

ORGANOZINC COORDINATION CHEMISTRY AND CATALYTIC EFFECTS OF ORGANOZINC COORDINATION COMPOUNDS

G. J. M. VAN DER KERK

*Institute for Organic Chemistry TNO and Organic Chemistry Laboratory
of the State University, Utrecht, The Netherlands*

ABSTRACT

A review of the present state of organozinc coordination chemistry, with special emphasis on compounds of the type $RZnX$ is given. Their preparation as well as some factors determining their structure and stability are discussed. Certain organozinc coordination compounds have been found to be effective catalysts for cyclo-oligomerization and polymerization reactions, in particular of oxygen-containing monomers (isocyanates, aldehydes, lactones and epoxides). The present views on the mechanisms of these reactions are given.

INTRODUCTION

Organozinc chemistry is an old subject: it started around 1850 and contributed much to the early development of organometallic chemistry as a whole. Organozinc compounds, in particular the zinc dialkyls, for some decades found extensive laboratory use as alkylating agents, until their replacement around 1900 by the organomagnesium compounds. After having been somewhat dormant for about sixty years—one notable exception being the continuing and even extending use of the Reformatsky reaction—organozinc chemistry towards 1960 entered into its second stage. Partly this was caused by the general renaissance of organometallic chemistry as a whole in the early fifties, but it also was due to the discovery by Simmons and Smith in 1958¹ of the extremely useful zinc-containing organometallic reagent for the generation of carbene.

Our own interest in organozinc chemistry reaches back to 1962 when we were invited by the International Lead Zinc Research Organization at New York to start an exploratory programme of organozinc research. Since then we have been actively engaged at Utrecht in the synthesis of organozinc compounds and their use in organic synthesis, but in particular in the study of organozinc coordination chemistry and of the catalytic effects of organozinc coordination compounds. My lecture deals with the two latter aspects of this work.

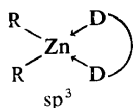
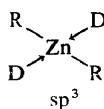
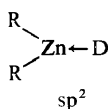
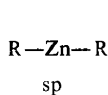
For bivalent zinc two basic types of organozinc compounds must be considered: R_2Zn and $RZnX$, R being hydrocarbon groups or, more generally groups attached to zinc via a zinc-carbon bond, and X being a

halogen or groups being attached to zinc via oxygen, nitrogen, sulphur, phosphorus and the like.

All organozinc compounds are strongly electron-deficient since four low-lying orbitals are available for bonding and only two valence electrons are supplied by zinc. The electrophilic character of zinc both in its inorganic and its organic compounds is one of the significant aspects of the chemical behaviour of zinc compounds, the organozinc compounds included. The most pronounced consequence is the capacity for complex formation. Since zinc has a fully closed 3d shell, for complex formation use is made of the unoccupied valence shell orbitals. In most cases only 4s and 4p orbitals are involved, leading to the preponderant occurrence of tetra-coordination by means of sp^3 hybridization. Higher coordination numbers (five and mostly six) are common in inorganic zinc chemistry but until very recently had not been observed in organozinc chemistry. They are brought about by the involvement of 4d orbitals (sp^3d and sp^3d^2 hybridization). All zinc complexes known so far are *outer* complexes, although a few cases are known where back-bonding from 3d orbitals may be involved.

In this lecture a few aspects of the Utrecht work on organozinc coordination chemistry will be discussed. Part of this work has been published².

I shall omit the relatively simple coordination chemistry of the compounds R_2Zn , where the following cases may be distinguished:



D = monodentate donor molecule

$\begin{array}{c} D \\ \diagup \quad \diagdown \\ D \end{array}$ = bidentate donor molecule

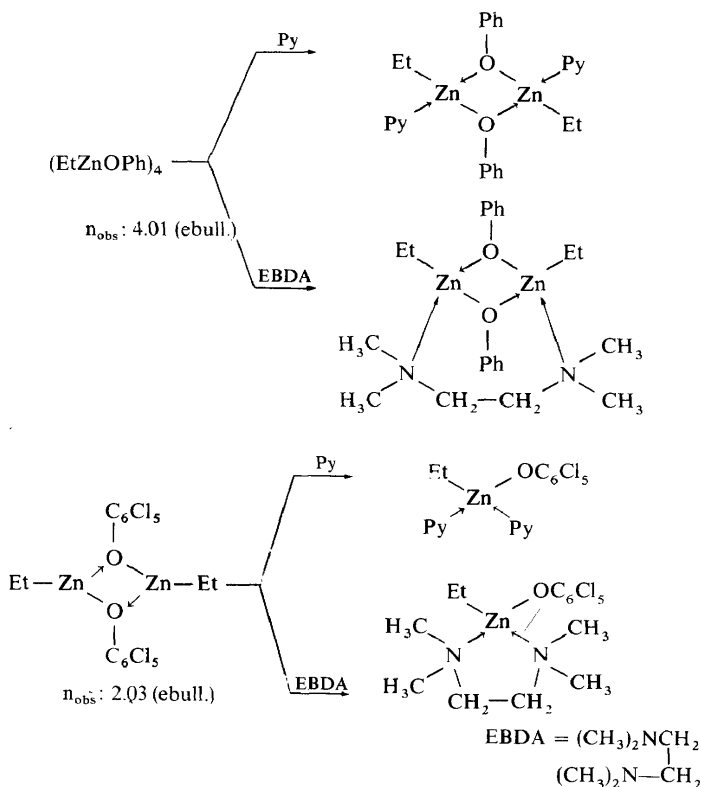
Among compounds of this type examples of three-coordinated zinc are rare, tetra-coordination being the rule.

In the following a few cases will be discussed involving the coordination chemistry of compounds $RZnX$.

THE COORDINATION CHEMISTRY OF COMPOUNDS $RZnX$

In the compounds $RZnX$ the electron-deficient zinc atom is bonded to an atom with donor properties. It must be expected that in order that both atoms become coordinatively saturated intermolecular association will occur both in the solid state and in solution. In fact none of this type of compounds appears to be monomeric. As an example the coordination behaviour of ethylzinc phenoxides is mentioned. Ethylzinc phenoxide is tetrameric in benzene solution and the structure is likely to be the same as that proven by x-ray analysis for methylzinc methoxide by Shearer and Spencer³. The latter compound contains both tetra-coordinate zinc and tetra-coordinate oxygen

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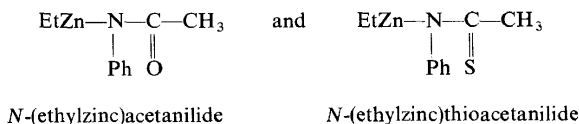


in a cubic framework, the zinc and oxygen atoms occupying the angular points of the cube. In the same way the ethylzinc phenoxide tetramer consists of two dimer units coordinated face to face via zinc-oxygen bridges. This structure is broken down by suitable donors such as pyridine, which forms a dimeric 2:2 complex, and EBDA which forms a bridged binuclear 2:1 complex. In both cases the binuclear zinc-oxygen complex is stable enough to withstand further attack, even by the strong donor EBDA.

In contrast, ethylzinc pentachlorophenoxide is dimeric in benzene which reflects the much greater negative inductive (−I) effect of the pentachlorophenyl as compared with the phenyl group. The donor character of the 3-coordinate oxygen has now become too weak to allow tetramer formation by face to face coordination. Also in the dimer the Zn—O bridges are much weaker than in the unsubstituted phenolate, as appears from the formation of a mononuclear 1:2 complex with pyridine and a mononuclear 1:1 complex with EBDA. These observations clearly illustrate the importance of electronic factors for the coordination behaviour.

More complicated situations arise if we are dealing with organozinc compounds of the type R—Zn—X—Y, in which Y is an organic group containing at least one additional atom with donor properties, the substituent —X—Y in total serving at least as a bidentate ligand. A few recent examples taken from partly unpublished work of Drs Noltes and Boersma at Utrecht will be discussed.

The first example deals with the different coordination behaviour of the two compounds *N*-(ethylzinc)acetanilide and *N*-(ethylzinc)thioacetanilide.

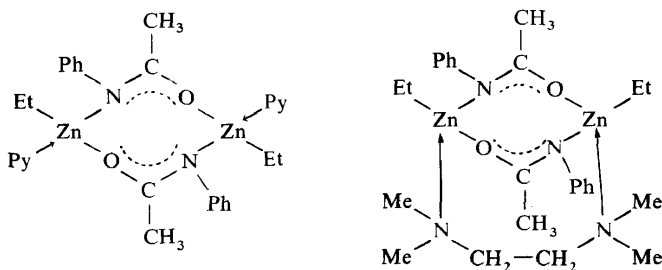


In boiling benzene the acetanilide is a tetramer but the thioacetanilide is a dimer. The compounds are easily obtained by the 1:1 reaction in benzene of diethylzinc with acetanilide and thioacetanilide, respectively. Both compounds are broken down by pyridine to coordination compounds which, according to analysis and molecular weight determinations, represent a 2:2 and a 1:1 pyridine complex, respectively. With EBDA, however, the acetanilide forms a 2:1 and the thioacetanilide a 1:1 complex.

The following values for the carbonyl stretching frequencies were of importance for establishing the structures of the several ethylzinc acetanilide complexes:

	$\nu(\text{C}=\text{O})$
PhNH—CO—Me	1706 cm^{-1}
EtZn—NPh—CO—Me	1563 cm^{-1}
Py complex	1563 cm^{-1}
EBDA complex	1560 cm^{-1}

The fact that both in the Py and in the EBDA complex of ethylzinc acetanilide a binuclear organozinc unit is present suggests that the original tetramer is formed from two relatively weakly associated dimers, in which the coordinate bonds are clearly much stronger. For these dimeric units an eight-membered ring structure is strongly indicated by the infrared results.

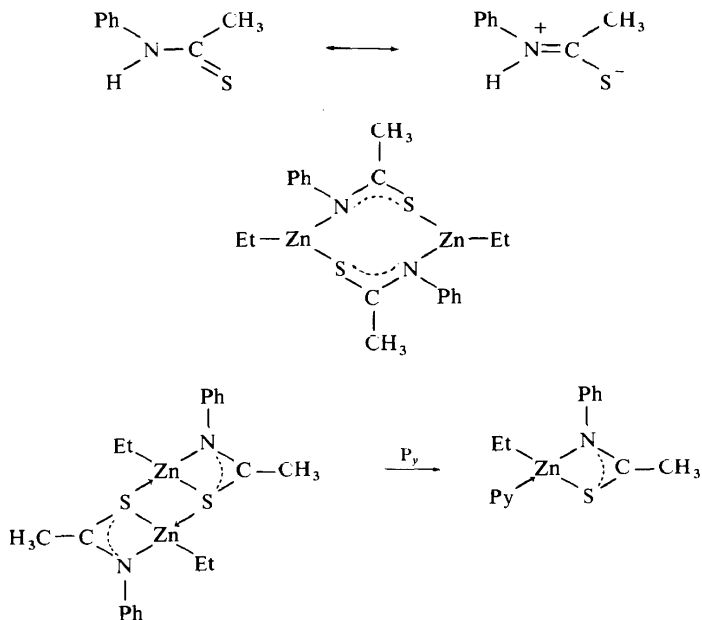


The position of the carbonyl absorption band in *N*-(ethylzinc)acetanilide is shifted quite considerably to smaller wave numbers as compared with acetanilide, indicating a coordinated carbonyl group in the zinc compound. This band does not shift towards higher frequencies upon complex formation with Py or EBDA. This also indicates that in the dimeric building block a coordinated carbonyl group is present. From n.m.r. data it follows that the pyridine complex occurs in two quickly interconvertible configurations.

carrying the Py ligands *cis* and *trans* with respect to the eight-membered ring (broad signal belonging to the acetanilide methyl group). On the other hand, a sharp methyl signal is observed for the EBDA complex, in agreement with the exclusive *cis* configuration occurring here.

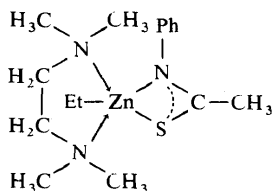
In conclusion, it seems well established that tetrameric *N*-(ethylzinc)acetanilide is built up from two dimer units, consisting of coordinatively stable eight-membered rings, which are weakly coordinated face to face via zinc-oxygen or zinc-nitrogen bonds.

For the dimeric *N*-(ethylzinc)thioacetanilide two structures may be envisaged. The first one, containing an eight-membered ring and coordinatively unsaturated zinc is formally identical with the structure of the dimeric units occurring in the ethylzinc acetanilide tetramer and in the ethylzinc acetanilide Py and EBDA complexes. The second one, containing a four-membered zinc-sulphur ring where tetra-coordination of zinc is attained both by inter- and by intramolecular coordination takes into account the much stronger nucleophilicity of sulphur in thioamides than of oxygen in amides:



The fact that with Py no 2:2 but a 1:1 complex is formed makes the eight-membered structure very improbable. Positive evidence for the four-membered ring structure was obtained from n.m.r. spectra. In the presence of pyridine the intermolecular Zn-S bridge is broken, but the intramolecular Zn-S bridge is retained. As said before, with EBDA a 1:1 complex is formed. The n.m.r. evidence points to the presence of a chelated EBDA ligand. Since the spectral characteristics of the thioacetanilide are identical for the 1:1 pyridine and the 1:1 EBDA complexes of ethylzinc thioacetanilide

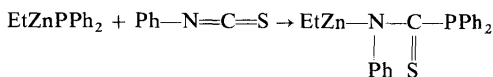
it must be concluded that in the EBDA complex the zinc atom is penta-coordinated:



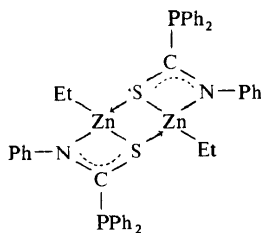
Several configurations may be postulated for either a trigonal bipyramidal or a square pyramidal structure. This was one of the first occasions where penta-coordination was met in an organozinc compound.

A second example of the more complicated behaviour of organozinc coordination compounds containing a multidentate substituent at the zinc is taken from very recent work on the synthetic uses of the zinc-phosphorus bond.

Upon reacting *P*-(ethylzinc)diphenylphosphine with phenylisothiocyanate in a 1:1 molar ratio (1 h at 60°C in benzene solution) the following insertion reaction occurs:



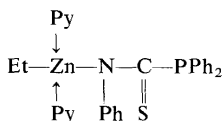
The pure compound appeared to be a dimer in dilute benzene solution. On the basis of spectral evidence we concluded a structure containing a Zn_2S_2 ring with intramolecular zinc-nitrogen coordination, fully analogous to the structure discussed a few moments ago:



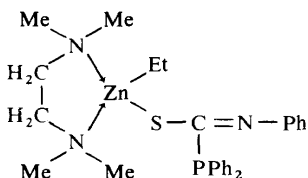
This compound forms a weak monomeric 2:1 complex with pyridine and a strong monomeric 1:1 complex with EBDA. The following table summarizes a few relevant molecular formulae and the i.r. characteristics of the carbon-sulphur bonds.

	$\nu(\text{C}=\text{S})$
(I) $\text{HNPh} \cdot \text{CS} \cdot \text{PPh}_2$	980 cm^{-1}
(II) $[\text{EtZnNPh} \cdot \text{CS} \cdot \text{PPh}_2]_2$	968 cm^{-1}
(III) $\text{EtZnNPh} \cdot \text{CS} \cdot \text{PPh}_2 \cdot 2 \text{ Py}$	987 cm^{-1}
(IV) $\text{EtZnNPh} \cdot \text{CS} \cdot \text{PPh}_2 \cdot \text{EBDA}$	925 cm^{-1}

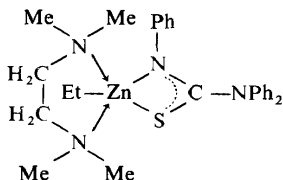
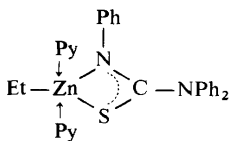
Compound (I) shows the characteristic frequency of a non-coordinated thiocarbonyl group in this type of environment. The lower frequency in compound (II) points to a diminished bond order of the thiocarbonyl group, due to coordination. The increase of $\nu(\text{C}=\text{S})$ in compound (III) indicates the breaking of the zinc-sulphur coordinate bond and the absolute value of $\nu(\text{C}=\text{S})$ points to the presence of a thiocarbonyl group of a character similar to that in compound (I). Tetra-coordination around zinc is maintained by the attachment of two pyridine molecules:



The very strong decrease of $\nu(\text{C}=\text{S})$ upon complexation with EBDA points to a considerable weakening of the carbon-sulphur bond. At the same time $\text{C}=\text{N}$ has shifted to higher frequency which indicates an increased bond order of the carbon-nitrogen bond. On the additional spectral evidence for the bidentate character of the EBDA ligand the following structure for the EBDA complex seems likely:

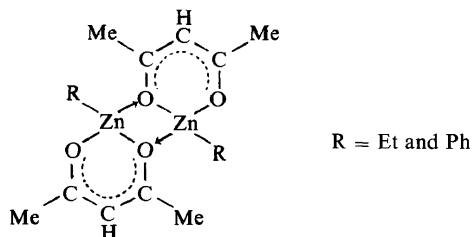


No definite information is yet available about the mechanism underlying the different course of the opening of the coordinated ring by means of pyridine and of EBDA respectively. It is, however, interesting to point in this connection to the different behaviour of the nitrogen analogue of the phosphorus compound under discussion. *N*-(ethylzinc)triphenylthiourea, $\text{EtZnNP} \cdot \text{CS} \cdot \text{NPh}_2$, is a dimer with the same structure as the one shown for the corresponding phosphorus compound. Although the Py and EBDA complexes of the nitrogen and phosphorus analogues have the same molecular composition their structures appeared to be different. N.m.r. evidence suggests that in the monomeric complexes $\text{EtZnNPh} \cdot \text{CS} \cdot \text{NPh}_2 \cdot 2 \text{Py}$ and $\text{EtZnNPh} \cdot \text{CS} \cdot \text{NPh}_2 \cdot \text{EBDA}$ both the zinc-nitrogen and the zinc-sulphur coordination is retained, the zinc atom in these two cases being penta-coordinated:



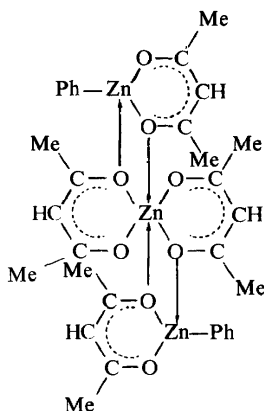
A third example deals with the coordination chemistry of organozinc derivatives of acetylacetonate.

In earlier work it has been observed that upon reaction of compounds R_2Zn (R = ethyl and phenyl) with acetylacetonate in a 1:1 molar ratio (in benzene, room temperature) one mole of RH is eliminated and the following dimeric coordination compounds are formed:



In agreement with the lower acceptor quality of ethyl substituted than of phenyl substituted zinc one would expect the ethyl derivative to be less stable than the phenyl derivative. However, upon recrystallization of the two compounds from boiling n-hexane (b.p. 69°C) the surprising observation was made that the phenylzinc compound which crystallized had not the composition PhZn acac but the one $(\text{PhZn acac})_2 \cdot \text{Zn(acac)}_2$. This composition was established by analysis and confirmed by a molecular weight determination in benzene (found: 740; calc. 746). On the other hand, the ethylzinc acetylacetonate after recrystallization had not changed its original composition.

The i.r. spectrum of the recrystallized phenylzinc compound showed the exclusive presence of chelated acetylacetonate ligands. This leads to the following structural picture for this compound:

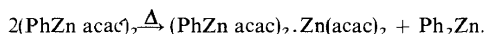


In this three-nuclear complex the two peripheral zinc atoms are tetra-coordinated, whereas the central zinc atom is hexa-coordinated. This picture is in agreement with the result of the x-ray structure determination for zinc bisacetylacetonate. In the solid state this compound has a trinuclear structure with one hexa- and two penta-coordinated zinc atoms⁴.

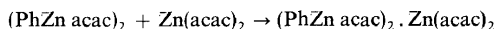
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The n.m.r. spectrum of our trinuclear complex at room temperature reveals one signal for the CH_3 and one signal for the CH protons. This indicates a fast exchange of 'central' and 'peripheral' acetylacetonate ligands. At low temperatures these signals are split.

It is supposed that the trinuclear compound is formed in a disproportionation reaction:



Additional proof for this view is the formation of the trinuclear compound in high yield upon reaction of phenylzinc acetylacetonate and zinc bisacetylacetonate in a 2:1 molar ratio:

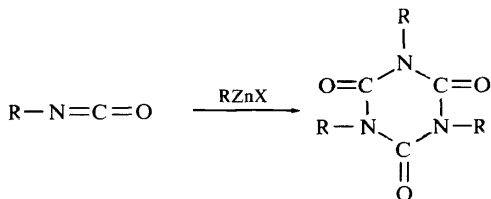


As said before, ethylzinc acetylacetonate does not undergo disproportionation. Neither does it react with zinc bisacetylacetonate, not even after prolonged heating at 60°C , to give a trinuclear species.

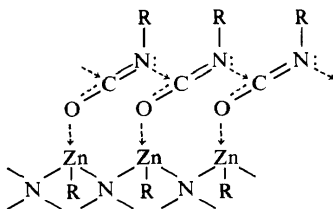
THE CATALYTIC EFFECTS OF ORGANOZINC COORDINATION COMPOUNDS

During the past five years or so much attention has been paid to the catalytic effects of organozinc compounds, in particular in polymerization reactions.

Early observations at Utrecht regarding the properties of compounds RZnX suggested their use as oligomerization and polymerization catalysts. Our first observation of this kind involved the cyclotrimerization of aliphatic and aromatic isocyanates⁵:



It was found that only such types of compounds RZnX which are trimeric in solution are catalysts for this reaction. The following trimerization mechanism could be proven. The trimeric, i.e. trimetallic, catalyst coordinates three isocyanate molecules, with oxygen coordinated to zinc as follows:



For simplicity the picture shows an open chain instead of the cyclic formula.

As a result of the charge displacements accompanying this coordination, interaction occurs between the nucleophilic nitrogen and the electrophilic carbon of neighbouring isocyanate molecules. The three isocyanate molecules are present in the coordination compound as a 'pre-trimer'. Upon addition of a sufficiently strong complexing agent, e.g. excess isocyanate, this pre-trimer is displaced from the catalyst and under suitable electronic rearrangements the trimeric isocyanurate is formed. Thus, we are dealing here with a *coordination-template mechanism* in which a trimetallic organozinc species forces three coordinated isocyanate molecules into a configuration which is, both sterically and electronically, favourable for trimerization to occur. Covalent bonds between the activated monomeric species are established upon breaking the initial coordinate bonds with the catalyst, but not before. Significantly, the organozinc catalyst has no coordinating capacity at all with respect to the trimeric end products of isocyanate oligomerization, the isocyanurates. The reason is of course that the non-bonding electron pairs at each of the three oxygen atoms are situated in the plane of the almost flat isocyanurate molecule and are thus sterically unfit to coordinate simultaneously with the three zinc atoms in the catalyst. Originally we supposed that this coordination-template mechanism might be a general feature of organozinc catalysis. Further work showed this not to be true, in most cases a coordination-insertion mechanism being involved.

So far organozinc compounds as such have not been found suitable for the oligomerization or polymerization of carbon-carbon unsaturated compounds. In Utrecht it was found that combination of certain organozinc and transition metal compounds gives rise to rather specific and active catalytic systems for the cyclotrimerization of butadiene and for the mono- and polyalkylation of aromatics by means of terminal alkenes. I shall not discuss these systems further at this moment.

Certain organozinc systems have been found to be excellent and stereospecific catalysts for the polymerization of aldehydes, lactones and epoxides.

In the last few years the linear homopolymerization of epoxides, in particular of ethylene oxide, propylene oxide and epichlorohydrin, and the copolymerization of epoxides have become of great practical significance. For these polymers quite a number of important applications have been developed, their uses ranging from water-soluble thickeners to special purpose elastomers. Among the systems suitable for the catalysis of epoxide homo- and copolymerizations organozinc compounds have gained prominence, mainly through the work of the groups around Tsuruta⁶ and around Furukawa⁷ in Japan. In particular the system diethylzinc/water has been the subject of Tsuruta's studies on the mechanism of the organozinc-catalysed stereoregular polymerization of propylene oxide. It is supposed that species like $\text{Et}(\text{ZnO})_n\text{-H}$ and $\text{HO}(\text{ZnO})_n\text{-H}$, which are formed during the controlled hydrolysis of diethylzinc, are the catalytically active agents⁶.

In Utrecht completely different organozinc-based catalysts for epoxide polymerizations have been developed. Ethylene oxide and propylene oxide can be homo- and copolymerized to yield extremely high molecular weight and, as far as propylene oxide is concerned, stereoregular polymers of great

strength. To my regret no particulars can be given at this moment about the nature of these catalysts.

At Utrecht the mechanisms of aldehyde and lactone polymerization have been studied in some detail⁸. These results and a few yet unpublished ones will be discussed here.

The polymerization of aldehydes

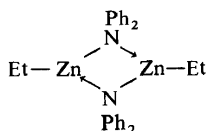
The simplest aldehyde, formaldehyde, can be polymerized to high molecular weight products by a range of catalysts. One basic problem in the commercialization of polyformaldehyde, which has nothing to do with the polymerization step, has been the stabilization against thermal degradation.

Until recently satisfactory systems for the polymerization of higher aldehydes, in the first place acetaldehyde, were not known. The reactivity of certain types of organozinc compounds towards the carbonyl function led us to a systematic study of the organozinc-catalysed polymerization of aldehydes. One problem with all aldehydes beyond formaldehyde is that upon polymerization an asymmetric carbon atom is generated and that useful polymer properties may only be expected if stereoregular polymerization can be achieved. Our work towards organozinc compounds as potential catalysts for the polymerization of aldehydes has resulted in the discovery by Mr Overmars of surprisingly stereoselective catalyst systems which convert, e.g. acetaldehyde, in high yields into almost completely stereoregular (isotactic) polyacetaldehyde. Polymerization has to be carried out below the ceiling temperature of polyacetaldehyde which is at about -40°C . At higher temperatures no polymerization occurs. Mostly we worked at -70°C at which temperature, when really active catalysts were being used, polymerization went very fast. The isotactic structure of the polymers was proven by means of i.r. spectroscopy.

Two different catalytic systems, which lead to similar end products, must be distinguished:

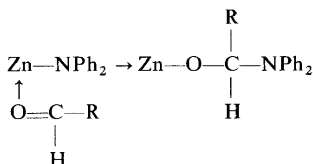
- (a) a combination of a *diarylzinc* compound (e.g. diphenylzinc) and an *N*-arylamide (e.g. acetanilide) as a co-catalyst in a hydrocarbon solvent. The presence of water, even in trace amounts, has a strongly deactivating influence;
- (b) a combination of a *dialkylzinc* compound (e.g. diethylzinc), an organic amide or other compounds containing the structural element —N—C=O as a co-catalyst and water as an activator in a hydrocarbon solvent.

For the activities of both systems a proper ratio of the components is essential. In particular, the catalyst system (b) is very effective and conveniently prepared. Whereas diethylzinc alone is inactive, extensive studies by Japanese workers⁶ have shown the system diethylzinc/water to be a catalyst for acetaldehyde polymerization, but a lengthy and tedious mixing procedure is required to prepare the active catalyst. By including an organic amide we found that an extremely active system is obtained within minutes. Although this is the most active system found so far, many other organozinc compounds are reasonably active catalysts for the polymerization of aldehydes. In order to shed light on the polymerization mechanism we selected the compound *N*-(ethylzinc)diphenylamine, EtZnNPh_2 , as a model catalyst. This is a well-defined, hydrocarbon-soluble compound with moderate catalytic activity.



The purpose was to elucidate the nature of the initiation and propagation steps of the ethylzinc diphenylamine-catalysed polymerization of aliphatic aldehydes.

When *N*-(ethylzinc)diphenylamine in benzene solution is treated in a 1:1 molar ratio at room temperature with acetaldehyde or butyraldehyde, or at 80°C with formaldehyde, in all three cases well-defined crystalline adducts are obtained with a 1:1 stoichiometry. Upon redissolution these 1:1 adducts are, at -70°C, as active catalysts for aldehyde polymerization as the starting compound *N*-(ethylzinc)diphenylamine. Upon following these 1:1 reactions by n.m.r. spectroscopy it was found that in each case the aldehyde proton signal at about $\delta = 9.5$ ppm disappears rapidly, and that a new signal appears in the region $\delta = 6.0$ ppm, normally associated with acetal-like protons. This indicates the occurrence of an insertion reaction of the type



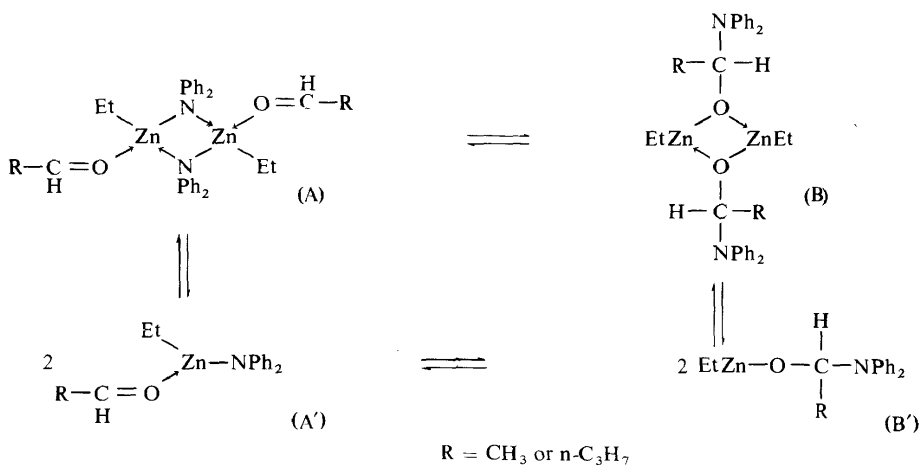
(R = H, Me or Prⁿ)

leading to the zinc derivatives of the elusive α -amino alcohols. Whereas the n.m.r. spectrum of the formaldehyde adduct consists of sharp signals, broad bands are present in the spectra of the acetaldehyde and butyraldehyde adducts.

Cryometric molecular weight determinations in benzene showed the formaldehyde adduct to be a non-dissociating tetramer, $[\text{EtZnOCH}_2\text{NPh}_2]_4$, which has the cubic structure, like the simple alkylzinc alkoxides. The acetaldehyde and butyraldehyde adducts, which mutually show much the same behaviour, were found to be extensively dissociating dimers. From their i.r. spectra the presence of a Zn_2O_2 ring could be derived (a prominent band in the 530–560 cm^{-1} region). In addition, both adducts show absorption in the 1500 cm^{-1} region, characteristic for a coordinated carbonyl group.

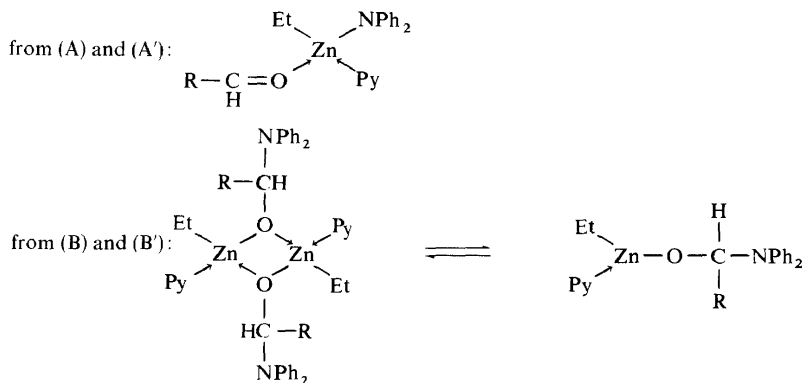
These data point to the occurrence of the following system of equilibria for the *N*-(ethylzinc)diphenylamine-acetaldehyde and butyraldehyde adducts in solution.

The first step in the interaction between the coordinatively unsaturated dimeric ethylzinc diphenylamine and an aldehyde in a 1:1 ratio is the formation of the coordinatively saturated dimeric complex (A). From n.m.r. measurements it may be concluded that following this coordination step a rapid insertion of the carbonyl group into the zinc-nitrogen bond occurs, leading to the coordinatively unsaturated dimeric species (B). The molecular weight determinations suggest a partial dissociation of the dimeric species

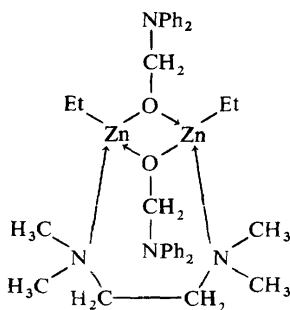


(A) and (B) in solution into the corresponding monomeric species (A') and (B'). Whether between (A') and (B') a similar equilibrium exists as between (A) and (B) has not been ascertained.

The ethylzinc diphenylamine-aldehyde adducts react with pyridine to form complexes with 1:1:1 stoichiometry which, according to molecular weight determinations, are dissociating dimers. No aldehyde is set free upon the addition of pyridine, indicating that the latter is too weak a donor species to replace coordinated aldehyde in (A) or (A') but that it only occupies available acceptor places at zinc. Thus, the following pyridine adducts may be formed:

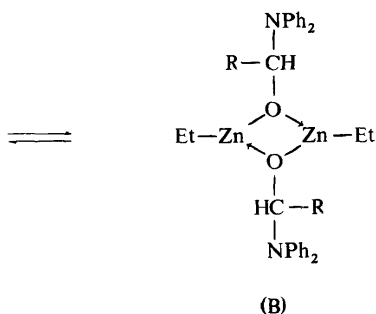
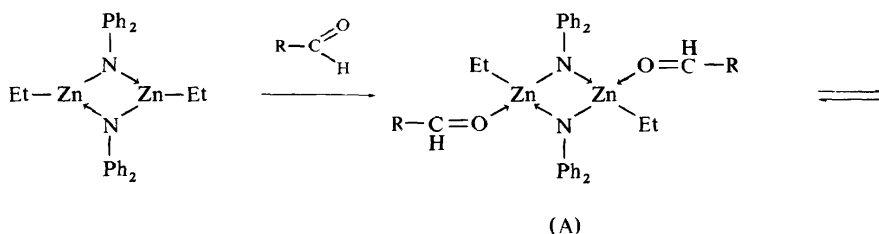


With the much stronger coordinating agent EBDA a radical disruption of the dissociating dimeric ethylzinc diphenylamine-acetaldehyde and butyraldehyde adducts occurs with total elimination of the aldehyde moieties. On the other hand, EBDA breaks down the non-dissociating tetrameric ethylzinc diphenylamine-formaldehyde adduct to the 2:1 complex $[(\text{EtZnOCH}_2\text{NPh}_2)_2]$. EBDA, which has the following bridged structure:



This complex, again, is extensively dissociated in solution.

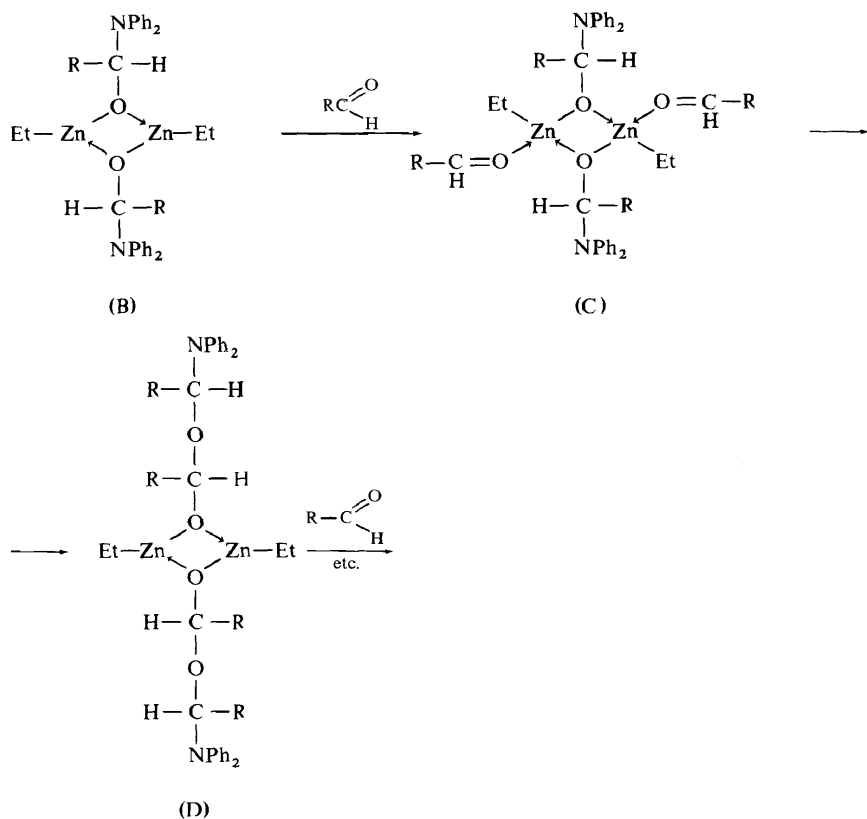
From all these results the following picture arises about the mechanism of aldehyde polymerization by means of organozinc catalysts. As outlined before, at room temperature the following reaction occurs between ethylzinc diphenylamine and an aldehyde:



Both (A) and (B) are in equilibrium with monomeric species as well. The coordinatively unsaturated species (B) may be able to coordinate aldehyde but above the ceiling temperature no insertion of the coordinated carbonyl group into a zinc-oxygen bond occurs, or if it occurs this reaction is reversible. Below the ceiling temperature a fast coordination-insertion mechanism becomes operative which leads to high molecular weight, highly stereoregular polyaldehydes.

The stereoregular nature of the polymerization may be the result of the stereocontrol both of the coordination step (B)→(C) and of the insertion step (C)→(D). In the catalyst-growing polymer complex both the zinc atom and the carbon atom attached to coordinated oxygen are sites of asymmetry

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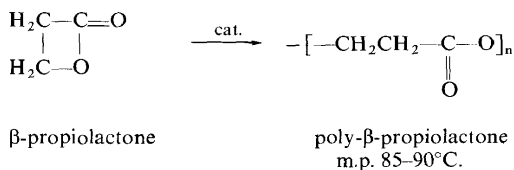


and it would seem that the presence of both is a prerequisite for stereoregular polymerization to occur.

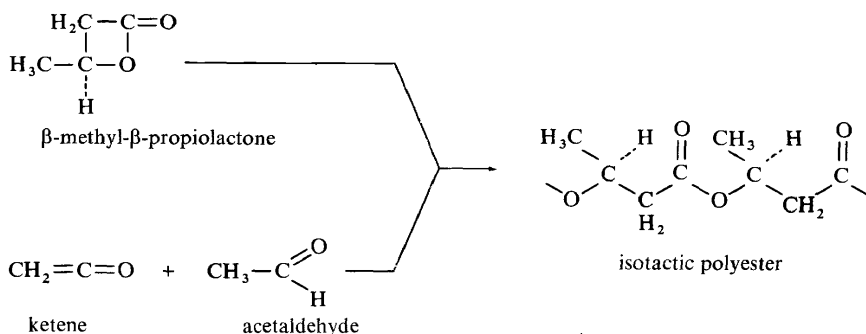
So far the very high melting points, the insolubility and the thermal instability of the polyaldehydes obtained have prevented a proper evaluation of their usefulness. Since the thermal instability is entirely related to the characteristic 'unzipping' process also observed with polyformaldehyde an important step forward would be to find means for end group stabilization.

The polymerization of β -lactones

In the course of our study of the catalytic effects of organozinc compounds it was found that certain types of compounds RZnX are excellent catalysts for the ring-opening polymerization of β -lactones:



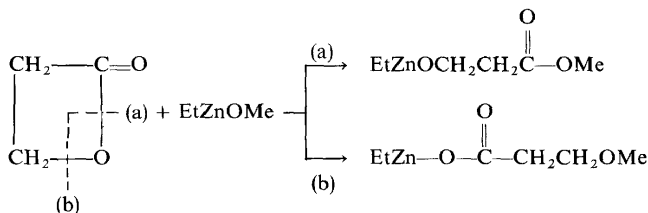
This polymer which in fact is a polyester has, like other types of aliphatic polyesters, too low a melting point for practical purposes. With a view to the high stereospecificity exhibited by organozinc catalysts in the polymerization of aldehydes it was envisaged to study such catalysts for the polymerization of appropriate β -lactones and the direct alternating copolymerization of suitable ketenes and aldehydes into stereoregular polyesters, e.g.



Considerably higher melting points are to be expected for such isotactic polyesters, e.g. for the one pictured a m.p. of at least 170°C . While work towards this goal is still in progress we found it desirable to study the mechanism of the organozinc-catalysed, ring-opening polymerization of β -lactones.

As in the case of aldehyde-polymerization we used easily handled, model systems, viz. the combinations β -propiolactone-ethylzinc methoxide and β -propiolactone-ethylzinc diphenylamine, for the study of the polymerization mechanism.

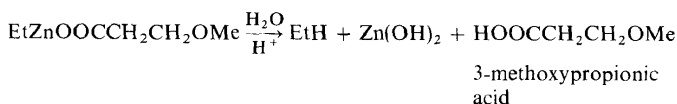
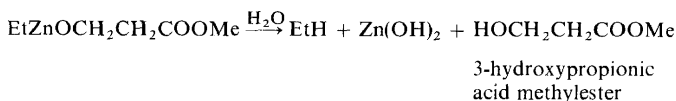
When β -propiolactone was reacted at room temperature in a 1:1 molar ratio with ethylzinc methoxide or with ethylzinc diphenylamine in benzene solution very complex reaction mixtures were formed. From the concomittant changes in the i.r. and n.m.r. spectra it followed that the lactone ring was opened and that the ethyl group remained attached at the zinc atom. Opening of the lactone ring by the organozinc compound may occur in two ways, either by acyl-oxygen cleavage (a), which yields an alkylzinc alkoxide, or by alkyl-oxygen cleavage (b), leading to an alkylzinc carboxylate, e.g.



Ishii *et al.* have shown that both trimethylsilyl⁹ and trimethylgermyl¹⁰ dialkylamines react with β -propiolactone with alkyl-oxygen cleavage (b), but that the corresponding trimethylstannyl compound brings about

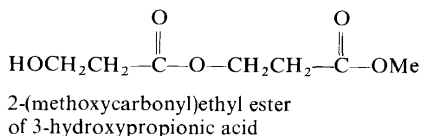
acyl-oxygen cleavage (a)¹⁰. The latter was reported¹¹ to dominate with trimethylstannyl methoxide, but the selectivity decreased with increasing polarity of the solvent.

In our case the complexity of the reaction mixture prevented the direct identification of the reaction product. Therefore the following procedure was applied. Ethylzinc methoxide and β -propiolactone in a 1:1 molar ratio were reacted in benzene at 75°C. After three hours the i.r. absorption at 1848 cm⁻¹ characteristic for the lactone ring had disappeared. Instead, a broad ester absorption band, centred at 1736 cm⁻¹, was found, but a carboxylate absorption around 1600 cm⁻¹ was notably absent. This already suggested that exclusively acyl-oxygen cleavage (a) had occurred. Upon hydrolysis of the reaction mixture the formation of zinc hydroxide and ethane was established. The less volatile organic fraction consisted mainly of two products which could be isolated in about equal amounts by distillation. The lowest boiling component was characterized as the methylester of 3-hydroxypropionic acid, whereas no trace of 3-methoxypropionic acid could be detected.



Reaction of β -hydroxypropionic acid methylester with diethylzinc afforded a product with the spectral characteristics of the original reaction mixture, whereas diethylzinc and 3-methoxypropionic acid yielded a different product. These reactions prove that the opening of the lactone ring has exclusively occurred according to reaction path (a), i.e. by acyl-oxygen cleavage.

The second, higher boiling hydrolysis product was characterized as the 2-(methoxycarbonyl)ethyl ester of 3-hydroxypropionic acid:



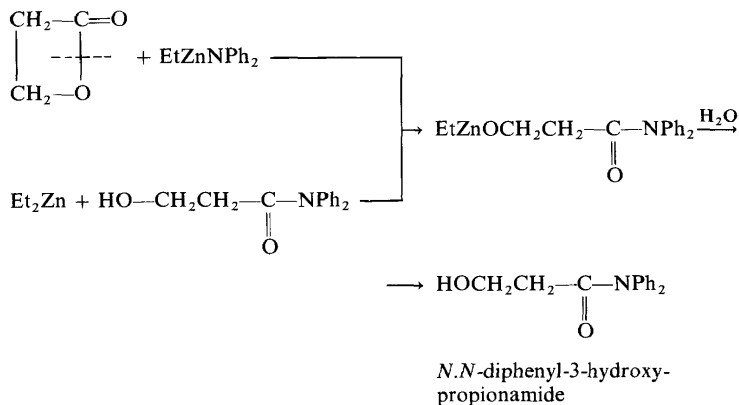
The isolation of this compound strongly suggests that the ethylzinc methoxide-catalysed polymerization of β -propiolactone proceeds by the successive insertion of monomer units into the Zn—O bond of the growing polymer-catalyst complex through acyl-oxygen cleavage of the lactone ring.

The i.r. carbonyl absorptions of the compound $\text{EtZn}-\text{OCH}_2\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{OMe}$

and of the corresponding hydroxy ester are identical, which proves that in the zinc compound the ester group is not coordinated to zinc. Surprisingly, the cryoscopically established molecular weight of this compound in

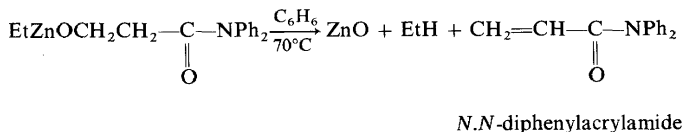
benzene points to a pentameric association for which no distinct structure can as yet be given.

Ethylzinc diphenylamine reacts much faster with β -propiolactone than the methoxide. In a similar way it could be demonstrated that here again exclusively acyl-oxygen cleavage of the lactone ring occurs:



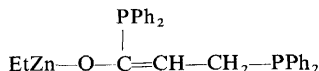
No accurate molecular weight could be determined for the ethylzinc complex, erratic values of $\bar{n}$ between 3 and 4 being found, but the i.r. spectrum showed the presence both of coordinated and of uncoordinated carbonyl groups.

Whereas the corresponding methyl ester appeared to be thermally stable, the diphenylamide already decomposed at 70°C in benzene solution with formation of *N,N*-diphenylacrylamide:

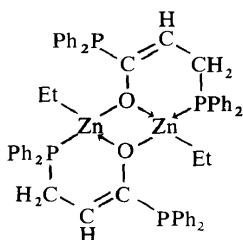


It would seem that the mechanism of the ethylzinc diphenylamine-catalysed polymerization of β -propiolactone is very similar to that discussed for ethylzinc methoxide.

It has been found that the system β -propiolactone-ethylzinc diphenylphosphine behaves quite differently. No high molecular weight polyester is formed; instead the curious compound

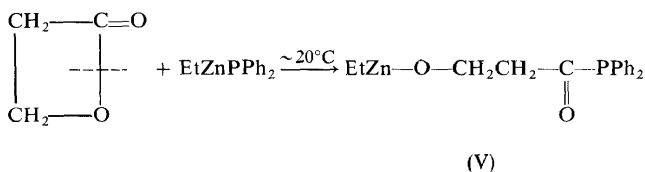


is formed in a yield of 56 per cent calculated on ethylzinc diphenylphosphine. The new compound is a dimer in solution which suggests the following structure:

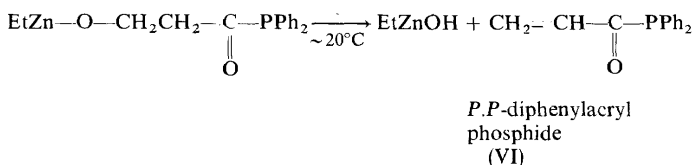


The following reaction sequence is proposed to account for the formation of this product.

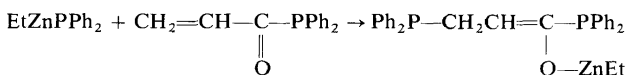
- (i) the reaction of β -propiolactone with the Zn—P bond of ethylzinc diphenylphosphine. As for the corresponding reactions with ethylzinc methoxide and diphenylamine acyl-oxygen cleavage is supposed to occur :



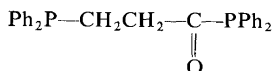
- (ii) In view of the marked thermolability of the corresponding nitrogen compound, discussed a few moments before, we assume a similar, but faster, decomposition of the phosphorus analogue (V) which already occurs at room temperature :



- (iii) Finally a 1,4 addition of the Zn—P bond of ethylzinc diphenylphosphine to compound (VI) may occur :



Upon hydrolysis the compound



should be obtained which, however, proved to be very unstable. Conjugate additions of organozinc phosphines of this type have not been described before.

CONCLUDING REMARKS

At the end of my lecture I should like to make one general remark. Restricting myself mainly to Utrecht work I have tried to emphasize the structure and reactivity of organozinc coordination compounds *in solution*. The structural pictures shown have been derived from spectral data (u.v., i.r., n.m.r.), but it should be realized that they merely represent a snapshot of an in reality *dynamic* situation. Here, I think, I am touching upon one of the most essential aspects of (organo)metal coordination chemistry which sometimes tends to be forgotten. Valuable as they are, the results of x-ray examinations of coordination compounds should not be used to interpret the behaviour of such compounds under the usual reaction conditions. X-ray results inform us about the *static* situation existing in the solid state, where lattice energies are of predominant significance. On the other hand, the same compounds in solution represent highly dynamic systems, since even small differences in polarity of the solvent system may result in drastic effects upon the coordination behaviour and thus upon chemical reactivity.

To illustrate my point I recall the trimeric organozinc catalysts for the cyclotrimerization of isocyanates, mentioned a few moments ago. One of the catalytically active compounds in benzene solution appeared to be a dissociating trimer. Its x-ray picture revealed, however, a tetrameric structure in the solid state.

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