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Harder, Sjoerd; Spielmann, Jan

Published in:
Chemical Communications

DOI:
[10.1039/c1cc14689k](https://doi.org/10.1039/c1cc14689k)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2011

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Harder, S., & Spielmann, J. (2011). Unprecedented reactivity of an aluminium hydride complex with ArNH₂BH₃: nucleophilic substitution versus deprotonation. *Chemical Communications*, 47(43), 11945-11947. <https://doi.org/10.1039/c1cc14689k>

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SUPPLEMENTARY MATERIAL

Unprecedented reactivity of an aluminium hydride complex with ArNH_2BH_3 : nucleophilic substitution *versus* deprotonation

Sjoerd Harder^{*a} and Jan Spielmann^b

^a*Stratingh Institute, University of Groningen, Nijenborgh 4, 9747AG, Groningen, Netherlands*
E-mail: s.harder@rug.nl; Fax: +31 50 3634296; Tel: +31 50 3634322

^b*Fachbereich Chemie, Universitätsstraße 5, 45117 Essen, Germany.*

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1. General experimental procedures

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: DIPPnacnacAlH₂,¹ DIPPnacnacAlCl₂,² *i*PrNH₂BH₃³ and DIPPNH₂BH₃.³

NMR spectra were measured on Bruker DPX300 and DRX500 spectrometer using predried deuterated solvents. Crystals were measured on a Siemens Smart diffractometer with APEXII area detector system.

2. Synthesis of DIPPnacnacAl(BH₄)₂

DIPPnacnacAlH₂ (200 mg, 0.45 mmol) and DIPPNH₂BH₃ (172 mg, 0.90 mmol) were dissolved in 4 mL of dry benzene and subsequently stirred for one hour. The solvent was removed under high vacuum and the residue was dissolved in 2 mL of dry hexane. After concentration to 1 mL the solution was slowly cooled to -27 °C. Crystals were isolated and the remaining mother liquor was concentrated further and again slowly cooled to -27 °C for further crystallization. The yield of the combined batches of crystals is 125 mg, 0.26 mmol, 58%. Elemental analysis (%) calcd. for C₂₉H₄₉AlB₂N₂ (MW = 474.30): C 73.43, H 10.41; found C 73.27, H 10.16. ¹H{¹¹B} NMR (500 MHz, [benzene-*d*₆], 20 °C): δ = 1.06 (s br, 8H, BH₄), 1.06 (d, ³J(H,H) = 6.8 Hz, 12H, *i*-Pr), 1.40 (d, ³J(H,H) = 6.8 Hz, 12H, *i*-Pr), 1.51 (s, 6H, Me backbone), 3.29 (sept, ³J(H,H) = 6.8 Hz, 4H, *i*-Pr), 4.92 (s, 1H, backbone), 7.08-7.12 (m, 6H, aryl); ¹¹B NMR (160 MHz, [benzene-*d*₆], 20 °C): δ = -36.6 (quintet, ¹J(B,H) = 85.3 Hz, BH₄); ¹³C NMR (75 MHz, [benzene-*d*₆], 20 °C): δ = 22.6 (Me backbone), 24.4 (*i*-Pr), 25.5 (*i*-Pr), 28.9 (*i*-Pr), 99.0 (backbone), 125.1 (aryl), 128.2 (aryl), 139.3 (aryl), 144.8 (aryl), 172.0 (backbone).

3. Synthesis of KNH(DIPP)BH₃

DIPPNH₂BH₃ (500 mg 2.62 mmol) and KN(SiMe₃)₂ (522 mg 2.62 mmol) were dissolved in 10 mL of dry benzene. The solution was stirred for one hour during which time a colourless precipitate was formed. This was isolated by centrifugation, washed with 6 mL of dry hexane and dried under high vacuum. Yield: 524 mg, 2.29 mmol 87%. Elemental analysis (%) calcd. for C₁₂H₂₁BKN (MW = 229.21): C 62.88, H 9.24; found C 61.58, H 9.23. ¹H NMR (500 MHz, [THF-*d*₈], 20 °C): δ = 1.15 (d, ³J(H,H) = 6.8 Hz, 6H, *i*-Pr), 1.88 (d, ³J(H,H) = 3.8 Hz, 3H, BH₃), 2.70 (q, ³J(H,H) = 3.8 Hz, 1H, NH), 3.56 (sept, ³J(H,H) = 6.8 Hz, 4H, *i*-Pr), 6.36 (t, ³J(B,H) = 7.5 Hz, 1H, aryl), 6.75 (d, ³J(B,H) = 7.5 Hz, 2H, aryl); ¹¹B NMR (160 MHz, [THF-*d*₈], 20 °C): δ = -17.5 (q, ¹J(B,H) = 85.3 Hz, BH₃); ¹³C NMR (75 MHz, [THF-*d*₈], 20 °C): δ = 24.5 (*i*-Pr), 28.4 (*i*-Pr), 115.8 (aryl), 123.0 (aryl), 137.0 (aryl), 154.7 (aryl).

4. New synthetic route to DIPPnacnacAlH₂

DIPPnacnacAlCl₂ (330 mg, 0.642 mmol) and KNH(DIPP)BH₃ (290 mg, 0.90 mmol) were dissolved in 6 mL of dry benzene (with gentle heating). The formation of a white precipitate was observed immediately. The reaction was monitored by ¹H NMR and was completed after stirring overnight at room temperature. The main product, DIPPnacnacAlH₂, is according to ¹H NMR present in quantities > 80%. After centrifugation, the mother liquor was isolated and all solvents were removed under high vacuum. The residue was dissolved in 2 mL of hexane and this solution was slowly cooled to -27 °C. After harvesting the first batch of colourless plate-like crystals, the mother liquor was concentrated and again slowly cooled to -27 °C. The yield of the combined batches of crystals is 177 mg, 0.397 mmol, 62%. The ¹H NMR spectrum equals that published earlier for DIPPnacnacAlH₂. ¹H NMR (300 MHz, [benzene-*d*₆], 20 °C): δ = 1.14 (d, ³J(H,H) = 6.8 Hz, 12H, *i*-Pr), 1.39 (d, ³J(H,H) = 6.8 Hz, 12H, *i*-Pr), 1.55 (s, 6H, Me backbone), 3.42 (sept, ³J(H,H) = 6.8 Hz, 4H, *i*-Pr), 4.51 (br, 2H, AlH₂), 4.87 (s, 1H, backbone), 7.08-7.14 (m, 6H, aryl).

5. Crystal structure determination of DIPPnacnacAl(BH₄)₂

Crystal data are summarized in Table 1. The structures were solved by Direct Methods (SHELXS-97) and refined with SHELXL-97.^{4, 5} All geometry calculations and graphics were performed with PLATON.⁶

The crystal structure contains one cocrystallized molecule of benzene which was slightly disordered and refined with high anisotropy. No further voids were detected. All H atoms have been placed on calculated positions, except for the H atoms on the BH₄ units. These were located in the Difference-Fourier map and refined isotropically. The crystal was twinned but the independent crystal lattices could be separated. Although overlapping reflexes were rejected (giving rise to measurement of 96% of all total reflections) some intensities might be falsified which explains the relatively high R1 value of 0.0689.

Table 1. Crystal data for DIPPnacnacAl(BH₄)₂.

CCDC Nr.	837323
Formula	C ₂₉ H ₄₉ AlB ₂ N ₂ , C ₆ H ₆
MW	552.41
Size (mm ³)	0.5 x 0.4 x 0.3
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	8.4532(5)
<i>b</i> (Å)	12.1566(8)
<i>c</i> (Å)	18.6362(12)
α	75.871(4)
β	78.335(4)
γ	69.729(4)
<i>V</i> (Å ³)	1727.5(2)
<i>Z</i>	2
ρ (g.cm ⁻³)	1.062
μ (MoK α) (mm ⁻¹)	0.083
<i>T</i> (°C)	-150
θ (max)	27.3
refl. total, unique	18224, 7453
R _{int}	0.037
obsvd refl. (<i>I</i> > 2 σ (<i>I</i>))	6161
parameter	403
<i>R</i> ₁	0.0689
<i>wR</i> ₂	0.2178
GOF	1.14
min/max resd (e.Å ⁻³)	-0.31/0.67

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