Borane-Substituted Imidazol-2-ylidenes: Syntheses, Structures, and Reactivity☆

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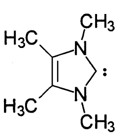
Received January 26, 1998

Keywords: Boranes / Carbenes / Carbene complexes / Heterocycles / Imidazoles

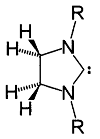
Reactions of the Lewis acids BH_3 and BEt_3 with trimethylimidazole (**1**) lead to the borane adducts **2a** and **2b**. Deprotonation of **2a** with *n*-butyllithium results in the formation of the novel *N*-borane-substituted imidazol-2-ylidene anion **3a**$^-$ whereas deprotonated **2b** rearranges unexpectedly to the anionic compound **3b**$^-$. This can be transformed into the carbene–borane adduct **4** by methylation. The reaction of **3a**$^-$ with $[Mn(CO)_5Br]$ yields the carbene complex **5**. Surprisingly, **3a**$^-$ attacks $Fe(CO)_5$ at a carbon atom which leads to the iron acyl complex anion **6**$^-$. The compositions of the products follow from spectroscopic and analytical data and from X-ray structure analyses for $Li(thp)^+$**3a**$^-$, $Li(thf)_2{}^+$**3b**$^-$ and $Li(thp)_3{}^+$**6**$^-$.

Introduction

The chemistry of nucleophilic carbenes has become an area of particular interest since the discovery of the first stable carbenes, synthesized by Arduengo et al. in 1991[1]. Several derivatives of the imidazol-2-ylidene **A** as well as the imidazolin-2-ylidene **B**[2] and the chain-like carbene compound **C** have been reported[3]. Based on the heterocycles triazole and thiazole, the carbenes **D**[4] and **E**[5] have also been synthesized. Recently, a review of the chemistry of N-heterocyclic carbenes was published by Herrmann et al.[6].

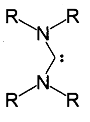


A



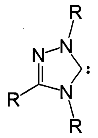
R = mesityl

B



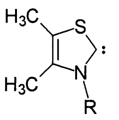
R = *i*-Pr

C



R = Ph

D



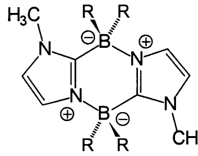
R = 2,6-diisopropylphenyl

E

Compounds **A**–**E** have in common the presence of only organic substituents attached to the nitrogen atoms, whereas other main-group element substituted carbenes are not known. Fehlhammer et al.[7] synthesized a tris(carbene)iron complex in which the carbene units are connected via a BH group.

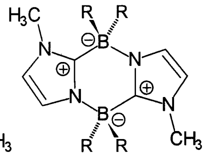
In 1994 Contreras, Wrackmeyer, et al.[8] published the synthesis of the imidazabole **F** (R = H) which may also be regarded as an intramolecular carbene–borane adduct **F'**. Its BH_2 groups function as Lewis acid centers for the carbene carbon atoms (see below).

Imidazol-2-ylidenes (e.g. **A**) have also proved to be excellent ligands in transition-metal complexes[9]. In particular, ligand exchange reactions with carbonylmetal compounds work easily yielding the expected carbene complexes. The reactions occur at room temperature and, depending on the stoichiometry of the reactants, mono-substituted products of type **H** are formed as well as bis- and tris(carbene) complexes in the case of Mo, W, and Ni[10][11]. Beside complexes with the monodentate ligand **A**, compounds **J** with a bidentate ligand are known as well[10][11].

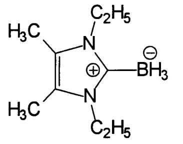


F

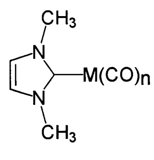
R = H, mesityl



F'

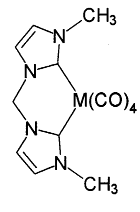


G



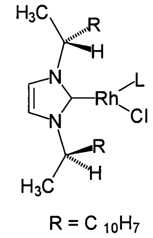
M = Cr, Mo, W; n = 5
M = Fe ; n = 4
M = Ni ; n = 3

H



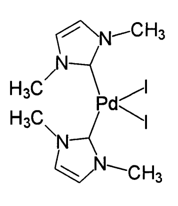
M = Cr, W

J



R = C ${}_{10}H_7$
L = 1,4-cyclooctadien

K



L

In complexes of imidazol-2-ylidenes the metal–carbene bond has weak π-backbonding character[6][10]. Therefore, these carbenes appear comparable to phosphanes, and could therefore also prove important in homogeneous catalytic processes[6][9e][10]. In fact, **K** and **L** are examples of useful carbene catalysts for asymmetric hydrosilylations (**K**)[12] and for the Heck reaction (**L**)[13].

In the following we report the deprotonation of the trimethylimidazol–borane adducts **2a** and **2b** with *n*-butyl-

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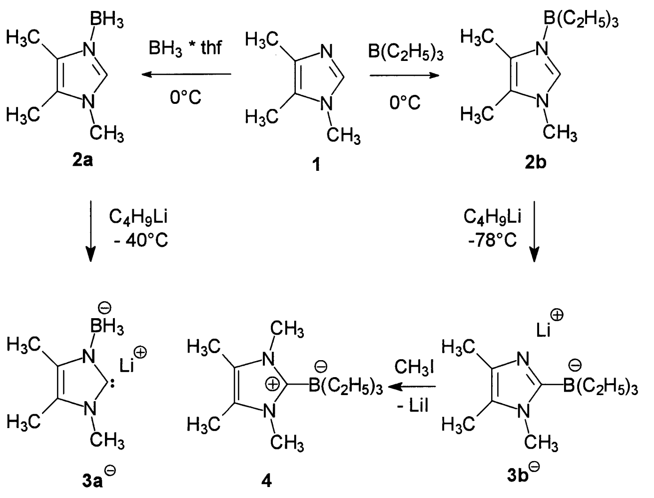
lithium which results in the formation of the novel anions **3a**$^-$ and **3b**$^-$. **3a**$^-$ forms the metal complexes **5** and **6**$^-$.

Results and Discussion

Synthesis

Analogous to the reaction of imidazoles with boranes[14], 1,4,5-trimethylimidazole (**1**) reacts with $BH_3 \cdot$ thf at 0 °C to yield 3-borane-1,4,5-trimethylimidazole (**2a**), a colorless, crystalline, and air-stable solid. Its composition follows from NMR and MS data. Deprotonation of **2a** leads to the formation of the 3-borane−1,4,5-trimethylimidazol-2-ylidene anion **3a**$^-$. The salt Li(thp)$^+$**3a**$^-$, thp being tetrahydropyran, is obtained as a colorless crystalline solid, which is sensitive to air and moisture. This first example of a borane-substituted nucleophilic carbene is dimeric in the solid state (see below). It is derived from **A** by formal substitution of a methyl group by the isoelectronic BH_3^- unit.

Scheme 1



A characteristic feature of nucleophilic carbenes is the low-field ^{13}C-NMR shift of the carbene carbon atom signal (δ = 211−256 for **A**−**E**)[1][2][3][4][5]. **3a**$^-$ shows a resonance at δ = 191.3 which is shifted 22.4 ppm to high field compared to that of the corresponding carbene **A**[1]. Obviously, there is a transfer of electron density from the negatively charged boron atom to the carbene carbon atom. The remaining ^{13}C-NMR data are very similar to those of **A**. The signals for C4 and C5 appear at δ = 121.8 and 128.7 while those for the three methyl groups appear at δ = 8.3, 10.4, and 33.8. The ^{11}B-NMR spectrum shows one signal at δ = −21.1 which is broadened so that coupling with the hydrogen atoms is not observed, in contrast to **2a** ($^1J_{B\text{-}H}$ = 94 Hz).

Treatment of **1** with BEt_3 at 0°C leads to 3-(triethylborane)−1,4,5-trimethylimidazole (**2b**) in quantitative yield. **2b** is a crystalline, colorless solid which is, in contrast to **2a**, sensitive to air. By analogy to the formation of **3a**$^-$, treatment of **2b** with *n*-butyllithium was expected to yield a carbene; however, surprisingly the rearranged anion **3b**$^-$ was obtained. After deprotonation, migration of the triethylborane from the nitrogen to the carbene carbon atom took place. This follows from the NMR data and from an X-ray structural analysis of $Li(thf)_2{}^+$**3b**$^-$. Obviously, the different Lewis acidities of BH_3/BEt_3 are responsible for this result.

The ^{13}C-NMR spectrum of **3b**$^-$ exhibits two signals at δ = 119.9 and 123.8 for the C4 and C5 atoms, the one for C2 not being observed. The resonances for the methyl groups are found at δ = 8.3, 9.4, and 32.0 while the ethyl substituents show two signals at δ = 10.7 and 14, the latter for the CH_2 carbon atom being broadened.

The different electronic behavior of BH_3 and BEt_3 as Lewis acids is reflected in the ^{11}B-NMR spectra. **2a** exhibits a resonance at δ = −20.9 whereas for **2b** a low-field shift to δ = −1.5 is observed. Comparing the shifts of **2a** and **2b** with those of **3a**$^-$ and **3b**$^-$ it is striking that for **3a**$^-$ (δ = −21.1) there is only a slight difference relative to **2a** whereas in the case of **3b**$^-$ (δ = −14.6) compared with **2b** a significant shift to higher field is observed. These data indicate that the migration of the triethylborane from the nitrogen to the carbon atom results in a larger electronic saturation of the boron atom. This is supported by comparing the ^{11}B-NMR shifts for tetraalkyl- and trialkyl(amino)-borates. $[BEt_4]^-$ shows a resonance at δ = −17.5[15] whereas for $[Et_3BNH_2]^-$ a low-field shift to δ = −9.8 is observed[16].

The reaction of **3b**$^-$ with iodomethane results in the formation of the 2-(triethylborane)−1,3,4,5-tetramethylimidazoline (**4**). Carbene adducts of this kind are known for a large variety of electrophiles and are usually obtained by addition of the Lewis acid to the free imidazol-2-ylidene[17]. Thus, carbene adducts with BH_3 and BF_3 have been described[18]. The method presented herein is a new route to generate triethylborane−carbene adducts. In the first step the trialkylborane is introduced, which on deprotonation and rearrangement gives **3b**$^-$. In the last step methylation of the anion **3b**$^-$ with CH_3I leads to the carbene adduct **4**.

4 is characterized by ^1H-, ^{13}C-, ^{11}B-NMR spectroscopy, and mass spectrometry. The ^1H-NMR spectrum shows the expected two signals at δ = 1.29 and 3.26 for the two sets of equivalent methyl substituents. In the ^{13}C-NMR spectrum only one signal for the imidazole carbon atoms C4 and C5 (δ = 123.6) is found, while that of C2 is, as for **3b**$^-$, not observed. The methyl substituents give rise to two signals at δ = 12.1 and 32.9. The ^{11}B-NMR shift of δ = −12.6 is comparable with that of **3b**$^-$.

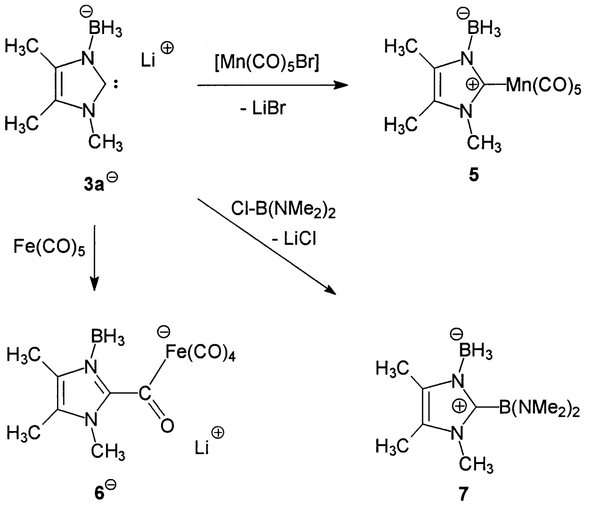
Complex Formation

The reactivity of **3a**$^-$ in ligand-exchange reactions was studied. When $[Mn(CO)_5Br]$ is added to a solution of **3a**$^-$, the expected complex **5** is obtained. In contrast to this, the reaction of **3a**$^-$ with $Fe(CO)_5$ results in the formation of the acyl complex **6**$^-$. Treatment of **3a**$^-$ with chlorobis(dimethylamino)borane leads to the borane compound **7** (Scheme 2).

The orange-yellow complex **5** is extremely sensitive to air and moisture, and is obtained by reaction of the in situ generated carbene **3a**$^-$ with $[Mn(CO)_5Br]$ at −40°C. The IR spectrum of the reaction mixture indicates the presence of several products, for which pure **5** can be isolated by column chromatography in 33% yield. **5** is characterized by

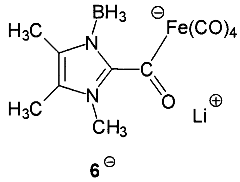
^{1}H-, ^{13}C-, ^{11}B-NMR, IR spectroscopy, and mass spectrometry. The ^{1}H-NMR spectrum shows two signals at δ = 2.22 and 2.24 for the C-CH$_3$ groups and one for the N-CH$_3$ group at δ = 3.81. In the ^{13}C-NMR spectrum the signals of the imidazole carbon atoms are found at δ = 129.0, 130.9 (C4, C5) and 146.9 (C2). This high-field shift of 44.4 ppm relative to that of **3a**$^-$ is in the same range as those for other carbenes and their complexes[10]. For the carbonyl ligands two signals at δ = 214.6 and 256.1 are observed. The assumption that **5** possesses a structure analogous to **6**$^-$ can be ruled out on the basis of the NMR data. The ^{11}B-NMR shift of $\delta = -22.3$ is comparable with the data mentioned above. Again the signal is broadened so that no coupling to the hydrogen atoms can be observed. The IR spectrum of **5** shows four absorptions at $\tilde{\nu}$ = 2081, 2004, 1992 and 1974 cm^{-1}. In the mass spectrum (EI) of **5** the molecular ion of *m*/*z* = 318 with the expected isotopic distribution is observed as well as the fragmentation pattern for the sequential loss of up to five CO molecules, with the resulting base peak at *m*/*z* = 178 [M$^+$ − 5 CO].

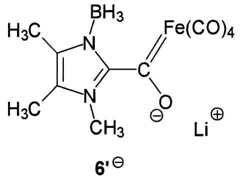
Scheme 2



At room temperature **3a**$^-$ attacks one carbonyl ligand in Fe(CO)$_5$, analogously to the reaction of alkyllithium with carbonyl complexes[19], with formation of the complex anion **6**$^-$. The reaction occurs rapidly and quantitatively as monitored by IR spectroscopy. This behavior represents an important difference relative to the reactivity of the imidazol-2-ylidenes known today. Obviously, **3a**$^-$ is much more nucleophilic than the classic nucleophilic carbenes. In the presence of tetrahydropyran, Li(thp)$_3$$^+$**6**$^-$ is obtained as a crystalline yellow solid which is extremely sensitive to air and moisture. It decomposes slowly even at temperatures < −10°C.

For the anion **6**$^-$ two structures may be expected, the acyl complex **6**$^-$ with an Fe−C single bond or the carbene complex **6′**$^-$. The X-ray diffraction study of Li(thp)$_3$$^+$**6**$^-$ reveals that in the solid state the complex has the acyl structure **6**$^-$ (see below). In case of an equilibrium between the two structures in solution, it should be possible to transform the complex into a Fischer carbene complex by methylation as preliminary experiments indicate.


6$^{\ominus}$


6'$^{\ominus}$

The NMR data for **6**$^-$ reveal the expected pattern: In the ^{13}C-NMR spectrum a low-field shift to δ = 154.3 for the C2 atom is observed, compared with δ = 135.7 in **2a**. This can be explained by the electron-withdrawing effect of the acyl group. Its carbon atom shows a resonance at δ = 280.8 while for the four other carbonyl groups only one signal is observed at δ = 219.4. The ^{11}B-NMR shift of $\delta = -22.9$ differs little from those for **2a** and **3a**$^-$. Again, the signal is broadened so that no coupling with the hydrogen atoms can be observed. Its IR spectrum shows four CO absorptions at $\tilde{\nu}$ = 2031, 1949, 1928, and 1911 cm^{-1}.

The reaction of **3a**$^-$ with chlorobis(dimethylamino)borane at −30°C leads to **7** in 72% yield. It was characterized by ^{1}H-, ^{13}C-, ^{11}B-NMR spectroscopy, and mass spectrometry. The ^{1}H-NMR spectrum shows two signals for the aminoboryl and the N-CH$_3$ groups at δ = 2.56 and 3.39, in an intensity ratio of 4:1. This indicates a free rotation of the dimethylamino substituents. The two C-CH$_3$ groups show resonances at δ = 2.10 and 2.11. In the ^{13}C-NMR spectrum two signals can be found in the aromatic region at δ = 123.4 and 131.0 for the atoms C4 and C5, while that of C2 is not observed. The four CH$_3$ substituents resonate at δ = 8.5, 10.0, 31.4, and 40.0. The ^{11}B-NMR shift of the BH$_3$ group is nearly unchanged with $\delta = -21.8$, and the second boron signal is observed at δ = 27.8, a typical shift for a diamino(organo)borane.

Crystal Structures

To elucidate the structure of **3a**$^-$, an X-ray diffraction study was carried out (crystal data and structure refinement for **3a**$^-$, **3b**$^-$, and **6**$^-$ are shown in Table 1). A single crystal of Li(thp)$^+$**3a**$^-$ was grown from a tetrahydropyran solution at 4°C. Its structure (Figure 1) is built up by dimeric units of two carbene anions which are connected by the two lithium cations.

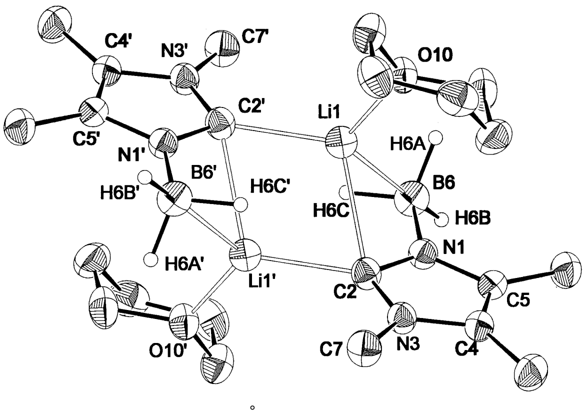
It was found that for imidazoles and imidazol-2-ylidenes the distances and angles at C2 show characteristic differences[1]. In imidazol-2-ylidenes the angle N1−C2−N3 (101.4−102.2°) is significantly smaller than that in imidazoles and imidazolium ions (107−109°)[20]. The C2−N distances are a little elongated and approximately equal (1.363−1.373 Å)[1], while in imidazoles an alternation of bond lengths is observed (e.g. 1.32 and 1.37 Å[21]). The C2−N1 and C2−N3 bond lengths (1.373 and 1.368 Å) in **3a**$^-$ are in good agreement with those of **A**[1], while the N1−C2−N3 angle of 104.0° is enlarged by 2.5°. This slight increase can be explained by the interaction of the carbene center with the lithium cation. The imidazole ring is almost planar with deviations from the best plane through the ring

Table 1. Crystal data and structure refinement for Li(thp)$^+$**3a**$^-$, Li(thf)$_2$$^+$**3b**$^-$, and Li(thp)$_3$$^+$**6**$^-$

	Li(thp)$^+$**3a**$^-$	Li(thf)$_2$$^+$**3b**$^-$	Li(thp)$_3$$^+$**6**$^-$
Empirical formula	$C_{11}H_{22}BLiN_2O$	$C_{20}H_{40}BLiN_2O_2$	$C_{26}H_{42}BFeLiN_2O_8$
Formula weight	216.1	358.3	584.2
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Unit cell			
a [Å]	8.218(4)	9.723(11)	10.873(8)
b [Å]	8.669(4)	13.853(14)	14.426(11)
c [Å]	11.108(6)	17.274(19)	20.307(15)
α [°]	79.44(3)	90	90
β [°]	75.19(3)	93.03(9)	93.37(6)
γ [°]	61.89(3)	90	90
Volume [Å^3]	673.0(6)	2323(4)	3180(4)
Z	2	4	4
Calc. density [g/cm^3]	1.066	1.024	1.220
Adsorp.coeff. [mm^{-1}]	0.066	0.063	0.519
F(000)	236	792	1240
Crystal size [mm]	0.65×0.55×0.50	0.7×0.5×0.5	0.7×0.7×0.5
Θ-range [°]	1.9−25.0	1.9−26.0	1.7−27.0
Index-ranges	−9/+9, −9/+10, 0/+13	−11/+11, 0/+17, 0/+21	−13/+13, 0/+18, 0/+25
No. of reflections			
unique	2375	4558	6932
observed [I>2σ(I)]	1619	2604	4836
Transmission	0.933−1.00	0.94−1.00	0.87−1.00
Parameters	228	239	527
Final R indices			
*R*1 [I > 2σ(I)]	0.059	0.091	0.045
*wR*2	0.165	0.271	0.117
Largest diff.peak/hole[e/Å^3]	+0.17 / −0.40	+0.48 / −0.43	+0.31 / −0.22

atoms being less than 0.006 Å. The B6−N1 distance of 1.572 Å is characteristic for a B−N single bond. For each of the lithium cations a short (Li−C2′ 2.169 Å) and a longer contact (Li1−C2 2.339 Å) with the carbene carbon atoms are observed. The coordination around the Li cation is completed by the thp molecule and a weak interaction with the BH_3 group.

Figure 1. Structure of Li(thp)$^+$**3a**$^-$ in the crystal[a]



[a] Selected bond lengths [Å] and angles [°]: N1−C2 1.373(3), C2−N3 1.368(3), N3−C4 1.393(3), C4−C5 1.355(3), C5−N1 1.398(3), B6−N1 1.572(3), Li1−B6 2.417(5), Li1−N1 2.489(5), Li1−C2 2.339(5), Li1−C2′ 2.169(5), Li1−H1 2.315(5), Li1−H3 2.214(5), B6−H1 1.156(32), B6−H3 1.185(30), B6−H2 1.102(30), N1−C2−N3 104.0(2), C2−N3−C4 112.2(2), N3−C4−C5 105.7(2), C4−C5−N1 107.9(2), C5−N1−C2 110.3(2).

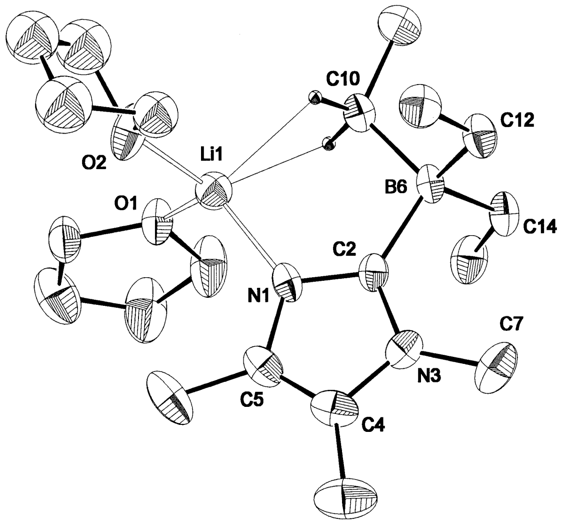
3a$^-$ is the first example of an isolable borane-substituted imidazol-2-ylidene, although carbene−borane adducts such as 2-borane−1,3-diethyl-4,5-dimethylimidazoline (**G**) are already known[18]. **F** has not attracted any attention as a carbene although the structural data[8] support the assumption that it may be regarded as a carbene−borane adduct (**F′**) as well.

In **F′** (R = mesityl)[8b] the C2−N bonds (1.356 and 1.357 Å) are nearly identical and match the distances found in **G**. The N−C−N angle of 106.4° has increased by 1.7° compared with that in **G**, but is still significantly smaller than in an imidazole or imidazolium ion. The C2−B distance in **F′** is 1.635 Å (**G**: 1.603 Å) which may be explained by the effect of the sterically demanding mesityl substituents. In contrast, **F** represents a description as an adduct in which the BH_2 group of a 2-boryl-substituted imidazole acts as Lewis acid and the imidazole nitrogen atom as Lewis base. This should lead to a characteristic imidazole structure with alternation of the C2−N bond lengths and a larger N−C−N angle. Another indication for the carbene character of **F′** (R = H) is its ^{13}C-NMR shift of δ = 161.0[8a] which is observed in the typical low-field area of carbene adducts and is comparable with the shift of δ = 166.6 for **G**[18].

A different structure is found for Li(thf)$_2$$^+$**3b**$^-$. A single crystal was grown from a hexane solution at 4°C and the structure is shown in Figure 2. The crystal-structure determination reveals the occurrence of a migration of the BEt_3 group from the nitrogen to the carbon atom, leading to a 1-methyl-2-borane-substituted imidazole anion.

The C2−N1 and C2−N3 bond lengths of 1.337 Å and 1.373 Å show the typical alternation of a 1-substituted imi-

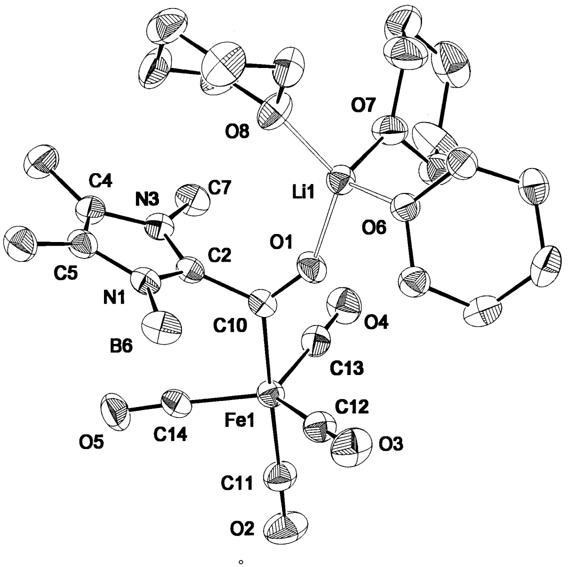
Figure 2. Structure of Li(thf)$_2{}^+$**3b**$^-$ in the crystal[a]



[a] Selected bond lenghts [Å] and angles [°]: N1−C2 1.337(4), C2−N3 1.373(4), N3−C4 1.389(5), C4−C5 1.346(5), C5−N1 1.388(5), N2−C7 1.464(5), B6−C2 1.645(5), B6−C10 1.655(5), B6−C12 1.646(5), B6−C14 1.639(5), Li1−N1 1.932(7), Li1−C10 2.511(7), N1−C2−N3 107.4(3), N1−C5−C4 109.4(3), C2−N1−N3 108.2(3), N3−C4−C5 105.7(3), C2−N3−C4 109.3(3).

dazole[21] and the N1−C2−N3 angle of 107.4° has increased considerably when compared to that of **A**[1] and Li(thp)$^+$**3a**$^-$. The N1 atom interacts strongly with the lithium cation (Li1−N1 1.932 Å), whose coordination is completed by the two thf molecules and weak agostic interactions with the hydrogen atoms of the methylene group at C10.

Figure 3. Structure of Li(thp)$_3{}^+$**6**$^-$ in the crystal[a]



[a] Selected bond lengths [Å] and angles [°]: N1−C2 1.326(3), C2−N3 1.347(3), N3−C4 1.395(3), C4−C5 1.351(4), C5−N1 1.397(4), N1−B6 1.596(4), N3−C7 1.465(4), C2−C10 1.512(4), Fe1−C10 1.966(3), C10−O1 1.237(3), Li1−O1 1.905(5), Fe1−C11 1.800(3), Fe1−C12 1.792(3), Fe1−C13 1.781(3), Fe1−C14 1.787(3), N1−C2−N3 109.4(2), C2−N1−C5 107.7(2), C2−N3−C4 108.3(2), N3−C4−C5 106.4(2), N1−C5−C4 108.2(2), C2−C10−O1 114.6(2), C2−C10−Fe1 118.7(2), Fe1−C10−O1 126.6(2), C10−Fe1−C11 178.3(1).

The bonding in Li(thp)$_3{}^+$**6**$^-$ is of significant interest in order to distinguish whether it is an acyl or a carbene compound. The answer was found by carrying out an X-ray diffraction study. Single crystals were grown from a thp solution at 4°C. The X-ray structure of **6**$^-$ shows the complex anion with Li(thp)$_3{}^+$ as counter ion that is attached to the acyl oxygen atom (Figure 3). There is no doubt that **6**$^-$ must be regarded as an acyl complex. It exhibits a trigonal-bipyramidal coordination of the iron atom by four CO ligands and the acyl group, derived from the addition of **3a**$^-$ to one of the axial carbon monoxide in Fe(CO)$_5$. The C10−Fe1−C11 axis is nearly linear with an angle of 178.7°. The Li(thp)$_3{}^+$ ion is coordinated by the oxygen atom of the acyl group. The length of the Fe1−C10 bond (1.966 Å) is in agreement with the formulation as an acyl complex, for which Fe−C distances between 1.92 and 1.99 Å[22] are typically observed, compared with 1.84−1.87 Å for carbene complexes[23]. The C2−C10 (1.512 Å) and C10−O1 (1.237 Å) distances also fit with the data found for acyl complexes[22]. Obviously the acyl ligand has nearly no influence on the *trans*-CO group, with the Fe1−C11 bond length of 1.800 Å being comparable to those for the equatorial carbonyl groups (1.781−1.792 Å). The distances and angles of the imidazole ring indicate the loss of carbene character. The alternating bond lengths N1−C2 (1.326 Å) and C2−N3 (1.347 Å) as well as the large N1−C2−N3 angle of 109.4° are typical for an imidazole.

Experimental Section

General: Reactions were carried out under dry argon, using standard Schlenk techniques. Solvents were dried, distilled, and saturated with nitrogen. Glassware was dried with a heat-gun in high vacuum. − ^{1}H-, ^{13}C-, ^{11}B-NMR: Bruker AC 200 spectrometer, NMR references are $(CH_3)_4Si$ and $BF_3 \cdot Et_2O$. − IR spectra were recorded with a Bruker IFS 28 Fourier transformation spectrometer with CaF_2 cells. − Mass spectra were obtained with a Finnigan MAT 8200 plus spectrometer using the EI technique. − Melting points (uncorrected) were obtained with a Büchi apparatus, using a capillary which was filled under argon and sealed. − 1,4,5-trimethylimidazole (**1**)[24a] and [Mn(CO)$_5$Br][24b] were prepared according to literature procedures.

3-Borane−1,4,5-trimethylimidazole (**2a**): To a solution of 790 mg (7.2 mmol) of **1** in 20 ml of thf, 7.2 ml of $BH_3 \cdot$ thf (1.0 M in thf) was added dropwise at 0°C, after which the mixture was allowed to warm to room temp. and stirred for 24 h. By that time a white solid had precipitated. The product was dissolved by heating and then allowed to crystallize at −30°C. Yield: 760 mg (85%) colorless, air-stable needles, m.p.: 160°C. − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.10 (s, 3 H, C-CH$_3$), 2.14 (s, 3 H, C-CH$_3$), 3.53 (s, 3 H, N-CH$_3$), 7.62 (s, 1 H, N=CH-N). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 9.2 (C-*C*H$_3$), 10.6 (C-*C*H$_3$), 33.2 (N-CH$_3$), 125.3 (C=*C*-N), 132.2 (C=*C*-N), 135.7 (N=CH-N). − ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = −20.9 (q, $^1J_{B\text{-}H}$ = 94 Hz). − $C_6H_{13}BN_2$ (124.0): calcd. C 58.12, H 10.56, N 22.59; found C 57.72, H 10.40, N 22.43.

3-(Triethylborane)−1,4,5-trimethylimidazole (**2b**): To a solution of 1.52 g (13.8 mmol) of **1** in 20 ml of toluene, 2.2 ml of BEt_3 was added dropwise at 0°C. The mixture was allowed to warm to room temp. and stirred for 24 h. The solvent was evaporated in vacuo and the colorless oil was allowed to crystallize at −30°C, and then washed with pentane and dried. Yield: 2.84 g (99%); colorless crystals, m.p.: 65°C. − ^{1}HNMR (200.1 MHz, CDCl$_3$): δ = 0.37 (t, 9 H, CH$_2$-C*H*$_3$), 0.57 (q, 6 H, C*H*$_2$-CH$_3$), 2.11 (s, 3 H, C-CH$_3$), 2.20 (s, 3 H, C-CH$_3$), 3.54 (s, 3 H, N-CH$_3$), 7.45 (s, 1 H, N=CH-N). − ^{13}C-NMR (50.3 MHz, CDCl$_3$): δ = 8.0 (C-*C*H$_3$), 9.3 (CH$_2$-*C*H$_3$), 11.0 (C-*C*H$_3$), 14 (br., *C*H$_2$-CH$_3$), 32.2 (N-CH$_3$), 124.5 (C=C-N), 130.8 (C=C-N), 134.2 (N=CH-N). − ^{11}B-NMR (64.2 MHz, CDCl$_3$): δ = −1.5 ($\Delta\nu_{1/2}$ = 290 Hz).

Lithium 3-Borane−1,4,5-trimethylimidazol-2-ylidene [Li(thp)$^+$-**3a**$^-$]: To a suspension of 860 mg (6.9 mmol) of **2a** in 25 ml of thf 3.2 ml of *n*-butyllithium (2.5 N in hexane) was added dropwise at −40°C. The mixture was allowed to warm to room temp. and stirred for 24 h. The solvent was evaporated in vacuo and the resulting solid was recrystallized from thf/hexane at −30°C. Yield: 1.14 g (82%) colorless crystals, m.p.: 210−220°C (decomp.). − ^{1}H NMR (200.1 MHz, C$_6$D$_6$): δ = 1.38 (m, 12 H, thf), 1.74 (s, 3 H, C-CH$_3$), 2.34 (s, 3 H, C-CH$_3$), 3.43 (s, 3 H, N-CH$_3$), 3.57 (m, 12 H, thf). − ^{13}C NMR (50.3 MHz, C$_6$D$_6$): δ = 8.3 (C-*C*H$_3$), 10.4 (C-*C*H$_3$), 25.1 (thf), 33.8 (N-CH$_3$), 67.6 (thf), 121.8 (C=C-N), 128.7 (C=C-N), 191.3 (N=C-N). − ^{11}B NMR (64.2 MHz, C$_6$D$_6$): δ = −21.1 ($\Delta\nu_{1/2}$ = 290 Hz).

Lithium Triethyl(1,4,5-trimethylimidazolyl)borate [Li(thf)$_2$$^+$**3b**$^-$]: To a suspension of 950 mg (4.6 mmol) of **2b** in 20 ml of thf 2.0 ml of *n*-butyllithium (2.5 N in hexane) were added dropwise at −78°C. The mixture was allowed to warm to room temp. and stirred for 24 h. The solvent was evaporated in vacuo and the resulting white solid was recrystallized from thf/hexane. Yield: 1.07 g (77%) colorless crystals, m.p.: 150−160°C (decomp.). − ^{1}H NMR (200.1 MHz, CDCl$_3$): δ = 0.29 (q, 6 H, C*H*$_2$-CH$_3$), 0.59 (t, 9 H, CH$_2$-C*H*$_3$), 1.83 (m, 8 H, thf), 2.06 (s, 3 H, C-CH$_3$), 2.10 (s, 3 H, C-CH$_3$), 3.58 (s, 3 H, N-CH$_3$), 3.72 (m, 8 H, thf). − ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 8.3 (C-*C*H$_3$), 9.4 (C-*C*H$_3$), 10.7 (CH$_2$-*C*H$_3$), 14.0 (br., *C*H$_2$-CH$_3$), 25.6 (thf), 32.0 (N-CH$_3$), 67.9 (thf), 119.9 (C=C-N), 123.8 (C=C-N), C2 not observed. − ^{11}B NMR (64.2 MHz, C$_6$D$_6$): δ = −14.6.

2-(Triethylborane)−1,3,4,5-tetramethylimidazoline (**4**): 810 mg (3.9 mmol) of **2b** was dissolved in 15 ml of thf and 1.7 ml of *n*-butyllithium (2.5 N in hexane) was added dropwise at −78°C. The mixture was allowed to warm to room temp. and stirred for 1 h. Then 0.5 ml of iodomethane was added at −30°C, the solution was warmed to room temp. and stirred for another hour. The solvent was evaporated in vacuo, the resulting white solid was dissolved in hexane and filtered. After cooling to −30°C, a white precipitate had formed which was filtered and dried. Yield: 600 mg (69%) white powder. − ^{1}H NMR (200.1 MHz, C$_6$D$_6$): δ = 1.01 (q, 6 H, C*H*$_2$-CH$_3$), 1.18 (t, 9 H, CH$_2$-C*H*$_3$), 1.29 (s, 6 H, C-CH$_3$), 3.26 (s, 6 H, N-CH$_3$). − ^{13}C NMR (50.3 MHz, C$_6$D$_6$): δ = 8.3 (C-*C*H$_3$), 12.1 (CH$_2$-*C*H$_3$), 15.0 (br., *C*H$_2$-CH$_3$), 32.9 (N-CH$_3$), 123.6 (C=C-N), C2 signal not observed. − ^{11}B NMR (64.2 MHz, C$_6$D$_6$): δ = −12.6. − EI-MS; *m/z* (%): 193 (45) [M$^+$ − C$_2$H$_5$], 137 (100), 124 (44) [M$^+$ − BEt$_3$].

(3-Borane−1,4,5-trimethylimidazol-2-ylidene)pentacarbonylmanganese (**5**): To a suspension of 240 mg (1.9 mmol) of **2a** in 20 ml of thp was added 0.85 ml of *n*-butyllithium (2.5 N in hexane) dropwise at −40°C. The reaction mixture was allowed to warm to room temp. and stirred for 1 h. Then 535 mg (1.9 mmol) of [Mn(CO)$_5$Br] were added at −40°C and the solution was again warmed to room temp. and stirred for another hour. While warming, the solid dissolved, the solution became orange-colored and at room temp. deep red. The solvent was evaporated in vacuo, the residue dissolved in toluene and separated by column chromatography (SiO$_2$/toluene). Yield: 200 mg (33%) yellow powder. − ^{1}H NMR (200.1 MHz, [D$_8$]thf): *δ* = 2.22 (s, 3 H, C-CH$_3$), 2.24 (s, 3 H, C-CH$_3$), 3.81 (s, 3 H, N-CH$_3$). − ^{13}C NMR (50.3 MHz, [D$_8$]thf): δ = 8.3 (C-*C*H$_3$), 9.6 (C-*C*H$_3$), 32.3 (N-CH$_3$), 129.0 (C=C-N), 130.9 (C=C-N), 146.9 (N-C-N), 214.6 (CO), 256.1 (CO). − ^{11}B NMR (64.2 MHz, C$_6$D$_6$): δ = −22.3. − IR (hexane): $\tilde{\nu}$(CO) [cm^{-1}] = 2081 (w), 2004 (s), 1992 (vs), 1974 (s). − EI-MS; *m/z* (%): 318 (22) [M]$^+$, 290 (17) [M − CO]$^+$, 262 (20) [M − 2 CO]$^+$, 234 (48) [M − 3 CO]$^+$, 206 (29) [M − 4 CO]$^+$, 178 (100) [M − 5 CO]$^+$.

Lithium (3-Borane−1,4,5-trimethylimidazol-2-ylcarbonyl)tetracarbonyliron [Li(thp)$_3$$^+$**6**$^-$]: To a suspension of 500 mg (4.0 mmol) of **2a** in 20 ml of thp was added 1.8 ml of *n*-butyllithium (2.5 N in hexane) dropwise at −40°C. The mixture was allowed to warm to room temp. and stirred for 1 h. Then 0.55 ml of Fe(CO)$_5$ was added at −40°C. At −30°C a yellow solid was formed which dissolved at 5°C. The orange-colored solution was stirred for 1 h at room temp. and afterwards half of the solvent was removed in vacuo. Crystallization at −30°C yielded 1.29 g (78%) yellow needles, m.p.: 120−127°C (decomp.). − ^{1}H NMR (200.1 MHz, C$_6$D$_6$): δ = 1.29 (m, 24 H, thp), 1.44 (s, 3 H, C-CH$_3$), 2.01 (s, 3 H, C-CH$_3$), 3.42 (s, 3 H, N-CH$_3$), 3.52 (m, 16 H, thp). − ^{13}C NMR (50.3 MHz, [D$_8$]thf): δ = 8.2 (C-*C*H$_3$), 10.0 (C-*C*H$_3$), 24.7 (thp), 27.8 (thp), 31.1 (N-CH$_3$), 69.3 (thp), 121.1 (C=C-N), 128.1 (C=C-N), 154.3 (N-C-N), 219.4 (CO), 280.8 (CO). − ^{11}B NMR (64.2 MHz, C$_6$D$_6$): δ = −22.9 (br.). − IR (thp): $\tilde{\nu}$(CO) [cm^{-1}] = 2031 (s), 1949 (s), 1928 (vs), 1911 (vs).

3-Borane−2-[bis(dimethylamino)boryl]-1,4,5-trimethylimidazoline (**7**): To a suspension of 500 mg (4.0 mmol) of **2a** in 20 ml of thf was added 1.6 ml of *n*-butyllithium (2.5 N in hexane) dropwise at −40°C with dissolving of the solid. The mixture was allowed to warm to room temp. and stirred for 1 h. Then 540 mg (4.0 mmol) of chlorobis(dimethylamino)borane was added at −30°C, the solution warmed to room temp. and stirred for another hour. The solvent was removed in vacuo and the white precipitate dissolved in toluene. LiCl was separated by filtration and the product was allowed to crystallize from a toluene/hexane solution. Yield: 640 mg (72%) colorless needles, m.p.: 74°C. − ^{1}H NMR (200.1 MHz, CDCl$_3$): δ = 2.10 (s, 3 H, C-CH$_3$), 2.17 (s, 3 H, C-CH$_3$), 2.56 (s, 12 H, N-CH$_3$), 3.39 (s, 3 H, N-CH$_3$). − ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 8.5 (C-*C*H$_3$), 10.0 (C-*C*H$_3$), 31.4 (N-CH$_3$), 40.0 (N-CH$_3$), 123.4 (C=C-N), 131.0 (C=C-N), C2 signal not observed. − ^{11}B NMR (64.2 MHz, CDCl$_3$): δ = −21.9 (br., BH$_3$), 27.8 [br., B(NMe$_2$)$_2$]. − EI-MS; *m/z* (%): 221 (13) [M$^+$ − H], 207 (7) [M$^+$ − CH$_3$], 123 (100) [M$^+$ − B(NMe$_2$)$_2$].

Crystal-Structure Determinations of Li(thp)$^+$**3a**$^-$, Li(thf)$_2$$^+$**3b**$^-$, *and* Li(thp)$_3$$^+$**6**$^-$: Crystal data and details of the structure determinations are listed in Table 1. Unique sets of intensity data were collected at −70°C with a four-circle diffractometer (Mo-K_α radiation λ = 0.7107 Å, graphite monochromator, ω-scan). Empirical absorption corrections (ψ-scans) were applied. The structures were solved by direct methods [SHELXS86][25] and refined by least-squares methods based on F^2 with all measured reflections [SHELXL97][26]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in **3b**$^-$ were included in calculated positions or as part of rigid groups (CH$_3$), in **3a**$^-$ and **6**$^-$ hydrogen atoms were located in difference Fourier maps and refined. The thf molecules in **3b**$^-$ and one of the thp molecules in **6**$^-$ are disordered.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallograhpic Data Center as supplementary publication no. CCDC-101057. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: int. code + 44(0)1223/336-001; e-mail: deposit@ccdc.cam.ac.uk

☆ Dedicated to Prof. Dr. *Heinrich Nöth* on the occasion of his 70th birthday.

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