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Synthesis and reactivity of triethylborane adduct of *N*-heterocyclic carbene: versatile synthons for synthesis of *N*-heterocyclic carbene complexes†

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The reaction of an imidazolium salt with $LiBEt_3H$ afforded triethylborane adduct of imidazol-2-ylidene, which can act as a carbene precursor for the synthesis of a transition metal complex as well as a main group element complex.

N-Heterocyclic carbenes (NHCs) are an increasingly useful class of ligands for not only transition metals but also main group elements.[1] One of the most widely used methods is the thermal cleavage of the enetetramines, so-called electron-rich olefins, in the presence of metal species.[2] However the metal precursor and/or product of the NHC are occasionally decomposed due to the high temperature requirement for enetetramine cleavage. The successful isolation of the free NHCs by Arduengo and co-workers in 1991[3] afforded the most common method of direct complexation of the free NHC, either isolated or generated *in situ*, produced by deprotonation of the corresponding salt. However manipulation of the free carbenes was often difficult due to their highly reactive nature. Recently the employment of NHC adducts as "protected" forms of the free carbene attracted much attention for synthesis of the metal complexes bearing these ligands. Grubbs and co-workers reported the utilization of NHC–alcohol or –chloroform adducts for saturated NHCs (imidazolin-2-ylidenes),[4] and Lin *et al.* reported the carbene transmetallation of silver complexes for unsaturated NHCs (imidazol-2-ylidenes).[5] Recent studies have revealed that the latter method is reliable for the preparation of the unsaturated NHC complexes.[6]

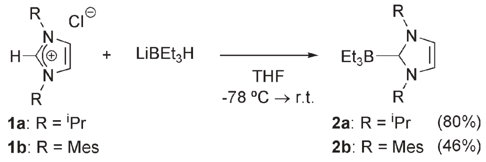
During the course of our research on NHC complexes, a BEt_3 adduct of NHC was obtained unexpectedly by the reaction of an imidazolium salt with $LiBEt_3H$; the latter acts not only as a base for the generation of a carbene but also the protecting group for it. We herein report the preparation, characterization, and utilization of $NHC{\cdot}BEt_3$ compounds.

Treatment of 1,3-diisopropylimidazolium chloride ($I^iPr{\cdot}HCl$, **1a**) with one equivalent of $LiBEt_3H$ in THF at −78 °C yielded a homogeneous reaction mixture from which pale yellow crystals of **2a** were isolated in 80% yield. In the case of **1b** (IMes·HCl), the 2,4,6-trimethylphenyl (mesityl) analogue of **1a**, a similar reaction took place to give a pale yellow solid **2b** (46%). Elemental analyses, and ^1H, ^{13}C, and ^{11}B NMR spectra established the formation of BEt_3-adduct NHC compounds (**2a** and **2b**) (Scheme 1). In the ^1H NMR spectra, the BEt_3 coordinated carbene carbon in both compounds displayed a triplet and a quartet for the methyl and methylene groups, respectively, in a region of high magnetic field (*ca.* −0.1 to 0.6 ppm). The ^{13}C NMR spectra showed the broad signals assignable to the carbene carbons at 174.0 ppm for **2a** and at 180.4 ppm for **2b**, respectively. The broadening may be caused by the influence of the binding boron. A singlet signal assignable to BEt_3 was observed at −12.6 ppm for **2a** and at −13.3 ppm for **2b**, respectively, in the ^{11}B NMR spectra. These chemical shifts are consistent with that of the reported carbene–BEt_3 compound.[7]

The X-ray analyses of **2a** and **2b** were undertaken.‡ The structures of **2a** and **2b** are shown in Fig. 1 and are consistent with their spectroscopic data. The B–C(carbene) bond distances are 1.683(5) Å for **2a** and 1.678(6) Å for **2b**. The B–C bond distances in **2** are remarkably longer than those in the BH_3-adduct of imidazol-2-ylidene compounds (1.596(4) Å for $IMes{\cdot}BH_3$ and 1.603(3) Å for 1,3-diethyl-4,5-dimethylimidazol-2-ylidene·BH_3),[8] and are slightly longer than those for the BF_3-adduct of imidazol-2-ylidene (1.635(5) Å for $IMes{\cdot}BF_3$ and 1.669(6) Å for 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene·BF_3).[9]

Recent study on the carbene adducts with Group 13 elements such as B, Al, Ga, and In revealed that these adducts have the remarkable thermal stability because of the formation of the stable acid–base adduct.[10] However, we focused attention on the elongated B–C(carbene) bond distance in the compounds **2**, because, if the bond cleavage would occur under mild conditions, compounds **2** could be utilized as the precursor for the HNCs. So, we investigated the reaction of compounds **2** with some metal compounds (Scheme 2).

On treating **2a** with $BH_3{\cdot}THF$ complex, a clean substitution



Scheme 1

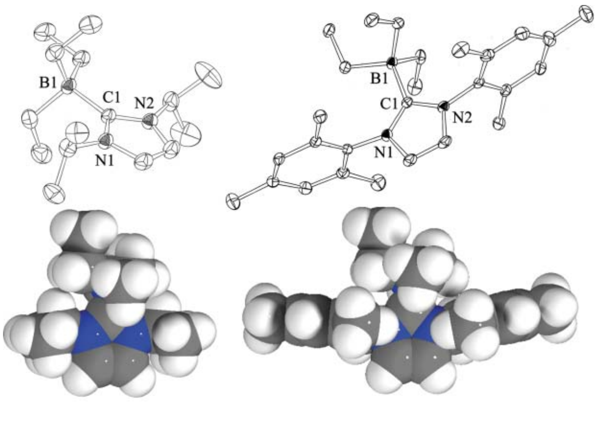


Fig. 1 Molecular structures of **2a** (left) and **2b** (right). ORTEP diagrams drawn at 30% probability (upper) and space filling diagrams (bottom).

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† Electronic supplementary information (ESI) available: full experimental data. See http://www.rsc.org/suppdata/cc/b4/b405459h/

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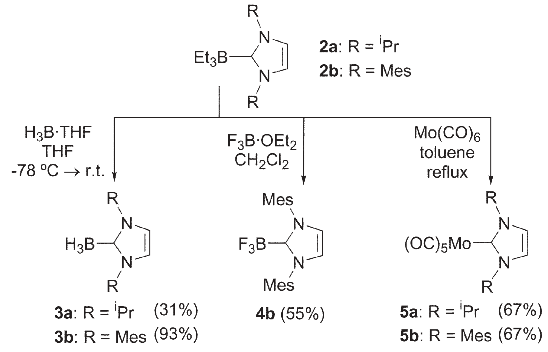


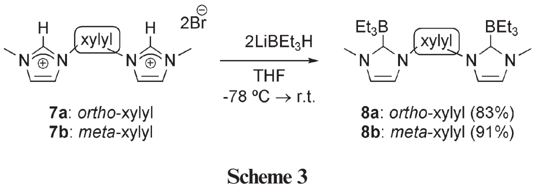
Scheme 2

reaction took place to give the BH$_3$-adduct of I^{i}Pr (**3a**). However, **3a** was so highly soluble toward hydrocarbons that a low isolated yield (31%) resulted. The similar reaction employing **2b** in the place of **2a** also afforded the BH$_3$-adduct **3b** as a white powder in a good yield (93%).[11] ^{11}B NMR spectra of **3a** and **3b** displayed quartet signals at -36.4 ppm ($^1J_{\mathrm{BH}} = 88.0$ Hz) and at -36.8 ppm ($^1J_{\mathrm{BH}} = 88.0$ Hz), respectively, whose data are consistent with the reported data for the related compound.[8] Other spectroscopic data supported the formation of BH$_3$-adducts **3**. Secondly the reaction of BF$_3$·OEt$_2$ with **2b** was examined, and thus the BF$_3$ adduct of IMes (**4b**) was formed as a colorless solid. The characterization of **4b** was done by ^{1}H and ^{11}B NMR measurements and these spectral data are consistent with the reported data by Arduengo.[9] Treatment of **2a** with Mo(CO)$_6$ in toluene under reflux conditions afforded a carbene complex of molybdenum **5a** as a pale yellow solid in moderate yield (67%). In the case of **2b**, Mo(CO)$_5$(IMes) (**5b**) was also obtained as a pale yellow solid in 67% yield. These complexes were characterized by elemental analyses, IR, and ^{1}H and ^{13}C NMR spectra.[12]

It is of interest to compare the behavior of BH$_3$- and/or BF$_3$-adducts toward Mo(CO)$_6$ to that of the BEt$_3$-adduct with a view to find possible reagents capable of carbene transfer to transition metals. Treatment of BH$_3$ adduct **3b** with Mo(CO)$_6$ under the same conditions, *i.e.*, refluxing in toluene, afforded the carbene complex **5b**, accompanied by the formation of Mo(η-toluene)(CO)$_3$ (**6**) (the ratio **5b**/**6** being *ca.* 1/1). On the other hand, from the reaction of Mo(CO)$_6$ with BF$_3$ adduct **4b**, the carbene complex **5b** was not formed and 82% of **4b** was recovered unreacted. These results clearly show that the BEt$_3$ adduct of NHC (**2**) effectively acts as a carbene precursor for a metal complex, which might be due to the weak Lewis acidity[13] and the steric bulk of BEt$_3$ compared with BF$_3$ and BH$_3$.

In order to investigate whether this method is applicable to the bidentate system or not, we examined the reaction of xylyl bridged bis(imidazolium) salts (**7a**: *ortho*-form, **7b**: *meta*-form) with two equivalents of LiBEt$_3$H. In both reactions, BEt$_3$-adducts of bis-(imidazol-2-ylidene) (**8a** and **8b**) were obtained as white powders in good yield (Scheme 3).

In summary, we showed the one-pot synthesis of BEt$_3$ adduct of NHC (**2**) by the reaction of imidazolium salt (**1**) with LiBEt$_3$H. The manipulation of BEt$_3$ adducts of NHC (**2**) is very easy due to their stability toward air and moisture. We also demonstrated the utilization of these adducts for the preparation of metal complexes.



Scheme 3

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Notes and references

‡ Crystal data for **2a**: C$_{15}$H$_{31}$BN$_2$, $M = 250.23$, orthorhombic, $a = 16.033(8)$, $b = 9.904(8)$, $c = 10.58(1)$ Å, $U = 1680(2)$ Å^3, $T = 223$ K, space group *Pnma* (no. 62), $Z = 4$, μ(Mo–Kα) = 0.56 cm^{-1}, 2788 measured reflections, 2575 unique reflections. $R1 = 0.082$, $wR2 = 0.212$, for 1754 reflections. For **2b**: C$_{27}$H$_{39}$BN$_2$, $M = 402.43$, orthorhombic, $a = 16.929(10)$, $b = 17.29(1)$, $c = 8.511(8)$ Å, $U = 2490(3)$ Å^3, $T = 173$ K, space group $P2_12_12_1$ (no. 19), $Z = 4$, μ(Mo–Kα) = 0.61 cm^{-1}, 4085 measured reflections, 4058 unique reflections. $R1 = 0.062$, $wR2 = 0.173$, for 3219 reflections. CCDC numbers: **2a**: 236673; **2b**: 236674. See http://www.rsc.org/suppdata/cc/b4/b405459h/ for crystallographic data in .cif format.

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