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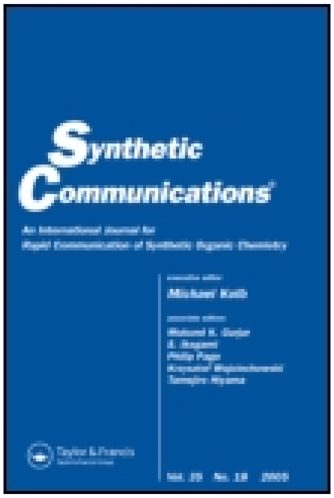

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DICHLOROBIS[1,4-DIAZABICYCLO(2,2,2)OCTANE]-(TETRAHYDROBORATO)ZIRCONIUM, [Zr(BH_4)$_2$$CL_2$(dabco)$_2$] (ZrBDC), A NEW STABLE, EFFICIENT, AND SELECTIVE REDUCING AGENT

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DICHLOROBIS[1,4-DIAZABICYCLO(2,2,2)OCTANE]-(TETRAHYDROBORATO)ZIRCONIUM, [Zr(BH_4)$_2$$Cl_2$(dabco)$_2$] (ZrBDC), A NEW STABLE, EFFICIENT, AND SELECTIVE REDUCING AGENT

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ABSTRACT

High yield preparation of a new stable zirconium borohydride, [Zr(BH_4)$_2$$Cl_2$(dabco)$_2$] is described and its application for the selective and efficient reduction of aldehydes and ketones is presented.

After the discovery of $NaBH_4$, many research groups have put their efforts into preparation of modified borohydride agents in order to decrease the problems encountered with this reagent. Some of the drawbacks of $NaBH_4$ for the reduction of functional groups may be mentioned as follows; poor chemo- and regio-selective reduction, high rate of decomposition in

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solvents like H_2O and CH_3OH, inability to work in aprotic solvents and also a limited number of the functional groups that can be reduced by the reagent.[1]

Transition metal borohydrides are mostly very reactive, volatile, unstable, difficult to handle and as such can not be used in organic synthesis as reducing agents without modification.[2] Ligand–metal borohydride complexes $[L_XM(BH_4)_n]$ form a category of modified borohydride agents that some of them have been used effectively for the reductive transformation of functional groups in organic synthesis.[2–6] The typical examples are; $Cu(BH_4)(PPh_3)_2$,[3] $Cu_2(BH_3CN)_2(PPh_3)_4$,[4] $Zn(BH_4)_2$ dabco,[5] $Zn(BH_4)_2PPh_3$[6] and $Zn(BH_4)_2$.crown ethers.[7]

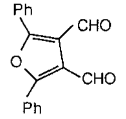
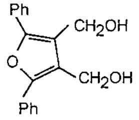
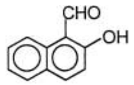
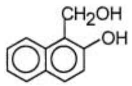
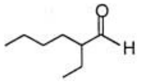
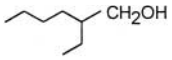
Zirconium borohydride, $Zr(BH_4)_4$, is a highly volatile colorless solid, inflames in air, hydrolyzes rapidly with explosion and not easy to handle.[2,8,9] A practical, easy to handle reducing agent of borohydride bearing zirconium cation is rare. To the best of our knowledge, there are onyl two reagents, $[Cp_2Zr(Cl)BH_4]$[10] and [crosslinked PVP_4-$Zr(BH_4)_4$][11] are reported as hydride tranfering agents for the reduction of a limited number of carbonyl compounds.

We here report the high yield (97%) easy preparation of a new stable ligand-metal zirconium borohydride $[Zr(BH_4)_2Cl_2(dabco)_2]$ (ZrBDC) as a white, stable, non-hygroscopic powder. This compound can be stored at room temperature for months without significant change in its reducing ability. This zirconium borohydride is much more stable than $NaBH_4$ in H_2O, CH_3OH and also in mild aqueous acidic conditions. Chemical formula of the compound has been established by quantitative chemical analysis and also by IR, ^1H NMR and ^{13}C NMR spectroscopy.[12]

The results of the reduction of carbonyl compounds in our study with $[Zr(BH_4)_2Cl_2(dabco)_2]$ (ZrBDC) are summarized in Table 1. High yield reduction of aldehydes and ketones were conducted by this reagent in isopropyl alcohol under reflux conditions. We have observed that functional groups like $-NO_2$, -CN and $-CO_2R$ remained intact during the progress of the reaction by this reagent. The effect of the nature of the substituted groups on the aromatic rings of the carbonyl compounds is quite clear. In comparison with benzaldehyde, electron-withdrawing groups facilitate the reduction reactions and electrons-donating groups retard the rate of the reactions. Selective and high yield reduction of benzaldehydes with different substituted groups was performed smoothly in the presence of this reducing agent. We have shown the selectivity between benzaldehyde derivatives in Table 2.

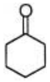
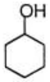
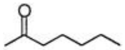
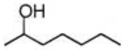
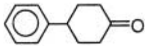
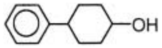
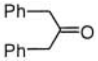
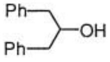
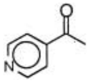
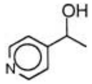
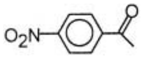
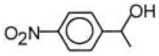
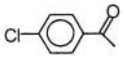
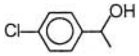
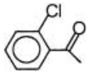
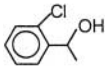
Selective reduction of aldehydes in the presence of ketones is of synthetic value. Therefore, we have presented the ability of the reagent for this kind of reaction. We have observed that ZrBDC reduces aldehydes in

Table 1. Reduction of Carbonyl Functional Groups with (ZrBDC) in Isopropyl Alcohol Under Reflux Conditions

Entry	Substrate(s)	Product[a]	Molar Ratio of Reagent/Subs.	Time (h)	% Yield (Isolated)
1	Benzaldehyde	Benzyl alcohol	0.5	3.5	80
2	*p*-Nitrobenzaldehyde	*p*-Nitrobenzyl alcohol	0.5	1.2	92
3	*m*-Nitrobenzaldehyde	*m*-Nitrobenzyl alcohol	0.5	0.8	96
4	*o*-Nitrobenzaldehyde	*o*-Nitrobenzyl alcohol	0.5	0.5	94
5	*p*-Chlorobenzaldehyde	*p*-Chlorobenzyl alcohol	0.5	2.2	92
6	*p*-Bromobenzaldehyde	*p*-Bromobenzyl alcohol	0.5	2.0	96
7	*p*-Cyanobenzaldehyde	*p*-Cyanobenzyl alcohol	0.5	0.8	93
8	*p*-Methoxybenzaldehyde	*p*-Methoxybenzyl alcohol	0.5	3.0	95
9	*m*-Methylbenzaldehyde	*m*-Methylbenzyl alcohol	0.5	4.5	85
10	Salicylaldehyde	Salicyl alcohol	0.5	3.0	87
11	Furfural	Furfuryl alcohol	0.5	1.5	82
12	4-(Me_2N)-C_6H_4CHO	4-(Me_2N)-$C_6H_4CH_2OH$	0.5	34	16[b]
13			1.0	3.5	97
14			0.5	1.5	91
15			0.5	1.5	83

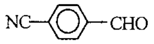
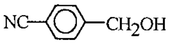
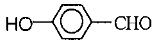
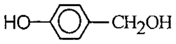
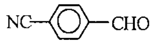
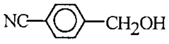
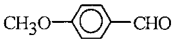
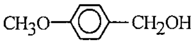
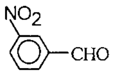
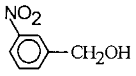
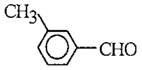
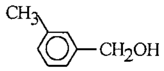
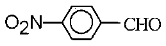
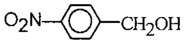
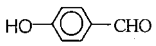
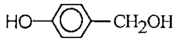
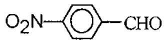
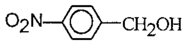
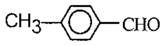
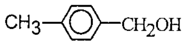
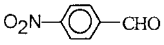
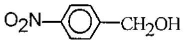
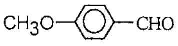
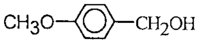
(*continued*)

Table 1. Continued

Entry	Substrate(s)	Product[a]	Molar Ratio of Reagent/Subs.	Time (h)	% Yield (Isolated)
16			0.75	2.8	86
17			0.75	6.0	88
18			0.75	2.5	98
19			0.75	5.0	97
20			0.75	5.0	97
21			0.75	0.8	97
22			0.75	1.5	93
23			0.75	0.8	91

[a]All compounds gave satisfactory spectral analysis; [b]Yield based on NMR analysis.

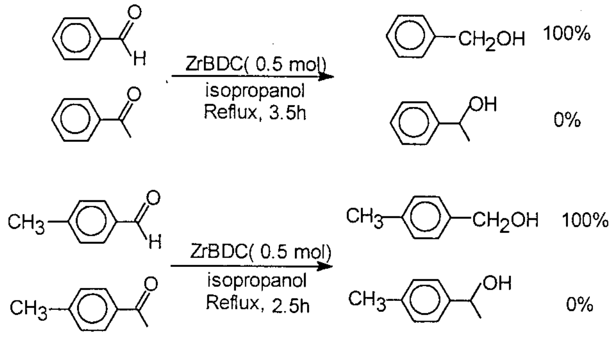
Table 2. Selective Reduction of Benzaldehyde Derivatives with (ZrBDC) in Isopropyl Alcohol Under Reflux Conditions[a]

Entry	Substrate (1, 2)	Product (1, 2)	Time (h)	% Yield[b]
1			1.0	100
				0
2			1.0	100
				12
3			0.8	94
				7
4			1.2	100
				15
5			1.2	100
				20
6			1.2	100
				25

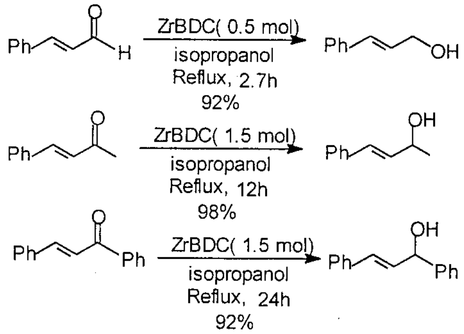
[a]The molar ratio of the reagents/subs.1/subs.2 is 0.5/1.0/1.0; [b]Yields based on NMR analysis.

the presence of ketones with absolute chemoselectivity that has been determined by ^{1}H NMR spectroscopy (Sch. 1).

High yield and selective production of allyl alcohols via 1,2-reduction of α,β-unsaturated carbonyl compounds is an important reaction. Reduction of α,β-unsaturated carbonyl compounds by ZrBDC was performed smoothly and the corresponding allyl alcohols were produced in high yields (Sch. 2).



Scheme 1.



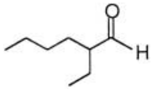
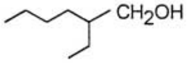
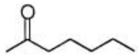
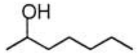
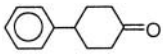
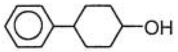
Scheme 2.

Recently, much attention has been paid to the reactions conducted in water in which the vast majority of biochemical processes take place.[13] We have found that ZrBDC is quite stable in aqueous media therefore, we have presented the potential of this reagent in aqueous media for the reduction of carbonyl compounds. Our studies showed that the rate of the reactions in water were faster than those performed in isopropyl alcohol under similar reaction conditions. The yields of the products were more or less similar to that observed for the reductions in isopropyl alcohol (Table 3).

In order to show the advantages and the drawbacks of ZrBDC for the reduction of carbonyl groups, we have compared the results with some of those reported with other modified borohydride reagents in Table 4.

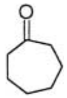
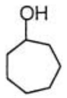
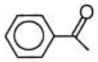
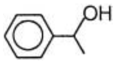
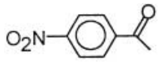
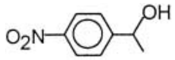
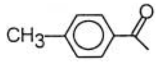
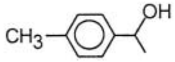
In conclusion, (ZrBDC) as a white powder, unlike its mother compound $Zr(BH_4)_4$, is thermally stable and could be stored for months without appreciable loss of its reducing ability at room temperature.

Table 3. Reduction of Carbonyl Functional Groups with (ZrBDC) in H_2O Under Reflux Conditions

Entry	Substrate	Product[a]	Molar Ratio of Reagent/Subs.	Time (h)	% Yield (Isolated)
1	Benzaldehyde	Benzyl alcohol	0.5	2	79
2	*p*-Nitrobenzaldehyde	*p*-Nitrobenzyl alcohol	0.5	0.8	90
3	*m*-Nitrobenzaldehyde	*m*-Nitrobenzyl alcohol	0.5	1.0	94
4	*o*-Nitrobenzaldehyde	*o*-Nitrobenzyl alcohol	0.5	0.7	97
5	*o*-Chlorobenzaldehyde	*o*-Chlorobenzyl alcohol	0.5	0.5	96
6	*p*-Cyanobenzaldehyde	*p*-Cyanobenzyl alcohol	0.5	0.7	98
7	*p*-Methoxybenzaldehyde	*p*-Methoxybenzyl alcohol	0.5	1.5	91
8	*p*-Methylbenzaldehyde	*p*-Methylbenzyl alcohol	0.5	2.0	88
9	Salicylaldehyde	Salicyl alcohol	0.5	0.8	93
10	Furfural	Furfuryl alcohol	0.5	1.0	87
11	PhCH=CH-CHO	PhCH=CH-CH_2OH	0.5	1.7	90
12			0.5	0.5	85
13			0.75	0.5	85
14			0.75	1.5	94

(*continued*)

Table 3. Continued

Entry	Substrate	Product[a]	Molar Ratio of Reagent/Subs.	Time (h)	% Yield (Isolated)
15			0.75	3.0	87
16			0.75	8.0	90
17			0.75	2.0	96
18			0.75	24	89

[a] All compounds gave satisfactory spectral analysis.

Table 4. Comparison of (ZrBDC) with Other Borohydride Reagents for the Reduction of Aldehydes and Ketones to Their Corresponding Alcohols

		ZrBDC		Other Borohydride Reagnet			
Entry	Substrate(s)	Time (h)	% Yield	Time (h)	% Yield	Time (h)	% Yield
1	Cinammaldehyde	2.7	92	7	87^a	–	49^b
2	*p*-Nitrobenzaldehyde	1.2	92	7	85^a	–	–
3	Cyclohexanone	2.8	86	24	77^c	1	88^d
4	2-Heptanone	6	88	72	35^c	4	84^d
5	Benzaldehyde	3.5	76	24	78^c	4	87^d
6	Ph-CH=CH-CO-CH_3	12	98	0.5	15^e	0.25	0^e

[a] Silica gel supported $Zn(BH_4)_2$;[14] [b] $Cp_2Zr(Cl)BH_4$;[10] [c] $LiBH_3CN$;[15] [d] $NaBH_3CN$;[16] [e] $Zn(BH_4)_2$.[17]

The preparation of the reagent is easy (in 97% yield) and unlike its polymer supported analogue [cross-linked PVP4-$Zr(BH_4)_4$] is quite reproducible by different hands.[18] This reagent has been applied successfully for the reduction of structurally different carbonyl compounds in organic media and water as well. Moreover, the mildness, easy reaction work up, efficiency, selectivity, high reaction yields, lack of requirement of an inert atmosphere make this new stabilized transition-metal borohydride a practical bench top modified zirconium borohydride reagent and a useful addition to borohydride chemistry.

Reduction of imines, enamines, acid chlorides, azides, reductive amination of aldehydes and ketones, and also methylation of amines are under investigation in our laboratories.

EXPERIMENTAL

All yields refer to isolated products. The products were purified by column chromatography and the purity determination of the products were accomplished by GLC on a Shimadzu model GC-8A instrument or by TLC on Silica-gel polygram SIL G/UV254 plates, mass spectra were run on a Shimadzu GC MS-QP 1000EX at 20 eV. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. The NMR spectra were recorded on a Bruker Avance DPX 250 MHz instrument.

Reduction of cinnamaldehyde, a typical procedure for the reduction of α,β-unsaturated carbonyl compounds in *iso*-PrOH or in H_2O: To a solution of cinnamaldehyde (2.0 mmol) in *iso*-PrOH (5–10 mL), the reducing agent (1.0 mmol) was added and refluxed with stirring (2.7 h). The mixture was cooled to room temperature, silica gel (2 g) was added and the solvent was evaporated. The resulting solid was applied on a silica gel column and eluted with petroleum benzene (60–80°C)/Et_2O (2/1). Evaporation of the solvent afforded pure cinnamyl alcohol in 92% yield (Sch. 2). In the case of the reaction in H_2O, after 1.7 h, the reaction was quenched by the addition of 10% HCl (aq.) and extracted with EtOAc or Et_2O (3×30 mL). The organic layer was washed with H_2O, brine, dired over anhydrous $MgSO_4$, and was evaporated to afford cinnamyl alcohol in 90% yield (Table 3).

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12. **Preparation and identification of $[Zr(BH_4)_2Cl_2(dabco)_2]$ (ZrBDC):** A slurry was produced by the addition of an ethereal solution of $LiBH_4$ (0.344 mol) to anhydrous $ZrCl_4$ (0.069 mol) under inert atmosphere and the resulting mixture[19] was stirred for 12 h. Then an ethereal solution of dabco (0.138 mol) was added dropwise to the slurry and stirring was continued for 10 h to produce a dark brown solid. The resulting solid was filtered and washed with Et_2O and dried under vacuum to afford a white powder. For further purification, the resulting powder was washed with dry THF and dry Et_2O respectively and was left under vacuum overnight. ZrBDC was isolated as a white, stable, non-hygroscopic powder in 97% yield. This reducing agent could be stored at room temperature for months without significant change in its reducing ability. The chemical formula of the reagent was established by IR and NMR studies.[9] IR (KBr, dabco species), ν (cm^{-1}): 2974s, 2963s, 2897s, 1623m, 1458s, 1324s, 1056s, 993s, 846s, 702b, and for $BH_4{}^-$ species, ν (cm^{-1}): 2383s, 2373s, 2306s, 2268s, 1155s. ^1H NMR ($CDCl_3$, 250 MHz): δ (ppm) 1.42 (broad band, 8H, two BH_4^-), that its coupling constant and pattern are similar to $Zr(BH_4)_4$,[9b] 2.9 ($AA'BB'$ pattern,[20] 24H of CH_2 groups). ^{13}C NMR ($CDCl_3$, 63 MHz): δ (ppm) 51.7, 52.1 (two different CH_2 groups). Determination of BH_4^- content was conducted by iodometric titration method,[21] quantitative measurement of chloride content was proceeded by potentiometric titration technique,[22] and quantitative

measurement of Zr was conducted by UV/Vis. spectrophotometric method.[23]

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