



Carbenes Hot Paper

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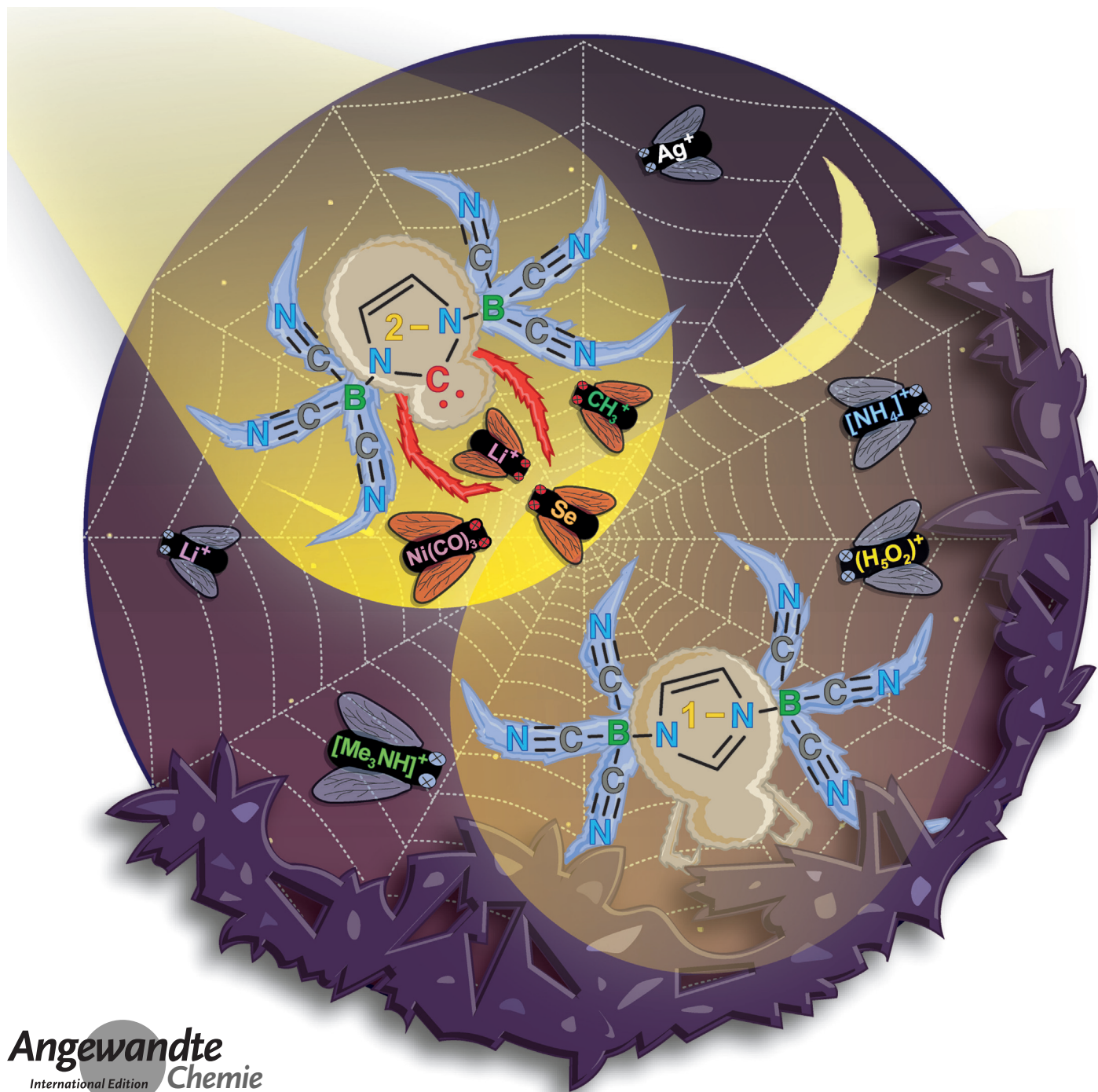
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1,3-Bis(tricyanoborane)imidazoline-2-ylidene Anion— A Ditopic Dianionic N-Heterocyclic Carbene Ligand

Ludwig Zapf, Udo Radius, and Maik Finze*

Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 80th birthday



Abstract: The 1,3-bis(tricyanoborane)imidazolate anion **1** was obtained in high yield from lithium imidazolate and $B(CN)_3^-$ pyridine adduct. Anion **1** is chemically very robust and thus allowed the isolation of the corresponding $H_3O_2^+$ salt. Furthermore, monoanion **1** served as starting species for the novel dianionic N-heterocyclic carbene (NHC), 1,3-bis(tricyanoborane)imidazoline-2-ylidene anion **3** that acts as ditopic ligand via the carbene center and the cyano groups at boron. First reactions of this new NHC **3** with methyl iodide, elemental selenium, and $[Ni(CO)_4]$ led to the methylated imidazolate ion **4**, the dianionic selenium adduct **5**, and the dianionic nickel tricarbonyl complex **6**. These NHC derivatives provide a first insight into the electronic and steric properties of the dianionic NHC **3**. Especially the combination of properties, such as double negative charge, different coordination sites, large buried volume and good σ -donor and π -acceptor ability, make NHC **3** a unique and promising ligand and building block.

Introduction

The isolation of the first N-heterocyclic carbene (NHC), 1,3-bis(adamantyl)imidazoline-2-ylidene, in 1991^[1] opened a novel field of research. Since then, N-heterocyclic carbenes were utilized for the stabilization of reactive compounds, for the activation of strong bonds, and as ligands in transition metal chemistry with a wealth of applications, for example, in organocatalysis, transition metal catalysis, and as pharmacophores.^[2] In contrast to neutral Arduengo carbenes (**I**, Figure 1), which are easily accessible from imidazolium cations by deprotonation, only few examples of anionic or even dianionic NHCs are known.^[3] One approach for the synthesis of anionic NHCs is the deprotonation of neutral or anionic imidazole derivatives, which bear borane instead of alkyl or aryl substituents at nitrogen. Following this strategy, the anionic triscarbene **II** was obtained in 1996 (Figure 1)^[4] and a number of related monoanionic tris- and biscarbenes have been investigated and used as chelating ligands in coordination chemistry.^[5] In 1998, the first anionic NHC was published that had a BH_3 moiety bonded to nitrogen (**III**, Figure 1).^[6] A further, rare example for a related anionic borane-substituted NHC (**IV**, Figure 1) was presented in 2012, but the weakly coordinating tris(pentafluorophenyl)borane group was attached to the backbone of the heterocyclic ring.^[7]

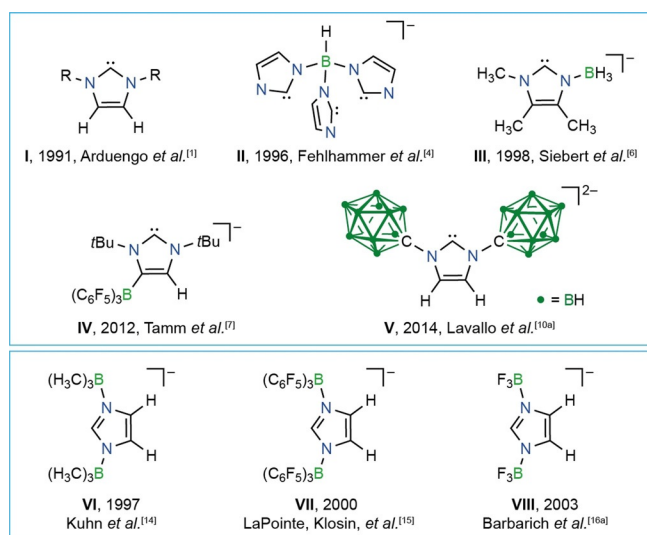


Figure 1. First class of neutral NHCs (**I**) and selected anionic borane-substituted NHCs (**II–V**, top) and examples of 1,3-bis(borane)-imidazolates (**VI–VIII**, bottom), which are conceivable precursors for dianionic NHCs.

In recent years it was demonstrated that this type of anionic borane-substituted NHC is a versatile tool for the synthesis of unusual group 13, 16, and 17 derivatives,^[8] for the activation of organic compounds, and for the preparation of catalytically active transition metal complexes.^[7,8c,9]

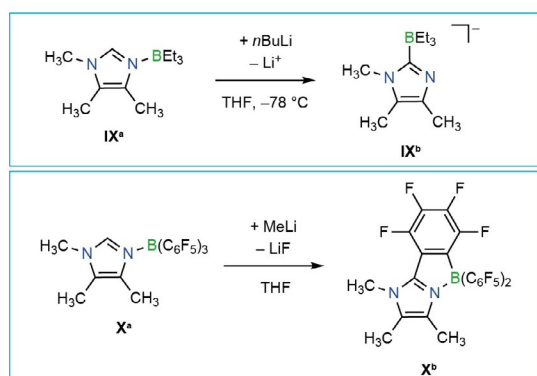
In 2014, anionic carboranyl units were introduced as substituents at the imidazole nitrogen atoms,^[10] for example in the dianion **V** (Figure 1).^[10a] The concept of using anionic boron clusters as substituents at NHCs via $C_{cluster}-N$ bonds was extended to other boron cages such as $\{nido-7,8-C_2B_9\}$,^[11] and recently, halogenated $\{closo-1-CB_{11}\}$ cages have been attached as well.^[12] To the best of our knowledge, no other dianionic NHCs are known. In contrast, many carbenes with two tethered anionic groups have been studied in the past.^[3,13]

In the first place it is surprising that no dianionic NHCs in which both nitrogen atoms are substituted with a borane have been described so far, although potential 1,3-bis(borane)imidazolate precursors are known: The 1,3-bis(trimethylborane)imidazolate ion **VI** was reported in 1997,^[14] the 1,3-bis[tris(pentafluorophenyl)borane]imidazolate ion **VII** in 2000,^[15] and the analogous bis(trifluoroborane) derivative **VIII** in 2003 (Figure 1).^[16] Most likely, these 1,3-bis(borane)imidazolate ions would undergo immediate follow-up reactions upon initial formation of the related carbene by deprotonation. This hypothesis is supported by reports on the reactivity of 3-triethylborane-1,4,5-trimethylimidazole (**IX^a**)^[6] and 3-tris(pentafluorophenyl)borane-1-methylimidazole (**X^a**) (Scheme 1).^[17] Deprotonation of **IX^a** is followed by migration of the Et_3B moiety even at $-78^\circ C$ to give the NHC- BEt_3 adduct **IX^b**.^[6] This behavior reflects the low Lewis basicity of the borane and the corresponding weakness of the B–N bond. In contrast, the stronger B–N bond in **X^a** remains intact after deprotonation, but an intramolecular nucleophilic attack of the carbene C atom at one of the C_6F_5 rings occurs to result in **X^b**.^[17]

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Scheme 1. Intramolecular reactions induced by deprotonation of a *N*-trialkylborane- (top)^[6] and a *N*-tris(pentafluorophenyl)boraneimidazole (bottom).^[17]

Cyano groups are well known to stabilize both boranes and borate ions due to their strong electron-withdrawing nature and their chemical and electrochemical stability.^[18] Tricyanoborane $B(CN)_3$, which is a coordination polymer due to $B-C\equiv N-B$ units,^[19] is a strong Lewis acid as is obvious from its high fluoride ion affinity (FIA, 540 kJ mol^{-1}).^[20] The Brønsted acidity of its hydride adduct $[BH(CN)_3]^-$ ^[21] was demonstrated by deprotonation to give the $B(CN)_3^{2-}$ dianion.^[22] Furthermore, the large number of chemically stable tricyanoborate ions $[RB(CN)_3]^-$ with different substituents ($R = CN$,^[19,23] F ,^[24] perfluoroalkyl,^[25] CO_2H ,^[22a] OH ,^[26] ...) shows the large stabilization effect of the $B(CN)_3$ group. The cyano groups attached to boron are the reason for the unprecedented stability of the $[B_2(CN)_6]^{2-}$ dianion as well.^[27] Keeping this high thermodynamic and kinetic stability of heteroatom- $B(CN)_3$ bonds in mind, we were interested to use tricyanoborane substituents for the preparation of a dianionic 1,3-bis(borane)-functionalized NHC and herein, we report its synthesis, structural and spectroscopic properties as well as first metal- and non-metal derivatives.

Results and Discussion

Lithium 1,3-bis(tricyanoborane)imidazolate (**Li1**) was formed by nucleophilic substitution starting from two equivalents of tricyanoborane-pyridine adduct ($B(CN)_3 \cdot py$; $py = \text{pyridine}$)^[28] and lithium imidazolate in tetrahydrofuran (THF, Figure 2). Since the starting materials are easily accessible and because of the high yield of more than 90%, **Li1** is accessible on a multigram scale. The Li salt is stable towards air, moisture, and even against aqueous acids and bases and it is thermally stable up to 336°C (onset, DSC). It was characterized by NMR and vibrational spectroscopy and by single-crystal X-ray diffraction (SC-XRD). The intermediate of the formation of **Li1**, the mono-substituted lithium tricyanoboraneimidazolate (**Li2**) was isolated from a reaction mixture of $B(CN)_3 \cdot py$ with lithium imidazolate in CH_2Cl_2 and characterized by NMR spectroscopy and SC-XRD (Figure 2).

Both salts **Li1** and **Li2** form three-dimensional coordination polymers in the crystals with tetrahedrally coordinated Li ions (Figure 2). The Li ion in **Li2** is coordinated by the N atom

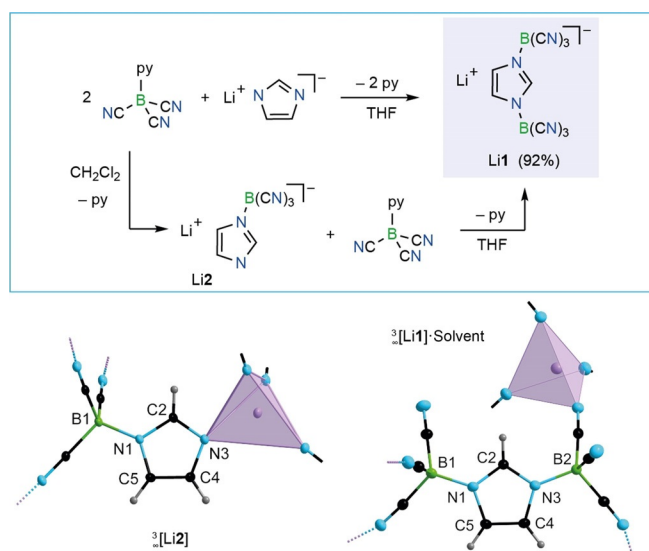


Figure 2. Synthesis of **Li1** and crystal structures of **Li1** and **Li2** (ellipsoids are drawn at the 25% probability level except for the H atoms that are depicted with arbitrary radii).^[43]

of the imidazolate ion and three cyano N atoms. In **Li1** solely cyano N atoms are involved in the coordination to the metal ions. So, four of the six nitrogen atoms of the cyano groups are bonded to lithium, leaving one cyano group of each $B(CN)_3$ moiety without coordination. The bond lengths of the imidazolate rings in **1** and **2** reveal some differences that reflect the different numbers of bonded $B(CN)_3$ groups.

As exemplified by the coordination motif in crystalline **Li1**, anion **1** acts as bridging ligand that forms coordination polymers. The silver salt **Ag1**, which was obtained from the reaction of **Li1** and $AgNO_3$ in water in 86% yield, is an example for a transition metal salt of **1** (Figure 3). **Ag1** forms a complex three-dimensional coordination polymer with 6 independent formula units in the unit cell (monoclinic, $I2/a$, $Z = 48$, Figure S46 in the Supporting Information). The silver ions are distorted tetrahedrally coordinated. Like **Li1**, two cyano groups per $B(CN)_3$ unit are bonded to Ag^+ and the

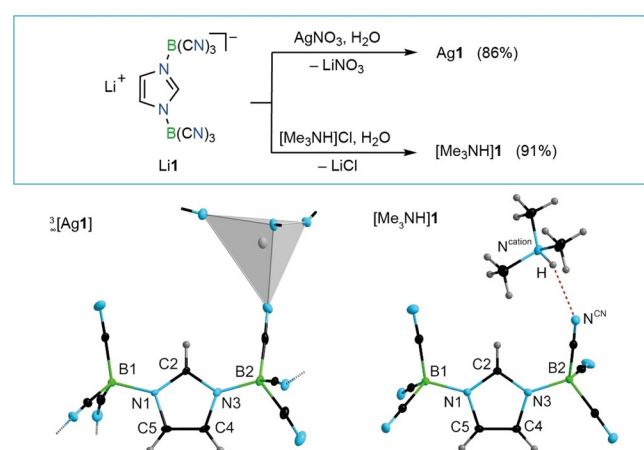


Figure 3. Syntheses and crystal structures of **Ag1** (bottom, left) and $[Me_3NH]1$ (bottom, right); (ellipsoids are drawn at the 25% probability level except for the H atoms that are depicted with arbitrary radii).^[43]

remaining third CN group is not coordinated. The reaction of aqueous solutions of $[\text{Me}_3\text{NH}]\text{Cl}$ and **Li1** gave the corresponding trimethylammonium salt of **1** (91%), which is an example for an organic salt of **1**. Discrete $[\text{Me}_3\text{NH}]\text{1}$ units are present in the crystal. The ions, $[\text{Me}_3\text{NH}]^+$ and **1**, are connected by a single H bond from the ammonium hydrogen atom to one CN group (Figure 3). The salts **Ag1** and $[\text{Me}_3\text{NH}]\text{1}$ are thermally very robust. **Ag1** melts under decomposition at 313 °C. $[\text{Me}_3\text{NH}]\text{1}$ melts at 161 °C and decomposition starts at 220 °C (onset, DSC).

Treatment of **Li1** with hydrochloric acid followed by extraction with diethyl ether resulted in $(\text{H}_5\text{O}_2)\text{1}$ in 77% yield (Figure 4). $(\text{H}_5\text{O}_2)\text{1}$ is an example for a non-metal coordination polymer in which the Zundel ions and **1** form a three-dimensional network. The non-hygroscopic salt $(\text{H}_5\text{O}_2)\text{1}$ melts at 141 °C, which is accompanied by loss of one equivalent of water. At 164 °C release of HCN, CO, and minor amounts of H_2O was observed by DTA measurements. The thermal analysis was repeated in a melting capillary, which gave crystals of $[\text{NH}_4]\text{1}$. Similar to $(\text{H}_5\text{O}_2)\text{1}$, cations and anions are connected by albeit weak H bonds (Figure 4). This latter thermal behavior is close to that of $(\text{H}_5\text{O})[\text{B}(\text{CN})_4]$.^[29]

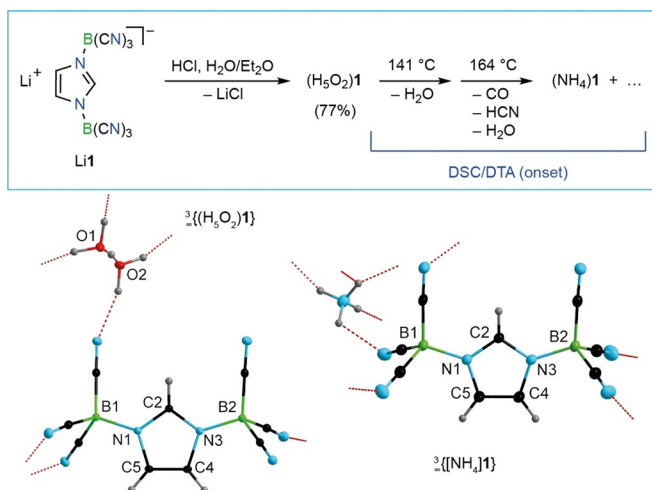


Figure 4. Synthesis of $(\text{H}_5\text{O}_2)\text{1}$ and its transformation into $[\text{NH}_4]\text{1}$ and crystal structures of both salts; (ellipsoids are drawn at the 30% probability level except for the H atoms that are depicted with arbitrary radii).^[43]

With the lithium and the trimethylammonium salt of **1** as starting materials in hand, we investigated the deprotonation of **1** to give the 1,3-bis(tricyanoborane)imidazoline-2-ylidene dianion (**3**). LiHMDS and *n*BuLi proved to be suitable bases. For example, **Li1** and one equivalent of *n*BuLi were used for the synthesis of $\text{Li}_2\text{3}$ in a yield of 95% (Figure 5). The dilithium salt $\text{Li}_2\text{3}$ contains one equivalent of THF per formula unit according to NMR spectroscopy, elemental analysis, and SC-XRD. Deprotonation of **1** under formation of dianion **3** is confirmed by NMR spectroscopy (Figure 5). The ^{11}B NMR signal is shifted from -25.4 (**1**) to -24.1 ppm (**3**). In the ^1H NMR spectrum of **3** only one resonance for the backbone H atoms was detected. The most significant difference was observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for the

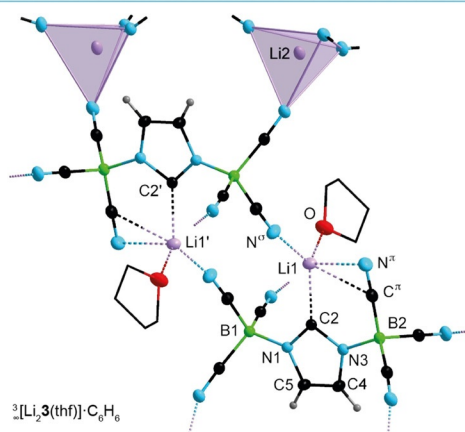
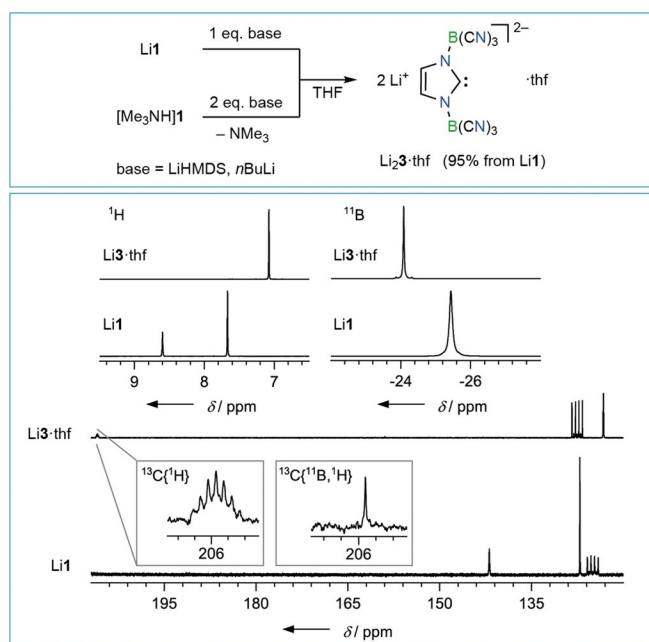


Figure 5. Syntheses of $\text{Li}_2\text{3}\text{-thf}$, NMR spectra of **Li1** and $\text{Li}_2\text{3}\text{-thf}$, and a dimer in the crystal structure of $^3[\text{Li}_2\text{1}(\text{thf})]\cdot\text{C}_6\text{H}_6$ (ellipsoids are drawn at the 25% probability level except for the H atoms that are depicted with arbitrary radii, disorder and H atoms of the THF solvate molecules are omitted for clarity and the C atoms are shown as stick model; bottom).^[43]

signal of the C2 nucleus. This signal was shifted from 140.9 ppm for **1** to 205.9 ppm for **3**, which is in the typical range observed for carbene carbon nuclei, for example, 213.2 ppm for 1,3-di(*tert*-butyl)imidazoline-2-ylidene (*t*Bu) or 211.2 ppm for **IV**.^[30] The signal is split into a septet due to the coupling to two ^{11}B nuclei with $^2J(^{13}\text{C},^{11}\text{B})$ of 11.7 Hz. In contrast, the signal of C2 of **1** reveals no coupling to ^{11}B .

Single crystals of $^3[\text{Li}_2\text{3}(\text{thf})]\cdot\text{C}_6\text{H}_6$ were obtained from a saturated benzene solution of the dilithium salt. The benzene molecules are severely disordered and their contribution to the structure factors was taken into account using the SQUEEZE routine as implemented in the Platon program.^[31] Two carbene units form cyclic dimers via bridging Li1 atoms (Figure 5). Li1 is coordinated to the C2 carbene carbon atom and to one CN group of the second NHC moiety. In addition, Li1 is oriented towards a $\text{B}(\text{CN})_3$ unit of the

parent dianionic NHC resulting in CN π -coordination. The coordination sphere of Li1 is completed by a THF ligand. The Li2–C2 distance of 215.1(6) pm is similar to related $d(\text{Li}\cdots\text{C}^{\text{carbene}})$, for example 215.5(4) pm in $[(t\text{Bu}_2\text{Im})\text{Li}(\eta^5\text{-}1,2,4\text{-}(\text{Me}_3\text{Si})_3\text{C}_5\text{H}_2)]^{[32]}$ or 209.2(2)/209.4(3) pm in $[(\text{IV})\text{Li}(\text{thf})_2]$.^[7] The lithium atom Li2 is tetrahedrally coordinated by CN groups of different anions **3**. The bond lengths of **3** differ from those of **1**. Noteworthy, the B–N distances are slightly shorter, whereas $d(\text{C}2\text{--N})$ are a little longer. Both differences reflect the increased electron density at the C2 carbene atom in **3**, which results in a slight weakening of the C2–N bonds, an increased basicity of the N atoms in the ring, and in turn stronger B–N bonds.

The lithium salt $\text{Li}_2\mathbf{3}\cdot\text{thf}$ starts to lose THF at ca. 100 °C in the solid state and is stable to temperatures higher than 150 °C. $\text{Li}_2\mathbf{3}$ was reacted with methyl iodide, selenium, and nickel tetracarbonyl as archetypical reactions for organic, main-group, and transition-metal substrates (Figure 6). Methylation of **3** with methyl iodide afforded anion **4** that was isolated as tetraethylammonium salt, which melts at 125 °C and decomposes at 326 °C (DSC, onset). The bond parameters of the imidazolium ring and the $\text{B}(\text{CN})_3$ units in **4** (Figure 6) are close to those of the parent protonated species **1** (Figures 2–4).

The reaction of elemental selenium with $\text{Li}_2\mathbf{3}\cdot\text{thf}$ in tetrahydrofuran gave the selenourea **5**. Its dilithium salt was isolated as tetrahydrate after aqueous work-up. The ⁷⁷Se chemical shift was observed at 139.1 and 147.6 ppm in $(\text{CD}_3)_2\text{CO}$ and $[\text{D}_8]\text{THF}$, respectively. These values are indicative for a higher π -acceptor ability of **5** than that of related backbone-unsaturated NHCs. For the corresponding Se adducts of 1,3-bis(mesityl)imidazoline-2-ylidene (IMes), 1,3-bis(2,6-diisopropylphenyl)imidazoline-2-ylidene (IDipp), and the 1,3-bis(2,6-diisopropylphenyl) derivative of anionic carbene **IV** ⁷⁷Se NMR shifts of 35, 87 ($(\text{CD}_3)_2\text{CO}$),^[33] and 114 ppm ($[\text{D}_8]\text{THF}$)^[8c] were reported previously. The ⁷⁷Se–¹³C coupling constant of 214.5 Hz (Figure 6) indicates that **5** is a potent σ -donor. However, a comparison to literature values is rather vague as the data reported were measured in CDCl_3 , for example, $^1J(^{77}\text{Se},^{13}\text{C})=231$ Hz for IMes and 219 Hz for SIMes (1,3-dimesitylimidazolidine-2-ylidene).^[33b]

Crystallization of $\text{Li}_2\mathbf{5}$ from water afforded crystals of $^3_\infty[\text{Li}_2\mathbf{5}(\text{H}_2\text{O})_3]$ while a mixed solvent system of THF and dichloromethane gave single crystals of $^2_\infty[\text{Li}_2\mathbf{5}(\text{thf})_2]\cdot\text{thf}$ (Figure 6). The Li atoms are tetrahedrally coordinated in both structures. All cyano groups are involved in coordination, which is complemented by the O atoms of THF or water in $^2_\infty[\text{Li}_2\mathbf{5}(\text{thf})_2]\cdot\text{thf}$ and $^3_\infty[\text{Li}_2\mathbf{5}(\text{H}_2\text{O})_3]$, respectively. In $^3_\infty[\text{Li}_2\mathbf{5}(\text{H}_2\text{O})_3]$ two crystallographically independent water molecules are arranged to cyclic hexamers with chair conformation^[34] (Figure 6). These water clusters are coordinated to four Li atoms ($\text{Li}\cdots\text{O}1$). The C=Se distances in both related structures are significantly different ($>3\sigma$) with 183.34(14) and 185.2(2) pm for $^3_\infty[\text{Li}_2\mathbf{5}(\text{H}_2\text{O})_3]$ and $^2_\infty[\text{Li}_2\mathbf{5}(\text{thf})_2]\cdot\text{thf}$, respectively. Both values are in the typical range for $d(\text{C}=\text{Se})$ in selenoureas. A close inspection of the structure of $^3_\infty[\text{Li}_2\mathbf{5}(\text{H}_2\text{O})_3]$ shows the presence of three weak $\text{Se}\cdots\text{H}$ bonds^[35] (263(3) (2 \times) and 262(6) pm (1 \times)) with H_2O as hydrogen bond donor (Figure 6). This intermolecular sele-

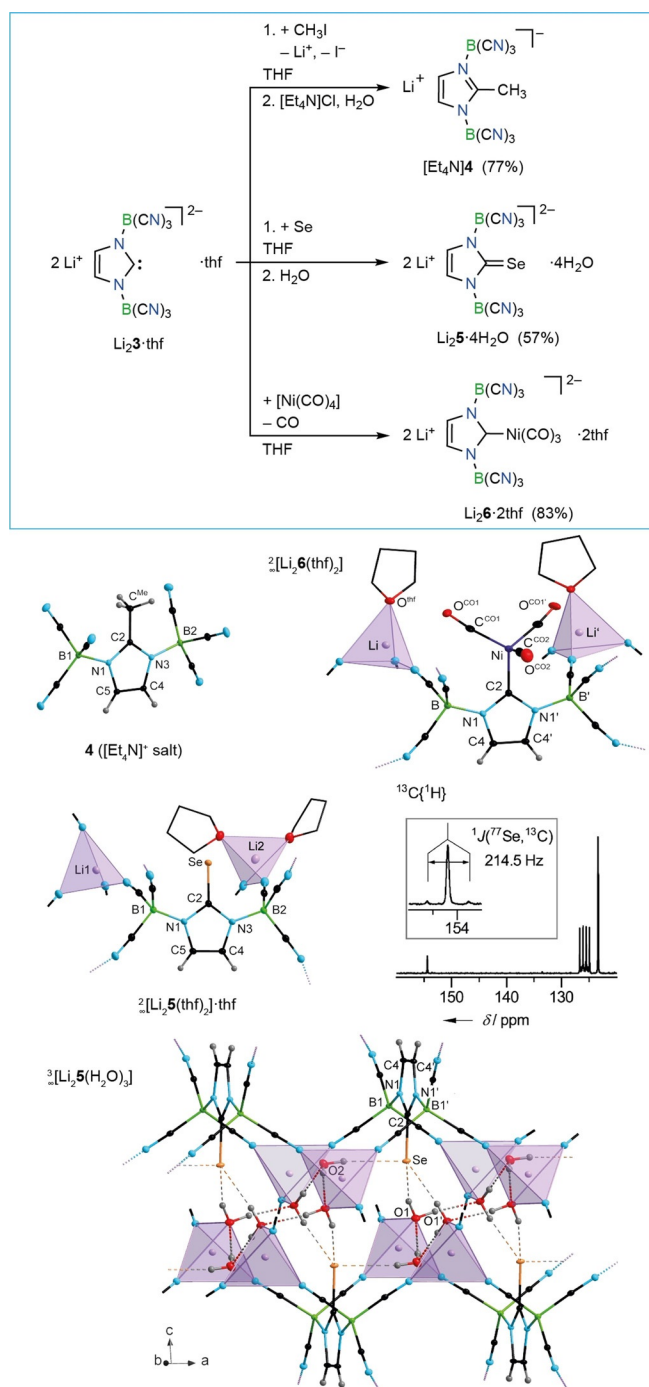


Figure 6. Syntheses of $[\text{Et}_4\text{N}]\mathbf{4}$, $\text{Li}_2\mathbf{5}\cdot 4\text{H}_2\text{O}$, and $\text{Li}_2\mathbf{6}\cdot 2\text{thf}$, related crystal structures and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Li}_2\mathbf{5}\cdot 4\text{H}_2\text{O}$, with $^1J(^{77}\text{Se},^{13}\text{C})$ coupling (ellipsoids are drawn at the 25% probability level except for the H atoms that are depicted with arbitrary radii, partial disorder of the imidazoline-2-ylidene ring in $^2_\infty[\text{Li}_2\mathbf{5}(\text{thf})_2]\cdot\text{thf}$, disorder of the THF molecules in $^2_\infty[\text{Li}_2\mathbf{5}(\text{thf})_2]\cdot\text{thf}$ and $^2_\infty[\text{Li}_2\mathbf{6}(\text{thf})_2]$, and disorder of the H atoms of the water molecules in $^3_\infty[\text{Li}_2\mathbf{5}(\text{H}_2\text{O})_3]$ are not shown. H atoms of the thf solvate molecules are omitted for clarity and the C atoms are shown as stick model).^[43]

nium hydrogen bonding might be the reason for a slight lengthening of the C=Se bond in $^3_\infty[\text{Li}_2\mathbf{5}(\text{H}_2\text{O})_3]$. The importance of intramolecular $\text{Se}\cdots\text{H}$ interaction was mentioned earlier.^[36] Recently, intermolecular selenium–hydrogen inter-

actions were used to rationalize deviations of $\delta(^{77}\text{Se})$ from expected values.^[37] The difference in $d(\text{C}=\text{Se})$ observed for dianion **5** in ${}^2_{\infty}[\text{Li}_2\mathbf{5}(\text{thf})_2]\cdot\text{thf}$ and ${}^3_{\infty}[\text{Li}_2\mathbf{5}(\text{H}_2\text{O})_3]$ thus provides further evidence for the sensitivity of the carbon selenium double bond against H bonding. A further comparison of the bond lengths of the N-heterocyclic ring in both dilithium salts is arbitrary since in ${}^2_{\infty}[\text{Li}_2\mathbf{5}(\text{thf})_2]\cdot\text{thf}$ the ring is in part disordered over two positions.

The reaction of nickel tetracarbonyl and $\text{Li}_2\mathbf{3}\cdot\text{thf}$ resulted in the formation of the dianionic nickel tricarbonyl complex **6**, which was isolated as dilithium salt $\text{Li}_2\mathbf{6}\cdot 2\text{thf}$ in 83% yield. The coordination of the carbene C atom to Ni is evident from the crystal structure analysis of ${}^2_{\infty}[\text{Li}_2\mathbf{6}(\text{thf})_2]$ (Figure 6). Similar to the solid state structure of ${}^2_{\infty}[\text{Li}_2\mathbf{5}(\text{thf})_2]\cdot\text{thf}$, two THF molecules are coordinated to lithium per formula unit. However, in case of the Ni complex **6** each Li cation is coordinated by one THF molecule and three CN moieties. The Ni–C2 bond of 198.4(5) pm is in the range typically observed for neutral $[(\text{NHC})\text{Ni}(\text{CO})_3]$ complexes, for example, $[(\text{IMes})\text{Ni}(\text{CO})_3]$ (197.1(3) pm) or $[(\text{IDipp})\text{Ni}(\text{CO})_3]$ (197.9(3) pm).^[38] From the structural data, the buried volume ($\%V_{\text{bur}}$)^[39] of the free dianionic NHC **3** was estimated to 39.9%. It is thus larger than $\%V_{\text{bur}}$ determined for bulky neutral type **I** NHCs (Figure 1), for example t^{Bu} (37%),^[38] and it is similar to $\%V_{\text{bur}}$ of sterically crowded cyclic (alkyl)aminocarbenes (cAACs)^[40] due to the bulky $\text{B}(\text{CN})_3$ substituents.

In the IR spectrum of solid $\text{Li}_2\mathbf{6}\cdot 2\text{thf}$ the A_1 symmetrical CO stretching frequency was assigned to a band at 2049 cm^{-1} (Figure S45 in the Supporting Information). The $\nu_{\text{CO}}(A_1)$ band position, the well-established Tolman electronic parameter (TEP),^[41] which is used for the assessment of the donor ability of a two valence electron donor ligand L in $[\text{LNi}(\text{CO})_3]$, is in the range typical for NHCs,^[42] for example, $[(\text{IMes})\text{Ni}(\text{CO})_3]$ (2051 cm^{-1}).^[38]

Conclusion

First salts of the imidazolate anion **1** and the related dianionic NHC **3** have been obtained on gram scale in high yield. Both anions **1** and **3** possess unprecedented stabilities compared to related species (Figure 1), which is due to a stabilization by the strong Lewis acid $\text{B}(\text{CN})_3$ bonded to both N atoms of the central heterocycle. Monoanion **1** and dianion **3** are promising ligands in coordination chemistry as exemplified by their salts and complexes described in the present contribution. Dianion **3** has a high potential as ditopic ligand with coordination being possible at the carbene center and the cyano groups alike. Furthermore, it can provide π -stabilization of a metal fragment coordinated to the carbene center via a cyano group as exemplified by the crystal structure of ${}^3_{\infty}[\text{Li}_2\mathbf{1}(\text{thf})]\cdot\text{C}_6\text{H}_6$ (Figure 4). According to the NMR spectroscopic study on the selenium adduct, the selenourea **5**, dianion **3** is a potent σ -donor and π -acceptor compared to related unsaturated NHCs. In addition, adduct **5** is a potential ligand in its own right. The combination of electronic properties, the large buried volume ($\%V_{\text{bur}}$), the

double negative charge, the possibility to act as ditopic ligand, and the ease of accessibility render **3** a unique novel NHC.

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Conflict of interest

The authors declare no conflict of interest.

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