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EFFECT OF COMPLEX FORMATION ON THE REACTION OF DIALKYLZINC WITH DIPHENYLAMINE

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SUMMARY

The reaction of dialkylzinc with diphenylamine is accelerated by the presence of an equimolar amount of bipyridine, 8-(dimethylamino)quinoline or pyridine. *N,N,N',N'*-Tetramethylethylenediamine, triethylamine, 1,2-dimethoxyethane, and tetrahydrofuran exhibited no accelerating effect. Back-donation from zinc atom is considered to play an important role in the specific effect of complexing agents having conjugated structures.

INTRODUCTION

In the course of our studies on the polymerization of alkylene oxides by optically active catalyst systems based on organometallic compounds[1], we found that the reaction of bis[(*S*)-2-methylbutyl]zinc with diphenylamine was accelerated by the presence of an equimolar amount of 8-(dimethylamino)quinoline. This finding prompted us to study the effect of complexing agents in the reaction of dialkylzinc with diphenylamine and the reaction was found to be accelerated by some complexing agents with conjugated structure, such as 2,2'-bipyridine, but not by *N,N,N',N'*-tetramethylethylenediamine.

RESULTS

The reaction of diethylzinc with diphenylamine

The equimolar reaction of diethylzinc with diphenylamine in benzene solution at 40° was followed by measuring the decrease in absorbance of N–H stretching vibration at 3400 cm^{-1} in the IR spectrum of the reaction mixture. As shown in Fig. 1, the reaction of diethylzinc with diphenylamine in benzene at 40° was very slow, only about five percent of the amine having reacted after twelve hours. In the presence of an equimolar amount of 2,2'-bipyridine, 8-(dimethylamino)quinoline or pyridine, the reaction was much accelerated. *N,N,N',N'*,-Tetramethylethylenediamine, triethylamine and 1,2-dimethoxyethane, on the other hand, showed no accelerating effect.

The reaction of diethylzinc with diphenylamine in the presence of bipyridine was studied in further detail. In the IR spectrum of diethylzinc–bipyridine complex,

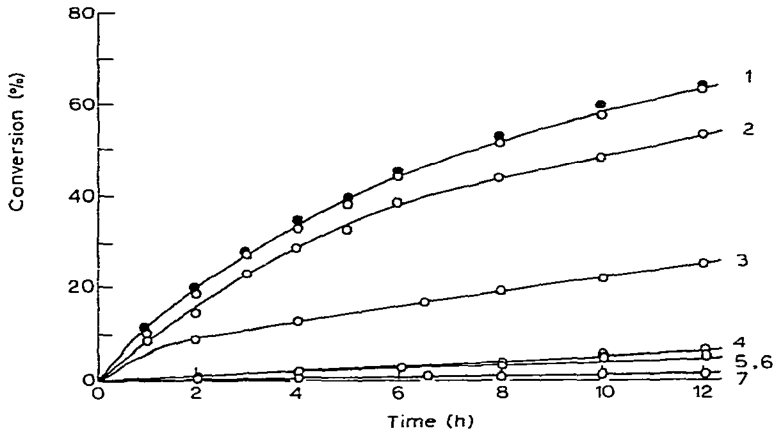


Fig. 1. Reaction of diethylzinc with diphenylamine in benzene at 40°. Initial conc.: diethylzinc, 0.30 *M*; diphenylamine, 0.30 *M*. Complexing agent (mole ratio to zinc): 1. bipyridine (1); 2. 8-(dimethylamino)-quinoline (1); 3. pyridine (1); 4. none; 5. tetramethylethylenediamine (1); 6. triethylamine (2); 7. 1,2-dimethoxyethane (1). ○ as determined by ν(N–H) of diphenylamine. ● as determined by ν_s(C–Zn–C) of diethylzinc.

an absorption due to C–Zn–C symmetrical stretching vibration occurs at 450 cm^{-1}, and in the course of the reaction with diphenylamine, this absorption decreased with time (Fig. 2). The extent of reaction estimated from the decrease in ν_s(C–Zn–C) of diethylzinc was in very good agreement with that deduced from the ν(N–H) of diphenylamine (Fig. 1, No. 1 ○ ●).

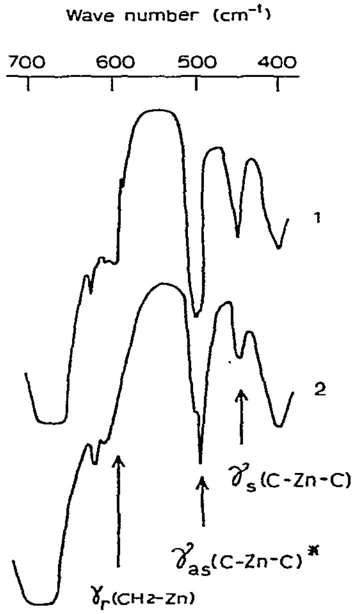


Fig. 2. Reaction of diethylzinc–bipyridine complex with diphenylamine. Infrared spectra. In benzene at 40°. 1. after 0 h and 2. after 12 h. * Superimposed on an absorption due to diphenylamine.

Ethylzinc diphenylamide separately prepared was mixed with an equimolar amount of bipyridine and further reaction of this mixture with diphenylamine was attempted. Under the same condition as in Figs. 1 and 2, no decrease in ν(N–H) absorption of diphenylamine was observed even after ten hours, indicating that there was no further reaction of diphenylamine with the ethylzinc diphenylamide formed. Since dialkylzinc[2] and alkylzinc diphenylamide[3] are known to form complexes with bipyridine or pyridine, the present reaction may be expressed as eqn. (1), but does not proceed to step (2) under the given conditions.

$$Et_2Zn \cdot Bipy + HNPh_2 \rightarrow EtZnNPh_2 \cdot Bipy + EtH \qquad (1)$$

$$EtZnNPh_2 \cdot Bipy + HNPh_2 \rightarrow Zn(NPh_2)_2 \cdot Bipy + EtH \qquad (2)$$

The reaction product, a yellowish brown solid soluble in benzene, gave satisfactory analysis. (Found: Zn, 15.1. $C_{24}H_{23}N_3Zn$ calcd.: Zn, 15.6%.) The IR spectrum of the product coincided with $EtZnNPh_2 \cdot Bipy$ complex separately prepared by mixing each component.

The reaction of diethylzinc with diphenylamine in the presence of complexing agent may be described in terms of second-order kinetics, first-order for each reactant (Fig. 3). Rate constants calculated on the basis of data given in Fig. 3 are summarized in Table 1. When the reaction of diethylzinc with diphenylamine was attempted in tetrahydrofuran as solvent, instead of benzene, at 40°, no appreciable reaction was observed even after twelve hours.

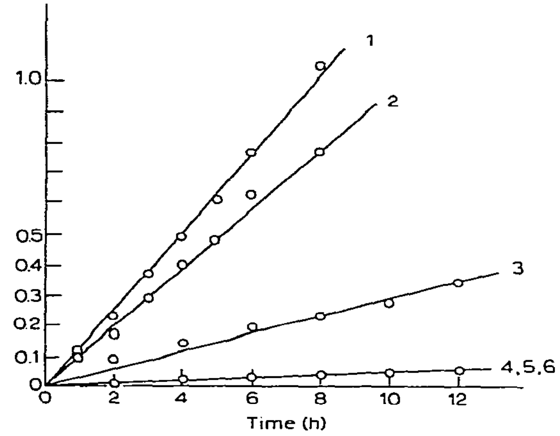


Fig. 3. Second-order plot of diethylzinc/diphenylamine reaction. $1-x$: Extent of reaction: 1. bipyridine; 2. 8-(dimethylamino)quinoline; 3. pyridine; 4. none; 5. tetramethylethylenediamine; 6. triethylamine.

Reaction of di-n-butylzinc and bis[(S)-2-methylbutyl]zinc with diphenylamine

The reactions of di-n-butylzinc and bis[(*S*)-2-methylbutyl]zinc with diphenylamine were also studied. In the case of di-n-butylzinc, the rate of reaction was determined as described above for diethylzinc, and the second-order rate constants thus obtained are summarized in Table 2.

Addition of five molar equivalents of 1,2-dimethoxyethane to di-n-butylzinc did not change the rate from that obtained with one molar equivalent.

The reaction of bis[(*S*)2-methylbutyl]zinc with diphenylamine without any

TABLE 1

RATE CONSTANTS FOR THE DIETHYLZINC/DIPHENYLAMINE REACTION[a]

Complexing agent[b]	Rate constant ($l \cdot mole^{-1} \cdot h^{-1}$)	Complexing agent[b]	Rate constant ($l \cdot mole^{-1} \cdot h^{-1}$)
None	1.6×10^{-2}	Bipy	4.1×10^{-1}
Triethylamine[c]	1.1×10^{-2}	8-DMAQ	3.2×10^{-1}
TMED	1.2×10^{-2}	DME	7×10^{-3}
Pyridine	9.6×10^{-2}		

[a] In benzene at 40°; diethylzinc 0.30 *M*, diphenylamine 0.30 *M*; equimolar ratio of complexing agent to zinc. [b] TMED: *N,N,N',N'*-tetramethylethylenediamine, 8-DMAQ: 8-(dimethylamino)quinoline, DME: 1,2-dimethoxyethane. [c] Mole ratio to zinc: two.

TABLE 2

RATE CONSTANTS FOR THE DI-n-BUTYLZINC/DIPHENYLAMINE REACTION[a]

Complexing agent	Rate constant ($l \cdot mole^{-1} \cdot h^{-1}$)
None	1.5×10^{-2}
TMED	1.5×10^{-2}
Bipy	3.5×10^{-1}
DME	8×10^{-3}

[a] For the reaction conditions, see Table 1.

complexing agent was rather slow, only 10% of reaction occurring in 24 h at 80° in benzene (0.30 *M*). Reaction in tetrahydrofuran at 66° proceeded at a similar rate. Even when the temperature was raised to 110° with toluene as solvent, only 27% of reaction took place in 26 h.

That acceleration of the reaction occurs upon addition of an equimolar amount of 8-(dimethylamino)quinoline (8-DMAQ) even at room temperature was indicated by the change in optical rotation of the reaction mixture (Fig. 4), since the rotation of the bis[(*S*)-2-methylbutyl]zinc·8-DMAQ complex is positive while that

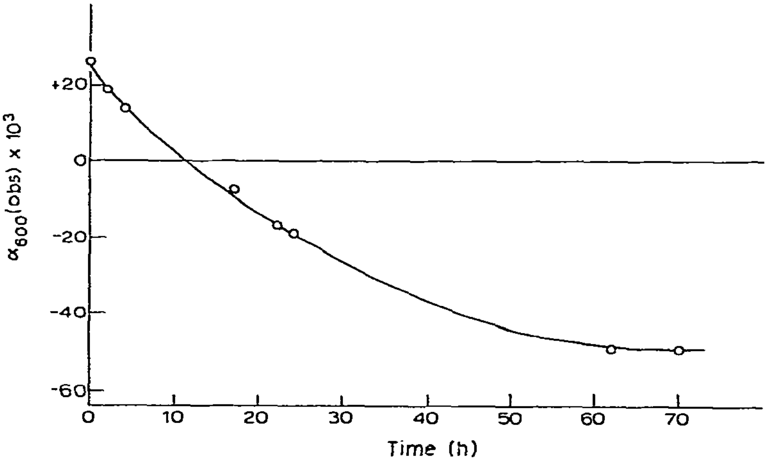


Fig. 4. Reaction of bis[(*S*)-2-methylbutyl]zinc with diphenylamine in the presence of 8-(dimethylamino)quinoline. Optical rotation: 0.20 *M* in benzene at 20°; cell length 0.1 dm.

of the (*S*)-2-methylbutylzinc diphenylamide·8-DMAQ complex is negative (see Experimental Part).

$$R^*_2Zn \cdot 8\text{-DMAQ} + HNPh_2 \rightarrow R^*ZnNPh_2 \cdot 8\text{-DMAQ} + RH \qquad (3)$$

[R* = (*S*)-2-methylbutyl]

Reaction (3) proceeded to the extent of 66% in 24 h at room temperature in benzene. When the reaction mixture was kept at room temperature for a longer period, *e.g.*, 70 h, the sign of the optical rotation remained negative, showing that reaction (4) [corresponding to reaction (2)] did not occur under the given conditions; if reaction (4) had occurred, the reaction mixture would have lost its optical activity.

$$R^*ZnNPh_2 \cdot 8\text{-DMAQ} + HNPh_2 \rightarrow Zn(NPh_2)_2 \cdot 8\text{-DMAQ} + RH \qquad (4)$$

The low reactivity of the second alkyl group attached to zinc is in agreement with the results obtained with diethylzinc.

DISCUSSION

As mentioned above, complexing agents with conjugated structures such as bipyridine, 8-(dimethylamino)quinoline and pyridine accelerate the reaction of dialkylzinc with diphenylamine, whereas N,N,N',N'-tetramethylethylenediamine, triethylamine and 1,2-dimethoxyethane do not.

Enhancement of the reactivity of organolithium or organomagnesium compounds when coupled with similar complexing agents has been considered at least partly due to the decrease in the degree of association of the organometallic compounds by the complex formation.

Dialkylzinc itself, however, is monomeric in benzene solution and the reactivity increase in the present reaction thus cannot be ascribed to a change in the degree of association. The remarkable increase in reactivity of alkyllithium when coordinated by N,N,N',N'-tetramethylethylenediamine (TMED) as a strong Lewis base has been considered to be caused by the enhancement of the carbanionic character of carbon–lithium linkage, and the ineffectiveness of TMED in the reaction of dialkylzinc with diphenylamine is significant.

In comparing the reactivities of the TMED complex and the bipyridine complex, the stability of the complexes should be taken into account. Results obtained by dielectric constant titration[2] show that the dissociation constant in benzene of diethylzinc–bipyridine complex is larger than that of TMED complex (30×10^{-5} and 1×10^{-5}, respectively); thus more of the complexed form is present in the case of TMED than in that of bipyridine. Thus it is safe to conclude that the TMED complex has no enhanced reactivity while the bipyridine complex exhibits high reactivity.

As for the strength of the coordination, examination of the IR absorptions of the complexes in low wavenumber region is helpful. The shifts in the C–Zn–C stretching vibrations and the rocking vibration of the methylene group adjacent to the zinc atom were studied in various solvents including ethers and tertiary amines[4], and the degree of the shift of ν_{as}(C–Zn–C) to lower wavenumber was found to be related to the strength of the coordination. With the diethylzinc–bipyridine and –TMED complexes, the shifts in ν_{as}(C–Zn–C) are of the same order (Table 3).

Such small difference in coordination strength are unlikely to account for the

TABLE 3

IR SPECTRA OF DIETHYLZINC COMPLEXES[a]

Complexing agent	Absorption (cm^{-1})		
	$\gamma_r(CH_2\text{–}Zn)$	$\nu_{as}(C\text{–}Zn\text{–}C)$	$\nu_s(C\text{–}Zn\text{–}C)$
None	620 s	561 s	484 s
Triethylamine	604 s	552 w	458 w
		525 s	
TMED	600	498 s	456 s
	585		430
Pyridine	602 s	528 s	444 w
		500 s	
Bipy	594 s	501 s	450 s

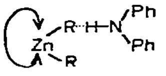
[a] In benzene. Ratio of complexing agent as mentioned in Table 1.

difference in the reactivity of these two complexes.

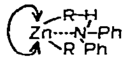
Recently, it was reported[5] that the reaction of dimethylmagnesium with benzophenone was retarded by TMED, but accelerated by 1,2-dimethoxyethane, and the retardation by TMED was ascribed to steric hindrance, which prevents the coordination of the carbonyl group of benzophenone to magnesium. In the reaction of dialkylzinc with diphenylamine, 1,2-dimethoxyethane was also ineffective. The low reactivity of dialkylzinc–TMED complex is thus not due to steric hindrance specific for TMED.

The light of the considerations above, the high reactivity of the dialkylzinc–bipyridine complex, for example, is thought to be related to back donation from the zinc atom to the coordinated complexing agent, which is possible only for complexing agents with conjugated structures such as bipyridine, 8-DMAQ and pyridine. Such a back donation (π-bonding) has been suggested to be responsible for the trends observed in the stability of such complexes[2], which have characteristic colours due to charge transfer.

Since the reaction of dialkylzinc with diphenylamine is a second-order process, the transition state of this reaction can be depicted as in (I) or (II)[6].



(I)



(II)

Acceleration by bipyridine but not by TMED strongly favours (II), with back donation from zinc to bipyridine increasing the electron accepting ability of the zinc atom and thus facilitating the coordination of diphenylamine. In case of transition state (I), TMED would also be effective.

An accelerating effect of some polar solvents such as tetrahydrofuran, dimethoxyethane, dimethylformamide, dimethyl sulfoxide and hexamethylphosphoric triamide has been reported in the reaction of diethylzinc with phenylacetylene[7], but the reactivity enhancement was ascribed to the increase in nucleophilicity of the organozinc compound by solvation. The present report is the first to ascribe an important role to back donation involving zinc atom in the reactivity of organozinc compounds.

EXPERIMENTAL

Organometallic compounds

Diethylzinc was purified by distillation in nitrogen atmosphere. B.p. 40°/40 mm.

Di-n-butylzinc was prepared by the reaction of n-butyl halide with zinc/copper couple[8]. B.p. 59°/5 mm.

Bis[(*S*)-2-*methylbutyl*]*zinc* was prepared by the method used for di-n-butylzinc. To a mixture of 100 g of (*S*)-2-methylbutanol {b.p. 129–131°, $[\alpha]_D^{24}$ –4.47} and phosphorus (16 g) was added slowly 160 g of iodine. When the initial exothermic reaction ceased, the mixture was heated at 80° for 4 h. Distillation under reduced pressure gave crude (*S*)-2-methylbutyl iodide, which was washed with aqueous sodium bisulfite, then with aqueous sodium hydroxide, dried over calcium chloride and rectified, b.p. 45.0–46.0°/20 mm; $[\alpha]_D^{21}$ +5.81. The (*S*)-2-methylbutyl iodide (100 g) thus obtained was reacted with zinc/copper couple, prepared from zinc dust (90 g) and cupric citrate (17.5 g), under nitrogen at 70–80°. Bis[(*S*)-2-methylbutyl]zinc was obtained by distillation; b.p. 66.5–67.5°/4 mm; $[\alpha]_D^{20}$ +9.37; d^{21} 0.96.

Ethylzinc diphenylamide was prepared by the reaction of diphenylamine with a slight excess of diethylzinc in benzene at 80°[9,10]. After 24 h volatile materials were removed by freeze-drying and the product was recrystallized from n-hexane, m.p. 108–110°.

(*S*)-2-*Methylbutylzinc diphenylamide* was prepared by the procedure described above but the reaction was carried out without solvent at 90° for 24 h. Repeated recrystallization of the product from n-hexane gave a white solid. (Found: Zn, 21.9 $C_{17}H_{21}NZn$ calcd.: Zn, 21.2%.) The NMR spectrum (in dioxane) indicated the ratio of aliphatic and aromatic hydrogens to be 11.2/10.0. The IR spectrum (in benzene) showed no absorption due to ν(N–H). $[\alpha]_D$ +5.52 (c = 8.4, in benzene).

Other reagents

Benzene, toluene and tetrahydrofuran were purified by the usual methods. Diphenylamine was purified by distillation under reduced pressure, b.p. 119°/3 mm. Bipyridine was recrystallized from n-hexane, m.p. 72.0–72.5°. *N,N,N',N'*-Tetramethylethylenediamine and 1,2-dimethoxyethane were purified by distillation over sodium metal in a nitrogen atmosphere. Pyridine was distilled over potassium hydroxide.

8-(*Dimethylamino*)*quinoline*. 8-Hydroxyquinoline (50 g) was added to a mixture of conc. aqueous ammonia (200 ml) and sulfur dioxide (45 g), and the mixture was heated at 150° for 8 h in an autoclave. The precipitate formed was washed out with ice-cold water, potassium hydroxide (2 g) was added, and the mixture steam distilled. The solid product was recrystallized from ligroin to give light yellow crystals of 8-aminoquinoline[11], m.p. 64.5–65.0°. 8-Aminoquinoline (35 g) in ether was slowly added to a suspension of sodium amide (10.3 g) in ether, then the mixture was refluxed until evolution of ammonia was over (about 1.5 h). An ether solution of dimethyl sulfate (16 g) was added slowly with stirring, then the mixture was refluxed for one hour. The addition of sodium amide (10.3 g), refluxing, and reaction with dimethyl sulfate (16 g) were then repeated. Water was added and the mixture was made alkaline and extracted with ether. The ether extracts were dried over potassium carbonate, the ether was removed, and the residue distilled. Rectification over sodium metal gave 10 g (24%) of 8-(dimethylamino)quinoline as a yellow liquid, b.p. 110–112°/1 mm. (Found: C, 76.74; H, 6.98. $C_{11}H_{12}N_2$ calcd.: C, 77.04; H, 6.94%.)

Complex formation of (S)-2-methylbutylzinc diphenylamide with 8-(dimethylamino)quinoline

When a toluene solution of (*S*)-2-methylbutylzinc diphenylamide was added to a toluene solution of 8-(dimethylamino)quinoline (8-DMAQ), a large change in optical rotation of the mixture occurred (Fig. 5.). The Figure indicates the formation of a 1/1 complex with a negative rotation. The IR spectrum shows the disappearance of an absorption at 2780 cm^{-1} due to ν(C–H) of the methyl group on the tertiary nitrogen atom, indicating quaternarization of the nitrogen. The methyl signal of $N\text{–}CH_3$ in the NMR spectrum shifted from the τ value 7.06 to 7.43. The red color of the solution indicates back donation from the zinc atom to the quinoline, as suggested for the dialkylzinc–bipyridine complex[2]. (*S*)-2-Methylbutylzinc diphenylamide · 8-DMAQ, $[\alpha]_{630}$–7.4 (c=24.8, in benzene); bis[(*S*)-2-methylbutyl]zinc · 8-DMAQ, $[\alpha]_D$+3.5 (c=24.8, in benzene).

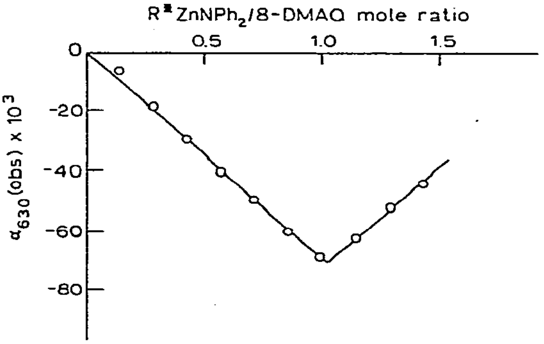


Fig. 5. Complex formation between (*S*)-2-methylbutylzinc diphenylamide and 8-(dimethylamino)quinoline (0.397 *M*) in toluene. Cell length 0.1 dm.

Reaction of dialkylzinc with diphenylamine

All reactions were carried out under nitrogen in a constant temperature bath, usually at 40°. To a mixture of diphenylamine and complexing agent in benzene, dialkylzinc was added. At suitable time intervals samples of the reaction mixture were transferred to an IR cell. The measurement was made under nitrogen at 20° with a Hitachi model EPI-G3 spectrophotometer.

The reaction of bis[(*S*)-2-methylbutyl]zinc with diphenylamine in the presence of 8-(dimethylamino)quinoline was studied using a Nippon Bunko model ORD/UV-5 automatic recording spectropolarimeter (error in $\alpha_{obs} = \pm 0.001$).

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