Optical Resolution of π-Thiophene Complexes $(C_6Me_6)Ru(2\text{-}RC_4H_3S)^{2+}$ and Related Studies

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Diastereomeric iminium thiolato complexes were prepared by the addition of *S*-(−)-α-methylbenzylamine to the π-thiophene complexes $[(C_6Me_6)Ru(2\text{-}RC_4H_3S)]^{2+}$, where R = Me (**1**$^{2+}$), CH_2OH (**3**$^{2+}$), and 2-C_4H_3S (**6**$^{2+}$). After chromatographic separation, the diastereomers were treated with HOTf to generate optically pure π-thiophene complexes. The absolute configuration of $[(C_6Me_6)RuSCMeC_2H_2(CHNHCHMePh)]OTf$, (−)-**2**(OTf), was determined by a single-crystal X-ray diffraction; the monohydrate crystallized in the acentric space group $P2_12_12_1$. Acetone solutions of (−)-**1**$^{2+}$ and (−)-**3**$^{2+}$ are optically stable for days in solution (25 °C), while the bithiophene complex was unstable with respect to dissociation of the bithiophene ligand. Optical resolution of $[(cymene)Os(2\text{-}MeC_4H_3S)](OTf)_2$ was not possible due to the instability of the iminium thiolato. Base hydrolysis of (−)-**1**$^{2+}$ gave the formyl thiolato complex (−)-**9**$_{kin}$, which isomerized to (+)-**9**$_{therm}$ with inversion of configuration at Ru, as indicated by circular dichroism measurements. The methyl ester of the amino acid (L)-phenylalanine was shown to add to $(C_6Me_6)Ru(C_4H_4S)^{2+}$ to give a 2:1 mixture of diastereomeric iminium thiolato complexes.

Introduction

Metal complexes which exhibit "planar chirality", such as metallocenes, have been of continuous interest almost since the discovery of ferrocene.[1] These studies have led to the optical resolution of many η^5-cyclopentadienyl and η^6-arene complexes,[2,3] some of which have emerged as synthetically and catalytically useful.[4] The optical resolution of π-thiophene complexes[5] has however not been reported. Such species could be of interest as mechanistic probes of C−S bond scission processes, which are relevant to desulfurization catalysis.[6] In addition, such complexes could also be of interest in asymmetric synthesis[7] and for their nonlinear optical properties.[8]

Our interest in the optical resolution of π-thiophene complexes was prompted by the finding that dicationic ruthenium thiophene complexes react readily with amines to give iminium thiolato derivatives.[9] The amination is reversed by treatment with acid, such as HOTf. In certain cases, the initial iminium thiolato complexes isomerize to a second, so-called thermodynamic isomer, which does not revert to the original π-thiophene complex upon protonation. Of further relevance to the optical resolution is the regioselectivity of the amination process. As for other nucleophiles,[10] amines attack complexes of 2-substituted thiophenes exclusively at the unsubstituted carbon α to sulfur.[9] With these facts in mind, it should be possible to generate adducts of chiral amines to give a single pair of diastereomers. This reactivity provides the basis of an optical resolution, provided that the diastereomers can be separated.

Results

Optical resolution of $[(C_6Me_6)Ru(2\text{-}MeC_4H_3S)](OTf)_2$. Addition of (*S*)-(−)-α-methylbenzylamine to a CH_2Cl_2 slurry of $[(C_6Me_6)Ru(2\text{-}MeC_4H_3S)](OTf)_2$, **1**$(OTf)_2$, causes a color change from yellow to cherry red (OTf^- is $CF_3SO_3^-$). The red product, **2**(OTf), was separated from the (*S*)-(−)-α-methylbenzylammonium triflate by chromatography on a short silica gel column and was isolated as a microcrystalline powder. The ^{1}H NMR spectrum of **2**(OTf) shows the presence of an equimolar

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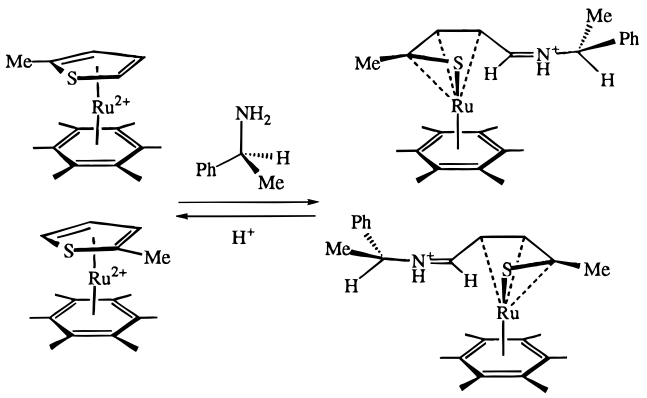
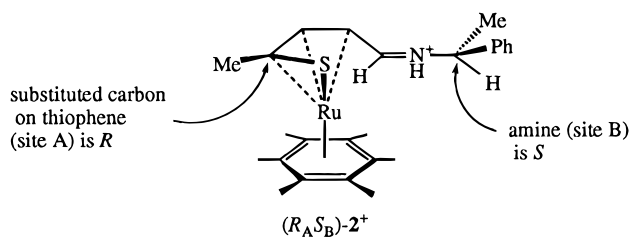
Scheme 1



mixture of the diastereomers, as indicated by pairs of resonances which integrate in a 1:1 ratio (Scheme 1, Figure 1). The resonances of each diastereomer were assigned through homonuclear decoupling experiments.

Tests using thin layer chromatography revealed that under optimal conditions the diastereomeric forms of **2**(OTf) separate on silica gel with a ΔR_f of ca. 0.06. Preparative-scale purifications were shown to be feasible, although multiple elutions were required. In the first elution, the initial 20% of the red band was collected and shown to be diastereomerically pure. The remaining band, which is enriched in the more polar diastereomer, was subjected to a second column. Three to four such separations afforded a 42% yield of the less polar diastereomer. Note that the separations become progressively easier as the mixture becomes enriched in the more polar isomer. The diastereomeric purity of the fractions was determined by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the less polar diastereomer coincides with one of the two subspectra seen in the original mixture. The C*H*=N*H* signals at δ 8.78 and 7.60 for the less polar diastereomer are shifted further downfield relative to the corresponding signals for the other diastereomer (δ 8.52 and 7.53, respectively). Polarimetry measurements show that this less polar diastereomer is levorotatory, with a specific rotation of −1800° at the sodium D line (all subsequent rotations are quoted for this wavelength).

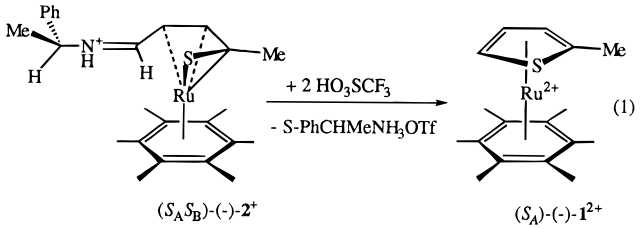
The absolute configuration of (−)-**2**(OTf) was determined by single-crystal X-ray crystallography, the salt crystallizing as the monohydrate in the acentric space group $P2_12_12_1$. Like other complexes of this type,[9] this species consists of a sandwich complex containing an η^6-arene ligand and an η^4-allyl-thiolato complex (Figure 2). The allyl thiolato ligand is functionalized with an iminium group derived from the resolving agent. The C6−Ru nonbonding distance of 2.79 Å is slightly longer than that found in the anilinium adduct [(C_6Me_6)Ru(SCMeC_2H_2(CHNHPh)]OTf (2.63 Å) (Table 1). Having determined the absolute configuration of this complex, we can apply the labeling shown as follows



(R_AS_B)-**2**$^+$

These labels are relevant to the description of other derivatives of **1**$^+$.

The less polar isomer of [(C_6Me_6)RuSCMeC_2H_2(CHNHCHMePh)]OTf reacts with 2 equiv of HOTf, resulting in an abrupt color change from red to pale yellow. In this process, the amine resolving agent is released as the ammonium salt, which is easily filtered off, concomitant with the regeneration of [(C_6Me_6)Ru(2-MeC_4H_3S)](OTf)$_2$, (*S*)-(−)-**1**(OTf)$_2$, in ∼80% yield (eq 1).



(S_AS_B)-(-)-**2**$^+$ (S_A)-(-)-**1**$^{2+}$ (1)

In acetone solutions $[\alpha]_D^{25} = -29°$. Solutions of (−)-**1**(OTf)$_2$ are quite optically stable: after 5 days in an acetone solution (25 °C), the optical rotation of (−)-**1**(OTf)$_2$ declined less than 5%. A fraction enriched in the more polar diastereomer of **2**(OTf)$_2$ was shown to consist of a 2:1 ratio of diastereomers. Protonolysis and workup of this species gave **1**(OTf)$_2$ with a rotation of ca. +14°. After the contamination by the levorotatory isomer was corrected for (as indicated by the diastereomer ratio), the specific rotation of the second enantiomer is approximately twice this value.

Optical Resolution of [(C_6Me_6)Ru(2-HOCH_2-C_4H_3S)](OTf)$_2$. In an effort to extend the scope of the resolution experiments, we examined a complex of the hydroxymethyl-functionalized thiophene 2-HOC$H_2C_4H_3S$. The new complex [(C_6Me_6)Ru(2-HOC$H_2C_4H_3S$)](OTf)$_2$, **3**(OTf)$_2$, was obtained as yellow crystals in 76% yield from the reaction of (C_6Me_6)Ru(OTf)$_2$[11] and an excess of 2-HOC$H_2C_4H_3S$. Evidence supporting π-complexation of this thiophene comes from the ^{1}H NMR resonances of the diastereotopic methylene (2-HOC$H_2C_4H_3S$) protons with signals centered at δ 4.96 and 4.82. For the uncomplexed heterocycle, these ^{1}H NMR signals appear as a doublet (δ 4.79).

There was some concern that amines, such as the resolving agent, might deprotonate the hydroxyl group in **3**(OTf)$_2$ leading to undesired side reactions. This possibility was tested by the treatment of **3**(OTf)$_2$ with *t*-BuNH_2. This reaction proceeded smoothly giving a 65% yield of the red iminium thiolato complex, [(C_6Me_6)RuSC(CH_2OH)C_3H_3(NH-*t*-Bu)]OTf, **4**(OTf).

Having confirmed the compatibility of π-complexed 2-HOC$H_2C_4H_3S$ and amines, **3**(OTf)$_2$ was treated with (*S*)-(−)-α-methylbenzylamine to give [(C_6Me_6)RuSC(CH_2-OH)C_2H_2(CHNHCHMePh)]OTf, **5**(OTf). This diastereomeric salt was isolated as a waxy red solid in 88% yield after chromatographic purification. The ^{1}H NMR data indicate equimolar quantities of the diastereomers, e.g., the doublets at δ 1.59 and 1.46 assigned to PhCH_3-CHNH. The less polar diastereomer of **5**(OTf) was purified chromatographically, as described for **2**(OTf). For CH_2Cl_2 solutions of the less polar isomer, $[\alpha]_D^{25} = -1850°$.

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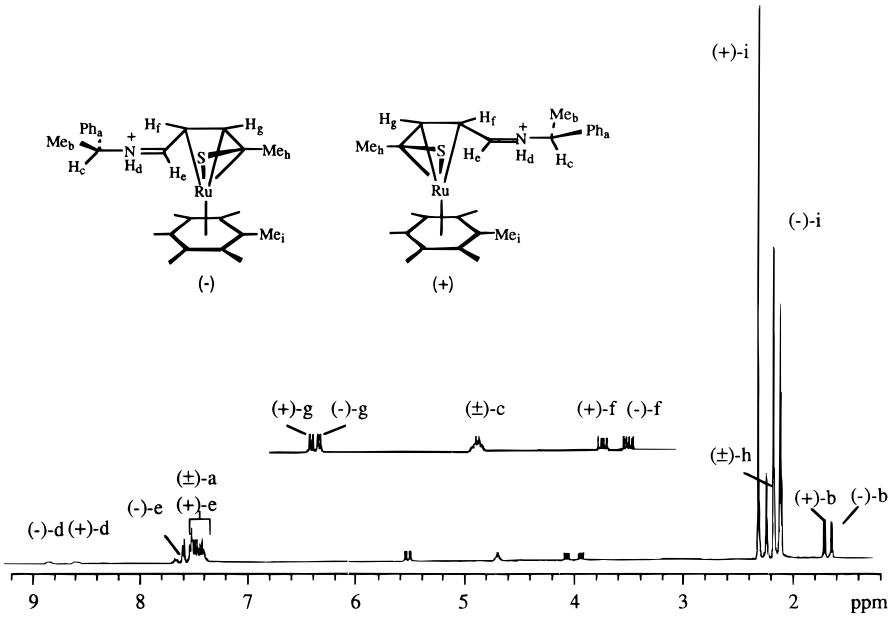


Figure 1. 400 MHz ^{1}H NMR spectrum of the two diastereomers of $\mathbf{2}^{2+}$ (acetone-d_6, inset: an expansion of the δ 6−3.5 range).

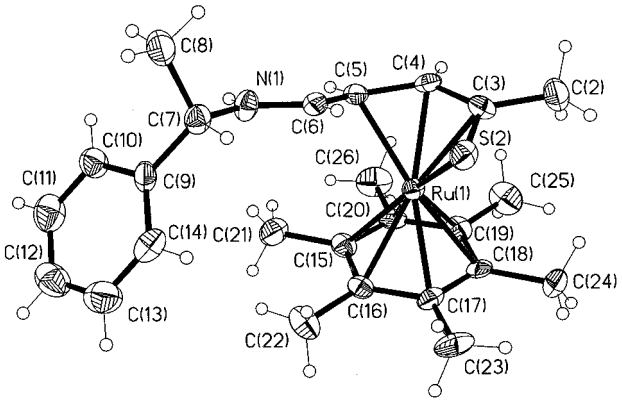


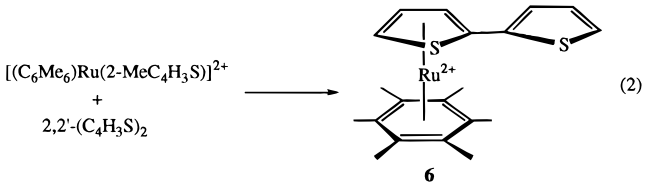
Figure 2. Structure of the cation in the less polar isomer of $[(C_6Me_6)RuSCMeC_2H_2(CHNHCHMePh)]OTf$, (−)-**2**-$(OTf)\cdot H_2O$, with thermal ellipsoids drawn at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for (−)-[(C_6Me_6)RuSCMeC$_2$H$_2$-(CHNHCHMePh)]OTf, (−)-2(OTf)

Ru−S1	2.402(2)	C4−C5	1.445(8)
Ru−C3	2.194(6)	C5−C6	1.390(8)
Ru−C4	2.155(5)	S−C3	1.735(7)
Ru−C5	2.223(5)	Ru−C_6Me_6 centroid	1.707(2)
Ru−C6	2.797(5)	Ru−SC_3 centroid	1.689(3)
Ru−C15−20	2.218(3)−2.222(3)	C4−C3−S	119.9(5)
N−C6	1.325(7)	C3−C4−C5	126.2(6)
N−C7	1.472(7)	C5−C6−N	122.3(5)
C3−C4	1.406(8)	C6−N−C7	122.5(5)

Optically pure (−)-**3**(OTf) was generated in approximately 85% yield from the less polar diastereomer by treatment with HOTf, the progress of the reaction being indicated by the discharge of the red color of the iminium thiolato complex and the precipitation of a yellow solid. The value of $[\alpha]_D^{25}$ for (−)-**3**$(OTf)_2$ was −29°. The optical rotation of solutions of this enantiomer declined a few percent over a period of days. This decline is attributed to decomposition, not racemization, since the addition of (*S*)-(−)-α-methylbenzylamine to the recovered polarimetry samples gave exclusively the less polar diastereomer.

Optical Resolution of $[(C_6Me_6)Ru(2,2'\text{-}C_4H_3SC_4H_3S)](OTf)_2$. In a final test of this resolution method, we examined the 2,2′-bithiophene complex $[(C_6Me_6)Ru(C_4H_3SC_4H_3S)](OTf)_2$, **6**$(OTf)_2$, which was prepared in the usual way (eq 2, one of two enantiomers shown).



(2)

The ^{1}H NMR spectrum of **6**$(OTf)_2$ shows two subspectra in the thiophenic region. The subspectrum assigned to the coordinated thienyl group consists of overlapping doublets at δ 8.08 and a doublet of doublets at δ 7.39. The second set of signals were assigned to the uncoordinated thienyl group: doublets at δ 7.61 and 7.36 and a doublet of doublets at 7.32. The assignments were confirmed by a ^{1}H{^{1}H} NMR experiment. The resonances assigned to the coordinated thienyl unit are similar to those found in **1**$(OTf)_2$ and **3**$(OTf)_2$.

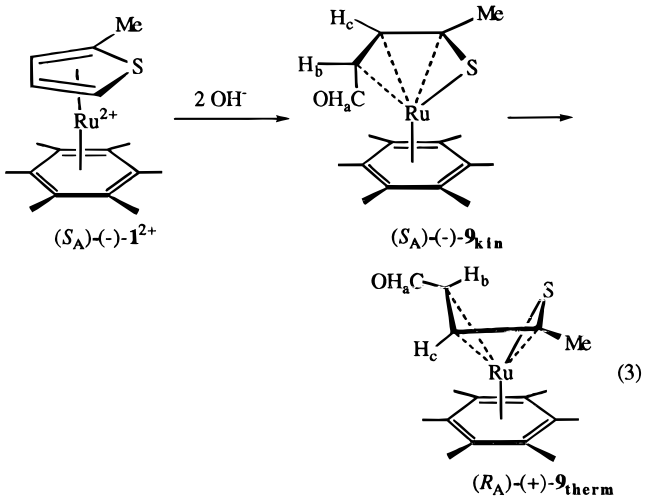
In a test reaction, a CH_2Cl_2 solution of **6**$(OTf)_2$ was treated with 2.1 equiv of *tert*-butylamine to give $[(C_6Me_6)RuSC(C_4H_3S)C_2H_2(CHNH\text{-}t\text{-}Bu)]OTf$, **7**(OTf). The ^{1}H NMR spectrum of **7**(OTf) indicates C−S scission of the coordinated thiophene unit. The shift of C*H*NH-*t*-Bu is found at δ 7.82, vs 7.60 in **4**(OTf). ^{1}H NMR measurements indicate that, unlike **6**$(OTf)_2$ (vide infra), acetone solutions of **7**(OTf) are stable for days.

The reaction of **6**$(OTf)_2$ and (*S*)-(−)-α-methylbenzylamine proceeded as expected to give a 1:1 mixture of the diastereomers of the formula $[(C_6Me_6)RuSC(C_4H_3S)C_2H_2(CHNHCHMePh)]OTf$, **8**(OTf). The chromatographic separation of these diastereomers was particularly straightforward, such that almost the first half of a single diastereomer was collected after one column. ^{1}H NMR measurements show that the signals for the less polar isomer are shifted upfield relative to the other

diastereomer. Again, polarimetry of the less polar diastereomer revealed a levorotatory rotation, $[\alpha]_D^{25} = -1750°$. Approximately 40% of the more polar diastereomer of **8**(OTf) was recovered; it exhibited a specific rotation of +1700°. Regeneration of (−)-[$(C_6Me_6)Ru(C_4H_3SC_4H_3S)$](OTf)$_2$, (−)-**6**(OTf)$_2$, involved the now routine protonolysis to give (−)-**6**(OTf)$_2$, $[\alpha]_D^{25} = -37°$. In addition to the levorotatory enantiomer, (+)-**6**(OTf)$_2$ was also isolated ($[\alpha]_D^{25} = +37°$).

The rotation of solutions of (−)-**6**(OTf)$_2$, however, declined more swiftly than for (−)-**1**(OTf)$_2$ and (−)-**3**(OTf)$_2$. After 7 h, it declined by almost 50% and the ^{1}H NMR spectrum showed the presence of free 2,2′-bithiophene. Recovery of the sample from the polarimetry cell and treatment with (*S*)-(−)-α-methylbenzylamine gave only the levorotatory diastereomer of **8**(OTf). It, therefore, appears that [$(C_6Me_6)Ru(C_4H_3SC_4H_3S)$](OTf)$_2$ is only moderately stable in solution.

Base Hydrolysis of (−)-[$(C_6Me_6)Ru(2\text{-}MeC_4H_3S)$](OTf)$_2$. Base hydrolysis of (*S*)-(−)-**2** with 0.03 M KOH gave the formyl thiolato complex $(C_6Me_6)Ru(SCMeC_2H_2CHO)$, **9**$_{kin}$ (eq 3, kin = kinetic). The ^{1}H NMR data for



(3)

this bright orange species indicate exclusive nucleophilic attack of the unsubstituted α-carbon, resulting in the formation of the formyl thiolato. Noteworthy ^{1}H NMR resonances include the C*H*O signal at δ 9.00 and the doublet of doublets at ca. δ 2.85 for H_b (labeling indicated in eq 3).

In contrast to the iminium thiolato complexes **2**$^{2+}$, **4**$^{2+}$, and **6**$^{2+}$, which do not isomerize, **9**$_{kin}$ isomerizes to **9**$_{therm}$ (therm = thermodynamic), as indicated by ^{1}H NMR measurements. Integration of the doublet for H_c at δ 4.62 (**9**$_{kin}$) relative to the doublet at δ 4.97 (**9**$_{therm}$) allowed us to monitor the progress of this isomerization, which requires ∼24 hours at 25 °C. The linear dependence of ln[**9**$_{kin}$] vs time indicates that the isomerization follows first order kinetics ($k = 7.4 \times 10^{-6}$ s^{-1}). Our studies were somewhat limited by the fact that in solution, **9**$_{therm}$ decomposes after ca. 6 days.

The isomerization of (−)-**9** was also monitored by polarimetry. Acetone solutions of **9**$_{kin}$ exhibit $[\alpha]_D^{25} = -3295°$. The optical rotation of its solutions changed sign over a period of several days. Purified samples of the orange/brown species **9**$_{therm}$ exhibited a specific rotation of +1100°. The change from a negative to a positive value of $[\alpha]_D^{25}$ suggests that the isomerization of **9**$_{kin}$ to **9**$_{therm}$ involves inversion at the chiroptical

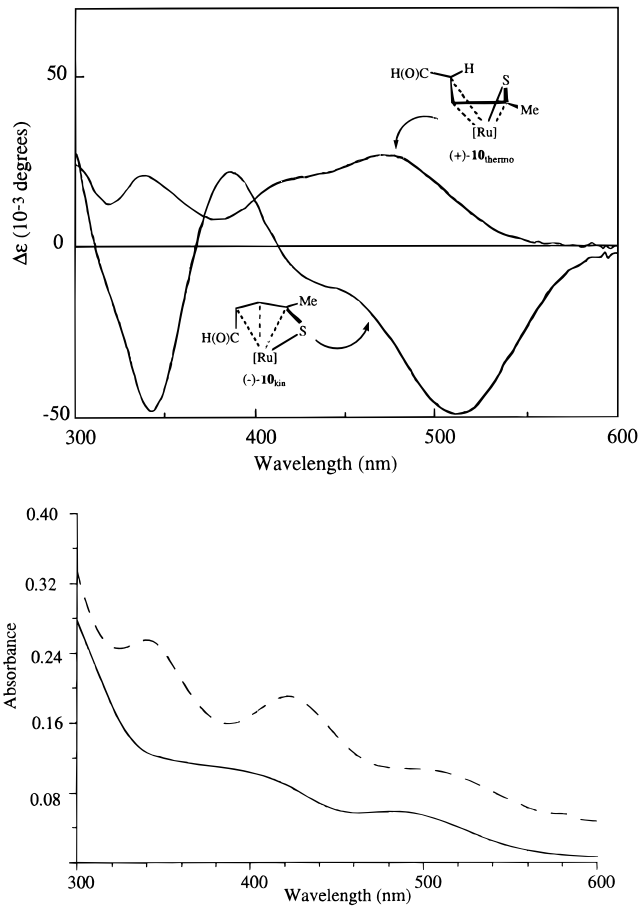


Figure 3. CD spectra of (−)$_{kin}$ and (+)$_{therm}$ isomers of (C_6Me_6)Ru($SCMeC_2H_2CHO$) (**9**). The UV−vis spectrum is shown below (dashed line = kin isomer, solid line = therm isomer). All spectra were recorded on CH_2Cl_2 solutions.

center. To support the polarimetry measurements, circular dichroism spectra were recorded on CH_2Cl_2 solutions of (−)-**9**$_{kin}$ and (+)-**9**$_{therm}$. The CD spectra are approximately mirror images, displaying Cotton effects of opposite sign (Figure 3). These spectra are not perfect mirror images since (−)-**9**$_{kin}$ and (+)-**9**$_{therm}$ are diastereomers not enantiomers ((−)-**9**$_{kin}$ and (+)-**9**$_{kin}$ would be enantiomers). The fact that the spectra approximate mirror images indicates that the chiroptical properties are dominated by the Ru(allyl thiolato) core, with the epimerizable center, *C*H(CHO), serving only as a minor perturbation.

Amination of [(Cymene)Os(2-MeC_4H_3S)](OTf)$_2$. Attempts to effect the optical resolution of osmium thiophene complexes were unsuccessful due to the instability of the iminium derivatives. This problem was revealed by studies of the reaction of [(cymene)Os(2-MeC_4H_3S)](OTf)$_2$, **10**(OTf)$_2$, and *t*-$BuNH_2$. Nucleophilic addition of the amine is followed by a relatively rapid isomerization of the iminium thiolato complex with a half-life of ∼53 min at 40 °C. Since thermodynamic isomers cannot be used to regenerate the η^5-RC_4H_3S complexes, this part of the study was discontinued. The isomerization is also accompanied by decomposition, as indicated by the formation of free cymene as well as other unidentified products. Note that isomerization is not observed for any of the aforementioned iminium thiolatos of ruthenium, for example solutions of [$(C_6Me_6)RuSCRC_2H_2(CHNH\text{-}t\text{-}Bu)$]OTf are stable for days at 40 °C.

Addition of Phenylalanine Methyl Ester to $[(C_6Me_6)Ru(C_4H_4S)](OTf)_2$. The reaction of $[(C_6Me_6)Ru(C_4H_4S)](OTf)_2$ with (L)-phenylalanine methyl ester afforded the iminium thiolato complex $[(C_6Me_6)RuSC_3H_3(CHNHCH(CH_2Ph)CO_2Me]OTf$, **11**(OTf), in 72% yield. IR and NMR measurements confirmed the attachment of the amino acid. The diastereomer ratio was 3:2, as indicated by $^1H\{^1H\}$ NMR data. The spectra of the diastereomers are typical of those presented above for kinetic isomers of the amine adducts. Comparison of the ^1H NMR data of $\mathbf{11}^+$ and $\mathbf{2}^+$ indicate that the major isomer of $\mathbf{11}^+$ corresponds to that for (−)-$\mathbf{2}^+$.

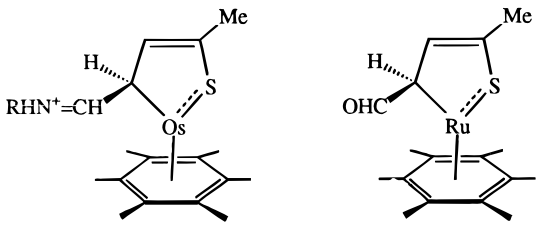
Discussion

The facile amination of dicationic π-thiophene complexes allowed us to develop a method for the optical resolution of this family of complexes. The approach begins with the generation of diastereomeric adducts of (*S*)-(−)-α-methylbenzylamine, which is cheaply available in optically pure form. After chromatographic separation of the diastereomers and removal of the chiral auxiliary, enantiomerically pure complexes of the type $(C_6Me_6)Ru(2\text{-}RC_4H_3S)^{2+}$ were obtained.[12] The use of (−)-$PhCH(Me)NH_2$ lends itself to the isolation of the levorotatory isomer, although we did confirm in one case that the more polar diastereomer was derived from the opposite enantiomer of the π-thiophene complex. Solutions of (−)-$(C_6Me_6)Ru(2\text{-}RC_4H_3S)^{2+}$ show a decline in their optical activity in the time of days for R = Me, CH_2OH. Our measurements showed that this is due to dissociation of the complexes, not racemization.

We were intrigued by the possibility that the racemization of (−)-(arene)$Ru(2\text{-}(2\text{-}C_4H_3S)C_4H_3S)^{2+}$ would be facilitated by the formation of either an *S*,*S*′-bound or η^2:η^2-bithiophene complex. The optical rotation of acetone solutions of (−)-$[(C_6Me_6)Ru(2,2'\text{-}C_4H_3SC_4H_3S)]^{2+}$ indeed decline at an accelerated rate, but the loss of optical activity is due to dissociation of the bithiophene not to racemization. These results are consistent with the report of Mann and co-workers who have observed that the $CpRu^+$ adduct of 2,2′-bithiophene is unstable in coordinating solvents.[13] It is, however, interesting to note that although the complex of the bithiophene is only modestly stable, its iminium thiolato derivatives are robust. Thus, it may be possible to use amination to stabilize metal complexes of oligothiophenes.

The resolution methodology was, unfortunately, not transferable to the analogous Os complexes, since the resulting iminium thiolato complexes are not configurationally stable. Instead, they rapidly isomerize and then decompose. We attribute the high isomerization rate in the Os species to enhanced stabilization of the 16e intermediate, depicted in Chart 1. The stabilization of such intermediates is expected to be greater for Os than that of Ru because of the increased importance of ligand to metal π-interactions for the heavier metal. This trend is illustrated by the finding that ruthenium analogs[14] of the imido compounds (η^6-arene)OsNAr[15] tend to dimerize.

Chart 1



Optically pure (−)-$[(C_6Me_6)Ru(2\text{-}MeC_4H_3S)](OTf)_2$ was utilized to probe the mechanism of the base hydrolysis of π-thiophene complexes.[16] It has been previously shown that treatment of $[(arene)Ru(C_4R_4S)](OTf)_2$ with excess aqueous KOH gives acyl thiolato complexes. The initial products ("kinetic isomers") of these reactions isomerize via a intramolecular pathway proposed to involve an $\eta^3-\eta^1$ conversion of the allyl group (Chart 1). According to this mechanism, isomerization should proceed with inversion of stereochemistry at the metal. Our study of the base hydrolysis of (−)-$[(C_6Me_6)Ru(2\text{-}MeC_4H_3S)](OTf)_2$ confirms that the isomerization of the formyl thiolato complex inverts the configuration at Ru, as previously proposed.[16]

The methodology developed could be used to determine the optical purity of primary amines. Dicationic ruthenium π-thiophene complexes offer some attractive features for this application: the diastereomeric iminium salts are quite stable, adduct formation is signaled by a dramatic color change, the diastereomers exhibit distinctive ^1H NMR spectra, the diastereomers can be separated chromatographically, and, finally, the chiral Ru auxiliary, as well as the amines in question, can be efficiently recovered.

Experimental Section

Syntheses and workups were performed under an inert atmosphere of purified nitrogen unless otherwise stated. $[(C_6Me_6)Ru(2\text{-}MeC_4H_3S)](OTf)_2$ and $[(C_6Me_6)Ru(C_4H_4S)](OTf)_2$ were prepared as described previously.[9,16] The AgOTf, (L)-phenylalanine methyl ester hydrochloride, $2\text{-}HOCH_2C_4H_3S$, and 2,2′-bithiophene were used as obtained from Aldrich. The *tert*-butylamine and (*S*)-(−)-α-methylbenzylamine (Aldrich) were distilled before use. Solvents used in chromatography were used without further purification, while the methylene chloride used in syntheses was distilled from CaH_2. The silica gel (0.040−0.063 mm, 230−400 mesh ASTM) for the chromatographic separations was procured from Merck. Celite 545 was obtained from Fisher Scientific and dried before use.

IR spectra were acquired on KBr pellets, using a Mattson Galaxy Series FTIR 3000 spectrometer, and the data are reported in cm^{-1}. NMR spectra were collected on a Varian U-400 spectrometer. Fast atom bombardment mass spectra (FABS-MS) were measured on a VG ZAB-SE. Mass spectrometry data are reported in units of *m*/*z*. UV−vis spectra were obtained with a HP-8452A diode array spectrophotometer.

Polarimetry data were collected from a JASCO DIP-360 Digital Polarimeter at the sodium D line (589 nm). The quartz polarimetry cell had a 1 mL capacity and a path length of 5 cm. Specific rotations were calculated as $[\alpha]_D^{25} = \alpha/cl$, where α (degrees) is the average of 10 measurements, *c* is the concentration in g/mL, and *l* is the path length in dm (10 cm). Circular dichroism spectra were recorded on a JASCO J720 spectropolarimeter.

(12) We also successfully applied these methods to the corresponding complexes of *p*-cymene in place of C_6Me_6.

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(+)- and (−)-[(C$_6$Me$_6$)RuSCMeC$_2$H$_2$(CHNHCHMePh)]-OTf, (+)- and (−)-2(OTf). To a slurry of 0.157 g (0.238 mmol) of **1** in 15 mL of CH_2Cl_2 was added 0.064 mL (0.500 mmol) of (*S*)-(−)-α-methylbenzylamine by syringe. The color immediately changed from yellow to cherry red, and the solids dissolved. The solution was stirred at 25 °C for 40 min, after which time the solvent was removed under vacuum. The α-methylbenzylammonium triflate was removed by chromatography through a column of silica gel (10 × 2.5 cm), eluting with THF. The red band was collected in its entirety. Yield: 0.137 g (91%). The diastereomers were found in a 1:1 ratio and are referred to as the (−) and (+) isomers. ^{1}H NMR (acetone-d_6): δ 8.78 (br dd, 1H, (−)), 8.52 (br dd, 1H, (+)), 7.60 (overlapping dd, 2H, (±)), 7.55−7.33 (overlapping m, 10H, (−) and (+)), 5.48 (d, 1H, (+)), 5.44 (d, 1H, (−)), 4.63 (overlapping q, 2H, (±)), 4.00 (dd, 1H, (+)), 3.87 (dd, 1H, (−)), 2.24 (s, 18H, (+)), 2.17 (s, 3H, (−)), 2.17 (s, 3H, (+)), 2.10 (s, 18H, (−)), 1.64 (d, 3H, (+)), 1.58 (d, 3H, (−)). UV−vis: 282, 354, 428, 516 nm. IR: 3510 and 3468 (ν_{NH}), 1600 ($\nu_{C=N}$) cm^{-1}. FAB-MS: 482 (M$^+$). Anal. Calcd for $C_{26}H_{24}NF_3O_3RuS_2$: C, 49.5; H, 5.43; N, 2.22; Ru, 16.02; S, 10.17. Found: C, 48.76; H, 5.36; N, 2.14; Ru, 15.15; S, 9.59. The (−)-diastereomer was purified by chromatography on 12 × 2.5 cm silica gel columns, eluting with a 90% Et_2O/10% CH_2Cl_2 solution. The first 20% of the red band was collected and checked by ^{1}H NMR for purity. The remainder of the red band was collected and subjected to a second column, following the same procedure. Using four such columns, 0.021 g (42%) of (−)-**2**(OTf) was obtained from ca. 0.100 g of (±)-**2**(OTf). The last 80% of the fourth column was collected and was determined to contain a 2:1 mixture of diastereomers, enriched in the (+)-isomer. $[\alpha]_D^{25}$ (−)-**2** = −1840° ($c = 5 \times 10^{-5}$, CH_2Cl_2).

(−)-(C$_6$Me$_6$)Ru(2-MeC$_4$H$_3$S)](OTf)$_2$, (−)-1(OTf)$_2$. A 50 mL Schlenk tube was charged with 0.087 g (0.138 mmol) of (−)-**2**(OTf) and 10 mL of CH_2Cl_2. Upon addition of 0.036 mL (0.414 mmol) of HOTf, the cherry red solution immediately blanched and a light yellow solid precipitated. After 1 h, the solid was filtered off and washed with 2 ×10 mL CH_2Cl_2 and 3 ×10 mL Et_2O. Yield: 0.072 g (79%). The ^{1}H NMR spectrum (acetone-d_6) was identical to that for the racemate. On the basis of the ∼2:1 mixture of diastereomers of **2**(OTf), $[\alpha]_D^{25}$ for the dextrarotatory enantiomer was calculated as ∼+33° ($c = 2 \times 10^{-3}$, acetone). Optical rotations were collected over a period of 5 days at 25 °C. The sample ($c = 2 \times 10^{-2}$, acetone) showed no visible sign of decomposition over this time, but the rotation decreased to −27°. The polarimetry sample was evaporated and treated with (*S*)-(−)-α-methylbenzylamine to give pure (−)-**1**(OTf)$_2$.

[(C$_6$Me$_6$)Ru(2-HOCH$_2$C$_4$H$_3$S)](OTf)$_2$, 3(OTf)$_2$. A 100 mL Schlenk flask was charged with 0.338 g (0.506 mmol) of [(C$_6$Me$_6$)RuCl$_2$]$_2$, 0.519 g (2.02 mmol) of AgOTf, and 15 mL of CH_2Cl_2. This reaction mixture was stirred for 4 h, followed by filtration through Celite. Approximately 1 mL (7.76 mmol) of 2-HOCH$_2$C$_4$H$_3$S was added to the orange solution. Precipitation of a dark brown solid began after ∼15 min; the reaction mixture was allowed to stir for a further 5 h. The solid was filtered off in air. The brown solid was repeatedly extracted with CH_2Cl_2 to give a yellow solution Removal of the solvent from the filtrate left lemon yellow microcrystals. Yield: 0.520 g (76%). ^{1}H NMR (acetone-d_6): δ 7.24 (d, 1H), 7.21 (d, 1H), 7.16 (dd, 1H), 5.96 (dd, 1H), 4.96 (d, 1H), 4.82 (d, 1H), 2.70 (s, 18H). ^{13}C{^{1}H} NMR (acetone-d_6): δ 120.0, 109.3, 99.0, 94.6, 93.1, 57.3. IR: 3390 (ν_{OH}) cm^{-1}. Anal. Calcd for $C_{19}H_{24}NF_6O_7RuS_3$: C, 33.77; H, 3.58; Ru, 14.96; S, 14.24. Found: C, 33.82; H, 3.68; Ru, 14.70; S, 13.90.

[(C$_6$Me$_6$)RuSCMeC$_2$H$_2$(CHNH-*t*-Bu)]OTf, 4(OTf). The synthesis is similar to that of **2**, using 0.058 g (0.086 mmol) of [(C$_6$Me$_6$)Ru(HOCH$_2$C$_4$H$_3$S)](OTf)$_2$, 10 mL of CH_2Cl_2, and 0.019 mL (0.180 mmol) of *t*-BuNH$_2$. Recrystallization of **4**(OTf) from a CH_2Cl_2 solution layered with hexane gave red crystals. Yield: 0.031 g (61%). ^{1}H NMR (acetone-d_6): δ 8.98 (br d, 1H), 7.60 (dd, 1H), d.76 (d, 1H), 4.45 (d, 1H), 3.94 (dd, 1H), 3.83 (d, 1H), 2.23 (s, 18H), 1.30 (s, 9H). UV−vis (CH_2Cl_2): 278, 354, 424, 510 nm. IR: 3454 (ν_{OH}), 1603 ($\nu_{C=N}$) cm^{-1}. FAB-MS: 449 (M$^+$). Anal. Calcd for $C_{22}H_{34}NF_3O_3RuS_2$: C, 44.13; H, 5.72; N, 2.34; Ru, 16.88; S, 10.71. Found: C, 44.06; H, 5.89; N, 2.40; Ru, 17.39; S, 10.91.

(+)- and (−)-[(C$_6$Me$_6$)RuSC(CH$_2$OH)C$_2$H$_2$(CHNHCHMePh)]OTf, (+)- and (−)-5(OTf). In air, approximately 10 mL of CH_2Cl_2 was added to 0.119 g (0.176 mmol) of **3**(OTf)$_2$. The resulting yellow slurry was treated with 0.048 mL (0.370 mmol) of (*S*)-(−)-α-methylbenzylamine, causing the mixture to change to a cherry red color. The reaction was stirred for 45 min, and then the solvent was removed by rotary evaporation. The red product was purified by chromatography on a 10 × 2.5 cm silica gel column using THF as the eluent. The entire red band was collected. The red, waxy solid was obtained by concentration of the solution, followed by the addition of hexane. Yield: 0.100 g (88%). The diastereomers are formed in a 1:1 mixture and are referred to as (−) and (+). ^{1}H NMR (acetone-d_6): δ 8.77 (br dd, 1H, (−)), 8.53 (br dd, 1H, (+)), 7.55−7.36 (phenyl region and 1 thiophene H, 12H, (±)), 5.84 (d, 1H, (+)), 5.79 (d, 1H, (−)), 4.62 (m, 2H, (±)), 4.44 (d, 1H, (+)), 4.42 (d, 1H, (−)), 4.08 (dd, 1H, (+)), 3.94 (dd, 1H, (−)), 3.81 (d, 1H, (+)), 3.78 (d, 1H, (−)), 2.24 (s, 18H, (+)), 2.09 (s, 18H, (−)), 1.59 (d, 3H, (+)), 1.46 (d, 3H, (−)). UV−vis: 232, 278, 348, 426, 510 nm. IR: 3463 (ν_{OH}) cm^{-1}. FAB-MS: 498 (M$^+$). Anal. Calcd for $C_{26}H_{34}NF_3O_4RuS_3$: C, 48.28; H, 5.30; N, 2.17; Ru, 15.63; S, 9.91. Found: C, 48.01; H, 5.34; N, 2.20; Ru, 15.95; S, 10.34. A sample of **5**(OTf) was chromatographed on a 10 × 2.5 cm silica gel column eluting with a 9:1 Et_2O/CH_2Cl_2 solvent mixture. The first ∼20% of the red band was collected. The remaining 80% was then rechromatographed until the desired amount of (−)-**5** was isolated. $[\alpha]_D^{25}$ = −1850° ($c = 4 \times 10^{-5}$, CH_2Cl_2).

(−)-[(C$_6$Me$_6$)Ru(2-HOCH$_2$C$_4$H$_3$S)](OTf)$_2$, (−)-3(OTf)$_2$. A 50 mL Schlenk flask was charged with 0.016 g (0.025 mmol) of (−)-**5**(OTf) and 5 mL of CH_2Cl_2. To this red solution, ca. 0.003 mL (0.030 mmol) of HOTf was added by microsyringe. The reaction mixture immediately blanched, and a light colored solid precipitated. The solid was filtered (in air) and washed with CH_2Cl_2. The pale yellow powder was dried under vacuum. Yield: 0.013 g (77%). Its ^{1}H NMR spectrum (acetone-d_6) was identical to the racemic isomer. IR: 3390 (ν_{OH}) cm^{-1}. $[\alpha]_D^{25} = -29°$ ($c = 8 \times 10^{-3}$, acetone).

[(C$_6$Me$_6$)Ru(2-(2-C$_4$H$_3$S)C$_4$H$_3$S)](OTf)$_2$, 6(OTf)$_2$. A 100 mL Schlenk flask was charged with 0.486 g (0.748 mmol) of [(C$_6$Me$_6$)RuCl$_2$]$_2$, 0.746 g (2.91 mmol) of AgOTf, and 20 mL of CH_2Cl_2. After the mixture was stirred for 2 h, the orange solution was filtered through Celite and then concentrated to approximately 15 mL. The solution was treated with 0.746 g (4.49 mmol) of 2,2′-bithiophene, after which a yellow precipitate immediately appeared. After 2 h, the precipitate was filtered off (in air) using a fine frit and washed with 10 mL of CH_2Cl_2 and 3 × 10 mL of hexane. Yield: 0.95 g (90%). ^{1}H NMR (acetone-d_6): δ 8.08 (m, 2H), 7.61 (dd, 1H), 7.40 (dd, 1H), 7.37 (dd, 1H), 7.33 (t, 1H), 2.51 (s, 18H). Anal. Calcd for $C_{22}H_{24}F_6O_6RuS_4$: C, 36.31; H, 3.32; Ru, 13.89; S, 16.62. Found: C, 35.96; H, 3.43; Ru, 13.69; S, 16.34.

[(C$_6$Me$_6$)RuSC(C$_4$H$_3$S)C$_2$H$_2$(CHNH-*t*-Bu)]OTf, 7(OTf). The synthesis is similar to that of **4**(OTf), using 0.072 g (0.100 mmol) of **6**(OTf)$_2$, 12 mL of CH_2Cl_2, and 0.022 mL (0.210 mmol) of *t*-BuNH$_2$. Red crystals precipitated upon addition of hexane to a concentrated CH_2Cl_2 solution. Yield: 0.050 g (77%). ^{1}H NMR (acetone-d_6): δ 9.36 (br d, 1H), 7.82 (dd, 1H), 7.58 (d, 1H), 7.48 (d, 1H), 7.14 (dd, 1H), 6.14 (d, 1H), 4.04 (dd, 1H), 2.05 (s, 18H), 1.33 (s, 9H). UV−vis (CH_2Cl_2): 298, 380, 514 nm. IR: 1602 ($\nu_{C=N}$) cm^{-1}. FAB-MS: 500 (M$^+$). Anal. Calcd for $C_{25}H_{34}NF_3O_3RuS_3 \cdot H_2O$: C, 44.90; H, 5.43; N, 2.09; Ru, 15.11; S, 14.38. Found: C, 44.98; H, 5.27; N, 2.02; Ru, 15.53; S, 14.32.

(+)- and (−)-[(C$_6$Me$_6$)RuSC$_3$H$_3$(CHNHCHMePh)]OTf, (+)- and (−)-8(OTf). In air, a 100 mL round-bottom flask was charged with 0.180 g (0.250 mmol) of **6**(OTf)$_2$ and 14 mL

of CH_2Cl_2, followed by 0.068 mL (0.525 mmol) of (*S*)-(−)-α-methylbenzylamine. The reaction mixture immediately changed from a yellow slurry to a cherry red solution. After 1 h, the solvent was removed under vacuum. This mixture of diastereomers was first purified by chromatography on a silica gel column (10 × 2.5 cm), using THF as the eluent. The entire red band was collected. The red product precipitated upon addition of hexane to the concentrated solution. Yield: 0.150 g (86%). The diastereomers are formed as a 1:1 mixture and are labeled as the (−)-isomer and the (+)-isomer. ^{1}H NMR (acetone-d_6): δ 9.43 (br s, 1H, (+)), 9.11 (br s, 1H, (−)), 7.77 (dd, 1H, (−)), 7.58 (dd, 1H, (+)), 7.55 (dd, 2H, (±)), 7.49 (dd, 2H, (±)), 7.50−7.30 (phenyl region and thiophene, 12H, (±)), 7.12 (dd, 2H, (±)), 6.17 (d, 1H, (+)), 6.12 (d, 1H, (−)), 4.65 (overlapping q, 2H, (±)), 4.16 (dd, 1H, (+)), 4.04 (dd, 1H, (−)), 2.04 (s, 18H, (+)), 1.87 (s, 18H, (−)), 1.66 (d, H, (+)), 1.62 (s, 3H, (−)). UV−vis (CH_2Cl_2): 242, 300, 376, 514 nm. IR: $\nu_{C=N}$ 1597 cm^{-1}. FAB-MS: 550 (M^+). Anal. Calcd for $C_{29}H_{34}NF_3O_3RuS_3$: C, 49.84; H, 4.90; N, 2.00; Ru, 14.46; S, 13.36. Found: C, 49.53; H, 4.91; N, 2.11; Ru, 14.52; S, 13.11. The (−)-diastereomer was purified by chromatography on a 12 × 2.5 cm silica gel column, eluting with 90% Et_2O/10% CH_2Cl_2. Starting with 0.100 g of (±)-**8**(OTf), approximately the first 50% of the red band was collected and shown by ^{1}H NMR measurements to be diastereomerically pure. The second half of the band (enriched in (+)-**8**(OTf)) was collected and then subjected to another such column. After three such columns, ca. 0.035 g (70%) of (−)-**8**(OTf) was isolated. The red product precipitated from Et_2O/CH_2Cl_2 upon addition of hexane. For (+)-**8**(OTf), $[\alpha]_D^{25} = +1700°$ ($c = 2 \times 10^{-5}$, CH_2Cl_2). The last 20% of the bands contained pure (+)-**8**(OTf) (unlike the separations of **2**(OTf) and **5**(OTf)). Approximately 0.020 g (40%) of (+)-**8**(OTf) was recovered: $[\alpha]_D^{25} = +1700°$ ($c = 2 \times 10^{-5}$, CH_2Cl_2).

(−)-(C$_6$Me$_6$)Ru(C$_4$H$_3$SC$_4$H$_3$S)](OTf)$_2$, (−)-6(OTf)$_2$. A 50 mL Schlenk flask was charged with 0.025 g (0.036 mmol) of (−)-**8**(OTf), to which ∼7 mL of CH_2Cl_2 was added to yield a red solution. By syringe, 0.009 mL (0.102 mmol) of HOTf was added. The solution immediately changed from a red color to yellow. After 10 min, the solution was concentrated and a lemon yellow powder precipitated upon addition of Et_2O. The solid was filtered off and washed with Et_2O. Yield: 0.022 g (85%). Its ^{1}H NMR spectrum was identical to racemic **6**(OTf)$_2$. $[\alpha]_D^{25} = -37°$ ($c = 2 \times 10^{-3}$, acetone). (+)-**6**(OTf)$_2$ was prepared analogously from (+)-**8**(OTf): $[\alpha]_D^{25} = +37°$ ($c = 2 \times 10^{-3}$, acetone).

(−)-[(C$_6$Me$_6$)RuSCMeC$_2$H$_2$CHO], (−)-9$_{kin}$ and (+)-9$_{therm}$. In air, 0.042 g (0.064 mmol) of (−)-**1**(OTf)$_2$ was treated with 7 mL of 0.03 M KOH (0.191 mmol). The color of the reaction mixture immediately changed from yellow to orange, and after 10 min, an orange solid began to precipitate. After 1 h, the aqueous layer was extracted with 3 ×7 mL CH_2Cl_2, using a separatory funnel. The combined CH_2Cl_2 fractions were dried over $NaSO_4$. The solvent was removed under vacuum leaving an orange residue, (−)-[(C$_6$Me$_6$)Ru(SCMeC$_2$H$_2$CHO)], (−)-**9**$_{kin}$. Yield: 0.016 g (67%). ^{1}H NMR: (acetone-d_6, kinetic) δ 9.09 (d, 1H), 4.73 (d, 1H), 2.80 (dd, 1H), 2.20 (s, 3H), 2.11 (s, 18H); (CD_2Cl_2, kinetic) δ 9.00 (d, 1H), 4.62 (d, 1H), 2.85 (dd, 1H), 2.21 (s, 3H), 2.09 (s, 18H). UV−vis (CH_2Cl_2): 340, 422, 504 nm. IR: 1610 (ν_{CO}) cm^{-1}. CD (CH_2Cl_2, nm (10^{-3} degrees)): 342 (−48), 422 (−8), 510 (−49). $[\alpha]_D^{25} = -3270°$ ($c = 2.5 \times 10^{-4}$, CH_2Cl_2). The thermodynamic isomer (+)-**9**$_{therm}$ was obtained by heating a CH_2Cl_2 solution of (−)-**9**$_{kin}$ for 5 days at 40 °C and purified by chromatography on a silica gel column, eluting with THF. Solutions of this isomer are orange/brown. ^{1}H NMR: (acetone-d_6, therm isomer) δ 8.97 (d, 1H), 5.08 (d, 1H), 2.17 (s, 3H), 2.12 (s, 3H), 1.82 (dd, 1H); (CD_2Cl_2, thermo) δ 9.01 (d, 1H), 4.97 (d, 1H), 2.18 (s, 3H), 2.10 (s, 18H), 1.85 (dd, 1H). UV−vis (CH_2Cl_2): 234, 266, 392, 486 nm. IR: 1660 and 1649 (ν_{CO}) cm^{-1}. CD (CH_2Cl_2, nm (10^{-3} degrees)): 340 (21), 422 (20), 470 (27). $[\alpha]_D^{25} = +1100°$ ($c = 4 \times 10^{-5}$, CH_2Cl_2). Kinetic data were collected from ^{1}H NMR spectra of CD_2Cl_2 solutions. Five data points were collected in roughly 24 h intervals at 25 °C. The sample is largely decomposed after 5−6 days in solution. The plot of ln(% kin isomer) vs time was linear with a slope of -7.41×10^{-6} s^{-1}.

[(Cymene)Os(2-MeC$_4$H$_3$S)](OTf)$_2$, 10(OTf)$_2$. A 100 mL Schlenk flask was charged with 0.260 g (0.329 mmol) of [(cymene)$OsCl_2$]$_2$, 0.338 g (1.32 mmol) of AgOTf, and 15 mL of CH_2Cl_2. The mixture was stirred for 3 h and filtered through Celite. The orange filtrate was treated with 1 mL (10.33 mmol) of 2-MeC$_4$H$_3$S. A few minutes following the addition a white precipitate appeared. After a further 6 h, the mixture was filtered and the colorless solid **10**(OTf)$_2$ was rinsed with 2 × 5 mL CH_2Cl_2. The solvent was removed under vacuum to yield a fine, white powder. Yield: 0.400 g (96%). ^{1}H NMR (acetone-d_6): δ 7.70 (d, 1H), 7.66 (t, 1H), 7.55 (d, 1H), 7.33 (overlapping dd, 2H), 7.27 (d, 1H), 7.23 (d, 1H), 3.09 (m, 1H), 0.77 (s, 3H), 1.39(d, 6H). Anal. Calcd for $C_{17}H_{20}F_6OsO_6S_3$: C, 28.33; H, 2.80; S, 13.35. Found: C, 29.97; H, 2.76; S, 13.43.

[(Cymene)Os(SCMeC$_2$H$_2$(CHNH-*t*-Bu)]OTf. To the white slurry of 0.103 g (0.163 mmol) of (cymene)Os(2-MeC$_4$H$_3$S)](OTf)$_2$ in 10 mL of CH_2Cl_2 was added 0.045 mL (0.424 mmol) of *t*-$BuNH_2$. The solution immediately changed to orange and then eventually to brown, accompanied by formation of a white precipitate. The reaction mixture was filtered in air through Celite. The solvent was removed under vacuum to yield a brown oil. The kinetics of isomerization were examined on an acetone-d_6 solution that was sealed in a 5 mm NMR tube containing CH_2Cl_2 as an integration standard. The isomerization was monitored at 40 °C by integration of δ 2.47 (kin isomer) and 2.39 (therm isomer) vs δ 5.6 (CH_2Cl_2). Eleven data points were collected at 10 min intervals. Plots of ln[complex] vs time were linear with a slope of 2.19×10^{-4} s^{-1}. ^{1}H NMR (acetone-d_6, kin isomer): δ 9.46 (br d, 1H), 8.05 (d, 1H), 6.47 (d, 1H), 6.17 (d, 1H), 6.01 (dd, 1H), 5.86 (d, 1H), 4.68 (dd, 1H), 2.72 (quintet, 1H), 2.47 (s, 3H), 2.30 (s, 3H), 2.29 (d, 6H), 1.27 (s, 9H). ^{1}H NMR (acetone-d_6, therm isomer): δ 8.29 (d, 2H), 6.63 (d, 1H), 6.08 (d, 1H), 5.93 (d, 1H), 5.83 (d, 1H), 5.42 (d, 1H), 5.42 (d, 1H), 2.66 (m, 1H), 2.37 (s, 3H), 2.25 (s, 3H), 1.52 (s, 9H), 1.29 (dd, 6H).

Reaction of [(C$_6$Me$_6$)Ru(C$_4$H$_4$S)](OTf)$_2$ with (L)-Phenylalanine Methyl Ester, 11(OTf). The same procedure as with the 2-MeC$_4$H$_3$S derivative was followed, using 0.160 g (0.248 mmol) of [(C$_6$Me$_6$)Ru(C$_4$H$_4$S)](OTf)$_2$, 0.053 g (0.248 mmol) of (L)-phenylalanine methyl ester hydrochloride, 20 mL of CH_2Cl_2, and 0.069 mL (0.496 mmol) of NEt_3. Yield: 0.120 g (72%). The diastereomers are formed in a 3:2 ratio. The more abundant isomer will be referred to as A and the lesser as B. ^{1}H NMR (acetone-d_6): δ 8.22 (br dd, 1H, A), 8.01 (br dd, 1H, B), 7.36−7.16 (phenyl region, 10H, A and B), 7.25 (dd, 1H, B), 6.95 (br dd, 1H, A), 6.11 (d, 2H, B), 6.02 (d, 1H, A), 5.72 (dd, 1H, B), 5.63 (dd, 1H, A), 4.42 (br m, 1H, B), 4.23 (m, 3H, A and B), 3.80 (s, 3H, A), 3.68 (s, 3H, B), 3.26−2.99 (m, 4H, A and B), 2.25 (s, 18H, A), 2.18 (s, 18H, B). UV−vis: 278, 498 nm. IR: 1745 (ν_{CO}), 1594 ($\nu_{C=N}$) cm^{-1}. FAB-MS: 525 (M^+). Anal. Calcd for $C_{27}H_{34}NF_3O_5RuS_2$: C, 48.06; H, 5.08; N, 2.08; Ru, 14.98; S, 9.50. Found: C, 47.81; H, 5.30; N, 1.89; Ru, 15.35; S, 8.81.

Structure of (−)-[(C$_6$Me$_6$)RuSCMeC$_2$H$_2$(CHNHCHMePh)]OTf. The crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fiber. The sample was bound by faces (−1,−1,0),(1,1,0),(1,−1,0),(−1,1,0),(0,0,1),(1,1,−3), and (−1,1,2). Distances from the crystal center to these facial boundaries were 0.030, 0.030, 0.045, 0.045, 0.18, 0.16, and 0.12 mm, respectively. Crystal structure and refinement details are given in Table 2. Systematic conditions led to the unambiguous space group $P2_12_12_1$. Standard intensities monitored during frame collection showed no decay; decay correction was not applied. Intensity data were reduced by a three-dimensional profile analysis using SAINT[17] and were corrected for

(17) SAINT V4, SHELXTL V5, SMART V4, Siemens Industrial Automation, Inc., Madison, WI.

Table 2. Crystal Data and Structure Refinement for (−)-2(OTf)·H_2O

mol formula	$C_{26}H_{36}F_3NO_4RuS_2$
mol wt	648.75
temp	298(2) K
wavelength	0.710 73 Å
cryst syst	orthorhombic
space group	$P2_12_12_1$
unit cell dimens	$a = 11.7033(5)$ å, $\alpha = 90°$
	$b = 13.8198(7)$ Å, $\beta = 90°$
	$c = 17.2576(8)$ Å, $\gamma = 90°$
volume (V)	2791.2(2) Å^3
z	4
density (calcd)	1.544 mg/m^3
abs coeff	0.764 mm^{-1}
cryst size	0.35 × 0.09 × 0.06 mm
θ range	1.89−28.29°
index ranges	$-15 \le h \le 15$, $-11 \le k \le 18$, $-22 \le l \le 21$
collection method	ccd area detector frames
rflns collcd	18379 ($R_{int} = 0.0705$)
independent rflns	6654 (5198 obs, $I > 2\sigma(I)$)
abs corr	integration
refinement	(shift/err = −0.002)
data/restraints/parameters	6649/0/334
goodness-of-fit on F^2	1.107
final R indices (obs data)†	$R_1 = 0.0523$, w$R_2 = 0.0887$
R indices (all data)†	$R_1 = 0.0845$, w$R_2 = 0.1054$
absolute structure param	−0.03(4)
largest diff. peak and hole	0.46 and −0.500 e$^-$ Å^{-3}†

† $w = 1/[\sigma^2(F_o^2) + (0.0109P)^2 + 7.5500P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Lorentz-polarization effects and absorption. Scattering factors and anomalous dispersion terms were taken from standard tables.[18] The structure was solved by direct methods.[19] Subsequent cycles of isotropic least-squares refinements, followed by an unweighted difference Fourier synthesis, revealed positions for the remaining non-H atoms. Methyl H-atom positions were optimized by rotation about C−C bonds with idealized C−H, C···H and H···H distances. The remaining H atoms were included as fixed idealized contributors. The U values for the H atoms were assigned as 1.5 times U_{eq} of the adjacent C atoms for methyl and 1.2 times U_{eq} of the adjacent C atoms for methylene and methine groups. H atoms were not assigned to O4, the oxygen in the water molecule. Non-H atoms were refined with anisotropic thermal coefficients. Successful convergence of the full-matrix least-squares refinement on F^2 was indicated by the maximum shift/error for the last cycle.[20] The highest peaks in the final difference Fourier map were in the vicinity of the O4 atom; the final map had no other significant features. A final analysis of the variance between the observed and calculated structure factors showed no dependence on the amplitude or resolution.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, bond lengths and angles, and torsion angles and an ORTEP diagram for (−)-**2**(OTf)·H_2O (13 pages). Ordering information is given on any current masthead page.

OM9607659

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