A New and Convenient Method for the Preparation of Complex Metal Hydrides of Group II Metals

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Summary A new and convenient method for the preparation of complex metal hydrides of zinc and other Group II metals has been found which involves the reduction of an "ate" complex with $LiAlH_4$ or AlH_3.

COMPLEX metal hydrides of aluminium ($LiAlH_4$) and boron ($NaBH_4$) have proved to be invaluable in organic synthesis. These compounds are prepared by the reaction of a Group IA metal hydride with a derivative of the Group IIIA metal. Recently we reported the preparation of the first complex metal hydride of magnesium ($KMgH_3$) by the hydrogenolysis of an "ate" complex of magnesium. The necessity for this synthetic scheme is due to the fact that the reaction of KH directly with $MgCl_2$ (analogous to the preparation of $LiAlH_4$) produces MgH_2 and not $KMgH_3$.[1] The particular R_2Mg compound used ($Bu^s{}_2Mg$) is difficult to prepare but its use is necessitated by the fact that it is the only known R_2Mg compound soluble in benzene and benzene solvent is necessitated by the fact that $MMgR_2H$ compounds (where M = Li, Na, or K) cleave ether solvents.[2,3]

$$4\,LiH + AlCl_3 \longrightarrow LiAlH_4 + 3\,LiCl \qquad (1)$$

$$4\,NaH + MeO_3B \longrightarrow NaBH_4 + 3\,NaOMe \qquad (2)$$

$$KH + Bu^s{}_2Mg \longrightarrow KMgBu^s{}_2H \xrightarrow{H_2} KMgH_3 + 2\,C_4H_{10} \qquad (3)$$

We have discovered a considerably more convenient and economical method for the preparation of complex metal hydrides of Group IIA and B metals. The method consists in the formation of an "ate" complex of the Group II metal followed by reaction with $LiAlH_4$ or AlH_3. The method is demonstrated by the following reaction:

$$n\,MeLi + Me_2Zn \xrightarrow{Et_2O} Li_nZnMe_{2+n} \xrightarrow{LiAlH_4} Li_nZnH_{2+n} + LiAlMe_2H_2 \qquad (4)$$

where n = 1, 2, or 3

When methyl-lithium was added to dimethylzinc in diethyl ether in ratios of 1:1, 2:1, and 3:1 followed by the addition of lithium aluminium hydride, the intermediate "ate" complexes were reduced to the corresponding hydrides $LiZnH_3$, Li_2ZnH_4, and Li_3ZnH_5 rapidly and quantitatively at room temperature. The hydrides are white crystalline solids, insoluble in ether and hence easily separated from the by-product aluminium compounds by filtration. Elemental analyses are consistent with the empirical formulae. *X*-Ray powder diffraction data show that each of the compounds are different from a mixture of LiH and ZnH_2 and are also different from each other. I.r. studies (Nujol mull) for the hydrides showed broad peaks which were not well resolved. In each case, i.r. spectra of the ethereal solutions left after filtration of the hydrides showed a strong well resolved peak in the Al–H stretching region centred at 1700 cm^{-1} and a moderate peak in the Al–H deformation region centred at 760 cm^{-1}. Both these peaks are characteristic of the species $LiAlMe_2H_2$.

Advantages of the above method are as follows: (1) the reactions are instantaneous and quantitative, (2) no ether cleavage products are formed, (3) high-pressure hydrogenation is not required, (4) methyl metal compounds in ether are much easier to prepare than the s-butyl compounds in hydrocarbon solvent, and (5) it is easier to work with solutions of methyl-lithium rather than solid lithium or sodium hydride.

Using $LiAlH_4$, $NaAlH_4$, or AlH_3 as reducing agents and starting with various "ate" complexes of zinc with potassium or sodium resulted in the preparation of $KZnH_3$, KZn_2H_5, and $NaZnH_3$. High-vacuum DTA–TGA analysis of the above compounds is in progress along with attempted synthesis of other complex metal hydrides of zinc. Complex metal hydrides of magnesium, copper, and cadmium have also been prepared by reduction of the "ate" complex with lithium aluminium hydride.

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