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$$\Delta_{\varphi\varphi^*}E^{(2)} = -2\frac{(\langle\varphi|h^F\varphi*\rangle)^2}{\varepsilon_{\varphi*} - \varepsilon_{Gf}} \qquad (3)$$

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A Homoleptic Carbene–Lithium Complex[**]

Robert Fränkel, Christine Birg, Ulrich Kernbach,
Tassilo Habereder, Heinrich Nöth, and
Wolf P. Fehlhammer[*]

The coordination chemistry of N-heterocyclic carbenes was given great impetus by the isolation of stable, free species by Arduengo.[1] Since then carbene complexes of nearly all the metals of the periodic table have been synthesized and studied in detail.[2, 3] As strongly nucleophilic two-electron donors the N,N-carbenes even form stable complexes with metals that normally show no tendency for π back-donation. Thus, a few years ago, Arduengo et al. were able to prepare a series of carbene complexes from the elements of Group 2.[4] However, to date there are very few examples of carbene complexes with Group 1 metals;[5–8] this is surprising as for the formation of "free" carbenes from the corresponding formamidinium and imidazolinium salts, even by the ammonia method of Herrmann et al.,[9] alkali metal containing bases such as KO*t*Bu, NaH, or lithiumdiisopropylamide are used in stoichiometric amounts as deprotonating agents. Thus, knowledge of the interactions between carbenes and alkali metals is essential for the understanding of the reactivity and properties of these complexes in solution.

In 1995 we were able to synthesize, for the first time, an Fe^{III} complex of the monoanionic, tridentate hydrotris(3-methyl-

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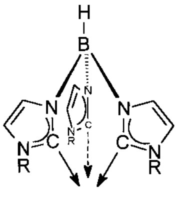
[*] Prof. Dr. W. P. Fehlhammer, Dr. U. Kernbach
Deutsches Museum
Museumsinsel 1, 80306 München (Germany)
Fax: (+49) 89-2179-425
E-mail: wpf@deutsches-museum.de

Dipl.-Chem. R. Fränkel, Dr. C. Birg, Dr. T. Habereder,[+]
Prof. Dr. H. Nöth[+]
Department Chemie der Ludwig-Maximilians-Universität München
Butenandtstrasse 5–13 (Haus D), 81377 München (Germany)

[+] X-ray analysis

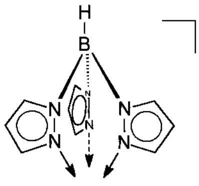
[**] Homoleptic carbene complexes part 10. This work was supported by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and by the Studienstiftung des Deutschen Volkes. Part 9 ref. [14].

imidazolin-2-ylidene)borate carbene ligand (**1**; TRIS^{Me}),[10] which has a topology analogous to that of the known tris(pyrazolyl)borate (**2**; Tp) [11] of Trofimenko.



R = Me, Et

1



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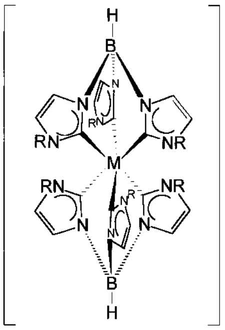
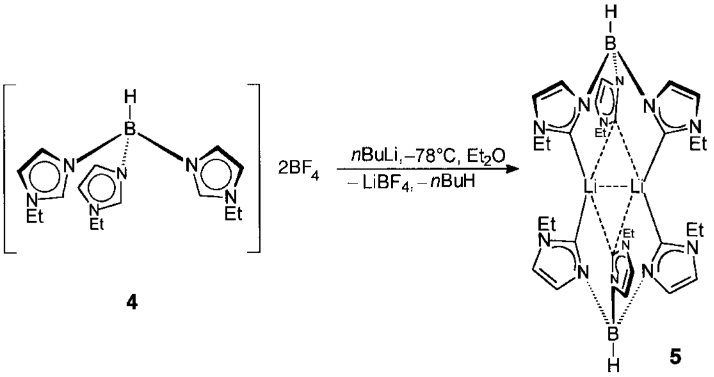


M / R	Fe	Co
Me	**3a**	**3b**
Et	**3c**	**3d**

Further Fe^{III}, Co^{III}[12] (**3**), and Re^{VII} complexes[13] with this ligand, as well as the corresponding ethyl derivate hydrotris(3-ethylimidazolin-2-ylidene)borate (TRIS^{Et}), were reported recently. In the synthesis of these compounds the "free" monoanionic carbenes (TRIS^R), formed in situ from the corresponding hydrotris(3-alkylimidazolium)borate tetrafluoroborates by deprotonation with *n*BuLi, were treated directly with the corresponding metallic precursor. We have always assumed that these syntheses proceed via saltlike lithium carbene intermediates. Recently we have concentrated on isolating such intermediates, whereby the possible uses of the TRIS^R ligands should be considerably broadened as *n*BuLi residues in the "in situ reaction mixture" frequently led to undesired side reactions. Deprotonation experiments with less aggressive amides (NaN(SiMe$_3$)$_2$) or oxo bases (KO*t*Bu) resulted in substitution reactions at the boron center, just as in the preparation of the bidentate bis(3-alkylimidazolin-2-ylidene)dihydroborate ligands[14] reported recently. However, no reaction occurred in a two-phase system with NaH and a catalytic amount of KO*t*Bu. On the other hand if **4**, suspended in diethylether, is deprotonated with *n*BuLi at −78 °C then LiTRIS^{Et} (**5**) precipitates in high yield, together with LiBF$_4$, [Eq. (1)]; thus it is easily separated from excess base and can be reacted further in polar solvents.



4 **5** (1)

The isolated almost colorless material is extremely moisture sensitive and decomposes slowly at room temperature turning yellow even under an inert atmosphere. At −30 °C, however, the substance can be kept for months without losing any of its reactivity.

Single crystals of the hexacarbene dilithium complex **5**, suitable for X-ray diffraction, were obtained by cooling a saturated diethyl ether solution to −30 °C.[15] The most surprising feature in the molecular structure of **5** is the unusual solvent-free complexation of each lithium atom by four carbene carbon atoms (Figure 1).[16, 17] This arrangement comes about by the terminal binding to the lithium centers of two carbon atoms (C3 (C3A), C7 (C7A)) from each hydrotris(3-ethylimidazolin-2-ylidene)borate anion while the third carbene carbon atoms (C4, C4A) adopt a bridging mode of coordination. At 68.2(2)° the Li1-C4-Li1A angle in the central Li$_2$C$_2$ four-membered ring is very similar to the corresponding angle (67.4(1)°) in the phenyl-bridged dimer [{Li(Ph)tmeda}$_2$].[18, 19] The LiC$_4$ coordination geometry is highly twisted forming a tetrahedron that is "flattened on one side": the C4A-Li1-C4 angle of 111.8(2)° approaches the ideal tetrahedral angle, the C7-Li1-C4 angle (92.7(2)°) is compressed, and the C3A-Li1-C7 angle (140.3(2)°) is greatly expanded. The planes of the bridging rings are almost perpendicular

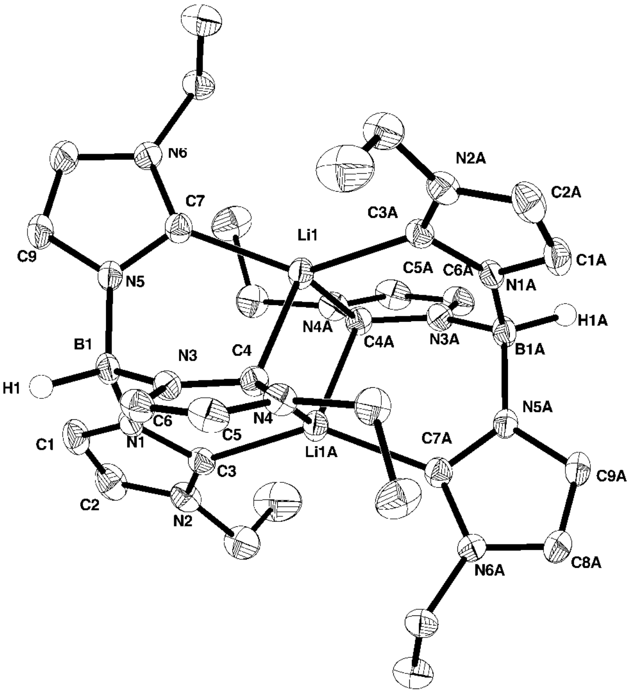
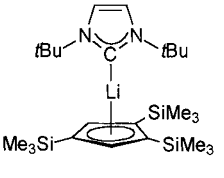
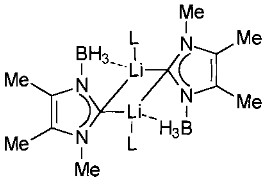


Figure 1. Molecular structure of **5** (for clarity the carbon-bound hydrogen atoms are omitted). The thermal ellipsoids are set at the 30% level. Selected bond lengths [Å] and angles [°]: N-C(carbene) 1.361(3) – 1.370(3), (C=C)-N 1.373(3) – 1.388(3), C=C 1.331(4) – 1.336(4), N-B 1.545(3) – 1.553(4); N-C(carbene)-N 103.7(2) – 103.8(2), C7-Li1-C3A 140.3(2), C7-Li1-C4 92.7(2), C4A-Li1-C4 111.8(2), Li1-C4-Li1A 68.2(2), N-B-N 110.4(2) – 111.6(2).

(93.8°) to the plane determined by Li1, C4, (C4A), and Li1A. The Li–C bonds to the terminal carbene atoms are 2.138(4) and 2.147(4) Å and thus resemble those in 1,2,4-tris(trimethylsilyl)cyclopentadienyl-[1,3-di(*tert*-butyl)imidazolin-2-ylidene]lithium (**6**; 2.155(4) Å).[6] In aryllithium compounds the terminal Li–C bonds are usually around this length.[20, 21] The two bonds to the bridging carbon atoms C4 (C4A) are significantly longer (2.201(4) and 2.311(4) Å, respectively) and of strikingly different length to each other. In the carbene-bridged dimeric [3-borane-(1,4,5-trimethylimidazolin-2-ylidene)]lithium (**7**) the Li-μ-C bonds (2.169(5) and 2.339(5) Å) vary even more.[8]

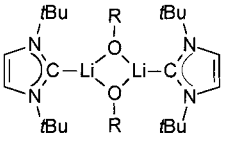


6



L = THF

7



R = 2,4,6-Me$_3$C$_6$H$_2$

8

Arduengo and Tamm have investigated the structural influence of the Lewis acid Li$^+$ on a neutral N,N-heterocylic carbene. The comparison of the free and coordinated carbene in **8** shows that neither the N–C(carbene) bond lengths nor the N-C(carbene)-N angle are influenced by the Li cation.[5a, 22] However, on coordination to a transition metal both opening of the N-C-N angle from 101–102° to 103–105° and a slight shortening of the N–C(carbene) bond compared to that in the free N-heterocylic carbene have been discussed.[1, 2] The comparison of **5** (103.7(2)–103.8(2)°; 1.361(3)–1.370(3) Å) with the hexacarbene complex **3** that we have studied by X-ray diffraction[10, 12] (104.5(4)–106.1(4)°; 1.345(6)–1.378(6) Å) shows that the differences here lie within 3σ; nor do other bond lengths, for example, those in the ring, show significant differences between **5** and the hexacarbene transition metal complexes **3**. However, there are significant differences when the data are compared to those of the crystal structure of the trisimidazolinium salt **4**.[23–26]

In the ^{1}H NMR spectrum of **5** ([D$_3$]acetonitrile) the resonance signals arising from the ring protons appear as two doublets at $\delta = 6.91$ and 7.05 and are thus shifted significantly to higher field than the corresponding resonances in **4** ($\delta = 7.55$ and 7.83). The signal arising from the acidic H atom at C2 in **4** ($\delta = 8.86$) has disappeared.

In the room-temperature ^{13}C NMR spectrum the resonance signal for the carbene carbon atom is missing. This effect can be attributed to signal broadening as a result of the exchange processes commonly observed in organolithium complexes. A low-temperature measurement could not shed any more light on this problem. In the spectrum recorded at 65 °C for a concentrated sample however, the averaged signal for the C2 carbon atom was observed in the expected region ($\delta = 191.8$). The solutions show no decomposition even after several weeks at 0 °C, an observation that Arduengo[27] also made for free carbenes.[6, 7]

Experimental Section

5: Under Argon a suspension of **4**[12] (500 mg, 1.06 mmol) in diethyl ether (5.0 mL) at −78 °C was treated with a solution of *n*BuLi in hexane (1.6 M, 3.17 mmol; 1.98 mL). The reaction mixture was stirred for 2 h and at the same time allowed to warm slowly to room temperature. The almost colorless solid, a mixture of **5** and LiBF$_4$, was collected on a D4-sinter. Extraction of the solid with diethyl ether (3 × 10 mL), concentration of the solution to about half the original volume, and cooling to −30 °C afforded pure **5** as colorless prismlike crystals. ^{1}H NMR (400 MHz, CD$_3$CN, 25 °C): $\delta = 1.38$ (q, 18H; CH$_3$), 4.00 (t, 12H; CH$_2$), 6.91 (d, 6H; CH), 7.05 (d, 6H; CH); ^{13}C NMR (68 MHz, CD$_3$CN, 65 °C): $\delta = 15.7$ (CH$_3$), 41.7 (CH$_2$), 119.0 (CH), 128.3 (CH), 191.8 (C2); ^{7}Li NMR (155 MHz, CD$_3$CN, 25 °C): $\delta = 2.56$ (s); IR (KBr): $\tilde{\nu} = 3064$, 2982 (C–H), 2479 (B–H), 1560, 1543, 1146 cm^{-1}.

The solid mixture of **5** and LiBF$_4$ collected by filtration (see above) is completely soluble in THF and can be used in this form for the preparation of metal complexes.[12]

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[16] Of the isomeric tris(pyrazolyl)borates (Tp)[11] that have been studied extensively to date, only one lithium compound phenyltris(3-*tert*-butylpyrazolyl)boratolithium has been characterized by X-ray crystallography. Because of the sterically demanding substituents a dimer is not formed, instead the cation exists as a LiTp species coordinated by three N groups.[17a] The isoelectronic compound tris(pyrazolyl)-methanelithiumtetrahydroborate [{HC(3,5-Me$_2$pz)$_3$}Li(η^3-BH$_4$)] is also a monomer.[17b]

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[23] Suitable crystals of **4** could be obtained from a saturated toluene solution at −30 °C.[24]. The endocyclic N-C(carbene)-N angles (between 109.8(4) and 110.9(4)°) lie in the range typical for imidazolinium salts and are clearly larger than the corresponding values for **5** (103.7 ± 1°). A second significant difference concerns the N-C(carbene) bonds in the carbene complex **5** (1.361(3) to 1.370(3) Å) which are clearly longer than the corresponding bonds in the imidazolinium precursor **4** (1.318(5)–1.328(5) Å); apart from these the bonding parameters differ only slightly.[1, 25, 26]

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Domino Hydroformylation/Knoevenagel/Hydrogenation Reactions**

Bernhard Breit* and Stephan K. Zahn

Dedicated to Professor Barry M. Trost
on the occasion of his 60th birthday

Efficient synthetic transformations are those forming new carbon–carbon bonds with complete control of chemo-, regio-, and stereoselectivity.[1] Reactions in accord with the criteria of atom economy are particularly useful.[2] In this context, the industrially important hydroformylation of olefins would be an ideal transformation if selectivity, in particular stereoselectivity, could be controlled.[3] We recently devised one solution to this problem by making more efficient use of substrate control with the aid of a substrate-bound catalyst-directing group.[4]

Although the hydroformylation of a carbon–carbon double bond introduces the preparatively useful aldehyde functionality, in terms of synthetic efficiency the reaction suffers from the fact that it provides only a one carbon chain elongation. One way to overcome this deficiency could be to incorporate this reaction as a key step in a domino-type process.[5, 6] In this context we recently developed a domino hydroformylation/Wittig olefination protocol.[7] In an extension of this study we herein report on the first domino hydroformylation/Knoevenagel reaction/hydrogenation process of acyclic olefinic substrates, which occurs with concomitant control of regio- and stereoselectivity and, additionally, provides useful building blocks for polyketide synthesis.

When the methallyl *ortho*-diphenylphosphanylbenzoate (±)-**1** was subjected to hydroformylation conditions in the presence of 1.5 equivalents of dimethylmalonate and 0.3 equivalents of piperidinium acetate (Scheme 1), the substituted malonate (±)-**2** could be isolated in satisfactory yield and with good diastereoselectivity (*syn*/*anti* 96:4, Table 1, entry 6). Malonate (±)-**2** is obviously the final product of a sequential domino hydroformylation/Knoevenagel reaction/

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[*] Prof. Dr. B. Breit, Dipl.-Chem. S. K. Zahn
Organisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
Fax: (+49) 6221-54-4205
E-mail: bernhard.breit@urz.uni-heidelberg.de

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