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Reactions of zinc dihydride with donor molecules containing acidic hydrogen atoms

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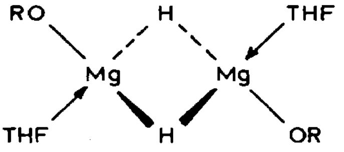
Abstract

Zinc dihydride reacts with an equimolar quantity of 2-dimethylaminoethanol or 3-dimethylaminopropanol in THF evolving hydrogen to form the dimers $[HZnO(CH_2)_nNMe_2]_2$ ($n = 1,2$) containing terminal zinc hydrogen bonds. Spectroscopic evidence points to the fluxional nature of $[HZnOC_2H_4NMe_2]_2$ in solution. Reaction with 2-methyl-2-propanethiol gave $Bu^tSZnH \cdot THF$, which would not redissolve once isolated from solution and is therefore probably polymeric. With 2-methoxyethanol, 2-methoxyphenol, 2,4,6-tri-t-butylphenol and 8-hydroxyquinoline no pure zinc hydride complexes could be obtained. No reaction occurred with diphenylamine and di-isobutylamine; diethylamine reacted on its own without hydrogen evolution to form the insoluble polymer $[Et_2NH \cdot ZnH_2]_n$, but in the presence of an excess of TMED gave polymeric $(Et_2NH)(TMED)_2(ZnH_2)_3$.

Introduction

Complex metal hydrides have found ready application as reducing agents in organic chemistry. The more common complex metal hydrides are based on the group III hydrides, borane (BH_3) and alane (AlH_3), and there is an extensive literature on them [1]. Except for those of beryllium [2], which have been fairly extensively studied, group II metal hydrides are less well known.

The following types of complex magnesium hydrides have been described: ROMgH [3]; R_2NMgH [4]; HMgX (X = halogen) [5]; $ROMg_2H_3$ [6]; RMgH [7]. In dilute tetrahydrofuran solution almost all of them are dimers with the type of structure shown in **1**, although dialkylaminomagnesium hydrides show increasingly higher degrees of association in solutions of increasing concentration [4]:



(1)

0022-328X/88/$03.50

Zinc dihydride and complex zinc hydrides are less well known. Reactions of alkali metal hydrides with R_2Zn produce anionic zinc hydrides, $MH(ZnR_2)_n$ ($n = 1,2$) as etherates or ether-free compounds for $n = 1$, but exist only in solution for $n = 2$ [8–12]. Little is known about the structure of such compounds, though it is generally believed that the hydride atoms act in a bridging capacity between zinc atoms, as is probably the case for other anionic zinc hydrides M_nZnH_{n+2} ($n = 1,2,3$) [12–15]. Although RZn_2H_3 ($R = Ph, C_5H_5$) [16] and H_3ZnX ($X = Cl, Br$) [17] have been prepared and are insoluble in inert solvents, the simple species RZnH are not known. They have however been obtained as coordination complexes $RZnH \cdot py$ ($R = Et, Ph, MeO(CH_2)_4$) [18] by reaction of R_2Zn with ZnH_2 in the presence of pyridine. When R = Et or Ph the compounds are trimeric in benzene solution, with hydride bridging between zinc atoms, and are converted by tetramethylethylenediamine (TMED) into the hydride-enriched species $R_2Zn_3H_4(TMED)$ through a combination of ligand exchange and disproportionation [18]. Zinc dihydride itself adds to pyridine to give a 1,4-dihydropyridine zinc hydride complex $(C_5H_6ZnH)(ZnH_2)_2py_2$ [19]. The first stable and soluble neutral zinc hydride complex was made in 1968 by the reaction of zinc dihydride with *N,N,N′*-trimethylethylenediamine [20]. Crystallographic studies have confirmed that the dimeric arrangement contains terminal zinc–hydrogen bonds, with nitrogen acting as bridging atoms in a Zn_2N_2 four-membered ring [21].

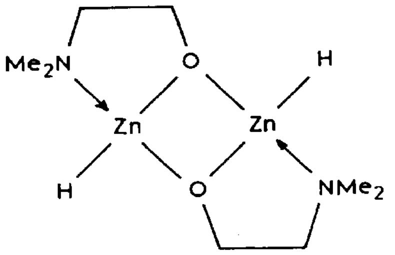
We report below the results of our studies of other reactions of zinc dihydride with donor molecules containing acidic hydrogen atoms.

Results and discussion

When equimolar amounts of zinc dihydride and 2-dimethylaminoethanol react in THF the following process takes place:

$$2ZnH_2 + 2Me_2NC_2H_4OH \xrightarrow{THF} (Me_2NC_2H_4OZnH)_2 + 2H_2$$

The crystalline complex so formed, $(HZnOC_2H_4NMe_2)_2$, is dimeric in benzene solution. A singlet at 4.47 ppm downfield from TMS in the ^1H NMR spectrum of the complex can be unambiguously assigned to the hydride hydrogen since the addition of D_2O or Ph_2CO to a solution of the complex in C_6D_6 in an NMR tube leads to disappearance of the absorption. The singlet lies close to that found at 4.2 ppm for $(HZnN(Me)C_2H_4NMe_2)_2$ [18]. Two absorptions are found in the infrared spectrum of the complex, recorded as a Nujol mull, in the 1500–1800 cm^{-1} region where Zn–H vibrations are likely to be found. These absorptions at 1740 and 1650 cm^{-1} are assigned to terminal Zn–H stretching vibrations, and these frequencies are comparable with the broad band at 1695 cm^{-1} in $(HZnN(Me)C_2H_4NMe_2)_2$ assigned to a terminal Zn–H vibration [22]. In a THF solution of $(HZnOC_2H_4NMe_2)_2$ only one absorption which could be ascribed to a terminal zinc–hydrogen stretching vibration was observed. There are substantial changes in the chemical shifts of the *O*-methylene, *N*-methyl and *N*-methylene protons of the aminoalcohol on going to the zinc hydride derivatives. Thus $[HZnOC_2H_4NMe_2]_2$ has an analogous structure, **2**, to that found for $(HZnN(Me)C_2H_4NMe_4)_2$ [21], containing a terminal Zn–H bond:

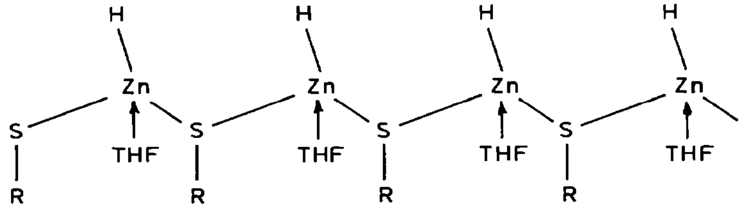


(**2**)

Dimethylaminoethoxyzinc alkyl compounds are thought to be fluxional in solution on the basis of multiple Zn–C rocking and stretching vibrations [23,24], and the appearance of two Zn–H stretching vibrations in the solid state and only a single vibration in a THF solution of $(HZnOC_2H_4NMe_2)_2$ may be ascribed to the same effect. The single broad ^1H NMR absorption for the hydride at room temperature unfortunately broadens further on cooling, so we were unable to confirm the presence of two species at low temperature. The making and breaking of the N–Zn donor bond will relieve the ring angle strain at O caused by the use of sp^2 hybrid orbitals by oxygen. In contrast such strain at oxygen is absent in the 6-membered ring formed by 3-dimethylaminopropanol and in the trimethylethylenediamine analogue where the ideal bond angle at the sp^3 NMe approaches that required by the 5-membered ring, and only one Zn–H infrared vibration is found in both the solid state and in solution in these two complexes.

Zinc dihydride reacts similarly with 3-dimethylaminopropanol to give a white gum which could not be crystallised but which was also dimeric in benzene solution. The broad infrared absorption at 1800–1640 cm^{-1} due to Zn–H stretching and the singlet in the ^1H NMR spectrum at 3.95 ppm downfield from TMS are indicative of the presence of a terminal Zn–H bond. Thus this compound doubtless has a similar structure to the 2-dimethylaminoethoxy and trimethylethylenediamino analogues. Although equimolar quantities of 2-methoxyethanol, 2-methoxyphenol, 2,4,6-tri-t-butylphenol, and 8-hydroxyquinoline reacted with zinc dihydride, either no zinc hydride complexes were formed or satisfactory analyses could not be obtained.

Equimolar quantities of zinc dihydride and 2-methyl-2-propanethiol reacted in THF to give an initially soluble material but on standing a white solid separated from solution and analysed as $(Bu^tCSZnH \cdot THF)_n$. This complex was unusually thermally stable for a zinc hydride, melting at 225 °C with decomposition (in contrast zinc dihydride decomposes at ~ 130 °C), and reacts unusually slowly with water. The complex showed a broad infrared stretching band from 1800–1220 cm^{-1} with a maximum at ~ 1500 cm^{-1}. The evidence points to a polymeric arrangement as in 3, although in view of its thermal stability, low reactivity towards

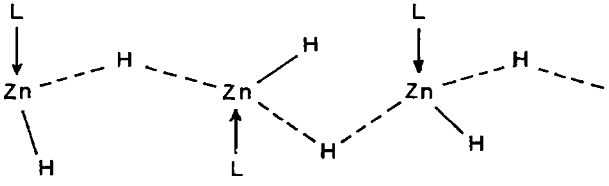


$R = Bu^t$

(**3**)

water, and the appearance of IR absorption down at 1220 cm^{-1}, hydrogen may also be acting in a bridging capacity.

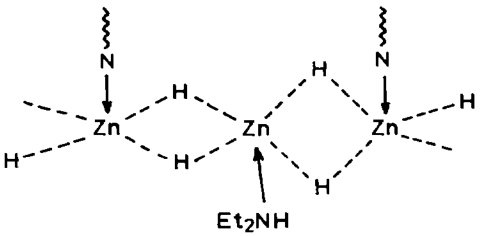
Zinc dihydride did not react readily with secondary amines. With diphenylamine and di-isobutylamine there was no reaction even after long periods and starting materials were recovered almost quantitatively. With diethylamine and zinc dihydride there was an endothermic reaction, but surprisingly there was no copious evolution of gas even at 50 ° C. The product isolated from solution had the empirical formula $Et_2NH \cdot ZnH_2$, and melted sharply at 155 ° C, and is therefore unlikely to be a mixture of products containing zinc dihydride. Unfortunately, once the product was obtained in a solid microcrystalline state it could not be redissolved in any inert solvent. The infrared spectrum contained a very broad absorption at 1800–1220 cm^{-1} which is assigned to terminal and bridging zinc–hydrogen stretching vibrations on the basis of the aforementioned terminal zinc–hydrogen stretching vibration frequencies. Thus the compound is believed to have the polymeric arrangement shown in **4**.



(**4**)

Before the complex was crystallised from solution an ^1H NMR spectrum of the solution showed a resonance at 4.18 ppm that can be assigned to a terminal hydridic hydrogen by analogy with earlier assignments. The signal from methylene and amino protons were shifted between 1 and 2 ppm downfield from those for the free amine, indicating strong coordination of the amine, while the methyl proton resonances stayed essentially the same. Thus a monomeric arrangement is present in solution but crystallisation results in polymerisation.

In an attempt to form a more soluble, less associated compound, the reaction between zinc dihydride and diethylamine was carried out in the presence of TMED in benzene solution in order to avoid coordinating solvents which might complicate the reaction. Reaction was slow, and after 60 h $(Et_2NH)(TMED)_2(ZnH_2)_3$ was isolated from solution. It is unlikely that the product is a physical mixture of $Et_2NH \cdot ZnH_2$ and $TMEDZnH_2$ because it melted sharply at 129 ° C (cf. $(Et_2NH \cdot ZnH_2)_n$ m.p. 155 ° C) and because tetramethyldiaminoethane does not react with zinc dihydride [19]. As the complex could not be re-dissolved after it had been obtained in a solid form, it is considered to be polymeric. The ^1H NMR spectrum of a solution of the oil before crystallisation showed that the resonances due to TMED are not shifted appreciably (0.05 ppm) from those of the free ligand, and thus there is little change in electron density around the $Me_2N \rightarrow Zn$ bond. It is therefore unlikely that TMED is acting as a chelating ligand, since where a five-membered ring to zinc is formed by a ligand containing the Me_2N group there is a significant upfield shift of the resonances of the Me_2N protons on ring formation. Thus a polymeric arrangement shown below is suggested, with both TMED and hydrogen acting in a bridging capacity, so that each zinc is 5-coordinate.



Reactions of these and other zinc hydrides with organic substrates will be discussed elsewhere.

Experimental

Reactions were performed under nitrogen by use of Schlenk tube techniques. Infrared spectra were recorded with a SP200 Pye Unicam grating infrared spectrometer. Solution spectra were obtained using matched cells of 0.15 mm pathlength with KBr windows. ^1H NMR spectra were recorded with an R600 Hitachi Perkin–Elmer FT spectrometer. Gas analysis was carried out by hydrolysing samples with a mixture of 2-methoxyethanol, water, and dilute hydrochloric acid on a standard vacuum line equipped with a Toepler pump. Zinc was determined by EDTA titration at pH 10. Lithium aluminium hydride solutions in diethyl ether were prepared by standard methods and were standardised by determination of their hydrolysable hydrogen content.

Preparation of zinc dihydride [25]

Diethylzinc (2 cm^3, 19.6 mmol) was added to diethyl ether (40 cm^3) at 0 °C in one arm of a double Schlenk tube, and this was followed by dropwise addition of lithium aluminium hydride (25 cm^3, 0.65 *M* solution in diethyl ether, 19.6 mmol). The mixture was stirred for 1 h and the white zinc dihydride (1.31 g, 19.6 mmol) so formed was filtered off, washed with dry diethyl ether (2×20 cm^3) and dry tetrahydrofuran (2×20 cm^3), and then dried briefly under reduced pressure.

Reactions of zinc dihydride

(a) With 2-dimethylaminoethanol. 2-Dimethylaminoethanol (2.11 g, 19.6 mmol) was added dropwise to a stirred slurry of zinc dihydride (1.31 g, 19.4 mmol) at room temperature. The reaction was stirred until most of the solid had dissolved, and then filtered. The solvent was removed from the filtrate under reduced pressure to leave a white oil, which gave a white solid on addition of hexane (yield 1.79 g, 57.8%), m.p. 176–180 °C decomp. (Found: hydrolysable H, 0.60; Zn, 42.0%; $M = 303$ (cryoscopically, 0.029 *M* in benzene). $(Me_2NC_2H_4OZnH)_2$ calc: hydrolysable H, 0.65; Zn, 42.2%; $M = 308$). Infrared absorptions: (Nujol mull), 2700s, 1740m, 1650m, 1420m, 1345m, 1290vs, 1260vs, 1200s, 1170m, 1110vs.br, 1060vs.br, 960vs, 890vs, 790vs.br cm^{-1}; (THF solution), 2800m, 1700vs, 1390m, 1370m, 1280m, 1150m.br, 1000m.br, 900–700 w.br, 790vs cm^{-1}. The ^1H NMR spectrum in C_6D_6 contained

resonances at δ(H), 4.47 (s,1H,ZnH), 4.25 (t,2H,OCH_2), 2.32, 2.80 ppm (m,8H,$(CH_3)_2NCH_2$).

(b) With 3-dimethylpropanol. 3-Dimethylpropanol (2.2 cm^3, 18.6 mmol) was added dropwise during 10 min to a slurry of zinc dihydride (1.31 g, 19.4 mmol) in THF (40 cm^3). After gas evolution ceased, the mixture was stirred for 2 h at 60 ° C then filtered, and the solvent was then removed under reduced pressure. Attempts to recrystallise the white gummy residue, which decomposed without melting at 120 ° C, were unsuccessful. (Found: hydrolysable H, 0.60; Zn, 38.0%; $M = 325$, 329 cryoscopically, (0.025, 0.036 M in benzene). $(Me_2NC_3H_6OZnH)_2$ calc: hydrolysable H, 0.60 Zn, 38.7%; $M = 336$.) Infrared absorptions: (Nujol mull), 2800vs, 1800–1640m.br, 1620m, 1320w.br, 1275m, 1240w.br, 1180m.br, 1060vs.br, 780m, 760m cm^{-1}. The ^{1}H NMR spectrum in C_6D_6 contained resonances at 4.05, 3.95(3), 2.32, 2.13(8), 1.66(2) ppm downfield from TMS.

(c) With 2-methyl-2-propanethiol. 2-Methyl-2-propanethiol (2.1 cm^3, 18.6 mmol) was added to a suspension of zinc dihydride (1.31 g, 19.4 mmol) in THF (30 cm^3) at −40 ° C. The mixture was allowed to warm to room temperature with stirring, and most of the solid dissolved during 1.5 h. The solution was filtered then kept overnight, and the white solid that had separated was filtered off and dried in vacuo (yield 1.74 g, 41%), m.p. 225 ° C decomp. (Found: hydrolysable H, 0.55; Zn, 29.6%. $Bu^tSZnH \cdot THF$ calc: hydrolysable H, 0.54; Zn, 28.7%.) Infrared absorptions: (Nujol mull), 3050–2800vs, 1800–1400vs, br, 1502vs, 1367s, 1207w, 1157vs, 1036vs, 976m.br, 886m, 815w, 717w, 667w cm^{-1}.

(d) With diethylamine. A mixture of zinc dihydride (1.31 g, 19.4 mmol), diethylamine (1.43 g, 19.6 mmol), and THF (35 cm^3) was stirred overnight at 50 ° C, during which most of the solid dissolved. The straw-coloured solution was then filtered and the solvent removed under reduced pressure to leave a brown oil that crystallised on the addition of hexane as a very fine brown powder. This was filtered off and dried in vacuo (yield 0.76 g, 28%), m.p. 155 ° C (Found: hydrolysable H, 1.52; Zn, 43.9%. $(Et_2NH)ZnH_2$ calc: hydrolysable H, 1.44; Zn, 46.4%.) Infrared absorptions: (Nujol mull), 2900vs, 1800–1220vs,br, 1180m, 1150m, 1110m, 1040m.br, 900w,br, 855m, 795m.br cm^{-1}.

(e) With diethylamine and N,N,N′,N′-tetramethylethylenediamine. Diethylamine (2 cm^3, 19.6 mmol) was added dropwise to a slurry of zinc dihydride (1.31 g, 19.4 mmol) and tetramethylethylenediamine (5 cm^3, 33 mmol) in benzene (30 cm^3). The mixture was stirred at room temperature for 60 h then filtered, and the solvent was removed from the filtrate to leave a clear oil which was redissolved in benzene. Addition of hexane yielded a white microcrystalline solid, which was filtered off and dried in vacuo (yield 1.06 g, 32%), m.p. 129 ° C (decomp. 135 ° C). (Found: hydrolysable H, 1.22; Zn, 39.8%. $(Et_2NH)(Me_2NC_2H_4NMe_2)_2(ZnH_2)_3$ calc: hydrolysable H, 1.19; Zn, 38.6%.). Infrared absorptions: (Nujol mull), 3000–2700vs, 1800–1550vs.br, 1290m, 1140m.br, 1100m.br, 1060–990m.br, 950m, 790m.br cm^{-1}. The ^{1}H NMR spectrum of the oil in C_6D_6 contained resonances at: δ(H) 1.20 (t,6H,CH_3), 3.32(q,4H,CH_2), 2.78(s(br),1H,NH), 2.16(s,24H,CH_3), 2.32 s,8H,CH_2).

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References

1 H.C. Brown and S. Krishnamurthy, Tetrahedron, 35 (1979) 567, and references therein.
2 N.A. Bell, in E.W. Abel, F.G.A. Stone and G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, Vol. I, Pergamon, Oxford, 1982, p. 121.
3 E.C. Ashby and A.B. Goel, Inorg. Chem., 18 (1979) 1306.
4 E.C. Ashby and A.B. Goel, Inorg. Chem., 17 (1978) 1862.
5 E.C. Ashby and A.B. Goel, Inorg. Chem., 16 (1977) 2941.
6 E.C. Ashby, A.B. Goel and J.J. Lin, Tetrahedron Lett., (1977) 3133.
7 E.C. Ashby and A.B. Goel, Chem. Commun., (1977) 169.
8 G. Wittig and P. Hornberger, Liebigs Ann. Chem., 577 (1952) 11.
9 G.J. Kubas and D.F. Shriver, J. Am. Chem. Soc., 92 (1970) 1949.
10 G.J. Kubas and D.F. Shriver, Inorg. Chem., 9 (1970) 1951.
11 P. Kobetz and W.E. Becker, Inorg. Chem., 2 (1963) 859.
12 D.F. Shriver, G.J. Kubas and J.A. Marshall, J. Am. Chem. Soc., 93 (1971) 5076.
13 E.C. Ashby and R.G. Beach, Inorg. Chem., 10 (1971) 2486.
14 E.C. Ashby and J.J. Watkins, Inorg. Chem., 12 (1973) 2493.
15 A.B. Goel, S. Goel and E.C. Ashby, Inorg. Chem., 18 (1979) 1433.
16 E.C. Ashby and A.B. Goel, Inorg. Chem., 20 (1981) 1096.
17 E.C. Ashby and H.S. Prosad, Inorg. Chem., 14 (1975) 1608.
18 A.J. de Koning, J. Boersma and G.J.M. van der Kerk, J. Organomet. Chem., 195 (1980) 1.
19 A.J. de Koning, J. Boersma and G.J.M. van der Kerk, J. Organomet. Chem., 186, (1980) 159.
20 N.A. Bell and G.E. Coates, J. Chem. Soc. (A), (1968) 823.
21 N.A. Bell, P.T. Moseley, H.M.M. Shearer and C.B. Spencer, Acta Crystallogr., B, 36 (1980) 2950.
22 N.A. Bell, P.T. Moseley, H.M.M. Shearer and C.B. Spencer, Chem. Commun., (1980) 359.
23 G.E. Coates and D. Ridley, J. Chem. Soc. A, (1966) 1064.
24 J. Boersma and J.G. Noltes, J. Organomet. Chem., 13 (1968) 291.
25 J.J. Watkins and E.C. Ashby, Inorg. Chem., 13 (1974) 2350.