# Complex Formation between Diethylzinc and Triethylamine

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Dialkylzinc has generally been held to be unable to form a coordination complex with aliphatic amines.[1,2] Recently, however, Noltes and Van Den Herk have reported a series of complexes of dialkylzinc with various amines.[3] Ishimori *et al.* have also found, by means of IR measurements, that the coordination of diethylzinc with triethylamine occurs.[4] Reported herein will be evidence to support the formation of a complex between diethylzinc and triethylamine.

The present author has proposed a method to detect the mild complex-formation of triethylaluminum with electron-donor compounds, such as amines, ethers, and stibines, on the basis of the fact that the alkyl groups of the resulting complexes clearly show proton chemical shifts different from those of the free ligands. The internal chemical shift between $\alpha$ and $\beta$ protons of the alkyl group is the most convenient measure for the above purpose.[5]

The nuclear magnetic resonance spectra of mixtures of diethylzinc and triethylamine over a wide range of molar ratios were measured. An example of the spectra is given in Fig. 1, while the $\tau$ values of each proton are summarized in Table 1.

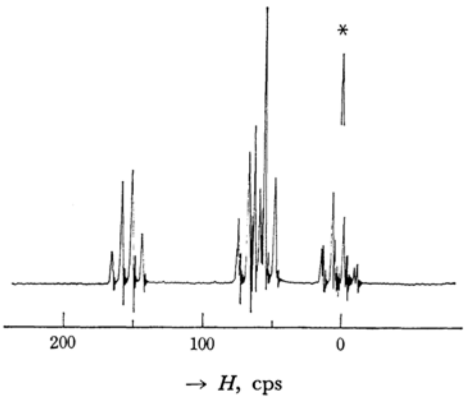

Fig. 1. NMR spectrum of the mixture of $ZnEt_2$ and $NEt_3$ (1:1). (* $SiMe_4$)

The internal chemical shifts ($\delta$) between the methylene and methyl protons of the ethyl group which was bound to zinc decreased as the molar ratios of triethylamine to diethylzinc increased, attaining a constant value at a molar ratio of 1.0.

This result suggests the formation of the 1 : 1 coordination compound $ZnEt_2 \cdot NEt_3$. The above constant $\delta$ value is considered to be that of the resulting complex. At a molar ratio of 0.5, the mean $\delta$ value between the values of free diethylzinc and the 1 : 1 complex was obtained; only one type

TABLE 1. NMR DATA FOR THE MIXTURES OF $ZnEt_2$ AND $NEt_3$ (60 Mc, 20°C)

| $NEt_3/ZnEt_2$ | $ZnEt_2$ |  |  | $NEt_3$ |  |  |
|---|---|---|---|---|---|---|
|  | $\tau$ for |  | $\delta$ | $\tau$ for |  | $\delta$ |
| mole ratio | $>CH_2$ | $-CH_3$ | ppm | $>CH_2$ | $-CH_3$ | ppm |
| 0 | 9.70 | 8.83 | −0.87 | — | — | — |
| 0.5 | 9.87 | 8.88 | −0.99 | 7.39 | 9.07 | 1.68 |
| 1.0 | 9.96 | 8.88 | −1.08 | 7.40 | 9.07 | 1.67 |
| 1.5 | 10.01 | 8.93 | −1.08 | 7.50 | 9.13 | 1.63 |
| 2.0 | 10.05 | 8.97 | −1.08 | 7.57 | 9.17 | 1.60 |
| 4.9 | 10.11 | 9.03 | −1.08 | 7.70 | 9.23 | 1.53 |
| 10.9 | 10.15 | 9.07 | −1.08 | 7.77 | 9.29 | 1.52 |

* The internal chemical shifts $\delta$ for the ethyl groups of triethylamine in a pure state and in a 10 percent benzene solution were measured to be 1.87 and 1.48 ppm respectively.

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1) J. Boor, Jr., *J. Polymer Sci.*, **A3**, 995 (1965).

2) G. E. Coates, "Organo-Metallic Compounds," Methuen, London (1965), p. 39.

3) J. G. Noltes and J. W. G. Van Den Hurk, *J. Organometal. Chem.*, **1**, 377 (1964).

4) M. Ishimori and T. Tsuruta, "High Polymer Discussion in Tokyo" (1964), p. 183.

5) Y. Takashi, to be published.

of signals assigned to the ethyl group bound to zinc was observed. This fact indicates that a rapid ligand exchange reaction occurs between diethylzinc and the 1 : 1 complex $ZnEt_2 \cdot NEt_3$ at room temperature.

Dailey and Shoolery have shown a direct dependency of the internal chemical shifts of the ethyl derivatives on the electronegativity of the substituent.[6] For this correlation several equations have been proposed for many ethyl compounds.[7,8] According to Narashimhan's equation,[8] the electronegativities of the zinc atoms in the $ZnEt_2 \cdot NEt_3$ complex and in free diethylzinc were evaluated as 1.40 and 1.53 respectively:

$$x = 0.62\,\delta + 2.07 \qquad (1)$$

where $x$ is electronegativity. It is estimated, therefore, that the ethyl group bound to zinc in this complex is more polarized than that of free diethylzinc.

In respect to the ethyl group bound to nitrogen, similar considerations hold, and the formation of a 1 : 1 complex is reasonably supported by the results shown in Table 1.

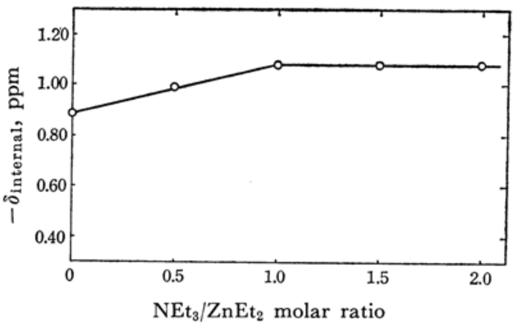

Fig. 2. Variation of the internal chemical shift of the ethyl group bound to zinc in the mixture of $ZnEt_2$ and $NEt_3$ as a function of the molar ratios.

### Experimental

**Materials.** A commercial diethylzinc (Sankyo Yûki Co.) was distilled at 116°C under a dry oxygen-free nitrogen atmosphere. A commercial triethylamine (Reagent Grade) was purified as usual, and distilled under a nitrogen atmosphere before use.

**Reaction Procedure.** Diethylzinc and triethylamine were simply mixed at room temperature with stirring under a nitrogen atmosphere. The reaction mixture was allowed to stand overnight at room temperature, and then used for the following measurements.

**NMR Measurements.** The proton magnetic resonance spectra were obtained with liquid samples in sealed tubes (5 mm o.d.). The spectra were recorded with a Varian A-60 spectrometer operating at 60 Mc. All values are given with tetramethylsilane as the external standard. The determination of the chemical shifts of the ethyl group were made on the basis of a first-order approximation; *i. e.,* the center line of the methyl triplet and the average of the two center lines of the methylene quartet were chosen as the chemical shifts for $CH_3$ and $CH_2$ groups respectively.

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6) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.,* **77**, 3977 (1956).

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8) P. J. Narashimahn and M. T. Rogers, *J. Am. Chem. Soc.,* **82**, 5983 (1961).