Supporting Information for

Nitrile hydroboration reactions catalysed by simple nickel salts, bis(acetylacetonato)nickel(II) and its derivatives

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Experimental Details and Compound Characterization Data

General considerations

Unless otherwise noted, all manipulations were performed under a nitrogen atmosphere using Schlenk techniques or a glove box. Benzene, toluene, hexane, and THF were purified by a solvent purification system (MBraun SPS-800 or Glass Contour Ultimate Solvent System). Other solvents (1,2-dichloroethane, benzene-$d_6$) were dried over CaH$_2$ or sodium benzophenone ketyl and distilled. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Catecholborane was purchased from Sigma-Aldrich Ltd. and purified by distillation. $^1$H, $^{11}$B, and $^{13}$C{${^1}$H} NMR spectra ($^1$H, 400 MHz; $^{11}$B, 128 MHz; $^{13}$C, 101 MHz) were recorded using a Bruker AVANCE 600 spectrometer. Chemical shifts are reported in $\delta$ (ppm) and are referenced to the residual solvent signals for $^1$H and $^{13}$C, and to boron trifluoride diethyl ether complex (BF$_3$·OEt$_2$, 0.0 ppm) as an external reference for $^{11}$B.

Catalytic Hydroborations

A typical procedure (Table 2, entry 1) is as follows. All reactions were carried out under nitrogen atmosphere. To a stirred solution of bis(2,2,6,6-tetramethyl-3,5-heptanedionato)nickel(II) (3) (0.001 mmol) in benzene (0.5 mL), was added benzonitrile (20.6 mg, 0.20 mmol) at 25 °C. After the mixture was stirred for 1 min, catecholborane (52.8 mg, 0.44 mmol) was added, and then the solution was stirred at room temperature for 18 hours. PhSiMe$_3$ (13.1 mg, 0.087 mmol) as an internal standard was added to the reaction mixture, and $^1$H NMR was measured to determine the NMR yield of PhCH$_2$N(Bcat)$_2$ (>99%). The resulting solution was then diluted by benzene (30 mL) and filtered to remove precipitates. The filtrate was concentrated to dryness to give analytically pure PhCH$_2$N(Bcat)$_2$ (65.9 mg, 0.19 mmol, 93%).

Compound Characterization Data

The final product was characterized by $^1$H, $^{13}$C{${^1}$H} and $^{11}$B{${^1}$H} NMR due to the instability of the hydroborated products under air. CH$_3$CH$_2$N(Bcat)$_2$ and PhCH$_2$N(Bcat)$_2$ were identified by comparing their $^1$H, $^{11}$B, and $^{13}$C{${^1}$H} NMR data with those previously reported.$^1$
$CH_3CH_2(Bcat)_2$

$^1$H NMR (C$_6$D$_6$, 25 °C): 7.03 (m, 4H, Bcat), 6.76 (m, 4H, Bcat), 3.34 (q, 2H, CH$_2$N, $J$ = 7.2 Hz), 1.11 (t, 3H, CH$_3$, $J$ = 7.2 Hz). $^{11}$B NMR (C$_6$D$_6$, 25 °C): 26.8 (bs, Bcat). $^{13}$C {$^1$H} NMR (C$_6$D$_6$, 25 °C): 148.9, 122.5, 112.3, 39.4, 17.7.

$^1$H NMR:

$^{13}$C {$^1$H} NMR:
CH$_3$CH$_2$CH$_2$N(Bcat)$_2$

$^1$H NMR (C$_6$D$_6$, 25 °C): 7.04 (m, 4H, Bcat), 6.76 (m, 4H, Bcat), 3.34 (t, 2H, CH$_2$N, $J = 7.6$ Hz), 1.56 (m, 2H, NCH$_2$-CH$_2$-CH$_3$), 0.80 (t, 3H, CH$_3$, $J = 7.2$ Hz). $^{11}$B NMR (C$_6$D$_6$, 25 °C): 27.0 (bs, Bcat). $^{13}$C {$^1$H} NMR (C$_6$D$_6$, 25 °C): 148.9, 122.5, 112.3, 46.2, 25.6, 11.2.

$^1$H NMR:

$^{13}$C {$^1$H} NMR:
$^{1}PrCH_{2}N(Bcat)_{2}$

$^{1}$H NMR (C$_{6}$D$_{6}$, 25 °C): 7.05 (m, 4H, Bcat), 6.76 (m, 4H, Bcat), 3.25 (d, 2H, CH$_{2}$N, $J = 7.6$ Hz), 1.90 (m, 1H, (CH$_{3})_{2}$CH), 0.84 (d, 6H, CH$_{3}$, $J = 6.4$ Hz).

$^{11}$B NMR (C$_{6}$D$_{6}$, 25 °C): 26.9 (bs, Bcat). $^{13}$C {$^{1}$H} NMR (C$_{6}$D$_{6}$, 25 °C): 148.9, 122.6, 112.3, 51.9, 30.4, 20.0.

$^{1}$H NMR:

$^{13}$C {$^{1}$H} NMR:
\[ \text{BuCH}_2N(B\text{cat})_2 \]

$^1$H NMR (C\(_6\)D\(_6\), 25 °C): 7.05 (m, 4H, Bcat), 6.77 (m, 4H, Bcat), 3.32 (s, 2H, CH\(_2\)N), 0.86 (s, 9H, CH\(_3\)). $^{11}$B NMR (C\(_6\)D\(_6\), 25 °C): 27.0 (bs, Bcat). $^{13}$C ($^1$H) NMR (C\(_6\)D\(_6\), 25 °C): 148.8, 122.6, 112.2, 55.3, 33.2, 27.4.

$^1$H NMR:

$^{13}$C ($^1$H) NMR:
CyCH₂N(Bcat)₂

¹H NMR (CD₆, 25 °C): 7.06 (m, 4H, Bcat), 6.76 (m, 4H, Bcat), 3.32 (d, 2H, CH₂N, J = 7.2 Hz), 1.63 (m, 6H, Cy-H), 0.99 (m, 5H, Cy-H). ¹¹B NMR (CD₆, 25 °C): 26.9 (bs, Bcat). ¹³C{¹H} NMR (CD₆, 25 °C): 148.9, 122.55, 112.3, 50.8, 39.8, 30.9, 26.8, 26.2.

¹H NMR:

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¹³C{¹H} NMR:
PhCH₂CH₂N(Bcat)₂

¹H NMR (C₆D₆, 25 °C): 7.15 (d, 2H, J = 7.2 Hz, Ar-H), 7.10 (t, 2H, J = 7.2 Hz, Ar-H), 7.05 (m, 4H, Bcat), 7.00 (t, 1H, J = 7.2 Hz, Ar-H), 6.77 (m, 4H, Bcat), 3.60 (t, 2H, J = 7.6 Hz, CH₂N), 2.80 (t, 2H, J = 7.6 Hz, PhCH₂). ¹¹B NMR (C₆D₆, 25 °C): 27.0 (bs, Bcat). ¹³C{¹H} NMR (C₆D₆, 25 °C): 148.8, 139.3, 129.3, 128.7, 128.5, 128.3, 122.6, 112.3, 46.2, 39.0.

¹H NMR:

¹³C{¹H} NMR:
PhCH₂N(Bcat)₂

¹H NMR (C₆D₆, 25 °C): 7.40 (d, 2H, \( J = 7.2 \) Hz, Ar-H), 7.11 (t, 2H, \( J = 7.6 \) Hz, Ar-H), 7.05 (m, 1H, Ar-H), 6.99 (m, 4H, Bcat), 6.73 (m, 4H, Bcat), 4.55 (s, 2H, CH₂N). ¹¹B NMR (C₆D₆, 25 °C): 27.2 (bs, Bcat). ¹³C{¹H} NMR (C₆D₆, 25 °C): 148.8, 140.6, 139.4, 128.8, 127.4, 122.6, 112.3, 47.9.

¹H NMR:

¹³C{¹H} NMR:
(o-tolyl)CH₂N(Bcat)₂

¹H NMR (C₆D₆, 25 °C): δ 7.28 (d, 2H, J = 8.0 Hz, Ar-H), 6.98 (m, 6H, Ar-H and Bcat), 6.88 (d, 1H, J = 7.6 Hz, Ar-H), 6.72 (m, 4H, Bcat), 4.57 (s, 2H, CH₂N), 2.15 (s, 3H, CH₃). ¹¹B NMR (C₆D₆, 25 °C): δ 27.1 (bs, Bcat).

¹³C⁻¹H NMR (C₆D₆, 25 °C): δ 148.8, 138.0, 135.1, 130.4, 128.3, 126.9, 126.7, 125.1, 122.6, 112.4, 45.38, 19.0.

¹H NMR:

¹³C⁻¹H NMR:
(m-toly)CH₂N(Bcat): 

¹H NMR (C₆D₆, 25 °C): δ 7.27 (m, 2H, Ar-H), 7.11 (m, 1H, Ar-H), 6.99 (m, 4H, Bcat), 6.88 (d, 1H, J = 7.6 Hz, Ar-H), 6.72 (m, 4H, Bcat), 4.59 (s, 2H, CH₂N), 2.05 (s, 3H, CH₃). ¹¹B NMR (C₆D₆, 25 °C): δ 27.0 (bs, Bcat). ¹³C{¹H} NMR (C₆D₆, 25 °C): δ 148.8, 140.5, 138.2, 128.9, 127.9, 124.6, 122.6, 112.3, 47.9, 21.3.

¹H NMR:

¹³C{¹H} NMR:
(p-tolyl)CH$_2$N(Bcat)$_2$

$^1$H NMR (C$_6$D$_6$, 25 °C): 7.37 (d, 2H, $J$ = 8.0 Hz, Ar-H), 7.00 (m, 4H, Bcat), 6.95 (d, 2H, $J$ = 8.0 Hz, Ar-H), 6.72 (m, 4H, Bcat), 4.57 (s, 2H, CH$_2$N), 2.06 (s, 3H, CH$_3$). $^{11}$B NMR (C$_6$D$_6$, 25 °C): 27.1 (bs, Bcat).

$^{13}$C{$^1$H} NMR (C$_6$D$_6$, 25 °C): 148.9, 137.7, 136.8, 129.5, 122.5, 112.3, 47.7, 21.0.

$^1$H NMR:

![H NMR spectrum](image)

$^{13}$C{$^1$H} NMR:

![C NMR spectrum](image)
(p-MeOC₆H₄)CH₂N(Bcat)₂;

¹H NMR (C₆D₆, 25 °C): 7.38 (d, 2H, J = 8.8 Hz, Ar-H), 7.02 (m, 4H, Bcat), 6.73 (m, 6H, Ar-H and Bcat), 4.54 (s, 2H, CH₂N), 3.26 (s, 3H, OCH₃). ¹¹B NMR (C₆D₆, 25 °C): 27.2 (bs, Bcat). ¹³C{¹H} NMR (C₆D₆, 25 °C): 159.4, 148.9, 132.8, 136.8, 129.1, 122.6, 114.2, 112.3, 54.8, 47.4.

¹H NMR:

¹³C{¹H} NMR:
(p-F₃CC₆H₄)CH₂N(Bcat)₂

¹H NMR (C₆D₆, 25 °C): 7.24 (d, 2H, J = 8.0 Hz, Ar-H), 7.11 (d, 2H, J = 8.0 Hz, Ar-H), 7.01 (m, 4H, Bcat), 6.75 (m, 4H, Bcat), 4.39 (s, 2H, CH₂N). ¹¹B NMR (C₆D₆, 25 °C): 26.8 (bs, Bcat). ¹³C{¹H} NMR (C₆D₆, 25 °C): 148.7, 144.2, 136.8, 129.5, 125.8, 127.5, 122.8, 112.4, 47.3.

¹H NMR:

![¹H NMR spectrum]

¹³C{¹H} NMR:

![¹³C{¹H} NMR spectrum]
(m-ClC₆H₄)CH₂N(Bcat)₂

¹H NMR (C₆D₆, 25 °C): 7.47 (s, 1H, Ar-H), 7.10 (d, 1H, J = 8.0 Hz, Ar-H), 6.98 (m, 5H, Ar-H and Bcat), 6.74 (m, 5H, Ar-H and Bcat), 4.35 (s, 2H, CH₂N). ¹¹B NMR (C₆D₆, 25 °C): 26.9 (bs, Bcat). ¹³C{¹H} NMR (C₆D₆, 25 °C): 148.7, 142.6, 134.7, 130.2, 128.3, 125.5, 122.7, 112.4, 47.3.

¹H NMR:

¹³C{¹H} NMR:
$(p$-$ClC_{6}H_{4})CH_{2}N(Bcat)_{2}$

$^1$H NMR (C\textsubscript{6}D\textsubscript{6}, 25 °C): 7.04 (m, 8H, Ar-$H$ and Bcat), 6.74 (m, 4H, Bcat), 4.35 (s, 2H, CH\textsubscript{2}N). $^{11}$B NMR (C\textsubscript{6}D\textsubscript{6}, 25 °C): 26.9 (bs, Bcat).

$^{13}$C{$^1$H} NMR (C\textsubscript{6}D\textsubscript{6}, 25 °C): 148.7, 138.9, 133.2, 129.0, 128.3, 122.7, 112.4, 47.1.

$^1$H NMR:

$^{13}$C{$^1$H} NMR:
§(2-furyl)CH2N(Bcat):

1H NMR (C6D6, 25 °C): 7.00 (m, 5H, furyl-H and Bcat), 6.73 (m, 4H, Bcat), 6.15 (d, 1H, J = 3.2 Hz, furyl-H), 5.98 (m, 1H, furyl-H), 4.50 (s, 2H, CH2N).

11B NMR (C6D6, 25 °C): 27.0 (bs, Bcat).

13C{1H} NMR (C6D6, 25 °C): 159.9, 148.8, 142.2, 122.6, 112.3, 110.6, 107.2, 41.0.

1H NMR:

13C{1H} NMR:
(2-thienyl)CH₂N(Bcat)₂

$^1$H NMR (C₆D₆, 25 °C): 7.00 (m, 4H, Bcat), 6.74 (m, 6H, thienyl-H and Bcat), 6.65 (m, 1H, thienyl-H), 4.63 (s, 2H, CH₂N). $^{11}$B NMR (C₆D₆, 25 °C): 26.8 (bs, Bcat). $^{13}$C {$^1$H} NMR (C₆D₆, 25 °C): 148.8, 143.6, 127.0, 126.0, 125.0, 122.6, 112.4, 42.7.

$^1$H NMR:

$^{13}$C {$^1$H} NMR:
Reaction of 3 with HBcat. A J-young NMR tube was charged with a C₆D₆ solution (0.4 mL) of 3 (5.0 mg, 0.012 mmol) and HBcat (5.5 mg, 0.046 mmol). After 15 min at room temperature, formation of black precipitate was observed. Formation of [tBuCOCHC(tBu)O–κO,κO']*Bcat was supported by both ¹H and ¹¹B{¹H} NMR although all the signals appeared as significantly broad signals due to the existence of paramagnetic nickel species. In addition, formation of several unidentified products, which exhibit broad signals as δ 28.9, 23.3, 18.7 ppm in the ¹¹B NMR spectrum, was also confirmed. After filtration, slow evaporation of the filtrate afforded single crystals of [tBuCOCHC(tBu)O–κO,κO']*Bcat.

[tBuCOCHC(tBu)O–κO,κO']*Bcat: ¹H NMR (C₆D₆, 25 °C): 7.11 (dd, 2H, J = 5.4, 3.6 Hz, Bcat), 6.84 (dd, 2H, J = 5.4, 3.6 Hz, Bcat), 5.82 (s, 1H, CH), 0.84 (s, 18H, tBu). ¹¹B NMR (C₆D₆, 25 °C): 9.7 (bs, Bcat). ¹³C{¹H} NMR (C₆D₆, 25 °C): 201.3, 151.9, 120.1, 110.2, 92.9, 39.5, 26.9.

Single-crystal X-ray diffraction studies. The single crystal X-ray diffraction measurements of [tBuCOCHC(tBu)O–κO,κO']*Bcat was performed under a cold nitrogen stream on a Rigaku XtaLAB P200 diffractometer with a Pilatus 200K detector using multi-layer mirror monochromated Mo Kα radiation. The determination of crystal systems and unit cell parameters and data processing were performed with the CrystalClear program package. The data sets were corrected for Lorentz and polarization effects and absorption. The structure was solved by direct methods using SIR97 program,² and refined by full-matrix least squares calculations on F² for all reflections (SHELXL-97)³. The structure was not fully refined due to the bad quality of the crystal and the final R values remain 0.1208 (R₁) and 0.2771 (wR₂).

Figure 1. Molecular structure of [tBuCOCHC(tBu)O–κO,κO']*Bcat with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): B–O1 1.463(3), B–O2 1.452(3), B–O3 1.490(2), O1–B–O2 107.1(2), O3–B–O3* 108.9(2).
Table S1. Crystal data and details of the crystal structure determination for tBuCOCHC(tBu)OBcat.

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References