In a wider empirical context, the result adds to an awareness that the behavior of the formally closo, formally 24-electron, 11-vertex cluster system may in fact quite regularly deviate from that expected on the basis of the straightforward Williams-Wade[6,7] formalism. Thus, of structurally characterized species, the present compound, the related ruthenadicarbaborane [2,4-Me_2-1-(η^6-MeC_6H_4-*p*-^{i}Pr)-1,2,4-$RuC_2B_8H_8$],[17] and the substituted dicarbaborane [2,3-$Me_2C_2B_9H_6$-4,7-$(OH)_2$-10-Br][20] all exhibit very significant deviations from straightforward closo structure, the osmadicarbaborane [(η^6-C_6Me_6)$OsC_2Me_2B_8H_8$] can adopt a conventional nido structure,[21] and the high fluxionalities of the closo-structured $[CB_{10}H_{11}]^-$ anion[22] and of $[B_{11}H_{11}]^{2-}$ itself[23] show that transition states of presumably open structure must be energetically very near to the closed deltahedral configuration for these simpler species also. The open structure reported here in fact resembles that proposed as the intermediate for the series of diamond–square–diamond steps in the "pentagonal belt rotation" mechanism suggested[22] for these fluxionalities.

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Registry No. 5,6-$C_2B_8H_{12}$, 41655-26-9; [1,1-$(PPh_3)_2$-1-H-1,2,4-$IrC_2B_8H_{10}$], 61214-59-3; [$IrCl(PPh_3)_3$], 16070-58-9; 1,8-bis(dimethylamino)naphthalene, 20734-58-1.

Supplementary Material Available: Tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, hydrogen atom parameters, bond lengths, and bond angles (8 pages). Ordering information is given on any current masthead page.

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Production of an Optically Active Sulfoxide by Use of Colloidally Dispersed Λ-Tris(2,2′-bipyridyl)ruthenium(II) Montmorillonite as a Photosensitizer

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Recently an ion-exchanged adduct of a clay and an optically active metal complex has been used as a chiral adsorbent in optical resolution and asymmetric syntheses, motivated by the finding that some metal chelates were adsorbed stereoregularly on a clay.[1,2] Tris(1,10-phenanthroline)iron(II) ($[Fe(phen)_3]^{2+}$), for example, is adsorbed in the form of a racemic pair of its Δ- and Λ-enantiomers. When a pure enantiomer of the same chelate, $[\Lambda\text{-}Fe(phen)_3]^{2+}$, for example, is added, the enantiomer is adsorbed, leaving half of the surface unoccupied.

In a comparison of the surfaces of the clays ion-exchanged with enantiomeric and racemic metal chelates, it was postulated that an empty space on the former surface would become a stereoselective site for adsorption or chemical reactions on a clay surface. In fact, an ion-exchange adduct of a clay with optically active $[Ru(phen)_3]^{2+}$ has been proved to be quite effective in resolving racemic mixtures.[1,2]

As an extension of these results, photoinduced asymmetric reactions have been attempted on an adduct of a clay and a photosensitive metal complex. It was intended to produce an optically active sulfoxide by illuminating a sulfide in the presence of optically active tris(2,2′-bipyridyl)ruthenium(II) [$(Ru(bpy)_3]^{2+}$) montmorillonite. As a result, optically active alkyl phenyl sulfoxides were obtained with the optical purity of 15–20% at room temperature.

Experimental Section

The clay used in these studies is sodium montmorillonite, purchased from Kunimine Ind. Co.; the cation-exchange capacity (CEC) is 115 mequiv/100 g. The complex $[Ru(bpy)_3]Cl_2$ was prepared and resolved according to the literature.[3,4] Alkyl phenyl sulfides were synthesized by reacting alkyl iodides with thiophenol in alkaline solutions.[5] Water containing ^{18}O (97.1 atom %) was purchased from ISOTECC Inc. The electronic spectra were recorded with a spectrophotometer, UVIDEC-430A (JEOL). The high-performance liquid chromatography (HPLC) was performed with a BIP-1 chromatograph (JEOL) equipped with a UV detector, UVIDEC-100-VI (JEOL). The circular dichroism spectra were measured with a polarimeter, J-20 (JEOL). The *m*/*e* of a sulfoxide was determined with a mass spectrometer, GCMS-QP1000 (Shimazu).

A clay–chelate adduct is prepared as follows: 1 g of sodium montmorillonite is dispersed in 100 mL of water. About 90 μL of this clay suspension is added to 10 mL of water. An aqueous solution of $[\Lambda\text{-}Ru(bpy)_3]Cl_2$ (5×10^{-7} mol) is then slowly added to it. The mixture is centrifuged and the supernatant solution is discarded.

Oxidation of the sulfide is performed in the following way: a sulfide (1×10^{-6} mol) in 5 mL of methanol is mixed with the clay–chelate adduct as prepared above. The mixture is illuminated with a 500-W tungsten lamp under bubbling oxygen gas. The light is focused on the sample solution. The temperature of the sample is kept constant by circulating water or methanol. After some interval, the medium is centrifuged and the supernatant liquid separated. The precipitate is washed with a few milliliters of methanol. The organic components are extracted with dichloromethane from the combined supernatant solution and methanol wash liquid. After evaporation of the dichloromethane, the residue is dissolved in 200 μL of methanol and analyzed by HPLC. The solutions eluting under peaks corresponding to sulfide or sulfoxide are collected and the concentrations of the compounds determined from the absorbances in the UV spectra ($\epsilon = 6460$ at 257 nm for cyclohexyl phenyl sulfide, and $\epsilon = 4390$ at 242 nm for cyclohexyl phenyl sulfoxide). The optical purity of the sulfoxide is estimated by resolving the mixtures into each enantiomer with a liquid column chromatograph of Λ-tris(1,10-phenanthroline)iron(II) montmorillonite. From the amplitude of the circular dichroism (CD) spectrum, $\Delta\epsilon$ at 242 nm is determined to be 30 for (*R*)-cyclohexyl phenyl sulfoxide.

The above procedures were repeated two or three times, using the same clay–chelate adduct as a catalyst. Reproducible results within the experimental errors of 5% of the reaction yields and optical purities were obtained.

Results

(i) Photoinduced Oxidation of a Sulfide in the Presence of $[Ru(bpy)_3]^{2+}$. Electronically excited $[Ru(bpy)_3]^{2+}$ is known to act as an oxidizing or reducing agent. We first examined how excited $[Ru(bpy)_3]^{2+}$ reacts with a sulfide in a methanol–water mixture.

About 1×10^{-6} mol of cyclohexyl phenyl sulfide was added to 5 mL of 1:4 (v/v) methanol–water containing 5×10^{-5} mol of $[\Lambda\text{-}Ru(bpy)_3]Cl_2$. The solution was illuminated with a 500-W tungsten lamp under 1 atm of oxygen for 180 min. When we analyzed the solution, the sulfide was found to be completely converted to the sulfoxide and no sulfone was produced. Oxidation

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did not take place when the above solution was placed in the dark for 24 h. When the same reaction proceeded under argon atmosphere, the sulfide was not oxidized at all. The addition of 0.001 M $HClO_4$ or $N(CH_3)_4OH$ did not affect the yield of sulfoxide.

The reaction was carried out in the presence of 1×10^{-4} M methyl viologen, which had no effect on the yield of sulfoxide from the sulfide.

When pure methanol or pure acetonitrile was used as a solvent, no sulfoxide was produced even in the presence of oxygen.

The oxidation of methyl phenyl sulfide (1×10^{-4} mol) was performed in 0.1 mL of H_2O or $H_2{}^{18}O$ in presence of 10^{-5} mol of $[Ru(bpy)_3]^{2+}$. The reaction products were extracted with dichloromethane and analyzed with a mass spectrometer. The molecular weight of methyl phenyl sulfoxide (C_7H_8OS) is 140. The ratio of the peak intensities at m/e = 140–142 were found to be 21 and 16 for H_2O and $H_2{}^{18}O$ solvents, respectively. Thus, the amount of methyl phenyl sulfoxide with ^{18}O was negligible when $H_2{}^{18}O$ was used as a solvent. In other words, the oxygen atom in a sulfoxide did not come from a water molecule but an oxygen molecule.

We have thus concluded that the photosensitized oxidation of a sulfide proceeds when the following components are present: $[Ru(bpy)_3]^{2+}$, oxygen, and water. $[Ru(bpy)_3]^{2+}$ absorbed light energy to be excited to the metal-to-ligand charge-transfer state (MLCT) as

$$[Ru(bpy)_3]^{2+} \rightarrow [Ru(bpy)_3]^{2+*} \qquad (1)$$

There are two possible ways conceivable for the fate of $[Ru(bpy)_3]^{2+*}$ in the present system. One is the direct reaction of $[Ru(bpy)_3]^{2+*}$ with a sulfide:

$$[Ru(bpy)_3]^{2+*} + R\text{-}S\text{-}Ph \rightarrow [Ru(bpy)_3]^{+} + R\text{-}S^{+}\text{-}Ph \qquad (2)$$

The other is the reaction of $[Ru(bpy)_3]^{2+*}$ with an oxygen molecule:

$$[Ru(bpy)_3]^{2+*} + O_2 \rightarrow [Ru(bpy)_3]^{3+} + O_2^{-} \qquad (3)$$

From the energetic point of view, reaction 2 is hardly possible because the oxidation–reduction potential of $[Ru(bpy)_3]^{2+*}/[Ru(bpy)_3]^{+}$ at 0.84 V vs hydrogen electrode[6] is much smaller than that of the oxidation of phenyl cyclohexyl sulfide, 1.4 V. On the other hand, the oxidation–reduction potential of $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+*}$ is 0.84 V, which is much higher than that of O_2/O_2^{-}, 0.56 V.[9] It is also reported that an oxygen molecule acts as an electron-transfer quencher of $[Ru(bpy)_3]^{2+*}$ as in reaction 3.[6] Thus, we presume that reaction 3 is more probable than reaction 2. The fact that the presence of methyl viologen showed no effect on the sulfoxide formation also reinforces this conclusion. Methyl viologen is known to be an electron-transfer quencher of $[Ru(bpy)_3]^{2+*}$.[10] If reaction 2 is the main path, the production of a sulfoxide would be lowered due to the competitive quenching of $[Ru(bpy)_3]^{2+*}$ by methyl viologen.

The Ru(III) complex produced in reaction 3 might react with a sulfide to result in the one-electron-oxidized species of the sulfide, $R\text{-}S^{+}\text{-}Ph$:

$$[Ru(bpy)_3]^{3+} + R\text{-}S\text{-}Ph \rightarrow [Ru(bpy)_3]^{2+} + R\text{-}S^{+}\text{-}Ph \qquad (4)$$

Reaction 4 is energetically accessible, since the oxidation–reduction potential of $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ is 1.27 V, which is only 0.13 V below the oxidation potential of a sulfide. The fact that water is necessary to produce a sulfoxide in the present system suggests that a water molecule might play some role in solvating reactants such as $[Ru(bpy)_3]^{2+}$ or $[Ru(bpy)_3]^{3+}$ or $R\text{-}S^{+}\text{-}Ph$. However, a detailed mechanism for the participation of water molecules is not certain. As a final step, an oxygen molecule attacks $R\text{-}S^{+}\text{-}Ph$ to form a sulfoxide.

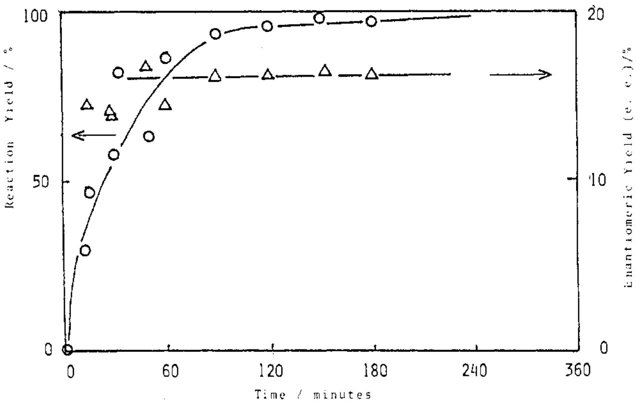

Figure 1. Changes of the reaction yield and the enantiomeric excess (ee) with time when cyclohexyl phenyl sulfide was photooxidized into the sulfoxide in the presence of $[\Lambda\text{-}Ru(bpy)_3]^{2+}$ montmorillonite. The solvent was 1:4 (v/v) methanol–water.

In order to obtain additional support for the above mechanisms, we attempted to react the oxidized species of $[Ru(bpy)_3]^{2+}$ with cyclohexyl phenyl sulfoxide. $[Ru(bpy)_3]^{2+}$ (1×10^{-6} mol) was mixed in 5 mL of water with an excess of PbO_2 powder. The resultant green mixture was filtered and the filtrate mixed with 1 mL of methanol containing 1×10^{-6} mol of cyclohexyl phenyl sulfide. Since PbO_2 does not dissolve in neutral water, the mixture contained only $[Ru(bpy)_3]^{3+}$ as an oxidizing reagent. The solution was kept in the dark under 1 atm of oxygen gas for 180 min. The sulfide was changed to the sulfoxide with the yield of 87% in this procedure. That is, 1 mol of Ru(III)-chelate molecule was consumed to produce 0.87 mol of sulfoxide. Since the sulfoxide is a two-electron-oxidation product of a sulfide, the results imply that other oxidizing agents should be included in the overall reaction of a sulfide to a sulfoxide. Most probably an oxygen molecule oxidizes the one-electron-oxidized form of a sulfide, $R\text{-}S^{+}\text{-}Ph$.

When the CD spectrum of a solution of the produced cyclohexyl phenyl sulfoxide was measured, no optical activity was observed in the sulfoxide. Therefore, the oxidation took place with no stereoselectivity in a homogeneous solution although an optically active $[\Lambda\text{-}Ru(bpy)_3]^{2+}$ chelate was used as a photosensitizer.

(ii) Photooxidation of a Sulfide in the Presence of Optically Active Λ-Tris(2,2′-bipyridyl)ruthenium(II) Montmorillonite. Oxidation of cyclohexyl phenyl sulfide was attempted by illuminating a 1:4 (v/v) methanol–water mixture containing the sulfide and $[\Lambda\text{-}Ru(bpy)_3]^{2+}$ montmorillonite. An ion-exchange adduct of montmorillonite with $[\Lambda\text{-}Ru(bpy)_3]^{2+}$ was prepared as described in the Experimental Section. Oxygen gas was bubbled during the reaction. Figure 1 shows the change of the conversion from a sulfide to a sulfoxide with reaction time. The sulfide was completely converted to the sulfoxide in 2 h. No sulfone was produced when illumination was continued after the sulfide had completely changed to the sulfoxide. The figure also includes the enantiomeric excess (ee) of the sulfoxide produced at various times. The produced sulfoxide was optically active, and the enantiomeric excess was constant at about 15% during the reaction. In order to confirm that the optical activity in the produced sulfoxide arose from the interaction of a reactant with optically active $[\Lambda\text{-}Ru(bpy)_3]^{2+}$, the photoinduced oxidation was carried out in the presence of $[\Delta\text{-}Ru(bpy)_3]^{2+}$ montmorillonite, $[\Lambda\text{-}Ru(bpy)_3]^{2+}$ montmorillonite, and $[rac\text{-}Ru(bpy)_3]^{2+}$ montmorillonite. The CD spectra of solutions of sulfoxide are shown in Figure 2. *S* and *R* enantiomers were produced in excess when $[\Delta\text{-}Ru(bpy)_3]^{2+}$ and $[\Lambda\text{-}Ru(bpy)_3]^{2+}$ were used, respectively, while racemic sulfoxide was produced when racemic $[Ru(bpy)_3]^{2+}$ was used. The results

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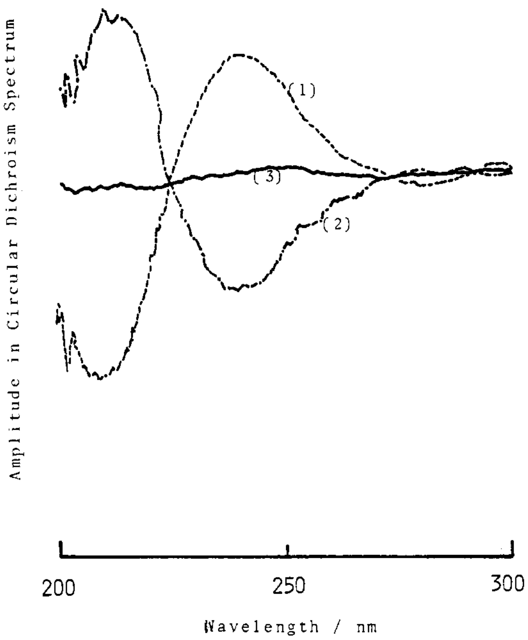

Figure 2. CD spectrum of a solution of the sulfoxide produced by photoxidation of cyclohexyl phenyl sulfide. The catalyst was (1) [Δ-Ru(bpy)$_3$]$^{2+}$ montmorillonite, (2) [Λ-Ru(bpy)$_3$]$^{2+}$ montmorillonite, and (3) [*rac*-Ru(bpy)$_3$]$^{2+}$ montmorillonite.

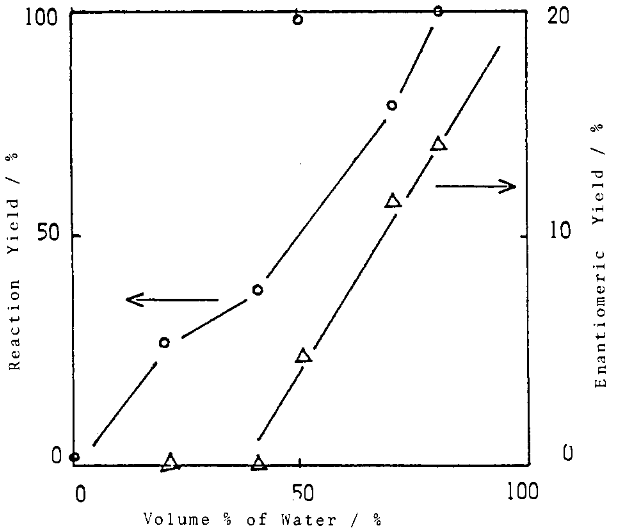

Figure 3. The dependence of the reaction yield and the enantiomeric excess (ee) on the volume percent of water in a water–methanol mixed solvent. The reaction was the photooxidation of cyclohexyl phenyl sulfide into the sulfoxide in 1:4 (v/v) methanol–water.

confirm that the chirality in the Ru(II) chelate is a cause for the production of optically active sulfoxide.

Figure 3 exhibits the results when the reaction was carried out in the various ratios of methanol–water mixtures. In these experiments, the amount of sulfoxide produced and its enantiomeric excess were determined after 180 min. At 100% of methanol no sulfoxide was formed. The sulfoxide amount increased as the content of water in a solvent increased. Oxidation was complete when water content attained 80%. The enantiomeric excess also increased with the increase of water. The effect of reaction temperature on the enantiomeric excess of the produced sulfoxide was investigated. The reaction was carried out in a 1:4 (v/v) methanol–water mixture in the temperature range from −12 to 56 °C. The enantiomeric excess was almost constant at about 14 from −12 to 10 °C. Above 10 °C, it decreased gradually until the value was 5.2 at 56 °C.

Sulfides with various alkyl groups were photooxidized with [Λ-Ru(bpy)$_3$]$^{2+}$ montmorillonite in 1:4 (v/v) methanol–water at room temperature. Table I gives the results of the enantiomeric excesses for six alkyl phenyl sulfoxides. It is seen that the *S* enantiomer was produced in excess for methyl, ethyl, *n*-butyl, and isobutyl sulfoxides, while the *R* enantiomer was produced in excess for cyclohexyl and benzyl sulfoxides. Selectivity depends delicately on the nature of the alkyl group.

Table I. Effect of Alkyl Group (R) on Selectivity in Photooxidation of Phenyl Alkyl Sulfide (Ph–S–R) in the Presence of Λ-Tris(2,2′-bipyridyl)ruthenium(II) Montmorillonite[a]

R	excess enantiomer	% opt yield	R	excess enantiomer	% opt yield
CH_3	*S*-(−)	15	$CH_2CH(CH_3)_2$	*S*-(−)	15
C_2H_5	*S*-(−)	15	C_6H_{11}	*R*-(+)	17
$(CH_2)_3CH_3$	*S*-(−)	20	$CH_2C_6H_5$	*R*-(+)	15

[a] Chemical yields 100%.

Discussion

The present results confirm that an optically active sulfoxide is produced by photooxidizing a sulfide on a surface of a clay–optically active chelate. The finding is the first example that a clay can be used as an adsorbent for photochemical asymmetric syntheses.

Extensive studies have been carried out on the photophysical and photochemical behavior of [Ru(bpy)$_3$]$^{2+}$. The problems relating to its optical activity, however, have been ignored except for a few examples.[13] One of the difficulties in developing a photochemical system with stereoselectivity may lie in the fact that the steric control by a single excited molecule cannot be large enough to direct a reaction in a stereoselective way. In fact, in the present system stereoselectivity was not induced when the reaction was carried out in a homogeneous solution. The present results provide the possibility that stereoselectivity in the photochemical processes will be enhanced when a reactant or a catalyst is adsorbed on a solid surface.

One of the possible reasons for such enhancement is that a surface reaction may proceed under the cooperative interactions among two or three chelates. Adsorption of the pure enantiomer of a tris-chelated complex with bulky ligands such as [M(phen)$_3$]$^{2+}$ and [M(bpy)$_3$]$^{2+}$ leaves half of the surface sites unoccupied. We propose that a sulfide molecule is adsorbed in the empty space, oxidized by [Ru(bpy)$_3$]$^{3+}$, and then attacked by an oxygen molecule according to the postulated mechanisms.

The present method produces a sulfoxide with the optical yield of 15–20%. The values are not high in comparison with the best known results reported by Pitchen et al.[15] They used Ti(OPr)–(*R*,*R*)-diethyl tartarate–water–BuOOH (modified Sharpless reagent) as an oxidizing reagent. They obtained various alkyl methyl sulfoxides with the optical yields of 50–91% at −17 to −21 °C.

In spite of its low selectivity, however, the present method has several interesting aspects from a practical point of view: (i) The system is a heterogeneous catalytic system, (ii) the optical yields are almost constant between −12 and 10 °C, and (iii) clay minerals are inexpensive adsorbents in comparison to the other ion-exchanging materials. These characteristics might promise potential utility of an ion-exchange adduct of clay–chelate as a chiral adsorbent for asymmetric organic syntheses.

Registry No. [Λ-Ru(bpy)$_3$]Cl$_2$, 85893-99-8; PhSCH$_3$, 100-68-5; PhSC$_2$H$_5$, 622-38-8; PhS(CH$_2$)$_3$CH$_3$, 1126-80-3; PhSCH$_2$CH(CH$_3$)$_2$, 13307-61-4; PhSC$_6$H$_{11}$, 7570-92-5; PhSCH$_2$C$_6$H$_5$, 831-91-4; (*S*)-(−)-PhS(O)CH$_3$, 18453-46-8; (*S*)-(−)-PhS(O)C$_2$H$_5$, 104113-36-2; (*S*)-(−)-PhS(O)(CH$_2$)$_3$CH$_3$, 77448-93-2; (*S*)-(−)-PhS(O)CH$_2$CH(CH$_3$)$_2$, 72174-22-2; (*R*)-(+)-PhS(O)C$_6$H$_{11}$, 114578-82-4; (*R*)-(+)-PhS(O)-CH$_2$C$_6$H$_5$, 20246-02-0; sodium montmorillonite, 1318-93-0.

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