Supporting information

to the article

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

by Andrey Y. Khalimon, Razvan Simionescu, and Georgii I. Nikonov*

gnikonov@brocku.ca

Catalytic reactivity of complex 3. We found that compound **3** catalyzes a variety of hydrosilylation processes details of which are given in (Tables SI1 - 4). Thus, the 1:1 reaction of benzaldehyde with $PhSiH_3$ in the presence of 0.5 mol. % of complex **3** gives 100 % conversion after 16 hours, affording a mixture of mono- and bis(substituted) silyl ethers $PhH_2Si(OBn)$ and $PhHSi(OBn)_2$ in 43 % and 57 % yield, respectively (Table SI1, entry 1).[1, 2] Changing the ratio of PhC(O)H and $PhSiH_3$ to 2:1 leads (at 1.3 mol. % catalyst load) to increased reaction time, achieving 100 % conversion of the benzaldehyde after one week at room temperature, but almost exclusive formation of $PhHSi(OBn)_2$ (95 % by integration of the ^1H NMR spectrum) is observed (Table SI1, entry 2).

The catalytic hydrosilylation of benzaldehyde proved highly sensitive to the Lewis acidity and steric hindrance of the silane. Thus, treatment of PhC(O)H with $PhMeSiH_2$ in the presence of 1.6 mol. % of **3** gives after 6 days at room temperature only 28 % conversion of benzaldehyde to form exclusively PhMeHSi(OBn)[2] (Table SI1, entry 3). At the same time, the reaction with more Lewis acidic $(EtO)_3SiH$[3] (1.0 % load of **3**) results in even lower conversion of PhC(O)H: 10 % after 4 days at room temperature (entry 4). At 50 ºC, the reaction of PhC(O)H with $(EtO)_3SiH$ goes to completion after 12 days, giving only 10 % of $(EtO)_3Si(OBn)$[3a]. The other 90 % were found to be $(EtO)_2Si(OBn)_2$ (32 %), $(EtO)Si(OBn)_3$ (47 %), and $Si(OBn)_4$ (11 %), produced by catalytic redistribution of the benzoxy(triethoxy)silane (Table SI1, entry 5).[4]

The catalytic hydrosilylation of ketones (acetophenone and acetone) by $PhSiH_3$ at room temperature is very sluggish (Table SI1, entries 6 and 7). An increase of the reaction time and/or temperature leads to competing silane redistribution and to partial carbonyl reduction to alkane.[5]

Table SI1. Catalytic hydrosilylation of ketones and aldehydes mediated by complex **3**.

Entry	Substrate[a]	Silane	Cat., mol. %	T, °C / time	Products[b]	Substr. conv.[c]	Yield[c]
1	PhC(O)H	$PhSiH_3$	0.5	RT / 16 h	$PhH_2Si(OBn)$	100 %	43 %
					$PhHSi(OBn)_2$		57 %
2[d]			1.3	RT / 7 days	$PhH_2Si(OBn)$	100 %	5 %
					$PhHSi(OBn)_2$		95 %
3		$PhMeSiH_2$	1.6	RT / 6 days	PhMeHSi(OBn)	28 %	28 %
4		$(EtO)_3SiH$	1.0	RT / 4 days	$(EtO)_3Si(OBn)$	10 %	8 %
					$(EtO)Si(OBn)_3$		< 2 %
5				50 °C / 12 days	$(EtO)_3Si(OBn)$	100 %	10 %
					$(EtO)_2Si(OBn)_2$		32 %
					$(EtO)Si(OBn)_3$		47 %
					$Si(OBn)_4$		11 %
6	PhC(O)Me	$PhSiH_3$	1.0	RT / 20 days	$PhH_2Si[OCH(Me)Ph]$	100 %	44 %
					$PhHSi[OCH(Me)Ph]_2$		29 %
					$PhHSi[OCH(Me)Ph]_3$		21 %
					$PhCH_2CH_3$		6 %
7	$Me_2C(O)$	$PhSiH_3$	1.0	RT / 5 days	$PhH_2Si(O^iPr)$	79 %	34 %
					$PhHSi(O^iPr)_2$		42 %

[a] The substrate/silane ratio with is 1:1. [b] Reactions with $PhSiH_3$ give Ph_2SiH_2 and SiH_4 by-products.[6] [c] Detected by ^1H NMR spectroscopy using tetramethylsilane as an internal standard. [d] 2:1 ratio of PhC(O)H and $PhSiH_3$, respectively.

Complex **3** turned out to be inactive in the hydrosilylation of alkenes and alkynes (Table SI2). Thus, reactions of $PhSiH_3$ with 1-hexene, cyclohexene, and styrene result only in partial reduction to the corresponding alkanes.[7] For instance, stoichiometric treatment of 1-hexene with $PhSiH_3$ in the presence of 5.0 mol. % of **3** leads after three days at room temperature to only 20 % conversion of the substrate, forming hexane in 15 % yield. 5 % of the isomerized product, 2-hexene,[8] was also observed by ^1H NMR (Table SI2, entry 1). Increase of the reaction time (37 days) and temperature (50 ºC) affords 100 % conversion of 1-hexene and production of 71 % of hexane in a mixture with 2-hexene (26 %) and hydrosilylation products[9] (less than 3 %) (Table SI2, entry 2). Treatment of the less sterically hindered olefin, ethylene, by $PhSiH_3$ gives, however, hydrosilylation products (a mixture of $PhEtSiH_2$, $PhEt_2SiH$, and $PhEt_3Si$) in 49 % yield after 15 hours at 50 ºC (Table 2, entry 9). Similarly to other alkenes, the formation of 31 % of ethane was also detected by ^1H NMR.

Table SI2. Reactions alkenes and alkynes with hydrosilanes in the presence of complex **3**

Entry	Substrate[a]	Silane	Cat., mol. %	T, °C / time	Products[b]	Subst. conv.[c]	Yield[c]
1	1-hexene	$PhSiH_3$	5.0	RT/3 days	2-hexene	20 %	5 %
					Hexane		15 %
2				50 °C / 37 days	2-hexene	100 %	26 %
					Hexane		71 %
					Hydrosilylation products		< 3 %
3	Cyclohexene	$PhSiH_3$	5.0	RT / 2 days	Cyclohexane	< 5 %	< 5 %
4				50 °C / 39 days	Cyclohexane	28 %	28 %
5	Styrene	$PhSiH_3$	3.0	50 °C / 23 h	$PhCH_2CH_3$	6 %	6 %
6	PhC≡CH	$PhSiH_3$	2.7	RT / 17 h	Polyphenylacetylene	100 %	100 %
7		—	3.0	RT / 24 h	Polyphenylacetylene	25 %	25 %

8				50 °C / 24 h	Polyphenylacetylene	45 %	45 %
9	Ethylene	$PhSiH_3$	3.3	50 °C / 15 h	$PhEtSiH_2$	80 %	19 %
					$PhEt_2SiH + PhEt_3Si$		30 %
					Ethane		31 %

[a] The substrate/ silane ratio with is 1:1 [b] Formation of Ph_2SiH_2 and SiH_4 as by-products was observed.[6] [c] Detected by ^1H NMR spectroscopy using tetramethylsilane as an internal standard.

Neither hydrosilylation nor reduction were observed upon the room temperature reaction of phenylacetylene with $PhSiH_3$ in the presence of 2.7 mol. % of **3**. Instead, catalytic polymerization[10] takes place, leading to 100 % conversion of the phenylacetylene and formation of polyphenylacetylene (TON = 34, TOF = 2; Table 2, entry 6) after 17 h. Surprisingly, in the absence of silane the turnover number decreases significantly, and only 25 % conversion of the alkyne is achieved after 24 h at room temperature. The increase of temperature up to 50 ºC does not affect significantly the yield of the polymer (Table SI2, entries 7 and 8). These observations suggest that $PhSiH_3$ plays an important role, presumably, in the recovery of the catalyst during polymerization.

Catalytic alcoholysis of $PhSiH_3$ by an equivalent of ethanol or isopropanol is a fast process and gives 100 % conversion in only 5 min. at room temperature (TON = 20, TOF = 241; Table SI3, entries 3 and 5).[11-13] The stoichiometric reaction of $PhSiH_3$ with either EtOH or ^{i}PrOH in the presence of 5.0 mol. % of **3** affords a mixture of mono- and disubstituted products $PhH_2Si(OR)$ (R = Et (33 %), ^{i}Pr (18 %)) and $PhHSi(OR)_2$ (R = Et (67 %), ^{i}Pr (82 %)), [1b,14] respectively. Addition of two equivalents of ethanol to phenylsilane results in a longer reaction time (25 min), but provides more selective formation of diethoxyphenylsilane (89 %; TON = 41, TOF = 98; Table SI3, entry 4).

Similar high catalytic activity of **3** was also found in the aminolysis of $PhSiH_3$ by aniline (5.0 mol. % cat. load, TON = 20, TOF = 60; Table SI3, entry 6).

Finally, the agostic silylamide **3** was found to mediate the addition of phenylsilane to nitriles. Only traces (< 3 %) of the hydrosilylation product $EtN(SiH_2Ph)_2$ were observed in the reaction of $PhSiH_3$ with CH_3CN even after heating the reaction mixture at 50 ºC for 51 h (Table SI3, entry 1). On the other hand, a 1:1 reaction of PhCN with $PhSiH_3$ in the presence of 5.0 mol. % of **3** results in 20 % conversion of the nitrile into the silylated imine $PhCH{=}N(SiH_2Ph)$ after 6 days at 50 ºC (TON = 4, Table SI3, entry 2). Such a selective monoaddition in the hydrosilylation of nitriles is very rare, [15-19] and only few reactions were achieved catalytically. [20,21]

Table SI3. Hydrosilylation of nitriles and alcoholysis and aminolysis of silanes mediated by complex **3**

Entry	Substrate[a]	Silane	Cat., mol. %	T, °C / time	Products[b]	Substrate conv.[c]	Yield[c]
1	CH_3CN	$PhSiH_3$	5.0	50 °C / 51 h	$EtN(SiH_2Ph)_2$	< 3 %	< 3 %
2	PhCN	$PhSiH_3$	5.0	50 °C / 6 days	$PhHC{=}N(SiH_2Ph)$	20 %	20 %
3	EtOH	$PhSiH_3$	5.0	RT / 5 min	$PhH_2Si(OEt)$	100 %	33 %
					$PhHSi(OEt)_2$		67 %
4[d]				RT / 25 min	$PhH_2Si(OEt)$	100 %	11 %
					$PhHSi(OEt)_2$		89 %
5	$^{i}PrOH$	$PhSiH_3$	5.0	RT / 5 min	$PhH_2Si(O^{i}Pr)$	100 %	18 %
					$PhHSi(O^{i}Pr)_2$		82 %
6	$PhNH_2$	—	5.0	RT / 20 min	$PhHN(SiH_2Ph)$	100 %	100 %

[a] The substrate/ silane ratio with is 1:1 [b] Reactions with $PhSiH_3$ give Ph_2SiH_2 and SiH_4 as by-products.[6] [c] Detected by ^1H NMR spectroscopy using tetramethylsilane as an internal standard. [d] 2:1 ratio of EtOH and $PhSiH_3$, respectively.

NMR scale reaction of (ArN=)$_2$Mo(η^2-C$_2$H$_4$)(PMe$_3$)$_2$ with PhSiH$_3$

A. PhSiH$_3$ (14.5 μL, 0.118 mmol) was added to a solution of (ArN=)$_2$Mo(η^2-C$_2$H$_4$)(PMe$_3$)$_2$ (32.4 mg, 0.059 mmol) in 0.6 mL of C_6D_6 in an NMR tube. No visual changes were observed after the silane addition. The reaction mixture was left at room temperature overnight. During this time the colour of the solution changed from purple to dark-green. NMR analysis showed the formation of a difficult-to-separate mixture of **3**, **4**, and unidentified polyhydride species, along with the formation of PhEtSiH$_2$.

B. A solution of BPh$_3$ (13.9 mg, 0.057 mmol) and PhSiH$_3$ (14.2 μL, 0.115 mmol) in 0.6 mL of C_6D_6 was added to a solid (ArN=)$_2$Mo(η^2-C$_2$H$_4$)(PMe$_3$)$_2$ (36.0 mg, 0.057 mmol). The colour of the solution turned brown. The reaction mixture was left at room temperature for 5 min. NMR analysis showed quantitative formation of **3** and Ph$_3$B·PMe$_3$.

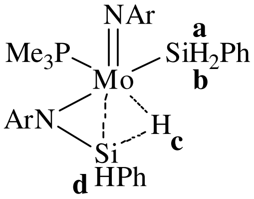
Preparation of (ArN=)Mo(SiD$_2$Ph)(PMe$_3$)(η^3-N(Ar)-SiDPh-D) (3d$_4$). The reaction was performed analogously to the preparation of **3** described above, using 0.72 g (1.061 mmol) of (ArN=)$_2$Mo(PMe$_3$)$_3$, 0.27 mL (2.121 mmol) of PhSiD$_3$, and 30 mL of hexanes. Yield: 0.41 g, 68 %. The spectral data for **3d$_4$** are the same as for **3** except for Si*H* resonances, which are not seen in the ^{1}H NMR spectrum of **3d$_4$** due to full substitution with deuterium.

NMR scale reaction of complex 3 with PhSiH$_3$. PhSiH$_3$ (4.14 μL, 0.034 mmol) was added to a solution of **3** (24.7 mg, 0.034 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The ^{1}H-^{1}H EXSY NMR experiment established proton exchange between the silyl substituent in **3** and free silane. After overnight at room temperature, NMR analysis showed the formation of a mixture of PhSiH$_3$ (30 %), Ph$_2$SiH$_2$ (34 %), SiH$_4$ (34 %) and PhSiH$_2$-

SiH_2Ph (2 %). At 50 °C, an analogous overnight reaction leads to full conversion of $PhSiH_3$ into Ph_2SiH_2 (47 %), SiH_4 (47 %) and $PhSiH_2$-SiH_2Ph (6 %).

NMR scale reaction of complex 3 with $PhSiD_3$. Compound **3** (23.0 mg, 0.031 mmol) was dissolved in 0.6 mL of toluene-d_8 to give a clear brown solution. The ^1H NMR spectrum of **3** acquired at -50 °C was carefully integrated. $PhSiD_3$ (3.85 μL, 0.031 mmol) was added to a solution, and the reaction mixture was left for 5 min. The extent of deuterium incorporation into each position was calculated from the difference of integration of the residual protons in the ^1H NMR spectra recorded at -50 °C.

H position	H, %	D, %
A(b)	55	45
B(a)	55	45
c	54	46
d	58	42



NMR scale reaction of complex 3 with (*m*-Tol)SiH_3. (*m*-Tol)SiH_3 (5.0 μL, 0.037 mmol) was added to a solution of complex **3** (27.3 mg, 0.037 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The reaction mixture was left at room temperature for 10 min. All volatiles were pumped off; the residue was dried under vacuum and then redissolved in toluene-d_8. VT NMR spectra showed the formation of a mixture (ArN=)Mo{SiH_2(*m*-Tol)}(PMe_3)(η^3-N(Ar)-SiHPh-H) (**3_{tol}**, 43 % by ^1H NMR analysis) and **3**, accompanied by the release of $PhSiH_3$. No exchange between the agostic silicon centre of **3** and $PhSiH_3$ was observed.

3_{tol}: ^1H NMR (300 MHz; C_6D_6; δ, ppm): 8.14 (m, 2H, *o*-H, *m-Tol*SiH_2), 2.25 (s, 3H, CH_3, *m-Tol*SiH_2), other signals are overlapping with those for **3**. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, δ, ppm): 10.5 (s, *P*Me_3). ^1H NMR (600 MHz; C_6D_6; - 30 °C; δ, ppm): 8.45 (d, $^3J_{H\text{-}H}$

= 7.2 Hz, 2H, *o*-H, *m-Tol*SiH$_2$), 7.38 (d, $^3J_{\text{H-H}}$ = 7.8 Hz, 2H, *o*-H, *Ph*SiH), 6.12 (m, 1H, (Ar)NSi*H*Ph-H), 5.97 (bs, 1H, *m*-TolSi*H*$_2$), 5.64 (bs, 1H, *m*-TolSi*H*$_2$), 4.36 (m, 1H, (Ar)NSiHPh-*H*), 2.30 (s, 3H, *CH$_3$*, *m-Tol*SiH$_2$), other signals are overlapping with those for **3**. ^{31}P{^{1}H} NMR (243 MHz; toluene-d$_8$; - 20 °C; δ, ppm): 12.2 (s, *P*Me$_3$).

General procedure for catalytic hydrosilylation mediated by complex 3. A solution of substrate, silane (when needed), and tetramethylsilane (5 mol. %) in 0.6 mL of C_6D_6 was added in one portion at room temperature to complex **3**. The mixture was immediately transferred to an NMR tube and the reaction was monitored by NMR spectroscopy at the appropriate temperature. Conversion of the substrate and the yield and structure of products were determined by NMR.

MePhHSi(OBn): ^{1}H NMR (300 MHz; C_6D_6; *δ*, ppm): 0.34 (d, $^3J_{\text{H-H}}$ = 2.7 Hz, 3H, Si*Me*), 4.62 (s, 2H, *CH$_2$*, O*Bn*), 5.26 (q, $^3J_{\text{H-H}}$ = 2.7 Hz, 1H, *H*Si), 7.13 (m, 3H, *m-H* and *p-H*, *Ph*, O*Bn*), 7.23 (m, 3H, *m-H* and *p-H*, Si*Ph*), 7.43 (m, 2H, *o-H*, *Ph*, O*Bn*), 7.57 (m, 2H, *o-H*, Si*Ph*). ^{29}Si INEPT+ NMR (119.2 MHz; C_6D_6; *J* = 200 Hz; *δ*, ppm): - 0.9 (d, $^1J_{\text{Si-H}}$ = 209.9 Hz, PhMe*Si*H).

(EtO)$_2$Si(OBn)$_2$: ^{1}H NMR (300 MHz; C_6D_6; selected resonances: *δ*, ppm): 4.88 (s, 4H, 2 *CH$_2$*, O*Bn*). ^{29}Si INEPT+ NMR (119.2 MHz, C_6D_6, *J* = 7 Hz, *δ*, ppm): - 81.6 (bm, overlapping with other $(EtO)_nSi(OBn)_{4-n}$ products).

(EtO)Si(OBn)$_3$: ^{1}H NMR (300 MHz; C_6D_6; selected resonances: *δ*, ppm): 4.91 (s, 6H, 3 *CH$_2$*, O*Bn*). ^{29}Si INEPT+ NMR (119.2 MHz; C_6D_6; *J* = 7 Hz; *δ*, ppm): - 81.6 (bm, overlapping with other $(EtO)_nSi(OBn)_{4-n}$ products).

Si(OBn)$_4$: ^{1}H NMR (300 MHz; C_6D_6; selected resonances: δ, ppm): 4.99 (s, 8H, 4 *CH$_2$*, O*Bn*). ^{29}Si INEPT+ NMR (119.2 MHz; C_6D_6; J = 7 Hz; δ, ppm): - 81.6 (bm, overlapping with other $(EtO)_nSi(OBn)_{4-n}$ products).

PhSiH$_2$[OCH(Me)Ph]: ^{1}H NMR (300 MHz; C_6D_6; selected resonances: δ, ppm): 1.38 (d, $^3J_{H\text{-}H}$ = 6.3 Hz, 3H, *CH$_3$*), 4.80 (q, $^3J_{H\text{-}H}$ = 6.3 Hz, 1H, *CH*), 5.20 (s, 2H, PhSi*H$_2$*). ^{29}Si NMR (59.6 MHz; C_6D_6; δ, ppm): - 20.4 (t, $^1J_{Si\text{-}H}$ = 220.0 Hz, Ph*Si*H$_2$); ^{29}Si{^{1}H}-NMR (59.6 MHz; C_6D_6; δ, ppm): - 20.4 (s, Ph*Si*H$_2$).

PhSiH[OCH(Me)Ph]$_2$: ^{1}H NMR (300 MHz; C_6D_6; selected resonances; δ, ppm): 1.42 (d, $^3J_{H\text{-}H}$ = 6.3 Hz, 3H, *CH$_3$*); 4.98 (m, $^3J_{H\text{-}H}$ = 6.0 Hz, 2H, *CH*); 5.30 (s, 1H, PhSi*H*). ^{29}Si NMR (59.6 MHz; C_6D_6; δ, ppm): - 32.6 (d, $^1J_{Si\text{-}H}$ = 248.6 Hz, Ph*Si*H); ^{29}Si{^{1}H}-NMR (59.6 MHz; C_6D_6; δ, ppm): - 32.6 (s, Ph*Si*H).

PhSi[OCH(Me)Ph]$_3$: ^{1}H NMR (300 MHz; C_6D_6; selected resonances; δ, ppm): 1.36 (d, $^3J_{H\text{-}H}$ = 6.0 Hz, 3H, *CH$_3$*), 5.03 (m, $^3J_{H\text{-}H}$ = 6.0 Hz, 3H, *CH*). ^{29}Si NMR (59.6 MHz; C_6D_6; δ, ppm): -32.7 (s, Ph*Si*).

PhH$_2$Si(OEt): ^{1}H NMR (300 MHz, C_6D_6; selected resonances; δ, ppm): 5.19 (s, 2H, *H$_2$*Si). ^{29}Si INEPT+ NMR (119.2 MHz; C_6D_6; J = 200 Hz; δ, ppm): - 28.6 (t, $^1J_{Si\text{-}H}$ = 210.0 Hz, PhH$_2$*Si*).

PhSiH(OEt)$_2$: ^{1}H NMR (300 MHz, C_6D_6; selected resonances; δ, ppm): 5.22 (s, 1H, *H*Si). ^{29}Si INEPT+ NMR (119.2 MHz; C_6D_6; J = 200 Hz; δ, ppm): - 30.8 (d, $^1J_{Si\text{-}H}$ = 241.3 Hz, PhH*Si*).

PhH$_2$Si(O^{i}Pr): ^{1}H NMR (300 MHz, C_6D_6; δ, ppm): 7.61 (m, 2H, *o*-H, *Ph*Si); 7.10-7.20 (m, 3H, *m*-H and *p*-H, *Ph*Si), 5.23 (s, 2H, *H$_2$*Si), 3.91 (sept, $^3J_{H\text{-}H}$ = 6.1 Hz, 1H, *CH*, SiO^i*Pr*), 1.08 (d, $^3J_{\text{H-H}}$ = 6.1 Hz, 6H, 2 *CH$_3$*, SiO^i*Pr*). ^{29}Si INEPT+ NMR (119.2 MHz; C_6D_6; *J* = 200 Hz; *δ*, ppm): - 22.5 (t, $^1J_{\text{Si-H}}$ = 213.4 Hz, Ph*Si*H$_2$).

PhSiH(O^{i}Pr)$_2$: ^{1}H NMR (300 MHz, C_6D_6; *δ*, ppm): 7.79 (m, 2H, *o*-H, *Ph*Si), 7.20-7.10 (m, 3H, *m*-H and *p*-H, *Ph*Si), 5.28 (s, 1H, Si*H*), 4.20 (sept, $^3J_{\text{H-H}}$ = 6.1 Hz, 2H, 2 *CH*, Si(O^i*Pr*)$_2$), 1.16 (d, $^3J_{\text{H-H}}$ = 6.1 Hz, 12H, 4 *CH$_3$*, Si(O^i*Pr*)$_2$). ^{29}Si INEPT+ NMR (119.2 MHz; C_6D_6; *J* = 200 Hz; *δ*, ppm): - 34.8 (d, $^1J_{\text{Si-H}}$ = 239.7 Hz, Ph*Si*H).

EtN(SiH$_2$Ph)$_2$: ^{1}H NMR (300 MHz, C_6D_6; selected resonances: *δ*, ppm): 5.19 (s, 2H, Si*H$_2$*Ph), 4.00 (s, 2H, C*H$_2$*Ph).

PhH$_2$Si(N=CHPh): ^{1}H NMR (300 MHz, C_6D_6; selected resonances: *δ*, ppm): 8.90 (s, 1H, C*H*Ph), 7.70 (m, 2H, Ph), 7.63 (m, 2H, Ph), 5.42 (s, 2H, Si*H$_2$*Ph).

NMR scale reaction of complex 3 with PhCN. Benzonitrile (3.8 μL, 0.037 mmol) was added to a solution of **3** (27.2 mg, 0.037 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The reaction was left at room temperature for 1 h. NMR analysis showed the formation of an intermediate tentatively formulated as (ArN=)(PMe$_3$)Mo(η^2-NAr=SiHPh)(η^2-N≡CPh) (**11b**), which was unstable and rearranged slowly into another product. All volatiles were pumped off; the oily residue was dried under vacuum, redissolved in fresh C_6D_6 and left at room temperature overnight for complete rearrangement. NMR spectra showed the formation of (ArN=)Mo(PMe$_3$)(η^2-NAr-SiHPh-CPh=N) (**12b**). Complex **12b** is unstable at room temperature in solution and completely decomposes within few days.

11b: ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): -6.4 (s, *P*Me$_3$).

12b: ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 8.83 (d, $^3J_{\text{H-H}}$ = 6.9 Hz, 2H, *o*-H, C*Ph*), 8.06 (m, 2H, *o*-H, Si*Ph*), 7.75-6.96 (m, 12H, *p*-H and *m*-H of C*Ph*, Si*Ph* and N*Ar*), 5.34 (s, 1H, Si*H*), 3.75 (m, 4H, 4*CH*, N*Ar*), 1.41 (d, $^3J_{\text{H-H}}$ = 6.6 Hz, 3H, *CH$_3$*, N*Ar*), 1.25 (d, $^3J_{\text{H-H}}$

= 7.2 Hz, 3H, *CH₃*, N*Ar*), 1.14 (d, $^2J_{\text{H-P}}$ = 8.7 Hz, 9H, P*Me₃*), 1.05 (d, $^3J_{\text{H-H}}$ = 7.2 Hz, 6H, 2*CH₃*, N*Ar*), 0.98 (d, $^3J_{\text{H-H}}$ = 6.9 Hz, 6H, 2*CH₃*, N*Ar*), 0.89 (m, 3H, *CH₃*, N*Ar*), 0.61 (d, $^3J_{\text{H-H}}$ = 7.2 Hz, 3H, *CH₃*, N*Ar*). $^{31}P\{^1H\}$ NMR (121.5 MHz; C_6D_6; δ, ppm): - 3.5 (s, *P*Me₃). ^{29}Si INEPT+ NMR (59.6 MHz; C_6D_6; *J* = 200 Hz; δ, ppm): - 44.4 (d, $^1J_{\text{Si-H}}$ = 225.4 Hz, *Si*H). $^{13}C\{^1H\}$ NMR (75.5 MHz; C_6D_6; δ, ppm): 16.9 (d, $^1J_{\text{C-P}}$ = 22.6 Hz, P*Me₃*), 21.5 (s, *CH₃*, N*Ar*), 23.2 (s, *CH₃*, N*Ar*), 23.6 (s, *CH₃*, N*Ar*), 24.1 (s, *CH₃*, N*Ar*), 24.7 (s, *CH₃*, N*Ar*), 24.9 (s, *CH₃*, N*Ar*), 27.8 (s, *CH*, N*Ar*), 28.0 (s, *CH*, N*Ar*), 28.3 (s, *CH*, N*Ar*), 29.1 (s, *CH*, N*Ar*), 122.4 (s, *p*-C, N*Ar*), 122.7 (s, *p*-C, N*Ar*), 122.8 (s, *m*-C, N*Ar*), 123.3 (s, *m*-C, N*Ar*), 125.2 (s, *m*-C, N*Ar*), 126.8 (s, *m*-C, N*Ar*), 127.0 (s, *m*-C, Si*Ph*), *m*-C of C*Ph*, obscured by benzene signal, 128.5 (s, *p*-C, Si*Ph*), 129.0 (s, *p*-C, C*Ph*), 133.4 (s, *o*-C, C*Ph*), 133.9 (s, *o*-C, C*Ph*), 135.5 (s, *o*-C, Si*Ph*), 136.9 (s, *o*-C, Si*Ph*), 141.5 (s, *o*-C, N*Ar*), 141.6 (s, *o*-C, N*Ar*), 143.5 (s, *o*-C, N*Ar*), 151.2, 153.6, 158.4 (all singlets, aromatic *i*-C), 192.4 (s, Ph*C*=N). IR (nujol): 2118 cm^{-1} (medium, Si-H).

NMR scale reaction of complex 3 with ^{i}PrCN. ^{i}PrCN (1.9 μL, 0.021 mmol) was added to a solution of **3** (15.3 mg, 0.021 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The reaction mixture was left at room temperature for 5 min. NMR analysis showed the formation of only one product, rationalized as the nitrile adduct (ArN=)Mo(PMe₃)(η^2-N(Ar)=SiHPh)(η^2-N≡C^{i}Pr) (**11c**). This product was unstable and slowly rearranged into the compound (ArN=)Mo(PMe₃)(η^2-NAr-SiHPh-C(^{i}Pr)=N) (**12c**). After 80 minutes at room temperature, the rearrangement was complete. At this point all volatiles were pumped off, the oily residue was dried under vacuum and redissolved in fresh C_6D_6. Further NMR analysis showed the presence of only **12c** in solution.

11c: ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 5.74 (d, $^3J_{H\text{-}P}$ = 3.9 Hz, 1H, Si*H*), 1.59 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 6H, 2*CH₃*, ^{i}*Pr*C≡N). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): - 4.4 (s, *P*Me₃).

12c: ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.94 (m, 2H, *o*-H, Si*Ph*), 7.09-6.89 (m, 3H, 9H, *m*-H and *p*-H of Si*Ph*, *m*-H and *p*-H of N*Ar*), 5.31 (s, 1H, Si*H*), 3.95 (m, 1H, *CH*, N*Ar*), 3.78 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 1H, *CH*, ^{i}*Pr*C=N), 3.70 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, 2*CH*, N*Ar*), 3.63 (sept, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H, *CH*, N*Ar*), 1.69 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 6H, 2CH_3, ^{i}*Pr*C=N), 1.36 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 3H, CH_3, N*Ar*), 1.30 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 3H, CH_3, N*Ar*), 1.22 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 3H, CH_3, N*Ar*), 1.18 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 6H, 2CH_3, N*Ar*), 1.12 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 6H, 2CH_3, N*Ar*), 1.05 (d, $^2J_{H\text{-}P}$ = 8.7 Hz, 9H, P*Me*₃), 0.60 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 3H, CH_3, N*Ar*). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): - 3.8 (s, *P*Me₃). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; δ, ppm): 14.3 (d, $^1J_{C\text{-}P}$ = 21.9 Hz, P*Me*₃), 22.55 (s, CH_3, ^{i}*Pr*C=N), 22.60 (s, CH_3, N*Ar*), 23.76 (s, CH_3, N*Ar*), 23.83 (s, CH_3, N*Ar*), 24.2 (s, CH_3, N*Ar*), 26.8 (s, CH_3, N*Ar*), 28.0 (s, *CH*, N*Ar*), 28.1 (s, *CH*, N*Ar*), 28.2 (s, *CH*, N*Ar*), 28.6 (s, *CH*, ^{i}*Pr*C=N), 122.5 (s, *p*-C, N*Ar*), 122.6 (s, *p*-C, N*Ar*), 122.8 (s, *m*-C, N*Ar*), 123.0 (s, *m*-C, N*Ar*), 125.3 (s, *m*-C, N*Ar*), *m*-C of Si*Ph* signal is overlapping with the benzene signal, 129.7 (s, *p*-C, Si*Ph*), 136.9 (s, *o*-C, Si*Ph*), 141.3 (s, *o*-C, N*Ar*), 141.8 (s, *o*-C, N*Ar*), 143.7 (s, *o*-C, N*Ar*), 153.8, 155.6, 155.8 (all singlets, aromatic *i*-C), 195.9 (s, ^{i}Pr*C*=N). ^{29}Si INEPT+ NMR (59.6 MHz; C_6D_6; 200 Hz; δ, ppm): - 46.6 (d, $^1J_{Si\text{-}H}$ = 218.3 Hz, *Si*H). IR (nujol): 2103 cm^{-1} (medium, Si-H).

NMR scale reaction of complex 12c with PhSiH₃. $PhSiH_3$ (12.0 μL, 0.097 mmol) was added to a solution of **12c** (21.5 mg, 0.031 mmol) in 0.6 mL of C_6D_6 in an NMR tube. No visual changes were observed. The reaction mixture was left at room temperature for 4 days. NMR analysis showed the selective formation of **3**. Mo-free silicon containing by-products were not identified.

NMR scale reaction of complex 3 with *ᵗ*BuCN. *ᵗ*BuCN (3.7 μL, 0.034 mmol) was added at to a solution of **3** (24.8 mg, 0.034 mmol) in 0.6 mL of toluene-d_8 in an NMR tube. The reaction mixture was left at room temperature for 5 min. NMR analysis showed the formation of a single product (ArN=)Mo(PMe_3)(η^2-NAr=SiHPh)(η^2-N≡C^{t}Bu) (**11d**). Complex **11d** decomposes slowly in solution, affording a difficult-to-analyze mixture of compounds. One of the components of this mixture appears to be similar to **12c** (see above) and was formulated as (ArN=)Mo(PMe_3)(η^2-NAr-SiHPh-C(^{t}Bu)=N) (**12d**). The latter is also not stable and decomposes completely in solution after one day at room temperature.

11d: ^{1}H NMR (600 MHz; toluene-d_8; δ, ppm): 7.98 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o*-H, Si*Ph*), 6.87-7.10 (m, overlapping with residual toluene-d_8 signals, *p*-H and *m*-H of *Ar*N and Si*Ph*), 5.66 (d, $^3J_{H-P}$ = 3.6 Hz, 1H, Si*H*), 3.95 (m, 2H, 2*CH*, N*Ar*), 3.86 (sept, $^3J_{H-H}$ = 6.6 Hz, 1H, *CH*, N*Ar*), 2.50 (sept, $^3J_{H-H}$ = 6.6 Hz, 1H, *CH*, N*Ar*), 1.45 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, N*Ar*), 1.42 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, N*Ar*), 1.39 (s, 9H, ^{t}*Bu*C), 1.28 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, 2CH_3, N*Ar*), 1.17 (m, 6H, 2CH_3, N*Ar*), 1.03 (d, $^2J_{H-P}$ = 9.0 Hz, 9H, PMe_3), 0.26 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, N*Ar*), 0.13 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3, N*Ar*). ^{1}H{^{31}P} NMR (600 MHz; toluene-d_8; δ, ppm): 5.66 (s, 1H, Si*H*), 1.03 (s, 9H, PMe_3). ^{31}P{^{1}H} NMR (121.5 MHz, toluene-d_8, δ, ppm): -1.9 (s, *P*Me$_3$). ^{13}C{^{1}H} NMR (151 MHz; toluene-d_8; - 30 °C; δ, ppm): 17.5 (d, $^1J_{C-P}$ = 27.2 Hz, PMe_3), 23.3 (s, CH_3, N*Ar*), 23.9 (s, CH_3, N*Ar*), 24.5 (s, CH_3, N*Ar*), 25.4 (s, CH_3, N*Ar*), 27.5 (s, *CH*, N*Ar*), 28.1 (s, *CH*, N*Ar*), 29.1 (s, *CH*, N*Ar*), 30.2 (s, CH_3, ^{t}*Bu*C), 35.0 (s, Me$_3$*C*C), 135.2 (s, *o*-C, Si*Ph*), 122.3 (s, *p*-C, Si*Ph*), 122.7 (s, *p*-C, N*Ar*), 123.3 (s, *p*-C, N*Ar*), 123.3 (s, *m*-C, N*Ar*), 123.9 (s, *m*-C, N*Ar*), 124.6 (s, *m*-C, N*Ar*), 126.4 (s, *m*-C, N*Ar*), 129.9 (s, *m*-C, Si*Ph*), 135.9 (s, *o*-C, Si*Ph*), 140.3 (s, *o*-C, N*Ar*), 141.2 (s, *o*-C, N*Ar*), 144.6 (s, *o*-C, N*Ar*), 145.6 (s, *o*-C, N*Ar*), 148.7 (s, *i*-C, Si*Ph*), 153.1 (s, *i*-C, N*Ar*), 153.4 (s, *i*-C, N*Ar*), 204.4 (s, ^{t}Bu*C*). ^{29}Si INEPT+ NMR (119.2 MHz; toluene-d$_8$; *J* = 200 Hz; - 30 °C; δ, ppm): -50.9 (d, $^1J_{\text{Si-H}}$ = 223.0 Hz, *Si*H).

12d: ^{1}H NMR (600 MHz; toluene-d$_8$; δ, ppm): 6.56 (s, 1H, Si*H*), 1.00 (d, $^2J_{\text{H-P}}$ = 7.2 Hz, 9H, P*Me*$_3$). ^{31}P{^{1}H} NMR (121.5 MHz; toluene-d$_8$; δ, ppm): 3.3 (s, *P*Me$_3$). ^{29}Si INEPT+ NMR (119.2 MHz; toluene-d$_8$; *J* = 200 Hz; - 30 °C; δ, ppm): -20.6 (d, $^1J_{\text{Si-H}}$ = 224.2 Hz, *Si*H).

NMR scale reaction of complex 3 with acetophenone. PhC(O)Me (3.3 μL, 0.028 mmol) was added at to a solution of **3** (20.6 mg, 0.028 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The reaction mixture was left at room temperature for 2 h. During this time the reaction was monitored by NMR analysis showing 100 % conversion of the starting material and the formation of (ArN=)$_2$Mo(η^2-O=CMePh)(PMe$_3$) (**14**) accompanied by the release of 1 equiv. of PhSiH$_3$. Other silicon containing products were not detected. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.63 (d, $^3J_{\text{H-H}}$ = 7.2 Hz, 2H, *o*-H, C*Ph*), 7.24 (t, $^3J_{\text{H-H}}$ = 7.2 Hz, 2H, *m*-H, C*Ph*), 7.07-6.87 (m, 7H, *p*-H of C*Ph* and *m*-H and *p*-H of N*Ar*), 3.97 (sept, $^3J_{\text{H-H}}$ = 6.6 Hz, 2H, *CH*, N*Ar*), 3.27 (sept, $^3J_{\text{H-H}}$ = 6.6 Hz, 2H, *CH*, N*Ar*), 2.60 (s, 3H, C*Me*), 1.25 (d, $^2J_{\text{H-P}}$ = 9.9 Hz, 9H, P*Me*$_3$), 1.23 (d, $^3J_{\text{H-H}}$ = 6.6 Hz, 6H, 2*CH*$_3$, N*Ar*), 1.15 (d, $^3J_{\text{H-H}}$ = 6.6 Hz, 6H, 2*CH*$_3$, N*Ar*), 0.98 (d, $^3J_{\text{H-H}}$ = 6.6 Hz, 12H, 4*CH*$_3$, N*Ar*). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): 8.5 (s, *P*Me$_3$). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; δ, ppm): 13.3 (d, $^1J_{\text{C-P}}$ = 27.9 Hz, P*Me*$_3$), 23.8 (s, *CH*$_3$, N*Ar*), 24.0 (s, *CH*$_3$, N*Ar*), 24.1 (s, *CH$_3$*, N*Ar*), 27.9 (s, *CH*, N*Ar*), 28.1 (s, *CH*, N*Ar*), 30.3 (s, *CH$_3$*, η^2-O=C*Me*Ph), 85.7 (s, η^2-O=*C*), 122.4 (s, *m*-C, N*Ar*), 122.7 (s, *m*-C, N*Ar*), 124.0 (s, *p*-C, N*Ar*), 124.1 (s, *p*-C, N*Ar*), 125.3 (s, *o*-C, η^2-O=C*Ph*), 125.3 (s, *p*-C, η^2-O=C*Ph*), signal for the *m*-C of η^2-O=CMe*Ph*, obscured by benzene resonance, 141.3 (s, *o*-C, N*Ar*), 141.9 (s, *o*-C, N*Ar*), 151.6 (s, *i*-C, η^2-O=CMe*Ph*), 153.8 (s, *i*-C, N*Ar*), 154.0 (s, *i*-C, N*Ar*). Elem. Anal. (%): calc. for $C_{35}H_{51}MoN_2OP$ (642.706) C 65.41, H 8.00, N 4.36; found: C 64.96, H 8.12, N 4.28.

Preparation of (ArN=)Mo(Et)(PMe$_3$)(η^3-NAr-SiDPh-CH=CH$_2$) (17$_D$). The reaction was done analogously to the preparation of **17**, using 262.4 mg (0.461 mmol) of **3d$_4$** and 30 mL of Et_2O. The spectral data of **17$_D$** are the same as for **17** except for the Si*H* resonances, which were not observed in the ^{1}H NMR spectrum due to full substitution with deuterium. Yield: 92.2 mg, 29 %.

NMR scale generation of (ArN=)$_2$Mo(η^2-O=CMe$_2$)(PMe$_3$) (13). Acetone (1.7 μL, 0.023 mmol) was added to a solution of $(ArN=)_2Mo(PMe_3)_3$ (15.4 mg, 0.023 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The colour of the reaction mixture turned from dark-green to brown almost immediately. The mixture was left at room temperature for 5 min. NMR analysis showed the release of 2 equiv. of PMe_3 and formation of **13**. All volatiles were pumped off; the brown oily residue was dried under vacuum and redissolved in fresh C_6D_6. NMR spectra showed the presence of only complex **13** in solution (see the characterization above). Addition of $PhSiH_3$ (28 μL; 0.23 mmol) to a solution of **13** in C_6D_6 resulted in exclusive formation of **3** and $PhH_2Si(O^iPr)$ in 10 h at room temperature.

Preparation of $(ArN=)_2Mo(\eta^2\text{-}O=CMePh)(PMe_3)$ (14)

A. Generated similarly to **13** from acetophenone (4.3 µL, 0.036 mmol) and $(ArN=)_2Mo(PMe_3)_3$ (24.4 mg, 0.036 mmol) in 0.6 mL of C_6D_6 in an NMR tube. NMR spectra showed the presence of complex **14** only.

B. Acetophenone (90 µL, 0.76 mmol) was added to a solution of $(ArN=)_2Mo(PMe_3)_3$ (515.2 mg, 0.76 mmol) in 40 mL of hexanes. The colour of the mixture changed from dark-green to brown almost immediately. The mixture was stirred at room temperature with N_2 purging for 20 min. All volatiles were pumped off to give an oily brown residue, which was dried under vacuum. The product was recrystallized from Hex/Et_2O (1/1) at -80 °C to give a brown solid. Yield: 201 mg, 41 %. See the characterization of **14** above.

NMR scale reaction of complex 14 with $PhSiH_3$. A solution of **14** (21.9 mg, 0.034 mmol) in 0.5 mL of C_6D_6 was added to a solution of $PhSiH_3$ (21.0 µL, 0.17 mmol) in 0.1 mL of C_6D_6 in an NMR tube. The reaction mixture was left at room temperature for 3 days. NMR analysis showed the release of 1 equiv. of PhC(O)Me and selective formation of **3**. Formation of H_2, $PhSiH_2[OCH(Me)Ph]$, and ethylbenzene was also observed by NMR spectroscopy.

Hydrosilylation of PhC(O)Me with $PhSiH_3$ mediated by complex 14. A solution of **14** in C_6D_6 (33.3 µL, 0.002 mmol; C = 0.06 M; 1.0 mol %) was added to a mixture of acetophenone (25.0 µL, 0.214 mmol) and $PhSiH_3$ (26.4 µL, 0.214 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The reaction mixture was left at room temperature for 20 days. NMR analysis showed 35 % conversion of PhC(O)Me and the formation of a mixture of $PhSiH_2[OCH(Me)Ph]$ (76 %) and $PhSi[OCH(Me)Ph]_3$ (24 %). TON: 38.

NMR scale generation of (ArN=)$_2$Mo(η^2-O=CHPh)(PMe$_3$) (16). PhC(O)H (6.1 μL, 0.06 mmol) was added to a solution of (ArN=)$_2$Mo(PMe$_3$)$_3$ (40.1 mg, 0.06 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The colour of the reaction mixture turned from dark-green to brown almost immediately. The reaction mixture was left at room temperature for 10 min. NMR analysis showed the formation of only one complex **16** and release of 2 equivs. of PMe$_3$. All volatiles were pumped off; the oily brown residue was dried under vacuum and redissolved in C_6D_6. NMR spectra showed the presence of only complex **16** in solution. The same product can be also obtained by the NMR scale reaction of (ArN=)$_2$Mo(η^2-C_2H_4)(PMe$_3$)$_2$ with PhC(O)H (15 min at room temperature). All attempts to isolate complex **16** in analytically pure form by recrystallization were unsuccessful. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.54 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H, *o*-H, C*Ph*), 7.19 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, *m*-H, C*Ph*), 7.06 (m, 3H, *p*-H, C*Ph* and N*Ar*), 6.89 (m, 4H, *m*-H, N*Ar*), 5.69 (s, 1H, C(O)*H*), 3.91 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, 2*CH*, N*Ar*), 3.45 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, 2*CH*, N*Ar*), 1.24 (m, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, 4*CH$_3$*, N*Ar*, $^2J_{H\text{-}P}$ = 6.6 Hz, 9H, P*Me*$_3$), 1.03 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, N*Ar*). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, δ, ppm): 8.6 (s, *P*Me$_3$). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; δ, ppm): 13.3 (d, $^1J_{C\text{-}P}$ = 29.4 Hz, P*Me$_3$*); 23.3 (s), 23.5 (s), 23.8 (s), 24.0 (s), 79.0 (s, *CH*, *C*(O)HPh), 122.3 (s, *m*-C, N*Ar*), 122.5 (s, *m*-C, N*Ar*), 124.0 (s, *p*-C, N*Ar*), 124.3 (s, *o*-C, C*Ph*), 125.6 (s, *p*-C, N*Ar*), 128.2 (s, *m*-C, C*Ph*), 141.4 (s, *o*-C, N*Ar*), 141.8 (s, *o*-C, N*Ar*), 148.7 (s, *i*-C, C*Ph*), 153.7 (s, *i*-C, N*Ar*), 153.9 (s, *i*-C, N*Ar*), *p*-C of C*Ph* is obscured by the residual signal of C_6D_6. IR (nujol): 1597 cm^{-1} (strong, O=C).

NMR scale reaction of complex 16 with $PhSiH_3$. $PhSiH_3$ (37.0 µL, 0.3 mmol) was added to a solution of **16** (37.3 mg, 0.06 mmol) in 0.6 mL of C_6D_6 in an NMR tube. The mixture was left at room temperature for 2 days. NMR analysis showed selective formation of **3**. Production of H_2, toluene, $PhH_2Si(OBn)$, and $PhHSi(OBn)_2$[1, 2] was also observed by NMR spectroscopy.

NMR scale reaction of 21 with $PhSiH_3$ and PMe_3. $PhSiH_3$ (3.9 µL, 0.032 mmol) and PMe_3 (3.3 µl, 0.032 mmol) were added to a solution of **21** (21.0 mg, 0.032 mmol) in 0.6 mL of C_6D_6 in an NMR tube. No reaction was observed after 10 min. at room temperature. The mixture was heated overnight at 50 °C showing full conversion of the starting complex and the formation of $(PhCH_2CH_2)SiH_2Ph$ (confirmed by ^1H-^1H COSY and ^1H-^{13}C HMBC) and **20**. A decomposition side-process leading to a difficult-to-characterize mixture of hydride compounds and traces of complex **18** was also observed.

NMR scale reaction of complex 25 with $PhSiD_3$. The reaction was done analogously to the one with $PhSiH_3$ (see above) using 3.7 µL (0.03 mol) of $PhSiD_3$ and ~ 0.03 mmol of **25** (generated *in situ* from 20.5 mg (0.03 mmol) of **17** (see above)). NMR analysis after 24 h at RT showed the formation of Ph(Et)SiHD. Scrambling of deuterium was also observed for the agostic complex $(ArN=)Mo(SiX_2Ph)(PMe_3)(\eta^3\text{-}NAr\text{-}Si(X)Ph\text{-}X)$ (X = H, D). ^2D NMR (92.1 MHz; benzene-h_6, δ, ppm): 4.65 (bs, Ph(Et)SiH*D*).

NMR scale reaction of complex 25 with (*m*-Tol)SiH_3. (*m*-Tol)SiH_3 (8.0 µL, 0.059 mmol) was added to a solution of **25** (generated *in situ* by the reaction of **17** (20.1 mg, 0.029 mmol) with $PhSiH_3$ (3.6 µL, 0.029 mmol) and BPh_3 (7.1 mg, 0.029 mmol), followed by the addition of 3.0 µL (0.029 mmol) of PMe_3) in 0.6 mL of C_6D_6 in an NMR tube. After 10 min at RT, NMR analysis revealed incorporation of the *m*-Tol group in the

Mo-bound silyl position of complex **24**. The reaction mixture was left at room temperature for 2 weeks. NMR analysis showed the presence of $PhSiH_3$ and scrambling of the *m*-Tol group (confirmed by ^1H-^{13}C HMBC) between the two silicon positions of the agostic complex $(ArN=)Mo(SiH_2R)(PMe_3)(\eta^3\text{-}NAr\text{-}Si(H)R\text{-}H)$ (R = Ph, *m*-Tol).

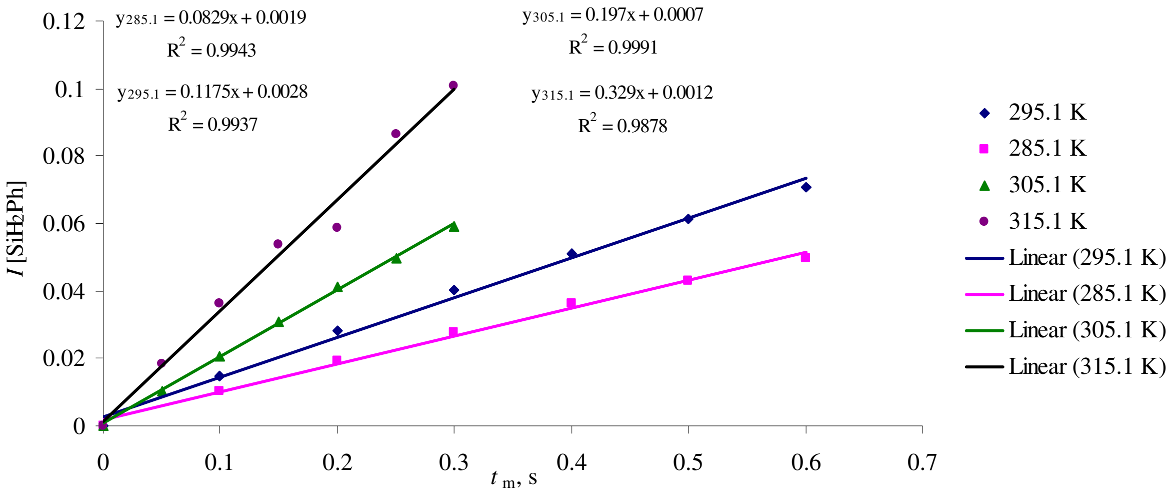


Figure SI1. Dependence of the integral intensity of the Si*H* resonances of the classical SiH_2Ph ligand of **3** (*I*[SiH_2Ph]) in the 1D ^1H EXSY NMR on the mixing time (t_m) upon selective excitement of the Si*H* protons of free $PhSiH_3$ (integrals of $PhSiH_2$ group and $PhSiH_3$ were normalized to 100. Four temperatures (285.1, 2951.1, 305.1, and 315.1 K) were applied).

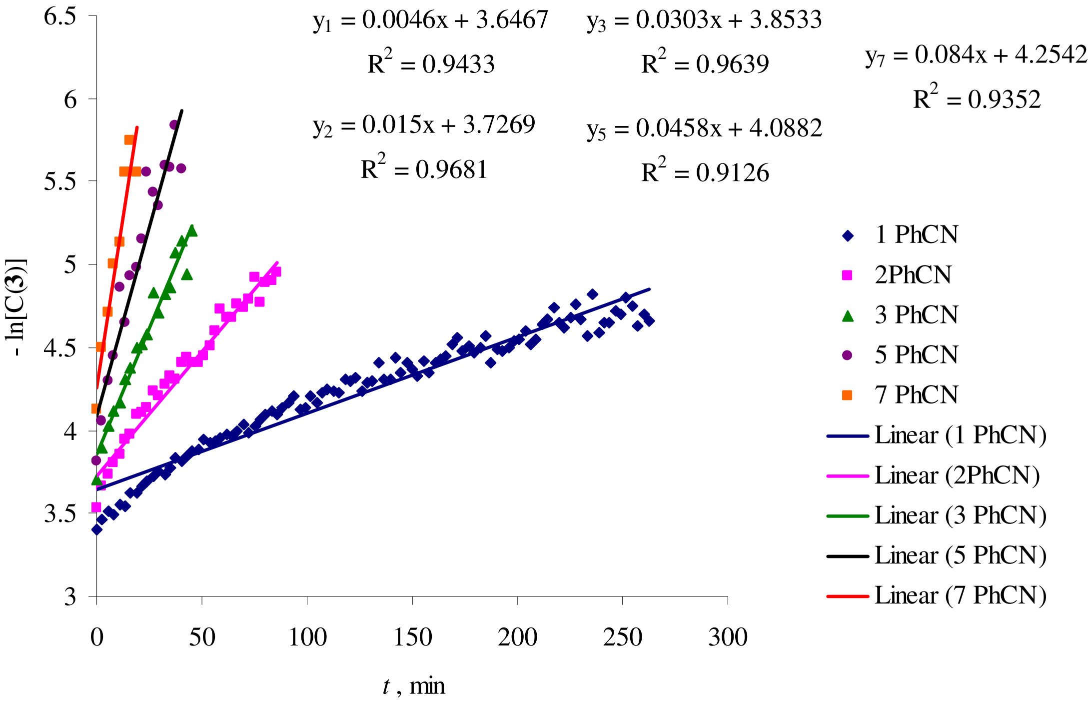


Figure SI2. –Ln[C]/time dependence for reactions of complex **3** with benzonitrile (1-3, 5, and 7 equivs.) at 22 °C.

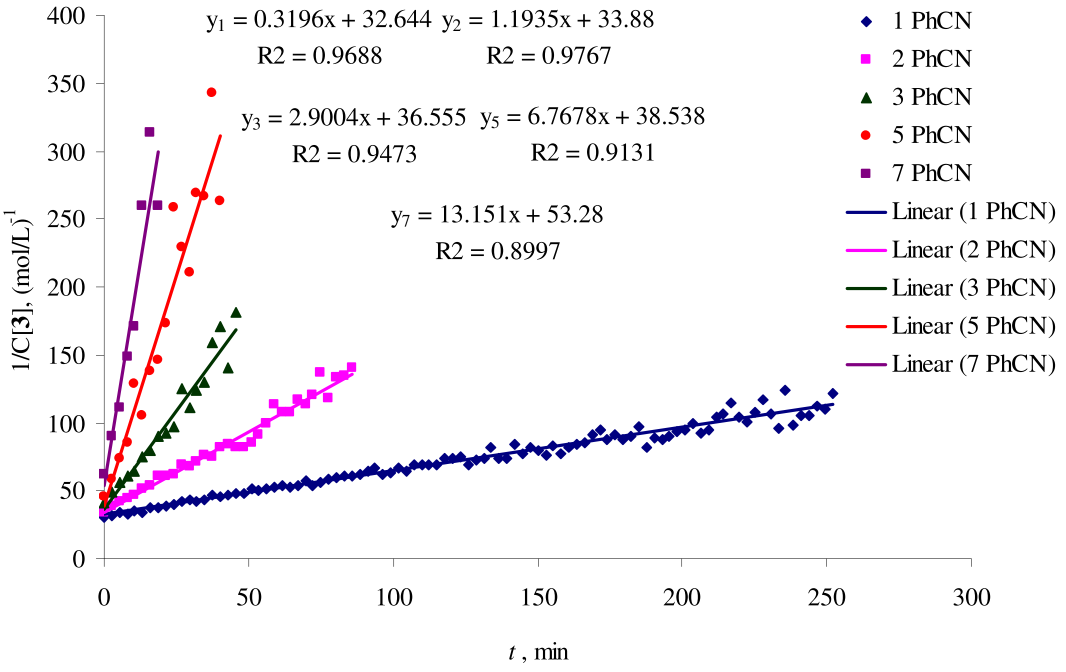


Figure SI3. (1/C)/time dependence for reactions of complex **3** with benzonitrile (1-3, 5, and 7 equivs.) at 22 °C.

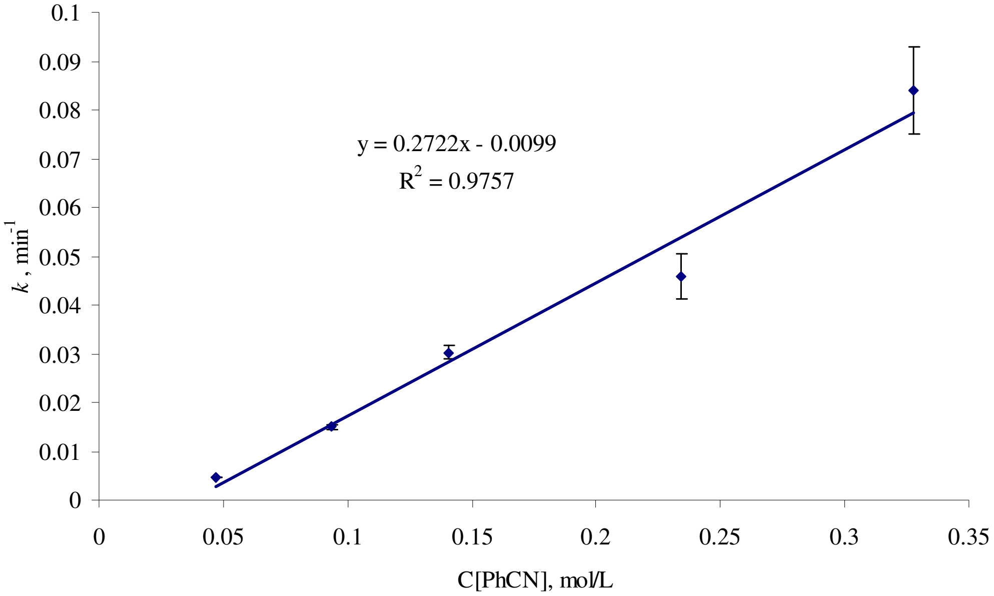


Figure SI4. Dependence of the effective rate constant on the concentration of nitrile in the reaction of **3** with benzonitrile at 22 °C (rate constants for each PhCN concentration were obtained by linearization of the data in –Ln(C[**3**])/time coordinates (Figure 2)).

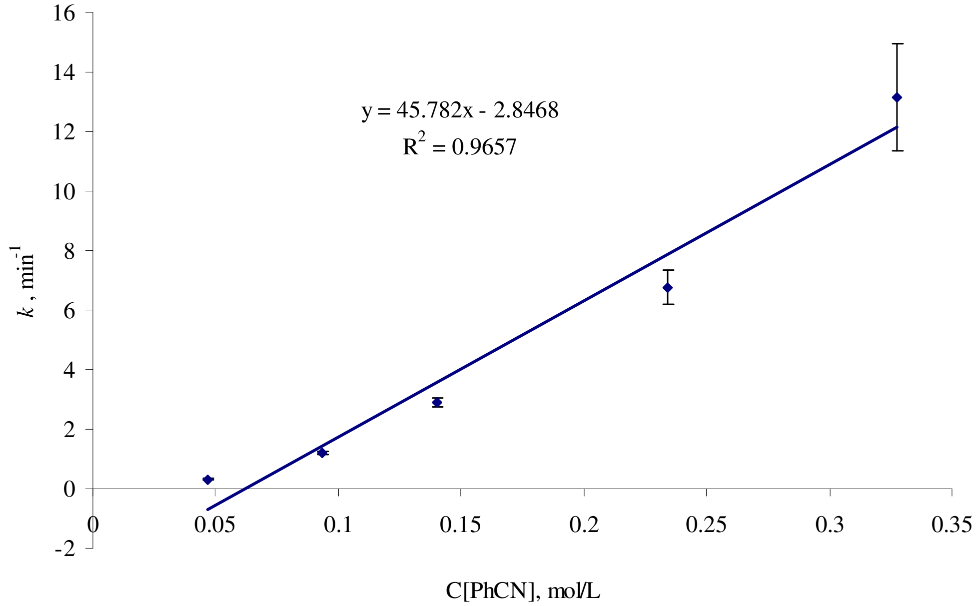
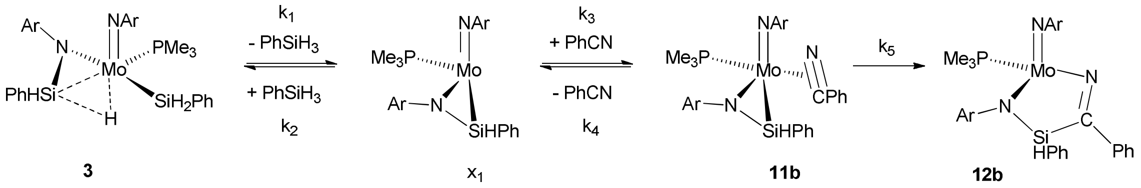


Figure SI5. Dependence of the effective rate constant on the concentration of nitrile in the reaction of **3** with benzonitrile at 22 °C (rate constants for each PhCN concentration were obtained by linearization of the data in (1/C[**3**])/time coordinates (Figure 3)).



[PhSiH$_3$] = [**3**]$_0$ - [**3**], where [**3**]$_0$ - starting concentration of agostic complex **3**

(**1**): $-d[\mathbf{3}]/dt = k_1[\mathbf{3}] - k_2x_1[PhSiH_3] = k_1[\mathbf{3}] - k_2[\mathbf{3}]_0x_1 + k_2[\mathbf{3}]x_1$

(**2**): $-dx_1/dt = k_2x_1[PhSiH_3] - k_1[\mathbf{3}] + k_3x_1[PhCN] - k_4[\mathbf{11b}] = k_2[\mathbf{3}]_0x_1 - k_2[\mathbf{3}]x_1 - k_1[\mathbf{3}] + k_3x_1[PhCN] - k_4[\mathbf{11b}] = 0$

(**3**): $-d[\mathbf{11b}]/dt = k_3x_1[PhCN] - k_4[\mathbf{11b}] + k_5[\mathbf{11b}] = 0$

(**4**): $d[\mathbf{12b}]/dt = k_5[\mathbf{11b}]$

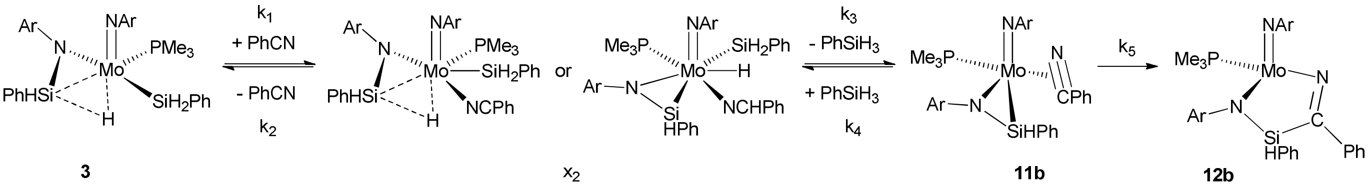
from (**3**): $[\mathbf{11b}] = k_3x_1[PhCN]/(k_4 + k_5)$

then from (**2**): $x_1 = \dfrac{(k_1k_4 + k_1k_5)[\mathbf{3}]}{k_2k_4[\mathbf{3}]_0 + k_2k_5[\mathbf{3}]_0 - k_2k_4[\mathbf{3}] - k_2k_5[\mathbf{3}] + k_3k_5[PhCN]}$

then from (**1**): $-d[\mathbf{3}]/dt = \dfrac{2k_1k_2k_4[\mathbf{3}]^2 + k_3k_5[PhCN][\mathbf{3}]}{(k_2k_4 + k_2k_5)[\mathbf{3}]_0 + (k_2k_4 - k_2k_5)[\mathbf{3}] + k_3k_5[PhCN]}$ or $\boxed{-\dfrac{d[\mathbf{3}]}{dt} = \dfrac{A[\mathbf{3}]^2 + B[PhCN][\mathbf{3}]}{C[\mathbf{3}]_0 + D[\mathbf{3}] + B[PhCN]}}$

where $A = 2k_1k_2k_4$ $C = k_2k_4 + k_2k_5$
$B = k_3k_5$ $D = k_2k_4 - k_2k_5$

Scheme SI1. Dissociative pathway of the reaction of complex **3** with PhCN and kinetic equations for this mechanism.



[PhSiH$_3$] = [**3**]$_0$ - [**3**], where [**3**]$_0$ - starting concentration of agostic complex **3**

(**1**): $-d[\mathbf{3}]/dt = k_1[PhCN][\mathbf{3}] - k_2x_2$

(**2**): $-dx_2/dt = k_2x_2 - k_1[PhCN][\mathbf{3}] + k_3x_2 - k_4[PhSiH_3][\mathbf{11b}] = k_2x_2 - k_1[PhCN][\mathbf{3}] + k_3x_2 - k_4[\mathbf{3}]_0[\mathbf{11b}] + k_4[\mathbf{3}][\mathbf{11b}] = 0$

(**3**): $-d[\mathbf{11b}]/dt = k_4[PhSiH_3][\mathbf{11b}] - k_3x_2 + k_5[\mathbf{11b}] = k_4[\mathbf{3}]_0[\mathbf{11b}] - k_4[\mathbf{3}][\mathbf{11b}] - k_3x_2 + k_5[\mathbf{11b}] = 0$

(**4**): $d[\mathbf{12b}]/dt = k_5[\mathbf{11b}]$

from (**3**): $[\mathbf{11b}] = k_3x_2/(k_4[\mathbf{3}]_0 - k_4[\mathbf{3}] + k_5)$

then from (**2**): $x_2 = \dfrac{k_1k_4[PhCN][\mathbf{3}]_0[\mathbf{3}] - k_1k_4[PhCN][\mathbf{3}]^2 - k_1k_5[PhCN][\mathbf{3}]}{k_2k_4[\mathbf{3}]_0 - k_2k_4[\mathbf{3}] + k_2k_5 + k_3k_5}$

then from (**1**): $-d[\mathbf{3}]/dt = \dfrac{(2k_1k_2k_5 + k_1k_3k_5)[PhCN][\mathbf{3}]}{k_2k_4[\mathbf{3}]_0 - k_2k_4[\mathbf{3}] + k_2k_5 + k_3k_5}$ or $\boxed{-\dfrac{d[\mathbf{3}]}{dt} = \dfrac{A[PhCN][\mathbf{3}]}{B[\mathbf{3}]_0 - B[\mathbf{3}] + C}}$ where $A = 2k_1k_2k_5 + k_1k_3k_5$
$B = k_2k_4$
$C = k_2k_5 + k_3k_5$

Scheme SI2. Associative pathway of the reaction of complex **3** with PhCN and kinetic equations for this mechanism.

---

(1) (a) Yun, S. S.; Kim, T. S.; Kim, C. H. *Bull. Korean Chem. Soc.* **1994**, *15*, 522. (b) Yun, S. S.; Lee, J.; Lee, S. *Bull. Korean. Chem. Soc.* **2001**, *22*, 623.

(2) Leelasubcharoen, S.; Zhizhko, P. A.; Kuzmina, L. G.; Churakov, A. V.; Howard, J. A. K.; Nikonov, G. I. *Organometallics* **2009**, *28*, 4500.

(3) (a) Onaka, M.; Higuchi, K.; Nanami, H.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2638. (b) Baba, T.; Kawanami, Y.; Yuasa, H.; Yoshida, S. *Catal. Lett.* **2003**, *91*, 31.

(4) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(5) For reduction of carbonyl compounds to alkanes, see: (a) West, C. T.; Donnelly, S. J.; Kooistra, D. A.; Doyle, M. P. *J. Org. Chem.* **1973**, *38*, 2675. (b) Barclay, L. R. C.; Sonawane, H. R.; MacDonald, M. C. *Can. J. Chem.* **1972**, *50*, 281. (c) Fry, J. L.; Orfanopoulos, M.; Adlington, M. G.; Dittman, W. R.; Silverman, S. B. *J. Org. Chem.* **1978**, *43*, 374.

(6) (a) Sadow, A. D.; Tilley, T. D. *Organometallics* **2001**, *20*, 4457. (b) Kim, B. H.; Woo, H.-G. *Adv. Organomet. Chem.* **2004**, *52*, 143

(7) Randolph, C. L.; Wrington, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366.

(8) For example: (a) Yue, C. J.; Liu, Y.; He, R. *J. Mol. Catal. A* **2006**, *259*, 17. (b) Stapleton, R. L.; Chai, J.; Taylor, N. J.; Collins, S. *Organometallics* **2006**, *25*, 2514.

(9) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7151.

(10) Ejfler, J.; Kobulka, M.; Hojniak, M.; Sobota, P. *J. Mol. Catal. A* **2004**, *224*, 93.

---

(11) Kocienski, P. J. *Protecting Groups*, Thieme: Stuttgart **1994**, pp. 28-42.

(12) (a) Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147. (b) Schubert, U.; Lorenz, C. *Chem. Ber.* **1995**, *128*, 1267.

(13) (a) Pillot, J.-P.; Roux, P.; Richard, C.; Birot, M.; Dunogues, J. in *Progress in Organosilicon Chemistry*, Marciniec, B.; Chojnowski, J. (Eds.), Gordon and Breach Publishers, Basel, 1995, p. 465 and refs. therein. (b) Blum, Y.; McDermott, G. A. in *Inorganic and Organometallic Polymers and Oligomers*, Harrod, J. F.; Laine, R. M. (Eds.), Kluwer, Dordrecht, The Netherlands, 1991 and refs therein.

(14) Gunji, Y.; Yamashita, Y.; Ikeno, T.; Yamada, T. *Chem. Lett.* **2006**, *35*, 714.

(15) Ochiai, M.; Hashimoto, H.; Tobita, H. *Angew. Chem. Int. Ed.* **2007**, *46*, 8192.

(16) Hashimoto, H.; Aratani, I.; Kabuto, C.; Kira, M. *Organometallics* **2003**, *22,* 2199.

(17) (a) Tanabe, M.; Osakada, K. *Organometallics* **2001**, *20*, 2118. (b) Kim, J.; Kang, Y.; Lee, J.; Kong, Y. K.; Gong, M. S.; Kang, S. O.; Ko, J. *Organometallics* **2001**, *20*, 937.

(18) For catalytic double hydrosilylation, see: (a) Chalk, A. J. *J. Organomet. Chem.* **1970**, *21*, 207. (b) Murai, T.; Sakane, T.; Kato, S. *Tetrahedron Lett.* **1985**, *26*, 5145. (c) Murai, T.; Sakane, T.; Kato, S. *J. Org. Chem.* **1990**, *55*, 449. (d) Caporusso, A. M.; Panziera, N.; Petrici, P.; Pitzalis, E.; Salvadori, P.; Vitulli, G.; Martra, G. *J. Mol. Catal. A* **1999**, *150*, 275.

---

(19) Mitzel, N. W.; Riede, J.; Schier, A.; Paul, M.; Schmidbaur, H. *Chem. Ber.* **1993**, *126*, 2027.

(20) (a) Calas, R.; Frainnet, E.; Bazouin, A.; Hebd, C. R. *Compt. Rend.* **1961**, *252*, 420. (b) T. Takamasa, I. Isao, *Jap. Patent Appl.* JP11228579 (**1999**).

(21) (a) Gutsulyak, D. V.; Nikonov, G. I. *Angew. Chem. Int. Ed.* **2010**, *49*, 7553. (b) Peterson, E.; Khalimon, A. Y.; Simionescu, R.; Kuzmina, L. G.; Howard, J. A. K.; Nikonov, G. I. *J. Am. Chem. Soc*. **2009**, *131*, 908.