ORGANOMETALLICS

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Stereospecific Syntheses and Structures of Planar Chiral Bidentate η^5:κS-Indenyl-Sulfanyl and -Sulfinyl Complexes of Rhodium(III)

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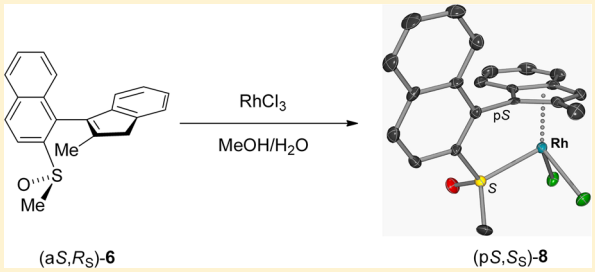
Supporting Information

ABSTRACT: Axially chiral *rac*-1-(2-methyl-1*H*-inden-3-yl)-2-(methylsulfanyl)naphthalene (*rac*-**3**) was synthesized from methyl 2-(methylsulfanyl)-1-naphthoate through reaction with the di-Grignard reagent derived from 1-bromo-2-(2-bromopropyl)benzene, followed by acid-catalyzed dehydration of the intermediate indanol. Oxidation of *rac*-**3** with *m*-CPBA gave the diastereomeric sulfoxides (a*R**,R_S*)-**5** and (a*R**,S_S*)-**6**, with the relative configuration of **5** established using single-crystal X-ray diffraction. The dichloro[η^5:κS-indenyl-sulfanyl and -sulfinyl]rhodium complexes *rac*-**4**, (p*R**,S_S*)-**7**, and (p*R**,R_S*)-**8** were synthesized through reaction of the ligands *rac*-**3**, (a*R**,R_S*)-**5**, and (a*R**,S_S*)-**6**, respectively, with rhodium trichloride in 9:1 methanol/water solution heated under reflux. The use of water as a cosolvent was found to be critical for obtaining good yields in the complexation reactions. Solid-state structures for the racemic rhodium complexes were determined through single-crystal X-ray diffraction. The enantiomers of the ligands **3**, **5**, and **6** were obtained in high enantiopurity through subjecting *rac*-**3** to a series of Kagan asymmetric sulfoxidation, deoxygenation, and resulfoxidation reactions. The enantiomeric relationship of the rhodium complexes derived from the enantio-enriched ligands was confirmed by CD spectroscopy, and the high enantiopurity of the complexes established by ^{1}H NMR analysis using the chiral shift reagent Eu(hfc)$_3$. The absolute configurations of the nonracemic ligands and rhodium complexes were established by a single-crystal X-ray diffraction determination of the solid-state structure of (pS,S_S)-**8**, with the Flack parameter refining to 0.00(2).

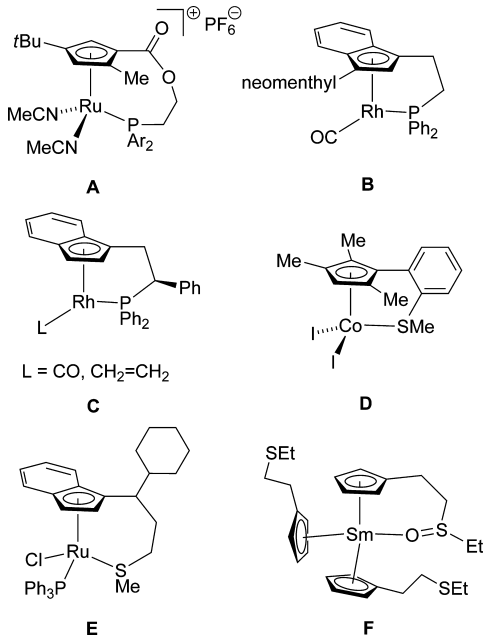


INTRODUCTION

Planar chiral ferrocenyl ligands have been successfully utilized in a wide range of asymmetric transition-metal-catalyzed reactions. While the iron center does not participate directly in the catalytic cycle of these reactions, the chemical robustness of ferrocenes has the advantage of enabling numerous synthetic transformations that allow for the introduction of a variety of different coordinating groups, together with specific strategies for the stereoselective creation of the planar chiral element.[1] Planar chiral transition-metal complexes where the metal involved in the planar chiral element is also the site for catalysis have also been examined as asymmetric catalysts. The most successful examples to date are early transition-metal and lanthanide metallocenes, in particular *ansa*-metallocenes, where a tether between the cyclopentadienyl (Cp; we also use this abbreviation to cover related indenyl and fluorenyl systems) rings prevents the normally facile rotation around the Cp−metal axis, creating a well-defined steric and electronic environment around the metal.[2] As an extension of this development, planar chiral constrained-geometry half-sandwich metal complexes would appear to be an attractive target for use in asymmetric catalysis. Takahashi and Onitsuka and their co-workers have, for example, demonstrated that planar chiral ruthenium complexes **A** (Chart 1) are highly effective asymmetric catalysts for a range of allylic substitution reactions.[3] An ongoing difficulty in the progress of planar chiral metallocenes and half-sandwich metal complexes as asymmetric catalysts is accessing stereochemically pure compounds, with the reactivity of the metal often significantly limiting the manipulations that are possible following Cp complexation. As a result, there has been considerable interest in approaches to facially selective π-complexation.[4] In the case of constrained-geometry ligands, where attention has been particularly focused on Cp-phosphane ligands, the most common approach involves the introduction of chiral substituents onto either the Cp ring or the tether. The diastereoselectivities obtained are, however, usually modest and the outcome is unpredictable. For example, Tani and co-workers[5] obtained the rhodium complex **B** through reaction of the indenyllithium precursor and [Rh(μ-Cl)(CO)$_2$]$_2$ with 24% de, and the diastereomerically pure complex was available only through repeated recrystallizations; the related neoisomenthyl complex was obtained with 74% de, but this was unable to be purified beyond 86% de. Whitby[6] and Salzer[7] and their co-workers have prepared the rhodium complexes **C** (L = CO or CH$_2$=CH$_2$) employing the same indenyllithium precursor; formation of the complex using [Rh(μ-Cl)(CO)$_2$]$_2$ occurs with 50% de, but with only 22% de using [Rh(μ-Cl)(η^2-CH$_2$=CH$_2$)$_2$]$_2$. Salzer also observed that the reaction of

Received: June 25, 2012
Published: July 24, 2012

Chart 1. Literature Examples of Planar Chiral Constrained-Geometry Half-Sandwich Metal Complexes Featuring Phosphane and Sulfane Tethers (A–E) and a Cp Complex Featuring a Sulfoxide Tether (F)



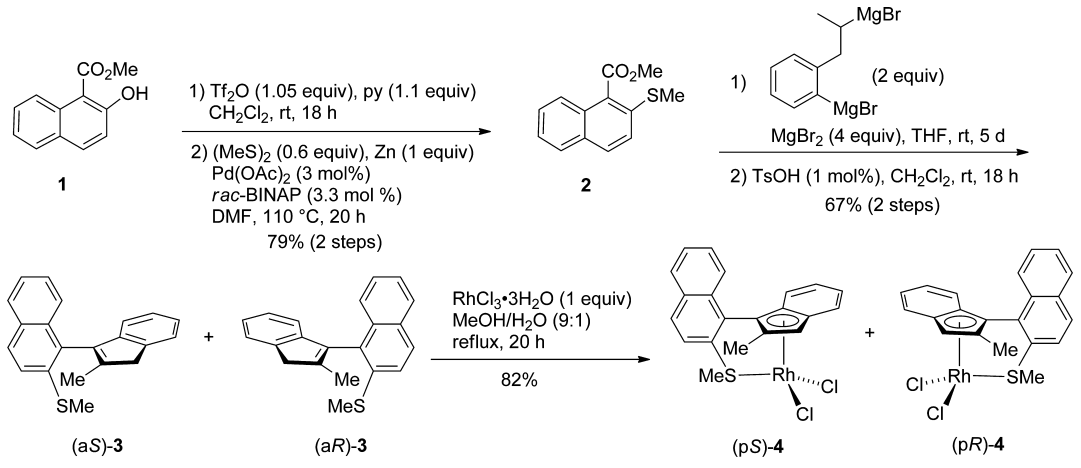
$[Rh(\mu\text{-}Cl)(\eta^2\text{-}CH_2{=}CH_2)_2]_2$ with an analogous indenyllithium precursor having 4,7-dimethyl substitution on the indenyl ring resulted in a 70% de, but with the opposite planar configuration now preferred.

In previous work we have used axially chiral Cp ligands, where a second coordination site is tethered to a nonsymmetrically substituted Cp ring via an aromatic ring and rotation about the Cp–aromatic axis is restricted, for the enantiospecific syntheses of a planar chiral bidentate indenyl-alkoxide complex of zirconium[8a] and a planar chiral fluorenyl-indenyl *ansa*-zirconocene.[8b] In extending this approach to examples involving late transition metals, we have initially focused on a bidentate indenyl-sulfur system, for which convenient access to ligands of high enantiopurity proved possible (*vide infra*). While a large number of chiral sulfur ligands have been examined for use in asymmetric catalysis,[9] bidentate Cp-sulfur ligands remain unexplored. A survey of literature reports of bidentate Cp-sulfur metal complexes reveals that a range of sulfur-containing functional groups, such as thiophene,[10] thiolate,[11] dithiocarboxylate and thioamide,[12] dithioacetal and trithioortho ester,[13] and, most commonly, thioether,[14] have been incorporated, but the majority of the complexes are achiral. There are only two previous examples of planar chiral bidentate Cp-sulfur metal complexes, both prepared in racemic form: the cobalt complex **D**[14m] and the ruthenium complex **E**[14g] (which was obtained as a 1:1 mixture of two of the four possible diastereomers resulting from the generated planar and metal-centered chiral elements, with the nature of the isomerism not unambiguously determined). The only nonracemic chiral bidentate Cp-sulfur metal complex described to date is $[Ru\{\eta^5{:}\kappa S\text{-}C_5H_4CH_2CH_2S[(1R)\text{-neomenthyl}]\}(PPh_3)_2][OTf]$, prepared by van der Zeijden and co-workers,[14d] which was found to undergo decomposition within a few hours at room temperature. We are aware of only one example of a bidentate Cp-sulfinyl metal complex, the samarium complex **F** (prepared by reaction of $(EtSCH_2CH_2C_5H_4)_3Sm$ with O_2), where the metal coordinates to the sulfoxide oxygen.[14k] In this paper we report the first enantio- and diastereospecific syntheses of planar chiral bidentate Cp-sulfanyl and -sulfinyl metal complexes, utilizing axially chiral indenyl ligands.

RESULTS AND DISCUSSION

Synthesis of the Racemic Ligands and Rhodium(III) Complexes. The methylsulfanyl ligand *rac*-**3** (Scheme 1) was prepared through our previously reported di-Grignard approach to the synthesis of 3-substituted-1*H*-indenes,[15] with the required ester **2** available through a cross-coupling reaction of the triflate derived from methyl 2-hydroxy-1-naphthoate **1**. Initially we adapted the procedure of McWilliams and co-workers for the synthesis of butyl(4-chlorophenyl)sulfane,[16] reacting the triflate of **1** with commercially available solid sodium methanethiolate in the presence of $Pd(OAc)_2$ (6 mol %), *rac*-BINAP (6.6 mol %), and LiCl (3 equiv) in toluene solution for 20 h at 100 °C, which gave the desired ester **2** in 67% yield (two steps from **1**). In looking to improve upon this result, we particularly wanted to find a more convenient and less expensive source of methanethiolate ion. The nickel- and palladium-catalyzed cross-coupling of aryl iodides or bromides with disulfides and zinc in DMF or THF solution has been previously reported,[17] and so we examined the viability of using dimethyl disulfide and zinc, while retaining the $Pd(OAc)_2$/BINAP catalyst. Using a combination of 0.6 equiv of dimethyl disulfide and 1 equiv of zinc in

Scheme 1. Synthesis of the Racemic Methylsulfanyl Ligand *rac*-3 and the Corresponding Racemic Rh(III) Complex *rac*-4



dx.doi.org/10.1021/om300581r | *Organometallics* 2012, 31, 5622–5633

DMF solution at 110 °C for 20 h, we obtained an improved yield of 79% (two steps from **1**) with a lower catalyst loading (3 mol %) and without the need for LiCl additive. The reaction of the ester **2** with the di-Grignard reagent prepared from 1-bromo-2-(2-bromopropyl)benzene (2 equiv) produced erratic results. In a modification of our original procedure,[15] we found that the addition of $MgBr_2$ (2 equiv per equivalent of di-Grignard) gave a reliable outcome. The crude indanol from this reaction was then dehydrated with catalytic TsOH to give the desired ligand *rac*-**3** in 67% yield (two steps from **2**).

Our initial efforts toward the complexation of *rac*-**3** focused on the reaction of the indenyllithium derived from *rac*-**3** (reaction with BuLi in diethyl ether solution followed by removal of the solvent) with either $[Rh(\mu\text{-}Cl)(\eta^2\text{-}CH_2{=}CH_2)_2]_2$, $[RhCl(PPh_3)_3]$, or $[RuCl_2(PPh_3)_3]$ in a range of solvents and at different temperatures. In all cases a mixture of products was formed, and it was evident that a significant degree of complexation was occurring on the face of the indene *anti* to the sulfur. This was clearly seen in the ^{1}H NMR spectra of the mixtures (although not quantifiable because of the overall complexity of the spectra), which revealed a doublet ($^3J \approx 8.8$ Hz) at $\delta \approx 11$ ppm attributable to the naphthalene 8-hydrogen, which is significantly deshielded through steric interaction with the metal fragment. A similar observation has been made for a 1,2,4,6-tetrasubstituted benchrotrene where the 1-substituent is 2-hydroxymethyl-1-naphthyl and the naphthalene 8-hydrogen is *syn* to the $Cr(CO)_3$ fragment.[18] We therefore sought to complex *rac*-**3** under conditions where the sulfur was likely to coordinate to the metal prior to π-complexation, ensuring this complexation takes place *syn* to the sulfur. Lewis and Welch[19] have reported the formation of the complex $[(C_9H_7)RhCl_2]_x$ on heating a solution of indene and rhodium trichloride trihydrate in methanol under reflux, and these conditions were thought likely to be conducive to our aims. On heating a mixture of the ligand *rac*-**3** and rhodium trichloride trihydrate (1 equiv) in methanol under reflux, a yellow-orange precipitate initially formed (presumably sulfur-coordinated rhodium species; the ^{1}H NMR spectrum of the isolated solid was very broad and complex, and the material not studied further), which on continued heating gradually dissolved to afford a dark red-brown solution. Eventually we succeeded in isolating, after several days of heating under reflux, and in less than 10% yield, the desired *rac*-**4** from a complex reaction product mixture (^{1}H NMR analysis). Marder and co-workers[20] have described the preparation of $[(\eta^5\text{-}C_9Me_7)RhCl(\mu\text{-}Cl)]_2$ through reaction of heptamethylindene and rhodium trichloride trihydrate in a 30:1 methanol/water mixture at reflux. While the purpose of the added water was not discussed, we decided to investigate the effect of adding water in the reaction of *rac*-**3** and observed a remarkable improvement in the rate of π-complexation and the isolated yield of *rac*-**4**. On heating a mixture of *rac*-**3** and rhodium trichloride trihydrate (1 equiv) in 9:1 methanol/water under reflux for 20 h, followed by removal of the volatiles, the ^{1}H NMR spectrum of the crude reaction product was now quite clean, consisting largely of signals for *rac*-**4** and unreacted ligand only, with the pure complex isolated by precipitation from CH_2Cl_2/benzene solution in 82% yield. The function of the water in this reaction may be to facilitate the dissociation of chloride ion from rhodium through improved solvation of the halide, as seen in the efficient formation of $[Cp^*Ru(\eta^6\text{-arene})]Cl$ complexes using $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ in aqueous solution,[21] or it may be more direct, since Bercaw and Labinger and their co-workers[22] have observed a role for coordinated hydroxyl and water ligands in rhodium, palladium, and platinum C−H bond activation in indene.

The dark brown complex *rac*-**4** has a very high melting point, decomposing above 350 °C, and has only modest solubility in CH_2Cl_2 and $CHCl_3$ and very low solubility in other solvents. Solutions of the complex are indefinitely stable in air, and no special precautions are required during the synthesis and purification. The complex precipitates from solution with variable amounts of solvate molecules, depending on the solvent composition and rate of precipitation. The solvate molecules are quite tenaciously retained; however, they could be completely removed from the complex after drying for several days under high vacuum. The η^5-hapticity in *rac*-**4** is confirmed by the presence of scalar couplings in the $^{13}C\{^1H\}$ NMR spectrum between the ^{103}Rh nucleus and all five carbon atoms of the indenyl C5 ring, with $^1J_{C,Rh}$ ranging from 6.1 to 8.3 Hz. The only resolved scalar coupling to ^{103}Rh in the ^{1}H NMR spectrum involves the methyl group on sulfur, with $^3J_{H,Rh} = 1.1$ Hz; that this is a scalar coupling rather than two distinct methyl signals was confirmed by examining the spectra at different field strengths. The solid-state molecular structure of *rac*-**4** was determined by X-ray diffraction (Figure 1) and shows a (p*R**,*S*$_S$*)-relative

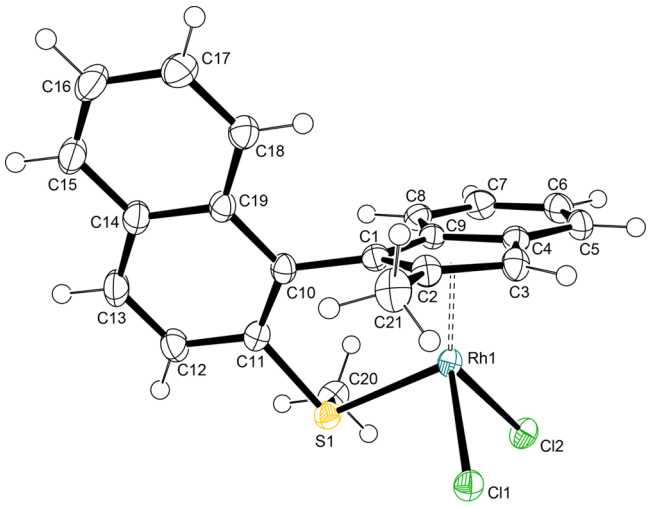


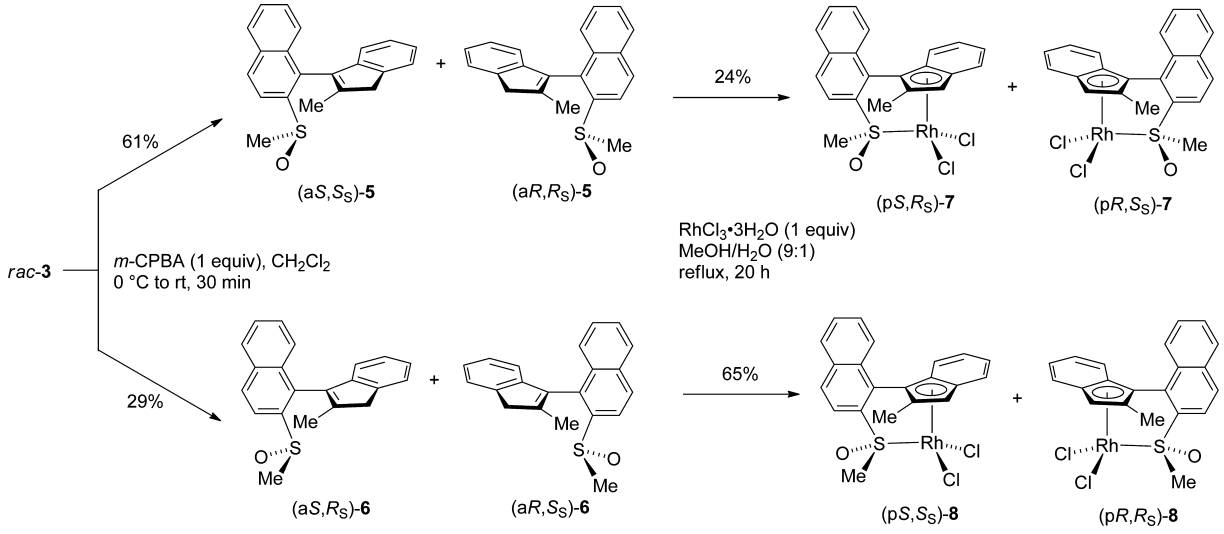
Figure 1. Solid-state molecular structure of *rac*-**4** with 50% displacement ellipsoids (p*S*-enantiomer illustrated and $CDCl_3$ molecules omitted for clarity).

configuration at the stereogenic sulfur. Since the barrier to pyramidal inversion at sulfur in sulfane−metal complexes is known to be low (10−20 kcal/mol),[23] this configuration must be thermodynamically preferred in the solid state. In solution the same preferred configuration at sulfur is also observed, as evident from a strong cross-peak in the NOESY spectrum of *rac*-**4** between the methyl group on sulfur and the indenyl 7-hydrogen (the hydrogen at C8 in Figure 1; further discussion of the structure of *rac*-**4** appears later in the paper).

The racemic ligands bearing a tethered methylsulfinyl group were next prepared through oxidation of *rac*-**3** using *m*-CPBA (Scheme 2). The resulting diastereomers were separable by column chromatography; the more mobile diastereomer **5** was isolated in 61% yield and the less mobile isomer **6** in 29% yield. The solid-state structure of diastereomer **5** was determined by X-ray diffraction (Figure 2) and shows a (a*R**,*R*$_S$*)-relative configuration. Each of the isomers was then complexed with rhodium trichloride under the same conditions as *rac*-**3**. While

dx.doi.org/10.1021/om300581r | *Organometallics* 2012, 31, 5622−5633

Scheme 2. Synthesis of the Racemic Methylsulfinyl Ligands *rac*-5 and *rac*-6 and the Corresponding Racemic Rh(III) Complexes *rac*-7 and *rac*-8



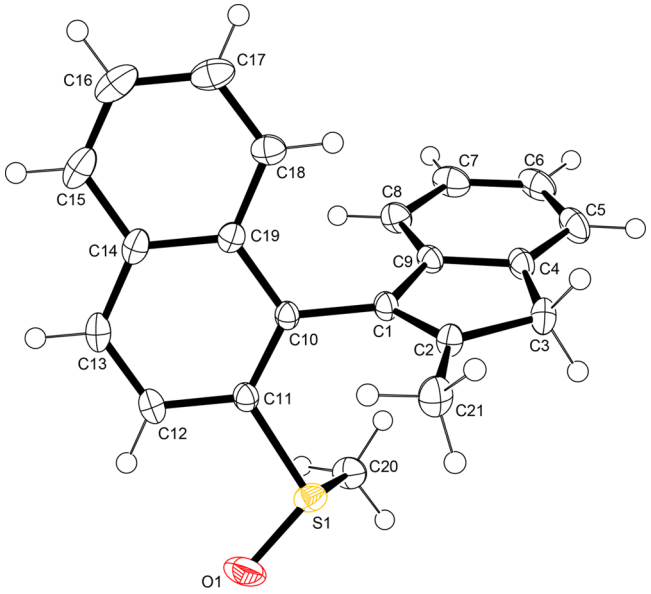


Figure 2. Solid-state molecular structure of *rac*-**5** with 50% displacement ellipsoids ((aS,S_S)-enantiomer illustrated). Selected bond lengths (Å) and bond and torsion angles (deg): S1−O1 1.4983(7), S1−C11 1.8082(6), S1−C20 1.7978(7), C1−C2 1.3579(9), C2−C3 1.5122(9), C3−C4 1.5076(11), C4−C9 1.4073(9), C1−C9 1.4767(9), C1−C10 1.4832(8); C11−S1−O1 106.23(3), C11−S1−C20 105.46(4), C9−C1−C10−C11 110.52(7).

the formation of a precipitate was not observed in the early stages of the reaction, as was the case for *rac*-**3**, there was a distinct color change from dark red to dark orange, suggesting the initial complexation of the sulfoxides to rhodium; continued heating of the reactions gave dark red-brown mixtures. Following removal of the volatiles, the ^{1}H NMR spectra of the crude reaction mixtures revealed the formation of a single metal complex in each case; that is, there was no evidence of any epimerization at either the chiral axis or sulfur during the course of the reactions. The spectrum of the reaction of *rac*-**6** was, as in the case of *rac*-**3**, quite clean, consisting largely of signals for *rac*-**8** and unreacted ligand only, with the pure complex isolated by precipitation from CH_2Cl_2/benzene solution in 65% yield.

In the case of *rac*-**5**, however, there were additional very broad and featureless signals associated with the formation of unidentified byproduct. Attempts to purify this reaction mixture through chromatography on a number of different stationary phases were unsuccessful; however, fractional crystallization did provide the pure complex *rac*-**7** in 24% yield.

Complexes *rac*-**7** and *rac*-**8** are, like complex *rac*-**4**, dark brown, very high melting point solids, with similar solubility properties to *rac*-**4**, with the solutions also being indefinitely stable in air. In common with *rac*-**4**, the complexes precipitate from solution with variable amounts of solvate molecules; however in the cases of *rac*-**7** and *rac*-**8** the solvate could be only partially removed, despite drying for several days under high vacuum at elevated temperatures. The complexes did however give satisfactory elemental analyses taking into account the presence of solvate, which was quantified by ^{1}H NMR spectroscopy, employing a long relaxation delay between transients. The η^5-hapticity in *rac*-**7** and *rac*-**8** is confirmed by the presence of scalar couplings in the ^{13}C{^{1}H} NMR spectrum between the ^{103}Rh nucleus and all five carbon atoms of the indenyl C5 rings, with $^1J_{C,Rh}$ ranging from 4.6 to 8.5 Hz. An additional scalar coupling, not seen in *rac*-**4**, occurs between ^{103}Rh and the naphthalene 2-carbon, with $^2J_{C,Rh}$ = 2.2 and 2.1 Hz for *rac*-**7** and *rac*-**8**, respectively. Conversely, there are no scalar couplings observed between ^{103}Rh and the sulfinyl methyl groups in the ^{1}H NMR spectra of the sulfoxide complexes. The IR spectra of the ligands *rac*-**5** and *rac*-**6** both show the vibration for the sulfoxide S=O bond at $\tilde{\nu}$ = 1054 cm^{-1}. In the complexes the S=O vibration occurs at $\tilde{\nu}$ = 1119 and 1099 cm^{-1} for *rac*-**7** and *rac*-**8**, respectively, these increases in frequency being typical for S-bonded sulfoxide−metal complexes.[24] The solid-state structures of *rac*-**7** and *rac*-**8** were determined by X-ray diffraction (Figures 3 and 4) and show the expected relative configurations of the chiral plane and sulfur based on the previously determined structure for *rac*-**5** (further discussion of these structures appears later in the paper).

Synthesis of the Enantiomeric Ligands and Rhodium(III) Complexes. To gain access to the enantiomeric forms of the ligands **3**, **5**, and **6**, we investigated subjecting *rac*-**3** to asymmetric sulfoxidation, which could open up the possibility of either a kinetic resolution of *rac*-**3** or, in the event of low

dx.doi.org/10.1021/om300581r | *Organometallics* 2012, 31, 5622−5633

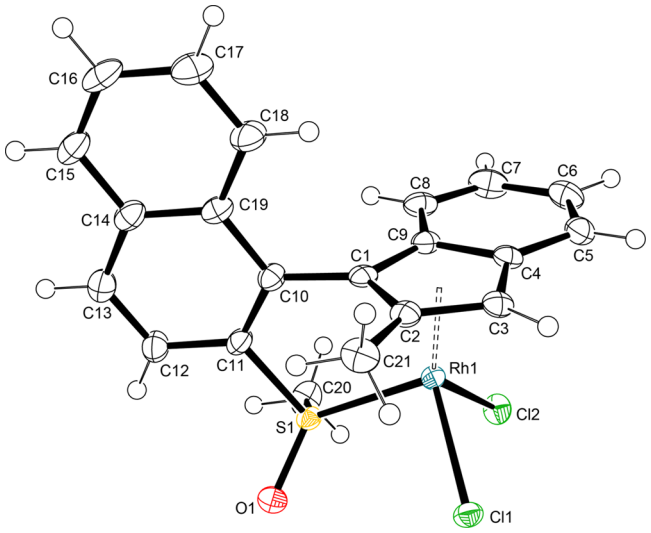


Figure 3. Solid-state molecular structure of *rac*-**7** with 50% displacement ellipsoids (molecule A of the two independent molecules of **7** in the asymmetric unit is illustrated (as the (p*S*,*R*$_S$)-enantiomer); solvent molecules omitted for clarity).

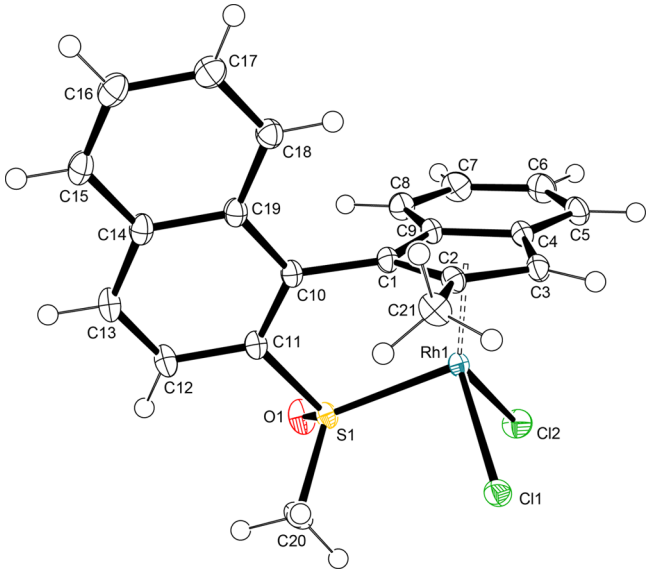
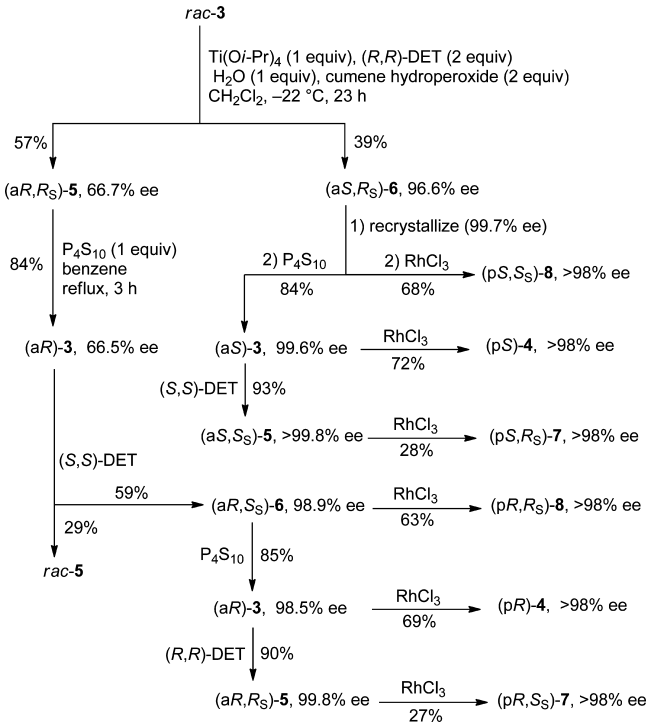


Figure 4. Solid-state molecular structure of *rac*-**8** with 50% displacement ellipsoids ((p*S*,*S*$_S$)-enantiomer illustrated; $CDCl_3$ molecule omitted for clarity).

substrate diastereocontrol but high catalyst enantiocontrol, access to **5** and **6** of high enantiopurity, with the sulfoxides subsequently converted back into the enantiomers of **3**. While there have been some reports of successful kinetic resolutions of racemic sulfides through asymmetric sulfoxidation,[25] the partial oxidation of *rac*-**3** using the Kagan system[26] gave unreacted sulfide with low enantiomeric enrichment (ca. 10% ee at 50% conversion), and so the oxidation was allowed to go to completion (Scheme 3). Using diethyl (*R*,*R*)-tartrate (DET) as the ligand on titanium, the diastereomers (a*R*,*R*$_S$)-**5** and (a*S*,*R*$_S$)-**6** were isolated in 57% and 39% yield, respectively, and with 66.7% and 96.6% ee, respectively (chiral HPLC analysis). The assignment of the *R*-configuration at sulfur was initially made on the basis of the substantial number of precedents for this stereochemistry for the Kagan sulfoxidation of a wide range of aryl- and heteroaryl-alkyl sulfides using (*R*,*R*)-DET[26,27] and

Scheme 3. Synthesis of the Enantiomeric Forms of Ligands 3, 5, and 6, and of the Corresponding Enantiomeric Forms of the Rh(III) Complexes 4, 7, and 8



was later confirmed unambiguously (see below). It should be noted that (a*R*,*R*$_S$)-**5** is the product of matched substrate and catalyst stereocontrol (consistent with the 2:1 dr favoring *rac*-**5** seen in the oxidation of *rac*-**3** with *m*-CPBA), accounting for the high enantiopurity of (a*S*,*R*$_S$)-**6**; conversely, the lower enantiopurity of (a*R*,*R*$_S$)-**5** is a result of mismatched substrate and catalyst stereocontrol during the formation of (a*S*,*R*$_S$)-**6**. A single recrystallization of (a*S*,*R*$_S$)-**6** provided material of 99.7% ee, which was then deoxygenated using phosphorus pentasulfide,[28] affording (a*S*)-**3** in 84% yield and with 99.6% ee (chiral HPLC analysis). Kagan sulfoxidation of (a*S*)-**3** employing (*S*,*S*)-DET then provided (a*S*,*S*$_S$)-**5** in 93% yield and with >99.8% ee, confirming the rationalization of substrate versus catalyst stereocontrol made above. Deoxygenation of (a*R*,*R*$_S$)-**5** (84% yield) followed by Kagan sulfoxidation employing (*S*,*S*)-DET provided (a*R*,*S*$_S$)-**6** in 59% yield and with 98.9% ee, accompanied by essentially racemic sulfoxide **5** in 29% yield. Deoxygenation of (a*R*,*S*$_S$)-**6** then provided (a*R*)-**3** in 85% yield and with 98.5% ee, which was then resulfoxidized employing (*R*,*R*)-DET, to afford (a*R*,*R*$_S$)-**5** in 90% yield and with 99.8% ee, thus completing the syntheses of the enantiomeric forms of all three of the ligands **3**, **5**, and **6**.

The enantiomers of the ligands **3**, **5**, and **6** were complexed with rhodium trichloride under the same conditions as the racemic ligands, to provide the enantiomers of the rhodium complexes **4**, **7**, and **8** in comparable yields to the racemic syntheses. The enantiopurity of each of the complexes was able to be assessed through ^{1}H NMR analysis in the presence of the chiral shift reagent europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] (Eu(hfc)$_3$), with all three complexes displaying resolved signals for the indenyl 2-methyl and 3-hydrogen; in addition the sulfoxide complexes displayed resolved signals for the methyl group on sulfur. The absence of signals for the opposite enantiomer in the spectra of each of the

dx.doi.org/10.1021/om300581r | *Organometallics* 2012, 31, 5622−5633

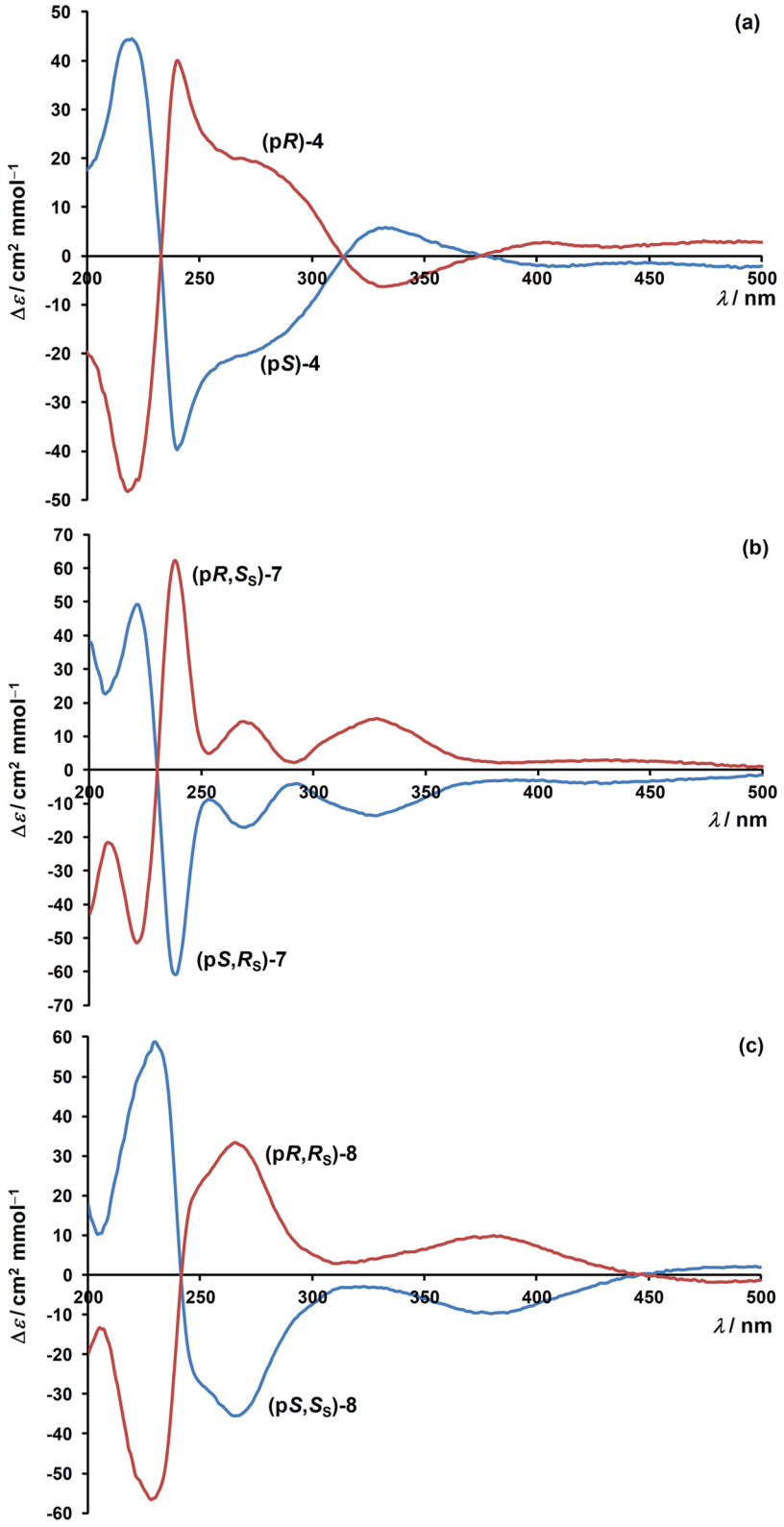


Figure 5. (a–c) CD spectra of enantiomeric forms of the Rh(III) complexes **4**, **7**, and **8**, respectively.

complexes confirmed their high enantiopurity (estimated to be >98% ee). While we were reasonably confident with the assignments of absolute configuration made above, we felt it prudent to confirm the assignments through X-ray crystallography. The solid-state structure of (p*S*,*S*S)-**8** was determined by X-ray diffraction, and the absolute structure established with the Flack parameter[29] refining to 0.00(2), confirming the assignments previously made. Solutions of the enantiomeric rhodium complexes were too dark (down to *c* 0.05 in a 1 dm cell), at all the available wavelengths from sodium- and mercury-vapor lamps, to measure specific rotations; however, circular dichroism (CD) spectra were obtained for the enantiomers of each of the

dx.doi.org/10.1021/om300581r | *Organometallics* 2012, 31, 5622–5633

Table 1. Selected Bond Distances (Å) and Bond and Torsion Angles (deg) for the Rhodium(III) Complexes

	rac-**4**	*rac*-**7** (A)	*rac*-**7** (B)	*rac*-**8**	(p*S*,*S*$_S$)-**8**
Rh1−C1	2.086(2)	2.086(3)	2.084(3)	2.0911(14)	2.094(2)
Rh1−C2	2.149(2)	2.140(3)	2.135(3)	2.1512(14)	2.154(3)
Rh1−C3	2.181(2)	2.210(3)	2.196(3)	2.1969(14)	2.185(3)
Rh1−C4	2.261(2)	2.300(3)	2.308(3)	2.2954(14)	2.279(3)
Rh1−C9	2.187(2)	2.192(3)	2.205(3)	2.2036(14)	2.217(2)
Rh1−S1	2.3921(6)	2.3188(7)	2.3101(7)	2.3305(4)	2.3304(8)
Rh1−Cl1	2.3888(6)	2.3846(7)	2.3740(7)	2.3738(4)	2.3616(7)
Rh1−Cl2	2.3859(7)	2.3933(7)	2.3949(7)	2.3773(4)	2.3802(7)
S1−O1		1.474(2)	1.469(2)	1.4807(12)	1.471(2)
Cl1−Rh1−Cl2	88.31(2)	91.74(3)	91.31(3)	89.303(14)	88.21(2)
Cl1−Rh1−S1	93.63(2)	94.96(2)	93.85(3)	93.983(14)	94.64(3)
Cl2−Rh1−S1	88.90(2)	90.85(2)	89.48(2)	91.130(14)	93.66(2)
C11−S1−Rh1	98.40(7)	101.49(10)	98.40(7)	100.55(5)	100.52(9)
C11−S1−C20	100.77(10)	101.12(15)	100.85(9)	100.41(7)	100.63(13)
C11−S1−O1		109.06(13)	109.44(13)	108.58(7)	108.50(13)
C9−C1−C10−C11	70.4(3)	87.7(4)	84.9(4)	75.74(11)	72.9(3)
C10−C1−Rh1−S1	13.40(14)	3.3(2)	5.90(19)	15.01(9)	16.18(19)
C10−C1−Rh1−Cl1	−77.01(15)	−87.8(2)	−84.7(2)	−75.44(10)	−75.3(2)
C10−C1−Rh1−Cl2	92.36(16)	88.0(2)	88.1(2)	97.49(11)	101.0(2)
C20−S1−Rh1−Cl1	−137.98(8)	−124.32(12)	−131.34(11)	5.97(6)	0.47(12)
C20−S1−Rh1−Cl2	−49.74(8)	−32.50(12)	−40.06(11)	95.35(6)	88.97(12)
O1−S1−Rh1−Cl1		6.23(11)	0.36(11)	−127.18(7)	−132.79(11)
O1−S1−Rh1−Cl2		98.05(11)	91.64(11)	−37.80(7)	−44.30(11)

complexes **4**, **7**, and **8** (Figure 5a−c, respectively), which show the expected mirror-image relationship. A common feature of all the spectra is the presence of an intense bisignate Cotton effect centered between 230 and 240 nm. For all three complexes the longer wavelength extremum is positive and the shorter extremum is negative for the complex with a p*R*-configuration.

Solid-State Structures of the Rhodium(III) Complexes and *rac*-5. Crystal data and details of the structure determinations for the complexes *rac*-**4**, *rac*-**7**, *rac*-**8**, and (p*S*,*S*$_S$)-**8** and the ligand *rac*-**5** are listed in Table 1SI, Supporting Information. Selected bond lengths and bond and torsion angles for *rac*-**5** are given in Figure 2 and are listed together for the rhodium complexes in Table 1 for the purposes of comparison; indenyl-related structural parameters are listed in Table 2. The structures of the four rhodium complexes all show the expected three-legged "piano-stool" arrangement, with bonding angles involving rhodium, sulfur, and the two chlorides all around 90°. Comparing the Rh1−S1 bond length in the sulfane complex *rac*-**4** with the average Rh1−S1 bond length for the sulfoxide complexes, a shortening by 0.070(2) Å is observed for the latter. The shortening of the S1−O1 bond length seen in the sulfoxide ligand *rac*-**5** (1.4983(7) Å) on complexation to rhodium (average of 1.472(2) Å for the two independent molecules of *rac*-**7**) is typical for S-bonded sulfoxide−metal complexes[24] and consistent with the increase in the S=O vibration frequency noted above. The indenyl rings of the rhodium complexes show typical slip-fold distortions[20,30] in the solid state (Table 2), with the slip distortions ranging from 0.090(3) to 0.116(3) Å, hinge angles ranging from 3.2° to 5.8°, and fold angles ranging from 2.4° to 6.0°. These values are all at the lower end of the range classified as distorted η^5-coordination.[20,30] In addition, the rhodium is displaced toward the pendant sulfur ligand, with the Rh1−C1 bond 0.095(4) Å shorter than the Rh1−C3 bond, and the Rh1−C9 bond 0.074(4) Å shorter than the Rh1−C4 bond, for the sulfane complex *rac*-**4**; for the sulfoxide complex *rac*-**7**, the corresponding differences are 0.118(6) and 0.106(6) Å (averages for the two independent molecules), while the average corresponding differences for *rac*-**8** and (p*S*,*S*$_S$)-**8** are 0.098(3) and 0.077(6) Å. Comparing the structures of the diasteromeric sulfoxide complexes, the most noticeable difference is the angle between the planes of the indenyl C_5 ring (C1−C4,C9) and the substituted ring (C10−14,19) of the naphthyl group. The average angle for the two independent molecules of *rac*-**7** is 89.5°, while the average for *rac*-**8** and (p*S*,*S*$_S$)-**8** is 76.8°, similar to the angle for the sulfane complex *rac*-**4** (73.7°). When comparing differences in the structures of the two independent molecules of *rac*-**7**, and between *rac*-**8** and (p*S*,*S*$_S$)-**8**, the torsion angles around the Rh1−S1 bond are most apparent. For example, for molecule A of *rac*-**7** the O1−S1−Rh1−Cl1 torsion angle is 6.23(11)°, while for molecule B the value is 0.36(11)°. Similar differences are apparent between the structures of *rac*-**8** and (p*S*,*S*$_S$)-**8**, after taking into consideration the transposition of the methyl and oxygen groups on sulfur; the C20−S1−Rh1−Cl1 torsion angle is 5.97(6)° for *rac*-**8**, while for (p*S*,*S*$_S$)-**8** the value is 0.47(12)°.

Table 2. Comparison of Indenyl-Related Structural Parameters for the Rhodium(III) Complexes and Ligand 5

complex	Δ_{M-C} (Å)[a]	HA (deg)[b]	FA (deg)[c]	Ind-Naph (deg)[d]
rac-**4**	0.090(3)	5.2	3.3	73.7
rac-**7** (A)	0.098(3)	3.2	2.4	90.2
rac-**7** (B)	0.116(3)	4.7	6.0	88.7
rac-**8**	0.106(1)	5.1	3.5	77.6
(p*S*,*S*$_S$)-**8**	0.108(3)	5.8	5.5	75.9
rac-**5**				112.3

[a] Δ_{M-C} = slip distortion = [average of Rh−C4,C9] − [average of Rh−C1,C3]. [b] HA = hinge angle = angle between planes C1−C3 and C1,C3,C4,C9. [c] FA = fold angle = angle beween planes C1−C3 and C4−C9. [d] Ind-Naph = angle beween planes of indenyl C_5-ring (C1−C4,C9) and substituted ring (C10−14,19) of the naphthyl group. Angles < 90° indicate that the naphthyl 2-substituent leans toward the benzo ring of the indenyl, while angles > 90° indicate that the naphthyl 2-substituent leans toward the indenyl methyl group.

dx.doi.org/10.1021/om300581r | *Organometallics* 2012, 31, 5622−5633

CONCLUSIONS

The axially chiral indenyl-sulfanyl ligand *rac*-**3** has been efficiently prepared on a multigram scale, and through a series of Kagan asymmetric sulfoxidation, deoxygenation, and resulfoxidation reactions, the enantiomers of **3** and the enantiomers of the diastereomeric sulfoxide ligands **5** and **6** have been obtained in high enantiopurity. Using these ligands, the first example of a nonracemic planar chiral bidentate Cp-sulfanyl half-sandwich metal complex and the first examples of bidentate Cp-sulfinyl half-sandwich metal complexes featuring κS-bonding have been reported. These complexes were prepared in an enantio- and diastereospecific approach, which was dependent on performing the metal complexation reactions under conditions where sulfur coordination precedes π-coordination of the metal. Water as a cosolvent was found to play a critical role in obtaining good yields for the complexation reactions of the ligands with rhodium trichloride. A combination of single-crystal X-ray crystallography, CD spectroscopy, and ^{1}H NMR analysis using the chiral shift reagent Eu(hfc)$_3$ confirms the stereospecificity of the approach. In future work we will be examining potential applications of the rhodium complexes in catalysis, in addition to examining the preparation and potential applications of complexes of the ligands with other transition metals.

EXPERIMENTAL SECTION

General Considerations. Reactions involving air- or moisture-sensitive compounds were performed under an atmosphere of argon using standard Schlenk techniques. No special precautions were required for the preparations of the rhodium complexes. Anhydrous tetrahydrofuran was obtained by distillation from sodium benzophenone ketyl immediately prior to use. Benzene was dried by standing over sodium wire for at least 72 h prior to use. Anhydrous dichloromethane was distilled from calcium hydride immediately prior to use. Dimethylformamide was dried by standing over activated 4A molecular sieves for at least 72 h prior to use. Pyridine was dried by standing over potassium hydroxide pellets for at least 72 h prior to use. The conversion of 2-hydroxy-1-naphthoic acid to the methyl ester **1** was carried out according to the procedure of Guo and co-workers.[31] The preparation of 1-bromo-2-(2-bromopropyl)benzene from 2-bromobenzaldehyde was carried out according to our previously described sequence.[15]

NMR spectra were recorded on a Bruker Avance 300, Bruker Avance III 400, or Bruker Avance III 500 spectrometer. ^{1}H and ^{13}C NMR chemical shifts were referenced to signals of the solvent. ^{13}C NMR DEPT experiments were used to assist the assignment of the ^{13}C NMR spectra, and ^{1}H–^{1}H COSY experiments were used in assigning the ^{1}H NMR spectra. A 60 s relaxation delay was employed when acquiring the ^{1}H NMR spectra used to determine the ratio of solvate molecules present in the rhodium complexes. Low-resolution EI mass spectra were recorded on a Thermo-Finnigan GC Trace with a Thermo-Finnigan Polaris ion trap mass spectrometer. High-resolution EI mass spectra were recorded on a VG Autospec (EBE) Sector mass spectrometer at the Australian National University (Canberra). Low-resolution ESI mass spectra were recorded using a Thermo-Finnigan LCQ Classic ion trap mass spectrometer. High-resolution ESI mass spectra were recorded on a Bruker Apex III 7T Fourier Transform Ion Cyclotron resonance mass spectrometer with Apollo II ESI/MALDI dual source in positive ion ESI mode. The most abundant ion in an isotopic envelope is quoted, with the relative intensities of all ions in each envelope agreeing with that calculated for the proposed formulas. Elemental analyses were conducted by the Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago.

Optical rotations were measured for solutions in chloroform at ambient temperature using a Perkin-Elmer model 341 polarimeter and a 1 dm quartz cell. Circular dichroism spectra were recorded for solutions in methanol at ambient temperature using a Jasco J-710 spectropolarimeter and a 1 mm quartz cell. Analytical chiral HPLC was carried out on a Waters chromatography system consisting of a model 510 pump, U6K injector, and model 2487 absorbance detector operating at 254 nm. A 25 cm × 4.6 mm i.d. Chiracel OD-H column was used with the indicated mobile phase at a flow rate of 0.6 mL min^{-1}. Infrared spectra were recorded with a Bruker IFS66 spectrometer equipped with a Spectra-Tech diffuse reflectance accessory using a KBr matrix. The spectra were manipulated using the Kubelka–Munk mathematical function in the Bruker OPUSTM software (Version 3.01, Bruker Analytik, Germany) to convert the spectra from reflectance into absorbance. Melting points were determined using a Stanford Research Systems OptiMelt apparatus in glass capillaries and are uncorrected.

Methyl 2-(Methylsulfanyl)-1-naphthoate (2). A solution of triflic anhydride (10.0 g, 35.4 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise via cannula to a solution of the naphthol **1** (6.83 g, 33.8 mmol) and dry pyridine (3.0 mL, 37.1 mmol) in dry CH_2Cl_2 (50 mL) at 0 °C under an atmosphere of Ar. The mixture was stirred at rt for 18 h, then diluted with diethyl ether (200 mL) and washed with dilute HCl (2 M, 200 mL), water (200 mL), and saturated aqueous NaCl (100 mL). The organic phase was dried with $MgSO_4$ and the solvent removed under reduced pressure, affording the triflate as a colorless oil, which solidified on standing overnight. The triflate was dissolved in dry DMF (50 mL), and the solution degassed by several cycles of alternately boiling the stirred solution under high vacuum followed by backfilling with Ar. Pd(OAc)$_2$ (225 mg, 1.0 mmol) and *rac*-BINAP (685 mg, 1.1 mmol) were added, and the mixture was warmed to complete dissolution of the *rac*-BINAP. Dimethyl disulfide (1.8 mL, 20.0 mmol) and Zn powder (2.2 g, 33.6 mmol) were then added, and the mixture was stirred at 110 °C (bath) for 20 h. The mixture was diluted with diethyl ether (200 mL) and filtered through Celite, washing the solid residue with further diethyl ether. The filtrate was washed four times with water (200 mL) and once with saturated aqueous NaCl (100 mL). The organic phase was dried with $MgSO_4$, and the solvent removed under reduced pressure, affording an orange solid. The solid was dissolved in CH_2Cl_2 (100 mL) and passed through a short column of silica (silica gel 60, 70–230 mesh), eluting with further CH_2Cl_2 (200 mL). The solvent was removed under reduced pressure, affording a colorless solid, which was recrystallized from CH_2Cl_2/hexane. Yield: 6.19 g (79% calculated from **1**). Mp: 70–71 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.55 (s, 3H, SCH_3), 4.07 (s, 3H, CO_2CH_3), 7.47 (ddd, 1H, $^3J_{H5,H6}$ = 8.0 Hz, $^3J_{H6,H7}$ = 6.9 Hz, $^4J_{H6,H8}$ = 1.2 Hz, *H*6), 7.51 (d, 1H, $^3J_{H3,H4}$ = 8.7 Hz, *H*3), 7.53 (ddd, 1H, $^3J_{H7,H8}$ = 8.4 Hz, $^3J_{H6,H7}$ = 6.9 Hz, $^4J_{H5,H7}$ = 1.4 Hz, *H*7), 7.76 (br d, 1H, $^3J_{H7,H8}$ = 8.4 Hz, *H*8), 7.81 (br d, 1H, $^3J_{H5,H6}$ = 8.0 Hz, *H*5), 7.85 (d, 1H, $^3J_{H3,H4}$ = 8.7 Hz, *H*4). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 17.9 (SCH_3), 52.6 (CO_2CH_3), 124.6, 126.0, 126.3, 127.8, 128.3 (5 × *C*H), 130.3 (C_q), 130.4 (*C*H), 131.6, 131.9, 134.0 (3 × C_q), 169.0 (CO_2CH_3). EI-MS: *m*/*z* 232 ([M]$^+$, 100%), 217 (27), 201 (98), 158 (43). EI-HRMS: *m*/*z* 232.0554 ([M]$^+$, calcd 232.0558).

***rac*-1-(2-Methyl-1*H*-inden-3-yl)-2-(methylsulfanyl)-naphthalene (*rac*-3).** 1,2-Dibromoethane (0.5 mL, 5.8 mmol) was added to a stirred suspension of Mg granules (20 mesh, 5.0 g, 206 mmol) in dry THF (20 mL) under an atmosphere of Ar. Upon cessation of effervescence, a solution of 1-bromo-2-(2-bromopropyl)benzene (14.4 g, 51.8 mmol) in dry THF (250 mL) was added dropwise via cannula over 1 h at rt. The mixture was then stirred overnight at rt (a pale green solid may precipitate). A solution of $MgBr_2$ in THF was prepared by dropwise addition of a solution of 1,2-dibromoethane (8.8 mL, 102 mmol) in dry THF (250 mL) to stirred Mg granules (20 mesh, 3.0 g, 123 mmol), under an atmosphere of Ar, at such a rate as to prevent the solution from boiling. Upon cessation of effervescence, the warm solution was transferred via cannula to the di-Grignard solution, and the combined solution (which may require warming to redissolve any precipitated solids) was added rapidly via cannula (leaving behind excess Mg) to a solution of the ester **2** (6.00 g, 25.8 mmol) in dry THF (50 mL) at 0 °C. The mixture was stirred for 5 d at rt and then quenched by the addition of 10% aqueous NH_4Cl (250 mL). The organic layer was separated, the aqueous layer was extracted with diethyl ether (200 mL), and the combined organic phases were washed with saturated aqueous NaCl (250 mL).

dx.doi.org/10.1021/om300581r | *Organometallics* 2012, 31, 5622–5633

The organic phase was dried with $MgSO_4$, and the solvent removed under reduced pressure, affording a pale yellow oil. The oil was dissolved in CH_2Cl_2 (100 mL), and *p*-toluenesulfonic acid monohydrate (50 mg, 0.26 mmol) added. The mixture was stirred for 18 h at rt, then diluted with diethyl ether (200 mL) and washed with saturated aqueous $NaHCO_3$ (200 mL) and saturated aqueous NaCl (100 mL). The organic phase was dried with $MgSO_4$, and the solvent removed under reduced pressure, affording a pale yellow oil. Flash chromatography (silica gel 60, 230−400 mesh) eluting with 30:70 CH_2Cl_2/hexane provided the indene as a colorless solid. Yield: 5.24 g (67% calculated from **2**). Mp: 121−123 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.94 (s, 3H, 2′-CH_3), 2.46 (s, 3H, SCH_3), 3.65 (s, 2H, (*H*1′)$_2$), 6.67 (br d, 1H, $^3J_{H4',H5'}$ = 7.3 Hz, *H*4′), 7.10−7.18 (m, 2H, *H*5′/*H*6′), 7.33 (ddd, 1H, $^3J_{H7,H8}$ = 8.3 Hz, $^3J_{H6,H7}$ = 6.9 Hz, $^4J_{H5,H7}$ = 1.3 Hz, *H*7), 7.41 (ddd, 1H, $^3J_{H5,H6}$ = 8.1 Hz, $^3J_{H6,H7}$ = 6.9 Hz, $^4J_{H6,H8}$ = 1.2 Hz, *H*6), 7.51 (br d, 1H, $^3J_{H6',H7'}$ = 7.5 Hz, *H*7′), 7.52 (br d, 1H, $^3J_{H7,H8}$ = 8.3 Hz, *H*8), 7.53 (d, 1H, $^3J_{H3,H4}$ = 8.8 Hz, *H*3), 7.86 (br d, 1H, $^3J_{H5,H6}$ = 8.1 Hz, *H*5), 7.89 (d, 1H, $^3J_{H3,H4}$ = 8.8 Hz, *H*4). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 15.1 (2′-CH_3), 16.0 (SCH_3), 43.1 (C1′), 119.7, 123.2, 123.5, 124.1, 125.1, 125.6, 126.3, 126.7, 128.2, 128.4 (10 × *C*H), 130.2, 131.3, 132.6, 135.9, 136.0, 142.5, 144.6 (8 × C_q). EI-MS: *m*/*z* 302 ([M]$^+$, 40%), 287 (100), 272 (44), 254 (20), 240 (12). Anal. Calcd for $C_{21}H_{18}S$: C, 83.40; H, 6.00; S, 10.60. Found: C, 83.52; H, 6.13; S, 10.65.

***rac*-Dichloro[(1,2,3,3a,7a-*η*)-1-[2-(methylsulfanyl-*κS*)-1-naphthyl]-2-methyl-1*H*-inden-1-yl]rhodium (*rac*-4).** To a stirred suspension of the ligand *rac*-**3** (300 mg, 0.99 mmol) in a mixture of methanol (27 mL) and water (3 mL) was added rhodium trichloride trihydrate (260 mg, 0.99 mmol). The mixture was stirred and heated under reflux for 20 h. The methanol was removed under reduced pressure, and the residual water removed under high vacuum. The dark red-brown residue was dissolved in CH_2Cl_2 (15 mL) and then diluted with benzene (15 mL). The mixture was filtered through Celite, washing the solid residue with 1:1 CH_2Cl_2/benzene (10 mL). The filtrate was then concentrated under reduced pressure to ca. 20 mL. After standing overnight, the dark brown solid was collected, washed with 1:1 hexane/benzene, and dried at 0.5 mmHg for 5 d at rt to remove CH_2Cl_2 and benzene solvate. Yield: 385 mg (82%). Mp: >350 °C (dec). Single crystals suitable for X-ray diffraction were obtained through slow evaporation of a $CDCl_3$ solution. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.89 (s, 3H, 2-CH_3), 2.72 (d, 3H, $^3J_{H,Rh}$ = 1.1 Hz, SCH_3), 6.25 (br s, 1H, *H*3), 6.92 (dddd, 1H, $^3J_{H6,H7}$ = 8.8 Hz, $^5J_{H3,H7}$ = 0.9 Hz, $^5J_{H4,H7}$ = 0.9 Hz, $^4J_{H5,H7}$ = 0.9 Hz, *H*7), 7.46 (ddd, 1H, $^3J_{H4,H5}$ = 8.8 Hz, $^4J_{H4,H6}$ = 0.9 Hz, $^5J_{H4,H7}$ = 0.9 Hz, *H*4), 7.50 (ddd, 1H, $^3J_{H6,H7}$ = 8.8 Hz, $^3J_{H5,H6}$ = 6.7 Hz, $^4J_{H4,H6}$ = 0.9 Hz, *H*6), 7.55−7.62 (m, 2H, *H*7′/*H*8′), 7.686 (ddd, 1H, $^3J_{H5',H6'}$ = 8.3 Hz, $^3J_{H6',H7'}$ = 6.4 Hz, $^4J_{H6',H8'}$ = 1.8 Hz, *H*6′), 7.688 (d, 1H, $^3J_{H3',H4'}$ = 8.8 Hz, *H*3′), 7.84 (ddd, 1H, $^3J_{H4,H5}$ = 8.8 Hz, $^3J_{H5,H6}$ = 6.7 Hz, $^4J_{H5,H7}$ = 0.9 Hz, *H*5), 8.05 (br d, 1H, $^3J_{H5',H6'}$ = 8.3 Hz, *H*5′), 8.15 (d, 1H, $^3J_{H3',H4'}$ = 8.8 Hz, *H*4′). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 11.4 (2-CH_3), 23.2 (SCH_3), 73.1 (d, $^1J_{C,Rh}$ = 6.8 Hz, *C*3), 89.8 (d, $^1J_{C,Rh}$ = 6.8 Hz, C_q), 101.6 (d, $^1J_{C,Rh}$ = 7.4 Hz, C_q), 102.2 (d, $^1J_{C,Rh}$ = 8.3 Hz, C_q), 111.4 (d, $^1J_{C,Rh}$ = 6.1 Hz, C_q), 121.4, 123.9, 126.4, 128.8, 128.9, 129.00, 129.03 (7 × *C*H), 131.4 (C_q), 131.8 (*C*H), 131.9 (C_q), 133.1 (*C*H), 133.5 (C_q), 137.4 (*C*H), 144.4 (C_q). ES-MS: *m*/*z* 915 ([2M − Cl]$^+$, 21%), 843 ([2M − 3Cl]$^+$, 26), 439 ([M − Cl]$^+$, 100). Anal. Calcd for $C_{21}H_{17}Cl_2RhS$: C, 53.07; H, 3.61; S, 6.75. Found: C, 53.03; H, 3.55; S, 6.65.

(a*R,*R*$_S$*)-1-(2-Methyl-1*H*-inden-3-yl)-2-(methylsulfinyl)-naphthalene (*rac*-5) and (a*R**,*S*$_S$*)-1-(2-Methyl-1*H*-inden-3-yl)-2-(methylsulfinyl)naphthalene (*rac*-6).** *m*-Chloroperbenzoic acid (3.22 g, 50% purity, 9.3 mmol) was added to a stirred solution of *rac*-**3** (2.82 g, 9.3 mmol) in CH_2Cl_2 (50 mL) at 0 °C. After 15 min at 0 °C, the solution was warmed to rt over 15 min. The mixture was then diluted with diethyl ether (150 mL) and washed with saturated aqueous $NaHCO_3$ (200 mL) and saturated aqueous NaCl (100 mL). The organic phase was dried with $MgSO_4$, and the solvent removed under reduced pressure, affording a pale yellow oil. Flash chromatography (silica gel 60, 230−400 mesh) eluting with 70:30 EtOAc/hexane provided the sulfoxides as pale yellow solids. Sulfoxide *rac*-**5** eluted first (R_f = 0.44; yield: 1.82 g, 61%), followed by *rac*-**6** (R_f = 0.36; yield: 848 mg, 29%). Single crystals of *rac*-**5** suitable for X-ray diffraction were obtained through slow evaporation of a CH_2Cl_2/hexane solution.

rac-**5**. Mp: 157−158 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.03 (s, 3H, 2′-CH_3), 2.39 (s, 3H, S(O)CH_3), 3.62 and 3.69 (ABq, 2H, $^2J_{AB}$ = 22.8 Hz, (*H*1′)$_2$), 6.55 (br d, 1H, $^3J_{H4',H5'}$ = 7.6 Hz, *H*4′), 7.10 (br dd, 1H, $^3J_{H4',H5'}$ = 7.6 Hz, $^3J_{H5',H6'}$ = 7.6 Hz, *H*5′), 7.18 (ddd, 1H, $^3J_{H5',H6'}$ = 7.6 Hz, $^3J_{H6',H7'}$ = 7.4 Hz, $^4J_{H4',H6'}$ = 1.1 Hz, *H*6′), 7.41 (ddd, 1H, $^3J_{H7,H8}$ = 8.6 Hz, $^3J_{H6,H7}$ = 6.9 Hz, $^4J_{H5,H7}$ = 1.2 Hz, *H*7), 7.52 (br d, 1H, $^3J_{H6',H7'}$ = 7.4 Hz, *H*7′), 7.56−7.60 (m, 2H, *H*6/*H*8), 7.97−7.99 (m, 1H, *H*5), 8.16 (d, 1H, $^3J_{H3,H4}$ = 8.7 Hz, *H*4), 8.23 (d, 1H, $^3J_{H3,H4}$ = 8.7 Hz, *H*3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 15.3 (2′-CH_3), 43.21 (S(O)CH_3), 43.25 (C1′), 119.1, 119.3, 123.8, 124.7, 126.6, 126.7, 127.2, 127.7, 128.6, 130.0 (10 × *C*H), 130.8, 132.0, 132.8, 134.7, 142.31, 142.34, 145.3, 146.7 (8 × C_q). FTIR: $\tilde{\nu}$ (cm^{-1}) = 1054 (s, $\nu_{S=O}$). ES-MS: *m*/*z* 659 ([2M + Na]$^+$, 100%), 637 ([2M + H]$^+$, 19), 341 ([M + Na]$^+$, 25), 319 ([M + H]$^+$, 28). Anal. Calcd for $C_{21}H_{18}OS$: C, 79.21; H, 5.70; S, 10.07. Found: C, 79.55; H, 5.90; S, 10.11.

rac-**6**. Mp: 169−171 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.88 (s, 3H, 2′-CH_3), 2.60 (s, 3H, S(O)CH_3), 3.61 and 3.70 (ABq, 2H, $^2J_{AB}$ = 22.8 Hz, (*H*1′)$_2$), 6.81−6.83 (m, 1H, *H*4′), 7.14−7.22 (m, 2H, *H*5′/*H*6′), 7.46 (ddd, 1H, $^3J_{H7,H8}$ = 8.4 Hz, $^3J_{H6,H7}$ = 6.9 Hz, $^4J_{H5,H7}$ = 1.2 Hz, *H*7), 7.50 (br d, 1H, $^3J_{H6',H7'}$ = 7.2 Hz, *H*7′), 7.59 (ddd, 1H, $^3J_{H5,H6}$ = 8.1 Hz, $^3J_{H6,H7}$ = 6.9 Hz, $^4J_{H6,H8}$ = 1.1 Hz, *H*6), 7.67 (br d, 1H, $^3J_{H7,H8}$ = 8.4 Hz, *H*8), 7.98 (br d, 1H, $^3J_{H5,H6}$ = 8.1 Hz, *H*5), 8.16 (d, 1H, $^3J_{H3,H4}$ = 8.8 Hz, *H*4), 8.26 (d, 1H, $^3J_{H3,H4}$ = 8.8 Hz, *H*3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 15.5 (2′-CH_3), 43.16 (S(O)CH_3), 43.21 (*C*1′), 119.0, 119.9, 123.6, 125.0, 126.1, 127.0, 127.5, 127.9, 128.8, 130.2 (10 × *C*H), 131.1, 131.6, 133.9, 135.0, 141.9, 142.5, 145.4, 145.7 (8 × C_q). FTIR: $\tilde{\nu}$ (cm^{-1}) = 1054 (s, $\nu_{S=O}$). ES-MS: *m*/*z* 341 ([M + Na]$^+$, 73%), 319 ([M + H]$^+$, 100). Anal. Calcd for $C_{21}H_{18}OS$: C, 79.21; H, 5.70; S, 10.07. Found: C, 79.01; H, 5.78; S, 10.21.

(p*R,*S*$_S$*)-Dichloro[(1,2,3,3a,7a-*η*)-1-[2-(methylsulfinyl-*κS*)-1-naphthyl]-2-methyl-1*H*-inden-1-yl]rhodium (*rac*-7).** To a stirred solution of the ligand *rac*-**5** (200 mg, 0.63 mmol) in a mixture of methanol (9 mL) and water (1 mL) was added rhodium trichloride trihydrate (166 mg, 0.63 mmol). The mixture was stirred and heated under reflux for 20 h. On cooling to rt, the mixture was filtered through Celite, washing the solid residue with methanol (5 mL). The methanol was removed from the filtrate under reduced pressure, and the residual water removed under high vacuum. The dark red-brown residue was dissolved in CH_2Cl_2 (10 mL) and then diluted with benzene (20 mL). The solution was filtered through Celite, washing the solid residue with 1:1 CH_2Cl_2/benzene (10 mL). The filtrate was then concentrated under reduced pressure to ca. 25 mL, and the mixture then filtered, washing the solid residue with benzene (2 mL). After standing the filtrate overnight, the dark brown solid was collected, washed with benzene, and dried at 0.5 mmHg for 5 d at 60 °C to partially remove CH_2Cl_2 and benzene solvate. ^{1}H NMR analysis indicated the sample retained 0.15 and 0.4 molar equiv of CH_2Cl_2 and benzene, respectively. Yield: 80.0 mg (24%). Mp: >350 °C (dec). Single crystals suitable for X-ray diffraction were obtained through slow evaporation of a CH_2Cl_2/benzene solution. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.91 (s, 3H, 2-CH_3), 3.47 (s, 3H, SCH_3), 6.50 (br s, 1H, *H*3), 6.71 (br d, 1H, $^3J_{H6,H7}$ = 8.8 Hz, *H*7), 7.47 (br dd, 1H, $^3J_{H6,H7}$ = 8.8 Hz, $^3J_{H5,H6}$ = 6.7 Hz, *H*6), 7.51 (br d, 1H, $^3J_{H4,H5}$ = 8.8 Hz, *H*4), 7.67−7.72 (m, 2H, *H*7′/*H*8′), 7.76−7.82 (m, 2H, *H*5/*H*6′), 8.14 (br d, 1H, $^3J_{H5',H6'}$ = 8.3 Hz, *H*5′), 8.21 (d, 1H, $^3J_{H3',H4'}$ = 8.9 Hz, *H*3′), 8.37 (d, 1H, $^3J_{H3',H4'}$ = 8.9 Hz, *H*4′). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 11.0 (2-CH_3), 44.2 (S(O)CH_3), 79.1 (d, $^1J_{C,Rh}$ = 5.5 Hz, *C*3), 93.3 (d, $^1J_{C,Rh}$ = 6.0 Hz, C_q), 103.4 (d, $^1J_{C,Rh}$ = 7.5 Hz, C_q), 106.9 (d, $^1J_{C,Rh}$ = 8.2 Hz, C_q), 111.7 (d, $^1J_{C,Rh}$ = 4.7 Hz, C_q), 121.0, 121.9, 125.2, 125.4 (4 × *C*H), 126.5 (C_q), 129.2, 129.8, 130.19 (3 × *C*H), 130.22 (C_q), 132.8, 134.3 (2 × *C*H), 135.6 (C_q), 137.1 (*C*H), 158.8 (d, $^2J_{C,Rh}$ = 2.2 Hz, *C*2′). FTIR: $\tilde{\nu}$ (cm^{-1}) = 1119 (s, $\nu_{S=O}$). ES-HRMS: *m*/*z* 946.91459 ([2M − Cl]$^+$, calcd 946.91431, 14%), 908.94049 ([2M − 2Cl − H]$^+$, calcd 908.94036, 19), 512.93291 ([M + Na]$^+$, calcd 512.93244, 48), 454.97397 ([M − Cl]$^+$, calcd 454.97382, 100). Anal. Calcd for $C_{21}H_{17}Cl_2ORhS{\cdot}0.15CH_2Cl_2{\cdot}0.4C_6H_6$: C, 52.85; H, 3.71; S, 5.99. Found: C, 52.59; H, 3.99; S, 5.64.

dx.doi.org/10.1021/om300581r | *Organometallics* 2012, 31, 5622−5633

(p*R,R_S*)-Dichloro[(1,2,3,3a,7a-η)-1-[2-(methylsulfinyl-κS)-1-naphthyl]-2-methyl-1*H*-inden-1-yl]rhodium (*rac*-8).** To a stirred solution of the ligand *rac*-**6** (200 mg, 0.63 mmol) in a mixture of methanol (9 mL) and water (1 mL) was added rhodium trichloride trihydrate (166 mg, 0.63 mmol). The mixture was stirred and heated under reflux for 20 h. The methanol was removed under reduced pressure, and the residual water removed under high vacuum. The dark red-brown residue was dissolved in CH_2Cl_2 (15 mL) and then diluted with benzene (10 mL). The mixture was filtered through Celite, washing the solid residue with 1:1 CH_2Cl_2/benzene (10 mL). The filtrate was then concentrated under reduced pressure to ca. 15 mL. After standing overnight, the dark brown solid was collected, washed with benzene, and dried at 0.5 mmHg for 5 d at 60 °C to partially remove CH_2Cl_2 and benzene solvate. ^{1}H NMR analysis indicated the sample retained 0.05 and 0.6 molar equiv of CH_2Cl_2 and benzene, respectively. Yield: 220 mg (65%). Mp: >350 °C (dec). Single crystals suitable for X-ray diffraction were obtained through slow evaporation of a $CDCl_3$ solution. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 1.79 (s, 3H, 2-C*H*$_3$), 3.48 (s, 3H, SC*H*$_3$), 6.23 (br s, 1H, *H*3), 7.02 (br d, 1H, $^3J_{H6,H7}$ = 8.8 Hz, *H*7), 7.47 (br d, 1H, $^3J_{H4,H5}$ = 8.8 Hz, *H*4), 7.52 (ddd, 1H, $^3J_{H6,H7}$ = 8.8 Hz, $^3J_{H5,H6}$ = 6.7 Hz, $^4J_{H4,H6}$ = 0.6 Hz, *H*6), 7.68−7.76 (m, 2H, *H*7′/*H*8′), 7.82 (ddd, 1H, $^3J_{H5',H6'}$ = 8.2 Hz, $^3J_{H6',H7'}$ = 6.6 Hz, $^4J_{H6',H8'}$ = 1.5 Hz, *H*6′), 7.87 (ddd, 1H, $^3J_{H4,H5}$ = 8.8 Hz, $^3J_{H5,H6}$ = 6.7 Hz, $^4J_{H5,H7}$ = 0.8 Hz, *H*5), 8.12 (d, 1H, $^3J_{H3',H4'}$ = 8.9 Hz, *H*3′), 8.17 (br d, 1H, $^3J_{H5',H6'}$ = 8.2 Hz, *H*5′), 8.40 (d, 1H, $^3J_{H3',H4'}$ = 8.9 Hz, *H*4′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 11.5 (2-*C*H$_3$), 43.4 (S(O)*C*H$_3$), 76.6 (d, $^1J_{C,Rh}$ = 5.6 Hz, *C*3), 95.1 (d, $^1J_{C,Rh}$ = 6.7 Hz, C_q), 104.8 (d, $^1J_{C,Rh}$ = 8.5 Hz, C_q), 107.5 (d, $^1J_{C,Rh}$ = 6.7 Hz, C_q), 115.9 (d, $^1J_{C,Rh}$ = 4.6 Hz, C_q), 121.1, 121.4, 125.8, 127.3 (4 × *C*H), 127.8 (C_q), 129.5, 130.0 (2 × *C*H), 130.5 (*C*H and C_q), 133.0, 134.7 (2 × *C*H), 136.0 (C_q), 138.4 (*C*H), 157.9 (d, $^2J_{C,Rh}$ = 2.1 Hz, *C*2′). FTIR: $\tilde{\nu}$ (cm^{-1}) = 1099 (s, $\nu_{S=O}$). ES-HRMS: *m*/*z* 946.91464 ([2M − Cl]$^+$, calcd 946.91431, 6%), 908.94112 ([2M − 2Cl − H]$^+$, calcd 908.94036, 17), 512.93305 ([M + Na]$^+$, calcd 512.93244, 24), 454.97414 ([M − Cl]$^+$, calcd 454.97382, 100). Anal. Calcd for $C_{21}H_{17}Cl_2ORhS{\cdot}0.05CH_2Cl_2{\cdot}0.6C_6H_6$: C, 54.59; H, 3.85; S, 5.91. Found: C, 54.21; H, 3.82; S, 5.77.

General Procedure for Asymmetric Sulfoxidation: Synthesis of (a*S*,R_S)-6. Titanium tetraisopropoxide (4.9 mL, 16.6 mmol) was added rapidly to a stirred solution of diethyl (*R*,*R*)-tartrate (6.8 g, 33.0 mmol) in dry dichloromethane (60 mL) at rt under an atmosphere of Ar. After 2.5 min, water (300 μL, 16.7 mmol) was added dropwise over 10 min with vigorous stirring. The mixture was stirred for 20 min at rt, followed by cooling to −22 °C over 20 min. The solid sulfide *rac*-**3** (5.00 g, 16.6 mmol) was added, and upon dissolution, cumene hydroperoxide (88% purity, 5.5 mL, 33.0 mmol) was added dropwise. After 23 h at −22 °C the mixture was diluted with diethyl ether (200 mL). The mixture was then poured into a solution of ferrous sulfate heptahydrate (15.3 g, 59.5 mmol) and citric acid (5.1 g, 26.5 mmol) in water (150 mL) and was stirred for 15 min. The organic phase was separated and then stirred vigorously with aqueous NaOH (2 M, 300 mL) for 1 h. The organic phase was separated, washed with saturated aqueous NaCl (100 mL), dried over $MgSO_4$, and evaporated under reduced pressure, to afford a pale yellow oil. Flash chromatography (silica gel 60, 230−400 mesh) eluting with 70:30 EtOAc/hexane afforded (a*R*,R_S)-**5** as a pale yellow oil (yield: 3.01 g, 57%) with 66.7% ee (HPLC, 20:80 2-propanol/hexane, t_R = 11.3 and 15.2 min for (a*S*,S_S)- and (a*R*,R_S)-**5**, respectively) and (a*S*,R_S)-**6** as a pale yellow solid (yield: 2.03 g, 39%) with 96.6% ee (HPLC, 20:80 2-propanol/hexane, t_R = 12.9 and 14.7 min for (a*R*,S_S)- and (a*S*,R_S)-**6**, respectively). Recrystallization of (a*S*,R_S)-**6** from CH_2Cl_2/hexane gave a pale yellow solid (1.63 g) with 99.7% ee. Mp: 197−200 °C. $[\alpha]_D$ = +507 (*c* 1.0, $CHCl_3$). The spectroscopic data were identical to those of *rac*-**6** within experimental error.

General Procedure for Sulfoxide Deoxygenation: Synthesis of (a*S*)-3. Phosphorus pentasulfide (1.9 g, 4.3 mmol) was added to a stirred solution of (a*S*,R_S)-**6** (99.7% ee, 1.38 g, 4.3 mmol) in dry benzene (55 mL) under an atmosphere of Ar. The mixture was heated under reflux for 3 h and then diluted with diethyl ether (200 mL). The mixture was filtered through Celite, washing the solid residue with further diethyl ether. The filtrate was washed twice with aqueous NH_3 (3M, 200 mL), then once with water (200 mL) and saturated aqueous NaCl (100 mL). The organic phase was dried with $MgSO_4$, and the solvent removed under reduced pressure, affording a pale orange oil. Flash chromatography (silica gel 60, 230−400 mesh) eluting with 30:70 CH_2Cl_2/hexane provided the sulfide as a pale yellow solid with 99.6% ee (HPLC, 0.5:99.5 2-propanol/hexane, t_R = 15.0 and 17.7 min for (a*S*)- and (a*R*)-**3**, respectively). Yield: 1.10 g (84%). Mp: 122−124 °C. $[\alpha]_D$ = −69.4 (*c* 1.0, $CHCl_3$). The spectroscopic data were identical to those of *rac*-**3** within experimental error.

Synthesis of (a*R*,S_S)-6. Following the general procedure, (a*R*,R_S)-**5** (3.01 g, 9.5 mmol, 66.7% ee) was deoxygenated to afford (a*R*)-**3** as a pale yellow oil (yield: 2.35 g, 84%) with 66.5% ee (HPLC). Following the general procedure, the sulfide was resulfoxidized using diethyl (*S*,*S*)-tartrate. This provided sulfoxide **5** as a pale yellow solid (yield: 720 mg, 29%) with negligible ee (0.5%, HPLC), and (a*R*,S_S)-**6** as a pale yellow solid (yield: 1.49 g, 59%) with 98.9% ee (HPLC). Mp: 197−200 °C. $[\alpha]_D$ = −504 (*c* 1.0, $CHCl_3$). The spectroscopic data were identical to those of *rac*-**6** within experimental error.

Synthesis of (a*R*)-3. Following the general procedure, (a*R*,S_S)-**6** (1.21 g, 3.8 mmol, 98.9% ee) was deoxygenated to afford (a*R*)-**3** as a pale yellow solid with 98.5% ee (HPLC). Yield: 980 mg (85%). Mp: 122−124 °C. $[\alpha]_D$ = +70.5 (*c* 1.0, $CHCl_3$). The spectroscopic data were identical to those of *rac*-**3** within experimental error.

Synthesis of (a*S*,S_S)-5. Following the general procedure, (a*S*)-**3** (834 mg, 2.8 mmol, 99.6% ee) was resulfoxidized using diethyl (*S*,*S*)-tartrate. This provided (a*S*,S_S)-**5** as a pale yellow oil (yield: 813 mg, 93%) with >99.8% ee (HPLC). $[\alpha]_D$ = −393 (*c* 1.0, $CHCl_3$). The spectroscopic data were identical to those of *rac*-**5** within experimental error.

Synthesis of (a*R*,R_S)-5. Following the general procedure, (a*R*)-**3** (625 mg, 2.1 mmol, 98.5% ee) was resulfoxidized using diethyl (*R*,*R*)-tartrate. This provided (a*R*,R_S)-**5** as a pale yellow oil (yield: 595 mg, 90%) with 99.8% ee (HPLC). $[\alpha]_D$ = +388 (*c* 1.0, $CHCl_3$). The spectroscopic data were identical to those of *rac*-**5** within experimental error.

Synthesis of (p*R*)- and (p*S*)-4. Following the procedure described for the synthesis of *rac*-**4**, (a*R*)-**3** (200 mg, 0.66 mmol, 98.5% ee) and (a*S*)-**3** (200 mg, 0.66 mmol, 99.6% ee) were complexed with rhodium trichloride trihydrate. The workup was as described for the synthesis of *rac*-**4**; however, trituration with hexane was required in the last step to facilitate precipitation of the complexes. The dark brown solids were dried at 0.5 mmHg for 3 d at rt to partially remove benzene solvate. ^{1}H NMR analysis indicated the samples retained 0.6 and 0.45 molar equiv of benzene for (p*R*)- and (p*S*)-**4**, respectively. Yields: 237 mg (69%) and 242 mg (72%) for (p*R*)- and (p*S*)-**4**, respectively. Mps: >350 °C (dec). The spectroscopic data were identical to those of *rac*-**4** within experimental error. The enantiomeric excess of the complexes was >98% by ^{1}H NMR ($CDCl_3$, 300 MHz) analysis in the presence of Eu(hfc)$_3$ (ca. 2 mg of the complex dissolved in 0.5 mL of a 16 mM solution of Eu(hfc)$_3$): δ 1.97 and 2.00 (2-C*H*$_3$ for (p*S*)- and (p*R*)-**4**, respectively), 6.55 and 6.61 (*H*3 for (p*S*)- and (p*R*)-**4**, respectively). CD (MeOH) λ_{ext}/nm 219 ($\Delta\varepsilon$/cm^2 mmol^{-1} −47.9): 240 (+40.0), 268 (sh, +20.1), 331 (−6.3), 409 (+2.7), 490 (+ 3.1) for (p*R*)-**4**; 220 (+44.5), 240 (−39.7), 268 (sh, −20.5), 333 (+5.8), 410 (−2.1), 490 (−2.5) for (p*S*)-**4**.

Synthesis of (p*R*,S_S)- and (p*S*,R_S)-7. Following the procedure described for the synthesis of *rac*-**7**, (a*R*,R_S)-**5** (180 mg, 0.57 mmol, 99.8% ee) and (a*S*,S_S)-**5** (230 mg, 0.72 mmol, >99.8% ee) were complexed with rhodium trichloride trihydrate. The workup was as described for the synthesis of *rac*-**7**; however, the filtration immediately preceding precipitation of the complexes was omitted. The dark brown solids were dried at 0.5 mmHg for 2 d at rt to partially remove CH_2Cl_2 and benzene solvate. ^{1}H NMR analysis indicated that both samples retained 0.05 molar equiv of CH_2Cl_2, together with 0.25 and 0.65 molar equiv of benzene for (p*R*,S_S)- and (p*S*,R_S)-**7**, respectively. Yields: 79 mg (27%) and 109 mg (28%) for (p*R*,S_S)- and (p*S*,R_S)-**7**, respectively. Mps: >350 °C (dec). The spectroscopic data were identical to those of *rac*-**7** within experimental error. The enantiomeric excess of the complexes was >98% by ^{1}H NMR (CD_2Cl_2, 300 MHz)

dx.doi.org/10.1021/om300581r | *Organometallics* 2012, 31, 5622−5633

analysis in the presence of Eu(hfc)$_3$ (ca. 2 mg of the complex dissolved in 0.5 mL of a 8 mM solution of Eu(hfc)$_3$): δ 2.34 and 2.36 (2-CH_3 for (pS,R_S)- and (pR,S_S)-**7**, respectively), 4.23 and 4.41 (S(O)CH_3 for (pS,R_S)- and (pR,S_S)-**7**, respectively), 6.92 and 6.97 (*H*3 for (pS,R_S)- and (pR,S_S)-**7**, respectively). CD (MeOH) λ_{ext}/nm 221 ($\Delta\varepsilon$/cm^2 mmol^{-1} −51.5): 238 (+62.2), 269 (+14.3), 328 (+15.2), 431 (+2.9) for (pR,S_S)-**7**; 221 (+49.3), 238 (−60.9), 269 (−17.1), 328 (−13.6), 432 (−4.0) for (pS,R_S)-**7**.

Synthesis of (pR,R_S)- and (pS,S_S)-8. Following the procedure described for the synthesis of *rac*-**8**, (aR,S_S)-**6** (200 mg, 0.63 mmol, 98.9% ee) and (aS,R_S)-**6** (200 mg, 0.63 mmol, 99.7% ee) were complexed with rhodium trichloride trihydrate. The workup was as described for the synthesis of *rac*-**8**. The dark brown solids were dried at 0.5 mmHg for 3 d at rt to partially remove CH_2Cl_2 and benzene solvate. ^{1}H NMR analysis indicated that the samples retained 0.2 and 0.15 molar equiv of CH_2Cl_2 and 0.9 and 0.95 molar equiv of benzene for (pR,R_S)- and (pS,S_S)-**8**, respectively. Yields: 231 mg (63%) and 246 mg (68%) for (pR,R_S)- and (pS,S_S)-**8**, respectively. Mps: >350 °C (dec). The spectroscopic data were identical to those of *rac*-**8** within experimental error. Single crystals of (pS,S_S)-**8** suitable for X-ray diffraction were obtained through slow evaporation of a CH_2Cl_2/benzene solution. The enantiomeric excess of the complexes was >98% by ^{1}H NMR (CD_2Cl_2, 300 MHz) analysis in the presence of Eu(hfc)$_3$ (ca. 2 mg of the complex dissolved in 0.5 mL of a 8 mM solution of Eu(hfc)$_3$): δ 2.26 and 2.31 (2-CH_3 for (pS,S_S)- and (pR,R_S)-**8**, respectively), 4.66 and 4.76 (S(O)CH_3 for (pS,S_S)- and (pR,R_S)-**8**, respectively), 6.89 and 6.95 (*H*3 for (pS,S_S)- and (pR,R_S)-**8**, respectively). CD (MeOH) λ_{ext}/nm 228 ($\Delta\varepsilon$/cm^2 mmol^{-1} −56.7): 253 (sh, +25.2), 266 (+33.4), 381 (+9.9), 491 (−1.7) for (pR,R_S)-**8**; 230 (+58.7), 253 (sh, −28.8), 265 (−35.5), 380 (−9.8), 489 (+2.1) for (pS,S_S)-**8**.

X-ray Crystallographic Studies. Crystal data and details of the structure determinations are listed in Table 1SI, Supporting Information. Crystals were attached with Exxon Paratone N to a short length of fiber supported in a copper mounting pin, then quenched in a cold nitrogen stream from an Oxford Cryosystems Cryostream. Data were collected at 150(2) K using Mo Kα radiation using either a Bruker SMART-1000 diffractometer (sealed tube, graphite monochromated; *rac*-**4**), a Bruker-Nonius FR591 Kappa APEX II diffractometer (fine-focus rotating anode, graphite monochromated; *rac*-**5** and *rac*-**8**), or an Agilent SuperNova diffractometer (microsource, mirror monochromated; *rac*-**7** and (pS,S_S)-**8**). The data processing were undertaken with SAINT and XPREP[32] (*rac*-**4**, *rac*-**5**, *rac*-**8**) or CrysAlisPro[33] (*rac*-**7**, (pS,S_S)-**8**). A multiscan absorption correction was applied to the data.[32−34] The structures were solved by direct methods with SHELXS-97[35] or SIR-97[36] ((pS,S_S)-**8**) and extended and refined with SHELXL-97.[35] The non-hydrogen atoms in the asymmetric unit were modeled with anisotropic displacement parameters except where noted below. A riding atom model with group displacement parameters was used for the hydrogen atoms.

Special Conditions/Variations. *rac*-**4**: One of two molecules of $CDCl_3$ in the asymmetric unit is disordered and was modeled over two positions. The carbon (C22′) and chlorine (Cl13′, Cl14′, Cl15′) atoms in the minor orientation (0.1 occupancy) were modeled isotropically.

rac-**7**: The asymmetric unit contains two crystallographically independent complex molecules, both with a (pR*,S_S*)-configuration, along with disordered solvent (1.8 × benzene, 0.1 × dichloromethane). One solvent site in the structure was modeled with benzene in two orientations rotationally disordered about the plane of the C6 ring; a second site contains benzene (0.8 total occupancy over 3 orientations) and dichloromethane (0.1 occupancy). The solvent molecules were modeled with rigid body constraints and isotropic disaplacement parameters.

rac-**8**: The crystal faces were indexed, and combined numerical absorption and multiscan scaling corrections were applied to the data with SADABS.[34] A rotationally disordered $CDCl_3$ molecule in the asymmetric unit was modeled over two sites with 0.92:0.08 occupancies; the deuterium was refined as isotropic.

(pS,S_S)-**8**: The asymmetric unit contains an ordered benzene molecule that sits between the indenyl and naphthyl groups of neighboring molecules. The absolute structure was established with the Flack parameter[29] refining to 0.00(2).

Crystallograpic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre: CCDC Nos. 881854 (*rac*-**4**), 881855 (*rac*-**5**), 881856 (*rac*-**7**), 881857 (*rac*-**8**), and 881858 ((pS,S_S)-**8**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Drs. Paul Jensen, Rene Macquart, and Jason Price, of the Crystal Structure Analysis Facility, University of Sydney, are thanked for assistance with X-ray diffraction data collection and analysis.

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