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Preliminary communication

Investigations on organozinc compounds
XIII. Organozinc-catalyzed polymerization of aldehydes. Preparation and characterization of some catalyst-monomer complexes*

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In the course of our study of organozinc compounds with the general formula $RZnX$[2] several types of highly stereospecific catalysts for the polymerization of aliphatic aldehydes have been discovered[3]. In order to shed light on the polymerization mechanism, we have studied more closely the interaction of *N*-(ethylzinc) diphenylamine with aliphatic aldehydes in benzene solution. In view of the recent interest in related organoaluminium reactions[4-6] we report in preliminary form some data on catalyst-monomer complexes studied in our work.

When *N*-(ethylzinc) diphenylamine is treated at room temperature with acetaldehyde and butyraldehyde, or at 80° with formaldehyde (1/1 molar ratio; benzene solution), well-defined adducts with a 1/1 stoichiometry are formed which have been isolated in crystalline form**. NMR spectroscopic study of these reactions reveals that in each case the aldehyde proton signal ($\delta \approx 9.5$ ppm) disappears rapidly, whereas a new signal appears in the region normally associated with acetal-like protons. This result indicates the occurrence of an insertion reaction, making these compounds organozinc derivatives of the elusive α-amino alcohols. Whereas the NMR spectrum of the formaldehyde adduct (I) consists of sharp signals, only broad bands are present in the spectra of the acetaldehyde (II) and n-butyraldehyde (III) adducts.

Molecular weight determinations in benzene solution (cryometric) show adduct I to be a tetramer (no concentration dependence of the molecular weight). The combined NMR and molecular weight results suggest that the reaction product of *N*-(ethylzinc) diphenylamine with formaldehyde, $[EtZnOCH_2NPh_2]_4$, has the cubic structure previously observed for simple alkylzinc alkoxides[7,8]. However, the adducts II and III are extensively dissociating dimers. The presence of a Zn_2O_2-ring in each of the adducts is confirmed by their IR spectra which show $\nu_a(O{-}Zn{-}O)$[9] as a prominent band in the 530–560 cm^{-1} region. The acetaldehyde and butyraldehyde adducts II and III show an absorption in the

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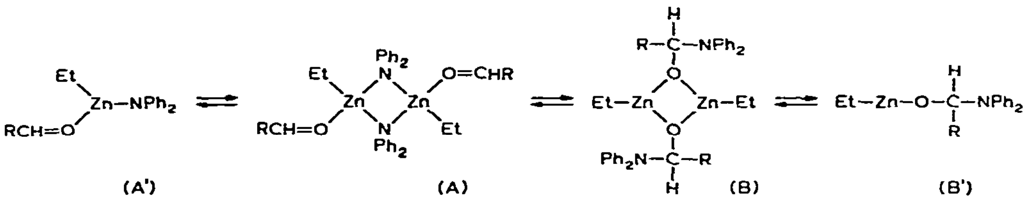
*For part XII see ref. 1.
**Satisfactory analytical data have been obtained for these compounds.

1500 cm^{-1} region (*e.g.* II at 1490 cm^{-1}) which may be assigned tentatively to a coordinated carbonyl group[10].

The data (NMR, IR and molecular weight) for adducts II and III can be explained in terms of the following equilibria (R = Me or n-Pr):



All three adducts react with pyridine to form complexes with 1/1 stoichiometry which have been isolated in crystalline form★. Again, the NMR spectra of the complexes of II and III, contrary to that of I, show broadened signals. In none of these reactions was the liberation of aldehydes detected. Pyridine is apparently unable to cleave the aldehyde coordinate bonds in A or A'. Molecular weight determinations show these pyridine complexes to be dissociating dimers (*cf.* also the presence of ν_a(O–Zn–O) in their IR spectra). It is of interest that exactly the same species are present in solution (identical IR and NMR spectra) and the same crystalline products are isolated regardless of whether the pyridine complex of *N*-(ethylzinc) diphenylamine is treated with acetaldehyde and butyraldehyde or the adducts II and III are treated with pyridine. This confirms that in solution the various monomeric and dimeric species are in rapid equilibrium with each other.

Adduct I reacts with TMED (*N,N,N',N'*-tetramethylethylenediamine) in benzene solution to give a complex which according to the NMR spectrum has 2/1 stoichiometry [$(EtZnOCH_2NPh_2)_2 \cdot TMED$; $\delta(CH_2O)$ 5.67 ppm]. This complex, again, is extensively dissociated in solution. In contrast, both adducts II and III react with TMED to give an equimolar mixture of Ph_2NH and $EtZnNPh_2 \cdot TMED$[11], together with an unidentified oil. These products can be rationalized in terms of equilibrium A $\rightleftharpoons$ B. TMED displaces coordinated aldehyde from A or A'. The free aldehyde is converted under the catalytic influence of $EtZnNPh_2 \cdot TMED$, into the corresponding aldol, which is sufficiently acidic to react with $EtZnNPh_2 \cdot TMED$ to give Ph_2NH, free TMED and the ethylzinc derivative of the aldol (*cf.* the reaction of Et_2AlNR_2 with CH_3OH[12]). In the process the equilibrium A $\rightleftharpoons$ B is shifted to the left side.

The significance of our results for the mechanism of the $EtZnNPh_2$-catalyzed stereospecific polymerization of aldehydes will be discussed in the full paper[13].

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★Satisfactory analytical data have been obtained for these complexes.

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