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The Molecular Structures of (+)-6-Benzylsparteine, (Ethyl)(bromo)[(+)-6-benzylsparteine]magnesium(II),† and Dibromo[(+)-6-benzylsparteine]magnesium(II).†† Structure and Reactivity of the Grignard Reagent–(−)-Sparteine Derivative Complexes for Asymmetric Selective Polymerization of Racemic Methacrylates.

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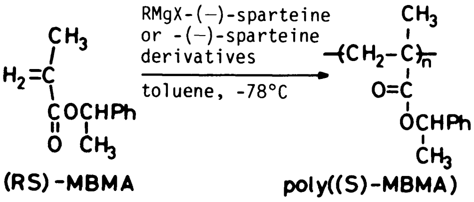
(+)-6-Benzylsparteine (**a**) crystallizes in orthorhombic systems; $P2_12_12_1$, a=10.711(1), b=25.868(4), c=6.804(1) Å, and Z=4; EtMgBr-(+)-6-benzylsparteine (**b**) also belongs to orthorhombic system; $P2_12_12_1$, a=11.020(4), b=23.660(10), c=8.666(6) Å and Z=4; and $MgBr_2$–(+)-6-benzylsparteine toluene solvate (**c**), orthorhombic system; $P2_12_12_1$, a=16.654(3), b=19.723(4), c=8.637(2) Å and Z=4. The structure of **a** was solved by the direct method and those of **b** and **c** by the heavy atom method. Refinements were carried out by the block-diagonal least-squares procedure; R values are: (**a**) 0.055. (**b**) 0.169, and (**c**) 0.118, respectively for 1342, 1445, and 1501 reflections. The **a** molecule takes a one-boat form, whereas by coordination to the Mg atom it changes into all-chair form in **b** and **c** molecules. The Mg atom has a distorted tetrahedral geometry; **b**, Mg–N=2.13(4) and 2.19(4), Mg–C 2.34(5) and Mg–Be=2.506(16) Å and N–Ng–N=83.1(14)°; **c**, Mg–N=2.08(3) and 2.17(3), Mg–Br=2.454(12) and 2.473(12) Å and N–Mg–N=85.8(10)°. The structures of these molecules are compared with those of (−)-sparteine complexes with EtMgBr, *t*-BuMgCl, and $MgCl_2$. On the basis of the molecular structures determined the activity of these Grignard reagent–(−)-sparteine derivatives for the enantiomer-selective polymerization of MBMA is discussed.

Asymmetric selective (enantiomer-selective) polymerization of racemic (*RS*)-α-methylbenzyl methacrylate (MBMA) has been investigated with homogeneous Grignard reagent–(−)-sparteine derivative catalysts in toluene at −78 °C.1) Sparteines combined with the Grignard reagents were (−)-sparteine, (−)-α-isosparteine, (−)-6-ethylsparteine, (+)-6-benzylsparteine, (−)-Δ^5-dehydrosparteine, and (−)-$\Delta^{5,11}$-didehydrosparteine. Among the complexes formed between Grignard reagent and (−)-sparteine (or its derivatives), EtMgBr–(−)-sparteine has a high activity, whereas *t*-BuMgCl–(−)-sparteine and EtMgBr–(−)-α-isosparteine has no activity, in the asymmetric selective polymerization of racemic (*RS*)-MBMA (Table 1). EtMgBr–(+)-6-benzylsparteine was also found active for the polymerization mentioned above but it is less active than EtMgBr–(−)-sparteine.



In order to obtain informations on the structural dependence of the reactivity and monomer-selectivity of these catalysts, molecular structures of EtMgBr–(−)-sparteine2), *t*-BuMgCl–(−)-sparteine3) and related complex $MgCl_2$–(−)-sparteine3), and EtMgBr–(−)-α-

TABLE 1. ASYMMETRIC SELECTIVE POLYMERIZATION OF (*RS*)MBMA WITH GRIGNARD REAGENT–(−)-SPARTEINE(OR SPARTEINE DERIVATIVE) COMPLEXES IN TOLUENE AT −78 °C1)

Sparteine ligand and Grignard reagent	Time / h	Yield / %	$[\alpha]^{20}_D$(OP) polymer / °(%)	$[\alpha]^{20}_D$(OP) recovered monomer / °(%)	Tacticity/% I	H	S
(−)-Sparteine							
EtMgBr	1	41.4	−102.2(82)	+30.4(57)	94	5	1
t-BuMgCl	96	0.4	0	0 (0)			
(+)-6-Benzylsparteine							
EtMgBr	99	14.1	−82.9(66)	+6.2(12)	77	14	9
(−)-α-Isosparteine							
EtMgBr	22	0					

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† Abbreviated as EtMgBr-(+)-6-benzylsparteine.

†† Abbreviated as $MgBr_2$-(+)-6-benzylsparteine.

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isosparteine[4] have been determined by means of X-ray diffraction. This paper deals with the molecular structure of EtMgBr–(+)-6-benzylsparteine and related complex $MgBr_2$–(+)-benzylsparteine. Interests on the molecular conformation promoted the crystal structure analysis of (+)-6-benzylsparteine.

Experimental

(+)-6-Benzylsparteine was recrystallized from a methanol solution. EtMgBr–(+)-6-benzylsparteine was prepared by mixing the crystalline powder of (+)-6-benzylsparteine and ether solution of EtMgBr under nitrogen atmosphere, because the reaction of a toluene solution of (+)-6-benzylsparteine and ether solution of EtMgBr gave $MgBr_2$–(+)-6-benzylsparteine instead of EtMgBr–(+)-6-benzylsparteine.

Crystals of (+)-6-benzylsparteine, EtMgBr–(+)-6-benzylsparteine, and $MgBr_2$–(+)-6-benzylsparteine used had approximate dimensions of 0.38×0.25×0.23, 0.68×0.33×0.25, and 0.13×0.25×0.5 mm, respectively. Crystals of EtMgBr–(+)-6-benzylsparteine and $MgBr_2$–(+)-6-benzylsparteine are both sensitive to moisture in air, and they were sealed in glass capillary tubes under nitrogen. Each crystal was mounted on a Rigaku automated, four-circle diffractometer. Nickel-filtered Cu $K\alpha$ radiation (λ=1.5418 Å) was used for the former organic crystal, and graphite monochromatized Mo $K\alpha$ radiation (λ=0.7107 Å) for the later two Mg-complexes, respectively. Unit-cell dimensions of each crystal were determined by the least-squares fit using 2θ values of high order, strong reflections.

Crystal Data. (+)-6-Benzylsparteine (**a**), $C_{22}H_{32}N_2$, M 324.5, orthorhombic, space group $P2_12_12_1$, a=10.711(1), b=25.868(4), c=6.804(1) Å, V=1885.1(4) Å^3, D_c=1.143 g cm^{-3} for Z=4, μ(Cu $K\alpha$)=5.07 cm^{-1}; EtMgBr–(+)-6-benzylsparteine (**b**), $C_{24}H_{37}N_2MgBr$, M 457.8, orthorhombic, space group $P2_12_12_1$, a=11.020(4), b=23.660(10), c=8.666(6) Å, V=2260(2) Å^3, D_c=1.350 g cm^{-3} for Z=4, μ(Mo $K\alpha$)=19.7 cm^{-1}; $MgBr_2$–(+)-6-benzylsparteine toluene solvate(c), $C_{22}H_{32}N_2MgBr_2\cdot C_7H_8$, $F.W.$ 600.8, orthorhombic, space group $P2_12_12_1$, a=16.654(3), b=19.723(4), c=8.637(2) Å, V=2836.8(9) Å^3, D_c=1.407 g cm^{-3} for Z=4, μ(Mo $K\alpha$)=30.7 cm^{-1}.

Reflection intensities were measured by the θ–2θ scan technique at a 2θ rate of 4° min^{-1}. The scan widths were $\Delta 2\theta$=(2.0+0.3tanθ)° for the former organic crystal and $\Delta 2\theta$=(2.4+0.7tanθ)° for the latter two Mg-complexes. Backgrounds were counted for 7.5 s at both ends of a scan. Four standard reflections were measured after every 60 reflections, which showed less than 5% fluctuations throughout the data collection. A total of 1408 reflections was measured for (+)-6-benzylsparteine, of which 1346 were non-zero reflections. The reflection profiles of EtMgBr–(+)-sparteine were not so sharp, and only 1445 reflections ($|F_o|>3\sigma(F_o)$) out of 2369 measured were used for the structure analysis. For $MgBr_2$–(+)-6-benzylsparteine 2942 reflections were measured but only 1501($|F_o|>3\sigma(F_o)$) could be used. Usual Lp corrections were applied but corrections for absorption and extinction were ignored.

Structure Solution and Refinement

(a) (+)-6-Benzylsparteine. The structure was solved by the direct method (*MULTAN* 78),[5] and all the C and N atoms could be located on the E map. The refinement of the structure was carried out by the block-diagonal least-squares procedure (*HBLS* V).[6] The function minimized was $\sum w(\Delta F)^2$. During the course of the refinement four strong reflections (200, 230, 031, and 160), which were considered largely affected by the extinction, were excluded. Hydrogen atoms were located on a difference Fourier map, which were refined isotropically while the other anisotropically. The final R index was 0.055 (R_W=0.092) for 1342 non-zero reflections. The weighting schemes used at the final stage of the refinement were $w=\{\sigma^2(F_o)+0.01024|F_o|^2\}^{-1}$ for $|F_o|>0$ and w=0.63654 for $|F_o|=0$. The final atomic parameters are listed in Table 2.[††††]

(b) EtMgBr-(+)-6-benzylsparteine. The Br atom

Table 2. Final atomic positional parameters, of (+)-6-benzylsparteine, with estimated standard deviaitions in parentheses

a) Anisotropic atoms.

Atom	x	y	z	B_{eq}[12)]/Å^2
N(1)	0.9110(3)	0.4216(2)	0.0795(6)	3.9
N(2)	0.6163(3)	0.3744(2)	-0.1125(5)	3.0
C(2)	0.4936(4)	0.3781(2)	-0.2008(6)	3.9
C(3)	0.4005(4)	0.4050(2)	-0.0636(8)	4.8
C(4)	0.3965(4)	0.3785(2)	0.1376(7)	4.1
C(5)	0.5299(4)	0.3734(2)	0.2187(6)	3.2
C(6)	0.6218(4)	0.3464(2)	0.0767(6)	2.9
C(7)	0.7575(4)	0.3515(2)	0.1553(6)	3.0
C(8)	0.8493(4)	0.3273(2)	0.0108(6)	3.5
C(9)	0.8424(4)	0.3592(2)	-0.1764(6)	3.4
C(10)	0.7103(4)	0.3581(2)	-0.2558(6)	3.5
C(11)	0.8921(4)	0.4150(2)	-0.1343(7)	3.5
C(12)	1.0145(4)	0.4246(2)	-0.2409(8)	4.4
C(13)	1.0676(5)	0.4777(2)	-0.1915(10)	6.0
C(14)	1.0763(5)	0.4856(2)	0.0296(10)	6.0
C(15)	0.9518(5)	0.4740(2)	0.1277(9)	5.1
C(17)	0.7964(4)	0.4091(2)	0.1882(6)	3.7
C(18)	0.5837(4)	0.2878(2)	0.0541(6)	3.2
C(19)	0.5941(4)	0.2549(2)	0.2381(6)	3.0
C(20)	0.6943(4)	0.2214(2)	0.2642(7)	3.7
C(21)	0.7019(5)	0.1902(2)	0.4323(7)	4.3
C(22)	0.6103(5)	0.1923(2)	0.5734(7)	4.4
C(23)	0.5101(4)	0.2246(2)	0.5475(7)	4.1
C(24)	0.5009(4)	0.2552(2)	0.3801(7)	3.7

b) Isotropic atoms.

Atom	x	y	z	B/Å^2
H(2a)	0.464(5)	0.341(2)	-0.226(8)	3.4(11)
H(2b)	0.497(4)	0.401(2)	-0.327(7)	2.7(10)
H(3a)	0.316(5)	0.405(2)	-0.123(8)	3.0(10)
H(3b)	0.427(4)	0.442(2)	-0.047(8)	3.3(11)
H(4a)	0.353(5)	0.344(2)	0.122(8)	3.0(10)
H(4b)	0.349(5)	0.400(2)	0.234(9)	3.8(11)
H(5a)	0.527(4)	0.353(2)	0.343(7)	2.9(10)
H(5b)	0.562(5)	0.409(2)	0.249(8)	2.7(10)
H(7)	0.761(4)	0.333(2)	0.283(7)	2.0(9)
H(8a)	0.825(4)	0.290(2)	-0.017(6)	1.8(9)
H(8b)	0.938(4)	0.328(2)	0.067(7)	2.3(9)
H(9)	0.898(5)	0.345(2)	-0.282(8)	3.6(11)
H(10a)	0.706(5)	0.385(2)	-0.368(8)	3.3(11)
H(10b)	0.691(4)	0.322(2)	-0.298(7)	2.7(10)
H(11)	0.826(4)	0.441(2)	-0.178(7)	2.3(10)
H(12a)	1.002(5)	0.422(2)	-0.390(9)	3.5(11)
H(12b)	1.077(5)	0.398(2)	-0.197(8)	3.5(11)
H(13a)	1.005(5)	0.504(2)	-0.256(8)	4.7(13)
H(13b)	1.151(6)	0.482(2)	-0.264(8)	4.5(12)
H(14a)	1.103(5)	0.523(2)	0.063(8)	3.5(11)
H(14b)	1.141(5)	0.461(2)	0.087(9)	3.9(11)
H(15a)	0.887(5)	0.501(2)	0.076(8)	3.5(11)
H(15b)	0.957(6)	0.478(2)	0.281(9)	4.6(13)
H(17a)	0.722(4)	0.430(2)	0.139(8)	2.6(10)
H(17b)	0.815(5)	0.419(2)	0.332(9)	3.9(12)
H(18a)	0.637(5)	0.271(2)	-0.059(9)	3.5(11)
H(18b)	0.493(4)	0.286(2)	0.003(7)	2.4(10)
H(20)	0.763(4)	0.221(2)	0.156(7)	1.5(9)
H(21)	0.779(4)	0.166(2)	0.449(7)	3.2(11)
H(22)	0.618(4)	0.171(2)	0.698(7)	2.5(10)
H(23)	0.445(5)	0.226(2)	0.647(9)	3.2(11)
H(24)	0.420(5)	0.278(2)	0.369(8)	3.0(10)

was located by three-dimensional Patterson function. Positions of the Mg, N, and C atoms except the C(16) were determined by the subsequent Fourier synthesis. The structure was first refined isotropically by the block-diagonal least-squares procedure (*HBLS* V) with unit weight. The temperature factor of the C(1) atom fell on a negative value, and it was corrected and fixed as B=4.67 Å^2 which was derived from the Wilson statistics of structure amplitudes. The C(16) atom could be located on a difference Fourier map and fixed at the position. At the final stage of the anisotropic refinement the anomalous dispersion of all the non-hydrogen atoms was considered. However, the R index converged to a rather high value of 0.169(R_w=0.188) for 1445 reflections. The final atomic parameters are listed in Table 3.††††

(c) $MgBr_2$-(+)-6-benzylsparteine Toluene Solvate. The crystal of this complex was expected as that of EtMgBr-(+)-6-benzylsparteine, but the three-dimensional Patterson function could not be interpreted well. Three big peaks, found on the E map based on the phases using the *MULTAN* 78 program, supported to interprete the Patterson function as the complex was $MgBr_2$-(+)-6-benzylsparteine. The N and C atoms were then located on the Fourier synthesis based on the phases of the Mg and two Br atoms. The structure was refined by the *HBLS* V program with unit weight. Subsequent Fourier and difference syntheses revealed the location of seven C atoms of toluene, the solvent of crystallization. None of the hydrogen atoms could be located. The R index was 0.118 (R_w= 0.126) for 1501 reflections at the final stage of the anisotropic refinement: the anomalous dispersion of Br, Mg, N, and C atoms was considered. The final atomic parameters are given in Table 4.††††

TABLE 3. FINAL ATOMIC POSITIONAL PARAMETERS, OF EtMgBr-(+)-6-BENZYLSPARTEINE, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

a) Anisotropic atoms.

Atom	x	y	z	B_{eq}[12)] /Å^2
Br	0.3580(4)	0.3635(2)	-0.0705(6)	5.3
Mg	0.536(2)	0.3805(6)	0.1038(15)	4.0
N(1)	0.458(3)	0.3966(11)	0.325(4)	3.2
N(2)	0.639(3)	0.3164(11)	0.231(3)	2.8
C(2)	0.714(3)	0.2910(13)	0.102(5)	3.5
C(4)	0.549(4)	0.2211(16)	0.056(6)	5.3
C(5)	0.483(4)	0.2481(16)	0.182(5)	3.7
C(6)	0.567(4)	0.2722(16)	0.308(4)	3.6
C(7)	0.494(3)	0.2996(14)	0.442(5)	3.2
C(8)	0.579(3)	0.3263(14)	0.567(6)	4.4
C(9)	0.649(4)	0.3747(14)	0.467(6)	6.0
C(10)	0.712(3)	0.3490(13)	0.334(4)	2.1
C(11)	0.560(4)	0.4291(17)	0.420(6)	5.5
C(12)	0.509(4)	0.4547(13)	0.566(6)	4.0
C(13)	0.423(4)	0.5041(18)	0.513(5)	4.7
C(14)	0.312(4)	0.4710(16)	0.448(6)	5.5
C(15)	0.359(4)	0.4440(15)	0.287(5)	4.3
C(17)	0.397(4)	0.3451(16)	0.401(6)	5.6
C(18)	0.640(4)	0.2246(16)	0.373(5)	4.8
C(19)	0.584(3)	0.1763(14)	0.459(4)	2.6
C(20)	0.575(3)	0.1737(14)	0.621(5)	3.9
C(21)	0.532(4)	0.1274(15)	0.703(5)	4.8
C(22)	0.489(4)	0.0796(17)	0.613(6)	5.4
C(23)	0.490(4)	0.0803(16)	0.456(6)	5.0
C(24)	0.542(4)	0.1261(12)	0.373(5)	3.5

b) Isotropic atoms.

Atom	x	y	z	B/Å^2
C(3)	0.650(4)	0.2698(14)	-0.021(4)	4.0(8)
C(1)	0.674(4)	0.4436(16)	-0.007(5)	4.7(9)
C(16)	0.765	0.4218	-0.100	15(3)

TABLE 4. FINAL ATOMIC POSITIONAL PARAMETERS, OF $MgBr_2$-(+)-6-BENZYLSPARTEINE TOLUENE SOLVATE, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B_{eq}[12)] /Å^2
Br(1)	0.4524(3)	0.1648(3)	-0.4109(6)	6.7
Br(2)	0.3287(3)	0.1758(3)	-0.8188(6)	7.2
Mg	0.3250(7)	0.1949(5)	-0.5359(12)	3.9
N(1)	0.235(2)	0.141(2)	-0.422(3)	3.3
N(2)	0.247(2)	0.282(2)	-0.507(3)	3.0
C(2)	0.289(2)	0.336(2)	-0.594(5)	5.0
C(3)	0.374(3)	0.351(2)	-0.526(4)	4.8
C(4)	0.372(2)	0.362(2)	-0.336(4)	3.8
C(5)	0.317(2)	0.308(2)	-0.269(4)	3.7
C(6)	0.238(2)	0.301(2)	-0.336(4)	3.8
C(7)	0.181(2)	0.245(2)	-0.263(3)	2.6
C(8)	0.099(2)	0.237(2)	-0.338(4)	3.7
C(9)	0.118(2)	0.211(2)	-0.513(4)	4.2
C(10)	0.174(2)	0.268(2)	-0.594(4)	3.8
C(11)	0.163(2)	0.139(2)	-0.512(4)	3.3
C(12)	0.093(2)	0.088(2)	-0.461(5)	5.4
C(13)	0.136(2)	0.016(2)	-0.447(4)	4.3
C(14)	0.207(2)	0.018(2)	-0.342(6)	5.9
C(15)	0.270(2)	0.071(2)	-0.389(5)	4.1
C(17)	0.226(2)	0.172(2)	-0.259(4)	4.5
C(18)	0.188(3)	0.371(2)	-0.328(5)	5.4
C(19)	0.161(2)	0.389(2)	-0.157(4)	3.1
C(20)	0.085(2)	0.382(2)	-0.117(4)	3.7
C(21)	0.055(3)	0.402(2)	0.027(5)	7.4
C(22)	0.114(3)	0.433(2)	0.132(5)	6.4
C(23)	0.189(3)	0.444(2)	0.087(5)	6.1
C(24)	0.218(3)	0.422(2)	-0.072(5)	5.8
C(25)	-0.055(4)	0.023(3)	-0.102(6)	11.6
C(26)	-0.017(4)	0.077(3)	-0.045(6)	11.5
C(27)	0.060(3)	0.069(3)	0.015(6)	9.1
C(28)	0.098(4)	0.124(3)	0.072(6)	10.9
C(29)	0.059(4)	0.198(3)	0.072(7)	12.6
C(30)	-0.006(3)	0.199(4)	0.010(5)	10.4
C(31)	-0.057(3)	0.139(2)	-0.053(5)	6.4

Atomic scattering factors[7)] and coefficients of anomalous dispersion[8)] used were taken from International Tables for X-Ray Crystallography, Vol. IV. All the computations were done on an ACOS 700S computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Results and Discussion

Molecular Structures. Perspective views(*ORTEP* II)[9)] of (+)-6-benzylsparteine, EtMgBr-(+)-6-benzylsparteine, and $MgBr_2$-(+)-6-benzylsparteine molecules are depicted in Figs. 1, 2, and 3, respectively. Bond lengths and bond angles in these complexes are given in Figs. 4, 5 and 6, respectively.

(a) (+)-6-Benzylsparteine: The remarkable feature of the structure is that this molecule takes a one-boat form: six-membered ring made by the C(7), C(8), C(9), C(11), N(1), and C(17) atoms is in a boat form, whereas all of the other rings in chair forms. The C(2)-N(2)-C(6)-[115.5(3)°] and C(11)-N(1)-C(15) angles[111.7(4)°] are respectively larger than the corresponding angles in

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†††† Tables of observed and calculated structure factors and anisotropic thermal parameters of (+)-6-benzylsparteine, EtMgBr-(+)-6-benzylsparteine, and $MgBr_2$-(+)-6-benzylsparteine toluene solvate, are kept at the Chemical Society of Japan, Document No. 8417.

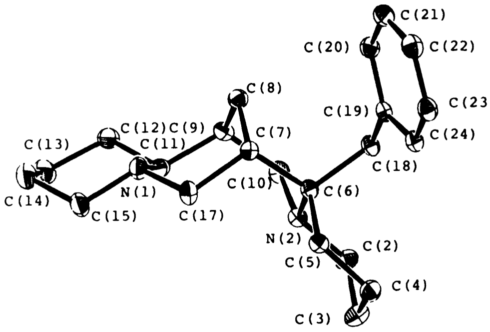


Fig. 1. A perspective view of (+)-6-benzylsparteine molecule with the numbering scheme of atoms. Non-hydrogen atoms are drawn as thermal ellipsoids with 20% probability level.[9]

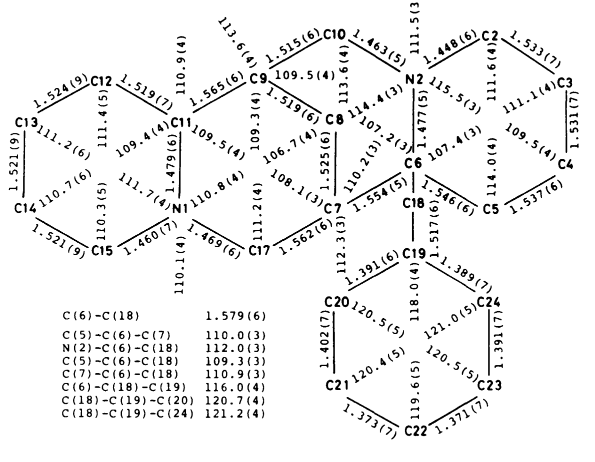


Fig. 4. Selected bond lengths [l/Å] and bond angles [ϕ/°] in (+)-6-benzylsparteine molecule.

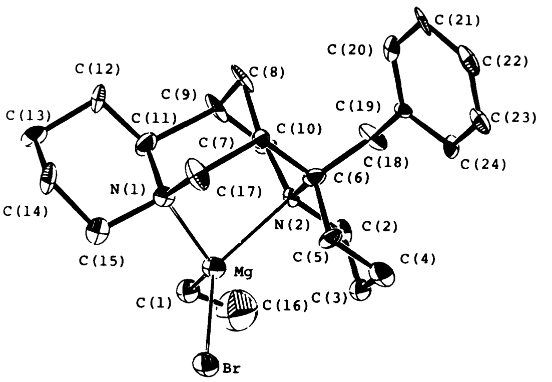


Fig. 2. A perspective view of EtMgBr–(+)-6-benzylsparteine molecule with the numbering scheme of atoms. Non-hydrogen atoms are drawn as thermal ellipsoids with 20% probability level.[9]

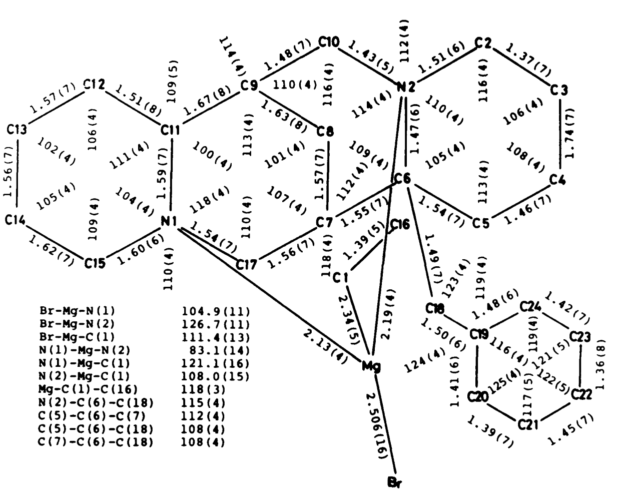


Fig. 5. Selected bond lengths [l/Å] and bond angles [ϕ/°] in EtMgBr–(+)-6-benzylsparteine molecule.

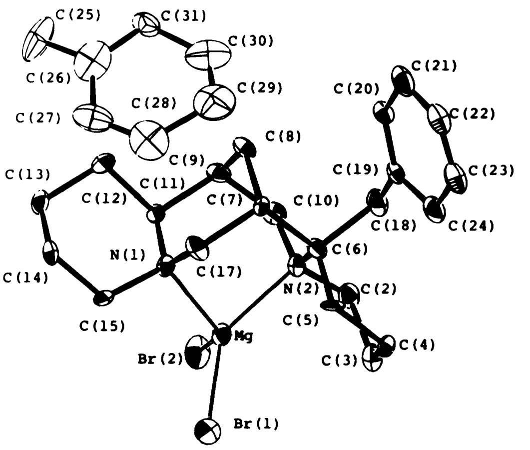


Fig. 3. A perspective view of $MgBr_2$–(+)-6-benzylsparteine and toluene, the crystalline solvent molecules with the numbering scheme of atoms. Non-hydrogen atoms are drawn as thermal ellipsoids with 20% probability level.[9]

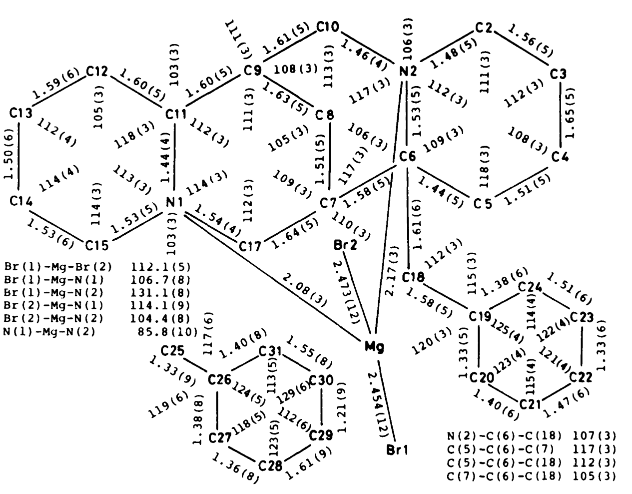
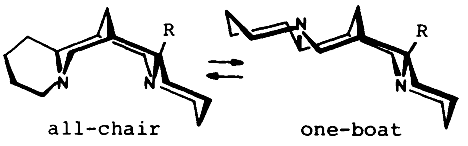


Fig. 6. Selected bond lengths [l/Å] and bond angles [ϕ/°] in $MgBr_2$–(+)-6-benzylsparteine and toluene, the crystalline solvent molecule.

sparteine skeleton in 17β-methylsparteine diperchlorate [109.6(6) and 107.9(5)°][10] and episparteine N(16)-oxide sesquiperchlorate [110.6(3) and 109.0(3)°],[11] of which the sparteine moieties have one-boat form. Whereas the C(5)-C(6)-(7) angle [110.0(3)°] is smaller than those [115.8(7) and 116.5(3)°] in the two sparteine derivatives mentioned below.



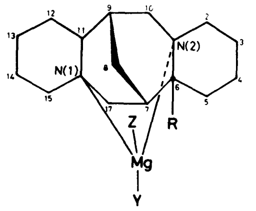
R = H, Et, CH$_2$Ph

(b) EtMgBr-(+)-6-benzylsparteine: The sparteine skeleton in the (+)-6-benzylsparteine moiety has an all-chair form, and its structure is similar to those found in EtMgBr-(−)-sparteine,[2] *t*-BuMgCl-(−)-sparteine,[3] and MgCl$_2$-(−)-sparteine.[3] The spatial arrangement of the alkyl and halogen ligands the sparteine skeleton through the Mg atom is, similar to that in *t*-BuMgCl-(−)-sparteine,[3] reverse to that in EtMgBr-(−)-sparteine.[2] The coordination geometry around the Mg atom is distorted tetrahedral, which is similar to those observed in Grignard reagent-(−)-sparteine complexes.

(c) MgBr$_2$-(+)-6-benzylsparteine: The sparteine skeleton in the present complex also has an all-chair conformation. Distorted tetrahedral geometry is observed around the Mg atom.

(d) Structure of the Sparteine Skeleton in RMgX-(−)-sparteine Derivative Complexes. Through the five

Table 5. Comparison of the coordination geometry around the Mg atom with estimated standard deviations in parentheses



R=H or CH$_2$Ph

(a) Bond length[*l*/Å]

	Mg-N(1)	Mg-N(2)	Mg-Y			Mg-Z		
			Mg-C	Mg-Cl	Mg-Br	Mg-C	Mg-Cl	Mg-Br
EtMgBr-(−)-sparteine	2.14(2)	2.16(3)	2.24(3)					2.482(9)
t-BuMgCl-(−)-sparteine	2.171(12)	2.175(12)		2.332(7)		2.19(2)		
MgCl$_2$-(−)-sparteine	2.150(9)	2.160(9)		2.269(5)			2.279(6)	
EtMgBr-(+)-6-benzylsparteine	2.13(4)	2.19(4)			2.506(16)	2.34(5)		
MgBr$_2$-(+)-6-benzylsparteine	2.08(3)	2.17(3)			2.452(12)			2.473(12)
EtMgBr-(−)-α-isosparteine	2.165(13)	2.195(13)	2.224(15)					2.506(6)

(b) Bond angle[*ϕ*/°]

	N(1)-Mg-N(2)	Y-Mg-N(1)	Y-Mg-N(2)	Z-Mg-N(1)	Z-Mg-N(2)	Y-Mg-Z
EtMgBr-(−)-sparteine	84.0(8)	114.4(10)	129.6(10)	108.3(6)	103.4(7)	115.1(8)
t-BuMgCl-(−)-sparteine	83.9(5)	100.8(4)	117.4(4)	119.5(6)	116.2(6)	114.7(5)
MgCl$_2$-(−)-sparteine	85.0(4)	108.0(3)	123.3(3)	112.6(3)	105.8(3)	117.6(2)
EtMgBr-(+)-6-benzylsparteine	83.1(14)	104.9(11)	126.7(11)	121.1(16)	108.0(15)	111.4(13)
MgBr$_2$-(+)-6-benzylsparteine	85.8(10)	106.7(8)	131.1(8)	114.1(9)	104.4(8)	112.1(5)
EtMgBr-(−)-α-isosparteine	83.9(5)	106.1(6)	129.7(6)	122.9(4)	101.4(4)	112.1(5)

RMgX-(−)-sparteine derivative complexes except EtMgBr-(−)-α-isosparteine, the (−)-sparteine ligand and sparteine skeleton of (+)-6-benzylsparteine ligand take all-chair form, and all of them have the same structure: corresponding bond lengths and bond angles are respectively equal within the range of error.

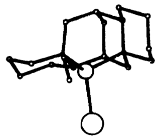
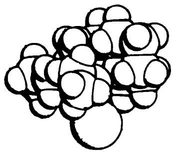
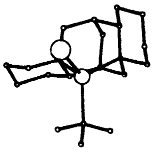
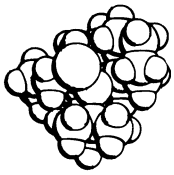
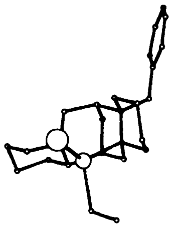
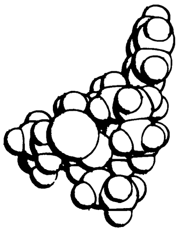
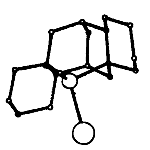
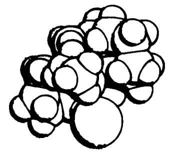
The (−)-sparteine ligand (or sparteine skeleton) consists of four fused N-containing six-membered rings; the fusion of N(1)-containing ring to the central symmetrically-fused two rings is different from that of N(2)-containing ring. The approximately Λ-shaped (−)-sparteine ligand has a cavity in which a Mg atom can coordinate. The C(7)-side of the cavity is spatially less open than the C(9)-side because of the unsymmetrical structure of (−)-sparteine ligand.

The (−)-α-isosparteine ligand has a C_2 symmetry. A half of its cavity is very similar to that of the C(7)-side of (−)-sparteine. The whole cavity of this ligand is more likely Λ-shaped and spatially less open than that of (−)-sparteine.

(e) Coordination Geometry around the Mg Atom in RMgX-(-)-sparteine Derivative Complexes: The geometry around the Mg atom is summarized in Table 5. In each complex the Mg atom has a distorted tetrahedral geometry. As shown in Table 5, two Mg–N bond lengths are equal [av. 2.15 Å], and the N–Mg–N angle is sharp and solid [83.1—85.8, av. 84.3°]. Regardless the geometrical relation of the alkyl and halogen ligands to the sparteine skeleton mentioned before, the Y–Mg–N(2) angle is larger than the Y–Mg–N(1), whereas the Z–Mg–N(2) angle is smaller than the Z–Mg–N(1). The Y–Mg–Z angle is slightly larger than the tetrahedral angle. Among the Mg–Y and Mg–Z bond lengths, the Mg–Cl lengths in *t*-BuMgCl-(−)-sparteine [2.332(7) Å] is much longer than those in dichloride, $MgCl_2$-(−)-sparteine [2.269(5) Å]. Similarly, the Mg–Br bond lengths in EtMgBr-(−)-sparteine, EtMgBr-α-isosparteine and EtMgBr-(+)-6-benzylsparteine look like longer than those in dibromide, $MgBr_2$-(+)-6-benzylsparteine though it is not fully significant. The Mg–C bond lengths in four complexes are equal [2.19(2)—2.34(5), av. 2.25 Å] within the range of error.

(f) Structure-dependence of Reactivity of RMgX-(−)-sparteine Derivative Complexes for the Asymmetric Selective Polymerization of (RS)-*MBMA*: In Table 6 summarized are molecular structures of EtMgBr-(−)-sparteine,[2] *t*-BuMgCl-(−)-sparteine,[3] EtMgBr-(+)-6-benzylsparteine (present study), and EtMgBr-(−)-α-isosparteine[4] and also results of enantiomer-selective

Table 6. Structure and reactivity of RMgX-(−)-sparteine derivative complexes

Complex	Molecular	Structure		Reactivity for the enantiomer selective polymerization of (*RS*)-MBMA (Ref. Table 1)
	Solid ball and spoke model[13]	Space-filling model[13]	Substrate-accomodation in the neighborhood of Mg atom	
EtMgBr-(−)-sparteine			Sufficiently large	Good
t-BuMgCl-(−)-sparteine			No	No
EtMgBr-(+)-6-benzylsparteine			Small	Poor
EtMgBr-(−)-α-isosparteine			No	No

polymerization of (*RS*)-MBMA initiated by these complex catalysts.[1] Discussion will be limited on the structural feature because the activity and selectivity of these complex catalysts has already been discussed in detail.[1]

It has been reported that the polymerization of MBMA proceeds in a coordination mechanism: the structure of the active center, which presumably depend on the structure of the sparteine skeleton and the geometry around the Mg atom, is considered of most importance.

In catalytically active EtMgBr-(−)-sparteine, the Et group coordinates to the Mg atom at the spatially less opened C(7)-side of the cavity (Y=Et) whereas the bulky Br ligand at the more opened C(9)-side. The Et group is not so large. The Mg atom, therefore, has a sufficient space to accommodate the MBMA, the substrate in its neighborhood.

On the other hand, in the inactive *t*-BuMgCl-(−)-sparteine, the bulky *t*-Bu ligand covers the Mg atom at the spatially more opened C(9)-side and the Cl ligand at the C(7)-side of the cavity (Y=Cl and Z=*t*-Bu). The spatial arrangement of alkyl and halogen ligands is reverse to that of EtMgBr-(−)-sparteine. As is clearly seen from the space-filling model[13] of this molecule (Table 6), there is no room spatially to accommodate the substrate in the neighborhood of the Mg atom.

In the poorly active EtMgBr-(+)-6-benzylsparteine, the all-chair form (+)-6-benzylsparteine ligand has a structure very close to the (−)-sparteine ligand except the benzyl group. The cavity under Λ-shaped sparteine skeleton is therefore very close to that of (−)-sparteine ligand. The Et ligand in this complex coordinates to the Mg atom at the more opened C(9)-side of the cavity. The alkyl and halogen ligands spatially arranged reverse to that of EtMgBr-(−)-sparteine (Y=Br and Z=Et).

In EtMgBr-(−)-*α*-isosparteine, the cavity of (−)-*α*-isosparteine is less opened than that of (−)-sparteine. The Mg atom coordinate deep in the cavity covered with Et and Br ligands, which leads the inactivity of this complex.

Crystal Structure. The packing of molecules in crystals of (+)-6-benzylsparteine, EtMgBr-(+)-6-benzylsparteine, and $MgBr_2$-(+)-6-benzylsparteine toluene solvate are drawn in Figs. 7, 8, and 9.

(a) (+)-6-Benzylsparteine: Rather loose molecular contacts are observed between carbon atoms of the benzyl group in one molecule and those of bridge-head carbons in the other molecule: The closest intermolecular atomic contact being 3.682(6) Å [C(24) (x, y, z)···C(9) $(-0.5+x,\ 0.5-y,\ -z)$].

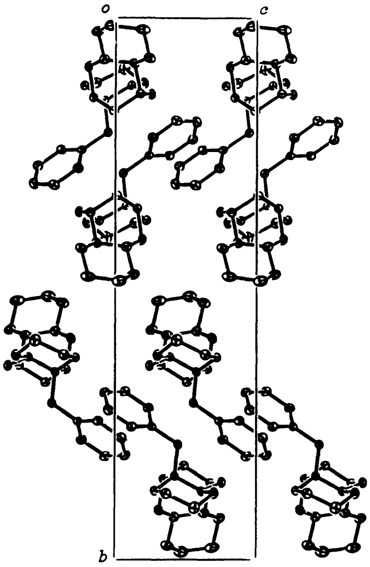


Fig. 7. The crystal structure of (+)-6-benzylsparteine.[9]

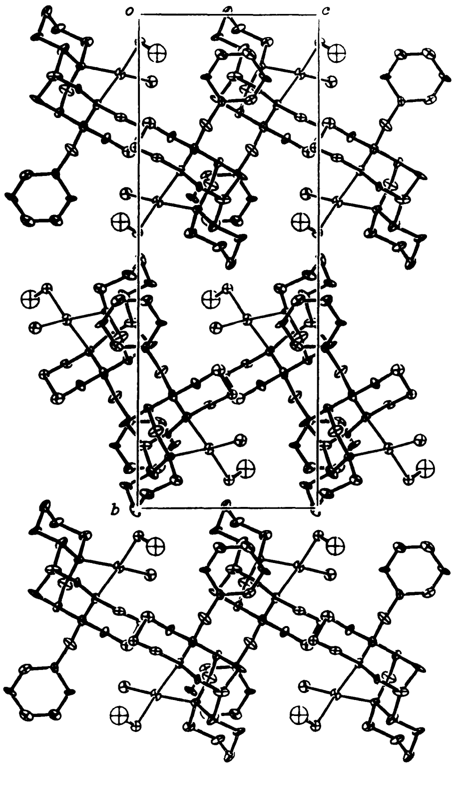


Fig. 8. The crystal structure of EtMgBr-(+)-6-benzylsparteine.[9]

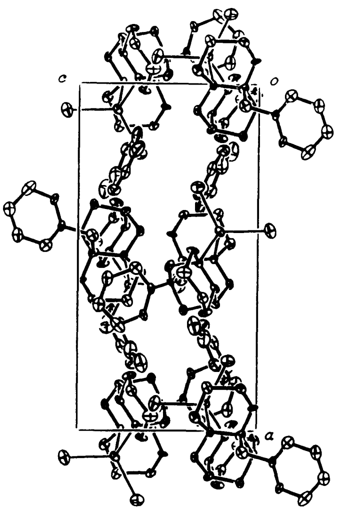


Fig. 9. The crystal structurre of $MgBr_2$-(+)-6-benzylsparteine toluene solvate.[9]

(b) EtMgBr-(+)-6-benzylsparteine: The molecular packing in the crystal is determined by the van der Waals contacts between carbon atoms of the benzyl group in one molecule to those of sparteine skeleton in the other molecule. The shortest intermolecular atomic contact is found between C(22) (x, y, z) and C(10) $(-0.5+x, 0.5-y, 1-z)$ [3.52(7) Å].

(c) MgBr₂-(+)-6-benzylsparteine Toluene Solvate: The Mg complexes in the crystal are loosely bound to toluene molecules by van der Waals forces. The closest intermolecular atomic contact is 3.56(7) Å [both C(30) $(x, y, z)\cdots$C(8) (x, y, z) and C(31) $(x, y, z)\cdots$C(4)$(-0.5+x$ $0.5-y, -z)$], whereas the shortest distance between Mg complexes is 3.74(4) Å [C(9) $(x, y, z)\cdots$Br $(-0.5+x, 0.5-y, -1-z)$].

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