Supporting Information

1,3-Bis(tricyanoborane)imidazoline-2-ylidenate Anion—A Ditopic Dianionic N-Heterocyclic Carbene Ligand

Ludwig Zapf, Udo Radius, and Maik Finze*

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1. General Synthetic Aspects

Unless stated otherwise all reactions involving air-sensitive compounds were performed under an argon atmosphere using standard Schlenk line techniques in tubes equipped with PTFE stems (Rettberg, Göttingen and Young, London).

2. Analytical Instruments and Details

$^1$H, $^7$Li, $^{11}$B, $^{13}$C, and $^{77}$Se NMR spectra were recorded at 25 °C either in [D$_8$]THF, (CD$_3$)$_2$CO, CD$_3$CN, (CD$_3$)$_2$SO, or D$_2$O on a Bruker Avance 500 spectrometer, a Bruker Avance III 400 Nanobay, or a Bruker Avance Neo 400 spectrometer. NMR signals were referenced against TMS ($^1$H and $^{13}$C with $\varepsilon$($^{13}$C) = 25.145020 MHz), LiCl 1.0 M in D$_2$O ($\varepsilon$($^7$Li) = 38.863797 MHz), BF$_3$·OEt$_2$ in CDCl$_3$ ($\varepsilon$($^{11}$B) = 32.083974 MHz), and Me$_2$Se in C$_6$D$_6$ ($\varepsilon$($^{77}$Se) = 19.071513). Chemical shifts were calibrated against the residual solvent signal, respectively ($\delta$($^1$H): [D$_7$]THF 3.58 and 1.72 ppm, (CD$_2$H)(CD$_3$)CO 2.05 ppm, (CD$_2$H)CN 1.94 ppm, (CD$_2$H)(CD$_3$)SO 2.50 ppm, and DHO 4.79 ppm; $\delta$($^{13}$C): [D$_8$]THF 67.21 and 25.31 ppm, (CD$_3$)$_2$CO 206.26 and 29.84 ppm, CD$_3$CN 118.26 and 1.32 ppm, and (CD$_3$)$_2$SO 39.52 ppm). IR spectra were recorded at room temperature with a Bruker Alpha-FT-IR spectrometer with an apodized resolution of 1 or 4 cm$^{-1}$ in the attenuated total reflection (ATR) mode in the region of 4000–400 cm$^{-1}$ using a setup with a diamond crystal. Raman spectra were measured at room temperature on a Bruker MultiRAM FT spectrometer with an apodized resolution of 4 cm$^{-1}$ in the region of 4000–400 cm$^{-1}$. The samples contained in melting point capillaries were excited with 1064 nm line of a Nd/YAG laser. Thermal analyses were performed with a DSC 204 F1 Phoenix (Netzsch) in the temperature range of −150 to 500 °C with a heating rate of 10 K min$^{-1}$. Elemental analyses (C, H, N) were performed either with a Euro EA3000 instrument (HEKA-Tech, Germany) or with an Elementar Vario MICRO cube instrument (Elementar Analysensysteme, Germany).

3. Chemicals

All standard chemicals were obtained from commercial sources and used without further purification. Solvents were dried according to standard protocols and stored under argon atmosphere in flasks with valves with PTFE stems (Rettberg, Göttingen and Young, London). B(CN)$_3$·py and lithium imidazolate were synthesized according to known procedures.
4. Syntheses

Lithium bis(tricyanoborane)imidazolate Li1
Tricyanoborane-pyridine adduct (3.44 g, 20.5 mmol) and lithium imidazolate (740 mg, 10.0 mmol) were dissolved in THF (30 mL). Under stirring, the solution was heated in a closed reaction tube to 90 °C for three days. The solvent was distilled off under vacuum. The air stable residue was dissolved in a minimum of THF and the product was precipitated by slow addition of CHCl3. The product was filtered off, washed with CHCl3 (3 × 10 mL), and dried in vacuum. Yield: 2.32 g (9.23 mmol, 92% calculated for lithium imidazolate). 1H NMR (500.1 MHz, (CD3)2CO): δ = 8.60 (s, 1H, NCHN), 7.67 ppm (s, 2H, NCHCHN). 13C(1H) NMR (125.8 MHz, (CD3)2CO): δ = 140.9 (s, 1C, NCN), 126.1 (s, 2C, NCCN), 124.0 ppm (q, 6C, 1J(13C,11B) = 74.4 Hz, CN). 13C(11B,1H) NMR (75.4 MHz, (CD3)2CO): δ = 140.9 (s, 1C, NCN), 126.1 (s, 2C, NCCN), 124.0 ppm (s, 6C, CN). 7Li NMR (194.4 MHz, (CD3)2CO): δ = −25.4 ppm (s, 2B). The vibrational spectra are depicted in Figure S38. Elemental analysis: calculated (%) for C9H5B3LiN6: C 42.94, H 1.20, N 44.51; found, C 42.72, H 1.73, N 44.78. Crystals of 3[Li1]1 solvent suitable for an X-ray diffraction study were obtained by slow diffusion of CH2Cl2 into an acetonitrile solution.

Lithium tricyanoboraneimidazolate Li2
Tricyanoborane-pyridine adduct (739 mg, 4.40 mmol) and lithium imidazolate (148 mg, 2.00 mmol) were suspended in CH2Cl2 (5 mL). Under stirring, the solution was heated in a closed reaction tube to 65 °C for two days. The solid, which had precipitated, was filtered off and washed with CH2Cl2 (3 × 5 mL). A sample of the isolated solid showed two sets of signals in the 1H and 11B NMR spectrum, which were assigned to the above described Li1 and to Li[B(CN)3]2LiN6 (Li2). 1H NMR (400.3 MHz, (CD3)2CO): δ = 7.63 (s, 1H, NCHN), 7.08 (s, 1H, NCHCHN), 7.02 ppm (s, 1H, NCHCHN). 13C(1H) NMR (100.7 MHz, (CD3)2CO): δ = 140.8 (s, 1C, NCN), 130.1 (s, 1C, NCCN), 125.9 (q, 3C, 1J(13C,11B) = 71.7 Hz, CN), 122.0 ppm (s, 1C, NCCN). 11B NMR (100.9 MHz, (CD3)2CO): δ = −25.7 ppm (s, 2B). Crystals of 3[Li2]1 suitable for an X-ray diffraction study were obtained from a THF solution by slow evaporation of the solvent.

Silver bis(tricyanoborane)imidazolate Ag1
Li1 (126 mg, 0.50 mmol) was dissolved in H2O (25 mL) and a solution of silver nitrate (84.9 mg, 0.50 mmol) in H2O (15 mL) was added. The solid that had formed was filtered off, washed with water (3 × 10 mL), and dried in vacuum. Yield: 152 mg (0.43 mmol, 86% calculated for Li1). 1H NMR (500.1 MHz, CD3CN): δ = 8.29 (s, 1H, NCHN), 7.46 ppm (s, 2H, NCHCHN). 13C(1H) NMR (125.8 MHz, CD3CN): δ = 141.3 (s, 1C, NCN), 126.1 (s, 2C, NCCN), 124.3 ppm (q, 6C, 1J(13C,11B) = 74.4 Hz, CN). 11B NMR (160.5 MHz, CD3CN): δ = −25.5 ppm (s, 2B). The vibrational spectra are depicted in Figure S39. Elemental analysis: calculated (%) for C9H5Ag2B3N6: C 30.65, H 0.86, N 31.77; found, C 30.23, H 1.12, N 31.93. Crystals of 3[Ag1]1 suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into an acetonitrile solution.
Oxonium-hydrate bis(tricyanoborane)imidazolate (H₂O)₁
Li₁ (126 mg, 0.500 mmol) was dissolved in hydrochloric acid (10 mL, 18.5% w/w). Diethyl ether (10 mL) was added and the emulsion was stirred for 10 minutes. The organic layer was separated and the aqueous phase was extracted three times with diethyl ether (10 mL). The combined organic phases were dried over Na₂SO₄ and concentrated in a vacuum to yield a colorless solid. Yield: 109 mg (0.387 mmol, 77% calculated for Li₁). ¹H NMR (500.1 MHz, (CD₃)₂SO): δ = 8.70 (s, 1H, NCHN), 7.71 (d, 2H, ⁴J(¹H,¹H) = 1.4 Hz, NCHCHN), 5.83 ppm (s br, 5H, H₆O₂). ¹³C [¹H] NMR (125.8 MHz, (CD₃)₂SO): δ = 140.6 (s, 1C, NCN), 125.4 (s, 2C, NCCN), 123.4 ppm (q, 6C, ¹J(¹³C,¹¹B) = 72.1 Hz, CN). ¹¹B NMR (160.5 MHz, (CD₃)₂SO): δ = −25.5 ppm (s, 2B). The vibrational spectra are depicted in Figure S40. Elemental analysis: calculated (%) for C₉H₅B₂N₆O₂, C 38.36, H 2.86; found, C 38.31, H 3.01, N 40.30. Crystals of ³{(H₂O)₁} suitable for an X-ray diffraction study were obtained from a diethyl ether solution by slow evaporation of the solvent.

Trimethylammonium bis(tricyanoborane)imidazolate [Me₃NH]₁
Li₁ (2.52 g, 10.0 mmol) was dissolved in a minimum amount of H₂O and trimethylammonium chloride (956 mg, 10.0 mmol) was added, whereupon a precipitate formed. The precipitate was filtered off and dried in vacuum to yield [Me₃NH]₁. Yield: 2.79 g (0.387 mmol, 91% calculated for Li₁). ¹H NMR (500.1 MHz, (CD₃)₂CO): δ = 8.61 (s, 1H, NCHFN), 8.44 (s br, 1H, NH), 7.68 (s, 2H, NCHCHN), 3.22 ppm (s, 9H, CH₃). ¹³C [¹H] NMR (125.8 MHz, (CD₃)₂CO): δ = 141.0 (s, 1C, NCN), 126.2 (s, 2C, NCCN), 124.1 (q, 6C, ¹J(¹³C,¹¹B) = 73.9 Hz, CN), 46.2 ppm (s, 3C, HNC₃). ¹¹B NMR (160.5 MHz, (CD₃)₂CO): δ = −25.4 ppm (s, 2B). The vibrational spectra are depicted in Figure S41. Elemental analysis: calculated (%) for C₁₂H₁₃B₂N₆, C 47.27, H 4.30, N 41.34; found, C 47.32, H 4.44, N 42.82. Crystals of [Me₃NH]₁ suitable for an X-ray diffraction study were obtained from an aqueous solution by slow evaporation of the solvent.

Dilithium bis(tricyanoborane)imidazoline-2-ylidenate Li₂⁻thf
Li₁ (504 mg, 2.00 mmol) was dissolved in THF (15 mL), cooled to −78 °C, and under vigorous stirring, nBuLi (8.80 mL 0.25 M in hexanes, 2.20 mmol) was added, slowly. The reaction mixture was allowed to warm to room temperature and was concentrated in vacuum. The resulting solid was dried in a vacuum to yield the product. Yield: 600 mg (1.90 mmol, 95% calculated for Li₁). ¹H NMR (500.1 MHz, [D₆]THF): δ = 7.07 (s, 2H, NCHCHN), 3.62 ppm (m, 4H, thf²⁻5H₂), 1.78 ppm (m, 4H, thf³⁻⁴H₂). ¹³C [¹H] NMR (125.8 MHz, [D₆]THF): δ = 206.0 (sept, 1C, ²J(¹³C,¹¹B) = 11.7 Hz, NCN), 127.5 (q, 6C, ¹J(¹³C,¹¹B) = 71.4 Hz, CN), 123.3 (s, 2C, NCCN), 68.3 (s, 2C, thf²⁻⁵C), 26.4 ppm (s, 2C, thf³⁻⁴C). ¹¹B NMR (194.4 MHz, [D₆]THF): δ = −0.1 ppm (s, 2Li). ¹¹B NMR (160.5 MHz, [D₆]THF): δ = −24.1 ppm (s, 2B). The vibrational spectra are depicted in Figure S42. Elemental analysis: calculated (%) for C₁₃H₁₀B₂Li₂N₆O, C 47.35, H 3.06, N 33.98; found, C 47.62, H 3.46, N 32.49. Crystals of
$^{3}$[Li$_2$1(thf)]-C$_8$H$_6$ suitable for an X-ray diffraction study were obtained from a saturated solution in the mixed solvent system THF/benzene.

**Tetraethylammonium bis(tricyanoborane)-2-methyl-imidazolate [Et$_4$N]4**

Li$_3$·thf (165 mg, 0.50 mmol) and was dissolved in THF (5 mL). Under vigorous stirring, iodomethane (50.0 µL, 114 mg, 0.80 mmol) was added and the solution was stirred at room temperature for 10 minutes. The solvent and the excess of iodomethane was distilled off under reduced pressure and the remaining solid was dissolved in H$_2$O (5 mL). A solution of tetraethylammonium chloride (82.9 mg, 0.50 mmol) in H$_2$O (5 mL) was added to yield a solid that was collected by filtration. The colorless solid was washed with H$_2$O (3 × 2 mL) and dried in vacuum. Yield: 149 mg (0.38 mmol, 77% calculated for Li$_3$·thf). $^1$H NMR (500.1 MHz, CD$_3$CN): δ = 7.31 (s, 2H, NCHCHN), 3.16 (q, 8H, $^3$J($^1$H, $^1$H) = 7.3 Hz, CH$_2$), 2.81 (s, 3H, CCH$_3$), 1.21 ppm (tt, 12H, $^3$J($^1$H, $^1$H) = 7.3 Hz, $^3$J($^{14}$N,$^1$H) = 1.9 Hz, CH$_2$). $^{13}$C($^1$H) NMR (125.8 MHz, CD$_3$CN): δ = 149.7 (s, 1C, NCN), 124.9 (q, 6C, $^1$J($^{13}$C,$^{11}$B) = 73.7 Hz, CN), 124.3 (s, 6C, CN), 53.1 (t, 4C, $^1$J($^{15}$N,$^{13}$C) = 3.1 Hz, CH$_2$), 14.0 (s, 1C, CCH$_3$), 7.7 ppm (s, 4C, CH$_3$). $^{13}$C($^{11}$B,$^1$H) NMR (75.4 MHz, CD$_3$CN): δ = 149.7 (s, 1C, NCN), 124.9 (s, 2C, NCCN), 124.3 (s, 2C, NCCN), 53.1 (t, 4C, $^1$J($^{15}$N,$^{13}$C) = 3.1 Hz, CH$_2$), 14.0 (s, 1C, CCH$_3$), 7.7 ppm (s, 4C, CH$_3$). $^{11}$B NMR (160.5 MHz, CD$_3$CN): δ = -25.7 ppm (s, 2B). The vibrational spectra are depicted in Figure S43. Elemental analysis: calculated (%) for C$_{18}$H$_{22}$B$_2$N$_9$: C 55.57, H 6.48, N 32.40; found, C 55.57, H 6.53, N 33.59. Crystals of [Et$_4$N]4 suitable for an X-ray diffraction study were obtained by slow evaporation of an acetone solution.

**Dilithium bis(tricyanoborane)imidazoline-2-ylidene-selenium Li$_2$5·4H$_2$O**

Li$_3$·thf (165 mg, 0.50 mmol) and selenium (43.4 mg, 0.55 mmol) were dissolved in THF (5 mL) and stirred at room temperature for 14 h. The reaction mixture was filtered through celite, the celite was washed with THF (3 × 5 mL) and the combined organic phases were concentrated in a vacuum to yield the product as a colorless solid. To substitute the THF, which is coordinated to the lithium cations, by H$_2$O, the crude product was dissolved in H$_2$O and subsequently, the solvent was pumped off in vacuum. Yield: 116 mg (0.284 mmol, 57% calculated for Li$_3$·thf). $^1$H NMR (500.1 MHz, (CD$_3$)$_2$CO): δ = 7.07 (s, 2H, NCHCHN), 3.15 ppm (s, 8H, H$_2$O). $^{13}$C($^1$H) NMR (125.8 MHz, (CD$_3$)$_2$CO): δ = 162.3 (s, 1C, NCN), 126.7 (q, 6C, $^1$J($^{13}$C,$^{11}$B) = 73.0 Hz, CN), 122.2 ppm (s, 2C, NCCN). $^{13}$C($^{11}$B,$^1$H) NMR (75.4 MHz, D$_2$O): δ = 155.2 (s, 1C, NCN), 126.7 (s, 6C, CN), 124.2 ppm (s, 2C, NCCN). $^7$Li NMR (194.4 MHz, (CD$_3$)$_2$CO): δ = 1.0 ppm (s, 2Li). $^{11}$B NMR (160.5 MHz, (CD$_3$)$_2$CO): δ = -24.8 ppm (s, 2B). $^{77}$Se($^1$H) NMR (76.3 MHz, (CD$_3$)$_2$CO): δ = 139.1 ppm (s, 1Se). $^{77}$Se($^1$H) NMR (76.3 MHz, [D$_8$]THF): δ = 147.6 ppm (s, 1Se). The vibrational spectra are depicted in Figure S44. Elemental analysis: calculated (%) for C$_9$H$_{16}$B$_2$Li$_2$N$_8$O$_4$S$_2$: C 26.45, H 2.47, N 27.42; found, C 26.70, H 2.29, N 27.13. Crystals of $^3$[Li$_2$5(thf)$_2$]·thf suitable for an X-ray diffraction study were obtained by slow diffusion of CH$_2$Cl$_2$ into a THF solution. Crystals of $^{3}$[Li$_2$5(H$_2$O)$_3$] suitable for an X-ray diffraction study were obtained by slow evaporation of an aqueous solution.
Dilithium bis(tricyanoborane)imidazoline-2-ylidenate-nickeltricarbonyl Li₂6·2thf

Caution: [Ni(CO)₄] is a flammable, volatile (boiling point: 43 °C) and toxic reagent. All steps involving [Ni(CO)₄] should be performed in a well-ventilated fume hood wearing gloves, safety glasses, and a lab coat. Half concentrated nitric acid can be used for the disposal of [Ni(CO)₄].

Li₂3·thf (165 mg, 0.50 mmol,) was dissolved in THF (5 mL) and cooled to −40 °C. Under vigorous stirring, [Ni(CO)₄] (77.6 µL, 102 mg, 0.60 mmol) was added and the solution was stirred at −40 °C for 10 minutes. After warming to room temperature the solvent and the excess [Ni(CO)₄] was distilled off under reduced pressure. The remaining solid was dried in vacuum to yield a solid product. Yield: 225 mg (0.41 mmol, 83% calculated for Li₂3·thf). ¹H NMR (500.1 MHz, [D₈]THF): δ = 7.25 (s, 2H, NCHCHN), 3.62 (m, 8H, thf₂,5H₂), 1.78 ppm (m, 8H, thf³,4H₂). ¹³C{¹H} NMR (125.8 MHz, [D₈]THF): δ = 200.0 (s, 3C, CO), 198.0 (m, 1C, NCN), 127.7 (q, 6C, ¹J(¹³C,¹¹B) = 71.8 Hz, CN), 124.3 (s, 2C, NCCN), 68.4 (s, 2C, thf²,5C), 26.5 ppm (s, 4C, thf³,4C). ¹³C{¹¹B,¹H} NMR (75.4 MHz, [D₈]THF): δ = 200.0 (s, 3C, CO), 198.0 (s, 1C, NCN), 127.7 (s, 6C, CN), 124.3 (s, 2C, NCCN), 68.4 (s, 2C, thf²,5C), 26.5 ppm (s, 4C, thf³,4C). ⁷Li NMR (194.4 MHz, [D₈]THF): δ = −0.83 ppm (s, 2Li). ¹¹B NMR (160.5 MHz, [D₈]THF): δ = −24.0 ppm (s, 2B).

The IR spectrum is depicted in Figure S45. Elemental analysis: calculated (%) for C₂₀H₁₈B₂Li₂N₈NiO₅, C 44.11, H 3.33, N 20.58; found, C 43.10, H 3.29, N 20.90. Crystals of ²[Li₂6(thf)₂] suitable for an X-ray diffraction study were obtained by slow diffusion of CH₂Cl₂ into a THF solution.
5. NMR Spectra

Figure S1. \(^1\)H NMR spectrum of Li1 in (CD\(_3\))\(_2\)CO.

Figure S2. \(^7\)Li NMR spectrum of Li1 in (CD\(_3\))\(_2\)CO.
Figure S3. $^{11}$B NMR spectrum of Li1 in (CD$_3$)$_2$CO.

Figure S4. $^{13}$C($^1$H) NMR spectrum of Li1 in (CD$_3$)$_2$CO.
**Figure S5.** $^{13}$C($^{11}$B, $^1$H) NMR spectrum of Li1 in (CD$_3$)$_2$CO.

**Figure S6.** $^1$H NMR spectrum of a mixture of Li2 and Li1 in (CD$_3$)$_2$CO.
**Figure S7.** $^{11}$B NMR spectrum of a mixture of Li2 and Li1 in (CD$_3$)$_2$CO.

**Figure S8.** $^{13}$C($^1$H) NMR spectrum of a mixture of Li2 and Li1 in (CD$_3$)$_2$CO.
Figure S9. $^1$H NMR spectrum of Ag1 CD$_3$CN.

Figure S10. $^{11}$B NMR spectrum of Ag1 CD$_3$CN.
Figure S11. $^{13}$C-$^{1}$H NMR spectrum of Ag1 CD$_3$CN.

Figure S12. $^{1}$H NMR spectrum of (H$_5$O)$_2$1 in (CD$_3$)$_2$SO.
Figure S13. $^{11}\text{B}$ NMR spectrum of (H$_5$O$_2$)1 in (CD$_3$)$_2$SO.

Figure S14. $^{13}\text{C}^{[1\text{H}]}$ NMR spectrum of (H$_5$O$_2$)1 in (CD$_3$)$_2$SO.
**Figure S15.** $^1$H NMR spectrum of $[\text{Me}_3\text{NH}]_1$ in (CD$_3$)$_2$CO.

**Figure S16.** $^{11}$B NMR spectrum of $[\text{Me}_3\text{NH}]_1$ in (CD$_3$)$_2$CO.
Figure S17. $^{13}\text{C}^{(1)}\text{H}$ NMR spectrum of [Me$_3$NH]$_1$ in (CD$_3$)$_2$CO.

Figure S18. $^1\text{H}$ NMR spectrum of Li$_2$3·thf in [D$_8$]THF.
Figure S19. $^7$Li NMR spectrum of Li$_2$3·thf in [D$_8$]THF.

Figure S20. $^{11}$B NMR spectrum of Li$_2$3·thf in [D$_8$]THF.
Figure S21. $^{13}$C{$^{1}$H} NMR spectrum of Li$_2$3·thf in [D$_8$]THF.

Figure S22. $^{13}$C{$^{11}$B, $^{1}$H} NMR spectrum of Li$_2$3·thf in [D$_8$]THF.
Figure S23. $^1$H NMR spectrum of [Et₄N]₄ in CD₃CN.

Figure S24. $^{11}$B NMR spectrum of [Et₄N]₄ in CD₃CN.
Figure S25. $^{13}$C\textsuperscript{1}H NMR spectrum of [Et\textsubscript{4}N]\textsubscript{4} in CD\textsubscript{3}CN.

Figure S26. $^{13}$C\textsuperscript{11}B,\textsuperscript{1}H NMR spectrum of [Et\textsubscript{4}N]\textsubscript{4} in CD\textsubscript{3}CN.
Figure S27. $^1$H NMR spectrum of Li$_2$5·4H$_2$O in (CD$_3$)$_2$CO.

Figure S28. $^7$Li NMR spectrum of Li$_2$5·4H$_2$O in (CD$_3$)$_2$CO.
Figure S29. $^{11}B$ NMR spectrum of Li$_2$Li$_5$·4H$_2$O in (CD$_3$)$_2$CO.

Figure S30. $^{13}C$($^1$H) NMR spectrum of Li$_2$Li$_5$·3H$_2$O in (CD$_3$)$_2$CO.
Figure S31. $^{13}$C($^{11}$B, $^1$H) NMR spectrum of Li$_2$5·4H$_2$O in D$_2$O.

Figure S32. $^{77}$Se($^1$H) NMR spectrum of Li$_2$5·4H$_2$O in (CD$_3$)$_2$CO (left) and in [D$_8$]THF (right).
Figure S33. $^1$H NMR spectrum of Li$_2$6·2thf in [D$_8$]THF.

Figure S34. $^7$Li NMR spectrum of Li$_2$6·2thf in [D$_8$]THF.
Figure S35. $^{11}$B NMR spectrum of Li$_2$6·2thf in [D$_8$]THF.

Figure S36. $^{13}$C{${}^1$H} NMR spectrum of Li$_2$6·2thf in [D$_8$]THF.
Figure S37. $^{13}$C($^{11}$B, $^1$H) NMR spectrum of Li$_2$6·2thf in [D$_8$]THF.
6. Vibrational Spectra

Figure S38. Vibrational spectra of Li1.

Figure S39. Vibrational spectra of Ag1.
Figure S40. Vibrational spectra of (H₂O)₁.

Figure S41. Vibrational spectra of [Me₃NH]₁.
Figure S42. Vibrational spectra of Li$_2$3·thf.

Figure S43. Vibrational spectra of [Et$_4$N]4.
Figure S44. Vibrational spectra of Li$_2$5·2thf.

Figure S45. IR spectrum of Li$_2$6·2thf.
7. Crystal Structure Determination

Crystal data of $\text{[Li}_2\text{]·}$-solvent, $\text{[Ag}_1\text{]·}$, $\text{[Me}_2\text{NH}]_1$, $\text{[H}_2\text{O}_2]_1$, $\text{[NH}_3]_1$, $\text{[Li}_2\text{3(thf)·}]$-CeH$_6$, $\text{[Et}_3\text{N]}_4$, $\text{[Li}_2\text{5(thf)·}]$-thf, $\text{[Li}_2\text{5(H}_2\text{O}_3]_3$], and $\text{[Li}_2\text{6(thf)·}]$ were collected on a XtaLAB Synergy, Dualflex diffractometer with a hybrid pixel array detector, using Cu$_{K\alpha}$ radiation (micro-focus sealed X-ray tube, $l = 1.54184$ Å). The structures were solved by intrinsic phasing methods (SHELXT) and refinement is based on full-matrix least-squares calculations on $F^2$ (SHELXL). All nonhydrogen atoms were refined anisotropically. Unless specified differently, for CH idealized bond lengths and angles were used. Calculations were carried out using the ShelXle graphical interface. Molecular structure diagrams were drawn with the program Diamond 4.6.3. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Selected bond length are collected in Table S1. Experimental details, crystal data, and CCDC numbers are summarized in Tables S2 and S3. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Additional refinement details for $\text{[Li}_1\text{]·}$-solvent: The structure was solved and refined as a two-component twin with occupancies of approximately 56 and 44%. Twin component 2 is rotated by 179.973 ° around [-0.24 0.00 0.97] (reciprocal) or [0.00 0.00 1.00] (direct). Contributions of strongly disordered solvent molecules to the structure factors were removed using the SQUEEZE routine as implemented in the Platon program. Additional refinement details for $\text{[Ag}_1\text{]·}$: The structure was solved and refined as a two-component twin with occupancies of approximately 66 and 34%.

Additional refinement details for $\text{[H}_2\text{O}_2]_1$·: The H atoms were refined freely.

Additional refinement details for $\text{[NH}_3]_1$·: The structure was refined as an inversion twin with occupancies of 80 and 20%. Restraints were applied to the N–H distances of the hydrogen atoms of the ammonium cations (SADI 0.02).

Additional refinement details for $\text{[Li}_2\text{3(thf)·}]$-CeH$_6$: Contributions of the strongly disordered benzene solvent molecule to the structure factors were removed using the SQUEEZE routine as implemented in the Platon program. The thf reveals fourfold disorder. Restraints had to be applied to the atoms of the thf molecule to ensure a stable refinement.

Additional refinement details for $\text{[Li}_2\text{5(thf)·}]$: Contributions of the strongly disordered thf solvent molecule to the structure factors were removed using the SQUEEZE routine as implemented in the Platon program. Both thf ligands are disordered over two positions, respectively. Thus, restraints had to be applied to the atoms of the thf ligands to ensure a stable refinement. The nitrogen heterocycle is disordered over two positions except for the C2 atom that is bonded to selenium. So, restraints had to be applied to the disordered atoms to achieve a stable refinement.

Additional refinement details for $\text{[Li}_2\text{5(H}_2\text{O}_3]_3$]: The structure was solved and refined as a two-component twin with occupancies of approximately 73 and 27%. All H atoms were refined without any restraints.

Additional refinement details for $\text{[Li}_2\text{6(thf)·}]$: The thf ligands are disordered over three positions. Thus, restraints were introduced to ensure a stable refinement of these ligands.
Selected bond lengths:

$^3$[Li1]-solvent (solvent = CH$_2$Cl$_2$/CH$_3$CN): B1–N1 153.4(4), B2–N3 155.8(4), B–CN 159.2(4), C=N 115.0(4), B–CN$^\text{Li}$ 159.9(5), C≡N$^\text{Li}$ 114.0(4), N1–C2 133.0(4), N3–C2 133.1(3), N1–C5 139.1(4), N3–C4 138.1(4), C4–C5 134.9(4), Li···N 202.6(5).

$^3$[Li2]: B1–N1 153.2(2), B1–CN$^\text{Li}$ 160.2(2), C≡N$^\text{Li}$ 114.2(2), N1–C2 133.2(2), N3–C2 131.1(2), N1–C5 135.5(2), N3–C4 135.3(2), C4–C5 136.1(2), Li···N 201.0(3), Li···NC 204.1(3).

$^3$[Ag1] (distances ranges for all three independent formula units): B–N 153.4(8)–155.7(8), B–C 156.9(9)–161.4(8), C≡N 112.9(8)–115.5(8), N1–C2 133.2(7)–134.2(7), N3–C4 137.2(8)–140.0(8), C4–C5 132.7(10)–135.4(8), Ag···N 221.6(8)–234.2(8).

[Me$_3$NH]$_1$ (mean values where applicable): B1–N1 155.4(2), B2–N3 155.6(3), B–CN 159.7(3), C≡N 114.4(3), N1–C2 133.0(2), N3–C2 133.9(2), N1–C5 138.6(2), N3–C4 138.5(2), C4–C5 134.6(3), N$^\text{cation}$···H 96(2), N$^\text{CN}$···H 216(2), N$^\text{cation}$···N$^\text{CN}$ 296.6(2).

$^3${(H$_5$O)$_2$}$_1$: B1–N1 154.38(14), B2–N3 155.26(15), B–CN 159.1(2), C≡N 114.5(2), N1–C2 133.53(14), N3–C2 133.38(13), N1–C5 138.42(14), N3–C4 138.57(14), C4–C5 134.73(15), O1–H 91(2) and 93(2), O2–H 89(2) and 90(2), O1–H$^\text{bridge}$ 124(3), O2–H$^\text{bridge}$ 119(3), O1···O$^\text{range}$ 242.9(1), N···H$^\text{range}$ 178(2)–197(2), N···O$^\text{range}$ 270.98(14)–283.54(14).

$^3$[[NH$_4$]$_1$]: B–N 155.1(5), B–CN 159.5(5), C≡N 114.5(4), N–C2 132.8(4), N1–C5/N3–C4 137.9(5), C4–C5 134.8(5).

$^3$[[Li$_2$(thf)]$^\text{C}_6$H$_6$]$: B1–N1 152.7(3), B2–N3 153.0(4), B–CN 160.0(5), C≡N 114.5(5), N1–C2 136.2(3), N3–C2 136.9(3), N1–C5 139.3(4), N3–C4 138.6(4), C4–C5 133.9(5), Li1···C2 215.1(6), Li1···N$^\text{c}$ 200.2(5), Li1···N$^\text{c}$ 243.4(7), Li1···C$^\text{c}$ 259.5(6), Li1···O1 190.1(12), Li2···N$^\text{range}$ 200.9(5)–203.5(5).

[Et$_4$N]$_4$: C2–CMe 149.04(13), B1–N1 155.75(13), B2–N3 155.46(12), B–CN 159.9(2), C≡N 114.5(2), N1–C2 134.06(11), N3–C2 134.25(12), N1–C5 138.82(12), N3–C4 138.72(11), C4–C5 134.63(11).

$^2$[Li$_2$(thf)$_2$]$: C2=Se 183.34(14), B1–N1 152.7(9), B2–N3 153.1(10), B–CN 160.3(3), C≡N 114.3(2), N1–C2 136.7(9), N3–C2 136.9(9), N1–C5 139.4(8), N3–C4 139.5(8), C4–C5 134.7(5), Li1···N 203.3(4), Li2···N 202.8(4), Li2···O 189.6(19).

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$^3[\text{Li}_2\text{Se}(\text{H}_2\text{O})_3]:$ C2=Se 185.2(2), B1–N1 153.5(3), B1–CN 160.5(3), C≡N 114.4(3), N1–C2 135.5(2), N1–C4 139.7(2), C4–C4' 134.4(3), Li···N 203.2(4), Li···O 192.5(4), O1···O1” 274.6(2), O1···O2 277.6(2), Se···O1 331.48(17), Se···H O1 263(3), Se···O2 343.1(2), Se···H O2 262(6).

$^3[\text{Li}_2\text{Ni}(\text{thf})_2]:$ C2–Ni 198.4(5), C≡O 115.2(8), B–N1 152.3(5), B–CN 160.8(5), C≡N 114.1(5), N1–C2 136.5(4), N1–C4 139.6(4), C4–C4' 133.5(5), Li···N 203.4(7), Li···O 190(2).
Table S1. Selected bond lengths of $\text{3}[\text{Li}_2]$, $\text{3}[\text{Li}1]$: solvent, $\text{3}[\text{Ag}1]$, $\text{[Me}_3\text{NH}]_1$, $\text{3}[\text{H}_2\text{O}]_1$, $\text{3}[\text{Li}_3\text{(thf)}]: \text{C}_6\text{H}_6$, $\text{[Et}_4\text{N}]_4$, $\text{2}[\text{Li}_2\text{((H}_2\text{O})_2]]$, and $\text{2}[\text{Li}_2\text{(thf)}]$.  

| $\text{3}[\text{Li}_2]$ | $\text{3}[\text{Li}1]$: solvent | $\text{3}[\text{Ag}1]$ | $\text{[Me}_3\text{NH}]_1$ | $\text{3}[\text{H}_2\text{O}]_1$ | $\text{3}[\text{NH}_4]_1$ | $\text{3}[\text{Li}_3\text{(thf)}]: \text{C}_6\text{H}_6$ | $\text{[Et}_4\text{N}]_4$ | $\text{2}[\text{Li}_2\text{((H}_2\text{O})_2]]$ | $\text{2}[\text{Li}_2\text{(thf)}]$ |
|---|---|---|---|---|---|---|---|---|---|
| C2–X | n.a.$^\text{[1]}$ | n.a.$^\text{[1]}$ | n.a.$^\text{[1]}$ | 0.93(2) | n.a.$^\text{[1]}$ | 215.1(6) | 149.04(13) | 183.34(14) | 185.2(2) |
| N1–B1/ | 153.2(2) | 153.4(4) | 153.4(8)–155.7(8)$^\text{[2]}$ | 155.4(2) | 154.38(14) | 155.1(5)$^\text{[3]}$ | 152.7(3) | 155.75(13) | 152.7(9) |
| N3–B2 | 155.8(4) | 155.6(3) | 155.26(15) | 153.0(4) | 153.0(4) | 153.5(10) | 153.5(3) | 152.3(5) | 152.3(5) |
| B–C$_\text{N}$$^\text{[1]}$ | 160.2(2) | 159.2(4) | 156.9(9)–161.4(8)$^\text{[2]}$ | 159.7(3) | 159.1(2) | 159.5(9) | 160.0(5) | 159.9(2) | 160.3(3) |
| C$_\text{N}$$^\text{[1]}$ | 114.2(2) | 115.0(4) | 112.9(8)–115.5(8)$^\text{[2]}$ | 114.4(3) | 114.5(2) | 114.5(4) | 114.5(5) | 114.3(2) | 114.4(3) |
| C2–N1/ | 135.1(2) | 133.0(4) | 133.2(7)–134.2(7)$^\text{[2]}$ | 133.0(2) | 133.53(14) | 132.8(4)$^\text{[3]}$ | 136.2(3) | 134.06(11) | 136.7(9) |
| C2–N3 | 131.1(2) | 133.1(3) | 133.2(7)–134.2(7)$^\text{[2]}$ | 133.9(2) | 133.38(13) | 136.9(3) | 134.25(12) | 136.9(9) | 136.9(9) |
| N1–C5/ | 135.5(2) | 139.1(4) | 137.2(9)–140.0(9)$^\text{[2]}$ | 138.6(2) | 138.42(14) | 137.9(5)$^\text{[2]}$ | 139.3(4) | 138.82(12) | 139.4(8) |
| N3–C4 | 135.3(2) | 138.1(4) | 138.5(2) | 138.5(2) | 138.57(14) | 138.6(4) | 138.72(11) | 139.5(8) | 139.5(8) |
| C4–C5 | 136.1(2) | 134.9(4) | 132.7(10)–135.4(8)$^\text{[2]}$ | 134.6(3) | 134.73(15) | 134.8(5) | 133.9(5) | 134.63(11) | 134.7(5) |

$^\text{[1]}$ n.a. = not applicable, H atoms placed on calculated positions. $^\text{[2]}$ Range of distances. $^\text{[3]}$ Mean value. $^\text{[4]}$ The anion is located on a mirror plane; thus, some bond lengths (e.g. N1–B1 and N3–B2) are not crystallographically independent.
|                         | $\frac{1}{2}$[Li2] | $\frac{1}{2}$[Li1]·solvent$^{[1]}$ | $\frac{1}{2}$[Ag1] | $\frac{1}{2}$[Me·NH]1 | $\frac{1}{2}$[(H2O)1] | $\frac{1}{2}$[(NH4)1] | $\frac{1}{2}$[Li3(thf)]·C6H6$^{[1]}$ |
|-------------------------|----------------------|----------------------------------|------------------|----------------------|----------------------|----------------------|----------------------------------|
| **Formula**             | C6H5BLiN6           | C6H5BLiN6                         | C6H5AgB12:N4     | C6H5B2N6           | C6H5B2NN2O           | C6H5B2N6           | C6H5B2NN2O           |
| **Mw**                  | 162.88               | 251.75                           | 2616.10          | 304.93              | 281.85               | 262.86               | 329.79               |
| **T (K)**               | 99.96(13)            | 100.00(10)                        | 100.00(10)       | 99.86(6)            | 99.98(10)            | 99.98(10)            | 100.03(3)            |
| **Crystal system**      | orthorhombic         | monoclinic                        | monoclinic       | orthorhombic        | monoclinic           | orthorhombic         | monoclinic           |
| **Space group**         | Cmca                 | P2/c                             | P2/a             | P2/c                | P2/c                | Cmc2 1              | C2PC               |
| **a (Å)**               | 7.5675(1)            | 10.2649(2)                        | 37.10320(13)     | 7.6339(1)           | 11.2034(1)           | 25.8993(3)           | 10.9743(2)           |
| **b (Å)**               | 18.0740(3)           | 22.7589(3)                        | 11.73968(3)      | 11.7385(1)          | 18.6366(2)           | 9.0133(1)            | 10.9968(2)           |
| **c (Å)**               | 12.1331(2)           | 7.9468(2)                         | 37.82374(10)     | 18.5952(2)          | 6.9028(1)            | 17.8423(2)           | 22.3892(6)           |
| **β**                   |                      |                                  |                  |                     |                      |                     |                    |
| **Volume (Å³)**         | 1659.50(4)           | 1822.03(6)                        | 16227.97(8)      | 1666.33(3)          | 1426.33(3)           | 4165.07(8)           | 2635.41(10)          |
| **Z**                   | 8                    | 4                                | 8                | 4                   | 4                   | 12                  | 4                  |
| **ρ (calcd) (Mg m⁻³)**  | 1.304                | 0.916                            | 1.732            | 1.215               | 1.313               | 1.258               | 0.831               |
| **μ (mm⁻¹)**            | 0.701                | 0.501                            | 11.973           | 0.655               | 0.810               | 0.707               | 0.449               |
| **F(000)**              | 656                  | 504                              | 8160             | 632                 | 576                 | 1608                | 672                |
| **No. of collected reflections** | 10281            | 5593                             | 29232            | 10294               | 30983               | 21830               | 65515               |
| **No. of unique reflections** | 923              | 5593                             | 29232            | 3335                | 3042                | 4205                | 5394                |
| **R(int)**              | 0.0274               | 0.0761                           | 0.0897           | 0.0341              | 0.0540              | 0.0355              | 0.0916              |
| **No. of parameters / restraints** | 73 / 0           | 182 / 0                          | 1083 / 0         | 223 / 0             | 222 / 0             | 316 / 58            | 374 / 637           |
| **R1 (I > 2σ(I))**      | 0.0381               | 0.0700                           | 0.0562           | 0.0316              | 0.0370              | 0.0370              | 0.0816              |
| **wR2 (all)**           | 0.1109               | 0.2107                           | 0.1686           | 0.0829              | 0.1024              | 0.1046              | 0.1887              |
| **GOF on F²**           | 1.091                | 1.139                            | 1.102            | 1.032               | 1.075               | 1.092               | 1.642               |
| **Largest diff. peak / hole / e Å⁻³** | 0.257 / −0.243   | 0.462 / −0.301                    | 6.857 / −2.835   | 0.136 / −0.210      | 0.233 / −0.264       | 0.190 / −0.193      | 0.715 / −0.430       |
| **CCDC no.**            | 2079436              | 2079435                          | 2079437          | 2079438             | 2079439             | 2079440             | 2079441             |

$^{[1]}$ The contributions of the solvent molecules to the structure factors were removed using the SQUEEZE routine as implemented in the Platon program.$^{[11]}$
Table S3. Selected Crystal Data and Details of the Refinement of the Crystal Structures of [Et₄N]₄, [Li₂5(thf)₂]:thf, [Li₂5(H₂O)₃], and [Li₂6(thf)₂].

|                  | [Et₄N]₄ | [Li₂5(thf)₂]:thf | [Li₂5(H₂O)₃] | [Li₂6(thf)₂] |
|------------------|---------|------------------|--------------|-------------|
| Formula          | C₁₈H₂₅B₂N₉ | C₁₇H₁₈B₂Li₂N₈O₂Se | C₁₇H₁₈B₂Li₂N₈O₃Se | C₂₀H₁₈B₂Li₂N₈NiO₃ |
| M₀               | 389.09  | 480.85           | 390.69       | 544.63      |
| T (K)            | 99.98(16)| 99.98(18)        | 100.0(3)     | 100.0(2)    |
| Crystal system   | monoclinic | monoclinic       | monoclinic   | orthorhombic |
| Space group      | P2₁/n   | P2₁/c            | P2/m         | Pnma        |
| a (Å)            | 10.3596(1)| 17.2869(2)       | 7.7198(2)    | 17.1662(5)  |
| b (Å)            | 15.5798(1)| 7.8990(1)        | 19.3711(4)   | 20.7305(7)  |
| c (Å)            | 14.4198(1)| 21.7458(2)       | 11.4566(2)   | 7.7228(3)   |
| β                | 109.848(1)| 105.933(1)       | 92.912(2)    |             |
| Volume (Å³)      | 2189.11(3)| 2855.30(6)       | 1711.02(6)   | 2748.27(16) |
| Z                | 4        | 4                | 4            | 4           |
| ρ (calcd) (Mg m⁻³)| 1.181   | 1.119            | 1.517        | 1.316       |
| μ (mm⁻¹)         | 0.598   | 1.979            | 3.204        | 1.393       |
| F(000)           | 824     | 968              | 768          | 1112        |
| No. of collected reflections | 25784 | 62202           | 5387         | 15103       |
| No. of unique reflections | 4648 | 6049            | 5387         | 2858        |
| R(int)           | 0.0323  | 0.0363           | 0.0330       | 0.0621      |
| No. of parameters / restraints | 267 / 0 | 406 / 636       | 141 / 0      | 271 / 532   |
| R1 (I > 2σ(I))   | 0.0353  | 0.0329           | 0.0303       | 0.0707      |
| wR2 (all)        | 0.0749  | 0.0699           | 0.0847       | 0.1382      |
| GOF on F²        | 1.281   | 1.357            | 1.087        | 1.394       |
| Largest diff. peak / hole / e Å⁻³ | 0.253 / −0.216 | 0.392 / −0.361 | 0.641 / −0.422 | 0.942 / −0.590 |
| CCDC no.         | 2079442 | 2079443         | 2079444      | 2079445     |

[1] The contributions of the thf solvent molecule to the structure factors were removed using the SQUEEZE routine as implemented in the Platon program. [11-13]
Figure S46. Crystal packing of $\text{AgI}_2$. Color code: Ag silver, B green, C black, N blue, H grey, O red.
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