

INVESTIGATIONS ON ORGANOZINC COMPOUNDS VIII*. THE INFLUENCE OF π -BONDING ON THE STABILITY OF DIALKYLZINC-2,2'-BIPYRIDINE COMPLEXES

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INTRODUCTION

The electronic absorption spectra of 2,2'-bipyridine and 1,10-phenanthroline complexes of dialkylzincs^{1,2} display long-wavelength charge-transfer bands which have been proposed to arise from the transition of metal d -electrons to vacant π -type ligand orbitals¹. The extent to which d_{π} -bonding may occur with d^{10} -metal ions has generally been considered unimportant in view of the high ionization potential of the non-bonding d^{10} -shell of these ions^{3,4}. This is not necessarily true for organo- d^{10} -metal complexes. In dialkylzinc compounds the Zn-C bond has a largely covalent character ($\sim 80\%$ using Pauling's formula⁵). Therefore, the formal positive charge on the Zn atom and, accordingly, the ionization energy of a $3d$ -electron will be considerably less for R_2Zn than for Zn^{2+} complexes (the 2,2'-bipyridine complex of *e.g.* $ZnBr_2$ fails to display a charge-transfer band in its electronic absorption spectrum^{1,6}).

Because of the synergism between σ - and π -bonding⁷ the occurrence of any significant back-coordination in organozinc complexes is likely to be reflected in the complex stability. Therefore, we have compared the stability of a series of dialkylzinc complexes with two extreme types of ligands, *e.g.* N,N,N',N'-tetramethylethylenediamine (TMED) and 2,2'-bipyridine (Bipy). TMED can take part in dative σ -bonding only, because it lacks the necessary vacant orbitals for back-acceptance of electron-density. Bipy, apart from being a σ -donor, is capable of π -bonding by accepting electron-density from filled metal π -orbitals with the appropriate symmetry into the π^* -antibonding orbitals of the ring system.

The complex stability of $R_2Zn \cdot TMED$ ($R = Me, Et, iso-Pr$ and *tert*-Bu) and of $R_2Zn \cdot Bipy$ ($R = Me, Et, iso-Pr, n-Bu, iso-Bu$ and *tert*-Bu) was investigated using a dielectric constant titration technique⁸.

EXPERIMENTAL PART

Materials

Dialkylzinc compounds were prepared following the Grignard ($R = Me,$

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tert-Bu) or direct synthesis ($R = \text{Et, iso-Pr, n-Bu, iso-Bu}$) route.

Di-tert-butyizinc was freed from the last traces of ether by repeated sublimation *in vacuo*. It was obtained as a colourless, crystalline solid with m.p. 28.8° (reported⁹: ca. 25°). (Found: Zn, 35.84. $\text{C}_8\text{H}_{18}\text{Zn}$ calcd.: Zn, 36.40%) The NMR spectrum (toluene solution) consists of one sharp singlet ($\delta = +1.06$ ppm; TMS internal standard). tert-Bu₂Zn forms a colourless, crystalline 1:1 complex (m.p. $91-92^\circ$) with TMED. (Found: Zn, 22.13. $\text{C}_{14}\text{H}_{34}\text{N}_2\text{Zn}$ calcd.: Zn, 22.14%) The 1:1 complex with Bipy is a dark-purple, crystalline solid with m.p. 94° . (Found: Zn, 19.23. $\text{C}_{18}\text{H}_{28}\text{N}_2\text{Zn}$ calcd.: Zn, 19.47%)

Procedure

Details concerning the dielectric constant titration technique for determining complex stabilities are reported in a separate publication⁸.

RESULTS AND DISCUSSION

Whereas both R_2Zn^{10} and the symmetrical molecules TMED and Bipy have

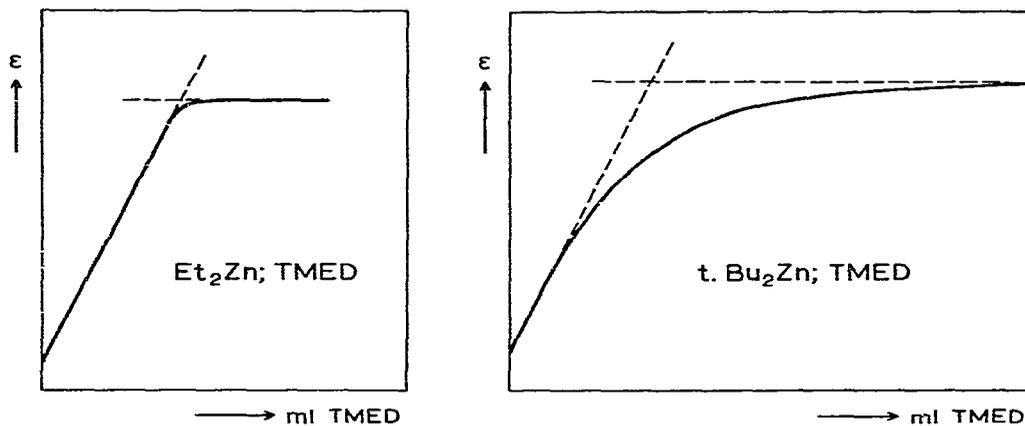


Fig. 1. Dielectric constant titration of Et_2Zn and tert-Bu₂Zn with TMED in benzene

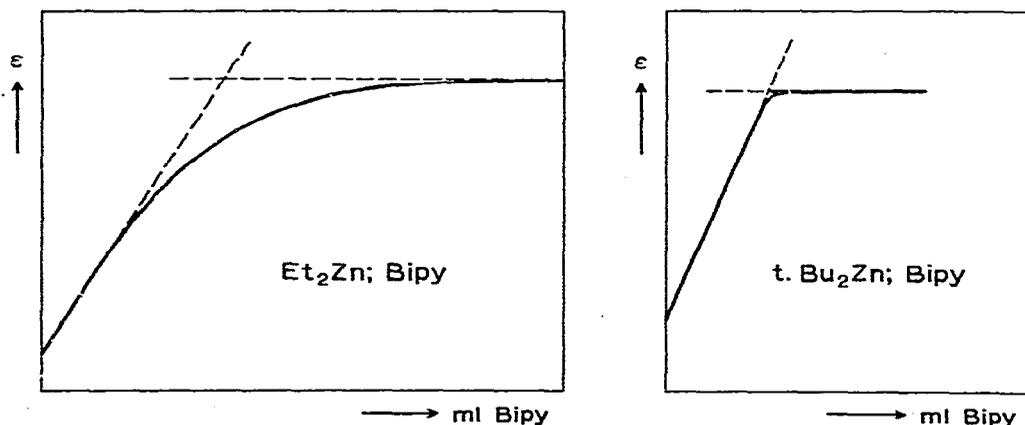


Fig. 2. Dielectric constant titration of Et_2Zn and tert-Bu₂Zn with Bipy in benzene.

zero or negligibly small dipole moments, the complexes $R_2Zn \cdot TMED$ and $R_2Zn \cdot Bipy$ have a considerable dipole moment. Thus, upon adding TMED or Bipy to R_2Zn in a non-polar solvent the dielectric constant ϵ of the solution will increase until complex formation is complete. In a plot of ϵ as a function of the amount of complexing agent added the difference between the value of ϵ in the equivalence point and the value of ϵ obtained by extrapolating to a large excess of complexing agent is a function of the dissociation constant of the complex⁸.

Representative titration curves are presented in Figs. 1 and 2. Dissociation constants derived from the titration curves⁸ are summarized in Table 1.

TABLE 1

DISSOCIATION CONSTANTS ($10^5 K$) OF SOME $R_2Zn \cdot TMED$ AND $R_2Zn \cdot Bipy$ COMPLEXES

R	$R_2Zn \cdot TMED$		$R_2Zn \cdot Bipy$	
	Benzene	Cyclohexane	Benzene	Cyclohexane
Me	<0.04		80	
Et	1	4	30	145
iso-Pr	4		6	
tert-Bu	60	~600	0.3	2

Our results show that for the TMED complexes the order of stability is $Me > Et > iso-Pr > tert-Bu$. This is the expected sequence, because electron-releasing substituents increase the electron-density on the metal thereby weakening the coordinative bonds with TMED which has a pure σ -donor function only. Complex stability will also be influenced by steric effects (*cf.* ref. 11). The order of stability follows the order of both the polar and steric substituent constants¹² of the alkyl groups.

For the Bipy complexes the observed order of stability is $tert-Bu > iso-Pr > Et > Me$. This sequence cannot be explained if only dative σ -bonding is taken into account. Both electronic and steric effects would suggest the order found for the TMED complexes. However, the discrepancy is removed, if it is accepted that π -bonding occurs in the Bipy complexes. π -Bonding in transition metal complexes is strongly favoured, if the metal atom carries a formal negative charge or if the metal is substituted with electron-donating groups^{3,7}. Taking into account the relative electron-donating properties of alkyl groups¹² synergic σ - π bonding in the $R_2Zn \cdot Bipy$ complexes would be expected to become more effective going from Me to tert-Bu in the above sequence. Whereas the n-Bu and iso-Bu group have about the same electron-releasing properties, the iso-Bu has higher steric requirements¹². We found the Bipy complex of n-Bu₂Zn ($10^5 K = 40$) and of iso-Bu₂Zn ($10^5 K = 38$) to have approximately the same stability in benzene solution. This result suggests that for this type of complexes electronic effects are more important than steric effects in determining complex stability.

After the completion of this work Thiele and Zdunneck¹¹ have reported a stability sequence $Et > n-Pr > n-Pent > n-Bu > Me$ for $R_2Zn \cdot Bipy$ complexes. This order was based on the results of cryoscopic molecular weight determinations in benzene. The complexes (R = n-Pent and n-Bu) were found to absorb at longer wavelength than the more stable complexes (R = Et and n-Pr). However, a deep colour of a charge-transfer complex is usually associated with high complex stability¹³. Indeed,

purple-coloured $\text{tert-Bu}_2\text{Zn} \cdot \text{Bipy}$ which we found to be the most stable absorbs at considerably longer wavelength (λ_{max} 485 μ) than *e.g.* orange-coloured $\text{Et}_2\text{Zn} \cdot \text{Bipy}$ (λ_{max} 420 $\text{m}\mu^{1,11}$). The solvation effect of solvent benzene cited by Thiele *et al.*¹¹ to explain their anomalous results would not seem to be important, since we observed an identical stability sequence in benzene and cyclohexane (Table 1).

We conclude from our results that π -bonding is operative in $\text{R}_2\text{Zn} \cdot \text{Bipy}$ complexes and that, in fact, this is the predominant factor determining the stability of this type of complexes.

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SUMMARY

The stability of a number of complexes of dialkylzinc compounds R_2Zn with N,N,N',N'-tetramethylethylenediamine (TMED) and with the potentially π -bonding ligand 2,2'-bipyridine (Bipy) has been compared using a dielectric constant titration technique. The stability of the $\text{R}_2\text{Zn} \cdot \text{TMED}$ complexes decreases in the expected order: $\text{Me} > \text{Et} > \text{iso-Pr} > \text{tert-Bu}$. The reversed stability sequence: $\text{Me} < \text{Et} < \text{iso-Pr} < \text{tert-Bu}$ has been observed for the $\text{R}_2\text{Zn} \cdot \text{Bipy}$ complexes. It is concluded that π -bonding is the predominant factor determining the stability of the latter type of complexes.

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