

## Polymer Supported Zirconium Borohydride: a Stable, Efficient and Regenerable Reducing Agent

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The unstable zirconium borohydride,  $Zr(BH_4)_4$ , is stabilized on polyvinylpyridine and used as a new, stable, efficient and regenerable polymer supported transition-metal borohydride reagent for reduction of a variety of carbonyl compounds.

A number of covalent transition-metal borohydride complexes are known.<sup>1</sup> They are volatile unstable solids and as such cannot be used in organic synthesis as reducing agents without modification. There are a few reports in the literature of the use of modified stable forms of such compounds in reduction reactions, such as,  $(Ph_3P)_2CuBH_4$ ,<sup>2</sup>  $[(Ph_3P)_2CuBH_3CN]_2$ ,<sup>3</sup> and  $(C_5H_5)_2Zr(Cl)BH_4$ .<sup>4</sup> Zinc borohydride is the only reported transition-metal borohydride which has been used frequently in reduction reactions, however, because of its instability it should always be used as its freshly prepared ethereal solutions, and even when it is supported on silica gel, it should be used on the same day of preparation.<sup>5</sup>

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.<sup>6</sup> The only reported polymer supported borohydride reagents are Amberlyst anion exchange resin supported borohydride and cyanoborohydride.<sup>7</sup> Recently, we reported preparation and the use of polyvinylpyridine supported zinc borohydride as a stable polymeric transition-metal borohydride reducing agent.<sup>8</sup>

Now we report the stabilization of zirconium borohydride,  $Zr(BH_4)_4$ , on a polymeric ligand poly(4-vinylpyridine) and its use as a new bench top, stable, efficient and regenerable polymer supported transition-metal borohydride reducing agent for reduction of carbonyl compounds.  $Zr(BH_4)_4$  itself is a highly volatile solid, decomposing around room temperature, inflaming in air and hydrolysing explosively.

Crosslinked poly(4-vinylpyridine) (2% divinyl benzene) supported zirconium borohydride reagent  $[XP4-Zr(BH_4)_4]$  was prepared using a modified procedure<sup>9</sup> by the exchange reaction between poly(4-vinylpyridine) supported zirconium chloride complex and lithium borohydride in dimethoxy ether. It was a white-cream, stable, non-hygroscopic powder and could be kept for months without significant change in its efficiency. The capacity of the reagent obtained by iodometry and checked by atomic absorption technique was 5.4 mmol  $BH_4$  per gram. The data obtained by these two techniques showed, within experimental error, that the reducing species

are in the form of  $Zr(BH_4)_4$  supported on the polymeric ligand.

Reduction of various carbonyl compounds in high yields were performed using this reagent and representative results are listed in Table 1. In a typical experiment, to a solution of the carbonyl compound (2 mmol) in tetrahydrofuran (20 ml), polymeric reagent (0.5 g) was added and stirred at room temp. Progress of the reaction was monitored by TLC or GC. On completion of the reaction methanol was added and stirred for 3 h. The reaction mixture was then filtered and solvent evaporated to give the pure alcohol in high yield. Regeneration of the dead reagent was accomplished by simply washing it with acid and base to obtain the original polymer followed by the above mentioned complexation and exchange reactions.

In conclusion  $[XP4-Zr(BH_4)_4]$  unlike its unsupported analogue  $Zr(BH_4)_4$  is a stable, easily prepared, and regenerable polymeric reducing agent. Its capacity is appreciably higher compared to other reported polymer supported borohydrides. Moreover, the mildness, easy reaction work-up with no boron moiety in the final product solution, and high reaction yields will make this new stabilized transition-metal borohydride reagent useful in the field of organic synthesis. Preliminary results obtained shows that this polymeric reagent is also active in reduction of acid chlorides to aldehydes, epoxides to the more substituted alcohols, azides to amines, disulfides to thiols, and nitro compounds to amines. It is inactive in reduction of esters, amides, halides, oximes, quinones and lactones.

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**Table 1** Reduction of carbonyl compounds to their corresponding alcohols with  $[XP4-Zr(BH_4)_4]^a$

Substrate	Red/sub <sup>b</sup>	t/h	Yield (%) <sup>c</sup>
Heptanal	1	10	88
Benzaldehyde	1	4	96
<i>p</i> -Nitrobenzaldehyde	1	3	95
Acetophenone	2	12	80
2-Phenylethanal	1	6	84
Cyclohexanone	2	15	80
Ph-CH=CH-CO-Ph	2	12	80 <sup>d</sup>
Ph-CH=CH-CHO	1	6	95 <sup>d</sup>

<sup>a</sup> All reactions carried out in THF at room temp. <sup>b</sup> Molar ratio: reducing agent/substrate. <sup>c</sup> Isolated yield. <sup>d</sup> No reduction of C=C bond was observed.