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REACTION OF ZINC HYDRIDE WITH PYRIDINE; FORMATION OF A COMPLEX OF 1,4-DIHYDRO-1-PYRIDYLZINC HYDRIDE, ZINC HYDRIDE AND PYRIDINE

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Notwithstanding its simple stoichiometry, zinc hydride, ZnH_2, is not a well-defined compound which has been little studied. Although a few syntheses have been reported[1-3], none of these so far has provided an analytically pure product.

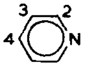
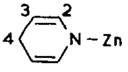
ZnH_2, a very insoluble and presumably highly associated hydrogen-bridged polymer, does not appear to be very reactive; even with water a freshly prepared sample reacts only slowly.

In an attempt to activate the Zn-H bond we tried to depolymerize ZnH_2 by means of suitable ligand molecules. Although several strong donor compounds such as 2,2′- bipyridyl, triethylamine and HMPT failed to achieve depolymerization, ZnH_2, surprisingly, appeared to dissolve in pyridine. In addition it was found that also a secondary reaction took place between this solvent and ZnH_2.

When ZnH_2 (1g), prepared according to ref 1, was dissolved in pyridine (20 ml) in an oxygen-free nitrogen atmosphere at 0°, a clear yellow solution resulted which gradually turned orange. After 30 minutes this solution was evaporated in vacuo giving an orange-brown sticky mass, which after washing with pentane changed into a yellow powder. Hydrolysis of this compound, which analyses as $ZnH_2.C_5H_5N$, yielded hydrogen and a mixture containing pyridine and 1,4-dihydropyridine in a molar ratio of 2:1. Although the compound was insoluble in non polar and weakly polar organic solvents, it readily dissolved in strongly coordinating solvents like DMSO and DMF.

The ^{1}H NMR spectra of the yellow product in deuterated pyridine or DMSO showed absorptions belonging to pyridine, the 1,4-dihydropyridyl system and hydrogen atoms bound to zinc. As after hydrolysis, the ratio pyridine/1,4-dihydropyridyl groups appeared to be 2:1. The absorptions attributed to hydrogen bound to zinc disappeared selectively upon hydrolysis, a reaction which was accompanied by the evolution of hydrogen. The ^{1}H NMR data are summarized in table 1.

Table 1. ^{1}H NMR chemical shifts (in ppm rel. to TMS) of the complex of 1,4-dihydro-1-pyridylzinc hydride, zinc hydride and pyridine in pyridine-d5 (a) and DMSO-d6 (b).

protons at positions		2	3	4	
	a)	8.73	ca 7.20	ca 7.60	
	b)	8.63	ca 7.40	ca 7.85	
	a)	6.55	4.27	3.67	
	b)	5.86	3.73	3.13	
Zn — H	a)				4.34
	b)				2.76

When these observations are combined with the analytical data, which point to a Zn:N ratio of one, it follows that the complex must be formulated as (C_5H_6NZnH. 2 ZnH_2. 2 pyridine). The following experiments corroborate this formulation:

a) Upon hydrolysis 5.1 moles of hydrogen were evolved for each mole of complex as formulated above. This indicates that only one out of six hydrogens of three zinc hydride units has been used for the reduction of pyridine.

b) ^{1}H NMR spectra recorded at low temperatures (-50 to 0^o) in pyridine-d5 showed the presence of at least 2 different kinds of hydrogen atoms bound to zinc, the signals of which coalesced at 10^o.

c) The molecular weight of the complex was determined by cryoscopy in DMSO. The value found indicated an apparent degree of association of 0.42. This low value is due to the displacement of 2 pyridine ligands in the complex by DMSO, which is evident from ^{1}H NMR spectra of DMSO solutions. This implies that each mole of complex gives rise to 3 moles of solute, resulting in an apparent degree of association of 0.33, which value compares not unfavourably with the observed one.

The data presented here are in accord with the following structure proposal (fig 1) or an open, non cyclic equivalent of this:

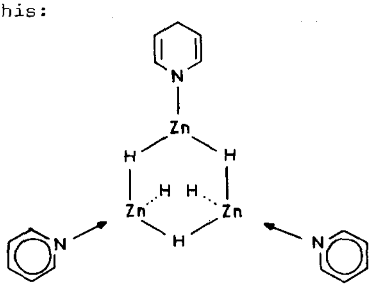


Figure 1. Tentative structure for the complex of 1,4-dihydro-1-pyridylzinc hydride, zinc hydride and pyridine.

Preliminary experiments showed the title complex to be a selective reducing agent for carbonyl compounds. The mechanism of this hydride-transfer reaction is under investigation.

It is tempting to suggest a relation between the present observations and the yet unknown function of zinc in the hydride-transfer step assumed in the mechanism of action of the zinc-containing alcohol dehydrogenases. Also this aspect is a subject of further research.

Acknowledgement

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References

1. G.D. Barbaras, C. Dillard, A.E. Finholt, T. Wortik, K.E. Wilzbach, H.I. Schlesinger, J. Amer. Chem. Soc., 73, 4585 (1951)
2. E. Wiberg, W. Henle, R. Bauer, Z. Naturforsch., 6, 393 (1951)
3. J.J. Watkins, E.C. Ashby, Inorg. Chem., 13, 2350 (1974)