Simple manganese complexes as efficient catalysts of ketone hydroboration

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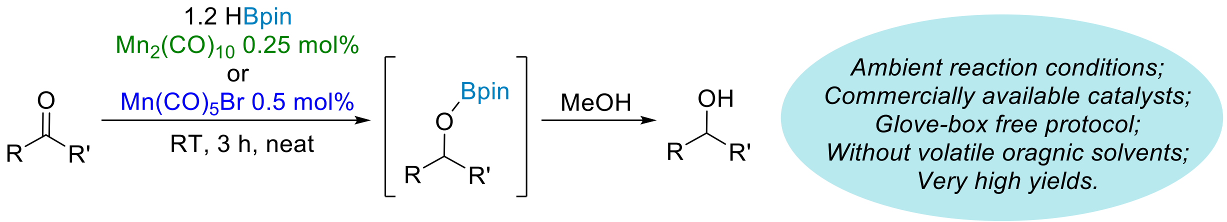
Hydroboration of carbonyl compounds has emerged as highly effective technique for the synthesis of bulk and fine chemicals.[1] This method facilitates the synthesis of valuable boronate ethers but also the large scale production of primary and secondary alcohols. Conventional methods for the reduction of carbonyl compounds to alcohols require highly reactive and difficult to handle reagents, such as explosive hydrogen gas or metal hydrides.[2,3] The hydroboration offers a convenient alternative as the addition of alkoxyboranes, typically catalyzed by transition metals, allows for milder reaction conditions and selective reduction of C=O group in the presence of the other unsaturated bonds in the substrates structure.[4] Therefore, it is still desirable to develop catalysts that will be characterized by high selectivity and productivity. Manganese is especially attractive for preparing the catalysts due to its abundance in the Earth's crust (as a third metal after iron and titanium) and low toxicity.



Ambient reaction conditions;
Commercially available catalysts;
Glove-box free protocol;
Without volatile oragnic solvents;
Very high yields.

In this communication, the application of simple manganese complexes such as $Mn(CO)_5Br$ and $Mn_2(CO)_{10}$ as efficient catalysts for the hydroboration of ketones will be presented. A detailed studies on reaction conditions tuning through the proper choice of the solvent, reaction time and catalyst concentration will be discussed. Moreover, the versatility of developed protocol based on utilization of various ketones with different functional groups including those with unsaturated bonds, e.g. C=C or C≡N will be considered. Additionally, mechanism of the reaction will be investigated based on NMR and DFT studies.

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