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SUPPLEMENTARY MATERIAL

Synthesis and Structure of a Magnesium-Amidoborane Complex and its Role in Catalytic Formation of a New *bis*-Aminoborane Ligand

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1) Syntheses

All experiments were carried out under argon using standard Schlenk-techniques and freshly dried solvents. The following starting materials have been prepared according to literature: (DIPP-nacnac)Mg[N(SiMe$_3$)$_2$],[1] [(DIPP-nacnac)MgH]$_2$,[2] NH$_2$(DIPP)BH$_3$,[3] (DIPP-nacnac = CH{(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)}$_2$). Di-*n*-butylmagnesium solution in heptane was purchased from Acros Organics and used as received.

(DIPP-nacnac)MgBH$_4$

Method a): 20 mg (0.03 mmol) (DIPP-nacnac)Mg[N(SiMe$_3$)$_2$] was dissolved in 0.5 mL of benzene-*d*$_6$. To this solution six equivalents of NH$_2$(DIPP)BH$_3$ were added stepwise over a period of three hours and the reaction was followed using ^{1}H-NMR spectroscopy. After the reaction was completed, the mixture was cooled slowly to 8 °C. This resulted in precipitation of colourless blocks of (DIPP-nacnac)Mg(BH$_4$) suitable for X-Ray analysis.

Method b): 360 mg (0.41 mmol) [(DIPP-nacnac)MgH]$_2$ was dissolved in 6 mL of benzene. To this solution 61 mg (0.81 mmol) BH$_3$(SMe$_2$) was added. Overnight colourless crystals of (DIPP-nacnac)Mg(BH$_4$) precipitated. Yield: 236 mg, 0.27 mmol, 64 %. Elemental analysis (%) calcd for $C_{58}H_{90}B_2Mg_2N_4$ (M_r = 913.60): C 76.24, H 9.93; found C 75.93, H 9.92. ^{1}H{^{11}B} NMR (500 MHz, [benzene-*d*$_6$], 20 °C): δ = 0.05 (s (br), 8H, BH$_4$), 0.99 (br, 24H, *i*Pr), 1.12 (d, ^{3}J(H,H) = 6.5 Hz, 24H, *i*Pr), 1.51 (s, 12H, Me backbone), 3.12 (sept, ^{3}J(H,H) = 6.5 Hz, 8H, *i*Pr), 4.76 (s, 2H, H backbone), 7.03-7.11 (m, 12H, aryl). ^{11}B NMR (160 MHz, [benzene-*d*$_6$], 20 °C): δ = –38.3 (br). ^{13}C{^{1}H} NMR (75 MHz, [benzene-*d*$_6$], 20 °C): 24.3 (Me backbone), 24.8 (*i*Pr), 24.9 (*i*Pr), 28.5 (*i*Pr), 95.5 (backbone), 124.3 (aryl), 126.2 (aryl), 142.9 (aryl), 144.2 (aryl), 170.4 (backbone).

(DIPP-nacnac)MgNH(Dipp)BH$_3$

500 mg (0.56 mmol) [(DIPP-nacnac)MgH]$_2$ were dissolved in 10 mL of toluene. This solution was cooled to 0 °C and 216 mg (1.13 mmol) NH$_2$(DIPP)BH$_3$ in 2 mL of toluene was added slowly. The temperature was allowed to rise to 25 °C and the reaction mixture was stirred for one hour. Then the reaction mixture was concentrated to a volume of about 3 mL and slowly cooled to –27 °C to give colourless crystals of (DIPP-nacnac)MgNH(DIPP)BH$_3$. Yield: 422

mg, 0.67 mmol, 59 %. Elemental analysis (%) calcd for $C_{41}H_{62}BMgN_3$ (M_r = 632.07): C 77.91, H 9.89; found C 77.13, H 9.84. $^{1}H\{^{11}B\}$ NMR (500 MHz, [benzene-*d*$_6$], 20 °C): δ = 1.00 (d, $^{3}J(H,H)$ = 6.6 Hz, 12H, *i*Pr amidoborane), 1.10 (d, $^{3}J(H,H)$ = 6.8 Hz, 12H, *i*Pr nacnac), 1.24 (d, $^{3}J(H,H)$ = 6.8 Hz, 12H, *i*Pr nacnac), 1.65 (s, 6H, Me backbone), 1.97 (sept, $^{3}J(H,H)$ = 6.6 Hz, 4H, *i*Pr amidoborane), 2.44 (d (br), 3H, BH_3), 2.86 (q, $^{3}J(H,H)$ = 4.8 Hz, 1H, NH), 3.29 (sept, $^{3}J(H,H)$ = 6.8 Hz, 4H, *i*Pr), 4.95 (s, 1H, H backbone), 6.88-6.56 (m, 3H, aryl), 7.06-7.14 (m, 6H, aryl). ^{11}B NMR (160 MHz, [benzene-*d*$_6$], 20 °C): δ = –17.7 (br). $^{13}C\{^{1}H\}$ NMR (75 MHz, [benzene-*d*$_6$], 20 °C): 24.2 (*i*Pr amidoborane), 24.5 (*i*Pr), 24.6 (*i*Pr), 25.1 (Me backbone), 28.7 (*i*Pr amidoborane), 29.2 (*i*Pr), 95.4 (backbone), 122.8 (aryl amidoborane), 123.8 (aryl), 124.7 (aryl), 126.3 (aryl amidoborane), 139.1 (aryl amidoborane), 142.8 (aryl), 170.6 (backbone).

HB[NH(DIPP)]$_2$

Method a): to a solution of 1.50 g (7.85 mmol) NH_2(DIPP)BH_3 in 20 of mL toluene was added 240 mg (0.40 mmol) (DIPP-nacnac)Mg[N$(SiMe_3)_2$] (5 mol%, calculated on the active rest). The solution was heated to 60 °C for 14 hours and afterwards the solvent was evaporated. To the residue was added 5 mL of hexane and the insoluble precipitate, presumably (DIPP-nacnac)MgBH_4, was filtered off. Hexane was evaporated to give HB[NH(DIPP)]$_2$ quantitatively as a colourless powder. This reaction can equally well be performed with the commercially available *n*Bu_2Mg (solution in heptane) as a catalyst. In this case 2.5 mol% (or 5 mol% calculated on the active butyl rest) of the catalyst gave HB[NH(DIPP)]$_2$ in nearly quantitative yield (1.40 g, 3.8 mmol, 98%).

Method b): Two equivalents of DIPP-aniline (6.23 g, 35.14 mmol) and one equivalent of $BH_3(SMe_2)$ (1.37 g, 17.60 mmol) were mixed with 18 mL of toluene in a 50 mL steel reactor. To this solution 0.88 mL of a 0.5 M solution of *n*Bu_2Mg in heptane (2.5 mol%) was added. The reactor was closed and heated to 60 °C for 14h. After the reaction was completed the evolved gas was released slowly and the solvent was evaporated. 30 mL of hexane were added to the residue and the insoluble Mg salts were filtered off. The mother liquor was isolated and the hexane was removed under vacuum to give HB[NH(DIPP)]$_2$ nearly quantitatively as a colourless powder (6.37 g, 17.50 mmol, 99%).

It should be mentioned that the reactions outlined above in principal also can be performed without a catalyst. However, the conversions are extremely slow and, even after prolonged reaction times, never complete (< 50%). In these cases the product HB[NH(DIPP)]$_2$ cannot be separated from the starting compound DIPP-aniline. Purification by multiple recrystallization from hexane failed due to the high solubility of the product and cocrystallization of the unreacted DIPP-aniline. Therefore Mg-catalyzed reactions should be the method of choice.

Crystals suitable for X-Ray analysis could be obtained by slowly cooling a concentrated hexane solution of HB[NH(DIPP)]$_2$ to 8 °C. Elemental analysis (%) calcd for $C_{24}H_{37}BN_2$ (M_r = 364.37): C 79.11, H 10.24 found C 78.72, H 10.31. ^{1}H NMR spectra in benzene show two sets of signals which likely arise from two different conformations. The B-N bonds have double bond character and free rotation around this bond is hindered. This could explain the two different conformations with DIPP-substituents in either *endo*- or *exo*- positions. Due to steric hindrance an (*endo*, *endo*) conformation is unlikely and only (*endo*, *exo*) and (*exo*, *exo*) conformations are possible. ^{1}H{^{11}B} NMR (500 MHz, [benzene-*d*$_6$], 20 °C): conformer 1: δ = 1.16-1.23 (br, 12H, *i*Pr), 3.40 (br, 4H, *i*Pr), 3.89 (br, 2H, NH), 4.40 (br, 1H, BH), 7.08-7.14 (m, 6H, aryl); conformer 2: δ = 1.16-1.23 (br,12H, *i*Pr), 3.58 (br, 4H, *i*Pr), 3.98 (br, 2H, NH), 4.40 (br, 1H, BH), 7.08-7.14 (m, 6H, aryl). ^{1}H NMR (500 MHz, [benzene-*d*$_6$], 70 °C): δ = 1.20 (d, ^{3}J(H,H) = 6.9 Hz, 12H, *i*Pr), 3.50 (sept., ^{3}J(H,H) = 6.9 Hz, 4H, *i*Pr), 3.97 (br, 2H, NH), 4.50 (br, 1H, BH), 7.09-7.12 (m, 6H, aryl). ^{11}B NMR (160 MHz, [benzene-*d*$_6$], 20 °C): δ = 27.6 (br). ^{13}C{^{1}H} NMR (75 MHz, [benzene-*d*$_6$], 70 °C): δ = 23.7 (*i*Pr), 28.6 (*i*Pr), 123.6 (aryl) 126.1 (aryl), 128.3 (aryl), 145.5 (aryl).

2) Crystal structure determination

Single crystals have been measured on a Siemens SMART CCD diffractometer or a STOE IPDS II two-circle-diffractometer. Structures have been solved and refined using the programs SHELXS-97 and SHELXL-97, respectively.[4] All geometry calculations and graphics have been performed with PLATON.[5]

Crystal structure determination for HB(NHDIPP)$_2$.

The crystal was twinned but the reflections in the two domains could be well separated from each other. The structure was refined by merging the data from the two domains. The Flack parameter for this non-centrosymmetric structure refined to 1.9(19). The large error is likely due to the two domain refinement. All hydrogen atoms have been observed and could be refined isotropically.

Crystal structure determination for [(DIPP-nacnac)MgBH$_4$]$_2$.

Most hydrogen atoms have been placed on idealized calculated positions, however, the hydrogen atoms for the BH$_4$ fragment have been observed and were refined isotropically.

Crystal structure determination for (DIPP-nacnac)MgNH(DIPP)BH$_3$.

Although the crystal was small and showed poor diffraction a structure could be determined. All hydrogen atoms have been placed on idealized calculated positions, except for that on N3 which was located and could be refined. The hydrogen atoms on the BH$_3$ could not be located and its positions have been calculated.

Data for HB(NHDIPP)$_2$

Formula			C24 H37 B N2
Formula Weight			364.37
Crystal System			Monoclinic
Space group		P21	(No. 4)
a, b, c [Angstrom]	10.2052(9)	10.3128(9)	11.5048(11)
alpha, beta, gamma [deg]	90	108.727(5)	90
V [Ang**3]			1146.71(18)
Z			2
D(calc) [g/cm**3]			1.055
Mu(MoKa) [/mm]			0.060
F(000)			400
Crystal Size [mm]			0.20 x 0.20 x 0.50

Data Collection

Temperature (K)		123
Radiation [Angstrom]	MoKa	0.71073
Theta Min-Max [Deg]		1.9, 30.1
Dataset		-14: 14 ; -14: 14 ; -16: 15
Tot., Uniq. Data, R(int)		14398, 6317, 0.054
Observed data [I > 2.0 sigma(I)]		5329

Refinement

Nref, Npar	6317, 391
R, wR2, S	0.0474, 0.1133, 1.05
w = 1/[\s^2^(Fo^2^)+(0.0487P)^2^+0.0160P] where P=(Fo^2^+2Fc^2^)/3	
Max. and Av. Shift/Error	0.00, 0.00
Flack x	1.9(19)
Min. and Max. Resd. Dens. [e/Ang^3]	-0.21, 0.17

Data for [(DIPP-nacnac)MgBH$_4$]$_2$

Formula	C58 H90 B2 Mg2 N4
Formula Weight	913.58
Crystal System	Monoclinic
Space group	P21/n (No. 14)
a, b, c [Angstrom]	14.3266(11) 13.9025(8) 15.1584(13)
alpha, beta, gamma [deg]	90 106.287(6) 90
V [Ang**3]	2898.0(4)
Z	2
D(calc) [g/cm**3]	1.047
Mu(MoKa) [/mm]	0.079
F(000)	1000
Crystal Size [mm]	0.43 x 0.44 x 0.47

Data Collection

Temperature (K)	173
Radiation [Angstrom]	MoKa 0.71073
Theta Min-Max [Deg]	3.5, 25.6
Dataset	-17: 17 ; -16: 16 ; -14: 18
Tot., Uniq. Data, R(int)	18615, 5409, 0.049
Observed data [I > 2.0 sigma(I)]	4369

Refinement

Nref, Npar	5409, 317
R, wR2, S	0.0460, 0.1298, 1.05
w = 1/[\s^2^(Fo^2^)+(0.0760P)^2^+0.4462P] where P=(Fo^2^+2Fc^2^)/3	
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-0.20, 0.46

Data for (DIPP-nacnac)MgNH(DIPP)BH$_3$

Formula	C41 H62 B Mg N3
Formula Weight	632.06
Crystal System	Monoclinic
Space group	P21/c (No. 14)
a, b, c [Angstrom]	18.295(4) 11.8119(14) 18.846(3)
alpha, beta, gamma [deg]	90 103.004(15) 90
V [Ang**3]	3968.2(12)
Z	4
D(calc) [g/cm**3]	1.058
Mu(MoKa) [/mm]	0.075
F(000)	1384
Crystal Size [mm]	0.16 x 0.17 x 0.19

Data Collection

Temperature (K)	173
Radiation [Angstrom]	MoKa 0.71073
Theta Min-Max [Deg]	3.5, 25.0
Dataset	-21: 17 ; -12: 14 ; -22: 22
Tot., Uniq. Data, R(int)	17455, 6903, 0.109
Observed data [I > 2.0 sigma(I)]	2340

Refinement

Nref, Npar	6903, 421
R, wR2, S	0.0924, 0.2375, 0.87
w = 1/[\S^2^(FO^2^)+(0.0769P)^2^] WHERE P=(FO^2^+2FC^2^)/3'	
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-0.30, 0.34

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