Generation and Reactivity of Substitution-Labile Dichloromethane and Chlorobenzene Adducts of the Chiral *Pentamethyl*cyclopentadienyl Rhenium Lewis Acid $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)]^+$

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Received January 12, 1994®

Reactions of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CH_3)$ (**5**) and $HBF_4\cdot OEt_2$ in CH_2Cl_2 (−80 °C) or C_6H_5Cl (−45 °C) give the chlorohydrocarbon complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**3**) and $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**4**). The latter is a mixture of linkage and constitutional isomers. Reactions of **3** and halide ions X^- give mainly $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Cl)$ (**6**) and XCH_2Cl, but **4** and $Ph_3PCH_3{}^+I^-$ yield $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(I)$ (84%). Reaction of **3** and $Et_4N^+CN^-$ gives comparable amounts of **6** and $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CN)$. The latter forms in 90% ee when (−)-(*R*)-**5** (>95% ee) is employed. When **3** is warmed to −35 °C, the oxidative addition product $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Cl)(CH_2Cl)]^+BF_4^-$ (**10**) forms. Reaction of **3** and CH_3I gives $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ICH_3)]^+BF_4^-$, but **3** converts to **10** in the presence of excess styrene or ethyne. Reactions of **4** and 1-pentene or styrene give the alkene complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+BF_4^-$ as mixtures of *RS*,*SR*/*RR*,*SS* diastereomers. Equilibration (50–100 °C) gives only the *RS*,*SR* diastereomers, indicating high enantioface binding selectivities. Similar substitutions involving ethyne and nonracemic **4** are described.

Chiral transition metal Lewis acids are proving to be of exceptional utility in enantioselective organic syntheses, and developmental efforts are underway in numerous laboratories.[1,2] We have conducted an extensive study of the pyramidal cyclopentadienyl rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**), which binds a variety of chiral and prochiral organic donor ligands in a highly stereoselective manner.[3-6] The coordinated ligands frequently undergo diastereoselective nucleophilic or electrophilic additions.[6] These compounds are usually accessed via the substitution-labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**1**)[7] or chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**2**),[8] which serve as functional equivalents of **I**. Most importantly, when **1** or **2** are generated from enantiomerically pure precursors, the resulting Lewis base adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+BF_4^-$ are obtained with essentially complete retention of configuration at rhenium. The mechanism of substitution of **1** has been examined in detail.[9]

Chiral transition metal Lewis acids are normally amenable to a variety of steric and electronic modifications. Thus, we sought to optimize certain properties of the Lewis acid **I**. In particular, we wondered whether replacement of the cyclopentadienyl ligand by a *pentamethyl*cyclopentadienyl ligand—which is bulkier and more basic[10]—would give enhanced binding or reaction selectivities. The resulting Lewis acid $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)]^+$ (**II**) would have a d orbital HOMO analogous to that of **I**, as shown in Chart 1.[11] This donor orbital is frequently an important determinant of ligand conformation.

For example, monosubstituted alkenes give two diastereomeric adducts with I.[4a-c] These have, in accord with the Dewar–Chatt–Duncanson bonding model, the idealized structures **III** and **IV** depicted in Chart 1. In both cases, the larger =CHR termini are *anti* to the bulky PPh_3 ligand. However, **III** and **IV** differ in the C=C enantioface bound to rhenium. Thermodynamic binding selectivities are high (90:10 to ≥99:≤1), consistent with a destabilizing steric interaction between the =CH*R* substituent and cyclopentadienyl ligand in **IV**. Since the pentamethylcyclopentadienyl ligand in **II** should give rise to a much greater interaction, we anticipated that binding selectivities would increase.

In this paper, we describe the synthesis, NMR properties, and reactivity of the unstable pentamethylcyclopentadienyl chlorohydrocarbon complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**3**) and $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$

® Abstract published in *Advance ACS Abstracts*, May 15, 1994.

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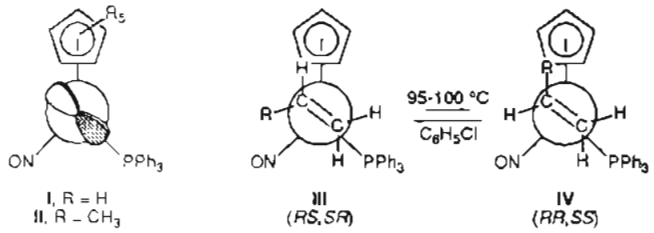
Chart 1. I, II: Pyramidal Rhenium Fragment $[(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)]^+$ with d-Orbital HOMO. III, IV: Newman Projections of Diastereomeric Monosubstituted Alkene Complexes of I



I, R = H
II, R = CH_3

III (*RS,SR*)

IV (*RR,SS*)

enantioface binding selectivities	
R = CH_3	96:4
$CH_2CH_2CH_3$	97:3
C_6H_5	90:10

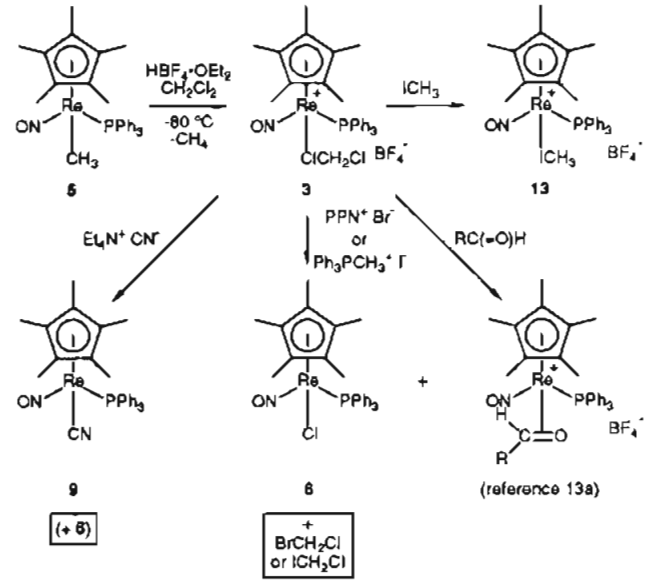
(**4**). Both compounds can be generated in enantiomerically enriched form, and subject to limitations detailed below serve as functional equivalents of the chiral Lewis acid **II**. Alkene binding selectivities are compared to those in the cyclopentadienyl series. Some data for **3** have been communicated,[12] and selected reactions of **3** and **4** have been independently reported.[13,14]

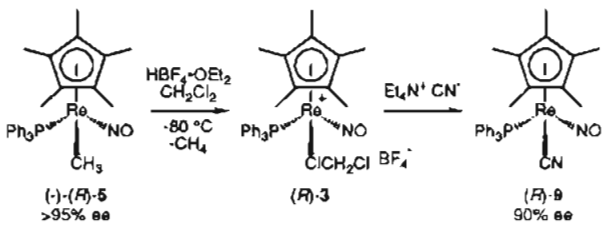
Results

1. Synthesis of a Dichloromethane Complex. Reactions with Anionic Lewis Bases. The cyclopentadienyl dichloromethane complex **1** can be generated by reaction of the corresponding methyl complex with HBF_4-OEt_2 in CH_2Cl_2 at –80 °C.[7] At lower temperatures, traces of intermediate cationic methyl hydride complexes can be detected by NMR. Accordingly, the pentamethylcyclopentadienyl methyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CH_3)$ (**5**)[14a] and HBF_4-OEt_2 (1.0 equiv) were combined in CH_2Cl_2 or CD_2Cl_2 in NMR tubes at –80 °C. Spectra (^1H, $^{13}C\{^1H\}$, ^{13}C, $^{31}P\{^1H\}$, ^{19}F) were immediately recorded at –85 °C, and showed the formation of methane (^1H NMR δ 0.14) and the pentamethylcyclopentadienyl dichloromethane complex **3** or **3**-d_2 (Scheme 1). In some runs, minor impurities were present (≤5%; ^{31}P NMR 25.6, 18.3 ppm). Similar experiments were conducted at –95 °C. No precursors to **3**-d_2 were detected by ^1H, $^{13}C\{^1H\}$, or $^{31}P\{^1H\}$ NMR. However, the resonances of **5** broadened markedly prior to its apparent consumption.

The preceding structural assignment was based primarily upon the characteristic $ReClCH_2Cl$ ^{13}C NMR signal (75.8 ppm), which was 22 ppm downfield from that of the free ligand and coupled to the PPh_3 phosphorus ($^3J_{CP}$ = 5.0 Hz), as illustrated in Figure 1. Similar downfield shifts and couplings have been observed for **1** and other alkyl halide adducts of **I**.[7,15,16] Also, a proton-coupled ^{13}C NMR spectrum showed a triplet of doublets, consistent with two directly-bound hydrogens (Figure 1B).[17] The PPh_3 ^{31}P resonance (16.2 ppm) was 3.7 ppm downfield from that of **1** (12.5 ppm)[7]—a shift typical of corresponding pentamethylcyclopentadienyl and cyclopentadienyl complexes.[13,14c,e] The BF_4^- ^{19}F chemical shift (–152.7 ppm) was nearly coincident with that of the cyclopentadienyl carbonyl complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (–152.6 ppm).[7] The $ReClCH_2Cl$ ^1H resonances could not be located due to overlap with the solvent resonance.

Scheme 1. Generation and Reactions of Racemic and Enantiomerically Enriched Dichloromethane Complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**3**)





Reactions were conducted to further support the structure assigned to **3**. In separate experiments, 1.2–1.4 equivalents of the halide salts $[Ph_3P{=}N{=}PPh_3]^+Br^-$ (PPN^+Br^-) and $Ph_3PCH_3^+I^-$ were added at –80 °C (Scheme 1). Workups gave *mixtures* of the chloride complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Cl)$ (**6**)[14c] and the bromide complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Br)$ (**7**)[14c] or iodide complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(I)$ (**8**).[14c] In each case, **6** greatly dominated (92–95% absolute yields). GC and GC/MS analysis of the second reaction showed ICH_2Cl (88%). Dichloromethane is normally inert towards halide ions below room temperature. Hence, these reactions are interpreted as involving nucleophilic attack of halide ions upon the dichloromethane carbon of **3**. Similar processes have been observed in the cyclopentadienyl series,[7,15,16] and the enormous rate accelerations vs analogous substitutions of free alkyl halides have been quantified.[15]

Non-racemic adducts of **II** were sought next. The enantiomers of cyclopentadienyl cyanide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$[7] are easily differentiated by chiral NMR shift reagents and HPLC.[18] Thus, the pentamethylcyclopentadienyl analog was

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(17) Since the $ReClCH_2Cl$ protons of **3** are diastereotopic, a doublet of doublets might have been observed. Apparently, the two $^1J_{CH}$ values are accidentally degenerate.
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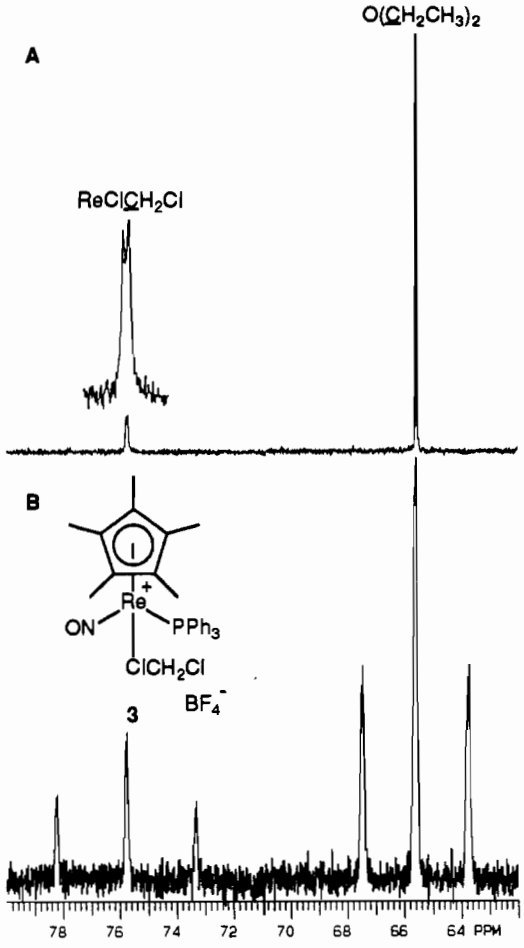
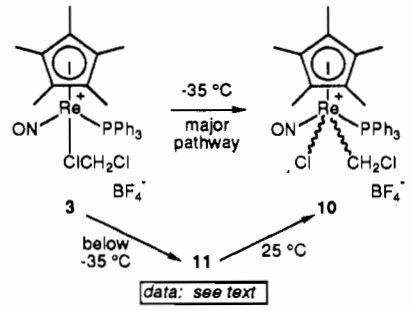


Figure 1. A. Partial $^{13}C\{^1H\}$ NMR spectrum of $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**3**) with inset showing $^3J_{CP}$ = 5.0 Hz. B. Partial ^{13}C NMR spectrum of **3** showing $^1J_{CH}$ = 186.0 Hz. All spectra were recorded at –62 °C in CH_2Cl_2.

targeted. First, the reaction of racemic **3** and cyanide salt $Et_4N^+CN^-$ (2.0 equiv) was monitored by ^{31}P NMR. After 15 min at –80 °C, a 44:35:13:4:3 mixture[19] of the chloride complex **6** (18.5 ppm), cyanide complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CN)$ (**9**; 19.6 ppm), methyl complex **5** (24.8 ppm),[20] and two unknown species (24.6, 28.6 ppm) had formed. When the sample was warmed to room temperature, the product ratio was unaffected. Chromatography gave **6**, **9**, and **5** in 39%, 32%, and 12% yields. Complex **9** was characterized by microanalysis and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy (experimental section). When $CDCl_3$ solutions of **9** were treated with the chiral NMR shift reagent (+)-Eu(hfc)$_3$, the C_5Me_5 ^1H resonances of the two enantiomers exhibited baseline resolution.

The optically active methyl complex (–)-(*R*)-**5**,[14d,21] >95% ee,[22] was then converted to dichloromethane complex **3** in a manner analogous to the racemate (Scheme 1, bottom). A similar reaction with $Et_4N^+CN^-$ gave **6**, **9**, and (–)-(*R*)-**5** (>95% ee) in 35%, 34%, and 11% yields after workup. Analysis with (+)-Eu(hfc)$_3$ showed **9** to be a 95:5 mixture of enantiomers (90% ee). After 6 days at room temperature, the enantiomer ratio was unchanged. This

Scheme 2. Decomposition of Dichloromethane Complex **3**



establishes the configurational stability of **9**, and indicates a modest loss of configuration during the conversion of (–)-(*R*)-**5** to **9**. By analogy to the stereochemistry established for related transformations in the cyclopentadienyl series (retention),[7,9] (–)-(*R*)-**5** was presumed to be converted to (*R*)-**3** and then (*R*)-**9**.

2. Decomposition of a Dichloromethane Complex. Reactions with Neutral Lewis Bases. The cyclopentadienyl dichloromethane complex **1** decomposes at –25 to –10 °C to the bridging chloride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+BF_4^-$.[7] A first-order rate law is followed, with k_{obs} = (3.5 ± 0.2) × 10^{-4} s^{-1} at –10.1 °C. Initial attack of the BF_4^- anion upon the dichloromethane carbon has been proposed, and supported by the detection of organofluorine decomposition products with related complexes.[16b]

However, in contrast to many pentamethylcyclopentadienyl complexes, **3** exhibited *lower* thermal stability than its cyclopentadienyl analog. Samples were generated at –80 °C, and transferred to –35 °C NMR probes. Spectra showed **3** and two new species (**10**, **11**) in 61–64%, 7–12%, and 24–32% yields, respectively (Scheme 2). Complex **3** then underwent first-order decomposition (k_{obs} = (5.0 ± 0.2) × 10^{-4} s^{-1}) to **10** (k_{obs} (appearance) = (5.0 ± 0.2) × 10^{-4} s^{-1}). The concentration of **11** did not change. The probe was warmed to 25 °C, whereupon **11** underwent first-order decomposition to **10** (k_{obs} = (5.1 ± 0.2) × 10^{-4} s^{-1}). Hence, **10** is formed by two pathways.

Preparative reactions gave **10** as a spectroscopically pure gold-yellow powder (60–70%), which was characterized identically to **9**. Although a satisfactory microanalysis could not be obtained, **10** was assigned as the Re(III) oxidative addition product $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Cl)(CH_2Cl)]^+BF_4^-$ upon the basis of the following: (1) a mass spectral parent ion for the cation (FAB), (2) a CH_2 ^{13}C NMR signal (47.7 ppm) upfield of those of CH_2Cl_2 and **3**, (3) a CH_2 phosphorus coupling (15.5 Hz) much greater than those of alkyl halide (or alkyl) complexes of **I**, and (4) an IR ν_{NO} value (1739 cm^{-1}) significantly greater than those of cationic complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(L)]^+X^-$.[13,14a,d] A similar IR ν_{NO} trend occurs with analogous cyclopentadienyl Re(III) and Re(I) complexes.[7] The NMR features also resembled those of the labile cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)(CH_3)]^+X^-$ (X = Br, I), which have been generated and studied *in situ*.[15,23]

(19) All ratios are normalized to 100, and error limits on each integer are ±2; e.g., 45:55 ≡ (45 ± 2):(55 ±2).

(20) The regeneration of methyl complex **5** is puzzling, and has no counterpart in other reactions of **3**. A similar phenomenon occurs in the cyclopentadienyl series.[7] Perhaps one of the protonated forms of **5**, such as a cationic methyl hydride complex with a *trans* geometry, is slow to eliminate methane. Some donor ligands might induce reductive elimination, but the more basic cyanide ion (pK_a(HCN) = 9.2) could effect deprotonation. Although we are unable to detect any protonated forms of **5** by NMR, the resonances of **5** broaden prior to its apparent consumption. If the reaction vessel is purged with nitrogen, **5** still forms, excluding the possibility of reversible methane elimination.

(21) (a) The absolute configuration at rhenium (specified first in alkene complexes that also contain =CHR stereocenters) is assigned by a variant of the Cahn–Ingold–Prelog rules in which the $\eta^5\text{-}C_5Me_5$ ligand is viewed as a pseudoatom of atomic number 30. This gives the priority sequence $\eta^5\text{-}C_5Me_5$ > ClR > PPh_3 > C=C, C≡C > NO > CN > CH_3. (b) A synclinal (*sc*) Re-(C=C) conformer is one in which the highest priority substituent on rhenium ($\eta^5\text{-}C_5Me_5$) and the C=C centroid (=*C*HR > =*C*H_2) 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 **V**/**VI** and **VII**/**VIII** are 45° and 135°, respectively. (c) See previous papers in this series for background literature on the preceding points.[4a,d]

(22) As assayed by chiral HPLC (hexane/2-propanol, 97:3, 0.30 mL/min; t_1 = 15.4 min, t_2 = 16.8 min).[18b]

(23) For data on other Re(III) complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Y)(Z)]^+X^-$, see: (a) Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 751. (b) Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 309.

Complex **10** was presumed to adopt, like well-known isoelectronic neutral tungsten analogs, a square pyramidal structure with the pentamethylcyclopentadienyl ligand in the apical position. Three geometric isomers would then be possible, which differ in the arrangement of the four basal ligands. However, **10** appeared by all criteria to be a single isomer. Over the course of 24 h in CH_2Cl_2, **10** slowly decomposed.

A CD_2Cl_2 solution that contained ca. 30% of the other decomposition product, **11**, was cooled to −85 °C. NMR spectra were recorded, and selected resonances were assigned.[24] Most importantly, the ^{19}F NMR spectrum showed only uncoordinated BF_4^-. Complex **11** also formed under argon, excluding the possibility of a dinitrogen adduct. When $[Ph_3P{=}N{=}PPh_3]^+I^-$ was added, **11** immediately converted to iodide complex **7**. Similar phenomena have been noted in reactions of the cyclopentadienyl dichloromethane complex **1** and weaker nucleophiles.[7,15] Most of the substitution product would form directly, but small amounts of a "transient" were also generated. At higher temperatures, the transient gave identical products. In efforts to identify this species, ethyl ether and fluorine donor adducts of **I** were prepared.[25] However, in no case did the NMR properties match. The ^{31}P NMR chemical shift relationship between the transient (19.1 ppm, −40 °C) and **11** (22.2 ppm, −85 °C)[24] is similar to that between **1** and **3**. We therefore suggest that the transient and **11** have analogous structures. Possibilities not eliminated by the preceding data would include dirhenium species with bridging dichloromethane or nitrosyl ligands.

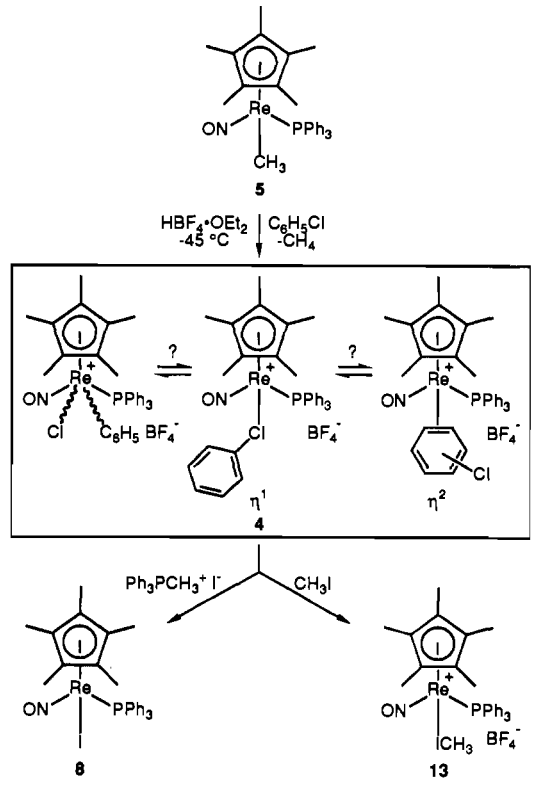
We next sought to react **3** and neutral Lewis bases. First, **3**-d_2 and CH_3I (2.0 equiv) were combined in an NMR tube at −80 °C (Scheme 1). Conversion to the methyl iodide complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ICH_3)]^+BF_4^-$ (**13**) was complete within 5 min, as assayed by ^1H and ^{31}P NMR. The probe was gradually warmed. At 20 °C, **13** slowly decomposed with a half-life of ca. 3 h to numerous products with ^{31}P resonances ranging from 21.8 to 10.7 ppm. The 10.7 ppm species, which may be a Re(III) complex analogous to **10**, constituted 35% of the product when decomposition was 68% complete. After an additional 12 h, only 21.9, 17.8, 14.2, and 11.9 ppm resonances remained. A preparative reaction was conducted with a large excess of methyl iodide. Workup gave crude **13** in 72% yield. However, an analytically pure sample could not be obtained.

As detailed elsewhere, reactions of **3** and aldehydes (3 equiv) gave analytically pure aldehyde complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(O{=}CHR)]^+BF_4^-$ in 85–89% yields (Scheme 1).[13a] We wondered if **3** and less nucleophilic Lewis bases would react. Accordingly, **3** was treated with styrene (3 equiv) and ethyne (1.5 atm). Only the independent decomposition of **3** to **10** occurred, as assayed by ^{31}P NMR. Hence, **3** has a variety of limitations as a functional equivalent of the Lewis acid **II**. This prompted the development of alternatives as described below.

3. Generation and Reactions of a Chlorobenzene Complex. The cyclopentadienyl chlorobenzene complex **2** is generated by reaction of the corresponding methyl complex with $HBF_4{\cdot}OEt_2$ in C_6H_5Cl at −45 °C.[8] As reported earlier, **2** exists as a mixture of linkage isomers, stereoisomers, and constitutional isomers. Nonetheless, all components serve as functional equivalents of the chiral Lewis acid **I**. Thus, the pentamethylcyclopentadienyl analog was sought.

The pentamethylcyclopentadienyl methyl complex **5** and $HBF_4{\cdot}OEt_2$ were combined in C_6H_5Cl in an NMR tube at −45 °C (Scheme 3), and ^{31}P spectra were recorded as the sample was gradually warmed (Figure 2). At −45 °C (Figure 2B), the spectrum was dominated by an apparent multiplet at 22.4 ppm

Scheme 3. Generation of Chlorobenzene Complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**4**) and Reactions with Iodine Nucleophiles



and a sharp singlet at 15.9 ppm (51:49, 85% of integral trace). The latter was 3.4 ppm downfield from the resonance of the η^1 isomer of cyclopentadienyl analog **2** (12.5 ppm, −45 °C, C_6H_5Cl) and close to that of dichloromethane complex **3** (16.2 ppm, −85 °C, CH_2Cl_2). Hence, it was assigned to the η^1 chlorobenzene complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\eta^1\text{-}ClC_6H_5)]^+BF_4^-(\eta^1\text{-}\mathbf{4})$.

After 1 h at −45 °C, the spectrum showed only qualitative changes (Figure 2C). After 5 min at 0 °C (Figure 2D), the resonance assigned to η^1-**4** had noticeably diminished, as resonances at 23.7, 22.6, 22.5, 22.4, 20.2, and 17.8 ppm appeared and/or intensified. These persisted at room temperature (Figure 2F). Multiple runs were conducted, and the spectra in Figure 2 were, with minor variations, reproduced. The cyclopentadienyl analog **2** gave similar spectra.[8] Although η^1-**4** could logically decompose to oxidative addition products, most resonances in Figure 2F are far downfield from that of Re(III) species **10**. They are also downfield from those of alkene complexes of **II** (below) and the cyclopentadienyl η^2-benzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}C_6H_6)]^+BF_4^-$ (8.1 ppm).[26] Nonetheless, on the basis of reactivity characteristics established in the cyclopentadienyl series, all species are presumed to be of the composition **4**.

Selected reactions of **4** with anionic or heteroatomic Lewis bases were investigated. Addition of $Ph_3PCH_3^+I^-$ (−45 °C) gave iodide complex **8** in 84% yield after workup (Scheme 3). No chloride complex **6**—the major product in the analogous reaction of **3**—was detected. Surprisingly, reaction of **4** and $Et_4N^+CN^-$ did not give observable quantities of cyanide complex **9**. NMR monitored experiments showed no reaction at room temperature, and numerous products formed upon warming to 80 °C. Finally, **4** and CH_3I were combined in NMR tubes at −45 °C. In all cases, the methyl iodide complex **13** was generated in spectroscopically pure form (Scheme 3). However, as noted with the reaction of **3** and CH_3I above, decomposition occurred upon warming to room temperature.

(24) Data on **11** (−85 °C, CD_2Cl_2): ^1H NMR (δ) 1.60 (s, C_5Me_5); $^{13}C\{^1H\}$ NMR (ppm) 101.4 (s, C_5Me_5), 9.7 (s, $C_5\mathit{Me}_5$); $^{31}P\{^1H\}$ NMR (ppm) 22.2 (s); ^{19}F NMR (δ) −152.2 (s).

(25) (a) Agbossou, S. K.; Fernández, J. M.; Gladysz, J. A. *Inorg. Chem.* **1990**, *29*, 476. (b) Agbossou, S. K.; Roger, C.; Igau, A.; Gladysz, J. A. *Inorg. Chem.* **1992**, *31*, 419.

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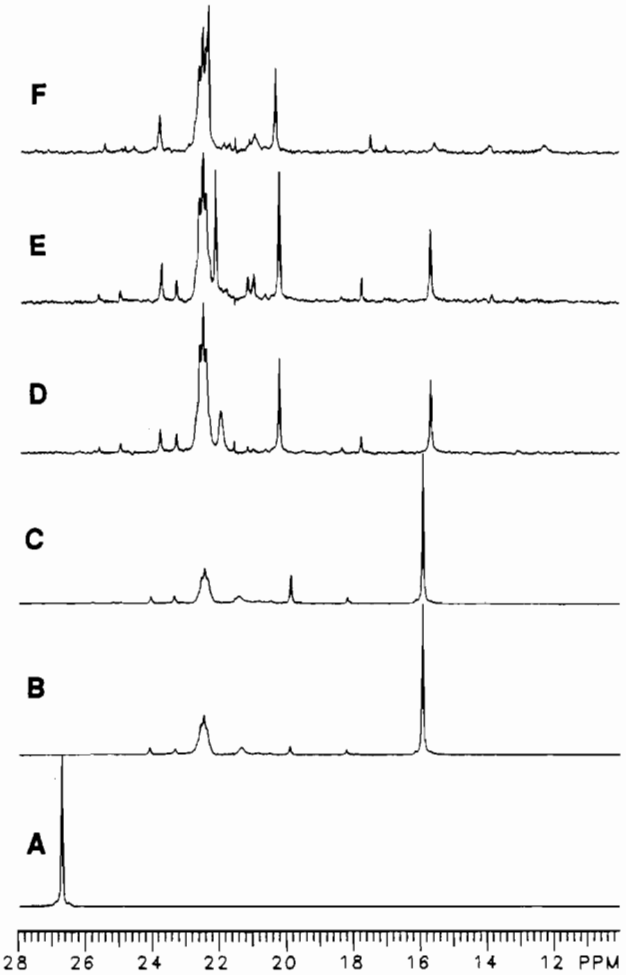


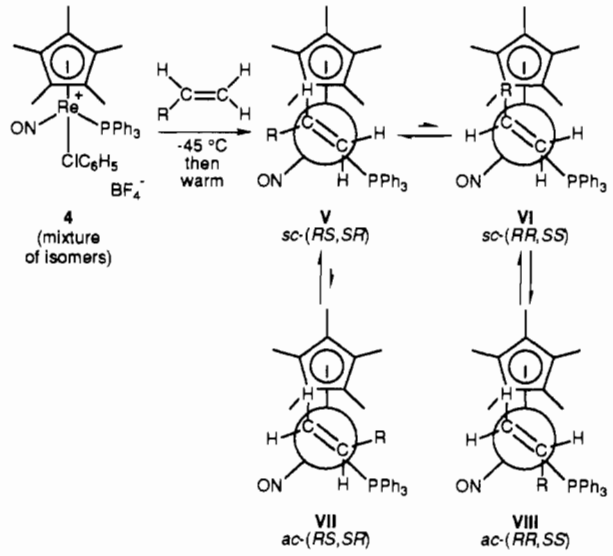
Figure 2. $^{31}P\{^1H\}$ NMR spectra of products from the reaction of methyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CH_3)$ (**5**) and $HBF_4{\cdot}OEt_2$ in chlorobenzene. Key: (A) before mixing at −45 °C; (B) after mixing at −45 °C; (C) after 1 h at −45 °C; (D) after 5 min at 0 °C; (E) after 1 h at 0 °C; (F) after 1 h at 20 °C.

4. Reactions of the Chlorobenzene Complex with Alkenes and Alkynes. We sought to determine whether the Lewis acid **II** would bind alkenes with greater selectivity than **I**, as outlined in the introduction. Thus, **4** and 1-pentene (5 equiv) were combined in an NMR tube (Scheme 4). After 0.5 h at −45 °C, a ^{31}P NMR spectrum showed that **4** had undergone 55% conversion to a 39:61 mixture of *RS,SR*/*RR,SS*[21] diastereomers ((**V** + **VII**)/(**VI** + **VIII**)) of the 1-pentene complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2CH_2CH_3)]^+BF_4^-$ (**14a**; 12.4/12.6 ppm). After 6 h, a low temperature workup gave **14a** in 81% yield as a 39:61 mixture of *RS,SR*/*RR,SS* diastereomers. In contrast, the reaction of cyclopentadienyl analog **2** and 1-pentene gave a 67:33 *kinetic* mixture of *RS,SR*/*RR,SS* diastereomers.[4b]

A similar reaction was kept at room temperature for 12 h. Workup gave **14a** in 87% yield as a 64:36 mixture of *RS,SR*/*RR,SS* diastereomers, indicating some interconversion. In contrast, diastereomers of the analogous cyclopentadienyl complex isomerize only at elevated temperatures.[4b] A similar reaction was kept at 100 °C for 12 h. Workup gave diastereomerically pure (*RS,SR*)-**14a** in 97% yield. A separate NMR experiment showed isomerization to be complete after 1.5 h. In both cases, as little as 1% of (*RR,SS*)-**14a** would have been detected. As shown in Chart 1, the cyclopentadienyl analog gives a 97:3 *RS,SR*/*RR,SS* equilibrium mixture. Thus, the Lewis acid **II** exhibits higher thermodynamic 1-pentene binding selectivity.

Complex **4** and styrene (5 equiv) were also combined in an NMR tube (Scheme 4). After 0.5 h at −45 °C, a ^{31}P NMR spectrum showed that **4** had undergone ca. 80% conversion to a

Scheme 4. Reactions of Chlorobenzene Complex **4** with Alkenes



14

R	temperature (°C) before workup	yield (%)	*RS,SR*/*RR,SS*
a, C_3H_7	-45	81	39 : 61
	23	87	64 : 36
	100	97	>99 : <1
b, C_6H_5	-45	--[a]	80 : 20
	23	97	81 : 19
	100	92	>99 : <1

[a] NMR experiment.

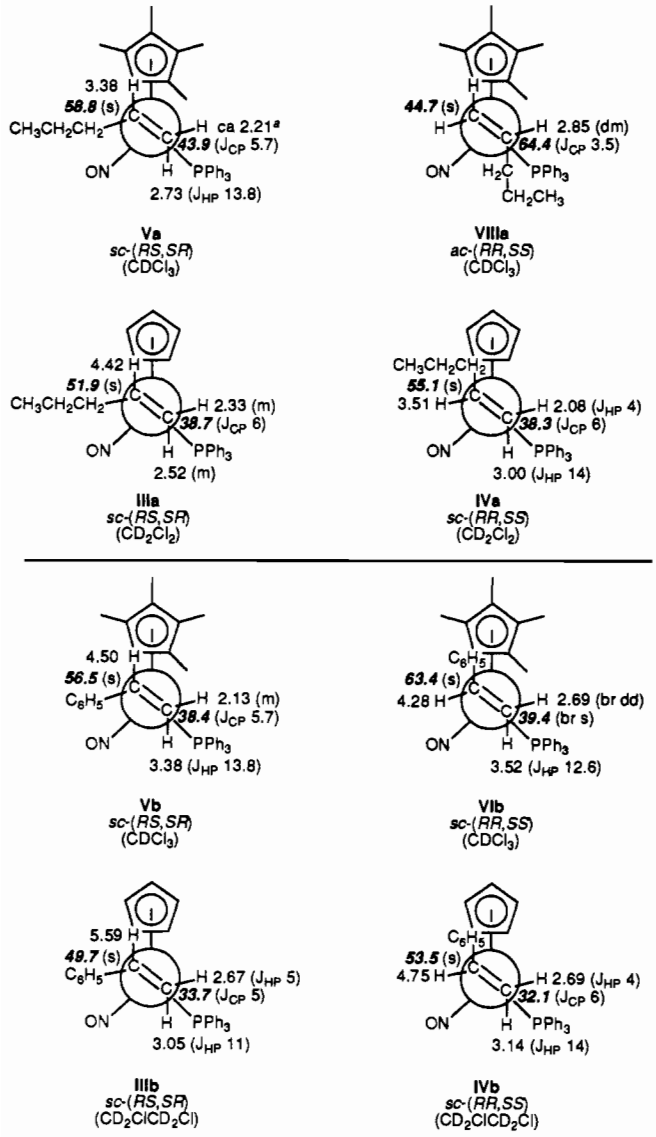
80:20 mixture of *RS,SR*/*RR,SS* diastereomers of the styrene complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(H_2C{=}CHC_6H_5)]^+BF_4^-$ (**14b**). The corresponding reaction of cyclopentadienyl analog **2** gives an identical kinetic mixture of diastereomers.[4b] The probe was warmed to room temperature. A ^{31}P NMR spectrum indicated >95% conversion to **14b** (76:24 *RS,SR*/*RR,SS*).

The probe was then warmed to 50 °C. Over the course of 5 h, (*RR,SS*)-**14b** completely isomerized to (*RS,SR*)-**14b** according to a first-order rate law, with $k_{obs} = (2.06 \pm 0.03) \times 10^{-4}$ s^{-1}. Thus, in contrast to 1-pentene, styrene gives parallel kinetic and thermodynamic binding selectivities with **II**. Furthermore, isomerization of the cyclopentadienyl *RR,SS* diastereomer occurs with the 10-fold *lower* first order rate constant of 2.77×10^{-5} s^{-1} at the much *higher* temperature of 96.5 °C.[4c] Also, only a 90:10 *RS,SR*/*RR,SS* equilibrium mixture is obtained (Chart 1). Thus, the Lewis acid **II** again exhibits a higher thermodynamic binding selectivity. Preparative reactions gave analogous data and high isolated yields, as summarized in Scheme 4.

Complexes **14a,b** were characterized analogously to other new compounds isolated above (Experimental Section). Most NMR properties were similar to those of the cyclopentadienyl analogs. For example, the $=CH_2$ ^{13}C resonances of (*RS,SR*)-**14a,b** (43.9, 38.4 ppm) were coupled to the PPh_3 phosphorus ($^2J_{CP}$ = 5.7 Hz; $w_{1/2}$ = 12.2–11.8 Hz), but the =CHR resonances were not (58.8, 56.5 ppm; $w_{1/2}$ = 5.9–6.6 Hz). This indicates that *sc* Re—(C–C) conformations, which place the smaller $=CH_2$ termini *syn* to the bulky PPh_3 ligand (**V**, Scheme 4), greatly dominate in solution.[4,21b] These and other NMR data are compared with those of cyclopentadienyl complexes in Chart 2 (**Va** vs **IIIa**; **Vb** vs **IIIb**). The $=CH_2$ and =CHR ^{13}C resonances of the less stable *RR,SS* diastereomer of styrene complex **14b** (39.4, 63.4 ppm) were not coupled to phosphorus, but the former was much broader ($w_{1/2}$ = 8.0, 4.8 Hz). This also suggests that a *sc* conformer (**VI**, Scheme 4) dominates in solution.

However, the less stable *RR,SS* diastereomer of 1-pentene complex **14a** exhibited a =CHR ^{13}C resonance that was coupled to phosphorus (64.4 ppm, $^2J_{CP}$ = 3.5 Hz, $w_{1/2}$ = 11.6 Hz), and

Chart 2. Comparison of ^1H (Plain Type) and ^{13}C (Bold, Italic Type) NMR Chemical Shifts (ppm) of Alkene Complexes of **II** and **I**

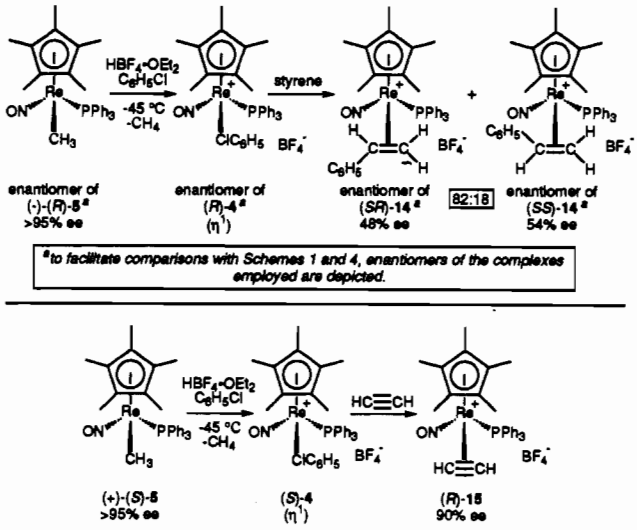


[a] overlapped with CH_2CH_2 resonances.

a $=CH_2$ resonance that was not (44.7 ppm, $w_{1/2}$ = 6.5 Hz). This implied that an *ac* Re—(C=C) conformer (**VIII**, Scheme 4) dominated in solution. In order to verify the assignment, a ^{13}C NMR spectrum was recorded without proton decoupling. The 64.4 ppm resonance gave a broad doublet ($^1J_{CH}$ = 149 Hz), indicative of one directly bound hydrogen. The 44.7 ppm resonance gave a triplet ($^1J_{CH}$ = 159 Hz), indicative of two directly bound hydrogens. Thus, (*RR,SS*)-**14a** is the first alkene complex of **I** or **II** in which the larger C=C terminus is preferentially directed *syn* to the PPh_3 ligand.

We next sought to utilize chlorobenzene complex **4** to prepare nonracemic complexes. Thus, the methyl complex (–)-(*R*)-**5** (>95% ee) was converted to **4** in a manner analogous to the racemate (Scheme 5). Styrene was added, and the sample was kept at room temperature for 0.5 h. Workup gave **14b** in 97% yield as a 82:18 mixture of *SR*/*SS* diastereomers. Analysis with (+)-Eu(hfc)$_3$ showed (*SR*)-**14b** and (*SS*)-**14b** to be 48% and 54% ee, respectively. An identical reaction was conducted, and the sample was kept at 100 °C for 24 h. This gave (*SR*)-**14b** that was only 7% ee. No racemization occurs in the cyclopentadienyl series under identical conditions.[4c] Configurations were assigned by analogy to the stereochemistry established in the cyclopentadienyl series (retention).

Scheme 5. Generation and Reaction of Enantiomerically Enriched Chlorobenzene Complex **4**



As described earlier, racemic **4** can be used to prepare alkyne complexes of **II**.[13b] In connection with other projects, we needed an ethyne complex of high enantiomeric purity. Thus, **4** was generated from (–)-(*R*)-**5** as above in an NMR tube. Excess ethyne was added, and ^{31}P NMR spectra were recorded. After 0.5 h at –45 °C, only the ethyne complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(HC{\equiv}CH)]^+BF_4^-$ (**15**; 19.5 ppm) was present.[13b] A preparative reaction with a room temperature workup gave (+)-(*R*)-**15** in 91% yield. Analysis with (+)-Eu(hfc)$_3$ established an ee of 90%. In an attempt to increase the ee, the sample was crystallized from CH_2Cl_2/ether. Yellow-orange prisms formed (42%) that were 84% ee. The (+)-(*R*)-**15** recovered from the mother liquor (55%) was 94% ee. Column chromatography did not give any fractionation (silica gel, CH_2Cl_2/acetone, 95:5 v/v).

Discussion

1. Preparative Merits of Lewis Acid Equivalents. The preceding reactions show that both dichloromethane complex **3** and chlorobenzene complex **4** can serve as functional equivalents of the chiral Lewis acid **II**. However, in the cases investigated, **3** reacts with anionic Lewis bases chiefly at the dichloromethane *carbon*. The much lower reactivity of aryl chloride linkages prevents such complications with **4**. However, we do not have a rationale for the apparent lack of reaction with cyanide ion. Furthermore, **4** is distinctly more reactive than **3** towards styrene at –45 °C.

Unfortunately, we have not been able to devise protocols that give substitution products of **3** or **4** that are >90% ee. Importantly, any unreacted methyl complex **5** is recovered with its original optical purity. Thus, racemization could occur (a) during the conversion to **5** to **3** or **4**, (b) due to the independent configurational instability of **3**, **4**, or substitution products, or (c) during the substitution step. Some compounds, such as styrene complex **14b**, are clearly less configurationally stable than cyclopentadienyl analogs.

We have previously shown that PPh_3 dissociates from the pentamethylcyclopentadienyl methoxide complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(OCH_3)$ 60–80 times faster than from the cyclopentadienyl analog at 14–19 °C.[14f,27] This occurs with anchimeric assistance of the methoxide oxygen lone pairs, and good evidence has been obtained for the subsequent formation of a trigonal planar species. The more electron-releasing pentamethylcyclopentadienyl ligand should stabilize an electron deficient intermediate better than a cyclopentadienyl ligand.

(27) See also Dewey, M. A.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1351.

Furthermore, the greater bulk provides an additional steric driving force for lowering the coordination number.

Hence, the lower configurational stabilities of Lewis base adducts of **II** may be due to enhanced rates of PPh_3 *or* Lewis base dissociation. However, it should be emphasized that the cyclopentadienyl dichloromethane complex **1** undergoes substitution by an *associative* mechanism.[9] Furthermore, no evidence has yet been found for any process involving the intermediacy of the unencumbered Lewis acid **I**.[4c] Thus, additional experiments will be required to firmly establish the mechanism(s) of racemization.

The cyclopentadienyl triflate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ provides a useful functional equivalent of the Lewis acid **I**.[28] Although this is one of the more configurationally labile complexes, it is easily generated and reacted *in situ*.[5d] Many substitution products have been isolated in >98% ee.[5d,18a,29] Thus, the pentamethylcyclopentadienyl analog may provide a valuable complement to the above methodology.

2. Chiral Recognition. In accord with the expectations in the introduction, monosubstituted alkenes give higher thermodynamic enantioface binding selectivities with Lewis acid **II** than Lewis acid **I**. Data for 1-pentene and styrene are summarized in Chart 1 and Scheme 4. This trend follows logically from the enhanced bulk of the pentamethylcyclopentadienyl ligand in **II**. In fact, the actual equilibrium values may be much greater than our >99:<1 detection limits. To our knowledge, no other chiral receptor gives a comparable level of discrimination between the enantiofaces of monosubstituted alkenes.

The thermodynamic binding selectivities of **I** and a variety of other alkenes have been measured.[4d-f] It is probable that those of **II** will be significantly higher, particularly with geminally-substituted alkenes $H_2C{=}CRR'$. Also, aldehydes are roughly isosteric with monosubstituted alkenes, and give π adducts with **II**.[13a] Although only one set of NMR resonances can be detected at low temperature, the possibility that two rapidly equilibrating diastereomers (analogous to **V**/**VI**, Scheme 4) are present has not yet been excluded. However, on the basis of the preceding data, aldehyde enantioface binding selectivities must similarly be very high.

The Re–(C=C) conformations of **14a,b** are also of interest. For the more stable *RS,SR* diastereomers, orientations are analogous to those of the cyclopentadienyl analogs (**V**, Scheme 4). However, for the less stable 1-pentene complex (*RR,SS*)-**14a**, the dominant Re–(C=C) conformation is opposite to that in the cyclopentadienyl series. This places the propyl C=C substituent in the congested interstice[30] between the large PPh_3 and small nitrosyl ligands (**VIII**, Scheme 4). This is apparently energetically preferable to the alternative (**VI**, Scheme 4), in which the propyl group would interact with the pentamethylcyclopentadienyl ligand. However, the latter conformation dominates with the less stable styrene complex (*RR,SS*)-**14b**. We have documented related equilibria in which a phenyl group has a smaller effective size than an alkyl group.[4f]

Potential applications of these impressive levels of chiral recognition are compromised, at least in some cases, by seemingly modest configurational stabilities. However, it may be possible to eliminate these problems by modifying the Lewis acid **II**. For example, the trifluorinated pentamethylcyclopentadienyl ligand $C_5Me_4CF_3$ has an inductive effect similar to that of cyclopentadienyl.[10d] However, its steric properties are identical with those of pentamethylcyclopentadienyl. Thus, the Lewis acid $[(\eta^5\text{-}C_5Me_4CF_3)Re(NO)(PPh_3)]^+$ should give alkene binding selectivities comparable to those of **II**. However, ligand dissociation should on electronic grounds be slower than with adducts of **II**. Properties could be "fine tuned" through further addition or subtraction of fluorines. Hence, there is now a wealth of literature data and precedent that should facilitate the rational design and optimization of chiral transition metal Lewis acids.

3. Chlorohydrocarbon Ligands. Oxidative additions of organic halides to coordinatively unsaturated metal centers are key steps in a variety of important reactions. Examples involving commodity chemicals include the Monsanto methanol to acetic acid process, related acetic anhydride and vinyl acetate syntheses, and the BASF butadiene to adipic acid process.[31] Other examples include the many metal-catalyzed cross-coupling reactions of organic halides used in fine chemical syntheses[32] and new halocarbon or halohydrocarbon environmental remediation technologies.[33] Thus, the mechanisms of organic halide oxidative additions have been studied in detail.[34]

The Lewis acid **II** constitutes the first metal fragment in which alkyl halide coordination can be observed prior to an oxidative addition event. We believe that oxidative addition occurs directly from **3**, in a conceptually analogous fashion to the pre-coordination established for arene carbon-hydrogen bond oxidative addition.[35] We favor the inner-sphere electron transfer mechanism illustrated in eq 1.[34] However, our present data do not rule out prior

$$M\text{—}ClR \longrightarrow \overline{M\text{—}Cl + \cdot R} \longrightarrow \underset{\displaystyle R}{\overset{\displaystyle |}{M\text{—}Cl}} \qquad (1)$$

dichloromethane dissociation from **3**, followed by an oxidative addition pathway not involving **3**.

Although only a few chlorohydrocarbon complexes have been isolated,[36] many others have now been characterized in solution.[37] In particular, Strauss and Waters have reported crystal structures of silver and ruthenium complexes that contain bidentate dichloromethane ligands.[36a,c] Also, numerous oxidative additions of dichloromethane to metal fragments have been observed.[38] At least some of these likely involve intermediate dichloromethane

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complexes. We are not aware of other chlorine-ligated chlorobenzene complexes analogous to η^1-**4**. However, numerous η^6 π complexes exist, and chlorobenzene solvates have been detected as intermediates in substitution reactions.[39]

4. Summary. This study has consolidated a wide variety of data involving the chiral rhenium Lewis acid **II** and addressed two principal themes: (1) the development of chlorohydrocarbon complexes that serve as functional equivalents of **II** and (2) chiral recognition in the binding of monosubstituted alkenes. Although some limitations remain in the synthetic procedures, the preceding compounds and protocols will see extensive use in future studies from this laboratory.

Experimental Section[40]

$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (3). A 5 mm NMR tube was charged with $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CH_3)$ (**5**, 0.031 g, 0.050 mmol)[14a] and CH_2Cl_2 or CD_2Cl_2 (ca. 0.6 mL) and capped with a septum. The tube was cooled to −80 °C (acetone/CO_2), and $HBF_4{\cdot}OEt_2$ (5.4 μL, 0.050 mmol) was added. The tube was shaken and quickly transferred to a −85 °C NMR probe, and spectra were recorded. Preparative reactions were conducted in Schlenk flasks with stirring. The dark orange solutions were kept at −80 °C for 15–30 min before Lewis base addition.

NMR (−62 °C, CH_2Cl_2): ^1H (δ) 7.62–7.00 (m, PPh_3), 1.68 (s, C_5Me_5); $^{13}C\{^1H\}$ (ppm) 135.5–130.5 (*o,p,i*-Ph),[41] 129.0 (d, J_{CP} = 9.7, *m*-Ph), 102.6 (s, C_5Me_5), 75.8 (d, J_{CP} = 5.0, CH_2), 9.4 (s, C_5Me_5); $^{31}P\{^1H\}$ (ppm) 16.2 (s); ^{19}F (ppm) −152.7 (s).

$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (4). Complex **5** (0.031 g, 0.050 mmol), C_6H_5Cl (0.8 mL), and $HBF_4{\cdot}OEt_2$ (5.4 μL, 0.050 mmol) were combined in an NMR tube at −45 °C (CH_3CN/CO_2) in a procedure analogous to that given for **3**. The tube was shaken and quickly transferred to a −45 °C NMR probe, and $^{31}P\{^1H\}$ (22.6, 21.6, 16.0 ppm; 3s, 39:9:52) and ^1H spectra (δ 1.51, 1.43, 1.29; 3s, 12:39:50; C_5Me_5) were recorded. Figure 2 shows data from a second experiment. Preparative reactions were conducted in Schlenk flasks with stirring. The dark orange solutions were kept at −45 °C for 15–30 min before Lewis base addition.

Reactions of 3 and 4 with Halide Ions. A. Complex **3** was generated from **5** (0.081 g, 0.13 mmol), CH_2Cl_2 (5 mL), and $HBF_4{\cdot}OEt_2$ (19 μL, 0.15 mmol). After 10 min, PPN^+Br^- (0.092 g, 0.15 mmol) was added with stirring. The cold bath was removed. After 30 min, the deep red solution was filtered through a 3-cm silica plug and washed with CH_2Cl_2 (40 mL). Solvent was removed by rotary evaporation, and the orange red powder was dried under oil pump vacuum. This gave a mixture (0.081 g) of the known halide complexes[14e,42] $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Cl)$ (**6**, 92%) and $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Br)$ (**7**, 4%), as assayed by ^1H NMR ($CDCl_3$, δ 1.63/1.66, C_5Me_5).

B. Complex **5** (0.095 g, 0.15 mmol), CH_2Cl_2 (5 mL), $HBF_4{\cdot}OEt_2$ (22 μL, 0.17 mmol), and $Ph_3PCH_3^+\ I^-$ (0.076 g, 0.19 mmol) were combined in a procedure analogous to method A. An identical workup gave a mixture (0.096 g) of halide complexes **6** (95%; δ 1.63) and $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(I)$ (**8**, <2%; δ 1.74).[14e,42]

C. Complex **5** (0.052 g, 0.083 mmol), CH_2Cl_2 (5 mL), $HBF_4{\cdot}OEt_2$ (11 μL, 0.10 mmol), and $Ph_3PCH_3^+\ I^-$ (0.046 g, 0.11 mmol) were combined in a procedure analogous to method A. Decane (18 μL, 0.092 mmol) was added, and GC[40b] (35–125 °C) showed ICH_2Cl to be present in 88% yield (verified by GC/MS).

D. Complex **4** was generated from **5** (0.063 g, 0.10 mmol), C_6H_5Cl (2 mL), $HBF_4{\cdot}OEt_2$ (12 μL, 0.11 mmol). After 10 min, $Ph_3PCH_3^+I^-$ (0.051 g, 0.13 mmol) was added with stirring. Workup as in procedure A gave **8** (0.062 g, 0.084 mmol, 84%).

$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CN)$ (9). A. Complex **3** was generated in an NMR tube from **5** (0.063 g, 0.10 mmol), CH_2Cl_2 (0.8 mL), and $HBF_4{\cdot}OEt_2$ (11.8 μL, 0.110 mmol). The tube was shaken and quickly transferred to a −80 °C NMR probe. A ^{31}P spectrum showed **5** to be consumed. Then $Et_4N^+\ CN^-$ (0.031 g, 0.20 mmol) was added with shaking. Over the course of 15 min, **3** (16.3 ppm) disappeared (data: see text). The probe was warmed to room temperature, and solvent was removed under oil pump vacuum. The residue was chromatographed on a silica column (15 × 1.3 cm, CH_2Cl_2). Solvent was removed from orange, red, and yellow bands (the last was eluted with CH_2Cl_2/acetone, 90:10 v/v) to give **5** (0.007 g, 0.01 mmol, 12%), **6** (0.026 g, 0.039 mmol, 39%), and **9**, respectively. Complex **9** was dissolved in CH_2Cl_2 (1 mL), and pentane (2 mL) was added. After 1 h, yellow needles formed, which were collected by filtration and dried under oil pump vacuum (0.021 g, 0.032 mmol, 32%); dec pt 248-249 °C. Anal. Calcd for $C_{29}H_{30}N_2OPRe$: C, 54.45; H, 4.73. Found: C, 54.22; H, 4.79. IR (cm^{-1}, thin film) ν_{NO} 1652 vs, ν_{CN} 2090 s. A 5-mm NMR tube was charged with **9** (0.003 g, 0.005 mmol), $CDCl_3$ (0.6 mL), and (+)-Eu(hfc)$_3$ (0.006 g, 0.005 mmol). After 15 h,[43] a ^1H spectrum showed C_5Me_5 resonances at δ 3.75 and 3.07 (50:50).

B. Procedure A was repeated on an identical scale but utilizing (−)-(*R*)-**5** (>95% ee).[14d,22] An identical workup gave (−)-(*R*)-**5** (0.007 g, 0.01 mmol, 11%; >95% ee, HPLC),[22] **6** (0.022 g, 0.035 mmol, 35%), and (*R*)-**9** (0.022 g, 0.034 mmol, 34%). A $CDCl_3$ solution of (*R*)-**9** was treated with (+)-Eu(hfc)$_3$ as above. ^1H NMR (δ): 4.53, 3.67 (95:5; 90% ee).[43]

NMR for **9** ($CDCl_3$): ^1H (δ) 7.58–7.36 (m, PPh_3), 1.80 (s, C_5Me_5); $^{13}C\{^1H\}$ (ppm) 134.3 (d, J_{CP} = 56.5, *i*-Ph), 133.8 (d, J_{CP} = 11.0, *o*-Ph), 130.4 (s, *p*-Ph), 129.3 (d, J_{CP} = 12.1, CN), 128.3 (d, J_{CP} = 10.4, *m*-Ph), 100.7 (s, C_5Me_5), 10.1 (s, C_5Me_5); $^{31}P\{^1H\}$ (ppm) 19.6 (s).

$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(Cl)(CH_2Cl)]^+BF_4^-$ (10). Complex **3** was generated from **5** (0.138 g, 0.219 mmol), CH_2Cl_2 (10 mL), and $HBF_4{\cdot}OEt_2$ (30 μL, 0.24 mmol). The cold bath was removed. After 1 h, solvent was removed by rotary evaporation. The residue was extracted with THF (10 mL) and ether (75 mL) was added. The resulting tan powder was collected by filtration and dried under oil pump vacuum to give **10** (0.131 g, 0.167 mmol, 76%), mp 90–95 °C. Anal. Calcd for $C_{29}H_{32}BCl_2F_4NOPRe$: C, 44.35; H, 4.11; Cl, 9.03. Found: C, 45.06; H, 4.11; Cl, 7.89. IR (cm^{-1}, KBr): ν_{NO} 1739 vs. MS:[44] 698 (M^+, 26%), 649 ($M^+ - CH_2Cl$, 84%), 436 ($M^+ - PPh_3$, 59%).

NMR ($CDCl_3$): ^1H (δ) 7.75–7.36 (m, PPh_3), 4.58 (dd, J_{HH} = 7.2, J_{HP} = 3.1, C*H*H′), 4.22 (dd, J_{HH} = 7.2, J_{HP} = 3.0, CH*H*′), 1.93 (s, C_5Me_5); $^{13}C\{^1H\}$ (ppm) 135.1 (d, J_{CP} = 9.0, *o*-Ph), 133.5 (s, *p*-Ph), 132.9 (d, J_{CP} = 52.5, *i*-Ph), 129.1 (d, J_{CP} = 11.0, *m*-Ph), 115.9 (s, C_5Me_5), 47.7 (d, J_{CP} = 15.5, CH_2), 10.2 (s, C_5Me_5); $^{31}P\{^1H\}$ (ppm) 10.9 (s).

$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ICH_3)]^+BF_4^-$ (13). A. Complex **3**-d_2 was generated in an NMR tube from **5** (0.063 g, 0.10 mmol), CD_2Cl_2 (0.6 mL), and $HBF_4{\cdot}OEt_2$ (12 μL, 0.11 mmol). Then CH_3I (12.5 μL, 0.200 mmol) was added. The tube was shaken and quickly transferred to a −80 °C NMR probe. Both ^{31}P (16.0 ppm) and ^1H (δ 2.51, 1.75) spectra showed complete conversion to **13**. The probe was gradually warmed to 20 °C as NMR spectra were recorded. Data: see text.

B. Complex **4**-d_5 was generated in an NMR tube from **5** (0.063 g, 0.10 mmol), C_6D_5Cl (0.6 mL), and $HBF_4{\cdot}OEt_2$ (12 μL, 0.10 mmol). Then CH_3I (62.3 μL, 1.00 mmol) was added. The tube was shaken and quickly transferred to a −45 °C NMR probe. A ^{31}P spectrum (16.2 ppm) showed complete conversion to **13**.

C. A Schlenk flask was charged with **5** (0.169 g, 0.269 mmol), CH_2Cl_2 (10 mL), CH_3I (5 mL, 80 mmol), and a stir bar and was cooled to −80 °C. Then $HBF_4{\cdot}OEt_2$ (36 μL, 0.28 mmol) was added with stirring. The cold bath was removed. After 15 min, the flask was again cooled to −80 °C, and ether (60 mL) was added with stirring. The resulting tan-yellow powder was collected by filtration and dried under oil pump vacuum to give **13** (0.164 g, 0.195 mmol, 72%). IR (cm^{-1}, KBr): ν_{NO} 1680 vs.

NMR (CD_2Cl_2): ^1H (δ) 7.54–7.26 (m, PPh_3), 2.44 (s, ICH_3), 1.85 (s, C_5Me_5); $^{13}C\{^1H\}$ (ppm) 133.7 (d, J_{CP} = 11.3, *o*-Ph), 132.0 (s, *p*-Ph), 129.6 (d, J_{CP} = 10.8, *m*-Ph),[45] 103.4 (s, C_5Me_5), 10.5 (s, C_5Me_5), −4.2 (s, ICH_3); $^{31}P\{^1H\}$ (ppm) 15.8 (s).

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(40) (a) General procedures and chemical sources were identical with those given in a previous paper.[4b] Additiional reagents used were as follows: CH_3I (Aldrich), distilled from P_2O_5; ethyne (Matheson, ≥99.6%), passed through Drierite; $Et_4N^+\ CN^-$ (Kluka), $PPN^+\ Br^-$, $Ph_3PCH_3^+\ I^-$, and alkenes (Aldrich), used without purification. (b) GC data were obtained on an HP-5890 chromatograph with an HP-5 fused silica capillary column. (c) NMR spectra were recorded at ambient probe temperature unless noted and referenced as follows: ^1H (δ), $Si(CH_3)_4$ (0.00), CH_2Cl_2 (5.40), or $CHDCl_2$ (5.32); ^{13}C (ppm), $CDCl_3$ (77.0) or CD_2Cl_2 (53.8); ^{31}P (ppm), external 85% H_3PO_4 (0.00); ^{19}F (ppm), C_6F_6 (−162.9). All coupling constants (*J*) are given in Hz.

(41) Complex PPh_3 ^{13}C resonance patterns were observed, presumably due to restricted rotation about the Re–P and/or P–C bonds.

(42) The IR, ^1H NMR, and ^{31}P NMR spectra were identical with those of an authentic sample of the racemate.

(43) The difference in chemical shifts of the enantiomers (Δδ) increases with time.

(44) Conditions: (+)-FAB, 7 kV, Ar, 3-nitrobenzyl alcohol/$CHCl_3$ matrix, *m/Z* (relative intensity), $^{187}Re/^{35}Cl$.

(45) The *ipso* carbon was not located.

[(η^5-C_5Me_5)Re(NO)(PPh_3)(H_2C=$CHCH_2CH_2CH_3$)]$^+BF_4^-$ (14a). A. Complex **4** was generated in an NMR tube from **5** (0.063 g, 0.10 mmol), C_6H_5Cl (1 mL), and HBF_4·OEt_2 (12 μL, 0.11 mmol). After 15 min, 1-pentene (55 μL, 0.50 mmol) was added. The tube was shaken and quickly transferred to a −45 °C NMR probe (data: see text). After 6 h, the solution was added to cold pentane (20 mL, −80 °C). The resulting precipitate was collected by filtration and dried under oil pump vacuum to give **14a** (0.063 g, 0.081 mmol, 81%; 39:61 *RS,SR/RR,SS*).

B. Complex **4** was generated from **5** (0.126 g, 0.200 mmol), C_6H_5Cl (5 mL), and HBF_4·OEt_2 (24 μL, 0.22 mmol). After 15 min, 1-pentene (110 μL, 1.00 mmol) was added with stirring. The cold bath was removed. After 12 h, the solution was added dropwise to hexane (50 mL). The resulting tan powder was collected by filtration, washed with pentane (2 × 3 mL), and dried under oil pump vacuum to give **14a** (0.134 g, 0.174 mmol, 87%; 64:36 *RS,SR/RR,SS*).

C. Complex **5** (0.063 g, 0.10 mmol), C_6H_5Cl (2.5 mL), HBF_4·OEt_2 (12 μL, 0.11 mmol), and 1-pentene (55 μL, 0.50 mmol) were combined in a procedure analogous to B. The solution was then stirred at 100 °C for 24 h. An identical workup gave **14a** (0.075 g, 0.097 mmol, 97%; >99:<1 *RS,SR/RR,SS*) as a tan powder, dec pt 85–88 °C. Anal. Calcd for $C_{33}H_{40}BF_4NOPRe$: C, 51.43; H, 5.23. Found: C, 51.17; H, 5.21. IR (cm^{-1}, thin film): ν_{NO} 1694 s.

NMR for (*RS,SR*)-**14a** ($CDCl_3$): ^1H (δ) 7.70–7.30 (m, PPh_3), 3.38 (dm, J_{HH} = 10.0, =CHR), 2.73 (ddd, J_{HH} = 3.8, 10.0, J_{HP} = 13.8, H_Z),[46] 2.21–1.20 (m, CH_2CH_2 and H_E), 1.74 (s, C_5Me_5), 0.73 (t, J_{HH} = 7.3, CH_3); $^{13}C\{^1H\}$ (ppm) 133.2 (m, *o*-Ph),[41] 132.0 (s, *p*-Ph), 129.4 (d, J_{CP} = 10.1, *m*-Ph),[45] 106.6 (s, C_5Me_5), 58.8 (s, $w_{1/2}$ = 5.9, =CHR), 43.9 (d, J_{CP} = 5.7, $w_{1/2}$ = 12.2, $=CH_2$), 39.7 (s, $=CHCH_2$), 27.0 (CH_2CH_3), 13.8 (s, CH_3), 9.6 (s, C_5Me_5); $^{31}P\{^1H\}$ (ppm) 12.6 (s). NMR for (*RR,SS*)-**14a** (partial): ^1H (δ) 2.85 (dm, J_{HH} = 13.1, =CHR), 1.70 (s, C_5Me_5), 0.57 (t, J_{HH} = 7.3, CH_3); $^{13}C\{^1H\}$ (ppm) 133.6 (d, J_{CP} = 9.6, *o*-Ph), 132.1 (s, *p*-Ph), 129.3 (d, J_{CP} = 9.6, *m*-Ph),[45] 106.7 (s, C_5Me_5), 64.4 (d, J_{CP} = 3.5, $w_{1/2}$ = 11.6, =CHR), 44.7 (s, $w_{1/2}$ = 6.5, $=CH_2$), 38.7 (s, $=CHCH_2$), 29.1 (CH_2CH_3), 13.8 (s, CH_3), 9.8 (s, C_5Me_5); $^{31}P\{^1H\}$ (ppm) 12.7 (s).

[(η^5-C_5Me_5)Re(NO)(PPh_3)(H_2C=CHC_6H_5)]$^+BF_4^-$ (14b). A. Complex **5** (0.126 g, 0.200 mmol), C_6H_5Cl (5 mL), HBF_4·OEt_2 (24 μL, 0.22 mmol), and styrene (114 μL, 1.00 mmol) were combined in a reaction analogous to procedure B for **14a**. An identical workup gave **14b** (0.156 g, 0.194 mmol, 97%; 81:19 *RS,SR/RR,SS*) as a pale-yellow powder.

B. Complex **5** (0.063 g, 0.10 mmol), C_6H_5Cl (2.5 mL), HBF_4·OEt_2 (12 μL, 0.11 mmol), and styrene (57 μL, 0.50 mmol) were combined as in procedure A. The solution was then stirred at 100 °C for 24 h. An identical workup gave **14b** (0.074 g, 0.092 mmol, 92%; >99:<1 *RS,SR/RR,SS*) as a pale-yellow powder, mp 154–158 °C dec. Anal. Calcd for $C_{36}H_{38}BF_4NOPRe$: C, 53.73; H, 4.76. Found: C, 53.10; H, 4.79. IR (cm^{-1}, thin film): ν_{NO} 1706 s. An NMR tube was charged with (*RS,SR*)-**14b** (0.004 g, 0.005 mmol), $CDCl_3$ (0.5 mL), and (+)-Eu(hfc)$_3$ (0.012 g, 0.010 mmol) and then shaken. After 12 h, a ^1H spectrum showed C_5Me_5 resonances at δ 2.63 and 2.56 (50:50).[43]

C. Complex (−)-(*R*)-**5** (0.031 g, 0.05 mmol, >95% ee),[14d,22] C_6H_5Cl (2 mL), HBF_4·OEt_2 (5.9 μL, 0.055 mmol), and styrene (29 μL, 0.55 mmol) were combined as in procedure A. The cold bath was removed and the solution was stirred for 30 min. An identical workup gave **14b** (0.039 g, 0.048 mmol, 97%; 82:18 *SR/SS*). A $CDCl_3$ solution was treated with (+)-Eu(hfc)$_3$ as above. ^1H NMR (δ): 2.22, 2.18 (26:74 *RS/SR*, 48% ee), 1.84, 1.82 (23:77 *RR/SS*, 54% ee).[43]

NMR for (*RS,SR*)-**14b** ($CDCl_3$): ^1H (δ) 7.70–6.90 (m, PPh_3 and 3H of CPh), 6.44 (d, J_{HH} = 7.5, 2H of CPh), 4.50 (ddd, J_{HH} = 10.5, 10.5, J_{HP} = 2.2, =CHR), 3.38 (ddd, J_{HH} = 4.9, 10.5, J_{HP} = 13.8, H_Z), 2.13 (m, H_E), 1.77 (s, C_5Me_5); $^{13}C\{^1H\}$ (ppm) 134.2–132.1 (m, PPh_3),[41] *CPh* at 139.4 (s), 127.9 (s), 127.4 (s), 126.0 (s), 107.0 (s, C_5Me_5), 56.5 (s, $w_{1/2}$ = 6.6, =CHR), 38.4 (d, J_{CP} = 5.7, $w_{1/2}$ = 11.8, $=CH_2$), 9.7 (s, C_5Me_5); $^{31}P\{^1H\}$ (ppm) 11.2 (s). NMR for (*RR,SS*)-**14b** (partial): ^1H (δ) 4.28 (dd, J_{HH} = 14.8, 9.1, =CHR), 3.52 (ddd, J_{HH} = 3.4, 9.1, J_{HP} = 12.6, H_E), 2.69 (br dd, J_{HH} = 3.4, 14.8, H_Z), 1.54 (s, C_5Me_5): $^{13}C\{^1H\}$ (ppm) *CPh* at 137.9 (s), 128.5 (s), 128.1 (s), 126.3 (s), 107.0 (s, C_5Me_5), 63.4 (s, $w_{1/2}$ = 4.8, =CHR), 39.4 (br s, $w_{1/2}$ = 8.0, $=CH_2$), 9.5 (s, C_5Me_5); $^{31}P\{^1H\}$ (ppm) 13.5 (s).

(+)-(*R*)-[(η^5-C_5Me_5)Re(NO)(PPh_3)(HC≡CH)]$^+BF_4^-$ (15). Complex (+)-(*S*)-**5** (0.164 g, 0.260 mmol, >95% ee),[14d,22] C_6H_5Cl (5 mL), and HBF_4·OEt_2 (28 μL, 0.26 mmol) were combined in a reaction analogous to procedure C for **14b**, except that a Schlenk tube with an O-ring-sealed Teflon stopcock was employed. The tube was evacuated. Excess ethyne was condensed into the mixture, the stopcock was closed, and the cold bath was removed. After 4 h, an identical workup gave (+)-(*R*)-**15** (0.173 g, 0.238 mmol, 91%) as a tan powder.[13b,42] A $CDCl_3$ solution was treated with (+)-Eu(hfc)$_3$. ^1H NMR (δ): 2.54, 2.48 (95:5, 90% ee).[43]

B. A portion of (+)-(*R*)-**15** from procedure A (0.050 g, 0.069 mmol) was dissolved in CH_2Cl_2 (2 mL) and layered with ether. This gave yellow-orange prisms of (+)-(*R*)-**15** (0.021 g, 0.029 mmol, 42%; 84% ee, (+)-Eu(hfc)$_3$). Solvent was removed from the mother liquor, and the residue was precipitated from CH_2Cl_2/ether. This gave (+)-(*R*)-**15** as a yellow powder (0.028 g, 0.038 mmol, 55%; 94% ee, (+)-Eu(hfc)$_3$), dec pt 106–111 °C, $[\alpha]_{589}^{25}$ 160.8 ± 2.7° (*c* = 0.648 mg/mL, $CHCl_3$).[47]

Acknowledgment. We thank the NSF for support of this research.

(46) The vinylic protons H_Z and H_E are defined with reference to the =CHR substituent; see also Chart 2.

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