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Preparation of NHC Borane Complexes by Lewis Base Exchange with Amine− and Phosphine−Boranes

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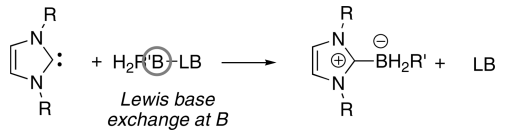

A versatile new method for the preparation of NHC boranes starting from two stable, readily available reactants—an heterocyclic salt and an amine or phosphine−borane—is reported. It uses a Lewis base exchange at boron and provides easy access to new NHC boranes, in particular B-substituted borane ones.

There is growing interest in the chemistry of borane complexes of N-heterocyclic carbenes (NHC boranes). Work focused first on structural determinations,[1] then gradually encompassed inorganic,[2] organic (in particular as tin hydride surrogates),[3] and organometallic[4] chemistries as well.

Further progress in NHC borane chemistry would be expedited by the development of a general, operationally simple and reliable pathway for the synthesis of such complexes. Until now, the only access to NHC boranes has been the complexation of isolated NHCs with solutions of reactive boranes, like BH_3−THF or BH_3−SMe_2.[2b−f,5] This methodology suffers some drawbacks. For example, BH_3−THF cannot be stored over prolonged periods (as are most isolable boranes) and BH_3−SMe_2 releases the foul-smelling and toxic volatile dimethyl sulfide upon complexation.

The formation of IPr−BH_3 from BH_3−THF is formally an exchange at the boron atom of a weakly coordinated Lewis base (THF) with the stronger NHCs. Boranes are known to lead to a variety of highly stable complexes with other, switchable, Lewis bases. In particular DABCO is used to decomplex sensitive phosphines from borane.[6] It thus seemed interesting to examine whether more tightly associated Lewis bases could also be exchanged with NHCs to generate the NHC boranes. We selected easily accessible amine−boranes[7] and phosphine−boranes.[8] We describe herein a new access to NHC boranes by Lewis base exchange at boron.

The well-known 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene carbene (IPr) was initially chosen as a representative NHC to probe exchanges with various amine−boranes. IPr is generated by deprotonation of the corresponding chloride imidazolium salt, and is an air-stable compound that can be stored for weeks.[9]

In a typical experiment, a benzene solution of IPr and a slight excess of Me_3N−BH_3 (**1a**, 1.1 equiv, Table 1, entry 1) was refluxed overnight, and the conversion was monitored by ^{11}B NMR. A new resonance (−36 ppm) appeared upfield from that of **1a** (−7 ppm). NHC borane **2** was isolated in 93% yield after a quick filtration over silica gel. The same

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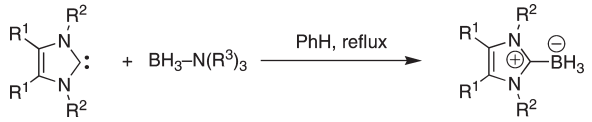
TABLE 1. Formation of NHC Borane Complexes from Amine–Boranes



entry	R^1	R^2	$N(R^3)_3$	NHCB, yield (%)
1	**H**	Ar[b]	Me_3N (**1a**)	**2**, 93
2	**H**	Ar	NH_3 (**1b**)	–[a]
3	**H**	Ar	Me_2NH (**1c**)	–[a]
4	**H**	Ar	*t*-Bu_2NH (**1d**)	–[a]
5	**H**	Ar	Et_3N (**1e**)	**2**, 91
6	**H**	Ar	pyridine (**1f**)	**2**, 87
7	**H**	Ar	DMAP (**1g**)	**2**, 70
8	**Me**	iPr	Me_3N (**1a**)	**3**, 89

[a]No reaction. [b]Ar = 2,6-iPrC_6H_3–.

compound was isolated in only 40% yield when the borane source was BH_3–THF.[3b]

A rapid screening of the commercially available amine–boranes as well as the easily accessible DMAP–BH_3[10] was examined next. No ^{11}B signal of **2** was observed in the crude mixture after one night with borane complexes of ammonia or primary and secondary amines (Table 1, entries 2–4). The acidity of such amine–boranes may account for these failures. On the other hand, good yields of **2** were obtained from triethylamine–borane (**1e**), pyridine–borane (**1f**, entry 6), and DMAP–borane (**1g**, entry 7). Overall, we were pleased to observe that the highest yielding amine–borane complex (**1a**) is also cheaper than the alternatives (1 mmol costs \$0.18, or 0.13€). The methodology was applicable to other stable NHCs. It delivered **3** in 89% yield (entry 8).

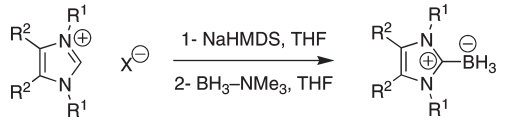
Most NHCs are prepared in situ so we looked for a more convenient procedure that starts directly from the imidazolium salts (Table 2). The latter were deprotonated in situ with a THF solution of NaHMDS (1 M) for 1 h at −78 °C in THF. Amine–borane **1a** was then added in one portion and the resulting solution was refluxed overnight (method A). To compare this new method to the standard methodology, we did a parallel series of experiments with BH_3–THF solution as boron source (method B).

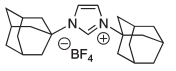
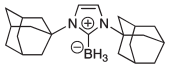
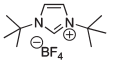
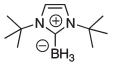
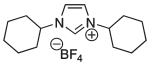
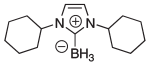
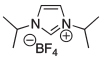
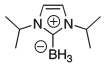
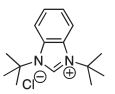
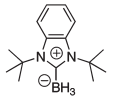
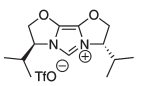
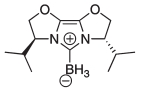
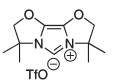
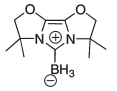
For all the in situ generated complexes but three, the yields with the new procedure were similar or slightly better than when BH_3–THF was used. Sterically hindered imidazolium yielded more desired product with the BH_3–THF solution than with **1a** (Table 2, entries 1, 3, and 11). The less tightly bound and less hindered BH_3–THF complex is probably better suited when steric hindrance becomes the main obstacle to reactivity.

Substituted boranes were examined next. The scattered example of NHC boranes with a substituent at B were prepared from stable boranes by direct complexation.[2b–f] We felt that our Lewis base exchange methodology might broaden the structural space that could be accessed since it would extend it to boranes that cannot be isolated pure, yet can be stabilized by amine complexation.

We selected two procedures from the literature to prepare *pyridine*-B-substituted borane complexes from the corresponding

TABLE 2. Variation of the NHC Unit



Entry	Imidazolium salt	Product	Meth.[a]	NHCB Yd. (%)
1			A	-[b]
2			B	**4**, 26
3			A	**5**, 6
4			B	**5**, 51
5			A	**6**, 71
6			B	**6**, 53
7			A	**7**, 65
8			B	**7**, 64
9			A	**8**, 50
10			B	**8**, 47
11			A	-[b]
12			B	**9**, 30
13			A	**10**, 87
14			B	**10**, 83
15			A	**11**, 47
16			B	**11**, 47

[a]Method A: NaHMDS (1 M in THF, 1.2 equiv), THF, −78 °C, 1 h then Me_3N–BH_3 (1.1 equiv), THF, reflux overnight. Method B: NaHMDS (1 M in THF, 1.2 equiv), THF, −78 °C, 1 h then BH_3–THF (1.1 equiv), THF, −78 °C to rt, overnight. [b]No reaction.

boronic acids[11] or boronates.[12] The complexed boranes were obtained by reduction of the corresponding boronate derivatives with LAH in diethyl ether, followed by quenching by pyridine (see the SI for detail).

The borane–pyridine complexes were then converted into the corresponding NHC boranes by using the previously established procedures, either from the isolated (method C) or from the in situ prepared (method A) NHCs (see Table 3). The yields were modest to satisfactory. Nonetheless there is to date no other way to access compounds **13**–**14**.

The reaction of IPr with (*S*)-Alpine–Boramine led to the corresponding NHC borane **13e** in 67% yield (entry 5), which shows that B-substituted amine–boranes also undergo the Lewis base exchange at boron.

Finally, we looked at phosphine–boranes as the borane source. In a typical experiment, triphenylphosphine borane was added to a benzene solution of iPr and led to 94% of **2**, after 24 h at 80 °C (see Scheme 1). The triphenylphosphine was fully recovered after a short purification. A similar result was obtained with secondary di-*tert*-butylphosphine–borane (81%).

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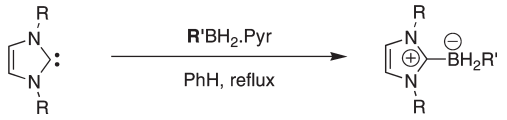
TABLE 3. Access to B-Substituted NHC Boranes



Entry	R	R'	Methods[a]	Yield (%)
1	2,6-iPrC$_6$H$_3$		C	**13a**, 16
2	2,6-iPrC$_6$H$_3$		C	**13b**, 65
3	2,6-iPrC$_6$H$_3$		C	**13c**, 66
4	2,6-iPrC$_6$H$_3$		C	**13d**, 68
5	2,6-iPrC$_6$H$_3$		C	**13e**, 67
6	Me		A	**14a**, 32
7	Me		A	**14b**, 49
8	Me		A	**14c**, 40
9	Me		A	**14d**, 58

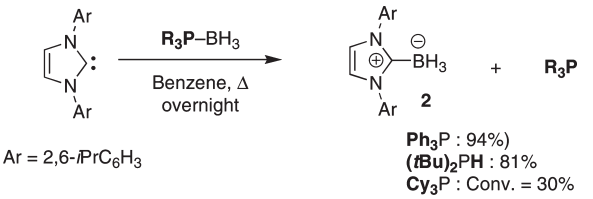
[a]Method A: See Table 2. Method C: Borane−amine complex (1.1 equiv), benzene, reflux overnight.

On the other hand, the reaction with tricyclohexylphosphine stopped at around 30% conversion after 4.5 days. The reverse reaction (PCy_3 on **2**) did not progress at all, so the former poor conversion cannot be explained by an equilibrium reached in a reversible reaction. Nonetheless the exchange methodology might be another way to decomplex specific phosphine−borane complexes.

To conclude, we have introduced a versatile new method for the preparation of NHC boranes starting from two stable, readily available reactants—an heterocyclic salt and an amine or phosphine−borane.[13] NHCs proved to be among the most tightly associated neutral ligands to boron. Thus, Lewis base exchange at boron provides an easy access to new substituted complexes, which should help in learning more about the reactivity of the title compounds.

(13) An alternative way to NHC boranes has been proposed by Braunschweig while this manuscript was under review. It involves carboxylate derivatives of NHCs as the NHC source, but uses borane−dimethyl sulfide as the boron source. See: Bissinger, P.; Braunschweig, H.; Kupfer, T.; Radacki, K. *Organometallics* **2010**, *29*, 3987−3990. This paper introduces NHC boranes as ligands for transition metals.

SCHEME 1. Phosphine/NHC Exchange



Experimental Section

General Procedure for the Synthesis of NHC Borane Complexes from Isolable NHCs. Trimethylamine−borane (7 mmol, 1.1 equiv) was added to a solution of IPr (250 mg, 6.43 mmol) in benzene (5 mL). The reaction mixture was refluxed overnight, and concentrated in vacuo. The crude product was purified by flash chromatography.

General Procedure for the Synthesis of NHC Borane Complexes from in Situ Generated NHC (Method A). NaHMDS (1 M in THF, 1.2 equiv) was added to a suspension of imidazolium salt (250 mg, 1 equiv) in dry THF (5 mL) at −78 °C. The resulting mixture was stirred for 1 h at −78 °C then warmed to rt. Trimethylamine−borane (1.1 equiv) was added and the resulting solution was refluxed overnight and concentrated in vacuo. The crude product was purified by flash chromatography.

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Supporting Information Available: Procedures and characterization of all new compounds, copies of spectra of products, and CIF files of the crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.