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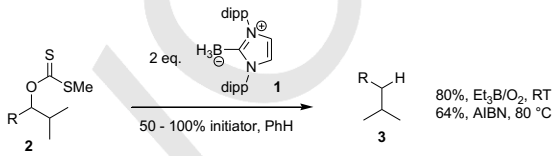
Aminopyridine-Borane Complexes as Hydrogen Atom Donor Reagents – Reaction Mechanism and Substrate Selectivity

Florian Barth, Florian Achrainer, Alexander M. Pütz, and Hendrik Zipse*[a]

Abstract: Lewis base-borane complexes are shown to be potent hydrogen atom donors in radical chain reduction reactions. Results obtained in ^{1}H, ^{11}B, and ^{13}C NMR measurements and kinetic experiments support a complex reaction mechanism involving the parent borane as well as its initial reaction products as active hydrogen atom donors. Efficient reduction reactions of iodides, bromides, and xanthates in apolar solvents rely on initiator systems generating oxygen-centered radicals under thermal conditions and pyridine-borane complexes carrying solubilizing substituents. In contrast to tin hydride reagents, the pyridine-boranes reduce xanthates faster than the corresponding iodides.

Introduction

Organotin compounds are versatile reagents in organic chemistry, the tin hydrides[1] being of particular importance in free-radical reduction reactions of appropriate alkyl, vinyl or aryl precursors such as halides or xanthates. In order to reduce problems caused by the toxicity of organotin compounds, methods catalytic in tin have been developed,[2] along with modified tin reagents to facilitate their removal.[3] In addition, a number of tin-free reagents[4,5] have been introduced including cyclohexadienes, germanes, thiols, hypophosphorous acid, different transition metal hydrides and silanes, such as the commercially available $(Me_3Si)_3SiH$.[6] Following earlier work by Roberts *et al.* documenting the ability of Lewis base-borane complexes (L-BH_3, L = NR_3, PR_3, SR_2)[7-9] to reduce oxygen- and carbon-centered radicals to the respective alcohols and hydrocarbons in moderate yields, Ueng *et al.* demonstrated the utility of borane complexes derived from *N*-heterocyclic carbenes (NHC) as Lewis bases.[10] Yields of more than 80% were obtained for the reduction of secondary xanthates **2** to the respective hydrocarbons **3** using the sterically demanding carbene borane **1** (Scheme 1).[10,11] While these experiments required larger amounts of initiator for good conversions, notable improvements were observed for NHC-boranes carrying smaller substituents, such as **12** (Figure 1).[12] Kinetic measurements show that this may be due to faster hydrogen abstraction rates for borane complex **12** (k_H(**12**) = 8 x 10^4 M^{-1} s^{-1}) than for the more shielded complex **1** (k_H(**1**) = 2 x 10^4 M^{-1} s^{-1}).[12] For selected Lewis base-borane complexes we recently calculated B-H bond dissociation energies (BDEs) using accurate quantum mechanical methods (Figure 1).[13]



Scheme 1. Radical reduction of xanthate **2** using "first-generation" NHC-borane **1** (dipp = 2,6-di*iso*propylphenyl, R = $(CH_2)_5OBn$).[10,11]

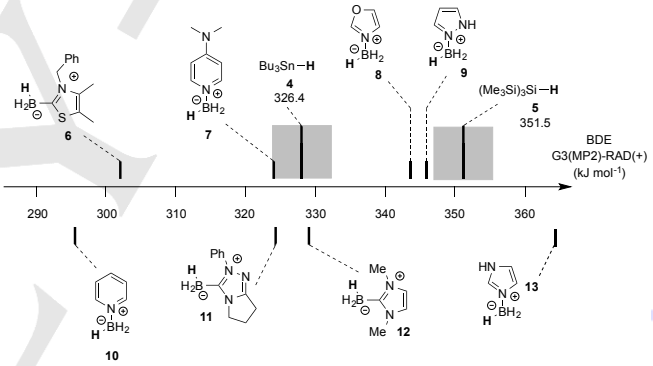


Figure 1. Theoretically calculated BDE(B-H) values (in kJ mol^{-1}) for selected borane complexes,[13] together with literature values for the Sn-H bond in Bu_3SnH (**4**),[14] and the Si-H bond in silane **5**.[15]

The BDE(B-H) value for borane complex **12** (BDE(**12**) = +328.6 kJ mol^{-1}) is closely similar to the BDE(Sn-H) value for tin hydride **4** (BDE(**4**) = +326.4 kJ mol^{-1}), which implies closely similar energetics for hydrogen transfer steps to carbon centered radicals. This is also true for DMAP-borane **7** (BDE (**7**) = +324.8 kJ mol^{-1}), whose utility in actual reduction reactions has not been explored much. In one of the few studies only activated α-iodo esters could be reduced in a radical chain process to the dehalogenated esters in moderate yields.[16] In the following we explore the utility of pyridine borane complexes such as **7** in radical reduction reactions and show that the success of these types of transformations is tightly linked to the type of radical precursor and initiator system used. We also show that the reaction mechanisms of these borane reductions are significantly more complex as compared to the well-known tin hydride reductions.

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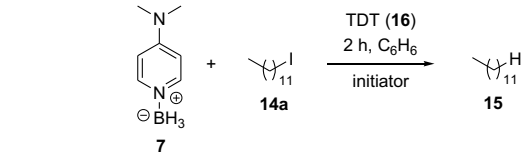
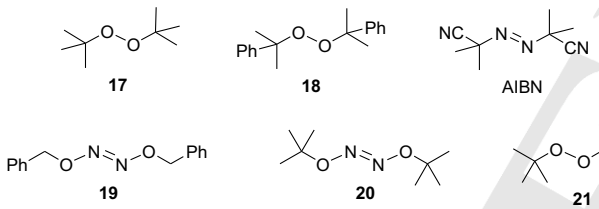
Results and Discussion

The reduction of 1-iodododecane (**14a**) to dodecane (**15**) in benzene was chosen as the test reaction for the radical experiments with DMAP borane (**7**) as hydrogen atom donor. Initial experiments with standard initiators (BEt_3/O_2 at room temperature and Azobisisobutyronitrile (AIBN) at 80 °C) were not successful, and alternative initiators were therefore tested for this system in the presence of small amounts of *tert*-dodecanethiol (TDT, **16**) as a "polarity reversal catalyst" to mediate hydrogen transfer steps.[7a,18] The underlying assumption here is that hydrogen atom transfer (HAT) reactions from TDT to a C-radical followed by HAT from borane **7** to TDT radical are faster than direct HAT between C-radical and borane **7**.

Table 1. Reduction of 1-iodododecane (**14a**) by borane complex **7** using different initiation systems.[a]



initiators:

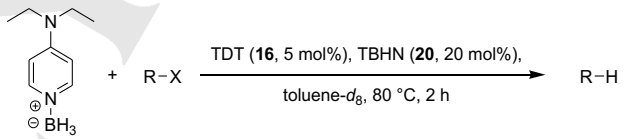


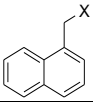
Radical Initiator	Amount of Initiator[b]	Temp. (°C)	Yield (%)
DTBP[c] (**17**)	20 mol%	80	0
Dicumoyl peroxide (**18**)	20 mol%	80	0
BEt_3/O_2	50 mol%	RT	13
AIBN	50 mol%	80	30
DBHN[d] (**19**)	20 mol%	80	17
TBHN[e] (**20**)	20 mol%	80	69
TBPP[f] (**21**)	20 mol%	90	88[g]

[a] Using 1.1 eq. **7** and 0.05 eq. TDT relative to **14a**. [b] Relative to **14a** employed. [c] Di-*tert*-butyl peroxide. [d] Dibenzyl hyponitrite. [e] Di-*tert*-butyl hyponitrite. [f] *Tert*-butyl peroxypivalate. [g] After 2 min reaction time.

Practically no conversion of iodide **14a** was observed in the presence of dialkylperoxides such as DTBP (**17**) and dicumyl peroxide (**18**) at a temperature of 80 °C. Higher reaction temperatures do, however, lead to ionic side reactions and also to decomposition of borane complex **7**, making these peroxides unsuitable for the reaction studied here. In addition, irradiation at a wavelength of 254 nm causes faster decomplexation of the borane than any effective initiation, which also eliminates the option of triggering the decomposition of peroxide **17** photochemically. Moderate conversion of iodide **14a** is observed for room temperature initiation with BEt_3/O_2 and also for AIBN at 80 °C. Significantly improved results are obtained at this latter temperature for di-*tert*-butyl hyponitrite (TBHN, **20**), whose decomposition generates two *tert*-butyloxy radicals. These latter species are also generated from perester *tert*-butyl peroxypivalate (TBPP, **21**), whose use leads to 88 % yield of dodecane **15**. The successful reduction of iodide **14** with borane complex **7** thus appears to require initiators generating oxygen-centered radicals in a temperature range around 80 °C. That the reaction is not successfully initiated by hyponitrite **19** may be due to the low thermal stability of this compound, whose decomposition sets in notably already below 20 °C. Taken together this leaves us with TBHN (**20**)/ DMAP borane (**7**) and TBPP (**21**)/ DMAP borane (**7**) as the only two protocols for the efficient reduction of alkyl iodides. Although the best results in these initial experiments were obtained for TBPP (**21**, Table 1), further experiments employed TBHN (**20**) as the initiating system in order to simplify comparison with earlier work using this initiator.[18]

Table 2. TDT-meditated reduction of different substrates using borane complex **22**.



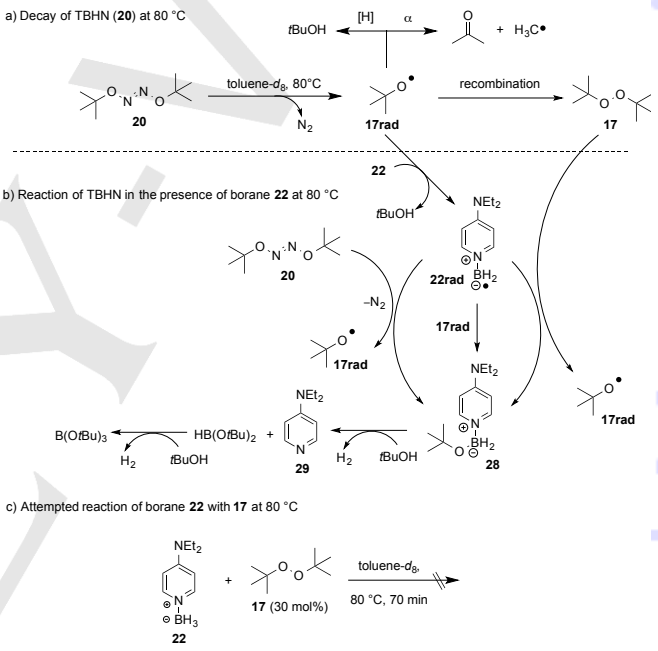
Entry	R-X		Yield (%)[a]
1		X = I (**14a**)	69
2		X = Br (**14b**)	37
3		X = OCS_2Me (**14c**)	99
4		X = I (**23a**)	51
5		X = I (**23a**)	82[b]
6		X = Br (**23b**)	0
7		X = OCS_2Me (**23c**)	0
8		X = OCS_2Me (**24**)	99
9		X = OCS_2Me (**25**)	10[c]

[a] Determined by ^1H NMR. [b] Ref. [18] using 0.1 eq. TBHN (**20**) and NHC-borane **12**. [c] Using 5 mol% TBHN (**20**).

The solubility of DMAP borane (**7**) in apolar solvents is rather limited, and further experiments have therefore been performed using 4-diethylaminopyridine borane (DEAP borane, **22**). This compound is easily soluble in toluene and benzene even at room temperature. Its reactivity in radical reactions is closely similar to that of DMAP borane (**7**) as can be seen from the

substrate screening results shown in Table 2. The reduction of 1-iododododecane (**14a**) with DEAP borane (**22**) leads to 69 % dodecane (entry 1). This is practically identical to the result obtained for DMAP borane (**7**) in benzene and demonstrates that the longer alkyl substituents in **22** have little influence on the reactions occurring at the boron center. For the reduction of 1-bromododecane (**14b**) a yield of 37 % was obtained (entry 2), while reduction of xanthate **14c** is quantitative under these conditions (entry 3). Full conversion was also observed for the secondary xanthate **24** (entry 8), while no reaction occurred for adamantyl bromide **23b** and adamantyl xanthate **23c** (entries 6 and 7). The reduction of adamantyl iodide **23a** with **22** proceeds with a moderate yield of 51 % (entry 4), while a yield of 82 % was reported earlier when using NHC-borane **12** as the reducing agent.[17] Only 10 % 1-methylnaphthalene were obtained from the reduction of xanthate **25** in the presence of 5 mol% TBHN (**20**, entry 9). In this case the reaction outcome seems to correlate with the amount of TBHN (**20**). This may imply that the rate of hydrogen abstraction from aminopyridine boranes by the stabilized benzylic substrate radical is too low to drive the chain reaction efficiently. In summary, primary iodides and xanthates as well as secondary xanthates can be effectively reduced using TBHN as the initiator and borane complex **22** as the reductant.

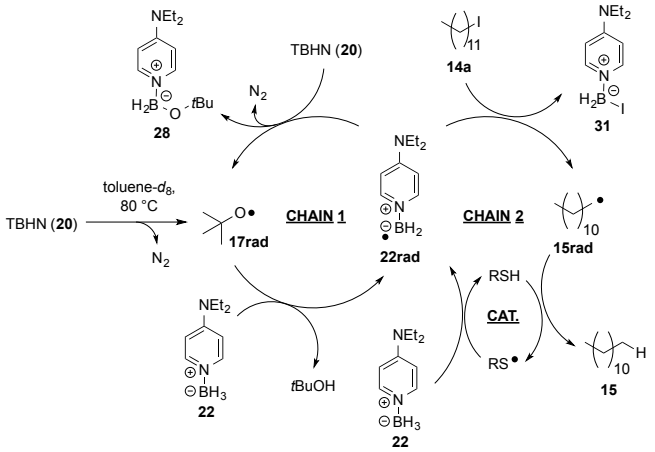
In order to better understand the decomposition pathways of TBHN (**20**), its decomposition in toluene-d_8 at 80 °C was monitored by ^{1}H NMR spectroscopy (initial concentration of TBHN was 0.1 M) implying a half-life time of 520 seconds and *tert*-butanol (**26**) and acetone (**27**) as the major products. This can be rationalized assuming the mechanism shown in Scheme 2a involving initial formation of *tert*-butyloxy radical **17rad**. Subsequent hydrogen abstraction (presumably from the solvent) generates *tert*-butanol, while C-C bond cleavage leads to acetone and a methyl radical. The latter can be identified as methane by ^{1}H NMR.[24] Recombination of radical **17rad** to yield peroxide **17** appears to play only a minor role under these conditions. The formation of methyl-*tert*-butyl ether as a possible recombination product of **17rad** and a methyl radical was also not observed. It should be added that the known high temperature initiator **17** is stable at 80 °C (as shown in a control experiment). Monitoring the decomposition of TBHN (**20**, 20 mol%) in toluene-d_8 at 80 °C in the presence of DEAP-borane (**22**) leads to a more complex sequence of events (Scheme 2b). That *tert*-butanol, but neither acetone nor DTBP (**17**), are formed under these conditions can be rationalized by assuming rapid reaction of the initially formed *tert*-butyloxy radical **17rad** with borane complex **22**. The boryl radical **22rad** generated in this step is then transformed to borane **28**, whose intermediate formation can be detected spectroscopically. Several pathways seem conceivable for this latter step (Scheme 2b): direct recombination of boryl radical **22rad** with a *tert*-butyloxy radical **17rad**, reaction of boryl radical **22rad** with TBHN, or reaction of boryl radical **22rad** with peroxide **17** (if formed). Whether borane complex **22** reacts directly with peroxide **17** was tested in a control experiment, but no reaction was detected after 70 min at 80 °C (Scheme 2c). However, repeating this experiment in the presence of TBHN (20 %) leads to complete consumption of peroxide **17** within 10 min at 80 °C, which can most easily be rationalized by reaction of boryl radicals **22rad** with peroxide **17**. In this case TBHN (**20**) acts as the true initiator of the reaction, whose presence is necessary for the generation of **22rad**. The final step of the reaction is the formation of di-*tert*-butoxy borane and tri-*tert*-butyl borate accompanied by decomplexation from the Lewis base as determined by ^{11}B NMR. These reactions may proceed along radical pathways, or simply result from the (non-radical) reaction of *tert*-butanol with borane complex **28**. This latter option implies formation of molecular hydrogen, whose release can indeed be detected by ^{1}H NMR spectroscopy.[24] Further control experiments show no ionic reaction of acetone or *tert*-butanol with DEAP-borane (**22**) after 30 minutes at 80 °C, yielding neither free DEAP (**29**), di-*tert*-butoxy borane or tri-*tert*-butyl borate.



Scheme 2. Decomposition of TBHN (**20**) in the (a) the absence and (b) the presence of borane complex **22**.

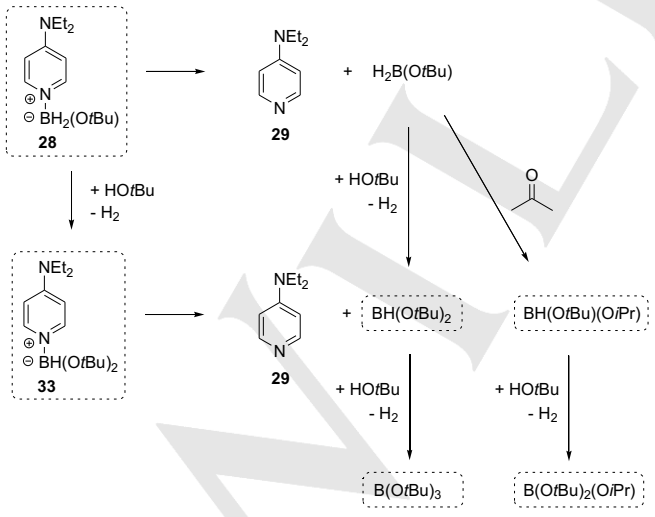
A plausible mechanism for the TDT (thiol)-catalyzed reduction of 1-iododododecane (**14a**) with DEAP borane (**22**) listed as entry 1 in Table 2 is shown in Scheme 3. Initiation with TBHN (**20**) leads to *tert*-butoxy radicals (**17rad**), whose subsequent reaction with DEAP borane (**22**) generates boryl radical **22rad** and *tert*-butanol. Two competitive chain reactions branch off from boryl radical **22rad**: in chain 1 reaction with the initiator TBHN (**20**) occurs, regenerating a *tert*-butoxy radical (**17rad**) and borane complex **28** under the release of nitrogen. In chain 2 boryl radical **22rad** reacts with precursor **14a** to yield iodo borane **31** and a dodecyl radical. Subsequent hydrogen transfer forming dodecane (**15**) as the desired product is possible either from borane complex **22**, or from thiol TDT (**16**). The thiyl radical generated in this latter case is catalytic in the sense that its reaction with borane complex **22** regenerates thiol **16**. Important

termination steps in the combined chain reactions 1 and 2 include the recombination of *tert*-butyloxyl **17rad** with boryl radical **22rad** leading to borane complex **28** observed by ^{1}H and ^{11}B NMR spectroscopy.



Scheme 3. Mechanism of the TDT-catalyzed reduction of iodododecane **14a** with borane complex **22** using TBHN (**20**) as initiator.

Detailed analysis of the reaction mixture for the reduction of iodide **14** using ^{1}H and ^{11}B NMR spectroscopy indicates that the fate of borane complex **22** is significantly more complex than described in Scheme 3. In addition to alkoxyborane **28** several more highly oxidized borane species are detected, whose identity was clarified through spectral parameters and comparison to reference compounds. A minimal mechanism rationalizing the formation of these compounds is shown in Scheme 4.



Scheme 4. Oxidation of borane complex **28** to boron species detected in the reduction of iodide **14a**. Dotted frames indicate species observed by ^{11}B NMR spectroscopy.

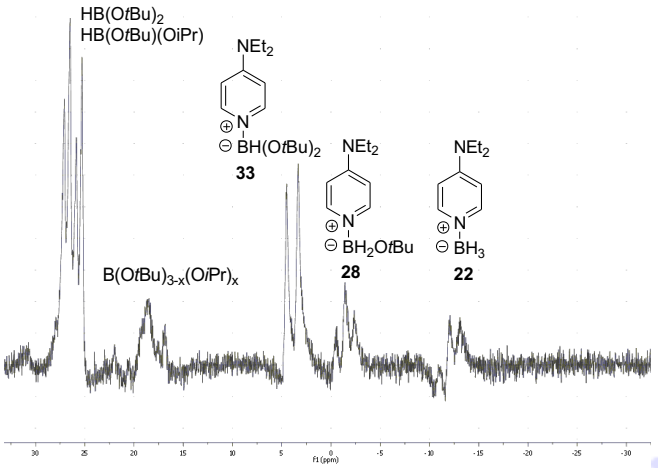
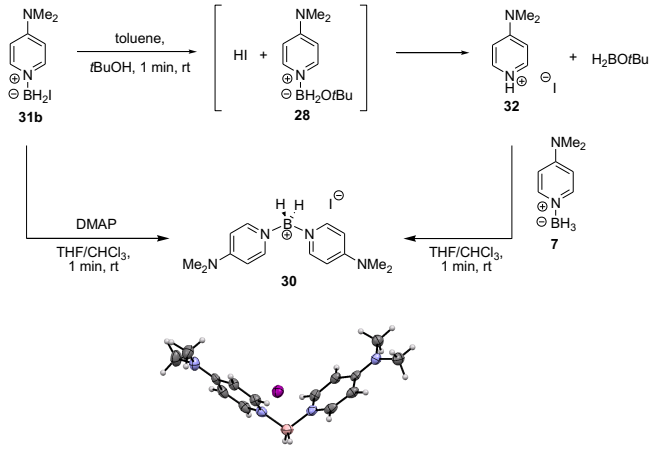


Figure 2. ^{11}B NMR spectrum of the TDT-catalyzed reduction of alkyl iodide **14a** with DEAP-BH_3 (**22**) in toluene-d_8 at 80 °C.

One of the most prominent species in the reaction mixture is bis-alkoxyborane complex **33**, possibly formed from complex **28** through reaction with *tert*-butanol. Dissociation of this species liberates pyridine **29** together with bis(*tert*-butyloxy)borane. This latter compound may alternatively be formed through dissociation of complex **28** and reaction of *tert*-butyloxyborane with *tert*-butanol. *Tert*-butylborate as the end product of the oxidation sequence most likely derives from direct reaction of *tert*-butanol with bis(*tert*-butyloxy)borane. The presence of boranes carrying isopropyloxy substituents is most easily rationalized through reduction of initiator-derived acetone with one of the borane species.

A final observation for the reduction of 1-iodododecane (**14a**) with aminopyridine boranes can be made at longer reaction times at 80 °C, when in all cases a colorless solid precipitates from the initially clear toluene solution. Formation of this precipitate is, at least in part, responsible for the noisy baseline observed for all ^{11}B NMR measurements performed in toluene-d_8 Using a combination of X-ray analysis, NMR spectroscopy, and mass spectrometry, the precipitate in the case of DMAP borane **7** can be identified as iodide **30**, which is air stable and resistant to water for several hours.[25] The formation of bispyridyl complex **30** can be rationalized assuming nucleophilic substitution of initially formed iodo borane **31b** by free DMAP generated in the dissociation of more highly oxidized borane complexes as described in Scheme 4. In support of this hypothesis iodide **31b** was independently synthesized by the addition of iodine to a solution of DMAP borane (**7**) in toluene as shown in Scheme 5 (^{11}B NMR, $CDCl_3$: t, -11.3 ppm). Addition of *tert*-butanol leads directly to the formation of 4-dimethyl aminopyridine hydroiodide **32**. This salt reacts immediately with DMAP borane **7** to bispyridyl complex **30**. Both pathways appear equally viable and responsible for the absence of NMR signals for free iodoborane of type **31** and aminopyridine in the reaction mixture. Replacing DMAP by DEAP (**29**) in Scheme 5 gives rise to DEAP-complex **30b**, which is equally insoluble in toluene as **30** (see SI for structural details).[25]



Scheme 5. Formation and independent synthesis of iodide **30**.

To avoid precipitation of the bispyridyl species and for testing its role in the mechanism as intermediate or even its suitability as hydrogen atom donor, the reduction of iodododecane (**14a**) was repeated under essentially identical reaction conditions as listed in Table 2, entry 1, using dihexylaminopyridine borane (DHAP borane, **34**). Although the corresponding bispyridyl species stays in solution in this case, the dodecane yield of 60% is slightly lower as compared to the 69% obtained with DEAP borane (**22**). It thus appears that cationic bispyridyl borane complexes such as **30** are not suitable hydrogen atom donors under these conditions.

The rich portfolio of boranes and borane complexes observed in the reduction of iodide **14a** with borane complex **22** raises the question whether some of these species are equally good (or even better) hydrogen atom donors as compared to the originally used borane complex in radical chain reduction reactions. Radical stabilization energies (RSEs) and B-H bond dissociation energies (BDEs) have therefore been calculated for the most relevant species using the same G3(MP2)-RAD(+) approach as before. From the results collected in Table 3 and shown graphically in Figure 3 it can easily be seen that the complexation of boranes by Lewis-basic amino pyridines has an enormous effect on the stabilization of the unpaired spin. As expected the B-H bond energy in DEAP borane **22** (BDE(**22**) = +330.4 kJ mol^{-1}) is closely similar to that in the respective dimethyl derivative **7** (BDE(**7**) = +324.8 kJ mol^{-1}), and both compounds thus fall into the BDE region marked by frequently employed reducing agents such as tin hydride **4** and ethanethiol (**37**) (used here as a model for TDT (**16**)). Replacing one of the B-H bonds in borane complex **22** by a *tert*-butyloxy substituent as in borane complex **28** reduces the B-H bond energy dramatically to BDE(**28**) = +288.4 kJ mol^{-1}, which implies that complex **28** is a much better hydrogen atom donor in thermochemical terms.

Table 3. Radical stabilization energies (RSEs) for selected boryl radicals together with BDE(B-H) values of the corresponding boranes (G3(MP2)-RAD(+), in kJ mol^{-1}).

$HBX_2 + {\bullet}BH_2 \xrightarrow[(=\,RSE)]{\Delta H_{298}} {\bullet}BX_2 + BH_3$

	RSE ($\bullet BX_2$)	BDE[a] ($H\text{-}BX_2$)
$HB(OtBu)_2$	+4.15	+445.3
BH_3	0.0	+441.1
H_2BOtBu	-6.5	+434.6
$H_2BSCOSMe$	-14.3	+426.8
$HB(SCOSMe)_2$	-34.7	+406.4

$LB{-}BHX_2 + {\bullet}BH_2 \xrightarrow[(=\,RSE)]{\Delta H_{298}} LB{-}BX_2 + BH_3$

	RSE ($LB\text{-}BX_2^{\bullet}$)	BDE[a] ($LB\text{-}BX_2\text{-}H$)
35	-68.0	+373.1
36	-78.2	+362.9
DEAP-BH_3 (**22**)	-110.7	+330.4
NHC-BH_3 (**12**)[b]	-112.5	+328.6
DMAP-BH_3 (**7**)	-116.4	+324.8
33	-129.7	+311.4
37	-136.0	+305.1
28	-152.5	+288.6

[a] With BDE($H\text{-}BX_2$) = RSE($\bullet BX_2$) + BDE($H_2B\text{-}H$) or BDE($LB\text{-}BX_2\text{-}H$) = RSE($LB\text{-}BX_2^{\bullet}$) + BDE($H_2B\text{-}H$) and using BDE($H_2B\text{-}H$) = +441.1 kJ mol^{-1} from ref. [13]. [b] From ref. [13].

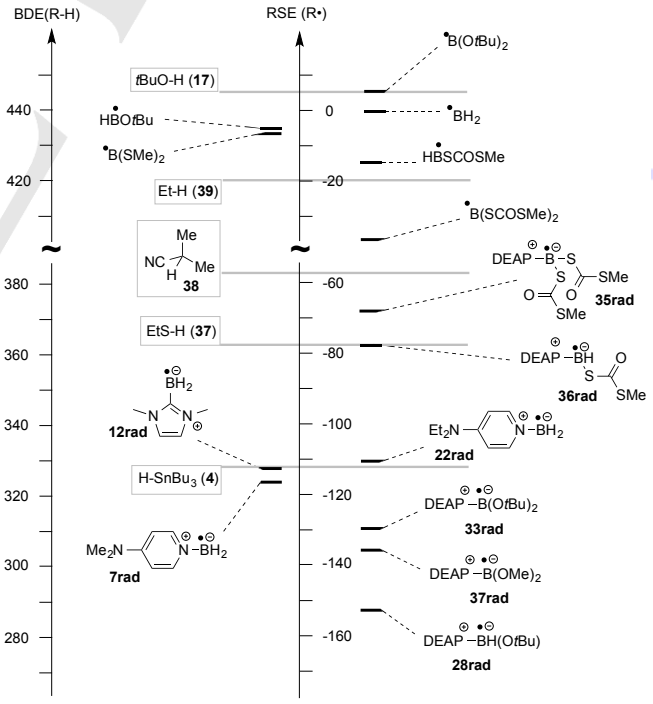
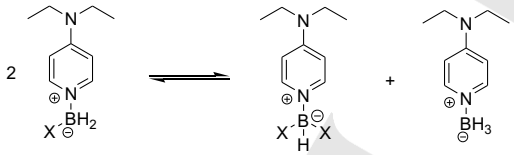


Figure 3. Graphical representation of radical stabilization energies (RSE, in kJ mol^{-1}) and the corresponding BDE(B-H) values of boryl radicals shown in Table 4 (DEAP = 4-diethyl aminopyridine).

Replacing a second B-H bond in **28** by a *tert*-butyloxy substituent leads to borane complex **33**, whose remaining B-H bond is somewhat stronger than in complex **28** at BDE(**33**) = +311.4 kJ mol^{-1}, but still weaker than in the original borane complex **22**. The introduction of sulfur substituents as in borane complexes **36** and **35**, in contrast, leads to an increase in B-H bond energies. These latter complexes are likely intermediates in the radical chain reduction of xanthate precursors (see below). Figure 3 also includes BDE values for radicals formed *in-situ* from established initiators like AIBN, BEt_3 or TBHN (**20**) as grey bars. From this comparison it is evident that the *tert*-butoxyl radical (**17rad**) is the least stable on thermochemical grounds.[17] Still, a reason why initiation is only accomplished by oxygen-centered radical is not immediately apparent from these energies.

The thermochemical data required for the calculation of B-H bond energies in pyridine borane complexes can also be used to quantify the driving force for the disproportionation of singly substituted complexes. This is particularly relevant for alkoxyborane complex **28** formed in larger amounts in the reduction reaction of iodide **14a**. Disproportionation of this complex to original borane complex **22** and dialkoxyborane complex **33** is exergonic by -31.8 kJ mol^{-1} at the G3(MP2)-RAD(+) level of theory (Table 4). This implies that, in addition to ionic reactions with *tert*-butanol and radical reactions involving initiator TBHN, a third pathway for the conversion of complex **28** to **33** involves disproportionation of the former as described by the process in Table 4. In contrast, the same disproportionation process is endergonic by +18.2 kJ mol^{-1} for xanthate-derived borane complex **36**.

Table 4. Thermochemical analysis of disproportionation reactions of borane complexes **28** and **36** at various levels of theory (in kJ mol^{-1}).

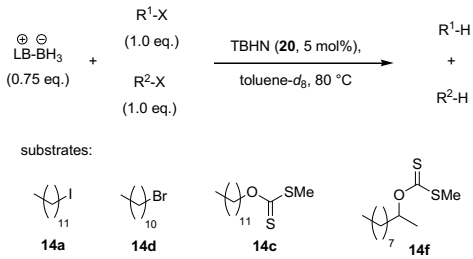


28/36 **33/35** **22**

X	mPW1K/6-31+G(d)			G3(MP2)-RAD(+)		
	ΔH_{dis}	ΔG_{dis}	K	ΔH_{dis}	ΔG_{dis}	K
O*t*Bu (**28**)	-18.3	-17.4	$1.1 \cdot 10^3$	-30.4	-31.8	$3.7 \cdot 10^5$
SCOSMe (**36**)	+37.5	+34.5	$8.9 \cdot 10^{-7}$	+21.9	+18.2	$6.6 \cdot 10^{-4}$

From a synthetic point of view the rather different yields obtained in the reduction of dodecyl iodides, bromides, and xanthates (Table 2) deserve further attention. In particular, the large differences in turning over bromides and xanthates appear at variance with results in other radical reduction reactions. The relative reactivities of these precursors were therefore tested in competition reactions with two dodecyl derivatives present in a 1:1 ratio and the reducing agent added in less than stoichiometric amounts. Reactions were run with TBHN (**20**) as the initiator and without added TDT (**16**). With DMAP-borane (**7**) as the commercially most viable borane complex conversion of dodecyl xanthate (**14c**) is actually faster than that of dodecyl iodide (**14a**) (Table 5, entry 1). A rather different result is obtained in reactions with NHC-borane **12**, where practically no turnover of xanthate **14c** is observed. Addition of TDT as a hydrogen transfer catalyst increases the turnover of iodide **14a** in this latter case, but has no impact on the reduction of xanthate **14c**. Tin hydride **4**, in contrast, turns over both precursors with a small preference for iodide **14a** and acts quite effectively in that the combined turnover approaches the theoretically possible maximum of 75%. In competition experiments involving dodecyl bromide (**14d**) and dodecyl xanthate (**14c**) the reduction with DMAP-borane (**7**) shows a large preference for the xanthate, which now is quite similar to that observed for NHC-borane **12** (Table 4, entries 5 and 6). Reduction with tin hydride **4** is unselective in that both precursors are reduced with comparable yield. Competition experiments using secondary xanthates such as **14f** show that these react substantially faster than primary xanthates. The combined turnover of xanthates and iodides/bromides in these last cases clearly exceeds the mark of 75%, which implies that more than one of the B-H bonds present in DMAP-borane is actively involved in the reduction reaction. With respect to the multi-step mechanism shown in Scheme 3 the selectivities documented in Table 5 most likely arise in the substrate radical generation step and thus reflect different rates of reaction between radical precursors and pyridine boryl radical **7rad** as compared to the reagent-derived radicals from NHC borane (**12**) or tin hydride (**4**).

Table 5. Competion of various iodides, bromides and xanthates with different hydrogen atom donors.



substrates:

14a **14d** **14c** **14f**

entry	LB-BH_3	Substrates	Conversion
1	DMAP-BH_3 (**7**)	**14a+14c**	18 % (**14a**), 78 % (**14c**)
2	NHC-BH_3 (**12**)	**14a+14c**	25 % (**14a**), <1 % (**14c**)
3[a]	NHC-BH_3 (**12**)	**14a+14c**	45 % (**14a**), <1 % (**14c**)
4	Bu_3SnH (**4**)	**14a+14c**	55 % (**14a**), 20 % (**14c**)
5	DMAP-BH_3 (**7**)	**14d+14c**	4 % (**14d**), 71 % (**14c**)
6	NHC-BH_3 (**12**)	**14d+14c**	13 % (**14d**), 70 % (**14c**)
7	Bu_3SnH (**4**)	**14d+14c**	35 % (**14d**), 35 % (**14c**)
8	DMAP-BH_3 (**7**)	**14a+14f**	35 % (**14a**), 94 % (**14f**)
9	DMAP-BH_3 (**7**)	**14b+14f**	10 % (**14b**), 96 % (**14f**)

[a] Addition of 5 mol% TDT (**16**).

Conclusions

Aminopyridine-borane complexes represent a class of easily accessible, air- and moisture-insensitive reducing agents for organic syntheses. They serve as a promising alternative for established hydrogen atom donors such as tin hydrides. The effectivity of DMAP-borane (**7**) as reducing agent in radical reactions is similar to that of DEAP-borane (**22**), which has a better solubility in apolar solvents. Effective radical reduction reactions with these borane complexes require an initiator system generating oxygen-centered radicals and a temperature range between 80 ºC and 90 °C. As an initiator perester **21** (TBPP) is equally effective as hyponitrite **20** (TBHN) used in earlier studies with NHC-boranes as reducing reagents.[18] Primary iodides as well as primary and secondary xanthates can be defunctionalised by use of these systems. As compared to tin hydrides an inverted selectivity was found for the reduction of 1-iodododecane (**14a**) and dodecyl xanthate **14c** in a "one-pot" reduction, where mainly the xanthate was reduced in the presence of DMAP-borane (**7**). This may offer a new strategy for the selective defunctionalisation of multiply functionalised substrates.

Experimental Section

All air and water sensitive manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. All commercial chemicals were of reagent grade and used as received unless otherwise noted. Hyponitrites were synthesized based on a procedure published by Mendenhall.[19] ^{1}H NMR and ^{13}C NMR spectra were recorded on *VARIAN Mercury 200*, *BRUKER ARX 300*, *VARIAN VXR 400 S* and *BRUKER AMX 600* instruments. ^{11}B NMR spectra were recorded on a *Jeol GSX-270* spectrometer. All measurements were done in standard NMR glass tubes (diameter: 5 mm). Chemical shifts are reported as δ values in ppm relative to tetramethylsilane. High resolution (HRMS) and low resolution (MS) spectra were recorded on a *FINNIGAN MAT 95Q* mass spectrometer. Electron impact ionization (EI) was conducted with an ionization energy of 70 eV.

General procedure for radical experiments with DTBP (17), dicumoyl peroxide (18), AIBN, DBHN (19), TBHN (20) and TBPP (21): For a typical kinetic experiment a 0.20 M stock solution of the respective radical starter in toluene-d_8 was prepared. This solution was stored under nitrogen atmosphere at -18 °C. At that temperature, the solutions can be kept for several weeks. Nevertheless it seemed advisable to limit the volume of stock solutions to 1 mL. A second stock solution for TDT (**16**, 0.1 M in toluene-d_8) was prepared similarly and stored at room temperature. Under an inert gas atmosphere a flask (or microwave vessel) was charged with 0.10 mmol of the substrate. Afterwards, the desired equivalents of borane complex and a defined amount of 1,3,5-trimethoxy benzene as internal standard (usually 0.1 to 0.15 mmol) were added. If desired, TDT (**16**) was added via Hamilton syringe from the stock solution. The same was done for the radical starter. Finally, the flask was filled with toluene-d_8 to a total volume of 0.60 mL and the solution was stirred until all solids had dissolved. This solution was subsequently reacted (in a preheated oil bath or in the microwave as closed vessel) or transferred to an NMR tube to follow the reaction progress directly by ^{1}H NMR spectroscopy.

General procedure for radical experiments with BEt_3: A suspension of 0.2 mmol of the respective borane complex in 2.0 ml solvent (benzene or toluene) was prepared in a pre-dried flask under nitrogen atmosphere. Afterwards, the substrate was added, followed by a defined amount of 1,3,5-trimethoxy benzene as internal standard (usually 0.1 to 0.15 mmol). If desired, TDT (**16,** 5 mol%) was added via Hamilton syringe. For experiments at 0 °C, the reaction flask was cooled by an external ice-bath. Finally, BEt_3 (1 M solution in hexanes, 0.2 ml, 0.2 mmol, 1 eq.) was added and the septum of the flask was pierced with a needle to provide oxygen. After two hours, the reaction mixture was analysed by NMR spectroscopy. If the reaction was carried out in a non-deuterated solvent, the solvent was removed under reduced pressure and the crude mixture was taken up in $CDCl_3$ prior to NMR analysis.

Setup for competition experiments: The setup is representative for all competition experiments. The two substrates (here: 1-bromoundecane (**14d**, 23.5 µl, 0.1052 mmol, 1.0 eq.) and xanthate **14c** (29.1 mg, 0.1052 mmol, 1.0 eq.)) were transferred into an NMR tube by a Hamilton syringe Afterwards, 0.75 eq. of the reducing agent (here: Bu_3SnH (**4**, 21.2 µl, 0.0789 mmol, 0.75 eq.)) and a defined amount of 1,3,5-trimethoxy benzene (here: 25.7 mg, 0.1528 mmol) as internal standard (usually 0.1 to 0.2 mmol) was added. The initiator was added as stock solution (here: TBHN (**20**, 0.201 M in toluene-d_8, 26.2 µl, 5 mol%)) and the NMR tube was filled with toluene-d_8 to a total volume of 0.60 mL. For thiol-catalyzed experiments, TDT (**16**) was also added as stock solution in toluene-d_8. The sample was then immediately used for NMR measurement at 80 °C (otherwise the NMR tube was stored at -18 °C). The sample was put into the pre-heated NMR spectrometer and the reaction was monitored by the decay of starting materials. After completion of the reaction (when no more decay of the starting materials could be observed) the crude reaction mixture was mixed with 1 mL isohexane, solids were filtered off on a celite plug and the filtrate was analyzed by GCMS.

Synthesis of dibenzyl hyponitrite (DBHN, 19): An aluminium foil-wrapped flask equipped with a dropping funnel and stirring bar was charged with sodium hyponitrite (2.11 g, 19.91 mmol, 1.00 eq.) dissolved in distilled water (15 mL). A silver nitrate solution (7.44 g, 43.80 mmol, 2.20 eq. in 50 mL distilled water) was added over ten minutes to the hyponitrite solution and a yellow solid precipitated immediately. After the addition, the yellow solid was filtered off, and washed twice with distilled water (50 mL) and ethanol (30 mL). Residues of solvent were removed under reduced pressure and silver hyponitrite was obtained as a yellow solid (2.60 g, 9.50 mmol) in 48 % yield, which decomposes readily at room temperature

A solution of freshly distilled benzyl bromide (1.32 mL, 11.14 mmol, 2.00 eq. in 8 mL CH_2Cl_2) was cooled to 0 °C under nitrogen atmosphere. Afterwards silver hyponitrite (1.53 g, 5.57 mmol, 1.00 eq.) was added in small portions over five minutes. After three hours the reaction mixture was filtered off and the solvent was removed under reduced pressure (without heating). The crude product was dissolved in pentane (20 mL) and cooled externally with liquid nitrogen until white crystals began to precipitate. The crystals were filtered off quickly and residual pentane was removed under reduced pressure (without heating). Hyponitrite **19** was obtained as colorless, light-sensitive crystals (0.53 g, 2.19 mmol, 39 %). The compound can be stored at −78 °C over a longer period. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 10H, $H_{aromatic}$), 5.27 (s, 4H, CH_2) ppm.

Synthesis of di-*tert*-butyl hyponitrite (TBHN, 20): To a Schlenk flask equipped with stirring bar und septum was added *tert*-butyl bromide (5.30 mL, 47.17 mmol, 10.00 eq.) and zinc chloride (1 M in Et_2O, 5.20 mL, 5.19 mmol, 1.10 eq.). The resulting suspension was cooled to 0 °C and stirred for 5 minutes before sodium hyponitrite (0.50 g, 4.72 mmol, 1.00 eq.) was added in portions over 5 minutes. Stirring was continued

for 90 minutes at 0 °C. The solvent was removed under reduced pressure at a water bath temperature lower than 20 °C. The residue was suspended in DCM, the undesired solid side products were filtered off and the filtrate concentrated under reduced pressure and cooled conditions (< 20 °C). This procedure was repeated with pentane (50 mL) with vigorous stirring for 3 minutes. At that point a brownish tar began to deposit at the bottom of the flask. The clear and colorless pentane phase was separated from this deposit and concentrated *in vacuo* below 20 °C. **20** was obtained as colorless solid (0.29 g, 1.64 mmol, 35 %) which can be stored at −18 °C over months, but should not be kept at room temperature for a longer period. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 18H, $C(CH_3)_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 81.09 ($C(CH_3)_3$), 27.71 ($C(CH_3)_3$) ppm.

Synthesis of TBPP (21): A commercially available solution of *tert*-butyl hydroperoxide (5.5 M in decane, 1.00 mL) was mixed with pentane (10 mL) and cooled to −20 °C. Afterwards, *n*-butyllithium (2.5 M in hexane, 2.20 mL) was slowly added. After five minutes pivaloyl chloride (0.68 mL, 5.50 mmol) was added and the mixture brought to room temperature. Water (10 mL) was added, the organic layer removed and dried over $MgSO_4$. Volatile components were removed under reduced pressure (300 mbar, 40 °C) by rotary evaporation for five minutes. Remaining decane was not removed and a *tert*-butyl peroxypivalate (**21**) solution in decane was obtained in quantitative yield. For determination of the content of **21** in solution, 10.00 mg of the solution were weighed into an NMR tube and 20.00 mg of 1,3,5-trimethoxy benzene were added as internal standard. The concentration of **21** in the solution was determined by ^{1}H NMR spectroscopy (0.003 mmol/mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 9H, $O_2C(CH_3)_3$), 1.24 (s, 9H, $OC(CH_3)_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.99 (CO), 83.31 ($O_2C(CH_3)_3$), 38.82 ($OC(CH_3)_3$), 27.21 ($O_2C(CH_3)_3$), 26.07 ($OC(CH_3)_3$) ppm.

General procedure for the synthesis of Lewis-base borane complexes (LB-BH_3): A Schlenk flask equipped with stirring bar and septum was charged with a solution of the respective Lewis base in dry THF and cooled to 0 °C. Afterwards 1.10 eq. of BH_3 (5 M solution of $H_3B{\bullet}SMe_2$ in Et_2O) were added slowly at 0 °C and the mixture stirred for 10 min. The air-stable borane complexes were purified by precipitation upon addition of isohexane (usually 5-10 fold excess). Vigorous stirring during the precipitation leads to the best results. The solid was then filtered off (frit N4) and washed three times with isohexane. Residual solvent was removed under reduced pressure to give the pure LB-BH_3 complexes in good to excellent yields. Single crystals suitable for X-ray analysis were obtained by slow evaporation of saturated chloroform solutions.

Synthesis of 4-dimethyl aminopyridine borane (DMAP borane, 7): Following the general procedure for the synthesis of LB-BH_3 complexes, 4-dimethyl aminopyridine (1.00 g, 8.18 mmol) was reacted with BH_3 (5 M H3B•SMe_2 in Et_2O, 1.80 mL) in 10 mL dry THF. **7** was obtained as a colourless solid (0.90 g, 6.63 mmol) in 81 % yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.91 – 7.89 (m, 2H, H-C2 and H-C6), 6.70 – 6.67 (m, 2H, H-C3, H-C5), 3.02 (s, 6H, NMe_2), 2.44 – 1.91 (broad, q, 3H, BH_3) ppm. ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.84 (C7), 146.46 (C2 and C3), 107.22 (C1 and C4), 39.42 (C5 and C6) ppm. {^{1}H} ^{11}B NMR (270 MHz, DMSO-d_6) δ -13.02 (s) ppm. HRMS (70 eV, EI): $C_7H_{13}BN_2$ calc. 136.1172 g/mol $[M]^+$, found 136.1173 g/mol.

Synthesis of 1,3-dimethyl imidazol-2-ylidene-borane (12):[17] A dry Schlenk flask equipped with stirring bar and reflux condenser was charged with 1,3-dimethyl imidazolium dimethyl phosphate (5.40 g, 24.30 mmol, 1.00 eq.), dissolved in THF (20 mL) and cooled to -78 °C with acetone/dry ice. Sodium bis(trimethylsilyl)amide (5.32 g, 29.01 mmol, 1.20 eq.) was added slowly and the mixture stirred for one hour to complete the carbene formation. The acetone/dry ice bath was removed and borane-ammonia complex (0.74 g, 23.81 mmol, 0.98 eq.) was added in small portions. The reaction mixture was then refluxed for two hours. The solvent was removed under reduced pressure and the crude orange-colored solid was purified by column chromatography on silica (0.035-0.070 mm, 60 Å/ DCM; R_f = 0.7) to give pure **12** as colourless solid (1.12 g, 10.21 mmol, 42 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78 (s, 2H, H-C1, H-C2), 3.70 (s, 6H, NMe), 1.41-0.55 (broad, q, 3H, BH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 119.91 (C1 and C2), 35.88 (NMe) ppm. {^{1}H} ^{11}B NMR (270 MHz, $CDCl_3$) δ −37.49 (s) ppm. HRMS (70 eV, EI): $C_5H_{11}BN_2$ calc. 109.0932 g/mol $[M]^+$, found 109.0935 g/mol.

Synthesis of 4-diethylaminopyridine (DEAP, 29): *4*-Aminopyridine (3.00 g, 31.88 mmol, 1.00 eq.) was dissolved in 200 mL dry THF. Afterwards *n*-butyllithium (1.6 M in hexane, 22.90 mL, 36.66 mmol, 1.15 eq.) was slowly added at room temperature. The reaction mixture was vigorously stirred for 30 minutes until a homogeneous suspension had formed. Afterwards ethyl iodide (2.95 mL, 36.66 mmol, 1.15 eq.) was added at room temperature and the mixture was stirred for ca. 20 minutes until a clear yellow solution had formed. Subsequently, *n*-butyllithium (1.6 M in hexane, 22.90 mL, 36.66 mmol, 1.15 eq.) was again slowly added at room temperature. The clear dark solution was stirred for 20 minutes, followed by the addition of ethyl iodide (2.95 mL, 36.66 mmol 1.15 eq.). After stirring for 15 minutes, distilled water (30 mL) was added to quench the reaction. The aqueous phase was extracted three times with chloroform, dried over $MgSO_4$ and concentrated under reduced pressure. To the brown oily residue isohexane (10 mL) was added and vigorously stirred for one minute to form two layers. The upper turbid isohexane layer was discared before additional isohexane (10 mL) was added to complete the precipitation of unwanted side products. The solvent was removed under reduced pressure and ethyl acetate (30 mL) was added to the crude product. After stirring for one minute a brown tar had deposited at the bottom of the flask and the organic layer above had become cloudy due to precipitation of pyridinium salts. This suspension was filtered off and the clear yellow solution was concentrated *in vacuo* to yield **29** as a slightly yellow wax (1.39 g, 9.25 mmol, 29 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (dd, J = 5.0 Hz, 1.6 Hz, 2H, H-C2 and H-C6), 6.39 (dd, J = 5.0 Hz, 1.6 Hz, 2H, H-C3 and H-C5), 3.29 (q, J = 7.1 Hz, 4H $N(CH_2CH_3)_2$), 1.11 (t, J = 7.1 Hz, 6H, $N(CH_2CH_3)_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.01 (C4), 149.64 (C2 and C6), 106.18 (C3 and C5), 43.69 ($N(CH_2CH_3)_2$), 12.22 ($N(CH_2CH_3)_2$) ppm. HRMS (70 eV, EI): $C_9H_{14}N_2$ calc. 150.1157 g/mol $[M]^+$, found 150.1150 g/mol.

Synthesis of 4-diethylaminopyridine borane (DEAP borane, 22): Following the general procedure for the synthesis of LB-BH_3 complexes, 4-diethyl aminopyridine (1.50 g, 9.96 mmol, 1.0 eq.) was reacted with BH_3 (5 M $H_3B{\bullet}SMe_2$ in Et_2O, 2.19 mL, 1.10 eq.) in 4 mL dry THF. After addition of isohexane the colorless preciptitate was filtered off and digested in benzene (10 mL). After filtration and concentration under reduced pressure, **22** was finally obtained by recrystallization from benzene as colourless solid in 59 % yield (0.96 g, 5.88 mmol). ^{1}H NMR (300 MHz, C_6D_6) δ 7.94 (d, J = 7.4 Hz, 2H, H-C2 and H-C6), 5.66 (d, J = 7.5 Hz, 2H, H-C3 and H-C5), 2.51 (q, J = 7.1 Hz, 4H, $N(CH_2CH_3)_2$), 0.55 (t, J = 7.1 Hz, 6H, $N(CH_2CH_3)_2$), 3.93-2.98 (broad, q, 3H, BH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6) δ 152.04 (C4), 146.78 (C2 and C6), 105.81 (C3 and C5), 43.62 ($N(CH_2CH_3)_2$), 11.46 ($N(CH_2CH_3)_2$) ppm. {^{1}H} ^{11}B NMR (270 MHz, C_6D_6) δ −12.28 (s) ppm. HRMS (70 eV, EI): $C_9H_{17}BN_2$ calc. 164.1485 g/mol $[M]^+$, found 164.1420 g/mol.

Synthesis of 4-dihexylaminopyridine (DHAP): *4*-Aminopyridine (3.00 g, 42.50 mmol, 1.00 eq.) was dissolved in 200 mL dry THF. Afterwards *n*-butyllithium (2.5 M in hexane, 37.40 mL, 93.50 mmol, 2.20 eq.) was slowly added at room temperature. A chewy precipitate was formed, which was vigorously stirred for 30 minutes. Afterwards *n*-hexyl iodide

(13.80 mL, 93.5mmol, 2.20 eq.) was added at room temperature and the mixture was stirred for ca. 30 minutes until a clear solution had formed. Distilled water (30 mL) was then added and the aqueous phase was extracted three times with DCM. The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure. ^{1}H NMR and GC/MS analysis of the residue indicated a mixture of the desired product, mono-alkylated aminopyridine, aminopyridinum hexyl iodide salts and unreacted hexyl iodide. Column chromatography on silica (0.035-0.070 mm, 60 Å/ DCM : Et_3N = 10 : 1; R_f =0.55) led to a crude product fraction containing 4-dihexylaminopyridine and 4-dihexylaminopyridinium hexyl iodide. The iodide salt could be precipitated by addition of isohexane (50 mL). The solid was filtered off and the solvent of the liquid phase was removed under reduced pressure. This yielded DHAP as a yellow oil (2.68 g, 10.20 mmol, 24 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (dd, J = 5.0 Hz, J = 1.6 Hz, 2H, H-C1 and H-C5), 6.40 (dd, J = 5.0 Hz, J = 1.6 Hz, 2H, H-C2 and H-C4), 3.25 (t, J = 7.6 Hz, 4H, H_2-C11 and H_2- C12), 1.63-1.49 (m, 4H, H_2-C10 and H_2-C7, H_2-C8, H_2-C9, H_2-C14, H_2-C15 and H_2-C16), 0.88 (t, J = 6.6 Hz, 6H, H_3-C6 and H_3-C17) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.36 (C3), 149.88 (C1 and C5), 106.29 (C2 and C4), 50.14 (C11 and C12), 31.60 (C8 and C15), 26.91 (C10 and C13), 26.66 (C9 and C14), 22.60 (C7 and C17), 13.97 (C6 and C17) ppm. HRMS (70 eV, EI): $C_{17}H_{30}N_2$ calc. 262.2409 g/mol $[M]^+$, found 262.2400 g/mol.

Synthesis of 4-dihexylaminopyridine borane (DHAP borane, 34): Following the general procedure for the synthesis of LB-BH_3 complexes, 4-dihexylaminopyridine (1.01 g, 3.83 mmol, 1.00 eq.) was dissolved in 5 mL THF under nitrogen atmosphere. The solution was cooled to 0 °C and a solution of H_3B•SMe_2 (5 M in Et_2O, 0.77 mL, 1.01 eq.) was added. After 10 minutes the external cooling was removed. After removing all residues of solvent under reduced pressure, **34** was obtained as a colourless oil (1.06 g, 3.83 mmol, 100 %). ^{1}H NMR (300 MHz, C_6D_6) δ 7.99 (d, J = 7.4 Hz, 2H, H-C1 and H-C5), 6.41 (d, J = 7.5 Hz, 2H, H-C2 and H-C4), 3.31 (t, J = 7.7 Hz, 4H, H_2-C11 and H_2-C12), 1.70 – 1.45 (m, 4H, H_2-C10 and H_2-C13), 1.44 – 1.11 (m, 12H, H_2-C7, H_2-C8, H_2-C9, H_2-C14, H_2-C15 and H_2-C16), 0.89 (t, J = 6.7 Hz, 6H, H_3-C6 and H_3-C17) 3.04-1.85 (broad, q, 3H, H_3-B) ppm. ^{13}C NMR (75 MHz, C_6D_6) δ 153.12 (C3), 146.87 (C1 and C5), 106.24 (C2 and C4), 50.66 (C11 and C12), 31.48 (C8 and C15), 26.74 (C10 and C13), 26.52 (C9 and C14), 22.53 (C7 and C17), 13.93 (C6 and C17) ppm. {^{1}H} ^{11}B NMR (270 MHz, C_6D_6) δ −13.87 (s) ppm. HRMS (70 eV, EI): $C_{17}H_{33}BN_2$ calc. 276.2737 g/mol $[M]^+$, found 276.2736 g/mol.

Synthesis of *O*-dodecyl *S*-methyl carbonodithioate (14c): In a Schlenk flask equipped with stirring bar and septum 1-Dodecanol (5.00 mL, 22.35 mmol, 1.00 eq.) was dissolved in 200 mL THF and the solution cooled to 0 °C. Afterwards sodium hydride (60 % suspension in mineral oils, 1.16 g, 29.06 mmol, 1.30 eq.) was added and the mixture stirred at 0 °C for 30 minutes, followed by the addition of CS_2 (2.02 mL, 33.53 mmol, 1.5 eq.). The external cooling was removed and the reaction mixture stirred for one hour. Subsequently methyl iodide (2.38 mL, 38.00 mmol, 1.7 eq.) was added and stirring was continued for 20 minutes. The crude mixture was quenched with distilled water (30 mL) and extracted three times with chloroform. The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography on silica (0.035-0.070 mm, 60 Å/ isohexane; R_f = 0.70) led to analytically pure **18c** which was isolated as pale yellow oil (5.19 g, 18.74 mmol, 84 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.51 (t, J = 6.7 Hz, 2H, H_2CO), 2.48 (s, 3H, OCS_2CH_3), 1.78 – 1.66 (m, 2H, $H_{aliphatic}$), 1.40 – 1.10 (m, 18H, $H_{aliphatic}$), 0.81 (t, J = 6.9 Hz, 3H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.95 (C=S), 74.28 (CO), 31.94 ($C_{aliphatic}$), 29.66 ($C_{aliphatic}$), 29.65 ($C_{aliphatic}$), 29.58 ($C_{aliphatic}$), 29.51 ($C_{aliphatic}$), 29.37 ($C_{aliphatic}$), 29.25 ($C_{aliphatic}$), 28.27 ($C_{aliphatic}$), 25.91 ($C_{aliphatic}$), 22.71 (CH_2CH_3), 18.91 (OCS_2CH_3), 14.14 (CH_2CH_3) ppm. HRMS (70 eV, EI): $C_{14}H_{28}OS_2$ calc. 276.1582 g/mol $[M]^+$, found 276.1578 g/mol.

Synthesis of *O*-(adamantan-1-yl) *S*-methyl carbonodithioate (23c): 1-Adamantanol (3.00 g, 19.71 mmol, 1.00 eq.) was dissolved in 200 mL THF and the solution cooled to 0 °C. Afterwards sodium hydride (60 % suspension in mineral oils, 1.02 g, 25.62 mmol, 1.30 eq.) was added, the external cooling was removed and the mixture stirred for 30 minutes, followed by the addition of CS_2 (1.78 mL, 29.56 mmol, 1.5 eq.). The suspension was warmed up to 40 °C and stirred for 3.5 hours. Subsequently, methyl iodide (2.09 mL, 33.50 mmol, 1.7 eq.) was added and the mixture stirred for 30 minutes at room temperature. All solids were filtered off and the solvent was removed from the crude product under reduced pressure. **23c** was obtained by repeated extraction with warm isohexane, in which the remaining alcohol is insoluble. The pure xanthate begins to grow as yellow needles from the clear isohexane solution by cooling with ice (2.06 g, 8.51 mmol, 43 %). ^{1}H NMR (300 MHz $CDCl_3$) δ 2.44 (s, 3H, OCS_2CH_3), 2.43 – 2.41 (m, 6H, $(CH_2)_3CO$,), 2.26 – 2.20 (m, 6H, $CH_{2,ad}$), 1.70 – 1.65 (m, 3H, CH_{ad}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.58 (C=S), 91.24 (CO), 41.11 ($(CH_2)_3CO$), 36.06 ($CH_{2,ad}$), 31.42 (CH_{ad}) ppm. HRMS (70 eV, EI): $C_{12}H_{18}OS_2$ calc. 242.0799 g/mol $[M]^+$, found 242.0797 g/mol.

Synthesis of *O*-(decan-2-yl) *S*-methyl carbonodithioate (24): 2-Decanol (2.49 g, 13.38 mmol, 1.00 eq.) was dissolved in 100 mL THF and cooled to 0 °C. Afterwards *n*-butyllithium (2.5 M solution in hexane, 5.90 mL, 14.72 mmol, 1.10 eq.) was added and stirred at 0 °C for 20 minutes, followed by the addition of CS_2 (1.00 mL, 17.39 mmol, 1.3 eq.). The external cooling was removed and the reaction mixture stirred for one hour. Finally, methyl iodide (1.30 mL, 20.07 mmol, 1.5 eq.) was added via syringe and stirring continued for 20 minutes. The crude mixture was quenched with water (30 mL) and extracted three times with chloroform. The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography on silica (0.035-0.070 mm, 60 Å/ *iso*hexane; R_f = 0.60) led to analytically pure xanthate **24** which was isolated as pale yellow oil (2.59 g, 10.44 mmol, 78 %).^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68 – 5.55 (m, 1H, CH), 2.47 (s, 3H, OCS_2CH_3), 1.77 – 1.48 (m, 2H, CH_2CH), 1.28 (d, J = 6.2 Hz, 3H, $CHCH_3$) 1.35 – 1.12 (m, 14H, $H_{aliphatic}$), 0.80 (t, J = 6.9 Hz, 3H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.43 (C=S), 81.43 (CH), 35.60 ($CHCH_2$), 31.86 ($C_{aliphatic}$), 29.45 ($C_{aliphatic}$), 29.41 ($C_{aliphatic}$), 29.22 ($C_{aliphatic}$), 25.26 ($C_{aliphatic}$), 22.67 (CH_2CH_3), 19.27 ($CHCH_3$), 18.77 (OCS_2CH_3), 14.12 (CH_2CH_3) ppm. HRMS (70 eV, EI): $C_{12}H_{24}OS_2$ calc. 248.1269 g/mol $[M]^+$, found 248.1237 g/mol.

Synthesis of *S*-methyl *O*-(naphthalen-1-ylmethyl) carbonodithioate (25): 1-Naphthylmethanol (1.65 g, 10.41 mmol, 1.00 eq.) was dissolved in 50 mL THF and cooled to 0 °C. Then, *n*-butyllithium (2.5 M solution in hexane, 5.00 mL, 12.49 mmol, 1.20 eq.) was added and the mixture stirred at 0 °C for 10 minutes, followed by the addition of CS_2 (0.94 mL, 15.62 mmol, 1.5 eq.). The external cooling was removed and the solution stirred for one hour. Afterwards, methyl iodide (1.11 mL, 17.70 mmol, 1.7 eq.) was added via syringe and stirring continued for 15 minutes. The crude reaction mixture was quenched with water (15 mL) and extracted three times with chloroform. The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography on silica (0.035-0.070 mm, 60 Å/ isohexane; R_f=0.75) led to the pure **25** which was isolated as viscous yellow oil (0.66 g, 2.66 mmol, 26 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 8.2 Hz, 1H, $H_{aromatic}$), 7.87 – 7.81 (m, 2H, $H_{aromatic}$), 7.57 – 7.46 (m, 3H, $H_{aromatic}$), 7.42 (dd, J = 8.2 Hz, 7.1 Hz, 1H, $H_{aromatic}$), 6.02 (s, 2H, CH_2), 2.50 (s, 3H, OCS_2CH_3). ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.65 (C=S), 133.79 ($C_{aromatic,q}$), 131.84 ($C_{aromatic,q}$), 130.38 ($C_{aromatic,q}$), 129.92 ($C_{aromatic}$), 128.82 ($C_{aromatic}$), 128.39 ($C_{aromatic}$), 126.88 ($C_{aromatic}$), 126.17 ($C_{aromatic}$), 125.27 ($C_{aromatic}$), 123.62 ($C_{aromatic}$), 73.80 (CH_2), 19.16 (OCS_2CH_3) ppm. HRMS (70 eV, EI): $C_{13}H_{12}OS_2$ calc. 248.0330 g/mol $[M]^+$, found 248.0327 g/mol.

Computational Details

Geometry optimization of all systems has been performed at the (U)mPW1K/6-31+G(d) level of theory. Thermal corrections to 298.15 K have been calculated without scaling at the same level of theory using the rigid rotor/harmonic oscillator model. Relative enthalpies were obtained using the G3(MP2)-RAD scheme proposed by Radom and co-workers.[20] Since the B3LYP functional in combination with the 6-31G(d) basis set gives unsatisfactory results for zwitterionic systems,[21] the (U)mPW1K/6-31+G(d) level was employed. All enthalpies mentioned in this text have been obtained using this modified G3(MP2)-RAD(+) procedure. The required (U)CCSD(T)/6-31G(d)//(U)mPW1K/6-31+G(d) calculations have been performed with MOLPRO,[22] all other calculations have been done with Gaussian 09.[23]

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Keywords: hydrogen atom transfer • radical reactions • Lewis base borane complexes • mechanism • NMR

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Organometallics, **2010**, 29 (9), 2176–2179; page S2). The signal for H_2 can be found in toluene-d_8 at 4.50 ppm, in line with literature reports (*ibid.*).

[25] Details of the solid state structures can be obtained from the CCDC database at www.ccdc.cam.ac.uk/structures using the following identifiers: compound **30b** (1552523); compound **30** (1552524); compound **23c** (1552525).

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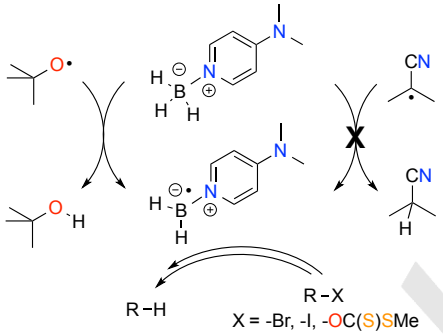
FULL PAPER

Alternative for tin hydrides: The crucial choice of initiators and reaction conditions for Lewis-base borane mediated radical chain reduction reactions has been investigated in detail. An inverted selectivity was found for the reduction of iodides vs. xanthates as compared to tin hydride reagents.



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Aminopyridine-Borane Complexes as Hydrogen Atom Donor Reagents – Reaction Mechanism and Substrate Selectivity