

# Polyvinylpyridine Chloroaluminum Borohydride As a New Stable, and Efficient Reducing Agent in Organic Synthesis

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## ABSTRACT

The unstable chloroaluminum borohydride is stabilized on polyvinylpyridine, and it is used as an efficient and regenerable polymer supported transition-metal borohydride reagent for reduction of variety of organic compounds such as, aldehydes, ketones, acid chlorides, epoxides and azides. The reagent is unable to reduce, esters, amides, oximes, and nitro compounds.

**Key Words:** reducing agent, transition metal borohydride, supported reagent, polyvinylpyridine, synthesis

## INTRODUCTION

Reduction is one of the most fundamental and useful reactions in organic chemistry. There must be a few organic syntheses of any complexity which do not involve a reduction at some stage. Reduction by hydride transferring agents has widely been used in organic synthesis by well known alkali metal borohydrides,  $\text{NaBH}_4$ ,  $\text{LiBH}_4$  and their modified forms [1-4]. Although a large number of covalent transition-metal borohydride complexes are known [5], there are few reports in the literature on the use of such compounds as reducing agents. This is primarily because almost all of them are volatile unstable solids and as such cannot be used in organic synthesis unless modified. A few reported modified stable forms of such compounds are  $(\text{Ph}_3\text{P})_2\text{CuBH}_4$  [6],  $\{(\text{Ph}_3\text{P})_2\text{CuBH}_3\text{CN}\}_2$  [7], and  $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{Cl})\text{BH}_4$  [8]. Zinc borohydride is the only reported unmodified transition-metal borohydride which has been used frequently in reduction

reactions [9a]. However, because of its instability it should always be used as its freshly prepared ethereal solution, and even when it is supported on silica gel it should be used on the same day of preparation [9b]. Very recently stable modified complex forms of this reagent have been reported [9c, 9d].

The immobilization of reagents on polymeric backbone has been investigated extensively [10, 11]. This is primarily because insoluble polymeric reagents expand the range of applicable solvents, increase the ease of work-up and product purification and isolation and in most cases provide for recovery and regeneration of the supported reagent. Polymer supported reducing agents have received considerable attention in recent years and a variety of them, while exhibiting the advantages of polymeric reagents, have been used in the mild and selective reduction of organic compounds [10]. Among these the only reported polymer supported borohydride reagents are Amberlyst anion exchange resin supported borohydride and cyanoboro-

hydride [12]. These reagents have been used in a number of organic transformations [13]. Recently, we reported the stabilization of zinc borohydride [14, 15] and zirconium borohydride [16] on polyvinylpyridine and their uses as new stable polymeric reducing agents. Very recently, in continuation of our studies on stabilization of reactive metal borohydrides on polymer supports we came across the fact that the unstable chloroaluminum borohydride can be stabilized on polyvinylpyridine and can be used as an efficient polymeric reducing agent especially for regioselective reductive cleavage of terminal epoxides [17]. Now, we wish to report in full the preparation and uses of this new polymeric reducing agent for a variety of organic reductive transformations.

## EXPERIMENTAL

### General

Chemicals were either prepared in our laboratory or were purchased from Fluka AG, Merck and Synthetic Chemicals Ltd. Poly(4-vinylpyridine) cross-linked with 2% divinylbenzene was purchased from Fluka AG. Capacity of the reagent was determined by a standard iodometric titration procedure [18] and atomic absorption technique using Philips Atomic Absorption instrument. All reduction products were known compounds and they were identified by comparison of their spectra and physical data with those of the authentic samples [19]. Reaction monitoring and purity determination of the products were accomplished by GLC or TLC. The IR and NMR spectra were recorded on Perkin-Elmer IR 157G and Hitachi R-2413, 60 MHz spectrophotometers.

### Preparation of Poly(4-vinylpyridine) Supported Chloroaluminum Borohydride [PVP-Al(BH<sub>4</sub>)Cl<sub>2</sub>]

Cross-linked poly(4-vinylpyridine) (5.0 g) was suspended in methanol (50 mL) and stirred for 1 h. A solution of AlCl<sub>3</sub> (20 g, 0.15 mol) in THF/MeOH (4:1, 150 mL) was added to the polymer suspension. The mixture was stirred for 12 h at room temperature and the precipitate was filtered off,

washed with excess methanol and ether, and it was finally dried in vacuum at 40 °C to yield 7.39 g polymer supported aluminum chloride [PVP-AlCl<sub>3</sub>], as a light yellow powder.

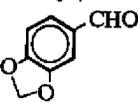
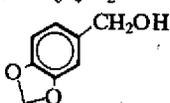
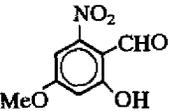
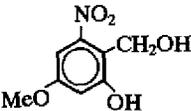
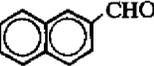
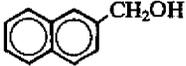
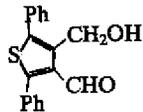
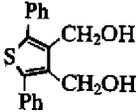
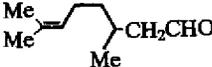
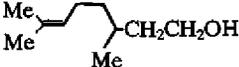
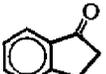
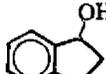
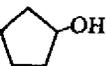
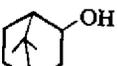
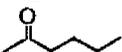
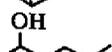
To a solution of LiBH<sub>4</sub> (3.0 g, 0.14 mol) in dry THF (100 mL), PVP-AlCl<sub>3</sub> was added portionwise at 0–5 °C and stirred for 3 h. The resulting material was separated and washed several times with THF and ether and dried under vacuum to produce a white cream coloured, stable and nonhygroscopic powder. The IR spectrum showed characteristic bands at 2400–1600 cm<sup>-1</sup> due to stretching vibration of B–H<sub>i</sub> (strong doublet), 1600–1700 cm<sup>-1</sup> due to bridge stretching vibration of B–H<sub>b</sub> (strong shoulder), 1300–1400 cm<sup>-1</sup> due to asymmetric bridge stretching vibration (strong shoulder) and 1000–1100 cm<sup>-1</sup> due to BH<sub>2</sub> deformation bands. Capacity of the reagent determined by iodometric titration method was 1.8 mmol BH<sub>4</sub> per gram polymer supported AlCl<sub>3</sub>. The amount of aluminum determined by atomic absorption technique and the Cl<sup>-</sup> content determined by potentiometric titration method were 1.90 and 3.85 mmol/g of polymer, respectively.

### General Procedure for Reduction of Carbonyl Compounds, Acid Chlorides, Azides and Epoxides with [PVP-Al(BH<sub>4</sub>)Cl<sub>2</sub>]

In a round bottomed flask (100 mL) equipped with a condenser and a magnetic stirrer, a solution of the substrate (1 mmol) in the proper solvent (10 mL) was prepared. The polymer supported reagent (1.5–2.8 g) was added and the reaction mixture was stirred while being refluxed. Progress of the reaction was monitored by TLC (eluent: CCl<sub>4</sub>/ether, 5/1) or GC. On completion of the reaction (1.5–24 h) water (100 mL) was added and stirred for 5 min. The mixture was then filtered and the filter cake was washed several times with ether. The organic layer was separated and dried over MgSO<sub>4</sub>. The resulting material was purified, if needed, on a silica gel plate using CCl<sub>4</sub>/ether as eluent.

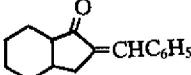
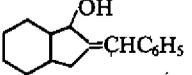
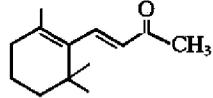
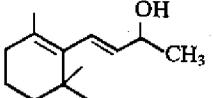
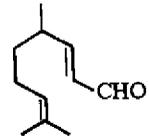
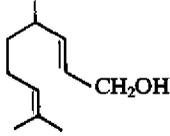
On evaporation of the solvent the pure products were obtained in 20–98% yield, as presented in Tables 1–3.

Table 1. Reduction of carbonyl compounds to their corresponding alcohols with [PVP-Al(BH<sub>4</sub>)Cl<sub>2</sub>]<sup>a</sup>.

Entry	Substrate	Product	Red.Sub. <sup>b</sup>	Time (h)	Yield Isolated (%)
1	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2.7	3	93
2	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2.7	5	88
3	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2.7	4	98
4			2.7	5	98
5			2.7	1.5	92
6	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CHO	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> OH	2.7	2.5	90
7			2.7	9	98
8			2.7	3	92
9			2.7	2.5	98 <sup>c</sup>
10	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CHOHCH <sub>3</sub>	5	8	75
11	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> COCH <sub>3</sub>	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> CHOHCH <sub>3</sub>	5	16	98
12	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CHOHC <sub>6</sub> H <sub>5</sub>	5	20	90
13			5	20	98
14	PhCH <sub>2</sub> COCH <sub>3</sub>	PhCH <sub>2</sub> CHOHCH <sub>3</sub>	3.6	4	95
15	C <sub>6</sub> H <sub>5</sub> COCHOHC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CHOHCHOHC <sub>6</sub> H <sub>5</sub>	3	5.5	92
16	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> COCHOH   C <sub>6</sub> H <sub>5</sub> OMe	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CHOHCHOH   C <sub>6</sub> H <sub>5</sub> OMe	5	10	98
17			5	15	85 <sup>c</sup>
18			5	15	85 <sup>c</sup>
19			3.6	3	83 <sup>c</sup>
20	C <sub>6</sub> H <sub>5</sub> CH=CHCOCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH=CHCHOHCH <sub>3</sub>	5	4	96

continued

Table 1. continued.

Entry	Substrate	Product	Red.Sub. <sup>b</sup>	Time (h)	Yield isolated (%)
21	$C_6H_5CH=CHCHO$	$C_6H_5CH=CHCH_2OH$	5	4	98
22			5	9	60
23			5	9	35 <sup>c</sup>
24			5	6.5	90 <sup>c</sup>

(a) Reactions performed in absolute ethanol under reflux; (b) Molar ratio of reducing agent substrate; (c) Progress of reactions monitored by GLC.

### Regeneration of the Reagent

The spent reagent (5g) was treated with hydrochloric acid (20 mL, 0.1 N), stirred for 0.5 h and filtered. The resulting filter cake was washed first with sodium hydroxide (3×100 mL, 0.1 N) and then with distilled water, acetone and finally with ether. The solid was dried in vacuum at 60 °C to give the original polymer (4.8 g) as a fine precipitate which was used as a support for preparation of the polymeric reagent according to the procedure given in the preceding section.

## RESULTS AND DISCUSSION

Preparation and characterization of some of the coordination complexes of polyvinylpyridine with a large number of metal salts have been reported in the literature [20]. These complexes are easily formed when alcoholic solutions of the metal salts are added to the solution or suspension of the polymer. Aluminum chloride was supported on cross-linked poly(4-vinylpyridine) by adding a THF/CH<sub>3</sub>OH solution of the metal salt to an alcoholic suspension of the polymer. Polymeric reagent was then obtained by an exchange reaction between

the polymer supported aluminum chloride and lithium borohydride in THF. It was a white-cream, stable, nonhygroscopic powder which could be stored as a bench top reagent without appreciable change in its capacity. The IR spectra of the reagent confirmed the presence of BH<sub>4</sub> species on the support. The capacity of the reagent obtained by iodometry was 1.8 mmol BH<sub>4</sub> per gram of polymer supported AlCl<sub>3</sub>. Data obtained on Al and Cl contents by atomic and potentiometric titration techniques, respectively, showed within experimental error that the reducing species are in the form of Al(BH<sub>4</sub>)Cl<sub>2</sub> supported on the polymeric ligand. Such species are known to be formed as unstable intermediates in the formation of aluminum borohydride from reaction of AlCl<sub>3</sub> and LiBH<sub>4</sub> [20]. Several attempts to prepare polymer supported aluminum borohydride were not successful.

It is known that solvents can play an important role in the stability, reducing power, and selectivity of borohydride reagents in reduction reactions [4, 21]. It is also known that for using a polymeric reagent in an organic reaction a solvent should be chosen in which it can swell to a considerable extent [10]. Considering these facts, solvent optimization reactions for each organic functional group

**Table 2.** Reduction of acid chlorides<sup>a</sup> and azides<sup>b</sup> with [PVP-Al(BH<sub>4</sub>)Cl<sub>2</sub>].

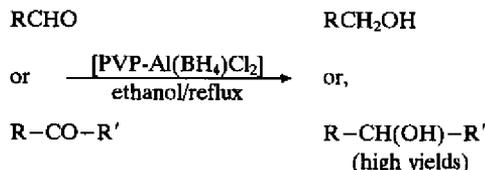
Entry	Substrate	Product	Red. sub. <sup>b</sup>	Time (h)	Yield isolated (%)
1	PhCOCl	PhCH <sub>2</sub> OH	2.7	3	7.3
2	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCl	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2.7	3	90
3	<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCl	<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2.7	2.5	95
4	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> COCl	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2.7	3	94
5			2.7	1	98
6	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COCl	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> OH	2.7	3.5	90
7	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>3</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	3.6	6	40
8	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> N <sub>3</sub>	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	3.6	0.7	95
9			3.6	6	80
10	PhCH <sub>2</sub> N <sub>3</sub>	PhCH <sub>2</sub> NH <sub>2</sub>	3.6	24	20
11	C <sub>6</sub> H <sub>5</sub> CHOHCH <sub>2</sub> N <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CHOHCH <sub>2</sub> NH <sub>2</sub>	3.6	24	20
12			3.6	24	25

(a) Reactions performed in dry THF under reflux; (b) Reactions performed in absolute ethanol under reflux.

reduction was performed using different solvents and the best was chosen on the basis of efficiency of the reagent in that solvent. The solvents of choice are mentioned in the tables. In these solvents the polymeric reagent was completely insoluble and aluminum and boron moieties before and after the reduction remained firmly bound to the insoluble polymeric support. The product isolation and purification were performed simply by filtration of the reaction mixture, evaporation of the solvent, and if necessary, further separation of the starting material by column chromatography. Molar ratios of the reducing agent to substrates were chosen in such a way to obtain reasonable yields of different products in acceptable times. Obviously, some functional groups were more resistant to reduction than others due to their inherent character and therefore higher amounts of the reagent were used.

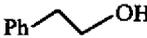
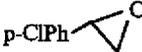
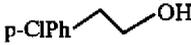
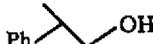
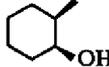
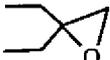
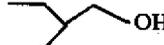
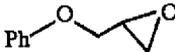
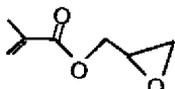
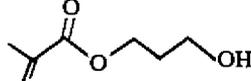
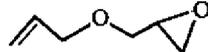
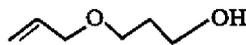
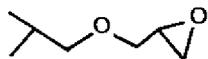
Reduction of carbonyl compounds to their

corresponding alcohols is one of the most important transformation in organic synthesis and equally important is the chemoselective reduction of aldehydes in the presence of ketones [4]. Table 1 shows the reduction of various carbonyl compounds with PVP-Al(BH<sub>4</sub>)Cl<sub>2</sub>. This reagent can reduce aldehydes to their corresponding alcohols in high yields. In using higher molar ratio of the reducing agent to the substrate and longer reaction time, ketones are also reduced to their corresponding alcohols in good yields.



The reagent is, therefore, chemoselective towards

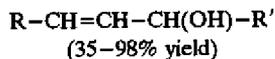
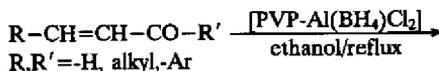
Table 3. Reductive cleavage of terminal epoxides with [PVP-Al(BH<sub>4</sub>)Cl<sub>2</sub>]<sup>a</sup>.

Epoxide	Product	Time (h)	Yield isolated (%)
		8	98
		10	95
		5	90
		6	85
		9	90
		10	92
		7	98
		10	89
		10	87

(a) All reactions are carried out in refluxed absolute ethanol.

the reduction of aldehydes with respect to ketones.

Selective 1,2-reduction of  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds without disturbing the carbon-carbon double bond is a frequent synthetic problem and it has stimulated considerable interest into the development of new reagents and methods [4]. As shown in Table 1, the polymeric reagent shows a complete regioselectivity in reduction of  $\alpha$ ,  $\beta$ -unsaturated aldehydes as well as ketones.



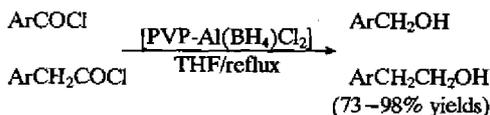
Direct conversion of readily available acid chlorides into the corresponding aldehydes without further reduction to alcohols is a useful reaction in

**Table 4.** Comparison of polymer-supported chloroaluminum, zinc and zirconium borohydrides in reduction of different organic functional groups [14–17].

Entry	Compound	Product	[PVP-Al(BH <sub>4</sub> )Cl <sub>2</sub> ] <sup>a</sup>		[PVP-Zn(BH <sub>4</sub> ) <sub>2</sub> ] <sup>b</sup>		[PVP-Zr(BH <sub>4</sub> ) <sub>4</sub> ] <sup>c</sup>	
			ratio	yield(%)	ratio	yield(%)	ratio	yield(%)
1	Piperonal	Piperonal	2.7	5 98	1	8 65	1	5 78
2	PhCH <sub>2</sub> CHO	PhCH <sub>2</sub> CH <sub>2</sub> OH	2.7	2.5 90	1	15 75	1	6 84
3	PhCOCH <sub>3</sub>	PhCHOHCH <sub>3</sub>	5	8 75	2	15 5	2	12 80
4	PhCOPh	PhCH(OH)Ph	5	20 90	2	45 0.0	2	18 75
5	Cinnamaldehyde	Cinnamyl alcohol	5	4 98	1	9 90	1	6 95
6	Benzalacetone	PhCH=CHCH(OH)Me	5	4 96	2	15 10	2	15 85
7	Chalcone	PhCH=CHCH(OH)Ph	5	7 95	2	24 0.0	2	12 80
8	PhCH <sub>2</sub> COCl	PhCH <sub>2</sub> CH <sub>2</sub> OH	2.7	3.5 90	2	20 70	–	–
		PhCH <sub>2</sub> CHO	–	–	–	20	2	15 90
9	PhCH=CHCOCl	Cinnamyl alcohol	2.7	1 98	2	12 85	–	–
		Cinnamaldehyde	–	–	–	5	2	12 75
10	Benzyl azide	Benzylamine	3.6	24 20	3	18 64	2	24 0.0
11	PhCH(OH)CH <sub>2</sub> N <sub>3</sub>	PhCH(OH)CH <sub>2</sub> NH <sub>2</sub>	3.6	24 20	4	24 0.0	2	24 0.0
12	Styrene oxide	PhCH <sub>2</sub> CH <sub>2</sub> OH	3.5	8 98	3	7 18	2	7 10
		PhCH(OH)Me	–	–	–	54	–	90
13	Phenyl-2,3-epoxy propylether	PhO(CH <sub>2</sub> ) <sub>3</sub> OH	3.6	10 92	–	–	–	–
		PhOCH <sub>2</sub> CH(OH)CH <sub>3</sub>	–	–	3	5 85	2	3 90

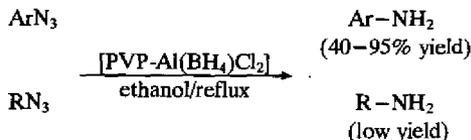
(a) Polyvinylpyridine supported chloroaluminum borohydride; (b) Polyvinylpyridine supported zinc borohydride; (c) Polyvinylpyridine supported zirconium borohydride.

organic synthesis and several mild reagents have been developed for this purpose [4, 7, 15, 22]. Transformation of acid chlorides to the corresponding alcohols can be effected by several hydride reagents [4]. Attempts to reduce acid chlorides to the corresponding aldehydes with PVP-Al(BH<sub>4</sub>)Cl<sub>2</sub> were not successful and in all cases alcohols were obtained as the sole products (Table 2).



Reduction of azide to the corresponding amine is an important reaction especially in nucleotide and carbohydrate chemistry. For this, several reagents have been introduced in the literature [2, 13d, 15]. As shown in Table 2, the polymeric reagent proved to be a suitable reducing agent for conversion of especially aryl azides to

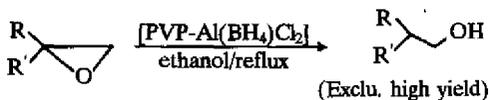
arylamines.



Reductive cleavage of epoxides to alcohols is another very useful reaction in organic synthesis [1]. Cleavage of unsymmetrical substituted epoxides with most conventional reducing agents generally produced the more substituted alcohol [4]. Considerable efforts have been focussed on the development of reagents for regioselective epoxide cleavage to the less substituted alcohols, with only a limited number of reagents being successful [9b, 23].

However, even with these reagents mixture of alcohols were obtained. As shown in Table 3, surprisingly, [PVP-Al(BH<sub>4</sub>)Cl<sub>2</sub>] was able to reduce

mono- and di-substituted epoxides exclusively to the less substituted alcohols in almost quantitative yields.



Regeneration of the polymeric reagent was accomplished by simple washing reactivation procedure in which the spent reagent was first washed with an acid to remove the metal complex and then with a base to obtain the original polymer followed by activation reactions. No change in the capacity of the regenerated reagent was observed and loss of the original polymer during this process was negligible.

Table 4 shows the comparison of polymer supported chloroaluminum borohydride with the only other two reported polymer supported transition metal borohydrides [14–16] in reduction of various organic functional groups.

As shown in many reduction reactions the efficiency of PVP-Al(BH<sub>4</sub>)Cl<sub>2</sub> is higher than those of polyvinylpyridine supported zinc borohydride [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] and in most cases similar to those of polyvinylpyridine supported zirconium borohydride [PVP-Zr(BH<sub>4</sub>)<sub>4</sub>].

One point worth mentioning is that while reductive cleavage of epoxides with [PVP-Al(BH<sub>4</sub>)Cl<sub>2</sub>] gives exclusively the terminal alcohols, more substituted alcohols are obtained with the other reagents.

## CONCLUSION

The unstable chloroaluminum borohydride stabilized on polyvinylpyridine is used as an efficient and regenerable polymer supported transition-metal borohydride reagent for reduction of variety of organic compounds.

In conclusion regioselectivity, easy reaction work-up with no boron moiety in the final product

solution, and high reaction yields make this new stabilized transition metal borohydride reagent useful in the field of organic synthesis.

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