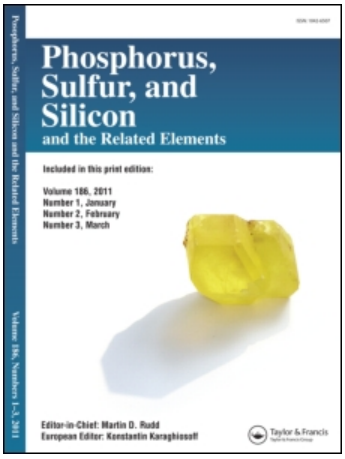

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MODIFIED BOROHYDRIDE AGENTS, BIS (TRIPHENYLPHOSPHINE) (TETRA-HYDROBORATO)ZINC COMPLEX [$Zn(BH_{42}(PPh_3)_2$] AND (TRIPHENYLPHOSPHINE) (TETRAHYDROBORATO)ZINC COMPLEX [$Zn(BH_4)_2(PPh_3)$]. NEW LIGAND METAL BOROHYDRIDES AS STABLE, EFFICIENT, AND VERSATILE REDUCING AGENTS

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MODIFIED BOROHYDRIDE AGENTS, BIS(TRIPHENYLPHOSPHINE) (TETRA-HYDROBORATO)ZINC COMPLEX $[Zn(BH_4)_2(PPh_3)_2]$ AND (TRIPHENYLPHOSPHINE) (TETRAHYDROBORATO)ZINC COMPLEX $[Zn(BH_4)_2(PPh_3)]$. NEW LIGAND METAL BOROHYDRIDES AS STABLE, EFFICIENT, AND VERSATILE REDUCING AGENTS

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Bis(triphenylphosphine)(tetrahydroborato)zinc and (triphenylphosphine)(tetrahydroborato) zinc complexes have been used for the efficient reductions of varieties of organic compounds in THF or under solvent free conditions. Selective reduction of aldehydes, ketones, α,β-unsaturated carbonyl compounds, and acyl chlorides to their corresponding alcohols and aryl, alkyl, aroyl, and sulfonyl azides to their corresponding amines and amides are described. Bis(triphenylphosphine)(tetrahydroboratro)zinc complex shows promising shelf stability and is much more stable than its mono triphenylphosphine analogue. The reducing ability of the two complexes is more or less the same.

Keywords: Borohydride; Modified Zinc Borohydride; Reducing Agent; Reduction; Tetrahydroborate; Carbonyl Compounds; Azides

* Correspondence Author.

INTRODUCTION

Reduction is one of the most fundamental chapters in chemistry. After the discovery of sodium borohydride in 1943 a revolutionary change in the methodology of reduction of various functional groups has occurred. Since then, many research groups have put their efforts to prepare modified borohydride agents in order to bring about more chemo-, regio- and stereoselective reductions, increasing the rate and versatility of the reaction conditions in comparison with the mother compound; $NaBH_4$. Recently, we have extensively reviewed modified borohydride agents and their applications in organic synthesis.[1] One of the encountered modifications is the preparation of ligand-metal borohydrides $[LXM(BH_4)_n]$.[2–7] The use of the ligand (Lx) can induce considerable relative stability and sometimes variation in the reactivity of the B-H bond[3,4] in comparision with the parent metal borohydride. Therefore, such modified tetrahydroborate complexes can constitute a class of reducing agents which could be useful for performing selective reductions of organic compounds. There are, however, few reports in the literature on the use of such compounds as reducing agents in organic synthesis. Bis(triphenylphosphine)(tetrahydroborato)copper(I), $[Cu(BH_4)(Ph_3P)_2]$ is an example in which the BH_4^- moiety is deactivated to the extent that it only reduces acyl chlorides to aldehydes, whereas, $NaBH_4$ reduces them to their alcohols.[4,7] The other examples are μ-bis(cyanotrihydroborato)-tetrakis(triphenylphosphine) dicopper (I), $[Cu_2(BH_3CN)_2\ (Ph_3P)_4]$[6], chlorobis(cyclopentadienyl)(tetrahydroborato) zirconium(IV) $[Zr(BH_4)(CP)_2Cl]$[5] and polymer-supported $AlCl_2(BH_4)$[8].

Zinc tetrahydroborate, $[Zn(BH_4)_2]$ is a potential modified borohydride reducing agent, which has attracted attention in recent years.[9] This compound is unstable at room temperature and for satisfactory results, its freshly prepared ethereal solution should be used. Silica gel supported zinc tetrahydroborate also suffers from the same drawback.[10,11] $Zn(BH_4)_2$ is neutral and in contact with water hydrolyzes vigorously.[3] Combination systems like Zn(BH4)2/N,N,N',N'-tetramethylethylenediamine, $Zn(BH_4)_2$/ Me_3SiCl, and $Zn(BH_4)_2/(CF_3Co)_2O$/ DME have also been used for various reduction purposes.[12] Supported polyvinylpyridinezinc tetrahydroborate is reported as a stable polymeric transition-metal borohydride. Poly[(1,4-η)pyrazine][tetrahydroborato]zinc, $[Zn(BH_4)_2(PYZ)]_n$ is also reported.[14] This polymeric reagent is stable to heat and light, but in con-

tact with water explodes violently. Recently, we have reported a new metal-ligand borohydride; (1,4-diazabicyclo[2.2.2]octane)(tetrahydroborato)zinc complex, $[Zn(BH_4)_2(dabco)]$, as a stable white fluffy powder whose reducing activity is more or less the same as $Zn(BH_4)_2$[15,16]. The effect of triphenylphosphine ligand upon the stability and reactivity of $CuBH_4$ and $Cu_2(BH_3CN)_2]$ are reported.[4,6,7]

The influence of the phosphorus ligands on the behavior of $Zn(BH_4)_2$ with respect to its stability, solubility, reactivity, and selectivity for the reduction of organic compounds has not been studied yet. Therefore, we have paid attention to the preparation of $Zn(BH_4)_2(Ph_3P)]$ and $[Zn(BH_4)_2(Ph_3P)_2]$ as new modified $Zn(BH_4)_2$ and studied their bench-top stability, solubility in organic solvents, reactivity, and their reducing abilities in organic syntheses. We have also discussed the limitations and advantages of the reagents in comparison with each other and with some other metal-ligand borohydrides.

RESULTS AND DISCUSSION

A. Reductions with $[Zn(BH_4)_2(Ph_3P)_2]$

1. Preparation of $[Zn(BH_4)_2(Ph_3P)_2]$

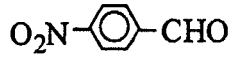
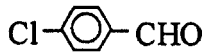
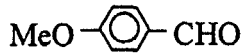
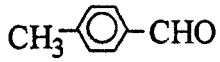
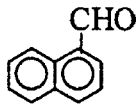
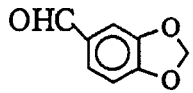
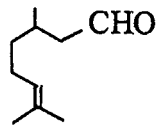
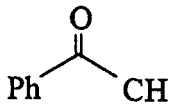
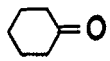
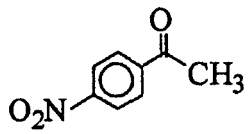
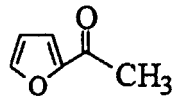
Bis(tetrahyhydroborato)bis(triphenylphosphine)zinc(II), $[Zn(BH_4)_2(Ph_3P)_2]$ was prepared by the addition of a two molar ethereal solution of triphenylphosphine to a one molar ethereal solution of $Zn(BH_4)_2$.[17] The formation of the complex was fast and the reagent was formed in good yield (84%) as a white fine powder. This compound reacted vigorously with acids and slowly with water. The zinc percentage in the complex was determined by atomic absorption and the amount of BH_4^- has been determined by iodometric titration method.[18]. This reagent is soluble in THF, CH_3CN, CH_2Cl_2 and $CHCl_3$. We have performed our reactions in THF which is safer than chlorinated solvents and shows a reasonable boiling point when it is required. The shelf-top stability of the reagent has been determined by measuring the volume of the hydrogen gas liberated from the reagent at different time intervals for the portions of 0.05 g of the compound and also by the iodometric titration of the reagent. The results show that the freshly prepared compound liberates hydrogen gas slowly for the first 20 days and reaches a stable state which contains

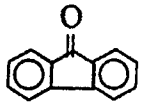
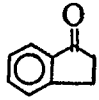
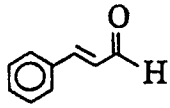
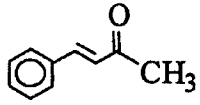
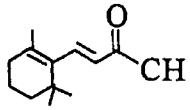
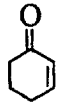
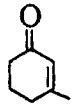
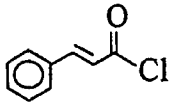
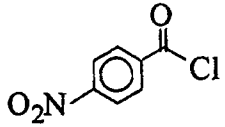
>85% of its original active hydride and could be stored for weeks without further losing its activity.

2. Reduction of Aldehydes, Ketones and Acyl Chlorides

Reductive transformation of carbonyl compounds to their corresponding alcohols is of importance in organic synthesis. $[Zn(BH_4)_2(Ph_3P)_2]$ reduces aldehydes to their corresponding alcohols very fast in THF at room temperature with high yields (80–100%) (Table I). Ketones are usually reduced with slower rates than aldehydes. This is also observed with this reagent and it reduces ketones usually under reflux conditions with longer reaction times in high yields (85-100%) (Table I). We have also studied the reaction of acyl chlorides with $[Zn(BH_4)_2(Ph_3P)_2]$ in THF at room temperature. The reaction was performed in a short reaction time and produced the corresponding alcohols in high yields (Table I). Attempts for the direct reduction of acyl chlorides to their corresponding aldehydes were not successful. In order to show the abilities and weaknesses of this reagent for the reduction of carbonyl compounds we have compared our results with the other reported zinc modified borohydride agents in Table II. The results show that $[Zn(BH_4)_2(Ph_3P)_2]$ is more reactive than the reagents presented in Table II. e.g, $Zn(BH_4)_2$ is not able to reduce acetophenone,[9] $[XP4\text{-}Zn(BH_4)_2]$[8,13] reduces this compound in <5% yield after 15 h and $[PYZ\text{-}Zn(BH_4)_n]$[14] reduces acetophenone in 85% after 30 h, whereas the presented reagent reduces the compound with 98% yield in 0.5 h. This is the reflection of the attachment of phosphorus ligand to $Zn(BH_4)_2$. Allyl alcohols are important synthetic precursors. Reductive transformation of the corresponding carbonyl compounds is an easy way to obtain the alcohols. Reduction of α,β-unsaturated carbonyl compounds with sodium borohydride is a highly solvent dependent reaction and generally does not result in useful regioselectivity.[19,20] Therefore, developed systems have been introduced for selective 1,2-reductions of α,β-unsaturated aldehydes and ketones.[2,19,21–24] Selective 1,2-reduction is usually achieved using modified hydride reagents, which are formed by the replacement of hydride with sterically bulky substitutions or electron-withdrawing groups in order to discriminate between the structural or electron environments of the carbonyl groups.[2,19,21,23,25,26]

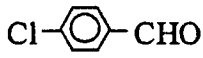
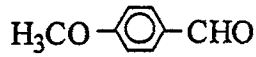
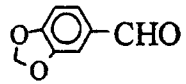
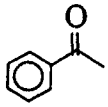
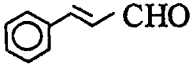
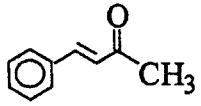
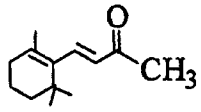
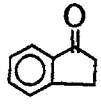
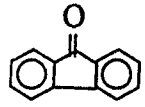
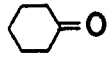
TABLE I Reduction of Aldehydes, Ketones, and Carboxylic Acid Chlorides to Their Corresponding Alcohols with $[Zn(BH_4)_2(Ph_3P)_2]$ in THF at Room Temperature or Under Reflux Conditions

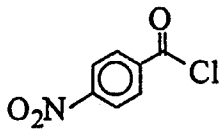
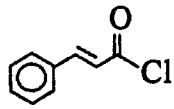
Entry	*Substrate*	*Red/Subs*	*Yield%,(h)*	*Mp or bp (°C)*
1		1	80(-)[a]	92–94
2		1	88(-)[a]	70–72
3		1	89(-.17)	23–25
4		1	87(-)[a,b]	59–61
5		1.5	100(-)[a]	60–62
6		1.5	100(-)[a]	53–55
7		1	100(-)[a]	-
8		2	98(0.5)[b]	204/745 mmHg
9		1	95(1)[b,c]	161
10		2	100(0.17)[b]	-
11		1	92(1)[b]	-

Entry	*Substrate*	*Red/Subs*	*Yield%,(h)*	*Mp or bp (°C)*
12		2	85(0.33)	153–154
13		1	50(2)	50–54
14		1	90(0.25)[b]	33–35
15		2	90(0.5)[b]	144/21 mmHg
16		1	80(0.08)[c]	-
17		1	90(-)[a,c]	-
18		1	80(2.25)[c]	-
19		1.5	90(0.25)	33–35
20		1.5	98(-)[a]	92–94

a) Immediate reaction.
b) Under reflux.
c) C.G. yield.

TABLE II Comparison of Reductions of Some Carbonyl Compounds and Carboxylic Acid Chlorides to Their Corresponding Alcohols with $[Zn(BH_4)_2(Ph_3P)_2]$ (I), $[Zn(BH_4)_2(dabco)]$ (II), $[Zn(BH_4)_2]$-XP4[a] (III), $Zn(BH_4)_2$, (IV), $[Zn(BH_4)_2(PYZ)]_n$ (V)

Entry	*Substrate*	*(I) Yield%, (h)*	*(II)[15] Yield%, (h)*	*(III)[8,13] Yield%, (h)*	*(IV)[9] Yield%, (h)*	*(V)[14] Yield%, (h)*
1		88(-)[b]	97(0.4)	95(5)	100(-)	95(3)
2		89(0.17)	96(12)	75(12)	-	-
3		100(-)[b]	96(6.5)	65(8)	-	-
4		98(0.5)	95(5.4)	<5(15)	0(-)	85(30)
5		92(0.25)	94(4.5)	90(9)	100(0.5)	93(6)
6		90(0.5)	92(2.3)	10(15)	15(30)	95(8)
7		80(0.08)	95(3)	10(15)	-	-
8		50(2)	95(6)	-	-	-
9		85(0.33)	95(2.3)	-	-	-
10		95(1)		10(24)		85(18)

Entry	*Substrate*	*(I)* *Yield%, (h)*	*(II)*[15] *Yield%, (h)*	*(III)*[8,13] *Yield%, (h)*	*(IV)*[9] *Yield%, (h)*	*(V)*[14] *Yield%, (h)*
11		98(-)[b]	88(20)	70(10)	93(0.25)	98(6)
12		90(0.25)	91(0.8)	85(12)	86(0.5)	93(3.5)

a) Cross-linked poly(4-vinylpyridine) supported zinc tetrahydroborate.
b) Immediate reaction.

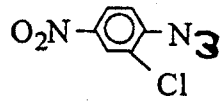
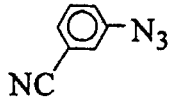
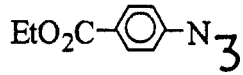
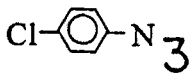
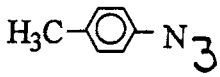
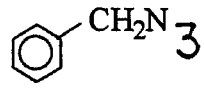
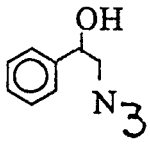
Reduction of α,β-unsaturated aldehydes and ketones proceeded well with $[Zn(BH_4)_2(Ph_3P)_2]$ in THF under reflux conditions (< 1 min-2.25 h) with high yields (80–90%)(Table I). Reduction of cyclohexenone and 3-methylcyclopentenone with hydride transfer agents afforded a mixture of alcohols via 1,2- and 1,4-hydride addition reactions. Reduction of these compounds were studied with $[Zn(BH_4)_2(Ph_3P)_2]$ in THF at room temperature. The reactions proceeded by 1,2-addition and the products were isolated in 90% and 80% respectively (Table I). We have compared our results with the nitrogen ligand $Zn(BH4)_2$ complexes in Table II. The comparisons show that $[Zn(BH_4)_2(Ph_3P)_2]$ is more reactive than $Zn(BH_4)_2$ and the closely related nitrogen ligand analogues. e.g. $Zn(BH_4)_2$[9] reduces benzalacetone via 1,2-reduction to produce the corresponding alcohol in 15% yield after 30 h. $[Zn(BH_4)_2$- XP4][8,13] effected the same reduction after 15h in only 10% yield and $[Zn(BH_4)_2$- $PYZ]_n$[14] produced the allylic alcohol in 95% yield in 8h with 4 molar ratios of the reducing agent. $[Zn(BH_4)_2(Ph_3P)_2]$ effected this reduction in 0.5 h with 90% yield with 2 molar ratios of the reducing agent. This enhancement in the rate and the efficiency of the reaction is also attributed to the phosphorus ligands.

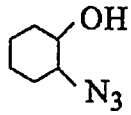
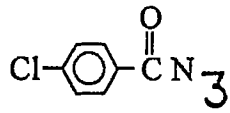
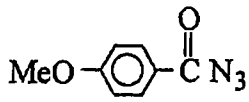
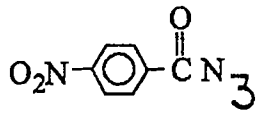
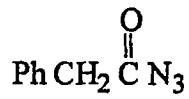
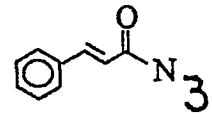
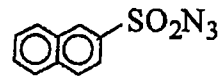
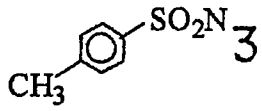
3. Reductions of Aryl-, Alkyl-, Aroyl-, and Arylsulfonyl Azides

The reduction of azides to amines constitutes a synthetically useful process. We have observed that $[Zn(BH_4)_2(Ph_3P)_2]$ in THF reduces alkyl and aryl azides to the corresponding amines in high reaction rates (<lmin-0.25h) and in excellent yields (Table III). Aroyl and arylsulfonyl

azides were also converted to their corresponding amides in good yields (80–95%) with short reaction times (Table III). Phenylacetyl azide was not reduced with this reagent under the same reaction conditions and the starting material was isolated intact after 24 h. 4-Nitrobenzoyl azide reduction gave its corresponding alcohol and amide in 50% yields respectively. Generally, $[Zn(BH_4)_2(Ph_3P)_2]$ is more efficient than the other closely reported analogues (Table IV) for this purpose.

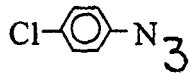
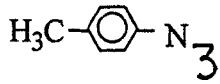
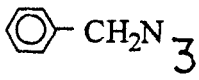
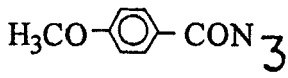
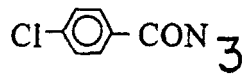
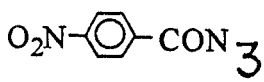
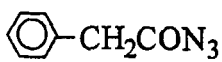
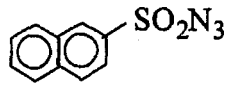
TABLE III Reductions of Alkyl and Aryl Azides to Their Corresponding Amines and Aroyl and Suylfonyl Azides to Their Correpsonding Amides with $[Zn(BH_4)_2(PH_3P)_2$ in THF

Entry	*Substrate*	*Yield%,(h)*	*Mp or bp (°C)*
1		93(-)[a]	107–109
2		91(0.25)	51–53
3		90(0.08)	88–90
4		85(0.3)	67–71
5		89(0.16)	41–46
6		100(0.25)[b]	-
7		N_3 100(-)[ab]	-

Entry	*Substrate*	*Yield%,(h)*	*Mp or bp (°C)*
8		100(-)[ab]	-
9		95(1.25)[c]	179
10		90(2)[c]	166–1168
11		50(-)[a,c] 50(-)[a,d]	92–94201
12		-	-
13		88(1)	-
14		93(0.17)[c]	
15		85(0.5)	-

a) Immediate reaction.
b) Under reflux.
c) Molar ratio of reducing agent/substrate: 2.
d) Alcohol is formed.

TABLE IV Comparison of the Results of the Reductive Conversion of Azides by $[Zn(BH_4)_2(Ph_3P)_2]$ (I), with $[Zn(BH_4)_2(dabco)]$ (II), $[Zn(BH_4)_2]$ (III), and $[Zn(BH_4)_2$-XP4] (IV)

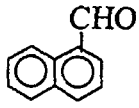
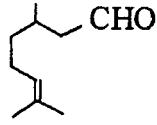
Entry	*Substrate*	*(I) Yield%,(h)*	*(II)*[15] *Yield%,(h)*	*(III)*[9] *Yield%,(h)*	*(IV)*[8,13] *Yield%,(h)*
1		85(0.3) amine	92(12)	92(3)	85(7.5)
2		89(0.16) amine	95(12)	-	70(14)
3		100(0.25) amine	100(11)	65(8)	64(18)
4		90(2) amide	97(48) amide	92(6) amide	-
5		95(1.25) amide	93(24) amide	94(5.5) alcohol	-
6		50(-)[c] alcohol 50 amide	88(3) amide	95(3.5) alcohol	-
7		N.R.	98(0.75) amide	85(3) amide	-
8		93(0.17)	-	90(4)	-

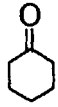
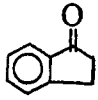
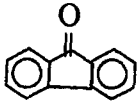
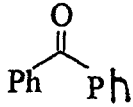
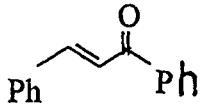
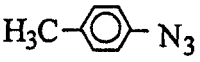
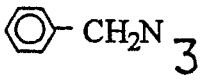
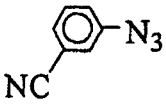
4. Solvent-Free Reduction of Some Functional Groups

Solid state reactions have found interests in recent years in organic chemistry.[27] The solid state reduction of ketones has also been achieved by mixing with sodium borohydride and storing the mixture in a dry box for five days. The major disadvantage in the heterogeneous reaction with $NaBH_4$ is that solvent reduces the reaction rate while in the solid state reactions time period is too long (5 days) for it to be of any practical utility.[28] Microwave assisted reductions of aldehydes and ketones with $NaBH_4$-Al_2O_3 in the absence of solvents has been reported very recently.[29] In this report it has been shown that reduction of benzophenone with $NaBH_4$-Al_2O_3 in an oil bath at 130°C with 5 molar ratios of the reagent stopped at 40% conversion even after 4h. The same reduction under microwave radiation requires 5 molar ratios of $NaBH_4$-Al_2O_3 to produce diphenylcarbinol in 92% yield.

We have studied the reducing ability of $[Zn(BH_4)_2(Ph_3P)_2]$ under neat conditions in the absence of microwave and ultrasound radiations. In most of the reactions in our studies only one molar ratio of the reagent was required. The reactions were carried out at room temperature at 30°C, and 60°C. The condition of the reaction was dependent upon the structure of the substrates. The rates of the reactions were also dependent upon the structure of the compounds and the reactions proceeded from immediate to 5h. The yields of the products were excellent (Table V). Reaction was also chemo- and regioselective. α,β-Unsaturated carbonyl compounds were reduced via a 1,2- reduction and produced the corresponding allyl alcohols in almost quantitative yields (Table V). In order to show the utility of the solventless method, we have compared the results with those reported in solution (Table VI).

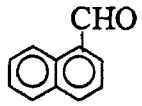
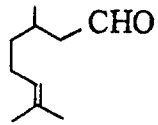
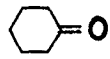
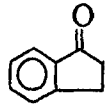
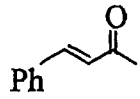
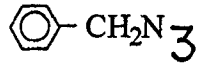
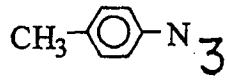
TABLE V Solvent- Free Reduction of Some Carbonyl Compounds to Their Corresponding Alcohols and Some Azides to Their Amines with $[Zn(BH_4)_2(Ph_3P)_2]$

Entry	*Substrate*	*Molar ratio*	*Temp (°C)*	*Yield%, (h)*	*Mp or bp (°C)*
1		1	60	98(0.3)	60–62
2		1	rt	98(-)[a,b]	-

Entry	*Substrate*	*Molar ratio*	*Temp (°C)*	*Yield%, (h)*	*Mp or bp (°C)*
3		1	rt	100(-)[a,b]	161
4			60	90(2.5)	50–54
5		2	60	90(4)	153–154
6		1	60	90(5)	65–67
7		1	60	100(0.16)	144/21 mmHg
8		1	rt	98(-)[a,b,c]	41–46
9		1	60	100(2)[c]	-
10		1	30	92(-)[a,c]	51–53

a) Immediate reaction.
b) G.C. Yield.
c) In the presence of silica gel 1:1 in order to control the vigorous reaction.

TABLE VI Comparison of the Results of Solvent-Free and in Solution Reductions of Carbonyl Compounds and Azides to Their Corresponding Alcohols or Amines with $[Zn(BH_4)_2(Ph_3P)_2]$

Entry	*Substrate*	*Solvent Free*[a]		*In Solution*	
		Molar ratio	*Yield%,(h)*	*Molar ratio*	*Yield%,(h)*
1		1	98(0.3)	1.5	100(-)[a]
2		1	90(-)[a]	1	100(-)[a]
3		1	100(-)[a]	1	95(1)
4		1	90(2.5)	2	50(2)
5		1	100(0.16)	2	90(0.5)
6		1	100(2)	1	100(0.25)
7		1	98(-)[a]	1	89(0.16)

a) Immediate reaction.

B. Reductions with $[Zn(BH_4)_2(Ph_3P)]$

1. Preparation of $[Zn(BH_4)_2(Ph_3P)]$

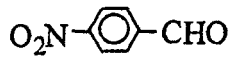
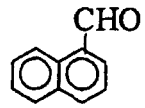
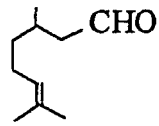
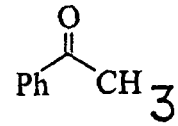
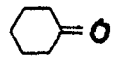
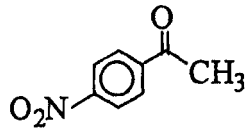
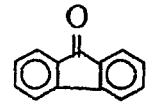
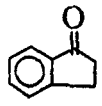
(Tetrahydroborato)(triphenylphosphine)zinc (II) was prepared in two steps. First, by the addition of one molar solution of Ph_3P in dry Et_2O to a one molar solution of anhydrous $ZnCl_2$ in the same solvent. The resulting white precipitate of $[ZnCl_2(Ph_3P)]$ was dissolved in dry THF and more than two equimolar amounts of $NaBH_4$ were added to the solution. After 12h stirring, the mixture was filtered to remove NaCl and unreacted $NaBH_4$. Evaporation of the solvent afforded a white precipitate of $[Zn(BH_4)_2(Ph_3P)]$ with a total yield of 70%. This compound reacts vigorously with acids and slowly with water. After few days, the color of the reagent changed to a pale gray with loosing its reducing ability. The measurement of the amount of the gas generated at different time intervals by this compound and also iodometric titration of BH_4^- content of the compound indicate appreciable decomposition of the reagent at room temperature. This compound lost ~50% of its active hydride within 20 days; therefore, it is less stable than $[Zn(BH_4)_2\ (Ph_3P)_2]$. Purification of the compound for the elemental analysis encounters difficulties. Zn^{2+} and BH_4^- contents of the freshly prepared reagent were determined by atomic absorption technique and iodometric titration method[18]. The results were consistent with the proposed structure within the experimental error.

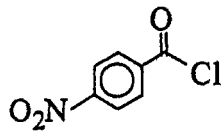
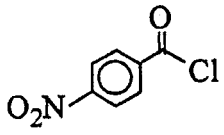
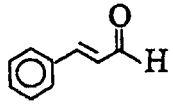
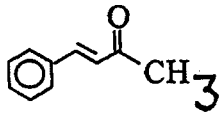
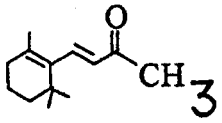
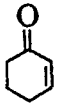
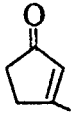
2. Reduction of Aldehydes, Ketones, and Acyl Chlorides

Aldehydes and ketones in THE were reduced by $[Zn(BH_4)_2(Ph_3P)]$ with high yields (75-100%)(Table VII). The results indicated that ketones were reduced with slower rates than aldehydes. $[Zn(BH_4)_2(Ph_3P)]$ reduced acyl chlorides to the corresponding alcohols in THF at room temperature in excellent yields (95–100%)(Table VII). Our efforts for the reduction of acyl chlorides to their corresponding aldehydes in varieties of solvents and with different molar ratios of the reducing agent were not successful. Reductive transformation of α,β-unsaturated aldehydes and ketones to their corresponding allyl alcohols was also achieved by $[Zn(BH_4)_2(Ph_3P)]$ in THF under reflux conditions within 0.17–2.5 h in high yields (85–100%) (Table VII). High yields of 1,2 reduction of cyclohexenone and 3-methylcyclopentenone (80–85%) and high chemo- and regioselectivity of the reagent for this type of reduction were obtained (Table VII). The comparison of the results showed that the rates of the reactions were usually faster for $[Zn(BH_4)_2(Ph_3P)_2]$ reduction than $[Zn(BH_4)_2(Ph_3P)]$ and

the yields of the products were more or less the same. The results are compared with other related reagents in Table VIII.

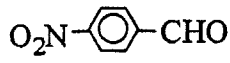
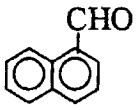
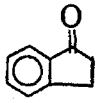
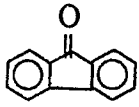
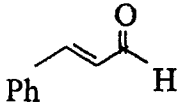
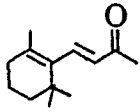
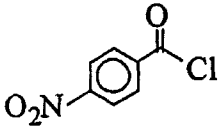
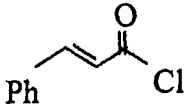
TABLE VII Reduction of Aldehydes, Ketones, and Carboxylic Acid Chlorides to Their Corresponding Alcohols with $[Zn(BH_4)_2(Ph_3P)]$ in THF

Entry	*Substrate*	*Molar ratio*	*Temp(°C)*	*Yield%,(h)*	*Mp or bp (°C)*
1		1.2	rt	95(0.25)[a]	92–94
2		2	Δ	90(0.5)[b]	60–62
3		2	Δ	95(0.17)[c]	-
4		2	Δ	75(1.25)[b]	204/745 mmHg
5		2	Δ	95(1)[b,c]	161
6		2	Δ	90(1)[b]	-
7		2	Δ	88(0.5)[b]	153–154
8		2	Δ	NR(20)	50–54

Entry	*Substrate*	*Molar ratio*	*Temp(°C)*	*Yield%,(h)*	*Mp or bp (°C)*
9		1	rt	95(-)[c]	33–35
10		1	rt	100(-)[c]	92–94
11		1.5	Δ	100(0.4)[b]	33–35
12		2	Δ	87(2.5)[b]	144/21 mmHg
13		2	Δ	100(1.3)[b]	-
14		1	rt	85(0.17)[a,c]	-
15		1	rt	80(12)[a,c]	-

a) Reaction proceeded at room temperature.
b) Reaction proceeded under reflux conditions.
c) G.C. yield.

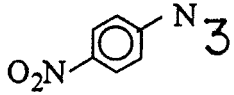
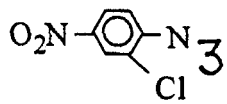
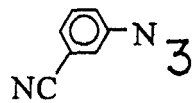
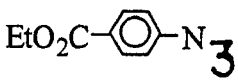
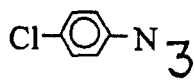
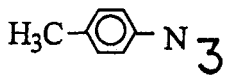
TABLE VIII Comparison of the Results of Reduction of Carbonyl Compounds and Carboxylic Acid Chlorides to Their Corresponding Alcohols with $[Zn(BH_4)_2(Ph_3P)]$ (I), $[Zn(BH_4)_2(Ph_3P)_2)]$(II), $[Zn(BH_4)_2(dabco)]$(III), and $Zn(BH_4)_2$ (IV)

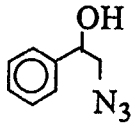
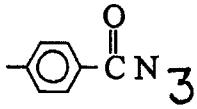
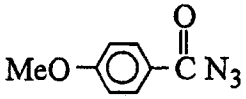
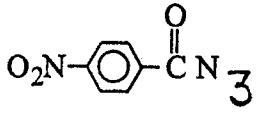
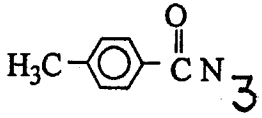
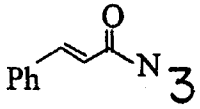
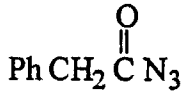
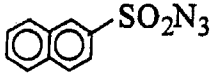
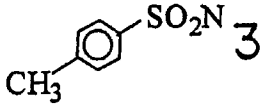
Entry	*Substrate*	*(I) Yield%, (h)*	*(II) Yield%, (h)*	*(III)*[15] *Yield%, (h)*	*(IV)*[9] *Yield%, (h)*
1		95(0.25)	80(-)[a]	-	-
2		90(0.5)	100(-)-a-	-	-
3		75(1.25)	98(0.5)	92(5.4)	-
4		95(1)	95(1)	-	-
5		0(20)	50(2)	95(6)	-
6		88(0.5)	85(0.33)	95(2.3)	-
7		100(0.4)	90(0.25)	94(4.5)	100(0.5)
8		100(1.3)	80(0.08)	95(3)	-
9		100(-)	98(-)	88(20)	93(0.25)
10		95(-)	90(0.25)	90(0.8)	86(0.5)

3. Reduction of Aryl-, Alkyl-, Aroyl-, and Aryl Sulfonyl Azides

Reduction of alkyl, aryl, aroyl and arylsulfonyl azides proceeded well and the corresponding amines and amides were obtained in excellent yields in THF with $[Zn(BH_4)_2(Ph_3P)]$ (Table IX). Phenylacetyl azide was resistant towards reduction and after 24 h stirring with this reagent in THF the starting material was isolated intact. 4-Nitrobenzoyl azide gave the corresponding alcohol in 35% and the amide in 65% yields respectively. We have compared the results with other modified zinc borohydrides in Table X which indicates that $[Zn(BH_4)_2(Ph_3P)]$ is a more efficient reagent than its related nitrogen ligand analogues and $Zn(BH_4)_2$ for this purpose but is less effective than $[Zn(BH_4)_2(Ph_3P)_2]$ for the above mentioned reactions (Table X).

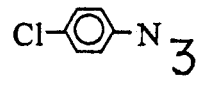
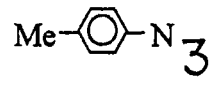
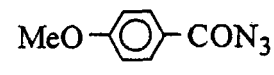
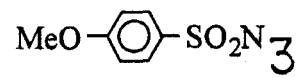
TABLE IX Reduction of Aldehydes, Ketones, and Carboxylic Acid Chlorides to Their Corresponding Alcohols with $[Zn(BH_4)_2(Ph_3P)]$ in THF

Entry	*Substrate*	*Molar ratio*	*Yield%,(h)*	*Mp or bp (°C)*
1		1	90(-)[a]	148.5–149.5
2		2	100(1)[b]	107–109
3		1.5	93(1)[b]	51–53
4		2	96(1)[b]	88–90
5		2	94(1)[c]	67–71
6		2	92(1)[b]	41–46
7	$PhCH_2N_3$	2	100(3)[c,d]	-

Entry	*Substrate*	*Molar ratio*	*Yield%,(h)*	*Mp or bp (°C)*
8		2	100(1)[c,d]	-
9		2	99(2.5)[b]	179
10		2	85(0.16)[c]	166–168
11		2	65(0.25)[b]	201
12		2	66(2)[b]	-
13		1	85(1)	-
14		N.R	-	-
15		2	86(1.5)	-
16		1	76(2.25)	-

a) Immediate reaction.
b) Reaction proceeded at room temperature.
c) Reaction proceeded under reflux conditions.
d) G.C. yield.

TABLE X Comparison of the Results of Some Reductive Transformation of Azides to Their Amines and Aroyl and Sulfonyl Azides to Their Amides with $[Zn(BH_4)_2(Ph_3P)]$ (I), $[Zn(BH_4)_2(Ph_3P)_2)]$(II), $[Zn(BH_4)_2(dabco)]$(III), and $Zn(BH_4)_2$ (IV)

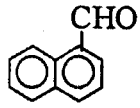
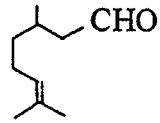
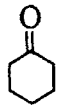
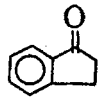
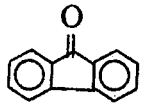
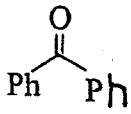
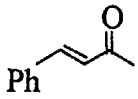
Entry	*Substrate*	*(I) Yield%, (h)*	*(II) Yield%, (h)*	*(III)[15] Yield%, (h)*	*(IV)[9] Yield%, (h)*
1		94(1)	85(0.3)	92(12)	92(3)
2.		92(1)	89(0.16)	92(2)	-
3	$PhCH_2N_3$	100(3)	100(0.25)	100(11)	65(8)
4		85(0.16)	90(2)	97(48)	92(6)
5		76(2.25)	85(0.5)	-	95(3.5)

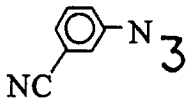
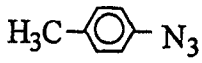
4. Solvent-Free Reductions of Some Functional Groups

$[Zn(BH_4)_2(Ph_3P)]$ has also proved to be an effective reagent for the reduction of various carbonyl compounds and azides in the absence of solvent. Reduction of aldehydes occurred immediately with excellent yields in the presence of one molar ratio of the reducing agent at room temperature. Cyclohexanone was also reduced immediately to cyclohexanol in 94% yield with one molar ratio of the reagent at room temperature. Hindered ketones were also reduced to their alcohols in 88%, 50% and 87% yields at 60°C (Entries; 4–6, Table XI). In order to show the regio- and chemoselectivity of the reagent in the absence of solvent, reduction of an α-β-unsaturated ketone was performed and the corresponding allyl alcohol was obtained in 98% within 6 min. with one molar ratio of the reagent. Azides are also reduced to their corresponding amines in 70–90% yields. The results are tabulated in Table XI. Generally, reactions with this reagent, under solvent free conditions are more efficient than the reactions in solu-

tion (Table XII). $[Zn(BH_4)_2(Ph_3P)]$ behaves similarly as $[Zn(BH_4)_2(Ph_3P)_2]$ in the absence of solvent (Tables VI and XII).

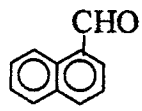
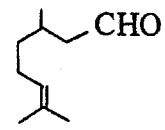
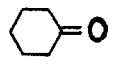
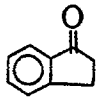
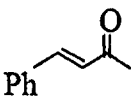
TABLE XI Solvent-Free Reduction of Carbonyl Compounds to Their Corresponding Alcohols and Azides to Their Amines with $[Zn(BH_4)_2(Ph_3P)]$

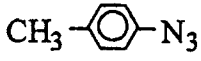
Entry	*Substrate*	*Molar ratio*	*Temp(°C)*	*Yield%,(h)*	*Mp or bp (°C)*
1		1	rt	100(-)[a]	60–62
2		1	rt	90(-)[a,b,d]	-
3		1	rt	94(-)[a,b,d]	161
4		1	60	88(2)[c]	50–54
5		2	60	50(4)[c]	153–154
6		1	60	87(10)[c]	65–67
7		1	60	98(0.08)[b]	144/21 mmHg

Entry	*Substrate*	*Molar ratio*	*Temp(°C)*	*Yield%,(h)*	*Mp or bp (°C)*
8		1	rt	90(0.08)[c]	51–53
9		1.5	60	89(0.08)[c]	41–46
10	$PhCH_2N_3$	1	60	70(2.3)[c,d]	-

a) Immediate reaction.
b) Reaction proceeded at room temperature.
c) Reaction proceeded at 60°C.
d) G.C. Yield.

TABLE XII Comparison of the Results of Solvent-Free and in Solution Reduction of Carbonyl Compounds and Azides to Their Corresponding Alcohols or Amines with $[Zn(BH_4)_2(Ph_3P)_2]$

Entry	*Substrate*	*Solvent-Free*		*In Solution*	
		Molar ratio	*Yield%,(h)*	*Molar ratio*	*Yield%,(h)*
1		1	100(-)[a]	2	90(0.5)
2		1	90(-)[a]	2	95(0.17)
3		1	94(-)[a]	2	100(1)
4		1	88(2)	2	0(20)
5		1	98(0.08)	2	87(2.5)

Entry	*Substrate*	*Solvent-Free*		*In Solution*	
		Molar ratio	*Yield%,(h)*	*Molar ratio*	*Yield%,(h)*
6	$PhCH_2N_3$	1	70(2.3)	2	100(3)
7		1.5	89(0.08)	2	92(1)

a) Immediate reaction.

CONCLUSION

In this study we have shown that unstable $Zn(BH_4)_2$ could be stabilized by Ph_3P ligands. Bis(triphenylphosphine)(tetrahydroborato)zinc is much more stable than (triphenylphosphine)(tetrahydroborato)zinc which shows the effect of the number of triphenylphosphine ligands upon the stability of $Zn(BH_4)_2$. Both reagents are more efficient than $Zn(BH_4)_2$ and their nitrogen ligand analogues. This is a reflection of the nature of the phosphorus ligand upon the reactivity of $Zn(BH_4)_2$. $[Zn(BH_4)_2(Ph_3P)]$ a stable reagent and should be used within a few days after its preparation whereas, $[Zn(BH_4)_2(Ph_3P)_2]$ shows reasonable stability and could be considered as a bench top reagent. Ease of preparation of the reagents from commercially available materials, easy work-up, high rates, and yields of the reactions, low molar ratios of the reagent towards substrates, and high regio- and chemoselectivity of the reagents are worthy of mention for these reagents.

EXPERIMENTAL

General: Reactions proceeded in THE or under solvent-free conditions. Yields refer to isolated products. The products were characterized by comparison with authentic samples (IR, ^{1}HNMR, GLC, and TLC).

Preparation of Bis(triphenylphosphine)(tetrahydroborato)zinc Complex $[Zn(BH_4)_2(PPh_3)_2]$.

A mixture of anhydrous $ZnCl_2$ (4 g, 0.029 mol) in dry ether (50ml) was stirred until most of the solid was dissolved. The mixture was allowed to

stand for 1h and the liquid was decanted from insoluble material. The ethereal zinc chloride solution was added dropwise to a stirred suspension of sodium borohydride (3 g, 0.98 mol) in absolute ether (150 ml) at room temperature followed by the addition of two more portions of $NaBH_4$ (3 g, 0.08 mol). Stirring was continued overnight and then the suspension was filtered quickly and the solution was stored in a stopped bottle at 5°C. To the resulting zinc borohydride ethereal solution, triphenylphosphine (15.2 g, 0.058 mol) in Et_2O (100 ml) was added. The precipitate was formed immediately which was filtered and the filter cake was washed with dry ether (50 ml). The resulting white powder was dried under vacuum to give a white non-hygroscopic stable powder in 84% yield. The amounts of $BH_4^-$and Zn^{2+} content were determined by iodometric titration[18] and atomic absorption techniques: Calc for $[Zn(BH_4)_2(Ph_3P)_2]$; BH_4^- 4.5 %, Zn^{2+} 10.5% , Found ; BH_4^- 4.4 %, Zn^{2+} 10.1%.

Reduction of 4-Methoxybenzaldehyde to 4-Methoxybenzyl Alcohol with $[Zn(BH_4)_2(PPh_3)_2]$. A Typical Procedure for the Reduction of Aldehydes

To a solution of 4-methoxybenzaldehyde (0.083 g, 0.6 mmol) in THF (10 ml) in a round-bottomed flask (25 ml) equipped with a magnetic stirrer, the reducing agent (0.38 g, 0.6 mmol) was added and the resulting mixture was stirred at room temperature for 10 min. Progress of the reaction was monitored by TLC (eluent; CCl_4/Acetone: 5/1). After completion of the reaction, CH_3OH (3 ml) was added to the mixture and stirring was cotinued for 1 h. Evaporation of the solvent and purification by preparative layer chromatography afforded 4-methoxybenzyl alcohol (0.075 g, 98% yield, Table I).

Reduction of Cinnamaldehyde to Cinnamyl Alcohol with $[Zn(BH_4)_2(PPh_3)_2]$: A Typical Procedure for the Selective 1,2-Reduction of α,β-Unsaturated Carbonyl Compounds

To the stirring solution of cinnamaldehyde (0.07 g, 0.53 mmol) in THF (10 ml) the reducing agent (0.33 g, 0.53 mmol) was added and the resulting mixture was refluxed for 0.25 h. CH_3OH (3 ml) was added to the resulting mixture and was stirred for 1 h. Evaporation of the solvent and purification of the crude material by column chromatography afforded cinnamyl alcohol (0.064 g, 90% yield, Table I).

Reduction of Cinnamoyl Chloride to Cinnamyl Alcohol with $[Zn(BH_4)_2(PPh_3)_2]$. A Typical Procedure for the Reduction of Acyl Chlorides

In a round-bottomed flask (25 ml), equipped with a magnetic stirrer, a solution of acid chloride (0.1 g, 0.6 mmol) in THF (10 ml) was prepared. The reducing agent (0.56 g, 0.3 mmol) was added and the reaction mixture was stirred at room temperature for 0.25 h. After completion of the reaction (monitored by TLC), CH_3OH (3 ml) was added to the mixture and was stirred for 1 h. The resulting mixture was filtered and the solvent was evaporated to give the crude product which was purified by preparative layer chromatography to afford pure cinnamyl alcohol (0.09 g, 90% yield, Table I).

Reduction of 4-Methylphenyl Azide to 4-Methylphenyl Amine with $[Zn(BH_4)_2(PPh_3)_2]$. A Typical Procedure for the Reduction of Azides to Amines

$[Zn(BH_4)_2(PPh_3)_2]$ (0.24 g, 0.4 mmol) was added to a stirring solution of 4-methylphenyl azide (0.053 g 0.4 mmol) in THE (10 ml) and the resulting mixture was stirred at room temperature for 0.16 h. Progress of the reaction was followed by TLC (eluent; CCl_4/Et_2O: 5/2). After completion of the reaction, CH_3OH (3ml) was added to the mixture and stirring continued for 1 h. The resulting mixture was filtered and the solvent was evaporated. The crude material was purified by chromatography on a silica gel plate to afford 4-methylphenyl amine (0.039 g, 89% yield, Table III).

Reduction of 4-Methylsulfonyl Azide to 4-Methylsulfonamide with $[Zn(BH_4)_2(PPh_3)_2]$. A Typical Procedure for the Reduction of Sulfonyl Azides

In a round-bottomed flask (25 ml), equipped with a magnetic stirrer, a solution of 4-methylsulfonyl azide (0.079 g, 0.4 mmol) in THF (10 ml) was prepared. The reducing agent (0.26 g, 0.4 mmol) was added and the reaction mixture was stirred at room temperature for 0.5 h. Progress of the reaction was monitored by TLC (eluent; CCl_4/Et_2O: 5/3). After completion of the reaction, CH_3OH (3 ml) was added to the mixture and stirring cotinued for 1 h. The resulting mixture was purified by chromatography on

a silica gel plate to afford 4-methylsulfonamide (0.057 g, 85% yield, Table III).

Reduction of Benzalacetone to 4-Phenyl-3-butene-2-ol with $[Zn(BH_4)_2(PPh_3)_2]$ Under Neat Conditions. A Typical Procedure for the Reductions in the Absence of Solvent

Benzalacetone (0.1 g, 0.68 mmol) was mixed with $[Zn(BH_4)_2(PP_3)_2]$ (0.42 g, 0.68 mmol) and was magnetically agitated at 60°C in an oil bath. Reduction was performed after 10 min., CH_3OH (6 ml) was added to the mixture and stirring was cotinued for 1 h. The resulting mixture was filtered and the solvent was evaporated. Purification of the crude material was carried out by chromatography on a silica gel plate to give 4-phenyl-3-butene-2-ol in a quantitative yield (Table V).

Preparation of (triphenylphosphine)(tetrahydroborato)zinc Complex $[Zn(BH_4)_2(Ph_3P)_2]$

An ethereal solution of Ph_3P (4.4 g, 16.8 mmol) was added to a stirred solution of anhydrous $ZnCl_2$ (2.3 g, 16.8 mmol) in Et_2O (50 ml) to afford immediate formation of a white precipitate of $[ZnCl_2(Ph_3P)]$ (6.7 g, 100% yield). After filtration, the precipitate was dissolved in THF (300 ml) and NaBH4 (3.8 g, 0.1 mol) was added and the mixture allowed to stir at room temperature for 12 h. The resulting mixture was filtered to remove the precipitated NaCl and the excess of $NaBH_4$. The solvent was evaporated under diminished pressure and the resulting white powder was washed with absolute ether (30 ml) and dried in the vacuum to afford $[Zn(BH_4)_2(PPh_3)]$ in 70% yield. BH_4^- and Zn^{2+} contents were determined by iodometric titration and atomic absorption techniques.Calc. for $[Zn(BH_4)_2(Ph_3P)]$; BH_4^- 7.8 %, Zn 18.3, Found; BH_4^- 7.5%, Zn 17.9 %.

Reduction of 4-Nitroacetophenone to 1-(4-Nitrophenyl)ethanol with $[Zn(BH_4)_2(PPh_3)]$, A Typical Procedure for the Reduction of Ketones

To a solution of 4-nitroacetophenone (0.1 g, 0.6 mmol) in THF (10 ml) in a round-bottomed flask (25 ml) equipped with a magnetic stirrer and a condenser, the reducing agent (0.42, 1.2 mmol) was added and the resulting mixture was stirred for 1 h while being refluxed. Progress of the reaction was monitored by TLC (eluent; CCl_4/Et_2O: 5/2). After completion of

the reaction, CH_3OH (3 ml) was added to the mixture and was stirred for 1 h and filtered. Evaporation of the solvent and purification of the crude material by column chromatography afforded 1-(4-nitrophenyl)ethanol (0.1 g, 98% yield, Table XI).

Reduction of β-Ionone to the Corresponding Alcohol with $[Zn(BH_4)_2(PPh_3)]$, A Typical Procedure for Selective 1,2-Reduction of α,β-Unsaturated Carbonyl Compounds

In a round-bottomed flask(25 ml) equipped with a condenser, a solution of b-ionone (0.1 g, 0.5 mmol) in THF (10 ml) was prepared. The reducing agent (0.36 g, 1 mmol) was added and the resulting mixture was stirred for 1.3 h under reflux condition. Progress of the reaction was followed by TLC (eluent, CCl_4/Et_2O: 5/1) and G.C. After completion of the reaction, CH_3OH (3 ml) was added and the mixture was stirred for 1 h and filtered. Evaporation of the solvent and purification of the crude material by chromatography on a silica gel plate afforded the desired alcohol in a quantitative yield (Table VII).

Reduction of 4-Nitrobenzoyl Chloride to 4-Nitrobenzyl Alcohol with $[Zn(BH_4)_2(PPh_3)]$ A Typical Procedure for the Reduction of Acyl Chlorides

In a round-bottomed flask (25 ml) equipped with a magnetic stirrer, a solution of 4-nitrobenzoyl chloride (0.1 g, 0.54 mmol) in THF (10 ml) was prepared. The reducing agent (0.19 g, 0.54 mmol) was added and the reaction was completed immediately (TLC, eluent; CCl_4/Et_2O: 5/1). CH_3OH (3 ml) was added to the reaction mixture and was magnetically stirred for 1 h and filtered. Evaporation of the solvent and purification by preparative layer chromatography afforded pure 4-nitrobenzyl alcohol in a quantitative yield (Table VII).

Reduction of 4-Nitrophenyl Azide to 4-Nitrophenyl Amine with $[Zn(BH_4)_2(PPh_3)]$ A Typical Procedure for the Reduction of Azides

To a stirring solution of 4-nitrophenyl azide (0.06 g, 0.37 mmol) in THF (10 ml) the reducing agent (0.13 g, 0.37 mmol) was added at room temper-

ature. The reaction was completed immediately. CH_3OH (3 ml) was added to the mixture and was stirred for 1 h and filtered. Evaporation of the solvent and purification of the crude product by chromatography on a silica gel plate (eluent; CCl_4/Et_2O: 5/1) afforded 4-nitrophenyl amine in a quantitative yield (Table IX).

Reduction of 1-Naphthaldehyde to 1-Naphthylmethanol with $[Zn(BH_4)_2(PPh_3)]$ Under Neat Conditions. A Typical Procedure for the Reduction of Aldehydes in the Absence of Solvent

A mixture of 1-naphthaldehyde (0.06 g, 0.38 mmol) and $[Zn(BH_4)_2(PPh_3)]$ (0.14 g, 0.38 mmol) was prepared and was magnetically agitated at room temperature. Reduction was completed immediately. CH_3OH (3 ml) was added to the mixture and stirring continued for 1 h. The mixture was filtered and evaporation of the solvent followed by chromatography on a silica gel plate gave pure 1-naphthylmethanol in a quantitative yield (Table XI).

Acknowledgements
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