Supporting Information

Unmasking Representative Structures of TMP-Active Hauser and Turbo Hauser Bases


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General Methods.
n-Hexane, toluene and THF were distilled from sodium-benzophenone. All synthetic work was carried out under an inert argon atmosphere using standard Schlenk techniques. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for $^1$H, 155.50 MHz for $^7$Li and 100.62 MHz for $^{13}$C. Data for X-ray crystal structure determination were obtained with a Nonius Kappa CCD and a Bruker SMART 1K CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Satisfactory elemental analyses of the compounds 1 and 2 could not be obtained due to their high air- and moisture-sensitive nature.
Crystal Data

Crystal Data for 1-toluene: C_{33}H_{60}Cl_{2}Mg_{2}N_{2}O_{2}; A colourless crystal with approximate dimensions 0.25 x 0.10 x 0.05 mm gave a monoclinic space group P2_1/n, \( a = 7.6748(2) \) \( b = 11.7489(4) \) c = 20.5222(5) \( \text{Å} \), \( \beta = 95.243(2) \)°, \( V = 1842.75(9) \) \( \text{Å}^3 \), \( T = 123 \) K, \( Z = 2 \), \( \rho_{\text{calc}} = 1.147 \) Mg m\(^{-3}\), \( 2\theta_{\text{max}} = 60.10 \)°, MoK\( \alpha \) \( \lambda = 0.71073 \)Å. Both structures were solved by direct methods and refined to convergence on \( F^2 \) (SHELXL-97; G. M. Sheldrick, University of Göttingen, Germany). \( R_1 = 0.0467 \) (for 3389 reflections with \( I > 2\sigma(I) \)) \( wR_2 = 0.1135 \) and \( S = 1.015 \) for 222 parameters and 5400 unique reflections. Minimum/maximum residual electron density \(-0.353/0.386 \) e\( \text{Å}^{-3} \). Crystallographic data (excluding structure factors) for the compounds reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 690058 and 690059. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

Crystal Data for 2: C_{21}H_{42}Cl_{2}LiMgNO_{3}; A colourless block of approximate dimensions 0.25 x 0.20 x 0.10 mm gave a monoclinic space group P2_1/c, \( a = 8.3132(4) \) \( b = 26.2139(15) \) c = 14.1160(7) \( \text{Å} \), \( \beta = 120.529(2) \)°, \( V = 2649.7(2) \) \( \text{Å}^3 \), \( T = 123 \) K, \( Z = 4 \), \( \rho_{\text{calc}} = 1.150 \) Mg m\(^{-3}\), \( 2\theta_{\text{max}} = 55.08 \)°, MoK\( \alpha \) \( \lambda = 0.71073 \)Å. \( R_1 = 0.0561 \) (for 3735 reflections with \( I > 2\sigma(I) \)) \( wR_2 = 0.1365 \) and \( S = 1.030 \) for 283 parameters and 6039 unique reflections. Minimum/maximum residual electron density \(-0.314/0.338 \) e\( \text{Å}^{-3} \).
Figure 1. Molecular structure of 1 with hydrogen atoms and disordered toluene of crystallization omitted for clarity. Symmetry operator A: \(-x + 1, -y + 1, -z\). Selected bond lengths (Å) and angles (°): Mg1–N1 1.9558(14), Mg1–O1 2.0070(13), Mg1–Cl1 2.4271(6), Mg1–Cl1* 2.4281(7), Mg1···Mg1* 3.5041(10), N1-Mg1-O1 113.54(6), N1-Mg1-Cl1 123.10(5), O(1)-Mg(1)-Cl(1) 102.05(4), N(1)-Mg(1)-Cl1* 126.06(5), O1-Mg1-Cl1* 98.96(4), Cl1-Mg1-Cl1* 87.61(2), Mg1-Cl1-Mg1* 92.39(2).
Figure 2. Molecular structure of 2 with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Li1–O2 1.921(5), Li1–O3 1.933(5), Li1–Cl1 2.361(5), Li1–Cl2 2.364(5), Mg1···Li1 3.195(5), Mg1–N1 1.981(2), Mg1–O1 2.026(2), Mg1–Cl1 2.4000(11), Mg1–Cl2 2.4042(11), O2-Li1-O3 113.9(3), O2-Li1-Cl1 108.4(2), O3-Li1-Cl1 114.7(2), O2-Li1-Cl2 109.2(2), O3-Li1-Cl2 114.1(3), Cl1-Li1-Cl2 94.88(17), N1-Mg1-O1 110.86(9), N1-Mg1-Cl1 122.47(7), O1-Mg1-Cl1 100.82(7), N1-Mg1-Cl2 126.74(7), O1-Mg1-Cl2 97.98(7), Cl1-Mg1-Cl2 92.84(4), Li1-Cl1-Mg1 84.29(12), Li1-Cl2-Mg1 84.12(12).
Synthesis of [TMP(THF)Mg(μ-Cl)₂Mg(THF)TMP] (I): To a solution of "BuMgCl (5 mmol, 2.5 mL of a 2.0 M solution in THF) in bulk THF (10 mL) was added TMP(H) (5 mmol, 0.85 mL). The resultant mixture was heated to reflux for 5 h and then stirred at RT overnight. Removal of the solvent yielded an off-white solid, which was recrystallised from hot toluene to give colourless crystals of I (0.68 g, 50 %). ¹H NMR (400 MHz, d₈-THF, 293 K): δ = 3.61 (m, 8H, CH₂-O, THF), 1.76 (m, 8H, CH₂, THF), 1.60 (m, 4H, γ-CH₂, TMP), 1.19 (m, 8H, β-CH₂, TMP), 1.12 (s, 24H, CH₃, TMP). ¹³C {¹H} NMR (100 MHz, d₈-THF, 293 K): 68.5 (CH₂-O, THF), 52.1 (α-C, TMP), 42.6 (β-CH₂, TMP), 36.1 (CH₃, TMP), 26.6 (CH₂, THF), 20.9 (γ-CH₂, TMP). A small amount of TMP(H) is also detected in the spectrum presumably due to a small amount of hydrolysis during the measurement.

¹H NMR spectrum of I in d₈-THF solution:
Isolation of crystalline [(THF)$_2$Li(μ-Cl)$_2$Mg(THF)TMP] (2) from the reaction of $i$PrMgCl.LiCl with TMP(H): To a solution of $i$PrMgCl.LiCl in THF (28.8 mmol, 30.0 mL of a 0.96 M solution in THF) was added TMP(H) (30.24 mmol, 5.14 mL, 1.05 equivalents) dropwise at RT and the resultant pale grey yellowish solution was allowed to stir for 24 h (slightly modified procedure of the one described by Knochel[8]). The solvents were removed under vacuum yielding an off-white oily solid. This solid was recrystallised from hexane/THF 3:2 mixtures at –27 °C affording colourless crystals of 2 (2.90 g, 26 %, considering the loss of one molecule of THF of 2) suitable for X-ray crystallographic analysis. $^1$H NMR (400 MHz, d$_8$-THF, 293 K): 3.61 (m, 8H, CH$_2$-O, THF), 1.76 (m, 8H, CH$_2$, THF), 1.57 (m, 2H, γ-CH$_2$, TMP), 1.17 (4H, m, β-CH$_2$, TMP), 1.16 (12H, s, CH$_3$, TMP). $^{13}$C{$^1$H} NMR (100.59 MHz, d$_8$-THF, 293 K): 68.5 (CH$_2$-O, THF), 52.3 (α-C, TMP), 43.0 (β-CH$_2$, TMP), 36.2 (CH$_3$, TMP), 26.6 (CH$_2$, THF), 21.0 (γ-CH$_2$, TMP). $^7$Li NMR (155 MHz, d$_8$-THF, 293K, reference LiCl in D$_2$O at 0.00 ppm): 0.29.

$^{13}$C{$^1$H} NMR spectrum of 1 in d$_8$-THF solution:
$^1$H NMR spectrum of 2 in d$_8$-THF solution:

$^{13}$C{$_1^1$H} NMR spectrum of 2 in d$_8$-THF solution:
Alternative synthesis of 2 from the reaction of LiTMP with anhydrous MgCl₂. A Schlenk tube was charged with 5 mmol (0.85 ml) of TMP(H) in 10 mL of hexane and a molar equivalent of n-BuLi (3.15 mL of a 1.6 M solution in hexane) was added dropwise and the resultant pale yellow solution was allowed to stir for 2 h. The solvent was removed under vacuum obtaining a pale yellow oily solid of LiTMP. MgCl₂ (0.48 g) was added to the LiTMP residue and 10 mL of THF were added dropwise at 0 °C. The resultant suspension was allowed to stir and turned to a very pale yellow transparent solution after 1 hour. The solution was then stirred for 1 day. Over the yellowish white-off oily residue obtained after solvent removal 30 mL of hexane were added and the mixture was stirred for 1 h. An off-white suspension was obtained which was filtered off obtaining a white solid identified by ¹H, ¹³C{¹H}, ⁷Li NMR and IR in nujol as 2 (0.95 g, 49 % considering the loss of one molecule of THF of 2). A unit cell checked of a crystal obtained from hexane/THF 3:2 mixtures at – 27 °C also confirmed this was the same compound of that obtained via reaction of ⁷PrMgCl₂LiCl with TMP(H).
Magnesiation of ethyl-3-chlorobenzoate followed by the reaction with iodine. The procedure used mimics the conditions used by Knochel in the synthesis of ethyl-3-chloro-2-iodobenzoate.\[9\]  

**Method (a):** To a cooled solution at 0 °C of 1 mmol of ethyl-3-chlorobenzoate (0.16 mL) in 3 mL of THF, a solution obtained by dissolving crystalline 2 in 1 mL of THF (1.2 equiv; concentration of the solution was titrated by using benzoic acid in dry THF and 4-(phenylazo)diphenylamine as an indicator) was added dropwise and stirred for 6 h. After this time the initially colourless solution turned gradually to dark orange. An aliquot of 0.25 mL of the crude reaction was taken and, after solvent removal, was analyzed by \(^1\)H and \(^7\)Li NMR showing as the major product to be the 2-magnesiated derivative of ethyl-3-chlorobenzoate (74 %, only complexes different from TMP(H) were taken into account to calculate the percentages, elaborated from the \(^1\)H NMR integrals of the methylene resonances of the ethylcarboxylate groups) together with the TMP(H) released in the metallation, a trace amount of ethyl-3-chlorobenzoate (4 %) and other(s) products non identified (22 %). I\(_2\) (381 mg, 1.5 equiv.) dissolved in dry THF (5 mL) was then added at 0 °C, and the resulting mixture was warmed to RT and stirred for 1 h. The reaction mixture was quenched with sat. aq. Na\(_2\)S\(_2\)O\(_3\) solution, extracted with CH\(_2\)Cl\(_2\) (3 × 40 mL) and dried over anhydrous Na\(_2\)SO\(_4\). After filtration, the solvent was evaporated in vacuo. Purification by flash-chromatography furnished the product ethyl-3-chloro-2-iodobenzoate as a yellow oil (0.21 g, 68 %) identified by \(^1\)H and \(^{13}\)C NMR spectra.  

**Method (b):** To a cooled solution at 0 °C of 1 mmol of ethyl-3-chlorobenzoate (0.16 mL) in 3 mL of THF, a solution of LiTMP/MgCl\(_2\) (1.20 M solution in THF; obtained by stirring 1 day a mixture of 1.2 mmol of LiTMP and anhydrous MgCl\(_2\) in 1 mL of THF) was added dropwise and stirred for 6 h. After this time the initially colourless solution turned gradually to dark orange. An aliquot of 0.50 mL of the crude reaction was taken and, after solvent removal, was analyzed by \(^1\)H and \(^7\)Li NMR showing as the major product to be the 2-magnesiated derivative of ethyl-3-chlorobenzoate (74 %; only complexes different from TMP(H) were taken into account to calculate the percentages, elaborated from the \(^1\)H NMR integrals of the methylene resonances of the ethylcarboxylate groups) together with the TMP(H) released in the metallation, a trace amount of ethyl-3-chlorobenzoate (7 %) and other(s) products non identified (19 %). I\(_2\) (381 mg, 1.5 equiv.) dissolved in dry THF (5 mL) was then added at 0 °C, and the
resulting mixture was warmed to RT and stirred for 1 h. The reaction mixture was quenched with sat. aq. Na$_2$S$_2$O$_3$ solution, extracted with CH$_2$Cl$_2$ (3 × 40 mL) and dried over anhydrous Na$_2$SO$_4$. After filtration, the solvent was evaporated in vacuo. Purification by flash-chromatography furnished the product ethyl-3-chloro-2-iodobenzoate as a yellow oil (0.18 g, 58 %) identified by $^1$H and $^{13}$C NMR.
A $^1$H NMR spectrum in d$_8$-THF solution (Method a) of the aliquot taken before the quench with iodine, showing the 2-magnesiated derivative and TMP(H) as the major products:
A $^7$Li NMR spectrum in d$_8$-THF solution (Method a) of the aliquot taken before the quench with iodine, confirmed the presence of Li in the 2-magnesiated derivative of ethyl-3-chlorobenzoate:
A $^1$H NMR spectrum in $d_8$-THF solution (Method b) of the aliquot taken before the quench with iodine, showing the 2-magnesiated derivative and TMP(H) as the major products:
A $^7$Li NMR spectrum in d$_8$-THF solution (Method b) of the aliquot taken before the quench with iodine, confirmed the presence of Li in the 2-magnesiated derivative of ethyl-3-chlorobenzoate: