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Carboranylamidinates

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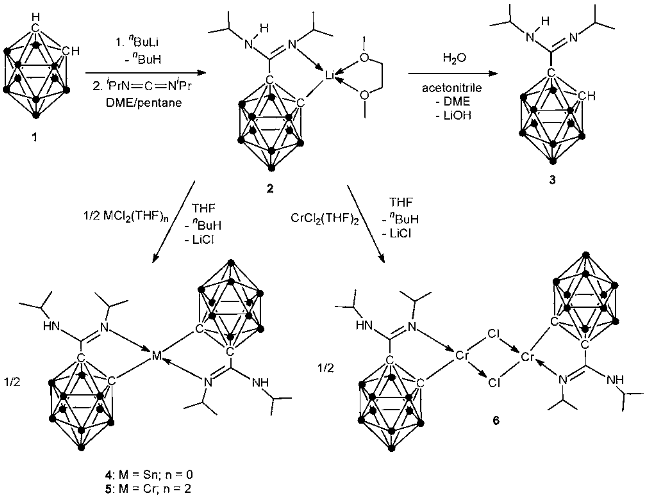
Abstract: Carboranylamidinate anions are readily accessible *via* addition of *N*,*N*′-dialkylcarbodiimides to lithio-*ortho*-carborane. They represent a novel difunctional boron-rich ligand system for main group and transition elements (Li, Sn, Cr). Initial structural investigations revealed an unexpected *N*,*C*-coordination mode instead of *N*,*N*′-chelation.

Ever since the discovery of 1,2-dicarba-*closo*-dodecaborane (**1**) in the 1960s, the chemistry of this exceptionally stable carborane has generated considerable interest.[1] Their unusual properties have provided a wide range of applications for carborane derivatives,[2] including the synthesis of polymers,[2c] ceramics,[2c] catalysts,[2d,f,g] complexes with nonlinear optical properties,[2e] or radiopharmaceuticals, although the medicinal chemistry of carborane has been mostly focused on the BNCT (Boron Neutron Capture Therapy) technique.[1b] Recent reports on unusually stable *C*,*N*-,[3] *C*,*P*-,[4] *N*,*S*-,[5] *N*,*P*-,[6] and *S*,*S*′-chelating[7] *o*-carboranyl metal complexes imply that the rigid chelate conformation and the *ortho*-carboranyl ligand backbone might be ideal for the stabilization of possible metal intermediates in organometallic reactions. Thus, the design of such ligand systems containing one functional group strongly bound to a transition metal center and another one coordinatively labile is of great interest.[8]

The search for alternatives of the ubiquitous cyclopentadienyl ligand and its derivatives has attracted much attention and made spectacular progress in recent years.[9] Among these ligands, amidinate anions have been widely employed as spectator ligands in main group, transition metal, and *f*-element coordination chemistry.[10] Amidinate anions of the general formula $[RC(NR')_2]^-$ offer a large degree of variability through the use of different substituents at carbon and nitrogen. Given the promising and versatile characteristics of both the carborane and amidinate ligands it appeared to be a highly promising goal to combine them in a single ligand system. The resulting *carboranylamidinate anions* (Scheme 1) have never before been described in the literature.

We now report that carboranylamidinates are readily accessible in a straightforward manner by insertion of *N*,*N*′-dialkylcarbodiimides into the Li−C bond of 1-Li-1,2-$C_2B_{10}H_{11}$. *In situ* monolithiation of **1** followed by treatment with *N*,*N*′-diisopropylcarbodiimide in DME (= 1,2-dimethoxyethane)/*n*-pentane provided the lithium carboranylamidinate **2** as a DME adduct in the form of colorless crystals in 65% isolated yield (Scheme 1). An X-ray analysis of **2** revealed that the newly formed carboranylamidinate anion unexpectedly does not act as an *N*,*N*′-chelating ligand. Instead, a five-membered $LiNC_3$ chelate ring is formed through coordination of the Li^+ ion to the nitrogen of the amidinate C═N unit and C2 of the carborane cage (Figure 1 left). A strong IR band at 3407 cm^{-1} is consistent with the presence of a N−H functionality in **2** and metalation of the carborane cage instead of the amidinate moiety. Controlled hydrolysis of **2** provided the free carboranylamidine **3**, which was isolated as colorless, needle-like crystals in 85% yield (Scheme 1, Figure 1 right). With 1.274(3) Å (C═N) and 1.3620(15) Å (C−NH) the bond lengths in the amidine functionality are favorably comparable with the corresponding distances e.g. in (*E*)-*N*,*N*′-diisopropyl-3-phenylpropiolamidine (C═N, 1.266(4) Å; C−NH, 1.373(4) Å).[11]

Scheme 1. Synthesis of Carboranylamidinates



Initial experiments showed that the novel carboranylamidinate anion is an excellent difunctional ligand system for main group elements as well as transition metals. Novel carboranylamidinate complexes can be prepared in simple one-pot reactions by *in situ* formation of **2** followed by addition of an appropriate main group or transition metal halides. In this manner, a reaction of **2** with anhydrous $SnCl_2$ (molar ratio 2:1) in THF afforded the novel stannylene derivative **4** as colorless crystals in 82% isolated yield. An X-ray diffraction study of **4** revealed again the *C*,*N*-chelating coordination mode of the carboranylamidinate ligands with nearly planar five-membered $SnNC_3$ rings. Figure 2 shows a monomeric structure with a *pseudo*-trigonal bipyramidal arrangement at the Sn center, although there is severe distortion from the regular polyhedron. The stereochemically active lone pair on Sn(II) presumably occupies an equatorial site (axial angle N1−Sn−N1A: 161.40(9)°). This geometry is fairly common for four-coordinate Sn(II) complexes.[12]

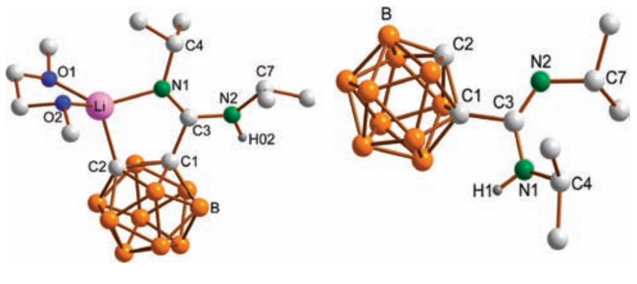


Figure 1. Molecular structures of **2** (left) and **3** (right).

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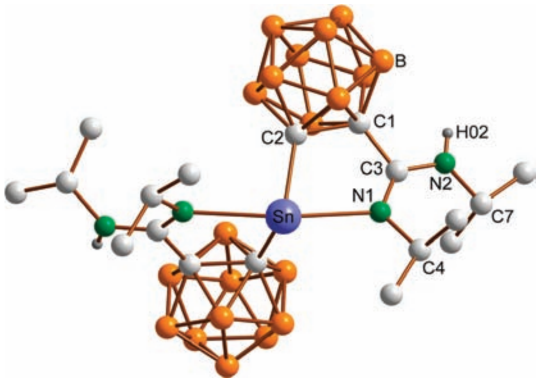

Figure 2. Molecular structure of **4**.

In a similar manner, two chromium(II) carboranylamidinates have been synthesized as first examples for transition metal complexes comprising the novel ligand system. Treatment of $CrCl_2(THF)_2$ with 2 equiv of **2** in THF afforded the homoleptic chromium(II) complex **5** in moderate yield (45%). The highly air-sensitive dichroitic (blue/green) needle-like crystals show a bluish metallic reflectance. According to the X-ray structural analysis, the *C,N*-coordination of the carboranylamidinates is favored with transition metals as well, leading to a distorted tetrahedral overall molecular structure (Figure 3).

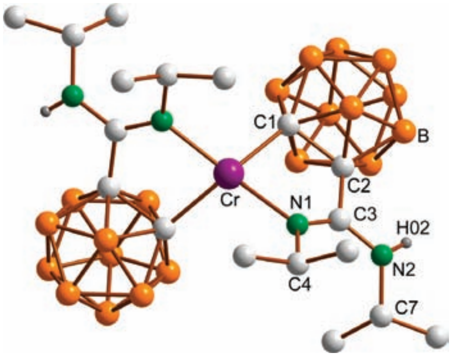

Figure 3. Molecular structure of **5**.

The same reaction carried out in a 1:1 molar ratio of the reactants (**6**, Scheme 1) gave access to the first mono(carboranylamidinate) complex of a transition metal, albeit in low yield (23%). While the blue-green color of crystalline **6** is virtually undistinguishable from that of **5**, the crystals have a more plate-like habit.

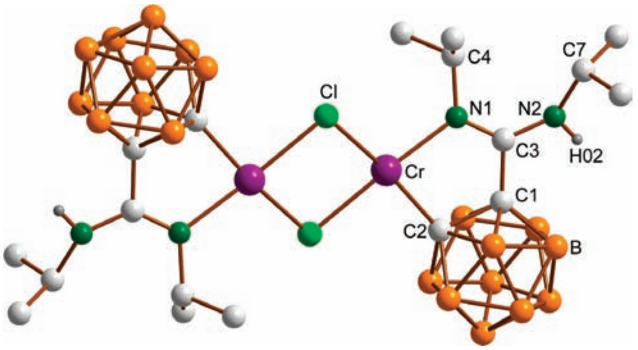

Figure 4. Molecular structure of **6**.

The structure of **6** was also verified by single-crystal X-ray diffraction (Figure 4). The mono(carboranylamidinato) Cr(II) derivative is dimerized *via* chloro-bridges. The entire tricyclic central unit is nearly planar with dihedral angles between the N−Cr−N and the Cl−Cr−Cl planes of only 15.9°. The Cr−C bond length of 2.0854(18) Å is typical for Cr−C(aryl) bonds.[13]

In summary, we found a straightforward route leading to the hitherto unknown carboranylamidinate anions *via* insertion of *N,N′*-dialkylcarbodiimides into the Li−C bond of $1\text{-Li-}1,2\text{-}C_2B_{10}H_{11}$. Initial reactivity studies lead to the isolation and structural characterization of novel Li, Sn, and Cr complexes, which all comprise an unexpected *C,N*-chelating coordination mode of the carboranylamidinates. Quite remarkable is the presence of free N−H functionalities in the products. Given the remarkable versatility of amidinate ligands, it is easy to foresee a bright future for carboranylamidinates in coordination chemistry.

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Supporting Information Available: CIF files giving X-ray structural data for **2**−**6** as well as experimental details on the preparation and characterization of **2**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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