REACTIONS OF ZINC HYDRIDE AND MAGNESIUM HYDRIDE WITH PYRIDINE; SYNTHESIS AND CHARACTERIZATION OF 1,4-DIHYDRO-1-PYRIDYLZINC AND -MAGNESIUM COMPLEXES *

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Summary

The synthesis and characterization of 1,4-dihydro-1-pyridylzinc and -magnesium complexes are described. Zinc hydride and magnesium hydride dissolve in and react with pyridine, and the reaction has been studied in detail in the case of zinc hydride. Evaporation of the solvent after 1—2 hours at 0°C yielded a product containing pyridine, a 1,4-dihydropyridyl moiety and zinc hydrogen bonds, and two alternative structures are proposed for this complex. When the reaction was carried on for a long period, a yellow precipitate began to separate after about 40 hours, and reaction was complete after 7 days. The yellow product was identified as the pyridine complex of bis(1,4-dihydro-1-pyridyl)zinc. The corresponding magnesium complex was obtained from the reaction between magnesium hydride and pyridine for 50 hours at room temperature.

Introduction

Zinc hydride was first prepared more than 25 years ago, yet it has been little studied. Several syntheses have been reported [2—6], but none yielded an analytically pure product. Zinc hydride is a thermolabile, non-volatile solid, virtually insoluble in non-polar and almost all polar organic solvents. It is presumably a highly associated, hydrogen-bridged coordination polymer like beryllium hydride and magnesium hydride. It appears to be very unreactive, and a freshly prepared sample reacts only slowly even with water.

As an alternative route to functionally-substituted organozinc compounds [7], we considered the possibility of adding Zn—H bonds to (functionally-substituted) olefins and acetylenes. Since ZnH₂ itself is very unreactive, we attempted to activate the zinc—hydrogen bonds by ligand-induced depolymer-
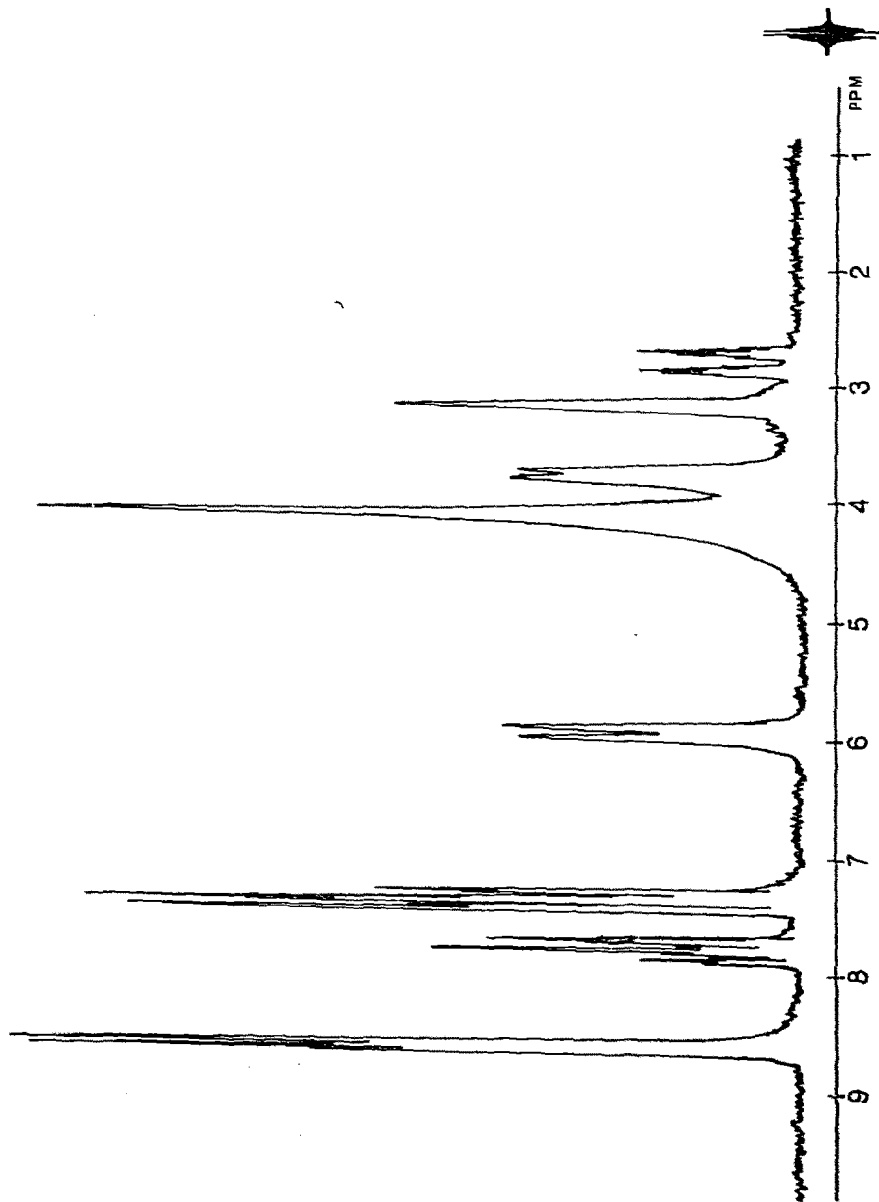
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* For a preliminary communication see ref. 1.

Fig. 1. The ^{1}H NMR spectrum of the complex of 1,4-dihydro-1-pyridylzinc hydride, zinc hydride and pyridine (complex A) recorded in DMF-d_7 at room temperature. For assignment of the absorptions see Table 1.

ization. Contrary to expectation, depolymerization did not occur, either in coordinating solvents like DMF and HMPT or with strong donor compounds such as triethylamine, 2,2'-bipyridyl and $N,N,N,'N'$-tetramethylethylenedi-amine (TMED). In pyridine, however, zinc hydride not only dissolved but also appeared to react, and we deal below with the nature of this reaction and the products. The reaction between magnesium hydride and pyridine was examined for comparison, but the route leading to the final product was not investigated in detail.

Results and discussion

Treatment of zinc hydride with pyridine at $0°C$ gives a clear yellow solution which gradually turns orange. Evaporation of the solvent in vacuo after one hour at $0°C$ gives an orange-brown sticky residue, which upon washing with pentane or hexane is changed into a pale yellow powder. Elemental analysis of this product, complex A, indicates the composition $(ZnH_2 \cdot C_5H_5N)_x$. Hydrolysis of complex A yields, in addition to hydrogen and zinc hydroxide, a mixture of pyridine and 1,4-dihydropyridine in a molar ratio of 2 : 1. The complex is extremely sensitive to moisture and air. Like zinc hydride, it undergoes thermal decomposition at $115°C$ (DTA, heating rate $10°C/min$). It is insoluble in non-polar or weakly polar organic solvents such as pentane, benzene, chloroform, ether and THF, but readily dissolves in strongly coordinating solvents such as pyridine, DMSO and DMF. The solutions in these solvents at room temperature are unstable because there is a slow reduction of the solvents by the solute.

The ^1H NMR spectra of complex A in fully deuterated pyridine, DMSO or DMF contain peaks indicating the presence of pyridine, the 1,4-dihydropyridyl system, and hydrogen atoms bound to zinc, in the molar ratio 2 : 1 : 5 (Fig. 1). The resonance attributed to zinc-bound hydrogen selectively disappears upon hydrolysis of complex A in a reaction which is accompanied by evolution of hydrogen. To our knowledge this is the first time that hydrogen bound to zinc has been identified by means of ^1H NMR spectroscopy; no signal of hydrogen bound to zinc was reported in the ^1H NMR spectrum (in benzene) of the dimeric compound, 2-dimethylaminoethyl(methyl)aminozinc hydride, prepared from zinc hydride and trimethylethylenediamine [8], but on reinvestigating this compound we observed the signal from the hydride atom at 4.17 ppm.
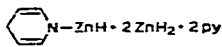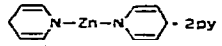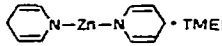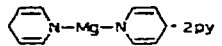
The chemical shifts of the signals from the pyridine protons in solutions of complex A in deuterated DMSO, DMF or pyridine are identical to those of free pyridine in the same solvents, and we conclude that in these solutions the pyridine is no longer coordinated to zinc. On the other hand, the signals from the 1,4-dihydropyridyl group are clearly shifted relative to those of free 1,4-dihydropyridine. Study of the corresponding ^{13}C NMR spectra leads to the same conclusions. The ^1H NMR and ^{13}C NMR data are summarized in Tables 1 and 2.

When the NMR data are combined with the analytical data, if follows that complex A must be formulated as $(C_5H_6NZn_3H_5 \cdot 2 \text{ pyridine})_n$. The following experiments corroborate this conclusion:

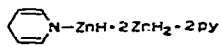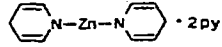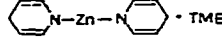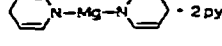(i) Upon hydrolysis 5 moles of hydrogen are evolved for each mole of com-

TABLE 1

^{1}H NMR CHEMICAL SHIFTS (IN PPM RELATIVE TO TMS) OF FRESHLY PREPARED SAMPLES OF 1,4-DIHYDROPYRIDINE AND SOME 1,4-DIHYDRO-1-PYRIDYLZINC AND -MAGNESIUM COMPLEXES

Compound	solvent	Zn—H	2	3	4	α	β	γ
N—H	py-d_5		5.87	4.24	2.98			
N—ZnH·2ZnH₂·2py (A)	py-d_5	4.34	6.55	4.27	3.67	8.73	7.24	7.62
	DMSO-d_6	2.76	5.86	3.73	3.13	8.63	7.43	7.86
	DMF-d_7	4.14	5.98	3.78	3.19	8.64	7.40	7.85
N—Zn—N ·2py (B)	py-d_5		6.30	4.30	3.62	8.69	7.18	7.57
	DMF-d_7		5.92	3.75	3.20	8.67	7.47	7.90
N—Zn—N ·TMED (C)	py-d_5		6.21	4.24	3.55			
	DMF-d_7		5.95	3.80	3.12			
N—Mg—N ·2py (D)	py-d_5		6.30	4.23	3.70	8.68	7.18	7.56
	DMF-d_7		6.03	3.65	3.32	8.67	7.45	7.90

plex A, as formulated above. This indicates that only one out of six hydrogens of three zinc hydride units has been utilized for the reduction of a pyridine molecule to a 1,4-dihydropyridyl group. This is in accord with the amount of hydrogen bound to zinc as derived from the ^{1}H NMR spectra of complex A before hydrolysis.

TABLE 2

^{13}C NMR CHEMICAL SHIFTS OF 1,4-DIHYDROPYRIDINE AND OF THE 1,4-DIHYDROPYRIDYL GROUPS BOUND TO ZINC OR MAGNESIUM IN SOME NITROGEN LIGAND COORDINATION COMPLEXES

Compound	2	3	4
N—H	127.3	95.3	22.3
N—ZnH·2ZnH₂·2py (A)	139.3	91.0	24.5
N—Zn—N ·2py (B)	138.2	92.4	24.2
N—Zn—N ·TMED (C)	138.2	92.4	24.2
N—Mg—N ·2py (D)	141.1	90.6	25.7

solvent: pyridine-d_5; temperature: 0°C. Shifts in ppm relative to TMS.

(ii) The ^{1}H NMR spectra at low temperatures show the presence of different kinds of hydrogen atoms bound to zinc; the spectra were studied in pyridine-d_5 since DMSO solidifies at 18.5°C and DMF is unsuitable because at low temperatures all the signals from the 1,4-dihydropyridyl group are broadened in this solvent. Since in pyridine solution the hydrogens bound to zinc have almost the same chemical shifts as the 3-hydrogens of the 1,4-dihydropyridyl group, we treated ZnH$_2$ with fully deuterated pyridine at 0°C:

$$(ZnH_2)_m \xrightarrow[0°C, 2h]{pyridine-d_5} \frac{m}{3n} (C_5D_5HNZn_3H_5 \cdot 2 \ C_5D_5N)_n$$
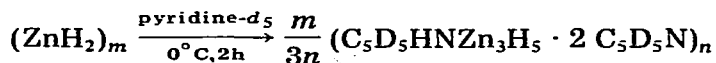
Upon cooling to below 0°C (temperature range 0°C to —50°C) the original absorption of the hydrogen atoms splits up into two broad bands indicating the presence of at least two kinds of hydrogen atoms bound to zinc. At 10°C the signals coalesce. This experiment with deuterated pyridine proved also that the hydrogen atom transferred from zinc hydride appears exclusively at the 4-position, and excludes the primary formation of a 1,2-dihydropyridyl moiety which subsequently rearranges to the 1,4-isomer.

(iii) The molecular association of complex A was determined cryoscopically in DMSO. In this solvent, the pyridine ligands are dissociated from the zinc as shown by ^{1}H NMR spectroscopy, and so each mole of complex A is expected to yield three moles of solute, to give an apparent degree of association of 0.33 if the complex is monomeric. The value obtained, viz. 0.42, is in reasonable agreement with that calculated for a monomeric complex.

On the basis of these data, two possible structures of complex A are presented in Fig. 2.

In both structures the zinc atoms are coupled by $2e$—$3c$ hydrogen bridges. Structures corresponding to the cyclic structure (I) were previously suggested for the pyridine complexes of ethylzinc hydride and phenylzinc hydride [9].

When zinc hydride is reacted at 0°C with pyridine for a long period a yellow precipitate starts to separate from the dark red solution after about 40 hours, and the reaction is complete after 7 days. The extremely air- and moisture-sensitive yellow product, which did not contain zinc—hydrogen bonds, was identified as the bis pyridine complex of bis(1,4-dihydro-1-pyridyl)zinc (complex B). Like complex A, complex B dissolves only in strongly coordinating solvents such as DMF and DMSO. However, complex B reduces these solvents even faster than complex A, and so the solutions are unsuitable for characterization of the original compound by spectroscopy or molecular association measurements. In the ^{1}H NMR spectrum of a freshly prepared sample of complex B in pyridine-d_5 no hydrogen atoms bound to zinc were detected and no gas evolution took place upon hydrolysis. The only products apart from Zn(OH)$_2$ obtained upon hydrolysis were pyridine and 1,4-dihydropyridine, in 1/1 molar ratio. Both hydrogen atoms originally bound to zinc have thus been used for the reduction of pyridine to the 1,4-dihydropyridyl moiety.

The ^{1}H NMR spectrum of complex B recorded in deuterated pyridine at room temperature changes with time (Fig. 3).

This behaviour can be explained as shown in Scheme 1.

The pyridine ligands in complex B are rapidly replaced by deuterated pyridine molecules when the latter are present in large excess. In an intra- or
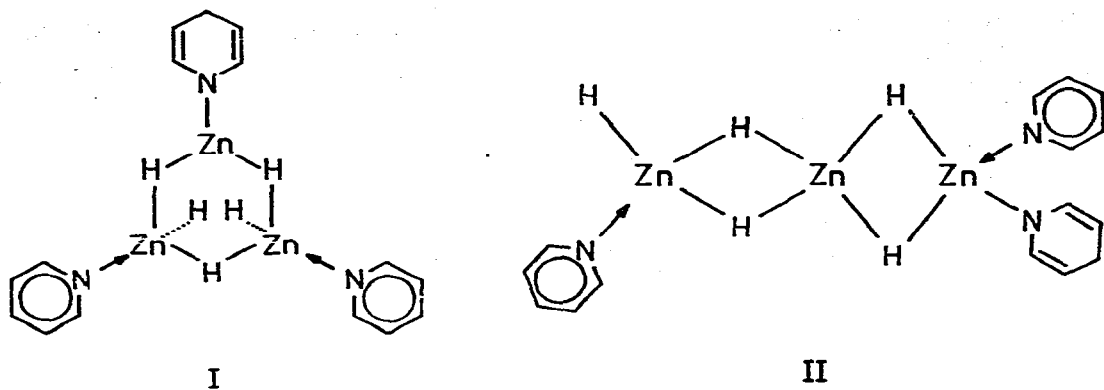
Fig. 2. Structure proposals for the complex of 1,4-dihydro-1-pyridylzinc hydride, zinc hydride and pyridine (complex A).
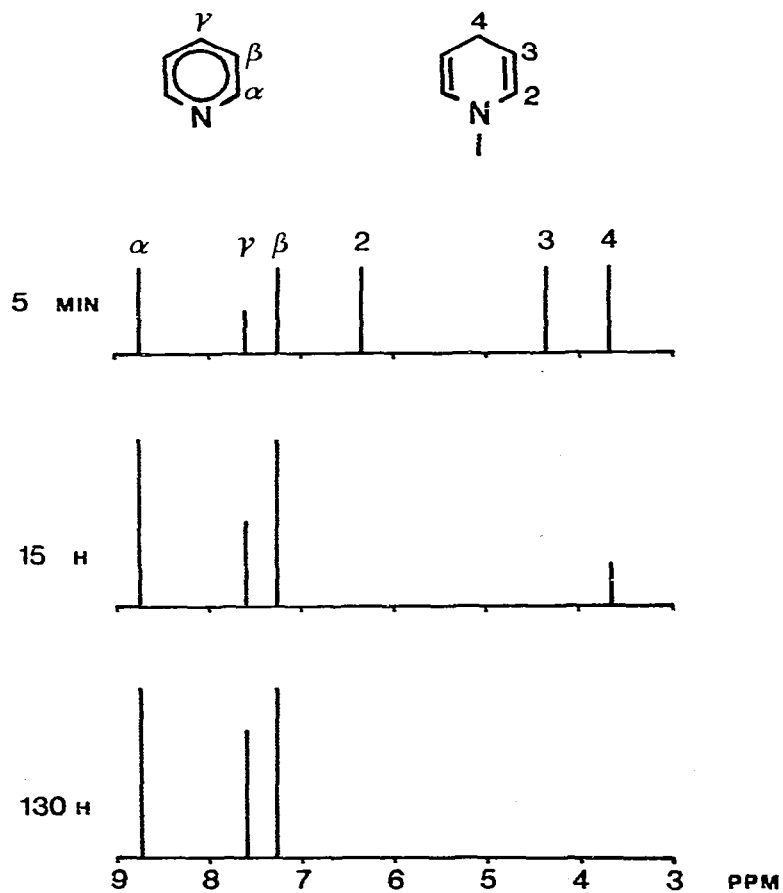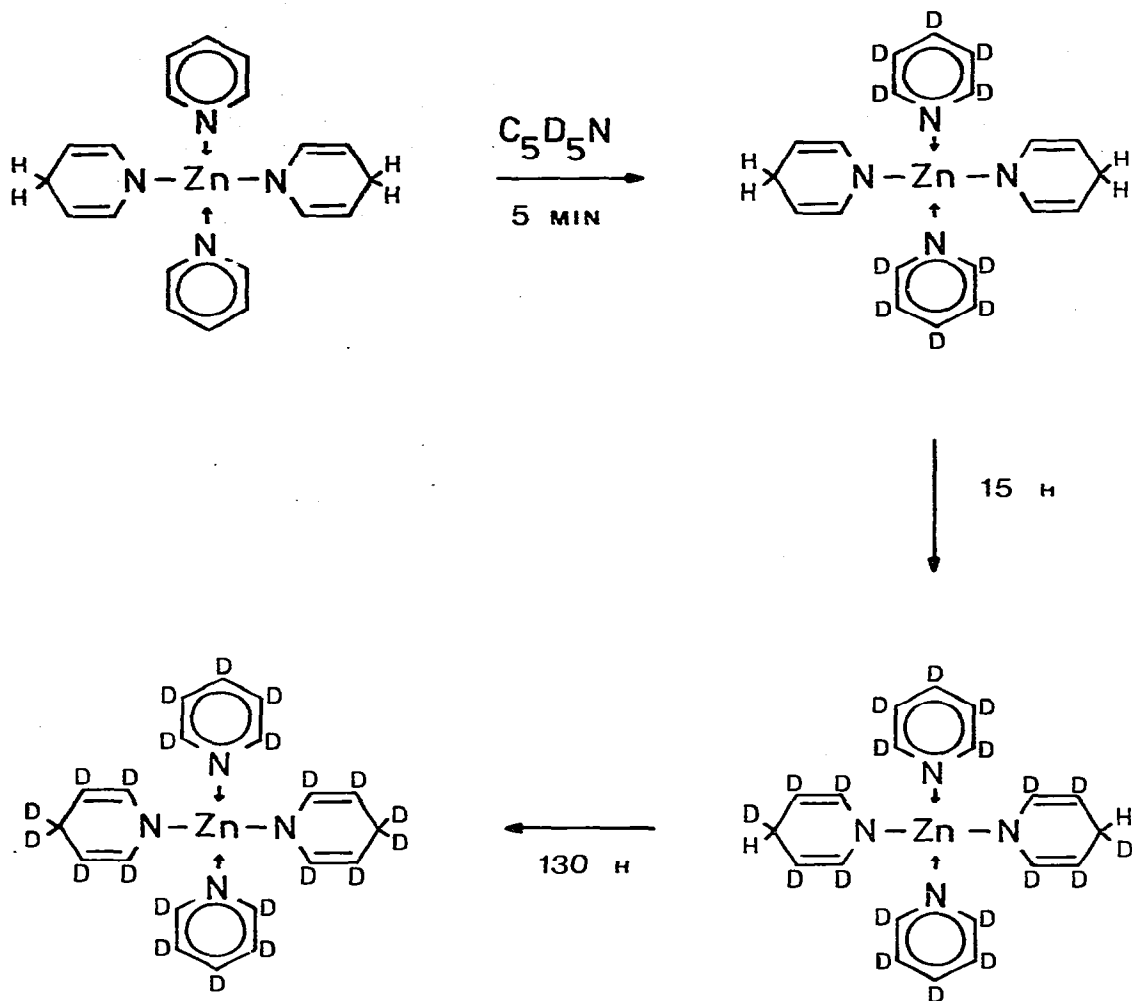

Fig. 3. Schematic picture of dynamic ^{1}H NMR spectra of the pyridine complex of bis(1,4-dihydro-1-pyridyl)zinc, complex B, in pyridine-d_5.

Scheme 1. Proposed reaction-pathway for the hydride transfer between the pyridine complex of bis(1,4-dihydro-1-pyridyl)zinc, complex B, and pyridine-d_5.

intermolecular reaction a coordinated pyridine-d_5 molecule is then reduced by a 1,4-dihydropyridyl group bound to zinc, the hydride atom being transferred exclusively from the 4-position of the 1,4-dihydropyridyl group to the γ-position of the pyridine-d_5 molecule. The absorptions at 6.30 ppm and 4.30 ppm of the hydrogen atoms at the 2- and 3-positions of the 1,4-dihydropyridyl group disappear completely in 15 hours, while the multiplet at 3.62 ppm of the hydrogen atoms at the 4-position of the 1,4-dihydropyridyl group diminishes to about half its original magnitude. Further decrease of this signal and a concurrent increase of the multiplet of the γ-atom of pyridine occur only slowly. Apparently this is due to an isotope effect, the H$^-$ transfer proceeding faster than D$^-$ transfer ($k_H/k_D \approx 7$). The multiplet of the hydrogen atoms at the 4-position of the 1,4-dihydropyridyl group has completely disappeared in 130

hours. At that time only pyridine signals are visible in the ^{1}H NMR spectrum and the integral ratio of the α, β and γ hydrogen atoms is then 4 : 4 : 3. This ratio is in full agreement with the proposed reaction pathway.

The hydride transfer probably involves an one-electron transfer mechanism, as may be concluded from an ESR signal which was observed during the reaction. The exact nature of this mechanism is being investigated at the moment.

The overall reaction between zinc hydride and pyridine can be represented as in Scheme 2.

$$ZnH_2 \;+\; \underset{N}{\bigcirc} \quad \xrightarrow{\text{fast}} \quad (ZnH_2)_n (py)_m$$

$$\Big\downarrow \; 1-3\,h$$

COMPLEX B $\qquad\xleftarrow[\text{slow}]{160\,h}\qquad$ COMPLEX A
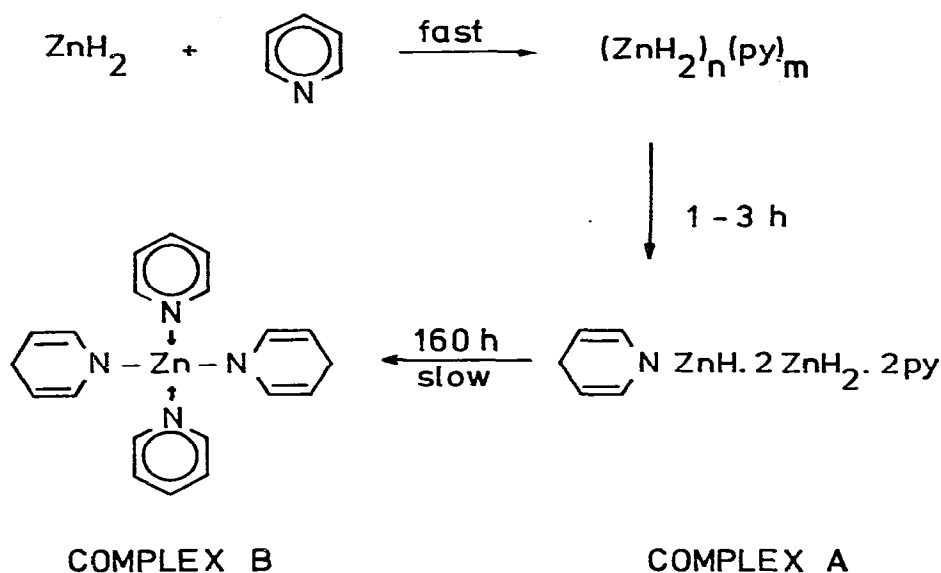
Scheme 2. Reaction between zinc hydride and pyridine at $0°$C.

The reaction between ZnH_2 and pyridine at room temperature is complete in 24 hours, but the purities of the intermediate product A and especially of the final complex B are much lower, the products being contaminated with zinc metal.

Magnesium hydride reacts with pyridine in the same way. The far greater thermal stability of magnesium hydride, compared to zinc hydride, allows this reaction to be carried out at room temperature without impairing the purity of the final product. After 50 hours at room temperature, a yellow, sometimes greenish, product can be isolated, which appears to be the pyridine complex of bis(1,4-dihydro-1-pyridyl)magnesium.

Under the conditions used no 1,2-dihydropyridyl-containing products were observed in the reaction of either ZnH_2 or MgH_2 with pyridine, contrary to what happens in the corresponding reaction of lithium aluminium hydride with this coordinating solvent [10—12]. $LiAlH_4$ does not react selectively with pyridine and the final product, lithium tetrakis(N-dihydropyridyl)aluminate, contains both 1,2-dihydropyridyl and 1,4-dihydropyridyl groups in a ratio which depends on the reaction temperature used.

The pyridine ligands in complex B are displaced by TMED or TEED (N,N,N',N'-tetraethylethylenediamine) on treatment with an excess of either of

these bidentate nitrogen ligands. The resulting TMED and TEED complexes of bis(1,4-dihydro-1-pyridyl)zinc are white solids with properties very similar to those of the parent compound. The pyridine complex of bis(1,4-dihydro-1-pyridyl)magnesium, surprisingly does not undergo these ligand exchange reactions with TMED or TEED.

Some ^{1}H NMR and ^{13}C NMR data for the pyridine and TMED complexes described above, are reported in Tables 1 and 2. The decomposition temperatures of the novel bis(1,4-dihydro-1-pyridyl)metal complexes, which are all stable at room temperature, are given in Table 3.

Quantitative analysis of the products formed in the endothermic decomposition reactions showed that the complexes B, C and D decompose in the following way:
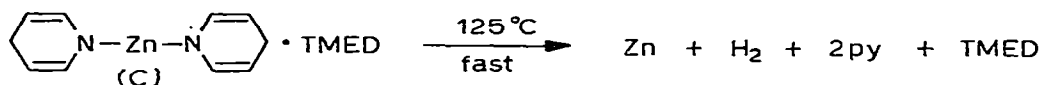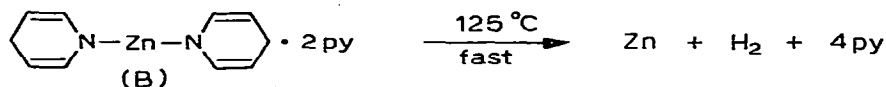
It is assumed that in the decompositions at 125°C hydride transfer occurs between the 1,4-dihydropyridyl groups and the metal, leading to the regeneration of the metal hydride and pyridine. In contrast to magnesium hydride, zinc hydride is not stable at 125°C and immediately decomposes to hydrogen and

TABLE 3

DECOMPOSITION TEMPERATURES ^{a} OF ZINC HYDRIDE, MAGNESIUM HYDRIDE AND OF SOME 1,4-DIHYDRO-1-PYRIDYLZINC AND -MAGNESIUM COMPLEXES

Compound	decomposition temperatures (°C)
MgH_2	310, exothermic
ZnH_2	115, exothermic
$N-ZnH \cdot 2 ZnH_2 \cdot 2py$ (A)	115, exothermic
$N-Zn-N \cdot 2py$ (B)	110, endothermic
$N-Zn-N \cdot TMED$ (C)	101, endothermic
$N-Mg-N \cdot 2py$ (D)	64, small endothermic effect
	170, exothermic

^{a} Determined by DTA using a heating rate of 10°C/min.

zinc metal. The decomposition of the zinc complexes B and C at 125°C proceeds much faster than of the magnesium complex D. These decompositions are considered to be the reverse of the reactions in which the bis(1,4-dihydro-1-pyridyl)metal complexes are formed. That is, a reversible hydride transfer takes place between zinc hydride or magnesium hydride and pyridine, a process which is thermally controlled.

Conclusions

The hydrogen-bridged coordination polymers zinc hydride and magnesium hydride dissolve in pyridine and react with this coordinating solvent. As final products novel coordination compounds are formed, viz. the pyridine complexes of bis(1,4-dihydro-1-pyridyl)zinc and bis(1,4-dihydro-1-pyridyl)magnesium. Both hydrogen atoms originally bound to the metal are used for the selective reduction of pyridine molecules to 1,4-dihydropyridyl groups, without formation of intermediate 1,2-dihydropyridyl isomers. The pyridine ligands of the zinc-containing complex B are displaced by TMED or TEED upon treatment with these bidentate ligands. The corresponding magnesium compound, although very similar to complex B in almost every respect, does not undergo this ligand-exchange.

At 125°C the bis(1,4-dihydro-1-pyridyl)metal complexes decompose by a reaction which is the reverse of that in which they are formed; hydride transfer occurs from the 1,4-dihydropyridyl groups to the metal with regeneration of the metal hydride and of pyridine.

The bis(1,4-dihydro-1-pyridyl)metal complexes, which do not contain metal—hydrogen bonds, nevertheless possess interesting reducing properties. Hydride transfer from 1,4-dihydropyridyl groups bound to zinc or magnesium occurs to a variety of substrates. The reduction of carbonyl groups and its possible biochemical implications is the subject of the following paper [13].

Experimental

General

All experiments were carried out under dry oxygen-free nitrogen. Solvents were carefully purified, dried, distilled, and stored under nitrogen. Solvents, solutions and liquid reagents were handled with syringes.

NMR spectra were recorded on Varian EM 390, XL 100 and CFT 20 spectrometers. The ^{1}H δ values are believed to be accurate to ±0.02 ppm, and ^{13}C δ values to ±0.1 ppm.

Infrared spectra were recorded on a Perkin-Elmer 457 double beam grating spectrometer with Nujol suspensions between KBr discs. The frequencies given are believed to be accurate within 3 cm^{-1}.

The gas evolved upon hydrolysis of hydride-containing samples was measured with a calibrated gasometer. Decomposition temperatures were measured by differential thermal analysis using samples sealed in vacuo in glass ampoules; accuracy ±2°C. Molecular weights were determined cryoscopically in DMSO [14].

Elemental analyses were carried out under the supervision of Mr. W.J. Buis in

the Analytical Department of the Institute for Organic Chemistry TNO at Utrecht.

Preparation of zinc hydride

There are several methods for preparing zinc hydride [2—6].

The zinc hydride used throughout this work was obtained by treating diethylzinc with lithium aluminium hydride in diethyl ether:

$$Et_2Zn + 2 LiAlH_4 \xrightarrow{Et_2O} ZnH_2 + 2(LiAlH_3Et)$$
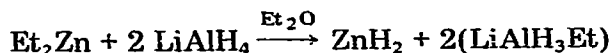
The LiAlH$_4$ was purified by adding diethyl ether, filtering the resulting suspension and evaporating the filtrate to dryness. Et$_2$Zn was prepared as described by Noller [15]. 5.0 g of Et$_2$Zn (40 mmol) in diethyl ether (25 ml) was added dropwise to a stirred solution of 3.1 g of LiAlH$_4$ (82 mmol) in diethyl ether (75 ml) at 0°C and the mixture was then stirred for one hour at 0°C. The white precipitate of ZnH$_2$ was isolated by centrifugation, washed six times with ether (6 × 80 ml), and dried in vacuo (0°C, 0.1 mm); yield 2.6 g (95%).

Analysis: found: H, 3.3; Zn, 93.7; Al, 0.5; Li, 1.0. ZnH$_2$ calcd.: H, 3.0; Zn, 97.0; Al, 0.0; Li, 0.0%. No ethane was developed upon hydrolysis.

Zinc hydride is a white, non-volatile solid. It usually turns grey within one or two days at room temperature, presumably as a result of slight decomposition into its elements. When stored at dry ice temperature ZnH$_2$ loses its reactivity during two weeks. When freshly prepared, the hydride reacts only very slowly with air, but samples in which decomposition has occurred may ignite spontaneously on contact with air. A freshly prepared sample of ZnH$_2$ decomposes at 115°C, as determined by DTA (heating rate 10°C/min). The IR spectrum of ZnH$_2$ shows very broad absorptions in the regions 1900—1300, 1150—850 and 650—500 cm^{-1}.

Zinc hydride may also be prepared by treating NaH with ZnCl$_2$ or LiH with ZnBr$_2$ in THF at room temperature as described by Watkins and Ashby [5], who claim that this route is more convenient and yields ZnH$_2$ which is more reactive than that prepared by any of the other methods. We do not agree with their views, and prefer the method described above.

Preparation of magnesium hydride

Magnesium hydride may also be prepared in several ways [2,16—19]. We used an active form of magnesium hydride obtained from the reaction of LiAlH$_4$ with Et$_2$Mg in diethyl ether [2]. Diethylmagnesium was prepared by the procedure of Storfer and Becker [20].

Magnesium hydride is a white solid which decomposes at 310°C to magnesium and hydrogen. It is stable indefinitely at room temperature when protected from moisture and oxygen. It is pyrophoric in air and reacts violently with water. The infrared spectrum of MgH$_2$ shows two broad band envelopes, one at 1400—800 cm^{-1} and one at 800—400 cm^{-1}.

Preparation of the complex of 1,4-dihydro-1-pyridylzinc hydride, zinc hydride and pyridine (complex A)

Zinc hydride (1.0 g) was dissolved in pyridine (25 ml) at 0°C. The clear yel-

low solution obtained gradually turned orange. After one hour the excess of pyridine was evaporated off ($0°C$, 0.1 mm) to leave a sticky orange-brown residue, which upon washing with pentane or hexane gave a pale yellow powder. The whole procedure took 3 to 4 hours. The supernatant liquid was decanted and the precipitate washed three times with pentane (3×50 ml). After drying at $0°C$ (0.1 mm), 2.1 g (96%) of complex A was obtained.

Analysis *, found: C, 40.93; H, 5.02; N, 8.96; Zn, 41.55. C_5H_7NZn calcd.: C, 40.99; H, 4.82; N, 9.56; Zn, 44.63%.

Thermal decomposition of complex A occurs at $115°C$ as determined by DTA (heating rate $10°C$/min). The IR spectrum shows very broad absorptions comparable to those of ZnH_2.

Complex A can also be obtained by reacting ZnH_2 (15 mmol) with an excess of pyridine (75 mmol) in benzene (30 ml); the pale yellow complex is formed in about 3 hours. If the reaction is continued the compound gradually turns green, probably because of decomposition. We prefer the other method of preparation described above because it is a homogeneous process with better reproducibility.

Preparation of the pyridine complex of bis(1,4-dihydro-1-pyridyl)zinc (complex B)

3.0 g of ZnH_2 was dissolved in 40 ml of pyridine at $0°C$ and the solution was kept at that temperature. The yellow solution gradually turned orange and then dark-red. After two days a yellow precipitate started to form and was complete after 7 days. The precipitate was filtered off, washed three times with diethyl ether (3×80 ml) and twice with pentane (2×80 ml), then dried in vacuo ($25°C$, 0.1 mm). Yield: 13.7 g (80%). The dark-red pyridine solution also contained a small amount of complex B, which was isolated by evaporation of the solvent and washing as described above. Yield: 2.7 g (16%).

Analysis, found: C, 61.38; H, 5.75; N, 13.85; Zn, 16.60. $C_{20}H_{22}N_4Zn$ calcd.: C, 62.59; H, 5.78; N, 14.60; Zn, 17.03%.

The IR spectrum shows absorptions at 1633 and 1568 cm^{-1} which can be assigned to the C=C and C=N stretching modes of the 1,4-dihydropyridyl moiety [21].

When the reaction between ZnH_2 and pyridine is carried out at room temperature, it is complete after 24 hours, but the product is contaminated with zinc metal.

Preparation of the TMED complex of bis(1,4-dihydro-1-pyridyl)zinc (complex C)

4 ml of TMED was added to a stirred suspension of 2 g of complex B in diethyl ether (25 ml) at room temperature. The yellow suspension gradually turned white. After 2 hours the white precipitate was filtered off, washed twice with diethyl ether (2×50 ml) and twice with pentane (2×25 ml), then dried in vacuo ($25°C$, 0.1 mm) to give the TMED complex of bis(1,4-dihydro-1-pyridyl)zinc in quantitative yield.

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* Taking into account the extreme sensitivity of the complex to air and moisture the analytical data are satisfactory.

Analysis, found: C, 55.34; H, 8.25; N, 15.62; Zn, 19.78. $C_{16}H_{28}N_4Zn$ calcd.: C, 56.22; H, 8.26; N, 16.39; Zn, 19.13%.

The IR spectrum shows absorptions at 1642 and 1577 cm^{-1} characteristic for the C=C and C=N stretching vibrations of the 1,4-dihydropyridyl group.

The TEED complex of bis(1,4-dihydro-1-pyridyl)zinc can be obtained similarly.

Preparation of the pyridine complex of bis(1,4-dihydro-1-pyridyl)magnesium (complex D)

2.0 g of MgH_2 was dissolved in 80 ml of pyridine at room temperature. The yellow solution gradually turned orange and then became red. No precipitate had formed even after 50 hours. The pyridine was evaporated off in vacuo and the yellow residue washed three times with diethyl ether (3 × 80 ml) and twice with pentane (2 × 80 ml) then dried in vacuo (25°C, 0.1 mm) to give complex D in quantitative yield (25.8 g).

Analysis, found: C, 68.64; H, 6.43; Mg, 7.22; N, 15.67. $C_{20}H_{22}MgN_4$ calcd.: C, 70.09; H, 6.47; Mg, 7.09; N, 16.35%.

The IR spectrum shows absorptions at 1638 and 1562 cm^{-1}, which are assigned to the C=C and C=N stretching vibrations of the 1,4-dihydropyridyl group.

Depending on the purity of the MgH_2 used, the reaction time varies and the product is sometimes green.

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