Syntheses and Structures of Unsymmetrically 1,1- and 1,2-Disubstituted Alkene Complexes of the Chiral Rhenium Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$: Enantioface Binding Selectivities and Conformational Equilibria

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Reactions of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClR)]^+BF_4^-$ (R = CH_2Cl (**1**), C_6H_5 (**2**)) and $H_2C{=}C(CH_3)R$ (R = CH_2CH_3 (**a**), $CH_2CH_2CH_3$ (**b**), C_6H_5 (**c**)) at room temperature (RT) give the alkene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}C(CH_3)R)]^+BF_4^-$ (**3a–c**; 53–98%) as (35–50):(65–50) mixtures of *RS,SR*/*RR,SS* diastereomers. At 95 °C, equilibration to (68–70):(32–30) (**3a,b**) and 36–64 (**3c**) mixtures occurs. Reactions of **2** and *cis*-$CH_3HC{=}CHR$ (R = CH_2CH_3 (**a**), $CH(CH_3)_2$ (**b**)) at RT or 95 °C give (*Z*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3HC{=}CHR)]^+BF_4^-$ ((*Z*)-**4a,b**; 90–99%) as (51–79):(49–21) mixtures of *RSR,SRS*/*RRS,SSR* diastereomers. Two Re—(C=C) conformers of each (*Z*)-**4a** diastereomer are detected by NMR (–60 °C) and interconvert with 11.6–11.9 kcal/mol barriers. Reactions of **2** and *trans*-$CH_3HC{=}CHR$ (R = CH_2CH_3 (**a**), $CH(CH_3)_2$ (**b**), C_6H_5 (**c**)) at RT give (*E*)-**4a–c** (85–97%) as 59:41, >99:<1, and 59:41 mixtures of *RSS,SRR*/*RRR,SSS* diastereomers. Similar reactions at 95 °C give ≥99:1 mixtures (89–96%). The Re—(C=C) conformers of the *RRR,SSS* diastereomer of (*E*)-**4c** readily interconvert ($\Delta G^{\ddagger}(T_c)$ = 10.3–10.4 kcal/mol), but those of the *RSS,SRR* diastereomers of (*E*)-**4a,c** show higher barriers (≥17.0 kcal/mol). Reactions of **2** and $CH_3HC{=}C(CH_3)_2$ give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3HC{=}C(CH_3)_2)]^+BF_4^-$ as mixtures of *RS,SR*/*RR,SS* diastereomers that slowly equilibrate at RT ((91–94):(9–6) after 64–336 h). The equilibrium diastereomer and conformer ratios are rationalized stereoelectronically and compared to those of analogous $H_2C{=}CHR$ and *cis*/*trans*-$RHC{=}CHR$ complexes, thus providing a comprehensive picture of alkene binding equilibria for the chiral Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$.

The binding of prochiral alkenes to chiral metal receptors is a key step in a host of metal-mediated asymmetric transformations.[1] Two configurational diastereomers are possible, which differ in the C=C enantioface coordinated to the metal. Both kinetic and thermodynamic binding selectivities are of obvious importance. Although such data are available for a few transition-metal Lewis acids,[2–4] a comprehensive study involving many types of substituted alkenes has not been undertaken for any one system. Thus, over the last 7 years, we have methodically investigated the binding of a variety of alkenes to the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**). This effort began with simple monosubstituted alkenes[4] and continued with symmetrically substituted *cis*- and *trans*-alkenes,[5] α,β-unsaturated aldehydes and ketones,[6] and conjugated and nonconjugated dienes.[7] Related studies of analogous allene[8] and alkyne[9] complexes have also been reported.

This endeavor has now amassed as many installments as popular genre movies have sequels. In this spirit, we present below the "final chapter", featuring the synthesis of unsymmetrically *di*substituted alkene complexes of **I** and equilibrium binding data. To help ensure that this corpus will not be resurrected, data for a trisubstituted alkene complex of **I** are also given. In order to provide a context for the results that follow, relevant properties of **I** and previously characterized alkene complexes are summarized first.

The pyramidal fragment **I** possesses the high-lying d donor orbital shown in Scheme 1. Accordingly, alkene ligands adopt Re—(C=C) conformations that allow high degrees of overlap of their π^* acceptor orbitals. As sketched in **II** (Scheme 1), the steric environments of the four resulting C=C substituent positions (a–d) have been mapped.[4–7] A large group is best accommodated in position a and is particularly disfavored in position d. Thus,

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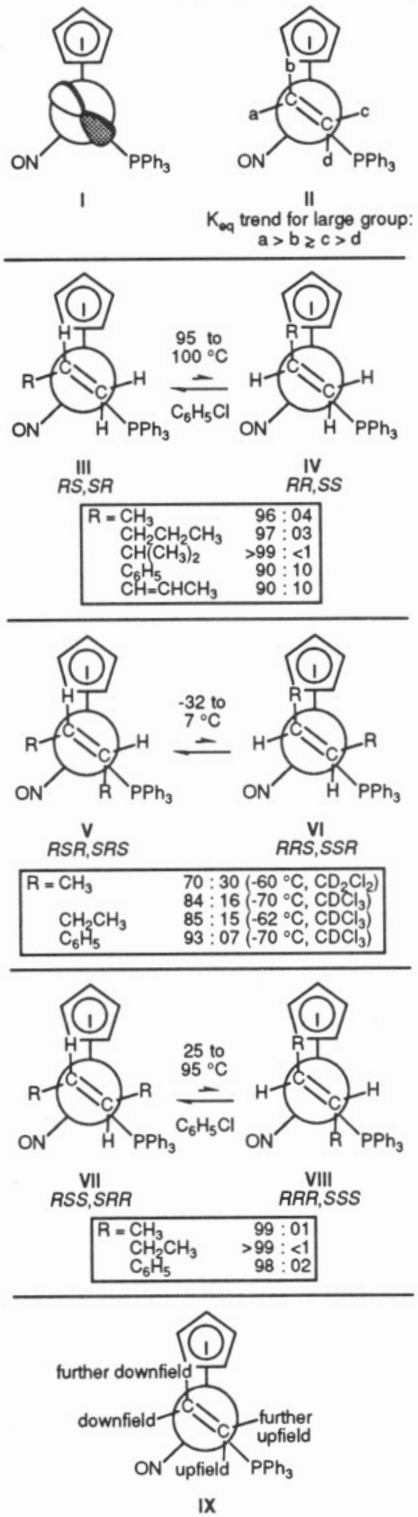
Scheme 1[a]



[a] Legend: **(I)** d-orbital HOMO of the pyramidal 16-valence-electron rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$; **(II)** steric environment in alkene complexes of **I**; **(III–VIII)** idealized structures of diastereomeric monosubstituted and symmetrical *cis*- and *trans*-disubstituted alkene complexes of **I**; **(IX)** ^{1}H NMR trends.

monosubstituted alkene ligands preferentially adopt the Re—(C=C) conformations shown in idealized structures **III** and **IV**, with the larger =CHR termini *anti* to the bulky PPh_3 ligand.[4,10] Although rotational barriers about the Re—(C=C) axes should not be significantly greater than those of the corresponding *cis*-alkene complexes (11–13 kcal/mol),[5b] no evidence has yet been observed for conformers with alkyl or aryl substituents in positions c and d.

Adducts **III** and **IV** are configurational diastereomers that differ in the C=C enantioface bound to rhenium. They are usually generated as ca. 2:1 mixtures from the substitution-labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]BF_4^-$ (**1**) or the chlorobenzene analog $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**2**).[11] Equilibrations occur at 95–100 °C in chlorohydrocarbon solvents by nondissociative mechanisms to give ≥96:4 **III**/**IV** mixtures when R = alkyl or 90:10 mixtures when R = phenyl or vinyl (Scheme 1).[4c,d,7a]

Symmetrically substituted *cis*-alkene ligands adopt Re—(C=C) conformations as in the idealized structures **V** and **VI** (Scheme 1).[5] The C=C faces of such ligands are *homotopic* or identical. Thus, although **V** and **VI** qualify as configurational diastereomers, they can—unlike **III** and **IV**—interconvert by a 180° rotation about the Re—(C=C) axis. This is normally rapid on the NMR time scale at room temperature. The thermodynamic binding selectivities are generally lower than for **III** and **IV**, reflecting the mismatched additive effects of the steric trends summarized in **II** (positions a + d vs b + c).[5b] Symmetrical *trans*-alkene ligands give the idealized structures **VII** and **VIII**, which differ in the C=C enantioface bound to rhenium and equilibrate at 25–95 °C. The thermodynamic binding selectivities are higher than for **III** and **IV**, in accord with the matched additive effects of the steric trends in **II** (positions a + c vs b + d). The Re—(C=C) rotational barriers are much greater for **VII** (>17.6 kcal/mol) than for **VIII** (11.6 kcal/mol, R = C_6H_5), and rationales have been suggested.[5b]

All of the preceding types of alkene complexes have been crystallographically characterized.[4b,c,5,6,7a] Their structures have been probed in solution by ^{1}H difference NOE experiments.[12] Importantly, irradiation of the cyclopentadienyl ligand resonance enhances the resonance of the group in position b in **II**.[4b,5–8] Many NMR chemical shift and coupling constant trends have been identified. For example, the ^{13}C and ^{1}H resonances of =CH groups *syn* to the PPh_3 ligand give J_{CP} and J_{HP} values larger than those *anti* to the PPh_3 ligand. The ^{1}H chemical shifts of allylic methyl (=CHC*H*$_3$) groups follow the trend shown in **IX** (Scheme 1).[5b] Other diagnostic features are noted below.

(10) (a) The absolute configuration at rhenium is specified first and is assigned by a variant of the Cahn–Ingold–Prelog rules in which the η^5-C_5H_5 and alkene ligands are viewed as pseudoatoms of atomic numbers 30 and 12, respectively. This gives the priority sequence η^5-C_5H_5 > PPh_3 > C=C > NO. (b) In alkene complexes with two =CHR stereocenters, the configuration of the carbon with the greater Cahn–Ingold–Prelog priority (=C*H*CH$_2$CH$_3$ > =C*H*CH$_3$) is given first. If the priorities are equal, the configuration of the =CHR group *anti* to the PPh_3 ligand is given first. (c) A synclinal (*sc*) Re—(C=C) conformer is one in which the highest priority substituent on rhenium (η^5-C_5H_5) and the C=C centroid (e.g., =CHCH$_2$CH$_3$ > =CHCH$_3$) define a (60 ± 30)° torsion angle. An anticlinal (*ac*) conformer is one in which the highest priority substituents define a (120 ± 30)° torsion angle. The torsion angles in the idealized structures **XIV**/**XVII** and **XV**/**XVI** are 45 and 135°, respectively. (d) Note that as long as a *cis* or *trans* relationship is maintained, the configurations of the RHC=CHR′ stereocenters are fixed relative to each other. Also, the configuration of a given carbon is not affected by a 180° rotation about the Re—(C=C) axis. However, with complexes of symmetrical *cis*-alkenes (**V**/**VI**, Scheme 1), the protocol in b leads to an *apparent* inversion. (e) See previous papers in this series for background literature on the preceding points.[5b,6]

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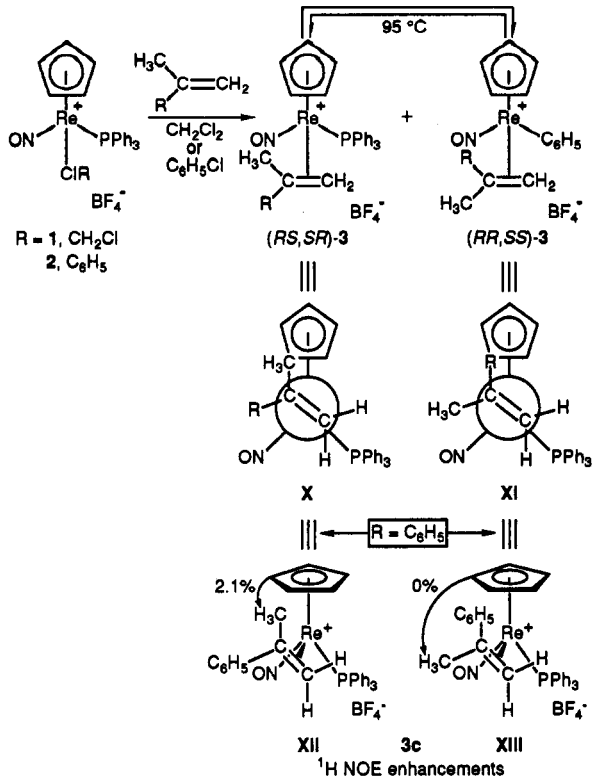
Scheme 2. Binding of Unsymmetrical Geminal Alkenes to the Chiral Lewis Acid I



	yield (*RS,SR*/*RR,SS* ratio)			
	room temperature		95 °C	
	from **1**	from **2**	from **2**[a]	from **3**[b]
R = **a**, CH_2CH_3	82% (42 : 58)	81% (48 : 52)	98% (69 : 31)	>99% (68 : 32)
b, $CH_2CH_2CH_3$	53% (49 : 51)	54% (50 : 50)	82% (70 : 30)	66% (68 : 32)
c, C_6H_5	97% (42 : 58)	98% (35 : 65)	96% (36 : 64)	— (36 : 64)

[a] Ratios are before *and* after workup. [b] These experiments utilized unequilibrated mixtures of diastereomers (**3a**, C_6D_5Cl; **3b**, C_6H_5Cl) or pure *RS,SR* and *RR,SS* diastereomers (**3c**, CD_2ClCD_2Cl).

In extending the preceding studies to unsymmetrically disubstituted alkene ligands, we generally expected to encounter additional isomers. For example, unsymmetrical *cis*-alkenes should give two configurational diastereomers that differ in the C=C enantioface bound to rhenium. Each will in turn have two conformers (*ac*/*sc*)[10c] that differ by ca. 180° rotations about the Re—(C̄–C) axes. Unsymmetrical *trans*-alkenes should give an analogous array of isomers. However, geminally disubstituted alkenes should have an even greater energetic bias than monosubstituted alkenes for Re—(C̄–C) conformers in which the substituted C=C terminus is *anti* to the PPh_3 ligand. Hence, we investigated this potentially simpler class of complexes first. The symmetrically substituted isobutylene complex of **I** has been described previously.[4b,13]

Results

1. Binding of 1,1-Disubstituted Alkenes. The dichloromethane complex **1** was generated at −80 °C in dichloromethane solvent as reported earlier.[11a] In separate experiments, 2-methyl-1-butene, 2-methyl-1-pentene, and α-methylstyrene were added (5 equiv; Scheme 2). After 3–12 h at room temperature, workups gave the corresponding alkene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}C(CH_3)R)]^+BF_4^-$ (**3a–c**) in 53–97% yields as (42–49):(58–51) mixtures of *RS,SR*/*RR,SS* configurational diastereomers (**X**/**XI**, Scheme 2).[10,14] Similar reactions with the chlorobenzene complex **2** (−45 °C, then room temperature; chlorobenzene solvent) gave **3a–c** in 54–98% yields as comparable mixtures of diastereomers. Complexes (*RS,SR*)-**3c** and (*RR,SS*)-**3c** were separated by column chromatography. Diastereomer configurations were assigned as described below.

A C_6D_5Cl solution of **3a** (48:52 *RS,SR*/*RR,SS*) was kept in a 95 °C NMR probe. After 1 h, a ^1H NMR spectrum showed a 68:32 *RS,SR*/*RR,SS* diastereomer mixture. This ratio was unchanged after an additional 8 h, or upon cooling. The corresponding propene and 1-pentene complexes require at least 12 h to attain equilibrium in C_6D_5Cl at 100 °C.[4c,d] Thus, the diastereomers of **3a** interconvert more rapidly. However, as would be intuitively expected from the relative sizes of the =CRR′ substituents, the enantioface binding selectivity is lower. A similar thermolysis of **3b** (50:50 *RS,SR*/*RR,SS*) gave a 68:32 *RS,SR*/*RR,SS* mixture (12 h, C_6H_5Cl, 95 °C).

In separate experiments, CD_2ClCD_2Cl solutions of (*RS,SR*)-**3c** and (*RR,SS*)-**3c** were kept in a 95 °C NMR probe, and ^1H spectra were taken every 15 min. Over the course of 1 h, both samples equilibrated to 36:64 *RS,SR*/*RR,SS* mixtures, indicating an *opposite* enantioface binding selectivity. Ratios were unchanged after an additional 2 h. In order to directly access equilibrium mixtures of diastereomers, the preceding reactions of chlorobenzene complex **2** and alkenes were repeated, but the samples were kept at 95 °C for 4–6 h before workup. Data are given in Scheme 2.

Complexes **3a–c** were characterized by microanalysis and IR and NMR ($^1H/^{13}C/^{31}P$) spectroscopy, as summarized in the Experimental Section. Most properties were similar to those of monosubstituted alkene complexes of **I**. The =CHH′ ^{13}C NMR resonances gave larger $^2J_{CP}$ values (4.8–6.1 Hz, $w_{1/2}$ = 11.1–12.3 Hz) than the =CRR′ resonances (s, $w_{1/2}$ = 5.3–7.5 Hz),[15] as expected from the Re—(C̄–C) conformations in **X** and **XI**. The downfield =CHH′ ^1H resonances of **3a,b** (δ 2.73–2.80) were assigned to the protons in position d, consistent with shielding trends shown by both diastereomers of monosubstituted alkene complexes,[4b,c] and gave larger $^3J_{HP}$ values (12.4–13.2 Hz) than the upfield =CHH′ resonances (δ 2.45–2.50, 5.4–6.3 Hz).[16]

Diastereomers were assigned from the relative chemical shifts of the =CHCH_3 ^1H resonances, per the trend in **IX**.[16] Furthermore, the cyclopentadienyl ^1H resonance of (*RR,SS*)-**3c** (δ 5.14) was upfield of that of (*RS,SR*)-**3c** (δ 5.78). A similar shift occurs in the analogous styrene complexes (δ 5.22, 5.77)[4b] and is plausibly ascribed to shielding from a phenyl group in position b. Finally, the assignments for **3c** were confirmed by ^1H difference NOE experiments.[12] As shown in **XII** (Scheme 2), irradiation of the cyclopentadienyl resonance of (*RS,SR*)-**3c** gave a 2.1% enhancement of the =CHCH_3 resonance (δ 2.54).

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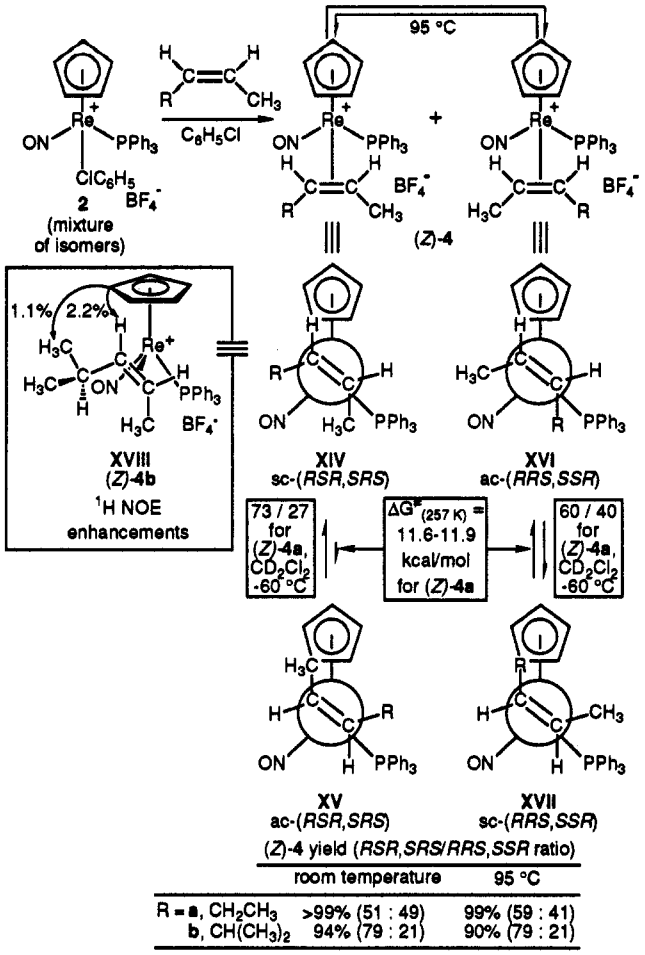
(14) All isomer ratios are normalized to 100, and error limits on each integer are ±2; e.g., 42:58 ≡ (42 ± 2):(58 ± 2). For comparison purposes, ratios involving more than two isomers must sometimes also be expressed with a subset of values normalized to 100. In these cases, the components normalized are italicized.

(15) Alkene complexes of **I** give C=C ^{13}C NMR resonances upfield from those of the free alkenes, but with parallel chemical shift trends.[4b,6,7a] Thus, the upfield C=C resonances of **3a–c** were assigned to the =CH_2 carbons, analogously to the free alkenes and the corresponding monosubstituted alkene complexes.[4b]

(16) These data are illustrated pictorially in the supplementary material.

Scheme 3. Binding of Unsymmetrical *cis*-Alkenes to the Chiral Lewis Acid I



(Z)-4 yield (RSR,SRS/RRS,SSR ratio)

	room temperature	95 °C
R = a, CH_2CH_3	>99% (51 : 49)	99% (59 : 41)
b, $CH(CH_3)_2$	94% (79 : 21)	90% (79 : 21)

However, similar irradiation of (*RR,SS*)-**3c** did not affect the =CHC*H*$_3$ resonance (δ 2.30).[17]

2. Binding of Unsymmetrical *cis*-Alkenes. The reaction of chlorobenzene complex **2** and *cis*-2-pentene (5 equiv) was monitored by ^{31}P NMR. After 1.5 h at room temperature, the alkene complex (*Z*)-[(η^5-C_5H_5)-Re(NO)(PPh_3)(CH_3HC=$CHCH_2CH_3$)]$^+BF_4^-$ ((*Z*)-**4a**) had formed in quantitative yield as a 50:50 mixture of *RSR,SRS*/*RRS,SSR* configurational diastereomers (8.1/8.8 ppm, (**XIV** + **XV**)/(**XVI** + **XVII**), Scheme 3). A similar preparative reaction gave (*Z*)-**4a** in >99% yield as a 51:49 mixture of *RSR,SRS*/*RRS,SSR* diastereomers. The preceding reaction was repeated, but the sample was kept at 95 °C for 48 h. Workup gave (*Z*)-**4a** in 99% yield as a 59:41 *RSR,SRS*/*RRS,SSR* equilibrium mixture, indicating modest enantioface binding selectivity. Reaction of dichloromethane complex **1**, which independently decomposes above −20 °C,[11a] and *cis*-2-pentene gave (*Z*)-**4a** in ca. 72% yield by NMR. Diastereomer configurations were assigned as described below.

Analogous preparative reactions of **2** and *cis*-4-methyl-2-pentene at *either* room temperature or 95 °C gave (*Z*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3HC=$CHCH(CH_3)_2$)]$^+$-BF_4^- ((*Z*)-**4b**) in 90–94% yields as 79:21 mixtures of *RSR,SRS*/*RRS,SSR* diastereomers (Scheme 3). Chromatography gave some fractions that contained 87:13 *RSR,SRS*/*RRS,SSR* mixtures, showing that the diastereomers do not readily interconvert at room temperature. Thus, the kinetic and thermodynamic enantioface binding selectivities are fortuitously equal.

Complexes (*Z*)-**4a,b** were characterized similarly to **3a–c**. Some ^{1}H and ^{13}C NMR peaks of (*Z*)-**4a** were broad at room temperature. Hence, these spectra were recorded at 59 °C. Decoupling experiments (Experimental Section) confirmed the ^{1}H assignments. The C=*C*HCH$_3$ ^{13}C resonances of the major *RSR,SRS* diastereomers gave detectable phosphorus couplings ($^2J_{CP}$ = 3.3–4.8 Hz, $w_{1/2}$ = 9.0–11.7 Hz),[18] but the *C*=CHCH$_3$ resonances did not (s, $w_{1/2}$ = 5.7–6.8 Hz). This indicates that *sc* Re—(C=*C*) conformers, in which the smaller =CHCH$_3$ termini are *syn* to the PPh_3 ligand (**XIV**), dominate in solution.

The Re—(C=*C*) conformation of the *RSR,SRS* diastereomer of (*Z*)-**4b** was also probed in a ^{1}H difference NOE experiment.[12] As depicted in **XVIII** (Scheme 3), irradiation of the cyclopentadienyl resonance gave a 2.2% enhancement in the =C*H*CH(CH$_3$)$_2$ resonance, consistent with a *sc* conformer. The downfield isopropyl methyl resonance also showed an enhancement, but the =C*H*C*H*$_3$ resonances did not. Importantly, neither Re—(C=*C*) conformer of the *RRS,SSR* diastereomer (**XVI**/**XVII**) should give an enhanced =C*H*CH(CH$_3$)$_2$ resonance. Hence, the NOE data also confirm the diastereomer assignment. Finally, the C=C ^{13}C resonances of the *RRS,SSR* diastereomers did not give detectable phosphorus couplings, and the peak widths varied only slightly ($w_{1/2}$ (Hz): (*Z*)-**4a**, 5.9 (=*C*HCH$_3$), 6.9 (=*C*HCH$_2$CH$_3$); (*Z*)-**4b**, 7.3 (=*C*HCH(CH$_3$)$_2$), 8.7 (=*C*HCH$_3$)). This suggests that appreciable amounts of both conformers are present.[19]

A ^{1}H NMR spectrum of (*Z*)-**4a** was recorded at −60 °C in CD_2Cl_2. Each diastereomer now exhibited two Re—(C=*C*) conformers. The major *RSR,SRS* diastereomer gave a 73:27 (*sc*/*ac*) (**XIV**/**XV**) mixture, as assigned from the =CHC*H*$_3$ resonance chemical shift pattern in **IX** (δ 1.70/2.34, $\Delta\nu$ = 192.7 Hz), in accord with the trend in C=C ^{13}C resonance $^2J_{CP}$ values noted above.[16] The minor *RRS,SSR* diastereomer gave a 60:40 *ac*/*sc* (**XVI**/**XVII**) mixture, as assigned from the =CHC*H*$_3$ resonance chemical shifts (δ 2.10/0.67, $\Delta\nu$ = 428.8 Hz), in accord with the slight trend in C=C ^{13}C resonance $w_{1/2}$ values.[19] Further, the relative chemical shifts of all four =CHC*H*$_3$ resonances were in agreement with the diastereomer assignments. These data also indicate a 43:16:25:16 *sc-RSR,SRS*/*ac-RSR,SRS*/*ac-RRS,SSR*/*sc-RRS,SSR* (**XIV**/**XV**/**XVI**/**XVII**) equilibrium ratio, provided that the 59:41 *RSR,SRS*/*RRS,SSR* equilibrium value determined at 95 °C is maintained at −60 °C.

When the −60 °C CD_2Cl_2 solutions of (*Z*)-**4a** were warmed, the *sc*/*ac* =CHC*H*$_3$ ^{1}H resonances of each diastereomer broadened, shifted, and then coalesced at −16 °C (T_c = 257 K). Standard analyses gave $\Delta G^*(T_c)$ values of 11.9 (*RSR,SRS*) and 11.6 (*RRS,SSR*) kcal/mol for the conversions of the minor to major conformers.[20]

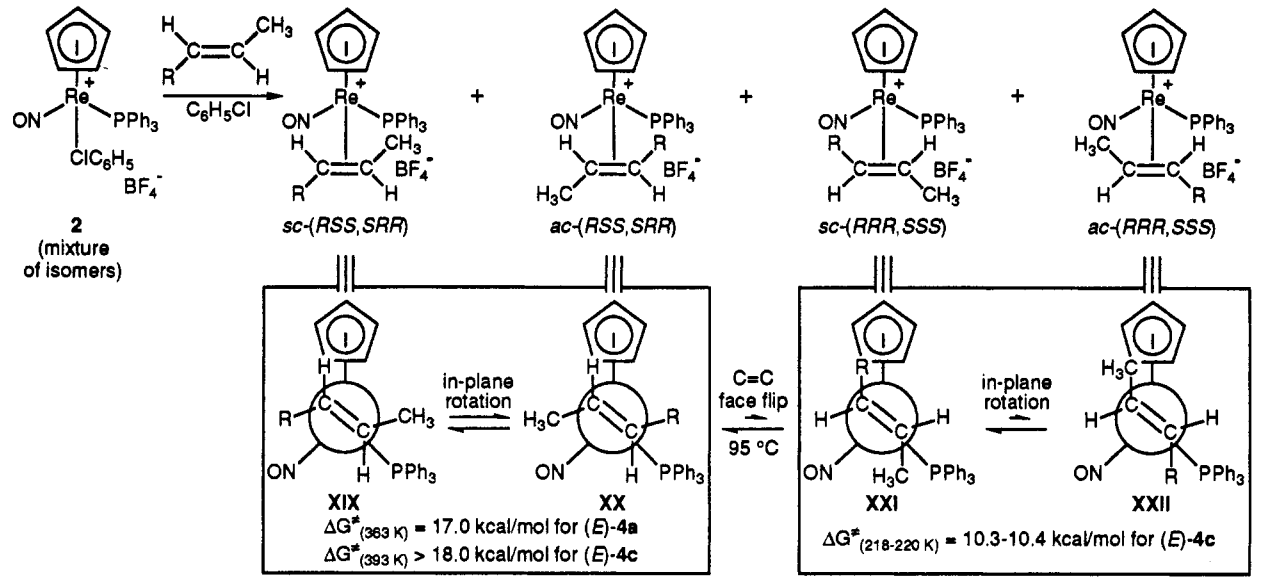
(17) Upon irradiation of the cyclopentadienyl ^{1}H resonances, most complexes of **I** show 0.2–0.5% enhancements of the PPh_3 *ortho* proton resonances. Thus, any enhancement of the overlapping =CPh resonances of (*RR,SS*)-**3c** could not be quantified.

(18) The C=C ^{13}C resonances of the *cis*-2-butene complex of **I** (53, 50 ppm) are 5–6 ppm upfield from those of the *cis*-3-hexene complex of **I** (58, 56 ppm),[5b] similar to the case for the free alkenes.[15] Thus, the upfield C=C resonances of (*Z*)-**4a,b** were assigned to the =CHCH$_3$ carbons. This was confirmed for both diastereomers of (*Z*)-**4b** by ^{13}C NMR spectra acquired with single-frequency ^{1}H decoupling (Experimental Section).

(19) In the absence of other effects, the broader resonance would correspond to the =CHR terminus with the greater probability of being *syn* to the PPh_3 ligand.

(20) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; Chapters 6 and 7. All $\Delta G^*(T_c)$ calculations utilized equation 6.5c.

Scheme 4. Binding of Unsymmetrical *trans*-Alkenes to the Chiral Lewis Acid I



	(*E*)-4 yield (XIX : XX / XXI : XXII ratio)	
	room temperature	95 °C
R = **a**, CH_2CH_3	97% (33 : 26 / 31 : 10)[a]	96% (64 : 35 / 1 : <1)[a]
b, $CH(CH_3)_2$	85% (>99 : <1 / <1 : <1)	92% (>99 : <1 / <1 : <1)
c, C_6H_5	92% (27 : 32 / 28 : 13)[b]	89% (45 : 55 / <1 : <1)

[a] Some (*Z*)-**4a** is present; see text for details. [b] From −65 °C ^{31}P NMR data: resonances of *sc-RRR,SSS* and *ac-RRR,SSS* isomers coalesce above −33 °C.

Thus, the barriers for 180° rotations about the Re—(C=C) axes are between those of the *cis*-2-butene complex of **I** (11.0–11.1 kcal/mol) and the *cis*-3-hexene complex of **I** (12.6–12.8 kcal/mol).[5b]

When ^1H NMR spectra of (*Z*)-**4b** were recorded in CD_2Cl_2 between −80 and +40 °C, no decoalescence was detected. However, the chemical shifts of *some* resonances of each diastereomer were strongly temperature dependent.[21] We suggest, on the basis of the above NOE data, that only the *sc* conformer of the major *RSR,SRS* diastereomer (**XIV**) is present in any appreciable amount in solution. From steric considerations, a much greater **XIV**/**XV** ratio would be expected for (*Z*)-**4b** than (*Z*)-**4a**. With the minor *RRS,SSR* diastereomer, the marked upfield shift of the =CHCH_3 resonance, particularly at lower temperature (δ 0.83, 20 °C; δ 0.47, −80 °C),[21] suggests that the *sc* conformer **XVII** dominates—in contrast to the comparable *sc*/*ac* populations implied by the $w_{1/2}$ values of the C=C ^{13}C resonances.[19] Since we were unable to obtain samples that contained more than 21% of the *RRS,SSR* diastereomer, we could not probe this equilibrium in greater detail.

3. Binding of Unsymmetrical *trans*-Alkenes. The chlorobenzene complex **2** and *trans*-2-pentene (10 equiv) were combined in an NMR tube. Reaction was complete within 5 h at room temperature to give (*E*)-**4a** as a 38:21:41 mixture of *sc-RSS,SRR*/*ac-RSS,SRR*/*RRR,SSS* diasteromers, as assayed by ^{31}P NMR (7.7/7.8/7.0 ppm, **XIX**/**XX**/(**XXI** + **XXII**); Scheme 4).[22] Rationales for these assignments are given below. Also, ca. 16% of the *cis*-2-pentene complex (*Z*)-**4a** was present. Accordingly, a ^{13}C NMR spectrum showed that the free alkene was a (98–99):(2–1) *trans*/*cis* mixture. An analogous phenomenon was observed in reactions of **2** and *trans*-2-butene and was attributed to the greater nucleophilicity of the *cis*-alkene isomer.[5b] Interestingly, the corresponding reaction of **2** and *trans*-3-hexene required days to go to completion.[5b]

A preparative reaction of **2** and *trans*-2-pentene gave a 97% yield of a material that consisted of a 33:26:31:10 mixture of *sc-RSS,SRR*/*ac-RSS,SRR*/*sc-RRR,SSS*/*ac-RRR,SSS* diastereomers of (*E*)-**4a** (81%) and a 40:60 mixture of *RSR,SRS*/*RRS,SSR* diastereomers of (*Z*)-**4a** (19%). An analogous reaction at 95 °C (48 h) gave a 96% yield of a material that consisted of a 64:35:1 mixture of *sc-RSS,SRR*/*ac-RSS,SRR*/*sc-RRR,SSS* diastereomers of (*E*)-**4a** (94%) and a 60:40 mixture of *RSR,SRS*/*RRS,SSR* diastereomers of (*Z*)-**4a** (6%). This established a high enantioface binding selectivity (99:1 *RSS,SRR*/*RRR,SSS*) but only a slight thermodynamic preference for the *sc* conformer of the *RSS,SRR* diastereomer (64:35 or *65:35*[14] **XIX**/**XX**). The similarity to the data for symmetrical *trans*-alkene complexes in Scheme 1 (**VII**/**VIII**) provided the primary basis for assigning configurations.

As with (*Z*)-**4a**, the *sc*/*ac* conformers of (*E*)-**4a** were assigned from the =CHCH_3 ^1H NMR shielding trends shown in **IX**. Accordingly, for the more stable *RSS,SRR* diastereomer, the =CHCH_3 resonance of the *sc* conformer was upfield from that of the *ac* conformer (δ 1.35/2.11, **XIX**/**XX**). Similarly, for the less stable *RRR,SSS* diastereomer, the =CHCH_3 resonance of the *sc* conformer was upfield of that of the *ac* conformer (δ 1.87/2.19, **XXI**/**XXII**).[16] The relative chemical shifts of all four =CHCH_3 resonances were in agreement with the diastereomer assignments.

A C_6D_5Cl solution of (*E*)-**4a** was warmed in an NMR probe. The =CHCH_3 ^1H resonances of the *sc*/*ac* conformers of the *RSS,SRR* diastereomer (20 °C: δ 1.47, 2.20,

(21) Selected data (δ, CD_2Cl_2, 20/0/−30/−50/−80 °C): *RSR,SRS*, =C*H*CH_3 2.82/2.74/2.64/2.58/2.45, =C*H*$CH(CH_3)_2$ 4.31/4.27/4.22/4.19/4.15, =$CHCH_3$ 1.86/1.86/1.85/1.85/1.84; *RRS,SSR*, =$CHCH_3$ 4.16/4.11/4.07/4.04/3.99, =C*H*$CH(CH_3)_2$ 3.27/3.26/3.25/3.25/3.24, =CHCH_3 0.83/0.74/0.64/0.57/0.47.

(22) The ^{31}P NMR chemical shifts of the *sc*/*ac* conformers of the *RRR,SSS* diastereomer of (*E*)-**4a** are identical in C_6H_5Cl.

72:28; $\Delta\nu$ = 219.9 Hz) broadened and then coalesced at 90 °C (T_c = 363 K). This gave a $\Delta G^{\ddagger}(T_c)$ value of 17.0 kcal/mol for the conversion of the *ac* to the *sc* conformer.[20] Thus, the barrier for a 180° rotation about the Re—(C⁻⁻C) axis is comparable to that for the corresponding *trans*-2-butene complex (18.6 kcal/mol).[5b] However, the conformers of the *RRR,SSS* diastereomer isomerized to the *RSS,SRR* diastereomer prior to any coalescence. Nonetheless, on the basis of previous work[5b] and new data below, the rotational barrier should be much lower. Hence, the *sc*/*ac* ratios obtained at room temperature (31:10 or 76:24)[14] can be taken as equilibrium values.

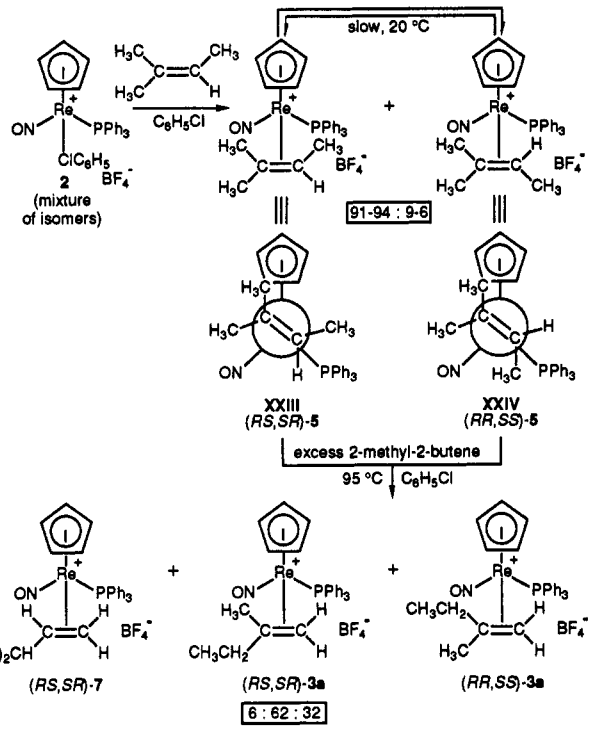
Reactions of **2** and the bulkier alkene *trans*-4-methyl-2-pentene at either room temperature or 95 °C gave only the *sc* conformer of the *RSS,SRR* diastereomer of (*E*)-**4b** (85–92%; Scheme 4). No other isomers could be detected in the crude reaction mixtures by ^{31}P or ^{1}H NMR. The *RSS,SRR* diastereomer of (*E*)-**4b** should give a much higher *sc*/*ac* equilibrium ratio than (*E*)-**4a**, as the *ac* conformer would direct an isopropyl-substituted C=C terminus *syn* to the PPh_3 ligand. As expected, the $=CHCH_3$ ^{13}C resonance of (*E*)-**4b** gave a larger $^2J_{CP}$ value (5.1 Hz, $w_{1/2}$ = 10.5 Hz) than the $=CHCH(CH_3)_2$ resonance (s, $w_{1/2}$ = 6.6 Hz).

The data for α-methylstyrene complex **3c** in Scheme 2 suggest that a phenyl group can have a smaller effective size than a methyl group. We wondered if similar phenomena might occur with isomeric alkenes. Thus, **2** and *trans*-β-methylstyrene were reacted at room temperature (Scheme 4). Workup gave the alkene complex (*E*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3HC{=}CHC_6H_5)]^+BF_4^-$ ((*E*)-**4c**, 92%) as a 27:32:41 mixture of *sc-RSS,SRR*/*ac-RSS,SRR*/*RRR,SSS* diastereomers (**XIX**/**XX**/(**XXI** + **XXII**)). A similar reaction at 95 °C (12 h) gave only the more stable *RSS,SRR* diastereomer (89%) as a 45:55 equilibrium mixture of *sc*/*ac* conformers.

The *sc*/*ac* assignment was made as described for other compounds above. First, the $=CHCH_3$ ^{1}H resonance of the *sc* conformer was upfield from that of the *ac* conformer (δ 1.62/2.36 **XIX**/**XX**), as expected from the trends in **IX**. Second, the $=CHCH_3$ ^{13}C resonance of the *sc* conformer was coupled to phosphorus ($^2J_{CP}$ = 4.7 Hz, $w_{1/2}$ = 10.5 Hz), but the =CHPh resonance was not (s, $w_{1/2}$ = 6.6 Hz). Conversely, the =CHPh resonance of the *ac* conformer was coupled to phosphorus ($^2J_{CP}$ = 3.4 Hz, $w_{1/2}$ = 9.6 Hz), but the $=CHCH_3$ resonance was not (s, $w_{1/2}$ = 6.4 Hz). Thus, the phenyl group of *trans*-β-methylstyrene is slightly better accommodated in the more congested position c than the methyl group.

The less stable *RRR,SSS* diastereomer of (*E*)-**4c** was isolated by chromatography and gave only one set of ^{1}H, ^{13}C, and ^{31}P NMR resonances at room temperature. Both C=C ^{13}C resonances were broad singlets ($w_{1/2}$ = 9.0–9.1 Hz). When a $CDCl_3$ solution was cooled to −65 °C, two ^{31}P resonances were observed (68:32; 7.5, 4.7 ppm). When a CD_2Cl_2 solution was cooled to −80 °C, two $=CHCH_3$ (71:29; δ 1.80, 2.08; $\Delta\nu$ = 79.7 Hz) and cyclopentadienyl (71:29; δ 5.18, 5.67; $\Delta\nu$ = 147.0 Hz) ^{1}H resonances were observed. These were assigned to *sc* (**XXI**, major) and *ac* (**XXII**, minor) conformers on the basis of the $=CHCH_3$ *and* cyclopentadienyl ^{1}H chemical shifts. As noted for **3c** and other complexes above, the cyclopentadienyl ^{1}H resonance moves upfield to δ 5.14–5.22 when a phenyl group occupies position b. Thus, the methyl group of *trans*-β-methylstyrene is more readily accommodated in the highly congested position d than the phenyl group.[23]

Scheme 5. Binding of 2-Methyl-2-butene to the Chiral Lewis Acid I



The *sc*/*ac* $=CHCH_3$ and cyclopentadienyl ^{1}H resonances of the *RRR,SSS* diastereomer coalesced upon warming to −55 °C (218 K) and −53 °C (220 K), respectively. This gave $\Delta G^{\ddagger}(T_c)$ values of 10.4–10.3 kcal/mol for the conversion of the *ac* to the *sc* conformer. Thus, the barrier to a 180° rotation about the Re—(C⁻⁻C) axis is comparable to that of the *RRR,SSS* diastereomer of the stilbene complex of **I** (11.6 kcal/mol).[5b] However, the *sc*/*ac* ^{31}P resonances of the more stable *RSS,SRR* diastereomer did not coalesce at 120 °C (4.3, 7.7 ppm, $CDCl_2CDCl_2$; $\Delta\nu$ = 410.1 Hz), at which temperature decomposition began. These data give a $\Delta G^{\ddagger}$(393 K) value of >18.0 kcal/mol, also paralleling the corresponding stilbene complex (>17.6 kcal/mol).[5b]

4. Binding of a Trisubstituted Alkene. The chlorobenzene complex **2** and 2-methyl-2-butene (10 equiv) were combined in an NMR tube at −45 °C (Scheme 5). The sample was gradually warmed, and ^{31}P NMR spectra were recorded. The trisubstituted alkene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3HC{=}C(CH_3)_2)]^+BF_4^-$ (**5**) began to slowly form at −25 °C as a mixture of *RS,SR*/*RR,SS* diastereomers (6.2/6.6 ppm, **XXIII**/**XXIV**), together with another alkene complex **6** that was assumed to arise from a contaminant in the 2-methyl-2-butene (8.6 ppm).[24] The sample was kept at 20 °C for an extended period. After 6 h, the NMR yield of **5** reached 49% (area percent of all

(23) When the $=CHCH_3$ ^{1}H NMR chemical shifts of the four isomeric β-methylstyrene complexes are measured under identical conditions, the shielding trends for positions a and b (**IX**) are reversed.[16] Other chemical shift patterns are sometimes switched in aryl-substituted alkene complexes of **I**. These are logically attributed to diamagnetic anisotropy effects, as evidenced by the upfield shifts in cyclopentadienyl ^{1}H resonances when phenyl groups occupy position b.

(24) On the basis of ^{1}H NMR data (Experimental Section), **6** was assigned as the 2,3-dimethyl-1-butene complex (*RS,SR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}C(CH_3)CH(CH_3)_2)]^+BF_4^-$. We could not detect commensurate quantities of any C_6 alkenes in the 2-methyl-2-butene by NMR or GC/MS. A FAB mass spectrum of the **5**/**6** mixture showed parent ions for each cation. The mechanism of formation of **6** is under investigation.

^{31}P resonances) and remained at 47–57% through 336 h. However, the *RS,SR*/*RR,SS* ratio, which was 64:36 after 6 h, continued to rise and reached 94:6 after 336 h (15 min, 58:42, 22%; 6 h, 64:36, 49%; 12 h, 68:32, 52%; 24 h, 71:29, 54%; 50 h, 82:18, 57%; 80 h, 87:13, 56%; 128 h, 89:11, 51%; 264 h, 93:7, 47%; 336 h, 94:6, 47%). The yield of **6** increased to 17% over 24 h and then remained at 17–19% (15 min, 1%; 6 h, 11%; 12 h, 12%; 24 h, 17%; 50 h, 18%; 80 h, 19%; 128 h, 17%; 264 h, 17%; 336 h, 19%).

The previous reaction was repeated. Workup after 12 h gave a 65:15:20 or *81:19*:25[14] (*RS,SR*)-**5**/(*RR,SS*)-**5**/**6** mixture in 75% yield. The diastereomers of **5** were assigned primarily on the basis of the anticipated stability order. The $=CHCH_3$ ^1H resonance of (*RS,SR*)-**5** (δ 3.18) was downfield from that of (*RR,SS*)-**5** (δ 3.06), consistent with the pattern for the =CHH′ resonances of **3a,b**.[16] However, the $^3J_{HP}$ values (9.4 vs 8.6 Hz) did not differ as much as with the =CHH′ resonances of **3a,b** (12.4–13.2 vs 5.4–6.3 Hz). Complexes (*RS,SR*)-**5** and (*RR,SS*)-**5** also gave similar $=CHCH_3$ ^1H chemical shifts (δ 1.59, 1.58) and very broad $=CHCH_3$ ^{13}C resonances (s, $w_{1/2}$ 21.6, 13.2 Hz).

A portion of the preceding sample was dissolved in $CDCl_3$ and stored in a freezer. After 240 h, a 70:7:23 or *91:9*:30 (*RS,SR*)-**5**/(*RR,SS*)-**5**/**6** mixture had formed, as measured by ^{31}P NMR. No significant amounts of other species were detected. A second portion was dissolved in chlorobenzene and kept at room temperature. After 64 h, a 72:8:20 or *91:9*:25 (*RS,SR*)-**5**/(*RR,SS*)-**5**/**6** mixture had formed. Two decomposition products were also present (15.7/15.5 ppm, 24:76; 17%). A third portion was dissolved in chlorobenzene and kept at 95 °C. After 24 h, a multitude of products had formed. Thus, although several factors complicate the preceding attempts to equilibrate (*RS,SR*)-**5** and (*RR,SS*)-**5**, the equilibrium ratio can be confidently bounded as (91–94):(9–6).

Complex **2** and 2-methyl-2-butene (10 equiv) were reacted in an NMR tube at −45 °C and then room temperature (8 h) to give a 51:28:21 (*RS,SR*)-**5**/(*RR,SS*)-**5**/**6** mixture (60% combined NMR yield). The sample was kept at 95 °C and monitored by ^{31}P NMR. Over the course of 12 h, **5** (and essentially all byproducts) disappeared as the 2-methyl-1-butene complexes (*RS,SR*)-**3a** and (*RR,SS*)-**3a** appeared (Scheme 5). Integration indicated a 56:25:19 (*RS,SR*)-**3a**/(*RR,SS*)-**3a**/**6** mixture (>90% combined yield). After 36 h total, the proportion of **6** had decreased. The previously characterized 3-methyl-1-butene complex (*RS,SR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH(CH_3)_2)]^+BF_4^-$ ((*RS,SR*)-**7**)[4c] and an unidentified species (7.2 ppm) were detected. Workup gave a 56:29:5:11 or *62:32:6*:12 mixture of (*RS,SR*)-**3a**, (*RR,SS*)-**3a**, (*RS,SR*)-**7**, and the unidentified species in 73% yield. Thus, when **5** is thermolyzed in the presence of excess 2-methyl-2-butene (and possibly small amounts of $HBF_4{\cdot}OEt_2$ remaining from the generation of **2**), complexes of isomeric alkenes form.

Finally, similar NMR experiments were conducted with **2** and the tetrasubstituted alkene 2,3-dimethyl-2-butene (10 equiv). No evidence was observed for the formation of any significant quantity of the target complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)((CH_3)_2C{=}C(CH_3)_2)]^+BF_4^-$ by ^{31}P or ^1H NMR. A preparative reaction mixture was then kept at 95 °C for 6 h. Workup gave chiefly the C_6 alkene complex **6** that was a byproduct in the synthesis of **5** (84% crude yield).[24] Further details of these isomerization processes, which complicate access to polysubstituted alkene complexes of **I**, will be reported at a later date.

Discussion

1. Background Considerations. Numerous binding phenomena involving prochiral alkenes and the chiral rhenium Lewis acid **I** are described above. Several aspects merit discussion prior to analysis of the thermodynamic binding selectivities. First, note that most of the alkenes give kinetic enantioface binding selectivities that are lower than the thermodynamic enantioface binding selectivities. The rhenium and carbon stereocenters should be much closer in the complexes than in the progenitor transition states. Consequently, the energy differences between diastereomeric transition states should be less than those between the diastereomeric complexes, leading to lower kinetic binding selectivities. However, *trans*-4-methyl-2-pentene gives only the *RSS,SRR* diastereomer of (*E*)-**4b** at both room temperature and 95 °C (Scheme 4). Similarly, the isomeric *cis*-4-methyl-2-pentene gives a 79:21 mixture of *RSR,SRS*/*RRS,SSR* diastereomers of (*Z*)-**4b** under all conditions (Scheme 3). These bulkier, isopropyl-substituted alkenes would logically have later, more productlike transition states. Also, a recent mechanistic study has shown that dichloromethane complex **1** and ketones react predominantly by *associative* mechanisms.[25] Thus, the Lewis acid **I** is not likely an intermediate in the preceding reactions.

As established in earlier reports,[4,5b,6,7] diastereomeric monosubstituted and disubstituted alkene complexes of **I** generally equilibrate with little or no decomposition in chlorohydrocarbon solvents at or below 100 °C. This is reflected in the present work by the absence of detectable byproducts in NMR experiments and high isolated yields for most of the thermolyses in Schemes 2–4. Hence, equilibrium ratios are not artificially enhanced by the selective destruction of one diastereomer. However, the 2-methyl-2-butene complex **5** (Scheme 5) is much more labile. Thus, equilibrium measurements involving diastereomeric trisubstituted alkene complexes of **I** require extended periods under carefully controlled conditions at or below room temperature.

All solvents investigated to date give identical alkene enantioface binding selectivities, within experimental error.[14] Chlorobenzene has been utilized in most experiments. However, some alkene complexes of **I** are very sparingly soluble in chlorobenzene. In these cases, the more polar solvents 1,2-dichloroethane and 1,1,2,2-tetrachloroethane have also been employed. Alkene complexes of **I** are not soluble in ethers and alkanes and often decompose when diastereomer equilibrations are attempted in more polar solvents. Valid data can be acquired in acetone or acetonitrile, provided that conditions are closely monitored to avoid substitution.[4c]

As shown in Scheme 1, the Re—(C=C) conformers of the *cis*-2-butene complex of **I** (**V**/**VI**) exhibit different equilibrium ratios in $CDCl_3$ (84:16) and CD_2Cl_2 (70:30).[5b] A comparable solvent effect upon another conformational equilibrium is shown in Scheme 6. Hence, if solvent can appreciably affect conformational equilibria that involve positions of C=C substitutents, it would logically follow that solvent can affect configurational equilibria that involve positions of C=C substituents. Thus, it is possible

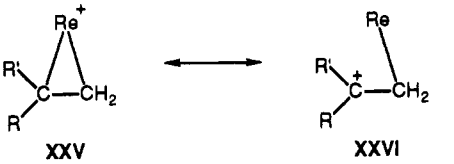
(25) Dewey, M. A.; Zhou, Y.; Liu, Y.; Gladysz, J. A. *Organometallics* **1993**, *12*, 3924.

that examples of the latter phenomenon will found in the future—although as noted above, none have been observed to date.

The potential temperature dependence of configurational and conformational equilibria is also an important issue. For all disubstituted alkene complexes of **I**, configurational equilibria have been established at 95 °C. In many cases, diastereomer ratios have been measured *both* at 95 °C and after the samples were cooled to room temperature. Diastereomer ratios have also been monitored as samples were slowly cooled. In all cases, diastereomer ratios are identical within experimental error. However, enantioface binding selectivities of π aromatic aldehyde complexes of **I** do show modest temperature effects.[26] Furthermore, we sometimes compare configurational equilibria determined above room temperature with conformational equilibria determined below room temperature. While this is unlikely to affect any of the qualitative conclusions of this study, there is the potential for overinterpretation of certain data.

Although the C=C substituent positions a–d diagrammed in the idealized structure **II** (Scheme 1) are useful for reference, it should be emphasized that they are not spatially invariant. For example, in the seven crystal structures published to date,[4b,c,5,6,7a] the angles of the Re—(C=C) planes with the Re—P bonds range from 8.8 to 22.6°, as opposed to the 0° in **II**. In each case, the alkene ligand is rotated counterclockwise from that in **II**. We also suspect that differences in the $^3J_{HP}$ values of =CH ^{1}H NMR resonances, several of which were noted above, arise from slight differences in P—Re—C—H conformations in solution. This degree of freedom, as well as those associated with the PPh_3 ligand,[27] potentially complicates any attempt to parameterize our equilibrium data based upon simple additive C=C substituent effects.

2. Thermodynamic Binding Selectivities. To a first approximation, the thermodynamic enantioface binding selectivities of monosubstituted alkene complexes of **I** (**III/IV**, Scheme 1) and geminally disubstituted alkene complexes **3** (**X/XI**, Scheme 2) should be a function of the relative sizes of the C=C substituents that occupy positions a (least congested) and b. Thus, all monosubstituted alkenes give high binding selectivities (H vs R). Furthermore, 3-methyl-1-butene, which has a branched isopropyl substituent, gives a higher **III/IV** equilibrium ratio than propene and 1-pentene, which have unbranched substituents (Scheme 1).[4c] However, the corresponding substituents in 2-methyl-1-butene and 2-methyl-1-pentene are much closer in size (CH_3 vs $CH_2CH_3/CH_2CH_2CH_3$). Hence, the binding selectivities of **3a,b** are lower ((68–70):(32–30) **X/XI**). There is also a possible contributing electronic factor. The two geminal C=C substituents in **3** should enhance structural contributions from resonance forms with positive charges localized on the CRR′ carbons (**XXVI**, eq i). This should increase the distances between rhenium and carbon stereocenters ("slippage"),[28] diminishing energy differences between diastereomers.



(i)

Interestingly, α-methylstyrene shows an enantioface binding selectivity (36:64 **IX/X**) *opposite* to those of the geminally methyl/alkyl disubstituted alkenes. Any slippage should be nearly equal in the two diastereomers. Thus, the phenyl group exhibits a smaller effective size than the methyl group. As summarized in Scheme 1, styrene and the terminal C=C linkage of *trans*-piperylene also give lower enantioface binding selectivities (90:10 **III/IV**) than aliphatic analogs.[4c,7a] Hence, the effective sizes of sp^2-hybridized C=C substitutents, in which the "allylic" carbon bears only two attached groups, can be smaller than those of alkyl groups—even methyl. Other equilibria have been reported in which phenyl groups have smaller effective sizes than methyl groups ("small phenyl effect").[29] However, such phenomena are strongly substrate dependent and must be extrapolated conservatively. For example, alkenes with formyl or acyl C=C substituents, such as acrolein, methyl vinyl ketone, and ethyl vinyl ketone, give higher enantioface binding selectivities (≥94:6 **III/IV**).[6]

The unsymmetrical *trans*-alkene complexes (*E*)-**4** all show high thermodynamic enantioface binding selectivities (≥99:≤1 (**XIX + XX**)/(**XXI + XXII**), Scheme 4), similar to the symmetrical analogs (**VII/VIII**, Scheme 1). However, now Re—(C=C) conformers are possible in each series of configurational diastereomers. The *sc/ac* equilibrium ratio for the less stable *RRR,SSS* diastereomer of *trans*-2-pentene complex (*E*)-**4a** (31:10 or *76:24*[14] **XXI/XXII**) follows from the relative sizes of the ethyl and methyl substituents and the steric environments of positions b and d (most congested). The *sc/ac* ratio for the *RRR,SSS* diastereomer of *trans*-β-methylstyrene complex (*E*)-**4c** (28:13 or *71:29* **XXI/XXII**) favors the conformer with the methyl group in the crowded position d and the phenyl group in position b. Thus, this complex does not exhibit a small phenyl effect.

The *sc/ac* ratio for the more stable *RSS,SRR* diastereomer of *trans*-2-pentene complex (*E*)-**4a** increases from 33:26 (**XIX/XX**, Scheme 4) or *56:44*[14] to 65:35 after heating at 95 °C. We presume that the latter represents the equilibrium value. The direction of equilibrium again follows from the relative sizes of the ethyl and methyl substituents and the steric environments of positions a (least congested) and c. The slightly lower ratio compared to that of the *RRR,SSS* diastereomer (65:35 vs 76:24) suggests that the steric environments of positions a and c differ less than those of b and d.

When the ethyl group in the *RSS,SRR* diastereomer of (*E*)-**4a** is replaced by the bulkier isopropyl group, the *sc/ac* equilibrium ratio increases from 65:35 to >99:<1 ((*E*)-**4b**, Scheme 4). However, when the ethyl group is replaced by a phenyl group, the *sc/ac* ratio *reverses* to 45:55 ((*E*)-**4c**, Scheme 4)—indicating that the phenyl group has a slightly smaller effective size than the methyl group. A complex of **I** and another unsymmetrical *trans*-alkene, 4-hexen-5-one, has also been characterized.[6] As shown in Scheme 6, the *RSS,SRR* diastereomer similarly gave a "reversed", 29:71 *sc/ac* (**XXVII/XXVIII**) ratio. This

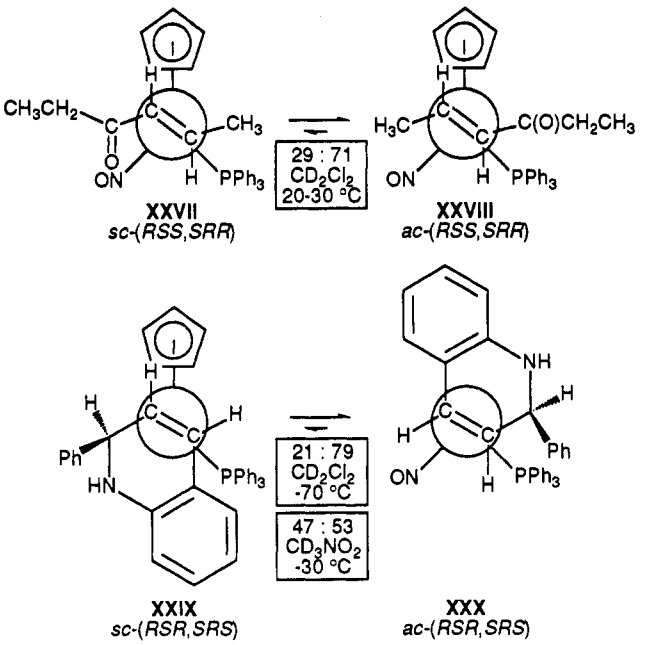
(26) (a) Quirós Méndez, N.; Mayne, C. L.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1475. (b) Boone, B. J.; Klein, D. P.; Seyler, J. W.; Quirós Méndez, N.; Arif, A. M.; Gladysz, J. A. Manuscript in preparation.

(27) (a) Garner, S. E.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1993**, *553*. (b) Davies, S. G.; Derome, A. E.; McNally, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2854. (c) Brunner, H.; Hammer, B.; Krüger, C.; Angermund, K.; Bernal, I. *Organometallics* **1985**, *4*, 1063.

(28) (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308. (b) Cameron, A. D.; Smith, V. H., Jr.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1988**, 1037.

(29) Eliel, E. L.; Manoharan, M. *J. Org. Chem.* **1981**, *46*, 1959.

Scheme 6. Other Unsymmetrical *trans*- and *cis*-Alkene Complexes of I



XXVII *sc*-(*RSS,SRR*) **XXVIII** *ac*-(*RSS,SRR*)

XXIX *sc*-(*RSR,SRS*) **XXX** *ac*-(*RSR,SRS*)

indicates that the sp^2-hybridized acyl C=C substituent has a smaller effective size than the methyl substituent.

The unsymmetrical *cis*-alkene complexes investigated do not give high thermodynamic enantioface binding selectivities (Scheme 3). However, analyses of the conformational equilibria are instructive. First, the more stable *RSR,SRS* diastereomer of the *cis*-2-pentene complex (*Z*)-**4a** gives an *sc*/*ac* equilibrium ratio (73:27 **XIV**/**XV**) slightly greater than the **V**/**VI** ratio of the *cis*-2-butene complex of **I** *when measured in the same solvent* (70:30, Scheme 1). Conversely, the less stable *RRS,SSR* diastereomer gives an *ac*/*sc* ratio (60:40 **XVI**/**XVII**) lower than the **V**/**VI** ratio of the *cis*-2-butene complex. These perturbations follow logically from the relative sizes of the ethyl and methyl substituents, and the positions occupied by the ethyl group in **XIV**/**XV** (a vs c) and **XVI**/**XVII** (d vs b).

The more stable *RSR,SRS* diastereomer of the *cis*-4-methyl-2-pentene complex (*Z*)-**4b** appears to give a much higher *sc*/*ac* (**XIV**/**XV**) equilibrium ratio, consistent with the preceding analysis and the greater size difference of the isopropyl and methyl substituents. However, we were unable to conclusively identify the dominant conformer of the less stable *RRS,SSR* diastereomer. Nonetheless, we suggest that the *ac*/*sc* (**XVI**/**XVII**) equilibrium ratio is less than unity—as would be expected when the size difference of the *cis* substituents becomes sufficiently large. Accordingly, the related heterocyclic *cis*-alkene complex partially sketched in Scheme 6 gives a 21:79 **XXIX**/**XXX** ratio in CD_2Cl_2 at −70 °C, as determined by crystallography and from NMR data.[30]

The **XIV**/**XV**/**XVI**/**XVII** equilibrium ratio for (*Z*)-**4a**, 43:16:25:16, is formulated from data at markedly different temperatures and must be viewed as provisional. Nonetheless, several comparisons can be attempted. First, the **XIV**/**XVI** ratio, 43:25 or *63:37*,[14] should reflect the thermodynamic partitioning of methyl and ethyl groups between positions a and d. The **XV**/**XVII** ratio, 16:16 or *50:50*, would be an analogous measure for positions b and c.[31] The **XIX**/**XX** and **XXI**/**XXII** ratios for (*E*)-**4a** (65:35 and 76:24; derived from Scheme 4) similarly compare positions a and c, and b and d. Finally, the **X**/**XI** ratio for **3a** (68:32, Scheme 2) gives the partitioning for positions a and b. Obviously, the preceding data (especially the **XIV**/**XVI** ratio) are *not* internally consistent—a feature we emphasize in the context of the caveats given in the previous section.

The equilibrium ratio for the diastereomeric trisubstituted alkene complexes (*RS,SR*)-**5** and (*RR,SS*)-**5** ((91–94):(9–6) **XXIII**/**XXIV**, Scheme 5) provides a direct measure of the relative steric environments of positions c and d. The difference is comparable to that given by the propene complexes of **I** for positions a and b (96:4 **III**/**IV**, Scheme 1). Thus, high thermodynamic enantioface binding selectivities can be expected for trisubstituted alkene complexes of **I** whenever the size of the *trans* geminal substituent is greater than or equal to that of the *cis* geminal substituent. This allows the larger groups on each C=C terminus to occupy positions a and c.

3. Summary and Prospective. This study of unsymmetrically disubstituted alkene complexes **3** and **4** and trisubstituted alkene complex **5** concludes our investigation of the binding of alkenes to the chiral rhenium Lewis acid **I**. Although more data on alkene complexes of **I** will be accumulated in connection with other research objectives,[30–32] we anticipate that future results will be readily accommodated in the context of the bonding models and analyses given above.

To summarize, we have developed stereoelectronic rationales that account for (1) the high enantioface binding selectivities exhibited by monosubstituted alkenes, (2) the very high enantioface binding selectivities of *trans*-alkenes, (3) the appreciable binding selectivities of symmetrically substituted *cis*-alkenes (a conformational equilibrium), (4) the generally lower enantioface binding selectivities of unsymmetrically substituted *cis*-alkenes and geminally disubstituted alkenes, and (5) the high enantioface binding selectivities of some types of trisubstituted alkenes. Rationales have also been developed, based upon parallel considerations, for the directions of Re—(C=C) conformational equilibria in unsymmetrically substituted alkene complexes.

Some complementary studies in progress merit brief mention. First, enantioface binding selectivities of π aromatic and aliphatic aldehyde complexes of **I** have been measured, and a comprehensive full paper is nearly complete.[26b] Equilibrium ratios are similar to those of the corresponding monosubstituted alkane complexes. Data have also been acquired for alkene complexes of the *pentamethyl*cyclopentadienyl analog of **I**.[32] In these compounds, the steric environments of positions b and d are sometimes reversed. All of these results will be reviewed together in the near future.

We also anticipate that other chiral metal fragments will exhibit alkene binding properties similar to those of **I**. In particular, there should be many other receptors in which the steric environments about one set of geminal positions (a and b in **II**) are less congested than about the other (c and d). At least to some extent, parallel trends should be observed, governed by the relative steric

(30) Stark, G. A.; Arif, A. M., Gladysz, J. A. Manuscript in preparation.

(31) Of all the possible pairs of positions, the steric environments of b and c appear to differ least. A recently prepared ethyl acrylate complex of **I** gives an 86:7:7 *sc*-(*RS,SR*)/*sc*-(*RR,SS*)/*ac*-(*RS,SR*) equilibrium mixture (97 °C, $CHCl_2CHCl_2$)—reflecting the partitioning of a carboethoxy group among positions a, b, and c: Wang, Y. Unpublished results, University of Utah.

(32) Peng, T.-S.; Winter, C. H.; Gladysz, J. A. Submitted for publication to *Inorg. Chem.*

properties of positions a and b and/or positions c and d.[33] Furthermore, it is apparent that alternative environments should more selectively bind certain classes of alkenes. For example, enantioface binding selectivities for unsymmetrical *cis*-alkenes should be higher with receptors for which steric congestion increases in the order a < d ≪ b, c. Indeed, it should be emphasized that there are only a finite number of types of chiral receptors for alkenes based upon steric permutations of positions a–d—a tractable situation for theoretical analysis, and one that is further simplified in receptors with C_2 symmetry (a = c, b = d).[34]

Finally, this study provides the necessary foundation for further investigation of the mechanism by which diastereomeric alkene complexes of **I** interconvert. Results to date for monosubstituted alkene complexes show that the rhenium can migrate from one enantioface to the other *without* dissociation.[4d] In this context, the absence of *Z*/*E* isomerization in thermolyses of the *cis*-/*trans*-alkene complexes **4** (Schemes 3 and 4) is noteworthy. The preceding compounds will enable a variety of tests of the unusual mechanism proposed.[4d] Other novel bond activation processes involving alkene complexes of **I** will also be fully described in future reports.[35]

Experimental Section[36]

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H$_2$C=C(CH$_3$)CH$_2$CH$_3$)]$^+$BF$_4^-$ (3a). A. A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_3$) (**8**; 0.224 g, 0.400 mmol),[37] CH_2Cl_2 (1.5 mL), and a stirbar, and the mixture was cooled to −80 °C. Then HBF_4·OEt_2 (43 μL, 0.40 mmol) was added with stirring. After 30 min, 2-methyl-1-butene (216 μL, 2.00 mmol) was added. The mixture was stirred at −80 °C for 1 h, and the cold bath was removed. After 2 h, solvent was removed by rotary evaporation. The residue was extracted with THF (10 mL). Hexane (30 mL) was added, and the resulting precipitate was collected by filtration, washed with pentane (2 × 3 mL), and dried *in vacuo* to give **3a** (0.230 g, 0.329 mmol, 82%; 42:58[14] *RS,SR*/*RR,SS*) as a tan powder, mp 134–137 °C dec. IR (cm^{-1}, thin film): ν_{NO} 1717 vs. MS:[38] 614 (M^+, 22%), 544 ($M^+ - C_5H_{10}$, 100%).

B. Complex **8** (0.028 g, 0.050 mmol), C_6H_5Cl (1.0 mL), HBF_4·OEt_2 (5.9 μL, 0.055 mmol), and 2-methyl-1-butene (27 μL, 0.25 mmol) were combined as in procedure A at −45 °C (CH_3CN/CO_2 bath). After 15 min, the cold bath was removed. After 12 h, the mixture was added dropwise to hexane (30 mL) and the resulting precipitate was collected as in procedure A to give **3a** (0.029 g, 0.041 mmol, 81%; 48:52 *RS,SR*/*RR,SS*) as a tan powder.

C. A 5-mm NMR tube was charged with some of the preceding sample (0.007 g) and C_6D_5Cl (0.5 mL), capped with a septum, and transferred to a 95 °C probe. Data: see text. After 9 h, workup as in procedure B gave complete recovery of **3a**.

D. Procedure B was repeated on an identical scale. The mixture was warmed to room temperature and then stirred at 95 °C for 4 h. Workup as in procedure B gave **3a** (0.034 g, 0.049 mmol, 98%; 69:31 *RS,SR*/*RR,SS*) as a tan powder. Anal. Calcd for $C_{28}H_{30}BF_4NOPRe$: C, 48.01; H, 4.32; N, 2.00. Found: C, 47.99; H, 4.31; N, 2.06.

NMR (*RS,SR*):[36b] ^{1}H (δ) 7.65–7.35 (m, PPh$_3$), 5.71 (s, C_5H_5), 2.74 (dd, J_{HH} = 3.8, J_{HP} = 12.4, =CH$_Z$), 2.59 (dq, J_{HH} = 7.2, 14.4, =CC*H*H′), 2.46 (dd, J_{HH} = 3.8, J_{HP} = 6.3, =CH$_E$), 2.20 (s, =CCH$_3$), 1.66 (dq, J_{HH} = 7.2, 14.4, =CCH*H*′), 1.12 (t, J_{HH} = 7.2, CHH′C*H*$_3$); ^{13}C{^{1}H} (ppm) 133.4 (d, J_{CP} = 9.7, *o*-Ph), 132.2 (s, *p*-Ph), 129.6 (d, J_{CP} = 50.7, *i*-Ph), 129.6 (d, J_{CP} = 10.3, *m*-Ph), 98.0 (s, C_5H_5), 76.1 (s, $w_{1/2}$ = 5.3, *C*=CH$_2$), 44.7 (d, J_{CP} = 5.3, $w_{1/2}$ = 11.5, =CH$_2$),[15] 38.6 (s, *C*H$_2$CH$_3$), 28.6 (s, =C*C*H$_3$), 14.5 (s, CH$_2$*C*H$_3$); ^{31}P{^{1}H} (ppm) 8.9 (s). NMR (*RR,SS*; partial): ^{1}H (δ) 5.70 (s, C_5H_5), 2.75 (dd, J_{HH} = 3.6, J_{HP} = 12.9, =CH$_E$), 2.50 (m, =CH$_Z$), 2.40 (m, =CC*H*H′), 2.07 (s, =CCH$_3$), 1.78 (m, =CCH*H*′), 1.22 (t, J_{HH} = 7.2, CHH′C*H*$_3$); ^{13}C{^{1}H} (ppm) 97.7 (s, C_5H_5), 78.1 (s, $w_{1/2}$ = 6.2, *C*=CH$_2$), 44.4 (d, J_{CP} = 5.4, $w_{1/2}$ = 12.3, =CH$_2$), 38.4 (s, *C*H$_2$CH$_3$), 27.6 (s, =C*C*H$_3$), 17.8 (s, CH$_2$*C*H$_3$); ^{31}P{^{1}H} (ppm) 9.1 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H$_2$C=C(CH$_3$)CH$_2$CH$_2$-CH$_3$)]$^+$BF$_4^-$ (3b). A. Complex **8** (0.112 g, 0.200 mmol), CH_2Cl_2 (5.0 mL), HBF_4·OEt_2 (24 μL, 0.22 mmol), and 2-methyl-1-pentene (123 μL, 1.00 mmol) were reacted as in procedure A for **3a**. After 12 h, workup as in procedure B for **3a** gave **3b** (49:51 *RS,SR*/*RR,SS*) with several minor impurities (^{1}H NMR ($CDCl_3$): δ 6.26, 6.02, 5.46, 5.41, 5.30; 5s, C_5H_5). Column chromatography (silica, 15 × 1.3 cm, 2:98 v/v acetone/CH_2Cl_2) gave **3b** (0.075 g, 0.11 mmol, 53%; 49:51 *RS,SR*/*RR,SS*) as a yellow powder, mp 123–126 °C dec. IR (cm^{-1}, thin film): ν_{NO} 1716 vs. MS:[38] 628 (M^+, 28%), 544 ($M^+ - C_6H_{12}$, 100%). Anal. Calcd for $C_{29}H_{32}BF_4NOPRe$: C, 48.75; H, 4.51, N, 1.96. Found: C, 48.55; H, 4.79; N, 1.93.

B. Complex **8** (0.112 g, 0.200 mmol), C_6H_5Cl (3.0 mL), HBF_4·OEt_2 (24 μL, 0.22 mmol), and 2-methyl-1-pentene (123 μL, 1.00 mmol) were reacted as in procedure B for **3a**. An identical workup gave **3b** (0.077 g, 0.11 mmol, 54%; 50:50 *RS,SR*/*RR,SS*) as a yellow powder.

C. A Schlenk flask was charged with some of the preceding sample (0.048 g, 0.067 mmol) and C_6H_5Cl (2.0 mL). The solution was stirred at 95 °C for 12 h. Workup as in preparation B for **3a** gave **3b** (0.032 g, 0.044 mmol, 66%; 68:32 *RS,SR*/*RR,SS*) as a tan powder.

D. Complex **8** (0.056 g, 0.10 mmol), C_6H_5Cl (1.5 mL), HBF_4·OEt_2 (12 μL, 0.11 mmol), and 2-methyl-1-butene (62 μL, 0.50 mmol) were reacted as in procedure B. The mixture was warmed to room temperature and then stirred at 95 °C for 6 h. Workup as in procedure B for **3a** gave **3b** (0.059 g, 0.082 mmol, 82%; 70:30 *RS,SR*/*RR,SS*) as a tan powder.

NMR (*RS,SR*): ^{1}H (δ) 7.80–7.20 (m, PPh$_3$), 5.69 (s, C_5H_5), 2.73 (dd, J_{HH} = 3.8, J_{HP} = 12.4, =CH$_Z$), 2.45 (dd, J_{HH} = 3.8, J_{HP} = 5.9, =CH$_E$), 2.25 (m, =CC*H*H′), 2.18 (s, =CCH$_3$), 1.85–1.35 (m, =CCH*H*′C*H*H′CH$_3$), 0.88 (t, J_{HH} = 7.2, CHH′C*H*$_3$); ^{13}C{^{1}H} (ppm) 133.3 (d, J_{CP} = 9.6, *o*-Ph), 132.2 (s, *p*-Ph), 129.5 (d, J_{CP} = 11.0, *m*-Ph),[39] 97.9 (s, C_5H_5), 75.3 (s, $w_{1/2}$ = 7.5, *C*=CH$_2$), 47.7 (s, =*C*CH$_2$), 45.0 (d, J_{CP} = 5.4,[40] =CH$_2$), 29.0 (s, =C*C*H$_3$), 23.6 (s, *C*H$_2$CH$_3$), 14.0 (s, CH$_2$*C*H$_3$); ^{31}P{^{1}H} (ppm) 9.4 (s). NMR (*RR,SS*; partial): ^{1}H (δ) 5.69 (s, C_5H_5), 2.80 (dd, J_{HH} = 3.7, J_{HP} = 13.2, =CH$_E$), 2.49 (dd, J_{HH} = 3.7, J_{HP} = 5.4, =CH$_Z$), 2.07 (s, =CCH$_3$), 0.98 (t, J_{HH} = 7.2, CHH′C*H*$_3$); ^{13}C{^{1}H} (ppm) 97.7 (s, C_5H_5), 76.8 (s,[40] *C*=CH$_2$), 47.5 (s, =*C*CH$_2$), 44.9 (d, J_{CP} = 5.6,[40] =CH$_2$), 28.0 (s, =C*C*H$_3$), 26.1 (s, *C*H$_2$CH$_3$), 14.0 (s, CH$_2$*C*H$_3$); ^{31}P{^{1}H} (ppm) 9.5 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H$_2$C=C(CH$_3$)C$_6$H$_5$)]$^+$BF$_4^-$ (3c). A. Complex **8** (0.168 g, 0.300 mmol), CH_2Cl_2 (1.5 mL), HBF_4·OEt_2 (32 μL, 0.30 mmol), and α-methylstyrene (195 μL, 1.50 mmol) were reacted as in procedure A for **3a**. After 6 h, workup as in procedure B for **3a** gave **3c** (0.217 g, 0.290 mmol, 97%; 42:58 *RS,SR*/*RR,SS*) as a tan powder. Column chromatography (silica, 15 × 1.3 cm, CH_2Cl_2) gave a yellow band, which was collected in three fractions. The first gave (*RR,SS*)-**3c** (0.053 g, 0.071 mmol, 25%) as a yellow powder, mp 189–190 °C dec. IR (cm^{-1}, thin

(33) For a conceptually similar analysis couched in different terms, see: Conticello, V. P.; Brard, L.; Giardello, M. A.; Tsuji, Y.; Sabat, M.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 2761.

(34) Whitesell, J. K. *Chem. Rev.* **1988**, *88*, 1581.

(35) (a) Peng, T.-S.; Gladysz, J. A. *Organometallics* **1990**, *9*, 2884. (b) Peng, T.-S.; Gladysz, J. A. Manuscript in preparation.

(36) (a) General procedures were identical with those described in a previous paper.[4c] Alkenes were used as received from Aldrich. (b) NMR spectra were recorded in $CDCl_3$ at ambient probe temperature and referenced to Si(CH$_3$)$_4$ (^{1}H, δ 0.00), $CDCl_3$ (^{13}C, 77.0 ppm), or external 85% H_3PO_4 (^{31}P, 0.00 ppm) unless noted. All coupling constants (*J*) and $w_{1/2}$ values are in Hz. (c) The ^{1}H difference NOE spectra[12] were acquired as described previously with 80–95% cyclopentadienyl resonance irradiation.[8]

(37) Agbossou, F.; O'Connor, E. J.; Garner, C. M.; Quirós Méndez, N.; Fernández, J. M.; Patton, A. T.; Ramsden, J. A.; Gladysz, J. A. *Inorg. Synth.* **1992**, *29*, 211.

(38) Conditions: (+)-FAB, 5 kV, Ar, 3-nitrobenzyl alcohol/$CHCl_3$ matrix, *m*/*z* (relative intensity), ^{187}Re.

(39) The *ipso* carbon was not located, or one line of the doublet was obscured.

(40) The $w_{1/2}$ value could not be measured due to overlapping resonances.

film): ν_{NO} 1722 vs. MS:[38] 662 (M^+, 31%), 544 ($M^+ - C_9H_{10}$, 100%). The second gave **3c** as a 50:50 *RS,SR/RR,SS* mixture (0.035 g, 0.047 mmol, 16%). Anal. Calcd for $C_{32}H_{30}BF_4NOPRe$: C, 51.34; H, 4.04, N, 1.87. Found: C, 51.25; H, 4.11; N, 1.85. The third gave (*RS,SR*)-**3c** (0.020 g, 0.027 mmol, 9%). Crystallization from $CHCl_3$ gave yellow needles, mp 184–186 °C dec. IR (cm^{-1}, thin film): ν_{NO} 1729 vs. MS:[38] 662 (M^+, 16%), 544 ($M^+ - C_9H_{10}$, 100%).

B. Complex **8** (0.028 g, 0.050 mmol), C_6H_5Cl (1.0 mL), HBF_4·OEt_2 (5.9 μL, 0.055 mmol), and α-methylstyrene (33 μL, 0.25 mmol) were reacted as in procedure B for **3a**. After 9 h, an identical workup gave **3c** (0.037 g, 0.049 mmol, 98%; 35:65 *RS,SR/RR,SS*) as a yellow powder.

C. Procedure B was repeated on an identical scale except with 6.0 mL of C_6H_5Cl. The mixture was warmed to room temperature and then stirred at 95 °C for 6 h. Workup as in procedure B gave **3c** (0.036 g, 0.048 mmol, 96%; 36:64 *RS,SR/RR,SS*) as a yellow powder.

D. Two 5-mm NMR tubes were charged with CD_2ClCD_2Cl (0.5 mL) and (*RS,SR*)-**3c** or (*RR,SS*)-**3c** (0.008 g, 0.01 mmol), capped with septa, and transferred to 95 °C probes. Data: see text.

NMR (*RS,SR*):[41] ^1H (δ) 7.70–7.00 (m, PPh_3 and CPh), 5.78 (s, C_5H_5), 3.53 (dd, J_{HH} = 4.9, J_{HP} = 13.5, $=CH_Z$), 2.54 (s, $=CCH_3$), 2.36 (dd, J_{HH} = 4.9, J_{HP} = 4.9, $=CH_E$); $^{13}C\{^1H\}$ (ppm) 133.6 (d, J_{CP} = 10.0, *o*-PPh), 133.5 (d, J_{CP} = ca. 52,[39] *i*-PPh), 132.6 (s, *p*-PPh), 129.8 (d, J_{CP} = 11.2, *m*-PPh), 145.6, 128.4, 127.6, 126.4 (4s, *C*Ph), 98.6 (s, C_5H_5), 70.0 (s, $w_{1/2}$ = 6.6, *C*=CH_2), 39.3 (d, J_{CP} = 6.1, $w_{1/2}$ = 12.3, =CH_2), 33.0 (s, CH_3); $^{31}P\{^1H\}$ (ppm) 12.6 (s). NMR (*RR,SS*): ^1H (δ) 7.80–7.20 (m, PPh_3 and CPh), 5.14 (s, C_5H_5), 3.27 (dd, J_{HH} = 4.5, J_{HP} = 4.5, $=CH_Z$), 3.09 (dd, J_{HH} = 4.5, J_{HP} = 14.0, $=CH_E$), 2.30 (s, CH_3); $^{13}C\{^1H\}$ (ppm) 133.5 (d, J_{CP} = 9.9, *o*-PPh), 132.7 (s, *p*-PPh), 130.5 (d, J_{CP} = ca. 58,[39] *i*-PPh), 130.0 (d, J_{CP} = 10.6, *m*-PPh), 146.6, 129.3, 128.9, 128.5 (4s, *C*Ph), 99.8 (s, C_5H_5), 74.2 (s, $w_{1/2}$ = 6.3, *C*=CH_2), 39.5 (d, J_{CP} = 4.8, $w_{1/2}$ = 11.1, =CH_2), 30.4 (s, CH_3); $^{31}P\{^1H\}$ (ppm) 12.0 (s).

(*Z*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3HC=$CHCH_2CH_3$)]$^+BF_4^-$ ((*Z*)-4a). A. Complex **8** (0.167 g, 0.300 mmol), C_6H_5Cl (5.0 mL), HBF_4·OEt_2 (33 μL, 0.30 mmol), and *cis*-2-pentene (160 μL, 1.50 mmol) were reacted as in procedure B for **3a**. After 3 h, the mixture was filtered, and solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (2.0 mL). Workup as in procedure B for **3a** gave (*Z*)-**4a** (0.222 g, 0.310 mmol, >99%; 51:49 *RSR,SRS/RRS,SSR*) as a tan powder, mp 126–127 °C dec. Anal. Calcd for $C_{28}H_{30}BF_4NOPRe$: C, 48.01; H, 4.32. Found: C, 47.29; H, 4.23. IR (cm^{-1}, thin film): ν_{NO} 1717 vs.

B. Complex **8** (0.111 g, 0.200 mmol), C_6H_5Cl (2.0 mL), HBF_4·OEt_2 (22 μL, 0.20 mmol), and *cis*-2-pentene (105 μL, 0.986 mmol) were reacted as in procedure A. The mixture was warmed to room temperature and then stirred at 95 °C for 48 h. Workup as in procedure A gave (*Z*)-**4a** (0.133 g, 0.199 mmol, 99%; 59:41 *RSR,SRS/RRS,SSR*) as a tan powder.

NMR (*RSR,SRS*): ^1H (δ, 59 °C) 7.56–7.34 (m, PPh_3), 5.72 (s, C_5H_5), 4.31 (m, =*CH*CHH'), 3.39 (m, =*CH*CH_3),[42] 2.10 (m, *CHH'*), 1.75 (d, J_{HH} = 6.1, =CHCH_3),[42] 1.12 (t, J_{HH} = 7.0, CHH'CH_3); $^{13}C\{^1H\}$ (ppm, 59 °C) 133.4 (d, J_{CP} = 9.8, *o*-Ph), 132.0 (s, *p*-Ph), 130.4 (d, J_{CP} = 57.2, *i*-Ph), 129.4 (d, J_{CP} = 10.7, *m*-Ph), 97.6 (s, C_5H_5), 56.5 (s, $w_{1/2}$ = 5.7, =*C*CH_2), 51.6 (d, J_{CP} = 3.3, $w_{1/2}$ = 9.0, =*C*CH_3),[18] 26.3 (s, CH_2), 18.2 16.3 (2s, $2CH_3$); $^{31}P\{^1H\}$ (ppm) 8.1 (s). NMR (*RRS,SSR*; partial): ^1H (δ, 59 °C) 5.72 (s, C_5H_5), 4.31 (m, =*CH*CH_3),[42] 3.25 (m, =*CH*CHH'),[42] 1.90 (m, *CHH'*), 1.82 (d, J_{HH} = 6.1, =CHCH_3),[42] 0.88 (d, J_{HH} = 7.0, CHH'CH_3); $^{13}C\{^1H\}$ (ppm, 59 °C) 97.7 (s, C_5H_5), 60.5 (s, $w_{1/2}$ = 6.9, =*C*CH_2), 49.8 (s, $w_{1/2}$ = 5.9, =*C*CH_3), 25.3 (s, CH_2), 17.2, 15.8 (2s, $2CH_3$); $^{31}P\{^1H\}$ (ppm) 8.8 (s).

^1H NMR (δ, partial, –60 °C):[41] *sc-RSR,SRS*, 5.65 (s, C_5H_5), 1.70 (d, J_{HH} = 5.8, =CHCH_3), 1.13 (t, J_{HH} = 7.0, CHH'CH_3); *ac-RSR,SRS*, 5.68 (s, C_5H_5), 2.34 (d, J_{HH} = 5.7, =CHCH_3); *sc-RRS,SSR*, 5.63 (s, C_5H_5), 1.20 (t, J_{HH} = 7.1, CHH'CH_3), 0.67 (d, J_{HH} = 6.4, =CHCH_3); *ac-RRS,SSR*, 5.64 (s, C_5H_5), 2.10 (d, J_{HH} = 5.9, =CHCH_3), 0.60 (t, J_{HH} = 6.3, CHH'CH_3).

(*Z*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3HC=$CHCH(CH_3)_2$)]$^+BF_4^-$ ((*Z*)-4b). A. Complex **8** (0.112 g, 0.200 mmol), C_6H_5Cl (2.0 mL), HBF_4·OEt_2 (24 μL, 0.22 mmol), and *cis*-4-methyl-2-pentene (251 μL, 2.00 mmol) were reacted as in procedure B for **3a**. After 12 h, an identical workup gave (*Z*)-**4b** (0.134 g, 0.187 mmol, 94%; 79:21 *RSR,SRS/RRS,SSR*) as a tan powder, mp 128–131 °C dec. Anal. Calcd for $C_{29}H_{32}BF_4NOPRe$: C, 48.75; H, 4.51. Found: C, 48.04; H, 4.46. IR (cm^{-1}, thin film): ν_{NO} 1713 vs. MS:[38] 628 (M^+, 42%), 544 ($M^+ - C_6H_{12}$, 100%).

B. Procedure A was repeated on an identical scale. The mixture was warmed to room temperature and then stirred at 95 °C for 24 h. An identical workup gave (*Z*)-**4b** (0.129 g, 0.181 mmol, 90%; 79:21 *RSR,SRS/RRS,SSR*) as a tan powder.

NMR[21] (*RSR,SRS*): ^1H (δ) 7.65–7.25 (m, PPh_3), 5.73 (s, C_5H_5), 4.37 (dd, J_{HH} = 10.3, 10.3, =*CH*CH$(CH_3)_2$),[42] 2.90 (m, =*CH*CH_3), 2.04 (m, *CH*$(CH_3)_2$),[42] 1.85 (d, J_{HH} = 6.0, =CHCH_3), 1.27, 1.20 (2d, J_{HH} = 6.6/6.3, CH$(CH_3)_2$);[42] $^{13}C\{^1H\}$ (ppm) 133.6 (d, J_{CP} = 9.9, *o*-Ph), 132.1 (s, *p*-Ph), 130.3 (*i*-Ph),[39] 129.4 (d, J_{CP} = 10.7, *m*-Ph), 97.8 (s, C_5H_5), 60.5 (s, $w_{1/2}$ = 6.8; =*C*HCH$(CH_3)_2$),[42] 48.5 (d, J_{CP} = 4.8, $w_{1/2}$ = 10.7, =*C*HCH_3), 32.1 (s, *C*H$(CH_3)_2$), 24.5, 24.0 (2s, CH(*C*$H_3)_2$), 16.1 (d, J_{CP} = 4.3, =CH*C*H_3); $^{31}P\{^1H\}$ (ppm) 8.4 (s). NMR (*RRS,SSR*): ^1H (δ, partial) 5.56 (s, C_5H_5), 4.07 (m, =*CH*CH$_3$), 3.17 (dd, J_{HH} = 9.9, 9.9, =*CH*CH$(CH_3)_2$),[42] 2.29 (m, *CH*$(CH_3)_2$),[42] 1.35, 1.31 (2d, J_{HH} = 6.4/6.3, CH$(CH_3)_2$),[42] 0.84 (d, J_{HH} = 6.6, =CHCH_3); $^{13}C\{^1H\}$ (ppm) 132.9 (d, J_{CP} = 9.3, *o*-Ph), 132.2 (s, *p*-Ph), 129.2 (*i*-Ph),[39] 129.8 (d, J_{CP} = 11.3, *m*-Ph), 92.2 (s, C_5H_5), 70.2 (s, $w_{1/2}$ = 7.3; =*C*HCH$(CH_3)_2$),[42] 50.5 (br s, $w_{1/2}$ = 8.7; =*C*HCH$_3$), 32.6 (s, *C*H$(CH_3)_2$), 25.8, 23.7 (2s, CH(*C*$H_3)_2$), 15.9 (s, =CH*C*H_3); $^{31}P\{^1H\}$ (ppm) 10.4 (s).

(*E*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3HC=$CHCH_2CH_3$)]$^+BF_4^-$ ((*E*)-4a). A. Complex **8** (0.223 g, 0.400 mmol), C_6H_5Cl (8.0 mL), HBF_4·OEt_2 (44 μL, 0.40 mmol), and *trans*-2-pentene (200 μL, 1.85 mmol) were reacted as in procedure A for (*Z*)-**4a**. After 24 h, an identical workup gave **4a** (0.272 g, 0.390 mmol, 97%) as a tan powder that was a 81:19 mixture of (*E*)-**4a** (33: 26:31:10 *sc-RSS,SRR/ac-RSS,SRR/sc-RRR,SSS/ac-RRR,SSS*) and (*Z*)-**4a** (40:60 *RSR,SRS/RRS,SSR*). IR (cm^{-1}, thin film): ν_{NO} 1721 vs.

B. Complex **8** (0.111 g, 0.199 mmol), C_6H_5Cl (2.0 mL), HBF_4·OEt_2 (22 μL, 0.20 mmol), and *trans*-2-pentene (110 μL, 1.02 mmol) were reacted as in procedure A. The mixture was warmed to room temperature and stirred at 95 °C for 48 h. An identical workup gave a 94:6 mixture (0.134 g, 0.191 mmol, 96%) of (*E*)-**4a** (64:35:1 *sc-RSS,SRR/ac-RSS,SRR/sc-RRR,SSS*) and (*Z*)-**4a** (60:40 *RSR,SRS/RRS,SSR*).

NMR (*sc-RSS,SRR*): ^1H (δ) 7.72–7.59 (m, PPh_3), 5.86 (s, C_5H_5), 4.35 (m, =*CH*CHH'), 3.03 (m, =*CH*CH_3),[42] 1.93 (m, *CHH'*),[42] 1.35 (d, J_{HH} = 5.8, =CHCH_3),[42] 1.19 (t, J_{HH} = 7.1, CHH'CH_3);[42] $^{31}P\{^1H\}$ (ppm) 7.6 (s). NMR (*ac-RSS,SRR*; partial): ^1H (δ) 5.85 (s, C_5H_5), 4.43 (m, =*CH*CH$_3$),[42] 2.90 (m, =*CH*CHH'), 2.18 (m, *CHH'*),[42] 2.11 (d, J_{HH} = 5.8, =CHCH_3),[42] 0.81 (t, J_{HH} = 6.7, CHH'CH_3);[42] $^{31}P\{^1H\}$ (ppm) 7.7 (s). NMR (*sc-RRR,SSS*; partial): ^1H (δ) 5.68 (s, C_5H_5), 4.43 (m, =*CH*CH$_3$), 3.26 (m, =*CH*CHH'), 1.87 (d, J_{HH} = 5.7, =CHCH_3), 0.98 (t, J_{HH} = 7.1, CHH'CH_3); $^{31}P\{^1H\}$ (ppm) 7.2 (s). NMR (*ac-RRR,SSS*; partial): ^1H (δ) 5.70 (s, C_5H_5), 2.19 (d, J_{HH} = 7.2, =CHCH_3); $^{31}P\{^1H\}$ (ppm) 7.5 (s).

(41) These NMR spectra were recorded in CD_2Cl_2 and referenced to $CHDCl_2$ (^1H, δ 5.32), CD_2Cl_2 (^{13}C, 53.8 ppm), or external 85% H_3PO_4 (^{31}P, 0.00 ppm).

(42) These assignments were verified by decoupling experiments. (*Z*)-**4a**: Irradiation of the δ 4.31 and 3.39 =*CH* resonances collapsed the δ 1.82 and 1.75 CH_3 resonances, respectively, to singlets. Irradiation of the δ 3.25 resonance did not affect any CH_3 resonances. (*Z*)-**4b**: Irradiation of the δ 2.04 $CH(CH_3)_2$ resonance collapsed the δ 1.27 and 1.20 CH_3 resonances to singlets and the δ 4.37 =*CH* resonance to a doublet. Irradiation of the δ 2.29 $CH(CH_3)_2$ resonance collapsed the δ 1.35 and 1.31 CH_3 resonances to singlets and the δ 3.17 =*CH* resonance to a doublet. Irradiation of the δ 4.37 and 3.17 =*CH* resonances collapsed the 60.5 and 70.2 ppm =CH resonances, respectively, to singlets. (*E*)-**4a**: Irradiation of the δ 3.03 and 4.43 =*CH* resonances collapsed the δ 1.35 and 2.11 CH_3 resonances, respectively, to singlets. Irradiation of the δ 2.11, 1.35, 1.19, and 0.81 CH_3 resonances simplified the δ 4.43, 3.03, 1.93, and 2.18 =CH and CH_3 resonances, respectively. (*E*)-**4c** (CD_2Cl_2): Irradiation of the δ 3.68 and 5.10 =*CH* resonances collapsed the δ 1.60 and 2.39 CH_3 resonances, respectively, to singlets and the δ 5.61 and 3.92 =*CH* resonances, respectively, to doublets.

(*E*)-[(η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_3$HC=CHCH(CH$_3$)$_2$)]$^+$BF$_4^-$ ((*E*)-4b). A. Complex **8** (0.056 g, 0.10 mmol), C_6H_5Cl (1.0 mL), HBF_4·OEt_2 (12 μL, 0.11 mmol), and *trans*-4-methyl-2-pentene (126 μL, 1.00 mmol) were reacted as in procedure B for **3a**. After 24 h, an identical workup gave (*E*)-**4b** (0.060 g, 0.085 mmol, 85%) as a tan powder. Minor impurities were evident (^{31}P NMR ($CDCl_3$): 21.2, 18.3, 14.6, 4.2 ppm).

B. Procedure A was repeated on an identical scale. The mixture was warmed to room temperature and stirred at 95 °C for 5 h. Workup as in procedure B for **3a** gave (*E*)-**4b** (0.066 g, 0.092 mmol, 92%; >99% *sc-RSS,SRR*), mp 136–139 °C dec. Anal. Calcd for $C_{29}H_{32}BF_4NOPRe$: C, 48.75; H, 4.51; N, 1.96. Found: C, 48.28; H, 4.17; N, 2.06. IR (cm^{-1}, thin film): ν_{NO} 1722 vs. MS:[38] 628 (M^+, 45%), 544 ($M^+ - C_6H_{12}$, 100%).

NMR: ^{1}H (δ) 7.65–7.25 (m, PPh_3), 5.86 (s, C_5H_5), 4.11 (dd, J_{HH} = 9.9, 9.9, =C*H*CH(CH$_3$)$_2$), 2.97 (m, =C*H*CH$_3$), 1.53 (m, C*H*(CH$_3$)$_2$), 1.33, 1.24, 1.19 (3d, J_{HH} = 6.0/7.0/6.5, 3CH$_3$); ^{13}C{^{1}H} (ppm) 133.2 (d, J_{CP} = 9.6, *o*-Ph), 132.1 (s, *p*-Ph), 130.5 (*i*-Ph),[39] 129.5 (d, J_{CP} = 10.9, *m*-Ph), 97.6 (s, C_5H_5), 62.6 (s, $w_{1/2}$ = 6.8, =*C*HCH(CH$_3$)$_2$), 51.8 (d, J_{CP} = 5.1, $w_{1/2}$ = 11.3, =*C*HCH$_3$), 37.9 (s, *C*H(CH$_3$)$_2$), 28.1 (s, =CH*C*H$_3$), 23.2 (s, CH(*C*H$_3$)$_2$); ^{31}P{^{1}H} (ppm) 7.3 (s).

(*E*)-[(η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_3$HC=CHC$_6$H$_5$)]$^+$BF$_4^-$ ((*E*)-4c). A. Complex **8** (0.112 g, 0.200 mmol), C_6H_5Cl (2.0 mL), HBF_4·OEt_2 (24 μL, 0.22 mmol), and *trans*-β-methylstyrene (130 μL, 1.00 mmol) were reacted as in procedure B for **3a**. After 12 h, an identical workup gave (*E*)-**4c** (0.138 g, 0.184 mmol, 92%; 27:32:41 *sc-RSS,SRR/ac-RSS,SRR/RRR,SSS*) as a tan powder. Column chromatography (silica, 15 × 1.3 cm, 2:98 v/v acetone/CH_2Cl_2) gave (*E*)-**4c** (0.076 g, 0.10 mmol, 50%; 28:34:38 *sc-RSS,SRR/ac-RSS,SRR/RRR,SSS*) as a yellow powder. Anal. Calcd for $C_{32}H_{30}BF_4NOPRe$: C, 51.34; H, 4.04; N, 1.87. Found: C, 51.23; H, 4.06; N, 1.90. IR (cm^{-1}, thin film): ν_{NO} 1726 vs. MS:[38] 662 (M^+, 27%), 544 ($M^+ - C_6H_{10}$, 100%).

B. Complex **8** (0.056 g, 0.10 mmol), C_6H_5Cl (1.0 mL), HBF_4·OEt_2 (12 μL, 0.11 mmol), and *trans*-β-methylstyrene (65 μL, 0.50 mmol) were reacted as in procedure B for **3a**. After 12 h, the mixture was kept at 95 °C for 12 h. An identical workup gave (*E*)-**4c** (0.066 g, 0.089 mmol, 89%; 45:55 *sc-RSS,SRR/ac-RSS,SRR*) as a tan powder.

NMR (*sc-RSS,SRR*): ^{1}H (δ) 7.80–6.90 (m, PPh_3 and 3H of CPh), 6.07 (d, J_{HH} = 7.0, 2H of CPh), 5.93 (s, C_5H_5), 5.60 (d, J_{HH} = 11.7, =C*H*Ph), 3.57 (m, =C*H*CH$_3$), 1.62 (d, J_{HH} = 6.2, =CHC*H*$_3$); ^{13}C{^{1}H} (ppm) 133.2 (d, J_{CP} = 10.0, *o*-PPh), 132.0 (s, *p*-PPh), 129.5 (d, J_{CP} = 10.8, *m*-PPh),[39] 141.6, 128.2, 127.3, 126.5 (4s, C*Ph*), 97.8 (s, C_5H_5), 53.8 (s, $w_{1/2}$ = 6.6, =*C*HPh), 49.6 (d, J_{CP} = 4.7, $w_{1/2}$ = 10.5, =*C*HCH$_3$), 22.6 (s, =CH*C*H$_3$); ^{31}P{^{1}H} (ppm) 5.0 (s). NMR (*ac-RSS,SRR*; partial): ^{1}H (δ) 5.83 (s, C_5H_5), 5.18 (m, =C*H*CH$_3$), 3.83 (dd, J_{HH} = 12.2, J_{HP} = 7.5, =C*H*Ph), 2.36 (d, J_{HH} = 5.9, =CHC*H*$_3$); ^{13}C{^{1}H} (ppm) 141.4, 128.6, 127.0, 126.5 (4s, C*Ph*), 98.5 (s, C_5H_5), 64.5 (d, J_{CP} = 3.4, $w_{1/2}$ = 9.6, =*C*HPh), 47.0 (s, $w_{1/2}$ = 6.4, =*C*HCH$_3$), 25.6 (s, =CH*C*H$_3$); ^{31}P{^{1}H} (ppm) 8.1 (s). NMR (*RRR,SSS*; partial): ^{1}H (δ) 5.44 (s, C_5H_5), 4.21 (d, J_{HH} = 12.8, =C*H*Ph), 3.70 (m, =C*H*CH$_3$), 1.98 (d, J_{HH} = 5.9, =CHC*H*$_3$); ^{13}C{^{1}H} (ppm) 133.6 (d, J_{CP} = 10.0, *o*-PPh), 131.9 (s, *p*-PPh), 129.2 (d, J_{CP} = 11.0, *m*-PPh),[39] 141.8, 128.8, 127.7, 126.5 (4s, C*Ph*), 100.3 (s, C_5H_5), 57.8 (br s, $w_{1/2}$ = 9.1, =*C*HPh), 46.5 (br s, $w_{1/2}$ = 9.0, =*C*HCH$_3$), 23.4 (s, =CH*C*H$_3$); ^{31}P{^{1}H} (ppm) 6.2 (s). NMR (*sc-RRR,SSS*): ^{31}P{^{1}H} (ppm, −65 °C) 7.5 (s). NMR (*ac-RRR,SSS*): ^{31}P{^{1}H} (ppm, −65 °C) 4.7 (s).

^{1}H NMR (δ; C_5H_5, =C*H*Ph, =C*H*CH$_3$, =CHC*H*$_3$):[41] *sc-RSS,SRR*, 5.91 (s), 5.61 (dd, J_{HH} = 11.7, J_{HP} = 1.7),[42] 3.68 (m),[42] 1.60 (d, J_{HH} = 6.4);[42] *sc-RSS,SRR* (−80 °C), 5.86 (s), 5.48 (d, J_{HH} = 11.1), 3.50 (m), 1.44 (d, J_{HH} = 6.1); *ac-RSS,SRR*, 5.81 (s), 3.92 (dd, J_{HH} = 12.2, J_{HP} = 7.4),[42] 5.10 (ddd, J_{HH} = 5.9, 12.2, J_{HP} = 1.8),[42] 2.39 (d, J_{HH} = 5.7);[42] *ac-RSS,SRR* (−80 °C), 5.72 (s), 3.76 (dd, J_{HH} = 12.4, J_{HP} = 6.8), 4.94 (m), 2.34 (d, J_{HH} = 5.0); *sc-RRR,SSS* (−80 °C), 5.18 (s), 4.66 (d, J_{HH} = 13.0), 3.10 (m), 1.80 (d, J_{HH} = 5.4); *ac-RRR,SSS* (−80 °C), 5.67 (s), 3.48 (dd, J_{HH} = 11.6, J_{HP} = 8.6), 4.46 (m), 2.07 (d, J_{HH} = 5.1).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_3$HC=C(CH$_3$)$_2$)]$^+$BF$_4^-$ (5). A. A 5-mm NMR tube was charged with **8** (0.028 g, 0.050 mmol) and C_6H_5Cl (0.8 mL), capped with a septum, and cooled to −45 °C. Then HBF_4·OEt_2 (5.9 μL, 0.055 mmol) was added. After 15 min, 2-methyl-2-butene (0.053 mL, 0.50 mmol) was added. The tube was transferred to a −45 °C NMR probe, which was warmed as ^{31}P spectra were acquired. Complexes **5** (*RS,SR/RR,SS*, 6.2/6.6 ppm), (*RS,SR*)-[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H$_2$C=C(CH$_3$)CH(CH$_3$)$_2$)]$^+$BF$_4^-$ ((*RS,SR*)-**6**, 8.6 ppm),[24] and byproducts (22.8, 21.1, 21.0, 19.3, 14.7, 4.2, −0.7 ppm) formed between −25 °C and room temperature, as further detailed in the text.

B. Procedure A was repeated on an identical scale. After 12 h, the solution was added dropwise to ether (50 mL). The resulting precipitate was collected by filtration, washed with pentane (2 × 3 mL), and dried *in vacuo* to give a tan powder (0.026 g, ca. 0.038 mmol, 75%) that was an 80:20 mixture of **5** (65:15 or *81:19 RS,SR/RR,SS*) and (*RS,SR*)-**6**. IR (cm^{-1}, thin film): ν_{NO} 1721, 1716 vs. MS:[38] 628 (M^+ for **6**; 16%), 614 (M^+ for **5**; 41%), 544 ((η^5-C_5H_5)Re(NO)(PPh$_3$)$^+$, 100%).

C. Procedure A was repeated on an identical scale. After 8 h, the tube was transferred to an ambient-temperature NMR probe and then kept at 95 °C for 36 h. Data: see text. Workup as in procedure B gave a tan powder (0.026 g, ca. 0.037 mmol, 73%) that was a 56:29:5:11 mixture of (*RS,SR*)-**3a**, (*RR,SS*)-**3a**, (*RS,SR*)-**7**, and an unidentified species (^{31}P NMR, 7.2 ppm). The cyclopentadienyl ^{1}H and ^{13}C resonances and alkene ligand ^{13}C resonances of (*RS,SR*)-**7** were identical with those reported previously.[4c]

NMR ((*RS,SR*)-**5**): ^{1}H (δ) 7.65–7.31 (m, PPh_3), 5.73 (s, C_5H_5), 3.18 (m, J_{HP} = 9.4, =C*H*CH$_3$),[42] 2.13, 2.07 (2s, =CCH$_3$ positions b/a), 1.59 (d, J_{HH} = 6.4, =CHC*H*$_3$);[42] ^{13}C{^{1}H} (ppm) 133.3 (d, J_{CP} = 11.0, *o*-Ph), 132.1 (s, *p*-Ph), 129.4 (d, J_{CP} = 9.0, *m*-Ph),[39] 98.3 (s, C_5H_5), 69.5 (s, $w_{1/2}$ = 6.0, *C*=CHCH$_3$), 58.4 (br s, $w_{1/2}$ = 21.6, =*C*HCH$_3$), 35.3, 27.9, 19.3 (3s, 3CH$_3$); ^{31}P{^{1}H} (ppm) 6.0 (s). NMR ((*RR,SS*)-**5**; partial): ^{1}H (δ) 5.64 (s, C_5H_5), 3.06 (m, J_{HP} = 8.6, =C*H*CH$_3$),[42] 2.17, 1.96 (2s, =CCH$_3$ positions b/a), 1.58 (d, J_{HH} = 6.4, =CHC*H*$_3$);[42] ^{13}C{^{1}H} (ppm) 99.0 (s, C_5H_5), 68.3 (s, $w_{1/2}$ = 5.3, *C*=CHCH$_3$), 58.2 (br s, $w_{1/2}$ = 13.2, =*C*HCH$_3$), 33.7, 27.2, 17.8 (3s, 3CH$_3$); ^{31}P{^{1}H} (ppm) 6.7 (s).

NMR ((*RS,SR*)-**6**): ^{1}H (δ) 7.80–7.00 (m, PPh_3), 5.70 (s, C_5H_5), 2.74 (dd, J_{HH} = 4.0, J_{HP} = 12.3, =CH$_Z$), 2.37 (dd, J_{HH} = 4.0, J_{HP} = 6.5, =CH$_E$), 2.08 (s, =CCH$_3$), 1.58 (m, C*H*(CH$_3$)$_2$), 1.19, 1.12 (2d, J_{HH} = 6.7/6.7, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} (ppm, partial) 98.1 (s, C_5H_5), 80.1 (s, $w_{1/2}$ = 6.8, *C*=CH$_2$), 44.7 (d, J_{CP} = 5.6, $w_{1/2}$ = 13.6, C=*C*H$_2$), 42.8 (s, *C*H(CH$_3$)$_2$), 25.9, 23.0, 21.2 (3s, 3CH$_3$); ^{31}P{^{1}H} (ppm) 8.9 (s).

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Supplementary Material Available: Charts summarizing NMR data utilized in structural assignments (7 pages). Ordering information is given on any current masthead page.

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