mol^{-1}.[11] A lengthening of the sulfur–sulfur bond (2.26 Å in $[(Fe(CNC_6H_4CF_3)_2(\eta\text{-}C_5H_5))_2(Ph_2S_2)](BF_4)_2$[4] vs. 2.023 (1) Å in Ph_2S_2[12]) occurs in conjunction with the observed decrease in bond strength.

We should qualify this comparison of bond strengths by observing that the free-ligand value was obtained from gas-phase measurements whereas our result comes from a solution reaction and will presumably be influenced by solvation effects. Also, it seems reasonable that repulsion of positive charges for the two monomers may be contributing to the weakening of the sulfur–sulfur bond in the disulfide-bridged complex. This point certainly warrants further study. Nonetheless, we still believe that there is merit to our earlier contention[2,3] that the sulfur–sulfur bond is weakened by back-bonding from the metal to a sulfur–sulfur antibonding orbital. It is also conceivable that the monomer, a radical species, is stabilized by ligands that are good donors. More study needs to be directed to this question in the future.

Registry No. $[Fe(SPh)(CO)(P(OEt)_3)(\eta\text{-}C_5H_5)]PF_6$, 76452-73-8; $[Fe(SPh)(CO)(P(OPh)_3)(\eta\text{-}C_5H_5)]PF_6$, 76468-63-8; $[Fe(SPh)(n\text{-}CNC_6H_4OMe)_2(\eta\text{-}C_5H_5)]BF_4$, 87681-64-9; $[Fe(SPh)(n\text{-}CNC_6H_4CF_3)_2(\eta\text{-}C_5H_5)]BF_4$, 87681-66-1.

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Cleavage of the Rhenium–Methyl Bond of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ by Protic and Halogen Electrophiles: Stereochemistry at Rhenium

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Reaction of (+)-(*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ ((+)-(*S*)-**1**) with HX gives (+)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ (X = Cl, (+)-(*S*)-**2**; X = Br, (+)-(*R*)-**3**; X = I, (+)-(*R*)-**4**; X = OSO_2CF_3, (+)-(*R*)-**5**; X = $OCOCF_3$, (+)-(*R*)-**6**; X = OCHO, (+)-(*R*)-**7**; X = $OSO_2\text{-}p\text{-}C_6H_4CH_3$, (+)-(*R*)-**8**) in 63–85% yields and ≥99% retention of configuration at rhenium. The corresponding reactions of (±)-**1** give (±)-**2**–(±)-**8** (69–89%). Triflate (+)-(*R*)-**5** and halides (+)-(*S*)-**2** and (+)-(*R*)-**3** are configurationally and chemically less stable than the other cleavage products. Reactions of (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ with (+)-(*R*)-**5**, (+)-(*S*)-**2**/$AgPF_6$, (+)-(*R*)-**3**/$AgPF_6$, and (+)-(*R*)-**4**/$AgPF_6$ give (+)-(*SS*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+X^-$ ((+)-(*SS*)-**9**$^+$X$^-$) of ≥99% diastereomeric purity. Reaction of (+)-(*R*)-**7** with $(CH_3)_3SiCl$ gives $HCO_2Si(CH_3)_3$ and (+)-(*S*)-**2** in 98% ee. Reaction of (+)-(*R*)-**5** with CO (2000 psi) gives (+)-(*S*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+CF_3SO_3^-$ in 78% ee. Reaction of (+)-(*S*)-**1** with Cl_2, Br_2, and I_2 gives essentially racemic **2**, **3**, and **4**, respectively. The mechanisms of these reactions, and absolute configuration assignments, are discussed. Products **2**–**8** are characterized by microanalysis and NMR, IR, mass, UV, ORD, and CD spectroscopy.

Introduction

There have been numerous studies of the stereochemistry of metal–carbon bond cleavage by electrophilic reagents.[3] The majority of these have focused on the stereochemistry at carbon.[3,4] In many cases where the stereochemistry at the metal was examined,[3,5] substantial racemization was observed.[5a–c]

We have found that a number of remarkably stereospecific ligand-based transformations[6] can be observed with easily resolved[7] chiral $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(L)$ compounds. Many of these have obvious applications in asymmetric organic synthesis, provided that the ligand (L) can be detached from the rhenium without significant epimerization or racemization of its chiral centers. Our preliminary results indicate that this is easily accomplished.[8] However, another important consideration in any ligand detachment reaction is the stereochemical fate of the rhenium. If the metal moiety can be recovered in enantiomerically pure form, then it can be recycled without an additional optical resolution and its utility as a "chiral auxiliary"[9] for asymmetric organic synthesis is greatly enhanced.

In this paper, we describe reactions of racemic and optically active forms of the methyl complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**)[7,10] with a series of protic acids HX and halogens X_2. High chemical yields of the new complexes $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(X)$[11] are obtained. The reactions with HX are shown to proceed with essentially complete retention of configuration at rhenium. Chemical transformations that establish the reaction stereochemistry are also described.

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(2) To whom correspondence should be addressed at the University of Utah; Fellow of the Alfred P. Sloan Foundation (1980–1984) and Camille and Henry Dreyfus Teacher-Scholar Grant Recipient (1980–1985).

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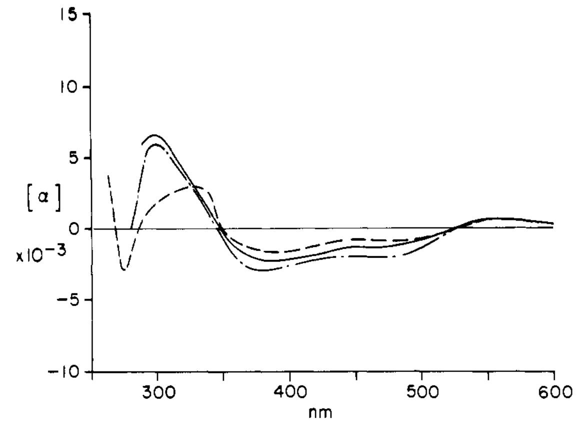


Figure 1. ORD spectra of (+)-(*S*)-(η-C_5H_5)Re(NO)(PPh_3)(Cl) ((+)-(*S*)-**2**) (—), (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(Br) ((+)-(*R*)-**3**) (-·-), and (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(I) ((+)-(*R*)-**4**) (--).

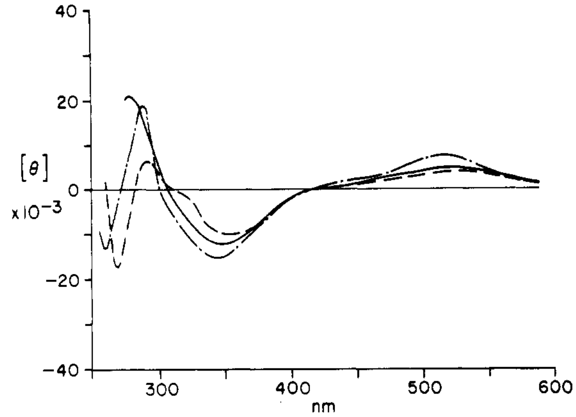


Figure 2. CD spectra of (+)-(*S*)-(η-C_5H_5)Re(NO)(PPh_3)(Cl) ((+)-(*S*)-**2**) (—), (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(Br) ((+)-(*R*)-**3**) (-·-), and (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(I) ((+)-(*R*)-**4**) (--).

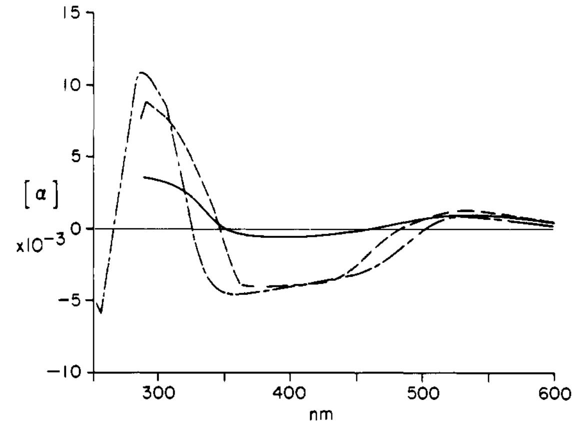


Figure 3. ORD spectra of (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(OSO_2CF_3) ((+)-(*R*)-**5**) (--), (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)($OCOCF_3$) ((+)-(*R*)-**6**) (---), and (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(OCHO) ((+)-(*R*)-**7**) (—).

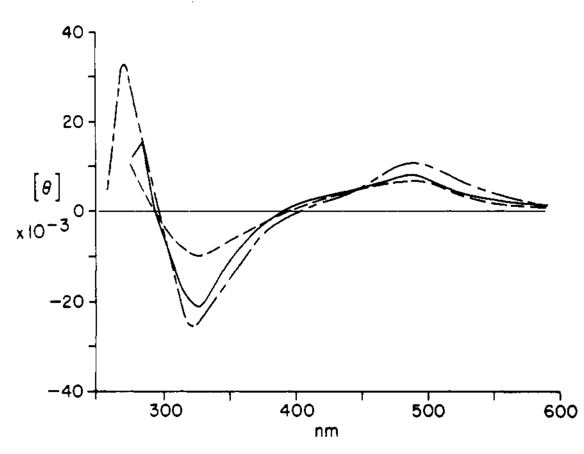


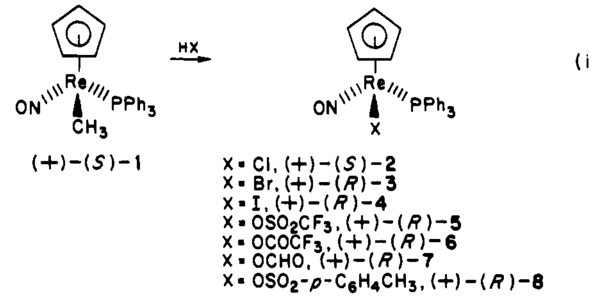
Figure 4. CD spectra of (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(OSO_2CF_3) ((+)-(*R*)-**5**) (--), (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)($OCOCF_3$) ((+)-(*R*)-**6**) (---), and (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(OCHO) ((+)-(*R*)-**7**) (—).

Results

A 0 °C CH_2Cl_2 solution of racemic (η-C_5H_5)Re(NO)(PPh_3)(CH_3) ((±)-**1**) was treated with aqueous HCl. Workup gave red prisms of the chloride (η-C_5H_5)Re(NO)(PPh_3)(Cl) ((±)-**2**) in 78% yield. Similar reactions of (±)-**1** with HBr, HI, CF_3SO_3H, CF_3CO_2H, HCO_2H, and *p*-$CH_3C_6H_4SO_3H$ gave the crystalline bromide (η-C_5H_5)Re(NO)(PPh_3)(Br) ((±)-**3**, 73%), iodide (η-C_5H_5)Re(NO)(PPh_3)(I) ((±)-**4**, 82%), triflate (η-C_5H_5)Re(NO)(PPh_3)(OSO_2CF_3) ((±)-**5**, 69%), trifluoroacetate (η-C_5H_5)Re(NO)(PPh_3)($OCOCF_3$) ((±)-**6**, 83%), formate (η-C_5H_5)Re(NO)(PPh_3)(OCHO) ((±)-**7**, 79%), and tosylate (η-C_5H_5)Re(NO)(PPh_3)(OSO_2-*p*-$C_6H_4CH_3$) ((±)-**8**, 89%), respectively. Experiments with other rhenium alkyl complexes (η-C_5H_5)Re(NO)(PPh_3)(R) have established that alkanes RH are formed in high yield in these protonation reactions.[8]

In crystalline form, **2**–**8** were very stable. However, in solution some were labile and the relative stability order **8** ≈ **7** ≈ **6** >> **4** > **3** ≈ **2** > **5** was observed. Products **2**–**8** were characterized by IR, ^1H NMR, ^{13}C NMR, ^{31}P NMR, and UV spectroscopy (Table I), mass spectrometry, and microanalysis (Experimental Section).

Optically active, >99% ee (+)-(*S*)-**1**[7,12] reacted analogously at 0 °C with the above acids to give products in 63–85% yields and with high specific rotations, as summarized in eq i and Table I. Optically active iodide (+)-(*R*)-**4** could be crystallized, but the other cleavage products were isolated as powders. Enantiomeric complexes were analogously prepared from (–)-(*R*)-**1**. Justifications for the configurational assignments (eq i)[12] will be given in the Discussion. When the reactions of (+)-(*S*)-**1** with HCl, HBr, and CF_3SO_3H were conducted at room temperature, rhenium complexes of slightly lower optical rotations were obtained. Room-temperature reactions of (+)-(*S*)-**1** with HI, CF_3CO_2H, and HCO_2H gave complexes with the same optical rotations as listed in Table I. Optically active **2**–**7** were also characterized by ORD and CD spectroscopy, as illustrated in Figures 1–4.



(i)

In solution, the relative configurational stabilities of complexes (+)-(*S*)-**2**–(+)-(*R*)-**8** paralleled the relative thermal stabilities of the corresponding racemates. The optical rota-

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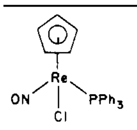
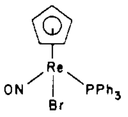
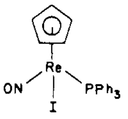
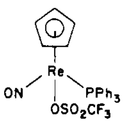
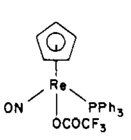
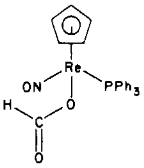
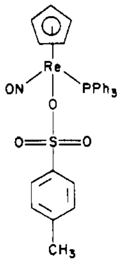
[12] (a) Absolute configurations are assigned according to the Baird–Sloan modification of the Cahn–Ingold–Prelog priority rules.[12c] The C_5H_5 ligand is considered to be a pseudoatom of atomic number 30, which gives the following sequences: I, Br > η^5-C_5H_5 > PPh_3 > NO; η^5-C_5H_5 > Cl > PPh_3 > NO; η^5-C_5H_5 > PPh_3 > –OCOR, –OSO_2CF_3 > NO; η^5-C_5H_5 > PPh_3 > NO > NCR. In complexes with more than one chiral center, the rhenium configuration is specified first. (b) Prefixes (+) and (–) refer to rotations at 589 nm. (c) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1.

Table I. Spectroscopic Characterization of the New Rhenium Complexes (η-C_5H_5)Re(NO)(PPh_3)(X)

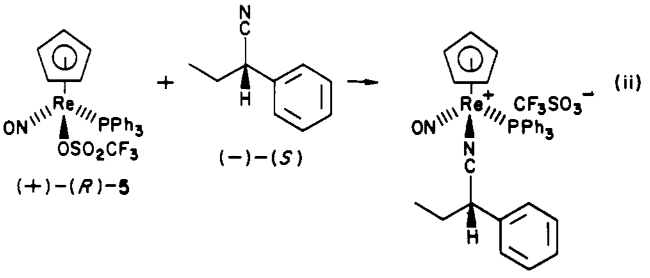
complex	IR ($CHCl_3$) $\nu_{N\equiv O}$, cm^{-1}	^{1}H NMR[a] ($CDCl_3$), δ	^{13}C NMR[b] ($CDCl_3$), ppm	^{31}P NMR,[c] ppm	UV ($CHCl_3$), nm	$[\alpha]^{25}_{589}$ (*c*. g/mL ($CHCl_3$)), deg
 **2**	1674 s	7.51–7.39 (m, 15 H), 5.22 (s, 5 H)	135.7 (d, *J* = 48.8 Hz), 133.8 (d, *J* = 10.3 Hz), 133.0 (s), 128.4 (d, *J* = 10.3 Hz), 91.1 (s, C_5H_5)	16.71[d]	261 (pk, ϵ = 7200), 315 (sh, ϵ = 2400)	307 (0.28)
 **3**	1673 s	7.51–7.39 (m, 15 H), 5.21 (s, 5 H)	134.9 (d, *J* = 52.8 Hz), 133.9 (d, *J* = 9.9 Hz), 130.5 (s), 128.3 (d, *J* = 10.4 Hz), 90.9 (s, C_5H_5)	15.06,[d] 15.78[e]	259 (pk, ϵ = 6600), 312 (sh, ϵ = 2400)	375 (0.34)
 **4**	1677 s	7.54–7.38 (m, 15 H), 5.19 (s, 5 H)	135.8 (d, *J* = 53.7 Hz), 135.5 (d, *J* = 9.9 Hz), 129.9 (s), 128.3 (d, *J* = 9.8 Hz), 89.3 (s, C_5H_5)	12.85[d]	262 (pk, ϵ = 7400), 330 (sh, ϵ = 2200)	233 (0.19)
 **5**	1680 s	7.49–7.33 (m, 15 H), 5.20 (s, 5 H)	134.0 (d, *J* = 53.8 Hz), 132.9 (d, *J* = 11.2 Hz), 131.0 (s), 128.8 (d, *J* = 10.8 Hz), 116.5 (q, $J_{^{13}C-^{19}F}$ = 318.6 Hz, CF_3), 90.7 (s, C_5H_5)	17.42,[d] 17.94[e]	262 (pk, ϵ = 7900), 305 (sh, ϵ = 3200)	571 (0.19)
 **6**	1655 s; 1710 m ($\nu_{C=O}$)	7.45–7.35 (m, 15 H), 5.29 (s, 5 H)	164.0 (q, $J_{^{13}C-^{19}F}$ = 37.6 Hz, C=O), 133.8 (d, *J* = 11.4 Hz), 132.9 (d, *J* = 51.0 Hz), 130.8 (s), 128.6 (d, *J* = 11.1 Hz), 112.9 (q, $J_{^{13}C-^{31}P}$ = 289.8 Hz, CF_3), 90.7 (s, C_5H_5)	21.15[e,f]	260 (pk, ϵ = 8100), 330 (sh, ϵ = 2900)	559 (0.21)
 **7**	1670 s; 1616 s ($\nu_{C=O}$), 2850 w (ν_{H-CO_2})	8.06 (s, 1 H), 7.50–7.26 (m, 15 H), 5.29 (s, 5 H)	171.4 (s, C=O), 134.0 (d, *J* = 11.2 Hz), 132.7 (d, *J* = 55.1 Hz), 130.6 (s), 128.5 (d, *J* = 11.0 Hz), 90.7 (s, C_5H_5)	20.80[e]	263 (pk, ϵ = 7000), 301 (sh, ϵ = 2800)	529 (0.72)
 **8**	1680 s	7.87–7.00 (m, 19 H), 5.37 (s, 5 H), 2.34 (s, 3 H)[g]	141.4 (s), 134.1 (d, *J* = 11.0 Hz), 133.5 (s), 131.1 (s), 129.1 (d, *J* = 67.7 Hz),[h] 129.1 (d, *J* = 10.8 Hz),[h] 129.1 (s),[h] 127.1 (s), 91.2 (s, C_5H_5), 21.5 (s, CH_3)[i]	18.67[e]	261 (pk, ϵ = 6900), 313 (sh ϵ = 2100)	453[j] (0.12)

[a] At 200 MHz and ambient probe temperature unless noted. [b] At 50 MHz and ambient probe temperature unless noted; all couplings (*J*) are to ^{31}P unless noted. [c] At 32 MHz and ambient probe temperature and referenced to external 85% H_3PO_4. [d] In acetone-d_6. [e] In $CDCl_3$. [f] At −30 °C. [g] At 300 MHz. [h] When an extra digit is included, these chemical shifts become 129.12, 129.09, and 129.09 ppm, respectively. [i] At 75 MHz. [j] In CH_2Cl_2.

tions of formate (+)-(*R*)-**7**, trifluoroacetate (+)-(*R*)-**6**, and iodide (+)-(*R*)-**4** (all (2.0–2.1) × 10^{-3} M) were unchanged after 30 h at 25.1 °C in CH_2Cl_2. Tosylate (+)-(*R*)-**8** showed <10% optical activity loss. Under identical conditions, bromide (+)-(*R*)-**3**, chloride (+)-(*S*)-**2**, and triflate (+)-(*R*)-**5** racemized with k_{obsd} = 6.15 × 10^{-5}, 8.90 × 10^{-5}, and 1.03 × 10^{-4} s^{-1}, respectively. These rates could only be followed for a period of 1 half-life due to increasing opaqueness of the polarimeter cell solution. After 16 h, **2**, **3**, and **5** were recovered in ca. 80% yield from the polarimeter cell. Hence, the optical activity loss can be attributed to racemization and not merely chemical decomposition to optically inactive materials.

In benzene, chloride (+)-(*S*)-**2** and bromide (+)-(*R*)-**3** showed no optical activity loss over the course of 30 h at 25 °C. Triflate (+)-(*R*)-**5** racemized in benzene, but at a much slower rate (k_{obsd} = 3.9 × 10^{-5} s^{-1}). The chemical decomposition of **2**–**5** was also retarded in benzene. The rate of racemization of chloride (+)-(*S*)-**2** in CH_2Cl_2 (25.0 °C, 2.0 × 10^{-3} M) was decreased by $[(C_6H_5)_3P{=}N{-}P(C_6H_5)_3)]^+Cl^-$ (PPN^+Cl^-). In the presence of 1 equiv of PPN^+Cl^-, a k_{obsd} of 3.1 × 10^{-5} s^{-1} was obtained. In the presence of 5 equiv of PPN^+Cl^-, a k_{obsd} of 1.5 × 10^{-5} s^{-1} was obtained.

Means of establishing the optical purities and absolute configurations of complexes (+)-(*S*)-**2**–(+)-(*R*)-**8** were sought. Racemic triflate **5** was treated with either (±)- or (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$.[13] Substitution occurred to give the nitrile complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+CF_3SO_3^-$ ($\mathbf{9}^+CF_3SO_3^-$) in high yield (see eq ii).



(+)-(*R*)-**5**

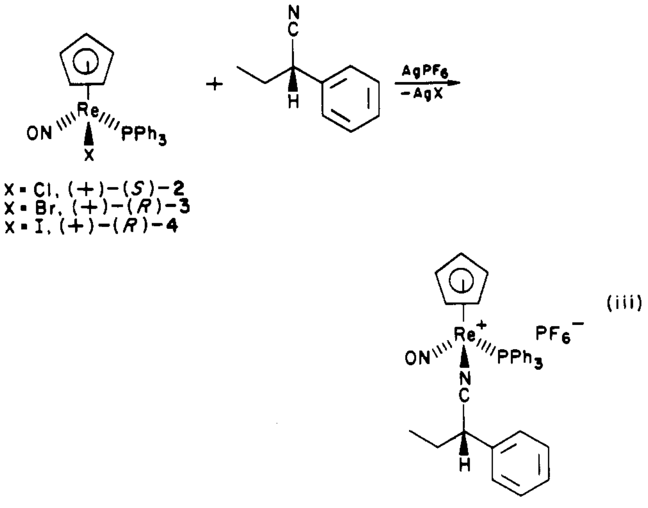
(−)-(*S*)

(+)-(*SS*)-$\mathbf{9}^+CF_3SO_3^-$

Both diastereomers of the closely related complex $\mathbf{9}^+PF_6^-$ have been previously isolated and characterized.[6e] The ^1H NMR spectra of these samples of $\mathbf{9}^+CF_3SO_3^-$ showed approximately equal amounts of each diastereomer.

The absolute configuration of nitrile complex (+)-(*SS*)-$\mathbf{9}^+PF_6^-$ has been previously established by X-ray crystallography.[6e] Hence, optically active triflate (+)-(*R*)-**5** was treated with (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ (eq ii). Subsequent ^1H NMR analysis,[6e] both in situ and after isolation, showed the product to be (+)-(*SS*)-$\mathbf{9}^+CF_3SO_3^-$ of ≥99% diastereomeric purity.

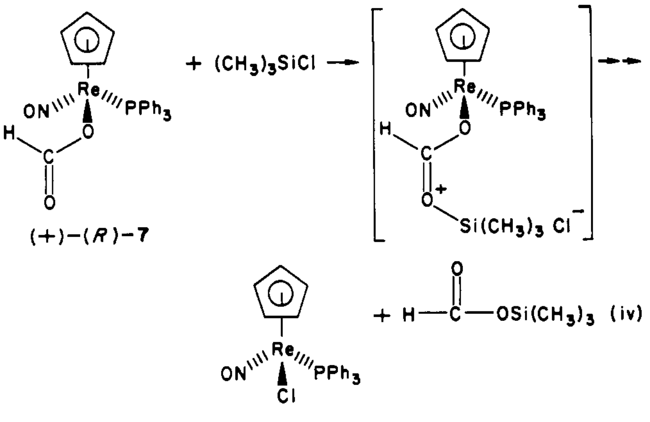
No reaction occurred between halides **2**–**4** and $CH_3CH_2CH(C_6H_5)CN$ at room temperature. However, in the presence of $AgPF_6$, rapid reaction occurred between −78 and −24 °C to give nitrile complex $\mathbf{9}^+PF_6^-$ in high yields (see eq iii). In situ ^1H NMR analysis[6e] of the reactions of chloride (+)-(*S*)-**2**, bromide (+)-(*R*)-**3**, and iodide (+)-(*R*)-**4** with (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN/AgPF_6$ indicated the formation of (+)-(*SS*)-$\mathbf{9}^+PF_6^-$ of ≥99% diastereomeric purity. Complex (+)-(*SS*)-$\mathbf{9}^+PF_6^-$ was subsequently isolated from the reactions of bromide (+)-(*R*)-**3** and iodide (+)-(*R*)-**4**. The corresponding reactions of chloride (−)-(*R*)-**2**, bromide (−)-(*S*)-**3**, and iodide (−)-(*S*)-**4** with (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN/AgPF_6$ gave exclusively the diastereomeric nitrile complex (−)-(*RS*)-$\mathbf{9}^+PF_6^-$.



X = Cl, (+)-(*S*)-**2**
X = Br, (+)-(*R*)-**3**
X = I, (+)-(*R*)-**4**

(+)-(*SS*)-$\mathbf{9}^+PF_6^-$

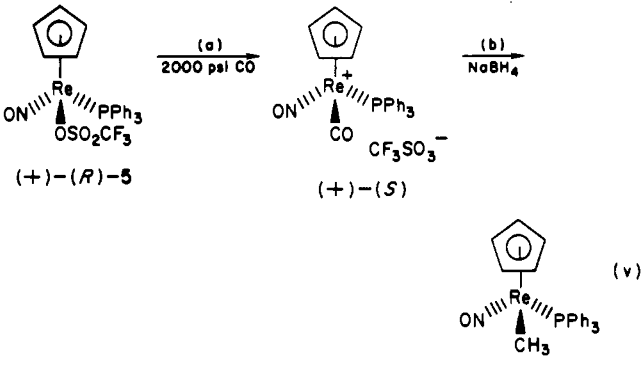
Trifluoroacetate **6** and formate **7** did not react with $CH_3CH_2CH(C_6H_5)CN$ at room temperature in either the presence or absence of $AgPF_6$. However, formate (+)-(*R*)-**7** cleanly reacted with $(CH_3)_3SiCl$ at 0 °C to give chloride (+)-(*S*)-**2** in 93% yield and 98% ee (eq iv). In separate experiments conducted with (±)-**7**, formate ester $HCO_2Si(CH_3)_3$ was detected by IR and ^1H NMR spectroscopy and GLC.



(+)-(*R*)-**7**

(+)-(*S*)-**2**

A benzene solution of racemic triflate **5** was treated with 2000 psi of CO. A quantitative yield of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+CF_3SO_3^-$ was obtained (eq v). When this reaction was repeated with (+)-(*R*)-**5**, (+)-(*S*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+CF_3SO_3^-$ was obtained in 78% ee, as assayed by subsequent $NaBH_4$ reduction[7] to methyl complex (+)-(*S*)-**1**.



(+)-(*R*)-**5**

(+)-(*S*)

(+)-(*S*)-**1**

Halogens Cl_2, Br_2, and I_2 reacted with methyl complex (±)-**1** to give halide complexes (±)-**2**, (±)-**3**, and (±)-**4** in 81–84% yields. When corresponding reactions were conducted with (+)-(*S*)-**1**, halide complexes (+)-(*S*)-**2**, (+)-(*R*)-**3**, and (+)-(*R*)-**4** were obtained, but only in 6%, 11%, and 7% ee, respectively. Identical experiments were conducted with (+)-(*S*)-**1** and 0.25 equiv of Br_2 and I_2. The starting material (+)-(*S*)-**1** was recovered from these reactions in 43% and 79% ee, respectively. Experiments with other rhenium alkyls $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(R)$ have established that alkyl halides RX are formed in high yields in these halogenation reactions.[8]

Discussion

The preceding data indicate that all reactions described except those involving halogens X_2 are essentially stereospecific at rhenium. All of the products of eq i except (+)-(*R*)-**6** and (+)-(*R*)-**8** were converted to other complexes of known optical purity and absolute configuration. In order to assign absolute configurations to optically active complexes **2**–**8**, the mechanisms of these transformations must be considered. However, it should be noted in advance that, with a single exception,[14] absolute configurations of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ complexes are correctly predicted by the signs of their ORD or CD spectra at >500 nm (or the sign of the region between the

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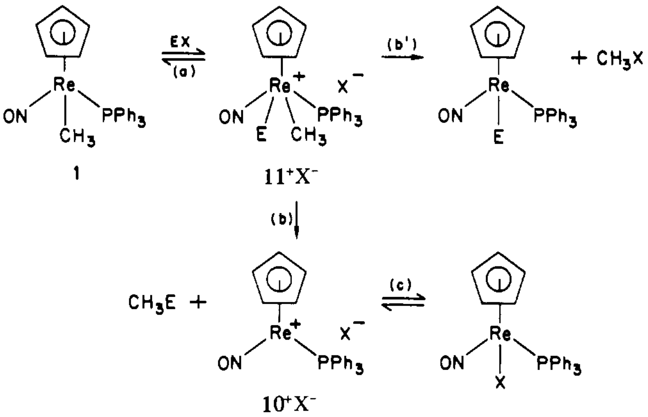
(13) Cram, D. J.; Haberfield, P. *J. Am. Chem. Soc.* **1961**, *83*, 2354.

(14) Buhro, W. E.; Wong, A.; Merrifield, J. H.; Lin, G.-Y.; Constable, A. G.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1852.

Scheme I. Some Possible Mechanisms for the Reactions of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (1) with Electrophiles



two *X*-axis crossings). By these criteria, every reaction in eq i proceeds with *retention* at rhenium.

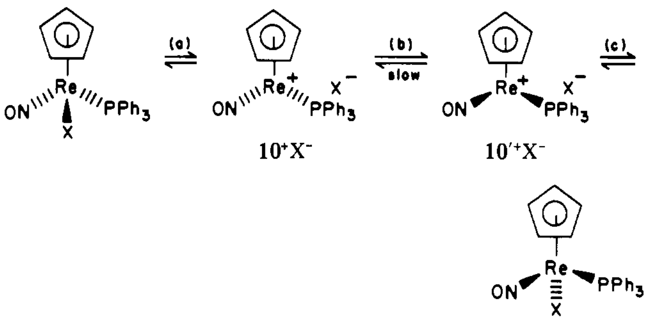
Equation iii is the most straightforward to interpret stereochemically. Silver ion promoted halide displacement reactions nearly always involve initial generation of AgX and a coordinatively unsaturated intermediate.[15] Hence, we suggest that $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)^+$ ($\mathbf{10^+}$) is initially formed in eq iii. Either retention or racemization, but not 100% inversion, is a plausible stereochemical fate for such an intermediate. Since eq iii proceeds in high optical yield, we conclude that it proceeds with overall retention at rhenium. Since the absolute configuration of product (+)-(*SS*)-$\mathbf{9^+}PF_6^-$ is known,[6c] the absolute configurations of optically active halides **2**–**4** are thereby established. This in turn requires, since the absolute configuration of (+)-(*S*)-**1** has been previously established,[7] that optically active halides **2**–**4** are formed with retention of configuration in eq i.

Faller has described a Ag^+-promoted substitution reaction of a molybdenum iodide complex that proceeds with retention at molybdenum.[16] Furthermore, Brunner has shown that substitution reactions of compounds closely related to **2**–**8**, such as $(\eta\text{-}C_5H_5)Mn(NO)(L)(CO_2CH_3) \rightarrow (\eta\text{-}C_5H_5)Mn(NO)(L')(CO_2CH_3)$, occur dissociatively with retention or partial racemization at manganese.[3b,17] Apparently the pyramidal 16-electron fragment $(\eta\text{-}C_5H_5)Mn(NO)(CO_2CH_3)$, and isoelectronic homologues such as $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)^+$ ($\mathbf{10^+}$), have appreciable configurational stability.[18]

In view of Brunner's precedent and eq iii, we interpret eq ii as a dissociative substitution proceeding with retention at rhenium and assign absolute configuration to the optically active triflate **5** accordingly. If **5** were assigned the opposite configuration, then the stereochemistry of triflate formation in eq i, and triflate substitution in eq ii, would have to be *opposite* to that found for halides **2**–**4**. We consider this possibility to be highly implausible.

We suggest that the initial step of the reaction of optically active formate (+)-(*R*)-**7** with $(CH_3)_3SiCl$ is silylation of the formate carbonyl oxygen, as shown in eq iv. This would generate a superb leaving group, the ester $HCO_2Si(CH_3)_3$. Subsequent dissociation to give $\mathbf{10^+}$ would be followed by chloride ion attack with retention. Again, if eq iv were to proceed with overall inversion, then the reaction of (+)-(*S*)-**1** with formic acid would have to proceed with stereochemistry *opposite* to that of HCl and the other acids. A similar reaction of a molybdenum *acetate* with $(CH_3)_3SiCl$ has been recently reported by M. L. H. Green.[19]

Scheme II. Proposed Racemization Mechanism



Some previously proposed mechanisms for the electrophilic cleavage of metal–carbon bonds that rationalize our data are given in Scheme I.[3a] We suggest that the protic electrophiles initially attack the HOMO of **1**[6b] to give square-pyramidal intermediate $\mathbf{11^+}$ (E = H). Reductive elimination of aliphatic C–H bonds (step b) is generally rapid,[20] so we propose that the protonation of **1** is essentially irreversible. However, reductive elimination of C–X bonds where X = halogen is less rapid.[21] Hence, in the reactions of optically active **1** with Cl_2, Br_2, and I_2, intermediate $\mathbf{11^+}$ (E = halide) may be of sufficient lifetime to racemize by pseudorotation or an equivalent process. Reversal of step a (Scheme I) would then give the partially racemized recovered **1** we observed. Alternatively, the reactions of **1** with X_2 may involve additional intermediates (e.g., odd-electron species) that are substitutionally and/or configurationally labile.[22] Also, many metal alkyl/X_2 reactions likely proceed via the S_N2 step b′, as inferred from *inversion* of configuration at the ligating carbon.[3a,4,23]

On the basis of two key observations, we propose that the coordinatively unsaturated cation $\mathbf{10^+}$ is also involved in the racemization of optically active chloride **2**, bromide **3**, and triflate **5**. First, the significantly greater configurational stability of optically active **2**, **3**, and **5** in benzene is consistent with an initial ionization step. Second, the inhibition of racemization of (+)-(*S*)-**2** by added Cl^- requires an intermediate that is capable of reacting with Cl^- (common ion effect). Hence, as shown in Scheme II, racemization would occur via pyramidal inversion of $\mathbf{10^+}$.[18] Brunner has obtained excellent evidence for the operation of a similar racemization mechanism in related manganese complexes.[3b,24] We plan a much more detailed and quantitative study of the equilibria in Scheme II.

Previously, Brunner has reported that chloride $(\eta\text{-}C_5H_5)Fe(CO)(L^*)(Cl)$ (L^* = chiral phosphine) epimerizes faster ($t_{1/2}$ = 181 min, benzene, 20 °C) than bromide $(\eta\text{-}C_5H_5)Fe(Cl)(L^*)(Br)$ ($t_{1/2}$ = 185 min, 45 °C).[5b] Under identical conditions, iodide $(\eta\text{-}C_5H_5)Fe(CO)(L^*)(I)$ does not significantly epimerize. This parallels our observation that optically active iodide **4** is the most configurationally stable of the halide

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(15) Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186.

(16) Faller, J. W.; Shvo, Y.; Chao, K.; Murray, H. H. *J. Organomet. Chem.* **1982**, *226*, 251.

(17) Brunner, H.; Aclais, J.; Langer, M.; Steger, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 810.

(18) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536.

(19) Green, M. L. H.; Parkin, G.; Bashkin, J.; Fail, J.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1982**, 2519.

(20) (a) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. (b) Norton, J. *Ibid.* **1979**, *12*, 139.

(21) For example, $(\eta\text{-}C_5Me_5)Ir(PMe_3)(R)(Br)$ is much more stable toward reductive elimination than $(\eta\text{-}C_5Me_5)Ir(PMe_3)(R)(H)$: Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. See also: Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562.

(22) (a) Hershberger, J. W.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1982**, 212. (b) McCullen, S. B.; Walker, H. W.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4007. (c) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *Ibid.* **1982**, *104*, 4032.

(23) Our preliminary results indicate retention of configuration at carbon with chlorination (two substrates), inversion with bromination (four substrates), and retention with protonation (CF_3CO_2H, one substrate).[8]

(24) (a) Brunner, H.; Schindler, H.-D. *Chem. Ber.* **1971**, *104*, 2467. (b) Brunner, H.; Langer, M. *J. Organomet. Chem.* **1975**, *87*, 223. (c) Brunner, H.; Aclais, J. A. *Ibid.* **1976**, *104*, 347.

complexes. Triflates are orders of magnitude better leaving groups than halides in S_N1 reactions at carbon,[25] so the much lower configurational stability of optically active **5** is understandable.

We also propose that ionization to $\mathbf{10}^+$ plays an important role in the thermal decomposition of **2–8**. Note that thermal stabilities are greater in benzene and that the complex with the best leaving group, triflate **5**, is the most labile. We have previously shown that when intermediate $\mathbf{10}^+$ is generated with a nonnucleophilic counterion, decomposition to $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)_2]^+X^-$ (and other products) occurs.[6e] We have also suggested that the thermal decarboxylation of formate **7** to hydride $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ may occur via the ion pair $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)^{+}\,{}^{-}OCHO$.[11]

Several observations of other researchers provide interesting contrasts to our data. Flood has reported that alkyls $(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)(R)$ (R = CH_3, CH_2CH_3) react with CF_3CO_2H to give trifluoroacetate $(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)(OCOCF_3)$ in 56–37% ee; recovered starting material showed substantial racemization.[5c] The corresponding reaction of (+)-(*S*)-**1** with CF_3CO_2H is essentially stereospecific. However, the reactions of $(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)(CH_3)$ and related cyclopentadienyliron methyl complexes[5a–c] with I_2 are more stereoselective than that of (+)-(*S*)-**1** with I_2.[5a–c] We speculate that perhaps iron homologues of intermediate $\mathbf{11}^+$ (Scheme I) are shorter lived or that **1** is more susceptible than $(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)(CH_3)$ to initial electron transfer and generation of a configurationally labile odd-electron intermediate.

The transformation shown in eq v closes (together with eq i) another stereochemical cycle and adds further support to our stereochemical assignments. More importantly, however, it shows that rhenium alkyl cleavage products can be recycled to new optically active rhenium alkyls. We made no attempt to optimize the 78% ee obtained in the carbonylation step a. Furthermore, halides **2–4** are useful substrates for other types of rhenium–carbon bond-forming reactions.[26]

Conclusion

We have shown that the rhenium–carbon bond in (+)-(*S*)-**1** can be cleaved by a variety of protic (HX) and halogen (X_2) electrophiles. Good chemical yields of rhenium complexes $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ are obtained. Protic electrophiles also give rhenium products in high optical yield (retention). It has been demonstrated that these cleavage products can be recycled to new rhenium alkyls. These data provide a necessary foundation for the rational application of optically active alkyl complexes of the type $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(R)$ in asymmetric organic synthesis.

Experimental Section

General Considerations. Procedures and instruments employed in this study were generally identical with those given in an earlier paper.[7] The ^{31}P NMR spectra were recorded on a Varian FT-80A spectrometer. Racemization rate constants (k_{obsd}) were obtained with use of thermostated polarimeter cells and $-\log\,[\alpha]$ vs. *t* plots.[24]

Reagents Br_2, I_2, HBr, and HI were purchased from Mallinckrodt. Acids HCl and HCO_2H were obtained from Baker, CF_3CO_2H and CF_3SO_3H were obtained from Aldrich, and *p*-$CH_3C_6H_4SO_3H\cdot H_2O$ was obtained from MCB. Gases Cl_2 and CO were purchased from Matheson. Salts $AgPF_6$ and PPN^+Cl^- were obtained from Alfa and Strem, respectively. All of the above reagents were used without purification. Silane $(CH_3)_3SiCl$ was obtained from Silar and was distilled from CaH_2 prior to use.

Methyl complexes (±)-**1**, (+)-(*S*)-**1**, and (−)-(*R*)-**1** were synthesized by the $NaBH_4$ reduction of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ as described previously.[7,10] Racemic $CH_3CH_2CH(C_6H_5)COOH$ was obtained from Aldrich, resolved by the method of Pettersson,[27] and converted to (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ as described by Cram and Haberfield.[13] An authentic sample of $HCO_2Si(CH_3)_3$ was prepared from formic acid, $(CH_3)_3SiCl$, and pyridine by following standard procedures.[28]

Preparation of (±)-$\mathbf{(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)}$ ((±)-2). A 100-mL Schlenk flask was charged with (±)-**1** (0.300 g, 0.540 mmol), CH_2Cl_2 (20 mL), and a magnetic stir bar and was cooled to 0 °C. Then 37% aqueous HCl (0.10 mL, 1.00 mmol) was slowly added. The reaction was stirred for 30 min, and the crude reaction mixture was poured through a fritted-glass funnel containing a 1-cm layer of silica gel. The product was eluted from the silica gel with CH_2Cl_2 (30 mL) and then 95:5 CH_2Cl_2/acetone (30 mL). Solvent was removed from the eluate via oil-pump vacuum, and the resulting red solid was recrystallized from CH_2Cl_2/hexane to give red prisms (0.245 g, 0.421 mmol, 78%) of (±)-**2**; mp 228–234 °C dec. Mass spectrum (*m*/*e*, 70 eV): 581 (M^+, $^{187}Re^{37}Cl$, 18%), 262 (Ph_3P^+, 100%). Anal. Calcd for $C_{23}H_{20}ClNOPRe$: C, 47.69; H, 3.46; Cl, 6.13; N, 2.42; O, 2.73; P, 5.37; Re, 32.17. Found: C, 47.47; H, 3.69; Cl, 6.23; N, 2.55; O, 2.59; P, 5.50; Re, 32.16.

Preparation of (±)-$\mathbf{(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(Br)}$ ((±)-3). This compound was prepared in a manner identical with that for (±)-**2** from (±)-**1** (0.360 g, 0.650 mmol) and 48% aqueous HBr (0.20 mL, 1.00 mmol). The crude red product was recrystallized from CH_2Cl_2/hexane to give red prisms (0.296 g, 0.475 mmol, 73%) of (±)-**3**; mp 234–236 °C dec. Mass spectrum (*m*/*e*, 70 eV): 625 (M^+, $^{187}Re^{81}Br$, 16%), 262 (Ph_3P^+, 100%). Anal. Calcd for $C_{23}H_{20}BrNOPRe$: C, 44.28; H, 3.20; Br, 12.82; N, 2.24; O, 2.46; P, 4.98; Re, 30.01. Found: C, 44.14; H, 3.16; Br, 12.92; N, 2.18; O, 2.36; P, 5.11; Re, 30.09.

Preparation of (±)-$\mathbf{(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(I)}$ ((±)-4). This compound was prepared in a manner identical with that for (±)-**2** from (±)-**1** (0.280 g, 0.502 mmol) and 47% aqueous HI (0.30 mL, 1.00 mmol). The crude purple product was recrystallized from CH_2Cl_2/hexane to give purple prisms (0.279 g, 0.416 mmol, 82%) of (±)-**4**; mp 209–212 °C. Mass spectrum (*m*/*e*, 70 eV): 671 (M^+, ^{187}Re, 90%), 544 ($M^+ - I$, 12%), 262 (Ph_3P^+, 100%). Anal. Calcd for $C_{23}H_{20}INOPRe$: C, 41.25; H, 2.98; I, 18.84; N, 2.09; O, 2.38; P, 4.63; Re, 27.81. Found: C, 41.02; H, 3.05; I, 18.78; N, 2.10; O, 2.41; P, 4.74; Re, 27.77.

Preparation of (±)-$\mathbf{(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OSO_2CF_3)}$ ((±)-5). This compound was prepared in a manner identical with that for (±)-**2** using (±)-**1** (0.380 g, 0.681 mmol), CF_3SO_3H (0.150 g, 1.00 mmol), and a 15-min reaction time. The crude light red solid was recrystallized from CH_2Cl_2/hexane to give red prisms (0.325 g, 0.470 mmol, 69%) of (±)-**5**; mp 222–228 °C. Mass spectrum (*m*/*e*, 70 eV): 693 (M^+, ^{187}Re, 40%), 544 ($M^+ - CF_3SO_3$, 4%), 262 (Ph_3P^+, 100%). Anal. Calcd for $C_{24}H_{20}F_3NO_4PReS$: C, 41.62; H, 2.91. Found: C, 41.41; H, 3.10.

Preparation of (±)-$\mathbf{(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCOCF_3)}$ ((±)-6). This compound was prepared in a manner identical with that for (±)-**2** using (±)-**1** (0.480 g, 0.860 mmol), CF_3CO_2H (0.122 g, 1.07 mmol), and a 15-min reaction time. The crude red product was recrystallized from CH_2Cl_2/hexane to give red prisms (0.468 g, 0.714 mmol, 83%) of (±)-**5**; mp 228–231 °C. Mass spectrum (*m*/*e*, 70 eV): 657 (M^+, ^{187}Re, 23%), 544 ($M^+ - CF_3CO_2$, 2%), 262 (Ph_3P^+, 100%). Anal. Calcd for $C_{25}H_{20}F_3NO_2PRe$: C, 45.70; H, 3.07; F, 8.65; N, 2.13; P, 4.73. Found: C, 45.50; H, 3.22; F, 8.51; N, 2.02; P, 4.70.

Preparation of (±)-$\mathbf{(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCHO)}$ ((±)-7). A 100-mL Schlenk flask was charged with (±)-**1** (0.310 g, 0.556 mmol), CH_2Cl_2 (20 mL), and a magnetic stir bar and was cooled to −24 °C (CH_3CN/CO_2 bath). Then 88% aqueous formic acid (0.035 g, 0.667 mmol) was slowly added. The reaction was stirred for 1 h, and the solvent was then removed via oil-pump vacuum. The resulting red residue was dissolved in CH_2Cl_2 and poured into a fritted-glass funnel containing a 1-cm layer of silica gel. The product was eluted from the silica gel with 90:10 CH_2Cl_2/acetone. The eluate was concentrated under oil-pump vacuum. Subsequent diffusion addition of hexanes gave red needles (0.286 g, 0.438 mmol, 79%) of (±)-**7**$\cdot 0.75CH_2Cl_2$ solvate. Alternatively, rapid CH_2Cl_2/hexane precipitation gave solvate-free (±)-**7**; mp 126–127 °C dec. Mass spectrum (*m*/*e*, 16

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(25) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; Table 4.12.

(26) (a) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1983**, *241*, 45. (b) Bodner, G. S. University of Utah, unpublished results.

(27) Pettersson, K. *Ark. Kemi* **1956**, *10*, 283.

(28) Pierce, A. E. "Silylation of Organic Compounds"; Pierce Chemical Co.: Rockford, IL, 1968; pp 19–20, 163.

eV): 589 (M^+, ^{187}Re, 2%), 545 ($M^+ - CO_2$, 100%), 467 ($M^+ - CO_2 - C_6H_6$, 74%). Anal. Calcd for $C_{24}H_{21}NO_3PRe\cdot 0.75CH_2Cl_2$: C, 45.57; H, 3.48; N, 2.15; P, 4.75. Found: C, 45.84; H, 3.66; N, 2.21; P, 4.85.

Preparation of (±)-(η-C_5H_5)Re(NO)(PPh_3)(OSO_2-*p*-$C_6H_4CH_3$) ((±)-8). A 250-mL Schlenk flask was charged with (±)-**1** (0.500 g, 0.896 mmol), CH_2Cl_2 (100 mL), *p*-$CH_3C_6H_4SO_3H\cdot H_2O$ (0.188 g, 0.986 mmol), and a magnetic stir bar. The reaction was monitored by TLC using 70:30 (v/v) hexane/acetone (R_f of (±)-**1** 0.52; R_f of (±)-**8** 0.20). The reaction was stirred for 1 h at room temperature, and the solvent was then removed under oil-pump vacuum. The resulting red solid was extracted with benzene. Ether was slowly added to the filtered extract by vapor diffusion. Red crystals of (±)-**8** deposited and were collected by filtration (0.572 g, 0.800 mmol, 89%); mp 188 °C. Mass spectrum (*m*/*e*, 15 eV): 715 (M^+, ^{187}Re, 1%), 262 (Ph_3P^+, 100%). Anal. Calcd for $C_{30}H_{27}NO_4PReS$: C, 50.41; H, 3.81. Found: C, 50.60; H, 3.97.

Preparation of (+)-(*S*)-(η-C_5H_5)Re(NO)(PPh_3)(Cl) ((+)-(*S*)-2). A 100-mL Schlenk flask was charged with (+)-(*S*)-**1** (0.512 g, 0.917 mmol), CH_2Cl_2 (20 mL), and a magnetic stir bar and was cooled to 0 °C. Then 37% aqueous HCl (0.20 mL, 2.00 mmol) was slowly added. The reaction was stirred for 30 min, and the crude reaction mixture was poured through a fritted-glass funnel containing a 1-cm layer of silica gel. The product was eluted from the silica gel with cold CH_2Cl_2 (30 mL) and then cold 95:5 CH_2Cl_2/acetone (30 mL). The eluate was maintained at −24 °C, and then solvent was removed at 0 °C under oil-pump vacuum to give (+)-(*S*)-**2** as a red solid (0.389 g, 0.669 mmol, 73%); mp 218–225 °C dec. All attempts to recrystallize this material gave oils. The enantiomer (−)-(*R*)-**2** was synthesized in an identical manner from (−)-(*R*)-**1**.

Preparation of (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(Br) ((+)-(*R*)-3). This compound was prepared in a manner identical with that for (+)-(*S*)-**2** from (+)-(*S*)-**1** (0.422 g, 0.756 mmol) and 48% aqueous HBr (0.30 mL, 1.50 mmol). The product was obtained as a red solid (0.364 g, 0.582 mmol, 77%); mp 235–237 °C dec. All recrystallization attempts gave oils. The enantiomer (−)-(*S*)-**3** was synthesized in an identical manner from (−)-(*R*)-**1**.

Preparation of (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(I) ((+)-(*R*)-4). This compound was prepared in a manner identical with that for (+)-(*S*)-**2** from (+)-(*S*)-**1** (0.292 g, 0.523 mmol) and 47% aqueous HI (0.20 mL, 0.67 mmol). The product was obtained as a purple solid (0.284 g, 0.424 mmol, 81%). Recrystallization from CH_2Cl_2/hexane gave purple prisms of (+)-(*R*)-**4**; mp 230–232 °C dec. The enantiomer (−)-(*S*)-**4** was synthesized in an identical manner from (−)-(*R*)-**1**.

Preparation of (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(OSO_2CF_3) ((+)-(*R*)-5). This compound was prepared in a manner identical with that for (+)-(*S*)-**2** from (+)-(*S*)-**1** (0.401 g, 0.719 mmol) and CF_3SO_3H (0.180 g, 1.20 mmol). The product was obtained as a red solid (0.314 g, 0.453 mmol, 63%); mp 215–220 °C dec. All recrystallization attempts gave oils. The enantiomer (−)-(*S*)-**5** was synthesized in an identical manner from (−)-(*R*)-**1**.

Preparation of (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)($OCOCF_3$) ((+)-(*R*)-6). This compound was prepared in a manner identical with that for (+)-(*S*)-**2** from (+)-(*S*)-**1** (0.338 g, 0.605 mmol) and CF_3CO_2H (0.102 g, 0.895 mmol). The product was obtained as a red solid (0.338 g, 0.514 mmol, 85%); mp 220–225 °C dec. All recrystallization attempts gave oils. The enantiomer (−)-(*S*)-**6** was synthesized in an identical manner from (−)-(*R*)-**1**.

Preparation of (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(OCHO) ((+)-(*R*)-7). This compound was prepared in a manner identical with that for (±)-(*S*)-**2** from (+)-(*S*)-**1** (0.392 g, 0.703 mmol) and 88% aqueous formic acid (0.065 g, 1.24 mmol). The product was obtained as a red solid (0.298 g, 0.506 mmol, 72%); mp 134–136 °C dec. All recrystallization attempts gave oils. The enantiomer (−)-(*S*)-**7** was synthesized in an identical fashion from (−)-(*R*)-**1**.

Preparation of (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(OSO_2-*p*-$C_6H_4CH_3$) ((+)-(*R*)-8). A 50-mL Schlenk flask was charged with (+)-(*S*)-**1** (0.100 g, 0.179 mmol), CH_2Cl_2 (5 mL), and a magnetic stir bar and was cooled to −24 °C. A solution of *p*-$CH_3C_6H_4SO_3H\cdot H_2O$ (0.0341 g, 0.179 mmol) in acetone (1 mL) was added dropwise. The reaction was then placed in a 0 °C bath and stirred for 30 min. Solvents were removed in vacuo, and the resulting orange solid was extracted with benzene (2 mL). The extract was filtered, and ether (10 mL) was added to the filtrate. The product precipitated as an orange powder, which was collected, washed with additional ether, and air-dried (0.080 g, 0.112 mmol, 63%); dec pt 208–210 °C.

Reaction of (±)-5 with (±)-$CH_3CH_2CH(C_6H_5)CN$. A 100-mL Schlenk flask was charged with (±)-**5** (0.210 g, 0.303 mmol), CH_2Cl_2 (20 mL), and a magnetic stir bar and was cooled to −24 °C. Then (±)-$CH_3CH_2CH(C_6H_5)CN$ (0.220 g, 1.515 mmol) was added. The solution was stirred for 0.5 h at −24 °C and was then allowed to warm to room temperature over the course of 0.5 h. The solvent was then removed under vacuum, and the resulting brown oil was washed with 3 × 15 mL of hexanes. The resulting solid was extracted with benzene, leaving a dark residue. The benzene was removed under vacuum to give the two diastereomers of $\mathbf{9}^+CF_3SO_3^-$ as a light brown solid (0.216 g, 0.267 mmol, 88%). A ^1H NMR spectrum of this material was identical[6e] with that of an authentic sample of $\mathbf{9}^+PF_6^-$.

Reaction of (+)-(*R*)-5 with (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$. A. A 5-mm septum-capped NMR tube was charged with (+)-(*R*)-**5** (0.028 g, 0.040 mmol) and $CDCl_3$ (0.400 mL) and was cooled to −78 °C. Then (−)-(*S*)-$CH_3CH_2CH(C_6H_5)(CN)$ (0.029 g, 0.202 mmol) was added. The reaction mixture was warmed to −24 °C and was vigorously shaken. The color of the solution immediately changed from red to light brown. The solution was maintained at −24 °C. Subsequent ^1H NMR analysis showed only the C_5H_5 resonance of (+)-(*SS*)-$\mathbf{9}^+CF_3SO_3^-$ to be present (δ 5.54). Doping experiments[6e] indicated as little as 0.5% of (−)-(*RS*)-$\mathbf{9}^+CF_3SO_3^-$ would have been detected.

B. A preparative reaction was conducted on a scale identical with that described with (±)-**5** and (±)-$CH_3CH_2CH(C_6H_5)CN$ above. An identical workup gave (+)-(*SS*)-$\mathbf{9}^+CF_3SO_3^-$ (0.218 g, 0.270 mmol, 89%) as a brown viscous oil. Only oils were obtained upon attempted recrystallization.

Reactions of (+)-(*S*)-2 and (−)-(*R*)-2 with $AgPF_6$/(−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$. A 5-mm NMR tube was charged with (+)-(*S*)-**2** (0.031 g, 0.053 mmol), (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ (0.038 g, 0.265 mmol), and $CDCl_3$ (0.400 mL). The tube was cooled to −78 °C, and $AgPF_6$ (0.015 g, 0.057 mmol) was added under a N_2 stream. The tube was vigorously shaken as it was allowed to warm to −24 °C. The red reaction mixture instantly turned brown when the solvent thawed. Subsequent ^1H NMR analysis showed (+)-(*SS*)-$\mathbf{9}^+PF_6^-$ (δ 5.54)[6e] of ≥99% diastereomeric purity. An identical experiment with (−)-(*R*)-**2** gave (−)-(*RS*)-$\mathbf{9}^+PF_6^-$ of ≥99% diastereomeric purity.

Reactions of (+)-(*R*)-3 and (−)-(*S*)-3 with $AgPF_6$/(−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$. A. NMR tube experiments were conducted identically to those described above for (+)-(*S*)-**2** and (−)-(*R*)-**2**. Identical results were obtained.

B. A 10-mL Schlenk flask was charged with (+)-(*R*)-**3** (0.177 g, 0.284 mmol), (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ (0.206 g, 1.420 mmol), 0.400 mL of CH_2Cl_2, and a micro magnetic stir bar. The solution was cooled to −78 °C, and $AgPF_6$ (0.074 g, 0.291 mmol) was added. The solution was then warmed to −24 °C. The reaction was stirred for 15 min and filtered. Solvent was removed from the filtrate under vacuum. The resulting brown oil was washed with hexane until TLC analysis of the washes indicated that starting nitrile was no longer being extracted. The brown residue was then extracted with benzene until the extracts were colorless. The benzene was then removed under vacuum to give a light brown solid, which was recrystallized from CH_2Cl_2/hexane to give gold prisms (0.203 g, 0.244 mmol, 86%) of (+)-(*SS*)-$\mathbf{9}^+PF_6^-$.[6e]

C. Diastereomer (−)-(*RS*)-$\mathbf{9}^+PF_6^-$ was prepared in an identical fashion from (−)-(*S*)-**3**. It was obtained as a light brown solid (0.198 g, 0.238 mmol, 84%) by rapidly removing the solvent from a concentrated CH_2Cl_2 solution under oil-pump vacuum. Recrystallization attempts gave only oils.

Reactions of (+)-(*R*)-4 and (−)-(*S*)-4 with $AgPF_6$/(−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$. Two NMR and two preparative experiments were conducted as described above for (+)-(*R*)-**3** and (−)-(*S*)-**3**. Identical diastereomeric purities were obtained in the NMR experiments, and comparable isolated yields were obtained in the preparative experiments.

Reaction of (+)-(*R*)-5 with CO. An autoclave was charged with (+)-(*R*)-**5** (0.229 g, 0.330 mmol), benzene (10 mL), and CO (2000 psi). The reaction was allowed to stand for 20 h, and the pressure was then slowly released. The insoluble product[10] (+)-(*S*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+CF_3SO_3^-$ was isolated by filtration (0.219 g, 0.304 mmol, 92%) and converted to (+)-(*S*)-**1**, $[\alpha]^{25}_{589} = 138°$ ($CHCl_3$, 78% ee), as previously described.[7]

Reaction of (+)-(*R*)-7 with $(CH_3)_3SiCl$. A. A 50-mL Schlenk flask was charged with (+)-(*R*)-**7** (0.113 g, 0.192 mmol), CH_2Cl_2 (10 mL), and a stir bar and was cooled to 0 °C. Then a weighed amount of $(CH_3)_3SiCl$ (0.040 g, 0.384 mmol) was added and the reaction was stirred for 0.5 h. The solvent was removed under oil-pump vacuum, and the red residue was taken up in CH_2Cl_2 and poured through a fritted-glass funnel containing a 1-cm layer of silica gel. The product was eluted from the silica gel with 95:5 CH_2Cl_2/acetone. Solvent was removed from the eluate under oil-pump vacuum to give (+)-(*S*)-**2** (0.103 g, 0.178 mmol, 93%); $[\alpha]^{25}_{589}$ = 300° (*c* 0.38, $CHCl_3$). Mass spectrum (*m*/*e*, 70 eV): 581 (M^+, $^{187}Re^{37}Cl$, 65%), 262 (Ph_3P^+, 100%).

B. A 5-mm septum-capped NMR tube was charged with (±)-**7** (0.026 g, 0.044 mmol) and CD_2Cl_2 (0.400 mL). Then $(CH_3)_3SiCl$ (0.006 mL, 0.005 g, 0.046 mmol) was added by syringe. The clean formation of $HCO_2Si(CH_3)_3$ was noted by ^1H NMR spectroscopy (δ 8.05 (s, 1 H), δ 0.02 (s, 9 H); authentic sample δ 8.09, 0.03). A similar experiment in CH_2Cl_2 verified the formation of $HCO_2Si(CH_3)_3$ by IR spectroscopy ($\nu_{C=O}$ 1723 cm^{-1}; authentic sample (neat) 1718 cm^{-1}) and GLC.

Reaction of (±)-(η-C_5H_5)Re(NO)(PPh_3)(CH_3) ((±)-1) with Cl_2. A 50-mL Schlenk flask was charged with (±)-**1** (0.172 g, 0.308 mmol), CH_2Cl_2 (15 mL), and a magnetic stir bar. The flask was cooled to 0 °C, and gaseous Cl_2 (10.0 mL, 0.41 mmol) was slowly bubbled into the solution via syringe. The reaction was stirred for 15 min, and then the solvent was removed under vacuum. The resulting light red residue was taken up in CH_2Cl_2, and (±)-**2** was isolated as red crystals (0.136 g, 0.234 mmol, 76%) as described above.

Reaction of (±)-1 with Br_2. A 50-mL Schlenk flask was charged with (±)-**1** (0.192 g, 0.344 mmol), CH_2Cl_2 (15 mL), and a magnetic stir bar. The flask was cooled to 0 °C, and Br_2 (0.083 g, 0.027 mL, 0.519 mmol) was then added via syringe. The solution was stirred for 15 min, and the solvent was then removed under vacuum. The resulting red residue was taken up in CH_2Cl_2, and (±)-**3** was isolated as red crystals (0.180 g, 0.289 mmol, 84%) as described above.

Reaction of (±)-1 with I_2. This reaction was conducted identically with that of (±)-**1** and Br_2 above. Product (±)-**4** was isolated as purple prisms (83%) as described above.

Reaction of (+)-(*S*)-1 with Cl_2. This reaction was conducted at −24 °C in a manner otherwise identical with that of (±)-**1** with Cl_2. Product (+)-(*S*)-**2** was isolated (81%) as described in the synthesis of (+)-(*S*)-**2** above; $[\alpha]^{25}_{589}$ = 17° (*c* 0.11, $CHCl_3$).

Reaction of (+)-(*S*)-1 with Br_2. A. A 50-mL Schlenk flask was charged with (+)-(*S*)-**1** (0.217 g, 0.389 mmol), CH_2Cl_2 (15 mL), and a magnetic stir bar. The flask was cooled to −24 °C, and Br_2 (0.087 g, 0.027 mL, 0.544 mmol) was then added by syringe. The reaction was stirred for 15 min, and solvent was then removed at 0 °C under oil-pump vacuum. The residue was filtered through a fritted-glass funnel containing a 1-cm layer of silica gel with use of first cold CH_2Cl_2 (30 mL) and then cold 95:5 CH_2Cl_2/acetone (30 mL). The eluate was maintained at −24 °C. The solvent was then removed under oil-pump vacuum at 0 °C to give a red solid; $[\alpha]^{25}_{589}$ = 15° (*c* 0.17, $CHCl_3$). This material was recrystallized from CH_2Cl_2/hexane to give (±)-**3** (0.196 g, 0.315 mmol, 81%).

B. A 50-mL Schlenk flask was charged with (+)-(*S*)-**1** (0.210 g, 0.378 mmol),CH_2Cl_2 (15 mL), and a stir bar. The flask was cooled to −24 °C, and Br_2 (0.014 g, 0.091 mmol) was added by syringe. The reaction was stirred for 15 min, and solvent was then removed under oil-pump vacuum. The resulting residue was rapidly chromatographed on a silica gel column with use of 15:85 ethyl acetate/hexane. The band corresponding to **1** was collected, and the column was then eluted with 95:5 CH_2Cl_2/acetone to give **3**. The identity and purity of these materials were confirmed by ^1H NMR. Recovered (+)-(*S*)-**1** gave $[\alpha]^{25}_{589}$ = 79° (*c* 0.13, $CHCl_3$), and product (+)-(*R*)-**3** gave $[\alpha]^{25}_{589}$ = 11° ($CHCl_3$).

Reaction of (+)-(*S*)-1 with I_2. A. A reaction with excess I_2 was conducted in an identical manner and on an identical scale with that of (+)-(*S*)-**1** and excess Br_2 above. Crude iodide (+)-(*R*)-**4** gave $[\alpha]^{25}_{589}$ = 21° (*c* 0.16, $CHCl_3$). Recrystallization from CH_2Cl_2/hexane gave (±)-**4** in 87% yield.

B. A reaction with 0.25 equiv of I_2 was conducted in an identical manner and on an identical scale with that of (+)-(*S*)-**1** and 0.25 equiv of Br_2 above. Recovered (+)-(*S*)-**1** gave $[\alpha]^{25}_{589}$ = 146° (*c* 0.21, $CHCl_3$), and product (+)-(*R*)-**4** gave $[\alpha]^{25}_{589}$ = 17° (*c* 0.18, $CHCl_3$).

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Registry No. (±)-**1**, 71763-18-3; (+)-(*S*)-**1**, 82336-24-1; (−)-(*R*)-**1**, 82336-23-0; (±)-**2**, 92761-70-1; (+)-(*S*)-**2**, 85702-43-8; (−)-(*R*)-**2**, 92761-71-2; (±)-**3**, 92695-33-5; (+)-(*R*)-**3**, 92761-72-3; (−)-(*S*)-**3**, 92761-73-4; (±)-**4**, 92695-34-6; (+)-(*R*)-**4**, 92761-74-5; (−)-(*S*)-**4**, 92761-75-6; (±)-**5**, 92695-35-7; (+)-(*R*)-**5**, 92761-76-7; (−)-(*S*)-**5**, 92761-77-8; (±)-**6**, 92695-36-8; (+)-(*R*)-**6**, 92761-78-9; (−)-(*S*)-**6**, 92761-79-0; (±)-**7**, 85702-40-5; (+)-(*R*)-**7**, 85719-07-9; (−)-(*S*)-**7**, 92761-80-3; (±)-**8**, 92695-37-9; (+)-(*R*)-**8**, 92761-81-4; $\mathbf{9}^+CF_3SO_3^-$ (isomer 1), 92761-83-6; $\mathbf{9}^+CF_3SO_3^-$ (isomer 2), 92761-85-8; (+)-(*SS*)-$\mathbf{9}^+CF_3SO_3^-$, 92761-86-9; (+)-(*SS*)-$\mathbf{9}^+PF_6^-$, 85702-45-0; (−)-(*RS*)-$\mathbf{9}^+PF_6^-$, 86594-81-2; (+)-(*S*)-[(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+CF_3SO_3^-$, 92761-87-0; $HCO_2Si(CH_3)_3$, 18243-21-5.