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INVESTIGATIONS ON ORGANOZINC COMPOUNDS
XI*. COORDINATION CHEMISTRY OF ORGANOZINC COMPOUNDS RZnX: ORGANOZINC–NITROGEN COMPOUNDS OF THE TYPE EtZnNPhCOZ**

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SUMMARY

The coordination chemistry of the organozinc–nitrogen compounds $EtZnNPh_2$ and EtZnNPhCOZ (Z=H, Me, OMe, SMe and NPh_2) has been studied. Whereas $EtZnNPh_2$ is dimeric [as is $Zn(NPh_2)_2$], with three-coordinate zinc, replacement of a Ph group in $EtZnNPh_2$ by COZ leads to higher association and four-coordination of zinc. Such compounds are trimeric in solution with Z=OMe and NPh_2, tetrameric with Z=Me, and polymeric ($n > 6$) with Z=H. The compound with Z=SMe decomposes into EtZnSMe and PhNCO above 5°. All compounds readily form four-coordinate complexes with pyridine (Py) and *N,N,N′,N′*-tetramethylethylenediamine (TMED). $EtZnNPh_2$ and EtZnNPhCOZ (Z=OMe, SMe, NPh_2) yield mononuclear complexes (RZnX·2 Py and RZnX·TMED). The organozinc amides (Z=H, Me) yield binuclear complexes [$(RZnX\cdot Py)_2$ and $(RZnX)_2\cdot$TMED]. Possible structures for these compounds in benzene solution are considered.

INTRODUCTION

The reaction between diethylzinc and diethylamine was reported by Frankland in 1867[1], but the chemistry of organozinc–nitrogen derivatives received no further attention until quite recently. In 1965 well-defined organozinc amines $RZnNR'_2$ (R and R′ alkyl or aryl) were prepared by controlled acidolysis of diorganozincs with secondary amines[2,3]. A mechanistic study of this reaction (using primary amines) was undertaken[4].

Recent studies of organozinc–oxygen derivatives RZnOR′ have shown that although such compounds may contain three-coordinate zinc[5–8], the zinc atom is usually four-coordinate[3,5,7,9]. The coordination may involve exclusively the oxygen bound to zinc which is then four-coordinate (*e.g.* simple alkoxides or phenoxides[3,5,7]) or the oxygen bound to zinc (three-coordinate in that case) and an additional donor atom present in R′ (*e.g.* derivatives of bidentate hydroxy compounds[5,7,9]).

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* For part X see ref. 9.

** Part of this research has been communicated at the XIth International Conference on Coordination Chemistry, Haifa, Israel, 1968.

Simple $RZnNR'_2$ compounds differ fundamentally from simple RZnOR' compounds in that the nitrogen atom has only one lone electron pair available for coordination. Methylzinc diphenylamine $MeZnNPh_2$ occurs as a dimer with three-coordinate zinc both in benzene solution[3] and in the solid state[10]. The dimeric ketenimine derivatives $RZnN{=}CPh_2$ (R=Me, Et, Ph)[11] likewise contain three-coordinate zinc. Introduction of suitably located donor atoms in the amine part of the molecule may lead to coordination saturation of the zinc atom. A few examples of such compounds have been reported, *i.e.* dimeric $MeZnNMeCH_2CH_2NMe_2$[3] and tetrameric RZnNPhCOR (R=Et, Ph)[5]. The latter compounds are of particular interest from a structural point of view[5].

As part of our general study of organozinc coordination chemistry[12], we have investigated organozinc–nitrogen compounds which contain additional donor atoms, *i.e.* those of the general type EtZnNPhCYZ (Y=O, S; Z=H, Me, OMe, SMe, NPh_2). This work was carried out in order to establish the relation between the coordination behaviour of such compounds and their catalytic activity in the cyclotrimerization of organic isocyanates (a preliminary account of the template effect of trimeric RZnX species in this reaction has been published[13]). Moreover, we wished to study the nature of the adducts obtained from organozinc alkoxides or amines and isocyanates or isothiocyanates[2] where addition of Zn–O or Zn–N across either C=O (C=S) or C=N bonds may occur.

The present paper deals with compounds EtZnNPhCOZ (Z=H, Me, OMe, SMe, NPh_2) and furthermore describes the coordination behaviour of $EtZnNPh_2$ and $Zn(NPh_2)_2$. The corresponding thiocarbonyl derivatives are discussed separately[14].

RESULTS AND DISCUSSION

The compounds EtZnNPhCOZ (Z=H, Me, OMe) have been prepared by the 1/1 reaction of Et_2Zn with the appropriate PhNHCOZ compound in dilute benzene solution. Problems connected with the synthesis of EtZnNPhCOSMe are discussed below. A second synthetic route to the organozinc carbamate (Z=OMe) involves the addition of EtZnOMe to PhNCO[2]. The organozinc urea (Z=NPh_2) was preferably prepared by the addition route ($EtZnNPh_2$ + PhNCO[2]), since the reaction of diethylzinc with triphenylurea is very slow. The compounds (Z=OMe, NPh_2) prepared by the two routes proved to be identical. All compounds are colourless, crystalline, air-sensitive solids, mostly insoluble in aliphatic, but soluble in aromatic hydrocarbons.

For each of these compounds and for $EtZnNPh_2$[2,3] the complex-forming behaviour towards pyridine (Py) and *N,N,N',N'*-tetramethylethylenediamine (TMED) has been investigated. The stoichiometry, melting points, molecular weights and analytical data of the various compounds and complexes isolated are given in Table 1.

*N-(Ethylzinc)diphenylamine, $EtZnNPh_2$ [(Ia)–(Ig)]**

In line with the presence of three-coordinate zinc in $(EtZnNPh_2)_2$[3] (Ia) com-

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* Numbers correspond with those in Table 1.

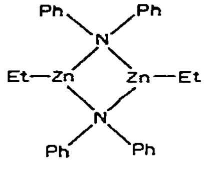
TABLE 1

STOICHIOMETRY, MELTING POINTS, ANALYTICAL DATA AND MOLECULAR WEIGHTS OF ORGANOZINC–NITROGEN COMPOUNDS

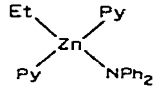
No.	Compound	M.p. (°C)	% Zn found (calcd.)	% N found (calcd.)	Molecular weight[a] found (calcd.)	concn. (wt.-%)
(Ia)	$(EtZnNPh_2)_2$[b]	106	24.71 (24.84)	5.76 (5.33)	518 (525.2)	3.10
(Ib)	$EtZnNPh_2 \cdot 2\ Py$	111	15.66 (15.53)			
(Ic)	$EtZnNPh_2 \cdot TMED$	134 (dec.)	17.41 (17.26)	11.07 (11.09)	382[c] (378.8)	0.44
(Id)	$EtZnNPh_2 \cdot Bipy$	103	15.98 (15.61)	10.47 (10.05)		
(Ie)	$[Zn(NPh_2)_2]_2$	282	16.32 (16.27)	6.96 (6.97)	780[d] (803.6)	0.16
(If)	$Zn(NPh_2)_2 \cdot TMED$	>260	12.58 (12.60)	10.82 (10.80)		
(Ig)	$Zn(NPh_2)_2 \cdot Bipy$	194	11.80 (11.72)	10.40 (10.05)	578[c] (558.0)	0.43
(IIa)	$(EtZnNPhCOMe)_4$	140	28.36 (28.59)	6.17 (6.14)	900 (914.4)	2.06
(IIb)	$(EtZnNPhCOMe)_2 \cdot 2\ Py$	125	20.84 (21.21)	8.60 (9.11)	598 (615.0)	4.14
(IIc)	$(EtZnNPhCOMe)_2 \cdot TMED$	55–60	22.74 (22.80)	9.46 (9.77)	573 (562.3)	4.31
(IIIa)	$(EtZnNPhCOH)_{\sim 6}$	132	29.44 (30.48)	6.87 (6.53)	1270 (214.5[e])	4.35
(IIIb)	$(EtZnNPhCOH)_2 \cdot 2\ Py$	66–72	22.28 (22.26)	8.71 (9.54)	568 (583.0)	5.98
(IIIc)	$(EtZnNPhCOH)_2 \cdot TMED$	70–75	23.35 (23.89)	9.75 (10.27)		
(IVa)	$(EtZnNPhCOOMe)_3$	158	26.89 (26.72)	6.87 (5.73)	690[f] (733.8)	4.67
(IVb)	$EtZnNPhCOOMe \cdot 2\ Py$	48	20.69 (20.21)	8.56 (8.66)		
(IVc)	$EtZnNPhCOOMe \cdot TMED$	85–89	18.57 (18.12)	11.43 (11.65)		
(Va)	$(EtZnNPhCOSMe)_n$[g]					
(Vb)	$EtZnNPhCOSMe \cdot Py$				304[c] (339.6)	1.42
(Vc)	$EtZnNPhCOSMe \cdot TMED$				334[c] (377.0)	1.11
(VIa)	$(EtZnNPhCONPh_2)_3$	239	16.31 (17.12)	7.78 (7.34)	1135 (1145.4)	2.03
(VIb)	$EtZnNPhCONPh_2 \cdot 2\ Py$	99	12.06 (12.12)	8.64 (9.12)		
(VIc)	$EtZnNPhCONPh_2 \cdot TMED$	88	12.56 (13.12)	10.77 (11.24)		

[a] Molecular weights were determined by ebulliometry in benzene, unless otherwise stated. Concentration dependency was observed only for compounds IIIa and IVa. [b] Reported[3]: M.p. 99–100°; Mol.wt.: 514 (1.5 wt.-%), 540 (1.79 wt.-%). [c] Cryometric determination. [d] Estimated error: ±100, due to very slight solubility in boiling benzene. [e] Calculated for monomer; mol.wt. concentration dependent. [f] Mol.wt. concentration dependent: 495 (1.4 wt.-%), 575 (2.0 wt.-%), 665 (3.5 wt.-%). [g] Decomposes above 5°.

plex-formation with Py (Ib), TMED (Ic) and Bipy (Id)* readily occurs. However, unlike $(EtZnOPh)_4$, which forms binuclear complexes with Py[3,7] and TMED[7], $(EtZnNPh_2)_2$ forms mononuclear complexes. The formation of $MeZnNPh_2 \cdot 2$ Py has been reported by Coates *et al.*[3] Ebulliometric titration of $(EtZnNPh_2)_2$ with Py



(Ia)



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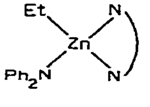
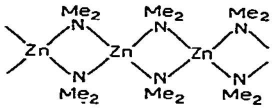
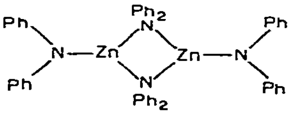


(Ic),(Id)

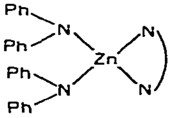
failed to provide evidence for the intermediate formation of binuclear $(EtZnNPh_2 \cdot Py)_2$. $(EtZnNPh_2)_2$ does not show the tendency to form disproportionation products in the presence of Py as observed for $(MeZnNPh_2)_2$[3].

The weakness of the diphenylamino group as a donor is again illustrated by the different coordination behaviour of $Zn(NPh_2)_2$[2] and $Zn(NMe_2)_2$[3]. $Zn(NMe_2)_2$ occurs as a coordination polymer insoluble in donor solvents such as DMF and Py or in a solution of Bipy in benzene[3]. In contrast, $Zn(NPh_2)_2$ (Ie) most probably occurs as a dimer in benzene solution. In accord with the presence of three-coordinate zinc, (Ie) readily forms 1/1 complexes with both TMED [(If); colourless] and Bipy [(Ig); deep-red].





(Ie)



(If),(Ig)

N-(Ethylzinc)acetanilide, EtZnNPhCOMe [(IIa)–(IIc)]

EtZnNPhCOMe (IIa) is a tetramer in benzene solution, the molecular weight being independent of the concentration. Upon reaction with an excess of Py or TMED the binuclear complexes $(EtZnNPhCOMe)_2 \cdot 2$ Py(IIb) and $(EtZnNPhCOMe)_2 \cdot$ TMED (IIc) are formed. Apparently, complete breakdown of the tetrameric structure

TABLE 2

IR AND PMR DATA OF $(EtZnNPhCOMe)_4$ AND ITS COMPLEXES[a]

No.	Compound	$\delta(CH_2)$	$\delta(CH_3)$	$\delta[C(O)CH_3]$	$\delta(NCH_3)$	$\delta(NCH_2)$	$\nu(C{=}O)$
	HNPhCOMe			1.70			1706
(IIa)	$(EtZnNPhCOMe)_4$	0.42	1.44	1.93			1563[b]
(IIb)	$(EtZnNPhCOMe)_2 \cdot 2$ Py	0.66	1.61	1.87[c]			1563[b]
(IIc)	$(EtZnNPhCOMe)_2 \cdot$TMED	0.20	1.50	1.89	2.08	2.08	1563[b]

[a] All IR and PMR spectra were recorded in benzene solution. [b] Stretching vibration of the bridging N=C=O group. [c] Very broad band.

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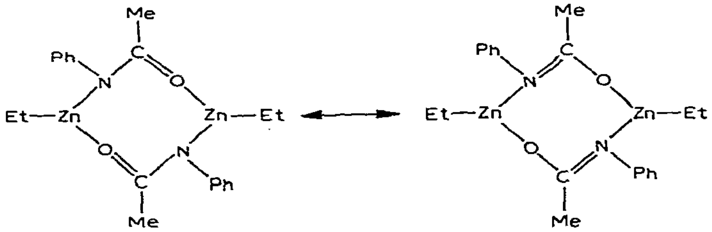
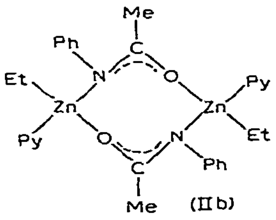
* The orange-coloured Bipy complex shows an intense charge-transfer band (λ_{max} 522 nm) in its UV spectrum (*cf.* refs. 15 and 16).

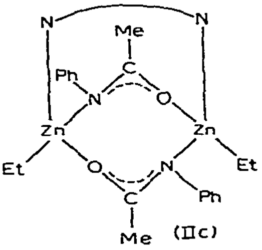
does not occur. This suggests that the tetramer is formed by a relatively weak association of two dimeric units, within which the coordinate bonds are clearly much stronger.

The ν(C=O) of $(EtZnNPhCOMe)_4$ is shifted as much as 143 cm^{-1} to lower frequency relative to PhNHCOMe (see Table 2). Although part of this effect must be attributed to a mass effect of the heavy zinc atom (*cf.* the shift of 65 cm^{-1} of ν(C=O) in $Et_3SnNPhCOH$[17]), coordinate bonding between the C=O group and the zinc atom must be mainly responsible. Since complexation with Py and TMED does not result in a shift of ν(C=O) (Table 2), coordinated carbonyl groups must be assumed to be present in the dimer units as well. Based on these data, the following structures are proposed for the dimeric unit and its Py and TMED complex:





(IIb)



(IIc)

In the absence of suitable ligands two coordinatively unsaturated dimeric units combine to form tetramers by face-to-face coordination via Zn–O or Zn–N bridges. This picture for the structure of tetrameric organozinc amides was first put forward by Coates and Ridley for $(RZnNPhCOR)_4$ (R = Et, Ph)[5]. Similar structures with NCO as a three-atom bridging group have recently been proposed for dimeric dialkylaluminium derivatives of N-substituted acid amides[18] (*cf.* ref. 19), where further coordination is, of course, not possible.

PMR data of compounds (IIa)–(IIc) are given in Table 2.

The high value of $\delta(CH_2)$ of $(EtZnNPhCOMe)_2 \cdot 2$ Py is probably caused by a deshielding effect of the pyridine rings. In the TMED complex, where this effect is absent, $\delta(CH_2)$ has a lower value than in the parent compound. The low-field shift of $\delta(COCH_3)$ of $(EtZnNPhCOMe)_4$ as compared to the parent amide is in agreement with coordination of the carbonyl groups in the organozinc compound. A notable feature is the broadening of the $C(O)CH_3$ singlet in the Py complex (IIb). In pyridine solution, this band appears at 2.30 ppm, again appreciably broadened. At −30° the band splits up into two singlets of nearly equal intensity at 2.19 and 2.52 ppm, indicating the presence of two different kinds of $C(O)CH_3$ groups. This effect can be explained by assuming that two configurations are possible for the pyridine complex, *i.e.* with the pyridine ligands in either a *cis*- or a *trans*-position relative to the eight-membered $Zn_2N_2C_2O_2$ ring. Interconversion between these configurations may occur via a dissociation process involving the Zn–Py coordinate bonds. It is revealing that no such broadening is observed in the spectrum of the TMED complex (IIc), in which the presence of a bridging TMED ligand keeps the ethyl groups in *cis*-position.

N-(Ethylzinc)formanilide, EtZnNPhCOH [(IIIa)–(IIIc)]

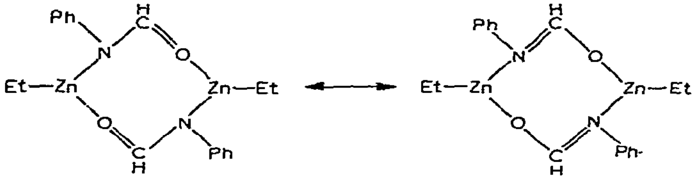
This compound differs from $(EtZnNPhCOMe)_4$ (IIa) in that it is more highly associated in benzene solution (*cf.* Table 1). Its behaviour towards Py and TMED is identical to that of $(EtZnNPhCOMe)_4$, binuclear complexes [(IIb) and (IIc)] being formed with both ligands. Some relevant IR and PMR data are given in Table 3. The IR data show that in both (IIIa) itself and in the complexes (IIIb) and (IIIc), the carbonyl groups are coordinated. The stoichiometry of the Py (2/2) and TMED (2/1) complexes is in agreement with the assumption that polymeric EtZnNPhCOH is built up from dimeric sub-units:

TABLE 3

IR AND PMR DATA OF $(EtZnNPhCOH)_n$ AND ITS COMPLEXES

No.	Compound	$\delta(CH_2)$	$\delta(CH_3)$	$\delta[C(O)H]$	$\delta(NCH_3)$	$\delta(NCH_2)$	$\nu(C=O)$
	HNPhCOH			8.30, 8.43			1695
(IIIa)	$(EtZnNPhCOH)_n$	0.41, 0.58[a]	1.29, 1.43[a]	8.14, 8.30[b] 8.53, 8.69			1582[d]
(IIIb)	$(EtZnNPhCOH)_2 \cdot 2$ Py	0.66[c]	1.60[c]	8.36, 8.40			1582[d]
(IIIc)	$(EtZnNPhCOH)_2 \cdot$TMED	0.26	1.44	8.73	1.90	1.90	1582[d]

[a] Collapse upon heating at 60°. [b] Broaden, but do not collapse, upon heating at 60°. [c] Relatively broad bands. [d] Stretching vibration of the bridging N=C=O group.



It is surprising that substitution of group Z in $(EtZnNPhCOZ)_4$ (Z=Me or Et[5]) by a hydrogen atom has so much influence on the mode of association between the dimeric sub-units. In particular the presence of at least two different kinds of C(O)H groups, as indicated by the complexity of the PMR spectrum, is difficult to explain (see Table 3).

The broadness of the PMR absorptions of the Py complex and the sharpness of those of the TMED complex can be explained along the same lines as for $(EtZnNPhCOMe)_4$. It is to be noted, that the TMED complexes of both $(EtZnNPhCOMe)_4$ (IIc) and $(EtZnNPhCOH)_n$ (IIIc) show only one signal for all TMED protons.

In complexes in which TMED acts as a chelating ligand, we have observed two separate signals for the NCH_3 (at lower field) and NCH_2 (at higher field) protons (*cf.* ref. 9).

Methyl N-(ethylzinc)carbanilate, EtZnNPhCOOMe [*(IVa)*–*(IVc)*]

The molecular weight of this compound shows a large concentration dependence in boiling benzene. Since the limiting value of n appears to be three, this compound is very probably a dissociating trimer in solution. A preliminary X-ray crystallographic study* of this compound has shown that the crystals are monoclinic, space group $P2_1/n$ with unit cell dimensions $a = 12.227$, $b = 21.538$ and $c = 17.200$ Å, $\beta = 91°26'$ and D(flotation) = 1.427 g/cc, indicating the presence of 16 monomer units per unit cell. Most probably these monomers are arranged in the unit cell as four tetramers. This observation contrasts with the trimeric association in benzene solution. It is of interest that $Me_2AlNPhCOMe$ recently has been found to be trimeric in the crystal and dimeric in solution[18] [*cf.* also the association of Me_2GaOH in the crystal (tetrameric) and in solution (trimeric)[20]].

Since all measurements on and reactions of EtZnNPhCOOMe were carried out in relatively concentrated solution, they will be discussed in terms of trimeric association.

The weakness of the coordinate bonds in (IVa), which is apparent from the occurrence of dissociation, is also reflected by the complete breakdown of the trimeric structure upon reaction with Py or TMED, which results in the formation of the monomeric 1/2 Py complex (IVb) and the monomeric 1/1 TMED complex (IVc).

TABLE 4

IR AND PMR DATA OF $(EtZnNPhCOOMe)_3$ AND ITS COMPLEXES

No.	Compound	$\delta(CH_2)$	$\delta(CH_3)$	$\delta(OCH_3)$	$\delta(NCH_3)$	$\delta(NCH_2)$	$\nu(C{=}O)$
	HNPhCOOMe			3.41			1748
(IVa)	$(EtZnNPhCOOMe)_3$	0.45	1.36	3.54			1587
(IVb)	EtZnNPhCOOMe·2 Py	0.79	1.68	3.56			1667
(IVc)	EtZnNPhCOOMe·TMED	0.26	1.56	3.58	1.92	1.85	1681

The PMR and IR data are shown in Table 4. It appears that the strong band at 1587 cm^{-1} in the carbonyl region observed for $(EtZnNPhCOOMe)_3$ (IVa) is shifted to lower frequency relative to the $\nu(C{=}O)$ of HNPhCOOMe. Upon complexation with Py or TMED, this band shifts partly back to higher frequency. If the band at 1587 cm^{-1} of (IVa) and those at 1667 cm^{-1} and 1681 cm^{-1} of its Py and TMED complexes [(IVb) and (IVc)] are taken as carbonyl stretching absorptions, the remaining difference between the $\nu(C{=}O)$ value of HNPhCOOMe and those of the complexes (IVb) and (IVc) can be ascribed to the mass effect of the ethylzinc group [*cf.* the discussion of the IR spectrum of $(EtZnNPhCOMe)_4$; see also ref. 21].

Although a structure containing a Zn_3O_3 ring cannot be ruled out, we propose a structure for trimeric EtZnNPhCOOMe consisting of a Zn_3N_3 ring, in which the carbonyl groups effect coordination saturation of the zinc atoms. The formation of a

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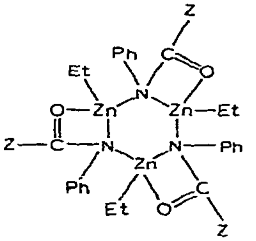
* This study was kindly performed by Dr. J. J. Daly (Monsanto Research S.A., Zürich, Switzerland).

six-membered ring in solutions of this compound can be explained on the basis of valency angle strain (*cf.* ref. 9).



(IVa), Z = OMe
(VIa), Z = NPh_2

S-Methyl N-(ethylzinc)thiocarbanilate, EtZnNPhCOSMe [(*Va*)–(*Vc*)]

The unstability of this compound above 5° prevents its synthesis by the reaction between Et_2Zn and HNPhCOSMe, since below 5° the reaction rate is extremely low. When the reaction is carried out at room temperature in benzene solution, a voluminous white precipitate is formed, accompanied by the evolution of ethane. The presence of PhNCO in the supernatant solution was detected by IR spectroscopy (strong band at 2275 cm^{-1}). Upon addition of Py or TMED to the reaction mixture, the precipitate redissolved completely and the NCO absorption vanished from the IR spectrum. When the isolated precipitate was dissolved in benzene containing Py or TMED, the IR spectra of the resulting clear solutions were superimposable with those of the corresponding complexes of EtZnSMe, which itself is a highly polymeric, insoluble compound[3]. These results indicate the following mode of decomposition:

$$\text{EtZnNPhCOSMe} \rightarrow \text{EtZnSMe} + \text{PhNCO}$$

When the initial reaction mixture of Et_2Zn and HNPhCOSMe was treated with one equivalent of TMED, the IR spectrum of the resulting solution was superimposable with that of a 1/1/1 mixture of EtZnSMe, PhNCO and TMED in benzene. Again, the NCO absorption was lacking from the IR spectrum. The presence of a strong band in the carbonyl region at 1704 cm^{-1} indicates that, under the influence of TMED, the following reaction has occurred:

$$\text{EtZnSMe} + \text{PhNCO} + \text{TMED} \rightarrow \text{EtZnNPhCOSMe}\cdot\text{TMED}$$

The alternative possibility—reaction of the PhNCO with the Zn–C bond of EtZnSMe—can be excluded, since the PMR spectrum of the solution indicated only ethyl groups bound to zinc.

EtZnNPhCOSMe forms monomeric 1/1 complexes both with Py (Vb) and TMED (Vc). The coordination behaviour towards Py is different from that of $(EtZnNPhCOOMe)_3$ which yields a 1/2 complex with Py. Because of the instability of EtZnNPhCOSMe itself, it was impossible to obtain more information regarding its structure. The easy decomposition into EtZnSMe suggests the presence of Zn–S coordinate bonds in this compound.

N-(Ethylzinc)-N,N′,N′-triphenylurea, EtZnNPhCONPh₂, [(*VIa*)–(*VIc*)]

This compound is trimeric in benzene, the molecular weight being independent of the concentration. The behaviour of $(EtZnNPhCONPh_2)_3$ towards complexing agents is completely analogous to that of $(EtZnNPhCOOMe)_3$. Here also, complete breakdown of the trimeric structure occurs upon addition of complexing agents, resulting in a 1/2 Py complex (VIb) and a 1/1 TMED complex (VIc).

IR and PMR data are shown in Table 5.

In the IR spectrum, the absorption in the carbonyl region observed at 1515 cm^{-1} for $(EtZnNPhCONPh_2)_3$, shifts back to higher frequency upon complexation with Py and TMED, indicating the breaking of coordinate bonds [*cf.* the IR data of (IVa)–(IVc)].

TABLE 5

IR AND PMR DATA OF $(EtZnNPhCONPh_2)_3$ AND ITS COMPLEXES

No.	Compound	$\delta(CH_2)$	$\delta(CH_3)$	$\nu(C=O)$
	$HNPhCONPh_2$			1678
(VIa)	$(EtZnNPhCONPh_2)_3$	0.13	0.75	1515
(VIb)	$EtZnNPhCONPh_2 \cdot 2\ Py$	0.71	1.63	1704
(VIc)	$EtZnNPhCONPh_2 \cdot TMED$	0.23, 0.31[a]	1.55, 1.59[a]	1704

[a] Relatively broad bands.

The PMR data show that the introduction of a diphenylamino group has interesting consequences. The ethyl group absorptions of $(EtZnNPhCONPh_2)_3$ are found at extremely high field, $\delta(CH_3)$ being even smaller than in Et_2Zn [*cf.* also the values for $(EtZnNPhCOOMe)_3$: $\delta(CH_2)=0.45$ ppm and $\delta(CH_3)=1.36$ ppm]. This must be the result of a shielding effect of the diphenylamino group since in general the methyl protons are rather insensitive to changes in the electron density at zinc. At the same time this phenomenon shows that the trimer has a sterically congested structure, since the shielding effect can be active only in the direct environment of the anisotropic group. The PMR spectrum of the monomeric Py complex (VIb) again shows $\delta(CH_3)$ with the normal value of 1.63 ppm. The influence of steric factors on the molecular structure of $(EtZnNPhCONPh_2)_3$, as apparent from its PMR spectrum, is nicely illustrated by the spectrum of the TMED complex. In the latter, the ethyl group absorptions are found at lower field than in the parent compound, although normally complexation with TMED results in a high-field shift of the methylene absorptions. This abnormal shift is clearly caused by the removal of the shielding effects mentioned earlier, through breakdown of the trimeric structure. It is not clear why, contrary to the Py complex, the likewise monomeric TMED complex should display two sets of ethyl group absorptions (of equal height) in its PMR spectrum.

Although, as for (IVa) a structure with a Zn_3O_3 ring cannot be ruled out, we propose a structure with a six-membered Zn_3N_3 ring in which the zinc atoms have become four-coordinate by carbonyl coordination.

EXPERIMENTAL

Experimental techniques are identical to those described in ref. 7.

N-(Ethylzinc)diphenylamine (Ia)

1.18 g (9.57 mmole) of Et_2Zn was mixed with 1.20 g (7.10 mmole) of Ph_2NH and the mixture heated at 90° for 30 min. After that time the ethane evolution had subsided and the reaction mixture had solidified. It was recrystallized from 10 ml of n-hexane, washed three times with 5 ml of cold n-hexane and dried *in vacuo*. Yield: 1.42 g (76%):

Zinc bis(diphenylamide) (Ie)

A solution of 2.28 g (1.04 mmole) of Ph_2Zn and 3.51 g (2.08 mmole) of Ph_2NH in 20 ml of toluene was heated under reflux for 3 h. During the reaction a greenish-white precipitate settled out. After cooling to room temperature the supernatant liquid was removed and the residue washed once with 10 ml of toluene and twice with 10 ml of n-hexane, resulting in a nearly quantitative yield of colourless, crystalline product.

N-(Ethylzinc)acetanilide (IIa)

By consecutive addition of pellets weighing about 0.2 g each, 2.0 g (14.8 mmole) of acetanilide was added to a solution of 2.0 g (16.2 mmole) of Et_2Zn in 15 ml of benzene, cooled at 10°. The reaction was instantaneous and slightly exothermic. When all of the acetanilide had been added, the reaction mixture was heated at 60° for 15 min. The excess of Et_2Zn and the solvent were removed *in vacuo* and the residue —a glassy solid—was dissolved in 20 ml of n-hexane. After cooling down to −78°, the product crystallized out, was washed three times with 10 ml of n-hexane and dried *in vacuo* at room temperature.

(IIIa) and (IVa) were prepared in an essentially similar way. Also the attempted preparation of *S*-methyl *N*-(ethylzinc)thiocarbanilate was carried out in this way.

N-(Ethylzinc)-N,N',N'-triphenylurea (VIa)

1.42 g (5.42 mmole) of $EtZnNPh_2$ was dissolved in 50 ml of boiling n-pentane and 0.65 g (5.42 mmole) of PhNCO was added with stirring. A colourless solid precipitated from the solution. The reaction mixture was boiled under reflux for 1 h. Thereafter, the supernatant solution was removed and the residue washed three times with 10 ml of hot n-pentane. After drying *in vacuo*, the product was recrystallized from n-hexane. Crystallization, even from very concentrated solutions, took several days.

Py complex of N-(ethylzinc)acetanilide (IIb)

To a stirred solution of 3.06 g (13.4 mmole) of $(EtZnNPhCOMe)_4$ in 20 ml of benzene was added dropwise with stirring 1.42 g (18.0 mmole) of pyridine. After heating at 60° for 30 min the solvent and the excess of pyridine were removed *in vacuo*. The residual oil was made to crystallize by stirring with 20 ml of n-pentane at −78°. The crystalline product was washed two times with 20 ml of n-pentane and dried *in vacuo*.

TMED complex of N-(ethylzinc)acetanilide (IIc)

2.35 g (20.2 mmole) of TMED were added dropwise to a stirred solution of 4.62 g (20.2 mmole) of EtZnNPhCOMe in 15 ml of benzene. After heating for 30 min at 60° the solvent was removed *in vacuo*. 20 ml of n-pentane were added to the oily residue and the resulting inhomogeneous mixture cooled down to −78°. Upon scratching with a glass rod the oil crystallized out. The product was washed two times with 20 ml of n-pentane and dried *in vacuo*.

All other Py and TMED complexes reported in this paper were prepared in a fully similar way.

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