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SYNTHESIS AND CHARACTERIZATION OF SOME ω-DIMETHYLAMINO-1-ALKYNYLZINC COMPOUNDS *,**

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Summary

Ethyl(ω-dimethylamino-1-alkynyl)zinc compounds and bis(ω-dimethylamino-1-alkynyl)zinc compounds were prepared by metalation of the dimethylamino alkynes $HC{\equiv}C(CH_2)_nNMe_2$ (n = 1—4) with diethylzinc and diphenylzinc. All compounds show oligomeric or polymeric association in benzene, the degree of association being dependent on the value of n. The presence of coordinating dimethylamino groups and/or bridging alkynyl groups was established by IR and NMR spectroscopy. Plausible structures for all compounds, based on spectroscopic and molecular weight data, are presented.

Introduction

Few organozinc compounds containing one or more alkynyl groups directly bound to zinc are known. Durand [2] obtained diethynylzinc from the reaction of diethylzinc with acetylene. Later, Podall, Petree and Zietz [3] concluded that, because of its insolubility and non-volatility, the zinc acetylide thus prepared is polymeric. Potassium tetraethynylzincate, $K_2Zn(C{\equiv}CH)_4$, synthesized from ethynylpotassium and zinc rhodanide in liquid ammonia [4], was found to be a salt containing covalently-bound ethynyl groups. Three organozinc compounds derived from 1-alkynes have been reported, viz. $PhZnC{\equiv}CPh$ [5], $Zn(C{\equiv}CPh)_2$ [5] and $Zn(C{\equiv}CC_6H_{13})_2$ [6]. The last two compounds are believed to be associated into linear polymers via bridging acetylenic groups. $PhZnC{\equiv}CPh$ slowly disproportionates in solution into diphenylzinc and bis(phenylethynyl)zinc.

In order to study the relatively unknown tendency and capacity of zinc to

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* Part of this work has been published as a Preliminary Communication [1].

** This article is dedicated to Professor Dr. E. Havinga on the occasion of his 70th Birthday and of his retirement from the Chair of Organic Chemistry at the State University of Leyden.

engage in coordinate bonding with carbon—carbon multiple bonds and to compare the strengths of such bonds with those of normal σ-type coordinate bonds, we have synthesized and characterized a series of organozinc compounds of the type EtZnR and ZnR_2 in which R = $C{\equiv}C(CH_2)_nNMe_2$ (n = 1—4). In these compounds coordinate bonding involving the triple bonds and σ-coordination by the dimethylamino groups may both be present.

Results and discussion

Synthesis and properties

Compounds of the type $EtZnC{\equiv}C(CH_2)_nNMe_2$ (n = 1—4) are prepared by metalation of the dimethylaminoalkyne with one equivalent of diethylzinc in benzene at 60° C:

$$Me_2N(CH_2)_nC{\equiv}CH + Et_2Zn \xrightarrow[50\ h]{C_6H_6,\ 60^\circ C} EtZnC{\equiv}C(CH_2)_nNMe_2 + EtH$$

(I.1—I.4, n = 1—4)

Among the unsymmetric organozinc compounds (I.1—I.4) only I.2 is soluble in benzene; the other products separate as colourless solids during the reaction.

The ethyl groups in I.2, I.3 and I.4 are so unreactive towards the parent alkynes, that it is impossible to prepare the dialkynylzinc compounds from diethylzinc and two equivalents of the dimethylaminoalkyne. *N,N*-Dimethylpropargylamine, however, is acidic enough to react with both ethyl groups of diethylzinc to give $Zn[C{\equiv}CCH_2NMe_2]_2$ (II.1).

The remaining dialkynylzinc compounds (II.2—II.4) were synthesized by treatment of the appropriate alkynes in a 2/1 ratio with diphenylzinc, which is known to be a better metalating agent than diethylzinc [5,7]:

$$2\ Me_2N(CH_2)_nC{\equiv}CH + Ph_2Zn \xrightarrow[50\ h]{C_6H_6,\ 60^\circ C} Zn[C{\equiv}C(CH_2)_nNMe_2]_2 + 2\ C_6H_6$$

(II.2—II.4, n = 2—4)

When *N,N*-dimethylpropargylamine is treated with diphenylzinc, the reaction is complete after 3 h at 60° C in benzene and the product precipitates as a colourless solid. For n = 2, 3, or 4, the products II.2 to II.4 are soluble in benzene, and are isolated by evaporation of the solvent or by precipitation with pentane.

The alkynylzinc compounds thus obtained are all white solids which are sensitive towards oxygen and moisture, but completely lack shock-sensitivity. They are moderately to slightly soluble in solvents like THF or benzene, and insoluble in aliphatic hydrocarbons. The solubility of the ethylzinc derivatives, I.1 to I.4, in benzene decrease in the order I.2 >> I.3 > I.4 > I.1, I.1 being virtually insoluble, whereas the solubility of the dialkynylzinc compounds in this solvent is moderate to good for II.2, II.3 and II.4, but again very low for II.1. All the compounds dissolve readily in strongly coordinating solvents such as pyridine and DMSO.

The melting points and decomposition temperatures of the alkynylzinc compounds as determined by DTA are given in Table 1.

It is remarkable, that only I.1 and II.1, the propargylamine derivatives,

TABLE 1

MELTING POINTS AND DECOMPOSITION TEMPERATURES [a] OF MONO- AND DI-ALKYNYLZINC COMPOUNDS EtZnR AND ZnR_2 ($R = C{\equiv}C(CH_2)_nNMe_2$; n = 1—4)

n	EtZnR		ZnR_2	
	M.p.	Decomposition temperature	M.p.	Decomposition temperature
1	—	168	—	230
2	137	150	110	186
3	164	176	138	213
4	158	199	125	212

[a] Determined by DTA using a heating rate of 8°C/min.

decompose without melting and are insoluble in non-coordinating organic solvents. This may indicate a high degree of association. The polymeric dialkynylzinc compounds diphenylethynylzinc and dioctynylzinc exhibit similar behaviour [5,6].

In all cases, the decomposition temperatures of the monoalkynylzinc compounds are lower than those of the dialkynylzinc derivatives. This may be connected with the fact that in the monoalkynylzinc compounds insufficient nitrogen atoms are available to allow coordination-saturation of the zinc atoms.

The molecular weights of the compounds were determined by ebulliometry in benzene and in pyridine (cf. Table 2).

The degrees of association in benzene decrease with increasing value of n both for the mono- and for the dialkynylzinc compounds. This may be connected with the increasing flexibility of the alkyl chains linking the zinc and nitrogen atoms, enabling association into smaller intra- of inter-molecular units.

TABLE 2

MOLECULAR WEIGHTS [a] AND DEGREES OF ASSOCIATION OF MONO- AND DI-ALKYNYLZINC COMPOUNDS EtZnR AND ZnR_2 ($R = C{\equiv}C(CH_2)_nNMe_2$; n = 1—4)

Compound	Solvent [b]	Molecular weight (found (calcd. for monomer))	Degree of association
$EtZnC{\equiv}CCH_2NMe_2$ (I.1)	P	171 (176.6)	0.97
$Zn[C{\equiv}CCH_2NMe_2]_2$ (II.1)	P	241 (229.6)	1.05
$EtZnC{\equiv}C(CH_2)_2NMe_2$ (I.2)	B	575 (190.6)	3.02
	P	187 (190.6)	0.98
$Zn[C{\equiv}C(CH_2)_2NMe_2]_2$	B	768 (257.7)	2.98
	P	259 (257.7)	1.01
$EtZnC{\equiv}C(CH_2)_3NMe_2$ (I.3)	B	416 (204.6)	2.03
	P	209 (204.6)	1.02
$Zn[C{\equiv}C(CH_2)_3NMe_2]_2$ (II.3)	B	553 (285.7)	1.94
	P	290 (285.7)	1.02
$EtZnC{\equiv}C(CH_2)_4NMe_2$ (I.4)	P	222 (218.6)	1.02
$Zn[C{\equiv}C(CH_2)_4NMe_2]_2$ (II.4)	B	900 [a] (313.8)	~3
	P	312 (313.8)	0.99

[a] Determined by ebulliometry. In no case, was concentration dependence observed. Concentration range used: 5—20 mg/ml. [b] P = pyridine; B = benzene. [c] Estimated accuracy ± 100; molecular weights in this range cannot be determined accurately by ebulliometry.

In pyridine, all the intermolecular coordination is broken and the compounds are monomeric.

Spectroscopic data

The IR spectra of the compounds, in solution (pyridine or benzene) and in the solid state, show characteristic shifts of the carbon—carbon triple bond stretching vibrations (cf. Table 3).

The ν(C≡C) values of the monoalkynylzinc compounds in benzene or in Nujol suspension are shifted 20—40 cm^{-1} to frequencies below those of the parent aminoalkynes. These shifts disappear when the spectra are recorded in pyridine. In II.2, II.3 and II.4 two different C≡C stretching vibrations occur in benzene solution. The vibrations around 2090 cm^{-1} are absent from the spectra of solutions in pyridine. In II.2 and II.3, the vibrations around 2090 cm^{-1} are absent in spectra of solid samples (as Nujol mulls). In II.1 only one C≡C stretching vibration appears and this is not shifted relative to that of the parent alkyne and has the same value in the solid state and in pyridine solution.

The lowering of the frequencies of the C≡C stretching vibration in the monoalkynylzinc compounds is similar to that reported for alkynylmetal compounds of beryllium [8] and aluminium [9]. These shifts are generally considered to provide evidence for the existence of bridging alkynyl groups involved in 2-electron—3-centre bonds. A few examples are listed in Table 4. In a few cases, the proposed bridged structure has been confirmed by X-ray analysis [10,11] or electron diffraction [12].

On the basis of these data, it seems reasonable to assume the presence of bridging alkynyl groups in the monoalkynylzinc compounds. The change in ν(C≡C) upon dissolving these compounds in pyridine is then attributed to their monomeric character in pyridine solution.

In view of the zinc/nitrogen ratio of 1/2 in the dialkynylzinc compounds, sufficient ligand atoms being present to saturate the four-coordination of all zinc atoms, it might be expected that alkynyl bridges would be absent. This implies that the ν(C≡C) should be about 2120 cm^{-1} and recording the spectrum in pyridine should have no influence on this value. This is the case for II.1; benzene solutions of II.2, II.3 and II.4, however, exhibit a second low-frequency vibration which disappears in pyridine, as for the monoalkynylzinc

TABLE 3

TRIPLE-BOND STRETCHING VIBRATIONS OF COMPOUNDS EtZnR AND ZnR$_2$ (R = C≡C(CH$_2$)$_n$-NMe$_2$; n = 1—4), AND OF THEIR PARENT ALKYNES RH

n	Alkyne	EtZnR		ZnR$_2$	
		Nujol [a]	Pyridine [b]	Nujol	Pyridine
1	2104	2084	— [c]	2110	2115
2	2121	2099	2117	2120 [d]	2121
3	2118	2081	2118	2119 [d]	2119
4	2118	2089	2117	2091, 2119	2118

[a] Measured as a solid suspended in Nujol. [b] Measured as a solution in pyridine. [c] Intensity too small for detection. [d] Splits up into two bands upon dissolution in benzene (2094 and 2127 cm^{-1} for *n* = 2, 2089 and 2111 cm^{-1} for *n* = 3).

TABLE 4

TRIPLE-BOND STRETCHING VIBRATIONS OF SOME ALKYNYLBERYLLIUM AND ALKYNYLALUMINIUM COMPOUNDS AND OF THEIR PARENT ALKYNES

Compound	$\nu(C\equiv C)$	Reference
$MeC\equiv CH$	2135	
$[MeC\equiv CBeMe \cdot NMe_3]_2$	2110	8
$[(MeC\equiv C)_2Be \cdot NMe_3]_2$	2115, 2134	
$t\text{-}BuC\equiv CH$	2112	
$[t\text{-}BuC\equiv CBeMe \cdot NMe_3]_2$	2092	8
$[(t\text{-}BuC\equiv C)_2Be \cdot NMe_3]_2$	2091, 2111	
$PhC\equiv CH$	2110	
$[PhC\equiv CAlMe_2]_2$	2050	9
$PhC\equiv CAlMe_2 \cdot THF$	2110	

compounds. We attribute this vibration to bridging alkynyl groups. This implies that in benzene solutions of compounds II.1, II.3 and II.4 both bridging and non-bridging alkynyl groups are present. The appearance of only one band, at about 2120 cm^{-1}, in the solids II.2 and II.3 indicates that in the solid state of these compounds bridging alkynyl groups are absent. Apparently, coordination-saturation of the zinc is then brought about by zinc—nitrogen coordination only. It seems reasonable to assume that solid-state effects, such as lattice energy and the influence of crystal packing, are responsible for the difference in coordination behaviour between solid state and solute species.

Both ^{13}C and ^{1}H NMR spectra of the title compounds were recorded in fully deuterated benzene or toluene, as far as solubility allowed, and in pyridine. The relevant data are given in Tables 5 and 6.

The NMR spectra of all the compounds in pyridine consist of sharp lines at normal shift positions, confirming the identities of the compounds. No structural information can be gained from these spectra, since in all cases monomeric species are present. However, the spectra of II.2, II.3 and II.4 in deuterobenzene or deuterotoluene show temperature-dependent line broadening both in the ^{1}H and in the ^{13}C NMR spectra. Since these effects are most pronounced for II.3, the spectra of this compound will be discussed in some detail.

The ^{1}H NMR spectrum of II.3 at ambient temperature consists of three very broad resonances which sharpen on heating to 60° C. At that temperature the expected multiplicity of the signals appears. On cooling to —30° C in deuterotoluene, the multiplets of H_δ and $H_{\gamma+\epsilon}$ (overlapping) split up in two multiplets each, and H_ω shifts 0.2 ppm to lowfield. Unfortunately, the peak-overlaps hamper a thorough interpretation of this spectrum.

The ^{13}C spectrum of II.3 is much more clear-cut (Fig. 1). At +60° C, the ^{13}C signals of C_γ, C_ϵ and C_ω are relatively sharp (linewidth about 0.4 ppm), whereas those of C_δ and C_β and in particular that of C_α, are broad (linewidths 1, 1 and 2 ppm, respectively). Upon cooling to —30° C the lines split up into doublets, except C_ω which splits up into a doublet and a singlet. The positions of the lines at +60° C are in all cases the exact average of the positions of the doublets, indicating that the population of both forms visible at —30° C is the same. We interpret these results in terms of the presence of equal amounts of two

(Continued on p. 136)

TABLE 5

^{1}H AND ^{13}C NMR DATA FOR THE COMPOUNDS EtZnR AND ZnR_2 (R = $C{\equiv}C(CH_2)_nNMe_2$; n = 1—4) IN PYRIDINE

$$-Zn-\underset{\alpha}{C}{\equiv}\underset{\beta}{C}-\underset{\gamma}{CH_2}-\underset{\delta}{CH_2}-\underset{\epsilon}{CH_2}-\underset{\zeta}{CH_2}-\underset{\omega}{N(CH_3)_2}$$

Compound	C_α	C_β	C_γ	C_δ	C_ϵ	C_ζ	C_ω	H_γ	H_δ	H_ϵ	H_ζ	H_ω
$EtZnC{\equiv}CCH_2NMe_2$	—[a]	102.2	50.2				44.1	3.55				2.45
$Zn[C{\equiv}CCH_2NMe_2]_2$	106.6	102.4	50.0				44.0	3.56				2.42
$EtZnC{\equiv}C(CH_2)_2NMe_2$	104.0	105.0	19.2	59.9			44.4	2.71	2.71			2.20
$Zn[C{\equiv}C(CH_2)_2NMe_2]_2$	101.8	105.5	19.4	60.0			44.6	2.69	2.69			2.20
$EtZnC{\equiv}C(CH_2)_3NMe_2$	103.6	107.4	18.7	28.7	58.9		45.2	2.58	1.86	2.51		2.15
$Zn[C{\equiv}C(CH_2)_3NMe_2]_2$	101.3	107.7	18.7	28.7	59.0		45.3	2.56	1.85	2.50		2.15
$EtZnC{\equiv}C(CH_2)_4NMe_2$	102.7	106.6	19.9	26.2	27.4	58.4	44.3	2.54	1.80	1.80	2.26	2.14
$Zn[C{\equiv}C(CH_2)_4NMe_2]_2$	101.3	107.6	20.6	26.9	28.1	59.1	45.1	2.51	1.70	1.70	2.26	2.14

[a] The intensity of this line was too low to be detected.

TABLE 6

^{1}H AND ^{13}C NMR DATA FOR COMPOUNDS EtZnR AND ZnR_2 (R = $C{\equiv}C(CH_2)_nNMe_2$; n = 2—4)[a] IN DEUTEROBENZENE OR DEUTEROTOLUENE

$$-Zn-\underset{\alpha}{C}{\equiv}\underset{\beta}{C}-\underset{\gamma}{CH_2}-\underset{\delta}{CH_2}-\underset{\epsilon}{CH_2}-\underset{\zeta}{CH_2}-\underset{\omega}{N(CH_3)_2}$$

Compound	C_α	C_β	C_γ	C_δ	C_ϵ	C_ζ	C_ω	H_γ	H_δ	H_ϵ	H_ζ	H_ω
$EtZnC{\equiv}C(CH_2)_2NMe_2$	109.8	107.2	19.2	59.3			45.7	2.3	2.3			2.26
$Zn[C{\equiv}C(CH_2)_2NMe_2]_2$ [b]	104.8	107.0	19.8	59.6			45.7	2.4	2.4			2.26
$EtZnC{\equiv}C(CH_2)_3NMe_2$ [b]	—[c]	—[c]	—[c]	—[c]	—[c]		—[c]	2.2	1.3	2.2		2.19
$Zn[C{\equiv}C(CH_2)_3NMe_2]_2$ [b]	109.0	98.9	18.3	25.8	58.9		44.6	2.5	1.6	2.5		2.13
$Zn[C{\equiv}C(CH_2)_4NMe_2]_2$ [b]	111.6[d]	96.7	21.3	25.8	27.9	59.2	44.9	2.6	1.8	1.8	2.6	2.41

[a] Compounds I.1, II.1 and I.4 are insufficiently soluble in benzene or toluene to permit recording of ^{1}H and ^{13}C NMR spectra. [b] Spectra recorded at +60° C, at ambient temperatures both ^{1}H and ^{13}C absorptions are broadened. [c] ^{13}C NMR spectrum could not be recorded because of insufficient solubility. [d] Very broad line even at +60° C.

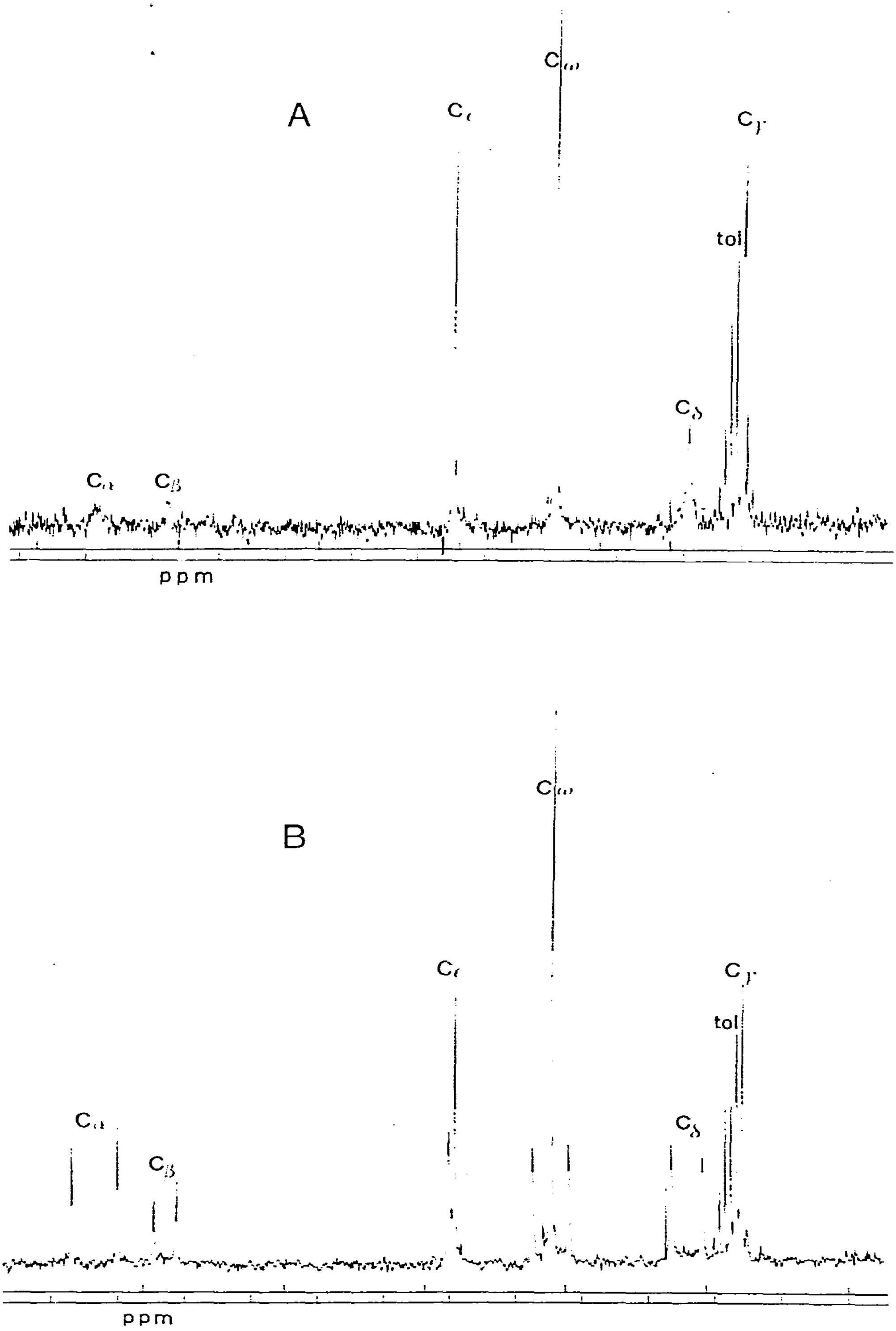


Fig. 1. ^{13}C NMR spectra of Zn[C≡C(CH$_2$)$_3$NMe$_2$]$_2$ (II.3) recorded in toluene-d_8 at +60°C (A) and −30°C (B).

different 5-dimethylaminopentynyl groups in the molecule, which start exchanging above —30° C. In one of these species the methyl groups bound to nitrogen are non-equivalent, since they appear as a doublet at —30° C, whereas in the other species they are equivalent and show up as a singlet. The most likely explanation for this difference is that in the first species nitrogen—zinc coordination occurs, and this immobilizes the dimethylamino group and gives rise to non-equivalence of the methyl groups. In the second species such coordination is absent, allowing the nitrogen atom to invert rapidly.

Similar effects are present in the NMR spectra of II.2 and II.4. At +60° C, the ^{13}C NMR spectrum of II.4 looks very similar to that of II.3, but on cooling to —30° C, the lines broaden and finally disappear with the exception of the very broad C_ω resonance. Apparently, at that temperature nearly all resonances are in a coalescence state, indicating that here the exchange is faster than in II.3. Unfortunately, the strong increases in the viscosity of the solutions below —30° C in deuterotoluene made recording of meaningful NMR spectra at lower temperatures impossible.

The results of the NMR measurements are in full accord with those of the IR spectra (vide supra). Again, in solution the presence of two types of dimethylaminoalkynyl groups in II.2, II.3 and II.4 was confirmed, one with bridging and one with non-bridging alkynyl groups.

Conclusions

On the basis of the observed degrees of association in benzene and the spectroscopic data given above, plausible structures can be assigned to the title compounds.

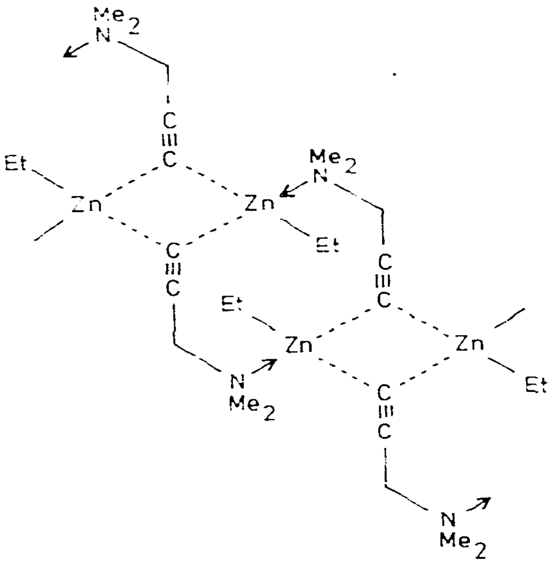
Ethyl(ω-dimethylamino-1-alkynyl)zinc compounds (I.1—I.4)

In the ethyl(ω-dimethylamino-1-alkynyl)zinc compounds, in which the N/Zn ratio is one, the favoured four-coordination of the zinc atoms is attained by alkynyl bridging and zinc—nitrogen coordination. Under no circumstances has disproportionation of the monoalkynylzinc compounds into diethylzinc and the corresponding dialkynylzinc compounds been observed. The complete absence of this feature, common to unsymmetric organozinc compounds, e.g. PhZnC≡CPh [5], may be connected with the presence of intra- or inter-molecular zinc—nitrogen coordination.

Several structures are possible for polymeric ethyl(3-dimethylamino-1-propynyl)zinc (I.1). One such structure, in which both alkynyl bridges and coordinating dimethylamino groups are present, is given in Fig. 2.

Structural proposals for trimeric $EtZnC{\equiv}C(CH_2)_2NMe_2$ (I.2) and dimeric $EtZnC{\equiv}C(CH_2)_3NMe_2$ (I.3) are given in Fig. 3. The different degrees of association of I.2 and I.3 in benzene may be connected with the size of the chelate ring formed. This is in line with earlier observations on the degrees of association of organozinc alkoxides, derived from monoprotic bidentate ligands, containing an electron-donating atom or group in a position suitable for chelate formation [13]. On the other hand, the rigidity of the carbon chain may also be an important factor determining the degree of association.

The molecular weight of the ethyl(alkynyl)zinc compound derived from



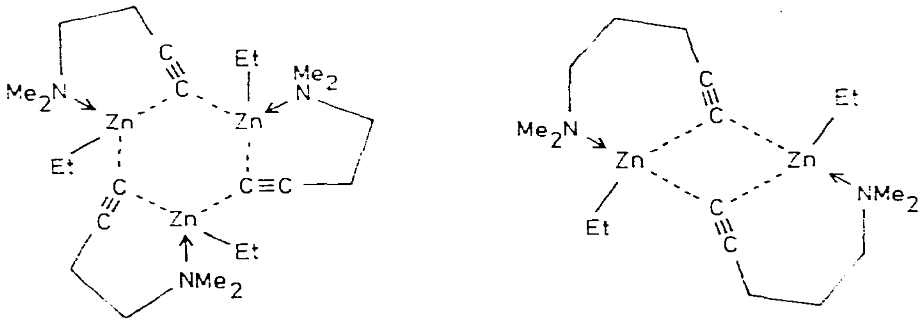
I.1

Fig. 2. Structure proposed for polymeric $EtZnC{\equiv}CCH_2NMe_2$ (I.1).

1-dimethylamino-5-hexyne (I.4) could not be measured by ebulliometry in benzene because of insufficient solubility. In view of the spectroscopic data a structure involving zinc—nitrogen coordination and alkynyl bridges is again obvious.

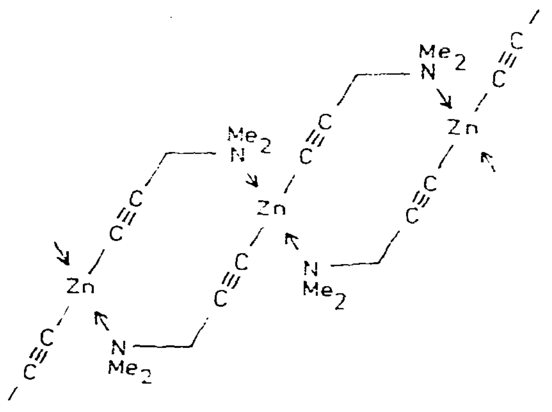
Bis(ω-dimethylamino-1-alkynyl)zinc compounds (II.1—II.4)

In all dialkynylzinc compounds in which the N/Zn ratio is two, the tetracoordination of zinc can in principle be attained by zinc—nitrogen coordination only. Since the IR spectra of polymeric $Zn[C{\equiv}CH_2NMe_2]_2$ (II.1) point to the absence of bridging alkynyl groups, the structure of this compound is probably built up as shown in Fig. 4.



I.2 I.3

Fig. 3. Structures proposed for trimeric $EtZnC{\equiv}C(CH_2)_2NMe_2$ (I.2) and dimeric $EtZnC{\equiv}C(CH_2)_3NMe_2$ (I.3).

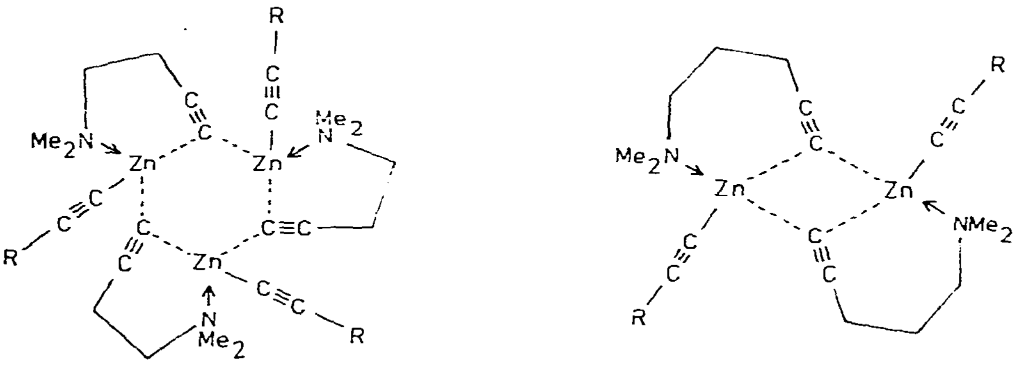


II.1

Fig. 4. Structure proposed for polymeric $Zn[C{\equiv}CCH_2NMe_2]_2$ (II.1).

In the remaining dialkynylzinc compounds (II.2—II.4), however, spectroscopic data indicate the presence both of bridging and non-bridging alkynyl groups and of two different types of dimethylamino groups. In these compounds the coordination saturation of the zinc atoms is attained by equal contributions of alkynyl bridges and zinc—nitrogen coordinate bonds. Consequently, for trimeric $Zn[C{\equiv}C(CH_2)_2NMe_2]_2$ (II.2) and dimeric $Zn[C{\equiv}C(CH_2)_3NMe_2]_2$ (II.3) structures analogous to those of the monoalkynylzinc derivatives are proposed (Fig. 5).

For $Zn[C{\equiv}C(CH_2)_4NMe_2]_2$ (II.4), also, a structure in which both types of coordination occur can be envisaged.



II.2 $R = -(CH_2)_2-NMe_2$

II.3 $R = -(CH_2)_3-NMe_2$

Fig. 5. Structures proposed for trimeric $Zn[C{\equiv}C(CH_2)_2NMe_2]_2$ (II.2) and dimeric $Zn[C{\equiv}C(CH_2)_3NMe_2]_2$ (II.3).

Experimental

General

All organozinc compounds were synthesized and handled under dry, oxygen-free nitrogen. Solvents were carefully purified, dried, and distilled under nitrogen before use. Solvents, solutions and liquid reagents were handled using syringes.

IR spectra were recorded on a Perkin—Elmer 457 infrared spectrometer using Nujol mulls between KBr disks or solutions in KBr cuvettes; frequencies are accurate to ±1 cm^{-1}. NMR spectra were recorded on Varian EM-390 and XL 100/15 FT NMR spectrometers.

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.

Starting materials

1-Dimethylamino-2-propyne was commercially available (Fluka) and was distilled under nitrogen before use. 1-Dimethylamino-3-butyne was prepared in 28% yield by Campbell, Fatora and Campbell's method [14] from sodium acetylide and *N,N*-dimethyl-β-bromoethylamine hydrobromide. 1-Dimethylamino-4-pentyne was synthesized in 32% yield by treatment of 1-chloro-4-pentyne with anhydrous dimethylamine according to ref. 14, and 1-dimethylamino-5-hexyne was made analogously in 48% yield.

Diethylzinc and diphenylzinc were prepared as described by Noller [15] and Strohmeier [16], respectively.

TABLE 7

ANALYTICAL DATA

Compound	Analysis (Found (calcd.)(%))			
	C [a]	H	N	Zn
$EtZnC{\equiv}C{-}CH_2NMe_2$	46.88	7.36	7.89	37.33
	(47.62)	(7.42)	(7.93)	(37.03)
$Zn[C{\equiv}CCH_2NMe_2]_2$	51.83	7.02	11.44	28.77
	(52.30)	(7.02)	(12.20)	(28.47)
$EtZnC{\equiv}C(CH_2)_2NMe_2$	50.15	8.04	7.31	34.17
	(50.41)	(7.93)	(7.35)	(34.30)
$Zn[C{\equiv}C(CH_2)_2NMe_2]_2$	53.74	7.83	10.77	25.25
	(55.93)	(7.82)	(10.87)	(25.37)
$EtZnC{\equiv}C(CH_2)_3NMe_2$	50.26	7.94	6.77	31.87
	(52.83)	(8.37)	(6.85)	(31.95)
$Zn[C{\equiv}C(CH_2)_3NMe_2]_2$	57.53	8.27	9.54	22.80
	(58.85)	(8.47)	(9.80)	(22.88)
$EtZnC{\equiv}C(CH_2)_4NMe_2$	53.77	8.76	6.37	29.79
	(54.93)	(8.76)	(6.41)	(29.90)
$Zn[C{\equiv}C(CH_2)_4NMe_2]_2$	59.90	9.11	8.75	20.84
	(61.24)	(8.99)	(8.93)	(20.84)

[a] The carbon percentage, determined by combustion analysis, is systematically low; this may be due to zinc carbide formation.

Synthesis of compounds $EtZnC{\equiv}C(CH_2)_nNMe_2$ *(n = 1—4)*

Dimethylaminoalkyne (30 mmol) was added to a solution of 35 mmol of diethylzinc in 30 ml of benzene and the mixture was heated with stirring at 50—60° C. After 50 h, the solvent was removed in vacuo and the solid residue was washed with pentane (3 × 30 ml) and dried in vacuo at room temperature. Yields were generally 70—85%.

Synthesis of compounds $Zn[C{\equiv}C(CH_2)_nNMe_2]_2$ *(n = 1—4)*

Bis(3-dimethylamino-1-propynyl)zinc. A solution of 55 mmoles of dimethylpropargylamine in 10 ml of benzene was added to a solution of 25 mmol of diphenylzinc in 40 ml of benzene and the mixture was stirred at room temperature for 3 h. After evaporation of the solvent, the solid product was washed with pentane (3 × 50 ml) and dried in vacuo during 5 h. The yield was 85%.

$Zn[C{\equiv}C(CH_2)_nNMe_2]_2$ *(n = 2—4).* These compounds were made as described for the dimethylpropargylamine derivative, but the reaction time was increased to 50 h and the temperature to 50—60° C. Yields were 70—85%.

The analytical data are listed in Table 7.

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