**Novel inorganic heterocycles from dimetalated carboranylamidinates†‡**

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Mono- and dianionic carboranylamidinates are readily available in one-pot reactions directly from o-carborane (1). In situ-monolithiation of 1 followed by treatment with $N,N'$-diisopropylcarbodiimide, $PrN=CN=Pr$, or $N,N'$-dicyclohexylcarbodiimide, $CyN=C=NCy$, provided the lithium carboranylamidinates (o-C$_2$B$_{10}$H$_{12}$C(NPr)(H)(NPr))$-x^2$C$_2$N)Li(DME) (2a) and (o-C$_2$B$_{10}$H$_{12}$C(NCy)(H)(NCy))$-x^2$C$_2$N)Li(DME) (2b). Controlled hydrolysis of 2a,b afforded the free carboranylamidines o-C$_2$B$_{10}$H$_{12}$C(NHPr)(H)(NHR)$-x^2$C$_2$N (3a: R = Pr, 3b: R = Cy). The first dimetalted carboranylamidinates, o-C$_2$B$_{10}$H$_{12}$C(NPr)(H)(NPr)Li$_2$(DME) (4a) (DME = 1,2-dimethoxyethane) and o-C$_2$B$_{10}$H$_{12}$C(NPr)(H)(NPr)Li$_2$(THF)$_4$ (4b), were prepared in high yield (83% yield) directly from 1 using a simple one-pot synthetic protocol. Treatment of 4b with 2 equiv. of Me$_2$SiCl afforded the disilylated derivative o-C$_2$B$_{10}$H$_{12}$-C$_2$N-[C(NPr)SiMe$_3$]$_2$($-x^2$C$_2$N) (5). Dianionic 4b also served as an excellent precursor for novel inorganic heterocycles incorporating the closo-1,2-C$_2$B$_{10}$H$_{11}$ cage, including the unsymmetrical distannene [C$_2$B$_{10}$H$_{11}$C(NiPr)(H)(NiPr)] (6) and the azaphosphole derivative [C$_2$B$_{10}$H$_{11}$C(NPPr)SiMe$_3$]$_2$($-x^2$C$_2$N)PPh$_2$ (7). Surprisingly, it was found that the synthesis of new inorganic ring systems from dianionic carboranylamidinates can also be achieved by employing only 1 equiv. of n-butyllithium in the generation of the anionic carboranylamidinate intermediates. Using this straightforward one-pot synthetic protocol, the Group 14 metallacycles [o-C$_2$B$_{10}$H$_{11}$C(NCy)($-x^2$C$_2$N)]$_2$SiR$_2$ (R = Cl (8), Me (9), Ph (10)) and [o-C$_2$B$_{10}$H$_{11}$C(NCy)($-x^2$C$_2$N)]GeCl$_2$ (11) have become accessible. The same synthetic strategy could be successfully adapted to prepare the corresponding Group 4 metallocene derivatives Cp$_2$Ti[o-C$_2$B$_{10}$H$_{11}$C(NCy)($-x^2$C$_2$N)] (12) and Cp$_2$Zr[o-C$_2$B$_{10}$H$_{11}$C(NCy)($-x^2$C$_2$N)] (13). The molecular structures of 2a, 3b, 4b, 5, 6, 7, 10, 12, and 13 were confirmed by single-crystal X-ray diffraction.

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**Introduction**

Carboranes (= dicarba-closo-dodecaboranes)

Carboranes continue to attract tremendous interest due to their wide range of applications, including the synthesis of polymers, ceramics, catalysts, complexes with non-linear optical properties or radiopharmaceuticals, as well as the important BNCT (= Boron Neutron Capture Therapy) technique. $\alpha$-Carboranyl ligands providing $C,N^1$, $C,P^2$, $N,S^6$, $N,P^7$, and $S,S^8$-chelating coordination modes have been reported to form a variety of interesting new transition metal complexes. Carboranylamidinates, which combine the versatile characteristics of both carboranes and the widely used amidinates in one system, were first synthesized in our laboratory in 2010. In situ-monolithiation of $o$-carborane (1)$^{10,11,12}$ followed by treatment with $N,N'$-diisopropylcarbodiimide in DME (= 1,2-dimethoxyethane)–n-pentane directly provided the novel lithium carboranylamidinate (o-C$_2$B$_{10}$H$_{12}$C(NPr)(H)(NPr))$-x^2$C$_2$N)Li(DME) (2a) as a DME adduct. Even more surprising was the finding that the resulting carboranylamidinate anion unexpectedly did not act as the normal $N,N'$-chelating amidinate ligand but rather adopted an unexpected $C,N'$-chelating coordination mode (Scheme 1).$^{10}$ The dicyclohexyl derivative could be prepared in an analogous manner.$^{13}$

In our previous work, besides the formation of 2a, we reported the corresponding free carboranylamidine as well as one Sn(u) and two Cr(u) carboranylamidinate complexes. More recently, the area has been significantly broadened through very interesting contributions by Jin et al. These authors not only expanded the range of transition metal...
carboranylamidinate complexes to elements like Ru, Co, Rh, Ir, Ni, and Cu, they also demonstrated that the carboranylamidinate system can be modified by attaching thiolate or selenolate functional groups or by generating novel nido-carboranylamidinate-type ligands. Meanwhile, the chemistry of carboranylamidinate complexes has already been summarized in two recent review articles. One of the most surprising initial findings was that in the products a N–H functionality remained uncoordinated and available for further deprotonation reactions. Subsequently, we as well as Jin et al. reported the preparation of the free carboranylamidines o-C$_2$B$_{10}$H$_{11}$C(NHiPr)(=NPr) (3a, 85% yield) and o-C$_2$B$_{10}$H$_{11}$C(NHCy)(=NCy) (3b, 78% yield) using a straightforward synthetic protocol (monolithiation of 1, followed by treatment with R–N=C=N-R (R = 1Pr, Cy) and subsequent hydrolysis). It was then attempted to force the imine N atom to coordinate to suitable metal centers by the addition of a base. It was found that the free carboranylamidines 3a and 3b could be doubly deprotonated upon the addition of two equivalents of $^8$BuLi as illustrated in Scheme 2. The resulting C$_2$N-dilithiocarboranylamidinates were used in situ for reactions with [Cp*MCl$_2$]$_2$ (M = Rh, Ir; Cp* = C$_5$Me$_5$) to give the corresponding 16-electron half-sandwich Rh and Ir carboranylamidinate complexes [o-C$_2$B$_{10}$H$_{11}$C(NHCy)(=NCy)]M(Cp*) (M = Rh, Ir). Thus far, the intermediate C$_2$N-dilithiocarboranylamidinates have not been structurally authenticated through X-ray diffraction. In this contribution we report the synthesis and structures of C$_2$N-dilithiocarboranylamidinates and their use as precursors for novel carboranylamidinate-derived inorganic heterocycles comprising Si, Ge, Sn, P, Ti, and Zr as heteroatoms.

Results and discussion

Starting materials

The key starting materials for studying carboranylamidinates are the easily accessible lithium derivatives 2a and 2b as well as the free carboranylamidines 3a and 3b. Thus far, only carboranylamidinates comprising N-isopropyl or N-cyclohexyl substituents have been prepared. Apparently, this has a simple reason in that N$_2$N'-diisopropylcarbodiimide and N$_2$N'-dicyclohexylcarbodiimide are both available in large quantities from commercial sources. In the course of the present study we set out with a more detailed structural characterization of two of these potentially useful starting materials. The N-cyclohexyl-substituted carboranylamidinate (o-C$_2$B$_{10}$H$_{11}$C(NHCy)(=NCy))$_2$Li(THF)$_2$ (2b) was prepared in the same manner as shown in Scheme 1 by reaction of in situ-prepared o-lithiocarborane with N$_2$N'-dicyclohexylcarbodiimide followed by crystallization from THF. Colorless, block-like, moisture-sensitive crystals of 2b were isolated in 58% yield. As in 2a, an IR band at 3404 cm$^{-1}$ clearly showed the presence of an N–H functionality in the molecule. A very strong band at 2547 cm$^{-1}$ is characteristic for B–H vibrations. A $^1$H NMR signal at δ = 4.63 ppm could be unequivocally assigned to the N–H proton, while the $^{13}$C NMR resonance of the amidinate carbon (NCN) was observed at δ = 155.5 ppm. The presence of only one resonance at δ = −4.3 ppm in the $^7$Li NMR spectrum confirmed the formation of a single Li-containing species. The $^{13}$B NMR spectrum displayed three signals at δ = −3.5, −6.4, and −9.3 ppm in the intensity ratio of 2 : 4 : 4. An EI mass spectrum of 2b showed the molecular ion at m/z 501, albeit with very low intensity (1%). The molecular structure of 2b was also verified by X-ray diffraction analysis. Suitable single-crystals were obtained directly by cooling the concentrated reaction mixture in THF to 4°C. Fig. 1 shows the molecular structure of 2a. Crystal data for all crystal structures reported in this contribution are listed in Table 1, while Table 2 summarizes selected bond lengths and angles.
In the solid state, the lithium carboranylamidinate 2b shows the typical \(C,N\)-chelating coordination mode which is by now well established for various carboranylaminidates and differs from the normal \(N,N'\)-coordination mode of other amidinate anions. This results in the formation of a nearly planar five-membered \(\text{LiNC}_3\) chelate ring. The exocyclic \(C-N\)-bond (C3–N2) is slightly longer (0.1 \(\AA\)) than the C3–N1 bond within the ring. The tetrahedral coordination geometry around Li is completed by the addition of two THF ligands.

The corresponding cyclohexyl-substituted free amidine \(\sigma\text{-C}_{10}B_{11}H_{12}C(N\text{HiPr})(\equiv\text{NCy})\) (3b) has already been mentioned in the previous literature by Jin et al. and used as a precursor for preparing various transition metal carboranylaminidates. These authors prepared 3b in 78% yield by hydrolysis of \(\sigma\text{-C}_{10}B_{11}H_{12}C(N\text{HiPr})(\equiv\text{NCy})\) in \(\text{DME}\) solution. We employed careful hydrolysis of isolated 2b in acetonitrile solution, a method which also gave a high yield (85%) in the case of 3a. However, following this procedure the cyclohexyl-substituted carboranylamidine 3b could only be isolated in 36% yield. Apparently, in this case the method using isolated lithium carboranylamidinate offers no preparative advantages over the original route. Carboranylamidine 3b was also structurally characterized by X-ray diffraction (Fig. 2; Tables 1 and 2). Colorless, needle-like single crystals were grown from a saturated solution in MeCN.

Fig. 2 gives a good impression of the high steric demand of the \(-\text{C(NHiPr)}(\equiv\text{NCy})\) moiety as compared to the smaller \(-\text{C(NHiPr)}(\equiv\text{NPr})\) group in 3a. Apart from that, all important structural features of 3b are very similar to those of the isopropyl derivative 3a. The N2–C3–N1 angle of the amidine functional group is 131.59(10)°. With a bond length of 1.3734(14) \(\AA\) the \(C-N\) single bond (C3–N1) is again significantly longer than the formal C=N double bond C3–N2 with 1.2788(14) \(\AA\). In 3a the corresponding distances are 1.3620(15) \(\AA\) (C–NH) and 1.274(3) \(\AA\) (C=N) and for (E)-\(N,N'\)-diisopropyl-3-phenylpropiolamidine they were reported to be 1.373(4) \(\AA\) (C–NH) and 1.266(4) \(\AA\), respectively.

Of central importance for the present study are dianionic carboranylaminidates. As illustrated in Scheme 2, the formation of \(C,N'\)-dilithiocarboranylaminidates and their use as intermediates for the preparation of 16-electron

![Fig. 1 Molecular structure of \((\sigma\text{-C}_{10}B_{11}H_{12}C(N\text{HiPr})(\equiv\text{NCy})\)-\(\kappa^\sigma\text{C,N})\text{Li(THF)}_2\) (2b). Most of the hydrogen atoms are omitted for clarity.](image-url)
half-sandwich Rh and Ir carboranylamidinate complexes have already been reported by Jin et al.13 Independently, a simple one-pot preparation leading to the C,N-dilithiocarboranylamidinates \( o-C_2B_{10}H_{10}C(NiPr)(vNiPr)Li_2(DME)_2 \) (4a) and \( o-C_2B_{10}H_{10}C(NiPr)(vNiPr)Li_2(THF)_4 \) (4b) has been developed in our laboratory. This route involves in situ-preparation of the lithium carboranylamidinate 2a according to Scheme 1 followed by the addition of a second equivalent of \( ^{6}LiBu \) to achieve deprotonation of the uncoordinated N–H group. Using this synthetic protocol, the solvated C,N-dilithiocarboranylamidinates \( o-C_2B_{10}H_{10}C(N^Pr)Li_2(DME)_2 \) (4a) and \( o-C_2B_{10}H_{10}C(N^Pr)Li_2(THF)_4 \) (4b) have become available for the first time as colorless, crystalline materials in high yields of >80% (Scheme 3).

The presence of isolable C,N-dilithiocarboranylamidinates was clearly established by a single-crystal X-ray analysis of 4a (Fig. 3; Tables 1 and 2). The carboranylamidinate dianion is coordinated to one lithium in the now familiar \( κ^2C,N \)-coordination mode resulting in formation of a nearly planar five-membered chelate ring (Li–N 1.988(3) Å). This Li+ ion (Li2) is tetrahedrally coordinated through the addition of a DME ligand, while the second lithium is only tricoordinated (trigonal planar) through \( κ^1 \)-bonding to N1 (Li–N 1.948(3) Å) and coordination of a chelating DME. It should be noted that such a type of \( κ^1 \)-bonding between lithium and monodentate amidine anions is quite rare in amidinate coordination chemistry. Examples are so far limited to lithium amidinates containing very bulky terphenyl20 or triptycenyl21 substituents.

Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Selected bond lengths (Å) and angles (°) for compounds 2b, 3b, 4a, 5, 6, 7, 10, 12, and 13</th>
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</thead>
<tbody>
<tr>
<td>2b</td>
<td>C23H49B10LiN2O2</td>
</tr>
<tr>
<td>3b</td>
<td>C15H34B10N2</td>
</tr>
<tr>
<td>4a</td>
<td>C17H44B10Li2N2O4</td>
</tr>
<tr>
<td>5</td>
<td>C15H42B10N2Si2</td>
</tr>
<tr>
<td>6</td>
<td>C31H70B10N6Sn2·C6H6</td>
</tr>
<tr>
<td>7</td>
<td>C15H29B10N2PC</td>
</tr>
<tr>
<td>8</td>
<td>27H42B10N2Si</td>
</tr>
<tr>
<td>9</td>
<td>C29H49B10N2OTi</td>
</tr>
<tr>
<td>10</td>
<td>C25H42B10N2Zr</td>
</tr>
</tbody>
</table>

Table 3

| Scheme 3 | Synthesis of the C,N-dilithiocarboranylamidinates \( o-C_2B_{10}H_{10}C(N^Pr)(vNiPr)Li_2(DME)_2 \) (4a) and \( o-C_2B_{10}H_{10}C(N^Pr)Li_2(THF)_4 \) (4b).

Fig. 2 Molecular structure of \( o-C_2B_{10}H_{11}C(NH)(N^Pr)(vNiPr)Li_2(DME)_2 \) (3b). Most of the hydrogen atoms are omitted for clarity.

1. \( ^{6}LiBu \)
2. iPr–N=C=N–iPr
3. \( ^{6}LiBu \)
4a: \( S_2 = DME \)
4b: \( S_2 = (THF)_2 \)
bonding environment around Li2 is distorted trigonal planar with an angle sum around Li2 = 355.9(2)°. The latter value can be favorably compared to those found in other structurally characterized bulky lithium amidinates comprising tricoordinate Li, e.g. 357.5° in [Li(THF)][(triphenyl)C(N′Pr)2]21 358.4 (3)° in (dimb)Li(TMEDA) (dimb = N,N′-diisopropyl[2,6-dimethyl]benzamidinate),20b and 354.4(4)° in (LPr)Li(TMEDA) (LPr = N,N′-diisopropyl[2,6-bis(2,4,6-triisopropylphenyl)]benzamidinate).20b Interestingly, it has been reported that in the molecular structure of (dimb)Li(TMEDA) the Li atom appears to have a weak interaction with one aromatic C-centre of the triptycyl substituent (Li···C = 2.690(6) Å). In 4a the tricoordinate Li resides directly above the centre (XIA) of a B-B bond (B4–B5) of the carborane cage (distance Li···XIA = 2.582 Å).

Colorless, block-like single crystals of the THF adduct 4b could also be obtained by slow cooling of a concentrated solution in THF to 5 °C. Unfortunately the low crystal quality did not permit a full refinement of the crystal structure. However, the X-ray diffraction study clearly showed the presence of a molecule analogous to 4a, again with two differently coordinated Li atoms (one tetrahedral and one trigonal planar) just with each of the DME ligands in 4a replaced by two THF ligands. Thus the present study clearly demonstrates that pure, crystalline C,N-dilithiocarboranylamidinates are readily available in high yields by a simple one-step synthetic route. With these promising materials in hand we started exploring their use as precursors for the synthesis of novel carboranyl-amidinate-based inorganic heterocycles.

Carboranyl amidinate-based heterocycles containing Group 4 and 5 elements (Si, Ge, Sn, and P)

The first experiments in this direction clearly demonstrated that new inorganic ring systems can be synthesized from di-anionic carboranylamidinates. Scheme 4 summarizes the results obtained with different Group 4 and 5 element halides. In the first step, the C,N-dilithiocarboranylamidinate 4b was prepared directly from α-carborane (1) using the one-pot synthetic protocol outlined in Scheme 3. It was found that the use of in situ-prepared 4b gave excellent results in subsequent reactions. The use of isolated 4a or 4b afforded similar or even lower yields so that this modification does not offer any advantages.

Silylation of 4b using Me3SiCl afforded the C,N-bis(tri-methylsilyl) derivative o-C2B10H10κ2C,N-(C(N′PrSiMe3)(N′Pr))SiMe3 (5) as colorless, block-like crystals. Its formation can be seen as a chemical proof for the presence of a C,N-dilithiocarboranylamidinate species in solution. The comparably low isolated yield (32%) can be explained by the very high solubility of 5 in hydrocarbon solvents including n-pentane. Compound 5 was fully characterized by spectroscopic methods, elemental analysis, and single-crystal X-ray diffraction. Single-crystals were obtained by cooling a concentrated solution in n-pentane to ~32 °C. Occasionally the product tends to form an oil, which is difficult to obtain free from n-pentane even under prolonged heating in a vacuum. The X-ray analysis confirmed the presence of the expected bis-silylated product (Fig. 4; Tables 1 and 2). The carbon–nitrogen bond lengths in the amide moiety in 5 are N(1)–C(3) 1.425(3) Å and N(2)–C(3) 1.249(3) Å, clearly corresponding to a carbon–nitrogen single and double bond, respectively. In the free carboranyl amidine o-C2B10H10C(N′Pr)2(N′Pr) (3a) the corresponding C–N distances are 1.3620(15) Å (C–N) and 1.274(3) Å (C=N), respectively.10 Future work will show if the bis(trimethylsilyl) derivative 5 might serve as a potentially useful starting material for the synthesis of new transition metal carboranylamidinates through reactions with high-valent transition metal halides. Such reactions have been explored many years ago by Roessky et al.22 and Dehnicek et al.23 for the closely related fully silylated benzamidine precursors PhC[=N(SiMe3)2][N(SiMe3)2]. For example, reaction of this compound with the tantalum(v) complex (C5Me5)TaF4 was found to result in the elimination of Me3SiF and clean formation of the mixed-ligand tantalum(v) amidinate complex [PhC(NSiMe3)2](C5Me5)TaF4.22

In marked contrast to the easily foreseeable formation of 5, the reaction of 4b with tin(n) chloride, which was carried out with the goal of making the carboranyl amidinate-stannylene [o-C2B10H10C(N′Pr)(N′Pr)]κ2C,NSn, had a surprising result (Scheme 4). Reaction of 4b with anhydrous SnCl4 in THF solution reproducibly yielded red/blue dichroic crystals for which an X-ray diffraction study revealed the presence of the unsymmetrical distannene [o-C2B10H10C(N′Pr)(N′Pr)]κ2C,NSn = Sn([PrNCl)2C2Bu]6 (6). Suitable single-crystals of 6 could be grown from concentrated solutions in toluene, while other methods of crystallization, e.g. diffusion of n-pentane into solutions of 6 in THF, diethyl ether or toluene, only led to separation of 6 in the form of a purple oil. As shown in Fig. 5, an unexpected structural feature of 6 is the presence of two n-butylamidinate ligands [[PrNCl)2C2Bu] which are attached to one Sn atom, while the second Sn atom forms the expected metallacycle with the formally di-anionic carboranylamidinate ligand (cf. Tables 1 and 2). The formation of the n-butylamidinate anion [[PrNCl)2C2Bu]− can be explained by the presence of both N,N′-diisopropylcarbodiimide and 8BuLi in the reaction mixture of the in situ-preparation of 4b. The easy formation of such n-butylamidinates from 8BuLi and carbodiimides has already been reported in the literature.24 This can explain why
$n$-butylamidinate ligands $[\text{(iPrN)}_2C\text{Bu}^-]$ are present in compound 6, but it remains unclear why this unsymmetrical distannene is the only reaction product instead of the expected stannylene $o$-$C_2B_{10}H_{10}C(\text{NiPr})\kappa^2C,N\text{Sn}$ or the symmetrical distannene $o$-$C_2B_{10}H_{10}C(\text{NiPr})\kappa^2C,N\text{Sn}_2$. Attempts to deliberately prepare the latter, i.e. by varying the stoichiometric ratios of the reactants, have thus far not been met with success. The binuclear tin carboranylamidinate 6 belongs to the small group of unsymmetrical distannenes. It is well known that the tin–tin bond distance in distannenes...
R₃Sn₂ can vary in the wide range between ca. 2.67 and 3.64.²⁶ With a distance of 2.9869(8) Å the Sn-Sn bond in 6 is fairly long, which can be seen as an indication for steric congestion in this molecule. A very similar value (2.961(1) Å) was reported by Lappert et al. for the unsymmetrically substituted distannene Cl₃SnSn[C(H)SiMe₂C₆H₅]₂.²⁵a On the Sn[[(iPrN)₂C-<br>1.8249(13) (P<br>in the [[(iPrN)₂C-<br>1.318(4) and 1.337(5) Å), a situation which is characteristic for N,N'-chelating amidinate ligands.⁹ The Sn2–N bond lengths are in the range of 2.139(3)–2.302(3) Å.<br><br>So far the isolation of the unsymmetrical distannene 6 is unique among Group 4 element carboranylamidinate derivatives. Several attempts were made to prepare the analogous compounds. However, reactions of 4a or 4b with GeCl₂(dioxane) in our hands invariably produced unstable red oils, which we could not characterize, while similar reactions with PbCl₂ afforded dark solutions which were very thermolabile and easily decomposed under the precipitation of metallic lead. Thus, until now carboranylamidinate-based germynes, digermenes, plumbynes, or diplumbynes remain elusive classes of main-group compounds.<br><br>The synthetic protocol illustrated in Scheme 4 also allowed the preparation of the first P-containing carboranylamidinate-based inorganic heterocycle. Treatment of in situ-prepared 4b with PhPCl₂ gave the azaphosphole derivative [o-C₂B₁₀H₁₀C{(NiPr)₂C₂B₁₀H₁₀C(NCy)κ²C,N}PPh (7) which was isolated in the form of colorless, air-sensitive crystals (33% yield). A singlet at δ = 50.7 ppm in the ³¹P NMR spectrum confirmed the formation of a single reaction product. Compound 7 was also structurally authenticated by X-ray diffraction. Large, colorless single-crystals could be obtained by recrystallization from CH₂Cl₂ at room temperature. The molecular structure of 7 is shown in Fig. 6 (cf. Tables 1 and 2). The P–N distance in 7 is 1.7174(14) Å, while the two P–C bond lengths are 1.8475(12) Å (P–C2) and 1.8249(13) Å (P–C10), respectively. With 1.2605(17) Å (C3–N2) the C=≡N double bond within the amidinate unit can be clearly distinguished from the single bond C3–N1 (1.4123(15) Å). The five-membered C₃PN ring is nearly planar. Clearly this potentially useful new phospine derivative awaits further exploration as a novel ligand for transition metals.<br><br>Further in the course of this investigation the important observation was made that the synthesis of new inorganic ring systems from dianionic carboranylamidinates can also be achieved by using only one equivalent of n-butyllithium for the generation of the anionic carboranylamidinates. Obviously the desired ring formation easily takes place under spontaneous elimination of HCl. This was successfully demonstrated by the straightforward synthesis of the novel Group 14 element heterocycles [o-C₂B₁₀H₁₀C(NCy)κ²C,N]SiR₂ (R = Cl (8), Me (9), Ph (10)) and [o-C₂B₁₀H₁₀C(NCy)κ²C,N]GeCl₂ (11) which have become accessible according to Scheme 5. The dichlorosilyl derivative [o-C₂B₁₀H₁₀C(NCy)κ²C,N]SiCl₂ (8) was synthesized following a simple one-pot synthetic protocol by treatment of in situ-generated 2b (cf. Scheme 3) with 1 equiv. of SiCl₄. In the same manner, the diorganosilyl derivatives [o-C₂B₁₀H₁₀C(NCy)κ²C,N]SiMe₂ (9) and [o-C₂B₁₀H₁₀C(NCy)κ²C,N]SiPh₂ (10) were made using Me₂SiCl₂ or Ph₂SiCl₂ as starting materials. These results clearly demonstrate that the easily accessible monoanionic carboranylamidinates 2a and 2b can be advantageously employed for the synthesis of new inorganic ring systems formally derived from dianionic carboranylamidinates.<br><br>All four compounds were isolated as colorless crystals in moderate to good yields (8: 57%, 9: 46%, 10: 76%, 11: 76%). As expected, the dichloro derivatives 8 and 11 are highly moisture-sensitive. The products 8–11 were fully characterized by spectroscopic methods and elemental analyses. In all cases the EI mass spectra showed the molecular ion, indicating significant volatility under MS conditions. The ²⁹Si NMR spectra of the three silicon derivatives each show only one singlet at δ ~−15.3 (8), 8.7 (9), and ~−15.1 (10) ppm. As a typical representative of this series of carboranylamidinate-based inorganic ring systems, the diphenyl derivative 10 has been structurally characterized by X-ray diffraction. Fig. 7 displays the molecular structure of 10 (cf. Tables 1 and 2). Incorporation of the SiPh₂ unit into the carboranylamidinate dianion affords a
five-membered 1,2-azasilole ring system which is anellated to the carbaborane cage. The five-membered SiNC₃ ring is once again nearly planar. As in the 1,2-azaphosphole derivative 7 the C≡N double bond in the amidinate moiety (C₃–N₂ 1.2619(16) Å) can be clearly distinguished from the C–N single bond within the five-membered ring (C₃–N₁ 1.4128(15) Å). It may be noted here that an initial attempt to reduce the dichlorosilane within the five-membered ring (C₃(N)₂(C₃(N))₂Si₂ was unsuccessful under the chosen reaction conditions. However, the results reported in the present study clearly demonstrate the high potential of both mono- and dianionic carbaboranylamidinates as precursors for novel inorganic ring systems.

Early transition metal carbaboranylamidinates

Previously reported carbaboranylamidinate complexes of middle and late transition metals include derivatives of Cr, Ru, Co, Rh, Ir, Ni, and Cu.¹⁰⁻¹³⁻¹⁸ Among them, only the 16-electron half-sandwich Rh and Ir carbaboranylamidinate complexes [o-C₃B₁₀H₁₀C(NCy)(=NCy)-κ²C₂N]MCP*(M = Rh, Ir) are formally derived from dianionic carbaboranylamidinates,¹³ and complexes of early transition metals have not yet been reported. In the course of the present study we found that the simple strategy leading to the carbaboranylamidinate-based Group 14 element heterocycles 8-11 could be successfully adapted to prepare the corresponding Group 4 metal metallocene derivatives according to Scheme 6.

Once again a solution of 2b was prepared from o-carborane (1), ⁷⁷BuLi, and N,N'-dicyclohexylcarbodiimide (molar ratio 1:1:1) in THF and treated directly with 1 equiv. of either Cp₂TiCl₂ or Cp₂ZrCl₂. Work-up was done by evaporation of the reaction mixtures to dryness, extraction of the product with n-pentane, and recrystallization of the crude product from a minimum amount of hot THF. The titanium complex Cp₂Ti[o-C₃B₁₀H₁₀C(NCy)(=NCy)-κ²C₂N] (12) was isolated in 69% yield in the form of glistening, copper-colored needles, while the zirconium derivative Cp₂Zr[o-C₃B₁₀H₁₀C(NCy)(=NCy)-κ²C₂N] (13) (44% yield) forms orange, needle-like crystals. Both compounds were readily characterized by their spectroscopic and analytical data. In the ¹H NMR spectra the cyclopentadienyl protons give rise to a singlet at δ 6.30 (12) and 6.39 (13) ppm, respectively. The EI mass spectrum of 12 shows the molecular ion at m/z 527 with very low relative intensity (1%), while in the mass spectrum of 13 the molecular ion at m/z 570 is the base peak with 100% intensity. Typical for all complexes formally derived from dianionic carbaboranylamidinates is the absence of an N–H band at ca. 3400 cm⁻¹ in the IR spectra. The molecular structures of both 12 and 13 were determined by X-ray diffraction. In both cases single-crystals were obtained by slow cooling of concentrated solutions of the complexes in THF to room temperature. The molecular structures are depicted in Fig. 8 and 9 (cf. Tables 1 and 2).

The Ti and Zr carbaboranylamidinate metallacycles 12 and 13 are almost identical in their structural parameters, but are not isostructural. The formally dianionic carbaboranylamidinate forms a nearly planar five-membered ring system incorporating the metal atom. In both compounds the angle between the metals and the cyclopentadienyl ring centroids is 127°. The bond lengths of the M–N σ-bonds are Ti–N 2.012(3) Å for 12 and Zr–N 2.0782(18) Å for 13. With 1.282(4) Å (12) and 1.271(3) Å (13) the exocyclic C₃–N₂ bonds have a clearly double bond character.
The ^1^H NMR (400 MHz), ^7^Li NMR (155.5 MHz), ^11^B NMR (128.4 MHz), ^13^C NMR (100 MHz), ^29^Si NMR (79.5 MHz) and ^3^P NMR (162 MHz) spectra were recorded on a Bruker DPX 400 spectrometer. IR (KBr) spectra were recorded using a Perkin-Elmer FT-IR 2000 spectrometer. Mass spectra (EI, 70 V) were recorded on a MAT 95 apparatus.

**Single crystal X-ray crystallography**

The intensity data of 2b, 4a, 5, 6, and 7 were collected on a Stoe IPDS 2 diffractometer with MoKα radiation. The data were collected with the Stoe XAREA program using ω-scans. The space groups were determined with the XRED32 program. The intensity data collected of 2b, 10, 12, and 13 were registered on an Oxford Diffraction Nova A diffractometer using mirror-focused CuKα radiation. Absorption corrections were applied using the multi-scan method. The structures were solved by direct methods (SHELLX-97) and refined by full matrix least-squares methods on F^2^ using SHEXL-97. The hydrogen atoms were refined as refined for 2b, 3b, 4a, 5, 6, as free for 7 and as constrained for 10, 12, 13.

**Synthesis of carboranylaminidanes**

\( (\text{O-C}_2\text{H}_4\text{H}_6\text{C}(\text{NH})(=\text{NCy})-\kappa^2\text{C},\text{N})\)Li(THF)_2 \)

(2b). In a 250 ml Schlenk flask, o-carborane (1.00 g, 7 mmol) was dissolved in 50 ml of THF and ^n^BuLi (1.6 M in hexane, 4.4 ml, 7 mmol) was added to the solution at r.t. while stirring. After stirring for 1 h, neat \(N\text{,}N\text{-dicyclohexylcarbodiimide} (1.44 \text{ g}, \text{ 7 mmol})\) was added and stirring at r.t. was continued for 12 h. The color of the solution changed from colorless to pale yellow. The solution was concentrated in a vacuum to a total volume of ca. 15 ml. Cooling to 4 °C for 72 hours afforded colorless, block-like crystals suitable for X-ray diffraction. Yield: 2.03 g (58%). ^1^H NMR (400 MHz, THF-d8, 25 °C): δ 4.63 (s br, 1 H, \(\text{Cy}=\text{C}(\text{NH})\)), 3.62 (O(CH_2)_2), 57.2 (NCH-CH(CH_2)_2), 3.23 (s br, 2 H, \(\text{NCH}(\text{CH}_2)_2\), 1.77 (O(CH_2)_2)), 1.17 (−6.4 (4 B), −9.3 (4 B), MS (EI): m/z (%) 501 (1) [M^+], 350 (28) [M − Li(THF)_2], 269 (100) [M − C_2H_2N^+], 187 (73) [M − C_2H_2N^+], 168 (13) [NC−C_2H_2N^+]) were collected on a MAT 95 apparatus. flattering. Yield: 0.50 g (36%). ^1^H NMR (400 MHz, THF-d8, 25 °C): δ 4.81 (s, \[−\text{C}−\text{CH}\]_2^+10H_10^+))

**Conclusions**

In summarizing the work reported here, the first dimetalated carboranylaminidanes were shown to be excellent precursors for novel inorganic heterocycles incorporating the closo-1,2-C_2B_10H_10 cage, including an unsymmetrical distannene and the novel azaphosphate derivative [o-C_2B_10H_10C(N^+P^−)](−N^+P^−)-κ^2C,N]PPH (7). For these syntheses the dimetalated carboranylaminidanes are most conveniently generated and employed in situ. The synthetic route could be simplified even further by employing only 1 equiv. of n-ButLi in the generation of the anionic carboranylamidinates. Using this simplified approach, a series of Group 4 (Ti, Zr) and Group 14 (Si, Ge) metallacycles have been prepared and fully characterized, including X-ray diffraction studies. These results clearly demonstrate that the combination of o-carborane and amidinate anions in one ligand system provides a highly useful platform for promising further studies in the field of inorganic ring systems.

**Experimental**

**General procedures**

All operations were performed with rigorous exclusion of air and water in oven-dried or flame-dried glassware under an inert atmosphere of dry argon, employing standard Schlenk, high-vacuum and glove box techniques (MBraun MBLab; <1 ppm O_2, <1 ppm H_2O). THF and toluene were dried over sodium/benzophenone and freshly distilled under a nitrogen atmosphere prior to use. Filtrations were done using the cannula technique. All glassware were oven-dried at 115 °C for at least 24 h, assembled while hot and cooled under a high vacuum prior to use. The starting materials o-carborane (1), N,N′-diisopropylcarbodiimide, \(N\text{,}N\text{-dicyclohexylcarbodiimide, n-butyllithium, SiCl}_4, \text{Me}_3\text{SiCl, Ph}_3\text{SiCl}_2, \text{GeCl}_4, \text{anhydrous SnCl}_4, \text{PhPCl}_2, \text{Cp}_2\text{TiCl}_2\) and C_p2ZrCl_2 were all obtained from commercial sources and used as received. Every sample of o-carborane (1) was dried under a high vacuum prior to use.

All hydrogen atoms are omitted for clarity.

![Molecular structures of Cp2Zr(o-C2B10H10C(NH)(=NCy)-2,13,14](Image)
(14 mmol) was dissolved in THF (150 ml) and \( n \)-BuLi (1.6 M in \( n \)-hexane, 8.8 ml, 14 mmol) was added to the solution at r.t. while stirring. After stirring for 30 min, neat \( N,N' \)-diisopropylcarbodiimide (2.4 ml, 14 mmol) was added. After further stirring for 12 h at r.t., a second equivalent of \( n \)-BuLi (1.6 M, 8.8 ml, 14 mmol) was added. After stirring for another 30 min, the THF was removed in vacuo and the remaining white solid was dissolved in 20 ml of DME. Cooling to 5 °C afforded colorless, block-like crystals. Yield: 5.3 g (82%). \(^1\)H NMR (400 MHz, \( CD_2Cl_2 \), 25 °C): \( \delta 3.89-2.00 \) (m, 10 H, BH), 3.94 (m, 2 H, CH(CH\(_3\))\(_2\)), 3.05 (s, 6 H, \( CH_3 \) (DME)). 2.83 (s, 4 H, CH(2) (DME)), 1.17 (d, 6 H, \( CH(CH_3)_2 \)), \( J = 6.0 \) Hz. \(^3\)C{\(^1\)H} NMR (100.6 MHz, \( CD_2Cl_2 \), 25 °C): \( \delta 161.9 \) (\( N \equiv C-N \)), 88.4 ([\( C-\text{Li} \]Br\(_2\)H\(_{10}\)), 70.1 (\( CH_2 \) (DME)), 68.5 ([\( C-\text{Li} \]Br\(_2\)H\(_{10}\)), 59.1 ([\( CH_3 \) (DME)), 45.8 (=N=C\(_3\)H)), 45.7 (=N-Li=CH)), 25.3 ([\( CH_2 \) (DME)), 25.1 ([\( CH_2 \) (DME)). \(^1\)Li NMR (155.5 MHz, \( CD_2Cl_2 \), 25 °C) \( \delta 1.3 \) (1 Li), 0.2 (1 Li). \(^{11}\)B{\(^1\)H} NMR (128.4 MHz, \( CD_2Cl_2 \), 25 °C) \( \delta -3.82 \) (2B), -5.96 (4B), -8.88 (4B). MS (EI): \( m/z \) % 294 (10) \([ M - \text{Li} \] (DME), \( N' \)Pr\(_2\)H), 220 (15) \([ M - \text{Li} \] (DME), \( N\)C\(_3\)H\(_5\)), 206 (15) \([ M - \text{Li} \] (DME), \( N\)C\(_3\)H\(_5\)), 164 (15) \([ C\_H\_13\_B\_10\_Li\_3\) (DME)). 142 (10) \([ CH_{10}B_{10}\) (100) \]. Anal. Found: C, 49.10; H, 6.36; N, 5.91. Calc. for C\(_{12}\)H\(_{18}\)B\(_{10}\)Li\(_2\) (462.50 g mol\(^{-1}\)): C, 49.58; H, 6.24; N, 5.87.

\( o-C\_B\_6\_H\_4\_C\_N\_H\_C\_N\_C\_C\_C\_C\_C\_\) (4a). \( o \)-Carborane (1, 0.5 g, 3.5 mmol) was dissolved in THF (70 ml) and \( n \)-BuLi (1.6 M in \( n \)-hexane, 2.2 ml, 3.5 mmol) was added to the solution at r.t. while stirring. After stirring for 20 min, neat \( N,N' \)-diisopropylcarbodiimide (0.6 ml, 3.5 mmol) was added and stirring at r.t. was continued for 90 min. Then \( Me_2\)SiCl (0.5 ml, 3.5 mmol) was added and the solution at r.t. The THF was removed in vacuo after stirring for another 12 min. \( n \)-Pentane was added to the remaining white solid giving a white suspension, which was filtered. The resulting colorless solution was concentrated in vacuo to a total volume of ca. 10 ml. Cooling to -32 °C for 2 days afforded colorless, block-like crystals suitable for X-ray diffraction. Yield: 0.16 g (32%). \(^1\)H NMR (400 MHz, \( CD_2Cl_2 \), 21 °C): \( \delta 3.65, \delta_{JHH} = 6.2 \) Hz, 1 H, NCH(\(_{CH_2}\)), 3.26 (sept, 1 H, \( \delta_{JHH} = 6.6 \) Hz, SiNC\(_{CH_2}\)), 1.09 (d, 3 H, \( \delta_{JHH} = 8.0 \) Hz, CH(\(_{CH_2}\)), 1.00 (d, 3 H, \( \delta_{JHH} = 8.0 \) Hz, CH(\(_{CH_2}\)), 0.92 (d, 3 H, \( \delta_{JHH} = 6.4 \) Hz, CH(\(_{CH_2}\)), 0.24 (s, 9 H, \( [C\_C\_10\_H_{10}\_Si(CH_2)\_3\_2\) (0.95) (S, 9 H, \( N\)C\(_3\)H\(_5\)). \(^{13}\)C{\(^1\)H} NMR (128.4 MHz, \( CD_2Cl_2 \), 25 °C): \( \delta -0.3 \) (2 B), -2.0 (1 B), -7.6 (3 B), -10.1 (4 B). \( ^{29}\)Si NMR (79.5 MHz, \( CD_2Cl_2 \), 23 °C): \( \delta 7.8 \) (1 Si), 8.6 (1 Si). MS (EI): \( m/z \) % 299 (100) \([ M - SiC\_H\_13\_H\_2\_H\_2\) (DME)). 143 (10) \([ C\_C\_10\_H_{10}\_Si(CH_2)\_3\_2\) (8.8 % (Si=CH)). \(^{13}\)B{\(^1\)H} NMR (128.4 MHz, \( CD_2Cl_2 \), 25 °C): \( \delta -3.82 \) (2B), -5.96 (4B), -8.88 (4B). MS (EI): \( m/z \) % 294 (10) \([ M - \text{Li} \] (DME), \( N' \)Pr\(_2\)H), 220 (15) \([ M - \text{Li} \] (DME), \( N\)C\(_3\)H\(_5\)), 206 (15) \([ M - \text{Li} \] (DME), \( N\)C\(_3\)H\(_5\)), 164 (15) \([ C\_H\_13\_B\_10\_Li\_3\) (DME)). 142 (10) \([ CH_{10}B_{10}\) (100) \]. Anal. Found: C, 49.10; H, 6.36; N, 5.91. Calc. for C\(_{12}\)H\(_{18}\)B\(_{10}\)Li\(_2\) (462.50 g mol\(^{-1}\)): C, 49.58; H, 6.24; N, 5.87.
The dilithium precursor was then cooled to 0 °C and treated with PhPCl2 (3.6 ml, 26.6 mmol). The solution was heated up and immediately turned yellow. After stirring for 12 h, the THF was removed in vacuo and a mixture of pentane–dichloromethane (3 : 2, 50 ml) was added to the remaining yellow solid. A white solid, which separated from the golden yellow solution, was removed by filtration. The solution was concentrated in vacuo to a total volume of ca. 20 ml. After 1 week colorless, rectangular single-crystals suitable for X-ray diffraction were obtained. Yield: 2.82 g (33%).1H NMR (400 MHz, THF-d8, 25 °C): δ 7.55–7.40 (m, 5 H, P–C–Ph), 4.57–4.44 (m, 2 H, δ NCH(CH3)2, −NPh(CH3)2), 1.18 [d, 6 H, CH(CH3)2, J = 6.4 Hz], 1.14 [dd, 7 H, −NPh(CH3)2, Jα = 8.7, Jβ = 3.6 Hz, JHP = 3.6 Hz] ppm.13C{1H} NMR (100.6 MHz, THF-d8, 25 °C): δ 145.5 (d, J = 10.1 Hz, PrN=N=C–NPr), 138.7 (d, J = 36.2 Hz, P–C(phenyl)).

The dilithium precursor was then cooled to 0 °C and treated with PhPCl2 (3.6 ml, 26.6 mmol). The solution was heated up to separate the LiCl after stirring for at least 48 hours at r.t. Yield: 2.83 g (76%).1H NMR (400.1 MHz, THF-d8, 25 °C): δ 7.81, 7.57, 7.48 (10 H, Si–C(CH3)2), 3.26–3.44 (2 H, NCH2), 2.00–3.15 (br, 10 H, B–H), 1.09–1.93 (m, 20 H, NCH(C6H7)), 11.5 (3 B), 14.1 (2 B). 29Si NMR (79.5 MHz, THF-d8, 25 °C): δ −5.6 (2 B), −6.6 (1 B), −8.1 (6 B), −11.6 (3 B), −15.3 (3 B). 25Si NMR (79.5 MHz, THF-d8, 25 °C): δ −15.1. MS (EI): m/z (%): 531 (22) [M+1], 499 [M−1], 367 (15) [M−1C(CH3)2], 350 (38) [M−1C2H4SiH3], 269 (100) [M−1C2H4Si2H5].

Following the procedure given for 8 using Ph2SiCl (1.50 ml, 7 mmol) instead of SiCl4 and crystallization of the product from DME (10 ml) at 4 °C for 48 hours afforded colorless, block-like crystals suitable for X-ray diffraction. Yield: 2.83 g (76%).1H NMR (400.1 MHz, THF-d8, 25 °C): δ 7.81, 7.57, 7.48 (10 H, Si–C(CH3)2), 3.26–3.44 (2 H, NCH2), 2.00–3.15 (br, 10 H, B–H), 1.09–1.93 (m, 20 H, NCH(C6H7)), 11.5 (3 B), 14.1 (2 B). 29Si NMR (79.5 MHz, THF-d8, 25 °C): δ −5.6 (2 B), −6.6 (1 B), −8.1 (6 B), −11.6 (3 B), −15.3 (3 B). 25Si NMR (79.5 MHz, THF-d8, 25 °C): δ −15.1. MS (EI): m/z (%): 531 (22) [M+1], 499 [M−1], 367 (15) [M−1C(CH3)2], 350 (38) [M−1C2H4SiH3], 269 (100) [M−1C2H4Si2H5].

Following the procedure given for 8 using GeCl4 (0.80 ml, 7 mmol) instead of SiCl4 and crystallization of the product from THF (15 ml) at r.t. afforded yellow, needle-shaped crystals which were not suitable for X-ray structure analysis. Yield: 2.61 g (76%).1H NMR (400.1 MHz, THF-d8, 25 °C): δ 4.04 (NCH2(CH3)2), 3.27 (NCH3(CH3)2), 2.10–3.15 (br, 10 H, B–H), 1.12–2.05 (m, 20 H, NCH(C6H7)), 1.31 [H NMR (100.6 MHz, THF-d8, 25 °C): δ −1.8 (1 B), −3.7 (1 B), −8.0 (3 B), −11.5 (3 B), −14.1 (2 B). 29Si NMR (79.5 MHz, THF-d8, 25 °C): δ −15.3. MS (EI): m/z (%): 448 (8) [M+2], 366 (90) [M−1C6H5], 351 (25) [M−1SiCl3, +2H2], 284 (30) [M−1C2H19], 269 (100) [M−1C2H7Si], 187 (77) [M−1C2H7Si], 143 (8) [C6H5Si2H10].

Following the procedure given for 8 using titanocene dichloride (1.74 g, 7 mmol) instead of SiCl4 and crystallization of the red product from hot THF (15 ml) afforded copper-colored, needle-shaped crystals which were suitable for X-ray structure analysis. Yield: 2.53 g (69%).1H NMR (400 MHz, THF-d8, 25 °C): δ 6.30 (s, 10 H, Cp), 3.57 (THF), 3.30 (s br, 1 H, NCH2(CH3)2), 3.26 (s br, 1 H, NCH(C6H7)), 2.00–3.20 (br m, 20 H, B–H), 1.72 (THF), 1.15–1.89 (m, 20 H, CH2(CH3)2).11C{1H} NMR (100.6 MHz, THF-d8, 25 °C): δ 143.1 ([(CyN=)C(NCy)], 137.5 (Cp), 77.1 [(CyN=)C–Cage], 68.1 (THF), 56.4 (NCH(CH3)2), 54.8 (NCH2), 52.9 (Cage–Tig), 26.3 (THF), 34.9, 26.7, 26.2, 25.8, 25.6, 25.1 (NCH(C6H7)).11B{1H} NMR (128.4 MHz, THF-d8, 25 °C): δ −3.9 (2 B), −10.0 (3 B), −13.6 (5 B). MS (EI): m/z (%): 527 (1)

74.6 (Cage–Si), 56.1 (NCH(CH3)2), 54.4 (NCH(CH3)2), 34.8, 33.0, 26.6, 26.1, 25.7, 25.1 (NCH(CH3)2), 0.3 (–Si–(CH3)).
[M’], 350 [22] [M – C10H4Ti’], 269 (100) [M – C10H4Ti, C4H9], 187 [76] [M – C10H4Ti, C12H16], 98 [34] [C6H12N2], 83 (43) [C6H11’]. Anal. Found: C, 56.96; H, 8.13; N, 5.29. Calc. for C25H21B10N2Ti (526.58 g mol⁻¹): C, 57.02; H, 8.04; N, 5.32.

\[ \text{Cp}_2\text{Zr}[\text{C}_6\text{H}_{11}]\text{C}(\text{CN})_2\text{N}=\text{CN}] \times \text{C}_3\text{N} \] (13). Starting from \( \text{o-} \)carborane (1, 0.75 g, 5.2 mmol), \( \text{BuLi} \) (1.6 M in \( \text{n-} \)hexane, 3.25 ml, 5.2 mmol) and \( \text{N}^+\text{N}^- \)-dicyclohexylcarbodiimide (1.07 g, 5.2 mmol) a solution of 2b was prepared and treated with zinc oxide and then with two equivalents of \( \text{BuLi} \) under reflux until no more 

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**Notes and references**


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