Synthesis and Characterization of Tetrahedral Ru_3O Clusters with Intrinsic Framework Chirality: A Chiral Probe of the Intact Cluster Catalysis Concept†

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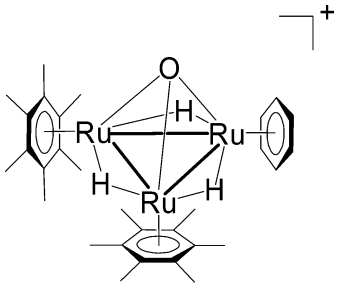
To bring evidence for or against the hypothesis of catalytic hydrogenation by intact trinuclear arene ruthenium clusters containing an oxo cap, cationic Ru_3O clusters with three different arene ligands (intrinsically chiral tetrahedra) have been synthesized as racemic mixtures. By introduction of a chiral auxiliary substituent at one of the three different arene ligands, the separation of the two diastereomers was possible. The chiral Ru_3O framework was evidenced by X-ray crystallography, by circular dichroism in the UV and IR regions, and by chiral shift reagents in the NMR spectra. The catalytic hydrogenation of the prochiral substrate methyl 2-acetamidoacrylate using a chiral Ru_3O cluster showed no asymmetric induction, suggesting that the catalytically active species is not the intact Ru_3O cluster.

Introduction

In 1999 one of our groups (Süss-Fink et al.) observed that the trinuclear cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ (**1**), accessible from the dinuclear percursor $[H_3Ru_2(C_6Me_6)_2]^+$ and the mononuclear percursor $[Ru(C_6H_6)(H_2O)_3]^{2+}$ and employed as the water-soluble tetrafluoroborate salt, efficiently catalyzes (or acts as an efficient catalyst precursor) the hydrogenation of benzene to cyclohexane under biphasic conditions.[1]



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From the mass spectroscopic observation of the host−guest complex $[C_6H_6\subset\mathbf{1}]^+$, from molecular modeling studies, and on the basis of the fact that after the hydrogenation of C_6D_6 to give $C_6D_6H_6$ catalyzed by **1**, >95% of the cluster cation could be recovered unchanged without the C_6H_6 ligand being exchanged by C_6D_6, it was hypothesized that the substrate molecule is incorporated in the hydrophobic pocket spanned by the three arene ligands in **1**, suggesting the catalytic reaction occurs within this host−guest complex, while the Ru_3O cluster stays intact throughout the catalytic process.[2]

However, for benzene hydrogenation catalysts derived from organometallic precursors, the true nature of the catalytic species remained a debatable point ("is it homogeneous or heterogeneous catalysis?").[3] In the case of the putative homogeneous $[(C_8H_{17})_3Me][RhCl_4]$ ion pair catalyst,[4] Finke and co-workers were able to demonstrate that rhodium(0) nanoclusters are the true catalysts ("soluble analogs of heterogeneous catalysts").[5] Homogeneous arene hydrogenation catalysts have been reviewed recently by Finke[6] and by Dyson,[7] and the question of the true nature of the catalytic species in arene hydrogenation with soluble metal complexes has been critically addressed by Finke et al.[8]

The water-soluble cluster cation **1**, reported by Süss-Fink et al. to catalyze efficiently the hydrogenation of benzene and benzene derivatives,[1] seemed to be a molecular catalyst that works under biphasic conditions. The high substrate selectivity,[9] which can be tuned by

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† This paper is dedicated to Professor Brian F. G. Johnson, University of Cambridge (Cambridge, U.K.), and to Prof. Heinrich Vahrenkamp, University of Freiburg (Freiburg, Germany), on the occasion of their retirement.

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§ X-ray crystallography.

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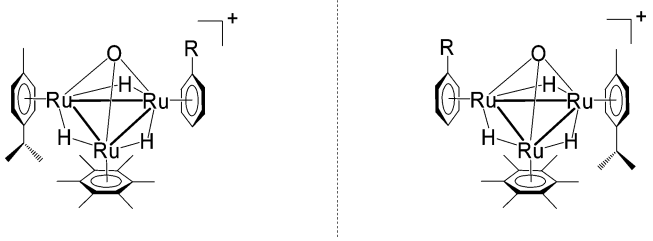
substituents on the arene ligands,[10] suggested a size effect of the hydrophobic pocket spanned by the three arene ligands in **1** and was thus interpreted in terms of supramolecular intact cluster catalysis.[2] The isolation and unambiguous X-ray characterization of the hexafluorophosphate or tetrafluoroborate salts of the host−guest complexes $[C_6H_6\subset\mathbf{2}]^+$ and $[C_6H_6\subset\mathbf{3}]^+$, **2** being $[H_3Ru_3\{C_6H_5(CH_2)_2OH\}(C_6Me_6)_2(O)]^+$ and **3** being $[H_3Ru_3\{C_6H_5(CH_2)_3OH\}(C_6Me_6)_2(O)]^+$, derivatives of the host−guest complex $[C_6H_6\subset\mathbf{1}]^+$, postulated as the catalytic intermediate, seemed to confirm this hypothesis.[11]

However, recent detailed studies revealed that the hydrogenation of benzene in the presence of **1** cannot be explained by molecular catalysis: In a collaborative study, we were able to show by a detailed analysis of the kinetics, by transmission electron microscopy of the reaction mixture, and by high-pressure in situ NMR measurements of the exchange process of H_2 and D_2O in the presence of **1** that cluster **1** is not the true catalyst; ruthenium(0) nanoparticles formed in small quantities from **1** under hydrogen pressure are implicated as the true catalytically active species (heterogeneous catalysis).[12]

To test the original hypothesis of intact cluster catalysis by an independent method, we decided to use the chirality transfer criterion in the catalytic hydrogenation of prochiral substrates: does this hydrogenation occur within the hydrophobic pocket of the intact trinuclear cluster **1**, or not?



We set out to synthesize triruthenium clusters analogous to **1** with three different arene ligands at the three ruthenium atoms. Such a Ru_3O cluster would be intrinsically chiral due to its tetrahedral structure, since the four vertices of the Ru_3O skeleton are different. Provided that the two enantiomers can be separated, the use of the enantiopure Ru_3O cluster in the catalytic hydrogenation of a prochiral substrate may induce an enantiomeric excess, if the intact cluster acts as a catalyst with the substrate being transformed within the hydrophobic pocket of the cluster. If, however, the catalytically active species are mononuclear fragments or nanoparticles formed from the desintegration of the Ru_3O skeleton, the enantiomeric excess of the catalytic products should be zero, given that in this case the chiral information due to the Ru_3O tetrahedron with four different vertices (framework chirality) would be lost.

In this paper, we report on the synthesis of intrinsically chiral cationic Ru_3O clusters with three different arene ligands as a racemic mixture, the separation of the diastereomers obtained by introducing a chiral auxiliary substituent in one of the three different arene ligands, and their use as catalysts in the hydrogenation of the prochiral substrate methyl 2-acetamidoacrylate under biphasic conditions. These Ru_3O cluster cations are the first homometallic clusters with intrinsic framework chirality.

Results and Discussion

Metal clusters with a chiral framework have been extensively studied ever since the pioneering work of Vahrenkamp and Richter,[13] who were the first to prepare tetrahedral M_3S clusters with three different metal atoms.[14] The motivation for this work was to demonstrate the implication of intact metal clusters in catalytic reactions, since intrinsically chiral metal clusters used as catalysts for the conversion of prochiral substrates may give rise to an enantiomeric excess of the chiral products, subject to the condition that the metal cluster stays intact throughout the catalytic process. So far, this demonstration still remains to be done,[15] because only very few intrinsically chiral metal clusters have been separated into their enantiomers,[13a,16] and in these cases the clusters either showed no catalytic activity[17] or became active only under UV irradiation, which caused racemization of the cluster framework.[15a] Whereas the intrinsically chiral metal clusters known so far, based on a tetrahedral framework with four different vertices, contain a M_3S,[13,14,16] a $M_3(CR)$,[13a,b] or a M_4[18] framework with different metal atoms, we report here homometallic trinuclear clusters containing a chiral Ru_3O skeleton capped by a μ_3-oxo ligand, the three ruthenium atoms being coordinated to three different arene ligands. Because of the three different arene ligands, the tetrahedral Ru_3O framework is intrinsically chiral, as the four vertices of the tetrahedron are different.

General Synthetic Method for Trinuclear Arene Ruthenium Cluster Cations Containing a Chiral Ru_3O Tetrahedral Framework. The assembly of

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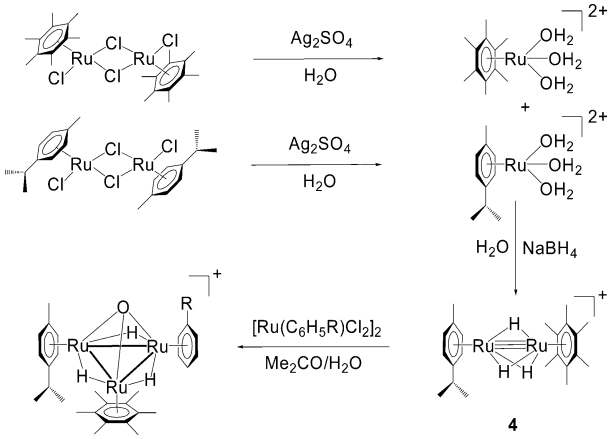
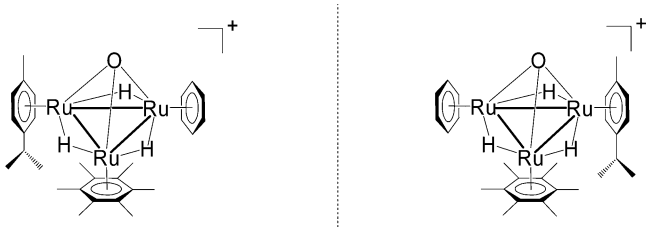
Scheme 1. Stepwise Assembly of Trinuclear Arene Ruthenium Cluster Cations Containing a Chiral Ru_3O Tetrahedral Framework



Ru_3O cluster cations containing three different arene ligands is based on the synthesis of a dinuclear precursor with two different arene ligands, which can react with a mononuclear complex containing another arene ligand. Treatment of an aqueous solution of the well-known chloro-bridged dinuclear arene ruthenium complexes $[Ru(C_6Me_6)Cl_2]_2$ and $[Ru(p\text{-}Pr^iMeC_6H_4)Cl_2]_2$[19] with Ag_2SO_4 gives a mixture of the mononuclear aqua complexes $[Ru(C_6Me_6)(H_2O)_3]^{2+}$ and $[Ru(p\text{-}Pr^iMeC_6H_4)(H_2O)_3]^{2+}$ with precipitation of AgCl. These aqua complexes react in situ with $NaBH_4$ to give the dinuclear trihydrido-bridged complex $[H_3Ru_2(C_6Me_6)(p\text{-}Pr^iMeC_6H_4)]^+$ (**4**), along with the analogues $[H_3Ru_2(C_6Me_6)_2]^+$ [20] and $[H_3Ru_2(p\text{-}Pr^iMeC_6H_4)]^+$ as byproducts. Complex **4** is isolated as its tetrafluoroborate salt and purified to a degree of purity of 95% (5% of residual $[H_3Ru_2(C_6Me_6)_2][BF_4]$) by column chromatography on silica gel, followed by preparative thin-layer chromatography on silica gel. The ^1H NMR spectrum of **4** in deuterated acetone shows a singlet (δ −15.52) in the hydride region, in accordance with its analogue $[H_3Ru_2(C_6Me_6)(indane)]^+$ already described in the literature.[21] The trihydrido complex **4** serves as a dinuclear building block to synthesize intrinsically chiral trinuclear ruthenium clusters by reaction with other triaqua complexes $[Ru(C_6H_5R)(H_2O)_3]^{2+}$ accessible in situ from the corresponding chloro-bridged dimers $[Ru(C_6H_5R)Cl_2]_2$ in aqueous solution, as summarized in Scheme 1.

Isolation and Characterization of an Intrinsically Chiral Trinuclear Ruthenium Cluster Cation as a Mixture of Enantiomers. The reaction of **4** with the well-known mononuclear triaqua complex $[Ru(C_6H_6)(H_2O)_3]^{2+}$,[22] formed in situ from the chloro-bridged precursor $[Ru(C_6H_6)Cl_2]_2$[23] in aqueous solution, gives the oxo-capped tetrahedral chiral trinuclear ruthenium cluster cation (containing a chiral Ru_3O tetrahedral framework) $[H_3Ru_3(C_6H_6)(C_6Me_6)(p\text{-}Pr^iMeC_6H_4)(O)]^+$ as a racemic mixture ((*S*)-**5** and (*R*)-**5**), crystallized



as the tetrafluoroborate salt. Crystals suitable for X-ray analysis have been obtained of the hexafluorophosphate salt, accessible by addition of KPF_6 to an aqueous solution of $[\mathbf{5}][BF_4]$.

Due to the asymmetric tetrahedral Ru_3O framework in (*S*)-**5** and (*R*)-**5**, the Cahn−Ingold−Prelog rules usually used for the designation of the absolute configuration of asymmetric carbon atoms can be applied in this case as well. The single-crystal X-ray structure analysis reveals both enantiomers (*S*)-**5** and (*R*)-**5** to be present in the same crystal. Figure 1 shows the centrosymmetric unit containing both enantiomers.

Due to the four chemically different vertices of the tetrahedron formed by the three arene ruthenium units and the oxo cap in **5**, the three hydrido ligands are inequivalent. This is reflected in the ^1H NMR spectrum, where the racemic mixture of (*S*)-**5** and (*R*)-**5** indeed gives rise to three different hydride signals; however, instead of the expected doublet of doublets multiplicity, the three signals show up as pseudotriplets.

Unfortunately, the separation of the two enantiomers (*S*)-**5** and (*R*)-**5** turned out to be unsuccessful in our hands. We tried fractional crystallization of the cationic enantiomers in the presence of chiral anions such as L-(+)-tartrate and (−)-camphor-10-sulfonate from acetone solution or HPLC on chiral phases (CHIRALPAK 50801 20 μm column in EtOH/MeOH 50/50) or ion-exchange chromatography in the presence of chiral ions (aqueous solution of L-(+)-tartrate as eluant through Sephadex-SP C-25 ion-exchange resin 40−120 μm). In no case did the chiral cluster **5** separate into the enantiomers (*S*)-**5** and (*R*)-**5**. Therefore, we decided to introduce a chiral auxiliary group tethered to one of the three different arene ligands, so that the clusters formed are obtained as a diastereomer mixture.

Isolation and Characterization of a Ruthenium Cluster Cation with Framework Chirality and a Chiral Substituent at One of the Arene Ligands as a Mixture of Diastereomers. To form diastereomers, the benzene ligand in **5** is replaced by an arene ligand containing an asymmetric carbon atom on a substituent. To minimize the distance between the two chiral centers (the chiral M_3O tetrahedron and the chiral substituent) for pronounced differences in the properties of the expected diastereomers, the asymmetric carbon atom should be in the benzylic position. Therefore, we decided to use (*R*)-1-phenylethanol as the chiral arene ligand. The synthesis of the starting chloro-bridged dimer (*R*,*R*)-$[Ru(1\text{-phenylethanol})Cl_2]_2$ (**6**) represents an inevitable step. The straightforward syn-

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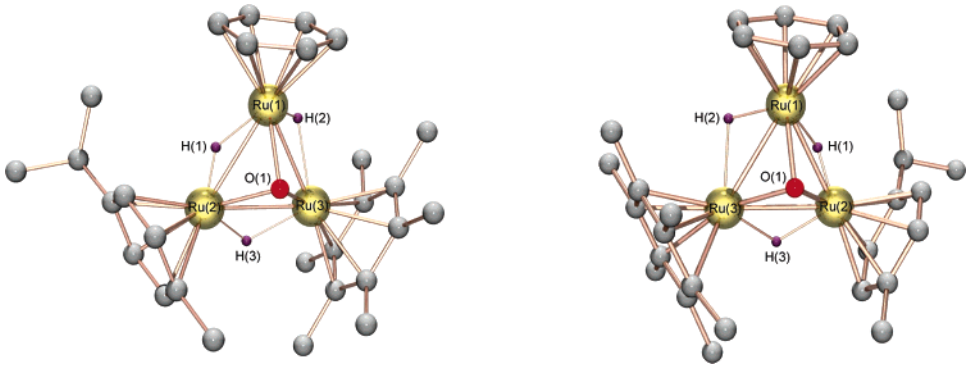
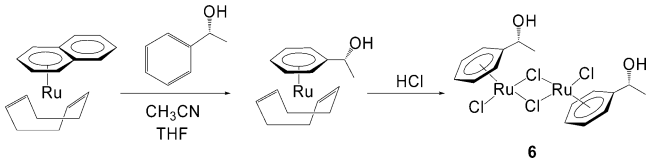


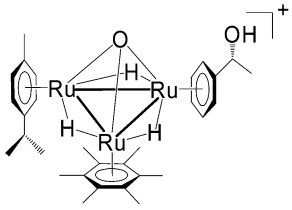
Figure 1. POV-Ray views[37] of cations (*S*)-5 (left) and (*R*)-5 (right). Hydrogen atoms (excepted hydride ligands) and counterions are omitted for clarity.

Scheme 2. Synthesis of the Chiral Chloro-Bridged Dimer (*R*,*R*)-[Ru(1-phenylethanol)Cl_2]$_2$ (6)

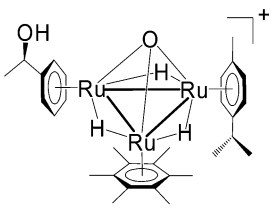


thetic method for this type of complexes, the dehydrogenation of the corresponding cyclohexadiene by $RuCl_3 \cdot nH_2O$ in refluxing ethanol,[23] cannot be used in this case, since the synthesis of the starting (1-hydroxyethyl)-cyclohexadiene implies a Birch reduction with metallic sodium in liquid ammonia,[24] which could cleave the C−O bond of the OH substituent to give ethylcyclohexadiene with loss of the chirality.[25] This is why **6** was synthesized by naphthalene displacement in [Ru(COD)-($C_{10}H_8$)],[26] followed by reaction with HCl,[27] an alternative way to prepare chloro-bridged arene-ruthenium dimers, as shown in Scheme 2.

The dinuclear trihydrido complex **4** reacts in a water/acetone solution with the mononuclear triaqua complex (*R*)-[Ru(1-phenylethanol)$(H_2O)_3$]$^{2+}$ formed in situ from **6** with water to give a diastereomeric mixture of the two trinuclear ruthenium cluster cations (S_{Ru_3O},R_C)-[H_3Ru_3(1-phenylethanol)(C_6Me_6)(*p*-Pr^{i}MeC$_6$H$_4$)(O)]$^+$ ((*S*,*R*)-**7**) and (R_{Ru_3O},R_C)-[H_3Ru_3(1-phenylethanol)(C_6Me_6)-



(*S*,*R*)-**7**

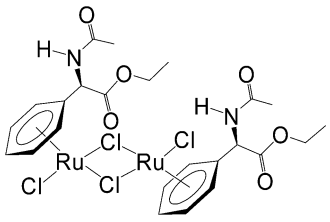


(*R*,*R*)-**7**

(*p*-Pr^{i}MeC$_6$H$_4$)(O)]$^+$ ((*R*,*R*)-**7**), being intrinsically chiral at the level of the Ru_3O framework and having a chiral ligand as well. The presence of the two diastereomers is reflected in the ^{1}H NMR and ^{13}C NMR spectra, where the mixture of (*S*,*R*)-**7** and (*R*,*R*)-**7** gives rise to two sets of signals, while the ESI-MS spectrum of the mixture shows only one peak with the characteristic Ru_3 isotope pattern centered at *m*/*z* 742.

Unfortunately, we did not succeed in separating the two diastereomers (*S*,*R*)-**7** and (*R*,*R*)-**7**, either by chromatographic methods (silica gel, dichloromethane/acetone as eluant) or by fractional crystallization of the tetrafluoroborate salts. Accordingly, the single-crystal analysis of [**7**][BF_4] shows both diastereomers being present in the same crystal in a 1:1 ratio, as shown in Figure 2.

Isolation and Characterization of a Ruthenium Cluster Cation with Framework Chirality and a Chiral Substituent on One of the Arene Ligands and Separation of the Diastereomers with Racemization of the Chiral Side Chain. Since the diastereomers (*S*,*R*)-**7** and (*R*,*R*)-**7** turned out to be inseparable in our hands, we synthesized an analogous cluster containing an amido and an ester function on the chiral substituent at one of the arene ligands. The chiral dimer (*S*,*S*)-[Ru{C_6H_5(CH(NHCOMe)CO_2Et)}Cl_2]$_2$ described in the literature[28] was used as the starting material for the reaction with the trihydrido dinuclear complex **4** in aqueous solution.



This reaction yields the cluster cation [H_3Ru_3-{C_6H_5(CH(NHCOMe)CO_2Et)}(C_6Me_6)(*p*-Pr^{i}MeC$_6$H$_4$)-(O)]$^+$ (**8**), which contains an asymmetric Ru_3O tetrahedron (framework chirality) and a chiral substituent in the (*R*)-C_6H_5(CH(NHCOMe)CO_2Et) ligand. With the ester and the amido substituents at the asymmetric carbon atom, it was possible to separate the diastereomers by preparative thin-layer chromatography on silica gel.

The two diastereomerically pure fractions show the same mass spectrum with a molecular peak centered

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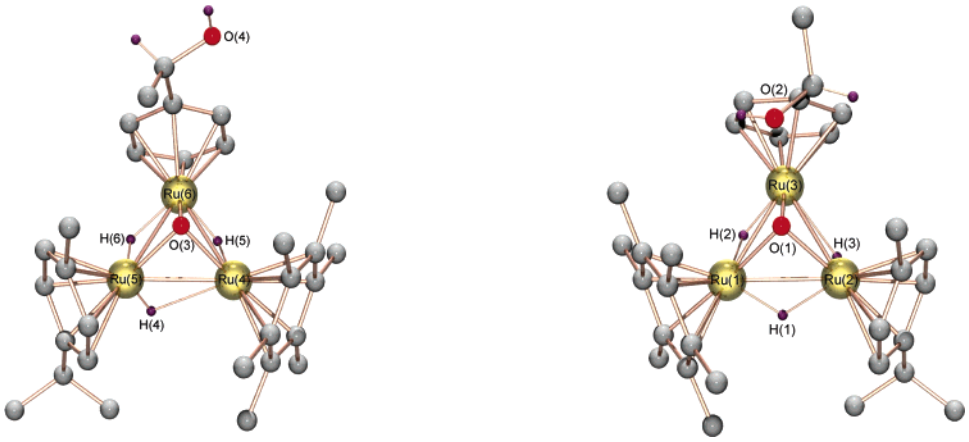


Figure 2. POV-Ray views[37] of cations (*S*,*R*)-**7** (left) and (*R*,*R*)-**7** (right). Counterions and hydrogen atoms, except for the hydroxide protons, the hydride ligands, and the α-hydrogen atoms of the phenylethanol moieties, are omitted for clarity.

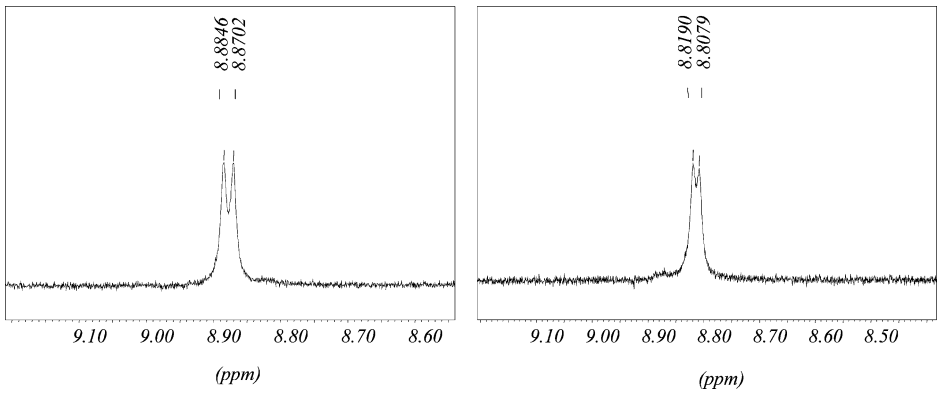


Figure 3. Enlarged ^{1}H NMR spectra (CD_2Cl_2, 400 MHz) (N*H* signals) of the first fraction (left) and the second fraction (right) isolated from the reaction of **4** with the chiral dimer (*S*,*S*)-[Ru{C_6H_5(CH(NHCOMe)CO_2Et)}Cl_2]$_2$. These spectra reflect the diastereopurity of each fraction.

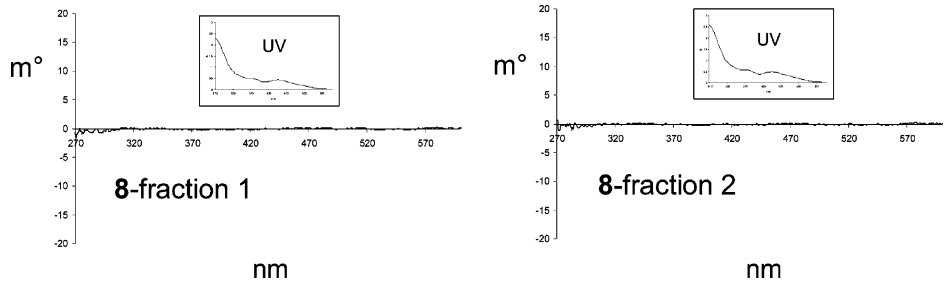


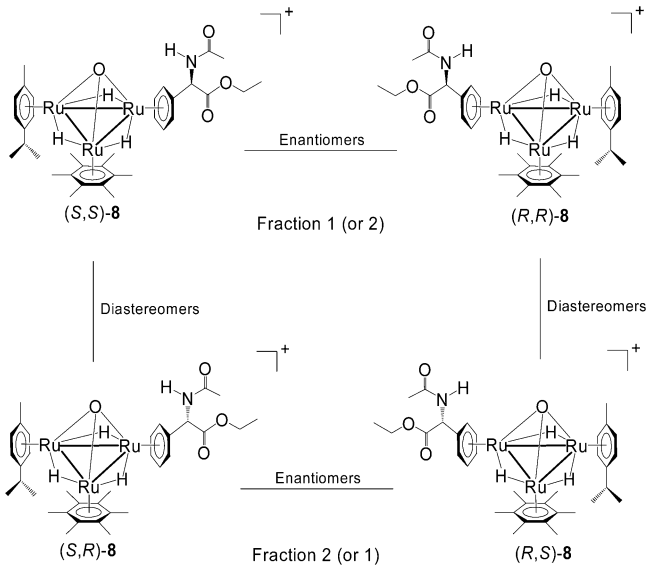
Figure 4. CD spectra (in MeOH) of the first and second fractions of **8**, isolated from the reaction of **4** with the chiral dimer (*S*,*S*)-[Ru{C_6H_5(CH(NHCOMe)CO_2Et)}Cl_2]$_2$ by preparative thin-layer chromatography on silica gel using dichloromethane/acetone as eluant. The corresponding UV spectra are shown in the frame.

at *m*/*z* 841. It is important to note that the change from *R* for the free ligand to *S* for the complex in the denomination is only due to the priority change in the Cahn−Ingold−Prelog rules, caused by coordination of the ligand to the ruthenium atom. The ^{1}H NMR spectra of both fractions show the same multiplicity but slightly different chemical shifts, as shown in Figure 3.

To find out if both diastereomers are optically active (i.e. enantiomerically enriched), we recorded the CD spectrum of both fractions of **8** (see Figure 4). Neither of the CD spectra shows any absorption band, suggesting that both isolated fractions contain a racemic mixture of chiral trinuclear clusters. This means that the asymmetric carbon atom has racemized during one of the different reaction steps. Indeed, the proton at the asymmetric carbon atom is relatively acidic, due to the electron-withdrawing ester group in the α-position; it can be removed easily by a base, causing the racemization of the asymmetric carbon atom.

The two separated fractions contain the racemic mixtures of (S_{Ru_3O},S_C)-[H_3Ru_3{C_6H_5(CH(NHCOMe)CO_2Et)}(C_6Me_6)(*p*-Pr^{i}MeC_6H_4)(O)]$^+$ ((*S*,*S*)-**8**) and (R_{Ru_3O},R_C)-[H_3Ru_3{C_6H_5(CH(NHCOMe)CO_2Et)}(C_6Me_6)(*p*-Pr^i-MeC_6H_4)(O)]$^+$ ((*R*,*R*)-**8**) as well as (S_{Ru_3O},R_C)-[H_3Ru_3-{C_6H_5(CH(NHCOMe)CO_2Et)}(C_6Me_6)(*p*-Pr^{i}MeC_6H_4)-(O)]$^+$((*S*,*R*)-**8**)and(R_{Ru_3O},S_C)-[H_3Ru_3{C_6H_5(CH(NHCOMe)-CO_2Et)}(C_6Me_6)(*p*-Pr^{i}MeC_6H_4)(O)]$^+$ ((*R*,*S*)-**8**); however, we do not know which fraction contains which racemic pair (Scheme 3).

Scheme 3. Representation of Isomers Isolated after the Reaction of 4 with the Chiral Dimer (*S*,*S*)-[Ru{C_6H_5(CH(NHCOMe)CO_2Et)}Cl_2]$_2$ by Preparative Thin-Layer Chromatography



Isolation and X-ray Characterization of a Ruthenium Cluster Cation without Framework Chirality but a Chiral Substituent on One of the Arene Ligands, Confirming the Racemization of the Chiral Side Chain in 8. The assumption that the synthesis of **8** involves the racemization of the chiral side chain could be proven irrefutably by single-crystal X-ray structure analysis. However, as no suitable crystals of **8** have been obtained in our hands, from either the first or the second fraction, we synthesized the analogous cluster cation [$H_3Ru_3(C_6Me_6)_2${C_6H_5-(CH(NHCOMe)CO_2Et)}(O)]$^+$ (**9**), containing an achiral Ru_3O framework but the same chiral substituent as **8**, hoping to see evidence for the racemization of the asymmetric carbon atom in the side chain. Indeed, crystals of [**9**][BF_4], suitable for single-crystal X-ray structure analysis, could be obtained, and the result shows that **9** crystallizes in a centrosymmetric space group, both enantiomers (*R*)-**9** and (*S*)-**9** being present in the same crystal, due to the racemization of the asymmetric carbon atom, as shown in Figure 5.

Because of this unequivocal proof of the racemization of the asymmetric carbon atom in the CH(NHCOMe)-CO_2Et side chain during the synthesis of **9**, it can be assumed that the same racemization also takes place during the synthesis of **8**, giving rise to the formation of two racemic diastereomer fractions, as shown in Scheme 3.

Isolation and Characterization of a Ruthenium Cluster Cation with Framework Chirality as Well as a Chiral Amido Substituent at One of the Arene Ligands as a Mixture of Diastereomers without Racemization of the Chiral Side Chain. Since **8** turned out to be separable into two fractions by preparative thin-layer chromatography on silica gel as two racemic mixtures, due to the racemization of the asymmetric carbon atom, it seemed promising to incorporate a chiral auxiliary containing a *NH* group into an intrinsically chiral trinuclear cluster at one of the three arene ligands, with an asymmetric carbon atom that cannot racemize. Therefore, we decided to replace the chiral arene ligand (*R*)-C_6H_5(CH(NHCOMe)CO_2Et) by a chiral ligand containing a *NH* group at the benzylic position, the asymmetric carbon atom of which does not racemize during the reaction. Starting from (*R*)-phenylglycinol, to avoid side reactions, N-terminal protection of the starting arene is necessary. Thus, (*R*)-phenylglycinol reacts with ethyl chloroformate under biphasic conditions (CH_2Cl_2/aqueous $NaHCO_3$) to give the protected ligand **10**,[29] as shown in Scheme 4.

The known chiral ligand (*R*)-C_6H_5(CH(NHCO$_2$Et)-CH_2OH) (**10**)[29] was used to prepare the new enantiopure dimer (*S*,*S*)-[Ru{C_6H_5(CH(NHCO$_2$Et)CH_2OH)}Cl_2]$_2$ (**11**) by a naphthalene displacement reaction in [Ru(COD)-($C_{10}H_8$)], followed by reaction with HCl, as illustrated in Scheme 5. Again, the formal change from *R* to *S* is only due to the priority change in the Cahn−Ingold−Prelog rules, caused by the coordination of the ligand to the ruthenium atom. As the proton at the asymmetric carbon atom is not labile, in contrast to that in (*S*,*S*)-[Ru{C_6H_5(CH(NHCOMe)CO_2Et)}Cl_2]$_2$, racemization is unlikely in this case. As expected, the ^{1}H and ^{13}C NMR spectra of **11** in CD_2Cl_2 display only a single set of signals.

Complex **11** is used as a chiral building block to prepare chiral trinuclear arene ruthenium cluster cations. To be sure that the asymmetric carbon atom does not racemize during the reaction with the dinuclear complex, we first prepared the trinuclear cluster cation (*S*)-[$H_3Ru_3(C_6Me_6)_2${C_6H_5(CH(NHCO$_2$Et)CH_2OH)}-(O)]$^+$ (**12**), containing an achiral Ru_3O framework and only the chiral carbon atom in the side-chain. Complex **11**, dissolved in water, gives rise to the in situ formation of the mononuclear aqua complex (*S*)-[Ru{C_6H_5-(CH(NHCO$_2$Et)CH_2OH)}(H_2O)$_3$]$^{2+}$, which reacts with the dinuclear complex [$H_3Ru_3(C_6Me_6)_2$]$^+$ to give the expected cation **12**, isolated as the tetrafluoroborate salt. Crystals of [**12**][BF_4] suitable for single-crystal X-ray structure analysis were easily obtained by a slow diffusion of hexane in a CH_2Cl_2 solution of the salt. The X-ray analysis shows that only the expected *S* enantiomer is present in the crystal (Figure 6).

The X-ray crystal structure analysis of [**12**][BF_4] also reveals the presence of strong intramolecular hydrogen bonds between the hydroxo proton and the oxo cap (d(O···H) = 1.842 Å, d(O···O) = 2.648 Å) as well as between the amido proton and the oxygen atom of the CH_2OH moiety (d(O···H) = 2.070 Å, d(O···N) = 2.722 Å), stabilizing the molecular edifice in the solid state. The hydrogen bond between the hydroxo proton and the oxo cap, found in the solid state, seems to persist also in dichloromethane solution: the ^{1}H NMR spectrum of **12** in CD_2Cl_2 shows a well-defined multiplet centered at 6.95 ppm, assigned to the OH proton coupled to the two diastereotopic protons of the neighboring CH_2 group. A similar phenomenon has already been observed in other trinuclear arene ruthenium cluster cations containing an alcohol function as a sidearm in one of the arene ligands.[30]

Having shown by the synthesis of **12** that the asymmetric carbon atom in **11** does not racemize in the

(29) Wu, Y.; Shen, X. *Tetrahedron: Asymmetry* **2000**, *11*, 4359.
(30) (a) Vieille-Petit, L.; Therrien, B.; Süss-Fink, G. *Eur. J. Inorg. Chem.* **2003**, 3707. (b) Vieille-Petit, L.; Karmazin-Brelot, L.; Labat, G.; Süss-Fink, G. *Eur. J. Inorg. Chem.* **2004**, 3907.

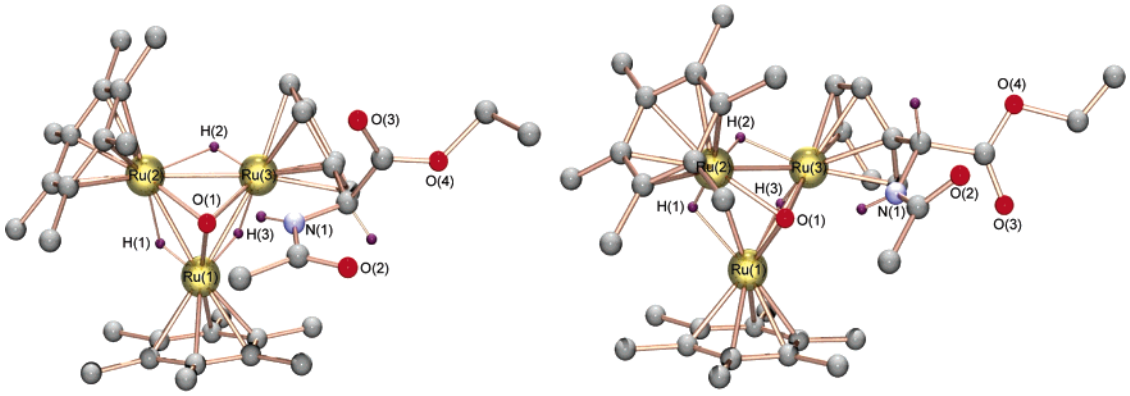
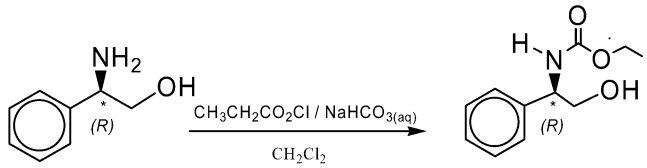


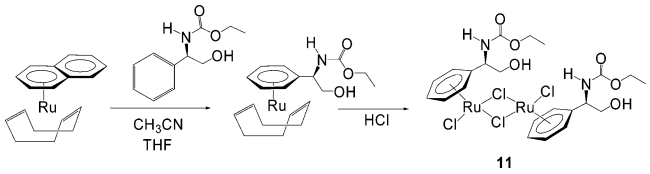
Figure 5. POV-Ray views[37] of both enantiomers of **9** ((*R*)-**9** on the left and (*S*)-**9** on the right) present in the same crystal. Anions, solvent molecules, and hydrogen atoms, except for the amide protons, the hydride ligands, and the α-hydrogen atoms of the chiral moieties, are omitted for clarity.

Scheme 4. Synthesis of the Protected Ligand (*R*)-C_6H_5((CH(NHCO$_2$ET)CH$_2$OH) (10)

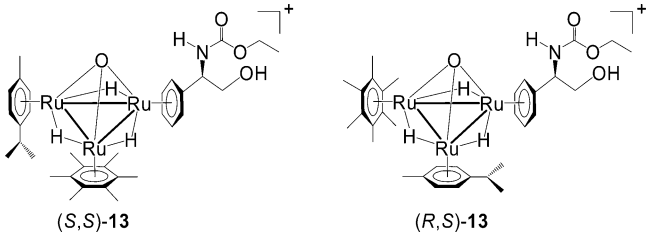


(*R*)-phenylglycinol

Scheme 5. Synthesis of the Chiral Dimer (*S*,*S*)-[Ru{C_6H_5((CH(NHCO$_2$Et)CH$_2$OH)}Cl$_2$]$_2$ (11)



reaction with $[H_3Ru_3(C_6Me_6)_2]^+$, we reacted the enantiopure dimer (*S*,*S*)-[Ru{C_6H_5(CH(NHCO$_2$Et)CH$_2$OH)}Cl$_2$]$_2$ (**11**) with the complex **4**, to prepare the diastereomeric cluster cations (S_{Ru_3O},S_C)-$[H_3Ru_3\{C_6H_5$-(CH(NHCO$_2$Et)CH$_2$OH)}$(C_6Me_6)(p$-Pr^{i}MeC$_6$H$_4$)(O)]$^+$ ((*S*,*S*)-**13**) and (R_{Ru_3O},S_C)-$[H_3Ru_3\{C_6H_5$(CH(NHCO$_2$Et)CH$_2$OH)}-



(*S*,*S*)-**13** (*R*,*S*)-**13**

$(C_6Me_6)(p$-Pr^{i}MeC$_6$H$_4$)(O)]$^+$ ((*R*,*S*)-**13**) with a chiral Ru_3O framework and an asymmetric carbon atom in the (*R*)-C_6H_5(CH(NHCO$_2$Et)CH$_2$OH) ligand.

The presence of the two diastereomers is reflected in the ^{1}H NMR and ^{13}C NMR spectra, where the mixture of (*S*,*S*)-**13** and (*R*,*S*)-**13** gives rise to two sets of signals (Figure 7), while the ESI-MS spectrum of the mixture shows only one peak with the characteristic Ru_3 isotope pattern centered at *m*/*z* 829.

Unfortunately, the separation of the two diastereomers (*S*,*S*)-**13** and (*R*,*S*)-**13** turned out to be unsuccessful in our hands, either by chromatographic methods

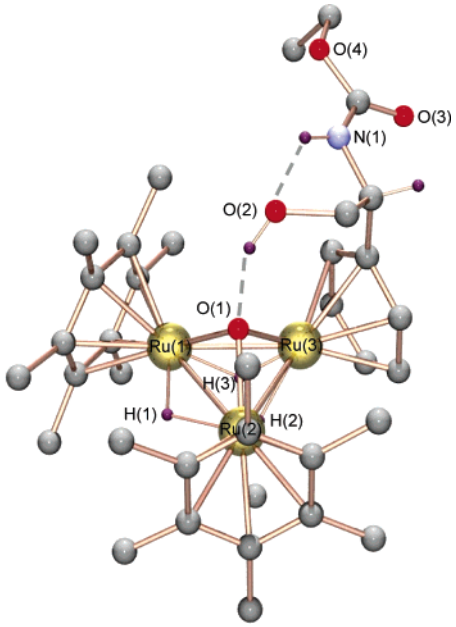


Figure 6. POV-Ray view[37] of the enantiopure trinuclear cluster cation (*S*)-$[H_3Ru_3(C_6Me_6)_2\{C_6H_5$(CH(NHCO$_2$Et)-CH$_2$OH)}(O)]$^+$ (**12**). Anion, solvent molecules, and hydrogen atoms, except for the amide proton, the hydroxide proton, the hydride ligands, and the α-hydrogen atom of the chiral moiety, are omitted for clarity.

(silica gel, dichloromethane/acetone as eluant) or by fractional crystallization of the tetrafluoroborate salts.

Isolation and Characterization of a Ruthenium Cluster Cation with Framework Chirality as Well as a Chiral Substituent at One of the Arene Ligands and Separation of the Diastereomers without Racemization of the Chiral Side Chain. Having shown that the presence of a NH group and an ester function is beneficial for the chromatographic separation of the two fractions of **8** and that, on the other hand, a methylene group at the α-position in the chiral auxiliary group prevents the racemization of the asymmetric carbon atom, we decided to esterify the alcohol function in **10** prior to coordination. Thus, **10** reacts with isobutyric acid at room temperature in the presence of coupling reagents to give the ester (*R*)-C_6H_5(CH(NHCO$_2$Et)CH$_2$OCOPr^i) (**14**) in good yield (see Scheme 6).

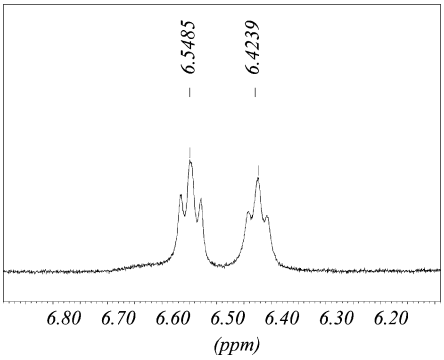
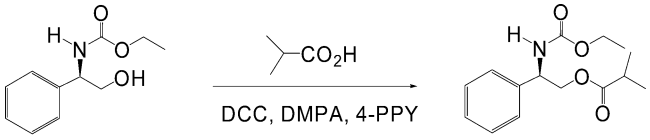


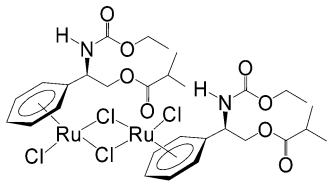
Figure 7. Enlarged ^1H NMR spectrum (CD_2Cl_2, 400 MHz) (O*H* signals) of the mixture of (*S*,*S*)-**13** and (*R*,*S*)-**13**. The spectrum shows two well-defined sharp triplets centered at 6.55 and 6.42 ppm, suggesting that both diastereomers form, in solution, a strong intramolecular hydrogen bond between the oxo cap and the proton of the OH group, as is the case in **12**.

Scheme 6. Synthesis of the Chiral Ligand (*R*)-C_6H_5(CH(NHCO$_2$Et)CH$_2$OCOPr^i) (14), Containing a NH Group as Well as an Ester Function in the *β*-Position



10 **14**

The new ligand (*R*)-C_6H_5(CH(NHCO$_2$Et)CH$_2$OCOPr^i) (**14**) was used to prepare the new enantiopure dimer (*S*,*S*)-[Ru{C_6H_5(CH(NHCO$_2$Et)CH$_2$OCOPr^i)}Cl$_2$]$_2$ (**15**),



15

again by a naphthalene displacement reaction in [Ru(COD)($C_{10}H_8$)], followed by reaction with HCl. Once again, the formal change from *R* to *S* is only due to the priority change in the Cahn−Ingold−Prelog rules, caused by the coordination of the ligand to the ruthenium atom. As expected, the ^1H and ^{13}C NMR spectra of **15** in CD_2Cl_2 display only a single set of signals.

Complex **15** is used as a chiral building block to prepare chiral trinuclear arene ruthenium cluster cations. Once again, to ensure that the asymmetric carbon atom does not racemize during the reaction with the dinuclear complex, we prepared at first the trinuclear cluster cation (*S*)-[$H_3Ru_3(C_6Me_6)_2${C_6H_5(CH(NHCO$_2$Et)CH$_2$OCOPr^i)}(O)]$^+$ (**16**), containing an achiral Ru_3O framework and only the chiral carbon atom in the side chain. Complex **15**, dissolved in water, gives rise to the in situ formation of the mononuclear aqua complex (*S*)-[Ru{C_6H_5(CH(NHCO$_2$Et)CH$_2$OCOPr^i)}(H$_2$O)$_3$]$^{2+}$, which reacts with the dinuclear complex [$H_3Ru_3(C_6Me_6)_2$]$^+$ to give the expected cation **16**, isolated as the hexafluorophosphate salt. Crystals of [**16**][PF$_6$] suitable for single-crystal X-ray structure analysis were easily obtained by

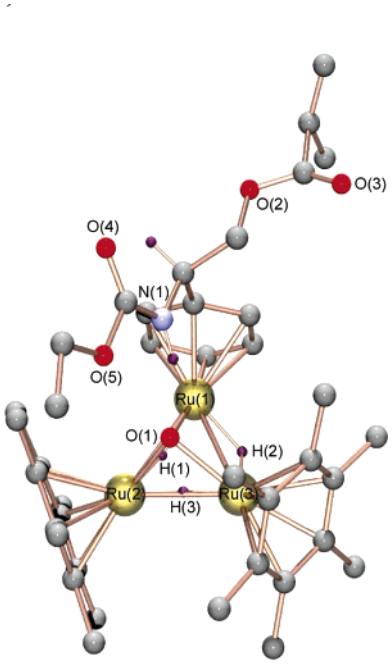


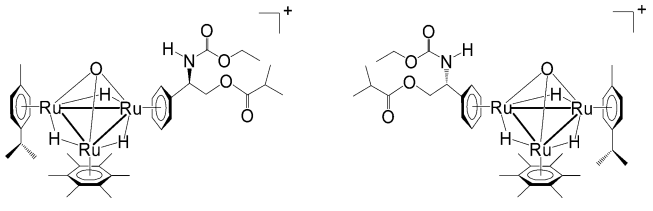
Figure 8. POV-Ray view[37] of the enantiopure trinuclear cluster cation (*S*)-[$H_3Ru_3(C_6Me_6)_2${C_6H_5(CH(NHCO$_2$Et)-CH$_2$OCOPr^i)}(O)]$^+$ (**16**). Anion, solvent molecules, and hydrogen atoms, except for the *NH* proton, the hydride ligands, and the α-hydrogen atom of the chiral moieties, are omitted for clarity.

the slow diffusion of hexane in a CH_2Cl_2 solution of the salt. The X-ray analysis shows that only the expected *S* enantiomer is present in the crystal (Figure 8).

Given that the crystal of [**16**][PF$_6$] selected for single-crystal X-ray structure analysis contains only the *S* enantiomer, we recorded the CD spectra of the bulk [**16**]-[PF$_6$] and of the single crystal used for X-ray analysis (Figure 9), to make sure that the total amount of the product obtained is enantiopure.

Surprisingly, both spectra show only weak absorption bands. However, the bulk of [**16**][PF$_6$] shows the same absorption and intensity as the single crystal of [**16**]-[PF$_6$] used for X-ray structure analysis. Since the single crystal is enantiopure, it can be concluded that the bulk of [**16**][PF$_6$] obtained is also enantiopure.

Having thus confirmed that the asymmetric carbon atom in **15** does not racemize in the reaction with [$H_3Ru_3(C_6Me_6)_2$]$^+$, we now reacted the enantiopure dimer (*S*,*S*)-[Ru{C_6H_5(CH(NHCO$_2$Et)CH$_2$OCOPr^i)}Cl$_2$]$_2$ (**15**) with the trihydrido complex **4**, to prepare the diastereomeric cluster cations (S_{Ru_3O},S_C)-[H_3Ru_3{C_6H_5(CH-(NHCO$_2$Et)CH$_2$OCOPr^i)}(C_6Me_6)(*p*-Pr^{i}MeC$_6$H$_4$)(O)]$^+$ ((*S*,*S*)-**17**) and (R_{Ru_3O},S_C)-[H_3Ru_3{C_6H_5(CH(NHCO$_2$Et)-



(*S*,*S*)-**17** (*R*,*S*)-**17**

CH$_2$OCOPr^i)}(C_6Me_6)(*p*-Pr^{i}MeC$_6$H$_4$)(O)]$^+$ ((*R*,*S*)-**17**), presenting both a chiral Ru_3O framework and an asym-

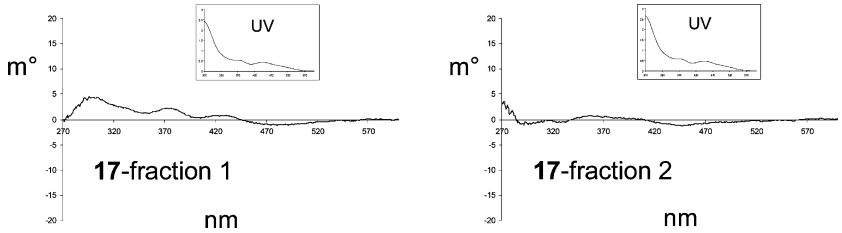


Figure 9. CD spectra (in MeOH) of [**16**][PF_6] (bulk) and of the single crystal of [**16**][PF_6] used for X-ray structure analysis. Both spectra display the same weak absorption bands. The corresponding UV spectra are shown in the frame.

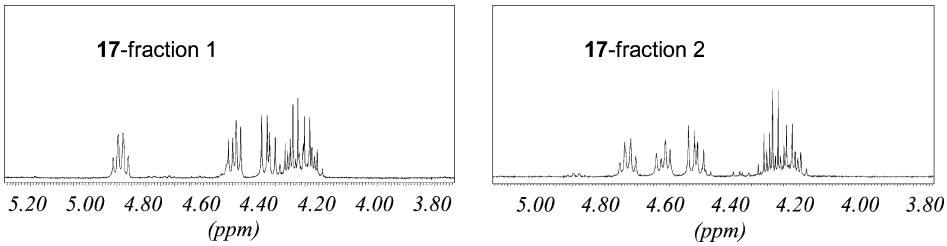


Figure 10. Enlarged ^{1}H NMR spectra (CD_2Cl_2, 400 MHz) of the first fraction (left) and the second fraction (right) isolated from the reaction of **4** with the chiral dimer (*S*,*S*)-[Ru{C_6H_5(CH(NHCO$_2$Et)CH_2OCOPr^i)}Cl_2]$_2$ (**15**). These spectra show the diastereopurity of the first fraction ((*S*,*S*)-**17** or (*R*,*S*)-**17**), whereas the second fraction ((*R*,*S*)-**17** or (*S*,*S*)-**17**) contains a small amount (not more than 5%) of fraction 1.

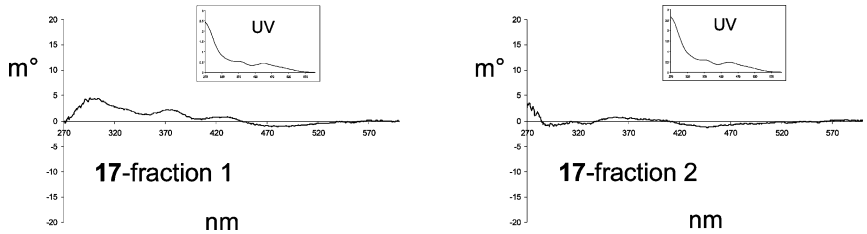


Figure 11. CD spectra (in MeOH) of the first ((*S*,*S*)-**17** or (*R*,*S*)-**17**) and the second ((*R*,*S*)-**17** or (*S*,*S*)-**17**) fraction isolated from the reaction of complex **4** with the chiral dimer (*S*,*S*)-[Ru{C_6H_5(CH(NHCO$_2$Et)CH_2OCOPr^i)}Cl_2]$_2$ (**15**) by preparative thin-layer chromatography. The corresponding UV spectra are shown in the frame.

metric carbon atom in the (*R*)-C_6H_5(CH(NHCO$_2$Et)-CH_2OCOPr^i) ligand.

As expected, it is possible to separate **17** into the two diastereomers (*S*,*S*)-**17** and (*R*,*S*)-**17** by preparative thin-layer chromatography on silica gel, using a CH_2Cl_2/acetone mixture as eluant. The two diastereomerically pure fractions show the same mass spectrum with a molecular peak centered at *m/z* 899. The ^{1}H NMR spectra of both fractions show the same multiplicity, but different chemical shifts, as shown in Figure 10.

Neither the tetrafluoroborate nor the hexafluorophosphate salts of (*S*,*S*)-**17** and (*R*,*S*)-**17** give crystals suitable for X-ray crystal analysis; therefore, the absolute configurations cannot be determined unequivocally. This means that, although we have clearly separated the two diastereomers of **17** into two fractions, we do not know which one of the two fractions contains the diastereomer (*S*,*S*)-**17** and which one contains the diastereomer (*R*,*S*)-**17**. Having shown that the asymmetric carbon atom in the chiral side chain does not racemize during the synthesis of **16**, it can be assumed that racemization does not take place during the synthesis of **17**, either. To make sure that both diastereomers are optically active as expected, we recorded the CD spectra of both fractions (see Figure 11).

Both spectra show several CD signals, suggesting that both diastereomers are indeed optically active. However, the weak intensity prompted us to analyze both fractions additionally by vibrational circular dichroism

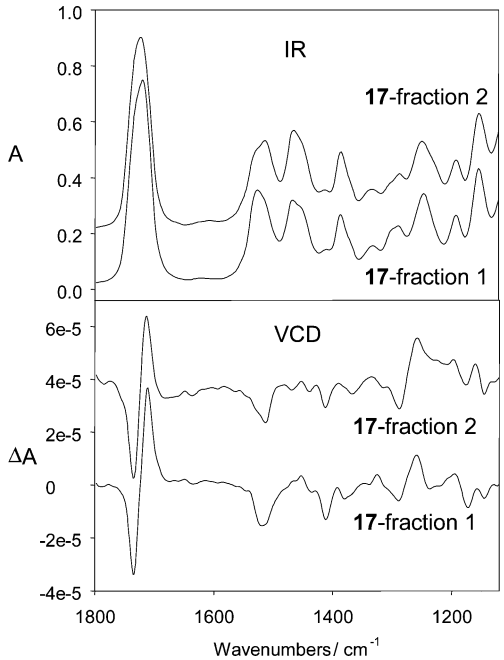


Figure 12. VCD spectra (in CD_2Cl_2) of the first ((*S*,*S*)-**17** or (*R*,*S*)-**17**) and the second ((*R*,*S*)-**17** or (*S*,*S*)-**17**) fraction isolated from the reaction of complex **4** with the chiral dimer (*S*,*S*)-[Ru{C_6H_5(CH(NHCO$_2$Et)CH_2OCOPr^i)}Cl_2]$_2$ (**15**) by preparative thin-layer chromatography. The corresponding IR spectra are shown in the frame above.

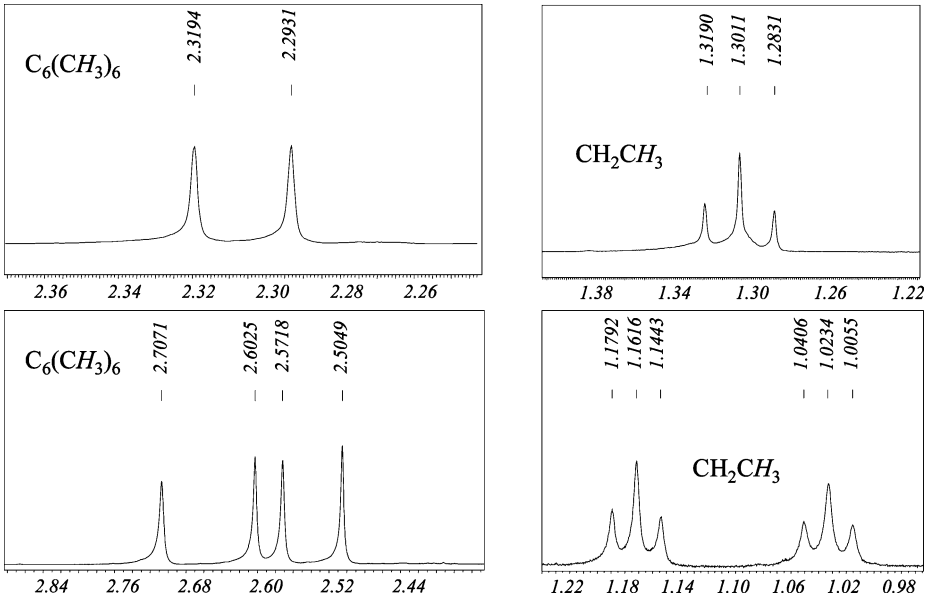


Figure 13. Selected enlargements of the ^{1}H NMR spectrum of **9** without [Eu(hfc)$_3$] (above) and of the ^{1}H NMR spectrum of **9** in the presence of 0.5 equiv of [Eu(hfc)$_3$] (below). As expected, after addition of the chiral shift reagent, both signals are shifted and duplicated, showing the presence of both enantiomers (*S*)-**9** and (*R*)-**9** in a 1:1 ratio, due to the fact that **9** is racemic.

(VCD) spectroscopy.[31] The VCD spectra of both diastereomers were recorded between 1800 and 1200 cm^{-1}, and the resulting spectra are shown in Figure 12.

Both fractions show significant VCD signals. The most prominent bands slightly above 1700 cm^{-1}, one negative and one positive, are associated with the C=O stretching vibrations. The VCD spectra of the two diastereomers are quite similar, in contrast to the CD spectra, which are significantly different. This indicates that the VCD is mainly sensitive to the chiral side chain, which has the same absolute configuration for both diastereomers. The result furthermore confirms that the absolute configuration of the side chain is retained during the synthesis of (*S*,*S*)-**17** and (*R*,*S*)-**17**.

Having shown by CD and VCD spectroscopy that both diastereomers (*S*,*S*)-**17** and (*R*,*S*)-**17** are indeed optically active, we decided to determine the enantiomeric purities of both fractions by NMR spectroscopy using a chiral lanthanide shift reagent.[32] NMR spectroscopy in the presence of chiral shift reagents represents a particularly well-adapted technique for determining the enantiomeric purity of chiral molecules.[33] Chiral lanthanide shift reagents, such as europium derivatives, have been used since the 1970s, and they form, via interaction with the electron donor sites, a weak addition complex with a large variety of compounds. Barton and Nowick were the first to report the use of chiral europium shift reagents for the determination of the enantiomeric purity of Ru(II) cationic complexes.[34]

We determined the enantiomeric purity of both fractions (*S*,*S*)-**17** and (*R*,*S*)-**17** by ^{1}H NMR spectroscopy in the presence of the commercially available chiral complex europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] ([Eu(hfc)$_3$]). In the presence of the chiral shift reagent, (*S*,*S*)-**17** should form only the (S_{Ru_3O},S_C)-(+)-[Eu(hfc)$_3$] complex and (*R*,*S*)-**17** only the (R_{Ru_3O},S_C)-(+)-[Eu(hfc)$_3$] complex, if both fractions are enantiopure. Therefore, the ^{1}H NMR spectra of (*S*,*S*)-**17** and (*R*,*S*)-**17** plus [Eu(hfc)$_3$] should display a single set of signals with a displacement of the original signals. However, a single set of signals in the NMR spectrum does not prove unequivocally the enantiopurity of a chiral compound: this could be due to the fact that the chiral shift reagent is not capable of binding to any of the functional groups present within the chiral molecule. Consequently, to make sure that the complex [Eu(hfc)$_3$] interacts adequately with (*S*,*S*)-**17** and (*R*,*S*)-**17**, we decided to compare the spectra to that of [Eu(hfc)$_3$] with the racemic cluster cation [$H_3Ru_3(C_6Me_6)_2${C_6H_5-(CH(NHCOMe)CO_2Et)}(O)]$^+$ (**9**). Indeed, the addition of [Eu(hfc)$_3$] to an NMR sample containing **9** causes a splitting of all NMR signals into two sets with a 1:1 ratio. A series of ^{1}H NMR spectra of [**9**][BF_4] in the presence of [Eu(hfc)$_3$] was recorded in CD_2Cl_2, the molar ratio of the chiral europium complex with respect to the substrate increasing from 0.1 to 1.2, a typical result being shown in Figure 13.

From this experiment, we can conclude that the complex [Eu(hfc)$_3$] interacts with **9** and it can be assumed that the same interactions take also place with (*S*,*S*)-**17** and (*R*,*S*)-**17**. Thus, the same NMR study was performed by starting from both diastereomeric cluster cations (*S*,*S*)-**17** and (*R*,*S*)-**17**, to determine their enantiomeric purity, having already shown their diastereopurity. Figure 14 shows the result in the area of the hexamethylbenzene signals. From this experiment, we can conclude that both diastereomers (*S*,*S*)-**17** and (*R*,*S*)-**17** are enantiomerically pure.

From CD and VCD spectroscopy and from NMR experiments in the presence of a chiral shift reagent, we conclude unequivocally that both cluster cations (*S*,*S*)-**17** and (*R*,*S*)-**17** containing a chiral Ru_3O frame-

(31) Nafie, L. A. *Annu. Rev. Phys. Chem.* **1997**, *48*, 357.
(32) (a) Morril, T. C. *Lanthanide Shift Reagents in Stereochemical Analysis*; VCH: New York, 1986. (b) Sullivan, G. R. *Top. Stereochem.* **1978**, *10,* 287.
(33) Parker, D. *Chem. Rev.* **1991**, *91*, 1441.
(34) Barton, J. K.; Nowick, J. S. *J. Chem. Soc., Chem. Commun.* **1984**, 1650.

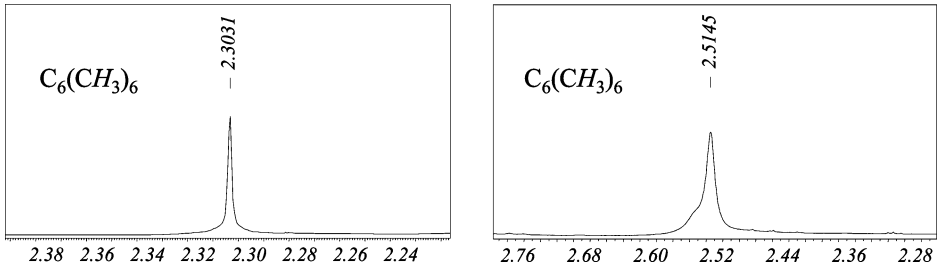
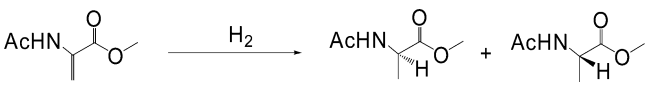


Figure 14. Selected enlargement of the ^{1}H NMR spectrum of the first fraction ((*S*,*S*)-**17** or (*R*,*S*)-**17**) without [Eu(hfc)$_3$] (left) and of the ^{1}H NMR spectrum of the same fraction in the presence of 0.5 equiv of [Eu(hfc)$_3$] (right). After addition of the chiral shift reagent, the signal is shifted and widened but not duplicated, showing the enantiopurity of the first fraction. A similar result was obtained with the second fraction in the presence of 0.5 equiv of [Eu(hfc)$_3$].

work and a chiral substituent at one of the arene ligands have been isolated as enantiopure diastereomers. In other words, we have been able to resolve the racemic mixture of the two chiral hydrophobic pockets spanned by the three different arene ligands in $[H_3Ru_3(C_6H_5R)(C_6Me_6)(p\text{-}Pr^iMeC_6H_4)(O)]^+$ into enantiomerically pure diastereomers. The ultimate goal would now consist in cleaving off the chiral auxiliary group in the side chain, to get the two Ru_3O framework enantiomers. Unfortunately, the chiral sidearm tethered to one of the arene ligands and containing the asymmetric carbon atom in (*S*,*S*)-**17** and (*R*,*S*)-**17** could not be removed in our hands, either by hydrogenolysis of the N-benzylic position under H_2 in the presence of Pd/C (50 bar of H_2, 110 °C in ethanol, 10 wt % Pd/C) or by a ligand exchange reaction (140 °C in 2-phenylethanol).

However, even the enantiomerically pure diastereomers can be used to test the intact cluster catalysis concept by hydrogenation of a prochiral substrate. Although they cannot give evidence for this mechanistic concept, they can give evidence against it: if the intact Ru_3O cluster is the catalytically active species, the catalytic conversions taking place inside the asymmetric hydrophobic pocket, we could observe asymmetric induction and thus an enantiomeric excess for the catalytic product. Such a result, however, will not be unequivocal, since not only do we have a chiral Ru_3O framework we also have a chiral auxiliary group in the diastereomers (*S*,*S*)-**17** and (*R*,*S*)-**17**. On the other hand, if no enantiomeric excess is found in the catalytic hydrogenation of a prochiral substrate despite the chirality of the hydrophobic pocket in (*S*,*S*)-**17** and (*R*,*S*)-**17**, the supramolecular cluster catalysis mechanism is unlikely.

Catalytic Activity of Both Enantiopure Diastereomeric Clusters (*S*,*S*)-17 and (*R*,*S*)-17 for the Hydrogenation of a Prochiral Substrate in Aqueous Solution. We decided to use methyl 2-acetamidoacrylate, a classical prochiral olefin used to test chiral hydrogenation catalysts, as a substrate to test the enantioselectivity of (*S*,*S*)-**17** and (*R*,*S*)-**17**.



In aqueous solution, both cluster cations (*S*,*S*)-**17** and (*R*,*S*)-**17** show a very weak catalytic activity for the hydrogenation of methyl 2-acetamidoacrylate under 50 bar of H_2 at room temperature (TON = 40 for the first fraction and 45 for the second fraction), as compared to other catalysts used for the same catalytic reaction.[35] Moreover, no enantiomeric excess was observed (ee < 0.2%), suggesting that (*S*,*S*)-**17** and (*R*,*S*)-**17** do not act as the true catalytic species but only as precursors for metallic nanoparticles, in line with kinetic studies and poisoning experiments published elsewhere.[12] However, it is important to remember that, in asymmetric catalysis, the presence of an optically active organometallic catalyst does not always give rise to enantioenriched products.

Conclusion

The results of this study, for which we synthesized and characterized the first homometallic tetrahedral clusters with intrinsic framework chirality, suggest that, in hydrogenation reactions catalyzed in the presence of the water-soluble cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ (**1**), the intact triruthenium cluster is not the actual catalyst, despite the hydrophobic pocket spanned by the three arene ligands suitable to accommodate small organic substrates, since there is no asymmetric induction in the hydrogenation of the prochiral substrate methyl 2-acetamidoacrylate, catalyzed by both optically active cluster cations (S_{Ru_3O},S_C)-$[H_3Ru_3\{C_6H_5(CH(NHCO_2Et)CH_2OCOPr^i)\}(C_6Me_6)(p\text{-}Pr^iMeC_6H_4)(O)]^+$ ((*S*,*S*)-**17**) and (R_{Ru_3O},S_C)-$[H_3Ru_3\{C_6H_5(CH(NHCO_2Et)CH_2OCOPr^i)\}(C_6Me_6)(p\text{-}Pr^iMeC_6H_4)(O)]^+$ ((*R*,*S*)-**17**). This is in line with kinetic studies, transition electron microscopic studies, and high-pressure in situ NMR studies,[12] which suggest that small quantities of ruthenium(0) nanoparticles formed from **1** under hydrogen pressure are the true catalytic species in hydrogenation reactions in the presence of **1**. However, these results should not be generalized: if in the case of benzene hydrogenation in the presence of **1** and water, the catalytically active species turned out to be ruthenium(0) nanoparticles formed in small quantities under catalytic conditions, this does not mean that in other catalytic processes intact metal clusters do not function as the active species.

Experimental Section

General Considerations. All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk

(35) (a) Landis, C. R.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1746. (b) Collot, J.; Gradinaru, J.; Humbert, N.; Skander, M.; Zocchi, A.; Ward, T. R. *J. Am. Chem. Soc.* **2003**, *125*, 9030.

techniques, unless indicated otherwise. Acetone was distilled over K_2CO_3, and acetonitrile and dichloromethane were purified, dried, and deoxygenated by distillation over CaH_2 under N_2. Tetrahydrofuran and diethyl ether were purified, dried and deoxygenated by distillation over Na/benzophenone under N_2. All other organic solvents and bidistilled water were deoxygenated by bubbling through a stream of N_2 prior to use. Room temperature (RT) corresponds to about 20 °C. Silica gel used for column chromatography (63−200, 60 Å) was purchased from Chemie Brunschwig AG, and silica gel G used for preparative thin-layer (20 × 20 cm) chromatography was purchased from Macherey-Nagel GmbH. Preparative thin-layer chromatography on silica gel, as well as column chromatography on silica gel, were performed in air. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. NMR spectra were recorded using a Bruker 400 MHz spectrometer and treated with WINNMR. Solvent shift references for ^{1}H NMR: acetone-d_6 δ_H 2.05, DMSO-d_6 δ_H 2.50, $CDCl_3$ δ_H 7.26, CD_2Cl_2 δ_H 5.36. Solvent shift references for ^{13}C NMR: acetone-d_6 δ_C 19.50, DMSO-d_6 δ_C 39.52, $CDCl_3$ δ_C 77.20, CD_2Cl_2 δ_C 54.20. The mass spectra were recorded at the University of Fribourg (Fribourg, Switzerland) by Prof. Titus Jenny. Microanalyses were carried out by the Mikroelementaranalytisches Laboratorium, ETH Zürich (Zürich, Switzerland). UV/vis absorption spectra were recorded on an Uvikon 930 spectrophotometer using precision cells made of quartz (10 mm) and exploited with Excel. Circular dichroism (CD) spectra were recorded on a JASCO J-710 spectropolarimeter (bandwidth 2 nm, step resolution 0.5 nm, response time 4 s, three accumulations) and exploited with Excel. Vibrational circular dichroism (VCD) spectra were recorded at 8 cm^{-1} in a cell equipped with CaF_2 windows and a 0.1 mm Teflon spacer. Solutions were made from 6 mg of sample in 300 μL of CD_2Cl_2. A VCD spectrum of the neat solvent served as reference and was subtracted from the sample VCD spectrum. For both sample and reference ca. 12 000 interferograms were averaged. The complexes $[Ru(C_6Me_6)Cl_2]_2$,[19] $[Ru(p\text{-}Pr^iMeC_6H_4)Cl_2]_2$,[19] $[Ru(C_6H_6)Cl_2]_2$,[23] $[Ru(COD)(C_{10}H_8)]$,[26a] (*S*,*S*)-$[Ru\{C_6H_5(CH(NHCOMe)CO_2Et)\}Cl_2]_2$,[28] and $[H_3Ru_2(C_6Me_6)_2]^+$ [36] were prepared according to literature procedures. Although the synthesis of the ligand **10** was already described in the literature,[29] the method employed here was slightly different. All other chemicals are commercially available and were used without further purification.

Syntheses and Characterizations. Synthesis of $[H_3Ru_2(C_6Me_6)(p\text{-}Pr^iMeC_6H_4)]^+$ (4). In a 250 mL brown glass Schlenk tube, 200 mg (0.30 mmol) of $[Ru(C_6Me_6)Cl_2]_2$ and 400 mg (0.65 mmol) of $[Ru(p\text{-}Pr^iMeC_6H_4)Cl_2]_2$ were mixed with a solution of 600 mg (1.92 mmol) of Ag_2SO_4 in 40 mL of water. The suspension was stirred at room temperature until the orange solids were completely dissolved to give a yellow mixture of $[Ru(C_6Me_6)(H_2O)_3]^{2+}$ and $[Ru(p\text{-}Pr^iMeC_6H_4)(H_2O)_3]^{2+}$ (around 1 h). The white precipitate of AgCl that formed was removed from the aqueous solution by filtration through filter pulp. The resulting clear yellow filtrate was cooled in an ice bath for 30 min. In a separate 50 mL Schlenk tube, 150 mg (3.95 mmol) of $NaBH_4$ was dissolved in 15 mL of water at room temperature. After it was stirred for 5 min, the $NaBH_4$ solution was transferred very slowly through a cannula into the cooled $[Ru(C_6Me_6)(H_2O)_3][SO_4]$/$[Ru(p\text{-}Pr^iMeC_6H_4)(H_2O)_3][SO_4]$ solution (ice bath). The solution turned black, due to the formation of $[H_3Ru_2(C_6Me_6)_2]^+$, $[H_3Ru_2(p\text{-}Pr^iMeC_6H_4)_2]^+$, and the expected cation $[H_3Ru_2(C_6Me_6)(p\text{-}Pr^iMeC_6H_4)]^+$ (**4**). The resulting solution was immediately filtered through filter pulp under argon to remove insoluble black particles. A large excess of $NaBF_4$ was then added in order to precipitate $[H_3Ru_2(C_6Me_6)_2][BF_4]$, $[H_3Ru_2(p\text{-}Pr^iMeC_6H_4)_2][BF_4]$, and $[H_3Ru_2(C_6Me_6)(p\text{-}Pr^iMeC_6H_4)][BF_4]$ ([**4**][BF_4]). The dark precipitate was centrifugated in air (1500 rpm, 10 min), and the aqueous solution was removed from the centrifuge tube with a glass pipet. The black solid was dissolved in CH_2Cl_2 and again filtered through filter pulp, to eliminate excess $NaBF_4$. Then the methylene chloride solution was concentrated and subjected to column chromatography on silica gel using CH_2Cl_2/acetone (10/0.1 to 10/1) as eluant. The first colored fraction containing $[H_3Ru_2(C_6Me_6)_2][BF_4]$ and the expected [**4**][BF_4] (appearing red in the silica gel under light) was collected, the second fraction containing $[H_3Ru_2(p\text{-}Pr^iMeC_6H_4)_2][BF_4]$ (appearing green in the silica gel under light) being discarded. After evaporation to dryness of the first fraction, the green residue was dissolved in 5 mL of CH_2Cl_2 and subjected to preparative thin-layer chromatography on silica gel using CH_2Cl_2/acetone (10/1) as eluant. [**4**][BF_4] was extracted from the second green band (the most important) with acetone. Evaporation of acetone under vacuum gave a green powder containing 95% of [**4**][BF_4] and 5% of residual $[H_3Ru_2(C_6Me_6)_2][BF_4]$ (shown by ^{1}H NMR). This starting material was used without further purification for the continuation of the experiments. Yield: 115 mg (32%). Anal. Calcd (found) for $C_{22}H_{35}BF_4Ru_2$: C, 44.90 (44.77); H, 5.99 (5.99).

Spectroscopic Data for 4. ^{1}H NMR (400 MHz, 2, 20 °C): δ 5.83 (d, 2H, ^3J = 6.18 Hz, H_{ar}), 5.75 (d, 2H, ^3J = 6.18 Hz, H_{ar}), 2.59 (hept, 1H, ^3J = 6.82 Hz, C*H*$(CH_3)_2$), 2.41 (s, 18H, $C_6(CH_3)_6$), 2.27 (s, 3H, $C_6H_4CH_3$), 1.28 (d, 6H, ^3J = 6.82 Hz, $CH(CH_3)_2$), −15.52 (s, 3H, Ru−*H*). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6, 20 °C): δ 108.80, 99.97, 96.24, 83.53, 82.28 (C_{ar}), 32.64 ($CH(CH_3)_2$), 24.19 ($CH(CH_3)_2$), 20.82 ($C_6H_4CH_3$), 18.47 ($C_6(CH_3)_6$). ESI-MS (in acetone): 503 $[M + 2H]^+$.

Synthesis of the Racemic Mixture of (S_{Ru_3O})-$[H_3Ru_3(C_6H_6)(C_6Me_6)(p\text{-}Pr^iMeC_6H_4)(O)]^+$ ((*S*)-5) and (R_{Ru_3O})-$[H_3Ru_3(C_6H_6)(C_6Me_6)(p\text{-}Pr^iMeC_6H_4)(O)]^+$ ((*R*)-5). At room temperature, 60 mg (0.102 mmol) of [**4**][BF_4] was dissolved in a mixture of 25 mL of acetone and 10 mL of water. A 65 mg portion (0.130 mmol) of solid $[Ru(C_6H_6)Cl_2]_2$ was added to the resulting clear green solution. The mixture was stirred at room temperature for 2 days. During this time the color of the solution changed from deep green to red. The red solution containing (*S*)-**5** and (*R*)-**5** was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and filtered through Celite in order to remove insoluble particles. Then the methylene chloride solution was concentrated to about 5 mL under vacuum. The resulting concentrate was subjected to preparative thin-layer chromatography on silica gel using CH_2Cl_2/acetone (2/1) as eluant. The racemate was extracted with acetone from the main red band. Evaporation of acetone under vacuum gave a red powder containing 95% of [**5**][BF_4] and 5% of $[H_3Ru_2(C_6Me_6)_2(C_6H_6)(O)][BF_4]$ as byproduct. Yield: 35 mg (44%). Anal. Calcd (found) for $C_{28}H_{41}OBF_4Ru_3$: C, 42.92 (42.64); H, 5.27 (5.49). Single crystals suitable for X-ray structure analysis were obtained of the hexafluorophosphate salt, accessible by addition of KPF_6 to an aqueous solution of [**5**][BF_4]. They were grown by slow diffusion of hexane into an acetone solution of [**5**][BF_4].

Spectroscopic Data for the Mixture of (*S*)-5 and (*R*)-5. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ 5.53 (s, 6H, C_6H_6), 5.48 (dd, 2H, ^3J = 9.17 Hz, ^4J = 5.75 Hz, H_{ar}), 5.37 (dd, 2H, ^3J = 9.17 Hz, ^4J = 5.75 Hz, H_{ar}), 2.52 (hept, 1H, ^3J = 6.82 Hz, C*H*$(CH_3)_2$), 2.28 (s, 18H, $C_6(CH_3)_6$), 2.20 (s, 3H, $C_6H_4CH_3$), 1.30 (d, 3H, ^3J = 6.82 Hz, $CH(CH_3)_2$), 1.28 (d, 3H, ^3J = 6.82 Hz, $CH(CH_3)_2$), −18.80 (t, 1H, ^2J = 4.12 Hz, Ru−*H*), −18.85 (t, 1H, ^2J = 4.12 Hz, Ru−*H*), −19.12 (t, 1H, ^2J = 4.12 Hz,

(36) Jahncke, M.; Neels, A.; Stoekli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1998**, *561*, 227. The complex was prepared according to the procedure described herein, and for further purification, it was subjected to column chromatography on silica gel using CH_2Cl_2/acetone as eluant (10/1 in the case of its tetrafluoroborate salt and 10/0.5 in the case of its hexafluorophosphate salt), the expected salt being isolated from the first (green) fraction. It is important to note that the tetrafluoroborate and hexafluorophosphate salts were obtained from the aqueous solution by precipitation after addition of an excess of $NaBF_4$ or KPF_6, respectively (analogously to the synthesis of **4** described in the present paper).

(37) Buck, D. K.; Collins, A. A. Persistence of Vision Ray-Tracer, POV−Ray Version 3.1.

Ru−*H*). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 20 °C): δ 107.83, 98.40, 95.43, 90.35, 83.63, 83.35, 82.98, 82.07 (C_{ar}), 32.72 ($CH(CH_3)_2$), 23.95 ($CH(CH_3)_2$), 23.60 ($CH(CH_3)_2$), 20.05 ($C_6H_4CH_3$), 17.94 ($C_6(CH_3)_6$). ESI-MS (in acetone): 698 $[M + 2H]^+$.

Synthesis of (*R,R*)-[Ru(1-phenylethanol)Cl$_2$]$_2$ (6). In a closed pressure Schlenk tube was dissolved 1.15 g (3.412 mmol) of [Ru(COD)($C_{10}H_8$)] in 100 mL of THF. To the resulting red solution were slowly added 6 mL (49.70 mmol) of (*R*)-1-phenylethanol and 2 mL of acetonitrile. The mixture was stirred at room temperature under pressure of argon (around 2 bar) for 2 days. During this time the color of the solution changed from red to brown. The solution was then concentrated to half of the volume under reduced pressure and siphoned under argon onto a column of alumina (neutral, activity III, approximately 15 cm long and 3 cm in diameter) covered with sand. Elution with THF gave a clear yellow-brown solution, which was evaporated to dryness. The resulting red-brown oily residue containing (*R*)-[Ru(COD)(1-phenylethanol)] was dissolved in 40 mL of acetone, and 2 mL of concentrated aqueous HCl was added dropwise at room temperature. An orange precipitate appeared after the addition of the first drops. The mixture was then stirred at room temperature for an additional 1 h. The orange precipitate was filtered, washed with 20 mL of acetone and 30 mL of diethyl ether, and dried under vacuum to give **6** as an orange powder. Yield: 620 mg (62%). Anal. Calcd (found) for $C_{16}H_{20}Cl_4O_2Ru_2$: C, 32.67 (32.89); H, 3.43 (3.43).

Spectroscopic Data for 6. ^1H NMR (400 MHz, DMSO-d_6, 20 °C): δ 6.01 (m, 3H, H_{ar}), 5.93 (m, 1H, H_{ar}), 5.84 (m, 1H, H_{ar}), 5.22 (br, 1H, CHO*H*), 4.67 (m, 1H, C*H*CH$_3$), 1.40 (d, 3H, ^3J = 6.65 Hz, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 20 °C): δ 108.99, 88.78, 88.48, 86.11, 85.21, 83.86 (C_{ar}), 66.23 (*C*HCH$_3$), 24.08 (CH*C*H$_3$). ESI-MS (in MeOH/EtOH): 545 [M − CH(OH)CH$_3$ + 2H]$^+$.

Synthesis of the Diastereomeric Mixture of (S_{Ru_3O},R_C)-[H$_3$Ru$_3$(1-phenylethanol)(C$_6$Me$_6$)(*p*-Pr^{i}MeC$_6$H$_4$)(O)]$^+$ ((*S,R*)-7) and (R_{Ru_3O},R_C)-[H$_3$Ru$_3$(1-phenylethanol)(C$_6$Me$_6$)(*p*-Pr^{i}MeC$_6$H$_4$)(O)]$^+$ ((*R,R*)-7). At room temperature, 150 mg (0.255 mmol) of [**4**][BF_4] was dissolved in a mixture of 40 mL of acetone and 15 mL of water. A 180 mg portion (0.306 mmol) of solid **6** was added to the resulting clear green solution. The mixture was stirred at room temperature for 6 days. During this time the color of the solution changed from deep green to red. The red solution containing (*S,R*)-**7** and (*R,R*)-**7** was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and filtered through Celite in order to remove insoluble particles. Then the methylene chloride solution was concentrated to about 5 mL in vacuo. The resulting concentrate was subjected to preparative thin-layer chromatography on silica gel using CH_2Cl_2/acetone (2/1) as eluant (two successive elutions on the same plate). The expected diastereomeric mixture was extracted with acetone from the main red band. Evaporation of acetone under vacuum gave a mixture of [(*S,R*)-**7**][BF_4] and [(*R,R*)-**7**][BF_4] as a red powder. Yield: 65 mg (31%). Anal. Calcd (found) for $C_{30}H_{45}BF_4O_2Ru_3 \cdot H_2O$: C, 42.61 (42.71); H, 5.60 (5.55). Single crystals suitable for X-ray diffraction analyses were grown by slow diffusion of hexane into an acetone solution of [(*S,R*)-**7**][BF_4] and [(*R,R*)-**7**][BF_4].

Spectroscopic Data for the Mixture of (*S,R*)-7 and (*R,R*)-7. ^1H NMR (400 MHz, acetone-d_6, 20 °C): δ 6.20 (d, 1H, J = 5.75 Hz, H_{ar}), 6.16 (d, 1H, J = 6.60 Hz, H_{ar}), 6.01 (t, 1H, J = 5.75 Hz, H_{ar}), 5.97 (t, 1H, J = 5.75 Hz, H_{ar}), 5.87 (m, 4H, H_{ar}), 5.64 (d, 2H, J = 5.12 Hz, H_{ar}), 5.61 to 5.53 (m, 6H, H_{ar}), 5.48 (d, 2H, J = 5.96 Hz, H_{ar}), 5.26 (br, 1H, CHO*H*), 5.21 (br, 1H, CHO*H*), 4.45 (m, 2H, C*H*CH$_3$), 2.60 (m, 2H, C*H*(CH$_3$)$_2$), 2.35 (s, 18H, C$_6$(C*H*$_3$)$_6$), 2.33 (s, 18H, C$_6$(C*H*$_3$)$_6$), 2.22 (s, 3H, C$_6$H$_4$C*H*$_3$), 2.19 (s, 3H, C$_6$H$_4$C*H*$_3$), 1.47 (d, 3H, ^3J = 6.39 Hz, CHC*H*$_3$), 1.46 (d, 3H, ^3J = 6.39 Hz, CHC*H*$_3$), 1.27 (m, 12H, CH(C*H*$_3$)$_2$), −18.50 (m, 2H, Ru−*H*), −18.55 (m, 1H, Ru−*H*), −18.59 (m, 1H, Ru−*H*), −18.71 (m, 2H, Ru−*H*). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6, 20 °C): δ 110.31, 110.23, 106.87, 106.82, 99.91, 99.86, 95.27, 95.22, 89.13, 88.17, 85.06, 84.93, 83.48, 83.09, 82.97, 82.76, 82.46, 82.35, 82.19, 81.94, 80.51, 80.19, 78.64, 78.31, 77.07, 76.56 (C_{ar}), 69.68 (*C*HCH$_3$), 32.34 (*C*H(CH$_3$)$_2$), 32.31 (*C*H(CH$_3$)$_2$), 23.91, 23.87, 23.65, 23.61 (CH(*C*H$_3$)$_2$), 23.37 (CH*C*H$_3$), 23.30 (CH*C*H$_3$), 19.29 (C$_6$H$_4$*C*H$_3$), 19.11 (C$_6$H$_4$*C*H$_3$), 17.39 (C$_6$(*C*H$_3$)$_6$). ESI-MS (in acetone): 742 $[M + 2H]^+$.

Synthesis of the Mixtures of Isomers of [H$_3$Ru$_3${C$_6$H$_5$-(CH(NHCOMe)CO$_2$Et)}(C$_6$Me$_6$)(*p*-Pr^{i}MeC$_6$H$_4$)(O)]$^+$: S_{Ru_3O},S_C ((*S,S*)-8), R_{Ru_3O},R_C ((*R,R*)-8), S_{Ru_3O},R_C ((*S,R*)-8), and R_{Ru_3O},S_C ((*R,S*)-8). At room temperature, 125 mg (0.212 mmol) of [**4**][BF_4] was dissolved in a mixture of 40 mL of acetone and 15 mL of water. A 220 mg portion (0.280 mmol) of solid (*S,S*)-[Ru{C_6H_5(CH(NHCOMe)CO_2Et)}Cl$_2$]$_2$ was added to the resulting clear green solution. The mixture was stirred in the dark at room temperature for 5 days. During this time the color of the solution changed from deep green to red. The red solution containing **8** was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and filtered through Celite in order to remove insoluble particles. Then the methylene chloride solution was concentrated to about 5 mL in vacuo. The resulting concentrated solution was subjected to preparative thin-layer chromatography on silica gel using CH_2Cl_2/acetone (2/1) as eluant. The expected mixture was extracted with acetone from the main badly defined red band. Evaporation of acetone under vacuum gave a red residue, which was dissolved in 5 mL of CH_2Cl_2. The methylene chloride solution was again subjected to preparative thin-layer chromatography on silica gel using CH_2Cl_2/acetone as eluant. The proportions used to separate the two diastereomers were as follows: first elution, 10/0.1; second elution, 10/0.5; third elution, 10/1; fourth elution, 10/3; three additional elutions using the 10/3 eluant. The separated two orange-red bands were extracted separately from silica with acetone. Evaporation of acetone under vacuum gave 30 mg of fraction 1 and 20 mg of fraction 2 as orange-red powders. Total yield: 50 mg (25%) containing 60% of fraction 1 and 40% of fraction 2. Anal. Calcd (found) for $C_{34}H_{50}NO_4BF_4Ru_3$ (fraction 1): C, 44.06 (44.19); H, 5.44 (5.65); N, 1.51 (1.29). Calcd (found) for $C_{34}H_{50}BF_4NO_4Ru_3 \cdot H_2O$ (fraction 2): C, 43.22 (43.43); H, 5.55 (5.55); N, 1.48 (1.28).

Spectroscopic Data for Fraction 1. ^1H NMR (400 MHz, CD_2Cl_2, 20 °C): δ 8.88 (d, 1H, ^3J = 5.96 Hz, N*H*), 5.85 (d, 1H, J = 5.75 Hz, H_{ar}), 5.82 (d, 1H, J = 5.54 Hz, H_{ar}), 5.67 (m, 2H, H_{ar}), 5.60 (m, 1H, H_{ar}), 5.46 (d, 1H, J = 5.75 Hz, H_{ar}), 5.39 (m, 2H, H_{ar}), 5.33 (d, 1H, J = 5.75 Hz, H_{ar}), 5.23 (d, 1H, ^3J = 5.96 Hz, C*H*NH), 4.34 (qd, 1H, ^2J = 10.76 Hz, ^3J = 7.14 Hz, C*H*$_2$CH$_3$), 4.30 (qd, 1H, ^2J = 10.76 Hz, ^3J = 7.14 Hz, C*H*$_2$CH$_3$), 2.57 (hept, 1H, ^3J = 7.04 Hz, C*H*(CH$_3$)$_2$), 2.31 (s, 18H, C$_6$(C*H*$_3$)$_6$), 2.29 (s, 3H, C$_6$H$_4$C*H*$_3$), 1.59 (s, 3H, NHCOC*H*$_3$), 1.35 (t, 3H, ^3J = 7.14 Hz, CH$_2$C*H*$_3$), 1.28 (d, 6H, ^3J = 7.04 Hz, CH(C*H*$_3$)$_2$), −18.71 (t, 1H, ^2J = 4.05 Hz, Ru−*H*), −18.77 (t, 1H, ^2J = 4.05 Hz, Ru−*H*), −18.85 (t, 1H, ^2J = 4.05 Hz, Ru−*H*). ESI-MS (in acetone): 841 $[M + 2H]^+$.

Spectroscopic Data for Fraction 2. ^1H NMR (400 MHz, CD_2Cl_2, 20 °C): δ 8.81 (d, 1H, ^3J = 4.48 Hz, N*H*), 5.96 (m, 1H, H_{ar}), 5.82 (m, 1H, H_{ar}), 5.63 (d, 1H, J = 5.75 Hz, H_{ar}), 5.60 (d, 1H, J = 5.75 Hz, H_{ar}), 5.55 (m, 1H, H_{ar}), 5.46 (d, 2H, J = 5.54 Hz, H_{ar}), 5.42 (m, 2H, H_{ar}), 5.01 (d, 1H, ^3J = 4.48 Hz, C*H*NH), 4.29 (qd, 1H, ^2J = 10.72 Hz, ^3J = 7.14 Hz, C*H*$_2$CH$_3$), 4.23 (qd, 1H, ^2J = 10.72 Hz, ^3J = 7.14 Hz, C*H*$_2$−CH$_3$), 2.56 (hept, 1H, ^3J = 6.82 Hz, C*H*(CH$_3$)$_2$), 2.32 (s, 18H, C$_6$(C*H*$_3$)$_6$), 2.27 (s, 3H, C$_6$H$_4$C*H*$_3$), 1.59 (s, 3H, NHCOC*H*$_3$), 1.31 (t, 3H, ^3J = 7.14 Hz, CH$_2$C*H*$_3$), 1.28 (d, 6H, ^3J = 6.82 Hz, CH(C*H*$_3$)$_2$), −18.76 (m, 2H, Ru−*H*), −18.83 (m, 1H, Ru−*H*). ESI-MS (in acetone): 841 $[M + 2H]^+$.

Synthesis of the Racemic Mixture of (R_C)-[H$_3$Ru$_3$-(C$_6$Me$_6$)$_2${C$_6$H$_5$(CH(NHCOMe)CO$_2$Et)}(O)]$^+$ ((*R*)-9) and (S_C)-[H$_3$Ru$_3$(C$_6$Me$_6$)$_2${C$_6$H$_5$(CH(NHCOMe)CO$_2$Et)}(O)]$^+$ ((*S*)-9). At room temperature, 125 mg (0.203 mmol) of [H_3Ru_2(C$_6$Me$_6$)$_2$]-[BF_4] was dissolved in a mixture of 40 mL of acetone and 15

mL of water. A 220 mg portion (0.280 mmol) of solid (*S*,*S*)-[Ru{C_6H_5(CH(NHCOMe)CO_2Et)}Cl_2]$_2$ was added to the resulting clear solution. The mixture was stirred in the dark at room temperature for 5 days. During this time the color of the solution changed from deep green to red. The red solution containing the racemic mixture of (*R*)-**9** and (*S*)-**9** was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and filtered through Celite in order to remove insoluble particles. Then the methylene chloride solution was concentrated to about 5 mL in vacuo. The resulting concentrated solution was subjected to preparative thin-layer chromatography on silica gel using CH_2Cl_2/acetone (2/1) as eluant. The main red band was coarsely collected, and the impure mixture was extracted with acetone. After evaporation, the orange-red residue was dissolved in 5 mL of CH_2Cl_2, and the methylene chloride solution was again subjected to preparative thin-layer chromatography on silica gel using CH_2Cl_2/acetone as eluant. The proportions used were as follows; first elution, 10/1; second elution, 10/2; third elution, 10/3 (successive elutions on the same plate). The expected pure racemic mixture was extracted with acetone from the main orange-red band. Evaporation of acetone under vacuum gave the mixture of [(*R*)-**9**][BF_4] and [(*S*)-**9**][BF_4] as an orange-red powder. Yield: 67 mg (34%). Anal. Calcd (found) for $C_{36}H_{54}BF_4NO_4Ru_3 \cdot H_2O$: C, 44.45 (44.45); H, 5.80 (5.77); N, 1.44 (1.18). Single crystals suitable for X-ray diffraction analyses were grown by slow diffusion of hexane into a methylene chloride solution of [(*R*)-**9**][BF_4] and [(*S*)-**9**][BF_4].

Spectroscopic Data for the Racemic Mixture of (*R*)-9 and (*S*)-9. ^{1}H NMR (400 MHz, acetone-d_6, 20 °C): δ 9.21 (br, 1H, N*H*), 6.15 (t, 1H, J = 5.75 Hz, H_{ar}), 6.12 (t, 1H, J = 5.54 Hz, H_{ar}), 5.86 (d, 1H, J = 5.54 Hz, H_{ar}), 5.63 (m, 2H, H_{ar}), 5.00 (d, 1H, ^3J = 4.05 Hz, C*H*NH), 4.22 (qd, 1H, ^2J = 10.87 Hz, ^3J = 7.03 Hz, CH_2CH$_3$), 4.20 (qd, 1H, ^2J = 10.87 Hz, ^3J = 7.03 Hz, CH_2CH$_3$), 2.37 (s, 18 H, C$_6$(CH_3)$_6$), 2.36 (s, 18 H, C$_6$(CH_3)$_6$), 2.31 (s, 3H, NHCOCH_3), 1.25 (t, 3H, ^3J = 7.03 Hz, CH$_2$CH_3), −18.97 (t, 1H, ^2J = 4.12 Hz, Ru−*H*), −19.05 (t, 1H, ^2J = 4.12 Hz, Ru−*H*), −19.67 (t, 1H, ^2J = 4.12 Hz, Ru−*H*). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6, 20 °C): δ 169.51 (N*C*O), 169.32 (*C*O_2), 101.26, 95.61, 95.64, 85.86, 85.66, 81.67, 78.91, 78.87 (*C*$_{ar}$), 61.69 (*C*H$_2$CH$_3$), 57.13 (*C*HNH), 21.91 (NHCO*C*H$_3$), 17.68 (C$_6$(*C*H$_3$)$_6$), 13.91 (CH$_2$*C*H$_3$). ESI-MS (in acetone): 869 [M + H]$^+$.

Synthesis of (*R*)-C_6H_5(CH(NHCO_2Et)CH_2OH) (10). In a 1 L two-necked round-bottom flask equipped with a bubbler, 15 g (0.11 mol) of (*R*)-phenylglycinol was dissolved in 170 mL of dichloromethane. A 200 mL portion of an aqueous solution of $NaHCO_3$ (5%) was added with stirring. A 13 g portion (0.12 mol) of ethyl chloroformate was slowly added to the mixture at room temperature. The biphasic mixture was stirred vigorously overnight. Phases were separated by decantation, and the aqueous phase was extracted with 2 × 100 mL of CH_2Cl_2. The organic phases were regrouped and dried over anhydrous $MgSO_4$. After evaporation, **10** was obtained as a white solid. Yield: 20.8 g (91%).

Spectroscopic Data for 10. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 7.29 (m, 5H, H_{ar}), 5.82 (br, 1H, N*H*), 4.80 (m, 1H, C*H*CH$_2$OH), 4.10 (q, 2H, ^3J = 7.02 Hz, CH_2CH$_3$), 3.80 (dd, 1H, ^2J = 11.31 Hz, ^3J = 4.1 Hz, CHCH_2OH), 3.72 (dd, 1H, ^2J = 11.31 Hz, ^3J = 6.72 Hz, CHCH_2OH), 3.26 (br, 1H, O*H*), 1.22 (t, 3H, ^3J = 7.02 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 20 °C): δ 157.36 (N*C*O_2), 139.98, 129.05, 128.03, 127.00 (C$_{ar}$), 66.52 (CH*C*H$_2$OH), 61.60 (*C*H$_2$CH$_3$), 57.93 (*C*HCH$_2$OH), 14.93 (CH$_2$*C*H$_3$).

Synthesis of (*S*,*S*)-[Ru{C_6H_5(CH(NHCO_2Et)CH_2OH)}Cl_2]$_2$ (11). In a closed pressure Schlenk tube were dissolved 2.72 g (8.071 mmol) of [Ru(COD)($C_{10}H_8$)] and 12.70 g (60.76 mmol) of **10** in 150 mL of THF. Then 5 mL of acetonitrile was added at room temperature. The mixture was stirred at room temperature under pressure of argon (around 2 bar) for 2 days. During this time the color of the solution changed from red to deep red-brown. The solution was then concentrated to half of the original volume under reduced pressure and siphoned under argon onto a column of alumina (neutral, activity III, approximately 15 cm long and 3 cm in diameter) covered with sand. Elution with THF gave a clear red-brown solution, which was evaporated to dryness. The resulting deep red-brown oily residue containing the [Ru(COD)(**10**)] complex was dissolved in 50 mL of diethyl ether, and 20 mL of a 2 M solution of HCl in diethyl ether was added at room temperature. A precipitate appeared after a few minutes, and the mixture was stirred at room temperature for an additional 1 h. Then the orange-brown precipitate was filtered, washed with diethyl ether (3 × 20 mL), and dried under vacuum. The resulting impure orange-brown powder containing **11** was then dissolved in dichloromethane and subjected to column chromatography on a silica gel column (approximately 25 cm long and 3 cm in diameter) using CH_2Cl_2/ethanol (10/0.1 to 10/1) as eluant. The first fractions were discarded, and the last fraction (orange) was collected. Evaporation of the solvent under reduced pressure gave **11** as a pure orange powder. Yield: 1.48 g (48%). Anal. Calcd (found) for $C_{22}H_{30}Cl_4N_2O_6Ru_2$: C, 34.66 (34.45); H, 3.97 (4.14); N, 3.67 (3.50).

Spectroscopic Data for 11. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ 7.43 (d, 1H, ^3J = 8.4 Hz, N*H*), 6.02 (m, 2H, H_{ar}), 5.94 (m, 3H, H_{ar}), 5.02 (t, 1H, ^3J = 5.42 Hz, O*H*), 4.60 (m, 1H, C*H*CH$_2$OH), 4.01 (q, 2H, ^3J = 7.03 Hz, CH_2CH$_3$), 3.81 (m, 2H, CHCH_2OH), 1.17 (t, 3H, ^3J = 7.03 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 20 °C): δ 156.76 (N*C*O_2), 102.23, 88.73, 88.51, 87.81, 86.74, 85.95 (C$_{ar}$), 62.45 (CH*C*H$_2$OH), 60.88 (*C*H$_2$CH$_3$), 54.06 (*C*HCH$_2$OH), 15.47 (CH$_2$*C*H$_3$). MS (ESI, in MeOH): *m/z* 727 [M − Cl]$^+$, 719 [M − OCH$_2$CH$_3$]$^+$, 693 [M − 2Cl]$^+$, 655 [M − 3Cl]$^+$.

Synthesis of (*S*)-[H_3Ru_3(C_6Me_6)$_2${C_6H_5(CH(NHCO_2Et)CH_2OH)}(O)]$^+$ (12). At room temperature, 122 mg (0.198 mmol) of [H_3Ru_2(C_6Me_6)$_2$][BF_4] was dissolved in a mixture of 40 mL of acetone and 15 mL of water. A 180 mg portion (0.237 mmol) of solid **11** was added to the resulting clear solution. The mixture was stirred in the dark at room temperature for 5 days. During this time the color of the solution changed from deep green to red. The red solution containing **12** was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and the solution filtered through Celite in order to remove insoluble particles. Then the methylene chloride solution was concentrated to about 5 mL in vacuo. The resulting concentrated solution was subjected to preparative thin-layer chromatography on silica gel using CH_2Cl_2/acetone (10/3) as eluant. The expected enantiopure cluster cation was extracted from the main orange-red fraction with acetone. Evaporation of acetone under reduced pressure gave [**12**][BF_4] as a pure orange-red powder. Yield: 65 mg (35%). Anal. Calcd (found) for $C_{35}H_{54}BF_4NO_4Ru_3$: C, 44.59 (44.56); H, 5.77 (5.53); N, 1.49 (1.45).

Spectroscopic Data for 12. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ 6.95 (m, 1H, O*H*), 5.91 (m, 1H, H_{ar}), 5.86 (m, 1H, H_{ar}), 5.52 (m, 1H, H_{ar}), 5.27 (d, 1H, J = 5.76 Hz, H_{ar}), 5.14 (d, 1H, J = 5.54 Hz, H_{ar}), 4.46 (m, 1H, C*H*CH$_2$OH), 4.15 (m, 2H, CH_2CH$_3$), 3.97 (m, 2H, CHCH_2OH), 2.29 (s, 18H, C$_6$(CH_3)$_6$), 2.28 (s, 18H, C$_6$(CH_3)$_6$), 1.30 (m, 3H, CH$_2$CH_3), −19.42 (m, 1H, Ru−H), −19.47 (m, 1H, Ru−H), −19.90 (t, 1H, ^2J = 3.62 Hz, Ru−H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 20 °C): δ 156.40 (N*C*O_2), 109.99, 95.53, 95.48, 86.52, 85.11, 77.38, 76.72, 76.57 (*C*$_{ar}$), 64.39 (CH*C*H$_2$OH), 61.73 (*C*H$_2$CH$_3$), 53.09 (*C*HCH$_2$OH), 18.08 (C$_6$(*C*H$_3$)$_6$), 18.03 (C$_6$(*C*H$_3$)$_6$), 14.83 (CH$_2$*C*H$_3$). ESI-MS (in acetone): 857 [M + 2H]$^+$.

Synthesis of the Diastereomeric Mixture of (S_{Ru_3O},S_C)-[H_3Ru_3{C_6H_5(CH(NHCO_2Et)CH_2OH)}(C_6Me_6)(*p*-Pr^{i}MeC$_6$H$_4$)(O)]$^+$ ((*S*,*S*)-13) and (R_{Ru_3O},S_C)-[H_3Ru_3{C_6H_5-(CH(NHCO_2Et)CH_2OH)}(C_6Me_6)(*p*-Pr^{i}MeC$_6$H$_4$)(O)]$^+$ ((*R*,*S*)-13). At room temperature, 145 mg (0.246 mmol) of [**4**][BF_4] was dissolved in a mixture of 40 mL of acetone and 15 mL of water. A 225 mg portion (0.295 mmol) of solid **11** was added

to the resulting clear green solution. The mixture was stirred in the dark at room temperature for 4 days. During this time the color of the solution changed from deep green to red. The red solution containing (*S*,*S*)-**13** and (*R*,*S*)-**13** was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and the solution filtered through Celite in order to remove insoluble particles. Then the methylene chloride solution was concentrated to about 5 mL in vacuo. The resulting concentrated solution was subjected to preparative thin-layer chromatography on silica gel using CH_2Cl_2/acetone (10/3) as eluant. The expected diastereomeric mixture was extracted with acetone from the main red band. Evaporation of acetone under vacuum gave a mixture of [(*S*,*S*)-**13**][BF_4] and [(*R*,*S*)-**13**][BF_4] as an orange-red powder. Yield: 70 mg (31%). Anal. Calcd (found) for $C_{33}H_{50}BF_4NO_4Ru_3$: C, 43.33 (43.13); H, 5.51 (5.34); N, 1.53 (1.33).

Spectroscopic Data for the Diastereomeric Mixture of (*S*,*S*)-13 and (*R*,*S*)-13. ^{1}H NMR (400 MHz, acetone-d_6, 20 °C): δ 6.55 (t, 1H, ^3J = 7.24 Hz, O*H*), 6.42 (t, 1H, ^3J = 6.60 Hz, O*H*), 5.98 (m, 2H, H_{ar}), 5.90 (m, 2H, H_{ar}), 5.82 (t, 1H, J = 5.54 Hz, H_{ar}), 5.73 (d, 1H, J = 5.54 Hz, H_{ar}), 5.66 (d, 1H, J = 5.11 Hz, H_{ar}), 5.60 (d, 2H, J = 5.11 Hz, H_{ar}), 5.51 (t, 2H, J = 5.54 Hz, H_{ar}), 5.49 (t, 1H, J = 5.54 Hz, H_{ar}), 5.39 to 5.31 (m, 4H, H_{ar}), 5.29 (d, 1H, J = 5.75 Hz, H_{ar}), 5.24 (d, 1H, J = 5.54 Hz, H_{ar}), 4.50 to 4.43 (m, 2H, C*H*CH_2OH), 4.18 to 4.07 (m, 4H, C$H_2$$CH_3$), 4.01 to 3.89 (m, 4H, CHCH_2OH), 2.55 (Hept, 1H, ^3J = 6.82 Hz, C*H*$(CH_3)_2$), 2.54 (hept, 1H, ^3J = 7.03 Hz, C*H*$(CH_3)_2$), 2.30 (s, 18H, C_6(CH_3)$_6$), 2.29 (s, 18H, C_6(CH_3)$_6$), 2.19 (s, 3H, $C_6H_4CH_3$), 2.18 (s, 3H, $C_6H_4CH_3$), 1.30 (m, 6H, CH_2CH_3), 1.27 (d, 6H, ^3J = 7.03 Hz, CH(CH_3)$_2$), 1.26 (d, 6H, ^3J = 6.82 Hz, CH(CH_3)$_2$), −18.92 (t, 2H, ^2J = 3.73 Hz, Ru−*H*), −19.03 (m, 2H, Ru−*H*), −19.13 (m, 2H, Ru−*H*). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 20 °C): δ 156.40 (N*C*O_2), 156.38 (N*C*O_2), 109.42, 109.15, 107.04, 106.82, 100.80, 100.55, 95.57, 92.16, 90.33, 89.10, 86.28, 85.92, 85.51, 85.24, 83.92, 83.59, 82.78, 82.73, 82.47, 82.35, 82.30, 81.92, 78.95, 78.87, 78.31, 78.08, 77.20, 77.09 (C_{ar}), 64.48 (CH-*C*H_2OH), 53.75 (*C*HCH$_2$OH), 52.89 (*C*HCH$_2$OH), 61.65 (*C*$H_2$$CH_3$), 32.37 (*C*H$(CH_3)_2$), 32.32 (*C*H$(CH_3)_2$), 24.11 (CH(*C*$H_3$)$_2$), 24.08 (CH(*C*$H_3$)$_2$), 19.78 ($C_6H_4CH_3$), 19.73 ($C_6H_4CH_3$), 17.98 ($C_6$(C$H_3$)$_6$), 14.84 ($CH_2CH_3$), 14.81 ($CH_2CH_3$). ESI-MS (in acetone): 829 $[M + 2H]^+$.

Synthesis of (*R*)-C_6H_5(CH(NHCO$_2$Et)CH_2OCOPr^i) (14). A solution of isobutyric acid (4.6 mL, 49.60 mmol), *N*,*N*-dicyclohexylcarbodiimide (15 g, 73 mmol), 4-(dimethylamino)-pyridine (2 g, 16 mmol), 4-pyrrolidinopyridine (2 g, 13 mmol), and **10** (8 g, 38.15 mmol) in CH_2Cl_2 (200 mL) was stirred at room temperature for 5 days. The resulting milky solution was filtered through Celite to remove insoluble *N*,*N*-dicyclohexylurea. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel using hexane/acetone (10/0.1 to 10/2) as eluant. The expected product **14** was isolated from the third fraction as a pure white solid. Yield: 7.70 g (72%).

Spectroscopic Data for 14. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 7.32 (m, 5H, H_{ar}), 5.41 (br, 1H, N*H*), 5.05 (m, 1H, C*H*CH_2O), 4.38 (m, 1H, CHCH_2O), 4.27 (dd, 1H, ^2J = 11.41 Hz, ^3J = 4.82 Hz, CHCH_2O), 4.11 (m, 2H, C$H_2$$CH_3$), 2.54 (hept, 1H, ^3J = 7.04 Hz, C*H*$(CH_3)_2$), 1.23 (t, 3H, ^3J = 6.90 Hz, CH_2CH_3), 1.13 (d, 3H, ^3J = 7.04 Hz, CH(CH_3)$_2$), 1.12 (d, 3H, ^3J = 7.04 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 20 °C): δ 177.45 (*C*O_2), 156.43 (N*C*O_2), 139.10, 129.08, 128.29, 126.99 (C_{ar}), 66.51 (CH*C*H_2O), 61.46 (*C*$H_2$$CH_3$), 54.70 (*C*HCH$_2$O), 34.32 (*C*H$(CH_3)_2$), 19.29 (CH(*C*$H_3$)$_2$), 19.21 (CH(*C*$H_3$)$_2$), 14.97 ($CH_2CH_3$).

Synthesis of (*S*,*S*)-[Ru{C_6H_5(CH(NHCO$_2$Et)-CH_2OCOPr^i)}Cl_2]$_2$ (15). In a closed pressure Schlenk tube were dissolved 816 mg (2.42 mmol) of [Ru(COD)($C_{10}H_8$)] and 7.50 g (26.88 mmol) of **14** in 80 mL of THF. Then 2 mL of acetonitrile was added to the resulting red solution. The mixture was stirred at room temperature under pressure of argon (around 2 bar) for 2 days. During this time, the color of the solution changed from red to yellow-brown. The solution was then concentrated to half of its original volume under reduced pressure and siphoned under argon into a column of alumina (neutral, activity III, approximately 15 cm long and 3 cm in diameter) covered with sand. Elution with THF gave a clear yellow-brown solution, which was evaporated to dryness under reduced pressure. The resulting yellow-brown oily residue containing the expected [Ru(COD)(**14**)] complex was dissolved in 15 mL of diethyl ether, and 10 mL of a solution of 2 M HCl in diethyl ether was added. An orange precipitate appeared quickly, and the mixture was then stirred for an additional 1 h at room temperature. Then the orange precipitate was filtered, washed with diethyl ether (3 × 15 mL), and dried under vacuum to give **15** as a pure orange powder. Yield: 550 mg (51%). Anal. Calcd (found) for $C_{30}H_{42}Cl_4N_2O_8Ru_2$: C, 39.92 (39.75); H, 4.69 (4.76); N, 3.10 (2.89).

Spectroscopic Data for 15. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ 6.39 (br, 1H, N*H*), 5.94 (t, 1H, J = 5.4 Hz, H_{ar}), 5.78 (d, 2H, J = 5.8 Hz, H_{ar}), 5.70 (t, 1H, J = 5.8 Hz, H_{ar}), 5.66 (t, 1H, J = 5.6 Hz, H_{ar}), 4.98 (m, 1H, C*H*-CH_2O), 4.67 (d, 2H, ^3J = 6.3 Hz, CHCH_2O), 4.16 (m, 2H, C$H_2$$CH_3$), 2.61 (Hept, 1H, ^3J = 7.0 Hz, C*H*$(CH_3)_2$), 1.29 (t, 3H, ^3J = 7.1 Hz, CH_2CH_3), 1.18 (d, 3H, ^3J = 7.0 Hz, CH(CH_3)$_2$), 1.17 (d, 3H, ^3J = 7.0 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 20 °C): δ 176.72 (*C*O_2), 156.76 (N*C*O_2), 95.00, 85.87, 81.87, 81.58, 81.23, 81.06 (C_{ar}), 64.35 (CH*C*H_2O), 61.84 (*C*$H_2$$CH_3$), 51.54 (*C*HCH$_2$O), 34.26 (*C*H−$CH_3$)$_2$), 19.09 (CH(*C*$H_3$)$_2$), 19.05 (CH(*C*$H_3$)$_2$), 14.82 ($CH_2CH_3$). ESI-MS (in MeOH): 859 $[M - CH(CH_3)_2]^+$.

Synthesis of (*S*)-[H_3Ru_3(C_6Me_6)$_2${C_6H_5(CH(NHCO$_2$Et)-CH_2OCOPr^i)}(O)]$^+$ (16). At room temperature, 170 mg (0.252 mmol) of [H_3Ru_2(C_6Me_6)][PF_6] was dissolved in a mixture of 60 mL of acetone and 30 mL of water. A 300 mg portion (0.332 mmol) of solid **15** was added to the resulting clear solution. The mixture was stirred in the dark at room temperature for 5 days. During this time the color of the solution changed from deep green to red. The red solution containing **16** was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and filtered through Celite in order to remove insoluble particles. Then the methylene chloride solution was concentrated to about 5 mL in vacuo. The resulting concentrated solution was subjected to preparative thin-layer chromatography on silica gel using CH_2Cl_2/acetone (10/3) as eluant. The expected enantiopure cluster cation was extracted from the main orange-red fraction with acetone. Evaporation of acetone under reduce pressure gave [**16**][PF_6] as a pure orange-red powder. Yield: 85 mg (31%). Anal. Calcd (found) for $C_{39}H_{60}F_6NO_5PRu_3 \cdot H_2O$: C, 43.01 (42.93); H, 5.74 (5.73); N, 1.29 (1.17). Single crystals suitable for X-ray analyses were obtained by a slow diffusion of hexane into a methylene chloride solution of [**16**][PF_6].

Spectroscopic Data for 16. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ 7.98 (br, 1H, N*H*), 5.86 (d, 1H, J = 5.33 Hz, H_{ar}), 5.83 (d, 1H, J = 5.11 Hz, H_{ar}), 5.55 (t, 1H, J = 5.75 Hz, H_{ar}), 5.32 (d, 1H, J = 5.96 Hz, H_{ar}), 5.27 (d, 1H, J = 5.54 Hz, H_{ar}), 4.75 (dd, 1H, ^2J = 10.23 Hz, ^3J = 4.05 Hz, CHCH_2O), 4.47 (m, 1H, C*H*CH_2O), 4.42 (dd, 1H, ^2J = 10.23 Hz, ^3J = 8.95 Hz, CHCH_2O), 4.28 (qd, 1H, ^2J = 10.65 Hz, ^3J = 7.03 Hz, C$H_2$$CH_3$), 4.18 (qd, 1H, ^2J = 10.65 Hz, ^3J = 7.03 Hz, C$H_2$$CH_3$), 2.51 (hept, 1H, ^3J = 7.03 Hz, C*H*$(CH_3)_2$), 2.30 (s, 18 H, C_6(CH_3)$_6$), 2.28 (s, 18 H, C_6(CH_3)$_6$), 1.36 (t, 3H, ^3J = 7.03 Hz, CH_2CH_3), 1.10 (d, 3H, ^3J = 7.03 Hz, CH(CH_3)$_2$), 1.08 (d, 3H, ^3J = 7.03 Hz, CH(CH_3)$_2$), −19.11 (t, 1H, ^2J = 4.12 Hz, Ru−*H*), −19.30 (t, 1H, ^2J = 4.12 Hz, Ru−*H*), −19.83 (t, 1H, ^2J = 4.12 Hz, Ru−*H*). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 20 °C): δ 176.68 (*C*O_2), 157.00 (N*C*O_2), 103.56, 95.56, 95.50, 86.35, 85.40, 80.93, 78.15, 76.57 (C_{ar}), 63.61 (CH*C*H_2O), 61.62 (*C*$H_2$$CH_3$), 54.41 (*C*HCH$_2$O), 34.18 (*C*H$(CH_3)_2$), 19.06 (CH(*C*$H_3$)$_2$), 18.98 (CH-(*C*$H_3$)$_2$), 18.14 ($C_6$(*C*$H_3$)$_6$), 18.07 ($C_6$(*C*$H_3$)$_6$), 14.93 ($CH_2CH_3$). ESI-MS (in acetone): 927 $[M + 2H]^+$.

Synthesis of (S_{Ru_3O},S_C)-[H_3Ru_3{C_6H_5(CH(NHCO$_2$Et)-CH_2OCOPr^i)}(C_6Me_6)(*p*-$Pr^iMeC_6H_4$)(O)]$^+$ ((*S*,*S*)-17) and (R_{Ru_3O},S_C)-[H_3Ru_3{C_6H_5(CH(NHCO$_2$Et)CH_2OCOPr^i)}-(C_6Me_6)(*p*-$Pr^iMeC_6H_4$)(O)]$^+$ ((*R*,*S*)-17). At room temperature, 120 mg (0.203 mmol) of [**4**][BF_4] was dissolved in a mixture of 60 mL of acetone and 20 mL of water. A 330 mg portion (0.366 mmol) of solid **15** was added to the resulting clear green solution. The mixture was stirred in the dark at room temperature for 6 days. During this time the color of the solution changed from deep green to red. The red solution containing the mixture of (*S*,*S*)-**17** and (*R*,*S*)-**17** was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and filtered through Celite in order to remove insoluble particles. Then the methylene chloride solution was concentrated to about 5 mL in vacuo. The resulting concentrate was subjected to preparative thin-layer chromatography on silica gel using CH_2Cl_2/acetone (10/3) as eluant. The expected mixture was extracted with acetone from the main badly defined red band. Evaporation of acetone under vacuum gave a red residue, which was dissolved in 5 mL of CH_2Cl_2. The methylene chloride solution was again subjected to preparative thin-layer chromatography on silica gel using CH_2Cl_2/acetone as eluant. The proportions used to separate (*S*,*S*)-**17** and (*R*,*S*)-**17** were as follows; first elution, 10/0.1; second elution, 10/0.5; third elution, 10/1; fourth elution, 10/3; three additional elutions using the 10/3 eluant. The two orange-red bands were extracted separately from silica with acetone. Evaporation of acetone under vacuum gave 52 mg of fraction 1 and 34 mg of fraction 2 as orange-red powders. Total yield: 86 mg (43%), containing 60% of fraction 1 and 40% of fraction 2. Anal. Calcd (found) for, $C_{37}H_{56}BF_4NO_5Ru_3 \cdot 2(CH_3)_2CO$ (fraction 1): C, 44.06 (44.19); H, 5.44 (5.65); N, 1.51 (1.29). Calcd (found) for $C_{37}H_{56}BF_4NO_5Ru_3 \cdot H_2O \cdot (CH_3)_2CO$ (fraction 2): C, 45.28 (45.31); H, 6.08 (6.02); N, 1.32 (1.16).

Spectroscopic Data for Fraction 1. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ 7.46 (br, 1H, N*H*), 5.84 (t, 1H, J = 5.54 Hz, H_{ar}), 5.81 (d, 1H, J = 5.75 Hz, H_{ar}), 5.67 (d, 1H, J = 5.75 Hz, H_{ar}), 5.60 (d, 1H, J = 5.75 Hz, H_{ar}), 5.57 (t, 1H, J = 5.54 Hz, H_{ar}), 5.42 (d, 1H, J = 5.75 Hz, H_{ar}), 5.38 (m, 2H, H_{ar}), 5.33 (d, 1H, J = 5.75 Hz, H_{ar}), 4.84 (m, 1H, C*H*CH$_2$O), 4.44 (dd, 1H, ^2J = 11.08 Hz, ^3J = 6.28 Hz, CHC*H*$_2$O), 4.32 (dd, 1H, ^2J = 11.08 Hz, ^3J = 7.78 Hz, CHC*H*$_2$O), 4.24 (qd, 1H, ^2J = 10.66 Hz, ^3J = 7.14 Hz, C*H*$_2$CH$_3$), 4.18 (qd, 1H, ^2J = 10.66 Hz, ^3J = 7.14 Hz, C*H*$_2$CH$_3$), 2.61 (hept, 1H, ^3J = 7.04 Hz, OCOC*H*(CH$_3$)$_2$), 2.53 (hept, 1H, ^3J = 6.82 Hz, C$_6$H$_4$C*H*(CH$_3$)$_2$), 2.30 (s, 18H, C$_6$(C*H*$_3$)$_6$), 2.21 (s, 3H, C$_6$H$_4$C*H*$_3$), 1.33 (t, 3H, ^3J = 7.14 Hz, CH$_2$C*H*$_3$), 1.28 (d, 3H, ^3J = 6.82 Hz, C$_6$H$_4$CH(C*H*$_3$)$_2$), 1.27 (d, 3H, ^3J = 6.82 Hz, C$_6$H$_4$CH(C*H*$_3$)$_2$), 1.18 (d, 6H, ^3J = 7.04 Hz, OCOCH(C*H*$_3$)$_2$), −18.78 (t, 1H, ^2J = 4.05 Hz, Ru−*H*), −18.85 (t, 1H, ^2J = 4.05 Hz, Ru−*H*), −18.98 (t, 1H, ^2J = 4.05 Hz, Ru−*H*). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 20 °C): δ 176.88 (*C*O$_2$), 156.67 (N*C*O$_2$), 107.58, 101.28, 100.16, 95.70, 87.44, 84.13, 83.43, 82.73, 82.33, 82.17, 80.46, 80.19, 78.76 (*C*$_{ar}$), 63.81 (CH*C*H$_2$O), 61.57 (*C*H$_2$CH$_3$), 52.11 (*C*HCH$_2$O), 34.26 (OCO*C*H-(CH$_3$)$_2$), 32.50 (C$_6$H$_4$*C*H(CH$_3$)$_2$), 24.19 (C$_6$H$_4$CH(*C*H$_3$)$_2$), 23.92 (C$_6$H$_4$CH(*C*H$_3$)$_2$), 20.00 (C$_6$H$_4$*C*H$_3$), 19.03 (OCOCH(*C*H$_3$)$_2$), 18.03 (C$_6$(*C*H$_3$)$_6$), 14.92 (CH$_2$*C*H$_3$). ESI-MS (in acetone): 899 [M + H]$^+$.

Spectroscopic Data for Fraction 2. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ 6.98 (br, 1H, N*H*), 5.90 (t, 1H, J = 5.75 Hz, H_{ar}), 5.79 (t, 1H, J = 5.75 Hz, H_{ar}), 5.63 (d, 1H, J = 5.75 Hz, H_{ar}), 5.60 (d, 1H, J = 5.75 Hz, H_{ar}), 5.52 (t, 1H, J = 5.75 Hz, H_{ar}), 5.41 (d, 1H, J = 5.75 Hz, H_{ar}), 5.35 (m, 3H, H_{ar}), 4.68 (m, 1H, C*H*CH$_2$O), 4.57 (dd, 1H, ^2J = 11.08 Hz, ^3J = 6.18 Hz, CHC*H*$_2$O), 4.47 (dd, 1H, ^2J = 11.08 Hz, ^3J = 7.68 Hz, CHC*H*$_2$O), 4.24 (qd, 1H, ^2J = 10.66 Hz, ^3J = 7.14 Hz, C*H*$_2$CH$_3$), 4.17 (qd, 1H, ^2J = 10.66 Hz, ^3J = 7.14 Hz, C*H*$_2$CH$_3$), 2.57 (m, 2H, OCOC*H*(CH$_3$)$_2$ plus C$_6$H$_4$C*H*(CH$_3$)$_2$), 2.31 (s, 18H, C$_6$(C*H*$_3$)$_6$), 2.19 (s, 3H, C$_6$H$_4$C*H*$_3$), 1.33 (t, 3H, ^3J = 7.14 Hz, CH$_2$C*H*$_3$), 1.28 (d, 3H, ^3J = 7.03 Hz, C$_6$H$_4$CH(C*H*$_3$)$_2$), 1.27 (d, 3H, ^3J = 7.03 Hz, C$_6$H$_4$CH(C*H*$_3$)$_2$), 1.16 (d, 3H, ^3J = 7.04 Hz, OCOCH(C*H*$_3$)$_2$), 1.15 (d, 3H, ^3J = 7.04 Hz, OCOCH(C*H*$_3$)$_2$), −18.86 (m, 2H, Ru−*H*), −18.90 (m, 1H, Ru−*H*). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 20 °C): δ 176.80 (*C*O$_2$), 156.63 (N*C*O$_2$), 107.52, 102.77, 99.91, 95.61, 85.89, 85.86, 83.32, 82.74, 82.60, 82.54, 80.74, 79.03, 78.63 (*C*$_{ar}$), 63.96 (CH*C*H$_2$O), 61.67 (*C*H$_2$CH$_3$), 52.20 (*C*HCH$_2$O), 34.24 (OCO*C*H(CH$_3$)$_2$), 32.53 (C$_6$H$_4$*C*H(CH$_3$)$_2$), 24.03 (C$_6$H$_4$CH(*C*H$_3$)$_2$), 23.95 (C$_6$H$_4$CH(*C*H$_3$)$_2$), 19.84 (C$_6$H$_4$*C*H$_3$), 19.06 (OCOCH(*C*H$_3$)$_2$), 19.03 (OCOCH-(*C*H$_3$)$_2$), 18.03 (C$_6$(*C*H$_3$)$_6$), 14.90 (CH$_2$*C*H$_3$). ESI-MS (in acetone): 899 [M + H]$^+$.

^{1}H NMR Study in the Presence of [Eu(hfc)$_3$]. In a typical experiment, in a classical NMR tube, 6 mg of [**9**][BF_4], [(*S*,*S*)-**17**][BF_4] or [(*R*,*S*)-**17**][BF_4] was dissolved in 500 μL of CD_2Cl_2. The complex [Eu(hfc)$_3$] was added incrementally by syringe as a concentrated solution in CD_2Cl_2, the molar ratio of the chiral europium complex with respect to the substrate increasing from 0.1 to 1.2. A series of spectra was thus recorded at room temperature using a Bruker 400 MHz spectrometer and treated with WINNMR.

Catalytic Study. In a typical experiment, a solution of [(*S*,*S*)-**17**][BF_4] or [(*R*,*S*)-**17**][BF_4] (10 mg) in 10 mL of water was placed in a 100 mL stainless steel autoclave equipped with a glass-lined vessel, and the water-soluble prochiral substrate methyl 2-acetamidoacrylate was added with a 1/50 catalyst/substrate ratio. After it was purged four times with hydrogen, the autoclave was pressurized with hydrogen (50 bar) and stirred vigorously at room temperature. After 48 h, the pressure was released. The catalytic product was extracted from the aqueous solution with 3 × 5 mL of ethyl acetate. After decanting, the organic phase was collected and dried over anhydrous $MgSO_4$. After evaporation to dryness, the residue was dissolved in ethanol to be analyzed by GC on a capillary column (Chirasyl-L-Val 25 m × 0.25 mm column, using pentadecane as internal standard, and/or heptakis-2,3,6-perethyl-β-cyclodextrin, 22 m × 0.32 mm column).

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Supporting Information Available: Details of the X-ray crystallographic studies, including CIF files, ORTEP drawings, and text describing experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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