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Strategy for the Resolution of a Chiral Dearomatization Agent:{TpRe(CO)(1-methylimidazole)} Coordination of α-Pinene (Tp = Hydridotris(pyrazolyl)borate)

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Abstract: A methodology for resolving TpRe(CO)(1-methylimidazole)(η^2-benzene) has been developed utilizing (R)-α-pinene. Each enantiomer of the {TpRe(CO)(MeIm)} system can be obtained with the enantiomer ratio (er) = 97:3 by taking advantage of differing rates of pinene substitution for the two diastereomers of TpRe(CO)(MeIm)(η^2-(R)-α-pinene).

The dearomatization agent pentaammineosmium(II) forms stable complexes with a variety of aromatic molecules and activates these ligands toward electrophilic addition reactions.[1] Many of these transformations of aromatic compounds are inaccessible by conventional synthetic methods and may become valuable synthetic tools if they can be carried out with absolute stereocontrol. Indeed, enantioselective dearomatization reactions have found synthetic utility for the formation of many complex organic compounds.[2-6] Although most of the reactions with pentaammineosmium(II) are highly stereocontrolled where both electrophile and nucleophile add to the ring face opposite that of metal coordination,[1] the rapid rate of racemization for the aromatic complexes has prevented the development of a general method for delivering dearomatized products with control of the absolute stereochemistry. The introduction of a chiral auxiliary has made enantioselective processes possible for anisole complexes of pentaammineosmium(II),[7] but the development of an effective general method calls for a resolved chiral-at-metal dearomatization agent. Since the pentaammineosmium-(II) system is not amenable to changes in the ligand set,[8] an analogous metal system was explored.

The second generation of η^2-dearomatization agents from our laboratories has the general formula TpRe(CO)(L)(L$_\pi$) (Tp = hydridotris(pyrazolyl)borate; L = ^{t}BuNC, PMe$_3$, pyridine, 1-methylimidazole (MeIm), NH$_3$; L$_\pi$ = dihapto-coordinated ligand).[9-11] Of these systems, that with L = MeIm has proven
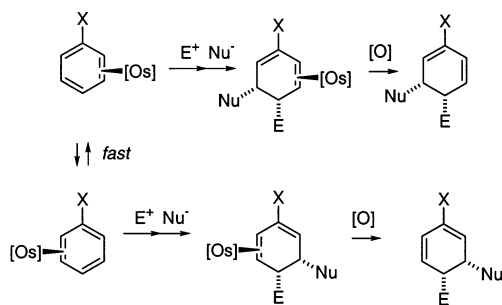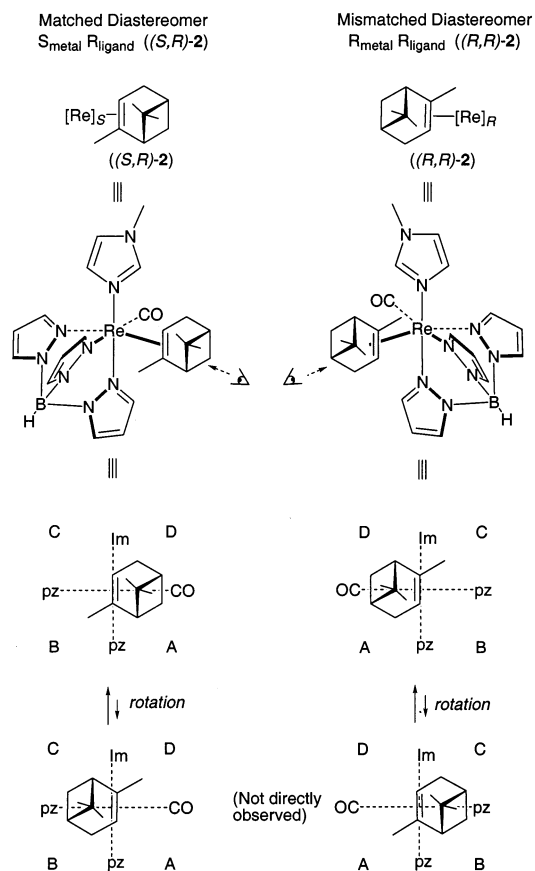

to bind the broadest range of aromatic molecules. More significantly, this system binds prochiral aromatic molecules with moderate stereocontrol (dr up to >20:1), and preliminary studies have shown that this rhenium system can activate the bound ligand toward reactions with electrophiles to an even greater degree than pentaammineosmium(II), often with high regio- and stereoselectivity.[12-14] Thus, an efficient method for resolving the complex TpRe(CO)(MeIm)(η^2-benzene) (**1**) was desired, given that this complex is the standard precursor to complexes of other aromatic ligands.

A quadrant analysis of the {TpRe(CO)(MeIm)} system was performed to ascertain the binding selectivity of a variety of substituted olefins, ketones, and aldehydes.[15] Two outcomes of this study are germane to the present work. First, trisubstituted olefins (e.g., 2-methyl-2-butene) bind selectively to avoid the placement of an alkyl substituent into the pyrazole/MeIm quadrant (quadrant C, Figure 1), which is sterically the most congested. Second, the system is intolerant of bulky substituents oriented toward the metal (e.g., as in η^2 -pinacolone).[15] Following these two guidelines, we selected (1R)-(+)-α-pinene

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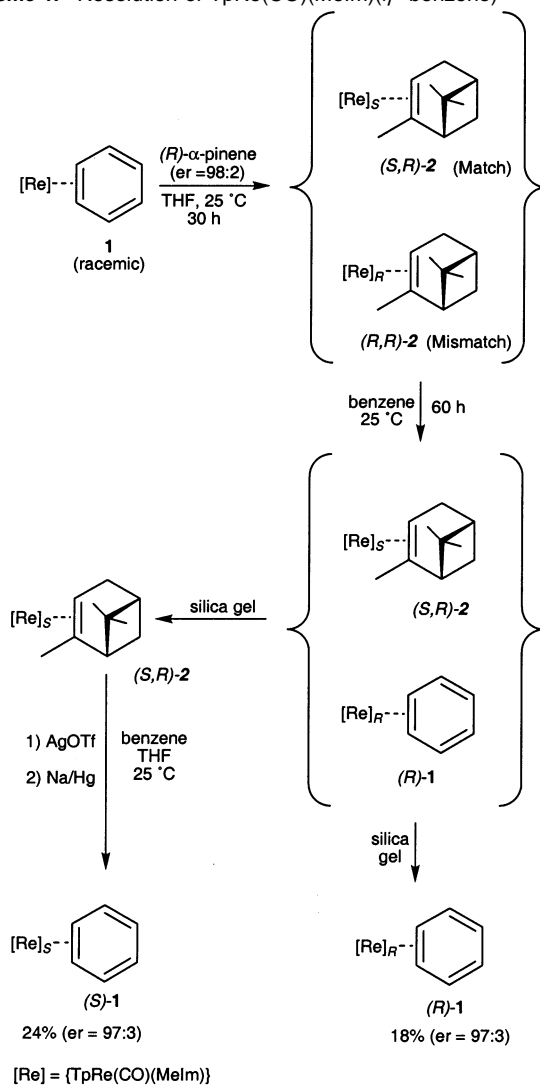(15) Meiere, S. H.; Harman, W. D. *Organometallics* **2001**, *18*, 3876.

Figure 1. Match ((S,R)-**2**) and mismatch ((R,R)-**2**) diastereomers of the (R)-α-pinene complex.

Scheme 1. Resolution of TpRe(CO)(MeIm)(η^2-benzene)

[Re] = {TpRe(CO)(MeIm)}

(97% ee; er = 98:2), a common reagent for the preparation of hydroboration agents,[16] as a readily available, inexpensive, chiral, trisubstituted olefin with a single hindered face.

Previous studies have shown that olefins will bind with the C=C bond orthogonal to the metal−CO bond in order to optimize back-bonding.[10,11] With this restriction in place, eight orientations (two diastereomers (face-flip of olefin) and two rotamers (180° rotation of olefin) for each configuration of the metal complex) are possible. For the (R)-α-pinene complex (**2**), four of these geometrical arrangements place the hindered face of the ligand (containing the geminal dimethyl bridge) toward the metal; thus, these forms are not observed. Of the remaining four orientations (Figure 1), the S metal fragment is observed as the rotamer which avoids placing any alkyl substituents into the hindered quadrant C. This form is designated the "match" diastereomer ((S,R)-**2**) (metal, pinene). The two remaining R metal rotamers place either a methyl group in quadrant C or extend the ring system over quadrants B and C. Although both rotamers are relatively unfavorable (cf. (S,R)-**2**), the former places less bulk toward the pyrazole ring *trans* to CO and, therefore, is the more stable complex. This diastereomer is assigned as the "mismatch" form ((R,R)-**2**) (see Figure 1).

The (R)-α-pinene complex (**2**) was synthesized from racemic TpRe(CO)(MeIm)(η^2-benzene) (**1**) by ligand substitution (18 pinene equiv, THF, 25 °C, 30 h).[9] Two diastereomers were observed by ^{1}H NMR in a 1:1 ratio, assigned according to ^{1}H, ^{13}C NMR, and NOE data and designated (R,R)-**2** and (S,R)-**2**. For the mismatch isomer ((R,R)-**2**), the steric strain between

the methyl group of the pinene and the pyrazole ring *trans* to CO (quadrant C) profoundly destabilizes this complex relative to the matched form ((S,R)-**2**).[15] After being stirred in benzene for 60 h at 25 °C, the mismatch complex ((R,R)-**2**) undergoes complete (>98%) ligand exchange with the solvent, while the matched form ((S,R)-**2**) is relatively stable under these conditions (<2% conversion). Thus, the resulting mixture consists of (S)-TpRe(CO)(MeIm)(η^2-(R)-α-pinene) ((S,R)-**2**) and (R)-TpRe-(CO)(MeIm)(η^2-benzene) ((R)-**1**). These two compounds can be separated on silica gel in order to isolate the resolved metal centers. To obtain (S)-TpRe(CO)(MeIm)(η^2-benzene) ((S)-**1**), one could simply use (S)-α-pinene (readily available at approximately the same cost as its enantiomer). However, to utilize fully the procedure above, an additional oxidation/reduction step (performed in our laboratory for other rhenium olefin complexes)[11,17] with the isolated matching form (S,R)-**2** yields the (S)-TpRe(CO)(MeIm)(η^2-benzene) complex ((S)-**1**) (Scheme 1). The isolated yield from racemic benzene complex **1** to the resolved benzene complexes (R)-**1** and (S)-**1** was 42% (18% and 24%, respectively).

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Scheme 2. Testing for Rhenium Epimerization Using β-Pinene
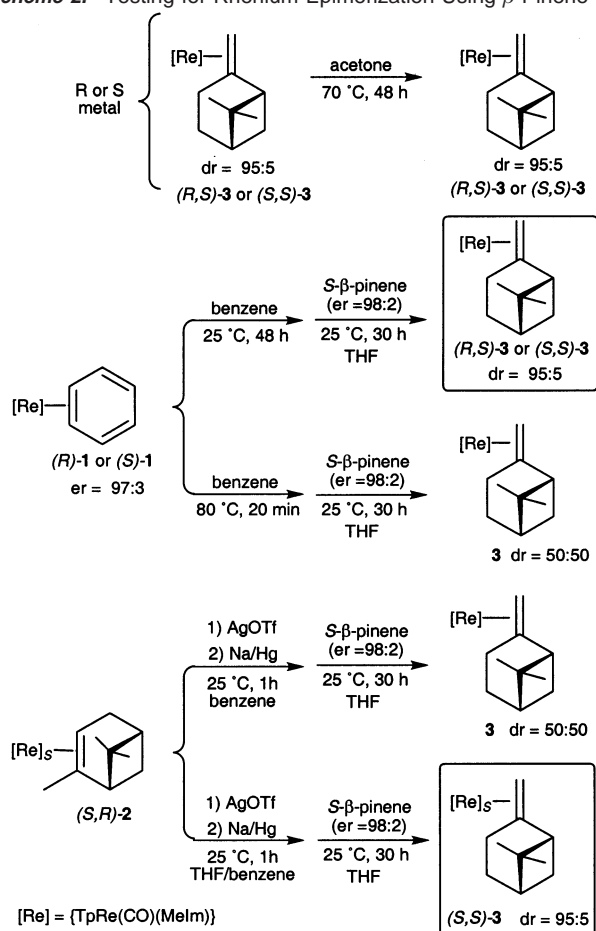
The enantiomer ratio (er) of these resolved benzene complexes ((R)-**1**, (S)-**1**), was measured using (1S)-(−)-β-pinene (er = 98:2) as a probe (Scheme 2). Although this ligand is similar to α-pinene in that only two rhenium complexes, *RS* ((R,S)-**3**) and *SS* ((S,S)-**3**), are observed by ^{1}H NMR, there is a key distinction. Because of the lack of a methyl group in quadrant C (both (R,S)-**3** and (S,S)-**3** orient olefinic protons toward quadrants C and D), these two diastereomers show no significant differences in thermal stability. Both β-pinene complexes (R,S)-**3** and (S,S)-**3** are more stable (<2% decomposition observed after 48 h at 70 °C, acetone-d_6) than their α-pinene analogues.

The benzene ligand of (R)-**1** and (S)-**1** was exchanged with (S)-β-pinene (18 equiv, THF, 25 °C, 30 h) to form a diastereomeric mixture of products. The diastereomer ratio (dr) for this mixture reflects the er of the initial metal complexes; thus, a racemic mixture of **1** yields a 1:1 ratio of diastereomers with (1S)-β-pinene. However, when this reaction is repeated with (R)-TpRe(CO)(MeIm)(η^2-benzene) ((R)-**1**), the complex (R)-TpRe(CO)(MeIm)(S-β-pinene) ((R,S)-**3**) is formed in a dr of 95:5. The same dr was obtained for (S)-TpRe(CO)(MeIm)(η^2-benzene) ((S)-**1**). Since the (S)-β-pinene that was used has an er of 98:2, the measured er of (R)-**1** and (S)-**1** approaches the theoretical maximum er of 97:3 (because of the er of (R)-α-pinene and (S)-β-pinene employed herein). We note that >99.5% ee α-pinene may be readily obtained by a procedure reported by Brown et al.[18]

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Racemization studies have been performed for both the rhenium benzene and pinene systems (Scheme 2). No racemization was observed at 25 °C (48 h) for the benzene complex ((R)-**1** and (S)-**1**) in benzene, suggesting that these compounds could indeed serve as precursors for other resolved η^2-aromatic complexes. Given that the substitution half-life for the benzene ligand is about 2 h at this temperature[9] and that this substitution is dissociative,[17,19] the five-coordinate intermediate is thought to be square pyramidal rather than trigonal bipyramidal.

The β-pinene complex ((R,S)-**3** and (S,S)-**3**) shows no detectable racemization at 70 °C over a period of 48 h in acetone-d_6. However, with the more labile benzene ligand, complete racemization occurs in <20 min at an elevated temperature (80 °C; (R)-**1** and (S)-**1** in benzene). Attempts to elucidate the mechanism have not been undertaken; however, a trigonal bipyramidal intermediate or transition state is thought to be responsible.[20]

Interestingly, utilizing the oxidation/reduction sequence for the conversion of the α-pinene complex ((S,R)-**2**) to the benzene complex ((S)-**1**) in the presence of only benzene (solvent) yields a racemic mixture of **1**, even at 25 °C. However, when a THF/benzene (1:1) cosolvent system is implemented, this procedure yields the product (S)-**1** with er = 96:4. This observation could be explained by invoking THF as a ligand for Re(II). Apparently, the putative THF complex is sufficiently inert that racemization does not occur. Without THF or another suitable ligand present, the weakly coordinating triflate apparently dissociates to form a square−pyramidal five-coordinate intermediate that rapidly inverts, leading to racemization of the Re(II) complex (Figure 2).

When racemization occurs at elevated temperatures for Re(I) and lower temperatures for Re(II) (in the absence of good σ-donor ligands), it may be possible during the substitution reaction between racemic benzene complex (**1**) and α-pinene to funnel all the rhenium to a single configuration. Such an asymmetric transfer process[21] would not only constitute a more efficient use of rhenium but also would eliminate a chromatography step. Efforts in this area are currently underway.

We chose to test this new methodology on the tandem addition of a proton and silyl ketene acetal to naphthalene (Scheme 3), a well studied organic transformation for the TpRe(CO) systems.[12] A 1.00-g sample of racemic benzene complex **1** was stirred with an excess of (R)-α-pinene in THF for 30 h to generate the matched and mismatched forms of **2**. The resulting mixture was then combined with naphthalene and again stirred in THF for 30 h. Addition of hexanes delivered a 1:1 mixture of the naphthalene complex[12] (R)-**4** and the matched pinene complex (S,R)-**2** in 48% yield. This mixture was then subjected to a sequence of steps in which the naphthalene ligand first protonates (HOTf·MeOH), then reacts with 1-methoxy-2-methyl-1-trimethylsiloxypropene (MMTP), and then is oxidatively decomplexed.[12] The resulting 2-alkylated 1,2-dihydronaphthalene (S)-**6** was isolated in 63% yield on the basis of available (R)-**4**. The optical purity was determined by analyzing a sample of **6** on a chiral GC coupled to an MS detector. The enantiomer ratio was found to be 93:7 (86% ee), a value which approaches the theoretical limit for this reaction, given that the pinene was

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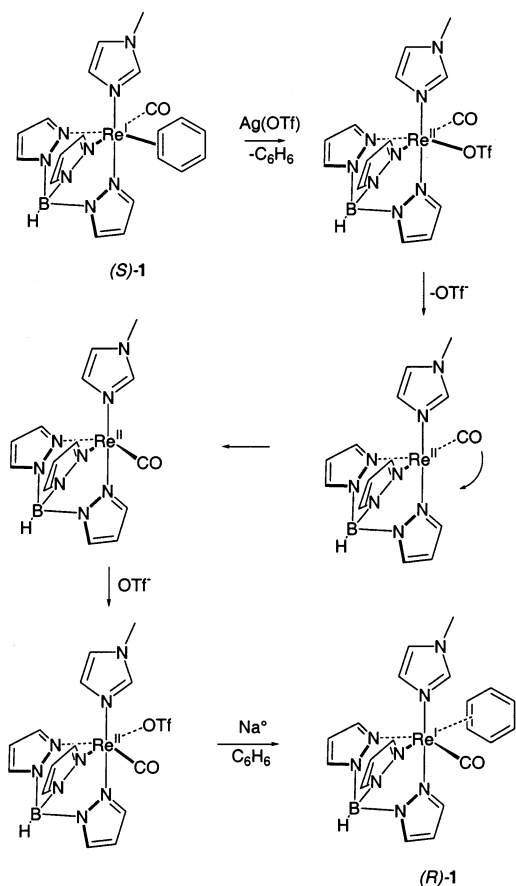
Figure 2. Racemization of TpRe(CO)(MeIm)(OTf).

Scheme 3. Preparation of an Enantio-enriched 2-Alkyl-1,2-dihydronaphthalene Using a Rhenium Dearomatization Agent
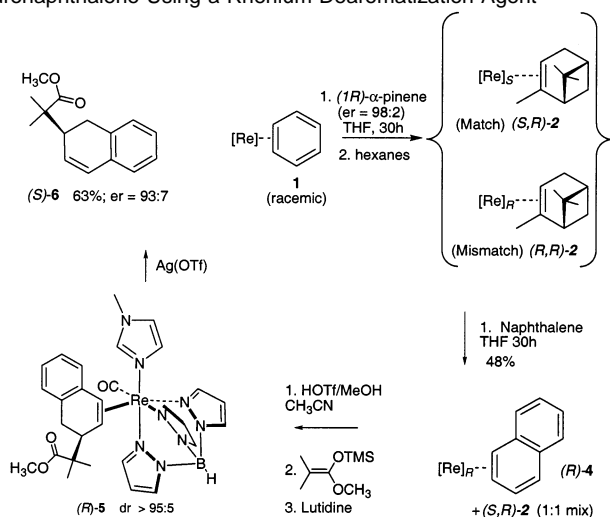
97% ee and that the dr for the complex (*R*)-**5** could be as low as 95:5. Of note, when the reaction was repeated with the stronger acid HOTf·CH₃CN, the enantiomer ratio for (*S*)-**6** was only 80:20, even though the diastereomer ratio for **5** was still >20:1. This observation suggests that acid may play a role in facilitating the epimerization of the rhenium stereogenic center and care must be taken to keep the acid strength and concentration as low as possible using this rhenium system for organic reactions.

In conclusion, both enantiomers of TpRe(CO)(MeIm)(η^2-benzene) ((*R*)-**1,** (*S*)-**1**) have been isolated in moderate yield (combined 42%) from a racemic mixture utilizing 97% ee (*R*)-α-pinene. Measured er's were 97:3 for both *R* and *S* forms, indicating a virtually complete transfer of chirality from ligand to metal. When a resolved rhenium system was used to carry out a tandem addition reaction to naphthalene, the chiral dihydronaphthalene product was obtained with good optical purity (er = 93:7). With an enantiomerically enriched dearomatization agent in hand, which also serves as a convenient precursor to other resolved aromatic complexes, enantioselective dearomatization reactions with dihapto-coordinated aromatic molecules are now generally accessible.

Experimental Section

General Methods. NMR spectra were obtained on a 300 or 500 MHz Varian INOVA spectrometer. All chemical shifts are reported in ppm and are referenced to tetramethylsilane (TMS) utilizing residual ¹H or ¹³C signals of the deuterated solvents as an internal standard. Coupling constants (*J*) are reported in hertz (Hz). Resonances in the ¹H NMR due to pyrazole ligands are listed by chemical shift and multiplicity only (all pyrazole coupling constants are 2 Hz). Infrared spectra (IR) were recorded on a MIDAC Prospect Series (Model PRS) spectrometer as a glaze (evaporated THF) on a Horizontal Attenuated Total Reflectance (HATR) accessory (Pike Industries). Values were reproducible within ±1 cm⁻¹. Electrochemical experiments were performed under a nitrogen atmosphere using a PAR model 362 potentiostat driven by a PAR model 175 universal programmer. Cyclic voltammograms (CV) were recorded (Kipp and Zonen BD90 XY recorder) at 100 mV/s (20 °C) in a standard three-electrode cell from +1.7 to −1.9 V with a glassy carbon working electrode, *N,N*-dimethylacetamide (DMAc) solvent, and tetrabutylammonium hexafluorophosphate (TBAH) electrolyte. All potentials are reported versus NHE (Normal Hydrogen Electrode) using cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) or ferrocene ($E_{1/2} = 0.55$ V) as an internal standard. The peak-to-peak separation was less than 100 mV for all reversible couples. Elemental analysis (EA) was performed with a Perkin-Elmer 2400 Series II CHNS/O Analyzer. All synthetic reactions and electrochemical experiments were performed under a dry nitrogen atmosphere. Benzene, THF (tetrahydrofuran), and hexanes were purged with nitrogen and purified by passage through a column packed with activated alumina.[22] Other solvents were thoroughly purged with nitrogen prior to use. Sodium amalgam (1 wt %), a liquid at 22 °C, was prepared by slowly adding small pieces of sodium to mercury under an inert atmosphere (exothermic!). Deuterated solvents were used as received from Cambridge Isotopes. (1*R*)-(+)-α-pinene (97% ee/GLC) and (1*S*)-(−)-β-pinene (97% ee/GLC) were used as received from Aldrich. Other reagents were used as received. Compound **1** has been reported previously.[9,17]

Synthesis of (*R*)-TpRe(CO)(MeIm)(η^2-benzene) ((*R*)-1) and (*S*)-TpRe(CO)(MeIm)(η^2-benzene) ((*S*)-1). In a glovebox, a 100-mL round-bottom flask was charged with a stir bar, TpRe(CO)(MeIm)(η^2-benzene) (**1**, 0.30 g, 0.51 mmol), (*R*)-α-pinene (97% ee, 1.27 g, 9.36 mmol), and THF (20 mL). Additionally, K₂CO₃ (~1 g) was added to eliminate any trace acid. The solution was stirred (30 h, 25 °C). The solvent was then removed under reduced pressure, and the resulting solid was redissolved in benzene (50 mL). The benzene solution was stirred (60 h, 25 °C), and the mixture was poured directly onto a column (20 cm × 2.5 cm) of silica gel (pretreated with benzene). Two bands were observed by eluting with 15% Et₂O in benzene and monitoring by IR: a beige fraction (ν_{CO} = 1773 cm⁻¹) followed by a bright yellow fraction (ν_{CO} = 1795 cm⁻¹).

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The yellow solution was placed into a round-bottom flask with a stir bar. The solvent volume was reduced by half under reduced pressure, and hexanes were added to twice the original volume. To complete the product precipitation, the solvent volume was reduced again by half and hexanes were added once more to restore original volume. The yellow suspension was filtered on a medium porosity frit. The precipitate was washed with hexanes (2 × 10 mL), and the product was dried in vacuo yielding a yellow powder ((*R*)-**1**) (0.053 g, 18%).

The beige solution was placed in a round-bottom flask with a stir bar. Under reduced pressure, the solvent volume was reduced to ∼20 mL. THF (15 mL) was added, and then a THF (5 mL) solution of AgOTf (0.064 g, 0.25 mmol) was added dropwise (∼ 1 min) to the stirring solution. An immediate darkening was observed, and solid silver appeared. After 5 min, Na/Hg (1 wt %, 7 g, 3 mmol) was added, and stirring was continued (1 h). Confirmation of complete oxidation and reduction can be obtained by IR (ν_{CO} = 1773 cm^{-1} (Re(I)-olefin) to ν_{CO} = 1855 cm^{-1} (Re(II)-THF) to ν_{CO} = 1795 cm^{-1} (Re(I)-benzene)). The solution was filtered through a Celite plug, and the yellow filtrate was placed in a round-bottom flask with a stir bar. The solvent volume was reduced by half under reduced pressure, and hexanes were added to twice the original volume. The solvent volume was reduced again by half, and hexanes were added to restore the original volume. The solvent volume was reduced by half once more, and the yellow suspension was filtered through a medium porosity frit. The precipitate was washed with hexanes (2 × 10 mL), and the product dried in vacuo yielding a yellow powder ((*S*)-**1**) (0.074 g, 24%).

Measuring % er with (1*S*)-(−)-β-Pinene. In a glovebox, a screw cap vial was charged with a stir bar, TpRe(CO)(MeIm)(η^2-benzene) (0.01 g, 0.02 mmol), (*S*)-β-pinene (97% ee, 0.04 g, 0.3 mmol), and THF (4 mL). Additionally, K$_2$CO$_3$ (∼100 mg) was added to eliminate any trace acid. The solution was stirred (30 h, 25 °C) and filtered to remove K$_2$CO$_3$. The solvent was removed from the resulting filtrate, and a ^{1}H NMR spectrum of the crude product was obtained. The dr (which relates directly to starting material er) was determined by the ratio of the Tp 4-position triplets at 6.18 (*R*,*S*)-**3** and 6.15 (*S*,*S*)-**3** ppm.

(*S*)-TpRe(CO)(MeIm)(η^2-(*R*)-α-pinene) ((*S*,*R*)-2). Assignments were made considering α-pinene bound to the 2,3-position. ^{1}H NMR (acetone-d_6, 20 °C, δ): 7.84, 7.74, 7.73, 7.67, 7.63, 7.21 (6H, 1:1:1:1:1:1, each a d (or fine dd with *J* < 1), Tp 3,5), 6.29, 6.20, 6.05, (3H, 1:1:1, each a t, Tp 4), 7.87 (1H, br t, Im), 7.07, 6.86 (2H, 1:1, each a t, *J* = 1.5, Im), 3.85 (3H, s, NMe), 3.02 (1H, d, *J* = 10, CH$_2$), 2.84 (1H, dddd, *J* = 14, 8, 3, 2, CH$_2$, 4-position), 2.72 (1H, d, *J* = 8, CH, 3-position), 2.64 (1H, dd, *J* = 14, 2, CH$_2$, 4-position), 2.19 (1H, dtd, *J* = 10, 7, 2, CH$_2$), 2.11 (1H, t, *J* = 6, CH, 1-position), 1.81 (1H, m, CH, 5-position), 1.39 (3H, s, gem CH$_3$), 1.09 (3H, s, gem CH$_3$), 0.55

(3H, s, CH$_3$). ^{13}C NMR (acetone-d_6, 20 °C, δ): (carbonyl not observed) 147.0, 142.4, 141.6, 141.4, 135.6, 134.5 (Tp 3,5), 136.2, 132.0, 121.8 (Im), 107.0, 106.2, 105.8 (Tp 4), 71.8 (olefin C), 57.7 (olefin CH), 57.2 (CH, 1-position), 43.2 (CH, 5-position), 41.9 (C), 33.6 (CH$_2$, 4-position), 32.4 (CH$_2$), 28.2 (gem CH$_3$), 28.1 (CH$_3$), 23.4 (gem CH$_3$), 34.3 (NMe). IR: ν_{CO} = 1773 cm^{-1} (vs), ν_{BH} = 2474 cm^{-1} (w). CV: $E_{p,a}$ = 0.04 V (II/I). EA Calculated for ReC$_{24}$H$_{32}$N$_8$BO: C, 44.65; H, 5.00; N, 17.36. Found: C, 44.86; H, 4.81; N, 17.74.

(*R*)-TpRe(CO)(MeIm)(η^2-(*R*)-α-pinene) ((*R*,*R*)-2). This product was not isolated but formed in situ. Tp and MeIm ^{1}H NMR resonances: 8.16, 7.87, 7.73, 7.63, 7.07 (6H, 1:1:2:1:1, each a d (or fine dd with *J* < 1), Tp 3,5), 6.26, 6.20, 6.05 (3H, 1:1:1, each a t, Tp 4), 7.42, 6.52 (2H, 1:1, each a br t, Im), 7.02 (1H, t, *J* = 1.5, Im), 3.80 (3H, s, NMe).

(*R*),(*S*)-TpRe(CO)(MeIm)(η^2-(*S*)-β-pinene) ((*R*,*S*)-3, (*S*,*S*)-3). This was reported as a 1:1 mixture of diastereomers. Significant broadening was observed for many ^{1}H and ^{13}C resonances. Measurements of dr were made utilizing the Tp 4 resonances which appear as sharp triplets. ^{1}H NMR (acetone-d_6, 22 °C, δ) (*R*,*S*)-**3** diastereomer: 8.16, 7.78, 7.61, 7.51, 7.10, 6.98 (6H, 1:1:1:1:1:1, each a br s, Tp 3,5 and Im), 7.85, 7.78 (2H, 1:1, each a d, Tp 3,5), 6.41 (1H, br s, Im), 6.26, 6.18, 5.99 (3H, 1:1:1, each a t, Tp 4), 3.78 (3H, s, NMe), 1.01 (3H, s, Me), 0.89 (3H, s, Me). ^{1}H NMR (acetone-d_6, 22 °C, δ) (*S*,*S*)-**3** diastereomer: 7.97, 7.79, 7.51, 7.03, 6.98 (5H, 1:1:1:1:1, each a br s, Tp 3,5 and Im), 7.85, 7.79 (3H, 1:2, each a d, Tp 3,5), 6.34 (1H, br s, Im), 6.27, 6.15, 5.99 (3H, 1:1:1, each a t, Tp 4), 3.78 (3H, s, NMe), 1.23 (3H, s, Me), 1.05 (3H, s, Me). Other pinene signals for both diastereomers: 3.17, 2.78, 2.29, 2.18 (4H, 1:1:1:1, each a br s, bound olefin), 1.95, 1.78, 1.66, 1.26 (13H, each a br m, pinene), 0.86 (3H, br m, pinene). ^{13}C NMR (acetone-d_6, 22 °C, δ): 199.7 (CO), 149.3, 146.1, 143.4, 142.6, 141.9, 137.1, 136.1, 135.8, 134.5, 134.4 (Tp 3,5, Im), 132.5, 121.7 (Im), 106.1 (2), 106.0 (2), 105.8, 105.7 (Tp 4), 65.0, 57.7, 57.6, 45.9, 41.1, 40.7 (bound CH$_2$, bound C, bridgehead CH, gem dimethyl C), 34.2 (NMe), 28.8, 27.6, 27.3, 26.9, 26.0, 23.9 (gem CH$_3$, ring CH$_2$). IR: ν_{CO} = 1785 cm^{-1} (vs), ν_{BH} = 2479 cm^{-1} (w). CV: $E_{1/2}$ = −0.11V (II/I) (overlapping diastereomers). EA Calculated for ReC$_{24}$H$_{32}$N$_8$BO: C, 44.65; H, 5.00; N, 17.36. Found: C, 44.56; H, 5.15; N, 17.60.