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Synthesis and Reactivity of Chiral Metal Fluoride and Water Complexes Derived from the Rhenium Fragment $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$

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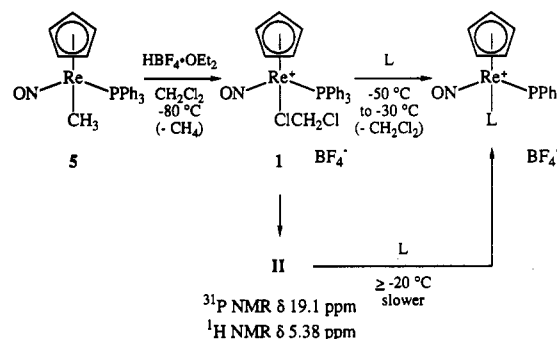
Reactions of triflate complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OTf})$ (**6**), chlorobenzene complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{THF})]^+\text{BF}_4^-$ with $(\text{Me}_2\text{N})_3\text{S}^+[\text{SiMe}_2\text{F}_2]^-$ give fluoride complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{F})$ (**3**) in $\geq 95\%$ NMR yields. Analytically pure **3** can be isolated from the last reaction in 65–75% yields, but decomposes on the time scale of hours in solution. The reaction of **3** with $\text{BF}_3\cdot\text{OEt}_2$ (-95 to -40°C) gives the dichloromethane complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{ClCH}_2\text{Cl})]^+\text{BF}_4^-$ (**1**), and that with MeOTf gives **6** and MeF . Reaction of **3** and $\text{P}(p\text{-tol})_3$ gives mainly the fluoride ligand substitution product $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{P}(p\text{-tol})_3)]^+\text{X}^-$. Reaction of **1** and H_2O gives the water complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OH}_2)]^+\text{BF}_4^-$ (**4**) (4^+BF_4^- , 87%), which in turn reacts with CH_3CN (3 equiv) to give $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NCCH}_3)]^+\text{BF}_4^-$ and H_2O . Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$ with $\text{Ph}_3\text{C}^+\text{PF}_6^-$ and then H_2O gives **4** (4^+PF_6^- , 91%). Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_3)$ and aqueous HF appears to give water complex 4^+X^- ($\text{X}^- = \text{F}^-$ or HF_2^-). Complex **3** is inert to water, but converts to **4** in the presence of HF or $\text{HBF}_4\cdot\text{OEt}_2$.

Fluoride complexes of low-oxidation-state, organometallic fragments are receiving increasing attention.¹ Anomalous and/or unusual reactivity patterns are frequently encountered, and useful applications of these properties are being developed. For example, the hydrogen-bonding capabilities of fluoride ligands have been exploited in some elegant host/guest chemistry described by Richmond.² Doherty has made use of the silaphilicity of fluoride ligands in condensation reactions that lead to novel bridging nitride complexes.³

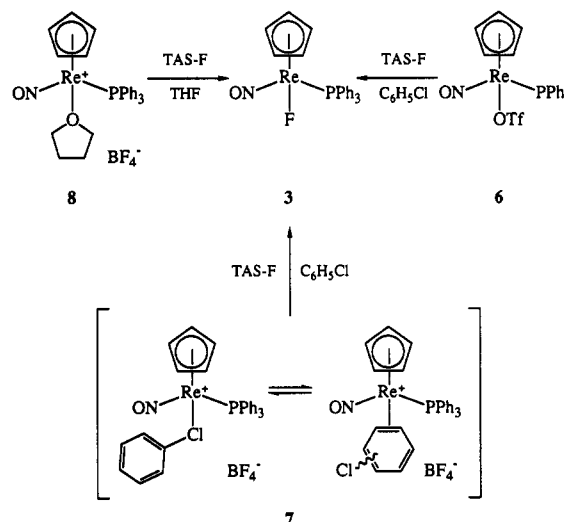
We have had an ongoing interest in the synthesis and physical and chemical properties of the chiral rhenium(I) chloride, bromide, and iodide complexes of the formula $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{X})$ ^{4,5} and the corresponding alkyl halide complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{XR})]^+\text{BF}_4^-$.^{6,7} Several factors turned our attention to fluorine-containing analogues. For example, the photoelectron spectra of the halide complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{L})(\text{X})$ ($\text{R} = \text{H}, \text{Me}$; $\text{L} = \text{PPh}_3, \text{CO}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been measured by Lichtenberger and co-workers.⁵ These reveal extensive mixing of filled metal d and halogen p orbitals—repulsive interactions that should be even more pronounced, possibly with important reactivity consequences, in the corresponding fluoride complexes.

Fluorine-containing complexes were also sought as part of a mechanistic investigation. The dichloromethane complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{ClCH}_2\text{Cl})]^+\text{BF}_4^-$ (**1**)^{6a} reacts with a variety of neutral donor ligands L at -50 to -30°C to give substitution products $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{L})]^+\text{BF}_4^-$ with retention of configuration at rhenium (Scheme I). Thus, **1** serves as the functional equivalent of the chiral Lewis acid $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$ (**I**), and numerous useful asymmetric transformations have been developed.⁸ However, reactions of **1** and less

Scheme I. Synthesis and Substitution Reactions of the Dichloromethane Complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{ClCH}_2\text{Cl})]^+\text{BF}_4^-$ (**1**)



Scheme II. Synthesis of the Fluoride Complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{F})$ (**3**)



reactive ligands L have been observed to proceed by two pathways:^{6b,7a} a direct route and one via a transient, **II** (up to 10%), that slowly converts to product at higher temperatures. One of several plausible structures for **II** would be the bridging tetra-

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fluoroborate complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{FBF}_3)$ (**2**).⁹ Thus, we envisioned accessing an authentic sample of **2**, and possibly other fluorine-ligated species, from the fluoride complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{F})$ (**3**).

In this paper, we describe several synthetic approaches to **3**, and its successful isolation in pure form. Basic reactivity patterns of **3** toward nucleophiles and electrophiles are also established. During the course of this study, we also had occasion to isolate and characterize some related water complexes, $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OH}_2)]^+\text{X}^-$ (4^+X^-).

Results

1. Syntheses of Fluoride Complexes. Halide complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{X})$ have been previously synthesized by reactions of methyl complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_3)$ (**5**) and aqueous acids HX in dichloromethane.^{4a} Thus, **5** and aqueous HF (1.5–2.0 equiv, 0 °C) were analogously reacted. A new complex cleanly formed, as assayed by ³¹P NMR spectroscopy (19.6 ppm, s). However, properties differed from those of authentic $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{F})$ (**3**) isolated below. Thus, study of this reaction was suspended while alternative syntheses involving fluoride salts were investigated.

Next, the substitution-labile triflate complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OTf})$ (**6**)^{4a} and $(\text{Me}_2\text{N})_3\text{S}^+[\text{SiMe}_3\text{F}_2]^-$ (TAS-F)¹⁰ were reacted in chlorobenzene at room temperature (Scheme II). A compound with plausible NMR properties for the target **3** cleanly formed. However, all attempts to isolate **3** in pure form from the reaction mixture were unsuccessful. In particular, it was not in our hands possible to separate **3** from the byproduct TAS-OTf, which remains partially soluble in nonpolar solvents. Purification was hampered by the instability of **3** in solution and on most chromatographic supports.

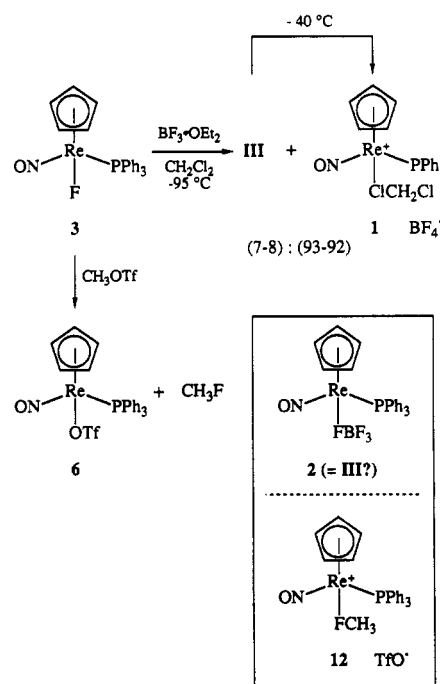
The chlorobenzene complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}_6\text{H}_5)]^+\text{BF}_4^-$ (**7**)^{6c} can be generated in a manner analogous to the dichloromethane complex **1** (Scheme I) and exists as a mixture of reactive linkage isomers. Thus, **7** and TAS-F were combined in chlorobenzene at –45 °C (Scheme II). Fluoride complex **3** formed cleanly, as assayed by ³¹P NMR spectroscopy. Workup gave **3** that was free of TAS-X byproducts. Unfortunately, all samples contained 3–5% of the methyl complex **5**—the precursor used to form chlorobenzene complex **7**. Attempts to circumvent this problem by adjusting the reactant stoichiometry were unsuccessful.

Thus, a substitution-labile cationic precursor that could be isolated in pure form was sought. Accordingly, the tetrahydrofuran complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{THF})]^+\text{BF}_4^-$ (**8**)¹¹ and TAS-F were reacted in THF at room temperature. An extraction/precipitation sequence separated the TAS-X byproducts and gave analytically pure **3** in 65–75% yields.

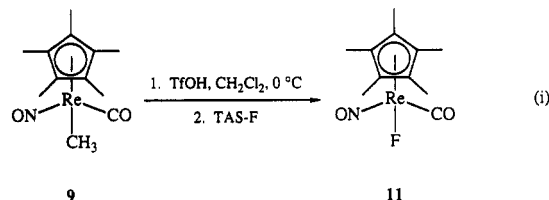
Complex **3** was characterized by IR and low-temperature NMR spectroscopy (¹H, ¹³C, ³¹P, ¹⁹F NMR; Experimental Section). The PPh₃ ³¹P NMR resonance (19.1 ppm, CD₂Cl₂) was strongly coupled to fluorine (d, ²J_{PF} = 41 Hz)—as is commonly observed for metal phosphine fluorides.¹ The fluoride ligand ¹⁹F NMR chemical shift (–475 ppm, d, ²J_{FP} = 41 Hz) was near the upfield extreme of the range previously found for fluoride ligands.¹ The IR ν_{NO} value (1631 cm^{–1}, KBr; 1651 cm^{–1}, CH₂Cl₂) was considerably lower than those of the homologous halide complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{X})$ (1673–1677 cm^{–1}, CHCl₃), as verified in replicate experiments.^{4a} The cyclopentadienyl ¹H NMR chemical shift (δ 5.26) and PPh₃ ³¹P NMR chemical shift were downfield of those of the other halide complexes (δ 5.19–5.22 and 12.9–16.7 ppm).^{4a}

Extensions of the above methodology were briefly investigated. First, the pentamethylcyclopentadienyl methyl complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_3)$ (**9**)¹² was treated with TfOH in di-

Scheme III. Reactions of the Fluoride Complex **3** with Electrophiles



chloromethane at 0 °C (eq i). This was presumed to generate,



by analogy to the previously reported synthesis of triflate complex **6**,^{4a} the new triflate complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{CO})(\text{OTf})$ (**10**). Subsequent addition of TAS-F and workup gave the fluoride complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{CO})(\text{F})$ (**11**) in 63% yield. Complex **11** was 95% pure by ¹H NMR spectroscopy. However, analogous reaction sequences starting with $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_3)$ ¹³ and $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})(\text{CH}_3)$ ^{12,14} gave considerably more byproducts.

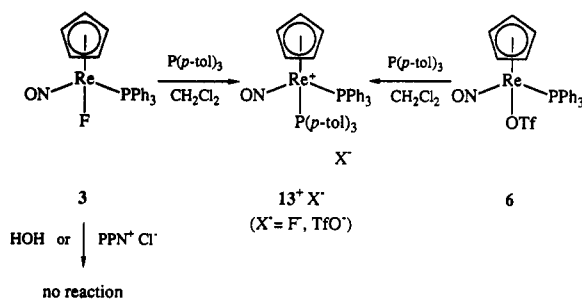
2. Reactivity of Fluoride Complex **3.** The thermal behavior of **3** was examined first. A chlorobenzene-*d*₂ solution of **3** was kept at 50 °C and monitored by ¹H and ³¹P NMR spectroscopy. Over the course of 20 h, a product appeared (³¹P NMR, 7.4 ppm, s; ¹H NMR, δ 4.93, s). After 24–30 h, a second compound began to form (23.0 ppm, v br; δ 5.19, v br) at the expense of the primary product. After 4 days, **3** had been consumed, and a third product was detectable (³¹P NMR, 25.6 ppm, s). No PPh₃ was present (–5.0 ppm, C₆D₅Cl). Complex **3** decomposed over the course of 7 days in benzene-*d*₆ at room temperature to three analogous products (³¹P NMR (ppm) 7.1 s, 23.0 v br, 28.0 s; ¹H NMR (δ) 5.25 s, 5.70 v br). In dichloromethane-*d*₂, **3** gave a multitude of decomposition products, of which the preceding three were the major components.

Reactions of **3** and electrophiles were studied next. First, dichloromethane-*d*₂ solutions of **3** were frozen in liquid nitrogen. Then BF₃·OEt₂ (1–3 equiv) was added (Scheme III). The samples were thawed, and ¹H and ³¹P NMR spectra were recorded at –95 °C. The ³¹P NMR spectra showed two complexes in

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Scheme IV. Reactions of the Fluoride Complex 3 with Nucleophiles



(93–92):(7–8) ratios (13.0 and 8.3–8.1 ppm). The solutions were warmed to -40°C , and the minor product (III) converted to the major product (^1H NMR, δ 5.62, s, C_5H_5). The NMR resonances of the major product exactly matched those of the dichloromethane complex 1. This assignment was verified by subsequent addition of propionaldehyde to give the previously characterized^{8a} π complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\eta^2\text{-O}=\text{CHCH}_2\text{CH}_3)]^+\text{BF}_4^-$ in quantitative spectroscopic yield. As is discussed below, one of several possible structures for the transient species III would be the bridging tetrafluoroborate complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})\text{-(PPh}_3)_2(\text{BF}_3)$ (2).

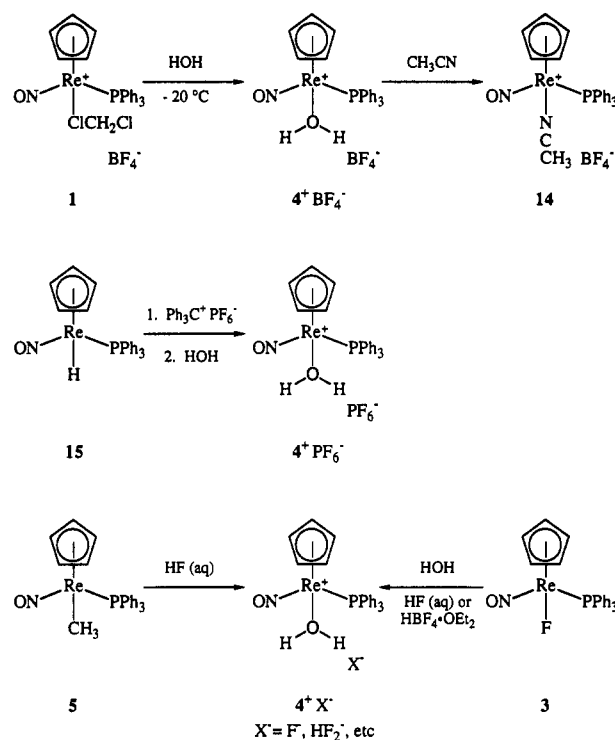
A dichloromethane- d_2 solution of 3 was similarly treated with methyl triflate (Scheme III). No reaction occurred over the course of 7 h at -60°C , as assayed by ^{31}P and ^1H NMR spectroscopy. The sample was warmed to room temperature. Over the course of 3 h, the triflate complex 6 and methyl fluoride (δ 4.32 d, $J_{\text{HF}} = 81.7$ Hz) formed as the only detectable products. No intermediates were noted. Workup of a preparative reaction gave 6 in 68% yield.

Next, reactions of 3 and nucleophiles were investigated. A dichloromethane solution of 3 was treated with $\text{P}(p\text{-tol})_3$ (20 equiv) at -95°C (Scheme IV). The sample was warmed, and reaction commenced at ca. -20°C , as assayed by ^{31}P NMR spectroscopy. Two products formed in a ca. 4:1 ratio. The major product exhibited two ^{31}P NMR resonances (7.4, 4.5 ppm) that were coupled to each other ($J_{\text{PP}} = 10$ Hz). The minor product gave a ^{31}P NMR resonance at 27.8 ppm. No free PPh_3 was observed.

Previous studies have shown that $\text{P}(p\text{-tol})_3$ analogues of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{X})$ complexes commonly exhibit ^{31}P NMR resonances that are shifted 2–4 ppm *upfield*.^{15,16} Hence, 3 (19.1 ppm) did not appear to have undergone PPh_3 ligand substitution. The ^{31}P NMR data for the major product were reminiscent of those previously reported for the bis(phosphine) complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{PPh}_2\text{CH}_2\text{Cl})]^+\text{Cl}^-$ (8.8 and 6.4 ppm, d, $J_{\text{PP}} = 8$ Hz).¹⁷ Thus, the triflate complex 6 and $\text{P}(p\text{-tol})_3$ (5 equiv) were combined in dichloromethane at -45°C (Scheme IV). Workup gave the bis(phosphine) complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})\text{-(PPh}_3)_2(\text{P}(p\text{-tol})_3)]^+\text{TfO}^-$ (13⁺TfO⁻) in 86% yield, which was characterized by IR and NMR spectroscopy (experimental section). The ^{31}P NMR spectrum (7.3 and 4.4 ppm, $J_{\text{PP}} = 11$ Hz) closely matched that obtained above.

Hence, the major product derived from 3 and $\text{P}(p\text{-tol})_3$ in dichloromethane was assigned as 13⁺F⁻ or a related salt 13⁺X⁻. However, reactions of 3 and $\text{P}(p\text{-tol})_3$ in THF and benzene gave a multitude of products. Some 13⁺X⁻ formed in benzene (ca. 30%). Free PPh_3 was not observed under any conditions. Finally, 3 did not react with excess water or PPN^+Cl^- over the course of 1 h in dichloromethane at room temperature.

3. Synthesis and Reactivity of Water Complexes. In order to help interpret the reaction of methyl complex 5 and aqueous HF described above, authentic samples of water complexes of the

Scheme V. Syntheses and Reactions of the Water Complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OH}_2)]^+\text{X}^-$ (4⁺X⁻)

formula $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OH}_2)]^+\text{X}^-$ (4⁺X⁻) were sought. Thus, syntheses analogous to those reported for the corresponding alcohol complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)\text{-(ROH)}]^+\text{X}^-$ were attempted.¹⁸

First, the dichloromethane complex 1 and excess water were reacted at -20°C (Scheme V). Workup gave the analytically pure water complex 4⁺BF₄⁻ in 87% yield. Complex 4⁺BF₄⁻ was characterized analogously to 3 (experimental section). Spectroscopic properties resembled those of the corresponding alcohol complexes.¹⁸ However, the ^1H NMR chemical shift of the water ligand protons was very temperature dependent (δ , CD_2Cl_2 , -70 and 25°C : 6.36 and 5.41). This may be a consequence of hydrogen bonding to the counter-anion, as further discussed elsewhere.^{18,19}

In order to provide chemical support for the structure of 4⁺BF₄⁻, a derivative was sought. Thus, 4⁺BF₄⁻ and CH_3CN were reacted in dichloromethane- d_2 in the presence of an internal standard (Scheme V). Over the course of 6 h at room temperature, quantitative conversion to the previously characterized acetonitrile complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NCCH}_3)]^+\text{BF}_4^-$ (14)^{8a} and water occurred, as assayed by ^1H and ^{31}P NMR spectroscopy.

Reactions of the hydride complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$ (15),²⁰ $\text{Ph}_3\text{C}^+\text{PF}_6^-$, and neutral donor ligands L have previously been shown to give the hexafluorophosphate salts $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{L})]^+\text{X}^-$ in high yields.¹⁸ Thus, 15 was sequentially treated with $\text{Ph}_3\text{C}^+\text{PF}_6^-$ and excess water at -80°C (Scheme V). Workup gave 4⁺PF₆⁻ in 91% yield, the spectroscopic properties of which (Experimental Section) closely matched those of 4⁺BF₄⁻. However, analytically pure samples were not obtained.

Next, the reaction of methyl complex 5 and aqueous HF (Scheme V) was reinvestigated. The product with a 19.6 ppm ^{31}P NMR resonance was generated as described above. Then an authentic sample of 4⁺BF₄⁻ was added (18.9 ppm). The resulting sample gave only one ^{31}P NMR resonance (19.2 ppm), suggestive of a single cationic rhenium entity. Thus, the product was for-

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mulated as the water complex 4^+X^- , where X^- is F^- , HF_2^- , or a related anion.

The above data suggested that aqueous HF and possibly other protic acids promote fluoride ligand substitution of **3**. Thus, dichloromethane solutions of **3** and excess water were treated with traces of aqueous HF or $HBf_4 \cdot OEt_2$. Complex 4^+X^- formed immediately, as assayed by ^{31}P NMR spectroscopy (Scheme V). A dichloromethane solution of **3** and PPN^+Cl^- was analogously treated with $HBf_4 \cdot OEt_2$. The chloride complex $(\eta^5-C_5H_5)Re(NO)(PPh_3)(Cl)$ formed in ca. 80% spectroscopic yield. Reaction of **3** and aqueous HCl also gave the chloride complex (>96%).

Discussion

Complex **3** is one of several low-oxidation-state rhenium fluorides that have been reported in the literature.^{1,21} Syntheses have recently been summarized in tabular format.¹ Scheme II shows that **3** is easily generated in solution by precedented types of procedures. However, the isolation of **3** in pure form is complicated by the removal of byproducts and its thermal instability in solution.

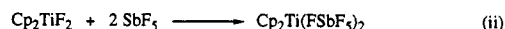
We have previously found that alkoxide complexes $(\eta^5-C_5H_5)Re(NO)(PPh_3)(OR)$ (**16**) and amido complexes $(\eta^5-C_5H_5)Re(NO)(PPh_3)(NRR')$ (**17**) undergo PPh_3 ligand dissociation slightly above room temperature.^{15,16} In the case of the dimethylamido complex $(\eta^5-C_5H_5)Re(NO)(PPh_3)(NMe_2)$, the amido-bridged dimer $[(\eta^5-C_5H_5)Re(NO)(\mu-NMe_2)]_2$ forms.^{15b,22} Complexes **3**, **16**, and **17** all contain related first-row heteroligands with π -donor capabilities. Thus, we had anticipated that **3** might readily convert to the fluoride-bridged dimer $[(\eta^5-C_5H_5)Re(NO)(\mu-F)]_2$. However, no PPh_3 is detected upon decomposition of **3**, nor is any product with fluorine-coupled ^{31}P NMR resonances observed. Thus, the fluoride ligand may be lost in a primary decomposition step.

Similarly, there is no evidence for PPh_3 ligand substitution when **3** is treated with $P(p\text{-tol})_3$ (Scheme IV). Rather, fluoride ligand displacement appears to be the kinetically preferred reaction pathway. In contrast, many metal fluoride complexes undergo ready substitution of spectator ligands.¹ For example, Doherty and Hoffman find that the carbonyl ligands in $(Ph_3P)_2Re(CO)_3(F)$ are even more readily displaced than those in the analogous chloride complex.^{21a}

The nucleophilicity and basicity of lone pairs on heteroatoms that ligate to the rhenium fragment $[(\eta^5-C_5H_5)Re(NO)(PPh_3)]^+$ (**I**) are significantly enhanced relative to those of organic analogues. Thus, phosphido complexes $(\eta^5-C_5H_5)Re(NO)(PPh_3)(PR_2)$,¹⁷ alkoxide complexes **16**,^{11,18} and amido complexes **17**,^{22,23} all readily react with alkylating agents to give isolable phosphine, ether, and amine complexes. In principle, the reaction of **3** and methyl triflate (Scheme III) might proceed similarly—i.e., via initial methylation of the fluoride ligand to give the methyl fluoride complex $[(\eta^5-C_5H_5)Re(NO)(PPh_3)(FCH_3)]^+TfO^-$ (**12**). Reaction of the iodide complex $(\eta^5-C_5H_5)Re(NO)(PPh_3)(I)$ and $Me_3O^+BF_4^-$ gives chiefly the analogous methyl iodide complex.^{7a} Also, Crabtree has reported that ruthenium iodide complexes $(\eta^5-C_5H_5)Ru(L)(L')(I)$ and methyl triflate react to give the corresponding methyl iodide complexes.²⁴ However, electrophiles have been observed to attack neutral $(\eta^5-C_5H_5)Re(NO)(PPh_3)(X)$ complexes at two other sites—the rhenium and nitrosyl ligand

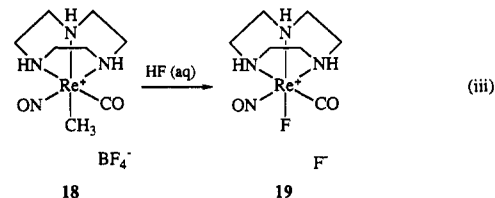
oxygen.²⁵ These pathways could also account for the observed products.

Similar mechanistic questions attend the reaction of **3** and $BF_3 \cdot OEt_2$. In this case, an intermediate is detectable (**III**), but is not present in sufficient concentration for a reliable spectroscopic assignment of structure. However, metal fluoride complexes have been found to react with related Lewis acids to give fluorine-bridged adducts, as shown in eq ii.²⁶ Also, Beck has described



molybdenum complexes for which corresponding $L_nM(FBF_3)$ and $[L_nM(ClCH_2Cl)]^+BF_4^-$ species are in detectable equilibria in dichloromethane.²⁷ Thus, any suggestion that **III** corresponds to the bridging tetrafluoroborate complex $(\eta^5-C_5H_5)Re(NO)(PPh_3)(FbF_3)$ (**2**) is chemically plausible. Furthermore, since the intermediate **II** in Scheme I is clearly distinct from **III**, it is unlikely to be the tetrafluoroborate complex **2**. Finally, it should be emphasized that Scheme III gives dichloromethane complex **1** of much higher spectroscopic purity than Scheme I.

The above data show that **3** is also activated toward fluoride ligand substitution by protic acids. This renders any preparative route to **3** involving aqueous HF impractical, since water will rapidly displace the fluoride ligand. Interestingly, Basolo and Pearson have shown that cobalt fluoride coordination complexes undergo acid-catalyzed substitution by water.²⁸ However, Wieghardt finds that the cationic rhenium methyl complex $[(\eta^3-1,4,7\text{-triazacyclononane})Re(NO)(CO)(CH_3)]^+BF_4^-$ (**18**), which is isoelectronic with **5**, and neat 40% aqueous HF react to give the corresponding fluoride complex $[(\eta^3-1,4,7\text{-triazacyclononane})Re(NO)(CO)(F)]^+F^-$ (**19**), as depicted in eq iii.^{21d}



Other reactions of **3** were investigated, but clean transformations were not observed. For example, bridging chloride, bromide, and iodide complexes of the formulas $[(\eta^5-C_5H_5)Re(NO)(PPh_3)]_2X^+BF_4^-$ are easily prepared.^{4c,6a} However, all attempts to access the corresponding bridging fluoride complex by reactions of **3** and chlorocarbon complexes **1** and **7** gave a multitude of products.

The electronic properties of fluoride ligands have been the subject of much interest.¹ Although the high electronegativity imparts considerable inductive electron-withdrawing capability, π -donor effects involving the fluoride lone pairs are also documented. As noted above, the IR ν_{NO} value of **3** is much lower than those of the corresponding chloride, bromide, and iodide complexes (1631–1651, 1674, 1673, 1677 cm^{-1} , respectively).^{4a} Analogous ν_{NO} and ν_{CO} trends are observed for the pentamethylcyclopentadienyl fluoride complex **11** (equation i) and the corresponding halide complexes (ν_{NO} 1673, 1682, 1683, 1703 cm^{-1} ; ν_{CO} 1933, 1946, 1949, 1963 cm^{-1}).⁵ This suggests that fluoride is *electron releasing* relative to other halide ligands toward rhenium fragments of the formulas $[(\eta^5-C_5R_5)Re(NO)(L)]^+$. However, these trends are reversed in the closely related rhenium nitrosyl halides $[(\eta^3-1,4,7\text{-triazacyclononane})Re(NO)(CO)(X)]^+X^-$, for which IR ν_{NO} and ν_{CO} values decrease in the order $F > Cl > Br \geq I$ (1720, 1710, 1700, 1700 cm^{-1} ; 1970, 1950, 1940, 1935 cm^{-1}).^{21d} Further, the substitution lability of the fluoride ligand in **3** may reflect, in part, repulsive interactions between fluoride lone pairs and filled rhenium d orbitals.

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In summary, we have devised convenient, high-yield protocols for the isolation of the labile fluoride complex **3** and the water complexes 4^+X^- . The rhenium–fluorine bond in **3** is readily cleaved by electrophiles and nucleophiles, and under thermal conditions. Although complexes 4^+X^- constitute an ancillary aspect of this study, water complexes of metals in low oxidation states are of considerable current interest,²⁹ and additional chemical properties will be described in future reports.

Experimental Section

General Data. All reactions were carried out under dry N_2 atmospheres. FT-IR spectra were recorded on Perkin-Elmer 1500 and Mattson Polaris spectrometers. NMR spectra were recorded on Varian XL-300 (1H , ^{13}C , ^{31}P) or VXR-500 (^{19}F) spectrometers: 1H (δ), referenced to $CDHCl_2$ at 5.32, $CHCl_3$ at 7.24, C_6D_5HCl at 7.30, or $Si(CH_3)_4$ at 0.00; ^{13}C (ppm), referenced to CD_2Cl_2 at 53.8, $CDCl_3$ at 77.0, or $Si(CH_3)_4$ at 0.0; ^{31}P (ppm), referenced to external 85% H_3PO_4 at 0.0; ^{19}F (ppm), referenced to $CFCl_3$ at 0.0. Microanalyses were conducted by Atlantic Microlab. Melting points were determined in evacuated capillaries.

Solvents and reagents were purified as follows: CH_2Cl_2 , C_6H_5Cl , and CH_3CN , distilled from P_2O_5 ; tetrahydrofuran, ethyl ether, and benzene, distilled from Na/benzophenone; hexane, distilled from sodium; $CDCl_3$, CD_2Cl_2 , C_6D_5Cl , and C_6D_6 , vacuum transferred from CaH_2 ; $HBf_4 \cdot OEt_2$ (Aldrich), standardized as previously described;^{6a} $Ph_3C^+PF_6^-$ (Aldrich), purified as described earlier;¹¹ $(Me_2N)_3S^+[SiMe_3F_2]^-$ (TAS-F), TfOH, MeOTf, $BF_3 \cdot OEt_2$, propionaldehyde (Aldrich), $P(p\text{-tol})_3$ (Strem), and Ph_3SiCH_3 (Pfaltz and Bauer), used as received.

Isolation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(F)$ (3**).** In a glovebox, a round-bottom flask was charged with $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(THF)]^+BF_4^-$ (**7**; ¹¹ 0.601 g, 0.855 mmol), TAS-F¹⁰ (0.295 g, 1.071 mmol), THF (20 mL), and a stir bar. The mixture was stirred for 15 min, and solvent was removed from the resulting solution under vacuum. The residue was extracted with benzene (50 mL), and the extract was filtered through a Kramer filter containing a 4-cm layer of cellulose.³⁰ The filtrate was concentrated to ca. 2 mL under vacuum, and hexane was added. A precipitate formed, which was collected by filtration, washed with hexane, and dried under vacuum to give **3** as a tan-pinkish powder (0.371 g, 0.659 mmol, 65%), mp 162–166 °C dec.

Data: IR (cm^{-1} , KBr/ CH_2Cl_2): ν_{NO} 1631/1651 s. 1H NMR (δ , $CDCl_3/CD_2Cl_2/C_6D_5Cl$): 7.58–7.34/7.55–7.35/7.58–7.34 (m, $3C_6H_5$), 5.26/5.31/5.02 (s, C_5H_5). $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3/CD_2Cl_2$): 133.8/133.4 (d, $J_{CP} = 51.9/51.4$ Hz, *i*-Ph), 133.7/134.2 (d, $J_{CP} = 10.8/10.6$ Hz, *o*-Ph), 130.5/131.0 (d, $J_{CP} = 2.3/2.4$ Hz, *p*-Ph), 128.5/128.9 (d, $J_{CP} = 10.3/10.5$ Hz, *m*-Ph), 91.0/91.4 (s, C_5H_5). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3/CD_2Cl_2/C_6D_5Cl$): 19.4/19.1/18.2 (d, $J_{PF} = 37/41/41$ Hz). ^{19}F NMR (ppm, CD_2Cl_2): –475 (d, $J_{PF} = 41$ Hz). Anal. Calcd for $C_{23}H_{20}FNOPRe$: C, 49.10; H, 3.58; N, 2.49. Found: C, 49.12; H, 4.06; N, 2.79.

Alternative Routes to **3.** A. A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ (**6**; ^{6a} 0.251 g, 0.362 mmol), C_6H_5Cl (5 mL), and a stir bar. The solution was freeze/pump/thaw degassed, and cooled to 0 °C. Then a solution of TAS-F (0.120 g, 0.436 mmol) in C_6H_5Cl (5 mL) was added. The mixture was stirred for 0.5 h and worked up in a manner analogous to the preceding procedure to give **3** as a pinkish tan powder (0.146 g, 0.260 mmol, 60%) that contained some TAS-OTf by 1H NMR spectroscopy (δ 2.95, s).

B. A Schlenk tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**5**; ³¹ 0.143 g, 0.255 mmol), C_6H_5Cl (5 mL), and a stir bar, and cooled to –40 °C. Then $HBf_4 \cdot OEt_2$ (0.033 mL, 0.255 mmol) was added with

stirring to generate $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**7**).^{6c} After 5 min, a solution of TAS-F (0.110 g, 0.399 mmol) in C_6H_5Cl (5 mL) was added. The cold bath was replaced with a room-temperature water bath. The mixture was stirred for 1 h and then worked up in a manner analogous to the preceding procedure. This gave **3** as a brown powder (0.066 g, 0.117 mmol, 46%) that contained **5** (3%) by 1H and ^{31}P NMR spectroscopy.

Generation of $(\eta^5\text{-}C_5Me_5)Re(NO)(CO)(F)$ (11**).** A Schlenk flask was charged with $(\eta^5\text{-}C_5Me_5)Re(NO)(CO)(CH_3)$ (**9**; ¹² 0.780 g, 1.98 mmol), CH_2Cl_2 (20 mL), and a stir bar, and cooled to 0 °C. Then TfOH (0.175 mL, 1.98 mmol) was slowly added with stirring. The red solution turned orange. After 5 min, a solution of TAS-F (0.545 g, 1.98 mmol) in CH_2Cl_2 (10 mL) was added via cannula. The reaction mixture was allowed to warm to room temperature over the course of 1 h, and solvent was removed under vacuum. The orange residue was extracted with benzene (20 mL), and the extract was filtered through a Kramer filter containing a layer of cellulose. The solvent was removed under vacuum and the residue taken up in CH_2Cl_2 (2 mL). This solution was poured into cold hexane (0 °C, 100 mL). The precipitate was collected by filtration, washed with hexane, and dried under vacuum to give **11** as a dark orange powder (0.496 g, 1.155 mmol, 58%). IR (cm^{-1} , KBr): ν_{CO} 1933 vs, ν_{NO} 1673 vs. 1H NMR (δ , $CDCl_3$): 2.03 (s, 5Me). $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$): 208.6 (s, CO), 104.9 (s, C_5Me_5), 9.8 (s, C_5Me_5).

Reaction of **3 and $BF_3 \cdot OEt_2$.** A 5-mm NMR tube was charged with **3** (0.030 g, 0.053 mmol) and CD_2Cl_2 (0.8 mL) and capped with a septum. The tube was immersed in a liquid nitrogen bath, and $BF_3 \cdot OEt_2$ (0.0194 mL, 0.159 mmol) was added. The tube was transferred to a –95 °C NMR probe. Data: see text.

B. Complex **3** (0.015 g, 0.023 mmol), CH_2Cl_2 (0.4 mL), and $BF_3 \cdot OEt_2$ (0.010 mL, 0.081 mmol) were combined in an analogous fashion. The tube was warmed to –45 °C, and propionaldehyde (0.006 mL, 0.083 mmol) was added. After 0.5 h, the tube was warmed to room temperature. A ^{31}P NMR spectrum showed $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O=CHCH_2CH_3)]^+BF_4^-$ (10.6 ppm)^{3a} to be the only product.

Reaction of **3 and CH_3OTf .** A Schlenk flask was charged with **3** (0.050 g, 0.089 mmol), CH_2Cl_2 (5 mL), and a stir bar, and cooled to –80 °C. Then CH_3OTf (0.030 mL, 0.27 mmol) was added with stirring. The solution was kept at room temperature for 3 h and then filtered through silica gel as in a previously described synthesis of **6**.^{6a} Precipitation from CH_2Cl_2 /hexane gave **6** as a red powder (0.042 g, 0.061 mmol, 68%).^{6a} 1H NMR (δ , CD_2Cl_2): 7.50–7.34 (m, 3 C_6H_5), 5.41 (s, C_5H_5). $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2): 134.0 (d, $J_{CP} = 11.0$ Hz, *o*-Ph), 133.3 (d, $J_{CP} = 54.1$ Hz, *i*-Ph), 131.4 (d, $J_{CP} = 2.3$ Hz, *p*-Ph), 129.2 (d, $J_{CP} = 10.8$ Hz, *m*-Ph), 119.1 (d, $J_{CF} = 316.5$ Hz, CF_3), 91.3 (s, C_5H_5). ^{31}P NMR (ppm, CD_2Cl_2): 18.5 s.

B. An analogous reaction was conducted in a NMR tube as described for **3** and $BF_3 \cdot OEt_2$. Data: see text.

Reaction of **3 and $P(p\text{-tol})_3$.** A 5-mm NMR tube was charged with **3** (0.007 g, 0.012 mmol), $P(p\text{-tol})_3$ (0.084 g, 0.27 mmol), and CH_2Cl_2 (0.5 mL), and capped with a septum. The sample was immediately transferred to a NMR probe, and ^{31}P NMR spectra were recorded. Data: see text.

Isolation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(P(p\text{-tol})_3)]^+TfO^-$ (13**;³ TfO^-).** A Schlenk tube was charged with **9** (0.370 g, 0.662 mmol), CH_2Cl_2 (5 mL), and a stir bar, and cooled to –45 °C. Then TfOH (59 μ L, 0.66 mmol) was added with stirring to generate **6**. After 10 min, $P(p\text{-tol})_3$ (1.000 g, 3.285 mmol) was added. The solution was allowed to warm to room temperature. After 20 h, hexane was added. The resulting precipitate was collected by filtration and dried under vacuum to give **13**³ TfO^- as a light tan powder (0.567 g, 0.569 mmol, 86%), mp 105–109 °C dec. IR (cm^{-1} , KBr): ν_{NO} 1701 s. 1H NMR (δ , CD_2Cl_2): 7.47 (m, 6H), 7.33 (m, 6H), 7.11 (m, 9H), 6.90 (m, 6H), 5.26 (s, C_5H_5), 2.38 (s, 3 CH_3). $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2): 142.3 (s, $p\text{-}C_6H_4CH_3$), 132.4–129.2 (other C_6H_4R), 94.5 (s, C_5H_5), 21.4 (s, 3 CH_3). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2): 7.3 (d, $J_{PP} = 11$ Hz, PPh_3), 4.4 (d, $J_{PP} = 11$ Hz, $P(p\text{-tol})_3$).

Isolation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OH)_2]^+BF_4^-$ (4**;⁴ BF_4^-).** A Schlenk flask was charged with **5** (1.000 g, 1.790 mmol), CH_2Cl_2 (25 mL), and a stir bar, and cooled to –80 °C. Then $HBf_4 \cdot OEt_2$ (0.250 mL, 1.97 mmol) was added with stirring to generate $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**1**).^{6a} Distilled, degassed water (1 mL) was added, and the mixture was kept at –20 °C for 5 min. The mixture was then cooled to –80 °C, and filtered into a Schlenk flask that had been charged with hexane (150 mL). A tan powder precipitated, which was collected by filtration, washed with hexane (3×10 mL), and dried under vacuum to give **4**⁴ BF_4^- (1.008 g, 1.555 mmol, 87%), mp 132–136 °C. IR (cm^{-1} , KBr): ν_{NO} 1685 s. 1H NMR (δ , CD_2Cl_2 , –70/25 °C): 7.63–7.31 (m, 3 C_6H_5), 5.53/5.48 (s, C_5H_5), 6.36/5.41 (br s, H_2O). $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2 , –70 °C): 133.2 (d, $J_{CP} = 10.7$ Hz, *o*-Ph), 133.1 (d, $J_{CP} = 55.0$ Hz, *i*-Ph), 130.9 (s, *p*-Ph), 128.7 (d, $J_{CP} = 11.1$ Hz, *m*-Ph), 91.2

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(s, C₅H₅). ³¹P{¹H} NMR (ppm, CD₂Cl₂) 19.1 (s). Anal. Calcd for C₂₃H₂₂BF₄NO₂Pr: C, 42.60; H, 3.42; N, 2.16. Found: C, 42.79; H, 3.54; N, 2.11.

Isolation of [(η⁵-C₅H₅)Re(NO)(PPh₃)(OH₂)]⁺PF₆⁻ (4⁺PF₆⁻). A Schlenk tube was charged with (η⁵-C₅H₅)Re(NO)(PPh₃)(H) (**15**, 0.106 g, 0.195 mmol),¹⁹ CH₂Cl₂ (5 mL), and a stir bar, and cooled to -80 °C. Then Ph₃C⁺PF₆⁻ (0.076 g, 0.196 mmol) was added with stirring. After 15 min, distilled, degassed water (100 μL, 5.56 mmol) was added. The solution was allowed to slowly warm to -20 °C and then transferred via cannula to a Schlenk flask that contained stirring hexane (40 mL). A brown powder precipitated, which was collected by filtration, washed with hexane (10 mL), and dried under vacuum to give 4⁺PF₆⁻ (0.125 g, 0.177 mmol, 91%), mp 123-127 °C dec. IR (cm⁻¹, KBr): ν_{NO} 1681 s, ν_{PF} 841 s. ¹H NMR (δ, CD₂Cl₂): 7.74-7.17 (m, 3 C₆H₅), 5.41 (br s, H₂O), 5.37 (s, C₅H₅). ³¹P{¹H} NMR (ppm, CD₂Cl₂, -80 °C): 19.8 (s, PPh₃), -144.5 (sept, J_{PF} = 713 Hz, PF₆).

Generation of [(η⁵-C₅H₅)Re(NO)(PPh₃)(OH₂)]⁺X⁻ (4⁺X⁻). A Schlenk tube was charged with **5** (0.314 g, 0.562 mmol), CH₂Cl₂ (20 mL), and a stir bar and cooled to 0 °C. Then aqueous HF (0.500 mL, 13.9 mmol) was added dropwise with stirring. After 1 h, the cold bath was removed. After an additional hour, solvents were removed under vacuum. The residue was washed with hexane and dissolved in CH₂Cl₂

(ca. 10 mL). Hexane was rapidly added, and the resulting precipitate was collected by filtration and dried under vacuum to give 4⁺X⁻ (0.270 g, ca. 0.45 mmol, 81%). IR (cm⁻¹, KBr): ν_{NO} 1683 s. ³¹P{¹H} NMR (ppm, CH₂Cl₂): 20.4 (s).

B. A 5-mm NMR tube was charged with **5** (0.036 g, 0.064 mmol) and CH₂Cl₂ (0.5 mL) and capped with a septum. The tube was cooled to 0 °C and aqueous HF (0.005 mL, 0.14 mmol) was added. The sample was kept at 0 °C for 5 min and then allowed to warm to room temperature. ³¹P{¹H} NMR (ppm, CH₂Cl₂): 19.6 (s).

Reaction of 4⁺BF₄⁻ and CH₃CN. A 5-mm NMR tube was charged with 4⁺BF₄⁻ (0.0157 g, 0.0241 mmol) and Ph₃SiCH₃ (0.0115 g, 0.0419 mmol) and capped with a septum. The tube was cooled to -80 °C, and CD₂Cl₂ (0.8 mL) and CH₃CN (0.0040 mL, 0.078 mmol) were sequentially added via syringe. The tube was warmed to 25 °C as ¹H and ³¹P NMR spectra were periodically recorded. After 6 h at room temperature, complete conversion to [(η⁵-C₅H₅)Re(NO)(PPh₃)(NCCH₃)]⁺BF₄⁻ (**14**, >99%)^{6a,c} and water (>99%) had occurred, as assayed by integration of their ¹H NMR resonances (δ 5.55 and 1.59) relative to the standard (δ 0.84).

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Chemistry of Copper(I) β-Diketonate Complexes. 2.¹ Synthesis, Characterization, and Physical Properties of (β-Diketonato)copper(I) Trimethylphosphine and Bis(trimethylphosphine) Complexes

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The volatile copper(I) complexes (β-diketonato)Cu(PMe₃)_n, where β-diketonate = hexafluoroacetylacetonate (hfac), trifluoroacetylacetonate (tfac), and acetylacetonate (acac) for n = 1 and 2 and β-diketonate = dipivaloylmethanate (dpm) and dibenzoylmethanate (dbm) for n = 1 have been prepared in high yield. These species have been characterized by spectroscopy and by elemental analysis. A number of derivatives have been characterized by single-crystal X-ray diffraction. The compound (hfac)Cu(PMe₃) crystallizes in the space group P $\bar{1}$ with a = 10.801 (2) Å, b = 12.676 (3) Å, c = 14.946 (3) Å, α = 91.10 (3)°, β = 100.65 (3)°, γ = 94.06 (3)°, Z = 6, R = 6.71%, and R_w = 7.26% for 3751 reflections. The compound (dpm)Cu(PMe₃) crystallizes in the space group P $\bar{1}$ with a = 10.193 (3) Å, b = 12.059 (3) Å, c = 14.547 (3) Å, α = 96.40 (2)°, β = 91.54 (2)°, γ = 90.65 (2)°, Z = 4, R = 5.34%, and R_w = 5.57% for 5261 reflections. The compound (dbm)Cu(PMe₃) crystallizes in the space group Cmc2₁ with a = 18.776 (6) Å, b = 7.995 (3) Å, c = 11.872 (4) Å, Z = 4, R = 2.72%, and R_w = 2.83% for 1620 reflections. While (acac)Cu(PMe₃) and (tfac)Cu(PMe₃) have only limited thermal stability, (hfac)Cu(PMe₃) is thermally stable for at least 4 days at its melting point (67 °C). The vapor pressure of (hfac)Cu(PMe₃) has been measured as a function of temperature, revealing reasonable volatility (100 mTorr at 60 °C). From the plot of log (vapor pressure) versus reciprocal temperature, an enthalpy of vaporization (ΔH_{vap}) of approximately 10 kcal/mol was obtained.

Introduction

The chemical vapor deposition (CVD) of metals from metal-organic molecules is the subject of much interest as a result of potential applications in the microelectronics industry.² The use of molecular metal-organic compounds as the source of the metal in CVD experiments, as distinct from the use of the metals themselves in physical vapor deposition (PVD) experiments, provides the potential advantages of conformal film coverage and selective deposition. However, until fairly recently, relatively little effort has been directed toward the design of metal-organic compounds specifically as precursors for CVD of metal films, especially with respect to selective deposition.

When metal-organic compounds are designed specifically for CVD of metals, the following criteria should be met. (i) The precursor should have a high vapor pressure to allow high deposition rates and controlled introduction of the precursor into the reactor. (ii) The precursor should be a liquid at the vaporization temperature used. This circumvents variable vaporization

rates due to surface area changes during evaporation associated with solid precursors. (iii) A suitable (thermal) decomposition mechanism should be in place to allow clean removal of the supporting ligands and produce pure films with low resistivity values close to those of the bulk metal. (iv) Selective deposition onto a specific material in the presence of several others is desirable over a wide temperature range.

The CVD of copper films has traditionally been carried out by using copper(II) β-diketonate compounds.³⁻⁹ While these

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