Synthesis and Reactivity of Chiral Rhenium Alcohol Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ROH)]^{\oplus}\,BF_4^{\ominus}$

Sénamé K. Agbossou, Whitney W. Smith, and John A. Gladysz*

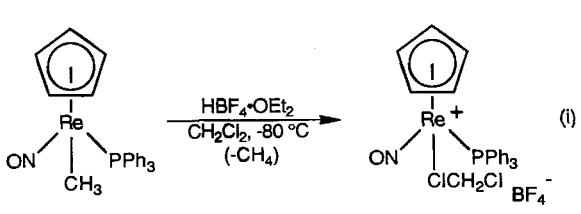
Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112

Received December 27, 1989

Key Words: Rhenium complexes / Alcohols as ligands / Chiral alcohol complexes

Reactions of dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^{\oplus}\,BF_4^{\ominus}$ (**2**$^{\oplus}$ $BF_4^{\ominus}$) and alcohols ROH give the title compounds $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ROH)]^{\oplus}\,BF_4^{\ominus}$; (**3**$^{\oplus}$ $BF_4^{\ominus}$; **a**: R = Me, **b**: Et, **c**: CH_2Ph, **d**: *t*-Bu) in 91–95% yields as air-stable powders after workup. Reactions of **3a–c**$^{\oplus}$ $BF_4^{\ominus}$ and Et_3N produce alkoxide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OR)$ (**4a–c**, 80–90%), which in turn react with HBF_4–OEt_2 to give **3a–c**$^{\oplus}$ $BF_4^{\ominus}$. Reactions of **3a–c**$^{\oplus}$ $BF_4^{\ominus}$ and $Ph_3PX^{\oplus}$ $Br^{\ominus}$ give the bromide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Br)$ (85–98%) and alcohols ROH. **3b,c**$^{\oplus}$ $BF_4^{\ominus}$ and aldehydes react to give π complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CHR')]^{\oplus}\,BF_4^{\ominus}$ (>94%). Reaction of **3b**$^{\oplus}$ $BF_4^{\ominus}$ and $HSi(OEt)_3$ generates the hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**5**, 77%). Reaction of **5** with $Ph_3C^{\oplus}$ $PF_6^{\ominus}$ and then ROH gives **3**$^{\oplus}$ $PF_6^{\ominus}$ (88–91%). NMR experiments establish the order O=CHR > ROH > ROR for ligand binding energies to the rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^{\oplus}$.

We have had an ongoing interest in complexes of the chiral rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^{\oplus}$ (**I**) and neutral donor ligands[1–3]. In previous work, we have found that the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**) is easily converted at low temperatures to the labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^{\oplus}\,BF_4^{\ominus}$ (**2**$^{\oplus}$ $BF_4^{\ominus}$; equation i)[1]. Complex **2**$^{\oplus}$$BF_4^{\ominus}$ reacts with a variety of neutral donor ligands L at −50°C to −30°C to give substitution products $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^{\oplus}\,BF_4^{\ominus}$ in high yields[1–3]. When **2**$^{\oplus}$ $BF_4^{\ominus}$ is generated in optically active form, substitution products are obtained in high optical yields and with retention of configuration at rhenium[1,2c–g]. Thus, **2**$^{\oplus}$ $BF_4^{\ominus}$ serves as the functional equivalent of the chiral, optically active Lewis acid **I**.



(i)

1 **2**$^{+}$ BF_4^{-}

We recently reported that reactions of **2**$^{\oplus}$ $BF_4^{\ominus}$ and symmetrical ethers (ROR) give ether complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ROR)]^{\oplus}\,BF_4^{\ominus}$ in high yields[3]. Hence, we sought to prepare analogous alcohol complexes, $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ROH)]^{\oplus}\,BF_4^{\ominus}$ (**3**$^{\oplus}$ $BF_4^{\ominus}$), and compare key properties such as stability, ligand donor strength, and reactivity. Furthermore, metal-complexed alcohols are plausible intermediates in a significant fraction of many industrially important metal-catalyzed reactions that produce or consume alcohols[4]. Surprisingly, fundamental studies of this ligand type are scarce[5–7]. In this paper, we describe several high-yield syntheses of alcohol complexes **3**$^{\oplus}$ $X^{\ominus}$, and selected physical and chemical properties of **3**$^{\oplus}$ $X^{\ominus}$.

Results

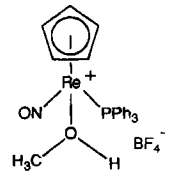
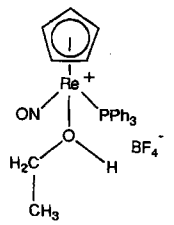
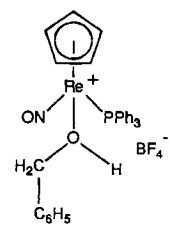
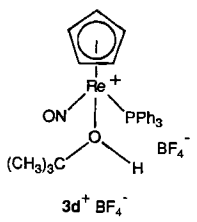
1) *Syntheses of Alcohol Complexes:* Dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^{\oplus}\,BF_4^{\ominus}$ (**2**$^{\oplus}$ $BF_4^{\ominus}$) was generated in CH_2Cl_2 at −80°C as previously described[1]. Then excess methanol was added. Workup gave methanol complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(MeOH)]^{\oplus}\,BF_4^{\ominus}$ (**3a**$^{\oplus}$ $BF_4^{\ominus}$) in 95% yield as an analytically pure powder (Scheme 1). Similar reactions with ethanol, benzyl alcohol, and *t*-butyl alcohol gave the corresponding alcohol complexes **3b–d**$^{\oplus}$ $BF_4^{\ominus}$ in 91–95% yields. Complexes **3a–d**$^{\oplus}$ $BF_4^{\ominus}$ were air-stable as solids, and could be stored for several months at −10°C without significant decomposition.

Alcohol complexes **3a–d**$^{\oplus}$ $BF_4^{\ominus}$ were characterized by IR and NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) spectroscopy, as summarized in Table 1. General features were similar to those found for ether complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ROR)]^{\oplus}\,X^{\ominus}$ [3]. The hydroxyl ^1H-NMR resonances of **3a–c**$^{\oplus}$ $BF_4^{\ominus}$ were broad singlets (δ = 5.99–6.46), whereas that of **3d**$^{\oplus}$ $BF_4^{\ominus}$ was not located. In all cases, weak and broad IR ν_{OH} bands were observed (3420–3430 cm^{-1}). Since the rhenium and alcohol oxygen are each stereogenic centers, diastereomers of **3a–d**$^{\oplus}$ $BF_4^{\ominus}$ are possible. However, only one set of ^1H- and ^{13}C-NMR resonances were observed in low-temperature spectra.

The preceding reactions were repeated with 5 equiv. of each alcohol, and monitored by ^{31}P NMR. In all cases, conversion to **3a–d**$^{\oplus}$ $BF_4^{\ominus}$ was ≥95% complete at −50°C. In analogous reactions with tetrahydrofuran[3], no reaction occurred below −50°C. Hence, alcohols are more nucleophilic towards **2**$^{\oplus}$ $BF_4^{\ominus}$ than ethers.

 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1990 0009–2940/90/0606–1293 $ 02.50/0

Table 1. Spectroscopic characterization of alcohol complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ROH)]^{\oplus}\ BF_4^{\ominus}$ ($3^{\oplus}\ BF_4^{\ominus}$)

Complex	IR [a] [cm^{-1}]	^1H NMR [b]	$^{13}C\{^1H\}$ NMR [c]	$^{31}P\{^1H\}$ NMR [d]
 **3a**$^+$ BF_4^-	ν_{OH} 3419 (w, br) ν_{NO} 1697 (vs)	7.50–7.24 (m, 3 C_6H_5), 6.38 (br, OH), 5.47 (s, C_5H_5), 3.85 (s, CH_3)	PPh_3 at: 133.4 (d, J = 10.5, *o*), 131.3 (d, J = 55.5, *i*), 131.2 (s, *p*), 128.9 (d, J = 10.4, *m*); 91.4 (s, C_5H_5), 71.6 (s, OC)	18.3 (s)
 **3b**$^+$ BF_4^-	ν_{OH} 3430 (w, br) ν_{NO} 1690 (vs)	7.52–6.98 (m, 3 C_6H_5), 5.99 (br, OH), 5.46 (s, C_5H_5), 4.24–4.08 (m, OC*H*H′), 3.85–3.40 (m, OCH*H*′), 1.07 (t, J = 7.0, CH_3)	PPh_3 at: 133.6 (d, J = 11.1, *o*), 131.2 (d, J = 55.8, *i*), 131.1 (s, *p*), 128.8 (d, J = 10.7, *m*); 91.3 (s, C_5H_5), 80.2 (d, J = 1.8, OC), 16.5 (s, CH_3)	18.6 (s)
 **3c**$^+$ BF_4^-	ν_{OH} 3419 (w, br) ν_{NO} 1677 (vs)	7.58–7.32 (m, 3 C_6H_5), 7.29–7.12 (m, 1 C_6H_5), 6.46 (br, OH), 5.33 (s, C_5H_5), 5.11 (dd, J = 11.5, 3.3, C*H*H′), 4.53 (dd, J = 11.5, 4.5, CH*H*′)	PPh_3 at: 133.4 (d, J = 10.9, *o*), 131.0 (s, *p*), 130.9 (d, J = 55.9, *i*), 128.7 (*m*) [e]; CPh at: 134.5 (s, *i*), 130.1 (s), 129.3 (s); 128.6 (s); 91.1 (s, C_5H_5), 84.0 (s, OC)	18.9 (s)
 **3d**$^+$ BF_4^-	ν_{OH} 3419 (w, br) ν_{NO} 1685 (vs)	7.55–7.24 (m, 3 C_6H_5) [f], 5.42 (s C_5H_5), 1.04 (s, 3 CH_3).	PPh_3 at: 133.6 (d, J = 10.3, *o*), 131.0 (s, *p*), 128.9 (*i*) [e], 128.6 (d, J = 10.3, *m*); 90.7 (s, C_5H_5), 84.5 (s, OC), 27.6 (s, CH_3)	19.0 (s)

[a] KBr. – [b] δ values recorded at 300 MHz in CD_2Cl_2 at −40°C (**2a–c**$^{\oplus}$ $BF_4^{\ominus}$) or −70°C (**2d**$^{\oplus}$ $BF_4^{\ominus}$) and referenced to $CDHCl_2$ at δ = 5.32. All couplings are in Hz. – [c] δ values recorded at 75 MHz in CD_2Cl_2 at −40°C (**2a, b**$^{\oplus}$ $BF_4^{\ominus}$) or −70°C (**2c, d**$^{\oplus}$ $BF_4^{\ominus}$) and referenced to CD_2Cl_2 (δ = 53.8). All couplings are in Hz and are to ^{31}P unless noted. Assignments of phenyl carbon resonances were made as described in footnote[c] of Table 1 in ref.[8]. – [d] δ values recorded at 121 MHz (unlocked) in CD_2Cl_2 at −40°C (**2a, b**$^{\oplus}$ $BF_4^{\ominus}$) or −70°C (**2c, d**$^{\oplus}$ $BF_4^{\ominus}$ and referenced to external 85% H_3PO_4. – [e] One line of doublet; other line obscured. – [f] Hydroxyl resonance not observed at −40°C or −70°C.

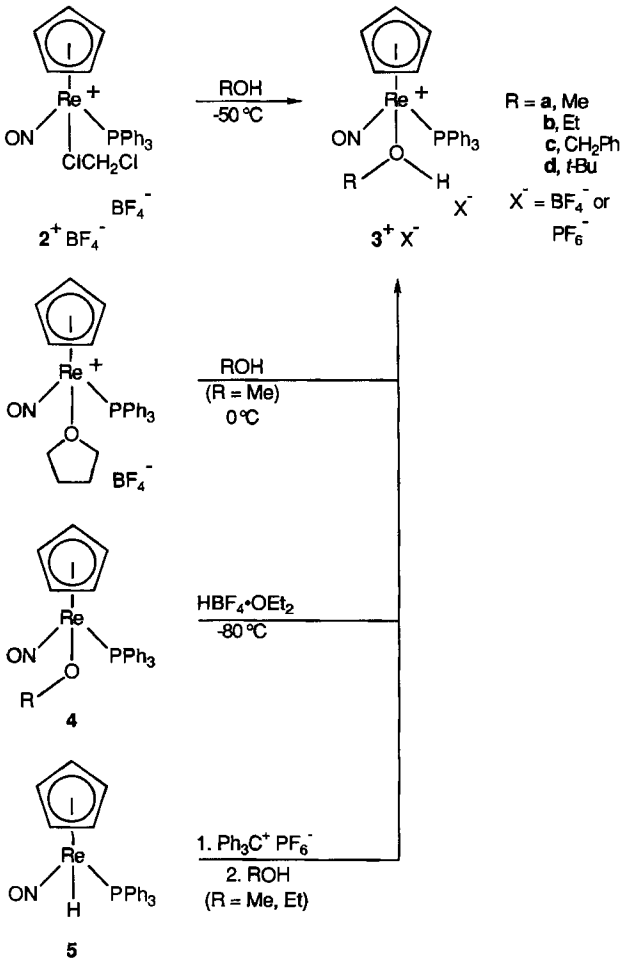
Independent routes to **3a–d**$^{\oplus}$ $BF_4^{\ominus}$ were examined. First, a CD_2Cl_2 solution of tetrahydrofuran complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(THF)]^{\oplus}$ $BF_4^{\ominus}$ was treated with 4 equiv. of methanol (Scheme 1). Methanol complex **3a**$^{\oplus}$ $BF_4^{\ominus}$ formed quantitatively, as assayed by ^1H and ^{31}P NMR [k_{obs}(0°C) = $1.8 \times 10^{-4}\ s^{-1}$]. This demonstrates that the binding constant of methanol to the Lewis acid **I** is greater than that of tetrahydrofuran.

Second, alkoxide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OR)$ (**4**) have previously been shown to react with oxonium salts $R_3O^{\oplus}\ X^{\ominus}$ to give ether complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ROR)]^{\oplus}\ X^{\ominus}$ [3]. Hence, dichloromethane solutions of **4a–c**[2a,f,8] were treated with HBF_4-OEt_2 (1 equiv., −80°C). Subsequent ^{31}P-NMR analysis indicated the spectroscopically quantitative formation of alcohol complexes **3a–c**$^{\oplus}$ $BF_4^{\ominus}$ (Scheme 1).

Finally, in order to clarify some unusual behavior of **3a, b**$^{\oplus}$ $BF_4^{\ominus}$ (below), hexafluorophosphate salts **3a, b**$^{\oplus}$ $PF_6^{\ominus}$ were sought. Since HPF_6-OEt_2 of good purity is not reliably available commercially, a previously described[3] alternative synthetic strategy was employed. First, hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**5**)[9] was treated with $Ph_3C^{\oplus}\ PF_6^{\ominus}$ in CH_2Cl_2 at −15°C (Scheme 1). Then excess methanol or ethanol was added. Workup gave **3a, b**$^{\oplus}$

$PF_6^\ominus$ as analytically pure powders (88–91%), which were characterized by IR, ^{1}H-NMR, and $^{31}P\{^1H\}$-NMR spectroscopy (Experimental). Interestingly, **3b**$^\oplus$ $PF_6^\ominus$ precipitated as a 1:1 ethanol solvate. Although the hydroxyl ^{1}H-NMR resonances of **3a,b**$^\oplus$ $PF_6^\ominus$ were not located, the methyl resonance of **3a**$^\oplus$ $PF_6^\ominus$ was a doublet. The IR ν_{OH} values differed somewhat from those of **3a,b**$^\oplus$ $BF_4^\ominus$ (cm^{-1}, KBr: **3a**$^\oplus$ $PF_6^\ominus$, 3444; **3b**$^\oplus$ $PF_6^\ominus$, 3550).

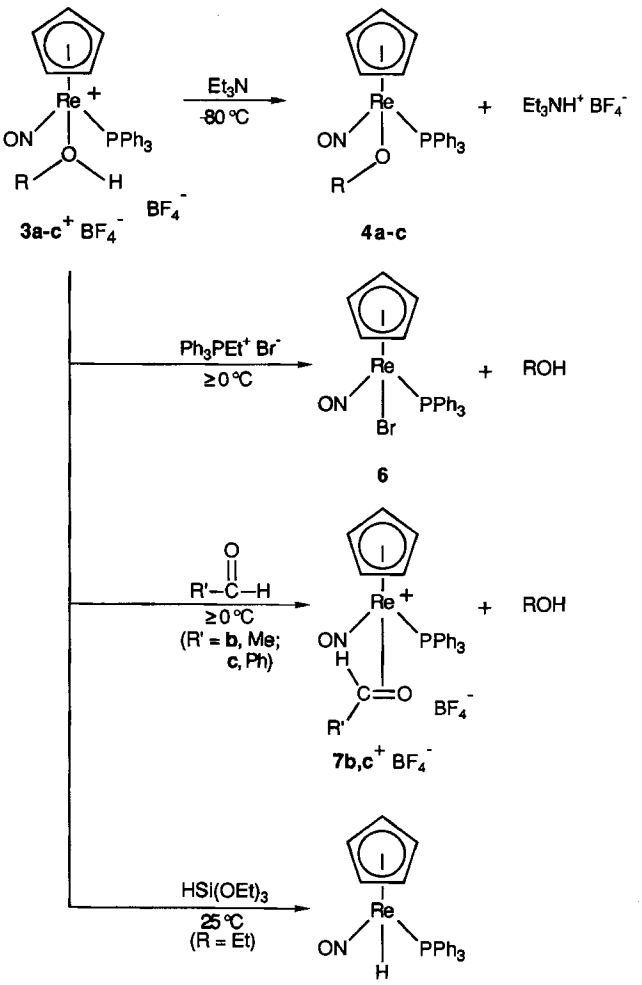
Scheme 1. Syntheses of alcohol complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ROH)]^\oplus X^\ominus$ (**3**$^\oplus$ $X^\ominus$)



2) *Reactions of Alcohol Complexes:* The base $K^\oplus$ *t*-$BuO^\ominus$ has previously been shown to deprotonate secondary phosphine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PR_2H)]^\oplus X^\ominus$ to the corresponding phosphido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PR_2)$[10]. Hence, the alcohol ligand protons of **3**$^\oplus$ $BF_4^\ominus$ were expected to be acidic. Accordingly, reactions of **3a–c**$^\oplus$ $BF_4^\ominus$ and Et_3N gave alkoxide complexes **4a–c** in 80–90% yields after workup (Scheme 2). Analogous reactions were conducted with crude **3a–c**$^\oplus$ $BF_4^\ominus$, providing a "one flask" entry into alkoxide complexes from methyl complex **1**.

Reactions of alcohol complexes **3**$^\oplus$ $BF_4^\ominus$ and nucleophiles were investigated. Treatment of **3a–c**$^\oplus$ $BF_4^\ominus$ with bromide salts PPN$^\oplus$ (PPN$^\oplus$ = $[Ph_3P{=}N{=}PPh_3]^\oplus$) or $Ph_3PEt^\oplus$ $Br^\ominus$ gave bromide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Br)$ (**6**)[10] in 85–98% yields after workup (Scheme 2). Analysis by GC and ^{1}H NMR showed the clean formation of the corresponding alcohols ROH. No alkyl bromides RBr, which would have resulted from nucleophilic attack at carbon, were observed. Analogous reactions of **3a–c**$^\oplus$ $BF_4^\ominus$ and cyanide salt $NEt_4^\oplus$ $CN^\ominus$ were monitored by ^{31}P NMR. These gave principally the cyanide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$[1]. However, several other minor rhenium-containing products were also observed.

Scheme 2. Reactions of alcohol complexes **3**$^\oplus$ $BF_4^\ominus$



We wondered whether similar substitution reactions would occur readily with neutral donor ligands. Hence, a CH_2Cl_2 solution of **3b**$^\oplus$ $BF_4^\ominus$ was treated with a large excess of acetaldehyde at −80 °C. No reaction occurred, as assayed by ^{31}P NMR. The sample was then warmed to room temperature. Acetaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CHR')]^\oplus$ $BF_4^\ominus$ (R′ = Me, **7b**$^\oplus$ $BF_4^\ominus$)[2a,f] formed in quantitative spectroscopic yield (Scheme 2), and was subsequently isolated in 94% yield. Complex **3d**$^\oplus$ $BF_4^\ominus$ and acetaldehyde reacted similarly. An analogous reaction was conducted with **3c**$^\oplus$ $BF_4^\ominus$ and 3 equiv. of benzaldehyde. Benzaldehyde complex **7c**$^\oplus$ $BF^\ominus$ (R′ = Ph) formed in quantitative spectroscopic yield under homogeneous conditions

at room temperature. This establishes that the binding constant of benzaldehyde to the Lewis acid **I** is greater than that of benzyl alcohol.

Next, ethanol complex **3b**$^{\oplus}$ $BF_4^{\ominus}$ was treated with the reductant[12] $HSi(OEt)_3$ (5 equiv.) at room temperature. Workup gave hydride complex **5** in 77% yield (Scheme 2). Alkoxide complexes **4a, b** also reacted with excess $HSi(OEt)_3$ to give **5**, but at much slower rates. An intermediate was observed when these reactions were monitored by ^{31}P NMR (δ = 18.3).

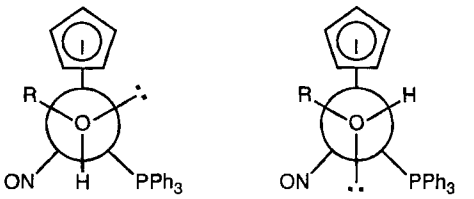
Interestingly, methanol complex **3a**$^{\oplus}$ $BF_4^{\ominus}$ underwent partial conversion in dichloromethane, even at $-80\,^{\circ}C$, to a new species (**8a**$^{\oplus}$ $BF_4^{\ominus}$). The **3a**$^{\oplus}$ $BF_4^{\ominus}$/**8a**$^{\oplus}$ $BF_4^{\ominus}$ ratio reached 80:20 at room temperature, at which point independent decomposition also occurred. The NMR spectra[13] of **8a**$^{\oplus}$ $BF_4^{\ominus}$ closely resembled those of **3a**$^{\oplus}$ $BF_4^{\ominus}$; the cyclopentadienyl ^1H and PPh_3 ^{31}P resonances were slightly shifted in a direction associated with neutral complexes. Ethanol complex **3b**$^{\oplus}$ $BF_4^{\ominus}$ underwent similar conversion to an analogous species (**8b**$^{\oplus}$ $BF_4^{\ominus}$)[13], with a 90:10 **3b**$^{\oplus}$ $BF_4^{\ominus}$/**8b**$^{\oplus}$ $BF_4^{\ominus}$ ratio at room temperature. However, benzyl alcohol complex **3c**$^{\oplus}$ $BF_4^{\ominus}$ gave only traces of an analogous species, and *t*-butyl alcohol complex **3d**$^{\oplus}$ $BF_4^{\ominus}$ did not appear to react.

Experiments were conducted to help interpret this behavior. First, a CD_2Cl_2 solution of **3a**$^{\oplus}$ $BF_4^{\ominus}$/**8a**$^{\oplus}$ $BF_4^{\ominus}$ was heated to 40 °C. No coalescence or broadening of ^1H-NMR resonances was observed. Second, ethoxide complex **4b** was treated with BF_3-OEt_2 at $-80\,^{\circ}C$ in an attempt to generate an authentic sample of the potential decomposition product $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(EtOBF_3)$. However, a multitude of species formed, as assayed by ^{31}P NMR at $-70\,^{\circ}C$. Third, when the **3**$^{\oplus}$ $BF_4^{\ominus}$/**8**$^{\oplus}$ $BF_4^{\ominus}$ mixtures were treated with Et_3N, alkoxide complexes **4** formed in quantitative yield, as assayed by ^{31}P NMR. Finally, analogous behavior was *not* exhibited by hexafluorophosphate salts **3a, b**$^{\oplus}$ $PF_6^{\ominus}$. The $BF_4^{\ominus}$ anion has previously been shown to be a much better hydrogen bond acceptor than $PF_6^{\ominus}$[14].

Discussion

Spectroscopic experiments described above, together with data from previous studies[3,15], establish the following order of thermodynamic binding affinities for the rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^{\oplus}$ (**I**): O=CHR > ROH > ROR > CH_2Cl_2 > η^2-C_6H_6. We ascribe the order ROH > ROR chiefly to the lower steric bulk of alcohols. However, the same trend is found for proton basicity in aqueous solution[16]. Interestingly, the order O=CHR > ROH is opposite to that found for proton basicity in solution[17]. This is likely due to the presence in **I**, but not in $H^{\oplus}$, of high-lying donor orbitals. Thus, **I** is more accurately described as an *amphotere*, as opposed to a "pure" Lewis acid. Hence, binding energies to ligands with low-lying acceptor orbitals, such as O=CHR, can be anomalously high relative to those found with $H^{\oplus}$. In the gas phase, binding energies to $H^{\oplus}$ follow the order MeOMe > O=CHMe > MeOH, whereas binding energies to $Li^{\oplus}$ follow the order O=CHMe > MeOMe > MeOH[18].

The conformations of rhenium complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^{n\oplus}$ have been extensively analyzed[2,19]. With ligands of the general type XLMS, where L/M/S denote large/medium/small substituents on the ligating atom X, the large substituent preferentially occupies the interstice between the small nitrosyl ligand and medium-sized cyclopentadienyl ligand[19]. Hence, alcohol complexes **3**$^{\oplus}$ $X^{\ominus}$ would be expected to adopt structures of the types **II** and **III**. These are diastereomeric, differing in the configuration at oxygen.



II **III**

However, complexes **3**$^{\oplus}$ $X^{\ominus}$ *appear* to be stereochemically homogeneous. Several interpretations are possible. First, one diastereomer might be much more stable than the other. However, diastereomers of the "isosteric" phosphido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PRH)$ exhibit equilibrium ratios that range from 50:50 (R = Ph) to 89:11 (R = Me)[20]. Alternatively, diastereomers **II** and **III** might simply undergo rapid equilibration on the NMR time scale at $-70\,^{\circ}C$. Importantly, the diastereotopic alkyl groups in symmetrical ether complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ROR)]^{\oplus}$ $X^{\ominus}$ exhibit a single set of ^1H- and ^{13}C-NMR resonances at $-70\,^{\circ}C$[3], indicative of low oxygen inversion barriers. Thus, we believe that **3**$^{\oplus}$ $X^{\ominus}$ exist as rapidly interconverting diastereomers. Finally, note that **II** and **III** can also be interconverted by a simple and potentially rapid proton loss/proton addition mechanism.

Some previous observations of other researchers are particularly relevant to this work. Although well-characterized, isolated complexes of alcohols and low-oxidation-state metal fragments are scarce[5–7], many of the reported examples involve rhenium. For example, hexafluoroarsenate complex $(CO)_5ReFAsF_5$ and methanol react to give the isolable Re(I) methanol complex $[(CO)_5Re(MeOH)]^{\oplus}$ $AsF_6^{\ominus}$ (ν_{OH} 3430 cm^{-1} m)[5b]. Pentabromide complex $(Et_4N^{\oplus})_2[(Br)_5Re(NO)]^{2\ominus}$ and ethanol react to give the *anionic* Re(II) ethanol complex $Et_4N^{\oplus}$ $[(Br)_4Re(NO)(EtOH)]^{\ominus}$, which was characterized crystallographically[5a]. In neither of these compounds was any evidence for hydrogen bonding involving the alcohol ligand noted.

Grundy has reported that the alkoxide complexes $(H)Re(NO)(CO)(PPh_3)_2(OR)$ (R = Me, Et) and $HClO_4$ react to give Re(I) alcohol complexes $[(H)Re(NO)(CO)(PPh_3)_2(ROH)]^{\oplus}$ $ClO_4^{\ominus}$[6]. These exhibit hydrogen bonding between the alcohol ligand proton and perchlorate anion, as evidenced by lower ν_{OH} (3140 cm^{-1}), splittings of $\nu(OClO_3)$ that are diagnostic of desymmetrization, and IR spectra of the corresponding deuterioalcohol complexes. The tris(phosphine) complex $[(H)Re(NO)(PPh_3)_3(ROH)]^{\oplus}$ $ClO_4^{\ominus}$ exhibits analogous properties[6b].

Complexes **3**$^{\oplus}$ $BF_4^{\ominus}$ do not exhibit spectroscopic properties that make a strong case for hydrogen bonding. However, it remains possible that **8a,b**$^{\oplus}$ $BF_4^{\ominus}$, which are in apparent equilibrium with **3a,b**$^{\oplus}$ $BF_4^{\ominus}$, might contain RO–H–FBF_3 linkages. The absence of similar equilibria with benzyl alcohol and *t*-butyl alcohol complexes **3c,d**$^{\oplus}$ $BF_4^{\ominus}$ would be rationalized by steric effects, and the absence of similar equilibria with **3a,b**$^{\oplus}$ $PF_6^{\ominus}$ would be rationalized by the poorer acceptor properties of the hexafluorophosphate anion[14]. The homogeneity of **3a,b**$^{\oplus}$ $PF_6^{\ominus}$ also argues against the assignment of **3**$^{\oplus}$ $BF_4^{\ominus}$/**8**$^{\oplus}$ $BF_4^{\ominus}$ as pairs of diastereomers. Interestingly, the water ligands in cationic complexes $[L_nM(HOH)]^{\oplus}$ $BF_4^{\ominus}$ show a marked tendency to hydrogen bond to $BF_4^{\ominus}$ counteranions[14].

Several of the reactions of alcohol complexes **3**$^{\oplus}$ $BF_4^{\ominus}$ in Scheme 2 merit comment. First, the deprotonation of **3**$^{\oplus}$ $BF_4^{\ominus}$ provides a very convenient synthetic entry into a variety of alkoxide complexes **4**. Further, the alcohol complex need not be isolated in pure form. As will be described in future publications[2g], this "one pot" synthesis of **4** from methyl complex **1** is frequently the method of choice.

Second, aldehyde complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CHR')]^{\oplus}$ $X^{\ominus}$ (**7**$^{\oplus}$ $X^{\ominus}$) undergo stereoselective nucleophilic (Nu) attack to give alkoxide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)[OCH(Nu)R]$ of high diastereomeric purities[2a,f,21]. This study establishes that such alkoxide complexes are readily protonated, and that the resulting alcohol complexes are easily converted back to the parent aldehyde complex **7**$^{\oplus}$ $X^{\ominus}$ with liberation of an alcohol product. This efficiently recycles the chiral rhenium auxiliary, as will be exemplified in a future report[20].

Finally, $HSi(OEt)_3$ is the first "external" reductant to provide a high-yield entry into hydride complex **5**. Normally, **5** is prepared by the decarboxylation of formate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)[O(C{=}O)H]$ in refluxing toluene[9]. We speculate that the reaction of **3b**$^{\oplus}$ $BF_4^{\ominus}$ and $HSi(OEt)_3$ involves some type of activating Si/$BF_4^{\ominus}$ interaction[12]. Accordingly, the reduction of **4a,b** by $HSi(OEt)_3$ is considerably slower. Silane reductions of alkoxide complexes to hydride complexes are precedented[22]. However, to our knowledge all reports involve complexes that, unlike **4**, should undergo ready oxidative addition.

In summary, we have devised protocols for the high-yield isolation of alcohol complexes **3**$^{\oplus}$ $BF_4^{\ominus}$, and defined key physical and chemical properties of the alcohol ligands. Future reports will describe the synthesis and properties of the analogous water complex[23], and extensions of this chemistry in directions that have potential for organic synthesis. In particular, attention should be drawn to the possibility of chiral recognition in the binding of chiral alcohols, both in kinetic and thermodynamic contexts.

We thank the *Department of Energy* for support of this research, and *J. M. Fernández* for preliminary experimental observations.

Experimental

General Data: General procedures and solvent purifications were identical to those given in a recent paper[3]. Methanol and ethanol were distilled from magnesium that had been activated with iodine[24]; benzyl alcohol, *t*-butyl alcohol, aldehydes, and Et_3N were used as received. Acid HBF_4–OEt_2 (Aldrich) was standardized as previously described[1], $Ph_3C^{\oplus}$ $PF_6^{\ominus}$ was purified as described earlier[3], and $Ph_3PEt^{\oplus}$ $Br^{\ominus}$, $PPN^{\oplus}$ $Br^{\ominus}$, and $HSi(OEt)_3$ (Aldrich) were used as received.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(MeOH)]^{\oplus}$ $BF_4^{\ominus}$ (**3a**$^{\oplus}$ $BF_4^{\ominus}$): A Schlenk tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**; 0.156 g, 0.279 mmol)[25], CH_2Cl_2 (6 ml), and a stir bar, and was cooled to –80°C. Then HBF_4–OEt_2 (0.036 ml, 0.279 mmol) was added as described previously to generate $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^{\oplus}$ $BF_4^{\ominus}$ (**2**$^{\oplus}$ $BF_4^{\ominus}$)[1]. Methanol (0.227 ml, 5.57 mmol) was added, and the cooling bath was allowed to slowly warm to –20°C. The tube was transferred to an ice bath, and the volatiles were removed under oil pump vacuum. The resulting solid residue was dissolved in CH_2Cl_2 at –15°C, and hexane was added with stirring. The resulting tan powder was collected by filtration, washed with hexane, and dried under vacuum to give **3a**$^{\oplus}$ $BF_4^{\ominus}$ (0.176 g, 0.266 mmol, 95%), mp 154–157°C (dec.).

$C_{24}H_{24}BF_4NO_2PRe$ (662.5) Calcd. C 43.51 H 3.65 N 2.11
Found C 43.58 H 3.67 N 2.09

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(EtOH)]^{\oplus}$ $BF_4^{\ominus}$ (**3b**$^{\oplus}$ $BF_4^{\ominus}$): Methyl complex **1** (0.125 g, 0.224 mmol), CH_2Cl_2 (5 ml), HBF_4–OEt_2 (0.029 ml, 0.224 mmol), and ethanol (0.258 ml, 4.37 mmol) were combined and worked up in a procedure analogous to that given for **3a**$^{\oplus}$ $BF_4^{\ominus}$. Complex **3b**$^{\oplus}$ $BF_4^{\ominus}$ was isolated as a tan powder (0.138 g, 0.204 mmol, 91%), mp 158–160°C (dec.).

$C_{25}H_{26}BF_4NO_2PRe$ (676.5) Calcd. C 44.39 H 3.87 N 2.07
Found C 44.28 H 3.88 N 2.04

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PhCH_2OH)]^{\oplus}$ $BF_4^{\ominus}$ (**3c**$^{\oplus}$ $BF_4^{\ominus}$): Complex **1** (0.144 g, 0.258 mmol), CH_2Cl_2 (5 ml), HBF_4–OEt_2 (0.033 ml, 0.258 mmol), and benzyl alcohol (0.500 ml, 4.83 mmol) were combined in a procedure analogous to that given for **3a**$^{\oplus}$ $BF_4^{\ominus}$. The mixture was allowed to warm to room temperature, and the CH_2Cl_2 was removed under vacuum to give a deep orange solution. Hexane (20 ml) and CH_2Cl_2 (0.5 ml) were added, and the mixture was vigorously stirred. After ca. 1 h, an orange precipitate formed. This was collected by filtration, washed with hexane, and dried under vacuum to give **3c**$^{\oplus}$ $BF_4^{\ominus}$ (0.181 g, 0.245 mmol, 95%), mp 145–147°C (dec.).

$C_{30}H_{28}BF_4NO_2PRe$ (738.5) Calcd. C 48.79 H 3.82 N 1.90
Found C 48.55 H 3.85 N 1.87

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(t\text{-}BuOH)]^{\oplus}$ $BF_4^{\ominus}$ (**3d**$^{\oplus}$ $BF_4^{\ominus}$): Complex **1** (0.137 g, 0.245 mmol), CH_2Cl_2 (5 ml), HBF_4–OEt_2 (0.032 ml, 0.245 mmol), and *t*-butyl alcohol (0.238 ml, 2.45 mmol) were combined in a procedure analogous to that given for **3a**$^{\oplus}$ $BF_4^{\ominus}$. The suspension was stirred for 10 min at –80°C. The tube was then transferred to a room temperature bath. The mixture was stirred for an additional 20 min, and hexane was added. The resulting mauve powder was collected by filtration, washed with hexane, and dried under vacuum to give **3d**$^{\oplus}$ $BF_4^{\ominus}$ (0.160 g, 0.227 mmol, 93%), mp 142–144°C (dec.).

$C_{27}H_{30}BF_4NO_2PRe$ (704.5) Calcd. C 46.03 H 4.29 N 1.99
Found C 46.06 H 4.34 N 2.03

Preparation of **3a**$^{\oplus}$ $PF_6^{\ominus}$: A Schlenk tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**5**[9], 0.282 g, 0.518 mmol), $Ph_3C^{\oplus}$ $PF_6^{\ominus}$ (0.201 g, 0.518 mmol), and a stir bar, and was cooled to –15°C. Then CH_2Cl_2 (4 ml) was added, and the mixture was stirred for 5 min. Then methanol (0.250 ml, 6.17 mmol) was added, and the mixture was stirred for 40 min. The cooling bath was removed, and the mixture was concentrated under vacuum to ca. 2 ml. The sample

was cooled to −15°C, and hexane was added with stirring. The resulting light brown powder was collected by filtration, washed with hexane, and dried under vacuum to give **3a**$^{\oplus}$ $PF_6^{\ominus}$ (0.328 g, 0.455 mmol, 88%), mp 150−152°C (dec.). − IR (cm^{-1}, KBr): $\tilde{\nu}$ = 3444 (w, ν_{OH}), 1698 (s, ν_{NO}). − ^1H NMR (CD_2Cl_2, −40°C): δ = 7.68−6.90 (m, 3 C_6H_5), 5.45 (s, C_5H_5), 3.88 (d, J_{HH} = 3.4 Hz); hydroxyl resonance not observed. − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40°C): δ = 18.4 (s, PPh_3), −144.2 (sept, J_{PF} = 712 Hz).

$C_{24}H_{24}F_6NO_2P_2Re$ (720.6) Calcd. C 40.00 H 3.36 N 1.94
Found C 40.02 H 3.38 N 1.95

Preparation of **3b**$^{\oplus}$ $PF_6^{\ominus}$: Hydride complex **5** (0.206 g, 0.378 mmol), $Ph_3C^{\oplus}$ $PF_6^{\ominus}$ (0.147 g, 0.378 mmol), and ethanol (0.350 ml, 5.96 mmol) were combined and worked up in a procedure analogous to that given for **3a**$^{\oplus}$ $PF_6^{\ominus}$. Solvate **3b**$^{\oplus}$ $PF_6^{\ominus}$ · EtOH was isolated as a brown powder (0.269 g, 0.345 mmol, 91%), mp 155−157°C (dec.). − IR (cm^{-1}, KBr): $\tilde{\nu}$ = 3550 (w, ν_{OH}), 1697 (s, ν_{NO}). − ^1H NMR (δ, CD_2Cl_2, −40°C) 7.71−7.01 (m, 3 C_6H_5), 5.44 (s, C_5H_5), 4.30−4.11 (m, C*H*H′) 3.63−3.45 (m, CH*H*′), 1.66 (t, J_{HH} = 6.9 Hz, CH_3); 2.99 (q, J_{HH} = 6.9 Hz) and 0.92 (t, J_{HH} = 6.6 Hz), free EtOH; hydroxyl resonances not observed. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40°C): δ = 18.4 (s, PPh_3), −144.2 (sept, J_{PF} = 712 Hz).

$C_{25}H_{26}F_6NO_2P_2Re \cdot C_2H_5OH$ (780.7)
Calcd. C 41.59 H 4.01 N 1.79
Found C 41.32 H 3.99 N 1.76

Reactions of **3**$^{\oplus}$ $BF_4^{\ominus}$ *and* Et_3N: The following procedures are representative. − A) A Schlenk tube was charged with **3a**$^{\oplus}$ $BF_4^{\ominus}$ (0.104 g, 0.157 mmol) and a stir bar, and was cooled to −80°C. Then CH_2Cl_2 (5 ml) and Et_3N (0.032 ml, 0.235 mmol) were added. The mixture was stirred for 5 min, transferred to a 0°C bath, and then stirred for 15 min. The volatiles were removed under oil pump vacuum, and the orange-red residue was extracted with benzene. The extract was filtered (under an inert atmosphere) through florisil (1 × 4 cm, deactivated with ca. 30 ml concentrated aqueous NH_3/100 g florisil) in a Kramer filter[26]. Solvent was removed from the filtrate under oil pump vacuum to give (η^5-C_5H_5)Re(NO)(PPh_3)(OCH_3) (**4a**)[10] as an orange powder (0.080 g, 0.139 mmol, 89%)[27].

B) Complex **3a**$^{\oplus}$ $BF_4^{\ominus}$ was generated as above from **1** (0.122 g, 0.218 mmol), CH_2Cl_2 (5 ml), HBF_4-OEt_2 (0.029 ml, 0.218 mmol), and MeOH (0.100 ml, 2.47 mmol). The volatiles were removed under oil pump vacuum and the crude **3a**$^{\oplus}$ $BF_4^{\ominus}$ was treated with Et_3N (0.040 ml, 0.277 mmol). Workup as in procedure A gave **4a** (0.114 g, 0.198 mmol, 91%).

Reactions of **3a−c**$^{\oplus}$ $BF_4^{\ominus}$ *and* $Ph_3PX^{\oplus}$ $Br^{\ominus}$: The following procedures are representative. − A) A Schlenk tube was charged with **3b**$^{\oplus}$ $BF_4^{\ominus}$ (0.102 g, 0.151 mmol) and a magnetic stir bar and cooled to 0°C. Then CH_2Cl_2 (3 ml) and $Ph_3PEt^{\oplus}$ $Br^{\ominus}$ (0.196 g, 0.528 mmol) were added, and the mixture was stirred while the cooling bath was allowed to warm to room temperature. After 4 h, the volatiles were pumped into a liquid-nitrogen-cooled trap for subsequent GC analysis. The solid residue was extracted with benzene. The extract was filtered through a fritted glass funnel containing a 2-cm layer of Celite. The solvent was removed from the filtrate by rotary evaporation, and the resulting purple foam was dried under vacuum to give (η^5-C_5H_5)Re(NO)(PPh_3)(Br) (**6**; 0.093 g, 0.139 mmol, 92%)[27].

B) A 5-mm NMR tube was charged with **3c**$^{\oplus}$ $BF_4^{\ominus}$ (0.028 g, 0.038 mmol) and PPN$^{\ominus}$ $Br^{\ominus}$ (0.023 g, 0.038 mmol), capped with a septum, and cooled to 0°C. Then CD_2Cl_2 (0.6 ml) was added. The tube was shaken and kept at 0°C for 10 min and room temperature for 1 h. Analysis by ^1H and $^{31}P\{^1H\}$ NMR showed the clean formation of benzyl alcohol (δ = 4.66 s, CH_2; 2.12 s, OH) and **6**.

Reactions of **3b,c**$^{\oplus}$ $BF^{\ominus}$ *and Aldehydes:* The following procedure is representative. A 5-mm NMR tube was charged with **3b**$^{\oplus}$ $BF_4^{\ominus}$ (0.021 g, 0.031 mmol) and capped with a septum. The tube was cooled to −80°C, and CH_2Cl_2 (0.6 ml) and acetaldehyde (0.050 ml, 0.894 mmol) were added. The tube was shaken, kept at −80°C for 3 h (no reaction by ^{31}P NMR), and gradually warmed to room temperature in an NMR probe. Reaction commenced at 20°C, and over the course of 1 h a yellow powder precipitated. Ether was added to the tube. The powder was collected by filtration, washed with ether, and dried under vacuum to give [(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-O=$CHCH_3$)]$^{\oplus}$ $BF_4^{\ominus}$ (**7b**$^{\oplus}$ $BF_4^{\ominus}$ [2g]; 0.020 g, 0.029 mmol, 94%)[27].

Reactions of **3**$^{\oplus}$ $BF_4^{\ominus}$ *and* **4** *with* $HSi(OEt)_3$: The following procedures are representative. − A) A Schlenk tube was charged with **3b**$^{\oplus}$ $BF_4^{\ominus}$ (0.130 g, 0.192 mmol), CH_2Cl_2 (3 ml), $HSi(OEt)_3$ (0.200 ml, 1.080 mmol), and a stir bar. The mixture was stirred for 2 h, and volatiles were then removed under oil pump vacuum. The solid residue was extracted with ethyl acetate (40 ml), and the extract was filtered through a 1- × 25-cm silica gel column. Solvent was removed from the filtrate by rotary evaporation, and the residue was dissolved in a minimum of ethyl acetate. Pentane was added, and the solution was stored at −10°C. An orange microcrystalline solid formed, which was collected by filtration, washed with pentane, and dried under vacuum to give **5**[9,27] (0.081 g, 0.149 mmol, 77%).

B) A 5-mm NMR tube was charged with **4b** (0.060 g, 0.102 mmol), C_6H_6 (0.6 ml), and $HSi(OEt_3)$ (0.056 ml, 0.306 mmol), and was capped with a septum. The tube was kept at 25°C and ^{31}P-NMR spectra were periodically recorded. After 3 h, peaks assigned to a transient (δ = 18.3, 7%) and **5** (δ = 29.4, <3%) were evident. These resonances intensified as that of **4b** (δ = 17.5) decreased. After four days, **4b** was consumed and the transient/**5** ratio was 10:90. After another day, only **5** remained. The volatiles were removed under oil pump vacuum. The residue was dissolved in CH_2Cl_2, and chromatographed on a silica gel column with ethyl acetate/hexane (20:80 v/v). A yellow band eluted. Solvent was removed from these fractions by rotary evaporation. The resulting yellow powder was dried under vacuum to give **5** (0.040 g, 0.73 mmol, 72%).

Reactions of **4** *and* HBF_4-OEt_2: The following procedure is representative. − A 5-mm NMR tube was charged with **4a** (0.050 g, 0.087 mmol) and capped with a septum. Then CH_2Cl_2 (0.6 ml) was added. A reference ^{31}P-NMR spectrum was recorded (−40°C; δ = 17.7, s). The tube was cooled to −80°C, and HBF_4-OEt_2 (0.012 ml, 0.087 mmol) was added. The tube was shaken and transferred to a −40°C NMR probe. A ^{31}P-NMR spectrum showed quantitative conversion to **3a**$^{\oplus}$ $BF_4^{\ominus}$ (δ = 18.2, s).

CAS Registry Numbers

1: 71763-18-3 / **2**$^{\oplus}$ $BF_4^{\ominus}$: 111470-01-0 / **3a**$^{\oplus}$ $BF_4^{\ominus}$: 126134-70-1 / **3a**$^{\oplus}$ $PF_6^{\ominus}$: 126134-75-6 / **3b**$^{\oplus}$ $BF_4^{\ominus}$: 126134-72-3 / **3b**$^{\oplus}$ $PF_6^{\ominus}$: 126134-76-7 / **3c**$^{\oplus}$ $BF_4^{\ominus}$: 126134-74-5 / **3d**$^{\oplus}$ $BF_4^{\ominus}$: 126134-78-9 / **4a**: 84369-20-0 / **4b**: 125050-42-2 / **5**: 79919-58-7 / **6**: 92695-33-5 / **7b**$^{\oplus}$ $BF_4^{\ominus}$: 126084-52-4 / **7c**$^{\oplus}$ $BF_4^{\ominus}$: 126186-43-4 / O=CHMe: 75-07-0 / O=CHPh: 100-52-7

[1] J. M. Fernández, J. A. Gladysz, *Organometallics* **8** (1989) 207.
[2] [2a] J. M. Fernández, K. Emerson, R. D. Larsen, J. A. Gladysz, *J. Am. Chem. Soc.* **108** (1986) 8268. − [2b] J. M. Fernández, K. Emerson, R. D. Larsen, J. A. Gladysz, *J. Chem. Soc., Chem. Commun.* **1988**, 37. − [2c] G. S. Bodner, J. M. Fernández, A. M. Arif, J. A. Gladysz, *J. Am. Chem. Soc.* **110** (1988) 4082. − [2d] C. H. Winter, W. R. Veal, C. M. Garner, A. M. Arif, J. A. Gladysz, *J. Am. Chem. Soc.* **111** (1989) 4766. − [2e] G. S. Bodner, T.-S. Peng, A. M. Arif, J. A. Gladysz, *Organometallics* 9 (1990) 1191. −

[20] C. M. Garner, N. Quirós Méndez, J. J. Kowalczyk, J. M. Fernández, K. Emerson, R. D. Larsen, J. A. Gladysz, *J. Am. Chem. Soc.*, in the press. – [2g] D. M. Dalton, J. M. Fernández, K. Emerson, R. D. Larsen, A. M. Arif, J. A. Gladysz, manuscript in preparation.

[3] S. K. Agbossou, J. M. Fernández, J. A. Gladysz, *Inorg. Chem.* **29** (1990) 476.

[4] R. P. A. Sneeden, in *Comprehensive Organometallic Chemistry* (G. Wilkinson, F. G. A. Stone, E. W. Abel, Eds.), vol. 8, chapter 50.2, see for example Scheme 19, Pergamon, Oxford 1982.

[5] [5a] G. Ciani, D. Giusto, M. Manassero, M. Sansoni, *J. Chem. Soc., Dalton Trans.* **1975**, 2156. – [5b] M. Oltmanns, R. Mews, *Z. Naturforsch., Teil B*, **35** (1980) 1324. – [5c] R. H. Crabtree, P. C. Demou, D. Eden, J. M. Mihelcic, C. A. Parnell, J. M. Quirk, G. E. Morris, *J. Am. Chem. Soc.* **104** (1982) 6994. – [5d] X. Xie, J. D. Simon, *J. Am. Chem. Soc.* **112** (1990) 1130.

[6] [6a] K. R. Grundy, K. N. Robertson, *Inorg. Chem.* **24** (1985) 3898. – [6b] J. Y. Chen, K. R. Grundy, K. N. Robertson, *Can. J. Chem.* **67** (1989) 1187.

[7] K. Sünkel, G. Urban, W. Beck, *J. Organomet. Chem.* **290** (1985) 231.

[8] W. E. Buhro, S. Georgiou, J. M. Fernández, A. T. Patton, C. E. Strouse, J. A. Gladysz, *Organometallics* **5** (1986) 956.

[9] G. L. Crocco, J. A. Gladysz, *J. Am. Chem. Soc.* **110** (1988) 6110.

[10] W. E. Buhro, B. D. Zwick, S. Georgiou, J. P. Hutchinson, J. A. Gladysz, *J. Am. Chem. Soc.* **110** (1988) 2427.

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

[12] R. J. P. Corriu, R. Perz, C. Reye, *Tetrahedron* **39** (1983) 999.

[13] NMR (CD_2Cl_2, −40°C); **8a**$^{\oplus}$ $BF_4^{\ominus}$, ^{1}H: δ = 6.22 (s, OH), 5.40 (s, C_5H_5), 3.43 (s, CH_3). – ^{13}C: δ = 91.1 (s, C_5H_5), 71.6 (s, CH_3). – ^{31}P: δ = 19.5 (s). – **8b**$^{\oplus}$ $BF_4^{\ominus}$, ^{1}H: δ = 6.16 (s, OH), 5.41 (s, C_5H_5). – ^{13}C: δ = 91.5 (s, C_5H_5). – ^{31}P: δ = 19.7 (s).

[14] W. Beck, K. Sünkel, *Chem. Rev.* **88** (1988) 1405.

[15] S. K. Agbossou, G. S. Bodner, A. T. Patton, J. A. Gladysz, *Organometallics* **9** (1990) 1184.

[16] pK_a (conjugate acid), MeOH: −2.5 (41% H_2SO_4); MeOMe: −3.83 (54% H_2SO_4). – N. C. Deno, J. O. Turner, *J. Org. Chem.* **31** (1966) 1969.

[17] pK_a (conjugate acid), O=CHMe: −10.2 (CF_3CO_2H/H_2SO_4). – G. C. Levy, J. D. Cargioli, W. Racela, *J. Am. Chem. Soc.* **92** (1970) 6238.

[18] [18a] R. H. Staley, J. L. Beauchamp, *J. Am. Chem. Soc.* **97** (1975) 5920. – [18b] S. G. Lias, J. F. Liebman, R. D. Levin, *J. Phys. Chem. Ref. Data* **13** (1984) 695.

[19] [19a] S. Georgiou, J. A. Gladysz, *Tetrahedron* **42** (1986) 1109. – [19b] G. L. Crocco, J. A. Gladysz, *J. Chem. Soc., Chem. Commun.* **1986**, 1154.

[20] [20a] W. E. Buhro, J. A. Gladysz, *Inorg. Chem.* **24** (1985) 3505. – [20b] B. D. Zwick, *Ph. D. Thesis*, University of Utah, 1987.

[21] C. M. Garner, J. M. Fernández, J. A. Gladysz, *Tetrahedron Lett.* **30** (1989) 3931.

[22] M. J. Fernández, M. A. Esteruelas, M. Covarrubias, L. A. Oro, M.-C. Apreda, C. Foces-Foces, F. H. Cano, *Organometallics* **8** (1989) 1158.

[23] S. K. Agbossou, unpublished results, University of Utah.

[24] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, New York 1980.

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

[26] H. C. Brown, *Organic Syntheses via Boranes*, figure 9.26, Wiley, New York 1975. – Aldrich catalog # Z10,139-7.

[27] The ^{1}H- and ^{31}P{^{1}H}-HMR spectra were identical to those of an authentic sample.

[416/89]