Supporting Information

to the article

Imido-hydrido Complexes of Mo(IV): Catalysis and Mechanistic Aspects of Hydroboration Reactions

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Experimental details

All manipulations were carried out under nitrogen atmosphere, using either conventional Schlenk techniques or an inert atmosphere MBraun glovebox. Dry solvents (THF, ether, hexane, dichloromethane, toluene, acetonitrile) were obtained using Innovative Technologies Pure Solv. purification system. DME was dried over sodium/benzophenone, ethyl acetate was dried over CaH₂. Benzene-d₆ and toluene-d₈ were dried by distillation over K/Na alloy. NMR spectra were obtained with Bruker DPX-300 (¹H: 300MHz; ¹³C: 75.5 MHz; ³¹P: 121.5 MHz; ¹¹B: 96.3 MHz) and Bruker DPX-600 (¹H: 600MHz; ²D: 92.1 MHz; ¹³C: 151 MHz; ³¹P: 243 MHz; ¹¹B: 192.6 MHz) spectrometers. IR spectra were measured on an ATI Mattson FTIR spectrometer. Elemental analyses were performed in “ANALEST” laboratories (University of Toronto). Organic substrates were purchased from Sigma-Aldrich and used without further purification. HBCat was additionally purified by distillation before use. Preparation and catalytic reactivity of (ArN)Mo(H)(Cl)(PMe₃)₃ (1) was described previously. Preparation of (ArN)Mo(Cl)(N=CHPh)(PMe₃)₃ (3) was reported in previously. Characterization of (ArN)MoCl₂(PMe₃)₃,¹⁸³ (ArN)MoCl(OCH₂Ph)(PMe₃)₁ and (ArN)Mo(Cl)(OEt)(PMe₃)₁ was reported previously. All catalytic, NMR scale reactions and kinetic experiments were done under nitrogen atmosphere using NMR tubes equipped with Teflon valves. The structures and yields of all hydroboration products were determined by NMR using tetramethylsilane as an internal standard.

Reaction of (ArN)Mo(H)(Cl)(PMe₃)₃ (1) with MeCN

A. Acetonitrile (1.1 µl, 0.02 mmol) was added in one portion at room temperature to a solution of 1 (10.4 mg, 0.02 mmol) in 0.6 ml of C₆D₆ in an NMR tube. No visual changes were observed after CH₃CN addition. The mixture was left at room temperature for 5 min. and then the reaction was monitored by NMR analysis for 24 h, showing full conversion of the starting material to give (ArN)Mo(Cl)(N=CHMe)(PMe₃)₂ (7) as a mixture of cis- and trans-isomers (ratio 1:1.6, according to the ³¹P NMR spectrum).

B. A solution of 1 (22.7 mg, 0.04 mmol) and CH₃CN (5.0 µl, 0.1 mmol) in 0.6 ml of C₆D₆ was added in one portion at room temperature to a solid BPh₃ (9.7 mg, 0.04 mmol). Immediate formation of a white precipitate of Ph₃B·PMe₃ was observed. The mixture was
transferred to an NMR tube and left at room temperature for 5 min. NMR analysis showed quantitative formation of 7 (1:1.3 mixture isomers, according to the $^{31}$P NMR spectrum). The mixture was filtered, all volatiles were removed under vacuum, and the residue was dried and extracted with 2.0 ml of hexanes. The solvent was removed under vacuum to give a brown oily substance (13.7 mg, 68%). All attempts to isolate complex 7 in the analytically pure form by recrystallisation were unsuccessful and only led to an oily material.

**Major isomer of 7**: $^1$H NMR (300 MHz; C$_6$D$_6$; δ, ppm): 6.86-7.13 (m, NAr aromatic protons overlapping with minor isomer); 6.15 (m, $^3$J$_{H-H}$ = 5.1 Hz, 1H, N=C(H)CH$_3$, found by $^1$H-$^1$C HMBC NMR); 4.12 (sept, $^3$J$_{H-H}$ = 6.9 Hz, 2H, 2 CH, NAr); 2.37 (ddd, $^3$J$_{H-H}$ = 5.1 Hz, $^3$J$_{H-P}$ = 1.5 Hz and 2.7 Hz, 3H, N=C(H)CH$_3$, found by $^1$H-$^1$C HMBC NMR); 1.29 (d, $^3$J$_{H-H}$ = 6.9 Hz, 12H, 4 CH$_3$, NAr); 1.16 (dd, $^2$J$_{H-P}$ = 7.2 Hz, $^4$J$_{H-P}$ = 3.6 Hz, 18H, 2 PMe$_3$, both isomers). $^1$H{$^{31}$P} NMR (300 MHz; C$_6$D$_6$; δ, ppm; selected resonances): 6.15 (q, $^3$J$_{H-H}$ = 5.1 Hz, 1H, N=C(H)CH$_3$); 2.37 (d, $^3$J$_{H-H}$ = 5.1 Hz, 3H, N=C(H)CH$_3$); 1.16 (s, 18H, 2 PMe$_3$, both isomers). $^{31}$P{$^1$H} NMR (121.5 MHz; C$_6$D$_6$; δ, ppm): -0.3 (s, 2 PMe$_3$, both isomers).

$^{31}$P NMR (121.5 MHz; C$_6$D$_6$; δ, ppm): -0.2 (br s, PMe$_3$, both isomers).

$^{13}$C{$^1$H} NMR (75.5 MHz, C$_6$D$_6$; both isomers; δ, ppm): 154.1, 147.1 (s, aromatic NAr); 146.6 (br s, N=C(H)CH$_3$, minor isomer, found by $^1$H-$^1$C HSQC NMR); 145.4 (d, $^3$J$_{C-P}$ = 11.3 Hz, N=C(H)CH$_3$, major isomer, found by $^1$H-$^1$C HSQC NMR); 125.7, 124.9, 123.6, 123.2, 115.9 (s, aromatic NAr); 27.9 (s, CH, NAr, major isomer); 27.7 (s, CH, NAr, minor isomer); 23.72 (s, CH$_3$, NAr, minor isomer); 23.67 (s, CH$_3$, NAr, major isomer); 23.0 (s, N=C(H)CH$_3$, major isomer); 19.1 (br s, N=C(H)CH$_3$, minor isomer); 14.0 (dd, $^3$J$_{C-P}$ = 11.3 Hz, $^1$J$_{C-P}$ = 22.6 Hz, 2 PMe$_3$, both isomers).
Hz, 2 PMe₃, minor isomer); 13.6 (dd, ²JC-P = 11.3 Hz, ¹JC-P = 21.9 Hz, 2PMe₃, major isomer).

**NMR scale reaction of (ArN)Mo(Cl)(N=CHMe)(PMe₃)₂ (7) with PhCN**

(ArN)Mo(Cl)(N=CHMe)(PMe₃)₂ (7) was generated in an NMR tube in 0.6 ml of C₆D₆ from the reaction of 1 (10.4 mg, 0.02 mmol) and acetonitrile (1.1 µl, 0.02 mmol) (see the procedure above). All volatiles were removed under vacuum and the residue was redissovled in 0.6 ml of C₆D₆. Benzonitrile (10.0 µl, 0.098 mmol) was added in one portion to the solution. The reaction mixture was left at room temperature for 24 h. NMR analysis showed full conversion of 7, evolution of one equivalent of CH₃CN, and formation of (ArN)Mo(Cl)(N=CHPh)(PMe₃)₂ (3).²

**NMR scale reaction of (ArN)Mo(Cl)(N=CHPh)(PMe₃)₂ (3) with benzaldehyde**

Benzaldehyde (2.6 µl, 0.026 mmol) and PMe₃ (2.7 µl, 0.026 mmol) were added at room temperature to a solution of 3 (10.5 mg, 0.019 mmol) in 0.6 ml of C₆D₆ in an NMR tube. No visual changes were observed and the reaction mixture was left at room temperature for two days. NMR analysis showed full conversion of the starting material and formation of PhCN and (ArN)Mo(Cl)(OBn)(PMe₃)₃ (12).¹ Traces of (ArN)MoCl₂(PMe₃)₃¹b were also observed by NMR.

**NMR scale reaction of (ArN)Mo(H)(Cl)(PMe₃)₃ (1) with trans-3-pentenenitrile**

Trans-3-pentenenitrile (5.1 µl, 0.054 mmol) was added in one portion at room temperature to a solution of 1 (28.7 mg, 0.054 mmol) in 0.6 ml of C₆D₆ in an NMR tube. The reaction progress was monitored by NMR analysis at room temperature for 3 days showing full conversion of 1 and formation of a mixture of the insertion product 8 (mixture of two isomers) and (ArN)MoCl₂(PMe₃)₃¹b in the ratio 1.3/1, according to ³¹P NMR. After 3 days all volatiles were removed under vacuum to leave an oily residue which was dried under vacuum and redissovled in C₆D₆ for NMR analysis. All attempts to isolate complex 8 in analytically pure form by recrystallisation were unsuccessful and led to the formation of an oily material. Major isomer of 8: ¹H NMR (600 MHz; C₆D₆; δ, ppm): 7.11-7.24 (m, aromatic protons overlapping with the signals of minor isomer); 7.09 (dt, ⁴JH-P = 3.1 Hz, ³JH-H = 8.2 Hz,
1H, N=CH): 6.65 (dd, $^3J_{H-H} = 8.2$ and 15.7 Hz, 1H, N=CH-CH); 5.28 (dt, $^3J_{H-H} = 7.2$ and 15.7 Hz, 1H, N=CH-CH=CH); 4.28 (sept, $^3J_{H-H} = 7.0$ Hz, 2H, 2 CH, NAr); 2.60 (dq, $^3J_{H-H} = 7.2$ Hz, 2H, CH=CHCH$_2$CH$_3$); 1.26 (vt, $^3J_{H-P} = 7.6$ Hz; 18H, 2 PMe$_3$); 1.18 (t, $^3J_{H-H} = 7.2$ Hz, 3H, CH=CHCH$_2$CH$_3$).

Minor isomer of 8: $^1$H NMR (600 MHz; C$_6$D$_6$; $\delta$, ppm): 8.35 (dt, $^4J_{H-P} = 3.5$ Hz, 3J$_{H-H} = 8.8$ Hz, 1H, N=CH); 7.11-7.24 (m, aromatic protons overlapping with the signals of major isomer); 6.51 (dd, $^3J_{H-H} = 8.8$ and 15.5 Hz, 1H, N=CH-CH); 5.62 (dt, $^3J_{H-H} = 7.2$ and 15.5 Hz, 1H, N=CH-CH=CH); 4.48 (sept, $^3J_{H-H} = 6.9$ Hz, 2H, 2 CH, NAr); 2.60 (dq, $^3J_{H-H} = 7.2$ Hz, 2H, CH=CHCH$_2$CH$_3$); 1.46 (d, $^3J_{H-H} = 6.9$ Hz, 12H, 4 CH$_3$, NAr); 1.26 (vt, $^2J_{H-P} = 7.6$ Hz; 18H, 2 PMe$_3$); 1.18 (t, $^3J_{H-H} = 7.2$ Hz, 3H, CH=CHCH$_2$CH$_3$).

NMR scale reaction of (ArN)Mo(H)(Cl)(PMe$_3$)$_3$(1) with 4-acetylbenzonitrile

A solution of 4-acetylbenzonitrile (5.4 mg, 0.037 mmol) in 0.6 ml of C$_6$D$_6$ was added in one portion at room temperature to 1 (19.9 mg, 0.037 mmol). The colour of the reaction mixture turned to red almost immediately and the mixture was transferred to an NMR tube. The reaction was monitored by NMR spectroscopy for 1.5 h, showing complete conversion of the starting material and formation of a difficult-to-separate mixture of methylenamide complex 9 and (ArN)MoCl$_2$(PMe$_3$)$_3$ in the ratio 6:1, according to $^{31}$P NMR. According to NMR, the carbonyl moiety remained unreacted. All attempts to purify complex 9 by recrystallisation were unsuccessful and resulted in a mixture of 9 and (ArN)MoCl$_2$(PMe$_3$)$_3$.

9: $^1$H NMR (600 MHz; C$_6$D$_6$; $\delta$, ppm): 7.95 (d, $^3J_{H-H} = 8.5$ Hz, 2H, o-H, 4-
CH₃C(O)C₆H₄); 7.26 (t, J_H,P = 2.5 Hz, 1H, N=CH, found by ¹H-³¹P HSQC NMR); 7.15 (m, obscured by the resonance of C₆D₆, 2H, m-H, 4-CH₃C(O)C₆H₄); 7.04-7.09 (m, 3H, NAr); 4.19 (sept, J_H-H = 6.9 Hz, 2H, 2 CH, NAr); 2.22 (s, 3H, 4-CH₃C(O)C₆H₄); 1.31 (d, J_H=CH = 8.6 Hz, 9H, PMe₃); 1.36 (d, J_H-P = 8.9 Hz, 9H, PMe₃); 1.31 (m, 12H, 4 CH₃, NAr). ³¹P{¹H} NMR (243 MHz; C₆D₆; δ, ppm): -2.36 (d, J_P-P = 98.8 Hz, PMe₃); -4.18 (d, J_P-P = 98.8 Hz, PMe₃). ¹³C{¹H} NMR (151 MHz; C₆D₆; δ, ppm): 153.8, 150.3, 146.6, 144.1, 126.3, 124.7, 123.0 (aromatic carbons of CPh and NAr); 126.4 (s, CN) 46.5 (d, J_C-P = 8.9 Hz, η²-CH₂=CHCN); 31.8 (d, J_C-P = 7.4 Hz, η²-CH₂=CHCN); 27.0 (s, CH, NAr); 25.2 (s, CH₂, NAr); 17.5 (d, J_C-P = 27.5 Hz, PMe₃); 16.3 (d, J_C-P = 26.9 Hz, PMe₃).

NMR scale reaction of (ArN)Mo(H)(Cl)(PMe₃)₃ (1) with acrylonitrile

Acrylonitrile (2.9 µl, 0.044 mmol) was added in one portion at room temperature to a solution of 1 (23.6 mg, 0.044 mmol) in 0.6 ml of C₆D₆ in an NMR tube. Immediately after the nitrile addition, the colour of the mixture changed to a different tint of brown. The reaction mixture was left at room temperature for 1h 20 min showing (by NMR) 56% conversion of the starting material and formation of trans-(ArN)Mo(H)(Cl)(η²-CH₂=CHCN)(PMe₃)₂ (10) in a mixture with (ArN)MoCl₂(PMe₃)₃ in the 1/1 ratio, according to ³¹P NMR. No further conversion of 1 was observed by NMR in the next 2 days. All attempts to purify complex 10 by recrystallisation were unsuccessful and resulted in a mixture of 10 and (ArN)MoCl₂(PMe₃)₃.

10: ¹H NMR (600 MHz; C₆D₆; δ, ppm): 6.90-7.21 (m, 8H, CPh and NAr); 6.28 (dd, J_H-P = 33.8 and 47.0 Hz, 1H, MoH); 4.24 (m, 2H, 2 CH, NAr); 2.87 (m, 1H, η²-C₂H₃CN); 2.51 (m, 1H, η²-C₂H₃CN); 2.45 (m, 1H, η²-C₂H₃CN); 1.61 (d, J_H-P = 8.6 Hz, 9H, PMe₃); 1.36 (d, J_H-P = 8.9 Hz, 9H, PMe₃); 1.31 (m, 12H, 4 CH₂, NAr). ³¹P{¹H} NMR (243 MHz; C₆D₆; δ, ppm): -2.36 (d, J_P-P = 98.8 Hz, PMe₃); -4.18 (d, J_P-P = 98.8 Hz, PMe₃). ¹³C{¹H} NMR (151 MHz; C₆D₆; δ, ppm): 153.8, 150.3, 146.6, 144.1, 126.3, 124.7, 123.0 (aromatic carbons of CPh and NAr); 126.4 (s, CN) 46.5 (d, J_C-P = 8.9 Hz, η²-CH₂=CHCN); 31.8 (d, J_C-P = 7.4 Hz, η²-CH₂=CHCN); 27.0 (s, CH, NAr); 25.2 (s, CH₂, NAr); 17.5 (d, J_C-P = 27.5 Hz, PMe₃); 16.3 (d, J_C-P = 26.9 Hz, PMe₃).
NMR scale reaction of (ArN)Mo(H)(Cl)(PMe₃)₃ (1) with 4-formylbenzonitrile

A solution of 4-formylbenzonitrile (4.6 mg, 0.035 mmol) was added in one portion at room temperature to solid 1 (18.6 mg, 0.035 mmol). Immediately after the nitrile addition, the colour of the mixture changed to a different tint of brown. The reaction mixture was monitored by NMR spectroscopy for 3 days at room temperature. After 5 min, the release of one equivalent of PMe₃ and formation of the bis(phosphine) complex \( \text{trans}-(\text{ArN})\text{Mo(H)(Cl)}(\eta^2-\text{O}=\text{CHC}_6\text{H}_4\text{CN})(\text{PMe}_3)_2 \) (a mixture of isomers) was observed by NMR. After 3 days at room temperature, NMR analysis showed complete rearrangement of the carbonyl adduct and formation of \( (\text{ArN})\text{Mo(Cl)(OCH}_2\text{C}_6\text{H}_4\text{CN})(\text{PMe}_3)_3 \) (11). Initially, small amount of \( (\text{ArN})\text{MoCl}_2(\text{PMe}_3)_3 \) (~14% by \( ^{31}\text{P} \) NMR) was also observed. Rearrangement of \( \text{trans}-(\text{ArN})\text{Mo(H)(Cl)}(\eta^2-\text{O}=\text{CHC}_6\text{H}_4\text{CN})(\text{PMe}_3)_2 \) to 11 leads to increased amount of \( (\text{ArN})\text{MoCl}_2(\text{PMe}_3)_3 \) by-product. All attempts to purify complex 11 by recrystallisation were unsuccessful and resulted in a mixture of 11 and \( (\text{ArN})\text{MoCl}_2(\text{PMe}_3)_3 \).

\( \text{trans}-(\text{ArN})\text{Mo(H)(Cl)}(\eta^2-\text{O}=\text{CHC}_6\text{H}_4\text{CN})(\text{PMe}_3)_2 \): Only the major isomer is described due to the very low abundance of the minor isomer. \( ^1\text{H} \) NMR (300 MHz; \( \text{C}_6\text{D}_6 \); \( \delta \), ppm): 7.41 (d, \( ^3J_{\text{H-H}} = 7.8 \) Hz, 2H, \( \text{C}_6\text{H}_4 \)); 7.3 (m, 1H, MoH; found by \( ^1\text{H}^{-^{31}\text{P}} \) HSQC NMR); 6.76-6.93 and 7.18-7.29 (m, 5H, \( \text{NAr} \) and \( \text{C}_6\text{H}_4 \)); 5.52 (br s, 1H, \( \eta^2-\text{O}=\text{CHC}_6\text{H}_4\text{CN} \)); 4.12 (sept, \( ^3J_{\text{H-H}} = 6.8 \) Hz, 2H, \( \text{NAr} \)); 1.39 (d, \( ^2J_{\text{H-P}} = 9.7 \) Hz, 9H, \( \text{PMe}_3 \)); 1.16 (m, 12H, \( \text{C}_3\text{H}_3 \), \( \text{NAr} \)).

\( ^{31}\text{P} \{^1\text{H}\} \) NMR (121.5 MHz; \( \text{C}_6\text{D}_6 \); \( \delta \), ppm): -1.77 (d, \( ^2J_{\text{P-P}} = 106.7 \) Hz, \( \text{PMe}_3 \)); -5.54 (d, \( ^2J_{\text{P-P}} = 106.7 \) Hz, \( \text{PMe}_3 \)).

\( ^{13}\text{C} \{^1\text{H}\} \) NMR (151 MHz; \( \text{C}_6\text{D}_6 \); \( \delta \), ppm): 150.6, 148.4, 147.6, 146.6, 130.3, 128.2, 123.7, 123.3, 119.6 (aromatic carbons of \( \text{NAr} \) and \( \text{C}_6\text{H}_4 \)); 108.7 (s, \( \text{C}_\text{N} \)); 85.2 (d, \( ^2J_{\text{C-P}} = 7.7 \) Hz, \( \eta^2-\text{O}=\text{CHC}_6\text{H}_4\text{CN} \)); 27.0 (s, \( \text{CH}_3 \), \( \text{NAr} \)); 25.2 (s, \( \text{CH}_3 \), \( \text{NAr} \)); 17.6 (d, \( ^1J_{\text{C-P}} = 28.5 \) Hz, \( \text{PMe}_3 \)); 13.9 (d, \( ^1J_{\text{C-P}} = 26.3 \) Hz, \( \text{PMe}_3 \)).

11: \( ^1\text{H} \) NMR (600 MHz; \( \text{C}_6\text{D}_6 \); \( \delta \), ppm): 6.90-7.28 (m, 7H, \( \text{NAr} \) and \( \text{C}_6\text{H}_4 \)); 4.96 (s, 2H, OCH₂C₆H₄CN); 4.24 (br s, 2H, 2 CH, \( \text{NAr} \)); 1.25 (br d, \( ^3J_{\text{H-H}} = 6.1 \) Hz, 12H, 4 CH₂, \( \text{NAr} \)); 1.18 (m, 27H, 3 PMe₃). \( ^{31}\text{P} \{^1\text{H}\} \) NMR (121.5 MHz; \( \text{C}_6\text{D}_6 \); \( \delta \), ppm): 8.11 (t, \( ^2J_{\text{P-P}} = 16.1 \) Hz, \( \text{PMe}_3 \)); -9.45 (d, \( ^2J_{\text{P-P}} = 16.1 \) Hz, \( \text{PMe}_3 \)). \( ^{13}\text{C} \{^1\text{H}\} \) NMR (151 MHz; \( \text{C}_6\text{D}_6 \); \( \delta \), ppm): 152.5, 150.6, 147.0, 131.5, 128.1, 124.4, 123.7, 119.3 (aromatic carbons of \( \text{NAr} \) and \( \text{C}_6\text{H}_4 \)); 109.8 (s, \( \text{CN} \)); 70.5 (s, OCH₂C₆H₄CN); 27.7 (s, \( \text{CH}, \text{NAr} \)); 27.2 (s, \( \text{CH}, \text{NAr} \)).
NMR scale reaction of (ArN)Mo(H)(Cl)(PMe$_3$)$_3$ (1) with PhCN and acetone

A solution of acetone (2.5 µl, 0.034 mmol) and PhCN (3.9 µl, 0.034 mmol) in 0.6 ml of C$_6$D$_6$ was added in one portion at room temperature to solid 1 (18.2 mg, 0.034 mmol). The mixture was immediately transferred into an NMR tube and monitored by NMR spectroscopy for 12 hours. After 50 min at room temperature, the NMR analysis showed full conversion of the starting material and selective formation of the methylenamide complex 3. Acetone remained unreacted. No changes were observed by NMR within the next 11 hours.

NMR scale reaction of (ArN)Mo(H)(Cl)(PMe$_3$)$_3$ (1) with PhCN and acetophenone

A solution of acetophenone (4.0 µl, 0.035 mmol) and PhCN (4.0 µl, 0.035 mmol) in 0.6 ml of C$_6$D$_6$ was added in one portion at room temperature to solid 1 (18.5 mg, 0.035 mmol). The mixture was immediately transferred into an NMR tube and monitored by NMR spectroscopy for 12 hours. After 1 hour at room temperature, the NMR analysis showed full conversion of the starting material and selective formation of complex 3. Acetophenone remained unreacted. No changes were observed by NMR within the next 11 hours.

NMR scale reaction of (ArN)Mo(H)(Cl)(PMe$_3$)$_3$ (1) with PhCN and cyclohexanone

A solution of cyclohexanone (4.5 µl, 0.043 mmol) and PhCN (5.0 µl, 0.043 mmol) in 0.6 ml of C$_6$D$_6$ was added in one portion at room temperature to solid 1 (23.2 mg, 0.043 mmol). The mixture was immediately transferred into an NMR tube and monitored by NMR spectroscopy for 12 hours. After 2 hours at room temperature NMR analysis showed full conversion of the starting material and formation of a mixture of complex 3 (84%) and (ArN)Mo(Cl)(OCy)(PMe$_3$)$_3$ 1b (16%). No changes were observed by NMR within the next 10 hours.

NMR scale reaction of (ArN)Mo(H)(Cl)(PMe$_3$)$_3$ (1) with acetonophenone

Acetophenone (3.3 µL; 0.028 mmol) was added in one portion at room temperature to a
solution of 1 (15 mg, 0.028 mmol) in 0.6 mL of C₆D₆ in an NMR tube. The brown solution immediately changed colour to a lighter green/brown. The reaction was monitored by NMR and the complete conversion of 1 was observed after 4.5 hours, with the formation of a mixture of (ArN)Mo(Cl)(OCH(Me)Ph)(PMe₃)₃ (13, 90%) and (ArN)Mo(Cl)₂(PMe₃)₃ (1b) (10%). All attempts to obtain complex 13 in analytically pure form by recrystallisation were unsuccessful.

13: ¹H NMR (300 MHz; C₆D₆; δ, ppm): 1.15 (d, 9H, J_H-P = 6.7 Hz, PMe₃); 1.38 (d, J_H-P = 6.3 Hz, 9H, PMe₃); 1.42 (m, 9H, PMe₃); 1.48 (d, 3H, OCH(Me)Ph); 1.50 (d, 12H, 4 Me, ArN); 3.69 (br s, 2H, 2 CH, ArN); 5.77 (br m, 1H, OCH(Me)Ph). ³¹P{¹H} NMR (121.5 MHz; C₆D₆; δ, ppm): -13.3 (d, J_P-P = 14.1 Hz, PMe₃); -12.9 (d, J_P-P = 14.5 Hz, PMe₃); 7.05 (t, J_P-P = 16.5 Hz, PMe₃). ¹H-¹³C HSQC NMR (f1: 300 MHz; f2: 75.5 MHz; C₆D₆; δ, ppm): 125.0, 122.1, 121.0 (m-C and p-C, NAr); 74.1 (OCH(Me)Ph); 29.2 (CH, NAr); 27.5 (OCH(Me)Ph); 24.8 (PMe₃); 23.7 (PMe₃); 23.5 (Me, NAr); 21.9 (PMe₃).

Addition of one equivalent of HBCat (3 µL, 0.028 mmol) resulted in the hydroboration product PhCH(OBCat)Me and a mixture of 1 (54%) and (ArN)MoCl₂(PMe₃)₃ (46%).

NMR reaction of (ArN)Mo(H)(Cl)(PMe₃)₃ (1) with ethyl acetate

1 (20 mg; 0.037 mmol) was dissolved in 0.6 mL of C₆D₆; ethyl acetate (1.8 µL; 0.0187 mmol) was added via syringe to the solution. The reaction was monitored by NMR and complete conversion was observed after 1 week at room temperature, associated with the color change from brown into dark green. NMR spectra showed the presence of (ArN)Mo(Cl)(OEt)(PMe₃)₃ (14; 96% by NMR) and (ArN)MoCl₂(PMe₃)₃ (1b; 4% by NMR).

An equivalent of HBCat (3.97 µL, 0.0373 mmol) was added to a solution of 14 resulting in the formation of the hydroboration product EtOBcat and regeneration of complex 1.

NMR scale reaction of (ArN)Mo(H)(Cl)(PMe₃)₃ (1) with HBCat

HBCat (3.9 µL; 0.037 mmol) was added in one portion to a frozen in liq. N₂ solution of 1 (20 mg; 0.037 mmol) in 0.6 mL of PhMe-d₈ in an NMR tube. The mixture was monitored by low temperature VT NMR and no significant reaction was observed. However, warming the sample up to room temperature and leaving for 24 h results in ~20 %
conversion of 1 to a mixture of (ArN)MoCl\(_2\)(PMe\(_3\))\(_3\)\(^{1b}\) and (ArN)Mo(H)\(_2\)(PMe\(_3\))\(_3\) (2). No formation of ClBCat was detected by NMR analysis.

**General procedure for catalytic hydroboration reactions**

All reactions were carried out under nitrogen atmosphere. A solution of HBCat (25 µl) organic substrate (or mixture of substrates) in a 1:1 mol ratio and tetramethylsilane (5 mol %) in 0.6 ml of C\(_6\)D\(_6\) was added in one portion at room temperature to solid catalyst (5 mol %) (either (ArN)Mo(H)(Cl)(PMe\(_3\))\(_3\) (1) or (ArN)Mo(H)\(_2\)(PMe\(_3\))\(_3\) (2) or Mo(H)\(_2\)(PMe\(_3\))\(_3\)(\(\eta^3\)-NAr-HBCat) (15)). The mixture was immediately transferred to an NMR tube and left at room temperature for 5 min. After that, the reaction was monitored by NMR spectroscopy. Conversion of organic substrates and yields were determined by \(^1\)H NMR by using tetramethylsilane as a standard. All hydroboration products were characterized without isolation. Characteristic NMR signals of new hydroboration products are presented below.

**trans-PhCH=CHBCat**: \(^1\)H NMR (300 MHz; C\(_6\)D\(_6\); δ, ppm): 8.00 (d, \(^3\)J\(_{H-H}\) = 18.6 Hz, 1H, PhC\(_H\)=CH); 7.45 (d, \(^3\)J\(_{H-H}\) = 7.0 Hz, 2H, o-Ph); 7.26 (m, 4H, m-Ph and CatB); 6.96 (m, 3H, p-Ph and CatB); 6.63 (d, \(^3\)J\(_{H-H}\) = 18.6 Hz, 1H, CH=CHBCat). \(^1\)H-\(^{13}\)C HSQC NMR (f1: 600 MHz; f2: 150 MHz; \(^3\)J = 145 Hz; C\(_6\)D\(_6\); \(^{13}\)C projection; δ, ppm): 152.0 (PhC\(_H\)=CH); 137.0 (o-Ph); 128.5-121.6 (m-H and p-H of Ph and CatB); 113.4 (s, PhCH=CHBCat). \(^{11}\)B NMR (96.3 MHz; C\(_6\)D\(_6\); δ, ppm): 31.5 (bs).

**Ph(CH\(_2\)\(_2\))BCat**: \(^1\)H NMR (300 MHz; C\(_6\)D\(_6\); δ, ppm): 7.21-7.35 (m, 5H, Ph); 7.09 (m, 2H, CatB); 6.87 (m, 2H, CatB); 2.97 (t, \(^3\)J\(_{H-H}\) = 8.1 Hz, 2H, PhCH\(_2\)CH\(_2\)BCat); 1.58 (t, \(^3\)J\(_{H-H}\) = 8.1 Hz, 2H, PhCH\(_2\)CH\(_2\)BCat). \(^1\)H-\(^{13}\)C HSQC NMR (f1: 600 MHz; f2: 150 MHz; \(^3\)J = 145 Hz; C\(_6\)D\(_6\); \(^{13}\)C projection; δ, ppm): 128.5-121.6 (aromatic CH); 31.4 (PhCH\(_2\)CH\(_2\)BCat); 29.0 (PhCH\(_2\)CH\(_2\)BCat). \(^{11}\)B NMR (96.3 MHz; C\(_6\)D\(_6\); δ, ppm): 35.0 (bs).

**PhCH(OBCat)Me**: \(^1\)H NMR (300 MHz; C\(_6\)D\(_6\); δ, ppm): 7.40 (d, \(^3\)J\(_{H-H}\) = 7.2 Hz, 2H, o-Ph); 7.21 (m, 3H, m-Ph and p-Ph); 6.99 (m, 2H, CatB); 6.83 (m, 2H, CatB); 5.50 (q, \(^3\)J\(_{H-H}\) = 6.6 Hz, 1H, PhCH(OBCat)Me); 1.50 (d, \(^3\)J\(_{H-H}\) = 6.3Hz, 3H, PhCH(OBCat)Me). \(^{11}\)B NMR (96.3 MHz; C\(_6\)D\(_6\); δ, ppm): 23.4 (bs). \(^1\)H-\(^{13}\)C HSQC NMR (f1: 300 MHz; f2: 75
MHz; \( J = 145 \text{ Hz} \); \(^{13}\text{C} \) projection; \( \delta, \text{ ppm} \): 125.6 (\( \text{o-Ph} \)); 74.2 (PhCH(OBCat)Me); 24.9 (PhCH(OBCat)Me).

\( ^{1}\text{Pr}_2\text{CH(OBCat)} \): \(^{1}\text{H} \) NMR (300 MHz; C\(_6\)D\(_6\); \( \delta, \text{ppm} \)): 6.90 (m, 4H, CatB); 3.99 (t, \(^{3}J_{\text{H-H}} = 5.7 \text{ Hz} \), 1H CH(OBCat)); 1.84 (m, 2H, 2CH, iPr); 1.14 (d, \(^{3}J_{\text{H-H}} = 6.6 \text{ Hz} \), 12H, 4CH\(_3\), iPr).

\(^{11}\text{B} \) NMR (96.3 MHz; C\(_6\)D\(_6\); \( \delta, \text{ppm} \)): 23.7 (bs).

\(^{1}H\)-\(^{13}\text{C} \) HSQC NMR (\( f_1: 300 \text{ MHz} \); \( f_2: 75 \text{ MHz} \); \( ^{13}\text{C} \) projection; \( \delta, \text{ppm} \)): 112.0, 122.3 (CatB); 86.5 (C\(_3\)H(OBcat)); 30.1 (C\(_3\)H, iPr); 16.8 (C\(_3\)H\(_3\), iPr).

\( \text{Ph}_2\text{CH(OBCat)} \): \(^{1}\text{H} \) NMR (300 MHz; C\(_6\)D\(_6\); \( \delta, \text{ppm} \)): 7.50 (d, \(^{3}J_{\text{H-H}} = 8.4 \text{ Hz} \), 4H, \( \text{o-H, Ph} \)); 7.17 (m, 6H, \( m\)-H and \( p\)-H of \( \text{Ph} \)) 6.80-6.96 (m, 4H, CatB); 6.55 (s, 1H, CH(OBcat)).

\(^{11}\text{B} \) NMR (96.3 MHz; C\(_6\)D\(_6\); \( \delta, \text{ppm} \)): 23.8 (bs).

\(^{1}H\)-\(^{13}\text{C} \) HSQC NMR (\( f_1: 300 \text{ MHz} \); \( f_2: 75 \text{ MHz} \); \( \delta, \text{ppm} \)): 148.2, 142.2, 130.0, 126.7, 122.3, 112.0, 79.6 (CH(OBCat)).

\( \text{EtOBCat} \): \(^{1}\text{H} \) NMR (300 MHz; C\(_6\)D\(_6\); \( \delta, \text{ppm} \)): 7.03 (m, 2H, CatB); 6.86 (m, 2H, CatB); 3.93 (q, \(^{3}J_{\text{H-H}} = 7.0 \text{ Hz} \), 2H, OCH\(_2\)CH\(_3\)); 1.11 (t, \(^{3}J_{\text{H-H}} = 7.0 \text{ Hz} \), 3H, OCH\(_2\)CH\(_3\)).

\(^{11}\text{B} \) NMR (96.3 MHz; C\(_6\)D\(_6\); \( \delta, \text{ppm} \)): 23.4 (bs, CatB).

\(^{1}H\)-\(^{13}\text{C} \) HSQC NMR (\( f_1: 300 \text{ MHz} \); \( f_2: 75 \text{ MHz} \); \( \delta, \text{ppm} \)): 121.2, 112.0 (CatB); 59.3 (OCH\(_2\)CH\(_3\)); 13.5 (OCH\(_2\)CH\(_3\)).

\( \text{CyOBCat} \): \(^{1}\text{H} \) NMR (300 MHz; C\(_6\)D\(_6\); \( \delta, \text{ppm} \)): 7.05 (m, 2H, B Cat); 6.86 (m, 2H, B Cat); 4.32 (m, 1H, CH-O); 1.92-2.04 (m, 2H, OCy); 1.67-1.80 (m, 2H, OCy); 1.53-1.11 (m, 6H, OCy).

\(^{11}\text{B} \) NMR (96.3 MHz; C\(_6\)D\(_6\); \( \delta, \text{ppm} \)): 23.3 (bs, CatB).

\(^{1}H\)-\(^{13}\text{C} \) HSQC NMR (\( f_1: 300 \text{ MHz} \); \( f_2: 75 \text{ MHz} \); \( \delta, \text{ppm} \)): 111.0, 122.0 (s, CatB aromatic); 75.1(s, C-OBcat); 39.8 (s, Cy); 27.2 (s, Cy); 26.3 (s, Cy).

\( \text{PhCH}_2\text{N(BCat)}_2 \): \(^{1}\text{H} \) NMR(300 MHz; CDCl\(_3\); \( \delta, \text{ppm} \)): 4.73 (s, 2H, CH\(_2\)N), 6.99-7.06 (m, 4H, B Cat), 7.18-7.24 (m, 4H, B Cat), 7.24-7.34 (m, 3H, Ph), 7.44-7.49 (m, 2H, Ph).

\(^{13}\text{C} \)\(^{1}\text{H} \) NMR (75.5 MHz; CDCl\(_3\); \( \delta, \text{ppm} \)): 47.96 (s, CH\(_2\)N), 112.47 (s, CH, B Cat), 122.59 (s, CH, B Cat), 127.52 (s, CH, Ph), 127.88 (s, CH, Ph), 128.72 (s, CH, Ph), 140.32 (s, i-C, B Cat), 148.46 (s, i-C, B Cat).\(^{11}\text{B} \) NMR (96.3 MHz; C\(_6\)D\(_6\); \( \delta, \text{ppm} \)): 27.6 (bs).
$\text{EtN(BCat)}_2$: $^1$H NMR (300 MHz; C$_6$D$_6$; δ, ppm): 7.02 (m, 2H, CatB); 6.76 (m, 2H, CatB); 3.35 (q, $^3\text{J}_{\text{H-H}} = 7.2$ Hz, 2H, NCH$_2$CH$_3$); 1.10 (t, $^3\text{J}_{\text{H-H}} = 7.2$ Hz, 3H, NCH$_2$CH$_3$). $^{13}$C (1H) NMR (75.5 MHz; C$_6$D$_6$; δ, ppm): 148.7 (s, CatB); 122.3 (s, CatB); 122.0 (s, CatB); 39.2 (s, NCH$_2$CH$_3$); 17.5 (s, NCH$_2$CH$_3$). $^{11}$B NMR (96.3 MHz; C$_6$D$_6$; δ, ppm): 27.8 (bs).

$\text{tBuCH}_2$-$\text{N(BCat)}_2$: $^1$H NMR (600 MHz; C$_6$D$_6$; δ, ppm): 7.09 (m, 2H, CatB); 6.89 (m, 2H, CatB); 3.32 (s, 2H, CH$_2$-N); 0.89 (s, 9H, 3CH$_3$). $^1$H-$^{13}$C HSQC NMR ($f_1$: 600 MHz; $f_2$: 150 MHz; $J = 145$ Hz; C$_6$D$_6$; $^{13}$C projection; δ, ppm): 122.0, 111.9 (CatB); 55.1 (H$_2$C-N), 27.2 (CH$_3$-C). $^{11}$B NMR (96.3 MHz; C$_6$D$_6$; δ, ppm): 27.0 (bs).

$\text{trans-NC(CH}_2)_3\text{CH=CHBCat}$: $^1$H NMR (300 MHz; C$_6$D$_6$; δ, ppm): 7.03-7.81 (m, 4H, CatB); 6.60 (dt, $^3\text{J}_{\text{H-H}} = 19.5$ and 6.6 Hz, 1H, CH=CHBCat); 5.59 (d, $^3\text{J}_{\text{H-H}} = 19.5$ Hz, 1H, CH=CHBCat). $^{11}$B NMR (96.3 MHz; C$_6$D$_6$; δ, ppm): 19.2 (bs).

$\text{CH}_3$-$\text{CHBcat-CN}$: $^1$H NMR (300 MHz; CDCl$_3$; δ, ppm): 7.00-6.78 (bm, 4H, BCat); 1.96 (q, $^2\text{J}_{\text{H-H}} = 7.1$ Hz, 1H, CH$_3$-CHBcat); 1.06 (d, $^2\text{J}_{\text{H-H}} = 7.8$ Hz, 3H, CH$_3$-CHBcat). $^1$H-$^{13}$C HSQC NMR ($f_1$: 300 MHz; $f_2$: 75 MHz; $J = 145$ Hz, CDCl$_3$; $^{13}$C projection; δ, ppm): 125.0 (s, C-N); 42.0 (CH$_3$-CHBcat); 13.8 (CH$_3$-CHBcat). $^{11}$B NMR (96.3 MHz; C$_6$D$_6$; δ, ppm): 32.5 (bs).

$\text{4-NO}_2$-$\text{C}_6\text{H}_4$-$\text{CH(OBcat)}$-$\text{CH}_3$: $^1$H NMR (300 MHz; C$_6$D$_6$; δ, ppm): 7.76 (d, $^3\text{J}_{\text{H-H}} = 6.6$ Hz, 2H, o-Ph); 6.90-6.50 (m, 6H ,CatB and m-Ph); 5.09 (q, $^3\text{J}_{\text{H-H}} = 6.4$ Hz, 1H, Ph-C(OBcat)H-CH$_3$); 1.14 (d, $^3\text{J}_{\text{H-H}} = 6.3$ Hz, 3H, Ph-C(OBcat)H-CH$_3$). $^{11}$B NMR (96.3 MHz; C$_6$D$_6$; δ, ppm): 22.4 (s). $^1$H-$^{13}$C HSQC NMR ($f_1$: 300 MHz; $f_2$: 75 MHz; J=145 Hz; C$_6$D$_6$; $^{13}$C projection; δ, ppm): 127.6 (o-Ph); 112.0-128.0 (aromatic); 73.9 (Ph-C(OBcat)H-CH$_3$); 25.6 (Ph-C(OBcat)H-CH$_3$).

$\text{HexBCat}$: $^1$H NMR (600 MHz; C$_6$D$_6$; δ, ppm): 7.13 (m, 2H, CatB); 6.89 (m, 2H, CatB); 1.41 (m, 4H, 2 CH$_2$); 1.31 (m, 4H, 2 CH$_2$); 1.21 (m, 2H, CH$_2$); 0.89 (t, $^3\text{J}_{\text{H-H}} = 7.2$ Hz, 3H, CH$_3$). $^1$H-$^{13}$C HSQC NMR ($f_1$: 600 MHz; $f_2$: 150 MHz; J = 145 Hz; C$_6$D$_6$; $^{13}$C projection δ, ppm): 122.3, 112.4 (CatB); 32.1 (H$_2$C-Bcat), 31.7, 24.0, 22.9, 14.0, 10.5 (CH$_2$, CH$_3$). $^{11}$B NMR (96.3 MHz; C$_6$D$_6$; δ, ppm): 35.9 (bs).
**Reaction of PhCH$_2$N(BCat)$_2$ with benzaldehyde:** For the hydroboration of PhCN with HBCat in C$_6$D$_6$ described above: after full conversion to PhCH$_2$N(BCat)$_2$, all volatiles were removed under vacuum and the residue was dissolved in 0.6 mL of CDCl$_3$. PhC(O)H (2.1 equivs to the starting HBCat) was added to the reaction tube and the mixture was left at room temperature for 1.5 hours showing full conversion of PhCH$_2$N(BCat)$_2$ to PhCH$_2$N=C(H)Ph and (CatB)$_2$O.

**Experimental details of EXSY NMR studies**

The EXSY NMR spectra were acquired on a Bruker Avance AV600 spectrometer equipped with a BBO-Z grad probe and VT accessory. A series of 1H 1D EXSY NMR spectra were recorded at different temperatures using the “selnogp” (1D NOESY using selective refocusing with a shaped pulse; dipolar coupling may be due to NOE or chemical exchange)$^4$ pulse sequence from the Bruker library. Each spectrum was acquired using 16 scans and 32K data points with a spectral width of 20 kHz. The offset frequency was always adjusted on the resonance with the analyzed signal. The acquired FIDs were processed using a line broadening of 0.3 Hz and zero-filled to 65K points. At each temperature a series of 5-8 1D EXSY spectra were recorded with a mixing time ranging from 25 to 2000 ms, optimized for each exchange rate, and a 1H 1D spectrum was used as a reference. The slopes of the buildup curves at 0 ms mixing time were determined by the initial rate approximation.$^6b$ More accurate measurements of the rates were also performed by employing the CIFIT2.0 software courtesy to Prof. Alex D. Bain from McMaster University (www.chemistry.mcmaster.ca/bain).$^5$ T1 relaxation times were measured by inversion recovery method using the Bruker “t1ir” pulse program.
Figure S1. Eyring plot for exchange between isomers of 20 (Rate constants of the exchange process at different temperatures were calculated using the initial rate approximation method\textsuperscript{6})
Figure S2. VT $^{31}$P{$^1$H} NMR traces for the reaction of complex 3 with HBCat in PhMe-d$_8$: (1) at 225 K; (2) at 249 K; (3) at 254 K; (4) at 254 K; (5) at 263 K; (6) at 273 K; (7) at 283 K; (8) at 295 K. An admixture of (ArN)MoCl$_8$: (1) at 225 K; (2) at 249 K; (3) at 254 K; (4) at 254 K; (5) at 263 K; (6) at 273 K; (7) at 283 K; (8) at 295 K. An admixture of (ArN)MoCl$_2$(PMe$_3$)$_3$ (14% by $^{31}$P{$^1$H} NMR) is coming from the starting material and, as was indicated by our previous experiments, does not react with HBCat.

Figure S3. $^{11}$B{$^1$H} NMR for the reaction of complex 3 with HBCat at 253 K in PhMe-d$_8$: resonance at 2.2 ppm corresponds to complex 4; resonance at 10.3 ppm corresponds to complex 5.
Figure S4. $^{11}$B NMR (A) and $^{11}$B{$^1$H} NMR (B) for the reaction of complex 3 with HBCat at 283 K in PhMe-d$_8$: resonance at 2.2 ppm corresponds to complex 4 ($^1J_{B-H} \approx 55$ Hz); resonance at 10.1 ppm corresponds to complex 5.

Figure S5. $^1$H NMR for the reaction of complex 3 with HBCat at 244 K in PhMe-d$_8$, showing formation of a mixture of complexes 4 and 5 along with the starting material 3 and (ArN)MoCl$_2$(PMe$_3$)$_3$. 

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Figure S6. $^1$H-$^{31}$P HSQC NMR for the reaction of complex 3 with HBCat at 254 K in PhMe-d$_8$, showing coupling between PMe$_3$ ligands and –N=CHPh of complex 4.

Figure S7. $^{13}$C($^1$H) NMR for the reaction of complex 3 with HBCat at 254 K in PhMe-d$_8$: resonances at 171.9 ppm and 154.2 ppm correspond to –N=CHPh of complexes 4 and 5, respectively (found by $^1$H-$^{13}$C HSQC NMR).
Figure S8. $^{31}$P NMR spectra (selectively decoupled from methyl groups) for the reaction of complex 3 with HBCat at 295 K in PhMe-$d_8$, showing no coupling of PMe$_3$ ligands to Mo-H in complex 5.
Figure S9. A series of $^1$H NMR spectra (at 283 K) for the reaction of 3 with HBCat in PhMe-d$_8$: (A) no decoupling; (B) $^1$H/$^{31}$P; (C) $^1$H/$^{11}$B.
**Figure S10.** $^{11}$B{$^1$H} NMR for the reaction of complex 3 with HBCat at 295 K in PhMe-d$_8$; resonance at 15.3 ppm corresponds to complex 6; resonance at 27.7 ppm corresponds to PhCH$_2$N(BCat)$_2$.

**Figure S11.** $^{31}$P NMR spectra (selectively decoupled from methyl groups at 1.80 ppm (A) and from methyl groups at 1.20 ppm (B) in the $^1$H NMR spectrum) for the reaction of complex 3 with HBCat at 295 K in PhMe-d$_8$, showing coupling of PMe$_3$ to Mo-H in 6.
Figure S12. $^1$H NMR for the reaction of complex 3 with HBCat at 295 K in PhMe-d$_8$, showing a mixture of complex 3, complex 6 and (ArN)MoCl$_2$(PMe$_3$)$_3$.

Figure S13. $^1$H-$^{31}$P HSQC NMR for the reaction of complex 3 with HBCat at 295 K in PhMe-d$_8$, showing a mixture of complex 3 (singlet $^{31}$P projection), complex 6 (two isomers, dd in $^{31}$P projection) and (ArN)MoCl$_2$(PMe$_3$)$_3$. 
Figure S14. $^1$H-$^{13}$C HSQC for the reaction of complex 3 with HBCat at 295 K in PhMe-d$_8$. 
Figure S15 (A) $^{31}$P($^1$H) NMR spectrum of the reaction of complex 1 with 4-formylbenzonitrile registered after leaving the reaction mixture in an NMR tube for 5 min at RT. Mutually coupled doublets at -5.54 ppm and -1.80 ppm correspond to trans-(ArN)Mo(H)(Cl)(η²-O=CHC₆H₄CN)(PMe₃). Signal at -62.5 ppm corresponds to PMe₃ released during the reaction. An admixture of (ArN)MoCl₂(PMe₃)₃ (14%; 2.64 ppm and 8.75 ppm) is coming from the starting material and, as was indicated by our control experiments, does not react with 4-formylbenzonitrile. (B) $^1$H NMR spectrum of the reaction of complex 1 with 4-formylbenzonitrile registered after leaving the reaction mixture in an NMR tube for 5 min at RT showing formation of trans-(ArN)Mo(H)(Cl)(η²-O=CHC₆H₄CN)(PMe₃) (signal at 5.52 ppm corresponds to η²-O=CH); hydride signal is located at 7.3 ppm (found by multinuclear 2D NMR) and obscured by the aromatic resonances of C₆H₄CN and NAr groups. (C) $^{13}$C($^1$H) DEPTQ NMR spectrum of the reaction of complex 1 with 4-formylbenzonitrile registered after leaving the reaction mixture in an NMR tube for 5 min at RT showing formation of trans-(ArN)Mo(H)(Cl)(η²-O=CHC₆H₄CN)(PMe₃) (resonances at 108.7 ppm (s) and 85.2 ppm (d, $^2J_{C-P} = 7.7$ Hz) correspond to CN and η²-O=CH carbons, respectively).
Figure S16. (A) $^1$H NMR spectrum of the reaction of complex 1 with 4-formylbenzonitrile registered after leaving the reaction mixture in an NMR tube for 3 days at RT showing formation of complex 11 (signal at 4.96 ppm corresponds to Mo-OCH$_2$ group; resonance of 4.12 ppm (sept) is coming from (ArN)MoCl$_2$(PMe$_3$)$_3$ by-product). Due to the presence of small amount of (ArN)MoCl$_2$(PMe$_3$)$_3$ integral intensities of the signals in the aliphatic region are a bit higher than can be expected for complex 11. (B) $^{13}$C[$^1$H] NMR spectrum of the reaction of complex 1 with 4-formylbenzonitrile registered after leaving the reaction mixture in an NMR tube for 3 days at RT showing formation of complex 11 (signal at 70.5 ppm corresponds to Mo-OCH$_2$; resonance at 109.8 ppm – CN group). (C) $^1$H-$^{13}$C HSQC NMR spectrum of the reaction of complex 1 with 4-formylbenzonitrile registered after leaving the reaction mixture in an NMR tube for 3 days at RT showing formation of complex 11. (D) $^{31}$P[$^1$H] NMR spectrum of the reaction of complex 1 with 4-formylbenzonitrile registered after leaving the reaction mixture in an NMR tube for 3 days at RT showing formation of complex 11 (signals at 8.11 ppm and 9.45 ppm correspond to complex 11; signals at 2.66 ppm and 8.81 ppm – to (ArN)MoCl$_2$(PMe$_3$)$_3$ by-product. (E) $^1$H-$^{31}$P HSQC NMR spectrum of the mixture of complex 11 and (ArN)MoCl$_2$(PMe$_3$)$_3$ produced in the reaction of 1 with 4-formylbenzonitrile (3 days at RT in C$_6$D$_6$).

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*Presence of 44% of (ArN)MoCl$_2$(PMe$_3$)$_3$ was observed by $^1$H NMR. 14% of (ArN)MoCl$_2$(PMe$_3$)$_3$ is coming from the starting material (see Fig. S6). The rest is presumably formed via redistribution at Mo during the reaction of complex 1 with 4-formylbenzonitrile. We consider formation of (ArN)MoCl$_2$(PMe$_3$)$_3$ as one of possible catalyst deactivation pathways (see ref. 1b).*
Figure S17. (A) $^{31}$P($^1$H) NMR spectrum of the reaction of complex 1 with acrylonitrile in C$_6$D$_6$ registered after leaving the reaction mixture in an NMR tube for 1 h 20 min at RT showing formation of a mixture of (ArN)MoCl$_2$(PMe$_3$)$_3$ and complex 10 (mutually coupled doublets at -4.18 ppm -2.36 ppm correspond to 10; signals at -8.80 ppm and 2.65 ppm – to (ArN)MoCl$_2$(PMe$_3$)$_3$; signals at -17.73 ppm and -1.38 ppm – to complex 1; 62.15 ppm – to free PMe$_3$ released during the reaction). (B) $^1$H NMR spectrum of the mixture of complexes 1, 10 and (ArN)MoCl$_2$(PMe$_3$)$_3$ obtained in the reaction of 1 with acrylonitrile. Resonances at 6.68 ppm (dd), 2.87 ppm (m), 2.51 ppm (m) and 2.45 (m) correspond to Mo-H and protons in $^\eta^2$-CH$_2$=CHCN ligand of 10, respectively. (C) $^1$H-$^{31}$P HMQC NMR spectrum of the mixture of complexes 1, 10 and (ArN)MoCl$_2$(PMe$_3$)$_3$ obtained in the reaction of 1 with acrylonitrile. The spectrum shows coupling between PMe$_3$ ligand, Mo-H and protons in $^\eta^2$-CH$_2$=CHCN ligand of 10. (D) $^{13}$C DEPTQ NMR spectrum of the mixture of complexes 1, 10 and (ArN)MoCl$_2$(PMe$_3$)$_3$ obtained in the reaction of 1 with acrylonitrile (doublets at 46.5 ppm and 31.8 ppm correspond to $^\eta^2$-CH$_2$=CHCN ligand; signal at 126.4 ppm (observed by the resonance of C$_6$D$_6$ and found by $^1$H-$^{13}$C HMBC NMR) correspond to the carbon of CN group). (E) A fragment of $^1$H-$^{13}$C HMBC NMR spectrum of the mixture of complexes 1, 10 and (ArN)MoCl$_2$(PMe$_3$)$_3$ obtained in the reaction of 1 with acrylonitrile. The spectrum shows long range correlation between carbon of CN group and protons in $^\eta^2$-CH$_2$=CHCN ligand.
Figure S18. NMR spectra of (ArN)Mo(Cl)(N=CHMe)(PMe$_3$)$_3$ (7; two isomers) in C$_6$D$_6$: (A) $^{31}$P-$^1$H NMR; (B) $^1$H NMR (signals at 6.15 ppm and 2.37 ppm correspond to N=C(H)CH$_3$ ligand of major isomer of 7).
Figure S19. NMR spectra for the reaction between complex 1 and 4-acetylbenzonitrile in C₆D₆ taken after 1.5 h at RT and showing the formation of complex 9: (A) $^{31}$P[$^1$H] NMR (signals at 2.66 ppm and 8.77 ppm correspond to (ArN)MoCl₂(PMe₃)₃ by-product (14%, see footnote for Figure S16); resonance at -62.35 ppm corresponds to free PMe₃ released during the reaction); (B) $^1$H NMR (signal at 7.26 ppm corresponds to N=C(H)C₆H₄-C(O)CH₃); (C) $^1$H-³¹P HSQC NMR showing coupling between PMe₃ and N=C(H)C₆H₄-C(O)CH₃ ligands in 9; (D) $^{13}$C DEPTQ NMR; (E) $^1$H-¹³C HSQC NMR; (F) $^1$H-¹³C HMBC NMR. (G) $^1$H-$^1$H COSY NMR.
Figure S20. $^1$H NMR spectrum of complex 3 in C$_6$D$_6$.

Figure S21. $^{31}$P($^1$H) NMR spectrum of complex 3 in C$_6$D$_6$.

Figure S22. $^{13}$C($^1$H) NMR spectrum of complex 3 in C$_6$D$_6$. 
Figure S23. $^1$H NMR spectrum of complex 8 (mixture of 2 isomers), generated on NMR scale by reaction of 1 with trans-pentenenitrile in $\text{C}_6\text{D}_6$. 41% of (ArN)MoCl$_2$(PMe$_3$)$_3$ is present, see Figure S24.

Figure S24. $^{31}$P-$^1$H NMR spectrum of complex 8 (mixture of 2 isomers), generated on NMR scale by reaction of 1 with trans-pentenenitrile in $\text{C}_6\text{D}_6$. 41% of (ArN)MoCl$_2$(PMe$_3$)$_3$ formed as a by-product of the reaction.
Figure S25. $^1$H–$^1$H COSY NMR spectrum of complex 8 (mixture of 2 isomers), generated on NMR scale by reaction of 1 with trans-pentenenitrile in C$_8$D$_6$. 41% of (ArN)MoCl$_2$(PMe$_3$)$_3$ is present, see Figure S24.

Figure S26. $^1$H–$^{31}$P HSQC NMR spectrum of complex 8 (mixture of 2 isomers), generated on NMR scale by reaction of 1 with trans-pentenenitrile in C$_8$D$_6$. 41% of (ArN)MoCl$_2$(PMe$_3$)$_3$ is present, see Figure S24.
Figure S27. $^{13}$C($^{1}$H) NMR spectrum of complex 8 (mixture of 2 isomers), generated on NMR scale by reaction of 1 with trans-pentenonitrile in C$_{6}$D$_{6}$. 41% of (ArN)MoCl$_{2}$(PMe$_{3}$)$_{3}$ is present, see Figure S24.

Figure S28. $^{1}$H-$^{13}$C HSQC NMR spectrum of complex 8 (mixture of 2 isomers), generated on NMR scale by reaction of 1 with trans-pentenonitrile in C$_{6}$D$_{6}$. 41% of (ArN)MoCl$_{2}$(PMe$_{3}$)$_{3}$ is present, see Figure S24.
Figure S29. $^1$H-$^{13}$C HMBC NMR spectrum of complex 8 (mixture of 2 isomers), generated on NMR scale by reaction of 1 with trans-pentenitrite in C₆D₆. 41% of (ArN)MoCl₂(PMe₃)₃ is present, see Figure S24.

Figure S30. $^{31}$P{$^1$H} NMR spectrum of complex 15, generated by the reaction of 2 with HBCat in PhMe-d₈ at 243 K.
Figure S31. $^{31}$P-$^{31}$P EXSY NMR spectrum of complex 15, generated by the reaction of 2 with HBCat in PhMe-d$_8$ at 243 K (an intramolecular PMe$_3$ exchange can be observed for complex 15).

Figure S32. $^{11}$B-$^1$H NMR (a) and $^{11}$B NMR (b) spectra of complex 15, generated by the reaction of 2 with HBCat in PhMe-d$_8$ at 243 K.
Figure S33. $^1$H NMR (a) and $^1$H$^{11}$B NMR (b) and $^1$H$^{31}$P NMR (c) spectra of complex 15, generated by the reaction of 2 with HBCat in PhMe-d$_8$ at 243 K.

Figure S34. A fragment of $^1$H-$^1$H COSY NMR spectrum of complex 15, generated by the reaction of 2 with HBCat in PhMe-d$_8$ at 243 K (showing mutual coupling of two Mo-H hydrides).
Figure S34. A fragment of $^1$H-$^{31}$P HSQC NMR spectrum of complex 15, generated by the reaction of 2 with HBCat in PhMe-$d_8$ at 243 K (showing coupling of PMe$_3$ ligands two Mo-H hydrides).

Figure S35. A fragment of $^1$H-$^{31}$P HSQC NMR spectrum of complex 15, generated by the reaction of 2 with HBCat in PhMe-$d_8$ at 243 K (showing coupling in PMe$_3$ ligands).
Figure S36. Fragments of $^{31}$P NMR spectra (selectively decoupled from methyl groups at 1.35 ppm in the $^1$H NMR spectrum (a) and selectively decoupled from methyl groups at 0.86 ppm in the $^1$H NMR spectrum (b)) of complex 15, generated by the reaction of 2 with HBCat in PhMe-$d_8$ at 243 K (showing coupling of PMe$_3$ ligands two Mo-H hydrides).

Figure S37. $^{31}$P{$^1$H} NMR (295 K) spectrum of complex 15, generated by the reaction of 2 with HBCat in PhMe-$d_8$ at 243 K (showing decomposition of 15 to complex 17 (singlet at 10.06 ppm)).
Figure S38. $^1$H NMR (a) and $^1$H$[^{31}$P$]$ NMR (b) (295 K) spectra of complex 15, generated by the reaction of 2 with HBCat in PhMe-$d_8$ at 243 K (showing decomposition of 15 to complex 17 (Mo-H at 3.9 ppm)).

Figure S39. $^1$H$-^{31}$P HSQC NMR spectrum of complex 17 in PhMe-$d_8$ at 295K showing coupling of Mo-H and PMe$_3$. 
**Figure S40.** $^{31}$P-$^1$H NMR spectrum of complex 19 in PhMe-d$_8$ at 258 K.

**Figure S41.** $^{31}$P-$^{31}$P EXSY NMR spectrum of complex 19 in PhMe-d$_8$ at 258 K showing exchange between two major isomers.
**Figure S42.** $^1$H NMR spectrum of complex 19 in PhMe-$d_8$ at 258 K.

**Figure S43.** $^1$H-$^1$H COSY NMR spectrum of complex 19 in PhMe-$d_8$ at 258 K.
Figure S44. A fragment of the $^1$H-$^{31}$P HSQC NMR spectrum of complex 19 in PhMe-d$_8$ at 258 K, showing coupling of protons in N=CHMe ligands with PMe$_3$ ligands.

Figure S45. A fragment of the $^1$H-$^{13}$C HSQC NMR spectrum of complex 19 in PhMe-d$_8$ at 258 K, showing coupling in N=CH ligands.
Figure S46. A fragment of the $^1$H-$^{13}$C HMBC NMR spectrum of complex 19 in PhMe-d$_8$ at 258 K, showing coupling in N=CHMe ligands.

Figure S47. $^{31}$P NMR spectrum for the reaction of complex 15 with 2 equiv. of MeCN in PhMe-d$_8$ at 258 K, showing formation of complex 20 (a mixture of isomers).
Figure S48. $^1$H NMR spectrum for the reaction of complex 15 with 2 equiv. of MeCN in PhMe-d$_8$ at 258 K, showing formation of complex 20 (a mixture of isomers).

Figure S49. Fragment of $^1$H-$^{31}$P HSQC NMR spectrum of complex 20 (a mixture of isomers) in PhMe-d$_8$ at 258 K, showing coupling between PMe$_3$ ligands and N(BCat)=CHMe and MeCN ligands.
Figure S50. $^1$H-$^1$H COSY NMR spectrum of complex 20 (a mixture of isomers) in PhMe-d$_8$ at 258 K, showing coupling in N(BCat)=CHMe ligands.

Figure S51. $^{11}$B NMR spectrum of complex 20 in PhMe-d$_8$ at 258 K.
Figure S52. $^1$H-$^{13}$C HSQC and $^1$H-$^{13}$C HMBC NMR spectra of complex 20 in PhMe-$d_8$ at 258 K, showing coupling in coordinated MeCN ligands.
References


