SUPPLEMENTARY MATERIAL

Unprecendented 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.*

Contents:

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: DIPPnacnacAlH$_2$,[1] DIPPnacnacAlCl$_2$,[2] *i*PrNH$_2$BH$_3$[3] and DIPPNH$_2$BH$_3$.[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(BH$_4$)$_2$

DIPPnacnacAlH$_2$ (200 mg, 0.45 mmol) and DIPPNH$_2$BH$_3$ (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 $C_{29}H_{49}AlB_2N_2$ (MW = 474.30): C 73.43, H 10.41; found C 73.27, H 10.16. ^{1}H{^{11}B} NMR (500 MHz, [benzene-d_6], 20 °C): δ = 1.06 (s br, 8H, BH$_4$), 1.06 (d, ^{3}J(H,H) = 6.8 Hz, 12H, *i-Pr*), 1.40 (d, ^{3}J(H,H) = 6.8 Hz, 12H, *i-Pr*), 1.51 (s, 6H, Me backbone), 3.29 (sept, ^{3}J(H,H) = 6.8 Hz, 4H, *i*-Pr), 4.92 (s, 1H, backbone), 7.08-7.12 (m, 6H, aryl); ^{11}B NMR (160 MHz, [benzene-d_6], 20 °C): δ = −36.6 (quintet, ^{1}J(B,H) = 85.3 Hz, BH$_4$); ^{13}C 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)BH_3

DIPPNH_2BH_3 (500 mg 2.62 mmol) and $KN(SiMe_3)_2$ (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 $C_{12}H_{21}BKN$ (MW = 229.21): C 62.88, H 9.24; found C 61.58, H 9.23. ^{1}H NMR (500 MHz, [THF-d_8], 20 °C): δ = 1.15 (d, ^{3}J(H,H) = 6.8 Hz, 6H, *i-Pr*), 1.88 (d, ^{3}J(H,H) = 3.8 Hz, 3H, BH_3), 2.70 (q, ^{3}J(H,H) = 3.8 Hz, 1H, NH), 3.56 (sept, ^{3}J(H,H) = 6.8 Hz, 4H, *i*-Pr), 6.36 (t, ^{3}J(B,H) = 7.5 Hz, 1H, aryl), 6.75 (d, ^{3}J(B,H) = 7.5 Hz, 2H, aryl); ^{11}B NMR (160 MHz, [THF-d_8], 20 °C): δ = −17.5 (q, ^{1}J(B,H) = 85.3 Hz, BH_3); ^{13}C 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 DIPPnacnacAlH_2

DIPPnacnac$AlCl_2$ (330 mg, 0.642 mmol) and KNH(DIPP)BH_3 (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 ^{1}H NMR and was completed after stirring overnight at room temperature. The main product, DIPPnacnacAlH_2, is according to ^{1}H 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 ^{1}H NMR spectrum equals that published earlier for DIPPnacnacAlH_2.[1] ^{1}H NMR (300 MHz, [benzene-d_6], 20 °C): δ = 1.14 (d, ^{3}J(H,H) = 6.8 Hz, 12H, *i-Pr*), 1.39 (d, ^{3}J(H,H) = 6.8 Hz, 12H, *i-Pr*), 1.55 (s, 6H, Me backbone), 3.42 (sept, ^{3}J(H,H) = 6.8 Hz, 4H, *i*-Pr), 4.51 (br, 2H, AlH_2), 4.87 (s, 1H, backbone), 7.08-7.14 (m, 6H, aryl).

5. Crystal structure determination of DIPPnacnacAl(BH_4)$_2$

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 BH_4 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 wich explains the relatively high R1 value of 0.0689.

Table 1. Crystal data for DIPPnacnacAl$(BH_4)_2$.

CCDC Nr.	837323
Formula	$C_{29}H_{49}AlB_2N_2$, C_6H_6
MW	552.41
Size (mm^3)	0.5 x 0.4 x 0.3
Crystal system	triclinic
Space group	*P*-1
a (Å)	8.4532(5)
b (Å)	12.1566(8)
c (Å)	18.6362(12)
α	75.871(4)
β	78.335(4)
γ	69.729(4)
V ($Å^3$)	1727.5(2)
Z	2
ρ ($g.cm^{-3}$)	1.062
$\mu(Mo_{K\alpha})$ (mm^{-1})	0.083
T (°C)	–150
θ(max)	27.3
refl. total, unique R_{int}	18224, 7453 0.037
obsvd refl.($I > 2\sigma(I)$)	6161
parameter	403
R_1	0.0689
*wR*2	0.2178
GOF	1.14
min/max resd ($e.Å^{-3}$)	–0.31/0.67

6. References

1 C. Cui, H. W. Roesky, H. Hao, H. G. Schmidt, M. Noltemeyer, *Angew. Chem. Int. Ed.*, 2000, **39**, 1815.

2 M. Stender, B. E. Eichler, N. J. Hardmann, P. P. Power, J. Prust, M. Noltemeyer, H. W. Roesky, *Inorg. Chem.*, 2001, **40**, 2794.

3 J. Spielmann, S. Harder, *J. Am. Chem. Soc.*, 2009, **131**, 5064.

4 G. M. Sheldrick, SHELXS-97, *Program for Crystal Structure Solution*, 1997, Universität Göttingen, Germany.

5 G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, 1997, Universität Göttingen, Germany.

6 A. L. Spek, PLATON, *A Multipurpose Crystallographic Tool* 2000, Utrecht University, Utrecht, The Netherlands.