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A Chiral Sulfoxide-Ligated Ruthenium Complex for Asymmetric Catalysis: Enantio- and Regioselective Allylic Substitution

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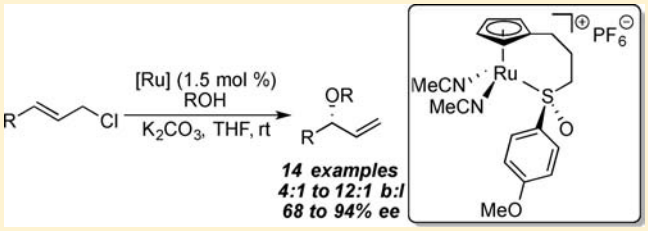
Supporting Information

ABSTRACT: The design and synthesis of a novel chiral sulfoxide-ligated cyclopentadienyl ruthenium complex is described. Its utility as an asymmetric variant of [CpRu-$(MeCN)_3$]PF_6 is demonstrated through its ability to function in the branched-selective asymmetric allylic alkylation of phenols and carboxylic acids. Water has also been shown to act as a competent nucleophile in this reaction to generate branched allyl alcohols with good regio- and enantioselectivities.

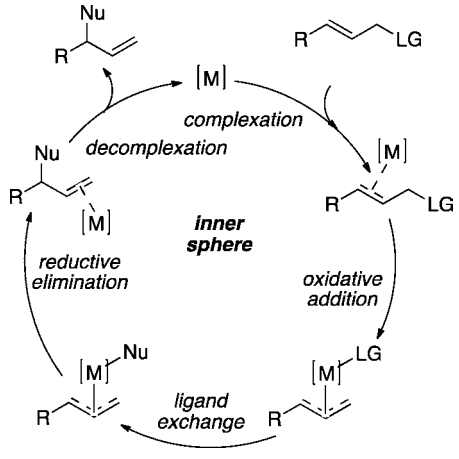


INTRODUCTION

Asymmetric catalysis has emerged as a powerful tool for the rapid and atom-economical construction of enantioenriched molecules.[1] As such, the development of new scaffolds for chiral catalysts is important. While alcohols and phosphines with chiral backbones have been heavily explored as ligands for asymmetric catalysis, *S*-chiral sulfoxides remain an underutilized ligand class.[2] A major breakthrough in the development of chiral sulfoxide ligands was recently disclosed by Dorta and coworkers.[3] In this report, a C_2-symmetric bis-sulfoxide ligand was successfully utilized in the Rh-catalyzed conjugate addition of arylboronic acids to cyclic enones. Subsequent work by Liao and others has resulted in the development of *S*-chiral monosulfoxide ligands, again utilized in Rh-catalyzed conjugate additions.[4] Though much progress has been made recently in the development of chiral sulfoxide ligands for Rh-catalyzed Hayashi−Miayura reactions, the use of such ligands for alternative processes remains limited. We herein report the synthesis of a novel chiral sulfoxide-ligated cyclopentadienylruthenium (CpRu) complex and its ability to catalyze branched-selective asymmetric allylic alkylation reactions.[5]

Asymmetric allylic alkylation (AAA) has emerged as a popular platform for the analysis of new ligand scaffolds due to its ability to construct optically enriched complex molecules from relatively simple building blocks. Much of the development of such reactions has involved the exploration of palladium catalysts with chiral phosphine ligands.[6] These palladium-catalyzed transformations are known to proceed through an "outer-sphere" mechanism, whereby the nucleophile attacks the cationic allyl complex without precoordination to the metal center. These outer-sphere mechanisms tend to favor linear products resulting from nucleophilic attack at the least hindered carbon. Recently, however, several groups have demonstrated the use of other transition metals as AAA catalysts, which can yield products that are complementary to the palladium-catalyzed processes. These reactions are believed to proceed through an "inner-sphere" mechanism, which is characterized by precoordination of the nucleophile to the metal center, followed by reductive elimination (Scheme 1). Such mechanisms tend to favor reductive elimination at the carbon that best stabilizes positive charge, leading to branched products.

Scheme 1. Inner-Sphere Mechanism for the Formation of Branched Allylic Alkylation Products



Early work in these branched-selective processes was performed with achiral rhodium and iridium catalysts.[7] Subsequent reports by Pfaltz and Helmchen disclosed the ability of chiral phosphine−oxazoline ligands on tungsten and iridium, respectively, to allylate soft carbon nucleophiles regio- and enantioselectively.[8] Later work by Trost and Pfaltz demonstrated the ability of molybdenum complexes to catalyze

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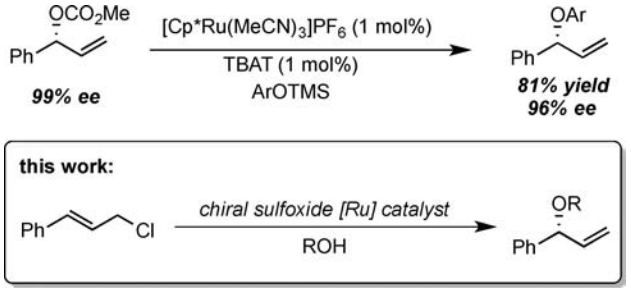
branched-selective AAA reactions, again with soft carbon nucleophiles.[9,10] Work by Bäckvall and others has demonstrated the use of Grignard and organozinc reagents as nucleophiles for the copper-catalyzed branched-selective AAA.[11]

Undoubtedly the most versatile catalysts for branched-selective AAA reactions, however, are the iridium−phosphoramidite complexes developed by Hartwig.[12] Using these complexes, the Hartwig group has effected the asymmetric allylation of amines, alcohols, silyl enol ethers, heteroarenes, and ammonia.[13] Elegant mechanistic studies have demonstrated the importance of an *in situ* cyclometalation event between the ligand and the metal to furnish the active catalyst.[14] Carreira and co-workers have also employed iridium catalysts bearing both chiral diene and phosphoramidite ligands to perform branched-selective allylic alkylations using oxygen nucleophiles.[15]

Despite the impressive scope of such catalysts, several groups have begun to explore the use of ruthenium in the branched-selective AAA in an attempt to overcome the cost barriers associated with iridium. The Trost group disclosed the first example of this approach, successfully coupling phenols and enantioenriched allyl carbonates with high levels of chirality transfer (Scheme 2).[16] Subsequently, Bruneau and Renaud

Scheme 2. Proposed Method for the Formation of Optically Active Branched Aryl Ethers and Esters



demonstrated the use of chiral bisoxazoline ligands with a ruthenium precatalyst in the branched-selective AAA reaction, albeit with modest regioselectivities.[17,18] Most recently, the Onitsuka group has pioneered the use of planar chiral tethered CpRu complexes as effective catalysts for the branched-selective AAA reaction (Figure 1a).[19] Although the regio- and enantioselectivities obtained with the Onitsuka system are very impressive, the complexity of the catalyst synthesis renders this method somewhat less practical (*vide infra*).[20]

We hypothesized that the design of a tethered, chiral sulfoxide-ligated CpRu complex might represent a modular,

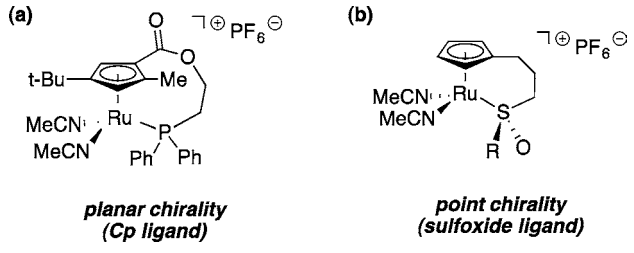


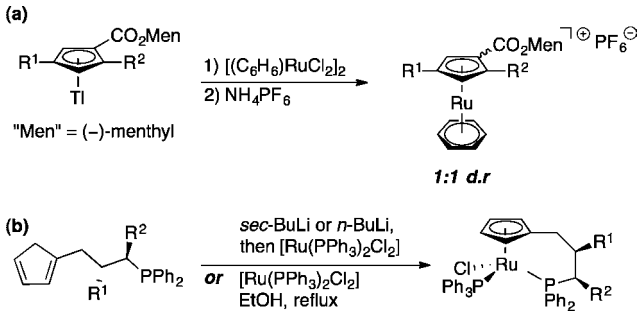
Figure 1. Two different approaches to chiral CpRu catalysts: (a) planar chiral Cp ligand pioneered by Onitsuka and co-workers and (b) point chiral sulfoxide ligand reported in this work.

easily accessible asymmetric variant of $[CpRu(MeCN)_3]PF_6$ (Figure 1b). We envisioned that the use of a chiral sulfoxide ligand would have two distinct advantages: (1) placement of the chiral information relatively close to the metal center and (2) the possibility of high levels of steric and electronic differentiation between a small oxygen substituent and a large aryl group on the sulfur atom. Furthermore, we believed that introduction of a tether from the cyclopentadienyl ring to the sulfoxide could aid both coordination of the sulfoxide and rigidification of the ligand framework. Our complex design differs fundamentally from that of the Onitsuka group, as the chirality in the proposed system contains point chirality at the sulfoxide rather than planar chirality at the Cp ligand (Figure 1). Finally, we sought to utilize an oxidative [3 + 2] coupling reaction as a highly modular and atom-economical approach to the installation of the cyclopentadienyl tether.

RESULTS AND DISCUSSION

Catalyst Design and Synthesis. Two standard methods have historically been employed to synthesize asymmetric, tethered CpRu complexes. The first approach, pioneered by Onitsuka, involves the preparation of trisubstituted planar-chiral CpRu complexes (Figure 1a).[20] In this strategy, trisubstituted cyclopentadienes containing a menthyl ester auxiliary are synthesized using the method of Ueda.[21] The thallium salt of the diene is then generated, and treatment of this salt with $[(C_6H_6)RuCl_2]_2$ results in the formation of a mixture of diastereomeric sandwich complexes (Scheme 3a).

Scheme 3. Established Approaches to the Synthesis of CpRu Complexes from Preformed Cyclopentadiene Ligands[a]



[a]Key: (a) Onitsuka's approach to the formation of planar chiral CpRu complexes; (b) formation of phosphine-tethered CpRu complexes through alkylation of a chloride salt.

The diastereomers are separated through a low-yielding fractional crystallization. Saponification of the menthyl auxiliary, introduction of the tether via the corresponding acid chloride, and photolysis to remove the benzene ligand complete the synthesis. Though many complexes with varying substitution and tethers have been synthesized by this approach, major drawbacks include the use of toxic thallium reagents to install the Cp ligand and the reliance on a kinetic resolution of ruthenium complexes to obtain enantiomerically pure catalysts.

A more common strategy for the formation of tethered CpRu complexes proceeds through the alkylation of $[Ru(PPh_3)_2Cl_2]$.[22] This approach enables the preparation of CpRu complexes containing chirality on the tether backbone. The monosubstituted cyclopentadiene is installed at the metal center via either an ethanolic reduction or substitution reaction (Scheme 3b). Inclusion of a phosphine on the tether is critical

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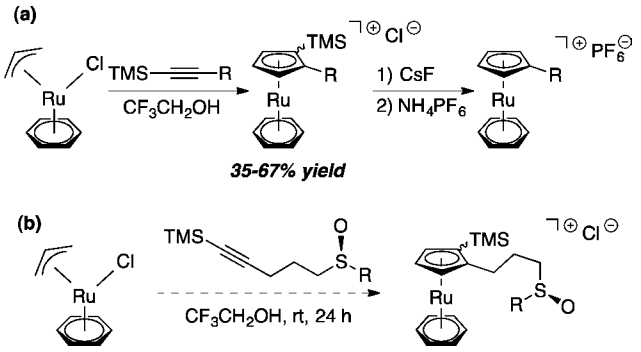
to effect an exchange with one of the PPh_3 ligands. This exchange, however, results in a mixture of complexes that are epimeric at ruthenium.[22c] The Trost group has synthesized a series of optically active tethered CpRu complexes using this method, and these complexes have been examined as chiral catalysts for the reconstitutive addition reaction.[22b,23]

An alternative strategy for accessing tethered CpRu complexes has recently been explored in the Trost group. This approach was inspired by previous work demonstrating the ability of ruthenium, rhodium, and cobalt π-allyl complexes to form cyclopentadienyl ligands in the presence of a symmetrical alkyne and a silver salt.[24,25] Unpublished work by Trost and Older has demonstrated the feasibility of such an oxidative [3 + 2] cycloaddition between $[(C_6H_6)Ru(\eta^3\text{-allyl})]Cl$ and unsymmetrically substituted internal alkynes to yield disubstituted sandwich complexes as racemic mixtures (Scheme 4a).[26] These complexes could subsequently be desilylated to remove the chirality at ruthenium and generate monosubstituted cyclopentadienyl ligands. Such an approach to Cp ligand formation is atom-economical, as the only byproduct of the reaction is hydrogen gas and avoids the use of toxic reagents. Furthermore, tethers lacking phosphine ligands can be accessed through this approach. Given these advantages, we decided to use the [3 + 2] cycloaddition as a key step in the synthesis of our desired chiral sulfoxide-containing CpRu complexes (Scheme 4b).

Scheme 4. Proposed [3 + 2] Cycloaddition Strategy[a]

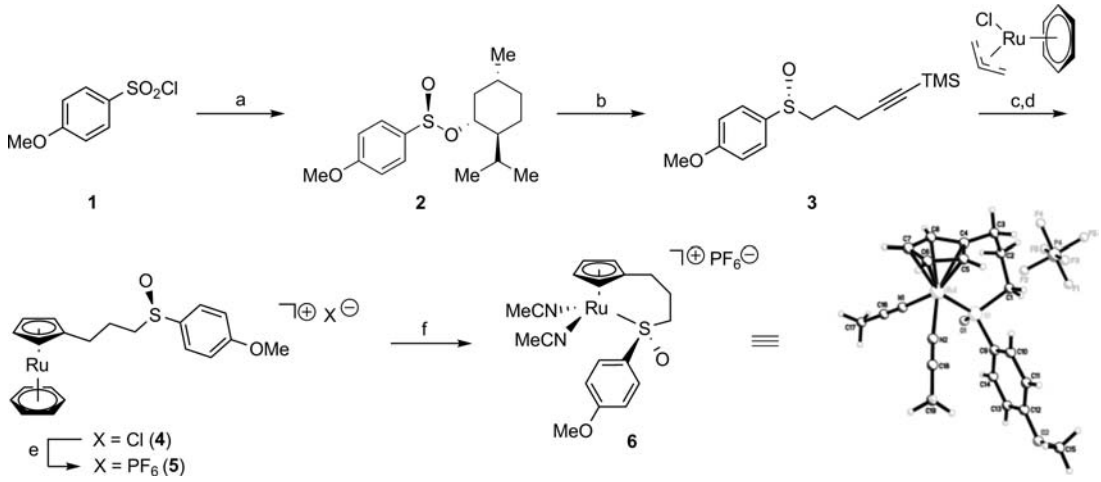


[a]Key: (a) [3 + 2] cycloaddition strategy for the formation of substituted CpRu complexes; (b) proposed key step for the synthesis of chiral sulfoxide-ligated CpRu complexes.

A library of five tethered sulfoxide CpRu complexes could be accessed using this [3 + 2] cycloaddition as a key step (see Table 2 and the Supporting Information). The synthesis of *p*-anisyl-substituted tethered sulfoxide complex **6** is shown as a representative example in Scheme 5. The synthesis of alkyne **3** was initially attempted through the alkylation of 4-(trimethylsilyl)pent-3-yn-1-yl iodide with lithiated methyl *p*-anisyl sulfoxide. Use of the homopropargyl iodide electrophile, however, resulted in an undesired elimination side reaction, prompting us to switch the reactivity of the coupling partners. To this end, reduction of sulfonyl chloride **1** to menthyl sulfinate ester **2** with PPh_3 was achieved using conditions developed by Toru.[27] Ester **2** could be obtained in 36% yield as a single diasteromer upon dynamic kinetic recrystallization with hot acetone and catalytic HCl. Coupling of **2** with the Grignard reagent derived from 5-(trimethylsilyl)pent-4-yn-1-yl iodide was found to proceed with inversion of configuration at sulfur to provide sulfoxide **3** in 91% yield as a single enantiomer.[28] This concise, two-step synthesis of the alkyne fragment allows for facile modification of the aryl group on the sulfoxide through judicious choice of the sulfonyl chloride starting material.

The key [3 + 2] cycloaddition reaction between alkyne **3** and $[(C_6H_6)Ru(\eta^3\text{-allyl})]Cl$ proceeded smoothly to provide the desired disubstituted CpRu complex in 85% yield as a mixture of diastereomers. A color change from bright orange to brown was observed upon conversion of the starting half-sandwich ruthenium complex to the final sandwich complex. To the best of our knowledge, this is the first example of the use of such a coupling reaction without the incorporation of stoichiometric silver salts.[24,25] Subsequent desilylation furnished sandwich complex **4** as the chloride salt. Ion exchange with NH_4PF_6, followed by photolytic ligand exchange to install two acetonitrile ligands, provided access to complex **6**. Irradiation with 350 nm blacklights was found to be crucial in the final

Scheme 5. Synthesis of the Catalyst[a]



[a]Key: (a) PPh_3, NEt_3, (−)-menthol, DCM, rt; then acetone/HCl (cat.) recrystallization, 36%; (b) (5-(trimethylsilyl)pent-4-yn-1-yl)magnesium iodide, THF, −78 °C to rt, 91%; (c) $[(\eta^3\text{-allyl})Ru(benzene)]Cl$, 2,2,2-trifluoroethanol, rt, 85% (1:1 dr); (d) CsF, MeCN, rt; (e) NH_4PF_6, H_2O/DCM/MeOH, rt (49% over two steps); (f) $h\nu$ (350 nm), MeCN, rt, 44%.

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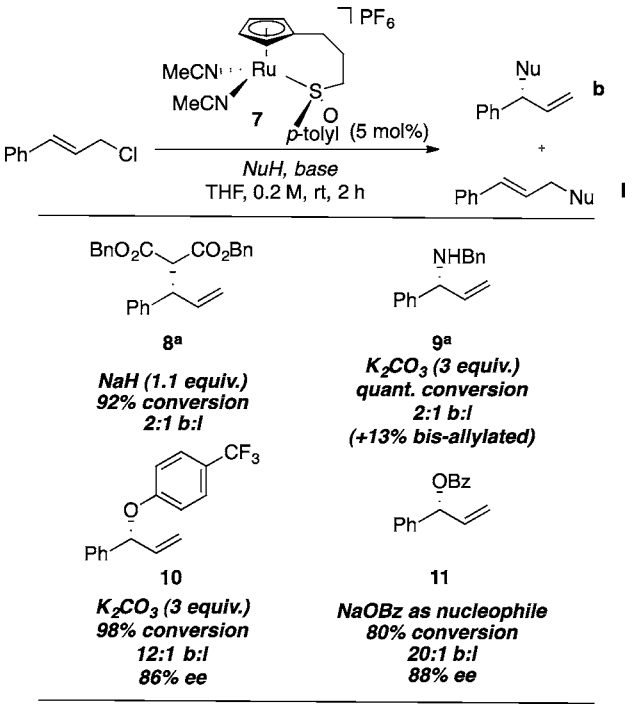
ligand exchange reaction, as irradiation at lower wavelengths resulted in decomposition of the complex. High dilutions were also observed to be necessary for the photolysis to proceed at a reasonable rate. Crystallographic analysis revealed that the sulfoxide ligand was bound to the metal center via the sulfur atom and confirmed the absolute stereochemistry of the sulfoxide ligand.

REACTION OPTIMIZATION

With a strategy in hand for accessing a variety of tethered sulfoxide CpRu complexes, we set our sights on examining their utility in the branched-selective AAA reaction. Our initial studies of this reaction involved the use of *p*-tolyl-substituted complex 7 and cinnamyl chloride as the electrophile (Table 1).

Table 1. Initial Experiments in the Branched-Selective AAA

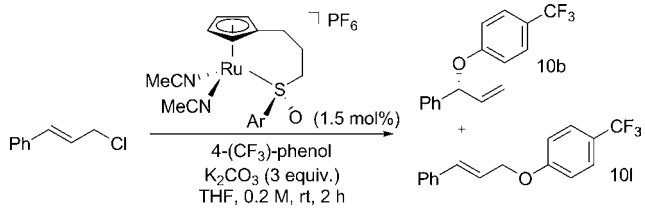


[a]ee not determined due to low regioselectivity.

Carbon-, nitrogen- and oxygen-based nucleophiles all participated in the desired transformation, though with varying levels of regioselectivity. Oxygen-based nucleophiles were found to react with the highest levels of branched-selectivity and displayed good enantioselectivities. The exploration of such oxygen-based nucleophiles was particularly attractive to us since heteroatom nucleophiles are known to be incompatible with the Mo-catalyzed branched-selective AAA.

With our focus set on oxygen nucleophiles, our attention was turned to optimization of the aryl group on the catalyst sulfoxide ligand (Table 2). The alkylation of cinnamyl chloride with *p*-(trifluoromethyl)phenol was employed as a test reaction. Introduction of an electron-rich anisyl substitutent resulted in the highest enantioselectivity (entry 3). Generally, enantioselectivities were found to increase with increased electron density of the aryl group. Such a trend could be attributed to the enhanced Lewis basicity of sulfoxide ligands containing electron-rich substituents, allowing for enhanced coordination to the metal center. Introduction of fused aromatics at the sulfur atom dramatically decreased the regio- and enantioselectivity of the allylic substutition reaction (entries 4 and 5). We hypothesized that the incorporation of a bulky aryl group might promote dissociation of the sulfoxide ligand. Indeed, control experiments suggest that this is the case, as the allylic alkylation of cinnamyl chloride and *p*-(trifluoromethyl)phenol with $[CpRu(MeCN)_3]PF_6$ led to the formation of products with comparably low regioselectivity (1:1 **10b**:**10l**).

Table 2. Effect of the Sulfoxide Ligand Substituent



entry	Ar	conversion (%)	**10b**:**10l**[a]	ee (%)
1	*p*-tolyl	99	10:1	78
2	*p*-*tert*-butylbenzene	99	14:1	53
3	*p*-anisyl	83	16:1	92
4	1-naphthyl	73	1:1	racemic
5	2-naphthyl	71	1:1	12

[a]Product ratio determined by ^{1}H NMR of unpurified reaction mixtures.

Optimization of the allylic substitution reaction conditions commenced with an examination of the effect of the leaving group (Table 3, entries 1−3). While use of cinnamyl acetate resulted in no observed alkylation, the corresponding carbonate was found to provide a low 14% yield of desired product. Use of cinnamyl chloride furnished the highest level of regio- and enantioselectivity. While inclusion of an organic base provided high levels of regio- and enantioselectivity (entry 4), the yield suffered. Finally, higher enantioselectivities were observed with more coordinating solvents, and THF was found to be optimal in this regard (entry 7). In the reactions run in acetone and THF, a minor side product was observed (18% conversion) corresponding to the addition of adventitious water to the branched position. This observed side product could be reduced with the inclusion of molecular sieves (entry 8).[29,30]

The substrate scope was initially examined with respect to the nucleophile (Table 4). Substituted phenol nucleophiles provided high levels of regio- and enantioselectivity. The utility of this method is nicely illustrated by entries 1 and 2, which represent formal syntheses of (−)-fluoxetine and (−)-tomoxetine.[16] Carboxylic acids were also found to be competent nucleophiles for this reaction to prepare branched allyl esters. The products obtained with unsaturated carboxylate nucleophiles (entries 3 and 4) are of particular interest, as they have been shown to provide access to optically active lactones through ring-closing metathesis.[31]

The scope was also examined with respect to the electrophile using phenol as a nucleophile (Table 5). Gratifyingly, *ortho*-substitution on the aryl group does not diminish regioselectivity (entry 1). Aliphatic electrophiles are tolerated in the reaction but provide products with diminished regio- and enantioselectivities. Notably, similar results can be obtained with the use of either the branched or linear regioisomer of the allyl chloride (entries 2 and 3). Interestingly, enyne substrate **20a** gave a product with higher enantioselectivity than those derived from saturated allyl chlorides, suggesting an electronic effect on the stereoselectivity.

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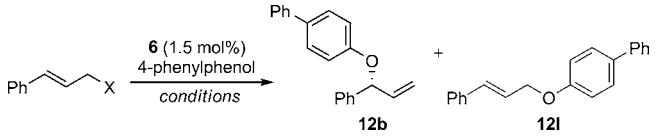
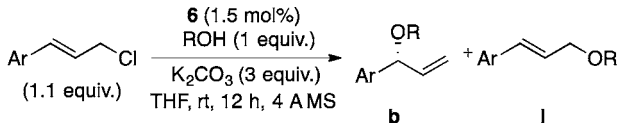
Table 3. Selected Optimization Experiments

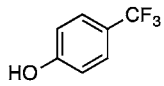
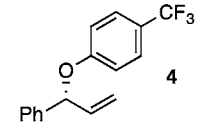
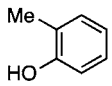
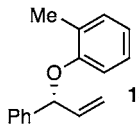
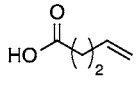
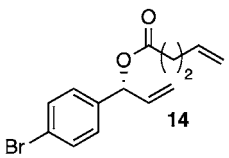
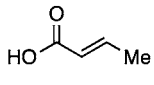
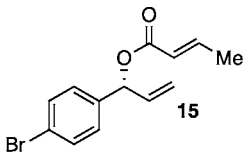
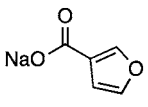
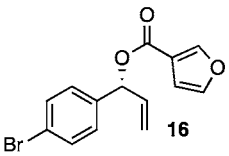
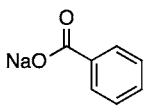
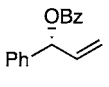


entry	X	base	solvent[a]	yield (%)	12b:12l[b]	ee (%)
1	OCO_2Me	K_2CO_3	DCM	14	1:1	23
2	Br	K_2CO_3	DCM	93	4:1	23
3	Cl	K_2CO_3	DCM	78	10:1	63
4	Cl	(2,5)-di-*tert*-butyl-4-methylpyridine	DCM	22	20:1	91
5	Cl	K_3PO_4	DCM	65	4:1	racemic
6	Cl	K_2CO_3	acetone	60	13:1	67
7	Cl	K_2CO_3	THF	64	9:1	75
8[c]	Cl	K_2CO_3	THF	72	20:1	91

[a]DCM = dichloromethane. [b]product ratio determined by ^{1}H NMR of unpurified reaction mixtures; [c]4 Å molecular sieves were used

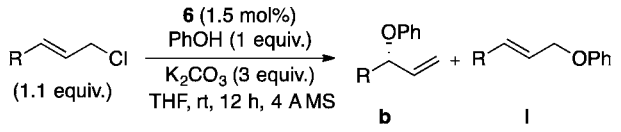
Table 4. Scope of the Nucleophile

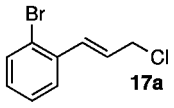
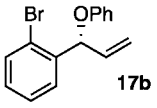
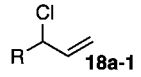
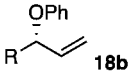
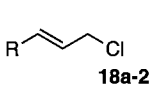
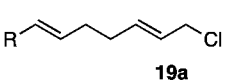
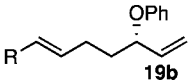
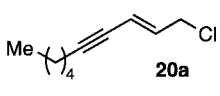
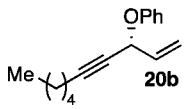


entry	nucleophile	product	result
1		 4	81% yield 12:1 b:l 82% ee (*R*)[a]
2		 13	60% yield 15:1 b:l 94% ee
3		 14	75% yield 5:1 b:l 88% ee
4[b]		 15	89% yield 6:1 b:l 87% ee
5[c]		 16	86% yield 8:1 b:l 91% ee
6[c]		 5	79% yield 8:1 b:l 93% ee

[a]Absolute configuration of **4** based on the sign of the specific rotation. Absolute configuration of all other products assigned by analogy to product **4**. [b]Na_2CO_3 (3 equiv) was used in place of K_2CO_3. [c]No exogenous base was added.

Table 5. Scope of the Electrophile



entry	electrophile	product	result
1	 17a	 17b	87% yield 10:1 b:l 88% ee
2[a,b]	 18a-1	 18b	57% yield 4:1 b:l 68% ee
3[a]	 18a-2		52% yield 5:1 b:l 68% ee
4[a]	 19a	 19b	72% yield 5:1 b:l 78% ee
5	 20a	 20b	58% yield 4:1 b:l 86% ee

[a]R = $-CH_2CH_2Ph$. [b]Racemic chloride was used.

During our optimization experiments, the formation of branched allylic alcohols were observed as minor products when molecular sieves were not employed. This observation, along with Onitsuka's report successfully employing water as a nucleophile, prompted us to examine the use of water as a potential nucleophile.[19f] Indeed, water can be used as a nucleophile using complex **6** as a catalyst to produce branched allylic alcohols with good levels of regio- and enantioselectivity (Scheme 6). The absolute configuration was established by comparison to known samples.

A model to predict the absolute stereochemistry of the products has also been developed (Figure 2). Mechanistic studies performed by Onitsuka suggest that the CpRu-catalyzed allylic alkylation occurs through an inner-sphere process.[19c] We envision that formation of the π-allyl complex should occur diastereoselectively at the metal center, placing the bulky allyl group *syn* to the small oxygen substituent of the sulfoxide. We

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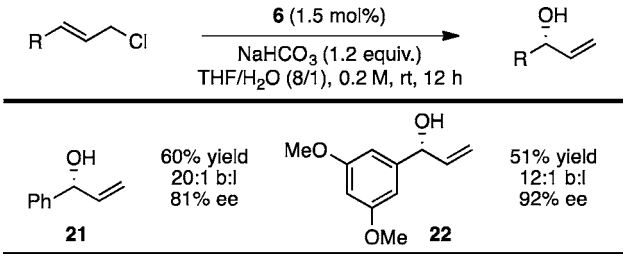
Scheme 6. Water as a Nucleophile



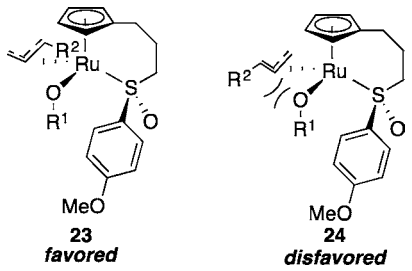


Figure 2. Stereochemical model to predict the absolute configuration of the allylation products.

also envision the central carbon atom of the allyl fragment pointing away from the Cp ligand. Such an orientation would allow for the formation of two diastereomeric π-allyl complexes (**23** and **24**). Steric interactions between the allyl substituent and the bulky phenoxy ligand should favor the formation of diastereomer **23**, which would lead to the observed absolute configuration of product.

CONCLUSION

Tethered CpRu chiral sulfoxide complexes represent a novel scaffold for asymmetric catalysis. They can be easily synthesized in six linear steps from the corresponding sulfonyl chloride and can function as an asymmetric surrogate for $[CpRu(MeCN)_3]PF_6$ in the branched-selective allylic alkylation using allyl chlorides. We envision that this oxidative [3 + 2] cycloaddition approach could easily be extended to the synthesis of other Cp−metal complexes containing tethered chiral sulfoxide ligands. Curiously, in contrast to the observation of complete substrate control of stereochemistry using $[CpRu(MeCN)_3]PF_6$ as the catalyst, complex **6** was observed to exhibit catalyst control when a branched electrophile was employed. We are currently evaluating this catalyst motif in other CpRu-catalyzed reactions.

EXPERIMENTAL SECTION

General Methods and Materials. ^{1}H and ^{13}C NMR spectroscopy were performed on a Varian Unity Inova NMR operating at 400 and 100 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^{1}H NMR, $CDCl_3$, and 77.0 ppm for ^{13}C NMR). In all ^{1}H NMR spectra, multiplicity is indicated as follows: bs (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), quin (quintuplet), or m (multiplet). Coupling constant values (in hertz) and number of protons for each signal are also indicated. Infrared spectroscopic data were recorded on sodium chloride plates as thin films on a Thermo Scientific Nicolet IR100 FT-IR spectrometer. Melting points were determined on a Thomas-Hoover Capillary Melting Point Apparatus and are uncorrected. Optical rotations were measured on a Jasco DIP-1000 digital polarimeter using 5 cm glass cells with a sodium 589 nm filter and are reported as $[\alpha]^{25}_D$, concentration (g/100 mL), and solvent. Thin-layer chromatography was performed on EMD silica gel 60 F254 plates (0.25 mm); visualization of the developed chromatogram was performed by fluorescence quenching and staining with aqueous potassium permanganate. Chromatographic purification of products was accomplished using forced-flow chromatography on Silicycle silica gel (particle size 0.040−0.063 mm). All isolated and characterized compounds were >95% pure as judged by ^{1}H NMR spectroscopic analysis. LC−MS (ESI) data were collected on a Micromass ZQ single quadrupole spectrometer. Isotopic abundance patterns observed alongside each major ion reported matched calculated ratios. GC−MS (EI) data were collected on an Agilent (HP) 7890/5975 instrument. Obtained data are expressed in mass/charge (m/z) units. Values between parentheses indicate relative intensities with regard to the base peak. Chiral HPLC analysis was performed on a Thermo Separation Products Spectra Series P-100 using Chiralcel and Chiralpak columns. Hexane and EtOAc were obtained and used without previous purification. All of the other reactants were obtained and also used without any previous treatment.

(1*R*,2*S*,5*R*)-(−)-Menthyl (*R*)-*p*-anisylsulfinate (2). A round-bottom flask with stir bar was charged with (−)-menthol (3.17 g, 0.0203 mol) and 4-methoxybenzenesulfonyl chloride (4.23 g, 0.0205 mol). DCM (50 mL) and NEt_3 (30 mL, 0.215 mol) were added, and the resulting solution was cooled to 0 °C. Triphenylphosphine (5.38 g, 0.0205 mol) was slowly added portionwise at 0 °C. The reaction mixture was allowed to warm to room temperature over 4 h. After this time, the reaction mixture was concentrated in vacuo, and the resulting crude solid was purified by silica gel chromatography. The resulting white solid was then recrystallized from hot acetone with a drop of 12 M HCl to yield sulfinate ester **2** as white needles (2.30 g, 7.40 mmol, 36%). R_f = 0.27 (10:1 petroleum ether/Et_2O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (m, 2H), 7.01 (m, 2H), 4.11 (td, J = 4.5 and 10.8 Hz, 1H), 3.85 (s, 3H), 2.27 (m, 1H), 2.13 (heptet of doublets, J = 2.6 and 6.8 Hz, 1H), 1.68 (m, 2H), 1.48 (m, 1H), 1.35 (ddt, J = 3.0, 10.2, and 12.7 Hz, 1H), 1.21 (m, 1H), 1.10−0.81 (m, 2H), 0.96 (d, J = 6.5 Hz, 3H), 0.86 (d, J = 7.0 Hz, 3H), 0.71 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 162.5, 137.8, 126.9, 114.4, 79.9, 55.6, 47.9, 43.0, 34.1, 31.8, 25.3, 23.2, 22.1, 20.9, 15.5. IR (thin film): 2947, 1590, 1494, 1253, and 1128 cm^{-1}. Mp = 116−118 °C. ^{1}H and ^{13}C NMR signals match literature values.[3b]

(*R*)-(5-((4-Methoxyphenyl)sulfinyl)pent-1-yn-1-yl)trimethylsilane (3). A 50 mL round-bottom flask with stir bar was charged with sulfinate ester **2**. The flask was evacuated and backflushed with Ar(g). Dry THF (15 mL) was added, and the resulting solution was cooled to −78 °C. 5-(Trimethylsilyl)pent-4-ynylmagnesium iodide (13.5 mmol, 1.0 M in diethyl ether) was added at −78 °C. The reaction mixture was allowed to warm to room temperature overnight. The next morning, the reaction mixture was diluted with diethyl ether (100 mL) and washed with saturated aqueous ammonium chloride (3 × 50 mL). The combined aqueous layers were extracted with diethyl ether (1 × 50 mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated in vacuo. The resulting crude oil was purified by silica gel chromatography (2:1 petroleum ether/EtOAc) to yield the sulfoxide **3** as a yellow oil (1.21 g, 4.11 mmol, 91%). R_f = 0.09 (2:1 petroleum ether/EtOAc). HR-MS (m/z): [M + H$^+$] calcd for $C_{15}H_{23}O_2SSi$ 295.1188, found 295.1180. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (m, 2H), 7.01 (m, 2H), 3.83 (s, 3H), 2.88 (m, 2H), 2.34 (m, 2H), 1.88 (m, 1H), 1.78 (m, 1H), 0.11 (s, 9H). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 162.0, 134.5, 125.9, 114.8, 105.0, 86.3, 56.0, 55.5, 21.2, 19.0, 0.1. IR (thin film): 2959, 2174, 1595, 1496, 1252, and 844 cm^{-1}. $[\alpha]^{23}_D$ = +97.7 (c = 1.05, CH_2Cl_2).

Preparation of Sandwich Complex 5. A 10 mL round-bottom flask with stir bar was charged with alkyne **3** (301 mg, 1.02 mmol) and [(benzene)Ru(π-allyl)]Cl (261 mg, 1.02 mmol). The flask was evacuated and backflushed with Ar(g). 2,2,2-Trifluoroethanol (4 mL) was added at room temperature, and the resulting orange solution was allowed to stir at room temperature for 24 h. A color change from orange to dark brown was observed over this time period. After 24 h, the resulting brown solution was concentrated in vacuo and purified by chromatography on acidic alumina (10% MeOH in DCM) to yield silylated sandwich complex **TMS-4** as a brown oil (1:1 mixture of

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diastereomers) (412 mg, 0.865 mmol, 85%). R_f = 0.13 (10% MeOH in DCM, basic alumina). HR-MS (m/z): [M − PF_6^-] calcd for $C_{21}H_{23}O_2RuS$ 441.0462, found 441.0458. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, J = 8.8 Hz, 4H), 7.03 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 6.28 (s, 6H), 6.26 (s, 6H), 5.78 (br s, 1H), 5.73 (br s, 1H), 5.64 (br s, 1H), 5.57 (br s, 1H), 5.13 (br s, 1H), 5.10 (br s, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.85 (m, 4H), 2.66 (m, 2H), 2.41 (m, 1H), 1.85 (m, 5H), 0.26 (s, 9H), 0.25 (s, 9H). IR (thin film): 3394, 2952, 1593, 1253, and 834 cm^{-1}. $[\alpha]^{24}_D$ = +60.7 (c = 1.00, $CHCl_3$). A round-bottom flask with stir bar was charged with ruthenium complex **TMS-4** (398 mg, 0.725 mmol) and CsF (524 mg, 3.45 mmol). The flask was evacuated and backflushed with Ar(g). Dry acetonitrile (4 mL) was added, and the reaction was allowed to stir at room temperature overnight. The next morning, the reaction mixture was concentrated in vacuo and passed through a plug of acidic alumina (10% MeOH in DCM). A new flask with stir bar was charged with the resulting crude brown oil and ammonium hexafluorophosphate (505 mg, 3.10 mmol). A 1:1:1 mixture of methanol, water, and DCM (3 mL) was added, and the reaction mixture was stirred at room temperature for 5 min. The reaction was then diluted with DCM (25 mL) and washed with water (2 × 10 mL). The combined aqueous layers were extracted with DCM (1 × 10 mL). The combined organic layers were then dried over magnesium sulfate, filtered, and concentrated in vacuo to yield sandwich complex **5** as a green-white solid (228 mg, 0.389 mmol, 49%). R_f = 0.48 (10% MeOH in DCM, basic alumina). HR-MS (m/z): [M − PF_6^-] calcd for $C_{21}H_{23}O_2RuS$ 441.0462, found 441.0458. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 9.0 Hz, 2H), 7.04 (d, J = 9.0 Hz, 2H), 6.12 (s, 6H), 5.37 (app t, J = 1.1 Hz, 2H), 5.30 (dd, J = 1.1 and 1.9 Hz, 2H), 3.84 (s, 3H), 2.82 (app octet, J = 8.2 Hz, 2H), 2.47 (m, 2H), 1.91 (m, 1H), 1.78 (m, 1H). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 162.1, 134.1, 126.0, 115.0, 103.9, 86.4, 80.7, 80.1, 55.7 (2C), 26.4, 23.3. IR (thin film): 3100, 2922, 1594, 1254, and 839 cm^{-1}. $[\alpha]^{23}_D$ = +68.1 (c = 0.67, CH_2Cl_2).

Preparation of Half-Sandwich Complex 6. A test tube was charged with ruthenium sandwich complex **5** (200 mg, 0.342 mmol) and was then dissolved in acetonitrile (280 mL). The test tube was capped with a septum and placed in a Rayonet Photochemical Reactor (equipped with F8T5-BL blacklight lamps, irradiating at 350 nm) and irradiated for 24 h. After 24 h, the resulting pale yellow solution was concentrated in vacuo to yield a bright yellow oil. The crude oil was passed through a plug of neutral alumina (acetonitrile eluent) and the yellow band was collected. The resulting yellow oil was recrystallized from acetonitrile/diethyl ether to yield half-sandwich complex **6** as yellow crystals (88.4 mg, 0.150 mmol, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 9.0 Hz, 2H), 7.14 (d, J = 9.0 Hz, 2H), 5.17 (td, J = 1.3 and 2.6 Hz, 1H), 5.07 (td, J = 1.3 and 2.6 Hz, 1H), 4.45 (br s, 1H), 4.30 (br s, 1H), 3.88 (s, 3H), 3.14 (m, 2H), 2.38 (s, 3H), 2.34 (ddd, J = 3.2, 7.8, and 14.4 Hz, 1H), 2.24 (ddd, J = 3.2, 9.9, and 14.4 Hz, 1H), 2.12 (m, 1H), 2.10 (s, 3H), 1.85 (m, 1H). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 162.5, 127.8, 126.2, 114.6, 93.4, 83.0, 81.9, 68.3, 67.5, 59.4, 55.8, 23.9, 21.2, 4.2, 3.7 (*C*N signals not detected). IR (thin film): 2894, 1570, 1474, 1238, 829 cm^{-1}. $[\alpha]^{25}_D$ = −52.5 (c = 1.49, $CDCl_3$).

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, crystallographic data, and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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