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Letter

4,4'-Bipyridyl-Catalyzed Reduction of Nitroarenes by Bis(neopentylglycolato)diboron

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Supporting Information

ABSTRACT: 4,4'-Bipyridyl worked as an organocatalyst for the reduction of nitroarenes by bis(neopentylglycolato)diboron (B_2nep_2), followed by hydrolysis to give the corresponding anilines. This reduction proceeded under aerobic conditions without any prepurification of substrates and reagents. We found broad functional group tolerance and compatibility for O- and N-protecting groups under the reaction conditions. The key in this catalytic system was the



addition of $B_2 nep_2$ to 4,4'-bipyridyl to form N,N'-bis[(neopentylglycolato)boryl]-4,4'-bipyridinylidene as a deoxygenating reagent of nitroarenes.

he deoxygenative reduction of nitroarenes is an important transformation for producing synthetically useful and profitable aniline derivatives. Although reduction by metal powders such as Al, Fe, Zn, In, Sn, and Sm upon combination with any proton source such as HCl, NH₄Cl, AcOH, or H₂O as well as hydrogenation catalyzed by heterogeneous catalysts such as Raney Ni, Pd/C, Pt/C, Rh/C, Pd/Al₂O₃, and Au/TiO₂ are practically and industrially utilized,^{1,2} recent demand has focused on high functional group tolerance to the nitro group reduction to expand the availability of highly functionalized anilines and allow for nitro group reduction in a later or final stage in the synthesis of aniline derivatives bearing various functional groups. In fact, various deoxygenation reactions with functional group tolerance were recently developed:³⁻⁵ A combination of HSiCl₃ and NEt₃ was used for nitro group reduction under mild reaction conditions. HSiEt₃, upon activation with $B(C_6F_5)_3$, exhibits high reduction ability for both nitroarenes and nitroalkanes, and diborons combined with KO^tBu or proton sources reduce nitroarenes under aerobic conditions.

Recently, we reported the chemoselective deoxygenative reduction of nitroarenes using N,N'-bis(trimethylsilyl)-4,4'-bipyridinylidene (**A**) as a reductant (Figure 1). A wide range of functional groups remained intact during single and double deoxygenation, selectively giving N,O-bis(trimethylsilyl)-phenylhydroxylamines and N,N-bis(trimethylsilyl)anilines.⁶ The corresponding pinacolatoboryl derivative, N,N'-bis(pinacolatoboryl)-4,4'-bipyridinylidene (**B**), was prepared by



Figure 1. *N*,*N*'-Bis(trimethylsilyl)- and *N*,*N*'-bis(pinacolatoboryl)-4,4'-bipyridinylidene.

the reaction of 4,4'-bipyridyl with bis(pinacolyl)diboron (B₂pin₂), and the "oxidative boryl transfer" of the boryl moieties from the 4,4'-bipyridinylidene to other heteroaromatic compounds such as pyrazine derivatives was also demonstrated.⁷ A notable application of B₂pin₂ in the presence of 4,4'-bipyridyl as an organocatalyst is the trans-1,2-diboration of acetylenedicarboxylates.8 We thus focused our attention on the reactivity of the N,N'-bis(boryl)-4,4'-bipyridinylidene skeleton for further utilization in the deoxygenative reduction of nitroarenes because N,N'-bis(boryl)-4,4'-bipyridinylidenes are easily synthesized by commercially available 4,4'-bipyridyl and diborons. Herein we report that 4,4'-bipyridyl acted as an efficient organocatalyst for the deoxygenative reduction of nitroarenes using bis(neopentylglycolato)diboron (B2nep2) as a reductant under aerobic conditions without the need to predry solvents and substrates. Control experiments revealed a reaction mechanism in which the addition of B2nep2 to 4,4'bipyridyl was the key to generating an efficient deoxygenating

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Table 1. Screening of Boron Compounds for the Reduction of Nitrobenzene $(1a)^a$

		NO ₂	1. 4,4'-bipyridyl (2 mol%) reductant (3.6 equiv)		NH ₂		
		1a 0.40 mmol	CH ₃ CN under a 2. hydroly	I, 100 °C, 6 h air rsis	2a		
entry	reductant	$\operatorname{conv}(\%)^{b}$	2a (%) ^b	entry	reductant	$\operatorname{conv}(\%)^{b}$	2a (%) ^b
1	B ₂ nep ₂	>99	93	7^d	B ₂ nep ₂	89	89
2^{c}	B ₂ nep ₂	91	85	8 ^e	B ₂ nep ₂	49	39
3	B ₂ hex ₂	3	3	9 ^f	B ₂ nep ₂	4	n.d.
4	B ₂ pin ₂	2	1	10	HBpin	8	6
5	B_2cat_2	83	4	11	H ₃ BNMe ₃	3	3
6	$B_2(OH)_4$	99	86	12	Me ₂ PhSiBpin	10	2

^{*a*}Conditions: nitrobenzene (0.40 mmol), boron compound (1.44 mmol), 4,4'-bipyridine (2 mol %, relative to nitrobenzene), CH_3CN (1.5 mL), 100 °C, 6 h, under air in J-young nuclear magnetic resonance (NMR) tube. ^{*b*}Determined by gas chromatography (GC) using dodecane as an internal standard. ^{*c*}Reaction under Ar. ^{*d*}1 mol % of 4,4'-bipyridyl. ^{*c*}Reaction at room temperature for 24 h. ^{*J*}No 4,4'-bipyridyl.



reagent for nitroarenes. In addition, N_1N -diborylanilines insitu-generated from nitroarenes with B₂nep₂/4,4'-bipyridyl were directly used to prepare ketimines upon the addition of ketones.

We began with searching for the best diboron to use for the reduction of nitrobenzene (1a) in the presence of a catalytic amount of 4,4'-bipyridyl (2 mol %), and the results are shown in Table 1. The reaction of 1a with B_2nep_2 (3.6 equiv) in the presence of a catalytic amount of 4,4'-bipyridyl (2 mol %) under air at 100 °C for 6 h resulted in the formation of aniline (2a) in 93% yield after hydrolysis (entry 1), whereas the yield of 2a was slightly decreased under an argon atmosphere (entry 2). The yield of 2a was significantly affected by the substituents on the boron atom: B₂hex₂ and B₂pin₂, with chelating diolato substituents on the boron atom, were less effective, and 2a was obtained in lower yield (entries 3 and 4). The treatment of 1a with catecholato-substituted diboron, B2cat2, gave 2a in 4% yield after workup, although the vast majority of B₂cat₂ was consumed (entry 5). 4,4'-Bipyridyl also acted as a catalyst of $B_2(OH)_4$, converting 1a to 2a in 86% yield (entry 6), although $B_2(OH)_4$ was reported to reduce nitroarenes in water or in organic solvents in the presence of metal catalysts.^{4c-e} Among the diborons we examined, B₂nep₂ was selected as the best for the deoxygenative reduction of the nitro group. The yield of B₂nep₂ was slightly decreased by lowering the catalyst loading to 1 mol % (entry 7). When the reaction was carried out at room temperature for 24 h, the yield of 2a was moderate (entry 8). Without 4,4'-bipyridyl, 2a was not obtained (entry 9), indicating that a 4,4'-bipyridyl-activated diboron reagent was indispensable for the initial deoxygenation (vide infra). We also checked other boron compounds: Reactions using hydroboranes, such as HBpin and H₃B·NMe₃, gave 2a in 6 and 3% yield, respectively (entries 10 and 11). Furthermore, Me₂PhSiBpin was not effective for the reduction (entry $12).^{9-11}$

With the optimized reaction conditions in hand, including 4,4'-bipyridyl as the organocatalyst,^{12,13} we explored the

substrate scope of the nitroarene reduction (Scheme 1). *para*-Alkyl-substituted nitroarenes **1b**,**c** were reduced to *p*-





^{*a*}Conditions: nitrobenzene (0.40 mmol), B_2nep_2 (1.44 mmol), 4,4'bipyridyl (2 mol %, relative to nitrobenzene), CH₃CN (1.5 mL), 100 °C, 6 h, under air, J-young NMR tube. Yield determined by ¹H NMR for p-substituted anilines **2b–k**, by GC for **2l**, and by isolation for **2m–u**. ^{*b*}One mmol scale in parentheses. See the detailed procedure in the Supporting Information. ^{*c*}24 h.

Organic Letters

toluidine (2b) and *p-tert*-butylaniline (2c) in 86 and 88% yield. Nitroarenes 1d,e, bearing electron-donating groups at the para position, afforded the reduced anilines 2d,e in moderate to good yield. The reduction of nitroarenes 1f-k with electronwithdrawing substituents at the para position proceeded without the dehalogenation or reduction of C=O and C= N moieties to give 2f-k in good to excellent yield. The sterically congested nitroarenes 11,m were also reduced to the corresponding anilines 21,m in moderate yield. In addition, a C-C double bond was tolerated to give styrylaniline 2n in excellent yield. When the scale-up reaction (1 mmol scale) was conducted for **1n**, the isolated vield was better under an argon atmosphere, although the purification of reagents and the solvent was unnecessary. The present catalytic system was successfully applied on nitro-containing heterocycles such as coumarin (10), pyridine (1p), unprotected indole (1q), and a benzofuran bearing an ester group (1r), affording 2o-r in good yield. Nitroarenes with OH (1s), CO₂H (1t), and NH₂ (1u) groups on the aromatic ring were reduced to 2s-u in moderate yield, demonstrating the stability of this catalytic system toward protic functionalities.

The $B_2nep_2/4,4'$ -bipyridyl system showed high functional group tolerance to various O- and N-protecting groups at the para position of nitroarenes, which are deprotected under acidic, basic, or hydrogenation conditions, as summarized in Table 2. A nitro group in **1v** was more reactive compared with

Table 2. Reduction of O- and N-protected Nitroarenes by $B_{2}nep_{2}/4,4'$ -bipyridyl^a

		NO ₂	1. 4,4'-bipyridyl (2 mol%) B ₂ nep ₂ (3.6 equiv)	NH ₂		
	PG _Z		CH ₃ CN, 100 °C, 6 h PG _Z under air 2. hydrolysis			
e	ntry	Z	protecting group (PG)	2 (%) ^b		
	1	0	C(=O)Me (Ac)	2v, 84		
	2	0	CH ₂ OMe (MOM)	2w , 80		
	3	0	SiMe2 ^t Bu (TBS)	2 x, 62		
	4	0	CH ₂ Ph (Bn)	2 y, 82		
	5	NH	$C(=O)OCH_2Ph$ (Cbz)	2z, 80		
	6	NH	$C(=O)O^{t}Bu$ (Boc)	2aa, 82		
	7	NH	C(=O)Me (Ac)	2ab, 82		
	8	NH	$S(=O)_2(C_6H_4CH_3-4)$ (Ts)	2ac , 84		
10	1			1)		

^{*a*}Conditions: nitrobenzene (0.40 mmol), B₂nep₂ (1.44 mmol), 4,4'bipyridyl (2 mol %, relative to nitrobenzene), CH₃CN (1.5 mL), 100 °C, 6 h, under air, J-young NMR tube. ^{*b*}Isolated yield.

the acetoxy functionality, giving 2v in 84% yield without any deprotection (entry 1). The methoxymethyl group in 1w was also tolerant under the reaction conditions to afford 2w in 80% yield (entry 2). The silicon-oxygen bond in 1x and benzyl protection in 1y remained intact for the catalyst system of $B_2nep_2/4,4'$ -bipyridyl to give 2x and 2y in 62 and 82% yield (entries 3 and 4). In addition, carbamate moieties in 1z,aa were retained to give 2z,aa in good yield (entries 5 and 6). Notably, both amide and sulfonyl amide in 1ab,ac were stable for the deoxygenation to give anilines 2ab,ac in good yield (entries 7 and 8), although the deoxygenation of sulfoxides by reduction using B_2pin_2 in the presence of a catalytic amount of 4-cyanopyridine was previously reported.^{13f} The 4,4'-bipyridylassisted diboron reduction was found to be an efficient and superior catalyst system for the reduction of highly functionalized nitroarenes, which is particularly important in multistep synthesis.

To clarify the reaction pathway and function of 4,4'bipyridyl as well as B_2nep_2 , we conducted some control experiments (Scheme 2). The reaction of 4,4'-bipyridyl with





 $B_2 nep_2$ at room temperature gave N, N'-bis-[(neopentylglycolato)boryl]-4,4'-bipyridinylidene (3) (Scheme 2a).⁷ The treatment of 1a with 3 (2.2 equiv) in CD₃CN at room temperature afforded N,O-bis-{(neopentylglycolato)boryl}hydroxyaniline (4) in 92% yield (Scheme 2b), whereas 3.6 equiv of 3 at 100 °C for 1 h produced N-(neopentylglycolato)borylaniline- d_1 (5) along with azobenzene (6) in 30 and 11% yield, respectively (Scheme 2c); 5 was generated by the deuteration of the transiently generated N,N-bis{(neopentylglycolato)boryl}aniline by CD₃CN, whereas 6 was formed by the dimerization of the phenylnitrene derived from the thermolysis of 4 (vide infra). In fact, the N-borylaniline (5) is the final compound generated under the optimized reaction conditions in Table 1 before hydrolysis. When nitrosobenzene (7), a singly deoxygenated derivative of 1a, was mixed with B_2nep_2 (1.1 equiv) in the absence of 4,4'-bipyridyl in C₆D₆ for 1 h at room temperature, 4 was obtained in 93% yield (Scheme 2d),

indicating that 4,4'-bipyridyl was not necessary in the diborylation of 7. Next, we conducted the thermolysis of 4 in the presence of B₂nep₂ at 100 °C in CD₃CN, and 5 was obtained as the major product, together with 6 and azoxybenzene 8 (Scheme 2e), the latter of which was probably formed by the reaction of 4 with in situ-generated phenylnitrene along with the elimination of B₂nep₂. The formation of 5 in Scheme 2e suggested the involvement of 4 as the reaction intermediate for the aniline formation. Under the optimized reaction conditions for nitroarene reduction, the N=N of 6 was partially reduced to afford 1,2-diphenylhydrazine 9 after hydrolysis in the presence of 4,4'-bipyridyl (2 mol %)/B₂nep₂ (2.5 equiv) (Scheme 2f), showing a similar behavior as the reported reduction of **6** with B_2pin_2 using 4-cyanopyridine as an organocatalyst.^{13f} To clarify the previously mentioned arylnitrene formation by the thermolysis of 4, the reaction of 2phenylnitrobenzene (10) with 2.2 equiv of 3 was conducted in C_6D_6 at ambient temperature for 1 h to allow the in situ formation of N-(2-biphenyl)-N,O-bis{(neopentylglycolato)boryl}-2-hydroxylamine; then, the reaction mixture was heated to 100 °C for 3 h, giving carbazole (11) in 60% yield along with 12% of 2-aminobiphenyl (12), the former of which was generated via the insertion of the arylnitrene into the ortho-C-H bond (Scheme 2g).¹⁶ The effectiveness of B_2nep_2 among the diborons screened (Table 1) was ascribed to the facile thermolysis of 4 to arylnitrenes because the reaction of 7 with B₂pin₂ quantitatively gave N,O-bis[(pinacolato)boryl]hydroxyaniline, whose thermolysis with B2pin2 afforded a complicated mixture including N-borylaniline as the only minor product. Thus both the high deoxygenating reactivity of 3 and the facile nitrene formation from 4 were indispensable factors in this deoxygenative reduction of nitroarenes to anilines.

On the basis of these controlled reactions in Scheme 2, we propose a reaction mechanism as outlined in Scheme 3. The

Scheme 3. Plausible Pathway for the Reduction of 1a by $B_2nep_2/4,4'$ -Bipyridyl (B = (neopentylglycolato)boryl)



initial step is the deoxygenation of nitrobenzene (1a) to nitrosobenzene (7) by 3 in-situ-generated from B_2nep_2 and 4,4'-bipyridyl. In this stage, 4,4'-bipyridyl functions as an organocatalyst for the deoxygenation of 1a. The second step is the reaction of 7 with B_2nep_2 or 3, giving *N*,*O*-bis-[(neopentylglycolato)boryl]hydroxyaniline 4. The thermolysis of 4 produces a nascent phenylnitrene **C**, presumably due to the substituent effect of neopentylglycolato at the boron atom. In fact, the thermolysis of 4 in the presence of HNEt₂ afforded the corresponding azepin, in which C was isomerized to benzazirine before reacting with HNEt₂.¹⁴ Under the optimized condition, C reacts with B_2nep_2 or 3 to give *N*,*N*diborylaniline D. Finally, D is basic enough to deprotonate CH₃CN, yielding *N*-borylaniline derivative 5. A pathway through azobenzene (6), which is formed by the dimerization of C, is excluded because there was no aniline formation from 6, as shown in Scheme 2f. The deoxygenation of 1a by radical species derived from B_2nep_2 with 4,4'-bipyridyl is the alternative mechanism, but it is assumed to be a minor pathway because of the low yield of 2a for substituted pyridine derivatives.¹²

The tolerance of a carbonyl group under the reduction conditions led us to examine the reduction of 1a using $B_2nep_2/4,4'$ -bipyridyl in the presence of acetophenone at 100 °C for 16 h, affording ketimine 13a in 78% yield (Scheme 4). On the

Scheme 4. Ketimine Formation^a



basis of a recent study for aldimine formation using *N*borylated anilines and aldehydes,¹⁵ we added acetophenone after the formation of **5** in the reaction mixture; however, we did not observe any formation of **13a**, suggesting that the insitu-generated *N*,*N*-diborylaniline **D** was the actual iminating reagent to ketones.¹⁶ Nitroarenes **1d** and **1k**, bearing parasubstituted electron-donating and electron-withdrawing groups, afforded the imines **13d** and **13k** in 75 and 56% yield, respectively. Upon the addition of 2 equiv of acetophenone to the reaction mixture, **13k** was obtained in 86% yield.

In summary, we developed a simple protocol for reducing nitroarenes under aerobic conditions to the corresponding anilines by using commercially available bis-(neopentylglycolato)diboron $(B_2 nep_2)$ and 4,4'-bipyridyl. During the reduction course, we revealed that in-situ-generated N,N'-bis[(neopentylglycolato)boryl]-4,4'-bipyridinylidene (3) worked as an actual reactive species for the deoxygenation of the nitro group. The superiority of B₂nep₂ was attributed to the thermal instability of the in-situ-generated N,O-bis-[(neopentylglycolato)boryl]hydroxyanilines, which decomposed to give the corresponding nitrenes, as trapped by B₂nep₂. The advantageous point of this reduction protocol was the high chemical tolerance to various functional groups as well as O- and N-protecting groups. In addition, ketimines were obtained in a one-pot manner from nitroarenes with acetophenone under the $B_2 nep_2/4,4'$ -bipyridyl system without any metal waste. Further reductive transformations of the nitro functionality by B2nep2 with a catalytic amount of 4,4'bipyridyl are ongoing in our laboratories.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b03419.

Experimental details, controlled experiment in Scheme 2, characterization of anilines, and NMR spectra (PDF)

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Organic Letters

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