#### **Supplementary Material for:**

# Bicyclic guanidinate compounds of magnesium and their activity as pre-catalysts in the Tishchenko reaction

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Expansion of nomenclature used to describe two bridging guanidinate ligands to two metal centres, illustrated for magnesium.

# Synthesis of [Mg(hpp)Cl(THF)] (1a)

A solution of MgMeCl (1.3 mL of a 3.0 M solution in THF, 3.9 mmol) was added dropwise to a clear colourless solution of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-a]pyrimidine (hppH) (0.544 g, 3.9 mmol) in THF (~15 mL) at ambient temperature. Gas evolved was observed on addition and a white precipitate formed within 15 mins. The reaction mixture was stirred for 1 hour before isolation of the precipitate by filtration. The solid product was washed with THF followed by the removal of any residual volitiles *in vacuo*, leaving a white powder of (**1a**). Yield 0.89 g, 85 %. X-ray quality crystals were grown by slow cooling a hot (~65 °C) saturated THF solution to room temperature.

**Analysis**: Calc'd. for C<sub>11</sub>H<sub>20</sub>N<sub>3</sub>ClMgO (*270.05*): C 48.92, H 7.46, N 15.56 %. Found C 48.82, H 7.35, N 15.44 %.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): *δ* 3.79 (m, 4H, THF), 3.35-3.00 (m, 8H, hpp-CH<sub>2</sub>), 2.10-1.70 (m, 8H, THF + hpp-CH<sub>2</sub>).

<sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): *δ* 164.1 (hpp-*C*N<sub>3</sub>), 68.8 (THF), 48.9, 42.8 (hpp-*C*H<sub>2</sub>), 25.7 (THF), 22.5 (hpp-*C*H<sub>2</sub>).

#### Synthesis of [Mg(tbo)Br(THF)<sub>1.5</sub>] (2a)

A solution of MeMgBr (1.6 mL of a 3.0 M solution in Et<sub>2</sub>O, 4.8 mmol) was added dropwise to a pale yellow solution of 1,4,6-triazabicyclo[3.3.0]oct-4-ene (Htbo) (0.511 g, 4.6 mmol,) in tetrahydrofuran (THF) (~15 mL) at ambient temperature. Gas evolved on addition and a small amount of a white precipitate formed within 15 mins. After stirring for 4 hours the solution was concentrated and warmed to ~65 °C. Filtration followed by slow cooling to ambient temperature yielded colourless crystals of **2a**. Yield 0.93 g, 60 % (based on Mg). Loss of THF (0.5 equiv / Mg) and formation of **2b** occured when preparing a sample of **2a** for elemental analysis.

**Analysis (2b)**: Calc'd. for C<sub>9</sub>H<sub>16</sub>N<sub>3</sub>BrMgO, corresponding to **2b**, (286.45): C 37.74, H 5.63, N 14.67 %. Found C 37.65, H 5.56, N 14.42 %.

<sup>1</sup>**H NMR (2a)** (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.80-3.65 (m, 10H, THF + tbo-CH<sub>2</sub>), 2.70 (m, 4H, tbo-CH<sub>2</sub>), 1.40 (m, 6H, THF).

<sup>13</sup>C NMR (2a) (125 MHz,  $C_6D_6$ ):  $\delta$ \*, 69.0 (THF), 54.7, 50.9 (tbo-*C*H<sub>2</sub>), 26.0 (THF). \* resonance for *C*N<sub>3</sub> not observed.

#### Synthesis of $Mg(hpp)(N{SiMe_3}_2)(3)$

0.16 mL of a 3.0 M solution of MgMeCl in THF (0.50 mmol) was added dropwise to a clear colourless solution of hppH (0.200 g, 0.50 mmol) in THF (~10 mL). The resultant clear, colourless solution was stirred at ambient temperature for 1 hour prior to dropwise addition to a clear colourless solution of K[N{SiMe<sub>3</sub>}<sub>2</sub>] (0.09 g, 0.50 mmol) in THF (~ 10 mL). Stirring for 16 hours at ambient temperature followed by removal of volatiles *in vacuo* afforded a crude white solid. Extraction with hot hexane and slow cooling to ambient temperature yielded colourless crystals of (**3**). Yield 0.22 g, 68 %

**Analysis**: Calc'd. for C<sub>13</sub>H<sub>30</sub>N<sub>4</sub>MgSi<sub>2</sub> (*322.88*): C 48.35, H 9.36, N 17.35 %. Found: C 48.20, H 9.13, N 17.41 %.

<sup>1</sup>**H** NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.00, 2.50, 1.62 (m, 4H, hpp-CH<sub>2</sub>), 0.34 (s, 18H, SiMe<sub>3</sub>).

<sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ163.1 (*C*N<sub>3</sub>), 47.4, 41.9, 23.6 (hpp-*C*H<sub>2</sub>), 5.6 (Si*Me*<sub>3</sub>).

# Synthesis of Mg(tbo)(N{SiMe<sub>3</sub>}<sub>2</sub>)(THF) (4)

A solution of MeMgBr (1.3 mL of a 3.0 M solution in Et<sub>2</sub>O, 3.9 mmol) was added dropwise to a pale yellow solution of 1,4,6-triazabicyclo[3.3.0]oct-4-ene (Htbo) (0.420 g, 3.8 mmol) in tetrahydrofuran (~15 mL) at ambient temperature. Gas evolution was observed and a small amount of a white precipitate formed within 15 mins. The solution was stirred for 4 hours before the dropwise addition of Li[N{SiMe<sub>3</sub>}<sub>2</sub>] (0.420 g, 3.8 mmol) in THF (~15 mL). The resulting solution was stirred for 20 hours followed by the removal of volatiles *in vacuo*. Extraction of the product with hot hexane and slow cooling of the solution to ambient temperature yielded colourless crystals of (**4**). Yield 1.00 g, 72 %.

**Analysis**: Calc'd. for C<sub>15</sub>H<sub>34</sub>N<sub>4</sub>MgOSi<sub>2</sub> (*366.93*): C 49.10, H 9.34, N 15.27 %. Found: C 49.05, H 9.35, N, 15.26 %.

<sup>1</sup>**H NMR** (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.93 (m, 4H, tbo-CH<sub>2</sub>), 3.75 (m, 4H, THF), 2.63 (m, 4H, tbo-CH<sub>2</sub>), 1.45 (m, 4H, THF), 0.37 (s, 18H, SiMe<sub>3</sub>).

<sup>13</sup>**C NMR** (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  180.6 (*C*N<sub>3</sub>), 69.6 (THF), 56.1, 50.7 (tbo-*C*H<sub>2</sub>), 25.6 (THF), 6.5 (Si*Me*<sub>3</sub>).

#### Crystallographic Details for 1-4

Crystals were covered in an inert oil and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. The structures were refined with SHELXL-97.<sup>1</sup> Additional features of note are described below:

 $Cl_2Mg(\mu-hpp)_2Mg(THF)_2$  (**1b**) Atoms C13 (hpp-ring) and C18 (THF) are each disordered over two positions and were refined with isotropic carbon atoms.

 ${(THF)BrMg}_{2}(\mu-tbo)_{2}(\mu-THF)$  (2a) The C3-N3-C4 unit of the tbo ligand is disordered over two positions and was refined with SADI restraints on the carbonnitrogen distances of each component; the disordered atoms were left isotropic. It was not possible to differentiate the oxygen and carbon atoms in the THF solvate. It was refined as fully disordered with each position 80% carbon and 20% oxygen.

 $[Mg(hpp)(N{SiMe_3}_2)]_2$  ([3]<sub>2</sub>) Atom C6 is disordered, with the lower occupancy site left isotropic.

 $[Mg(tbo)(N{SiMe_3}_2)(THF)]_2$  ([4]<sub>2</sub>) The SiMe<sub>3</sub> group around Si2 is disordered over two positions and was refined with SADI restraints; the carbon atoms of the lower occupancy site were left isotropic. The THF is also disordered over two positions and was refined with SADI restraints; the carbon atoms of both orientations were left isotropic.

#### **Reference**

1. G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Göttingen, 1997.

#### Procedure for NMR reactions for the dimerization of benzaldehyde.

In an inert atmosphere glovebox, two NMR tubes fitted with J. Youngs taps were charged with either 1 or 10 mol % of pre-catalyst followed by the addition of in 0.5 mL of a  $C_6D_6$  solution of 1,4-dimethoxybenzene (0.11 M). 0.1 mL of a  $C_6D_6$  solution of benzaldehyde (4.77 M) was added to one of the samples, which was used immediately to pre-lock and shim the NMR instrument. An experiment was then set up to record <sup>1</sup>H NMR spectra (1 scan every 30 seconds) for the duration of the experiment. 0.1 mL of the benzaldehdye solution was then added to the remaining NMR tube in the glovebox which was immediately sealed then taken and inserted into the NMR instrument. The experiment was started as soon as the sample was in the probe (maximum time elapsed after mixing ~ 2.5 mins).

# *Procedure for the NMR reactions for the dimerization of cyclohexanecarboxaldehyde, isovaleraldehyde and acetaldehyde.*

100  $\mu$ L of aldehyde was added, in an inert atmosphere glovebox, to an NMR tube, fitted with a J. Young's tapthat had previously been charged with 0.01 equivalents of **3** and 0.5 mL of C<sub>6</sub>D<sub>6</sub> solution of 1,4-dimethoxybenzene (0.11 M). The progress of the reactions were checked after 10 min, 1 h, 2 h and 24 h.

#### Procedure for the NMR reaction for the dimerization of pivaldehyde

0.3 ml of a  $C_6D_6$  solution of pivaldehyde (4.95 M, 1.5 mmol, 100 equiv.) was added, in an inert atmosphere glovebox, to an NMR tube fitted with J. Young's tap that had previously been charged with **3** (4.8 mg, 0.015 mmol, 1 equiv.) and 0.2 ml of a  $C_6D_6$ solution of 1,4-dimethoxybenzene (0.11M). The progress of the reaction was checked after 10 min, 1 h, 2 h and 24 h.

In each case, the data was worked up by integrating the methyl protons of the 1,4dimethoxybenzene standard against the RC(O)H proton of the aldehyde and the  $RC(O)OCH_2R$  protons of the ester.

The concentrations were calculated using the following formulas (I = integration):

 $[aldehyde] = ([standard] \times I_{aldehdye} \times 6) / I_{standard}$ 

 $[ester] = ([standard] \times I_{ester} \times 3) / I_{standard}$ 

**Figure S1** Plot of % yields of benzylbenzoate *vs.* time for experiments using (a) 1 mol% **3**, (b) 1 mol% **4**, (c) 10 mol% **3**, (d) 10 mol% **4**. Values calculated from NMR integrals relative to 1,4-dimethoxybenzene internal standard, monitored for 60 mins.



**Figure S2** Plot of % yields of ester *vs*. time for experiments using 1 mol% **3** and RC(O)H (R = Ph, <sup>t</sup>Bu, Cy). Values calculated from NMR integrals relative to 1,4-dimethoxybenzene internal standard, monitored for 120 mins.



**Figure S3** Expansion of nomenclature used to describe two bridging guanidinate ligands to two metal centres, illustrated for magnesium.



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