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Can a meso-type dinuclear complex be chiral?: dinuclear β -diketonato Ru(III) complexes†

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Dinuclear Ru(III) complexes, [Ru(III)(acac)₂(dabe)Ru(III)(acac)₂] (acacH = acetylacetone; dabeH₂ = 1, 2-diacetyl-1,2-dibenzoylethane) and [Ru(III)(acac)₂(tbet)Ru(III)(acac)₂] (tbetH₂ = 1,1,2,2-tetrabenzoylethane) were synthesized by reacting [Ru(acac)₂(CH₃CN)₂]PF₆ with dabeH₂ and tbetH₂ respectively, in toluene. The X-ray structural analysis of a meso-type dinuclear Ru(III) complex, $\Delta \Lambda$ -[Ru(III)(acac)₂-(dabe)Ru(III)(acac)₂], showed that the bridging part became chiral due to the orthogonal twisting of two non-symmetrical β-diketonato moieties. To confirm this conclusion, the complex was resolved chromatographically to provide a pair of optical antipodes. Such chirality in the bridging part was not generated for [Ru(III)(acac)₂(tbet)Ru(III)(acac)₂], because the β-diketonato moieties in tbet²⁻ are symmetrical.

Introduction

The chemistry of multi-nuclear metal complexes plays a significant role in metal-ion directed self-assembly processes.¹⁻³ Multi-nuclear complexes with various shapes (*e.g.* boxes and helicates) can be constructed and spatial arrangement of metal centres therein can be controlled on the basis of well-defined geometries of coordination spheres. In these architectures, *N*-coordination entities such as derivatized porphyrins and polypyridyl ligands are widely used for homo- and hetero-metallic connections. In contrast, less attention is paid to *O*-coordinating β -diketonato bridges in spite of the fact that tris- or bis- β -diketonato complexes of transition metals have unique electronic and magnetic properties.³⁻¹⁰

We have studied chirality effects on the multi-nuclear complexes consisting of β -diketonato moieties.⁷⁻⁹ In these multi-nuclear complexes, each tris-chelated centre has $\Delta\Lambda$ chirality, and a com-

^aGraduated School of Science and Engineering, Ehime University, Matsuyama, Ehime, 790-8577, Japan. E-mail: sato.hisako.my@ehime-u.ac.jp; Fax: +81-89-927-9599; Tel: +81-89-927-9599 bination thereof causes the diastereomers, which exhibit different spectroscopic properties. Now the question comes: Can chirality be induced in the bridging part? And if so, does the chirality affect any properties (*e.g.* dichroic properties and molecular recognition behaviour) of the multi-nuclear complexes? Recently dinuclear Ru(III) complexes, [Ru(III)(acac)₂(taet)Ru(III)(acac)₂] (taetH₂ = 1,1,2,2-tetraacetylethane), were synthesized by Hashimoto *et al.* and their stereochemical effects on electronic and electrochemical properties were studied.⁶ We extended this work to the syntheses of trinuclear and tetranuclear Ru(III) complexes bridged by the same taet ligands.^{8,9} In these complexes, tris- β -diketonato parts have $\Delta\Lambda$ -chirality, while the bridging parts are achiral since the orthogonal twisting of symmetrical β -diketonato moieties causes D_{2d} symmetry.

In this paper, we report the chiral induction of a bridging part by use of a non-symmetrical β -diketonato ligand, for which the twisting of two β -diketonato planes causes C_2 symmetry. As the precursor of such a ligand, 1,2-diacetyl-1,2dibenzoylethane (dabeH₂), was used (Chart 1(a)). The meso-type and racemic diastereomers of dinuclear complex, $\Delta \Lambda$ - and $\Delta \Delta$ -(or $\Lambda\Lambda$)-[Ru(III)(acac)₂(dabe)Ru(III)(acac)₂], were obtained and their stereochemical properties were investigated by ¹H NMR, mass spectrometry, X-ray crystallography and electronic and vibrational circular dichroism spectra. These results are compared with the dinuclear complex with a symmetrical bridging ligand, 1,1,2,2-tetrabenzoylethane (tbetH₂) (Chart 1(b)).

Results and discussion

[Ru(III)(acac)₂(dabe)Ru(III)(acac)₂]

 $[Ru(III)(acac)_2(CH_3CN)_2]PF_6$ and dabeH₂ were reacted in toluene (Experimental section). When the reactant was eluted on a HPLC

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[†] Electronic supplementary information (ESI) available: The results of chromatographic resolution of [Ru(III)(acac)₂(*S*- or *R*-dabe)Ru(III)(acac)₂)] and [Ru(III)(acac)₂(tbet)Ru(III)(acac)₂)]; mass spectra and 'H NMR of [Ru(acac)₂(CH₃(CN)₂]PF₆, dabeH₂ and tbetH₂; 'H NMR data of the isomers of [Ru(III)(acac)₂(*S*- or *R*-dabe)Ru(III)(acac)₂] and [Ru(III)(acac)₂(tbet)Ru(III)(acac)₂]; chiral chromatographic resolution of [Ru(III)(acac)₂(*S*- or *R*-dabe)Ru(III)(acac)₂(tbet)Ru(III)(acac)₂]; chiral chromatographic resolution of [Ru(III)(acac)₂(*S*- or *R*-dabe)Ru(III)(acac)₂]; and [Ru(III)(acac)₂(tbet)Ru(III)(acac)₂]; CD, UV and VCD of $\Delta \Delta$ -[Ru(III)(acac)₂(*S*- or *R*-dabe))Ru(III)(acac)₂] and DFT calculated results of $\Delta \Lambda$ -[Ru(III)(acac)₂(*S*-dabe)Ru(III)(acac)₂]. CCDC reference number 819545. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11133g



Chart 1 Structures of (a) 1,2-diacetyl-1,2-dibenzoylethane (dabeH₂), (b) 1,1,2,2-tetrabenzoylethane (tbetH₂) and (c) $\Delta\Lambda$ -[Ru(III)(acac)₂-(dabe)Ru(III)(acac)₂]

column packed with silica gel, three peaks (denoted as F₁, F₂ and F₃, respectively) were separated (see ESI†). All of the peaks gave the molecular weight of a dimeric species (m/z = 919 (obs.); 918.9 (calc.)). From the ¹H NMR spectra of these fractions in CDCl₃, the two tris- β -diketonato moieties were inequivalent for F₁, while they were equivalent for F₂ and F₃ (see ESI†). The results were rationalized by assuming that the bridging part (dabe^{2–}) was chiral (denoted as *S*-dabe^{2–} and *R*-dabe^{2–} tentatively), resulting in the diastereometic relation with the octahedral Ru(III) moieties. Based on this assumption, F₁ was assigned to be $\Delta\Lambda$ -[Ru(III)(acac)₂(*S*-or *R*-dabe)Ru(III)(acac)₂] (meso-type), while F₂ and F₃ were assigned to be either $\Delta\Delta$ - (or $\Lambda\Lambda$ -)[Ru(III)(acac)₂(*S*-dabe or *R*-dabe)Ru(III)(acac)₂] (racemic type) (Chart 1(c)).

The molecular structure was determined for the racemic mixture of the meso-type dimer by X-ray crystallographic analysis. The results are shown in Fig. 1. It was unequivocally confirmed that the two tris(β -diketonato)Ru(III) moieties had $\Delta\Lambda$ -antipodal structures. Notably the two non-symmetrical β -diketonato moieties in dabe²⁻ were orthogonally twisted in the C_{α} - $C_{\alpha'}$ bond. Thus the bridging part has axial chirality according to the sign of the twisting angle. It should be noted that the chirality in the bridging part is different from that in the keto-form of (R,R)- or (S,S)dabeH₂.^{11,12}



Fig. 1 The molecular structure of $\Delta\Lambda$ -[Ru(III)(acac)₂(dabe)-Ru(III)(acac)₂] in the crystal. H-atoms are omitted for clarity.

If the rotation of the β -diketonato planes around the $C_{\alpha}-C_{\alpha'}$ bond is prohibited, the enantiomers of F_1 , $\Delta\Lambda$ - $[Ru(III)(acac)_2(S-dabe)Ru(III)(acac)_2]$ and $\Delta\Lambda$ - $[Ru(III)(acac)_2(R-dabe)Ru(III)(Acac)_2(R-dabe)Ru(III)(Acac)$ dabe)Ru(III)(acac)₂], are stable against racemization in a solution. In order to examine the possibility of such interlocking of the two halves of the molecule, it was attempted to optically resolve a racemic mixture of meso-type dimers chromatographically. A methanol solution of F1 was mounted on a chiral column packed with Δ -[Ru(II)(phen)₃]²⁺/synthetic hectorite¹³ and eluted with 1:1(v/v) methanol/chloroform mixture. As a result, two peaks with the same area were obtained (see ESI[†]). As shown in Fig. 2(a), the more and less retained fractions gave mirror-imaged electronic circular dichroism (ECD) spectra. Chromatographic resolution was also obtained for racemic-type dimers, F_2 and F_3 (see ESI^{\dagger}). The comparison of their ECD spectra (Fig. 2(b) and (c)) with that of [Ru(acac)₃] allowed us to determine the configuration of the Ru(III) centres. In the case of F_2 , the more and less retained fractions were $\Delta\Delta$ -[Ru(III)(acac)₂(S- or R-dabe)Ru(III)(acac)₂] and $\Lambda\Lambda$ -[Ru(III)(acac)₂(*R*- or *S*-dabe)Ru(III)(acac)₂], respectively. In the case of F₃, the more and less retained fractions were $\Lambda\Lambda$ -[Ru(III)(acac)₂(S- or R-dabe)Ru(III)(acac)₂] and $\Delta\Delta$ -[Ru(III)(acac)₂(*R*- or *S*-dabe)Ru(III)(acac)₂], respectively. It should be noted that F_1 gave much weaker ECD peaks than F_2 and F_3 . This was reasonable, since the chirality due to the $\Delta\Lambda$ isomerism of the two tris-\beta-diketonato parts was cancelled out, leaving the chirality of the bridging part alone for F_1 .



Fig. 2 The circular dichroism spectra of the resolved enantiomers of fractions (1), (2), and (3) in methanol. (a), (b) and (c) are F_1 (meso-type), F_2 (racemic-type) and F_3 (racemic-type), respectively. Black and red lines are the less and more retained enantiomers, respectively.

The vibrational circular dichroism (VCD) spectroscopy, which is an extension into the infrared and near-infrared regions of the circular dichroism spectroscopy, provides a powerful tool to identify a chiral part in a molecule in a solution.¹⁴⁻¹⁷ Fig. 3(a), (b) and (c) show the VCD spectra of F_1 , F_2 and F_3 , respectively. These diastereomers gave mirror-imaged VCD spectra between the



Fig. 3 The vibrational circular dichroism spectra of $CDCl_3$ solutions of the dimeric species: (a), (b) and (c) are F_1 (meso-type), F_2 (racemic-type) and F_3 (racemic-type), respectively. Black and red lines are the less and more retained enantiomers, respectively.

opposite enantiomers. The intensities of VCD peaks were much lower for F_1 than for F_2 and F_3 as already noticed in the ECD spectra. In the case of F_2 and F_3 , the couplet bands around 1550 cm⁻¹ were assigned to C-O stretching vibrations. The signs of these couplets for the $\Delta\Delta$ - and $\Lambda\Lambda$ -dimer are in accord with those for Δ - and Λ -[Ru(acac)₃] respectively.¹⁷ In the case of F_1 , the triple multiple peaks with different signs were observed with lower intensity in the same wavenumber region. The appearance of these peaks might come from the stretching vibration of C-O bonds in the bridging part. The multiple peaks in the region of 1300–1400 cm⁻¹ were thought to give a clue to determining the RS configuration of the bridging part. As an attempt to determine the configuration, the VCD spectrum of $\Delta\Lambda$ -[Ru(III)(acac)₂(S-dabe)Ru(III)(acac)₂] was calculated (see ESI[†]). By comparing the observed and calculated spectra, it was tentatively assigned that the less and more retained enantiomers were $\Delta\Lambda$ -[Ru(III)(acac)₂(S-dabe)Ru(III)(acac)₂] and $\Delta\Lambda$ -[Ru(III)(acac)₂(*R*-dabe)Ru(III)(acac)₂], respectively. More detailed theoretical analyses are now in progress.

In order to estimate the barrier height for the rotation around the C–C bond in the coordinated dabe^{2–}, the enantiomeric meso-type dimer, $\Delta\Lambda$ -[Ru(III)(acac)₂(*S*-dabe)Ru(III)(acac)₂], was dissolved in toluene and kept at 90 °C. After the elapse of five days, the solution was evaporated and the residue was analyzed chromato-graphically on the chiral column. As a result, no racemization of the initial enantiomer to its antipode, $\Delta\Lambda$ -[Ru(III)(acac)₂(*R*-dabe)Ru(III)(acac)₂], took place after 120 h.

[Ru(III)(acac)₂(tbet)Ru(III)(acac)₂]

 $[Ru(III)(acac)_2(CH_3CN)_2]PF_6$ and tbetH₂ were reacted in toluene and the reaction mixture was eluted on a HPLC column packed with silica gel. Two peaks (denoted as F₁ and F₂, respectively) were separated (see ESI†). Both the peaks gave the molecular weight of a dimer (m/z = 1044 (obs.); 1043.0 (calc.)). According to the ¹H NMR spectra of these fractions in CDCl₃, four acac ligands were all equivalent, giving only two kinds of methyl groups for both F₁ and F2 (see ESI[†]). Thus the bridging part was achiral and the two tris-β-diketonato moieties were equivalent. When eluted on the chiral column, F₁ gave a single band with no indication of optical resolution, while F_2 gave two peaks with an equal area (see ESI^{\dagger}). Thus F1 and F2 were concluded to be achiral meso-type dimer, $\Delta\Lambda$ -[Ru(III)(acac)₂(tbet)Ru(III)(acac)₂], and chiral racemic-type dimer, $\Delta\Delta$ - (or $\Lambda\Lambda$ -)[Ru(III)(acac)₂(tbet)Ru(III)(acac)₂], respectively. The bridging part was achiral due to the orthogonal twisting of the symmetrical B-diketonato moieties. These situations were the same as previously observed for [Ru(III)(acac)₂(taet)Ru(III)(acac)₂].⁶ As for the racemic-type dimer, the less and more retaining isomers were assigned to be $\Delta\Delta$ and $\Lambda\Lambda$ -enantiomers, respectively, when their ECD spectra were compared with that of $[Ru(acac)_3]$ (see ESI^{\dagger}). The VCD spectra of these resolved enantiomers are given in the ESI[†]. They were similar to those of racemic [Ru(III)(acac)₂(dabe)Ru(III)(acac)₂]. It is interesting to note that the elution order of racemic $[Ru(III)(acac)_2(tbet)Ru(III)(acac)_2]$ on the chiral column was similar to that of racemic [Ru(III)(acac)₂(dabe)Ru(III)(acac)₂] in F_3 and opposite to that in F_2 . These situations might reflect the subtle orientational difference of phenyl groups at the bridging part among these molecules.

Experimental

Syntheses of ligands

The ligand, dabeH₂, was obtained by reacting sodium 1-pheny-1,3butanedionate (5.93 g, 0.032 mol) with iodine (4.06 g, 0.016 mol) in dioxane.⁶ The compound was identified to be *meso*-1,2-diacetyl-1,2-dibenzoylethane by ¹H NMR and mass spectra (see ESI[†]).^{10,11} The ¹H NMR spectrum showed that dabeH₂ took a keto form and was not converted to the enol form in CDCl₃ as was reported in the literature.¹⁰⁻¹² The ligand, tbetH₂, was obtained by reacting sodium 1,3-diphenyl-1,3-propanedionate (9.83 g, 0.040 mol) with iodine (5.13 g, 0.020 mol) in dioxane. The compound was identified by ¹H NMR.

Syntheses of metal complexes

A dinuclear complex, [Ru(III)(acac)₂(dabe)Ru(III)(acac)₂], was prepared by refluxing [Ru(III)(acac)₂(CH₃CN)₂]PF₆ (52.4 mg, 0.10 mmol) and dabeH₂ (17.3 mg, 0.054 mmol) in dehydrated toluene (120 mL) for 24 h. After evaporating the solvent, the residue was eluted on a silica gel column (40 mm (i.d.) \times 30 cm) with 9:1 (v/v) benzene-acetonitrile to remove [Ru(III)(acac)₂(dabeH)] and [Ru(III)(acac)₃]. The fraction collected was further eluted on a HPLC silica gel column (4 mm (i.d.) × 25 cm) (Inertsil, GL Science Inc., (Japan)) with 9:1 (v/v) benzene-acetonitrile. Three peaks (denoted as F_1 , F_2 and F_3 , respectively) were separated (see ESI[†]). Mass spectral measurements showed that all of these peaks corresponded to dinuclear complexes (m/z = 919 (obs.);918.9 (calc.)). The identification of these complexes is described in the Results and discussion section. The chromatographic resolution of F_1 was performed by use of a HPLC column (4 mm (i.d.) \times 25 cm) packed with Δ -[Ru(II)(phen)₃]²⁺/synthetic hectorite.13 This column has been developed in our laboratory,

showing high capability of resolving multi-nuclear β-diketonato complexes.⁹ \mathbf{F}_1 : $\Delta \Lambda$ -[Ru(III)(acac)₂(dabe)Ru(III)(acac)₂]. $\delta = -43.0$ (1H, CH), -34.22 (1H, CH), -17.62 (1H, CH), -14.31 (3H, CH₃), -12.70 (3H, CH₃), -12.48 (1H, CH), -11.59 (3H, CH₃), -11.03 (3H, CH₃), -9.70 (3H, CH₃), -6.52 (3H, CH₃), 0.12 (3H, CH₃), 2.29 (3H, CH₃), 3.77 (3H, CH₃), 4.52 (2H, aromatic), 4.67 (2H, aromatic), 5.47 (3H, CH₃), 7.25 (1H, aromatic), 8.02 (2H, aromatic), 8.28 (1H, aromatic), 8.34 (2H, aromatic). \mathbf{F}_2 : $\Delta\Delta$ - (or $\Lambda\Lambda$) -[Ru(III)(acac)₂(dabe)Ru(III)(acac)₂]. $\delta = -35.0$ (2H, CH), -16.12 (2H, CH), -15.31 (6H, CH₃), -10.13 (6H, CH₃), -6.90 (6H, CH₃), 0.77 (6H, CH₃), 4.00 (4H, aromatic), 4.70 (6H, CH₃), 6.26 (4H, aromatic), 7.58 (2H, aromatic). F_3 : $\Delta\Delta$ - (or $\Lambda\Lambda$) - $[Ru(III)(acac)_2(dabe)Ru(III)(acac)_2]$. $\delta = -40.5$ (2H, CH), -13.81 (6H, CH₃), -12.86 (6H, CH₃), -10.00 (2H, CH), -9.31 (6H, CH₃), $3.37 (6H, CH_3), 4.12 (4H, d, J = 7 Hz, aromatic), 6.65 (6H, CH_3),$ 7.89 (2H, aromatic), 8.92 (4H, aromatic).

The dinuclear complex, [Ru(III)(acac)₂(tbet)Ru(III)(acac)₂], was prepared by refluxing [Ru(III)(acac)₂(CH₃CN)₂]PF₆ (0.22 g, 0.42 mmol) and tbetH₂ (0.17 g, 0.380 mmol) in dehydrated toluene (70 mL) for 24 h. After evaporating the solvent, the residue was eluted on a silica gel column (40 mm (i.d.) × 30 cm) with 9:1 (v/v) benzene–acetonitrile to remove [Ru(III)(acac)₂(tbetH)] and [Ru(III)(acac)₃]. The desired fraction was further separated into the two peaks. Mass spectral measurements showed that both the peaks corresponded to dinuclear complexes (*m*/*z* = 1044 (obs.); 1043.0(calc.)): F₁ $\Delta\Lambda$ -[Ru(III)(acac)₂(tbet)Ru(III)(acac)₂]. δ = -30.10 (4H, CH), -7.03 (12H, CH₃), -3.51 (12H, CH₃), 6.10 (8H, aromatic), 7.70 (4H, aromatic), 8.26 (8H, aromatic); F₂: $\Delta\Delta$ -(or $\Lambda\Lambda$) -[Ru(III)(acac)₂(tbet)Ru(III)(acac)₂]. δ = -27.1 (4H, CH), -5.73 (12H, CH₃), -1.56 (12H, CH₃), 4.69 (8H, aromatic), 6.76 (8H, aromatic), 7.46 (4H, broad t, *J* = 6 Hz).

Spectroscopic measurements

¹H NMR spectra were measured with a JNM-AL400 (JEOL, Ltd.) in CDCl₃. UV-vis spectra were recorded with a U-2810 spectrophotomer (Hitachi, Ltd., Japan). Circular dichroism (CD) spectra were recorded with a J-720 spectropolarimeter (JASCO, Co., Japan). VCD and IR spectra were measured with a PRESTO-S-2007 spectrometer (JASCO, Co., Japan). The machine is the single PEM system, at which the central wavenumber of PEM was set at 1250 cm⁻¹. The calibration was made by use of a quarter wave-retardation and an analyzer. The spectra were recorded on the instrument implemented with the shuttle system. However, we did not use the shuttle system in this work because the signals were large enough for the conventional measurements. A CDCl₃ solution of each complex was injected into a cell (150 μ m in optical length) with BaF₂ windows. The signal was accumulated during 10000 scans (ca. 1.5 h) for each complex. The background correction was performed only by subtracting the solvent spectrum. The resolution of wavenumber was 4 cm⁻¹. The concentration was adjusted such that the absorbance of IR spectra below 1.0 for the optimal measurements.

X-Ray crystal analyses

A single crystal suitable for X-ray analysis was obtained by recrystallization from an ethanol solution of the racemic mixture of $meso-[Ru(III)(acac)_2(dabe)Ru(III)(acac)_2]$ (F₁). The intensity

Table 1 Crystallographic data of $\Delta\Lambda$ -[Ru(III)(acac)₂(dabe)Ru(III)-(acac)₂]

Empirical formula	$C_{40}H_{44}O_{12}Ru_2$
Formula weight	918.89
Crystal size/mm ³	$0.15 \times 0.05 \times 0.01$
Crystal system	Triclinic
a/Å	9.8075(16)
b/Å	13.263(2)
c/Å	15.335(3)
α/deg	79.540(2)
β/\deg	86.223(2)
γ/deg	82.549(2)
$V/Å^3$	1943.1(5)
Space group	PĪ
Z value	2
$D_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.571
F(000)	936
No. of reflections	13098
No. of observations	5647
Parameters	497
Temperature/K	90(2) K
Final $R_1, R_w(I > 2\sigma(I))$	0.0414, 0.0776
Final R_1 , R_w (all data)	0.0709, 0.0960
Goodness-of-fit	1.029

data were collected at 90 K on a Bruker Smart CCD diffractometer with graphite-monochromated Mo K α radiation. The structure was solved by the direct method and refined by the least-squares on F^2 . The crystallographic data and refinement parameters are listed in Table 1.†

Computational details

The IR and VCD spectra of the complex were theoretically calculated by the use of Gaussian 09 program.¹⁸ VCD intensities were determined by the vibrational rotational strength and magnetic dipole moments, which were calculated by the magnetic field perturbation (MFP) theory formulated using magnetic field gauge-invariant atomic orbitals. The calculated intensities were converted to Lorentzian bands with 4 cm⁻¹ half-width at half-height. Geometry optimization and frequency analysis were performed at the DFT level (B3LYP functional with Stuttgart ECP for Ru and 6-31G(d) for other atoms). Thus the peaks in the observed spectrum were assigned on the basis of the animation of molecular vibration with Gauss view 5.08 (Gaussian Inc.).

Conclusion

Ru(III) dimers bridged by the non-symmetrical β -diketonato ligand, [Ru(III)(acac)₂(dabe)Ru(III)(acac)₂], were synthesized and separated into the meso- and two racemic forms, each of which was resolved into a pair of enantiomers. Notably, the meso-form, in which Δ - and Λ -moieties are connected by the bridging ligand, is *chiral* in solid and solution states. This is the first example of optical resolution of the enantiomers due to the axial chirality of β -diketonato rings. The resolution was successfully achieved on the basis of the chiral recognition by Δ -[Ru(phen)₃]²⁺/synthetic hectorite. The enantiopure meso-form showed characteristic circular dichroism, particularly in the mid IR region, even though the chirality due to $\Delta\Lambda$ isomerism of the Ru(III) centers is cancelled out. In contrast to the non-symmetical bridging ligand, a symmetrical bridging ligand, tbetH₂, formed achiral meso-type and chiral racemic-type dimers. The situations were the same as taetH₂.

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