Supporting information

to the manuscript

Hydridosilylamido complexes of Ta and Mo isolobal with Berry's zirconocenes: syntheses, *β*-Si-H agostic interactions, catalytic hydrosilylation, and insight into mechanism

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Contents

Experimental

All manipulations were carried out using conventional inert atmosphere glove-box and Schlenk techniques. Dry diethyl ether, toluene, hexanes, and acetonitrile were obtained, using Grubbs-type purification columns, other solvents were dried by distillation from appropriate drying agents. Dimethoxyethane (DME) was dried over sodium benzophenone ketyl and collected through distillation. C_6D_6, PhMe-d_8 were dried by distillation from K/Na alloy, and $CDCl_3$ was dried by distillation from CaH_2. NMR spectra were obtained with a Bruker DPX-300 and Bruker DPX-600 instruments (^{1}H: 300 and 600 MHz; ^{2}H: 92.1 MHz; ^{13}C: 75.5 and 151 MHz; ^{29}Si: 59.6 and 119.2 MHz; ^{31}P: 121.5 and 243 MHz; ^{11}B: 96.3 and 192.6 MHz). NMR analysis was done at room temperature unless specified. IR spectra were measured on a Perkin-Elmer 1600 FT-lR spectrometer. $(RN)_2MoCl_2(DME)$ (R = Ar, ^{t}Bu; Ar = 2,6-diisopropylphenyl, ^{t}Bu = *tert*-butyl) were prepared *via* literature preparation.[1]

Preparation of Cp(ArN)Ta[N(SiHMe$_2$)^{t}Bu](Cl) (1)

Cp(ArN)$TaCl_2$ (0.102 g, 0.06 mmol) was dissolved in 10 mL of Et_2O. A solution of LiN(SiHMe$_2$)^{t}Bu·THF (0.014 g, 0.07 mmol) in 5 mL of Et_2O was added directly to this at room temperature. This was allowed to stir overnight upon which time all volatiles were removed. The product was extracted using 20 mL of hexanes. The resulting filtrate was reduced in volume (2 mL) and allowed to crystallize overnight at -30 °C. ^{1}H-NMR (300 MHz, Benzene-d_6, 22 °C, δ, ppm): 0.21 (d, 3H, SiH*Me*$_2$, $^3J_{H\text{-}H}$ = 3.6 Hz), 0.31 (d, $^3J_{H\text{-}H}$ = 3.6 Hz, 3H, SiH*Me*$_2$), 1.30 (s, 9H, ^{t}*Bu*N), 1.35 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 6H, C*H*$_3$, *Ar*N), 1.39 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 6H, C*H*$_3$, *Ar*N), 4.13 (sept. , $^3J_{H\text{-}H}$ = 6.3 Hz, 2H, C*H*, *Ar*N), 4.77 (sept, $^3J_{H\text{-}H}$ = 3.6 Hz, 1H, Si*H*Me$_2$), 6.04 (s, 5H, *Cp*), 6.94 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H, *p*- *Ar*N), 7.18 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H, *m*- *Ar*N). ^{13}C{^{1}H}-NMR (75.5 MHz; Benzene-d_6, 22 °C, δ, ppm): -1.62 (s, *C*H$_3$, Si*Me*$_2$), 1.47 (s, *C*H$_3$, Si*Me*$_2$), 24.65 (s, *C*H$_3$, *Ar*N), 25.17 (s, *C*H$_3$, *Ar*N), 27.18 (s, *C*H, *Ar*N), 35.31 (s, *C*H$_3$, ^{t}*Bu*N), 61.23 (s, N*C*(CH$_3$)$_3$, ^{t}*Bu*N), 110.4 (s, *C*$_5$H$_5$, *Cp*), 123.0 (s, *p*- *Ar*N), 124.2 (s, *m*-*Ar*N), 145.6 (s, *o*- *Ar*N), 150.7 (s, *i*- *Ar*N). ^{29}Si INEPT+ (119 MHz, Benzene-d_6, 22 °C, J = 200 Hz, δ, ppm): 26.1 (d, $^1J_{Si\text{-}H}$ = 183.6 Hz). Elem. Anal. (%): calc. for $C_{23}H_{38}ClTaN_2Si$ (587.05) C 47.06, H 6.52, N 4.77; found C 47.31. H 6.42, N 4.65.

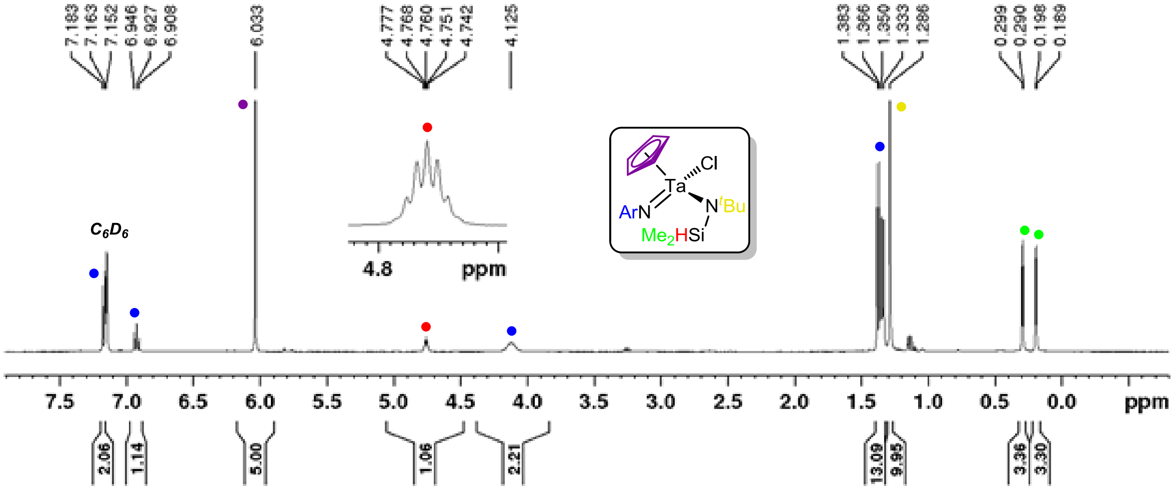

Figure SI1. ^{1}**H-NMR** (400 MHz, Benzene-d_6) – Cp(ArN=)Ta[N^{t}Bu(SiHMe$_2$)]Cl (**1**)

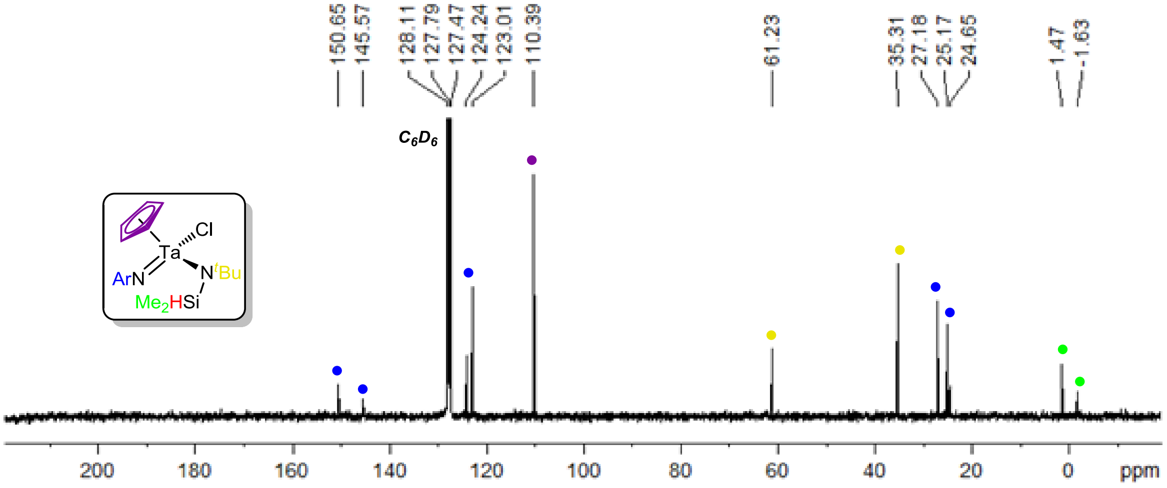

Figure SI2. ^{13}**C{^{1}H} NMR** (150.9 MHz, Benzene-d_6) - Cp(ArN=)Ta[N^{t}Bu(SiHMe$_2$)]Cl (**1**)

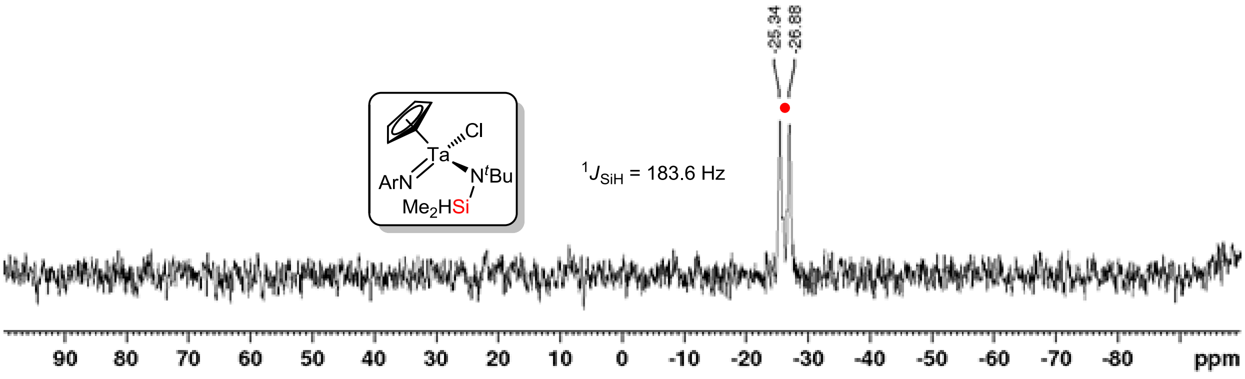

Figure SI3. ^{29}**Si INEPT+** (119 MHz, Benzene-d_6) - Cp(ArN=)Ta[N^{t}Bu(SiHMe$_2$)]Cl (**1**)

NMR scale generation of Cp(ArN)Ta{η^3-N^{t}Bu-SiMe$_2$-H}(H) (2)

Cp(ArN)Ta(H)(Cl)(PMe$_3$) (0.023 g, 0.04 mmol) and LiN(^{t}Bu)SiHMe$_2$·THF (0.009 g, 0.04 mmol) were added to two separate vials and dissolved in 0.3 mL of C$_6$D$_6$ each. BPh$_3$ (0.010 mg, 0.04 mmol) was added directly to the Cp(ArN)Ta(H)(Cl)(PMe$_3$) solution, quickly followed by the LiN(^{t}Bu)SiHMe$_2$·THF solution. This was mixed thoroughly and transferred to an NMR tube. ^{1}H-NMR (300 MHz, Benzene-d_6, 22 °C, δ, ppm): 0.08 (d, $^3J_{\text{H-H}}$ = 3.6 Hz, 3H, Si*Me$_2$*), 0.23 (d, $^3J_{\text{H-H}}$ = 3.6 Hz, 3H, Si*Me$_2$*), 1.31 (s, 9H, ^{t}*Bu*N), 1.37 (dd, $^3J_{\text{H-H}}$ = 6.9 Hz, 12H, C*H*$_3$, *Ar*N), 3.12 (d quart, $^2J_{\text{H-H}}$ = 3.6 Hz, $^3J_{\text{H-H}}$ = 3.3 Hz, 1H, Si-*H*), 4.84 (sept, $^3J_{\text{H-H}}$ = 6.9 Hz, 2H, C*H*, *Ar*N), 5.87 (s, 5H, *Cp*), 6.92 (t, $^3J_{\text{H-H}}$ = 7.5 Hz, 1H, *p*-Ar), 7.17 (d, $^3J_{\text{H-H}}$ = 7.5 Hz, 2H, *m*-Ar), 12.05 (d, $^2J_{\text{H-H}}$ = 3.6 Hz, 1H, Ta-*H*). ^{29}Si INEPT+ (119 MHz, Benzene-d_6, 22 °C, *J* = 200 Hz, δ, ppm): -59.7 (d, $^1J_{\text{Si-H}}$ = 155.0 Hz).

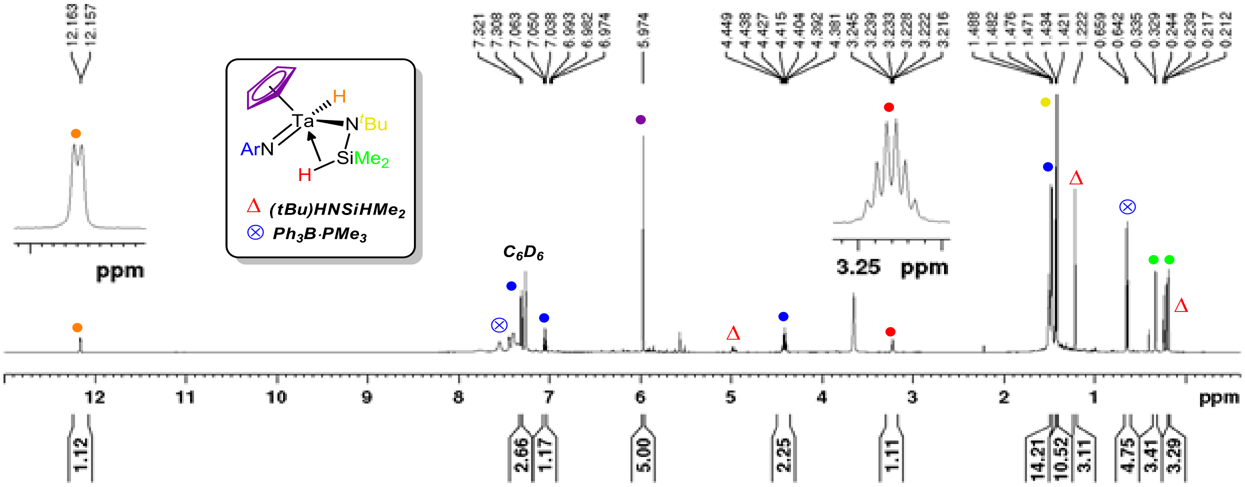

Figure SI4. ^{1}H-NMR (400 MHz, Benzene-d_6) – Cp(ArN)Ta{η^3-N^{t}Bu-SiMe$_2$-H}(H) (**2**)

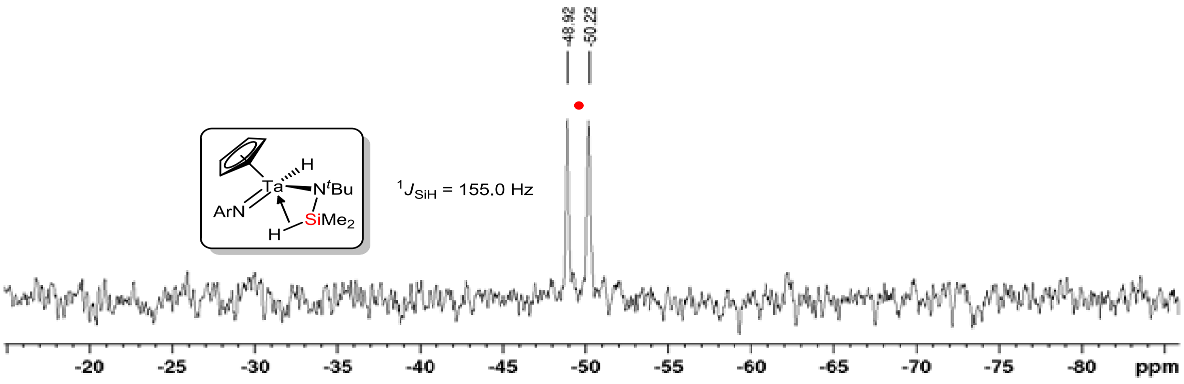

Figure SI5. ^{29}Si INEPT+ (119 MHz, Benzene-d_6) - Cp(ArN)Ta{η^3-N^{t}Bu-SiMe$_2$-H}(H) (**2**)

Preparation of $(ArN)_2Mo[N(SiHMe_2)^tBu](Cl)$ (3)

$(ArN)_2MoCl_2(DME)$ (0.877 g, 1.56 mmol) was added to a flask and dissolved in 50 mL of toluene. This solution was added to $Li(N(^tBu)SiHMe_2$ (0.317 g, 1.51 mmol) in 10 mL of toluene, to produce a dark red mixture with formation of a white precipitate. After stirring for one day at room temperature the mixture was filtered and product extracted with 10 mL of toluene. The solution was placed in the -80°C freezer for six days where large dark red crystals were seen. These were washed with cold (-30°C) hexane and dried in vacuum. Yield: 0.8142g, 88%. ^{1}H-NMR (300 MHz, Benzene-d$_6$, 22 °C, δ, ppm): 6.97 (d, $^3J_{H\text{-}H} = 7.4$ Hz, 4 H, *m*-Ar), 6.91 (t, $^3J_{H\text{-}H} = 7.4$ Hz, 2H, *p*-Ar), 5.64 (sept, $^3J_{H\text{-}H} = 3.3$ Hz, 1 H, Si*H*Me$_2$), 3.92 (sept, $^3J_{H\text{-}H} = 6.9$ Hz, 4 H, C*H*Me$_2$, Ar), 1.41 (s, 9 H, ^{t}Bu), 1.20 (d, $^3J_{H\text{-}H} = 6.9$ Hz, 12 H, CH*Me*$_2$, Ar), 1.13 (d, $^3J_{H\text{-}H} = 6.9$ Hz, 12 H, CH*Me*$_2$, Ar), 0.36 (d, $^3J_{H\text{-}H} = 3.3$ Hz, 6 H, SiH*Me*$_2$). ^{13}C{^{1}H}-NMR (75.5 MHz; Benzene-*d*$_6$, 22 °C, δ, ppm): 153.9 (*i*-Ar), 143.2 (*o*-Ar), 127.0 (*m*-Ar), 123.0 (*p*-Ar), 62.1 (N*C*(CH$_3$)$_3$), 34.2 (NC(*C*H$_3$)$_3$), 28.2 (Ar-*C*HMe$_2$), 24.4 (Ar-CH*Me*$_2$), 23.6 (Ar-CH*Me*$_2$), 0.6 (Si(*C*H$_3$)$_2$). ^{29}Si INEPT+ (119 MHz, Benzene-*d*$_6$, 22 °C, $J = 180$ Hz, δ, ppm): -25.18 (d sept, $^1J_{Si\text{-}H} = 172.9$ Hz). IR (Nujol): 1971 cm^{-1} (Si-H). Elem. Anal. (%): calc. for $C_{30}H_{50}ClMoN_3Si$ (612.22) C 58.85, H 8.23, N 6.86; found C 58.48. H 7.85, N 6.47.

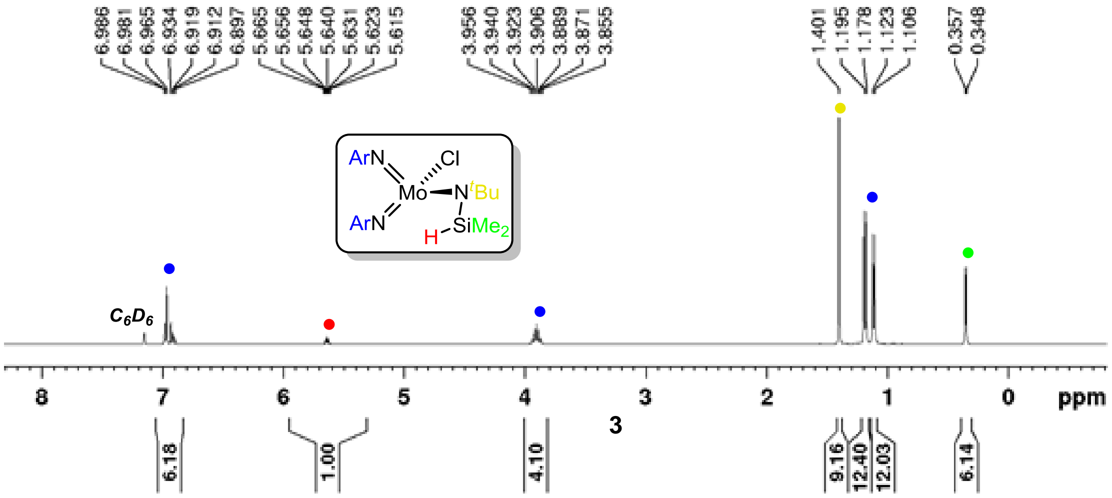

Figure SI6. **^{1}H-NMR** (400 MHz, Benzene-*d*$_6$) – $(ArN=)_2Mo[N^tBu(SiMe_2H)]Cl$ (**3**)

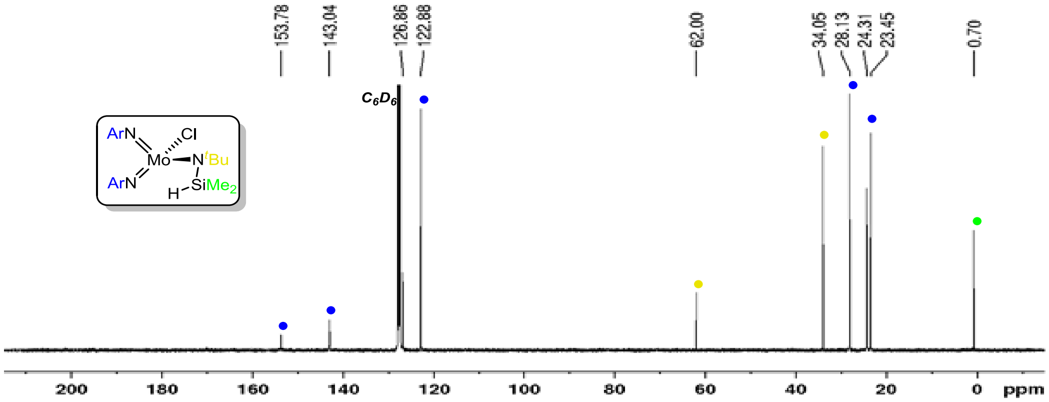

Figure SI7. **^{13}C{^{1}H}-NMR** (150.9 MHz, Benzene-d_6) **-** (ArN=)$_2$Mo[N^{t}Bu(SiMe$_2$H)]Cl (**3**)

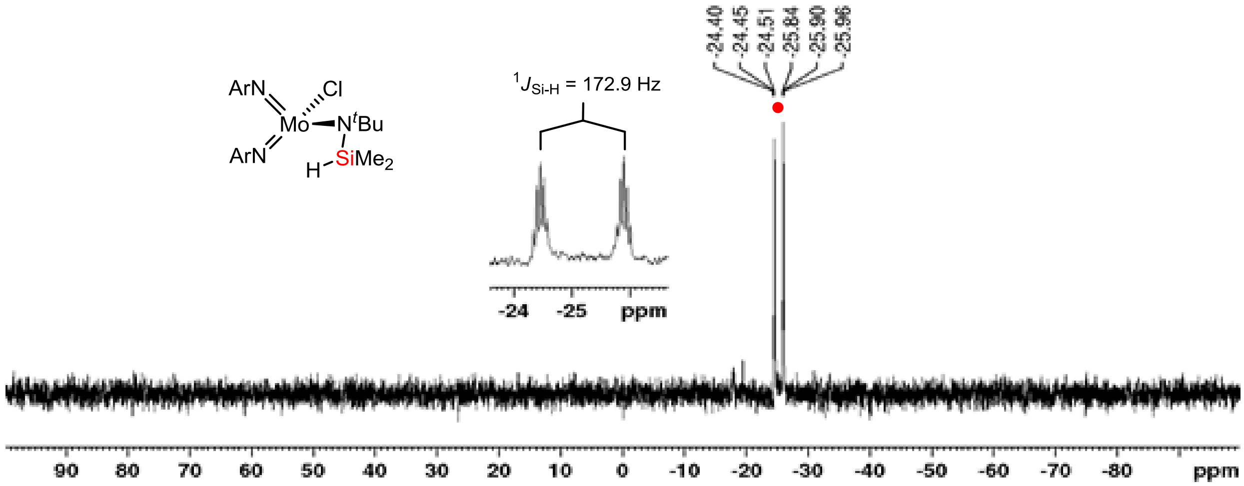

Figure SI8. **^{29}Si INEPT+** (119 MHz, Benzene-d_6) **-** (ArN=)$_2$Mo[N^{t}Bu(SiMe$_2$H)]Cl (**3**)

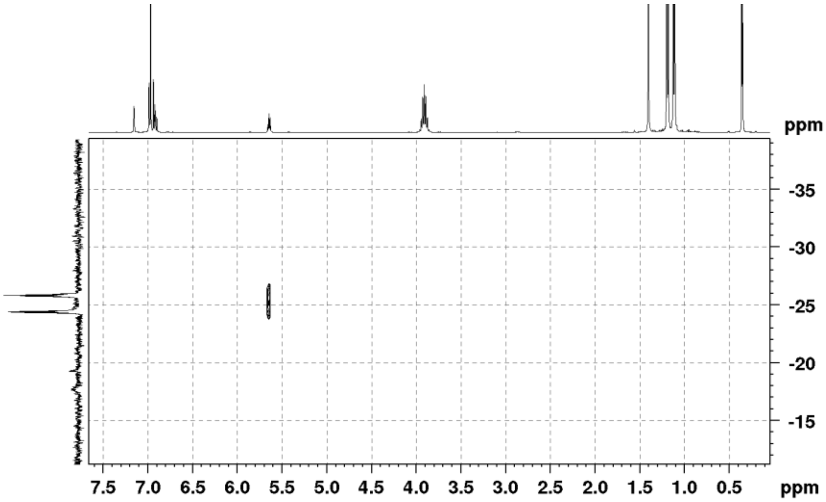

Figure SI9. **^{1}H-^{29}Si HSQC** (600 MHz/119 MHz, Benzene-d_6, 22 °C, J = 200 Hz) - (ArN=)$_2$Mo[N^{t}Bu(SiMe$_2$H)]Cl (**3**)

NMR scale preparation of (ArN)$_2$Mo(η^3-N^{t}Bu-SiMe$_2$-H)(H) (4)

(ArN)$_2$Mo[N(^{t}Bu)SiHMe$_2$]Cl (0.022 g, 0.04mmol) was dissolved in C$_6$D$_6$ and transferred to an NMR tube. L-Selectride (36.0 µL, 0.04 mmol, 1.6 M in THF) was added directly to the NMR tube via a 50 µL syringe. This solution was thoroughly mixed and after 15 minutes at room temperature, selective formation of **4**. Attempted scale-ups (1-2 mmol scale) of this reaction resulted in a red oily material which does not precipitate from hexane or ether even upon cooling to – 30 °C and – 80 °C, whereas slow removal of volatiles by vapour diffusion regenerates the original red oil. ^{1}H-NMR (300 MHz, Benzene-d_6, 22 °C, δ, ppm): 7.02 (d, $^3J_{\text{H-H}}$ = 6.98 Hz, 4 H, *m*-Ar), 6.94 (t, $^3J_{\text{H-H}}$ = 6.98 Hz, 2H, *p*-Ar), 6.49 (d, $^3J_{\text{H-H}}$ = 3.0 Hz, 1 H, Mo-H), 4.13 (d sept, $^3J_{\text{H-H}}$ = 3.0 Hz, $^2J_{\text{H(Mo)-H}}$ = 3.0 Hz, 1 H, Si*H*Me$_2$), 4.06 (sept, $^3J_{\text{H-H}}$ = 6.9 Hz, 4 H, C*H*Me$_2$, Ar), 1.35 (s, 9 H, ^{t}Bu), 1.21 (d, $^3J_{\text{H-H}}$ = 7.2 Hz, 12 H, CH*Me*$_2$, Ar), 1.18 (d, $^3J_{\text{H-H}}$ = 6.6 Hz, 12 H, CH*Me*$_2$, Ar), 0.22 (d, $^3J_{\text{H-H}}$ = 3.0 Hz, 6H, SiH*Me*$_2$). ^{13}C{^{1}H}-NMR (75.5 MHz; Benzene-d_6, 22 °C, δ, ppm): 153.1 (*i*-Ar), 141.9 (*o*-Ar), 125.5 (*m*-Ar), 122.5 (*p*-Ar), 59.0 (N*C*(CH$_3$)$_3$), 35.1 (NC(*C*H$_3$)$_3$), 27.9 ([Ar-*C*HMe$_2$]$_2$), 23.7 (Ar-CH*Me*$_2$), 23.1 (Ar-CH*Me*$_2$), 0.9 (Si(*C*H$_3$)$_2$). ^{29}Si INEPT+ (119 MHz, Benzene-d_6, 22 °C, *J* = 125 Hz, δ, ppm): -52.9 (d, $^1J_{\text{Si-H}}$ = 125.3 Hz). IR (Nujol): 1886 cm^{-1} (Si-H-Mo), 1710 cm^{-1} (Mo-H).

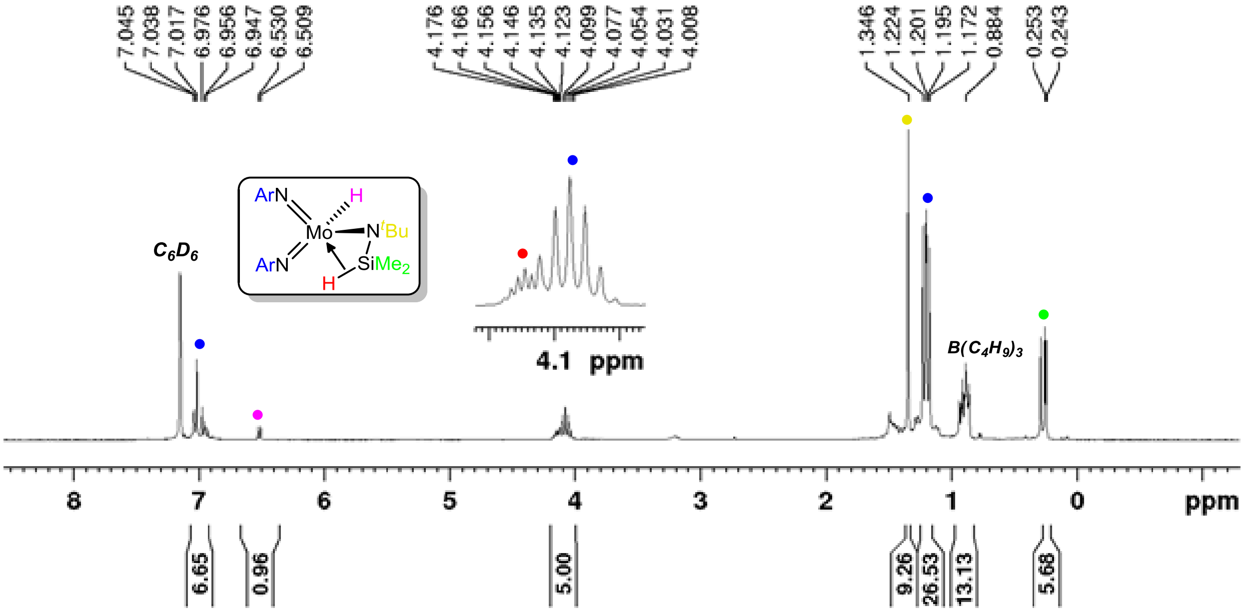

Figure SI10. ^{1}H-NMR (400 MHz, Benzene-d_6) – (ArN=)$_2$Mo(η^3-N^{t}Bu-SiMe$_2$-H)(H) (**4**)

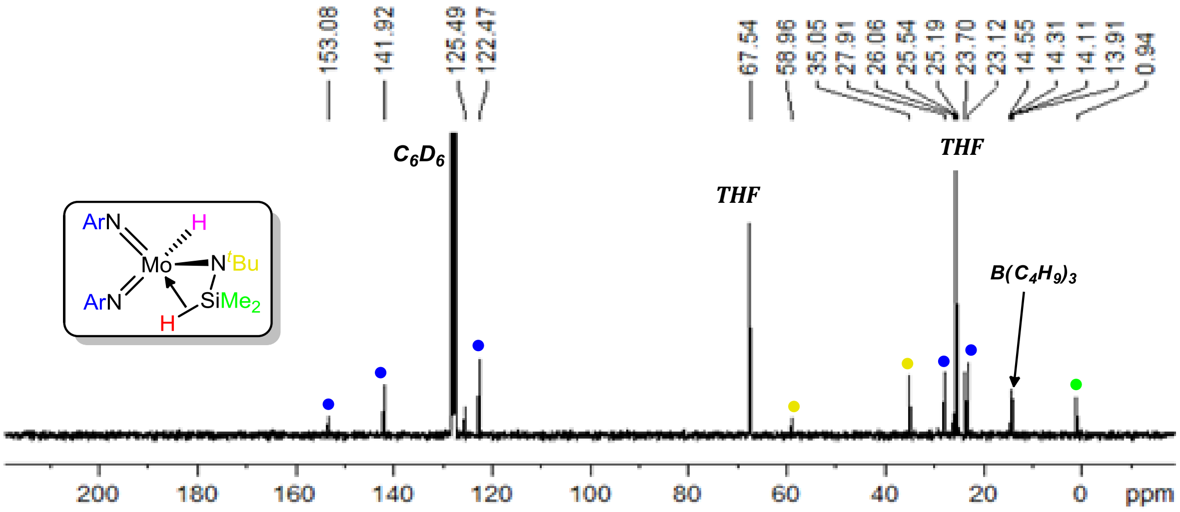

Figure SI11. ^{13}**C{^{1}H} NMR** - (150.9 MHz, Benzene-d_6) - (ArN=)$_2$Mo(η^3-N^{t}Bu-SiMe$_2$-H)(H) (**4**)

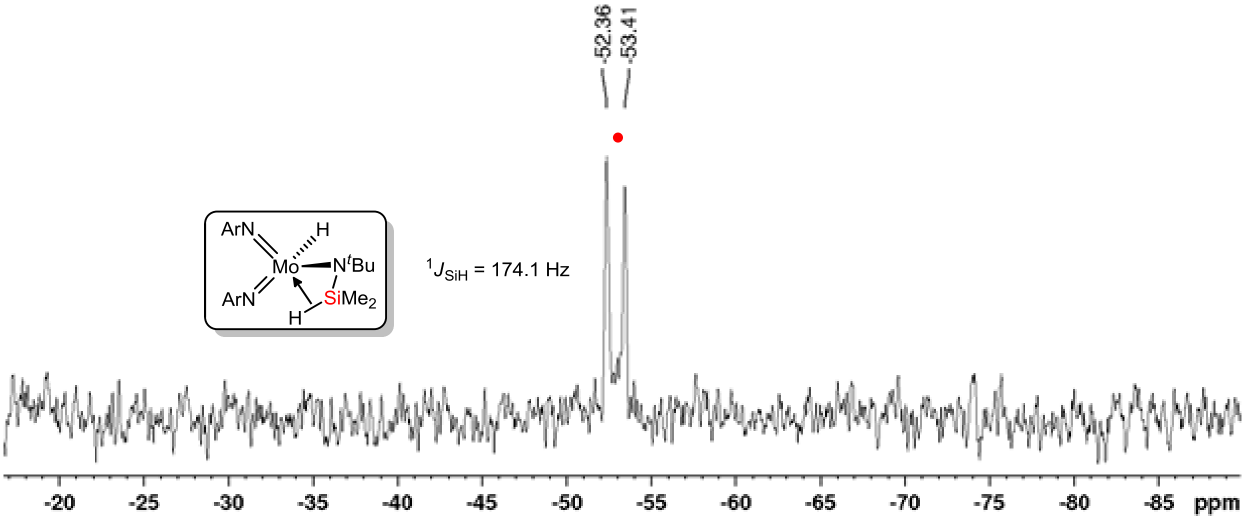

Figure SI12. ^{29}**Si INEPT+** (119 MHz, Benzene-d_6) - (ArN=)$_2$Mo(η^3-N^{t}Bu-SiMe$_2$-H)(H) (**4**)

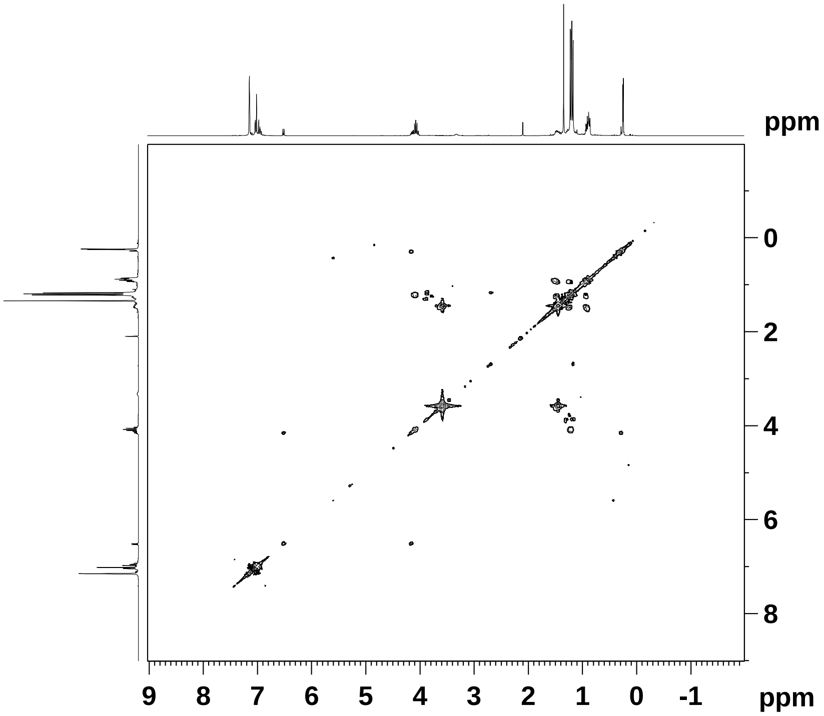

Figure SI13. ^{1}H-^{1}H COSY (600 MHz, Benzene-d_6) - (ArN=)$_2$Mo(η^3-N^{t}Bu-SiMe$_2$-H)(H) (**4**)

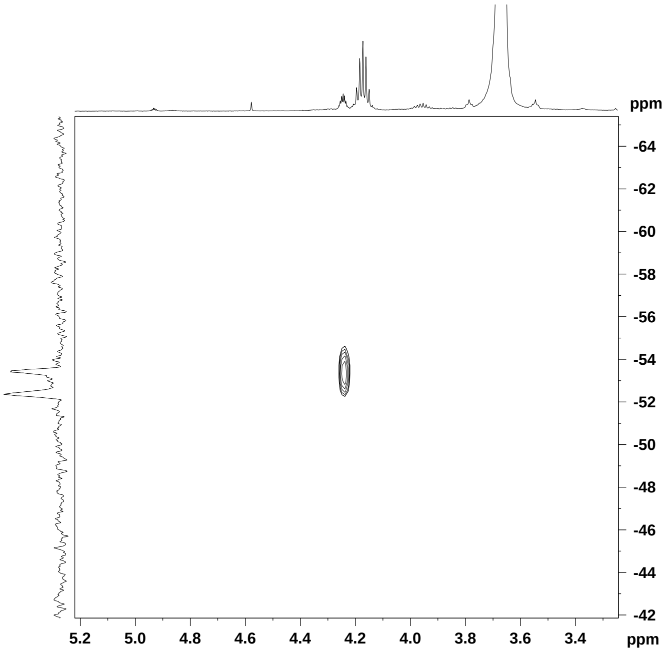

Figure SI14. ^{1}H-^{29}Si HSQC (600 MHz/119 MHz, Benzene-d_6, J = 200 Hz) - (ArN=)$_2$Mo(η^3-N^{t}Bu-SiMe$_2$-H)(H) (**4**)

Preparation of $(ArN)_2Mo[N(SiHMe_2)^tBu](Me)$ (5)

$(ArN)_2Mo[N(SiHMe_2)^tBu]Cl$ (0.252 g, 0.41 mmol) was dissolved in 10 mL of Et_2O and transferred to a small flask, along with a solution of LiMe (0.26 mL, 0.41 mmol; 1.6 M in Et_2O) at room temperature and stirred for 30 minutes. The mixture was filtered and washed with 2 x 3 mL of Et_2O followed by volume reduction in vacuum to 2 mL, then placed in a -30°C freezer for two days. After this time, light orange crystalline solid grew on the sides of the flask. The solution was decanted and the residue was dried in vacuum to give **5** as the sole product. (0.048 g; 20 % yield). ^1H-NMR (300 MHz, Benzene-d_6, 22 °C, δ, ppm): 7.01 (d, $^3J_{H-H}$ = 7.4 Hz, 4H, *m*-Ph, *Ar*N,), 6.95 (d, $^3J_{H-H}$ = 7.0 Hz, 1H, *p-Ar*N, $^3J_{H-H}$ = 7.0 Hz), 6.94 (d, $^3J_{H-H}$ = 7.0 Hz, 1H, *p-Ar*N), 5.18 (sept, $^3J_{H-H}$ = 3.3 Hz, 1H, Si*H*), 3.88 (sept, $^3J_{H-H}$ = 6.9 Hz, 4H, C*H*, *Ar*N), 1.54 (s, 3H, Mo*Me*), 1.36 (s, 9H, ^{t}*Bu*NSiHMe$_2$), 1.18 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, CH_3, *Ar*N), 1.14 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH_3, *Ar*N), 0.31 (d, $^3J_{H-H}$ = 3.4 Hz, 6H, Si*Me*$_2$). $^{13}C\{^1H\}$-NMR (75.5 MHz; Benzene-d_6, 22 °C, δ, ppm): 153.4 (*i*-Ar), 142.0 (*o*-Ar), 125.3 (*p*-Ar), 122.7 (*m*-Ar), 60.14 ($C(CH_3)$, ^{t}*Bu*N), 35.10 (CH_3, ^{t}*Bu*N), 28.09 (*C*H, *Ar*N), 24.16 (CH_3, *Ar*N), 23.55 (CH_3, *Ar*N), 20.57 (Mo*Me*), 0.85 (Si*Me*$_2$). ^{29}Si INEPT+ (119 MHz, Benzene-d_6, 22 °C, *J* = 150 Hz, δ, ppm): -32.60 (dsept, *Si*Me$_2$H, $^1J_{Si-H}$ = 166.0 Hz, $^2J_{Si-H}$ = 7.0 Hz). Elem. Anal. (%): calc. for $C_{31}H_{53}MoN_3Si$ (591.799) C 62.92, H 9.03, N 7.10; found C 61.01. H 9.53, N 6.55. Several attempts to obtain better elemental analyses from three different laboratories returned results consistently low in carbon even when single crystals of **5** were submitted. We attribute this failure to incomplete combustion due to the formation of molybdenum carbides as a result of the presence of direct Mo-C bond in the starting compound.

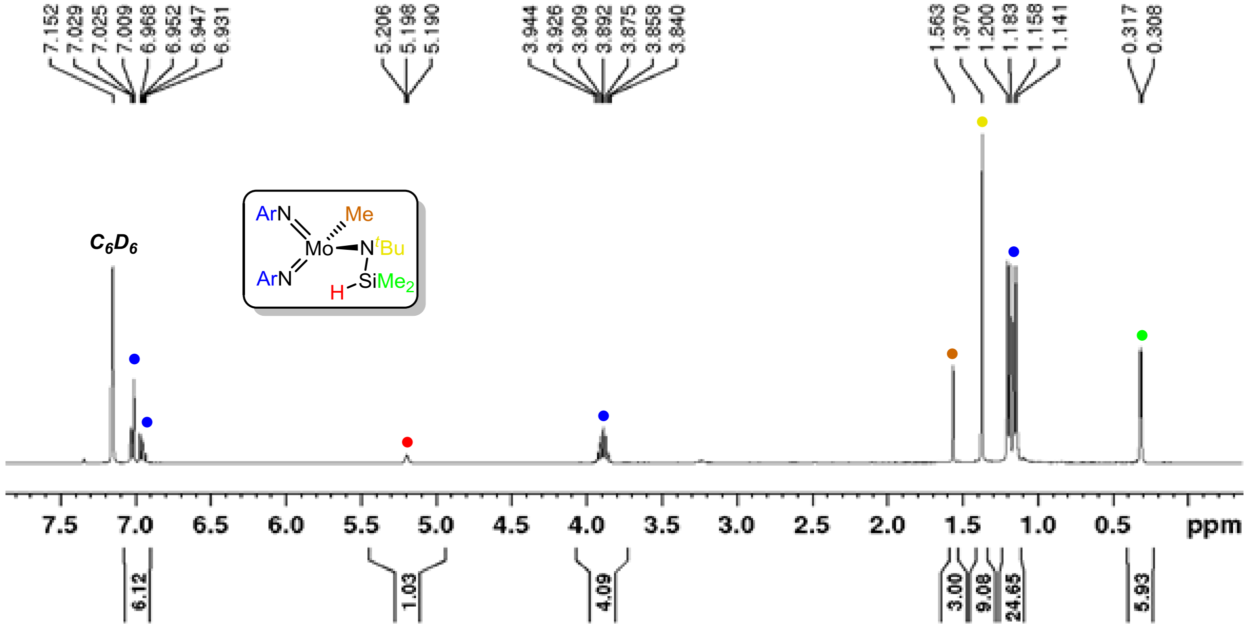

Figure SI15. **^{1}H-NMR** (400 MHz, Benzene-d_6) – (ArN=)$_2$Mo[N^{t}Bu(SiMe$_2$H)]Me (**5**)

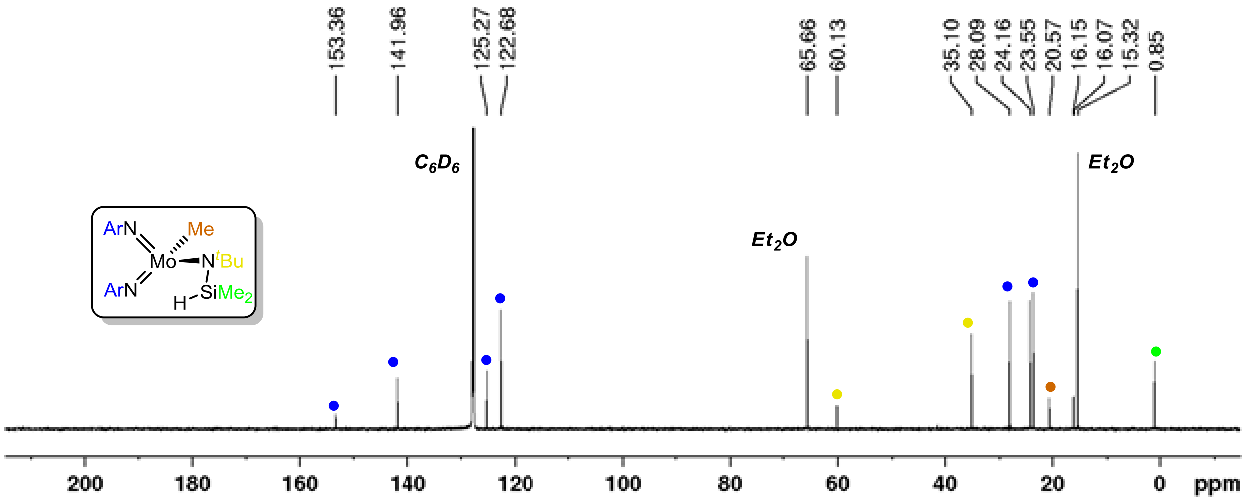

Figure SI16. **^{13}C{^{1}H}-NMR** (150.9 MHz, Benzene-d_6) - (ArN=)$_2$Mo[N^{t}Bu(SiMe$_2$H)]Me (**5**)

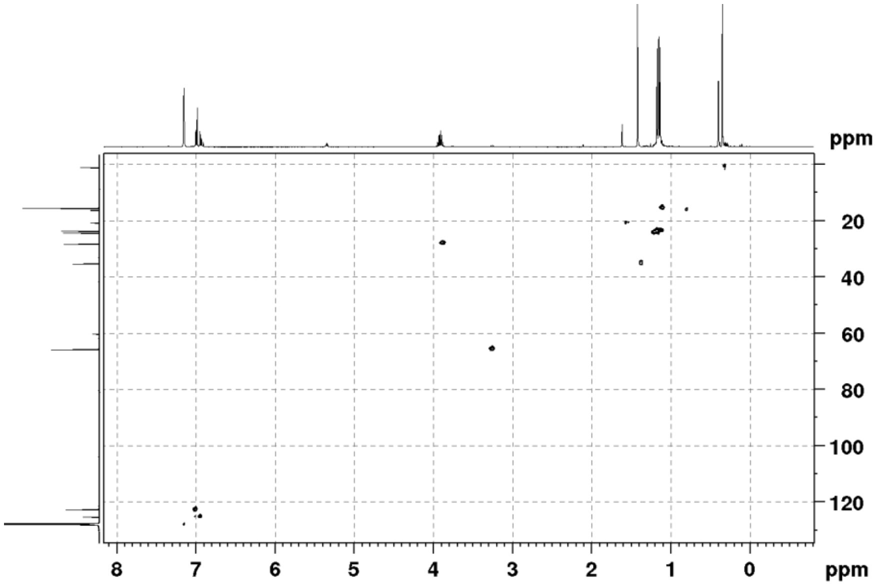

Figure SI17. ^{1}**H-**^{13}**C HSQC** (600 MHz/151 MHz, Benzene-d_6, J = 200 Hz) - (ArN=)$_2$Mo[N^{t}Bu(SiMe$_2$H)]Me (**5**)

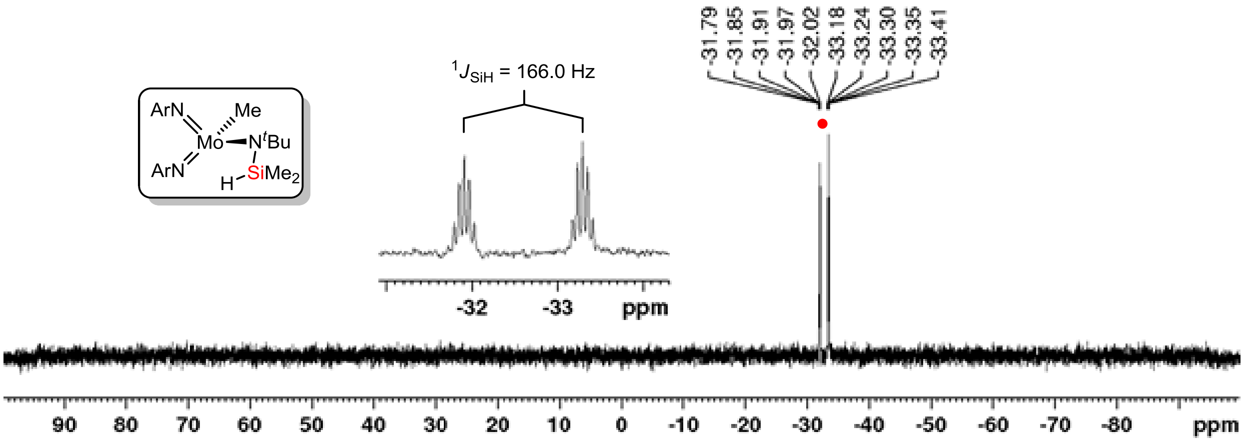

Figure SI18. ^{29}**Si INEPT+** (119 MHz, Benzene-d_6) **-** (ArN=)$_2$Mo[N^{t}Bu(SiMe$_2$H)]Me (**5**)

Preparation of (ArN)$_2$Mo[N(SiHMe$_2$)^{t}Bu](OBn) (8)

To a freshly prepared sample of (ArN)$_2$Mo(η^3-N(^{t}Bu)Si(Me$_2$)-H)(H) (0.764 mmol) in toluene (10 mL) using the procedure described above, benzaldehyde (77.9 µL, 0.400 mmol) was directly added *via* 100 µL syringe. The dark brown solution turned a light red colour. Volatiles were removed in vacuum to give a red oil. A small amount of hexanes was added and the solution was cooled to -80°C overnight. A light orange solid was observed after one night in the -80 °C freezer, so the solution was decanted and washed with cold hexane (2 mL) to give 0.160 g of pure (ArN)$_2$Mo(N(^{t}Bu)SiMe$_2$H)(OBn). Yield: 31 %. However, numerous attempts to obtain a satisfactory elemental analysis failed. ^{1}H-NMR (300 MHz, Benzene-d$_6$, 22 °C, δ, ppm): 0.37 (d, $^3J_{\text{H-H}}$ = 3.4 Hz, 6H, Si*Me*$_2$), 1.09 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 12 H, C*H*$_3$, *Ar*N), 1.16 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 12 H, C*H*$_3$, *Ar*N), 1.44 (s, 9H, ^{t}*Bu*N), 3.88 (sept, 4H, C*H*, *Ar*N, $^3J_{\text{H-H}}$ = 6.8 Hz), 5.55 (sept, $^3J_{\text{H-H}}$ = 3.3 Hz, 1H, Si*H*), 5.74 (s, 2H, C*H*$_2$, OBn), 6.92 (m, 2H, *p*-Ph, *Ar*N), 6.99 (m, 4H, *m*-Ph, *Ar*N). ^{13}C{^{1}H}-NMR (75.5 MHz; Benzene-*d*$_6$, 22 °C, δ, ppm): 1.85 (s, *C*H$_3$, Si*Me*$_2$), 23.47 (s, *C*H$_3$, *Ar*N), 24.33 (s, *C*H$_3$, *Ar*N), 28.09 (s, *C*H, *Ar*N), 34.51 (s, *C*H$_3$, ^{t}*Bu*N), 79.59 (s, *C*H$_2$, OBn), 122.83 (s, *p*-Ph, *Ar*N), 125.85 (s, *m*-Ph, *Ar*N). ^{29}Si INEPT+ (119 MHz, Benzene-*d*$_6$, 22 °C, *J* = 125 Hz, δ, ppm): -21.92 (d sept, H*Si*Me$_2$, $^1J_{\text{Si-H}}$ = 176.4 Hz, $^2J_{\text{Si-H}}$ = 6.9 Hz).

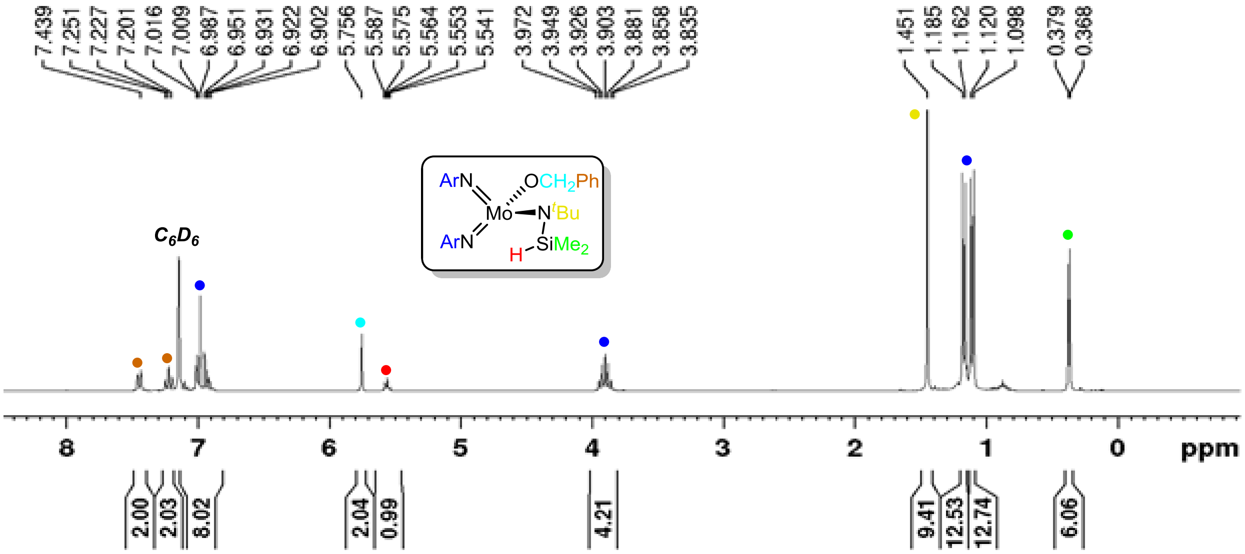

Figure SI19. **^{1}H-NMR** (400 MHz, Benzene-*d*$_6$) – (ArN=)$_2$Mo[N^{t}Bu(SiMe$_2$H)](OBn) (**8**)

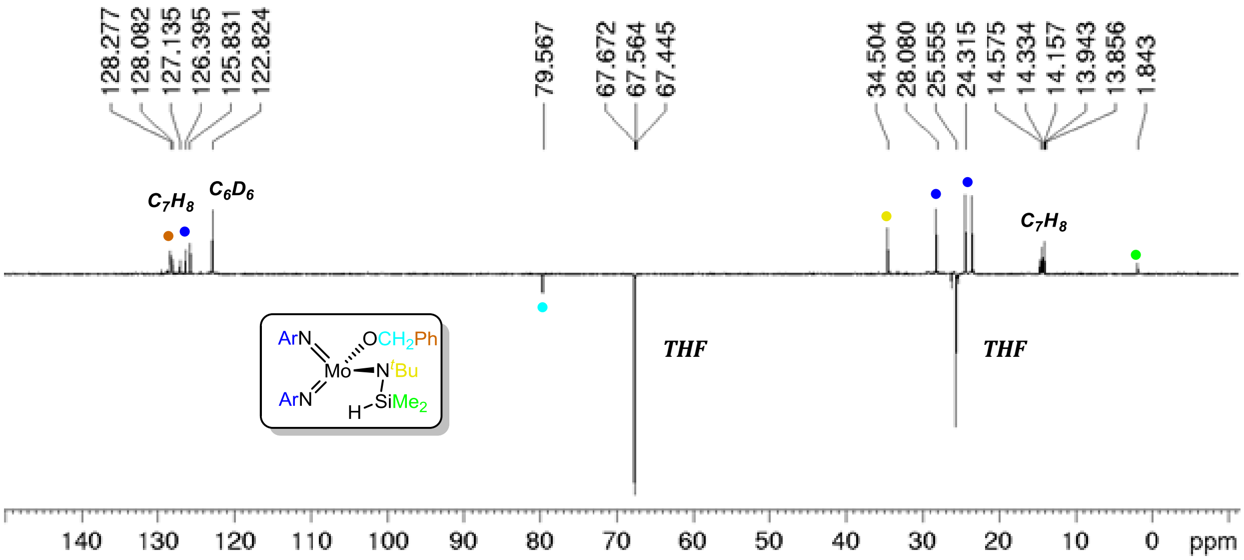

Figure SI20. $^{13}C\{^1H\}$ **DEPT-135 NMR** - (150.9 MHz, Benzene-d_6) - $(ArN=)_2Mo[N^tBu(SiMe_2H)](OBn)$ (**8**). This spectrum was taken from an NMR tube reaction sample containing THF from the hydride generation step.

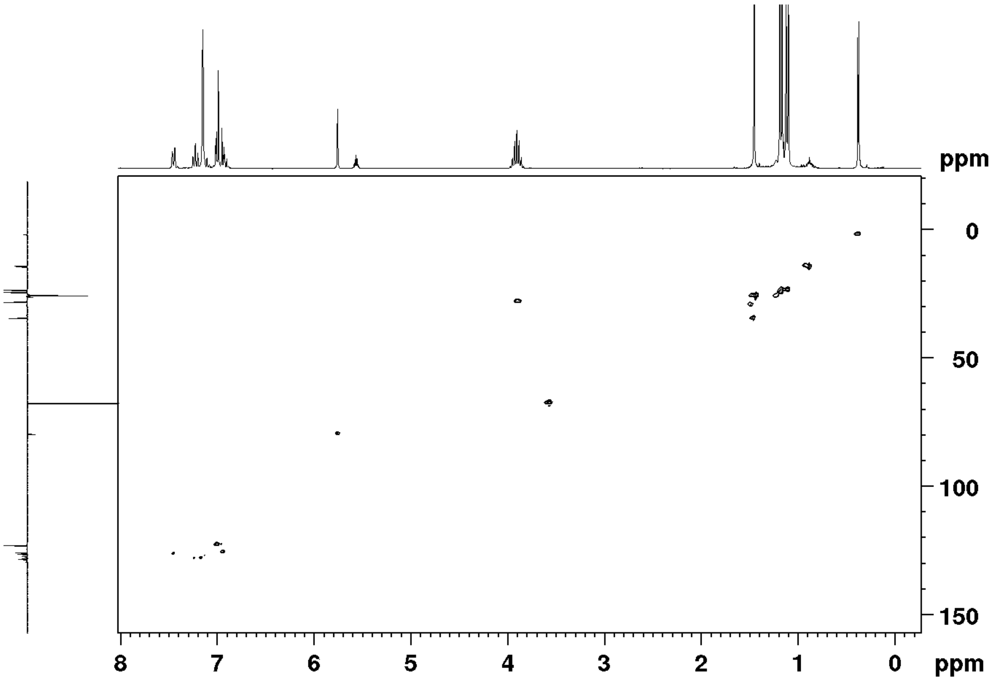

Figure SI21. ^1H-^{13}C **HSQC** (600 MHz/151 MHz, Benzene-d_6) - $(ArN=)_2Mo[N^tBu(SiMe_2H)](OBn)$ (**8**). This spectrum was taken from an NMR tube reaction sample containing THF from the hydride generation step.

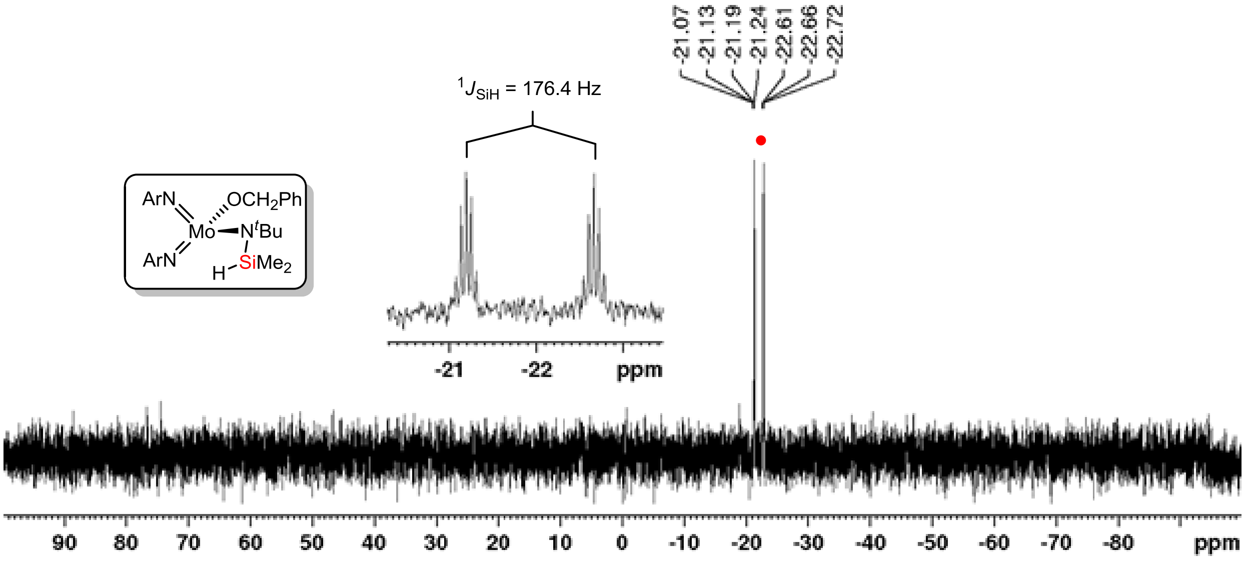

Figure SI22. ^{29}**Si INEPT+** (119 MHz, Benzene-*d*$_6$) - (ArN=)$_2$Mo[N^{t}Bu(SiMe$_2$H)](OBn) (**9**)

Reaction of (ArN)$_2$Mo[N(SiHMe$_2$)^{t}Bu](OBn) (8) with PhHC=O and D$_3$SiPh.

To the NMR tube containing 0.0249 g (0.0364 mmol) (ArN)$_2$Mo(η^3-N(^{t}Bu)Si(Me$_2$)-H)(OBu) in 0.6 mL of C_6D_6 were added benzaldehyde (2.95 µL, 0.0364 mmol) and D$_3$SiPh (3.69 µL, 0.0364 mmol). NMR spectrum taken 20 min after keeping at room temperature showed the formation of the partially deuterated hydrosilylation product PhH$_x$D$_y$SiOCH$_z$D$_k$Ph (x+y=2; z+k=2).

General Procedure for hydrosilylation using (ArN)$_2$Mo(N(SiHMe$_2$)^{t}Bu)(OBn) or (ArN)$_2$Mo(η^3-N^{t}Bu-SiMe$_2$-H)(H)

To an NMR tube loaded with either (ArN)$_2$Mo[N(SiHMe$_2$)^{t}Bu](OBn) (5 mol %) or (ArN)$_2$Mo(η^3-N(^{t}Bu)Si(Me$_2$)-H)(H) (5 mol %) in 0.6 mL of C_6D_6, silane and carbonyl were added in a 1:1 ratio sequentially. The reactions were monitored by ^{1}H-NMR spectroscopy at room temperature over the appropriate length of time. All structures were determined using 2D-NMR techniques or compared to known spectra.

Crystal structure determination

X-ray quality crystals of complex **3** were grown from a toluene solution at -80 °C. A single crystal of **3** was mounted in a film of perfluoropolyether oil on a glass fibre and transferred to a Siemens three-circle diffractometer with a CCD detector (SMART-1K system). The data were corrected for Lorentz and polarization effects.

Crystals of complex **5** were grown from an ether solution at -30 °C. A single crystal of **5** was mounted on a glass fibre using paraffin oil. Prior to data collection the crystal was cooled to 200 °K. Data were collected on a Bruker AXS SMART single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) APEX II CCD detector. The data collection results represent the best data sets obtained in several trials for each sample. Raw data collection and processing were performed with APEX II software package from BRUKER AXS.[2] Diffraction data were collected with a sequence of 0.5° ω scans at 0, 120, and 240° in φ. Initial unit cell parameters were determined from 60 data frames with 0.3° ω scan each collected at the different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.[3]

Both structures were solved by direct methods[4] and refined by full-matrix least squares procedures based on F^2.[5] The solutions yielded a chemically reasonable and computationally stable result of refinement. For all structures the positions of hydrogen atoms attached to silicon were found as residual electron density peaks from the Fourier maps and their positions were refined isotropically. The hydrogen atoms directly attached to carbon atoms were restrained to riding models and were consecutively treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.[6] Crystal and structure refinement data are given in Table SI1.

Table SI1 Crystal and structure refinement data for **3** and **5**.

	3	**5**
Empirical formula	$C_{30}H_{50}MoN_3ClSi$	$C_{31}H_{53}MoN_3Si$
Formula weight	612.21	591.79
Crystal size, mm^3	0.38 x 0.16 x 0.05	0.11 x 0.08 x 0.06
Crystal system	Triclinic	triclinic
Space group	P1	P1
Unit cell dimensions:		
a, Å	10.1926(8)	10.8122(14)
b, Å	10.7193(9)	10.8705(14)

c, Å	16.7763(17)	16.219(2)
α, deg	71.491(3)	108.896(2)
β, deg.	86.247(5)	90.882(3)
γ, deg	69.622(3)	110.844(2)
Volume, Å^3	1627.3(2) Å	1667.0(4)
Z	2	2
Density (calculated), g/cm^3	1.249	1.179
Absorption coefficient, mm^{-1}	0.544	0.451
F(000)	648	591.79
Diffractometer	Bruker SMART-1K	Bruker AXS SMART
Temperature, K	123(2)	200(2)
Radiation, (lambda, Å) ,	(0.71073) Mo K$_\alpha$	(0.71073) Mo K$_\alpha$
θ range for data collection, deg	1.28 to 28.50	2.04 to 24.86
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $-22 \leq l \leq 22$	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-19 \leq l \leq 19$
Reflections collected	14574	11842
Independent reflections	8098 [R(int) = 0.0669]	5716 [R(int) = 0.0497]
Absorption correction	Multi-scan (SADABS)	Semi-empirical from equivalents
Max. transmission	0.8456	0.7451
Min. transmission	0.5638	0.6227
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Data / restraints / parameters	8098 / 0 / 329	5716 / 0 / 331
Goodness-of-fit on F^2	0.928	1.012
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1366	R1 = 0.0487, wR2 = 0.0961
R indices (all data)	R1 = 0.0999, wR2 = 0.1477	R1 = 0.0757, wR2 = 0.1065
Largest diff. peak and hole, e.Å^{-3}	1.241 and -2.602	0.437 and -0.418

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