

Supporting information

to the article

The Unexpected Mechanism of Carbonyl Hydrosilylation Catalyzed by (Cp)(ArN)Mo(H)(PMe₃)

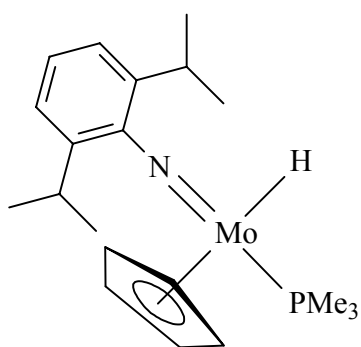
by Oleg Sherbrooke, Serge I. Gorelsky, Razvan Simionescu, Lyudmila G.

Kuzmina, and Georgii I. Nikonov*

Experimental details

All manipulations were carried out using conventional inert atmosphere glove-box and Schlenk techniques. Dry ether, THF, benzene, toluene and hexanes were obtained, using Grubbs-type purification columns. NMR spectra were obtained with a Bruker DPX-300 and Bruker DPX-600 instruments (¹H: 300 and 600 MHz; ¹³C: 75.5 and 151 MHz; ²⁹Si: 59.6 and 119.2 MHz; ³¹P: 121.5 and 243 MHz). IR spectra were measured on ATI Mattson FTIR spectrometer. (ArN)Mo(H)(Cl)(PMe₃)₃ (Ar = 2,6-(iPr)₂C₆H₃) was prepared by the literature procedure¹. PhSiH₃ was prepared from PhSiCl₃ by reaction with LiAlH₄. Organic substrates (PhC(O)H, PhC(O)Me, PhCN, cyclohexanone) were purchased from Aldrich. All catalytic, kinetic and NMR reactions were done under nitrogen atmosphere using “Young” type NMR tubes equipped with Teflon valves. The structures and the yields of all hydrosilylated products were determined by NMR analysis using tetramethylsilane as an internal standard.

Synthesis of (Cp)(ArN)Mo(H)(PMe₃)

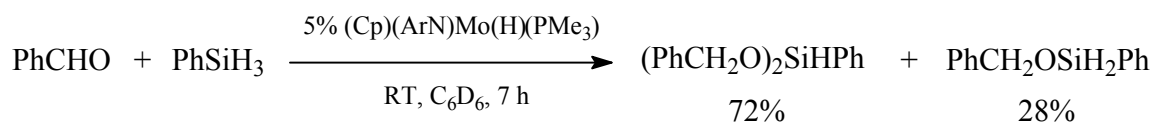


The THF solutions of (ArN)Mo(Cl)(H)(PMe₃)₃ (0.30 g, 0.56 mmol) and CpNa (0.12 g, 1.4 mmol) were mixed at room temperature, and the reaction mixture was stirred overnight. The

solvent was removed under vacuum, and the product was extracted with hexane giving 0.22 g of (ArN)Mo(Cp)(H)(PMe₃) as a dark-green solid. Yield: 95%. Yield: 95%. ¹H-NMR (300 MHz; C₆D₆; 298K; δ, ppm): -5.81 (d, ²J_{H-P} = 33.9 Hz, 1H, *Mo-H*), 1.06 (d, ²J_{H-P} = 9.0 Hz, 9H, *PMe*₃), 1.30 (d, ³J_{H-H} = 6.9 Hz, 6H, *iPr*), 1.37 (d, ³J_{H-H} = 6.9 Hz, 6H, *iPr*), 4.54 (sept, ³J_{H-H} = 6.9 Hz, 2H, *iPr*), 4.80 (s, 5H, *Cp*), 7.10 (m, 3H, *ArN*). ¹³C-NMR (75.5 MHz; C₆D₆; 298 K; δ, ppm): 23.7 (CH₃, *iPr*), 23.7 (d, ²J_{C-P} = 27.5 Hz, *PMe*₃), 24.0 (CH₃, *iPr*), 28.3 (CH, *iPr*), 87.0 (*Cp*), 123.0 (*Ar*), 124.5 (*Ar*), 144.2 (*Ar*). ³¹P-NMR (121.5 MHz; C₆D₆; 298 K; δ, ppm): 20.5 (s, 1P, *PMe*₃). IR (nujol, cm⁻¹): 1778 (*Mo-H*).

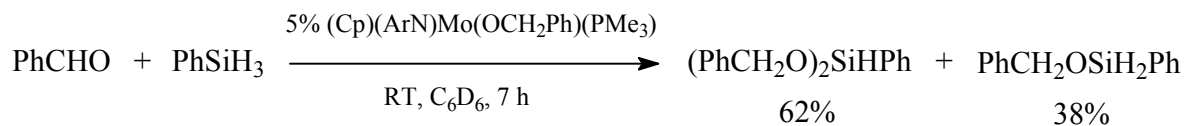
CATALYTIC HYDROSILYLATION

Hydrosilylation of benzaldehyde with phenylsilane catalyzed by (Cp)(ArN)Mo(H)(PMe₃)



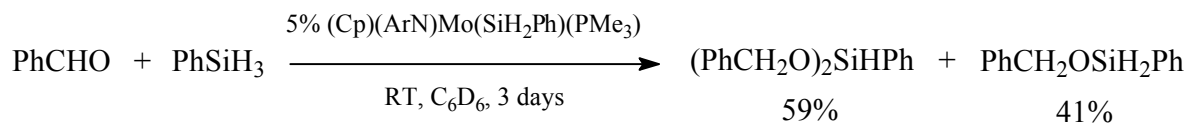
Benzaldehyde (0.026 g, 0.242 mmol) and phenylsilane (0.026 g, 0.242 mmol) were mixed in the presence of (Cp)(ArN)Mo(H)(PMe₃) (0.005 g, 5% mol) in C₆D₆ (0.65 mL) at room temperature. The reaction was monitored by ¹H NMR. The reaction was complete in 7h, yielding (PhCH₂O)₂SiHPh (72%) and PhCH₂OSiH₂Ph (28%).

Hydrosilylation of benzaldehyde with phenylsilane catalyzed by (Cp)(ArN)Mo(OCH₂Ph)(PMe₃)



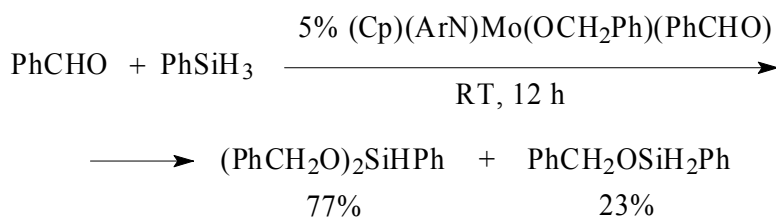
Benzaldehyde (0.026 g, 0.242 mmol) and phenylsilane (0.026 g, 0.242 mmol) were mixed in the presence of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) (0.006 g, 5% mol) in C₆D₆ (0.65 mL) at room temperature. The reaction was monitored by ¹H NMR. The reaction was complete in 7h, giving (PhCH₂O)₂SiHPh (62%) and PhCH₂OSiH₂Ph (38%).

**Hydrosilylation of benzaldehyde with phenylsilane catalyzed by
(Cp)(ArN)Mo(SiH₂Ph)(PMe₃)**



Benzaldehyde (0.026 g, 0.242 mmol) and phenylsilane (0.026 g, 0.242 mmol) were mixed in the presence of (Cp)(ArN)Mo(SiH₂Ph)(PMe₃) (0.006 g, 5% mol) in C₆D₆ (0.65 mL) at room temperature. The reaction was monitored by NMR. The reaction afforded (PhCH₂O)₂SiHPh (59%) and PhCH₂OSiH₂Ph (41%) in 3 days with the overall yield of 54%.

**Hydrosilylation of benzaldehyde with phenylsilane catalyzed by
(Cp)(ArN)Mo(OCH₂Ph)(PhCHO)**



Benzaldehyde (0.026 g, 0.242 mmol) and phenylsilane (0.026 g, 0.242 mmol) were mixed in presence of (Cp)(ArN)Mo(OCH₂Ph)(PhCHO) (0.005 g, 5% mol) in C₆D₆ (0.65 ml) at room temperature. The reaction was monitored by ¹H NMR. The reaction was complete in 12h, yielding (PhCH₂O)₂SiHPh (77%) and PhCH₂OSiH₂Ph (23%).

The diagram below (Figure S11) shows the profile of phenylsilane addition to benzaldehyde in the presence of four different catalysts: (Cp)(ArN)Mo(H)(PMe₃), (Cp)(ArN)Mo(OCH₂Ph)(PMe₃), (Cp)(ArN)Mo(OCH₂Ph)(PhCHO), and (Cp)(ArN)Mo(SiH₂Ph)(PMe₃):

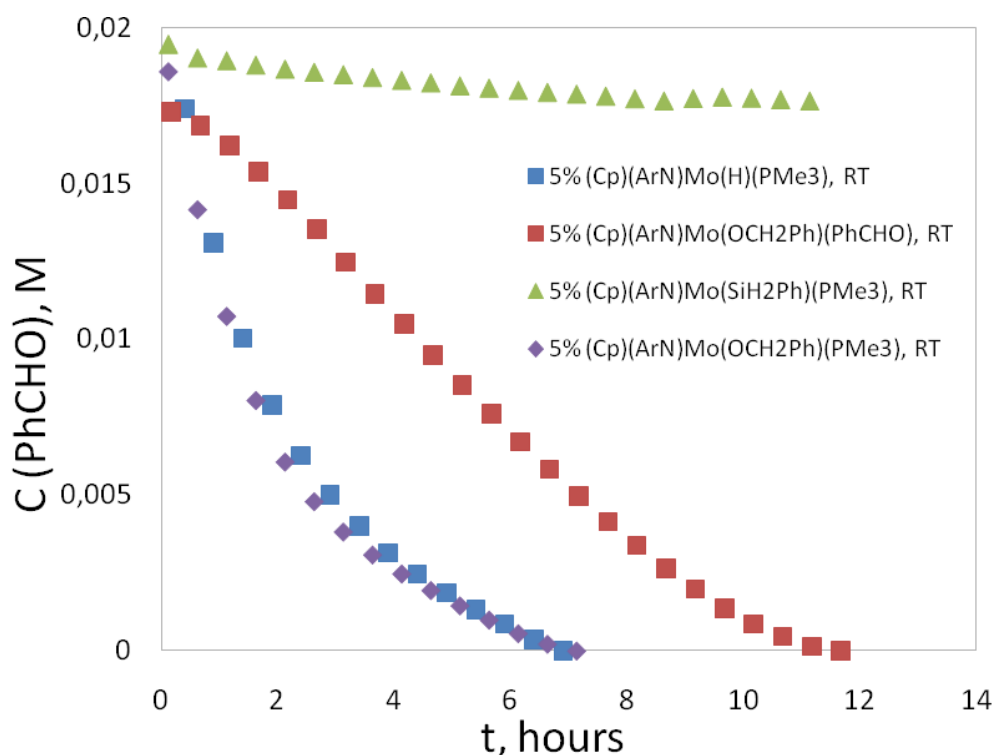
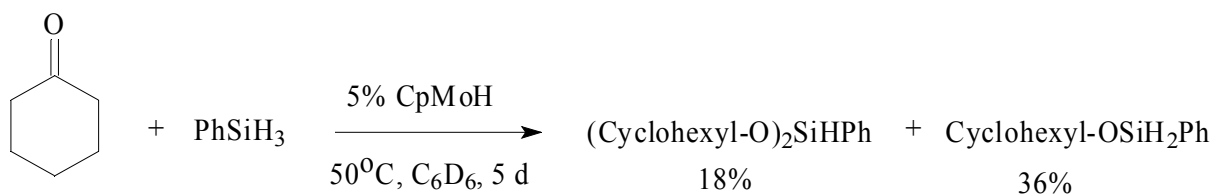


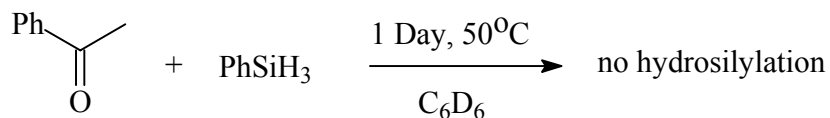
Figure S11. Catalytic profile for hydrosilylation of benzaldehyde with phenylsilane in the presence of (Cp)(ArN)Mo(H)(PMe₃), (Cp)(ArN)Mo(OCH₂Ph)(PMe₃), (Cp)(ArN)Mo(OCH₂Ph)(PhCHO), and (Cp)(ArN)Mo(SiH₂Ph)(PMe₃),

Hydrosilylation of cyclohexanone with phenylsilane catalyzed by (Cp)(ArN)Mo(H)(PMe₃)



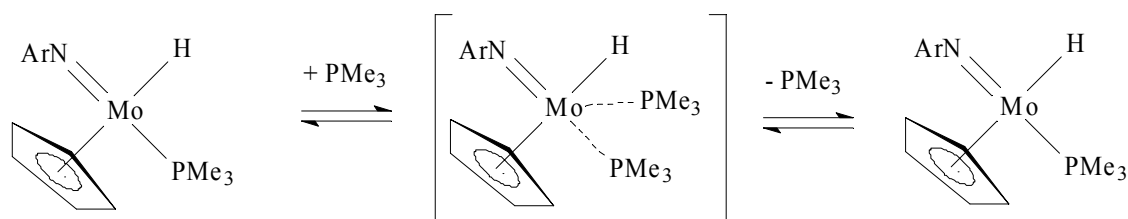
Cyclohexanone (0.035 g, 0.356 mmol) and phenylsilane (0.039 g, 0.356 mmol) were mixed in the presence of (Cp)(ArN)Mo(H)(PMe₃) (0.0074 mg, 0.018 mmol, 5% mol) in C₆D₆ (0.65 mL) and heated at 50 °C. The reaction afforded (cyclohexyl-O)₂SiHPh (18%) and cyclohexyl-OSiH₂Ph (36%) in five days in the overall yield of 54%.

Hydrosilylation of acetophenone with phenylsilane catalyzed by (Cp)(ArN)Mo(H)(PMe₃)



Acetophenone (0.0424 g, 0.356 mmol) and phenylsilane (0.0386 g, 0.356 mmol) were mixed in the presence of (Cp)(ArN)Mo(H)(PMe₃) (0.0074 mg, 0.018 mmol, 5% mol) in C₆D₆ (0.65 mL). The reaction mixture was heated at +50 °C for a day. There was no hydrosilylation observed. The catalyst only reacted with the phenylsilane to give (Cp)(ArN)Mo(SiH₂Ph)(PMe₃).

Activation parameters for phosphine exchange: (Cp)(ArN)Mo(H)(PMe₃) + PMe₃



Trimethylphosphine (0.0017 g, 0.022 mmol) was added to a solution of (Cp)(ArN)Mo(H)(PMe₃) (0.005 g, 0.012 mmol). Several SELNOGP (selective ge-1D EXSY) NMR experiments were carried out at four different temperatures, +12, +22, +32, and +42 °C, with the mixing times (d8) of 5, 7, 10, 12, 15, 20, 30, 40, 50, 60, 100 and 200 ms by irradiating the peaks of free and bound phosphines. Relaxation times (T₁) were also measured for the free and bound phosphines. The exchange rate constants and activation parameters parameters were calculated using the obtained data (Figure SI2): $(2.89 \pm 0.04) \cdot 10^1 \text{ s}^{-1}$ (+12.0 °C), $(4.29 \pm 0.07) \cdot 10^1 \text{ s}^{-1}$ (+22.0 °C), $(6.22 \pm 0.12) \cdot 10^1 \text{ s}^{-1}$ (+32.0 °C), $(8.56 \pm 0.15) \cdot 10^1 \text{ s}^{-1}$ (+42.0 °C)

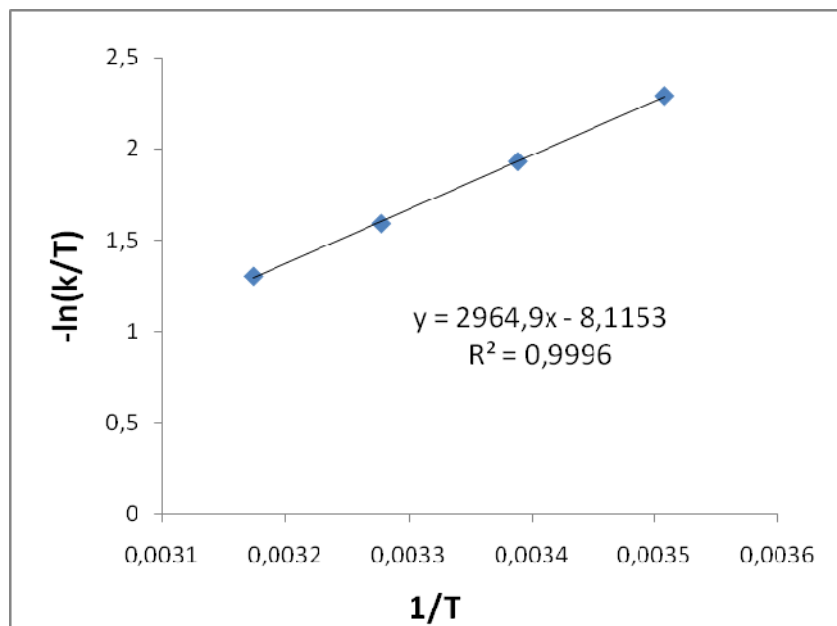


Figure SI2. Eyring plot for phosphine exchange in (Cp)(ArN)Mo(H)(PMe₃)/PMe₃

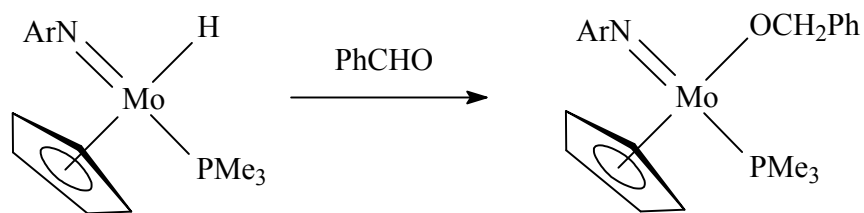
The activation parameters have been extracted from the Eyring plot (Figure SI2).

$$-\ln\left(\frac{k}{T}\right) = \frac{\Delta H^\ddagger}{RT} - \left(23.8 + \frac{\Delta S^\ddagger}{R}\right)$$

$$\Delta S^\ddagger = -(1.30 \pm 0.01) \cdot 10^2 \text{ J/(K} \cdot \text{mol)}$$

$$\Delta H^\ddagger = (2.47 \pm 0.04) \cdot 10^1 \text{ kJ/mol}$$

Synthesis of (ArN)Mo(Cp)(OCH₂Ph)(PMe₃)

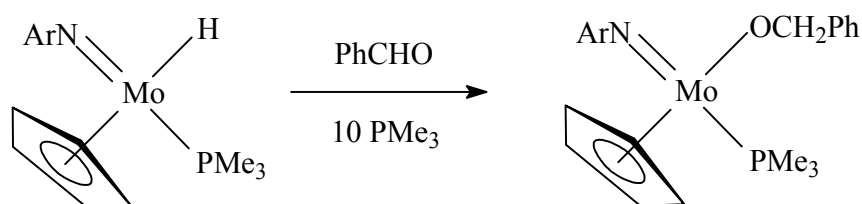


Benzaldehyde (0.053 g, 0.501 mmol) was added to a solution of (Cp)(ArN)Mo(H)(PMe₃) (0.207 g, 0.501 mmol) in 20 mL of hexane. The reaction mixture was left for several days at room temperature until the reaction is complete. The product, (Cp)(ArN)Mo(OCH₂Ph)(PMe₃), was filtered off, washed with hexane (2 x 10 ml) and dried in vacuum. Yield: 135 mg, 52%.

¹H-NMR (300 MHz; C₆D₆; 298K; δ, ppm): 1.01 (d, ²J_{H-P} = 9.3 Hz, 9H, PMe₃), 1.12 (d, ³J_{H-H} =

6.8 Hz, 6H, *iPr*), 1.26 (d, $^3J_{H-H} = 6.8$ Hz, 6H, *iPr*), 4.08 (sept, $^3J_{H-H} = 6.8$ Hz, 2H, *iPr*), 5.06 (s, 5H, Cp), 5.22 (dd, $^2J_{H-H} = 180.3$ Hz, $^3J_{H-P} = 14.3$ Hz, 2H, OCH₂Ph), 7.02-7.20 (m, 4H, Ar), 7.30-7.39 (m, 2H, Ar), 7.46-7.53 (m, 2H, Ar). ³¹P-NMR (121.5 MHz; C₆D₆; 298 K; δ, ppm): 16.1 (s, 1P, PMe₃). ¹³C-NMR (75.5 MHz; C₆D₆; 298 K; δ, ppm): 17.1 (d, $^2J_{C-P} = 25.2$ Hz, PMe₃), 24.1 (Me, *iPr*), 24.2 (Me, *iPr*), 28.3 (CH, *iPr*), 86.0 (d, $^3J_{C-P} = 5.3$ Hz, OCH₂Ph), 94.7 (Cp), 123.4 (CH, Ar), 125.2 (CH, Ar), 126.1 (CH, Ar), 126.4 (CH, Ar), 128.5 (CH, Ar, the position of this carbon was determined by HSQC NMR), 145.1 (ipso-C, Ar), 148.7 (ipso-C, Ar), 153.9 (ipso-C, Ar).

Kinetic study of the formation of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃)



Benzaldehyde (0.0027 g, 0.026 mmol) was added to a solution of (Cp)(ArN)Mo(H)(PMe₃) (0.0107 g, 0.026 mmol) in the presence of PMe₃ (0.0197 g, 0.259 mmol) in C₆D₆ (0.65 mL). The formation of the product was monitored by ¹H NMR at +26 (Figure SI3), +40 (Figure SI4), +50 (Figure SI5) and +60 °C (Figure SI6).

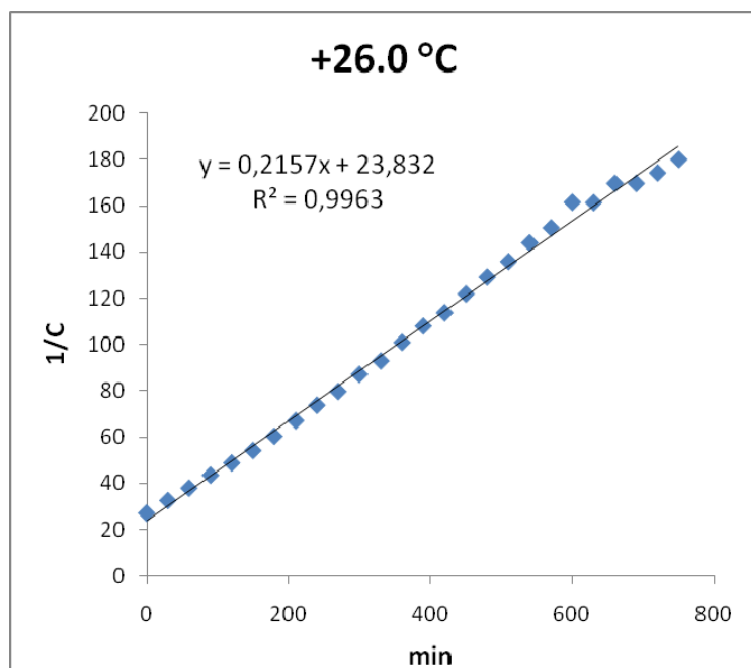


Figure SI3. (1/C)/time plot for the reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhCHO (1eq.) in presence of PMe₃ (10 eq.) at +26.0 °C

$$k (+26.0 \text{ °C}) = (2.157 \pm 0.027) \cdot 10^{-1} \text{ M}^{-1} \cdot \text{min}^{-1} = (3.60 \pm 0.05) \cdot 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

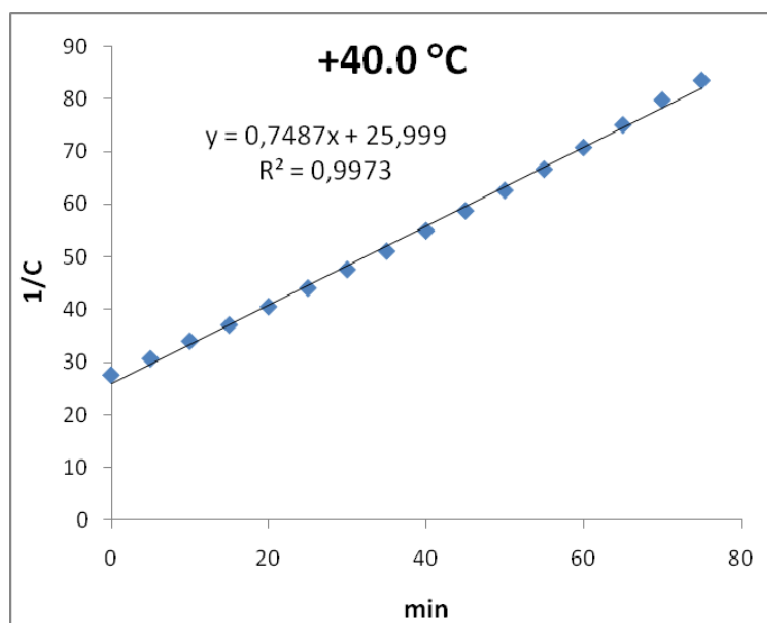


Figure SI4. (1/C)/time plot for the reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhCHO (1eq.) in the presence of PMe₃ (10 eq.) at +40.0 °C

$$k (+40.0 \text{ °C}) = (7.487 \pm 0.104) \cdot 10^{-1} \text{ M}^{-1} \cdot \text{min}^{-1} = (1.25 \pm 0.17) \cdot 10^{-2} \text{ M}^{-1} \cdot \text{s}^{-1}$$

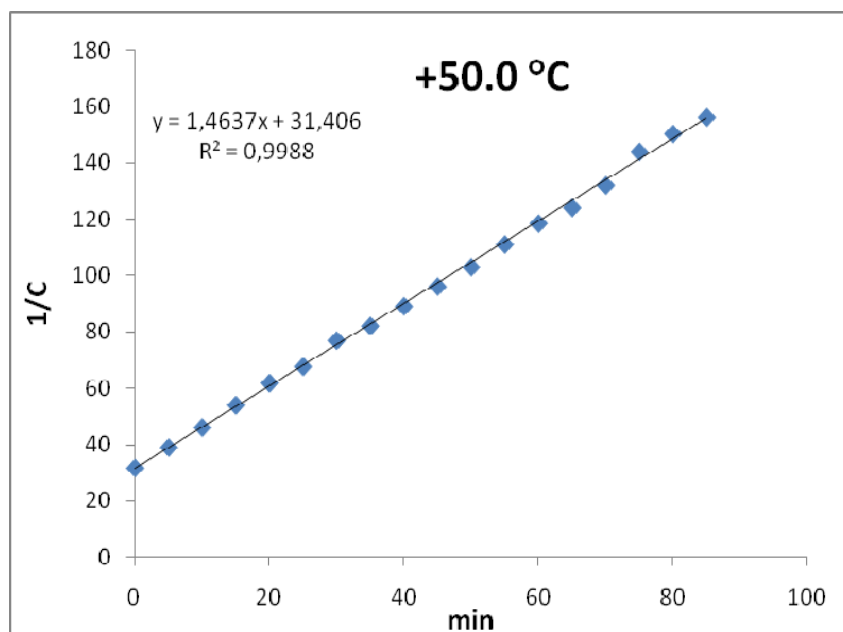


Figure SI5. (1/C)/time plot for the reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhCHO (1eq.) in the presence of PMe₃ (10 eq.) at +50.0 °C

$$k (+50.0 \text{ °C}) = (1.4637 \pm 0.0126) \text{ M}^{-1} \cdot \text{min}^{-1} = (2.44 \pm 0.17) \cdot 10^{-2} \text{ M}^{-1} \cdot \text{s}^{-1}$$

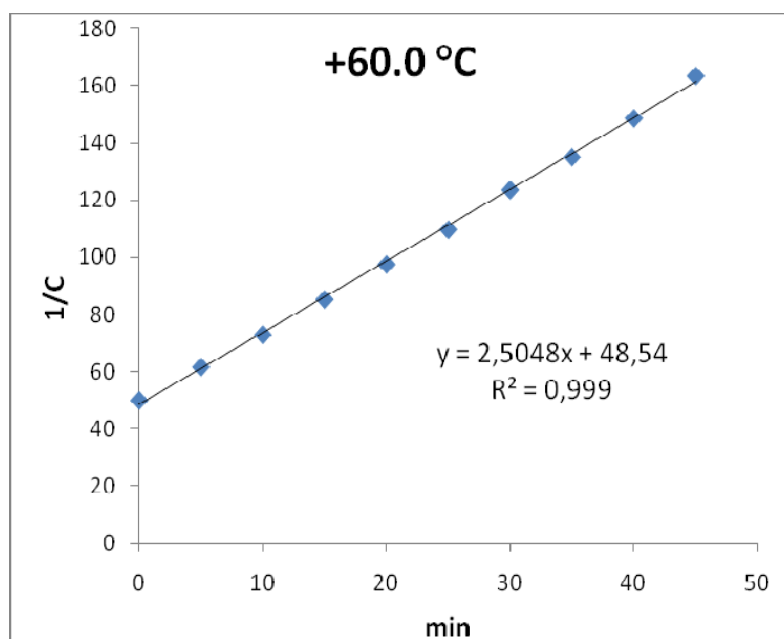


Figure SI6. (1/C)/time plot for the reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhCHO (1eq.) in the presence of PMe₃ (10 eq.) at +60.0 °C

$$k (+60.0 \text{ °C}) = (2.5048 \pm 0.0280) \text{ M}^{-1} \cdot \text{min}^{-1} = (4.17 \pm 0.05) \cdot 10^{-2} \text{ M}^{-1} \cdot \text{s}^{-1}$$

The activation parameters have been extracted from the Eyring plot.

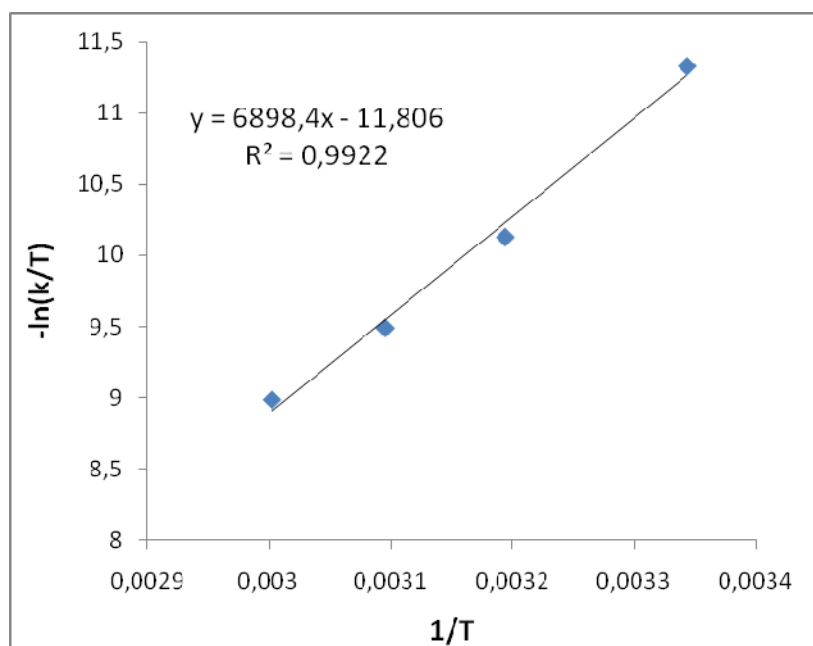


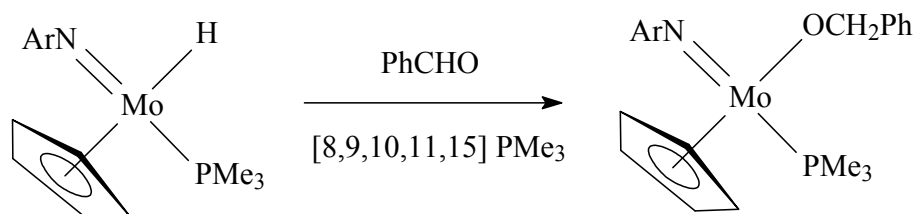
Figure si7. Eyring plot for the reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhCHO (1eq.) in the presence of PMe₃ (10 eq.)

$$-\ln\left(\frac{k}{T}\right) = \frac{\Delta H^\ddagger}{RT} - \left(23,8 + \frac{\Delta S^\ddagger}{R}\right)$$

$$\Delta S^\ddagger = -(9,97 \pm 1,14) \cdot 10^1 \text{ J/(K} \cdot \text{mol)}$$

$$\Delta H^\ddagger = (5,76 \pm 0,36) \cdot 10^1 \text{ kJ/mol}$$

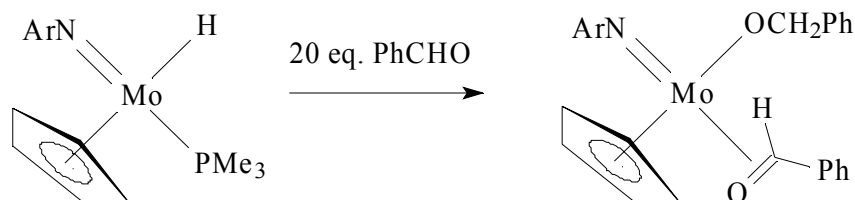
Formation of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃)



Benzaldehyde (0.0027 g, 0.026 mmol) was added to a solution of (Cp)(ArN)Mo(H)(PMe₃) (0.0107 g, 0.026 mmol) in the presence of PMe₃ (8 eq (0.0158 g, 0.207 mmol), 9 eq. (0.0177 mmol), 10 eq. (0.0197 g, 0.259 mmol), 11 eq. (0.0217 g, 0.285 mmol), 15 eq. (0.0296 g, 0.388 mmol,)) in C₆D₆ (0.65 mL). The formation of the product was monitored by ¹H NMR at +22.0

°C. Variation of the amount of PMe_3 did not influence the change in the reaction rate constant.

Formation of $(\text{Cp})(\text{ArN})\text{Mo}(\text{OCH}_2\text{Ph})(\text{PhCHO})$



Benzaldehyde (0.0257 g, 0.242 mmol) was added to a solution of $(\text{Cp})(\text{ArN})\text{Mo}(\text{H})(\text{PMe}_3)$ (0.053 g, 0.010 mmol) in C_6D_6 (0.65 ml). Two isomers of $(\text{Cp})(\text{ArN})\text{Mo}(\text{OCH}_2\text{Ph})(\text{PhCHO})$ (**A**, 71% and **B**, 29%) formed within an hour at room temperature.

Isomer A:

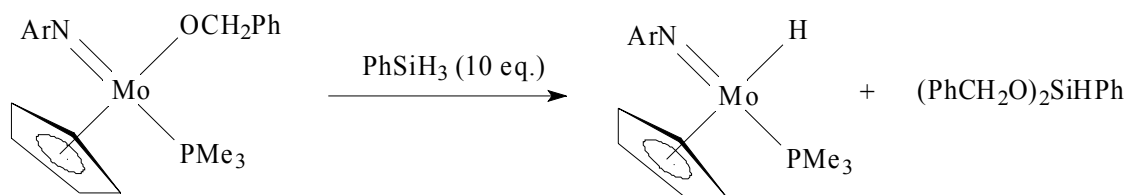
$^1\text{H-NMR}$ (300 MHz; C_6D_6 ; 298K; δ , ppm): 0.87 (d, $^3J_{\text{H-H}} = 6.85$ Hz, 6H, 2 CH_3 , iPr), 1.09 (d, $^3J_{\text{H-H}} = 6.85$ Hz, 6H, 2 CH_3 , iPr), 3.39 (sept, $^3J_{\text{H-H}} = 6.85$ Hz, 2H, iPr), 5.58 (s, 1H, PhCHO), 5.65 (s, 5H, Cp), 5.84 (d, $^2J_{\text{H-H}} = 13.8$ Hz, $\text{CH}^a\text{H-O}$), 6.25 (d, $^2J_{\text{H-H}} = 13.8$ Hz, $\text{CHH}^b\text{-O}$), 6.77-6.81 (m, 3H, Ar), 6.87-7.42 (mm, 8H, 2Ph), 7.72-7.77 (m, 2H, Ph, PhCHO).

Isomer B:

$^1\text{H-NMR}$ (300 MHz; C_6D_6 ; 298K; δ , ppm): 1.16 (d, $^3J_{\text{H-H}} = 6.92$ Hz, 6H, 2 CH_3 , iPr), 1.21 (d, $^3J_{\text{H-H}} = 6.92$ Hz, 6H, 2 CH_3 , iPr), 3.94 (sept, $^3J_{\text{H-H}} = 6.85$ Hz, 2H, iPr), 5.38 (s, 5H, Cp), 5.92 (d, $^2J_{\text{H-H}} = 13.8$ Hz, $\text{CH}^a\text{H-O}$), 6.08 (s, 1H, PhCHO), 6.15 (d, $^2J_{\text{H-H}} = 13.8$ Hz, $\text{CHH}^b\text{-O}$), 6.91-6.94 (m, 3H, Ar), 6.87-7.42 (mm, 8H, 2Ph), 7.69-7.74 (m, 2H, Ph, PhCHO).

$^{13}\text{C-NMR}$ (both isomers) (75.5 MHz; C_6D_6 ; 298 K; δ , ppm): 24.0 (CH_3 , iPr, A), 24.2 (CH_3 , iPr, B), 24.6 (CH_3 , iPr, B), 25.3 (CH_3 , iPr, A), 27.9 (CH , iPr, A), 28.5 (CH , iPr, B), 70.5 ($\text{CH}_2\text{-O}$, A), 71.3 ($\text{CH}_2\text{-O}$, B), 88.7 ($-\text{CHO}$, B), 89.0 ($-\text{CHO}$, A), 108.0 (Cp, B), 109.9 (Cp, A), 123.3 (CH , Ar, A), 123.5 (CH , Ar, B), 125.4 (CH , PhCHO, A), 126.8, 126.9, 127.3, 127.4, 127.5, 127.6, 127.6, 127.7, 128.0, 128.2, 128.6, 128.9, 146.0 (C-Pr^{-1} , Ar, B), 146.6, 146.7 (C-CHO , A), 147.0 (C-Pr^{-1} , Ar, A), 148.3 (C-CHO , B), 152.7 (C-N , Ar, A) 154.0 (C-N , Ar, B).

Kinetic study of the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with PhSiH₃ (10 eq.)



Phenylsialne (0.0117 g, 0.108 mmol) was added to a solution of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) (0.0056 g, 0.011 mmol) in C₆D₆ (0.65 mL). The reaction was monitored by NMR at +16 (Figure SI8), +26 (Figure SI9), +36 (Figure SI10) and +46 °C (Figure SI11).

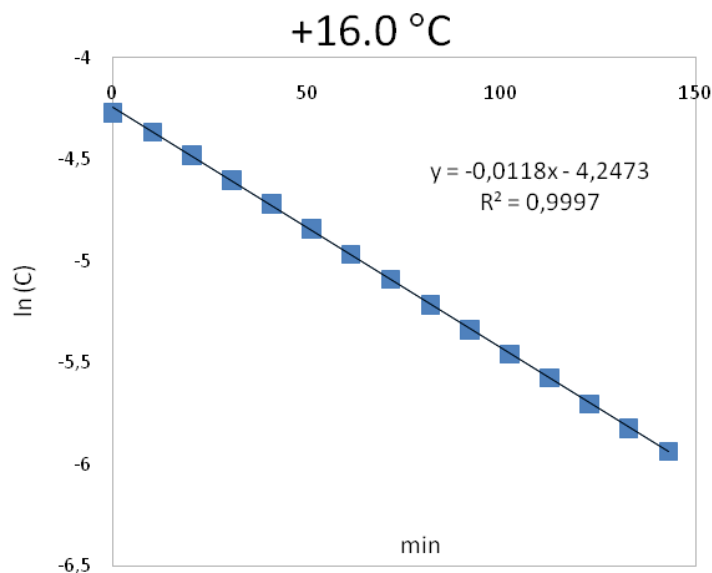


Figure SI8. ln(C)/time plot for the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with PhSiH₃ (10 eq.) at +16.0 °C

$$k_{\text{H}}(+16.0 \text{ } ^\circ\text{C}) = (1.18 \pm 0.01) \cdot 10^{-2} \text{ min}^{-1} = (1.97 \pm 0.02) \cdot 10^{-4} \text{ s}^{-1}$$

$$k_{\text{H}}^{\text{II}}(+16.0 \text{ } ^\circ\text{C}) = k_{\text{H}}(+16.0 \text{ } ^\circ\text{C})/C(\text{PhSiH}_3) = (1.09 \pm 0.01) \cdot 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

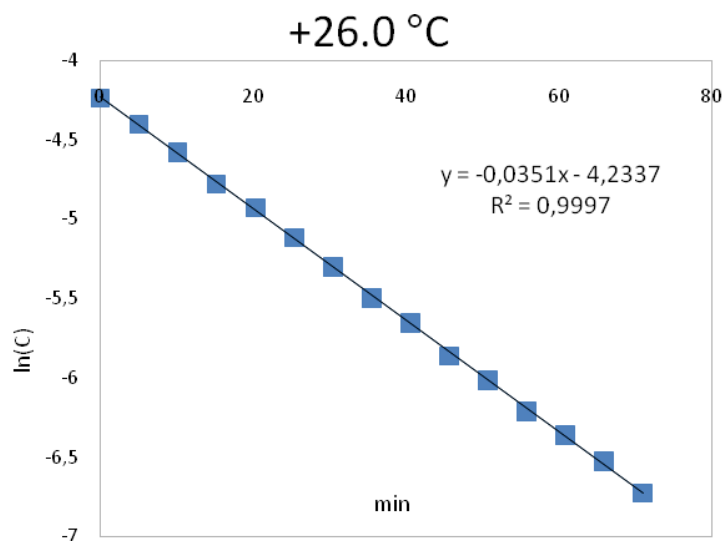


Figure SI9. ln(C)/time plot for the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with PhSiH₃ (10 eq.) at +26.0 °C

$$k_H(+26.0 \text{ °C}) = (3.51 \pm 0.02) \cdot 10^{-2} \text{ min}^{-1} = (5.85 \pm 0.03) \cdot 10^{-4} \text{ s}^{-1}$$

$$k_H^{\text{II}}(+26.0 \text{ °C}) = k_H(+26.0 \text{ °C})/C(\text{PhSiH}_3) = (3.25 \pm 0.02) \cdot 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

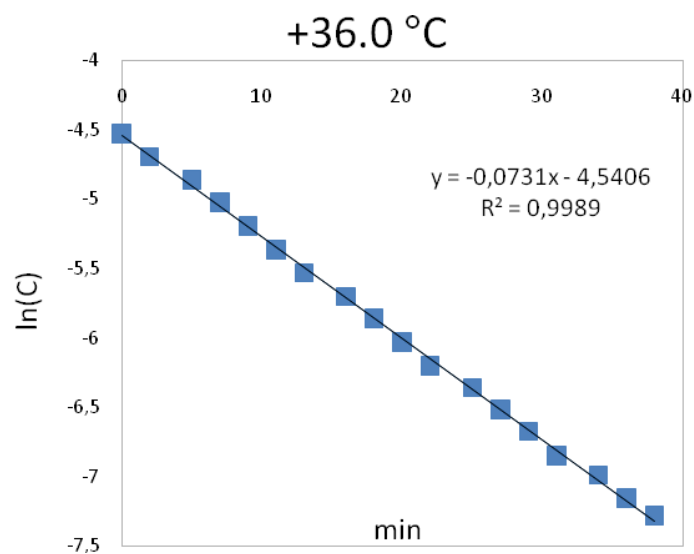


Figure SI10. ln(C)/time plot for the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with PhSiH₃ (10 eq.) at +36.0 °C

$$k_H(+36.0 \text{ °C}) = (7.31 \pm 0.06) \cdot 10^{-2} \text{ min}^{-1} = (1.22 \pm 0.01) \cdot 10^{-3} \text{ s}^{-1}$$

$$k_H^{\text{II}}(+36.0 \text{ °C}) = k_H(+36.0 \text{ °C})/C(\text{PhSiH}_3) = (6.78 \pm 0.06) \cdot 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

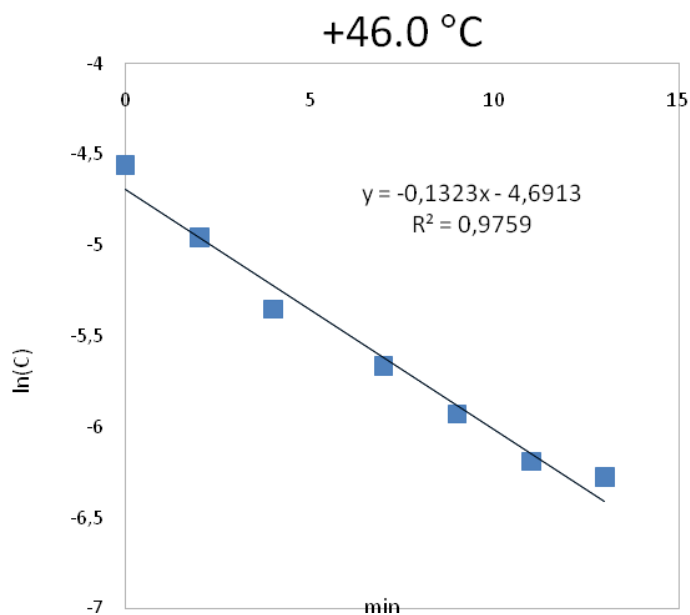


Figure SI11. ln(C)/time plot for the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with PhSiH₃ (10 eq.) at +46.0 °C

$$k_H(+46.0 \text{ °C}) = (1.323 \pm 0.093) \cdot 10^{-1} \text{ min}^{-1} = (2.21 \pm 0.16) \cdot 10^{-3} \text{ s}^{-1}$$

$$k_H^{\text{II}}(+46.0 \text{ °C}) = k_H(+46.0 \text{ °C})/C(\text{PhSiH}_3) = (1.23 \pm 0.09) \cdot 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

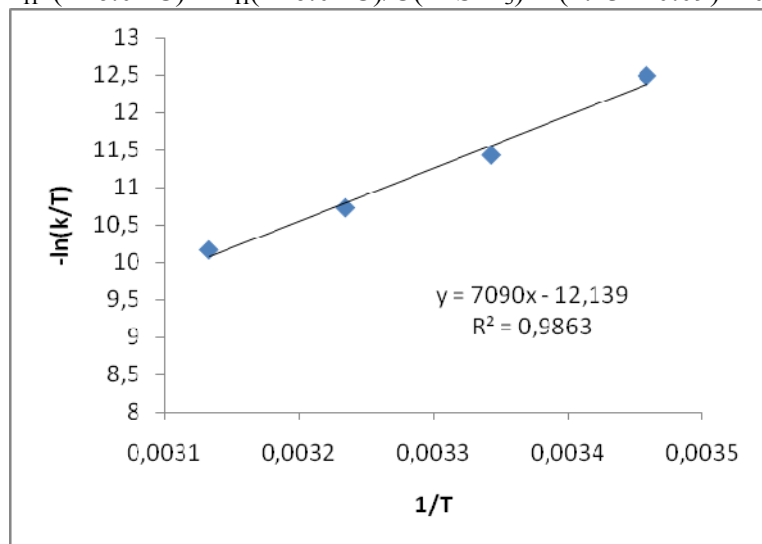


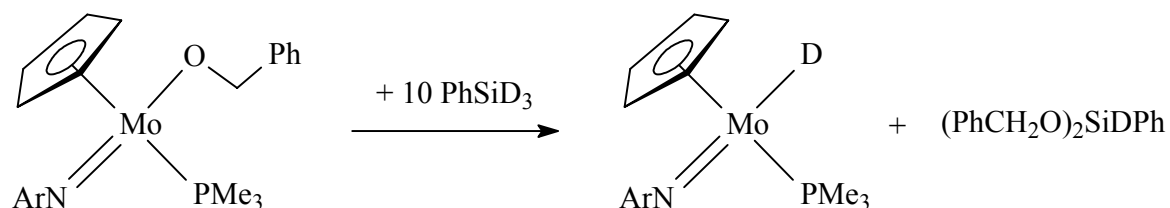
Figure 12. Eyring plot for the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with PhSiH₃ (10 eq.).

$$-\ln\left(\frac{k}{T}\right) = \frac{\Delta H^\ddagger}{RT} - \left(23.8 + \frac{\Delta S^\ddagger}{R}\right)$$

$$\Delta S^\ddagger = -(9.69 \pm 1.6) \cdot 10^1 \text{ J/(K} \cdot \text{mol)}$$

$$\Delta H^\ddagger = (5.89 \pm 0.49) \cdot 10^1 \text{ kJ/mol}$$

Kinetic study of the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with excess PhSiD₃ under pseudo-first order conditions



PhSiD₃ (0.012 g, 0.108 mmol) was added to a solution of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) (0.0056 g, 0.011 mmol) in C₆D₆ (0.65 mL). The reaction was monitored by ¹H NMR at +16 (Figure SI13), +26 (Figure SI14), +36 (Figure SI15) and +46 °C (Figure SI16).

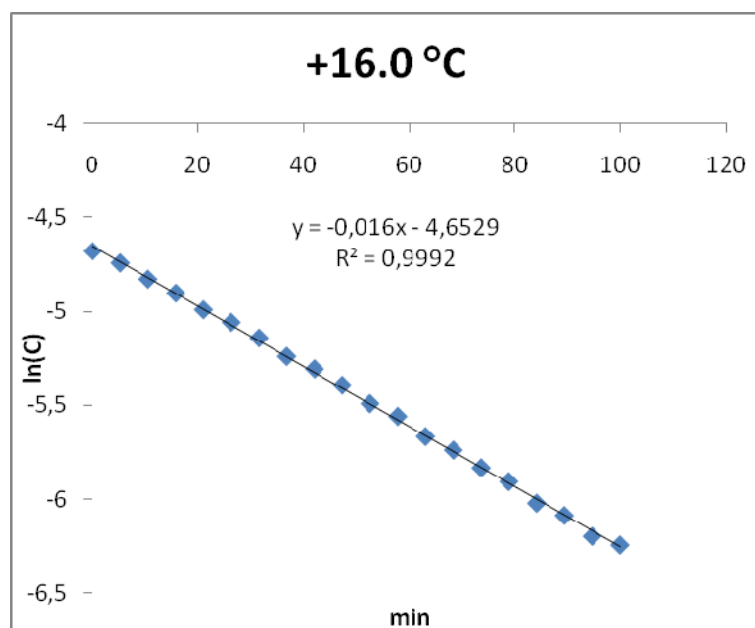


Figure SI13. ln(C)/time plot the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with PhSiH₃ (10 eq.) +16.0 °C.

$$k_D(+16 \text{ }^\circ\text{C}) = (1.60 \pm 0.01) \cdot 10^{-2} \text{ min}^{-1} = (2.7 \pm 0.02) \cdot 10^{-4} \text{ s}^{-1}$$

$$k_D^{\text{II}}(+16.0 \text{ }^\circ\text{C}) = k_D(+16.0 \text{ }^\circ\text{C})/C(\text{PhSiD}_3) = (1.48 \pm 0.01) \cdot 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

$$\frac{k_H(+16)}{k_D(+16)} = \frac{0.0118}{0.0160} \cong 0.7$$

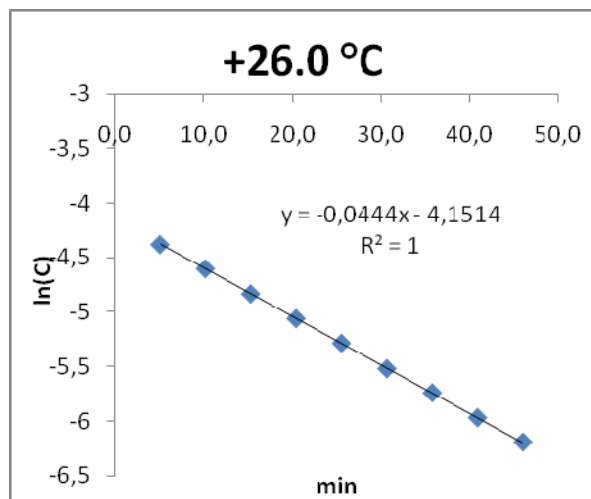


Figure SI14. ln(C)/time plot the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with PhSiH₃ (10 eq.) at +26.0 °C.

$$k_D(+26.0 \text{ °C}) = (4.44 \pm 0.01) \cdot 10^{-2} \text{ min}^{-1} = (7.40 \pm 0.02) \cdot 10^{-4} \text{ s}^{-1}$$

$$k_D^{\text{II}}(+26.0 \text{ °C}) = k_D(+26.0 \text{ °C})/C(\text{PhSiD}_3) = (4.11 \pm 0.01) \cdot 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

$$\frac{k_H(+26)}{k_D(+26)} = \frac{0.0351}{0.0444} \cong 0.8$$

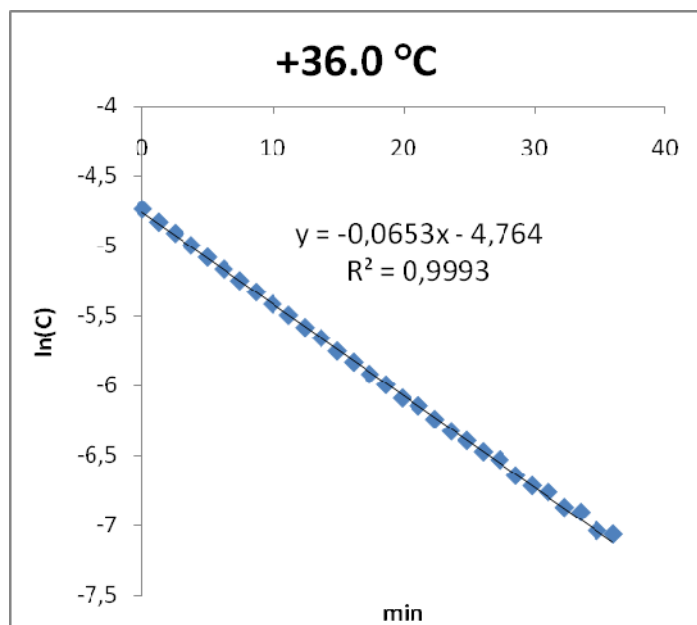


Figure SI15. $\ln(C)/\text{time}$ plot the reaction of $(\text{Cp})(\text{ArN})\text{Mo}(\text{OCH}_2\text{Ph})(\text{PMe}_3)$ with PhSiH_3 (10 eq.) at $+36.0\text{ }^\circ\text{C}$.

$$k_D(+36\text{ }^\circ\text{C}) = (6.53 \pm 0.03) \cdot 10^{-2} \text{ min}^{-1} = (1.09 \pm 0.01) \cdot 10^{-3} \text{ s}^{-1}$$

$$k_D^{\text{II}}(+36.0\text{ }^\circ\text{C}) = k_D(+36.0\text{ }^\circ\text{C})/C(\text{PhSiD}_3) = (6.05 \pm 0.06) \cdot 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

$$\frac{k_H(+36)}{k_D(+36)} = \frac{0.0731}{0.0653} \cong 1.1$$

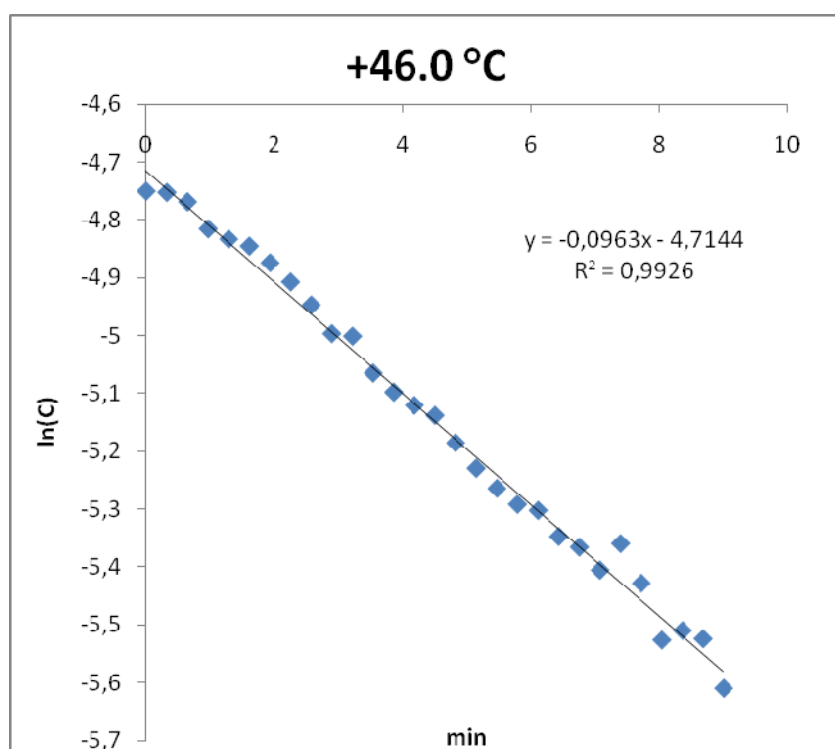


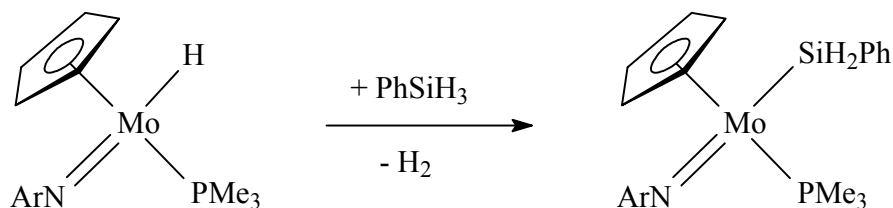
Figure SI16. $\ln(C)/\text{time}$ plot the reaction of $(\text{Cp})(\text{ArN})\text{Mo}(\text{OCH}_2\text{Ph})(\text{PMe}_3)$ with PhSiH_3 (10 eq.) at $+46.0\text{ }^\circ\text{C}$.

$$k_D(+46.0\text{ }^\circ\text{C}) = (9.63 \pm 0.16) \cdot 10^{-2} \text{ min}^{-1} = (1.60 \pm 0.03) \cdot 10^{-3} \text{ s}^{-1}$$

$$k_D^{\text{II}}(+46.0\text{ }^\circ\text{C}) = k_D(+46.0\text{ }^\circ\text{C})/C(\text{PhSiD}_3) = (8.92 \pm 0.20) \cdot 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

$$\frac{k_H(+46)}{k_D(+46)} = \frac{0.1323}{0.0963} \cong 1.4$$

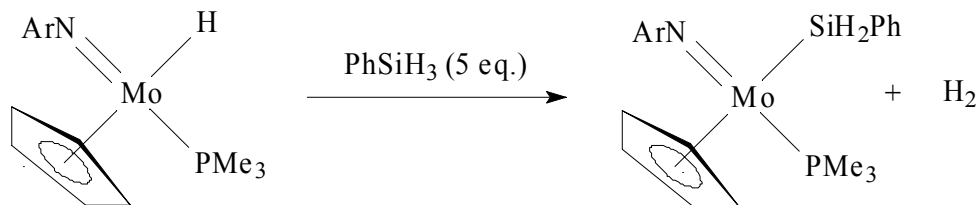
Synthesis of (Cp)(ArN)Mo(SiH₂Ph)(PMe₃)



Phenylsilane (0.140 g, 0.970 mmol) was added to a solution of (Cp)(ArN)Mo(H)(PMe₃) (0.270 g, 0.480 mmol) in Et₂O. The reaction mixture was left for one week at room temperature until the reaction was complete. Evaporation of all volatiles afforded (Cp)(ArN)Mo(SiH₂Ph)(PMe₃) (0.326 mg, 96% yield) as a brown-green oil.

¹H-NMR (300 MHz; C₆D₆; 298K; δ , ppm): 1.04 (d, ²*J*_{H-P} = 9.0 Hz, 9H, PMe₃), 1.16 (d, ³*J*_{H-H} = 6.9 Hz, 6H, iPr), 1.19 (d, ³*J*_{H-H} = 6.9 Hz, 6H, iPr), 4.30 (sept, ³*J*_{H-H} = 6.9 Hz, 2H, iPr), 4.70 (s, 5H, Cp), 5.18 (d, ³*J*_{H-P} = 1.5 Hz, 1H, SiH₂Ph), 5.56 (d, ³*J*_{H-P} = 4.2 Hz, 1H, SiH₂Ph), 6.89 (t, ³*J*_{H-H} = 7.5 Hz, 1H, *p*-H, ArN), 7.05 (m, 2H, *p*-H, ArN), 7.25 (m, 1H, *p*-H, SiPh), 7.34 (t, ³*J*_{H-H} = 7.5 Hz, 2H, *m*-H, SiPh), 8.12 (d, ³*J*_{H-H} = 6.5 Hz, 2H, *o*-H, SiPh). ¹³C-NMR (75.5 MHz; C₆D₆; 298 K; δ , ppm): 21.5 (d, ²*J*_{C-P} = 25.7 Hz, PMe₃), 23.8 (s, CH₃), 24.8 (s, CH₃), 28.2 (s, CH), 90.0 (s, Cp), 119.3, 123.4, 125.3, 127.8, 130.5, 136.4, 137.3, 145.0 (s, aromatic). ³¹P-NMR (121.5 MHz; C₆D₆; 298 K; δ , ppm): 18.60 (s, 1P, PMe₃). ²⁹Si-NMR (119.24 MHz; C₆D₆; 298 K; δ , ppm): -4.0 (dt, ¹*J*_{Si-P} = 29.8 Hz, ¹*J*_{Si-H} = 156.8 Hz, SiH₂Ph).

The study of dependence of the reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhSiH₃ on PMe₃ concentration



Phenylsilane (0.0136 g, 0.125 mmol) was added to a solution (Cp)(ArN)Mo(H)(PMe₃) (0.0105 g, 0.025 mmol) in C₆D₆ (0.65 mL). The reaction was monitored by ¹H NMR.

This experiment have been carried out also in presence of 10 eq. PMe_3 (0.0193 g, 0.250 mmol) and 20 eq. PMe_3 (0.0386 g, 0.508 mmol). The presence of phosphine has no effect on the course of this reaction.

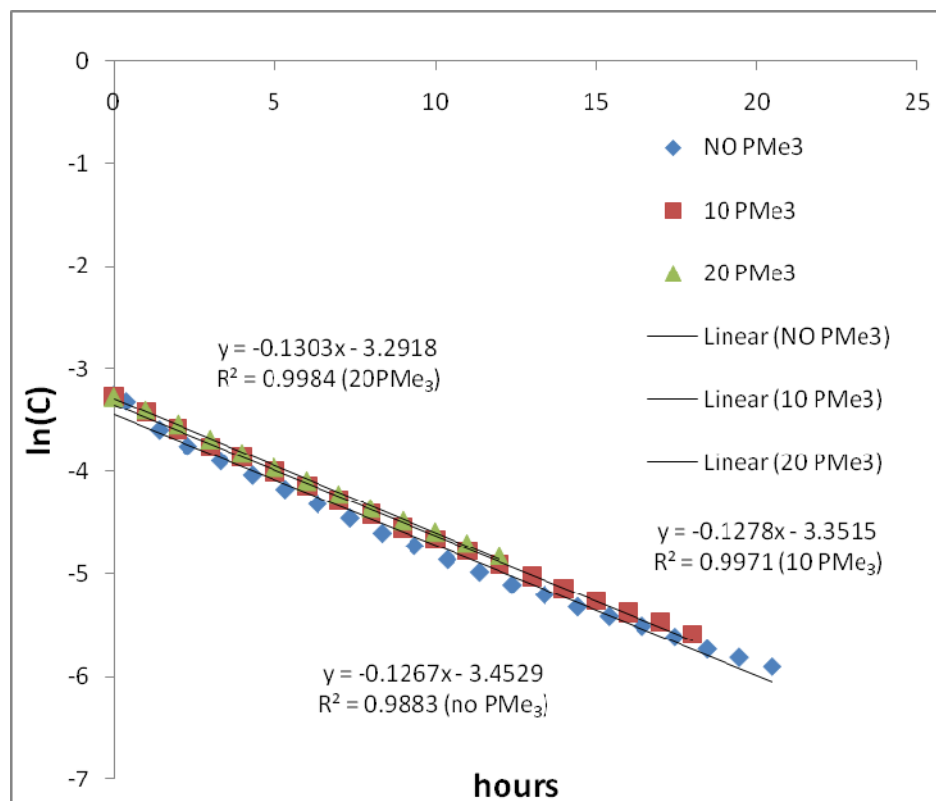


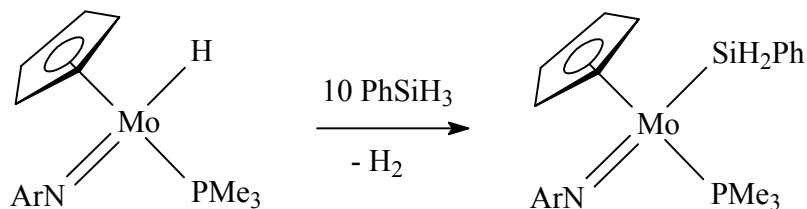
Figure 17. $\ln(C)/\text{time}$ plot for the reaction of $(\text{Cp})(\text{ArN})\text{Mo}(\text{H})(\text{PMe}_3)$ with PhSiH_3 (5 eq.) at $+26.0\text{ }^\circ\text{C}$ in presence of 0, 10, and 20 eq. of PMe_3

$$k(\text{no PMe}_3) = (1.27 \pm 0.03) \cdot 10^{-1} \text{ h}^{-1}$$

$$k(10 \text{ PMe}_3) = (1.28 \pm 0.02) \cdot 10^{-1} \text{ h}^{-1}$$

$$k(20 \text{ PMe}_3) = (1.30 \pm 0.02) \cdot 10^{-1} \text{ h}^{-1}$$

The reaction of (Cp)(ArN)Mo(H)(PMe₃) with 10 eq. PhSiH₃



Phenylsilane (0.0131 mg, 0.121 mmol) was added to a solution (Cp)(ArN)Mo(H)(PMe₃) (0.0105 mg, 0.025 mmol) in C₆D₆ (0.65 ml). The reaction was monitored by ¹H NMR at +25.0 (Figure SI18), +35.0 (Figure SI19), +45.0 (Figure SI20), and +55.0 °C (Figure SI21).

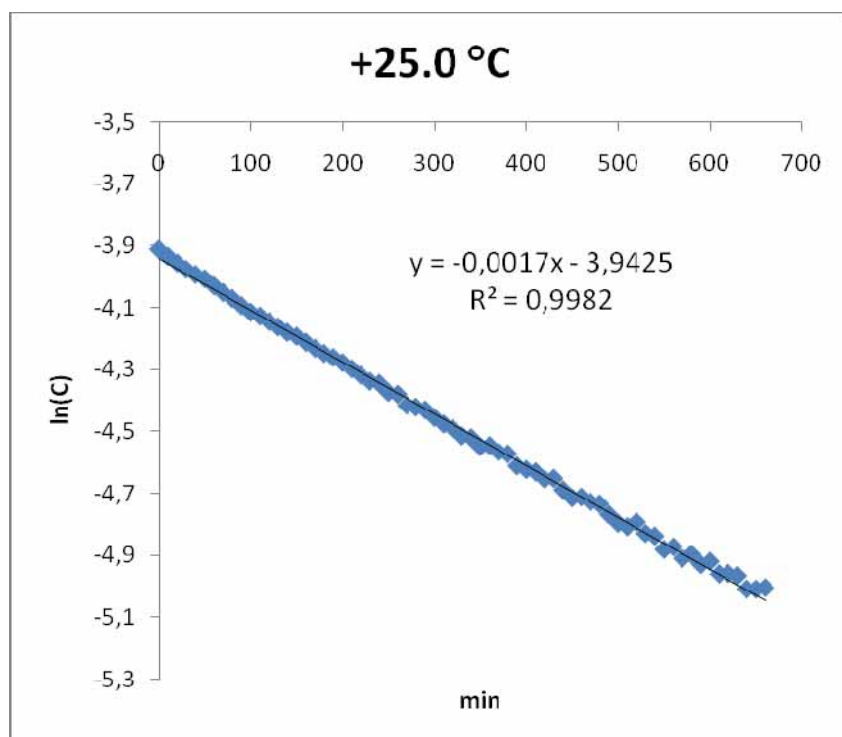


Figure SI18. Ln(C)/time plot for the reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhSiH₃ (10 eq.) at +25.0 °C.

$$k_H(+25.0 \text{ °C}) = (1.70 \pm 0.01) \cdot 10^{-3} \text{ min}^{-1} = (2.83 \pm 0.02) \cdot 10^{-5} \text{ s}^{-1}$$

$$k_H^{\text{II}}(+25.0 \text{ °C}) = k_H(+25.0 \text{ °C})/C(\text{PhSiH}_3) = (1.57 \pm 0.01) \cdot 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$$

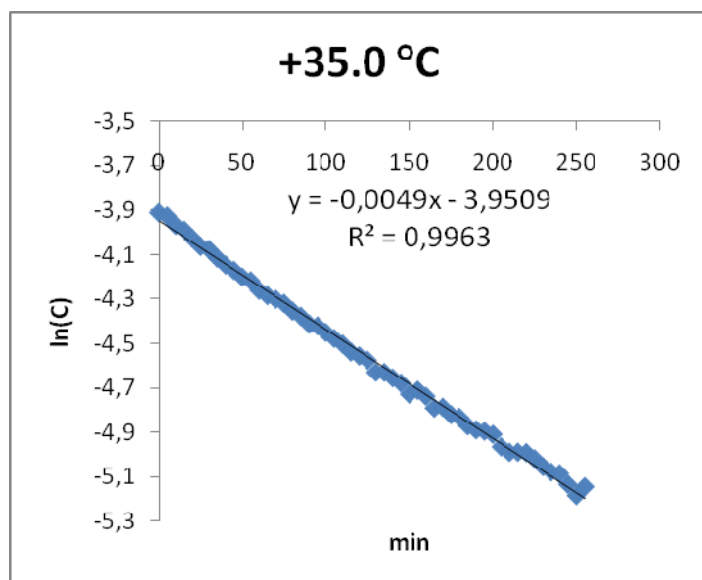


Figure SI19. Ln(C)/time plot for the reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhSiH₃ (10 eq.) at +35.0 °C.

$$k_H(+35.0 \text{ °C}) = (4.9 \pm 0.1) \cdot 10^{-3} \text{ min}^{-1} = (8.17 \pm 0.02) \cdot 10^{-5} \text{ s}^{-1}$$

$$k_H^{\text{II}}(+35.0 \text{ °C}) = k_H(+35.0 \text{ °C})/C(\text{PhSiH}_3) = (4.54 \pm 0.01) \cdot 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$$

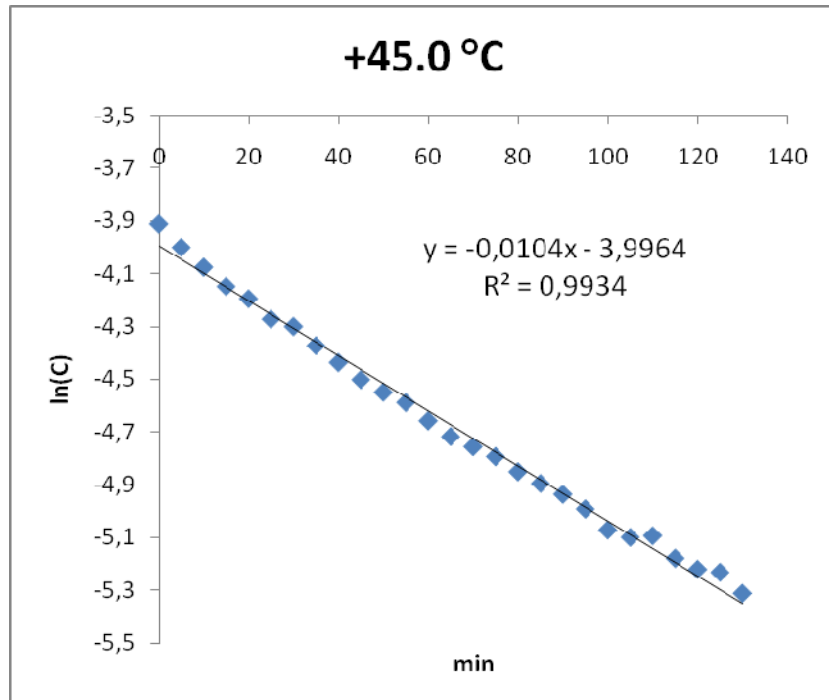


Figure SI20. Ln(C)/time plot for the reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhSiH₃ (10 eq.) at +45.0 °C.

$$k_H(+45.0\text{ }^\circ\text{C}) = (1.04 \pm 0.02) \cdot 10^{-2} \text{ min}^{-1} = (1.73 \pm 0.03) \cdot 10^{-4} \text{ s}^{-1}$$

$$k_H^{\text{II}}(+45.0\text{ }^\circ\text{C}) = k_H(+45.0\text{ }^\circ\text{C})/C(\text{PhSiH}_3) = (9.61 \pm 0.17) \cdot 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$$

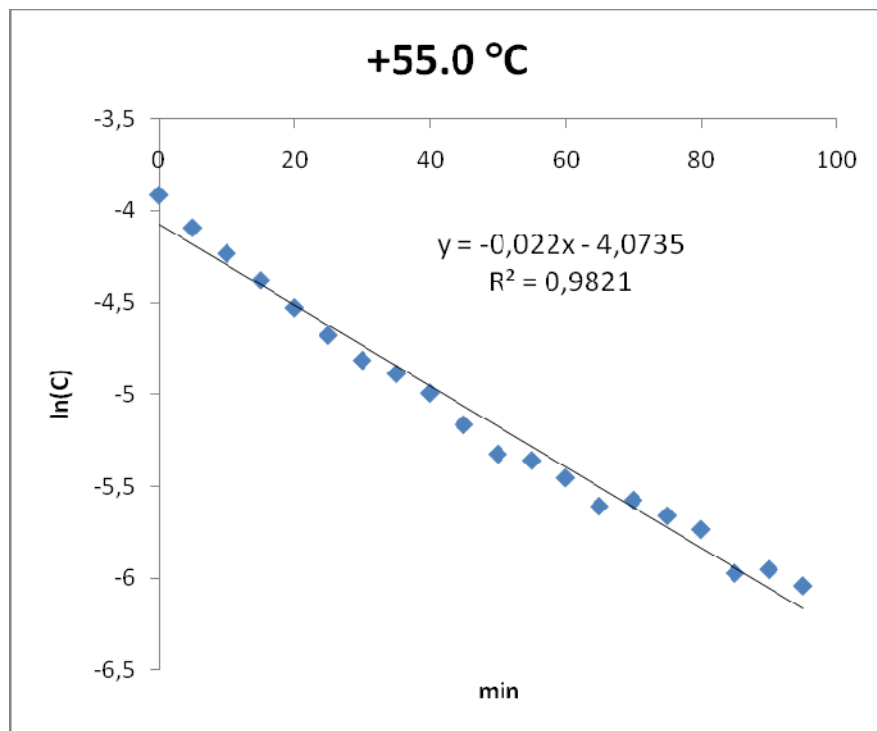


Figure SI21. Ln(C)/time plot for the reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhSiH₃ (10 eq.) at +55.0 °C.

$$k_H(+55.0\text{ }^\circ\text{C}) = (2.2 \pm 0.1) \cdot 10^{-2} \text{ min}^{-1} = (3.67 \pm 0.17) \cdot 10^{-4} \text{ s}^{-1}$$

$$k_H^{\text{II}}(+55.0\text{ }^\circ\text{C}) = k_H(+55.0\text{ }^\circ\text{C})/C(\text{PhSiH}_3) = (2.04 \pm 0.09) \cdot 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

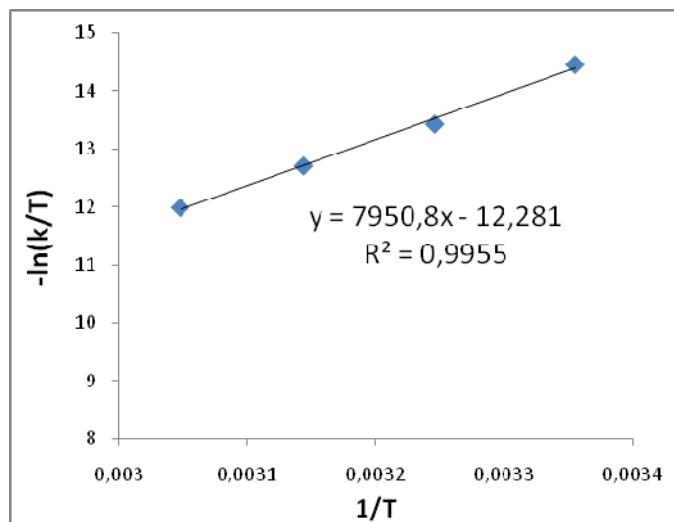


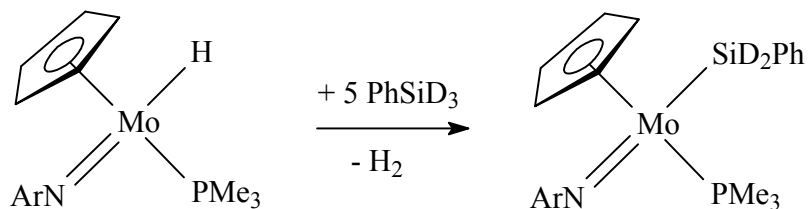
Figure SI22. Eyring plot for the reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhSiH₃ (10 eq.).

$$-\ln\left(\frac{k}{T}\right) = \frac{\Delta H^\ddagger}{RT} - \left(23.8 + \frac{\Delta S^\ddagger}{R}\right)$$

$$\Delta S^\ddagger = -(9.58 \pm 1.00) \cdot 10^1 \text{ J/(K} \cdot \text{mol)}$$

$$\Delta H^\ddagger = (6.61 \pm 0.31) \cdot 10^1 \text{ kJ/mol}$$

The reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhSiD₃ (5 eq.)



PhSiD₃ (0.0136 g, 0.121 mmol) was added to a solution (Cp)(ArN)Mo(H)(PMe₃) (0.0105 g, 0.025 mmol) in C₆D₆ (0.65 mL). The reaction was monitored by ¹H NMR at +25 °C .

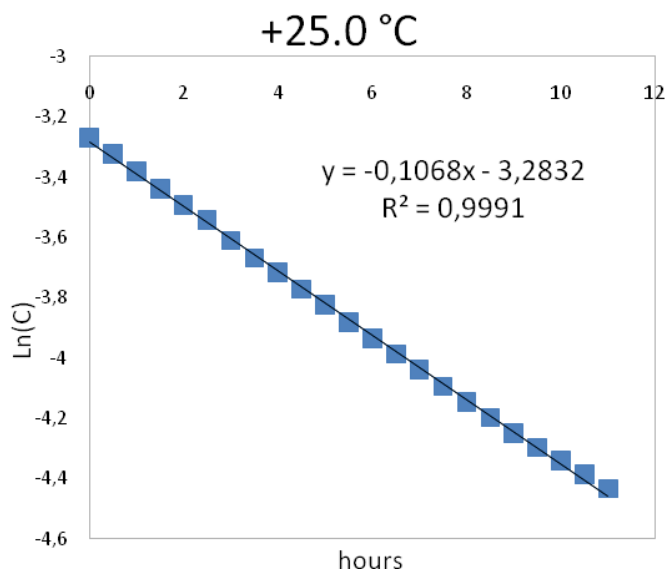


Figure SI23. Ln(C)/time plot for the reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhSiD₃ (5 eq) at +25.0 °C.

$$k_D(+25.0 \text{ °C}) = (1.068 \pm 0.007) \cdot 10^{-1} \text{ hours}^{-1} = (2.97 \pm 0.02) \cdot 10^{-5} \text{ s}^{-1}.$$

$$k_D^{\text{II}}(+25.0 \text{ °C}) = k_D(+25.0 \text{ °C})/C(\text{PhSiD}_3) = (1.65 \pm 0.01) \cdot 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$$

$$\frac{k_H(+25)}{k_D(+25)} = \frac{2.83 \cdot 10^{-5}}{2.97 \cdot 10^{-5}} \cong 1.0$$

The substitution of the Mo-bound hydride for the deuterium from PhSiD₃ was observed.

The picture below (Figure SI24) illustrates the concurrent formation of (Cp)(ArN)Mo(SiH₂Ph)(PMe₃) (blue marks) and the substitution of the Mo-H hydride by deuterium (red marks). After three hours, an equilibrium of the H/D exchange has been reached, while the formation of (Cp)(ArN)Mo(SiH₂Ph)(PMe₃) achieved only ~30%.

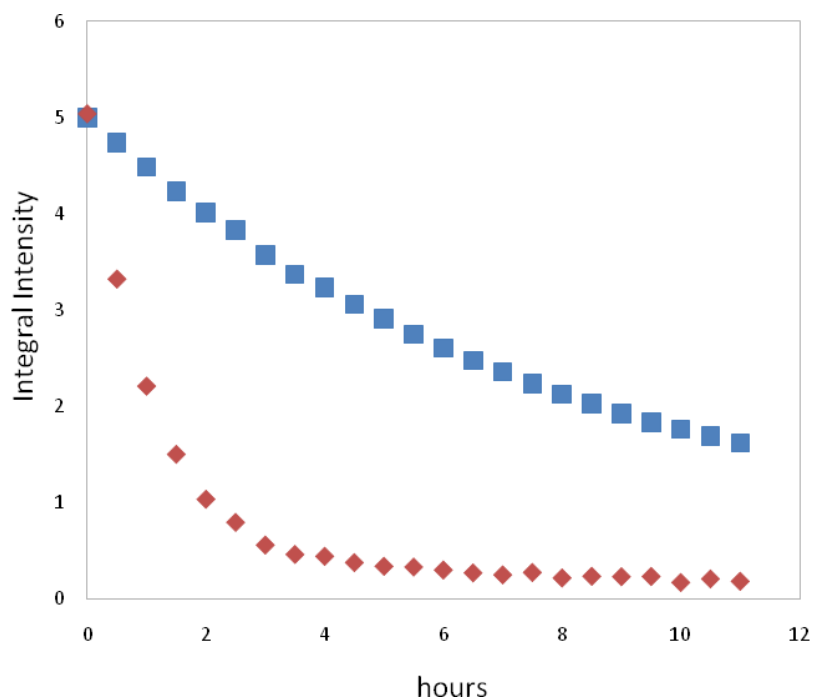


Figure SI24. Relative integral intensity vs. time. Concurrent formation of $(\text{Cp})(\text{ArN})\text{Mo}(\text{SiH}_2\text{Ph})(\text{PMe}_3)$ (blue marks) and substitution of Mo-H by deuterium (red marks) in the reaction of $(\text{Cp})(\text{ArN})\text{Mo}(\text{H})(\text{PMe}_3)$ with PhSiD_3 (5 eq) at $+25^\circ\text{C}$.

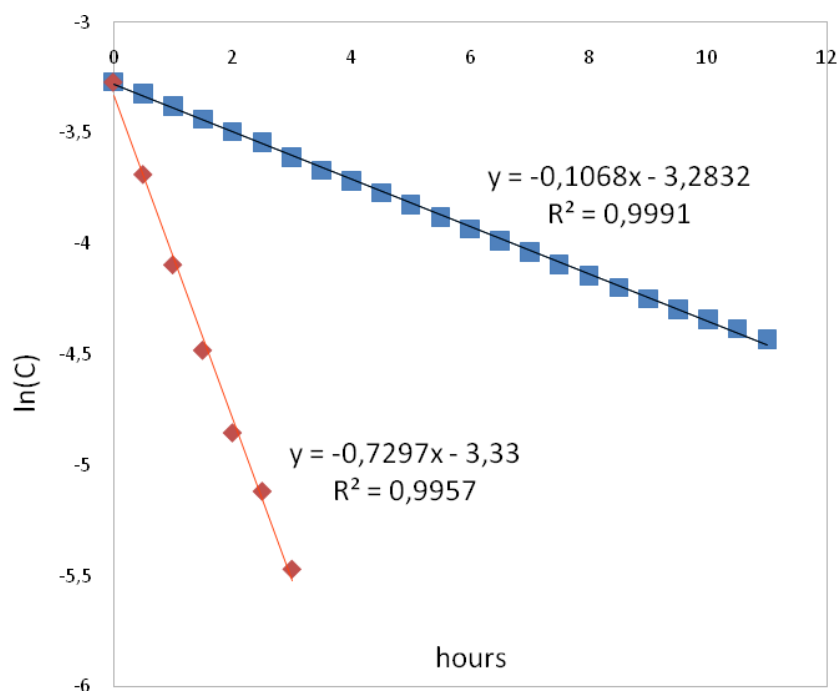


Figure SI25. Ln(C)/time plot for the reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhSiD₃ (5 eq) at +25 °C. Red line illustrates the disappearance of (Cp)(ArN)Mo(H)(PMe₃). Blue line indicates the conversion of (Cp)(ArN)Mo(H/D)(PMe₃) into (Cp)(ArN)Mo(SiD₂Ph)(PMe₃).

The blue line (Figure SI25) shows the progress of conversion of (Cp)(ArN)Mo(H/D)(PMe₃) into (Cp)(ArN)Mo(SiD₂Ph)(PMe₃). The red line shows the disappearance of (Cp)(ArN)Mo(H)(PMe₃), which is the result of both the H/D exchange and the conversion into the silyl-phosphine complex.

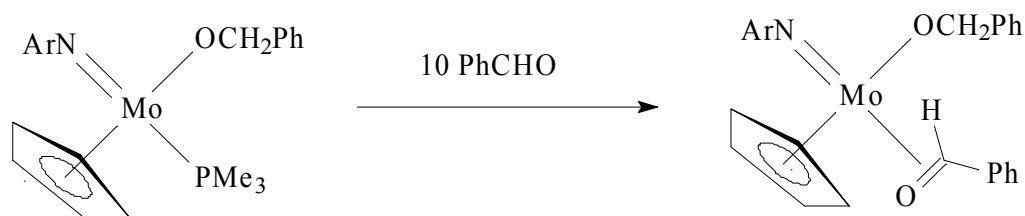
Taking these observations into account, it is possible to find both constants:

$k_1 = (0.1068 \pm 0.0007) \text{ hours}^{-1} = (2.97 \pm 0.02) * 10^{-5} \text{ s}^{-1}$ (the rate constant of the conversion to the silyl-phosphine complex),

$k_1 + k_2 = (0.7297 \pm 0.0214) \text{ hours}^{-1}$, where $k_2 = (0.6230 \pm 0.0207) \text{ hours}^{-1} = (1.73 \pm 0.06) * 10^{-4} \text{ s}^{-1}$ (the rate constant of substitution of H by D).

$$\frac{k_2}{k_1} = \frac{0.6230}{0.1068} \approx 5.8$$

The kinetic study of the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with PhCHO (10 eq.)



Benzaldehyde (0.0108 g, 0.102 mmol) was added to a solution of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) (0.0053 g, 0.010 mmol) in C₆D₆ (0.65 mL). The reaction was monitored by ¹H NMR at +26.0 (Figure SI26), +40.0 (Figure SI27), and +55.0 °C (Figure SI28).

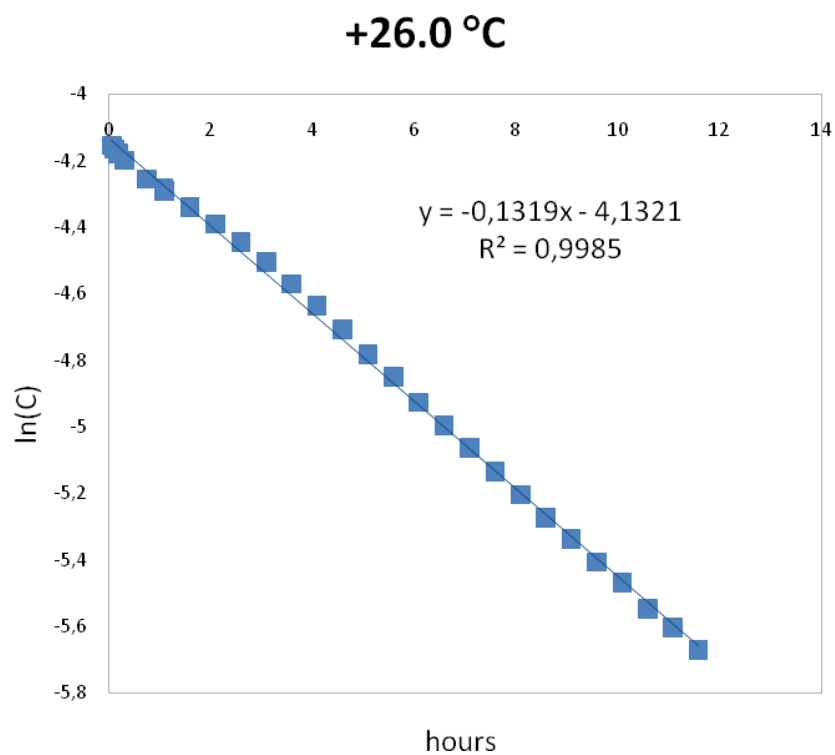


Figure SI26. Ln(C)/time plot for the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with PhCHO (10 eq.) at +26.0 °C.

$$k(+26.0 \text{ °C}) = (0.132 \pm 0.001) \text{ h}^{-1} = (3.66 \pm 0.03) \cdot 10^{-5} \text{ s}^{-1}$$

$$k^{\text{II}}(+26.0 \text{ °C}) = k(+26.0 \text{ °C})/C(\text{PhCHO}) = (2.15 \pm 0.02) \cdot 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$$

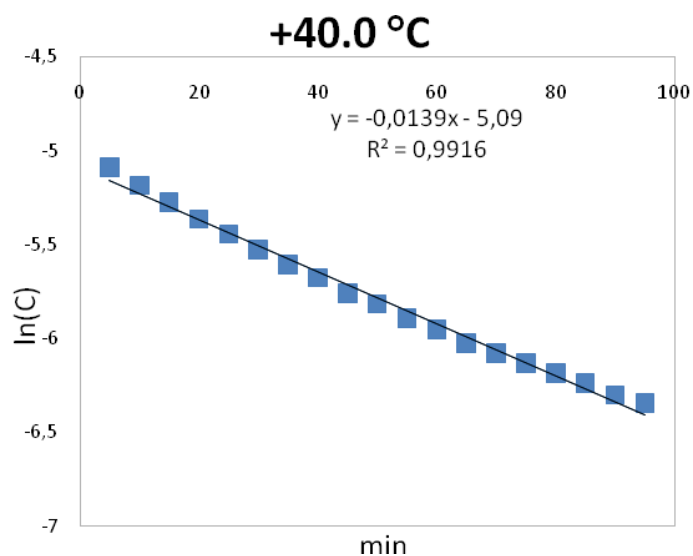


Figure SI27. Ln(C)/time plot for the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with PhCHO (10 eq.) at +40.0 °C.

$$k(+40.0\text{ °C}) = (1.39 \pm 0.03) \cdot 10^{-2} \text{ min}^{-1} = (2.31 \pm 0.05) \cdot 10^{-4} \text{ s}^{-1}$$

$$k^{\text{II}}(+40.0\text{ °C}) = k_{\text{H}}(+40.0\text{ °C})/C(\text{PhCHO}) = (1.36 \pm 0.03) \cdot 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

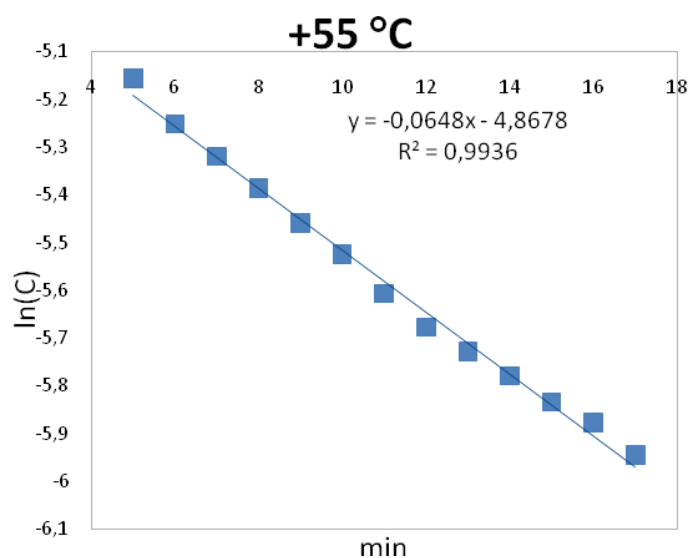


Figure SI28. Ln(C)/time plot for the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with PhCHO (10 eq.) at +55.0 °C.

$$k(+55.0\text{ }^\circ\text{C}) = (6.48 \pm 0.16) * 10^{-2} \text{ min}^{-1} = (1.08 \pm 0.03) * 10^{-3} \text{ s}^{-1}$$

$$k^{\text{II}}(+55.0\text{ }^\circ\text{C}) = k_{\text{H}}(+55.0\text{ }^\circ\text{C})/C(\text{PhCHO}) = (2.04 \pm 0.09) * 10^{-3} \text{ M}^{-1} * \text{s}^{-1}$$

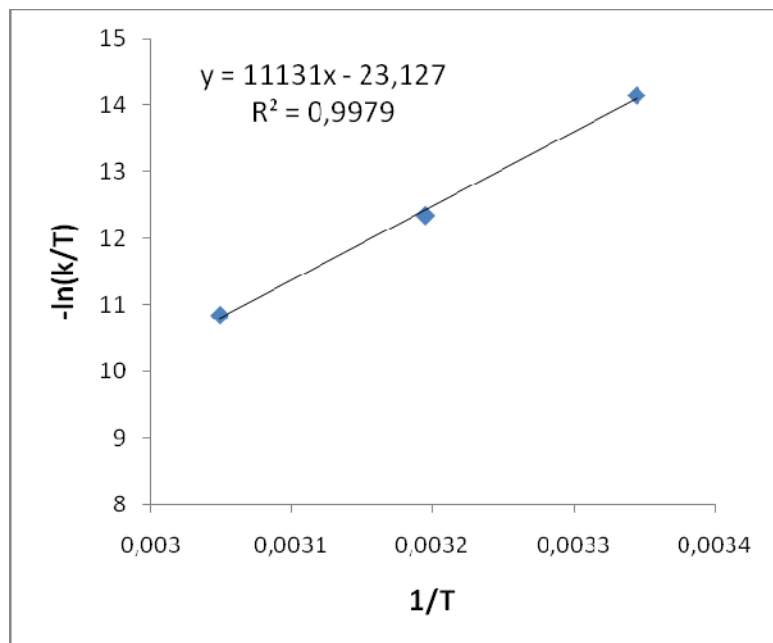


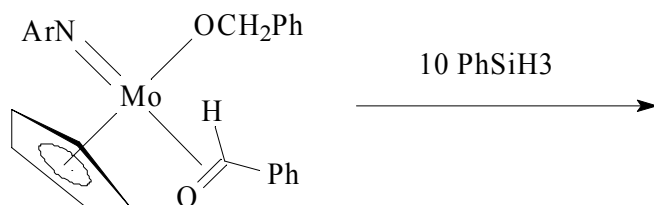
Figure SI29. Eyring plot for the reaction of (Cp)(ArN)Mo(OCH₂Ph)(PMe₃) with PhCHO (10 eq.)

$$-\ln\left(\frac{k}{T}\right) = \frac{\Delta H^\ddagger}{RT} - \left(23.8 + \frac{\Delta S^\ddagger}{R}\right)$$

$$\Delta S^\ddagger = -(5.6 \pm 13.6) \text{ J/(K}\cdot\text{mol)}$$

$$\Delta H^\ddagger = (9.25 \pm 0.43) * 10^1 \text{ kJ/mol}$$

Reaction of (Cp)(ArN)Mo(OCH₂Ph)(PhCHO) with excess of PhCHO



Phenylsilane (0.0257 g, 0.242 mmol) was added to a solution of (Cp)(ArN)Mo(H)(PMe₃) (0.053 g, 0.010 mmol) in C₆D₆ (0.65 ml). The reaction afforded (Cp)(ArN)Mo(OCH₂Ph)(PhCHO) in an hour at room temperature. All volatiles were evaporated, and the residue was dissolved in C₆D₆

(0.65 mL). Phenylsilane (0.013 g, 0.121 mmol) was added to the solution, and the reaction was monitored by ^1H NMR. The reaction did not afford an individual product. The reaction mixture contained some amounts of $(\text{Cp})(\text{ArN})\text{Mo}(\text{H})_2(\text{SiH}_2\text{Ph})$ and $(\text{Cp})(\text{ArN})\text{Mo}(\text{H})(\text{SiH}_2\text{Ph})(\text{H})$ distinguished by their characteristic peaks of the Mo-H protons, -0.51 ppm (d, $J = 4.9$ Hz, 1H) and 0.59 ppm (d, $J = 4.9$ Hz, 1H) and -1.30 ppm (s, 2H) respectively.

The kinetic data show the overall process of the reaction. The changes in the $(\text{Cp})(\text{ArN})\text{Mo}(\text{OCH}_2\text{Ph})(\text{PhCHO})$ concentration over the time have been linearized in the logarithmic coordinates.

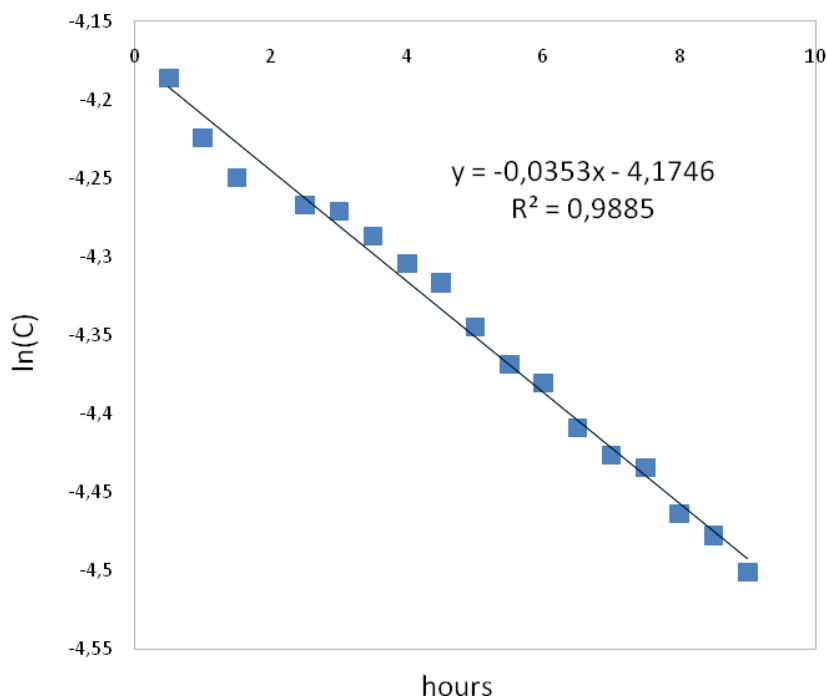
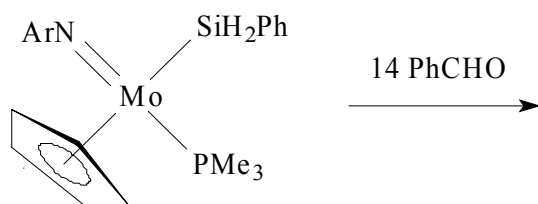


Figure SI30. Ln(C)/time plot for the reaction of $(\text{Cp})(\text{ArN})\text{Mo}(\text{OCH}_2\text{Ph})(\text{PhCHO})$ with PhSiH_3 (10 eq.).

$$k(+26.0\text{ }^\circ\text{C}) = (3.53 \pm 0.10) \cdot 10^{-2} \text{ h}^{-1} = (9.8 \pm 0.3) \cdot 10^{-6} \text{ s}^{-1}$$

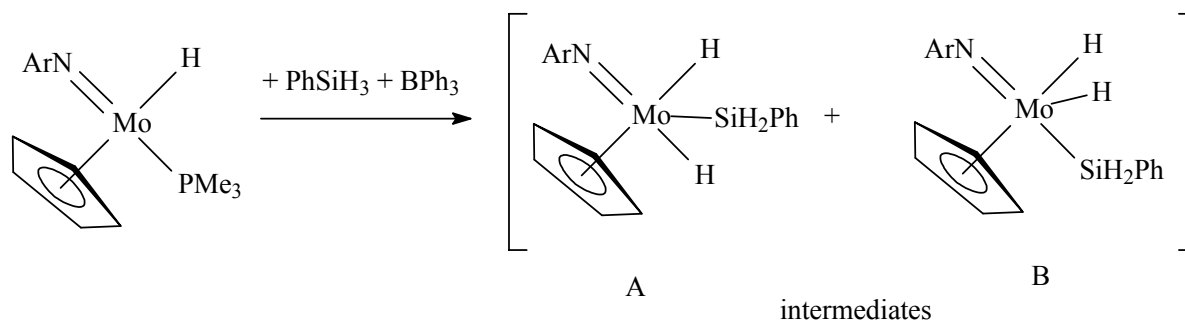
$$k^{\text{II}}(+26.0\text{ }^\circ\text{C}) = k_{\text{H}}(+26.0\text{ }^\circ\text{C})/C(\text{PhSiH}_3) = (1.08 \pm 0.03) \cdot 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

Reaction of (Cp)(ArN)Mo(SiH₂Ph)(PhCHO) with excess of PhCHO



Benzaldehyde (0.0143 g, 0.1347 mmol) was added to a solution of (Cp)(ArN)Mo(SiH₂Ph)(PMe₃) (0.005 g, 0.0096 mmol) in C₆D₆ (0.65 mL). No reaction was observed after one day at room temperature.

Reaction of (Cp)(ArN)Mo(H)(PMe₃) with PhSiH₃ (1 eq.) and Ph₃B (1 eq.)



Phenylsilane (7.1 μ L, 6.23 mg, 0.057 mmol) and Ph₃B (0.0139 g, 0.057 mmol) were added to a solution of (Cp)(ArN)Mo(H)(PMe₃) (0.0238 g, 0.057 mmol) in C₆D₆ at room temperature. The formation of intermediates **A** and **B** was detected by NMR (Figure SI31).

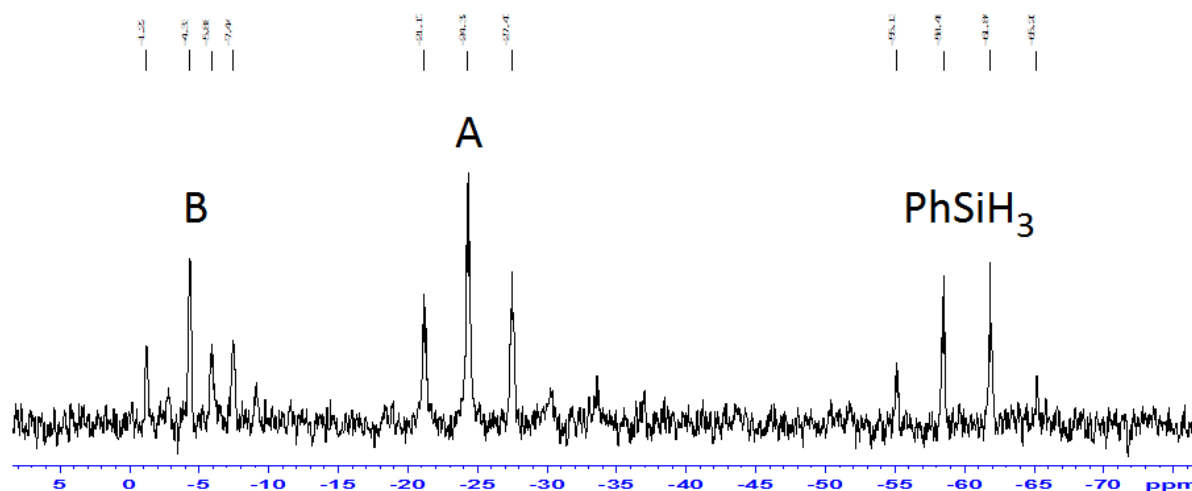
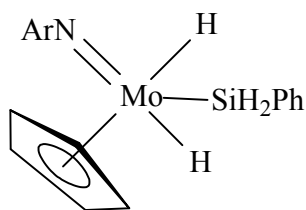


Figure SI31. ^{29}Si INEPT+ NMR spectrum of two isomers of $(\text{Cp})(\text{ArN})\text{Mo}(\text{H})_2(\text{SiH}_2\text{Ph})$ (**A** and **B**) were detected. Peaks have been assigned using ^1H - ^{29}Si HSQC and HMBS experiments.

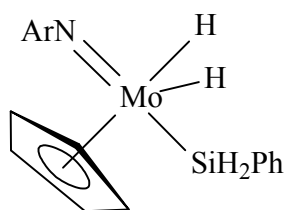
The intermediates were not stable and decomposed the next day.



$(\text{ArN})(\text{ArN})(\text{Cp})\text{Mo}(\text{H})(\text{SiH}_2\text{Ph})(\text{H})$, **A** – characteristic peaks only:

^1H -NMR (300 MHz; C_6D_6 ; 298K; δ , ppm): -1.30 (s, 2H, $\text{Mo}(\text{H})(\text{SiH}_2)(\text{H})$), 5.82 (s, 2H, SiH_2Ph).

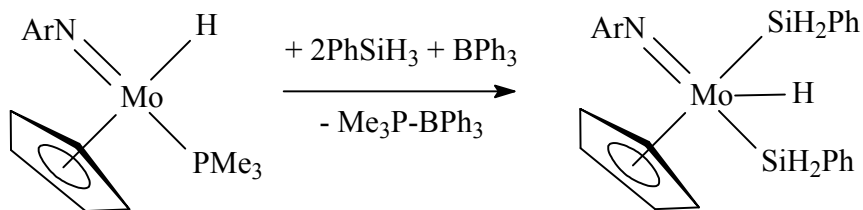
^{29}Si -NMR INEPT+ (300 MHz; C_6D_6 ; 298K; δ , ppm): -24.32 (tt, $^1J_{\text{Si-H}} = 188.2$ Hz, $^2J_{\text{Si-H}} = 6.9$ Hz, 1Si).



$(\text{ArN})(\text{Cp})\text{Mo}(\text{H})(\text{H})(\text{SiH}_2\text{Ph})$, **B** – characteristic peaks only:

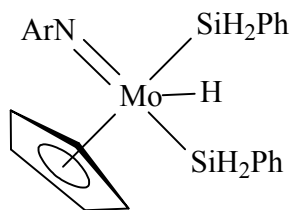
^1H -NMR (300 MHz; C_6D_6 ; 298K; δ , ppm): -0.52 (d, $^2J_{\text{H-H}} = 4.9$ Hz, 1H, Mo-H^a), 0.58 (d, $^2J_{\text{H-H}} = 4.9$ Hz, 1H, Mo-H^b). ^{29}Si -NMR INEPT+ (300 MHz; C_6D_6 ; 298K; δ , ppm): -4.33 (vt, $^1J_{\text{Si-H}} = 185.6$ Hz, 1Si).

Generation of $(\text{Cp})(\text{ArN})\text{Mo}(\text{H})(\text{SiH}_2\text{Ph})_2$.



Phenylsilane (0.400 g, 3.70 mmol) and Ph_3B (0.176 g, 0.726 mmol) were added to a solution of $(\text{Cp})(\text{ArN})\text{Mo}(\text{H})(\text{PMe}_3)$ (0.300 g, 0.726 mmol) in Et_2O . The reaction mixture was stirred for a week at room temperature until it was complete. All volatiles were removed in vacuum,

affording $(\text{Cp})(\text{ArN})\text{Mo}(\text{H})(\text{SiH}_2\text{Ph})_2$ (0.420 g, 76% by NMR) as a dark oil. The product was contaminated with Ph_2SiH_2 (~5%) and $(\text{Cp})(\text{ArN})\text{Mo}(\text{SiH}_2\text{Ph})(\text{PMe}_3)$ (~7-10%). All attempts to purify the compound by crystallization were unsuccessful.



$(\text{Cp})(\text{ArN})\text{Mo}(\text{SiH}_2\text{Ph})_2(\text{H})$ – characteristic peaks only:

^1H -NMR (300 MHz; C_6D_6 ; 298K; δ , ppm): 0.28 (m, 1H, Mo-*H*), 4.84 (s, 5H, *Cp*), 5.61 (dd, $^2J_{\text{H-H}} = 4.5$ Hz, $^3J_{\text{H-H}} = 2.1$ Hz, 2H, 2SiH^{*a*}HPh), 5.80 (dd, $^2J_{\text{H-H}} = 4.5$ Hz, $^3J_{\text{H-H}} = 2.1$ Hz, 2H, 2SiH^{*b*}HPh). ^{29}Si -NMR INEPT+ (300 MHz; C_6D_6 ; 298K; δ , ppm): -5.90 (t, $^1J_{\text{Si-H}} = 189.7$ Hz, 2Si).

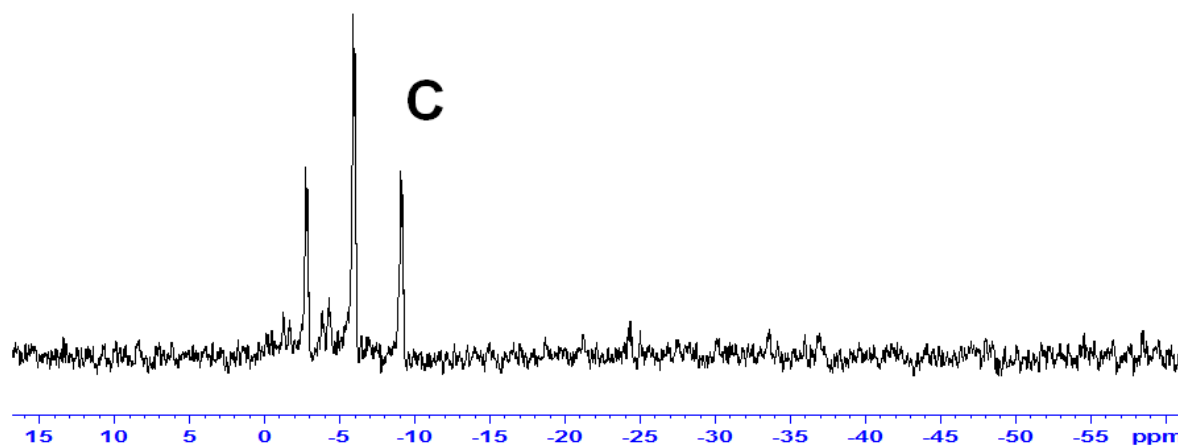


Figure SI32. ^{29}Si INEPT+ NMR spectrum of $(\text{Cp})(\text{ArN})\text{Mo}(\text{SiH}_2\text{Ph})_2(\text{H})$, C.

TABLES

Table SII. Kinetic parameters.

REACTION	Rate constant, <i>k</i>	ΔH^\ddagger , kJ/mol	ΔS^\ddagger , J/(mol*K)
(Cp)(ArN)Mo(H)(PMe ₃) + PMe ₃ , phosphine exchange	(2.89 ± 0.04)*10 ¹ s ⁻¹ (+12.0 °C) (4.29 ± 0.07)*10 ¹ s ⁻¹ (+22.0 °C) (6.22 ± 0.12)*10 ¹ s ⁻¹ (+32.0 °C) (8.56 ± 0.15)*10 ¹ s ⁻¹ (+42.0 °C)	(2.47±0.04)*10 ¹	-(1.30 ± 0.01)*10 ²
(Cp)(ArN)Mo(H)(PMe ₃) + PhCHO (1 eq) + PMe ₃ (10 eq) => (Cp)(ArN)Mo(OCH ₂ Ph)(PMe ₃)	(3.6 ± 0.1)*10 ⁻³ M ⁻¹ *s ⁻¹ (+26.0 °C) (1.25 ± 0.17)*10 ⁻² M ⁻¹ *s ⁻¹ (+40.0 °C) (2.44 ± 0.17)*10 ⁻² M ⁻¹ *s ⁻¹ (+50.0 °C) (4.17 ± 0.05)*10 ⁻² M ⁻¹ *s ⁻¹ (+60.0 °C)	(5.76 ± 0.36)*10 ¹	-(9.97 ± 1.14)*10 ¹
(Cp)(ArN)Mo(OCH ₂ Ph)(PMe ₃) + PhSiH ₃ (10 eq) => (Cp)(ArN)Mo(H)(PMe ₃) + (PhCH ₂ O) ₂ SiHPh	(1.09 ± 0.01)*10 ⁻³ M ⁻¹ *s ⁻¹ (+16.0 °C) (3.25 ± 0.02)*10 ⁻³ M ⁻¹ *s ⁻¹ (+26.0 °C) (6.78 ± 0.06)*10 ⁻³ M ⁻¹ *s ⁻¹ (+36.0 °C) (1.23 ± 0.09)*10 ⁻³ M ⁻¹ *s ⁻¹ (+46.0 °C)	(5.89 ± 0.49)*10 ¹	-(9.69 ± 1.6)*10 ¹
(Cp)(ArN)Mo(OCH ₂ Ph)(PMe ₃) + PhSiD ₃ (10 eq) => (Cp)(ArN)Mo(D)(PMe ₃) + (PhCH ₂ O) ₂ SiDPh	(1.48 ± 0.01)*10 ⁻³ M ⁻¹ *s ⁻¹ (+16.0 °C) (4.11 ± 0.01)*10 ⁻³ M ⁻¹ *s ⁻¹ (+26.0 °C) (6.05 ± 0.06)*10 ⁻³ M ⁻¹ *s ⁻¹ (+36.0 °C) (8.92 ± 0.20)*10 ⁻³ M ⁻¹ *s ⁻¹ (+46.0 °C)	(4.20 ± 0.76)*10 ¹	-(1.52 ± 0.25)*10 ²
(Cp)(ArN)Mo(H)(PMe ₃) + PhSiH ₃ (10 eq) => (Cp)(ArN)Mo(SiH ₂ Ph)(PMe ₃) + H ₂	(1.57 ± 0.01)*10 ⁻⁴ M ⁻¹ *s ⁻¹ (+25.0 °C) (4.54 ± 0.01)*10 ⁻⁴ M ⁻¹ *s ⁻¹ (+35.0 °C) (9.61 ± 0.17)*10 ⁻⁴ M ⁻¹ *s ⁻¹ (+45.0 °C) (2.04 ± 0.09)*10 ⁻³ M ⁻¹ *s ⁻¹ (+55.0 °C)	(6.61 ± 0.31)*10 ¹	-(9.58 ± 1.00)*10 ¹
(Cp)(ArN)Mo(H)(PMe ₃) + PhSiD ₃ (5 eq) => (Cp)(ArN)Mo(SiD ₂ Ph)(PMe ₃) + HD	(1.65 ± 0.01)*10 ⁻⁴ M ⁻¹ *s ⁻¹ (+26.0 °C)	-	-
(Cp)(ArN)Mo(OCH ₂ Ph)(PMe ₃) + PhCHO (10 eq) => (Cp)(ArN)Mo(OCH ₂ Ph)(PhCHO)	(2.15 ± 0.02)*10 ⁻⁴ M ⁻¹ *s ⁻¹ (+26.0 °C) (1.36 ± 0.03)*10 ⁻³ M ⁻¹ *s ⁻¹ (+40.0 °C) (6.35 ± 0.02)*10 ⁻³ M ⁻¹ *s ⁻¹ (+55.0 °C)	(9.25 ± 0.43)*10 ¹	-(5.6 ± 13.6)
(Cp)(ArN)Mo(OCH ₂ Ph)(PhCHO) + PhSiH ₃ => N/A	(1.08 ± 0.03)*10 ⁻⁴ M ⁻¹ *s ⁻¹ (+26.0 °C)	-	-

Table SI2. Hydrosilylation of PhCHO with PhSiH₃

CATALYST	Products	Reactions conditions	Yield, according to ¹ H-NMR	Catalyst mol, %	Turnover number (TON)
(Cp)(ArN)Mo(H)(PMe ₃)	PhCH ₂ OSiH ₂ Ph (PhCH ₂ O) ₂ SiHPh	7 h	21% 79% (Σ100%)	5	20
Cp)(ArN)Mo(OCH ₂ Ph)(PMe ₃)	PhCH ₂ OSiH ₂ Ph (PhCH ₂ O) ₂ SiHPh	7 h	38% 62% (Σ100%)	5	20
(Cp)(ArN)Mo(OCH ₂ Ph)(PhCHO)	PhCH ₂ OSiH ₂ Ph (PhCH ₂ O) ₂ SiHPh	12 h, RT	23% 77% (Σ100%)	5	20
(Cp)(ArN)Mo(SiH ₂ Ph)(PMe ₃)	PhCH ₂ OSiH ₂ Ph (PhCH ₂ O) ₂ SiHPh	3 d, RT	22% 32% (Σ54%)	5	11

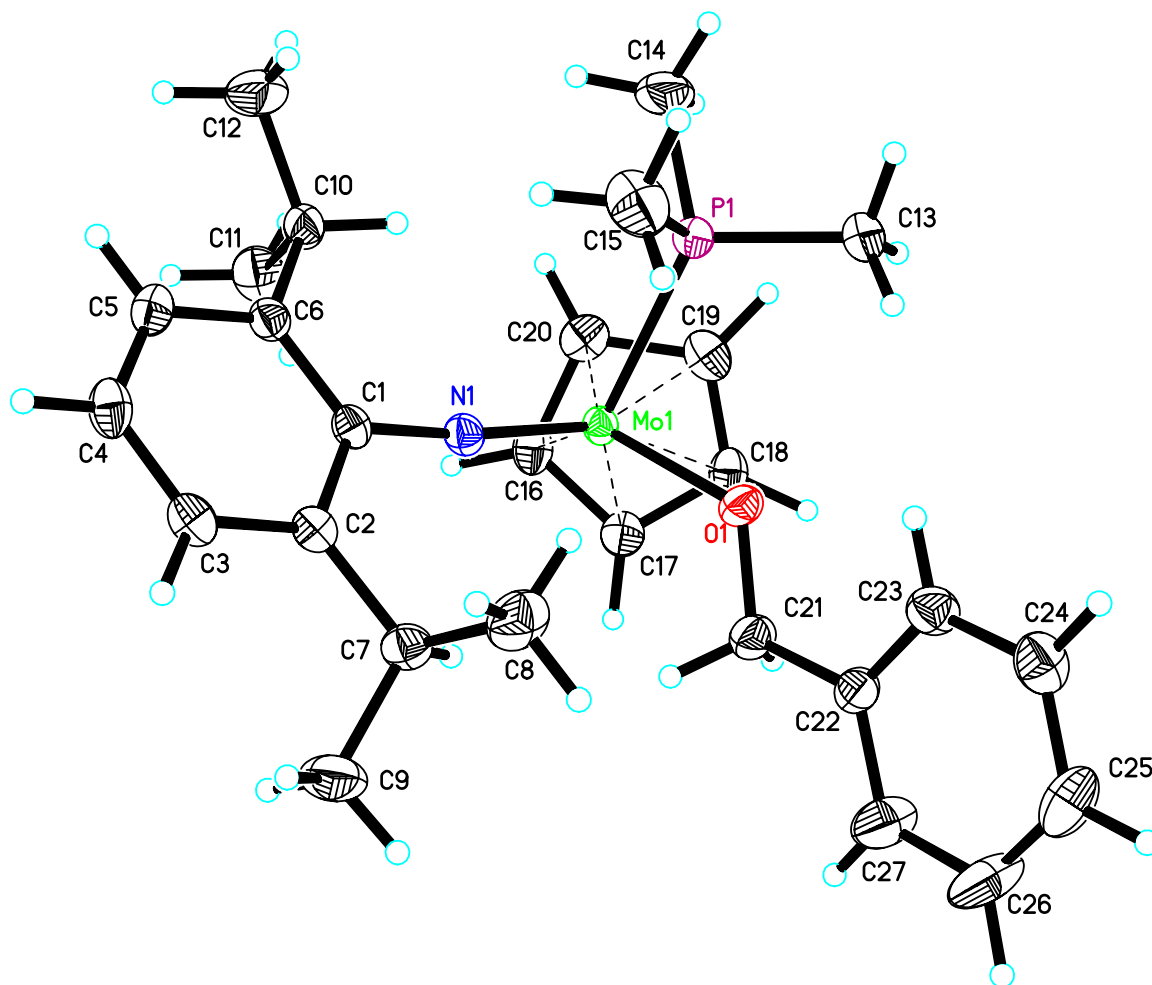


Figure SI33. Molecular structure of $(\text{Cp})(\text{ArN})\text{Mo}(\text{OCH}_2\text{Ph})(\text{PMe}_3)$

Computational Details.

Density Functional Theory (DFT) calculations have been performed using the *Gaussian 03* program.¹ In all calculations, the spin-restricted method was employed. Wave function stability calculations were performed to confirm that the calculated wave functions corresponded to the electronic ground state. The structures of all species were optimized using the B3LYP exchange-correlation (XC) functional^{2,3} with the all-electron, mixed basis set (DZVP⁴ on Mo and TZVP⁵ on all other atoms). Tight SCF convergence criteria (10^{-8} a.u.) were used for all calculations. Harmonic frequency calculations with the analytic evaluation of force gradients (OPT=CalcAll) were used to determine the nature of the stationary points. Intrinsic reaction coordinate (IRC)⁶ calculations were used to confirm the reaction pathways through transition states (TSs) for all reactions. Free energies of species were evaluated at 298K and 1 atm.

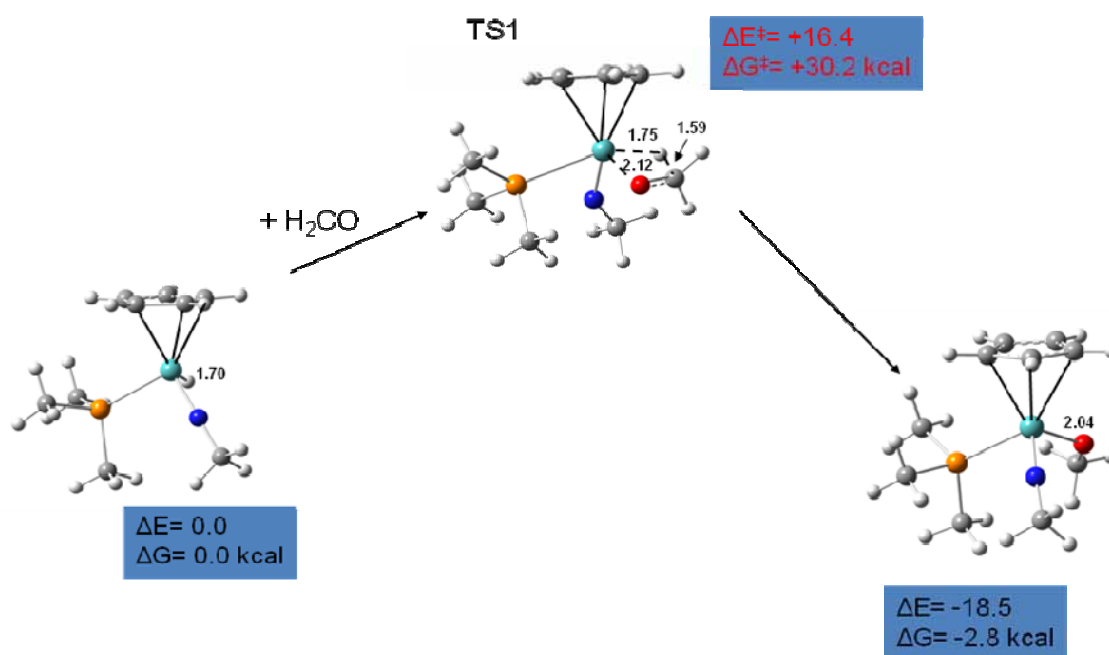


Figure SI34. Computed reaction pathways for the formation of Cp(MeN)Mo(PMe₃)(OCH₃) (at 298 K)

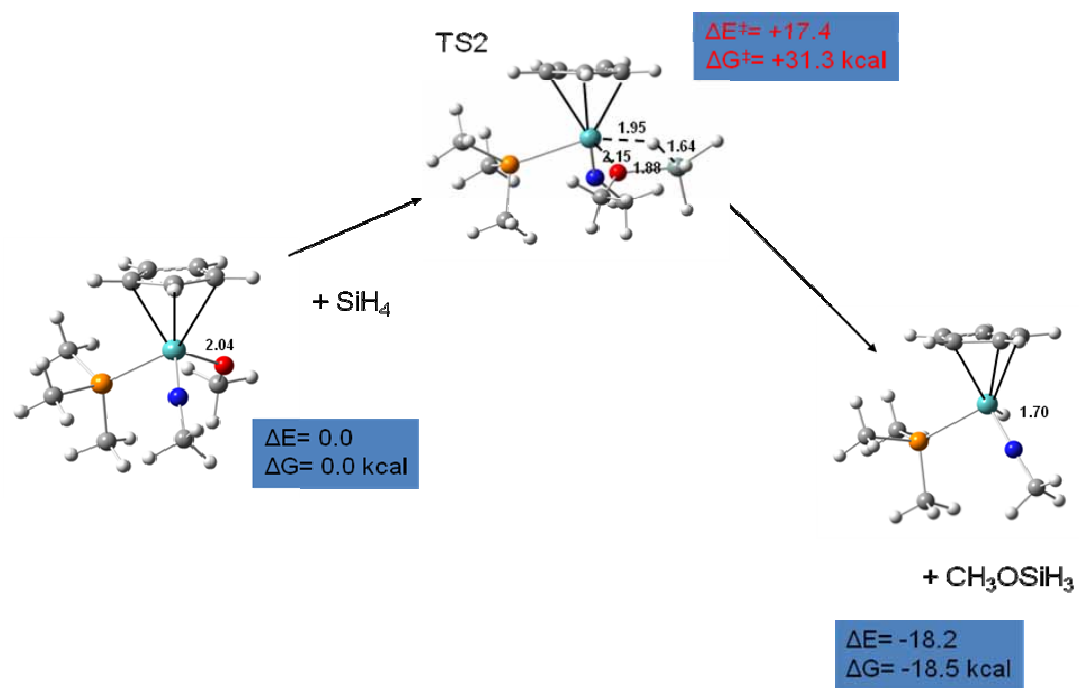


Figure SI35. Computed reaction pathways for the addition of SiH_4 to $\text{Cp}(\text{MeN})\text{Mo}(\text{PMe}_3)(\text{OCH}_3)$ (at 298 K)

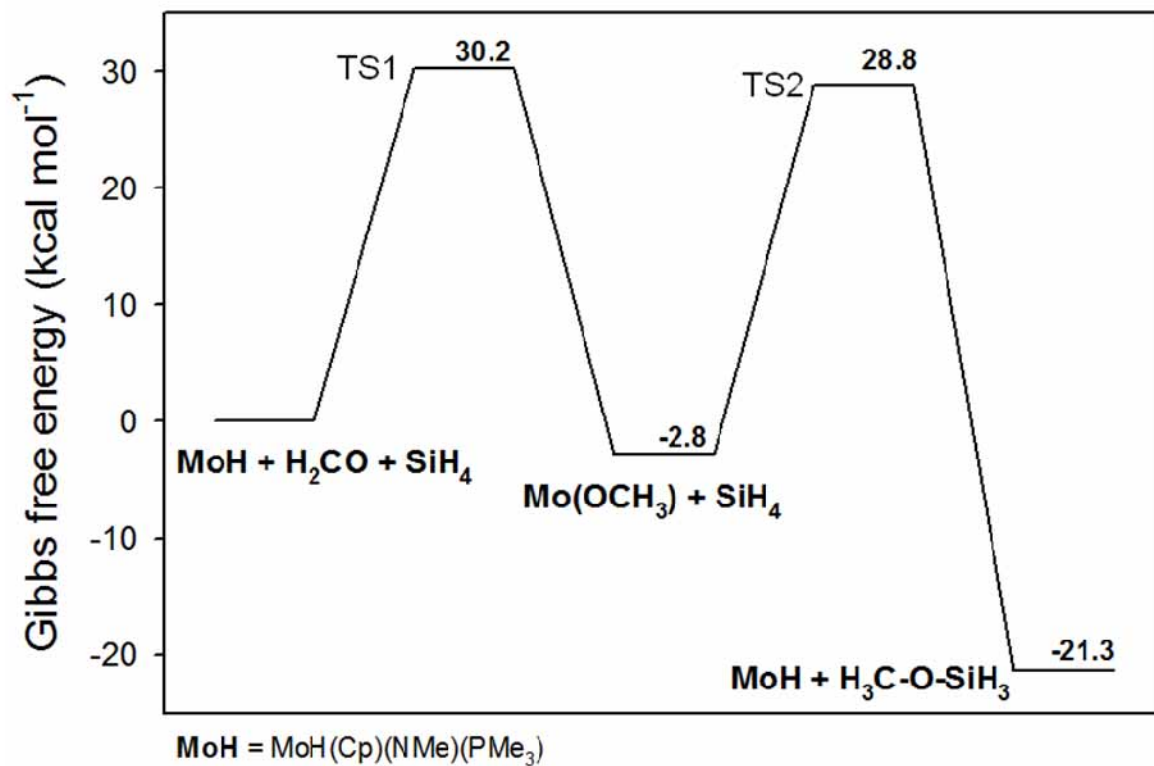


Figure SI36. Energy profile for the addition of SiH₄ to H₂C=O mediated by Cp(MeN)Mo(PMe₃)(H) (at 298 K)

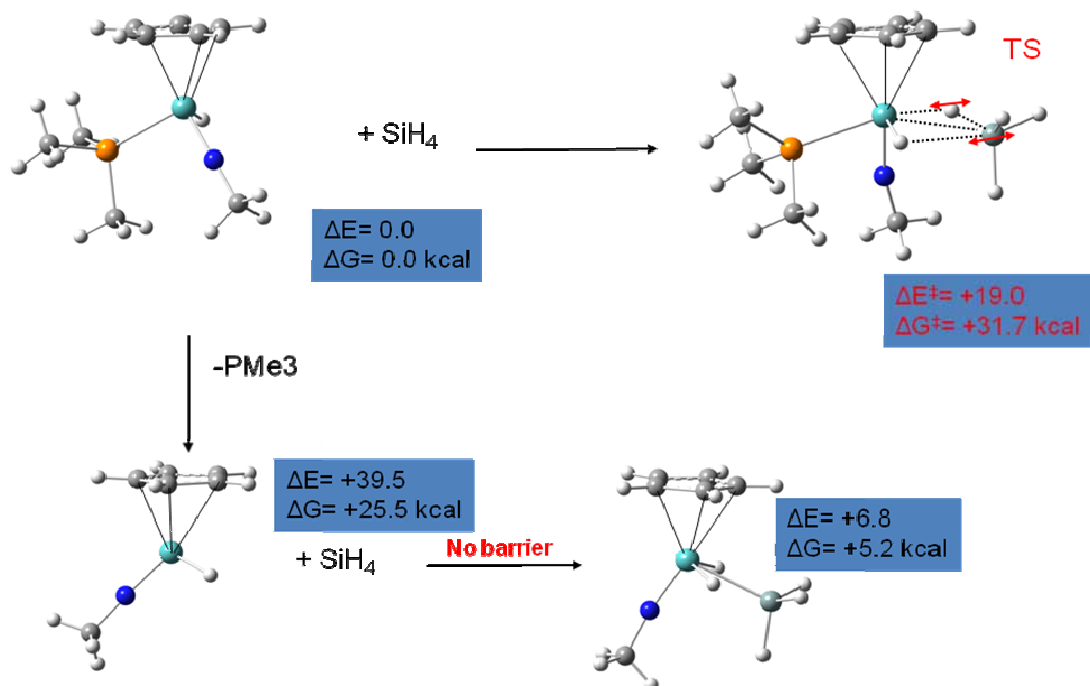


Figure SI37. Computed reaction pathways for the formation of Cp(MeN)MoH₂SiH₃ (at 298 K)

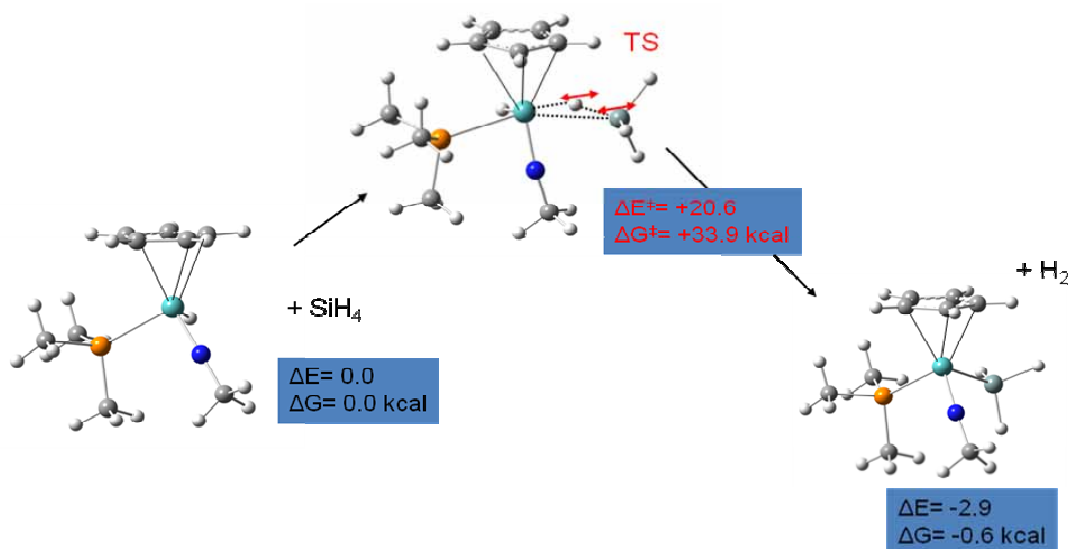


Figure SI38. Computed reaction pathway for the formation of Cp(MeN)Mo(PMe₃)(SiH₃) (at 298 K)

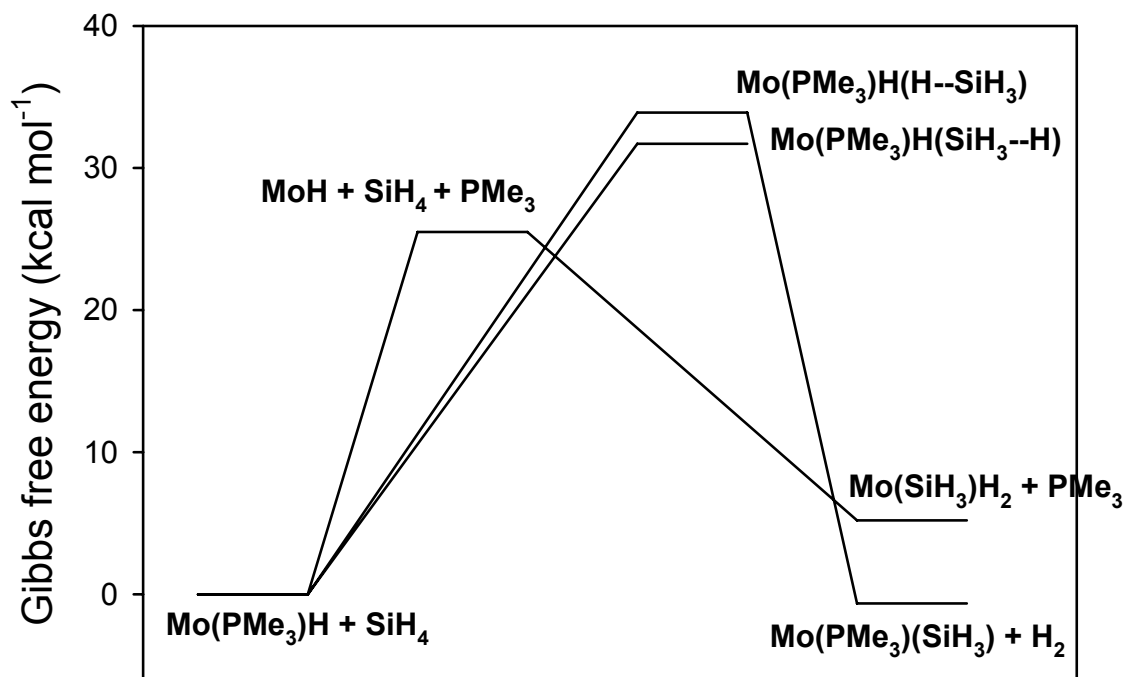


Figure SI39. Energy profile for the reactions of SiH_4 with $\text{Cp}(\text{MeN})\text{Mo}(\text{PMe}_3)(\text{H})$ (at 298 K)

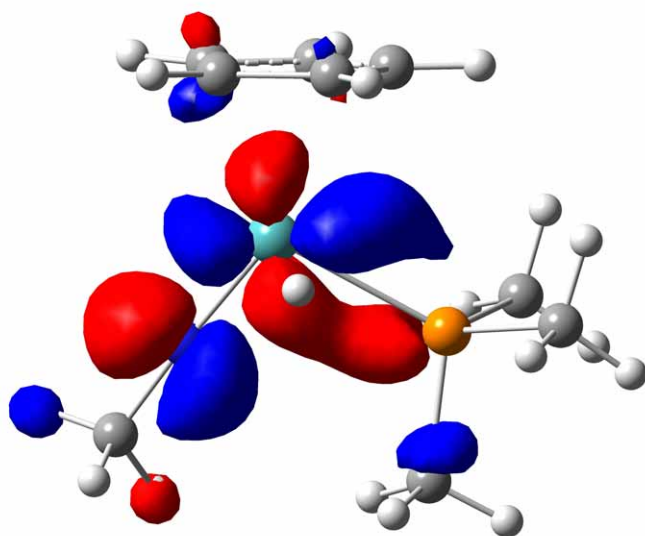


Figure SI40. The lowest unoccupied molecular orbital (LUMO) of $\text{Cp}(\text{MeN})\text{Mo}(\text{PMe}_3)(\text{H})$.

Crystallographic study

A crystal of **3** was coated with polyperfluoro oil and mounted on the Bruker Smart APEX three-circle diffractometer with CCD area detector at 123 K.⁷ The crystallographic data and characteristics of the structure solution and refinement are given in Table SI3. The Bruker SAINT program⁸ was used for data reduction. An absorption correction based on measurements of equivalent reflections was applied (SADABS).⁹ The structures were solved by direct methods¹⁰ and refined by full-matrix least squares procedures, using $\omega(|F_o|^2 - |F_c|^2)|^2$ as the refined function. All non-hydrogen atoms were found from the electron density map and refined with anisotropic thermal parameters, whereas all hydrogen atoms were calculate geometrically and refined using the “riding” model.

Table SI3. Crystal data, data collection, structure solution and refinement parameters

Empirical formula	C ₂₇ H ₃₈ MoNOP
Formula weight	519.49
Colour, habit	black plate
Crystal size, mm	0.38 × 0.32 × 0.04
Crystal system, space group	Triclinic, P $\bar{1}$
<i>a</i> , Å	9.9782(7)
<i>b</i> , Å	10.3691(7)
<i>c</i> , Å	14.1074(10)
α , deg	108.5940(10)
β , deg	96.9990(10)
γ , deg	105.3790(10)
<i>V</i> , Å ³	1299.42(16)
<i>Z</i>	2

d , g/cm ³	1.328
μ , mm ⁻¹	0.584
$F(000)$	544
Diffractometer	Bruker SMART-APEX-2
Temperature, K	123(2)
Radiation, (λ , Å)	graphite monochromatized MoK $_{\alpha}$ (0.71073)
Scan mode	ω
Step per scan, deg	0.3
Scan time, sec	15
Theta range, deg	1.56 to 30.00
Limiting indices	-14 $\leq h \leq 12$, -11 $\leq k \leq 14$, -19 $\leq l \leq 19$
Reflections collected / unique ?	16642 / 7517 [R(int) = 0.0238]
Completeness, %	99.2
Reflections with $I > 2\sigma(I)$	6610
Absorption correction	Semi-empirical from equivalents
Min. and Max. transmission	0.8085 and 0.9770
Solution method	Direct methods (SHELXS-97, G.M.Sheldrick, Acta Cryst., A46, 1990, 467-473)
Refinement method	Full-matrix least-squares on F^2 (SHELXL-97, Program for the Refinement of Crystal Structures. University of Gottingen, 1997)
Weighting scheme	$W = 1 / [\sigma^2(F_o^2) + (0.0372 P)^2 + 0.17 P]$
Hydrogen treatment	All H atoms were found from diff. Fourier synthesis and refined isotropically
Data / restraints / parameters	7517 / 0 / 280
GOOF on F^2	1.074
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0289$, $wR_2 = 0.0713$
R indices (all data)	$R_1 = 0.0358$, $wR_2 = 0.0740$
Largest diff. peak and hole, e/Å ³	1.016 and -0.383

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