

Preliminary communication

PREPARATION AND CHARACTERIZATION OF THE PYRIDINE  
 COMPLEXES OF ETHYLZINC HYDRIDE AND PHENYLZINC HYDRIDE

A.J. DE KONING, J. BOERSMA, and G.J.M. VAN DER KERK

*Laboratory for Organic Chemistry, State University, Utrecht (The Netherlands)*

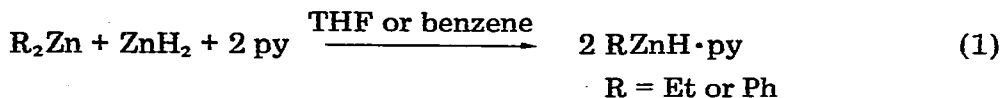
(Received May 11th, 1978)

Summary

The pyridine complexes of ethylzinc hydride and phenylzinc hydride were prepared by treatment of the corresponding diorganozinc compounds with zinc hydride and two equivalents of pyridine in THF or benzene solution. Both complexes of the type  $RZnH \cdot py$ , which were characterized by NMR spectroscopy, are trimeric in benzene solution.

Some years ago Coates and coworkers synthesized several  $RBeH$  compounds [1—3]. More recently, Ashby and coworkers reported the formation of  $PhZn_2H_3$  in the reaction of  $LiAlH_4$  with  $Ph_2Zn$  in THF solution [4]. They also prepared a number of  $RMgH$  compounds [5—6]. Simple organozinc hydrides,  $RZnH$ , or their complexes, however, were previously unknown. We now report the preparation and characterization of the pyridine complexes of ethyl- and phenyl-zinc hydrides.

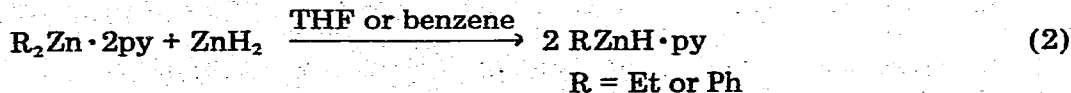
Only a few reactions of zinc hydride are known [7—9]. Zinc hydride is presumably a highly associated hydrogen-bridged polymer and is very insoluble in common organic solvents. When, however,  $ZnH_2$  is treated with diorganozinc compounds in THF or benzene at room temperature in the presence of two molequivalents of pyridine, it readily dissolves to give a clear solution within 1 h (eq. 1).  $ZnH_2$  reacts much faster with  $Et_2Zn$  than with  $Ph_2Zn$  in either solvent. Both reactions proceed faster in THF than in benzene.



Evaporation of the solvent in vacuo and washing of the residue with cold pentane yields the pyridine complexes of the corresponding  $RZnH$  compounds, for which satisfactory analytical data were obtained.  $PhZnH \cdot py$  is a white solid, whereas  $EtZnH \cdot py$  only was obtained as a viscous yellow oil.

The decomposition temperature for both complexes as measured by DTA at a heating rate of 10°C/min was about 100°C.

The same compounds, RZnH·py, were also obtained from the pre-formed pyridine complexes of the parent diorganozinc compounds, R<sub>2</sub>Zn·2py, and zinc hydride (eq. 2), the reaction conditions being the same as before.



The RZnH·py complexes were characterized by <sup>1</sup>H NMR spectroscopy; the signal of the hydrogen bound to zinc was found between 4 and 5 ppm downfield from TMS (Table 1). This chemical shift agrees very well with that found for the 2-dimethylaminoethyl(methyl)aminozinc hydride dimer, prepared according to Bell and Coates [8].

TABLE 1

<sup>1</sup>H NMR CHEMICAL SHIFTS (in ppm rel. to TMS) OF THE HYDROGEN ATOM BOUND TO ZINC IN SOME ZINC HYDRIDE DERIVATIVES (BENZENE SOLUTION)

Compound	Zn-H
EtZnH·py	4.04
PhZnH·py	4.58
2-Dimethylaminoethyl(methyl)aminozinc hydride <sup>a</sup>	4.17

<sup>a</sup>This <sup>1</sup>H NMR chemical shift was not reported by Bell and Coates [8].

Both EtZnH·py and PhZnH·py are trimeric in benzene solution, as was found by cryoscopy. The fact that these compounds are associated into non-dissociating trimers excludes the possibility that they consist of complexes of ZnH<sub>2</sub> with diorganozinc compounds, since in that case an even number of zinc atoms would be present in the associates. On the basis of these results we propose the structure for RZnH·py shown in Fig. 1. This structure has many features in common with the structure we suggested earlier for the complex of 1,4-dihydro-1-pyridylzinc hydride, zinc hydride and pyridine [9]. In both cases the zinc atoms attain the preferred four-coordination by bridging through hydrogen atoms.

The IR spectra of RZnH·py, recorded as Nujol mulls, do not show sharp

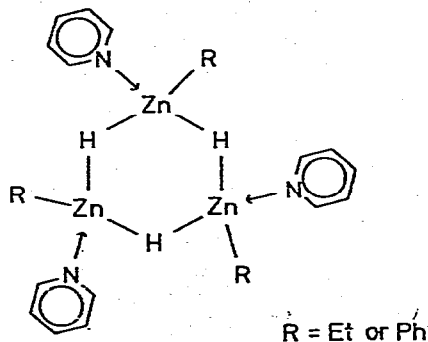


Fig. 1. Proposed structure for trimeric RZnH·py.

bands attributable to Zn—H terminal or bridging stretching vibrations; only some very broad absorptions are observed in the regions 1900—1300, 1150—850 and 650—500  $\text{cm}^{-1}$ . Similar broad absorptions are also found in the IR spectrum of  $\text{ZnH}_2$  itself.

When  $(\text{PhZnH}\cdot\text{py})_3$  is treated with an excess of TMED, the coordinated pyridine is replaced completely by this bidentate nitrogen ligand. The resulting TMED complex has the stoichiometry  $(\text{PhZnH})_2\cdot\text{TMED}$ . Preliminary molecular weight data indicate that this complex exists as a dissociating dimer in benzene solution. Similar reactions with  $(\text{EtZnH}\cdot\text{py})_3$  are being examined.

Ketones are rapidly reduced by the  $\text{RZnH}\cdot\text{py}$  complexes in THF solution. The Zn—H bond in the  $\text{RZnH}\cdot\text{py}$  compounds is also able to reduce any excess of pyridine, as was the case for zinc hydride itself [9]; in these reactions the pyridine is exclusively reduced to the 1,4-dihydropyridyl moiety. The scope of these and other reductions and the possible stereoselectivity involved, are under investigation.

### Acknowledgement

This investigation was supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

### References

- 1 N.A. Bell and G.E. Coates, *J. Chem. Soc.*, (1965) 692.
- 2 G.E. Coates and P.D. Roberts, *J. Chem. Soc. A*, (1969) 1008.
- 3 G.E. Coates and D.L. Smith, *J. Chem. Soc. (Dalton)*, (1974) 1737.
- 4 E.C. Ashby and A.B. Goel, *J. Organometal. Chem.*, 139 (1977) C89.
- 5 E.C. Ashby and A.B. Goel, *J. Chem. Soc. Chem. Commun.*, (1977) 169.
- 6 E.C. Ashby and A.B. Goel, *J. Org. Chem.*, 42 (1977) 3480.
- 7 G.D. Barbaras, C. Dillard, A.E. Finholt, T. Wortik, K.E. Wilzbach and H.I. Schlesinger, *J. Amer. Chem. Soc.*, 73 (1951) 4585.
- 8 N.A. Bell and G.E. Coates, *J. Chem. Soc. A*, (1968) 823.
- 9 A.J. de Koning, J. Boersma and G.J.M. van der Kerk, *Tetrahedron Lett.*, (1977) 2547.