INVESTIGATIONS ON ORGANOZINC COMPOUNDS

I. SOME COORDINATION COMPLEXES OF DIBUTYL-, DIPHENYL-, AND BIS(PENTAFLUOROPHENYL)ZINC

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INTRODUCTION

Since Wanklyn[1] in 1858 reported the isolation of $NaZnEt_3$, various anionic organozinc complexes have been reported in the literature. Examples of these include the complex anions ZnR_3^- (ref. 2), ZnR_2H^- (ref. 3), ZnR_4^{2-} (ref. 4), and $Zn(C{\equiv}CH)_4^{2-}$ (ref. 5).

Organozinc compounds were, however, generally held to be unable to form neutral donor–acceptor complexes, but very recently, the first examples of well-defined coordination complexes have been reported. An indication of their existence was the observation made in 1859 by Frankland[6] that the use of dimethyl or diethyl ether as a solvent greatly facilitates the formation of dimethylzinc from zinc and methyl iodide and that separation of the product from the solvent proved to be impossible. Thiele[7] recently studied the interaction of dimethylzinc with a variety of linear and cyclic, mono- and bivalent ethers and succeeded in isolating a number of well-defined crystalline or liquid, distillable 1:1 and 1:2 coordination complexes. The formation of crystalline mono-dioxane complexes of a number of arylzinc compounds had already been mentioned by Sheverdina *et al.*[8]. A crystalline 1:1 complex of diethylzinc and isoquinoline recently has been isolated by Pajaro *et al.*[9]. Coloured 2,2′-bipyridine complexes of dimethyl- and diethylzinc have recently been mentioned in the literature[10].

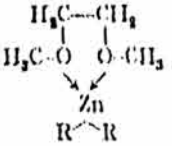
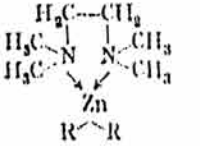
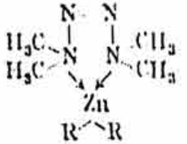
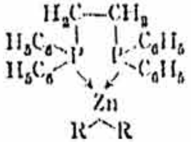
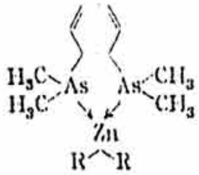
Current interest in this subject leads us to publish some of the results obtained in our study of the complex-forming behaviour of organozinc compounds.

RESULTS

In the present study we have found that organozinc compounds are capable of forming stable coordination complexes having well-defined stoichiometry with a variety of oxygen-, nitrogen-, phosphorus- and arsenic-containing ligands. The influence of the organic substituent R on the acceptor properties of the zinc atom has been investigated by suitable variation of R. Complexes have been prepared of dibutylzinc, diphenylzinc and the not previously reported bis(pentafluorophenyl)zinc. The latter compound has been obtained as a colourless crystalline solid (m.p. 91–93°) by the reaction of zinc chloride with pentafluoromagnesium bromide in diethyl ether:

$$ZnCl_2 + 2C_6F_5MgBr \rightarrow (C_6F_5)_2Zn + MgCl_2 + MgBr_2$$

TABLE I. SOME COORDINATION COMPLEXES OF ORGANOZINC COMPOUNDS

Complex	*No.*	*R*	*M.p. °C*	*Solvent*	*Formula*	*Zinc* % *Calcd.*	*Zinc* % *Found*
	(I,a) (I,b)	C_6H_5 C_6F_5	60–61 108–109	pentane pentane	$C_{16}H_{20}O_2Zn$ $C_{16}H_{10}F_{10}O_2Zn$	21.14 13.36	22.09 13.51
	(II,a) (II,b) (II,c)	C_4H_9 C_6H_5 C_6F_5	liquid 123–124 161–162	— benzene–pentane benzene–pentane	$C_{14}H_{34}N_2Zn$ $C_{18}H_{26}N_2Zn$ $C_{18}H_{16}F_{10}N_2Zn$	22.31 19.50 12.69	22.24 19.81 13.31
	(III,a) (III,b) (III,c)	C_4H_9 C_6H_5 C_6F_5	~ 45 54–55 136–137	— pentane pentane	$C_{12}H_{30}N_4Zn$ $C_{16}H_{22}N_4Zn$ $C_{16}H_{12}F_{10}N_4Zn$	22.31 19.50 12.69	22.72 19.90 13.25
	(IV,a) (IV,b)	C_6H_5 C_6F_5	142–143 166–167	benzene–pentane pentane	$C_{18}H_{40}P_2Zn$ $C_{18}H_{30}F_{10}P_2Zn$	8.78 7.08	8.68* 7.24
	(V,a) (V,b) (V,c)	C_4H_9 C_6H_5 C_6F_5	114 (sintering) 185–187 211–213	pentane benzene benzene–pentane	$C_{34}H_{42}P_2Zn$ $C_{38}H_{34}P_2Zn$ $C_{38}H_{24}F_{10}P_2Zn$	11.31 10.58 8.20	10.61** 10.44 8.28
	(VI,a) (VI,b) (VI,c)	C_4H_9 C_6H_5 C_6F_5	liquid 132–133 136–137	— benzene–pentane pentane	$C_{18}H_{34}As_2Zn$ $C_{22}H_{26}As_2Zn$ $C_{22}H_{16}As_2F_{10}Zn$	14.04 12.93 9.54	14.56 12.69 9.57

* P, calcd. 8.33%; found: 8.63%. ** P, calcd. 10.74%; found: 11.13%.

The ligands used include ethyleneglycol dimethyl ether (I,a,b), ethylenebis(dimethylamine) (II,a,b,c), tetramethyl-2-tetrazene (III, a,b,c), triphenylphosphine (IV,a,b), ethylenebis(diphenylphosphine) (V,a,b,c), and *o*-phenylenebis(dimethylarsine) (VI, a,b,c). The complexes prepared have been summarized in Table 1.

The properties of a series of 2,2'-bipyridine and *o*-phenanthroline complexes including those containing various other groups R, have been discussed in a separate paper[11].

Complexes of zinc bromide with the same ligands as mentioned in Table 1 (R = Br) have been prepared incidentally to this investigation. These are listed in Table 2.

TABLE 2

SOME COORDINATION COMPLEXES OF ZINC BROMIDE

Complex[*]	*M.p. °C*	*Solvent*	*Formula*	*Zinc*	
				% Calcd.	*% Found*
(I,c)	103–105	diglyme[**]	$C_4H_{10}Br_2O_2Zn$	20.76	20.42
(II,d)	182	ethanol	$C_6H_{16}Br_2N_2Zn$	19.18	19.53
(III,d)	dec.	ether	$C_4H_{12}Br_2N_4Zn$	19.18	19.17
(IV,c)	200 (dec.)	ethanol	$C_{36}H_{30}Br_2P_2Zn$	8.72	8.79
(V,d)	275	ethanol	$C_{26}H_{24}Br_2P_2Zn$	10.48	10.08
(VI,d)	200–202	ethanol	$C_{10}H_{16}As_2Br_2Zn$	12.79	12.85

[*] *Cf.* Table 1 (R = Br).
[**] Ethyleneglycol dimethyl ether.

DISCUSSION

It seems reasonable to assume a chelate structure (tetra-coordinated zinc) for the 1:1 complexes with bidentate ligands. Although the formation of sp^2-hybridized planar complexes (1:1 complex with monodentate ligand) recently has been reported[7,9], formation of tetrahedral complexes with sp^3 hybridization of the zinc atom is the expected situation in view of its $3d^{10}4s^2$ electron configuration. Indeed, the monodentate ligand triphenylphosphine yielded 2:1 complexes (IV,a and IV,b).

By increasing the electronegative character of the organic group R on zinc, the polar character of the zinc–carbon bond will be enhanced. Negative charge is being pulled away from the zinc atom causing the electron affinity of the vacant orbitals of zinc and, consequently, the tendency to form donor-acceptor complexes to be increased (compare ref. 12). In keeping with the fact that phenyl groups are more electron-attracting than butyl groups, diphenylzinc forms coordination complexes more readily than does dibutylzinc. Whereas diphenylzinc readily forms complexes with ethyleneglycol dimethyl ether (I,a) and with triphenylphosphine (IV,a), dibutylzinc forms a thermally very unstable complex with the first ligand (complete dissociation at 40° and 0.01 mm Hg) and fails to complex with triphenylphosphine. Similarly, the diphenylzinc complex of *o*-phenylenebis(dimethylarsine) (VI,b) is much more stable than the dibutylzinc complex (VI,a) which slowly loses dibutylzinc upon heating *in vacuo*.

The possibility must be taken into account that the complexes derived from phosphorus- or arsenic-containing ligands are stabilized by $d\pi$–$d\pi$ back-bonding of electrons from the filled $3d$ orbitals of zinc to empty d orbitals of phosphorus or arsenic. However, the dibutylzinc complexes (II,a and III,a) with nitrogen-containing ligands which lack the possibility of $d\pi$–$d\pi$ bonding are more thermally stable than the ditertiary arsine complex (VI,a). Lewis *et al.* recently considered the role of $d\pi$–$d\pi$ bonding in ditertiary arsine complexes of d^{10} metals unimportant in view of the high ionization potential of the non-bonding d^{10} shell of the metal atoms[13]. Moreover, introduction of more electronegative groups on zinc, while increasing the strength of the phosphorus (arsenic) to zinc σ-bond of the complex, at the same time will decrease the tendency towards $d\pi$–$d\pi$ back-bonding from zinc to ligand. The first effect is clearly dominant as appears from the fact that the diphenylzinc complexes are more stable than the dibutyl complexes. Unsuccessful attempts have been made to isolate coordination complexes of dibutylzinc with triphenylphosphine, triphenylarsine and ethylenebis(diphenylarsine). The latter ligands do coordinate with diphenylzinc, but analytically pure complexes with the arsenic-containing ligands could not be isolated.

In accordance with the recent finding that the pentafluorophenyl group and the bromine atom have approximately the same electron-attracting properties[14,15], bis(pentafluorophenyl)zinc was found to form coordination complexes readily (I,b; II,c; III,c; IV,b; V,c; VI,c).

Although quantitative data are lacking, the zinc–carbon bond in the complexes mentioned in Table 1 seems to be less sensitive towards hydrolysis than in the parent organozinc compounds.

Whereas the organozinc complexes with tetramethyl-2-tetrazene (III,a,b,c) appear to be stable at moderate temperatures, the zinc bromide complex of this ligand (III,d) decomposes upon heating with evolution of a gas. The chloride analogue is even more unstable and explosively decomposes above room temperature. In a few preliminary experiments samples of the chloride complex have been carefully decomposed in n-hexane at 40–60° C until the evolution of gas had ceased. A solid product remained, the analysis of which suggests the formation of zinc chloride–tetramethylhydrazine complex. This behaviour seems to be unique for zinc as the corresponding complexes of cadmium and mercury halides have been reported to melt normally (m.p. $CdCl_2$ complex: 250° C; m.p. $HgCl_2$ complex: 93° C)[16]. We plan to look more closely into the thermal behaviour of the complexes (III,a,b,c,d) (for a related study see ref. 17).

EXPERIMENTAL PART

The organozinc compounds and their complexes are very sensitive to atmospheric moisture. Their preparation was carried out using the techniques described in a recent publication from our Institute[18].

Analyses for zinc were made by decomposing a sample of the complex (*ca.* 0.15 mmole) in a mixture of fuming nitric acid and fuming sulphuric acid, adjusting the pH to 10, and titrating Zn^{2+} with EDTA to Eriochrome Black T end-point.

Melting points have been taken in sealed capillaries (nitrogen atmosphere) and have not been corrected.

Ethylenebis(dimethylamine)[19], tetramethyl-2-tetrazene[16], ethylenebis(diphenylphosphine)[20], ethylenebis(diphenylarsine)[21] and o-phenylenebis(dimethylarsine)[22] were prepared according to published procedures. The other ligands used were commercial preparations.

Dibutylzinc[23] and diphenylzinc[2] were obtained according to the literature.

Bis(pentafluorophenyl)zinc

In a 500 ml three-necked flask provided with stirrer, reflux condenser, dropping funnel and inlet and outlet tubes for maintaining a nitrogen atmosphere, a solution of pentafluorophenylmagnesium bromide[24] was prepared from 3.8 g magnesium, 35.0 g (0.14 mole) of pentafluorobromobenzene and 100 ml of diethyl ether. To the Grignard reagent a solution of 9.7 g (0.07 mole) of anhydrous zinc chloride in 150 ml of diethyl ether was added dropwise with stirring. The reaction mixture was kept at reflux temperature for one hour. Diethyl ether was removed by distillation and replaced by 300 ml of toluene. The mixture was kept at reflux temperature for two hours causing the precipitation of inorganic salts which were removed by filtration. The filtrate was diluted with 300 ml of *n*-pentane and allowed to stand for 16 hours. After filtration and evaporation of the solvents, crude bis(pentafluorophenyl)zinc–diethyl ether complex remained as a dark-brown viscous oil. The complex was decomposed upon distillation *in vacuo* (bath temperature *ca.* 140°C; 0.1 mm Hg) affording 5.9 g of a colourless oil which crystallized for the greater part. The adhering oil was removed by washing with a small quantity of *n*-pentane affording 4.2 g (15%) of colourless crystals with m.p. 91–93°C. (Found: Zn, 16.13. $C_{12}F_{10}Zn$ calcd.: Zn, 16.36%.)

Preparation of complexes (see Tables 1 and 2)

Complex (I,a) was prepared by dissolving diphenylzinc in ethyleneglycol dimethyl ether, heating at 60°, evaporating excess of ether *in vacuo*, and crystallizing the complex by addition of pentane.

Complexes (I,b) and (I,c) were obtained in the same way.

Complex (II,a) was obtained by heating a mixture of dibutylzinc and excess of ethylenebis(dimethylamine) at 70°, and removing excess of ligand at 80°C and 0.1 mm Hg. A colourless liquid remained which could not be made to crystallize.

Complex (II,b) crystallized upon addition of pentane to a solution of diphenylzinc and ethylenebis(dimethylamine) in a small volume of benzene followed by cooling. The crystals were washed with pentane and dried *in vacuo*.

Complexes (II,c), (III,b), (IV,a), (V,b), (V,c), and (VI,b) were obtained in the same way.

Complex (III,a) remained as a colourless liquid which crystallized at *ca.* —45° when a mixture of dibutylzinc and excess of tetramethyl-2-tetrazene was heated at 60°C followed by removing excess of ligand at 50°C and 0.1 mm Hg.

Complex (III,c) separated as colourless crystals upon addition of excess of tetramethyl-2-tetrazene to a solution of bis(pentafluorophenyl)zinc in pentane and cooling. The crystals were washed with pentane and dried *in vacuo*.

Complexes (IV,b) and (IV,c) were prepared similarly.

Complex (V,a) was obtained by heating a mixture of equimolar amounts of dibutylzinc and ethylenebis(diphenylphosphine) at 120°, adding pentane to the clear mixture obtained, cooling at 0°, washing the crystals thus obtained with pentane and drying the product *in vacuo*.

Complex (VI,a) was obtained as a colourless liquid by heating a mixture of *o*-phenylenebis(dimethylarsine) and excess of dibutylzinc at 70°C, and then removing excess of dibutylzinc at 40°C and 0.1 mm Hg.

Unsuccessful attempts were made to isolate well-defined complexes of dibutylzinc with ethyleneglycol dimethyl ether and triphenylphosphine and of both dibutyl- and diphenylzinc with triphenylarsine and with ethylenebis(diphenylarsine).

Complex (II,d) crystallized upon addition of excess of ethylenebis(dimethylamine) to a solution of zinc bromide in ethanol. The crystals were washed with ethanol and dried.

Complex (III,d) crystallized upon cooling a solution of zinc bromide and excess of tetramethyl-2-tetrazene in a large volume of diethyl ether. An explosive reaction occurs when these reactants are mixed in the absence of a solvent.

Complex (V,d) crystallized upon addition of a solution of zinc bromide in ethanol to a solution of excess of ethylenebis(diphenylphosphine) in benzene and cooling.

Complex (IV,c) was obtained similarly.

Complex (VI,d) was obtained by slowly evaporating *in vacuo* a solution of equimolar amounts of zinc bromide and *o*-phenylenebis(dimethylarsine) in absolute ethanol and washing the crystals thus obtained with acetone.

Synthesis and thermal decomposition of zinc chloride–tetramethyl-2-tetrazene complex

A solution of 2.7 g (0.02 mole) of anhydrous zinc chloride in 500 ml of anhydrous diethyl ether was filtered, cooled at 0° and added dropwise to a solution of 2.3 g (0.02 mole) of tetramethyl-2-tetrazene in 100 ml of diethyl ether kept at 0°. The crystalline solid which precipitated during the addition was collected by filtration and kept at 0°C under N_2. The product may explosively decompose when reaching room temperature. (Found: Zn, 26.31. $C_4H_{12}Cl_2N_4Zn$ calcd.: Zn, 25.92%.)

Upon heating a suspension of the complex in hexane at 40°C gas was evolved. The mixture was finally refluxed for one hour and evaporated *in vacuo* leaving a tan solid product. (Found: Zn, 29.81; Cl, 32.31. $C_4H_{12}Cl_2N_2Zn$ calcd.: Zn, 29.22; Cl, 31.60%.)

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SUMMARY

Dibutyl-, diphenyl-, and bis(pentafluorophenyl)zinc have been found capable of forming coordination complexes with various oxygen-, nitrogen-, phosphorus- and arsenic-containing ligands. Bidentate ligands yield 1:1 complexes, triphenylphosphine 2:1 complexes.

The influence of the organic groups attached to zinc on the stability of these complexes and the possible role of d_π–d_π bonding in complexes with phosphorus- and arsenic-containing ligands has been discussed.

Complexes with tetramethyl-2-tetrazene have been found to display interesting thermal behaviour.

The preparation of bis(pentafluorophenyl)zinc is reported.

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