Supporting information

to the article

Catalytic Hydroboration by an Imido-Hydrido Complex of Mo(IV)

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Experimental details

All manipulations were carried out using conventional inert atmosphere glove-box and Schlenk techniques. Dry diethyl ether, toluene, hexanes, and acetonitrile were obtained, using Grubbs-type purification columns, other solvents were dried by distillation from appropriate drying agents. C_6D_6, PhMe-d_8 were dried by distillation from K/Na alloy, and $CDCl_3$ was dried by distillation from CaH_2. NMR spectra were obtained with a Bruker DPX-300 and Bruker DPX-600 instruments (^{1}H: 300 and 600 MHz; ^{2}D: 92.1 MHz; ^{13}C: 75.5 and 151 MHz; ^{29}Si: 59.6 and 119.2 MHz; ^{31}P: 121.5 and 243 MHz; ^{11}B: 96.3 and 192.6 MHz). NMR analysis was done at room temperature unless specified. IR spectra were measured on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses were performed in "ANALEST" laboratories (University of Toronto). Preparation of (ArN)Mo(H)(Cl)(PMe_3)$_3$ (**1**) was reported earlier.[1] Benzaldehyde, acetone, acetophenone, benzophenone, cyclohexanone, ethyl acetate, *i*$Pr_2C(O)$, styrene, 3-hexyne, phenylacetylene, PhCN, MeCN, 5-hexynenitrile, 4-acetylbenzonitrile, 4-formylbenzonitrile, 3-(2-oxocyclohexyl)propanenitrile were purchased from Sigma-Aldrich and used without further purification. HBCat was purchased from Sigma-Aldrich and additionally purified by distillation. 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 hydrosilated and hydrogenated products were determined by NMR analysis using tetramethylsilane as an internal standard.

Reaction of (ArN)Mo(H)(Cl)(PMe_3)$_3$ (1) with MeCN

A. Acetonitrile (1.1 μl, 0.02 mmol) was added in one portion at room temperature to a solution of (ArN)Mo(H)(Cl)(PMe_3)$_3$ (**1**) (10.4 mg, 0.02 mmol) in 0.6 ml of C_6D_6 in an NMR tube. No visual changes were observed after CH_3CN 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)(PMe_3)$_2$ (**2**) as a mixture of *cis*- and *trans*- isomers (ratio 1:1.6, according to the ^{31}P{^{1}H} NMR spectrum).

B. A solution of (ArN)Mo(H)(Cl)(PMe_3)$_3$ (**1**) (22.7 mg, 0.04 mmol) and CH_3CN (5.0 μl, 0.1 mmol) in 0.6 ml of C_6D_6 was added in one portion at room temperature to a solid BPh_3 (9.7 mg, 0.04 mmol). Immediate formation of white precipitate of $Ph_3B{\cdot}PMe_3$ was

observed. The mixture was transferred to an NMR tube and left at room temperature for 5 min. NMR analysis showed quantitative formation of (ArN)Mo(Cl)(N=CHMe)(PMe_3)$_2$ (**2**) (1:1.3 mixture isomers, according to the $^{31}P\{^1H\}$-NMR spectrum). The mixture was filtered, all volatiles were pumped off, and the residue was dried and extracted with 2.0 ml of hexanes. The solvent was removed in vacuum to give a brown oily substance (13.7 mg, 68 %). All attempts to isolate complex **2** in analytically pure form by recrystallization were unsuccessful and led to the formation of oily material.

$^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6; both isomers; δ, ppm): 154.1, 147.1 (s, aromatic N*Ar*); 146.6 (bs, N=*C*(H)CH_3, minor isomer, found by ^1H-^{13}C HSQC NMR); 145.4 (d, $J_{C\text{-}P}$ = 11.3 Hz, N=*C*(H)CH_3, major isomer, found by ^1H-^{13}C HSQC NMR); 125.7, 124.9, 123.6, 123.2, 115.9 (s, aromatic N*Ar*); 27.9 (s, *CH*, N*Ar*, major isomer); 27.7 (s, *CH*, N*Ar*, minor isomer); 23.72 (s, *CH*$_3$, N*Ar*, minor isomer); 23.67 (s, *CH*$_3$, N*Ar*, major isomer); 23.0 (s, N=C(H)*CH*$_3$, major isomer); 19.1 (bs, N=C(H)*CH*$_3$, minor isomer); 14.0 (dd, $^3J_{C\text{-}P}$ = 11.3 Hz, $^1J_{C\text{-}P}$ = 22.6 Hz, 2 P*Me*$_3$, minor isomer); 13.6 (dd, $^3J_{C\text{-}P}$ = 11.3 Hz, $^1J_{C\text{-}P}$ = 21.9 Hz, 2P*Me*$_3$, major isomer).

Major isomer of **2**: ^1H NMR (300 MHz; C_6D_6; δ, ppm): 6.86-7.13 (m, N*Ar* aromatic protons overlapping with minor isomer); 6.15 (m, $^3J_{H\text{-}H}$ = 5.1 Hz, 1H, N=C(*H*)CH_3, found by ^1H-^{13}C HMBC NMR); 4.12 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, 2 *CH*, N*Ar*); 2.37 (ddd, $^3J_{H\text{-}H}$ = 5.1 Hz, $J_{H\text{-}P}$ = 1.5 Hz and 2.7 Hz, 3H, N=C(H)*CH*$_3$, found by ^1H-^{13}C HMBC NMR); 1.29 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, 4 *CH*$_3$, N*Ar*); 1.16 (dd, $^2J_{H\text{-}P}$ = 7.2 Hz, $^4J_{H\text{-}P}$ = 3.6 Hz, 18H, 2 P*Me*$_3$, both isomers). $^1H\{^{31}P\}$ NMR (300 MHz; C_6D_6; δ, ppm; selected resonances): 6.15 (q, $^3J_{H\text{-}H}$ = 5.1 Hz, 1H, N=C(*H*)CH_3); 2.37 (d, $^3J_{H\text{-}H}$ = 5.1 Hz, 3H, N=C(H)*CH*$_3$); 1.16 (s, 18H, 2P*Me*$_3$, both isomers). $^{31}P\{^1H\}$ NMR (121.5 MHz; C_6D_6; δ, ppm): -0.3 (s, 2*P*Me$_3$). ^{31}P NMR (121.5 MHz; C_6D_6; δ, ppm): -0.2 (bs, PMe_3, both isomers).

Minor isomer of **2**: ^1H NMR (300 MHz; C_6D_6; δ, ppm): 7.70 (m, $^3J_{H\text{-}H}$ = 4.8 Hz, 1H, N=C(*H*)CH_3, found through ^1H-^{13}C HMBC NMR); 6.86-7.13 (m, N*Ar* overlapping with major isomer); 4.27 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, 2 *CH*, N*Ar*); 2.26 (ddd, $^3J_{H\text{-}H}$ = 4.8 Hz, $J_{H\text{-}P}$ = 1.5 Hz and 3.6 Hz, 3H, N=C(H)*CH*$_3$, found by ^1H-^{13}C HMBC NMR); 1.27 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, 4 *CH*$_3$, N*Ar*); 1.16 (dd, $^2J_{H\text{-}P}$ = 7.2 Hz, $^4J_{H\text{-}P}$ = 3.6 Hz, 18H, 2 P*Me*$_3$, both isomers). $^1H\{^{31}P\}$ NMR (300 MHz; C_6D_6; δ, ppm; selected resonances): 6.15 (q, $^3J_{H\text{-}H}$ = 5.1 Hz, 1H, N=C(*H*)CH_3); 2.26 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 3H, N=C(H)*CH*$_3$); 1.16 (s, 18H,

2P*Me*$_3$, both isomers). $^{31}P\{^1H\}$ NMR (121.5 MHz; C_6D_6; δ, ppm): -0.1 (bs, 2*P*Me$_3$). ^{31}P NMR (121.5 MHz; C_6D_6; δ, ppm): -0.2 (bs, PMe$_3$, both isomers).

Preparation of (ArN)Mo(Cl)(N=CHPh)(PMe$_3$)$_2$ (3)

PhCN (36.0 µl, 0.352 mmol) was added in one portion at room temperature to a solution of (ArN)Mo(H)(Cl)(PMe$_3$)$_3$ (**1**) (188.9 mg, 0.352 mmol) in 15 ml of toluene. The mixture was stirred at room temperature for 50 min. All volatiles were pumped off, and the residue was extracted with 30 ml of diethyl ether. Et_2O solution was concentrated to 10 ml and left at -80 °C for a week to give a yellow powder of (ArN)Mo(Cl)(N=CHPh)(PMe$_3$)$_2$ (**3**), which was filtered off and dried in vacuum. Yield: 125.0 mg, 63 %. ^1H NMR (300 MHz; C_6D_6; δ, ppm): 7.38 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, *o*-H, -N=CH*Ph*); 7.27 (m, 2H, *m*-H, -N=CH*Ph*); 7.23 (t, $J_{H\text{-}P}$ = 6.0 Hz, 1H, -N=C*H*Ph, found by ^1H-^{31}P HSQC (J = 30 Hz) and ^1H-^{13}C HSQC NMR); 7.06 (m, 2H, *m*-H, N*Ar*); 6.85 (m, 1H, *p*-H, N*Ar*); 6.63 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, *p*-H, -N=CH*Ph*); 4.21 (sept, $^3J_{H\text{-}H}$ = 7.0 Hz, 2H, 2 *CH*, N*Ar*); 1.32 (d, $^3J_{H\text{-}H}$ = 7.0 Hz, 12H, 4 *CH$_3$*, N*Ar*); 1.10 (dd, $^2J_{H\text{-}P}$ = 7.2 Hz, 18H, 2 P*Me$_3$*). $^1H\{^{31}P\}$ NMR (300 MHz; C_6D_6; selected resonances; δ, ppm): 7.22 (s, 1H, Mo-N=C*H*Ph); 1.10 (s, 18H, 2 P*Me$_3$*). $^{31}P\{^1H\}$ NMR (121.6 MHz; C_6D_6; δ, ppm): -0.7 (s, 2 *P*Me$_3$). ^1H-^{13}C HSQC NMR (f1: 300 MHz; f2: 75.5 MHz, J = 145.0 Hz; C_6D_6; ^{13}C projection; δ, ppm): 150.2 (Mo-N=*C*HPh); 131.6, 128.7, 128.3, 123.5, 122.9, 122.3 (aromatic carbons of C*Ph* and N*Ar*); 27.6 (*C*H, N*Ar*); 23.5 (*C*H$_3$, N*Ar*); 13.0 (P*Me$_3$*). Elem. Anal. (%): calc. for $C_{25}H_{41}ClMoN_2P_2$ (562.947): C 53.34, H 7.34, N 4.98; found: C 53.04, H 7.30, N

NMR scale reaction of (ArN)Mo(Cl)(N=CHMe)(PMe$_3$)$_2$ (2) with PhCN

(ArN)Mo(Cl)(N=CHMe)(PMe$_3$)$_2$ (**2**) was generated in an NMR tube in 0.6 ml of C_6D_6 from (ArN)Mo(H)(Cl)(PMe$_3$)$_3$ (**1**) (10.4 mg, 0.02 mmol) and acetonitrile (1.1 µl, 0.02 mmol) (see procedure above). All volatiles were pumped off and the residue was dried in vacuum and redissovled in 0.6 ml of C_6D_6. Benzonitrile (10.0 µl, 0.098 mmol) was added in one portion to solution. The reaction mixture was left at room temperature for 24 h. NMR analysis showed full conversion of **2**, evolution of one equivalent of CH_3CN, and formation of (ArN)Mo(Cl)(N=CHPh)(PMe$_3$)$_2$ (**3**).

NMR scale reaction of (ArN)Mo(H)(Cl)(PMe_3)$_3$ (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 (ArN)Mo(H)(Cl)(PMe_3)$_3$ (**1**) (28.7 mg, 0.054 mmol) in 0.6 ml of C_6D_6 in an NMR tube. The reaction mixture was monitored by NMR analysis at room temperature for 3 days showing full conversion of **1** and formation of a difficult-to-separate mixture of insertion product **4** (mixture of two isomers) and (ArN)$MoCl_2(PMe_3)_3$[2] (1.3/1, respectively, according to $^{31}P\{^1H\}$ NMR spectroscopy). After 3 days all volatiles were pumped off to leave an oily residue which was dried in vacuum and redissolved in C_6D_6 for NMR analysis. All attempts to isolate complex **4** in analytically pure form by recrystallization were unsuccessful and led to the formation of oily material.

Major isomer of **4**: ^1H NMR (600 MHz; C_6D_6; δ, ppm): 7.11-7.24 (m, aromatic protons overlapping with the signals of minor isomer); 7.09 (dt, $^4J_{H\text{-}P}$ = 3.1 Hz, $^3J_{H\text{-}H}$ = 8.2 Hz, 1H, N=C*H*); 6.65 (dd, $^3J_{H\text{-}H}$ = 8.2 and 15.7 Hz, 1H, N=CH-C*H*); 5.28 (dt, $^3J_{H\text{-}H}$ = 7.2 and 15.7 Hz, 1H, N=CH-CH=C*H*); 4.28 (sept, $^3J_{H\text{-}H}$ = 7.0 Hz, 2H, 2 *CH*, N*Ar*); 2.48 (dq, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, CH=CH*CH*$_2$CH$_3$); 1.42 (d, $^3J_{H\text{-}H}$ = 7.0 Hz, 12H, 4 *CH*$_3$, N*Ar*); 1.27 (vt, $^2J_{H\text{-}P}$ = 7.3 Hz; 18H, 2 P*Me*$_3$); 1.11 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 3H, CH=CHCH$_2$*CH*$_3$). $^{31}P\{^1H\}$ NMR (243 MHz; C_6D_6; δ, ppm): -1.2 (s, 2 *P*Me$_3$). $^{13}C\{^1H\}$ NMR (151 MHz; C_6D_6; δ, ppm): 151.9 (bs, N=*C*H); 150.3 (s, *i*-C, N*Ar*); 145.4 (s, *o*-C, N*Ar*); 129.4 (s, N=CH-*C*H); 126.2, 125.9 (N*Ar*); 121.4 (s, N=CH-CH=*C*H); 27.7 (s, *C*H, N*Ar*); 25.1 (s, N=CH-CH=CH*C*H$_2$CH$_3$); 23.5 (s, *C*H$_3$, N*Ar*); 15.6 (s, N=CH-CH=CHCH$_2$*C*H$_3$); 13.1 (vt, $^1J_{C\text{-}P}$ = 22.1 Hz, 2 P*Me*$_3$).

Minor isomer of **4**: ^1H NMR (600 MHz; C_6D_6; δ, ppm): 8.35 (dt, $^4J_{H\text{-}P}$ = 3.5 Hz, $^3J_{H\text{-}H}$ = 8.8 Hz, 1H, N=C*H*); 7.11-7.24 (m, aromatic protons overlapping with the signals of major isomer); 6.51 (dd, $^3J_{H\text{-}H}$ = 8.8 and 15.5 Hz, 1H, N=CH-C*H*); 5.62 (dt, $^3J_{H\text{-}H}$ = 7.2 and 15.5 Hz, 1H, N=CH-CH=C*H*); 4.48 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, 2 *CH*, N*Ar*); 2.60 (dq, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, CH=CH*CH*$_2$CH$_3$); 1.46 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, 4 *CH*$_3$, N*Ar*); 1.26 (vt, $^2J_{H\text{-}P}$ = 7.6 Hz; 18H, 2 P*Me*$_3$); 1.18 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 3H, CH=CHCH$_2$*CH*$_3$). $^{31}P\{^1H\}$ NMR (243 MHz; C_6D_6; δ, ppm): -1.4 (s, 2 *P*Me$_3$). $^{13}C\{^1H\}$ NMR (151 MHz; C_6D_6; δ, ppm): 153.5 (bs, N=*C*H); 152.9 (s, *i*-C, N*Ar*); 145.6 (s, *o*-C, N*Ar*); 131.6 (s, N=CH-

CH=*C*H); 130.1 (s, N=CH-*C*H); 27.6 (s, *C*H, N*Ar*); 26.1 (s, N=CH-CH=CH*C*$H_2$$CH_3$); 23.6 (s, *C*$H_3$, N*Ar*); 15.6 (s, N=CH-CH=CHCH_2*C*H_3); 13.3 (vt, $^1J_{C\text{-}P}$ = 22.1 Hz, 2 P*Me*$_3$).

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_6D_6 was added in one portion at room temperature to a solid (ArN)Mo(H)(Cl)(PMe_3)$_3$ (**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 **5** and (ArN)$MoCl_2(PMe_3)_3$[2] (6:1, respectively, according to $^{31}P\{^1H\}$ NMR spectroscopy). According to NMR analysis, the carbonyl moiety remained unreacted. All attempts to purify complex **5** by recrystallization were unsuccessful and resulted in mixtures of **5** and (ArN)$MoCl_2(PMe_3)_3$.

5: ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.94 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 2H, o-H, 4-$CH_3C(O)C_6H_4$); 7.26 (bm, 1H, N=C*H*, found by ^{1}H-^{31}P HSQC NMR); 6.89-7.25 (m, 5H, aromatic protons); 4.18 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, 2 *CH*, N*Ar*); 2.21 (s, 3H, 4-*CH*$_3$C(O)C_6H_4); 1.31 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, 4 *CH*$_3$; N*Ar*); 1.07 (vt, $^2J_{H\text{-}P}$ = 7.1 Hz, 18H, 2 P*Me*$_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz; C_6D_6; δ, ppm): -0.8 (s, 2 *P*Me_3). ^{1}H-^{13}C HSQC NMR (f1: 300 MHz; f2: 75.5 MHz, *J* = 145.0 Hz; C_6D_6; ^{13}C projection; δ, ppm): 147.9 (N=*C*H); 129.0, 128.3, 123.3, 123.7 (all aromatic carbons); 27.4 (*C*H, N*Ar*); 25.4 (4-*C*H_3C(O)C_6H_4); 23.6 (*C*H_3, N*Ar*); 12.3 (2 P*Me*$_3$).

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

Acrylonitrile (2.9 μl, 0.044 mmol) was added in one portion at room temperature to a solution of (ArN)Mo(H)(Cl)(PMe_3)$_3$ (**1**) (23.6 mg, 0.044 mmol) in 0.6 ml of C_6D_6 in an NMR tube. Immediately after nitrile addition the colour of the mixture changed to a different tint of brown. The reaction mixture was left at room temperature for 20 min showing (by NMR) 56 % conversion of the starting material and formation of *trans*-(ArN)Mo(H)(Cl)(η^2-CH_2=CHCN)(PMe_3)$_2$ (**6**) in a mixture with (ArN)$MoCl_2(PMe_3)_3$[2] (1/1, respectively, according to $^{31}P\{^1H\}$ NMR spectroscopy) No further conversion of **1** was observed by NMR in next 2 days. All attempts to purify complex **6** by

recrystallization were unsuccessful and resulted in mixtures of **6** and $(ArN)MoCl_2(PMe_3)_3$.

6: ^{1}H NMR (600 MHz; C_6D_6; δ, ppm): 6.90-7.21 (m, 8H, C*Ph* and N*Ar*); 6.68 (dd, $^2J_{H-P}$ = 33.8 and 47.0 Hz, 1H, Mo*H*); 4.24 (m, 2H, 2 *CH*, N*Ar*); 2.87 (m, 1H, η^2-C_2H_3CN); 2.51 (m, 1H, η^2-C_2H_3CN); 2.45 (m, 1H, η^2-C_2H_3CN); 1.61 (d, $^2J_{H-P}$ = 8.6 Hz, 9H, P*Me$_3$*); 1.36 (d, $^2J_{H-P}$ = 8.9 Hz, 9H, P*Me$_3$*); 1.31 (m, 12H, 4 *CH$_3$*, N*Ar*). ^{31}P{^{1}H} NMR (243 MHz; C_6D_6; δ, ppm): -2.4 (d, $^2J_{P-P}$ = 98.8 Hz, *P*Me$_3$); -4.1 (d, $^2J_{P-P}$ = 98.8 Hz, *P*Me$_3$). ^{13}C{^{1}H} NMR (151 MHz; C_6D_6; δ, ppm): 153.8, 150.3, 146.6, 144.1, 126.3, 124.7, 123.7, 123.0 (aromatic carbons of C*Ph* and N*Ar*); 46.5 (d, $^2J_{C-P}$ = 8.9 Hz, η^2-*C*H_2=CHCN); 31.8 (d, $^2J_{C-P}$ = 7.4 Hz, η^2-CH_2=*C*HCN); 27.0 (s, *CH*, N*Ar*); 25.2 (s, *CH$_3$*, N*Ar*); 17.5 (d, $^1J_{C-P}$ = 27.5 Hz, P*Me$_3$*); 16.3 (d, $^1J_{C-P}$ = 26.9 Hz, P*Me$_3$*).

NMR scale reaction of (ArN)Mo(H)(Cl)(PMe$_3$)$_3$ (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 $(ArN)Mo(H)(Cl)(PMe_3)_3$ (**1**) (18.6 mg, 0.035 mmol). Immediately after 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 PMe_3 and formation of bis(phosphine) complex *trans*-$(ArN)Mo(H)(Cl)(\eta^2$-$O{=}CHC_6H_4CN)(PMe_3)_2$ (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 $(ArN)Mo(Cl)(OCH_2C_6H_4CN)(PMe_3)_3$ (**7**). Small amount of $(ArN)MoCl_2(PMe_3)_3$[2] (~15 % by ^{31}P{^{1}H} NMR) was also observed by NMR. All attempts to purify complex **7** by recrystallization were unsuccessful and resulted in mixtures of **7** and $(ArN)MoCl_2(PMe_3)_3$.

trans-(ArN)Mo(H)(Cl)(η^2-O=CHC$_6$H$_4$CN)(PMe$_3$)$_2$: Only major isomer described due to very low abundance of minor isomer. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.41 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, C*C$_6$H$_4$*); 7.38 (m, 1H, MoH; found by ^{1}H-^{31}P HSQC NMR); 6.76-6.93 and 7.18-7.29 (m, 5H, N*Ar* and C*C$_6$H$_4$*); 5.52 (bs, 1H, η^2-O=C*H*C$_6$H$_4$CN); 4.12 (sept, $^3J_{H-H}$ = 6.8 Hz, 2H, 2 *CH*, N*Ar*); 1.39 (d, $^2J_{H-P}$ = 9.7 Hz, 9H, P*Me$_3$*); 1.16 (m, 12H, 4 *CH$_3$*, N*Ar*); 1.08 (d, $^2J_{H-P}$ = 9.3 Hz, 9H, P*Me$_3$*). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): -1.7 (d, $^2J_{P-P}$ = 106.7 Hz, *P*Me$_3$); -5.5 (d, $^2J_{P-P}$ = 106.7 Hz, *P*Me$_3$). ^{13}C{^{1}H} NMR (151 MHz;

C_6D_6; δ, ppm): 150.6, 148.4, 147.6, 146.6, 130.3, 128.2, 123.7, 123.3 (aromatic carbons of N*Ar* and C*C*$_6$*H*$_4$); 108.7 (s, *C*N); 85.2 (s, η^2-O=*C*HC$_6$H$_4$CN); 27.0 (s, *C*H, N*Ar*); 25.2 (s, *C*H$_3$, N*Ar*); 17.6 (d, $^1J_{C\text{-}P}$ = 28.5 Hz, P*Me*$_3$); 13.9 (d, $^1J_{C\text{-}P}$ = 26.3 Hz, P*Me*$_3$).

7: ^{1}H NMR (600 MHz; C_6D_6; *δ*, ppm): 6.95-7.24 (m, 7H, N*Ar* and C*C*$_6$*H*$_4$); 5.06 (s, 2H, O*CH*$_2$C$_6$H$_4$CN); 4.35 (bs, 2H, 2 *CH*, N*Ar*); 1.36 (bs, 12H, 4 *CH*$_3$, N*Ar*); 1.29 (m, 18H, 2 P*Me*$_3$). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; *δ*, ppm): 8.1 (t, $^2J_{P\text{-}P}$ = 16.1 Hz, *P*Me$_3$); -9.5 (d, $^2J_{P\text{-}P}$ = 16.1 Hz, *P*Me$_3$). ^{13}C{^{1}H} NMR (151 MHz; C_6D_6; δ, ppm): 152.5, 150.6, 147.0, 131.5, 128.1, 124.4, 123.7 (aromatic carbons of N*Ar* and C*C*$_6$*H*$_4$); 109.8 (s, CN); 70.5 (s, O*C*H$_2$C$_6$H$_4$CN); 26.9 (s, *CH*, N*Ar*); 25.4 (s, *CH*$_3$, N*Ar*); 21.8 (d, $^1J_{C\text{-}P}$ = 21.6 Hz, PMe$_3$); 16.5 (vt, $^1J_{C\text{-}P}$ = 20.4 Hz, 2 P*Me*$_3$).

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_6D_6 was added in one portion at room temperature to solid (ArN)Mo(H)(Cl)(PMe$_3$)$_3$ (**1**) (18.2 mg, 0.034 mmol). The mixture was immediately transferred into an NMR and monitored by NMR spectroscopy for 12 hours. After 50 min at room temperature NMR analysis showed full conversion of the starting material and selective formation of methylenamide complex **3**. Acetone remained unreacted. No changes were observed by NMR within 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_6D_6 was added in one portion at room temperature to solid (ArN)Mo(H)(Cl)(PMe$_3$)$_3$ (**1**) (18.5 mg, 0.035 mmol). The mixture was immediately transferred into an NMR and monitored by NMR spectroscopy for 12 hours. After 1 hour at room temperature NMR analysis showed full conversion of the starting material and selective formation of methylenamide complex **3**. Acetophenone remained unreacted. No changes were observed by NMR within 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_6D_6 was added in one portion at room temperature to solid (ArN)Mo(H)(Cl)(PMe$_3$)$_3$ (**1**) (23.2 mg, 0.043 mmol). The mixture was immediately

transferred into an NMR 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 methylenamide complex **3** (84 %) and (ArN)Mo(Cl)(OCy)$(PMe_3)_3$[3] (16 %). Acetophenone remained unreacted. No changes were observed by NMR within next 10 hours.

NMR scale reaction of (ArN)Mo(H)(N=CHPh)$(PMe_3)_2$ (3) with HBCat

A: Room temperature reaction. A solution of HBCat (3.5 μl, 0.033 mmol) in 0.6 ml of C_6D_6 was added in one portion at room temperature to solid (ArN)Mo(H)(N=CHPh)$(PMe_3)_2$ (**3**) (18.5 mg, 0.033 mmol). The mixture was immediately transferred in to an NMR tube and left at room temperature for 10 min. During this time the colour of the mixture turned red. NMR analysis after 10 min showed formation of a difficult-to-separate mixture of starting material and (ArN)Mo(H)(Cl)(η^2-N(BCat)=CHPh)$(PMe_3)_2$ (**11**) (~1:1). Addition of another equivalent of HBCat to the reaction mixture leads to full conversion of **3** into **11**. All attempts to isolate complex **11** were unsuccessful due to its instability. The ^{31}P-^{31}P EXSY NMR of complex **11** revealed an intramolecular exchange of PMe_3 ligands; however, addition of PhCN to a solution of **11** in C_6D_6 does not afford CatBN=CHPh. On the other hand, addition of a stoichiometric mixture of PhCN and HBCat to a solution of **11** in C_6D_6 leads to slow (2 days) conversion of **11** into **3** and formation of $PhCH_2N(BCat)_2$.

A: Low temperature VT reaction. HBCat (3.6 μl, 0.033 mmol) was added in one portion at room temperature to a frozen in liq. N_2 solution of (ArN)Mo(H)(N=CHPh)$(PMe_3)_2$ (**3**) (23.5 mg, 0.042 mmol) in 0.6 ml of C_6D_6 in an NMR tube. The mixture was warmed up to -30 °C and placed into an NMR machine pre-cooled to -30 °C. The temperature was dropped down to -50 °C and the sample was warmed gradually and monitored by NMR spectroscopy. At -50 °C, NMR analysis revealed the presence of a mixture of the starting material **3**, (ArN=)Mo(Cl){η^3-N(=CHPh)(CatB-H$^{\cdots}$}$(PMe_3)_2$ (**9**), and (ArN)Mo(H)(Cl)(η^1-N(BCat)=CHPh)$(PMe_3)_2$ (**10**). Compound **9** is slowly transferred to **10** upon increase of the temperature of the reaction mixture. Warming the sample up to 25 °C leads to the formation of the hydride derivative (ArN)Mo(H)(Cl){η^2-CatBN=CHPh}$(PMe_3)_2$ (**11**). Addition of another equivalent of

HBCat affords $PhCH_2N(BCat)_2$ and a mixture of **1**, $(ArN)MoCl_2(PMe_3)_3$,[2] and unknown decomposition products.

(ArN=)Mo(Cl){ η^3-N(=CHPh)(CatB-H···}(PMe$_3$)$_2$ (**9**): ^{1}H NMR (600 MHz; 225 K; PhMe-d_8; δ, ppm): 8.91 (bs, 1H, C*H*Ph); 8.08 (d, $^3J_{H-H}$ = 7.4 Hz, 2H, *o*-H, CH*Ph*); 6.63-7.37 (m, overlapping aromatic signals of HBCat, **3**, **9**, and **10**); 4.33 (bm, 2H, 2*CH*, *Ar*N, overlapping with *CH* (*Ar*N) of **3**); 1.39 (bm, 6H, 2CH_3, *Ar*N); 1.29 (bm, 6H, 2CH_3, *Ar*N); 1.24 (bm, 18H, 2 P*Me*$_3$). ^{31}P{^{1}H} NMR (243 MHz; 225 K; PhMe-d_8; δ, ppm): -0.9 (bs, *P*Me$_3$). ^{11}B{^{1}H} NMR (193 MHz; 253 K; PhMe-d_8; δ, ppm): 2.3 (bs, H*B*Cat). ^{11}B NMR (193 MHz; 283 K; PhMe-d_8; δ, ppm): 2.2 (bd, $^1J_{B-H} \approx$ 55 Hz; H*B*Cat). ^{13}C{^{1}H} NMR (151 MHz; 253 K; PhMe-d_8; δ, ppm): 172.0 (s, N=*C*HPh, found by ^{1}H-^{13}C HSQC NMR); 129.7 (s, *o*-C, CH*Ph*); 27.5 (s, *CH*, *Ar*N); 23.8 (s, CH_3, *Ar*N); 23.6 (s, CH_3, *Ar*N); 14.3 (vt, $^1J_{C-P}$ = 24 Hz, 2 *trans*-P*Me*$_3$).

(ArN)Mo(H)(Cl)(η^1-N(BCat)=CHPh)(PMe$_3$)$_2$ (**10**): ^{1}H NMR (600 MHz; 225 K; PhMe-d_8; δ, ppm): 8.31 (bs, 1H, N=C*H*Ph); 6.63-7.37 (m, overlapping aromatic signals of HBCat, **3**, **9**, and **10**); 4.12 (bs, 1H, *CH*, *Ar*N); 3.92 (bs, 1H, *CH*, *Ar*N); 1.32 (bm, 6H, 2CH_3, *Ar*N); 1.29 (d, $^2J_{H-P}$ = 8.4 Hz, 9H, P*Me*$_3$); 1.21 (bm, 6H, 2CH_3, *Ar*N); 0.87 (d, $^2J_{H-P}$ = 8.1 Hz, 9H, P*Me*$_3$); -2.94 (bm, 1H, Mo*H*). ^{31}P{^{1}H} NMR (243 MHz; 225 K; PhMe-d_8; δ, ppm): -1.4 (d, $^2J_{P-P}$ = 212.0 Hz, *P*Me$_3$); -13.0 (d, $^2J_{P-P}$ = 212.0 Hz, *P*Me$_3$). ^{11}B NMR (193 MHz; 253 K; PhMe-d_8; δ, ppm): 10.1 (bs, *B*Cat). ^{11}B NMR (193 MHz; 283 K; PhMe-d_8; δ, ppm): 10.2 (bs, *B*Cat). ^{13}C{^{1}H} NMR (151 MHz; 253 K; PhMe-d_8; δ, ppm): 154.2 (s, N=*C*HPh, found by ^{1}H-^{13}C HSQC NMR); 27.2 (s, *CH*, *Ar*N); 26.9 (s, *CH*, *Ar*N); 25.7 (bs, CH_3, *Ar*N); 25.2 (s, CH_3, *Ar*N); 13.1 (d, $^1J_{C-P}$ = 22.8 Hz, P*Me*$_3$); 12.7 (d, $^1J_{C-P}$ = 21.7 Hz, P*Me*$_3$).

(ArN)Mo(H)(Cl){ η^2-CatBN=CHPh}(PMe$_3$)$_2$ (**11**): ^{1}H NMR (600 MHz; 295 K; PhMe-d_8; δ, ppm): 7.65 (d, $^3J_{H-H}$ = 7.7 Hz, 2H, *o*-H, CH*Ph*, major isomer); 7.45 (d, $^3J_{H-H}$ = 7.7 Hz, 2H, *o*-H, CH*Ph*, minor isomer); 7.06 (m, Mo*H* of major isomer, obscured by aromatic signals, found by ^{1}H-^{31}P HSQC NMR); 6.9-7.3 (m, overlapping aromatic signals of CPh and NAr of **3**, **10**, **11**, and $(ArN)MoCl_2(PMe_3)_3$); 6.91 (m, 2H, B*Cat*, major isomer); 6.78 (m, 2H, B*Cat*, major isomer); 6.73 (bm, Mo*H* of minor isomer, found by ^{1}H-^{31}P HSQC NMR); 5.00 (dd, $^3J_{H-P}$ = 3.0 Hz; 1H, N=C*H*Ph, major isomer); 4.39 (bs, 1H, N=C*H*Ph, minor isomer); 4.22 (sept, $^3J_{H-H}$ = 6.7 Hz, 1H, *CH*, *Ar*N, major isomer); 4.13 (sept, $^3J_{H-H}$

= 6.7 Hz, 1H, *CH*, *Ar*N, major isomer); 3.98 (bm, 1H, *CH*, *Ar*N, minor isomer); 3.84 (sept, $^{3}J_{H\text{-}H}$ = 6.7 Hz, 1H, *CH*, *Ar*N, minor isomer); 1.80 (d, $^{2}J_{H\text{-}P}$ = 10.1 Hz, 9H, P*Me*$_3$, major isomer); 1.72 (d, $^{2}J_{H\text{-}P}$ = 10.1 Hz, 9H, P*Me*$_3$, minor isomer); 1.35 (bm, 9H, P*Me*$_3$, minor isomer); 1.24 (d, $^{3}J_{H\text{-}H}$ = 6.7 Hz, 6H, 2*CH*$_3$, *Ar*N, major isomer); 1.20 (d, $^{2}J_{H\text{-}P}$ = 9.9 Hz, 9H, P*Me*$_3$, major isomer); 1.18 (d, $^{3}J_{H\text{-}H}$ = 6.7 Hz, 6H, 2*CH*$_3$, *Ar*N, major isomer). ^{31}P{^{1}H} NMR (243 MHz; 295 K; PhMe-d$_8$; *δ*, ppm): 2.4 (d, $^{2}J_{P\text{-}P}$ = 88.5 Hz, *P*Me$_3$, both isomers); -5.2 (d, $^{2}J_{P\text{-}P}$ = Hz, *P*Me$_3$, both isomers). ^{31}P NMR (selectively decoupled from methyl groups at 1.20 ppm in the ^{1}H NMR spectrum; 243 MHz; 295 K; PhMe-d$_8$; *δ*, ppm): 2.4 (dd, $^{2}J_{P\text{-}P}$ = 88.5 Hz, $^{2}J_{P\text{-}H}$ = 50.9 Hz, *P*Me$_3$); -5.2 (bm, *P*Me$_3$). ^{31}P NMR (selectively decoupled from methyl groups at 1.80 ppm in the ^{1}H NMR spectrum; 243 MHz; 295 K; PhMe-d$_8$; *δ*, ppm): 2.4 (bm, *P*Me$_3$); -5.2 (dd, $^{2}J_{P\text{-}P}$ = 88.5 Hz, $^{2}J_{P\text{-}H}$ = 45.0 Hz, *P*Me$_3$). ^{11}B NMR (193 MHz; 295 K; PhMe-d$_8$; *δ*, ppm): 27.5 (bs, *B*Cat). ^{1}H-^{13}C HSQC NMR (f1: 300 MHz; f2: 75.5 MHz; *J* = 145 Hz; 296 K; PhMe-d$_8$; ^{13}C projection for major isomer; *δ*, ppm): 128.9 (*o*-C, C*Ph*); 62.9 (N=*C*HPh); 27.2 (*C*H, *Ar*N); 26.6 (*C*H, *Ar*N); 24.9 (*C*H$_3$, *Ar*N); 24.8 (*C*H$_3$, *Ar*N); 17.5 (P*Me*$_3$); 17.1 (P*Me*$_3$).

NMR scale reaction of (ArN)Mo(H)(N=CHPh)(PMe$_3$)$_2$ (3) with benzaldehyde

Benzaldehyde (2.6 µl, 0.026 mmol) and PMe$_3$ (2.7 µl, 0.026 mmol) were added at room temperature to a solution of (ArN)Mo(H)(N=CHPh)(PMe$_3$)$_2$ (**3**) (10.5 mg, 0.019 mmol) in 0.6 ml of C$_6$D$_6$ in an NMR tube. No visual changes were observed and the reaction mixture was left at room temperature for two days. NMR analysis after that showed full conversion of the starting material and formation of PhCN and (ArN)Mo(Cl)(OCH$_2$Ph)(PMe$_3$)$_3$ (**8**).[1] Traces of (ArN)MoCl$_2$(PMe$_3$)$_3$[2] were also observed by NMR spectroscopy.

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

(ArN)Mo(H)(Cl)(PMe$_3$)$_3$ (**1**) (15 mg, 0.028 mmol) was dissolved in C$_6$D$_6$ to which acetophenone (3.3 µL; 0.028 mmol) was added via syringe. The brown solution immediately changed colour to a lighter green/brown. The reaction was monitored by NMR and the complete conversion of the starting complex was observed after 4.5 hours, with the formation of a mixture of (ArN)Mo(Cl){OCH(Me)Ph}(PMe$_3$)$_3$ (90%) and (ArN)Mo(Cl)$_2$(PMe$_3$)$_3$ (10%). All attempts to obtain (ArN)Mo(Cl){OCH(Me)Ph}(PMe$_3$)$_3$ in analytically pure form by recrystallization were unsuccessful.

(ArN)Mo(Cl){OCH(Me)Ph}(PMe$_3$)$_3$: ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 1.15 (d, 9H, $^2J_{H\text{-}P}$ = 6.7 Hz, P*Me$_3$*); 1.38 (d, $^2J_{H\text{-}P}$ = 6.3 Hz, 9H, P*Me$_3$*); 1.42 (m, 9H, P*Me$_3$*); 1.48 (d, 3H, OCH(*Me*)Ph); 1.50 (d, 12H, 4Me, *Ar*N); 3.69 (bs, 2H, 2CH, *Ar*N); 5.77 (bm, 1H, O-*CH*). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): -13.3 (d, $^2J_{P\text{-}P}$ = 14.1 Hz, *P*Me$_3$); -12.9 (d, $^2J_{P\text{-}P}$ = 14.5 Hz, *P*Me$_3$); 7.05 (t, $^2J_{P\text{-}P}$ = 16.5 Hz, *P*Me$_3$). ^{1}H-^{13}C HSQC NMR (f1: 300 MHz; f2: 75.5 MHz; C_6D_6; δ, ppm): 125.0, 122.1, 121.0 (*m*-C and *p*-C, N*Ar*); 74.1 (O-*C*H-); 29.2 (*C*H, N*Ar*); 27.5 (OCH(*Me*)Ph); 24.8 (P*Me$_3$*); 23.7 (P*Me$_3$*); 23.5 (*Me*, N*Ar*); 21.9 (P*Me$_3$*).

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)MoCl$_2$(PMe$_3$)$_3$ (46%)[2].

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

HBCat (3.9 μL; 0.037 mmol) was added in one portion to a frozen in liq. N_2 solution of (ArN)Mo(H)(Cl)(PMe$_3$)$_3$ (**1**) (20 mg; 0.037 mmol) in 0.6 mL of PhMe-d$_8$ 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$_3$)$_3$[2] and (ArN)Mo(H)$_2$(PMe$_3$)$_3$ (**12**). No formation of ClBCat was detected by NMR analysis.

(ArN)Mo(H)$_2$(PMe$_3$)$_3$ (**12**): compound is highly fluxional at room temperature. ^{1}H NMR (600 MHz; toluene-d$_8$; 244 K; δ, ppm): -5.31 (dtd, $^2J_{H\text{-}P}$ = 60.6 Hz, $^2J_{H\text{-}P}$ = 46.2 Hz, $^2J_{H\text{-}H}$ = 7.2 Hz, 1H, Mo*H*); 1.35 (m, 21H, 4 *CH$_3$* of N*Ar* and P*Me$_3$*); 1.49 (bm, 18H, 2 P*Me$_3$*); 2.08 (m, overlapping with residual toluene-d$_8$ signal, $^2J_{H\text{-}P}$ = 43.2 Hz, $^2J_{H\text{-}H}$ = 7.2 Hz, 1H, Mo*H*, found by ^{1}H-^{1}H COSY and ^{1}H-^{31}P HSQC NMR); 4.43 (sept, $^3J_{H\text{-}H}$ = 6.6 Hz, 2H, 2 *CH*, N*Ar*); 6.91-7.32 (m, overlapping with residual toluene-d$_8$ resonances, 3H, *m*-H and *p*-H of N*Ar*). ^{1}H{^{31}P} NMR (600 MHz; toluene-d$_8$; 243 K; selected resonances; δ, ppm): -5.31 (d, $^2J_{H\text{-}H}$ = 7.2 Hz, 1H, Mo*H*); 1.38 (s, 9H, P*Me$_3$*); 1.50 (s, 18H, 2 P*Me$_3$*); 2.09 (d, $^2J_{H\text{-}H}$ = 7.2 Hz, 1H, Mo*H*). ^{31}P{^{1}H} NMR (243 MHz; toluene-d$_8$; 247 K; δ, ppm): 14 8 (d, $^2J_{P\text{-}P}$ = 19.4 Hz, 2P, 2 *P*Me$_3$); 13.1 (t, $^2J_{P\text{-}P}$ = 19.4 Hz, 1P, *P*Me$_3$). ^{1}H-^{13}C HSQC NMR (f1: 600 MHz; f2: 151 MHz; toluene-d$_8$; 243 K; ^{13}C projection; δ, ppm): 124.9, 122.0, 121.9, (*m*-C and *p*-C, N*Ar*); 26.3 (*C*H, N*Ar*); 26.2 (*CH$_3$*, N*Ar*); 25.9 (PMe$_3$), 25.0 (*CH$_3$*, N*Ar*); 24.2 (P*Me$_3$*). IR (nujol): 1620 cm^{-1} (broad, medium, Mo-H).

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_6D_6 was added in one portion at room temperature to solid (ArN)Mo(H)(Cl)$(PMe_3)_3$ (**1**) (5 mol %). 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_6D_6; δ, ppm): 8.00 (d, $^3J_{H\text{-}H}$ = 18.6 Hz, 1H, PhC*H*=CH) ;7.45(d, $^3J_{H\text{-}H}$ = 7.0 Hz, 2H, *o*-Ph); 7.26(m, 4H, *m*-Ph and *Cat*B); 6.96 (m,3H, *p*-Ph and *Cat*B); 6.63 (d, $^3J_{H\text{-}H}$ = 18.6 Hz, 1H, CH=C*H*BCat). ^{1}H-^{13}C HSQC NMR (f1: 600 MHz; f2: 150 MHz; *J* = 145 Hz; C_6D_6; ^{13}C projection; δ, ppm): 152.0 (Ph*C*H=CH); 137.0 (*o*-Ph); 128.5-121.6 (*m*-H and *p*-H of Ph and *Cat*B); 113.4 (s, PhCH=*C*HBCat). ^{11}B NMR (96.3 MHz; C_6D_6; δ, ppm): 31.5 (bs).

Ph(CH$_2$)$_2$BCat: ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.21-7.35 (m, 5H, *Ph*); 7.09 (m, 2H, *Cat*B); 6.87 (m, 2H, *Cat*B); 2.97 (t, $^3J_{H\text{-}H}$ = 8.1 Hz, 2H,PhCH$_2$*CH$_2$*BCat); 1.58 (t, $^3J_{H\text{-}H}$ = 8.1 Hz, 2H,Ph*CH$_2$*CH$_2$BCat). ^{1}H-^{13}C HSQC NMR (f1: 600 MHz; f2: 150 MHz; *J* = 145 Hz; C_6D_6; ^{13}C projection; δ, ppm): 128.5-121.6 (aromatic CH); 31.4 (PhCH$_2$*CH$_2$*BCat); 29.0 (Ph*CH$_2$*CH$_2$BCat). ^{11}B NMR (96.3 MHz; C_6D_6; δ, ppm): 35.0 (bs).

PhCH(OBCat)Me: ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.40 (d, $^3J_{H\text{-}H}$= 7.2 Hz, 2H, *o*-Ph); 7.21 (m, 3H, *m*-Ph and *p*-Ph); 6.99 (m, 2H, *Cat*B); 6.83 (m, 2H, *Cat*B); 5.50 (q, $^3J_{H\text{-}H}$ = 6.6 Hz, 1H, PhC*H*(OBCat)Me); 1.50 (d, $^3J_{H\text{-}H}$ = 6.3Hz, 3H, PhCH(OBCat)*Me*). ^{11}B NMR (96.3 MHz; C_6D_6; δ, ppm): 23.4 (bs). ^{1}H-^{13}C HSQC NMR (f1: 300 MHz; f2: 75 MHz; *J* = 145 Hz; ^{13}C projection; δ, ppm): 125.6 (*o*-Ph); 74.2 (Ph*C*H(OBCat)Me); 24.9 (PhCH(OBCat)*Me*).

iPr$_2$CH(OBCat): ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 6.90 (m, 4H, *Cat*B); 3.99 (t, $^3J_{H\text{-}H}$ = 5.7 Hz, 1H *CH*(OBcat)); 1.84 (m, 2H, 2*CH*, *i*Pr); 1.14 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 12H, 4*CH$_3$*, *i*Pr). ^{11}B NMR (96.3 MHz; C_6D_6; δ, ppm): 23.7 (bs). ^{1}H-^{13}C HSQC NMR (f1: 300 MHz; f2:

75 MHz; *J* = 145 Hz; ^{13}C projection; δ, ppm): 112.0, 122.3 (*Cat*B); 86.5 (*C*H(OBcat)); 30.1 (*C*H, *i*Pr); 16.8 (*C*H$_3$, *i*Pr).

Ph$_2$CH(OBCat): ^{1}H NMR (300 MHz; C$_6$D$_6$ δ,ppm): 7.50 (d, $^{3}J_{H\text{-}H}$ = 8.4 Hz, 4H, *o*-H, *Ph*); 7.17 (m, 6H, *m*-H and *p*-H of *Ph*) 6.80-6.96 (m, 4H, *Cat*B); 6.55 (s, 1H, *CH*(OBCat)). ^{11}B NMR (96.3 MHz; C$_6$D$_6$; δ, ppm): 23.8 (bs). ^{1}H-^{13}C HSQC NMR (f1: 300 MHz; f2: 75 MHz; *J* = 145 Hz; ^{13}C projection; δ, ppm): 148.2, 142.2, 130.0, 126.7, 122.3, 112.0, 79.6 (*C*H(OBCat)).

EtOBCat: ^{1}H NMR (300 MHz; C$_6$D$_6$; δ, ppm): 7.03 (m, 2H, *Cat*B); 6.86 (m, 2H, *Cat*B); 3.93 (q, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 2H, O*CH$_2$*CH$_3$); 1.11 (t, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 3H, OCH$_2$*CH$_3$*). ^{11}B NMR (96.3 MHz; C$_6$D$_6$; δ, ppm): 23.4 (bs, Cat*B*). ^{1}H-^{13}C HSQC NMR (f1: 300 MHz; f2: 75 MHz; *J* = 145 Hz, ^{13}C projection; δ, ppm): 121.2, 112.0 (*Cat*B); 59.3 (O*C*H$_2$CH$_3$); 13.5 (OCH$_2$*C*H$_3$).

PhCH$_2$N(BCat)$_2$: ^{1}H NMR(300 MHz; CDCl$_3$; *δ*, 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}C{^{1}H} NMR (75.5 MHz; CDCl$_3$; *δ*, ppm): 47.96 (*CH$_2$*N), 112.47 (*CH*, B*Cat*), 122.59 (*CH*, B*Cat*), 127.52 (*CH*, *Ph*), 127.88 (*CH*, *Ph*), 128.72 (*CH*, *Ph*), 140.32 (*i*-C, B*Cat*), 148.46 (*i*-C, B*Cat*). ^{11}B NMR (96.3 MHz; C$_6$D$_6$; *δ*, ppm): 27.6 (bs).

EtN(BCat)$_2$: ^{1}H NMR(300 MHz; C$_6$D$_6$; *δ*, ppm): 7.02 (m, 2H, *Cat*B); 6.76 (m, 2H, *Cat*B); 3.35 (q, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, N*CH$_2$*CH$_3$); 1.10 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 3H, NCH$_2$*CH$_3$*). ^{13}C{^{1}H} NMR (75.5 MHz; C$_6$D$_6$; *δ*, ppm): 148.7 (s, *Cat*B); 122.3 (s, *Cat*B); 122.0 (s, *Cat*B); 39.2 (s, N*C*H$_2$CH$_3$); 17.5 (s, NCH$_2$*C*H$_3$). ^{11}B NMR (96.3 MHz; C$_6$D$_6$; *δ*, ppm): 27.8 (bs).

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

Table SI1. Hydroboration of organic substrates with HBCat mediated by **1** (5 mol. %, C_{subst} = 0.4 M, 22 °C).

Entry	Substrate[a]	Conv.[b]	Product(s)	*t*,	Yield, %[d]	TON[e]	TOF, h^{-1}[e]
1	$PhCH{=}CH_2$	100 %	$PhCH_2CH_2B(Cat)$	20 h	32	20.0	1.00
			trans-PhCH=CHB(Cat)		53		
			$PhCH_2CH_3$		15		
2	3-hexyne	94 %	EtCH=C(Et)B(Cat)	21 h	94	18.8	0.89
3	PhC≡CH	99 %	*trans*-PhCH=CHB(Cat)	20 h	99	19.8	0.99
4	$iPr_2C(O)$	91 %	$(iPr)_2CH(OBCat)$	24 h	91	18.2	0.76
5	MeC(O)OEt	100 %	EtOBCat)	24 h	100	20.0	0.83
6	$Ph_2C(O)$	100 %	$Ph_2CH(OBCat)$	24 h	100	20.0	0.83
7	PhC(O)Me	99 %	PhCH(OBCat)Me	24 h	99	19.8	0.83
8	MeCN	100 %	$EtN(BCat)_2$	12 h	100	20.0	1.67
9	PhCN	100 %	$PhCH_2N(BCat)_2$	12 h	100	20.0	1.67
10	5-hexynenitrile	50 %	*trans*-$NC(CH_2)_3CH{=}CHB(Cat)$	20 h	50	10.0	0.50
11	$Ph_2C(O)$ / PhCN (1:1)	100 %	$Ph_2CH(OBCat)$	12 h	67	20.0	1.67
			$PhCH_2N(BCat)_2$		33		
12	4-acetylbenzonitrile	100 %[c]	4-CN-C_6H_4-CH(OBCat)Me /	12 h	67	20.0	1.67
			4-$(CatB)_2NCH_2$-C_6H_4-CH(OBCat)Me		33		
13	acrylonitrile	65 %	$(CatB)CH_2CH_2CN$	48 h	55	13.0	0.27
			$(CatB)CH_2(CH_2)_2N(BCat)_2$		10		
14	3-(2-oxocyclohexyl)propanenitrile	100 %	2-$NC(CH_2)_2$-C_6H_{10}-OBCat	5 min	100	20.0	240.1
		100 %[c]	2-$NC(CH_2)_2$-C_6H_{10}-OBCat	48 h	32	20.0	0.42
			2-$(CatB)_2N(CH_2)_3$-C_6H_{10}-OBCat		68		

[a] The ratio of substrate/HBCat is 1/1. [b] Conversion of organic substrate, except entries 5, 8, 11 and 12 where conversion of HBCat was calculated. [c] The substrate/HBCat ratio is 1/2. [d] Yields were determined by ^1H NMR using tetramethylsilane as an internal standard. [e] TON and TOF were calculated at maximum conversion.

Table SI2. Crystal structure determination parameters for complex **3**.

Empirical formula	$C_{25}H_{41}ClMoN_2P_2$	
Formula weight	562.93	
Temperature, K	153(2)	
Wavelength, Å	0.71073	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions:		
	a = 22.805(4) Å	α = 90.00 °
	b = 16.318(3) Å	β = 110.478(3) °
	c = 16.590(3) Å	γ = 90.00 °
Volume, $Å^3$	5783.4(19)	
Z	8	
Density (calculated), mg/m^3	1.293	
Absorption coefficient, mm^{-1}	0.671	
F(000)	2352	
Crystal size, mm	0.19 x 0.12 x 0.06	
Theta range for data collection, °	0.95 to 28.00	
Index ranges	-30<=h<=30, -21<=k<=21, -21<=l<=21	
Reflections collected	13937	
Independent reflections	7310	
Completeness to theta = 28.00°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13937/ 0 / 559	
Goodness-of-fit on F^2	0.863	
Final R indices [I>2sigma(I)]	R1 = 0.0610, wR2 = 0.1332	
R indices (all data)	R1 = 0.1480, wR2 = 0.1109	

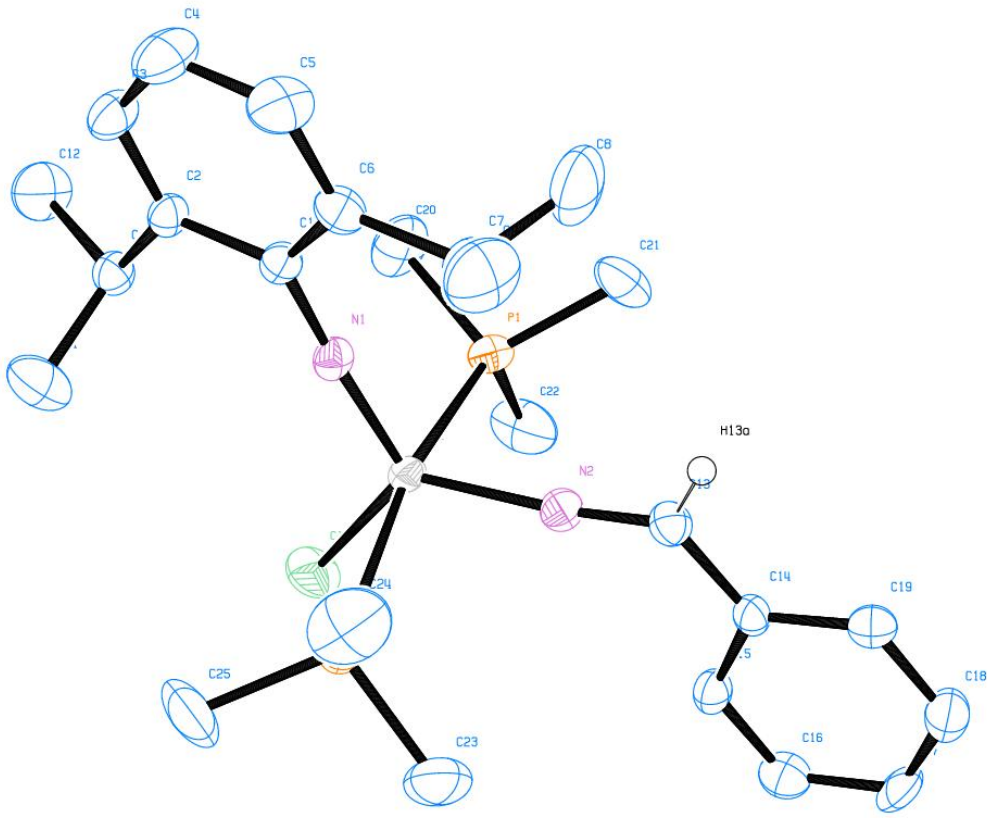

Figure SI1. Molecular structure of complex **3**.

Table SI3. Bond distances (Å) for complex **3**.

Mo1-N1	1.761(4)	C2-C10	1.515(6)
Mo1-N2	1.843(4)	C3-C4	1.388(7)
Mo1-Cl1	2.4341(14)	C4-C5	1.374(7)
Mo1-P2	2.4846(15)	C5-C6	1.376(7)
Mo1-P1	2.4929(14)	C6-C7	1.525(7)
P1-C20	1.804(5)	C7-C8	1.500(8)
P1-C21	1.808(5)	C7-C9	1.527(7)
P1-C22	1.809(6)	C10-C12	1.511(7)
P2-C25	1.794(6)	C10-C11	1.532(7)
P2-C23	1.803(6)	C13-C14	1.477(6)
P2-C24	1.806(6)	C14-C15	1.387(6)
N1-C1	1.387(6)	C14-C19	1.392(6)
N2-C13	1.279(6)	C15-C16	1.378(7)
C1-C6	1.403(6)	C16-C17	1.374(7)
C1-C2	1.419(6)	C17-C18	1.382(7)
C2-C3	1.369(7)	C18-C19	1.396(7)

Table SI4. Bond angles (°) for complex **3**.

N1-Mo1-N2	116.45(17)	C6-C1-C2	120.7(4)
N1-Mo1-Cl1	121.14(13)	C3-C2-C1	118.2(4)
N2-Mo1-Cl1	122.42(13)	C3-C2-C10	122.2(4)
N1-Mo1-P2	97.51(13)	C1-C2-C10	119.6(4)
N2-Mo1-P2	86.99(12)	C2-C3-C4	121.7(5)
Cl1-Mo1-P2	85.47(5)	C5-C4-C3	119.1(5)
N1-Mo1-P1	97.86(12)	C4-C5-C6	122.2(5)
N2-Mo1-P1	87.12(12)	C5-C6-C1	118.2(5)
Cl1-Mo1-P1	85.70(5)	C5-C6-C7	120.7(5)
P2-Mo1-P1	164.60(5)	C1-C6-C7	121.2(4)
C20-P1-C21	104.7(3)	C8-C7-C9	111.0(5)
C20-P1-C22	103.3(3)	C8-C7-C6	110.9(5)
C21-P1-C22	102.3(3)	C9-C7-C6	113.2(5)
C20-P1-Mo1	113.6(2)	C2-C10-C12	114.5(4)
C21-P1-Mo1	115.20(19)	C2-C10-C11	109.1(4)
C22-P1-Mo1	116.2(2)	C12-C10-C11	110.6(4)
C25-P2-C23	102.4(3)	N2-C13-C14	123.7(4)
C25-P2-C24	103.6(4)	C15-C14-C19	118.1(4)
C23-P2-C24	102.6(3)	C15-C14-C13	121.9(4)
C25-P2-Mo1	120.7(2)	C19-C14-C13	119.9(4)
C23-P2-Mo1	112.7(2)	C16-C15-C14	120.9(5)
C24-P2-Mo1	112.8(2)	C17-C16-C15	120.9(5)
C1-N1-Mo1	175.0(3)	C16-C17-C18	119.4(5)
C13-N2-Mo1	172.3(4)	C17-C18-C19	119.8(5)
N1-C1-C6	121.4(4)	C14-C19-C18	120.8(5)
N1-C1-C2	117.9(4)		

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