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Metal complexes of anionic 3-borane-1-alkylimidazol-2-ylidene derivatives

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Dedicated to Professor Rolf Gleiter on the occasion of his 65th birthday

Abstract

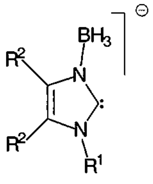
Addition of BH_3·thf to 1-alkylimidazoles (alkyl = methyl, butyl) and 1-methylbenzimidazole leads to BH_3 adducts, which are deprotonated by BuLi to yield the organolithium compounds (L)Li$^+$(**1b**–**d**)$^-$. In the solid state (thf)Li$^+$**1b**$^-$ is dimeric. The acyl–iron complexes (thf)$_3$Li$^+$(**3b**,**d**)$^-$ are formed from (thf)Li$^+$(**1b**,**d**)$^-$ and Fe(CO)$_5$. (L)Li$^+$(**1a**–**c**)$^-$ react with [CpFe(CO)$_2$X], however, the only complex obtained is [CpFe(CO)$_2$**1a**] (**5a**). The analogous reaction of (L)Li$^+$**1a**$^-$ with the pentadienyl complex [(C_7H_{11})Fe(CO)$_2$Br] yields the corresponding iron compound **6a**. Their compositions follow from spectroscopic data. Treatment of Cp_2TiCl with (L)Li$^+$**1a**$^-$ leads to [Cp_2Ti**1a**] (**7a**), which could not be oxidized with $PbCl_2$ to give the corresponding Ti(IV) complex. The compounds [Li(py)$_4$]$^+$**9a**$^-$ and [Li(L)$_4$]$^+$(**10b**–**d**)$^-$ are obtained when (L)Li$^+$**1**$^-$ are reacted with VCl_3 and $ScCl_3$. The X-ray structure analysis of the vanadium complex reveals a distorted tetrahedron of the anion [V(**1a**)$_4$]$^-$ with two smaller and four larger C–V–C angles. The scandium compound [Li(dme)$_2^+$**10c**$^-$] has a different structure: the distorted tetrahedron of the anion [Sc(**1c**)$_4$]$^-$ contains two larger (140.2 and 142.9°) and four smaller C–Sc–C angles (93.9–98.7°). This arrangement allows the formation of four bridging B–H–Sc 3c,2e bonds to give an eight-fold coordination. The anion **10c**$^-$ is formally a 16e complex. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carbenes; Carbene complexes; Heterocycles; 3-Borane-imidazoles

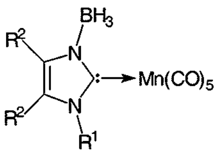
1. Introduction

One of the most interesting properties of imidazol-2-ylidenes is their ability to coordinate to transition metals [1]. Recently, we reported the synthesis [2] and structure [3] of 3-borane-1,4,5-trimethylimidazole and of the 3-borane-1,4,5-trimethylimidazol-2-ylidene anion (**1a**$^-$), a new kind of nucleophilic carbene, which allowed the formation of the neutral manganese complex **2a** and the anionic iron compound **3a**$^-$ in reactions with BrMn(CO)$_5$ and Fe(CO)$_5$, respectively [2].

This work describes further investigations with **1a**$^-$ and the new anionic derivatives (**1b**–**d**)$^-$. Various transition metals have been used as well as additional ligands to determine how these complexes are stabilized. Several early and late transition metal compounds were obtained and investigated by spectroscopic methods including X-ray crystallographic analyses.



1$^-$



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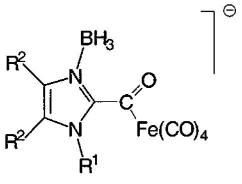

3$^-$

	a	b	c	d
R^1	CH_3	CH_3	C_4H_9	CH_3
R^2	CH_3	H	H	C_2H_2

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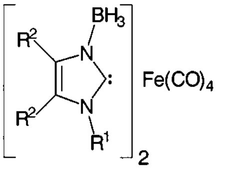
2. Results and discussion

2.1. Syntheses of the 3-borane-1-alkylimidazol-2-ylidene complexes

Addition of BH_3·thf to THF solutions of 1-methylimidazole, 1-butylimidazole, and 1-methylbenzimidazole gave the corresponding 3-borane adducts, which were deprotonated with BuLi at low temperature to yield the new derivatives $(L)Li^{+}$(**1b**–**d**)$^{-}$. In the solid state $(thf)Li^{+}$**1b**$^{-}$ is dimeric as observed for $(thp)Li^{+}$**1a**$^{-}$. The latter organolithium compound [2] reacted with $Fe(CO)_5$ and formed the crystalline acyl–iron complex $(thp)_3Li^{+}$**3a**$^{-}$, in which the lithium ion is coordinated by three tetrahydropyrane ligands and by the oxygen atom of the acyl group. In THF the analogous products $(thf)_3Li^{+}$**3b**$^{-}$ and $(thf)_3Li^{+}$**3d**$^{-}$ were obtained from $(thf)Li^{+}$(**1b**,**d**)$^{-}$ and $Fe(CO)_5$. Their compositions followed from spectroscopic data and X-ray structure analyses, which do not show any significant differences with the structure of $(thf)Li^{+}$**3a**$^{-}$ (for further details see Section 5). Attempts to synthesize ironcarbonyl compounds **4** from acyl–iron complexes $(L)_3Li^{+}$**3**$^{-}$ and elemental iodine led to dark red solutions, however, the expected products were not formed. Also, reactions of $(L)_3Li^{+}$**3**$^{-}$ with $(OC)_4FeI_2$ did not yield **4**.



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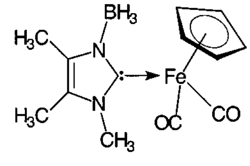
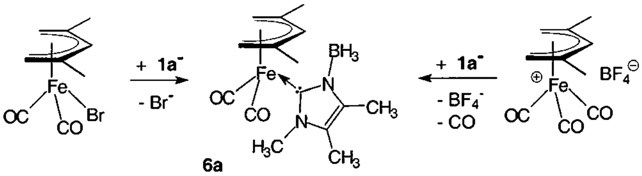


5a

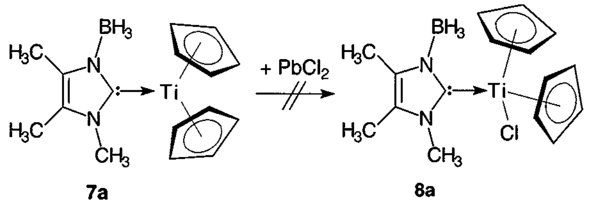
When derivatives of $(L)Li^{+}$(**1a**–**c**)$^{-}$ were allowed to react with $[CpFe(CO)_2X]$ (X = Cl, Br, I), the neutral iron complex **5a** was obtained only from $CpFe(CO)_2Br$ and $(L)Li^{+}$**1a**$^{-}$ (35% yield). In addition $[CpFe(CO)_2]_2$ was identified as side or as main product, the derivatives **5b**,**c** were not formed. The composition of **5a** followed from its spectroscopic data. In the ^{1}H-NMR spectrum three signals for the carbene ligand appear at $\delta = 1.73$, 2.13 and 3.59 as well as a singlet for the Cp protons at $\delta = 5.17$. Corresponding resonances are found in the ^{13}C-NMR spectrum at $\delta = 9.5$, 11.9 and 35.1 for the methyl groups as well as at $\delta = 127.4$ and 134.5 for the olefinic carbon atoms (C4, C5) of the heterocycle. The carbene atom (C2) was not observed due to its weakness. The Cp ligand resonance appears at $\delta = 87.7$ while a singlet at $\delta = 214.1$ is found for the carbonyl groups. In the ^{11}B-NMR spectrum a signal at $\delta = -17.2$ is indicative for the coordinated BH_3 Lewis acid. The IR spectrum exhibits two absorptions for the CO ligands at $\nu = 2035$ and 1975 cm^{-1}.

The analogous reaction of $(L)Li^{+}$**1a**$^{-}$ with the pentadienyl complex $[(C_7H_{11})Fe(CO)_2Br]$ led to the formation of the iron compound **6a**. In this case no hint for the dimeric side product $[(C_7H_{11})Fe(CO)_2]_2$ [4] was found. Nevertheless, the yield of brown **6a** (33%) was not higher when compared with **5a**. A better route is the reaction of $(L)Li^{+}$**1a**$^{-}$ with the cationic complex $[(C_7H_{11})Fe(CO)_3]^{+}BF_4^{-}$ leading to **6a** in 42% yield. Spectroscopic data of **6a** support its proposed composition. Beside signals for the carbene ligand in the ^{1}H-NMR spectrum at $\delta = 1.23$, 2.25 and 3.43, the pentadienyl unit shows resonances at $\delta = 0.89$ (*endo*) and 2.05 (*exo*) for the hydrogen atoms at C1,5. The methyl groups are found at $\delta = 2.12$ and a low-field signal for C3–H is observed at $\delta = 5.39$. In the ^{13}C-NMR the carbene ligand exhibits the expected signals at $\delta = 8.3$, 10.7, 31.2 (methyl groups), 123.9, 130.4 (C4,5) and 144.4 for the C2 atom, the remaining peaks at $\delta = 28.8$, 43.8, 94.8, 104.7 are assigned to the pentadienyl ligand, and the carbonyl resonance is found at $\delta = 212.5$. In the IR spectrum ($\nu = 2037$ and 1963 cm^{-1}) almost no shift is observed when compared with those of **5a**.



6a

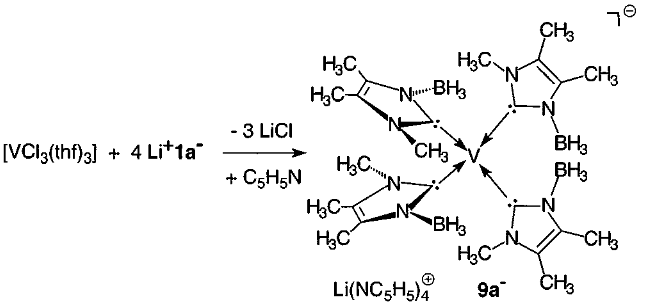
Attempts to synthesize molybdenum complexes analogous to **5** by reacting the anion **1**$^{-}$ with $[CpMo(CO)_3I]$ gave no hint on the formation of a carbene–molybdenum compound. Instead $[CpMo(CO)_3I]$ was reduced to the $[CpMo(CO)_3]^{-}$ anion, identified by its IR spectrum. In contrast, compounds of early transition metals in higher oxidation states formed new products with $(L)Li^{+}$**1**$^{-}$. From $(L)Li^{+}$**1a**$^{-}$ and Cp_2TiCl, prepared in situ by reducing Cp_2TiCl_2 with zinc powder, the Ti(III) complex **7a** was obtained. The reaction took place even at −70 °C when the carbene anion was added to a solution of the titanium compound. Work-up led to the extremely air-sensitive, blue–violet complex in 78% yield. Although Ti(III) complexes are typically oxidized to the corresponding Ti(IV)chloro compounds with lead(II) chloride [5], attempts to obtain diamagnetic **8a** have not been successful.



7a **8a**

The reaction of $(L)Li^{+}$**1a**$^{-}$ with vanadium chloride $[VCl_3(thf)_3]$ at low temperature resulted in a complete substitution with formation of a purple, paramagnetic anion $[V(\mathbf{1a})_4]^-$. An interesting color change was observed, when the purple tetrahydrofurane solution was treated with stronger donor ligands. Upon addition of pyridine a deep red solution formed from which the ion pair $[Li(NC_5H_5)_4]^+[V(\mathbf{1a})_4]^-$ crystallized.

Its structure was elucidated by an X-ray crystallographic study, which showed the presence of the anionic tetracarbene complex **9a**$^-$. After formation of $V(\mathbf{1a})_3$ a fourth ligand **1a**$^-$ coordinated at the metal center to yield the anion **9a**$^-$. An explanation for the change of color may be that in the originally formed complex the lithium cation interacted with nitrogen atoms of carbene ligands. Upon addition of the stronger donor pyridine the Li^+ ion was removed from the carbene ligand and the separated ion pair was formed. Compound **9a**$^-$ is paramagnetic due to d^2 vanadium [6]. The only known anionic homoleptic V(III) species is the complex $[Li(thf)_4]^+[VR_4]^-$ (R = mesityl) [7]. In contrast to the formation of $[Li(py)_4]^+$ **9a**$^-$, the substitution of $[VCl_3(thf)_3]$ with lithium mesityl can be halted at the neutral three-coordinated complex. Preliminary investigations showed that the anion **9a**$^-$ may be oxidized by ferricinium tetrafluoroborate to form a neutral V(IV) complex.



When $Li^+\mathbf{1c}^-$ was reacted with scandium trichloride in THF solution, the formation of the anionic tetracarbene complex **10c**$^-$ similar to **9a**$^-$ occurred. After complete substitution of $ScCl_3$ a fourth ligand coordinated at scandium, even when the molar ratio of the ligand to metal chloride was 3:1. Analogously, the anions **1b**$^-$ and **1d**$^-$ reacted to give the anionic tetracarbene complexes **10b**$^-$ and **10d**$^-$. Their compositions followed from the ^1H-, ^{13}C-, ^{11}B-NMR spectra and an X-ray structure analysis of $[Li(dme)_2]^+$ $[Sc(\mathbf{1c})_4]^-$, which confirms a tetrahedral arrangement of the anion.

$$ScCl_3 + 4\ Li^+\mathbf{1}^- \xrightarrow{L} [Li(L)_n]^+[Sc(\mathbf{1})_4]^- + 3\ LiCl$$

$[Li(L)_n]^+\mathbf{10}^-$

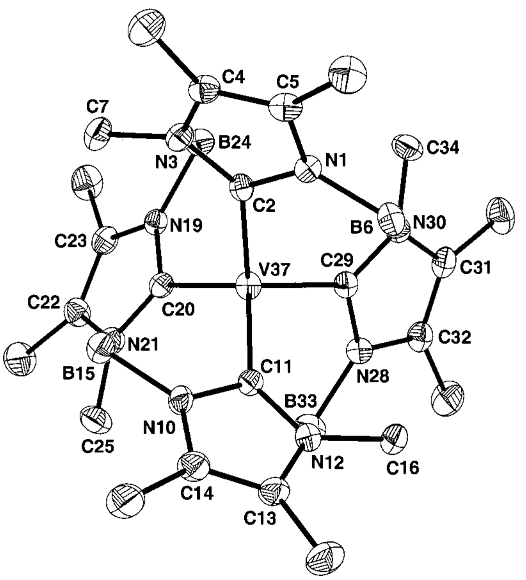


Fig. 1. Structure of the anion **9a**$^-$ in the crystal. The cation $[Li(NC_5H_5)_4]^+$ is omitted for clarity. Selected bond lengths (Å) and bond angles (°): V37–C 2.119–2.132(6), N1–C2 1.365(6) (1.354, average of all N1–C2 analogous bond lengths), C2–N3 1.357(7) (1.359), N3–C4 1.372(7) (1.390), C4–C5 1.343(8) (1.342), C5–N1 1.401(7) (1.392), N1–B6 1.566(8) (1.557); C2–V37–C11 95.9(2), C20–V37–C29 93.3(2), C2–V37–C20 116.3(2), C2–V37–C29 117.4(2), C11–V37–C20 120.3(2), C11–V37–C29 115.4(2), angle between least-square planes C2–V37–C11 and C29–V37–C20 87.5.

2.2. Structures of the metal complexes

The X-ray structure analysis of $[Li(NC_5H_5)_4]^+\mathbf{9a}^-$ (Fig. 1) shows the typical observations that can be made for imidazol-2-ylidene complexes. The vanadium atoms are coordinated in a pseudo tetrahedral geometry with two smaller (93.3, 95.5°) and four larger C–V–C angles (115.4–120.3°), the V–C bond lengths are almost identical (2.119–2.132 Å). The bond lengths and angles in the four ligands exhibit only small differences compared with the free carbene. Some angles and distances in the heterocycle N1,N3 are given. The N1–C2–N3 angle is slightly increased in the complex by 1.1° compared with that of **1a** (104.0°). Unfortunately, the boron hydrogen atoms could not be located. The V···B distances are between 3.20 and 3.31 Å. In the complex $V(\eta^1\text{-}BH_4)_2(dmpe)_2$ [8] V···B is 2.833(4) Å.

Fig. 2 shows the molecular structure of the anionic complex **10c**$^-$. The cell contains two independent anions and two $[Li(dme)_2]^+$ cations. The scandium atom is coordinated by four carbene ligands and has four Sc···H–B interactions with one hydrogen atom of each BH_3 group. This indicates that the scandium atom possesses an eight-fold coordination. The two planes of coordinating atoms (C1, C8, H2BC, H4BA and C15, C22, H1BA, H3BA) are nearly perpendicular (89.7°). A large increase of the tetrahedral angles C1–Sc–C8 and

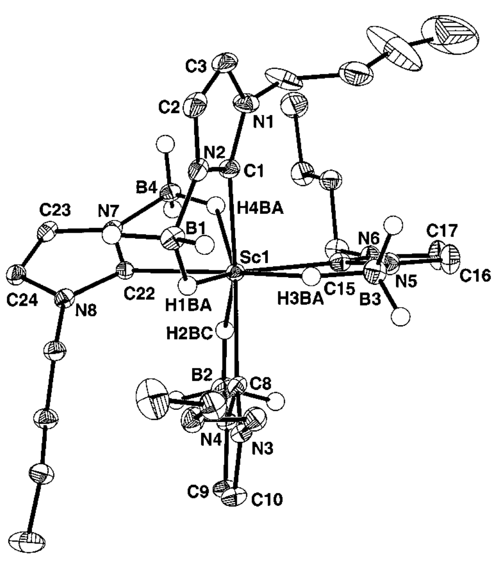


Fig. 2. Structure of the anion **10c**$^-$ in the crystal. The cation $[Li(dme)_2]^+$ and hydrogen atoms at carbon are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Sc–C 2.295–2.322(4), Sc–H_B 2.17–2.39(3), C1–Sc1–C8 142.3(1), C15–Sc1–C22 140.2(1), C29–Sc2–C36 142.9(2); C43–Sc2–C50 141.8(2), all other C–Sc–C angles between 93.3 and 98.7(2), angle between least-square planes C22–H1BA–H3BA–C15–Sc1 and C8–H2BC–H4BA–C1–Sc1 89.7.

C15–Sc–C22 allows the formation of four agostic B–H$\rightharpoonup$Sc interactions. This might prevent the heterocycles to rotate around the Sc–C axes. As a consequence the butyl groups are locked in pairs and the four-carbene ligands form a pseudo tetrahedral geometry. The Sc–C bond lengths are almost identical (2.295–2.322 Å). There are two large C–Sc–C angles (140.2–142.9°) in each anion and four C–Sc–C angles in the range from 93.3 to 98.7°. The bond lengths and angles in the four ligands exhibit only small differences compared with that of the ligand **1c**$^-$. The bridging hydrogen atoms (H1BA, H2BC, H3BA, H4BA) are involved in 3c,2e bonds with scandium (Sc···B 3.14–3.17 Å), the bond lengths Sc–H_B are between 2.17 and 2.39 Å. In the dicarbollide scandium hydride $[Cp^*(C_2B_9H_{11})ScH]_2[Li(thf)_n]_2$ the two anionic fragments are held together by two 3c,2e B–H$\rightharpoonup$Sc bonds (Sc–H_B 2.196, 2.173 Å) to give a remarkably unreactive dimer [9]. Shorter Sc–H_B [2.03(4) Å] and Sc···B [2.52(3) Å] bond lengths appear in the complex $[\{C_5H_3(SiMe_3)_2\}_2Sc(\mu\text{-}H)_2BH_2]$, and confirm the bidentate mode of BH_4 bonding [10]. A theoretical study of the coordination mode of BH_4 ligands (η^1, η^2 or η^3) in $Sc(BH_4)_3(PH_3)_2$ shows that the (η^2, η^3, η^3) structure is the most stable one, in agreement with experimental data. The structures (η^1, η^3, η^3), (η^2, η^3, η^3) and (η^3, η^3, η^3) are formally 18 electron complexes [11].

Our anion **10c**$^-$ is formally a 16e complex, which is a rare bonding situation for an early transition metal in an organometallic compound. In the organovanadium complex anion **9a**$^-$, only 10 VE are present. Because the boron hydrogen atoms could not be located, we will not speculate if any weak B–H···V interactions might be present. It is remarkable that the B···Sc distances in **10c**$^-$ (3.14–3.17 Å) are only slightly shorter than B···V (3.20–3.31 Å) in **9a**$^-$. The main differences between the two distorted tetrahedral anions are two large C–Sc–C angles and four smaller ones in **10c**$^-$, whereas in **9a**$^-$ two smaller C–V–C angles and four larger are present.

3. Conclusions

In this work, we report the synthesis of new metal complexes with anionic 3-borane-1-alkylimidazol-2-ylidene derivatives **1**$^-$. The formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2$**1a**$]$ and $[(\eta^5\text{-}C_7H_{11})Fe(CO)_2$**1a**$]$ as well as $[Cp_2Ti$**1a**$]$ demonstrate that the organolithium compounds $(L)Li^+$**1**$^-$ are suitable reagents to introduce anionic ligands **1**$^-$. However, in several cases reductions were observed, which avoided the formation of the desired products. Reaction of anions **1**$^-$ with VCl_3 and $ScCl_3$ did not stop at the neutral species, but led to anionic complexes. $[V($**1a**$)_4]^-$ and $[Sc($**1c**$)_4]^-$ are distorted tetrahedrons with a four- and eight-fold coordination, respectively. In addition to four Sc–C bonds there are four B–H$\rightharpoonup$Sc 3c,2e interactions. We do not know if B–H···M interactions function in the vanadium complex **9a**$^-$, however, they are active in the scandium compound **10c**$^-$.

4. Experimental

General: Reactions were carried out under dry Ar, 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 or AC 300 spectrometer, NMR references are $(CH_3)_4Si$ and $BF_3{\cdot}Et_2O$. IR spectra were recorded on a Bruker IFS 28 Fourier transformation spectrometer with CaF_2 cells. Mass spectra were obtained with a Finnigan MAT 8200 plus spectrometer using EI technique. Melting points (uncorrected) were obtained with a Büchi apparatus, using a capillary which was filled under Ar and sealed. $[CpFe(CO)_2X]$ [12], $[(C_7H_{11})Fe(CO)_3]^+BF_4^-$ [13], and $[VCl_3(thf)_3]$ [14] were prepared according to literature procedures. Solutions of the anion **1a**$^-$ were prepared from 3-borane-1,4,5-trimethylimidazole [2] which was deprotonated with *n*-butyllithium in THF at -40 °C and then allowed to warm to room temperature (r.t.).

4.1. 2-Lithium-3-borane-1-methylimidazole [(thf)Li**1b**]

To a solution of 1.18 g (14.4 mmol) of 1-methylimidazole in 40 ml of THF, 14.4 ml of BH_3·thf (1.0 M in THF) was added dropwise at −40 °C, after which the mixture was allowed to warm to r.t. and stirred for 24 h. The solvent was removed in vacuum to yield a colorless liquid adduct (1.32 g, 96%). ^{1}H-NMR (200.1 MHz, $CDCl_3$): $\delta = 3.66$ (s, 3H, N–CH_3), 6.64 (s, 1H, CH), 6.78 (s, 1H, CH), 7.69 (s, 1H, N=CH–N). ^{13}C-NMR (50.3 MHz, $CDCl_3$): $\delta = 35.1$ (N–CH_3), 121.1, 128.3 (C=C), 137.1 (N–C–N). ^{11}B-NMR (64.2 MHz, CD_2Cl_2): $\delta = -19.6$ (q, $^1J_{(B-H)} = 93$ Hz). Calc. for $C_4H_9BN_2$ (95.94): C 50.08, H 9.46, N 29.20. Anal. Found: C 49.70, H, 8.72, N 28.80%. Deprotonation of the adduct with BuLi in THF occurred at −40 °C, and evaporation of the solvent yielded crystalline (thf)Li**1b**.

4.2. Lithium-3-borane-1-butylimidazole [(thf)Li**1c**]

The same procedure as for preparation of [(thf)Li**1b**] was used by reacting 1.79 g (14.4 mmol) of 1-butylimidazole with 14.4 ml of BH_3·thf to give an oily residue which solidified slowly, m.p. 35–36 °C (1.85 g, 93%). ^{1}H-NMR (200.1 MHz, $CDCl_3$): $\delta = 0.87$ (t, $^3J_{(H-H)} = 7.2$ Hz, 3H, CH_3), 1.17–1.35 (m, 2H, CH_2–CH_3), 1.60–1.85 (m, 2H, $\mathit{CH_2}$–CH_2–CH_3), 3.86 (t, 2H, $^3J_{(H-H)} = 7.2$ Hz, NCH_2), 6.79 (s, 1H, CH), 7.00 (s, 1H, CH), 7.65 (s, 1H, N=CH–N). ^{13}C-NMR (50.3 MHz, $CDCl_3$): $\delta = 13.6$ (CH_3), 19.8 (CH_2–CH_3), 32.7 ($\mathit{CH_2}$–CH_2–CH_3), 48.6 (N–CH_2), 119.9, 128.2 (C=C). ^{11}B-NMR (64.2 MHz, CD_2Cl_2): $\delta = -19.1$ (q, $^1J_{(B-H)} = 95$ Hz). Calc. for $C_7H_{15}BN_2$ (138.0): C 60.92, H 10.96, N 20.30. Anal. Found: C 60.74, H, 10.91, N 19.95%. Deprotonation of the adduct with BuLi in THF led to a solution of Li**1c**.

4.3. 2-Lithium-3-borane-1-methylbenzimidazole [(thf)Li**1d**]

The same procedure as for preparation of [(thf)Li**1b**] was used by reacting 5.29 g (40.0 mmol) of 1-methylbenzimidazole with 40.0 ml of BH_3·thf to give a white solid, m.p. 105–106 °C (5.56 g, 95%). ^{1}H-NMR (200.1 MHz, $CDCl_3$): $\delta = 3.80$ (s, 3H, N–CH_3), 7.34 (m, 3H, benz), 7.84–7.88 (m, 1H, benz), 8.05 (s, 1H, N=CH–N). ^{13}C-NMR (50.3 MHz, $CDCl_3$): $\delta = 32.3$ (N–CH_3), 110.6, 117.7, 125.0, 125.4, 133.2, 137.5 (C_6H_4), 142.4 (N=C–N). ^{11}B-NMR (64.2 MHz, CD_2Cl_2): $\delta = -21.5$ (q, $^1J_{(B-H)} = 93$ Hz). Calc. for $C_8H_{13}BN_2$ (146.0): C 65.81, H 7.59, N 19.19. Anal. Found: C 65.34, H, 7.59, N 18.70%. Deprotonation of the adduct with BuLi in THF yielded a solution of Li**1d**.

4.4. Lithium (3-borane-1-methylimidazol-2-ylcarbonyl)-tetracarbonyl iron [(thf)$_3$Li$^+$**3b**$^-$]

To a suspension of 384 mg (4.0 mmol) of **1b** in 30 ml of THF was added 1.8 ml of *n*-butyllithium (2.5 N in hexane) dropwise at −40 °C. The mixture was allowed to warm to r.t. and stirred for 1 h. Then 0.6 ml of $Fe(CO)_5$ was added at −78 °C. The solution turned slowly red when it was allowed to warm to r.t. and stirred overnight. The largest part of the solvent was removed in vacuum and crystallization at −18 °C gave 1.64 g (80%) orange crystalls of [(thf)$_3$Li$^+$**3b**$^-$], m.p. 76–77 °C. ^{1}H-NMR (200.1 MHz, C_6D_6): $\delta = 1.36$ (m, 12H, THF), 3.38 (s, 3H, N–CH_3), 3.54 (m, 12H, THF), 5.57 (s, 1H, CH=), 6.65 (s, 1H, CH=). ^{13}C-NMR (50.3 MHz, C_6D_6): $\delta = 24.2$ (THF), 33.9 (CH_3), 66.8 (THF), 117.5, 123.7 (CH=CH), 151.8 (C–O), 216.8 (CO). ^{11}B-NMR (64.2 MHz, C_6D_6): $\delta = -20$ (br.). IR (THF); ν (cm^{-1}): 1912 (vs), 1929 (vs), 1949 (s), 2032 (s).

4.5. Lithium (3-borane-1-butylimidazol-2-ylcarbonyl)-tetracarbonyl iron [(thf)$_3$Li$^+$**3c**$^-$]

The same procedure as for preparation of [(thf)$_3$Li$^+$**3b**$^-$] was used by reacting 276 mg (0.20 mmol) of **1c**. After workup 1.09 g (98%) of red oily [(thf)$_3$Li$^+$**3c**$^-$] were obtained. ^{1}H-NMR (200.1 MHz, C_6D_6): $\delta = 0.71$ (t, $^3J_{(HH)} = 7.0$ Hz, 3H, CH_3), 0.95–1.06 (m, 2H, $\mathit{CH_2}$–CH_3), 1.25–1.45 (m, 14H, $\mathit{CH_2}$–CH_2–CH_3 + THF), 3.57 (m, 12H, THF), 4.29 (t, $^3J_{(HH)} = 7.0$ Hz, 2H, N–CH_2), 5.81 (s, 1H, CH=), 6.72 (s, 1H, CH=). ^{13}C-NMR (50.3 MHz, C_6D_6): $\delta = 13.6$ (CH_3), 19.8 (CH_2), 25.5 (THF), 33.4 (CH_2), 48.0 (N–CH_2), 68.2 (THF), 117.4, 125.0 (CH=CH), 218.1 (CO). ^{11}B-NMR (64.2 MHz, C_6D_6): $\delta = -18$ (br).

4.6. Lithium (3-borane-1-methylbenzimidazol-2-ylcarbonyl)tetracarbonyl iron [(thf)$_3$Li$^+$**3d**$^-$]

The same procedure as for preparation of [(thf)$_3$Li$^+$**3b**$^-$] was used by reacting 438 mg (0.30 mmol) of **1d**. After workup 1.34 g (79%) of orange crystals of [(thf)$_3$Li$^+$**3d**$^-$] were obtained, m.p. 93–94 °C. ^{1}H-NMR (200.1 MHz, CD_2Cl_2): $\delta = 1.75$ (m, 12H, THF), 3.66 (m, 12H, THF), 3.83 (s, 3H, N–CH_3), 7.37 (m, 3H, C_6H_4), 7.79–7.80 (m, 1H, C_6H_4). ^{13}C-NMR (50.3 MHz, CD_2Cl_2): $\delta = 25.7$ (THF), 31.4 (N–CH_3), 68.3 (THF), 110.7, 110.8, 117.4, 124.9, 125.0 (C_6H_4), 162.4 (C–O), 217.5 (CO). ^{11}B-NMR (64.2 MHz, CD_2Cl_2): $\delta = -24$ (br). IR (THF); ν (cm^1): 1914 (vs), 1931 (vs), 1952 (m), 2033 (s).

4.7. (3-Borane-1,4,5-trimethylimidazol-2-ylidene)-(cyclopentadienyl)dicarbonyliron (**5a**)

To a solution of 260 mg (2.1 mmol) of Li**1a** in 20 ml of THF 490 mg (1.9 mmol) [CpFe(CO)$_2$Br] was added at -35 °C and slowly warmed to r.t. yielding a brown suspension. After filtration the solvent was evaporated and the resulting solid extracted with toluene. This solution contained mainly of [CpFe(CO)$_2$]$_2$ and a small amount of **5a**. Most of it remained undissolved and was separated by filtration. The solid was washed with toluene and recrystallized from THF. Yield: 220 mg yellow powder (35%). ^{1}H-NMR (200.1 MHz, [D$_8$]-THF): $\delta = 1.73$ (s, 3H, C–CH$_3$), 2.13 (s, 3H, C–CH$_3$), 3.59 (s, 3H, N–CH$_3$), 5.17 (s, 5H, Cp). ^{13}C-NMR (50.3 MHz, [D$_8$]-THF): $\delta = 9.5$ (C–*C*H$_3$), 11.9 (C–*C*H$_3$), 35.1 (N–CH$_3$), 87.7 (Cp), 127.4 (C=*C*–N), 134.5 (C=*C*–N), 214.1 (CO), C2 not observed. ^{11}B-NMR (64.2 MHz, C$_6$D$_6$): $\delta = -17.2$ (q, $^1J_{(B-H)} = 79$ Hz). IR (THF); ν (cm^{-1}): 1975 (s), 2035 (vs). EIMS; *m/z* (%): 123 (100) [C$_6$H$_{12}$BN$_2$]$^+$.

4.8. (2,4-Dimethylpentadienyl)dicarbonylironbromide

The bromide was prepared following a procedure for the synthesis of the iodine compound [4], using 580 mg (1.8 mmol) [(C$_7$H$_{11}$)Fe(CO)$_3$]$^+$BF$_4^-$ and 260 mg (2.5 mmol) NaBr. Yield: 200 mg dark red needles (39%). ^{1}H-NMR (300.1 MHz, C$_6$D$_6$): $\delta = 0.33$ (br, 2H, C1,5-H$_{endo}$), 1.75 (br, 8H, C1,5-H$_{exo}$ + C–CH$_3$), 5.82 (br, 1H, C3–H). ^{13}C-NMR (75.5 MHz, C$_6$D$_6$): $\delta = 26.4$ (C–*C*H$_3$), 55 (br, C1,5), 97.0 (C3), 129.3 (C2,4), CO not observed. IR (toluene); ν (cm^{-1}): 2001 (s), 2031 (s). EIMS; *m/z* (%): 286 (4) [M]$^+$, 258 (38) [M − CO]$^+$, 230 (100) [M − 2CO]$^+$, 95 (76) [C$_7$H$_{11}$]$^+$.

4.9. (3-Borane-1,4,5-trimethylimidazol-2-ylidene)-(2,4-dimethylpentadienyl)dicarbonyliron (*6a*)

4.9.1. Compound *6a* from [(C$_7$H$_{11}$)Fe(CO)$_2$Br]

A solution of 494 mg (4.0 mmol) of Li**1a** in 20 ml of THF was slowly added to 1.13 g (3.9 mmol) [(C$_7$H$_{11}$)Fe(CO)$_2$Br], dissolved in 30 ml of THF at -30 °C. The mixture was allowed to warm to r.t. and stirred for 1 h after which a brown solution is obtained. The solvent was removed in vacuum, the remaining solid extracted with toluene and filtered. The product was recrystallized from a toluene–hexane mixture at -30 °C. Yield: 420 mg brown solid (33%). ^{1}H-NMR (300.1 MHz, THF-d_8): $\delta = 0.89$ (t, 2H, C1,5$_{\rm pdl}$-H$_{\rm endo}$), 1.23 (s, 3H, C$_{\rm Im}$–CH$_3$), 2.05 (s, 2H, C1,5$_{\rm pdl}$-H$_{exo}$), 2.12 (s, 6H, C$_{\rm pdl}$–CH$_3$), 2.25 (s, 3H, C$_{\rm Im}$–CH$_3$), 3.43 (s, 3H, N–CH$_3$), 5.39 (s, 1H, C3$_{\rm pdl}$–H). ^{13}C-NMR (75.5 MHz, THF-d_8): $\delta = 8.3$, 10.7 (C$_{\rm Im}$–*C*H$_3$), 28.8 (C$_{\rm pdl}$–*C*H$_3$), 31.2 (N–CH$_3$), 43.8 (C1,5$_{\rm pdl}$), 94.8 (C2,4$_{\rm pdl}$), 104.7 (C3$_{\rm pdl}$), 123.9, 130.4 (C=*C*–N), 144.4 (N–C–N), 212.5 (CO). ^{11}B-NMR (96.2 MHz, C$_6$D$_6$): $\delta = -22$ (br). IR (toluene); ν (cm^{-1}): 1963 (s), 2037 (vs). EIMS; *m/z* (%): 316 (1) [M − BH$_3$]$^+$, 302 (6) [M − CO]$^+$, 288 (14) [M − BH$_3$ − CO]$^+$, 274 (35) [M − 2CO]$^+$, 260 (100) [M − BH$_3$ − 2 CO]$^+$, 207 (12) [M − C$_6$H$_{12}$BN$_2$]$^+$, 123 (23) [C$_6$H$_{12}$BN$_2$]$^+$.

4.9.2. Compound *6a* from [(C$_7$H$_{11}$)Fe(CO)$_3$]$^+$ BF$_4^-$

To a solution of 420 mg (3.4 mmol) of Li**1a** in 20 ml of THF a suspension of 1.10 g (3.4 mmol) [(C$_7$H$_{11}$)Fe(CO)$_3$]$^+$BF$_4^-$ in 30 ml of THF was added at -30 °C. After slowly warming to r.t. and stirring, a brown solution was formed. The solvent was removed in vacuum and the remaining solid extracted with toluene. After filtration most of the toluene was removed, hexane added and **6a** obtained at -30 °C. Yield: 470 mg brown solid (42%), analytical data see above.

4.10. (3-Borane-1,4,5-trimethylimidazol-2-ylidene)-bis(cyclopentadienyl)titanium (*7a*)

A solution of Cp$_2$TiCl was prepared by stirring 1.00 g (4.0 mmol) of Cp$_2$TiCl$_2$ with 1.20 g (18.5 mmol) of zinc dust in 50 ml of THF for 10 h. Following filtration, a solution of 500 mg (4.0 mmol) of Li**1a** in 20 ml of THF was added at -78 °C. During this procedure the solution turned dark blue and after slowly warming to r.t., a brown solution was formed. The solvent was removed in vacuum and the remaining solid extracted with toluene. After filtration, a blue violet solution was obtained, hexane was added and the mixture left for crystallization at -30 °C. Yield: 940 mg blue violet microcrystalline solid (78%). ^{11}B-NMR (96.2 MHz, C$_6$D$_6$): $\delta = -25$ (br). EIMS; *m/z* (%): 301 (40) [M]$^+$, 287 (10) [M − BH$_3$]$^+$, 178 (47) [Cp$_2$Ti]$^+$, 123 (31) [C$_6$H$_{12}$BN$_2$]$^+$, 110 (100) [C$_6$H$_{10}$N$_2$]$^+$. HREI; *m/z*: 301.1359. Calc. for C$_{16}$H$_{22}$BN$_2$Ti: 301.1356 (Δ mmu 0.3).

4.11. Lithium-tetrakis(pyridin) tetrakis(3-boran-1,4,5-trimethylimidazol-2-ylidene)vanadium [Li(py)$_4$*9a*]

A solution of 1.00 g (8.1 mmol) of Li**1a** in 20 ml of THF was slowly added to a solution of 1.01 g (2.7 mmol) [VCl$_3$(thf)$_3$] in 40 ml of THF at -78 °C. After the addition the solution turned deep violet. The mixture was slowly warmed to r.t. and stirred for 5 h. The solvent was removed in vacuum and the remaining solid extracted with toluene. [Li(py)$_4$**9a**] crystallized from a THF–Py–hexane mixture at 0 °C. Yield: 1.24 g dark red needles (56%). ^{11}B-NMR (96.2 MHz, C$_6$D$_6$): $\delta = -19.9$ (q, $^1J_{(B-H)} = 94$ Hz).

4.12. Lithium-bis(dimethoxiethane) tetrakis(3-boran-1-methylimidazol-2-ylidene)scandium [Li(dme)$_2$*10b*]

To a solution of 768 mg (8.0 mmol) of 3-borane-1-methylimidazole in 40 ml of THF 3.20 ml of butyllithium (2.5 N in hexane) was added dropwise at -78 °C. The mixture was allowed to warm to r.t. and stirred for 1 h. Then 301 mg (2.0 mmol) of anhydrous scandium chloride was added at −78 °C and the mixture was warmed to r.t. and stirred for 48 h to give a light yellow solution. The solvent was removed in vacuum and the remaining solid was extracted with 50 ml of toluene. Removing the solvent in vacuum and recrystallization in DME–toluene at −18 °C gave 841 mg (57%) of [Li(dme)$_2$**10b**], m.p. 65–68 °C. ^{1}H-NMR (200.1 MHz, CD_2Cl_2): $\delta = 3.28$ (s, 6H, dme), 3.62 (s, 4H, dme), 3.73 (s, 3H, N–CH_3), 6.47 (s, 1H, CH), 6.53 (s, 1H, CH). ^{13}C-NMR (50.3 MHz, CD_2Cl_2): $\delta = 34.9$ (N–CH_3), 58.9 (dme), 72.0 (dme), 121.4 (CH), 127.8 (CH), N–C–N not observed. ^{11}B-NMR (64.2 MHz, CD_2Cl_2): $\delta = -18$ (br).

4.13. *Lithium-bis(dimethoxiethane) tetrakis(3-borane-1-butylimidazol-2-ylidene)scandium [Li(dme)$_2$**10c**]*

The same procedure as for preparation of [Li(dme)$_2$**10b**] was used by reacting 714 mg (5.16 mmol) of 3-borane-1-butylimidazole with 2.20 ml (5.50 mmol) of butyllithium (2.5 N in hexane) and 260 mg (1.72 mmol) of $ScCl_3$. Crystallization from a mixture of dme and toluene at −18 °C yielded 573 mg (48%) of [Li(dme)$_2$**10c**], m.p. 45–47 °C. ^{1}H-NMR (200.1 MHz, CD_2Cl_2): $\delta = 0.79$, (t, $^3J_{(HH)} = 7.2$ Hz, 3H, CH_3), 1.14 (m, 2H, *CH_2*–CH_3), 1.39 (m, 2H, *CH_2*–CH_2–CH_3), 3.29 (s, 18H, CH_3 of dme), 3.47 (s, 12H, CH_2 of dme), 4.02 (t, $^3J_{(HH)} = 7.2$ Hz, 1H, N–CH_2), 6.52 (s, 1H, CH), 6.60 (s, 1H, CH). ^{13}C-NMR (50.3 MHz, CD_2Cl_2): $\delta = 14.1$ (C–CH_3), 20.4 (*CH_2*–CH_3), 33.9 (*CH_2*–CH_2–CH_3), 49.2 (N–CH_2), 59.1 (CH_3 in dme), 71.8 (CH_2 in dme), 117.2 (CH), 122.5 (CH), N–C–N not observed. ^{11}B-NMR (64.2 MHz, CD_2Cl_2, B{H}): $\delta = -17.6$.

Table 1
Crystal data and structure refinement parameters for [Li(py)$_4$**9a**] and [Li(dme)$_2$**10c**]

	[Li(py)$_4$**9a**]	[Li(dme)$_2$**10c**]
Empirical formula	$C_{59}H_{83}B_4LiN_{15}V$	$C_{47}H_{94}B_4N_8O_6$-LiSc
Formula weight	1103.52	962.44
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$Pna2_1$
Unit cell dimensions		
a (Å)	13.3342(6)	44.815(3)
b (Å)	18.2483(5)	12.4845(9)
c (Å)	13.3115(6)	21.271(2)
β (°)	93.775(3)	90
V (Å^3)	3232.0(2)	11901(1)
Z	2	8
$D_{calc.}$ (g cm^3)	1.134	1.074
Adsorption coefficient (mm^{-1})	0.201	0.171
F(000)	1176	4192
Crystal size (mm)	0.25·0.18·0.13	0.70·0.43·0.20
Θ-Range (°)	3.34–36.35	2 – 25
Index ranges	$0 \le h \le 22$, $0 \le k \le 26$, $-21 \le l \le 21$	$0 \le h \le 53$, $0 \le k \le 14$, $-24 \le l \le 25$
Number of reflections unique	11 884	19 500
Number of reflections observed [$I > 2\sigma(I)$]	6029	14 074
Parameters	710	1276
Final R indices R_1 [$I > 2\sigma(I)$]	0.088	0.059
wR_2	0.263	0.162
Largest differential peak and hole (e Å^3)	0.37 and −0.34	0.48 and −0.36

4.14. *Lithium-tetrakis(tetrahydrofurane) tetrakis(3-borane-1-methylbenzimidazol-2-ylidene)-scandium [Li(thf)$_4$**10d**]*

The same procedure as for preparation of [Li(dme)$_2$**10b**] was used by reacting 292 mg (2.00 mmol) of 3-borane-1-methylbenzimidazole with 0.80 ml (2.00 mmol) of butyllithium (2.5 N in hexane) and 76 mg (0.50 mmol) of $ScCl_3$. Crystallization from a mixture of toluene and THF at −18 °C yielded 314 mg (68%) of [Li(thf)$_4$**10d**], m.p. 54–56 °C. ^{1}H-NMR (200.1 MHz, CD_2Cl_2): $\delta = 1.71$ (m, 16H, THF), 3.56 (m, 16H, THF), 3.91 (s, 3H, N–CH_3), 6.24–6.54 (m, 2H, C_6H_4), 7.03–7.22 (m, 2H, C_6H_4). ^{13}C-NMR (50.3 MHz, CD_2Cl_2): $\delta = 25.7$ (THF), 34.4 (N–CH_3), 68.3 (THF), 109.5, 115.6, 122.7, 125.5, 128.4, 129.2 (C_6H_4). ^{11}B-NMR (64.2 MHz, CD_2Cl_2, B{H}): $\delta = -19.0$.

4.15. *Crystal structure determination of [Li(py)$_4$**9a**] and [Li(dme)$_2$**10c**] (see Section 5)*

Crystal data and details of the structure determinations are listed in Table 1. Intensity data were collected for [Li(py)$_4$**9a**] with a Nonius Kappa CCD (Mo–K$_\alpha$-radiation, $T = 293$ K), for [Li(dme)$_2$**10c**] with a Bruker AXS CCD diffractometer (Mo–K$_\alpha$-radiation, $T = 190$ K). Structures were solved by direct methods and refined by least-squares based on F^2. Hydrogen atoms in [Li(py)$_4$**9a**] were inserted in calculated positions, while in [Li(dme)$_2$**10c**] they were located and refined isotropically.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 171658–171661 for compounds [(thf)$_3$Li$^+$**3b**$^-$], [(thf)$_3$Li$^+$**3d**$^-$], [Li(py)$_4$**9a**] and [Li(dme)$_2$**10c**], respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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