Carbene Chemistry

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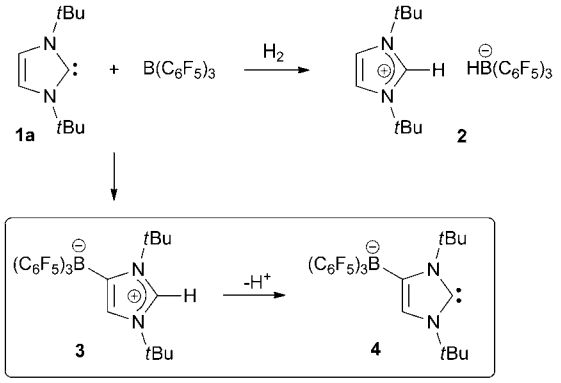
Anionic N-Heterocyclic Carbenes That Contain a Weakly Coordinating Borate Moiety

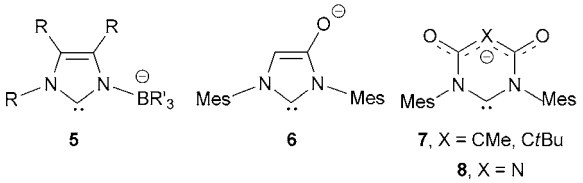
*Sabrina Kronig, Eileen Theuergarten, Constantin G. Daniliuc, Peter G. Jones, and Matthias Tamm**

Frustrated carbene-borane Lewis pairs, such as **1**/$B(C_6F_5)_3$, that are prevented from normal adduct formation by steric factors[1] were recently shown to exhibit a very strong propensity for the activation of small molecules, such as dihydrogen, ammonia, tetrahydrofuran, alkynes, white phosphorus, and sulfur.[2–9] Thus, heterolytic H_2 splitting and clean formation of the imidazolium hydroborate **2** occurs under an atmosphere of H_2, whereas self-deactivation and irreversible formation of the abnormal carbene-borane adduct **3** occurs in the absence of H_2 or other substrates (Scheme 1).[2,4,6] It was



Scheme 1. Reactivity of a frustrated carbene-borane Lewis pair.

immediately realized that the zwitterion **3** might become useful for generating the anionic carbene **4**, which bears a weakly coordinating anionic borate moiety in the backbone and could be regarded as a potentially useful addition to the comparatively small family of anionic N-heterocyclic carbenes (NHCs). Amongst the NHCs that have been described to date, numerous bi- and tridentate systems that contain tethered anionic binding sites such as thiolate,[10] alkoxide,[11] enolate,[12] imido,[13] or amido[14] groups are known, and thus afford chelating carbene ligands that are able to bind strongly to hard, electropositive metal ions.[15] In contrast, a significantly smaller number of anionic carbene-borate ligands of type **5** are known (Scheme 2), in which the borate moiety acts as a noncoordinating N-substituent and can also serve as a bridge between two or three imidazolin-2-ylidene fragments.[16]



Scheme 2. Selected examples of anionic N-heterocyclic carbenes. Mes = 2,4,6-trimethylphenyl.

A different approach that is based on the presence of a remote anionic functional group within the heterocyclic backbone was developed by Lavigne and co-workers.[17] Thus, the imidazolin-2-ylidene-4-olate **6** as well as the malonate- and imidato-type six-membered carbenes **7** and **8** were presented.[17–20] Although the coordination of **6–8** (and of related fluorinated species)[21] to transition metals in most cases does not involve metal interactions with the potentially reactive backbone moieties in the solid state, the possibility of such interactions is likely to affect the catalytic performance of homogeneous transition-metal catalysts that contain these carbene ligands.[19] Therefore, to minimize the accessibility of an additional basic site during catalytic processes, the introduction of a non-nucleophilic and chemically robust anionic functionality is required. Carbenes, such as **4**, can be expected to fulfill these prerequisites, as the steric and electronic effects of the $B(C_6F_5)_3$ unit are perfectly suited for the design of weakly coordinating anions (WCAs).[22]

Unfortunately, all attempts to generate the weakly coordinating, anionic, N-heterocyclic carbene (WCA-NHC) **4** by deprotonation of the zwitterion **3** proved unsuccessful. Consequently, an alternative approach was adapted that builds on the report by Robinson and co-workers on the possibility of generating anionic "dicarbene" **9a** by selective deprotonation of **1a** at the 4-position.[23] This procedure allows carbene functionalization by reaction with various electrophiles[23,24] and, accordingly, the reaction of lithiated carbenes **9** with $B(C_6F_5)_3$ should generate a borate moiety in the carbene backbone (Scheme 3). Indeed, the addition of *n*-butyllithium (*n*BuLi) to solutions of **1a** (R = *t*Bu) and **1b** (R = 2,6-diisopropylphenyl (Dipp)) in *n*-hexane afforded **9a** and **9b** as white precipitates, which, after suspension in toluene, were treated with $B(C_6F_5)_3$ to form the lithium salts of the

[*] Dipl.-Chem. S. Kronig, M. Sc. E. Theuergarten, Dr. C. G. Daniliuc, Prof. Dr. P. G. Jones, Prof. Dr. M. Tamm
Institut für Anorganische und Analytische Chemie
Technische Universität Carolo-Wilhelmina
Hagenring 30, 38106 Braunschweig (Germany)
E-mail: m.tamm@tu-bs.de
Homepage: http://www.tu-braunschweig.de/iaac

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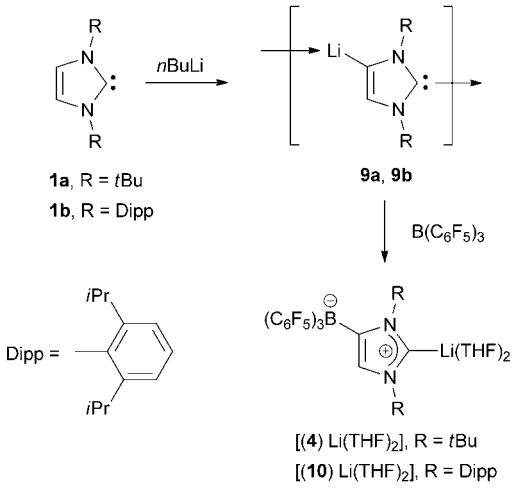


Scheme 3. Preparation of lithium carbene complexes.

desired WCA-NHCs. The addition of THF produced the lithium bis(tetrahydrofuran) complexes [(**4**)Li(THF)$_2$] by crystallization and [(**10**)Li(THF)$_2$] by precipitation. The resonances for the carbene carbon atoms are at $\delta =$ 211.2 ppm for [(**4**)Li(THF)$_2$] and at $\delta = 217.2$ ppm for [(**10**)Li(THF)$_2$] in the ^{13}C NMR spectra in [D$_8$]THF, which is, in both cases, slightly upfield from the resonances for the neutral carbenes **1a** ($\delta = 213.2$ ppm, [D$_8$]THF) and **1b** ($\delta =$ 220.6 ppm, C$_6$D$_6$).[25,26] The introduction of the borate moiety renders the N-substituents magnetically inequivalent, and two different sets of resonances in the ^{1}H NMR and ^{13}C NMR spectra are detected for the *t*Bu and Dipp groups. In a similar fashion to that described for **3** (Scheme 1), the rotation of the borane moiety around the B–C bond in [(**4**)Li(THF)$_2$] is hindered on the NMR timescale, as indicated by the detection of 14 separate signals for the 15 fluorine atoms, with two resonances for the *meta*-fluorine atoms overlapping at $\delta = -167.0$ ppm. As a result of this interlocking of the *t*Bu and C$_6$F$_5$ groups, the backbone CH group gives rise to a broad doublet at $\delta = 6.40$ ppm in the ^{1}H NMR spectrum, and has a coupling constant of $J_{HF} = 5.10$ Hz, which can be ascribed to long-range ^{1}H–^{19}F coupling.[27,28] In contrast, this resonance in the less sterically encumbered [(**10**)Li(THF)$_2$] appears as a broad singlet at $\delta = 6.11$ ppm, and the ^{19}F NMR spectrum contains only three resonances for the *meta*-, *para*-, and *ortho*-fluorine atoms, of which the latter is significantly broadened.

The molecular structures of [(**4**)Li(THF)$_2$] and [(**10**)Li(THF)$_2$] were also established by X-ray diffraction analysis and are shown in Figure 1. In both cases, the lithium atom is bound to the carbene carbon atom as well as two THF molecules and resides in a distorted trigonal-planar coordination sphere with angle sums of 359.7° and 359.9°, respectively. The C1–Li distances of 2.094(3) and 2.092(2) Å fall in the typical range of Li–C$_{carbene}$ interactions that are found in the literature, and these values are also in very good agreement with the values that have been reported for other Lewis acid adducts derived from **9b**.[11d,14a,b,16b,f,23a,29]

To study transmetalation reactions with the anionic carbenes **4** and **10**, their lithium complexes were added to

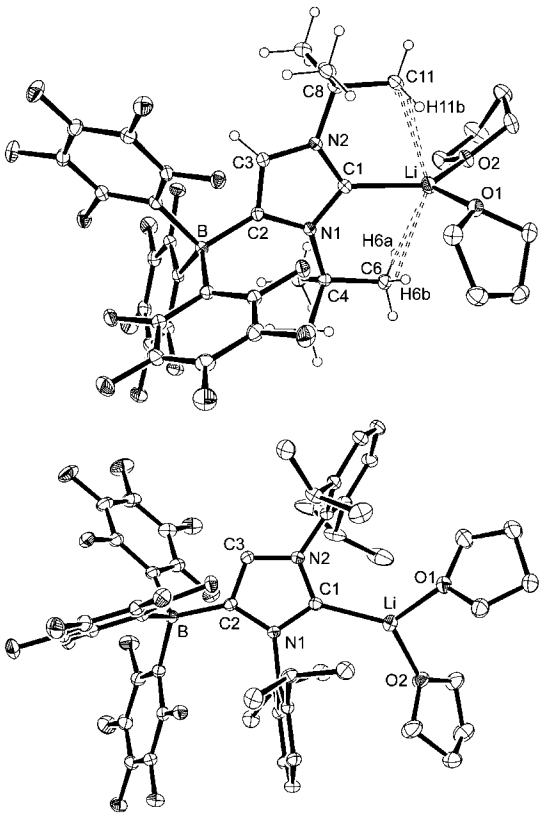
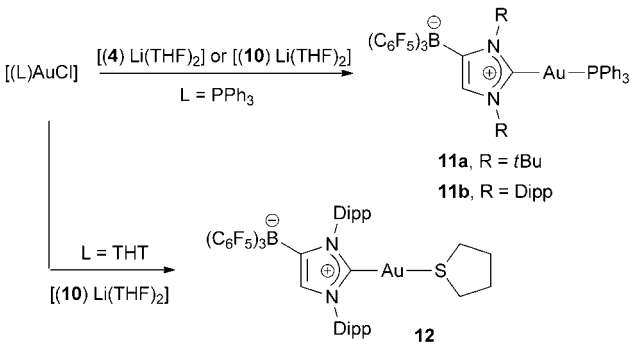


Figure 1. ORTEP diagram of [(**4**)Li(THF)$_2$] (top) and [(**10**)Li(THF)$_2$] (bottom) with thermal ellipsoids drawn at 30% probability. The hydrogen atoms on the THF ring are omitted for clarity. Selected bond lengths [Å] and angles [°] in [(**4**)Li(THF)$_2$]/[(**10**)Li(THF)$_2$]: Li–O1 1.910(2)/1.905(3), Li–O2 1.895(2)/1.889(3), Li–C1 2.092(2)/2.094(3), B–C2 1.6470(15)/1.6513(19); N1–C1–N2 103.71(9)/102.78(11), O1–Li–O2 113.48(10)/103.87(13), O1–Li–C1 118.35(11)/125.95(15), O2–Li–C1 127.89(11)/130.12(15). In [(**4**)Li(THF)$_2$], four short C–H···Li contacts with the *t*Bu groups that range from 2.23 to 2.47 Å were detected.

toluene suspensions of [AuCl(PPh$_3$)], which affords the neutral gold(I) complexes [(**4**)Au(PPh$_3$)] (**11a**) and [(**10**)Au(PPh$_3$)] (**11b**) as colorless, crystalline solids after separation from LiCl by filtration and crystallization from toluene/



Scheme 4. Preparation of neutral WCA-NHC gold(I) complexes; formal charges within the carbene ligand are shown to illustrate the ylidic nature of the metal-bound carbenes.

hexane or toluene/pentane solutions at −34 °C (Scheme 4). Carbene coordination to the $Au(PPh_3)$ complex fragment can be unequivocally confirmed by the detection of resonances at $\delta = 185.5$ (**11a**) and $\delta = 187.4$ ppm (**11b**) in the ^{13}C NMR spectrum for the carbene carbon atoms, which appear as doublets ($^2J_{CP} = 126$ Hz) as a result of ^{13}C–^{31}P coupling with the *trans*-phosphorus atom. The corresponding resonances in the ^{31}P NMR spectrum are detected at $\delta = 39.2$ (**11a**) and $\delta =$ 40.5 ppm (**11b**). X-ray diffraction analysis confirmed the expected, almost linear, two-coordinate gold environment for both complexes (Figure 2).

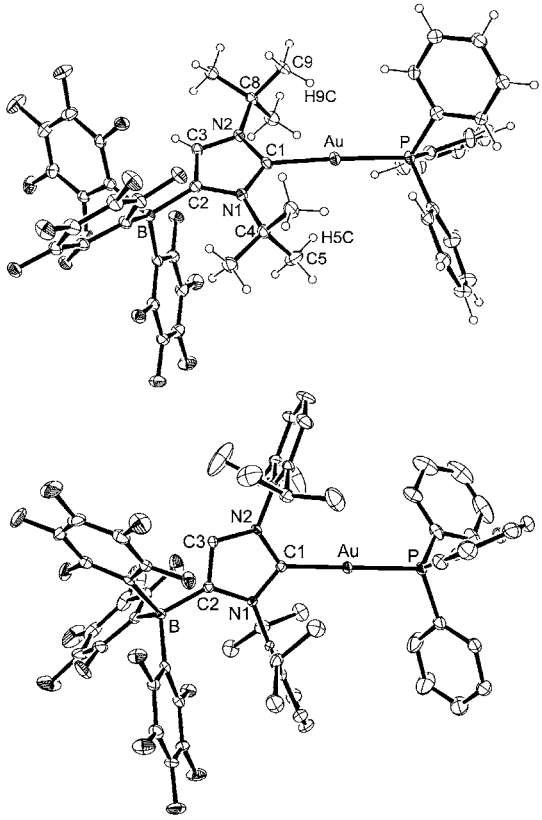


Figure 2. ORTEP diagram of **11a** (top) and **11b** (bottom) with thermal ellipsoids drawn at 30% (**11a**) and 50% (**11b**) probability. Selected bond lengths [Å] and angles [°] in **11a**/**11b**: Au–C1 2.071(2)/2.037(2), Au–P 2.2732(6)/2.2851(7), B–C2 1.658(3)/1.647(4); C1–Au–P 176.93(7)/177.84(7), N2–C1–N1 107.4(2)/105.3(2).

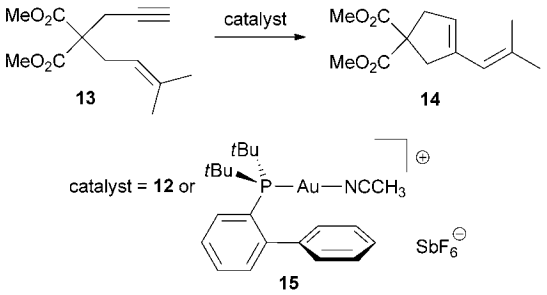
Since the first catalytic application of an NHC-gold(I) complex for the addition of water to 3-hexyne in the presence of the Lewis acid $B(C_6F_5)_3$ by Herrmann and co-workers in 2003,[30] gold(I) complexes that contain N-heterocyclic carbenes as stabilizing ligands have been employed in a wide variety of organic transformations.[31] Based on the alkynophilic nature of gold complexes, they proved to be excellent catalysts for promoting the cyclization and isomerization of enynes by skeletal rearrangement or alkoxycyclization in the presence of alcohols as nucleophiles,[32] and also for other organic transformations that involve alkynes.[33]

Most commonly, AuCl complexes that are supported by an N-heterocyclic carbene or a bulky phosphine ligand are employed in combination with a silver(I) salt (AgX, X = BF_4, PF_6, SbF_6) or other chloride scavengers to generate the corresponding cationic gold(I) complex as the catalytically active species in the presence of a WCA.[34] Examples in which a silver-free activation of neutral gold(I) precursors was employed are rare, and such protocols still remain highly desirable.[35] Furthermore, the cationic nature of the active catalysts usually requires the reactions to be carried out in polar solvents, such as dichloromethane or acetonitrile, which might be regarded as a limitation. The WCA-NHC systems **4** and **10**, on the other hand, offer the possibility of producing neutral, single-source, carbene-gold catalysts for application in less polar solvents and without the use of silver salts in any of the reaction steps, if a co-ligand is used that is more labile than the PPh_3 ligand in complexes **11** and that will readily dissociate during the catalytic process.

Therefore, [(THT)AuCl] (THT = tetrahydrothiophene) was treated with the lithium complexes [(**4**)Li$(THF)_2$] or [(**10**)Li$(THF)_2$] in toluene at 0 °C. In the case of [(**4**)Li-$(THF)_2$], the formation of elemental gold and decomposition occurred, whereas the formation of Au^0 was largely suppressed by use of [(**10**)Li$(THF)_2$], and the corresponding complex [(**10**)Au(THT)] (**12**) was isolated as a white crystalline solid in acceptable yield after filtration and crystallization from diethyl ether/dichloromethane/pentane solution at −34 °C (Scheme 4). The two broad resonances at $\delta = 1.64$–1.75 ppm and $\delta = 2.76$–3.05 ppm in the ^1H NMR spectrum, which can be assigned to the coordinated THT ligand, clearly indicate the formation of complex **12**. The resonance for the carbene carbon atom is at $\delta = 175.7$ ppm in the ^{13}C NMR spectrum, which is significantly shifted to higher field relative to the lithium complex [(**10**)Li$(THF)_2$] ($\delta = 217.2$ ppm) and the corresponding triphenylphosphine complex **11b** ($\delta =$ 187.4 ppm). The molecular structure of **12** was also confirmed by X-ray diffraction analysis, which revealed a linear S–Au–$C_{carbene}$ arrangement. Unfavorably, the Au(THT) moiety is disordered over two positions (the structure is presented in the Supporting Information).

To test the performance of **12** as a catalyst, the skeletal rearrangement of enyne **13** was chosen as a model reaction, which usually affords the 1,3-diene **14** as the single product.[32a,34e] The reaction was performed in various solvents with one mol % catalyst loading at room temperature and was monitored by GC (Table 1). In toluene, diethyl ether, and dichloromethane, full conversion of the starting material occurred in short times, and **14** was isolated in excellent yields. In contrast, the reaction did not proceed in hexane, and the starting material **13** remained unconverted even after 90 min, which is in agreement with the observation that **12** did not dissolve during the reaction. Relative to catalytic studies on the skeletal rearrangement reaction of **13** by gold(I) catalysts,[32a,34e,i,35b] amongst which the cationic complex **15** showed the best performance, the neutral catalyst **12** has comparable or even improved activity in this model reaction, and it also performs well in less polar solvents, such as toluene. Furthermore, **12** acts as a single-source catalyst and does not require activation by silver(I) salts. This underlying principle can be extended to various other catalytic processes in which cationic catalysts are involved, and the potential use

Table 1: Gold-catalyzed skeletal rearrangement of enyne **13**.



Catalyst	Catalyst loading [mol%]	Solvent	*t* [min]	Conversion [%][a]	Yield[b] [%]
12	1	toluene	5	>98	86
12	1	diethyl ether	5	>98	96
12	1	CH_2Cl_2	10	>98	98
12	1	hexane	90	–	–
15	2	CH_2Cl_2	5	–	98[34e]
$(PPh_3)AuCl/AgSbF_6$	2	CH_2Cl_2	25	–	91[32a, 34e]

[a] Conversion determined by GC by using *n*-decane as an internal standard. [b] Yield of isolated product after chromatography on a silica-gel column (hexane/ethyl acetate).

of WCA-NHCs as ancillary ligands in homogeneous catalysis will be further exploited.

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