Stable Spirocyclic Neutral Radicals: Aluminum and Gallium Boraamidinates**

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Supplementary Information

Experimental Section

All reactions and the manipulations of products were carried out under anaerobic and anhydrous conditions using Schlenk techniques and an inert-atmosphere (argon) glove box. The reagents $AlCl_3$ and I_2 were sublimed prior to use. Filtrations were performed using a PTFE filter disk (Acrodisc syringe filter; diameter: 25 mm; pore size: 0.45 μm). The compounds $Li_2[PhB(\mu\text{-}N^tBu)_2]$ and $\{\mu\text{-}Li(OEt_2)[PhB(\mu\text{-}N^tBu)_2]_2Ga\}$ (**4b**) were prepared by literature procedures.[1, 2] X-band EPR spectra were recorded on a Bruker EMX 113 spectrometer equipped with a variable-temperature accessory. NMR spectra were obtained on C_6D_6 solutions at 298 K using a Bruker DRX 400 spectrometer. ^1H, ^{27}Al, ^{11}B, ^{13}C, ^{71}Ga, and ^7Li NMR spectra were referenced to the external standards Me_4Si in $CDCl_3$, $Al(NO_3)_3$ in D_2O, $BF_3{\cdot}OEt_2$ in C_6D_6, Me_4Si in $CDCl_3$, $Ga(NO_3)_3$ in D_2O, and 1.0 M LiCl in D_2O, respectively. EPR spectral simulations were carried out by using the XEMR v. 0.7[3a] and WINEPR SimFonia v. 1.25[3b] programs.

$\{[PhB(\mu\text{-}N^tBu)_2]AlCl(OEt_2)\}$, 3: A colourless solution of $Li_2[PhB(\mu\text{-}N^tBu)_2]$ (0.46 g, 1.86 mmol) in Et_2O (50 mL) was added to solid $AlCl_3$ (0.25 g, 1.86 mmol) cooled to 195 K producing a bright purple reaction mixture. After 15 min., the reaction mixture was allowed to reach 295 K affording a clear colourless solution. After 15 min. at 295 K, a cloudy pale yellow reaction mixture was produced that was stirred for 18 h. The resulting mixture was filtered to remove LiCl. Removal of solvent in vacuo and addition of cold *n*-hexane afforded a pale yellow precipitate of **3** (0.41 g, 1.11 mmol, 60 %) that was washed twice with cold *n*-hexane. Elemental analysis calcd (%) for $C_{14}H_{23}AlClBN_2$: C 58.95, H 9.07, N 7.64; found: C 58.42, H 9.25, N 7.72; ^{1}H NMR: δ = 7.63 (d, 2H; $-C_6H_5$), 7.24 (m, 3H; $-C_6H_5$), 3.76 [q, 4H; $(CH_3C\underline{H}_2)_2O$], 1.22 [s, 18H; $-C(C\underline{H}_3)_3$], 0.81 ppm [t, 6H; $(C\underline{H}_3CH_2)_2O$]; ^{11}B NMR: δ = 36 ppm (br s); ^{13}C NMR: δ = 155.0 ($-C_6H_5$), 132.7 ($-C_6H_5$), 127.4 ($-C_6H_5$), 126.3 ($-C_6H_5$), 66.4 [$(CH_3\underline{C}H_2)_2O$], 49.7 [$-\underline{C}(CH_3)_3$], 35.6 [$-C(\underline{C}H_3)_3$], 15.8 ppm [$(\underline{C}H_3CH_2)_2O$].

{μ-Li(OEt$_2$)[PhB(μ-N^{t}Bu)$_2$]$_2$Al}, 4a: A colourless solution of Li$_2$[PhB(μ-N^{t}Bu)$_2$] (0.10 g, 0.43 mmol) in benzene (50 mL) was added to solid **3** (0.16 g, 0.43 mmol) cooled to 273 K. The reaction mixture was allowed to reach 295 K affording a clear colourless solution to which Et_2O (2 mL) was added. The mixture was heated at reflux for 18 h and then filtered to remove LiCl. After removal of solvent in vacuo, the residue was taken up in *n*-hexane affording colourless crystals of **4a** (0.08 g, 0.14 mmol, 33 %) at 258 K (4 d). Elemental analysis calcd (%) for $C_{32}H_{56}AlB_2N_4LiO$: C 67.62, H 9.93, N 9.86; found: C 67.31, H 10.12, N 10.01; ^{1}H NMR: δ = 7.60 (d, 4H; $-C_6H_5$), 7.33 (t, 4H; $-C_6H_5$), 7.21 (m, 2H; $-C_6H_5$), 3.16 [q, 4H; $(CH_3C\underline{H}_2)_2O$], 1.36 [s, 36H; $-C(C\underline{H}_3)_3$], 0.92 ppm [t, 6H; $(C\underline{H}_3CH_2)_2O$]; ^{27}Al NMR: δ = 488.2 ppm (s); ^{11}B NMR: δ = 39 ppm (br s); ^{13}C NMR: δ = 157.4 ($-C_6H_5$), 132.7 ($-C_6H_5$), 127.7 ($-C_6H_5$), 126.6 ($-C_6H_5$), 66.0 [$(CH_3\underline{C}H_2)_2O$], 50.9 [$-\underline{C}(CH_3)_3$], 35.7 [$-C(\underline{C}H_3)_3$], 14.7 ppm [$(\underline{C}H_3CH_2)_2O$]; ^{7}Li NMR: δ = 0.89 ppm (s).

{[PhB(μ-N^{t}Bu)$_2$]$_2$Al}$^\bullet$, 2a: A solution of I_2 in Et_2O (0.81 ml, 0.024 M, 0.019 mmol) was added to a colourless solution of **4a** (0.022 g, 0.039 mmol) in Et_2O (15 ml) at 295 K instantly producing a dark red solution. After concentration followed by cooling (258 K, 24 h), the radical **2a** was isolated as dark red crystals (0.016 g, 0.033 mmol, 84 %). Elemental analysis calcd (%) for $C_{28}H_{46}AlB_2N_4$: C 69.01, H 9.51, N 11.50; found: C 68.78, H 9.48, N 11.56; UV/Vis (Et_2O): λ_{max} = 364 (br), 461 (br), 551 nm (br); ^{27}Al NMR: δ = 262.1 ppm (s).

{[PhB(μ-N^{t}Bu)$_2$]$_2$Ga}$^\bullet$, 2b: A solution of I_2 in Et_2O (1.10 ml, 0.0432 M, 0.048 mmol) was added to a colourless solution of **4b** (0.058 g, 0.095 mmol) in Et_2O (15 ml) at 295 K instantly producing a dark green solution. The reaction mixture was filtered to remove LiI and after removal of solvent in vacuo from the filtrate, the radical **2b** was isolated as a dark green powder (0.035 g, 0.066 mmol, 70 %). Dark green crystals of **2b** were isolated from a concentrated solution in Et_2O (258 K, 1 d). Elemental analysis calcd (%) for $C_{28}H_{46}B_2GaN_4$: C 63.45, H 8.75, N 10.57; found: C 63.95, H 8.73, N 10.32; UV/Vis (Et_2O): λ_{max} = 355 (br), 604 nm (br); ^{71}Ga NMR: δ = –443.9 ppm (s).

[1] T. Chivers, C. Fedorchuk, G. Schatte, M. Parvez, *Inorg. Chem.* **2003**, *42*, 2084–2093.

[2] T. Chivers, C. Fedorchuk, G. Schatte, J. K. Brask, *Can. J. Chem.* **2002**, *80*, 821−831.

[3] a) J. Eloranta, University of Jyväskylä, Finland, XEMR version 0.7, **2004**; b) Bruker Analytische Messtechnik GmbH, *WINEPR SimFonia* version 1.25, **1996**.

Computational Details

The structures of diamagnetic monoanions $\{[\mathrm{PhB}(\mu\text{-NMe})_2]_2\mathrm{M}\}^-$ and paramagnetic radicals $\{[\mathrm{PhB}(\mu\text{-NMe})_2]_2\mathrm{M}\}^\bullet$ (M = Al, Ga) were optimized in their ground states using density functional theory. Hybrid PBE0 exchange-correlation functional[1] and Ahlrichs' triple-zeta valence basis set augmented by one set of polarization functions (TZVP)[2] were used in all optimizations. Hyperfine coupling constants were then calculated by single point calculations employing the optimized geometries, PBE0 functional, and unrestricted Kohn-Sham formalism. For B, N and Al, the single point calculations utilized the IGLO-III basis set[3] in its completely uncontracted form and augmented with one additional steep s-function as well as f-polarization functions from the cc-pVTZ basis set.[3] For C, H and Ga, the calculations utilized the cc-pVTZ basis[3] in its standard form. A pruned (99,590) integration grid was used in all single point calculations to ensure numerical convergence of calculated hfc constants. All geometry optimizations were done with the Turbomole 5.7[4] program package whereas Gaussian 03[5] was used in all single point calculations.

[1] a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868; *ibid.* **1997**, *78*, 1396; b) J. P. Perdew, K. Burke, M. Ernzerhof, *J. Chem. Phys.* **1996**, *105*, 9982–9985; c) M. Ernzerhof, G. E. Scuseria, *J. Chem. Phys.* **1999**, *110*, 5029–5036.

[2] The TZVP basis set was used as referenced in the Turbomole 5.7[4] internal basis set library.

[3] The basis set was taken from EMSL basis set library: http://www.emsl.pnl.gov/forms/basisform.html. Site accessed December 2004.

[4] TURBOMOLE, Program Package for *ab initio* Electronic Structure Calculations, Version 5.7. R. Ahlrichs, *et al.* Theoretical Chemistry Group, University of Karlsruhe, Karlsruhe, Germany, 2004.

[5] Gaussian 03, Revision C.02, M. J. Frisch, *et al.* Gaussian, Inc., Wallingford CT, 2004.

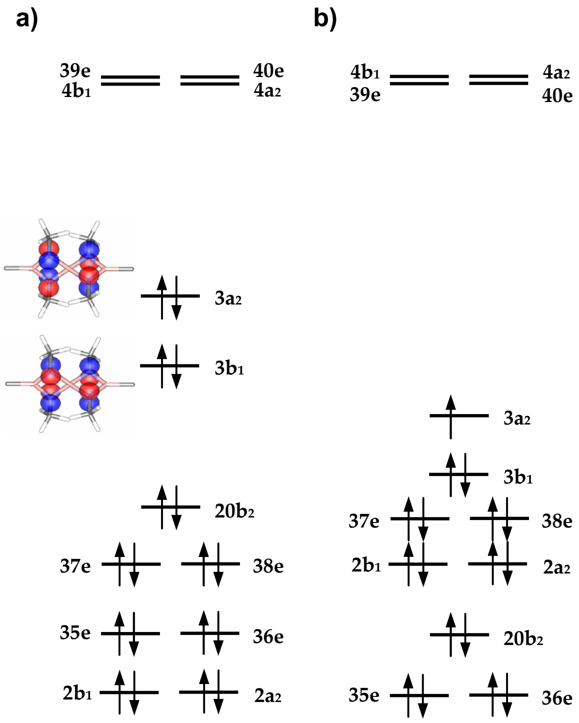

Figure S1. Schematic frontier KS-orbital diagrams of a) $\{[PhB(\mu\text{-}NMe)_2]_2Al\}^-$ and b) $\{[PhB(\mu\text{-}NMe)_2]_2Al\}^\bullet$.