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**Electronic Supporting Information** 

## Magnesium Hydridotriphenylborate [Mg(thf)<sub>6</sub>][HBPh<sub>3</sub>]<sub>2</sub>:

## A Versatile Hydroboration Catalyst

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### General remarks.

All manipulations were performed under argon atmosphere using standard Schlenk or glove box techniques. Prior to use, glassware was dried overnight at 130 °C and solvents were dried, distilled and degassed using standard methods. NMR measurements were performed on a Bruker DRX 400 at ambient temperature unless otherwise mentioned. The chemical shifts ( $\delta$ ppm) in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane.<sup>S1</sup> Abbreviations for NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), sep (septet), br. (broad). IR spectra were measured on KBr pellets using an AVATAR 360 FT-IR spectrometer. Abbreviations for IR spectra: w (weak), m (medium), s (strong), br. (broad). BPh<sub>3</sub> (95%) was purchased from abcr and recrystallized from Et<sub>2</sub>O solution at -35 °C. [Mg{N(SiHMe<sub>2</sub>)<sub>2</sub>}<sub>2</sub>] was synthesized following literature procedure.<sup>S2</sup> All the substrates and HBpin were purchased from the suppliers like Sigma-Aldrich, Alfa Aesar, and abcr. CO<sub>2</sub> (purity level 5.0, equals to 99.990% purity) was purchased from Westfalen, Germany and passed through a column of  $P_4O_{10}$  with moisture indicator while using in the Schlenk line. Elemental analyses were performed on an elementar vario EL machine. X-ray diffraction data were collected on a Bruker APEX II diffractometer. Single crystal diffraction data of 9 is reported in crystallographic information file (cif) accompanying this document.

# [Mg(thf)<sub>6</sub>][HBPh<sub>3</sub>]<sub>2</sub> (1).

 $[Mg{N(SiHMe_2)_2}_2]$  (0.100 g, 0.346 mmol) and BPh<sub>3</sub> (0.168 g, 0.694 mmol) were dissolved together in 5 mL of THF. The solution mixture was stirred at room temperature for 12 h,

during which a white crystalline solid precipitated. The solid was isolated by filtration and washed with THF ( $3\times5$  mL). Subsequent drying under reduced pressure afforded [Mg(thf)<sub>6</sub>][HBPh<sub>3</sub>]<sub>2</sub> (1, 0.257 mg, 0.272 mmol, 79% yield) as colorless crystals.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  1.76 (m, THF), 3.26-3.65 (br, q, <sup>1</sup>*J*<sub>BH</sub> = 80 Hz, 2 H, *H*B), 3.61 (m, THF), 6.76 (t, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 6 H, *p*-C<sub>6</sub>H<sub>5</sub>), 6.91 (t, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 12 H, *m*-C<sub>6</sub>H<sub>5</sub>), 7.16 (br, m, 12 H, *o*-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  25.1 (THF), 67.0 (THF), 121.4 (*p*-C<sub>6</sub>H<sub>5</sub>), 125.5 (*m*-C<sub>6</sub>H<sub>5</sub>), 135.0 (*o*-C<sub>6</sub>H<sub>5</sub>), 163.0-164.5 (m, *ipso*-C<sub>6</sub>H<sub>5</sub>). <sup>11</sup>B NMR (128 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  -8.3 (d, <sup>1</sup>*J*<sub>BH</sub> = 80 Hz). IR (KBr, cm<sup>-1</sup>): 2202-2004 (multiple absorptions, v<sub>BH</sub>). Anal. Calcd. for C<sub>60</sub>H<sub>80</sub>B<sub>2</sub>O<sub>6</sub>Mg: C, 76.40; H, 8.55; N, 0.00. Found: C, 75.98; H, 8.44; N, 0.29.



Figure S1. <sup>1</sup>H NMR spectrum of [Mg(thf)<sub>6</sub>][HBPh<sub>3</sub>]<sub>2</sub> in DMSO-d<sub>6</sub>.



Figure S2. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $[Mg(thf)_6][HBPh_3]_2$  in DMSO-*d*<sub>6</sub>.



Figure S3. <sup>11</sup>B NMR spectrum of [Mg(thf)<sub>6</sub>][HBPh<sub>3</sub>]<sub>2</sub> in DMSO-d<sub>6</sub>.



wave number (cm<sup>-1</sup>)

Figure S4. Solid-state IR (KBr pellet) spectrum of [Mg(thf)<sub>6</sub>][HBPh<sub>3</sub>]<sub>2</sub>.

#### [Mg(HCO<sub>2</sub>BPh<sub>3</sub>)<sub>2</sub>(thf)<sub>4</sub>] (9).

A suspension of  $[Mg(thf)_6][HBPh_3]_2$  (0.050 g 0.053 mmol) in 2 mL of THF was charged in a 25 mL Schlenk tube. The mixture was degassed by three cycles of freeze-pump-thaw, followed by filling up the head-space with CO<sub>2</sub> (1 atm). A homogeneous solution was obtained within 15 min indicating reaction completion. All the volatiles were removed under reduced pressure to obtain analytically pure  $[Mg(thf)_4(HCO_2BPh_3)_2]$  (9, 0.041 g, 0.046 mmol,

87% yield) as a white powder. X-ray quality single crystals were grown from its concentrated THF solution at -35 °C.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  1.76 (m, THF), 3.60 (m, THF), 6.95 (t, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 6 H, *p*-C<sub>6</sub>H<sub>5</sub>), 7.06 (t, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 12 H, *m*-C<sub>6</sub>H<sub>5</sub>), 7.22 (d, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 12 H, *o*-C<sub>6</sub>H<sub>5</sub>), 8.14 (s, 1 H, *H*CO<sub>2</sub>BPh<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  25.1 (THF), 67.0 (THF), 123.4 (*p*-C<sub>6</sub>H<sub>5</sub>), 126.1 (*m*-C<sub>6</sub>H<sub>5</sub>), 133.1 (*o*-C<sub>6</sub>H<sub>5</sub>), 157.3 (*ipso*-C<sub>6</sub>H<sub>5</sub>), 167.3 (HCO<sub>2</sub>BPh<sub>3</sub>). <sup>11</sup>B NMR (128 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  2.9 (s, br). IR (KBr, cm<sup>-1</sup>): 1633 (v<sub>CO, asym</sub>). Anal. Calcd. for C<sub>54</sub>H<sub>64</sub>B<sub>2</sub>O<sub>8</sub>Mg: C, 73.12; H, 7.27; N, 0.00. Found: C, 72.77; H, 7.16; N, 0.24.



Figure S5. <sup>1</sup>H NMR spectrum of [Mg(HCO<sub>2</sub>BPh<sub>3</sub>)<sub>2</sub>(thf)<sub>4</sub>] in DMSO-d<sub>6</sub>.



Figure S6.  ${}^{13}C{}^{1}H$  NMR spectrum of [Mg(HCO<sub>2</sub>BPh<sub>3</sub>)<sub>2</sub>(thf)<sub>4</sub>] in DMSO-d<sub>6</sub>.



Figure S7. <sup>11</sup>B NMR spectrum of [Mg(HCO<sub>2</sub>BPh<sub>3</sub>)<sub>2</sub>(thf)<sub>4</sub>] in DMSO-*d*<sub>6</sub>.



Figure S8. Solid-state IR (KBr pellet) spectrum of [Mg(HCO<sub>2</sub>BPh<sub>3</sub>)<sub>2</sub>(thf)<sub>4</sub>].

## [Mg(thf)<sub>6</sub>][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sub>2</sub> (10).

 $[Mg{N(SiHMe_2)_2}_2]$  (0.050 g, 0.173 mmol) and  $B(C_6F_5)_3$  (0.090 g, 0.176 mmol) were dissolved together in 5 mL of THF. The solution mixture was stirred at room temperature for 12 h. All the volatiles were removed to give a white solid, which was washed with pentane (3×5 mL) and dried under vacuum to give analytically pure  $[Mg(thf)_6][HB(C_6F_5)_3]_2$  (10, 0.214 g, 0.144 mmol, 83% yield) as a white powder.

<sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>):  $\delta$  1.77 (m, THF), 3.30-4.00 (br, 2 H, *H*B), 3.62 (m, THF). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, THF-*d*<sub>8</sub>):  $\delta$  26.5 (THF), 136.1 (*C*<sub>6</sub>F<sub>5</sub>), 137.5 (*C*<sub>6</sub>F<sub>5</sub>), 138.6 (*C*<sub>6</sub>F<sub>5</sub>), 139.9 (*C*<sub>6</sub>F<sub>5</sub>), 148.1 (*C*<sub>6</sub>F<sub>5</sub>), 150.5 (*C*<sub>6</sub>F<sub>5</sub>). <sup>11</sup>B NMR (128 MHz, THF-*d*<sub>8</sub>):  $\delta$  –25.4 (d, <sup>1</sup>*J*<sub>BH</sub> = 90 Hz). <sup>19</sup>F NMR (THF-*d*<sub>8</sub>, 377 MHz):  $\delta$  –133.7, –165.9, –168.6. IR (KBr, cm<sup>-1</sup>): 2363 (v<sub>BH</sub>). Anal. Calcd. for C<sub>60</sub>H<sub>50</sub>B<sub>2</sub>O<sub>6</sub>F<sub>30</sub>Mg: C, 48.60; H, 3.40; N, 0.00. Found: C, 48.94; H, 3.70; N, 0.31.



**Figure S9.** <sup>1</sup>H NMR spectrum of  $[Mg(thf)_6][HB(C_6F_5)_3]_2$  in THF- $d_8$ .



Figure S10. <sup>13</sup>C $\{^{1}H\}$  NMR spectrum of [Mg(thf)<sub>6</sub>][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sub>2</sub> in THF-d<sub>8</sub>.



Figure S11. <sup>11</sup>B NMR spectrum of  $[Mg(thf)_6][HB(C_6F_5)_3]_2$  in THF- $d_8$ .



Figure S12. <sup>19</sup>F NMR spectrum of  $[Mg(thf)_6][HB(C_6F_5)_3]_2$  in THF- $d_8$ .



wave number (cm<sup>-1</sup>)

Figure S13. Solid-state IR (KBr pellet) spectrum of [Mg(thf)<sub>6</sub>][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sub>2</sub>.

# Catalysis. Typical NMR-scale catalytic hydroboration using HBpin.

A J.Young-style NMR tube was charged with substrate, HBpin and 0.45 mL of a 0.06 M stock solution of 1,3,5-trimethoxybenzene (internal standard) in THF (THF:THF- $d_8 = 2:1$ ). Desired catalyst loading was achieved either by adding an appropriate volume of DMSO stock solution of the catalyst of known concentration using a microliter syringe, or by weighing out the solid catalyst and transferring into the reaction mixture. For catalysis at elevated temperature, preheated oil bath was used. In case of CO<sub>2</sub>, the reaction mixture was degassed following the standard cycle of freeze-pump-thaw three times prior refilling the headspace with CO<sub>2</sub> (1 bar). Reaction progress was monitored using <sup>1</sup>H NMR spectroscopy. The products were characterized by <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C NMR spectroscopy and compared with the literature. <sup>1</sup>H NMR spectra of the catalytic reaction mixture are provided below to show the completion of reduction.



Figure S14. <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of PhCHO in the presence of DMSO. 12.5% of DMSO got reduced to  $Me_2S$  after 12 h at room temperature.



**Figure S15.** <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of p-Me-C<sub>6</sub>H<sub>4</sub>-CHO in the presence of DMSO. 2.7% of DMSO got reduced to Me<sub>2</sub>S after 12 h at room temperature.



**Figure S16.** <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of p-OMe-C<sub>6</sub>H<sub>4</sub>-CHO in the presence of DMSO. Only 0.9% of DMSO got reduced to Me<sub>2</sub>S.



**Figure S17.** <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of p-Br-C<sub>6</sub>H<sub>4</sub>-CHO in the presence of DMSO. 5.6% of DMSO got reduced to Me<sub>2</sub>S.



**Figure S18.** <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of p-F-C<sub>6</sub>H<sub>4</sub>-CHO in the presence of DMSO. Only 0.9% of DMSO got reduced to Me<sub>2</sub>S.



**Figure S19.** <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of p-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CHO in the presence of DMSO. Only 0.3% of DMSO got reduced to Me<sub>2</sub>S.



**Figure S20.** <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of p-CN-C<sub>6</sub>H<sub>4</sub>-CHO in the presence of DMSO. Only 0.4% of DMSO got reduced to Me<sub>2</sub>S.



**Figure S21.** <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of PhCH=CH-CHO in the presence of DMSO. Partial (52%) reduction was achieved after 12 h at room temperature. 11.4% of DMSO got reduced to  $Me_2S$ .



**Figure S22.** <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of PhC(O)Me in the presence of DMSO. Partial (64%) reduction was achieved after 12 h at room temperature. 13.0% of DMSO got reduced to  $Me_2S$ .



**Figure S23.** <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of Ph<sub>2</sub>CO in the presence of DMSO. Only 11% reduction was achieved after 12 h at room temperature. 25% of DMSO got reduced to Me<sub>2</sub>S.



Figure S24. <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of Ph<sub>2</sub>CO in the absence of DMSO.



Figure S25. <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of DMSO in the absence of carbonyls.



Figure S26. <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of MePhS(O).



Figure S27. <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of pyridine.



Figure S28. <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of *tert*-butylnitrile.



Figure S29. <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of N-benzylideneaniline.



Figure S30. <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of ethylacetate.



Figure S31. <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of *N*,*N*-dimethylacetamide.



Figure S32. <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of CO<sub>2</sub>.



Figure S33. <sup>11</sup>B NMR of the catalytic reaction mixture for the hydroboration of CO<sub>2</sub>.



Figure S34. <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of *N*,*N*-diisopropylcarbodimide.



Figure S35. <sup>1</sup>H NMR of the catalytic reaction mixture for the hydroboration of *tert*-butylisocyanate.

### Catalytic hydroboration of benzophenone on mmol scale.

A 20 mL screw-cap vial fitted with a magnetic stir bar was charged with  $Ph_2CO$  (500 mg, 2.74 mmol), HBpin (350 mg, 2.74 mmol), **1** (26 mg, 0.027 mmol) and 2 mL of THF. The resulting solution mixture was stirred for 1 h at room temperature. It was filtered through a plug of silica. All the volatiles were then removed to obtain  $Ph_2CHOH$  (473 mg, 2.56 mmol, 93%) as a colorless crystalline solid. The product was characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR and FT-IR spectroscopy and compared with the results obtained from using the lithium catalyst.

# **Crystal Structure Analysis**

The single-crystal X-ray diffraction measurement on a colorless crystal of 9 (0.35  $\times$  0.25  $\times$ 0.24 mm) was performed at 100(2) K on a Bruker AXS diffractometer equipped with an Incoatec microsource and an APEX area detector using MoKa radiation, multilayer optics and ω-scans. The data reduction was performed with the Bruker SAINT software.<sup>S3a</sup> The compound  $C_{54}H_{64}B_2MgO_8$  (*fw* = 886.98 g·mol<sup>-1</sup>) crystallizes in the monoclinic space group  $P2_1/n$  with a = 11.3567(9) Å, b = 12.2346(10) Å, c = 18.4353(15) Å,  $\beta = 108.1883(13)^\circ$ ,  $V = 108.1883(13)^\circ$ 2433.5(3) Å<sup>3</sup> with Z = 2, F(000) = 948,  $\mu$ (MoK $\alpha$ ) = 0.090 mm<sup>-1</sup>. The absorption correction was carried out using the program SADABS.<sup>S3b</sup> 29142 reflections were collected (1.88  $\leq \theta \leq$ 26.55), of which 5066 were unique and 4261 were observed ( $I > 2\sigma(I)$ ),  $R_{int} = 0.0421$ . The structure was solved by direct methods using the program SIR-92.<sup>S3c</sup> The refinement was carried out by the full-matrix least squares method using SHELXL-2013 as implemented in the WinGX program system with anisotropic displacement parameters for all non-hydrogen atoms.<sup>S3d,e</sup> All hydrogen atoms were refined in their position with isotropic displacement parameters. The refinement led to final R indices of RI = 0.0387 and wR2 = 0.0954 (I > 0.0954)  $2\sigma(I)$ ), as well as R1 = 0.0476 and wR2 = 0.1002 (all data); GooF = 1.054. The graphical representation was obtained with the computer program DIAMOND.<sup>S3f</sup> CCDC-1498969 (9) contains the supplementary crystallographic data for this paper. These data can be obtained the free of charge from Crystallographic Data Centre via www.ccdc.cam.ac.uk/dada request/cif.

The measurement on a colorless crystal of 1 ( $0.42 \times 0.32 \times 0.22$  mm) was also performed at 100(2) K on a Bruker AXS diffractometer equipped with an Incoatec microsource and an APEX area detector using MoK $\alpha$  radiation, multilayer optics and  $\omega$ -scans. The data reduction was performed with the Bruker SAINT software.<sup>S3a</sup> The compound  $C_{60}H_{80}B_2MgO_6$  (fw = 943.17 g·mol<sup>-1</sup>) crystallizes in the monoclinic space group  $P2_1/c$  with a = 16.924(3) Å, b =17.299(3) Å, c = 18.192(3) Å,  $\beta = 95.767(3)^\circ$ , V = 5299.1(16) Å<sup>3</sup> with Z = 4, F(000) = 2040,  $\mu$ (MoK $\alpha$ ) = 0.084 mm<sup>-1</sup>. The absorption correction was carried out using the program SADABS.<sup>S3b</sup> 42927 reflections were collected (1.21  $\le \theta \le 25.11$ ), of which 9422 were unique and 4260 were observed ( $I \ge 2\sigma(I)$ ),  $R_{int} = 0.0998$ . The structure was solved by direct methods using the program SIR-92.<sup>S3c</sup> The solution revealed two crystallographically independent units of  $Mg(C_4H_8O)_6$  with each magnesium atom located on a centre of symmetry (0.50, 0.00, 0.00) and 0.00, 0.50, 0.00). Strong disorder within the thf ligands as well as within the two crystallographically independent units of  $HB(C_6H_5)_3$  could be modelled with split positions. The refinement was carried out with anisotropic displacement parameters for the nonhydrogen atoms that were not disordered and with isotropic parameters for the disordered atoms.<sup>S3d,e</sup> All hydrogen atoms were included in calculated positions. Due to the strong disorder, the refinement led to poor final R indices of RI = 0.1085 and wR2 = 0.3012 (I > $2\sigma(I)$ , as well as R1 = 0.1985 and wR2 = 0.3662 (all data); GoF = 1.087. For this reason, the data are not discussed in detail and were not deposited at the Cambridge Crystallographic Data Centre. Figure S36 and S37 show the molecular structure of 1 in the crystal packing. The wire/stick representation in S37 shows the disorder, but clearly shows the connectivity and the separated ion pair.



**Figure S36**. Molecular structure of **1** showing the displacement parameters within the crystal packing. Only one of the two crystallographically independent units is shown. Only one of two crystallographic split positions for the disordered atoms are depicted. Hydrogens are omitted for clarity.



**Figure S37**. Wire/stick model showing the disorder within the two crystallographically independent molecules of **1** and their orientation in the crystal lattice. Hydrogens are omitted for clarity.

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