Contributions to the Chemistry of Boron, 223[1]

Hetero-*ansa*-Bridged Main Group Metallocenes – a Structural and NMR Study

Ralf Littger, Nils Metzler, Heinrich Nöth*, and Matthias Wagner

Institute of Inorganic Chemistry, University of Munich,
Meiserstraße 1, D-80333 München, Germany

Received March 24, 1994

Key Words: Diborane(4) dianion, 1,2-bis(dimethylamino)-1,2-di-9-fluorenyl- / Li, Na, K, Cs salts / Ca, Ba salts / Main group metallocenes / Hetero-*ansa*-bridged metallocenes

1,2-Bis(dimethylamino)-1,2-di-9-fluorenyldiborane(4) (**1**) is doubly metallated with group 1 and 2 metals to yield metal 1,2-bis(dimethylamino)-1,2-di-9-fluorenyldiborate(4) **2**-Li to **2**-Ba. The conformations of these compounds in solution are investigated by NMR spectroscopy, and the solid-state structures of **2**-Li · 5 THF, **2**-K · 4 THF, **2**-K · 2 DME, and **2**-Ca · 2 THF are determined by X-ray diffraction. All four structures can be described as main group metallocenes. The potassium derivatives form contact ion pairs, leading to polymeric chain-like structures. In contrast, **2**-Li · 5 THF exhibits the rare combination of a contact ion pair with a solvent-separated ion pair, giving the monomeric structure $[Li(THF)_4][(fl_2B_2(NMe_2)_2)Li \cdot THF]$. **2**-Ca · 2 THF, which is also monomeric, adapts a severely distorted geometry.

Organolithium compounds and Grignard reagents are among the most frequently used and intensely studied compounds in organic and organometallic chemistry[2,3]. Much less is known about the structures and chemistry of organometallic compounds of the heavier group 1 and 2 metals. Due to their extreme reactivity a detailed investigation of their structures and coordination chemistry has started only recently[2,4,5].

In the course of our investigations of diborane(4) derivatives, we studied the solution and solid-state structures of alkali and alkaline earth metal salts of difluorenyldiborane(4)[6,7] in order to obtain information about possible B–C-π interaction. However, these compounds proved to be suitable starting materials for new heterocycles[8]. In this paper, we report on the synthesis, crystal structures and NMR-spectroscopic properties of metal 1,2-bis(dimethylamino)-1,2-di-9-fluorenyldiborate(4) compounds $M_x(fl)_2B_2(NMe)_2$, where M is an alkali ($x = 2$) or an alkaline earth metal ($x = 1$, fl = 9-fluorenyl). We suggest to name this new class of compounds (**2**) hetero-*ansa*-bridged, since in contrast to most previously described organometallic compounds, the *ansa*-bridge is not a carbon chain but a diborane(4) moiety. After presentation of the crystal structures, the NMR data will be discussed in terms of probable structures in solution as well as of boron-carbon π bonding. To our knowledge, this paper is the first systematic study on *ansa*-bridged main group organometallic compounds.

Formation and Characterization of Bis(dimethylamino)difluorenyldiborane(4) Anions 2

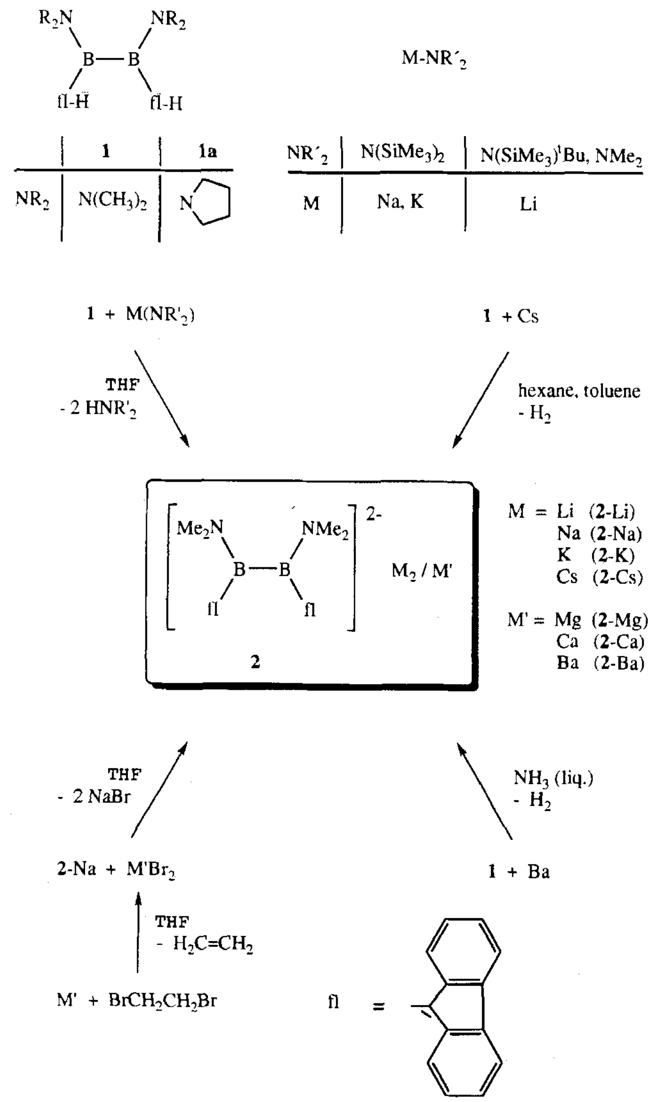
The synthesis and spectroscopic properties of 1,2-bis(dialkylamino)-1,2-di-9-fluorenyldiborane(4) derivatives with dimethylamino (**1**) and pyrrolidinyl (**1a**) groups attached to the boron atoms as well as the X-ray single crystal structure of **1a** have been described before[9]. In a dianion of **1**, the negative charge is delocalized not only on the fluorenyl rings, but also in a p orbital on the boron atom. Consequently, **1** can easily be deprotonated to yield compounds **2**, which are the subject of this study.

Deprotonation of **1** with alkali metal (M) amides in tetrahydrofuran (THF) yields pure **2**-Li, **2**-Na, and **2**-K after removal of the solvent and washing of the residue with hexane. **2**-Cs can more easily be prepared from **1** and Cs metal in hexane/THF. All these compounds were characterized by NMR spectroscopy (^1H, ^7Li, ^{11}B, and ^{13}C). For **1**-Li · 5 THF, **2**-K · 4 THF, and **2**-K · 2 DME (DME = 1,2-dimethoxyethane) the solid-state structure was determined by single-crystal X-ray diffraction in order to elucidate the molecular geometry of the hetero-*ansa*-bridging ligand and the coordination sphere of the metal atoms.

Alkaline earth metal (M′) compounds **2**-Mg, **2**-Ca, and **2**-Ba were obtained by reaction of **2**-Na with freshly prepared $M'Br_2$ solutions (from M′ metal and 1,2-dibromoethane in THF). **2**-Na proved to be the most suitable starting material for these metathesis reactions due to the insolubility of the resulting NaBr in THF. **2**-Ba, however, was accessible in analogy to $Bafl_2$[10] by reaction of **1** with Ba metal in liquid ammonia. **2**-Mg proved to be fairly insoluble and could not be further characterized, but the constitution of **2**-Ca and **2**-Ba in solution was elucidated by NMR spectroscopy. Furthermore, the solid-state structure of **2**-Ca · 2 THF was determined by a single-crystal X-ray diffraction analysis.

0009–2940/94/1010–1901 $ 10.00+.25/0

Scheme 1



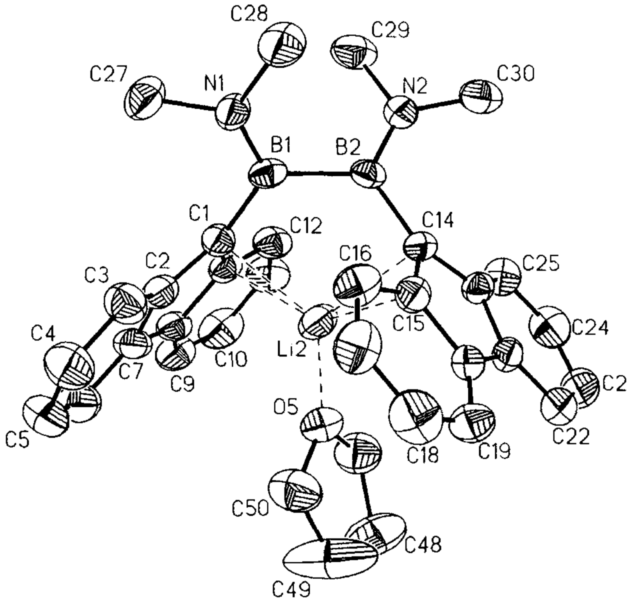


Figure 1. ORTEP plot of 2-Li, 25% probability, H atoms and Li(THF)$_4$ omitted for clarity. Selected bond lengths [Å] and angles [deg]: B1–B2 1.714(13), B1–N1 1.431(11), B2–N2 1.407(12), B1–C1 1.526(12), B2–C14 1.537(12), B1–Li2 2.683(17), B2–Li2 2.662(17), Li2–C1 2.217(15), Li2–C13 2.383(16), Li2–C14 2.211(16), Li2–C15 2.402(17), Li2–O5 1.831(16); B2–B1–N1 119.9(7), B1–B2–N2 120.2(7), B2–B1–C1 119.4(7), B1–B2–C14 118.7(7), N1–B1–C1 120.7(7), N2–B2–C14 121.0(7), B1–C1–Li2 89.6(6), B2–C14–Li2 88.6(6), C2–C1–C13 102.9(8), C15–C14–C26 103.0(7); N1–B1–B2/B1–B2–N2 65.8, C1 to C13/N1–B1–B2 46.8, C14 to C26/N2–B2–B1 40.2, C1 to C13/C14 to C26 74.1

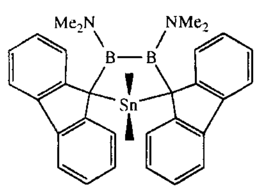
Crystal Structure of 2-Li · 5 THF

Single crystals of 2-Li · 5 THF were obtained from a THF solution at −18°C. An ORTEP plot of 2-Li · 5 THF, which crystallizes in the monoclinic space group $P2_1/n$ ($Z = 4$), is shown in Figure 1 [the Li(THF)$_4$ cation has been omitted for clarity].

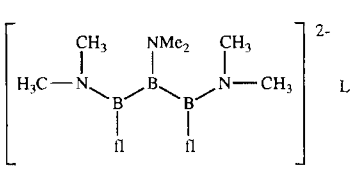
The most remarkable feature of 2-Li is the fact that one lithium ion is coordinated by four THF molecules and completely separated from the rest of 2-Li, which consists of the $fl_2B_2(NMe_2)_2^{2-}$ unit and a lithium ion (complexed by one additional THF molecule) forming a 1,2-dibora-4-lithiacyclopentane ring which is twisted. This non-planarity is not unexpected, as diborane(4) derivatives generally prefer an orthogonal disposition of substituents. In this case, the steric requirement of Li complexation causes a lowering of the dihedral angle N1–B1–B2–N2 to 65°. In the LiCB$_2$C ring, the lithium atom is not only bound to C1 and C14, but rather bridges C14/C15 [2.21(2)/2.40(2) Å] and C1/C13 [2.22(2)/2.38(2) Å]. An allyl-like bridging as in Lifl · quinuclidine[11] is not found in 2-Li [Li–C26 2.80(2), Li–C2 2.75(2) Å]. The structure of 2-Li closely resembles that of the stanna-3,4-diborolane 3, which is also a synthetic equivalent of the $fl_2B_2(NMe_2)_2^{2-}$ dianion[8]. In comparison with 2-Li the longer B–C bond in 3 (1.61 Å) reflects the covalent character of tin-carbon bonds and the reduced negative charge on C1 and C14 in 3 as compared to the predominantly ionic 2-Li.

In contrast to the results of Streitwieser[12] and Schleyer[13,14], who predicted 1,4-double lithium-bridged structures for 1,4-dilithiated butadienes and biphenyls to be the most stable isomers theoretically[13,14] and indeed found this coordination by X-ray crystallography[15–17], the structure of 2-Li features only one bridging lithium atom, the other one being completely separated and complexed by four THF molecules. A comparable combination is only found in [Li(THF)$_4$][Li{C(SiMe$_3$)$_3$}$_2$][18], where steric hindrance may account for the observed structure. A reason for this unusual lithium coordination mode[19] in 2-Li may be the twisting of the LiCB$_2$C ring, making the C1–C14 distance [3.472(17) Å] considerably longer than in the dilithiated biphenyl, where the two phenyl rings are coplanar[15].

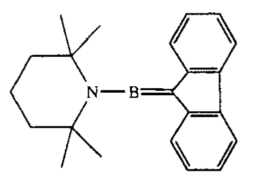
Furthermore, the extent of B–C double bonding in 2-Li is difficult to quantify: A comparison of the crystal structures of 1[9] and 2-Li shows no elongation of the B–N bonds in 2-Li, which would be expected if electron density is delocalized from the carbanionic centre into the empty p orbital of boron, thereby reducing the degree of B–N π bonding. On the other hand, a shortening of the B–C bond by 0.09 Å results upon lithiation of **1**. In 9-fluorenylidene(2,2,6,6-tetramethylpiperidino)borane (**4**) a compound with a "genuine" B–C double bond[20], the B–C distance is 1.422(7) Å or 0.1 Å shorter than the corresponding bond in **2**-Li. On the other hand, this shortening is partly due to a rehybridization of the carbon atom (sp^3 to sp^2 from **1** to **2**-Li, but also sp^2 to sp for the boron atom from **2**-Li to **4**), an influence which will solely affect σ bonds. From the data available for mesitylboron compounds (mes = mesityl = 2,4,6-trimethylphenyl)[21] and alkynylboranes[22] this σ influence can be estimated to be about 0.02 Å, and thus is of minor importance. Another indication of the presence of a B–C π interaction in **2**-Li is the reduction of the angles between the fluorene and the NBB planes from **1** to **2**-Li (from 73.2°/81.1° to 40.2°/46.8° in **2**-Li) as a consequence of lithiation.



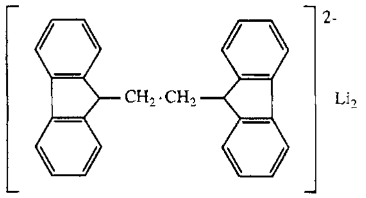
3



5



4



6

From these data and from a comparison with related systems[21,23,24] one can deduce a bond order of about 1.5 for the B–C bond in **2**-Li, which is in good agreement with the NMR data presented later.

Crystal Structure of 2-K · 4 THF and 2-K · DME

Crystallization of the potassium salt of **2** from THF yielded **2**-K · 4 THF as established by the integrals in the ^{1}H-NMR spectrum. The X-ray structure determination of these crystals had to be carried out at room temperature, since the crystals underwent an irreversible phase transition at −20°C and broke in the glass capillary. Due to the fact that only very small crystals suitable for an X-ray analysis could be found and that a decay of the intensities during measurement (probably by slow loss of THF at room temperature) occurred, it was not possible to obtain a high-quality data set at high angles. Although the structure solution and refinement proceeded almost smoothly it turned out to be impossible to adequately refine the parameters for the THF molecules due to thermal motion. Consequently, C–O and C–C bond lengths within these molecules do not correspond with the expected single bond lengths. Therefore, although the principal structural features of **2**-K · 4 THF are certainly beyond doubt, the data do not allow a critical discussion of structural details (Figure 2).

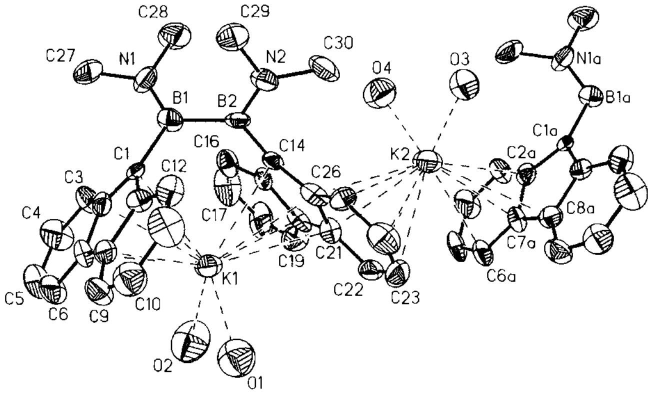


Figure 2. ORTEP plot of **2**-K · 4 THF, 25% probability, H and C atoms of THF molecules omitted for clarity. Selected bond lengths [Å] and angles [deg]: B1–B2 1.68(3), B1–N1 1.38(3), B2–N2 1.46(3), B1–C1 1.59(3), B2–C14 1.53(3), K1–C1 3.06(2), K1–C2 3.05(2), K1–C7 3.15(2), K1–C8 3.22(2), K1–C13 3.09(2), K1–C14 3.09(2), K1–C15 2.97(2), K1–C20 3.14(2), K1–C21 3.24(2), K1–C26 3.18(2), K2–C21 3.07(2), K2–C22 3.18(2), K2–C23 3.36(2), K2–C24 3.45(3), K2–C25 3.42(2), K2–C26 3.26(2), K2–C2a 3.27(2), K2–C7a 3.01(2), K2–C6a 3.28(2), K2–C8a 3.42(2), K1–O1 2.67(2), K1–O2 2.67(2), K2–O3 2.63(1), K2–O4 2.71(2); B2–B1–N1 123(2), B1–B2–N2 121(2), B2–B1–C1 118(2), B1–B2–C14 120(2), N1–B1–C1 120(2), N2–B2–C14 119(2), B1–C1–K1 104(1), B2–C14–K1 104(1), C2–C1–C13 104(2), C15–C14–C26 103(2), O1–K1–O2 78.8(7), O3–K2–O4 90.1(6); N1–B1–B2/B1–B2–N2 112.6, C1 to C13/N1–B1–B2 49.8, C14 to C26/N2–B2–B1 42.7, C1 to C13/C14 to C26 108.3

The need of potassium atoms for higher coordination numbers as compared to lithium atoms results in a chain-like structure for **2**-K · 4 THF. There are two different potassium atoms: K1 is situated between the two fluorenyl rings of 2^{2-} (resulting in a double η^5 coordination), whereas K2 is bridging two neighbouring molecules in a η^4-η^6 fashion. Although a shift of the metal from the five- to the six-membered ring is known for transition metal fluorenyl complexes[25] as well as for main group metals[26], the structure of **2**-K · 4 THF presents a unique example in the sense that η^5-five ring and η^6-six ring coordination are realized at the same time in the same molecule. To complete the coordination sphere, each K atom is bound to two additional THF molecules.

In order to overcome disorder and decomposition problems in **2**-K · 4 THF, **1** was metallated with $KN(SiMe_3)_2$ · DME in benzene and the product recrystallized from a DME/diethyl ether mixture. At 4°C, **2**-K · 2 DME crystallized as orange-coloured crystals of X-ray quality. An ORTEP plot of **2**-K · 2 DME is shown in Figure 3.

Again, the central K1 atom is coordinated in a bis-η^5-like fashion to the fluorenyl rings in 2^{2-}, whereas K2 is bridging two neighbouring molecules in a η^5-η^4 fashion. The coordination sphere of each K atom is completed by the two oxygen atoms of one DME ligand. There are several points noteworthy: K1 is situated almost centrally over one five-membered ring (C14, 15, 20, 21, 26) with distances ranging between 2.981(5) (to C14) and 3.238(6) Å (to C20), but shifted towards one six-memberd ring of the other fluo-

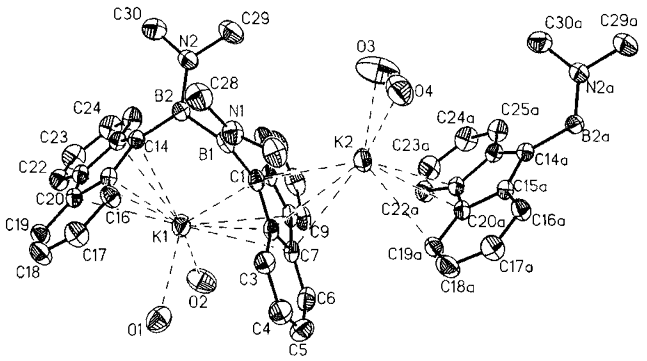


Figure 3. ORTEP plot of **2**-K · 2 DME, 25% probability, H and C atoms of DME molecules omitted for clarity. Selected bond lengths [Å] and angles [deg]: B1–B2 1.722(8), B1–N1 1.415(6), B2–N2 1.429(8), B1–C1 1.552(8), B2–C14 1.553(7), K1–C1 3.087(4), K1–C2 3.294(4), K1–C7 3.365(5), K1–C8 3.155(5), K1–C13 2.947(5), K1–C14 2.981(5), K1–C15 3.042(6), K1–C20 3.238(6), K1–C21 3.236(6), K1–C26 3.045(6), K2–C1 2.987(5), K2–C2 3.166(5), K2–C7 3.354(5), K2–C8 3.259(4), K2–C13 3.026(4), K2–C19a 3.069(6), K2–C20a 3.071(5), K2–C21a 3.164(6), K2–C22a 3.338(7), K1–O1 2.702(5), K1–O2 2.697(6), K2–O3 2.624(8), K2–O4 2.793(5); B2–B1–N1 120.1(5), B1–B2–N2 119.3(4), B2–B1–C1 118.1(4), B1–B2–C14 119.6(4), N1–B1–C1 121.8(5), N2–B2–C14 121.1(5), B1–C1–K1 101.5(3), B2–C14–K1 102.7(3), C2–C1–C13 102.3(4), C15–C14–C26 103.8(4), O1–K1–O2 61.3(2), O3–K2–O4 61.7(2); N1–B1–B2/B1–B2–N2 108.6, C1 to C13/N1–B1–B2 40.4, C14 to C26/N2–B2–B1 44.9, C1 to C13/C14 to C26 105.0

renyl ligand [distances: K1–C13 2.947(5) to 3.365(5) Å to C7]. The observed K–C distances are similar to those observed in Kfl · TMEDA (TMEDA = tetramethylethylenediamine) (3.04 to 3.35 Å)[27] and Kfl · 2 tmeda (3.07 to 3.32 Å)[26]. In Kcp compounds (cp = cyclopentadiene), metal atom coordination is far more symmetrical with bond lengths between 2.96 and 3.1 Å, and the K atom is situated exclusively above the centre of the cp rings[4,28–30].

Since the C14 to C26 fluorene ring is far from being perpendicular to the K1–K2 line it cannot adopt an η^5 coordination to K2. There are two short [K2–C19a/C20a 3.069(6) Å/3.071(5) Å] and two longer K–C distances [K2–C21a/C22a 3.164(6) Å/3.338(7) Å]. This results in a position of the K2 atom outside of the C_5 ring if K2 is perpendicularly projected onto the plane defined by atoms C14a, C15a, C20a, C21a, and C26a.

The different coordination modes described for potassium fluorenide in this and previous papers[26,27] is another conclusive experimental proof of the calculated flat energy surface for metal atom coordination to delocalized carbanions[12,31,32], resulting in different structures with only slight alteration of conditions.

Crystal Structure of 2-Ca · 2 THF

2-Ca crystallized from a THF solution at 4°C. Its X-ray single-crystal structure determination reveals the composition [**2**-Ca · 2 THF] · THF (Figure 4). There are two crystallographically independent molecules in the unit cell ($P\bar{1}$, Z = 4). The two independent molecules prove to be very similar with respect to bond lengths and angles, and thus the following discussion concentrates on only one of the two molecules.

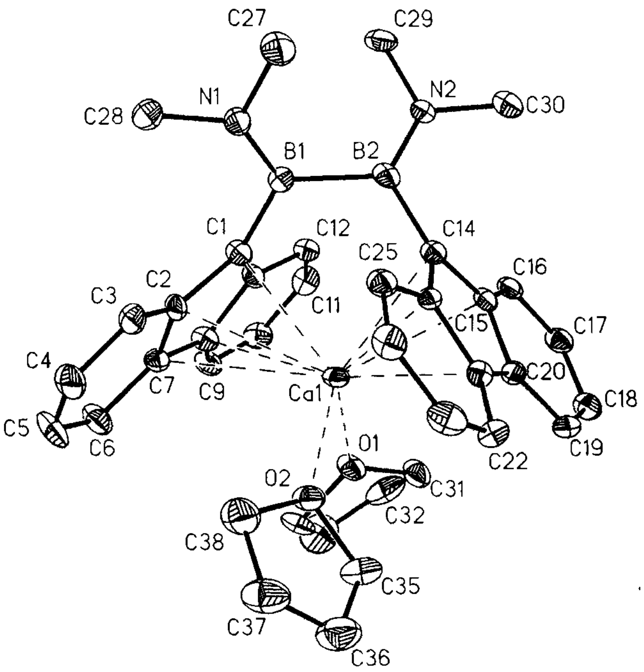


Figure 4. ORTEP plot of **2**-Ca · 2 THF, 25% probability, H atoms omitted for clarity. Selected bond lengths [Å] and angles [deg]: B1–B2 1.755(12), B1–N1 1.405(10), B2–N2 1.402(10), B1–C1 1.560(12), B2–C14 1.555(11), Ca1–C1 2.640(7), Ca1–C2 2.914(7), Ca1–C7 3.147(8), Ca1–C8 3.036(7), Ca1–C13 2.687(7), Ca1–C14 2.674(8), Ca1–C15 2.835(7), Ca1–C20 2.980(8), Ca1–C21 2.914(7), Ca1–C26 2.685(8), Ca1–O1 2.343(5), Ca1–O2 2.344(5); B2–B1–N1 122.5(7), B1–B2–N2 123.7(7), B2–B1–C1 115.5(6), B1–B2–C14 114.5(6), N1–B1–C1 121.8(6), N2–B2–C14 121.5(6), B1–C1–Ca1 107.0(4), B2–C14–Ca1 107.5(5), C2–C1–C13 104.1(6), C15–C14–C26 104.2(5), O1–Ca1–O2 82.3(2); N1–B1–B2/B1–B2–N2 63.9, C1 to C13/N1–B1–B2 43.4, C14 to C26/N2–B2–B1 131.0, C1 to C13/C14 to C26 106.5

2-Ca · 2 THF consists of discrete molecules of the formula $fl_2B_2(NMe_2)_2Ca$ · 2 THF in the solid state. Its structure closely resembles that of **2**-Li · 5 THF, the major difference being that the Ca atom is approximately η^5-bound to the five-membered rings. Due to the larger atomic radius of Ca compared to Li, the Ca^{2+} ion is moved away from the B–B bond (which probably for the same reason is lengthened by about 4 pm), but it is a striking observation that the Ca1–C1/C13 and the Ca1–C14/C26 distances (approx. 2.68 Å) are significantly shorter than the remaining Ca–C distances (2.8 to 3.1 Å). This is similar to the case of **2**-Li, where the central Li atom is bridging the same two carbon atoms. If a best plane through the fluorene rings is defined (C2 to C13 and C15 to C26, respectively, omitting C1 and C14, which are moved slightly out of the fl plane towards the Ca atom), the distance from Ca to these planes is 2.49 and 2.50 Å, respectively, and thus about 0.1 Å longer than e.g. in $Ca(MeC_5H_4)_2$ · DME[33] and $Ca[Me_4C_2(C_5H_4)_2]$ · (*t*BuNCH–CHN*t*Bu) (= A)[34], an *ansa*-bridged $Cacp_2$ complex (2.39 Å and 2.39 Å). The angle ring centroid –Ca–ring centroid in **2**-Ca (131.3°) is the smallest one found for substituted cp_2Ca derivatives[5] except for A (119.0°)[34]. We ascribe the considerably distorted geometry in 2-Ca (as compared to all crystallographically characterized calcocene derivatives[5,34]) to the *ansa*-bridging diborane(4) moiety.

Structure in Solution and NMR Data of 2

In contrast to the solid-state structure of hetero-*ansa*-bridged **2**-Li which exhibits a bridging lithium atom, the homo-*ansa*-bridged 1,2-bis(9-lithio-9-fluorenyl)ethane (**6**) adopts a *trans* configuration of the anionic centres in the crystal lattice. It seems that the preferred orthogonal confomation of the substituents at the boron-boron bond in **2** exerts some structure-determining force, leading to a closer proximity of the anionic centres. In solution, methanolysis of **2**-Li in THF with one equivalent of methanol yields a 1:1 mixture of **2**-Li and unreacted **1**. According to NMR data, no monolithiated $\mathbf{2}^-/Li^+$ is formed. The same products are observed upon reaction of **1** with one equivalent of $LiN(SiMe_3)(tBu)$ only. Thus, lithiation of the first fluorene ring in **1** faciliates lithiation of the second fluorenyl group in the same molecule. In order to shed more light on this neighbouring group effect, we studied the conformation of **2**-Li to **2**-Ba in solution by NMR spectroscopy.

Similar to the structure of the 1,3,4-stannadiborolane **3**[8], **2**-Ca and **2**-Ba exhibit twelve ^{13}C-NMR signals (a "double" set) for the carbon atoms of the fluorene rings, indicative of a C_2-symmetric structure with a twisted MCB_2C ring, and the twofold axis containing the metal atom and bisecting the boron-boron bond. Thus, the bis-η^5 coordination adopted in the solid state is retained in solution for the alkaline earth metal derivatives. In contrast, all group 1 derivatives **2**-Li, -Na, -K, and -Cs show only six ^{13}C-NMR signals in the fluorenyl region which can easily be explained by a looser coodination of the fluorenyl rings to the metal centre, thus allowing rotation of the fluorenyl rings around the B–C bond via a species with a strong B–C π interaction. This assumption is supported by the ^1H- and ^{13}C-NMR data of the 1,2,3-tris(dimethylamino)-1,3-difluorenyltriborane(5) dianion **5** which can be prepared similarly to **2**-Li. The fact that only one signal for the terminal dimethylamino groups is observed at 55°C is an indication of a strong B–C π interaction which lowers the barrier of rotation around the B–N bond. At −55°C this rotation is slow as indicated by two signals for the terminal dimethylamino groups in **5**. This unexpected behaviour is probably due to the larger six-membered $LiCB_3C$ ring in **5**, in which for steric reasons the coordination of the carbanions to the lithium centres may be weaker.

Previous investigations have shown a significant cation dependence of the ^{13}C- and ^1H-NMR shifts of fluorenyl anions[35]: Not only are the resonances spread over a wider range in all fluroenyl anions, but on formation of contact ion pairs (CIP) in solution rather than solvent-separated ion pairs (SSIP) a significant downfield shift is observed. The same is true for compounds **2**: For instance, the ^1H-NMR signals of **2**-Na are generally about 0.15 to 0.2 ppm downfield from those of **2**-Li, indicative of the larger cation (Na) forming CIPs rather than SSIPs, which are preferred by lithium[36,37]. The same tendency is disclosed for **2**-Ca to **2**-Ba in their ^{13}C- and ^1H-NMR spectra in the fluorenyl region, although in this case the more pronounced magnetic anisotropy of the larger cation certainly exerts an effect on the NMR shifts as well.

Finally, the NMR data of the dianions provide another means of estimating the extent of B–C double bonding. The tendency of forming SSIPs in solution (and thus observing a rather "free" anion) is strongest for **2**-Li. Therefore, its ^{13}C-NMR data will be compared to those of 1,2-bis(9-lithio-9-fluorenyl)ethane (**6**)[38] (delocalization of the negative charges only into the aromatic ring) and 9-fluorenylidene(2,2,6,6-tetramethylpiperidino)borane (**4**)[20] (B–C double bond), which are all structurally very similar so that differences in their chemical shifts can solely be attributed to the varying degree of B–C π bonding. Summing up all the differences of the chemical shifts [aromatic region only, 22.0 ppm (**2**-Li − **7**) and 23.2 (**4** − **2**-Li)] between **2**-Li and **7** or **4**, respectively, we find **2**-Li to be placed right in the middle between the "full" B–C double bond (**4**) and **7** (no π bonding at all to outside the fluorene ring system). We believe these NMR data to confirm the conclusion drawn from the bond lengths in **2**-Li, suggesting a considerable amount of B–C double bonding in the dianion.

The authors are grateful to *J. Turner* for helpful hints and discussions and to *F. Oehme* for technical assistance. The help of Dr. *M. Thomann* and *M. Schmidt*, who collected the X-ray data for **2**-Li and **2**-Ca, is also gratefully acknowledged. In addition, we are grateful for the support of our research by *Fonds der Chemischen Industrie, BASF Aktiengesellschaft* and *Chemetall GmbH*.

Experimental

All manipulations were carried out in dry nitrogengas in Schlenk glassware that was dried in vacuo. Solvents were dried by standard procedures, distilled and stored under nitrogen. – ^{11}B NMR: Bruker AC-P 200 (ext. $BF_3 \cdot OEt_2$). – ^1H and ^{13}C NMR: Jeol EX 400 (TMS or internal C_6D_6 as secondary standards). A positive sign indicates a downfield shift relative to the standard. The NMR spectra of all anions were recorded in $[D_8]$THF (**2**-Li and **2**-Na) or in undeuterated THF with three drops of C_6D_6 for locking and shimming. The assignment of NMR signals (especially for the fluorene rings) was confirmed by 2D-NMR spectra (H-H-COSY and ^{13}C-^1H-HECTOR). No effort was made, however, to find an unambiguous assignment for the pairs of C2/C13, C3/C12, etc. The numbering of the fluorenyl substituent follows that given in Figure 5, ^1H- and ^{13}C-NMR shifts are summarized in Table 1. – Due to the extreme reactivity of all compounds, no elemental analysis could be carried out (except **2**-Li, microanalytical department of the institute). – Melting points (uncorrected): Sealed glass capillaries under nitrogen.

Crystallographic Data: In all cases, a suitable specimen was sealed under argon in a dry glas capillary (for **2**-K and **2**-Ca in a glove box equipped with a microscope). The measurements were carried out either with a Nicolet R3m/V or a Siemens P4 four-circle diffractometer using Mo-K_α radiation and a highly oriented graphite crystal monochromator. Relevant crystallographic data are presented in Table 2[39]. It should be noted that all crystals were weakly diffracting and only few reflections with $I > 3\sigma(I)$ were observed at higher angles.

2-Li · 5 THF: 0.32 g (0.70 mmol) of **1**[9] was dissolved in 15 ml of THF. At room temp. 2.15 ml (1.5 mmol) of a 0.68 M solution of $LiN(SiMe_3)(tBu)$ in THF was added dropwise with stirring. After

Table 1. NMR data of all dianions of **2**. ^{1}H-NMR signals are generally multiplets (except NMe_2), only the centres are given (n.m.: not measured)

^{1}H-NMR	**2**-Li	**2**-Na	**2**-K	**2**-Cs
3, 12 - H	7.66	7.83	7.70	7.61
4, 11 - H	6.86	6.97	6.84	6.82
5, 10 - H	6.42	6.53	6.39	6.38
6, 9 - H	7.74	7.92	7.70	7.61
NMe_2	3.43 / 3.16	3.43 / 3.16	3.19 / n. m.	3.13 / n.m.

^{1}H-NMR	**2**-Ca	**2**-Ba
4, 11, 5, 10, 3, 12, 6, 9 - H	8.00 / 7.80 / 7.63 / 7.08 / 7.03 / 6.67	7.94 / 7.79 / 7.55 / 7.08 / 7.05 / 6.69 / 6.62
NMe_2	3.08 / n. m.	3.16 / n. m.
NH_3		- 0.95 (3H, s. br)

^{13}C-NMR	**2**-Li	**2**-Na	**2**-K	**2**-Cs
1 - C	95.0	n. m.	102.4	103.8
2, 13 - C	141.7	141.1	140.4	141.0
3, 12 - C	118.4	118.5	118.5	119.9
4, 11 - C	121.2	120.6	120.3	124.3
5, 10 - C	111.8	110.7	110.5	110.4
6, 9 - C	119.6	119.7	119.8	120.3
7, 8 - C	128.4	125.7	123.9	124.9
NMe_2	44.7 / 43.9	44.5 / 43.8	44.5 / 43.5	44.3 / 43.1

^{13}C-NMR	**2**-Ca	**2**-Ba
1 - C	n. m.	104.0
2, 13 - C	138.0 / 135.6	140.9 / 136.9
3, 12 - C	120.0 / 119.3	119.8 / 119.8
4, 11 - C	122.9 / 122.6	122.2 / 121.8
5, 10 - C	115.1 / 114.3	113.5 / 112.8
6, 9 - C	121.8 / 120.5	121.5 / 120.0
7, 8 - C	124.1 / 122.9	123.8 / 123.9
NMe_2	44.0 / 42.6	44.0 / 42.4

addition of about one third of the base the yellow reaction mixture instantaneously turned orange. Stirring was continued for another 6 h at room temp. During this time the colour gradually changed to deep red. The solvent was evaporated in vacuo, and a brown powder remained as residue which was washed with 10 ml of hexane to yield bright yellow **2**-Li · 5 THF, m.p. 155–160°C (dec.). After filtration the product was dried in vacuo. No complete loss of THF was achieved. Yield: 0.37 g (65%). – $C_{50}H_{68}B_2Li_2N_2O_5$ (812.6): calcd. C 73.90, H 8.43, N 3.45; found C 73.16, H 8.53, N 3.38. – ^{11}B NMR (64.16 MHz, THF): $\delta = 50$ ($h_{1/2} = 1300$ Hz).

2-Na: 0.35 g (0.80 mmol) of **1**[9] was dissolved in 15 ml of THF. At room temp. 3.10 ml (1.6 mmol) of a 0.53 M solution of $NaN(SiMe_3)_2$ in THF was added dropwise. Workup is as described for **2**-Li. After drying in vacuo for 5 h **2**-Na was obtained free of solvent as a bright yellow powder which spontaneously ignited in air. The compound decomposed between 60 and 70°C. Yield: 0.29 g (75%). – ^{11}B NMR (64.16 MHz, THF): $\delta = 50$ ($h_{1/2} = 1500$ Hz).

5: 0.96 g (1.9 mmol) of 1,3,2-tris(dimethylamino)-1,3-di-9-fluorenyltriborane(5)[9] was dissolved in 10 ml of THF. At room temp. 6.5 ml (3.9 mmol) of a 0.60 M solution of $LiN(SiMe_3)(t\text{Bu})$ in THF was added dropwise with stirring. After the addition was complete, the solution was orange-coloured. Upon stirring at room temp. for an additional 12 h the colour changed to deep red. The volatile products were removed in vacuo, and 10 ml of pentane was added to the waxy residue. After stirring for 2 h a yellow precipitate separated from the red supernatant liquid. The precipitate was filtered, washed with pentane and then dried in vacuo to give yellow **5** · THF. The compound was extremly air- and moisture-sensitive. It decomposed at 80°C under argon and gave a red-coloured THF solution. The exact yield could not be determined due to varying amounts of coordinated THF which could not be removed completely. – ^{1}B NMR (64.16 MHz, THF): $\delta = 53$ ($h_{1/2} = 3000$ Hz). – NMR at +50°C: ^{1}H NMR (400 MHz, $[D_8]$THF, TMS): δ = 7.80 (d, 4H, 6,9-H), 7.71 (d, 4H, 3,12-H), 6.87 (pseudo-t, 4H, 4,11-H), 6.46 (pseudo-t, 4H, 5,10-H), 3.20 [s, 6H, $N(CH_3)_2$], 2.87 [s, 12H, terminal $N(CH_3)_2$]. – ^{13}C NMR (100 MHz, $[D_8]$THF, TMS): δ = 141.3 (C-2,13), 127.1 (C-7,8), 120.0 (C-4,11), 119.9 (C-6,9), 117.9 (C-3,12), 110.4 (C-5,10), C-1,14 not found, 46.0 [$N(CH_3)_2$], 43.4 [terminal $N(CH_3)_2$]. – NMR at −50°C: ^{1}H NMR (400 MHz, $[D_8]$THF, TMS): δ = 7.83 (br, 4H, 6,9-H), 8.15, 7.38 (br, 2H, 2H, 3,12-H), 6.80 (br, 4H, 4,11-H), 6.40 (br, 4H, 5,10-H), 2.96 [s, 6H, $N(CH_3)_2$], 2.87, 2.70 [s, 6H, s, 6H, terminal $N(CH_3)_2$]. – ^{13}C NMR (400 MHz), $[D_8]$THF, TMS): δ = 142.6, 140.3 (C-2,13), 125.3 (C-7,8), 120.3, 119.2 (C-4,11), 118.3 (br, C-6,9), 117.7, 117.4 (C-3,12), 107.8, 107.5 (C-5,10), 103.6 (C-1,14), 45.5 [central $N(CH_3)_2$], 43.9, 42.4 [terminal $N(CH_3)_2$].

2-K · THF: To a solution of 1.19 g (2.70 mmol) of **1** in 15 ml of THF was added dropwise at room temp. a solution of 1.08 g (5.41 mmol) of $KN(SiMe_3)_2$ in 15 ml of the same solvent. After stirring at room temp. for 5 min an orange powder precipitated from the red solution. After a further 3 h all volatile products were removed in vacuo, the residue was washed with 30 ml of hexane and separated from the colourless solution by filtration. After drying in vacuo 1.52 g (ca. 80%) of **2**-K was obtained as an orange powder, which decomposed in a sealed melting point tube at 96°C. Due to varying amounts of THF no exact yield could be given. Single crystals were obtained from a saturated THF solution at 4°C. – ^{11}B NMR: $\delta = 50.0$ ($h_{1/2} = 2100$ Hz).

2-K · 2 DME: At room temp. to a solution of 0.82 g (1.86 mmol) of **1** in 20 ml of benzene a solution of 0.74 g (3.71 mmol) of $KN(SiMe_3)_2$ and 0.6 ml (0.52 g, 5.77 mmol) of DME in 20 ml of benzene was added rapidly. After stirring for 15 h at room temp. a red preticipate formed, from which all volatile compounds are removed in vacuo. The waxy residue was dissolved in DME/Et_2O (1:1). From the saturated solution big orange crystals separated after several days at 4°C (0.81 g, 1.16 mmol, 63% yield of **2**-K · 2 DME). After a second crystallization under the same conditions, single crystals suitable for an X-ray structure analysis were obtained.

2-Cs: 1.00 g (7.52 mmol) of Cs metal was suspended in 100 ml of warm hexane with efficient stirring. After cooling of the suspension to room temp. a solution of 1.62 g (3.68 mmol) of **1** in 25 ml of THF was added. After stirring for 18 h at room temp. gas evolution had ceased, and all Cs metal was used up. An orange powder of **2**-Cs · x THF (ca. 2.5 g) separated from the colourless solution which was washed twice with hexane and dried several hours in vacuo. Due to changing amounts of THF no exact yield could be given.

2-Mg: A freshly prepared solution of $MgBr_2$ in THF was allowed to react with a solution of **2**-Na in THF as described for **2**-Ca. A fine orange precipitate formed immediately, which proved to be insoluble in all common solvents.

2-Ca: To a suspension of 3.2 mmol of $CaBr_2$ in 40 ml of THF (freshly prepared from Ca metal and an excess of 1,2-dibromoethane) was added dropwise at room temp. a solution of **2**-Na in the same solvent. After stirring for 16 h the colourless precipitate was removed by centrifugation (56.11 mg of Ca found by titration with a 0.1 M Titriplex III solution, 43.8% of all Ca). From the red solution, **2**-Ca · 2 THF crystallized at 4°C. – ^{11}B NMR: $\delta = 48.4$ ($h_{1/2} = 960$ Hz).

2-Ba: To a blue-black solution of 0.56 g (4.08 mmol) of Ba metal in liquid ammonia was added 1.80 g (4.09 mmol) of **1** at −78°C.

Table 2. Crystallographic data[39]

	2-Li · 5 THF	**2**-K · 4 THF	**2**-K · 2 DME	**2**-Ca · 2 THF
Formula	$C_{50}H_{68}B_2Li_2$ N_2O_5	$C_{46}H_{44}$ B_2K_2 N_2O_4	$C_{38}H_{44}B_2K_2$ N_2O_4	$C_{38}H_{44}B_2Ca$ $N_2O_2 \cdot THF$
Formula weight	812.6	788.7	692.6	694.6
Colour, Habit	Light yellow rhomb	Orange-red plate	Orange yellow plate	Orange plate
Crystal size (mm^3)	1.0 * 0.7 * 0.4	0.1 * 0.3 * 0.4	0.16 * 0.35 * 0.4	0.2 * 0.3 * 0.3
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	C2/c	$P\bar{1}$	$P\bar{1}$
Z	4	8	2	4
a (Å)	11.597(4)	17.021(3)	9.677(3)	15.366(7)
b (Å)	24.964(7)	14.968(3)	10.770(3)	15.550(8)
c (Å)	17.000(9)	37.068(7)	20.329(5)	17.280(8)
α (°)	90.0	90.0	103.83(1)	91.29(1)
β (°)	90.03(4)	97.09(3)	93.80(2)	111.82(1)
γ (°)	90.0	90.0	105.09(1)	95.78(1)
Absorpt. coeff. (mm^{-1})	0.064	0.242	0.279	0.206
F(000)	1752	3312	732	1488
Diffractometer	R3m/V	P4	P4	P4
Temperature (°C)	24	20	20	-100
2 θ	3.0 to 42.0	2.0 to 45	2.0 to 48	2.0 to 46.0
Scan speed (°/min)	2.6 to 29.3	2.0 to 60.0	2.0 to 60.0	3.6 to 60.0
Scan range (°)	0.80	1.6	1.0	1.2
Index range (h / k / l)	0-12 / 0-26 / -17-18	0-18 / 0-16 / -40-40	0-11 / -11-11 / -23-23	0-17 / -17-17 / -19-18
Indep. refl. (R_{int}, %)	4604 (4.35)	6341 (4.57)	6106 (3.15)	11615 (10.8)
Obs. reflections (F >...σ(F))	2606 (3)	1995 (3)	3415 (4)	5653 (4)
Parameters	550	456	433	901
Data : Parameter	4.7 : 1	4.4 : 1	7.9 : 1	6.3 : 1
Weighting factor	0.0027	0.001	0.0005	0.0022
R / R_w	8.6 / 10.66	11.43 / 10.78	6.59 / 7.50	7.01 / 8.20
Larg. diff. peak / hole (eÅ^{-3})	0.2 / -0.28	0.40 / -0.38	0.3 / -0.28	0.43 / -0.37

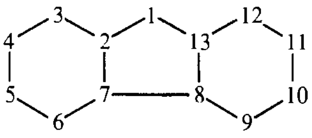


Figure 5. Numbering scheme for fluorene rings

When no reaction occurred at −78°C the solution was allowed to reach the boiling temp. of ammonia (−33°C). At this time the colour changed rapidly to orange. The mixture was subsequently cooled to −40°C, and 25 ml of THF was added dropwise. After warming to room temp. the residual THF solution was cooled to −78°C, the orange precipitate was isolated after 2 d with a cooled glas frit and dried several hours in vacuo. Yield: 1.32 g of **2**-Ba · $(NH_3) \cdot x$ THF. One molecule of ammonia and changing amounts of THF are bound to **2**-Ba.

---

[1] Contribution 222: D. Loderer, H. Nöth, W. Rattay, H. Schick, *Chem. Ber.* **1994**, *127*, 1605–1611.

[2] E. Weiss, *Angew. Chem.* **1993**, *105*, 1565–1587; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1501–1523.

[3] P. R. Markies, O. S. Akkerman, F. Bickelhaupt, W. J. J. Smeets, A. L. Spek, *Adv. Organomet. Chem.* **1991**, *32*, 147–226.

[4] C. Schade, P. v. R. Schleyer, *Adv. Organomet. Chem.* **1987**, *27*, 169–227.

[5] T. P. Hanusa, *Polyhedron* **1990**, *9*, 1345–1362.

[6] M. Wagner, Dissertation, Universität München, **1992**.

[7] R. Littger, Diplomarbeit, Universität München, **1992**.

[8] R. Littger, H. Nöth, M. Thomann, M. Wagner, *Angew. Chem.* **1993**, *105*, 275–277; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 295.

[9] H. Nöth, M. Wagner, *Chem. Ber.* **1991**, *124*, 1963–1972.

[10] G. Mösges, F. Hampel, P. v. R. Schleyer, *Organometallics* **1993**, *11*, 1769–1770.

[11] J. J. Brooks, W. Rhine, G. D. Stucky, *J. Am. Chem. Soc.* **1972**, *94*, 7339–7346.

[12] A. Streitwieser Jr., *Acc. Chem. Res.* **1984**, *17*, 353–357.

[13] W. Neugebauer, A. J. Kos, P. v. R. Schleyer, *J. Organomet. Chem.* **1982**, *228*, 107–118.

[14] A. J. Kos, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1980**, *102*, 7928–7929.

[15] U. Schubert, W. Neugebauer, P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.* **1982**, 1184–1185.

[16] M. Kranz, H. Dietrich, W. Mahdi, G. Müller, F. Hampel, T. Clark, R. Hacker, W. Neugebauer, A. J. Kos, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1993**, *115*, 4698–4704.

[17] M. F. Lappert, C. L. Raston, B. W. Skelton, A. J. White, *J. Chem. Soc., Chem. Commun.* **1982**, 14–15.

[18] C. Eaborn, P. B. Hitchcock, J. D. Smith, A. C. Sullivan, *J. Chem. Soc., Chem. Commun.* **1983**, 827–828.

[19] W. N. Setzer, P. v. R. Schleyer, *Adv. Organomet. Chem.* **1985**, *24*, 353–451.

[20] B. Glaser, H. Nöth, *Chem. Ber.* **1986**, *119*, 3253–3267.

[21] M. Pilz, J. Allwohn, P. Willershausen, W. Massa, A. Berndt, *Angew. Chem.* **1990**, *102*, 1085–1087; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1030–1032.

[22] B. Ederer, N. Metzler, H. Nöth, *Chem. Ber.* **1993**, *126*, 2003–2010.

[23] G. Herberich, B. Heßner, M. Hostalek, *Angew. Chem.* **1986**, *98*, 637–638; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 642–643.

[24] M. M. Olmstead, P. P. Power, K. J. Weese, R. J. Doedens, *J. Am. Chem. Soc.* **1987**, *109*, 2541–2542.

[25] J. W. Johnson, P. M. Treichel, *J. Am. Chem. Soc.* **1977**, *99*, 1427–1436.

[26] C. Janiak, *Chem. Ber.* **1993**, *126*, 1603–1607.

[27] R. Zerger, W. Rhine, G. D. Stucky, *J. Am. Chem. Soc.* **1974**, *96*, 5441–5448.

[28] P. Jutzi, W. Leffers, B. Hampel, S. Pohl, W. Saak, *Angew. Chem.* **1987**, *99*, 563–564; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 583–584.

[29] J. Lorberth, S.-H. Shin, S. Wocadlo, W. Massa, *Angew. Chem.* **1989**, *101*, 793–794; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 735–736.

[30] G. Rabe, H. W. Roesky, D. Stalke, F. Pauser, G. M. Sheldrick, *J. Organomet. Chem.* **1991**, *403*, 11–19.

[31] P. v. R. Schleyer, *Pure Appl. Chem.* **1983**, *55*, 355–362.

[32] P. v. R. Schleyer, *Pure Appl. Chem.* **1984**, *56*, 151–162.

[33] A. Hammel, W. Schwarz, J. Weidlein, *J. Organomet. Chem.* **1989**, *378*, 347–361.

[34] M. Rieckhoff, U. Pieper, D. Stalke, F. T. Edelmann, *Angew. Chem.* **1993**, *105*, 1102–1104; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1079–1081.

[35] U. Edlund, *Organic Magnetic Resonance* **1979**, *12*, 661–666.

[36] D. H. O'Brien, C. R. Russell, A. J. Hart, *J. Am. Chem. Soc.* **1979**, *101*, 633–639.

[37] M. Szwarc, *Ions and Ion Pairs in Organic Reactions*, 1st ed., Wiley, New York, **1972**.

[38] B. Becker, V. Enkelmann, K. Müllen, *Angew. Chem.* **1989**, *101*, 501–503; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 458–460.

[39] Further details of the crystal structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58178, the names of the authors, and the complete journal citation.

[119/94]