Doubly Helical, Chiral Crown Thioether fully preorganized for Planar Coordination

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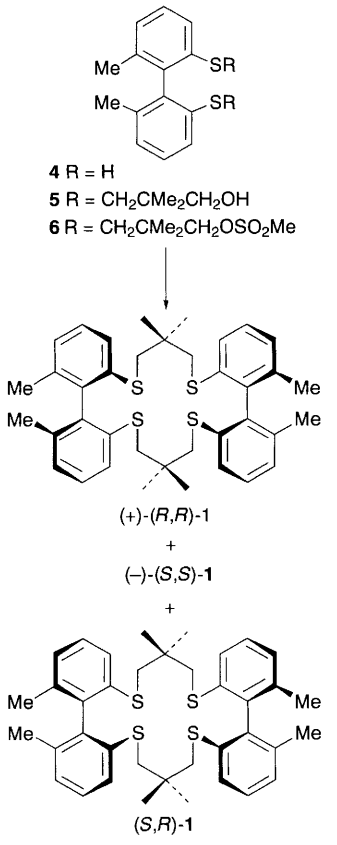
Optically active 18-membered quadridentate crown thioethers with double helicity, (+)-(*R,R*)- and (−)-(*S,S*)-bitol$_2$Me$_4$[18]S$_4$ and the non-helical *meso*-compound are prepared and their reactions with ruthenium(II) give *trans*-[RuCl$_2${(+)-(*R,R*)-bitol$_2$Me$_4$[18]S$_4$}] and the *meso*-analogue of D_2 and C_{2h} symmetries, respectively; free (+)-(*R,R*)-bitol$_2$Me$_4$[18]S$_4$ and the racemic ruthenium(II) complex have been structurally characterized.

There is increasing interest in the transition metal complexes of crown thioethers;[1] however, those of chiral crown thioethers are extremely rare.[2] Here we report the preparation, characterization and optical resolution of an 18-membered quadridentate crown thioether bitol$_2$Me$_4$[18]S$_4$ **1** and its coordination to ruthenium(II). The ligand **1** consists of two 2,2′-bitolyl-3,3′-dithiolato groups bonded alternately to two 2,2-dimethylpropane subunits. Incorporation of two structurally rigid and axially chiral bitolyl groups determines unequivocally doubly helical and non-helical arrays for the racemate and *meso*-isomer of **1**, respectively. This is also the case for the ruthenium complexes *trans*-[RuCl$_2${(+)-(*R,R*)-**1**}] **2** and *trans*-[RuCl$_2${(*R,S*)-**1**}] **3**. The former represents the first example of an optically active and doubly helical transition metal complex containing sulfur ligands. Almost all helicates so far reported have been produced with open-chain and macrocyclic polydentate ligands containing nitrogen donors such as pyridine and bipyridine.[3]

The macrocycle **1** was prepared through S-alkylation of the disodium salt of (±)-2,2′-dimethyl-6,6′-disulfanylbiphenyl **4**[4] with 3-bromo-2,2-dimethylpropan-1-ol in EtOH under reflux, mesylation of the resulting diol **5** with mesyl chloride in pyridine, and cyclization of the dimesylate **6** with **4** in the presence of Cs$_2$CO$_3$ in DMF (Scheme 1).[5] The total yield is 13.5%. Complete optical resolution of the three diastereoisomers was achieved by HPLC with a column packed with cellulose tris(3,5-dimethylphenylcarbamate) on silica gel;[6] elution with 0.1% Pr^{i}OH–hexane gave optically pure (−)-(*S,S*)-**1**, (+)-(*R,R*)-**1** {[α]$_D$^{20} −157 and +152 (*c* 0.4, hexane), respectively} and the *meso*-compound (*R,S*)-**1** in a 1 : 1 : 2 ratio. The absolute configuration of the two chiral diastereoisomers was deduced by comparing their CD spectra with those of (6,6′-dimethylbiphenylene-2,2′-diyl)bis(diphenylphosphine)[7] and was determined unequivocally by an X-ray structural study for the (+)-(*R,R*) enantiomer.† (+)-(*R,R*)-**1** assumes a quadrangular structure of approximate D_2 symmetry with an *endo*-orientation of all S atoms directed towards the centre of the macrocycle (Fig. 1). Owing to the inherent twist about the pivotal bond of 2,2′-bitolyl groups, the four S atoms adopt an up-down-up-down conformation where up and down indicate the direction of the lone electron pair orbitals on the S atoms with respect to the approximately square plane (4S) defined by the four S atoms. Two aromatic rings of the 2,2′-bitolyl groups are orthogonal with a mean dihedral angle of 87.8°. The corresponding angle between the least-squares 4S plane and each aromatic ring is 79.3°. The non-bonded S···S distances of 3.873(6)–4.031(8) Å are longer than the sum of the van der Waals radius (3.7 Å). The D_2 structure is retained in solution as deduced from ^{1}H NMR spectra of the two optically resolved enantiomers, which exhibit one Me singlet and two CH$_2$ doublets due to the two CH$_2$CMe$_2$CH$_2$ groups.‡ The observation of two signals for each proton of the *meso*-compound is consistent with C_{2h} symmetry with an up-up-down-down (*syn*) conformation.

The X-ray structure suggests that the chiral crown thioether with double helicity is fully preorganized for planar coordination to metal ions. Indeed, treatment of (+)-(*R,R*)-**1** with K$_2$[RuCl$_5$(H$_2$O)] in MeOCH$_2$CH$_2$OH under reflux for 24 h followed by chromatography (silica gel, CHCl$_3$) and recrystallization from CH$_2$Cl$_2$–hexane gave *trans*-[RuCl$_2${(+)-(*R,R*)-**1**}] (**2**) {[α]$_D$^{20} +35 (*c* 0.1, CHCl$_3$)} as reddish brown crystals in



Scheme 1

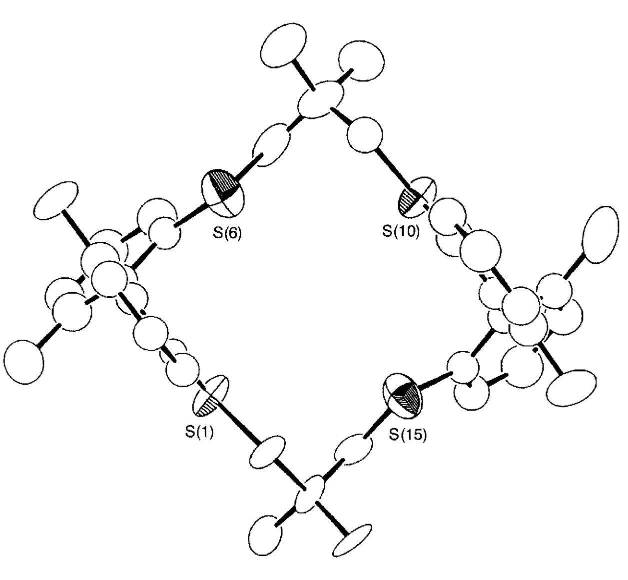


Fig. 1 Molecular structure of (+)-(*R,R*)-bitol$_2$Me$_4$[14]S$_4$-**1**

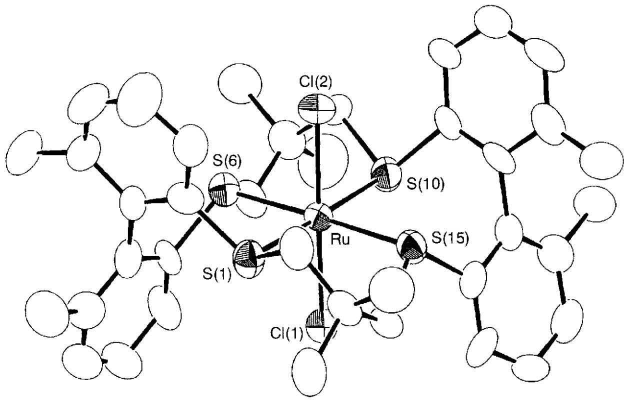


Fig. 2 Molecular structure of *trans*-[$RuCl_2${(+)-(*R*,*R*)-**1**}] **2** in the racemate. Selected bond distances (Å) and angles (°): Ru–S(1) 2.373(7), Ru–S(6) 2.368(5), Ru–S(10) 2.361(7), Ru–S(15) 2.370(5), Ru–Cl(1) 2.417(5), Ru–Cl(2) 2.395(5); S(1)–Ru–S(6) 89.0(2), S(1)–Ru–S(10) 179.1(2), S(1)–Ru–S(15) 90.2(2), S(6)–Ru–S(10) 90.2(2), S(6)–Ru–S(15) 178.7(2), S(10)–Ru–S(15) 90.7(2), S(1)–Ru–Cl(1) 90.7(2), S(1)–Ru–Cl(2) 89.7(2), S(6)–Ru–Cl(1) 89.8(2), S(6)–Ru–Cl(2) 91.1(2), S(10)–Ru(Cl(1) 89.6(2), S(10)–Ru–Cl(12) 90.1(2), S(15)–Ru–Cl(1) 89.2(2), S(15)–Ru–Cl(2) 89.9(2).

82% yield. A similar reaction with (*R*,*S*)-**1** afforded *trans*-[$RuCl_2${(*R*,*S*)-**1**}] (**3**) (43% yield). The ^{1}H NMR spectra of **2** and **3** indicate D_2 and C_{2h} structures as observed for the corresponding free ligands, respectively.‡ Although attempts to obtain a single crystal of **2** failed, recrystallization of the racemic mixture from toluene–EtOH gave crystals suitable for an X-ray analysis (Fig. 2).‡ The geometry at Ru is octahedral, with four S atoms in the equatorial plane and two Cl atoms in the axial sites. An up-down-up-down conformation of a co-ordinated quadridentate thiamacrocycle is rare, having a sole precedent in the seven-coordinate [Hg([16]$aneS_4$)$(ClO_4)_2$].[9] The Ru–S distance (average 2.368 Å) is significantly longer than those [2.291(3)–2.308(2) Å] found for the saturated quadridentate thiamacrocycle with a *syn*-conformation in *trans*-[RuH(Cl)(L)] (L = Me_4[14]$aneS_4$, Me_6[15]$aneS_4$) and [Ru_2H(μ-H)Cl(Me_4[14]$aneS_4$)$_2$]$^{2+}$.[10] The Cl–Ru–Cl angle [179.1(2)°] is essentially linear. To reduce the steric strain induced by the planar coordination, the dihedral angle (average 76.5°) between two tolyl planes becomes more acute than that of the free ligand, while the decrease in the corresponding angle (74.5°) between the 4S and tolyl planes is not so extensive. As expected from the observed conformation of the thiamacrocycle, the Ru atom lies exactly in the least-squares 4S plane, the deviation being only 0.009(5) Å.

The above results suggest that the M[(+)-(*R*,*R*)-**1**] moiety possesses the helical cavity at the axial sites capable of discriminating the chirality of prochiral substrates through coordination and may serve as a novel type of chiral catalyst. Indeed, the latter possiblility is shown by the asymmetric hydrosilylation of PhCOMe with Ph_2SiH_2 with the catalyst prepared from [$RhCl(C_8H_{12})_2$]$_2$ and (+)-(*R*,*R*)-**1** *in situ* which gave (*S*)-PhCH(OH)Me after hydrolysis in 35 and 57% chemical and optical yields, respectively.

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Footnotes

† The structures were solved by direct methods for (+)-(*R*,*R*)-**1** and by the Patterson method for the racemate of *trans*-[$RuCl_2$(**1**)] and refined by full-matrix least-squares for intensity data collected on a Rigaku AFC-5R diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

Crystal data for (+)-(*R*,*R*)-**1**: $C_{38}H_{44}S_4$, M = 629.0, monoclinic, $P2_1$, a = 11.671(7), b = 25.839(8), c = 12.687(5) Å, β = 110.10(3)°, U = 3592(5) Å^3, Z = 4, D_c = 1.163 g cm^{-3}, μ(Mo-Kα) = 2.76 cm^{-1}, F(000) = 1344, final $R(R_w)$ = 0.0677 (0.0534) for 3984 reflections [$I > 3.0\sigma(I)$] and 415 variables. There are two independent molecules in the asymmetric unit, the structures of which are essentially the same. The possibility of the alternative enantiomer, (−)-(*S*,*S*)-**1** is ruled out by Roger's test,[8] the final $R(R_w)$ factors then being 0.0681(0.0537).

For *trans*-[$RuCl_2$(**1**)] (racemate): $C_{38}H_{44}S_4Cl_2Ru\cdot 2C_6H_5Me\cdot EtOH$, M = 1031.3, triclinic, $P\bar{1}$, a = 15.174(4), b = 15.977(5), c = 13.304(4) Å, α = 114.13(2), β = 109.07(2), γ = 66.51(2)°, U = 2647(1) Å^3, Z = 2, D_c = 1.294 g cm^{-3}, μ(Mo-Kα) = 5.78 cm^{-1}, F(000) = 1080, final $R(R\text{w})$ = 0.066 (0.057) for 2839 reflections [$I > 3.0\sigma(I)$] and 444 variables.

‡ (+)-(*R*,*R*)-**1**: mp 168–169 °C; EI-MS (70 eV) *m*/*z* 628 ([M]$^+$). (−)-(*S*,*S*)-**1**: mp 167–168 °C; EI-MS (70 eV) *m*/*z* 628 ([M]$^+$). ^{1}H NMR (δ, $CDCl_3$) for both enantiomers 0.97 (s, 12H, MeC), 1.92 (s, 12H, MeAr), 2.65 (d, *J* 11.6 Hz, 4H, CH_2), 2.85 (d, *J* 11.6 Hz, 4H, CH_2), 7.06 (d, *J* 7.6 Hz, 4H, Ar), 7.11 (d, *J* 7.6 Hz, ArH), 7.18 (dd, *J* 7.6, 7.6 Hz, 4H). (*R*,*S*)-**1**: mp 282–283 °C; EI-MS (70 eV) *m*/*z* 628 ([M]$^+$); ^{1}H NMR (δ, $CDCl_3$) 0.77 (s, 6H, MeC), 1.05 (s, 6H, MeC), 1.91 (s, 12H, MeAr), 2.52 (d, *J* 11.8 Hz, 4H, CH_2), 3.01 (d, *J* 11.8 Hz, 4H, CH_2), 7.03 (d, *J* 7.8 Hz, 4H, Ar), 7.09 (d, *J* 7.8 Hz, ArH), 7.18 (dd, *J* 7.8, 7.8 Hz, 4H). *trans*-[$RuCl_2${(+)-(*R*,*R*)-**1**}]: mp >300 °C; FAB-MS (3-nitrobenzyl alcohol) *m*/*z* 802 ([M]$^+$); ^{1}H NMR (δ, $CDCl_3$) 1.25 (s, 12H, MeC), 1.91 (s, 12H, MeAr), 2.74 (d, *J* 11.2 Hz, 4H, CH_2), 3.45 (d, *J* 11.2 Hz, 4H, CH_2), 7.19–7.26 (m, 12H, Ar). *trans*-[$RuCl_2${(*R*,*S*)-**1**}]: mp >300 °C; FAB-MS (3-NOBA) *m*/*z* 802 ([M]$^+$); ^{1}H NMR (δ, $CDCl_3$) 1.04 (s, 6H, MeC), 1.17 (s, 6H, MeC), 1.98 (s, 12H, MeAr), 2.62 (brd, *J* 11.3 Hz, 4H, CH_2), 3.29 (d, *J* 11.3 Hz, 4H, CH_2), 7.28 (d, *J* 7.8 Hz, 4H ArH), 7.32 (dd, *J* 7.8, 7.8 Hz, 4H, Ar), 7.47 (d, *J* 7.8 Hz, 4H, Ar).

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