Synthetic Approaches to the Chiral, Pyramidal, Transition-Metal Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+X^-$. Generation, Characterization, and Reactions of a Dichloromethane Adduct

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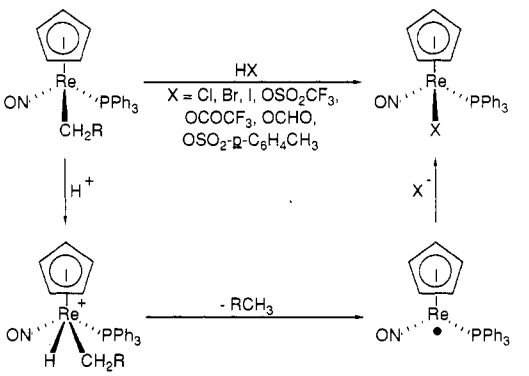
Reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**2**) with $HBF_4{\cdot}O(C_2H_5)_2$ and $HPF_6{\cdot}O(C_2H_5)_2$ (CH_2Cl_2, −78 °C) gives reactive intermediates ($\mathbf{1}^+BF_4^-$, $\mathbf{1}^+PF_6^-$) that are functional equivalents of the chiral, pyramidal, 16-valence-electron, transition-metal Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$. Low-temperature ^{13}C NMR spectra show that $\mathbf{1}^+X^-$ contains coordinated CH_2Cl_2. Reactions of $\mathbf{1}^+X^-$ with Lewis bases (RCN, CO, $H_2C{=}CH_2$, $O{=}PPh_3$, ^-CN) give adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^{n+}$ (65–86%). Optically active (*S*)-$\mathbf{1}^+X^-$ is generated from optically active methyl complex (+)-(*S*)-**2**, as assayed by the formation of Lewis base adducts in 98–99% ee and with overall retention of configuration. Low-temperature NMR data suggest methyl hydride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)(H)]^+X^-$ to be a precursor of $\mathbf{1}^+X^-$. This is supported by the characterization of more stable analogues $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)(H)]^+BF_4^-$ (R = H, $CH_2C_6H_5$). While $\mathbf{1}^+PF_6^-$ decomposes to many products, $\mathbf{1}^+BF_4^-$ decomposes (2–4 h, −20 °C) chiefly to bridging chloride complex (*SS,RR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+BF_4^-$ ((*SS,RR*)-$\mathbf{13}^+BF_4^-$, 64%). This structural assignment is confirmed by an independent synthesis of (+)-(*SS*)-$\mathbf{13}^+BF_4^-$ from (*S*)-$\mathbf{1}^+BF_4^-$ and chloride complex (+)-(*S*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ ((+)-(*S*)-**9**). When (*SS,RR*)-$\mathbf{13}^+BF_4^-$ is refluxed in CH_3CN or acetone, $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+BF_4^-$ (L = CH_3CN, acetone; 92–96%) and **9** (96–98%) form.

Introduction

Transition-metal complexes of weakly coordinating ligands are important from both synthetic and mechanistic viewpoints.[1-10] Such complexes are often in facile equilibrium with their coordinatively unsaturated, "Lewis acid",[1,11] counterparts. These are in turn capable of coordinating and activating Lewis bases. This provides a convenient route to several important classes of transition-metal complexes and constitutes a key reaction sequence in a variety of catalytic reactions.[12]

In view of the large number of stable transition-metal complexes with less than 18 valence electrons, there are an abundance of transition-metal "Lewis acids". However, the BF_4^- and PF_6^- complexes in Figure 1 deserve emphasis, as they are well-studied and contain ligand arrays similar to our target complex described below. In nearly every case

Scheme I. Cleavage of Rhenium–Carbon σ Bonds by Acids with Retention of Configuration at Rhenium



where experimental data has been sought, evidence has been found for BF_4^- binding to coordinatively unsaturated metal cations in solution and the solid state.[2a,c-g,4a,7b,10,13] Other important classes of weakly coordinating anionic ligands include SbF_6^-,[7] $B_{11}CH_{12}^-$,[8] and $^-OTeF_5$.[9]

Lewis acids catalyze a number of organic transformations, and there has been a great deal of recent interest in the development of chiral, optically active Lewis acids for use in asymmetric organic synthesis.[14] Some examples,

(1) (a) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, in press. (b) Lawrence, G. A. *Ibid.* **1986**, *86*, 17.

(2) (a) Beck, W.; Schloter, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1214. (b) Schloter, K.; Beck, W. *Ibid.* **1980**, *35B*, 985. (c) Sünkel, K.; Ernst, H.; Beck, W. *Ibid.* **1981**, *36B*, 474. (d) Olgemöller, B.; Bauer, H.; Löbermann, H.; Nagel, U.; Beck, W. *Chem. Ber.* **1982**, *115*, 2271. (e) Sünkel, K.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1983**, *251*, 227. (f) Sünkel, K.; Urban, G.; Beck, W. *Ibid.* **1983**, *252*, 187. (g) Raab, K.; Nagel, U.; Beck, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1466. (h) Raab, K.; Beck, W. *Chem. Ber.* **1985**, *118*, 3830. (i) Bauer, H.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1985**, *290*, 219. (j) Beck, W.; Sacher, W.; Nagel, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 270. (k) Appel, M.; Schloter, K.; Heidrich, J.; Beck, W. *J. Organomet. Chem.* **1987**, *322*, 77. (l) Appel, M.; Sacher, W.; Beck, W. *Ibid.* **1987**, *322*, 351.

(3) (a) LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312. (b) Markman, J.; Menard, K.; Cutler, A. R. *Inorg. Chem.* **1985**, *24*, 1581.

(4) (a) Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186. (b) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1981**, *217*, C37. (c) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135.

(5) Regina, F. J.; Wojcicki, A. *Inorg. Chem.* **1980**, *19*, 3803.

(6) Legzdins, P.; Martin, D. T. *Organometallics* **1983**, *2*, 1785.

(7) (a) Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599. (b) Honeychuck, R. V.; Hersh, W. H., submitted for publication.

(8) (a) Shelly, K.; Reed, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 3117. (b) Liston, D. J.; Reed, C. A.; Eigenbrot, C. W.; Scheidt, W. R. *Inorg. Chem.* **1987**, *26*, 2740.

(9) (a) Noirot, M. D.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1987**, *26*, 2216. (b) Abney, K. D.; Long, K. M.; Anderson, O. P.; Strauss, S. H. *Ibid.* **1987**, *26*, 2638.

(10) Thomas, R. R.; Venkatasuryanarayana, C.; Sen, A. *J. Am. Chem. Soc.* **1986**, *108*, 4096.

(11) Jensen, W. B. *Chem. Rev.* **1978**, *1*.

(12) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980; pp 5–21.

(13) (a) Buffagni, S.; Vallarino, L. M.; Quagliano, J. V. *Inorg. Chem.* **1964**, *3*, 671. (b) Brown, D. S.; Lee, J. D.; Melsom, B. G. A.; Hathaway, B. J.; Procter, I. M.; Tomlinson, A. A. G. *J. Chem. Soc., Chem. Commun.* **1967**, 369. (c) Tomlinson, A. A. G.; Dessy, G.; Fares, V.; Scaramuzza, L. *J. Chem. Soc., Dalton Trans.* **1972**, 1671. (d) Gaughan, A. P.; Dori, Z.; Ibers, J. A. *Inorg. Chem.* **1974**, *13*, 1657. (e) Boniface, S. M.; Clark, G. R.; Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1981**, *206*, 109. (f) Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1082.

(14) (a) Hashimoto, S.; Komeshima, N.; Koga, K. *J. Chem. Soc., Chem. Commun.* **1979**, 437. (b) Kelly, T. R.; Whiting, A.; Chandrakumar, N. S. *J. Am. Chem. Soc.* **1986**, *108*, 3510. (c) Bednarski, M.; Danishefsky, S. *Ibid.* **1986**, *108*, 7060. (d) Reetz, M. T.; Kunisch, F.; Heitmann, P. *Tetrahedron Lett.* **1986**, *27*, 4721. (e) Paterson, I.; Lister, M. A.; McClure, C. K. *Ibid.* **1986**, *39*, 4787. (f) Maruoka, K.; Sakurai, M.; Fujiwara, J.; Yamamoto, H. *Ibid.* **1986**, *27*, 4895. (g) Sakane, S.; Maruoka, K.; Yamamoto, H. *Tetrahedron* **1986**, *42*, 2203. (h) Quimpère, M.; Jankowski, K. *J. Chem. Soc., Chem. Commun.* **1987**, 676. (i) Bir, G.; Kaufmann, D. *Tetrahedron Lett.* **1987**, *28*, 777. (j) Takemura, H.; Komeshima, N.; Takahashi, I.; Hashimoto, S.; Ikota, N.; Tomioka, K.; Koga, K. *Ibid.* **1987**, *28*, 5687. (k) Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310.

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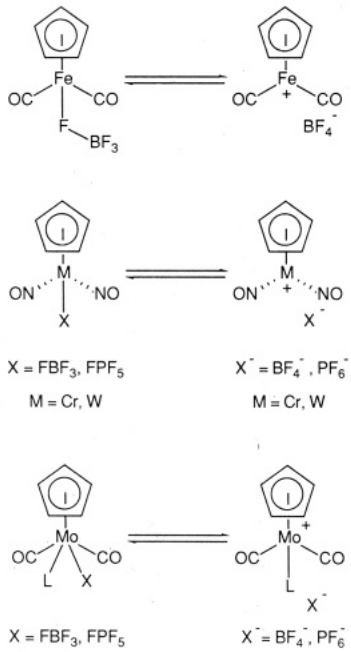


Figure 1. Some transition-metal Lewis acids.

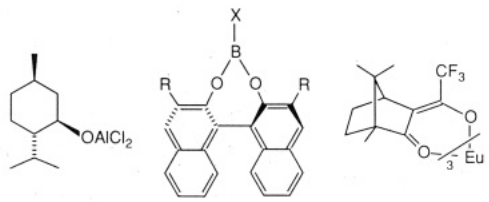


Figure 2. Representative chiral, optically active Lewis acids.

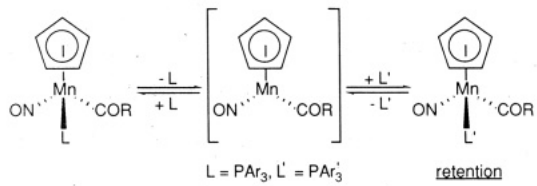


Figure 3. Likely intermediacy of a chiral, transition-metal, Lewis acid in a dissociative substitution reaction.

all of which contain main-group or lanthanide element binding sites, are given in Figure 2. Note, however, that common trivalent group 13 Lewis acids R_3E (E = B, Al, etc.) are generally *planar* at the binding site.

Surprisingly, there has been little effort directed at the synthesis or generation of *chiral-at-metal, optically active, transition-metal Lewis acids*. In a key study, Brunner showed that manganese phosphine complex $(\eta^5\text{-}C_5H_5)$-$Mn(NO)(COR)(PAr_3)$ underwent substitution by PAr'_3 by a *dissociative* mechanism and with *retention* of configuration (Figure 3).[15] This suggests the intermediacy of a *pyramidal*, 16-valence-electron, Lewis acidic complex that retains configuration, although it should be noted in passing that an η^2-acyl complex might be an additional (possibly lower energy) intermediate. Subsequent theoretical work by P. Hofmann established that such d^6 $(\eta^5\text{-}C_5H_5)MLL'$ complexes should have pyramidal ground states.[16] Hence, we wondered if it would be possible to synthesize and perhaps isolate chiral, opically active,

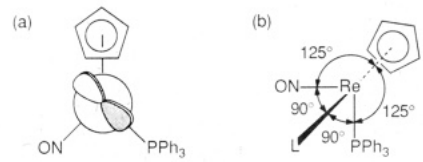
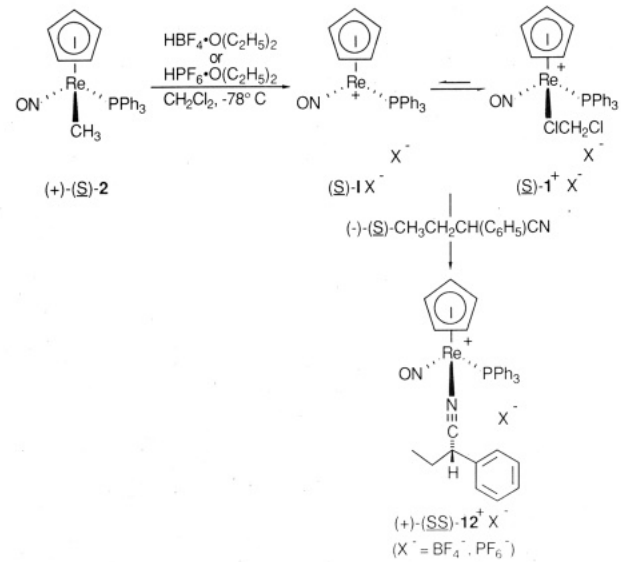


Figure 4. (a) d orbital HOMO of the chiral Lewis acid fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I). (b) Key geometric features of Lewis base adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^{n+}$.

Scheme II. Generation and Trapping of a Chiral, Optically Active Rhenium Lewis Acid



transition-metal Lewis acids and apply them in a rational way in asymmetric organic synthesis.

The chiral, d^6, 16-valence-electron rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I) is a powerful π donor that is capable of stabilizing normally reactive unsaturated ligands.[17,18] It also can efficiently transmit its chirality to new ligand-based chiral centers.[19] The d-orbital HOMO and key geometric features of fragment I are shown in Figure 4. The corresponding alkyl complexes $(\eta^5\text{-}C_5H_5)$-$Re(NO)(PPh_3)(CH_2R)$ are readily available in optically pure form.[20] Interestingly, these react with protic acids HX (Scheme I) to give new complexes $(\eta^5\text{-}C_5H_5)Re$-$(NO)(PPh_3)(X)$ in high chemical yields and with essentially complete retention of configuration at rhenium (as well as carbon).[19c,21] It has been suggested that these transformations occur by initial protonation of the metal, followed by reductive elimination of alkane to give the chiral Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I), as shown in Scheme I. Hence, we set out to attempt the synthesis of I, and its physical and chemical characterization. A portion of this study has been communicated.[22]

(15) (a) Brunner, H.; Aclasis, J.; Langer, M.; Steger, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 810. (b) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151.

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

(17) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

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

(19) (a) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (b) Crocco, G. L.; Gladysz, J. A. *Ibid.* **1985**, *107*, 4103. (c) O'Connor, E. J.; Kobayashi, M.; Floss, H. G.; Gladysz, J. A. *Ibid.* **1987**, *109*, 4837. (d) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P.-C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *Ibid.* **1987**, *109*, 7688.

(20) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

(21) Merrifield, J. H.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

(22) Fernández, J. M.; Gladysz, J. A. *Inorg. Chem.* **1986**, *25*, 2672.

Table I. Comparison of ^{13}C NMR Chemical Shifts of the α-Carbon Atoms of Lewis Bases before and after Coordination to the Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)^+]$

ligand	uncoordinated[a] (ppm)	coordinated (ppm)	Δ (ppm)
CH_3CN	117.7	140.4[b,c]	22.7
CH_3COCH_3	206.0	232.7[c,d]	26.7
CH_3I	−20.7	0.8[d,e]	21.5
CH_2Cl_2	54.0	78.3[f,g]	24.3

[a] Neat vs TMS, from ref 24a, pp 269–272. [b] In $CDCl_3$ and at ambient probe temperature. [c] Referenced to TMS. [d] In CD_2Cl_2 and at ambient probe temperature. [e] Referenced to CD_2Cl_2 at 53.8 ppm. [f] In CH_2Cl_2 at −85 °C. [g] Referenced to CH_2Cl_2 at 54.0 ppm.

Results

1. Attempted Generation of Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I). We sought to repeat the rhenium–carbon bond protonolyses shown in Scheme I, but utilizing acids with less coordinating anions. Hence, methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**2**) and $HBF_4{\cdot}O(C_2H_5)_2$, $HPF_6{\cdot}O(C_2H_5)_2$, and $HBF_4{\cdot}O(CH_3)_2$ were reacted at −78 °C in CD_2Cl_2 or CH_2Cl_2 (see Scheme II). These mixtures were immediately analyzed by ^1H or $^{31}P\{^1H\}$ NMR at −85 °C. In all cases, resonances due to transient species were observed. These diminished to <10% by briefly annealing the samples at −60 °C.

Subsequent to annealing, each sample contained a complex ($1^+BF_4^-$ or $1^+PF_6^-$) of ≥85% spectroscopic purity with the following selected spectral characteristics: ^1H NMR (δ) 5.62 (s); $^{31}P\{^1H\}$ NMR 12.4 (s) ppm; $^{13}C\{^1H\}$ NMR 92.0 (s) ppm; IR (−90 °C)[23] $\nu_{N\equiv O}$ 1714 cm^{-1}. The ^1H and $^{13}C\{^1H\}$ NMR spectra also showed CH_4 (δ 0.14 (s); −4.0 (s))[24] and *uncomplexed* ethers $O(C_2H_5)_2$ or $O(CH_3)_2$. Hence, $1^+BF_4^-$ and $1^+PF_6^-$ are not ether complexes.

Complex $1^+BF_4^-$ exhibited a ^{19}F NMR BF_4^- resonance (−152.45 ppm vs CCl_3F) that was nearly coincident with that of free BF_4^- in the coordinatively saturated cationic carbonyl complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (−152.64 (s) ppm, −90 °C, CD_2Cl_2).[17] Interestingly, one transient precursor to $1^+BF_4^-$ showed a large ^{19}F NMR coupling (−156.9 (d, J = 91.9 Hz) ppm, ≃ 3%), possibly to phosphorus or a bridging fluorine. Complex $1^+PF_6^-$ exhibited ^{19}F and ^{31}P NMR PF_6^- resonances that were coincident with those of free PF_6^- in the coordinatively saturated cationic ethylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$ (CH_2Cl_2, −90 °C: ^{19}F NMR, −73.5 (d, J_{FP} = 710.0 Hz) ppm; ^{31}P NMR, −145.0 (sep, J_{PF} = 712.0 Hz) ppm).[18] Hence, it is unlikely that either BF_4^- or PF_6^- coordinate to rhenium in $1^+BF_4^-$ and $1^+PF_6^-$.

Complexes $1^+BF_4^-$ and $1^+PF_6^-$ did not exhibit unusual IR or NMR features that might be diagnostic of an agostic interaction.[25] Thus, in view of their reactions with Lewis bases described below, we considered formulating them as salts of the target Lewis acid I. However, solvent interactions with coordinatively unsaturated metal centers are increasingly being documented.[26] Furthermore, Lewis base adducts did not form "immediately" but required 2–3 h at −50 °C. Thus, the possibility of CH_2Cl_2 coordination in $1^+BF_4^-$ and $1^+PF_6^-$ was considered. The generation or

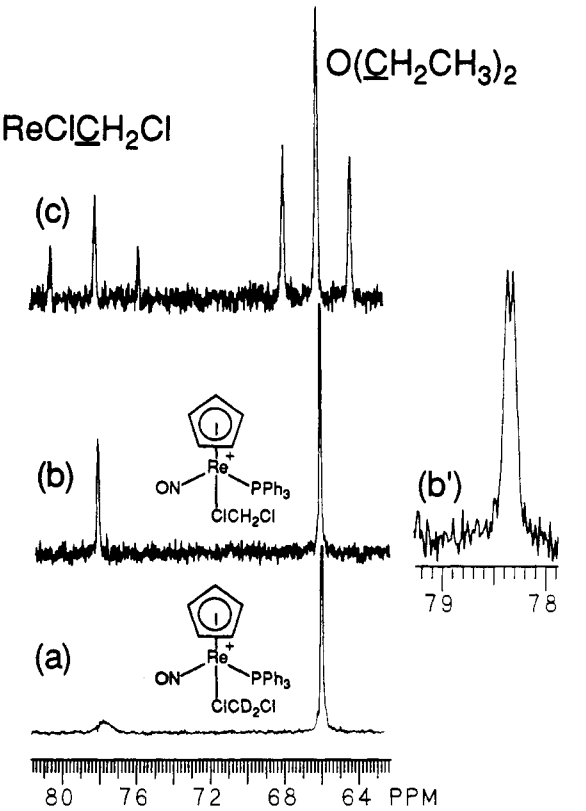


Figure 5. (a) $^{13}C\{^1H\}$ NMR spectrum of $1^+\text{-}d_2BF_4^-$. (b) $^{13}C\{^1H\}$ NMR spectrum of $1^+BF_4^-$, with inset (b′) showing $^3J_{CP}$ = 3.8 Hz. (c) ^{13}C NMR spectrum of $1^+BF_4^-$ showing $^1J_{CH}$ = 185.5 Hz. All spectra are at −85 °C.

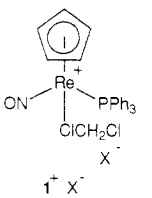
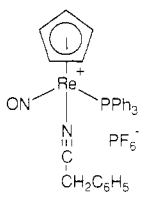
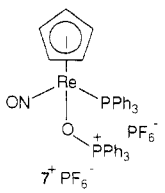
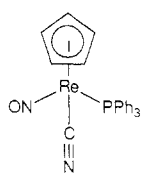
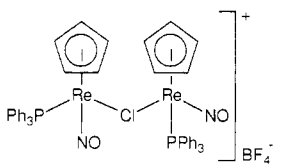
intermediacy of dichloromethane complexes has been proposed previously,[2a,g,4a,27,28] but direct experimental evidence is scant. Hence, we probed for CH_2Cl_2 coordination by ^{13}C NMR.

Complex $1^+BF_4^-$ was generated in CD_2Cl_2 and a $^{13}C\{^1H\}$ NMR spectrum was recorded at −85 °C (Figure 5a). A broad resonance was noted at 78 ppm. Free CH_2Cl_2 exhibits a ^{13}C NMR resonance at 54.0 ppm. As shown in Table I, σ coordination of heteroatomic Lewis bases to I reproducibly shifts any α-carbon ^{13}C NMR resonance 22–27 ppm downfield.

In order to remove any peak broadening due to deuterium coupling, $1^+BF_4^-$ was generated in CH_2Cl_2 and a $^{13}C\{^1H\}$ NMR spectrum again recorded (Figure 5b). A sharper resonance was noted at 78.3 ppm, which an expansion (b′) showed to be a doublet (J = 3.8 Hz). Of the two high-abundance, undecoupled spin $^1/_2$ nuclei in the sample (^{31}P of PPh_3, ^{19}F of BF_4^-), this coupling is most logically attributed to ^{31}P. The chemical shift and coupling constant did not significantly change in spectra recorded

(23) Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325.
(24) (a) Silverstein, R. M.; Bassler, G. C.; Morril, T. C. *Spectroscopic Identification of Organic Compounds*, 4th ed.; Wiley-Interscience: New York, 1981; p 269. (b) Pavia, D. L.; Lampman, G. M.; Kriz, G. S. *Introduction to Spectroscopy*; W. B. Saunders: Philadelphia, 1979; p 93.
(25) Brookhart, M.; Green, M. L. H.; Wong, L.-T. *Prog. Inorg. Chem.* **1988**, *36*, 1.
(26) (a) Simon, J. D.; Peters, K. S. *Chem. Phys. Lett.* **1983**, *98*, 53. (b) Yang, G. K.; Peters, K. S.; Vaida, V. *Ibid.* **1986**, *125*, 566.
(27) (a) Green, M. L. H.; Whiteley, R. N. *J. Chem. Soc. A* **1971**, 1943. (b) Ferguson, J. A.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 1025. (c) Boyle, P. F.; Nicholas, K. M. *J. Organomet. Chem.* **1976**, *114*, 307. (d) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099; see footnote 13. (e) Reger, D. L.; Coleman, C. J.; McElligot, P. J. *J. Organomet. Chem.* **1979**, *171*, 73. (f) Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3155. (h) Jernakoff, P.; Cooper, N. J. *Organometallics* **1986**, *5*, 747. (i) An X-ray crystal structure of a complex with 3.354-Å metal–$ClCH_2Cl$ distance has been reported: Cotton, F. A.; Ilsley, W. H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 3475. Baral, S.; Cotton, F. A.; Ilsley, W. H. *Inorg. Chem.* **1981**, *20*, 2696.
(28) (a) Scherer, O. J.; Jungmann, H. *J. Organomet. Chem.* **1981**, *208*, 153. (b) Werner, H.; Paul, W. *Ibid.* **1982**, *236*, C71. (c) Olson, W. L.; Nagaki, D. A.; Dahl, L. F. *Organometallics* **1986**, *5*, 630. (d) Burns, E. G.; Chu, S. S. C.; de Meester, P.; Lattman, M. *Ibid.* **1986**, *5*, 2383. (e) Chang, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4298. (f) Marder, T. B.; Fultz, W. C.; Calabrese, J. C.; Harlow, R. L.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1543.

Table II. Characterization of New Rhenium Compounds

complex	IR (cm^{-1}, KBr)	^1H NMR[a,b] (δ)	$^{13}C\{^1H\}$ NMR[b,c] (ppm)	$^{31}P\{^1H\}$ NMR[b,d] (ppm)	anal.
 $1^+ X^-$	$\nu_{N\equiv O}$ 1714 vs	7.51–7.16 (m, $3C_6H_5$), 5.62 (s, C_5H_5)[e]	PPh_3 at 132.5 (d, J = 10.6), 130.6 (s, para), 130.2 (d, J = 57.8, ipso), 128.6 (d, J = 10.9); 92.0 (s, C_5H_5); 78.3 (d, J = 3.7, $ClCH_2Cl$)[e,f]	12.50 (s)[e]	NA
 $6^+ PF_6^-$	$\nu_{N\equiv O}$ 1700 vs	7.55–6.91 (m, $4C_6H_5$), 5.53 (s, C_5H_5), 4.31 (d, J = 2.84, *H*CH), 4.29 (d, J = 2.93, HC*H*)	CPh at 129.7 (s), 129.4 (s), 129.3 (s);[g] PPh_3 at 134.3 (d, J = 11.2), 132.6 (s, para), 132.5 (d, J = 57.3, ipso), 130.2 (d, J = 11.3); 143.0 (s, CN); 93.1 (s, C_5H_5); 26.1 (s, CH_2)	14.50 (s)	Calcd for $C_{31}H_{27}F_6P_2N_2ORe\cdot(CH_2Cl_2)_{0.25}$: C, 45.49; H, 3.33; N, 3.39; Found: C, 45.64; H, 3.22; N, 3.42
 $7^+ PF_6^-$	$\nu_{N\equiv O}$ 1676 vs, ν_{P-O} 1028 w, 1058 m	7.76–7.29 (m, $6C_6H_5$), 5.02 (s, C_5H_5)	$OPPh_3$ at 134.6 (d, J = 2.7, para), 129.9 (d, J = 12.7), 126.1 (d, J = 108.5, ipso); $RePPh_3$ at 133.0 (d, J = 55.4, ipso), 131.8 (d, J = 2.2, para), 129.6 (d, J = 10.6); other PPh_3 at 134.0 (d, J = 10.9), 133.3 (d, J = 10.6);[h] 91.1 (s, C_5H_5)	19.11 (d, J = 12.0, $RePPh_3$), 62.30 (d, J = 11.4, $OPPh_3$)[e]	Calcd for $C_{41}H_{35}F_6O_2P_3Re$: C, 50.98; H, 3.62; Found: C, 50.83; H, 3.68
 11	$\nu_{N\equiv O}$ 1679 vs, $\nu_{C\equiv N}$ 2091 s	7.53–7.26 (m, $3C_6H_5$), 5.25 (s, C_5H_5)	PPh_3 at 134.1 (d, J = 56.3, ipso), 133.3 (d, J = 11.0), 130.8 (d, J = 1.6, para), 128.6 (d, J = 10.7); 121.5 (d, J = 11.9, CN); 90.4 (s, C_5H_5)	17.37 (s)	Calcd for $C_{24}H_{20}N_2OPRe$: C, 50.66; H, 3.52; N, 4.92; Found: C, 50.70; H, 3.78; N, 4.99
 (SS,RR)-$13^+ BF_4^-$	$\nu_{N\equiv O}$ 1662 vs, ν_{B-F} 1034, 1046, 1068	7.63–7.10 (m, $3C_6H_5$), 5.40 (s, C_5H_5)	PPh_3 at 133.6 (d, J = 9.9), 133.0 (d, J = 56.0, ipso), 131.5 (d, J = 2.1, para), 129.1 (d, J = 11.3); 93.1 (s, C_5H_5)	15.12 (s)[e]	Calcd for $C_{46}H_{40}BF_4N_2O_2P_2Re\cdot(CH_2Cl_2)_{0.45}$: C, 44.70; H, 3.25; Cl, 5.41; Found: C, 44.41; H, 3.29; Cl, 5.18

[a] At 300 MHz and ambient probe temperature and referenced to internal $(CH_3)_4Si$ or residual protio solvent; all couplings (Hz) are to hydrogen unless noted. [b] NMR solvents: $1^+BF_4^-$, $6^+PF_6^-$, $7^+PF_6^-$, and (*SS,RR*)-$13^+BF_4^-$, CD_2Cl_2; **11**, $CDCl_3$. [c] At 75 MHz and ambient probe temperature and referenced to internal $(CH_3)_4Si$ or to the solvent; all couplings (Hz) are to phosphorus unless noted. [d] At 32.2 MHz and ambient probe temperature unless noted; referenced to external 85% H_3PO_4. [e] Spectrum taken at −85 °C. [f] Spectrum taken in CH_2Cl_2. [g] One phenyl carbon resonance obscured by the triphenylphosphine resonances. [h] These resonances could not be unambiguously assigned to $RePPh_3$ or $OPPh_3$.

at −30 °C (5–10% decomposition during data acquisition) and −3.3 °C (extensive decomposition; see below).

Next, a proton-coupled ^{13}C NMR spectrum was recorded (Figure 5c). The triplet ($^1J_{CH}$ = 185 Hz) observed establishes that two protons are bound to the 78 ppm carbon. Hence, $1^+BF_4^-$ and $1^+PF_6^-$ are formulated as dichloromethane complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+X^-$. Accordingly, the IR $\nu_{N\equiv O}$ and cyclopentadienyl ^1H and ^{13}C NMR chemical shifts of 1^+X^- (Table II) are in ranges typical of cationic complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+X^-$, where L is a σ-bound heteroatomic Lewis base (RCN, R_3P, $R_2C{=}O$, etc.). This assignment is further supported by the recent isolation and crystallographic characterization of analogous alkyl iodide complexes.[29] Note that the CH_2Cl_2 ligand protons are diastereotopic and can in principle show different $^1J_{CH}$.

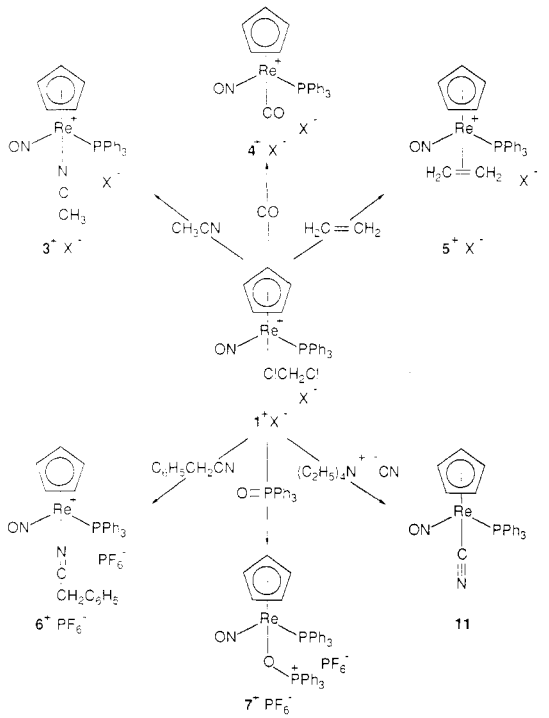
Deuteriodichloromethane complex $1^+\text{-}d_2BF_4^-$ was generated in CD_2Cl_2 (0.40 mL) as above and treated with CH_2Cl_2 (0.25 mL) at −78 °C. A $^{13}C\{^1H\}$ NMR spectrum (−85 °C) showed only $1^+\text{-}d_2BF_4^-$ to be present. The probe was warmed to −65 °C, and a $^{13}C\{^1H\}$ NMR spectrum showed a small amount of unlabeled dichloromethane complex $1^+BF_4^-$. The probe was then kept at −40 °C for 2 h, and a $^{13}C\{^1H\}$ NMR spectrum was subsequently recorded at −85 °C. Appreciable quantities of both $1^+\text{-}d_2BF_4^-$ (78 ppm, br s) and $1^+BF_4^-$ (78.5 ppm, d) were present (peak area ratio ca. 65:35).

Finally, reactions of methyl complex **2** and $HBF_4\cdot O(C_2H_5)_2$ were repeated in the presence of 20–25 equiv of (a) $O(C_2H_5)_2$ and (b) $(CH_3)_4N^+BF_4^-$. In each case, $1^+BF_4^-$ formed cleanly as above, as assayed by ^1H and ^{13}C NMR.

2. Reactions of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+X^-$ (1^+X^-). Although we had established the presence of CH_2Cl_2 in the coordination spheres of $1^+BF_4^-$ and $1^+PF_6^-$, we nonetheless anticipated that these compounds would serve as functional equivalents of chiral, transition-metal Lewis acids. Hence, reactions of $1^+BF_4^-$ and $1^+PF_6^-$ with Lewis bases were examined.

(29) Winter, C. H.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7560.

Scheme III. Reactions of Lewis Bases with the Dichloromethane Complex 1^+X^- ($X^- = BF_4^-, PF_6^-$)



Treatment of $1^+BF_4^-$ with CH_3CN (5.0 equiv) and CO (excess, 225 psi) at −78 °C, followed by warming, gave the known cationic complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+BF_4^-$ ($3^+BF_4^-$, 73%)[18] and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ ($4^+BF_4^-$, 82%), respectively (Scheme III). Reactions of $1^+PF_6^-$ with CH_3CN and CO proceeded analogously to give $3^+PF_6^-$ and $4^+PF_6^-$. Reaction of $1^+BF_4^-$ and ethylene (excess, 180 psi) gave the known ethylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+BF_4^-$ ($5^+BF_4^-$, 78%).[18]

Treatment of $1^+PF_6^-$ with $C_6H_5CH_2CN$ (5.0 equiv) and $O{=}PPh_3$ (1.0 equiv) gave new cationic complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_2C_6H_5)]^+PF_6^-$ ($6^+PF_6^-$, 75%) and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}PPh_3)]^+PF_6^-$ ($7^+PF_6^-$, 86%), respectively (Scheme III). All new compounds were characterized by NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) and IR spectroscopy and microanalysis (Table II). The phosphine oxide ligand in $7^+PF_6^-$ was assigned an η^1-binding mode by analogy to other phosphine oxide complexes.[30] Accordingly, it exhibited a decrease in IR ν_{P-O} (1028 (w), 1058 (m) cm^{-1}) relative to that of free $O{=}PPh_3$ (1220 cm^{-1}).[31] The cyclopentadienyl ligand ^1H NMR chemical shift (δ 5.02) was typical of neutral complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$, implying substantial $Re{-}O{-}P^+Ph_3$ or phosphonium salt character.

Treatment of $1^+BF_4^-$ with bromide salts $[Ph_3P{=}N{=}PPh_3]^+Br^-$ (PPN^+Br^-) or $Ph_3PCH_3^+Br^-$ gave varying, condition-dependent ratios of the known[21] bromide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Br)$ (**8**) and chloride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ (**9**). The latter always predominated. Similar reactivity was observed with iodide salt $Ph_3PCH_3^+I^-$. In all cases iodide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**10**)[21] was the minor product and chloride complex **9** was the major product. The organic product ICH_2Cl was detected by GLC, and this reactivity mode of the CH_2Cl_2 ligand is described in more detail elsewhere.[32]

For the preparative objectives desired here, methyl complex **2** was treated with $HBF_4{\cdot}O(C_2H_5)_2$ in the *presence* of halide salts. With 1.1 equiv of PPN^+Br^-, a (90 ± 2):(10 ± 2) mixture of bromide complex **8** and chloride complex **9** formed, as assayed by ^1H NMR of the crude reaction mixture. With 15 equiv of $Ph_3PCH_3^+Br^-$, **8** was the exclusive product and was subsequently isolated in 70% yield. Identical experiments were conducted with 1.1 and 15 equiv of $Ph_3PCH_3^+I^-$. These gave (93 ± 2):(7 ± 2) and >99:1 mixtures of iodide complex **10** and chloride complex **9**, respectively, and **10** was isolated in 80% yield from the latter reaction.

Reaction of $1^+BF_4^-$ and cyanide salt $(C_2H_5)_4N^+CN^-$ (0.94 equiv) gave the new cyanide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ (**11**, Scheme III) in 56% yield after column chromatography. Surprisingly, methyl complex **2** was also reproducibly isolated in ca. 14% yield. Only small amounts of chloride complex **9** formed. Reaction of triflate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OSO_2CF_3)$[21] and $(C_2H_5)_4N^+CN^-$ (1.1 equiv) also gave **11** (79%). Complex **11** exhibited a characteristic IR $\nu_{C\equiv N}$ (Table II) and was assigned as a cyanide (as opposed to *isocyanide*) linkage isomer by analogy to other low-valent cyanide complexes.[33]

Attempts were next made to generate $1^+BF_4^-$ and $1^+PF_6^-$ in optically active form (Scheme II). Accordingly, optically active methyl complex (+)-(*S*)-**2**[20,34] and $HBF_4{\cdot}O(C_2H_5)_2$ were reacted as described for racemic **2** above. In a previous study, the diastereomeric, optically active nitrile complexes (+)-(*SS*)- and (−)-(*RS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^-$ ((+)-(*SS*)- and (−)-(*RS*)-$\mathbf{12}^+PF_6^-$) were independently synthesized, shown to be easily distinguished by NMR, and crystallographically characterized to establish absolute configuration.[18] Hence, the chiral, optically active nitrile (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ (≥99% ee, 2.0 equiv) was added. Nitrile complex (+)-(*SS*)-$\mathbf{12}^+BF_4^-$ formed (as assayed in situ by ^1H NMR) as a >99:1 mixture of diastereomers and was subsequently isolated in 90% yield, $[\alpha]^{23}_{589}$ 215°. Metathesis with $(CH_3)_4N^+PF_6^-$ gave the previously characterized salt (+)-(*SS*)-$\mathbf{12}^+PF_6^-$, $[\alpha]^{23}_{589}$ 203° (≥98% ee). Reaction of (+)-(*S*)-**2**, $HPF_6{\cdot}O(C_2H_5)_2$, and (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ gave (+)-(*SS*)-$\mathbf{12}^+PF_6^-$ with similar stereospecificity (after correction for a slightly lower nitrile optical purity).[35] Hence, 1^+X^- can serve as the functional equivalent of a chiral, *optically active*, rhenium Lewis acid.

(30) (a) Bertrand, J. A. *Inorg. Chem.* **1967**, *6*, 495. (b) Bombieri, G.; Brown, D.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1975**, 1873. (c) Kuhn, N.; Schumann, H. *J. Organomet. Chem.* **1986**, *304*, 181. (d) Che, C.-M.; Lai, T.-F.; Chung, W.-C.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1987**, *26*, 3907.

(31) Pouchert, C. J. *The Aldrich Library of Infrared Spectra*, 3rd ed.; Aldrich Chemical Co.: Wisconsin, 1981; p 1191.

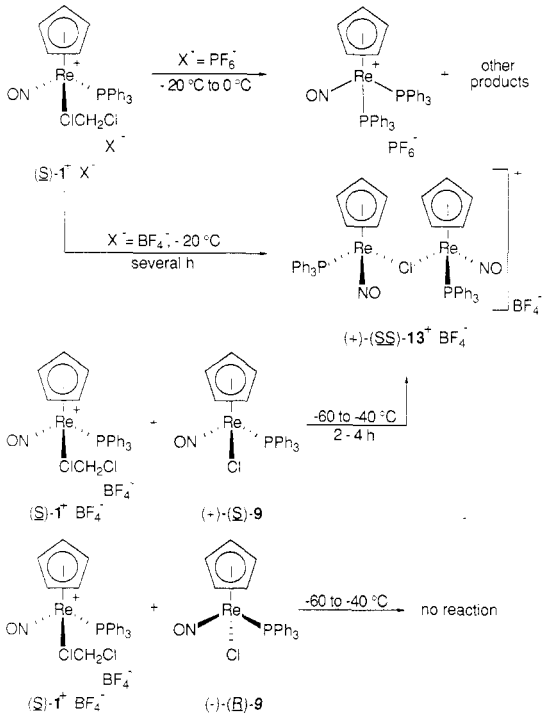
(32) Winter, C. H.; Gladysz, J. A. *J. Organomet. Chem.* **1988**, *354*, C33.

(33) (a) Rigo, P.; Turco, A. *Coord. Chem. Rev.* **1974**, *13*, 133. (b) Carter, S. J.; Stuhl, L. S. *Organometallics* **1988**, *7*, 1909. (c) Jennings, M. A.; Wojcicki, A. *Inorg. Chim. Acta* **1969**, *3*, 335.

(34) (a) Absolute configurations are assigned according to the Baird/Sloan modification of the Cahn-Ingold-Prelog priority rules. The $\eta^5\text{-}C_5H_5$ ligand is considered to be a pseudoatom of atomic number 30, which gives the following sequence: I > Br > $\eta^5\text{-}C_5H_5$ > PPh_3 > NO > NCR > CH_3. Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1. (b) In complexes with more than one chiral center, the rhenium configuration is specified first. (c) Prefixes (+) and (−) refer to rotations at 589 nm. Measurements are in CH_2Cl_2 ((+)-(*SS*)-$\mathbf{13}^+BF_4^-$) or $CHCl_3$ (other compounds) with *c* in the range of 0.3–0.2 mg/mL. All compounds are racemic unless noted.

(35) (a) Commercial $HPF_6{\cdot}O(C_2H_5)_2$ has been at best sporadically available since 1986, and samples have varied considerably in purity. Hence, we have been unable to optimize certain experiments (e.g., reaction of (*S*)-$\mathbf{1}^+PF_6^-$ with optically *pure* (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$) and caution that the decomposition behavior of $1^+PF_6^-$ is sample-dependent. (b) The optical rotation of (+)-(*SS*)-$\mathbf{12}^+PF_6^-$ is correct as given in Scheme III of ref 18 ($[\alpha]^{25}_{589}$ 207°); however, it is reversed with that of (+)-(*SR*)- and (−)-(*RS*)-$\mathbf{12}^+PF_6^-$ ($[\alpha]^{25}_{589}$ 170°) in the text and Experimental Section.

Scheme IV. Thermal Decomposition of Dichloromethane Complex (*S*)-1$^+$BF$_4^-$, and Independent Synthesis of Bridging Chloride Complex (+)-(*SS*)-13$^+$BF$_4^-$



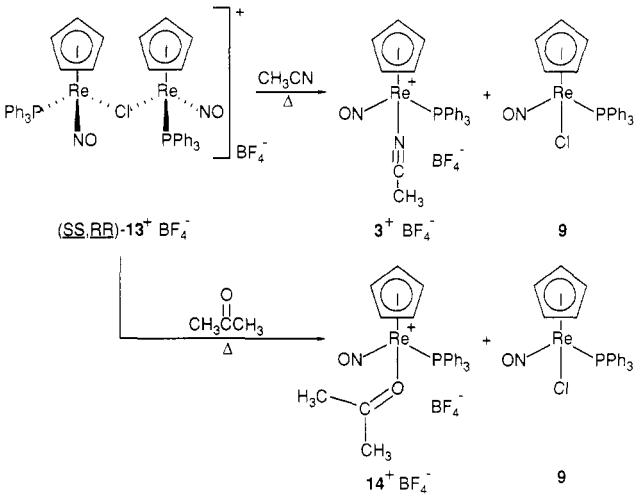
Similarly, methyl complex (+)-(*S*)-**2** was treated with $HBF_4{\cdot}O(C_2H_5)_2$ in the presence of halide salts $Ph_3PCH_3{}^+Br^-$ (15 equiv) and $Ph_3PCH_3{}^+I^-$ (15 equiv). Subsequently isolated were optically active bromide complex[21] (+)-(*R*)-**8** (65–70%) of ≥98% ee and optically active iodide complex[21] (+)-(*R*)-**10** (65–80%) of ≥98% ee.

Finally, the rate of reaction of 1$^+$-d_2BF$_4^-$ (0.036–0.037 M in CD_2Cl_2) and excess CH_3CN to give acetonitrile complex 3$^+$BF$_4^-$ was monitored by ^{1}H NMR at −38.5 °C. Standard logarithmic plots indicated the reaction to be first order in 1$^+$-d_2BF$_4^-$ through 85% completion. Importantly, the pseudo-first-order k_{obsd} depended upon the CH_3CN concentration over the range studied (representative data: $[CH_3CN]$ = 0.19 M, $k_{obsd} = (5.9 \pm 0.3) \times 10^{-4}$ s^{-1}, $t_{1/2}$ = 19.5 min; $[CH_3CN]$ = 0.56 M, $k_{obsd} = (17.3 \pm 1.3) \times 10^{-4}$ s^{-1}, $t_{1/2}$ = 6.7 min), consistent with either an associative substitution or a dissociative substitution with $k_{-1}[CD_2Cl_2] \gg k_2[CH_3CN]$. Reactions of 1$^+BF_4^-$ and 1$^+$PF$_6^-$ with a variety of other Lewis bases proceed on similar time scales (ca. 3 h, −50 to −40 °C; 3.0 equiv of aldehydes, ketones, primary alkyl halides).[29,36] A mechanistic study of these substitution reactions is in progress.

3. Decomposition of Dichloromethane Complexes 1$^+$X$^-$. Complexes 1$^+$BF$_4^-$ and 1$^+$PF$_6^-$ decomposed upon attempted isolation. Hence, their thermal stabilities were probed by NMR. Complex 1$^+$PF$_6^-$ decomposed to a multitude of products between −20 and 0 °C, as evidenced by numerous cyclopentadienyl ^{1}H NMR resonances. The decomposition rate and product distribution depended somewhat on the sample of $HPF_6{\cdot}O(C_2H_5)_2$ utilized.[35a] The known bis(phosphine) complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)_2]^+PF_6^-$ was spectroscopically identified (^{1}H NMR (δ) 5.29 (s, C_5H_5); $^{31}P\{^1H\}$ NMR 15.8 (s) ppm)[17] as one (10–31%) of the products (Scheme IV).[35a]

In contrast, 1$^+$BF$_4^-$ decomposed quite cleanly to a new complex (13$^+$BF$_4^-$) over the course of several hours at −20 °C. The rate of disappearance of 1$^+$-d_2 (0.033 M in CD_2Cl_2) was monitored at −10.1 °C by ^{1}H NMR and was found to be first order in 1$^+$-d_2BF$_4^-$ ($k_{obsd} = (3.5 \pm 0.2) \times 10^{-4}$; $t_{1/2}$ = 33 min).[37] Significant quantities of an intermediate accumulated (δ 5.43, up to 30% of total cyclopentadienyl resonance integration) before conversion to 13$^+$BF$_4^-$ was complete. A ^{19}F NMR spectrum of the reaction mixture showed $BF_3{\cdot}O(C_2H_5)_2$ (−152.8 ppm, 43% of total fluorine resonances), BF$_4^-$ (−152.5 ppm, 43%), and minor products at −134.3 (3%), −145.7 (2%), −150.9 (6%), and −155 (v br, 4%) ppm. Workup gave the crystalline solvate 13$^+$-BF$_4^-{\cdot}(CH_2Cl_2)_{1.0}$, which partially desolvated when separated from the mother liquor. Vacuum drying gave light orange, microcrystalline 13$^+$BF$_4^-{\cdot}(CH_2Cl_2)_{0.45}$ in 65–75% yields.

Scheme V. Cleavage Reactions of Bridging Chloride Complex (*SS*,*RS*)-[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)]$_2$Cl$^+$BF$_4^-$



The IR spectrum of 13$^+$BF$_4^-$ clearly showed the presence of the BF$_4^-$ ion (Table II). However, the cyclopentadienyl ^{1}H and ^{13}C NMR chemical shifts were intermediate between those of cationic complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+BF_4^-$ (L = CO, $H_2C{=}CH_2$) and neutral complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ (e.g., **11**, Table II). The FAB mass spectrum of 13$^+$BF$_4^-$ showed a parent ion at m/z 1123, indicating a dirhenium complex. Furthermore, a peak at m/z 579 suggested the presence of a $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ moiety. Hence, 13$^+$BF$_4^-$ was provisionally assigned as the bridging chloride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+BF_4^-$ (see Scheme IV). Although 13$^+$BF$_4^-$ contains two chiral rhenium centers, it apparently forms as one of two possible diastereomers.

Reactions of 13$^+$BF$_4^-$ provided further evidence for the proposed structure. First, 13$^+$BF$_4^-$ was converted in refluxing CH_3CN to a (50 ± 2):(50 ± 2) mixture of acetonitrile complex 3$^+$BF$_4^-$ and chloride complex **9** (Scheme V). These were subsequently isolated in 96% and 98% yields (based upon a theoretical maximum of 0.5 equiv), respectively. A similar reaction in refluxing acetone gave acetone complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)_2)]^+BF_4^-$ (14$^+$BF$_4^-$)[36b] and chloride complex **9** in 92% and 96% yields, respectively. The rate of the reaction in CD_3CN was monitored by ^{1}H NMR at 40.1 °C: k_{obsd} = $(1.91 \pm 0.07) \times 10^{-4}$ s^{-1}; $t_{1/2}$ = 60 min.[37]

The structure of 13$^+$BF$_4^-$, including the diastereomer assignment, was unequivocally established by additional syntheses. First, optically active (*S*)-1$^+$BF$_4^-$ decomposed to give *optically active* 13$^+$BF$_4^-$, $[\alpha]^{23}_{589}$ 549°.[34c] This

(36) (a) Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8268. (b) Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1988**, 37.

(37) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 13, 30.

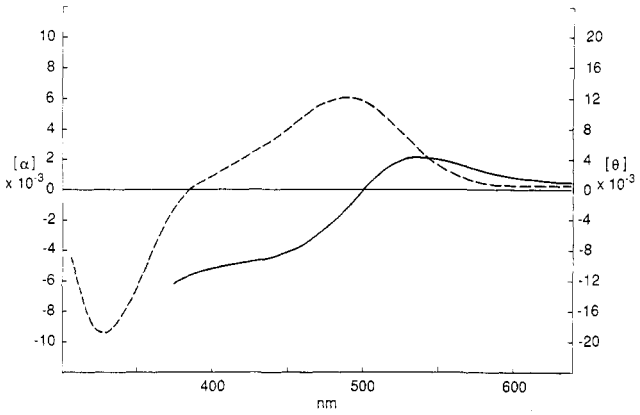


Figure 6. ORD spectrum (solid line, left y axis) and CD spectrum (dashed line, right y axis) of (+)-(*SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+BF_4^-$.

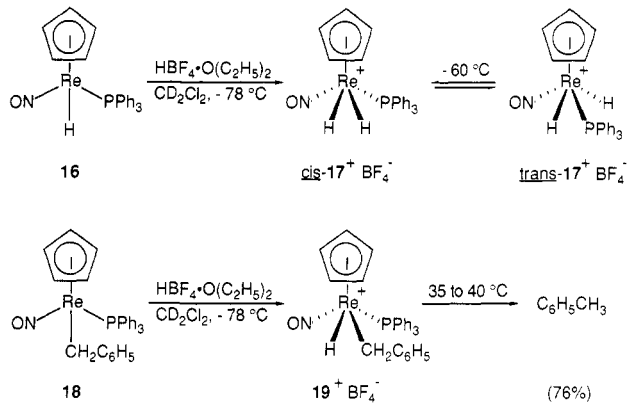
shows that racemic $\mathbf{13}^+BF_4^-$ forms as a *dl* or (*SS,RR*) diastereomer. The alternative meso diastereomer would be optically inactive. Second, reaction of racemic $\mathbf{1}^+BF_4^-$ with racemic chloride complex **9** independently gave (*SS,RR*)-$\mathbf{13}^+BF_4^-$ (80%). No trace of the meso diastereomer was noted. Finally, optically active (*S*)-$\mathbf{1}^+BF_4^-$ was treated with optically active chloride complex of *identical* relative configuration, (+)-(*S*)-**9** (Scheme IV). The reactants were thus appropriately matched to give one enantiomer of a *dl* diastereomer, as opposed to a meso diastereomer. Reaction occurred smoothly at −60 to −40 °C, as assayed by ^1H and ^{31}P NMR. Bridging chloride complex (+)-(*SS*)-$\mathbf{13}^+BF_4^-$, $[\alpha]^{23}_{589}$ 528°, was isolated in 74% yield. The absolute configuration was assigned by analogy to Scheme II. The ORD and CD spectra of (+)-(*SS*)-$\mathbf{13}^+BF_4^-$ are given in Figure 6.

Interestingly, attempted syntheses of the meso diastereomer of $\mathbf{13}^+BF_4^-$ failed. Optically active (*S*)-$\mathbf{1}^+BF_4^-$ was treated with optically active chloride complex (−)-(*R*)-**9** (Scheme IV). These are of *opposite* relative configuration and are thus appropriately matched to give a meso diastereomer. At −40 °C, independent decomposition of (*S*)-$\mathbf{1}^+BF_4^-$ began. At 0 °C, (−)-(*R*)-**9** started to react. Addition of ether precipitated extensively racemized (+)-(*SS*)-$\mathbf{13}^+BF_4^-$ ($[\alpha]^{23}_{589}$ 116°). A ^1H NMR spectrum of the supernatant showed <5% of any resonances that could possibly be ascribed to the meso diastereomer.

4. Mechanism of Formation of Dichloromethane Complexes $\mathbf{1}^+X^-$. When reactions of methyl complex **2** with $HBF_4{\cdot}O(C_2H_5)_2$ or $HPF_6{\cdot}O(C_2H_5)_2$ were monitored by NMR as described above, transient ^1H NMR resonances were observed at −85 °C in characteristic cyclopentadienyl (δ 6.01, 5.20, 5.17, 5.13), methyl (δ 1.44 (dd, J = 5.42, 23.7 Hz); 1.04 (d, J = 11.71 Hz)), and hydride (δ −3.45 (d, J_{HP} = 65.44 Hz); −2.20 (br d, $J_{HP} \simeq$ 50 Hz)) ligand regions. The δ 1.04 resonance overlapped with a $O(C_2H_5)_2$ resonance and was assigned from a reaction with $HBF_4{\cdot}O(CH_3)_2$. The ^{13}C NMR spectrum showed corresponding cyclopentadienyl (96.4, 91.5, 91.0 ppm) and methyl (−32.4 (d, J_{CP} = 6.7 Hz); −10.9 (d, J_{CP} = 12.7 Hz) ppm) ligand resonances. The ^{31}P NMR spectrum showed transients at 19.19, 17.92, 16.51, and 16.33 ppm. An IR spectrum (−90 °C)[23] showed a broad, transient $\nu_{N\equiv O}$ at 1764 cm^{-1}.

As the transients disappeared, CH_4 NMR resonances increased. These data suggest the generation of isomeric square-pyramidal complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)(H)]^+X^-$ ($\mathbf{15}^+X^-$), close relatives of which have been described in the literature.[38-41] In order

Scheme VI. Protonation of Rhenium Hydride and Benzyl Complexes 16 and 18



16 cis-17+ BF4- trans-17+ BF4-

18 19+ BF4-

to support this structural assignment, syntheses of more stable analogues were attempted.

The reaction of hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**16**)[42] and $HBF_4{\cdot}O(C_2H_5)_2$ (CD_2Cl_2, −78 °C) was immediately analyzed by ^1H and $^{13}C\{^1H\}$ NMR at −85 °C (Scheme VI). A product with two hydride resonances (*cis*-$\mathbf{17}^+BF_4^-$) cleanly formed (^1H NMR δ −0.49 (br d, J_{HP} = 33.5 Hz), −1.97 (br s)).[43] The sample was gradually warmed. At −60 °C, a new complex with a *single* hydride resonance (*trans*-$\mathbf{17}^+BF_4^-$) appeared (^1H NMR δ −2.53 (d, J_{HP} = 50.23 Hz)).[43] At −35 °C, *cis*- and *trans*-$\mathbf{17}^+BF_4^-$ were present in a (88 ± 2):(12 ± 2) ratio, and the hydride resonances of *cis*-$\mathbf{17}^+BF_4^-$ (J_{HP} = 27.2) broadened. The resonances sharpened when the sample was cooled to −60 °C. At 22 °C, the hydride resonances of *cis*-$\mathbf{17}^+BF_4^-$ coalesced ($\Delta G^{\ddagger}_{295\,K}$ = 13.0 ± 0.1 kcal/mol),[44] and *cis*- and *trans*-$\mathbf{17}^+BF_4^-$ were present in a (40 ± 2):(60 ± 2) ratio. This ratio remained unchanged after 1 day.

Addition of ether precipitated a (40 ± 2):(60 ± 2) mixture of *cis*- and *trans*-$\mathbf{17}^+BF_4^-$ (86%) as a spectroscopically pure off-white powder. After 10–15 min in the presence or absence of oxygen, the powder turned purple. No decomposition was evident in subsequent ^1H or ^{13}C NMR spectra. Attempts to crystallize the sample gave powders. Addition of $N(C_2H_5)_3$ regenerated hydride complex **16**. On the basis of these data, *cis*- and *trans*-$\mathbf{17}^+BF_4^-$ were assigned as the isomeric dihydride complexes *cis*- and *trans*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)_2]^+BF_4^-$, respectively.[43]

Deuteride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(D)$ (**16**-d_1)[42b] and $HBF_4{\cdot}O(C_2H_5)_2$ were analogously reacted. Complex *cis*-$\mathbf{17}^+$-$d_1BF_4^-$ formed with an equal amount of deuterium

(38) Kubáček, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

(39) (a) Fischer, E. O.; Frank, A. *Chem. Ber.* **1978**, *111*, 3740. (b) Dong, D. F.; Hoyano, J. K.; Graham, W. A. G. *Can. J. Chem.* **1981**, *59*, 1455. (c) Hoyano, J. K.; Graham, W. A. G. *Organometallics* **1982**, *1*, 783. (d) Einstein, F. W. B.; Oliva, H. K.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53. (e) Pasman, P.; Snel, J. J. M. *J. Organomet. Chem.* **1986**, *301*, 329. (f) Herrmann, W.; Hecht, C.; Herdtweck, E.; Kreuper, H. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 132.

(40) (a) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852. (b) Faller, J. W.; Anderson, A. S.; Jakubowski, A. *J. Organomet. Chem.* **1971**, *27*, C47. (c) Todd, L. J.; Wilkinson, J. R.; Hickey, J. P.; Beach, D. L.; Barnett, K. W. *Ibid.* **1978**, *154*, 151.

(41) Sanderson, L. J.; Baird, M. C. *J. Organomet. Chem.* **1986**, *307*, C1.

(42) (a) Merrifield, J. H.; Gladysz, J. A. *Organometallics* **1983**, *2*, 782. (b) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6110.

(43) (a) Summary of NMR data for *cis*-$\mathbf{17}^+BF_4^-$ (CD_2Cl_2): ^1H NMR (δ, −35 °C) 5.85 (s, C_5H_5), −0.82 (d, J_{HP} = 27.24 Hz, ReH), −1.56 (d, J_{HP} = 7.09 Hz, ReH'); $^{13}C\{^1H\}$ NMR (ppm, −85 °C) 95.0 (s, C_5H_5); $^{31}P\{^1H\}$ NMR (ppm, −85 °C) 19.89 (s). (b) Summary of NMR data for *trans*-$\mathbf{17}^+BF_4^-$ (CD_2Cl_2): ^1H NMR (δ, −60 °C) 6.00 (s, C_5H_5), −2.43 (d, J_{HP} = 50.61 Hz, ReH$_2$); $^{13}C\{^1H\}$ NMR (ppm, −85 °C) 93.6 (s, C_5H_5); $^{31}P\{^1H\}$ NMR (ppm, −85 °C) 11.64 (s). (c) IR of mixture (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1769, 1718 cm^{-1} (s).

(44) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; p 96.

in each site. The reaction was repeated with 0.15 equiv of $HBF_4{\cdot}O(C_2H_5)_2$. Over the course of 10 min at −60 °C, ca. 10% of the unreacted **16**-d_1 converted to **16**-d_0. This suggests that the protonation of **16** by $HBF_4{\cdot}O(C_2H_5)_2$ is reversible.

The reaction of benzyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ (**18**)[19a] and $HBF_4{\cdot}O(C_2H_5)_2$ (CD_2Cl_2, −78 °C) was immediately analyzed by ^1H and $^{13}C\{^1H\}$ NMR at −85 °C (Scheme VI). A single species formed, which on the basis of characteristic hydride ligand ^1H NMR and alkyl ligand CH_α ^1H and ^{13}C NMR resonances[45] was assigned as the benzyl hydride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)(H)]^+BF_4^-$ (**19**$^+BF_4^-$). The sample was gradually warmed. At room temperature, slow decomposition began with formation of toluene. No isomerization was noted. At 35–40 °C, toluene formed in 76% yield (integration vs cyclopentadienyl resonances of the homogeneous sample) over the course of 1.5 h.

Finally, benzyl hydride complex **19**$^+BF_4^-$ was generated in situ as above and treated with PPN^+Cl^- (1.0 equiv) at −60 °C. An immediate reaction occurred to give chloride complex **9** (29% vs cyclopentadienyl resonances), toluene (31%), and a species with a broad cyclopentadienyl resonance at δ 4.76 (possibly benzyl complex **18** and HCl in dynamic equilibrium with **19**$^+Cl^-$). As the sample was warmed, the δ 4.76 species slowly converted to **9** and toluene. At 20 °C, **9** and toluene were present in 78% and 86% yields, respectively. Hence, exogenous agents can greatly affect the rate of alkane reductive elimination from alkyl hydride complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)(H)]^+BF_4^-$.

Discussion

1. Routes to Transition-Metal Lewis Acids. A number of methods for the generation of functional equivalents of cationic transition-metal Lewis acids L_nM^+ have been described in the literature. These include the chemical and electrochemical oxidation of transition-metal dimers L_nMML_n (e.g., $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$)[27b,c] and the abstraction of halide ion from halide complexes L_nMX (e.g., $(\eta^5\text{-}C_5H_5)Fe(P(OPh)_3)_2(I)$,[27a] $(\eta^5\text{-}C_5H_5)Fe(CO)(L)(I)$,[27e,f] $(\eta^5\text{-}C_5H_5)W(NO)_2(Cl)$).[6] Beck has shown that the trityl cation $Ph_3C^+X^-$ can abstract hydride from metal hydride complexes (e.g., $(\eta^5\text{-}C_5H_5)M(CO)_3(H)$, M = Mo, W)[2a] to give L_nM^+ intermediates. Graham reported that $Ph_3C^+X^-$ and the tropylium ion ($C_7H_7^+X^-$) abstract hydride from rhenium complex $(\eta^5\text{-}C_5H_5)Re(NO)(CO)(H)$ to give η^2-complexes of the resulting hydrocarbons (Ph_3CH, C_7H_8), presumably via the Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)]^+$.[4b,c]

We sought a precursor to rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I) that would be (1) thermally stable, (2) air stable, (3) readily available in optically pure form, (4) configurationally stable, and (5) amenable to NMR monitoring. We reported earlier that treatment of halide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ with $Ag^+PF_6^-$ in the presence of donor ligands L gave adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+PF_6^-$ in high yield.[21] However, ^1H NMR spectra acquired during these reactions showed only broad resonances.[46] Preliminary data indicated that hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**16**) and $Ph_3C^+BF_4^-$ or $Ph_3C^+PF_6^-$ reacted (CH_2Cl_2, −78 °C) to give functional equivalents of I.[46] However, **16** is not readily available in optically active form,[42] and we wanted to avoid the possible complication of a Lewis acid/Ph_3CH adduct as observed by Graham. Wojcicki had shown that reaction of $HPF_6{\cdot}O(C_2H_5)_2$ and $(\eta^5\text{-}C_5H_5)Cr(NO)_2(CH_3)$ generated a functional equivalent of the chromium Lewis acid $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]^+PF_6^-$.[5] This result, and our earlier study outlined in Scheme I, prompted the evaluation of methyl complex **2** as a precursor to I. Complex **2** satisfies all five criteria given above.

2. Bonding Considerations in Transition-Metal Lewis Acids. As noted in the Introduction, there are many isolable transition-metal Lewis acids. However, complexes of very weak donor ligands, including saturated hydrocarbons, with coordinatively unsaturated metal centers are increasingly being identified.[26] Hence, attempts to generate reactive transition-metal Lewis acids in solution may give instead some lower energy solvate. Furthermore, a variety of weak intramolecular Lewis base interactions are possible.

For example, Beck has shown that coordinatively unsaturated metal cations L_nM^+ can bind BF_4^- in solution.[2a,c–g] He finds that adducts such as $(\eta^5\text{-}C_5H_5)M(CO)_2(L)(FBF_3)$ (M = Mo, W; L = CO, PPh_3, $P(OPh)_3$) exhibit distinctive ^{19}F NMR chemical shifts (−350 to −400 ppm) for the bridging fluorine. Since coordination lowers the BF_4^- symmetry, additional IR ν_{B-F} are also observed. Anion PF_6^- is less coordinating than BF_4^-,[2a,7b] but L_nMFPF_5 complexes have been identified by analogous spectroscopic criteria.[2a,f,i,7b] Our data clearly exclude such bonding in $1^+BF_4^-$ and $1^+PF_6^-$.

Interestingly, Beck finds that the fluorine bridges in $(\eta^5\text{-}C_5H_5)M(CO)_2(L)(FBF_3)$ are maintained in CH_2Cl_2 solution. Under analogous conditions, the BF_4^- salt of rhenium Lewis acid I binds CH_2Cl_2. Hence, the CH_2Cl_2/BF_4^- binding constant ratio must be significantly greater for I than for molybdenum and tungsten Lewis acids $[(\eta^5\text{-}C_5H_5)M(CO)_2(L)]^+BF_4^-$. Also, no evidence for an ether complex is observed when $1^+BF_4^-$ is generated in the presence of 20–25 equiv of ether. Protons and common first-row Lewis acids (e.g., BR_3) bind ethers in chlorinated solvents. Although our experiment may not be under thermodynamic control, it suggests that I has an abnormally high binding constant for CH_2Cl_2 vs ether. We suggest, as will be detailed in future papers, that these trends arise from the marked *π-donor* capability of I. Hence, certain transition-metal "Lewis acids" are best described as amphoteres, and Lewis base acceptor orbitals should play an important role in determining binding affinities.

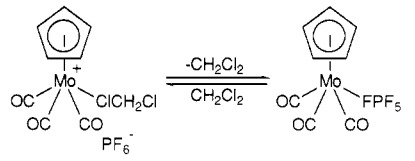
Our demonstration of CH_2Cl_2 coordination in $1^+BF_4^-$ provides support for several previous proposals[2a,f,4a,6,27] of dichloromethane complexes in the literature.[47] The best documented cases are due to Beck, who has reported IR ν_{C-Cl} and carbon/hydrogen analyses for $[(\eta^5\text{-}C_5H_5)M(CO)_3(ClCH_2Cl)]^+PF_6^-$ (**20**; **a**, M = Mo; **b**, M = W).[2a,f] These species are generated in CH_2Cl_2 under conditions analogous to those that gave the BF_4^- complexes $(\eta^5\text{-}C_5H_5)M(CO)_2(L)(FBF_3)$ noted above. Hence, Lewis acids $[(\eta^5\text{-}C_5H_5)M(CO)_3]^+$ exhibit a greater affinity for BF_4^- than PF_6^-. However, above 15 °C molybdenum complex **20a** dissociates CH_2Cl_2 to give (as assayed by ^{19}F NMR) detectable quantities of $(\eta^5\text{-}C_5H_5)Mo(CO)_3(FPF_5)$ (**21a**; eq

(45) Summary of spectroscopic data for **19**$^+BF_4^-$: ^1H NMR (δ, CD_2Cl_2, 22 °C) 7.81–7.23 (m, $4C_6H_5$), 5.68 (s, C_5H_5), 3.62 (dd, J_{HHR_e} = 3.80 Hz, $J_{HH'}$ = 11.51 Hz, J_{HP} = 16.25 Hz, CHH'), 3.12 (dd, $J_{H'H}$ = 11.13 Hz, $J_{H'P}$ = 5.02 Hz, CHH'), −3.72 (dd, J_{HR_eH} = 3.81 Hz, J_{HR_eP} = 65.72 Hz, ReH); $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2, −85 °C) 97.0 (s, C_5H_5), 15.96 (d, J_{CP} = 6.3 Hz, CH_2); $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2, −65 °C) 16.50 (s); IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1752 (s).

(46) Fernández, J. M., University of Utah, unpublished results.

(47) The syntheses and crystal structures of silver *chelate* complexes of dichloromethane and 1,2-dichloroethane have recently been reported: Colsman, M. R.; Noirot, M. D.; Miller, M. M.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1988**, *110*, 6886.

1). Complex **21a** reverts to **20a** upon cooling.[2f]

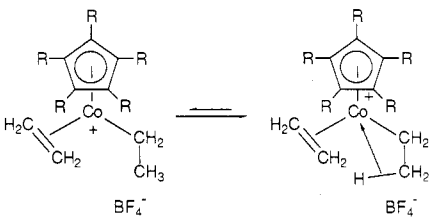


(1)

20a **21a**

Although Lewis acid I clearly binds CH_2Cl_2 solvent, can detectable quantities of I be generated in less polar media? Experiments to probe this possibility are in progress. However, lowering the solvent dielectric may simply increase the likelihood of L_nMFBF_3 and/or L_nMFPF_5 adduct formation. It should also be emphasized that our present data do not require the intermediacy of I in substitution reactions of $1^+BF_4^-$ and $1^+PF_6^-$ (Schemes II and III). Rate studies to address this point are being pursued.

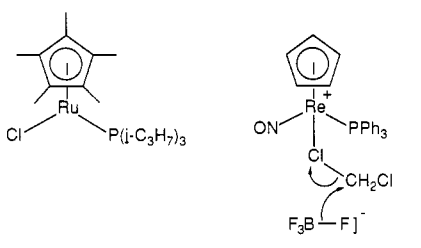
Interestingly, data on only a limited number of other d^6, 16-valence-electron $(\eta^5\text{-}C_5H_5)MLL'$ complexes are available in the literature. For example, good evidence exists for the intermediacy of ethyl cobalt complex $[(\eta^5\text{-}C_5R_5)Co(H_2C{=}CH_2)(C_2H_5)]^+BF_4^-$ (**22**) in CH_2Cl_2.[48] However, this Lewis acid acquires an 18-valence-electron configuration by forming an agostic bond with an ethyl ligand β-hydrogen, giving isolable complex **23** (eq 2). Molecular models indicate that Lewis acid I cannot form agostic bonds (PPh_3 or $\eta^5\text{-}C_5H_5$ C–H) without introducing considerable strain.



(2)

22 **23**

Tilley has recently reported the synthesis and crystal structure of the *neutral* d^6 ruthenium Lewis acid $(\eta^5\text{-}C_5Me_5)Ru(P(i\text{-}C_3H_7)_3)(Cl)$ (**24**).[49] This complex is substituted with two bulky ligands and a good π-donor (Cl). Accordingly, **24** has a very short Ru–Cl bond and a near-planar geometry at ruthenium.



24 **25**

3. Properties of Dichloromethane Complexes 1^+X^-. We were initially surprised at the observation of a separate ^{13}C NMR resonance (and a $^3J_{CP}$) for the CH_2Cl_2 ligand in $1^+BF_4^-$ (Figure 5). We had anticipated that the CH_2Cl_2 ligand would undergo rapid exchange with CH_2Cl_2 solvent, resulting in one resonance. However, the chemical shift data set a minimum $\Delta G^{\ddagger}_{270\,K}$ of 10.4 kcal/mol for any process capable of exchanging the CH_2Cl_2 ligand and solvent. As noted above, CH_2Cl_2/CD_2Cl_2 exchange does occur over the course of several hours between –60 and –40 °C, and attempts to measure an exact rate are in progress.

The ^{13}C NMR spectra of dihalomethanes show geminal couplings $^1J_{CH}$ that are larger than normal for sp^3 carbon–hydrogen bonds (CH_2F_2, 184.5 Hz;[50] CH_2Cl_2 (–85 °C, from the solvent resonance in the spectrum partially depicted in Figure 5c), 178.3 Hz). This follows from the greater p character in the carbon–halogen bonds and hence greater s character in carbon–hydrogen bonds. Since the CH_2Cl_2 $^1J_{CH}$ increases upon coordination to I (185.5 Hz), there must be even greater p character in the carbon–chlorine bonds of 1^+X^-.

In Scheme II, the absolute configurations of the starting methyl complex **2** and product (+)-(*SS*)-$\mathbf{12}^+X^-$ have been independently determined.[18,20] Hence, the conversion of **2** to Lewis base adducts of I occurs with overall retention at rhenium. We presume, by analogy to Brunner's studies with manganese complexes $(\eta^5\text{-}C_5H_5)Mn(NO)(PAr_3)(COR)$ (Figure 3),[15] that substitution of the CH_2Cl_2 ligand in 1^+X^- proceeds with retention at rhenium. Hence, dichloromethane complexes 1^+X^- must in turn form with retention of configuration at rhenium. If substitution of the CH_2Cl_2 ligand were for some reason to occur with inversion, then exchange of the CH_2Cl_2 ligand with CH_2Cl_2 solvent should similarly occur with inversion. This would effect racemization. However, CH_2Cl_2 ligand/solvent exchange is much *faster* than the decomposition of optically active (*S*)-$1^+BF_4^-$. Since this decomposition gives optically *active* products (Scheme IV), exchange cannot occur with inversion.

Complexes $1^+BF_4^-$ and $1^+PF_6^-$ decompose to different products (Scheme IV). This suggests the possibility (in at least one case) of counteranion participation. Anion BF_4^- is a better fluoride ion donor than PF_6^-,[51] and the chlorine in $1^+BF_4^-$ decomposition product (*SS,RR*)-$\mathbf{13}^+BF_4^-$ must come from CH_2Cl_2. Hence, the BF_4^- anion might mediate the displacement of chloride complex **9** from coordinated CH_2Cl_2, as shown in **25**. It has been shown that analogous alkyl iodide complexes are markedly activated toward nucleophilic attack relative to free alkyl iodides.[29] One expected fluorine-containing product, $BF_3{\cdot}O(C_2H_5)_2$, is clearly observed by ^{19}F NMR. However, the other (FCH_2Cl; 168.7 (*t*, J_{FH} = 49.4 Hz) ppm)[52] is not found among the numerous minor fluorinated products.

As noted above, optically active (*S*)-$1^+BF_4^-$ thermally decomposes to *optically active* bridging chloride complex (+)-(*SS*)-$\mathbf{13}^+BF_4^-$ (Scheme IV). Thus, its decomposition rate is faster than its inversion rate. Hence, it will not be possible to obtain an inversion barrier for the chiral Lewis acid I from $1^+BF_4^-$ (and likely the other compounds in this study). This quantity is likely best acquired by study of optically active triflate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$, which undergoes slow racemization in benzene.[21] Finally, a model that accounts for the greater stability of bridging chloride complex diastereomer (*SS,RR*)-$\mathbf{13}^+BF_4^-$ is given in the following paper.[53]

4. Mechanism of Formation of Dichloromethane Complexes 1^+X^-. Although the cleavage of metal–carbon σ bonds by electrophiles is common,[5,19c,21,41,54] reaction

(48) (a) Brookhart, M.; Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Chem. Commun.* **1983**, 691. (b) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *Ibid.* **1984**, 326. (c) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443.

(49) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278.

(50) Levy, G. C.; Lichter, R. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley: New York, 1980; pp 33–36.

(51) (a) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766. (b) Haartz, J. C.; McDaniel, D. H. *Ibid.* **1973**, *95*, 8562.

(52) Sartori, P.; Habel, W. *J. Fluorine Chem.* **1980**, *16*, 265.

(53) Winter, C. H.; Arif, A. M.; Gladysz, J. A. *Organometallics*, following paper in this issue.

(54) (a) Rogers, W. N.; Baird, M. C. *J. Organomet. Chem.* **1979**, *182*, C65. (b) Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37.

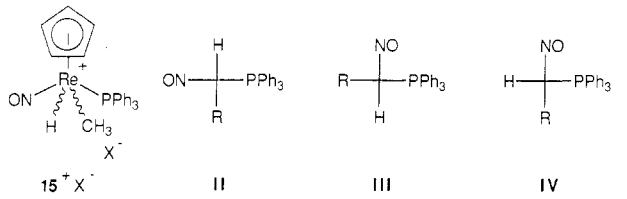


Figure 7. Possible isomeric arrays of basal ligands in square-pyramidal rhenium alkyl hydride complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)(H)]^+X^-$.

intermediates are less frequently observed. For protonolysis, initial attack at the metal has usually been proposed.[54] Hence, the intermediacy of methyl hydride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)(H)]^+X^-$ ($\mathbf{15}^+X^-$, Figure 7) is expected in Scheme II. Several rhenium complexes of the formula $(\eta^5\text{-}C_5H_5)Re(L)(L')(L'')(L''')$ have been structurally characterized.[39] All are square pyramids with the cyclopentadienyl ligands in the apical positions.

The four basal ligands of alkyl hydride complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)(H)]^+X^-$ can in principle exist in three isomeric arrays (II–IV, Figure 7). Literature NMR data suggest means by which such geometric isomers can be distinguished. For example, molybdenum complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PR_3)(H)$ exhibit $^2J_{PH}$ of 64–73 Hz when the phosphine and hydride ligands are cis and $^2J_{PH}$ of 21–29 Hz when the phosphine and hydride ligands are trans.[40a] Similarly, halide complexes $(\eta^5\text{-}C_5H_5)M(CO)_2(PR_3)(X)$ (M = Mo, W) exhibit larger CO ligand $^2J_{CP}$ when the phosphine and CO ligands are cis.[40c]

Accordingly, one hydride ligand in dihydride complex *cis*-$\mathbf{17}^+BF_4^-$ has a much larger $^2J_{HP}$ (27–33 Hz) than the other (7 Hz). This is assigned to the hydride ligand cis to the PPh_3 ligand. In *trans*-$\mathbf{17}^+BF_4^-$, where both hydride ligands must be cis to the PPh_3 ligand, the $^2J_{HP}$ is also large (50 Hz). Interestingly, some ruthenium complexes closely related to *cis*-$\mathbf{17}^+BF_4^-$ have been shown to be dihydrogen complexes $[(\eta^5\text{-}C_5H_5)Ru(L)(PR_3)(\eta^2\text{-}H_2)]^+X^-$.[55] However, these exhibit *equivalent* hydrogen ^1H NMR resonances and small J_{HP}.

Benzyl hydride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)(H)]^+BF_4^-$ ($\mathbf{19}^+BF_4^-$) shows a large hydride ligand $^2J_{HP}$ (66 Hz). Thus, the hydride ligand must be cis to the PPh_3 ligand as in isomers II or III. Further, C_α of the benzyl ligand exhibits a small $^2J_{CP}$ (6 Hz). This suggests that the benzyl ligand is trans to the PPh_3 ligand as in III. This in turn places the benzyl and hydride ligands cis, appropriate for the reductive elimination of toluene from $\mathbf{19}^+BF_4^-$ (Scheme VI).

One of the transient methyl ^{13}C NMR resonances assigned to methyl hydride complex $\mathbf{15}^+X^-$ exhibits a $^2J_{CP}$ (−32.4 ppm, 6.7 Hz) similar to that of $\mathbf{19}^+BF_4^-$, and is tentatively assigned to isomer III. Another methyl resonance exhibits a larger $^2J_{CP}$ (−10.9 ppm, 12.7 Hz). Since reactions proceeding via $\mathbf{15}^+X^-$ are capable of giving optically active products, any geometric isomers must interconvert without racemization. Isomer interconversion would most likely occur by either deprotonation/reprotonation or intramolecular rearrangement. A detailed topological analysis by Faller shows that rearrangement can take place without racemization.[40a] Hence, optically active reaction products can be expected provided that racemization does not occur concurrently with protonation of methyl complex **2** (e.g., formation of one enantiomer of any given geometric isomer of $\mathbf{15}^+X^-$).

(55) (a) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1986**, 506; **1987**, 1675. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865.

Several studies have shown that methane is more rapidly eliminated from methyl hydride complexes than hydrogen is from analogous dihydride complexes.[56] Hence, the stability order *cis*-$\mathbf{17}^+BF_4^- \gg \mathbf{15}^+BF_4^-$ has precedent. Our data further establish that methane is more readily eliminated from $\mathbf{15}^+BF_4^-$ than toluene is from $\mathbf{19}^+BF_4^-$. However, the observation that chloride ion promotes toluene formation from $\mathbf{19}^+BF_4^-$ hints that reductive elimination may be mechanistically complex. In particular, the possibility of CH_2Cl_2-, ether-, BF_4^--, or PF_6^--assisted reductive elimination in Scheme II must be considered. To aid in probing this point, we are continuing to attempt the isolation of an analytically pure alkyl hydride complex of formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)(H)]^+X^-$. Interestingly, alkene-promoted reductive eliminations have recently been documented.[57]

5. Summary. Our systematic attempts to prepare the chiral rhenium Lewis acid I have resulted in the generation and characterization of novel functional equivalents, dichloromethane complexes $\mathbf{1}^+BF_4^-$ and $\mathbf{1}^+PF_6^-$. These species are readily generated in optically active form and show, as reported elsewhere, many promising applications for use in asymmetric organic synthesis.[36,58] However, the actual intermediacy of Lewis acid I in CH_2Cl_2 substitution and exchange reactions of $\mathbf{1}^+BF_4^-$ and $\mathbf{1}^+PF_6^-$ (Schemes II and III), and in reductive elimination reactions leading to $\mathbf{1}^+BF_4^-$ and $\mathbf{1}^+PF_6^-$, remains to be rigorously established. Experiments designed to address these and other mechanistic questions are in progress.

Experimental Section

General Data. All reactions were conducted under a dry N_2 atmosphere. IR spectra were recorded on a Perkin-Elmer 1500 (FT) spectrometer. NMR spectra were recorded on Varian XL-300 (^1H, ^{13}C, ^{31}P, ^{19}F) and FT-80A (^{31}P) spectrometers as outlined in Table II (^{19}F NMR spectra were referenced to external C_6F_6 at −162.9 ppm vs CCl_3F). Probe temperatures in dynamic NMR and rate experiments were calibrated with methanol (low temperatures) and ethylene glycol (high temperatures). Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter. ORD and CD spectra were recorded on a JASCO J-20c ORD-CD spectropolarimeter. Mass spectra were obtained on a VG 7070E spectrometer. Microanalyses were conducted by Galbraith and Schwarzkopf Laboratories. Melting points were determined in evacuated capillaries and were not corrected.

Acids $HBF_4{\cdot}O(C_2H_5)_2$ (Aldrich) and $HPF_6{\cdot}O(C_2H_5)_2$ (Columbia) were ≥98% pure by ^{19}F NMR and were standardized by titration vs **2** (followed by ^1H and ^{31}P NMR). Reagents $HBF_4{\cdot}O(CH_3)_2$ (Columbia), $[Ph_3{=}N{=}PPh_3]^+Br^-$ (PPN^+Br^-; Aldrich), $Ph_3PCH_3^+Br^-$ (Aldrich), $Ph_3PCH_3^+I^-$ (Aldrich), carbon monoxide (Matheson), ethylene (Matheson), $C_6H_5CH_2CN$ (Aldrich), $O{=}PPh_3$ (Aldrich), $(C_2H_5)_4N^+CN^-$ (Fluka), $(CH_3)_4N^+BF_4^-$ (Fluka), and $(CH_3)_4N^+PF_6^-$ (Fluka) were used as received. Deuteriated acid CF_3COOD was prepared from $(CF_3CO)_2O$ (Aldrich, distilled from P_2O_5) and D_2O (Aldrich, 99.8% D).[59] Acid (+)-(*S*)-$CH_3CH_2CH(C_6H_5)COOH$ (Aldrich) was converted to (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$, $[\alpha]^{23}_{589}$ −22.8°, by a literature procedure (lit.[60] $[\alpha]^{24}_{589}$ −23.0°).

Solvents were purified as follows: ether and benzene, distilled from Na/benzophenone; hexane, pentane, and toluene, distilled from Na; CH_2Cl_2, distilled from P_2O_5; acetone, distilled from $CaSO_4$; CH_3CN, distilled from CaH_2; ethyl acetate, used as received; $CDCl_3$, vacuum transferred from P_2O_5; C_6D_6, CD_2Cl_2, and

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

(57) Kurosawa, H.; Emoto, M.; Ohnishi, H.; Miki, K.; Kasai, N.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 6333.

(58) Bodner, G. S.; Fernández, J. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 4082.

(59) Summerville, R. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 1110.

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

CD_3CN, vacuum transferred from CaH_2.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ ($1^+BF_4^-$). A (NMR experiment). A 5-mm NMR tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**2**, 0.098 g, 0.179 mmol)[17] and CD_2Cl_2 (ca. 0.60 mL). The tube was cooled to −78 °C, and $HBF_4{\cdot}O(C_2H_5)_2$ (18.9 μL, 0.179 mmol) was added by syringe. The tube was shaken and placed in a −85 °C broad-band NMR probe. ^1H, ^{31}P, ^{19}F, and ^{13}C NMR spectra were recorded: see text for data. Reactions with $HBF_4{\cdot}O(CH_3)_2$ were performed in an identical manner. **B** (preparative experiment). A Schlenk flask was charged with **2** (0.131 g, 0.234 mmol), CH_2Cl_2 (ca. 25 mL), and a stir bar. The resulting orange solution was cooled to −78 °C, and $HBF_4{\cdot}O(C_2H_5)_2$ (25.3 μL, 0.234 mmol) was added by syringe. This gave a dark orange solution of $1^+BF_4^-$, which was normally stirred for 15–30 s before Lewis base addition.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+PF_6^-$ ($1^+PF_6^-$). Experiments were conducted in a manner identical with those given for $1^+BF_4^-$. The following scales are representative. NMR experiment: **2** (0.098 g, 0.179 mmol), $HPF_6{\cdot}O(C_2H_5)_2$ (25.3 μL, 0.179 mmol), CD_2Cl_2 (ca. 0.60 mL). Preparative experiment: **2** (0.330 g, 0.591 mmol), $HPF_6{\cdot}O(C_2H_5)_2$ (86.7 μL, 0.591 mmol), CH_2Cl_2 (ca. 40 mL).

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+BF_4^-$ ($3^+BF_4^-$). Complex **2** (0.200 g, 0.358 mmol), CH_2Cl_2 (ca. 25 mL), and $HBF_4{\cdot}O(C_2H_5)_2$ (38.7 μL, 0.358 mmol) were combined as described in preparation B of $1^+BF_4^-$. Then CH_3CN (74.0 μL, 1.80 mmol) was added by syringe with stirring, and the solution was slowly warmed to room temperature. After 1 h, the solvent was removed in vacuo and the flask was taken into a glovebox. The yellow-orange residue was dissolved in CH_2Cl_2 (ca. 3 mL). The solution was filtered, and ether was added by vapor diffusion. Orange rosettes of $3^+BF_4^-$ formed, which were collected by filtration and dried in vacuo (0.172 g, 0.260 mmol, 73%); mp 204–207 °C dec (lit.[18] 208 °C dec). Complex $3^+PF_6^-$ was prepared from **2** and $HPF_6{\cdot}O(C_2H_5)_2$ in an analogous manner; mp 177–180 °C dec. The ^1H NMR spectra of $3^+BF_4^-$ and $3^+PF_6^-$ were identical.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ ($4^+BF_4^-$). Complex **2** (0.065 g, 0.117 mmol), CH_2Cl_2 (ca. 10 mL), and $HBF_4{\cdot}O(C_2H_5)_2$ (38.7 μL, 0.358 mmol) were combined at −78 °C in a Fischer-Porter bottle as described in the preparation of $1^+BF_4^-$. The solution was stirred under CO (225 psi) and allowed to warm to room temperature. IR monitoring showed complete conversion to product after 22 h. The solvent was removed in vacuo and the residue dissolved in CH_2Cl_2 (ca. 2 mL). The solution was filtered, and ether was added by vapor diffusion. Yellow plates of $4^+BF_4^-$ formed, which were collected by filtration and dried in vacuo (0.063 g, 0.096 mmol, 82%); mp 274–277 °C dec (lit.[17] 277–278 °C dec). Complex $4^+PF_6^-$ was prepared from **2** and $HPF_6{\cdot}O(C_2H_5)_2$ in an analogous manner; mp 224–228 °C dec. The ^1H NMR spectra of $4^+BF_4^-$ and $4^+PF_6^-$ were identical.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+BF_4^-$ ($5^+BF_4^-$). Complex **2** (0.053 g, 0.095 mmol), CH_2Cl_2 (ca. 10 mL), and $HBF_4{\cdot}O(C_2H_5)_2$ (10.3 μL, 0.095 mmol) were combined as described for the preparation of $4^+BF_4^-$. The solution was stirred under ethylene (ca. 180 psi) and allowed to warm to room temperature. IR monitoring showed complete conversion to product after 12 h. Solvent was removed in vacuo and the reaction flask taken into a glovebox. The residue was dissolved in CH_2Cl_2 (ca. 2 mL). The solution was filtered, and ether was added by vapor diffusion. Dark yellow plates of $5^+BF_4^-$ formed, which were collected by filtration and dried in vacuo (0.053 g, 0.072 mmol, 78%); mp 224–230 °C. A ^1H NMR spectrum was identical with that of an authentic sample of $5^+PF_6^-$.[18]

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_2C_6H_5)]^+PF_6^-$ ($6^+PF_6^-$). Complex **2** (0.250 g, 0.448 mmol), CH_2Cl_2 (ca. 25 mL), and $HPF_6{\cdot}O(C_2H_5)_2$ (65.7 μL, 0.448 mmol) were combined as described in preparation B of $1^+PF_6^-$. Then $C_6H_5CH_2CN$ (270 μL, 2.24 mmol) was added by syringe with stirring. The solution was slowly warmed to room temperature. After 1 h, solvent was removed in vacuo to give a dark yellow oil. Ether (ca. 25 mL) was added, and the mixture was stirred to precipitate a yellow powder. The powder was collected by filtration, taken into a glovebox, and dissolved in CH_2Cl_2 (ca. 5 mL). The solution was filtered, and ether was added by vapor diffusion. Yellow rods of $6^+PF_6^-{\cdot}(CH_2Cl_2)_{0.25}$ formed, which were collected by filtration and dried in vacuo (0.272 g, 0.344 mmol, 75%): mp 222–224 °C dec; mass spectrum ((+)-FAB, 7 kV, Ar, 3-nitrobenzyl alcohol; *m/z* (relative intensity), ^{187}Re) 661 (M^+, 32), 544 (M^+ − NCC$H_2C_6H_5$, 100), 262 (Ph_3P^+, 5).

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}P(C_6H_5)_3)]^+PF_6^-$ ($7^+PF_6^-$). Complex **2** (0.283 g, 0.507 mmol), CH_2Cl_2 (ca. 25 mL), and $HPF_6{\cdot}O(C_2H_5)_2$ (74.2 μL, 0.507 mmol) were combined as described in preparation B of $1^+PF_6^-$. Then $O{=}PPh_3$ (0.143 g, 0.504 mmol) was added with stirring. The solution was slowly warmed to room temperature. After 1 h, solvent was removed in vacuo and the flask taken into a glovebox. The residue was dissolved in CH_2Cl_2 (ca. 5 mL). The solution was filtered, and ether was added by vapor diffusion. Red rosettes of $7^+PF_6^-$ formed, which were collected by filtration and dried in vacuo (0.423 g, 0.434 mmol, 86%): mp 222–226 °C dec; mass spectrum ((+)-FAB, 7 kV, Ar, 3-nitrobenzyl alcohol; *m/z* (relative intensity), ^{187}Re) 822 (M^+, 19), 560 (M^+ − PPh_3, 7), 544 (M^+ − $OPPh_3$, 100), 530 (M^+ − PPh_3 − NO, 3), 467 (M^+ − $OPPh_3$ − Ph, 4), 262 (Ph_3P^+, 6).

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Br)$ (8). A Schlenk flask was charged with **2** (0.098 g, 0.176 mmol), CH_2Cl_2 (ca. 15 mL), and $Ph_3PCH_3^+Br^-$ (0.978 g, 2.63 mmol). The orange solution was cooled to −78 °C, and $HBF_4{\cdot}O(C_2H_5)_2$ (19.0 μL, 0.176 mmol) was added by syringe with stirring. After 10 min, the solution was warmed to 0 °C, and the solvent was removed in vacuo. The light red residue was dissolved in CH_2Cl_2 (ca. 5 mL) and rapidly eluted through a 2–3 cm plug of silica gel with CH_2Cl_2. Solvent was removed in vacuo at 0 °C to give **8** as a light red powder (0.076 g, 0.123 mmol, 70%), mp 234–236 °C dec (lit.[21] mp 234–236 °C dec). A ^1H NMR spectrum of **8** was identical with that of an authentic sample.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (10). Complex **2** (0.192 g, 0.344 mmol), CH_2Cl_2 (ca. 15 mL), $Ph_3PCH_3^+I^-$ (2.086 g, 5.163 mmol), and $HBF_4{\cdot}O(C_2H_5)_2$ (44.0 μL, 0.351 mmol) were combined as in the preparation of **8** above and worked up analogously. This gave **10** as a purple powder (0.184 g, 0.275 mmol, 80%), mp 207–210 °C dec (lit.[21] mp 209–212 °C dec). A ^1H NMR spectrum of **10** was identical to that of an authentic sample.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ (11). A (from $1^+BF_4^-$). Complex **2** (0.232 g, 0.416 mmol), CH_2Cl_2 (ca. 25 mL), and $HBF_4{\cdot}O(C_2H_5)_2$ (44.9 μL, 0.416 mmol) were combined as described in preparation B of $1^+BF_4^-$. Then $(C_2H_5)_4N^+CN^-$ (0.061 g, 0.392 mmol) was added with stirring. The solution was slowly warmed to room temperature. After 1 h, the solvent was removed in vacuo, and the yellow-orange residue was dissolved in CH_2Cl_2 (ca. 2 mL). This was eluted through a 125-cm silica gel column with 90:10 (v/v) hexanes/ethyl acetate. An orange band eluted first. Solvent was removed by rotary evaporation to give **2** (0.042 g, 80% pure by ^1H NMR; 0.060 mmol, 14%). A red band eluted next. Solvent was removed by rotary evaporation to give chloride complex **9** (0.005 g, 0.008 mmol, 2%). A yellow band then eluted with acetone. Solvent was removed by rotary evaporation to give a yellow solid that was extracted with benzene (2 × 2–3 mL). The extract was filtered through a 3-cm Celite plug. Pentane was added by vapor diffusion. Yellow rosettes formed, which were collected by filtration and dried in vacuo to give **11** (0.124 g, 0.218 mmol, 56% based upon ^-CN), decomp pt 194–196 °C. The yield of **2** decreased to 4% when the $1^+BF_4^-$ solution was stirred for 1.5 h at −78 °C prior to ^-CN addition. **B** (from triflate complex). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OSO_2CF_3)$[21] (0.204 g, 0.293 mmol), CH_2Cl_2 (ca. 25 mL), and a stir bar. Then $(C_2H_5)_4N^+CN^-$ (0.052 g, 0.323 mmol) was added with stirring. After ca. 10 h, the solution turned yellow; an IR spectrum showed the absence of starting material. The solvent was removed in vacuo. The residue was extracted with benzene (2 × 5 mL), and the extract was filtered through a 2-cm Celite plug. The resulting yellow solution was concentrated to ca. 2–3 mL. Pentane was added by vapor diffusion. Yellow-orange plates formed, which were collected by filtration and dried in vacuo to give **11** (0.133 g, 0.233 mmol, 79%): decomp pt 194–196 °C; mass spectrum (*m/e* (relative intensity), 17 eV, ^{187}Re) 570 (M^+, 22), 435 (M^+ − CN − NO − Ph, 3), 262 (Ph_3P^+, 100).

Preparation of (+)-(*R*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Br)$ ((+)-(*R*)-8). This compound was prepared from (+)-(*S*)-**2** (0.220 g, 0.394 mmol),[20] $HBF_4{\cdot}O(C_2H_5)_2$ (42.6 μL, 0.395 mmol), and $Ph_3PCH_3^+Br^-$ (2.241 g, 5.914 mmol) in a manner identical with that of the racemate. Thus obtained was (+)-(*R*)-**8** (0.163 g, 0.252

mmol, 65%), $[\alpha]^{23}_{589}$ 373° (99% ee; lit.[21] $[\alpha]^{23}_{589}$ 375°).

Preparation of (+)-(*R*)-(η^5-C_5H_5)Re(NO)(PPh_3)(I) ((+)-(*R*)-10). This compound was prepared from (+)-(*S*)-**2** (0.206 g, 0.364 mmol), $HBF_4{\cdot}O(C_2H_5)_2$ (39.9 μL, 0.364 mmol), and $Ph_3PCH_3{}^+I^-$ (2.237 g, 5.554 mmol) in a manner identical with that of the racemate. Thus obtained was (+)-(*R*)-**10** (0.160 g, 0.238 mmol, 65%), $[\alpha]^{23}_{589}$ 228° (98% ee, lit.[21] $[\alpha]^{23}_{589}$ 233°).

Preparation of (+)-(*SS*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]$^+X^-$ ((+)-(*SS*)-12$^+X^-$). A (NMR experiment). A 5-mm NMR tube was charged with (+)-(*S*)-**2** (0.016 g, 0.029 mmol), CD_2Cl_2 (ca. 0.6 mL), and $HBF_4{\cdot}O(C_2H_5)_2$ (3.1 μL, 0.029 mmol) as described for the preparation of $1^+BF_4^-$ above. Then (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ (12.8 μL, 0.145 mmol) was added by syringe. The tube was shaken and placed in a 0 °C bath. After 15 min, the tube was transferred to a NMR probe. A ^1H NMR spectrum showed the formation of (+)-(*SS*)-**12**$^+BF_4^-$, with at best possible traces of another diastereomer (≃99.4:0.6). **B** (preparative experiment). Complex (+)-(*S*)-**2** (0.175 g, 0.314 mmol), CH_2Cl_2 (ca. 25 mL), and $HBF_4{\cdot}O(C_2H_5)_2$ (33.9 μL, 0.314 mmol) were combined as described in preparation B of $1^+BF_4^-$. Then (−)-$CH_3CH_2CH(C_6H_5)CN$ (93.5 μL, 0.628 mmol) was added by syringe with stirring, and the solution was slowly warmed to 0 °C. After 0.5 h, solvent was removed in vacuo to give a dark yellow oil. Ether (ca. 30 mL) was added, and the mixture was stirred for 15 min. The ether was decanted (extracting excess nitrile), and the remaining dark yellow oily solid was dissolved in CH_2Cl_2 (ca. 2 mL). Ether (ca. 25 mL) was added with stirring, and a yellow powder precipitated. The powder was collected by filtration and dried in vacuo to give (+)-(*SS*)-**12**$^+BF_4^-$ (0.220 g, 0.284 mmol, 90%): $[\alpha]^{23}_{589}$ 215°; decomp pt 78–82 °C. A ^1H NMR spectrum indicated a ca. 99.2:0.8 diastereomer ratio. The yellow powder (0.215 g, 0.278 mmol) was dissolved in acetone (ca. 20 mL), and $(CH_3)_4N^+PF_6^-$ was added with stirring. After 16 h the solvents were removed in vacuo to give a yellow-white residue. This was extracted with CH_2Cl_2 (2 × 10 mL). The extract was filtered through a 2-cm Celite plug, and the yellow filtrate was concentrated to ca. 3 mL in vacuo. Hexanes (ca. 25 mL) was added, and the mixture was concentrated by rotary evaporation to precipitate a yellow powder. This was extracted with benzene (2 × 5 mL). The extract was filtered, and solvent was removed by rotary evaporation. The resulting dark yellow oil was recrystallized from CH_2Cl_2/hexanes to give yellow-orange needles of (+)-(*SS*)-**12**$^+PF_6^-$ (0.197 g, 0.236 mmol, 84%; diastereomer ratio ca. 99.3:0.7): $[\alpha]^{23}_{589}$ 203° (lit.[18,35] $[\alpha]^{25}_{589}$ 207°); mp 165–169 °C dec (lit.[18] mp 177–178 °C dec).

Preparation of (*SS,RR*)-[(η^5-C_5H_5)Re(NO)(PPh_3)]$_2Cl^+BF_4^-$ ((*SS,RR*)-13$^+BF_4^-$). A (from $1^+BF_4^-$). Complex **2** (0.172 g, 0.308 mmol), CH_2Cl_2 (ca. 40 mL), and $HBF_4{\cdot}O(C_2H_5)_2$ (33.3 μL, 0.310 mmol) were combined as described in preparation B of $1^+BF_4^-$. The orange solution was warmed to room temperature and stirred for ca. 8 h. An orange solid precipitated, and the solvent was concentrated in vacuo to ca. 10 mL. Ether (ca. 25 mL) was added via cannula to precipitate additional orange solid. The flask was transferred to a glovebox, and the solid was collected by filtration and dissolved in CH_2Cl_2 (ca. 10 mL). The orange solution was filtered, and ether was added by vapor diffusion. Orange needles of (*SS,RR*)-13$^+BF_4^-{\cdot}(CH_2Cl_2)_{1.0}$ formed (solvate assayed by ^1H NMR), which were collected by filtration and dried in vacuo for 7 days at 78 °C. During this time the sample lost crystallinity, giving (*SS,RR*)-13$^+BF_4^-{\cdot}(CH_2Cl_2)_{0.45}$ (0.121 g, 0.101 mmol, 65%). **B** (from chloride complex **9**). Complex **2** (0.193 g, 0.343 mmol), CH_2Cl_2 (ca. 40 mL), and $HBF_4{\cdot}O(C_2H_5)_2$ (374 μL, 0.346 mmol) were combined as described in preparation B of $1^+BF_4^-$. Then **9** (0.202 g, 0.348 mmol)[21] was added with stirring. The orange-red solution was warmed to room temperature, and an orange solid precipitated. The powder was collected by filtration, transferred to a glovebox, and worked up as described in A to give (*SS,RR*)-13$^+BF_4^-{\cdot}(CH_2Cl_2)_{0.45}$ (0.332 g, 0.276 mmol, 81%): mp 244–248 °C dec; mass spectrum ((+)-FAB, 7 kV, Ar, 3-nitrobenzyl alcohol; *m/z* (relative intensity), ^{187}Re, ^{35}Cl) 1123 (M^+, 14), 579 (M^+ − (C_5H_5)Re(NO)(PPh_3), 13), 544 (M^+ − (C_5H_5)Re(NO)(PPh_3)(Cl), 100), 262 (Ph_3P^+, 29).

Preparation of (+)-(*SS*)-[(η^5-C_5H_5)Re(NO)(PPh_3)]$_2Cl^+BF_4^-$ ((+)-(*SS*)-13$^+BF_4^-$). A. Complex (+)-(*S*)-**2** (0.121 g, 0.210 mmol),[20] CH_2Cl_2 (ca. 40 mL), and $HBF_4{\cdot}O(C_2H_5)_2$ (23.2 μL, 0.213 mmol) were combined as described in the preparation of $1^+BF_4^-$. The solution was warmed to room temperature and stirred for 8 h. The solvent was concentrated in vacuo to ca. 10 mL. Ether (ca. 25 mL) was added by cannula to precipitate a light orange powder, which was collected by filtration, washed with ether (2 × 15 mL), and dried in vacuo to give (+)-(*SS*)-**13**$^+BF_4^-$ (0.184 g, 0.153 mmol, 72%), $[\alpha]^{23}_{589}$ 546°. **B.** Complex (+)-(*S*)-**2** (0.252 g, 0.452 mmol), CH_2Cl_2 (ca. 40 mL), and $HBF_4{\cdot}O(C_2H_5)_2$ (49.3 μL, 0.456 mmol) were combined as described in the preparation of $1^+BF_4^-$. Then (+)-(*S*)-**9** (0.266 g, 0.454 mmol)[21] was added with stirring. The orange-red solution was warmed to room temperature and stirred for 2–3 h. The solvent was concentrated in vacuo to ca. 10 mL, and ether (ca. 25 mL) was added to precipitate a light orange powder. The powder was collected by filtration, washed with ether (2 × 15 mL), and dried in vacuo to give (+)-(*SS*)-**13**$^+BF_4^-$ (0.433 g, 0.362 mmol, 79%): decomp pt 145–150 °C, $[\alpha]^{23}_{589}$ 528°.

Reaction of (*SS,RR*)-13$^+BF_4^-$ with CH_3CN. A Schlenk flask was charged with (*SS,RR*)-13$^+BF_4^-$ (0.203 g, 0.168 mmol), CH_3CN (ca. 40 mL), and a stir bar. The orange solution was refluxed with stirring for 5 h. Solvent was removed in vacuo to give a heterogeneous yellow-red residue that was transferred to a glovebox. The residue was extracted with benzene (2 × 5 mL). The extract was filtered to give an orange-red solution of neutral products. Cationic complexes were left behind as a yellow residue. Pentane was added to the extract by vapor diffusion. This gave red rods of **9**, which were collected by filtration (0.048 g, 0.083 mmol, 98%). The ^1H NMR and mass spectra were identical with those of an authentic sample.[21] The yellow residue was washed with benzene (2 × 5 mL) and dissolved in CH_2Cl_2 (ca. 2 mL). The solution was filtered, and ether was added by vapor diffusion. This gave yellow plates of **3**$^+BF_4^-$,[18] which were collected by filtration (0.052 g, 0.083 mmol, 96%). A ^1H NMR spectrum of **3**$^+BF_4^-$ was identical with that of an authentic sample.

Reaction of (*SS,RR*)-13$^+BF_4^-$ with Acetone. A Schlenk flask was charged with (*SS,RR*)-13$^+BF_4^-$ (0.262 g, 0.213 mmol), acetone (ca. 40 mL), and a stir bar. The orange solution was refluxed with stirring for 4 h. Solvent was removed in vacuo to give an orange residue that was transferred to a glovebox. The residue was extracted with benzene (2 × 5 mL). The extract was filtered to give an orange-red solution of neutral products. Cationic complexes were left behind as an orange residue. Pentane was added to the extract by vapor diffusion. This gave red rods of **9** (0.061 g, 0.102 mmol, 96%),[21] which were characterized as described above. The orange residue was washed with benzene (2 × 5 mL) and dissolved in acetone (ca. 2 mL). Ether was added by vapor diffusion. This gave orange rods of [(η^5-C_5H_5)Re(NO)(PPh_3)(η^1-O=$C(CH_3)_2$)]$^+BF_4^-$ (**14**$^+BF_4^-$) that were collected by filtration (0.073 g, 0.106 mmol, 92%), mp 178–182 °C dec. A ^1H NMR spectrum was identical with that of an authentic sample of **14**$^+PF_6^-$.[36b]

Preparation of *cis*- and *trans*-[(η^5-C_5H_5)Re(NO)(PPh_3)(H)$_2$]$^+BF_4^-$ (*cis*- and *trans*-17$^+BF_4^+$). A (NMR experiment). A 5-mm NMR tube was charged with (η^5-C_5H_5)Re(NO)(PPh_3)(H) (**16**, 0.031 g, 0.056 mmol)[40] and CD_2Cl_2 (ca. 0.6 mL). The tube was cooled to −78 °C and $HBF_4{\cdot}O(C_2H_5)_2$ (5.9 μL, 0.060 mmol) was added by syringe. The tube was shaken and placed in a −85 °C NMR probe; ^1H and ^{13}C NMR spectra were recorded at −85 and −60 °C. Data:[41] see text. **B** (preparative experiment). A Schlenk flask was charged with **16** (0.303 g, 0.556 mmol), CH_2Cl_2 (ca. 25 mL), and a stir bar. The resulting yellow solution was cooled to −78 °C, and $HBF_4{\cdot}O(C_2H_5)_2$ (54.0 μL, 0.555 mmol) was added by syringe with stirring. The solution immediately became colorless and after ca. 10 min turned light purple. The solution was warmed to 0 °C, and ether (ca. 25 mL) was added to precipitate an off-white powder, which was collected by filtration in a glovebox. After ca. 10–15 min the powder turned light purple. The powder was dried in vacuo to give a (40 ± 2):(60 ± 2) mixture of *cis*- and *trans*-17$^+BF_4^-$ (0.307 g, 0.476 mmol, 86%).[43] Crystallization attempts yielded only powders.

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$)(H)]$^+$-BF_4^- (19$^+BF_4^-$). A (NMR experiment). A 5-mm NMR tube was charged with (η^5-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) (**18**, 0.022 g, 0.032 mmol)[19a] and CD_2Cl_2 (ca. 0.6 mL). The tube was cooled to −85 °C, and $HBF_4{\cdot}O(C_2H_5)_2$ (4.0 μL, 0.03 mmol) was added by syringe. The tube was shaken and placed in a −85 °C NMR probe; ^1H and ^{13}C NMR spectra were recorded.[45] **B** (preparative experiment).

A Schlenk flask was charged with **18** (0.197 g, 0.311 mmol), CH_2Cl_2 (ca. 10 mL), and a stir bar. The resulting orange solution was cooled to −78 °C, and $HBF_4{\cdot}O(C_2H_5)_2$ (41.0 μL, 0.312 mmol) was added by syringe with stirring. The solution turned light orange, and after 10 min ether (ca. 15 mL) was added. A dark yellow powder precipitated (0.154 g, 0.214 mmol, 69%), and the flask was transferred to a glovebox. The powder was collected by filtration and dried in vacuo. A portion of the solid was dissolved in CD_2Cl_2. A ^1H NMR spectrum at −60 °C showed $\mathbf{19}^+BF_4^-$ of ca. 85% purity.[45]

Rate Measurements. The following experiment is representative. A 5-mm NMR tube was charged with **2** (0.013 g, 0.023 mmol) and CD_2Cl_2 (0.60 mL) in a glovebox and capped with a septum. The tube was placed in a −78 °C bath, and after 10 min, $HBF_4{\cdot}O(C_2H_5)_2$ (2.7 μL, 0.023 mmol) was added by syringe. The tube was shaken and placed in a −85 °C NMR probe. A ^1H NMR spectrum was recorded and showed formation of $\mathbf{1}^+BF_4^-$. The tube was returned to the −78 °C bath and precooled CH_3CN (11.9 μL, 0.230 mmol) was added by syringe. The tube was shaken and transferred to a −38.5 °C NMR probe. The disappearance of $\mathbf{1}^+BF_4^-$ and appearance of $\mathbf{3}^+BF_4^-$ was monitored through 85% completion by integration of the cyclopentadienyl ^1H NMR resonances. Identical rate constants were obtained from ln $[\mathbf{1}^+BF_4^-]$ and ln $(1 - [\mathbf{3}^+BF_4^-])$ vs time plots (k_{obsd} = (11.6 ± 1.0) × 10^{-4} s^{-1}).[37]

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Synthesis, Structure, and Reactivity of Bridging Halide Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2X^+BF_4^-$. Preferential Binding of One Enantiomer of Halide Complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ by the Chiral Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$

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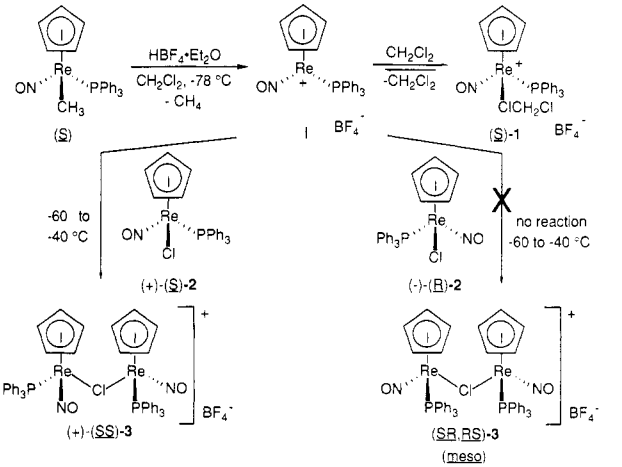
Reactions of halide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ (X = I, **7**; X = Br, **8**) and $AgBF_4$ in refluxing benzene gives bridging halide complexes (*RR,SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2X^+BF_4^-$ exclusively as *dl* diastereomers (X = I, (*RR,SS*)-**4**, 59%; X = Br, (*RR,SS*)-**5**, 54%). Reaction of optically active (+)-(*R*)-**7** and dichloromethane complex (*S*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ ((*S*)-**1**) gives a complex mixture of products, including species derived from $-CH_2Cl$ transfer from (*S*)-**1** to (+)-(*R*)-**7**. In no case is evidence for a meso diastereomer of a bridging halide complex observed. The structure of solvate (*RR,SS*)-**4**·$(CHCl_2CHCl_2)_{0.7}$ is verified by X-ray crystallography (monoclinic, $P2(1)/c$ (No. 14), a = 14.975 (4) Å, b = 18.219 (4) Å, c = 20.855 (4) Å, β = 108.20 (2)°, Z = 4). A "W" conformation is found for the P–Re–I–Re–P bonds, and a stereoelectronic rationale is given. Models show that if meso bridging halide complex diastereomers were to adopt analogous "W" conformations, severe steric interactions would occur between two syn cyclopentadienyl ligands. Complexes (*RR,SS*)-**4** and (*RR,SS*)-**5** react with acetonitrile (95 °C, 1.25 and 0.25 h, respectively) to give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+BF_4^-$ and halide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ (93–99% of theory).

Introduction

The chiral, transition-metal Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**) is easily generated in optically active form as a dichloromethane adduct (**1**), as described in the previous paper and summarized in Scheme I.[1] Lewis acid **I** binds and activates several types of prochiral organic Lewis bases.[2] These coordinated bases can in many cases be stereospecifically elaborated into chiral organic molecules. However, the binding of *chiral* Lewis bases to **I** has not yet been systematically examined. With chiral, *racemic* bases, there is the attractive possibility that one enantiomer might be preferentially complexed, affording an optical resolution.

In the previous paper, we reported that optically active dichloromethane complex (*S*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ ((*S*)-**1**) and optically active chloride

Scheme I. Binding of Optically Active Chloride Complex 2 to the Chiral Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I)



complex (+)-(*S*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ ((+)-(*S*)-**2**) react at −60 to −40 °C (Scheme I) to give the optically active bridging chloride complex (+)-(*SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+BF_4^-$ ((+)-(*SS*)-**3**).[1,3] Since both reactants

(1) Fernández, J. M.; Gladysz, J. A. *Organometallics*, preceding paper in this issue.

(2) (a) Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8268. (b) Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1988**, 37. (c) Bodner, G. S.; Fernández, J. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 4082.

0276-7333/89/2308-0219$01.50/0