(Pyridine)(tetrahydroborato)zinc Complex, $[Zn(BH_4)_2(py)]$, as a New Stable, Efficient and Chemoselective Reducing Agent for Reduction of Carbonyl Compounds

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(Pyridine)(tetrahydroborato)zinc complex, $[Zn(BH_4)_2(py)]$, as a stable white solid, was prepared quantitatively by complexation of an equimolar amount of zinc tetrahydroborate and pyridine at room temperature. This reagent can easily reduce variety of carbonyl compounds such as aldehydes, ketones, acyloins, α-diketones and α,β-unsaturated carbonyl compounds to their corresponding alcohols in good to excellent yields. Reduction reactions were performed in ether or THF at room temperature or under reflux conditions. In addition, the chemoselective reduction of aldehydes over ketones was accomplished successfully with this reducing agent.

Key Words : Reduction, Tetrahydroborato, Carbonyl compounds, Chemoselective, Pyridine

Introduction

Reduction is one of the most fundamental and useful reactions in organic synthesis. The discoveries of sodium borohydride and lithium aluminum hydride in 1940s have provided an efficient route for the reduction of functionalized molecules and they are commonly used in organic laboratory nowadays.[1] In spite of their efficiency and convenience, these two hydride reagents stand at the extreme ends: lithium aluminum hydride being capable for reducing nearly all of the functionalized groups and sodium borohydride being very weak reducing agent only for aldehydes, ketones and acid chlorides.[1] So, controlling the reducing power of such reagents has been one of the main interests for organic chemists in many years. In fact, advances in such a field have been realized by: a) substitution of the hydride(s) with other groups which may exert marked steric and electronic influences upon the reactivity of the substituted complex ion, b) variation in the alkali metal cation and metal cation in the complex hydride which would alter the reducing power of the reagent, c) by concurrent cation and hydride exchange, d) use of ligands to alter behavior of the metal hydrides, e) combination of borohydrides with metal, metal salts, Lewis acids, mixed solvent systems and some other agents, f) changing the cation to quaternary and phosphonium borohydrides, and g) finally use of the polymers and solid beds for supporting the hydride species. Preparation of modified hydroborates reagents and their uses in organic synthesis has been reviewed recently.[2]

Zinc tetrahydroborate, $Zn(BH_4)_2$, as a non-conventional hydride transferring agent, has been reported to effect very efficient chemo-, regio- and stereoselective reductions in several compelex substrates.[3a] This potential reducing agent is a neutral and can be used in a range of aprotic solvents such as ether, THF and DME. High coordination ability of zinc makes zinc tetrahydroborate more selective in its hydride transferring reactions. In spite of this, zinc tetrahydroborate has been used less than regular reducing agents in laboratory for the reduction of organic compounds, probably because of non-availability as a commercial reagent, being freshly prepared solution just prior to use and limitation to handling and storage. The reducing abilities of zinc tetrahydroborate have been reviewed recently.[3] In addition to using zinc tetrahydroborate alone as a mild reducing agent, its combination systems *e.g.*, $Zn(BH_4)_2$/TMEDA,[4a] $Zn(BH_4)_2$/Me_3SiCl[4b] and $Zn(BH_4)_2$/TFA/DME[4c] are of interest and have been used for different reduction purposes.

Along the outlined strategies some modifications of zinc tetrahydroborate such as poly[(tetrahydroborato)(η-pyrazinc)zinc] complex, $[Zn(BH_4)_2(pyz)]_n$,[5] (1,4-diazabicyclo-[2,2,2]octane)(tetrahydroborato)zinc complex, $[Zn(BH_4)_2$-(dabco)][2b,6] and bis(tetrahydroborato)(triphenylphosphine) zinc, $[Zn(BH_4)_2(Ph_3P)_X]$ (X=1 & 2)[7] have been made by our research group and used for reduction of organic compounds. In continuation of our interest for preparation of new modified tetrahydroborates, we now wish to report the preparation of new stable ligand-zinc tetrahydroborate such as (pyridine)(tetrahydroborato)zinc complex, $[Zn(BH_4)_2(py)]$ and its reducing ability in the reduction of carbonyl compounds such as aldehydes, ketones, acyloins, α-diketones and α,β-unsaturated carbonyl compounds to their corresponding alcohols.

Results and Discussion

(Pyridine)(tetrahydroborato)zinc, $[Zn(BH_4)_2(py)]$, is a stable white solid which can be readily prepared by complexation of 1 : 1 ethereal solution of zinc tetrahydroborate and pyridine at room temperature. The complex is readily formed quantitatively to give a white solid. Filtration and evaporation of the solvent result in a white fluffy powder which could be stored in a sealed bottle for months without losing its activity. The Zn content in the complex is determined by both gravimetric and atomic absorption techniques. The measurements data are in good agreement with the proposed structure of the reagent as $[Zn(BH_4)_2(py)]$

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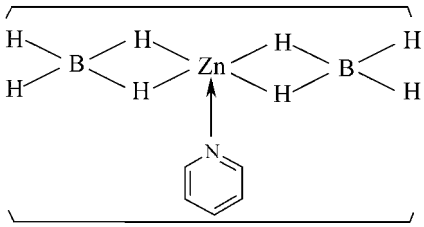


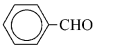
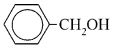
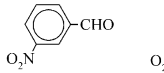
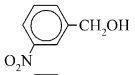
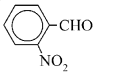
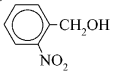
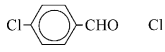
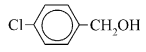
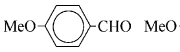
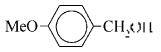
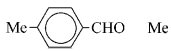
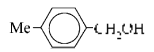
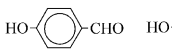
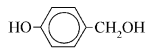
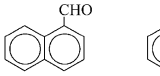
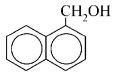
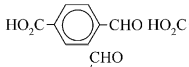
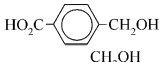
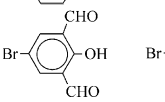
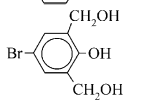
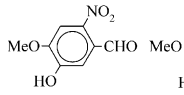
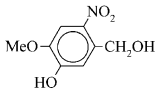
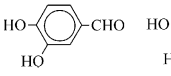
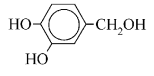
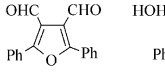
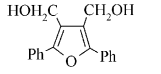
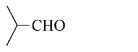
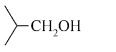
Figure 1. (Pyridine)(tetrahydroborato)zinc complex.

(Figure 1).

The solubility behavior of $[Zn(BH_4)_2(py)]$ in various aprotic solvents such as Et_2O, CH_2Cl_2, $CHCl_3$, CH_3CN and THF was studied and observed that this reagent is slightly soluble in these solvents. $[Zn(BH_4)_2(py)]$ in protic solvents such as methanol and ethanol is unstable and decomposed with the evolution of hydrogen gas. For the selection of appropriate solvent in reduction reactions, 4-chlorobenzaldehyde and acetophenone as model compounds was adopted in dry Et_2O, CH_3CN, $CHCl_3$ and THF. Our observation reveals that all these solvents are suitable for reduction, but especially the reduction of aldehydes in Et_2O and ketones in THF provided a fast reaction rate and efficiency. The required molar ratio of the reducing agent varies between 1-4 molar equivalents according to the nature of carbonyl group in a molecule.

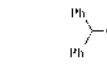
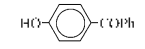
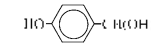
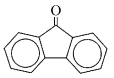
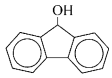
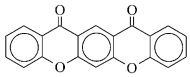
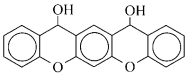
Reduction of Aldehydes and Ketones. Transformation of aldehydes and ketones to their alcohols is one of the most important reactions in organic synthesis. $NaBH_4$ is usually used for the reduction of aldehydes and ketones to their corresponding alcohols in protic solvents such as ethanol or isopropyl alcohol. This goal could be easily achieved by $[Zn(BH_4)_2(py)]$ in aprotic solvents such as ether and THF. Reduction of a variety of structurally different aromatic and aliphatic aldehydes to their corresponding alcohols is performed efficiently with this reducing agent (Table 1).

Table 1. Reduction of Aldehydes to Alcohols with $[Zn(BH_4)_2(py)]$[a]

Entry	Substrate	Product	Molar Ratio Reag./Subs.	Time/ h	Yield/ %[b]
1			1	0.5	91
2			1	0.25	98
3			1	0.45	97
4			1	0.2	99
5			1	1.3	96
6			1	0.7	94
7			1	0.3	91
8			1	0.8	95
9			1	1.7	94
10			1.3	0.4	90
11			1	0.5	92
12			1	1.6	98
13			2	3.9	95
14			1	0.35	85

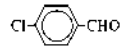
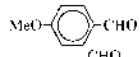
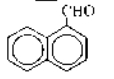
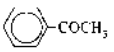
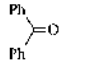
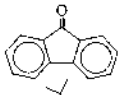
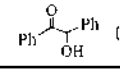
[a]All reactions were performed in ether at room temperature. [b]Yields referred to isolated products.

Table 2. Reduction of Ketones to Alcohols with $[Zn(BH_4)_2(py)]$[a]

Entry	Substrate	Product	Molar Ratio Reag./Subs.	Time/ h	Yield/ %[b]
1			2	4.3	97
2			2	2.4	92
3			2	4.2	96
4			2	5.3	98
5			4	3.2	93
6			2	1	99
7			2	2	94
8			2	2	89
9			2	3	89
10			4	2	94
11			2	4.5	94
12			4	2	92
13			2	1.4	97
14			2	4.5	90
15			2	2.3	83
16			2	2	80

[a]All reactions were performed in THF under reflux conditions. [b]Yields referred to isolated products.

Table 3. Comparison of Reduction of Aldehydes and Ketones to Alcohols with [Zn(BH$_4$)$_2$(py)] and Other Reported Reagents

Entry	Substrate	Molar Ratio (Reag. Subs.), Time/h and Yield/%									
		I	II[2b]	III[5]	IV[7]	V[7]	VI[8]	VII[9]	VIII[10]	IX[11]	X[12]
1		1(0.5)(91)	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		1(0.2)(99)	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		1(1.3)(96)	0.75(12)(96)	2(1.5)(96)	–	1(0.17)(89)	–	1(12)(75)	1(Im)(83)	2(0.8)(85)	–
4		1(0.8)(95)	–	–	2(0.5)(90)	1.5(Im)(100)	–	1(8)(84)	1(Im)(100)	1(0.25)(90)	–
5		2(2)(94)	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		2(4.3)(97)	1.5(8.5)(94)	–	–	–	–	2(48)(0)	–	2(21.5)(90)	–
7		2(2)(89)	–	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		2(5.3)(98)	1.5(2.3)(95)	–	2(0.5)(88)	2(0.33)(85)	–	–	1.6(18)(80)	–	–
9		2(4.5)(94)	2.4(72)(70)	–	–	–	–	–	1(24)(77)	–	–
10		0.5(0.5)(97)	1(0.17)(92)	3(5)(85)	–	–	–	–	–	–	–

[1]|Zn(BH$_4$)$_2$(py)|; [II]|Zn(BH$_4$)$_2$(dabco)|; [III]|Zn(BH$_4$)$_2$(pyz)|$_n$; [IV]|Zn(BH$_4$)$_2$(Ph$_3$P)|; [V]|Zn(BH$_4$)$_2$(Ph$_3$P)$_2$|; [VI]Zn[BH$_4$]$_2$; [VII][Zn(BH$_4$)$_2$-XP4]; [VIII]Ph$_3$PMe[BH$_4$]; [IX][PhCH$_2$(dabco)]BH$_4$; [X]Bu$_4$N[BH$_4$]; [a]THF, −10 °C. [b]DME, −78 °C; Im means immediately.

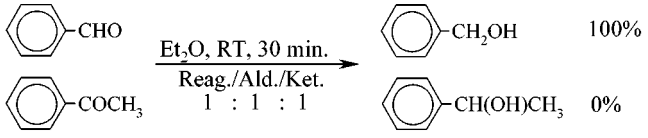
Aldehydes are reduced with 1-2 molar amounts of the reagent in ether at room temperature in high to excellent yields (85-99%). In Table 1, the reduction of aromatic aldehydes substituted with electron-withdrawing groups is generally faster than that of those substituted with electron-releasing groups. Reduction of ketones is also performed well with 2-4 molar amounts of the reagent in refluxing THF. The efficiency of these reactions were also excellent (80-99%) (Table 2). The work-up procedure of the reaction mixture is easy: employing dilute mineral acid (5% HCl) affects the procedure to afford the crude product for further purification by a column chromatography packed with silica gel.

In order to show the efficiency of the reagent, we compared our results with those of reported in the literature for [Zn(BH$_4$)$_2$(dabco)],[2b] [Zn(BH$_4$)$_2$(pyz)]$_n$,[5] [Zn(BH$_4$)$_2$(Ph$_3$P)],[7] [Zn(BH$_4$)$_2$(Ph$_3$P)$_2$],[7] Zn[BH$_4$]$_2$,[8] [Zn(BH$_4$)$_2$-XP4],[9] Ph$_3$PMe[BH$_4$],[10] 4-aza-N-benzylbicyclo[2.2.2]octylammonium tetrahydroborate[11] and tetrabutylammonium tetrahydroborate[12] (Table 3).

Chemoselective Reduction of Aldehydes and Ketones. It is often necessary in organic synthesis to reduce one particular carbonyl group without affecting other carbonyl group in a molecule. In the case of hydridic agents with respect to both steric and electronic influence, aldehydes generally are more susceptible to reduction than ketones. NaBH$_4$, LiAlH$_4$ and BH$_3$, as usually employed reagents for reduction reactions, are too reactive under normal conditions to take advantage of the inherent difference in reactivity between aldehydes and ketones. Thus most of the reported chemoselective methods involve the modification of one of the above reagents in order to attenuate reactivity. A numerous modified tetrahydroborate reagents have been reported to show the discrimination ability between aldehydes and ketones.[13]

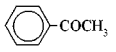
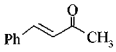
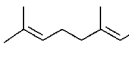
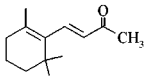
Along the outlined strategy and showing the chemoselectivity of [Zn(BH$_4$)$_2$(py)] for discrimination of aldehydes over ketones, we underwent competition experiments of a variety of structurally different aldehydes and ketones. In the preceding section, we notified that, reduction of aldehydes and ketones were both temperature and solvent dependent (Tables 1 and 2). Therefore, this goal could be easily achieved by reduction of acetophenone in the presence of an equimolar amount of benzaldehyde with [Zn(BH$_4$)$_2$(py)] at room temperature. In Scheme 1 we see that this reducing agent discriminates exclusively between aldehyde and ketone. In Table 4, we see the general trend of this discrimination ability for reduction of aldehydes in the presence of ketones by [Zn(BH$_4$)$_2$(py)]. The bulky nature of reagent induces special steric selectivity for the reduction of sterically hindered carbonyl groups *vs* non-hindered ones (Entry 6) (Table 4).

Regioselective 1,2-Reduction of α,β-Unsaturated Carbonyl Compounds. Reduction of α,β-unsaturated carbonyl compounds by metal hydrides can follow two pathways: addition



Scheme 1

Table 4. Competitive Reduction of Aldehydes and Ketones to Alcohols with $[Zn(BH_4)_2(py)]$

Entry	Substrate 1	Substrate 2	Molar Ratio Reag. Subs. 1/Subs. 2	Solvent	Condition	Time/h	Conv. 1 %[a]	Conv. 2 %[a]
1			1:1:1	Et_2O	RT	0.5	100	0
2			1:1:1	Et_2O	RT	1.85	100	3
3			1:1:1	Et_2O	RT	1.9	100	5
4			2:1:1	THF	Reflux	2.6	100	7
5			1:1:1	Et_2O	RT	0.7	100	5
6			2:1:1	THF	Reflux	2.1	100	13

[a]Conversions referred to TLC monitoring and isolated products.

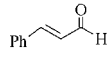
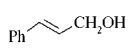
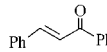
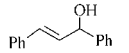
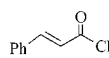
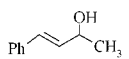
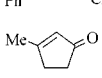
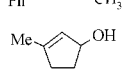
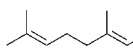
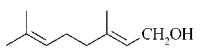
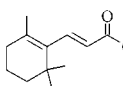
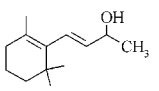
to carbonyl group (1,2-reduction) to give allylic alcohols or addition to the conjugated double bond (1,4-addition) to give saturated carbonyl compounds.

In spite of substantial evidence, the tendency for sodium borohydride to reduce conjugated enones is highly solvent dependent and generally does not result in a useful regioselectivity.[14a-c] On the other hand, the need for reduction of conjugated enones to the corresponding allylic alcohols has led to the development of several new specific reagents.[14d-i] Selective 1,2-reduction is usually achieved by using modified tetrahydroborate agents, which are formed: a) by the replacement of hydride(s) with sterically bulky substituents or electron-withdrawing/releasing groups in order to discriminate between the structural and electronic environments of the carbonyl groups.[15] b) combination with Lewis acids and mixed solvents.[16] c) using of transition metal tetrahydroborates and its new modifications.[17] d) using of quaternary ammonium and phosphonium tetrahydroborates[18] and e) finally, immobilization on polymeric supports and anion exchange resins.[19]

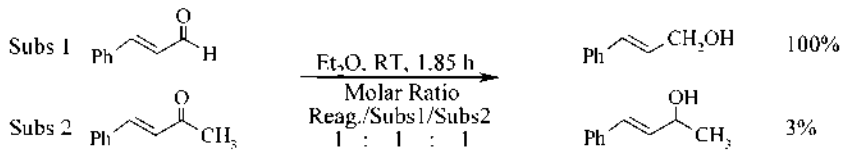
Reduction of α,β-unsaturated aldehydes and ketones by $[Zn(BH_4)_2(py)]$ proceeds with excellent regioselectivity and final allylic alcohol products are obtained in high yields. Aldehydes were readily reduced with equimolar amount of the reagent in ether at room temperature (93-97%) (Table 5), but the reduction of ketones required drastic reaction conditions of higher molar ratios of the reagent and refluxing THF. The efficiency of the reactions was also excellent to provide the corresponding secondary allylic alcohols in 89-96% (Table 5).

Previously, we recognized that reduction of α,β-unsaturated aldehydes and ketones is solvent and temperature dependent, so we take this advantage for chemo- and regioselective reduction of α,β-unsaturated aldehydes over ketones. This goal is demonstrated by competitive reduction of cinnamaldehyde in the presence of an equimolar amount of benzylideneacetone in ether at room temperature by the reagent. Scheme 2 shows such a reduction which reveals that aldehyde is reduced to alcohol in excellent selectivity in the presence of ketone. Table 4 shows the general trend of chemoselectivity for reduction of α,β-unsaturated aldehydes over ketones.

Table 5. Reduction of α,β-Unsaturated Carbonyl Compounds to Allyl Alcohols with $[Zn(BH_4)_2(py)]$[a]

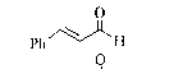
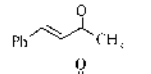
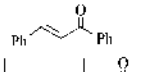
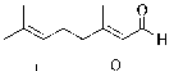
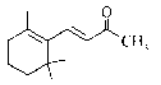
Entry	Substrate	Product	Molar Ratio (Reag./Subs.)	Ratio of 1,2:1,4	Time/h	Yield/%[b]
1			1	100:0	1.5	97
2			2	100:0	3	94
3			2	100:0	1	97
4			2	100:0	1.3	89
5			1	100:0	1.8	93
6			2	100:0	1.5	92

[a]All reactions of aldehydes were performed in ether at room temperature and ketones in THF under reflux conditions. [b]Yields referred to isolated products.



Scheme 2

Table 6. Comparison of Reduction of α,β-Unsaturated Carbonyl Compounds to Their Alcohols with $[Zn(BH_4)_2(py)]$ and Other Reported Reagents

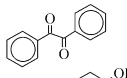
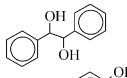
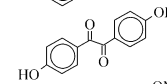
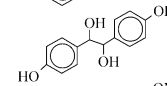
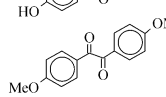
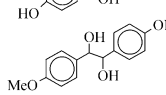
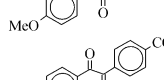
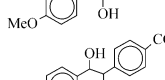
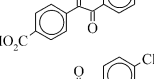
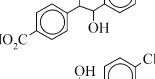
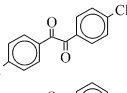
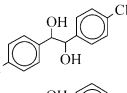
Entry	Substrate	Molar Ratio (Reag./Subs.), Time/h and Yield/%									
		I	II[2b]	III[5]	IV[7]	V[7]	VI[8]	VII[9]	VIII[10]	IX[11]	X[12]
1		1(1.5)(97)	0.75(4.5)(94)	3(6)(93)	1.5(0.4)(100)	1(0.25)(90)	1(0.5)(100)[a]	1(9)(90)	1(1m)(95)	1(0.33)(90)	1.5(17)(73)
2		2(1)(97)	1.2(2.2)(92)	4(8)(95)	2(2.5)(87)	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		2(3)(94)	1.3(7.5)(95)	4(30)(90)	–	–	–	2(24)(0)	1.2(6)(90)	2(3.2)(85)	1(3.3)(75)
4		1(1.8)(93)	1.5(2.7)(93)	3(6)(87)	–	–	1(0.25)(100)[b]	1(18)(80)	–	–	–
5		2(1.5)(92)	1.3(3)(95)	–	2(1.3)(100)	1(0.08)(80)	–	2(15)(10)	1(6)(71)	–	–

[I] $[Zn(BH_4)_2(py)]$; [II] $[Zn(BH_4)_2(dabco)]$; [III] $[Zn(BH_4)_2(pyz)]_n$; [IV] $[Zn(BH_4)_2(Ph_3P)]$; [V] $[Zn(BH_4)_2(Ph_3P)_2]$; [VI] $Zn[BH_4]_2$; [VII] $[Zn(BH_4)_2\text{-}XP_4]$; [VIII] $Ph_3PMe[BH_4]$; [IX] $[PhCH_2(dabco)]BH_4$; [X] $^nBu_4N[BH_4]$; [a] THF, −10 °C; [b] DME, −78 °C; 1m means immediately.

For showing the efficiency of $[Zn(BH_4)_2(py)]$ for 1,2-regioselective reduction of α,β-unsaturated carbonyl compounds, we compared our results with those of reported by $[Zn(BH_4)_2(dabco)]$,[2b] $[Zn(BH_4)_2(pyz)]_n$,[5] $[Zn(BH_4)_2(Ph_3P)]$,[7] $[Zn(BH_4)_2(Ph_3P)_2]$,[7] $Zn[BH_4]_2$,[8] $[Zn(BH_4)_2\text{-}XP4]$,[9] $Ph_3PMe[BH_4]$,[10] 4-aza-N-benzylbicyclo[2.2.2]octylammonium tetrahydroborate[11] and tetrabutylammonium tetrahydroborate[12] (Table 6). A comparison shows that this reagent is also more efficient than the other reagents.

Reduction of Acyloins and α-Diketones. Synthetic applications of α-hydroxy ketones and α-diketones are well known and their reductions to vicinal diols and/or acyloins are the subject of interests in organic synthesis. Reduction of α-diketones usually gives a mixture of α-hydroxy ketones and vicinal diols. In spite of this, some chemical or biochemical reagents can undergo selective reduction of α-diketones to only one of the mentioned products. For example; Zn/aq.DMF,[20] Zn/H_2SO_4,[21] $TiCl_3$ or VCl_2/THF,[22] $(C_2H_5O)_3P$,[23] H_2S/piperidine/DMF[24] and heating with benzpinacol[25] performed reduction of α-diketones to acyloins, whereas *Cryptococcus macerans*[26] did this reduction to vicinal diols. Reduction of α-diketones with modified tetrahydroborate agents is also subject of the interest[2b] and easily achieved by $[Zn(BH_4)_2(py)]$. This reagent with 1-2 molar equivalents efficiently reduces α-diketones to their vicinal diols in THF under reflux condition (Table 7). Our attempts for reduction of α-diketones to acyloins were unsatisfactory and only vicinal diols were detected as products (Table 7) (84-98%). In addition to the reduction of α-diketones, reduction of acyloins to vicinal diols is also important in organic synthesis. For this transformation using $H_2/CuCr_2O_4$,[27] *Saccharomyces cerevisiae* (bakers yeast)[28] and modified tetrahydroborate agents[2b] have been reported. In continuation of our study, this goal also easily achieved by $[Zn(BH_4)_2(py)]$ and we observed that benzoin is reduced to hydrobenzoin efficiently in refluxing THF by utilizing 0.5 molar equivalent of the reagent (Table 7). In Table 3, we see a comparison for reduction of this compound with $[Zn(BH_4)_2(py)]$ and other reported reagents.

Table 7. Reduction of α-Diketones and Acyloins to Their Alcohols with $[Zn(BH_4)_2(py)]$[a]

Entry	Substrate	Product	Molar Ratio Reag./Subs.	Time/ h	Yield/ %[b]
1			1.5	2	98
2			2	1	91
3			2	1.5	89
4			1.5	1	84
5			2	0.8	94
6[c]			0.5	0.5	97

[a] All reactions were performed in THF under reflux conditions. [b] Yields referred to isolated products. [c] This reaction was performed at room temperature.

Conclusion

In this study, we prepared (pyridine)(tetrahydroborato)-zinc complex, $[Zn(BH_4)_2(py)]$, as a new stable ligand-metal

tetrahydroborate and utilized it as an efficient reducing agent. Preparation of this complex reagent is carried out simply and quantitatively by complexation of $Zn(BH_4)_2$ and pyridine at room temperature. Our observation shows that pyridine has a good ligand behavior for stabilizing of $Zn(BH_4)_2$ at room or higher temperature. Furthermore, the reducing ability of $Zn(BH_4)_2$ appears almost constant. $[Zn(BH_4)_2(py)]$ appears a suitable reagent for the reduction of a variety of carbonyl compounds such as aldehydes, ketones, α-diketones and acyloins to their corresponding alcohols at room temperature or under reflux conditions. A high regioselectivity has been observed for the 1,2- *vs* 1,4-reduction of α,β-unsaturated carbonyl compounds. Chemoselective reduction of aldehydes over ketones was also achieved successfully. Comparison of the obtained results with $[Zn(BH_4)_2(py)]$ and $Zn(BH_4)_2$ or other reported reagents shows that the reduction reaction with $[Zn(BH_4)_2(py)]$ in most cases was very efficient. Easy work-up procedure as well as the previous advantages makes this new modified tetrahydroborate agent as an attractive practical bench-top reagent and a synthetically useful metal tetrahydroborate complex.

Experimental Section

All products were characterized by a comparison with those of authentic samples (mp or bp) and their IR, ^{1}H-NMR spectral. All yields referred to isolated products. TLC accomplished the purity determination of the substrates, products and reactions monitoring over silica gel PolyGram SILG/UV 254 plates.

Preparation of (Pyridine)(tetrahydroborato)zinc Complex; $[Zn(BH_4)_2(py)]$. An ethereal solution of $Zn(BH_4)_2$ (0.16 M, 250 mL) (1 M = 1 mol dm^{-3}) was prepared from $ZnCl_2$ (5.452 g, 0.04 mol) and $NaBH_4$ (3.177 g, 0.084 mol) according to an available procedure in the literature.[29] Then, pyridine (3.164 g, 0.04 mol) in ether (50 mL) was added dropwise to the ethereal solution of $Zn(BH_4)_2$ and stirred for 30 min. Evaporation of the solvent under vacuum at room temperature gave $[Zn(BH_4)_2(py)]$ as a white powder in a quantitative yield (6.83 g, 98%) which decomposes to dark material at 106-108 °C.

A Typical Procedure for Reduction of Aldehydes to Alcohols with $[Zn(BH_4)_2(py)]$. In a round-bottomed flask (15 mL), equipped with a magnetic stirrer, a solution of *p*-tolualdehyde (0.12 g, 1 mmol) in ether (8 mL) was prepared. The complex reducing agent (0.174 g, 1 mmol) was then added as a solid and the mixture was stirred at room temperature. TLC monitored the progress of the reaction (eluent; CCl_4/Et_2O : 5/2). After completion of the reaction in 42 min, a solution of 5% HCl (7 mL) was added to the reaction mixture and stirred for 30 min. The mixture was extracted with CH_2Cl_2 (3 × 15 mL) and dried over the anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel by eluent of CCl_4/Et_2O : 5/2 affords pure crystals of *p*-methylbenzyl alcohol (0.114 g, 94% yield, Table 1).

A Typical Procedure for Reduction of Ketones to Alcohols with $[Zn(BH_4)_2(py)]$. In a round-bottomed flask (15 mL) equipped with a magnetic stirrer and a condenser, a solution of 1-indanone (0.132 g, 1 mmol) in THF (8 mL) was prepared. The reducing agent (0.35 g, 2 mmol) was then added as a solid and the mixture was heated to gentle reflux with stirring. TLC monitored the progress of the reaction (eluent; CCl_4/Et_2O : 5/2). After completion of the reaction in a 1 h, a solution of 5% HCl (7 mL) was added to the reaction mixture and stirred for 30 min. The mixture was extracted with CH_2Cl_2 (3 × 15 mL) and dried over the anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel by eluent of CCl_4/Et_2O : 5/2 affords pure 1-indanol (0.133 g, 99% yield, Table 2).

A Typical Procedure for Regioselective 1,2-Reduction of α,β-Unsaturated Aldehydes to Their Alcohols with $[Zn(BH_4)_2(py)]$. In a round-bottomed flask (15 mL) equipped with a magnetic stirrer, a solution of cinnamaldehyde (0.132 g, 1 mmol) in ether (8 mL) was prepared. The reducing agent (0.174 g, 1 mmol) was then added as a solid and the mixture was stirred at room temperature. TLC monitored the progress of the reaction (eluent: CCl_4/Et_2O : 5/2). After completion of the reaction in 1.5 h, a solution of 5% HCl (7 mL) was added to the reaction mixture and stirred for 30 min. The mixture was extracted with CH_2Cl_2 (3 × 15 mL) and dried over the anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel by eluent of CCl_4/Et_2O : 5/2 affords pure liquid cinnamyl alcohol (0.129 g, 97% yield, Table 5).

A Typical Procedure for Selective 1,2-Reduction of α,β-Unsaturated Ketones to Their Alcohols with $[Zn(BH_4)_2(py)]$. In a round-bottomed flask (15 mL) equipped with a magnetic stirrer and a condenser, a solution of benzylideneacetone (0.146 g, 1 mmol) in THF (8 mL) was prepared. The reducing agent (0.35 g, 2 mmol) was then added as a solid and the mixture was heated to gentle reflux with stirring. TLC monitored the progress of the reaction (eluent; CCl_4/Et_2O : 5/2). After completion of the reaction in 1 h, a solution of 5% HCl (7 mL) was added to the reaction mixture and stirred for 30 min. The mixture was extracted with CH_2Cl_2 (3 × 15 mL) and dried over the anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel by eluent of CCl_4/Et_2O : 5/2 affords pure 4-phenyl-3-buten-2-ol (0.143 g, 97% yield, Table 5).

A Typical Procedure for the Competitive Reduction of Aldehydes and Ketones with $[Zn(BH_4)_2(py)]$. 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 ether (8 mL) was prepared. The reducing agent (0.174 g, 1 mmol) was then added as a solid and the mixture was stirred at room temperature. TLC monitored the progress of the reaction. After 0.5 h, the reaction is quenched by addition of a solution of 5% HCl (7 mL) and stirred for

30 min. The mixture was extracted with CH_2Cl_2 (3 × 15 mL) and dried over the anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel by eluent of CCl_4/Et_2O : 5/2 affords pure liquid benzyl alcohol as a sole product of reduction (Table 4).

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