

SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF SOME ORGANOZINC HYDRIDE COMPLEXES

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(Received March 5th, 1980)

Summary

The synthesis and characterization of the monopyridine complexes of ethylzinc hydride and phenylzinc hydride are described. On treatment with TMED these complexes are converted into $R_2Zn_3H_4$. TMED species through a combination of ligand-exchange and disproportionation. The formation of organozinc hydrides from ω -functionally-substituted diorganozinc compounds is only successful when the intramolecular coordination in these starting materials is weak and easily broken by pyridine. The results of these investigations are used as a basis for a discussion of the factors governing the formation of stable organozinc hydrides.

The $RZnH.py$ complexes easily reduce ketones and aldehydes, but no unusual stereoselectivity was observed in the reduction of substituted cyclohexanones. $EtZnH.py$ reacts with an excess of pyridine with formation of the bis pyridine complex of ethyl(1,4-dihydro-1-pyridyl)zinc, a soluble compound, which is monomeric in benzene. The corresponding phenylzinc complex, however, cannot be isolated; disproportionation to $Ph_2Zn.2py$ and the bis pyridine complex of bis(1,4-dihydro-1-pyridyl)zinc occurs.

Introduction

Our interest in the chemistry of zinc hydride is twofold. In the first place, we have been engaged in a study of the reaction of zinc hydride with pyridine [1] which yields the bis pyridine complex of bis(1,4-dihydro-1-pyridyl)zinc; this reagent, which does not contain metal–hydrogen bonds, nevertheless exhibits very interesting reducing properties [2,3]. Secondly, the synthesis of compounds of the type $RZnH$ has been the objective of some of our studies [4].

Although some organoberyllium hydride complexes [5–8] and more recently organomagnesium hydride compounds [9–11] have been described, little is known about organozinc hydrides. The main reason for this discrepancy is

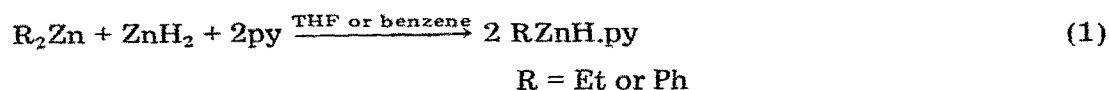
probably the thermolability of the Zn—H bond relative to the Be—H and Mg—H bonds. Recently, however, Ashby and Goel reported the formation of a stable organozinc hydride, PhZn_2H_3 from the reaction of LiAlH_4 with Ph_2Zn in THF solution [12]. We succeeded in preparing mono pyridine complexes of ethylzinc hydride and phenylzinc hydride by reactions between zinc hydride and the corresponding diorganozinc compound in the presence of two mole-equivalents of pyridine [4].

In this paper we give an account of the synthesis and characterization of organozinc hydride complexes. The scope of the methods of preparation is indicated and, in addition, the reactions of the new organozinc hydride complexes with a variety of substrates are described.

Results and discussion

a. Synthesis and characterization of compounds RZnH.py

Only a few reactions of zinc hydride are known [1,13,14]. Zinc hydride is presumably a highly associated hydrogen-bridged coordination polymer, like beryllium hydride and magnesium hydride, and is very insoluble in common organic solvents. However, when ZnH_2 is treated with diorganozinc compounds in THF or benzene at room temperature in the presence of two mole-equivalents of pyridine it readily dissolves to give a clear solution within 1 h (eq. 1).



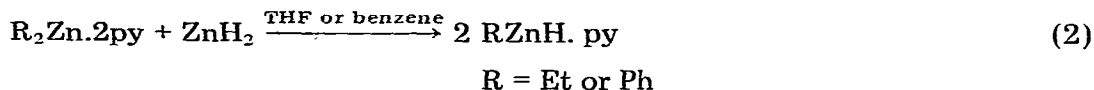
The dissolution of insoluble zinc hydride in THF or benzene in the presence of the diorganozinc compound and pyridine suggests the occurrence of the reaction shown in eq. 1. In the absence of pyridine no reaction occurs in contrast to the formation of RMgH compounds from MgH_2 and R_2Mg in THF [9,11]. If the diorganozinc compound is omitted, again a clear solution is not formed; under these circumstances ZnH_2 reacts slowly with pyridine yielding a complex of (1,4-dihydro-1-pyridyl)zinc hydride, zinc hydride and pyridine [1,15]. This heterogeneous reaction also gives rise to decomposition products [1].

Zinc hydride reacts much faster with Et_2Zn than with Ph_2Zn in either solvent and both reactions are faster in THF than in benzene. Evaporation of the solvent in vacuo and washing the residue with pentane yields the pyridine complexes of the corresponding organozinc hydrides. PhZnH.py is a white solid, whereas EtZnH.py was obtained as a viscous yellow oil. Solutions of the pyridine complexes of the organozinc hydrides are not very stable at room temperature; decomposition occurs within a few hours as shown by the appearance of zinc metal.

No reaction took place between THF-insoluble dicyclopentadienylzinc, Cp_2Zn , and zinc hydride in the presence of pyridine. This may be due to the insolubility of the reactants.

The compounds RZnH.py ($\text{R} = \text{Et or Ph}$) were also obtained from the preformed pyridine complexes of the parent diorganozinc compounds, $\text{R}_2\text{Zn.2py}$,

and zinc hydride (eq. 2), the reaction conditions being the same as before.



The RZnH.py complexes were characterized by NMR and IR spectroscopy. In the ^1H NMR spectrum 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 we found for the 2-dimethylaminoethyl(methyl)-aminozinc hydride dimer prepared as described by Bell and Coates [14,16]. The signal of the hydrogen bound to zinc in the RZnH.py complexes broadens considerably upon cooling, but no different types of hydride atoms could be distinguished. At -50°C (solvent toluene- d_8) the hydride absorption is found as a very broad signal between 3.3 and 5.3 ppm, and at that temperature the absorptions of the ethyl or phenyl group and of pyridine also broaden. Upon further cooling (to -95°C) there is only further broadening of all the signals of RZnH.py.

The ^{13}C NMR data of the pyridine complexes of ethylzinc hydride, phenylzinc hydride, and the bis pyridine complexes of the corresponding diorganozinc compounds are given in Table 2. No substantial shift differences between the carbon atoms of the same groups in RZnH.py and $\text{R}_2\text{Zn} \cdot 2\text{py}$ are observed. However, the intensity of the signal of the carbon atom directly bound to zinc (C_1) was much greater in PhZnH.py than in $\text{Ph}_2\text{Zn} \cdot 2\text{py}$. The strong increase in signal-intensity of C_1 in PhZnH.py relative to that of the corresponding carbon atom in $\text{Ph}_2\text{Zn} \cdot 2\text{py}$ cannot be explained only in terms of an extra contribution of the dipole-dipole relaxation mechanism arising from the local magnetic field associated with the (zinc-bound) β hydrogen atom. Apparently, the contributions of other relaxation mechanisms, particularly spin-rotation relaxation and chemical shift anisotropy, which depend on the size of the molecule and the electronic environment of the carbon atom under consideration, are also different for the two molecules. The results thus clearly indicate that we are dealing with two totally different compounds, and that PhZnH.py is not simply a mixture of $\text{Ph}_2\text{Zn} \cdot 2\text{py}$ and ZnH_2 .

The IR spectra of RZnH.py do not show sharp bands attributable to terminal

TABLE 1

^1H NMR CHEMICAL SHIFTS (in ppm rel. to TMS) OF THE HYDROGEN ATOM BOUND TO ZINC IN SOME ZINC HYDRIDE DERIVATIVES

Compound	Solvent	Zn-H
EtZnH · py	benzene	4.0
PhZnH · py	benzene	4.6
$\text{CH}_3\text{O}(\text{CH}_2)_4\text{ZnH} \cdot \text{py}$	benzene	4.1
$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{ZnH}^a$	benzene	4.2
$(\text{PhZnH})_2 \cdot \text{TMED}$	benzene	3.6
$\text{Et}_2\text{Zn}_3\text{H}_4 \cdot \text{TMED}$	pyridine	4.0
$\text{Ph}_2\text{Zn}_3\text{H}_4 \cdot \text{TMED}$	pyridine	4.1

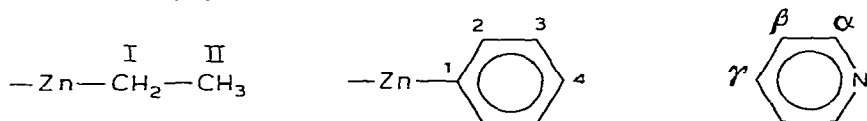
^a This ^1H NMR chemical shift was not reported by Bell and Coates [14].

TABLE 2

^{13}C NMR CHEMICAL SHIFTS ^a (in ppm rel. to TMS) OF THE PYRIDINE COMPLEXES OF ETHYLZINC HYDRIDE AND PHENYLZINC HYDRIDE AND OF THE PARENT $\text{R}_2\text{Zn} \cdot 2\text{py}$ COMPOUNDS

Compound	I	II	1	2	3	4	α	β	γ
$\text{EtZnH} \cdot \text{py}$	1.5	14.4					149.3	124.5	137.8
$\text{PhZnH} \cdot \text{py}$			159.6	140.3	127.1	125.5	149.4	124.7	138.2
$\text{Et}_2\text{Zn} \cdot 2\text{py}$	2.6	13.5					149.1	124.2	136.9
$\text{Ph}_2\text{Zn} \cdot 2\text{py}$			160.6	140.3	127.3	125.6	149.5	124.3	137.4

^a Solutions in C_6D_6 .



or bridging Zn—H stretching vibrations; only some very broad absorptions are observed in the regions 1900–1300, 1150–850 and 650–500 cm^{-1} . Similar broad absorptions are also found in the IR spectrum of ZnH_2 itself, and indicate the presence of bridging hydrogen atoms in both cases.

Both $\text{EtZnH} \cdot \text{py}$ and $\text{PhZnH} \cdot \text{py}$ 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_2 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 $\text{RZnH} \cdot \text{py}$ as 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-pyridyl)zinc hydride, zinc hydride and pyridine [1,15]. In both cases the zinc atoms attain the preferred four-coordination by bridging through hydrogen atoms.

The pyridine complexes of ethylzinc hydride and phenylzinc hydride thermally decompose at about 100°C, as was determined by DTA (heating rate 10°C/min). In the case of $\text{PhZnH} \cdot \text{py}$ the decomposition products are hydrogen, zinc and $\text{Ph}_2\text{Zn} \cdot 2\text{py}$. The thermal decomposition is thus the result of the thermolability of the zinc—hydrogen bond. (A freshly prepared sample of ZnH_2 decomposes into its elements at 115°C.)

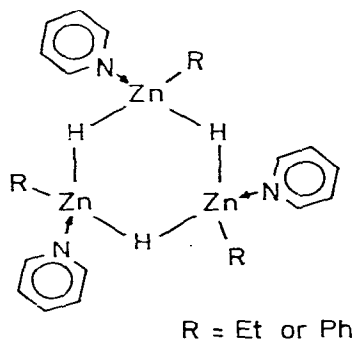
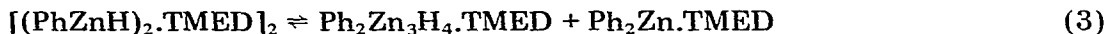


Fig. 1. Proposed structure for trimeric $\text{RZnH} \cdot \text{py}$.

b. Reactions with donor molecules

Reaction of PhZnH.py with the bidentate nitrogen ligand N,N,N',N' -tetramethylethylenediamine (TMED) results in the formation of $(\text{PhZnH})_2\cdot\text{TMED}$, a substance which is soluble in THF and benzene. This compound can also be prepared by treatment of $\text{Ph}_2\text{Zn}\cdot\text{TMED}$ with ZnH_2 in THF. Molecular association studies in benzene indicate that $(\text{PhZnH})_2\cdot\text{TMED}$ exists as a dissociating dimer. One should, however, be careful in interpreting this observed degree of association because the compound also tends to disproportionate. With diethyl ether 1 equivalent of $\text{Ph}_2\text{Zn}\cdot\text{TMED}$ can be easily washed away from the solid $(\text{PhZnH})_2\cdot\text{TMED}$, leaving an insoluble residue (eq. 3).



The remaining compound has the composition $\text{Ph}_2\text{Zn}_3\text{H}_4\cdot\text{TMED}$, as found by elemental analysis and ^1H NMR spectroscopy. It also disproportionates, but the disproportionation constant for this complex must be very small, since large amounts of diethyl ether are necessary to remove more $\text{Ph}_2\text{Zn}\cdot\text{TMED}$ and to leave a still further hydride-enriched residue.

The complex $(\text{EtZnH})_2\cdot\text{TMED}$, prepared from $\text{Et}_2\text{Zn}\cdot\text{TMED}$ and ZnH_2 in THF, is also unstable; washings with pentane or diethyl ether yield $\text{Et}_2\text{Zn}_3\text{H}_4\cdot\text{TMED}$. Like $\text{Ph}_2\text{Zn}_3\text{H}_4\cdot\text{TMED}$, the ethyl analogue is very resistant to disproportionation into $\text{R}_2\text{Zn}\cdot\text{TMED}$ and a hydride-enriched product. The hydride-containing products, formed on disproportionation of $(\text{RZnH})_2\cdot\text{TMED}$ species, are increasingly insoluble in THF.

The reactions of the pyridine complexes of the organozinc hydrides with TMED were carried out in order to obtain bidentate mononuclear $\text{RZnH}\cdot\text{TMED}$ species. The latter complexes, in which the zinc atoms have already reached their favoured four-coordination, may contain terminal zinc-hydrogen bonds. They could, therefore, be expected to be more reactive towards olefins and acetylenes than ZnH_2 , which contains bridging hydrogen atoms and does not react. The ligand-exchange reactions described above, however, did not yield mononuclear $\text{RZnH}\cdot\text{TMED}$. The bidentate nitrogen ligand is apparently unable to break the Zn-H-Zn bridges. The initial complexes $(\text{RZnH})_2\cdot\text{TMED}$ disproportionate, and when $\text{R}_2\text{Zn}\cdot\text{TMED}$ is gradually removed the final product is ZnH_2 in which zinc is tetrahedrally surrounded by bridging hydrogen atoms only.

In this context we also carried out some reactions of zinc hydride with ω -functionally-substituted dialkylzinc compounds, viz. bis(3- N,N -dimethylamino-propyl)zinc and bis(4-methoxybutyl)zinc. These organozinc compounds contain a built-in ligand enabling intramolecular coordination [17]. The internal coordination between zinc and the hetero-atoms present is strong in the case of $\text{Zn}[(\text{CH}_2)_3\text{NMe}_2]_2$ and weak in $\text{Zn}[(\text{CH}_2)_4\text{OMe}]_2$. Bis(3- N,N -dimethylamino-propyl)zinc does react with zinc hydride in THF, but upon attempted isolation, the product appears to dissociate and an ill-defined hydride-containing product results. Bis(4-methoxybutyl)zinc, on the other hand, reacts with ZnH_2 just as Et_2Zn does and, in the presence of two molequivalents of pyridine, $\text{MeO}(\text{CH}_2)_4\text{-ZnH.py}$ is formed. The ^1H NMR chemical shift of the metal-bound hydrogen atom of the latter compound is listed in Table 1. In conclusion, stable RZnH complexes are formed from $\text{R}_2\text{Zn}\cdot 2\text{py}$ and ZnH_2 . When, however, the bidentate

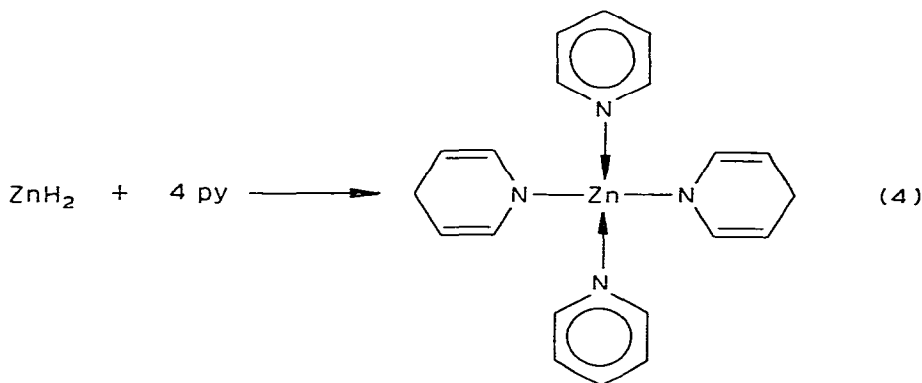
nitrogen ligand TMED is added or a strong intramolecular coordinative interaction is possible, the primary complexes dissociate to varying degrees.

c. Reactions with ketones and aldehydes

The pyridine complexes of the organozinc hydrides react readily with ketones and aldehydes and yield the corresponding alcohols after hydrolysis. No alkylation or arylation products were obtained. We also tested the novel class of compounds, described in this paper, as selective reducing agents for cyclic ketones. Both EtZnH.py and PhZnH.py were allowed to react with 4-tert-butylcyclohexanone, 2-methylcyclohexanone, 3,3,5-trimethylcyclohexanone and camphor in order to study the stereoselectivity of these new hydrides. The results are summarized in Table 3. The first important observation is that the organozinc hydride complexes behave very much like ZnH_2 towards the four ketones studied in spite of the insolubility of the latter in THF. It is also interesting to note, that EtZnH.py and PhZnH.py display a nearly identical stereoselectivity in their reductions. Apparently, since stereoselectivity is very much a function of the steric requirement of the reagent, the ethyl and phenyl group provide the same steric hindrance to attack of the carbonyl groups. Although the RZnH.py compounds are attractive reducing agents they do not, unfortunately, exhibit any unusual stereoselectivity.

d. Reactions with pyridine




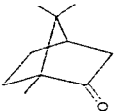
Zinc hydride reacts with pyridine with the ultimate formation of the bis pyridine complex of bis(1,4-dihydro-1-pyridyl)zinc (eq. 4) [1].



In this reaction the hydride atoms originally bound to zinc, are transferred exclusively to the 4-positions of the pyridine molecules. In the RZnH.py complexes both pyridine and Zn-H bonds are present but no reduction of the pyridine ligands is observed. Even when RZnH.py is allowed to react with a small excess of pyridine in THF only a very slow reduction of pyridine takes place. In pure pyridine, however, complete reaction between the Zn-H bonds and the coordinating solvent takes place within 24 hours. In the case of EtZnH.py, the bis pyridine complex of ethyl(1,4-dihydro-1-pyridyl)zinc was isolated on evaporat-

TABLE 3

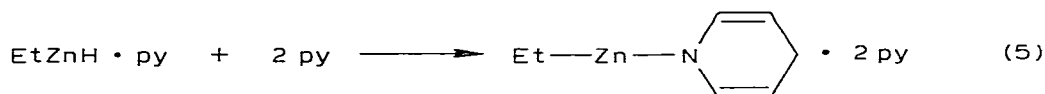
RELATIVE YIELDS^a OF *axial*, *cis* OR *exo* ALCOHOL IN THE REDUCTION OF SOME SUBSTITUTED CYCLOHEXANONES AND CAMPHOR BY ZnH₂ AND THE PYRIDINE COMPLEXES OF ETHYLZINC HYDRIDE AND PHENYLZINC HYDRIDE (THF, room temperature, 24 h)

Reducing agent ^b				
	4-tert. Bu-cyclohexanone	2-Me-cyclohexanone	3,3,5-triMe-cyclohexanone	camphor
ZnH ₂	35	52	85	92
EtZnH · py	16	35	94	97
PhZnH · py	17	35	93	98

^a Normalized as % axial alcohol + % equatorial alcohol = 100%; the ratio is measured by GLC analysis. All reductions are complete.

^b The molar ratio of reducing agent to ketone was 1:1.

ing the solvent and washing of the residue with pentane (eq. 5).

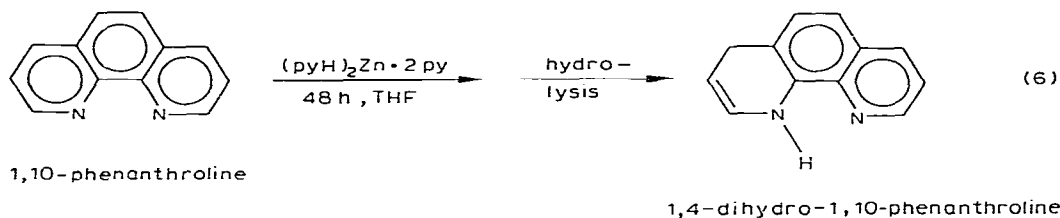


This new compound is soluble in benzene, in contrast to (pyH)₂Zn.2py and (pyH)₂Zn.TMED complexes [1]. A cryoscopic molecular association determination showed that the compound is monomeric in benzene, the molecular weight being concentration-independent. The same product, Et(pyH)Zn.2py, was also obtained from the redistribution reaction between Et₂Zn and (pyH)₂Zn.2py in pyridine. Although the Zn—H bond present in PhZnH.py also reacts in the same specific way with pyridine, no definite complex could be isolated; instead a mixture of (pyH)₂Zn.2py and Ph₂Zn.2py was obtained. Redistribution experiments, as expected, gave the same results. Et(pyH)Zn.2py thus appears to be a stable compound whereas Ph(pyH)Zn.2py disproportionates. Although such a difference is not exceptional in organozinc chemistry, an explanation for it cannot be given at present.

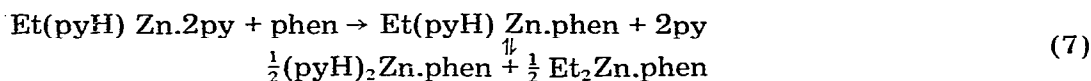
The pyridine complex of ethyl(1,4-dihydro-1-pyridyl)zinc possesses only weak reducing properties. In a typical reaction, in which the molar ratio of reducing agent to ketone was 1 : 1, cyclohexanone was reduced for 44% in 24 hours. In the reactions of (pyH)₂Zn.2py and (pyH)₂Zn.TMED with ketones and aldehydes, it was also noted that the first 1,4-dihydropyridyl group bound to zinc was more reactive than the second [2]. The situation in which one of the two 1,4-dihydropyridyl groups in the latter complexes has reacted, is comparable to that in Et(pyH)Zn.2py.

One of the most striking properties of the 1,4-dihydropyridyl groups bound to zinc (or magnesium) is their highly specific and selective reducing capacity in reactions with aromatic nitrogen heterocycles [3]. E.g. 1,10-phenanthroline (phen) is reduced to 1,4-dihydro-1,10-phenanthroline exclusively (eq. 6); no

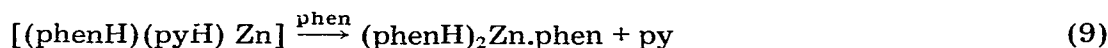
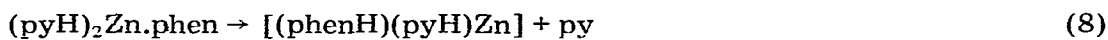
isomers are formed and no further reduction of the pyridine ring takes place.



The metal-bound 1,4-dihydropyridyl group of $\text{Et}(\text{pyH})\text{Zn} \cdot 2\text{py}$ also exhibits this unique specificity and selectivity. Substrates containing one pyridine ring unit, e.g. quinoline or isoquinoline, are reduced to the 1,4-dihydro- and 1,2-dihydro-derivative, respectively. These reduction products have been identified after hydrolysis. When phen, a bidentate ligand containing two pyridine ring units, is used as a substrate, a product identical to that obtained from the reaction between $(\text{pyH})_2\text{Zn} \cdot 2\text{py}$ and phen, viz. $(\text{phenH})_2\text{Zn} \cdot \text{phen}$, was isolated from the reaction mixture. Apparently, the two coordinating pyridine molecules are replaced by phen in a ligand-exchange reaction and the resulting complex $\text{Et}(\text{pyH})\text{Zn} \cdot \text{phen}$ disproportionates into $(\text{pyH})_2\text{Zn} \cdot \text{phen}$ and $\text{Et}_2\text{Zn} \cdot \text{phen}$ (eq. 7).



In an inter- or intra-molecular reaction the coordinated ligand is reduced by a zinc-bound 1,4-dihydropyridyl group [3] (eq. 8 and eq. 9).



The final zinc complex contains two equivalents of reduced phen and one equivalent of the unreduced ligand. The suggested disproportionation of $\text{Et}(\text{pyH})\text{Zn} \cdot 2\text{py}$ in the presence of phen is supported by the fact that disproportionation also occurs when TMED, an "unreducible" bidentate nitrogen ligand, is added to a solution of $\text{Et}(\text{pyH})\text{Zn} \cdot 2\text{py}$ in diethyl ether. From this reaction $(\text{pyH})_2\text{Zn} \cdot \text{TMED}$ has been isolated and characterized.

e. Other reactions

The pyridine complexes of ethylzinc hydride and phenylzinc hydride react with triphenyltin hydride in a protonolysis-type reaction in which the zinc-carbon bond is attacked by the Ph_3SnH hydrogen. Preliminary results showed that the same product, $\text{Ph}_3\text{SnZnH} \cdot \text{py}$, was obtained in both cases. We are expanding our studies on this interesting new complex metal hydride and analogous zinc-transition metal compounds.

Conclusions

$\text{RZnH} \cdot \text{py}$ complexes can be prepared from ZnH_2 , R_2Zn and two equivalents of pyridine in THF. This method is successful for $\text{R} = \text{Et}, \text{Ph}$ or $(\text{CH}_2)_4\text{OMe}$.

However, no reaction took place for $R = \text{cyclopentadienyl}$ and no organozinc hydride was obtained for $R = (\text{CH}_2)_3\text{NMe}_2$. The RZnH.py complexes disproportionate on treatment with TMED, and in a few cases intermediate disproportionation products can be isolated. In conclusion, the formation of RZnH.py compounds is only possible when:

- i. R_2Zn and the corresponding pyridine complex, $\text{R}_2\text{Zn.2py}$ are soluble in THF (ZnH_2 is totally insoluble in this solvent). This is not the case for $R = \text{Cp}$ and therefore no detectable reaction took place. Pyridine is necessary for reaction to occur. The preparation of organomagnesium-hydrides [9–11], however, does not require this nitrogen ligand. In this case the solvent, THF, probably takes over the coordinating role of pyridine.
- ii. formation of a stable complex between R_2Zn and pyridine occurs. This does not happen with bis(3-*N,N*-dimethylaminopropyl)zinc and accordingly no stable product has been obtained in this case.
- iii. an active form of zinc hydride is used. Only zinc hydride freshly prepared from Et_2Zn and LiAlH_4 is useful in the synthesis of RZnH.py complexes. Even when stored at dry ice temperature, ZnH_2 loses its reactivity after a period of two weeks.

So far all attempts to obtain organozinc hydride complexes containing a terminal zinc–hydrogen bond failed. Apparently even the gain in energy from complexation of the electron-deficient organozinc hydrides with strong donor compounds is not enough to break the Zn–H–Zn bridges. A species like PhZn_2H_3 , reported by Ashby and Goel [12], would, therefore, contain three hydrogen bridges for each unit, leaving one coordination place open. This, in view of our results on organozinc hydride chemistry, is not very likely.

The RZnH.py complexes do not exhibit any unusual stereoselectivity as reducing agents towards substituted cyclohexanones. THF-soluble alkylmagnesium hydrides [9] and halogenomagnesium hydrides [18] are also not very selective in their reduction reactions. Dialkylaminomagnesium hydrides [19, 20] and alkoxy- and aroxymagnesium hydrides [21–24], however, function very well as selective reducing agents. This is probably due to the higher effective bulk of the organic groups, since selectivity is very much a function of the steric requirement of the reagent. Similar organic zinc hydrides may thus also exhibit this stereoselectivity in the reduction of cyclic ketones. The main difficulty in the synthesis of such compounds, however, is the insolubility of nearly all $\text{Zn}(\text{OR})_2$ and $\text{Zn}(\text{NR}_2)_2$ compounds.

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 ^1H 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 spectrometer using Nujol suspensions between KBr discs. Decomposition

temperatures were measured by differential thermal analysis using samples sealed in vacuo in glass ampoules. Molecules weights were determined cryoscopically.

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.

Starting materials

Details of the preparation of an active form of ZnH_2 from LiAlH_4 and Et_2Zn in diethyl ether are given in ref. 1 as are the syntheses of the pyridine and TMED complexes of bis(1,4-dihydro-1-pyridyl)zinc. Et_2Zn and Ph_2Zn were prepared according to Noller [25] and Strohmeier [26], respectively. Bis(3-*N,N*-dimethylaminopropyl)zinc and bis(4-methoxybutyl)zinc were synthesized from ZnCl_2 and the corresponding Grignard reagent in THF [17]. Dicyclopentadienylzinc was prepared as described by Lorberth [27]. Commercially available substrates were purified by distillation, sublimation, or recrystallization.

Synthesis of RZnH.py

To a well-stirred suspension of 1.0 g of ZnH_2 (14.8 mmol) in 50 ml of THF at room temperature was added a solution of $\text{R}_2\text{Zn.2py}$ (12 mmol) or R_2Zn (12 mmol) and pyridine (24 mmol) in 50 ml of THF. The mixture was stirred for 1 h during which almost all the zinc hydride dissolved. The small excess of insoluble ZnH_2 was removed by filtration and clear colourless solutions of RZnH.py were obtained. After evaporation of the solvent in vacuo and washing of the resulting residues with pentane (3×50 ml) followed by drying in vacuo (25°C , 0.5 h, 0.1 mm) the RZnH.py complexes were isolated in 95% yield. PhZnH.py is a white solid, whereas EtZnH.py was obtained as a highly viscous yellow liquid. The compounds prepared by the method described above may contain small amounts ($\sim 5\%$) of THF.

Pure RZnH.py complexes were obtained when the same procedure was followed in benzene. The redistribution reactions, however, are slower in this solvent. RZnH.py complexes, prepared in this way, were used for molecular association studies and elemental analysis. Analytical data: PhZnH.py : Found: C, 58.62; H, 4.69; N, 6.02; Zn, 28.69; $\text{C}_{11}\text{H}_{11}\text{NZn}$ calcd.: C, 59.35; H, 4.98; N, 6.29; Zn, 29.37%. The pyridine complex of 4-methoxybutylzinc hydride can only be prepared in THF.

Reaction of PhZnH.py with TMED

An excess of the amine (5 ml) was added to a solution of 1.0 g of PhZnH.py in 40 ml of THF at room temperature. No precipitate was formed. After 30 minutes the solvent was evaporated in vacuo and the sticky residue was washed with pentane (3×50 ml). A white solid, $(\text{PhZnH})_2\text{.TMED}$, resulted which was dried in vacuo (25°C , 0.5 h, 0.1 mm). The same product was obtained from a redistribution reaction between ZnH_2 and $\text{Ph}_2\text{Zn.TMED}$ in THF. Analytical data: $(\text{PhZnH})_2\text{.TMED}$: Found: C, 52.26; H, 6.88; N, 6.81; Zn, 32.22; $\text{C}_{18}\text{H}_{28}\text{N}_2\text{Zn}_2$ calcd.: C, 53.62; H, 7.00; N, 6.95; Zn, 32.43%.

When 1.5 g of $(\text{PhZnH})_2\text{.TMED}$ was washed three times with 70 ml of diethyl ether and once with pentane, the residue analyzed as $\text{Ph}_2\text{Zn}_3\text{H}_4\text{.TMED}$. Analytical

data: $\text{Ph}_2\text{Zn}_3\text{H}_4\cdot\text{TMED}$: Found: C, 45.82; H, 6.41; N, 5.89; Zn, 41.73; $\text{C}_{18}\text{H}_{30}\text{N}_2\text{-Zn}_3$ calcd.: C, 45.94; H, 6.43; N, 5.95; Zn, 41.68%. When $\text{Ph}_2\text{Zn}_3\text{H}_4\cdot\text{TMED}$ was washed 5 more times with 70 ml of diethyl ether, the hydride content of the resulting solid was hardly increased. More washings with ether were necessary to obtain a hydride-enriched product.

Reaction of EtZnH.py with TMED

The reaction of EtZnH.py with TMED proceeds in the same way as the reaction involving of PhZnH.py. When the solvent of a clear THF solution of the reaction product was evaporated in vacuo, $(\text{EtZnH})_2\cdot\text{TMED}$ was obtained quantitatively. Washings with pentane (3×50 ml) yielded $\text{Et}_2\text{Zn}_3\text{H}_4\cdot\text{TMED}$. Analytical data: $\text{Et}_2\text{Zn}_3\text{H}_4\cdot\text{TMED}$: Found: C, 31.84; H, 7.60; N, 7.09; Zn, 52.19; $\text{C}_{10}\text{H}_{30}\text{N}_2\text{Zn}_3$ calcd.: C, 32.07; H, 8.07; N, 7.48; Zn, 52.37%.

Reduction of cyclic ketones with RZnH.py

The reductions were carried out in a 100 ml flask equipped with a magnetic stirrer. To a known amount of reducing agent (ca. 10 mmol) was added the appropriate volume of a 0.2 M solution of substrate in THF. The reactions were carried out at room temperature with a 1 : 1 molar ratio of reducing agent to ketone. Distilled water was added after 24 hours. After filtration and evaporation of most of the solvent, the product mixtures were analyzed by GLC. The experimental conditions for the analysis of the products are described in ref. 2.

Reactions of RZnH.py with pyridine

Both EtZnH.py and PhZnH.py dissolve in pyridine giving an orange solution. After 24 h the reactions between the organozinc hydride complexes and the coordinating solvent are complete. Orange crystals were formed when the solution of phenyl(1,4-dihydro-1-pyridyl)zinc in pyridine was stored at -20°C for two days. These crystals, however, appeared to be a mixture of $\text{Ph}_2\text{Zn}\cdot 2\text{py}$ and $(\text{pyH})_2\text{Zn}\cdot 2\text{py}$. No formation of crystals was observed in the case of the ethyl-(1,4-dihydro-1-pyridyl)zinc pyridine complex. Evaporation of the excess of pyridine yielded a yellow solid which after washing with pentane and drying in vacuo analyzed as $\text{C}_{17}\text{H}_{21}\text{N}_3\text{Zn}$. Analytical data: $\text{Et}(\text{pyH})\text{Zn}\cdot 2\text{py}$: Found: C, 61.02; H, 6.32; N, 12.77; Zn, 19.73; $\text{C}_{17}\text{H}_{21}\text{N}_3\text{Zn}$ calcd.: C, 61.36; H, 6.36; N, 12.63; Zn, 19.65%. ^1H NMR chemical shifts (C_6D_6): $-\text{CH}_2-$, 0.61 (q); $-\text{CH}_3$, 1.53 (t); 1,4-dihydropyridyl group: 2-protons, 6.26 (m); 3-protons, 4.42 (m); 4-protons, 3.47 (m) ppm. ^{13}C NMR chemical shifts (C_6D_6): C_α , -1.5 ; C_β , 14.1; 1,4-dihydropyridyl group: C_2 , 140.2; C_3 , 95.8; C_4 , 24.9 ppm.

The same results were obtained from redistribution reactions between equimolar amounts of $(\text{pyH})_2\text{Zn}\cdot 2\text{py}$ and Ph_2Zn or Et_2Zn in pyridine.

Acknowledgement

This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advancement of Pure Research (ZWO).

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