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*The chemistry of zinc hydrides.*

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THE CHEMISTRY OF ZINC HYDRIDES

by

ANDREW L KASSYK B.Sc

A Thesis submitted to the Council  
for National Academic Awards in  
partial fulfilment of the  
requirement for PhD.

Sponsoring establishment,  
Sheffield City Polytechnic.

Collaborating establishment, I C I  
Catalysis Division, Billingham.

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A. Abstract

The thesis reviews structural and chemical properties of complex zinc, magnesium and beryllium hydrides. Least is known about complex zinc hydrides and this thesis records the results of a range of reactions between zinc dihydride and substrates containing acidic protons or unsaturated bonds.

Zinc dihydride reacts with compounds containing N-H, O-H, S-H and P-H bonds. The hydride products ranged from dimers, in cases where intramolecular steric effects allowed this, to polymers where intramolecular coordination bonds could not be formed e.g.  $[m\text{-Me}_2\text{NC}_6\text{H}_4\text{OZnH}]_n$ .

Several unusual complex zinc hydrides were obtained, where the reacting substrate appeared to undergo condensation before reacting with the zinc dihydride e.g. a product with a stoichiometry of  $(\text{C}_9\text{H}_{17}\text{O})_2\text{ZnH}$  was obtained from the reaction of zinc dihydride with camphor.

Zinc dihydride was found to react unexpectedly with diethylamine. The expected product,  $(\text{Et}_2\text{NZnH})_x$ , was not obtained. Instead, a coordination polymer,  $[\text{Et}_2\text{NHZnH}_2]_n$ , was obtained.

Attempts at trapping a monomeric species from the reaction, using N,N,N',N'-tetramethylethylenediamine failed.

Zinc dihydride was found to undergo exchange with zinc chloride in the presence of donor solvents to give chlorozinc hydride complexes.

In general, the structural features exhibited by complex zinc hydrides were, as expected, terminal zinc hydrogen bonds and four coordinate zinc in a tetrahedral environment.

The reactivity of complex zinc hydrides towards ketones was intermediate to that of lithium tetrahydridoaluminate and zinc dihydride. This was explained on the basis of steric hindrance and electronic repulsion in the transition state. Addition of hydride took place at the carbonyl group in trans-cinnamaldehyde rather than at the alkene, while with phenylacetylene, matters were complicated by competing elimination reactions. Product distribution was controlled by steric effects in the complex zinc hydrides. A possible mechanism for the addition of  $[\text{Me}_2\text{NC}_2\text{H}_4\text{OZnH}]_2$  to trans-2-pentene was advanced on the basis of kinetic experiments.

## B. Statement of Objectives

The objectives of the study presented here were to obtain complex zinc hydrides which were soluble in inert organic solvents by the reaction of zinc dihydride with ligands containing electron rich functional groups and acidic protons or unsaturated functions. The behaviour of these complex zinc hydrides towards organic compounds containing unsaturated functions was then to be investigated.

### C. Acknowledgements

The author wishes to thank Dr.N.A.Bell and Dr.J.R.Jennings for all their help and encouragement during the progress of this work. Thanks are also due to other members of the chemistry department at Sheffield City Polytechnic for helpful discussions and suggestions. The help of the technical staff of the chemistry department at Sheffield City Polytechnic, particularly Mr.P.Ash and Mr.B.Christian as also greatly appreciated.

Finally my thanks go to everyone who encouraged me while I was writing my thesis and to Ms. J.Harbutt for typing it.

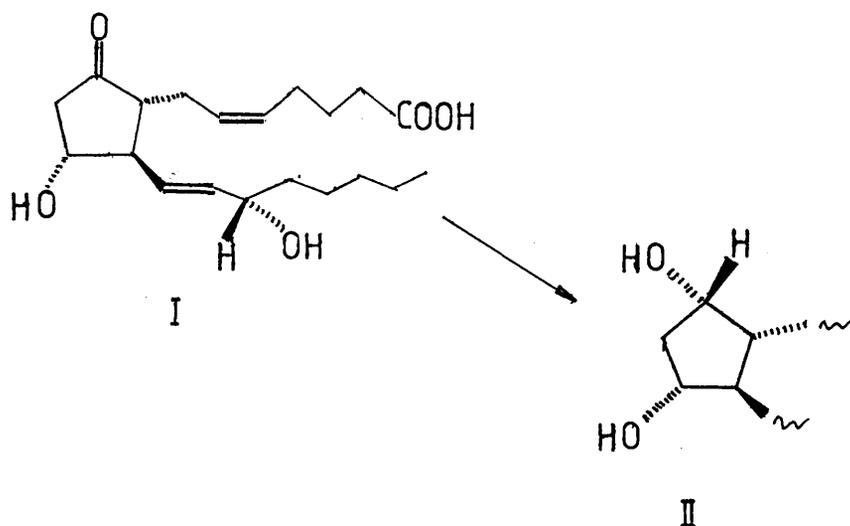
1.1 Factors which affect the reducing power of complex metal hydrides

Complex metal hydrides are a well known class of compounds, but those which have found a ready application in organic chemistry as reducing agents are based on the group III hydrides, borane ( $\text{BH}_3$ ) and alane ( $\text{AlH}_3$ ), e.g. sodium tetrahydridoborate and lithium tetrahydridoaluminate<sup>1</sup>.

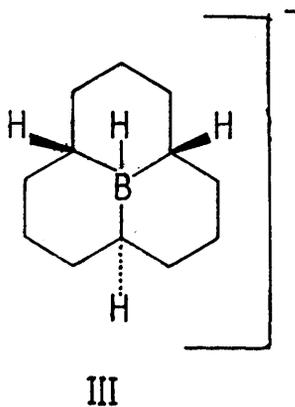
Lithium tetrahydridoaluminate and sodium tetrahydridoborate may be said to represent opposite ends of the strength of reducing agents. Lithium tetrahydridoaluminate reacts with protic solvents, usually violently, and reduces a wide variety of organic functional groups while sodium tetrahydridoborate is commonly employed in aqueous ethanol or methanol, since it reacts only very slowly with these solvents and it will only reduce aldehydes or ketones.

Complex molecules with many functional groups are of interest to the organic chemist and reducing agents are employed in most synthetic strategies. Problems arise when a particular functional group has to be reduced without reducing other functional groups present.

As an example consider the reduction of I to give II.



The use of  $\text{LiAlH}_4$  would result in the reduction of other functional groups present and the correct stereochemistry would not be maintained. Such a transformation has been achieved in 99% yield by the use of the very sterically hindered borane<sup>2</sup>, lithium perhydro-9b-boraphenyl hydride which has the following structure (III)<sup>3</sup>.



Thus by altering the steric environment around the metal in the complex metal hydride it is possible to alter its

reducing behaviour. The effect of the increase in steric crowding around the metal atom can also be seen in Table 1 which shows how substituted hydridoaluminates react with various organic functional groups<sup>1</sup>. Increasing the steric

Table 1. Reducing agents.

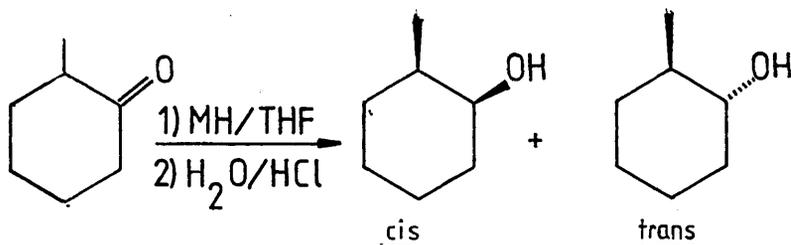
Substrate	(Bu <sup>t</sup> O) <sub>3</sub> AlH <sup>-</sup>	(MeO) <sub>3</sub> AlH <sup>-</sup>	AlH <sub>4</sub> <sup>-</sup>
$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{H} \end{array}$	*	*	*
$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{R}' \end{array}$	*	*	*
$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{Cl} \end{array}$	*	*	*
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{H}_2\text{C}-\text{CH}_2 \end{array}$	-	*	*
$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{O}-\text{R}' \end{array}$	-	*	*
$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{OH} \end{array}$	-	*	*
$\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{NR}'_2 \end{array}$	-	*	*
R-C≡N	-	*	*

Key: \* reduction

- no reduction

environment around the metal atom decreases the reactivity of the reducing agent, thus the very bulky tri-tertiarybutoxy-hydridoaluminate reduces only aldehydes, ketones and acyl chlorides while the trimethoxyhydridoaluminate reacts similarly to the tetrahydridoaluminate.

The steric effect of substituents on the metal atom is not the only factor which affects the reducing behaviour of complex metal hydrides. Changing the central metal atom can have a drastic effect on the product distribution of a reduction. Table 2 shows the effect of different complex metal hydrides on the reduction of 2-methylcyclohexanone<sup>1</sup> in the following reaction



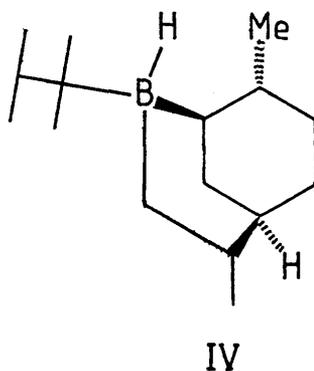
The very sterically hindered hydridoaluminate gives the more sterically favoured trans alcohol in high yield while all the sterically hindered hydridoboronates, which might also be expected to give the trans alcohol on steric grounds, give the less stable, sterically unfavourable, cis alcohol. This is presumably due to electronic factors in the transition state.

Table 2.

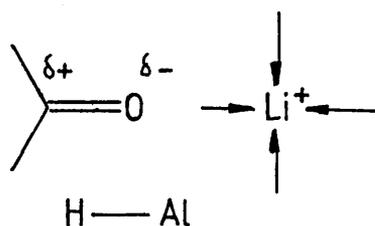
Reducing agent	cis-alcohol	trans-alcohol
$\text{NaBH}_4$	31%	69%
$\text{LiAlH}(\text{Bu}^t\text{O})_3$	27%	73%
$\text{K}(\text{Pr}^i\text{O})_3\text{BH}$	92%	8%
$\text{PBPH}^a$	97%	3%
$\text{TLBH}^b$	94%	6%
$\text{Li}(\text{Bu}^s)_3\text{BH}$	99%	-

a) PBPH - lithium perhydro-9b-boraphenanyl hydride<sup>3</sup> III

b) TLBH - Thexyllimonylborane<sup>4</sup> IV



The metal counter ion also affects the product distribution presumably by polarising the ketonic double bond prior to attack by the hydride



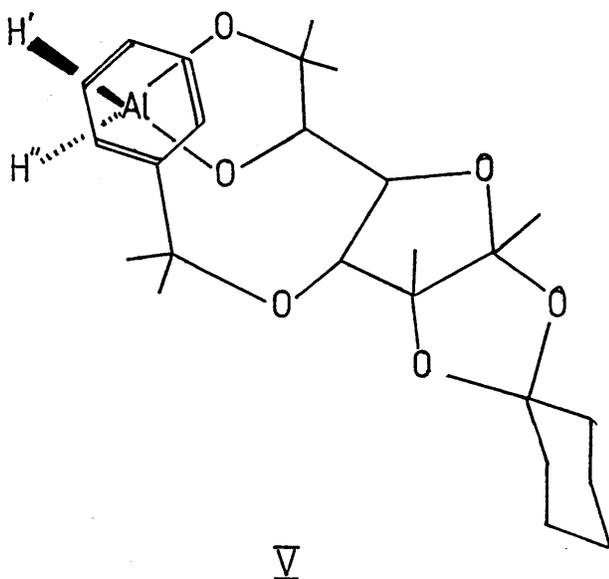
Experiments in which the metal counterion is removed by sequestering agents such as crown ethers and cryptands<sup>5</sup> shows that the reaction rate is decreased and that regioselectivity is altered (or reversed) by the addition of such sequestering agents to the reaction mixture.

Two other factors, changes of solvent and temperature, have an effect on product distribution. Of the two, the change in solvent from say ether to tetrahydrofuran has the greater effect. For  $\text{LiAlH}_4$  and  $\text{NaBH}_4$  reductions, coordinating solvents and low temperatures were found to increase the selectivity of the reaction<sup>6</sup>. The same should hold true for more complex metal hydrides.

## 1.2 Asymmetric reduction by complex metal hydrides

Particularly spectacular effects have been achieved with complex metal hydrides obtained from the reaction of chiral alcohols with  $\text{LiAlH}_4^{7,8}$ .

The lithium tetrahydridoaluminate-3-O-benzyl-1,2-O-cyclohexylidene- $\alpha$ -D-glucofuranose complex is thought to have the following structure<sup>8</sup>.



$\text{H}'$  is shielded by the benzyl group thus  $\text{H}''$  is responsible for reduction. The approaching ketone orientates in such a way as to keep the carbonyl oxygen furthest away from the oxygen atoms in the aluminium complex. Upon transfer of the hydride moiety the (S)-carbinol is obtained. Optically active (S)-alcohols with 40% enantiomeric excess have been obtained using this complex. If  $\text{H}''$  is replaced by an ethoxy group<sup>9</sup> then the (R)-carbinol is obtained with a

maximum 70% enantiomeric excess.

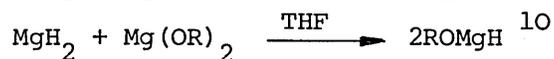
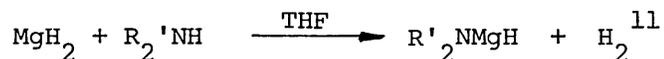
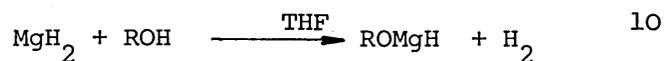
Thus by controlling the steric environment around the metal-hydrogen bond and by changing the metal it should, in theory at least, be possible to achieve any desired reduction with good selectivity and high yield.

We have so far dealt exclusively with group III metal hydrides. Group II metals are also well known in organic chemistry. Magnesium is at the basis of those ubiquitous compounds, the Grignard reagents, and zinc is to be found in the Reformatsky reaction among others.

However, until recently complex zinc and magnesium hydrides were virtually unknown and the organic chemistry of those which had been discovered had been almost totally ignored on the grounds that the metal dihydrides were insoluble in any solvent with which they did not react and were therefore ill suited to the needs of the organic chemist. The chemistry of magnesium dihydride has since received some attention and is discussed in section 1.3. Beryllium dihydride has also received attention and its chemistry is reviewed in section 1.4. Hydrides of cadmium and mercury are known<sup>79</sup> but they decompose very readily even at low temperature ( $-40^{\circ}\text{C}$ ) and there is no evidence in the literature as yet, of organocadmium or mercury hydrides. The chemistry of zinc dihydride forms the main body of this work.

### 1.3 Magnesium dihydride and its complexes

The chemistry of magnesium dihydride and its complexes has been studied in some depth. Alkoxy, aryloxy and aminomagnesium hydrides have been synthesised according to the following reaction schemes.



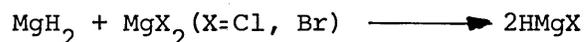
where: R = Me, Pr<sup>i</sup>, Bu<sup>t</sup>, Bu<sup>t</sup>CH<sub>2</sub>, PhCH<sub>2</sub>CH<sub>2</sub>, cyclo C<sub>6</sub>H<sub>11</sub>,

Ph, Ph<sub>3</sub>C, Ph<sub>2</sub>(Me)C, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-diisopropylphenyl  
and 2,6-ditertiarybutyl-4-methylphenyl.

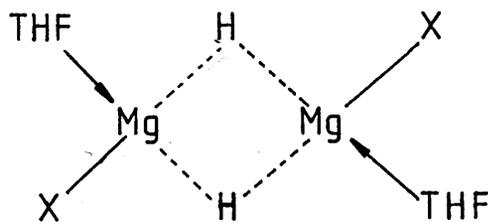
R' = Et, Pr, Pr<sup>i</sup>, Bu<sup>n</sup>, Bu<sup>s</sup> and Ph

R'<sub>2</sub>N = piperidinyl, 2,6-dimethylpiperidinyl, Pr<sup>i</sup>(Me)N  
and Me<sub>3</sub>Si(t-Bu)N.

Other classes of complex magnesium hydride have also been prepared. Halomagnesium hydrides have been prepared by the redistribution reaction of magnesium dihydride with the anhydrous magnesium halide in tetrahydrofuran at room temperature<sup>12</sup>.



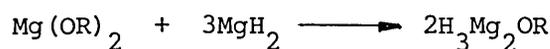
These compounds are believed on the basis of IR spectroscopic evidence to have the following structure VI in dilute THF solution.



## VI

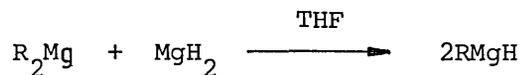
In more concentrated tetrahydrofuran solution they exist as trimers or are even more highly associated<sup>12</sup>.

ROMg<sub>2</sub>H<sub>3</sub> compounds have also been prepared<sup>13</sup> by the following scheme.



No information is available on the structure of such complexes but X-ray powder diffraction studies show the complexes to be discrete compounds and not physical mixtures of HMgOR and MgH<sub>2</sub>.

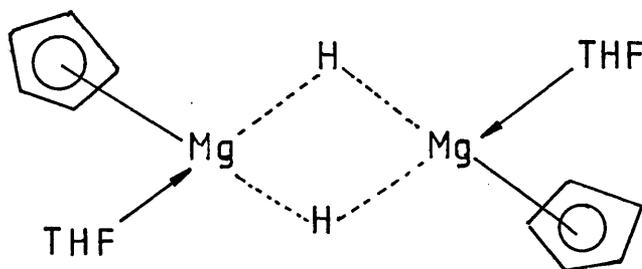
Organomagnesium hydrides have also been prepared<sup>14</sup> by redistribution reactions



where R = Me, Et, isopropyl, cyclopentadienyl.

MeMgH exhibits increasing molecular association with increasing concentration in THF, but cyclopentadienylmagnesium hydride was found to crystallize as CpMgH·THF and was suggested to have the following structure on the basis of infrared and

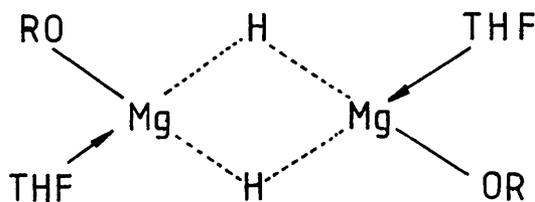
n.m.r. spectroscopic evidence and colligative properties.



VII

The hydridic hydrogens were found to resonate at 5.3 ppm downfield from TMS in the nuclear magnetic spectrum of a THF solution of this compound<sup>23</sup>. Solutions of RMgH in THF were stable except for EtMgH which cleaved the solvent. The reaction of Me<sub>2</sub>Mg with MgH<sub>2</sub> in one to three molar ratio results in the formation of MeMg<sub>2</sub>H<sub>3</sub><sup>14</sup>.

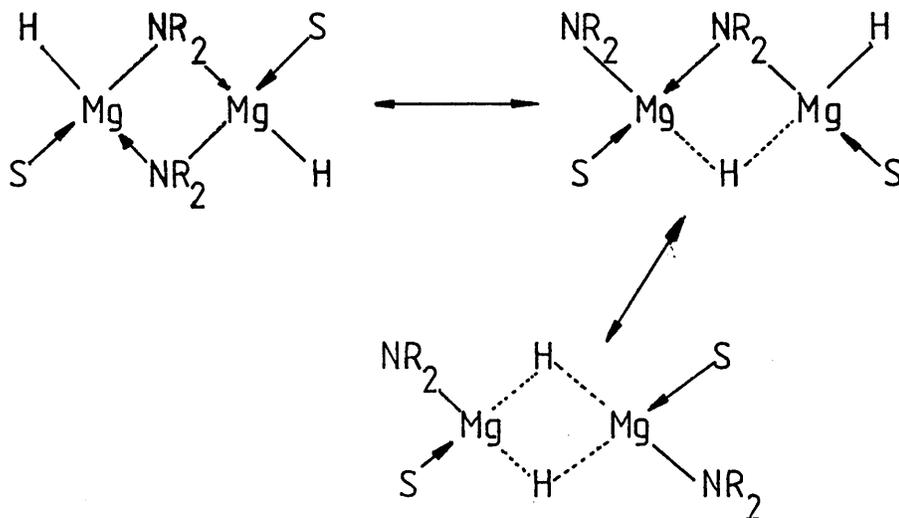
Generally, alkoxy and aroxy magnesium hydrides are dimeric in dilute THF solution<sup>10</sup> but dialkylaminomagnesium hydrides show increasing association in more concentrated solutions<sup>11</sup>. The alkoxy magnesium hydrides are believed to have bridging hydride atoms in the following type of structure



VIII

The infrared spectra of these compounds show broad absorptions from 1480 - 1400  $\text{cm}^{-1}$ . Some doubt must therefore be attached to the above structure since the terminal stretching vibration of the Mg-H bond is found to lie between 1497 and 1598  $\text{cm}^{-1}$  in the electronic vapour phase spectrum of  $\text{MgH}^{15}$  and the bridging Mg-H stretch would therefore be expected to occur at a much lower wavenumber.

Dialkylaminomagnesium hydrides show magnesium-hydride stretching vibrations in the range 1630 to 1580  $\text{cm}^{-1}$ . These are almost certainly due to terminal magnesium-hydridic hydrogen bonds. The authors who prepared these compounds suggest<sup>11</sup> that in solution both dialkylamino groups and hydride hydrogens act as bridging groups, as well as competing with the solvent for coordination to the metal.



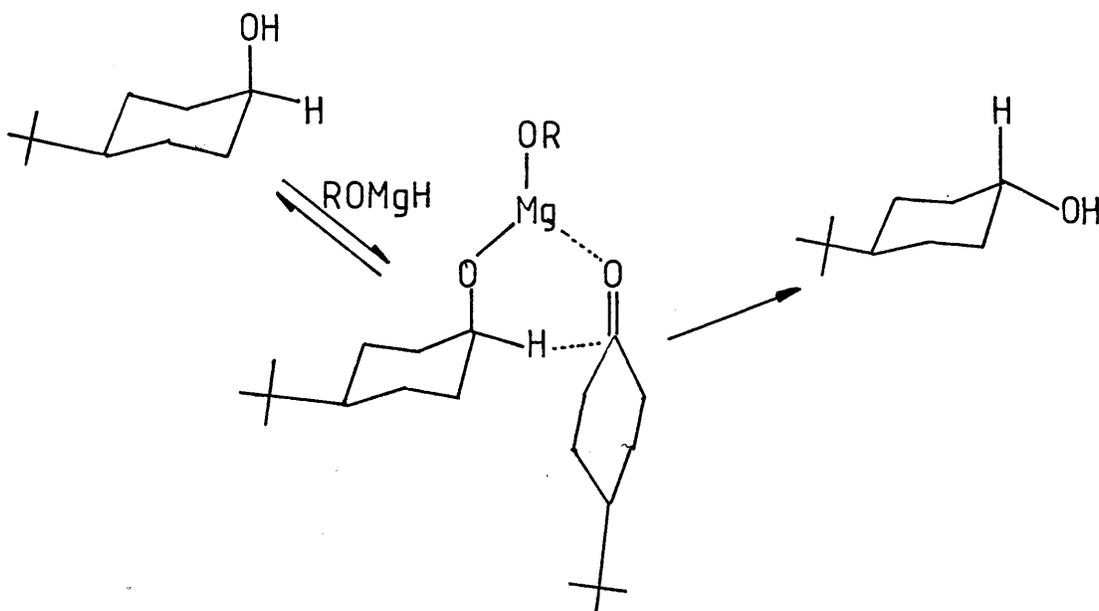
This may account for the increased association with increased concentration shown by these compounds.

### 1.3.1 The organic chemistry of complex magnesium hydrides

The reduction of cyclic ketones by magnesium dihydride and complex magnesium hydrides has been studied<sup>13,16-19</sup>. The reduction of cyclic ketones by magnesium dihydride depends on the molar ratio of magnesium dihydride to ketone. Different workers have reported different product distributions for reductions of the same ketone by  $MgH_2$ <sup>13,20</sup>. Presumably the intermediate complex magnesium hydrides formed during the reaction determine the stereochemistry of the reaction.

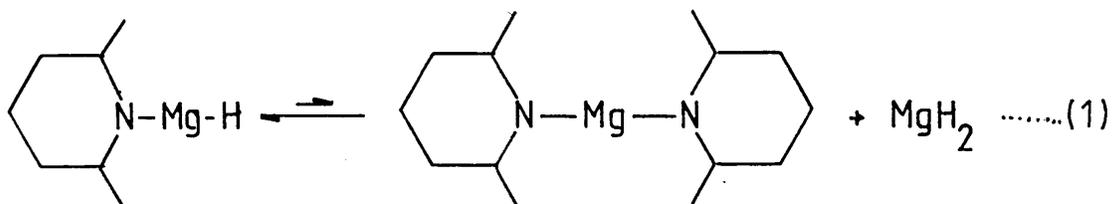
Alkoxymagnesium hydrides have been found to reduce cyclic and bicyclic ketones in excellent yield under mild conditions<sup>16,17</sup>. Reductions proceed with high stereoselectivity. The stereoselectivity is controlled by the steric requirement of the alkoxy group and the degree of molecular association of the hydride in solution.

An unusual feature in complex magnesium hydride is that the product mixture can equilibrate by a Meerwein-Ponndorf process through an  $Mg(OR)_2$  intermediate thus -

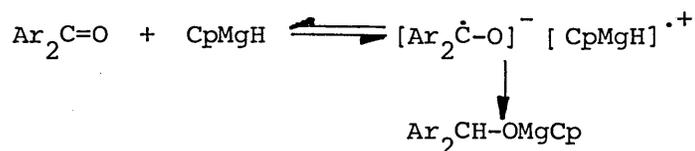


This kind of equilibration has not been seen in either aluminohydride or borohydride reductions.

Trimethylsilyl-*t*-butylaminomagnesiumhydride<sup>18</sup> was the most selective aminomagnesium hydride studied, giving the less stable isomeric alcohols in high yields. This is not surprising when the steric bulk of the reducing agent is considered. More surprising is the lack of stereoselectivity of the 2,6-dimethylpiperidino-magnesium hydride which also has a large steric requirement. It is believed that this complex reducing agent exists in an equilibrium (1) in solution and the reducing agent is the one which reacts faster with the organic substrate, in this case  $\text{MgH}_2$ .



The reaction of cyclopentadienylmagnesium hydride with dimesitylketone was found to proceed with the formation of an intermediate ketyl by a simple electron transfer mechanism



These solvent separated radical pairs were unusually stable, persisting in solution for several days. Similar reactions were reported with polyaromatic hydrocarbons and trityl halides<sup>21</sup>.

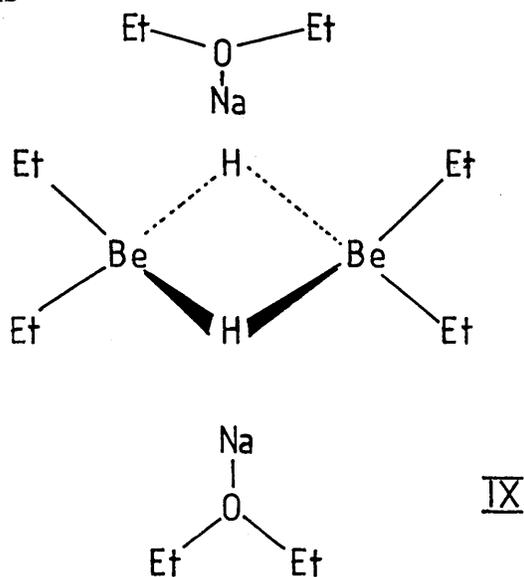
Magnesium dihydride has also been found to react with pyridine. A 1:1 molar ratio of pyridine to magnesium dihydride gave a complex of stoichiometry  $\text{HMgNC}_5\text{H}_6$ <sup>21</sup>. Reduction of pyridine by this complex gave exclusively a bis(1,4-dihydropyridyl)magnesium bis pyridine complex<sup>22</sup>. If the pyridine was present in five-fold excess then a complex was obtained with a stoichiometry of  $\text{H}_3\text{Mg}_2\text{NC}_5\text{H}_6$ <sup>21</sup>. However, nothing is known about the structure of these complexes.

## 1.4 Beryllium hydride and its complexes

The chemistry of beryllium hydrides have been relatively well studied and both anionic and neutral complex beryllium hydrides are known.

### 1.4.1 Anionic hydride complexes of beryllium

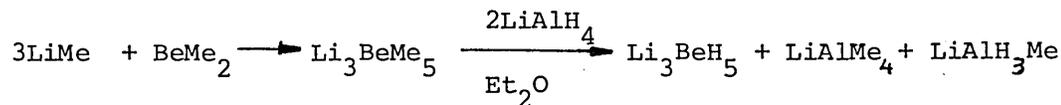
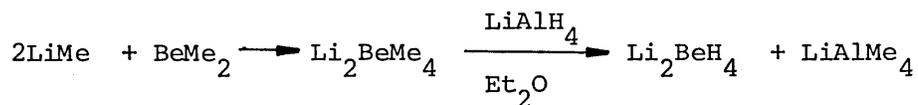
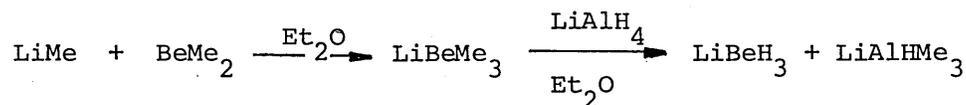
Complexes of the type  $MR_2BeH$  ( $M = Li$ ,  $R = Et$ <sup>24</sup>;  $M = Na$ ,  $R = Me$ <sup>25</sup>,  $Et$ <sup>26</sup>,  $Pr^n$ ,  $Pr^i$ ,  $Bu$ <sup>27</sup>) have been synthesised from the beryllium dialkyls and the alkali metal hydrides in boiling diethylether. The complex  $LiBe(Bu^i)_2H$  has been prepared by a metathetic reaction of the sodium complex with lithium bromide in diethylether<sup>27</sup>. The structure of the etherate of sodium diethylberyllium hydride has been determined by X-ray diffraction methods<sup>28</sup> and it has been found to consist of  $[Et_4Be_2H_2]^{2-}$  ions with diethylether coordinating to the sodium cations



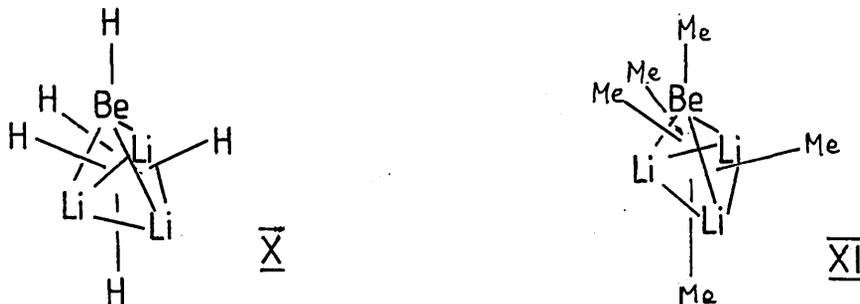
Such complexes are soluble in coordinating solvents.

Ditert. butylberyllium was found to react with sodium hydride to give a crystalline complex with a stoichiometry of  $\text{Na}(\text{OEt})_4 \text{Bu}_4^t\text{Be}_2\text{H}$ .<sup>27</sup> The tertiary butyl groups are believed to inhibit the formation of  $\text{BeH}_2\text{Be}$  bridges due to steric crowding around the beryllium atoms.<sup>27</sup>

Mixed metal hydrides are also known. Complexes of the type  $\text{M}_2\text{BeH}_4$  ( $\text{M} = \text{Li}, \text{Na}$ ) have been prepared by heating the product from the reaction of  $\text{MR}_2\text{BeH}$  with  $\text{BeCl}_2$  in 4:1 molar ratio at  $180^\circ\text{C}$  after removal of  $\text{NaCl}$ .<sup>29</sup> The compounds  $\text{M}_2\text{BeH}_4$  were characterised by their X-ray diffraction patterns and they were found to be insoluble in solvents with which they did not react. Preparation of  $\text{MBeH}_3$  was attempted in a similar manner<sup>29</sup> using a 3:1 molar ratio of hydride to chloride but in all cases a mixture of  $\text{M}_2\text{BeH}_4$  and  $\text{BeH}_2$  was obtained. The following lithium hydridoberyllates,  $\text{LiBeH}_3$ ,  $\text{Li}_2\text{BeH}_4$  and  $\text{Li}_3\text{BeH}_5$  have been synthesized<sup>30</sup> by reacting the corresponding methyl complexes of methyllithium and dimethylberyllium with  $\text{LiAlH}_4$  in diethyl ether according to the following schemes



These complexes were characterised by elemental analysis, X-ray powder diffraction patterns and DTA-TGA analysis. These complexes were believed to have structures similar to the corresponding methyl complexes<sup>31</sup>, e.g.



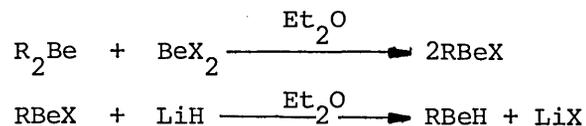
#### 1.4.2 Neutral organoberyllium hydride complexes

Organoberyllium hydrides have been synthesised by a variety of routes. The reaction of alkalimetal dialkylberyllium hydrides with beryllium chloride in diethyl ether resulted in solutions in which the complex had a stoichiometry of  $R_4Be_3H_2$ <sup>25</sup>.

Viscous oils were obtained when the removal of solvent from these solutions was attempted and these oils were found to contain diethyl ether which could not be totally removed. Reaction of such an oil of stoichiometry  $Me_4Be_3H_2$  with the donor molecule  $Me_3N$  resulted in the formation of a mixture of products,  $Me_2BeNMe_3$  and  $(MeBeHNMe_3)_2$ <sup>25</sup>.

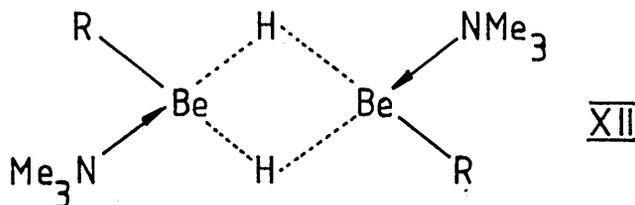
Solutions of stoichiometry  $RBeH$  ( $R = Me, Et, Bu^t, n-C_5H_{11}, Ph, o-Tol, m-Tol$ ) were prepared from the reaction of equimolar quantities of  $R_2Be$  and  $BeX_2$  ( $X = Cl, Br$ ) with  $LiH$  in boiling

diethyl ether<sup>32-34</sup> according to the following scheme

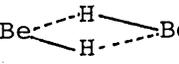


Attempts to obtain RBeH free from diethyl ether failed even after heating under reduced pressure. Some etherate complexes have been isolated however, e.g. (MeBeH.OEt<sub>2</sub>)<sub>2</sub> which was found to be dimeric in benzene solution<sup>34</sup> as was (Bu<sup>i</sup>BeH.THF)<sub>2</sub><sup>35</sup>.

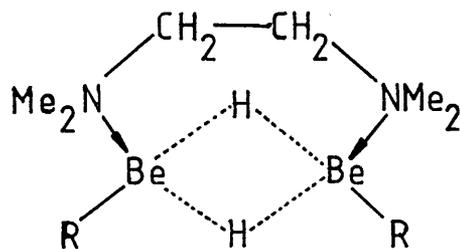
A range of trimethylamine complexes of organoberyllium hydrides (RBeH.NMe<sub>3</sub>)<sub>2</sub> (R = Me, Et, Ph, n-C<sub>5</sub>H<sub>11</sub>, o-tol, m-tol) are known<sup>30-32, 36, 37</sup>. They have all been found to be dimeric in benzene solution and are believed to have the following structure



An infrared spectrum of (MeBeH.NMe<sub>3</sub>)<sub>2</sub> showed<sup>37</sup> a band at 1344 cm<sup>-1</sup> in cyclohexane which shifts to 1020cm<sup>-1</sup> in (MeBeD.NMe<sub>3</sub>)<sub>2</sub>. This band was assigned to a stretching vibration of the BeH<sub>2</sub>Be bridge.

These complexes have been studied by <sup>1</sup>H nmr spectroscopy and the splitting of the trimethylamine proton resonance has been attributed to cis-trans isomerism around the Be—Be bridge<sup>39</sup>. A bridging hydride resonance has been observed

in the  $^1\text{H}$  nmr spectrum of  $(\text{EtBeH.NMe}_3)_2$  but this resonance was not detected in any other  $(\text{RBeH.NMe}_3)_2$  complexes. The failure to detect this resonance was attributed to an unfavourable relaxation time for the bridging hydridic hydrogens on account of their proximity to the beryllium nuclei, which have a quadrupole moment ( $I = 3/2$ ) and which are in an unsymmetrical electrical environment<sup>39</sup>. The  $\text{BeH}_2\text{Be}$  bridge is strong enough to withstand cleavage by bidentate donor ligands such as TMEDA and 1,2-dimethoxyethane. Complexes of the following type  $(\text{RBeH})_2\text{TMEDA}$  are known where  $\text{R} = \text{Me}, \text{Et}, \text{Bu}^i, \text{Bu}^s, \text{Bu}^t, n\text{-C}_5\text{H}_{11}, \text{Me}_3\text{CCH}_2, \text{Ph}, o\text{-Tol}, m\text{-Tol}$ <sup>25,32,35,37,40</sup>. and of these  $(\text{RBeH})_2\text{TMEDA}$  complexes when  $\text{R} = \text{Me}$  and  $\text{Bu}^t$  they have been found to be monomeric in benzene solution<sup>35,37</sup>. They are believed to have the following structure



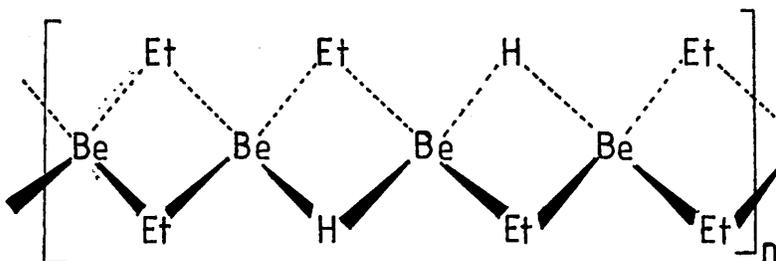
XIII

The complex  $(\text{MeBeH})_2\text{DME}$  which was obtained as an oil<sup>25</sup> probably has a similar structure.

A phosphine-organoberyllium hydride  $(\text{PhBeH.PMe}_3)_2$  is also known but this dissociates<sup>36</sup> with loss of phosphine.

Other routes to organoberyllium hydrides have been investigated. Alkyl hydrogen exchange reactions between  $\text{R}_2\text{Be}$  ( $\text{R} = \text{Me}, \text{Et}$ ) and  $\text{Et}_3\text{SnH}$  in diethyl ether yielded  $\text{RBeH}$  compounds which were characterised as their trimethylamine complexes<sup>25,36</sup> but if non-coordinating solvents were used, complexes contaminated by tin compounds were obtained.

Pyrolysis of secondary or tertiary alkyl organoberyllium compounds leads to the elimination of alkenes to form organoberyllium hydrides, e.g. on heating ditertiarybutylberyllium to  $110^\circ\text{C}$ , 2-methyl prop-2-ene was eliminated leaving a mixture of isobutyl and tertiary butylberyllium hydrides.<sup>35</sup> Pyrolysis of  $(\text{RBeBu}^t)_2$  ( $\text{R} = \text{o-tol}, \text{m-tol}$ ) in boiling xylene leads to the formation of  $\text{RBeH}$ <sup>32</sup>.  $\text{Et}_3\text{Be}_2\text{H}$  was obtained by heating  $(\text{EtBeBu}^t)_2$  with diethylberyllium<sup>37</sup>. This compound was believed to be polymeric and on the basis of infrared spectroscopy it was assigned the following structure

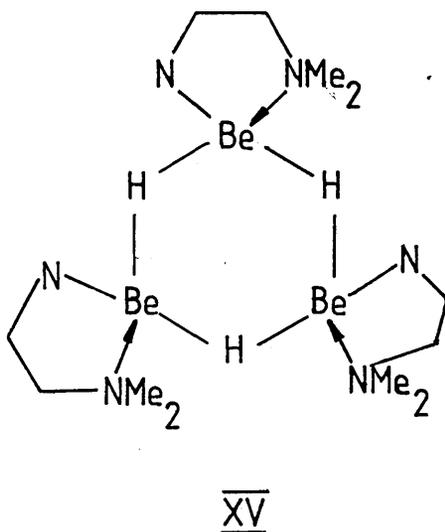


XIV

Another route to RBeH compounds was found when equimolar mixtures of  $R_2Be$  and  $BeCl_2$  were allowed to react with  $NaEt_3BH$  in diethyl ether<sup>36</sup>. After filtration from  $NaCl$ , triethylborane was evaporated off and RBeH ( $R = Et, Ph^{36}, Me_3CCH_2^{40}$ ) complexes were obtained.

Complex beryllium hydrides formed by the reaction of beryllium dihydride with compounds containing an acidic hydrogen atom or by addition to a carbon-heteroatom double bond are also known<sup>41</sup>.

Beryllium dihydride and trimethylethylene diamine eliminate hydrogen yielding a crystalline complex which was found to be trimeric in benzene solution. The following structure was proposed<sup>41</sup> for this complex.



More recent work has shown that in the solid state this complex has a structure<sup>42</sup> similar to that of the zinc analogue<sup>43</sup>.

Benzophenone was reduced by beryllium dihydride and in tetrahydrofuran the intermediate, diphenylmethoxyberyllium hydride was isolated. In benzene solution the complex was found to be oligomeric with a degree of association of  $7 - 8^{41}$ .

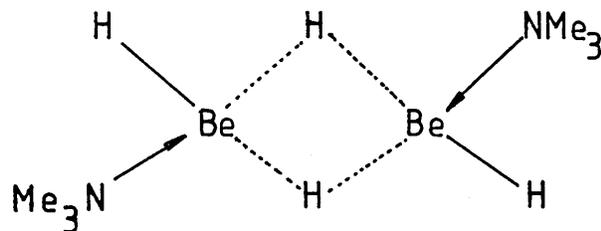
Similarly benzylideneaniline was reduced by beryllium dihydride and a complex amino beryllium hydride was isolated as a THF adduct. This complex (HBeNPhCH<sub>2</sub>Ph.THF) had a much lower degree of association in benzene solution but the fractional degree of association (1.2-1.3) was thought to be due to dissociation of the complex<sup>41</sup>. It was also found that 4-dimethylaminopyridine could replace THF in the aminoberyllium hydride but the new complex was too insoluble in benzene for its degree of association to be determined<sup>41</sup>.

Beryllium dihydride forms complexes with tertiary amines. Me<sub>3</sub>NBeH<sub>2</sub> was prepared in low yield by the reaction of the diethylaluminium hydride-diethylberyllium adduct with an excess of trimethylamine<sup>44</sup>.



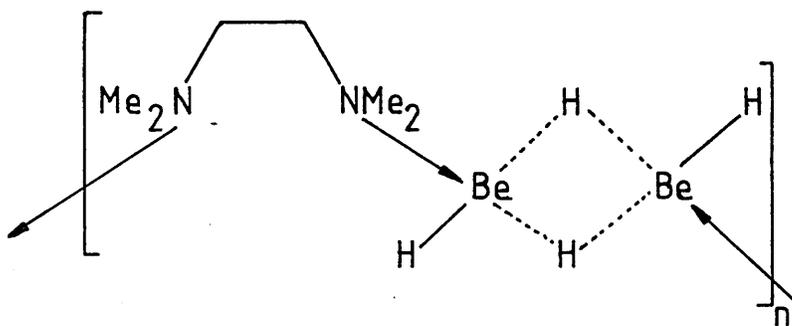
The complex was moderately soluble in benzene, but in diethyl ether, the complex first dissolved and then precipitated out having lost some trimethylamine. The complex was found to be dimeric in benzene solution and together with evidence from infrared spectroscopy which showed a BeH<sub>2</sub>Be bridge stretching mode at  $1340 \text{ cm}^{-1}$  this suggests that the structure of the

complex is



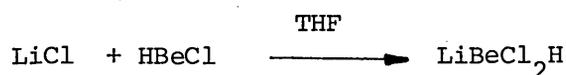
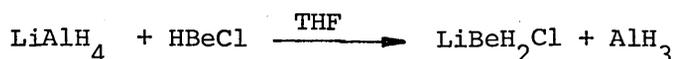
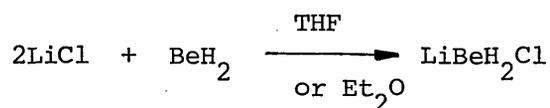
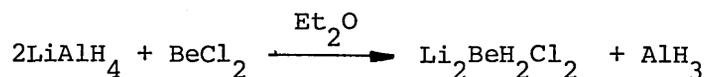
XVI

Other tertiary amine complexes were prepared by heating an excess of the tertiary amine with beryllium dihydride at  $120^{\circ} - 180^{\circ}\text{C}$  for some time or by ball-milling the reactants in a sealed vessel. Both of these methods gave high yields of product<sup>44</sup>, and complexes of the following tertiary amines were obtained:  $\text{Me}_3\text{N}$ ,  $\text{EtNMe}_2$ ,  $\text{Et}_2\text{NMe}$ ,  $\text{Et}_3\text{N}$ ,  $\text{Me}_2\text{NCH}_2\text{Ph}$ ,  $(\text{CH}_2)_4\text{NMe}$ ,  $(\text{CH}_2)_5\text{NMe}$ , TMEDA. All of these complexes were found to be dimeric in benzene with the exception of  $\text{TMEDA}\cdot 2\text{BeH}_2$  which was believed to be a linear polymer with a structure similar to that which methyl beryllium hydride TMEDA adduct was believed<sup>45</sup> to have.

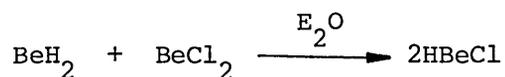
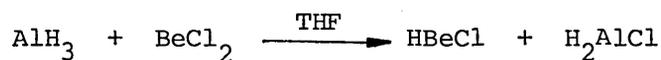


XVII

Investigation of the reaction of lithium tetrahydridoaluminate with beryllium chloride in ether solvents<sup>46</sup> led the authors to believe that the following complexes could be obtained,  $\text{Li}_2\text{BeH}_2\text{Cl}_2$ ,  $\text{LiBeH}_2\text{Cl}$ ,  $\text{LiBeHCl}_2$ , by the following reactions

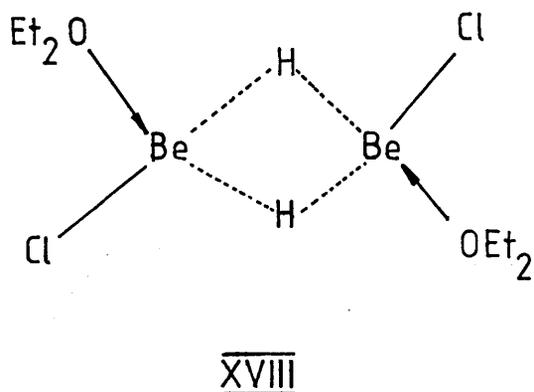


These complexes were characterised by infrared spectroscopy and chemical analysis. They were found to decompose on standing in diethyl ether to give mixtures of  $\text{LiCl}$  and  $\text{BeH}_2$ . When beryllium chloride was allowed to react with alane in THF a hydridoberyllium chloride was obtained<sup>47</sup>. The same complex was obtained by the reaction of beryllium dihydride with beryllium chloride in diethyl ether<sup>47</sup>.

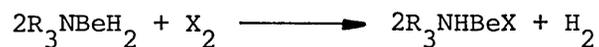
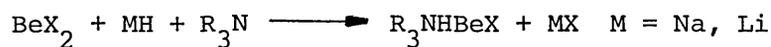
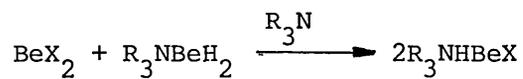


A molecular weight study of  $\text{HBeCl}$  in diethyl ether showed it to be dimeric. An infrared spectrum of  $\text{HBeCl}$  showed a band at

1330  $\text{cm}^{-1}$  while in that of  $\text{DBeCl}$  the band at 1330  $\text{cm}^{-1}$  had disappeared and a new band had appeared at 985  $\text{cm}^{-1}$ . Taken together the evidence shows that  $\text{HBeCl}$  has the following structure in the solid state<sup>38,47</sup>.

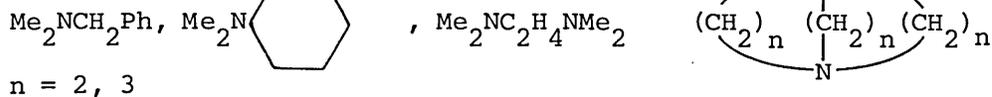


Tertiary amine complexes of hydridoberyllium halides were synthesised by a number of routes<sup>48</sup>.



The tertiary amines used in these reactions were:

$\text{Me}_3\text{N}$ ,  $\text{Me}_2\text{NEt}$ ,  $\text{MeNEt}_2$ ,  $\text{Et}_3\text{N}$ ,  $\text{Me}_2\text{NR}$  ( $\text{R} = (\text{CH}_2)_n\text{CH}_3$   $n = 2-11$ ),



The complexes were characterised by molecular weight studies, which showed that all the complexes were dimeric in benzene solution, and by chemical analysis<sup>48</sup>.

#### 1.4.3 Some reactions of beryllium hydrides.

Reactions of organoberyllium hydrides with organic substrates have also been studied. Reduction of both C=O bonds occurs rapidly e.g.  $\text{MeBeH}$  reduces benzylideneaniline, benzaldehyde and benzophenone quantitatively<sup>34</sup>. Benzonitrile is also reduced by  $\text{MeBeH}$  and a complex  $(\text{MeBeN} = \text{CHPh})_4$  was isolated<sup>49,50</sup> but it was found that further addition of Be-H did not take place.

Ethylberyllium hydride reacts rapidly with terminal alkenes but much slower with non terminal double bonds and not at all with sterically hindered double bonds<sup>34</sup>. There is evidence to suggest that the metal migrates to the terminal carbon as in hydroboration reactions. The formation of donor complexes was found to enhance the rate of reaction thus the relative rates of reaction of  $\text{Bu}^{\text{pt}}\text{BeH}$ ,  $\text{Bu}^{\text{i}}\text{BeH.OEt}_2$  and  $(\text{Bu}^{\text{i}}\text{BeH.NMe}_3)_2$  with pent-1-ene were found to be in the ratio of 1:40:110<sup>35</sup>.

Organoberyllium hydrides were also found to add to alkynes but the products were complicated by other addition and disproportionation reactions<sup>51</sup>.

## 1.5 Anionic complex zinc hydrides

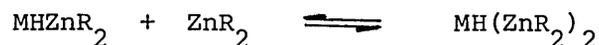
Zinc dihydride was first prepared in 1951<sup>52</sup> by the reaction of dimethylzinc and lithium tetrahydridoaluminate in diethylether and by the reaction of anhydrous zinc iodide with sodium hydride in diethylether. It was obtained as a white solid, insoluble in any solvent with which it did not react. No reactions were reported.

In 1952 the first anionic zinc hydride was reported<sup>53</sup>.  $\text{LiHZn}(\text{C}_6\text{H}_5)_2$  was isolated as a monoetherate after a mixture of lithium hydride and diphenylzinc was heated to  $90^\circ\text{C}$  and the resulting solid had been extracted with diethylether. A period of some ten years elapsed before hydrides of zinc reappeared in the literature! It was reported briefly<sup>54</sup> that sodium hydride dissolved in diethylzinc in dimethoxyethane but it was not until later<sup>55</sup> that the solution was shown to contain  $\text{NaH}[\text{ZnEt}_2]_2$  in the presence of excess sodium hydride. This complex could not be obtained in the solid state due to its decomposition upon removal of the solvent. The preparation of such 1:2 complexes was subsequently repeated and complexes of the type  $\text{MH}(\text{ZnR}_2)_2$ ,  $\text{M} = \text{Li}, \text{Na}$ ;  $\text{R} = \text{Me}, \text{Et}$  were obtained as concentrated dimethoxyethane solutions but all attempts at obtaining them in the solid state failed. 1:1 complexes of the type  $\text{MHZnR}_2$ ,  $\text{M} = \text{Li}, \text{Na}$ ;  $\text{R} = \text{Me}, \text{C}_6\text{H}_5$ ; were also prepared<sup>56</sup> by the reaction of the alkali metal hydride with the diorganozinc in an ether solvent, and isolated in the solid state as

etherates from diethylether or ether-free from tetrahydrofuran.

In dimethoxyethane however, only 1:2 complexes were obtained.

When these reactions were investigated by  $^1\text{H}$  n.m.r. spectroscopy, a mobile equilibrium was demonstrated in solution<sup>56</sup>.

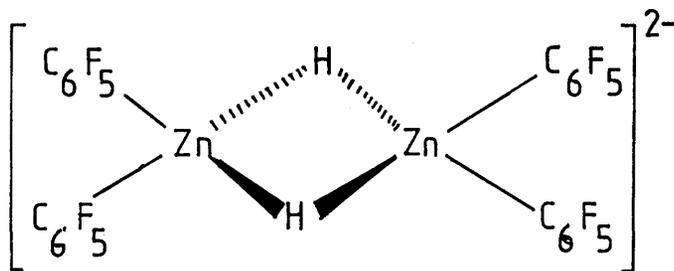


At room temperature a single resonance was found between 7 and 4 ppm downfield from TMS due to the average of individual hydridic hydrogen resonances. When the sample was cooled to  $-60^\circ\text{C}$  the separate resonances due to individual species appeared. When excess dialkylzinc was added, keeping the equilibrium well to the right, the hydride resonance was assigned to a bridging hydride species. The resonance due to the terminal hydride hydrogen in a solution of  $\text{NaR}_2\text{ZnH}$  in tetrahydrofuran was found to occur at 3.40 ppm downfield from TMS.

The infrared spectra of these complexes were less informative. Neither 1:1 nor 1:2 dialkylzinc hydride complexes showed bands in the region  $2100\text{ cm}^{-1}$  to  $1600\text{ cm}^{-1}$  where terminal zinc hydride stretching vibrations might be expected to occur, even though molecular weight data showed that  $\text{NaHZn}(\text{CH}_3)_2$  was monomeric in solution<sup>56</sup>. No reason was given for this. Only the ether-free lithium hydridodiphenyl zincate showed a broad band from  $1650 - 1200\text{ cm}^{-1}$  which shifted to  $1200 - 900\text{ cm}^{-1}$  on formation of the dietherate. The dietherate was believed to have a structure in the solid state similar to  $[\text{NaHBe}(\text{C}_2\text{H}_5)_2]_2 \cdot 2\text{Et}_2\text{O}$ <sup>28</sup> with the ether molecules coordinating to the alkali metal cation rather than to the zinc. Pressure composition studies indicated

that this was so<sup>56</sup>.

When bis(pentafluorophenyl)zinc was treated with sodium hydride or lithium hydride in diethylether at 0°C an ether-soluble complex was obtained<sup>57</sup>. The complex was found to be a tight (inner sphere) ion pair between Na<sup>+</sup> and the anion and to be dimeric in diethylether solution. It was thought to have the following structure

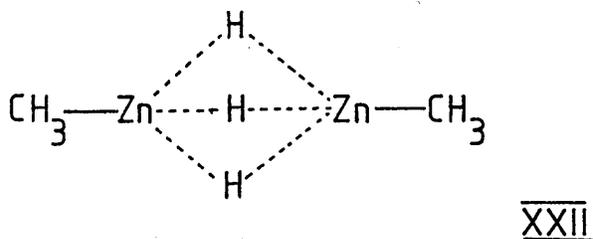
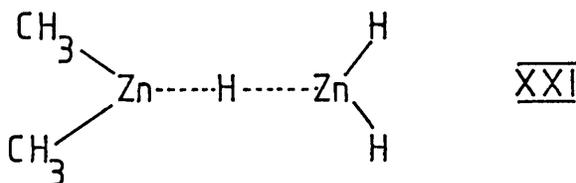
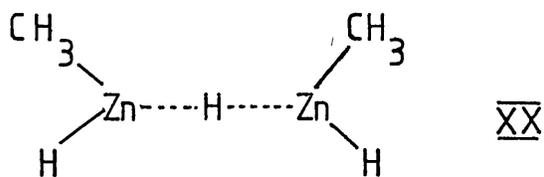


XIX

No proton n.m.r. spectrum could be obtained in diethylether solution but an infrared spectrum showed an underlying absorption from 1700 cm<sup>-1</sup> to 1300 cm<sup>-1</sup> which shifted to ca. 1100 cm<sup>-1</sup> on deuteration and was therefore assigned to Zn-H vibrations. The above structure was assumed because an X-ray structure determination of [Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>N(Me)ZnH]<sub>2</sub> showed the presence of terminal zinc-hydrogen bonds<sup>43</sup> and the zinc-hydrogen stretching frequency had been erroneously reported at 1825 cm<sup>-1</sup><sup>41</sup>. In fact the zinc-hydrogen stretching vibration occurs at 1694 cm<sup>-1</sup><sup>43</sup>. Thus it is entirely possible that the underlying band from

1700 - 1300  $\text{cm}^{-1}$  in the infrared spectrum of  $[\text{NaHZn}(\text{C}_6\text{F}_5)_2]_2$ <sup>57</sup> is also due to vibrational modes of the terminal zinc-hydrogen bonds. Thus there must be some doubt as to the assumed structure for  $[\text{NaHZn}(\text{C}_6\text{F}_5)_2]_2$ .

A further type of complex zinc hydride was prepared by the reaction of methylzinc hydride (formally)\* with an alkali metal hydride<sup>58</sup>. This complex was prepared in tetrahydrofuran and the isolated product contained non-stoichiometric amounts of this solvent. Various structures XX–XXII were postulated since no one structure satisfactorily accounted for all the experimental data obtained.

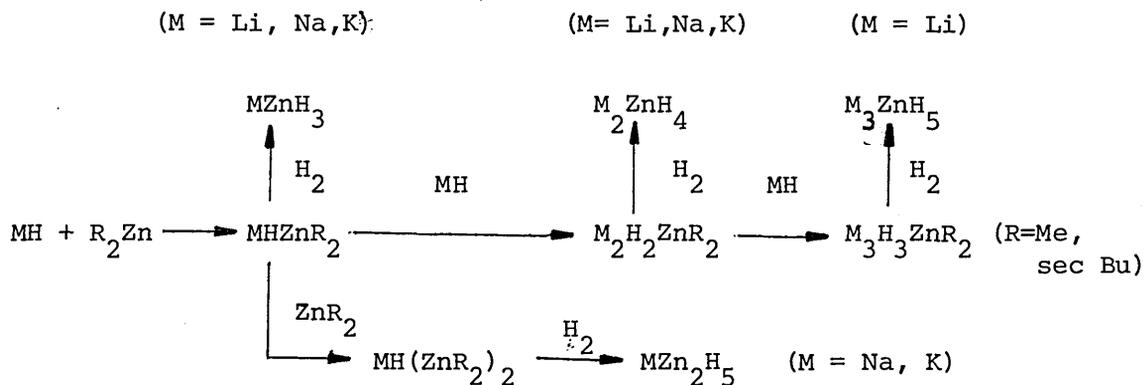



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\* Note: Methylzinc hydride has never been isolated but the stoichiometry of the reaction is such that  $\text{MeZnH}$  may be said to take part rather than a mixture of  $\text{Me}_2\text{Zn}$  and  $\text{ZnH}_2$ .

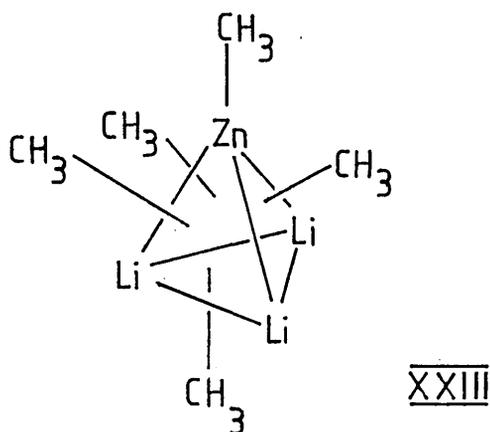
Infrared data supported the presence of a terminal zinc-hydrogen bond since there were broad bands at  $1500\text{ cm}^{-1}$  and from  $800\text{ cm}^{-1}$  to  $500\text{ cm}^{-1}$  due to the Zn-H stretching and the Zn-H wagging modes respectively. The Raman spectrum showed a weak broad band at  $1029\text{ cm}^{-1}$  which could be due to the vibration of a bridging hydride. The proton n.m.r. spectrum showed a resonance of 2.91 ppm downfield from TMS which was assigned to a terminal hydride species. This complex lost dimethylzinc very easily so structure  $\overline{\text{XXI}}$  is most probable. Reactions of organic substrates with  $\text{NaZn}_2(\text{CH}_3)_2\text{H}_3$  were investigated<sup>58</sup>. See section 1.7.

Other complex zinc hydrides have been prepared.<sup>58-62</sup>  $\text{Li}_3\text{ZnH}_5$ ,  $\text{Li}_2\text{ZnH}_4$ ,  $\text{LiZnH}_3$ ,  $\text{Na}_2\text{ZnH}_4$ ,  $\text{NaZnH}_3$ ,  $\text{NaZn}_2\text{H}_5$ ,  $\text{K}_2\text{ZnH}_4$ ,  $\text{KZnH}_3$ ,  $\text{KZn}_2\text{H}_5$  and  $\text{MgZnH}_4$  have been mainly prepared by the reaction of the corresponding alkali metal dimethylzincate with either lithium tetrahydridoaluminate, or alane in tetrahydrofuran. All of these complexes are insoluble and are presumably either ionic in nature or polymeric in the solid state. It is believed, however that  $\text{Li}_3\text{ZnH}_5$  has a structure analogous to that proposed<sup>63</sup> for  $\text{Li}_3\text{Zn}(\text{CH}_3)_5$  (XXIII). A scheme has been presented for the reaction pathways by which the hydrogenolysis of complex organozinc hydrides give rise to new complexes. (Scheme 1),

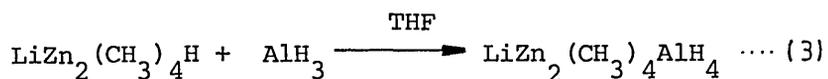


Scheme 1.

These complexes were characterised by infrared spectroscopy and X-ray powder diffraction and elemental analysis.

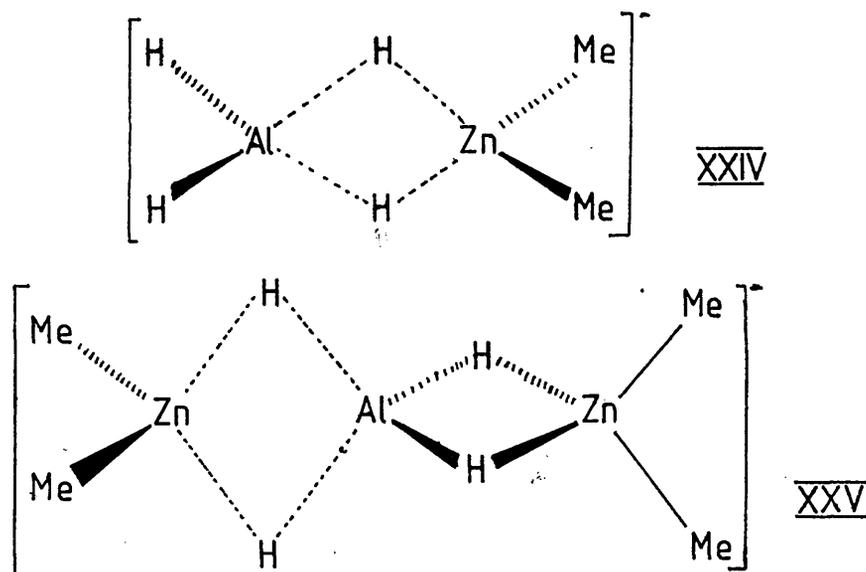


Mixed metal complex hydrides containing zinc have also been synthesised<sup>64-67</sup> by the reaction of complex zinc hydrides with alane.



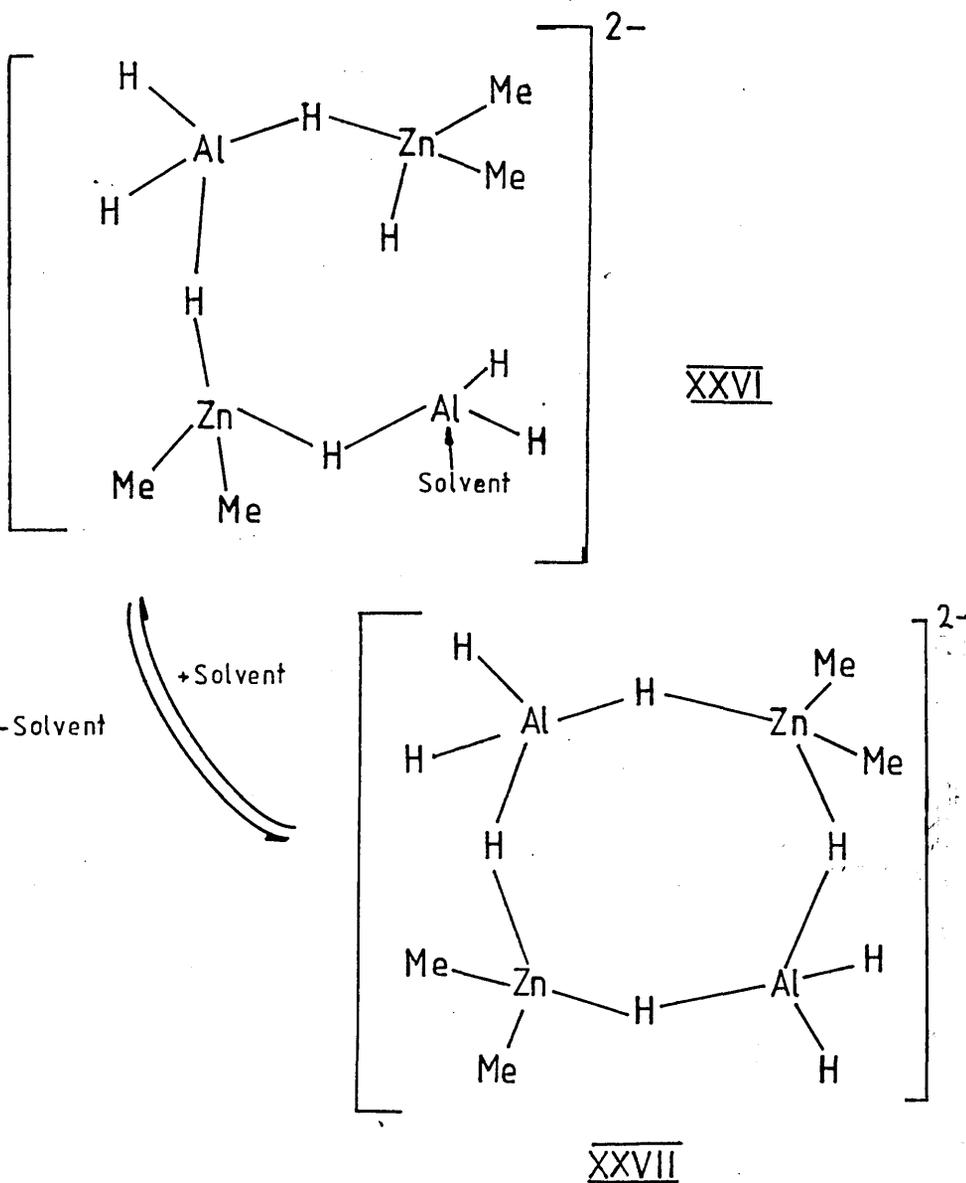
Originally it was hoped that reactions (2) and (3) would provide synthetic routes to  $\text{LiAlZnH}_6$  as an extension of the

reaction scheme 1 on page 43. but the complexes XXIV and XXV were isolated instead. On the basis of infrared spectroscopy and molecular weight studies,  $\text{LiZn}(\text{CH}_3)_2\text{AlH}_4$  XXIV and  $\text{LiZn}_2(\text{CH}_3)_4\text{AlH}_4$  XXV have been shown to have the following structures respectively in dilute tetrahydrofuran solution



In more concentrated tetrahydrofuran or diethylether solutions the degree of association of complex XXIV was found to lie between 1 and 2 and proton n.m.r. and infrared spectroscopy indicated the presence of monomeric and dimeric forms of XXIV

In solutions of higher concentration the complexes can best be described by an equilibrium involving solvated intermediates<sup>64</sup> e.g.



Attempts at obtaining these complexes in the solid state failed. Gums, which turned black at room temperature were obtained on removal of solvent.

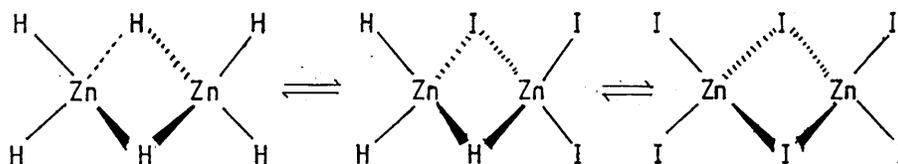
These complexes XXVI and XXVII were shown to be present during the reaction of dimethylzinc with lithium tetrahydridoaluminates in tetrahydrofuran or diethylether<sup>65,66</sup> and were

shown to be intermediates in the alkyl-hydrogen exchange reaction leading to the formation of zinc dihydride.

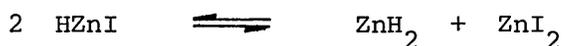
## 1.6 Neutral complex zinc hydrides

While anionic complex zinc hydrides have received some detailed attention, little work has been done on neutral complexes of zinc dihydride.

A white solid, analysing as hydrido-zinc iodide  $\text{HZnI}$  was obtained in 1952<sup>68</sup>. To account for the difficulty in obtaining a pure product, the authors suggested that the product could be described by the following structures, 'connected by equilibria'.<sup>68</sup>

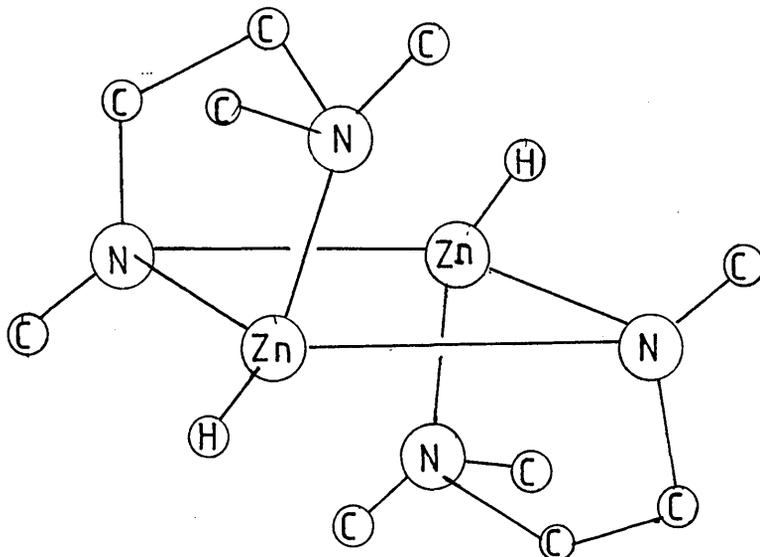


It is most likely that the product simply disproportionates according to the following scheme.



leaving the hydrido-zinc iodide contaminated with zinc dihydride.

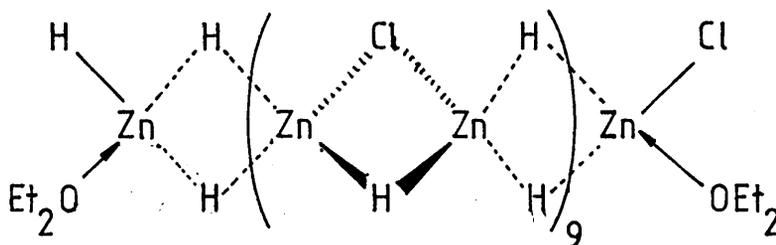
No further work was carried out in the field of neutral zinc hydrides until 1968 when Bell and Coates prepared the  $N,N,N'$ -trimethylethylenediaminozinc hydride dimer<sup>41</sup>. This product was obtained in a crystalline form and X-ray and neutron diffraction studies have since shown the compound to have the following structure<sup>43</sup>



This complex has terminal zinc hydrogen bonds. The zinc hydrogen bond length has been determined from neutron diffraction to be  $1.618 \text{ \AA}$  - close to the sum of the covalent radii<sup>69</sup> thus suggesting that the bond is predominantly covalent in character<sup>43</sup>. The zinc hydrogen stretching frequency was reported erroneously as occurring at  $1825 \text{ cm}^{-1}$  but as has already been stated (p.40) in fact this band occurs at  $1694 \text{ cm}^{-1}$ . The band is broad with a half height width of  $120 \text{ cm}^{-1}$ . No n.m.r. resonance due to the hydridic hydrogen was reported but the complex was found to be dimeric in dilute benzene solution and thus it presumably has the same structure in solution as in the solid state.

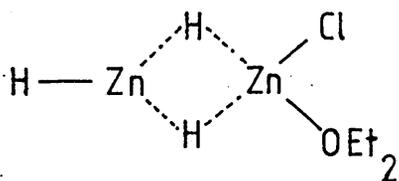
Since then halozinhydrides have received renewed attention. Compounds of stoichiometry  $\text{H}_3\text{Zn}_2\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) were prepared by the reaction of alane with the corresponding anhydrous zinc dihalide in diethylether<sup>70</sup>. Zinc iodide however, did not exchange with alane to give an iodozinc hydride but formed the coordination complex,  $\text{AlH}_3 \cdot \text{ZnI}_2 \cdot n\text{Et}_2\text{O}$  instead. The halozinc-hydrides,  $\text{H}_3\text{Zn}_2\text{X}$ , were found to be insoluble in all inert solvents and they showed very broad absorptions in their infrared

spectra at ca.  $1550\text{ cm}^{-1}$  which were considered to be rather low for terminal zinc hydrogen stretching vibrations but rather high for bridging zinc hydrogen stretching vibrations.  $\text{H}_3\text{Zn}_2\text{Cl}$  showed a far infrared absorption at  $280\text{ cm}^{-1}$  which was very similar to an absorption in the far infrared spectrum of  $\text{ZnCl}_2$  which was assigned to a terminal zinc-chlorine stretching vibration. Chemical analysis of the complexes always showed the presence of diethylether, typically  $\text{H}_3\text{Zn}_2\text{X} \cdot 0.2 - 0.3\text{Et}_2\text{O}$ . A stoichiometry of  $\text{H}_3\text{Zn}_2\text{Cl} \cdot 0.2\text{Et}_2\text{O}$  can be accounted for by the following structure

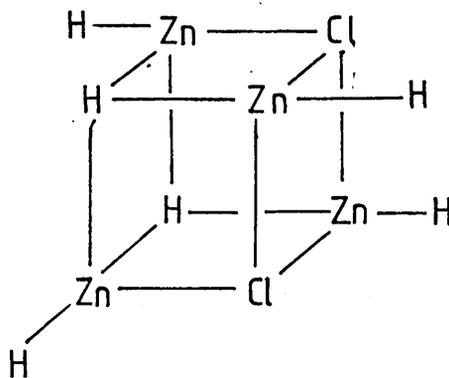


XXVIII

Such a chain length would account for the insolubility of the product in inert solvents, unlike the structural possibilities suggested by the authors<sup>70</sup>, XXIX, XXX



XXIX

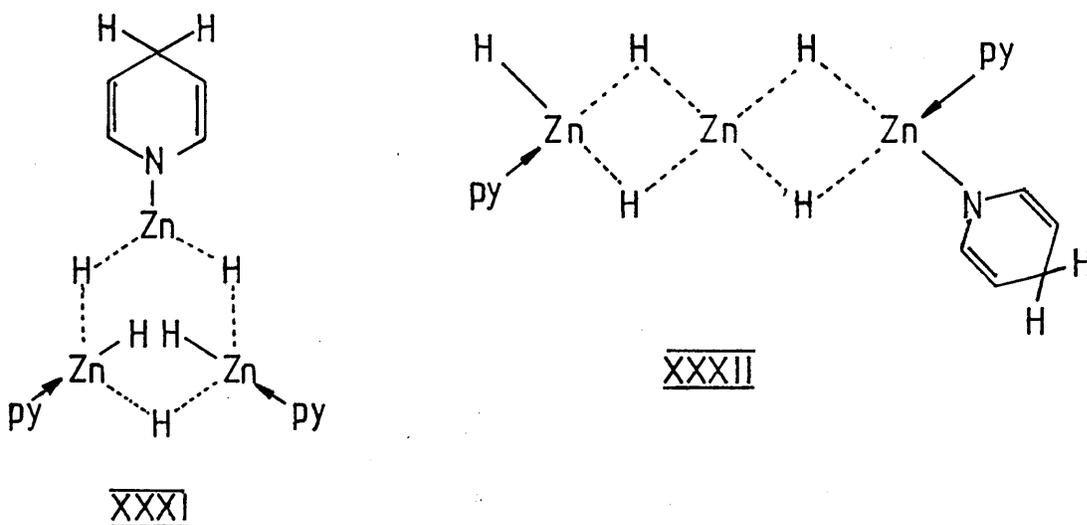


XXX

No conclusive evidence was found for the existence of discrete  $\text{HZnX}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) species though they must exist as intermediates in the formation of the isolable halozinohydride compounds.

The reaction of zinc dihydride with pyridine has received considerable attention. Zinc dihydride was observed to dissolve in pyridine and evaporation of a freshly prepared solution yielded a 1,4-dihydropyridylzinc hydride complex having the stoichiometry  $\text{C}_5\text{H}_6\text{NZnH} \cdot (\text{ZnH}_2)_2 \cdot \text{py}_2$ <sup>71</sup>.

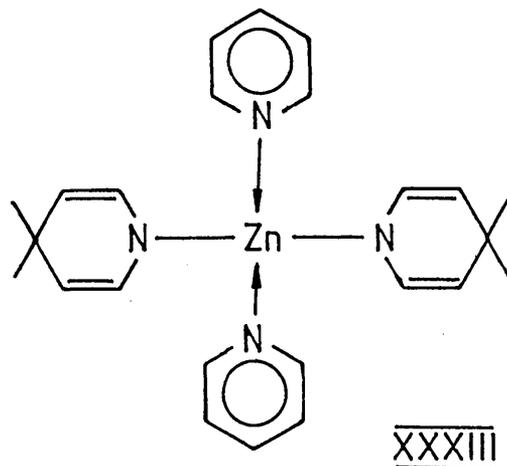
Two structures have been suggested<sup>72</sup> to account for the spectroscopic data obtained for this complex.



XXXI is unusual in that both three and four coordinate zinc, are present in the same molecule but this six membered zinc-hydrogen ring is seen in  $\text{RZnH} \cdot \text{py}$  complexes<sup>74</sup>. XXXII has coordinatively saturated zinc and thus seems more likely but there are no means to distinguish between the two possible structures, on the basis of available evidence. The infrared

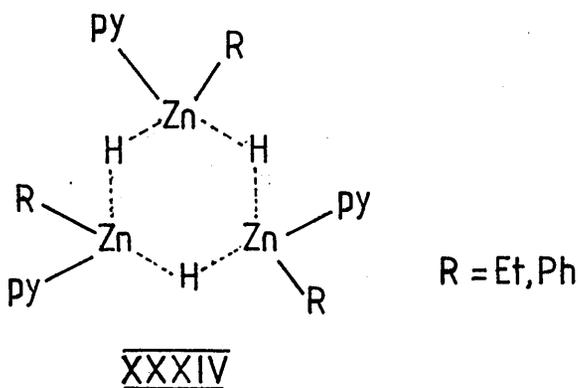
spectrum of this complex showed broad bands from 1900 - 1300  $\text{cm}^{-1}$ , 1150  $\text{cm}^{-1}$  - 850  $\text{cm}^{-1}$  and 650 - 500  $\text{cm}^{-1}$ , similar to that obtained for zinc dihydride itself. Ashby and co-workers have also prepared this complex but they find a band in the range 1720  $\text{cm}^{-1}$  - 1570  $\text{cm}^{-1}$  which they assign to terminal zinc-hydrogen modes<sup>21</sup>. Variable temperature proton n.m.r. showed that there were at least two different types of hydrogen bound to zinc, the signals of which coalesced at 10°C. This complex was also found to be soluble, without reacting with DMSO-d<sub>6</sub> and DMF-d<sub>7</sub>. The resonances due to the hydridic hydrogens varied widely with change in solvent, 4.34 ppm downfield from TMS in pyridine<sup>71</sup>, 4.1 ppm downfield from TMS for DMF-d<sub>7</sub><sup>72</sup> and 2.76 ppm downfield from TMS in DMSO-d<sub>6</sub><sup>71</sup>. Presumably this is due to the solvent displacing the coordinating pyridine molecules in the complex.

Surprisingly, if the pyridine solution of the complex was allowed to stand, a yellow precipitate separated out after 2 days and by seven days a maximum yield of the bis (1,4-dihydropyridyl) zinc pyridine complex was obtained, XXXIII.



This complex was found to be a stronger reducing agent than the hydrido zinc complex  $(C_5H_6N)ZnHZnH_2Py_2$  with the metal bound 1,4-dihydropyridyl groups acting as hydride donors<sup>72, 20, 74</sup>.

Pyridine complexes of phenylzinc hydride and ethyl zinc-hydride have also been isolated<sup>73, 75</sup>. They are believed to have the following structure with coordinatively saturated zinc atoms.



Proton n.m.r. spectroscopy showed that the hydridic hydrogens have resonance at  $\sim 4 - 5$  ppm downfield from TMS. Lowering the temperature resulted in a considerable broadening of the hydridic hydrogen resonances suggesting that there may be some inter- or intramolecular exchange process involving the zinc-hydrogen bridges in solution. The infrared spectrum of the  $RZnHpy$  complexes showed broad bands similar to those of zinc dihydride itself.

When allowed to react with the bidentate nitrogen-containing ligand  $N,N,N',N'$ -tetramethylethylenediamine (TMEDA),  $RZnHpy$

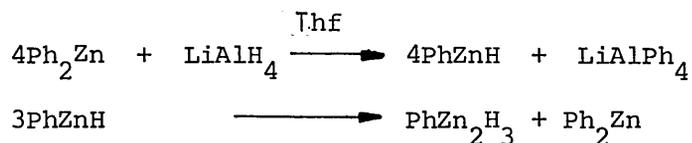
(R = Et, Ph) lost pyridine and a complex of stoichiometry  $(RZnH)_2$  TMEDA was obtained. This complex was soluble in benzene and tetrahydrofuran and molecular weight studies showed that the complex existed as a dissociating dimer in benzene.

These TMEDA  $(RZnH)_2$  complexes disproportionate very easily. Merely washing with diethylether gives a hydrido enriched product with a stoichiometry of  $R_2Zn_3H_4$ .TMEDA. The authors do not speculate on the structure of these hydrido zinc species but the hydridic hydrogen resonance has been assigned at  $\sim 4$  ppm downfield from TMS<sup>75</sup>.

Other complexes of zinc dihydride have been obtained by the redistribution reaction of zinc dihydride and the required diorganozinc compound. Bis(3-N,N'-dimethylaminopropyl)zinc reacted with zinc dihydride but a stable, stoichiometric product could not be obtained<sup>75</sup>. Bis(4-methoxybutyl)zinc reacted with zinc dihydride and in the presence of pyridine a complex of stoichiometry  $MeO.(CH_2)_4ZnHpy$  was obtained<sup>75</sup>. No structural information was given other than the proton n.m.r. resonance of the hydrogen bound to zinc. The same authors found that zinc dihydride did not react with strong donors such as 2,2'-bipyridyl, triethylamine and hexamethylphosphoramide<sup>71</sup> or with polymeric diorganozinc compounds like bis(cyclopentadienyl)zinc<sup>75</sup>.

A further type of reaction was briefly reported<sup>76</sup> in that a compound of stoichiometry  $PhZn_2H_3$  was obtained on

allowing diphenylzinc to react with lithium tetrahydridoaluminate in tetrahydrofuran. Very recently this reaction has been repeated<sup>77</sup> and the same product has been obtained by the reaction of zinc dihydride with diphenylzinc in tetrahydrofuran. Zinc dihydride was also found to react with cyclopentadiene to give a product with a stoichiometry of  $\text{CpZn}_2\text{H}_3$ <sup>77</sup>. These complexes have been found to be insoluble in all solvents with which they did not react so they were characterised by infrared spectroscopy and X-ray powder diffraction. It is believed that during the course of the reaction an intermediate complex of stoichiometry  $\text{RZnH}$  is formed and this disproportionates upon removal of solvent to give  $\text{RZn}_2\text{H}_3$ .



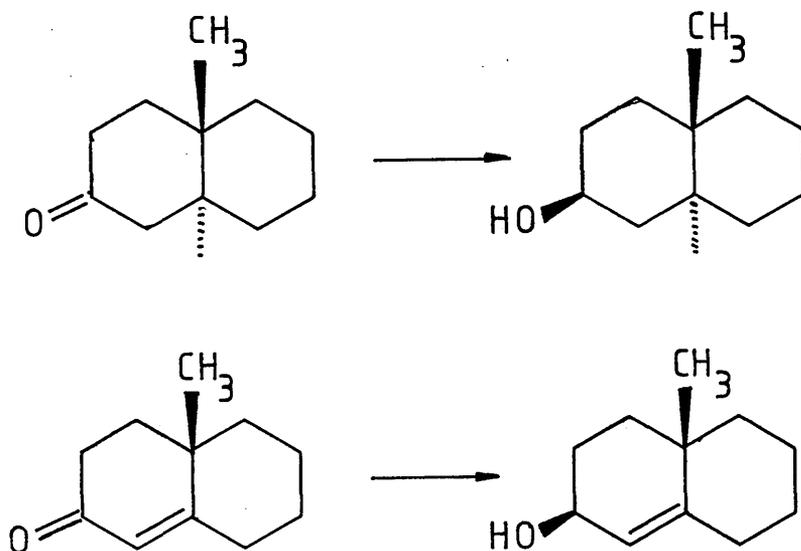
A similar reaction is believed to occur when dimethylzinc is allowed to react with zinc dihydride but no product having satisfactory analytical data could be obtained due to rapid decomposition of the isolated compound.

Zinc dihydride was found to react with cyclohexanol to give an insoluble solid with an empirical formula  $\text{cyclo-C}_6\text{H}_{11}\text{O}\cdot\text{ZnH}$ <sup>77</sup>. This product has an infrared absorption at  $1780\text{ cm}^{-1}$  which may be due to a terminal zinc hydrogen stretching vibration, but it has so far been incompletely characterised.

## 1.7 Anionic complex zinc hydrides as reducing agents

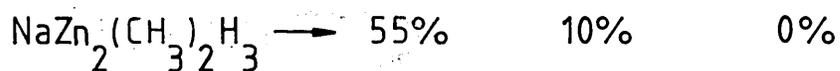
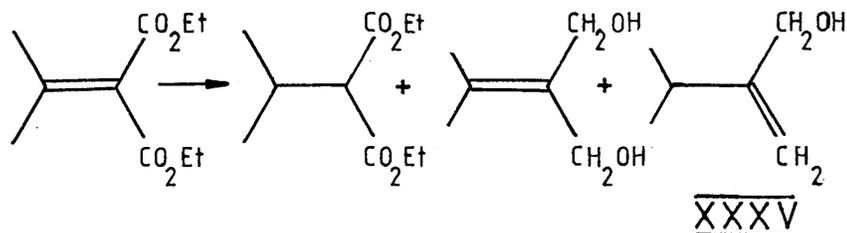
The reaction of the 1:2 sodium hydride-methylzinc hydride complex  $\text{NaZn}_2(\text{CH}_3)_2\text{H}_3$  with several organic substrates has been studied and a comparison made with lithium tetrahydridoaluminate as the reducing agent<sup>58</sup>.

In the addition to cyclic ketones,  $\text{NaZn}_2(\text{CH}_3)_2\text{H}_3$  showed similar stereoselectivity to  $\text{LiAlH}_4$ .



It was however found to be a milder reducing agent than  $\text{LiAlH}_4$ ; thus whereas  $\text{LiAlH}_4$  reduced benzonitrile to benzylamine over one hour, the same reaction took 24 hours when  $\text{NaZn}_2(\text{CH}_3)_2\text{H}_3$  was used. After one hour, however, a good yield of the corresponding imine was obtained.

Of interest also is the following reduction



The relative product distribution suggests that the zinc hydrogen bond adds mainly across the carbon-carbon double bond in a 1,2: mode of addition whereas the lithium tetrahydridoaluminate, being a much stronger reducing agent adds equally in 1,2 and 1,4 modes of addition. The presence of XXXV is indicative of a cyclic transition state involving the  $\text{AlH}_2$  moiety, formed by a 1,4 mode of addition.

Epoxides were also shown to be fairly resistant to ring opening by the zinc-containing reducing agent whereas lithium tetrahydridoaluminate effected ring opening easily<sup>58</sup>



No other reaction of complex anionic zinc hydrides has been reported in the literature to date.

## 1.8 Neutral complex zinc hydrides as reducing agents

The behaviour of pyridine zinc hydride complexes with organic substrates has been investigated<sup>20,75</sup> and the results are summarised in Table 3.

Table 3

Alcohol <sup>(b)</sup>	LiAlH <sub>4</sub>	ZnH <sub>2</sub>	DHPZ <sup>(a)</sup>	py.EtZnH	py.PhZnH
axial	9	35	27	16	17
cis	24	52	43	35	35
axial	78	85	88	94	93
cis	91	92	94	97	98

(a) DHPZ - 1,4-dihydro-1-pyridylzinc hydride.bis (zinc dihydride) bispyridine complex.

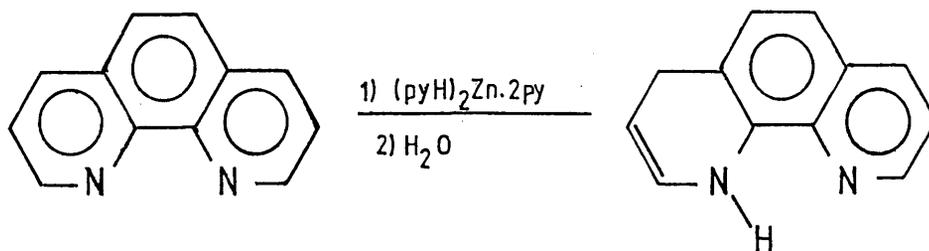
(b) These rows refer, in descending order, to the percentage of the less stable isomeric alcohol obtained by the reduction of 4-t-butylcyclohexanone; 2-methylcyclohexanone; 3,3,5-trimethylcyclohexanone and camphor

The product ratios were explained purely on steric grounds. Zinc dihydride, a hydrogen bridged coordination polymer has the highest steric requirement, and hence the highest percentage of the less stable alcohol is obtained, compared to other reducing agents for unhindered attack. Lithium tetrahydridoaliminate, a solvent separated ion pair<sup>77</sup>, has the lowest steric

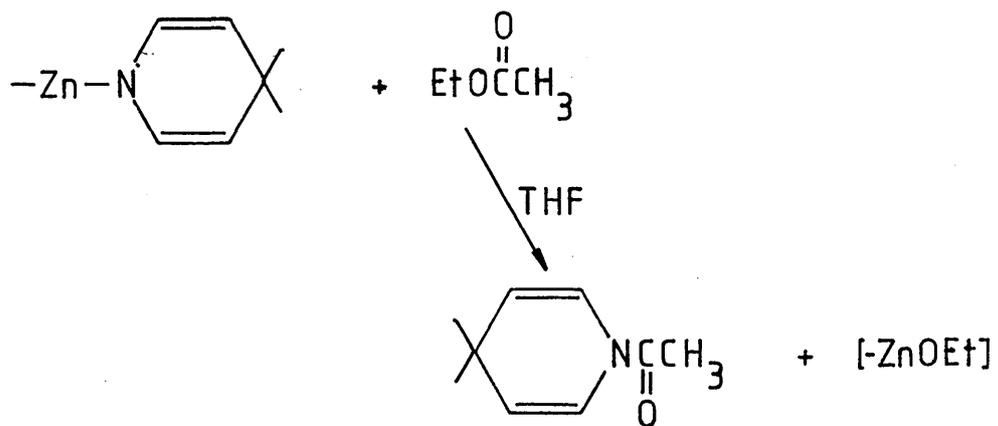
requirement and hence the lowest percentage of the less stable alcohol is obtained for unhindered attack. The complex zinc hydrides have product ratios that lie between those obtained for  $\text{ZnH}_2$  and  $\text{LiAlH}_4$  and their steric requirement also lies between that of  $\text{ZnH}_2$  and  $\text{LiAlH}_4$  (they are trimeric in benzene solution).  $\text{Py}\cdot\text{EtZnH}$  and  $\text{py}\cdot\text{PhZnH}$  have very similar product distributions so the ethyl and phenyl groups are thought to provide the same steric hindrance to attack on the carbonyl group<sup>75</sup>.

For cyclic ketones e.g. 3,3,5-trimethylcyclohexanone and camphor the attacking hydride is directed by the steric effect of the ring substituents to one predominant side, thus the syn-C-7 methyl group in camphor severely blocks exo attack by the hydride. This results in a less sensitive probe of the steric effect of the hydride containing reducing agent. Thus these complex zinc hydrides do not show any unusual stereoselectivity towards cyclic ketones.

As has been mentioned previously (p.52 ) the pyridine zinc hydride complexes are weaker reducing agents than bis(1,4-dihydropyridyl)zinc-bis pyridine complexes. These bis complexes show unusual stereoselectivity in reducing nitrogen containing heterocycles.

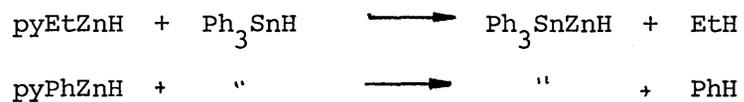


This is exclusively 1,4 addition<sup>75</sup>. In other reactions, the amine character of the zinc containing reagent predominates over its reducing behaviour.



### 1.9 Other reactions of neutral complex zinc hydrides

The complexes py.EtZnH and py.PhZnH undergo a hydrogenolysis type reaction with triphenyltin hydride to give a mixed metal zinc hydride<sup>75</sup>.



Nothing further is known about this unusual tin zinc hydride complex other than its existence.

## 2.1 General experimental techniques

All solvents with the exception of benzene and pentane were dried over molecular sieve (4A) or anhydrous magnesium sulphate and distilled immediately prior to their use. THF was distilled from sodium benzophenone ketyl or potassium metal under nitrogen. Diethylether was distilled under nitrogen from calcium hydride. Pentane and benzene were dried over sodium wire and were not distilled before use. Solutions of lithium tetrahydridoaluminates were prepared by refluxing solid lithium tetrahydridoaluminates in diethylether under nitrogen for 24 hours followed by filtration. The resulting clear solution was standardised by measuring the amount of hydrogen evolved from the reaction of an aliquot of the solution with 2-methoxyethanol on a standard high vacuum line equipped with a Toepler pump. Starting materials were dried over molecular sieve (4A) and distilled, or recrystallised prior to their use. Crude trimethylchlorosilane was purified by condensing it onto triethylamine on a vacuum line. Triethylamine hydrochloride, a solid with no appreciable vapour pressure, was formed from the HCl present as an impurity in  $\text{Me}_3\text{SiCl}$ . The pure trimethylchlorosilane was then condensed on the line into an ampoule under vacuum and used immediately. All reactions were carried out using Schlenk tube techniques described in 2.3

Air sensitive solutions

and diethylzinc were manipulated using glass syringes and 18 or 20 gauge 12" stainless steel needles. Gross manipulation of products and the preparation of samples for spectroscopic analysis

were carried out in a glove box (see p. 64 ).

The analysis of zinc was performed by digestion of a weighed sample of the complex zinc hydride with concentrated hydrochloric acid followed by its adjustment of pH and then titration with standard EDTA solution using Xylenol orange at pH 6 or Erio T at pH 10 as indicators.

The analysis of the hydridic hydrogen was carried out by hydrolysing a weighed sample of the complex metal hydride with 2-methoxyethanol, distilled water and dilute hydrochloric acid on a standard vacuum line and measuring the amount of hydrogen evolved using a Toepler pump. The figures quoted in the analytical data thus refer only to the hydrolysable hydrogen content.

<sup>1</sup>H Nmr spectra were recorded using C-60 HL Jeol Co. continuous wave and R.600 Hitachi Perkin Elmer Fourier transform spectrometers, with TMS as an internal standard. All resonances are quoted downfield from TMS with the TMS resonance occurring at 0 ppm.

Infrared spectra from 4000 to 650 or 400  $\text{cm}^{-1}$  were obtained from samples as Nujol mulls between NaCl or KBr plates or as solutions in benzene or THF using matched cells of 0.15 cm pathlength with KBr windows (Specac<sup>®</sup>) using SP200, SP400, SP1000 and SP1200 Pye Unicam grating infrared spectrometers. A thin film of polyethylene was used to calibrate the spectra obtained.

Gas-liquid chromatography was carried out using a GCV Pye Unicam Series 104 chromatograph.

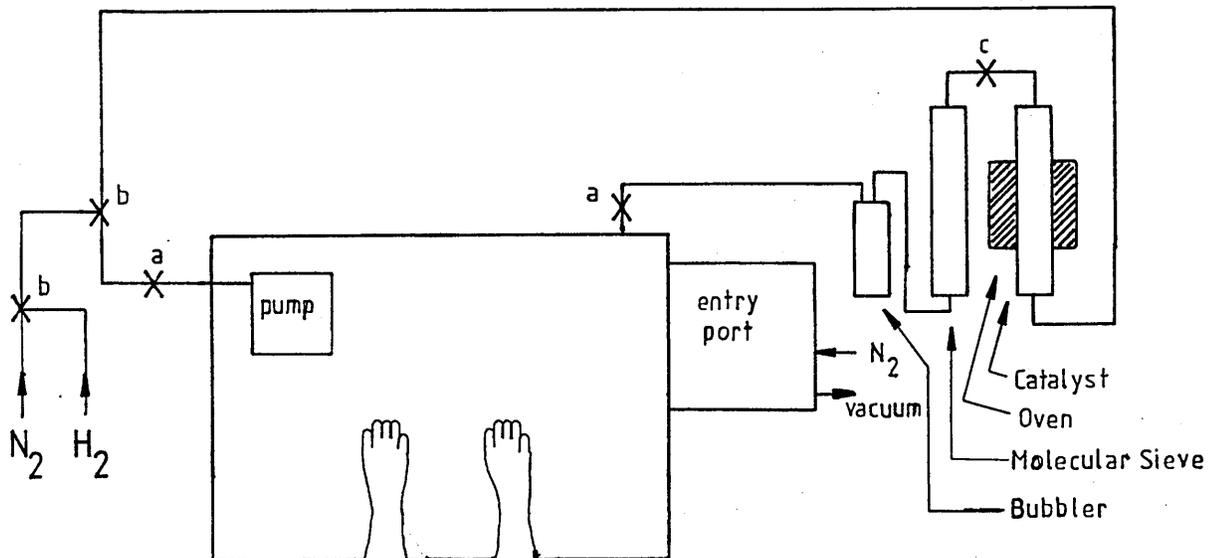
U.V. spectra were recorded using an SP800A ultraviolet spectrometer.

Molecular weight measurements were obtained using the Beckmann Thermometer freezing point depression method<sup>78</sup> with the apparatus slightly modified so that the procedure could be carried out under nitrogen.

## 2.2 The Glove Box

A Gallenkamp Manipulator glove box was modified so that the atmosphere contained within it could be continually recirculated and scrubbed free from oxygen. To this end, a small electrically driven air pump, inside the glove box, drove the atmosphere out through a column, 0.75 metres in length, charged with BASF R3-11 copper catalyst pellets which were maintained at 70°C then through another column, 0.75 metres in length, charged with molecular sieve 4A and finally back into the glove box. The catalyst was periodically regenerated by passing a mixture of hydrogen and nitrogen (1:10) through the catalyst column at 140°C. The regeneration was complete when the catalyst had changed to a black colour. A large amount of water vapour

was produced in the regeneration process, so the exhaust gases were vented directly to the atmosphere, the glove box being isolated from the recirculating system in the process. The glove box was equipped with an entry port which could be flushed with nitrogen independently. The doors in the entry port were of the interlocking type so that both doors could not be opened at the same time. The perspex front panel of the glove box was additionally sealed with an adhesive compound to prevent leaks from the outside. A schematic diagram is given below.



a) on/off taps

b) two way T taps

c) two way tap to vent

2.3 General procedures in the preparation of zinc dihydride and complex zinc hydrides

A double Schlenk tube (Fig. 1 ) was dried overnight in an oven and attached to a nitrogen/vacuum manifold (Fig. 2 )

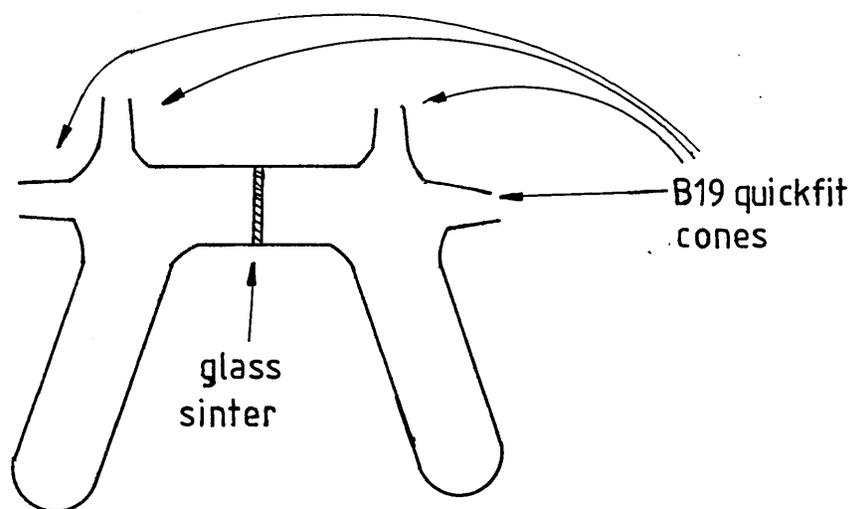


Fig. 1

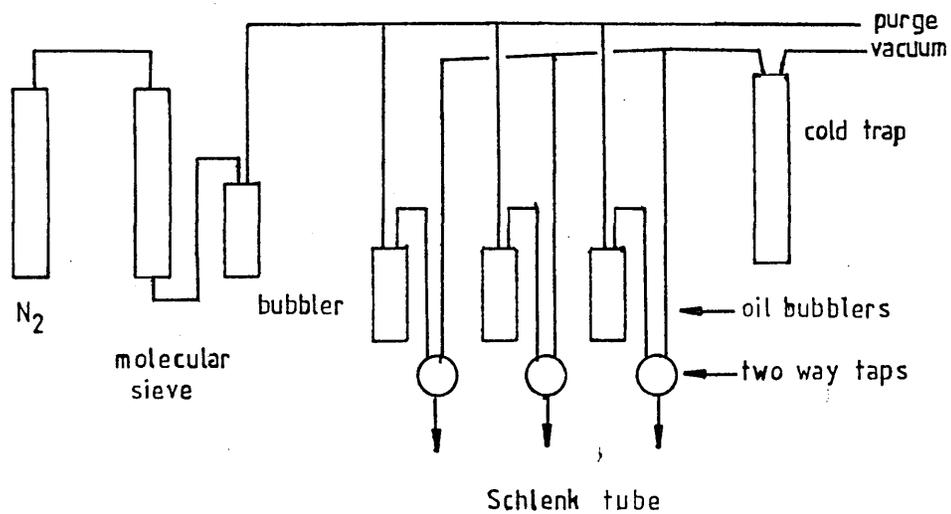


Fig. 2

The double Schlenk tube was evacuated, flushed with nitrogen and then allowed to cool under nitrogen. The reagents and solvent were then added to one arm of the double Schlenk tube under a positive pressure of nitrogen and allowed to react for the desired length of time. The reaction mixture was then passed through the sinter either under a positive pressure of nitrogen on the same side of the sinter as the reaction mixture, or under reduced pressure, applied from the opposite side. In this way any solid retained on the sinter could be dried under a flow of nitrogen or under vacuum. The solvent was removed from the filtrate under reduced pressure by continuous pumping or by condensing the solvent into the other arm of the double Schlenk tube, kept at  $-196^{\circ}\text{C}$  in a liquid nitrogen bath, until only the desired product remained.

## 2.4 Preparation of zinc dihydride

### 2.4.1 $\text{ZnI}_2 + 2\text{NaH}$

THF ( $20\text{ cm}^3$ ) was added to freshly sublimed zinc iodide (3.1 g, 10 mmoles) in one arm of a double Schlenk tube and the mixture was stirred until the  $\text{ZnI}_2$  had dissolved. A slurry of sodium hydride (0.55 g, 22 mmoles) in THF ( $20\text{ cm}^3$ ) was added to the other arm of the double Schlenk tube. The zinc iodide solution was drawn through the sinter and allowed to mix with

the sodium hydride slurry. The reaction mixture was stirred for 48 hours and then filtered. The zinc dihydride, thus obtained, was washed with THF and kept in the Schlenk tube for further reactions.

#### 2.4.2 $\text{ZnEt}_2 + \text{LiAlH}_4$ —

Diethylzinc ( $2 \text{ cm}^3$ , 19.6 mmoles) was added to diethylether ( $40 \text{ cm}^3$ ) at  $0^\circ\text{C}$  in one arm of a double Schlenk tube. Lithium tetrahydridoaluminate ( $25 \text{ cm}^3$ , 0.65 M solution in diethylether, 19.6 mmoles\*) was added dropwise to the diethylzinc solution. The reaction was exothermic and virtually instantaneous. The reaction mixture was then stirred for a further hour and the zinc dihydride (1.31 g, 19.6 mmoles) so formed was filtered off, washed with diethylether ( $2 \times 20 \text{ cm}^3$ ) and then the solvent in which it would be used. It was then briefly dried *in vacuo* and then it was ready for further use.

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\* In later preparations an excess of lithium tetrahydridoaluminate was used

2.5 Reactions of zinc dihydride with potentially bidentate ligands  
containing an acidic proton

2.5.1.1 N,N,N'-Trimethylethylenediamine\*

Zinc dihydride (1.9 g, 28 mmoles), prepared from zinc iodide and sodium hydride in THF, was washed with toluene and then formed into a slurry in toluene (60 cm<sup>3</sup>) in one arm of a double Schlenk tube. On addition of N,N,N'-trimethylethylenediamine (3 cm<sup>3</sup>, 36 mmoles) to the slurry, immediate evolution of gas was seen. When gas evolution had ceased, the reaction mixture was filtered and the clear filtrate was evaporated under reduced pressure until a yellow white product separated out. This was filtered off and dried *in vacuo* (yield, 0.12 g, 2%). The infrared spectrum of this compound as a Nujol mull revealed no bands due to N-H vibrations but a broad band with maximum absorbance at 1625 cm<sup>-1</sup>.

2.5.1.2 N,N,N'-Trimethylethylenediamine

N,N,N'-trimethylethylenediamine was added dropwise via syringe to zinc dihydride (1.31g, 19.6 mmoles), prepared from

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\* The reaction between ZnH<sub>2</sub> and Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(Me)H has been reported previously<sup>43</sup> and<sup>2</sup> yields<sup>2</sup> a<sup>2</sup> crystalline dimeric product [HZnN(Me)C<sub>2</sub>H<sub>4</sub>NMe<sub>2</sub>]<sub>2</sub>.

diethylzinc and lithium tetrahydridoaluminate, in toluene. (60 cm<sup>3</sup>). Slow evolution of gas was seen. The reaction mixture was heated to 70°C and after 2 hours most of the zinc dihydride had reacted. The solution was filtered from excess zinc dihydride and zinc metal and then cooled to 0°C. No crystallisation was observed so the solvent was removed under reduced pressure, leaving a very viscous white oil. Pentane was added to the oil, giving a white solid which was filtered off and dried *in vacuo* (yield, 1.20 g, 37%). Found: %H, 0.69; % Zn, 38.2; Calc. for [Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(Me)ZnH]<sub>2</sub> %H, 0.59; %Zn, 38.9. An infrared spectrum of the solid product, recorded as a Nujol mull, showed the following main absorptions: 2900, 2820s, 1700 m broad, 1405m, 1368m, 1300 s, 1172s sharp, 1120s broad, 1050s broad, 990 m, 950 m, 860 s, 790 m (cm<sup>-1</sup>). A THF solution of the product showed the following infrared absorptions: 2790 m, 1690 vs, 1650 sh, 1520 m.broad, 1405 m, 1170, 1010, 790 m. cm<sup>-1</sup>. An <sup>1</sup>H nmr spectrum of the product dissolved in deuterated toluene showed the following resonances (intensities in parentheses): 4.20 (1), 2.95 (2), 2.80 (3), 2.35 (2), 2.05 (6) ppm. A solution (0.0287M) of the product in THF showed an absorption of 37,037 cm<sup>-1</sup> with a half height width of 4800 cm<sup>-1</sup>. The extinction coefficient was found to be 1.175 x 10<sup>4</sup> g dm<sup>-2</sup>.

## 2.5.2 2-Dimethylaminoethanol

Zinc dihydride (1.31 g, 19.6  $\mu$ moles), freshly prepared according to the method described in 2.4.2, was washed with THF ( $2 \times 20 \text{ cm}^3$ ) and then formed into a slurry in THF ( $40 \text{ cm}^3$ ). 2-Dimethylaminoethanol (2.11 g, 19.6  $\mu$ moles) was added dropwise via syringe to the stirred slurry at room temperature. The reaction mixture was stirred until most of the zinc dihydride had dissolved, then it was filtered from unreacted solids. The solvent was removed *in vacuo* leaving behind a white oil which deposited a white solid on addition of hexane (yield, 1.79 g, 57.8%).

Found: %H, 0.60; % Zn, 42.0; Calc. for  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OZnH}$ : % H, 0.65; % Zn, 42.2. The white solid melted with decomposition between  $176^\circ\text{C}$  and  $180^\circ\text{C}$ . An infrared spectrum of the product, as a Nujol mull, showed the following main absorptions: 2700 s, 1740 m, broad, 1650 m., 1420 m, 1370 s, 1345 m, 1290 vs, 1260 vs, 1200 s, 1170 m, 1110 vs. broad, 1060 vs. broad, 960 vs, 890 vs, 790 vs. broad ( $\text{cm}^{-1}$ ).

In THF solution, the following absorptions were observed: 2800 m, 1700 vs, 1390 m, 1370 m, 1280 m, 1150 m. broad, 1000 m. broad, 900-700 w. broad, 790 vs ( $\text{cm}^{-1}$ ). The following resonances were observed in the  $^1\text{H}$  nmr spectrum of a solution of the product in deuterated benzene. 4.47 (1), 4.25 (2), 2.90, 2.32 (8), ppm. A solution (0.0291 M) in benzene was found to depress the freezing point of benzene by  $0.087^\circ\text{C} \pm 0.001^\circ\text{C}$ . The molecular weight of the species in solution was found to be 303. The calculated molecular weight for the dimer  $[\text{Me}_2\text{NCH}_2\text{CH}_2\text{OZnH}]_2$  is 308.

### 2.5.3.1 2-Methoxyethanol

Zinc dihydride (1.31 g, 19.6 mmoles) was washed with THF (2 x 20 cm<sup>3</sup>) and then formed into a slurry with THF (60 cm<sup>3</sup>). 2-Methoxyethanol (1.6 cm<sup>3</sup>, 20 mmole) was added to the stirred slurry at 0°C. When gas evolution had stopped (2 hours), the reaction mixture was filtered from unreacted solids and the solvent removed *in vacuo*, leaving a clear mobile oil. When pentane (30 cm<sup>3</sup>) was added to the oil, a white solid was gradually formed which was separated by filtration. (Yield; 0.5 g, 18%). Found: % H, 0.40, % Zn, 39.8; Calc. for MeOCH<sub>2</sub>CH<sub>2</sub>OZnH: % H, 0.71, % Zn, 46.0. The white solid decomposed at 165°C. An infrared spectrum of the product was recorded as a Nujol mull and the following absorptions were observed, 2840 vs, 2790 s, 2715 s, 1960 - 1690 m. broad (1780 max), 1410 m.sh., 1360 m, 1310 m, 1260 s, 1210 s, 1150 s. broad, 1100 s. broad, 1060 s, broad, 970 m, 900 m broad, 850s(cm<sup>-1</sup>). The <sup>1</sup>H nmr spectrum of the product as a solution in deuterated toluene showed the following resonances. 4.15 (2.1), 4.00 (2.1), 3.8, 3.5 (3.7), 3.26 (2.8), 3.24 (1), 3.14 (1) ppm.

### 2.5.3.2 2-Methoxyethanol

Zinc dihydride (1.25 g, 18 mmole) was slurried with toluene (40 cm<sup>3</sup>) in one arm of a double Schlenk tube. 2-Methoxyethanol (1.4 g, 18 mmole) was added dropwise to the stirred slurry at 0°C.

The reaction mixture was stirred for 12 hours, filtered from unreacted solids, and the solvent removed *in vacuo*, leaving a white oily solid which, on addition of pentane, formed a white powder. The white powder (0.24 g, 9%) was filtered off and dried *in vacuo*. An infrared spectrum of the product as a Nujol mull contained the following absorptions 2750 s, 2680 s, 1780 m.broad, 1610 sh, 1260 s, 1200 s, 1140 vs,broad, 1090 vs, 1030 s, 900 s, 840 s ( $\text{cm}^{-1}$ ).

#### 2.5.4.1 3-Dimethylaminopropan -1-ol

Zinc dihydride (1.31 g, 19.6 mmole) freshly prepared and washed with THF, was formed into a slurry with THF ( $40 \text{ cm}^3$ ). 3-Dimethylpropan-1-ol ( $2.2 \text{ cm}^3$ , 18.6 mmole) was added dropwise over a period of 10 minutes. The reaction mixture was stirred for 2 hours at  $60^\circ \text{C}$ , filtered from unreacted solids, and the solvent removed *in vacuo*. Attempts to obtain a crystalline product failed and the product was finally obtained as a white gum which decomposed without melting *in vacuo* at  $120^\circ \text{C}$ . Found: % H, 0.60; % Zn, 36.0. Calc for  $\text{Me}_2\text{NC}_3\text{H}_6\text{OZnH}$ : % H, 0.56; % Zn, 36.5. An infrared spectrum of the product as a Nujol mull showed the following absorptions: 2800 vs, 1800 - 1640 m.broad, 1620 m, 1320 w,broad, 1275 m, 1240 w,broad, 1180 m.broad, 1060 bs.broad, 780 m, 760 m( $\text{cm}^{-1}$ ). The following absorptions were observed in the infrared spectrum of a benzene solution of the product: 2800 s, 1800 - 1640 , 1684 s,

1550 w, 1480 vs, 1390 vs, 1300 s, 1260 s, 1225 s, 1180 s, broad,  
1080 vs. broad, 1000 m, 970 m, 940 m, 800 m, 780 s  $\text{cm}^{-1}$ .

The  $^1\text{H}$  nmr spectrum of the product as a solution in deuterated benzene showed the following resonances

4.05, 3.95 (3.2), 2.32, 2.13 (8.8), 1.66 (2.0) ppm.

#### 2.5.4.2 3-Dimethylaminopropan-1-ol

Zinc dihydride (1.31 g, 19.6 mmole), freshly prepared and washed with benzene, was formed into a slurry with benzene (20  $\text{cm}^3$ ) and 3-dimethylaminopropan-1-ol (2.3  $\text{cm}^3$ , 19.4 mmole) was added via syringe. A slightly exothermic reaction with rapid gas evolution at room temperature took place. The reaction mixture was heated to  $60^\circ\text{C}$  and when most of the zinc dihydride had dissolved, the reaction mixture was filtered and the solvent removed *in vacuo*. The product could not be crystallised but was finally obtained as a white gum. An infrared spectrum of the product as a Nujol mull showed the following absorptions: 2800 vs, 1820 - 1640 s. broad, 1300 m, 1260 s, 1240 m, 1175 s, 1080 s. broad, 980 m, 960 m, 900 m, 850 m, 770 s ( $\text{cm}^{-1}$ ).

#### 2.5.5.1 3-Dimethylaminophenol

Zinc dihydride (1.31 g, 19.6 mmole) was formed into a slurry with THF (40  $\text{cm}^3$ ). A solution of 3-dimethylaminophenol (2.64 g,

19.6 mmoles) in THF (20 cm<sup>3</sup>) was added to the zinc dihydride slurry via syringe. The reaction mixture was stirred overnight by which time it had taken on a yellow colouration. The reaction mixture was then filtered and the solvent removed under reduced pressure leaving a yellow/brown gum (1.2 g, 31%). Attempts at crystallising this gum failed. Found: % H, 0.53; % Zn, 32.2. Calc for Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OZnH: % H, 0.49; % Zn, 32.1. An infrared spectrum of a Nujol mull of the product showed the following absorptions 3000 (vs, broad), 1780 w, 1660 - 1540 m, 1360 m, 1300 - 1200 m, broad, 1180 - 1100 m, 1080 - 1020 m, 1020 - 940 m, 940 - 880 m, 880 - 800 m, 760 m, 695m(cm<sup>-1</sup>). The <sup>1</sup>H nmr spectrum of the product in deuterated benzene showed the following resonances: 6.87, 6.28 (4), 3.50 (3.5), 2.66 (6), 1.27 (3.3) ppm.

#### 2.5.5.2 3-Dimethylaminophenol

Zinc dihydride (1.31 g, 19.6 mmoles) was formed into a slurry with benzene (20 cm<sup>3</sup>) and 3-dimethylaminophenol (2.54 g, 18.9 mmoles) in benzene (20 cm<sup>3</sup>) was added via syringe. The reaction mixture was stirred for 48 hours at room temperature. No reaction appeared to take place so the reaction mixture was heated to 65°C for one hour, during which time a yellow colouration appeared. The reaction mixture was filtered and a yellow solid (yield, 3.41 g, 86%) , which turned white when dry, was obtained as the residue. An infrared spectrum of this product as a Nujol

mull showed the following absorptions: 2900 vs, 1610 s, 1580 s, 1510 m, 1360 m, 1240 s, 1170 m, 1150 m, 1000s, 980 w, 900 w, 840 m.broad, 760 m, 750 m, 695 m ( $\text{cm}^{-1}$ ). The solvent was removed from the filtrate to give a yellow powder (yield 0.09 g, 2%). An infrared spectrum of the Nujol mull of this powder showed the following absorptions: 3100 - 2800 vs, 1720 m, 1610 s, 1580 sh, 1360 m, sh. 1270 m.broad asym., 1180 - 1080 m. broad, asym 1060 m.broad, 1005 s, 985 m, 900 m, 840 m.broad, 760 m, 695 m ( $\text{cm}^{-1}$ ). The  $^1\text{H}$  nmr spectrum of the powder solution in benzene showed the following resonances: 6.93, 6.51, 6.10 (4), 3.25 (1), 2.44 (6), ppm.

#### 2,5,6 8-Hydroxyquinoline

8-Hydroxyquinoline (2.82 g, 19.4 mmoles) was added as a solid to freshly prepared zinc dihydride (1.31 g, 19.6 mmoles). Tetrahydrofuran ( $30 \text{ cm}^3$ ) was added at  $0^\circ\text{C}$  and a violent effervescence was seen. The reaction mixture was allowed to warm up to room temperature and was then stirred for 20 hours. After filtration a dark coloured solution was obtained which on removal of solvent yielded a dark brown/green solid (yield, 2.79 g). Found: % Zn, 14.6; Calc. for  $\text{C}_9\text{H}_6\text{NOZnH}$  %Zn., 30.9. Bis-(8-oxyquinolato) zinc requires 18.3% Zn. Addition of water to the solid did not result in the liberation of gas. The solid melted at  $310^\circ\text{C}$  without decomposition. An infrared spectrum

of the product as a Nujol mull showed the following absorptions: 3100 - 2800 s, broad, 1620 w, 1605 m, 1585 s, 1502 s, 1320 m, 1290 m.broad, 1220 sh, 1180 sh, 1100 s, 1060 s, broad, 995 m, 910 m, 825 s, 798 s, 790 s, ( $\text{cm}^{-1}$ ). The  $^1\text{H}$  nmr spectrum of the THF soluble product in deuterated acetone showed the following resonances: 8.44 - 7.87 (0.42), 7.37 - 6.27 (1.68), 3.61 (1), 2.97 (2.46), 2.03 (0.55), 1.76 (1.02), 1.24 (1.00), 0.85 (0,94) ppm. This product was found to react with acetone to give a bright yellow product.

The residue of the initial reaction mixture was a reddish coloured solid (yield, 2.00 g) which reacted with water, liberating a gas. This solid decomposed on heating. At  $130^\circ\text{C}$  it turned grey and at  $280^\circ\text{C}$  shrinking was observed. No further change was seen to the temperature limit of the melting point apparatus. An infra-red spectrum of the product, as a Nujol mull, showed the following absorptions: 3100 - 2800 s, 1800 - 1500 m.broad, 1605 m, 1580 m, 1502 s, 1320 m, 1280 m.broad, 1110 s, 1080 s, 1040 s.broad, 900 m, 825 m, 800 m, 790 m, 730 s.broad, 690 m ( $\text{cm}^{-1}$ ).

#### 2.5.7 2-Methoxyphenol

Zinc dihydride (1.31 g, 19.6 mmoles) was formed into a slurry with THF ( $20\text{ cm}^3$ ) and the slurry was cooled to  $-45^\circ\text{C}$ . 2-Methoxyphenol (2.34 g, 18.9 mmoles) was dissolved in THF ( $20\text{ cm}^3$ ) and

added to the slurry via syringe. \* The reaction mixture, as shown by gas evolution, proceeded sluggishly at  $-45^{\circ}\text{C}$ , due to problems in the mixing of the reactants. When the temperature of the reaction mixture was raised to  $-10^{\circ}\text{C}$  the reaction proceeded briskly. After stirring for 24 hours the reaction mixture was filtered. The THF insoluble solid in the residue (yield, 2.47 g) decomposed between  $110^{\circ}\text{C}$  and  $115^{\circ}\text{C}$ . Found: % H, 0.97; % Zn, 34.5. Calc. for  $\text{C}_7\text{H}_7\text{O}_2\text{ZnH}$ : % H, 0.53; % Zn, 34.4. An infrared spectrum of the insoluble product as a Nujol mull showed the following absorptions: 2940 vs, 2845 vs, 1800 - 1400 s.broad, 1610 s, 1510 s, 1450 vs, 1330 o, 1292 vs, 1268 vs, 1224 vs, 1185 vs, 1120 vs, 1075 s, 1042 m, 1030 vs, 910 s, 870 w, 842 s, 757 s, 740 s, 730 s ( $\text{cm}^{-1}$ ).

After the solvent had been distilled off from the filtrate, a white solid (yield 0.76 g) was obtained. This showed signs of degradation at  $157^{\circ}\text{C}$  and it melted between  $245^{\circ}\text{C}$  and  $250^{\circ}\text{C}$ . Found: % H, 0.0; % Zn, 22.9. Calc. for  $\text{C}_{14}\text{H}_{14}\text{O}_4\text{Zn}$ : % H, 0.0; % Zn, 20.9. An infrared spectrum of this product as a Nujol mull showed the following absorptions: 2960 vs, 2860 vs, 1610 s, 1590 sh, 1510 vs, 1420 w, 1350 s, 1295 vs, 1268 vs, 1224 vs, 1185 vs, 1120 vs, 1075 s, 1040 sh., 1030 s.broad, 910 s, 870 s.broad, 840 s, 760 s, 740 vs, 690 m ( $\text{cm}^{-1}$ ). The  $^1\text{H}$  nmr spectrum of the soluble product in deuterated toluene showed the following resonances:

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\* The reaction vessel and syringe were covered in aluminium foil because 2-methoxyphenol (Guaiacol) is sensitive to light.

6.91 - 6.20 (4.4), 3.58 (4.5), 3.35 - 3.12 (2.9), 1.51 (4.2) ppm.

#### 2.5.8 2-Methoxybenzenethiol

Zinc dihydride (1.31 g, 19.6 mmoles) was formed into a slurry with THF (40 cm<sup>3</sup>) at -45°C. The thiol (2.73 g, 19.5 mmoles) was added dropwise via syringe over a period of five minutes to the slurry. Since the reaction proceeded very slowly at -45°C, the reaction mixture was heated to 45°C and stirred for 2 hours until gas evolution had stopped. The reaction mixture was then filtered and the solvent distilled from the filtrate to give a colourless oil. Addition of hexane yielded a blue-white solid (yield 1.95 g). Found: % H, 0.29; % Zn, 16.3. Calc. for C<sub>7</sub>H<sub>7</sub>OSZnH: % H, 0.48; % Zn, 31.6 (MeOC<sub>6</sub>H<sub>4</sub>SH)<sub>2</sub>:ZnH requires: % H, 0.28, % Zn, 18.9. An infrared spectrum of the product as a Nujol mull showed the following absorptions: 2940 vs, 2850 vs, 1600 m.broad, 1577 vs, 1299 w, 1270 m, 1224 vs, 1178 w, 1130 w, 1068 s, 1041 m, 1018 s, 792 w, 743 s, 676 s (cm<sup>-1</sup>). An infrared spectrum of the product as a THF solution showed the following absorptions: 3100 s, 1661 w. broad, 1575 s, 1521 m.broad, 1440 m.broad, 1402 m.broad, 1011 w. broad asym. 792 sh, 745 s, 684 s (cm<sup>-1</sup>). The <sup>1</sup>H nmr spectrum of the product obtained in deuterated dimethylsulphoxide, a solvent with which the product was found to react, showed the following resonances: 7.40, 7.28 (0.42), 6.75 (0.68), 3.72 (1), 2.50 (0.07), ppm. Reaction of the complex with H<sub>2</sub>O and subsequent extraction with diethylether yielded white needle-like crystals. An infrared

spectrum of these crystals in Nujol was obtained and the following absorptions were observed: 2940 vs, 2850 s, 1580 m, 1305 w, 1272 m, 1240 s, 1150 m, 1130 m, 1060 s, 1040 m, 1022 s, 846 m, 795 m, 740 s ( $\text{cm}^{-1}$ ). The  $^1\text{H}$  nmr spectrum of these crystals in deuterated chloroform contained the following resonances: 7.60 - 6.75 (5.15), 5.12 (1.65), 3.85 (6.75), 2.12 (1.2), 1.25 (5.2) ppm. The complex exhibited shrinking at  $150^\circ\text{C}$  and decomposed with melting and bubbling between  $157^\circ\text{C}$  and  $167^\circ\text{C}$ .

## 2.6 Reactions of zinc dihydride with monodentate ligands containing an acidic hydrogen atom

### 2.6.1 2,4,6,- Tri-t-butylphenol

Zinc dihydride (1.31 g, 19.6 mmoles) was formed into a slurry with benzene ( $20\text{ cm}^3$ ). The phenol (5.13 g, 19.6 mmoles) was dissolved in benzene ( $20\text{ cm}^3$ ) and then added via syringe to the slurry at  $0^\circ\text{C}$ . A violent effervescence was observed. The reaction mixture was allowed to warm up to room temperature and then stirred for 24 hours after which time it was filtered and the solvent removed from the filtrate *in vacuo*. A crystalline yellow solid (4.59 g), was obtained. The product was analysed by infrared and  $^1\text{H}$  nmr spectroscopy. The infrared spectrum of the product as a Nujol mull showed the following absorptions: 3670 m, 2900 vs, 1760 w, 1605 w, 1300 sh, 1290 sh, 1280 s.broad, 1240 s, 1200 m, 1160 s, 1120 s, 1090 m, 1060 m, 1030 m, 940 w, 920 w, 900 s, 880 s, 840 m, 820 m, 790 m, 770 m, 740 m, 675 m ( $\text{cm}^{-1}$ ). The  $^1\text{H}$  nmr spectrum of the product in deuterated benzene

showed the following resonances: 7.42 (2), 7.32 (2), 4.79 (1), 1.66, 1.56 (20), 1.39, 1.36, 1.33 (45) ppm.

### 2.6.2 2-Methyl-2-propanethiol

Zinc dihydride (1.31 g, 19.6 mmoles) was formed into a slurry with THF (30 cm<sup>3</sup>) at -40°C. To this slurry was added 2-methyl-2-propanethiol (2.1 cm<sup>3</sup>, 18.6 mmoles). All of the zinc dihydride had dissolved within the space of 1.5 hours and the reaction mixture was then filtered. On standing overnight a white solid had precipitated out of the filtrate. This was filtered off (1.74 g, 57%). Found: % H, 0.55; % Zn 29.6. Calc for (CH<sub>3</sub>)<sub>3</sub>CSZnH: % H, 0.64; % Zn, 41.8. (CH<sub>3</sub>)<sub>3</sub>CSZnH.THF requires % H, 0.44, % Zn 28.6. This white solid decomposed with melting at 225°C. The remaining filtrate was concentrated and addition of hexane gave first a white oil and then a creamy white solid (1.36 g, 43%) which melted at 137°C with decomposition. An infrared spectrum of the white solid as a Nujol mull showed the following absorptions: 3050 - 2800 vs, 1800 - 1400 vs, br, 1652 sh, 1627 sh, 1502 vs, 1367 s, 1207 w, 1157 vs, 1036 vs, 976 m.broad, 886 m, 815 w, 717 w, 667 w. An infrared spectrum of creamy white solid product as a THF solution showed the following absorptions: 1734 w.sh, 1657 vs, 1531 vs.broad, 1411 vs. broad, 1159 s, 1004 m, 772 s, 682 s. The <sup>1</sup>H nmr of a THF solution of the creamy white solid product, before it had been desolvated,

was also obtained. This showed a resonance at 4.78 ppm downfield of the TMS resonance.

### 2.6.3 Diphenylphosphine

Zinc dihydride (1.31 g, 19.6 mmoles) was formed into a slurry with THF (30 cm<sup>3</sup>). Diphenylphosphine (3.5 cm<sup>3</sup>, 20.1 mmoles) was added dropwise to the stirred slurry at room temperature. The zinc dihydride was seen to dissolve and a fine solid gradually deposited from solution. The reaction mixture was filtered, leaving an ivory-coloured solid which did not liberate hydrogen from water, did not melt up to 340°C and which slowly turned pink on exposure to the atmosphere. The filtrate, a yellow/green solution decomposed on exposure to reduced pressure at room temperature.

### 2.6.4 Diphenylamine

Zinc dihydride (1.3 g, 19.4 mmoles) was formed into a slurry with toluene (30 cm<sup>3</sup>). Diphenylamine (3.3 g, 19.5 mmoles) was dissolved in toluene (20 cm<sup>3</sup>) and was added dropwise to the zinc dihydride slurry. The reaction mixture was stirred for 24 hours and then filtered. Concentration of the filtrate yielded colourless rectangular plate-like crystals (yield, 1.46 g) which melted

between 46°C and 54°C. A  $^1\text{H}$  nmr spectrum was obtained of the product in deuterated toluene and this showed the following resonances: 7.4 - 6.8 (12.3 ), 5.1 (0.8) ppm.

#### 2.6.5.1 Diethylamine

Zinc dihydride (1.31 g, 19.6 mmoles) was allowed to react with diethylamine (1.43 g, 19.6 mmoles) in THF (35 cm<sup>3</sup>). The reaction mixture was stirred overnight at 50°C and was then filtered yielding a straw coloured solution. The solvent was removed under reduced pressure, leaving a brown oil which crystallised on addition of hexane as a very fine brown powder (yield, 0.76 g, 28%), melting between 155°C and 160°C. Found: % H, 1.52; % Zn, 43.9. Calc. for  $\text{Et}_2\text{NZnH}$ : % H, 0.72; % Zn, 47.1.  $\text{Et}_2\text{NHZnH}_2$  requires % H, 1.44 ; % Zn, 46.4 An infrared spectrum of the product as a Nujol mull showed the following absorptions: 2900 vs, 1800 - 1220 vs.broad, 1180 m, 1150 m 1110 m, 1040 m.broad, 900 w.broad, 855 m, 795 m.broad. Prior to crystallisation of the brown oil by hexane, benzene was added. No crystallisation was seen but the brown oil did dissolve to some extent The  $^1\text{H}$  nmr of this benzene solution was obtained and the following resonances were observed: 4.18 (2), 3.78 (2), 2.82 (5.1), 1.55 (9), 1.08 (7) ppm.

## 2.5.6.2 Diethylamine in the presence of tetramethylethylenediamine(TMEDA)

Zinc dihydride (1.31 g, 19.6 mmoles) was formed into a slurry with benzene (30 cm<sup>3</sup>) and TMEDA (5 cm<sup>3</sup>, 33 mmoles). Diethylamine (2 cm<sup>3</sup>, 19.6 mmoles) was then added dropwise to the slurry. After stirring at room temperature for 60 hours, the reaction mixture was filtered. The solvent was then distilled off into a cold trap, leaving behind a clear oil, which was redissolved in benzene. An infrared spectrum of this benzene solution showed the following absorptions: 2950 vs, 2850 vs, 2800 vs, 2750 vs, 1750 sh, 1600 s.broad, 1580 sh, 1450 vs, 1380 s, 1290 s, 1260 s, 1160 sh, 1150 sh, 1125 vs.broad, 950 m, 932 m, 880 w, 830 m, 790 m. cm<sup>-1</sup>. Addition of hexane to the benzene solution yielded a white microcrystalline solid which was filtered off and collected (1.06 g, 30.1%).

Found: % H, 1.22; % Zn, 39.8. Calc. for Et<sub>2</sub>NZnH.TMEDA: % H, 0.39; % Zn, 25.5 (Et<sub>2</sub>NH.ZnH<sub>2</sub>)(TMEDA.ZnH<sub>2</sub>)<sub>2</sub> requires % H, 1.18; % Zn, 38.5. The white solid melted at 129°C and decomposed at 135°C. An infrared spectrum of the solid as a Nujol mull showed the following resonances: 3000 - 2700 vs, 1800 - 1550 vs, broad, 1290 m, 1140 m.broad, 1100 m.broad, 1060 - 990 m.broad, 950 m, 790 m. broad. cm<sup>-1</sup>. The <sup>1</sup>H nmr spectrum of a benzene solution of the white solid showed the following broad resonances: 3.22 (1), 2.13 (3.8), 1.56 (4.0) ppm.

### 2.6.6 Diisobutylamine

Zinc dihydride (1.31 g, 19.6 mmoles) was formed into a slurry with THF (20 cm<sup>3</sup>). Diisobutylamine (3.40 cm<sup>3</sup>, 19.5 mmoles) was added dropwise to the stirred slurry. Aliquots of the supernatant liquor of the reaction mixture did not liberate hydrogen from water even after the reaction mixture had been stirred for 120 hours, by which time the zinc dihydride in the reaction mixture had turned black.

## 2.7 The reaction of zinc dihydride with carbonyl groups

### 2.7.1 Benzophenone

Zinc dihydride (1.31 g, 19.6 mmoles) was formed into a slurry with THF (20 cm<sup>3</sup>). Benzophenone (3.58 g, 19.6 mmoles) was dissolved in THF (20 cm<sup>3</sup>) and the resulting solution was added to the slurry at room temperature via syringe. During the first half hour a pink colouration persisted in the reaction mixture. This was accompanied by exothermicity and after half an hour had elapsed, the reaction mixture had become white and opaque. Stirring for 50 hours at room temperature did not lead to the dissolution of more zinc dihydride, so the reaction mixture was filtered. The solvent was removed from the filtrate, leaving a green gum. Attempts to crystallise this gum failed. Found: % H, 0.02; Calc. for C<sub>13</sub>H<sub>11</sub>OZnH: % H, 0.44. An infrared spectrum

of a Nujol mull of this gum showed the following absorptions:

3050 m, 2950 vs, 2900 vs, 1660 w, 1610 m, 1500 m, 1360 m, 1265 m,  
1200 m.broad, 1000 m.broad, 930 m, 870 w, 760 w, 745 m, 708 m ( $\text{cm}^{-1}$ ).

A solution of the green gum in deuterated benzene was examined  
by  $^1\text{H}$  nmr spectroscopy and the following resonances were observed :  
7.34, 7.10 (8), 3.28 (1), 1.29 (3) ppm.

### 2.7.2 Benzaldehyde

Zinc dihydride (1.31 g, 19.6 mmoles) was formed into a slurry  
with benzene ( $20 \text{ cm}^3$ ). Benzaldehyde ( $1.98 \text{ cm}^3$ , 19.6 mmoles)  
was added dropwise to the slurry. A very exothermic reaction was  
noted. The reaction mixture was stirred for 24 hours and then  
filtered. The solvent was distilled off from the filtrate leaving  
a straw coloured oil. Addition of hexane ( $20 \text{ cm}^3$ ) to the oil  
gave a white creamy solid (0.88 g). Found: % H, 0.05; Calc.  
for  $\text{C}_7\text{H}_7\text{OZnH}$  : % H, 0.57. The solid melted between  $113^\circ\text{C}$  and  
 $120^\circ$  without decomposing. An infrared spectrum of a Nujol mull  
of the product showed the following absorptions: 2900 vs, 2750 w,  
1700 w, 1618 w.broad, 1320 s, 1270 m, 1200 s, 1160 m, 1100 m.  
broad, 1020 m.broad, 820 w.broad, 700 m ( $\text{cm}^{-1}$ ). The  $^1\text{H}$  nmr  
spectrum of the product in deuterated benzene showed the  
following resonances: 7.24, 7.15 (9.8), 4.90 (1.2) ppm.

### 2.7.3 (dl)-Camphor

Zinc dihydride (1.31 g, 19.6 mmoles) was formed into a slurry with THF (20 cm<sup>3</sup>). A solution of camphor (3.01 g, 19.8 mmoles) in THF (20 cm<sup>3</sup>) was added to the slurry via syringe at room temperature. A slightly exothermic reaction was noted during the first half hour of reaction time. The reaction mixture was stirred for 12 hours and then centrifuged yielding a white solid and a cloudy pink solution. The solution was removed via syringe to a Schlenk tube and the solvent removed to yield a pink/rose oil. This crystallised in hexane at -5°C as a pink-white solid which was dried *in vacuo* (1.84 g, 42.8%). Found: % H, 0.27; % Zn, 16.8. Calc. for C<sub>10</sub>H<sub>17</sub>OZnH: % H, 0.46; % Zn, 29.6. (C<sub>10</sub>H<sub>17</sub>O)<sub>2</sub>ZnH requires % H, 0.27, % Zn 17.5. The complex decomposed at 134°C.

An infrared spectrum of the complex as a Nujol mull showed the following absorptions: 2950 vs, 2750 m, 1790 w, 1580 vs, broad, shoulder, 1320 m, 1280 m, 1250 m, 1195 s, 1120 s, 1080 s. broad, 1025 s, 990 s, 955 m, 918 s. broad, 870 s, 855 s, 800 m, 738 s, 695 m (cm<sup>-1</sup>). The <sup>1</sup>H nmr spectrum of a deuterated benzene solution of the complex showed the following resonances: 4.11 (1), broad, 3.54 (0.99), 1.70 broad, 1.21, 1.06, 0.96, 0.86 (31.4) ppm. A sample of the complex was hydrolysed and worked up as described in 2.14. The organic layer was injected onto a 5 foot 10% PEGA chromatography column at 150°C. No free ketone was found and the ratio of exo alcohol to endo

alcohol was found to be 9:1.

#### 2,7,42-Acetylthiophene

Zinc dihydride (1.2 g, 17.9 mmoles) was formed into a slurry with THF (20 cm<sup>3</sup>). 2-acetylthiophene (2.21 g, 17.7 mmoles) was added dropwise via syringe to the slurry at room temperature. A very exothermic reaction took place and after the reaction mixture had been stirred for one hour, it was filtered. The filtrate was reduced to a small volume and addition of hexane resulted in the precipitation of a light white powder (0.12 g). Removal of solvent from the filtrate yielded a white gum. An infrared spectrum of the powder as a Nujol mull showed the following absorptions: 2900 vs.sh, 2750 vs, 1772 w.broad, 1585 m.broad, 1307 m, 1260 w, 1232 m, 1187 m.sh, 1152 w.broad, 1080 s.broad, 1040 w, 1010 w, 980 w, 910 m.sh, 890 m.broad, 850 m.sh, 830 w, 722 w, 698 vs (cm<sup>-1</sup>). The <sup>1</sup>H nmr spectrum of a deuterated benzene solution of the powder showed the following resonances: 7.15, 6.84 (8), 5.38 broad (2.3); 3.50 (3), 1.5 (8) ppm. The white gum decomposed at 90°C.

## 2.8 Reaction of zinc dihydride with triple bonds.

### 2.8.1.1 Acetonitrile

Zinc dihydride (1.31 g, 19.6 mmol) was formed into a slurry with THF (30 cm<sup>3</sup>). Acetonitrile (1 cm<sup>3</sup>, 19.6 mmol) was added to the stirred slurry via syringe. The reaction mixture was stirred for 24 hours at 60°C and the unreacted zinc dihydride was then filtered off. The yellow/green filtrate was concentrated but crystallisation could not be induced. The solvent was then completely removed under reduced pressure and a pale yellow crystalline solid (yield 1.34 g) was obtained (255°C dec.) Found: % H, 0.07; % Zn, 25.0. Calc. for C<sub>2</sub>H<sub>4</sub>NZnH: %H, 0.92; % Zn, 60.1. A mixture with a stoichiometry of 92% (MeC≡N)<sub>2</sub>Zn(MeCH=N)<sub>2</sub> + 7% HZnN=C(H)Me satisfies the above analysis. No attempts were made to separate the components of the mixture. An infrared spectrum of a Nujol mull of the mixture showed the following absorptions: 2940 vs, 2870 vs, 2180 m, 2060 w, 1862 w, 1610 w.broad, 1270 w, 1112 m.sh, 1067 s. broad, 890 s.broad, 800 m.broad (cm<sup>-1</sup>). The <sup>1</sup>H nmr spectrum was not obtained due to the very low solubility of the product in inert deuterated solvents.

### 2.8.1.2 (CH<sub>3</sub>CH=N)<sub>2</sub>Zn(N=CCH<sub>3</sub>)<sub>2</sub> + TMEDA

The complex (0.34 g, 1.5 mmol) was allowed to react with TMEDA (0.3 cm<sup>3</sup>, 1.9 mmol) in benzene (10 cm<sup>3</sup>). The starting

complex, though insoluble in benzene, dissolved completely on addition of the TMEDA. The reaction mixture was stirred for 48 hours and was then filtered. The solvent was removed *in vacuo*, leaving a white solid (yield 0.27 g, 68.3%). An infrared spectrum of a Nujol mull of the white solid showed the following absorptions, 2940 vs, 2860 vs, 2230 w, 1270 m, 1100 m.broad, 1030 m.broad, 825 m, 800 m, ( $\text{cm}^{-1}$ ).

### 2.8.2.1 2-Methyl-2-propionitrile

Zinc dihydride (1.31 g, 19.6 mmoles) was formed into a slurry with THF ( $30 \text{ cm}^3$ ). 2-Methyl-2-propionitrile ( $2.1 \text{ cm}^3$ , 19.0 mmoles) was added to the stirred slurry via syringe. The reaction mixture was then heated to  $66^\circ\text{C}$  and kept at this temperature until all the zinc dihydride had dissolved. The reaction mixture was then filtered and the solvent distilled off *in vacuo* into the other arm of the double Schlenk tube. A white solid (yield 2.87 g) was obtained ( $165^\circ\text{C}$  - dec.) Found: % H, 0.28. Calc for  $\text{C}_4\text{H}_{10}\text{NZnH}$ : % H, 0.66. A Nujol mull of the product exhibited the following infrared absorptions : 2950 vs, 2850 vs, 2690 w, 1699 m, 1670 m, 1220 m, 1185 m, 1060 vs.broad, 1015 s,broad, 895 m, 730 m.broad, 692 s ( $\text{cm}^{-1}$ ). An infrared spectrum of a THF solution of the product showed the following absorptions: 2800 w, 2710 w, 1670 vs, 1650 vs, 1500 m, 1400 vs, 1370 vs, 1150 w.sh, 1010 vs.broad, 780 vs, broad, 710 m.sh. The  $^1\text{H}$  nmr spectrum of a deuterated benzene solution of the product showed the following resonances: 3.64

broad (0.26), 1.21 broad, assym. (1) ppm. When the product was in contact with THF vapour *in vacuo* a very exothermic reaction was noted.

#### 2.8.2.2 2,2-Dimethylpropyliminozinc hydride + TMEDA

The complex (0.47 g, 1.5 mmoles) was allowed to react with TMEDA (0.2 cm<sup>3</sup>, 1.5 mmoles) in benzene (10 cm<sup>3</sup>). The reaction mixture was stirred for 96 hours at room temperature without any apparent reaction taking place. It was then filtered, leaving a brown/white solid (0.24 g). An infrared spectrum of a Nujol mull of the product showed the following absorptions: 2950 vs, 2840 vs, 1620 m.broad, 1280 m, 1070 s, broad, 1018 m, 960 m, 935 m, 885 m, 840 m, 790 s.broad, 657 m. (cm<sup>-1</sup>). The <sup>1</sup>H nmr spectrum of a deuterated benzene solution of the product showed the following resonances: 3.08 (5) broad, 2.31 (1), 2.11 (2.5), 1.08 (22) broad (ppm).

#### 2.9 Benzylidenemethylamine

Zinc dihydride (1.31g, 19.6 mmoles) was formed into a slurry with THF (20 cm<sup>3</sup>). Benzylidenemethylamine (2.2 cm<sup>3</sup>, 17.8 mmoles) was added to the stirred slurry via syringe. An exothermic reaction was noted, and a purple red colouration was observed

initially in the reaction mixture. The reaction mixture was filtered and the solvent was removed from the filtrate overnight by distillation *in vacuo* into a cold trap. A yellow oil was obtained and on addition of a 50/50 mixture of benzene and hexane a white microcrystalline solid was obtained (yield, 4.62 g). An infrared spectrum of a solution of the product in THF showed the following absorptions: 3270 m, 2990 s, 2690 m, 1663 s,sh, 1594 s, 1490 vs, 1381 vs. broad, 1349 vs,sh, 1138 m,broad, 815 vs. broad, 728 vs, 690 vs ( $\text{cm}^{-1}$ ). A solution of the product in deuterated benzene was examined by  $^1\text{H}$  nmr spectroscopy and the following resonances were observed: 7.34 (4.9), 4.29 (0.5), 3.74, 3.64 (1.0), 3.03 (0.4), 2.40, 2.31 (1.26) ppm. The solid decomposed on standing at room temperature under nitrogen.

## 2.10 Redistribution reactions of zinc dihydride

### 2.10.1 Trimethylchlorosilane in the presence of triethylamine

A three necked  $100\text{ cm}^3$  flask equipped with a magnetic stirrer bar, rubber septum inlet and greased stopper was charged with zinc dihydride (1.31 g, 19.6 mmoles) in the glove box. The flask was then attached to a vacuum line (see Fig. 3 ) at A. and evacuated. THF ( $40\text{ cm}^3$ ) was added, followed by trimethylchlorosilane (1.43 g, 13.2 mmoles) and triethylamine (2.11 g, 20.8 mmoles) via syringe through the septum inlet. Tap 6 was then closed and the

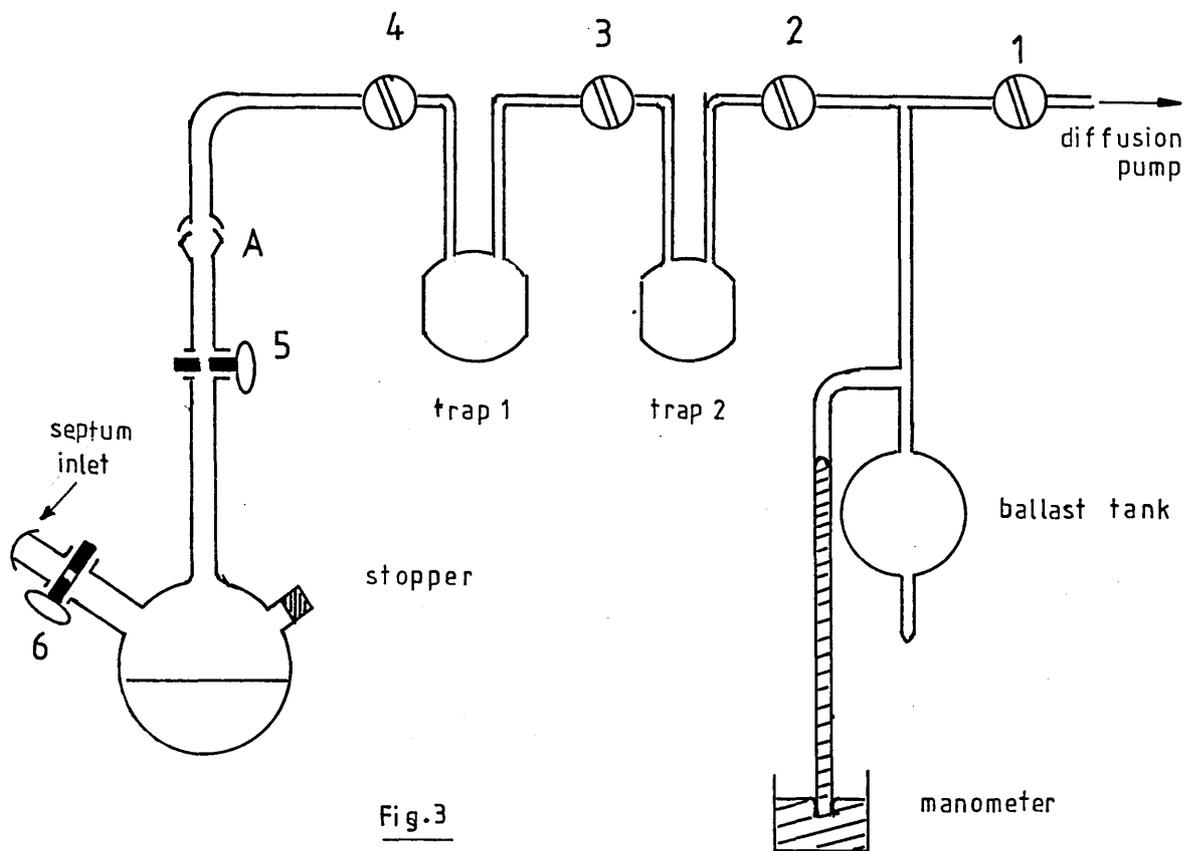


Fig. 3

flask was cooled with liquid nitrogen and evacuated. The vacuum line was then closed at tap 1 and the reaction mixture was stirred at room temperature for 12 hours. The pressure in the vacuum line increased to 60 mm Hg during this time. Taps 4 and 5 were then closed and the three necked flask was connected up to a nitrogen supply. It was flushed with nitrogen and the contents were then transferred to a double Schlenk tube. The contents of the vacuum line were condensed out into the freeze-out tip of the

ballast tank. A gas cell was attached to the vacuum line at A and evacuated. The system was then closed at tap 1. The contents of the ballast tank were then allowed to warm up to room temperature. The gas cell was then opened to the vacuum line and once the pressure had equilibrated, the gas cell was detached from the vacuum line and an infrared spectrum was obtained of the volatile contents of the vacuum line. This showed the following absorptions: 2980 vs, 2860 vs, 2370 m, 2130 vs, 1260 m.broad, 1145 m, 1138 m, 1084 s. broad, 913 vs, 906 vs, 850 m.broad ( $\text{cm}^{-1}$ ). The non-volatile reaction product in the double Schlenk tube was filtered and the filtrate was concentrated. Crystallisation of the concentrated liquor was attempted without success. The solvent was then completely distilled off leaving a green/yellow oil. This decomposed on standing to give a grey/white/orange solid mass. Analysis of this was not attempted.

#### 2.10.21 Trimethylamine hydrochloride

Zinc dihydride (0.66 g, 9.8 mmol) was allowed to react with trimethylamine hydrochloride (0.63 g, 6.6 mmol) in THF ( $40 \text{ cm}^3$ ) over a period of 24 hours at room temperature. The reaction mixture was then filtered, the filtrate was concentrated and benzene ( $20 \text{ cm}^3$ ) was added. This solvent was gradually distilled off until colourless needle-like crystals were observed in the benzene-THF solution. Some of these were filtered off and pumped

dry to yield white needles (yield, 0.26 g, ) which melted smoothly at 78 - 80°C and decomposed at 120°C with bubbling. Benzene (10 cm<sup>3</sup>) was added to the remaining THF-benzene solution. The solvent was then completely distilled off from the solution and a white crystalline solid (0.34 g) was obtained. This solid did not melt cleanly but showed shrinkage at 60°C with melting at 90°C and decomposition at 120°C. A colourless liquid was seen to condense in the cool top of the sealed melting point tube. Found: % H, 0.10; % Zn, 20.36. Calc. for Me<sub>3</sub>NHZnCl: % H, 0.62; % Zn, 40.5. Me<sub>3</sub>NHZnCl (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> requires % H, 0.31, % Zn, 20.53. An infrared spectrum of the white solid as a Nujol mull showed the following absorptions: 2960 vs, 2870 vs, 1600 m.broad, 1258 m, 1240 w, 1160 w.broad, 1115 m, 1010s, 825 s, 505 s, 400 s.broad (cm<sup>-1</sup>). A solution of the white solid in THF showed the following infrared absorptions: 2785 w, 1720 vs.broad, 1540 sh, 1490 vs, 1415 vs, 1255 w.broad, 1080 sh.broad, 1015 vs, 880 sh.broad, 825 vs, 692 m, 4950, 400s, broad (cm<sup>-1</sup>). The <sup>1</sup>H nmr spectrum of a solution of the product in deuterated benzene showed the following resonances: 7.18 (4), 2.05 (3) ppm.

#### 2.10.2.2 Trimethylaminechlorozinc hydride complex and triphenylphosphine

The complex zinc hydride (0.05 g, 0.15 mmoles) was allowed to react with triphenylphosphine (0.08 g, 0.30 mmoles) in deuterated benzene (2.5 cm<sup>3</sup>) over a period of 24 hours, during which time most of the complex had dissolved. The supernatant liquor was

extracted and the  $^1\text{H}$  nmr spectrum of this showed the following resonances: 7.40 (2.13), 7.08 (2.77), 4.50 (0.1), 2.01 (1) ppm.

### 2.10.2.3 Trimethylaminechlorozinc hydride complex and dimethoxyethane

The complex zinc hydride (0.1 g, 0.30 mmoles) was allowed to mix with 1,2-dimethoxyethane (0.028 g, 0.30 mmoles) in deuterated benzene ( $3\text{ cm}^3$ ) over a period of 24 hours. The supernatant liquor was then extracted and the  $^1\text{H}$  nmr spectrum of this showed the following resonances, 7.16 (1), 3.35 (2.1), 3.13 (3), 2.01 (2.5) ppm.

### 2.10.3 Zinc dichloride and tetramethylethylenediamine(TMEDA)

Zinc dihydride (1.31g, 19.6 mmoles) was formed into a slurry with THF ( $20\text{ cm}^3$ ). Anhydrous zinc chloride (2.28 g, 16.7 mmoles) and TMEDA ( $6.5\text{ cm}^3$ , 43.3 mmoles) were added to the stirred slurry. A rapid exothermic reaction was noted. The reaction mixture was filtered when most of the zinc dihydride had dissolved. Concentration of the filtrate led to the formation of some colourless crystals. Addition of hexane ( $7\text{ cm}^3$ ) to the concentrated filtrate precipitated out a white powder. This was washed with hexane and pumped dry overnight (yield 3.73 g, 43.9 %). The white powder melted at  $85^\circ\text{C}$  and decomposed with bubbling between  $110^\circ\text{C}$  and  $115^\circ\text{C}$ . Found: % H, 0.53; % Zn, 28.6. Calc. for  $\text{C}_6\text{H}_{16}\text{N}_2\text{ClZnH}$ : % H, 0.46; % Zn, 29.9. A Nujol mull of the product was examined

by infrared spectroscopy and the following absorptions were observed: 2950 vs, 2870 vs, 1701 vs broad, 1610 w, broad.sh., 1353 m, 1287 vs, 1247 m, 1191 w, 1168 m, 1126 s, 1104 w, 1061w, 1047 w, 1028 vs, 1011 vs, 952 vs, 936 w, 800 vs, 780 m, 730 w, 589 m, 512 vs. broad.sh, 482 vs. broad, 431 vs ( $\text{cm}^{-1}$ ). The  $^1\text{H}$  nmr spectrum of the product in deuterated benzene showed the following resonances: 4.43 (1), 2.06 (12), 1.84 (4.5) ppm.

#### 2.10.4 Zinc dichloride and dimethoxyethane

A mixture of zinc dihydride (1.31 g, 19.6 mmoles) and anhydrous zinc chloride (1.86 g, 13.7 mmoles) was formed into a slurry with THF ( $20 \text{ cm}^3$ ). 1,2-Dimethoxyethane ( $8 \text{ cm}^3$ , 77 mmoles) was added to the slurry via syringe. An exothermic reaction was noted and the zinc dihydride mostly dissolved in one and half hours and the reaction mixture was then filtered. Hexane ( $40 \text{ cm}^3$ ) was added producing a turbidity in the solution. This settled out to give a colourless oil. The solvent was then slowly distilled off and a cloudy viscous oil was obtained. Attempts to crystallise the oil were unsuccessful. The oil was then kept under reduced pressure to remove any remaining solvent. An infrared spectrum was obtained of a thin film of the oil and the following absorptions were observed: 2890 vs, 2800 s, 1590 m.v. broad asym, 1475 sh, 1460 vs, broad, 1380 m, 1350 vs, 1300 sh, 1280 m. broad, 1242s, 1190 s, 1136 vs, sh, 1109 vs, 1078 vs, 1016 vs, 945 m. broad asym, 873 s, 850 s. sh, 660 w, 530 vs, broad ( $\text{cm}^{-1}$ ). The

$^1\text{H}$  nmr spectrum of a solution of the oil in deuterated benzene showed the following resonances: 3.97 (0.58), 3.47 (1.75), 3.24 (1) ppm.

#### 2.10.5 Zinc dichloride and 2,5-dithiahexane

A mixture of zinc dihydride (1.2 g, 17.9 mmoles) and anhydrous zinc chloride (1.71 g, 12.5 mmoles) was formed into a slurry with THF (20 cm<sup>3</sup>). 2,5-Dithiahexane (8 cm<sup>3</sup>) was added dropwise to the slurry via syringe. No immediate exothermic reaction was noted. The reaction mixture was stirred at 45°C for 1.5 hours and then filtered. Hexane (20 cm<sup>3</sup>) was added to the filtrate and a clear oil settled out. The solvent was gradually distilled off leaving behind the clear oil. This oil could not be crystallized. The infrared spectrum of the oil as a thin film showed the following absorptions: 2940 vs, 2890 vs, 2830 vs sh, 1700 - 1500 w, v.broad, 1430 vs, 1321 w, 1269 m, 1204 s, 1135 m, 1068 m.sh, 1047 s, 1012 w, 963 s, 917 m, 891 m, 739 s, 688 vs, 410 vs.broad (cm<sup>-1</sup>). A THF solution of the oil was also examined by infrared spectroscopy and the following absorptions were observed: 1565 w.v.broad, 1450 vs, broad, 1320 m, 975 m.broad, 738 vs, 690 vs, 610 w.broad, 515 w broad, 418 vs broad (cm<sup>-1</sup>). The  $^1\text{H}$  nmr spectrum of a deuterated benzene solution of the product showed the following resonances: 3.72 (1), 3.15 (0.4), 2.58 (4.47), 1.94 (6.27) ppm. The oil showed some signs of decomposition on prolonged exposure to reduced pressure.

## 2.11 Reactions of zinc dihydride with coordinating ligands

### 2.11.1 Triphenylphosphine

An excess of triphenylphosphine (16 g, 61.0 mmoles) was added to zinc dihydride (2.0 g, 29.9 mmoles) in THF (60 cm<sup>3</sup>) and the reaction mixture was stirred overnight at room temperature. The reaction mixture was then filtered from unreacted solids and the solvent was removed under reduced pressure. A large amount of a white crystalline solid was obtained. A spot test for zinc<sup>80</sup> in this solid proved negative. Comparison of the infrared and <sup>1</sup>H nmr spectra of the solid with those of authentic triphenylphosphine showed that no reaction had in fact taken place.

### 2.11.2 Triethylamine

Zinc dihydride (1.0 g, 14.9 mmoles) was allowed to react with triethylamine (5 cm<sup>3</sup>, 68.1 mmoles) in THF (40 cm<sup>3</sup>) under reflux conditions until the reaction mixture started turning grey. (Under prolonged reflux conditions the zinc dihydride decomposed leaving behind a large mass of zinc). The reaction mixture was filtered and the solvent was removed from the filtrate leaving a trace of white oil which was insoluble in deuterated toluene. There was an insufficient quantity of the oil for a quantitative chemical analysis to be carried out.

### 2.11.3 Bisdimethylaminomethane

Zinc dihydride (0.3 g, 4.5 mmoles) was formed into a slurry with THF (40 cm<sup>3</sup>). Bisdimethylamino methane (0.6 cm<sup>3</sup>, 10.8 mmoles) was added to the slurry via syringe. The reaction mixture was stirred for 120 hours at room temperature and then filtered. When the solvent was removed from the filtrate no significant yield of product was obtained.

## 2.12 Reactions of diethylzinc

### 2.12.1 2-Methoxyethanol

2-Methoxyethanol (3.1 cm<sup>3</sup>, 50.9 mmoles) was added dropwise to a solution of diethylzinc (1.41 g, 19.6 mmoles) in toluene (40 cm<sup>3</sup>) at 0°C and with constant stirring. When gas evolution had ceased, the solvent was removed under reduced pressure leaving a white crystalline solid (135°C dec.). Found: % Zn, 30.8, Calc. for (MeOC<sub>2</sub>H<sub>4</sub>O)<sub>2</sub>Zn: % Zn, 30.2. An infrared spectrum of the complex as a Nujol mull showed the following absorptions: 2900 vs, 2710 w, 1340 w, 1300 w, 1250 w, 1210 w, 1170 - 1030 m. broad, 960 m, 930 sh, 900 m, 840 m (cm<sup>-1</sup>). The <sup>1</sup>H nmr spectrum of the complex in deuterated toluene showed the following resonances: 4.05 (4), 3.55, 3.45 (6), 3.35 (4) ppm.

### 2.12.2 2-Methoxyethanol

Diethylzinc (4.82 g, 39.1 mmol) was added to pentane (40 cm<sup>3</sup>) at -40°C followed by the dropwise addition of 2-methoxyethanol (2.98 g, 39.2 mmol) with repeated shaking. After 0.5 hours a clear solution was obtained. The solution was then filtered and the volume of the filtrate was reduced by half under reduced pressure. On cooling the filtrate, a large amount of white crystals were deposited on the sides of the reaction vessel. The crystals were filtered off and on warming to room temperature the crystals melted to give a colourless mobile liquid. Found: % C<sub>2</sub>H<sub>5</sub>, 15.2, % Zn, 38.0; Calc. for MeOC<sub>2</sub>H<sub>4</sub>OZnC<sub>2</sub>H<sub>5</sub>: % C<sub>2</sub>H<sub>5</sub>, 16.9, % Zn, 38.4. An infrared spectrum of a thin film of the product showed the following absorptions: 2960 vs, 2920 vs, 2880 vs, 2740 w, 1480 m, 1385 m, 1260 m, 1215 s, 1140 vs, 1082 vs, 1068s, 1036s, 1000 m, 970 w, 930 w, 904 vs, 851 m (cm<sup>-1</sup>). The <sup>1</sup>H nmr spectrum of a solution of the product in deuterated toluene showed the following resonances: 3.92 (2), 3.40 (1.8), 3.26 (3.2), 1.42 (2.9), 0.38 (2) ppm. After standing under nitrogen at room temperature for 7 days, the colourless mobile liquid decomposed to a yellow/orange solid of unknown stoichiometry.

### 2.12.3 N,N,N'-Trimethylethylenediamine

To a stirred solution of diethylzinc (2 cm<sup>3</sup>, 19.6 mmol) in THF (35 cm<sup>3</sup>) was added N,N,N'-trimethylethylenediamine (3.70 g,

36.2 mmoles) via syringe. The reaction mixture was heated to 65°C and stirred for 5 hours but the reaction appeared to proceed slowly. After filtration the reaction mixture was cooled to -78°C and colourless-white crystals were obtained overnight. The supernatant liquor was filtered off and the crystals were dried first in a stream of dry nitrogen and then *in vacuo*. The crystals melted between 76°C and 80°C without decomposition. Found: % Zn, 33.9. Calc for  $\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{Me})\text{ZnC}_2\text{H}_5$ : % Zn, 33.1.

An infrared spectrum of the product as a Nujol mull showed the following absorptions: 2980 vs, 2924 vs, 2832 w, 1363 m, 1295 m, 1270 w, 1165 s, 1128s, 1041vs, 1019w, 950 m, 860 m, 788 m, 725 m ( $\text{cm}^{-1}$ ). The  $^1\text{H}$  nmr spectrum of a solution of the product in deuterated benzene showed the following resonances: 3.02, 2.92 (1.7), 2.77 (3.0), 2.55, 2.42, 2.35 (2.0), 2.25, 2.05 (6.0), 1.80, 1.65, 1.50 (2.9), 0.55, 0.40, 0.25, 0.10 (2.0) ppm.

### 2.13 Dialkyl and Diarylamines. General reaction

In a typical reaction one equivalent of diethylzinc was refluxed with two equivalents of a secondary amine in toluene under nitrogen for up to 24 hours. The reaction mixture was then transferred to a double Schlenk tube via syringe and filtered. The solvent was removed from the filtrate *in vacuo* and the remaining product was analysed spectroscopically. With *s*-Bu<sub>2</sub>NH and Et<sub>2</sub>NH no reaction was observed. With (C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>NH and Ph<sub>2</sub>NH complexes of an indeterminate nature were observed. All of these reactions

were characterised by a blue/green colouration in the reaction mixture, during reflux.

#### 2.14 The reaction of complex zinc hydrides with organic substrates - experimental methods

A two necked flask ( $50 \text{ cm}^3$ ) was evacuated, flash flamed and allowed to cool under nitrogen. The flask was then weighed, charged with the complex zinc hydride in the glove box (p 64) and reweighed. The flask was then attached to a nitrogen/vacuum manifold and the organic substrate was added, via syringe, in solution with the solvent in which the reaction was to be carried out. After the desired time interval had elapsed, the reaction was quenched by the addition of either  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  as desired. If  $\text{H}_2\text{O}$  was used as the quenching agent then dilute hydrochloric acid was also added. The organic layer was then extracted with diethylether ( $3 \times 20 \text{ cm}^3$ ) and dried over anhydrous magnesium sulphate for one hour. The diethylether solution was then filtered through an oven dried filter paper and the solvent was then distilled off under reduced pressure leaving the desired product. This was then redissolved in the desired solvent and analysed in the chosen manner.

## 2.15 Reactions of complex zinc hydrides with carbonyl groups

### 2.15.1 $[\text{Me}_2\text{NC}_2\text{H}_4\text{OZnH}]_2 + 4\text{-t-butylcyclohexanone}$

The hydride (0.30 g, 1.9 mmoles) was allowed to react with 4-t-butylcyclohexanone (0.28 g, 1.8 mmoles) in THF (5 cm<sup>3</sup>) over a period of 24 hours at 20°C. The reaction was then quenched with distilled water (10 cm<sup>3</sup>) and the reaction mixture was worked up in the usual manner (described in 2.14). The white crystalline product which was obtained was dissolved in diethylether (10 cm<sup>3</sup>) and this solution was analysed by gas chromatography on a 5' 10% PEGA on Chromosorb W column at 138°C. The order of elution of the products were: ketone first, then the axial alcohol and lastly the equatorial alcohol. The relative percentage of the axial alcohol in the reaction product was 7.1% and that of the equatorial alcohol was 92.9%.

### 2.15.2 $[\text{Me}_2\text{NC}_2\text{H}_4\text{OZnH}]_2 + (\text{dl})\text{-camphor}$

The hydride (0.10 g, 0.63 mmoles) was allowed to react with camphor (0.10 g, 0.65 mmoles) in THF (8 cm<sup>3</sup>) over a period of 12 hours at room temperature. The reaction was then quenched with the addition of H<sub>2</sub>O (10 cm<sup>3</sup>) and the reaction mixture was then worked up. Dilute hydrochloric acid was added to remove the 2-dimethyl-aminoethanol formed during the work up from the organic layer and to dissolve the zinc hydroxide. The product which was thus obtained was dissolved in diethylether (10 cm<sup>3</sup>) and subsequently

analysed by gas chromatography on a 5', 10% PEGA on Chromosorb W column at 170<sup>o</sup>c. The order of elution of the products was: ketone first, then exo-alcohol and finally endo-alcohol. The relative percentage of the exo alcohol was 90%\* and that of the endo alcohol was 10%\*. The reaction proceeded with an overall conversion of ketone to alcohols of 76%.

2.15.3 [Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>OZnH]<sub>2</sub> + 2-methylcyclohexanone

The hydride (0.0636 g, 0.41 mmoles) was allowed to react with 2-methylcyclohexanone (0.05 cm<sup>3</sup>, 0.40 mmoles) in THF (5 cm<sup>3</sup>) over a period of 16 hours at room temperature. The reaction was then quenched by the addition of H<sub>2</sub>O (10cm<sup>3</sup>) and the reaction mixture was then worked up. The product which was thus obtained was dissolved in diethylether (10 cm<sup>3</sup>) and analysed by gas chromatography on a 5', 20% diethyleneglycol on Chromosorb W column at 110<sup>o</sup>C. The order of elution of the product was: ketone first, then the cis alcohol and lastly the trans alcohol. The relative percentages of the cis and trans alcohols were 39.5% and 60.5% respectively. The reaction proceeded with an overall conversion of ketone to alcohols of 89.6%.

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\*The percentages of alcohols quoted here and in subsequent sections are those obtained by assuming total alcohol percentage in reaction product is 100%.

2.15.4 (Et<sub>2</sub>NH.ZnH<sub>2</sub>)(TMEDA.ZnH<sub>2</sub>)<sub>2</sub> + 4-t-butylcyclohexanone

The hydride (0.0915 g, 0.18 mmoles) was allowed to react with 4-t-butylcyclohexanone (0.0578 g, 0.37 mmoles) in diethylether (5 cm<sup>3</sup>) over a period of 24 hours at room temperature. The reaction was then quenched by the addition of H<sub>2</sub>O (10 cm<sup>3</sup>) and the reaction mixture was then worked up. The product which was thus obtained was dissolved in diethylether (10 cm<sup>3</sup>) and analysed by gas chromatography on a 5', 10% PEGA on Chromosorb W column at 140°C. On elution the relative percentage of the axial and the equatorial alcohols were found to be 38.7% and 61.3% respectively. The overall conversion of ketone to alcohol was 92%.

2.15.5 (Et<sub>2</sub>NH.ZnH<sub>2</sub>)(TMEDA.ZnH<sub>2</sub>)<sub>2</sub> + (dl)-camphor

The hydride (0.0482 g, 0.09 mmoles) was allowed to react with (dl)-camphor (0.06 g, 0.39 mmoles) in THF (6 cm<sup>3</sup>) over a period of 24 hours at room temperature. The reaction was then quenched by the addition of H<sub>2</sub>O (10 cm<sup>3</sup>) and the reaction mixture was then worked up. The product which was thus obtained was dissolved in diethylether (10 cm<sup>3</sup>) and then analysed by gas chromatography on a 5', 10% PEGA on Chromosorb W column at 180°C. On elution the relative percentages of the exo and endo alcohols were found to be 74.9% and 25.1% respectively. The reaction proceeded with an overall conversion of ketone to alcohols of 73.2%.

2.15.6 (Et<sub>2</sub>NH.ZnH<sub>2</sub>)(TMEDA.ZnH<sub>2</sub>)<sub>2</sub> + 2-methylcyclohexanone

The hydride (0.0531 g, 0.10 mmoles) was allowed to react with 2-methylcyclohexanone (0.05 cm<sup>3</sup>, 0.4 mmoles) in THF (6 cm<sup>3</sup>) over a period of 24 hours at room temperature. The reaction was then quenched by the addition of H<sub>2</sub>O (10 cm<sup>3</sup>) and the reaction mixture was then worked up in the usual manner. The product which was thus obtained was dissolved in diethylether (10 cm<sup>3</sup>) and analysed by gas chromatography on a 5', 20% diethyleneglycol on Chromosorb W column at 100°C. On elution the relative percentages of the *cis* and *trans* alcohols were found to be 50% each. The reaction proceeded with an overall conversion of ketone to alcohols of 20%.

2.15.7 (CH<sub>3</sub>)<sub>3</sub>CSZnH.THF + 4-t-butylcyclohexanone

The hydride (0.1208 g, 0.53 mmoles) was allowed to react with 4-t-butylcyclohexanone (0.0744 g, 0.50 mmoles) in THF (5 cm<sup>3</sup>) over a period of 24 hours at room temperature. The reaction was then quenched by the addition of H<sub>2</sub>O (10 cm<sup>3</sup>) and the reaction mixture was worked up in the usual manner. The product which was thus obtained was dissolved in diethylether (10 cm<sup>3</sup>) and analysed by gas chromatography on a 5', 10% PEGA on Chromosorb W column at 140°C. On elution the relative percentages of axial and equatorial alcohols was found to be 13.3% and 86.7% respectively. The reaction proceeded with an overall conversion of ketone to alcohols of 99%.

2.15.8  $(\text{CH}_3)_3\text{CSZnH}\cdot\text{THF}$  + (dl)-camphor

The hydride (0.1180 g, 0.52 mmoles) was allowed to react with (dl)-camphor (0.0668 g, 0.44 mmoles) in THF (5 cm<sup>3</sup>) over a period of 24 hours at room temperature. The reaction was then quenched by the addition of H<sub>2</sub>O and the reaction mixture was worked up in the usual manner. The product which was thus obtained was dissolved in diethylether (10 cm<sup>3</sup>) and then analysed by gas chromatography on a 11', 10% PEGA on Chromosorb W column at 110°C. On elution, the relative percentage of exo and endo alcohols was found to be 90.3% and 9.7% respectively. The reaction proceeded with an overall conversion of ketone to alcohols of 88.4%.

2.15.9  $[\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{Me})\text{ZnH}]_2$  + 4-t-butylcyclohexanone

The hydride (0.0703 g, 0.41 mmoles) was allowed to react with 4-t-butylcyclohexanone (0.0624 g, 0.40 mmoles) in THF (5 cm<sup>3</sup>) over a period of 1 hour at room temperature. The reaction was then quenched with H<sub>2</sub>O (10 cm<sup>3</sup>) and the reaction mixture was worked up in the usual manner. The product which was thus obtained was dissolved in diethylether (10 cm<sup>3</sup>) and analysed by gas chromatography on a 5' 10% PEGA on Chromosorb W column at 140°C. On elution the relative percentages of axial and equatorial alcohols were found to be 19.1% and 80.9% respectively. The reaction proceeded

with an overall conversion of ketone to alcohols of 95.5%.

2.15.10  $[\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{Me})\text{ZnH}]_2$  + (dl)-camphor

The hydride (0.0690 g, 0.41 mmoles) was allowed to react with (dl)-camphor (0.0619 g, 0.38 mmoles) in THF (5 cm<sup>3</sup>) over a period of one hour at room temperature. The reaction was then quenched by the addition of distilled water (10 cm<sup>3</sup>) and worked up in the usual manner. The product thus obtained was dissolved in diethylether (10 cm<sup>3</sup>) and analysed by gas-chromatography on a 5', 10% PEGA on Chromosorb W column at 165°C. On elution the relative percentages of exo and endo alcohols were found to be 63.3% and 36.7% respectively. The reaction proceeded with an overall conversion of ketone to alcohols of 98.6%.

2.15.11 TMEDA.HZnCl + 4-t-butylcyclohexanone

The hydride (0.1776 g, 0.81 mmoles) was allowed to react with 4-t-butylcyclohexanone (0.122 g, 0.79 mmoles) in diethylether (10 cm<sup>3</sup>) at room temperature during a period of one hour. The reaction mixture was then quenched with H<sub>2</sub>O (10 cm<sup>3</sup>) and worked-up in the usual manner. The product thus obtained, was dissolved in diethylether (10 cm<sup>3</sup>) and analysed by gas chromatography on a 5', 10% PEGA on Chromosorb W column at 140°C. On elution the relative

percentages of the axial and equatorial alcohols were found to be 99% and 1% respectively. The reaction proceeded with an overall conversion of ketone to alcohols of 79%.

#### 2.15.12 TMEDA.HZnCl + (dl)-camphor

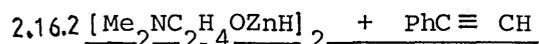
The hydride (0.1507 g, 0.69 mmoles) was allowed to react with (dl)-camphor (0.1053 g, 0.69 mmoles) in diethylether (10 cm<sup>3</sup>) over a period of one hour at room temperature. The reaction mixture was then quenched by the addition of H<sub>2</sub>O (10 cm<sup>3</sup>) and worked up in the usual manner. The product thus obtained was dissolved in diethylether (10 cm<sup>3</sup>) and analysed by gas chromatography on a 5', 10% PEGA on Chromosorb W column at 180°C. On elution the relative percentages of exo and endo alcohols were found to be 33.9% and 66.1% respectively. The reaction proceeded with an overall conversion of ketone to alcohols of 2%.

#### 2.16 Reactions of complex zinc hydrides with phenylacetylene

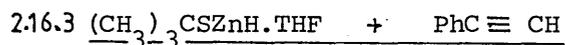
##### 2.16.1 [Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>OZnH]<sub>2</sub> + PhC≡CH

The hydride (0.1271 g, 0.89 mmoles) was allowed to react with phenylacetylene (0.09 cm<sup>3</sup>, 0.82 mmoles) in THF (10 cm<sup>3</sup>) over a period of one hour at room temperature. The reaction was then

quenched with  $D_2O$  ( $5\text{ cm}^3$ ) and the reaction was then worked up (see section 2.14 ). The yellow mobile oil obtained was dissolved in  $CDCl_3$  and analysed by  $^1H$  nmr spectroscopy. The resonances obtained and their integrated intensities in parentheses, are given. 7.40 (5.66), 3.76 (2.30, 3.09, 3.01 (1.0), 2.50, 2.31 (2.40), 1.84 (1.90)ppm.

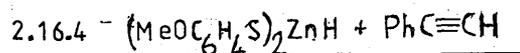


The hydride (0.0886 g, 0.57 mmoles) was allowed to react with phenylacetylene ( $0.06\text{ cm}^3$ , 0.54 mmoles) in benzene ( $10\text{ cm}^3$ ) over a period of 24 hours at room temperature. The reaction was then quenched with  $D_2O$  ( $2\text{ cm}^3$ ) and worked up as in 2.14 and the product was analysed by  $^1H$  nmr spectroscopy. The following resonances and intensities were obtained: 7.38 (13.2), 3.05 (1), 2.31 (1), doublet (ppm).

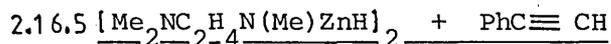


The hydride (0.2805 g, 1.23 mmoles) was allowed to react with phenylacetylene ( $0.13\text{ cm}^3$ , 1.18 mmoles) in diethylether ( $10\text{ cm}^3$ ) over a period of 24 hours at room temperature. The reaction was then quenched with  $D_2O$  ( $2\text{ cm}^3$ ) and the reaction mixture was extracted with diethylether ( $10\text{ cm}^3$ ). The ether was evaporated

off leaving a yellow solid. This was analysed by  $^1\text{H}$  nmr spectroscopy and the following resonances and intensities were obtained: 7.40 7.38 (1), 1.55, 1.37, 1.25 (1.97), 0.88 (0.68) (ppm).



The hydride (0.1946 g, 0.56 mmoles) was allowed to react with phenylacetylene (1.54 cm<sup>3</sup>, 0.56 mmoles) in diethylether (10 cm<sup>3</sup>) over a period of 24 hours at room temperature. The reaction was then quenched with D<sub>2</sub>O (3 cm<sup>3</sup>). The organic layer was separated, dried with anhydrous magnesium sulphate, filtered and then the solvent was removed under reduced pressure to give a mobile yellow oil. Analysis by  $^1\text{H}$  nmr spectroscopy showed the following resonances and intensities: 7.73 (1), 7.38, 7.08 (14.9), 4.89 (0.38), (ppm).



The hydride (0.1692 g, 0.99 mmoles) was allowed to react with phenylacetylene (0.11 cm<sup>3</sup>, 1.00 mmoles) in THF (5 cm<sup>3</sup>) over a period of 24 hours at room temperature. The reaction was then quenched with D<sub>2</sub>O (2 cm<sup>3</sup>). The organic layer was extracted with diethylether (50 cm<sup>3</sup>) dried over anhydrous MgSO<sub>4</sub>, filtered

and the solvent was removed under reduced pressure leaving a dark red-brown oil and a clear oil. A  $^1\text{H}$  nmr spectrum of both reaction products showed the following resonances and intensities: 7.38, 7.26 (2.13), 6.55 (0.65), 4.32, (1), doublet, 3.72 (2.04), 1.92 (2.23), 1.70 (1.98) (ppm).

#### 2.16.6 TMEDA. HZnCl + PhC $\equiv$ CH

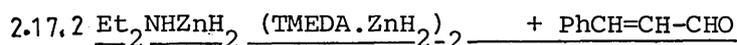
The hydride (0.2088 g, 0.96 mmoles) was allowed to react with phenylacetylene (0.105 cm<sup>3</sup>, 0.96 mmoles) in diethylether (10 cm<sup>3</sup>) over a period of 24 hours at room temperature. The reaction was then quenched by the addition of D<sub>2</sub>O (3 cm<sup>3</sup>). The organic layer was extracted with diethylether (50 cm<sup>3</sup>), dried over anhydrous magnesium sulphate, filtered and the solvent was removed under reduced pressure. A viscous white/colourless oil was obtained. This was analysed by  $^1\text{H}$  nmr spectroscopy and the following resonances and intensities were observed: 7.36, 7.24 (1), 3.05 (0.1), 2.58, 2.29 (1.8), 1.51, 1.21 (1.3) (ppm).

#### 2.17 Reaction of complex zinc hydrides with trans-cinnamaldehyde

##### 2.17.1 [Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>OZnH]<sub>2</sub> + PhCH = CH-CHO

The hydride (0.0952 g, 0.61 mmoles) was allowed to react with cinnamaldehyde (0.07 cm<sup>3</sup>, 0.55 mmoles) in diethylether (8 cm<sup>3</sup>)

over a period of 24 hours at room temperature. The reaction was quenched by the addition of  $D_2O$  ( $4\text{ cm}^3$ ). The organic layer was extracted with diethylether ( $40\text{ cm}^3$ ), dried with anhydrous magnesium sulphate and filtered. The ether was removed under reduced pressure. A golden yellow oil was obtained. This was analysed by  $^1H$  nmr spectroscopy and the following resonances and intensities were observed: 9.76, 9.64 (0.31), doublet, 7.47, 7.34 (3.92), 6.90, 6.77 (0.65), 6.55, 6.43 (1.14), 4.34, 4.26 (1.01), 3.65, 3.54, 3.43, 3.31 (0.34), 2.25 (0.60), 2.05 (0.60), 1.31, 1.25, 1.19, 1.07 (2.45) triplet and singlet (ppm).



The hydride (0.0896 g, 0.18 mmoles) was allowed to react with cinnamaldehyde ( $0.04\text{ cm}^3$ , 0.31 mmoles) in diethylether ( $10\text{ cm}^3$ ) over a period of 24 hours at room temperature. The reaction was then quenched by the addition of  $D_2O$  ( $3\text{ cm}^3$ ). The organic layer was extracted with diethylether ( $50\text{ cm}^3$ ), dried over anhydrous magnesium sulphate and then filtered. The solvent was then removed under reduced pressure, leaving a pale yellow oil. This was analysed by  $^1H$  nmr spectroscopy and the following resonances and intensities were observed: 9.76, 9.64 (1.0), 7.63, 7.48, 7.36 (8.97), 6.87, 6.77 (1.13), 6.63, 6.36 (1.32), 4.34, 4.27 (0.79), 3.64, 3.52, 3.41, 3.28 (1.96), 2.38, 2.23, 2.05 (1.31), 1.31, 1.25\*, 1.19, 1.08 (4.07) triplet and singlet\* (ppm).

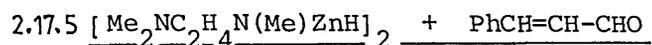
2.17.3  $(\text{CH}_3)_3\text{CSZnH.THF} + \text{PhCH=CH-CHO}$

The hydride (0.4178 g, 1.84 mmoles) was allowed to react with cinnamaldehyde (0.23 cm<sup>3</sup>, 1.82 mmoles) in diethylether (10 cm<sup>3</sup>) over a period of 24 hours. The reaction was then quenched by the addition of dilute hydrochloric acid (10 cm<sup>3</sup>). A yellow solid, insoluble in H<sub>2</sub>O was obtained. It and the organic layer were extracted with diethylether (50 cm<sup>3</sup>), dried with anhydrous magnesium sulphate and then filtered. The solvent was then removed under reduced pressure and the product thus obtained was analysed by <sup>1</sup>H nmr spectroscopy. The following resonances (and intensities) were observed: 9.70, 9.57 (1.0), 7.42, 7.28, 7.07, (26.6), 6.85, 6.73 (3.43), 6.49 (4.5), 4.48, 4.30, 4.25, 4.05 (5.99), 2.79, 2.60, 2.38 (2.95), 1.58, 1.21 (5.64) (ppm).

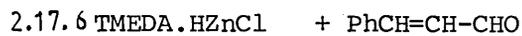
2.17.4  $(\text{MeOC}_6\text{H}_4\text{SZnH})(\text{1-MeOC}_6\text{H}_4\text{SH}) + \text{PhCH=CH-CHO}$

The hydride (0.2146 g, 0.62 mmoles) was allowed to react with cinnamaldehyde (0.0821 g, 0.62 mmoles) in diethylether during a period of 24 hours at room temperature. The reaction was then quenched by the addition of H<sub>2</sub>O (10 cm<sup>3</sup>). The organic layer was then extracted with diethylether (50 cm<sup>3</sup>), dried with anhydrous magnesium sulphate and filtered. The solvent was then distilled off under reduced pressure leaving a white solid which was dissolved in CDCl<sub>3</sub>. The resulting solution was analysed by <sup>1</sup>H nmr spectroscopy and the following resonances and intensities

were obtained: 9.78, 9.64 (1.0), 8.00 (2.30), 7.48, 7.34 (16.8), 6.91, 6.81 (1.90), 6.55, 6.43, 6.34 (3.99), 6.18, 6.10 (0.64), 4.32 (5.18), 3.86 (1.52), 3.54, 3.43 (1.82), 2.38 (2.26), 1.62 (5.27), 1.19 (3.97), 0.69 (1.75) (ppm).



The hydride (0.2008 g, 1.18 mmoles) was allowed to react with cinnamaldehyde (0.1571 g, 1.17 mmoles) in THF (5 cm<sup>3</sup>) over a period of 24 hours at room temperature. The reaction was then quenched by the addition of H<sub>2</sub>O (10 cm<sup>3</sup>). The organic layer was then extracted with diethylether (50 cm<sup>3</sup>), dried with anhydrous magnesium sulphate and filtered. The solvent was then removed leaving a yellow oil. This was analysed by <sup>1</sup>H nmr spectroscopy. The following resonances and intensities were observed: 9.90 (0.07), 7.83 (0.67), 7.32 (11.28), 6.79 (1.02), 6.53, 6.43, 6.34 (2.92), 6.14 (0.30), 4.34, 4.25 (3.60), 1.99 (3.33), 1.25(1) (ppm).



The hydride (0.2062 g, 0.95 mmoles) was allowed to react with cinnamaldehyde (0.1252 g, 0.95 mmoles) in diethylether (10 cm<sup>3</sup>) over a period of 24 hours at room temperature. The reaction was then quenched by the addition of D<sub>2</sub>O (4 cm<sup>3</sup>). The organic layer

was extracted with diethylether (50 cm<sup>3</sup>), dried over anhydrous magnesium sulphate and filtered. The solvent was then removed under reduced pressure leaving a mobile yellow oil. This was analysed by <sup>1</sup>H nmr spectroscopy and the following resonances and intensities were observed: 9.78, 9.66 (1.0), 8.12, 7.98 (1.0), 7.65, 7.47, 7.36 (8.9), 6.90, 6.76 (1.25), 6.55, 6.46, 6.37 (1.96), 6.18 (0.67), 4.36, 4.28 (1.57), 2.23 (0.39), 1.81 (0.65), 1.25 (0.72) (ppm).

2.18 Reaction of [Me<sub>2</sub>NC<sub>2</sub>H<sub>2</sub>N(Me)ZnH]<sub>2</sub> with trans-2-pentene.

A kinetic study

A nmr tube was charged with the aminozinc hydride (0.2144 g, 1.26 mmoles) in the glove box and sealed with a rubber septum. Deuterated benzene (0.55 cm<sup>3</sup>) and benzene (0.1 cm<sup>3</sup>), as an internal standard, were added via syringe. A 'blank' <sup>1</sup>H nmr spectrum was obtained and then the alkene (0.15 cm<sup>3</sup>, 1.38 mmoles) was injected via the rubber septum. The nmr tube was shaken thoroughly to allow mixing of the reactants and further spectra were recorded, after 15 seconds, 4, 6, 8 <sup>1</sup>/<sub>3</sub> and 10 <sup>1</sup>/<sub>2</sub> minutes had elapsed. In each case the relative intensities of the standard benzene and the olefinic protons were measured. A second order plot of the reciprocal of the concentration of the alkene against time was obtained and this showed a straight line within the

limits of experimental error. The rate constant  $k$  was determined to be  $1.7 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ sec}^{-1}$ .

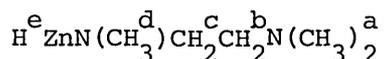
## Chapter 3. Discussion

### 3.1 Reaction of Zinc Dihydride with Bidentate Ligands containing Acidic Hydrogen Atoms

#### 3.1.1 N'N'N-Trimethylethylene diamine

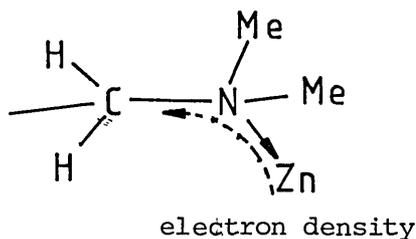
Two routes for preparing zinc dihydride were investigated since it was claimed that zinc dihydride prepared from sodium hydride and zinc iodide was more reactive than if prepared by other means. This was, in fact, found not to be so. This was demonstrated clearly in the case of its reaction with trimethylethylenediamine. When zinc dihydride, prepared from zinc iodide and sodium hydride, was used the product did not have the physical characteristics of the reported aminozinc hydride and only 2% yield was obtained. A much better synthetic yield (37%) was obtained when the zinc hydride used was prepared from diethylzinc and lithium tetrahydridoaluminate. However, even though the product had the correct melting point and analysis for  $[\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{Me})\text{ZnH}]_2$  the infrared spectrum did not show the reported absorption<sup>43</sup> at  $1694 \text{ cm}^{-1}$  for terminal Zn-H stretching vibrations but a very broad absorption from  $1800 - 1600 \text{ cm}^{-1}$ . However an infrared spectrum of a THF solution of this complex zinc hydride showed this vibration to occur at  $1690 \text{ cm}^{-1}$ . It is felt that the broad absorption observed in the Nujol mull spectrum is due to some long range association in the crystalline complex.

That this absorption is due to the zinc hydride bond was demonstrated by exposure of the mull to air. When the spectrum was re-recorded the intensity of the broad absorption had decreased significantly in relation to other absorptions due to the same molecule, indicating that the Zn-H bond had been hydrolysed to some extent. The nmr spectrum was assigned as follows:-

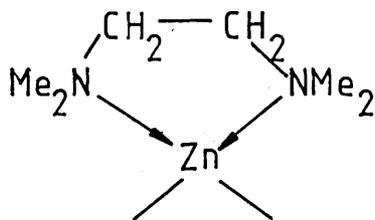


ppm	description	intensity	H
2.05	singlet	6	a
2.80	singlet	3	d
2.35	multiplet	2	b
2.95	multiplet	2	c
4.20	broad singlet	1	e

The chemical shift of the hydridic hydrogen at 4.20 ppm agrees with that previously reported<sup>43</sup>. The methyl and methylene resonances in the  $-CH_2-N(Me)-Zn-H$  moiety are shifted downfield by 0.4 ppm from those in the free amine suggesting a withdrawal of electron density from the carbon atoms to the nitrogen atom, bound to the zinc atom while the methyl and methylene resonances in the  $-CH_2-NMe_2$  moiety in the complex are shifted upfield by 0.1 ppm from those in the free amine suggesting a slight shift of electron density from the nitrogen atom co-ordinated to the zinc atom to the adjacent carbon atom.



This could be due to back donation from the zinc atom to a suitable orbital on the nitrogen atom. When such an upfield shift is observed in the N methyl protons of the dimethylamino group (see for example  $Me_2NC_2H_4OZnH$ , TMEDA  $HZnCl$ ) this is taken as evidence for the formation of a five membered chelate ring such as



This is in contrast to TMEDA ( $\text{BeH}_2$ )<sub>2</sub> where a downfield shift of 0.18 to 0.11 ppm in the N-methyl proton resonances is observed on complexation as a result of the reduction in electron density on the methyl protons when N atoms serve as donor ligands<sup>44</sup>.

When a solution of  $[\text{TriMEDZnH}]_2$  in diethylether was examined by u.v. spectroscopy an absorption was observed with  $\nu_{\text{max}}$  of  $37037 \text{ cm}^{-1}$  (270 nm) and with an extinction coefficient 11751. Such an absorption is typical of a charge transfer band, having a high extinction coefficient.

### 3.1.2 2-Dimethylaminoethanol

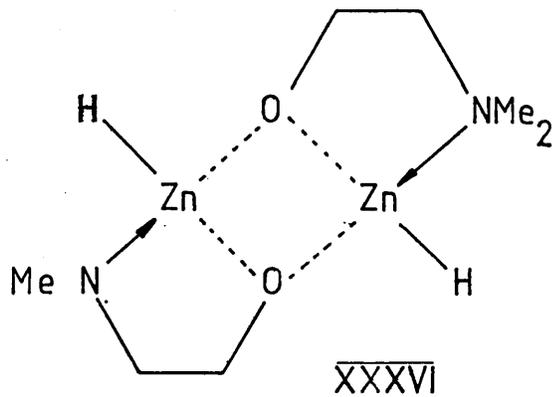
When equimolar amounts of zinc dihydride and 2-dimethylaminoethanol were allowed to react in THF, a complex formed readily without the need for elevated temperatures. Chemical analysis showed that the complex had a stoichiometry of  $\text{HZn-OC}_2\text{H}_4\text{NMe}_2$  and molecular weight (cryoscopic) techniques showed that the aminoethoxyzinc hydride complex was dimeric in benzene solution with a degree of association of 1.96.

The <sup>1</sup>H nmr spectrum of the complex in deuterated toluene was assigned as follows:

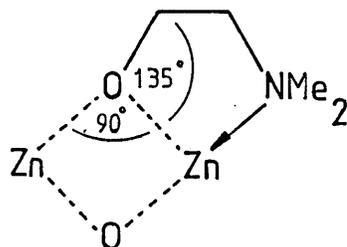
<u>ppm</u>	<u>intensity</u>	<u>description</u>	<u>assignment</u>
2.32	8	singlet	N-methyl protons
2.80		broad shoulder	-N-methylene protons
4.25	2	triplet	-Zn-O-methylene protons
4.47	1	singlet	Zn-H

The N-methyl singlet and N-methylene proton triplet could not be resolved on the instrument on which the spectrum was obtained so an overall intensity of the two resonances was recorded.

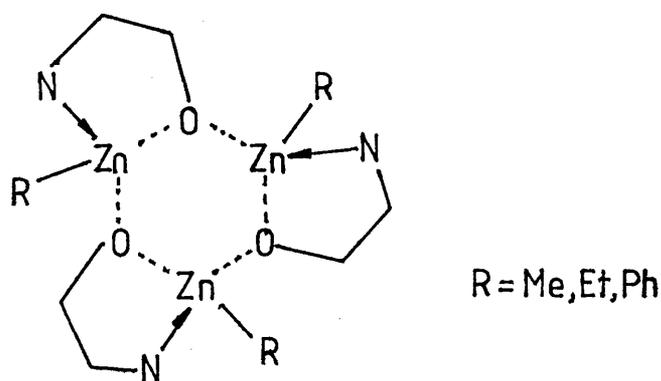
There were substantial differences in the chemical shifts of the O-methylene protons and the N-methyl and N-methylene protons in the aminoalcohol from the corresponding resonances. Thus both the oxygen and nitrogen atoms are involved in bonding in the complex. Both infrared and  $^1\text{H}$  nmr spectroscopy showed that the complex has terminal zinc hydrogen bonds. The infrared spectrum of the complex shows two bands which have been assigned to Zn-H vibrations. One fairly broad band at  $1740\text{ cm}^{-1}$  with a width at half height of  $60\text{ cm}^{-1}$  and the other a sharp band at  $1650\text{ cm}^{-1}$ . Both come in the region expected for terminal Zn-H stretching vibrations. The hydridic hydrogen resonance at 4.47 ppm is close to that of the Zn-H resonance in  $[\text{HZnN}(\text{Me})\text{C}_2\text{H}_4\text{N}(\text{Me})_2]_2$  (4.20 ppm) which is known to have terminal Zn-H bonds. Thus the structure of this complex in benzene solution is



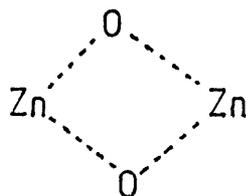
The dimeric structure was thought to be unlikely due to bond angle strain around the oxygen atoms



The oxygen atom is  $sp^2$  hybridised for bonding requirements, thus bond angles around the oxygen atom should be  $120^\circ$ . In dimeric and tetrameric  $RZnOR'$  the Zn-O-Zn bond angle is  $\sim 90^\circ$ . (In  $(MeOZnMe)_4$  it is  $92^\circ$ <sup>81</sup>, thus there will be a large departure from the ideal  $sp^2$  environment of the oxygen atoms in the dimeric structure and thus considerable angular strain around the oxygen atoms. A dimeric structure with a Zn-O-Zn bond angle of  $120^\circ$  is possible but in this case intramolecular coordination by the dimethylamino group is impossible without considerable angular strain in the ligand leading to either intermolecular co-ordination and thus a polymeric structure or no co-ordination at all. Thus on theoretical grounds, the trimeric structure (p.123 R=H) was expected, and indeed methyl, ethyl and phenylzinc dimethylaminoethoxide<sup>81,82</sup> were found to be trimeric in benzene solution with the following type of structure

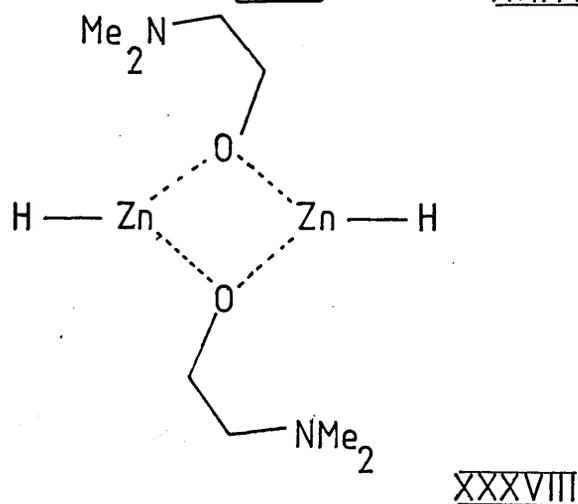
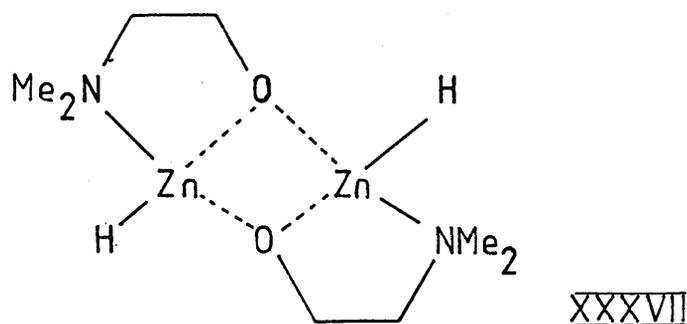


Since the complex zinc hydride actually exists as the dimer, thus there must be some other driving force which makes the



unit stable.

Since the dimethylaminoethoxyzinc alkyl compounds were thought to be fluxional in solution on the basis of multiple Zn-C rocking and stretching vibrations<sup>81,82</sup> the complex zinc hydride might exhibit the same behaviour. Thus the two Zn-H stretching vibrations could be due to the following species



The infrared spectrum of a THF solution of this complex showed one band at  $1710\text{ cm}^{-1}$  width at half-height  $50\text{ cm}^{-1}$  which is due presumably to an average of species and there is only one zinc hydride resonance in the proton n.m.r. spectrum of the complex at room temperature but this is broad as are the  $-\text{N}-\text{CH}_2$  and  $\text{O}-\text{CH}_2$  resonances and thus the complex with structure (XXXVII) could be fluxional in solution. The fluxional behaviour would also relieve some of the bond angle

strain around the oxygen atoms.

### 3.1.3 3-Dimethylaminopropan-1-ol

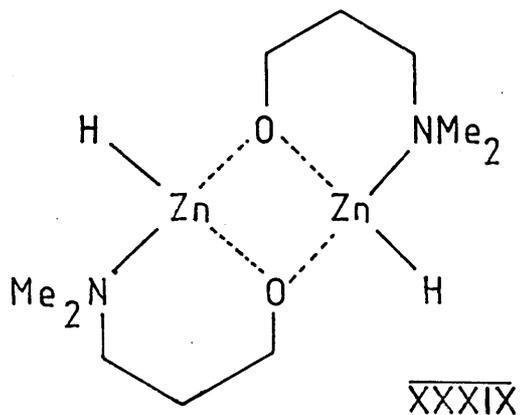
Though 2-dimethylaminoethoxyzinc hydride was expected to be trimeric from valence bond angle strain considerations, 3-dimethylaminopropoxyzinc hydride was expected to be dimeric on similar grounds (p.123 ) since, in this case, the chelate ring is six-membered. This latter complex was prepared in benzene and THF and the same product was obtained regardless of solvent. The  $^1\text{H}$  n.m.r. spectrum was assigned as follows:

<u>ppm</u>	<u>intensity</u>	<u>description</u>	<u>assignment</u>
1.66	2	multiplet	C-CH <sub>2</sub> -C
2.13	8	singlet	N-methyl protons
2.32		shoulder*	N-methylene protons
3.95	3	singlet	Zn-H
4.05		shoulder*	O-methylene protons

\*These multiplets could not be resolved from the singlets. No O-H resonance was seen and all the resonances have different chemical shifts from the free alcohol thus both the oxygen and nitrogen are involved in bonding.

The infrared spectrum, recorded as a Nujol mull shows a large asymmetric broad band from 1800 to 1640  $\text{cm}^{-1}$  due to Zn-H stretching and a weaker broad absorption at 1600  $\text{cm}^{-1}$  which may be due to Zn-H vibrations. When wet Nujol was added to the mull the broad strong absorption from 1800 to 1640  $\text{cm}^{-1}$  disappeared completely, but the absorption at 1600  $\text{cm}^{-1}$  remained, though much decreased in intensity. The broadness of the absorption due to the Zn-H stretching vibration would suggest that far from being dimeric, the complex is much more associated in the solid state. The complex  $\text{EtZnOC}_3\text{H}_6\text{NMe}_2$  is a mixture of dimer and tetramer in 7:3 ratio in solution,<sup>82</sup> but this does

not appear to be the case for  $\text{HZnOC}_3\text{H}_6\text{NMe}_2$  as only one resonance due to N-methyl protons was observed in the  $^1\text{H}$  nmr spectrum of the complex zinc hydride. Thus the structure of  $\text{HZnOC}_3\text{H}_6\text{NMe}_2$  is probably:



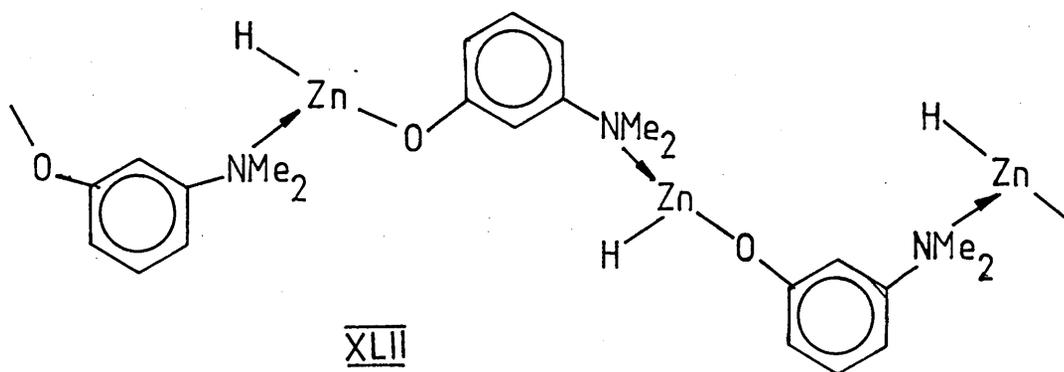
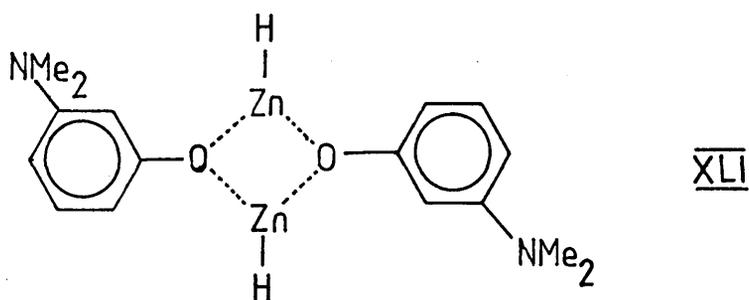
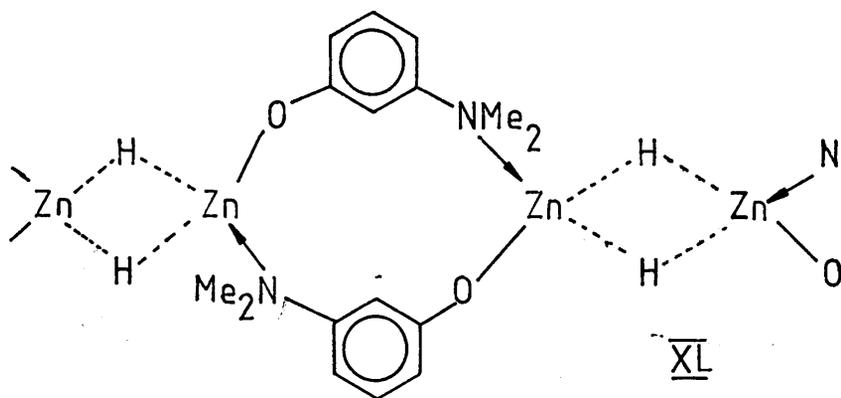
Also in favour of the dimeric structure is the bond angle strain, and the fact that the four membered zinc oxygen ring seems stable (cf.  $[\text{Me}_2\text{NC}_2\text{H}_4\text{OZnH}]_2$ ,  $[\text{TriMEDZnH}]_2$ .)

#### 3.1.4 3-Dimethylaminophenol

If the dimethylamino group in the dimethylamino alcohol is in such a position as to make intramolecular co-ordination impossible then the situation becomes much more complex.

The reaction of zinc hydride and 3-dimethylaminophenol was investigated in THF and benzene. The product was different for each solvent. In benzene a soluble product (yield, 2% as  $\text{HZnOC}_6\text{H}_4\text{NMe}_2$ ) and an insoluble product (yield, 86%, as  $\text{HZnOC}_6\text{H}_4\text{NMe}_2$ ) were obtained. The insoluble product was not a mixture of zinc hydride and 3-dimethylaminophenol. The I.R. spectrum showed changes in the C-N stretch region (much broader  $1280 - 1200 \text{ cm}^{-1}$ ) from that of the free ligand. Thus both nitrogen and oxygen are involved in bonding.

A broad underlying shape from 1700 to 1500  $\text{cm}^{-1}$  was assigned to zinc-hydride vibrations. Since intramolecular co-ordination is impossible due to the alignment of the oxygen-zinc and dimethylamino groups, a polymeric structure with intermolecular bridging by the ligand must exist. Several structural possibilities exist.

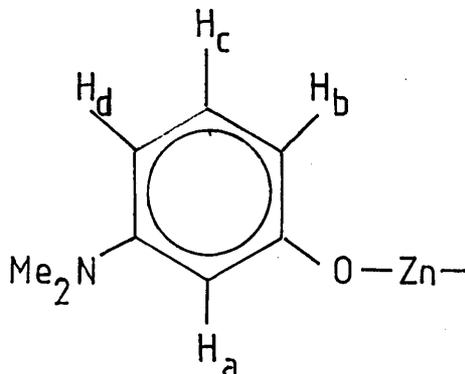


In XIII the vacant co-ordination positions of the zinc atom are filled by the  $-NMe_2$  groups from other linear polymeric units forming a 3 dimensional polymer. In XIV the vacant co-ordination positions of the zinc atoms are filled by dimethyl-amino groups from other dimeric units, forming a linear polymer.

Structural possibility XV has bridging hydridic hydrogen atoms and an arrangement of ligand groups which has low entropy (12 atoms in ring) and is therefore unlikely. No Zn-H-Zn stretching vibrations were detected in the infrared spectrum of the benzene insoluble product. The structure of the soluble product was deduced from the nmr and infrared spectroscopic data.

The  $^1H$  n.m.r. spectrum of the soluble product was assigned as follows:

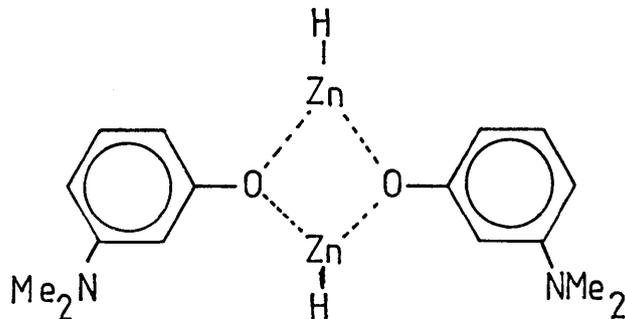
<u>ppm</u>	<u>intensity</u>	<u>description</u>	<u>assignment</u>
2.44	6	broad singlet	$-NMe_2$
3.25	1	broad-weak singlet	Zn-H
6.10	unresolved	multiplets	$H_a$ where $H_a, b, c, d$ , refer to the
6.51	4		$H_d, H_b$ benzene ring
6.93			$H_c$ protons shown left



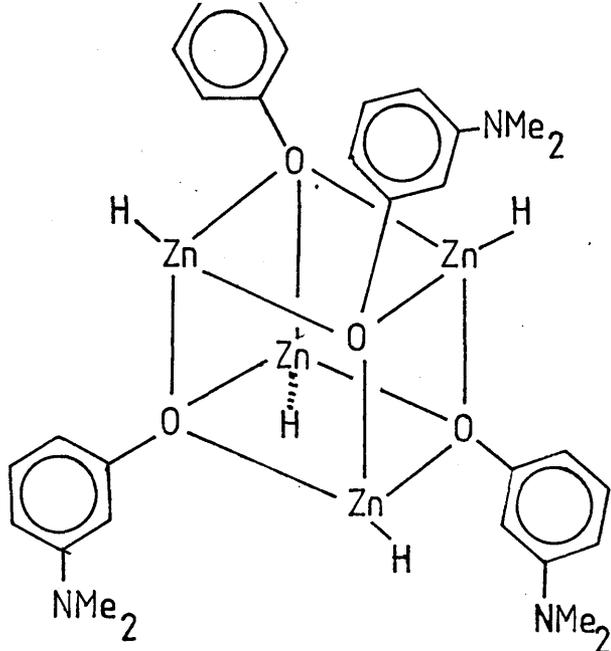
In the free phenol  $H_c$  shows a doublet at 6.93 ppm and a multiplet at 6.24 ppm contains resonances due to  $H_a, H_b$  and  $H_d$ .

Thus in the complex, electron density is withdrawn from the oxygen since the resonance due to  $H_b$  (ortho) and  $H_d$  (para) move downfield while  $-NMe_2$  is not involved in bonding since  $H_a$  (ortho to both  $-NMe_2$  and  $-O-Zn$ ) does not shift much. The infrared spectrum of this complex shows a band at  $1720\text{ cm}^{-1}$  attributed to Zn-H stretching. The  $-C-O$  stretch region shows a broad band from  $1310 - 1200\text{ cm}^{-1}$  (free phenol has  $-C-O$  stretch at  $1240 - 1220\text{ cm}^{-1}$ ), while the  $-C-N$  stretch does not shift in position from  $1380\text{ cm}^{-1}$ .

Since the dimethylamino group does not appear to be involved in the bonding in the benzene-soluble product then the structure of this product is likely to be



It is not unlikely to find the dimethylamino group not involved in bonding since, with the phenoxy  $O-Zn$  group withdrawing electrons, the dimethylamino group will be a weak base indeed. In the above structure the zinc atoms are co-ordinately unsaturated. Co-ordinative saturation might be achieved in a manner similar to that found for tetrameric methylzinc methoxide



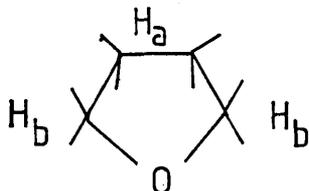
XLIII

In tetrahydrofuran a soluble product (30% yield as  $\text{HZnOC}_6\text{H}_4\text{NMe}_2$ ) was obtained.

The  $^1\text{H}$  n.m.r. spectrum of this complex was assigned as follows:

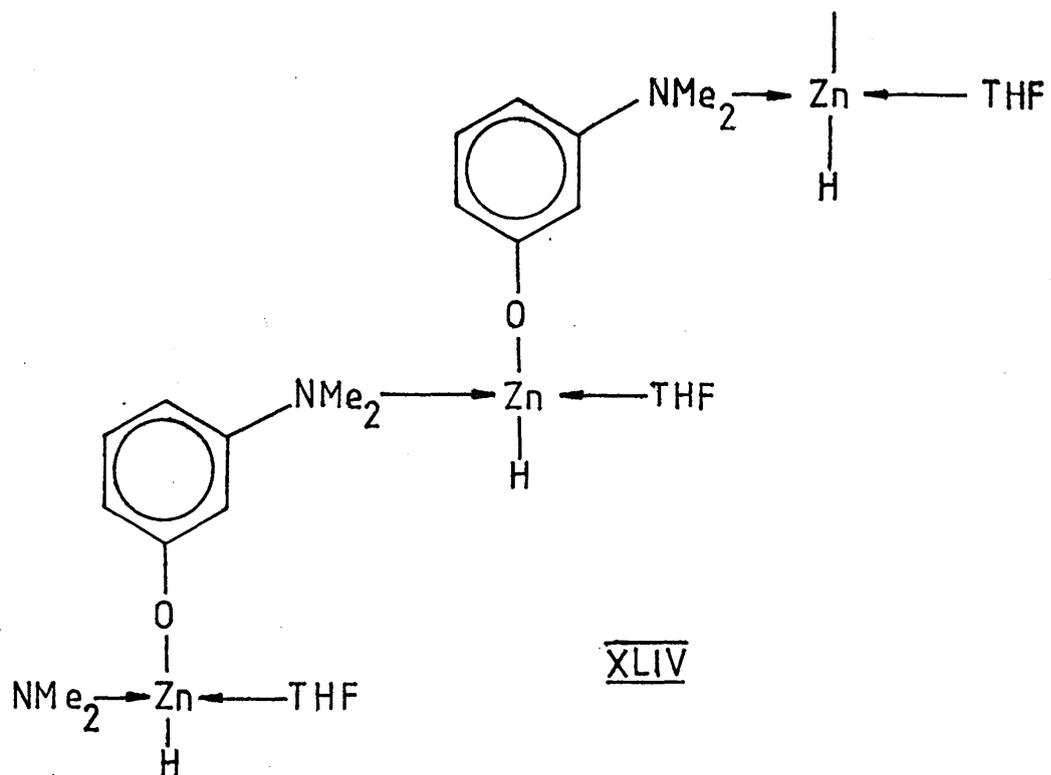
<u>ppm</u>	<u>intensity</u>	<u>description</u>	<u>assignment</u>
1.27	3.3	multiplet	$\text{H}_a$ (THF)
2.66	6	broad, asymmetric	-N-methyl protons
3.50	3.6	multiplet	$\text{H}_b$ (THF)
6.28 $\text{H}_w$	4	broad multiplet	phenyl ring protons
6.87 $\text{H}_{x,y,z}$			see below

The protons in THF are assigned as follows:

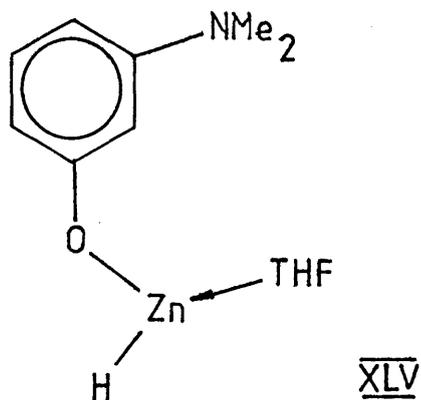


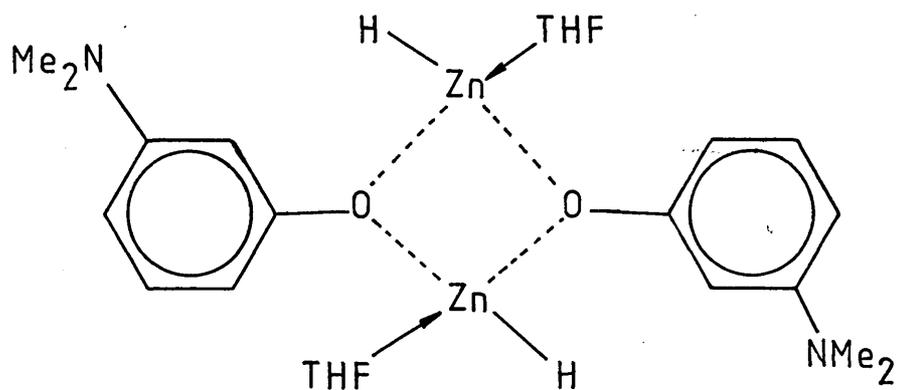
No hydridic resonance was observed but it could have been obscured either by phenyl ring protons if it were bridging, or by the THF  $H_b$  resonances. The N-methyl protons' chemical shift has moved downfield by 0.2 ppm indicating some involvement of the dimethylamino group in bonding. The reason for this is unclear since the resonances due to the phenyl ring protons do not appear to have shifted much (0.04 - 0.05 ppm).

The infrared spectrum of the complex suggests that both the dimethylamino group and the oxygen are involved in bonding. No band can be attributed to Zn-H vibration though it could be concealed by the carbon carbon in plane vibrations which give a broad band from 1660 to 1540  $cm^{-1}$ . It is thought that this complex is fluxional in solution - very broad resonances are seen in the  $^1H$  n.m.r. spectrum. Thus it is polymeric (XLIV) in the solid state, with tetrahydrofuran occupying one of the co-ordination sites and the dimethylamino group the other



but in THF solution the structure is unknown, other than that THF is still involved in co-ordination. The following type of structure might be feasible however





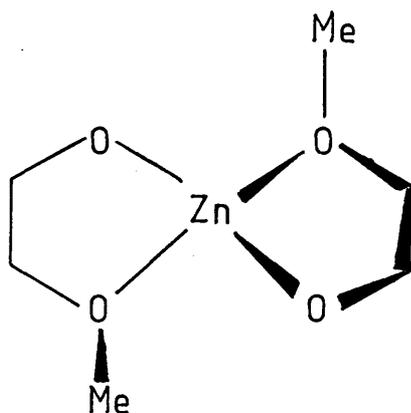
XLVI

XLV is unlikely on the grounds that, the zinc atom is co-ordinatively unsaturated and monomeric, there being no steric grounds for this situation to be stable. XLVI is likely provided that THF is a stronger donor than the dimethylamino group. This is quite likely in view of what has already been stated (p.129 ).

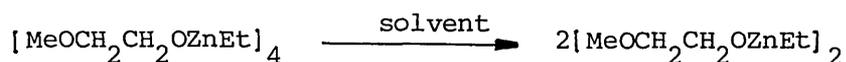
### 3.1.5 2-Methoxyethanol

The reaction of zinc hydride with 2-methoxyethanol is also complex. Yields of soluble, hydride containing products were low (one to nine per cent). In order to examine this system more closely, comparative reactions of diethylzinc and 2-methoxyethanol were carried out in one to one and one to two molar ratios.

Bis(2-methoxyethoxy)zinc, prepared from diethylzinc and 2-methoxyethanol in 1:2 molar ratio was found to have the following structure



It was characterised by chemical analysis, infrared and n.m.r. spectroscopy. The geminal protons are magnetically non-equivalent due to the O-methyl groups lying out of the plane of the molecule and this was deduced from the  $^1\text{H}$  n.m.r. spectrum. The geminal coupling constant was found to be 5 Hz. Ethylzinc-2-methoxyethoxide was isolated as a colourless mobile liquid which decomposed on standing under  $\text{N}_2$  after a few days. It was characterised by chemical analysis, infrared and  $^1\text{H}$  n.m.r. spectroscopy. The infrared spectrum suggested that it did have the cubane type structure of simple alkylzinc alkoxides or aroxides but the  $^1\text{H}$  n.m.r. showed that the ether-oxygen was involved in bonding to some extent. There was no evidence for fluxionality in solution thus it would appear that the following occurs on solvation.



Examination of the  $^1\text{H}$  n.m.r. spectrum of the product of the reaction between zinc dihydride and 2-methoxyethanol in tetrahydrofuran showed that the product  $\text{MeOCH}_2\text{CH}_2\text{OZnH}$  was a mixture of dimeric and tetrameric complexes in 2:1 ratio. Thus in solution the following equilibrium exists:



The  $^1\text{H}$  n.m.r. spectrum was assigned as follows:

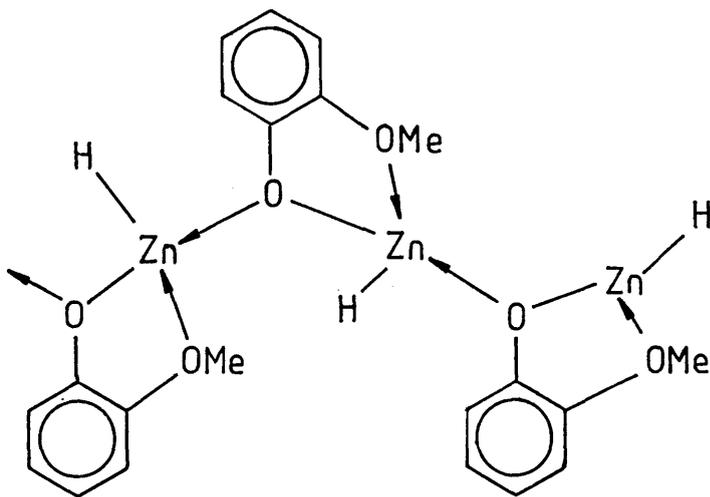
<u>ppm</u>	<u>intensity</u>	<u>assignment</u>
4.15	2.1	$-\text{CH}_2\text{OZn}$ dimer
4.00	2.1	$-\text{CH}_2\text{OZn}$ tetramer
3.8 - 3.5 (broad)	3.7	$-\text{CH}_2\text{OMe}$ , dimer, tetramer
3.34	3.2	$\text{CH}_3\text{-O-}$ tetramer
3.26	2.8	$\text{CH}_3\text{-O}$ dimer
3.24	1	Zn-H tetramer
3.14	1	Zn-H dimer

The infrared spectrum of the complex showed a very broad absorption centred on  $1800\text{ cm}^{-1}$  with a width at half height of  $200\text{ cm}^{-1}$ . This was assigned to a Zn-H stretching vibration. The  $-\text{C-O-Me}$  stretching vibrations in the complex were virtually the same as for free 2-methoxyethanol. Thus in the solid state the complex appears to be a mixture of dimers and tetramers with the tetramers predominating.

Unfortunately the complex appeared to decompose over a period of several hours after desolvation since a satisfactory chemical analysis could not be obtained.

### 3.1.6 2-Methoxyphenol

Zinc dihydride was also found to react with 2-methoxyphenol. An insoluble product was obtained and chemical analysis showed this to be 2-methoxyphenoxyzinc hydride. The infrared spectrum of this complex as a Nujol mull showed the characteristic bond absorption from  $1800 - 1550\text{ cm}^{-1}$  almost obscuring the phenyl ring carbon in plane vibration at  $1630\text{ cm}^{-1}$ . Nothing can be said with certainty about the structure of this hydrido zinc complex. A polymeric structure could be considered.



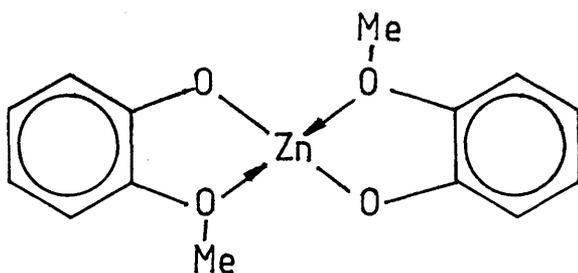
XLVII

Alternatively, a dimeric structure such as that postulated (p.134 ) for 2-methoxyethoxyzinc hydride is possible and even though such a structure might lead us to believe that the complex ought to be soluble, it might just be that the dipole moment of solvent just is not large enough cf.

TMEDA(BeH<sub>2</sub>)<sub>2</sub><sup>44</sup> .

A THF soluble product was obtained in low yield when the THF solute was removed under reduced pressure. Chemical analysis of this product showed it to be bis(2-methoxyphenoxy) zinc. No absorptions in the infrared spectrum of a Nujol mull of the complex were found in the region of 1800 - 1500 cm<sup>-1</sup> with the exception of the 1640 cm<sup>-1</sup> band due to phenyl ring carbon-carbon stretching vibration.

A <sup>1</sup>H n.m.r. spectrum of the complex showed a multiplet (or broad peak) at 5.2 ppm. This was assigned to the methoxy protons.



### XLVIII

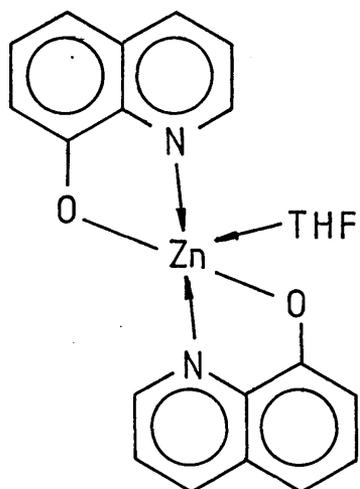
The methoxy protons in the complex would be expected to show a sharp singlet in the  $^1\text{H}$  n.m.r. spectrum of the product. However, a broad resonance is observed. This may be due to some fluxional behaviour in solution but without temperature dependence studies it is impossible to confirm.

#### 3.1.7 8-Hydroxyquinoline

The reaction of zinc dihydride with 8-hydroxyquinoline yielded two products. A THF soluble product was shown to be the bis(oxyquinolate) zinc tetrahydrofuranate  $(\text{C}_9\text{H}_7\text{ON})_2\text{Zn}$  THF on the basis of chemical analysis.

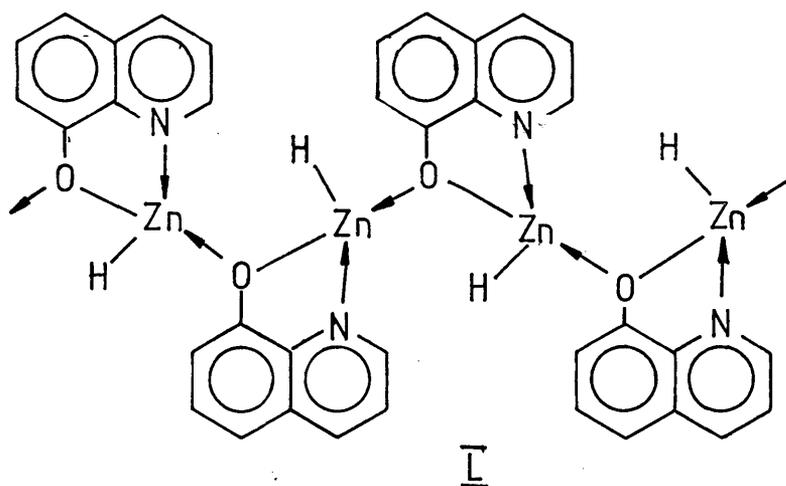
Bis(oxyquinolate) zinc tetrahydrofuranate reacted with deuterated acetone to give a yellow solution and a yellow solid. The yellow solution was examined by  $^1\text{H}$  n.m.r. spectroscopy and this showed the resonances due to aromatic protons at 8.44 - 7.87 and 7.37 - 6.27 ppm as well as resonances due to THF at 3.61 and 1.76 ppm. A strong unidentified resonance at 2.79 ppm was tentatively assigned to some alkoxy protons - presumably from acetone.

The structure of bis(oxyquinolate) zinc tetrahydrofuranate can be explained as follows



XLIX

The oxygen and nitrogen atoms are held in a rigid framework and the distance between these atoms is less than the optimum distance for maximum orbital overlap for the tetrahedral zinc, nitrogen and oxygen atoms, thus the tetrahedron becomes distorted and THF can approach closely enough to the zinc atom to form a co-ordinating bond. The THF insoluble product was not a physical mixture of zinc dihydride and 8-hydroxyquinoline since the infrared spectrum of this product did not show the broad absorptions recorded for zinc dihydride nor did the solid melt at  $74^{\circ}\text{C}$  which is the melting point of 8-hydroxyquinoline. The hydride, since it is insoluble in THF, is most likely to be a co-ordination polymer with the following type of structure



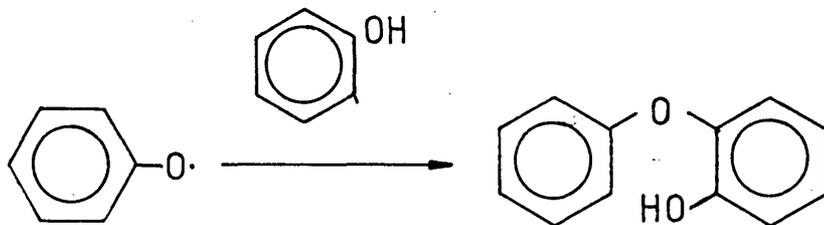
The infrared stretching frequency of the zinc hydride bond was observed at  $1800 - 1500 \text{ cm}^{-1}$  which is in the range for terminal Zn-H bonds. The vibrations assigned to C=N and C=C stretching vibrations were found in the same frequency range  $1605 - 1502 \text{ cm}^{-1}$  for both compounds, thus suggesting that they have similar bonding environments.

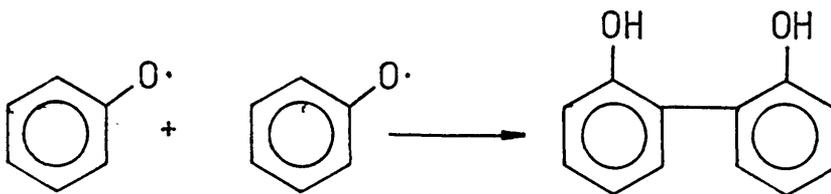
### 3.1.8 2-Methoxybenzenethiol

The reaction of zinc dihydride with 2-methoxybenzenethiol gave a product, soluble in THF, for which chemical analysis showed the stoichiometry to be  $(2\text{-MeOC}_6\text{H}_4\text{S})_2\text{ZnH}$ . Infrared spectroscopy showed the presence of a terminal Zn-H stretching vibration at  $1601 \text{ cm}^{-1}$ .

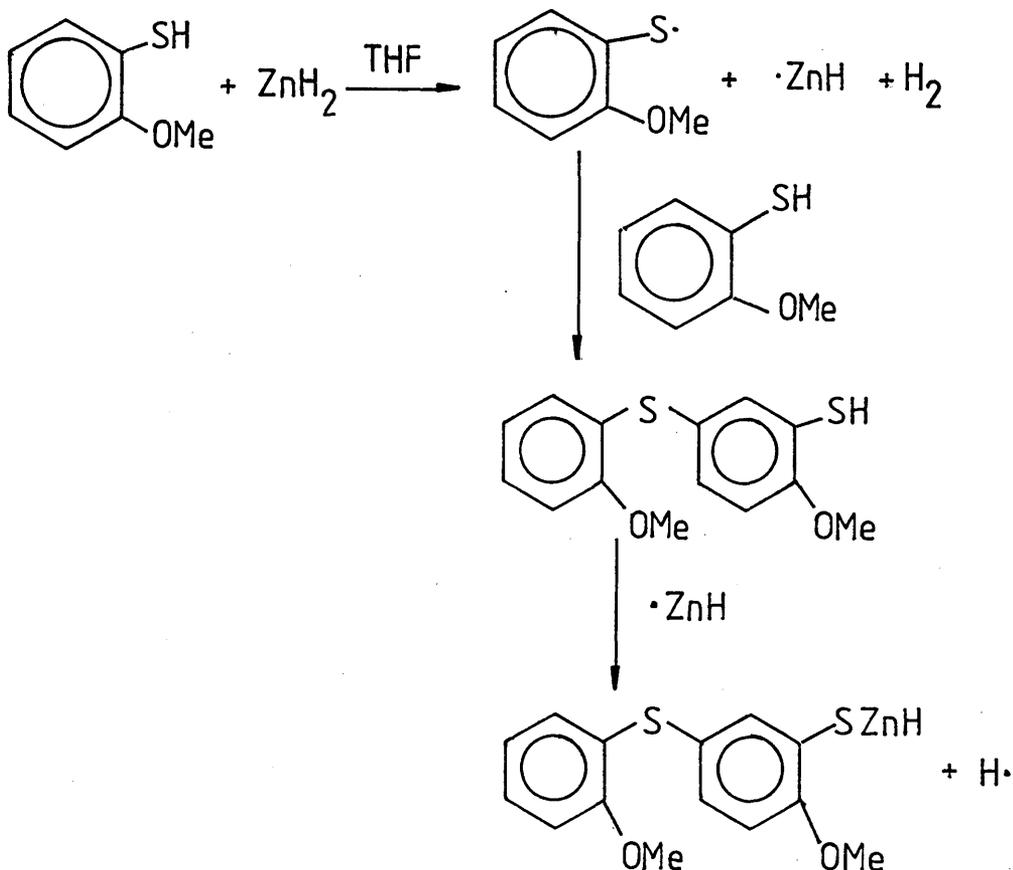
The  $^1\text{H}$  n.m.r. spectrum of this compound in deuterated DMSO showed resonances at 7.40, 7.28 and 6.75 ppm which were assigned to phenyl ring protons and a singlet at 3.72 ppm which was assigned to the methoxy group protons. In 2-methoxybenzenethiol the corresponding resonances are observed at 7.96, 7.83, 7.61, 7.48 and 7.32 ppm while the methoxy group protons resonate at 4.34 ppm and there is no evidence in either the infrared or the  $^1\text{H}$  n.m.r. spectrum of a sulphur-hydrogen bond thus 2-methoxybenzenethiol may undergo coupling during reaction with zinc dihydride.

It is well known<sup>83</sup> that phenols undergo oxidative coupling to give a large variety of products due to the formation of intermediate phenoxy radicals.



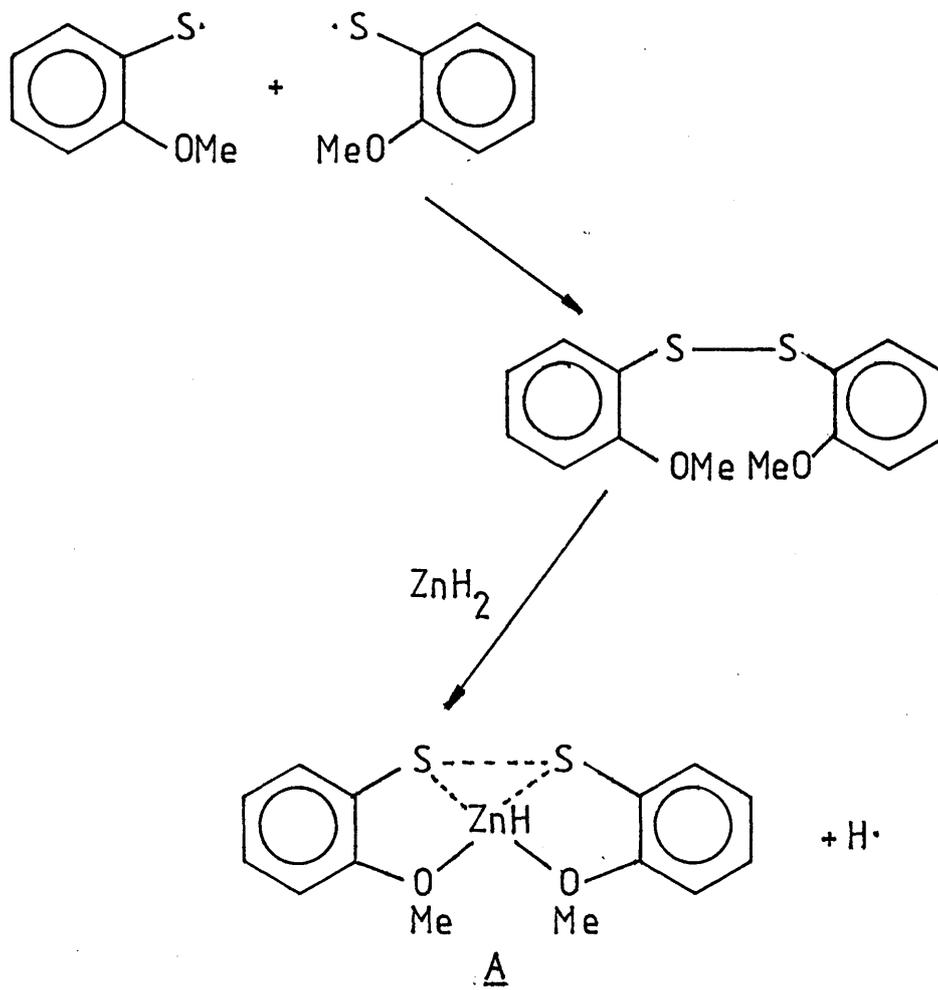


It is believed that hydride reaction <sup>84</sup> can proceed via single electron transfer processes thus a thiophenoxy radical which might undergo coupling might be formed.



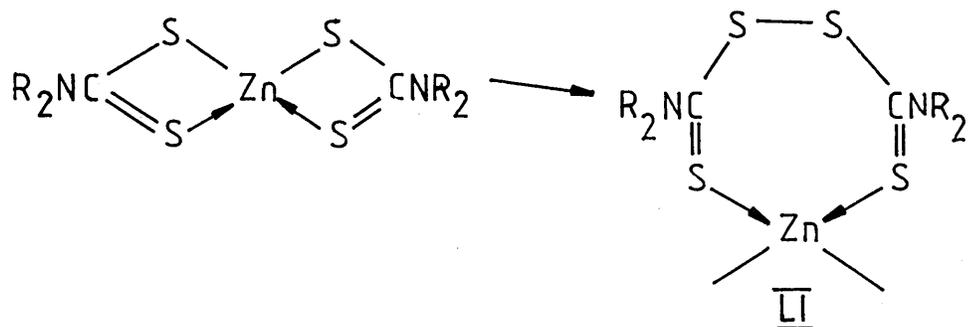
The product from the reaction shown above would be expected to give rise to a much more complex <sup>1</sup>H n.m.r. spectrum than is actually observed therefore it is unlikely that the

(2-MeOC<sub>6</sub>H<sub>4</sub>S)<sub>2</sub>ZnH has the above structure. Another type of structure might be obtained from the condensation of two thiophenoxy radicals. Thus:



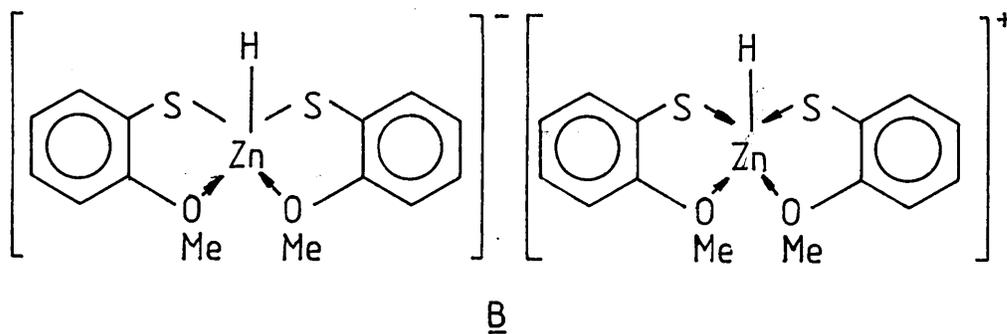
A complex with the above type of structure would be expected to give rise to a very simple <sup>1</sup>H n.m.r. spectrum, such as has been observed.

The formation of a disulphide, metal complex has been reported<sup>85</sup>. Oxidation of bis-dithiocarbamato complexes of zinc, cadmium and mercury yields thiuram disulphide complexes. II.



However in these complexes, the disulphide group does not take part in bonding with the metal.

One last possibility can be considered. If the disulphide is formed by oxidation then there must be a corresponding reduction somewhere. The following ionic product might be likely



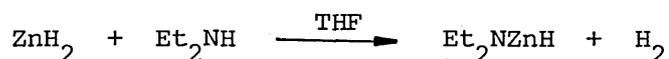
Hydrolysis of the complex followed by ether extraction yielded white crystals soluble in deuterated chloroform. Analysis of this product by  $^1\text{H}$  n.m.r. and infrared spectroscopy showed that it was not 2-methoxybenzenethiol.

There is therefore evidence to show that  $(2\text{-MeOC}_6\text{H}_4\text{S})_2\text{ZnH}$  has a symmetrical structure as shown in A and B but the present evidence cannot distinguish between these structural possibilities.

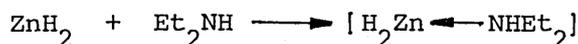
### 3.2 The reaction of zinc dihydride with monodentate ligands containing acidic protons

#### 3.2.1 The reaction of zinc dihydride with secondary amines

Zinc dihydride was found not to react readily with secondary amines. With diisobutylamine or diphenylamine no reaction was observed even after prolonged reaction periods and starting materials were recovered almost quantitatively. When zinc dihydride was allowed to react with diethylamine in equimolar quantities, an endothermic reaction was noted. Surprisingly, there was no copious evolution of gas even at elevated temperatures (50°C) as would have been expected if the reaction was proceeding according to the following scheme:



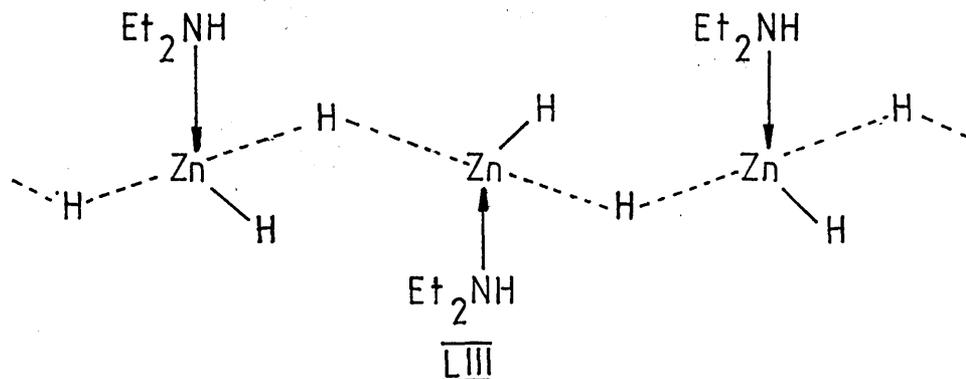
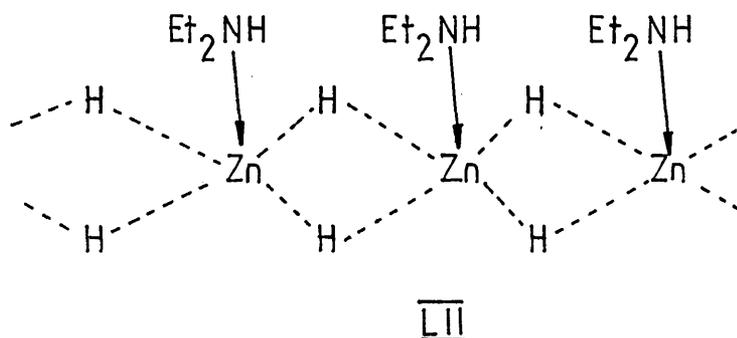
Furthermore, analysis of the product showed a zinc to hydridic hydrogen ratio of 1:2 and a stoichiometry of  $\text{Et}_2\text{NHZnH}_2$ . Since the product was found not to be a mixture of products containing zinc dihydride, because the compound melted sharply at 155°C, the reaction must thus proceed as follows with the formation of a coordination complex of zinc dihydride.



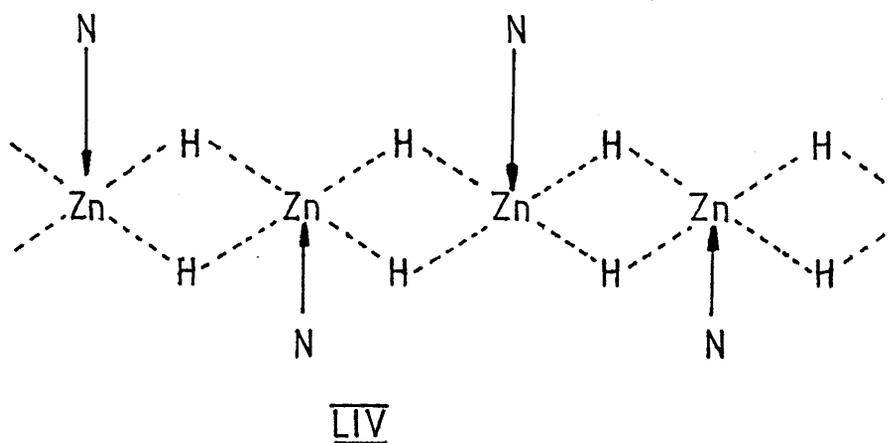
Unfortunately, once the product had been obtained in a solid microcrystalline state, it could not be redissolved satisfactorily in any inert solvent. The infrared spectrum of this complex, as a Nujol mull, showed a very broad absorption from 1800 to 1220  $\text{cm}^{-1}$  with a width at half height of This band is assigned to Zn-H stretching vibration on the basis of previously reported terminal zinc-hydrogen stretching vibration frequencies.<sup>43</sup> Presumably N-H deformation vibrations are also present but since these are usually weak for secondary amines<sup>86</sup> they might not be apparent. There were three bands at 1180, 1150 and 1110  $\text{cm}^{-1}$ , all of equal intensity, whereas in the infrared spectrum of neat diethylamine

only one band at  $1150\text{ cm}^{-1}$  was observed. These vibrations are assigned to mainly C-N stretching vibrations. The multiplicity of C-N stretching vibrations can be attributed to either a decrease in symmetry on complexation (i.e. more infrared active vibrations) or to the presence of different  $\text{Et}_2\text{NH}$  groups. Two sharp bands at  $2730\text{ cm}^{-1}$  and  $2670\text{ cm}^{-1}$  may be assigned to N-H stretching vibrations in the complex. The N-H stretching vibration in the free amine is found in the range  $3500 - 3300\text{ cm}^{-1}$  while in salts it is found at ca.  $2700\text{ cm}^{-1}$ <sup>86</sup>. Other bands at  $1070 - 1000\text{ cm}^{-1}$  and at  $790\text{ cm}^{-1}$  (broad) are assigned to possibly a Zn-H-Zn stretching mode and to a Zn-H wagging mode respectively.

The product is considered to be polymeric due to its apparent insolubility in inert solvents. There are therefore two structural possibilities.



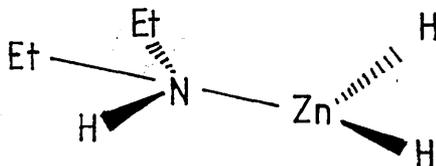
LIII might seem more favourable since the zinc atoms have a coordination number of four while in LII the coordination number of zinc is five. On the other hand, LII has a zinc hydridic hydrogen skeleton which is similar to that of the zinc dihydride which is believed to have a three-dimensional polymeric structure with bridging Zn-H-Zn units on the basis of infrared spectroscopy . LIII might be expected to show two infrared absorptions, one terminal Zn-H vibration in the region of  $1600\text{ cm}^{-1}$  to  $1700\text{ cm}^{-1}$  and a Zn-H-Zn mainly stretching vibration which may be expected around  $1300 - 1400\text{ cm}^{-1}$ , LII would be expected to show an infrared spectrum similar to that of zinc dihydride. The actual infrared spectrum of the complex as a Nujol mull showed a broad absorption from  $1800\text{ cm}^{-1}$  to  $1200\text{ cm}^{-1}$  as well as other absorptions which were assigned to the organic part of the complex. Thus the infrared spectrum supports structure LIII. Structure LII, does allow for the possibility of structural isomers thus



LIV has a different structure from LIII with the diethylamine groups, represented by N, being alternately above and below the 'plane' of the zinc atoms. This isomerism would be expected to complicate the infrared spectrum of the complex and it might lead to severe broadening of the zinc-hydrogen vibrations due to the presence of the different Zn-H-Zn units.

During attempts to crystallise out the complex a solution of the complex in benzene was obtained and this was analysed by  $^1\text{H}$  n.m.r. spectroscopy. The resonance which was observed at 4.18 ppm was assigned to the hydridic hydrogen. A similar resonance at 4.20 ppm observed in the  $^1\text{H}$  n.m.r. spectrum of  $[\text{TriMEDZnH}]_2$  was also assigned to the hydridic hydrogen. The quartet at 3.78 ppm was assigned to the N-methylene protons. The resonance due to these same protons in the free amine occurs at 2.58 ppm. A resonance at 1.08 ppm was assigned to the methyl protons in the ethyl groups and in the free amine these are found to resonate at 1.04 ppm. A resonance at 2.82 ppm was assigned to the amino proton whereas in the free amine this resonance is to be found at 0.90 ppm. Thus the resonances due to the protons in the methylene groups and in the amino proton, of the product in solution are shifted by between 1 and 2 ppm downfield from those in the free amine while the methyl proton resonances have essentially the same shift in the complex and in the free base. The size of this shift of the methylene and the amino protons shows that a strong coordination bond is formed. Usually the observed difference in the chemical shift of protons in  $-\text{CH}_2\text{X}$  ( $\text{X} = \text{N}, \text{O}$ ) on complexation is of the order of 0.5 ppm. e.g. a difference of 0.1 ppm in the chemical shift of the methylene group protons in  $-\text{CH}_2\text{NMe}_2$  on complexation during the formation of  $[\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}(\text{Me})\text{ZnH}]_2$ . No low field resonances (5-8 ppm) were seen apart from that due to the benzene solvent.

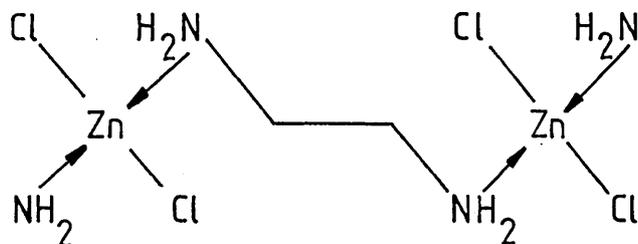
This is the region in which resonances due to bridging hydridic hydrogen atoms might be expected to be observed thus there does not appear to be any Zn-H-Zn species in solution. Most probably the hydridic species in solution is monomeric



and on removal of the solvent, the monomeric units join by forming Zn-H-Zn bridging, thus achieving coordinative saturation for zinc and leading to the formation of an insoluble complex.

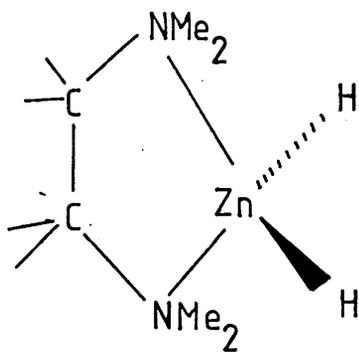
### 3.2.2 Diethylamine and TMEDA

Since the diethylamine zinc dihydride complex was polymeric and insoluble, it was thought that the presence of TMEDA in the reaction mixture might give a less associated, more soluble product. The reaction of zinc dihydride with diethylamine in the presence of TMEDA was carried out using benzene as a solvent so that there would not be any unwanted solvent effects and an approximate two-fold excess of TMEDA was used. The reaction was slow and a product was obtained in 30% yield as  $\text{Et}_2\text{NHZnH}_2 (\text{TMEDAZnH}_2)_2$  after 60 hrs. Chemical analysis of the product satisfied a stoichiometry of  $\text{Et}_2\text{NHZnH}_2 (\text{TMEDAZnH}_2)_2$ . The  $^1\text{H}$  n.m.r. spectrum of the product showed no spin-spin coupling in the methylene protons in the TMEDA ligand which might have been expected if the TMEDA was acting as a monodentate 'dangling' ligand. TMEDA must therefore be acting as a bridging or chelating ligand. It is known that  $(\text{en})\text{ZnCl}_2$  has the following structure<sup>87</sup>



with en having the trans form. TMEDA might be expected to adopt the type of structure shown above in the complex with zinc dihydride and diethylamine zinc dihydride.. There is no evidence in the solution or solid state infrared spectra for trans  $\text{CH}_2$  rocking vibrations. There are, however, two absorptions at  $960$  and  $932 \text{ cm}^{-1}$  which have been assigned to gauche  $\text{CH}_2$

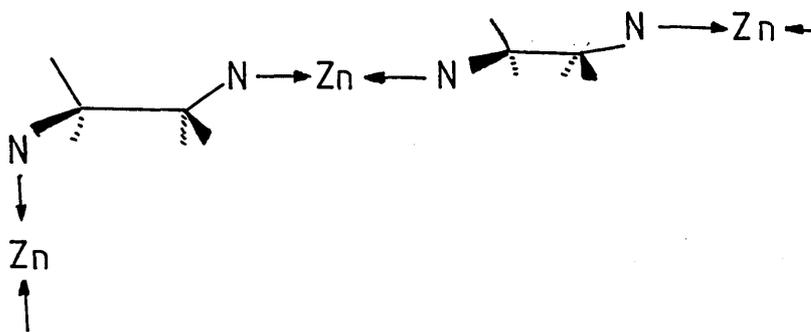
rocking modes. Such rocking modes are usually found in chelate complexes but there is no evidence that TMEDA is forming a chelate complex here. For instance, chelate complexes of  $\text{HZnCl}$ , show exothermicity during formation (p. 96 ) while in complexes where a 5-membered ring to zinc is formed by a ligand containing an  $\text{NMe}_2$  group, there is an upfield shift of the resonances in the  $^1\text{H}$  n.m.r. spectrum of the dimethylamine proton on the formation of the ring<sup>88</sup> thus the following arrangement of TMEDA within the overall structure of  $(\text{Et}_2\text{NHZnH}_2)(\text{TMEDAZnH}_2)_2$  can be excluded.



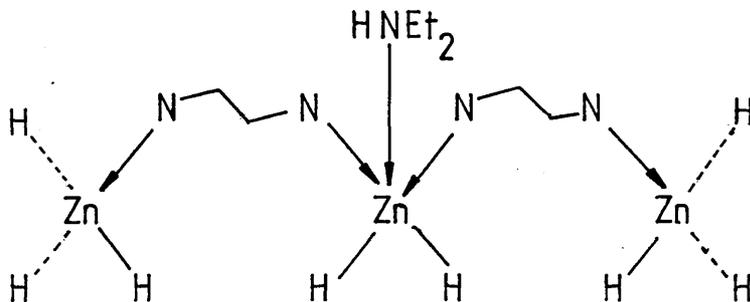
Furthermore, there is no evidence that the product is simply a physical mixture of  $\text{Et}_2\text{NHZnH}_2$  and  $\text{TMEDAZnH}_2$  because the product melted sharply at  $129^\circ\text{C}$  and while  $\text{Et}_2\text{NHZnH}_2$  is known (see p.143 ) it has been reported that zinc dihydride did not react with donor molecules like trimethylamine and hexamethylphosphoramide (HMPA)<sup>71</sup> and no reaction was observed to occur between zinc dihydride and tetramethyldiaminomethane in benzene.

This leaves as the only possible alternative, a linear structure containing TMEDA groups bridging between zinc atoms

with TMEDA molecules adopting a gauche conformation.



The diethylamine group is believed to coordinate to one zinc in three, making this zinc atom 5 co-ordinate and since the complex could not be redissolved satisfactorily after it had been obtained in a crystalline state it is considered to be polymeric with the following structure



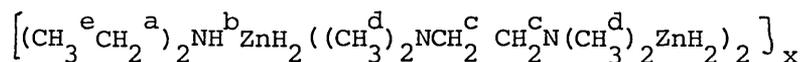
<sup>1</sup>H n.m. r. spectra were obtained both before and after desolvation of the product from benzene. Once the reaction mixture had been filtered and the filtrate concentrated to give

an oil, fresh benzene was added and the  $^1\text{H}$  n.m.r. spectrum of this solution was obtained. This is referred to as the  $^1\text{H}$  n.m.r. spectrum of product A. The benzene solution was then further concentrated and finally a crystalline solid was obtained. This was partially redissolved in benzene and the  $^1\text{H}$  n.m.r. spectrum of this product, product B, was obtained. As had already been seen, the  $^1\text{H}$  n.m.r. spectrum of product A shows that diethylamine and TMEDA are present in a molar ratio of 1:2. Unfortunately the  $^1\text{H}$  n.m.r. spectrum of product B showed only broadened resonances without any resolution at 3.2, 2.1 and at 1.2 ppm which were assigned to N-methylene ( $\text{Et}_2\text{NH}$ ), methylene and methyl protons in TMEDA and methyl protons ( $\text{Et}_2\text{NH}$ ) respectively. No resonances were observed which could be assigned to either N-H or Zn-H protons.

The  $^1\text{H}$  n.m.r. spectrum of product A was much more illuminating. The following resonances were observed (Table 4 ).

Table 4			
ppm	multiplicity	relative intensity	assignment <sup>(f)</sup>
3.32	quartet	4	a
2.78	broad singlet	1	b
2.32	singlet	7.8	c
2.16	singlet	24	d
1.20	triplet	6	e

(f) The labels are shown below with their relevant protons



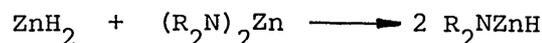
The resonances due to TMEDA in the complex are not shifted appreciably (0.05 ppm upfield) from those in free TMEDA. Thus there is little change in the electron density around the  $\text{Me}_2\text{N} \rightarrow \text{Zn}$  donor bonds. This means that the bonds formed by TMEDA and zinc in this complex are weak therefore it is highly unlikely that TMEDA is playing a chelating role.

The resonances due to the dimethylamine group protons in

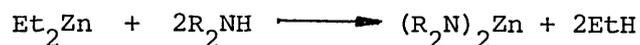
this complex have been shifted significantly but not by the same amount as in the diethylamine zinc dihydride complex (p.143 ). The diethylamine group may therefore have a slightly different environment in the  $\text{Et}_2\text{NHZnH}_2$  (TMEDAZnH<sub>2</sub>)<sub>2</sub> complex as opposed to in the  $\text{Et}_2\text{NHZnH}_2$  complex (p.143 ).

### 3.2.3 The reaction of secondary amines with diethylzinc

Although no other dialkylamino- or diarylaminozinc hydride complexes are known, several organozinc and zinc amides are known<sup>89</sup>  $(\text{EtZnNPh}_2)_2$ ,  $(\text{EtZnNEt}_2)_2$ ,  $\text{Zn}(\text{NPh}_2)_2$  and  $\text{Zn}(\text{NMe}_2)_2$  have been made by acidolysis of the diorganozinc by secondary amines. The crystal structure of  $(\text{MeZnNPh}_2)_2$  has been obtained<sup>90</sup> and this complex is dimeric in the solid state. It was thought that the redistribution reaction between zinc dihydride and bisdialkyl/diarylamino zinc would be a route to aminozinc hydride complexes



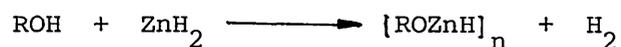
Since several aminomagnesium hydrides have been prepared from the redistribution reaction between magnesium dihydride and bisdialkyl/diarylamino magnesium<sup>18</sup>. However, the synthesis of bisdialkyl/diarylaminozinc complexes was complicated by solvent effects. A characteristic blue colour was observed in these reactions. This was believed to be due to partially oxidised organozinc species present in the reaction mixture



This reaction was attempted using  $\text{R}_2\text{NH}$  where  $\text{R} = \text{R}, \text{Et}, \text{Bu}^s, \text{cyclo C}_6\text{H}_{11}, \text{Ph}$ . In no case was the diaminozinc obtained, but complexes of an indeterminate nature were obtained instead.

### 3.2.4 The reaction of zinc dihydride with 2,4,6-tri-t-butylphenol

Complex alkoxyorganozinc compounds are known<sup>81</sup> and show varying degrees of association ranging from dimeric, to more highly associated<sup>82</sup>. It ought therefore to be possible to obtain alkoxyzinc hydrides by the reaction of alcohols with zinc dihydride



Since hydroxyl protons are much more acidic than amino protons it was anticipated that the reaction between alcohols and zinc dihydride would be rapid and would probably give a product with a high degree of association which would consequently be insoluble in the solvents in which the reactions would be performed. However, if an alcohol with severe steric crowding around the hydroxyl group is chosen then the bulky interfering groups may hinder intermolecular association in the complex and the complex may be soluble in the solvent used. Consequently 2,4,6-tri-t-butylphenol was chosen as an alcohol which fitted the above criterion.

The reaction between equimolar amounts of zinc dihydride and 2,4,6-tri-t-butylphenol in benzene was rapid but all the zinc dihydride did not react. A crystalline yellowish solid was obtained, on evaporation of the solvent, and the <sup>1</sup>H n.m.r. spectrum of this material in benzene solution was assigned as follows:

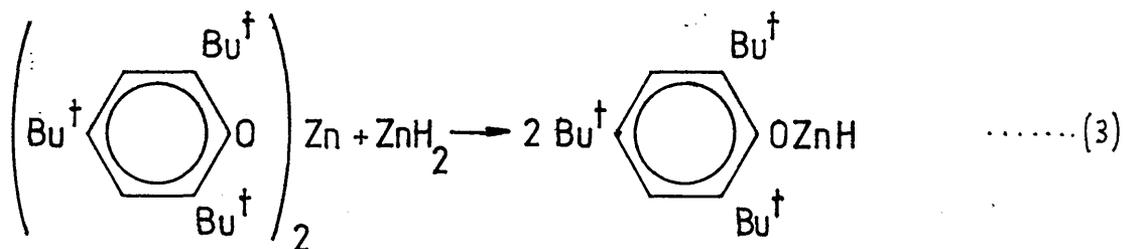
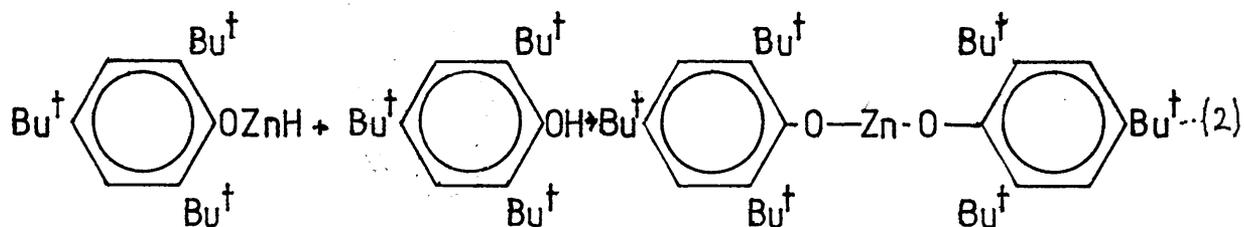
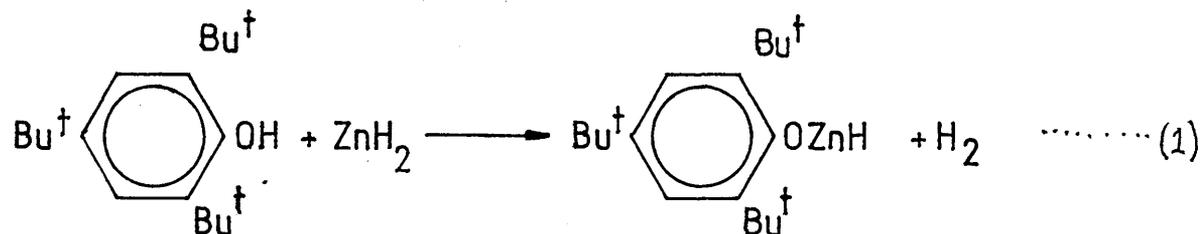
<u>ppm</u>	<u>intensity</u>	<u>multiplicity</u>	<u>assignment</u>
7.42	2	singlet	phenyl ring protons in phenoxide
7.32	2	singlet	phenyl ring protons in phenol
4.79	1	singlet	hydroxyl proton in phenol
1.66	} 20	singlet	tertiary butyl group
1.56		singlet	
1.39	} 45	singlet	protons in the phenol, phenoxide and hydride
1.36		singlet	
1.33		singlet	

The  $^1\text{H}$  n.m.r. spectrum of the reaction product showed five singlet peaks in the region 1 - 2 ppm where the tertiary butyl group proton signals are expected. Two of the signals can be assigned to unreacted alcohols (one due to the t-butyl groups ortho to the hydroxyl group and the other due to the t-butyl group para to the hydroxyl group). The remaining peaks must be due to more than one species since the 2,4,6-tri-t-butyl phenoxy group has only two magnetically non-equivalent t-butyl groups. On the basis of the intensities of the resonances due to the protons in the tertiary butyl groups it can be said that the reaction product is a mixture of bis (2,4,6-tri-t-butylphenoxy) zinc, the free phenol and an unknown component but presumably the hydride in 3:3:1 ratio. However no  $^1\text{H}$  n.m.r. resonance, which could be assigned to a hydridic hydrogen, was observed.

The infrared spectrum of the reaction product and the infrared spectrum of the free phenol were similar except in the region  $1300\text{ cm}^{-1}$  to  $1200\text{ cm}^{-1}$  where more and broader absorptions were observed. In this region we see C-O stretching vibrations and Zn-H-Zn stretching vibrations. The multiplicity of vibrational modes suggest the presence of different C-O

species thus the infrared spectra seem to bear out the fact that the reaction product is a mixture.

It would seem that at room temperature the following reactions occur.

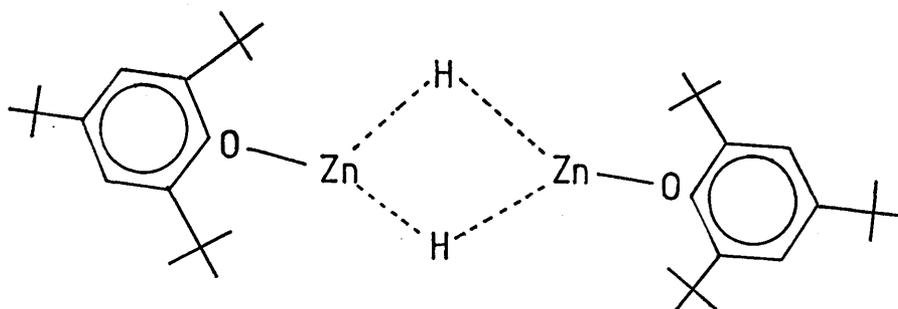


Steps 1 and 2 are very fast. This accounts for the non-reaction of all of the zinc dihydride. Step 3 is very slow due to the steric hindrance around the reactive centre and the fact that zinc dihydride is itself highly associated.

Thus the hydride complex will be a minor product.

Since no absorptions due to terminal Zn-H stretching vibrations were found in the infrared spectrum of the reaction product, the complex aroxyzinc hydride must have bridging hydride atoms.

The degree of association is unknown, but the complex aroxyzinc hydride may have the structure below



It would be impossible for the phenoxy groups to act as bridging ligands because the environment of the oxygen atom is too sterically hindered to allow close approach of two zinc atoms. The structure shown above has co-ordinatively unsaturated zinc atoms so it is unlikely to be simply dimeric.

### 3.2.5 The reaction of zinc dihydride with thiols

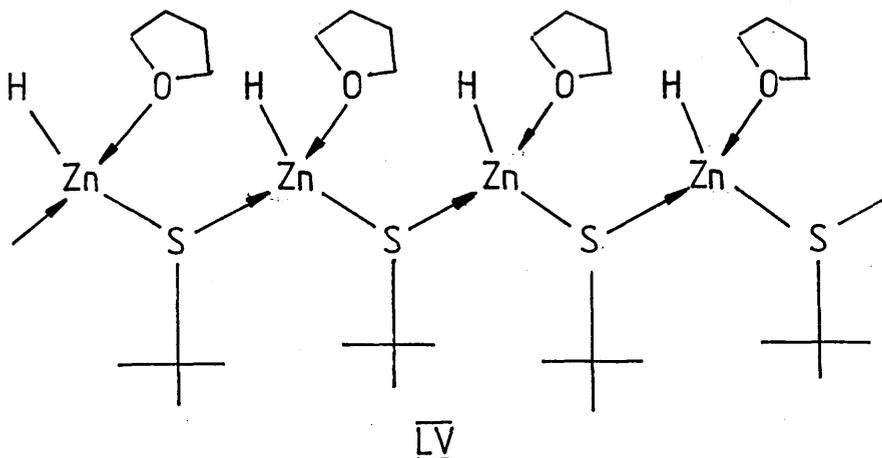
Since the reaction of zinc dihydride with the phenol did not lead to a high yield of a complex zinc hydride it was thought that the use of a thiol instead would result in a stable complex zinc hydride since:

- a) the thiol is not as acidic as the phenol
- b) the Zn-S bond is stronger than the Zn-O bond

Consequently the reaction of equimolar amounts of zinc dihydride and 2-methyl-2-propanethiol was investigated. An

initial product, soluble in THF, was obtained but on standing, a white solid precipitated out of the solution. This product analysed as  $(\text{CH}_3)_3\text{CSZnH}\cdot\text{THF}$ . An infrared spectrum of the white solid, as a Nujol mull, showed a broad band at  $1502\text{ cm}^{-1}$  with a width at half height of  $100\text{ cm}^{-1}$  and two high frequency shoulders at  $1627\text{ cm}^{-1}$  and  $1652\text{ cm}^{-1}$ . No such bands were apparent in the infrared spectrum of the free ligand so the band at  $1502\text{ cm}^{-1}$  was assigned to a terminal zinc hydrogen stretching vibration. Bands at  $1159\text{ cm}^{-1}$  ( $\nu_{\text{ring}}$ ),  $1036\text{ cm}^{-1}$  ( $\nu_{\text{ring}}$ ),  $976\text{ cm}^{-1}$  ( $\nu_{\text{C-C/C-O}}$ ) and  $886\text{ cm}^{-1}$  ( $\rho\text{ CH}_2$ ) have been assigned to vibrations of the THF ring on the basis of the assignments for THF by Driessen and den Heijer<sup>91</sup>.

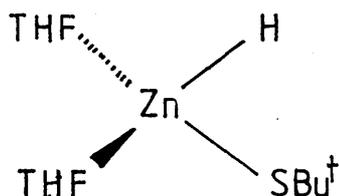
The complex zinc hydride was unusually thermally stable with a decomposition temperature of  $220^\circ\text{C}$  cf.  $\sim 130^\circ\text{C}$  for  $\text{ZnH}_2$ . The product also appeared to react unusually slowly with water as compared to most complex zinc hydrides. These facts point to a polymeric structure for the insoluble complex LV.



When the remaining supernatant THF solution was evaporated under reduced pressure, an oil was obtained. This oil dissolved in hexane and reevaporation yielded a white product which had

an identical infrared spectrum to that of the THF insoluble product. This new product had a lower melting point than that of the THF insoluble product. This was considered to be due to the presence of THF and hexane in the new product. Other than this the two products are identical.

Some of the supernatant THF solutions was examined by  $^1\text{H}$  n.m.r. spectroscopy and they showed a resonance of 4.78 ppm which was thought to be due to the terminal hydridic resonance in a soluble thiozinc hydride.



This is likely to have the above structure, since desolvation of this will lead to a coordinatively unsaturated product which will probably polymerise in order to achieve tetrahedral co-ordination.

An infrared spectrum of the reaction mixture as a THF solution showed similar bands to those obtained as Nujol mulls i.e. bands attributable to THF vibrations and t-butyl skeletal vibrations. Two strong bands at  $1657\text{ cm}^{-1}$  and at  $1531\text{ cm}^{-1}$  were assigned to terminal zinc-hydrogen stretching modes. The presence of two bands suggests that in solution there is strong coupling of  $\nu\text{Zn-H}$  to some other vibrational mode or that there are in fact two Zn-H species in THF solution. There is no other evidence for the latter however.

### 3.2.6 Diphenylphosphine

Since the reactions of zinc dihydride with secondary amines

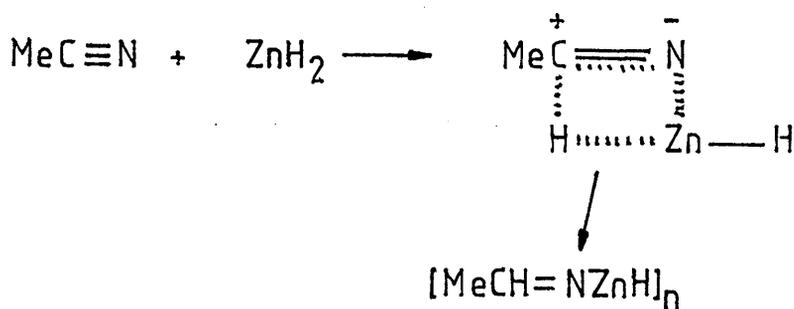


However, no chemical analyses were performed on any of the products so this interpretation cannot be considered conclusive.

### 3.3 Reaction of zinc dihydride with ligands containing C=N, C≡N, and C=O groups

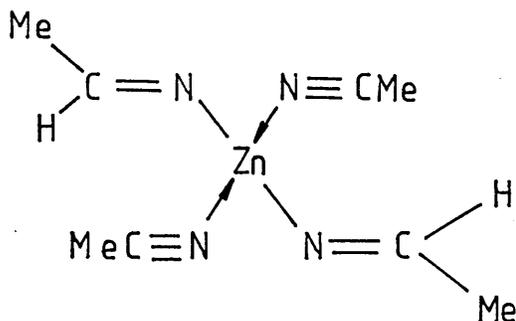
#### 3.3.1 Acetonitrile

The reaction of zinc dihydride with acetonitrile using equimolar ratios of reactants produced a yellow crystalline product but it was noted that the zinc dihydride did not all react. This crystalline product could not be redissolved satisfactorily in any inert solvent and this together with the fact that the solid showed no sign of melting up to 300°C suggests that the product was ionic or polymeric. Analyses of the hydrolysable hydrogen content of the product showed that both hydride atoms added to the acetonitrile. The zinc content of the product was found to be 25%, as opposed to the expected 60% for MeCH=NZnH. Clearly the reaction does not proceed according to the following scheme

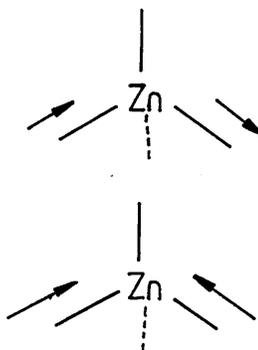
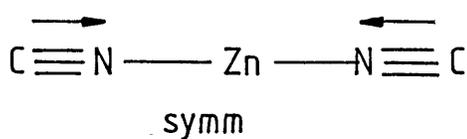
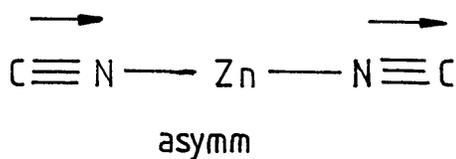


The infrared spectrum of the product showed a broad band of medium intensity from 1680 to 1590 cm<sup>-1</sup>. This band was assigned to C=N stretching modes. Sharp bands at 2180 and 2060 cm<sup>-1</sup>

were also observed in the complex. These were assigned to C≡N stretching modes. In neat acetonitrile an intense band observed at 2280 cm<sup>-1</sup> is assigned to the C≡N stretching vibration. From this evidence the major product of the reaction was believed to be (MeCH=N)<sub>2</sub>Zn(MeC≡N)<sub>2</sub> with the following structure

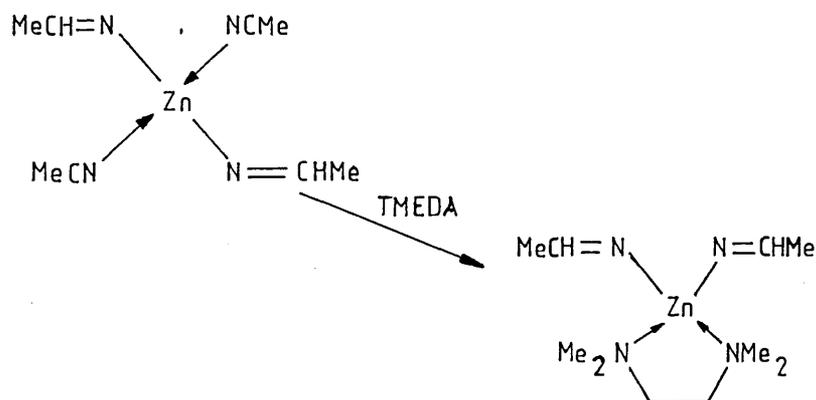


The fact that two C≡N stretching modes were observed can be explained by a coupling of the stretching modes of C≡N to give in effect a symmetric and an asymmetric C≡N stretching vibration thus:-



The analytical data suggests the presence of a hydridic species as a 7% impurity in the product. A weak absorption was observed at  $1860\text{ cm}^{-1}$  in the infrared spectrum of the product and this was tentatively assigned to some terminal Zn-H vibration but nothing could be said about the structure of this species.

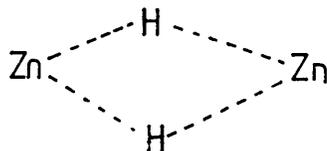
The product was allowed to react with TMEDA in benzene and the product, previously insoluble, dissolved in benzene. On standing, a white solid precipitated out, and an infrared spectrum of this solid as a Nujol mull showed a weak band at  $2240\text{ cm}^{-1}$  which was assigned to residual free acetonitrile in the product. Thus it would appear that TMEDA will replace acetonitrile in the complex.



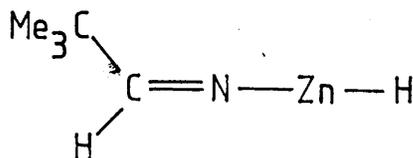
### 3.3.2 Pivalonitrile

The reaction of equimolar quantities of pivalonitrile and zinc dihydride produced a white product which proved to be more soluble than the product of the reaction of zinc dihydride and acetonitrile. The hydrolysable hydrogen content of 0.28% did not agree with that expected for  $\text{Bu}^t\text{CH}=\text{N}^+\text{ZnH}$  (0.66%) whereas  $\text{Bu}^t\text{CH}=\text{N}^+\text{ZnH}(\text{Bu}^t\text{C}\equiv\text{N})_2$  (0.31%) did not satisfy the spectroscopic data obtained for this product.

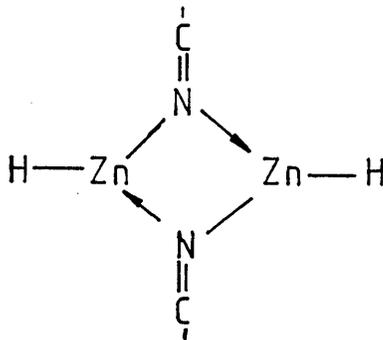
The  $^1\text{H}$  n.m.r. spectrum of this product exhibited only two broad peaks at 1.21 and 3.64 ppm with a 4:1 ratio of protons. Resolution of these peaks could not be improved. Infrared absorptions at 1699 and 1676  $\text{cm}^{-1}$  were assigned to C=N stretching vibrations. Significantly there were no absorptions in the range 2300 - 2000  $\text{cm}^{-1}$  where C $\equiv$ N stretching vibrations occur and thus  $\text{Bu}^+\text{C}\equiv\text{N}$  is not present in this complex. Furthermore there was no evidence for terminal Zn-H stretching vibrations in the region 1800 - 1500  $\text{cm}^{-1}$  where they are normally expected to occur. A broad band was observed at 1060  $\text{cm}^{-1}$  and this could be due to stretching vibrations in

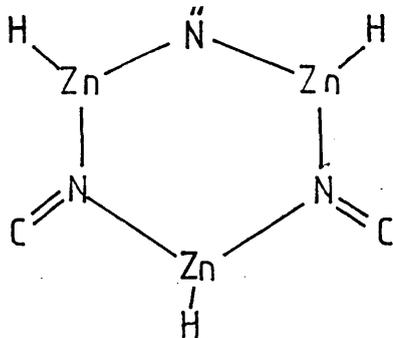


It is unlikely that the complex will be monomeric in solution at least

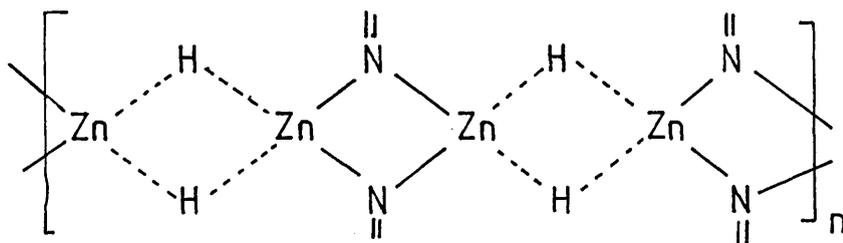


It is more likely that the lone pair of electrons on the nitrogen would form a dative bond with a nearby zinc atom thus increasing the co-ordination number of the zinc atom and leading to the formation of a dimeric or more associated species, e.g.



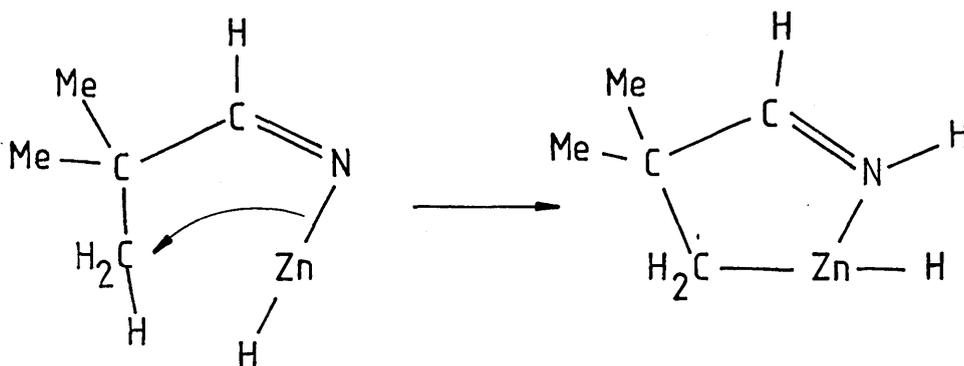


Since there is no evidence for terminal zinc hydridic hydrogen bonds in the  $^1\text{H}$  n.m.r. and infrared spectra of this complex the following structures may be considered

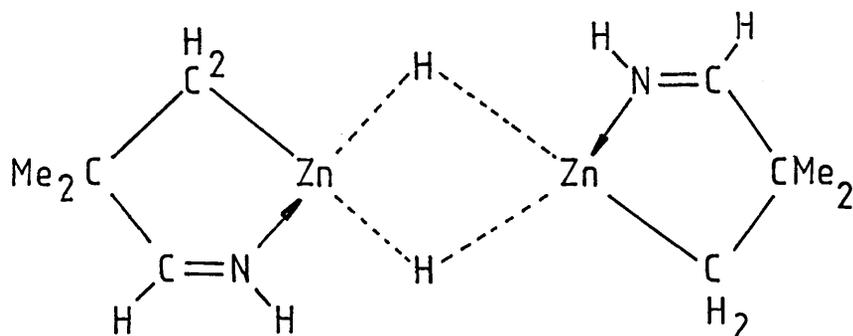


However, a complex with this type of structure might be expected to be insoluble due to its associated nature. It would also be expected that a  $^1\text{H}$  n.m.r. spectrum of a complex with this type of structure would show three resonances due to the methyl group protons, the hydridic hydrogens and the methylene proton. However the  $^1\text{H}$  n.m.r. spectrum of this complex actually shows only two broad resonances so the above structure can be dismissed.

Another structural possibility which can be considered is if we get intramolecular metalation in the complex thus:



The driving force for this might be the formation of a five membered ring and the formation of a donor bond by atoms with greatest electronegativity . The n.m.r. spectrum of this compound would be expected to show a complicated spectrum and if the imino and methylene protons had similar chemical shifts and the methyl and methylene protons also had similar chemical shift, the n.m.r. spectrum would show two broad peaks with a peak area ratio of 4:1 which is in fact observed. This complex would also be unlikely to be monomeric so it might have the following structure:



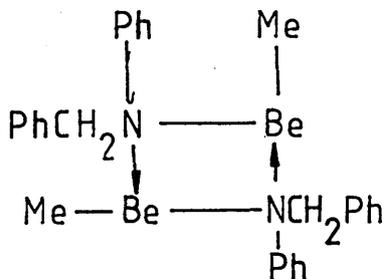
The fact that the C=N stretching vibrations are observed can now be explained by cis-trans isomerism around the  $ZnH_2Zn$  bridge. Such isomerism has been reported for complexes with a  $BeH_2Be$  bridge<sup>39</sup> .

A sample of the complex was hydrolysed using dilute HCl/ $H_2O$  and the organic part extracted with diethylether in an effort to shed light on the organic part of the complex. After extraction, a product was obtained which was liquid at room temperature. An infrared spectrum of this product showed absorptions due to both O-H (possibly hydrogen bonded) and C=N, stretching vibrations. This compound is thus likely to be 1 hydroxy-2-dimethylpropylimine  $HOCH_2CMe_2CH=NH$   
This complex did not react with TMEDA even after a reaction

time of 96 hours. The  $^1\text{H}$  n.m.r. spectrum of the reaction product in benzene showed resonances due to the presence of unchanged TMEDA.

### 3.3.3 Benzylidenemethylamine

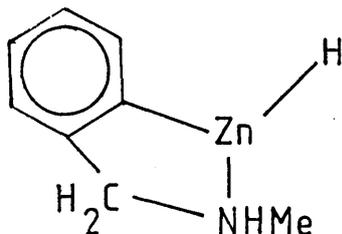
The reaction of zinc dihydride and benzylidene methylamine was investigated. A similar reaction has already been investigated for methylberyllium hydride and benzylideneaniline with the following product being obtained<sup>41</sup>.



A similar product might have been expected for zinc dihydride and benzylidenemethylamine but a very unstable product was obtained which was soluble in benzene and THF. A  $^1\text{H}$  n.m.r. spectrum of the product in benzene showed doublets at 3.68, and 2.35 ppm and a broad peak at 3.03 and 4.29 ppm, in ratios of 2:3:1:1 which were assigned to methylene protons in  $\text{PhCH}_2\text{NMeH}$ , and methyl protons in  $\text{PhCH}_2\text{NMeH}$ , NH and Zn-H protons and an asymmetric peak centred on 7.34 which was assigned to phenyl ring protons. The infrared spectrum of a THF solution of the product showed a sharp band at  $3280\text{ cm}^{-1}$  which was assigned to an N-H stretching vibration. The rest of the infrared spectrum was assigned as follows:

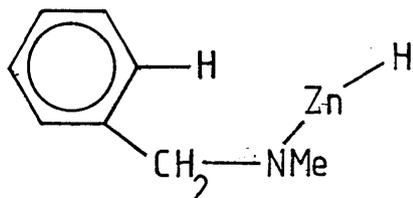
<u>cm<sup>-1</sup></u>	<u>intensity</u>	<u>due to:</u>
3000	s	aromatic proton stretching vibrations
2700	m	aliphatic C-H stretching vibrations
1668	m	Zn-H stretching vibrations (terminal)
1590	s	N-H bending vibrations and C=C stretching modes
1492	s	C=C stretching vibrations
1394	s	aliphatic C-H bending vibrations
1140	s	C-N stretching vibration
818	s	Zn-H wagging vibration
734	s	o-disubstituted ring vibration modes

The spectroscopic evidence suggests that the complex has the following type of structure

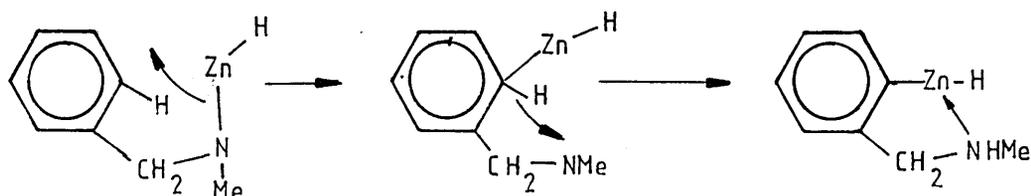


with an ortho-metalated phenyl ring. Such metalated species are known for aromatic imines with a number of transition metals.<sup>88</sup>

If, as is expected, the reaction proceeds by addition of zinc dihydride to the imino group, the initial product would be



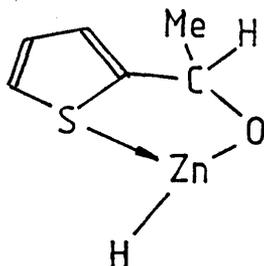
Obviously, in this structure zinc is coordinatively unsaturated but it might be expected that the solvent (in this case THF) would fill the vacant coordination sites. Clearly, the driving force for this reaction is the formation of a five membered ring and an increase in the coordination number of the zinc atoms.



Such a complex, whatever degree of association it might have, would be expected to be very unstable due to the presence of both a hydridic hydrogen and a slightly acidic secondary amino proton in the same molecule, and to decompose via an intramolecular elimination reaction, yielding hydrogen, zinc metal and an organic remnant (which might be a heterocyclic compound). An interesting observation on this reaction was the appearance of a transient red colour in the reaction mixture, which was thought to be due to the formation of an imine-zinc hydride complex prior to the addition reaction. Such complexes with ketones replacing the imine have been observed and are postulated to explain the reaction of zinc dihydride and camphor (see p.170 ).

### 3.3.4.2 Acetylthiophene

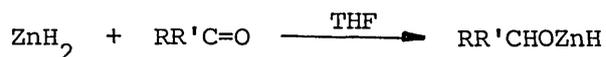
The reaction of zinc dihydride with 2-acetylthiophene was very exothermic. The product which precipitated out of solution on addition of a 1:3 mixture of benzene and hexane decomposed *in vacuo* at 90°C. Infrared and  $^1\text{H}$  n.m.r. spectra of this product showed that a reaction had taken place. A broad band of medium intensity at 1588  $\text{cm}^{-1}$  was assigned to a terminal Zn-H stretching vibration, the Zn-H wagging mode being found at 697  $\text{cm}^{-1}$ . The product appeared to have some solubility in benzene and a  $^1\text{H}$  n.m.r. spectrum of the product in benzene showed resonances at 7.15 - 6.84 ppm which were assigned to thiophene ring protons, at 5.38 ppm, hydridic hydrogen, 3.50, methane proton, 1.68 ppm methyl proton. The integrated intensities of the resonances suggest that the product has the following stoichiometry,  $\text{C}_6\text{H}_8\text{OSZn}$ , but without analytical and molecular weight data, nothing can be said with certainty about the exact structure of this complex. It is worth



noting that the hydridic resonance occurs at 5.38 ppm. This is 1 ppm downfield of the other known terminal hydridic hydrogen resonances e.g.  $\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{Me})\text{ZnH}_2$  where the hydridic hydrogen shows a resonance at 4.19 ppm. Thus there may be some bridging character in the Zn-H bond.

### 3.3.5 Carbonyl groups

The addition of zinc dihydride to ketones has been studied as a possible route to alkoxyzinc hydrides



The reaction of zinc dihydride with the carbonyl group in organic compounds was characterised by an initial period of exothermicity lasting about 30 minutes when the reaction was carried out at room temperature.

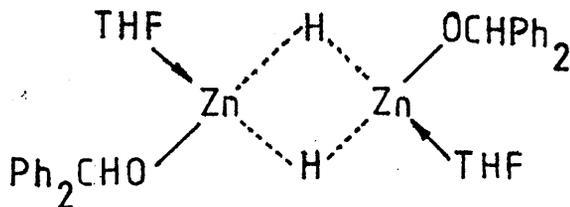
### 3.3.6 Benzophenone

The reaction of zinc dihydride with benzophenone in THF proceeded with a pink/purple colouration persisting in the reaction mixture during the first half hour of reaction. It was thought that this may be due to the formation of a ketyl. Evidence of ketyl formation has been produced in the reaction of carbonyl groups with metals and metal hydrides <sup>84</sup>. Though the reaction mixture was stirred for 50 hours, not all of the zinc dihydride dissolved. A green gum was obtained on evaporation of solvent after attempts at recrystallisation were unsuccessful. The <sup>1</sup>H n.m.r. spectrum of a benzene solution of the green gum was assigned as follows:

<u>ppm</u>	<u>description</u>	<u>assignment</u>
7.34	broad multiplet	phenyl ring protons in the benzophenoxy group
7.10	broad singlet	benzene (usually 7.20 ppm)
3.28	broad multiplet	THF: O-C-H
1.29	broad multiplet	THF

The n.m.r. spectrum does not show a Zn-H resonance (though this might be hidden). The infrared spectrum of the complex does not show any absorptions due to terminal Zn-H stretching vibrations. When air was admitted to the mull, a strong band at 3400 cm<sup>-1</sup> due to νOH stretching appeared and the shape and intensity of the absorption in the region 1200 - 1000 cm<sup>-1</sup> changed. It may be that this absorption is in part due to Zn-H-Zn vibrations. The complex hydride appears to have

the following structure

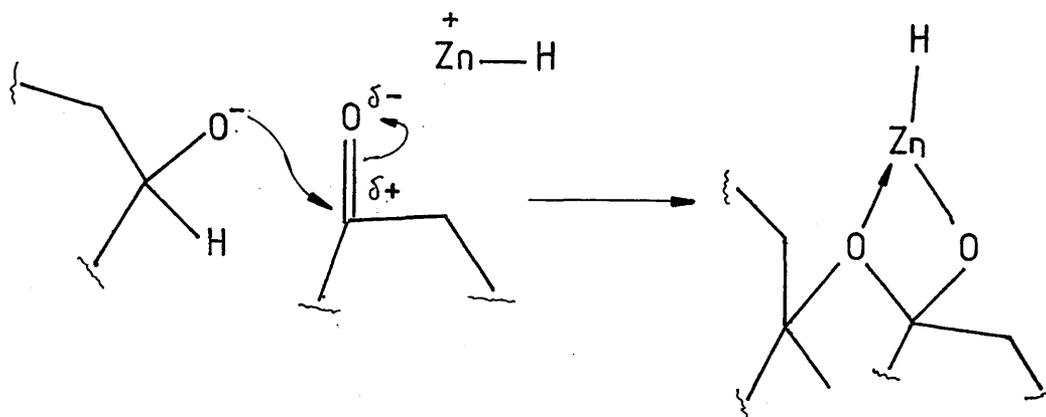


The low amount of hydrolysable hydrogen obtained when the reaction product was hydrolysed was explained on the basis of the reaction mixture being a mixture of the complex zinc hydride and bis(diphenylmethoxy)zinc.

### 3.3.7 Camphor

When zinc hydride was allowed to react with camphor a pink/white solid was obtained. The analysis of this complex suggests a stoichiometry of  $(C_{10}H_{17}O)_2ZnH$ . This is curious since zinc dihydride usually reacts in equimolar ratio. The infrared spectrum of the complex shows a broad band from 1760 to 1400  $cm^{-1}$  which is due to terminal Zn-H stretching. The -C-O stretching vibrations (1100-1060  $cm^{-1}$ ) not observed in camphor itself showed that the oxygen atom has a different environment in the complex. The proton n.m.r spectrum showed a very broad resonance centred on 4.11 ppm downfield from TMS and this was assigned to the Zn-H resonance. The resonances due to the methylene protons near the oxygen are shifted upfield suggesting an increase in electron density in that part of the molecule. The chemical shifts of the bridgehead methyl protons are the same as in camphor. It was originally thought that camphor itself must be involved in bonding by co-ordinating in the complex through the carbonyl group but on hydrolysis of a sample of the complex no camphor could be found after analysis by g.l.c. No structure consistent with the above information is possible unless some kind of condensation reaction occurs between camphor and

the alkoxy group, thus

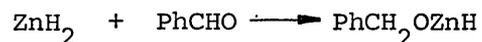


(most of the carbon skeleton has been omitted for the sake of clarity).

If such a structure is feasible then the reducing behaviour of this complex should be interesting due to the steric crowding in the environment of the zinc-hydride bond.

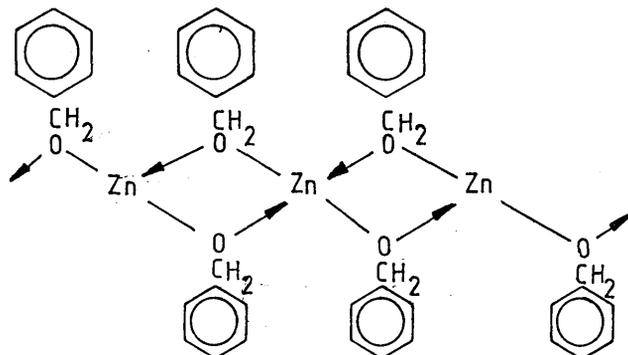
### 3.3.8 Benzaldehyde

The reaction of zinc dihydride with benzaldehyde proceeds according to the following scheme:

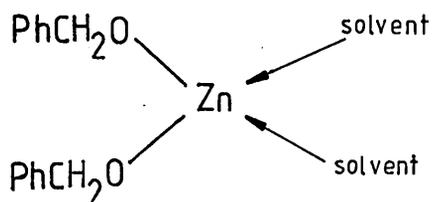


but the hydride was obtained on only 10% of the reaction product (based on the percentage of hydrolysable hydrogen obtained). The  $^1\text{H}$  n.m.r. spectrum of a benzene- $\text{d}_6$  solution of the reaction product showed only resonances due to phenyl ring protons at 7.24 ppm and a resonance at 4.90 ppm which was assigned to the methylene protons in the phenylmethoxy group. The infrared spectrum of the product did not show any absorption attributable to terminal zinc-hydride stretching vibrations. Absorptions at  $1100\text{ cm}^{-1}$  and at  $1020\text{ cm}^{-1}$  were assigned to C-O stretching vibrations since such absorptions were not

observed in the infrared spectrum of neat benzaldehyde. The evidence above points to the reaction product being a mixture of 10% phenylmethoxyzinc hydride and 90% bis(phenylmethoxy)zinc



Bis(phenylmethoxy)zinc probably has the above structure in the solid state but in solution with donor solvent, solvent molecules will depolymerise the complex and solvent molecules may take up the two vacant coordination sites thus:



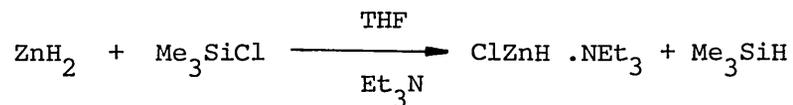
With benzaldehyde then, the reaction does not stop with the formation of a phenylmethoxyzinc hydride but the complex zinc hydride, which is presumably more reactive than the zinc hydride, reduces more benzaldehyde to give the bis(phenylmethoxy)zinc.

### 3.4 Reactions of zinc dihydride with halogen-containing compounds

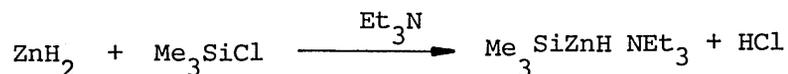
Several routes to hydrido zinc halides were investigated and since there was no evidence for the presence of  $\text{HZnCl}$  as a product of the reaction of metal hydrides with zinc dichloride in diethylether<sup>70</sup> it was thought that in the presence of a chelating agent the coordinatively unsaturated  $\text{HZnCl}$  may become trapped and thus isolated as a non-associated product.

### 3.4.1 Trichloromethylsilane

The reaction between trichloromethylsilane and zinc dihydride, in the presence of an excess of triethylamine, in THF was investigated as a route to hydrido-zinc chloride according to the following scheme



Another reaction, proceeding by a radical mechanism would be:



There was no evidence for the formation of HCl in the volatile products evolved from the reaction mixture but the presence of  $\text{Me}_3\text{SiH}$  was indicated by a strong sharp band in the infrared spectrum of the volatile products, at  $2130 \text{ cm}^{-1}$  due to the Si-H stretching mode.

Triethylamine may have formed a complex with the hydrido-zinc chloride but on removal of the solvent, the complex decomposed. It would therefore seem likely that the triethylamine hydrido-zinc chloride is a very weak complex and easily decomposes into zinc metal and other (unidentified) decomposition products.

### 3.4.2 Trimethylamine hydrochloride

A more successful route to stable hydrido-zinc halide was by the reaction of trimethylamine hydrochloride with zinc dihydride in tetrahydrofuran according to the following scheme:

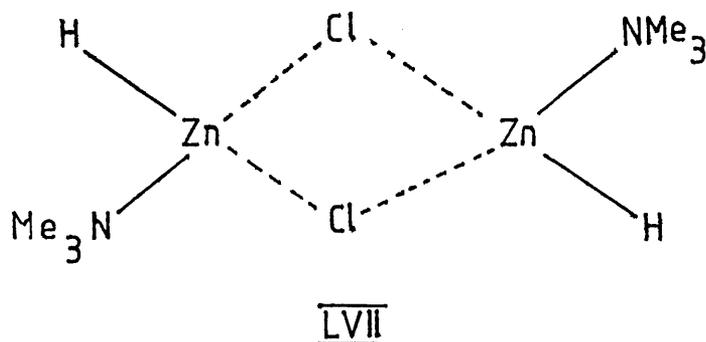
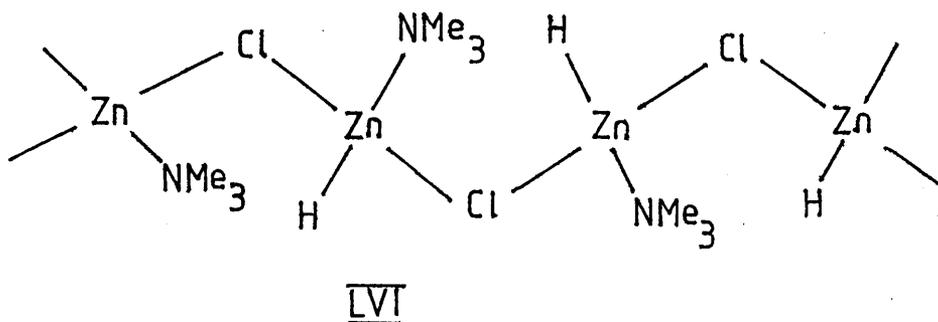


Though trimethylamine hydrochloride is insoluble in tetrahydrofuran, it was seen to dissolve in the presence of zinc

dihydride. The product was obtained as white crystalline needles from benzene and it was then dried in vacuo for several hours to remove traces of THF. The  $^1\text{H}$  n.m.r. spectrum did not show any resonances due to THF but it did show the presence of benzene. The ratio of benzene to trimethylamine was found to be 2:1. Analysis of the product by wet chemical techniques suggested a stoichiometry of  $\text{Me}_3\text{N}\cdot\text{HZnCl}\cdot 2\text{C}_6\text{H}_6$  and when the product was heated in a sealed tube to  $80^\circ\text{C}$  a liquid was seen to condense in the cool part of the tube at the same time as the solid melted. Thus it appears that when the product crystallises from THF solution on addition of benzene two moles of benzene are trapped in the crystal per mole of hydrido-zinc chloride. The resonance due to the protons in the  $\text{Me}_3\text{N}$  groups in the  $^1\text{H}$  n.m.r. spectrum of the complex is found at 2.05 ppm. In  $\text{Me}_3\text{NHCl}$  the corresponding resonance is found at 2.90 ppm, thus there is no trimethylamine hydrochloride present in the product. However, on the basis of the similarity in the chemical shifts of the methyl group protons in the trimethylamine moiety in the complex (2.05 ppm) and in free trimethylamine (2.00 ppm)<sup>93</sup> it seems likely that the trimethylamine group is not strongly coordinated in the complex since the electron density in a strongly coordinated trimethylamine group would be expected to be different from that of a weakly coordinated trimethylamine group.

No resonance due to the hydridic hydrogen could be detected. The infrared spectrum of the complex as a Nujol mull showed a broad absorption from  $1700 - 1540\text{ cm}^{-1}$  which is attributed to terminal Zn-H stretching vibrations. The vibrations due to trimethylamine showed that coordination had occurred. A strong band at  $1010\text{ cm}^{-1}$  was assigned to a  $\nu_{\text{asym}}$  C-N. This band is not present in the infrared spectra of  $\text{Me}_3\text{NHCl}$  or  $\text{Me}_3\text{N}$ . Many trimethylamine metal complexes have a strong vibration at  $\sim 1000\text{ cm}^{-1}$  which has been assigned to the asymmetric C-N stretch<sup>25</sup>. Thus the trimethylamine is coordinated to the metal but the assignment of the metal nitrogen

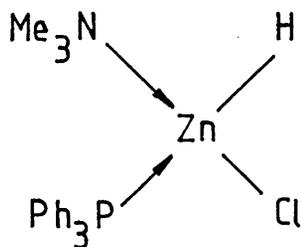
stretching vibration is less certain. Zinc-nitrogen stretching vibrations have been reported as occurring at  $437\text{ cm}^{-1}$  for  $\text{Zn}(\text{NH}_3)_4\text{Cl}_2$ , at  $300\text{ cm}^{-1}$  for  $\text{Zn}(\text{NH}_3)_6\text{Cl}_2$ <sup>94</sup>; at  $423\text{ cm}^{-1}$  from  $\text{Zn}(\text{en})_3\text{Cl}_2$  (en in ethylenediamine) and at  $450\text{ cm}^{-1}$  for  $\text{Zn}(\text{en})_2\text{Cl}_2$ <sup>87</sup>. In  $\text{Me}_3\text{NHZnCl} \cdot 2\text{C}_6\text{H}_6$  there are two low frequency vibrations. One at  $505\text{ cm}^{-1}$  is too high to be confidently assigned to a Zn-N vibration but the band at  $410\text{ cm}^{-1}$  can be assigned to a Zn-N stretching vibration. The position of the band and the strong  $\nu_{\text{asym}}\text{ N-C}$  at  $1010\text{ cm}^{-1}$  suggests that trimethylamine is acting as a coordinating ligand. Possibilities for the structure of this complex are



It seems likely that if a monomer exists then it will only do so in dilute solutions. In concentrated solution LVI will be most likely while in the crystalline or solid state LVI seems most likely because such an open structure can trap solvent molecules.

When LVI was allowed to react with an equimolar amount of 1,2-dimethoxyethane in an n.m.r. tube and the reaction was monitored by observing changes in the  $^1\text{H}$  n.m.r. spectrum of the reaction mixture over a period of time, no resonances due to coordinated 1,2-dimethoxyethane could be detected. Since a resonance due to  $\text{Me}_3\text{N}$  protons was still present it was likely that no reaction had taken place.

When LVI was allowed to react with triphenyl phosphine and the reaction was again monitored by  $^1\text{H}$  n.m.r., a resonance at 7.06 ppm due to coordinated triphenylphosphine was observed. A new resonance was observed at 4.50 ppm and this was assigned to a hydridic hydrogen. The intensities of the resonances suggested that a new complex had been formed, with a stoichiometry of  $\text{Zn}(\text{H})(\text{Cl})(\text{NMe}_3)(\text{PPh}_3)$ . A resonance due to  $\text{NMe}_3$  protons was also observed. This complex probably has the following structure:



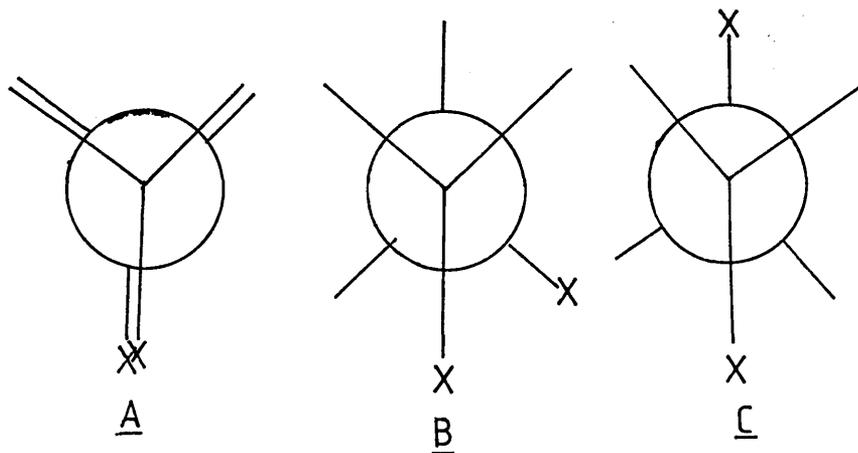
Thus it would seem that while 1,2-dimethoxyethane is not a strong enough donor ligand to break the chloride bridge, triphenylphosphine can.

### 3.4.3 Zinc chloride and TMEDA

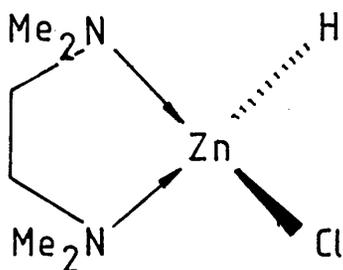
The reaction between zinc dihydride and anhydrous zinc chloride in 1:1 mole ratio was also investigated. In the presence of TMEDA, a white crystalline solid of stoichiometry  $\text{TMEDA} \cdot \text{HZnCl}$  was obtained. The complex was found to be soluble in benzene and a  $^1\text{H}$  n.m.r. spectrum of this solution showed a resonance due to hydridic hydrogen at 4.43 ppm. Signals due to protons in free TMEDA were shifted; on complex formation the methylene resonances being shifted to 0.5 ppm upfield. This effect is believed to be due to the formation of a chelate ring (see p.120).

The infrared spectrum of the complex as a Nujol mull showed a broad band at  $1701\text{ cm}^{-1}$ , width at half height  $80\text{ cm}^{-1}$  which was assigned to terminal Zn-H stretching vibrations. Two carbon-nitrogen stretching vibrations were observed at  $1028, 1011\text{ cm}^{-1}$ , these being due to Me-N and  $\text{CH}_2\text{-N}$ . The structure of the chelate part of the complex was assigned on the basis of conformations in disubstituted ethanes and their relationship to  $\text{CH}_2$  rocking modes of vibration which appear to be sensitive to changes in conformation<sup>95</sup>.

1,2-disubstituted ethane can exist in a variety of conformations depending upon the angle of internal rotation. In intramolecular coordination compounds the 1,2-disubstituted ethanes will have a cis A or gauche B form. In intermolecular coordination the ligand will have the trans form C.



The trans form has  $C_{2h}$  local symmetry thus there will be only one infrared active vibration (of  $A_u$  symmetry) due to  $CH_2$  rocking vibrations and this will be higher in frequency than those due to the cis or gauche forms in which the rocking mode will have A and B symmetry and these will show more than one infrared active vibration<sup>95</sup>. In TMEDA.HZnCl there are several bands which have been assigned to  $CH_2$  rocking vibrations between 1000 and 700  $cm^{-1}$ . The structure of the complex in the solid state will be



It is likely that the actual conformation of the chelating ligand will lie somewhere between the cis and gauche forms as relieving the eclipsing strain in the cis forms and maximising the metal-nitrogen bond interactions in the gauche form.

There are several low frequency vibrations which have been tentatively assigned to Zn-N vibrational modes with  $\nu_{sym}$  Zn-N at 482  $cm^{-1}$  and  $\nu_{asym}$  at 431  $cm^{-1}$ . There are other bands which cannot be definitely assigned. These will be in part due to skeletal vibration and overtones of Zn-Cl stretching vibrations.

#### 3.4.4 Zinc Chloride and 1,2-Dimethoxyethane

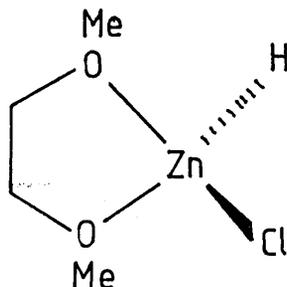
The reaction of zinc dihydride with anhydrous zinc chloride

in the presence of other bidentate ligands was also investigated. No crystalline products could be obtained but viscous oils which decomposed *in vacuo* to zinc metal, resulted on removal of solvent by evaporation.

In the presence of 1,2-dimethoxyethane (DME) a complex was obtained as an oil. The  $^1\text{H}$  n.m.r. spectrum of a deuterated benzene solution of the complex showed it to have a stoichiometry of  $\text{DME}\cdot\text{HZnCl}$ . The methylene proton resonances in the complexed DME showed a small upfield shift of 0.11 ppm indicative of chelate ring formation. A resonance at 3.97 ppm was assigned to the hydridic hydrogen.

The infrared spectrum of the complex as a thin film showed a broad band, width at half height  $150\text{ cm}^{-1}$  with a maximum at  $1590\text{ cm}^{-1}$  which was assigned to terminal Zn-H stretching vibrations. The methylene rocking modes in 1,2-dimethoxyethane have been assigned<sup>96</sup> to bands between  $1000\text{ cm}^{-1}$  and  $800\text{ cm}^{-1}$  with those due to the trans form occurring at higher frequency. In  $\text{DME}\cdot\text{HZnCl}$  there are strong bands at  $873$  and  $850\text{ cm}^{-1}$  which have been assigned to the rocking vibrations in gauche or cis DME while a weak broad band at  $945\text{ cm}^{-1}$  was assigned to a Zn-H wagging vibration. In free DME there is an absorption at  $980\text{ cm}^{-1}$  which is due to a methylene rocking vibration in trans 1,2-dimethoxyethane.

$\text{DME}\cdot\text{HZnCl}$  will therefore have the following structure



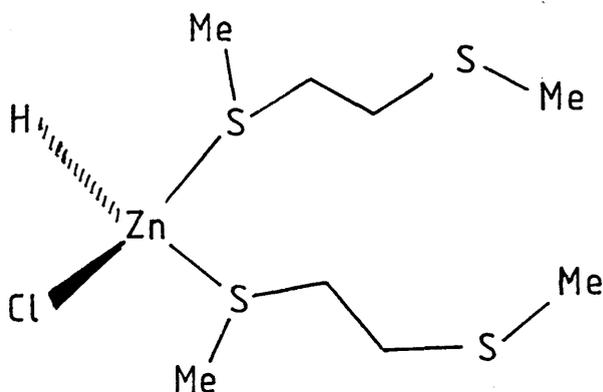
Since this complex could not be crystallised out successfully there must be some weak interaction between the individual molecules which, while not disrupting the above structure, interfere sufficiently with crystal packing forces to prevent the formation of a crystal. This may explain why the coordination of 1,2-dimethoxyethane is fairly weak, as shown by the small difference between chemical shifts of the protons in free and complexed ligand. The relatively small shift in C-O stretching frequency ( $11 \text{ cm}^{-1}$ ) and the lack of a definite zinc-oxygen stretching vibration. Zinc-oxygen stretching modes come between  $465 \text{ cm}^{-1}$  for bismethoxyzinc<sup>97</sup> and  $227$  for  $\text{Zn}(\text{DME})_3 \cdot (\text{SbCl}_6)_2$ <sup>97</sup>. A band at  $400 \text{ cm}^{-1}$  in  $\text{DME-HZnCl}$  can be assigned to a COC bending mode coupling to a ZnO stretch.

#### 3.4.5 Zinc Chloride and 1,2-bis(methylthio)ethane

When zinc dihydride and anhydrous zinc chloride were allowed to react in the presence of 1,2-bis(methylthio)ethane, -(DTH), a clear oil was obtained which would not yield crystals. On exposure to a vacuum of 1 mm Hg, a fine grey powder, presumably zinc metal, was seen to form in the oil. A  $^1\text{H}$  n.m.r. spectrum of the oil in benzene showed virtually no change in the resonances due to the ligand suggesting that no chelate complex was formed and that the bonding is particularly weak. This oil was found to have a stoichiometry of  $\text{HZnCl}(\text{DTH})_2 \cdot 0.25 \text{ THF}$  on the basis of the integrated intensities of the various proton resonances in the  $^1\text{H}$  n.m.r. spectrum of the oil in benzene. The resonances due to THF were observed at 1.50 ppm (1.89 free) and 3.72 ppm (normally 3.82 ppm) suggesting that THF is coordinating to the metal.

The infrared spectrum of the oil showed a broad weak band from  $1700$  to  $1500 \text{ cm}^{-1}$ , width at half height of  $100 \text{ cm}^{-1}$  which was assigned to terminal zinc hydrogen stretching vibrations. In THF solution this absorption had a maximum at  $1565 \text{ cm}^{-1}$ .

The methylene rocking vibrations and carbon-sulphur stretching vibrations of the ligand in the complex have been assigned on the basis of the vibrations of the free ligand reported in literature<sup>98</sup>. No C-S stretching vibration due to the gauche form, expected around  $650\text{ cm}^{-1}$  was observed. Instead an absorption at  $688\text{ cm}^{-1}$  was assigned to this stretching vibration in the trans form of the ligand. The methylene rocking vibrations at  $1204\text{ cm}^{-1}$  were matched to the vibrations seen in the trans form of the ligand. Spectroscopic evidence points to the following structure for the complex.



There must be some association of these molecules since one molecule of the hydridic complex is associated with a quarter of one THF molecule. It seems likely that zinc will have a coordination number greater than four.

Presumably the reason 1,2 bis(methylthio) ethane does not form a chelate complex is due to the incompatibility of the soft ligand and the hard metal so that the energy needed to overcome the rotational barrier between the trans and gauche conformations of the ligand is not offset by the energy recovered on the formation of a chelate ring.

This is consistent with the fact that no exothermic reaction was noted when  $\text{ZnH}_2$  and  $\text{ZnCl}_2$  were allowed to react in the presence of 1,2 bis(methylthio)ethane while in the presence of TMEDA and DME quite strong exothermic reactions were observed and chelate complexes were obtained.

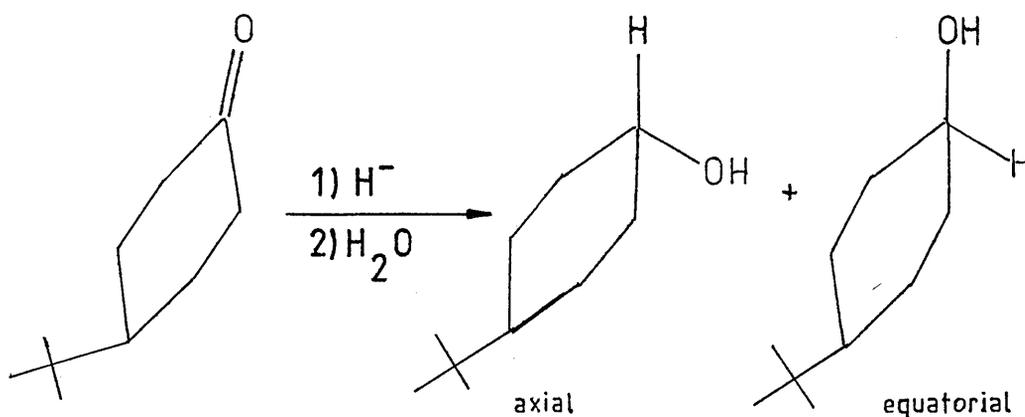
#### 4. The organic chemistry of zinc dihydride and some hydrido zinc complexes

##### 4.1 Introduction

In order to rationalise the behaviour of hydrido zinc complexes with organic substrates, it is necessary first of all to choose such organic molecules as will lead to a clear picture of any trends which may be discovered. Five organic compounds were chosen.

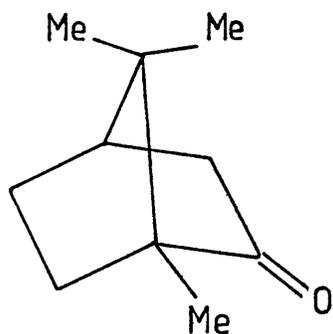
##### 4.1.1 4-t-Butylcyclohexanone

4-t-Butylcyclohexanone was chosen in order to examine the reactivity and stereochemistry of hydrido zinc compounds with carbonyl containing compounds. The reaction of 4-t-butylcyclohexanone with reducing compounds containing hydridic hydrogen atoms, e.g.  $\text{LiAlH}_4$ , gives rise to a mixture of isomeric alcohols on hydrolysis, whose conformation is fixed by the bulky 4-t-butyl group. This group is sterically bulky, but is far away from the reactive carbonyl centre.



##### 4.1.2 Camphor

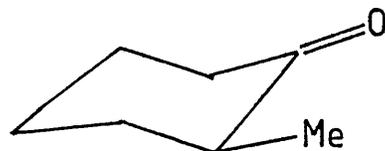
Camphor was chosen for the same reason as 4-t-butylcyclohexanone but whereas 4-t-butylcyclohexanone has a reactive carbonyl centre that is free from steric influence camphor has a highly hindered carbonyl group



The carbonyl group is protected by the bridgehead carbon atom and its methyl groups from attack by nucleophiles. Thus attack on the carbonyl group is strongly directed to the exo side.

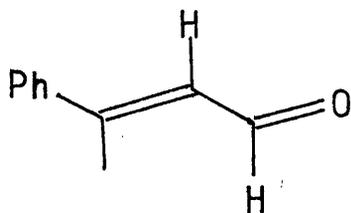
#### 4.1.3 2-methylcyclohexanone

Like 4-*t*-butylcyclohexanone and camphor, 2-methyl-cyclohexanone has a carbonyl group which can be attacked by hydride anion. In this ketone, the  $\beta$ -methyl group, one on the carbon



atom adjacent to the carbonyl group has an inhibiting effect on nucleophiles which have an equatorial approach to the carbonyl group.

#### 4.1.4 Trans-cinnamaldehyde



Trans-cinnamaldehyde was chosen as an example of a compound with two conjugated double bonds, an aldehyde carbonyl and an alkene double bond, and a slightly acidic proton. Possible modes of reaction are:

- i) Total reduction to 3-phenyl propan-1-ol.
- ii) 1,2 addition to the aldehyde to give 3-phenyl prop-2-ene-1-ol.
- iii) 1,2 addition to give 3-phenyl propanal.
- iv) 1,4 addition to give 3-phenyl prop-1-ene-1-ol.

#### 4.1.5 Phenylacetylene

Phenylacetylene was chosen as an example of an asymmetric alkyne ( $\text{PhC}\equiv\text{CH}$ ) with addition of hydride possible at either alkyne carbon atom as well as reaction with the acidic proton to give an initial acetylide which on hydrolysis yields phenylacetylene.

#### 4.2 The reaction of zinc dihydride and several hydrido zinc complexes with 4-t-butylcyclohexanone.

The results of these experiments are summarised in the table 5.

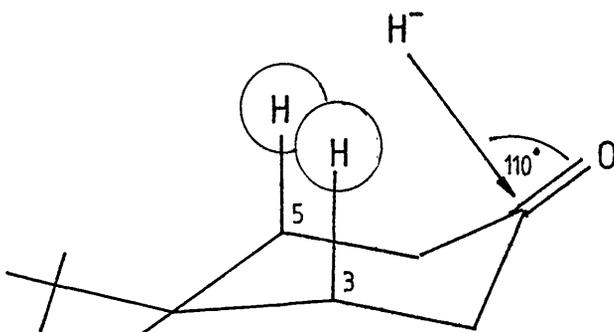
Axial attack occurs as shown in the following diagram with the hydride approaching at an angle of  $110^\circ$ . The axial hydrogen atoms at C3 and C5 will hinder the approach of the incoming hydride atom and as the incoming nucleophile becomes

Table 5

Hydride	Percentage of alcohol obtained on hydrolysis and extraction of reaction mixture	
	axial alcohol	equatorial alcohol
ZnH <sub>2</sub>	35	65
(Me <sub>2</sub> NC <sub>2</sub> H <sub>4</sub> OZnH) <sub>2</sub>	7	93
[ (Et <sub>2</sub> NH) (ZnH <sub>2</sub> ) <sub>3</sub> (TMEDA) <sub>2</sub> ] <sub>n</sub>	38	62
(Me <sub>2</sub> NC <sub>2</sub> H <sub>4</sub> N(Me)ZnH) <sub>2</sub>	19.1	80.9
( <sup>t</sup> BuSZnH.THF) <sub>n</sub>	13.2	86.8
TMEDA.HZnCl*	99	1
LiAlH <sub>4</sub> <sup>+</sup>	9	91

\*This complex zinc hydride only gave 78% yield of alcohols on hydrolysis. All percentages shown have been normalised.

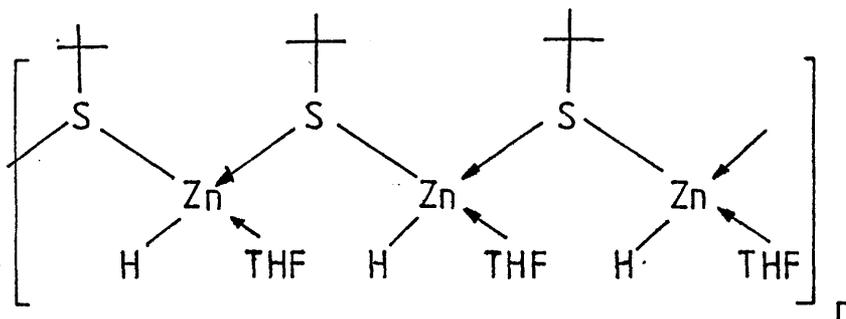
+The data for lithium tetrahydridoaluminate are included for comparison.<sup>13</sup>



larger the amount of axial attack, which yields the equatorial alcohol on hydrolysis would be expected to decrease. This has been observed for LiAlH<sub>4</sub>, (Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>OZnH)<sub>2</sub>, (Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>N(Me)ZnH)<sub>2</sub>, [Et<sub>2</sub>NH(TMEDA)<sub>2</sub>(ZnH<sub>2</sub>)<sub>3</sub>]<sub>n</sub> and ZnH<sub>2</sub>. In these cases, as the hydride becomes more associated or there is a greater steric influence on the Zn-H bond then the amount of axial attack does decrease. Lithium tetrahydridoaluminate shows the typical behaviour expected for a mobile, unassociated H<sup>-</sup>.

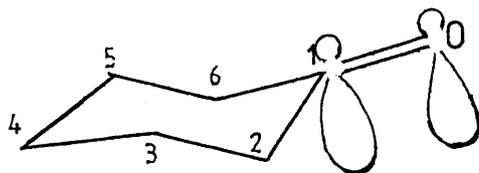
Two of the complex zinc hydrides, (<sup>t</sup>BuSZnH.THF)<sub>n</sub> and

TMEDA.HZnCl did not fall into the pattern shown by the other complex zinc hydrides.  $({}^t\text{BuSZnH}\cdot\text{THF})_n$  is believed to have the following structure with long chains of S-Zn-S-Zn,



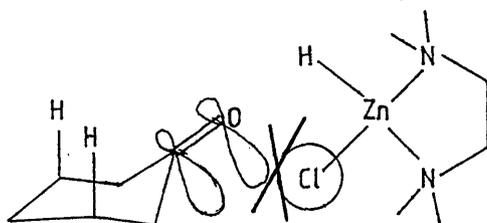
namely a very associated structure. However, its reaction behaviour with 4-*t*-butylcyclohexanone suggests that it behaves more like  $\text{LiAlH}_4$ , i.e. approach to the carbonyl group by  $\text{H}^-$ . This may be because the complex becomes depolymerised rapidly to give  ${}^t\text{BuSZnH}\cdot\text{THF}$  as a first step in the reaction, and the resulting monomer will obviously find it easier to give axial attack. Another possible reason is that the Zn-H bond is relatively weak (and therefore longer) than in the other complex hydrides, therefore the transition state for this reaction is far along the reaction coordinate and therefore the reduction is effectively carried out by  $\text{H}^-$ , thus minimising steric effects.

TMEDA.HZnCl on the other hand would be expected to behave very much like  $\text{LiAlH}_4$  in its reaction with 4-*t*-butylcyclohexanone because of the small size of the molecule and its low degree of association. However, it gave, almost exclusively, the alcohol due to equatorial attack on the carbonyl group. The chlorine atom obviously takes an important part in the reaction, probably by orienting the attacking molecule.

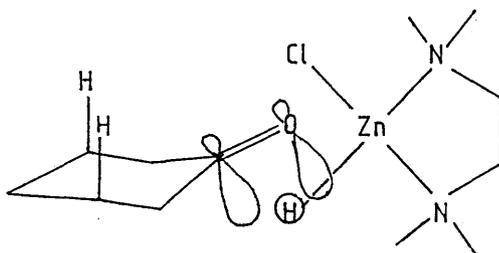


The diagram above shows the effect of the orbital interaction of p orbitals of the carbonyl group and the  $\beta$  carbon-carbon bonds ( $C_2-C_3$  and  $C_5-C_6$ ). This interaction gives rise to an unsymmetrical electron density on the two faces of the carbonyl group <sup>100</sup>. The approach by the TMEDA.HZnCl will be to minimise the interaction of the chlorine with the molecular orbitals (MO's) as shown below.

(A)



(B)



In A there is electronic repulsion between the chlorine atom and the MO while the hydride is still far away. Therefore there is little likelihood of the reaction taking place. In B, because of the small size of the hydridic hydrogen atom, it can approach the carbon atom much more closely and therefore the likelihood of the reaction taking place is much greater.

Another factor which makes axial attack less likely is the steric repulsion of the axial protons on the C<sub>3</sub> and C<sub>5</sub> atoms especially if the complex zinc hydride forms a compact transition state with the ketone.

4.3 The reaction of zinc dihydride and several hydrido-zinc complexes with camphor.

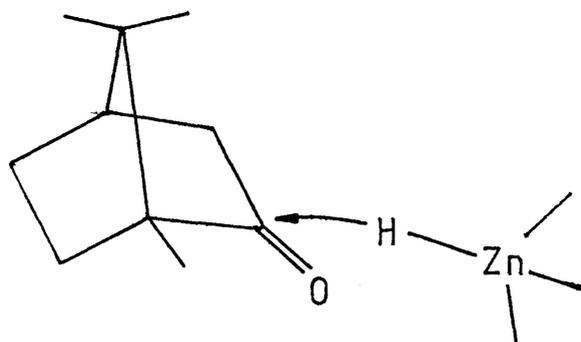
All of the complex zinc hydrides reacted with camphor and gave 75 - 99% yields of isomeric alcohols after hydrolysis, except for TMEDA.HZnCl which gave just 1% yield of isomeric alcohols. The following table gives the results of the experiments.

Table 6

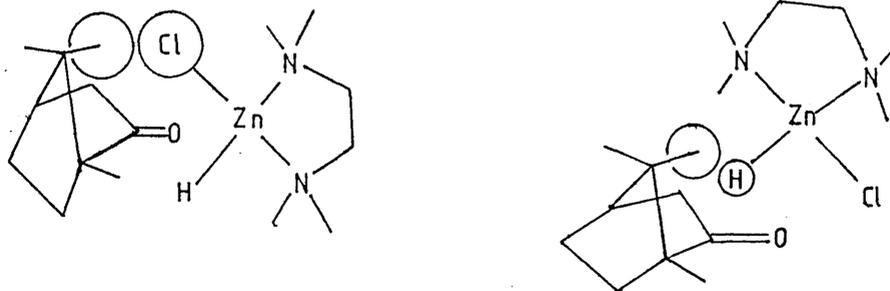
Hydride	Percentage of alcohols obtained after hydrolysis of reaction mixture	
	exo	endo
ZnH <sub>2</sub>	92	8
(Me <sub>2</sub> NC <sub>2</sub> H <sub>4</sub> OZnH) <sub>2</sub>	90	10
(Et <sub>2</sub> NH(ZnH <sub>2</sub> ) <sub>3</sub> (TMEDA) <sub>2</sub> ) <sub>n</sub>	74.9	25.1
(Me <sub>2</sub> NC <sub>2</sub> H <sub>4</sub> N(Me)ZnH) <sub>2</sub>	63.2	36.8
( <sup>t</sup> BuSZnH.THF) <sub>n</sub>	90.3	9.7
TMEDA.HZnCl	34	66
LiAlH <sub>4</sub> <sup>a</sup>	91	9

<sup>a</sup>The data for lithium tetrahydridoaluminate have been included for comparison.<sup>13</sup>

In every case but one the major product is the exo alcohol, formed by approach by the hydride from the least hindered side of the ketone.

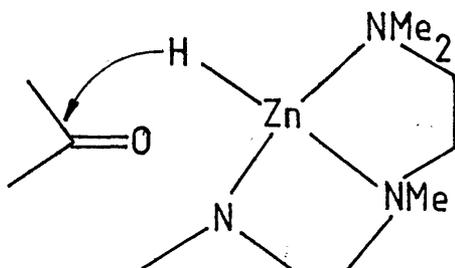


In the case of TMEDA.HZnCl, the hydride attacks from the hindered side of the ketone. Clearly, a different mechanism must operate in this reaction, since both highly associated hydrides e.g.  $\text{ZnH}_2$ , and hydrides which do not show any association, e.g.  $\text{LiAlH}_4$ , give the same type of product distribution, i.e. approach by the hydride from the least hindered side of the ketone. Unlike the corresponding reaction of TMEDA.HZnCl with 4-t-butylcyclohexanone which is governed by electronic repulsion between the chlorine atom and the excess electron density on one face of the carbonyl group (p 188), the dominant force here must be the steric repulsion of the bridge-head methyl groups and the chlorine atom. This is illustrated in diagram



The chlorine atom, having a much larger van der Waals radius than the hydridic hydrogen, will orientate itself in such a way as to be furthest away from the bridghead carbon atoms. This means that the hydride approaches from above the plane of the carbonyl group, thus giving rise to the endo alcohol as the major product. However this product is kinetically unfavourable, and so over the reaction period, only 1% of the ketone had been reduced to the alcohol.

Another complex zinc hydride, which gives a significant yield of the endo alcohol is trimethylethylenediaminozinc hydride. This is known to be dimeric in solution.<sup>43</sup> A similar sort of transition state can be envisaged as for TMEDA.HZnCl above



Since there is less steric hindrance by the nitrogen atom the favoured product is the exo-alcohol. The hydride,  $(\text{Me}_2\text{NC}_2\text{H}_4\text{OZnH})_2$ , might be expected to have shown reducing behaviour similar to that of  $(\text{TriMEDZnH})_2$  since both complexes have very similar structures. Clearly the strength of the zinc-hydridic hydrogen bond is an important factor here.

The more reactive hydride would be expected to show more sensitivity to the steric influence of the carbonyl compound, while the less reactive hydride would be expected to show more sensitivity to its own steric influence.

All of the other complex zinc hydrides, and zinc dihydride gave the exo-alcohol as the major product thus the steric effects of the bridgehead carbon atoms in the camphor molecule proved to be the dominating feature of these reductions.

4.4 The reaction of zinc dihydride and several hydrido zinc complexes with 2-methylcyclohexanone

The results of this experiment are shown in the table below.

Table 7

Hydride	Percentage yield (normalised) of alcohol obtained after hydrolysis of the reaction mixture	
	cis	trans
ZnH <sub>2</sub>	52	48
[Et <sub>2</sub> NH.(ZnH <sub>2</sub> ) <sub>3</sub> (TMEDA) <sub>2</sub> ] <sub>n</sub>	50	50
(Me <sub>2</sub> NC <sub>2</sub> H <sub>4</sub> OZnH) <sub>2</sub>	39.5	60.5
LiAlH <sub>4</sub> <sup>12</sup>	24	76

In this ketone, the 2-methyl group has an inhibiting effect on equatorial approach to the carbonyl group by nucleophiles.

The hydride [Et<sub>2</sub>NH.(ZnH<sub>2</sub>)<sub>3</sub>(TMEDA)<sub>2</sub>]<sub>n</sub>, showed reducing behaviour with this ketone which was similar to that of zinc dihydride itself. This might be expected since both hydrides are polymeric in nature and the reactive centre is similar in each. Similar results were seen in the reduction of 4-t-butyl-cyclohexanone by this complex zinc hydride (p. 186).

The hydride, (Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>OZnH)<sub>2</sub> shows behaviour similar to

that of  $\text{LiAlH}_4$  in its reduction of 2-methylcyclohexanone. Because of the smaller size of the hydridic reducing agent, the approach to the carbonyl is governed by the steric effect of the hydride and since the equatorial approach is preferred slightly, then trans-2-methylcyclohexanol will be the major product. This is indeed found, though  $(\text{Me}_2\text{NC}_2\text{H}_4\text{OZnH})_2$  gives more of the cis alcohol than does  $\text{LiAlH}_4$ , since the complex zinc hydride has a larger steric bulk than  $\text{LiAlH}_4$ .

#### 4.5 The reaction of complex zinc hydrides with trans-cinnamaldehyde

The table on page 194 summarizes the complex zinc hydrides which were investigated and the results which were obtained.

As was mentioned at the beginning of the chapter, trans-cinnamaldehyde was chosen because there are several different modes of addition of hydride to this molecule. The reaction mechanisms for these reductions are shown below with  $\text{AA}'\text{ZnH}$  representing the complex zinc hydride.

##### 1,2 addition to carbonyl

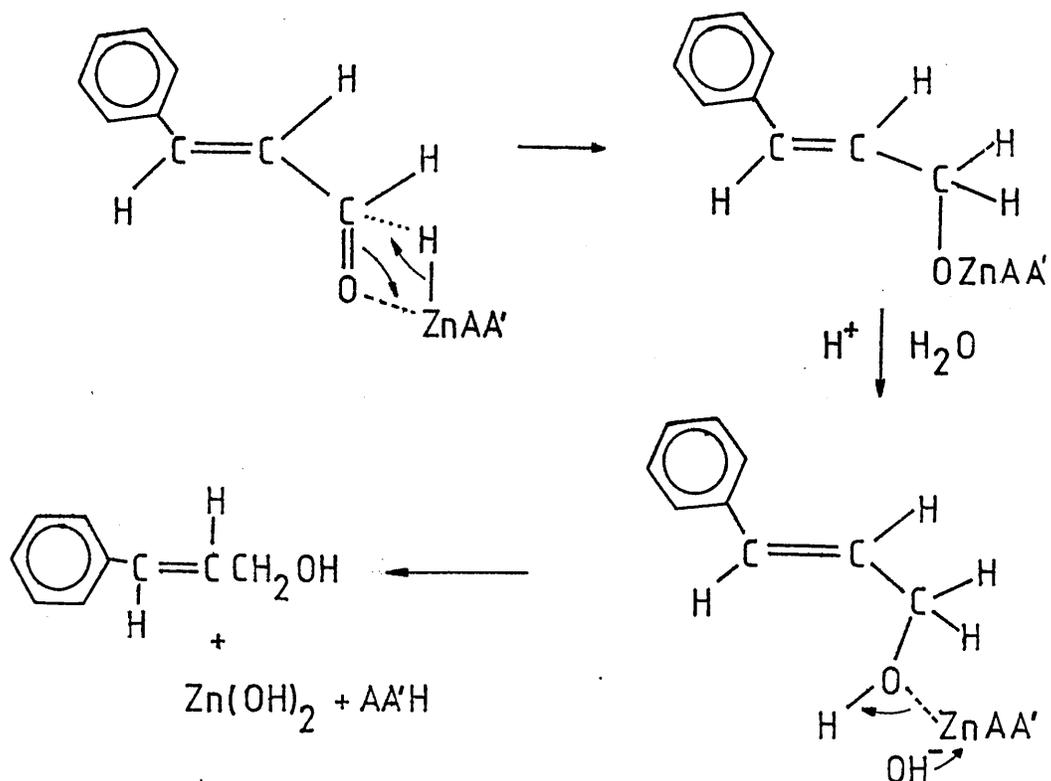
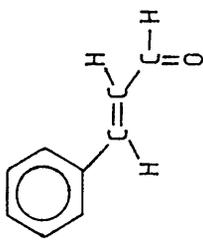
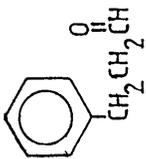
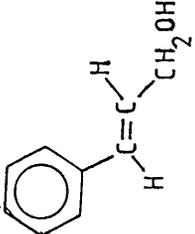
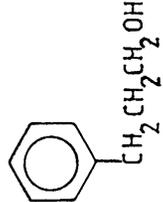


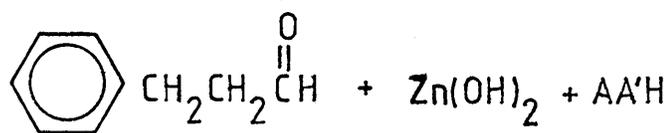
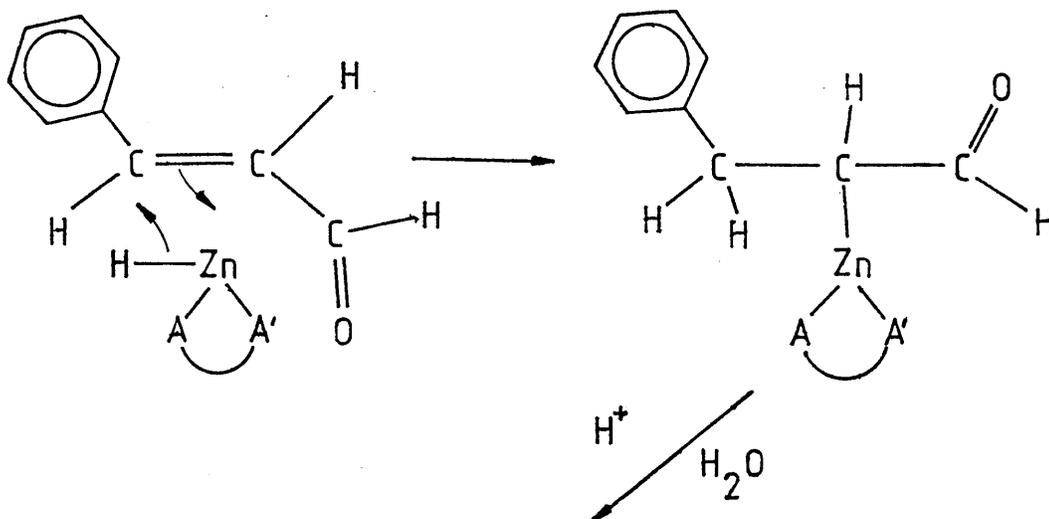
Table 8.

					Unidentified product
$(\text{Me}_2\text{NC}_2\text{H}_4\text{OZnH})_2$	36.2	-	63.8	-	
$(\text{Et}_2\text{NH}(\text{TMEDA})_2(\text{ZnH})_2)_3^n$	55.7	-	21.7	23.1	
$(\text{CH}_3)_3\text{CSZnH}\cdot\text{THF}^n$	20	-	60	20	
$(\text{MeOC}_6\text{H}_4\text{S})_2\text{ZnH}^n$	30	-	30	30	10
$(\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{Me})\text{ZnH})_2$	-	trace	75.3	-	24
TMEDA.HZnCl	44	-	38.9	-	17

<sup>a</sup>The numbers in this table refer to the percentage of product obtained or starting material recovered.

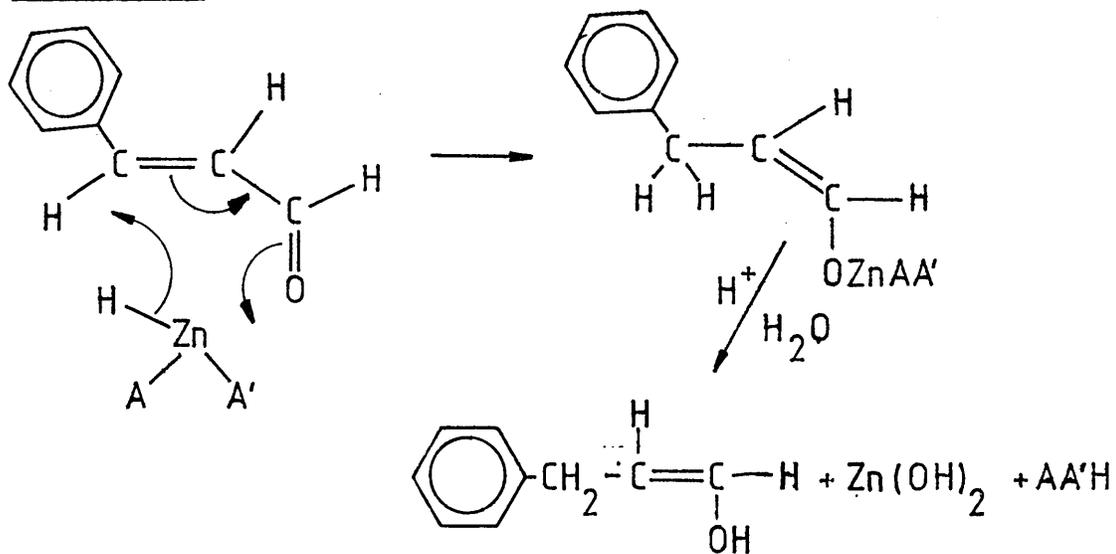
Scheme 1

3,4 addition to alkene

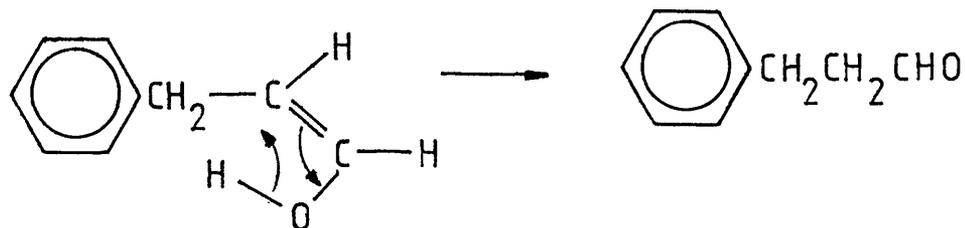


Scheme 2

1,4 addition



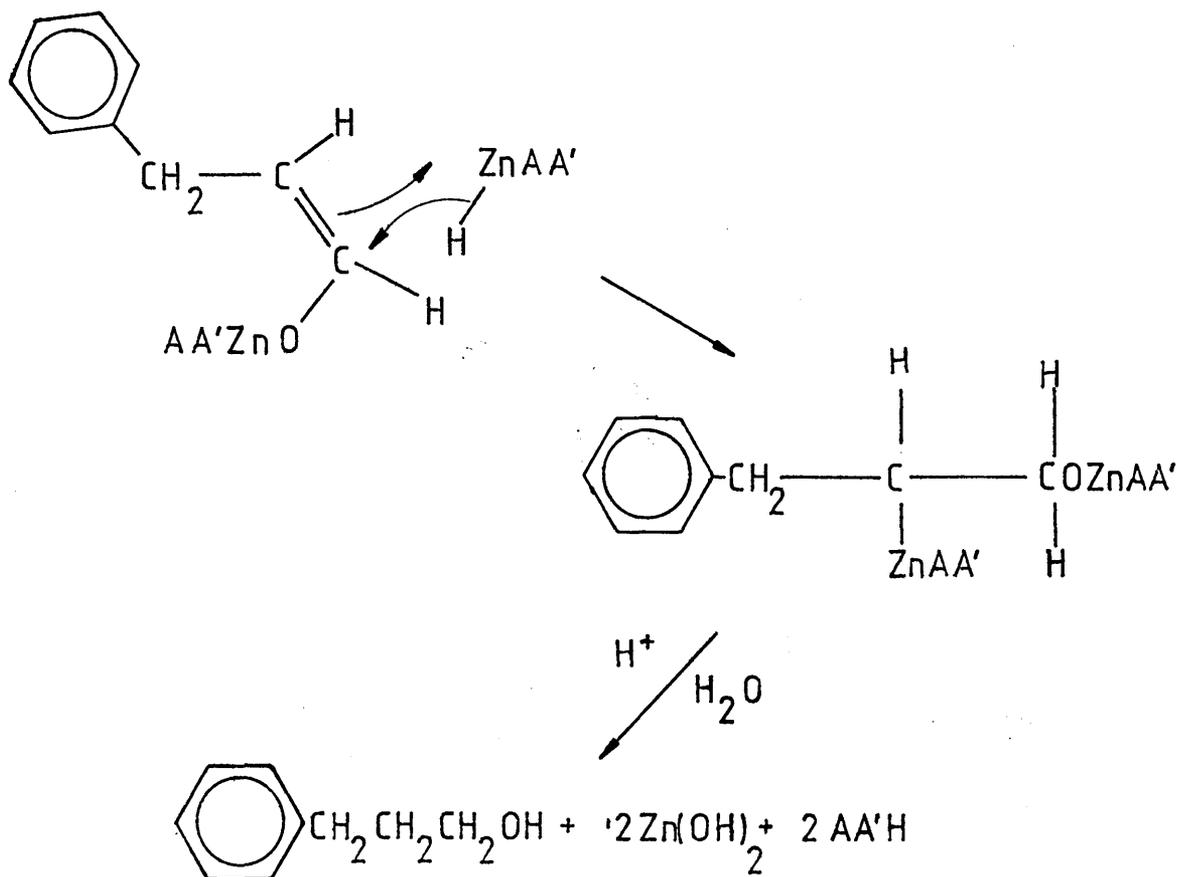
The vinyl alcohol obtained might be expected to rearrange to give the corresponding aldehyde



It is clear from Table 8, that the preferred mode of reduction of trans-cinnamaldehyde by the complex zinc hydrides is by 1,2 addition of the hydride to the carbonyl group of the ketone:  $[(Et_2NH(TMEDA)_2(ZnH_2)_3)_n]$  and  $[(MeOC_6H_4S)_2ZnH]_n$  however gave low yields of this 1,2 addition product.

No products from 1,2 addition to alkene were observed for any of the complex zinc hydrides except for a trace amount produced during the reduction of trans-cinnamaldehyde by  $(Me_2NC_2H_4N(Me)ZnH)_2$ . The reason for this is that 1,2-addition is likely to be a concerted process and thus the alkene bond will have to line up alongside the zinc-hydridic hydrogen bond. This means that steric crowding around the carbon-carbon double bond will hinder addition to that bond. The phenyl group in trans-cinnamaldehyde does just that and no 1,2 addition product (due to addition to alkene) is seen.

Several complex zinc hydrides  $((Et_2NH(TMEDA)_2(ZnH_2)_3)_n$ ,  $((CH_3)_3CSZnH.THF)_n$  and  $((MeOC_6H_4S)_2ZnH)_n$  produce some 1-phenylpropan-3-ol in the reduction of trans-cinnamaldehyde. Since no 1,2 addition to alkene was observed it is unlikely that 1-phenylpropan-3-ol is obtained by the reduction of the carbonyl group followed by addition to alkene. It is more likely that it is obtained as a result of 1,4 addition of the hydride to trans-cinnamaldehyde. The reaction mechanism probably proceeds as shown in scheme 2 on p. 195 and then the reaction continues as shown below.



The vinyl carbon-carbon double bond is polarised by the presence of the  $\text{OZnAA}'$  group which makes it attractive to attack by more of the complex zinc hydride. It is no coincidence that those complex zinc hydrides which give the highest yields of 1-phenylpropan-3-ol are those from which the highest percentage of unreacted 1-phenylprop-1-en-3-al (cinnamaldehyde) was recovered.

#### 4.6 The reaction of complex zinc hydrides with phenylacetylene

The results of reactions of various complex zinc hydrides with phenylacetylene are given in the table on p. 198

The reaction mixture was quenched with  $\text{D}_2\text{O}$  to reveal at

Table 9.

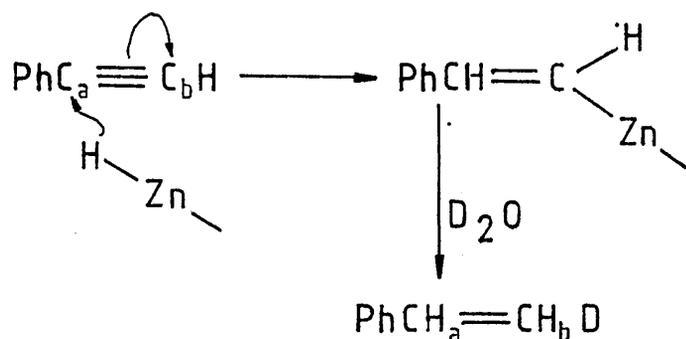
	PhCH=CH <sub>2</sub>	PhCH <sub>2</sub> CH <sub>3</sub>	PhCHR <sup>b</sup> CH <sub>3</sub>	PhCH <sub>2</sub> CH <sub>2</sub> R <sup>b</sup>	PhC≡CH
(Me <sub>2</sub> NC <sub>2</sub> H <sub>4</sub> OZnH) <sub>2</sub> /THF	-	50 <sup>a</sup>	-	-	50
(Me <sub>2</sub> NC <sub>2</sub> H <sub>4</sub> OZnH) <sub>2</sub> /C <sub>6</sub> H <sub>6</sub>	-	62	-	-	38
((CH <sub>3</sub> ) <sub>3</sub> CSZnH.THF) <sub>n</sub>	-	<1	-	99	-
((MeOC <sub>6</sub> H <sub>4</sub> S) <sub>2</sub> ZnH) <sub>n</sub>	11	-	69.2	19.6	-
(Me <sub>2</sub> NC <sub>2</sub> H <sub>4</sub> N(Me)ZnH) <sub>2</sub>	80	10	-	-	10
TMEDA.HZnCl	-	55	-	-	45

<sup>a</sup> The numbers in this table refer to the percentage of product obtained or starting material recovered

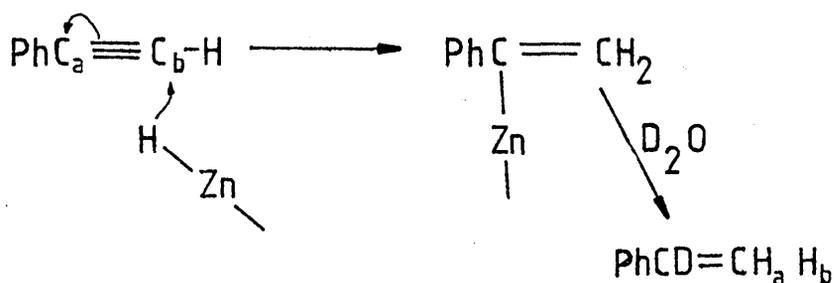
<sup>b</sup> R refers to a sulphur containing moiety

which carbon atom of the alkyne the hydride attacks, e.g.

Attack at  $C_a$

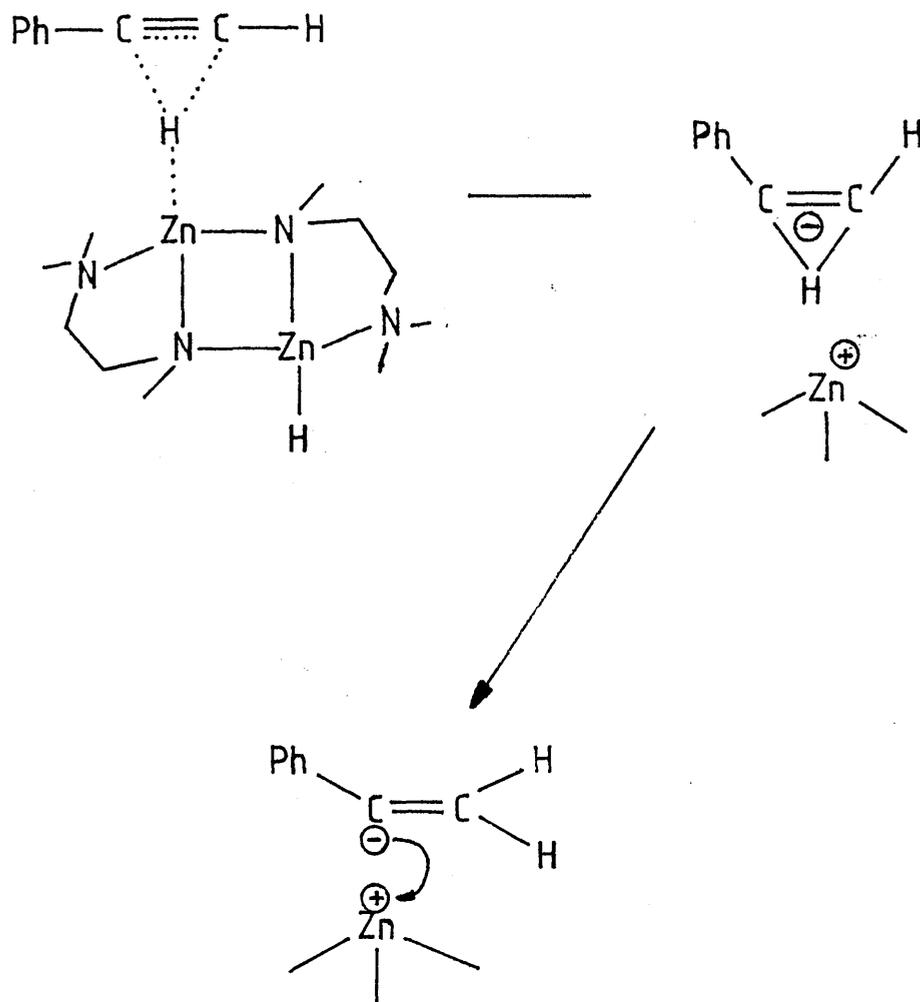


Attack at  $C_b$



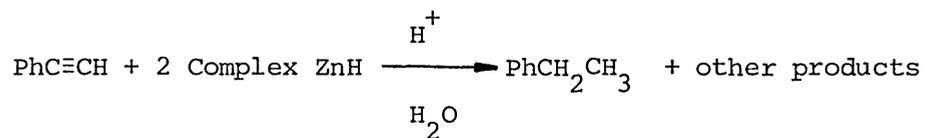
Thus by using  $^1\text{H}$  NMR spectroscopy it is possible to distinguish between  $\text{H}_a$  and  $\text{H}_b$  by their coupling constants and chemical shifts.

The results in Table 9 on p.198 show some surprises. Only  $(\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{Me})\text{ZnH})_2$  reduced phenylacetylene to styrene in significant yield. Also attack on  $C_a$  and  $C_b$  were equally favoured with 40% of  $\text{PhCD}=\text{CH}_2$  and 40% of  $\text{PhCH}=\text{CHD}$  being obtained from the reaction mixture. This would suggest that the reaction proceeds by initial attack of hydride followed later by attack by the zinc cation, after the carbanion had been formed:

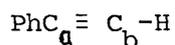


In all of the other cases investigated the major products were ethylbenzenes or substituted ethylbenzenes.

Both  $(\text{Me}_2\text{NC}_2\text{H}_4\text{OZnH})_2$  and  $\text{TMEDA}\cdot\text{HZnCl}$  gave ethyl benzene in 40 - 50% yield with 40 - 50% phenylacetylene being recovered at the end of the reaction. This is not surprising since the stoichiometry for the reaction is

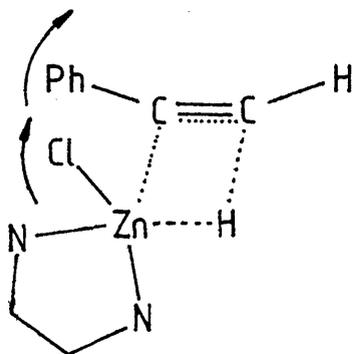


Since the reaction was carried out using 1:1 molar ratio of reactants it is expected to find 50% unreacted phenyl acetylene. However, the direction of addition of hydride to acetylene was different in each case, and further, in the case of  $(\text{Me}_2\text{NC}_2\text{H}_4\text{OZnH})_2$  the direction of addition was found to be dependent on the solvent in which the reaction was carried out. For  $(\text{Me}_2\text{NC}_2\text{H}_4\text{OZnH})_2$ , when the reaction was carried out in tetrahydrofuran, addition of the hydride took place at the carbon closest to the phenyl ring  $\text{C}_a$  while in benzene the addition took place at the carbon furthest away from the phenyl ring i.e. at  $\text{C}_b$



Clearly, in THF, the solvent must stabilise the 3-coordinate zinc cation after loss of hydride - allowing the most stable, primary carbanion to develop. In benzene, this solvent stabilisation is not possible, thus addition of hydride proceeds to the sterically favourable carbon atom i.e.  $\text{C}_b$ .

TMEDA.HZnCl in THF gives a reaction product like that of  $(\text{TriMED.ZnH})_2$  in benzene, there the chlorine atom has the major effect on the course of reaction



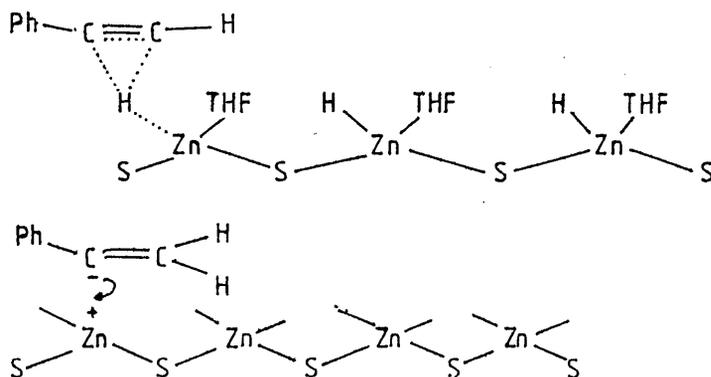
As the complex zinc hydride approaches the acetylene so the chlorine and the phenyl ring repel each other. This means that the phenyl ring moves trans <sup>101</sup> to the incoming hydride so

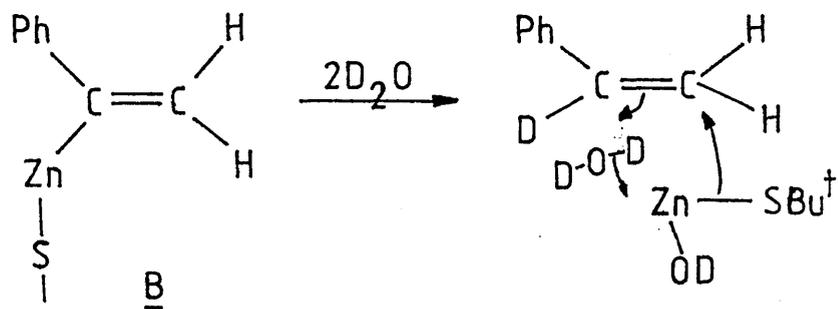
that the lowest unoccupied molecular orbital of the alkyne gives maximum overlap with the  $1s^2$  atomic orbital of the hydridic hydrogen .

It might, of course, be expected that the electronegative chlorine atom would try to orientate itself furthest from the phenyl ring and this leads to hydride addition at  $C_a$ , but there is in fact no evidence for this at all.

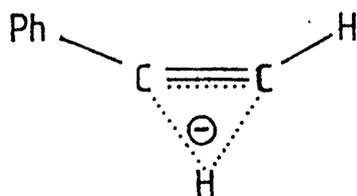
The main point of interest in the reactions of  $(CH_3)_3CSZnH \cdot THF$  and  $(MeOC_6H_4S)_2ZnH$  with phenyl acetylene is that both the hydride and a sulphur moiety add to the alkyne. The reaction of phenyl acetylene with  $(CH_3)_3CSZnH \cdot THF$  can be rationalised as a reaction taking place at a surface. See scheme below.

As the phenyl acetylene molecule approaches the surface of the hydride it will approach with the acidic proton first . because of the steric effect of the phenyl group, so addition will take place at the end carbon atom . Then a transition state is formed with the carbanion being stabilised by the zinc cation. The transition state then breaks leading to the formation of an organozinc intermediate B which undergoes intramolecular rearrangement through the formation of a six membered transition state to give the products .

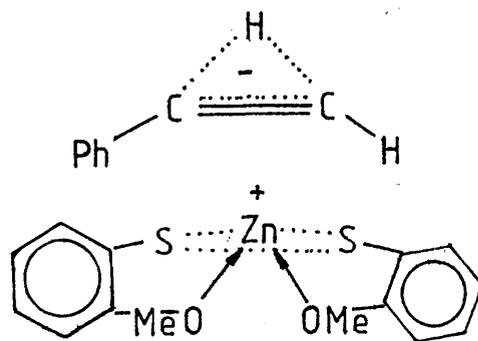




The reaction of  $(\text{MeOC}_6\text{H}_4\text{S})_2\text{ZnH}$  with phenyl acetylene is believed to proceed not as a surface reaction since this hydride is not polymeric, but as attack by  $\text{H}^-$  first to give the following type of transition state.

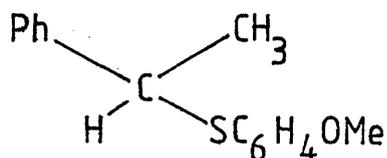


The approach of the metal is determined by the stereochemistry of the cationic group, and since this is a large group, approach will be to the favourable carbon furthest from the phenyl group.



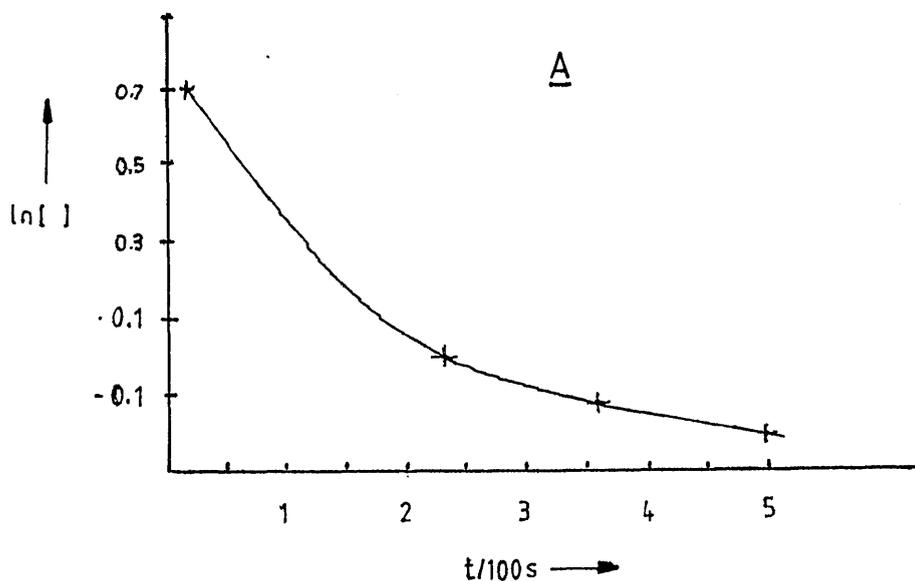
Since considerable doubt remains as to the actual structure of this sulphur-containing complex zinc hydride the mechanism of the addition of the sulphur moiety must be speculative.

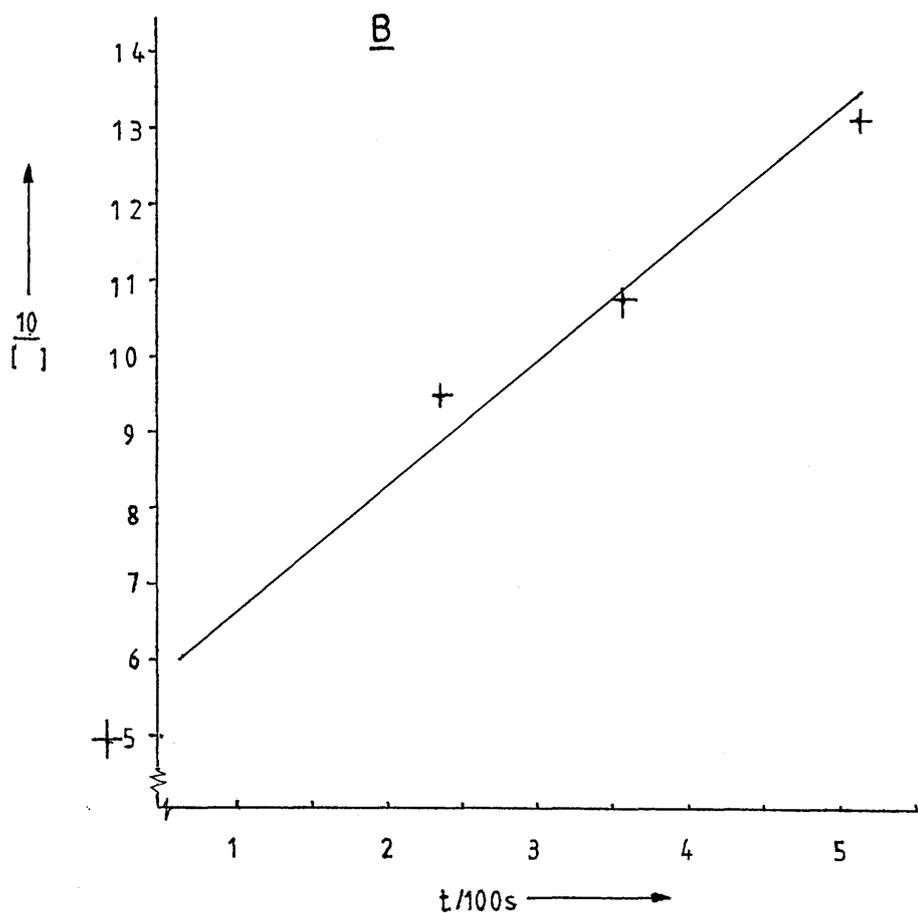
$^1\text{H}$  nmr spectroscopy does however show that the addition product has a stoichiometry of  $\text{PhCH}(\text{SC}_6\text{H}_4\text{OMe})\text{CH}_3$ , so the sulphur-containing zinc cation must undergo rearrangement on addition of water to give the product



4.7 The kinetics of addition of a complex zinc hydride to trans-pent-2-ene at 20°C

An experiment to examine the kinetics of addition of  $(\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{Me})\text{ZnH})_2$  to trans pent-2-ene was carried out using  $^1\text{H}$  nmr spectroscopy to monitor the decrease in concentration of the alkene proton resonances. Both 1st order (graph A) and 2nd order (graph B) plots (using the concentration of alkene against time) were inspected in order to establish the order of the reaction.

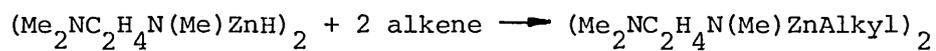




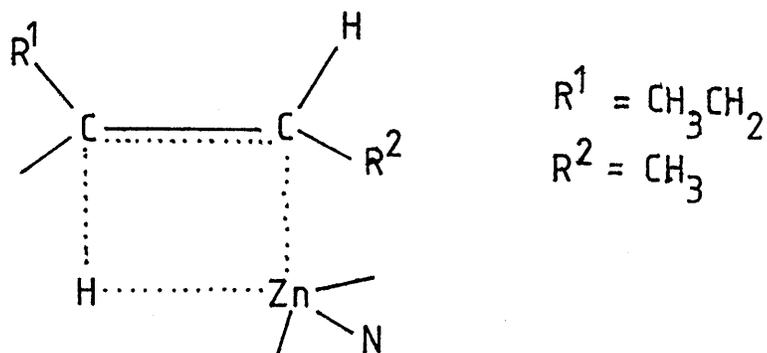
A straight line was obtained for the second order plot. This shows that the rate of reaction is proportional to the square of the concentration of alkene

i.e.  $k \propto [\text{alkene}]^2$

This is to be expected if one considers the stoichiometry of reaction.



This also suggests that the transition state is as expected,  
a simple 4-membered ring



Under the same conditions, the addition of  $(\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{Me})\text{ZnH})_2$   
to 1-decene was too rapid to measure.

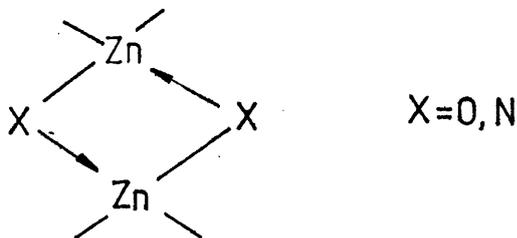
## 5. The chemistry of complex zinc hydrides

### 5.1 Structural Features

Aspects of the complex zinc hydrides studied in this thesis have been summarised below.

The following structural features appear to be general. Zinc tends to be 4 coordinate with a tetrahedral environment, wherever possible. Preferred degrees of association are 1, 2 and  $\infty$  ( $n = \text{large}$ ). Complex zinc hydrides have terminal zinc-hydridic hydrogen bonds with the infrared stretching vibration frequency in the range  $1800 - 1500 \text{ cm}^{-1}$ . Let us examine some of these structural features in greater detail.

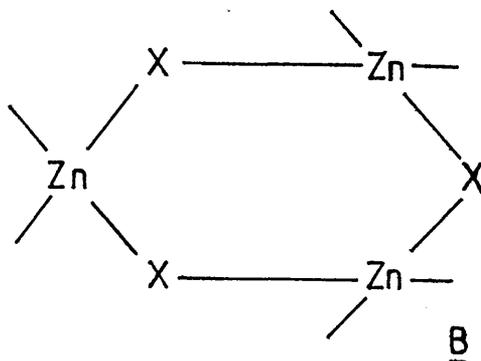
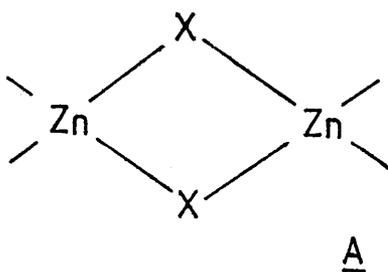
With bidentate ligands such as  $\text{Me}_2\text{NC}_2\text{H}_4\text{N}(\text{Me})\text{H}$ ,  $\text{Me}_2\text{NC}_2\text{H}_4\text{OH}$ ,  $\text{Me}_2\text{NC}_6\text{H}_4\text{OH}$  the basic structural unit of the complex molecule is a four membered ring containing alternate zinc and electronegative atoms.



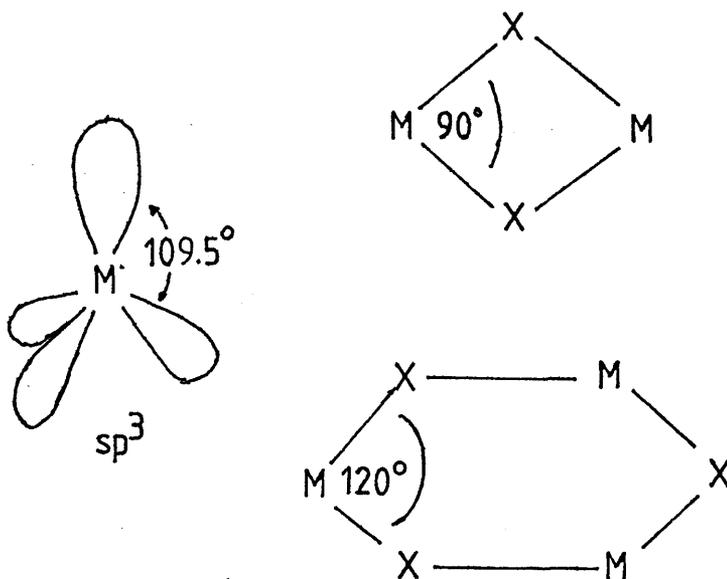
Evidence for larger rings has not been found even where it might have been expected on theoretical grounds, e.g.

$(\text{Me}_2\text{NC}_2\text{H}_4\text{OZnH})_2$  p. 121 The four membered  $\text{Zn}_2\text{X}_2$  type ring appears in a large number of complex zinc hydrides.

On the grounds of entropy the fewer the number of atoms in a particular arrangement the more stable will be the system. e.g.



In the diagram above, system A will have higher entropy than system B therefore system A will be favoured, if the hybridised orbitals involved in bonding are considered. Where zinc has a tetrahedral electronic environment, the atomic orbitals from which the coordinate bonds are formed during association will be  $sp^3$  hybridised.



In the cases where the four membered  $Zn_2X_2$  ring has been shown to exist in crystal structures of  $(Me_2NC_2H_4N(Me)ZnH)_2$ <sup>43</sup>

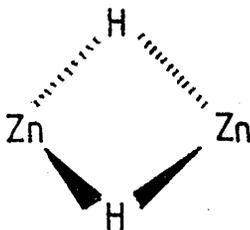
and  $(\text{Ph}_2\text{NZnMe})_2$ <sup>102</sup> the internal (ligand-atom-metal-ligand atom) angle is  $90^\circ$ . This represents a large departure from the tetrahedral angle of  $109^\circ$ . That this amount of valency angle strain is tolerated in these complex zinc hydrides is surprising but it may be that the increase in energy due to increased electrostatic repulsion is offset by the achievement of coordination saturation of the zinc atom. If this metal-ligand atom angle of  $90^\circ$  can be tolerated it is rather surprising to find the only evidence for a tetrameric species with the cubane type structure reported for  $(\text{MeZnOMe})_4$  is observed for  $(\text{MeOC}_2\text{H}_4\text{OZnH})_n$   $n = 2, 4$ .

Clearly the cubane type structure is not tolerated on a) the grounds of decreased entropy in the system and b) the fact that many more of the internal angles are  $90^\circ$  leading to a much larger degree of electrostatic repulsion.

In theory the six membered  $\text{Zn}_3\text{X}_3$  ring should be favoured on the grounds of relatively little valence angle strain. In practice there is no evidence for this arrangement at all. This may be due to the size of the internal angle of  $120^\circ$  which is significantly greater than the ideal tetrahedral angle and thus the remaining hybrid orbitals on the metal will be more constrained than in the case of the  $\text{Zn}_2\text{X}_2$  (Angle =  $90^\circ$ ) ring leading to increased electrostatic repulsion without the benefit of coordinative saturation.

Coordination polymers are common in the structural features of complex zinc hydrides. In cases where intramolecular bidentate coordination is not possible, e.g.  $(3-\text{Me}_2\text{NC}_6\text{H}_4\text{OZnH})_n$  (p. 126) or where there is no possibility of bidentate coordination e.g.  $(\text{Et}_2\text{NHZnH}_2)_n$  p. 143 or  $((\text{CH}_3)_3\text{CSZnH}\cdot\text{THF})_n$ . In these two cases also we can consider the effect of the solvent filling a vacant coordinate site. It is believed that in the diethylamine complex the hydride ligand acts as a bridging ligand, thus completing the fourth

coordination site on the zinc atom, while in the t-butylthiozinc hydride, THF complex, THF is a strong enough electron donor to fill the vacant coordination site and thus the hydride ligand does not have to act as a bridging ligand. The following type of structure has been observed in anionic metal hydride

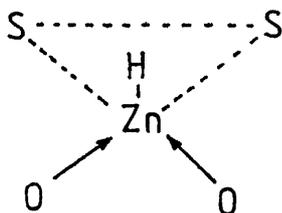


chemistry<sup>57</sup> but has not been observed in the complex zinc hydrides studied here. There is however some evidence to suggest that it may be present in  $(\text{Me}_2\text{CCH}_2\text{CH}=\text{NHZnH})_2$  and in  $(\text{Ph}_2\text{CH}_2\text{OZnH}\cdot\text{THF})$  as an absorption in the infrared spectrum of this complex at  $1060\text{ cm}^{-1}$  was assigned to a  $\text{Zn}\dots\text{H}\dots\text{Zn}$  vibration. Similarly in  $\text{Ph}_2\text{CH}_2\text{OZnH}\cdot\text{THF}$  an I.R. absorption at  $1040\text{ cm}^{-1}$  was assigned to a  $\text{Zn-H-Zn}$  vibration.

Some of the complex zinc hydrides, notably the chlorozinc hydrides  $\text{TMEDAHZnCl}$ ,  $\text{DMEHZnCl}$ ,  $\text{DTH}\cdot\text{HZnCl}$  (p. 177) appeared to be monomeric on the basis of infrared spectroscopic evidence. It seems that bidentate ligands are strong enough electron donors to maintain 4 coordination around the zinc. Any bridging by either hydride or chloride would mean an increase in the coordination number of zinc and this is not energetically favourable.

Two other features of the complex zinc hydrides must be mentioned. One is that coordination number of five for zinc is seen in some hydrides. In particular, in  $(\text{TMEDAZnH}_2)_2^-$   $\text{Et}_2\text{NHZnH}_2$  both four and five coordinate zinc is observed. Although this seems unusual.

... it is known for other zinc complexes.<sup>72</sup> Why it should occur for this complex is unclear. Another feature of complex zinc hydrides is that some of the ligands undergo coupling in the presence of zinc hydride to give  $L_2ZnH$  type complex zinc hydrides. In both these cases the zinc atom is believed to have a coordination number which is not four. In the case of camphor, the coupled ligand is so bulky that the zinc has a coordination number of three (p. 170). In the case of 2-methylbenzenethiol it has been postulated that a 3 centre, 2 electron bond is formed thus:



Here the zinc appears to have a coordination number of 5. Since the structure of this particular complex is uncertain as yet, this must be looked upon as being speculative.

## 5.2 Factors affecting the preparation of complex zinc hydrides

Zinc dihydride was found to react more rapidly with hydroxy protons which are considerably more acidic than with amine protons. Products of the type  $(ROZnH)_x$  were much more difficult to obtain than the corresponding  $(RNR'ZnH)_x$ , e.g.  $(MeOC_2H_4OZnH)_n$ , 2,4,6- $t$ Bu $_3$ C $_6$ H $_2$ OZnH, as compared to  $(Me_2NC_2H_4N(Me)ZnH)_2$  or  $(Et_2NH.ZnH_2)_n$ . Methoxy groups were found to be much weaker coordinating groups e.g.  $(MeOC_2H_4OZnH)_n$  as compared to  $(Me_2NC_2H_4OZnH)_2$ . The reason is because the hydroxy group proton is more acidic and therefore reacts faster with zinc dihydride and it also reacts with the complex zinc hydride already formed giving the bis alkoxy zinc or bis aroxy zinc complexes, which may or may not react with zinc dihydride.

Most of the alkoxy or aroxyzinc hydrides were found to be insoluble e.g. the complex product obtained from the reaction of 8-hydroxyquinoline and zinc dihydride, p.137, 2-methoxyphenoxy zinc hydride. It seems that the reactions of zinc dihydride with ligands containing acidic protons are governed by the following factors.

a) The acid strength of the acidic proton

If the acidic proton is relatively strongly acidic then the reaction with zinc dihydride is very rapid, not stopping at the intermediate complex zinc hydride stage but going on to react with both hydride hydrogen atoms. e.g. bis(methoxyethoxy) zinc, bis(oxyquinolate)zinc tetrahydrofuranate. There is other evidence to suggest that the intermediate hydrides are themselves, much more reactive than zinc dihydride since in the reactions of zinc dihydride with ketones, little amounts of oxyzinc hydrides were obtained and the major products were bis oxy zinc species with the exception of zinc dihydride and camphor. However, camphor is unusual since it is a highly hindered ketone so steric factors must play a part in the reaction.

Conversely where the proton had virtually no acidic character then the reaction did not take place at all, e.g. the reaction of zinc dihydride with secondary amines with the exception of diethylamine. With diethylamine the reaction did not involve elimination of hydrogen however. Diethylamine was a strong enough donor to depolymerise the polymeric zinc dihydride - the first known coordination complex of zinc dihydride.

b) The donor strength of the conjugate base

In the case of diphenylphosphine a very rapid reaction

was observed even though the phosphine proton shows little acidic character. The driving force for the reaction is the donor strength of the phosphorus.

c) The donor strength of any other electronegative atoms present

To some extent the degree of association of the complex zinc hydrides seems to depend on this factor and also whether chelate rings are formed.

In the case of TMEDA.HZnCl and (DTH)<sub>3</sub>HZnCl, 0.25 THF the nitrogen in TMEDA is the stronger donor and so the complex has a five membered chelate ring, while the sulphur atoms in dithiahexane are not as powerful donor atoms; no chelate ring is formed. The dithiahexane ligands 'dangle'.

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- 2 Inorganic reaction mechanisms-The University Sheffield.
- 3 Metals in organic synthesis The University Sheffield.
- 4 Inorganic research colloquia-The University Sheffield.
- 5 Chemical Society lectures,The University,Sheffield.
- 6 Departmental research colloquia-Sheffield City Polytechnic.

#### BOOKS

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