Crystal Structure of 1. Data were collected on a Syntex $P\bar{1}$ diffractometer as outlined in Table I. The unit cell was determined by using 15 centered reflections with $9° < 2\theta < 25°$. The structure was solved with standard heavy-atom techniques, using the UCLA Crystallographic Package. Programs used have been previously detailed.[34] The structure was refined to convergence at an R value of 0.031 (R_w = 0.040). Since molecules in polar space groups can give somewhat inaccurate heavy-atom positions if the incorrect enantiomer is chosen,[35] the atomic coordinates of all atoms were multiplied by −1 to give the enantiomeric molecule, which was refined further. The R value dropped to 0.028 (R_w = 0.035), indicating the enantiomeric molecule (R absolute configuration) to be present in the crystal. All data compiled correspond to (*R*)-**1**.

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Supplementary Material Available: Table of anisotropic thermal parameters for **1** (1 page); a table of calculated and observed structure factors for **1** (26 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Reactivity of Chiral Rhenium Alkene Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+X^-$

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Reaction of the dichloromethane complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ and monosubstituted alkenes gives $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+BF_4^-$ (**3**$^+BF_4^-$, 89–91%; R = CH_3 (**a**), *n*-C_3H_7 (**b**), $CH_2C_6H_5$ (**c**), C_6H_5 (**d**)) as (73–62):(27–38) mixtures of (*RS,SR*)/(*RR,SS*) diastereomers. Reactions of η^1-allyl complexes (*E*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH{=}CHR')$ (**4**; R′ = H (**a**), C_6H_5 (**c**)) and electrophiles E^+X^- (E^+ = H^+, D^+, R^+) give alkene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCHER')]^+X^-$ (79–92%) as (75–60):(25–40) mixtures of diastereomers. When (*RS,SR*)/(*RR,SS*)-**3a–c**$^+BF_4^-$ are heated (C_6H_5Cl, 95–100 °C), they equilibrate to ≃95:5 mixtures of diastereomers. Rationales are given for the modest kinetic and high thermodynamic stereoselectivities. The crystal structure of independently synthesized (*RR,SS*)-**3c**$^+PF_6^-$ shows the =CHR alkene terminus to be approximately anti to the PPh_3 ligand, with R syn to the C_5H_5 ligand. NOE experiments show that the =CHR terminus is anti to the PPh_3 ligand in both diastereomers of **3**$^+X^-$ in solution. Variable-temperature ^{13}C NMR spectroscopy gives $\Delta G^{\ddagger}_{369\,K}$ = 16.4 kcal/mol for Re–(C═C) rotation in the ethylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$. Also described are substitution reactions of **3**$^+X^-$, a detailed analysis of the spectroscopic properties of **3**$^+X^-$, and high 1,4-asymmetric induction in the reaction of **4c** and CF_3SO_3D to give **3c**-$d_1{}^+CF_3SO_3^-$.

Introduction

There is an extensive chemistry of transition-metal alkene complexes, the history of which dates back to the origins of organometallic chemistry.[1] There are also numerous chiral metal complexes that catalyze asymmetric reactions of alkenes.[2] Over the last dozen years, a variety of chiral-at-metal alkene complexes have been synthesized in optically active form.[3,4] However, applications of such complexes in asymmetric organic synthesis have not been extensively developed. For example, it should be possible to design chiral transition-metal receptors that can selectively bind and activate one enantioface of prochiral alkenes.

We have undertaken an extensive study of easily resolved,[5] chiral-at-metal rhenium complexes of the formula $[(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(L)]^+X^-$.[6] The pyramidal 16-valence-electron fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ possesses the high-lying d donor orbital shown in I (Scheme I),[7] and hence the Dewar–Chatt–Duncanson model[8] predicts the formation of alkene complexes with the general Re—C═C conformation in II. Monosubstituted alkenes $H_2C{=}CHR$ can give two diastereomeric complexes (*RS,SR* and *RR,SS*)[9] that differ in the alkene enantioface bound

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(6) Some leading references: (a) O'Connor, E. J.; Kobayashi, M.; Floss, H. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 4837. (b) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *Ibid.* **1987**, *109*, 7688. (c) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *Ibid.* **1988**, *110*, 6096. (d) Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1154. (e) Winter, C. H.; Veal, W. R.; Garner, C. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 4766. (f) Garner, C. M.; Méndez Quirós, N.; Kowalczyk, J. J.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *Ibid.*, in press. (g) Dalton, D. M.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Arif, A. M.; Glaydsz, J. A. Manuscript in preparation.
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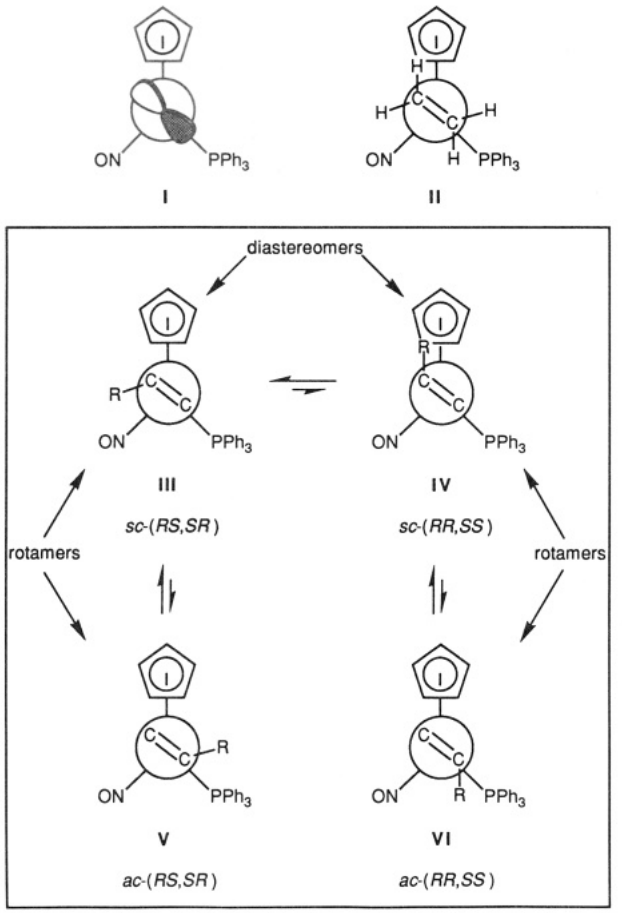
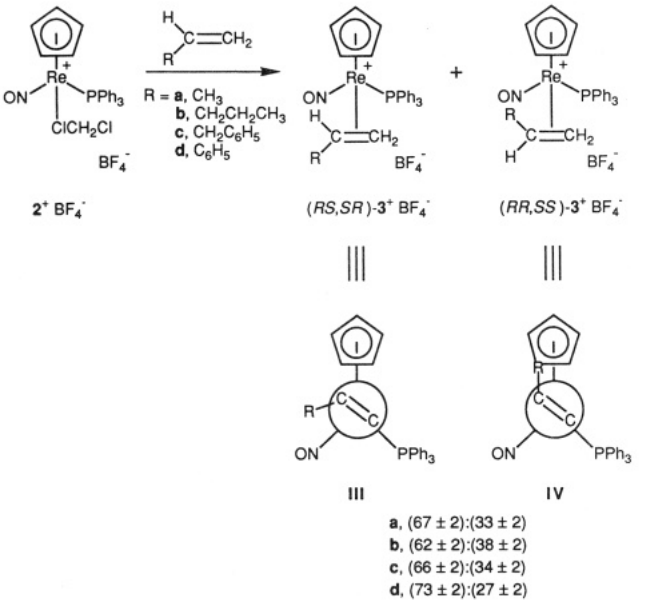
Scheme I. HOMO of the pyramidal 16-Valence-Electron Rhenium Fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I), Idealized Structure of the Ethylene Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+$ (II), and Possible Structures of Monosubstituted Alkene Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+$ (III–VI)[a]



[a] Legend: III, more stable rotamer of more stable diastereomer; IV, more stable rotamer of less stable diastereomer; V, less stable rotamer of more stable diastereomer; VI, less stable rotamer of less stable diastereomer.

to rhenium. For each diastereomer, two Re–(C=C) rotamers are possible (*sc* and *ac*).[10] Those of the *RS,SR* diastereomer are shown as III and V in Scheme I, and those of the *RR,SS* diastereomer are shown as IV and VI. We anticipated that the more stable rotamer of each diastereomer would be that with the substituted =CHR terminus opposite to the bulky PPh_3 ligand (III, IV). Note that, in III, the alkene substituent projects at the small nitrosyl ligand. In IV, the alkene substituent projects at the medium-sized cyclopentadienyl ligand. Hence, we anticipated that the *RS,SR* diastereomer would be the more stable and set out to determine whether one monosubstituted alkene enantioface might bind selectively to the $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ fragment.

Scheme II. Synthesis of the Monosubstituted Alkene Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+BF_4^-$ ($3^+BF_4^-$) from the Dichloromethane Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ ($2^+BF_4^-$)



In this paper, we report (1) high-yield reactions of the easily generated dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ and monosubstituted alkenes that give the complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+BF_4^-$ as ≃2:1 mixtures of *RS,SR* and *RR,SS* diastereomers, (2) reactions of the allyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH{=}CHR')$ and electrophiles (E^+X^-) that give monosubstituted alkene complexes as similar mixtures of diastereomers, and with high 1,4-asymmetric induction, (3) the detailed spectroscopic characterization of these complexes, (4) a crystal structure of an independently prepared *RR,SS* diastereomer, (5) NMR data that establish the preferred Re–(C=C) rotamers of the alkene complexes in solution, and their rotational barriers, (6) substitution and isomerization reactions that show the *RS,SR* diastereomers to be considerably more stable ($K_{eq} \simeq 95/5$), and (7) an analysis of the stereoselectivity in the preceding transformations. A portion of this study has been communicated.[11]

Results

1. Synthesis of Alkene Complexes from Monosubstituted Alkenes. The methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (1)[12] and $HBF_4{\cdot}O(C_2H_5)$ were reacted in CH_2Cl_2 at −78 °C to give the substitution-labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ ($2^+BF_4^-$) as previously reported.[13] Subsequent addition of excess (a) propene (130 psi), (b) 1-pentene, (c) allylbenzene, and (d) styrene gave alkene

(9) (a) The absolute configuration at rhenium is specified first and is assigned according to the Baird–Sloan modification of the Cahn–Ingold–Prelog priority rules. The $\eta^5\text{-}C_5H_5$ and $H_2C{=}CHR$ ligands are considered pseudoatoms of atomic numbers 30 and 12, respectively. This gives the following sequence: $\eta^5\text{-}C_5H_5 > PPh_3 > H_2C{=}CHR > NO > CHRR'$ (Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1). (b) The absolute configuration of the alkene-based stereogenic unit in 3^+X^- is assigned by drawing the complex as a metallacyclopropane and applying the Cahn–Ingold–Prelog rules to the resulting asymmetric carbon (Paiaro, G.; Panunzi, A. *J. Am. Chem. Soc.* **1964**, *88*, 5148). (c) Prefixes + and − refer to rotations at 589 nm. Measurements are in $CHCl_3$ with c = 0.8–1.2 mg/mL unless noted.

(10) (a) A synclinal (*sc*) conformer is one in which the highest priority[9a] substituent on the rhenium ($\eta^5\text{-}C_5H_5$) and the C=C centroid (=*C*HR) 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 idealized structures III/IV and V/VI (Scheme I) are 45° and 135°, respectively. See section E-5.6, p 24, of: *Pure Appl. Chem.* **1976**, *45*, 11. (b) A reviewer has noted that the terms exo and endo are sometimes used to designate alkene complex rotamers. However, these terms are also used to designate alkene complex diastereomers.[10c] (c) McNally, J. P.; Cooper, N. J. *Organometallics* **1988**, *7*, 1704.

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(13) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207.

complexes (*RS,SR*)- and (*RR,SS*)-[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CHR)]$^+BF_4^-$ ((*RS,SR*)- and (*RR,SS*)-**3a–d**$^+BF_4^-$) as (73–62):(27–38) mixtures of diastereomers, as assayed by ^{1}H and ^{31}P NMR spectra of the crude reaction mixtures (Scheme II). Hence, the diastereomers anticipated to be more stable (Scheme I) predominated, but not to a great extent.

Workup of the (*RS,SR*)-/(*RR,SS*)-**3a–d**$^+BF_4^-$ reaction mixtures (Experimental Section) gave analytically pure powders (89–91%) with identical diastereomer ratios. The styrene complex diastereomers (*RS,SR*)-/(*RR,SS*)-**3d**$^+BF_4^-$ were separable by silica gel chromatography. Alkene complexes (*RS,SR*)-/(*RR,SS*)-**3a–d**$^+BF_4$ were characterized spectroscopically as described below. Their properties closely matched those of the corresponding hexafluorophosphate salts (*RS,SR*)-**3a**$^+PF_6^-$, (*RR,SS*)-**3a**$^+PF_6^-$, (*RS,SR*)-**3d**$^+PF_6^-$, and (*RR,SS*)-**3d**$^+PF_6^-$, which were independently prepared by β-hydride abstraction from secondary alkyl complex precursors and stereochemically characterized previously.[14]

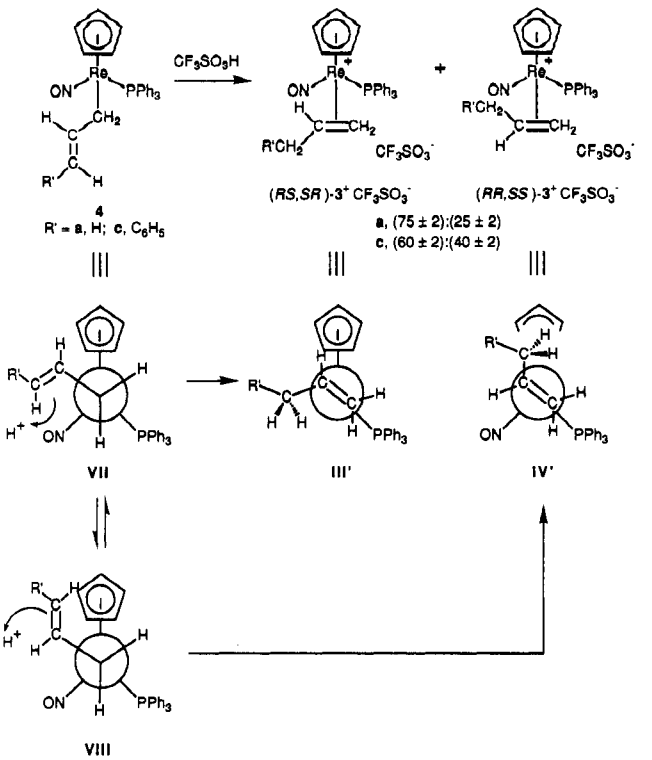
In separate experiments, styrene complex diastereomers (*RS,SR*)-**3d**$^+BF_4^-$ and (*RR,SS*)-**3d**$^+BF_4^-$ were treated with a chiral NMR shift reagent, (+)-Eu(hfc)$_3$ (3–4 equiv, CD_2Cl_2). The cyclopentadienyl ^{1}H NMR resonances of each pair of enantiomers exhibited near-base-line resolution ($\Delta\delta \simeq 0.03$ ppm), which increased to base-line resolution ($\Delta\delta \simeq 0.18$ ppm) over a period of hours. Similar experiments were conducted on mixtures of *RS,SR*/*RR,SS* diastereomers of propene, pentene, and allylbenzene complexes **3a–c**$^+BF_4^-$. Comparable enantiomer resolution was observed.

Next, the optically active methyl complex (–)-(*R*)-**1**[5a] was similarly converted to the optically active styrene complex (–)-(*SR*)-/(*SS*)-**3d**$^+BF_4^-$ ((74 ± 2):(26 ± 2)).[9c] The diastereomers were separated chromatographically ([α]$^{25}_{589}$ –357 ± 7, –120 ± 6°; c = 0.44 mg/mL, CH_2Cl_2), and shift reagent analysis showed no trace of the opposite enantiomers. When (–)-(*SR*)-**3d**$^+BF_4^-$ was spiked with 2% of the racemate, giving a sample of ≃98% ee, the enantiomer (+)-(*RS*)-**3d**$^+BF_4^-$ was readily observed. Hence, the optical purities of (–)-(*SR*)- and (–)-(*SS*)-**3d**$^+BF_4^-$ are >98% ee.

The optically active methyl complex (+)-(*S*)-**1** was similarly converted to the optically active propene complex (+)-(*RS*)-/(*RR*)-**3a**$^+BF_4^-$ (89%, (67 ± 2):(33 ± 2), [α]$^{23}_{589}$ 115°) and the optically active allylbenzene complex (+)-(*RS*)-/(*RR*)-**3c**$^+BF_4^-$ (85%, (66 ± 2):(34 ± 2), [α]$^{23}_{589}$ 86°).[9c] A number of related reactions have been shown to proceed with retention of configuration at rhenium, and absolute configurations of all preceding optically active alkene complexes have been assigned accordingly.[6f,g,13] The signs of [α]$_{589}$, which nearly always correlate with the absolute configuration at rhenium,[5] further support this conclusion.

2. Synthesis of Alkene Complexes from η^1-Allyl Complexes. We sought alternative routes to alkene complexes **3**$^+X^-$ that might exhibit improved diastereoselectivities. Cyclopentadienyliron allyl complexes (η^5-C_5H_5)Fe(CO)$_2$(CH_2CH=CHR′) have been shown to readily undergo C_γ protonation to give the cationic alkene complexes [(η^5-C_5H_5)Fe(CO)$_2$(H_2C=CHCH_2R′)]$^+$.[15] Hence, we examined analogous protonations of the rhenium allyl complexes (η^5-C_5H_5)Re(NO)(PPh$_3$)(CHRCH=CHR′) (**4**). Complexes **4** were prepared earlier by (among other routes) *t*-BuO$^-$K$^+$ deprotonation of the "allylic" carbon of alkene complexes **3**$^+BF_4^-$.[16]

Scheme III. Synthesis of the Monosubstituted Alkene Complexes [(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CHCH_2R′)]$^+CF_3SO_3^-$ by Protonation of the η^1-Allyl Complexes (*E*)-(η^5-C_5H_5)Re(NO)(PPh$_3$)(CH_2CH=CHR′) (4)



The reaction of the allyl complex (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH_2CH=CH_2) (**4a**) and CF_3SO_3H in CD_2Cl_2 (Scheme III) was monitored by ^{1}H NMR spectroscopy at –78 °C. A (75 ± 2):(25 ± 2) mixture of the propene complex diastereomers (*RS,SR*)-/(*RR,SS*)-**3a**$^+CF_3SO_3^-$ formed in quantitative yield within 5 min. No evidence for an intermediate cationic rhenium hydride complex[13] was noted. Workup of an analogous preparative reaction gave a (75 ± 2):(25 ± 2) mixture of (*RS,SR*)-/(*RR,SS*)-**3a**$^+$-$CF_3SO_3^-$ in 92% yield. Alkene complexes isolated from allyl complexes were in all cases analytically pure (Experimental Section) and were spectroscopically characterized as described below.

Similarly, the reaction of the cinnamyl complex (*E*)-(η^5-C_5H_5)Re(NO)(PPh$_3$)(CH_2CH=CHC_6H_5) (**4c**) and CF_3SO_3H in CD_2Cl_2 at –78 °C cleanly gave a (60 ± 2):(40 ± 2) mixture of the allylbenzene complex diastereomers (*RS,SR*)-/(*RR,SS*)-**3c**$^+CF_3SO_3^-$. Workup of a preparative reaction of **4c** and the stronger acid HPF_6·Et_2O gave a (60 ± 2):(40 ± 2) mixture of (*RS,SR*)-/(*RR,SS*)-**3c**$^+PF_6^-$ in 86% yield. Hence, the diastereoselectivity of this route to alkene complexes **3**$^+X^-$ is approximately the same as that found in Scheme II.

A preparative reaction of the methallyl complex (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH_2C(CH_3)=CH_2) (**4e**)[16] and CF_3SO_3H gave the isobutylene complex [(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=C(CH_3)$_2$)]$^+CF_3SO_3^-$ (**3e**$^+CF_3SO_3^-$, 88%). The two C=C faces of isobutylene are *identical* (not enantiotopic), and consequently **3e**$^+CF_3SO_3^-$ has no diastereomer. The analogous hexafluorophosphate salt **3e**$^+PF_6^-$ has been characterized previously.[14]

We wondered whether reactions of allyl complexes **4** and bulkier electrophiles might give alkene complexes with

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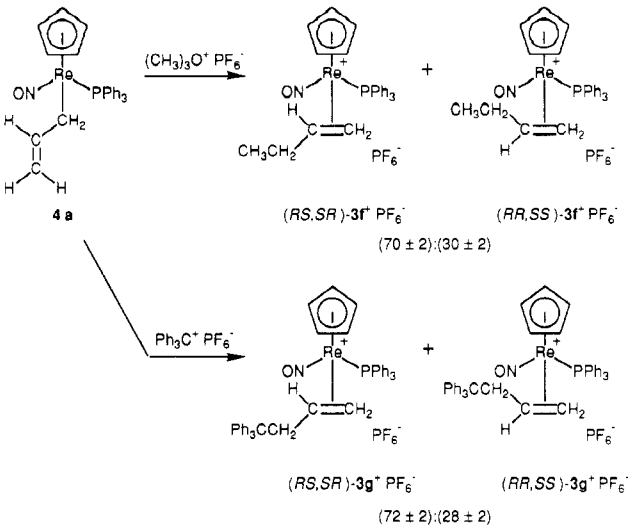
(15) Rosenblum, M. *J. Organomet. Chem.* **1986**, *300*, 191.
(16) Bodner, G. S.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *Organometallics* **1989**, *8*, 2399.

Scheme IV. Synthesis of the Monosubstituted Alkene Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2R')]^+PF_6^-$ by Alkylation of the η^1-Allyl Complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH{=}CH_2)$ (4a)



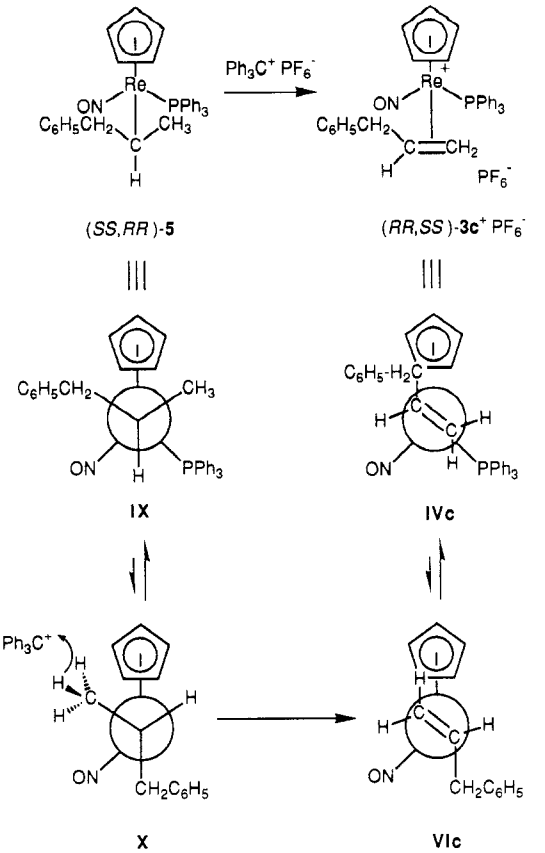
higher diastereoselectivities. Thus, reactions with alkylating agents were briefly studied (Scheme IV). First, the allyl complex **4a** was treated with $(CH_3)_3O^+PF_6^-$ (CH_2Cl_2, −15 °C). Workup gave a (70 ± 2):(30 ± 2) mixture of the 1-butene complex diastereomers (*RS,SR*)-/(*RR,SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHC_2H_5)]^+PF_6^-$ ((*RS,SR*)-/(*RR,SS*)-**3f**$^+PF_6^-$) in 88% yield.

Complex **4a** was similarly treated with $Ph_3C^+PF_6^-$ (Scheme IV). This reagent has previously been observed to act as a hydride abstractor toward the alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)$[14] and as an alkylating agent toward the vinyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CH_2)$.[6b] Interestingly, alkylation occurred exclusively to give a (72 ± 2):(28 ± 2) mixture of the 4,4,4-triphenyl-1-butene complex diastereomers (*RS,SR*)-/(*RR,SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2C(C_6H_5)_3)]^+PF_6^-$ ((*RS,SR*)-/(*RR,SS*)-**3g**$^+PF_6^-$), as assayed by ^1H NMR spectroscopy. Workup gave a (70 ± 2):(30 ± 2) mixture of diastereomers in 79% yield.

3. Other Syntheses of Alkene Complexes. We have previously reported that $Ph_3C^+PF_6^-$ effects α-hydride abstraction from the alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_2R)$ to give the alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2R)]^+PF_6^-$. However, when there is an additional C_α or C_β substituent on the alkyl ligand, β-hydride abstraction occurs to give alkene complexes.[14] Such branched-alkyl complexes are commonly prepared by multistep routes and, hence, are less attractive precursors to alkene complexes **3**$^+X^-$. However, as analyzed below, reactions of $Ph_3C^+PF_6^-$ and diastereomerically pure C_α-branched alkyl complexes are stereospecific, affording only one alkene complex diastereomer.[14]

Accordingly, the secondary alkyl complex (*SS,RR*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(CH_3)CH_2C_6H_5)$ ((*SS,RR*)-**5**) was synthesized by the diastereospecific route reported previously.[14] The reaction of (*SS,RR*)-**5** and $Ph_3C^+PF_6^-$ in CD_2Cl_2 was monitored by ^1H NMR spectroscopy at −96 °C. Hydride transfer occurred cleanly and rapidly (<5 min) to give an authentic sample of the less stable allylbenzene complex diastereomer (*RR,SS*)-**3c**$^+PF_6^-$. Some resonances were slightly broadened but sharpened as the sample was warmed. No evidence for distinct Re−(C═C) rotamers was noted. The complex (*RR,SS*)-**3c**$^+PF_6^-$ was isolated in 83% yield from an analogous preparative reaction. When samples of (*RR,SS*)-**3c**$^+PF_6^-$ were cooled,

Scheme V. Synthesis of the Allylbenzene Complex (*RR,SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2C_6H_5)]^+PF_6^-$ ((*RR,SS*)-3c**$^+PF_6^-$) by Hydride Abstraction from the Alkyl Complex (*SS,RR*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(CH_3)CH_2C_6H_5)$ ((*SS,RR*)-5)**



some ^1H NMR resonances again broadened, but no decoalescence behavior was observed.

4. Spectroscopic Characterization of Alkene Complexes. The complexes **3**$^+X^-$ were characterized by microanalysis and IR and NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) spectroscopy. As a result of substitution and equilibration reactions described below, complete spectroscopic assignments could generally be made for both diastereomers. Although the ^1H and ^{13}C NMR spectra of other salts (e.g., PF_6^-) of some alkene complexes have been previously reported, all data are included in Table I (obtained under similar conditions at uniform spectrometer fields etc.) in order to facilitate comparisons.

The IR ν_{NO} values (1715–1730 cm^{-1}), ^{31}P NMR PPh_3 chemical shifts (9.0–11.0 ppm), and ^1H and ^{13}C NMR cyclopentadienyl ligand chemical shifts (Table I: δ 5.2–5.8, 97–100 ppm) of **3**$^+X^-$ were typical of cationic $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+$ complexes. Diastereomers exhibited identical IR ν_{NO} values, and the PPh_3 ^{31}P NMR resonances were also identical or very similar (**3c**$^+X^-$, **3d**$^+BF_4^-$, **3g**$^+PF_6^-$).

The C═C ^{13}C NMR resonances and vinylic ^1H NMR resonances of **3**$^+X^-$ exhibited characteristic upfield shifts relative to those of the free alkenes.[17] The C═C resonances were assigned by analogy to shielding trends exhibited by free alkenes (═CHR downfield of ═CH_2) and

(17) (a) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981; Table 2.10. (b) Cutler, A.; Enhold, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. (c) Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73. (d) Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3155.

assignments made for related iron alkene complexes.[17d] The $=CH_2$ carbons, which are expected from Scheme I and data below to be syn to the PPh_3 ligand, exhibited larger $^2J_{CP}$ (4–6 Hz) values than the =CHR carbons (<2 Hz). Interestingly, the $=CH_2$ carbon resonances of the *RS,SR* diastereomers were slightly downfield of those of the *RR,SS* diastereomers, whereas the opposite shielding trend was observed for the =CHR resonances. The "allylic" carbon resonances of the *RR,SS* diastereomers were always slightly downfield of those of the *RS,SR* diastereomers.

The vinylic ^1H NMR resonance assignments in 3^+X^- were made on the basis of coupling constants ($^3J_{HH}$(trans) > $^3J_{HH}$(cis)) and by analogy to related alkene complexes.[14,17b-d] Several shielding trends were evident. First, the $=CH_Z$ resonances were downfield from the $=CH_E$ resonances in the *RS,SR* diastereomers but upfield in the *RR,SS* diastereomers. This indicates that the geminal proton that is directed anti to the cyclopentadienyl ligand in projections III and IV (Scheme I) is intrinsically deshielded relative to the other. Second, the =CHR resonances of the *RS,SR* diastereomers were downfield of those of the *RR,SS* diastereomers. Conversely, the chemical shifts of any "allylic" protons were generally at lower field in the *RR,SS* diastereomers. This indicates that the cyclopentadienyl ligand exerts a deshielding effect upon the "syn" group of the =CHR moiety (i.e., H in III, R in IV).

Interestingly, the larger geminal proton $^3J_{HP}$ value is found (when resolved) with $=CH_Z$ in the *RS,SR* diastereomers and $=CH_E$ in the *RR,SS* diastereomers. In each case, this corresponds to the proton that is directed anti to the cyclopentadienyl ligand in III and IV. On the basis of distortions observed in the crystal structure described below, this geminal proton should more closely eclipse the PPh_3 ligand than the other. Finally, the shielding trends noted above for "allylic" substituents suggest that the 32.7 ppm and δ 2.23 ^{13}C and ^1H NMR resonances of the isobutylene complex $\mathbf{3e}^+CF_3SO_3^-$ are associated with the methyl group that would be syn to the cyclopentadienyl ligand as in IV (pro-*S*).[9b]

5. Solid-State Structure of Allylbenzene Complex (*RR,SS*)-3c$^+$PF$_6^-$. We sought to verify the general structures anticipated for the alkene complexes 3^+X^- (Scheme I). We elected to structurally characterize one of the *RR,SS* diastereomers, as we thought that they might be more subject to steric structural perturbations and exhibit a smaller energy difference between the two idealized Re–(C=C) rotamers (IV, VI). Hence, X-ray data were acquired on (*RR,SS*)-$\mathbf{3c}^+PF_6^-$ as summarized in Table II. Refinement yielded the structures shown in Figure 1. Atomic coordinates, and key bond lengths and angles, are given in Tables III and IV. The remaining bond lengths and angles, anisotropic thermal parameters, and calculated and observed structure factors were included in the supplementary material of our preliminary communication.[11]

The angle of the Re—C=C plane with the Re—P vector was found to be 20°. In comparison to idealized structure IV, where this angle is 0°, the C=C moiety is rotated in a counterclockwise direction, moving the =CHR terminus further from the cyclopentadienyl ligand. The angle of the Re—C=C plane with the plane defined by the cyclopentadienyl centroid, rhenium, and the C=C centroid was 65°. The Re—C=C unit exhibited nearly equal Re—C=C bond angles (72.1 (11), 71.6 (11)°) and Re—C bond lengths (2.241 (18), 2.246 (19) Å), indicating negligible "slippage" of the alkene ligand. The distances between the benzylic

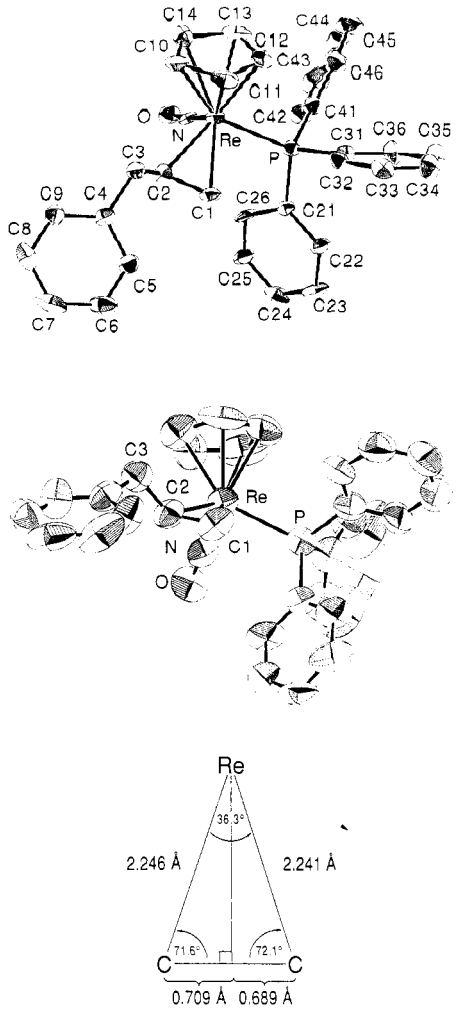


Figure 1. Structure of the cation of the allylbenzene complex (*RR,SS*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=$CHCH_2C_6H_5$)]$^+PF_6^-$ ((*RR,SS*)-$\mathbf{3c}^+PF_6^-$): (top) numbering diagram; (middle) Newman-type projection; (bottom) view of the Re—C=C plant.

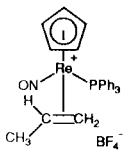
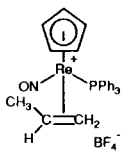
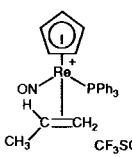
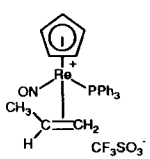
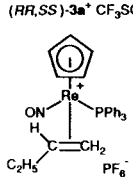
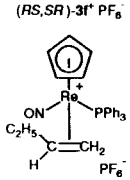
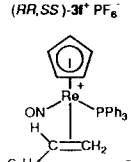
carbon (C3) and the nearest cyclopentadienyl ligand (C10, C11) were 3.13–3.41 Å. The C2—C3 bond was clearly bent out of the π nodal plane of the free alkene. In order to quantify this feature, a plane was defined that contained C2 and C1 but was perpendicular to the Re—C=C plane. The angle of the C2—C3 bond with this plane was 25°, as opposed to the 0° angle that would be expected from a free alkene.

6. Solution Structures and Dynamics of Alkene Complexes. We sought to test the assumption that Re–(C=C) rotamers of the types shown in Scheme I are readily interconvertible. Hence, the previously reported ethylene complex[18] [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=CH_2)]$^+PF_6^-$ was studied by variable-temperature ^{13}C NMR spectroscopy. Two resonances were observed for the ethylene ligand carbons in $C_2D_2Cl_4$ at 30 °C (31.9, 23.4 ppm (s); $\Delta\nu$ 631.1 Hz; 75.4 MHz). The downfield resonance was slightly broader ($w_{1/2}$ = 5.1, 2.3 Hz). As shown in Figure 2, the resonances further broadened upon warming and coalesced at 96.2 °C. At higher temperatures, a new resonance emerged (28.6 ppm, 140 °C). These data indicate that $\Delta G^*_{369\,K}$ = 16.4 kcal/mol for the process rendering the two carbons equivalent.

Since neither ethylene ligand ^{13}C NMR resonance exhibited a resolved J_{CP} involving the PPh_3 ligand, a disso-

(18) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.

Table I. ^1H and ^{13}C NMR Characterization of Rhenium Alkene Complexes

complex	^1H NMR[a], δ					$^{13}C\{^1H\}$ NMR,[b] ppm				
	C_5H_5	$=CH_Z$	$=CH_E$	$=CRH$	other	C_5H_5	$=CH_2$	$=CHR$	other	PPh_3
 (*RS,SR*)-**3a**$^+$ BF_4^-	5.75 (s)	2.66 (ddd, J_{HH} = 4, 15, J_{HP} = 11)	2.41 (ddd, J_{HH} = 4, 10, J_{HP} = 6)	4.64 (m)	2.09 (d, J_{HH} = 6, CH_3), 7.60–7.38 (m, 3 C_6H_5)	96.7 (s)[c]	40.7 (d, J = 6)	47.4 (s)	23.3 (s, CH_3)	133.2 (d, J = 10, *o*), 132.2 (d, J = 3, *p*), 130.3 (d, J = 59, *i*), 129.6 (d, J = 11, *m*)
 (*RR,SS*)-**3a**$^+$ BF_4^-	5.70 (s)	2.01 (ddd, J_{HH} = 4, 14, J_{HP} = 4)	2.90 (m)	3.60 (m)	2.22 (d, J_{HH} = 6, CH_3)	97.9 (s)[c]	39.2 (d, J = 6)	49.8 (s)	24.1 (s, CH_3)	
 (*RS,SR*)-**3a**$^+$ $CF_3SO_3^-$	5.72 (s)	2.56 (ddd, J_{HH} = 4, 14, J_{HP} = 11)	2.37 (m)	4.54 (m)	2.10 (d, J_{HH} = 6, CH_3), 7.60–7.36 (m, 3 C_6H_5)	98.4 (s)	40.4 (d, J = 5)	47.1 (s)	23.1 (s, CH_3)	134.7 (d, J = 9, *o*), 133.6 (s, *p*), 132.1 (d, J = 59, *i*), 130.9 (d, J = 9, *m*)
 (*RR,SS*)-**3a**$^+$ $CF_3SO_3^-$	5.66 (s)	1.97 (ddd, J_{HH} = 4, 14, J_{HP} = 4)	3.02 (ddd, J_{HH} = 4, 10, J_{HP} = 14)	3.66 (m)	2.27 (d, J_{HH} = 6, CH_3)	99.4 (s)	39.7 (d, J = 4)	50.8 (s)	24.5 (s, CH_3)	
 (*RS,SR*)-**3f**$^+$ PF_6^-	5.75 (s)	2.46 (ddd, J_{HH} = 4, 15, J_{HP} = 11)	2.28 (m)	4.55 (m)	1.49 (m, CH_2), 1.19 (t, J_{HH} = 7, CH_3), 7.60–7.39 (m, 3 C_6H_5)	98.4 (s)	38.5 (d, J = 5)	54.4 (s)	32.0 (s, CH_2), 17.9 (s, CH_3)	134.6 (d, J = 11, *o*), 133.5 (s, *p*), 132.0 (d, J = 59, *i*), 130.8 (d, J = 11, *m*)
 (*RR,SS*)-**3f**$^+$ PF_6^-	5.69 (s)	2.10 (ddd, J_{HH} = 4, 14, J_{HP} = 4)	2.95 (ddd, J_{HH} = 4, 9, J_{HP} = 14)	3.63 (m)	1.66 (m, CH_2), 1.26 (t, J_{HH} = 7, CH_3)	99.0 (s)	37.9 (d, J = 5)	57.5 (s)	33.6 (s, CH_2), 20.8 (s, CH_3)	
 (*RS,SR*)-**3b**$^+$ BF_4^-	5.74 (s)	2.52 (7)	2.33 (m)	4.42 (m)	1.54 (m, CH_2CH_2), 0.98 (t, J_{HH} = 7, CH_3), 7.58–7.23 (m, 3 C_6H_5)	96.9 (s)[c]	38.7 (d, J = 6)	51.9 (s)	40.6 (s, $=CHCH_2$), 27.1 (s, CH_2CH_3), 14.1 (s, CH_3)	133.1 (d, J = 10, *o*), 132.2 (d, J = 3, *p*),[d] 129.6 (d, J = 12, *m*)

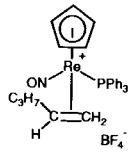
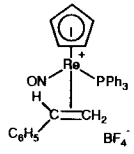
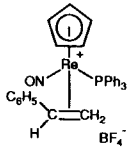
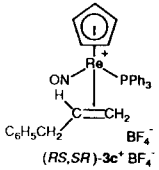
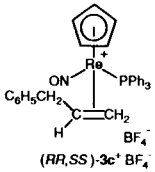
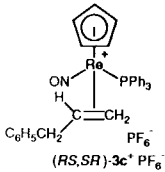
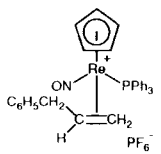
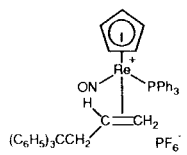
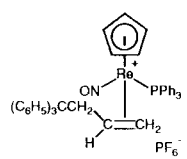
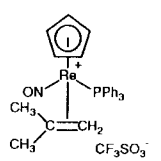
 (*RR,SS*)-**3b**$^+$ BF_4^-	5.67 (s)	2.08 (ddd, J_{HH} = 4, 14, J_{HP} = 4)	3.00 (ddd, J_{HH} = 4, 9, J_{HP} = 14)	3.51 (m)	1.70 (m, CH_2CH_2), 1.02 (t, J_{HH} = 7, CH_3)	97.7 (s)[c]	38.3 (d, J = 6)	55.1 (s)	42.0 (s, =**C**HCH$_2$), 29.6 (s, **C**H$_2$CH$_3$), 14.2 (s, **C**H$_3$)	
 (*RS,SR*)-**3d**$^+$ BF_4^-	5.77 (s)[e]	3.05 (ddd, J_{HH} = 5, 11, J_{HP} = 11)	2.67 (ddd, J_{HH} = 5, 11, J_{HP} = 5)	5.59 (ddd, J_{HH} = 11, 11 J_{HP} = 1)	7.70–6.92 (m, 4 C_6H_5)	97.5 (s)[e]	33.7 (d, J = 5)	49.7 (s)	CC_6H_5 at 140.0 (s, *i*), 128.6 (s), 128.1 (s), 126.9 (s, *p*)	133.3 (d, J = 10, *o*), 132.7 (s, *p*),[d] 129.9 (d, J = 11, *m*)
 (*RR,SS*)-**3d**$^+$ BF_4^-	5.22 (s)[e]	2.69 (ddd, J_{HH} = 5, 14, J_{HP} = 4)	3.14 (ddd, J_{HH} = 5, 9, J_{HP} = 14)	4.75 (dd, J_{HH} = 9, J_{HP} = 14)	7.70–7.20 (m, 4 C_6H_5)	99.9 (s)[e]	32.1 (d, J = 6)	53.5 (s)	CC_6H_5 at 141.9 (s, *i*), 129.7 (s), 129.5 (s), 128.8 (s, *p*)	133.4 (d, J = 10, *o*), 132.8 (s, *p*),[d] 130.1 (d, J = 11, *m*)
 (*RS,SR*)-**3c**$^+$ BF_4^-	5.58 (s)	2.56 (ddd, J_{HH} = 4, 15, J_{HP} = 11)	2.48 (m)	4.48 (m)	3.57 (dd, J_{HH} = 14, 7, C*H*H′), 3.18 (dd, J_{HH} = 14, 7, CH*H*′), 7.60–7.37 (m, 3 C_6H_5)	96.8 (s)[c]	39.0 (d, J = 6)	52.2 (s)	44.1 (s, CH_2); CC_6H_5 at 141.2 (s, *i*), 128.8 (s), 128.3 (s), 126.9 (s, *p*)	133.2 (d, J = 10, *o*), 132.3 (d, J = 3, *p*), 131.2 (d, J = 59, *i*), 129.7 (d, J = 11, *m*)
 (*RR,SS*)-**3c**$^+$ BF_4^-	5.76 (s)	2.10 (ddd, J_{HH} = 4, 15, J_{HP} = 4)	2.96 (ddd, J_{HH} = 4, 9, J_{HP} = 14)	3.68 (m)	3.72 (dd, J_{HH} = 13, 5, C*H*H′), 2.88 (dd, J_{HH} = 13, 11, CH*H*′)	97.7 (s)[c]	36.8 (d, J = 4)	53.2 (s)	44.9 (s, CH_2)	
 (*RS,SR*)-**3c**$^+$ PF_6^-	5.52 (s)	2.59 (ddd, J_{HH} = 4, 15, J_{HP} = 11)	2.46 (m)	4.42 (m)	3.56 (dd, J_{HH} = 14, 7, C*H*H′), 3.19 (dd, J_{HH} = 14, 7, CH*H*′), 7.60–7.33 (m, 3 C_6H_5)	96.8 (s)	38.9 (d, J = 6)	52.4 (s)	44.1 (s, CH_2); CC_6H_5 at 141.2 (s, *i*), 128.8 (s), 128.3 (s), 126.9 (s, *p*)	133.2 (d, J = 10, *o*), 132.3 (d, J = 3, *p*),[d] 129.7 (d, J = 11, *m*)

Table I (Continued)

complex	^{1}H NMR[a], δ					^{13}C{^{1}H} NMR,[b] ppm				
	C_5H_5	$=CH_Z$	$=CH_E$	$=CRH$	other	C_5H_5	$=CH_2$	$=CHR$	other	PPh_3
 (*RR,SS*)-**3c**$^+$ PF_6^-	5.73 (s)	2.23 (ddd, J_{HH} = 4, 15, J_{HP} = 4)	2.99 (ddd, J_{HH} = 4, 9, J_{HP} = 14)	3.64 (m)	3.73 (dd, J_{HH} = 13, 7, C*H*H′), 2.84 (dd, J_{HH} = 13, 9, CH*H*′)	98.7 (s)	37.5 (d, J = 5)	53.7 (s)	45.6 (s, CH_2); CC_6H_5 at 144.8 (s, *i*), 129.5 (s), 129.5 (s), 127.5 (s, *p*)	134.1 (d, J = 10, *o*), 133.0 (s, *p*), 131.2 (*i*),[d] 130.3 (d, J = 11, *m*)
 (*RS,SR*)-**3g**$^+$ PF_6^-	5.53 (s)	2.79 (ddd, J_{HH} = 4, 15, J_{HP} = 11)	2.62 (m)	4.49 (m)	3.75 (dd, J_{HH} = 14, 7, C*H*H′), 3.31 (dd, J_{HH} = 14, 7, CH*H*′), 7.62–7.14 (m, 6 C_6H_5)	98.6 (s)	40.0 (d, J = 5)	50.8 (s)	42.0 (s, CH_2); 61.1 (s, $C(C_6H_5)_3$); CC_6H_5 at 149.1 (s, *i*)[f]	134.7 (d, J = 9, *o*), 133.8 (s, *p*), 131.8 (d, J = 59, *i*), 131.1 (d, J = 11, *m*)
 (*RR,SS*)-**3g**$^+$ PF_6^-	5.68 (s)	2.42 (ddd, J_{HH} = 4, 14, J_{HP} = 5)	3.16 (ddd, J_{HH} = 4, 10, J_{HP} = 14)	3.54 (m)	3.92 (dd, J_{HH} = 13, 8, C*H*H′), 2.97 (dd, J_{HH} = 13, 10, CH*H*′)	99.4 (s)	38.0 (d, J = 5)	54.3 (s)	46.1 (s, CH_2); 62.7 (s, $C(C_6H_5)_3$); CC_6H_5 at 145.7 (s, *i*)[f]	
 **3e**$^+$ $CF_3SO_3^-$	5.59 (s)	2.87 (dd, J_{HH} = 4, J_{HP} = 13)	2.32 (dd, J_{HH} = 4, J_{HP} = 6)		2.23 (br s, CH_3), 2.16 (br s, CH′$_3$), 7.67–7.28 (m, 3 C_6H_5)	98.3 (s)	45.1 (d, J = 4)	71.1 (s)	32.7 (s, CH_3), 31.9 (s, CH′$_3$)	133.9 (d, J = 11, *o*), 132.9 (s, *p*), 130.7 (d, J = 58, *i*), 130.2 (d, J = 11, *m*)

[a] ^{1}H NMR spectra were taken at 300 MHz in CD_2Cl_2 at ambient probe temperature and referenced to $CHDCl_2$ (δ 5.32) unless noted. All couplings (J) are in Hz. The geminal protons of the alkene ligand that are cis and trans to the substituent are designated $=CH_Z$ and $=CH_E$, respectively. These assignments were accidentally reversed for (*RS,SR*)-**3d**$^+PF_6^-$ in Table IV of ref 14. [b] ^{13}C NMR spectra were taken at 75 MHz in CD_3CN at ambient temperature and referenced to CD_3CN (1.7 ppm) unless noted. All couplings (J) are to ^{31}P and are in Hz. Assignments of ipso (*i*), para (*p*), meta (*m*), and ortho (*o*) carbon resonances were made as described in footnote *c* of Table I in: Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956. [c] In $CDCl_3$ and referenced in internal $(CH_3)_4Si$. [d] Ipso carbon not located, or one line of doublet obscured. [e] In $C_2D_4Cl_2$ and referenced to $(C_2HD_3Cl_2$ (δ 3.72) and $C_2D_4Cl_2$ (43.6 ppm). [f] Other phenyl carbons not resolved.

Table II. Summary of Crystallographic Data for (*RR,SS*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2=$CHCH_2C_6H_5$)]$^+PF_6^-$ ((*RR,SS*)-3c$^+PF_6^-$)

molecular formula	$C_{32}H_{30}F_6NOP_2Re$
fw	806.74
cryst syst	monoclinic
space group	$C2/c$
cell dimens	
a, Å	19.828 (6)
b, Å	13.782 (2)
c, Å	24.168 (3)
β, deg	93.18 (2)
V, Å^3	6594.4
Z	8
d_{calcd}, g/cm^3 (15 °C)	1.625
d_{obsd}, g/cm^3 (22 °C)	1.62
cryst dimens, mm	0.22 × 0.30 × 0.32
radiation, Å	λ(Mo Kα), 0.710 73
data collection method	θ-2θ
scan speed, deg/min	2.0
range of indices (hkl)	0 to 23, 0 to 16, −28 to 28
scan range	$K\alpha_1$ − 1.0 to $K\alpha_2$ + 1.0
no. of reflns between stds	97
total no. of unique data	4626
no. of obsd data, $I > 3\sigma(I)$	3102
abs coeff (μ), cm^{-1}	38.88
min abs cor	0.817
max abs cor	0.968
no. of variables	388
$R = \sum(\|\|F_o\| - \|F_c\|\|)/\sum\|F_o\|$	0.062
$R_w = \sum(\|\|F_o\| - \|F_c\|\|)w^{1/2}/\sum\|F_o\|w^{1/2}$	0.076
goodness of fit	3.69
Δ/σ (max)	0.039
$\Delta\rho$ (max), e/Å^3	1.19 (1.09 Å from Re)

Table III. Atomic Coordinates of Non-Hydrogen Atoms in (*RR,SS*)-3c$^+PF_6^-$

atom	x	y	z
Re	0.1923 (0)	0.1488 (0)	0.1764 (0)
P	0.1102 (3)	0.1108 (4)	0.1017 (2)
N	0.1781 (7)	0.0362 (12)	0.2053 (6)
O	0.1745 (7)	−0.0434 (11)	0.2238 (6)
C1	0.1056 (10)	0.2394 (15)	0.2019 (9)
C2	0.1506 (11)	0.2281 (13)	0.2481 (8)
C3	0.1839 (10)	0.3105 (15)	0.2772 (8)
C4	0.1407 (11)	0.3506 (14)	0.3224 (9)
C5	0.0759 (13)	0.3889 (18)	0.3097 (10)
C6	0.0373 (14)	0.4229 (22)	0.3485 (16)
C7	0.0587 (18)	0.4149 (21)	0.4039 (16)
C8	0.1239 (19)	0.3780 (20)	0.4182 (10)
C9	0.1623 (12)	0.3442 (18)	0.3765 (10)
C10	0.2937 (11)	0.2177 (20)	0.2053 (11)
C11	0.2651 (13)	0.2752 (16)	0.1580 (14)
C12	0.2624 (13)	0.2110 (24)	0.1116 (10)
C13	0.2887 (13)	0.1184 (20)	0.1316 (15)
C14	0.3070 (13)	0.1284 (20)	0.1907 (11)
C21	0.0249 (10)	0.0832 (13)	0.1220 (8)
C22	0.0173 (12)	0.0177 (18)	0.1669 (10)
C23	−0.0424 (16)	−0.0063 (20)	0.1800 (10)
C24	−0.1001 (14)	0.0260 (20)	0.1540 (12)
C25	−0.0944 (13)	0.0982 (20)	0.1122 (13)
C26	−0.0318 (13)	0.1208 (17)	0.0958 (9)
C31	0.0988 (10)	0.1974 (15)	0.0456 (9)
C32	0.1105 (11)	0.2944 (15)	0.0541 (8)
C33	0.0967 (13)	0.3572 (18)	0.0105 (11)
C34	0.0735 (14)	0.3525 (21)	−0.0407 (11)
C35	0.0649 (15)	0.2288 (21)	−0.0496 (11)
C36	0.0745 (13)	0.1663 (16)	−0.0049 (9)
C41	0.1378 (12)	0.0015 (16)	0.0667 (9)
C42	0.1124 (13)	−0.0911 (17)	0.0798 (11)
C43	0.1329 (20)	−0.1741 (23)	0.0555 (17)
C44	0.1819 (26)	−0.1670 (34)	0.0179 (23)
C45	0.2101 (18)	−0.0825 (36)	0.0061 (17)
C46	0.1877 (14)	0.0052 (22)	0.0305 (11)

ciative mechanism for this process could not a priori be excluded. However, deuterium labeling experiments have shown that alkene complexes (*RS,SR*)-/(*RR,SS*)-3$^+X^-$ do not undergo alkene ligand dissociation over extended periods of time at 90 °C.[19] Hence, we conclude that the ethylene ligand carbons are equivalenced by Re–(C⋯C) rotation.

We next sought to test our assumptions regarding the more stable rotamer of each diastereomer of 3$^+BF_4^-$.

Table IV. Key Bond Lengths (Å) and Angles (deg) in (*RR,SS*)-3c$^+PF_6^-$

Re–P	2.419 (6)	Re–N	1.731 (17)
N–O	1.189 (18)	Re–C1	2.241 (18)
Re–C2	2.246 (19)	C1–C2	1.398 (26)
C2–C3	1.473 (25)	C3–C4	1.529 (27)
C4–C5	1.407 (29)	C4–C9	1.355 (27)
C5–C6	1.330 (33)	C6–C7	1.387 (43)
C7–C8	1.414 (39)	C8–C9	1.377 (33)
Re–C10	2.297 (26)	Re–C11	2.321 (20)
Re–C12	2.315 (22)	Re–C13	2.286 (22)
Re–C14	2.297 (26)	P–C21	1.827 (20)
P–C31	1.812 (21)	P–C41	1.826 (21)
C10–C11	1.477 (34)	C10–C14	1.311 (32)
C11–C12	1.428 (34)	C12–C13	1.452 (36)
C13–C14	1.460 (36)		
P–Re–N	89.3 (5)	Re–N–O	173.7 (14)
N–Re–C1	104.1 (8)	P–Re–C1	80.3 (6)
N–Re–C2	92.8 (7)	P–Re–C2	114.8 (6)
Re–C1–C2	72.1 (11)	Re–C2–C1	71.6 (11)
C1–C2–C3	123.0 (17)	C2–C3–C4	111.5 (17)
C3–C4–C9	120.4 (20)	C3–C4–C5	121.3 (19)
C4–C9–C8	121.7 (24)	C4–C5–C6	122.2 (25)
C5–C6–C7	119.7 (29)	C5–C4–C9	118.2 (21)
C7–C8–C9	118.6 (26)	C6–C7–C8	119.4 (26)
C11–C10–C14	111.7 (23)	C10–C11–C12	105.8 (21)
C12–C13–C14	108.0 (23)	C11–C12–C13	106.6 (24)
C13–C14–C10	108.0 (23)	Re–P–C21	116.1 (6)
Re–P–C31	117.9 (7)	Re–P–C41	108.5 (7)

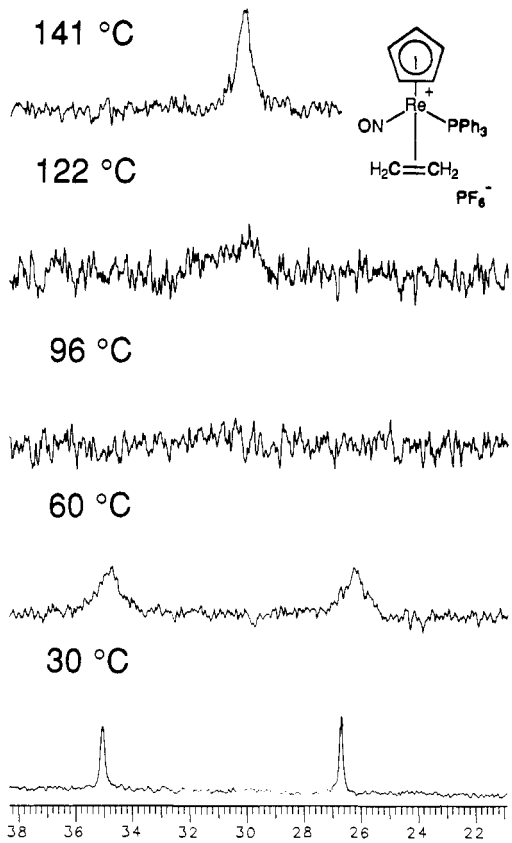
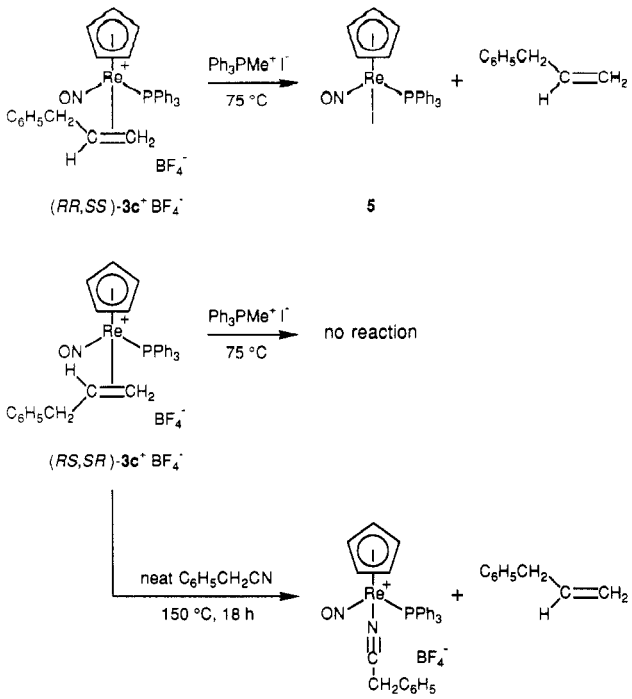


Figure 2. Variable-temperature ^{13}C NMR spectra of the ethylene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=CH_2)]$^+PF_6^-$ (ppm, $CDCl_2CDCl_2$, ethylene carbon region).

(19) Peng, T.-S.; Gladysz, J. A. Submitted for publication.

Scheme VI. Representative Alkene Ligand Substitution Reactions



Hence, in a difference NOE experiment,[20,21] the cyclopentadienyl ligand ^{1}H NMR resonance of the propene complex (*RS,SR*)-**3a**$^+$$BF_4^-$ was irradiated. Only the =C*H*R resonance exhibited an enhancement (5.0%), consistent with the dominance of rotamer III in solution (Scheme I). Analogous behavior was exhibited by the allylbenzene complex (*RS,SR*)-**3c**$^+$$BF_4^-$ (4.8% enhancement of the =C*H*R resonance). Next, the cyclopentadienyl ligand ^{1}H NMR resonance of (*RR,SS*)-**3a**$^+$$BF_4^-$ (minor component of a (67 ± 2):(33 ± 2) mixture of diastereomers) was irradiated. Only the $-CH_3$ resonance exhibited an enhancement (5.6%), consistent with the dominance of rotamer IV in solution (Scheme I).

7. Displacement of Alkene Ligands. Alkene ligands are readily displaced from the cationic iron complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(H_2C{=}CHR)]^+X^-$.[15] Hence, we sought to examine similar substitution reactions of rhenium complexes **3**$^+X^-$. First, a (66 ± 2):(34 ± 2) mixture of the diastereomeric allylbenzene complexes (*RS,SR*)-/(*RR,SS*)-**3c**$^+$$BF_4^-$ and the iodide salt $Ph_3PCH_3^+I^-$ (3.0 equiv) were reacted in C_6H_5Cl at 75 °C. Clean conversion of the minor diastereomer to the previously characterized iodide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**5**,[22] Scheme VI) slowly occurred, as assayed by ^{31}P NMR spectroscopy. After 2 days, the area ratio of the (*RS,SR*)-**3c**$^+$$BF_4^-$/(*RR,SS*)-**3c**$^+$$BF_4^-$/**5** ^{31}P NMR resonances was (64 ± 2):(5 ± 2):(31 ± 2). After 3 days, the ratio was (66 ± 2):(<1):(34 ± 2).

The complexes (*RS,SR*)-/(*RR,SS*)-**3c**$^+$$BF_4^-$ and the cyanide salt $(C_2H_5)_4N^+CN^-$ (1.2 equiv) were reacted in C_6H_5Cl at room temperature, and ^{31}P NMR spectra were periodically recorded. Over the course of 12 h, the minor diastereomer slowly converted to a mixture of the previously characterized cyanide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ (**6**, major), the cinnamyl complex **4a** (minor), and several lesser products.

An authentic sample of the optically active phenylacetonitrile complex (+)-(*S*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_2C_6H_5)]^+BF_4^-$ ((+)-(*S*)-**7**$^+$$BF_4^-$, $[\alpha]^{23}_{589}$ 226°)[9c] was prepared in a manner analogous to that for racemic **7**$^+$$PF_6^-$ and the optically active 2-phenylbutyronitrile complexes described previously.[13] Next, a (67 ± 2):(33 ± 2) mixture of the optically active allylbenzene complex diastereomers (+)-(*RS*)-/(*RR*)-**3c**$^+$$BF_4^-$ was heated at 150 °C in neat phenylacetonitrile. Complete conversion of **7**$^+$$BF_4^-$ occurred over the course of 18 h (Scheme VI). Workup gave **7**$^+$$BF_4^-$ that was nearly racemic (91%, $[\alpha]^{23}_{589}$ 35°, 15% ee). An analogous reaction of a (67 ± 2):(33 ± 2) mixture of the optically active propene complex diastereomers (+)-(*RS*)-/(*RR*)-**3a**$^+$$BF_4^-$ gave **7**$^+$$BF_4^-$ of 13% ee.

The preceding transformations show that complexes **3**$^+X^-$ undergo alkene ligand substitution much less readily than related iron complexes. The *RS,SR* diastereomers are much less reactive than the *RR,SS* diastereomers, suggestive of a greater thermodynamic stability.

8. Interconversion of Alkene Complex Diastereomers. The (67–62):(28–33) mixtures of alkene complex diastereomers (*RS,SR*)-/(*RR,SS*)-**3a–c**$^+$$BF_4^-$ obtained in Scheme II were heated at 100 °C in C_6H_5Cl for 24 h. Subsequently isolated in 89–97% yields were samples that had converted to (98 ± 2):(2 ± 2), (95 ± 2):(5 ± 2), and (96 ± 2):(4 ± 2) mixtures of diastereomers, respectively. When analogous reactions (95 °C) were monitored by ^{1}H NMR spectroscopy, similar product ratios were obtained (Experimental Section). Some crystallization was evident in the NMR tube reactions but not in the preparative reactions. In neither case was any evidence for thermal decomposition products observed.

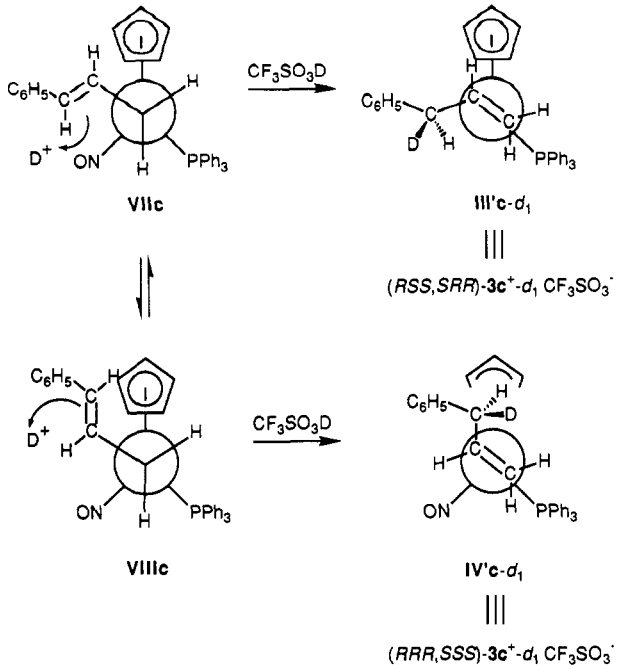
The preceding experiments clearly show that the *RS,SR* diastereomers of **3**$^+$$BF_4^-$ are more stable than the *RR,SS* diastereomers and establish the order of magnitude of K_{eq} ($\simeq$95/5). At 100 °C, a K_{eq} of 95/5 corresponds to a ΔG of 2.2 kcal/mol. However, conditions for the acquisition of data on these equilibrations are still being optimized. For example, use of more polar solvents such as CH_3CN results in some alkene ligand substitution.[14] Hence, the presentation of additional quantitative results will be deferred to a future publication.[19] Nonetheless, fascinating mechanistic features are evident at this stage (high to complete retention of configuration at rhenium, catalysis by external agents, etc.).

9. 1,4-Asymmetric Induction in Reactions of Allyl Complexes with Electrophiles. Finally, we sought to study a reaction of an allyl complex **4** and an electrophile that would give a new asymmetric carbon in the "allylic" position of the alkene complex product. We wondered if this third stereogenic center would form stereospecifically in each of the alkene complex diastereomers. Such 1,4-asymmetric induction would complement the highly efficient 1,2-asymmetric induction previously observed in reactions of nucleophiles with the alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+X^-$[6a,14] and 1,3-asymmetric induction previously observed in reactions of electrophiles with the vinyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CX{=}CHR)$.[6b]

Hence, the cinnamyl complex **4c** was treated with CF_3SO_3D in CD_2Cl_2 at −78 °C (Scheme VII). A (60 ± 2):(40 ± 2) mixture of the allylbenzene complex diastereomers (*RSS,SRR*)- and (*RRR,SSS*)-**3c**-$d_1$$^+$$CF_3SO_3^-$ formed, which was isolated as described above for the undeuterated complex (*RS,SR*)-/(*RR,SS*)-**3c**$^+$$PF_6^-$ (83%). Analysis by ^{1}H NMR spectroscopy showed that the upfield

(20) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: New York, 1987; Chapter 6.
(21) (a) Hunter, B. K.; Baird, M. C. *Organometallics* **1985**, *4*, 1481. (b) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Whittaker, M. *J. Am. Chem. Soc.* **1987**, *109*, 5711.
(22) Merrifield, J. H.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

Scheme VII. Reaction of the Cinnamyl Complex (*E*)-(η^5-C_5H_5)Re(NO)(PPh_3)($CH_2CH{=}CHC_6H_5$) (4c) and CF_3SO_3D To Give the Deuterated Allylbenzene Complex [(η^5-C_5H_5)Re(NO)(PPh_3)($H_2C{=}CHCHDC_6H_5$)]$^+CF_3SO_3^-$ (3c-$d_1$$^+CF_3SO_3^-$)



(δ 3.18) $-CH_2$ resonance of (*RS,SR*)-**3c**$^+X^-$ was absent in (*RSS,SRR*)-**3c**-$d_1$$^+CF_3SO_3^-$ (residual area <2% of downfield $-CH_2$ resonance). Similarly, the upfield (δ 2.88) $-CH_2$ resonance of (*RR,SS*)-**3c**$^+X^-$ was absent in (*RRR,SSS*)-**3c**-$d_1$$^+CF_3SO_3^-$ (residual area <2% of downfield $-CH_2$ resonance).

Thus, the reaction of the cinnamyl complex **4c** with CF_3SO_3D proceeds stereospecifically, with the incorporation of deuterium into a single site in each diastereomer of the resulting allylbenzene complex. Product stereochemistry (Scheme VII) is assigned as described below. Accordingly, the upfield methylene resonances of (*RS,SR*)- and (*RR,SS*)-**3c**$^+X^-$ can be assigned to the pro-*S* and pro-*R* protons, respectively, in Newman projections III′ and IV′ (Scheme III).

Discussion

1. Stereoselectivity in the Formation of Rhenium Alkene Complexes. The kinetic selectivities for the binding of monosubstituted alkene enantiofaces to the chiral Lewis acid [(η^5-C_5H_5)Re(NO)(PPh_3)]$^+$ (Scheme II) are modest and distinctly lower than the thermodynamic selectivities. Naturally, the separation of the alkene from the rhenium should be greater in the transition state leading to the complex than in the complex itself. This should reduce steric interactions and $\Delta\Delta G^{\ddagger}$ relative to $\Delta\Delta G$. Importantly, we have to date been unable to obtain any evidence that substitution reactions of the dichloromethane complex **2**$^+X^-$ are dissociative.[23] Hence, the kinetic binding selectivities are likely determined by a transition state more complex than a simple approach of alkene to [(η^5-C_5H_5)Re(NO)(PPh_3)]$^+$.

Importantly, the demonstration that each diastereomer of the styrene complex **3d**$^+BF_4^-$ is generated in optically pure form shows that the rhenium does not epimerize prior to or concurrent with alkene binding. Hence, the alkene ligands can in principle be elaborated to optically active organic compounds. Related cationic iron alkene complexes have been shown to be versatile substrates for a variety of stereospecific carbon–carbon and carbon–heteroatom bond-forming reactions.[15]

The kinetic selectivities observed when the alkene complexes **3**$^+X^-$ are prepared by reactions of the allyl complexes **4** with electrophiles (Schemes III and IV) are also modest but are amenable to a more detailed mechanistic analysis. The crystal structure of the cinnamyl complex **4c** exhibits two C_α–C_β rotamers that correspond to idealized Newman projections VII and VIII (Scheme III).[16] The populations refine to a 21.2 (2):78.8 (2) ratio. The Re–C_α–C_β–C_γ torsion angles in VII and VIII differ by ca. 180°, resulting in an anti arrangement of the $=C_\gamma$ allyl termini. As is best visualized in Scheme III, the geometric relationship of the $=C_\gamma$ allyl terminus and the diastereotopic C_α protons determines the alkene complex diastereomer formed upon C_γ electrophilic attack. Note also that the diastereomer formed is in principle *in*dependent of the direction of electrophilic attack or even the Re–C_α conformation.

The product ratios in Schemes III and IV suggest that the minor solid-state rotamer VII is more reactive than the major rotamer VIII. However, difference ^1H NOE experiments indicate appreciable concentrations of VII in solution.[16] Any enhanced reactivity of VII is likely due to the fact that it leads directly to the more stable alkene complex diastereomer. Further, as detailed elsewhere,[16] the $C_\beta{=}C_\gamma$ π and π^* orbitals of VII are better aligned with the d orbital HOMO of the [(η^5-C_5H_5)Re(NO)(PPh_3)]$^+$ fragment (I). Finally, note that repetitive deprotonation/protonation steps should eventually equilibrate the diastereomeric alkene complexes formed in Scheme III.

The iron allyl complexes (η^5-C_5H_5)Fe(CO)(PPh_3)(CHR′CH(R′)=CHR) have been shown to undergo C_γ electrophilic attack upon the $C_\beta{=}C_\gamma$ face that is anti to iron.[15] The C_γ deuteration of cinnamyl complex **4c** is similarly stereospecific (Scheme VII), and we presume analogous reaction pathways as shown in transition states VIIc and VIIIc. The configurations of the deuterated carbons in each diastereomer of the resulting allylbenzene complex **3c**-$d_1$$^+CF_3SO_3^-$ are assigned accordingly. Since the configurations are opposite, a common stereoisomer would not be obtained upon C⇄C enantioface as described above.

The stereospecificity observed when alkene complexes are synthesized by β-hydride abstraction as in Scheme V has been analyzed previously.[14] Basically, the conversion of (*SS,RR*)-**5** to (*RR,SS*)-**3c**$^+PF_6^-$ does not generate a new stereogenic unit. Hence, in the absence of epimerization pathways or parallel mechanisms that afford opposite stereochemistry, the reaction must be stereospecific.

It has been shown that Ph_3C^+ abstracts β-hydrides from a direction anti to the M–C_α bond.[24] In accord with our earlier model,[14] we suggest that the Re–C_α rotamer of (*SS,RR*)-**5** depicted in X (Scheme V) is the most reactive. This is the only *staggered* rotamer that allows participation of the rhenium d orbital HOMO (I) in hydride abstraction from the methyl group and delivers the product (*RR,SS*)-**3c**$^+PF_6^-$ as one of the two optimal Re–(C⇄C) rotamers VIc and IVc. Unfortunately, all attempts to detect distinct Re–(C⇄C) rotamers of (*RR,SS*)-**3c**$^+PF_6^-$ by low-temperature NMR spectroscopy were unsuccessful. Hence, we could not verify the kinetic formation of the less stable

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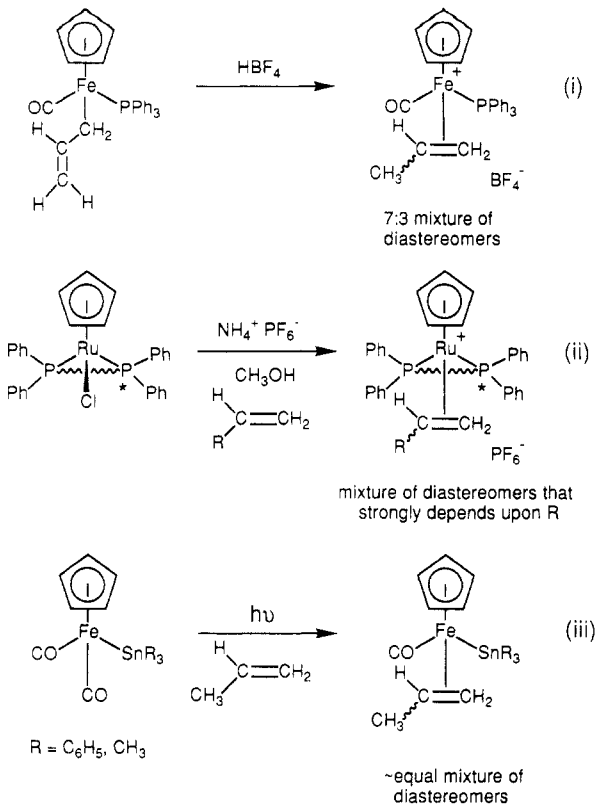
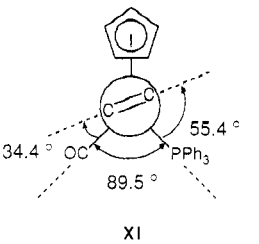
Scheme VIII. Stereoselectivity in the Formation of Monosubstituted Alkene Complexes of Chiral Metal Fragments from Allyl Complex Precursors or Free Alkenes



rotamer VIc predicted by Scheme V. Interestingly, no evidence is observed for hydride abstraction from the benzyl group of Re–C_α rotamer IX (Scheme V). We speculate that the phenyl ring might preferentially occupy the position on C_β that is anti to the Re–C_α bond.

2. Stereoselectivity in the Formation of Other Alkene Complexes. Several earlier syntheses of monosubstituted alkene complexes of chiral metal fragments are particularly relevant to our work. First, Brown has found that the reaction of the iron allyl complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CH_2CH{=}CH_2)$ and HBF_4 gives a 7:3 mixture of the diastereomeric propene complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H_2C{=}CHCH_3)]^+BF_4^-$ (Scheme VIII, eq i).[25] This parallels our findings in Scheme III. Second, Brookhart has reported that the iron propylidene complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(=CHCH_2CH_3)]^+TfO^-$ undergoes a 1,2-hydride shift at −78 °C to give the *less* stable diastereomer of the propene complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H_2C{=}CHCH_3)]^+TfO^-$.[26] Equilibration occurs between −40 and 0 °C to give chiefly the more stable diastereomer (>80:20), which is spectroscopically identical with the corresponding tetrafluoroborate salt prepared by Brown.

Consiglio has described reactions of monosubstituted alkenes with ruthenium complexes that should serve as precursors to the 16-valence-electron fragment $[(\eta^5\text{-}C_5H_5)Ru(L)(L')]^+$, where L and L′ are termini of a chiral chelating diphosphine (Scheme VIII, eq ii).[4] Representative *thermodynamic* enantioface binding selectivities include 95:5 (styrene), 89:11 (propene), 55:45 (methyl acrylate), and 23:77 (3-methyl-1-butene). Kinetic selectivities could be measured only for alkenes substituted with



XI

Figure 3. Newman-type projection of the structure of the cation of the ethylene complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H_2C{=}CH_2)]^+AsF_6^-$.

electron-withdrawing groups (e.g., ca. 20:80, methyl acrylate). Interestingly, propene and 3-methyl-1-butene appear to bind *opposite* faces. However, structural characterization has not yet proved possible.

Faller has reported that photolysis of the iron stannyl complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2(SnR_3)$ (R = Ph, CH_3) in the presence of propene gives the diastereomeric complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(SnR_3)(H_2C{=}CHCH_3)$ in essentially equal amounts (Scheme VIII, eq iii).[27a] One diastereomer is significantly less stable and appears to decompose by propene loss. Similarly, Dötz has found that photolysis of $(\eta^5\text{-}C_5Me_5)Mo(NO)(CO)_2$ in the presence of 1-octene gives a (57 ± 3):(43 ± 3) mixture of diastereomers of $(\eta^5\text{-}C_5Me_5)Mo(NO)(CO)(H_2C{=}CHC_6H_{13})$.[27b] Hence, there are, to our knowledge, no well-documented reactions of metal complexes and monosubstituted alkenes that serve to bind one alkene enantioface with high *kinetic* selectivity. Also, note that diastereomers of the alkene complexes shown in Scheme VIII appear to equilibrate much more readily than those of the rhenium complexes $\mathbf{3}^+X^-$.

3. Structures of Alkene Complexes. Several aspects of the structure of the allylbenzene complex (*RR,SS*)-$\mathbf{3c}^+PF_6^-$ (Figure 1) merit analysis. First, the C–C (C1–C2) bond length (1.40 (3) Å) is, as expected from the Dewar–Chatt–Duncanson model,[8] intermediate between that of the monosubstituted C=C double bond in propene (1.318 Å) and the carbon–carbon single bond in propane (1.526 Å).[28] We were not able to locate any structural data on free allylbenzene, but the crystal structure of the corresponding molybdenum bis(π-arene) complex $Mo(\eta^6\text{-}C_6H_5CH_2CH{=}CH_2)_2$ has been reported (C=C = 1.303 (11) Å).[29] The C–C bond lengths in a variety of structurally characterized alkene complexes have been tabulated and vary widely (e.g., 1.354–1.477 Å for ethylene complexes).[30]

The Re–(C–C) rotamer of (*RR,SS*)-$\mathbf{3c}^+PF_6^-$ that is expected to be more stable (IVc) is in fact found in the solid state. However, in all rotamers of the general type IV there is the potential for steric interactions between the alkene substituent and the cyclopentadienyl ligand. These appear to be minimized, but not eliminated, in (*RR,SS*)-$\mathbf{3c}^+PF_6^-$ by (1) the orientation of the phenyl ring and (2) a counterclockwise rotation of the allylbenzene ligand, opening the angle of the Re—P bond with the Re—C=C plane from 0° in idealized structure IV to 20°. The latter also likely lessens steric interactions of the $=CH_2$ terminus with

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the PPh_3 ligand. The difference ^1H NOE experiments establish that type IV (*sc*) rotamers of (*RR,SS*)-$\mathbf{3}^+X^-$ also dominate in solution.

Finally, the crystal structure of the "isoelectronic" iron ethylene complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H_2C{=}CH_2)]^+AsF_6^-$ has been determined.[31] Several features merit comparison with those of (*RR,SS*)-$\mathbf{3c}^+PF_6^-$. First, the C–C bond length (1.39 (2) Å) is similar. However, some shortening might have been expected from the reduced π basicity of the iron fragment (the HOMO of which is analogous to I).[32] Second, the angle of the Fe—P bond with the Fe—C–C plane is 55°, as depicted in Newman-type projection XI (Figure 3). Hence, the alkene ligand conformations in the two compounds differ by 35°. We therefore conclude that electronic factors are less important, and steric factors are more important, in determining alkene ligand conformations in the iron complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H_2C{=}CHR)]^+X^-$.

4. Interconversion of Alkene Complex Rotamers. The rotational barrier of the ethylene ligand in the rhenium complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$ (16.4 kcal/mol, 96.2 °C) is much higher than those found for the corresponding iron complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H_2C{=}CH_2)]^+BF_4^-$ (10.0 kcal/mol, −40 °C)[33] and the related species $(\eta^5\text{-}C_5H_5)Fe(CO)(SnR_3)(H_2C{=}CH_2)$ (R = Ph, CH_3; 12.8 kcal/mol, −40 to −50 °C).[27a] Since rhenium–ligand bonds are typically 5–10% longer than those in analogous iron complexes, the steric component of the rotational barrier should be lower in the rhenium complex, opposite to the trend observed. This provides additional evidence for the metal fragment π basicity order $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+ \gg [(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]^+$.[32]

Alkene ligand rotational barriers have been measured in nearly 100 complexes.[30b] That of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$ (16.4 kcal/mol) is among the higher recorded. For example, the 1,2-dimethoxyethylene ligand in (acac)Rh(*trans*-MeOCH=CHOMe)$_2$ and the propene ligand in $[(\eta^5\text{-}C_5H_5)_2W(H)(H_2C{=}CHCH_3)]^+PF_6^-$ have been assigned rotational barriers of 19.2 and 22.4 kcal/mol,[10c,30b] respectively. However, rotational barriers where the alkene ligand does not bear an electron-withdrawing group are commonly much lower and range from 7.6 to 14.0 kcal/mol in 12 complexes of $(\eta^5\text{-}C_5H_5)MLL'$ metal fragments.[27b,30b]

The magnitude of the ethylene ligand rotational barrier in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$ suggests that rotamers of the monosubstituted alkene complexes $\mathbf{3}^+X^-$ should rapidly interconvert at room temperature. However, decoalescence of rotamers might conceivably be observed in low-temperature NMR spectra. However, we are unable to detect any such phenomena or any sign of a second rotamer when complexes $\mathbf{3}^+X^-$ are generated at low temperatures in NMR-monitored experiments. Hence, we provisionally conclude that the alkene ligand rotational barriers in $\mathbf{3}^+X^-$ are somewhat lower than that of the ethylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$.

5. Conclusion. When monosubstituted alkenes and the dichloromethane complex $\mathbf{2}^+BF_4^-$ are reacted, diastereomeric complexes that differ in the alkene enantioface bound to rhenium form ((*RS,SR*)- and (*RR,SS*)-$\mathbf{3}^+BF_4^-$). The kinetic diastereoselectivities are modest. However, thermodynamic selectivities are considerably higher, as shown by the preliminary equilibration data. The direction of the equilibrium is easily rationalized from stereoelectronic factors (Scheme I). When optically active precursors are utilized, complexes $\mathbf{3}^+BF_4^-$ are obtained in high optical purities.

Considerable synthetic and mechanistic interest attends the diastereomer equilibration reactions. For example, the high degree of retention at rhenium[11,19] and the general synthetic versatility of cationic alkene complexes[15] suggest applications in asymmetric organic synthesis. Further, there are obvious strategies for the catalysis of these equilibrations. In summary, this study has provided the diastereomerically and enantiomerically pure starting materials, as well as fundamental structural, dynamic, and spectroscopic data, that are necessary for a thorough exploration of these important synthetic and mechanistic questions.

Experimental Section

General Data. General procedures were identical with those described in a recent paper.[16] Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter.[9c]

Solvents were purified as follows: benzene, ether, and THF, distilled from Na/benzophenone; hexane, distilled from Na; CH_2Cl_2, $CHCl_3$, and chlorobenzene, distilled from P_2O_5; CD_2Cl_2, $C_2D_4Cl_2$, $C_2D_2Cl_4$, CD_3CN, and acetone-d_6, vacuum transferred from CaH_2.

Reagent sources were as follows: propene (Matheson), 1-pentene (Alfa), allylbenzene and styrene (Aldrich), used as received; CF_3SO_3H (Aldrich), distilled under vacuum; CF_3SO_3D, synthesized as reported previously;[6b] $HPF_6{\cdot}Et_2O$ (Columbia) and $HBF_4{\cdot}Et_2O$ (Aldrich), standardized as described earlier;[13] (+)-Eu(hfc)$_3$, $Ph_3PCH_3{}^+I^-$, $C_6H_5CH_2CN$ (Aldrich) and $(C_2H_5)_4N^+CN^-$ (Fluka), used as received; $(CH_3)_3O^+PF_6^-$ (Aldrich), washed with CH_2Cl_2 and ether.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_3)]^+BF_4^-$ ($\mathbf{3a}^+BF_4^-$). A. A Fischer–Porter bottle was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**,[12] 0.496 g, 0.889 mmol), CH_2Cl_2 (30 mL), and a stirbar. The solution was cooled to −78 °C, and $HBF_4{\cdot}Et_2O$ (100 μL, 0.928 mmol) was added to generate a dark orange solution of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ ($\mathbf{2}^+BF_4^-$).[13] Then excess propene gas was condensed into the bottle. The reaction mixture was stirred for 24 h and was concurrently warmed to room temperature. The excess propene was vented whenever the bottle pressure reached 135 psi. The reaction mixture was then filtered, and solvent was removed from the filtrate by rotary evaporation. The residue was extracted with CH_2Cl_2 (20 mL), and ether (50 mL) was added. A yellow powder precipitated, which was collected by filtration and dried in vacuo to give $\mathbf{3a}^+BF_4^-$ (0.543 g, 0.808 mmol, 91%) as a (67 ± 2):(33 ± 2) mixture of *RS,SR*/*RR,SS* diastereomers; mp 218–222 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1727 s. ^{31}P NMR (ppm, CH_2Cl_2): 10.1 (s). Anal. Calcd for $C_{26}H_{26}BF_4NOPRe$: C, 46.54; H, 3.87. Found: C, 46.26; H, 3.84.

B. A Schlenk tube was charged with a (67 ± 2):(33 ± 2) mixture of (*RS,SR*)-/(*RR,SS*)-$\mathbf{3a}^+BF_4^-$ (0.300 g, 0.521 mmol), C_6H_5Cl (12 mL), and a stirbar. The solution was stirred and kept in a 100 °C oil bath for 24 h. Solvent was then removed by oil pump vacuum to give a dark yellow oil. The oil was extracted with CH_2Cl_2 (10 mL), and hexane (25 mL) was added to the extract. Solvents were removed by rotary evaporation to give $\mathbf{3a}^+BF_4^-$ as a yellow powder (0.291 g, 0.505 mmol, 97%) that was a (98 ± 2):(2 ± 2) mixture of *RS,SR*/*RR,SS* diastereomers.

C. A 5-mm NMR tube was charged with a (67 ± 2):(33 ± 2) mixture of (*RS,SR*)-/(*RR,SS*)-$\mathbf{3a}^+BF_4^-$ (0.015 g, 0.026 mmol) and C_6D_5Cl (0.6 mL). The tube was placed in a 95 °C oil bath and periodically monitored by ^1H NMR spectroscopy: 6 h, (82 ± 2):(18 ± 2); 12 h, (95 ± 2):(5 ± 2). A small amount of crystallization was evident after 6 h.

D. An experiment analogous to (A) was conducted with the optically active methyl complex (+)-(*S*)-$\mathbf{1}$[5a] (0.120 g, 0.215 mmol), $HBF_4{\cdot}Et_2O$ (25 μL, 0.230 mmol), and CH_2Cl_2 (5 mL). An identical workup gave (+)-$\mathbf{3a}^+BF_4^-$ (0.128 g, 0.191 mmol, 89%) as a (67 ±

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(32) This trend is evidenced by the large decrease in alkylidene and vinylidene ligand rotational barriers upon changing the metal fragment from $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ to $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]^+$.[6b,c]

(33) Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3270.

2):(33 ± 2) mixture of *RS/RR* diastereomers; $[\alpha]^{23}_{589}$ 115°.[9c]

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=CH-*n*-C_3H_7)]$^+BF_4^-$ (3b$^+BF_4^-$). A. A Schlenk flask was charged with **1** (0.250 g, 0.448 mmol), CH_2Cl_2 (25 mL), and a stirbar. The flask was cooled to −78 °C, and HBF_4·Et_2O (50 μL, 0.460 mmol) was added with stirring. After 0.5 h, 1-pentene (0.450 mL, 4.48 mmol, 10 equiv) was added. The reaction mixture was stirred at −78 °C for 1 h and was then warmed to room temprature and stirred for an additional 2 h. Solvent was removed under oil pump vacuum, and the resulting residue was extracted with THF (30 mL). Then hexene (60 mL) was added. A yellow powder precipitated, which was collected by filtration and dried under vacuum to give **3b**$^+BF_4^-$ (0.285 g, 0.408 mmol, 91%) as a (62 ± 2):(38 ± 2) mixture of *RS,SR/RR,SS* diastereomers; mp 134–136 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1718 s. ^{31}P NMR (ppm, CH_2Cl_2): 10.4 (s). Anal. Calcd for $C_{28}H_{30}BF_4NOPRe$: C, 47.99; H, 4.28. Found: C, 47.65; H, 4.09.

B. A Schlenk tube was charged with a (62 ± 2):(38 ± 2) mixture of (*RS,SR*)-/(*RR,SS*)-**3b**$^+BF_4^-$ (0.200 g, 0.286 mmol), C_6H_5Cl (8 mL), and a stirbar. Reaction and workup as described in preparation B of **3a**$^+BF_4^-$ above gave **3b**$^+BF_4^-$ (0.181 g, 0.258 mmol, 90%) that was a (95 ± 2):(5 ± 2) mixture of *RS,SR/RR,SS* diastereomers.

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=CH$CH_2C_6H_5$)]$^+BF_4^-$ (3c$^+BF_4^-$). A. Complex **1** (0.350 g, 0.627 mmol), CH_2Cl_2 (30 mL), HBF_4·Et_2O (70 μL, 0.650 mmol), and allylbenzene (0.850 mL, 6.3 mmol, 10 equiv) were reacted in a procedure analogous to that given for **3b**$^+BF_4^-$. An identical workup gave **3c**$^+BF_4^-$ (yellow powder, 0.420 g, 0.562 mmol, 90%) as a (64 ± 2):(36 ± 2) mixture of *RS,SR/RR,SS* diastereomers; mp 141–144 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1718 s. ^{31}P NMR (ppm, CH_2Cl_2): 10.5 (s, (*RR,SS*)-**3c**$^+BF_4^-$), 9.8 (s, (*RS,SR*)-**3c**$^+BF_4^-$). Anal. Calcd for $C_{27}H_{26}F_3NO_4PReS$: C, 44.13; H, 3.54. Found: C, 44.18; H, 3.64.

B. A Schlenk tube was charged with a (67 ± 2):(33 ± 2) mixture of (*RS,SR*)-/(*RR,SS*)-**3c**$^+BF_4^-$ (0.280 g, 0.374 mmol), C_6H_5Cl (8 mL), and a stirbar. Reaction and workup as described in preparation B of **3a**$^+BF_4^-$ gave **3c**$^+BF_4^-$ as a yellow powder (0.248 g, 0.332 mmol, 89%) that was a (96 ± 2):(4 ± 2) mixture of *RS,SR/RR,SS* diastereomers.

C. A 5-mm NMR tube was charged with a (67 ± 2):(33 ± 2) mixture of (*RS,SR*)-/(*RR,SS*)-**3c**$^+BF_4^-$ (0.015 g, 0.020 mmol) and C_6H_5Cl (0.7 mL). The tube was placed in a 95 °C oil bath and periodically monitored by ^1H NMR spectroscopy: 6 h, (79 ± 2):(21 ± 2); 12 h, (93 ± 2):(7 ± 2). A small amount of crystallization was evident after 6 h.

D. An experiment analogous to (A) was conducted with the optically active methyl complex (+)-(*S*)-**1** (0.120 g, 0.215 mmol), HBF_4·Et_2O (25 μL, 0.230 mmol), and allylbenzene (0.300 mL, 2.2 mmol). An analogous workup gave (+)-**3c**$^+BF_4^-$ (0.136 g, 0.182 mmol, 85%) as a (66 ± 2):(34 ± 2) mixture of *RS/RR* diastereomers; $[\alpha]^{23}_{589}$ 86°.[9c]

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=CHC_6H_5)]$^+BF_4^-$ (3d$^+BF_4^-$). A. Complex **1** (0.279 g, 0.500 mmol), CH_2Cl_2 (1 mL), HBF_4·Et_2O (54 μL, 0.500 mmol), and styrene (0.287 mL, 2.500 mmol, 5 equiv) were reacted in a procedure analogous to that given for **3b**$^+BF_4^-$. The reaction residue was extracted with CH_2Cl_2 (10 mL), and hexane (30 mL) was added to the extract. A tan powder precipitated, which was collected by filtration and dried under vacuum to give **3d**$^+BF_4^-$ (0.324 g, 0.442 mmol, 89%) as a (73 ± 2):(27 ± 2) mixture of *RS,SR/RR,SS* diastereomers, which were characterized after separation.

B. The preceding sample was dissolved in CH_2Cl_2 (20 mL), and $CHCl_3$ (5 mL) was added. A tan powder formed, which was collected as above to give (*RS,SR*)-**3d**$^+BF_4^-$ (0.147 g, 0.200 mmol, 40%), mp 244–247 °C dec. IR (cm^{-1}, thin film): ν_{NO} 1728 s. ^{31}P NMR (ppm, CD_2ClCD_2Cl): 10.46 (s). Mass spectrum ((+)-FAB (5 kV, Ar, 3-nitrobenzyl alcohol/$CHCl_3$), *m/z* (relative intensity), ^{187}Re): 648 (**3d**$^+$, 91%), 544 (**3d**$^+$ − C_8H_8, 100%). Anal. Calcd for $C_{31}H_{28}BF_4NOPRe$: C, 50.69; H, 3.84; N, 1.91. Found: C, 50.65; H, 3.84; N, 1.89.

C. The filtrate from the preceding experiment was chromatographed on a 5-mL silica gel column with CH_2Cl_2. Several fractions of a yellow band were collected. After preliminary ^1H NMR analysis, the initial fractions were combined, and solvent was removed to give (*RR,SS*)-**3d**$^+BF_4^-$ as a yellow powder (0.043 g, 0.059 mmol, 12%), mp 202–204 °C dec. IR (cm^{-1}, thin film): ν_{NO} 1726 s. ^{31}P NMR (ppm, CD_2ClCD_2Cl): 10.70 (s). Mass spectrum ((+)-FAB (5 kV, Ar, 3-nitrobenzyl alcohol/$CHCl_3$), *m/z* (relative intensity), ^{187}Re): 648 (**3d**$^+$, 62%), 544 (**3d**$^+$ − C_8H_8, 100%). Continued elution of the column with 95:5 (v/v) CH_2Cl_2/acetone completely removed the yellow band. These fractions were combined to give **3d**$^+BF_4^-$ (0.038 g, 0.051 mmol, 10%) as a (54 ± 2):(46 ± 2) mixture of *RS,SR/RR,SS* diastereomers.

D. A reaction was conducted identically with (A), but with (−)-(*R*)-**1**. The tan powder was chromatographed on a 25-mL silica gel column with 95:5 (v/v) CH_2Cl_2/acetone. Fractions were collected and grouped into four series on the basis of ^1H NMR analyses. The first series contained mainly byproducts (0.028 g). The second series gave (−)-(*SS*)-**3d**$^+BF_4^-$ (0.043 g, 0.059 mmol, 12%) as a yellow powder, $[\alpha]^{25}_{589}$ −120 ± 6° (*c* = 0.44 mg/mL, CH_2Cl_2). Yellow needles were obtained from CH_2Cl_2/hexane (1 mL/2 mL); mp 210–212 °C dec. The third series gave a (57 ± 2):(43 ± 2) mixture of (−)-(*SR*)-/(*SS*)-**3d**$^+BF_4^-$ (0.029 g, 0.040 mmol, 8%). The fourth series gave (−)-(*SR*)-**3d**$^+BF_4^-$ (0.183 g, 0.250 mmol, 50%) as a yellow powder: dec pt (no melting) 224–225 °C; $[\alpha]^{25}_{589}$ −357 ± 7° (*c* = 0.44 mg/mL, CH_2Cl_2).

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=CHCH_3)]$^+CF_3SO_3^-$ (3a$^+CF_3SO_3^-$). A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2CH=CH_2) (**4a**,[16] 0.150 g, 0.257 mmol), CH_2Cl_2 (15 mL), and a stirbar. The flask was cooled to −78 °C, and CF_3SO_3H (25 μL, 0.282 mmol) was added with stirring. After 0.25 h, the solution was slowly warmed to room temperature and was stirred an additional 2 h. Solvent was then removed under oil pump vacuum (7 h). The resulting yellow foam was washed with benzene (2 × 10 mL) and extracted with CH_2Cl_2 (20 mL). Hexane (40 mL) was added to the extract. The resulting suspension was concentrated by rotary evaporation. The yellow precipitate was collected by filtration and dissolved in CH_2Cl_2 (10 mL). Then ether was slowly added by vapor diffusion. Yellow prisms formed, which were collected by filtration and dried in vacuo to give **3a**$^+CF_3SO_3^-$ (0.173 g, 0.236 mmol, 92%) as a (75 ± 2):(25 ± 2) mixture of *RS,SR/RR,SS* diastereomers; mp 181–183 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1727 s. ^{31}P NMR (CH_2Cl_2, ppm): 10.2 (s). Mass spectrum ((+)-FAB (7 kV, Ar, thioglycerol), *m/z* (relative intensity), ^{187}Re): 586 (M^+, 17%), 544 (M^+ − C_3H_6, 100%). Anal. Calcd for $C_{27}H_{26}F_3NO_4PReS$: C, 44.13; H, 3.54. Found: C, 44.18; H, 3.64.

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=C$HCH_2C_6H_5$)]$^+PF_6^-$ (3c$^+PF_6^-$). Complex (*E*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2CH=CHC_6H_5) (**4c**,[16] 0.150 g, 0.227 mmol), HPF_6·Et_2O (25 μL, 0.450 mmol), and CH_2Cl_2 (15 mL) were combined in a procedure analogous to that given for **3a**$^+CF_3SO_3^-$. The yellow foam obtained was washed with benzene (2 × 10 mL) and extracted with CH_3CN (10 mL). Ether was added to the extract, and the solution was concentrated by rotary evaporation. A yellow powder precipitated, which was collected by filtration, washed with cold hexane, and dried in vacuo to give **3c**$^+PF_6^-$ (0.158 g, 0.195 mmol, 86%) as a (60 ± 2):(40 ± 2) mixture of *RS,SR/RR,SS* diastereomers; mp 204–206 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1718 s. ^{31}P NMR (CH_2Cl_2, ppm): 9.5 (s, *RS,SR*), 10.2 (s, *RR,SS*). Mass spectrum ((+)-FAB (7 kV, Ar, thioglycerol), *m/z* (relative intensity), ^{187}Re): 662 (M^+, 74%), 544 (M^+ − C_9H_{10}, 100%). Anal. Calcd for $C_{32}H_{30}F_6NOP_2Fe$: C, 47.63; H, 3.72. Found: C, 47.23; H, 3.75.

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=C$HCHDC_6H_5$)]$^+CF_3SO_3^-$ (3c-$d_1$$^+CF_3SO_3^-$). Complex **4c** (0.100 g, 0.151 mmol), CF_3SO_3D (15 μL, 0.165 mmol), and CH_2Cl_2 (10 mL) were combined in a procedure analogous to that given for **3c**$^+PF_6^-$. An identical workup gave **3c**-$d_1$$^+CF_3SO_3^-$ (0.102 g, 0.126 mmol, 83%) as a (60 ± 2):(40 ± 2) mixture of *RSS,SRR/RRR,SSS* diasteromers; mp 207–210 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1718 s. ^{31}P NMR (CH_2Cl_2, ppm): 9.4 (s, *RSS,SRR*), 10.1 (s, *RRR,SSS*). ^1H NMR (CD_2Cl_2, CHD only): δ 3.57 (*RSS,SRR*, d, J_{HH} = 7 Hz), 3.75 (*RRR,SSS*, d, J_{HH} = 5 Hz).

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=C-(CH_3)$_2$)]$^+CF_3SO_3^-$ (3e$^+CF_3SO_3^-$). Complex (η^5-C_5H_5)Re(NO)(PPh_3)($CH_2C(CH_3)$=CH_2) (**4e**,[16] 0.150 g, 0.251 mmol), CF_3SO_3H (25 μL, 0.275 mmol), and CH_2Cl_2 (15 mL) were combined in a procedure analogous to that given for **3a**$^+CF_3SO_3^-$. After 0.5 h, the reaction mixture was warmed to room temperature

and solvent was removed under oil pump vacuum. An identical workup gave **3e**$^+CF_3SO_3^-$ (0.165 g, 0.220 mmol, 88%) as gold-yellow prisms, mp 190–192 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1725 s. ^{31}P NMR (CH_2Cl_2, ppm): 9.0 (s). Mass spectrum ((+)-FAB (7 kV, Ar, thioglycerol), *m/z* (relative intensity), ^{187}Re): 600 (M^+, 14%), 544 ($M^+ - C_4H_8$, 100%). Anal. Calcd for $C_{28}H_{28}F_3NO_4PReS$: C, 44.91; H, 3.74. Found: C, 44.63; H, 3.48.

Preparation of [(η^5-C_5H_5)Re(NO)(PPh$_3$)(H$_2$C=CHC$_2$H$_5$)]$^+$PF$_6^-$ (3f$^+$PF$_6^-$). Complex **4a** (0.150 g, 0.257 mmol) and $(CH_3)_3O^+PF_6^-$ (0.106 g, 0.514 mmol) were combined at −20 °C in a procedure similar to that given for **3a**$^+CF_3SO_3^-$. The reaction mixture was stirred at −20 °C for 0.5 h and was then slowly warmed to room temperature and stirred for an additional 2 h. The suspension was filtered and solvent removed from the filtrate by rotary evaporation to give a yellow oil. The oil was dissolved in $CHCl_3$ (7 mL) and heptane added (20 mL). Solvents were removed by rotary evaporation, and the resulting yellow powder was washed with cold hexane and dried in vacuo to give **3f**$^+PF_6^-$ (0.168 g, 0.226 mmol, 88%) as a (70 ± 2):(30 ± 2) mixture of *RS,SR*/*RR,SS* diastereomers; mp 202–205 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1725 s. ^{31}P NMR (ppm, CH_2Cl_2): 10.0 (s). Mass spectrum ((+)-FAB (7 kV, Ar, thioglycerol), *m/z* (relative intensity), ^{187}Re): 600 (M^+, 3%), 544 ($M^+ - C_4H_8$, 100%). Anal. Calcd for $C_{27}H_{28}F_6NOP_2Re$: C, 43.54; H, 3.76. Found: C, 43.37; H, 3.77.

Preparation of [(η^5-C_5H_5)Re(NO)(PPh$_3$)(H$_2$C=CHC(C$_6$H$_5$)$_3$)]$^+$PF$_6^-$ (3g$^+$PF$_6^-$). A Schlenk flask was charged with **4a** (0.150 g, 0.257 mmol), CH_2Cl_2 (15 mL), and a stirbar and was cooled to −78 °C. Then $Ph_3C^+PF_6^-$ was added with stirring. After 1 h, the reaction mixture was slowly warmed to room temperature and was stirred for an additional 2 h. Solvents were then removed under oil pump vacuum. The resulting yellow foam was washed with benzene (2 × 15 mL) and extracted with CH_2Cl_2 (15 mL). The extract was filtered, and hexane (50 mL) was added to the filtrate. A yellow powder precipitated, which was collected by filtration, washed with cold acetone (2 × 10 mL), and dried in vacuo to give **3g**$^+PF_6^-$ (0.196 g, 0.202 mmol, 79%) as a (70 ± 2):(30 ± 2) mixture of *RS,SR*/*RR,SS* diastereomers; mp 211–215 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1722 s. ^{31}P NMR (CH_2Cl_2, ppm): 10.0 (s, *RS,SR*), 11.3 (s, *RR,SS*). Anal. Calcd for $C_{45}H_{40}F_6NOP_2Re$: C, 55.54; H, 4.11. Found: C, 55.68; H, 4.06.

Preparation of (*RR,SS*)-[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H$_2$C=CHCH$_2$C$_6$H$_5$)]$^+$PF$_6^-$ ((*RR,SS*)-3c$^+$PF$_6^-$). A Schlenk flask was charged with (*RR,SS*)-(η^5-C_5H_5)Re(NO)(PPh$_3$)(CH(CH$_3$)CH$_2$C$_6$H$_5$) ((*RR,SS*)-**5**,[14] 0.159 g, 0.240 mmol), CH_2Cl_2 (15 mL), and a stirbar and was cooled to −78 °C. Then $Ph_3C^+PF_6^-$ (0.096 g, 0.247 mmol) was added with stirring. After 0.5 h, hexane (25 mL) was added. Solvents were then removed under oil pump vacuum as the reaction mixture was warmed to room temperature. This gave a pale yellow solid, which was triturated with hexane to give (*RR,SS*)-**3c**$^+PF_6^-$ (0.160 g, 0.200 mmol, 83%). A sample (0.060 g) was dissolved in acetone (7 mL), and ether was slowly added by vapor diffusion over 5 days. This gave golden prisms of (*RR,SS*)-**3c**$^+PF_6^-$, mp 196–198 °C dec. Mass spectrum ((+)-FAB (7 kV, Ar, thioglycerol), *m/z* (relative intensity), 187 Re): 662 (M^+, 74%), 544 ($M^+ - C_9H_{10}$, 100%).

Reaction of 3c$^+$BF$_4^-$ and Ph$_3$PCH$_3^+$I$^-$. A 5-mm NMR tube was charged with a (67 ± 2):(33 ± 2) mixture of (*RS,SR*)-/(*RR,SS*)-**3c**$^+BF_4^-$ (0.017 g, 0.023 mmol), $Ph_3PCH_3^+I^-$ (0.028 g, 0.068 mmol), and C_6H_5Cl (0.9 mL) and was capped with a septum. The tube was shaken, and the solution turned green (<5 min). A ^{31}P NMR spectrum showed diastereomeric species (10.1, 9.8 ppm) that were assigned as the metathesis products (*RS,SR*)-/(*RR,SS*)-**3c**$^+I^-$. The tube was placed in a 75 °C oil bath, and the reaction was monitored by ^{31}P NMR spectroscopy. After 3 days, the resonance of (*RR,SS*)-**3c**$^+I^-$ had been replaced by one (13.7 ppm) coincident with that of the previously reported iodide complex (η^5-C_5H_5)Re(NO)(PPh$_3$)(I) (**5**).[22] The area ratio of (*RS,SR*)-**3c**$^+I^-$:**5** ^{31}P NMR resonances was (66 ± 2):(34 ± 2).

Preparation of (+)-(*S*)-[(η^5-C_5H_5)Re(NO)(PPh$_3$)(NCCH$_2$C$_6$H$_5$)]$^+$BF$_4^-$ ((+)-(*S*)-7$^+$BF$_4^-$). A Schlenk flask was charged with (+)-(*S*)-**1** (0.078 g, 0.140 mmol),[5] CH_2Cl_2 (5 mL), and a stirbar. The solution was cooled to −78 °C, and $HBF_4 \cdot Et_2O$ (17 μL, 0.160 mmol) was added with stirring. After 0.5 h, $C_6H_5CH_2CN$ (0.160 mL, 1.40 mmol, 10 equiv) was added. After 0.5 h, the solution was slowly warmed to room temperature and was stirred for an additional 1 h. The solvent was removed under oil pump vacuum to give a dark yellow oil. Then ether (15 mL) was added, and the mixture was stirred to precipitate a yellow powder, which was collected by filtration, washed with cold ether, and dried in vacuo to give (+)-(*S*)-7$^+BF_4$ (0.098 g, 0.131 mmol, 94%): mp 219–222 °C dec; $[\alpha]^{23}_{589}$ 226°.[9c] A ^1H NMR spectrum matched that of the racemate.[13]

Reaction of (+)-(*RS*)/(*RR*)-3c$^+$BF$_4^-$ and C$_6$H$_5$CH$_2$CN. A 5-mm NMR tube was charged with a (67 ± 2):(33 ± 2) mixture of (+)-(*RS*)-/(+)-(*RR*)-**3c**$^+BF_4^-$ (0.016 g, 0.021 mmol, $[\alpha]^{23}_{589}$ 86°) and $C_6H_5CH_2CN$ (0.7 mL) and was capped with a septum. The tube was shaken and a ^{31}P NMR spectrum of the starting materials recorded. The tube was placed in a 150 °C oil bath, and the reaction was monitored by ^{31}P NMR spectroscopy. Complete conversion to 7$^+BF_4^-$ occurred over the course of 18 h. The solution was transferred to a flask. Ether (20 mL) was added to precipitate a yellow powder, which was collected by filtration, washed with cold ether (2 × 10 mL), and dried in vacuo to give 7$^+BF_4^-$ (0.013 g, 0.020 mmol, 91%, $[\alpha]^{23}_{589}$ 35°, 15% ee).

NMR Experiments. A. The ^1H NOED experiments[20,21] were conducted as previously described.[16] In separate experiments, the following substrate T_1 values were obtained (20 °C, CD_2Cl_2). (*RS,SR*)-**3a**$^+BF_4^-$: $=CH_Z$, $=CH_E$, CH_3, 0.5 s; =CHR, 0.9 s. (*RS,SR*)-**3c**$^+BF_4^-$: $=CH_E$, =CHR, 0.1 s; $=CH_Z$, CCH_2C, 0.3 s.

B. Variable-temperature NMR experiments were conducted as previously described.[34] Spectra were acquired at 5 °C intervals in coalescence regions.

X-ray Crystal Structure of (*RR,SS*)-3c$^+$PF$_6^-$. This structure was solved analogously to that of an η^4-cyclopentadiene complex reported recently.[35]

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