The Molecular Structures of (*t*-Butyl)(chloro)[(−)-sparteine]magnesium(II)† and Dichloro[(−)-sparteine]magnesium(II)††

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Crystals of *t*-BuMgCl–(−)-sparteine (**1**) belongs to orthorhombic system; $P2_12_12_1$, $a=25.689(6)$, $b=10.030(2)$, $c=7.942(2)$ Å, and $Z=4$; $MgCl_2$–(−)-sparteine (**2**) also crystallizes in orthorhombic system; $P2_12_12_1$, $a=11.180(4)$, $b=11.957(4)$, $c=12.573(5)$ Å, and $Z=4$. Both structures were solved by the heavy atom method, and refined by the block-diagonal least-squares procedure; (**1**) $R=0.098$ for 1199 non-zero reflections and (**2**) $R=0.091$ for 1347 observed reflections. The Mg atom in each complex has a distorted tetrahedral geometry: (**1**) Mg–N= 2.17(2) and 2.18(2), Mg–C=2.19(2), and Mg–Cl=2.332(7) Å and N–Mg–N=83.9(5)°; (**2**) Mg–N=2.150(9) and 2.160(9), and Mg–Cl=2.269(5) and 2.279(6) Å, and N–Mg–N=85.0(4)°.

The kinetics[1] and the structure and reactivity of a series of Grignard reagent–(−)-sparteine (or its derivative) complexes in the asymmetric selective polymerization of α-methylbenzyl methacrylate have been studied. The molecular structure of EtMgBr–(−)-sparteine,[2] which chooses the (*S*)-monomer out of the racemic mixture of α-methylbenzyl methacrylate (or other methacrylates) and initiates the asymmetric selective polymerization, has been determined by means of X-ray diffraction. Molecular structures of the inactive EtMgBr–(−)-α-isosparteine[3] and *t*-BuMgCl–(−)-sparteine also have been determined. This paper deals with the crystal structure determination of inactive *t*-BuMgCl–(−)-sparteine (**1**) and of related complex $MgCl_2$–(−)-sparteine (**2**).

Experimental

Many trials to prepare the complex between *t*-BuMgBr and (−)-sparteine have been unsuccessful. The *t*-BuMgCl–(−)-sparteine was then prepared by mixing a toluene solution of (−)-sparteine and an ether solution of *t*-BuMgCl under nitrogen atmosphere. Crystals obtained were recrystallized from toluene, which were used for X-ray study. All of the crystals examined did not give any sharp diffraction profiles. The other crystals, obtained from the mother liquor at room temperature, were also recrystallized from toluene, which were first considered as *t*-BuMgCl–(−)-sparteine and were later found as $MgCl_2$–(−)-sparteine. *t*-BuMgCl–(−)-sparteine was then prepared again and recrystallized from toluene. The crystals were found useful for X-ray diffraction data collection.

As both crystals were sensitive to moisture in the air, they were sealed in thin-walled glass capillary tubes, which were mounted on a Rigaku automated, four-circle diffractometer. Graphite monochromatized Mo *Kα* radiation ($\lambda=0.71069$ Å) was used. Unit-cell dimensions were determined by the least-squares fit using 2θ values of 25 strong reflections. A prismatic crystal of *t*-BuMgCl–(−)-sparteine with approximate dimensions of $0.4\times0.20\times0.18$ mm³ was used for the X-ray experiment. The $MgCl_2$–(−)-sparteine crystal used had dimensions of $0.20\times0.18\times0.50$ mm³.

Crystal Data. *t*-BuMgCl–(−)-sparteine (**1**): $C_{19}H_{35}N_2$-MgCl, M 351.3, orthorhombic, space group $P2_12_12_1$, $a=25.689(6)$, $b=10.030(2)$, $c=7.942(2)$ Å, $V=2046.3(7)$ Å³, $D_c=1.140$ g cm⁻³ for $Z=4$, μ(Mo *Kα*)=2.22 cm⁻¹. $MgCl_2$–(−)-sparteine (**2**): $C_{15}H_{26}N_2MgCl$, M 329.6, orthorhombic, space group $P2_12_12_1$, $a=11.180(4)$, $b=11.957(4)$, $c=12.573(5)$ Å, $V=1680.7(10)$ Å³, $D_c=1.303$ g cm⁻³ for $Z=4$, μ(Mo *Kα*)= 4.18 cm⁻¹.

Integrated intensities for both crystals were measured by the θ-2θ scan technique (**1**) $2\theta\leqq46.0°$; (**2**) $2\theta\leqq50.5°$: the 2θ scan rate was 4° min⁻¹ and the scan width $\Delta2\theta=(2.4+0.7\ \tan\theta)°$. The background scattering was counted for 7.5 s at both ends of a scan. Four standard reflections measured after every 60 reflections were used in order to check the crystal orientation and X-ray damage. They showed less than 5% fluctuation throughout the data collection of *t*-BuMgCl–(−)-sparteine. For $MgCl_2$–(−)-sparteine, the intensities of the four standard reflections decreased; as they did so uniformly with time, the observed intensities were corrected linearly. Usual corrections for Lorentz and polarization effects were applied but those for absorption and extinction corrections were ignored. Totals of 1678 (1199 non-zero) and 1763 (1451 non-zero) reflections were collected for *t*-BuMgCl–(−)-sparteine and $MgCl_2$–(−)-sparteine, respectively.

Structure Solution and Refinement

Both structures were solved by the heavy atom method, and refined anisotropically for non-hydrogen atoms by the block-diagonal least-squares procedure (*HBLS* V).[4] The function minimized was $\sum w(\Delta F)^2$. The H atoms were located and fixed at the calculated positions with equal isotropic thermal parameters ($B=3.3$ Å²). At the final stage of the refinement the anomalous dispersion of all the non-hydrogen atoms were considered.

t-BuMgCl–(−)-sparteine. (1) Initial positional parameters of the Cl and Mg atoms were determined by a three-dimensional Patterson function with the aid of the direct method (*MULTAN* 78).[5] The N and C atoms were located on a subsequent Fourier map. The structure was then refined. The final R factor was 0.098 for non-zero (0.206 for all) reflections and R_w was 0.124. The weighting schemes used at the final stage were

† Abbreviated as *t*-BuMgCl–(−)-sparteine.
†† Abbreviated as $MgCl_2$–(−)-sparteine.
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TABLE 1. FINAL ATOMIC POSITIONAL PARAMETERS, OF *t*-BuMgCl-(−)-SPARTEINE, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*	B_{eq}[a)]/Å^2
Cl	0.04219(14)	0.0720(4)	0.0861(5)	4.4
Mg	0.1037(2)	0.0490(4)	0.3000(6)	2.7
N(1)	0.1347(4)	0.2502(10)	0.3113(12)	2.7
N(2)	0.0784(4)	0.0905(10)	0.5561(12)	3.0
C(1)	0.1570(5)	−0.1191(14)	0.2685(21)	5.0
C(2)	0.0522(6)	−0.0317(14)	0.6271(17)	4.5
C(3)	−0.0009(6)	−0.0534(14)	0.5246(18)	4.9
C(4)	−0.0345(6)	0.0665(15)	0.5460(19)	5.3
C(5)	−0.0070(5)	0.1945(12)	0.4890(17)	3.7
C(6)	0.0441(5)	0.2093(12)	0.5822(16)	3.5
C(7)	0.0741(5)	0.3374(12)	0.5315(17)	3.3
C(8)	0.1187(5)	0.3553(14)	0.6599(19)	4.7
C(9)	0.1567(5)	0.2412(13)	0.6174(15)	3.3
C(10)	0.1281(5)	0.1091(12)	0.6602(17)	3.8
C(11)	0.1780(5)	0.2510(13)	0.4395(15)	3.1
C(12)	0.2152(6)	0.3681(13)	0.4197(20)	4.4
C(13)	0.2377(6)	0.3759(15)	0.2402(19)	4.8
C(14)	0.1931(6)	0.3911(13)	0.1188(18)	4.5
C(15)	0.1563(5)	0.2664(14)	0.1402(16)	4.3
C(16)	0.1599(9)	−0.1386(21)	0.0811(26)	10.4
C(17)	0.0933(5)	0.3472(13)	0.3514(16)	3.6
C(18)	0.2118(7)	−0.1074(20)	0.3303(35)	11.0
C(19)	0.1320(8)	−0.2424(16)	0.3391(30)	8.8

a) After Hamilton.[6)]

$w=\{\sigma_{cs}^2(F_o)+0.03251|F_o|+0.00231|F_o|^2\}^{-1}$ for $|F_o|>0$ and $w=0.02855$ for $|F_o|=0$.

The final atomic positional and equivalent thermal parameters[6)] are listed in Table 1.††††

$MgCl_2$-(−)-sparteine (2). The crystals were expected to contain *t*-BuMgCl-(−)-sparteine, but the three-dimensional Patterson function could not be interpreted satisfactorily. The *E*-map calculated by using the *MULTAN* 78 program showed a good coincidence with the interpretation of the Patterson map for $MgCl_2$-(−)-sparteine instead of *t*-BuMgCl-(−)-sparteine. The Fourier synthesis based on the phases of the Mg and two Cl atoms revealed the remaining N and C atoms of the $MgCl_2$-(−)-sparteine. The anisotropic refinement gave the final *R* as 0.091 for 1347 observed ($|F_o|\leq 3\sigma(F_o)$) reflections ($R_w=0.104$). At the final stage the weighting scheme used was $w=\{\sigma^2(F_o)+0.10124|F_o|\}^{-1}$. The final atomic positional and equivalent thermal parameters are listed in Table 2.††††

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

†††† Tables of observed and calculated structure factors and anisotropic thermal parameters and calculated hydrogen positions of *t*-BuMgCl-(−)-sparteine and $MgCl_2$-(−)-sparteine are kept at the Chemical Society of Japan, Document No. 8335.

TABLE 2. FINAL ATOMIC POSITIONAL PARAMETERS, OF $MgCl_2$-(−)-SPARTEINE, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

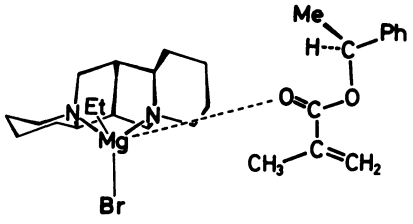
Atom	*x*	*y*	*z*	B_{eq}[a)]/Å^2
Cl(1)	0.2110(4)	0.1164(3)	0.0138(3)	4.4
Cl(2)	0.1761(4)	0.4379(3)	0.0491(3)	5.0
Mg	0.1941(4)	0.2655(3)	0.1245(3)	2.4
N(1)	0.0535(7)	0.2304(7)	0.2364(7)	2.0
N(2)	0.3045(7)	0.2883(7)	0.2637(7)	2.5
C(2)	0.4269(10)	0.3228(9)	0.2285(10)	3.1
C(3)	0.4870(10)	0.2277(12)	0.1643(12)	4.4
C(4)	0.4951(12)	0.1249(12)	0.2267(12)	4.9
C(5)	0.3706(11)	0.0927(10)	0.2696(10)	3.8
C(6)	0.3131(10)	0.1923(9)	0.3313(9)	3.0
C(7)	0.1912(10)	0.1645(10)	0.3825(9)	3.2
C(8)	0.1487(11)	0.2595(12)	0.4476(9)	4.1
C(9)	0.1321(10)	0.3544(10)	0.3769(9)	3.3
C(10)	0.2521(11)	0.3816(10)	0.3246(10)	3.8
C(11)	0.0296(10)	0.3308(9)	0.2979(8)	2.5
C(12)	−0.0933(11)	0.3261(10)	0.3540(10)	3.5
C(13)	−0.1945(10)	0.3024(10)	0.2780(10)	3.3
C(14)	−0.1689(11)	0.1950(11)	0.2237(11)	4.1
C(15)	−0.0496(10)	0.1987(11)	0.1636(11)	3.7
C(17)	0.0889(10)	0.1354(9)	0.3016(10)	3.2

a) After Hamilton.[6)]

Results and Discussion

Molecular Structure. Perspective views (*ORTEP* II)[9)] of *t*-BuMgCl-(−)-sparteine and $MgCl_2$-(−)-sparteine molecules with the numbering scheme of atoms are drawn in Figs. 1 and 2, respectively. Bond lengths and bond angles in the two complexes are given in Figs. 3 and 4, respectively.

t-BuMgCl-(−)-sparteine (1). The coordination geometry around the Mg atom is distorted tetrahedral: two N atoms of the sparteine skeleton, the C atom of the *t*-Bu group and the Cl bond to the Mg atom. Two Mg–N bond lengths are equal [2.171(12) and 2.175(12) Å] and the N(1)–Mg–N(2) angle is 83.9(5)°. The Mg–C(1) bond length of 2.19(2) Å is comparable with that in EtMgBr-(−)-sparteine [2.24(3) Å].[3)] The Mg–Cl bond length is 2.332(7) Å. The Cl–Mg–N(2) angle [117.4(4)°] is much larger than the Cl–Mg–N(1) angle [100.8(4)°]. The (−)-sparteine skeleton has a similar structure to that in EtMgBr-(−)-sparteine (an all-chair conformation). The remarkable feature of the structure is that the geometrical relation of the alkyl and halogen ligands to the (−)-sparteine skeleton in the present complex is reverse to that in EtMgBr-(−)-sparteine. The initial stage of the asymmetric selective polymerization of racemic methacrylate is considered to be coordination of the carbonyl oxygen of a substrate to the Mg atom of a Grignard reagent-(−)-sparteine complex.[1)]



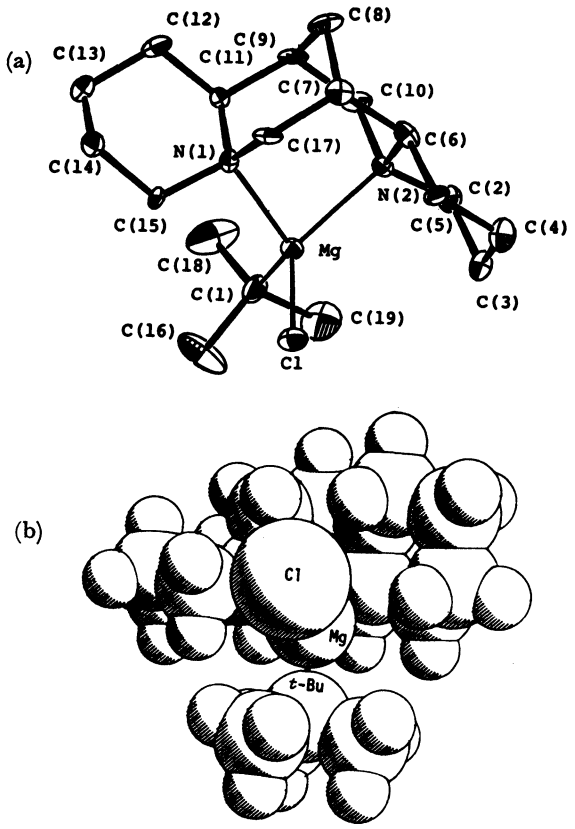


Fig. 1. (a): A perspective view[9] of the *t*-BuMgCl–(−)-sparteine molecule with the numbering scheme of atoms. Non-hydrogen atoms are drawn as thermal ellipsoids with 20% probability level. (b): A space-filling model[10] of the *t*-BuMgCl–(−)-sparteine molecule.

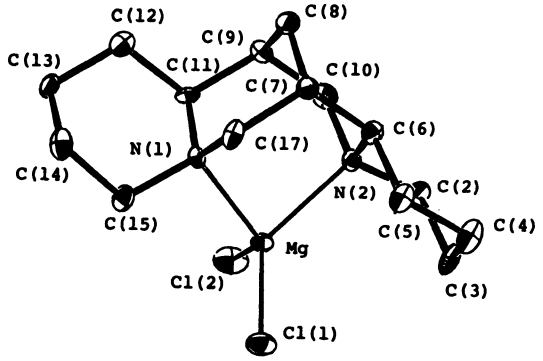


Fig. 2. A perspective view[9] of the $MgCl_2$–(−)-sparteine molecule with the numbering scheme of atoms. Non-hydrogen atoms are drawn as thermal ellipsoids with 20% probability level.

In the latter complex, the Et ligand is not so large and the Mg atom has a sufficient room to access the substrate in its neighborhood. In the former, however, the bulky *t*-Bu group blocks the central Mg atom from the substrate together with the Cl atom. This fact may explain the inactivity of the *t*-BuMgCl–(−)-sparteine on the asymmetric selective polymerization of methyl methacrylate.

$MgCl_2$–(−)-sparteine (2). As is seen in Fig. 2, the central Mg atom is tetrahedrally coordinated by

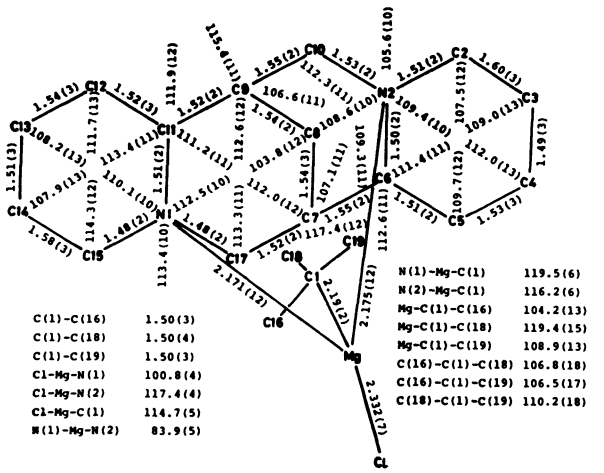


Fig. 3. Selected bond lengths [*l*/Å] and bond angles [ϕ/°] in the *t*-BuMgCl–(−)-sparteine molecule.

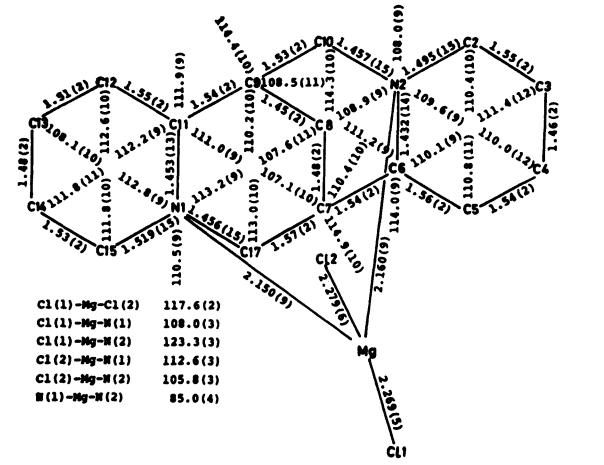


Fig. 4. Selected bond lengths [*l*/Å] and bond angles [ϕ/°] in the $MgCl_2$–(−)-sparteine molecule.

two N atoms of (−)-sparteine and two Cl ligands. Two Mg–N bond lengths [2.150(9) and 2.160(9) Å] are equal, and they are also equal to those in EtMgBr–(−)-sparteine [2.14(2) and 2.16(3) Å][2] and in *t*-BuMgCl–(−)-sparteine mentioned above. The N(1)–Mg–N(2) angle [85.0(4)°] is also equal to those in EtMgBr–(−)-sparteine [84.0(8)°] and *t*-BuMgCl–(−)-sparteine. Two Mg–Cl bonds are equal in length [2.269(5) and 2.279(6) Å], but they are significantly shorter than that in *t*-BuMgCl–(−)-sparteine. The Cl(1)–Mg–N(2) angle [123.3(3)°] is larger than the Cl(1)–Mg–N(1) [108.0(3)°] whereas the Cl(2)–Mg–N(2) [105.8(3)°] is smaller than Cl(2)–Mg–N(1) [112.6(3)°]. The (−)-sparteine skeleton in the present complex has nearly the same structure as those in EtMgBr–(−)-sparteine and *t*-BuMgCl–(−)-sparteine.

Crystal Structure. The crystal structures of *t*-BuMgCl–(−)-sparteine and $MgCl_2$–(−)-sparteine are depicted in Figs. 5 and 6, respectively. The closest intermolecular atomic contact in *t*-BuMgCl–(−)-sparteine is 3.73(3) Å (C(14) $(x, y, z)\cdots$C(12) $(1/2-x, 1-y, -1/2+z)$). Molecular contacts in the crystal are rather loose, which may explain poor quality of the

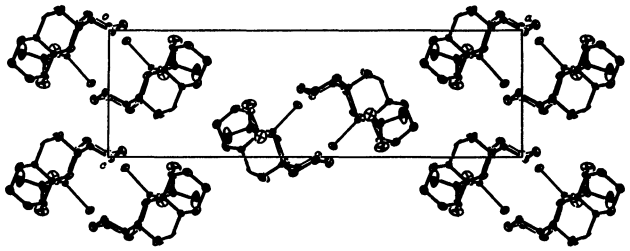


Fig. 5. The crystal structure of *t*-BuMgCl–(−)-sparteine.[9]

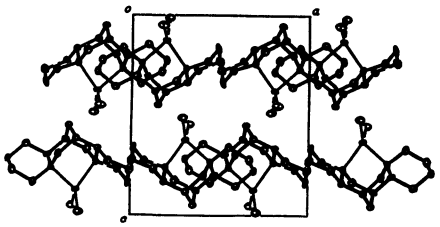


Fig. 6. The crystal structure of $MgCl_2$–(−)-sparteine.[9]

crystal. The shortest interatomic distance between molecules in contact in $MgCl_2$–(−)-sparteine is 3.64(2) Å (C(10) $(x, y, z)\cdots$C(12) $(1/2-x, 1-y, 1/2+z)$).

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