

Modified Hydroborate Agent: (2,2'-Bipyridyl)(tetrahydroborato)zinc Complex, $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$, as a New, Stable, Efficient Ligand-Metal Hydroborate and Chemoselective Reducing Agent

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(2,2'-Bipyridyl)(tetrahydroborato)zinc complex, $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$, is a new white stable compound which has been used for efficient reduction of variety of carbonyl compounds such as aldehydes, ketones, acyloins, α -diketones and α,β -unsaturated carbonyl compounds (1,2-reduction) to their corresponding alcohols in acetonitrile at room temperature. Excellent chemoselectivity was also observed for the reduction of aldehydes over ketones with this reducing agent.

The absence of a selective reduction of the carbonyl function of aldehydes, ketones, acids, esters and amides in the presence of carbon double bonds by catalytic hydrogenation, has led to the wide-spread use of certain complex metal hydrides for the reduction of carbonyl groups. In spite of the great convenience of lithium aluminum hydride and sodium tetrahydroborate in laboratory for organic synthesis, they suffer from certain limitations. LiAlH_4 as a powerful reducing agent shows poor selectivity for the reduction of multifunctional molecules. On the other hand, $\text{Na}[\text{BH}_4]$ is a mild reducing agent and is used for the reduction of few organic functional groups.¹ Thus developing means for controlling the reducing power of such reagents is desirable; such control could be achieved either by decreasing the reducing power of LiAlH_4 or by increasing that of $\text{Na}[\text{BH}_4]$.^{1,2} In fact, this has been achieved by different types of modifications. Methods can be summarized as: a) Substitution of the hydride(s) with other substituents which may exert marked steric and electronic influences upon the reactivity of the substituted complex ion, e.g., $\text{Na}[\text{BH}(\text{OAc})_3]$,^{3,4} $\text{Na}[\text{BH}_3(\text{OAc})]$,^{4,5} $\text{Na}[\text{BH}(\text{OMe})_3]$,^{3,6} sodium (dimethylamino) and (*t*-butylamino) trihydroborates,^{3,7} $\text{Na}[\text{BHEt}_3]$,⁸ $\text{Na}[\text{BH}(\text{O}_2\text{CCF}_3)_3]$,³ $\text{Na}[\text{BH}_3(\text{CN})]$ ⁹ and $\text{Na}[\text{BH}_2(\text{S}_3)]$,¹⁰ b) Variation of alkali-metal cation and metal cation in the hydride complex, e.g., $\text{Li}[\text{BH}_4]$,¹¹ $\text{K}[\text{BH}_4]$,¹² $\text{Ca}[\text{BH}_4]_2$,¹³ $\text{Cu}[\text{BH}_4]_2$,¹⁴ $\text{Zn}[\text{BH}_4]_2$,¹⁵ $\text{Ti}[\text{BH}_4]_3$,¹⁶ $\text{Zr}[\text{BH}_4]_4$ and the others;^{16b} c) A concurrent cation and hydride exchange, such as $\text{K}[\text{BH}(\text{OAc})_3]$,^{3,17} $\text{K}[\text{BH}(\text{i-PrO})_3]$,¹⁸ $\text{K}[\text{BHPH}_3]$,¹⁹ $\text{Li}[\text{BH}(\text{OAc})_3]$,²⁰ $\text{Li}[\text{BH}_3(\text{CN})]$,^{3,21} $\text{Li}[\text{BHEt}_3]$ (Super Hydride),²² $\text{Li}[\text{BH}(\text{n-butyl})]$,²³ lithium 9,9-di-*N*-butyl-9-borabicyclo[3.3.1]nonate,²⁴ lithium isopinocampheyl-9-borabicyclo[3.3.1]nonyl hydride,²⁵ lithium B-iso-2-ethylapopinocampheyl-9-borabicyclo[3.3.1]nonyl hydride,²⁶ lithium (amino)trihydroborate,²⁷ lithium trihydro(pyrrolidino)borate,²⁸ $\text{Li}[\text{BH}(\text{sec-butyl})_3]$ (L-Selectride),²⁹ $\text{K}[\text{BH}(\text{sec-butyl})_3]$ (K-Selectride),^{29a,c} $\text{Ca}[(\text{BH}_2(\text{S}_3))_2]$ ³⁰ and $\text{Ba}[(\text{BH}_2(\text{S}_3))_2]$,³¹ d) Use of the ligands to alter behavior of the metal hydroborates: $(\text{Ph}_3\text{P})_2\text{-Cu}[\text{BH}_4]$,³² $(\text{Ph}_3\text{P})_4\text{Cu}_2[\text{BH}_3(\text{CN})]_2$,³³ $(\text{C}_5\text{H}_5)_2\text{Zr}[\text{BH}_4]\text{Cl}$ ³⁴ and $(\text{i-PrO})_2\text{Ti}[\text{BH}_4]$ ³⁵ are examples in this area; e) Combination of

tetrahydroborates with metals, metal salts, Lewis acids, additives³⁶ and mixed solvent systems, especially those containing methanol;³⁷ f) Changing the cation to quaternary ammonium and phosphonium tetrahydroborates, such as $\text{Et}_4\text{N}[\text{BH}_4]$,^{38,39} $\text{Bu}_4\text{N}[\text{BH}_4]$,^{39,40} $\text{PhCH}_2(\text{Et})_3\text{N}[\text{BH}_4]$,⁴¹ $\text{Bu}_4\text{N}[\text{BH}(\text{OAc})_3]$,⁴² $\text{Bu}_4\text{N}[\text{BH}_3(\text{CN})]$,⁴³ 4-aza-*N*-benzylbicyclo[2.2.2]octylammonium tetrahydroborate⁴⁴ and $\text{Ph}_3\text{PMe}[\text{BH}_4]$,⁴⁵ g) Use of the polymers or solid supports to support hydride species: Amberlyst (A-26 or A-400), zeolite, alumina, silica gel and polyvinylpyridine are usually used as bed supports for different hydride species.⁴⁶

Zinc tetrahydroborate, $\text{Zn}[\text{BH}_4]_2$, as a transition metal hydroborate, is a potential reducing agent that has attracted much attention in the last two decades.⁴⁷ This reagent could be prepared conveniently from inexpensive zinc chloride and sodium tetrahydroborate in ether.¹⁵ The reagent must be used as its ethereal solution and should be stored in a cold place, which puts some restriction on its uses. This compound with high coordination ability is neutral and its combination systems such as $\text{Zn}[\text{BH}_4]_2/\text{TMEDA}$,⁴⁸ $\text{Zn}[\text{BH}_4]_2/\text{Me}_3\text{SiCl}$,⁴⁹ and $\text{Zn}[\text{BH}_4]_2/\text{TFA/DME}$ ⁵⁰ have also been used for different reduction purposes. Preparation and use of poly(4-vinylpyridine) supported zinc tetrahydroborate as a first polymeric transition metal hydroborate have been reported.^{46a} This reagent is very stable and has excellent chemoselectivity for reduction of aldehydes over ketones. The other reported modified tetrahydroborate is poly{tetrahydro[η -pyrazine]boratozinc} complex, $[\text{Zn}(\text{BH}_4)_2(\text{pyz})]_n$.⁵¹ This compound is stable to heat and light, but explodes violently into flames when in contact with water. Recently, we reported new tertiary amino and phosphino ligand complexes of zinc tetrahydroborate as (1,4-diazabicyclo[2.2.2]octane)(tetrahydroborato)zinc, $[\text{Zn}(\text{BH}_4)_2(\text{dabco})]$,^{2b,45b} and mono or bistrisphenylphosphinezinc tetrahydroborate, $[\text{Zn}(\text{BH}_4)_2(\text{Ph}_3\text{P})]$ or $[\text{Zn}(\text{BH}_4)_2(\text{Ph}_3\text{P})_2]$,⁵² of which we investigated the full reducing abilities. Continuing our mentioned strategies and our interest in preparation of modified ligand-metal tetrahydroborate, now we wish to report a new coordination complex of zinc tetrahydroborate and a commercially

cheap bidentate ligand, 2,2'-bipyridyl, as a stable bench-top reducing agent for the reduction of a variety of carbonyl compounds to their corresponding alcohols.

Results and Discussion

(2,2'-Bipyridyl)(tetrahydroborato)zinc, $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$, is a white stable compound which is prepared by the dropwise addition of an equimolar ethereal solution of 2,2'-bipyridyl to an equimolar ethereal solution of $\text{Zn}(\text{BH}_4)_2$ at room temperature. The formation of the complex is very fast and the reagent is formed quantitatively. Filtration and drying of the precipitate resulted in a white fluffy powder, which could be stored for months without losing its activity. The amount of Zn content in the complex is determined by both gravimetric and atomic absorption techniques, which confirmed the $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$ formula (Fig. 1).

1. Reduction of Aldehydes and Ketones. $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$ is a slightly soluble reagent and works efficiently in a range of aprotic solvents such as CH_2Cl_2 , Et_2O , THF and CH_3CN at room temperature. This reagent is unstable in protic solvents such as methanol, ethanol and water and decomposed vigorously with the evolution of hydrogen gas. Because of higher rate and efficiency of reduction in CH_3CN relative to other solvents, we selected it as a suitable solvent for the reduction reactions. The molar ratio of the reducing agent varies between 0.25–1.5 according to the nature of the carbonyl function in the molecules. As shown in Tables 1 and 2, different types of aldehydes and ketones were reduced with the reducing agent in acetonitrile at room temperature. Aldehydes are reduced rapidly with 0.25–0.5 molar amounts of the reagent in short times and 85–99% yields (Table 1). Ketones can also be reduced in acetonitrile in 50–99% yields (Table 2). Relative to aldehydes, reduction of ketones required higher molar amounts of the reagent (0.5–1.5 mol) and longer reaction times (Table 2).

Since aldehydes are reduced much more rapidly than ketones and the reagent has a bulky nature, this reagent can act as a good chemoselective reagent for discrimination of aldehydes over ketones or less hindered ketones over hindered ones. In order to show the chemoselectivity towards various carbonyl compounds, we performed the competitive reduction of acetophenone in the presence of an equimolar amount of benzaldehyde with 0.25 mol of the reagent at room temperature. We observed that aldehyde with excellent selectivity ratio was re-

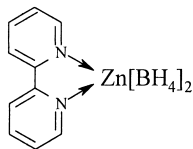
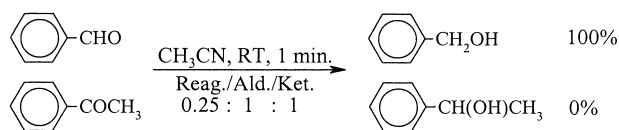


Fig. 1. (2,2'-Bipyridyl)(tetrahydroborato)zinc Complex.



Scheme 1.

duced by the reagent (Scheme 1). In Table 3, we see the general trend of chemoselective reduction of various carbonyl compounds. In most cases the selectivity ratio was excellent.

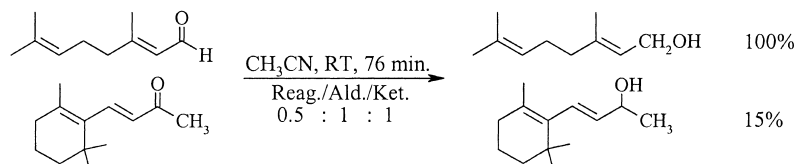
In order to show both advantages and limitations of the reducing agent, we compared our results with those reported for $[\text{Zn}(\text{BH}_4)_2(\text{dabco})]$,^{2b} $[\text{Zn}(\text{BH}_4)_2(\text{pyz})]$,⁵¹ $[\text{Zn}(\text{BH}_4)_2(\text{Ph}_3\text{P})]$,⁵² $[\text{Zn}(\text{BH}_4)_2(\text{Ph}_3\text{P})_2]$,⁵² $\text{Zn}[\text{BH}_4]_2$,^{47a-c} $[\text{Zn}(\text{BH}_4)_2\text{-XP4}]$,^{46a} $\text{Ph}_3\text{-PMe}[\text{BH}_4]$,^{45a, c} 4-aza-*N*-benzylbicyclo[2.2.2]octylammonium tetrahydroborate⁴⁴ and $\text{Bu}_4\text{N}[\text{BH}_4]$ ⁴⁰ (Table 4).

2. Reduction of α -Diketones and Acyloins. Reduction of α -diketones to their diols usually gives a mixture of the diols and the corresponding acyloins. With this reagent, α -diketones are reduced very easily to their corresponding vicinal diols with excellent yields (Table 5). Attempts to reduce α -diketones to their corresponding acyloins have been unsatisfactory and only the corresponding vicinal diols have been isolated from a mixture with high yields (92–98%). Acyloins are also reduced very easily to their vicinal diols by the reagent in excellent yields (90–96%) (Table 5).

3. Regioselective 1,2-Reduction of α,β -Unsaturated Carbonyl Compounds. A regioselective reduction of α,β -unsaturated aldehydes and ketones is an easy way to obtain allyl alcohols that are important synthetic materials in organic synthesis. This achievement with $\text{Na}[\text{BH}_4]$ is highly solvent-dependent and generally does not result in a useful regioselectivity.^{4,53} Regioselective 1,2-reduction is usually achieved using modified hydride reagents, which are formed a) by the replacement of hydride with sterically bulky substituents or electron-withdrawing/releasing groups in order to discriminate between the structural and electronic environments of the carbonyl groups, b) by changing the metal cation, c) by combination with metal salts and mixed solvents, and d) finally immobilization on polymeric supports.^{4,13,14b,23,53,54} $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$ is also regioselective in this case and α,β -unsaturated aldehydes and ketones are efficiently reduced to their corresponding allyl alcohols with 0.5–1 molar amount in CH_3CN at room temperature (92–98%) (Table 6).

The chemo- and regioselectivity of the reagent are also demonstrated by the following competitive reaction (Scheme 2). The selectivity ratio for the 1,2-reduction of citral over β -ionone is 6.7 (Table 3).

In this case, we also compared our results with those reported for $[\text{Zn}(\text{BH}_4)_2(\text{dabco})]$,^{2b} $[\text{Zn}(\text{BH}_4)_2(\text{pyz})]$,⁵¹ $[\text{Zn}(\text{BH}_4)_2(\text{Ph}_3\text{P})]$,⁵² $[\text{Zn}(\text{BH}_4)_2(\text{Ph}_3\text{P})_2]$,⁵² $\text{Zn}[\text{BH}_4]_2$,^{47a-c} $[\text{Zn}(\text{BH}_4)_2\text{-}$



Scheme 2.

Table 1. Reduction of Aldehydes to Their Alcohols with $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]^\text{a)}$

Entry	Substrate	Product	Molar ratio Reag./Subs.	Time/min	Yield/% ^{b)}
1			0.25	1	95
2			0.25	5	98
3			0.25	5	98
4			0.35	10	99
5			0.35	10	90
6			0.35	8	94
7			0.25	8	99
8			0.25	5	92
9			0.25	11	95
10			0.4	3	91
11			0.3	5	96
12			0.3	6	97
13			0.3	2	93
14			0.3	1	94
15			0.35	2	94
16			0.25	3	98
17			0.5	25	93
18			0.4	4	95
19			0.25	6	85

a) All reactions were performed in CH_3CN at room temperature.

b) Yields referred to isolated products.

XP4],^{46a} $\text{Ph}_3\text{PMe}[\text{BH}_4]$,^{45a,c} 4-aza-*N*-benzylbicyclo[2.2.2]octylammonium tetrahydroborate⁴⁴ and $\text{Bu}_4\text{N}[\text{BH}_4]$ ⁴⁰ (Table 7). A comparison shows that this reagent is more efficient and reactive than those reported.

Conclusion

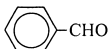
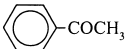
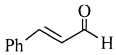
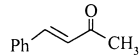
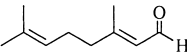
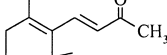
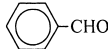
In this article we have shown that 2,2'-bipyridyl is a good ligand for stabilizing $\text{Zn}[\text{BH}_4]_2$ and does not affect the reduc-

Table 2. Reduction of Ketones to Their Alcohols with $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]^{\text{a)}$

Entry	Substrate	Product	Molar ratio Reag./Subs.	Time/h	Yield/% ^{b)}
1			1	0.75	99
2			1	1.3	93
3			1	1.75	96
4			1	1.5	94
5			1	0.15	93
6			0.5	0.25	98
7			0.5	0.15	88
8			1	0.25	89
9			0.5	2.15	97
10			1	1	98
11			1	3.5	97
12			1	1	95
13			2	1.5	93
14			2	0.25	89
15			1.5	3.5	97
16 ^{c)}			2	1.5	92
17			1	4.25	94
18			0.5	0.25	87
19			1	2	50

a) All reactions were performed in CH_3CN at room temperature. b) Yields referred to isolated products. c) Under reflux condition.

Table 3. Competitive Reduction of Aldehydes and Ketones to Their Alcohols with $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]^\text{a)}$

Entry	Substrate 1	Substrate 2	Molar ratio Reag./Subs 1/Subs 2	Time/min	Conv. 1/% ^{b)}	Conv. 2/% ^{b)}
1			0.25:1:1	1	100	0
2			0.5:1:1	1	100	0
3			0.5:1:1	76	100	15
4			0.5:1:1	15	100	0
5			0.25:1:1	1	100	< 5
6			1:1:1	3.5 h	100	< 1

a) All reactions were performed in CH_3CN at room temperature.

b) Conversions referred to TLC monitoring and isolated products.

ing ability of the reagent. $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$ is very suitable reagent for easy reduction of a variety of carbonyl compounds, such as aldehydes, ketones, α -diketones and acyloins, to their corresponding alcohols at room temperature. This reagent also reduces effectively α,β -unsaturated carbonyl compounds to their corresponding allyl alcohols. Reduction reactions need low molar ratios and short times. Comparison of obtained results with those reported for $\text{Zn}[\text{BH}_4]_2$ and other reagents shows that the reduction reactions with $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$ was very efficient and selective. The stability, ease of preparation from commercially available materials, high regio- and chemoselectivity of the reagent and also easy work-up of the reaction mixture can make this new modified hydroborate agent as an attractive practical bench-top reducing agent in organic synthesis.

Experimental

Products were characterized by a comparison with those of authentic samples (IR, ^1H NMR and TLC). All yields referred to isolated products. TLC was used for the purity determination of the substrates, products and reactions, monitoring over silica gel PolyGram SILG/UV 254 plates.

Preparation of (2,2'-Bipyridyl)(tetrahydroborato)zinc; $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$. A solution of $\text{Zn}[\text{BH}_4]_2$ (0.08 M, 250 mL) was prepared in dry ether from ZnCl_2 (2.725 g, 0.02 mol) and $\text{Na}[\text{BH}_4]$ (1.59 g, 0.042 mol) according to procedure available in the literature.¹⁵ Then, 2,2'-bipyridyl (3.123 g, 0.02 mol) in ether (50 mL) was added dropwise to solution of $\text{Zn}[\text{BH}_4]_2$ and stirred for 30 min. The resulting precipitate was filtered and dried in a vacuum to afford a fluffy white compound in a quantitative yield (4.92 g, 98%). This compound decomposed at 235 °C. Found: C, 47.42; H, 6.51; N, 11.06; Zn, 25.98%. Calcd for $\text{C}_{10}\text{B}_2\text{H}_{16}\text{N}_2\text{Zn}$: C, 47.80; H, 6.42; N, 11.15; Zn, 26.02%.

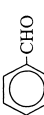
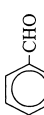
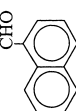
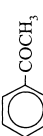
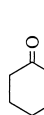
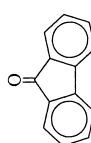
A Typical Procedure for Reduction of Aldehydes to Their Alcohols with $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$. In a round-bottomed

flask (15 mL), equipped with a magnetic stirrer, a solution of 4-chlorobenzaldehyde (0.14 g, 1 mmol) in CH_3CN (8 mL) was prepared. The reducing agent (0.062 g, 0.25 mmol) was added and the mixture was stirred magnetically at room temperature for 5 min. TLC monitored the progress of the reaction (eluent; $\text{CCl}_4/\text{Et}_2\text{O}$: 5/1). After completion of the reaction, a solution of 10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (7 mL) was added and the mixture was magnetically stirred for 20 min. Then, the mixture was extracted with CH_2Cl_2 (3×15 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and thick-layer chromatography of the resulting crude material over silica gel by eluent of $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2 afforded the pure crystals of 4-chlorobenzyl alcohol (0.14 g, 98% yield, Table 1).

A Typical Procedure for Reduction of Ketones to Their Alcohols with $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$. In a round-bottomed flask (15 mL) equipped with a magnetic stirrer, a solution of benzophenone (0.182 g, 1 mmol) in CH_3CN (8 mL) was prepared. The reducing agent (0.251 g, 1 mmol) was added and the mixture was magnetically stirred at room temperature for 45 min. TLC monitored the progress of the reaction (eluent; $\text{CCl}_4/\text{Et}_2\text{O}$: 5/1). After completion of the reaction, a solution of 10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (7 mL) was added and the mixture was magnetically stirred for 20 min. Then, the mixture was extracted with CH_2Cl_2 (3×15 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and thick-layer chromatography of the resulting crude material over silica gel by eluent of $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2 afforded pure crystals of diphenylmethanol (0.182 g, 99% yield, Table 2).

A Typical Procedure for Regioselective 1,2-Reduction of α,β -Unsaturated Aldehydes to Their Alcohols with $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$. In a round-bottomed flask (15 mL) equipped with a magnetic stirrer, a solution of cinnamaldehyde (0.132 g, 1 mmol) in CH_3CN (8 mL) was prepared. The reducing agent (0.126 g, 0.5 mmol) was added and the mixture was stirred magnetically at room temperature for 2 min. TLC monitored the progress of the reaction (eluent; $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2). After

Table 4. Comparison of Reductions of Aldehydes and Ketones to Their Alcohols with [Zn(BH₄)₂(bpy)] and Other Reported Reagents

Entry	Substrate	Molar ratio (Reag./Subs), Time/h, and Yield/%									
		I	II ^{2b}	III ⁵¹	IV ⁵²	V ⁵²	VI ^{47/a-c}	VII ^{46a}	VIII ^{45a, c}	IX ⁴⁴	X ⁴⁰
1		0.25(0.02)(95)	0.75(0.7)(90)	1(2.5)(73)	—	—	1(0.5)(100) ^{a)}	1(8)(80)	1(Im)(90)	1(0.25)(90)	4(0.67)(96)
2		0.25(0.08)(98)	0.75(0.4)(97)	1(3)(95)	—	1(Im)(88)	1(0.5)(100) ^{a)}	1(5)(95)	1(Im)(86)	1(0.23)(90)	—
3		0.35(0.17)(99)	0.75(12)(96)	2(1.5)(96)	—	1(0.17)(89)	—	1(12)(75)	1(Im)(83)	2(0.8)(85)	—
4		0.25(0.13)(99)	—	—	2(0.5)(90)	1.5(Im)(100)	—	1(8)(84)	1(Im)(100)	1(0.25)(90)	—
5		0.5(2.15)(97)	1.2(5.4)(92)	4(30)(85)	2(1.25)(75)	2(0.5)(80)	1(0.5)(0) ^{a)}	2(15)(0)	2(12)(96)	2(17)(80)	4(10)(98)
6		1(0.75)(99)	1.5(8.5)(94)	—	—	—	—	2(48)(0)	—	2(21.5)(90)	—
7		0.5(0.15)(88)	—	4(18)(85)	2(1)(100)	1(1)(95)	1(0.08)(100) ^{b)}	2(24)(0)	1(10)(95)	—	4(9.2)(98)
8		1(1.5)(94)	1.5(2.3)(95)	—	2(0.5)(88)	2(0.33)(85)	—	—	1.6(18)(80)	—	—
9		1.5(3.5)(97)	2.4(72)(70)	—	—	—	—	—	1(24)(77)	—	—
10		0.5(0.08)(91)	1(0.17)(92)	3(5)(85)	—	—	—	—	—	—	—

I: [Zn(BH₄)₂(bpy)]; II: [Zn(BH₄)₂(dabco)]; III: [Zn(BH₄)₂(pyz)]_n; IV: [Zn(BH₄)₂(Ph₃P)]; V: [Zn(BH₄)₂(Ph₃P)₂]; VI: Zn[BH₄]₂; VII: [Zn(BH₄)₂-XP4]; VIII: Ph₃PMc[BH₄];IX: [PhCH₂(dabco)]BH₄; X: Bu₄N[BH₄]; a) THF, -10 °C; b) DME, -78 °C; Im means immediately.

Table 5. Reduction of Acyloins and α -Diketones to Their Alcohols with $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]^\text{a)}$

Entry	Substrate	Product	Molar ratio (Reag./Subs.)	Yield/% ^{b)}
1			1	94
2			1	92
3			1	95
4			1	97
5			1	98
6			0.5	91
7			0.5	95
8			0.5	90
9			0.5	95
10			0.5	96
11			1	94
12			0.5	92

a) All reactions were performed in CH_3CN at room temperature for 3–5 minutes.

b) Yields referred to isolated products.

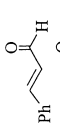
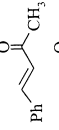
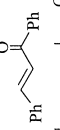
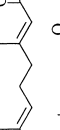
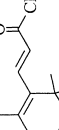
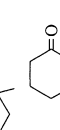
Table 6. Reduction of α,β -Unsaturated Carbonyl Compounds to Their Alcohols with $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]^\text{a)}$

Entry	Substrate	Product	Molar ratio (Reag./Subs.)	Time/h	Yield/% ^{b)}
1			0.5	2 min	92
2			1	1.3	97
3			1	3	98
4			0.5	0.5	90
5			0.5	0.2	89
6			0.5	1	95
7			1	1.6	96

a) All reactions were performed in CH_3CN at room temperature.

b) Yields referred to isolated products.

Table 7. Comparison of Reductions of α,β -Unsaturated Carbonyl Compounds to Their Alcohols with $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$ and Other Reported Reagents

Entry	Substrate	I	II ^{2b}	III ⁵¹	IV ⁵²	V ⁵²	VI ^{d/a-c}	VII ^{6a}	VIII ^{45a, c}	IX ⁴⁴	X ⁴⁰
1		0.5(0.03)(92)	0.75(4.5)(94)	3(6)(93)	1.5(0.4)(100)	1(0.25)(90)	1(0.5)(100) ^{a)}	1(9)(90)	1(Im)(95)	1(0.33)(90)	1.5(17)(73)
2		1(1.3)(97)	1.2(2.2)(92)	4(8)(95)	2(2.5)(87)	2(0.5)(90)	1(0.5)(15) ^{a)}	2(15)(10)	1(3.5)(90)	1(0.4)(85)	1(0.4)(80)
3		1(3)(98)	1.3(7.5)(95)	4(30)(90)	—	—	—	2(24)(0)	1.2(6)(90)	2(3.2)(85)	1(3.3)(75)
4		0.5(1)(95)	1.5(2.7)(93)	3(6)(87)	—	—	1(0.25)(100) ^{b)}	1(18)(80)	—	—	—
5		1(1.6)(96)	1.3(3)(95)	—	2(1.3)(100)	1(0.08)(80)	—	2(15)(10)	1(6)(71)	—	—
6		0.5(0.5)(90)	—	—	1(0.17)(85)	1(Im)(90)	1(0.08)(14) ^{b)}	—	—	—	—

I: $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$; II: $[\text{Zn}(\text{BH}_4)_2(\text{dabco})]$; III: $[\text{Zn}(\text{BH}_4)_2(\text{pyz})]_n$; IV: $[\text{Zn}(\text{BH}_4)_2(\text{Ph}_3\text{P})]$; V: $[\text{Zn}(\text{BH}_4)_2(\text{Ph}_3\text{P})_2]$; VI: $[\text{Zn}(\text{BH}_4)_2\text{-XP4}]$; VII: $[\text{Zn}(\text{BH}_4)_2\text{-XP4}]$; VIII: $\text{Ph}_3\text{PMel}[\text{BH}_4]$; IX: $[\text{PhCH}_2(\text{dabco})\text{BH}_4]$; X: $\text{Bu}_4\text{N}[\text{BH}_4]$; a) THF, -10°C ; b) DME, -78°C ; Im means immediately.

completion of the reaction, a solution of 10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (7 mL) was added and the mixture was magnetically stirred for 20 min. Then, the mixture was extracted with CH_2Cl_2 (3×15 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and thick-layer chromatography of the resulting crude material over silica gel by eluent of $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2 afforded pure liquid cinnamyl alcohol (0.123 g, 92% yield, Table 6).

A Typical Procedure for Selective 1,2-Reduction of α,β -Unsaturated Ketones to Their Alcohols with $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$. In a round-bottomed flask (15 mL) equipped with a magnetic stirrer, a solution of benzylideneacetone (0.146 g, 1 mmol) in CH_3CN (8 mL) was prepared. The reducing agent (0.251 g, 1 mmol) was added and the mixture was stirred magnetically at room temperature for 1.3 h. TLC monitored the progress of the reaction (eluent; $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2). After completion of the reaction, a solution of 10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (7 mL) was added and the mixture was magnetically stirred for 20 min. Then, the mixture was extracted with CH_2Cl_2 (3×15 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and thick-layer chromatography of the resulting crude material over silica gel by eluent of $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2 afforded pure 4-phenyl-3-buten-2-ol as a product (0.144 g, 97% yield, Table 6).

A Typical Procedure for the Competitive Reduction of Aldehydes and Ketones with $[\text{Zn}(\text{BH}_4)_2(\text{bpy})]$. In a round-bottomed flask (15 mL) equipped with a magnetic stirrer, a solution of benzaldehyde (0.106 g, 1 mmol) and acetophenone (0.12 g, 1 mmol) in CH_3CN (8 mL) was prepared. The reducing agent (0.062 g, 0.25 mmol) was added and the mixture was magnetically stirred at room temperature for 1 min. TLC monitored the progress of the reaction. Then, the mixture was quenched with a solution of 10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (7 mL) and this is magnetically stirred for 20 min. Then, the mixture was extracted with CH_2Cl_2 (3×15 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and thick-layer chromatography of the resulting crude material over silica gel by eluent of $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2 afforded the pure liquid benzyl alcohol as a sole product of reduction and acetophenone as an intact material (Table 3).

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