(C_8H_{17}) (0.61 g) with bp 100 °C (0.07 mmHg), which had spectroscopic data identical to that observed for the product obtained with Cp_2ZrCl_2/*n*BuLi.

Reaction of $H(PhMeSi)_2H$ with Cp_2ZrCl_2/*n*BuLi. In the same manner as performed for the coupling reaction of $PhMeSiH_2$, Cp_2ZrCl_2 (0.042 g, 0.14 mmol) and *n*BuLi (0.22 mL, 1.3 M, 0.28 mmol in 1 mL of toluene (degassed)) were reacted with $H(PhMeSi)_2H$ (0.63 g, 2.6 mmol, 95% by GC) at 90 °C. A dark brown solution formed, and bubbling was observed for a few minutes. Aliquots were removed to determine the distribution of products [time (h), wt % $PhMeSiH_2$/PhMeBuSiH/disilane/trisilane/tetrasilane/pentasilane/hexasilane]: 0.0 (–/0.6/94/0.7/–/–/–), 0.50 (13/4.1/59/8.6/11/–/–), 1.0 (18/4.3/46/12/15/0.9/–), 24 (17/4.4/14/25/20/3.8/0.5).

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Synthesis, Structure, and Reactivity of Chiral Rhenium Carboxylic and Carbonic Acid Ester Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(X)X')]^+X''^-$

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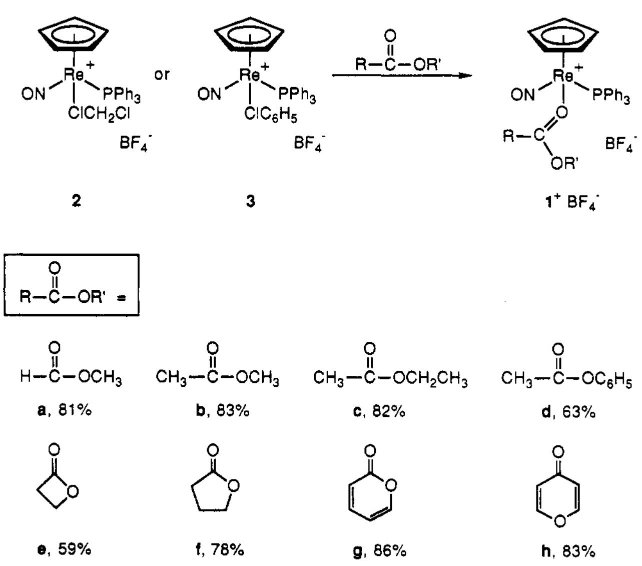
Reactions of chlorocarbon complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClX)]^+BF_4^-$ (X = CH_2Cl, C_6H_5) with (**a**) methyl formate, (**b**) methyl acetate, (**c**) ethyl acetate, (**d**) phenyl acetate, (**e**) propiolactone, (**f**) γ-butyrolactone, (**g**) 2*H*-pyran-2-one, (**h**) 4*H*-pyran-4-one, (**i**) dimethyl carbonate, (**j**) ethylene carbonate, and (**k**) imidazolidone give the corresponding σ complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(X)X')]^+BF_4^-$ (**1a–k**$^+BF_4^-$; 87–42% after workup). Reactions of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$, $Ph_3C^+PF_6^-$, and esters **b**,**f** give **1b**,**f**$^+PF_6^-$ (83–88%). Crystal structures of **1b**,**f**$^+PF_6^-$ show similar ON—Re—O=C torsion angles (27.6 (9)°, 12.1 (6)°) and C=O bond lengths (1.23 (1), 1.236 (7) Å), but the ester oxygen is *E* to the rhenium in the former and *Z* in the latter. Spectroscopic, structural, and dynamic properties of **1a–k**$^+X^-$ are analyzed in detail. The ester ligands in **1c**,**f**,**i**$^+BF_4^-$ are readily displaced by acetone and propionaldehyde at room temperature (Lewis basicity order: propionaldehyde > acetone > **c**,**f**,**i**). Analogous substitutions occur with alcohols.

The synthesis, structure and reactivity of Lewis acid/base adducts of transition-metal fragments and organic carbonyl compounds have been receiving increasing attention.[1] In particular, *chiral* transition-metal Lewis acid fragments offer numerous potential applications in chiral recognition and asymmetric organic synthesis. Remarkably, there have been few if any systematic studies of complexes of *nonchelated* carboxylic and carbonic acid ester functionalities.[1-4] This is surprising in view of the variety of metalloenzyme-catalyzed biological transformations of such compounds[5] and the many commercial transesterification processes that use metal catalysts.[6]

Scheme I. Syntheses of Ester Complexes 1a–h$^+BF_4^-$



We have conducted an extensive study of complexes of the chiral rhenium moiety $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I) and organic aldehydes and ketones O=CRR′.[7-10] These

(1) (a) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256. (b) Huang, Y.-H.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298.

(2) Structurally characterized transition-metal ester complexes: (a) Danielsen, J.; Rasmussen, S. E. *Acta Chem. Scand.* **1963**, *17*, 1971. (b) Brun, L.; *Acta Crystallogr.* **1966**, *20*, 739. (c) Bassi, I. W.; Calcaterra, M.; Intrito, R. *J. Organomet. Chem.* **1977**, *127*, 305. (e) Poll, T.; Metter, J. O.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 112. (f) Sobota, P.; Mustafa, M. O.; Lis, T. *J. Organomet. Chem.* **1989**, *377*, 69.

(3) Other transition-metal ester complexes: (a) Foxman, B. M.; Klemarczyk, P. T.; Liptrot, R. E.; Rosenblum, M. *J. Organomet. Chem.* **1980**, *187*, 253. (b) Schmidt, E. K. G.; Thiel, C. H. *J. Organomet. Chem.* **1981**, *209*, 373. (c) Chang, T. C. T.; Rosenblum, M. *J. Org. Chem.* **1981**, *46*, 4626. (d) Faller, J. W.; Ma, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1579.

(4) Some leading references to structurally characterized main-group and lanthanide Lewis acid/ester adducts: (a) Bart, J. C. J.; Bassi, I. W.; Calcaterra, M.; Albizzati, E.; Giannini, U.; Parodi, S. *Z. Anorg. Allg. Chem.* **1981**, *482*, 121; *Ibid.* **1983**, *496*, 205. (b) Lewis, F. D.; Oxman, J. D.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 466. (c) Rodriguez, I.; Alvarez, C.; Gomez-Lara, J.; Toscano, R. A.; Platzer, N.; Mulheim, C.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1987**, *1502*. (d) Shreve, A. P.; Mülhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409. (e) Power, M. B.; Bott, S. G.; Clark, D. L.; Atwood, J. L.; Barron, A. R. *Organometallics* **1990**, *9*, 3086.

(5) Chin, J. *Acc. Chem. Res.* **1991**, *24*, 145.

(6) (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; pp 209–214. (b) Marsi, M. *Inorg. Chem.* **1988**, *27*, 3062. (c) Otera, J.; Dan-oh, N.; Nozaki, H. *J. Org. Chem.* **1991**, *56*, 5307. (d) Ludewig, H. *Polyester Fibers*; Wiley: New York, 1971; pp 96–106.

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compounds are readily available in enantiomerically pure form, and the coordinated carbonyl groups are activated toward nucleophilic (Nu) attack. The resulting addition products, alkoxide complexes (η^5-C_5H_5)Re(NO)(PPh_3)-(OC(Nu)RR′), form in high diastereomeric excesses and are easily elaborated to optically active alcohols and derivatives. Hence, we sought to synthesize and study the properties of analogous ester complexes. In this paper, we report (1) high-yield syntheses of chiral rhenium σ carboxylic acid ester complexes [(η^5-C_5H_5)Re(NO)-(PPh_3)(η^1-O=C(R)OR′)]$^+X^-$ and related carbonic acid derivatives (1^+X^-), (2) crystal structures of methyl acetate and γ-butyrolactone complexes, (3) a detailed analysis of the spectroscopic, structural, and dynamic properties of these compounds, and (4) preliminary reactivity studies.

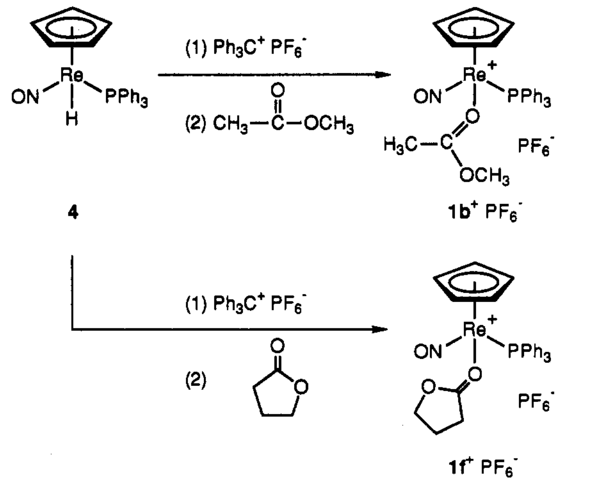
Results

1. Synthesis and Characterization of Carboxylic Acid Ester and Lactone Complexes. The chlorocarbon complexes [(η^5-C_5H_5)Re(NO)(PPh_3)($ClCH_2Cl$)]$^+BF_4^-$ (**2**) and [(η^5-C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]$^+BF_4^-$ (**3**) were generated at −80 °C in dichloromethane and −45 °C in chlorobenzene, respectively, as previously described.[11,12] These substitution-labile compounds have been shown to serve as functional equivalents of the chiral rhenium Lewis acid [(η^5-C_5H_5)Re(NO)(PPh_3)]$^+$ (I). Next, 2–10 equiv of (**a**) methyl formate, (**b**) methyl acetate, (**c**) ethyl acetate, and (**d**) phenyl acetate were added, as shown in Scheme I. Workup gave the formate and acetate ester complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(η^1-O=C(R)OR′)]$^+BF_4^-$ (**1a–d**$^+BF_4^-$) as tan to orange powders in 63–83% yields.

Reactions of the dideuteriodichloromethane complex **2**-d_2 (0.08 M in CD_2Cl_2) with 3 equiv of (**a**) methyl formate and (**c**) ethyl acetate were monitored by ^{31}P NMR spectroscopy. No reaction was observed at −80 °C. When the NMR probe was warmed to −40 °C, ester complexes **1a,c**$^+BF_4^-$ slowly appeared. Reactions were complete within 45 min at −20 °C. Complexes **1a–d**$^+BF_4^-$ all gave detectable decomposition on the time scale of minutes in CH_2Cl_2 at room temperature. For this and other reasons,[12,13] the chlorobenzene complex **3** was generally superior to **2** as a preparative precursor to $1^+BF_4^-$. Also, yields of the methyl acetate complex **1b**$^+BF_4^-$ were slightly higher when **3** was generated in the presence of methyl acetate.

Complexes **1a–d**$^+BF_4^-$ were characterized by microanalysis (Experimental Section) and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy (Table I). The σ binding mode was evidenced by the IR ν_{CO} values (1611–1625 cm^{-1}), which were lower than those of the corresponding free esters, and IR ν_{NO} criteria described earlier.[8b,9a] Also, ester ^{13}C NMR C=O resonances were observed at 179–187 ppm. These

Scheme II. Syntheses of Hexafluorophosphate Salts of Ester Complexes



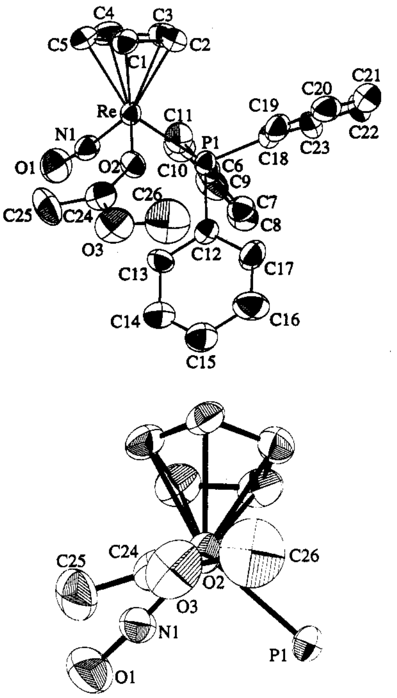


Figure 1. Structure of the cation of methyl acetate complex $1b^+PF_6^-$: (top) numbering diagram; (bottom) Newman-type projection down the O2–Re bond.

and most other spectroscopic properties (e.g., cyclopentadienyl ^1H and ^{13}C NMR chemical shifts) were quite similar to those reported previously for the σ-ketone complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(η^1-O=C(R)R′)]$^+BF_4^-$.[8] However, the ^{31}P NMR PPh_3 resonances were typically 2–3 ppm downfield.

Next, chlorocarbon complexes **2** and **3** were similarly treated with (**e**) propiolactone and (**f**) γ-butyrolactone. Workup gave the lactone complexes **1e,f**$^+BF_4^-$ as orange powders in 59–78% yields (Scheme I). These compounds were characterized analogously to **1a–d**$^+BF_4^-$, and spectroscopic properties are summarized in Table I. Complex **1e**$^+BF_4^-$ was much less stable in CH_2Cl_2 at room temperature than **1f**$^+BF_4^-$.

2. Crystal Structures of Ester and Lactone Complexes. We were unable to grow crystals of ester complexes **1a–f**$^+BF_4^-$ that were suitable for X-ray analysis. Attempts to metathesize these compounds to the corresponding hexafluorophosphate salts $1^+PF_6^-$ were compli-

(7) (a) Garner, C. M.; Quirós Méndez, N.; Kowalczyk, J. J.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5146. (b) Agbossou, F.; Ramsden, J. A.; Huang, Y.-H.; Arif, A. M.; Gladysz, J. A. *Organometallics*, accompanying paper in this issue.
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(9) (a) Quirós Méndez, N.; Arif, A. M.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1473. (b) Quirós Méndez, N.; Mayne, C. L.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1475.
(10) Dalton, D. M.; Garner, C. M.; Fernández, J. M.; Gladysz, J. A. *J. Org. Chem.* **1991**, *56*, 6823.
(11) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207.
(12) Kowalczyk, J. J.; Agbossou, S. K.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *397*, 333.
(13) Igau, A.; Gladysz, J. A. *Polyhedron* **1991**, *10*, 1903.

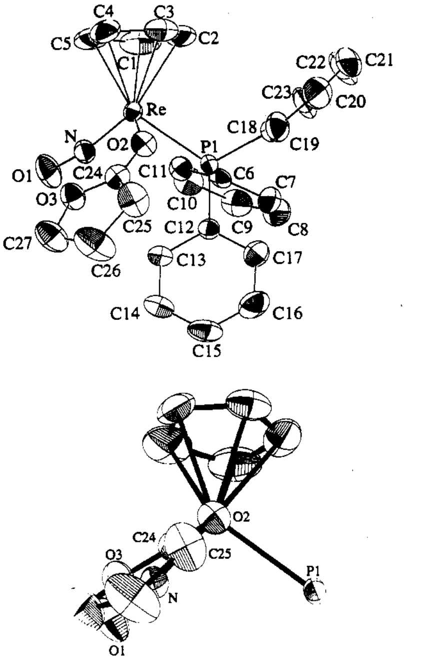


Figure 2. Structure of the cation of γ-butyrolactone complex $1f^+PF_6^-$: (top) numbering diagram; (bottom) Newman-type projection down the O2–Re bond.

cated by displacement of the ester ligands by solvent (see below). Thus, an alternative synthesis of hexafluorophosphate salts developed earlier for the corresponding alcohol complexes[14] was employed. First, the hydride complex (η^5-C_5H_5)Re(NO)(PPh_3)(H) (4)[15] was treated with $Ph_3C^+PF_6^-$ at –80 °C (Scheme II). Then (**b**) methyl acetate or (**f**) γ-butyrolactone (3 equiv) was added. Workup gave the ester complexes $\mathbf{1b,f}^+PF_6^-$ in 83–88% yields.

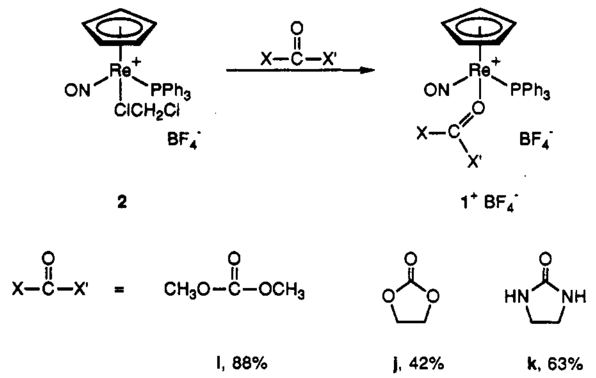
Burgundy crystals of $\mathbf{1b,f}^+PF_6^-$ were obtained from CH_2Cl_2/ether. X-ray data were collected as summarized in Table II. Refinement, described in the Experimental Section, yielded the structures shown in Figures 1 and 2. Both compounds contain similar arrays of non-hydrogen atoms, differing only by one ligand-based carbon. Thus, nearly identical atomic numbering schemes are employed. Atomic coordinates and key bond lengths, bond angles, and torsion angles are given in Tables III and IV. Additional data are provided in the supplementary material.

As is obvious from Figures 1 and 2, $\mathbf{1b,f}^+PF_6^-$ exhibit similar N—Re—O═C and P—Re—O═C torsion angles (27.6 (9)° and 12.1 (6)°; 119.0 (8)° and 107.6 (5)°), as well as PPh_3 ligand orientations. However, the ester oxygen is *E* (trans) to the rhenium in $\mathbf{1b}^+PF_6^-$ but *Z* (cis) to the rhenium in $\mathbf{1f}^+PF_6^-$. Additional geometric features were calculated. First, consider the planes defined by O2–C24–O3 and O2–C24–C25. The angles of the Re–N bonds with these planes were 30.9° and 29.2° ($\mathbf{1b}^+PF_6^-$) and 15.5° and 17.1° ($\mathbf{1f}^+PF_6^-$)—in good agreement with the N—Re—O═C torsion angles. The angles of the Re–PPh_3 bonds with these planes were 123.1° and 121.5° ($\mathbf{1b}^+PF_6^-$) and 113.9° and 115.7° ($\mathbf{1f}^+PF_6^-$).

The π nodal C═O planes in $\mathbf{1b,f}^+PF_6^-$ can be approximated by the O2/C24/C25/O3 least-squares planes. The Re–O bonds of $\mathbf{1b,f}^+PF_6^-$ made very small angles with this plane (3.1°, 4.6°), as would be expected of idealized σ complexes. The C26–O3 bond of the methoxy group in

(14) Agbossou, S. K.; Smith, W. W.; Gladysz, J. A. *Chem. Ber.* **1990**, *123*, 1293.
(15) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6110.

Scheme III. Syntheses of Complexes of Carbonic Acid Derivatives $\mathbf{1i\text{-}k}^+BF_4^-$



$\mathbf{1b}^+PF_6^-$ also made a small angle with this plane (4.6°). As shown in eq i, acyclic esters can adopt two limiting O–CO

(i)

II — *s-trans* or *Z*; III — *s-cis* or *E*

bond conformations, s–trans or *Z* (II), and s–cis or *E* (III). The former, which is the more stable in solution,[16] is found for the methyl acetate ligand in $\mathbf{1b}^+PF_6^-$. Accordingly, the C26–O3–C24–O2 and C26–O3–C24–C25 torsion angles (Table IV) are close to the idealized values of 0° and 180°.

3. Synthesis and Characterization of Pyranone- and Carbonate-Derived Complexes. The dichloromethane complex **2** was treated with (**g**) 2*H*-pyran-2-one and the vinylogous ester (**h**) 4*H*-pyran-4-one (Scheme I). Both of these compounds have a zwitterionic, aromatic resonance form that contributes significantly to the ground state. Workup gave the corresponding σ complexes $\mathbf{1g,h}^+BF_4^-$ as dark red or orange powders in 83–86% yields. These compounds were stable on the time scale of hours in CH_2Cl_2 at room temperature and were characterized analogously to $\mathbf{1a\text{–}f}^+BF_4^-$. Spectroscopic data are summarized in Table I. Alternative olefinic coordination modes would give HC═C ^{1}H and ^{13}C NMR chemical shifts considerably upfield from those of the free ligands.[17]

Next, the binding properties of carbonic acid derivatives were examined. Thus, **2** was similarly treated with (**i**) dimethyl carbonate, (**j**) ethylene carbonate, and the dialkylurea (**k**) imidazolidone (Scheme III). Workup gave the corresponding σ complexes $\mathbf{1i\text{–}k}^+BF_4^-$ as salmon or orange powders in 42–88% yields. Complexes $\mathbf{1i,j}^+BF_4^-$ showed detectable decomposition on the time scale of minutes in CH_2Cl_2 at room temperature. However, $\mathbf{1k}^+BF_4^-$ was much more stable. These compounds were characterized as described for the other new complexes.

Reactions of dideuteriodichloromethane complex **2**-d_2 and ligands **g,h,j,k** were monitored by ^{31}P NMR spectroscopy as described for $\mathbf{1a,c}^+BF_4^-$ above. In all cases, some product $\mathbf{1g,h,j,k}^+BF_4^-$ slowly formed at –80 °C. Reactions were complete within 10 min at –20 °C. Thus, these ligands are more nucleophilic than the simple esters **a–d**.

A byproduct was observed in the ^{31}P NMR experiments with imidazolidone. At –20 °C, $\mathbf{1k}^+BF_4^-$ and a second

(16) (a) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935. (b) Mark, H.; Baker, T.; Noe, E. A. *Ibid.* **1989**, *111*, 6551.
(17) Bodner, G. S.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1191.

Table I. Spectroscopic Characterization of New Complexes $[(\eta^5-C_5H_5)Re(NO)(PPh_3)(\eta^1-O{=}C(X)X')]^+BF_4^-$ ($1^+BF_4^-$)

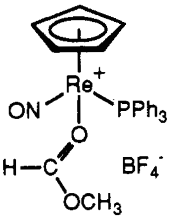
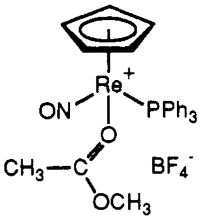
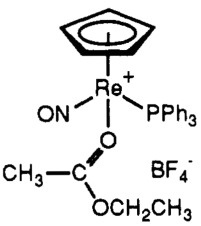
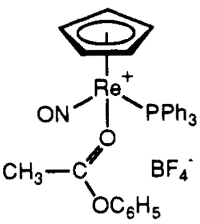
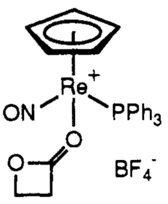
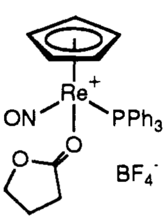
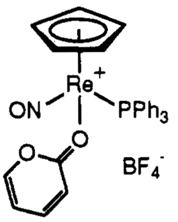
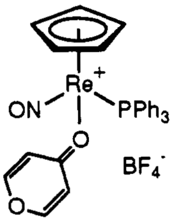
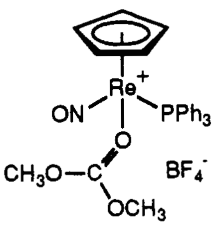
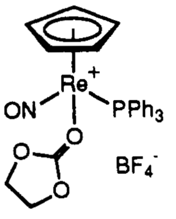
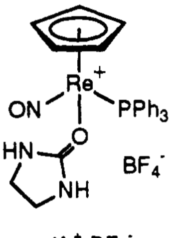
complex	IR (cm^{-1})[a]	^1H NMR (δ)[b,c]	$^{13}C\{^1H\}$ NMR (ppm)[c,d]	$^{31}P\{^1H\}$ NMR (ppm)[c,e]
 $1a^+ BF_4^-$	ν_{NO} 1698 vs, ν_{CO} 1618 s	8.29 (s, HC=O), 7.61–7.28 (m, 3 C_6H_5), 5.61 (s, C_5H_5), 3.31 (s, CH_3)	179.3 (s, C=O); PPh_3 at 133.0 (d, J = 11.0, o), 131.0 (s, p), 130.2 (i),[f] 128.7 (d, J = 10.3, m); 91.3 (s, C_5H_5), 55.3 (s, CH_3)	20.4 (s)
 $1b^+ BF_4^-$	ν_{NO} 1696 vs, ν_{CO} 1611 vs	7.65–7.37 (m, 3 C_6H_5), 5.60 (s, C_5H_5), 3.34 (s, OCH_3), 2.35 (s, CH_3)	186.9 (s, C=O); PPh_3 at 133.8 (d, J = 11.0, o), 132.1 (d, J = 55.0, i), 131.9 (d, J = 2.3, p), 129.1 (d, J = 10.8, m); 92.3 (s, C_5H_5), 56.4 (s, OCH_3), 22.5 (s, CH_3)	20.2 (s)
 $1c^+ BF_4^-$	ν_{NO} 1694 vs, ν_{CO} 1619 s	7.71–7.19 (m, 3 C_6H_5), 5.58 (s, C_5H_5), 3.89 (m, C*H*H′), 2.93 (m, CH*H′*), 2.42 (s, $CH_3C{=}O$), 1.03 (t, J = 7.0, CH_3)	185.8 (s, C=O); PPh_3 at 133.5 (d, J = 10.8, o), 131.7 (s, p), 130.9 (i),[f] 129.4 (d, J = 10.4, m); 92.1 (s, C_5H_5), 66.0 (s, CH_2), 23.2 (s, $CH_3C{=}O$), 13.4 (s, CH_3)	20.4 (s)
 $1d^+ BF_4^-$	ν_{NO} 1703 vs, ν_{CO} 1625 s	7.60–7.35 (m, 3 C_6H_5); CPh at 6.91 (br, s, 4 H), 6.40 (d, J = 7.5, 1 H); 5.43 (s, C_5H_5), 2.77 (s, CH_3)	185.8 (s, C=O); PPh_3 at 132.7 (d, J = 9.0, o), 132.1 (d, J = 55.4, i), 131.1 (s, p), 128.9 (d, J = 10.4, m); CPh at 149.1 (s, i), 129.8 (s), 127.0 (s), 120.3 (s); 91.8 (s, C_5H_5), 21.7 (s, CH_3)	17.9 (s)
 $1e^+ BF_4^-$	ν_{NO} 1684 vs, ν_{CO} 1719 s	7.64–7.30 (m, 3 C_6H_5), 5.56 (s, C_5H_5), 4.60 (m, OCH), 4.47 (m, OCH′), 3.64 (m, O=CCH), 3.06 (m, O=CCH′)	185.0 (s, C=O); PPh_3 at 133.1 (d, J = 11.1, o), 131.1 (s, p), 130.6 (d, J = 55.6, i), 128.6 (d, J = 10.5, m); 91.2 (s, C_5H_5), 65.0 (s, OCH_2), 35.5 (s, $O{=}CCH_2$)	19.9 (s)
 $1f^+ BF_4^-$	ν_{NO} 1703 vs, ν_{CO} 1635 s	7.60–7.27 (m, 3 C_6H_5), 5.51 (s, C_5H_5), 4.63 (m, OCH_2), 2.47–2.06 (m, 2 CH_2)	193.0 (s, C=O); PPh_3 at 133.6 (d, J = 13.9, o), 132.0 (d, J = 57.3, i), 131.5 (s, p), 129.1 (d, J = 13.2, m); 91.1 (s, C_5H_5), 75.5 (s, OCH_2), 30.4 (s, $O{=}CCH_2$), 23.1 (s, $CH_2CH_2CH_2$)	20.0 (s)

Table I (Continued)

complex	IR (cm^{-1})[a]	^1H NMR (δ)[b,c]	$^{13}C\{^1H\}$ NMR (ppm)[c,d]	$^{31}P\{^1H\}$ NMR (ppm)[c,e]
 **1g**$^+$ BF_4^-	ν_{NO} 1674 vs, ν_{CO} 1638 vs	7.83 (m, OCH), 7.54–7.27 (m, 3 C_6H_5), 6.72 (m, CH), 6.50 (m, CH),[g] 5.53 (s, C_5H_5)	220.7 (s, C=O), 152.9 (s, OCH), 146.3 (s, OC=CC); PPh_3 at 133.5 (d, *J* = 10.0, o), 132.2 (i),[f] 131.5 (s, p), 129.1 (d, *J* = 11.4, m); 116.3 (s, O=CC), 110.7 (s, OC=C), 91.8 (s, C_5H_5)	18.9 (s)
 **1h**$^+$ BF_4^-	ν_{NO} 1665 vs, ν_{CO} 1627 s	8.08 (m, OCH), 7.49–7.31 (m, 3 C_6H_5), 6.70 (m, O=CCH), 5.53 (s, C_5H_5)	220.8 (s, C=O), 159.0 (s, OCH); PPh_3 at 133.6 (d, *J* = 11.4, o), 132.1 (i),[f] 131.4 (s, p), 129.2 (d, *J* = 11.2, m); 117.4 (s, O=CC), 92.3 (s, C_5H_5)	18.5 (s)
 **1i**$^+$ BF_4^-	ν_{NO} 1680 vs, ν_{CO} 1622 s	7.68–7.24 (m, 3 C_6H_5), 5.53 (s, C_5H_5), 3.99 (s, OCH_3), 3.27 (s, $OC'H_3$)	220.0 (s, C=O); PPh_3 at 133.0 (d, *J* = 10.5, o), 131.0 (d, *J* = 54.2, i), 130.8 (s, p), 128.5 (d, *J* = 10.0, m); 91.0 (s, C_5H_5), 59.1 (s, OCH_3), 57.6 (s, $OC'H_3$)	21.3 (s)
 **1j**$^+$ BF_4^-	ν_{NO} 1708 vs, ν_{CO} 1663 vs	7.62–7.30 (m, 3 C_6H_5), 5.48 (s, C_5H_5), 4.72 (s, 2 CH_2)	220.0 (s, C=O); PPh_3 at 132.9 (d, *J* = 12.0, o), 130.8 (d, *J* = 56.8, i), 130.8 (s, p), 128.4 (d, *J* = 13.1, m); 91.0 (s, C_5H_5), 68.9 (s, 2 CH_2)	19.2 (s)
 **1k**$^+$ BF_4^-	ν_{NO} 1690 vs, ν_{CO} 1627 vs	7.72–7.37 (m, 3 C_6H_5), 5.46 (s, C_5H_5), 5.41 (br, s, NH), 3.63 (s, 2 CH_2)	247.8 (s, C=O); PPh_3 at 133.8 (d, *J* = 11.6, o), 132.9 (d, *J* = 55.3, i), 131.6 (s, p), 129.3 (d, *J* = 10.9, m); 92.0 (s, C_5H_5), 42.6 (s, 2 CH_2)	18.1 (s)

[a] KBr (pellet). [b] Recorded at 300 MHz in CD_2Cl_2 and referenced to internal $Si(CH_3)_4$. All couplings are in hertz and are to ^1H. [c] Recorded at −80 °C (**1a,c–e,i,j**$^+BF_4^-$) or ambient (**1b,f–h,k**$^+BF_4^-$) probe temperature. [d] Recorded at 75 MHz in CD_2Cl_2 and referenced to CD_2Cl_2 (53.8 ppm). All couplings are in hertz and are to ^{31}P. Assignments of phenyl carbon resonances are made as described in footnote *c* of Table I in: Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956. [e] Recorded at 121 MHz (unlocked) in CD_2Cl_2 and referenced to external 85% H_3PO_4. [f] One line of doublet; other line obscured. [g] One vinylic CH resonance obscured by PPh_3.

species were reproducibly present in (55–70):(45–30) ratios (18.2, 18.8 ppm). When the samples were warmed to room temperature, only **1k**$^+BF_4^-$ (18.1 ppm) remained. When the samples were subsequently cooled to −80 °C, NMR spectra were unaffected.

4. Dynamic Properties of Ester Complexes. Ester complexes **1**$^+BF_4^-$ have the potential for several types of dynamic NMR behavior. For example, Faller has recently observed isomers of coordinated esters by low-temperature ^1H NMR, and proposed provisional assignments as s-cis and s-trans conformers.[3d] Thus, ^1H NMR spectra of methyl acetate and ethyl acetate complexes **1b,c**$^+BF_4^-$ were recorded in CD_2Cl_2 over the temperature range of 0 to −95 °C. However, no broadening of resonances or other decoalescence phenomena were observed.

However, the dimethyl carbonate complex **1i**$^+BF_4^-$ exhibited *two* methoxy ^1H and ^{13}C NMR resonances of equal intensity at −80 °C (Table I, $\Delta\nu$ 218 Hz; see Figure 3,

Table II. Summary of Crystallographic Data for Ester Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)OCH_3)]^+PF_6^-$ ($1b^+PF_6^-$) and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{CCH_2CH_2CH_2O})]^+PF_6^-$ ($1f^+PF_6^-$)

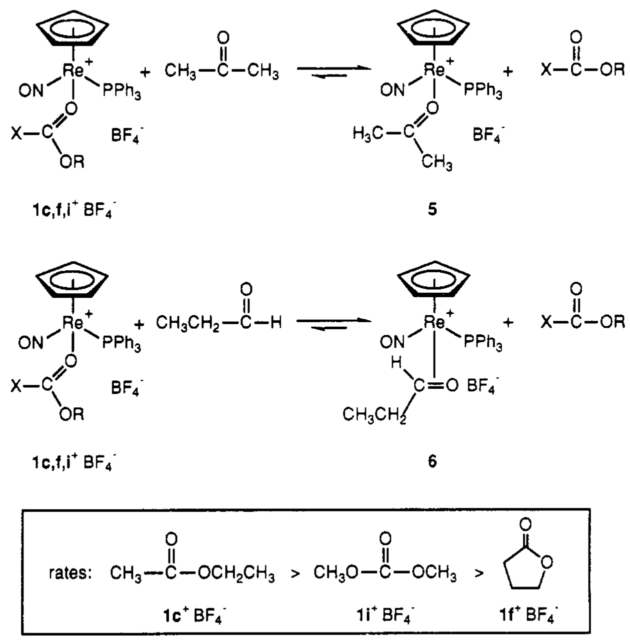
	$1b^+PF_6^-$	$1f^+PF_6^-$
molecular formula	$C_{26}H_{26}F_6NO_3P_2Re$	$C_{27}H_{26}F_6NO_3P_2Re$
molecular weight	762.640	774.652
crystal system	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
cell dimensions		
a, Å	7.816 (1)	13.024 (1)
b, Å	17.984 (2)	8.049 (1)
c, Å	20.156 (1)	27.072 (2)
β, deg	99.057 (7)	100.35 (1)
V, Å^3	2798.01	2791.55
Z	4	4
d_{calc}, g/cm^3	1.81	1.84
d_{obs}, g/cm^3 (CCl_4/CH_2I_2)	1.80	1.82
crystal dimensions, mm	0.38 × 0.15 × 0.12	0.31 × 0.28 × 0.18
diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
radiation, (λ, Å)	Cu Kα (1.540 56)	Cu Kα (1.540 56)
data collection method	θ–2θ	θ–2θ
scan speed, deg/min	variable	variable
reflections measured	5307	5361
range/indices (hkl)	0–9, 0–21, −23 to +23	0–15, 0–9, −31 to +31
scan range	0.80 + 1.40 (tan θ)	0.80 + 1.40 (tan θ)
2θ limit, deg	4.0–130.0	4.0–130.0
time between std	1 X-ray hour	1 X-ray hour
total no. of unique data	4737	4734
no. of obsd data, $I > 3\sigma(I)$	3661	4118
abs coefficient, cm^{-1}	99.126	99.476
min transmission, %	78.460	53.932
max transmission, %	99.654	99.442
no. of variables	352	362
goodness of fit	0.85	1.18
R (averaging) (I_{obs}, F_o)	0.025, 0.017	0.021, 0.014
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0387	0.0321
$R_w = \sum\|\|F_o\| - \|F_c\|\|w^{1/2}/\sum\|F_o\|w^{1/2}$	0.0438	0.0349
Δ/σ (max)	0.001	0.013
$\Delta\rho$ (max), e/Å^3	0.759	0.925

supplementary material). These were assigned to the groups Z and E to the rhenium. Under comparable conditions, the other complexes containing a symmetrically substituted carbonyl group ($1h,j,k^+BF_4^-$) gave only a single set of resonances for the Z/E substituents. A rationale is suggested below.

Next, variable-temperature ^{1}H NMR spectra of $1i^+BF_4^-$ were recorded in CD_2Cl_2 (Figure 3). The methoxy resonances coalesced at −12 °C (261 K). At 20 °C, the resulting singlet was still considerably broadened (δ 3.69; $\Delta\nu_{1/2}$ 6 Hz). Application of the coalescence formula[18] gave a $\Delta G^{\ddagger}$(261 K) of 12.0 ± 0.2 kcal/mol for the process that renders the methoxy groups equivalent. Spectra were also recorded in the presence of added dimethyl carbonate. Separate resonances were observed for the free and coordinated ligand under all conditions (−80 to +20 °C), thereby showing the exchange process to be intramolecular.

5. Reactions of Ester Complexes. The representative complexes $1c,f,i^+BF_4^-$ were dissolved in CD_2Cl_2 (0.08 M) and treated with 2.4 equiv of acetone at room temperature. The samples were monitored by ^{31}P NMR spectroscopy. As shown in Scheme IV, the ethyl acetate complex $1c^+BF_4^-$ reacted over the course of 15 min to give a (18 ± 2):(82 ± 2) equilibrium mixture of $1c^+BF_4^-$ and the previously characterized σ acetone complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)_2)]^+BF_4^-$ (**5**).[8a] The dimethyl carbonate complex $1i^+BF_4^-$ reacted over the course of 1 h to give a (20 ± 2):(80 ± 2) $1i^+BF_4^-/5$ equilibrium mixture. The γ-butyrolactone complex $1f^+BF_4^-$ reacted over the course of 24 h to give a (22 ± 2):(78 ± 2) $1f^+BF_4^-/5$ equilibrium mixture. All of these ratios are equal within experimental error. However, substitution lability varies significantly in the order $1c^+BF_4^- > 1i^+BF_4^- > 1f^+BF_4^-$. If acetone and the carboxylic and carbonic esters exhibited equal Lewis basicity toward I, 29:71 mixtures would have formed. Thus, acetone appears to have a slightly greater Lewis basicity.

Scheme IV. Substitution of Carboxylic and Carbonic Ester Ligands



Next, $1c,f,i^+BF_4^-$ were analogously treated with 2.4 equiv of propionaldehyde. The ethyl acetate complex $1c^+BF_4^-$ reacted over the course of 15 min to give a (10 ± 2):(90 ± 2) equilibrium mixture of $1c^+BF_4^-$ and the previously characterized π-propionaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CHCH_2CH_3)]^+BF_4^-$ (**6**).[7a] Complexes $1i,f^+BF_4^-$ reacted over the course of 30 min and 4 h to give (6 ± 2):(94 ± 2) and (8 ± 2):(92 ± 2) $1i^+BF_4^-/6$ and $1f^+BF_4^-/6$ equilibrium mixtures, respectively. These ratios are very close within experimental error and indicate that the Lewis basicity of propionaldehyde toward I is greater than that of carboxylic and carbonic acid esters.

Finally, reactions of representative ester complexes with alcohols were studied. First, the methyl acetate complex $1b^+BF_4^-$ (0.07 M in CD_2Cl_2) was treated with 95% aqueous ethanol (3 equiv) at room temperature. A rapid reaction occurred to give a mixture of the previously characterized[14] ethanol complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HOCH_2CH_3)]^+BF_4^-$ and the corresponding water complex.[19] A ^{1}H NMR spectrum showed free methyl acetate, but no ethyl acetate. Thus, no transesterification processes occurred.

Next, the ethyl acetate complex $1c^+BF_4^-$ (0.07 M in CD_2Cl_2) was similarly treated with methanol. An analogous reaction took place to give the previously characterized[14] methanol complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HOCH_3)]^+BF_4^-$ and a small amount of the water complex arising from adventitious moisture. A ^{1}H NMR spectrum showed free ethyl acetate, but no methyl acetate.

(18) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; Chapter 7.

(19) Agbossou, S. K.; Roger, C.; Igau, A.; Gladysz, J. A. *Inorg. Chem.* **1992**, *31*, 419.

Table III. Atomic Coordinates of Non-Hydrogen Atoms in $1b^+PF_6^-$ and $1f^+PF_6^-$

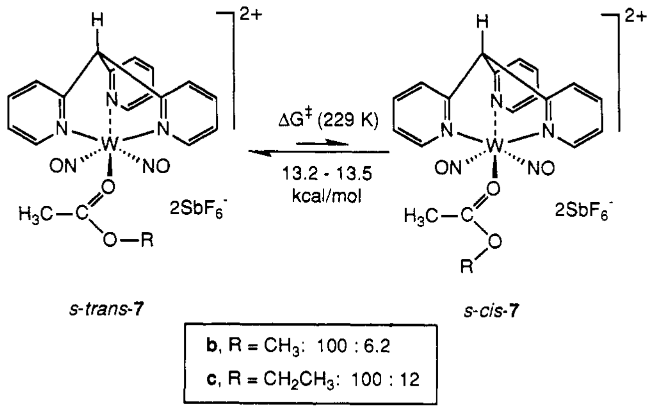
	$1b^+PF_6^-$			$1f^+PF_6^-$		
	x	*y*	*z*	*x*	*y*	*z*
Re	0.17006 (5)	0.16030 (2)	0.26897 (2)	0.10040 (2)	0.16012 (3)	0.09005 (1)
P1	0.0116 (3)	0.0577 (1)	0.2155 (1)	0.1985 (1)	0.3560 (2)	0.14621 (5)
P2	0.6111 (4)	0.2282 (2)	0.4906 (1)	0.3346 (2)	−0.1727 (3)	−0.11351 (8)
F1	0.616 (1)	0.1522 (4)	0.4526 (4)	0.4303 (4)	−0.0518 (8)	−0.1010 (2)
F2	0.609 (1)	0.3074 (4)	0.5259 (3)	0.2662 (6)	−0.027 (1)	−0.1351 (4)
F3	0.789 (1)	0.2082 (5)	0.5358 (4)	0.2379 (5)	−0.2925 (8)	−0.1268 (3)
F4	0.713 (1)	0.2645 (5)	0.4359 (4)	0.3593 (6)	−0.206 (1)	−0.1646 (3)
F5	0.515 (1)	0.1948 (5)	0.5462 (4)	0.3027 (7)	−0.136 (1)	−0.0647 (2)
F6	0.437 (1)	0.2484 (5)	0.4444 (4)	0.3985 (7)	−0.312 (1)	−0.0903 (5)
O1	−0.1431 (9)	0.2475 (4)	0.2802 (4)	−0.0505 (4)	0.3845 (7)	0.0304 (2)
O2	0.2072 (8)	0.0922 (3)	0.3566 (3)	0.2399 (3)	0.1543 (6)	0.0589 (1)
O3	0.196 (1)	0.0446 (5)	0.4566 (3)	0.1892 (3)	0.2801 (6)	−0.0141 (2)
N1	−0.0197 (9)	0.2081 (4)	0.2782 (4)	0.0201 (4)	0.3024 (6)	0.0535 (2)
C1	0.468 (1)	0.1844 (5)	0.2889 (4)	−0.0078 (6)	0.042 (1)	0.1359 (3)
C2	0.425 (1)	0.1429 (5)	0.2287 (4)	0.0893 (7)	−0.013 (1)	0.1555 (3)
C3	0.304 (1)	0.1850 (6)	0.1814 (4)	0.1319 (5)	−0.1021 (9)	0.1204 (3)
C4	0.277 (1)	0.2538 (5)	0.2144 (5)	0.0590 (6)	−0.1084 (9)	0.0761 (3)
C5	0.378 (1)	0.2519 (5)	0.2816 (5)	−0.0296 (6)	−0.020 (1)	0.0859 (4)
C6	−0.167 (1)	0.0833 (5)	0.1512 (4)	0.1236 (4)	0.4900 (7)	0.1805 (2)
C7	−0.297 (1)	0.0322 (5)	0.1287 (4)	0.1740 (5)	0.5864 (9)	0.2206 (2)
C8	−0.440 (1)	0.0528 (6)	0.0803 (5)	0.1155 (6)	0.6923 (9)	0.2453 (2)
C9	−0.449 (1)	0.1243 (6)	0.0545 (4)	0.0099 (6)	0.7046 (9)	0.2307 (2)
C10	−0.322 (1)	0.1755 (6)	0.0771 (4)	−0.0407 (5)	0.6091 (9)	0.1910 (2)
C11	−0.177 (1)	0.1548 (5)	0.1247 (4)	0.0161 (5)	0.5014 (8)	0.1661 (2)
C12	−0.096 (1)	0.0007 (4)	0.2720 (4)	0.2765 (4)	0.5032 (7)	0.1175 (2)
C13	−0.191 (1)	0.0366 (5)	0.3141 (4)	0.2379 (5)	0.5617 (7)	0.0694 (2)
C14	−0.277 (1)	−0.0055 (6)	0.3600 (5)	0.2922 (5)	0.6803 (9)	0.0478 (2)
C15	−0.260 (1)	−0.0794 (6)	0.3646 (5)	0.3847 (5)	0.7414 (9)	0.0727 (3)
C16	−0.158 (1)	−0.1187 (6)	0.3193 (5)	0.4234 (5)	0.686 (1)	0.1205 (3)
C17	−0.083 (1)	−0.0780 (5)	0.2739 (5)	0.3698 (5)	0.5673 (9)	0.1432 (3)
C18	0.144 (1)	−0.0087 (5)	0.1773 (4)	0.2902 (4)	0.2430 (8)	0.1931 (2)
C19	0.291 (1)	−0.0389 (5)	0.2177 (5)	0.3725 (5)	0.161 (1)	0.1777 (3)
C20	0.391 (1)	−0.0904 (5)	0.1907 (6)	0.4315 (6)	0.048 (1)	0.2093 (3)
C21	0.355 (1)	−0.1140 (6)	0.1266 (6)	0.4077 (6)	0.013 (1)	0.2556 (3)
C22	0.200 (1)	−0.0840 (6)	0.0842 (5)	0.3298 (6)	0.099 (1)	0.2715 (3)
C23	0.101 (1)	−0.0310 (5)	0.1096 (4)	0.2718 (5)	0.214 (1)	0.2408 (2)
C24	0.166 (1)	0.0990 (6)	0.4127 (4)	0.2603 (5)	0.2104 (8)	0.0192 (2)
C25	0.078 (1)	0.1636 (7)	0.4364 (5)	0.3654 (5)	0.212 (1)	0.0047 (3)
C26	0.267 (2)	−0.0227 (9)	0.4353 (7)	0.3510 (6)	0.322 (1)	−0.0400 (3)
C27	-	-	-	0.2370 (6)	0.341 (1)	−0.0562 (3)

Discussion

1. Synthesis and Spectroscopic Properties. Schemes I–III establish that carboxylic and carbonic acid ester complexes of the rhenium Lewis acid I are in general easily accessed and isolated. These data suggest that related functional groups such as carboxylic acid amides and urethanes should also give stable adducts. However, some ester complexes are considerably more labile than others. Those that are most robust (**1f–h,k**$^+BF_4^-$) tend to have more electron-releasing carbonyl substituents.

Schemes I–III further suggest that transition-metal ester complexes may be considerably more tractable than the sparse literature[2,3] suggests. Interestingly, the first such complex to be isolated was apparently $Mn(OP(=O)Cl_2)_2(\eta^1\text{-}O{=}C(CH_3)OCH_3)_2$—a substance reported in 1911.[20] However, the structure was not elucidated until considerably later.[2a] Very recently, Faller has characterized an important series of tungsten(0) acetate ester complexes $[HC(py)_3W(NO)_2(\eta^1\text{-}O{=}C(OR)CH_3)]^{2+}\ 2SbF_6^-$ (**7**) by ^1H NMR.[3d] These are illustrated, together with provisional isomer assignments, in Scheme V.

Scheme V. Proposed s-trans/s-cis Isomerism in Tungsten Ester Complexes 7



As summarized in Table V, the IR $\nu_{C=O}$ of **1a–k**$^+BF_4^-$ are generally 100–160 cm^{-1} lower than those of the free ligands. Similar shifts are observed for the corresponding σ ketone complexes (e.g., **5**)[8] and other Lewis acid adducts of organic carbonyl compounds.[2-4] However, the IR $\nu_{C=O}$ of 2*H*-pyran-2-one and imidazolidone, which are the lowest of the free ligands, change by only 31–48 cm^{-1} upon complexation.

Similarly, the C=O ^{13}C NMR resonances of **1a–k**$^+BF_4^-$ are downfield from those of the free ligands (Table V). Complexes **1a–e**$^+BF_4^-$ exhibit a uniform 16–18 ppm shift. Similar trends are observed for carbons β to the rhenium in σ-ketone complexes[8] and other heteroatomic Lewis base adducts of I (e.g., RCH_2X of alkyl halides[13,21] and RCN of nitriles[22]). However, the pyranone- and carbonate-derived

(20) (a) Bassett, H.; Taylor, H. S. *J. Chem. Soc.* **1911**, *99*, 1402. (b) Bassett, H.; Taylor, H. S. *Z. Anorg. Chem.* **1912**, *73*, 75.

(21) Winter, C. H.; Veal, W. R.; Garner, C. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 4766.

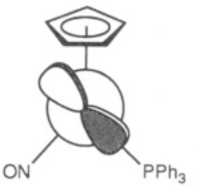
Table IV. Selected Bond Distances (Å), Bond Angles (deg) and Torsion Angles (deg) in $1b^+PF_6^-$ and $1f^+PF_6^-$

	$1b^+PF_6^-$	$1f^+PF_6^-$
Re–P1	2.383 (2)	2.394 (1)
Re–N	1.749 (8)	1.736 (4)
O1–N	1.210 (6)	1.210 (6)
Re–O2	2.132 (6)	2.137 (4)
C24–C25	1.47 (2)	1.491 (8)
C25–C26		1.48 (1)
C26–C27		1.48 (1)
O2–C24	1.23 (1)	1.236 (7)
O3–C24	1.31 (1)	1.299 (7)
O3–C26	1.43 (2)	
O3–C27		1.477 (7)
Re–C1	2.342 (9)	2.250 (7)
Re–C2	2.288 (9)	2.281 (7)
Re–C3	2.236 (9)	2.275 (6)
Re–C4	2.24 (1)	2.243 (6)
Re–C5	2.303 (9)	2.217 (7)
P1–C6	1.807 (9)	1.817 (5)
P1–C12	1.833 (9)	1.823 (5)
P1–C18	1.828 (9)	1.821 (5)
P1–Re–N	92.2 (3)	97.2 (2)
Re–N–O1	172.2 (7)	168.0 (4)
O2–Re–N	101.6 (3)	104.9 (2)
P1–Re–O2	85.6 (2)	82.6 (1)
Re–O2–C24	133.1 (7)	131.7 (4)
C24–O3–C26	118 (1)	
C24–O3–C27		109.5 (5)
O2–C24–O3	120 (1)	121.6 (5)
O2–C24–C25	126 (1)	125.6 (5)
O3–C24–C25	114.4 (9)	112.7 (5)
C24–C25–C26		103.4 (6)
C25–C26–C27		106.1 (6)
O3–C27–C26		106.0 (6)
N–Re–O2–C24	−27.6 (9)	−12.1 (6)
P1–Re–O2–C24	−119.0 (8)	−107.6 (5)
C26–O3–C24–O2	−4 (2)	
C26–O3–C24–C25	174 (1)	

complexes $1g–k^+BF_4^-$ exhibit considerably greater downfield shifts (42–82 ppm). Interestingly, the C═O chemical shift differences are much more pronounced in the complexes (220–248 ppm for $1g–k^+BF_4^-$ vs 179–187 ppm for $1a–f^+BF_4^-$) than in the free ligands (**a**–**k**, 155–178 ppm).

2. General Structural Properties. Complexes $1b,f^+PF_6^-$ exhibit general structural features quite similar to those previously found for the σ-acetone complex $[(\eta^5-C_5H_5)Re(NO)(PPh_3)(\eta^1-O{=}C(CH_3)_2)]^+PF_6^-$ (**5**),[8a] the σ-benzophenone complex $[(\eta^5-C_5H_5)Re(NO)(PPh_3)(\eta^1-O{=}C(CH_3)C_6H_5)]^+PF_6^-$ (**8**),[8a] and the σ-*p*-methoxybenzaldehyde complex $[(\eta^5-C_5H_5)Re(NO)(PPh_3)(\eta^1-O{=}C(H)\text{-}4\text{-}C_6H_4OCH_3)]^+PF_6^-$ (**9**).[9a] Although these five compounds are formally octahedral, all have O–Re–P bond angles that are somewhat less than 90° and O–Re–N bond angles that are somewhat greater than 90°: $1b^+PF_6^-$, $1f^+PF_6^-$, **5**, **8**, **9**: 85.6 (2)°/101.6 (3)°, 82.6 (1)°/104.9 (2)°, 84.1 (1)°/103.8 (2)°, 85.8 (1)°/103.0 (2)°, 83.3 (1)°/102.9 (2)°. Similar distortions are observed in analogous neutral alkoxide[8a] and amide[23] complexes.

Complexes $1b^+PF_6^-$, $1f^+PF_6^-$, **5**, **8**, and **9** exhibit essentially coplanar Re—O═C(C)(X) moieties. Also, all adopt quite similar rhenium–oxygen bond conformations, as indicated by the N–Re–O–C torsion angles (28°, 12°, 21°, 9°, and 0°, respectively). As noted earlier, when N–Re–O–C torsion angles are 0°, overlap of the rhenium fragment HOMO shown in I with the vacant C═O π* orbital lobe



I

on oxygen is maximized.[7a] However, this directs the C═O substituent that is *Z* to the rhenium toward the nitrosyl ligand. Accordingly, the torsion angle is lowest in **9**, which has a hydrogen *Z* to the rhenium. Also, the Re—O═C bond angles (133.1 (7)°, 131.7 (4)°, 136.3 (4)°, 138.3 (4)°, 129.5 (4)°) are greatest in the three complexes with methyl groups *Z* to the rhenium ($1b^+PF_6^-$, **5**, **8**). Finally, the C═O bond lengths span a relatively narrow range (1.23 (1), 1.236 (7), 1.248 (9), 1.245 (8), 1.271 (8) Å).

The methyl acetate ligand in $1b^+PF_6^-$ exhibits a structure similar to that of free methyl acetate.[24] For example, the C═O, C—C, and C—OCH_3 bond lengths are quite close (1.23 (1), 1.47 (2), and 1.31 (1) Å vs 1.200 (4), 1.493 (4), and 1.337 (4) Å). Also, no large deviations are found in the O═C—O, O═C—C, or C—CO—O bond angles (120 (1)°, 126 (1)°, and 114.4 (9)° vs 122.5 (3)°, 125.7 (3)°, and 111.8 (3)°) or C—O—C═O and C—O—C—C torsion angles (−4 (2)° and 174 (1)° vs −1.2 (5)° and −179.3 (3)°.

Accurate experimental structural data for free γ-butyrolactone do not appear to be available.[25–27] However, crystal structures of simple derivatives exhibit C═O, C—OCH_2, and H_2C—CO bond lengths of 1.20–1.22, 1.33–1.38, and 1.50–1.52 Å and C═C—O, O═C—CH_2, and H_2C—C-O—O bond angles of 121–122°, 127–128°, and 110–111°.[26c,28] The corresponding bond lengths and angles in $1f^+PF_6^-$ fall close to these ranges (1.236 (7), 1.299 (7), 1.491 (8) Å; 121.6 (5)°, 125.6 (5)°, 112.7 (5)°). Although the differences are not always statistically significant, $1b,f^+PF_6^-$, **5**, **8**, and **9** all appear to have C═O bonds that are slightly longer than those of the free ligands.[27] The data similarly suggest some contraction of the O–CO bonds in $1b,f^+BF_4^-$.[37]

The crystal structures of several six-coordinate titanium(IV) and zirconium(IV) ester complexes have been reported.[2] The nonchelated examples exhibit s–trans ester conformations and C═O bond lengths that range from 1.234 (5) to 1.275 (9) Å. To our knowledge, all structurally characterized main-group and lanthanide metal ester complexes also exhibit s–trans conformations.[4] However, we are not aware of any other crystal structures of ester complexes of transition metals in lower oxidation states.

3. Dynamic and Chemical Properties. The dynamic properties of transition-metal ester complexes have been previously studied by Faller.[3d] He finds that the tungsten methyl acetate and ethyl acetate complexes **7b,c** shown in Scheme V exist as 100:6.2 and 100:12 equilibrium mixtures of isomers at −44 °C. These were provisionally assigned as s–trans and s–cis isomers, respectively. In-

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(27) Two ab initio studies give γ-butyrolactone C═O bond lengths of ca. 1.194 Å.[26b,c]

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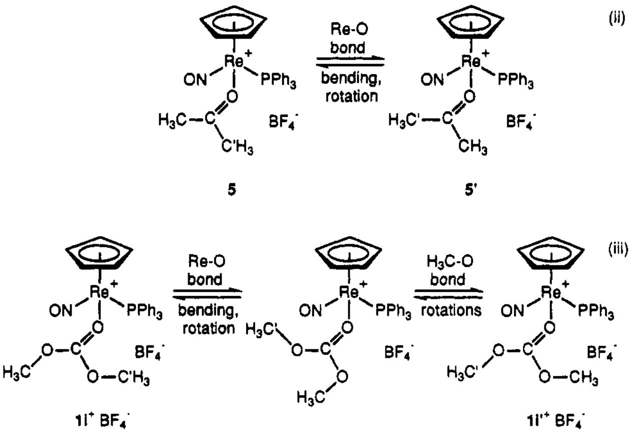
Table V. Comparison of Spectroscopic Properties of Free and Coordinated Ligands in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(X)X')]^+BF_4^-$ ($1^+BF_4^-$)

		IR ($\nu_{C=O}$, cm^{-1})			^{13}C NMR (C=O, ppm)		
	ligand	uncoordinated	coordinated[b]	Δ	uncoordinated[c]	coordinated[e]	Δ
a	methyl formate	1724[a]	1618	106	161.1	179.3	18.2
b	methyl acetate	1740[a]	1611	129	169.8[d]	186.9	17.1
c	ethyl acetate	1740[a]	1619	121	170.0[d]	185.8	15.8
d	phenyl acetate	1754[a]	1625	129	168.8	185.8	17.0
e	propiolactone	1835[a]	1719	116	168.6	185.8	17.2
f	γ-butyrolactone	1770[a]	1635	135	177.5	185.0	7.5
g	2*H*-pyran-2-one	1740[b]	1638	102	161.5	220.7	59.2
h	4*H*-pyran-4-one	1658[b]	1627	31	177.7	220.8	43.1
i	dimethyl carbonate	1754[a]	1622	132	155.9	220.0	64.1
j	ethylene carbonate	1800[b]	1663	137	155.5	220.0	64.5
k	imidazolidone	1675[b]	1627	48	165.4	247.8	82.4

[a] Neat. Data from: Pouchert, C. J. *The Aldrich Library of Infrared Spectra*; Aldrich Chemical Co.: Milwaukee, 1981. [b] KBr. [c] $CDCl_3$, unless noted. [d] Neat. Data from: Breitmaier E.; Haas, G.; Voelter, W. *Atlas of Carbon-13 NMR Data*; Heyden: Bristol, 1979. [e] CD_2Cl_2 at −80 °C (**1a,c–e,i,j**$^+BF_4^-$) or ambient (**1b,f–h,k**$^+BF_4^-$) probe temperature.

Scheme VI. Mechanisms for Exchange of *Z*/*E* C=O Substituents



terestingly, these ratios are not as large as those of free acetate esters. This may be due to the steric bulk of the metal fragment. Also, interconversion barriers (13.2–13.5 kcal/mol) are larger than those of free esters. This is a logical consequence of the increased RO⋯CO bond order in Lewis acid adducts of esters.

Under comparable conditions, s-trans/s-cis isomers of rhenium complexes **1b,c**$^+BF_4^-$ are not detectable, suggestive of lower interconversion barriers. Accordingly, the tungsten fragments in Faller's complexes are *di*cationic, which should confer stronger Lewis acidity. However, s-trans/s-cis isomerism may be an important aspect of the dynamic NMR behavior exhibited by dimethyl carbonate complex **1i**$^+BF_4^-$.

First, it is instructive to compare the dynamic properties of **1i**$^+BF_4^-$ with those previously reported for the acetone complex **5**.[8a] The *Z* and *E* C=O methyl groups of **5** undergo rapid intramolecular exchange, with a $\Delta G^\ddagger$(133 K) of 6.0 kcal/mol (Scheme VI, eq ii). Although several distinct mechanisms are possible,[8a,29] the reaction coordinate need only involve motion about the rhenium–oxygen bond. The corresponding 3-pentanone complex exhibits a $\Delta G^\ddagger$(151 K) of 7.0 kcal/mol for ethyl group exchange.[8c]

However, the $\Delta G^\ddagger$ for methoxy group exchange in **1i**$^+BF_4^-$ is considerably greater (12.0 kcal/mol, 261 K). Furthermore, NMR spectra of the related ethylene carbonate complex **1j**$^+BF_4^-$ show no sign of any broadening or decoalescence at −80 °C. A possible rationale is sketched in Scheme VI. First, note that the *E*/*Z* C=O substituents of **1j**$^+BF_4^-$ can be exchanged by a process analogous to that shown for acetone complex **5**. However, the acyclic dimethyl carbonate ligand in **1i**$^+BF_4^-$ likely adopts a structure with the *E*-methoxy group in an s-trans conformation as in crystalline **1b**$^+PF_6^-$ and the *Z*-methoxy group in an s-cis conformation to minimize interaction with the nitrosyl ligand (Scheme VI, eq iii).[30] Since the ligand now lacks a C_2 axis, additional steps—rotations about the CH_3O⋯CO bonds—are required to consummate methoxy group exchange. Thus, the $\Delta G^\ddagger$ for methoxy group exchange in **1i**$^+BF_4^-$ may reflect rate-determining CH_3O⋯CO bond rotation, analogous to the process proposed by Faller in Scheme V.

The dominant chemical property of ester complexes **1**$^+BF_4^-$ appears to be substitution lability, as exemplified by the transformations in Scheme IV. However, several observations suggest that dissociative processes involving the Lewis acid I are unlikely. First, acetone and propionaldehyde react with **1c,f,i**$^+BF_4^-$ at substantially different rates. Second, the kinetics of substitution reactions of the dichloromethane complex **2** and other halocarbon complexes have been studied in detail.[31] In all cases, data are best accommodated by *associative* mechanisms.

The reactions of **1b,c**$^+BF_4^-$ with simple alcohols show that ligand substitution is faster than addition to the ester carbonyl group. The latter would presumably lead to some type of detectable transesterification. However, in work in progress, we have been able to effect modifications of the ester ligands, such as deprotonation to the corresponding enolates.[32]

4. Summary. This study has established the ready accessibility, and fundamental spectroscopic and structural properties, of carboxylic and carbonic acid ester complexes of the chiral rhenium fragment I. Future reports will describe additional chemical properties of this emerging class of organometallic compounds.

Experimental Section

General Procedures. Instrumentation and general procedures (including dynamic NMR), were identical to those described in a previous paper.[8a] Solvents and reagents were purified as follows:

(29) With spherical Lewis acids, cis/trans C=O substituents are exchanged by simply migrating the Lewis acid from one side of the oxygen to the other in the π nodal plane. However, with *chiral* Lewis acids, a subsequent 180° rotation about the Lewis acid–oxygen bond (or inversion of the Lewis acid configuration) must occur.

(30) Structural studies of free dimethyl carbonate indicate that a C_{2v} isomer with both methoxy groups syn to the carbonyl oxygen is more stable: (a) Katon, J. E.; Cohen, M. D. *Can. J. Chem.* **1975**, *53*, 1378. (b) Evans, M. W.; Afsar, M. N.; Davies, G. J.; Ménard, C.; Goulon, J. *Chem. Phys. Lett.* **1977**, *52*, 388. (c) Mijlhoff, F. C. *J. Mol. Struct.* **1977**, *36*, 334.

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CH_2Cl_2 and C_6H_5Cl, distilled from P_2O_5; hexane and ether, distilled from Na/benzophenone; methanol, distilled from Mg; $Ph_3C^+PF_6^-$ (Columbia), dissolved in a minimum of CH_2Cl_2, precipitated with ethyl acetate, and washed with hexane; all organic carbonyl compounds (Aldrich, Merck, or Fluka), used as received.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(H)OCH_3)]^+BF_4^-$ (1a$^+$BF$_4^-$). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (10;[33] 299.8 mg, 0.537 mol), CH_2Cl_2 (5 mL), and a stir bar and the resultant mixture cooled to −80 °C. Then $HBF_4{\cdot}OEt_2$ (0.080 mL, 0.64 mmol) was added with stirring to give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (2).[11] After 5 min, methyl formate (0.100 mL, 1.62 mmol) was added. The solution was allowed to warm to 0 °C over the course of 2 h and kept at 0 °C (ice bath) for 1 h. The solvent was concentrated to 2 mL under oil pump vacuum, and ether (20 mL) was added dropwise. A salmon powder precipitated, which was collected by filtration, washed with ether, and dried under vacuum to give **1a**$^+BF_4^-$ (303.2 mg, 0.439 mmol, 82%), mp 138–141 °C dec. Anal. Calcd for $C_{25}H_{24}BF_4NO_3PRe$: C, 43.49; H, 3.50. Found: C, 43.39; H, 3.49.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)OCH_3)]^+BF_4^-$ (1b$^+$BF$_4^-$). A Schlenk flash was charged with **10** (232.9 mg, 0.417 mmol), C_6H_5Cl (2 mL), methyl acetate (0.330 mL, 4.151 mmol), and a stir bar and the resultant mixture cooled to −45 °C. Then $HBF_4{\cdot}OEt_2$ (0.055 mL, 0.44 mmol) was added with stirring to give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (3).[12] The solution was allowed to warm slowly to room temperature. An orange-red precipitate subsequently formed. Ether was added dropwise to precipitate additional product, which was collected by filtration, washed with ether, and dried under vacuum to give **1b**$^+BF_4^-$ (245.0 mg, 0.348 mmol, 83%), mp 159–164 °C dec. Anal. Calcd for $C_{26}H_{26}BF_4NO_3PRe$: C, 44.33; H, 3.72. Found: C, 44.43; H, 3.82.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)OCH_2CH_3)]^+BF_4^-$ (1c$^+$BF$_4^-$). A Schlenk flask was charged with **10** (301.2 mg, 0.539 mmol), C_6H_5Cl (5 mL), and a stir bar and the resultant mixture cooled to −45 °C. Then $HBF_4{\cdot}OEt_2$ (0.080 mL, 0.64 mmol) was added with stirring. After 5 min, ethyl acetate (0.100 mL, 1.02 mmol) was added. The solution was allowed to warm slowly to room temperature over the course of 2 h. A tan precipitate subsequently formed. The solvent was concentrated to 2 mL under oil pump vacuum. Ether (20 mL) was added to precipitate additional product, which was collected by filtration, washed with ether, and dried under vacuum to give **1c**$^+BF_4^-$ (317.6 mg, 0.443 mmol, 82%), mp 95–99 °C dec. Anal. Calcd for $C_{27}H_{28}BF_4NO_3PRe$: C, 45.13; H, 3.93. Found: C, 44.90; H, 3.92.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)OC_6H_5)]^+BF_4^-$ (1d$^+$BF$_4^-$). Complex **10** (301.6 mg, 0.540 mmol), C_6H_5Cl (5 mL), $HBF_4{\cdot}OEt_2$ (0.080 mL, 0.64 mmol), and phenyl acetate (0.200 mL, 1.58 mmol) were combined in a procedure analogous to that given for **1c**$^+BF_4^-$. A similar workup gave **1d**$^+BF_4^-$ as a dark orange powder (262.5 mg, 0.342 mmol, 63%), mp 164–166 °C dec. Anal. Calcd for $C_{31}H_{28}BF_4NO_3PRe$: C, 48.57; H, 3.68. Found: C, 48.39; H, 3.67.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{CCH_2CH_2O})]^+BF_4^-$ (1e$^+$BF$_4^-$). Complex **10** (301.2 mg, 0.539 mmol), C_6H_5Cl (5 mL), $HBF_4{\cdot}OEt_2$ (0.080 mL, 0.064 mmol), and propiolactone (0.100 mL, 1.59 mmol) were combined in a procedure analogous to that given for **1c**$^+BF_4^-$. A similar workup gave **1e**$^+BF_4^-$ as an orange powder (225.0 mg, 0.320 mmol, 59%), dec pt 138–144 °C. Anal. Calcd for $C_{26}H_{24}BF_4NO_3PRe$: C, 44.46; H, 3.44. Found: C, 44.29; H, 3.52.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{CCH_2CH_2CH_2O})]^+BF_4^-$ (1f$^+$BF$_4^-$). Complex **10** (302.1 mg, 0.541 mmol), CH_2Cl_2 (4 mL), $HBF_4{\cdot}OEt_2$ (0.080 mL, 0.064 mmol), and γ-butyrolactone (0.135 mL, 1.66 mmol) were combined in a procedure analogous to that given for **1a**$^+BF_4^-$. A similar workup gave **1f**$^+BF_4^-$ as an orange powder (301.6 mg, 0.421 mmol, 78%), dec pt 141–156 °C. Anal. Calcd for $C_{27}H_{26}BF_4NO_3PRe$: C, 45.26; H, 3.66. Found: C, 45.05; H, 3.48.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{CCH{=}CHCH{=}CHO})]^+BF_4^-$ (1g$^+$BF$_4^-$). Complex **10** (302.3 mg, 0.541 mmol), CH_2Cl_2 (5 mL), $HBF_4{\cdot}OEt_2$ (0.080 mL, 0.64 mmol), and 2*H*-pyran-2-one (0.150 mL, 1.85 mmol) were combined in a procedure analogous to that given for **1a**$^+BF_4^-$. A similar workup gave **1g**$^+BF_4^-\cdot 0.5CH_2Cl_2$ as a brick red powder (358.6 mg, 0.467 mmol, 86%), mp 120–122 °C. Anal. Calcd for $C_{28.5}H_{25}BClF_4NO_3PRe$: C, 44.52; H, 3.28; Cl, 4.61. Found: C, 44.40; H, 3.30; Cl, 4.57.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{CCH{=}CHOCH{=}CH})]^+BF_4^-$ (1h$^+$BF$_4^-$). Complex **10** (304.3 mg, 0.544 mmol), CH_2Cl_2 (4 mL), $HBF_4{\cdot}OEt_2$ (0.080 mL, 0.64 mmol), and 4*H*-pyran-4-one (107 mg, 1.11 mmol) were combined in a procedure analogous to that given for **1a**$^+BF_4^-$. A similar workup gave **1h**$^+BF_4^-$ as a dark orange powder (329.4 mg, 0.453 mmol, 83%), mp 183–185 °C dec. Anal. Calcd for $C_{28}H_{24}BF_4NO_3PRe$: C, 46.29; H, 3.33. Found: C, 46.13; H, 3.28.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(OCH_3)_2)]^+BF_4^-$ (1i$^+$BF$_4^-$). Complex **10** (301.0 mg, 0.539 mmol), CH_2Cl_2 (5 mL), $HBF_4{\cdot}OEt_2$ (0.080 mL, 0.64 mmol), and dimethyl carbonate (0.140 mL, 1.66 mmol) were combined in a procedure analogous to that given for **1a**$^+BF_4^-$. A similar workup gave a salmon powder that was recrystallized from CH_2Cl_2/ether at −80 °C to give **1i**$^+BF_4^-$ (340.0 mg, 0.472 mmol, 88%), mp 114–116 °C dec. Anal. Calcd for $C_{26}H_{26}BF_4NO_4PRe$: C, 43.34; H, 3.64. Found: C, 43.11; H, 3.70.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{COCH_2CH_2O})]^+BF_4^-$ (1j$^+$BF$_4^-$). Complex **10** (302.1 mg, 0.541 mmol), CH_2Cl_2 (3 mL), $HBF_4{\cdot}OEt_2$ (0.080 mL, 0.64 mmol), and ethylene carbonate (146.9 mg, 1.67 mmol; dissolved in 1 mL of CH_2Cl_2) were combined in a procedure analogous to that given for **1a**$^+BF_4^-$. A similar workup gave **1j**$^+BF_4^-$ as a salmon powder (164.0 mg, 0.228 mmol, 42%), mp 171–172 °C dec. Anal. Calcd for $C_{26}H_{24}BF_4NO_4PRe$: C, 43.47; H, 3.37. Found: C, 43.33; H, 3.73.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{CNHCH_2CH_2NH})]^+BF_4^-$ (1k$^+$BF$_4^-$). Complex **10** (225.7 mg, 0.405 mmol), CH_2Cl_2 (3 mL), $HBF_4{\cdot}OEt_2$ (0.054 mL, 0.43 mmol), and imidazolidone (39.9 mg, 0.46 mmol, dissolved in 1 mL of CH_2Cl_2) were combined in a procedure analogous to that given for **1a**$^+BF_4^-$. A similar workup gave **1k**$^+BF_4^-$ as an orange powder (181.0 mg, 0.253 mmol, 62%), mp 191–192 °C dec. Anal. Calcd for $C_{26}H_{26}BF_4N_3O_2PRe$: C, 43.59; H, 3.66. Found: C, 43.35; H, 3.73.

1b$^+$PF$_6^-$. A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (4;[15] 300.2 mg, 0.551 mmol), CH_2Cl_2 (10 mL), and a stir bar and the resultant mixture was cooled to −80 °C. Then solid $Ph_3C^+PF_6^-$ (238.1 mg, 0.613 mmol) was added with stirring. After 5 min, methyl acetate (0.130 mL, 1.64 mmol) was added. The solution was allowed to warm to 0 °C over a period of 2 h. The solvent was concentrated to 3 mL under oil pump vacuum, and ether (20 mL) was added dropwise. A dark orange powder precipitated, which was collected by filtration, washed with ether, and dried under vacuum to give **1b**$^+PF_6^-$ (347.0 mg, 0.455 mmol, 83%). A sample was crystallized from layered CH_2Cl_2/ether. This gave burgundy plates of **1b**$^+PF_6^-$, mp 173–176 °C. Anal. Calcd for $C_{26}H_{26}F_6NO_3P_2Re$: C, 40.95; H, 3.44. Found: C, 40.87; H, 3.48.

1f$^+$PF$_6^-$. Complex 4 (301.4 mg, 0.553 mmol), CH_2Cl_2 (10 mL), $Ph_3C^+PF_6^-$ (275.4 mg, 0.709 mmol), and γ-butyrolactone (0.135 mL, 1.66 mmol) were combined in a procedure analogous to that given for **1b**$^+PF_6^-$. The solution was allowed to warm slowly to room temperature over a period of 2 h. The solvent was concentrated to 2 mL under oil pump vacuum, and ether (15 mL) was layered onto the solution. After 12 h, the resulting burgundy prisms were collected by filtration, washed with ether, and dried under vacuum to give **1f**$^+PF_6^-$ (377.4 mg, 0.487 mmol, 88%), mp 166 °C dec. Anal. Calcd for $C_{27}H_{26}F_6NO_3P_2Re$: C, 41.86; H. 3.38. Found: C, 41.75; H, 3.40.

Substitution of Ester Ligands. The following experiment is representative. A 5-mm NMR tube was charged with **1c**$^+BF_4^-$ (28.0 mg, 0.039 mmol) and capped with a septum. Then CD_2Cl_2 (0.5 mL) was added. The tube was cooled to −80 °C, and acetone (0.0070 mL, 0.095 mmol) was added. The tube was shaken and transferred to a −80 °C NMR probe. The probe was gradually warmed while ^{31}P NMR spectra were recorded. At 20 °C, a resonance due to acetone complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)_2)]^+BF_4^-$ (**5**) appeared (18.7 ppm).[8a] After 15 min, an (18 ± 2):(82 ± 2) **1c**$^+BF_4^-$/**5** mixture had formed. A

(33) (a) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (b) Agbossou, F.; O'Connor, E. J.; Garner, C. M.; Quirós Méndez, N.; Fernández, J. M.; Patton, A. T.; Ramsden, J. A.; Gladysz, J. A. *Inorg. Synth.* **1992**, *29*, 337.

spectrum recorded after an additional 15 min gave an identical ratio.[34]

Crystal Structures. Crystals of **1b,f**$^+PF_6^-$ (above) were mounted for data collection on a Enraf-Nonius CAD-4 diffractometer as summarized in Table I. Cell constants were determined from 25 reflections with 20° < 2θ < 30° (**1b**$^+PF_6^-$) or 17° < 2θ < 25° (**1f**$^+PF_6^-$). The space groups were determined from systematic absences (**1b**$^+PF_6^-$, $h0l$ ($h + l = 2n$), $0k0$ ($k = 2n$); **1f**$^+PF_6^-$, $h0l$ ($l = 2n$), $0k0$ ($k = 2n$) and subsequent least-squares refinement. Standard reflections showed 8.1% decay during data collection for **1b**$^+PF_6^-$, but <1% for **1f**$^+PF_6^-$. Lorentz, polarization, anisotropic decay, and empirical absorption (Ψ scans) corrections were applied to the data. Intensities of equivalent reflections were averaged. The structures were solved by standard heavy-atom techniques with the SDP/VAX package.[35] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located for **1f**$^+BF_4^-$ and added to the structure factor calculations but were not refined. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[36]

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Supplementary Material Available: Figure 3 (variable-temperature ^{1}H NMR spectra of **1i**$^+BF_4^-$ in CD_2Cl_2) and tables of anisotropic thermal parameters for **1b,f**$^+PF_6^-$ (3 pages); tables of calculated and observed structure factors (28 pages). Ordering information is given on any current masthead page.

(34) For all reactions in Scheme IV, equilibrium ratios were checked by recording additional NMR spectra at *twice* the time interval after which equilibrium appeared to be initially reached.

(35) Frenz, B. A. The Enraf-Nonius CAD 4 SDP—A Real-time System for Concurrent X-ray Data Collection and Crystal Structure Determination. In *Computing and Crystallography*; Schenk, H., Olthof-Hazelkamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

(36) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, pp 72–98, 149–150; Tables 2.2B and 2.3.1.

(37) Wiberg has recently (a) established the basicity order **f** > **i** > **c** toward the oxonium salt $(CH_3CH_2)_3O^+BF_4^-$, which parallels our data in Scheme IV and solution lability trends, and (b) conducted ab initio calculations that show the more basic C=O lone pairs in *s-trans*-methyl acetate and γ-butyrolactone correspond to those bound to rhenium in crystalline **1b,f**$^+PF_6^-$ (Figures 1 and 2). See: Wiberg, K. B.; Waldron, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 7705.

Synthesis, Structure, and Reactivity of (Pentamethylcyclopentadienyl)rhenium Aldehyde Complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CHR)]^+BF_4^-$: Highly Diastereoselective Deuteride Additions

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Reactions of the dichloromethane complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ and RCH=O (R: **a**, CH_3; **b**, CH_2CH_3; **c**, $CH(CH_3)_2$; **d**, C_6H_5; **e**, $CH_2C_6H_5$) give π-aldehyde complexes (*RS,SR*)-$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CHR)]^+BF_4^-$ ((*RS,SR*)-**5a–e**, 85–89%). A crystal structure of (*RS,SR*)-**5b** shows the RCH=O carbon to be anti to the PPh_3 ligand and the ethyl group to be syn to the NO ligand, confirming the stereochemical assignment. The C–O bond length (1.325 (7) Å) is intermediate between that of a single and double bond. Reactions of (*RS,SR*)-**5a–e** and formyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ (**6**) give alkoxide complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(OCH_2R)$ (**7a–e**, 79–88%) and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (≥94%). Analogous reactions with deuterioformyl complex **6**-d_1 give **7a–e**-d_1 as 78–98:22–2 mixtures of *RR,SS* and *RS,SR* diastereomers. The mechanism of diastereoselection is analyzed. Complexes **7a–e**-d_1 epimerize at rhenium at room temperature.

The conversion of achiral aldehydes to enantiomerically pure alcohol derivatives is a major objective of asymmetric organic synthesis.[1] Accordingly, many chiral, optically active transition-metal compounds are now available[2] and would appear to have considerable untapped potential for effecting enantioselective nucleophilic additions in both catalytic and stoichiometric modes.

We have found that the chiral rhenium dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ is easily generated in enantiomerically pure form and serves as a functional equivalent of the chiral Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I).[3] This pyramidal fragment is a powerful π donor and possesses the d-orbital HOMO shown in Figure 1. Hence, aldehydes react to give π complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CHR)]^+BF_4^-$ (**1**) with structures IIa and IIIa.[4,5] In each case, the substituted =CHR terminus is oriented anti to the bulky PPh_3 ligand. Adducts IIa and IIIa are diastereomeric and differ in the aldehyde enantioface bound to rhenium. Note that the aldehyde substituent is directed at the small nitrosyl ligand in IIa and the larger cyclopentadienyl ligand in IIIa.

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