Supporting Information

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Supporting information

to the article

Agostic NSi—H⁺Mo Complexes: From Curiosity to Catalysis

by

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Experimental details

All manipulations were carried out using conventional inert atmosphere glove-box and Schlenk techniques. Dry ether, toluene and hexanes were obtained, using Grubbs-type purification columns, other solvents were dried by distillation from appropriate drying agents. NMR spectra were obtained with a Bruker DPX-300 and Bruker DPX-600 instruments (^1H : 300 and 600 MHz; ^{13}C : 75.5 and 151 MHz; ^{29}Si : 59.6 and 119.2 MHz; ^{31}P : 121.5 and 243 MHz). IR spectra were measured on a Perkin-Elmer 1600 FT-IR spectrometer. $(\text{ArN})_2\text{Mo}(\text{PMe}_3)_3$ ($\text{Ar} = 2,6\text{-}(^i\text{Pr})_2\text{C}_6\text{H}_3$) was prepared by a literature procedure.^[1] PhSiCl_3 , $\text{HSi}(\text{OEt})_3$, PhMeSiCl_2 and PMe_3 were purchased from Aldrich. PhSiH_3 and PhMeSiH_2 were prepared from corresponding chlorosilanes by treatment with LiAlH_4 . Organic substrates (PhCHO , PhMeCO , acetone, 1-hexene, cyclohexene, ethylene, styrene, PhCN , $^i\text{PrCN}$, $^t\text{BuCN}$, phenylacetylene, and pyridine), and (*m*-Tol) MgBr were purchased from Aldrich. (*m*-Tol) SiH_3 was prepared by a literature procedure from SiCl_4 and corresponding Grignard reagent.² All catalytic and NMR reactions were done under nitrogen atmosphere using NMR tubes equipped with Teflon valves. The structures and yields of all hydrosilated products were determined using NMR analysis.

Preparation of $(\text{ArN})(\text{PMe}_3)(\text{PhH}_2\text{Si})\text{Mo}(\eta^3\text{-NAr-SiHPh-H})$ (**3**)

PhSiH_3 (0.37 mL, 3.0 mmol) was added to a solution of $(\text{ArN})_2\text{Mo}(\text{PMe}_3)_3$ (1.01 g, 1.5 mmol) in 100 mL of hexane at room temperature. After the addition of PhSiH_3 , the colour of reaction mixture immediately turned from dark-green to brown, and the formation of a brown precipitate was observed. The reaction mixture was purged with N_2 under stirring at room temperature for 30 min., concentrated and left in a freezer (-30°C) overnight. More crystalline brown precipitate formed. The cold precipitate was filtered off, washed with cold hexane (10 mL) and dried in vacuum to give a fine brown powder of **3**. Yield: 0.7 g, 77 %.

^1H -NMR (300 MHz; C_6D_6 ; 293K; δ , ppm): 0.36 (bs, 3H, CH_3 , ArN); 1.04 (d, $^2J_{\text{H-P}} = 8.4$ Hz, 9H, PMe_3); 1.14 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 3H, CH_3 , ArN); 1.18 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6H, 2CH_3 , ArN); 1.23 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 3H, CH_3 , ArN); 1.27 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6H, 2CH_3 , ArN); 1.34 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 3H, CH_3 , ArN); 2.71 (sept., $^3J_{\text{H-H}} = 6.6$ Hz, 1H, CH , ArN); 3.46 (sept., $^3J_{\text{H-H}} = 6.9$ Hz, 1H, CH , ArN); 4.04 (sept., $^3J_{\text{H-H}} = 6.6$ Hz, 2H, 2CH , ArN); 4.30 (bs, 1H, ArN-Si-H, agostic); 5.57 (s, 1H, Mo-Si-H); 5.78 (bs, 1H, ArN-Si-H, terminal); 5.94 (s, 1H, Mo-Si-H); 6.91 – 6.94 and 6.99 – 7.24

(overlapping multiplets, 8H, *m*-H and *p*-H of NAr, and *p*-H of Si-Ph aromatic protons); 6.96 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 2H, *m*-H, Si-Ph); 7.32 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 2H, *m*-H, Si-Ph); 7.43 (d, $^3J_{\text{H-H}} = 7.2$ Hz, 2H, *o*-H, Si-Ph); 8.31 (d, $^3J_{\text{H-H}} = 7.2$ Hz, 2H, *o*-H, Si-Ph). ^1H -NMR (600 MHz; toluene- d_8 ; 293K; δ , ppm): 0.30 (bs, 3H, CH_3 , ArN); 1.05 (d, $^2J_{\text{H-P}} = 8.4$ Hz, 9H, PMe_3); 1.12 (bs, 3H, CH_3 , ArN); 1.17 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 6H, 2CH_3 , ArN); 1.20 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 3H, CH_3 , ArN); 1.27 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 6H, 2CH_3 , ArN); 1.35 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 3H, CH_3 , ArN); 2.68 (sept., $^3J_{\text{H-H}} = 6.6$ Hz, 1H, CH , ArN); 3.47 (bs, 1H, CH , ArN); 4.01 (sept., $^3J_{\text{H-H}} = 6.6$ Hz, 2H, 2CH , ArN); 4.25 (bs, 1H, ArN-Si-H, agostic); 5.46 (s, 1H, Mo-Si-H); 5.75 (bs, 1H, ArN-Si-H, terminal); 5.84 (s, 1H, Mo-Si-H); 6.86 – 6.95 and 6.96 – 7.03 and 7.13 (overlapping multiplets, 6H, *m*-H and *p*-H, NAr); 6.95 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 2H, *m*-H, Si-Ph); 7.06 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 1H, *p*-H, Si-Ph); 7.22 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 1H, *p*-H, Si-Ph); 7.29 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 2H, *m*-H, Si-Ph); 7.40 (d, $^3J_{\text{H-H}} = 7.2$ Hz, 2H, *o*-H, Si-Ph); 8.22 (d, $^3J_{\text{H-H}} = 7.2$ Hz, 2H, *o*-H, Si-Ph). ^1H -NMR (600 MHz; toluene- d_8 ; 223K; δ , ppm): 0.15 (bs, 3H, CH_3 , ArN); 0.962 (d, $^2J_{\text{H-P}} = 8.4$ Hz, 9H, PMe_3); 1.02 (bs, 3H, CH_3 , ArN); 1.16 (bs, 3H, CH_3 , ArN); 1.19 (bs, 6H, 2CH_3 , ArN); 1.28 (bs, 6H, 2CH_3 , ArN); 1.41 (bs, 3H, CH_3 , ArN); 2.75 (bs, 1H, CH , ArN); 3.52 (bs, 1H, CH , ArN); 3.97 (bs, 2H, 2CH , ArN); 4.35 (bm, $^2J_{\text{H-H}} = 5.4$ Hz, 1H, ArN-Si-H, agostic); 5.68 (s, 1H, Mo-Si-H); 5.97 (s, 1H, Mo-Si-H); 6.03 (bd, $^2J_{\text{H-H}} = 5.4$ Hz, ArN-Si-H, terminal); 6.80 – 7.02 and 7.06 – 7.16 (overlapping multiplets, 9H, *m*-H and *p*-H, NAr', and 1 *o*-H and 1 *p*-H, SiPh); 7.28 (bt, $^3J_{\text{H-H}} = 7.2$ Hz, 1H, *p*-H, Si-Ph); 7.37 (bt, $^3J_{\text{H-H}} = 7.2$ Hz, 2H, *o*-H, Si-Ph); 7.40 (bd, $^3J_{\text{H-H}} = 7.2$ Hz, 2H, *m*-H, Si-Ph); 8.49 (bd, $^3J_{\text{H-H}} = 7.2$ Hz, 2H, *m*-H, Si-Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz; C_6D_6 ; 293K; δ , ppm): 10.43 (s, PMe_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz; toluene- d_8 ; 293; δ , ppm): 10.55 (s, PMe_3). ^{31}P -NMR (selectively decoupled from methyl groups) (243 MHz; toluene- d_8 ; 293K; δ , ppm): 10.61 (d, $^2J_{\text{H-P}} = 9.3$ Hz, PMe_3). ^{13}C -NMR (150.9 MHz; toluene- d_8 ; 293K; δ , ppm): 17.8 (d, $^1J_{\text{C-P}} = 25.7$ Hz, PMe_3); 22.5 (s, CH_3 , ArN); 23.4 (s, 2CH_3 , ArN); 23.5 (s, CH_3 , ArN); 24.1 (s, 2CH_3 , ArN); 26.3 (s, CH_3 , ArN); 26.6 (s, CH_3 , ArN); 26.9 (s, CH , ArN); 27.8 (s, CH , ArN); 28.9 (s, 2CH , ArN); 122.2 (s, NAr); 122.9 (s, NAr); 123.0 (s, NAr); 123.1 (s, NAr); 125.0 (s, *o*-C, NAr); 126.1 (s, *p*-C, SiPh); 127.4 (s, *p*-C, SiPh); 127.6 (s, *m*-C, SiPh); 127.9 (s, *o*-C, NAr); 128.0 (s, *m*-C, SiPh); 128.2 (s, *o*-C, NAr); 128.8 (s, NAr); 130.6 (s, NAr); 136.0 (s, *o*-C, SiPh); 136.3 (s, *o*-C, SiPh); 136.9 (s, *o*-C, NAr); 140.2 (s, *i*-C, SiPh); 141.4 (s, *i*-C, SiPh); 144.5 (s, *i*-C, NAr); 153.6 (s, *i*-C, NAr). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (119.2 MHz; toluene- d_8 ; 223K; δ , ppm): -72.9 (dd, $^1J_{\text{Si-H}} = 113.0$ Hz, $^1J_{\text{Si-H}} = 245.3$ Hz, ArN-SiH₂Ph); 1.2 (t, $^1J_{\text{Si-H}} = 153.5$ Hz, Mo-SiH₂Ph). IR (nujol, cm^{-1} , selected bands): 1694 cm^{-1} , 2014 cm^{-1} , 2041 cm^{-1} and 2165 cm^{-1} . Elem. Anal. (%): calc. for

C₃₉H₅₇MoN₂PSi₂ (736.968) C 63.56, H 7.80, N 3.80; found C 62.76, H 7.48, N 3.86. Single crystals suitable for X-Ray analysis were obtained from hexane solution at -30 °C.

Preparation of (ArN)(PMe₃)(Et)Mo(η^3 -NAr-SiHPh-CH=CH₂) (4)

An ampoule containing a frozen solution of **3** (502.6 mg, 0.682 mmol) in 100 mL of Et₂O was put under vacuum and then refilled with ethylene at -80 °C. The reaction mixture was warmed up to ambient temperature and allowed to stir for 48 hours. Then all volatiles were pumped off, the residue was dried and extracted with 100 mL of hexane. The solvent was removed under reduced pressure to leave a dark-brown powder of **4**. Yield: 362.7 mg, 84 %. Single crystals suitable for X-Ray analysis were obtained by slow cooling of a warm (~35 °C) hexane solution to the ambient temperature.

¹H-NMR (300 MHz; C₆D₆; 297 K; δ , ppm): 7.67 (m, 2H, *o*-H, SiPh); 6.85-7.10 (m, 9H, *m*-H and *p*-H of NAr and SiPh); 6.48 (s, 1H, SiH); 4.30 (dd, ³J_{H-H} = 3.9 Hz, 13.0 Hz, 1H, H₂C=CHSi); 4.09 (m, 2H, H₂C=CHSi and CH of NAr); 3.83 (sept, ³J_{H-H} = 6.6 Hz, 1H, CH, NAr); 3.71 (sept, ³J_{H-H} = 6.9 Hz, 1H, CH, NAr); 2.95 (dd, ³J_{H-H} = 13.0 Hz, 15.6 Hz, 1H, H₂C=CHSi); 2.70 (sept, ³J_{H-H} = 6.9 Hz, 1H, CH, NAr); 2.54 (m, 1H, CH₂, MoEt); 2.04 (t, ³J_{H-H} = 7.2 Hz, 3H, CH₃, MoEt); 1.54 (m, 6H, 2CH₃, NAr); 1.47 (m, 1H, CH₂, MoEt); 1.40 (d, ³J_{H-H} = 6.6 Hz, 6H, 2CH₃, NAr); 1.15 (d, ³J_{H-H} = 6.9 Hz, 3H, CH₃, NAr); 1.10 (d, ³J_{H-H} = 6.6 Hz, 6H, 2CH₃, NAr); 0.70 (d, ²J_{P-H} = 7.5 Hz, 9H, PMe₃); 0.31 (d, ³J_{H-H} = 6.9 Hz, 3H, CH₃, NAr). ³¹P{¹H}-NMR (121.5 MHz; C₆D₆; 297 K; δ , ppm): -17.2 (s, PMe₃). ¹³C-NMR (75.5 MHz; C₆D₆; 297 K; δ , ppm): 14.0 (d, ¹J_{C-P} = 19.6 Hz, PMe₃); 15.5 (s, CH₃, NAr); 19.6 (d, ³J_{C-P} = 5.9 Hz, CH₃, MoEt); 22.1 (s, CH₃, NAr); 24.2 (s, CH₃, NAr); 24.3 (s, CH₃, NAr); 25.5 (s, CH₃, NAr); 27.2 (s, CH, NAr); 27.6 (s, CH₃, NAr); 27.9 (s, CH, NAr); 29.7 (s, CH₃, NAr); 30.2 (s, CH, NAr); 31.6 (d, ²J_{C-P} = 6.3 Hz, CH₂, MoEt); 49.9 (d, J_{C-P} = 4.7 Hz, SiCH=CH₂); 75.4 (d, J_{C-P} = 13.2 Hz, SiCH=CH₂); 123.0 (s, *p*-C, SiPh); 123.1 (s, *m*-C, NAr); 123.7 (s, *p*-C, NAr); 124.0 (s, *m*-C, NAr); 127.0 (s, *m*-C, NAr); 129.5 (s, *m*-C, SiPh); 134.3 (s, *o*-C, SiPh); 140.4 (s, *o*-C, NAr); 141.3 (s, *o*-C, NAr); 143.7 (s, *o*-C, NAr); 144.2 (s, *o*-C, NAr); 147.8 (s, *i*-C, SiPh); 150.4 (s, *i*-C, NAr); 152.0 (s, *i*-C, NAr). ²⁹Si INEPT+ NMR (59.6 MHz; C₆D₆; 200 Hz; δ , ppm): -28.2 (d, ¹J_{Si-H} = 207.8 Hz, SiH). IR (nujol): 2105 cm⁻¹ (Si-H). Elem. Anal. (%): calc. for C₃₇H₅₇MoN₂PSi (684.861) C 64.89, H 8.39, N 4.09; found: C 64.48, H 8.30, N 3.74.

NMR reaction of **3** with acetophenone to give **7**.

Acetophenone (3.3 μ L, 0.028 mmol) was added at room temperature to a solution of **3** (20.6 mg, 0.028 mmol) in 0.6 mL of C₆D₆ in NMR tube. The reaction mixture was monitored by NMR spectroscopy for 2 hours at room temperature until completion. NMR spectra showed quantitative formation of only one product, (ArN)₂Mo(PMe₃)(η^1 -O=CMePh) (**7**).

¹H-NMR (300 MHz; C₆D₆; δ , ppm): 7.63 (d, ³J_{H-H} = 7.2 Hz, 2H, *o*-H, CPh); 7.24 (t, ³J_{H-H} = 7.2 Hz, 2H, *m*-H, CPh); 7.07-6.87 (m, 7H, *p*-H of CPh and *m*-H and *p*-H of NAr); 3.97 (sept, ³J_{H-H} = 6.6 Hz, 2H, CH, NAr); 3.27 (sept, ³J_{H-H} = 6.6 Hz, 2H, CH, NAr); 2.60 (s, 3H, CMe); 1.25 (d, ²J_{H-P} = 9.9 Hz, 9H, PMe₃); 1.23 (d, ³J_{H-H} = 6.6 Hz, 6H, 2CH₃, NAr); 1.15 (d, ³J_{H-H} = 6.6 Hz, 6H, 2CH₃, NAr); 0.98 (d, ³J_{H-H} = 6.6 Hz, 12H, 4CH₃, NAr). ³¹P{¹H}-NMR (121.5 MHz; C₆D₆; δ , ppm): 8.48 (s, PMe₃). ¹³C-NMR (75.5 MHz; C₆D₆; δ , ppm): 13.3 (d, ¹J_{C-P} = 27.9 Hz, PMe₃); 23.8 (s, CH₃, NAr); 24.0 (s, CH₃, NAr); 24.1 (s, CH₃, NAr); 27.9 (s, CH, NAr); 28.1 (s, CH, NAr); 30.3 (s, CH₃, η^1 -O=CMePh); 85.7 (s, η^1 -O=CMePh); 122.4 (s, *m*-C, NAr); 122.7 (s, *m*-C, NAr); 124.0 (s, *p*-C, NAr); 124.1 (s, *p*-C, NAr); 125.3 (s, *o*-C, η^1 -O=CMePh); 125.3 (s, *p*-C, η^1 -O=CMePh); signal for the *m*-C of η^1 -O=CMePh overlaps with the signal for C₆D₆; 141.3 (s, *o*-C, NAr); 141.9 (s, *o*-C, NAr); 151.6 (s, *i*-C, η^1 -O=CMePh); 153.8 (s, *i*-C, NAr); 154.0 (s, *i*-C, NAr). IR (nujol): 2276 cm⁻¹ (O=C). Elem. Anal. (%): calc. for C₃₅H₅₁MoN₂OP (642.706) C 65.41, H 8.00, N 4.36; found: C 64.96, H 8.12, N 4.28.

NMR reaction of (ArN=)₂Mo(PMe₃)₃ with acetophenone

Acetophenone (4.3 μ L, 0.036 mmol) was added at room temperature to a solution of (ArN)₂Mo(PMe₃)₃ (24.4 mg, 0.036 mmol) in 0.6 mL of C₆D₆ in NMR tube. After addition of acetophenone, the colour of reaction mixture turned from dark-green to brown almost immediately. The reaction mixture was left at room temperature for 5 min. NMR spectra showed the formation of only one product, (ArN)₂Mo(PMe₃)(η^1 -O=CMePh) (**7**), and evolution of two equivalents of PMe₃. Then all volatiles were pumped off and the residue was dried in vacuum and redissolved in fresh C₆D₆. NMR spectra showed the presence of compound **7** only.

Preparation of (ArN)₂Mo(PMe₃)(η^1 -O=CMePh) (**7**)

Acetophenone (90 μ L, 0.76 mmol) was added by a syringe at room temperature to a solution of (ArN)₂Mo(PMe₃)₃ (515.2 mg, 0.76 mmol) in 40 mL of hexane. The reaction mixture was purged with N₂ under stirring at room temperature for 20 min. The colour of the mixture changed from

dark-green to brown almost immediately. Then all volatiles were pumped off to give an oily residue, which was dried in vacuum. Recrystallization from Hex/Et₂O (1/1) gave **7** as an oily solid. Yield: 201 mg, 41 %.

NMR reaction of (ArN)₂Mo(PMe₃)(η^1 -O=CMePh) (7**) with PhSiH₃**

A solution of **7** (21.9 mg, 0.034 mmol) in 0.5 mL of C₆D₆ was added at room temperature to a solution of PhSiH₃ (4.2 μ L, 0.034 mmol) in 0.1 mL of C₆D₆ in NMR tube. NMR monitoring of the reaction showed after 3 days at room temperature selective the formation of agostic complex **3**, as well as the release of H₂ and acetophenone, which then reacted with PhSiH₃, affording the hydrosilation product, (PhMeCO)SiH₂Ph. Ethylbenzene was also observed.

Catalytic hydrosilation of acetophenone with PhSiH₃, using **7**

A solution of **7** (33.3 μ L, 0.002 mmol; C = 0.06 M; 1.0 mol %) was added at room temperature to a mixture of acetophenone (25.0 μ L, 0.214 mmol) and PhSiH₃ (26.4 μ L, 0.214 mmol) in 0.6 mL of C₆D₆ in NMR tube. The reaction was monitored by NMR for 20 days at room temperature and showed the 35 % conversion of acetophenone and formation of a mixture of PhSiH₂(OCH(Me)Ph) (76 %) and PhSi(OCH(Me)Ph)₃ (24 %). TON: 37.5.

PhSiH₂(OCH(Me)Ph): ¹H-MNR (300 MHz; C₆D₆; δ , ppm): 1.38 (d, ³J_{H-H} = 6.3 Hz, 3H, CH₃); 4.80 (q, ³J_{H-H} = 6.3 Hz, 1H, CH); 5.20 (s, 2H, PhSiH₂). ¹H-¹³C HSQC NMR (¹H(F2): 600 MHz; ¹³C(F1): 150.9 MHz; C₆D₆; J = 145 Hz; δ , ppm): 73.6 ppm (O-CH(Me)(Ph)). ²⁹Si{¹H}-NMR (59.6 MHz; C₆D₆; δ , ppm): -20.4 (t, ¹J_{Si-H} = 220.0 Hz, PhSiH₂); ²⁹Si-NMR (59.6 MHz; C₆D₆; δ , ppm): -20.4 (s, PhSiH₂). PhSi(OCH(Me)Ph)₃: ¹H-MNR (300 MHz; C₆D₆; δ , ppm): 1.36 (d, ³J_{H-H} = 6.0 Hz, 3H, CH₃); 5.03 (m, ³J_{H-H} = 6.0 Hz, 3H, CH); ¹H-¹³C HSQC NMR (¹H(F2): 600 MHz; ¹³C(F1): 150.9 MHz; C₆D₆; J = 145 Hz; δ , ppm): 72.0 ppm (O-CH(Me)(Ph)). ²⁹Si-NMR (59.6 MHz; C₆D₆; δ , ppm): -32.7 (s, PhSi).

NMR reaction of **3 with acetone**

Acetone (1.6 μ L, 0.022 mmol) was added at room temperature to a solution of **3** (16.0 mg, 0.022 mmol) in 0.6 mL of C₆D₆ in NMR tube. The reaction mixture was monitored by NMR analysis and left for 2 hours at room temperature until completion. NMR spectra showed the formation of only one product, (ArN)₂Mo(PMe₃)(η^2 -O=CMe₂) (**6**).

^1H -NMR (300 MHz; C_6D_6 ; δ , ppm): 7.07-6.96 (m, 6H, *p*-H and *m*-H, *NAr*); 3.98 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 4H, *CH*, *NAr*); 2.30 (s, 6H, $\eta^2\text{-O=CMe}_2$); 1.19 (m, 33H, *CH*₃ of *NAr* and 9H of PMe_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz; C_6D_6 ; δ , ppm): 7.30 (s, PMe_3). ^{13}C -NMR (75.5 MHz; C_6D_6 ; δ , ppm): 13.3 (d, $^1J_{\text{C-P}} = 27.8$ Hz, PMe_3); 24.0 (s, *CH*₃, *NAr*); 24.1 (s, *CH*₃, *NAr*); 28.0 (s, *CH*, *NAr*); 32.3 (s, *CH*₃, $\eta^2\text{-O=CMe}_2$); 85.8 (s, $\eta^2\text{-O=CMe}_2$); 122.7 (s, *m*-C, *NAr*); 123.9 (s, *p*-C, *NAr*); 141.6 (s, *o*-C, *NAr*); 153.9 (s, *i*-C, *NAr*). IR (nujol): 1621 cm^{-1} (O=C).

NMR reaction of $(\text{ArN})_2\text{Mo}(\text{PMe}_3)_3$ with acetone

Acetone (1.7 μL , 0.023 mmol) was added at room temperature to a solution of $(\text{ArN})_2\text{Mo}(\text{PMe}_3)_3$ (15.4 mg, 0.023 mmol) in 0.6 mL of C_6D_6 in an NMR tube. After addition of acetophenone 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 spectra showed the formation of only one complex, $(\text{ArN})_2\text{Mo}(\text{PMe}_3)(\eta^2\text{-O=CMe}_2)$ (**6**), and evolution of two equivalents of PMe_3 . Then all volatiles were pumped off, the oily residue was dried in vacuum and redissolved in fresh C_6D_6 . NMR spectra showed the presence of only the compound **3** in solution.

NMR reaction of $(\text{ArN})_2\text{Mo}(\text{PMe}_3)_3$ with benzaldehyde

Benzaldehyde (6.1 μL , 0.06 mmol) was added at room temperature to a solution of $(\text{ArN})_2\text{Mo}(\text{PMe}_3)_3$ (40.1 mg, 0.06 mmol) in 0.6 mL of C_6D_6 in NMR tube. After addition of acetophenone, the colour of the reaction mixture almost immediately turned from dark-green to brown. The reaction mixture was left at room temperature for 10 min. NMR spectra showed the formation of only one complex, $(\text{ArN})_2\text{Mo}(\text{PMe}_3)(\eta^2\text{-O=CHPh})$ (**8**), and evolution of two equivalents of PMe_3 . All volatiles were pumped off, and the oily residue was dried in vacuum and redissolved in fresh C_6D_6 . NMR spectra showed the presence of only one compound **8** in solution.

^1H -NMR (300 MHz; C_6D_6 ; δ , ppm): 7.54 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 2H, *o*-H, $\eta^2\text{-O=CHPh}$); 7.19 (t, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, *m*-H, $\eta^2\text{-O=CHPh}$); 7.06 (m, 3H, *p*-H, $\eta^2\text{-O=CHPh}$ and *NAr*); 6.89 (m, 4H, *m*-H, *NAr*); 5.69 (s, 1H, $\eta^2\text{-O=CHPh}$); 3.91 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, 2*CH*, *NAr*); 3.45 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, 2*CH*, *NAr*); 1.24 (m, $^3J_{\text{H-H}} = 6.9$ Hz, 12H, 4*CH*₃, *NAr*; $^2J_{\text{H-P}} = 6.6$ Hz, 9H, PMe_3); 1.03 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 12H, *NAr*). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz; C_6D_6 ; δ , ppm): 8.62 (s, PMe_3). ^{13}C -NMR (75.5 MHz; C_6D_6 ; δ , ppm): 13.3 (d, $^1J_{\text{C-P}} = 29.4$ Hz, PMe_3); 23.3 (s); 23.5 (s); 23.8 (s); 24.0 (s); 79.0 (s, *CH*, $\eta^2\text{-O=CHPh}$); 122.3 (s, *m*-C, *NAr*); 122.5 (s, *m*-C, *NAr*); 124.0 (s, *p*-C, *NAr*); 124.3 (s, *o*-C, $\eta^2\text{-O=CHPh}$); 125.6 (s, *p*-C, *NAr*); 128.2 (s, *m*-C, $\eta^2\text{-O=CHPh}$); 141.4 (s, *o*-C, *NAr*); 141.8 (s,

o-C, *NAr*); 148.7 (s, *i*-C, η^2 -O=CHPh); 153.7 (s, *i*-C, *NAr*); 153.9 (s, *i*-C, *NAr*); *p*-C of η^2 -O=CHPh ligand is overlapping with signals from benzene- d_6 . IR (nujol): 1597 cm^{-1} (O=C).

NMR reaction of (ArN)₂Mo(PMe₃)(η^2 -O=CHPh) (**8**) with PhSiH₃

PhSiH₃ (7.5 μL , 0.06 mmol) was added at room temperature to a solution of **8** (37.3 mg, 0.06 mmol) in 0.6 mL of C₆D₆ in an NMR tube. The reaction was monitored by NMR for 2 days at room temperature and showed the formation of **3**. The formation of H₂, toluene and hydrosilation products, (PhCH₂O)SiH₂Ph and (PhCH₂O)₂SiHPh was also observed.

NMR reaction of **3** with styrene

Styrene (3.5 μL , 0.031 mmol) was added at room temperature to a solution of **3** (22.5 mg, 0.031 mmol) in 0.6 mL of C₆D₆ in NMR tube. The reaction mixture was left at room temperature for 2 hours and 30 min until completion and monitored with NMR analysis. NMR spectra showed the formation of only one product, (ArN)(PMe₃)Mo(H)(η^2 -NAr-SiHPh-CH=CHPh) (**5**).

¹H-NMR (600 MHz; C₆D₆; δ , ppm): 8.00 (d, ³*J*_{H-H} = 7.8 Hz, 2H, *o*-H, *CPh*); 7.41 (d, ³*J*_{H-H} = 7.8 Hz, 2H, *o*-H, *SiPh*); 7.27 (m, 2H, *m*-H, *CPh*); 7.06-6.88 (m, 10H, *p*-H of *CPh*, *m*-H and *p*-H of *SiPh*, *m*-H and *p*-H of *NAr*); 6.22 (d, ³*J*_{H-H} = 15.0 Hz, 1H, CH=CH); 6.15 (d, ⁴*J*_{H-P} = 6.6 Hz, 1H, *SiH*); 3.56 (sept, ³*J*_{H-H} = 6.6 Hz, 1H, *CH*, *NAr*); 3.36 (sept, ³*J*_{H-H} = 7.2 Hz, 1H, *CH*, *NAr*); 3.30 (d, ³*J*_{H-H} = 15.0 Hz, 1H, CH=CH); 3.05 (d, ²*J*_{H-P} = 43.2 Hz, 1H, Mo-*H*); 2.63 (sept, ³*J*_{H-H} = 7.2 Hz, 1H, *CH*, *NAr*); 1.78 (sept, ³*J*_{H-H} = 7.2 Hz, 1H, *CH*, *NAr*); 1.39 (d, ³*J*_{H-H} = 7.2 Hz, 3H, *CH*₃, *NAr*); 1.30 (d, ³*J*_{H-H} = 7.2 Hz, 3H, *CH*₃, *NAr*); 1.14 (d, ³*J*_{H-H} = 6.6 Hz, 6H, 2*CH*₃, *NAr*); 1.12 (d, ³*J*_{H-H} = 7.2 Hz, 3H, *CH*₃, *NAr*); 1.10 (d, ³*J*_{H-H} = 7.2 Hz, 3H, *CH*₃, *NAr*); 0.95 (d, ³*J*_{H-H} = 6.6 Hz, 3H, *CH*₃, *NAr*); 0.75 (d, ²*J*_{H-P} = 7.8 Hz, 9H, *PMe*₃); 0.47 (d, ³*J*_{H-H} = 7.2 Hz, 3H, *CH*₃, *NAr*). ³¹P{¹H}-NMR (243 MHz; C₆D₆; δ , ppm): -19.2 (s, *PMe*₃). ³¹P-NMR (selectively decoupled from methyl groups) (243 MHz; C₆D₆; δ , ppm): -19.2 (dd, ²*J*_{H-P} = 43.7 Hz, ⁴*J*_{H-P} = 7.3 Hz *PMe*₃). ²⁹Si INEPT+ NMR (119.2 MHz; C₆D₆; 200 Hz; δ , ppm): -8.2 (d, ¹*J*_{Si-H} = 197.9 Hz, *SiH*). ¹³C-NMR (75.5 MHz; C₆D₆; δ , ppm): 17.4 (d, ¹*J*_{C-P} = 21.1 Hz, *PMe*₃); 18.4 (s, *CH*₃, *NAr*); 24.0 (s, *CH*₃, *NAr*); 24.7 (s, *CH*₃, *NAr*); 25.2 (s, *CH*₃, *NAr*); 25.3 (s, *CH*₃, *NAr*); 26.4 (s, *CH*₃, *NAr*); 27.7 (s, *CH*₃, *NAr*); 28.2 (s, *CH*, *NAr*); 28.3 (s, *CH*, *NAr*); 28.5 (s, *CH*, *NAr*); 28.7 (s, *CH*, *NAr*); 37.5 (d, ⁴*J*_{C-P} = 6.8 Hz, Si-CH=CH₂); 83.4 (d, ⁵*J*_{C-P} = 3.4 Hz, Si-CH=CH₂); 123.1, 123.2, 123.4, 123.8, 125.0, 126.6, 126.8, 127.1, 127.8, 128.1 (s, *p*-C of *CPh*, *p*-C and *m*-C of *SiPh* and *NAr*); 128.2 (s, *m*-C, *CPh*); 130.2 (s, *m*-C, *CPh*); 135.5 (s, *o*-C, *CPh*); 136.0, 136.1, 136.4, 136.8 (s, *o*-C, *SiPh*); 138.5, 141.1, 141.4,

147.4, 147.6, 150.6, 150.7, 151.3 (s, aromatic quaternary carbons). IR(nujol): 1812 cm⁻¹ (Mo-H); 2098 cm⁻¹ (Si-H).

NMR reaction of **3** with benzonitrile

Benzonitrile (3.8 μ L, 0.037 mmol) was added at room temperature to a solution of **3** (27.2 mg, 0.037 mmol) in 0.6 mL of C₆D₆ in NMR tube. The reaction was left at room temperature for 1 hour. NMR spectra showed the formation an intermediate tentatively formulated as (ArN)(PMe₃)Mo(η^2 -N(Ar)=SiHPh)(NCPh) (**11**), which was unstable and rearranged slowly into another product.^[3] All volatiles were pumped off; the oily residue was dried in vacuum, redissolved in fresh C₆D₆ and left at room temperature overnight for complete rearrangement. NMR spectra showed the formation of only one rearranged product, formulated as (ArN)(PMe₃)Mo[N(Ar)-Si(H)(Ph)-C(Ph)=N-] (**15**). Complex **15** is thermally unstable at room temperature in solution, completely decomposing in the course of one day.

(ArN)(PMe₃)Mo(η^2 -N(Ar)=SiHPh)(NCPh) (**11**): ³¹P-NMR (121.5 MHz; C₆D₆; δ , ppm): -6.43 (s, PMe₃).

(ArN)(PMe₃)Mo[N(Ar)-Si(H)(Ph)-C(Ph)=N-] (**15**): ¹H-NMR (300 MHz; C₆D₆; δ , ppm): 8.83 (d, ³J_{H-H} = 6.9 Hz, 2H, *o*-H, CPh); 8.06 (m, 2H, *o*-H, SiPh); 7.75-6.96 (m, 12H, *p*-H and *m*-H of CPh, SiPh and NAr); 5.34 (s, 1H, SiH); 3.75 (m, 4H, 4CH, NAr); 1.41 (d, ³J_{H-H} = 6.6 Hz, 3H, CH₃, NAr); 1.25 (d, ³J_{H-H} = 7.2 Hz, 3H, CH₃, NAr); 1.14 (d, ²J_{H-P} = 8.7 Hz, 9H, PMe₃); 1.05 (d, ³J_{H-H} = 7.2 Hz, 6H, 2CH₃, NAr); 0.98 (d, ³J_{H-H} = 6.9 Hz, 6H, 2CH₃, NAr); 0.89 (m, 3H, CH₃, NAr); 0.61 (d, ³J_{H-H} = 7.2 Hz, 3H, CH₃, NAr). ³¹P-NMR (121.5 MHz; C₆D₆; δ , ppm): -3.50 (s, PMe₃). ²⁹Si INEPT+ NMR (59.6 MHz; C₆D₆; *J* = 200 Hz; δ , ppm): -44.4 (d, ¹J_{Si-H} = 225.4 Hz, SiH). ¹³C-NMR (75.5 MHz; C₆D₆; δ , ppm): 16.9 (d, ¹J_{C-P} = 22.6 Hz, PMe₃); 21.5 (s, CH₃, NAr); 23.2 (s, CH₃, NAr); 23.6 (s, CH₃, NAr); 24.1 (s, CH₃, NAr); 24.7 (s, CH₃, NAr); 24.9 (s, CH₃, NAr); 27.8 (s, CH, NAr); 28.0 (s, CH, NAr); 28.3 (s, CH, NAr); 29.1 (s, CH, NAr); 122.4 (s, *p*-C, NAr); 122.7 (s, *p*-C, NAr); 122.8 (s, *m*-C, NAr); 123.3 (s, *m*-C, NAr); 125.2 (s, *m*-C, NAr); 126.8 (s, *m*-C, NAr); 127.0 (s, *m*-C, SiPh); *m*-C of CPh signals are overlapping with benzene signal; 128.5 (s, *p*-C, SiPh); 129.0 (s, *p*-C, CPh); 133.4 (s, *o*-C, CPh); 133.9 (s, *o*-C, CPh); 135.5 (s, *o*-C, SiPh); 136.9 (s, *o*-C, SiPh); 141.5 (s, *o*-C, NAr); 141.6 (s, *o*-C, NAr); 143.5 (s, *o*-C, NAr); 151.2, 153.6, 158.4 (all singlets, aromatic *i*-C); 192.4 (s, PhC=N). IR (nujol): 2118 cm⁻¹ (Si-H).

NMR reaction of **3** with *i*PrCN

*i*PrCN (1.9 μ L, 0.021 mmol) was added at room temperature to a solution of **3** (15.3 mg, 0.021 mmol) in 0.6 mL of C₆D₆ in an NMR tube. The reaction mixture was left at room temperature for 5 minutes. NMR spectra showed the formation of only one product, rationalized as nitrile adduct (ArN)(PMe₃)Mo(η^2 -N(Ar)=SiHPh)(NC*i*Pr) (**9**). This product was unstable and slowly rearranged into the compound (ArN)(PMe₃)Mo[-N(Ar)-SiHPh-C(*i*Pr)=N-] (**13**), most likely via intermolecular insertion of the nitrile into the Mo-Si bond of the silanimine moiety.^[3] After 1 hour 20 minutes at room temperature, the rearrangement was complete, all volatiles were pumped off, the oily residue was dried in vacuum and redissolved in fresh C₆D₆. Further NMR analysis showed the presence of only one product **13** in solution.

(ArN)(PMe₃)Mo(η^2 -N(Ar)=SiHPh)(NC*i*Pr) (**9**): ¹H-NMR (300 MHz; C₆D₆; δ , ppm): 5.74 (d, ³J_{H-P} = 3.9 Hz, 1H, SiH); 1.59 (d, ³J_{H-H} = 6.9 Hz, 6H, 2CH₃, *i*PrC=N). ³¹P{¹H}-NMR (121.5 MHz; C₆D₆; δ , ppm): -4.35 (s, PMe₃).

(ArN)(PMe₃)Mo[-N(Ar)-SiHPh-C(*i*Pr)=N-] (**13**): ¹H-NMR (300 MHz; C₆D₆; δ , ppm): 7.94 (m, 2H, *o*-H, SiPh); 7.09-6.89 (m, 3H, 9H, *m*-H and *p*-H of SiPh, *m*-H and *p*-H of NAr); 5.31 (s, 1H, SiH); 3.95 (m, 1H, CH, NAr); 3.78 (sept, ³J_{H-H} = 6.9 Hz, 1H, CH, *i*PrC=N); 3.70 (sept, ³J_{H-H} = 6.9 Hz, 2H, 2CH, NAr); 3.63 (sept, ³J_{H-H} = 7.5 Hz, 1H, CH, NAr); 1.69 (d, ³J_{H-H} = 6.9 Hz, 6H, 2CH₃, *i*PrC=N); 1.36 (d, ³J_{H-H} = 6.6 Hz, 3H, CH₃, NAr); 1.30 (d, ³J_{H-H} = 6.6 Hz, 3H, CH₃, NAr); 1.22 (d, ³J_{H-H} = 6.6 Hz, 3H, CH₃, NAr); 1.18 (d, ³J_{H-H} = 6.9 Hz, 6H, 2CH₃, NAr); 1.12 (d, ³J_{H-H} = 6.9 Hz, 6H, 2CH₃, NAr); 1.05 (d, ²J_{H-P} = 8.7 Hz, 9H, PMe₃); 0.60 (d, ³J_{H-H} = 6.9 Hz, 3H, CH₃, NAr). ³¹P-NMR (121.5 MHz; C₆D₆; δ , ppm): -3.83 (s, PMe₃). ¹³C-NMR (75.5 MHz; C₆D₆; δ , ppm): 14.3 (d, ¹J_{C-P} = 21.9 Hz, PMe₃); 22.55 (s, CH₃, *i*PrC=N); 22.60 (s, CH₃, NAr); 23.76 (s, CH₃, NAr); 23.83 (s, CH₃, NAr); 24.2 (s, CH₃, NAr); 26.8 (s, CH₃, NAr); 28.0 (s, CH, NAr); 28.1 (s, CH, NAr); 28.2 (s, CH, NAr); 28.6 (s, CH, *i*PrC=N); 122.5 (s, *p*-C, NAr); 122.6 (s, *p*-C, NAr); 122.8 (s, *m*-C, NAr); 123.0 (s, *m*-C, NAr); 125.3 (s, *m*-C, NAr); *m*-C of SiPh signal is overlapping with the benzene signals; 129.7 (s, *p*-C, SiPh); 136.9 (s, *o*-C, SiPh); 141.3 (s, *o*-C, NAr); 141.8 (s, *o*-C, NAr); 143.7 (s, *o*-C, NAr); 153.8, 155.6, 155.8 (all singlets, aromatic *i*-C); 195.9 (s, *i*PrC=N). ²⁹Si INEPT+ NMR (59.6 MHz; C₆D₆; 200 Hz; δ , ppm): -46.6 (d, ¹J_{Si-H} = 218.3 Hz, SiH). IR (Nujol): 2103 cm⁻¹ (Si-H).

Preparation of (ArN)(PMe₃)Mo(-NAr-SiHPh-C(ⁱPr)=N-) (**13**)

ⁱPrCN (37.7 μ L, 0.42 mmol) was added at room temperature to a solution of **1** (281.3 mg, 0.38 mmol) in 15 mL of toluene. The reaction mixture was stirred at room temperature for 2 hours. Then all volatiles were pumped off, the residue was dried in vacuum, redissolved in fresh toluene and allowed to stir at room temperature overnight. All volatiles were removed under reduced pressure and the residue was extracted with hexane. The solvent was pumped off to leave an oily substance which was dissolved in Et₂O. The ether solution was left with stirring for 2 hours, and then ether was removed in vacuum to give a brown foam of **13**. Yield: 193.3 mg, 73 %. All attempts to recrystallize the product gave an oily substance. The product is not stable at room temperature in solution and after four days NMR analysis showed a slow decomposition of **13**.

NMR reaction of **13** with PhSiH₃

PhSiH₃ (12.0 μ L, 0.097 mmol) was added in one portion at room temperature to a solution of **13** (21.5 mg, 0.031 mmol) in 0.6 mL of C₆D₆ in NMR tube. No visual changes were observed after the addition of silane. The reaction mixture was left for four days at room temperature. NMR monitoring showed a slow but selective formation of **3**.

NMR reaction of **3** with ^tBuCN

^tBuCN (3.7 μ L, 0.034 mmol) was added at room temperature to a solution of **1** (24.8 mg, 0.034 mmol) in 0.6 mL of toluene-d₈ in NMR tube. The reaction mixture was left at room temperature for 5 minutes. NMR spectra showed the formation of a single product (ArN)(PMe₃)Mo(η^2 -N(Ar)=SiHPh)(η^2 -N $\equiv$ C^tBu) (**10**). This formulation was confirmed by the observation of nitrile carbon signal at 204 ppm in the ¹³C NMR spectrum, suggesting the η^2 -coordination of ^tBuCN ligand⁴), the ¹H-¹³C HMBC NMR spectrum showed the absence of coupling between the Si-H proton and nitrile carbon atom. Complex **10** decomposes slowly in solution, affording a difficult-to-analyze mixture of compounds. One of the components of the mixture, appearing to be similar to the insertion product **13**, was formulated as (ArN)(PMe₃)Mo[-N(Ar)-SiHPh-C(^tBu)=N-] (**14**). **14** is not stable and decomposes completely in solution after one day at room temperature.

Characteristic NMR signals for (ArN)(PMe₃)Mo(η^2 -N(Ar)=SiHPh)(η^2 -N $\equiv$ C^tBu) (**10**): ¹H-NMR (600 MHz; toluene-d₈; 295 K; δ , ppm): 7.98 (d, ³J_{H-H} = 7.2 Hz, 2H, *o*-H, SiPh); 6.87-7.10 (overlapping with toluene signals multiplet, *p*-H and *m*-H of ArN and SiPh); 5.66 (d, ³J_{H-P} = 3.6 Hz, 1H, SiH); 3.95 (m, 2H, 2CH, NAr); 3.86 (sept, ³J_{H-H} = 6.6 Hz, 1H, CH, NAr); 2.50 (sept, ³J_{H-H}

= 6.6 Hz, 1H, *CH*, *NAr*); 1.45 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 3H, *CH*₃, *NAr*); 1.42 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 3H, *CH*₃, *NAr*); 1.39 (s, 9H, *t*BuC); 1.28 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 6H, 2*CH*₃, *NAr*); 1.17 (m, 6H, 2*CH*₃, *NAr*); 1.03 (d, $^2J_{\text{H-P}} = 9.0$ Hz, 9H, *PMe*₃); 0.26 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 3H, *CH*₃, *NAr*); 0.13 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 3H, *CH*₃, *NAr*). $^1\text{H}\{^{31}\text{P}\}$ -NMR (600 MHz; toluene-*d*₈; 295 K; δ , ppm): 5.66 (s, 1H, SiH); 1.03 (s, 9H, *PMe*₃). $^{31}\text{P}\{^1\text{H}\}$ -NMR (121.5 MHz; toluene-*d*₈; 298 K; δ , ppm): -1.86 (s, *PMe*₃). ^{13}C -NMR (151 MHz; toluene-*d*₈; 243 K; δ , ppm): 17.5 (d, $^1J_{\text{C-P}} = 27.2$ Hz, *PMe*₃); 23.3 (s, *CH*₃, *NAr*); 23.9 (s, *CH*₃, *NAr*); 24.5 (s, *CH*₃, *NAr*); 25.4 (s, *CH*₃, *NAr*); 27.5 (s, *CH*, *NAr*); 28.1 (s, *CH*, *NAr*); 29.1 (s, *CH*, *NAr*); 30.2 (s, *CH*₃, *t*BuC); 35.0 (s, Me₃CC); 135.2 (s, *o*-C, SiPh); 122.3 (s, *p*-C, SiPh); 122.7 (s, *p*-C, *NAr*); 123.3 (s, *p*-C, *NAr*); 123.3 (s, *m*-C, *NAr*); 123.9 (s, *m*-C, *NAr*); 124.6 (s, *m*-C, *NAr*); 126.4 (s, *m*-C, *NAr*); 129.9 (s, *m*-C, SiPh); 135.9 (s, *o*-C, SiPh); 140.3 (s, *o*-C, *NAr*); 141.2 (s, *o*-C, *NAr*); 144.6 (s, *o*-C, *NAr*); 145.6 (s, *o*-C, *NAr*); 148.7 (s, *i*-C, SiPh); 153.1 (s, *i*-C, *NAr*); 153.4 (s, *i*-C, *NAr*); 204.4 (s, *t*BuC). ^{29}Si INEPT+ NMR (119.2 MHz; toluene-*d*₈; 200 Hz; 243 K; δ , ppm): -50.9 (d, $^1J_{\text{Si-H}} = 223.0$ Hz, SiH).

Characteristic NMR signals for (ArN)(PMe₃)Mo[-N(Ar)-SiHPh-C(*t*Bu)=N-] (**14**): ^1H -NMR (600 MHz; toluene-*d*₈; 295 K; δ , ppm): 6.56 (s, 1H, SiH); 1.00 (d, $^2J_{\text{H-P}} = 7.2$ Hz, 9H, *PMe*₃). ^{31}P -NMR (121.5 MHz; toluene-*d*₈; 298 K; δ , ppm): 3.30 (s, *PMe*₃). ^{29}Si INEPT+ NMR (119.2 MHz; toluene-*d*₈; 200 Hz; 243 K; δ , ppm): -20.6 (d, $^1J_{\text{Si-H}} = 224.2$ Hz, SiH).

NMR reaction of **3** with PhSiH₃

PhSiH₃ (4.14 μL , 0.034 mmol) was added at room temperature to a solution of **3** (24.7 mg, 0.034 mmol) in 0.6 mL of C₆D₆ in NMR tube. The reaction mixture was left at room temperature for nine days. The ^1H - ^1H EXSY NMR experiment (Fig. 10) established proton exchange between silyl substituent in **3** and free silane. After overnight at room temperature the reaction mixture contains the starting PhSiH₃ (30 %), Ph₂SiH₂ (34 %), SiH₄ (34 %) and PhSiH₂-SiH₂Ph (2 %).^[5] Analogous reaction with heating at 50 °C overnight gives full conversion of PhSiH₃ into Ph₂SiH₂ (47 %), SiH₄ (47 %) and PhSiH₂-SiH₂Ph (6 %).

NMR reaction of **3** with PhSiD₃

3 (23.0 mg, 0.031 mmol) was dissolved in 0.6 mL of toluene-*d*₈ to give a clear brown solution. At this point, a careful integration of signals of SiH protons in the ^1H NMR spectrum recorded at -50 °C was performed. Then, PhSiD₃ (3.85 μL , 0.031 mmol) was added at room temperature to the solution, and the reaction mixture was left at room temperature for 5 minutes. The extent of

deuterium incorporation into each position was calculated from the difference of integration of the residual protons in the ^1H NMR spectra (Fig. 11 and 12) recorded at $-50\text{ }^\circ\text{C}$. These data are listed below.

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

NMR reaction of **3** with (*m*-Tol)SiH₃

(*m*-Tol)SiH₃ (5.0 μL , 0.037 mmol) was added at room temperature to a solution of **3** (27.3 mg, 0.037 mmol) in 0.6 mL of C₆D₆ in NMR tube. The reaction mixture was left at room temperature for 10 minutes, then all volatiles were pumped off, the residue was dried in vacuum and dissolved in toluene-*d*₈. VT NMR spectra showed the formation of only one new product, (ArN)(PMe₃)[(*m*-Tol)H₂Si]Mo(-NAr-SiHPh-H-) (**3_{tol}**), accompanied by the release of an equivalent of PhSiH₃, which was rationalized in terms of reversible silane addition to the electron deficient silanimine intermediate (ArN)(PMe₃)Mo(η^2 -N(Ar)=SiHPh)^[31]. No exchange with the agostic silicon centre was observed. The conversion of the starting complex **3** into **3_{tol}** was 43 % (Fig. 16 and 17).

(ArN)(PMe₃)[(*m*-Tol)H₂Si]Mo(-NAr-SiHPh-H-) (**3_{tol}**): ^1H -NMR (300 MHz; C₆D₆; 297 K; δ , ppm): 8.14 (m, *o*-H, *m*-TolSiH₂); 2.25 (s, CH₃, *m*-TolSiH₂); all other signals are overlapping with those for starting material **3**. $^{31}\text{P}\{^1\text{H}\}$ -NMR (121.5 MHz; C₆D₆; 297 K; δ , ppm): 10.54 (s, PMe₃). ^1H -NMR (600 MHz; C₆D₆; 243 K; δ , ppm): 8.45 (d, $^3J_{\text{H-H}} = 7.2\text{ Hz}$, *o*-H, *m*-TolSiH₂); 7.38 (d, $^3J_{\text{H-H}} = 7.8\text{ Hz}$, *o*-H, PhSiH); 6.12 (m, (Ar)NSiHPh-H-, terminal); 5.97 (bs, *m*-TolSiH₂); 5.64 (bs, *m*-TolSiH₂); 4.36 (m, (Ar)NSiHPh-H-, agostic); 2.30 (s, CH₃, *m*-TolSiH₂); all other signals are overlapping with those for starting material **3**. ^{31}P -NMR (243 MHz; toluene-*d*₈; 252 K; δ , ppm): 12.22 (s, PMe₃).

CATALYSIS BY **3**

Hydrosilation of benzaldehyde with PhMeSiH₂

Complex **3** (3.2 mg; 0.004 mmol; 1.6 mol. %) was added at room temperature to a solution of benzaldehyde (25 μ L; 0.246 mmol) and PhMeSiH₂ (33.8 μ L; 0.246 mmol) in 0.6 mL of C₆D₆ in an NMR tube. After 10 min at room temperature, the colour of the solution changed from brown to green. The reaction mixture was left at room temperature for 6 days. NMR analysis showed a 28 % conversion of benzaldehyde and the formation of only one product, MePhHSi(OCH₂Ph). TON: 16. Characteristic NMR signals: ¹H-MNR (300 MHz; C₆D₆; δ , ppm): 0.34 (d, ³J_{H-H} = 2.7 Hz, 3H, *Me*); 4.62 (s, 2H, O-CH₂-Ph); 5.26 (q, ³J_{H-H} = 2.7 Hz, 1H, *H*-Si); 7.13 (m, 3H, *m*-H and *p*-H, *Ph*); 7.23 (m, 3H, *m*-H and *p*-H, SiPh); 7.43 (m, 2H, *o*-H, *Ph*); 7.57 (m, 2H, *o*-H, SiPh). ²⁹Si INEPT+ NMR (119.2 MHz; C₆D₆; *J* = 200 Hz; δ , ppm): -0.9 (d, ¹J_{Si-H} = 209.9 Hz, PhMeSiH).

Hydrosilation of benzaldehyde with (EtO)₃SiH

3 (1.8 mg; 0.0025 mmol; 1.0 mol. %) was added at room temperature to a solution of benzaldehyde (25 μ L; 0.246 mmol) and (EtO)₃SiH (45.1 μ L; 0.246 mmol) in 0.6 mL of C₆D₆ in an NMR tube. After 10 min at room temperature, the colour changed to dark-brown. The reaction mixture was left at room temperature for 4 days, showing only a 10 % conversion of benzaldehyde (TON: 9.8), and then heated at 50 °C for 12 days until the starting silane and benzaldehyde were consumed. The course of reaction was monitored by ¹H-NMR spectroscopy that showed a 100 % conversion of benzaldehyde and the formation of (EtO)₃Si(OCH₂Ph)^[6] (10 %), (EtO)₂Si(OCH₂Ph)₂ (32 %), (EtO)Si(OCH₂Ph)₃ (47 %) and Si(OCH₂Ph)₄ (11 %). TON: 98.4.

Characteristic NMR signals: ²⁹Si INEPT+ NMR (119.2 MHz; C₆D₆; *J* = 7 Hz; δ , ppm): -81.6 (bm, *J*_{Si-H} = 2.9 Hz, overlapping signals from all four products). (EtO)₃Si(OCH₂Ph): ¹H-MNR (300 MHz; C₆D₆; δ , ppm): 4.85 (s, OCH₂Ph). (EtO)₂Si(OCH₂Ph)₂: ¹H-MNR (300 MHz; C₆D₆; δ , ppm): 4.88 (s, OCH₂Ph). (EtO)Si(OCH₂Ph)₃: ¹H-MNR (300 MHz; C₆D₆; δ , ppm): 4.91 (s, OCH₂Ph); Si(OCH₂Ph)₄: ¹H-MNR (300 MHz; C₆D₆; δ , ppm): 4.99 (s, OCH₂Ph).

Reaction of cyclohexene with PhSiH₃

3 (7.5 mg; 0.01 mmol; 5.0 mol. %) was added at room temperature to a solution of cyclohexene (20.5 μ L; 0.203 mmol) and PhSiH₃ (25 μ L; 0.203 mmol) in 0.6 mL of C₆D₆ in an NMR tube. The reaction mixture was left at room temperature for 2 days (no reaction was observed during this

time) and then heated at 50 °C for 39 days until the starting silane disappeared. NMR spectra showed the formation of cyclohexane (28 %). TON: 5.8.

Reaction of hexene-1 with PhSiH₃

3 (7.5 mg; 0.01 mmol; 5.0 mol. %) was added at room temperature to a solution of 1-hexene (25.2 μ L; 0.203 mmol) and PhSiH₃ (25 μ L; 0.203 mmol) in 0.6 mL of dry C₆D₆ in an NMR tube. The reaction mixture was left at room temperature for 3 days, showing only 20 % conversion of hexene (TON: 4.1), and then heated at 50 °C for 37 days until the starting silane disappeared. The course of reaction was monitored by ¹H-NMR spectroscopy that showed a 100 % conversion of 1-hexene and the formation of a mixture of Ph₂SiH₂, 2-hexene (26 %), hexane (71 %) and traces of hydrosilation products (less than 3 %).^[7] TON: 20.3.

Hydrosilation of benzaldehyde with PhSiH₃

A: 3 (2.3 mg; 0.003 mmol; 1.3 mol %) was added to a mixture of benzaldehyde (54.3 μ L; 0.534 mmol) and PhSiH₃ (33 μ L; 0.267 mmol) in 0.6 mL of C₆D₆ in NMR tube. The reaction was monitored by ¹H-NMR spectroscopy at room temperature during 7 days to give a 100 % conversion of starting benzaldehyde and the formation of PhSiH₂(OCH₂Ph) (5 %) and PhSiH(OCH₂Ph)₂ (95 %).^[8,9] TON: 82.

B: 3 (0.96 mg; 0.0013 mmol; 0.5 mol. %) was added at room temperature to a solution of benzaldehyde (25.0 μ L; 0.25 mmol) and PhSiH₃ (32.8 μ L; 0.27 mmol) in 0.6 mL of C₆D₆ in an NMR tube. The mixture was left at room temperature for 16 hours to give a full conversion of benzaldehyde into PhSiH₂(OCH₂Ph) (43 %) and PhSiH(OCH₂Ph)₂ (57 %).^{8,9} TON: 192.3.

Hydrosilation of acetophenone with PhSiH₃

3 (1.6 mg; 0.002 mmol; 1.0 mol %) was added at room temperature to a mixture of acetophenone (25.0 μ L; 0.214 mmol) and PhSiH₃ (26.4 μ L; 0.214 mmol) in 0.6 mL of C₆D₆ in an NMR tube. The reaction was monitored by ¹H-NMR spectroscopy for 20 days at room temperature until 100 % conversion of acetophenone. NMR spectra showed the formation of a mixture of products: PhSiH₂(OCH(Me)Ph) (44 %), PhSiH(OCH(Me)Ph)₂ (29 %), PhSi(OCH(Me)Ph)₃ (21 %) and ethylbenzene (6 %). TON: 107.

Characteristic NMR signals. PhSiH₂(OCH(Me)Ph): ¹H-MNR (300 MHz; C₆D₆; δ , ppm): 1.38 (d, ³J_{H-H} = 6.3 Hz, 3H, CH₃); 4.80 (q, ³J_{H-H} = 6.3 Hz, 1H, CH); 5.20 (s, 2H, PhSiH₂). ²⁹Si-NMR (59.6

MHz; C₆D₆; δ , ppm): -20.4 (t, $^1J_{\text{Si-H}} = 220.0$ Hz, PhSiH₂); $^{29}\text{Si}\{^1\text{H}\}$ -NMR (59.6 MHz; C₆D₆; δ , ppm): -20.4 (s, PhSiH₂). PhSiH(OCH(Me)Ph)₂: ^1H -MNR (300 MHz; C₆D₆; δ , ppm): 1.42 (d, $^3J_{\text{H-H}} = 6.3$ Hz, 3H, CH₃); 4.98 (m, $^3J_{\text{H-H}} = 6.0$ Hz, 2H, CH); 5.30 (s, 1H, PhSiH). ^{29}Si -NMR (59.6 MHz; C₆D₆; δ , ppm): -32.6 (d, $^1J_{\text{Si-H}} = 248.6$ Hz, PhSiH); $^{29}\text{Si}\{^1\text{H}\}$ -NMR (59.6 MHz; C₆D₆; δ , ppm): -32.6 (s, PhSiH). PhSi(OCH(Me)Ph)₃: ^1H -MNR (300 MHz; C₆D₆; δ , ppm): 1.36 (d, $^3J_{\text{H-H}} = 6.0$ Hz, 3H, CH₃); 5.03 (m, $^3J_{\text{H-H}} = 6.0$ Hz, 3H, CH); ^{29}Si -NMR (59.6 MHz; C₆D₆; δ , ppm): -32.7 (s, PhSi).

Reaction of phenylacetylene with PhSiH₃

3 (4.1 mg; 0.006 mmol; 2.7 mol. %) was added at room temperature to a mixture of phenylacetylene (22.3 μL ; 0.203 mmol) and PhSiH₃ (25 μL ; 0.203 mmol) in 0.6 mL of C₆D₆ in an NMR tube. The reaction was monitored by ^1H -NMR spectroscopy for 17 hours at room temperature until 100 % conversion of phenylacetylene. NMR spectra showed only the formation of polyphenylacetylene^[10], with PhSiH₃ remaining unreacted. TON: 33.8.

Polymerization of phenylacetylene

3 (3.3 mg; 0.0045 mmol; 3.0 mol. %) was added at room temperature to a solution of phenylacetylene (16.4 μL ; 0.149 mmol) in 0.6 mL of C₆D₆ in an NMR tube. The reaction was monitored by ^1H -NMR spectroscopy for 24 hours at room temperature and stopped after a 25 % conversion of phenylacetylene (TON: 8.3) was reached. NMR spectra showed the formation of polyphenylacetylene^[10] (22 %). Further heating of the reaction mixture at 50 °C for 24 hours afforded 42 % (in total) of polyphenylacetylene with 45 % conversion of the starting phenylacetylene. TON: 14.9.

Reaction of styrene with PhSiH₃

3 (3.2 mg; 0.0044 mmol; 3.0 mol. %) was added at room temperature to a solution of styrene (25.0 μL ; 0.22 mmol) and PhSiH₃ (26.8 μL ; 0.22 mmol) in 0.6 mL of C₆D₆ in an NMR tube. The mixture was left at room temperature for 24 hours, showing no reaction. Then the mixture was heated at 50 °C for 23 hours to give only 6 % (according to ^1H -NMR) of ethylbenzene (TON: 1.3) at 18 % conversion of the starting PhSiH₃, the silicon products being a mixture of PhH₂Si-SiH₂Ph (36 %), Ph₂SiH₂ (32 %) and SiH₄ (32 %).

Alcoholysis of PhSiH₃ with ethanol

A: **3** (7.5 mg; 0.01 mmol; 5.0 mol. %) was added at room temperature to a solution of ethanol (11.9 μ L; 0.203 mmol) and PhSiH₃ (25.0 μ L; 0.203 mmol) in 0.6 mL of C₆D₆ in an NMR tube. Immediate gas evolution was observed after the addition of the catalyst. The reaction was left at room temperature for 5 minutes. NMR analysis showed a 100 % conversion of ethanol to give a mixture of mono- and bis(substituted) products: PhH₂Si(OEt) (33 %), and PhSiH(OEt)₂ (67 %).^{8, 11} TON: 20.3.

B: **3** (7.5 mg; 0.01 mmol; 5.0 mol. %) was added at room temperature to a solution of ethanol (23.8 μ L; 0.406 mmol) and PhSiH₃ (25.0 μ L; 0.203 mmol) in 0.6 mL of C₆D₆ in an NMR tube. Immediate gas evolution was observed after addition of the catalyst. The reaction was left at room temperature for 25 minutes. NMR analysis showed 100 % conversion of ethanol to give a mixture of mono- and bis(substituted) products: PhH₂Si(OEt) (11 %), and PhSiH(OEt)₂ (89 %).^[8, 11] TON: 40.6.

Characteristic NMR signals: ¹H-NMR (300 MHz, C₆D₆; δ , ppm): 5.22 (s, PhHSi(OEt)₂); 5.19 (s, PhH₂Si(OEt)). ²⁹Si INEPT+ NMR (119.2 MHz; C₆D₆; J = 200 Hz; δ , ppm): -28.6 (t, ¹ $J_{\text{Si-H}}$ = 210.0 Hz, PhH₂Si(OEt)); -30.8 (d, ¹ $J_{\text{Si-H}}$ = 241.3 Hz, PhHSi(OEt)₂).

Alcoholysis of PhSiH₃ with propanol-2

3 (7.5 mg; 0.01 mmol; 5.0 mol. %) was added at room temperature to a solution of propanol-2 (15.5 μ L; 0.203 mmol) and PhSiH₃ (25.0 μ L; 0.203 mmol) in 0.6 mL of C₆D₆ in an NMR tube. Immediate gas evolution was observed after addition of the catalyst. The reaction was left at room temperature for 5 minutes. NMR analysis showed 100 % conversion of propanol-2 to give a mixture of mono- and bis(substituted) products: PhH₂Si(O^{*i*}Pr) (18 %), and PhSiH(O^{*i*}Pr)₂ (82 %).^{11a} TON: 20.3.

Characteristic NMR signals: ¹H-NMR (300 MHz, C₆D₆; δ , ppm): 7.79 (m, *o*-H, PhHSi(O^{*i*}Pr)₂); 7.61 (m, *o*-H, PhH₂Si(O^{*i*}Pr)); 7.20-7.10 (m, overlapping *m*-H and *p*-H signals of PhHSi(O^{*i*}Pr)₂ and PhH₂Si(O^{*i*}Pr)); 5.28 (s, PhHSi(O^{*i*}Pr)₂); 5.23 (s, PhH₂Si(O^{*i*}Pr)); 4.20 (sept, ³ $J_{\text{H-H}}$ = 6.1 Hz, CH, PhHSi(O^{*i*}Pr)₂); 3.91 (sept, ³ $J_{\text{H-H}}$ = 6.1 Hz, CH, PhH₂Si(O^{*i*}Pr)); 1.16 (d, ³ $J_{\text{H-H}}$ = 6.1 Hz, CH, PhHSi(O^{*i*}Pr)₂); 1.08 (d, ³ $J_{\text{H-H}}$ = 6.1 Hz, CH, PhH₂Si(O^{*i*}Pr)). ²⁹Si INEPT+ NMR (119.2 MHz; C₆D₆; J = 200 Hz; δ , ppm): -34.8 (d, ¹ $J_{\text{Si-H}}$ = 239.7 Hz, PhSiH(O^{*i*}Pr)₂); -22.5 (t, ¹ $J_{\text{Si-H}}$ = 213.4 Hz, PhSiH₂(O^{*i*}Pr)).

Hydrosilation of acetonitrile with PhSiH₃

3 (7.5 mg; 0.01 mmol; 5.0 mol. %) was added at room temperature to a solution of acetonitrile (9.5 μ L; 0.203 mmol) and PhSiH₃ (25.0 μ L; 0.203 mmol) in 0.6 mL of C₆D₆ in an NMR tube. The mixture was left at room temperature for 14 hours, showing no reaction. Then the mixture was heated at 50 °C for 51 hours. NMR spectra showed the formation of traces (less than 3 %) of EtN(SiH₂Ph)₂.^[12b,c]

Characteristic NMR signals: ¹H-NMR (300 MHz, C₆D₆; δ , ppm): 5.19 (s, 2H, SiH₂Ph); 4.00 (s, 2H, CH₂Ph).

Hydrosilation of benzonitrile with PhSiH₃

3 (7.5 mg; 0.01 mmol; 5.0 mol. %) was added at room temperature to a solution of benzonitrile (20.7 μ L; 0.203 mmol) and PhSiH₃ (25.0 μ L; 0.203 mmol) in 0.6 mL of C₆D₆ in NMR tube. The mixture was left at room temperature for 24 hours, showing no reaction. Then the reaction mixture was heated at 50 °C for 6 days. NMR spectra showed 20 % conversion of benzonitrile and formation of only one product, PhH₂SiN=CHPh. TON: 4.1.

Characteristic NMR signals: ¹H-NMR (300 MHz, C₆D₆; δ , ppm): 8.90 (s, 1H, CHPh); 7.70 (m, 2H, Ph); 7.63 (m, 2H, Ph); 5.42 (s, 2H, SiH₂Ph).

Hydrosilation of acetone with PhSiH₃

3 (1.5 mg; 0.002 mmol; 1.0 mol. %) was added at room temperature to a solution of acetone (14.9 μ L; 0.203 mmol) and PhSiH₃ (25.0 μ L; 0.203 mmol) in 0.6 mL of C₆D₆ in an NMR tube. The reaction was left at room temperature for 5 days. NMR spectra showed 76 % conversion of acetone and the formation of a mixture of PhH₂Si(O^{*i*}Pr) (34 %) and PhHSi(O^{*i*}Pr)₂ (42 %).^{12a} TON: 77.1. For characteristic NMR signals, see the reaction of PhSiH₃ with ^{*i*}PrOH.

Hydrosilation of pyridine with PhSiH₃

3 (7.0 mg; 0.01 mmol; 0.6 mol. %) was added at room temperature to a mixture of pyridine (131 μ L; 1.62 mmol) and PhSiH₃ (200 μ L; 1.62 mmol). The reaction was left at room temperature for 5 days and was monitored by NMR, showing less than 5 % conversion of pyridine into N-(phenylsilyl)-4-hydropyridine and N-(phenylsilyl)-2-hydropyridine (approximately 1:1).^[13]

Hydrosilation of ethylene with PhSiH₃

Ethylene was added *via* vacuum transfer at -80 °C to a frozen mixture of PhSiH₃ (25.0 μL, 0.203 mmol) and **3** (5.0 mg, 0.007 mmol, 3.3 mol. %) in 0.6 mL of C₆D₆ in NMR tube. The reaction mixture was warmed up to room temperature and left for 30 minutes, showing no reaction. Then the mixture was heated at 50 °C for 15 hours. NMR analysis showed a 56 % conversion of PhSiH₃ to give a mixture of PhH₂Si-SiH₂Ph (4 %), Ph₂SiH₂ (15 %), ethane (31 %) and hydrosilation products: PhEtSiH₂^[14] (19 %), PhEt₂SiH and PhEt₃Si (both in total 30 %). TON (total, calculated for the conversion of PhSiH₃): 16.2.

HMBC

Figure 1. Long range ^1H - ^{13}C HMBC NMR spectrum of **13** from a sample taken directly from the reaction mixture, showing the coupling of SiH, CH and CH₃ signals (5.4, 3.9 and 1.8 ppm, respectively) to the imine carbon of the [PhHSi-(ⁱPr)C=N] fragment.

Figure 2. ^{31}P NMR spectra (297 K, C_6D_6) from the reaction mixture of **3** and $t\text{-BuCN}$, showing formation of **10** and its rearrangement into **14** at room temperature. The signals at 10.4, 3.7, and -1.9 ppm correspond to compounds **3**, **14** and **10**, respectively.

Figure 3. ^1H NMR spectrum (297 K, toluene- d_8) from the reaction mixture of **3** and $t\text{BuCN}$, showing the formation of **10** (the Si-H signal as a doublet at 5.7 ppm), the rearrangement product **14** (Si-H signal as a singlet at 6.7 ppm), the release of PhSiH_3 (the Si-H signal as a singlet at 4.2 ppm). The signals at 5.48 and 5.87 correspond to Si-H protons in silyl position in the starting material **3**; signals at 5.77 and 5.79 ppm correspond to a product of decomposition of **10**.

Figure 4. $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum (297 K, toluene-d_8) from the reaction mixture of **3** and $t\text{BuCN}$, showing a singlet for the Si-H proton (5.68 ppm) for **10** instead of a doublet in the ^{31}P -coupled spectrum.

Figure 5. ^1H - ^{31}P HSQC NMR spectrum (- 30 °C, toluene- d_8 , $I = 15$ Hz) of a sample taken from the reaction mixture of **3** and $t\text{BuCN}$.

Figure 6. ^1H - ^{29}Si HSQC NMR spectrum ($-30\text{ }^\circ\text{C}$, toluene- d_8 , $J = 200\text{ Hz}$) from the reaction mixture of **3** and $t\text{BuCN}$. Signals at 4.28, 5.63, 5.98, 6.19 ppm in ^1H NMR and -72.9 and 1.3 ppm in ^{29}Si NMR correspond to **3**; signals at 5.88, 5.92 ppm in ^1H NMR and -0.5 ppm in ^{29}Si NMR correspond to products of decomposition of **10**; signals at 6.65 ppm and -20.0 ppm in ^1H and ^{29}Si NMR spectra, respectively, correspond to **14**.

Figure 7. ^{29}Si INEPT + NMR spectrum ($-30\text{ }^{\circ}\text{C}$, toluene- d_8 , $J = 150\text{ Hz}$) from the reaction mixture of **3** and $t\text{BuCN}$. Signals at -72.7 ppm (dd) and -0.2 ppm (t) correspond to Si signals of starting **3**; the doublet at -50.9 ppm corresponds to nitrile adduct **10**; the doublet at -20.6 ppm corresponds to rearrangement product **14**; the triplet at -2.2 ppm and doublet at -59.6 ppm are from decomposition products.

Figure 8. ^1H - ^{13}C HMBC NMR spectrum (- 30 °C, toluene-d_8) from the reaction mixture of **3** and t -BuCN, showing coupling of protons in t -Bu group (at 1.39 ppm) to nitrile carbon at 204.4 ppm and no coupling between the Si-H proton (at 5.66 ppm) and $\text{C}\equiv\text{N}$ carbon in **10**.

Figure 10. Room temperature ^1H - ^1H EXSY NMR experiment from the reaction of **3** and PhSiH_3 in C_6D_6 , showing exchange of protons in the silyl position of **3** and the free PhSiH_3 . Signals at 5.6 and 6.08 ppm correspond to the Si-H protons in the classical silyl ligand in **3**; the signal at 4.25 ppm corresponds to the Si-H protons in PhSiH_3 .

Figure 11. Low temperature (223 K) ^1H NMR of **3** before addition of PhSiD_3 in toluene- d_8 . The signals at 8.37, 7.50, 5.91 and 5.50 ppm correspond to Si-H protons in another isomer of **3**.

Figure 12. Low temperature (223 K) ^1H NMR of **3** after the addition of PhSiD_3 in toluene- d_8 . The signals at 8.39 and 7.50 ppm correspond to ortho-protons in another isomer of **3**.

Figure 13. ^1H - ^{13}C HMBCGP NMR spectrum of **3** at room temperature in C_6D_6 showing coupling between the protons at silicon, the ortho-protons in the Ph group at silicon and the ipso-carbon in the Ph group at silicon in the silyl substituent.

Figure 14. ^{29}Si INEPT+ VT NMR spectra of **3** (as a mixture of two isomers) in PhMe-d_8 , showing the change of $^1J(\text{Si-H})$ (J_1 – agostic, J_2 – terminal) in the agostic silicon position: **A** (224 K, $J_{1A} = 111.4$ Hz, $J_{1B} = 103.2$ Hz, $J_{2A} = 244.5$ Hz, $J_{2B} = 244.2$ Hz), **B** (254 K, $J_{1A} = 111.4$ Hz, $J_{1B} = 103.2$ Hz, $J_{2A} = 244.5$ Hz, $J_{2B} = 244.2$ Hz), **C** (273.2 K, $J_1 = 117.9$ Hz, $J_2 = 242.3$ Hz), **D** (293.6 K, $J_1 = 141.7$ Hz, $J_2 = 230.0$ Hz), **E** (312.3 K, $J_1 = 142.0$ Hz, $J_2 = 215.5$ Hz), **F** (328.1 K, $J_1 = 142.1$ Hz, $J_2 = 211.4$ Hz), **G** (341.2 K, $J_1 = 145.1$ Hz, $J_2 = 211.0$ Hz). $^1J(\text{Si-H})$ in silyl position remains the same.

Figure 15. Dependence of $^1J(\text{Si-H})$ (Hz) in agostic [$J_{\text{ag}}(\text{T})$] and terminal [$J_{\text{term}}(\text{T})$] positions in **1** on temperature (K) showing that at 430.2 K the values of $^1J(\text{Si-H})$ for both protons become equal: 179.2 Hz.

Figure 16. ^{31}P NMR spectrum of the reaction mixture resulting from the reaction between **3** and (*m*-Tol)SiH₃ in C₆D₆, showing **3** and **3**_{tol} in the ratio 1.3:1.

Figure 17. ^1H NMR spectrum from the reaction mixture of **3** with (*m*-Tol)SiH₃ in C₆D₆, showing the change of appearance of the ortho-protons of Ph group in the classical silyl substituent (the doublet at 8.31 ppm corresponds to the ortho-protons of Ph in the silyl position in **3**; the multiplet at 8.13 ppm corresponds to the ortho-protons in *m*-Tolyl group in the silyl position in **3**_{tol}).

Figure 18. ^1H - ^{13}C HSQC JC NMR spectrum of **4** in C_6D_6 showing the $^1J_{\text{C-H}}$ coupling constants for the CH_2 (110 Hz and 112 Hz) and CH_3 (124 Hz) groups in the ethyl substituent of **4**.

Figure 19. ^1H projection of the ^1H - ^{13}C HSQC JC NMR spectrum of **4** in C_6D_6 (Fig. 11), showing the $^1J_{\text{C-H}}$ coupling constants for the CH_2 (110 Hz, only one of the protons) and CH_3 (124 Hz) groups in the ethyl substituent of **4**.

Figure 20. The change of concentration of $\text{PhSiH}_2(\text{OCH}_2\text{Ph})$ and $\text{PhSiH}(\text{OCH}_2\text{Ph})_2$ (at the 1.3 mol. % load of **3**) versus the reaction time (h)

Figure 21. Change of TOF in the hydrosilation of benzaldehyde with PhSiH_3 (1.3 mol. % load of **1**) versus the reaction time (h)

Table 1. Catalytic hydrosilation of aldehydes and ketones by **3**.

Entry	Organic substrate	Silane	Ratio	cat., mol. %	T, °C/time	Products*	Conversion of organic substrate	Yield, %	TON	TOF, h ⁻¹
1	benzaldehyde	PhSiH ₃	2:1	1.3	RT/7 days	PhSiH ₂ (OCH ₂ Ph) PhSiH(OCH ₂ Ph) ₂	100 %	5 % 95 %	82	0.5
			1.1:1	0.5	RT/16 h	PhSiH ₂ (OCH ₂ Ph) PhSiH(OCH ₂ Ph) ₂	100 %	43 % 57 %	192.3	12.0
		PhMeSiH ₂	1:1	1.6	RT/6 days	PhMeSiH(OCH ₂ Ph)	28 %	28 %	16	0.1
		HSi(OEt) ₃	1:1	1.0	RT/4 days	(EtO) ₃ Si(OCH ₂ Ph) (EtO)Si(OCH ₂ Ph) ₃	10 %	8 % 2 %	9.8	0.1
						(EtO) ₃ Si(OCH ₂ Ph) (EtO) ₂ Si(OCH ₂ Ph) ₂ (EtO)Si(OCH ₂ Ph) ₃ Si(OCH ₂ Ph) ₄	100 %	10 % 32 % 47 % 11 %	98.4	0.3
2	acetophenone	PhSiH ₃	1:1	1.0	RT/20 days	PhSiH ₂ OCH(Me)Ph PhSiHO(CH(Me)Ph) ₂ PhSiHO(CH(Me)Ph) ₃ PhCH ₂ CH ₃	100 %	44 % 29 % 21 % 6 %	107.0	0.2
3	acetone	PhSiH ₃	1:1	1.0	RT/5 days	PhH ₂ Si(O ⁱ Pr) PhHSi(O ⁱ Pr) ₂	79 %	34 % 42 %	77.1	0.6

* Reactions with PhSiH₃ gave Ph₂SiH₂ and SiH₄ as by-products produced by catalytic redistribution of substituents at the silicon centre. The increase of temperature of reaction increases the amount of Ph₂SiH₂ and SiH₄ formed in the reaction.

Table 2. Reactions of alkenes with phenylsilane in the presence of catalytic amount of **3**.

Entry	Organic substrate	Silane	Ratio	cat., mol. %	T, °C/time	Product*	Conversion of organic substrate	Yield, %	TON	TOF, h ⁻¹
1	1-hexene	PhSiH ₃	1:1	5.0	RT/3 days	2-hexene hexane	20 %	5 % 15 %	4.1	0.06
					50°C/37 days	2-hexene hexane	100 %	26 % 71 %	20.3	0.02
						hydrosilation products		<3 %		
2	cyclohexene	PhSiH ₃	1:1	5.0	RT/2 days	cyclohexane	less than 5 %	<5 %	—	—
					50°C/39 days	cyclohexane	28 %	28 %	5.8	—
3	styrene	PhSiH ₃	1:1	3.0	RT/24 h	no reaction	—	—	—	—
					50 °C/23 h	PhCH ₂ CH ₃	6 %	6 %	1.3	0.06
4	phenylacetylene	PhSiH ₃	1:1	2.7	RT/17 h	polyphenylacetylene	100 %	100 %	33.8	2.0
		—	—	3.0	RT/24 h	polyphenylacetylene	25 %	25 %	8.3	0.4
					50 °C/24 h	polyphenylacetylene	45 %	45 %	14.9	0.6
5	ethylene	PhSiH ₃		3.3	RT/0.5h	no reaction	—	—	—	—
					50 °C/15 h	PhEtSiH ₂ PhEt ₂ SiH and PhEt ₃ Si Ethane	Conversion of PhSiH ₃ : 56 %	19 % 30 % 31 %	16.2	1.1

* Reactions with PhSiH₃ gave Ph₂SiH₂ and SiH₄ as by-products produced by catalytic redistribution of substituents at the silicon centre. The increase of temperature of reaction increases the amount of Ph₂SiH₂ and SiH₄ formed in the reaction.

Table 3. Catalytic hydrosilation of nitriles, pyridines and alcoholysis of silanes by **3**.

Entry	Organic substrate	Silane	Ratio	cat., mol. %	T, °C/time	Product*	Conversion of organic substrate	Yield, %	TON	TOF, h ⁻¹
1	acetonitrile	PhSiH ₃	1:1	5.0	RT/14 h	no reaction	—	—	—	—
					50 °C/51 h	EtN(SiH ₂ Ph) ₂	less than 3 %	<3 %	—	—
2	benzonitrile	PhSiH ₃	1:1	5.0	RT/24 h	no reaction	—	—	—	—
					50 °C/6 days	PhHC=NSiH ₂ Ph	20 %	20 %	4.1	0.03
3	ethanol	PhSiH ₃	1:1	5.0	RT/5 min	PhH ₂ Si(OEt) PhHSi(OEt) ₂	100 %	33 % 67 %	20.3	244.6
			2:1	5.0	RT/25 min	PhH ₂ Si(OEt) PhHSi(OEt) ₂	100 %	11 % 89 %	40.6	97.4
4	propanol-2	PhSiH ₃	1:1	5.0	RT/5 min	PhH ₂ Si(O'Pr) PhHSi(O'Pr) ₂	100 %	18 % 82 %	20.3	244.6
5	pyridine	PhSiH ₃	1:1	0.6	RT/5 days	N-(phenylsilyl)-4-hydropyridine N-(phenylsilyl)-2-hydropyridine	less than 5 %	all together less than 5 %	—	—

* Reactions with PhSiH₃ gave Ph₂SiH₂ and SiH₄ as by-products produced by catalytic redistribution of substituents at the silicon centre. The increase of temperature of reaction increases the amount of Ph₂SiH₂ and SiH₄ formed in the reaction.

Table 4. Crystal data and structure refinement for **3**^a and **4**^b

Parameters	(ArN)(PMe ₃)(PhH ₂ Si)Mo(NAr-SiHPh-H)*hexane (3)	(ArN)(PMe ₃)(Et)Mo(η^2 -NAr-SiHPh-CH=CH ₂) (4)
Empirical formula	C ₄₄ H ₆₉ MoN ₂ PSi ₂	C ₇₄ H ₁₁₂ Mo ₂ N ₄ P ₂ Si ₂
Formula weight	809.10	1367.68
Colour	dark-orange	Brown
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 12(1)/c1'	<i>P</i> 2(1)/c
Crystal size, mm ³	0.35x0.18x0.12	0.28x0.16x0.08
Unit cell dimensions:		
a (Å)	8.5536(12)	20.7264(11)
b (Å)	22.691(3)	17.4162(10)
c (Å)	23.379(3)	22.0696(12)
$\alpha/\beta/\gamma$ (grad.)	90.00/97.423(3)/90.00	90.00/110.163(3)/90.00
Volume (Å ³)	4499.6(11)	7478.4(7)
Z	4	4
Density (calculated) (g/sm ³)	1.194	1.215
Temperature (K)	153.2	123.2
Absorption coefficient (mm ⁻¹)	0.411	0.451
F(000)	1728	2904
Theta range for data collection (grad.)	2.512-23.3245	1.05-30.00
Index ranges	-11≤h≤11, -30≤k≤30, -31≤l≤31	-29≤h≤29, -24≤k≤24, -29≤l≤31
Reflections collected	11725	83082
Independent reflections	7701	20834 [R(int) = 0.0721]
Data/restraints/parameters	11725/0/459	20834/0/755
Final R indices [I>2sigma(I)]	R ₁ = 0.0718, wR ₂ = 0.1749	R ₁ = 0.0537, wR ₂ = 0.0987
R indices (all data)	R ₁ = 0.1195, wR ₂ = 0.1600	R ₁ = 0.0986, wR ₂ = 0.1090
Goodness-of-fit on F ²	1.054	1.029
Largest diff. peak and hole	1.018 and -0.828 eÅ ⁻³	1.261 and -0.810 eÅ ⁻³
Max. and min. transmission		0.9648 and 0.8840
Refinement method	Full-matrix least squares on F ²	Full-matrix least squares on F ²
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents

^a Molecular formula and molecular weight were calculated for a mixture of **3** and a molecule of co-crystallized hexane.

^b The crystal data, empirical formula and molecular weight calculated for the fragment containing two molecules of **4**

Table 5. Selected distances (Å) and angles (°) for **3**.

Mo1–N1	2.062(4)	Mo1–N2–C13	169.5(3)
Mo1–N2	1.754 (4)	Mo1–N1–C1	140.0(3)
Mo1–Si2	2.4945(14)	Mo1–N1–Si1	88.50(16)
Mo1–Si1	2.6341(12)	N1–Si1–Mo	51.49(12)
Mo1–H1b	1.929	Si1–Mo1–N1	40.01(10)
Mo1–P1	2.4251(13)	Mo1–Si1–H1a	121.27
Si1–H1a	1.425	Mo1–Si1–H1b	46.11
Si1–H1b	1.484	Mo1–Si1–C25	130.93(14)
Si2–H2a	1.438	N1–Si1–H1a	116.17
Si2–H2b	1.541	N1–Si1–H1b	94.46
Si1–N1	1.694(4)	N1–Si1–C25	120.31(19)
Mo1–H1a	3.587	Mo1–Si2–H2a	115.03
N1–C1	1.430(6)	Mo1–Si2–H2b	112.53
N2–C13	1.392(6)	Mo1–Si2–C31	119.31(16)
Si1–C25	1.861(4)	N2–Mo1–Si1	121.87(12)
Si2–C31	1.887(6)	P1–Mo1–H1b	163.55
Mo1–H2a	3.365	Si2–Mo1–P1	89.61.5
Mo1–H2b	3.398		

Table 7. Selected distances (Å) and angles (°) for **12**.

Mo1–N1	1.769(2)	Mo1–N1–C1	161.3(2)
Mo1–C33	2.216(3)	Mo1–C33–C34	118.4(2)
Mo1–N2	2.068(2)	Mo1–C32–C31	73.32(16)
Mo1–Si1	2.9036(8)	Mo1–C31–Si1	88.82(11)
N2–Si1	1.740(2)	Mo1–N2–Si1	99.02(10)
Si1–C31	1.841(3)	C31–Si1–N2	95.92(11)
C31–C32	1.429(4)	P1–Mo1–C31	162.54(8)
C32–Mo1	2.238(3)	P1–Mo1–C32	160.41(8)
Mo1–P1	2.5757(8)	Mo1–N2–C13	135.24(17)
Mo1–C31	2.283(3)	N2–Mo1–N1	139.72(10)
C33–C34	1.536(4)	C33–Mo1–P1	82.52(8)
N1–C1	1.394(4)	N1–Mo1–C33	108.77(11)
N2–C13	1.437(3)	N2–Mo1–C33	111.01(10)
Si1–C25	1.882(3)	N2–Mo1–Si1	121.87(12)
		N2–Si1–C25	114.69(12)
		C31–Si1–C25	118.42(13)
		N2–Si1–Mo1	44.69(7)
		C32–C31–Mo1	69.86(15)

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