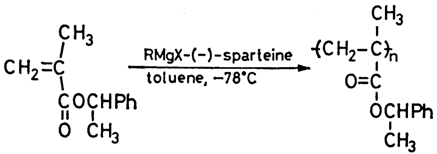
May, 1983] Bull. Chem. Soc. Jpn., 56, 1319—1321 (1983)

The Molecular Structure of Bromo(ethyl)[(−)-sparteine]magnesium(II),[†] a Catalyst for the Asymmetric-selective Polymerization of Racemic Methacrylates

Hiroyuki Kageyama, Kunio Miki, Nobuo Tanaka,[††] Nobutami Kasai,*
Yoshio Okamoto,** and Heimei Yuki**,[†††]
Department of Applied Chemistry, Faculty of Engineering, Osaka University,
Yamadaoka, Suita, Osaka 565
***Department of Chemistry, Faculty of Engineering Science, Osaka University,*
Machikaneyama, Toyonaka, Osaka 560
(Received September 18, 1982)

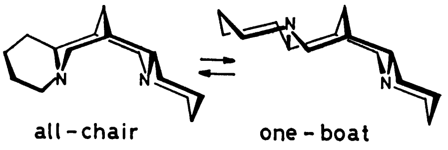
The molecular structure of EtMgBr-(−)-sparteine, which initiates asymmetric (enantiomer) selective polymerization of racemic methacrylates, has been determined by means of X-ray diffraction. The crystal is orthorhombic, space group $P2_12_12_1$, $a=11.278(2)$, $b=14.112(3)$, $c=11.746(2)$ Å, $Z=4$. The structure was established by the heavy atom method and refined by the block-diagonal least-squares procedure: $R=0.100$ for 1272 non-zero reflections. The Mg atom is tetrahedrally coordinated by the Et group, Br and two N atoms of the (−)-sparteine.

Recently, Okamoto, Yuki, and their co-workers have studied the asymmetric-selective (enantiomer selective) polymerization of racemic methacrylates, especially that of the (*RS*)-α-methylbenzyl methacrylate ((*RS*)-MBMA).[1–5)]



(RS)-MBMA poly((S)-MBMA)

In this reaction, in toluene at −78 °C, the (*S*)-monomer polymerizes preferentially over the (*R*)-monomer by the presence of a complex between a primary or secondary Grignard reagent and a chiral bidentate ligand, (−)-sparteine[††††] or its derivative. The activity and selectivity of the catalysts were discussed[6)] on the basis of the molecular structures determined by means of X-ray diffraction. This study deals with the molecular structure of the EtMgBr–(−)-sparteine complex which has a high catalytic activity on the asymmetric-selective polymerization of the MBMA. Interests on the structure and the reactivity of the present complex and also on the conformation of the (−)-sparteine ligand, either one-boat or all-chair form, promoted this study.



Experimental

Crystals used were obtained from a toluene solution. A crystal with approximate dimensions of 0.50×0.50×0.38 mm, sealed in a thin-walled glass capillary tube under nitrogen atmosphere, was mounted on a Rigaku automated, four-circle X-ray diffractometer. The unit-cell dimensions were precisely determined by the least-squares fit using 2θ values of 25 strong reflections.

Crystal Data. $C_{17}H_{31}N_2MgBr$, M 367.7, orthorhombic space group $P2_12_12_1$, $a=11.278(2)$, $b=14.112(3)$, $c=11.746(2)$ Å, $V=1869.5(5)$ Å^3, $D_C=1.306$ g cm^{-3} for $Z=4$, $\mu(\text{Mo } K\alpha)=23.62$ cm^{-1}.

Reflection intensities were measured on the diffractometer with Zr-filtered Mo $K\alpha$ radiation by the θ-2θ scan technique ($2\theta \leq 50.5°$). The 2θ scan rate was 4° min^{-1} and the scan width $\Delta 2\theta=(2.0+0.7\tan\theta)°$ Backgrounds were counted for 7.5 s at both ends of a scan. Four standard reflections measured after every 27 reflections showed less than 3% intensity fluctuations during the data collection. However the peak profiles of reflections were not so sharp, reflection intensities were rather low, and high order reflections were scarcely observed to have non-zero intensity. Of the 1937 reflections measured only 1272 had non-zero intensities. Usual Lorentz and polarization corrections were applied but absorption and extinction corrections were ignored.

Structure Solution and Refinement

The heavy atom method was applied to solve the structure. The position of the Br atom was determined from the three-dimensional Patterson function. The Mg, N, and C atoms except the C(16) were located by the subsequent Fourier synthesis. The structure was refined isotropically by the block-diagonal least-squares procedure (*HBLS* V).[7)] The remaining C(16) atom could be located on the difference Fourier synthesis. Further refinement was carried out anisotropically for non-hydrogen atoms except for the C(10), C(16), and C(17) atoms, because thermal parameters of these atoms could not be refined anisotropically. Hydrogen atoms could not be located on the difference Fourier synthesis. At the final stage of the refinement the anomalous dispersion of the Br and Mg atoms[8)] was considered; the R value became 0.100 for non-zero reflections ($R_w=0.103$). The final atomic positional parameters and equivalent[9)] (or isotropic) tem-

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[†] Abbreviated as EtMgBr-(−)-sparteine

[††] Present address: Institute for Protein Research, Osaka University, Yamadaoka, Suita, Osaka 565.

[†††] Present address: Tezukayama-Gakuin Women's Junior College, Tezukayama, Sumiyoshi-ku, Osaka 558.

[††††] Dodecahydro-7,14-methano-2*H*,6*H*-dipyrido[1,2-*a*:1′, 2′-*e*][1,5] diazocine.

TABLE 1. FINAL ATOMIC POSITIONAL PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B_{eq} or B/Å^2
Br	−0.04812(24)	0.56688(15)	0.41953(20)	5.4
Mg	−0.0501(7)	0.4081(5)	0.3286(6)	4.0
N(1)	0.0901(15)	0.4029(12)	0.2064(14)	4.6
N(2)	−0.1614(15)	0.4283(14)	0.1809(14)	5.1
C(1)	−0.0411(25)	0.2853(12)	0.4496(15)	5.4
C(2)	−0.2901(17)	0.4467(17)	0.2202(25)	7.0
C(3)	−0.3317(21)	0.3648(16)	0.2854(22)	6.5
C(4)	−0.3363(21)	0.2767(22)	0.2133(29)	8.5
C(5)	−0.1980(22)	0.2609(17)	0.1639(24)	6.4
C(6)	−0.1616(24)	0.3464(15)	0.1005(20)	6.3
C(7)	−0.0331(20)	0.3328(15)	0.0494(17)	5.0
C(8)	−0.0112(21)	0.4176(17)	−0.0244(18)	5.8
C(9)	−0.0044(26)	0.5053(16)	0.0568(21)	7.1
C(10)[a]	−0.1262(19)	0.5196(15)	0.1198(19)	4.8(5)
C(11)	0.0998(21)	0.4937(18)	0.1386(23)	6.3
C(12)	0.2212(26)	0.5081(20)	0.0796(23)	7.5
C(13)	0.3263(26)	0.4947(23)	0.1667(26)	8.7
C(14)	0.3194(17)	0.3991(21)	0.2177(23)	7.1
C(15)	0.1976(20)	0.3885(18)	0.2811(23)	6.2
C(16)[a]	−0.0802(37)	0.2959(27)	0.5428(32)	12.7(13)
C(17)[a]	0.0693(19)	0.3194(13)	0.1310(16)	4.2(5)

a) Refined isotropically.

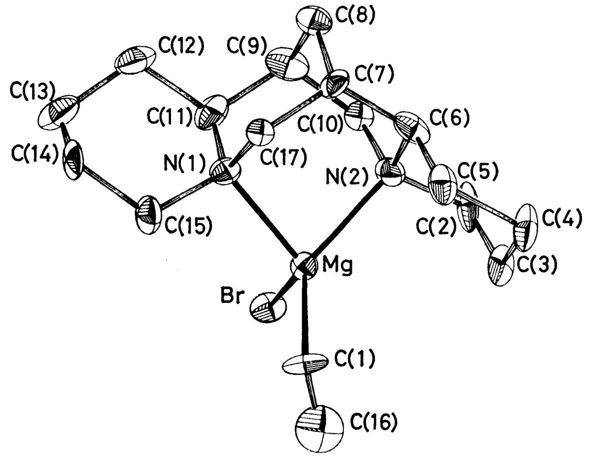

Fig. 1. A perspective view of the EtMgBr-(−)-sparteine molecule with the numbering scheme of atoms. Non-hydrogen atoms are drawn as thermal ellipsoids with 20% probability level.[11]

perature factors are listed in Table 1.†††††

The neutral atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[10] All the computations were done on an ACOS 700 or 900 computer at the Computation Center, Osaka University.

Results and Discussion

Molecular Structure. A perspective view (*ORTEP* II)[11] of the EtMgBr–(−)-sparteine complex with the numbering scheme of atoms is presented in Fig. 1.

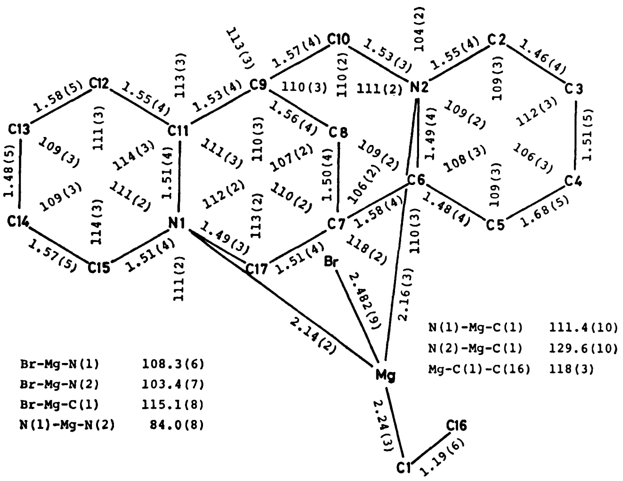

Fig. 2. Selected bond lengths (l/Å) and bond angles (ϕ/°) in the EtMgBr-(−)-sparteine molecule.

Selected bond lengths and bond angles are listed in Fig.2.

The Mg atom is tetrahedrally coordinated by the two N atoms of the (−)-sparteine, the C atom of the Et group, and the Br atom. The N(1)–Mg–N(2) angle [84.0(8)°] is equal to that observed in EtMgBr–(−)-α-isosparteine[12] but is smaller than the corresponding angles in dichloro[(−)-sparteine] cobalt(II) [90.4(3)°],[13] dichloro[(−)-α-isosparteine] cobalt(II) [89.0(2)°],[14] and dichloro[β-isosparteine] copper(II) [90.6(2)°].[15] This can be attributed to the fact that two N atoms of the (−)-sparteine ligand are spatially fixed, and hence the longer the coordination bonds between N atoms and the central metal atom(($\text{Mg–N})_{av}$=2.15††††††, $(\text{Co–N})_{av}$=2.05[13], Co–N=2.07[14], and

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††††† Tables of observed and calculated structure factors and anisotropic temperature factors are kept at the Chemical Society of Japan, Document No. 8321.

†††††† Present study.

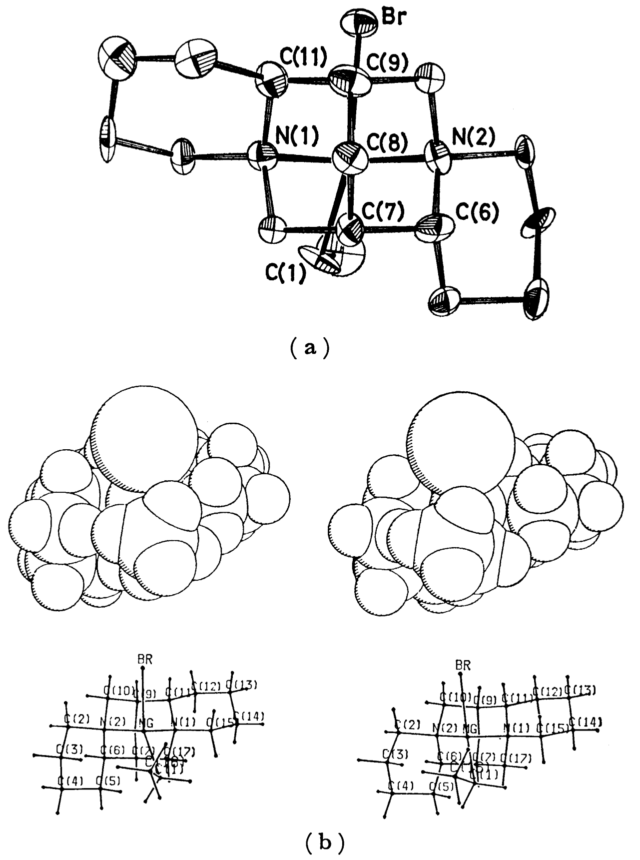

Fig. 3. (a) Molecular structure projected down along the bisector of the N(1)–Mg–N(2) angle. Non-hydrogen atoms are drawn as thermal ellipsoids with 20% probability level.[11] (b) Space-filling model of the molecule viewed up along the bisector.[17]

(Cu–N)$_{av}$=1.99[15]) is the smaller the N–Metal–N angle is expected to be. The C(1)–Mg–Br angle [115.1(8)°] in the present complex is slightly larger than the tetrahedral angle. The N(2)–Mg–C(1) [129.6(10)°] and N(2)–Mg–Br [103.4(7)°] angles largely deviated from the tetrahedral angle, whereas the N(1)–Mg–C(1) [111.4(10)°] and N(1)–Mg–Br [108.3(6)°] angles are similar to it.

Of the two possible conformations, the (−)-sparteine ligand takes the all-chair form. In addition to the bulky Br and ethyl group of the EtMgBr, the coordination of the (−)-sparteine to the Mg atom makes the space small around the N(1) atom but not the neighborhood of the N(2) as can be seen in Fig. 3. This fact may favor the selective coordination of the (*S*)-monomer to the Mg atom of the EtMgBr-(−)-sparteine at the initial stage of polymerization of the methacrylate, which is favorable to the subsequent (*S*)-monomer selection.

Crystal Structure. The packing of EtMgBr-(−)-sparteine molecules in a unit-cell is shown in Fig. 4. The dimeric association of molecules, observed in the crystal structures of Grignard reagents, [EtMgBr, Et$_3$N]$_2$[17] and [EtMgBr, (*i*-Pr)$_2$O]$_2$[18] is not observed. The closest intermolecular atomic contact is C(17) $(x, y, z)\cdots\mathrm{Br}(-x, -1/2+y, 1/2-z)$ (3.62(3) Å).

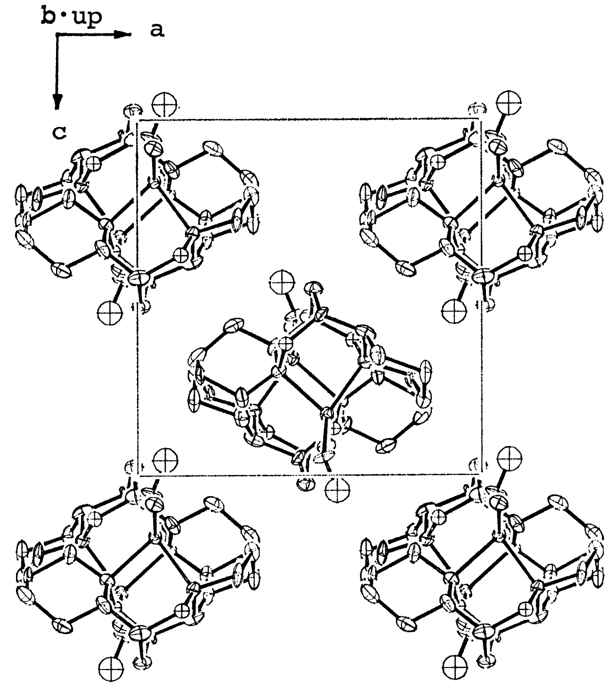

Fig. 4. The crystal structure of EtMgBr-(−)-sparteine.[11]

A part of the cost of this study was defrayed by the Grant-in-Aid (No. 434024) for Scientific Research from the Ministry of Education, Science and Culture.

References

1) Y. Okamoto, K. Ohta, and H. Yuki, *Chem. Lett.*, **1977**, 617.

2) Y. Okamoto, K. Urakawa, K. Ohta, and H. Yuki, *Macromolecules*, **11**, 719 (1978).

3) Y. Okamoto, K. Ohta, and H. Yuki, *Macromolecules*, **11**, 724 (1978).

4) Y. Okamoto, K. Suzuki, K. Ohta, and H. Yuki, *J. Polym. Sci., Polym. Lett. Ed.*, **17**, 293 (1979).

5) Y. Okamoto, H. Gamaike, and H. Yuki, *Makromol. Chem.*, **179**, 1341 (1978).

6) Y. Okamoto, K. Suzuki, T. Kitayama, H. Yuki, H. Kageyama, K. Miki, N. Tanaka, and N. Kasai, *J. Am. Chem. Soc.*, **104**, 4618 (1982).

7) T. Ashida, *HBLS* V, The Universal Crystallographic Computing System-Osaka The Computation Center, Osaka Univ., (1973), p. 55.

8) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham (1974), Vol. IV, p. 148.

9) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

10) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham (1974), Vol. IV, p. 71.

11) C. K. Johnson, *ORTEP* II, ORNL-5138, Oak Ridge National Laboratory, Tennessee (1976).

12) H. Kageyama, K. Miki, Y. Kai, N. Kasai, Y. Okamoto, and H. Yuki, *Acta Crystallogr., Sect. B*, **38**, 2264 (1982).

13) R. Kuroda and S. F. Mason, *J. Chem. Soc., Dalton Trans.*, **1977**, 371.

14) R. Kuroda and S. F. Mason, *J. Chem. Soc., Dalton Trans.*, **1979**, 727.

15) L. S. Childers, K. Folting, L. L. Merritt, Jr., and W. E. Streib, *Acta Crystallogr., Sect. B*, **31**, 924 (1975).

16) S. Motherwell, *PLUTO*, Cambridge Crystallographic Files User Mannual (1976).

17) J. Toney and G. D. Stucky, *J. Chem. Soc., Chem. Commun.*, **1967**, 1168.

18) A. L. Spek, P. Voorbergen, G. Schat, C. Blomberg, and F. Bickelhaupt, *J. Organomet. Chem.*, **77**, 147 (1974).