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Preliminary communication

1-ALKYNYLZINC COMPOUNDS DERIVED FROM 1-DIMETHYLAMINO-3-BUTYNE

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Summary

Ethyl(4-dimethylamino-1-butynyl)zinc was prepared by metalation of 1-dimethylamino-3-butyne with diethylzinc in benzene! Bis(4-dimethylamino-1-butynyl)zinc was synthesized similarly from diphenylzinc and two equivalents of the acetylenic amine. Both compounds are trimeric in benzene; structures are proposed on the basis of the spectroscopic evidence.

Only a few 1-alkynylzinc compounds are known, e.g. $PhZnC{\equiv}CPh$ [1], $Zn(C{\equiv}CPh)_2$ [1—3] and $Zn(C{\equiv}CC_6H_{13})_2$ [3]. The dialkynylzinc compounds are believed to be associated into linear polymers via bridging acetylenic groups [3]. As part of our work on the coordination chemistry of organozinc compounds containing terminal functional groups [4], we have metalated 1-dimethylamino-3-butyne with diethylzinc and diphenylzinc in order to obtain the corresponding ω-functionally substituted alkynylzinc compounds.

When diethylzinc is treated with one equivalent of 1-dimethylamino-3-butyne, $HC{\equiv}C(CH_2)_2NMe_2$, in benzene at 60°C for 50 h, a slow evolution of ethane occurs and a colourless solution is obtained. Evaporation of the solvent in vacuo and washing of the residue with pentane gives a colourless solid in 75% yield, which analyzes correctly for $EtZnC{\equiv}CC_2H_4NMe_2$ (compound A). Analysis: Found: C, 50.15; H, 8.04; N, 7.31; Zn, 34.17. $C_8H_{15}NZn$ calcd.: C, 50.41; H, 7.93; N, 7.35; Zn, 34.30%.

Because of the insufficient reactivity of the remaining ethyl group in compound A towards a second equivalent of 1-dimethylamino-3-butyne, bis(4-dimethylamino-1-butynyl)zinc (compound B) was prepared as a colourless solid by treating two equivalents of the acetylenic amine with diphenylzinc instead of diethylzinc. The conditions and the yield were the same as for A. Analysis: Found: C, 53.74; H, 7.83; N, 10.77; Zn, 25.25. $C_{12}H_{20}N_2Zn$ calcd.: C, 55.93; H, 7.82; N, 10.87; Zn, 25.37%.

Ebulliometry showed both A and B to be trimeric in benzene and monomeric in pyridine; no concentration dependence was observed.

The ^1H and ^{13}C NMR spectra of A and B show the presence of ethyl groups bound to zinc (in A) and of 4-dimethylamino-1-butynyl groups (in A and B). These spectra do not, however, give any simple indication of the way in which the acetylenic groups are involved in coordinative bonding.

In the IR spectrum of A, either as a Nujol suspension or in benzene solution, the triple bond stretching frequency is shifted 22 cm^{-1} towards lower frequency as compared with that in 1-dimethylamino-3-butyne (2099 vs. 2121 cm^{-1}). This shift is absent when the IR spectrum of A is recorded in pyridine solution, in which, according to molecular weight determinations, no intermolecular coordination exists. In the IR spectra of B, under all conditions the triple bond stretching frequency is the same (2121 cm^{-1}) as that for the parent acetylene. The shifts observed in the IR spectra of A are comparable to those found for certain other alkynylmetal compounds. Such shifts were taken as evidence for the presence of electron-deficient acetylenic bridges.

Bridging phenylethynyl groups were proposed for dimeric dimethyl(phenylethynyl)aluminium on the basis of ^1H NMR spectroscopy at various temperatures [5]. The IR spectrum of this compound recorded in benzene shows a C≡C stretching frequency of 2050 cm^{-1}. This frequency shifted to 2110 cm^{-1} in the donor solvent THF, in which the dimeric structure is disrupted.

Acetylenic bridges were also proposed for dimeric methyl(propynyl)beryllium trimethylamine and dimeric bis(propynyl)beryllium trimethylamine (cf. Fig. 1) on the basis of IR spectroscopic data. The C≡C stretching frequency in the former compound appeared to be 2110 cm^{-1}, while the latter compound shows absorptions at 2115 and 2134 cm^{-1}, ascribed to bridging propynyl and terminal propynyl groups respectively [6]. The C≡C stretching frequency of propyne in CCl_4 is 2135 cm^{-1}. The structural proposal for methyl(propynyl)beryllium trimethylamine was confirmed by X-ray structural analysis [7].

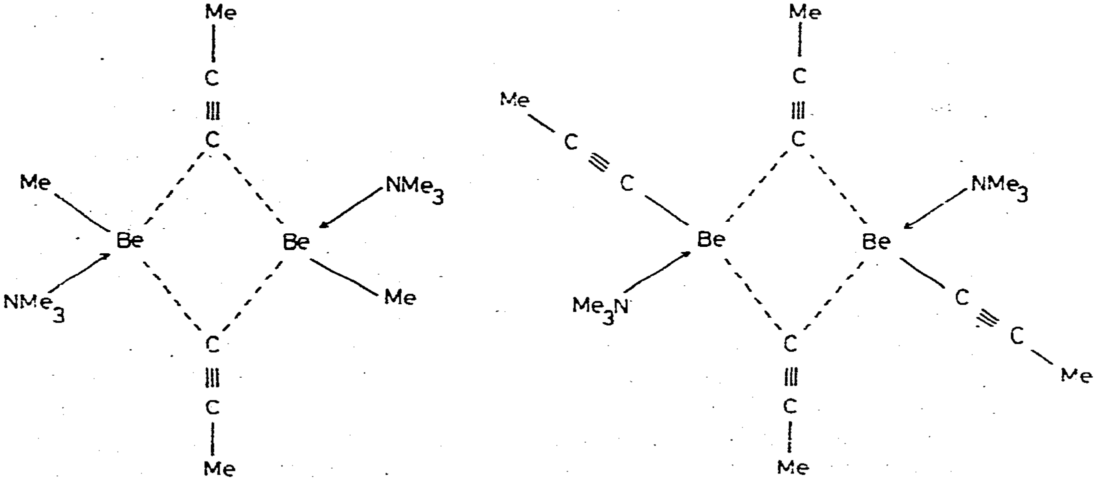

Fig. 1. Structures proposed by Coates and Francis [6] for the dimeric trimethylamine complexes of methyl(propynyl)beryllium and bis(propynyl)beryllium.

In the field of organozinc chemistry, bridging alkynyl groups were proposed for bis(phenylethynyl)zinc and bis(1-octynyl)zinc. In the IR spectra of these compounds the C≡C stretching frequency is shifted 30—50 cm^{-1} to lower wavenumber relative to that for the parent acetylene [3].

On the basis of these data, we interpret the shift observed for A in terms of the presence of bridging alkynyl groups.

Structural proposals for compounds A and B based on the observed degree of association in benzene and the spectroscopic data are given in Fig. 2.

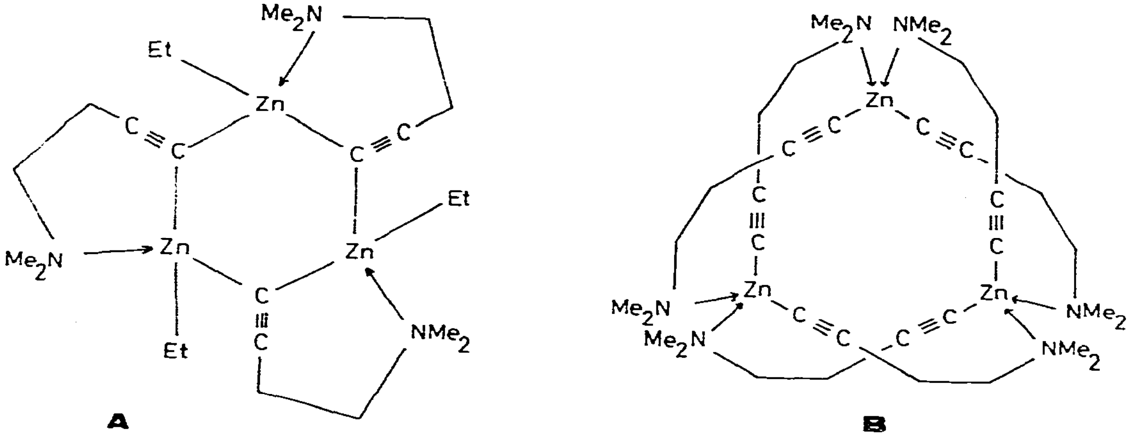

Fig. 2. Structural proposals for trimeric ethyl(4-dimethylamino-1-butynyl)zinc (A) and trimeric bis(4-dimethylamino-1-butynyl)zinc (B).

The structural differences between A and B can be rationalized in terms of the tendency of zinc to attain four-coordination in both cases. In A the N/Zn ratio is one, which implies that zinc can only reach four-coordination by coordinating both with nitrogen and the alkynyl groups. In B the N/Zn ratio is two, and coordination saturation of zinc can be attained by N-coordination only. The trimeric association of both compounds may be enforced by the rigidity of part of the carbon chain.

We are extending our study to other members of the series $EtZnC{\equiv}C(CH_2)_nNMe_2$ and $Zn[C{\equiv}C(CH_2)_nNMe_2]_2$, ($n = 1, 3, 4$), in order to investigate the relation between coordination behaviour and alkyl-chain length.

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