appears to be synchronous with this second step (Scheme IV).

Intramolecular linkage isomerizations are well documented, e.g., $[(NH_3)_5CoSCN]^{2+} \rightarrow [(NH_3)_5CoNCS]^{2+}$; $[(NH_3)_5CoONO]^{2+} \rightarrow [(NH_3)_5CoNO_2]^{2+}$.[29] None, however, have involved ambident functional groups incorporated into a chelate arm, and the present facile S- to O-sulfoxide rearrangement with synchronous ring expansion therefore assumes especial interest. It is also worthy of comment that while both O- and S-bound sulfoxide complexes are known, particularly for the noble metals, interconversion between these linkage isomers does not seem to have been observed. In this instance the cobalt(III) center is a rather hard acid and might be expected to prefer oxygen as the donor. Also the S-bound form is sterically crowded. Both would assist the rearrangement. Even so, it is a surprisingly rapid process.

A curious aspect of the chemistry is the resistance of the chelated sulfoxides toward chlorine oxidation. The crystallography establishes O-coordination for one of the two isomers in the solid state, and the lack of intense UV absorption typifying Co–S bonding indicates this linkage is retained in solution. It seems likely that chelation sterically inhibits sulfur from achieving the required trigonal-bipyramidal geometry which would result from addition of Cl^+ followed by the addition of H_2O to effect the oxidation to the sulfone. Oxidation of the monodentate sulfoxides, however, would not be inhibited in the same way, and it has been observed in at least two instances, i.e., $[(NH_3)_5CoO{=}S(Me)_2]^{2+}$ and $[(NH_3)_5CoO{=}\overline{S(CH_2)_3CH_2}]^{3+}$.[16]

A similar explanation may account for the difficulty in oxidizing the S-methylcysteamine chelate (Scheme I). An analogous trigonal bipyramid has to be achieved, and the chelate imparts a substantial restriction on the angles that can be adopted at the S atom during the process. The inverse process, however, is quite different. The oxidation of the bound mercaptide ion to the sulfenate ion and the subsequent use of the latter as a nucleophile for an alkyl halide require quite different and less demanding paths. The restrictions imposed by the chelate on the geometry about S do not impinge so effectively on this chemistry.

The O-bonded sulfoxide diastereoisomers have been prepared independently from *cis*-$[Co(en)_2(Me_2SO)_2]^{3+}$ and (racemic) free ligand and also from *cis*-$[Co(en)_2X(NH_2(CH_2)_2SOCH_3)]^{n+}$ (X = Br^-, Cl^-, N_3^-, Me_2SO, OH_2) by ring closure with substitution of X. The products were separated by fractional crystallization and chromatography. The hope that five-membered ring formation (with S bonding) would be preferred to six-membered (with O bonding) was not realized, and this is consistent with the rearrangement observed in the oxidation. The starting material in all these cases was a ~50:50 mixture of epimers, and the product was a similar mixture of the chelated sulfoxides; i.e., ring closure occurs largely with retention of the configuration about cobalt.[28]

It appears that chiral chelate sulfoxides may be synthesized from resolved cobalt(III) mercaptide complexes, utilizing the methods for the stereospecific addition of oxygen and followed by the stereospecific addition of the alkyl group to the sulfenate as described here. However the generality of the method has yet to be explored and the specificity should be confined largely to the chelate systems.

Acknowledgment. We thank the Microanalytical Section of the John Curtin School of Medical Research, A.N.U., for the C, H, N, and S analyses.

Supplementary Material Available: Thermal parameters (Table VII), amplitudes of root mean square vibrations (Table VIII), and a listing of observed and calculated structure factors for the 1394 reflections used in the refinement (12 pages). Ordering information is given on any current masthead page.

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Synthesis and Electrophile-Induced Disproportionation of the Neutral Formyl (η-C_5H_5)Re(NO)(PPh_3)(CHO)

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Abstract: The crystalline, thermally stable neutral formyl (η-C_5H_5)Re(NO)(PPh_3)(CHO) (**3**) is synthesized by reaction of cation $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**2a**) with either $Li(C_2H_5)_3BH$ in THF or $NaBH_4$ in THF/H_2O. Precursor **2a** is in turn prepared by the sequential treatment of $[(\eta\text{-}C_5H_5)Re(NO)(CO)_2]^+BF_4^-$ (**1**) with $C_6H_5I^+O^-/CH_3CN$ (oxidative removal of CO) and PPh_3. At 50–105 °C in appropriate solvents, **3** decomposes (in variable yields) to rhenium hydrides. **3** is reduced by BH_3·THF to (η-C_5H_5)Re(NO)(PPh_3)(CH_3) (**4**). When **3** is reacted with CH_3SO_3F or CF_3CO_2H, facile formyl ligand disproportionation occurs: **4** and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+$ salts form. Potential intermediates in these disproportionations are independently synthesized. Reaction of **4** with $Ph_3C^+X^-$ (X = PF_6, BF_4) at −78 °C affords the cationic methylidene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+X^-$ (**5**), which can be isolated as a stable solid. **5** is further characterized by preparing $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\text{–}L^+)]$ adducts where L = pyridine (**6a**), 2,6-dimethylpyridine (**6b**), PPh_3 (**7a**), and P(n-C_4H_9)$_3$ (**7b**). Reaction of **5** or **6a** with excess CH_3O^- yields (η-C_5H_5)Re(NO)(PPh_3)(CH_2OCH_3) (**8**). Addition of 0.5 equiv of CH_3SO_3F to **8** gives **4**, $(CH_3)_2O$, and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOCH_3)]^+SO_3F^-$ (**9a**) in a 1.0:1.0:1.1 ratio. On the basis of hydride transfer reactions observed between **3** and **5**, **3** and **9a**, and **8** and **5**, and low temperature ^1H NMR monitoring, the CH_3SO_3F-induced disproportionation of **3** is proposed to involve the sequence of intermediates **3** → **9a** → **8** → **5** → **4**. Reaction of **3** with CF_3CO_2H is suggested to occur similarly; initial formation of unstable hydroxymethylidene intermediate $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOH)]^+X^-$ (X = CF_3CO_2, **10a**) can be observed by ^1H and ^{13}C NMR spectroscopy. When X = CF_3SO_3, this salt can be isolated. Attempts to prepare the proposed hydroxymethyl intermediate (η-C_5H_5)Re(NO)(PPh_3)(CH_2OH) (**11**) are detailed. Syntheses of (η-C_5H_5)Re(NO)(PPh_3)(COOH) (**2a** + NaOH) and (η-C_5H_5)Re(NO)(PPh_3)(H) (**2a** + $(CH_3)_3N^+O^-/LiAlH_4$) are also described, and the relevance of the above reactions to catalytic CO reduction is discussed.

Declining domestic crude oil reserves have prompted a renewed interest in the chemistry of CO/H_2 gas mixtures ("synthesis gas"), which are readily available from coal and can be transformed by metal catalysts into a variety of organic molecules (methane, methanol, higher alkanes and alcohols, glycols, and gasoline hydrocarbons) normally derived from petroleum.[2,3] In particular,

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work in numerous laboratories is being directed at the development of milder and/or more selective CO reduction catalysts[3-9] and the delineation of CO reduction mechanisms.[2,10-18] Reactions of CO and H_2 can be effected over both homogeneous[5,6,19-21] and heterogeneous[2,7-9] catalysts, and diverse mechanistic pathways have been invoked to account for the variety of organic products which can be formed.[2,3,18,19c] In our laboratory, we have attempted to systematically synthesize homogeneous transition-metal complexes containing uncommon single-carbon ligand types (—CHO, =CHOH, $-CH_2OH$, $\overset{4}{-}C$, ≡CH, $=CH_2$, etc.) which are considered to be plausible intermediates in CO reduction.[22-25] By study of their basic chemistry, we have sought to gain insight into possible catalyst reaction pathways.

Catalyst-bound formyls are believed to be initial intermediates in the conversion of CO/H_2 gas mixtures to oxygen-containing organic products.[2,6,19,26] The first isolable homogeneous formyl complex, $(CO)_4Fe(CHO)^-$, was prepared in 1973 by Collman and Winter by reaction of $(CO)_4Fe^{2-}$ with formic acetic anhydride.[28,29] Subsequent work in Casey's laboratory,[11c] ours,[22] and elsewhere[30] established that trialkyl- and trialkoxyborohydrides react with a variety of neutral metal carbonyl compounds to yield anionic formyl complexes. These were found to be powerful hydride donors which reduced electrophiles such as ketones, alkyl halides, and metal carbonyls.[11c,22,29] However, formyl ligand reduction could be effected only under forcing conditions with hydridic reagents. We then turned our attention to the synthesis of *neutral* formyl complexes.[24] On the basis of literature precedent, the prospects for obtaining isolable complexes of this type were much less certain. However, it was felt that their chemistry might have a stronger parallel to that of catalyst-bound formyls. Initial studies on the reactions of metal carbonyl cations with $Li(C_2H_5)_3BH$ uncovered a series of neutral formyls which were kinetically unstable and/or incapable of rigorous purification,[24a] an account of which will be given elsewhere.[24d] One of these, $(\eta\text{-}C_5H_5)Re(NO)(CO)(CHO)$, has been independently synthesized and studied in detail by Casey[11a,b] and Graham.[13] Our ultimate objective, however, was to prepare a crystalline, analytically pure neutral formyl complex whose physical and chemical properties could be subjected to unambiguous definition.[31] In this paper, we describe (a) the attainment of this goal in the synthesis of the neutral formyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$, (b) remarkable low-temperature transformations of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ which result in formyl ligand disproportionation, and (c) independent syntheses of several intermediates in these disproportionations. These include $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+$ and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOH)]^+$ salts, which are the first isolable electrophilic methylidene and hydroxymethylidene complexes, respectively. As noted above, $=CH_2$ and =CHOH ligands may also be important intermediates in catalytic CO reduction.

Results

Synthesis of Precursor Carbonyl Cations. The rhenium carbonyl cation $[(\eta\text{-}C_5H_5)Re(NO)(CO)_2]^+BF_4^-$ (**1**)[32] was prepared from readily avalable $(\eta\text{-}C_5H_5)Re(CO)_3$ as shown in eq 1. However, the desired phosphine-substituted cation $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**2a**) could not be synthesized from **1** by standard thermal or photochemical substitution methods. The possibility of introducing the PPh_3 ligand at an earlier stage was therefore investigated. As described in the literature,[33] photolysis of $(\eta\text{-}C_5H_5)Re(CO)_3$ in the presence of PPh_3 afforded $(\eta\text{-}C_5H_5)Re(PPh_3)(CO)_2$ in modest (46%) yields. When $(\eta\text{-}C_5H_5)Re(PPh_3)(CO)_2$ was treated with $NO^+BF_4^-$ (eq 1), however, only a 41% yield of **2a** was obtained; interestingly, the major product (43%) was the dicarbonyl cation **1**.

Although the preceding synthesis of **2a** sufficed for exploratory studies, a higher yield route to **2a** was desired. Trimethylamine

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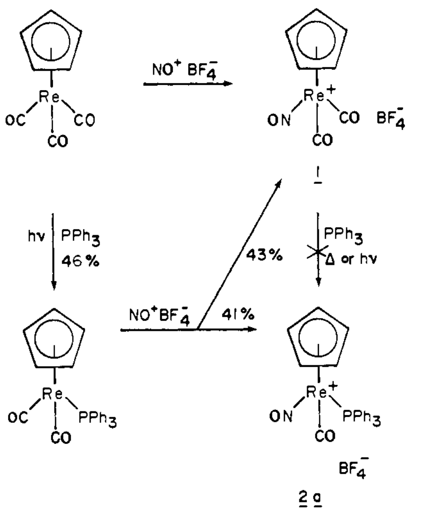
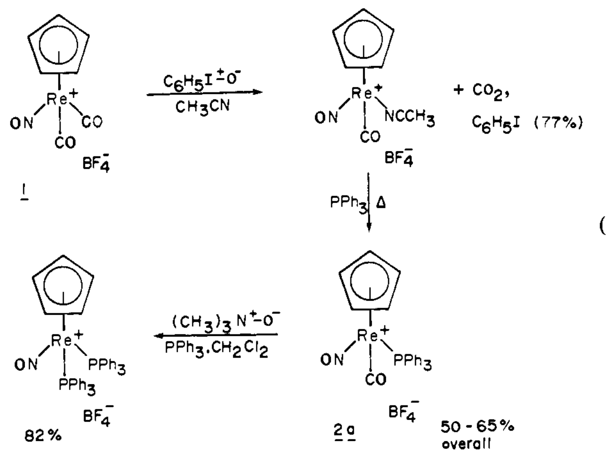


(1)

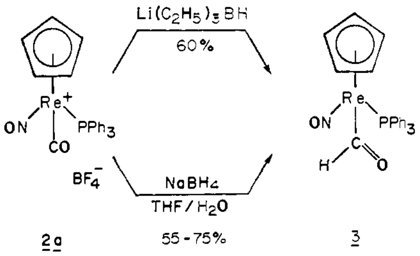
N-oxide has been recently popularized as a reagent for the oxidative removal of coordinated CO.[23a,34] Unfortunately, its reaction with **1** in the presence of PPh_3 did not yield any CO-containing products; gross decomposition of the starting material appeared to occur.

Consequently, a milder reagent for the oxidation of ligating CO to CO_2 was sought. After surveying several possibilities, it was found that the reaction of **1** in CH_3CN with commercially available iodosobenzene ($C_6H_5I^+O^-$) resulted in the smooth formation of $[(\eta\text{-}C_5H_5)Re(NO)(CO)(NCCH_3)]^+BF_4^-$ (eq 2). Analysis of this reaction by GLC indicated iodobenzene to be present in 77% yield. The $[(\eta\text{-}C_5H_5)Re(NO)(CO)(NCCH_3)]^+BF_4^-$ could be purified or simply refluxed in crude form with PPh_3 in 2-butanone (substitution was slow in refluxing acetone) to afford desired product **2a** (eq 2) in 50–65% overall yields. When **2a** was treated with $(CH_3)_3N^+O^-$ in the presence of PPh_3 (eq 2), substitution occurred to give the dark red bis(triphenylphosphine) complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)_2]^+BF_4^-$; we were not able to prepare this compound directly from **1**, $(CH_3)_3N^+O^-$, and PPh_3.



(2)

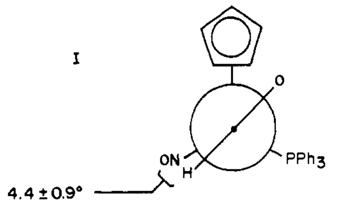
Synthesis and Properties of the Formyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ (3). Reaction of carbonyl cation **2a** with $Li(C_2H_5)_3BH$ afforded the thermally stable, air-sensitive neutral formyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ (**3**) in 60% isolated yield after column chromatography (eq 3). Alternatively, reaction of **2a** with $NaBH_4$ in THF/H_2O afforded **3** in 55–75% yields following recrystallization.



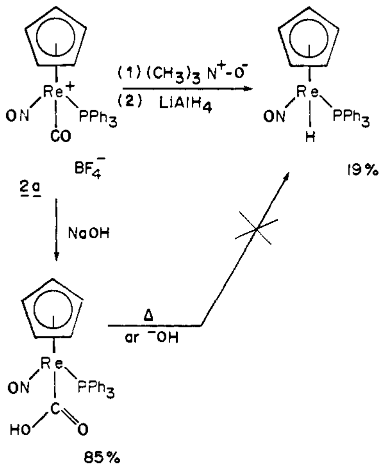
(3)

NMR spectral properties of **3** were in accord with those previously noted for formyl complexes (Experimental Section).[29] IR spectra showed $\nu_{C=O}$ to be between 1565 and 1558 cm^{-1}, which is unusually low for a >C=O functionality. Honey yellow crystals of **3** were obtained by THF/hexane recrystallization, and a single-crystal X-ray structure was determined, as described in a preliminary communication.[24b] The formyl ligand was found to be approximately trigonal (∠Re–C–O = 128.1 (8)°), and the rhenium–formyl bond distance was found to be 2.055 (10) Å. An additional significant structural feature is the near coplanarity of the formyl ligand with the C–Re–NO plane, as shown in the Newman projection, I (a view down the formyl carbon–rhenium bond). The dihedral angle subtended by these ligands is 4.4 ± 0.9°.

I



Since metal formyl complexes often decompose to metal hydrides,[29] authentic samples of cyclopentadienylrhenium hydrides were sought prior to studying the thermal chemistry of **3**. Graham had earlier reported the synthesis of $(\eta\text{-}C_5H_5)Re(NO)(CO)(H)$ by reaction of cation **1** with $(C_2H_5)_3N/H_2O$.[35] A Re–COOH species, which undergoes base-promoted decarboxylation, has been shown to be an intermediate in this preparation.[11b] We found that a homologous compound, $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COOH)$, could be prepared from **2a** as shown in eq 4. Disappointingly, subsequent thermal decomposition (or reaction with $(C_2H_5)_3N$) did not result in detectable quantities of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$. However, we were able to synthesize $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ in low but serviceable yield from **2a** as shown in eq 4.



(4)

When heated in solid form, formyl **3** underwent gradual (ca. 91 °C) decomposition. A sample was pyrolyzed for 2 h at 125 °C. ^{1}H NMR analysis of the decomposition residue did not indicate any $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (dec pt 183–186 °C) or $(\eta\text{-}C_5H_5)Re(NO)(CO)(H)$. These hydrides were also undetectable in partially decomposed samples of **3**. Decomposition of **3** at 105 °C in toluene-d_8 ($t_{1/2} \simeq 1$ h) cleanly gave a ca. 1:1 mixture of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (d, δ −9.29, $J_{^1H-^{31}P}$ = 29

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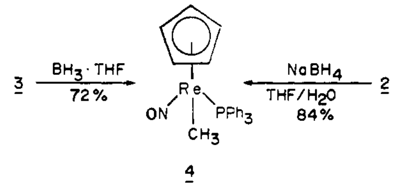
(35) Stewart, R. P.; Okamota, N.; Graham, W. A. G. *J. Organomet. Chem.* **1972**, *42*, C32.

Hz) and $(\eta\text{-}C_5H_5)Re(NO)(CO)(H)$ (s, δ −8.16). Formyl **3** decomposed over the course of 4 days at 60 °C or 10–12 days (sealed NMR tube) at 50 °C in THF-d_8; $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ and $(\eta\text{-}C_5H_5)Re(NO)(CO)(H)$ formed, but only in 1–13% yields (each) vs. internal standard. Rhenium hydrides were not detected when **3** was decomposed over ca. 40 min at 70 °C in $CDCl_2CDCl_2$. Decomposition rates were measured in THF-d_8 and toluene-d_8, but $d[\mathbf{3}]/dt$ followed neither first nor second-order rate laws.

Other experiments were conducted to assist in interpreting the above decomposition data. When **3** was decomposed in toluene-d_8 at 80 °C in the presence of 1.18 equiv of PEt_3, the normal decomposition products were accompanied by a new rhenium hydride (d, δ −10.48, $J_{^1H-^{31}P}$ = 29 Hz, and s, 4.71), assigned as $(\eta\text{-}C_5H_5)Re(NO)(PEt_3)(H)$. However, at 70% decomposition (24 h), no new formyl resonances were detectable; only **3** remained. In separate experiments, $(\eta\text{-}C_5H_5)Re(NO)(CO)(H)$ was reacted with PEt_3 and PPh_3 in toluene-d_8. With PEt_3, conversion to $(\eta\text{-}C_5H_5)Re(NO)(PEt_3)(H)$ was complete after 4 h at 95 °C. With PPh_3, reaction was much slower; $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ was present in ca. 1% yield after 2 days at 95 °C and 12% yield after an additional 2 days at 105 °C. No reaction occurred when $(\eta\text{-}C_5H_5)Re(NO)(CO)(H)$ was heated at 70 °C for 24 h in $CDCl_2CDCl_2$; after an additional 24 h at 95 °C, the hydride had disappeared and a new resonance at δ 3.96 ($CDHClCDCl_2$, also detectable in the formyl decomposition) was present (lit. δ 3.97, $CH_2ClCHCl_2$).[36]

Reductions of **3** were attempted. No reaction was observed between **3** and H_2 (150 psi, 2 days) at room temperature. Similarly, neither $(CH_3CH_2)_3SiH$ (excess, 25 °C, 2 days) nor $(\eta\text{-}C_5H_5)Re(NO)(CO)(H)$ (25 °C, 1 day) effected any reaction. However, $BH_3\cdot THF$ smoothly reduced **3** to the methyl complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**4**) in 72% yield. Compound **4** was also synthesized in a preparatively superior route (84% yield) by reacting **2a** with $NaBH_4$ in THF (eq 5).



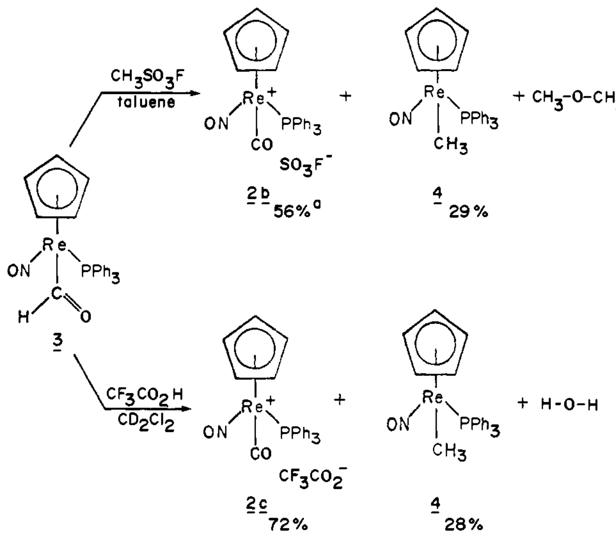
(5)

Electrophile-Induced Disproportionations of 3. The reaction of **3** with CH_3SO_3F was investigated with the objective of effecting a seemingly well-precedented[37] O-methylation. Addition of 1.0 equiv of CH_3SO_3F to **3** (ca. 0.1 M in toluene) at −78 °C, followed by warming to room temperature, afforded $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+SO_3F^-$ (**2b**) and $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**4**) in 56% and 29% isolated yields, respectively. When this reaction was repeated with CD_3SO_3F instead of CH_3SO_3F, the ratio of **4**-d_0:**4**-d_3 was ≥99.9:0.1, as determined by mass spectrometry. Thus the methyl ligand in **4** does not originate from the CH_3SO_3F. When **3** and CH_3SO_3F were similarly reacted in CH_2Cl_2, variable amounts of a third organometallic product (**9a**; vide infra) formed; small quantities of this species appeared sporadically in reactions conducted in toluene. ^1H NMR monitored experiments in CD_2Cl_2 indicated $(CH_3)_2O$ (confirmed by GLC) to be the only non-rhenium-containing product.

A similar reaction occurred between **3** and CF_3CO_2H. After adding 1.0 equiv of CF_3CO_2H to **3** (0.14 M in CD_2Cl_2) at −78 °C and warming to room temperature, $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+CF_3CO_2^-$ (**2c**, 72%) and **4** (28%) were detected by ^1H NMR spectroscopy. A broad resonance at δ 10.30 was assigned to a mixture of H_2O and unreacted CF_3CO_2H (Experimental Section).

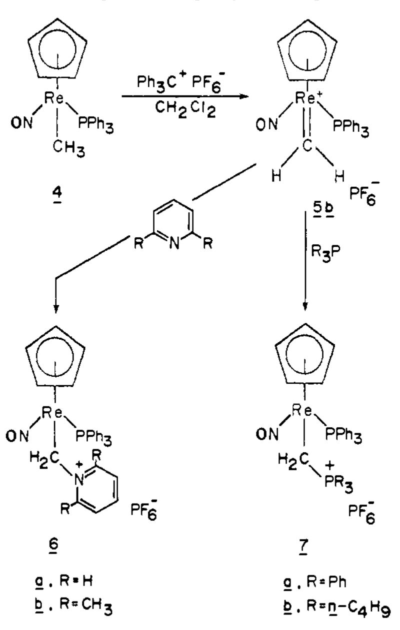
The above data are summarized and compared in Scheme I. The possibility that a general mechanism might be operative was considered. Carbonyl cation products **2** can be formally derived by hydride loss from formyl **3**. As a working hypothesis, species of the general formula $Re^+{=}CHOE$ (E = electrophile-derived groups CH_3 or H), $Re{-}CH_2OE$, and $Re^+{=}CH_2$ were postulated as plausible precursors to **4**. The following sections describe attempts to *synthesize* such compounds, *establish* their chemical properties, and *assay* for their intermediacy in Scheme I.

Scheme I. Electrophile-Induced Disproportionations of 3



[a] A third cationic product (**9a**) is detected in some reactions.

Reaction of 3 with CH_3SO_3F. Synthesis and Properties of Intermediates. When **4** was reacted with $Ph_3C^+BF_4^-$ or $Ph_3C^+PF_6^-$ (1.05–1.10 equiv) in CD_2Cl_2 at −70 °C, the cationic methylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+X^-$ (**5a**, X = BF_4; **5b**, X = PF_6) formed in 88–100% spectroscopic yield (eq 6). *Two* low-field methylidene protons were present in ^1H NMR spectra of **5** (**5a**, −33 °C, CD_2Cl_2; δ 15.65, 15.48; *no* coalescence up to 25 °C), and the methylidene ^{13}C NMR resonance was observed at 290.3 ppm. In solution, **5** decomposed slowly at −10 °C and rapidly at room temperature. However, when preparative-scale reactions were worked up at −23 °C, **5b** was obtained as an off-white powder which was pure by ^1H NMR spectroscopy. Methylidene **5b** could be stored at 0 °C under N_2 for over 1 week without visible deterioration and tolerated brief exposures to air at 25 °C.



(6)

As would be expected of an electrophilic methylidene ligand, **5b** formed adducts with numerous nitrogen and phosphorus nucleophiles. Some examples are given in eq 6. These reactions occurred rapidly; formation of **7a** from **5b** and PPh_3 (each 0.057

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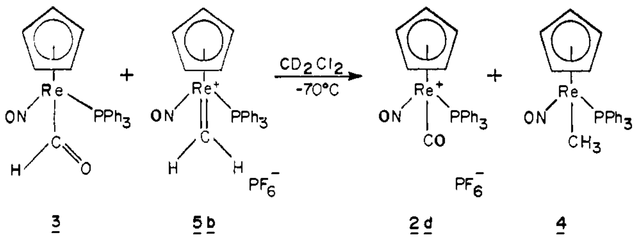
(36) "The Sadtler Standard NMR Spectra", Sadtler Research Laboratories: Philadelphia, PA, 1974; Vol. 26, spectrum 16882.

(37) Treichel, P. M.; Wagner, K. P. *J. Organomet. Chem.* **1975**, *88*, 199.

M in CD_2Cl_2) was complete within 3 min at −70 °C. Generally, adducts were crystalline and thermally stable. However, **6b** slowly decomposed to methylidene-derived products in solution at room temperature. No reaction was observed between **5b** and $(CH_3)_2O$.

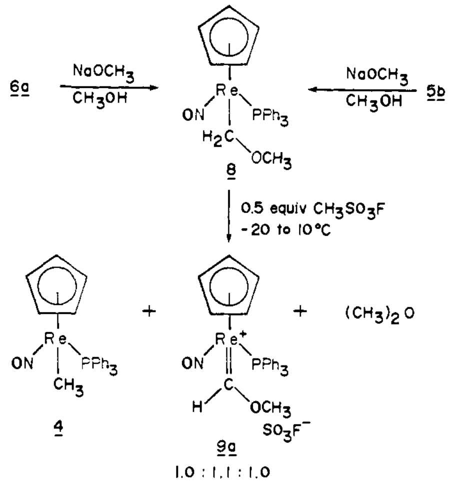
Of relevance to the disproportionation mechanism proposed below, an immediate reaction occurred when **5b** was treated with **3** in CD_2Cl_2 at −70 °C. ^1H NMR indicated the clean formation of **4** and **2d**, which were subsequently isolated in 60% and 90% yields, respectively (eq 7). Thus **5b** in sufficiently electrophilic to function as a hydride abstractor.



(7)

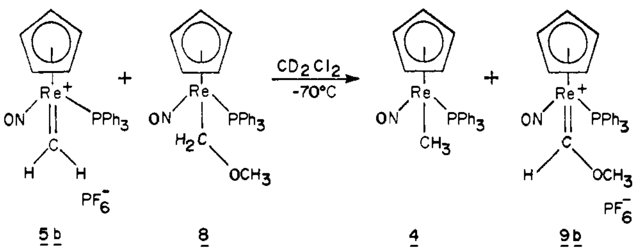
A second plausible intermediate in the reaction of **3** with CH_3SO_3F, (η-C_5H_5)Re(NO)(PPh_3)(CH_2OCH_3) (**8**), was easily synthesized by reacting **6a** (eq 7) with excess $NaOCH_3/CH_3OH$ (60–70% yields after recrystallization). Alternatively, direct reaction of **5b** with excess $NaOCH_3$, when carefully executed, also afforded high yields of **8**. Since **8** was viewed as a logical precursor (subsequent to initial O-methylation by CH_3SO_3F) to **5c** (**c** = SO_3F^- salt of **5**) and $(CH_3)_2O$, attempts were made to observe this transformation.

Reactions of **8** with CH_3SO_3F occurred slowly at −20 °C and rapidly at 10 °C. Even through $(CH_3)_2O$ was always observed to form in ^1H NMR monitored reactions, in no instance (even under optimum inverse addition conditions) could methylidene **5c** be detected as an intermediate or product. When **8** was treated with 0.5 equiv of CH_3SO_3F, approximately equimolar quantities of three products formed: **4**, [(η-C_5H_5)Re(NO)(PPh_3)($CHOCH_3$)]$^+SO_3F^-$ (**9a**), and $(CH_3)_2O$ (eq 8).



(8)

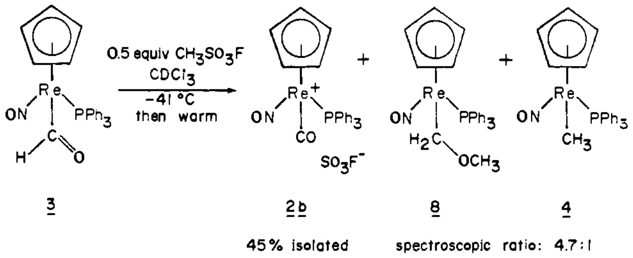
Equation 8 provides a means by which another possible intermediate in the formyl disproportionation, **9a**, can be synthesized. When the reaction of **8** with CH_3SO_3F is conducted in toluene, **9a** (formally O-methylated **3**) precipitates as a solvate.[38] Although methylidene **5c** is not an observed intermediate in eq 8, it should be noted that product **4** can be formally derived from **5c** + hydride. Also, product **9a** can be formally derived by hydride loss from starting material **8**. The logical inference that initially formed **5** might react rapidly with **8** was tested by mixing authentic independently prepared samples in CD_2Cl_2 at −78 °C (eq 9). A



(9)

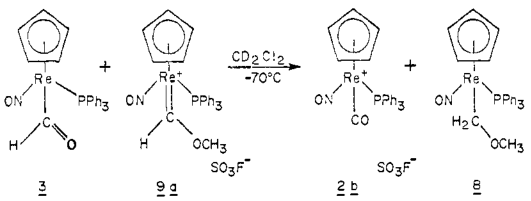
^1H NMR spectrum, recorded at −70 °C within a few minutes after mixing, indicated that complete hydride transfer had occurred to give **4** and **9b** (**9b** = PF_6^- salt of **9**).

Attempts of prepare [(η-C_5H_5)Re(NO)(PPh_3)($CHOCH_3$)]$^+$ (**9**) by direct reaction of formyl **3** with trimethyloxonium salts or CH_3SO_3F (even under inverse addition conditions) were uniformly unsuccessful. When **3** was treated with 0.5 equiv of CH_3SO_3F at −41 °C in $CDCl_3$, the product distribution shown in eq 10 was obtained. The two major products, **2b** and **8**, can



(10)

be formally derived by H⁻ loss from starting **3** and H⁻ attack upon **9a**, respectively. The logical inference that initially formed **9a** might rapidly react with **3** was tested by mixing authentic independently prepared samples in CD_2Cl_2 at −78 °C (eq 11). A



(11)

^1H NMR spectrum, recorded at −70 °C within a few minutes after mixing, indicated that complete hydride transfer had occurred. Compound **8** formed in quantitative spectroscopic yield, and **2b** was isolated (in a separate experiment) in 93% yield.

Reaction of 3 with CH_3SO_3F. ^1H NMR Monitoring. Having synthesized authentic samples of **5**, **8**, and **9**, we were able to rigorously interpret the ^1H NMR monitored reaction of **3** with CH_3SO_3F (1:1 ratio). Experiments in toluene-d_8 did not yield quantitative data due to the precipitation of cationic products, but CD_2Cl_2 solutions in which initial reactant concentrations were <0.10 M remained homogeneous. In a representative experiment, **3** and CH_3SO_3F were mixed at −78 °C in CD_2Cl_2 and a 200-MHz ^1H NMR spectrum (see Supplementary Material) was recorded 10 min after warming the sample to −73 °C. Additional spectra were recorded as the reaction was warmed further. Ratios of intermediates and products were determined by integration, as summarized in Table I.

Some disproportionation occurred (Table I) at −73 °C. In a few experiments, traces of **4** were also present at −73 °C. At −40 °C, **3** began to disappear rapidly, and **2b** and **8** were present in a 1:1 ratio. At this point, the reaction had essentially passed through a stage corresponding to eq 10.

Remaining **3** disappeared at −30 °C (Table I), and traces of **4** and $(CH_3)_2O$ increased. This stage of the reaction corresponds to the bottom portion of eq 8. At 25 °C, **8** had entirely reacted;

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[38] The 200-MHz ^1H NMR spectrum of **9a** is not temperature dependent from −70 to 25 °C. However, in spectra of optimized resolution, a second alkylidene complex (5–10%) is detectable. The amount of this complex remained in the 5–10% range after multiple recrystallizations from $CHCl_3$/petroleum ether. Accordingly, it is assigned to a second Re=C geometric isomer of **9a**; see ref 25 for a discussion of this phenomenon.

Table I. Intermediates and Products in the ^1H NMR Monitored Reaction of 3 with CH_3SO_3F in CD_2Cl_2

temp,[a] °C	3[b] (-CHO)	2b (-CO)$^+$	8 ($-CH_2OCH_3$)	4 ($-CH_3$)	9a ($=CHOCH_3$)$^+$	CH_3SO_3F	$(CH_3)_2O$
t_0	100					100	
−73	57	24	19			72	
−60	47	27	26			71	
−50	36	33	31			69	
−40	10	45	45			56	
−30	trace	51	49	trace		54	trace
−20		50	47	3		50	3
−10		53	42	5		49	5
0		51	32	9	7	27	8
10		50	22	14	14	44	11
20		49	11	19	21	43	14
25		56	0	20	23	39	17
25[c]		56[c]		28[c]	16[c]	51[c]	13[c]

[a] Product ratios were determined after ca. 15 min at the indicated temperature; the sample was subsequently warmed to the next temperature. Spectra are provided as supplementary material. [b] Ratios are based upon integrated intensities of the C_5H_5 and/or CH_3 resonances of the homogeneous reaction mixture; rhenium-containing products are normalized to 100. Accuracy is estimated to be ±10% for the major components at any given temperature; error limits are greater for the minor components. Some artifacts (e.g., absence of 9a at −10 °C; CH_3SO_3F concentrations above −10 °C) are apparent. [c] These data are for an identical experiment in which the sample was allowed to warm directly from −78 °C to room temperature.

in more concentrated reaction mixtures (as in eq 8), this step occurred more rapidly.

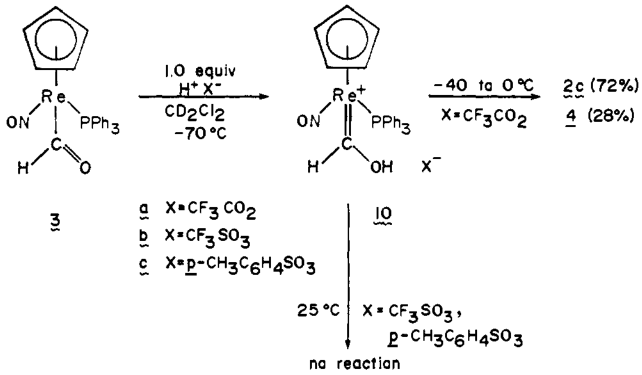
With additional standing, **4** reacted with CH_3SO_3F. Reaction of $(CH_3)_2O$ with CH_3SO_3F[39] did not appear to take place under the disproportionation conditions.

An analysis of the various limiting disproportionation stoichiometries is presented under Discussion. Final ratios of **4** to **9a** were somewhat higher (up to 2:1) when analogous reactions were *rapidly* brought from −78 °C to room temperature, as illustrated by the final entry in Table I.

Reaction of 3 with CF_3CO_2H. Attempted Syntheses of Intermediates. The reaction of **3** with CF_3CO_2H (1 equiv) in CD_2Cl_2 was NMR monitored at −70 °C. A single product formed rapidly and quantitatively. On the basis of ^1H and ^{13}C NMR data (Experimental Section), the hydroxymethylidene structure $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOH)]^+CF_3CO_2^-$ (**10a**) was assigned. Reaction of **10a** with $Li(C_2H_5)_3BH$ regenerated **3**, supporting the formulation of **10a** as a simple protonation product of **3**.

When CD_2Cl_2 solutions of **10a** were warmed, decomposition occurred starting at −40 °C. Mixtures of **2c** and **4** formed as described above (Scheme I), but without the intervention of ^1H NMR detectable intermediates.

Addition of stronger acids to **3** afforded more stable salts of **10**. Thus **3** and CF_3SO_3H reacted to give $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOH)]^+CF_3SO_3^-$ (**10b**; eq 12),[40] which was isolable as an off-white powder. **10b** showed no sign of decomposition when



(12)

warmed to 80 °C in $CDCl_2CDCl_2$. Similarly, **3** and $p\text{-}CH_3C_6H_4SO_3H$ reacted to give $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOH)]^+p\text{-}CH_3C_6H_4SO_3^-$ (**10c**), which showed no decomposition over the course of several days at 25 °C in CD_2Cl_2 (eq 12). No reaction took place between **3** and CH_3CO_2H at room temperature (1 day, CD_2Cl_2).

By analogy to the reaction of **3** with CH_3SO_3F, plausible intermediates in the reaction of **3** with CF_3CO_2H would also include methylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+CF_3CO_2^-$ and hydroxymethyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2OH)$ (**11**). Although BF_4^- and PF_6^- salts of the former are readily available (eq 6), the latter has proved elusive. Initial synthetic approaches were modeled after those which were successful for methoxymethyl **8** (eq 8). Thus, reactions of **5b**, **6a**, and **6b** (and other **5b**-amine adducts) were attempted under a variety of conditions with hydroxide ion sources such as NaOH and $(n\text{-}C_4H_9)_4N^+OH^-$. In most cases, the major neutral product was **4**. Some crude reaction mixtures contained ^1H NMR resonances which might be plausibly ascribed to **11**. However, separation of the putative **11** from **4** could not be effected by recrystallization (both are neutral), and $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2OR)$ compounds decompose upon attempted chromatography.

Since precedent exists for $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COOH)$ to serve as a OH^- donor,[41] its reaction with **5b** was investigated. However, ^1H NMR monitoring in CD_2Cl_2 at −73 °C indicated $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+PF_6^-$ (**2d**) and **4** to be the only products (ca. 2:1 ratio).

In view of the successful hydride transfer from formyl **3** to **9a** (eq 11), the synthesis of **11** from equimolar quantities of **3** and isolated **10b** was attempted. The reaction was monitored by ^1H NMR at −73 °C, at which temperature the low-field and C_5H_5 resonances of **3** and **10b** were replaced by single broad absorptions at δ 14.27 and 5.44, respectively. These shifted with additional warming, and at −13 °C individual C_5H_5 resonances due to $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+CF_3SO_3^-$ (**2e**) and **4** (ca. 3:1) emerged. Residual absorptions at δ 14.85 and 5.43 disappeared upon further warming, and some **3** reappeared. At 27 °C, only **2e**, **4**, and **3** remained (68:21:11 ratio).

Other approaches to **11** were modeled after successful syntheses of the carbonyl-substituted homologue $(\eta\text{-}C_5H_5)Re(NO)(CO)(CH_2OH)$.[11,13] Thus, numerous attempts were made to hydrolyze **8** ($CF_3CO_2H/(C_2H_5)_3N$) and partially reduce **2a** ($Na(C_2H_5)_2AlH_2$)[11,13] and **3**. These afforded **4** as the major product.

Discussion

Synthesis and Properties of 3. The synthesis of formyl **3** (eq 1–3) utilizes conventional reactions except for the step involving iodosobenzene (eq 2). The formation of byproducts CO_2 and iodobenzene in this reaction suggests that an initial $[(\eta\text{-}C_5H_5)$-

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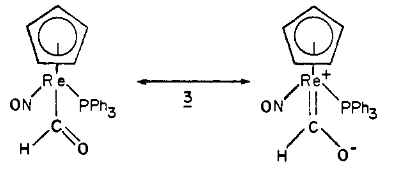
[39] Ahmed, M. G.; Alder, R. W.; James, G. H.; Sinnott, M. L.; Whiting, M. C. *J. Chem. Soc., Chem. Commun.* **1968**, 1533.

[40] Optimally resolved low-temperature ^1H NMR spectra of salts of 10 show as many as *four* geometric isomers (Re=C and C⋯OH) to be present (Experimental Section). This phenomenon has been noted with other $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOE)]^+$ species (but not with **9a**),[38] and will be fully treated in subsequent papers. Restricted carbon–oxygen bond rotation is well documented in M=CROR′ carbenes: Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Müller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237.

[41] Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627.

Re(NO)(CO)(COO–$^+IC_6H_5$)]BF_4^- adduct, similar to those which have been postulated for amine oxide decarbonylations,[23a,34] may form. A few previous reactions of iodosobenzene with organometallic compounds have been reported. For instance, Fischer-type carbenes L_nM=C(R)X can be oxidized to O=C(R)X compounds.[42] Iodosobenzene does not attack CO in neutral metal carbonyl complexes and is thus more selective than $R_3N^+O^-$ reagents; furthermore, a nonligating byproduct is formed (C_6H_5I vs. R_3N).

Physical properties of **3** provide some insight to the origins of its stability. The low IR stretching frequency associated with the formyl carbon–oxygen bond indicates an important resonance contribution by zwitterion **3b** to the ground state of **3**. The resultant back-bonding strengthens the rhenium–formyl carbon bond. Amides, which also have low $\nu_{C=O}$, have many properties which are best accounted for by a zwitterionic resonance form R_2N^+=C(R′)O^-.



3a 3b

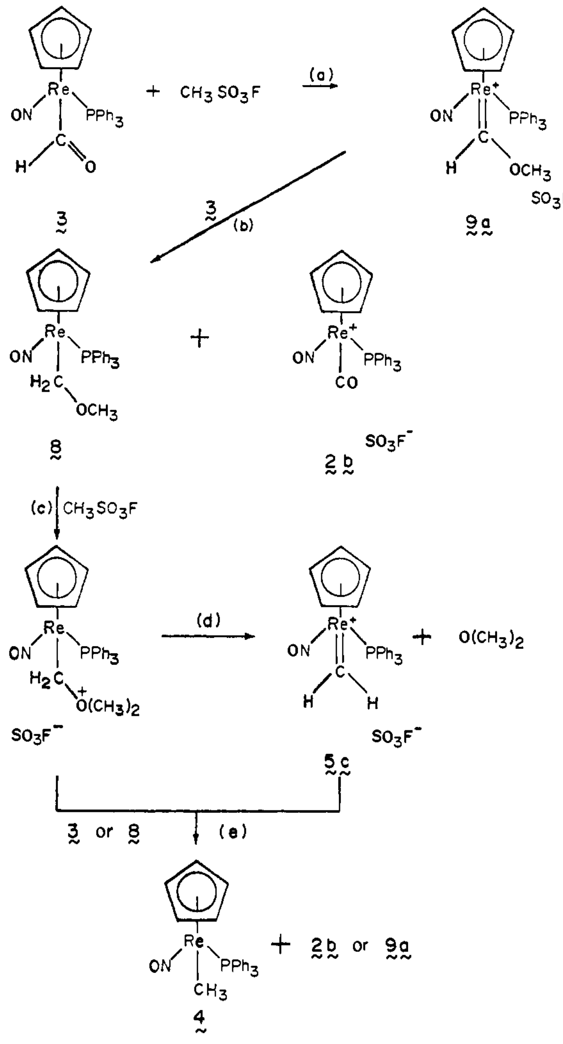
The eclipsing of the formyl and nitrosyl ligands in **3** (see Newman projection I) is significant in the following context. The homologous benzylidene complex [(η-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ has been synthesized[25] and its X-ray crystal structure determined.[43] The benzylidene ligand was found to similarly eclipse the nitrosyl ligand. Hückel MO calculations indicate that this orientation maximizes ligand p orbital overlap with a filled d donor orbital on rhenium.[44,45] Thus the formyl ligand in **3** adopts the "alkylidene-like" bonding geometry that would be expected if **3b** is an important resonance contributor.

Another contributing factor to the stability of **3** is that third row transition metals make stronger metal–ligand bonds than first row transition metals.[46] Thus decomposition modes which require ligand dissociation or bond homolysis should be retarded. For instance, (η-C_5H_5)Mn(NO)(CO)(CHO) is much less stable than the rhenium homologue.[24a,d] Rhenium is not unique among third row metals; stable neutral iridium and osmium formyls have also been isolated.[29,31]

Since the homologous carbonyl-substituted formyl (η-C_5H_5)-Re(NO)(CO)(CHO) decarbonylates (in dilute solution) to (η-C_5H_5)Re(NO)(CO)(H) over the course of a few hours at room temperature,[11a,b] the PPh_3 ligand is clearly critical to the stability of **3**. In the absence of any NO bending or η^5-C_5H_5 to η^3- or η^1-C_5H_5 isomerization,[47] decomposition of (η-C_5H_5)Re(NO)-(CO)(CHO) would be expected to be initiated by CO dissociation to give coordinatively unsaturated formyl.[29] Apparently PPh_3, which is a better donor ligand than CO, does not as readily dissociate from **3**; we were unable to demonstrate any exchange with PEt_3. The increased electron density on rhenium in going from (η-C_5H_5)Re(NO)(CO)(CHO) to **3** also enhances the back-bonding to the formyl ligand (**3b**).

When heated in appropriate solvents, **3** decomposes to rhenium hydrides (η-C_5H_5)Re(NO)(PPh_3)(H) and (η-C_5H_5)Re(NO)-(CO)(H). Since (η-C_5H_5)Re(NO)(CO)(H) does not significantly react with PPh_3 under the decomposition conditions, (η-C_5H_5)-Re(NO)(PPh_3)(H) appears to be (unless a substitution-labile 17 valence electron radical intermediate is involved)[48] a primary reaction product. Thus **3** is the first formyl complex to decompose to a metal hydride via loss of the formyl C=O.[29] The erratic, solvent-dependent decomposition rates observed and the variability of hydride yields suggest that both PPh_3 dissociation [leading to (η-C_5H_5)Re(NO)(CO)(H)] and bond homolysis may play important roles in the decomposition of **3**.

Scheme II. Proposed Mechanism for the Formation of 4 following the Reaction of 3 with CH_3SO_3F



Reduction and Disproportionation of 3. The reduction of the formyl ligand in **3** to a methyl ligand (**4**) with BH_3·THF (eq 5) is analogous to Masters' earlier reductions of metal acyls to alkyls.[49] Significantly, *N,N*-dialkylamides (RCONR′R″) are also reduced to amines ($RCH_2NR'R''$) by BH_3·THF.[50] This reinforces the analogy between **3** and amides and indicates that the rhenium should not be viewed as uniquely activating the C=O bond toward BH_3 reduction. Since BH_3 should be a byproduct when **3** is prepared from **2a** and $NaBH_4$ in THF/H_2O (eq 3), hydrolysis of BH_3 (or a **3**·BH_3 adduct) must be rapid under the reaction conditions. This route to **3** is modeled after earlier preparations of (η-C_5H_5)Re(NO)(CO)(CHO) by Casey and Graham.[11,13] Since **3** is inert to PEt_3 at temperatures below its decomposition, its lack of reaction with H_2 (which would similarly require a vacant coordination site) at 25 °C is not surprising.

The results in Scheme I show that the formyl ligand in **3** can be transformed into a methyl ligand under mild conditions and without the addition of an exogeneous reducing agent. Formyl reduction is of course accompanied by a stoichiometric amount of formyl oxidation. We propose that these disproportionations occur by similar overall mechanisms, as exemplified in Scheme

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II for the reaction of **3** with CH_3SO_3F. The conversion of **3** to **9a** (step a, Scheme II) is not directly observed by ^1H NMR (Table I), but this is understandable in view of the independently noted (eq 11) rapid reaction of **3** with **9a** at −70 °C (step b). Similarly, the conversion of **8** to **5c** (steps c, d) is not directly observed because of the rapid subsequent reaction (eq 7, 9) of **5c** with **3** and/or **8** (step e). Since no reaction was noted between **5b** and $(CH_3)_2O$, we believe it likely that step d (unimolecular) is rapid relative to step e (bimolecular). However, some **4** may arise directly from the oxonium ion formed in step c.

Scheme II has several limiting stoichiometries. When the initial CH_3SO_3F:**3** ratio is only 1:2 (eq 10), the reaction essentially stops after steps a and b. Another variable is the hydride donor in the final step e. Reactions in CD_2Cl_2 which were slowly brought to room temperature (Table I) gave 1:1 final ratios of **4** to **9a**, as would be expected if **8** were the exclusive hydride donor in step e. This mechanism requires an initial CH_3SO_3F:**3** ratio of at least 3:4. Reactions in CD_2Cl_2 which were rapidly brought from −78 °C to room temperature gave higher ratios of **4** to **9a** (up to 2:1). We suggest that in these experiments, some **3** is available to participate in step e; if this path were exclusively followed, an initial CH_3SO_3F:**3** ratio of only 2:3 would be required. Details of step e in toluene-d_8 could not be definitively probed due to the insolubility of **2b** and **9a**; however, some disproportionations were rigorously free of **9a**, as shown by solvent evaporation and CD_2Cl_2 extraction of the residue.

Methylidene **5** is the most interesting of the intermediates in Scheme II. Electrophilic methylidene complexes have been postulated as intermediates in many reactions,[51] but **5** is the first example to be detected or isolated. Apparently, some of the factors which help to stabilize formyl **3** also contribute to the stability of **5**. The most important of these is probably the high electron density on rhenium, which strengthens π back-bonding. Accordingly, ^1H NMR data indicate the rotational barrier about the rhenium–methylidene bond to be ≥15 kcal/mol. The synthesis of methylidene $[(\eta\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)(CH_2)]^+$ $CF_3CO_2^-$, in which the metal is similarly substituted with good donor ligands, has been more recently reported by Brookhart and Flood.[52] At −40 °C, $\Delta G^\ddagger$ for methylidene rotation was found to be 10.4 kcal/mol; this lower value may simply reflect differences in first row vs. third row metal–ligand π bond strengths. Higher alkylidene[25] and $C_5(CH_3)_5$[53] homologues of **5** have significantly greater kinetic stability (>150 °C as solids). Their physical and chemical properties will be fully treated in subsequent papers from our laboratory.

Reaction of **3** with CF_3CO_2H appears to follow a path qualitatively similar to Scheme II. However, proton transfer to **3** (analogous to step a) occurs much faster at −78 °C than subsequent hydride transfer; thus **10a** is an observable intermediate. Protonation should be reversible, and with warming, hydride transfer from small equilibrium quantities of **3** to **10a** (yielding hydroxymethyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2OH)$) is proposed to take place. Reaction between **3** and **10** does indeed give disproportionation products as described above in one of our unsuccessful attempts to prepare $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2OH)$. Significantly, when **10** is prepared from **3** and the stronger acids CF_3SO_3H and $p\text{-}CH_3C_6H_4SO_3H$ (eq 12), no hydride transfer chemistry is observed, even at 25 °C.

Since hydroxymethyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2OH)$ is not an observed intermediate in the reaction of **3** with CF_3CO_2H and numerous attempts at its independent synthesis have failed, we believe that the molecule is intrinsically unstable. $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2OH)$ would be expected to be amphoteric, serving as a source of H^+, HO^-, *and* H^-.[54] Thus it should undergo facile hydride transfer chemistry in the absence of external reagents. The isolable carbonyl-substituted homologue $(\eta\text{-}C_5H_5)Re(NO)(CO)(CH_2OH)$[11,13] should be a comparable acid, but not nearly as strong a HO^- or H^- donor.

Compounds **10a–c** are the first complexes containing ligands of the formula =CHOH to be generated and/or isolated. This result is of some historic interest, since catalyst-bound =CHOH species were once considered to be intermediates in the Fischer–Tropsch process.[55]

Related Hydride Transfer Chemistry. Several research groups have recently observed hydride transfer reactions which are closely related to the individual steps of Schemes I and II. For example, Cutler has attempted to dealkylate cationic iron alkoxycarbenes of the formula $[(\eta\text{-}C_5H_5)Fe(L)(CO)(CHOCH_3)]^+PF_6^-$ (**12**) with I^- (1.0–0.5 equiv).[56] Equimolar quantities of $[(\eta\text{-}C_5H_5)Fe(L)(CO)_2]^+PF_6^-$ and $(\eta\text{-}C_5H_5)Fe(L)(CO)(CH_2OCH_3)$ species formed. Our data support the postulated[56] initial formation of $(\eta\text{-}C_5H_5)Fe(L)(CO)(CHO)$ formyls; rapid subsequent hydride transfer from formyl to unreacted **12**, as in eq 11, would give the observed product distribution. Similarly, eq 9 has analogy in gas-phase work by Beauchamp and Stevens,[57] who reported the reaction $[(C_5H_5)Fe(CO)_2(CH_2)]^+ + (C_5H_5)Fe(CO)_2(CH_2OCH_3) \rightarrow (C_5H_5)Fe(CO)_2(CH_3) + [(C_5H_5)Fe(CO)_2(CHOCH_3)]^+$.

Casey has shown that concentrated solutions of the carbonyl-substituted formyl $(\eta\text{-}C_5H_5)Re(NO)(CO)(CHO)$ decompose to the novel bimetallic ester $[(\eta\text{-}C_5H_5)Re(NO)(CO)](\mu\text{-}CO_2CH_2)[(CO)(NO)Re(\eta\text{-}C_5H_5)]$ (1:1 mixture of diastereomers).[11a,b] This decomposition is accelerated approximately 2-fold by CH_3CO_2H. Casey has suggested the intermediacy of hydroxymethylidene $[(\eta\text{-}C_5H_5)Re(NO)(CO)(CHOH)]^+$, which rapidly abstracts hydride from formyl to give equal amounts of $(\eta\text{-}C_5H_5)Re(NO)(CO)(CH_2OH)$ and $[(\eta\text{-}C_5H_5)Re(NO)(CO)_2]^+$; subsequent combination would afford the bimetallic ester. In the presence of added base (which retards decomposition), the carbonyl group of $(\eta\text{-}C_5H_5)Re(NO)(CO)(CHO)$ has been proposed to serve as the electrophile which initiates (by attacking the formyl ligand of a second molecule) hydride transfer chemistry. The reaction of $(\eta\text{-}C_5H_5)Re(NO)(CO)(CHO)$ with benzaldehyde to yield the ester $(\eta\text{-}C_5H_5)Re(NO)(CO)(CO_2CH_2C_6H_5)$ is also CH_3CO_2H catalyzed.[11a]

Recently, Geoffroy and Steinmetz reported that reaction of the unstable anionic cluster formyl $[Os_3(CO)_{11}(CHO)]^-$ with H_3PO_4 yields the methylidene-bridged cluster $Os_3(CO)_{11}CH_2$ (0.20–0.30 equiv) and $Os_3(CO)_{12}$.[58] On the basis of deuterium labeling studies, a mechanism closely related to Scheme II has been proposed. Initial formation of an $Os_3(CO)_{11}(CHOH)$ species, analogous to **10**, is believed to be followed by hydride transfer from unreacted $[Os_3(CO)_{11}(CHO)]^-$. Loss of ^-OH from the resulting $[Os_3(CO)_{11}(CH_2OH)]^-$ would then afford the methylidene product.

Alkali-promoted bimolecular hydride transfer reactions are common in organic chemistry (e.g., Cannizarro reaction). Electrophile-promoted bimolecular hydride transfers such as in Scheme II are much less frequent, but do have precedent in purely organic systems. For instance, xanthydrol cleanly disproportionates in dilute HCl, as shown in eq 13.[59] Such reactions require rather specialized conditions (and substrates) so that hydride transfer can compete with solvolysis and/or ether formation.[59] Intramolecular variants of this reaction are much more common.[60]

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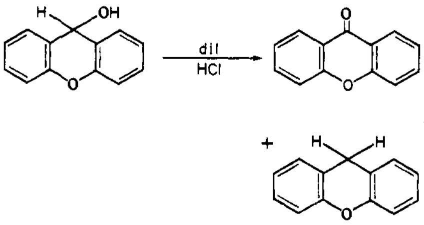

(13)

Overview

The elucidation of a new, electrophile-induced, disproportionative formyl reduction mechanism, as exemplified in Scheme II, suggests a possible means of catalytic CO reduction which has not been heretofore considered. Significantly, both heterogeneous and homogeneous CO reduction catalyst recipes often contain electrophilic components such as silica supports, metal oxides, and $AlCl_3$.[2a,4,7,9] These could play several key roles. For instance, Shriver has elegantly demonstrated that electrophiles can facilitate the migration of alkyl groups to coordinated CO;[61] Lewis acid adducts of metal acyl complexes are isolated. Catalyst-bound formyls might be generated by similarly promoted hydride migrations.

Electrophilic catalyst components could subsequently effect hydride transfer disproportionation of the formyl intermediates. However, it should be kept in mind that our model reactions are stoichiometric in electrophile "E^+X^-"; in each case, an "E–O–E" and two $(\text{metal})^+X^-$ species form. If an analogous mechanism is to operate catalytically, H_2 must be able to convert these back to "E^+X^-" and $(\text{metal})^0$, respectively. While the reduction of oxidized metal species by H_2 is commonplace, the suggestion that H_2 might regenerate "E^+X^-" species is more speculative. Water (a byproduct in most CO/H_2 reactions) would be formed concurrently.

Electrophilic species by no means play a role in all CO reduction catalysts.[26] However, there is a growing interest in mechanisms by which supports can interact with dispersed metals;[62] our study suggests a new possibility.

Finally, this work has resulted in the first isolations of parent members of two important families of ligands: $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+$ (**5**; electrophilic methylidene) and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOH)]^+$ (**10**; hydroxymethylidene). These will be the subject of future reports from our laboratory.

Experimental Section

General. All reactions were carried out under an atmosphere of dry N_2. THF and toluene were purified by distillation from benzophenone ketyl. Hexane and petroleum ether were distilled from potassium metal or benzophenone ketyl. Benzene was distilled from benzophenone ketyl or 4-Å molecular sieves. CH_2Cl_2 was distilled from P_2O_5. $CHCl_3$, CH_3CN, and other solvents were commercial reagent grade and simply degassed with N_2 prior to use. Deuterated solvents were also degassed, and some were additionally purified: CD_2Cl_2, distilled from P_2O_5; THF-d_8, distilled from $LiAlH_4$; toluene-d_8, distilled from benzophenone ketyl.

IR spectra were recorded on a Perkin-Elmer Model 521 spectrometer. ^1H NMR and ^{13}C NMR spectra were (unless noted otherwise) referenced to $(CH_3)_4Si$ and obtained on a Brüker WP-200 spectrometer at 200 and 50 MHz, respectively. Mass spectra were obtained on an AEI-MS9 instrument. Gas chromatographic analyses were conducted on a Hewlett-Packard Model 5720A chromatograph equipped with a flame ionization detector. Microanalyses were conducted by Galbraith. Melting points were recorded on a Büchi Schmeltzpunktbestimmungsapparat and were not corrected.

Starting Materials. $Re_2(CO)_{10}$ was purchased from either Pressure or Strem Chemical Co. Iodosobenzene was purchased from Pfaltz and Bauer or prepared from iodosobenzenediacetate (Fischer Scientific) by the method of Saltzman and Sharefkin.[63] NO^+ and Ph_3C^+ salts were purchased from Aldrich and stored under N_2 in the refrigerator. $(CH_3)_3N^+O^-$ was purchased from Aldrich (as a dihydrate) and dried by azeotropic distillation with benzene. CH_3SO_3F, CD_3SO_3F, and $Li(C_2H_5)_3BH$ (1.0 M in THF) were purchased from Aldrich and used without purification. $[(C_6H_5)_2(CH_3)Si]_2O$ was obtained from Petrarch. All other starting materials were available from common commercial sources and used without purification.

$(\eta\text{-}C_5H_5)Re(CO)_3$.[64] $Re_2(CO)_{10}$ (2.5 g) and dicyclopentadiene (5–7 mL, preferably solid material purified by vacuum distillation) were refluxed for 12 h under N_2 in a 200-mL round-bottomed flask with vigorous magnetic stirring and periodic TLC monitoring. The reaction mixture was allowed to cool overnight, whereupon (partial) solidification occurred. The mixture was extracted with hexane (removing hydrocarbon and any unreacted $Re_2(CO)_{10}$; these washings were stockpiled for the eventual recovery of the latter) and the residue (product and polymer) collected on a coarse sintered glass frit. The residue was extracted with CH_2Cl_2; evaporation of the CH_2Cl_2 afforded solid $(\eta\text{-}C_5H_5)Re(CO)_3$ (pure by TLC and ^1H NMR: δ 5.37, s, $CDCl_3$) in 65–85% yields.

$[(\eta\text{-}C_5H_5)Re(NO)(CO)_2]^+BF_4^-$ (**1**).[32] $(\eta\text{-}C_5H_5)Re(CO)_3$ (4.00 g, 11.93 mmol) was dissolved in 40–50 mL of dry degassed CH_2Cl_2, and $NO^+BF_4^-$ (2.00 g, 17.09 mmol) was added. Gas evolved and the reaction mixture was stirred for 8–12 h. The solvent was removed and the residue was extracted with acetone and filtered. The filtrate was concentrated and ethyl ether was added to precipitate the yellow product, which was collected by filtration, washed with additional ether, and dried; yield of **1**, 4.85 g (96%, 11.43 mmol).

$[(\eta\text{-}C_5H_5)Re(NO)(CO)(NCCH_3)]^+BF_4^-$. **A.** To 100 mL of CH_3CN was added 2.20 g (5.19 mmol) of $[(\eta\text{-}C_5H_5)Re(NO)(CO)_2]^+BF_4^-$ and 1.14 g (5.18 mmol) of iodosobenzene. After the mixture was stirred overnight, the solvent was removed and the residue was taken up in acetone and filtered through silica gel. The orange filtrate was concentrated, and ethyl ether was added to precipitate the product (1.53 g, 3.50 mmol, 67%). Recrystallization from acetone/ethyl ether yielded air-stable orange-yellow crystals. Data: mp 105–107 °C; IR (cm^{-1}, CH_2Cl_2) $\nu_{C\equiv O}$ 2028 s, $\nu_{N\equiv O}$ 1758 s; ^1H NMR (δ, acetone-d_6) 6.47 (s, 5 H), 2.95 (s, 3 H). Anal. Calcd for $C_8H_8BF_4N_2O_2Re$: C, 21.97; H, 1.84; N, 6.40; Re, 42.57. Found: C, 21.88; H, 1.98; N, 6.35; Re, 42.30.

B. A similar reaction was conducted with 0.163 g (0.383 mmol) of $[(\eta\text{-}C_5H_5)Re(NO)(CO)_2]^+BF_4^-$ and 0.093 g (0.420 mmol) of iodosobenzene in 25 mL of CH_3CN. GLC analysis indicated iodobenzene to be present in 77% yield. Identical workup afforded 0.145 g (0.306 mmol, 80%) of $[(\eta\text{-}C_5H_5)Re(NO)(CO)(NCCH_3)]^+BF_4^-$.

$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**2a**). **A.** To 50 mL of 2-butanone was added 1.03 g (2.36 mmol) of $[(\eta\text{-}C_5H_5)Re(NO)(CO)(NCCH_3)]^+BF_4^-$ and 1.50 g (5.72 mmol) of Ph_3P. The mixture was refluxed for 3 h and then allowed to cool. The product formed as a yellow or yellow-green precipitate, which was collected, washed with ethyl ether, and vacuum dried to yield 1.55 g (2.36 mmol, 100%) of **2a**. Recrystallization from CH_2Cl_2/ethyl ether yielded air-stable orange crystals. Data: mp 277–278 °C dec; IR (cm^{-1}, CH_2Cl_2) $\nu_{C\equiv O}$ 2001 s, $\nu_{N\equiv O}$ 1760 s; ^1H NMR (δ, CD_3CN) 7.63 (s, 15 H), 5.90 (s, 5 H). Anal. Calcd for $C_{24}H_{20}BF_4NO_2PRe$: C, 43.78; H, 3.06; N, 2.13; P, 4.70. Found: C, 42.90; H, 3.05; N, 2.15; P, 5.37.

B. Preparatively, **2a** was commonly synthesized from **1** without the purification of $[(\eta\text{-}C_5H_5)Re(NO)(CO)(NCCH_3)]^+BF_4^-$. Thus $[(\eta\text{-}C_5H_5)Re(NO)(CO)(NCCH_3)]^+BF_4^-$ was prepared as described above, but after the silica gel filtration step the solvent was removed and 2-butanone and Ph_3P (ca. 2 equiv) were added. Isolation of **2a** (50–65% yields) was then effected as described in A.

C. In a lower yield procedure (eq 1), 0.20 g (1.70 mmol) of $NO^+BF_4^-$ was added to 0.703 g (1.24 mmol) of $(\eta\text{-}C_5H_5)Re(PPh_3)(CO)_2$[33] in 30 mL of CH_2Cl_2. A yellow solid formed, and after 0.5 h, silica gel TLC indicated $(\eta\text{-}C_5H_5)Re(PPh_3)(CO)_2$ to be consumed. The yellow solid was isolated by filtration and recrystallized from acetone/ethyl ether to yield **2a** (0.333 g, 0.506 mmol, 41%). To the reaction filtrate was added ethyl ether, which precipitated **1** (0.228 g, 0.537 mmol, 43%).

$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)_2]^+BF_4^-$. To 15 mL of dry degassed CH_2Cl_2 was added 0.081 g (0.122 mmol) of **2a** and 0.035 g (0.134 mmol) of PPh_3. To this yellow solution was added (with stirring) 0.010 g (0.133 mmol) of anhydrous $(CH_3)_3N^+O^-$; the color immediately changed to orange-red. After 2 h, the resulting red-purple solution was rotary evaporated to dryness. The red-purple residue was taken up in $CHCl_3$ and hexane was added to precipitate the crude product. Subsequent diffusion recrystallization ($CHCl_3$/30–60 °C petroleum ether) afforded reddish crystals of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)_2]^+BF_4^-$ (0.090 g, 0.101 mmol) in 82% yield. Data: mp 232 °C dec; IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$

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1666 s; ^{1}H NMR (δ, $CDCl_3$) 7.54–7.42 (m, 30 H), 5.22 (s, 5 H); ^{13}C NMR (ppm, $CDCl_3$) 91.2 (C_5H_5) and phenyl carbons (137.9–128.6).

(η-C_5H_5)Re(NO)(PPh_3)(CHO) (3). A. To 1.035 g (1.573 mmol) of **2a** suspended in 30 mL of THF was added 1.60 mL (1.60 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF. The resulting orange solution was stirred for 10 min, and the solvent was then removed by vacuum distillation. The residue was dissolved in a minimum of THF and chromatographed under N_2 on a silica gel column; the column was eluted first with 1:3 (v/v) THF:hexane (to remove an impurity) and then with pure THF. Solvent removal yielded 0.536 g (0.937 mmol, 60%) of **3**.

B. To 0.506 g (0.768 mmol) of **2a** suspended in 50 mL of 1:1 (v/v) THF:H_2O at 0 °C was added 0.302 g (7.953 mmol) of $NaBH_4$. The reaction mixture was stirred for 1 h at 0 °C and then extracted with CH_2Cl_2 until the extract was colorless. The yellow CH_2Cl_2 solution was separated, dried over $MgSO_4$, and filtered, and the solvent was removed under vacuum at 25 °C. The resulting yellow powder was extracted with a small amount of THF and filtered. Hexane was added to the filtrate, which upon standing overnight gave 0.315 g of **3** (0.550 mmol, 72%) as air-sensitive honey-yellow crystals.

Data on **3**: dec pt gradual, ca. 91 °C (sealed capillary); IR (cm^{-1}, THF) $\nu_{N\equiv O}$ 1663 s, $\nu_{C=O}$ 1566 s; ^{1}H NMR (δ, CD_2Cl_2) 16.48 (s, 1 H), 7.50–7.36 (m, 15 H), 5.25 (s, 5 H); (THF-d_8) 16.48 (s, 1 H), 7.27 s + 7.17 s (15 H), 5.22 (s, 5 H); (C_6D_6, 60 MHz) 17.23, 7.62–7.05, 4.85; ^{13}C NMR (ppm, CD_2Cl_2, −30 °C) 251.3 (d, $J_{^{31}P-^{13}C} = 11$ Hz), 135.4 (d, $J = 55$ Hz), 133.5 (d, $J = 11$ Hz), 131.0 (s), 129.0 (d, $J = 11$ Hz), 94.0 (s). Anal. Calcd for $C_{24}H_{21}NO_2PRe$: C, 50.34; H, 3.70; N, 2.45; P, 5.41. Found: C, 50.14; H, 3.82; N, 2.39; P, 5.34.

(η-C_5H_5)Re(NO)(PPh_3)(COOH). To 0.382 g (0.580 mmol) of **2a** in 7 mL of degassed CH_3CN was added 0.585 mL of 1.0 N NaOH (0.585 mmol). The reaction mixture was stirred for 0.5 h and a yellow precipitate was removed by filtration. The precipitate was washed with hexane and vacuum dried to give 0.291 g (0.495 mmol, 85%) of (η-C_5H_5)Re(NO)(PPh_3)(COOH): mp 170 °C dec; IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1675 s, $\nu_{C=O}$ 1591 m, 1090 m; ^{1}H NMR (δ, $CDCl_3$) 1.62 (br s, 1 H), 5.30 (s, 5 H), 7.53–7.33 (m, 15 H). Anal. Calcd for $C_{24}H_{21}NO_3PRe$: C, 48.97; H, 3.60; N, 2.38; P, 5.26. Found: C, 48.87; H, 3.81; N, 2.68; P, 5.16.

(η-C_5H_5)Re(NO)(PPh_3)(H). To 0.102 g (0.154 mmol) of **2a** dissolved in 20 mL of CH_2Cl_2 was added 0.014 g (0.19 mmol) of anhydrous $(CH_3)_3N^+O^-$. The yellow solution turned orange, and after 10 min of stirring, solvent was removed by vacuum distillation. THF and excess $LiAlH_4$ were added to the reaction residue, which was stirred overnight. Solvent was then removed by vacuum distillation, and the residue was extracted with benzene and filtered. Solvent was removed from the yellow filtrate and the residue chromatographed on a silica column in 90:10 (v/v) hexane:ethyl acetate. Product was obtained (0.016 g, 19%) as an air-stable yellow powder: mp 183–186 °C dec; ^{1}H NMR (δ, C_6D_6) 7.72–6.96 (m, 15 H), 4.62 (s, 5 H), −9.15 (d, $J_{^{31}P-^1H} = 29$ Hz, 1 H); mass spectrum (16 eV, *m/e*) 545 (M$^+$, ^{187}Re, 28%), 467 (M$^+$ − C_6H_5, 28%), 262 (PPh_3, 100%). Anal. Calcd for $C_{23}H_{21}NOPRe$: C, 50.73; H, 3.89; N, 2.57; P, 5.69. Found: C, 50.62; H, 4.00; N, 2.38; P, 5.48.

Decomposition of 3. The following two experiments are representative.

Formyl **3** (0.016 g, 0.028 mmol) was dissolved in 0.400 mL of THF-d_8 in a NMR tube, and 0.0020 mL (0.005 mmol) of $[(C_6H_5)_2(CH_3)Si]_2O$ standard was added. The tube was sealed under vacuum and placed in a 50 °C oil bath. ^{1}H NMR spectra were recorded at the following intervals: 34 h (no rhenium hydrides), 64 h (trace quantities of (η-C_5H_5)Re(NO)(PPh_3)(H) and (η-C_5H_5)Re(NO)(CO)(H)), 137 h (hydrides ca. 10% each), and 227 h (hydrides ca. 13% each; **3** ca. 18%). Yields were determined by integration relative to the standard.

Formyl **3** (0.010 g, 0.017 mmol) was dissolved in 0.400 mL of toluene-d_8 in a NMR tube, and 0.0030 mL (0.020 mmol) of PEt_3 was added. The tube was capped with a septum and placed in an 80 °C oil bath. After 23 h a ^{1}H NMR spectrum indicated (η-C_5H_5)Re(NO)(CO)(H), (η-C_5H_5)Re(NO)(PPh_3)(H), (η-C_5H_5)Re(NO)(PEt_3)(H), and **3** to be present in a 20:46:13:21 ratio (see Results for chemical shifts). After 70 h, only (η-C_5H_5)Re(NO)(PPh_3)(H) and (η-C_5H_5)Re(NO)(PEt_3)(H) remained (52:48); no other C_5H_5 resonances were present.

(η-C_5H_5)Re(NO)(PPh_3)(CH_3) (4). A. To 1.368 g (2.08 mmol) of **2a** suspended in 100 mL of THF was added 0.237 g (6.24 mmol) of $NaBH_4$. The mixture was stirred for 4 h and then filtered. Solvent was removed by rotary evaporation, and the residue was taken up in benzene and filtered through silica gel, yielding a bright orange solution. The benzene was removed and the residue recrystallized from CH_2Cl_2/hexane. After refrigerator cooling, 0.923 g of **4** (1.74 mmol, 84%) was collected. Data: mp 198–200 °C; IR (cm^{-1}, THF) $\nu_{N\equiv O}$ 1630 s; ^{1}H NMR (δ, C_6D_6, 60 MHz) 7.8–6.8 (m, 15 H), 4.58 (s, 5 H), 1.43 (d, $J_{^{31}P-^1H} = 5$ Hz, 3 H); (CD_2Cl_2, 200 MHz) 7.43 s + 7.39 s (15 H), 4.96 (s, 5 H), 0.95 (d, $J = 5$ Hz, 3 H); ^{13}C NMR (ppm, CD_2Cl_2) 136.3 (d, $J_{^{31}P-^{13}C} = 53$ Hz), 133.8 (d, $J = 11$ Hz), 130.4 (s), 128.7 (d, $J = 10$ Hz), 90.2 (s), −25.2 (d, $J = 6$ Hz); mass spectrum (16 eV, *m/e*) 559 (M$^+$, ^{187}Re, 100%), 544 (M$^+$ − CH_3, 31%). Anal. Calcd for $C_{24}H_{23}NOPRe$: C, 51.60; H, 4.15; N, 2.51; P, 5.54. Found: C, 52.30; H, 4.60; N, 2.15; P, 5.82.

B. To 0.046 g (0.080 mmol) of **3** in 0.30 mL of THF at −78 °C was added 0.30 mL (0.30 mmol) of 1.0 M $BH_3 \cdot THF$. The reaction was allowed to warm to room temperature over 1.5 h, whereupon the orange solution was chromatographed on a silica gel column with 10:90 (v/v) ethyl acetate:hexane. Solvent removal from the orange band afforded 0.032 g (0.058 mmol, 72%) of **4**.

Reactions of 3 with CH_3SO_3F. A. To 0.116 g (0.202 mmol) of **3** in 20 mL of toluene at −78 °C was added 0.20 mL (0.20 mmol) of 0.99 M CH_3SO_3F in toluene. The mixture was allowed to warm to room temperature over the course of 1 h. A light yellow solid formed, which was isolated by filtration, washed with ethyl ether, and vacuum dried. Thus obtained was 0.073 g (0.113 mmol, 56%) of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+SO_3F^-$ (**2b**): IR (cm^{-1}, CH_2Cl_2) $\nu_{C\equiv O}$ 2025 s, $\nu_{N\equiv O}$ 1764 s; ^{1}H NMR (δ, CD_3CN) 7.83–7.25 (m, 15 H), 6.00 (s, 5 H). The solvent was removed from the filtrate by vacuum distillation, and the residue was chromatographed on a silica gel column with 10:90 (v/v) ethyl acetate:hexane. Thus obtained was 0.032 g (0.058 mmol, 29%) of **4**.

B. In a ^{1}H NMR tube was placed 0.0200 g (0.035 mmol) of **3** and 0.360 mL of CD_2Cl_2. The resulting orange solution was cooled to −78 °C and 0.0029 mL (0.036 mmol) of CH_3SO_3F was added. ^{1}H NMR spectra were recorded while the probe temperature was gradually warmed (see Table I for data).

C (**Eq 10**). In a ^{1}H NMR tube was placed 0.040 g (0.071 mmol) of **3** and 0.400 mL of $CDCl_3$. After the mixture was cooled to −41 °C (CH_3CN/N_2), 0.003 mL (0.037 mmol) of CH_3SO_3F was added. The solution was kept at −41 °C for 1.5 h, during which time a yellow solid precipitated. A 60-MHz ^{1}H NMR spectrum at ambient probe temperature indicated a 4.7:1 ratio of **8**:**4** (integration of C_5H_5 resonances at δ 5.04 and 4.92, respectively). The yellow solid was isolated by filtration, washed with hexane, and vacuum dried. Thus obtained was 0.022 g (0.033 mmol, 45%) of **2b**. Solvent was removed from the filtrate to yield 0.019 g (ca. 45%) of a mixture of **4** and **8**.

Reaction of 3 with CD_3SO_3F. A reaction similar to the one in procedure A immediately above was run utilizing 0.020 g (0.035 mmol) of **3**, 0.003 mL of CD_3SO_3F, and ca. 0.5 mL of toluene. Subsequently isolated was 0.0063 g (32%) of **4**, the mass spectrum of which (70 eV) contained peaks at *m/e* 562, 561, 560, and 559 in an intensity ratio (arbitrary units) of 5:104:1088:5440 (559 = ^{187}ReM$^+$ for **4**-d_0). From this and authentic mass spectra of **4**-d_0 and **4**-d_3, the ratio of **4**-d_0:**4**-d_3 obtained in this reaction was calculated as >99.9:0.1.

Preparation of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+X^-$ (5). A. In Situ. To a ^{1}H NMR tube was added 0.0187 g (0.0566 mmol) of $Ph_3C^+BF_4^-$ and 0.10 mL of CD_2Cl_2. After the mixture was cooled to −78 °C, 0.0296 g (0.0531 mmol) of **4** in 0.35 mL of CD_2Cl_2 was added. A ^{1}H NMR spectrum (−70 °C) of the resulting homogeneous solution showed immediate formation of **5a**. The following chemical shifts were recorded at −33 °C (δ, CD_2Cl_2): 15.65 (t, $J_{^1H-^1H'} = J_{^1H-^{31}P} = 4$ Hz, 1 H), 15.48 (d, $J_{^1H'-^1H} = 4$ Hz, $J_{^1H'-^{31}P} < 1$ Hz, 1 H), 6.05 (s, 5 H). A δ 5.58 resonance was assigned to Ph_3CH (s, 1 H), and phenyl protons (7.11–7.69, m) were present. A 91% yield of **5a** was calculated by relative integration to the only other C_5H_5 resonance, some unreacted **4**. A ^{13}C NMR spectrum of a similarly prepared solution was obtained (ppm, CD_2Cl_2, −70 °C, gated decoupled): 290.3 (t, $J_{^{13}C-^1H} = 151$ Hz), 100.5 (d, $J_{^{13}C-^1H} = 190$ Hz).

Solutions of **5b** (X = PF_6^-) were prepared similarly in spectroscopic yields ranging from 88 to 100%. ^{1}H NMR (δ, CD_2Cl_2, −70 °C) 15.67 (m, unresolved ABX system, 1 H; at 10 °C; t, $J_{^1H-^1H'} = J_{^1H-^{31}P} = 4$ Hz, 1 H), 15.42 (br d, $J_{^1H-^1H'} = 4$ Hz, $J_{^1H'-^{31}P} \leq 1$ Hz, 1 H), 6.03 (s, 5 H).

B. Isolation. To 30 mL of dry degassed CH_2Cl_2 was added 0.3415 g (0.611 mmol) of **4**. This solution was cooled to −78 °C, and 0.261 g (0.673 mmol) of $Ph_3C^+PF_6^-$ was added with stirring. The color immediately changed from orange to yellow-green. After 40 min at −78 °C, the CH_2Cl_2 solvent was removed under vacuum at −23 °C (CCl_4/CO_2 bath). The resulting yellow-green residue was washed with 5 mL of cold $CHCl_3$ at −23 °C, affording an off-white powder which was collected by filtration at 25 °C, washed with cold hexane, and dried under vacuum. Thus obtained was 0.3755 g (0.535 mmol, 87%) of **5b**, IR (cm^{-1}, KBr) ν_{C-H} 3110 m, 3054 w, $\nu_{N\equiv O}$ 1710 s.

$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2NC_5H_5)]^+PF_6^-$ (6a). To 0.2245 g (0.403 mmol) of **4** in 30 mL of CH_2Cl_2 at −78 °C was added 0.1625 g (0.419 mmol) of solid $Ph_3C^+PF_6^-$. The reaction was stirred for 0.5 h at −78 °C, and 0.15 mL (1.3 mmol) of pyridine was added. The resulting orange solution was allowed to warm to room temperature, after which the solvent was removed by rotary evaporation. The residue was washed with ethyl ether and recrystallized from CH_2Cl_2/ethyl ether. Thus isolated was 0.2483 g (0.318 mmol, 79%) of **6a** as air-stable orange-yellow crystals: mp 180 °C dec; IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1640 s; ^1H NMR (δ, $CDCl_3$) NC_5H_5 resonances at 8.82 (d, J = 5.6 Hz, 2 H), 8.14 (t, J = 7.8 Hz, 1 H), 7.75 (d of d, J = 7.8, 5.6 Hz, 2 H), other protons at 7.53–7.31 (m, 15 H), 5.81 (d of d, $J_{^1H-^1H'}$ = 12.5 Hz, $J_{^1H-^{31}P}$ = 1.8 Hz, 1 H), 5.67 (d of d, $J_{^1H'-^1H}$ = 12.5 Hz, $J_{^1H'-^{31}P}$ = 6.6 Hz, 1 H), 5.08 (s, 5 H); ^{13}C NMR (ppm, $CDCl_3$, 25 °C) 91.2, 35.4 (CH_2), and phenyl/pyridine carbons. Anal. Calcd for $C_{29}H_{27}F_6N_2OP_2Re$: C, 44.56; H, 3.48; N, 3.58; P, 7.93. Found: C, 44.45; H, 3.54; N, 3.66; P, 8.08.

$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2NC_5(2,6\text{-}CH_3)H_3)]^+PF_6^-$ (6b). To 0.3264 g (0.584 mmol) of **4** in 30 mL of CH_2Cl_2 at −78 °C was added 0.250 g (0.644 mmol) of solid $Ph_3C^+PF_6^-$. The reaction mixture was stirred for 0.5 h at −78 °C, and 0.340 mL (2.932 mmol) of 2,6-dimethylpyridine was added. The resulting orange-red solution was stirred for 1 h at −78 °C, after which solvent was removed under vacuum while the solution was being warmed to room temperature. The resulting orange-red residue was washed with ethyl ether and then redissolved in CH_2Cl_2. After filtration through glass wool, the solution was layered with hexane and stored in the refrigerator, whereupon **6b** crystallized (0.3324 g, 0.411 mmol, 70%); **6b** underwent substantial thermal decomposition over a period of several hours in solution at room temperature. Data: mp 127 °C dec; IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1640 s; ^1H NMR (δ, $CDCl_3$, 0 °C) 8.04–7.40 (m, 18 H, PPh_3 and pyridine protons), 5.38 (d of d, $J_{^1H-^1H'}$ = 12.8 Hz, $J_{^1H-^{31}P}$ = 6 Hz, 1 H), 5.01 (d of d, $J_{^1H'-^1H}$ = 12.8 Hz, $J_{^1H'-^{31}P}$ = 2 Hz, 1 H), 4.82 (s, 5 H), 2.65 (br s, 3 H), 2.73 (br s, 3 H); ^{13}C NMR (ppm, $CDCl_3$, 0 °C) 90.5 (C_5H_5), 22.7 (1 C), 22.4 (2 C), and phenyl/pyridine carbons.

$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]^+PF_6^-$ (7a). To 0.1970 g (0.354 mmol) of **4** dissolved in 30 mL of CH_2Cl_2 at −78 °C was added 0.1358 g (0.350 mmol) of solid $Ph_3C^+PF_6^-$. After the mixture was stirred for 0.5 h at −78 °C, 0.1336 g (0.510 mmol) of PPh_3 dissolved in 5 mL of CH_2Cl_2 was added. The solution was slowly warmed to room temperature, the solvent was vacuum distilled, and the residue was washed with 25 mL of ethyl ether. The residue was taken up in 1:1 (v/v) CH_2Cl_2:acetone and petroleum ether was allowed to slowly diffuse into the solution. Air-stable orange crystals of **7a** (0.1809 g, 0.188 mmol, 54%) were subsequently isolated. Data: mp >280 °C; IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1650 s; ^1H NMR (δ, CD_3CN) 7.58–7.50 (m, 30 H), 4.68 (s, 5 H), 3.23 (m, part of ABXY system, $J_{^1H-^1H'}$ = 14 Hz, $J_{^1H-^{31}P}$ = 11 Hz, $J_{^1H-^{31}P'}$ = 8 Hz, 1 H), 2.68 (m, $J_{^1H'-^1H}$ = 14 Hz, $J_{^1H'-^{31}P}$ = 16 Hz, $J_{^1H'-^{31}P'}$ = 1 Hz, 1 H); ^{13}C NMR (ppm, CD_3CN) 91.4, −28.6 (d, $J_{^{31}P-^{13}C}$ = 31 Hz), and phenyl carbons. Anal. Calcd for $C_{42}H_{37}F_6NOP_3Re$: C, 52.28; H, 3.86; P, 9.63; N, 1.45. Found: C, 52.36; H, 3.93; P, 9.89; N, 1.39.

$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2P(n\text{-}C_4H_9)_3)]^+PF_6^-$ (7b). $Ph_3C^+PF_6^-$ (0.1461 g, 0.377 mmol) was added to 0.2111 g (0.379 mmol) of **4** in 20 mL of CH_2Cl_2 at −78 °C. After the reaction was stirred for 0.5 h, 0.20 mL (0.80 mmol) of $P(n\text{-}C_4H_9)_3$ was added and the mixture was allowed to slowly warm to room temperature. The solvent was vacuum distilled, and the residue was washed with ether. The orange-yellow powder was dissolved in a minimum amount of THF and filtered. Crystallization was induced by slow diffusion of petroleum ether (bp 40–60 °C) into the filtrate. Thus isolated was 0.200 g (0.225 mmol, 60%) of **7b** as air stable orange crystals. Data: mp 229–235 °C; IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1647 s; ^1H NMR (δ, CD_2Cl_2) 7.51–7.29 (m, 15 H), 5.17 (s, 5 H), 2.15 (m, ABX system, J = 12, 14, and 9 Hz, 1 H), 1.20–2.00 (m, 18 H + 1 H), 0.94 (t, $J_{^1H-^1H}$ = 7 Hz, 9 H); ^{13}C NMR (ppm, CD_2Cl_2) 90.6, −33.6 (d of d, $J_{^{31}P-^{13}C}$ = 16 Hz, $J_{^{31}P'-^{13}C}$ = 3 Hz), and phenyl and butyl (24.6, 24.4, 24.3, 24.2, 23.2, 22.2, 13.6) carbons. Anal. Calcd for $C_{36}H_{49}F_6NOP_3Re$: C, 48.00; H, 5.46; P, 10.27; N, 1.55. Found: C, 48.48; H, 5.72; P, 10.56; N, 1.41.

Attempted Reaction of 5b with $(CH_3)_2O$. As described above, **5b** was prepared in a ^1H NMR tube from **4** (0.0240 g, 0.043 mmol) and $Ph_3C^+PF_6^-$ (0.0170 g, 0.044 mmol) in CD_2Cl_2 (total volume 0.50 mL). A ^1H NMR spectrum at −70 °C indicated quantitative formation of **5b**. After the mixture was cooled to −78 °C, 0.050 mL of $CDCl_3$ containing some $(CH_3)_2O$ was added. A subsequent ^1H NMR spectrum at −30 °C indicated a ca. 1:1 ratio of **5b** (δ 6.02) to $(CH_3)_2O$ (δ 3.29). No new products were present. No reaction was noted by ^1H NMR at −20 °C or −10 °C, whereupon **5b** began to slowly decompose.

Reaction of 3 with 5. As described above, **5a** was prepared at −78 °C in a ^1H NMR tube from **4** (0.0266 g, 0.048 mmol) and $Ph_3C^+PF_6^-$ (0.0156 g, 0.047 mmol) in 0.40 mL (total volume) of CD_2Cl_2. To this solution was added 0.0245 g (0.043 mmol) of **3** in 0.35 mL of CD_2Cl_2 (precooled). A ^1H NMR spectrum taken immediately thereafter at −70 °C indicated **3** to be completely reacted. Only **4** and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**2a**) remained; the latter then precipitated from solution.

A preparative reaction was conducted at −78 °C with **5b** prepared from **4** (0.0419 g, 0.075 mmol) and $Ph_3C^+PF_6^-$ (0.0306 g, 0.079 mmol) in 20 mL of CH_2Cl_2. After addition of **3** (0.0426 g, 0.075 mmol), the solution was warmed to room temperature. A yellow solid precipitated, which was collected, washed with hexane, and shown by ^1H NMR and IR spectroscopy to be $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+PF_6^-$ (**2d**; 0.0477 g, 0.067 mmol, 89%). Solvent was removed from the filtrate and the residue was chromatographed with 10:90 (v/v) ethyl acetate:hexane; 0.0244 g (0.044 mmol, 59%) of **4** was obtained.

$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2OCH_3)$ (8). A. To 0.4180 g (0.750 mmol) of **4** in 25 mL of CH_2Cl_2 at −78 °C was added 0.3083 g (0.795 mmol) of solid $Ph_3C^+PF_6^-$. The solution was stirred for 0.5 h at −78 °C to form **5b**. To 5 mL of CH_3OH was added 0.153 g (6.65 mmol) of Na; the resulting solution was added to the solution of **5b**. The mixture was allowed to slowly warm to room temperature. The solvent was vacuum distilled, and the residue was extracted with benzene until the extract was colorless. The extract was filtered and concentrated to 15 mL, whereupon 50 mL of hexane was layered on the benzene. Orange, air-stable crystals of **8** formed, which after 1 day were isolated by filtration and vacuum dried (0.2974 g, 0.506 mmol, 67%). Note: A 20-fold excess of $NaOCH_3$ gave a 99% yield of **8**; **8** should not be chromatographed as it transforms to **4** on silica gel.

B. To a stirred solution of **6a** (0.3951 g, 0.506 mmol) in 30 mL of anhydrous methanol was added excess $NaOCH_3$ in CH_3OH. The reaction mixture was stirred at ambient temperature for an hour. The solvent was vacuum distilled, and the residue was extracted with benzene. The resulting orange extract was filtered, and the solvent was removed from the filtrate by vacuum distillation. The residue was recrystallized from ethyl ether/hexane. Thus obtained was 0.170 g (0.289 mmol, 57%) of **8**. Data: mp 175–177 °C; IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1625 s; ^1H NMR (δ, $CDCl_3$) 7.40–7.25 (m, 15 H), 5.04 (d, $J_{^1H-^{31}P}$ = 0.5 Hz, 5 H), 5.09 (d of d, $J_{^1H-^1H'}$ = 10.5 Hz, $J_{^1H-^{31}P}$ = 5.6 Hz, 1 H), 5.45 (d of d, $J_{^1H'-^1H}$ = 10.5 Hz, $J_{^1H'-^{31}P}$ = 2.0 Hz, 1 H), 3.16 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3/Cr(acac)_3$, 22.5 MHz)[65] 135.7 (d, $J_{^{13}C-^{31}P}$ = 51.3 Hz), 133.0 (d, J = 9.8 Hz), 129.6 (s), 127.9 (d, J = 9.8 Hz), 89.9 (s), 59.4 (s, OCH_3), 53.5 (br s, $ReCH_2O$). Anal. Calcd for $C_{25}H_{25}NO_2PRe$: C, 51.01; H, 4.28; N, 2.38; P, 5.26. Found: C, 51.05; H, 4.30; N, 2.36; P, 5.49.

Reaction of 8 with CH_3SO_3F (Eq 8). To 0.0420 g (0.071 mmol) of **8** in 0.40 mL of $CDCl_3$ at −60 °C was added 0.0029 mL (0.036 mmol) of CH_3SO_3F. The mixture was allowed to warm to room temperature. After 45 min, a 60-MHz ^1H NMR spectrum indicated **8** to be consumed and a 1.0:1.0:1.1 mixture of **4** (δ 4.97, 1.03 d), **9a** (δ 13.70, 5.90, 4.00), and $(CH_3)_2O$ (δ 3.33) to be present. When N_2 was bubbled through this solution, the resonance at δ 3.33 vanished.

Reaction of 5b with 8. As described above, **5b** was prepared at −78 °C from 0.0147 g (0.026 mmol) of **4** and 0.0103 g (0.027 mmol) of $Ph_3C^+PF_6^-$ in 0.40 mL (total volume) of CD_2Cl_2. A ^1H NMR spectrum at −70 °C indicated quantitative formation of **5b**. This solution was treated at −78 °C with 0.0156 g (0.027 mmol) of **8** in 0.30 mL of CD_2Cl_2 and shaken. A ^1H NMR spectrum at −70 °C showed clean formation of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOCH_3)]^+PF_6^-$ (**9b**) and **4** (1.1:1.0).

$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOCH_3)]^+SO_3F^-$ (9a). To 0.5257 g (0.894 mmol) of **8** dissolved in 75 mL of toluene at −22 °C (CO_2/CCl_4 bath) was added 0.040 mL (0.490 mmol) of CH_3SO_3F. The mixture was slowly warmed to room temperature, and the reaction was allowed to stir overnight. An off-white precipitate formed which was collected by filtration, washed with hexane, and vacuum dried. Thus obtained was 0.2012 g of **9a** which was solvated with 0.33–0.40 equiv of toluene (0.280 mmol, 31%). Vacuum drying for 4 days did not alter the toluene content. Data: mp 103–110 °C dec; IR (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1711 s; ^1H NMR (δ, $CDCl_3$) 13.73 (s, 1 H), 7.58–7.26 (m, phenyl protons), 5.85 (s, 5 H), 3.95 (s, 3 H), and 2.35 (s, toluene). Integration indicated a 2.4:1.0 **9a**:toluene ratio. In 200-MHz ^1H NMR spectra of optimized resolution, additional resonances appeared at δ 13.84 and 5.94 (C_5H_5). These constituted 5–10% of the total alkylidene and C_5H_5 protons.[38] ^{13}C NMR (ppm, $CDCl_3$) 288.4, 133.2 (d, $J_{^{13}C-^{31}P}$ = 9.8 Hz), 132.0, 129.4 (d, J = 12.2 Hz), 96.6, 72.2. Anal. Calcd for $C_{25}H_{24}FNO_5PReS + 0.40C_7H_8$: C, 46.15; H, 3.79; N, 1.94; P, 4.28. Calcd for $C_{25}H_{24}FNO_5PReS + 0.33C_7H_8$: C, 45.74; H, 3.74; N, 1.95; P, 4.32. Found: C, 45.78, 45.78, 45.87; H, 3.83, 3.69; N, 2.06; P, 4.29.

Reaction of 9a with 3. To a ^1H NMR tube was added 0.0182 g (0.032 mmol) of **3** in 0.30 mL of $CDCl_3$. After the mixture was cooled to −23 °C (CCl_4/CO_2 bath), a solution of **9a** (0.0218 g, 0.030 mmol) in 0.30 mL of $CDCl_3$ was added. The mixture was warmed to room temperature, and a yellow precipitate formed. A 60-MHz ^1H NMR spectrum indicated that **8** had formed quantitatively (2.4:1.0 ratio of **8** to toluene of solvation from **9a**). The yellow solid was filtered, washed with hexane, and vacuum dried to yield 0.0187 g (0.028 mmol, 93%) of **2b**. This reaction was repeated on a 0.027-mmol scale at −78 °C in CD_2Cl_2. A ^1H NMR spectrum taken immediately after mixing (−70 °C) showed **3** to be completely consumed.

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(65) We thank Dr. F. McCormick for recording this spectrum.

Synthesis and Decomposition of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOH)]^+CF_3CO_2^-$ (10a). To a ^1H NMR tube was added 0.032 g (0.056 mmol) of **3** and 0.40 mL of CD_2Cl_2. The solution was cooled to −78 °C and 0.0045 mL (0.058 mmol) of CF_3CO_2H was added. ^1H NMR spectra taken at −70 to −50 °C indicated the quantitative formation of **10a**: (δ, −50 °C) 17.80 (br s, 1 H), 14.80 (s, 1 H), 7.64–7.34 (m, 15 H), 5.57 (s, 5 H). Upon warming to room temperature, **10a** disappeared as $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+CF_3CO_2^-$ (**2c**) and **4** appeared. By integration of the phenyl protons in the homogeneous sample relative to the C_5H_5 resonances at δ 5.85 and 4.85, yields of 72% and 28% were calculated, respectively. An additional broad resonance was present (δ 10.30) which integrated to 0.077 mmol of protons. Since only 0.058 mmol of CF_3CO_2H was employed, this resonance cannot be due solely to unreacted CF_3CO_2H. By analogy to the reactions of **3** with CH_3SO_3F, this resonance is presumed to arise from a mixture of CF_3CO_2H and H_2O. This quantity of H_2O is well below the sensitivity limit of conventional thermal conductivity gas chromatographs. The ^{13}C NMR spectrum of **10a** was obtained from a sample prepared from 0.187 g (0.327 mmol) of **3** and 0.026 mL (0.331 mmol) of CF_3CO_2H in 3.0 mL of CD_2Cl_2 at −78 °C (ppm, −60 °C): 277.8 (s), 160.7 (q, $J_{^{13}C-^{19}F} = 38$ Hz), 133.3 (d, $J_{^{13}C-^{31}P} = 11$ Hz), 131.9 (s), 129.3 (d, $J_{^{13}C-^{31}P} = 11$ Hz), 116.2 (q, $J_{^{13}C-^{19}F} = 290$ Hz), 95.7 (s); ipso phenyl carbon not observed.

Reaction of 10a with $Li(C_2H_5)_3BH$. As described above, 0.005 mL (0.065 mmol) of CF_3CO_2H was added to 0.035 g (0.061 mmol) of **3** in 0.350 mL of CD_2Cl_2 at −78 °C. After a ^1H NMR spectrum (−70 °C) indicating the clean formation of **10a**, 0.064 mL (0.064 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF was added. Within 3 min, **3** had re-formed quantitatively.

Isolation of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOH)]^+CF_3SO_3^-$ (10b). Formyl **3** (0.183 g, 0.320 mmol) was dissolved in 10 mL of CH_2Cl_2. The solution was cooled to −78 °C and 0.031 mL (0.053 g, 0.350 mmol) of CF_3SO_3H was added via syringe. After 15-min stirring at −78 °C, 20 mL of hexane was added. After an additional 15 min at −78 °C, the reaction was warmed to −23 °C (CCl_4/CO_2bath), and the solvents were removed under high vacuum. Thus obtained was an off-white powder, which was washed with hexane and dried under vacuum. Yield of **10b**: 0.220 g (0.305 mmol, 95%). Data: mp 102–103 °C dec; IR (cm^{-1}, CH_2Cl_2) $\nu_{N{\equiv}O}$ 1718 s; ^1H NMR (δ, CD_2Cl_2, phenyl protons omitted)[40] (−78 °C) 14.15, 13.74, 13.31, 12.84 (m, Re=CHOH, height ratio ca. 3:3:2:2), 11.83 (br s, OH), 5.65, 5.59 (overlapping s, C_5H_5, height ratio ca. 3:2); (−43 °C) 14.16, 13.76 (s, ca. 1:1), 11.90 (br s), 5.67, 5.62 (overlapping s, ca. 1:1); (25 °C) 14.20, 13.85 (br s, ca. 1:1), 11.48 (br s), 5.67 (s); ^{13}C NMR (ppm, $CDCl_3/Cr(acac)_3$) 25 °C, 283.6 (br s), 132.8 (d, $J_{^{13}C-^{31}P} = 10$ Hz), 132.1 (s), 129.4 (d, $J = 12$ Hz), 96.1 (s); (0 °C) 284.1 and 282.6 (ca. 5:2) resonances replace the one at 283.6; $CF_3SO_3^-$ not observed. Anal. Calcd for $C_{25}H_{22}F_3NO_5PSRe{\cdot}CH_2Cl_2$ (sample subsequently shown to have ca. 1 equiv of CH_2Cl_2 by ^1H NMR): C, 38.67, H, 3.00; N, 1.73; P, 3.84. Found: C, 37.97, 37.75; H, 3.48, 3.31; N, 1.76, 1.69; P, 3.78, 3.86.

Reaction of 10b with 3. To a ^1H NMR tube was added 0.017 g (0.024 mmol) of **10b**, 0.0016 mL (0.002 g, 0.004 mmol) of $[(C_6H_5)_2(CH_3)Si]_2O$, and 0.300 mL of CD_2Cl_2. To 0.200 mL of CD_2Cl_2 was added 0.014 g (0.024 mmol) of **3**. Each solution was cooled to −78 °C, and the latter was added to the former via syringe. The reaction was quickly transferred to a precooled NMR probe (−73 °C), and the data cited in the Results section were obtained. At 27 °C, integration vs. the standard indicated 0.027, 0.008, and 0.004 mmol of **2e**, **4**, and **3**, respectively.

Reaction of 5b with $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COOH)$. To a ^1H NMR tube was added 0.0167 g (0.024 mmol) of **5b**, 0.0030 mL (0.003 g, 0.008 mmol) of $[(C_6H_5)_2(CH_3)Si]_2O$, and 0.350 mL of CD_2Cl_2. To 0.400 mL of CD_2Cl_2 was added 0.0141 g (0.024 mmol) of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COOH)$. Each solution was cooled to −78 °C, and the latter was added to the former via syringe. The reaction was quickly transferred to a precooled NMR probe (−73 °C). A ^1H NMR spectrum showed a ca. 2:1 ratio of **2d**:**4**, and some unreacted **5b** due to an apparent measuring error. The sample was warmed. At −13 °C, integration vs. internal standard indicated 0.021 mmol of **2d** and 0.010 mmol of **4** to be present, and methylidene decomposition products began to appear.

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Registry No. 1, 31960-40-4; **2a**, 70083-73-7; **2b**, 71763-17-2; **2c**, 71763-20-7; **2d**, 79919-50-9; **2e**, 79919-51-0; **3**, 70083-74-8; **4**, 71763-18-3; **5a**, 71763-22-9; **5b**, 71763-23-0; **6a**, 71763-30-9; **6b**, 79919-53-2; **7a**, 71763-25-2; **7b**, 71763-27-4; **8**, 71763-31-0; **9a**, 71763-33-2; **9b**, 71763-34-3; **10a**, 72343-50-1; **10b**, 79919-54-3; $(\eta\text{-}C_5H_5)Re(CO)_3$, 12079-73-1; $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)_2]^+BF_4^-$, 79919-56-5; $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COOH)$, 79919-57-6; $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$, 79919-58-7; $Re_2(CO)_{10}$, 14285-68-8; $(\eta\text{-}C_5H_5)Re(PPh_3)(CO)_2$, 42766-75-6; $(\eta\text{-}C_5H_5)Re(NO)(CO)(H)$, 38814-46-9; $(\eta\text{-}C_5H_5)Re(NO)(PEt_3)(H)$, 79919-59-8; CH_3SO_3F, 421-20-5; $Ph_3C^+BF_4^-$, 341-02-6; $Ph_3C^+PF_6^-$, 437-17-2; PPh_3, 603-35-0; $P(n\text{-}C_4H_9)_3$, 998-40-3; CH_3OH, 67-56-1; $(CH_3)_2O$, 115-10-6; pyridine, 110-86-1; 2,6-dimethylpyridine, 108-48-5; **10c**, 79933-11-2.

Supplementary Material Available: Labeled spectra used to obtain the data in Table I (13 pages). Ordering information is given on any current masthead page.