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Letter

Inverse Hydroboration of Imines with NHC-Boranes Is Promoted by Diphenyl Disulfide and Visible Light

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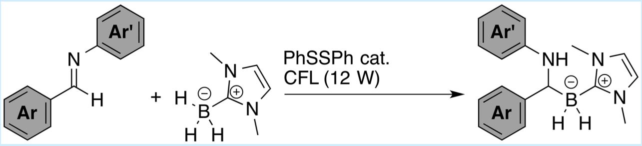
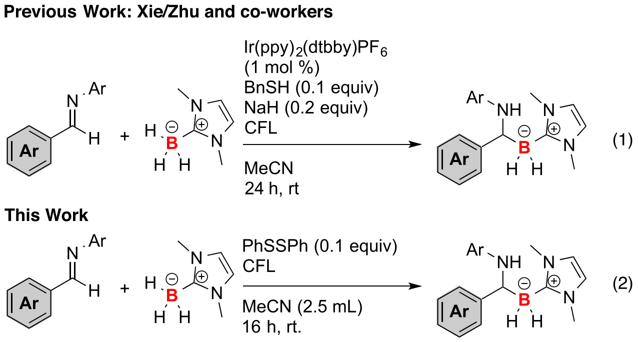
ABSTRACT: We describe a simple and efficient procedure for nucleophilic borylation of imines in the absence of a photoredox catalyst. Visible light irradiation of an acetonitrile solution of an imine, an NHC-borane, and diphenyl disulfide (10 mol %) provides various stable α-amino NHC-boranes in good yields. The reaction proceeds via addition of a nucleophilic boryl radical to an imine, followed by hydrogen abstraction from thiophenol, which is generated from NHC-borane and diphenyl disulfide.



Organoboron compounds are versatile building blocks in organic synthesis.[1] In the past two decades, boron-containing drugs[2] and functional materials[3] have attracted attention. In particular, α-amino boronic acids play an important role in pharmaceuticals.[4] Direct C-borylation of imines is an ideal method for the formation of α-amino boronic acids.[5,6] Standard ionic hydroboration cannot be used for this reaction because boranes behave as hydride sources and simple reduction to an amine typically ensues.[7] However, several valuable methods based on diborylation are known. In 2000, Baker and co-workers reported diborylation of imines with bis(catecholato)diboron in the presence of Pt(cod)Cl$_2$ catalyst.[6a] Elman developed asymmetric diborylation of chiral sulfinyl imines with copper catalyst,[6b] and Fernández reported enantioselective diborylation of tosylaldimines with chiral phosphine.[6c] The atom economy in these reactions is not ideal because one of the two boron functional groups is ultimately sacrificed for a proton.

In recent years, carbon−boron bond-forming reactions of *N*-heterocyclic carbene boranes (NHC-boranes) with alkenes and alkynes have been discovered.[8−10] These hydroboration reactions involve additions of NHC-boryl radicals to multiple bonds. The resulting NHC-borane adducts are stable compounds that nonetheless have a wide variety of reaction chemistry centering around the boron atom and its substituents.[11] In 2015, we reported radical cyanation of NHC-boranes with dinitriles.[9a] This reaction proceeds via addition of a nucleophilic boryl radical to a nitrile to give an iminyl radical, followed by β-cleavage.

Recently, Xie/Zhu and co-workers achieved inverse hydroboration of NHC-boranes to imines to afford α-amino boranes (eq 1).[12] This reaction requires a photocatalyst, benzyl thiol (0.1 equiv), sodium hydride (0.2 equiv), and light, and two nonchain mechanisms based on photoredox catalysis were proposed. In one, the new C−B bond is formed by radical−radical coupling, and in the other, it is formed by addition of an NHC-boryl radical to the imine. In traditional radical reactions, a radical Y adds to an unsaturated bond followed by hydrogen abstraction from Z−H to give a product along with a Z radical. The Z radical regenerates a Y radical thus keeping a radical chain.[13] If we could select an appropriate radical initiator and hydrogen donor, the α-amino boranes could be obtained through a radical chain mechanism under simple reaction conditions. We have now discovered that the inverse hydroboration reaction of imines with NHC-BH$_3$ proceeds efficiently by using PhSSPh as an additive under compact fluorescent light (CFL) irradiation conditions (eq 2).



Initially, we chose (*E*)-*N*-phenyl-1-(*p*-tolyl)methanimine (**1a**) as a model substrate in this study (Table 1). Curran reported hydrodehalogenation of aryl iodides and bromides using NHC-BH$_3$ and a catalytic amount of disulfide with a sun lamp.[14] These conditions are known to form thiols in situ. Thus, a reaction in acetonitrile was conducted with **1a** (0.5 mmol), diMeImd-BH$_3$ **2** (1.2 equiv), and PhSSPh (0.1 equiv)

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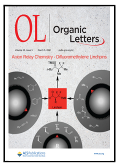

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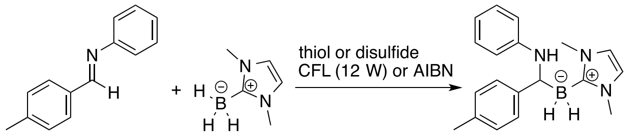
Table 1. Optimization

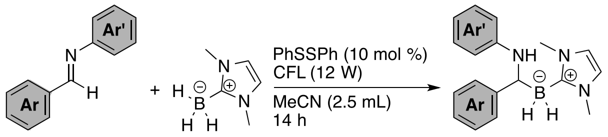


1 0.5 mmol **2** 1.2 equiv

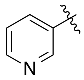
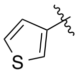
entry	light or initiator	thiol or disulfide	temp	yield[a]
1	CFL	PhSSPh (0.1 equiv)	–[c]	88% (78%)[b]
2	CFL	none	–[c]	0%
3	CFL	BnSSBn (0.1 equiv)	–[c]	0%
4	none (under dark)	PhSSPh (0.1 equiv)	80 °C	10%
5	AIBN (0.1 equiv)	PhSH (0.1 equiv)	80 °C	97%
6	AIBN (0.1 equiv)	PhSH (0.2 equiv)	80 °C	91%
7	AIBN (0.1 equiv)	BnSH (0.1 equiv)	80 °C	24%
8	AIBN (0.1 equiv)	BnSH (0.2 equiv)	80 °C	59%
9	AIBN (0.1 equiv)	none	80 °C	0%

[a] Determined by ^{1}H NMR using $CHCl_2CHCl_2$ as an internal standard. [b] Isolated yield after silica gel column chromatography. [c] The reaction was conducted at room temperature. However, the solution temp was increased using CFL to around 33 °C.

Table 2. Substrate Scope for Inverse Hydroboration Reactions of Imines[a]



1 0.5 mmol **2** 1.2 equiv

Entry	Ar	Ar'	1	3	Yield [b,c]
1	4-$CH_3C_6H_4$	Ph	**1a**	**3a**	88% (78%)
2	Ph	Ph	**1b**	**3b**	96% (87%)
3	4-FC_6H_4	Ph	**1c**	**3c**	94% (89%)
4	4-ClC_6H_4	Ph	**1d**	**3d**	89% (78%)
5	4-BrC_6H_4	Ph	**1e**	**3e**	98% (99%)
6	3-BrC_6H_4	Ph	**1f**	**3f**	98% (89%)
7	2-BrC_6H_4	Ph	**1g**	**3g**	90% (86%)
8	2-$C_{10}H_7$	Ph	**1h**	**3h**	95% (95%)
9		Ph	**1i**	**3i**	96% (82%)
10		Ph	**1j**	**3j**	90% (69%)
11	Ph	4-BrC_6H_4	**1k**	**3k**	78% (71%)
12	4-$CH_3C_6H_4$	4-BrC_6H_4	**1l**	**3l**	88% (85%)

[a] **1** (0.5 mmol), **2** (0.6 mmol), PhSSPh (0.05 mmol), CFL (12 W), MeCN (2.5 mL), 14 h. [b] Determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethame as an internal standard. [c] Yield of product, isolated after flash column chromatography on SiO_2, is given in parentheses.

under irradiation from a 12 W white CFL (compact fluorescence lamp) for 14 h. The target product **3a** was formed in 88% NMR yield and was isolated in 78% yield after column chromatography on silica gel (entry 1). No borylation product was observed in the absence of disulfide (entry 2). Importantly, BnSSBn is not an effective additive (entry 3).

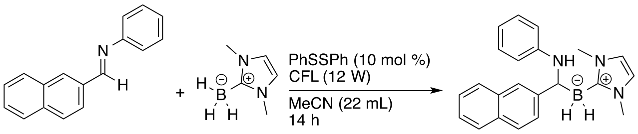
To understand why PhSSPh succeeds and BnSSBn fails, we conducted control experiments that omitted the imine. CFL irradiation of PhSSPh and **2** gave diMeImd-BH_2(SPh) and diMeImd-BH$(SPh)_2$.[15] In contrast, the reaction of BnSSBn with **2** afforded only trace amounts of NHC-boryl sulfides. These results suggest that PhSSPh is absorbing a little light from CFL to form an initial thiyl radical.

We next explored thermal reactions at 80 °C in the dark. In these, we used thiols in place of disulfides. Heating of **1**, **2a**, and 0.1 equiv of PhSSPh gave **3a** in only 10% yield (entry 4). Thermal initiation of PhSSPh is not effective.[15] However, when the traditional initiator AIBN was added, **3a** was formed in good yields (entries 5 and 6). The thermal reaction with BnSH gave poor results (entries 7 and 8). This difference in the reactivity may be based on the bond dissociation energies (BDE_{BnS-H} = 86.9 kcal mol^{-1} vs BDE_{PhS-H} = 79.1 kcal mol^{-1}).[16] This is suggested that the hydrogen abstraction by the iminyl radical from BnS−H would not proceed efficiently. No product was formed when AIBN was added and the thiol was omitted (entry 9). Taken together, these experiments support the notion that a radical chain is operating in both thermal and photoreactions and that PhSSPh is a precursor of PhSH in the photoreactions.

Next we explored the generality of this simple radical borylation of imines (Table 2). The reaction of **1b** gave corresponding product in 87% yield (entry 2). Substrates having halogen atoms at *para*, *meta*, and *ortho* positions, **1c**−**1g**, gave the corresponding products **3c**−**3g** in good yields (entries 3−7). The selectivity with aryl bromides (entries 5−7) is significant; no dehydrobromination products[14] were observed in these reactions. The reaction of imines **1h**−**1j**, which were prepared from aniline with 2-naphthaldehyde, 3-pyridinecarboxaldehyde, and thiophene-3-carbaldehyde, afforded *α*-amino boranes **3h**−**3j** in 95%, 82%, and 69% yields, respectively (entries 8−10). The reaction of imines **1k** and **1l**, which are prepared from 4-bromoaniline, also worked well (entries 11 and 12). The imines, which were prepared from the combination of aliphatic aldehydes with aliphatic or aromatic amines and aromatic aldehydes with aliphatic amines, were not suitable for this inverse hydroboration reaction in optimized conditions (Table 1, entry 1).

Finally, we conducted a gram-scale reaction of **1h** (4.34 mmol) under the standard conditions (Scheme 1). This furnished **3h** in 79% yield (1.17 g) after evaporation and flash chromatography.

Scheme 1. Gram Scale Reaction



1h 1.00 g 4.34 mmol **2** 1.2 equiv **3h** 1.17 g 3.43 mmol 79%

A chain mechanism for this inverse hydroboration of imines is proposed in Figure 1. In the initiation step, a thiyl radical **A** is formed from the disulfide under visible light irradiation conditions.[14] The thiyl radical abstracts hydrogen from NHC-borane **2** to give an NHC-boryl radical **B.**[17] In the key step, the NHC-boryl radical **B** adds to the imine **1** to give the α-NHC-boryl aminyl radical **C**. Addition to the C-atom of the imine is preferred over the N-atom due to the nucleophilicity of the NHC-boryl radical. Finally, **C** abstracts hydrogen from thiol to afford **3** and another thiyl radical **A**.

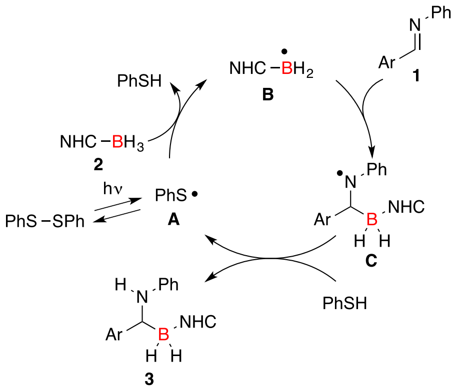


Figure 1. Possible mechanism.

In summary, we discovered a convenient photochemical procedure for inverse hydroboration of imines with NHC-borane **2** leading to α-amino boranes. PhSSPh was employed as a precursor of the thiyl radical and thiol. These reactions can also be conducted with AIBN under traditional thermal conditions, and this complementarity suggests that other types of PhSSPh/visible light-initiated radical borylation are worthy of investigation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00230.

Experimental procedure, compound characterization data, and copies of NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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