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SYNTHESIS AND COORDINATION PROPERTIES OF ω -FUNCTIONALLY-SUBSTITUTED DIALKYLZINC COMPOUNDS

H.K. HOFSTEE, J. BOERSMA, J.D. VAN DER MEULEN and G.J.M. VAN DER KERK
Laboratory for Organic Chemistry, State University, Utrecht (The Netherlands)

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Summary

The synthesis and characterization are described of ω -functionally-substituted dialkylzinc compounds of the type $Zn[(CH_2)_3X]_2$, ($X = OCH_3, SCH_3, N(CH_3)_2$). For comparison, one higher homologue, viz. $Zn[(CH_2)_4OCH_3]_2$, was also prepared and studied.

The chemical properties, degrees of association, dipole moments and NMR spectral data point to exclusive intramolecular coordination between zinc and the hetero-atoms present.

Introduction

α -Functionally-substituted organozinc compounds of the type $RZnCH_2X$, have a long history. The Reformatsky-reagent, $ROOCCH_2ZnBr$, has long been of importance in organic synthesis [1]. In 1959 Wittig [2] synthesized iodo-methylenezinc iodide ($IZnCH_2I$) by treating diazomethane with zinc iodide. Later on, Simmons and Smith [3] obtained the same compound from activated zinc and methylene iodide. They discovered its ability to act as a carbene generator in the synthesis of cyclopropanes, which led to its designation as the "Simmons-Smith reagent". Dialkynylzinc compounds of the type $Zn(CH_2C\equiv CR)_2$ were described by Thiele [4].

Until recently much less was known about organozinc compounds carrying a functional group beyond the α -position. Iodoalkylzinc iodides with 4 or 5 methylene groups between zinc and iodine were reported by Thiele [6]. Dialkenylzinc compounds were prepared by St. Denis et al. [7], who in the case of di-4-pentenylzinc presented evidence for a coordinative interaction between zinc and the carbon-carbon double bond.

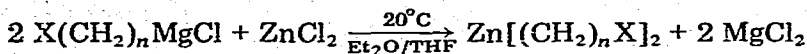
Very recently, Thiele et al. [8] reported the synthesis and associative behaviour of di-4-methoxybutylzinc, $Zn[(CH_2)_4OCH_3]_2$ and di-3-ethylmercaptopropylzinc, $Zn[(CH_2)_3SCH_2CH_3]_2$; both compounds are present as open-chain species,

chelate-ring formation by intramolecular coordination between zinc and the heteroatoms not occurring to a significant extent [8]. Their conclusions prompt us to report our studies on the synthesis and coordination chemistry of compounds of this type, viz. $Zn[(CH_2)_nX]_2$, ($n = 3$, $X = OCH_3, SCH_3, N(CH_3)_2$; and $n = 4$, $X = OCH_3$), which we required primarily for the synthesis of functionally-substituted alkyl compounds of copper, silver and gold [9].

Results

Synthesis and properties

The reaction of anhydrous zinc chloride with Grignard reagents of the type $X(CH_2)_nMgCl$ ($n = 3$, $X = OCH_3, SCH_3, N(CH_3)_2$ and $n = 4$, $X = OCH_3$) in a mixture of ether and THF affords dialkylzinc compounds of the type $Zn[(CH_2)_nX]_2$:



These compounds behave like common dialkylzinc compounds in being very sensitive to oxygen and moisture and very soluble in both polar and non-polar solvents. They can be stored indefinitely at room temperature under nitrogen. In contrast to non-substituted dialkylzinc compounds, they easily lose coordinating solvents such as ether and THF, as observed by Thiele [8], suggesting that in the functionally-substituted compounds the zinc atoms have already attained tetra-coordination. Ebulliometric molecular weight determinations (Table 1) show that all compounds are monomeric in benzene, the molecular weights being concentration independent. Therefore, the tetra-coordination of the zinc is not due to intermolecular association.

Spectroscopic data

In agreement with Thiele [8], we consider that the IR spectra of the functionally-substituted dialkylzinc compounds do not unambiguously indicate the

TABLE 1

EBULLIOMETRIC MOLECULAR WEIGHT MEASUREMENTS ON THE ω -FUNCTIONALLY-SUBSTITUTED DIALKYLZINC COMPOUNDS OF THE TYPE $Zn[(CH_2)_nX]_2$ ($n = 3$, $X = OCH_3, SCH_3, N(CH_3)_2$ AND $n = 4$, $X = OCH_3$) IN BENZENE

| Compound | Molecular weight Found (calcd.) (%) | Degree of association ^a |
|---------------------------------|--|---------------------------------------|
| $Zn[(CH_2)_3OCH_3]_2$ (I) | 216 (211.5) | 1.02 |
| $Zn[(CH_2)_3SCH_3]_2$ (II) | 244 (243.5) | 1.00 |
| $Zn[(CH_2)_3N(CH_3)_2]_2$ (III) | 234 (237.5) | 0.99 |
| $Zn[(CH_2)_4OCH_3]_2$ (IV) | 239 (239.6) | 1.00 |

^a All molecular weights were concentration independent.

presence or absence of coordinative interaction between zinc and the heteroatoms present.

The ^1H NMR spectral data for the compounds are presented in Table 2, together with those of the parent hydrocarbons and of dibutylzinc and its TMED complex. The resonance positions of the resonances for all compounds were concentration independent, and temperature independent within the range -90 to $+90^\circ\text{C}$. The chemical shifts of the α -hydrogens of the functionally-substituted dialkylzinc compounds are shifted to high field, but do not differ by more than 8–10 Hz from those of dibutylzinc. For intramolecular coordination one would have expected high-field shifts, comparable with those resulting from complexation of dibutylzinc with TMED, i.e. of about 20–25 Hz. On the other hand, the resonances from the hydrogen atoms neighbouring the functional substituents are shifted from their positions in the parent hydrocarbons. This suggests coordination of the heteroatoms involved. However, these shifts vary from an upfield shift of 25 Hz to a downfield shift of 25 Hz, and show no distinct pattern. These data show that ^1H NMR spectroscopy does not enable definite conclusions about the existence of intramolecular coordination.

It appeared that ^{13}C NMR spectroscopy might dissolve this dilemma, and the relevant data are summarized in Table 3. Again no concentration or temperature dependence was observed. In all the functionally-substituted compounds the absorptions of the α -carbon atoms are shifted upfield relative to those in dibutylzinc. A similar upfield shift is observed when dibutylzinc is complexed with 2,2'-bipyridine or TMED. On comparing the relative shifts ($\Delta = \delta(\text{R}_2\text{Zn}) - \delta(\text{RH})$) of the γ -carbon atoms for the functionally-substituted dialkylzinc compounds with those for dibutylzinc, it is found that the γ -carbon signals of the former appear at higher field. These high-field shifts can only be explained by the presence of fixed five- or six-membered ring systems. This so-called γ -effect is very general in the case of saturated ring systems [10–12]. Thus, in contrast

TABLE 2

THE ^1H NMR SPECTRA OF ω -FUNCTIONALLY-SUBSTITUTED DIALKYLZINC COMPOUNDS AND OF SOME REFERENCE COMPOUNDS IN C_6D_6

| Compound | Resonance positions (in ppm relative to internal TMS) ^a | | | | |
|--|--|---------|----------|----------|------------|
| | α | β | γ | δ | ϵ |
| $\text{H}(\text{CH}_2)_3\text{OCH}_3$ | 0.29 | 1.98 | 3.19 | | 3.17 |
| (I) | 0.88 | 1.52 | 3.24 | | 3.17 |
| $\text{H}(\text{CH}_2)_3\text{SCH}_3$ | 0.29 | 1.96 | 2.46 | | 1.82 |
| (II) | 0.90 | 1.42 | 2.15 | | 2.13 |
| $\text{H}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$ | 0.27 | 1.9 | 2.0 | | 2.0 |
| (III) | 0.88 | 1.47 | 2.29 | | 1.87 |
| $\text{H}(\text{CH}_2)_4\text{OCH}_3$ | 0.48 | 1.85 | 1.57 | 3.40 | 3.18 |
| (IV) | 0.92 | 1.5 | 1.5 | 3.28 | 3.21 |
| ZnBu_2 | 0.40 | 1.6 | 1.4 | 0.96 | |
| HBu | 0.91 | 1.4 | 1.4 | 0.91 | |
| $\text{ZnBu}_2 \cdot \text{TMED}$ | 0.18 | 1.8 | 1.6 | 1.16 | |

^a The spectra were recorded at room temperature. The resonance positions were concentration and temperature independent in the range -90 to $+90^\circ\text{C}$.

TABLE 3

¹³C NMR SPECTRA ^a OF ω -FUNCTIONALLY-SUBSTITUTED DIALKYLZINC COMPOUNDS AND OF SOME REFERENCE COMPOUNDS IN C₆D₆

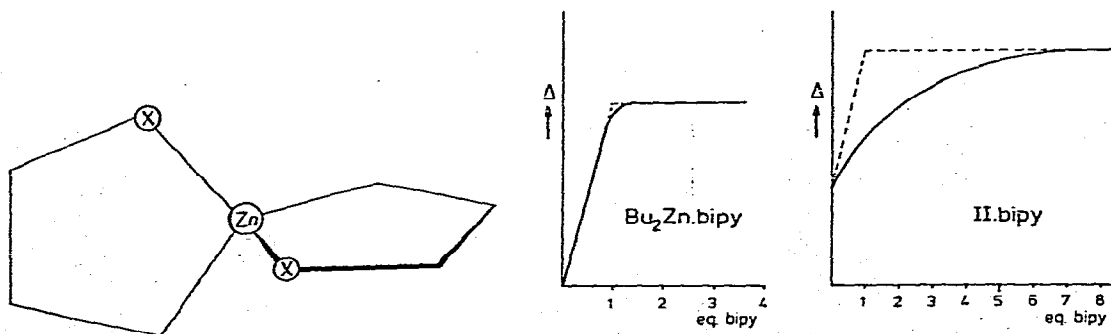
| Compound | Resonance positions Zn-C _{α} -C _{β} -C _{γ} -(C _{δ})-X-C _{ϵ} | | | | | Internal shift ^c Δ |
|--|---|---------|----------|----------|------------|---|
| | α | β | γ | δ | ϵ | |
| H(CH ₂) ₃ OCH ₃ (I) | 5.26 | 28.26 | 75.62 | | 58.10 | +1.02 |
| I · Bipy | 10.50 | 23.27 | 74.59 | | 58.04 | |
| I · TMED | 5.44 | 28.57 | 76.23 | | 58.07 | |
| H(CH ₂) ₃ SCH ₃ (II) | 5.69 | 30.05 | 79.72 | | 58.32 | |
| II · Bipy | 7.43 | 26.40 | 40.07 | | 14.09 | +4.43 |
| II · TMED | 13.45 | 22.82 | 36.64 | | 15.33 | |
| H(CH ₂) ₃ N(CH ₃) ₂ (III) | 7.76 | 26.79 | 40.17 | | 14.14 | |
| III · Bipy ^b | 10.25 | 29.80 | 41.87 | | 15.51 | +1.78 |
| III · TMED ^b | 4.09 | 26.40 | 63.86 | | 44.97 | |
| H(CH ₂) ₄ OCH ₃ (IV) | 11.88 | 21.35 | 62.08 | | 45.50 | |
| IV · Bipy | 4.06 | 26.43 | 63.83 | | 44.98 | |
| IV · TMED | 4.08 | 26.40 | 63.85 | | 44.96 | |
| ZnEt ₂ | 13.12 | 25.85 | 34.51 | 76.10 | 58.82 | |
| HBU | 14.00 | 19.71 | 32.21 | 72.59 | 58.19 | +2.31 |
| ZnBu ₂ · Bipy | 12.39 | 26.75 | 36.99 | 74.21 | 58.30 | |
| ZnBu ₂ · TMED | 11.12 | 26.91 | 37.89 | 73.94 | 58.36 | |
| | 16.06 | 29.01 | 29.73 | 14.27 | | +4.83 |
| | 13.10 | 24.90 | 24.90 | 13.10 | | |
| | 12.37 | 33.19 | 30.55 | 14.68 | | |
| | 11.06 | 33.09 | 30.74 | 14.73 | | |

^a Resonance positions in ppm relative to internal TMS. ^b Not isolated; data obtained from 1/1 solutions.^c Internal shift $\Delta = \delta(R_2Zn) - \delta(RH)$ of the γ -carbon atoms.

to the IR and ¹H NMR data, the ¹³C NMR data show clearly that intramolecular coordination occurs between zinc and the heteroatoms present. The resulting structures are schematically represented in Fig. 1.

Reactions of ω -functionally-substituted organozinc compounds with nitrogen-containing ligands

(a) With 2,2'-bipyridine (Bipy). In general dialkylzinc compounds form stable complexes with nitrogen-donor molecules [13]. The behaviour of the ω -func-

Fig. 1. Schematic structure of ω -functionally-substituted dialkylzinc compounds of the type Zn[(CH₂)₃X]₂.Fig. 2. Microwave titration of Bu₂Zn and II with bipy in benzene.

tionally-substituted dialkylzinc compounds towards such donor molecules was studied by microwave titrations and by reactions on a preparative scale. Reaction of the compounds with Bipy in hexane gave coloured solutions, from which crystalline 1/1 complexes were isolated for the compounds I, II, and IV (Table 4). Owing to extreme dissociation this was not possible for the Bipy-complex of III, indicating that in this case external coordination does not compete favourably with internal coordination.

An excellent way to study the reaction of these functionally-substituted dialkylzinc compounds with Bipy proved to be titration in benzene using the microwave technique developed by Adema and Schrama [14]. This technique provides information not only about the stoichiometry of the complexes formed, but also about their dissociation [15]. It appeared that the functionally-substituted dialkylzinc compounds have a considerable molecular damping, in contrast to simple dialkylzinc compounds such as Me_2Zn and Bu_2Zn , for which this damping is zero [16]. This implies that the former compounds have an appreciable dipole moment. As an example, in Fig. 2 the molecular damping is plotted as a function of the amount of Bipy added for dibutylzinc and for compound II ($\text{Zn}[(\text{CH}_2)_3\text{SCH}_3]_2$).

It appears that the complex of dibutylzinc is far less dissociated than that of the functionally-substituted dialkylzinc compound. All Bipy-complexes of compounds I–IV appeared to be more or less dissociated. Bipy was found to react in all cases in a one step reaction to give a coloured complex in which the zinc/bipy ratio is 1/1.

Because of the extreme dissociation of the final complexes accurate dissociation constants could not be derived from the microwave titration curves except for the Bipy-complex of IV. It appeared, however, that accurate values could be obtained from the ^{13}C NMR data. Only one set of Bipy signals was observed due to fast exchange in solution between complexed and uncomplexed Bipy. Consequently, the observed chemical shifts are the weight-averaged mean of those of free and of complexed Bipy and the dissociation constants can be calculated if these reference values are known. As reference values we took those of Bipy and of the Bipy complex of dibutylzinc, which has a very low dissociation constant ($K_D = 40 \times 10^{-5}$ mol/l).

TABLE 4

UV AND VISIBLE SPECTRAL DATA FOR 2,2'-BIPYRIDINE COMPLEXES OF ω -FUNCTIONALLY-SUBSTITUTED DIALKYLZINC COMPOUNDS AND OF SOME SIMPLE DIALKYLZINC COMPOUNDS IN BENZENE

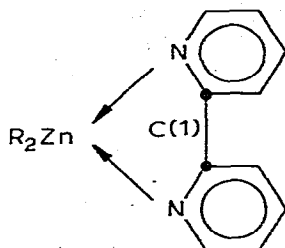
| Bipy-complex of compound | Colour | λ_{max} (nm) | Molar extinction ϵ_{max} at λ_{max} | Excitation energies E (kJ mol^{-1}) |
|--------------------------|------------|-----------------------------|--|--|
| I | orange-red | 405 | 300 | 293 |
| II | orange | 375 | 270 | 318 |
| III | purple | 530 | 250 | 226 |
| IV | red | 418 | 210 | 285 |
| Diethylzinc | red | 420 | — | 285 |
| Di-n-butylzinc | red | 425 | 360 | 281 |
| Di-t-butylzinc | purple | 551 | — | 218 |

The dissociation constants, which are presented in Table 5, were calculated using the C(1)-chemical shifts of the Bipy species, since these shifts are particularly sensitive to coordination. It appears that the dissociation constants increase in the order $K_D(\text{IV}) \ll K_D(\text{II}) < K_D(\text{I}) \ll K_D(\text{III})$, indicating that the strengths of internal zinc-heteroatom coordinate bonds increase in the same order. These data also show a five-membered ring (I), to be more stable than a six-membered ring (IV), other factors being equal. Partial or complete loss of internal coordination is also demonstrated by the ^{13}C NMR resonance positions of the γ -carbon atoms, shown in Table 3, which are shifted downfield compared to those in the uncomplexed compounds.

The colour of the Bipy-complexes of dialkylzinc compounds is caused by charge-transfer, and depends on the electronegativities of the organic groups bound to zinc [17]. The UV and visible absorption spectra of the complexes in benzene are given in Table 4 together with data for the Bipy-complexes of di-n-propyl-, di-n-butyl- and of di-t-butyl-zinc. [18]. The values of ϵ_{max} were calculated from the observed ϵ_{obs} taking into account the degree of dissociation. The excitation energies E were calculated from λ_{max} . The excitation energies of the Bipy-complexes of I, II and IV lie in the same range as those of the corresponding unsubstituted dialkylzinc compounds, viz. diethyl- and di-n-dibutyl-zinc. On the other hand the excitation energy of the Bipy-complex of compound III is much lower, and has about the same value as that of the complex of di-t-butyl-zinc. We believe that this exception cannot be accounted for by electronegativity differences of the organic groups bound to zinc, and that the zinc atom in the Bipy-complex of III must have a coordination number larger than four.

TABLE 5

SOME ^{13}C NMR SPECTRAL DATA FOR THE BIPY-COMPLEXES OF FUNCTIONALLY-SUBSTITUTED DIALKYLZINC COMPOUNDS AND SOME REFERENCE COMPOUNDS, AND THE DISSOCIATION CONSTANTS K_D OF THE ORGANOZINC COMPOUNDS CALCULATED FROM THESE DATA



| Compound | Resonance positions ^a of C(1) | Dissociation constants K_D (mol l ⁻¹ at 25°C) |
|---------------------------|---|---|
| I · Bipy | 155.87 | 1.1 |
| II · Bipy | 155.15 | 0.6 |
| III · Bipy ^b | 156.50 | >100 |
| IV · Eipy ^c | 152.49 | 45×10^{-4} ^c |
| Bipy | 156.52 | |
| Bu ₂ Zn · Bipy | 152.44 | 40×10^{-5} |

^a Resonance positions in ppm relative to internal TMS obtained from 0.25 M solutions in benzene. ^b Data obtained from a 1/1 solution. ^c The calculated K_D corresponds with the one calculated from the microwave titration curve ($K_D = 39 \times 10^{-4}$ (mol l⁻¹)).

(b) *With N,N,N',N'-tetramethylethylenediamine (TMED)*. The reactions of the functionally-substituted dialkylzinc compounds I, II and IV with TMED result in 1/1 complexes. Again, the TMED-complex of compound III could not be isolated because of extreme dissociation. The ^{13}C NMR spectral data, shown in Table 3, and the fact that even in high vacuum the former do not lose TMED, indicate that these complexes are dissociated only to a very small degree.

The difference in stability between the TMED- and Bipy-complexes can be accounted for by the better σ -donating properties of TMED relative to Bipy. A similar difference was observed for the corresponding complexes of e.g. dibutyl- or diethyl-zinc. The ^{13}C NMR spectra (Table 3) indicate that for compounds I, II, and IV coordination is lost in the presence of TMED, which is manifested by the disappearance of the so-called γ -effect.

Experimental

General

All experiments were carried out under dry, oxygen-free nitrogen. Solvents were carefully purified, dried, and distilled before use under nitrogen. NMR spectra were recorded on Varian EM-390 and CFT 20 NMR spectrometers using hexadeuterobenzene as solvent. UV and visible absorption spectra were recorded in benzene solution using a Cary 15 spectrophotometer. Molecular weights were measured by ebulliometry using a Gallenkamp MW 125, modified for operation in a nitrogen atmosphere. Elemental analyses were carried out under the supervision of Mr. W.J. Buis, in the Analytical Department of the Institute for Organic Chemistry TNO at Utrecht.

Synthesis of the starting materials

1-Bromo-3-methoxypropane (b.p. 131°C), 1-bromo-4-methoxybutane (b.p. 165°C) and 1-chloro-3-methylmercaptopropane (b.p. $52\text{--}56^\circ\text{C}/14\text{ mmHg}$) were prepared by literature procedures [19,20].

1-Chloro-3-*N,N*-dimethylaminopropane was obtained from the commercially available HCl-salt (Fluka) by treatment with sodium hydroxide solution and extraction with ether.

Synthesis of the ω -functionally-substituted dialkylzinc compounds

An ethereal solution of ZnCl_2 (100 g/l) was added dropwise with stirring, until a Gilman test [21] was negative, to the Grignard solution prepared from 0.25 mol of the alkyl halide and 0.25 mol Mg in 150 ml ether. The mixture was then refluxed for 0.5 h and extracted three times with 100 ml of ether. The combined ether extracts were freed from ether under vacuum at room temperature. The organozinc compounds were distilled from the residue in vacuo (0.1 mmHg) by cautious heating on an open flame. No boiling points were recorded. In all cases analytically and spectroscopically pure products were obtained in 70% yield. I, II and IV are colourless, slightly viscous liquids at room temperature; III is a colourless solid melting at 37°C . Analytical data *: I: Found: C, 44.7; H, 8.4; Zn, 29.90; $\text{C}_8\text{H}_{18}\text{O}_2\text{Zn}$ calcd.: C, 45.44; H, 8.51; Zn, 30.92%. II: Found:

* In view of the extreme sensitivity to air and moisture the analytical data are satisfactory.

C, 40.2; H, 7.7; S, 26.3; Zn, 25.5. $C_8H_{18}S_2Zn$ calcd.: C, 41.35; H, 7.40; S, 26.35; Zn, 26.90%. III: Found: C, 49.9; H, 10.2; N, 11.2; Zn, 27.5. $C_{10}H_{24}N_2Zn$ calcd.: C, 50.54; H, 10.18; N, 11.79; Zn, 27.50%. IV: Found: C, 49.7; H, 8.9; Zn, 26.8. $C_{10}H_{22}O_2Zn$ calcd.: C, 50.15; H, 9.19; Zn, 27.30%.

Synthesis of the Bipy complexes of I, II and IV

Upon adding 1.56 g (10 mmol) of Bipy to solutions of 10 mmol of the dialkylzinc compounds in 50 ml of n-hexane, the colourless solutions became orange to red. After stirring for 30 minutes at room temperature the solutions were slowly cooled to $-40^\circ C$. The Bipy complexes crystallized as yellow to orange needles, and analytically pure compounds were isolated after washing two times with 5 ml of n-hexane at $-40^\circ C$ in 80% yield. Analytical data: I · Bipy: Found: N, 7.7; Zn, 17.6. $C_{18}H_{26}N_2O_2Zn$ calcd.: N, 7.62; Zn, 17.79%. II · Bipy: Found: N, 7.1; Zn, 16.5. $C_{18}H_{26}N_2S_2Zn$ calcd.: N, 7.01; Zn, 16.36%. IV · Bipy: Found: N, 6.9; Zn, 16.6. $C_{20}H_{30}O_2N_2Zn$ calcd.: N, 7.08; Zn, 16.52%.

Attempted synthesis of the Bipy complex of III

When 1.56 g (10 mmol) of Bipy was added to a solution of 10 mmol of compound III, a purple solution was obtained. Upon cooling to $-40^\circ C$, pure Bipy crystallized out and the solution became colourless. The same results were obtained when the reaction was carried out in other solvents.

Acknowledgements

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