si center to metal, the nitrogen bridge is one of the best studied.[2,3a,4] Agostic silylamido compounds are usually prepared by salt-elimination reactions between a silylated amide $R'(HR_2Si)NM$ (M = an alkali metal) and a transition metal halide.[2]

[†] Dedicated to Prof. Dietmar Seyferth on the occasion of his 80th birthday.

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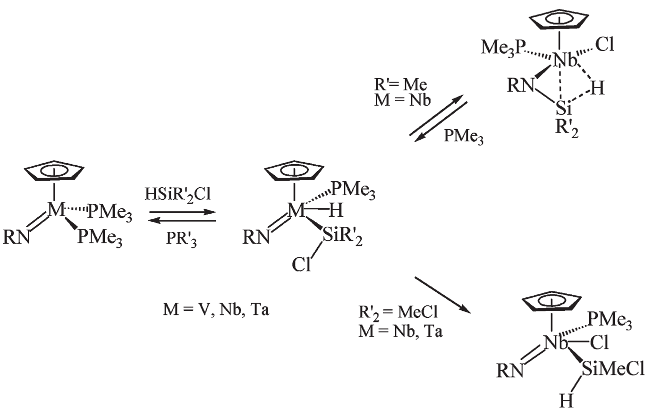
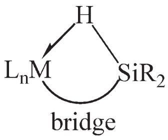
Scheme 1. Product Diversity in the Reactions of Group 5 Cp/Imido Compounds with Silanes



This approach puts severe limitations of the nature of R groups on silicon, hampering the investigation of substituent effects of the extent of the Si−H interaction.



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We have recently reported an alternative pathway to β−Si-H silylamido agostic species based on direct coupling between silanes and reactive transition metal imido compounds.[3−5] For Group 5 Cp/imido derivatives Cp(RN)M-$(PMe_3)_2$, their reactions with silanes $HSiR'_3$ (R′ = Me, Ph, Cl, H) afford three types of products: the silyl hydride compounds Cp(RN)M(PMe_3)H(SiR'_3) (M = V, Nb, Ta), the agostic compounds Cp(η^2-RN-SiR′$_2$-H$\cdots$)Nb(PMe_3)Cl, and the silyl chloride compounds Cp(RN)M(PMe_3)Cl-(SiR′HCl) (M = Nb, Ta) (Scheme 1). The formation and interconversion of these species is determined by the nature of the metal, M, and the substituents at silicon and nitrogen.[4]

Taking into account the isolobal relationship between the imide (RN^{2-}) and cyclopentadienide (Cp^-) groups,[6] we became interested in investigating the reactions of hydrosilanes with Group 6 bis(imido) compounds $(RN)_2M(PMe_3)_3$ (M = Mo, W), isolobal to Group 5 Cp/imido compounds Cp(RN)M$(PMe_3)_2$. Here we report that such reactions with hydrochlorosilanes $HSiCl_3R_{3-n}$ (n = 1−3) afford a wider spectrum of silylamido β−Si-H agostic species, and in one case (for the silane $HSiCl_3$) lead to a productive silane/imido coupling reaction furnishing an equivalent of silanimine. A preliminary communication of part of this work has been published.[7]

Results and Discussion

Starting Compounds. The reduction of precursors $(RN)_2MCl_2(DME)$ (M = Mo, W) has been earlier reported to give several types of compounds. Sodium amalgam reduction of $(ArN)_2WCl_2(DME)$ (Ar = 2,6-$^iPr_2C_6H_3$) in the presence of PMe_2Ph affords the bis(phosphine) compound $(ArN)_2W(PMe_2Ph)_2$.[8] Gibson has reported the X-ray structure of the related compound $(ArN)_2Mo(PMe_3)_2$.[9] On the other hand, Sundermeyer et al. provided evidence that for a less bulky imido group (R = Mes) the tris(phosphine) compound $(MesN)_2Mo(PMe_3)_3$ exists in equilibrium with its bis(phosphine) form and free PMe_3.[10] In contrast, magnesium reduction of $(^tBuN)_2MoCl_2(DME)$ was reported to furnish the imido-bridged dimer $[(^tBuN)(Me_3P)Mo(\mu\text{-}N^tBu)]_2$.[11] In this work, we found that magnesium reduction of $(RN)_2MCl_2(DME)$ (R = Ar or Ar′) in the presence of excess PMe_3 always gives tris(phosphine) compounds $(RN)_2M(PMe_3)_3$ (M = Mo, W) existing in solution in equilibrium with the corresponding bis(phosphine) derivative and free PMe_3.

In the case where R = ^{t}Bu, the magnesium reduction of $(^tBuN)_2MoCl_2(DME)$ in the presence of 5 to 7 equiv of PMe_3 affords a mixture of a new bis(phosphine) compound $(^tBuN)_2Mo(PMe_3)_2$ (**2a**) and the previously reported dimer $[(^tBuN)(PMe_3)Mo(\mu\text{-}N^tBu)]_2$. The yield of **2a** increases when more phosphine is used. Addition of excess PMe_3 to $[(^tBuN)(PMe_3)Mo(\mu\text{-}N^tBu)]_2$ does not convert it into monomeric **2a**, even upon heating to 70 °C for several days. However, we found that very prolonged heating (3 weeks) of a mixture of (**2a**) and $[(^tBuN)(PMe_3)Mo(\mu\text{-}N^tBu)]_2$ at 70 °C results in selective decomposition of the latter into insoluble product(s) of unknown composition, leaving **2a** as the single component of the solution. Interestingly, there is no formation of free phosphine during this decomposition, suggesting that the product is a higher oligomer of $\{(^tBuN)_2(PMe_3)Mo\}$ having the same composition. Furthermore, in the presence of excess PMe_3, degradation of $[(^tBuN)(PMe_3)Mo(\mu\text{-}N^tBu)]_2$ slows significantly, suggesting that phosphine elimination is the rate determining step. In summary, the thermolysis of a mixture of **2a** and

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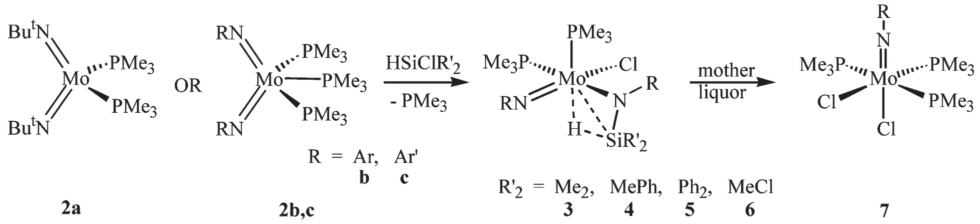

Scheme 2. Reactions of $(RN)_2Mo(PMe_3)_3$ with Silanes $HSiR'_2Cl$ and $HSiMeCl_2$

Table 1. Selected NMR Data for the β-Agostic Silylamido Compounds

compound	δ (^{1}H) Mo-H-Si, ppm [J(P−H), Hz]	δ ^{29}Si, ppm [a]	^1J(Si−H),Hz [a]
$(^tBuN)(\eta^2\text{-}^tBuNSiMe_2H)Mo(PMe_3)_2Cl$ (**3a**)	1.4[b,c]	−76.0	93
$(ArN)(\eta^2\text{-}ArNSiMe_2H)Mo(PMe_3)_2Cl$ (**3b**)	0.88 [t, 7.5]	−64.9	97
$(Ar'N)(\eta^2\text{-}Ar'NSiMe_2H)Mo(PMe_3)_2Cl$ (**3c**)	1.68[f] [dd, 3.5, 23.5]	−63.8[f]	98[f]
$(^tBuN)(\eta^2\text{-}^tBuNSiMePhH)Mo(PMe_3)_2Cl$ (**4a**)	1.83 [b,c,e]	−79.9	94
$(Ar'N)(\eta^2\text{-}Ar'NSiMePhH)Mo(PMe_3)_2Cl$ (**4b**)	2.14[c,d] [t, 22]	−69.3[d]	98[d]
$(^tBuN)(\eta^2\text{-}^tBuNSiMeClH)Mo(PMe_3)_2Cl$ (**6a**)	1.45 [dd, 3.6, 0.9]	−74.2	123
$(ArN)(\eta^2\text{-}ArNSiMeClH)Mo(PMe_3)_2Cl$ (**6b**)	1.23[b,c,f]	−68.7[f]	130[f]
$(Ar'N)(\eta^2\text{-}Ar'NSiMeClH)Mo(PMe_3)_2Cl$ (**6c**)	2.02[g] [dd, 4, 20]	−70.1	129
		−70.5[f]	135.6[f]

[a] At room temperature unless otherwise stated. [b] The signal is obscured by other resonances. [c] Found from $^1H-^{29}Si$ HMQC. [d] At −40 °C. [e] At −20 °C. [f] At −50 °C. [g] At −70 °C.

$[(^tBuN)(PMe_3)Mo(\mu\text{-}N^tBu)]_2$ allows for the production of pure compound **2a**.

Reactions of $(RN)_2Mo(PMe_3)_n$ (n = 2,3) with Mono- and Dichlorosilanes. Molybdenum compounds $(RN)_2Mo(PMe_3)_n$ (**2**; n = 2, R = Bu^t (**a**); n = 3, Ar (**b**); n = 3, Ar' (**c**)) react with mono- and dichlorosilanes to give exclusively the β−Si-H agostic compounds $(RN)(\eta^3\text{-}RN{-}SiR'_2H\cdots)MoCl(PMe_3)_2$ (R'_2 = Me_2 (**3a-c**), MePh (**4a-c**), Ph_2 (**5a-c**), MeCl (**6a-c**), Scheme 2). The isomeric silyl hydride compounds $(RN)_2Mo(SiR'_2Cl)H(PMe_3)$ were not observed even when the reactions were monitored by low temperature NMR.[12] The agostic compounds **3**−**6** are metastable, slowly decomposing in mother liquor to the thermodynamically stable products $(RN)MoCl_2(PMe_3)_3$ (**7**, Scheme 2).[13] The main silicon coproduct of this reaction is the silanimine dimer $(RNSiR'_2)_2$, whose formation manifests productive coupling of the imido ligand with the silane. Similar behavior has been previously observed for silane additions to the isolobal Group 5 compounds $Cp(RN)M(PR'_3)_2$ (R =Ar or Ar'), for which the initial agostic or silyl hydride products were found to be intermediates on the way to dichlorides $Cp(RN)MCl_2(PR'_3)$ and $CpMCl_2(PR'_3)_3$.[4]

The agostic compounds **3**−**6** were characterized by multinuclear NMR, IR, and X-ray structure determinations for compounds **3c** and **6c**.[7] For example, the ^{1}H NMR spectrum of compound **6a** exhibits the agostic $Si-H\cdots M$ hydride as a P-coupled signal at δ 1.45 [dd, J(P−H) = 3.6 Hz, J(P−H) = 0.9 Hz], two nonequivalent ^{t}Bu signals at δ 1.54 (imido) and δ 1.15 (amido), and the SiMe signal at δ 1.19. The agostic hydride gives rise to a band at 1851 cm^{-1} in the IR spectrum. Compounds **3c**, **4a**, **4c**, **5a**, and **6b,c** are fluxional in solution at room temperature.

The formulation of compound **6a** and its congeners as agostic species is unequivocally supported by the measurements of silicon-hydride coupling constants from the ^{29}Si NMR spectra (Table 1). These values are about half of those in the parent silanes but significantly larger than for non-interacting silyl and hydride groups (3−10 Hz).[14] Notably, the J(H−Si) of 97 Hz in **3b** and **3c** is the same as that observed for the isolobal compound $Cp(\eta^3\text{-}ArN{-}SiMe_2H\cdots)NbCl(PMe_3)$.[3a] Chlorine substitution at silicon leads to increased Si−H coupling constants (e.g., 123 Hz in **6a**); however, these increased values do not correspond to a stronger Si−H bonding but are instead a result of rehybridization at the silicon center.[7a]

The rate of silane addition in Scheme 2 appears to be controlled by steric factors. The relatively unhindered compounds **2a** and **2c** react over a period of several hours. Compound **2b** (bearing a more sterically demanding Ar group at nitrogen) reacts with silane $HSiMe_2Cl$ overnight, whereas its reaction with the more hindered HSiMePhCl takes several days and is accompanied by significant decomposition to **7b**. The bulkiest silane studied, $HSiPh_2Cl$, does not react at all with **2b**, even after several days.

The reaction of $(ArN)_2Mo(PMe_3)_3$ with $HSiMeCl_2$ was studied by low temperature NMR in toluene-d$_8$. At −40 °C, the reaction is 30% complete after 5 min. No intermediates or byproduct such as $(ArN)_2Mo(PMe_3)H(SiMeCl_2)$ or a Si−Cl−Mo bridged compound $(ArN)(\eta^2\text{-}ArNSiClH\text{-}Cl\cdots)Mo(PMe_3)_2Cl$ (vide infra) were observed, but traces of the decomposition product **7b** were detected in the ^{31}P NMR spectrum. On warming the

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[12] In the related Nb chemistry, the silyl hydride $Cp(ArN)Nb(PMe_3)H(SiMe_2Cl)$ is the kinetic product of silane addition to $Cp(ArN)Nb(PMe_3)_2$ which has the β-agostic compound $Cp(ArNSiMe_2\text{-}H)Nb(PMe_3)Cl$ as the thermodynamic product (ref 3a).

[13] (a) Compound $(tBuN)MoCl_2(PMe_3)_3$ has been previously prepared by another route: Green, M. L. H.; Konidaris, P. C.; Mountford, P.; Simpson, S. J. *Chem. Commun.* **1992**, 256. (b) X-ray structure of the related compound $(PhN)WCl_2(PPh_3)_3$ is available: Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2651.

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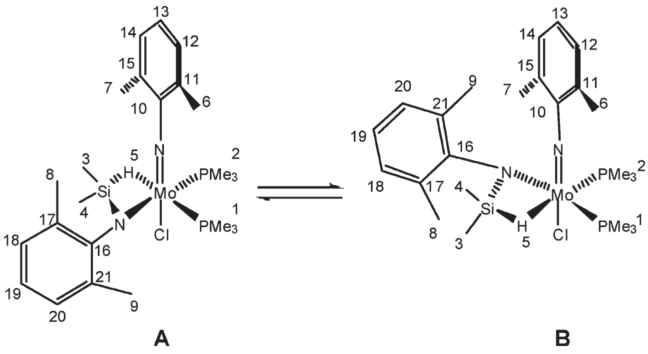
Scheme 3. Degenerate Exchange Equilibrium in Compound **3c** (Two Enantiomers, "**A**" and "**B**")



sample to 0 °C for 5 min, a fluxional agostic product **6b** forms quantitatively. Its ^{1}H NMR spectrum at −50 °C exhibits four nonequivalent signals for the CH protons of the Ar groups. The Si−H−Mo signal at about δ 1.23 is obscured by other groups, but its chemical shift could be determined from a ^{1}H−^{29}Si HMQC experiment. The corresponding ^{29}Si signal is found at δ −68.7 (at −50 °C). When the reaction was scaled up (diethyl ether, room temperature for 30 min) the products were compound **6b** and (ArN)Mo(PMe$_3$)$_3$Cl$_2$.

Variable Temperature (VT) NMR Study of 3c and 6c. As mentioned above, some of the agostic products in Scheme 2 are fluxional. To gain an understanding of the dynamic processes involved, VT NMR studies were performed for compounds **3c** and **6c**.

The room temperature ^{1}H NMR spectrum of **3c** shows only featureless signals in the aliphatic and aromatic regions. Lowering the temperature reveals the presence of only one compound, exhibiting nonequivalent methyl groups in the amido, imido, and silyl ligands. VT ^{1}H and ^{31}P NMR experiments between −40 and + 65 °C revealed the pairwise methyl group exchange processes Me^2 ↔ Me^1, Me^7 ↔ Me^6, Me^8 ↔ Me^9, and Me^3 ↔ Me^4 (see Scheme 3 for the numbering scheme). This exchange is degenerate, in the sense that species **A** and **B** in Scheme 3 are enantiomers and thus are isoenergetic and indistinguishable by NMR. The exchange rates for these four different processes resulted, within experimental error, in the same value of the free energy of activation 13.9(3) kcal mol^{-1} (Table 2).

The coincidence of the exchange rates in the silyl, amido, imido, and phosphine ligands suggests that there is a single, highly correlated mechanism of exchange as summarized in Scheme 4. This appears to proceed via the partial opening of the Si−H···Mo agostic bond, rotation around the N−Mo bond, and is completed by the ring closure on the other side of the compound, as shown in Scheme 4. The $\Delta S^{\ddagger}$ values (Table 2) are all somewhat negative which allows us to rule out phosphine dissociation as a possible step in exchange. The small negative entropy of activation is consistent with the process shown in Scheme 4 as it evidently proceeds via a very organized transition state, highly constrained by steric factors.

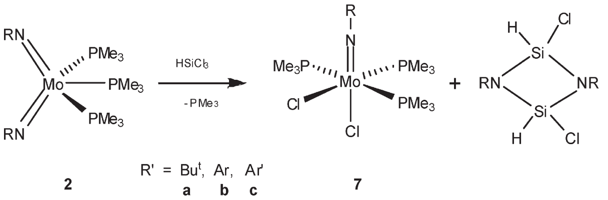
The observed fluxionality of the chlorosilyl derivative **6c** appears to follow the same mechanism. The quantitative analysis proved more difficult for it involves exchange between two diastereomers stemming from the presence of two chiral centers, molybdenum and silicon. Indeed, at −40 °C signals of the second diastereomer were observed by ^{1}H and ^{31}P NMR and coalesced signals were found at positions corresponding to weighted average shifts in the major and minor isomers. Unfortunately, the low abundance of the minor diastereomer (∼5%) hampered quantitative analysis. We, however, succeeded in measuring the rate constant for phosphine group exchange at 0 °C (ca. 120 s^{-1}), which is comparable to the PMe$_3$ exchange for the compound **3c** (ca. 78 s^{-1}) and suggests the occurrence of a similar mechanism.

Table 2. Activation Parameters for the Various Exchange Processes in Compound **3c**[a]

exchanging groups	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})	$\Delta G^{\ddagger}$ (285 K, kcal mol^{-1})
Me^1↔Me^2	10.9(2)	−10(1)	13.9(3)
Me^3↔Me^4	10.8(1)	−11(1)	13.9(2)
Me^6↔Me^7	10.2(3)	−13(1)	13.9(4)
Me^8↔Me^9	9.7(3)	−15(1)	13.9(4)

[a] See Scheme 3 for numbering scheme.

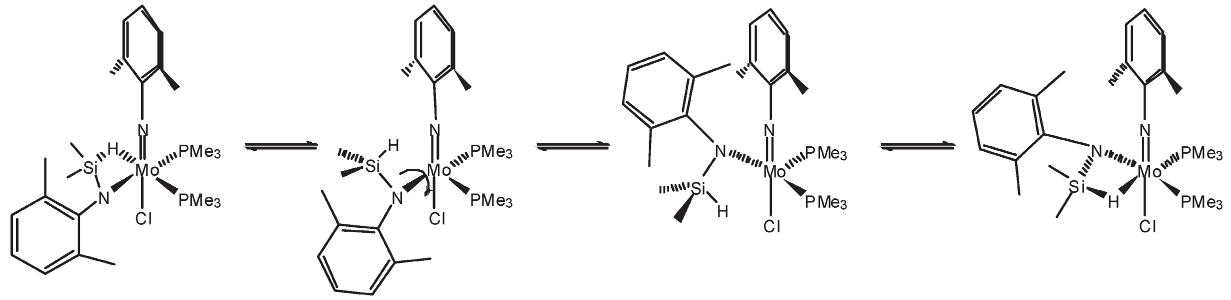
Reactions of (RN)$_2$Mo(PMe$_3$)$_3$ with HSiCl$_3$. Room temperature reactions of molybdenum compounds **2a**−**c** with HSiCl$_3$ afford the corresponding monoimido compounds **7a**−**c** and the silanimine dimers (-RN-SiHCl-)$_2$ (eq 1). Some variable amount of the free amine H$_2$NR was also observed, when the reaction was carried on the NMR tube scale.



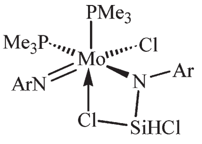
(1)

The reaction of (ArN)$_2$Mo(PMe$_3$)$_3$ with HSiCl$_3$ at low temperature was followed by NMR. At −30 °C, the formation of an initial bis(phopshine) product with two broad ^{31}P NMR singlets of equal intensity at 20.0 and −2.6 ppm was observed. This complex shows a downfield SiH signal at 7.10 ppm coupled in ^{1}H−^{29}Si HSQC with the ^{29}Si NMR signal at −31.8 ppm with ^1J(Si−H) = 337.5 Hz (from ^{29}Si INEPT). The large value ^1J(Si−H) and the fact that neither the SiH signal nor the ^{29}Si NMR signal are coupled to phosphorus suggest that the SiH group is not coordinated to metal. These structural features are consistent with the formation of a silylamido complex (ArN)(ArNSiHCl-Cl···)Mo(PMe$_3$)$_2$Cl (**8b**), which presumably has an additional coordination of one of the Si-bound chlorides to molybdenum, allowing for the formation of a 18e species. We have no evidence for the formation of the Si−Cl−Mo bridge, but this inference is a reasonable alternative to the otherwise 16-electron imido-amido species (ArN)(Ar{Cl$_2$HSi}N)-Mo(PMe$_3$)$_2$Cl. Further warming the reaction mixture to −15 °C − 0 °C leads to a slow rearrangement of the initial product into another bis(phosphine) compound exhibiting a large J(P−P) coupling constant of 223.5 Hz, suggesting the trans arrangement of phosphine ligands. In the ^{1}H NMR spectrum, this derivative shows a downfield SiH signal at 6.01 ppm coupled to one of the phosphines with the ^3J(H−P) = 9.0 Hz and also coupled

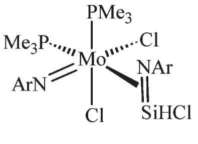
Scheme 4. Mechanism of Enantiomer Exchange for **3c**



(by ^{1}H−^{29}Si HSQC NMR) to the ^{29}Si signal at −42.4 ppm (dd, ^1J(Si−H) = 327.0 Hz, ^2J(Si−P) = 22.1 Hz). The large value of ^1J(Si−H) is consistent with the Si−H bond being uncoordinate to the metal, whereas the large ^2J(Si−P) and small ^3J(SiH-P) constants show that the silicon atom is directly bound to molybdenum. All together these NMR features suggest the formation of a silanimine complex (ArN)(η^2-ArN=SiHCl)Mo(PMe$_3$)$_3$Cl$_2$ (**9b**), which could be a direct precursor to the compound **7b**.[15] Consistent with this description, addition of an equivalent of PMe$_3$ to this mixture results in immediate formation of **7b**.



8b



9b

Reactions of (RN)$_2$W(PMe$_3$)$_3$ with Mono- And Dichlorosilanes. The reactions of the tungsten precursors (RN)$_2$W(PMe$_3$)$_3$ (R = Ar, Ar′) with silanes are more complicated and generally less clean than the analogous reactions of the molybdenum compounds **2a**−**c**. Addition of HSiMeCl$_2$ to (ArN)$_2$W(PMe$_3$)$_3$ (**10b**) in pentane, followed by the immediate removal of volatiles and recrystallization from diethyl ether, allows for the isolation of a yellow crystalline compound (ArN)$_2$W(PMe$_3$)H(SiMeCl$_2$) (**11b**). Compound **11b** was characterized by NMR, IR, and X-ray diffraction analysis. In particular, the W-bound hydride gives rise to a doublet at 10.24 ppm (J(P−H) = 59.5 Hz) flanked by ^{183}W satellites (J(W−H) = 35.0 Hz) in the ^{1}H NMR. The corresponding ν(W−H) band in the IR spectrum is seen at 1731 cm^{-1}. This hydride is coupled to a ^{29}Si NMR signal at 92.0 ppm (d, J(P−Si) = 7.5 Hz) with a coupling constant of −37 Hz. Such an increased magnitude of J(H−Si) compared to values observed in classical silyl hydride complexes (0−10 Hz)[1] suggests the presence of nonclassical Si−H bonding.[1e] Moreover, the negative sign of this coupling constant, measured by us in this study, is in accord with the presence of *direct* Si−H bonding.[16] Analogous negative J(Si−H) values with increased magnitudes have been previously found for the isolobal compounds Cp$_2$Ti(PMe$_3$)H(SiClR$_2$)[16] and Cp(RN)Ta(PMe$_3$)H(SiClR$_2$)[3b] which both exhibit an interligand hypervalent interaction (IHIs) between the hydride and silicon centers.[4b,17,18]

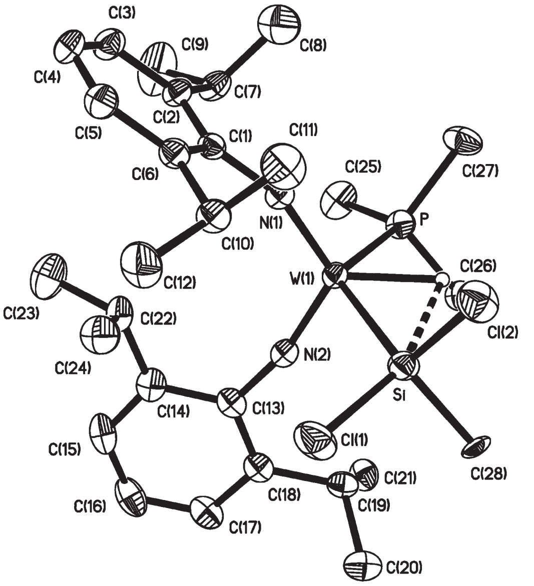


Figure 1. Molecular structure of compound **11b**. Hydrogen atoms, apart from the hydride, are omitted for clarity. Selected distances (Å) and angles (deg): W1−N2 1.779(3), W1−N1 1.789(3), W1−P 2.4778(9), W1−Si 2.5106(9), W1−H 1.78(4), Si−C28 1.900(3), Si−Cl2 2.0710(14), Si−Cl1 2.1075(13), N2−W1−N1 121.02(12), N2−W1−P 96.97(8), N1−W1−P 110.38(8), N2−W1−Si 96.16(8), N1−W1−Si 107.55(8), P−W1−Si 124.91(3), P−W1−H 66.6(13), Si−W1−H 60.2(13), Cl2−Si−Cl1 102.38(6), C28−Si−W1 115.28(11), Cl2−Si−W1 115.43(5), Cl1−Si−W1 113.25(5).

The molecular structure of **11b** is shown in Figure 1. The structure is isolobal with the previously structurally characterized compounds Cp$_2$Ti(PMe$_3$)H(SiCl$_2$Me)[16] and Cp(ArN)Ta(PMe$_3$)H(SiCl$_2$Me).[3b] Like the latter compounds, the phosphine, hydride, and silyl ligands lie in the bisecting plane of the pseudometallocene fragment (ArN)$_2$W.[6] The silyl ligand is oriented in such a way that one of the chloride substituents lies approximately trans to the hydride. This chloride forms a longer Si−Cl bond of 2.107(2) Å compared with the other Si−Cl (Si−Cl(2) = 2.071(2) Å). These values correspond well to the Si−Cl

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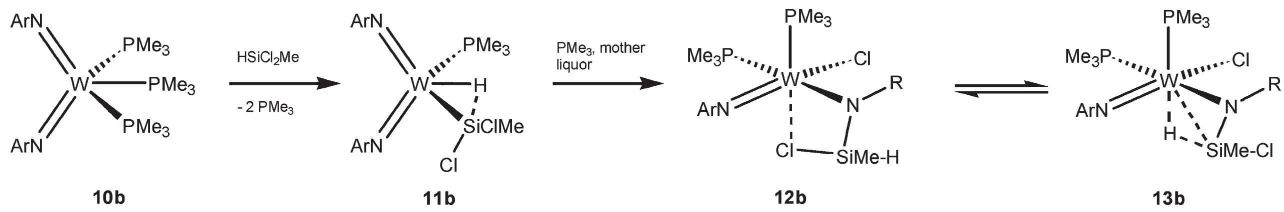
[15] For isolated silanimine complexes LnM(η^2-RNSiR′$_2$) see: (a) Procopio, L. J.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1991**, *113*, 1870–1872. (b) Procopio, L. J.; Carroll, P. J.; Berry, D. H. *Polyhedron* **1995**, *14*, 45–55. (c) For a transient silanimine complex see ref 7b.

[16] Ignatov, S. K.; Rees, N. H.; Tyrrell, B. R.; Dubberley, S. R.; Razuvaev, A. G.; Mountford, P.; Nikonov, G. I. *Chem.—Eur. J.* **2004**, *10*, 4991.

[17] Ignatov, S. K.; Rees, N. H.; Merkoulov, A. L.; Dubberley, S. R.; Razuvaev, A. G.; Mountford, P.; Nikonov, G. I. *Organometallics* **2008**, *27*, 5968–5977.

[18] Negative J(H-Si) was calculated for silane σ-complexes Cp(Me$_3$P)Ru(Cl)(η^2-HSiR$_3$): Osipov, A. L.; Vyboishchikov, S. F.; Dorogov, K. Y.; Kuzmina, L. G.; Howard, J. A. K.; Lemenovskii, D. A.; Nikonov, G. I. *Chem. Commun.* **2005**, 3349.

Scheme 5. Preparation of Compounds **11b** and **12b**



bonds in the related nonclassical compound Cp(ArN)Ta(PMe_3)H($SiCl_2Me$), 2.117(2) Å and 2.064(3) Å, respectively.[3c] The W−Si bond length (2.5108(13) Å) is relatively short in comparison to other silyl compounds of tungsten (range 2.533−2.685 Å),[19] although precise comparisons are not possible because none of the latter contain a dichlorosilyl ligand and/or supporting imido ligand.[20] The short M−Si bond and the elongated Si−Cl bond trans to the hydride are characteristic features of IHIs.[1e,3,4,16] The W−H bond length of 1.78(6) Å lies within normal ranges. Although the experimentally determined Si−H distance of 2.283 Å is too long to suggest the presence of a significant Si−H interaction, it should be taken into account that the precise location of a hydride in a heavy element environment is subject to significant uncertainty.

Monitoring the reaction between $HSiMeCl_2$ and $(ArN)_2W(PMe_3)_3$ by NMR shows that at room temperature **11b** forms within minutes but then decomposes *in the mother liquor* over 20−30 min into a new, highly fluxional bis(phosphine) compound **12b**. In contrast, pure **11b** is stable in solution for at least several hours. The salient feature of **12b** is that at −40 °C its ^1H NMR spectrum exhibits a downfield signal for the Si−H bond at 5.78 ppm (q, $J(H-H) = 2.4$ Hz) coupled to the Me signal at 0.19 ppm (d, $J(H-H) = 2.4$ Hz). The large value of $J(H-Si) = 264$ Hz clearly establishes that this Si−H bond is not coordinated to the metal. The corresponding ^{29}Si signal appears at 41.8 ppm. The presence of two chemically nonequivalent phosphine ligands in the ^{31}P NMR spectrum and the observation of three methine C−H signals in the ratio 1:2:1 in the ^1H NMR spectrum allow us to rule out unequivocally the formation of a compound such as $(ArN)_2W(PMe_3)Cl(SiMeClH)$ that would be isolobal to $Cp(ArN)Nb(PMe_3)Cl(SiMeClH)$.[3c] The spectroscopic data can best be rationalized in terms of the formation of a fluxional SiCl-W bridged species $(ArN)(\eta^2\text{-ArNSiMeH-Cl}\cdots)W(PMe_3)_2Cl$ (**12b**), similar to the Mo compound **8b** discussed above.[21] Interestingly, the ^{29}Si NMR spectrum measured at room temperature overnight showed the presence of a Si−H−W agostic signal at −90.6 ppm (d, $J(H-Si) = 92$ Hz) in addition to other signals. These signals come from the thermal decomposition of **12b**.

These observations are consistent with the reaction sequence presented in Scheme 5. The silyl hydride compound **11b** is formed as a kinetic product, which then reacts with an equivalent of phosphine to give **12b**. The latter slowly rearranges to (or is in equilibrium with) a *β*-Si-H agostic compound $(ArN)(\eta^2\text{-ArNSiClMe-H}\cdots)W(PMe_3)_2Cl$ (**13b**). This behavior is reminiscent of the reactions of the isolobal niobium compounds Cp(RN)Nb(PMe_3)$_2$ with silanes, where the initially formed compounds $Cp(RN)Nb(SiR'_2Cl)H(PMe_3)$ rearrange into the agostic product $Cp(\eta^2\text{-RN-SiR}'_2\text{-H}\cdots)NbCl(PMe_3)$ (for $R'_2 = Me_2$, MePh) or to the silyl chloride compounds Cp(RN)Nb(SiMeClH)Cl(PMe_3) in the case of $R'_2 = MeCl$. Both of these reactions are catalyzed by PMe_3.[4] The rearrangement proceeds via the same Lewis acid−base adduct/intermediate $Cp(RN\{\rightarrow SiMe_{2-n}Cl_nH\})Nb(PMe_3)_2$ that is formed upon silane addition to the imido nitrogen of $Cp(RN)Nb(PMe_3)_2$.[4] The only difference between this and tungsten chemistry is that a silyl chloride product of the type $(ArN)_2W(PMe_3)Cl(SiMeClH)$ is not formed according to the NMR data.

In accordance with this mechanism, the addition of PMe_3 to a solution of pure $(ArN)_2W(PMe_3)H(SiMeCl_2)$ (**11b**) results in immediate color change from yellow to brown and the formation of a mixture of compounds composed of **12b**, the starting compound $(ArN)_2W(PMe_3)_3$, and the free silane.

The reaction between $HSiCl_2Me$ and the less hindered precursor $(Ar'N)_2W(PMe_3)_3$ affords the agostic compound $(Ar'N)(\eta^3\text{-Ar}'\text{NSiClMe-H}\cdots)W(PMe_3)_2Cl$ (**13c**, eq 2). Compound **13c** was isolated in the form of dark crystals and characterized by NMR and IR spectroscopy. In contrast to its Mo analogue **6c** (Scheme 2), **13c** is non-fluxional at room temperature. Two nonequivalent

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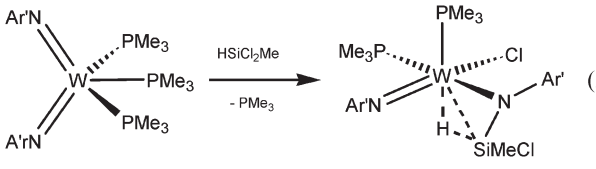
(19) (a) Sakaba, H.; Hirata, T.; Kabuto, C.; Horino, H. *Chem. Lett.* **2001**, 1078. (b) Sakaba, H.; Tsukamoto, M.; Hirata, T.; Kabuto, C.; Horino, H. *J. Am. Chem. Soc.* **2000**, *122*, 11511. (c) Ueno, K.; Sakai, M.; Ogino, H. *Organometallics* **1998**, *17*, 2138. (d) Figge, L. K.; Carrol, P. J.; Berry, D. H. *Organometallics* **1996**, *15*, 209. (e) Malisch, W.; Schmitzer, S.; Lankat, R.; Neumayer, M.; Prechtl, F.; Adam, W. *Chem. Ber.* **1995**, *128*, 1251. (f) Koloski, T. S.; Pestana, D. C.; Carrol, P. J.; Berry, D. H. *Organometallics* **1994**, *13*, 489. (g) Schmitzer, S.; Weis, U.; Käb, H.; Buchner, W.; Malisch, W.; Polzer, T.; Posset, U.; Kiefer, W. *Inorg. Chem.* **1993**, *32*, 303. (h) H Sharma, S.; Kapoor, R. N.; Cervantes-Lee, F.; Pannell, K. H. *Polyhedron* **1991**, *10*, 1177. (i) Barron, A. R.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *Dalton Trans.* **1987**, 837. (k) Darensbourg, D. J.; Bauch, C. G.; Reibenspies, J. H.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 4203. (l) Heyn, R. H.; Tilley, T. D. *Inorg. Chem.* **1990**, *29*, 4051. (m) Suzuki, E.; Okazaki, M.; Tobita, H. *Chem. Lett.* **2005**, *34*, 1026. (n) Begum, R.; Komuro, T.; Tobita, H. *Chem.Commun.* **2006**, 432. (o) Wagner, H.; Baumgartner, J.; Marschner, C. *Organometallics* **2005**, *24*, 4649. (p) Wang, B.; Zhu, B.; Xu, S.; Zhou, X. *Organometallics* **2003**, *22*, 4842. (q) Palitzsch, W.; Beyer, C.; Bohme, U.; Rittmeister, B.; Roewer, G. *Eur. J. Inorg. Chem.* **1999**, 1813. (r) Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2004**, *126*, 4375. (s) Ueno, K.; Asami, S.; Watanabe, N.; Ogino, H. *Organometallics* **2002**, *21*, 1326. (t) Ueno, K.; Sakai, M.; Ogino, H. *Organometallics* **1998**, *17*, 2138.

(20) There has been described only one silyl derivative of tungsten supported by the bis(imido) ligand set, $(ArN)_2W(Si\{SiMe_3\}_3)(CH_2CH_3)$, but its structure is not known. In the molybdenum analogue, the Mo-Si bond is 2.6048(9) Å; Casty, G. L.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1997**, *16*, 4746.

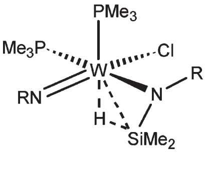
(21) Again, as in the case of molybdenum compound (ArN)(ArNSiClH-Cl···)Mo(PMe_3)$_2$Cl (**8b**), we have no direct evidence of the chloride lone pair donation to tungsten, but the formation of a Si-Cl···W bridge appears to be a good alternative to the otherwise 16e compound (ArN)(ArNSiMeHCl)W(PMe_3)$_2$Cl.

phosphines give rise to doublets (J(P−P) = 14 Hz) at −20.7 ppm and −29.9 ppm, flanked by ^{183}W satellites (J(P−W) = 204 and 168 Hz, respectively). The agostic W···$\underline{\text{H}}$-Si hydride is seen in the ^{1}H NMR as a multiplet at 2.46 ppm coupled to the Si-Me group and two phosphorus atoms (ddq, J(P−H) = 16.7 Hz, J(H−H) = 1.5 Hz, J(P−H) = 0.6 Hz). The corresponding ^{29}Si signal was found at −77.5 ppm. The H−Si coupling constant of 118 Hz determined from the ^{1}H-coupled ^{29}Si NMR unequivocally establishes the presence of an agostic W···H−Si interaction. The silyl hydride compound (Ar′N)$_2$W(PMe$_3$)H(SiMeCl$_2$) and the Si−Cl−W bridged compound (Ar′N)(η^2-Ar′NSiMeH-Cl···)W(PMe$_3$)$_2$Cl, which would be analogous to the products **11b** and **12b** formed in the corresponding reactions of (ArN)$_2$W(PMe$_3$)$_3$ (Scheme 5), were not observed.



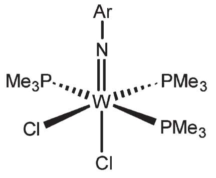
10c **13c** (2)

Addition of HSiClMe$_2$ to a pentane solution of (Ar′N)$_2$W(PMe$_3$)$_3$ affords a mixture of products, the predominant component of which is a highly fluxional agostic compound (Ar′N)(η^2-Ar′NSiMe$_2$−H···)WCl(PMe$_3$)$_3$ (**14c**) characterized by its ^{29}Si NMR signal at −68.3 ppm coupled to the Si-$\underline{\text{H}}$···W resonance at 2.24 ppm (d, J(P−H) = 23.6 Hz, ^1J($\underline{\text{Si}}$−H) = 87 Hz). The analogous reaction of (ArN)$_2$W(PMe$_3$)$_3$ with HSiClMe$_2$ gives an even more complicated mixture containing the agostic compound (ArN)(η^2-ArNSiMe$_2$-H···)WCl(PMe$_3$)$_2$ (**14b**), the dichloride (ArN)WCl$_2$(PMe$_3$)$_3$ (**15b**), and some other unidentified compounds. Compound (ArN)(η^2-ArNSiMe$_2$-H···)WCl(PMe$_3$)$_2$ is fluxional at room temperature. It was characterized by a ^{29}Si NMR signal at δ −70 ppm (J(Si−H) = 81 Hz, J(Si−P) = 9 Hz). Another compound, giving rise to a ^{29}Si NMR signal at δ −9.8 ppm with the J(Si−H) = 199 Hz, contains a free SiMe$_2$H group but other details of its structure are not known. Attempted separation of this mixture by recrystallization afforded only complex **15b** as the final decomposition product.

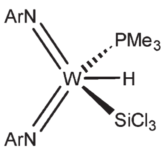


R = Ar Ar′

14b **14c**



15b



16b

Reactions of HSiCl$_3$ with (RN)$_2$W(PMe$_3$)$_3$. The reactions of (RN)$_2$W(PMe$_3$)$_3$ (R = Ar, Ar′) with HSiCl$_3$ afford the corresponding mono(imido) derivatives (RN)WCl$_2$(PMe$_3$)$_3$ (**15**) as the final products, but are generally less clean. Addition of HSiCl$_3$ to (ArN)$_2$W(PMe$_3$)$_3$ at room temperature results in a fast (few minutes) color change from purple to brown and the formation of a mixture of compounds, the main component of which is (ArN)WCl$_2$(PMe$_3$)$_3$ (**15b**). Apart from the latter compound, there are also other products formed, but their identities remain unknown. Similarly, (Ar′N)$_2$W(PMe$_3$)$_3$ (**10c**) reacts rapidly with HSiCl$_3$ (5 min) to furnish (Ar′N)WCl$_2$(PMe$_3$)$_3$ (**15c**) and (Ar′NSiHCl)$_2$ as the final products.

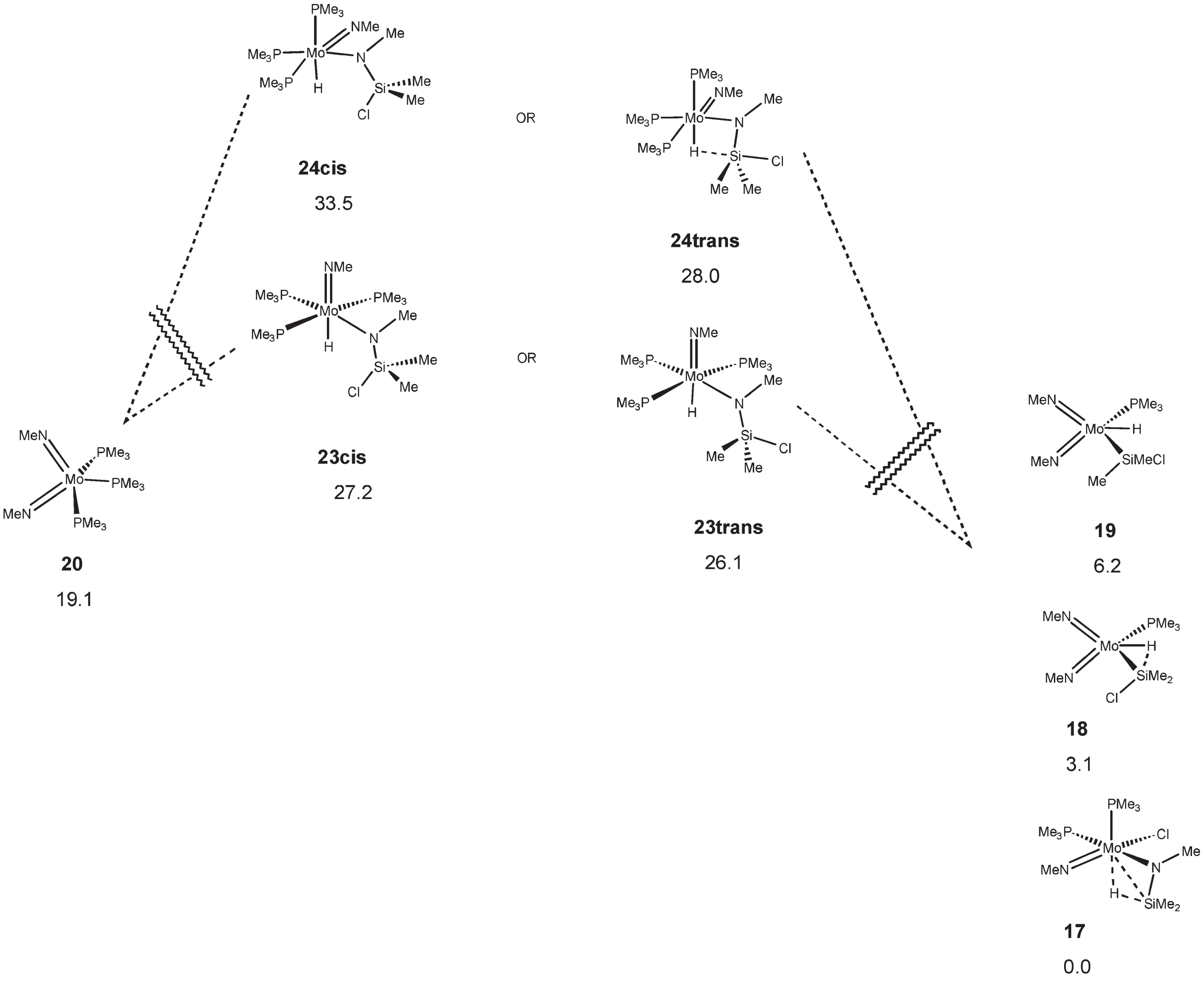
Unlike the related Mo chemistry, when (ArN)$_2$W(PMe$_3$)$_3$ reacts with HSiCl$_3$ in the presence of BPh$_3$ at low temperature, the initial product observed at −20 °C is the silyl hydride (ArN)$_2$W(H)(SiCl$_3$)(PMe$_3$) (**16b**). This compound shows a W-bound hydride at 11.04 ppm coupled to phosphine (^2J(H−P) = 58.8 Hz) and tungsten (J(W−H) = 31.8 Hz) but only weakly coupled to the ^{29}Si signal at 73.8 ppm (the cross-peak in ^{1}H−^{29}Si HSQC NMR is observed only when a small J(Si−H) = 7 Hz is used). These structural features resemble strongly the pattern observed for the silyl hydride complex **11b**. Upon the increase of temperature to room temperature, this product decomposes to a mixture of **15b** and several uncharacterized hydride species.

Density Functional Theory (DFT) Calculations. At first sight, the transformations described above for the Group 6 (RN)$_2$M(PMe$_3$)$_n$ (n = 2,3) systems are similar to the previously described reactions of Cp(RN)M(PMe$_3$)$_2$ (M = V, Nb, Ta) with silanes.[3,4] The significant difference, however, is that molybdenum compounds (RN)$_2$Mo(PMe$_3$)$_n$ (**2**; R = Ar, Ar′, Bu^t) react with mono- and dichlorosilanes HSiCl$_n$R′$_{3-n}$ (n = 1,2) to give exclusively the agostic compounds (RN)(η^3-RN−SiR′$_2$H···)MoCl(PMe$_3$)$_2$ (R = Ar, Ar′, Bu^t), whereas reactions of their niobium analogues Cp(RN)Nb(PMe$_3$)$_3$ (R = Ar, Ar′) afford a variety of products, namely Cp(RN)Nb(PMe$_3$)H(SiR$_3$), Cp(η^3-RN-SiR″$_2$-H···)Nb(PMe$_3$)Cl, and Cp(RN)Nb(PMe$_3$)Cl(SiRHCl), whose identity depends on the substituents at silicon and reaction conditions. In contrast, the tantalum congener forms only the silyl hydride derivatives Cp(RN)Ta(PMe$_3$)H(SiR$_3$) and, in a few cases, silyl chloride compounds Cp(RN)Ta(PMe$_3$)Cl(SiRHCl), whereas the reactions of the tungsten compounds (RN)$_2$W(PMe$_3$)$_3$ (R = Ar, Ar′) with HSiMe$_2$Cl and HSiMeCl$_2$ give several silyl hydride and agostic silylamido products. This difference between the 4d and 5d metals reflects (i) the better ability of the heavier metals to stabilize higher oxidation states and (ii) the diminished propensity of Group 6 metals to be in the highest Group oxidation state (VI) in comparison with Group 5 metals.

Our previous studies of the mechanism of silane addition to compounds Cp(RN)Nb(PMe$_3$)$_2$ revealed that the reaction goes via direct addition of silane to the imido moiety to give the intermediate Cp(RN)(RN→SiR$_2$ClH···)NbCl(PMe$_3$)$_2$ with a pentacoordinate silicon center, supported by agostic Si−H···Nb bonding rather than via phosphine dissociation followed by Si−H oxidative addition to the metal.[4] To shed more light on the mechanism of silane addition to Group 6 bis(imido) compounds and the bonding situation in the various products formed, we carried out DFT calculations on model compounds featuring a Me group on the imido center (Scheme 6).

In accord with our experimental observations, the most stable product of the addition of HSiMe$_2$Cl to the model compound (Me)$_2$Mo(PMe$_3$)$_3$ (**20**) is the agostic compound (MeN)(η^2-MeNSiMe$_2$-H···)MoCl(PMe$_3$)$_2$

Scheme 6. Non-Dissociative (with Regard to PMe_3) Pathways to Agostic Compound **17**[a]



[a] Gibbs free energies are expressed in kcal mol^{-1}.

(**17**, Scheme 6, Table 3). Next comes the silyl hydride derivative $(MeN)_2Mo(PMe_3)H(SiMe_2Cl)$ (**18**), having the chloride trans to the hydride ligand and stabilized by IHI. A "rotamer" of **18**, in which the silyl is rotated in such a way that chloride is cis to the hydride, *cis*-$(MeN)_2Mo(PMe_3)H(SiMe_2Cl)$ (**19**), does not have IHI and is further destabilized by 3.1 kcal/mol. All these compounds are thermodynamically allowed products.

As in our previous studies,[4] we considered two mechanisms of silane addition. The "text book" mechanism is based on phosphine(s) elimination from $(MeN)_2Mo(PMe_3)_3$ to give an unsaturated intermediate(s) that can add the Si–H bond to the metal center. An alternative mechanism which we have already described for related Cp/imido compounds of Group 5 metals[4,17] involves addition of the silane as a Lewis acid to the basic nitrogen center of the imido ligand to give a pentacoordinate silicon species which then transforms to products via Si–H or Si–Cl activation. Attempts to find an intermediate or transition state for direct addition of silane to the metal to give, for example, product **18** were unsuccessful.

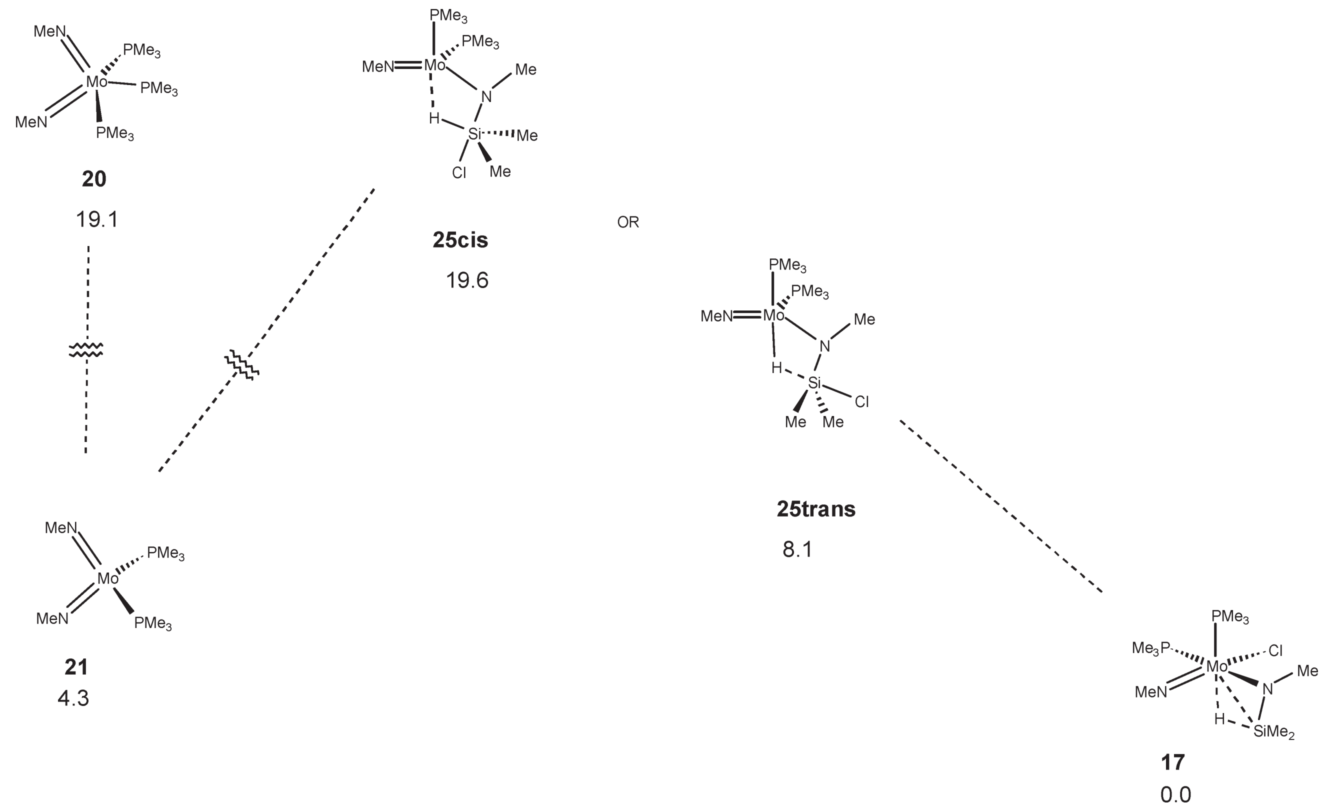
Table 3. Selected Interatomic Distances (Å) of the Mo Structures **17**–**22**

	structures					
	17	**18**	**19**	**20**	**21**	**22**
Mo–N^{im}	1.773	1.774	1.780, 1.773	1.838, 1.840	1.796	1.767
Mo–N^{am}	2.097					
Mo–P	2.465, 2.520	2.478	2.471	2.504, 2.508, 2.399[a]	2.414	2.435
Mo–H	1.946	1.766	1.751			
Mo–Si	2.664	2.503	2.513			
Mo–Cl	2.612					
Si–N	1.713					
Si–H	1.621	2.163	2.203			
Si–Cl		2.145	2.128			

[a] Central phosphine.

The main difference between the compound $(MeN)_2Mo(PMe_3)_3$ (**20**) and its Group 5 analogues $Cp(MeN)M(PMe_3)_2$ (M = Nb, Ta) is that the former has three phosphine ligands. Therefore, two dissociative and two associative pathways should be considered. Dissociation of one PMe_3 from **20** to give the bis(phosphine)

Scheme 7. Dissociative (with Regard to PMe_3) Pathway to Agostic Compound **17**[a]



[a] Gibbs free energies are expressed in kcal mol^{-1}.

$(MeN)_2Mo(PMe_3)_2$ (**21**) is a very thermodynamically profitable process (by 14.8 kcal mol^{-1}, Scheme 7), which accounts for the observed fluxionality of our starting tris(phosphines) **2b**,**c** and the fact that the *tert*-butylimido compound **2a** is a bis(phosphine) compound. In contrast, further phosphine dissociation from **21** to give a formally 14e species $(MeN)_2Mo(PMe_3)$ (**22**) costs 24.7 kcal mol^{-1}, which suggests that compound **21** is the most attractive candidate for silane addition. Nevertheless, in our first set of calculations we considered addition of $HSiClMe_2$ to both **20** and **21**.

Addition of $HSiClMe_2$ to the Mo=N bond of **20** affords a silylamido hydride compound (Scheme 6). Because this product is pseudo-octahedral, several isomers are possible. To minimize the computational cost, we assumed that the original cis arrangement of imido groups is preserved in the product. This assumption leads to two options: the hydride goes trans to imido to give the *mer*-isomer **23** or the hydride adds trans to a phosphine ligand as in the *fac*-isomer **24**.

For each isomer (**23**, **24**), we considered two possible rotamers, depending on the orientation of the silyl ligand (Scheme 6). The trans-rotamers, in which the Si-bound chloride is trans to the hydride on molybdenum (**23trans** and **24trans**) are preferred to cis rotamers; and compounds with a trans imido/hydride arrangement are preferred to trans hydride/phosphines. This selectivity is hard to rationalize in term of trans-influence because the most stable compounds **23cis** and **23trans** and the least stable compound **24cis** are virtually hydride derivatives (Mo−H: 1.806 Å, 1.837 Å, and 1.712 Å, respectively; Si···H: 3.347 Å, 2.852 Å, and 3.088 Å, respectively; Table 4), that is, have the strongest trans-influence ligands (imido and hydride) trans to each other. The Si−H distances are long, primarily as a result of very opened Mo−N−Si bond angles (139.0, 125.1, and 126.7°, respectively), which helps to minimize the interligand repulsion. The compound with an intermediate stability, **24trans**, has an acute Mo−N−Si bond angle (110.3°) but the Si−H distance (2.510 Å) is still too long to qualify for a Si···H interaction. It thus appears that the structure of the initial product of silane addition to **20** is determined primarily by steric factors.

Addition of $ClSiMe_2H$ to the bis(phosphine) $(MeN)_2$-$Mo(PMe_3)_2$ (**21**) is much more favorable and affords a trigonal bipyramidal silylamido hydride species stabilized by an additional interaction between the hydride and the silicon atom (Scheme 7). We again considered two orientations for silane addition. Silane attack on the imido group with the chloride lying cis to the hydride affords a silane/imido adduct **25cis** featuring a penta-coordinate silicon center with apical N and Cl groups (N−Si−Cl bond angle equals 155.4°). The hydride is found in the bridging position, forming elongated bonds to both molybdenum and silicon (1.838 Å and 1.610 Å, respectively). This additional agostic Mo···H−Si interaction, also found in related Cp/imido compounds of Nb and Ta,[4,17] helps to stabilize the silane/imido adduct. As a result of a strong Si−N interaction (1.832 Å), the trans Si−Cl bond is significantly elongated to 2.393 Å.

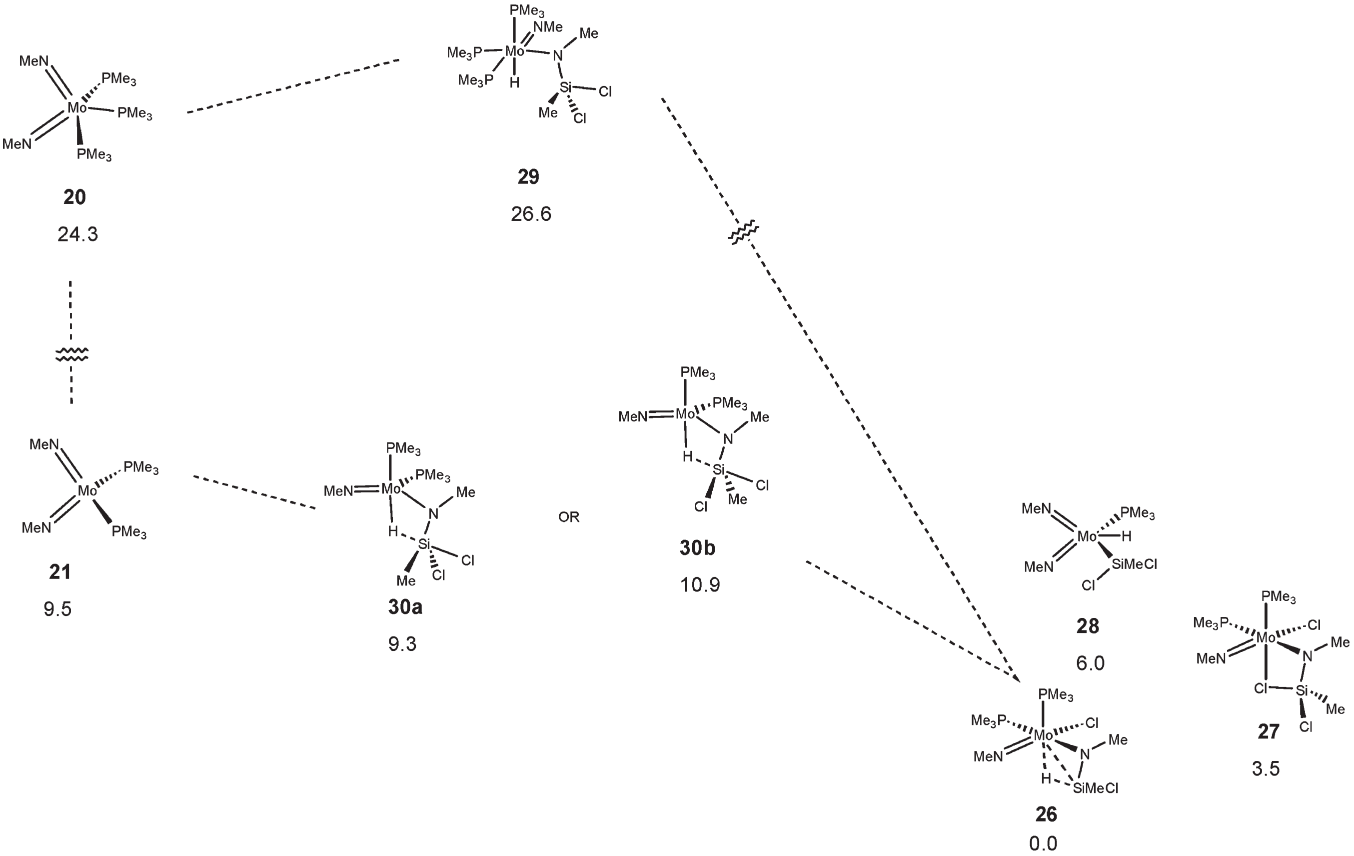
A more favorable isomer, **25trans**, lying only 3.8 kcal mol^{-1} above the starting bis(phosphine) compound **21**, is formed when silane adds to the imido center, bearing the chloride trans to the hydride atom. In this case, a more

Table 4. Selected Interatomic Distances (Å) for the Mo Structures **23**−**25**

	structures					
	23cis	**23trans**	**24cis**	**24trans**	**25cis**	**25trans**
Mo−N^{im}	1.792	1.791	1.750	1.748	1.763	1.753
Mo−N^{am}	2.200	2.163	2.131	2.110	1.964	2.025
Mo−P trans to imido	2.514[a]	2.549 [a]	2.817	2.840		
Mo−P trans to amido or vacant site	2.399	2.403	2.510	2.529	2.452	2.436
Mo−P trans to hydride	2.520[a]	2.549 [a]	2.514	2.536	2.485	2.549
Mo−H	1.806	1.837	1.712	1.736	1.838	1.747
Mo−Si	3.662	3.440	3.449	3.050	2.779	
Si−N	1.706	1.706	1.723	1.720	1.832	1.748
Si−H	3.347	2.852	3.088	2.510	1.610	2.114
Si−Cl	2.109	2.143	2.108	2.164	2.393	2.185

[a] This phopshine is trans to another phosphine.

Scheme 8. Dissociative and Non-Dissociative (with Regard to PMe$_3$) Pathways to Agostic Compound **26**[a]



[a] Gibbs free energies are expressed in kcal mol^{-1}.

advanced Si−H activation occurs, leading to a longer Si−H distance of 2.114 Å and a stronger Mo−H bond of 1.747 Å (Table 4). The geometry at silicon still can be described as penta-coordinate, with the chloride lying trans to the hydride and forming a H−Si−Cl bond angle of 175.2°. The computed Si−Cl bond length of 2.185 Å is elongated relative to experimental Si−Cl bonds in monochloro organosilanes (2.02 Å) but is comparable to values found in compounds where the Si−Cl bond is involved in hypervalent interactions.[22]

A qualitatively similar picture was observed for the addition of the dichlorosilane HSiCl$_2$Me (Scheme 8). The most stable product is the Si−H···Mo agostic compound **26** which is 3.5 kcal mol^{-1} more stable than the Si−Cl···Mo bridged isomer **27**, which is in turn structurally analogous to the proposed tungsten compound **12b** (Scheme 5). Structure **26** is also 6 kcal mol^{-1} more stable than the silyl hydride compound **28**, explaining why we do not observe this species in the experimental system. Given that the dissociative (with regard to PMe$_3$) pathway of silane addition is favorable (see above), we assessed only one regioisomer of the HSiCl$_2$Me attack on the tris(phosphine) **20**, namely, that having the Si−Cl bond trans to hydride. This intermediate is the silylamido hydride

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(22) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chap. 20.

Table 5. Selected Interatomic Distances (Å) for the Mo Structures **26**−**30**

	26	**27**	**28**	**29**	**30a**	**30b**
Mo−N^{im}	1.745	1.748	1.775, 1.770	1.748	1.752	1.746
Mo−N^{am}	2.103	2.100		2.135	2.029	2.029
Mo−P trans to imido				2.830		
Mo−P trans to amido	2.519	2.524		2.523	2.437[a]	2.434[a]
Mo−P trans to hydride	2.452		2.482 (trans to silyl)	2.526	2.533	2.537
Mo−H	1.982		1.763	1.733	1.752	1.756
Mo−Si	2.657	3.056		3.162	2.935	2.918
Mo−Cl	2.606	2.823				
Si−N	1.671	1.688		1.692	1.728	1.729
Si−H	1.578	1.494		2.552	1.933	1.937
Si−Cl	2.105	2.157	2.107, 2.123 (trans to H)	2.132, 2.130 (trans to H)	2.127, 2.171 (trans to H)	2.122, 2.174 (trans to H)

[a] This phosphine lies in the MoN_2P plane.

derivative **29**, closely resembling the monochloride analogue **24trans** (Scheme 6). Although the geometry at silicon can be seen as a highly distorted trigonal bipyramid (the sum of bond angles in the "equatorial plane" NSiClMe is 342.23°) with a chloride and the hydride in the apical positions, the long Si···H distance of 2.552 Å indicates the absence of any significant interaction. Also, there is no difference between the "apical" and "equatorial" Si−Cl bonds lengths of 2.130 and 2.132 Å, respectively (Table 5). The geometry of this species is evidently dictated by the steric hindrance of the octahedral Mo center. This intermediate lies 2.3 kcal mol^{-1} above the starting compound **20**, which suggests that competitive $HSiMeCl_2$ addition to the residual tris(phosphine) compound **2** present in the real reaction mixture could be possible.

For the more favorable addition of $HSiCl_2Me$ to the bis(phosphine) **21** we again considered two directions of attack. Attempted optimization of the structural analogue of compound **25cis** (Scheme 7), having a chloride group cis to hydride, resulted in compound **30a** (Scheme 8) which, in fact, is structurally analogous to the isomeric compound **25trans**. This intermediate had a Si-bound methyl group on the same side of the HMoSiN plane as the methylimido ligand and is 0.2 kcal mol^{-1} more stable than the starting compound **21**. Another, more sterically encumbered rotamer **30b**, which has the Si-bound methyl group facing the phosphine ligand lies above **30a** by only 1.6 kcal mol^{-1}. Structurally, both **30a** and **30b** are very similar: the Mo−H bond distances are 1.752 and 1.756 Å, respectively, and the Si−H contacts are 1.933 and 1.937 Å, respectively (Table 5). Compared with the corresponding parameters in compound **25trans** (Si−H distance of 2.114 Å, Mo−H bond of 1.747 Å) these data indicate stronger Si−H interactions, possibly, because the more chlorinated fragment $MeCl_2SiN$ is a stronger Lewis acid.

Despite the Si−H contact in **30a** and **30b** being relatively long, the overall geometry at silicon in both rotamers can be still described as pseudotrigonal bipyramidal (the sum of equatorial bond angles is 352.2° and 352.9°, respectively). The observation of a longer Si−Cl bond for the apical chloride (2.171 Å in **30a** and 2.174 Å in **30b**) than for the equatorial chloride (2.127 Å in **30a** and 2.122 Å **30b**) substantiates further this description.

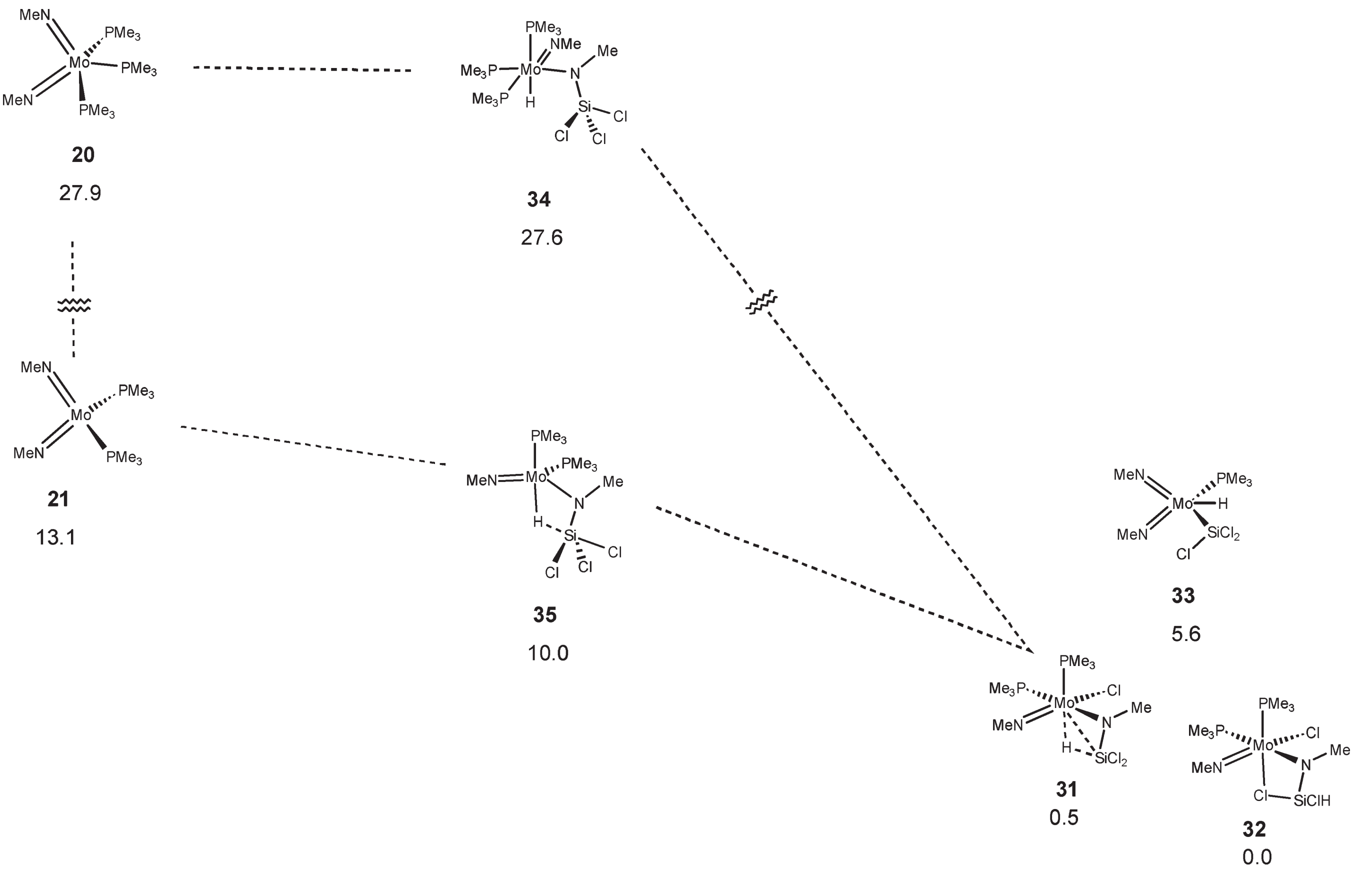
In the case of $HSiCl_3$ addition to **20** and **21**, the Si−H···Mo agostic product **31** is still more thermodynamically stable than the silyl hydride **33** (Scheme 9, Table 6), but very marginally (0.5 kcal mol^{-1}) less stable than the Si−Cl··· Mo bridged compound **32**. This result is in good accord with our inability to observe the analogues of **31** and **33** experimentally and is also in accord with the ease of double SiCl activation in $HSiCl_3$ to give the monoimide $(RN)MoCl_2(PMe_3)_3$ and the silanimine dimer $(RNSiHCl)_2$. The non-dissociative pathway goes via an intermediate **34** which is 0.3 kcal mol^{-1} more stable than the tris(phosphine) **20**. The dissociative pathway, that is, via silane addition to the bis(phosphine) species **21**, goes via the silylamido compound **35**. As in the case of $HSiMeCl_2$ addition discussed above, all attempts to find a rotamer of compound **35**, analogous to the agostic silane adduct **25cis** (Scheme 7), converged to the same compound **35**.

Overall, comparing the stability of the intermediates relative to the starting phosphine compounds, a clear trend emerges: the introduction of more chlorine groups at silicon lowers the energy of the intermediates, and also presumably the energy of the corresponding barriers. This trend agrees well with the following experimental order of reactivity (i.e., rates of reaction): $HSiMe_2Cl < HSiMeCl_2 < HSiCl_3$. This order correlates with the increased Lewis acidity of the respective silanes and qualitatively agrees with our conclusions that the reactions proceed via a donor/acceptor type of interaction between the Lewis basic imido N atoms and the Lewis acidic Si centers of the various silanes.

Comparison of the series of isostructural trigonal-bipyramidal compounds **25trans** (Scheme 7, Table 4), **30a** (Scheme 8, Table 5), and **35** (Scheme 9, Table 6) shows that the Si−H distance progressively contracts from 2.114 Å in **25trans** to 1.745 Å in **35**, accompanied by an elongation of the Mo−H bond from 1.747 Å to 1.786 Å. This trend can be rationalized in terms of increased Lewis acidity of the more chlorinated silicon centers.

Interestingly, a similar trend was found for β−Si-H agostic compounds **17**, **26**, and **31**. The Si−H bond shortens progressively and the Mo−H bond elongates as one goes from **17** to the more chlorinated derivative **31**. On the other hand, the Mo−Si distance contracts only slightly from 2.664 Å to 2.656 Å along this series. These trends agree well with our observations that the Si−H coupling constants in the experimental compounds increase from **3** to **6** and that **3c** has a slightly shorter Mo−Si distance than **6c**.[7] Note that the strengthening of the

Scheme 9. Dissociative and Non-Dissociative (with Regard to PMe_3) Pathways to Agostic Compound **31**[a]



[a] Gibbs free energies are expressed in kcal mol^{-1}.

Table 6. Selected Interatomic Distances (Å) for the Mo Structures **31**–**35**

	31	32	33	34	35
Mo–N^{im}	1.747	1.745	1.771	1.7420	1.748
Mo–N^{am}	2.125	2.118		2.160	2.020
Mo–P trans to imido				2.816	
Mo–P trans to amido	2.442	2.518		2.509	2.443 (equatorial phosphine)
Mo–P trans to hydride	2.518		2.479 (trans to silyl)	2.528	2.512
Mo–H	2.058		1.761	1.728	1.786
Mo–Si	2.656	3.082	2.471	3.197	2.826
Mo–Cl	2.564	2.858			
Si–N	1.655	1.669		1.676	1.724
Si–H	1.551	1.482	2.165	2.615	1.745
Si–Cl	2.084, 2.068	2.120	2.090, 2.102 (trans to H), 2.090	2.097, 2.103, 2.085	2.124, 2.116, 2.155

Si–H interaction from **17** to **31** contradicts the usual expectation that introduction of more electron-withdrawing groups at silicon should promote oxidative addition of the Si–H bond to the metal because of increased back-donation to the Si–H antibonding orbital.[1] An explanation of this abnormality in terms of interplay of the decreased direct donation and increased back-donation has been offered in a previous work.[7]

It appears that the reason for the increased relative stability of HSi-Cl···M bridged compounds in comparison to their ClSiH···M β-agostic isomers is the decreased donor ability of the Si–H bond in the more chlorinated systems.

Conclusions

The reactions of molybdenum compounds $(RN)_2Mo(PMe_3)_n$ (R = Ar or Ar′ for n = 3; R = ^tBu for n = 2) with silanes R'_2SiClH have some similarities and also some important differences in comparison with the reactions of the isolobal $Cp(RN)Nb(PMe_3)_2$ systems. Thus: (i) mono- and dichlorosilanes give only agostic compounds $(RN)(\eta^2\text{-RN–SiR'}_2\text{H}\cdots)MoCl(PMe_3)_2$; (ii) in no case are silyl hydride products $(RN)_2Mo(PMe_3)H(SiR'_2Cl)$ observed, even transiently when the reactions are followed by low temperature NMR; (iii) the reaction with $HSiCl_3$ affords a silanimine dimer and the dichloride compound $(RN)MoCl_2(PMe_3)_3$; (iv) the mechanism of silane addition involves Si attack on an imido nitrogen of the bis(phosphine) compound $(RN)_2Mo(PMe_3)_2$, which initially either exists as a bis(phosphine) species for R = ^tBu or is easily formed from the tris(phosphine) precursor for R = Ar or Ar′.

The related reactions of the tungsten compounds $(RN)_2W(PMe_3)_3$ (R = Ar or Ar′) proceed in a similar way with one notable exception: in the case of the reaction between

(ArN)$_2$W(PMe$_3$)$_3$ (**10b**) and HSiMeCl$_2$ we were able to intercept the silyl hydride oxidative addition intermediate (ArN)$_2$W(PMe$_3$)(H)(SiMeCl$_2$). This compound is thermally stable in the absence of free phosphine, but like its isolobal analogue Cp(ArN)Nb(PMe$_3$)(H)(SiMe$_2$Cl), instantaneously rearranges into a silylamido species upon addition of PMe$_3$. In contrast to our expectations, the first silylamido product of this rearrangement is not a Si−H···W agostic compound, according to NMR. In the absence of structural data, we tentatively assign this product the Si−Cl···W bridged structure (ArN)(η^2-ArNSiMeH-Cl···)W(PMe$_3$)$_2$Cl. DFT calculations for model Mo compounds do indeed find such a Cl-bridged form. This is 3.5 kcal mol^{-1} less stable than the alternative β−Si-H agostic isomer in the case of HSiCl$_2$Me addition, but is the global minimum for the addition of HSiCl$_3$. This result is in good accord with our inability to observe agostic products in reactions of Mo and W phosphine compounds with HSiCl$_3$. The Si−Cl···M bridged structure also appears to be a reasonable intermediate in the course of formation of the monoimide product (RN)MCl$_2$(PMe$_3$)$_3$ stemming from elimination of the silanimine RN=SiHCl from (RN)(η^2-ArNSiClH-Cl···)M(PMe$_3$)$_2$Cl.

Experimental Section

All manipulations were carried out using conventional Schlenk techniques. Solvents were dried over sodium or sodium benzophenone ketyl and distilled into the reaction vessel by high vacuum gas phase transfer. NMR spectra were recorded on a Varian Mercury-*vx* (^{1}H 300 MHz, ^{31}P 121.4 MHz, ^{13}C 75.4 MHz, ^{29}Si 59.6 MHz) and Unity-plus (^{1}H, 500 MHz; ^{31}P 202.4 MHz, ^{13}C 125.7 MHz) spectrometers. IR spectra were obtained as Nujol mulls with a FTIR Perkin-Elmer 1600 series spectrometer. Silanes were obtained from Sigma-Aldrich, apart from HSiClMePh, which was purchased from Lancaster.

Precursor Phosphine Compounds. Starting phosphine compounds (RN)$_2$M(PMe$_3$)$_n$ (M = Mo, W; n = 2,3) were prepared analogously to the literature method.[9] Correct elemental analyses were not obtained because these compounds are highly sensitive to air and for n = 3 easily loose the phosphine.

(^{t}BuN)$_2$Mo(PMe$_3$)$_2$ (1a). ^{1}H NMR (300 MHz, toluene-d$_8$, at 25 °C): 1.49 (s, 18, ^{t}Bu), 1.31 (broad d, J(P−H) = 7.5 Hz, 18, PMe$_3$). ^{31}P NMR (121.4 MHz, toluene-d$_8$, at 20 °C): 38.5 (bs, PMe$_3$).

^{1}H NMR (300 MHz, toluene-d$_8$, at −50 °C): 1.60 (s, 18, ^{t}Bu), 1.28 (d, J(P−H) = 7.8 Hz, 18, PMe$_3$). ^{13}C NMR (75.4 MHz, toluene-d$_8$, at −50 °C): 64.5 (CMe$_3$), 34.7 (s, Me of ^{t}Bu), 25.3 (d, J(P−C) = 24.0 Hz). ^{31}P NMR (121.4 MHz, toluene-d$_8$, at −50 °C): 39.5 (bs, PMe$_3$).

(ArN)$_2$Mo(PMe$_3$)$_3$ (1b). Compound **1b** is fluxional at room temperature. ^{1}H NMR (300 MHz, C$_6$D$_6$, at 25 °C): δ 7.16 (d, J(H−H) = 7.5 Hz, 4, m-Ar), 6.92 (t, J(H−H) = 7.5 Hz, 2, p-Ar), 3.77 (sept, J(H−H) = 6.9 Hz, 4, CH), 1.32 (d, J(H−H) = 6.9 Hz, 24, Me/Ar), 1.03 (bs, 27, PMe$_3$). ^{31}P NMR (121.4 MHz, C$_6$D$_6$): δ (bs, PMe$_3$). ^{1}H NMR (300 MHz, toluene-d$_8$, at −40 °C): δ 7.18 (d, J(H−H) = 7.5, 2, m-Ar), 7.09 (d, J(H−H) = 7.5, 2, m-Ar), 6.90 (t, J(H−H) = 7.5, 2, p Ar), 3.81 (sept, J(H−H) = 6.9 Hz, 2, CH), 3.66 (sept, J(H−H) = 6.9 Hz, 2, CH), 1.42 (d, J(P−H) = 6.9 Hz, 12, Ar), 1.29 (d, J(P−H) = 6.9 Hz, 12, Ar), 1.21 (d, J(P−H) = 7.5 Hz, 9, PMe$_3$), 0.89 (vt, J(P−H) = 2.3 Hz, 18, PMe$_3$). ^{13}C NMR (toluene-d$_8$, at −40 °C): δ 128.9, 127.9, 31.7 (CH), 31.2 (CH), 31.4 (Me/Ar), 29.6 (Me/Ar), 28.8 (PMe$_3$), 23.3 (PMe$_3$). ^{31}P NMR (121.4 MHz, toluene-d$_8$, at −20 °C): δ −29.9 (s, 1, PMe$_3$), −5.0 (s, 2, PMe$_3$).

(Ar′N)$_2$Mo(PMe$_3$)$_3$ (1c). Compound **1c** is fluxional at room temperature. ^{1}H NMR (300 MHz, toluene-d$_8$, 25 °C): δ 7.12 (bd, J(H−H) = 7.2 Hz, m-Ar′), 6.68 (t, J(H−H) = 7.2 Hz, p-Ar′), 2.32 (bs, 12, Me/Ar), 0.93 (bs, 27, PMe$_3$). ^{31}P NMR (121.4 MHz, toluene-d$_8$, 25 °C): δ 31.4 (bs, 1, PMe$_3$), −8.4 (bs, 2, PMe$_3$). ^{1}H NMR (300 MHz, toluene-d$_8$, at −10 °C): δ 7.23 (bs, 2, m-Ar′), 7.13 (bs, 2, m-Ar′), 6.74 (t, J(H−H) = 5.7 Hz, 2, p-Ar′), 2.43 (bs, 6, Me/Ar), 2.29 (bs, 6, Me/Ar), 1.27 (d, J(P−H) = 6.6 Hz, 9, PMe$_3$), 0.80 (bs, 18, PMe$_3$). ^{13}C NMR (75.4 MHz, toluene-d$_8$, at −10 °C): δ 158.7 (i-Ar′), 125.6, 123.3, 116.4 (all Ar′), 25.0 (Me/Ar), 24.7 (Me/Ar), 22.0 (PMe$_3$), 17.1 (2 PMe$_3$). ^{31}P NMR (121.4 MHz, toluene-d$_8$, at −10 °C): δ 31.7 (s, 1, PMe$_3$), −8.1 (s, 2, PMe$_3$).

(ArN)$_2$W(PMe$_3$)$_3$ (10b). Compound **10b** is fluxional at room temperature. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.7 (bs, Ar), 2.34 (bs, Ar′), 3.7 (bs, CH), 1.30 (bs, Ar), 1.1 (bs, PMe$_3$). ^{31}P NMR (121.4 MHz, C$_6$D$_6$): δ −14.1 (bs, 1, PMe$_3$), −24.0 (bs, 2, PMe$_3$). ^{1}H NMR (300 MHz, toluene-d$_8$, at −20 °C): δ 7.00 (d, J(H−H) = 7.5, 1, p- Ar), 6.90 (t J(H−H) = 7.5, 1, m- Ar), 3.83 (sept, J(H−H) = 6.6 Hz, 2, CH), 3.51 (sept, J(H−H) = 6.9 Hz, 2, CH), 1.46 (d, J(P−H) = 8.1 Hz, 8, PMe$_3$), 1.41 (d, J(P−H) = 6.6 Hz, Ar), 1.25 (d, J(P−H) = 6.6 Hz, Ar), 1.08 (vt, J(P−H) = 2.2 Hz, 18, PMe$_3$). ^{13}C NMR (75.4 MHz, toluene-d$_8$, at −20 °C): δ 128.6, 127.8, 31.6 (CH), 30.8 (CH), 32.7 (PMe3), 31.1 (Me/Ar), 31.1 (Me/Ar), 29.2 (PMe3). ^{31}P NMR (121.4 MHz, toluene-d$_8$, at −20 °C): δ −7.9 (t, J(P−P) = 18.2 Hz, J(W−P) = 461 Hz, 1, PMe$_3$), −17.7 (d, J(P−P) = 18.2 Hz, J(W−P) = 316 Hz, 2, PMe$_3$).

(Ar′N)$_2$W(PMe$_3$)$_3$ (10c). Compound **10c** is fluxional at room temperature. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.22 (bs, Ar′), 2.34 (bs, Ar′), 1.46 (bs, 1PMe$_3$), 0.94 (bs, 2PMe$_3$). ^{31}P NMR (121.4 MHz, C$_6$D$_6$): −11.9 (bs, 1, PMe$_3$), −26.5 (bs, 2, PMe$_3$).

(^{t}BuN)(^{t}BuNSiMe$_2$−H···)Mo(PMe$_3$)$_2$Cl (3a). To a solution of (^{t}BuN)$_2$Mo(PMe$_3$)$_2$ (0.654 g, 1.68 mmol) in 25 mL of pentane was added HSiClMe$_2$ (0.20 mL, 1.80 mmol). The mixture was stirred for an hour at room temperature during which time the color changed to gray. All volatiles were removed in vacuo, and the residue was extracted by pentane (2 × 15 mL), filtered, and dried in vacuo. Yield: 0.49 g. (1.01 mmol, 60%) of a brown oily compound. The compound does not crystallize from pentane upon cooling to −30 °C. IR (Nujol): $\nu_{\text{Si−H}}$ = 1992 cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.54 (s, 9, Bu^t), 1.47 (d, J(P−H) = 7.5 Hz, 9, PMe$_3$), 1.40 (d, J(P−H) = 6.6 Hz, 9, PMe$_3$), ~1.4 (found by ^{1}H−^{29}Si HMQC, Mo−H), 1.02 (s, 9, Bu^t), 1.27 (d, J(P−H) = 8.5, 0.81 (d, J(P−H) = 1.8 Hz, 3, SiMe$_2$), 0.55 (d, J(P−H) = 2.4 Hz, 3, SiMe$_2$). ^{13}C NMR (75.4 MHz, C$_6$D$_6$): δ 68.5 (s, CMe$_3$), 55.7 (s, CMe$_3$), 36.0 (s, CMe$_3$), 31.5 (s, CMe$_3$), 23.2 (d, J(P−C) = 23.6 Hz), 22.8 (d, J(P−C) = 21.1 Hz), 3.4 (s, SiMe), 0.9 (s, SiMe). ^{31}P NMR (121.4 MHz, C$_6$D$_6$): δ 6.9 (d, J(P−P) = 12 Hz, 1P), 5.0 (d, J(P−P) = 12 Hz, 1P). ^{29}Si NMR (59.6 MHz, 25 °C, C$_6$D$_6$): −76 (J(Si−H) = 93.2 Hz). C, H,N analysis (%) calcd for C$_{16}$H$_{34}$MoN$_2$P$_2$SiCl (484.63): C 39.63, H 8.94, N 5.78; found: C 38.46, H 8.03, N 5.78.

(^{t}BuN)(^{t}BuNSiPhMe−H···)Mo(PMe$_3$)Cl (4a). HSiPhMeCl (0.17 mL, 1.12 mmol) was added to a solution of (^{t}BuN)$_2$Mo(PMe$_3$)$_2$ (0.523 g, 1.34 mmol) in 20 mL of pentane. The mixture was left to stand at room temperature for an hour to give a dark-brown solution. Then the solution was filtered and dried in vacuo to give brown oil. According to the ^{1}H and ^{31}P NMR, a mixture of two isomers of (^{t}BuN)(^{t}BuNSiPhMeH)Mo(PMe$_3$)Cl (**4a**) contaminated with (^{t}BuN)MoCl$_2$(PMe$_3$)$_3$ (**6a**, about 30% of the mixture) is formed. The content of **6a** in the solution increases with time because of decomposition of the initial product. All attempts to purify **4a** from **6a** failed because of close solubility of both products. Yield: 0.61 g. NMR spectra at room temperature show the presence of a fluxional compound. IR (Nujol): $\nu_{\text{Si−H}}$ = 2121 cm^{-1}. ^{29}Si NMR (59.6 MHz, 25 °C, C$_6$D$_6$): δ −79.9 (J(Si−H) = 94 Hz, J(Si−H) = 3.1 Hz, J(Si−P) = 5.6 Hz).

Major Isomer of 4a. ^{1}H NMR (300 MHz, toluene-d$_8$, −20 °C): δ 7.92 (d, J(H−H) = 7.8 Hz, o-Ph), 7.23 (m, m-Ph), 7.14

(m, p-Ph), 1.64 (m, Mo−H, found from ^{1}H−^{29}Si HMQC experiment), 1.70 (s, Bu^{t}), 1.44 (d, J(P−H) = 8.1 Hz, 9, PMe$_3$), 1.37 (d, J(P−H) = 6.9 Hz, 9, PMe$_3$), 0.72 (s, ^{t}Bu). ^{13}C NMR (75.4 MHz, toluene-d$_8$, −20 °C): δ 140.3 (s, o-Ph), 133.4 (s, p-Ph), 133.0 (s, m-Ph), 55.1 (s, ^{t}Bu), 40.8 (s, Bu^{t}), 27.5 (s, PMe$_3$), 27.1 (s, PMe$_3$), 35.5 (s, ^{t}Bu). ^{31}P NMR (121.4 MHz, toluene-d$_8$, −20 °C): δ 12.2 (d, J(P−P) = 12.7 Hz, 1, PMe$_3$), 1.4 (d, J(P−P) = 12.7 Hz, 1, PMe$_3$).

Minor Isomer of 4a. ^{1}H NMR (300 MHz, toluene-d$_8$, −20 °C): δ 8.36 (d, J(H−H) = 7.8 Hz, o-Ph), 7.39 (m, m-Ph), 7.21(m, p-Ph), 1.95 (s, Bu^{t}), 1.83 (Mo−H, found from the ^{1}H−^{29}Si HMQC experiment), 1.46 (d, J(P−H) = 6.9 Hz, 9, PMe$_3$), 1.26 (d, J(P−H) = 7.2 Hz, 9, PMe$_3$), 1.05 (s, ^{t}Bu). ^{13}C NMR (75.4 MHz, toluene-d$_8$, −20 °C): δ 142.8 (s, o-Ph), 140.2 (s, m-Ph), 134.6 (s, p-Ph), 43.0 (s, Bu^{t}), 27.5 (s, PMe$_3$), 27.0 (s, PMe$_3$), 36.4 (s, ^{t}Bu). ^{31}P NMR (121.4 MHz, toluene-d$_8$, −20 °C): δ 12.3 (d, J(P−P) = 13.5 Hz, 1, PMe$_3$), −0.3 (d, J(P−P) = 13.5 Hz, 1, PMe$_3$).

(^{t}BuN)(^{t}BuNSiPh$_2$−H···)Mo(PMe$_3$)$_2$Cl (5a). HSiPh$_2$Cl (0.3 mL, 1.40 mmol) was added to a solution of (^{t}BuN)$_2$Mo(PMe$_3$)$_2$ (0.546 g, 1.40 mmol) in 25 mL of pentane. The mixture was left at room temperature for 4 days. Then the solution was filtered and dried in vacuo to give a brown powder. The yield is quantitative according to ^{1}H NMR. Yield: 0.806 g. (1.32 mmol, 94%). IR (Nujol): $\nu_{\mathrm{Si-H}}$ = 1950 cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 8.38 (dd, J(P−H) = 1.6 Hz, J(P−H) = 8.1 Hz, 2, o-Ph), 7.96 (dd, J(P−H) = 2.0 Hz, J(P−H) = 7.6 Hz, 2, o-Ph), 7.26−7.08 (m, 6, m,p-Ph), 2.32 (dd, J(P−H) = 25.9 Hz, J(P−H) = 9.2 Hz, 1, Mo−H), 1.67 (s, 9, Bu^{t}), 1.47 (d, J(P−H) = 7.7 Hz, 9, PMe$_3$), 1.37 (d, J(P−H) = 7.3 Hz, 9, PMe$_3$), 1.15 (s, 9, Bu^{t}), 0.66 (s, 9, Bu^{t}). ^{13}C NMR (75.4 MHz, C$_6$D$_6$): δ 138.7, 135.9, 129.7, 129.3, 128.5 (all Ph), 69.0 (s, $\underline{\mathrm{C}}$Me$_3$), 55.5 (s, $\underline{\mathrm{C}}$Me$_3$), 36.8 (s, C$\underline{\mathrm{Me}}_3$), 31.0 (s, C$\underline{\mathrm{Me}}_3$), 23.3 (d, J(P−C) = 23.9 Hz, PMe$_3$), 22.9 (d, J(P−C) = 21.3 Hz, PMe$_3$). ^{31}P NMR (121.4 MHz, C$_6$D$_6$): δ 5.7 (d, J(P−H) = 13.4 Hz, 1), −5.3 (d, J(P−H) = 13.4 Hz, 1). ^{29}Si NMR (59.6 MHz, 25 °C, C$_6$D$_6$): δ −87.4 (J(Si−H) = 103.3 Hz). C,H,N analysis (%): calcd for C$_{26}$H$_{47}$N$_2$MoClSiP$_2$ (609.10): 51.10, H 8.08, N 4.58; found: C 50.10, H 8.03, N 4.56.

(^{t}BuN)(^{t}BuNSiMeCl−H···)Mo(PMe$_3$)$_2$Cl (6a). HSiCl$_2$Me (0.25 mL, 2.40 mmol) was added to a solution of (^{t}BuN)$_2$Mo (PMe$_3$)$_2$ (0.75 g, 1.92 mmol) in 15 mL of ether. The mixture was stirred for 10 min, filtered, and dried in vacuo to give brown oil. The yield is quantitative according to ^{1}H NMR. The oil was extracted by 40 mL of hexane, filtered, and cooled to −30 °C for a month to produce dark-brown crystals. The cold solution was decanted, and the residue was quickly washed by 5 mL of pentane and dried. Yield: 0.30 g. (0.59 mmol, 31%). IR (Nujol): $\nu_{\mathrm{Si-H}}$ = 1851 cm^{-1}.

^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.54 (s, 9, Bu^{t}), 1.43 (dd, J(P−H) = 3.6 Hz, J(P−H) = 0.9 Hz, Mo−H), 1.35 (d, J = 8.0 Hz, 9, PMe$_3$), 1.28 (d, J(P−H) = 7.1 Hz, 9, PMe$_3$), 1.19 (s, 3, SiMeCl), 1.15 (s, 9, Bu^{t}). ^{13}C NMR (75.4 MHz, C$_6$D$_6$): δ 69.7 (s, $\underline{\mathrm{C}}$Me$_3$), 54.9 (s, $\underline{\mathrm{C}}$Me$_3$), 35.2 (s, C$\underline{\mathrm{Me}}_3$), 31.1 (s, C$\underline{\mathrm{Me}}_3$), 22.5 (dd, J(P−C) = 2.5 Hz, J(P−C) = 24.8 Hz, PMe$_3$), 22.2 (d, J(P−C) = 22.0 Hz, PMe$_3$), 3.2 (SiMe). ^{31}P NMR (121.4 MHz, C$_6$D$_6$): δ 9.8 (d, J(P−P) = 11.8 Hz, 1), −3.7 (d, J(P−P) = 11.8 Hz, 1). ^{29}Si NMR (59.6 MHz, 25 °C, C$_6$D$_6$): δ −74.2 (J(Si−H) = 123 Hz, J(Si−P) = 9 Hz). C,H,N analysis (%): calcd for C$_{15}$H$_{40}$N$_2$MoCl$_2$SiP$_2$ (505.37): 35.65, H 7.98, N 5.54; found: C 34.44, H 7.71, N 5.43.

(Bu^{t}N)Mo(PMe$_3$)$_3$Cl$_2$[13a] (7a). To 25 mL of ether solution of (Bu^{t}N)$_2$Mo(PMe$_3$)$_2$ (1.70 g, 4.35 mmol) was added an equivalent of PMe$_3$ followed by 0.7 mL of HSiCl$_3$ (6.94 mmol). Instantaneous reaction occurs, resulting in the formation of a brown precipitate. The mixture was cooled to −30 °C overnight. The cold solution was filtered off, and the residue was washed by 3 mL of ether and dried to give 1.11 g (2.39 mmol, 55%) of a light-amber powder of **6a**. Keeping the mother liquor at −30 °C over the period of 4 days afforded the second crop (0.225 g, 0.48 mmol, 11%) of the same compound. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.43 (vt, J = 3.6 Hz, 18, trans PMe$_3$), 1.25 (d, J(P−H) = 7.6 Hz, 9, cis PMe$_3$), 1.01 (s, 9, Bu^{t}). ^{31}P NMR (121.4 MHz, C$_6$D$_6$): δ 7.3 (bs, 1, cis PMe$_3$), −5.9 (bs, trans PMe$_3$), agrees with the literature data (ref 14a).

NMR Tube Preparation of (ArN)(ArNSiMe$_2$-H···)Mo(PMe$_3$)$_2$Cl (3b). To 0.0248 g (0.037 mmol) of (ArN)$_2$Mo(PMe$_3$)$_3$ in 1 mL of ether was added 0.004 mL (0.037 mmol) of HSiClMe$_2$. The mixture was left overnight at room temperature. All volatiles were removed in vacuo, and the residue was redissolved in 0.6 mL of C$_6$D$_6$. NMR spectra showed clean formation of **3b**. This product is not fluxional at room temperature. Scaling up the reaction resulted in a non-separable mixture of **3b** and (ArN)MoCl$_2$(PMe$_3$)$_3$ (**7b**). IR (Nujol): $\nu_{\mathrm{Si-H}}$ = 1943, cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.23 (t, J(H−H) = 4.5 Hz, 1), 7.07 (d, J(H−H) = 4 Hz, 2), 6.95 (pseudo t, J(H−H) = 3 Hz, 2), 6.84 (dd, J(H−H) = 3 Hz, J(H−H) = 6 Hz, 1), 4.33 (sept, J(H−H) = 6.6 Hz, 1, CH), 3.78 (sept, J(H−H) = 6.6 Hz, 1, CH), 3.45 (sept, J(H−H) = 6.8 Hz, 1, CH), 3.11 (sept, J(H−H) = 6.7 Hz, 1, CH), 1.52 (d, J(H−H) = 6.5 Hz, 3, Pr^{i}), 1.28 (d, J(H−P) = 6 Hz, 9, PMe), 1.25 (d, J(H−P) = 7.0 Hz, 3, Pr^{i}), 1.23 (d, J(H−H) = 6 Hz, 3, Pr^{i}), 1.22 (d, J(H−H) = 6.5 Hz, 3, Pr^{i}), 1.12 (d, J = 7.5, 9, PMe), 1.05 (d, J(H−H) = 6.5 Hz, 3, Pr^{i}), 1.02 (d, J(H−H) = 7 Hz, 3, Pr^{i}), 1.00 (d, J(H−H) = 7 Hz, 3, Pr^{i}), 0.98 (s, 3, SiMe$_2$), 0.93 (d, J(H−H) = 7 Hz, 3, Pr^{i}), 0.876 (t, J(P−H) = 7.5 Hz, 1, MoHSi), 0.65 (s, 3, SiMe$_2$). ^{13}C NMR (75.4 MHz, C$_6$D$_6$): δ 155.0 (s, i-Ar), 153.2 (s, i-Ar), 145.9 (s, o-Ar), 144.6 (s, o-Ar), 142.2 (s, o-Ar), 140.0 (s, o-Ar), 123.7, 123.5, 122.5, 121.9, 29.6 (s, Me-Pr^{i}), 27.6 (s, CH), 27.5 (s, CH), 27.3 (s, Me-Pr^{i}), 26.5 (s, 2CH), 24.6 (s, Me- Pr^{i}), 24.5 (s, Me Pr^{i}), 24.9 (s, Me Pr^{i}), 23.9 (s, Me-Pr^{i}), 23.2 (s, Me-Pr^{i}), 22.5 (s, Me-Pr^{i}), 21.5 (d, J(P−C) = 21.3 Hz, PMe), 20.3 (d, PMe), 2.8 (s, SiMe$_2$), −0.036 (s, SiMe$_2$). ^{31}P NMR (121.4 MHz, C$_6$D$_6$): δ 4.7 (d, J(P−P) = 7 Hz), −6.8 (d, J(P−P) = 8 Hz). ^{29}Si NMR (59.6 MHz, 25 °C, C$_6$D$_6$): δ −64.9 (^{1}J(Si−H) = 97 Hz, ^{2}J(Si−H) = 3.1 Hz).

NMR Tube Preparation of (ArN)(ArNSiMePh-H···)Mo(PMe$_3$)$_2$Cl (4b). To 0.0254 g (0.039 mmol) of (ArN)$_2$Mo(PMe$_3$)$_3$ in 0.6 mL of C$_6$D$_6$ was added an equivalent of HSiMePhCl. NMR monitoring showed slow formation of **3b** over a period of several days, accompanied by significant decomposition to (ArN)MoCl$_2$(PMe$_3$)$_3$ (**7b**). ^{31}P NMR (121.4 MHz, C$_6$D$_6$): δ 3.40 (b), −6.24 (b).

(ArN)(ArNSiMeCl-H···)Mo(PMe$_3$)$_2$Cl (6b). To 0.135 g (0.20 mmol) of **1b** in 50 mL of pentane was added 0.1 mL of silane HSiMeCl$_2$. Within few minutes the initial dark-green color changes to yellow-brown. All volatiles were removed in vacuo, affording a brown oil, which was shown by NMR to be a mixture of **6b** and **7b**. Attempts to recrystallize the mixture to isolate pure **6b** failed. The only crystalline material isolated from different solvents and under different regimes was **7b**. NMR scale preparation of **6b** showed the quick (within 7 s) formation of highly fluxional **6b** which then decomposes in solution to **7b**. IR (Nujol): $\nu_{\mathrm{Si-H}}$ = 1919 cm^{-1}. ^{1}H NMR (300 MHz, toluene-d$_8$, −50 °C): δ 4.27 (sept, J(H−H) = 6.6 Hz, 1, CH), 4.19 (sept, J(H−H) = 6.6 Hz, 1, CH), 3.74 (sept, J(H−H) = 6.3 Hz, 1, CH), 2.92 (sept, J(H−H) = 6.3 Hz, 1, CH), 1.50 (d, J(H−H) = 6.6 Hz, 3, CH$_3$), 1.47 (d, J(H−H) = 6.6 Hz, 3, CH$_3$), 1.45 (s, 3, SiMe), 1.39 (d, J(H−H) = 6.3 Hz, 3, CH$_3$), 1.28 (d, J(H−H) = 6.0 Hz, 3, CH$_3$), 1.23 (Mo−H−Si obscured by a PMe$_3$ signal but determined from ^{29}Si−^{1}H HMQC at −50 °C), 1.17 (multiplet of the Ar signal obscured by PMe$_3$, 6, CH$_3$), 1.16 (d, J(H−P) = 7.5 Hz, 9, PMe$_3$), 0.99 (doublet of the Ar signal obscured by PMe$_3$, 3, CH$_3$), 0.98 (d, J(H−P) = 8.7 Hz, 9, PMe$_3$), 0.89 (d, J(H−H) = 6.6 Hz, 3, CH$_3$). ^{13}C NMR (75.4 MHz, toluene-d$_8$, −50 °C): δ 152.6 (s, i-Ar), 151.4 (s, i-Ar), 145.1 (s, o-Ar), 144.9 (s, o-Ar), 143.9 (s, o-Ar), 140.0 (s, o-Ar), 124.0, 123.9, 123.5, 122.4, 122.3, 29.3 ($\underline{\mathrm{Me}}$-Ar), 28.4 ($\underline{\mathrm{Me}}$-Ar), 27.7 (CH), 27.4 (CH), 26.58 (CH), 26.27 (CH), 25.5 ($\underline{\mathrm{Me}}$-Ar), 24.6 ($\underline{\mathrm{Me}}$-Ar), 24.5 ($\underline{\mathrm{Me}}$-Ar), 24.3 (Me-Ar), 23.7 (Me-Ar), 22.1 (Me-Ar), 20.7 (PMe$_3$, obscured by toluene), 19.6 (PMe$_3$, obscured by toluene), 5.6 (SiMe). ^{31}P NMR (121.4 MHz, toluene-d$_8$, −50 °C): δ 10.5 (d, *J*(P−P) = 8.7 Hz, 1 PMe$_3$), −3.8 (d, *J*(P−P) = 8.7 Hz, 1 PMe$_3$). ^{31}P NMR (121.4 MHz, C$_6$D$_6$, 25 °C): δ 8.7 (bs), −4.5 (bs). ^{29}Si NMR (119.2 MHz, toluene-d$_8$, −50 °C): δ −68.5 (^{1}*J*(Si-H) = 130 Hz, ^{2}*J*(Si-P) = 16.2 Hz).

(ArN)Mo(PMe$_3$)$_3$Cl$_2$ (7b). A 0.2 mL portion (1.98 mmol) of HSiCl$_3$ was added to 15 mL of pentane solution of (ArN)$_2$Mo(PMe$_3$)$_3$ (0.274 g, 0.424 mmol). Within 10 min the color changed from dark-green to yellow-brown. The mixture was left at room temperature for 20 h. The solution was filtered off, and the residue was washed by 3 mL of cold pentane and dried. Yield 0.11 g (0.193 mmol, 42%), green crystals. Volatiles were removed from the mother liquor to give oil. According to NMR this product was mainly (ArNSiClH-)$_2$.

7b. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.01 (t, *J* = 7.7 Hz, 1, p-Ar), 6.87 (d, *J* = 7.7 Hz, 1, m-Ar), 4.12 (sept, *J*(H−H) = 6.8 Hz, 2, CH), 1.40 (vt, *J*(H−P) = 2.4 Hz, 18, PMe$_3$), 1.27 (d, *J*(P−H) = 8.4 Hz, 9, PMe$_3$), 1.17 (d, *J*(H−H) = 6.6 Hz, 12, CH$_3$). ^{13}C NMR (75.4 MHz, toluene-d$_8$, −50 °C): δ 146.8, 126.7 (p-Ar), 123.9 (m-Ar), 27.1 9s, CH), 25.4 (CH3), 23.1 (d, *J*(P−C) = 23.0 Hz, 1 PMe$_3$), 17.1 (vt, *J*(P−C) = 11.5 Hz, 1 PMe$_3$). ^{31}P NMR (121.4 MHz, C$_6$D$_6$): δ 3.6 (t, *J*(P−P) = 16.7 Hz, 1 PMe$_3$), −7.8 (d, *J*(P−P) = 16.7 Hz, 1 PMe$_3$). C,H,N analysis (%): calcd for C$_{21}$H$_{44}$NMoP$_3$Cl$_2$ (570.354): C 44.22, H 7.78, N 2.46; found: C 43.23, H 7.78, N 2.46.

(ArNSiClH)$_2$. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.03−6.90 (m), 5.48 (s) 3.40 (sept, *J*(H−H) = 6.6 Hz, 2, CH), 1.41 (d, *J*(H−H) = 6.6 Hz, 12, CH$_3$). ^{29}Si−^{1}H HMQC NMR (59.6 MHz, C$_6$D$_6$, 25 °C): δ 37.3.

NMR Reaction of (ArN)$_2$Mo(PMe$_3$)$_3$ with HSiCl$_3$ in the Presence of BPh$_3$. A solution of HSiCl$_3$ (4.0 μL, 0.04 mmol) and BPh$_3$ (9.5 mg, 0.04 mmol) in 0.3 mL of toluene-d$_8$ was added to an NMR tube containing a frozen solution of (ArN)$_2$Mo(PMe$_3$)$_3$ (26.5 mg, 0.04 mmol) in 0.4 mL of toluene-d$_8$. The mixture was placed to 600 MHz NMR spectrometer pre-cooled to −20 °C and was cooled down to −70 °C. The mixture was slowly warmed up, and the course of the reaction was monitored by NMR. At −30 °C, the formation of an initial product with the suggested structure (ArN)(ArNSiHCl-Cl···)Mo(PMe$_3$)$_2$Cl (**8b**) was observed. Warming the mixture up to −15 °C − 0 °C leads to a slow rearrangement of the initial product into another compound, whose NMR features are consistent with the structure (ArN)(η^2-ArN=SiHCl)Mo(PMe$_3$)$_3$Cl$_2$ (**9b**). Further increase of the temperature to >0 °C leads to fast decomposition to a mixture of (ArNSiHCl)$_2$ and (ArN)MoCl$_2$(PMe$_3$)$_3$ (**7b**).

(ArN)(ArNSiHCl-Cl···)Mo(PMe$_3$)$_2$Cl (8b). ^{1}H NMR (600 MHz, −30 °C, toluene-d$_8$) δ: 7.44 (bm, 1H, N*Ar*), 7.33 (bm, 1H, N*Ar*), 6.92−7.19 (multiplet overlapping with the residual toluene-d$_8$ resonances, 4H, N*Ar*), 7.10 (1H, Si-*H*, found by ^{1}H−^{29}Si HSQC), 4.85 (bs, 1H, *CH*, N*Ar*), 4.70 (bs, 1H, *CH*, N*Ar*), 3.98 (bs, 1H, *CH*, N*Ar*), 2.79 (bs, 1H, *CH*, N*Ar*), 1.60 (bs, 6H, CH_3, N*Ar*), 1.49 (bs, 3H, CH_3, N*Ar*), 1.37 (bs, 6H, 2CH_3, N*Ar*), 1.04 (bs, 9H, P*Me*$_3$), 0.94 (bs, 9H, P*Me*$_3$), 0.90 (bs, 3H, CH_3, N*Ar*), 0.77 (bs, 3H, CH_3, N*Ar*). ^{31}P NMR (243 MHz, −30 °C, toluene-d$_8$) δ: 20.0 (bs, *P*Me$_3$), −2.6 (bs, *P*Me$_3$). ^{29}Si INEPT+ NMR (119.2 MHz, −30 °C, toluene-d$_8$, *J*(Si−H) = 200 Hz) δ: −31.8 (d, ^{1}*J*(Si−H) = 337.5 Hz, *Si*-H). ^{1}H−^{13}C HSQC NMR (*J*(H−C) = 145 Hz, −30 °C, toluene-d$_8$) δ: 130.9, 125.1, 124.9, 124.7 124.1 (*m*-C and *p*-C of N*Ar*), 28.5, 27.9, 26.5, 25.7 (*CH*, N*Ar*), 30.5, 27.3, 26.4, 24.7, 23.8, 22.4 (CH_3, N*Ar*), 20.6, 18.8 (P*Me*$_3$).

(ArN)(η^2-ArN=SiHCl)Mo(PMe$_3$)$_3$Cl$_2$ (9b). ^{1}H NMR (600 MHz, toluene-d$_8$, −50 °C) δ: 6.81−7.38 (multiplet overlapping with the residual toluene-d$_8$ resonances, 6H, N*Ar*), 6.01 (bd, ^{3}*J*(H−P) = 9.0 Hz, 1H, Si-*H*), 4.41 (bs, 1H, *CH*, N*Ar*), 4.11 (bs, 1H, *CH*, N*Ar*), 3.70 (bs, 1H, *CH*, N*Ar*), 3.11 (bs, 1H, *CH*, N*Ar*), 1.60 (bs, 6H, 2CH_3, N*Ar*), 1.53 (bs, 3H, CH_3, N*Ar*), 1.49 (bs, 3H, CH_3, N*Ar*), 1.39 (bs, 6H, 2CH_3, N*Ar*), 1.23 (bs, 3H, CH_3, N*Ar*), 1.07 (bs, 3H, CH_3, N*Ar*), 1.19 (bs, 9H, P*Me*$_3$), 0.63 (bs, 9H, P*Me*$_3$). ^{31}P NMR (243 MHz, toluene-d$_8$, −50 °C) δ: −8.6 (d, ^{2}*J*(P−P) = 223.5 Hz, *P*Me$_3$), −17.1 (d, ^{2}*J*(P−P) = 223.5 Hz, *P*Me$_3$). ^{29}Si INEPT+ NMR (119.2 MHz, toluene-d$_8$, −50 °C, *J*(Si−H) = 200 Hz) δ: −42.4 (dd, ^{1}*J*(Si−H) = 327.0 Hz, ^{2}*J*(Si−P) = 22.1 Hz, *Si*-H). ^{1}H−^{13}C HSQC NMR (*J*(H−C) = 145 Hz, −30 °C, toluene-d$_8$) δ: 127.8, 124.8, 124.7 124.3, 123.6 (*m*-C and *p*-C of N*Ar*), 28.4, 28.2, 27.2, 26.7 (*CH*, N*Ar*), 30.5, 27.3, 25.9, 25.8, 24.8, 24.7, 24.5, 23.8 (CH_3, N*Ar*), 16.8, 15.3 (P*Me*$_3$).

(Ar′N)(Ar′NSiMe$_2$-H···)Mo(PMe$_3$)$_2$Cl (3c). To a solution of (Ar′N)$_2$Mo(PMe$_3$)$_3$ (0.381 g, 0.677 mmol) in 40 mL of ether was added HSiClMe$_2$ (0.25 mL, 2.25 mmol). In 5 min the color changed from dark-green to dark-brown. The solution concentrated to 15 mL, and 15 mL of hexane was added; the mixture was placed in a freezer (−30 °C) overnight to give dark well-defined crystals, which were isolated by filtration and drying in vacuo. Yield: 0.100 g. Two more crops were obtained by concentrating the solution and cooling to −30 °C. Total yield: 0.277 g (0.477 mmol, 70%). IR (Nujol): $\nu_{\mathrm{Si-H}}$ = 1910 cm^{-1}(weak). ^{1}H NMR (500 MHz, −40 °C, toluene-d$_8$): δ 7.24 (d, *J* (H−H) = 7.4 Hz, 1, *m*-Ar′NSi), 7.10 (d, *J* (H−H) = 7.5 Hz, 1, *m*-Ar′NSi), 7.00 (t, *J*(H−H) = 7.4 Hz, 1, *p*-Ar′NSi), 6.83 (d, *J*(H−H) = 7.53 Hz, 1, *m*-Ar′N), 6.78 (t, *J*(H−H) = 7.4 Hz, 1, *p*-Ar′N), 6.75 (d, *J*(H−H) = 7.6 Hz, 1, *m*-Ar′N), 2.85 (s, 3, Me-Ar′NSi), 2.49 (s, 3, Me-Ar′N), 2.07 (s, 3, Me-Ar′NSi), 2.06 (s, 3, Me-Ar′N), 1.68 (dqq, *J* = 2.2 Hz, *J* = 1.7 Hz, *J* = 23.3 Hz, 1, MoH), 1.23 (d, *J*(P−H) = 7.1 Hz, 9, PMe$_3$), 0.98 (d, *J* (P−H) = 8.5 Hz, 9, PMe$_3$), 0.71 (d, *J* = 1.7 Hz, 3, SiMe), 0.25 (d, *J* = 2.2 Hz, 3. SiMe). ^{13}C NMR (125.7 MHz, −40 °C, toluene-d$_8$): δ 158.2 (d, *J* (P−C) = 2.0 Hz, *i*-Ar′NSi), 154.5 (d, *J* (P−C) = 5.6 Hz, *i*-Ar′N), 135.4 (d, *J* (P−C) = 2.1 Hz, *o*-Ar′NSi), 133.7 (d, *J*(P−C) = 1.6 Hz, *o*-Ar′NSi), 131.3 (d, *J*(P−C) = 1.8 Hz, *o*-Ar′N), 128.8 (s, *m*-Ar′N), 128.5 (s, *m*-Ar′NSi), 128.3 (s, *m*-Ar′N), 128.1 (s, *m*-Ar′NSi), 128.0 (s, *o*-Ar′N), 123.3 (s, *p*-Ar′N), 121.0 (s, *p*-Ar′NSi), 21.6 (s, Me-Ar′NSi), 20.4 (s, Me-Ar′N), 20.0 (s, Me-Ar′NSi), 19.9 (s, Me-Ar′N), 19.5 (d, *J*(P−C) = 21.2 Hz, PMe$_3$), 18.6 (dd, *J*(P−C) = 25.0 Hz, *J*(P−C) = 0.8, PMe$_3$), ^{31}P NMR (121.4 MHz, −40 °C, toluene-d$_8$): δ 6.4 (d, *J*(P−P) = 9 Hz, 1, PMe$_3$), −7.0 (d, *J*(P−P) = 9 Hz, 1, PMe$_3$). ^{29}Si NMR (119.2 MHz, −50 °C, toluene-d$_8$): δ −63.8 (^{1}*J*(Si−H) = 98 Hz, ^{2}*J*(Si-Me) = 7.2 Hz, *J*(Si−P) = 21.5 Hz). C,H,N analysis (%): calcd for C$_{24}$H$_{43}$N$_2$MoP$_2$SiCl (581.045): C 49.63, H 7.46, N 4.82; found: C 48.99, H 6.92, N 4.82.

(Ar′N)(Ar′NSiMePh-H···)Mo(PMe$_3$)$_2$Cl (4c). To a dark-green solution of (Ar′N)$_2$Mo(PMe$_3$)$_3$ (0.267 g, 0.475 mmol) in 40 mL of ether was added HSiCl$_2$Me (0.1 mL, 0.67 mmol). The resultant solution was kept at room temperature for 2 h, developing brown color. The solution filtered from small amount of gray deposit and concentrated to 10 mL, and the mixture placed in a freezer (−30 °C) overnight to give a dark crystalline deposit. The cold solution was filtered off, and the product was washed by 5 mL of hexane and dried in vacuo. Yield: 0.186 g. (0.289 mmol, 61%). IR (Nujol): $\nu_{\mathrm{Si-H}}$ = 1906 cm^{-1}(weak). ^{1}H NMR (300 MHz, −40 °C, toluene-d$_8$): δ 8.15 (d, *J*(H−H) = 7.8 Hz, 4H,), 7.52 (d, *J*(H−H) = 6.9 Hz, 4H,), 7.23−6.93 (m,), 6.78 (m, 4H,), 2.64 (s, 3, C$_6$H$_4$Me$_2$), 2.69 (s, 3, C$_6$H$_4$Me$_2$), 2.45 (s, 3, C$_6$H$_4$Me$_2$), 2.29 (s, 3, C$_6$H$_4$Me$_2$), 2.24 (s, 3, C$_6$H$_4$Me$_2$), 2.19 (s, 3, C$_6$H$_4$Me$_2$), 2.17 (s, 3, C$_6$H$_4$Me$_2$), 2.14 (t, *J*(P−H) = 22 Hz, 2, Mo−H), 2.10 (s, 3, C$_6$H$_4$Me$_2$), 1.24 (d, *J*(P−H) = 7.0 Hz, 9, PMe$_3$), 1.23 (d, *J*(P−H) =7.0 Hz, 9, PMe$_3$), 1.15 (d, *J*(P−H) = 1.8 Hz, 3, SiMe), 1.00 (d, *J*(P−H) = 8.5 Hz, 9, PMe$_3$), 0.99 (d, *J*(P−H) = 8.5 Hz, 9, PMe$_3$), 0.58 (d, *J*(P−H) = 1.8 Hz, 3, SiMe). ^{13}C NMR (75.4 MHz, −40 °C, toluene-d$_8$): δ 157.5, 154.9, 154.4, 136.6, 136.0, 135.5, 135.1, 134.2, 133.3, 132.4, 131.4, 129.9, 127.2, 123.7, 123.6, 121.2, 21.9, 21.5, 20.8, 20.3, 30.0, 19.4 (d, *J*(P−C) = 21.0 PMe$_3$), 19.3 (d, *J*(P−C) = 216 PMe$_3$), 18.7 (d, *J*(P−C) = 25.2, PMe$_3$), 18.6 (d, *J*(P−C) = 25.1 PMe$_3$), 1.0 (SiMe), −3.4 (SiMe). ^{31}P

NMR (121.4 MHz, 25 °C, toluene-d_8): δ 5.5 (bs), −7.9 (bs). ^{29}Si NMR (59.6 MHz, 25 °C, C_6D_6): −74.0 (*J* = 100 Hz). ^{29}Si NMR (59.6 MHz, −40 °C, C_6D_6): −69.3 (*J* = 98 Hz). C,H,N analysis (%) calcd for $C_{24}H_{43}N_2MoP_2SiCl$ (643.116): 54.16, H 7.05, N 4.36; found: C 54.03, H 7.06, N 4.43.

(Ar′N)(Ar′NSiMeCl-H···)Mo(PMe_3)$_2$Cl (6c). To a solution of $(Ar'N)_2Mo(PMe_3)_3$ (0.326 g, 0.580 mmol) in 40 mL of ether was added $HSiCl_2Me$ (0.15 mL, 1.37 mmol). In 3−4 min the color changed from dark-green to dark-brown. The solution filtered from small amount of gray deposit and concentrated to 10 mL, 10 mL of hexane was accurately added, and the mixture was placed overnight in a freezer (−30 °C) to give dark, well-defined crystals. The cold solution was filtered off, and the product was dried in vacuo. Yield: 0.150 g. (0.249 mmol, 43%). IR (Nujol): ν_{Si-H} = 1920 cm^{-1} (weak). ^{1}H NMR (300 MHz, −10 °C, toluene-d_8): δ 7.07 (bd, *J*(H−H) = 7.6 Hz, 1, *m*-Ar′), 6.98 (bd, *J*(H−H) = 7.5 Hz, 1, *m*-Ar′), 6.87 (vt, *J*(H−H) = 7.5 Hz, 1, *p*-Ar′), 6.87 (bs, 3, *m* + *p*-Ar′), 2.60 (bs, 3, Me-Ar′), 2.39 (bs, 3, Me-Ar′), 2.37 (bs, 6, Me-Ar′), 1.76 (dq, *J*(H−P) = 18 Hz, *J*(H−H) = 1.5 Hz, 1, MoH), 1.18 (d, *J*(P−H) = 7.4 Hz, 9, PMe_3), 0.99 (d, *J*(P−H) = 8.5 Hz, 9, PMe_3), 0.97 (d, *J*(H−H) = 1.5 Hz, 3, SiMe). ^{13}C NMR (75.4 MHz, −10 °C, toluene-d_8): δ 154.9 (d, *J*(P−C) = 1.8 Hz, *i*-Ar′), 154.5 (dd, *J*(P−C) = 1.8, 3.5 Hz, *i*-Ar′), 134.6 (s, *o*-Ar′), 128.5 (s, *m*-Ar′), 128.4 (s, *m*-Ar′), 124.3 (s, *p*-Ar′), 121.7 (s, *p*-Ar′), 21.1 (s, Me-Ar′), 20.4 (s, Me-Ar′), 19.3 (d, *J*(P−C) = 22.8 Hz, PMe_3), 18.6 (d, *J*(P−C) = 25.8 Hz, PMe_3), 1.8 (s, SiMe). ^{31}P NMR (121.4 MHz, −60 °C, toluene-d_8): δ 10.2 (bd, *J*(P−P) = 6.5 Hz, 1, PMe_3), −5.0 (bd, *J*(P−P) = 6.5 Hz, 1, PMe_3). ^{29}Si NMR (59.6 MHz, 25 °C, C_6D_6): −70.1 (*J*(Si−H) = 129 Hz, *J*(Si−P) = 7.2 Hz). ^{29}Si NMR (119.2 MHz, −50 °C, toluene-d_8): −70.5 (*J*(Si−H) = 135.6 Hz, *J*(Si−P) = 20.6 Hz). C,H,N analysis (%) calcd for $C_{23}H_{40}N_2MoP_2SiCl_2$ (601.353): C 45.93, H 6.70, N 4.66; found: C 46.23, H 6.93, N 4.74.

(Ar′N)Mo(PMe_3)$_3$Cl$_2$ (7c). A 0.2 mL portion (1.98 mmol) of $HSiCl_3$ was added by syringe to 15 mL of an ether/pentane (1:2) solution of $(Ar'N)_2Mo(PMe_3)_3$ (0.380 g, 0.675 mmol). Within a minute the color changed from dark-green to yellow-brown, and a small amount of gray precipitate was formed. In 30 min the solution was filtered, cooled to −78 °C, and slowly concentrated in vacuo to 2 mL. The cold solution was filtered, the residue washed by 1 mL of cold pentane, and volatiles removed in an analogous fashion from the combined fractions to give a yellow-brown oil and green solid. Yield of $(Ar'N)Mo(PMe_3)_3Cl_2$: 0.237 g (0.461 mmol, 68%). The volatiles were removed from mother liquor to give 0.237 g of a yellow-brown oil, which mostly consisted of $(Ar'NSiClH)_2$ contaminated by $(Ar'N)Mo(PMe_3)_3Cl_2$.

7c. ^{1}H NMR (300 MHz, C_6D_6): δ 6.84 (pt, *J*(H−H) = 7.35 Hz, 1, *p*- Ar′), 6.70 (d, *J*(H−H) = 7.5 Hz, 1, *m*-Ar′), 2.42 (s, 6, Me), 1.23 (d, *J*(P−H) = 7.1 Hz, 9, PMe_3), 1.38 (vt, *J*(P−H) = 3.45 Hz, 18, trans PMe_3), 1.24 (d, *J*(P−H) = 7.5 Hz, cis PMe_3). ^{13}C NMR (75.4 MHz, C_6D_6): δ 135.2 (s, *o*-Ar′), 128.6 (s, *m*-Ar′), 125.5 (s, *p*-Ar′), 20.1 (s, Me), 22.2 (d, *J*(P−H) = 23.3 Hz, cis PMe_3), 17.1 (vt, *J* (P−H) = 11.5 Hz, trans PMe_3). ^{31}P NMR (121.4 MHz, C_6D_6): δ 3.69 (t, *J*(P−P) = 17.0, 1 trans P), −7.9 (d, *J* (P−P) = 17.0, 2 cis P). C,H,N analysis (%): calcd for (514.24): C 39.71, H 7.06, N 2.72; found: C 40.70, H 6.84, N 3.28.

[(Ar′N)HClSi-]$_2$: IR (Nujol). ν_{Si-H} = 2240 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 6.82 (m, 3, m + p- Ar′), 5.44 (s + d, *J* (H−Si) = 337 Hz, 1, Si−H), 2.19 (s, 6, Me). ^{13}C NMR (75.4 MHz, C_6D_6): δ 137.4 (s, *o*-Ar′), 129.7 (s, *m*-Ar′), 127.8 (*p*-Ar′), 19.9 (s, Me). ^{29}Si NMR (59.6 MHz, C_6D_6): δ - 20.9 (s). EI-HRMS: *m*/*z* found (calcd. for $C_{16}H_{20}Cl_2N_2Si_2$) 366.0540 (366.0542).

(ArN)$_2$W(PMe_3)H($SiCl_2Me$) (11b). A 0.15 mL portion (1.37 mmol) of $HSiCl_2Me$ were added to 10 mL of pentane solution of $(ArN)_2W(PMe_3)_3$ (0.259 g, 0.34 mmol) causing the color change from deep-purple to brown. In 10 s all volatiles were pumped off to give a purple residue. This was extracted with 5 mL of ether, filtered, and cooled to −30 °C. Yellow crystals were produced overnight. The cold solution was decanted, and the crystals were washed by 1 mL of pentane. The crystals were dried to afford 0.048 g of **11b**. The combined fractions were concentrated to 3 mL and cooled first to −30 °C and then to −80 °C to give the second crop. Total yield: 0.0655 g (0.90 mmol, 27%). IR (Nujol): 1731 cm^{-1}. ^{1}H NMR (300 MHz, 23 °C, C_6D_6): δ 11.24 (dd, *J*(P−H) = 59.5 Hz, *J*(W−H) = 35.0 Hz, *J*(Si−H) = 30.0 Hz 1, WH), 7.07 (m, 4, m- Ar), 7.03 (m, 2, p- Ar), 3.99 (sept, *J*(H−H) = 6.9 Hz, 2, CH), 3.66 (sept, *J*(H−H) = 6.9 Hz, 2, CH), 1.51 (s, 3, SiMe), 1.23 (d, *J*(H−H) = 6.6 Hz, 24, Ar), 1.15 (d, *J*(P−H) = 10.2 Hz, 9, PMe_3). ^{13}C NMR (75.4 MHz, 25 °C, C_6D_6): δ 153.5 (i-Ar), 143.1 (o-Ar), 125.4 (p-Ar), 122.7 (m-Ar), 28.0 (s, CH), 24.1 (s, Me/Ar), 23.9 (s, Me/Ar), 20.4 (SiMe), 19.0 (d, *J*(P−C) = 35.9 Hz, PMe_3). ^{31}P NMR (121.4 MHz, 23 °C, C_6D_6): δ 1.22 (*J*(P−W) = 316 Hz). ^{29}Si NMR (59.6 MHz, 23 °C, C_6D_6): δ 92.1 (*J*(Si−W) = 36.7 Hz). C,H,N analysis (%): calcd for $C_{28}H_{47}N_2WPSiCl_2$ (725.49): C 46.36, H 6.53, N 3.86; found: C 45.57, H 6.94, N 3.77.

Reaction of (ArN)$_2$W(PMe_3)H($SiCl_2Me$) (11b) with PMe_3. To a sample of **11b** in C_6D_6 were added 6 equiv of PMe_3. Immediate color change from yellow to brown-green occurred. NMR spectra revealed a mixture of the starting compound **11b** and the agostic (ArN)(ArNSiMeHCl···)W(PMe_3)$_2$Cl (**12b**) contaminated by some $(ArN)_2W(PMe_3)_3$ and $HSiCl_2Me$. At room temperature, the system converts to **12b**. **12b:** IR (Nujol): 2180 cm^{-1}. ^{1}H NMR (300 MHz, −40 °C, toluene-d_8): δ 7.25 (d, *J*(H−H) = 7.9 Hz, m-Ar), 7.22 (d, *J*(H−H) = 8.4 Hz, m-Ar), 6.99 (m obscured by toluene, m-Ar), 6.93 (m, p-Ar), 5.78 (badly resolved quartet, *J*(H−H) = 2.4 Hz, *J*(Si−H) = 263.8 Hz, 1H, SiH), 4.39 (q, *J*(H−H) = 6.6 Hz, 1 CH), 3.97 (q, *J*(H−H) = 6.9 Hz, 2 CH), 3.65 (q, *J*(H−H) = 6.6 Hz, 1 CH), 1.58 (d, *J*(H−H) = 6.6 Hz, 3, Ar), 1.54 (d, *J*(P−H) = 8.7 Hz, 9, PMe_3), 1.51 (d, *J*(H−H) = 6.6 Hz, 3, Ar), 1.48 (d, *J*(H−H) = 6.3 Hz, 3 Ar), 1.39 (d, *J*(H−H) = 6.9 Hz, 6, Ar), 1.31 (d, *J*(H−H) = 6.9 Hz, 6, Ar), 1.26 (d, *J*(P−H) = 8.4 Hz, 9, PMe_3), 1.18 (d, *J*(H−H) = 6.6 Hz, 3, Ar), 1.10 (d, *J*(H−H) = 6.6 Hz, 3, Ar), 0.19 (d, *J*(H−H) = 1.0 Hz, 3H, SiMe). ^{13}C NMR (75.4 MHz, −40 °C, toluene-d_8): δ 150.6 (i-Ar), 149.0 (i-Ar), 143.6 (o-Ar), 142.2 (o-Ar), 141.7 (o-Ar), 125.7 (m-Ar), 124.2 (m-Ar), 123.8 (p-Ar), 123.5 (m-Ar), 123.2 (m-Ar), 29.8 (CH), 28.8 (CH), 28.2 (CH), 27.1 (CH), 26.5 (Me-Ar), 25.8 (Me-Ar), 25.5 (Me-Ar), 25.4 (Me-Ar), 25.2 (Me-Ar), 25.1 (Me-Ar), 24.8 (d, *J*(P−C) = 21.0 Hz PMe_3), 23.9 (s, PMe_3). ^{13}P NMR (121.4 MHz, −40 °C, toluene-d_8): δ −8.8 (d, *J*(P−P) = 9.6 Hz, −22.6 (d, *J*(P−P) = 9.6 Hz. ^{13}P NMR (121.4 MHz, 25 °C, toluene-d_8): δ −12.4 (bs, 1P), −24.8 (bs, 1P). ^{29}Si HMQC: δ 41.8.

(Ar′N)(ArN’SiMeCl-H···)W(PMe_3)$_2$Cl (13c). To 0.284 g (0.437 mmol) of $(Ar'N)_2W(PMe_3)_3$ dissolved in 10 mL of pentane:toluene mixture (10:1) C_6D_6 was added by syringe 0.15 mL (1.37 mmol) of $HSiMeCl_2$. The color quickly changes from deep-purple to dark-brown. The reaction was allowed to proceed at room temperature for 1.5 h and then the reaction mixture was cooled to −30 °C. Dark crystals were formed during several days. The cold solution was decanted and the crystals were washed by small amount of cold pentane and dried. Yield: 0.112 g (0.112 g, 37%). IR (Nujol): 1914 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 7.11(d, *J* = 7.2 Hz,1, m-Ar′), 7.06 (d, *J* = 7.2 Hz, 1, m-Ar′), 6.91 (t, *J* = 7.7 Hz, 1, p-Ar′), 6.85 (t. *J* = 6.2 Hz, 1, p-Ar′), 6.85 (d, *J* = 6 Hz, 2, m-Ar′), 2.56 (s, Ar′NSi, 3), 2.51 (s, Ar′NSi, 3), 2.46 (ddq, *J*(P−H) = 16.7 Hz, *J*(H−H) = 1.5 Hz, *J*(P−H) = 0.6 Hz, 1, Si−H−W), 2.33 (s, Ar′, 6), 1.34 (d, *J* = 7.8 Hz, PMe), 1.14 (d, 8.7 Hz, PMe), 1.08 (d, *J* = 1.5 Hz, 3 SiMe), 0.87 (t, *J*(P−H) = 7.1 Hz, 1, W−H). ^{13}C NMR (75.4 MHz, C_6D_6): δ 156.4 (i, Ar′), 155.3 (i, Ar′), 135.1 (o, Ar′), 134.4 (o, Ar′), 128.5 (m, Ar′), 128.2 (m, Ar′), 127.9 (m, Ar′), 123.2 (p, Ar′), 122.2 (p, Ar′), 22.7 (d, *J*(P−C) = 27.1 Hz, PMe), 21.6 (d, *J*(P−C) = 29.6 Hz, PMe), 21.0 (C_6H_3Me), 20.8 (C_6H_3Me), 20.5 (C_6H_3Me), −1.2 (SiMe). ^{13}P NMR (121.4 MHz, C_6D_6): δ 20.7 (d + d, *J*(P−P) = 14 Hz, *J*(^{31}P−^{183}W) = 204.0 Hz 1, P), −29.9 (d + d, *J*(P−P) = 14 Hz, *J*(^{31}P−^{183}W) = 168.2 Hz). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −77.6 (^{1}*J*(Si−H) = 118 Hz). C,H,N analysis (%): calcd for $C_{23}H_{40}N_2WP_2SiCl_2$ (689.365): C 40.07, H 5.85, N 4.06; found: C 40.87, H 6.10, N 3.91.

NMR Tube Preparation of (ArN)(ArNSiMe$_2$-H$\cdots$)W(PMe$_3$)$_2$Cl (14b). To 0.069 g (0.090 mmol) of (ArN)$_2$W(PMe$_3$)$_3$ in 0.6 mL of C_6D_6 was added by syringe 0.011 mL (0.099 mmol) of HSiMe$_2$Cl. The course of the reaction was monitored by NMR. The reaction gave a mixture of compounds, the main component of which was highly fluxional at room temperature. The ^{29}Si NMR experiment (59.6 MHz, C_6D_6) revealed three products with a direct Si$-$H bond, one of which was assigned the agostic structure **14b** (δ $-$70 ppm, *J*(Si$-$H) = 81 Hz, *J*(Si$-$P) = 9 Hz).

(Ar′N)(Ar′NSiMe$_2$-H$\cdots$)W(PMe$_3$)$_2$Cl (14c). A 0.185 g portion (0.284 mmol) of (Ar\N)$_2$W(PMe$_3$)$_3$ dissolved in 30 mL of pentane was added 0.15 mL of silane HSiMe$_2$Cl. The mixture was stirred at room temperature for an hour, during which time the color changes from purple to dark-brown. Volatiles were removed in vacuo to give a green solid. Yield: 0.121 g (0.182 mmol, 64%). IR (Nujol): ν_{Si-H} = 1908 cm^{-1}, 1770 cm^{-1} (impurity). ^{1}H NMR (500 MHz, $-$50 °C, toluene-d$_8$): δ 7.21 (d, *J*(H$-$H) = 6.3 Hz, 1, Ar′), 7.09 (m, Ar′), 6.83 (d, *J*(H$-$H) = 7.5 Hz, 2, Ar′), 6.93 (m, Ar′), 6.82 (m, Ar′), 2.84 (s, 3, Me), 2.39 (s, 3, Me), 2.21 (m, *J*(P$-$H) = 23.6 Hz, W$-$H), 2.14 (s, 3, Me), 2.09 (s, 3, Me), 1.41 (d, *J*(P$-$H) = 7.2 Hz, 9, PMe$_3$), 1.12 (d, *J*(P$-$H) = 8.7 Hz, 9, PMe$_3$), 0.82 (s, 3, SiMe), 0.40 (s, 3. SiMe). ^{13}C NMR (125.7 MHz, $-$50 °C, toluene-d$_8$): δ 129.4, 128.9, 128.4. 125.8, 22.5 (d, *J*(P$-$C) = 25.8 Hz, PMe$_3$), 21.6 (s, Me), 21.1 (s, Me), 20.0 (s, Me), 0.44 (s, SiMe), $-$3.5 (s, SiMe). ^{31}P NMR (121.4 MHz, $-$50 °C, toluene-d$_8$): δ 13.1 (^{1}*J*(P$-$P) = 15.1 Hz), $-$27.1 (^{1}*J*(P$-$P) = 15.1 Hz). ^{29}Si NMR (59.6 MHz, 25 °C, toluene-d$_8$): δ $-$68.3 (^{1}*J*(Si$-$H) = 87 Hz).

(Ar′N)W(PMe$_3$)$_3$Cl$_2$ (15c). A 0.0012 mL portion of HSiCl$_3$ (0.012 mmol) was added to 5 mL of hexane solution of (Ar′N)$_2$W(PMe$_3$)$_3$ (0.077 g, 0.012 mmol). In 20 s all volatiles were removed in vacuo to give a dark-green solid. NMR showed the formation of a mixture of compounds, the main component of which is (Ar′N)W(PMe$_3$)$_3$Cl$_2$. IR(Nujol) 2274, 2167, 1778 cm^{-1} (silane and hydride impurities). ^{1}H NMR (300 MHz, 23 °C, toluene-d$_8$): δ 6.84 (m, 1, p-Ar), 6.78 (d, *J*(H$-$H) = 7.8 Hz, 2, m-Ar), 2.37 (s, 6, Me), 1.44 (vt, *J*(P$-$H) = 4.5 Hz, 18, trans-PMe$_3$), 1.42 (d, *J*(P$-$H) = 7.5 Hz, 9, cis-PMe$_3$). ^{13}C NMR (125.7 MHz, 23 °C, toluene-d$_8$): δ 169.0 (i), 142.2 (o), 129.0 (m), 128.1 (p), 26.5 (d, *J*(P$-$C) = 27.3 Hz, cis PMe$_3$), 20.4 (s, Me-Ar), 18.0 (vt, *J*(P$-$C) = 13.5 Hz, trans PMe$_3$). ^{31}P NMR (121.4 MHz, 23 °C, toluene-d$_8$): δ $-$23.0 (s), $-$24.1 (s).

(ArN)W(PMe$_3$)$_3$Cl$_2$ (15b). A 0.15 mL portion (1.47 mmol) of HSiCl$_3$ was added to 10 mL of ether solution of (ArN)$_2$W(PMe$_3$)$_3$ (0.152 g, 0.20 mmol) at 0 °C. The mixture was stirred for 20 s, and then all volatiles were removed in vacuo to give brown oil. This oil was dissolved in 5 mL of ether and charged with pentane, causing precipitation of a brown solid. The solution was filtered off, and the residue was washed with pentane and dried. ^{1}H NMR (300 MHz, 23 °C, C_6D_6): δ 7.13(m, 1, p-Ar), 6.92 (d, *J*(H$-$H) = 8.4 Hz, 2, m-Ar), 4.02 (sept, *J*(H$-$H) = 7.0 Hz, 2, CH), 4.01 (sept, *J*(H$-$H) = 6.3 Hz, 2, CH), 1.45 (vt, *J*(P$-$H) = 4.2 Hz, 18, trans-PMe$_3$), 1.44 (d, *J*(P$-$H) = 7.1 Hz, 9, cis-PMe$_3$), 1.18 (d, *J*(H$-$H) =7.2 Hz, 12, ArMe). ^{13}C NMR (125.7 MHz, 23 °C, C_6D_6): δ 151.5, 145.1, 125.5 (p-Ar), 123.7 (m-Ar), 27.4 (d, *J*(P$-$C) = 27.3 (CH), 27.6 Hz, cis-PMe$_3$), 25.3 (s, Ar-Me), 18.0 4 (vt, *J*(P$-$C) = 13.4 Hz, cis-PMe$_3$). ^{31}P NMR (121.4 MHz, 23 °C, C_6D_6): δ $-$27.8 (s, 2P), $-$28.8 (s, 1P).

NMR Reaction of (ArN)$_2$W(PMe$_3$)$_3$ with HSiCl$_3$ in the Presence of BPh$_3$. A solution of HSiCl$_3$ (4.2 μL, 0.041 mmol) and BPh$_3$ (10.0 mg, 0.041 mmol) in 0.4 mL of toluene-d$_8$ was added at $-$80 °C to a solution of (ArN)$_2$W(PMe$_3$)$_3$ (**10b**) (31.5 mg, 0.041 mmol) in 0.4 mL of toluene-d$_8$ in an NMR tube. The mixture was immediately frozen by liquid nitrogen and placed to a 600 MHz NMR spectrometer pre-cooled to $-$30 °C, and cooled down to $-$70 °C. The mixture was slowly warmed up, and the course of the reaction was monitored by NMR. At $-$20 °C, the selective formation of an initial product with the suggested structure (ArN)$_2$W(H)(SiCl$_3$)(PMe$_3$) (**16b**) was observed. Warming the mixture up to $-$10 °C leads to a slow rearrangement of the initial product into other hydride species, which do not contain a coordinated PMe$_3$ ligand. Addition of excess PMe$_3$ and warming the mixture to room temperature results in fast formation of (ArNSiHCl)$_2$ and (ArN)WCl$_2$(PMe$_3$)$_3$ (**15b**).

Table 7. X-ray Diffraction Crystal Data and Structure Refinement for **11b**

compound	**11b**
formula	$C_{28}H_{47}Cl_2N_2PSiW$
FW	725.49
color, habit	yellow, block
cryst size, mm	0.15 × 0.20 × 0.20
cryst sys	monoclinic
space group	$P2_1/n$
a, Å	10.0467 (2)
b, Å	32.2846 (3)
c, Å	10.5529 (2)
β, deg	107.754(5)
V, Å^3	2149.51(12)
Z	4
T, K	150
ρ_{calc}, g/cm^3	1.478
F(000)	1464
radiation	Mo
μ, mm^{-1}	3.812
transmission factors	0.466 - 0.583
$2\theta_{max}$, deg	54.96
total no. of reflns	14107
no. of unique reflns	7401
R_{merge}	0.02
no. with $I \geq n\theta(I)$	6229 (n = 2)
no. of variables	324
R	0.0295
R$_w$	0.0616
GOF	1.047
max Δ/σ	0.001

(ArN)$_2$W(H)(SiCl$_3$)(PMe$_3$) (16b). ^{1}H NMR (600 MHz, toluene-d$_8$, 226 K) δ: 11.04 (d, ^{2}*J*(H$-$P) = 58.8 Hz, 1H, W-*H*), 7.00$-$7.26 (multiplet overlapping with the residual toluene-d$_8$ resonances, 6H, N*Ar*), 4.01 (bs, 2H, 2*CH*, N*Ar*), 3.91 (bs, 1H, *CH*, N*Ar*), 3.56 (bs, 1H, *CH*, N*Ar*), 1.50 (bs, 6H, 2*CH*$_3$, N*Ar*), 1.42 (bs, 3H, *CH*$_3$, N*Ar*), 1.31 (m, 12H, 4*CH*$_3$, N*Ar*), 1.19 (bs, 3H, *CH*$_3$, N*Ar*), 1.05 (d, ^{2}*J*(H$-$P) = 7.8 Hz, 9H, P*Me*$_3$). ^{1}H-{^{31}P} NMR (600 MHz, toluene-d$_8$, 224 K) δ: 11.04 (bs, 1H, W-*H*), 1.05 (s, 9H, P*Me*$_3$). ^{31}P NMR (243 MHz, toluene-d$_8$, 223 K) δ: 3.01 (s + sat, ^{1}*J*(P$-$W) = 328.0 Hz, *P*Me$_3$). ^{1}H$-^{29}$Si HSQC NMR (*J*(Si$-$H) = 7 Hz, toluene-d$_8$, 253 K) δ: 73.8 (*Si*Cl$_3$). ^{1}H$-^{13}$C HSQC NMR (*J*(H$-$C) = 145 Hz, $-$30 °C, toluene-d$_8$) δ: 127.4, 126.4, 123.9, 123.4, 123.3, 121.9 (*m*-C and *p*-C of N*Ar*), 27.8, 27.6, 21.7 (*CH*, N*Ar*), 26.5, 25.9, 25.2, 24.8, 24.0, 23.5, 21.1 (*CH*$_3$, N*Ar*), 18.03 (P*Me*$_3$).

DFT Calculations. The unconstrained geometry optimization was carried out for all the considered structures with the Gaussian 03 program package,[23] using DFT and applying Becke three parameter hybrid exchange functional in

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conjunction with gradient-corrected nonlocal correlation functional of Perdew and Wang (B3PW91).[24] The 6-31G(d,p) basis set was used for the H, C, N, Si, P and Cl atoms. The Hay−Wadt effective core potentials (ECP) and the corresponding VDZ basis sets were used for the Mo atoms.[25] The same level of theory was used in the frequency calculations performed at the located stationary points. The thermodynamic parameters were calculated in the rigid rotor−harmonic oscillator approximation.

Crystal Structure Determinations for 11b. The crystals of **11b** were grown from diethyl ether by cooling to −30 °C. The crystals were mounted in a film of perfluoropolyether oil on a glass fiber and transferred to a Siemens three-circle diffractometer with a CCD detector (SMART system). The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by full-matrix least-squares procedures (Table 7).[26] All non-hydrogen atoms were refined anisotropically, the hydrogen atoms except the hydride (which was located from Fourier difference synthesis and positionally refined isotropically) were placed in calculated positions and refined in a "riding" model.

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Supporting Information Available: VT NMR spectra for compound **3c** and X-ray data in CIF format for compound **11b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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