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Supplementary Material Available: Tables of bond distances, angles, and anisotropic thermal parameters for $[Ir_2(SnCl)(CO)_2Cl_2(\mu\text{-dpma})_2][Ir(SnCl_3)_2CO(dpma)]\cdot 2.25CH_2Cl_2$, tables of atomic positional parameters, bond distances, angles, anisotropic thermal parameters, and hydrogen positions for $[Ir_2(AgCl)(CO)_2Cl_2(\mu\text{-dpma})_2]\cdot 1.8CH_2Cl_2$, and full details of data collection, solution, and refinement (18 pages). Ordering information is given on any current masthead page.

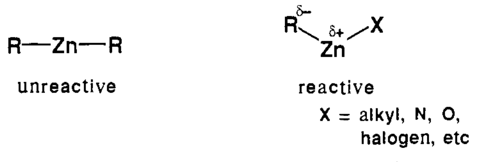
Enantioselective Addition of Dialkylzincs to Aldehydes Promoted by Chiral Amino Alcohols. Mechanism and Nonlinear Effect

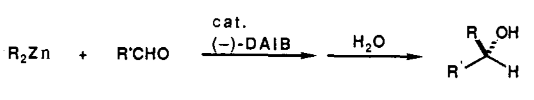
M. Kitamura, S. Okada, S. Suga, and R. Noyori*

Contribution from the Department of Chemistry, Nagoya University, Chikusa, Nagoya 464, Japan. *Received September 2, 1988*

Abstract: In the presence of a catalytic amount of (−)-3-*exo*-(dimethylamino)isoborneol (DAIB), reaction of dialkylzincs and aldehydes is accelerated markedly to give, after hydrolysis, the corresponding *S*-alcohols in high enantiomeric purity. The reaction mechanism and origin of the enantioselection have been elucidated on the basis of the kinetic measurement, alkyl-scrambling experiments, single-crystal X-ray analysis, ^{1}H NMR study, molecular weight determination of certain key intermediates. Reaction of DAIB and dimethylzinc in a 1:1 molar ratio produces a single dinuclear zinc chelate complex, which does not alkylate benzaldehyde but acts as catalyst precursor. The alkylation proceeds via a dinuclear zinc species containing the DAIB auxiliary, an aldehyde ligand, and three alkyl groups, where it is the bridging alkyl group, rather than the terminal alkyls, that migrates from zinc to the aldehyde carbon. Kinetic measurements and temperature effects on the enantioselectivity indicate that the alkyl transfer process is the turnover-limiting and stereodetermining step. A new type of nonlinear effect has been observed in this enantioselective alkylation. For example, reaction of benzaldehyde and diethylzinc in the presence of 8 mol % of (−)-DAIB in 15% ee leads to (*S*)-1-phenyl-1-propanol in 95% ee. This unusual phenomenon is a result of a marked difference in chemical properties of the diasteromeric dinuclear complexes formed from dialkylzincs and the DAIB auxiliary. Reaction of equimolar amounts of dimethylzinc and enantiomerically pure DAIB affords a dinuclear chelate complex with C_2 chirality, which acts as the active catalyst precursor of the alkylation. By contrast, dimethylzinc and racemic DAIB generate a more stable, but much less reactive, dinuclear complex possessing a meso, C_i structure, rather than a racemic mixture of the chiral complex.

Monomeric dialkylzincs having an sp hybridized, linear geometry are inert to simple carbonyl compounds, because the alkyl–metal bond is rather nonpolar. However, addition of certain donor ligands or auxiliaries can generate coordinatively unsaturated, bent structures possessing higher reactivity. Particularly, replacement of the alkyl group by an electronegative substituents increases polarity of the alkyl–Zn bond to a great extent and, consequently, enhancement of the donor property of the alkyl group and the acceptor character of the Zn atom is the result.[1] In 1986, we reported that dialkylzincs react with aldehydes in the presence of a catalytic amount of (−)-3-*exo*-(dimethylamino)isoborneol (DAIB) to give after hydrolysis the corresponding *S*-alcohols in high (up to 99%) enantiomeric purities.[2,3] The sterically constrained β-dialkylamino alcohol not only accelerates the alkylation reaction but also directs the stereochemical outcome in the absolute sense. Various para-substituted benzaldehydes give consistently high enantioselectivity, suggesting that the stereoselection is steric





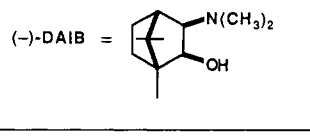


Table I. Effect of the C_6H_5CHO:$(C_2H_5)_2Zn$:(−)-DAIB Molar Ratio on Reactivity[a]

ratio			(*S*)-1-phenyl-1-propanol	
C_6H_5CHO	$(C_2H_5)_2Zn$	(−)-DAIB	% yield[b]	% ee[c]
1	1	0	0[d]	
1	1	1	1[e]	0
1	2	2	0[f]	
1	2	1	88[d]	98
2	2	1	49[g]	96
100	50	1	48[h]	98
50	50	1	97[d]	98

[a] All reactions were carried out under argon at 0 °C in degassed anhydrous toluene unless otherwise specified. [b] HPLC analysis (Develosil 100-5, ether–hexane). Based on benzaldehyde. [c] HPLC analysis (Bakerbond DNBPG covalent type, 2-propanol–hexane). [d] Benzyl alcohol was obtained in 1–3% yield. [e] After 170 h, 29% of benzyl alcohol was obtained. [f] After 1500 h, 64% of benzyl alcohol was obtained. [g] After 170 h, 13% of benzyl alcohol was obtained. [h] After 170 h, 12% of benzyl alcohol and 10% of propiophenone were obtained.

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(1) Boersma, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Chapter 16.

(2) Kitamura, M.; Suga, S.; Kawai, K.; Noyori, R. *J. Am. Chem. Soc.* **1986**, *108*, 6071.

(3) For related reactions, see: (a) Oguni, N.; Omi, T. *Tetrahedron Lett.* **1984**, *25*, 2823. (b) Smaardijk, A. A.; Wynberg, H. *J. Org. Chem.* **1987**, *52*, 135. (c) Itsuno, S.; Frêchet, J. M. J. *J. Org. Chem.* **1987**, *52*, 4140. (d) Soai, K.; Ookawa, A.; Ogawa, K.; Kaba, T. *J. Chem. Soc., Chem. Commun.* **1987** 467. Soai, K.; Ookawa, A.; Kaba, T.; Ogawa, K. *J. Am. Chem. Soc.* **1987**, *109*, 7111. (e) Chaloner, P. A.; Perera, S. A. R. *Tetrahedron Lett.* **1987**, *28*, 3013. (f) Corey, E. J.; Hannon, F. J. *Tetrahedron Lett.* **1987**, *28*, 5233. (g) Corey, E. J.; Hannon, F. J. *Tetrahedron Lett.* **1987**, *28*, 5237. (h) Evans, D. A. *Science* **1988**, *240*, 420.

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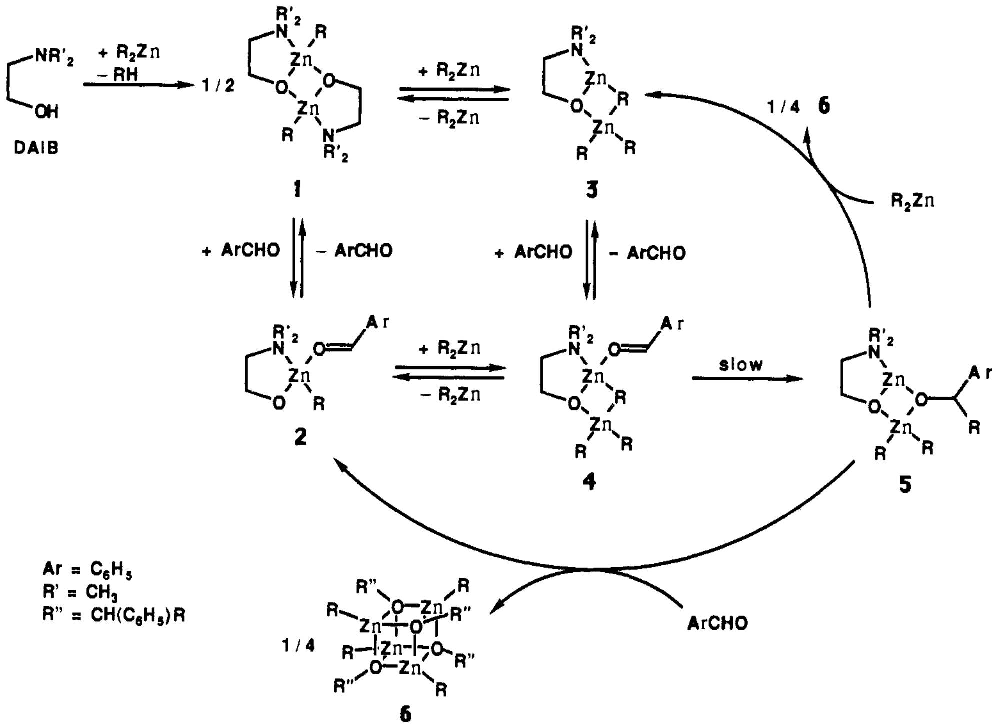
Scheme I



in origin. Certain α,β-unsaturated and aliphatic aldehydes can also be alkylated with a high degree of enantioselectivity. Dimethyl-, diethyl-, and di-*n*-butylzinc can be used as the alkylating agent. The methylation proceeds rather slowly but gives comparable results. Notably, the enantioselective reaction exhibits a unique nonlinear relationship between the enantiomeric purities of the chiral amino alcohols and alkylation products. This paper describes the mechanism of the enantioselective catalysis and the origin of the intriguing nonlinear effect.

Reaction Mechanism

We have found that stoichiometry of the aldehyde, alkylzinc, and DAIB auxiliary has marked effects on the reactivity and reaction course. Table I illustrates results of the ethylation reaction with varying stoichiometries, indicating the alkylation occurs only when dialkylzinc:DAIB ratio is greater than 1. A complex formed from equimolar amount of dialkylzinc and DAIB could not ethylate benzaldehyde but formed slowly benzyl alcohol. These results clearly indicate that two Zn atoms per aldehyde are responsible for the alkylation reaction.[2] This view was also supported by the experiments using a polymer-bound DAIB as auxiliary.[3c]

We now postulate the catalytic cycle of Scheme I for the ligand accelerated reaction, where structure of DAIB is simplified. Alkylzinc compounds are generally fluxional in nature and undergo ready interconversion with the possible structural isomers by intra- or intermolecular processes; only significant structures are formulated in the scheme.[4] The reaction pathway has been examined mainly by using dimethylzinc, because the methylzinc intermediates are less fluxional than other alkyl analogues and easier to monitor. Many lines of structural information support the mechanism of Scheme I which possesses a soft energy surface. (1) In the absence of DAIB, dialkylzincs and benzaldehyde have merely donor–acceptor type weak interactions in toluene. ^{1}H NMR spectra of the mixtures exhibited only the independent signals of each component. (2) When (–)-DAIB and dimethylzinc were mixed in a 1:1 mole ratio in toluene, methane was evolved[5] and a single dimeric compound **1** (R = CH_3), among three possible isomers, was produced. The dinuclear structure in hydrocarbon solution and solid state was substantiated by cryoscopic molecular weight (MW) determination in benzene, ^{1}H and ^{13}C NMR spectra, and single-crystal X-ray analysis [The detailed structure will be given later. See structure (–)(–)-**1** (R = CH_3) in Figure 4]. This complex is unable to alkylate aldehyde[6] but acts as a catalyst precursor. (3) The dinuclear framework of **1** (R = CH_3) is ruptured spontaneously by addition of benzaldehyde to form the mononuclear complex **2**.[7] This process is reversible and proceeds probably via a dissociative mechanism with respect to **1**.[8] A broad aldehydic proton signal is observed in the ^{1}H NMR spectrum at 0 °C. The position of equilibration, though favoring **2**, depends on the **1**:aldehyde ratio as revealed by MW measurement [MW calcd 383, obsd 338 (77 mM benzene solution, **1**:benzaldehyde = 1:2) corresponding to 74% conversion]. Reaction with a 1:6 **1**:aldehyde ratio provides 85% conversion. (4) Dimethylzinc also cleaves the dimeric structure of **1** (R = CH_3) equilibrating with the monomeric form,[8] leading to a new, unsymmetrical dinuclear complex, **3**. This methyl complex, unsaturated at Zn, is highly fluxional and the three different Zn–CH_3 groups undergo rapid exchange, exhibiting an ^{1}H NMR signal at δ –0.27 as a very sharp singlet at 25 °C and as a somewhat broad singlet at –50 °C. (5) The methyl complex **3** in a 95 mM benzene solution has MW of 352 [**1**:$(CH_3)_2Zn$ = 1:2, calcd 372]. The formation of **3** is also reversible as proved by MW measurement of the ethyl complex with varying **1**:$(C_2H_5)_2Zn$ ratio; 80% and 87% conversions were attained with a 1:2 and 1:8 molar ratio, respectively. No sign of the occurrence of higher aggregates is observed in a 52–170 mM concentration range; addition of large excess of diethylzinc does not affect the MW either. This phenomenon is characteristic of the DAIB-catalyzed system.[9] (6) When 1 equiv of dimethylzinc was introduced to a toluene solution

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[4] For example, the bicyclic structures **3** and **5** which possess an unsaturated, angular Zn(sp^3) atom are in equilibria with their positional isomers having an unsaturated Zn(sp^2) atom at the nonangular position. In a like manner, positional isomers are possible for **4**.

[5] (a) Coates, G. E.; Ridley, D. *J. Chem. Soc. A* **1966**, 1064. (b) Boersma, J.; Noltes, J. G. *J. Organomet. Chem.* **1968**, *13*, 291.

[6] Complex **2** (R = C_2H_5 or *n*-C_4H_9; Ar = C_6H_5) slowly gave benzyl alcohol after hydrolysis.

[7] Reetz, M. T.; Hüllmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, *108*, 2405.

[8] The results obtained by using polymer-anchored DAIB[3c] agree with this interpretation.

[9] Mixing diethylzinc and 2-(dimethylamino)-3-methyl-1-butanol, 3-(dicyclohexylamino)-2-propanol, or 2-(dimethylamino)-1-phenylethanol in a 2:1 molar ratio forms tetranuclear zinc complexes as judged by cryoscopic MW measurement: Matsuda, Y.; Tokumitsu, T.; Oguni, N., In *34th Symposium on Organometallic Chemistry*; Kyoto, Japan, 1987; PB 205.

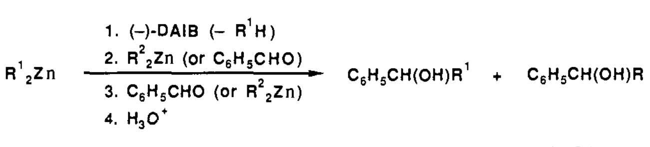
Table II. Scrambling Experiments Using DAIB, R^1_2Zn, R^2_2Zn, and Benzaldehyde in a 1:1:1:1 Molar Ratio[a]

dialkylzincs		product ratio		rel reactivity
R^1_2Zn	R^2_2Zn	C_6H_5-$CH(OH)R^1$	C_6H_5-$CH(OH)R^2$	R^1:R^2
CH_3	C_2H_5	2	93	1:21
C_2H_5	CH_3	76[b]	8[c]	19:1
C_2H_5	n-C_4H_9	44	35	2.5:1
C_2H_5[d]	n-C_4H_9	41	32	2.6:1
C_2H_5[e]	n-C_4H_9	38	32	2.4:1
n-C_4H_9	C_2H_5	14	68	1:2.4
n-C_4H_9[d]	C_2H_5	13	66	1:2.5
n-C_4H_9[e]	C_2H_5	14	67	1:2.4

[a] R^1_2Zn was first added to a toluene solution of (−)-DAIB at 30 °C and, after 15 min, R^2_2Zn was added. After the mixture was stirred for 10 min and cooled to 0 °C, benzaldehyde was added. The mixture was stirred at 0 °C for 6 h, quenched with water, and analyzed by HPLC. All reactions produced 3–14% benzyl alcohol. [b] *S* product in 98% ee. [c] *S* product in 94% ee. [d] R^2_2Zn was added to the initially formed R^1Zn complex and the mixture was stirred at −78 °C. Then benzaldehyde was added. [e] Benzaldehyde was added to the R^1Zn complex prior to addition of R^2_2Zn.

of **2** (R = CH_3) at 0 °C, a new dynamic system containing **4** was formed. The same equilibrating mixture was obtained by mixing **3** and benzaldehyde in a 1:1 mole ratio. The ^1H NMR spectrum, giving very broad signals (C_6H_5CHO, δ 9.7, and Zn–CH_3, δ −0.25), indicates the presence of an equilibrium, **2** ⇄ **4** ⇄ **3**. (7) Upon standing the mixture at 20 °C, a methyl-transfer reaction occurred slowly to give an alkoxide which may be assigned the structure **5** (R = CH_3). In the ^1H NMR spectrum, methyl and methine protons due to the bridged alkoxide afford a doublet at δ 1.93 and a quartet at δ 5.36, respectively, whereas the Zn–CH_3 signal appears as a broad singlet at δ −0.17. (8) Complex **5** (R = CH_3) was rather stable under such conditions and was very slowly converted to the cubic Zn alkoxide tetramer **6** (R = CH_3)[10] [MW calcd 806, obsd 759 (51 mM benzene solution), ^1H NMR δ −0.44 (singlet, Zn–CH_3), 1.72 (doublet, alkoxide methyl), and 5.13 (quartet, alkoxide methine)] and catalyst precursor **1**. Notably, upon exposure to benzaldehyde or dimethylzinc, **5** underwent instantaneous decomposition leading to stable tetramer **6**, and thus the catalytic process is greatly facilitated.

In accord with the fluxional nature of the intermediates, when two different alkylzinc agents were employed, a statistical distribution of the possible products was observed.[11] The results are summarized in Table II. The product ratio was governed only by a statistical ratio of the two alkyl groups and their relative reactivities (CH_3:C_2H_5:n-C_4H_9 = 1:20:8)[6] and not influenced by the order or conditions including temperature (−78 to 30 °C) of the mixing of the aldehyde and the second dialkylzinc to the initially formed dimeric Zn chelate complexes of type **1**.



$$R^1_2Zn \xrightarrow[\substack{3.\ C_6H_5CHO\ (\text{or } R^2_2Zn) \\ 4.\ H_3O^+}]{\substack{1.\ (-)\text{-DAIB}\ (-\ R^1H) \\ 2.\ R^2_2Zn\ (\text{or } C_6H_5CHO)}} C_6H_5CH(OH)R^1 + C_6H_5CH(OH)R$$

Preliminary results of the kinetic measurements, given in Figure 1, indicate that, under the standard catalytic conditions using a 0.3–1.3 M diethylzinc, 0.3–1.3 M benzaldehyde, and 2–25 mM DAIB solution in toluene at 0 °C, the reaction is first order in the DAIB auxiliary but the rate is not affected by concentration of the dialkylzinc and aldehyde substrate. With aldehyde concentration lower than 0.3 M, the rate was dependent on the concentration. The result is consistent with the presence of a preequilibrium consisting of **1**–**4** and suggests that the alkyl transfer is taking place in the mixed ligand complex **4**. The possibility of any bimolecular mechanisms involving free benzaldehyde or monomeric dialkylzinc agents is dismissed. The degree

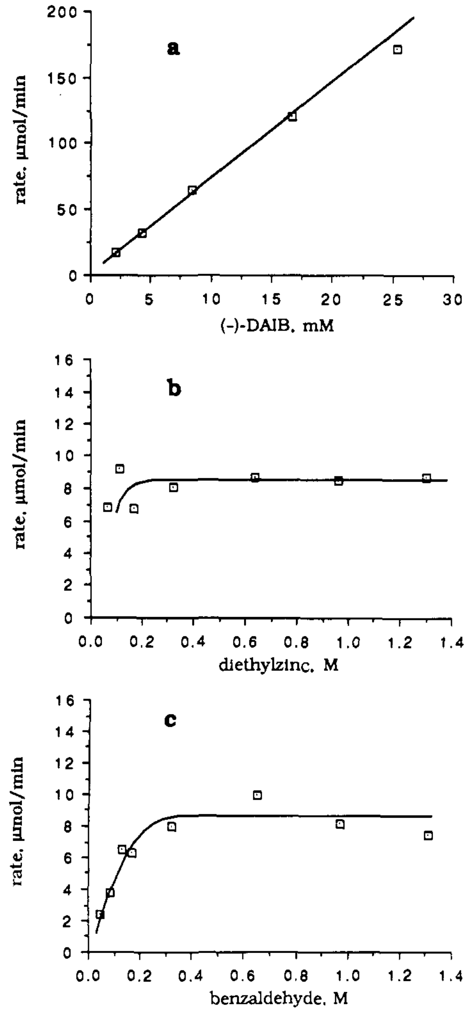


Figure 1. Rates of the reaction of benzaldehyde and diethylzinc in the presence of (−)-DAIB in toluene at 0 °C: a, The plot of the initial rate as a function of [(−)-DAIB] (0.41 M $(C_2H_5)_2Zn$, 0.41 M C_6H_5CHO); b, The plot of the initial rate as a function of [$(C_2H_5)_2Zn$] (2.1 mM (−)DAIB, 0.33 M C_6H_5CHO]; c, The plot of the initial rate as a function of [C_6H_5CHO] (2.1 mM (−)-DAIB, 0.33 M $(C_2H_5)_2Zn$).

of enantioselectivity was lowered considerably by raising the reaction temperature from −20 °C (*S*:*R* = 99:1) to 50 °C (94.5:5.5). These facts, coupled with the ^1H NMR observations, suggest that the alkyl-transfer step, **4** → **5**, is the turnover limiting, as well as the stereodetermining, step.

The sterically demanding DAIB auxiliary plays a significant role in the efficient and selective creation of the chiral Zn chelate complexes. The product-determining Zn complex **4** would have an "endo-fused" four-membered ring geometry with respect to DAIB skeleton as in the complex **1**, and the more Lewis acidic DAIB-chelated Zn_A atom accommodates the aldehyde substrate. Here the bridging R, rather than the terminal R, acts as the migrating group, because the Zn–$R_{bridging}$ linkage is more polarizable than the Zn–$R_{terminal}$ bond. In going from the ground state to the transition state, electrophilicity of the aldehyde and nucleophilicity of the alkyl group must be enhanced. As easily seen from the polar limiting structure **4b**, this electronic requirement is most satisfied by the ligand arrangement in **4**. Thus the bridging R migrates to the electron-deficient carbonyl carbon via the transition structure **7**. A tricoordinate structure of the migrating R features the transition-state structure **7**. Such a nonclassical mechanism involving a bicyclic transition structure has been advanced theoretically for the addition of dimeric methyllithium to formaldehyde.[12]

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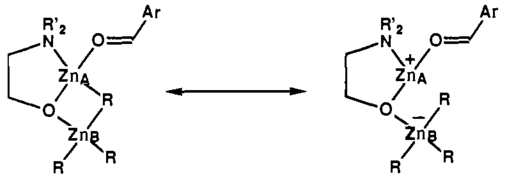
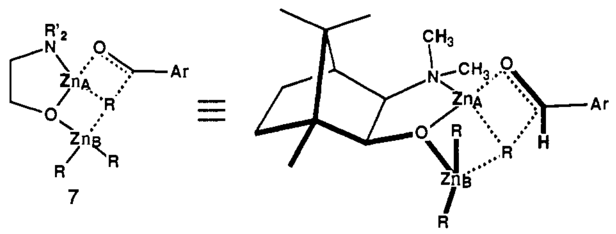
(10) Prepared independently from dimethylzinc and (*S*)-1-phenylethanol.

(11) Fréchet claimed an absence of such scrambling under his reaction conditions.[3c]

(12) Kaufmann, E.; Schleyer P. v. R.; Houk, K. N.; Wu, Y.-D. *J. Am. Chem. Soc.* **1985**, *107*, 5560.



4a **4b**



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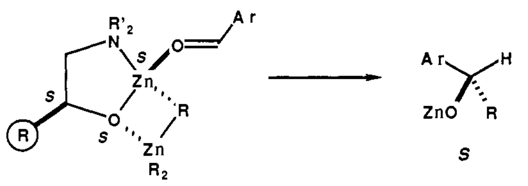
Inspection of molecular models suggests that the kinetic bias leading to the *S*-configurated alkoxide derives primarily from a nonbonded repulsion between the carbonyl substituents (Ar and H) and a terminal R group attached to Zn_B. Survey of the stereochemical results of this and related reactions[3] revealed that the general sense of the asymmetric induction is determined by the chirality of the product-forming 5/4-fused bicyclic intermediate. The (*S*)-Zn alkoxide is derived consistently from the dinuclear intermediate **8** possessing *S*-configurated Zn and O atoms at the angular positions, while the corresponding *R*-Zn, *R*-O, structure **9** leads to the *R* enantiomer. Here the stereogenic carbon bearing oxygen atom plays a crucial role in the selective creation of the chiral bicyclic structure. The adjacent nitrogen-bearing stereogenic center as well as nitrogen substituents also exerts influence, but is of secondary importance. The substituents in the amino alcohol thus define the chirality of the 5/4 bicyclic skeleton, which in turn is transmitted to the Zn-complexed aldehyde substrate by alkyl transfer. Direct nonbonded interaction between the auxiliary substituents and carbonyl substituents is not very significant in the enantioselection. In this context, DAIB among others serves as the best chiral auxiliary; the cis relationship of the C(1) and C(2) substituents as well as the sterically demanding backbone prohibits formation of the diasteromeric 5/4-fused system.



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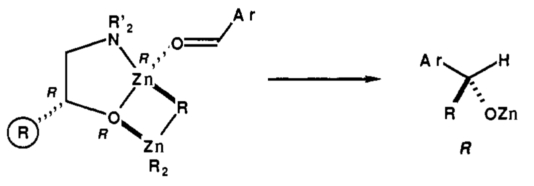

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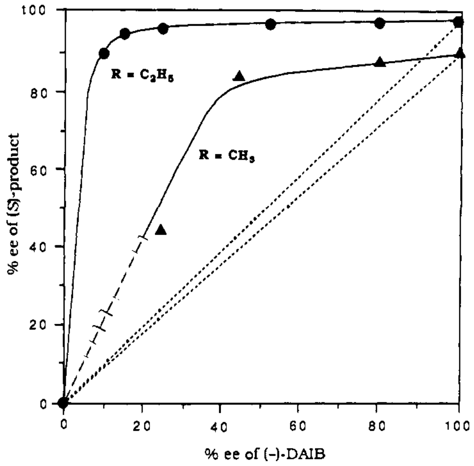


Figure 2. Correlation between the ee of the alkylation product and the ee of the chiral auxiliary: (●) Reaction using 0.42 M $(C_2H_5)_2Zn$, 0.42 M C_6H_5CHO, and 34 mM (−)-DAIB in toluene at 0 °C; (▲) 0.47 M $(CH_3)_2Zn$, 0.49 M C_6H_5CHO, 47 mM (−)-DAIB in toluene-d_8 at 32 °C.

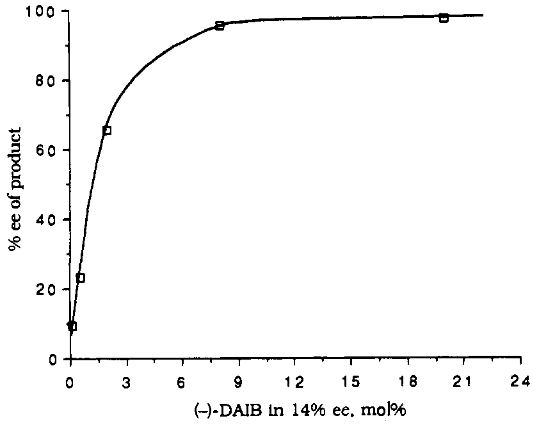
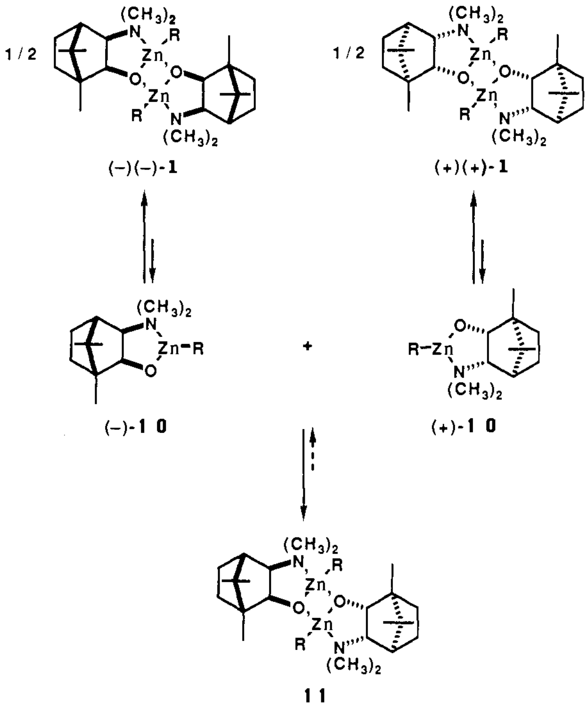


Figure 3. Effect of auxiliary concentration on nonlinearily in the ethylation of benzaldehyde aided by (−)-DAIB in 14% ee (0.42 M $(C_2H_5)_2Zn$, 0.42 M C_6H_5CHO, toluene, 0 °C).

Scheme II



Nonlinear Effect

In certain asymmetric catalyses, the extent of asymmetric induction deviates considerably from the enantiomeric excess of the starting chiral source. Enantioselective oxidation of prochiral sulfides or epoxidation of geraniol in the presence of titanium–tartrate complexes and the proline-catalyzed Hajos-Wiechert aldol reaction are examples,[13,14] and on the basis of simple kinetic studies these phenomena have been interpreted in terms of the participation of two auxiliary molecules, in either a homochiral or a

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(13) Puchot, C.; Samuel, O.; Duñach, E.; Zhao, S.; Agami, C.; Kagan, H. B. *J. Am. Chem. Soc.* **1986**, *108*, 2353. For enantiomeric recognition and interactions in stoichiometric reactions, see: Wynberg, H.; Feringa, B. *Tetrahedron* **1976**, *32*, 2831.

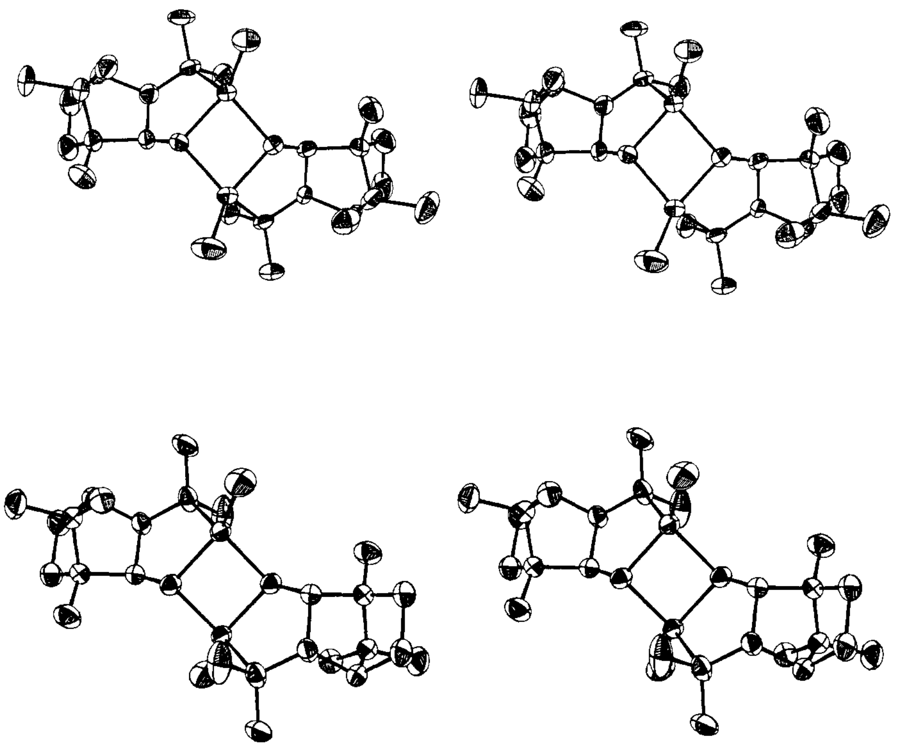

Figure 4. Stereoscopic view of (−)(−)-**1** (R = CH_3) (upper) and **11** (R = CH_3) (lower).

heterochiral manner, in the transition state of the enantiodifferentiating step. The present amino alcohol aided enantioselective alkylation exhibits unusually high deviation,[15] and the mechanism of the departure from linearity is somewhat different from those proposed earlier.[13,14]

Typically, when benzaldehyde and diethylzinc (1:1 mole ratio, 0.42 M) are reacted in the presence of 8 mol % of (−)-DAIB[16] (34 mM) in 15% ee in toluene (0 °C, 7 h), (*S*)-1-phenyl-1-propanol is produced in 95% ee (92% yield). This ee value achieved with the partially resolved DAIB auxiliary is close to the value of 98% obtained using enantiomerically pure DAIB.[2] The nonlinear effect is clear in Figure 2, which shows the ee of *S* product as a function of the ee of the chiral auxiliary. A similar chirality amplification has been observed in the reaction of dimethylzinc.[17] As illustrated in Figure 3, with a given ee of DAIB and a constant dialkylzinc and aldehyde concentration, a higher deviation is seen with higher auxiliary mole ratio. Thus the ethylation of benzaldehyde aided by (−)-DAIB in 14% ee gave the *S* product in 24% ee (2.1 mM DAIB, 0.42 M diethylzinc, 0.42 M benzaldehyde) to 98% ee (84 mM DAIB), implying that turnover efficiency of the chiral-catalyst system was twice to >600 times[18] greater than that of the coexisting achiral catalyst system.[19]

The enormous convexity of the curve with respect to a linear correlation (Figure 2) is not due to participation of two chiral auxiliary molecules per aldehyde in the *transition state* but results from unique enantiomer recognition in the dinuclear *catalyst precursors*, **1** and **11**, as illustrated in Scheme II. Structural examinations were done with dimethylzinc, which forms relatively unfluxional complexes. First, when equimolar amounts of enantiomerically pure (−)-DAIB and dimethylzinc were mixed in toluene at 25 °C, a single dimeric complex, (−)(−)-**1** (R = CH_3), was formed. The simple ^1H and ^{13}C NMR spectra indicate magnetic equivalency of the two daib[16] moieties. The stereochemistry was determined by a single-crystal X-ray analysis as shown in Figure 4. The structure indeed has C_2 symmetry, where the central Zn_2O_2 four-membered ring has syn geometry and is "endo-fused" to the adjacent daib/Zn five-membered rings. The dimeric nature in hydrocarbon solvents was proved by the cryoscopic molecular weight measurement in benzene (calcd 553, obsd 530). The observed MW of (−)(−)-**1** (R = C_2H_5), however, ranged from 536 in 63 mM solution to 484 in 18 mM solution (calcd 581), and the concentration effect indicates a propensity of **1** to dissociate to form the monomer **10**. In a like manner, reaction of racemic DAIB and dimethylzinc in a 1:1 molar ratio led to a single, highly crystalline dimeric complex, **11** (R = CH_3). This product, however, is not a racemic mixture of **1** but possesses achiral C_i symmetry, as proved by the simple patterns of the NMR spectra. The dimeric nature was supported by MW measurement of the ethyl complex, MW calcd 581, obsd 531 (34 mM benzene solution) and 513 (14 mM).[17] A single-crystal X-ray analysis of **11** (R = CH_3) revealed that the Zn_2O_2 four-membered ring is, like in **1**, endo-fused to the daib/Zn ring but has anti geometry, as illustrated in Figure 4. The same meso compound **11** (R = CH_3) was derived quantitatively by mixing equimolar amounts of (+)(+)-**1** and (−)(−)-**1** (R = CH_3) in toluene at ambient temperature.

The chiral complex **1** itself does not undergo alkyl-transfer reaction with aldehydes but acts as efficient catalyst precursors. As described above, the dimeric skeleton is cleaved instantaneously by exposure to a dialkylzinc and/or aldehyde entering the catalytic cycle to give the alkylation products. ^1H NMR spectrum of a 0.5:1:1 molar mixture of (−)(−)-**1** (R = CH_3), dimethylzinc, and benzaldehyde, generating a dynamic mixture of **1**–**4**, is illustrated in Figure 5b, where only a single Zn–CH_3 signal and broad aldehydic proton signal are seen. In addition, a small amount of **5** (R = CH_3) emerges. In striking contrast, the meso compound **11** (R = CH_3) is virtually inert to similar stoichiometric reaction conditions. The NMR monitoring revealed that the dimeric structure in a toluene solution was not affected by the addition of dimethylzinc and/or benzaldehyde. The spectrum of the mixture (Figure 5d) exhibited independent signals of unchanged **11** (R = CH_3), the dialkylzinc, and aldehyde substrate. The Zn–CH_3 signals are separated and the aldehydic proton signal remains sharp.

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[14] Agami, C.; Puchot, C. *J. Mol. Catal.* **1986**, *38*, 341. Agami, C. *Bull. Soc. Chim. Fr.* **1988**, 499.

[15] (a) Noyori, R.; Suga, S.; Kawai, K.; Okada, S.; Kitamura, M. *Pure Appl. Chem.* **1988**, *60*, 1597. (b) Oguni, N.; Matsuda, Y.; Kaneko, T. *J. Am. Chem. Soc.* **1988**, *110*, 7877.

[16] Daib = 3-*exo*-(dimethylamino)isoborneoxyl.

[17] Measurement at high concentration was difficult because of the low solubility of the methylzinc complex in aromatic hydrocarbons.

[18] The calculation was made by assuming the product ee to be >97%.

[19] Enantioselectivity of the ethylation using enantiomerically pure DAIB is not affected by concentration (4–34 mM).

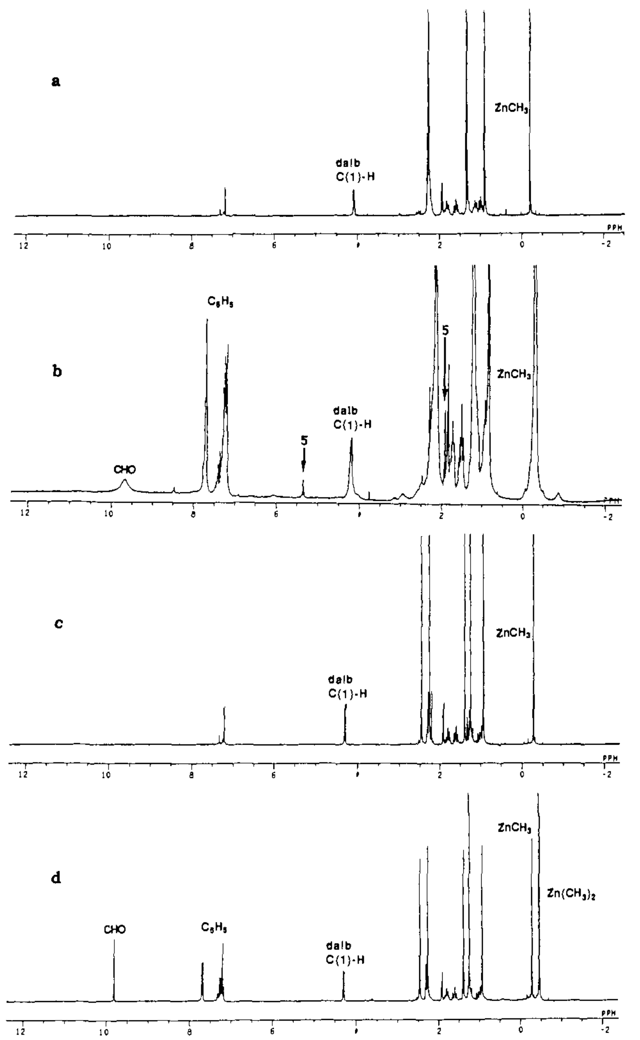

Figure 5. ^{1}H NMR spectra of the catalyst precursors and their mixtures with dimethylzinc and benzaldehyde (toluene-d_8, 25 °C): a, (−)(−)-**1** (R = CH$_3$); b, a 0.5:1:1 (−)(−)-**1**-(CH$_3$)$_2$Zn-C$_6$H$_5$CHO mixture; c, **11** (R = CH$_3$); d, a 0.5:1:1 **11**-(CH$_3$)$_2$Zn-C$_6$H$_5$CHO mixture.

The reaction rate appeared to be sensitive to enantiomeric purity of the DAIB auxiliary. The ethylation with enantiomerically pure DAIB was 6 times faster than the reaction with racemic DAIB under the same conditions using 8.4 mM DAIB, 0.42 M diethylzinc, and 0.42 M benzaldehyde in toluene at 0 °C. The rate of the alkylation using racemic DAIB, unlike that with homochiral auxiliary, is profoundly affected by the concentration of diethylzinc (0.07–0.96 M) and benzaldehyde (0.04–0.99 M). In addition, the reaction is first order in (±)-DAIB in low concentration (<15 mM), but considerable deviation is seen at high concentration. Some bimolecular reaction between **11** and dialkylzinc or benzaldehyde may be involved in the reaction using (±)-DAIB. Such different kinetic behavior results in marked dependency of the degree of nonlinearity on DAIB to dialkylzinc and aldehyde molar ratio (Figure 3).

Thus it is clear that the emergence of the intriguing nonlinearity is a result of conspicuous difference in chemical properties of the diastereomeric catalyst precursors, **1** and **11**. The meso dinuclear complex **11** is thermodynamically more stable than the chiral counterpart **1**. In the reaction with nonracemic but not enantiomerically pure DAIB, generating **1** and **11** in a thermodynamically controlled ratio, **1** possesses greater tendency to dissociate into active monomer **10**, thereby exhibiting a much higher turnover efficiency. The difference of the complexes is easily understandable by considering relative steric congestion of the central syn or anti 5/4/5-ring system. Indeed, the crystalline structures of the complexes in Figure 4 indicate that the dihedral angle of the five- and four-membered rings in (−)(−)-**1** (R = CH$_3$) is 135–146°, which is much larger than the 112–124° observed in **11** (R = CH$_3$).

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-GX270 spectrometer (toluene, external standard) with toluene-d_8 as solvent. Chemical shifts are reported in ppm (δ) downfield from the tetramethylsilane. Molecular weight was determined by depression of freezing point in benzene solution. X-ray crystallographic analysis was conducted on a Rigaku automated four-circle diffractometer RU-200 with graphite-monochromated Cu radiation. Gas chromatographic and liquid chromatographic analyses were conducted on a Shimadzu GC-15A and a Shimadzu LC-6A instrument, respectively. Flash chromatography was done on a column of silica gel (Fuji Davison BW300, 240–400 mesh). All experiments were performed under an argon atmosphere by using standard Schlenk techniques. Toluene and benzene were distilled from sodium benzophenone ketyl under argon and stored in a 2-L Schlenk flasks. Toluene-d_8 and benzene-d_6, dried on 4-Å molecular sieves, were distilled from Na–K alloy and stored in a 10-mL graduated Schlenk tube. A stock solution of dimethylzinc or diethylzinc was prepared by mixing toluene, toluene-d_8, or benzene and 99% dimethylzinc or 99% diethylzinc (Toyo Stauffer Chemical Co., Lot No DMZ EK-01 and DEZ 932) in a lecture bottle and was kept in a 20-mL Schlenk tube equipped with a Young's tap. (−)-, (+)-, and (±)-DAIB were prepared from (1*R*)-(+)-camphor (Nakarai Chemical Co., Lot No 070-07, $[\alpha]^{20}{}_{\rm D}$ +45.2° (*c* 9.7, ethanol)), (1*S*)-(−)-camphor (Aldrich Chemical Co., Lot No 27,967-6, $[\alpha]^{20}{}_{\rm D}$ −42.9° (*c* 10.0, ethanol)), and (±)-camphor (Tokyo Kasei Kogyo Co., Lot No C0011, $[\alpha]^{25}{}_{\rm D}$ +0.072° (*c* 9.9, ethanol)), respectively, by the reported method.[20] The ee's of nonracemic DAIB were determined by HPLC analysis as follows: 3,5-Dinitrophenyl isocyanate (20 mg, 0.089 mmol) and pyridine (5 μL) were added to a toluene solution (2 mL) of DAIB (10 mg, 0.051 mmol). After vigorous stirring of the mixture for 30 min at 20 °C, 2 μL of the reaction mixture containing the carbamate derivative was analyzed by HPLC (column, Sumitomo Chemical Co. SUMIPAX OA-4000; eluent, 98:2 hexane-ethanol mixture; flow rate, 1.0 mL/min; detection, 254-nm light; $t_{\rm R}$, 21 min (carbamate from (−)-DAIB) and 26 min (carbamate from (+)-DAIB)).

General Procedure for the Kinetic Runs. A dry 20-mL Schlenk tube containing a Teflon-coated stirring bar was evacuated and filled with argon. (−)-DAIB (0.15–1.77 mL of a 0.10 M toluene solution, 0.015–0.177 mmol) and toluene (2–5 mL) were charged. Diethylzinc (0.23–4.56 mL of a 2.0 M toluene solution, 0.46–9.12 mmol) was added at 25 °C. The mixture was stirred for 15 min and then cooled to 0 °C. To this was added benzaldehyde (32–973 mg, 0.30–9.17 mmol) in one portion. In all cases the total volume was 7.0 mL. At 1–10-min intervals, a portion (ca. 0.3 mL) was quickly transferred by using a cannula to a vigorously stirred mixture of saturated aqueous 3 N hydrochloric acid solution (1.5 mL) and ether (1.5 mL) at 0 °C. The consumption of benzaldehyde or the yield of 1-phenyl-1-propanol was quantitated by GC analysis of the organic layer (column, 20% SE-30 on Chromosorb WAW 3 mm × 3 m; column temperature, 170 °C; carrier gas, Ar; $t_{\rm R}$ of benzaldehyde, 5.6 min; $t_{\rm R}$ of 1-phenyl-1-propanol, 11.0 min). The initial rates were calculated from 4–8 experiment sets and were first-order-plotted. Correlations between concentration of (−)-DAIB (mM) and rate (conversion of benzaldehyde, μmol/min), concentration of diethylzinc (M) and rate (amount of consumed benzaldehyde, μmol/min). and concentration of benzaldehyde (M) and rate (amount of produced 1-phenyl-1-propanol, μmol/min) were as follows: (2.1, 17.0), (4.2, 32.5), (8.4, 65.5), (16.7, 121), (25.3, 172); (0.065, 6.83), (0.11, 9.20), (0.17, 6.8), (0.33, 8.13), (0.64, 8.73), (0.96, 8.53), (1.30, 8.73); (0.043, 2.37), (0.084, 3.77), (0.13, 6.51), (0.17, 6.31), (0.32, 8.03), (0.65, 10.0), (0.97, 8.22), (1.31, 7.44).

Typical Procedure for the Alkyl-Scrambling Experiments. A dry 10-mL Schlenk flask containing a small Teflon-coated stirring bar was evacuated and filled with argon. The flask was charged with (−)-DAIB (95.4 mg, 0.483 mmol) and toluene (1.2 mL), and the solution was degassed by three freeze–thaw cycles. Diethylzinc (0.267 mL of a 1.81 M solution in toluene, 0.483 mmol) was added at 30 °C by a microliter syringe. After stirring of the mixture for 15 min, dibutylzinc (0.353 mL of a 1.37 M solution in toluene, 0.484 mmol) was added at 30 °C. The mixture was stirred for 10 min and cooled to −78 °C. Benzaldehyde (51.4 mg, 0.484 mmol) was added and the mixture was allowed to warm to 0 °C and was kept there for 6 h. Then saturated aqueous ammonium chloride solution (5 mL) was added. The mixture was extracted three

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[20] (a) Beckett, A. H.; Lan, N. T.; McDonough, G. R. *Tetrahedron* **1969**, *25*, 5689. (b) Chittenden, R. A.; Cooper, G. H. *J. Chem. Soc. C* **1970**, 49. (c) Pauling, H. *Helv. Chim. Acta* **1975**, *58*, 1781.

Table III. Molecular Weight Determination by Cryoscopy Method

sample[a]	ω	ΔT	K_f	MW	n
A	14.7	0.143	5.16	530	1.92
B	31.5	0.258	4.63	565	1.94
C	43.0	0.630	5.16	352	0.95
D	24.9	0.341	5.16	377	0.91
D	60.9	0.847	5.16	371	0.90
D	83.2	1.107	5.16	388	0.94
E	57.6	1.54	5.16	193	*b*
F	32.8	0.50	5.16	338	0.88
G	51.4	1.37	5.16	194	*c*
H	46.8	0.318	5.16	759	3.8

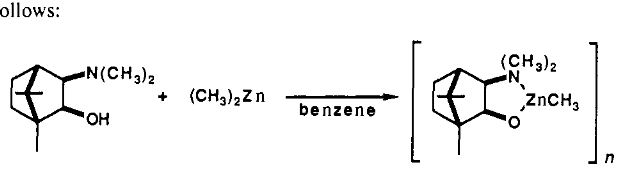
[a] A: prepared from (−)-DAIB and $(CH_3)_2Zn$ in a 1:1 molar ratio. B: (−)-DAIB:$(C_2H_5)_2Zn$ = 1:1. C: (−)-DAIB:$(CH_3)_2Zn$ = 1:2. D: prepared from (−)-DAIB and $(C_2H_5)_2Zn$ in a 1:2 molar ratio. E: prepared from (−)-DAIB and $(C_2H_5)_2Zn$ in a 1:5 molar ratio. F: prepared from (−)-DAIB, $(CH_3)_2Zn$, and benzaldehyde in a 1:1:1 molar ratio. G: prepared from (−)-DAIB, $(CH_3)_2Zn$, and benzaldehyde in a 1:1:3 molar ratio. H: prepared from (*S*)-1-phenylethanol and $(CH_3)_2Zn$ in a 1:1 molar ratio. [b] The average molecular weight calculated by assuming that the complex **3** and 1–3 equiv of $(C_2H_5)_2Zn$ form no highly aggregated complexes is 269, 220, and 196, respectively. [c] The average molecular weight calculated on the assumption that the complex **2** and 1 and 2 equiv of benzaldehyde form no highly aggregated complexes is 245 and 198.

times with ether (10 mL). The combined organic layers were washed with 1 N aqueous hydrochloric acid solution (10 mL), water (10 mL), and brine (10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude mixture was chromatographed on silica gel (5 g) by using a 1:2 ether–hexane mixture as eluent to give a mixture of 1-phenyl-1-propanol, 1-phenyl-1-pentanol, and benzyl alcohol (70 mg). The product ratio was determined by HPLC analysis (column, Develosil 100–5; flow rate, 1 mL/min; eluent, 1:2 ether–hexane mixture; detection, 254-nm light; t_R of benzyl alcohol, 10.8 min (14%); t_R of 1-phenyl-1-propanol, 7.8 min (44%); t_R of 1-phenyl-1-pentanol, 6.4 min (35%).

General Procedure for NMR Study. Samples for NMR study were prepared as follows: The complex (−)(−)-**1** (13.2 mg, 0.0238 mmol) was placed into a dry 5-mm NMR tube in an argon-filled drybox. The tube was then equipped with a Schlenk tube by using an adaptor, and this was connected to a vacuum line. Toluene-d_8 (0.6–1.5 mL) was distilled into the NMR tube, and the solution was degassed by three freeze–thaw cycles. To this was added $(CH_3)_2Zn$ (0.0110 mL of a 4.32 M toluene-d_8 solution, 0.0476 mmol) at 25 °C. After 10 min, the mixture was cooled to −78 °C, and benzaldehyde (0.0437 mL of a 1.09 M toluene-d_8 solution, 5.06 mg, 0.0476 mmol) was added. The NMR tube was sealed under vacuum or covered by a Teflon cap, and the sample was stored in a dry ice–acetone bath until the spectra were recorded. The NMR tube was removed from the −78 °C bath, wiped, inserted in the spinner, and placed in the magnet. All FID collections at the appropriate timing were stored on a floppy diskette.

Molecular Weight Determination. The determination of molecular weights was carried out with a standard freezing point depression apparatus equipped with a side arm through which the cell could be evacuated and filled with argon and later flushed with argon while solutions or solids were being added. Molecular weight was calculated in each case from: $\Delta T = K_f\omega/\mathrm{MW}$, where ΔT = depression (degrees), K_f = molal depression of the solvent, ω = weight (g) of solute in 1000 g of solvent, and MW = molecular weight. K_f value of this apparatus was calculated to be 5.16 on the basis of the depression of a benzene (10.53 g) solution of naphthalene (118.6–566.6 mg).

The procedure for the molecular weight determination of the complex **1** prepared from (−)-DAIB and $(CH_3)_2Zn$ in a 1:1 molar ratio is as follows:



A dry Schlenk-type cryoscopy cell was evacuated and filled with argon and was replaced with (−)-DAIB (111.6 mg, 0.566 mmol) and benzene (10.53 g). Dimethylzinc (0.193 mL of a 2.93 M solution in benzene) was added, and the mixture was stirred at 30 °C for 15 min. The benzene solution (ω = 14.7) was degassed by three freeze–thaw cycles to remove the generated methane gas and the cell was again filled with argon. The apparatus was immersed into an ice–salt bath, and the temperature was measured by a Beckmann thermometer at 30-s intervals until the solution froze. After warming up to room temperature, the same procedure was repeated three times. Since the averaged ΔT value obtained from four runs was 0.143, the molecular weight (MW) of this compound was calculated to be 530 (n = 1.92).

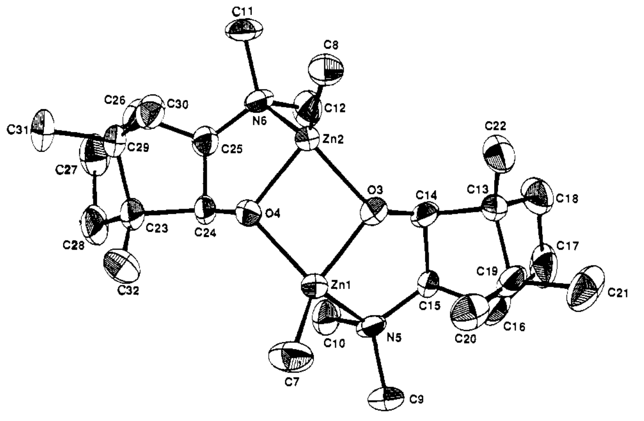


Figure 6. ORTEP drawing of (−)(−)-**1** (R = CH_3), showing the atom-numbering scheme. All hydrogen atoms have been omitted for clarity.

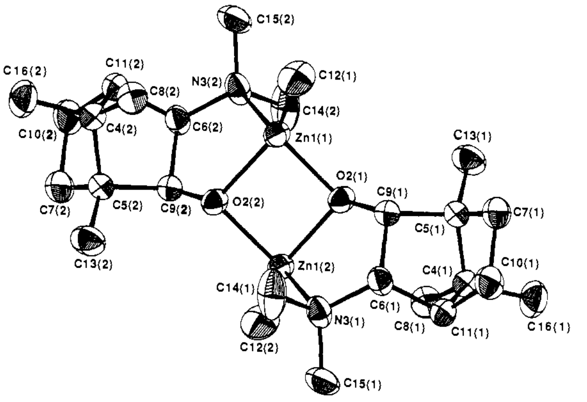


Figure 7. ORTEP drawing of **11** (R = CH_3), showing the atom-numbering scheme. All hydrogen atoms have been omitted for clarity.

The molecular weights and parameters of other complexes were shown in Table III. In the calculation of the MW of the zinc complexes the excess dialkylzinc compounds or benzaldehyde present in the mixture are assumed to exist as independent entities.

Chiral Amplification Experiments. Typical Procedure. (−)-DAIB (0.92 mL of a 0.0844 M solution in toluene, 0.0776 mmol), (+)-DAIB (0.79 mL of a 0.0807 M solution in toluene, 0.0638 mmol), toluene (1.60 mL), and diethylzinc (0.74 mL of a 2.38 M toluene solution, 1.76 mmol) were successively added at 25 °C to a dry argon-filled 20-mL Schlenk tube containing a Teflon-coated magnetic stirring bar by using gas-tight syringes. Gas evolution occurred when diethylzinc was mixed. The colorless solution was stirred for 15 min at the same temperature and cooled to 0 °C with an ice bath. Benzaldehyde (188 mg, 1.77 mmol) was added to this cold solution, and the resulting slightly yellow solution was kept at 0 °C. After 7 h, a portion of the reaction mixture was treated and analyzed as described in general procedure for the kinetic runs, showing 91.6% conversion. The enantiomeric excess was determined by HPLC analysis of the crude mixture (column, Bakerbond DNBPG covalent; eluent, 100:0.25 hexane–2-propanol mixture; flow rate, 1.0 mL/min; detection, 254-nm light; t_R of (*S*)-1-phenyl-1-propanol, 25.4 min (97.4%); t_R of *R* isomer, 26.8 min (2.6%), indicating 94.8% ee. In the reaction time of 29 h, the conversion and enantiomeric excess were 93.1% and 94.9%, respectively. Percent ee's of the *S*-ethylated product (% ee of (−)-DAIB) obtained under the same reaction conditions were as follows: 90 (10), 95 (15), 96 (24), 97 (53), 97 (81), 98 (100). Chiral amplification experiments using dimethylzinc were conducted at 32 °C in a similar manner as described above. In the GC analysis, the retention time of 1-phenylethanol was 7.5 min. The enantiomeric excess of 1-phenylethanol was analyzed by HPLC (column, Daicel Co. CHIRALCEL OB; eluent, 100:0.5 hexane–2-propanol mixture; flow rate, 1.0 mL/min; detection, 254-nm light; t_R of (*S*)-1-phenylethanol, 24.4 min; t_R of *R* isomer, 34.0 min. Percent ee's of the *S*-methylated product (% ee of (−)-DAIB) observed under the reaction conditions (46.8 mM (−)-DAIB, 0.47 M $(CH_3)_2Zn$, 0.49 M C_6H_5CHO, toluene-d_8, 32 °C)

Table IV. Crystallographic Data for (−)(−)-**1** and **11** (R = CH_3)

compound	(−)(−)-**1**	**11**
mol formula	$C_{13}H_{25}NOZn$	$C_{13}H_{25}NOZn$
mol wt	276.74	276.74
crystal size, mm	1.03 × 0.20 × 0.10	0.45 × 0.42 × 0.40
space group	P_{212121}	$P2_1/n$
cell dimens		
a, Å	13.430 (4)	13.109 (2)
b, Å	18.143 (3)	11.157 (1)
c, Å	11.521 (1)	9.911 (1)
α, deg	90	90
β, deg	90	104.77 (1)
γ, deg	90	90
vol, $Å^3$	2807.3 (10)	1401.7 (4)
Z	8	4
ρ measd, g cm^{-3}	1.305	1.635
ρ calcd, g cm^{-3}	1.310	1.640
diffractometer	Rigaku automated four-circle diffractometer, AFC-5R	same
radiation	Cu Kα (1.541 84 Å)	same
monochrometer	graphite crystal	same
scan type	$\theta-2\theta$	same
scan speed, deg min^{-1}	$0° \leq 2\theta \leq 76°$ 8 (2θ) $76° \leq 2\theta \leq 102°$ 4 (2θ) $102° \leq 2\theta \leq 126°$ 2 (2θ)	same $76° \leq 2\theta \leq 102°$ 6 (2θ) $102° \leq 2\theta \leq 126°$ 4 (2θ)
2θ scan limit, deg	126	same
"standard" reflections	3 every 100 reflections	same
indices	(−4, −8, −4), (−4, −8, 4), (−2, 3, −7)	(−2, 0, 4), (−3, 1, 3), (−6, 2, 0)
cryst stability	1.9–3.0% anisotropic decay during data collection	decay less than 2% during data collection
total reflections scanned	2242	2398
unique reflections with $I > \sigma(I)$	2352	2221
cryst dimensions, mm	1.03 × 0.20 × 0.10	0.45 × 0.42 × 0.40
cell dimensions	20 reflections, AFC-5 diffractometer	same
determination	$58° < 2\theta < 61°$, $t = 20 \pm 2$ °C	$30.7° < 2\theta < 50.4°$, $t = 20 \pm 2$ °C
μ, cm^{-1}	20.92	
transmission factors		
max	0.8112	
min	0.1159	
hkl range	$0 \leq h \leq 15$ $0 \leq k \leq 20$ $0 \leq l \leq 13$	$-15 \leq h \leq 14$ $0 \leq k \leq 12$ $0 \leq l \leq 11$
absorption	Katayama's method[a]	not done
scattering factor source	international tables[b] (dispersion corrected)	same
function minimized by refinement	$\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum\lvert F_o\rvert^2$	same
no. of reflections in refinement anal.	2352	2221
R	0.0802	0.0530
R_w[c]	0.0668	0.0506

[a] Katayama, C.; Sakabe, N.; Sakabe, K. *Acta Crystallogr., Sect. A* **1972**, *A28*, SS207. [b] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 91–101, 149–150. [c] $R_w = \{\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum\lvert F_o\rvert^2\}^{1/2}$.

Table V. Selected Interatomic Distances (Å) and Angles (deg) of (−)(−)-**1** (R = CH_3)

Bond Distances			
Zn(1)–O(3)	1.98 (1)	Zn(1)–O(4)	2.06 (1)
Zn(1)–N(5)	2.25 (2)	Zn(1)–C(7)	1.98 (3)
Zn(2)–O(3)	2.05 (1)	Zn(2)–O(4)	1.98 (1)
Zn(2)–N(6)	2.19 (2)	Zn(2)–C(8)	1.96 (3)
O(3)–C(14)	1.40 (3)	N(5)–C(10)	1.49 (3)
N(5)–C(9)	1.50 (3)	N(5)–C(15)	1.48 (3)
C(14)–C(15)	1.60 (3)	O(4)–C(24)	1.42 (3)
C(24)–C(25)	1.57 (3)	N(6)–C(25)	1.48 (3)
N(6)–C(11)	1.50 (3)	N(6)–C(12)	1.49 (3)
Bond Angles			
O(3)–Zn(1)–O(4)	82.3 (5)	O(3)–Zn(1)–N(5)	80.0 (6)
O(3)–Zn(1)–C(7)	144 (1)	O(4)–Zn(1)–N(5)	120.6 (6)
O(4)–Zn(1)–C(7)	116 (1)	N(5)–Zn(1)–C(7)	112 (1)
O(3)–Zn(2)–O(4)	82.7 (5)	O(3)–Zn(2)–N(6)	116.9 (6)
O(3)–Zn(2)–C(8)	117.6 (8)	O(4)–Zn(2)–N(6)	81.6 (6)
O(4)–Zn(2)–C(8)	140.7 (9)	N(6)–Zn(2)–C(8)	112.8 (9)
Zn(1)–O(3)–Zn(2)	95.2 (6)	Zn(1)–O(3)–C(14)	122 (1)
Zn(2)–O(3)–C(14)	130 (1)	Zn(1)–O(4)–Zn(2)	95.0 (5)
Zn(1)–O(4)–C(24)	126 (1)	Zn(2)–O(4)–C(24)	120 (1)
Zn(1)–N(5)–C(9)	114 (1)	Zn(1)–N(5)–C(10)	102 (1)
Zn(1)–N(5)–C(15)	110 (1)	C(10)–N(5)–C(15)	108 (2)
C(9)–N(5)–C(15)	114 (2)	C(9)–N(5)–C(10)	107 (2)
Zn(2)–N(6)–C(25)	110 (1)	Zn(2)–N(6)–C(12)	103 (1)
Zn(2)–N(6)–C(11)	113 (1)	C(11)–N(6)–C(12)	108 (2)
C(11)–N(6)–C(25)	113 (2)	C(12)–N(6)–C(25)	109 (2)

Table VI. Selected Interatomic Distances (Å) and Angles (deg) of **11** (R = CH_3)

Bond Distances			
Zn1(1)–O2(1)	2.028 (3)	Zn1(1)–O2(2)	2.001 (3)
Zn1(1)–N3(2)	2.168 (4)	Zn1(1)–C12(1)	1.985 (5)
O2(1)–C9(1)	1.411 (5)	N3(1)–C14(1)	1.476 (7)
N3(1)–C15(1)	1.475 (8)	N3(1)–C6(1)	1.503 (7)
C6(1)–C9(1)	1.577 (6)		
Bond Angles			
O2(2)–Zn1(1)–O2(1)	84.7 (1)	O2(2)–Zn1(1)–N3(2)	81.4 (1)
O2(2)–Zn1(1)–C12(1)	140.1 (2)	N3(2)–Zn1(1)–C12(1)	117.1 (2)
O2(1)–Zn1(1)–C12(1)	116.1 (2)	N3(2)–Zn1(1)–O2(1)	111.0 (1)
Zn1(2)–N3(1)–C15(1)	113.7 (3)	Zn1(2)–N3(1)–C14(1)	101.4 (4)
Zn1(2)–N3(1)–C6(1)	110.4 (3)	C15(1)–N3(1)–C6(1)	113.2 (4)
C14(1)–N3(1)–C15(1)	109.2 (5)	C6(1)–N3(1)–C14(1)	108.2 (4)
Zn1(2)–O2(1)–Zn1(1)	95.3 (1)	Zn1(1)–O2(1)–C9(1)	116.0 (2)
Zn1(2)–O2(1)–C9(1)	119.1 (3)		

were as follows: 44 (24), 85 (43), 88 (81), 91 (100).

Preparation of (−)(−)-**1 and 11 (R = CH_3).** (−)-DAIB (1.04 g, 5.27 mmol) and toluene (30 mL) were placed in a dry 80-mL Schlenk tube. Dimethylzinc (0.40 mL, 5.76 mmol) was added to this solution at 28 °C. During this time, methane gas was evolved. After stirring for 1 h, the mixture was evaporated to a volume of about 10 mL and the clear solution was allowed to stand for 6 h at 28 °C and 12 h at 5 °C. Crystals were separated by removing the supernatent by means of a cannula, washed two times with 5 mL of cold toluene, and dried in vacuo, affording (−)(−)-**1** (930 mg, 64% yield): ^1H NMR (270 MHz, toluene-d_8) δ −0.20 (s, 3, $ZnCH_3$), 0.91 (s, 3, CH_3), 0.96–1.05 (m, 1, CH), 1.10–1.20

(m, 1, CH), 1.35 (s, 6, 2 CH_3), 1.56–1.66 (m, 1, CH), 1.77–1.89 (m, 1, CH), 1.95 (d, 1, J = 4.4 Hz, CH), 2.27 (br s, 7, 2 NCH_3 and NCH), 4.10 (d, 1, J = 6.8 Hz, C*H*OH); ^{13}C NMR (67.8 MHz, toluene-d_8) δ −14.15, 12.63, 22.46, 23.01, 29.66, 33.32, 44.07, 46.00, 47.95, 49.65, 50.29, 77.53, 85.28; mp >160 °C dec. With use of (±)-DAIB (1.10 g, 5.59 mmol), **11** was prepared in 81% yield: ^1H NMR (270 MHz, toluene-d_8) δ −0.28 (s, 3, $ZnCH_3$), 0.93 (s, 3, CH_3), 0.91–1.01 (m, 1, CH), 1.15–1.34 (m, 1, CH), 1.25 (s, 3, CH_3), 1.39 (s, 3, CH_3), 1.53–1.65 (m, 1, CH), 1.74–1.86 (m, 1, CH), 1.92 (d, 1, J = 4.9 Hz, CH), 2.26 (s, 3, NCH_3), 2.29 (d, 1, J = 6.8 Hz, NCH), 2.46 (s, 3, NCH_3), 4.29 (d, 1, J = 6.8 Hz, C*H*OH); ^{13}C NMR (67.8 MHz, toluene-d_8) δ −16.57, 12.00, 22.66, 23.35, 29.68, 33.36, 44.39, 45.93, 48.23, 49.87, 50.70, 78.27, 84.35; mp >180 °C dec.

X-ray Analysis of the Complexes (−)(−)-1 and 11 (R = CH_3). Single crystals of (−)(−)-**1** and **11** suitable for diffraction experiments were obtained by recrystallization from toluene and benzene at room temperature. The crystals were sealed in thin-walled capillary tubes (Oversees X-ray Service Co., 0.3 mm i.d. for (−)(−)-**1** and 0.7 mm i.d. for **11**) in a glovebox. Crystallographic data, data collection details, data reduction and refinement details for (−)(−)-**1** and **11** are summarized in Table IV. Selected interatomic distance and angles are listed in Table V for (−)(−)-**1** and in Table VI for **11**. ORTEP drawings of (−)(−)-**1** and **11** with the numbering scheme are shown in Figures 6 and 7, respectively.

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Supplementary Material Available: Tables of atomic parameters, anisotropic temperature factors, and bond angles and distances for (−)(−)-**1** and **11** (48 pages); complete listings of observed and calculated structure factors for (−)(−)-**1** and **11** (12 pages). Ordering information is given on any current masthead page.

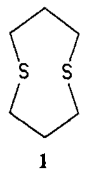
Sulfur–Sulfur Lone Pair and Sulfur–Naphthalene Interactions in Naphtho[1,8-*b*,*c*]-1,5-dithiocin

Richard S. Glass,* Stephen W. Andruski, Jeffrey L. Broeker, Habib Firouzabadi,[†]
L. Kraig Steffen, and George S. Wilson[‡]

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721. *Received September 12, 1988*

Abstract: Naphtho[1,8-*b*,*c*]-1,5-dithiocin (**4**), which has a unique geometry so constrained that the sulfur atoms are held close to one another and oriented such that their p orbitals are almost colinear and orthogonal to the naphthalene π-system, has been synthesized. Its crystal and molecular structure was determined by single-crystal X-ray analysis. It crystallizes in the orthorhombic space group *Pbca* with a = 8.140 (2) Å, b = 9.866 (1) Å, c = 28.302 (3) Å, and Z = 8. The structure was solved by direct methods. Full-matrix least-squares refinement led to a conventional R factor of 0.046 after several cycles of anisotropic refinement. For comparison purposes the crystal and molecular structure of the previously reported 1,8-bis(methylthio)naphthalene (**5**) was also determined by X-ray techniques. Semiempirical molecular orbital methods (MNDO and AM1) were used to analyze the five highest occupied molecular orbitals in 1,8-bis(methylthio)naphthalene as a function of the C(1)–S and C(8)–S torsion angles and to analyze the molecular orbitals of compound **4**. Of particular interest is the result that the energy of the highest occupied molecular orbital in 1,8-bis(methylthio)naphthalene is nearly independent of the C–S torsion angle and that the lowest ionization potential for **4** is predicted to be 7.75 eV and its lone pair–lone pair splitting due to transannular S–S interaction is 1.6–2.0 eV. The computations were correlated with the experimentally measured He I and He II photoelectron spectra of **4** and the AM1 method provided reasonable agreement with the experimental data. The electrochemical oxidation of **4** and **5** in acetonitrile was studied by cyclic voltammetry. They undergo irreversible oxidation with peak potentials of 0.70 and 0.47 V, respectively, versus a Ag/0.1 M $AgNO_3$ in acetonitrile reference electrode. Controlled-potential electrolysis of **4** gives the corresponding sulfoxide (**12**), which is consistent with removal of an electron from the highest occupied molecular orbital which is sulfur lone pair in character.

Oxidation of 1,5-dithiocane, **1**, to the corresponding, unusually stable, radical cation **2**[1–4] and dication **3**[2,3,5] occurs with remarkable ease. The peak potential for this reversible oxidation is 0.34 V in acetonitrile versus a Ag/$AgNO_3$ in acetonitrile reference electrode.[6,7] This oxidation can also be achieved chemically.[1,2] The basis for this facile oxidation has been ascribed to the destabilization of 1,5-dithiocane, **1**, by transannular lone-pair–lone-pair repulsion and the stabilization of the oxidized products by neighboring-group participation, that is, bond formation between the two sulfur atoms. The bonding between the sulfur atoms in the radical cation of 1,5-dithiocane has been convincingly established[8,9] as $\sigma^2\sigma^{*1}$ and a chemical consequence of this bonding is the unusual ease of removal of a second electron from 1,5-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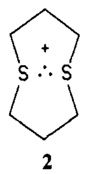
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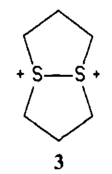
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[†] On leave from the Department of Chemistry, Shiraz University, Shiraz, Iran.

[‡] Present address: Department of Chemistry, University of Kansas, Lawrence, KS 66045.

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