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Bimetallic Anionic Formyl Complexes: Synthesis and Properties

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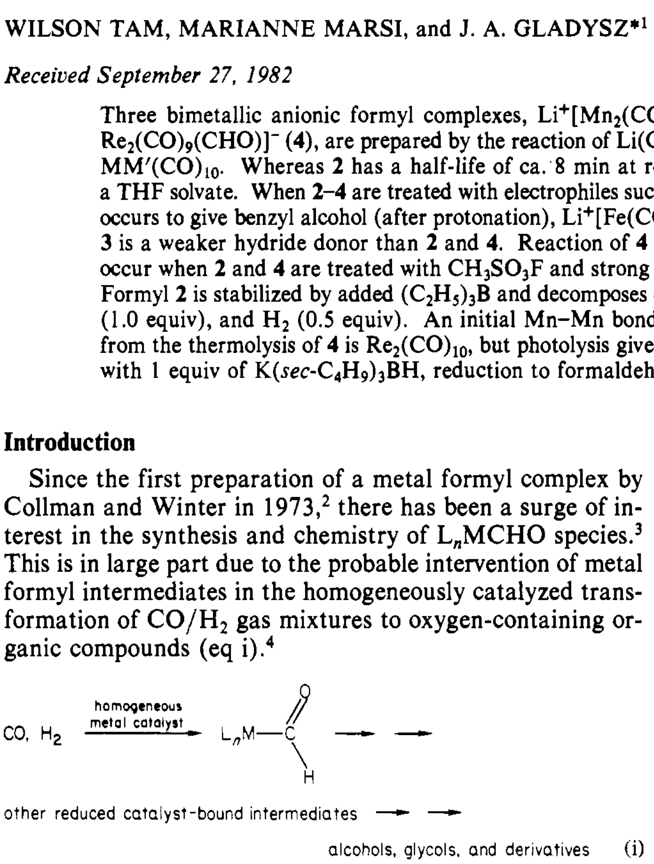
Three bimetallic anionic formyl complexes, $Li^+[Mn_2(CO)_9(CHO)]^-$ (**2**), $Li^+[ReMn(CO)_9(CHO)]^-$ (**3**), and $Li^+[cis\text{-}Re_2(CO)_9(CHO)]^-$ (**4**), are prepared by the reaction of $Li(C_2H_5)_3BH$ with the corresponding neutral metal carbonyl dimers $MM'(CO)_{10}$. Whereas **2** has a half-life of ca. 8 min at room temperature, **4** is stable for days and is easily isolated as a THF solvate. When **2**–**4** are treated with electrophiles such as benzaldehyde, $Fe(CO)_5$, and *n*-octyl iodide, hydride transfer occurs to give benzyl alcohol (after protonation), $Li^+[Fe(CO)_4(CHO)]^-$, and octane, respectively. Heterobimetallic formyl **3** is a weaker hydride donor than **2** and **4**. Reaction of **4** with CH_3I gives CH_4 (ca. 50%). However, complex reactions occur when **2** and **4** are treated with CH_3SO_3F and strong acids, contrary to our original report of CH_4 and H_2 evolution. Formyl **2** is stabilized by added $(C_2H_5)_3B$ and decomposes disproportionatively to $Mn_2(CO)_{10}$ (0.5 equiv), $Li^+[Mn(CO)_5]^-$ (1.0 equiv), and H_2 (0.5 equiv). An initial Mn–Mn bond cleavage step is proposed. The only characterizable product from the thermolysis of **4** is $Re_2(CO)_{10}$, but photolysis gives $Li^+[Re_2(CO)_9(H)]^-$. When $K^+[Re_2(CO)_9(CHO)]^-$ is treated with 1 equiv of $K(sec\text{-}C_4H_9)_3BH$, reduction to formaldehyde (21%) and $K_2[Re_2(CO)_9]$ (92%) occurs.

Introduction

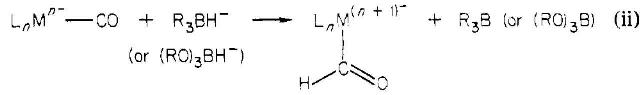
Since the first preparation of a metal formyl complex by Collman and Winter in 1973,[2] there has been a surge of interest in the synthesis and chemistry of L_nMCHO species.[3] This is in large part due to the probable intervention of metal formyl intermediates in the homogeneously catalyzed transformation of CO/H_2 gas mixtures to oxygen-containing organic compounds (eq i).[4]



(i)

Several synthetic routes to formyl complexes have been explored.[3] Although many transition-metal alkyls can be readily carbonylated to metal acyls, the carbonylation of a metal hydride to a metal formyl has been observed only in one instance.[5] Generally, metal hydride carbonylation is an endothermic reaction. Collman and Winter found that the anionic formyl complex $[Fe(CO)_4(CHO)]^-$ (**1**) could be synthesized from $[Fe(CO)_4]^{2-}$ and formic acetic anhydride.[2] Unfortunately, the reaction of formic acetic anhydride or related formylating agents with other transition-metal anions does not yield detectable quantities of formyl complexes.[6-8]

Since coordinated CO is readily attacked by a variety of carbon nucleophiles, the synthesis of formyl complexes by hydride attack upon metal carbonyl precursors has been investigated by several groups (eq ii). In 1976, the successful application of this strategy to the synthesis of anionic formyl complexes (eq ii, *n* = 0) was reported by Casey's laboratory,[6] ours,[9] and Winter's.[10]



$$L_nM^{n-}\text{—}CO + \underset{(\text{or }(RO)_3BH^-)}{R_3BH^-} \longrightarrow L_nM^{(n+1)-}\text{—}C(=O)H + R_3B\ (\text{or }(RO)_3B) \qquad \text{(ii)}$$

Although a variety of mononuclear anionic formyl complexes have been prepared via eq ii,[3,6,9-13] the majority have

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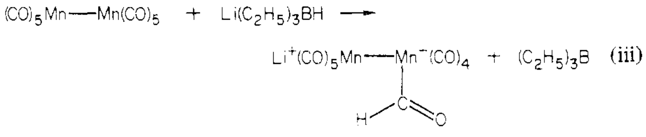
either been unstable at room temperature or simply derivatives of the formyl $[Fe(CO)_4(CHO)]^-$ (**1**) originally prepared by Collman and Winter. In this paper, we describe the synthesis and properties of a series of *binuclear* formyl complexes: $Li^+[Mn_2(CO)_9(CHO)]^-$ (**2**), $Li^+[MnRe(CO)_9(CHO)]^-$ (**3**), and $Li^+[cis\text{-}Re_2(CO)_9(CHO)]^-$ (**4**).[14] Since **4** can be isolated in pure form as a THF monosolvate, this work significantly extends the range of thermally stable anionic formyl complexes available for study. Salts of **4** have also been synthesized and studied by Casey and co-workers.[15] Separate full papers detail our work with similarly prepared neutral formyl complexes[16] and kinetically unstable mononucler anionic formyl complexes.[11b]

Results

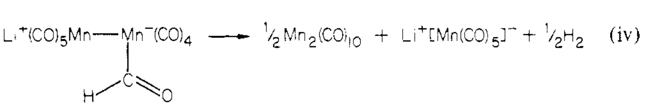
To a −20 °C THF solution of $Mn_2(CO)_{10}$ and an internal standard (*p*-xylene, *p*-di-*tert*-butylbenzene, or 1,2,4,5-tetrachlorobenzene) in a 5-mm NMR tube was added 1.0 equiv of $Li(C_2H_5)_3BH$ in THF. A new ^1H NMR resonance appeared (−20 °C) at δ 13.66 in 80–99% yields relative to the standard.[17] An IR spectrum recorded below ambient temperature showed absorbances at 2076 w, 1970 s, 1941 m, 1903 m, and 1540 w cm^{-1}. On the basis of the characteristic ^1H NMR chemical shift and IR $\nu_{C=O}$ stretch,[3] the product was formulated as the anionic formyl complex **2** (eq iii). The stereochemistry at the disubstituted manganese was not rigorously established but by analogy to the rhenium homologue (vide infra) is believed to be cis.



$(CO)_5Mn\text{—}Mn(CO)_5 + Li(C_2H_5)_3BH \longrightarrow Li^+(CO)_5Mn\text{—}Mn^-(CO)_4(C(=O)H) + (C_2H_5)_3B$ (iii)

2

At −20 °C, **2** was stable for hours. However, at room temperature it rapidly decomposed. By use of IR monitoring techniques previously described,[18] the primary organometallic decomposition products were noted to be $Mn_2(CO)_{10}$ and $Li^+[Mn(CO)_5]^-$ (ca. 1/2 ratio). Simultaneously, 0.39 equiv of H_2 (77%; verified by mass spectrometry) was collected via a Toepler pump. After the addition of Ph_3SnCl to the reaction mixture, $Mn_2(CO)_{10}$ and $Ph_3SnMn(CO)_5$ (from $Li^+[Mn(CO)_5]^-$)[18] were isolated in 86% and 88% yields, respectively. These yields are based upon the theoretical decomposition stoichiometry shown in eq iv.



$Li^+(CO)_5Mn\text{—}Mn^-(CO)_4(C(=O)H) \longrightarrow \frac{1}{2}Mn_2(CO)_{10} + Li^+[Mn(CO)_5]^- + \frac{1}{2}H_2$ (iv)

2

The decomposition of **2** followed the rate law

$$\frac{d[\mathbf{2}]}{dt} = -k_{obsd}[\mathbf{2}] \qquad (v)$$

over a wide range of temperatures and through 2.0 to >3.0 half-lives. For −15 °C solutions that were initially 0.20 ± 0.02 M in **2** and 0.21 ± 0.02 M in $(C_2H_5)_3B$, k_{obsd} values of $(5.33 \pm 0.60) \times 10^{-4}$ and $(6.17 \pm 0.75) \times 10^{-4}$ s^{-1} were measured (average 5.75×10^{-4} s^{-1}; $t_{1/2}$ = 20.0 min). At 21 °C, identically prepared solutions gave k_{obsd} values of $(12.95 \pm 0.75) \times 10^{-4}$ and $(15.16 \pm 0.85) \times 10^{-4}$ s^{-1} (average 14.06×10^{-4} s^{-1}; $t_{1/2}$ = 7.9 min).

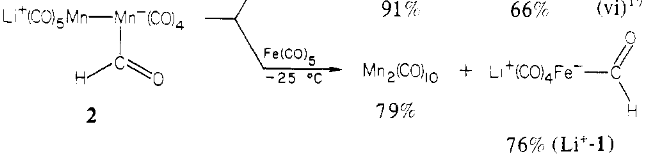
The decomposition of **2** was inhibited by added $(C_2H_5)_3B$. A 15 °C sample that was initially 0.18 ± 0.02 M in **2** and 0.74 ± 0.03 M in $(C_2H_5)_3B$ decomposed according to eq v with $k_{obsd} = (2.87 \pm 0.34) \times 10^{-4}$ s^{-1}. A second sample with $[\mathbf{2}]_0 = 0.16 \pm 0.02$ M and $[(C_2H_5)_3B] = 0.73 \pm 0.03$ M gave $k_{obsd} = (1.98 \pm 0.25) \times 10^{-4}$ s^{-1}.

Reaction of $Mn_2(CO)_{10}$ with $Li(C_2H_5)_3BD$ gave the deuterated formyl $Li^+[Mn_2(CO)_9(CDO)]^-$ (**2**-d_1). The rate of decomposition of **2**-d_1 was measured by ^2H NMR at 15 °C under conditions comparable to those above. In four experiments, k_{obsd} ranged from $(3.29 \pm 0.36) \times 10^{-4}$ to $(3.66 \pm 0.40) \times 10^{-4}$ s^{-1}, with an average value of 3.45×10^{-4} s^{-1}. This yields a deuterium isotope effect, k_H/k_D, of ca. 1.66.

The ^1H NMR chemical shift of **2** was temperature dependent. A THF solution that was 0.20 ± 0.02 M in **2** and 0.021 ± 0.02 M in $(C_2H_5)_3B$ exhibited a formyl resonance at δ 13.67 at −40 °C and δ 14.17 at 15 °C. A THF solution that was 0.18 ± 0.02 M in **2** and 0.74 ± 0.03 M in $(C_2H_5)_3B$ exhibited a resonance at δ 13.19 at −20 °C and δ 13.43 at 15 °C.

When 1 equiv of $Li(C_2H_5)_3BH$ was added to **2**, followed by warming, complete conversion to $Li^+[Mn(CO)_5]^-$ occurred (IR (cm^{-1}): 1898 m, 1958 s). The rate of disappearance of **2** under these conditions was within 10% of that in the absence of $Li(C_2H_5)_3BH$. A sample of **2** was treated with 1.25 equiv of $Li(C_2H_5)_3BD$ at −78 °C and then warmed to −30 °C. A ^2H NMR spectrum showed no **2**-d_1 to be present. A ^1H NMR spectrum showed that **2**-d_0 remained. If desired, solutions of $Li^+[Mn(CO)_5]^-$ (or $K^+[Mn(CO)_5]^-$) could be directly prepared by the addition of 2.5 equiv of $Li(C_2H_5)_3BH$ (or $K(C_2H_5)_3BH$) to $Mn_2(CO)_{10}$ in THF at room temperature. The utility of this methodology for the synthesis of $[Mn(CO)_5]^-$ and other metal carbonyl anions has been described in a separate publication.[18]

Reactions of **2** with electrophiles were examined. When **2** was treated with benzaldehyde, hydride transfer occurred to give, after protonation, benzyl alcohol (eq vi). When **2** was treated with $Fe(CO)_5$, net "transformylation" occurred to give $Mn_2(CO)_{10}$ and the lithium salt of the Collman/Winter formyl, Li^+-**1**.[2]



$Li^+(CO)_5Mn\text{—}Mn^-(CO)_4(C(=O)H) \xrightarrow[2.\ H_2O]{1.\ PhCHO} Mn_2(CO)_{10} + PhCH_2OH$ (vi)[17]

$Li^+(CO)_5Mn\text{—}Mn^-(CO)_4(C(=O)H) \xrightarrow[-25\ °C]{Fe(CO)_5} Mn_2(CO)_{10} + Li^+(CO)_4Fe^-\text{—}C(=O)H$

2

We encountered difficulty in reproducing two reactions of **2** reported in our original communication. The reaction of $HMn(CO)_5$ with **2** (−23 °C, followed by warming to room temperature) does, as previously described,[14a] give $Li^+[Mn(CO)_5]^-$ (98% as the Ph_3SnCl adduct) and $Mn_2(CO)_{10}$ (69%). However, the rate of this reaction, as monitored by ^1H NMR, varied from immediate to sluggish. Toepler pump analysis showed that 0.19 equiv of H_2 evolved (>90% pure by mass spectrometry) over the course of 2 h at −23 °C. Another 0.16 equiv of H_2 evolved upon warming the reaction to room tem-

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(14) Portions of this work have appeared in preliminary communcations: (a) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L. *J. Organomet. Chem.* **1977**, *140*, C1. (b) Gladysz, J. A.; Tam, W. *J. Am. Chem. Soc.* **1978**, *100*, 2545.

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(17) Depending upon the amount of standard employed, ^1H NMR and GLC yields reported in this paper are judged to be accurate within 5–10%. Yields are based upon the limiting reagent unless otherwise noted.

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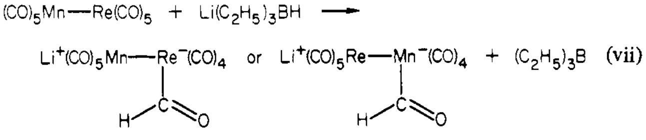
perature. This is approximately the amount of H_2 expected from eq iv alone. We also reported that **2** and CH_3SO_3F reacted to give methane (80%; confirmed by mass spectrometry).[14a] This observation has not proved repeatable. However, $Mn_2(CO)_{10}$ is consistently obtained in 72–82% isolated yields. The implications of these results will be discussed below.

To a −20 °C THF solution of $ReMn(CO)_{10}$ and an internal standard in a 5-mm NMR tube was added 1.0 equiv of $Li(C_2H_5)_3BH$ in THF. A new ^1H NMR resonance appeared at δ 14.30 in 80–98% yields relative to the standard.[17] At −53 °C, the resonance shifted to δ 13.78. By analogy to eq iii, the product was formulated as a binuclear anionic formyl of structure **3a** or **3b** (eq vii). The IR spectrum (cm^{-1}, THF: 2072 w, 2011 m, 1970 s, 1906 m, 1872 m, 1579 m) showed only one formyl $\nu_{C=O}$.



$$(CO)_5Mn{-}Re(CO)_5 + Li(C_2H_5)_3BH \longrightarrow Li^+(CO)_5Mn{-}Re^-(CO)_4(CHO) \text{ or } Li^+(CO)_5Re{-}Mn^-(CO)_4(CHO) + (C_2H_5)_3B \quad \text{(vii)}$$

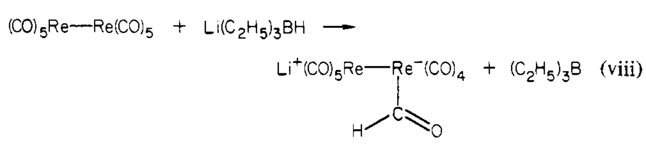
3a **3b**

Solvent was removed from a sample of **3** at −23 °C, and the resulting yellow residue was washed with hexanes and dried. A ^{13}C NMR spectrum (ppm, THF-d_8, −40 °C, 22.5 MHz: 283.9, 202.5, 199.0, 197.7, 191.6, 189.3) showed a single formyl resonance. The CO resonance pattern closely matched that of the Re_2 homologue (vide infra). The formyl ^1H NMR resonance of this material appeared at δ 15.36 (−40 °C, THF-d_8).

Heterobimetallic formyl **3** was more stable than **2** but decomposed according to the same rate law (eq v). At 32 °C, k_{obsd} was found to be $(8.8 \pm 0.4) \times 10^{-4}\ s^{-1}$ ($t_{1/2}$ = 13 min). The ^1H NMR spectrum of the decomposition products lacked resonances from δ 0.0 to −33.3, which indicated the absence of $HRe(CO)_5$ and $HMn(CO)_5$. The major decomposition product, $ReMn(CO)_{10}$, was isolated in 39–48% yields. Some $Li^+[Mn(CO)_5]^-$ and $Li^+[Re(CO)_5]^-$ also formed, as evidenced by IR spectroscopy and the formation of $Ph_3SnMn(CO)_5$ (27%) and $Ph_3SnRe(CO)_5$ (7%) after the addition of Ph_3SnCl to the decomposition mixture. Solid **3**, isolated as described above, was stored for 2 days at −5 °C. IR analysis showed, in addition to remaining **3**, the presence of $ReMn(CO)_{10}$, $Li^+[Mn(CO)_5]^-$, and $Li^+[Re(CO)_5]^-$.

Formyl **3** also underwent hydride transfer when treated with appropriate electrophiles. Reaction of **3** with benzaldehyde gave, after protonation, benzyl alcohol in 82% GLC yield.[17] Proton NMR monitoring showed hydride transfer to be complete within 5 min at −30 °C. When **3** was treated with $Fe(CO)_5$ at −30 °C, no $Li^+[Fe(CO)_4(CHO)]^-$ (Li^+-**1**) appeared. When the reaction mixture was warmed to room temperature, only a 13% yield of Li^+-**1** was obtained. Thus **3** is a weaker hydride donor than the homometallic formyl **2**.

To a room temperature THF solution of $Re_2(CO)_{10}$ and an internal standard in a 5-mm NMR tube was added 1.0 equiv of 1.0 M $Li(C_2H_5)_3BH$ in THF. A new ^1H NMR resonance appeared at δ 15.78 in 80–98% yields relative to the standard. By analogy to eq iii and vii, the product was formulated as the anionic formyl **4** (eq viii).



$$(CO)_5Re{-}Re(CO)_5 + Li(C_2H_5)_3BH \longrightarrow Li^+(CO)_5Re{-}Re^-(CO)_4(CHO) + (C_2H_5)_3B \quad \text{(viii)}$$

4

Solutions of **4** were stable at room temperature for periods of days. When the THF solvent was removed under vacuum until apparent dryness, the residue was dissolved in a minimum of ether, and pentane was added, a light yellow powder formed. After vacuum drying, this material gave a correct analysis for a THF monosolvate of **4**. When **4** was dissolved in $CDCl_3$ containing *p*-di-*tert*-butylbenzene standard, under which conditions decomposition occurred, a ^1H NMR spectrum indicated the presence of 0.93 ± 0.06 equiv of THF. Reasonably pure **4**·THF could also be obtained by simply washing the above residue with hexane and vacuum drying.

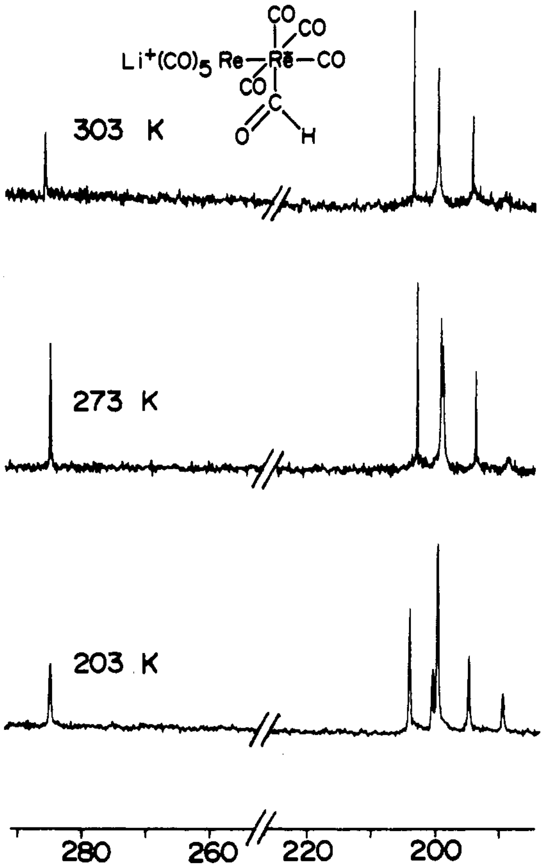


Figure 1. ^{13}C NMR spectra (50.32 MHz) of **4**·THF in THF-d_8 (0.02 M in $Cr(acac)_3$) at three temperatures. Spectra are hand aligned; for exact chemical shifts, see text.

Spectroscopic properties of **4**·THF were studied in detail. While only three CO ^{13}C NMR resonances were discernible at 30 °C (50 MHz, THF-d_8 0.02 M in $Cr(acac)_3$), the same sample displayed five CO resonances (203.0, 199.5, 198.7, 193.8, and 188.5 ppm) when the spectrum was recorded at −70 °C.[19] These data, and a spectrum recorded at 0 °C, are illustrated in Figure 1. The origin of the ^{13}C NMR temperature dependence will be discussed below. The −70 °C spectrum clearly excludes the more symmetrical trans stereochemistry for the disubstituted rhenium in **4**. The formyl carbon resonance appeared at 283.2 ppm in the spectrum recorded at −70 °C, and in a gated decoupled ^{13}C NMR spectrum, $J_{^{13}C-^1H}$ was 124 Hz.

The IR spectrum of **4**·THF was similar to that of **2** and **3** (cm^{-1}, THF: 2090 w, 2030 m, 1973 s, 1940 m, 1905 m, 1529 m). However, the formyl ^1H NMR resonance of isolated **4** in THF appeared at δ 15.97 and, unlike the corresponding resonance in **2** and **3**, was *not* temperature dependent from +32 to −40 °C. When 0.364 mmol of **4**·THF was dissolved in 0.4 mL of 1.0 M $(C_2H_5)_3B$ in THF, the formyl ^1H NMR resonance appeared at δ 14.05 at −45 °C and δ 14.46 at 32 °C.

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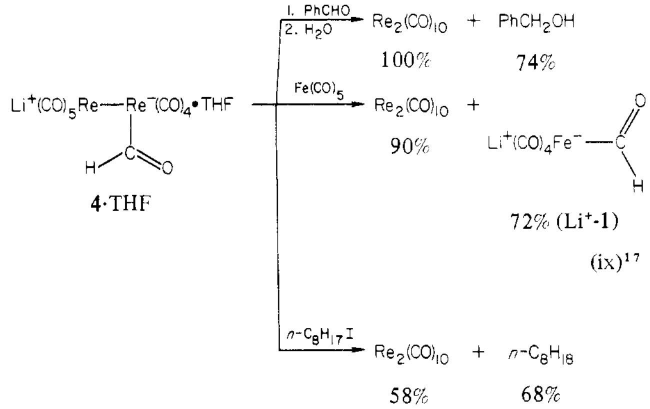
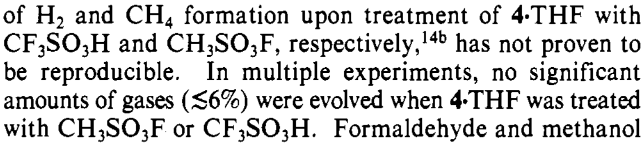
(19) We thank Professor C. P. Casey, University of Wisconsin, for suggesting the low-temperature ^{13}C NMR experiment to us.

Reactions of isolated **4**·THF with electrophiles were investigated. Benzaldehyde, $Fe(CO)_5$, and *n*-octyl iodide were reduced as summarized in eq ix.[17] However, our initial report of H_2 and CH_4 formation upon treatment of **4**·THF with CF_3SO_3H and CH_3SO_3F, respectively,[14b] has not proven to be reproducible. In multiple experiments, no significant amounts of gases (≲6%) were evolved when **4**·THF was treated with CH_3SO_3F or CF_3SO_3H. Formaldehyde and methanol assays were also negative. The dimer $Re_2(CO)_{10}$ could be routinely isolated from these reactions in 44–62% yields. Proton NMR and GLC monitoring of reactions of **4**·THF and CH_3SO_3F in THF-d_8 indicated that some $(CH_3)_2O$ formed, but acetone, ethanol, and isopropyl alcohol were absent. However, reaction of **4**·THF with the softer electrophile CH_3I (1 h, 25 °C) gave, by Toepler pump analysis, 1.03 equiv of gas. Mass spectral comparison with a standard CH_4/CO sample indicated this gas to be a (45 ± 5)/(55 ± 5) CH_4/CO mixture. Column chromatography of the reaction residue separated $Re_2(CO)_{10}$ (47%) from a yellow polar product.



(ix)[17]

Addition of 1.0 equiv of K(*sec*-$C_4H_9)_3BH$ (0.5 M in THF) to $Re_2(CO)_{10}$ gave $K^+[Re_2(CO)_9(CHO)]^-$ (**5**), as evidenced by a ^1H NMR resonance at δ 16.03 and an IR spectrum similar to that of **4** (cm^{-1}, THF: 2092 w, 2023 m, 1972 s, 1933 m, 1897 m, 1547 m). When **5** was treated with 1.0 equiv of K(*sec*-$C_4H_9)_3BH$ at room temperature, a new complex formed over the course of 10 min (eq x). An orange compound was isolated by solvent removal and precipitation from THF/hexanes. No protons were present by ^1H NMR, and microanalysis suggested the empirical formula $K_2[Re_2(CO)_9]$ (**6**; 91% yield). This dianion has been previously mentioned in the literature but has had minimal characterization.[20] The IR spectrum was unexceptional (cm^{-1}, THF: 2033 w, 2010 m, 1966 s, 1924 s, 1880 m, 1860 m), but the ^{13}C NMR spectrum (ppm, 50 MHz, THF-d_8 0.06 M in $Cr(acac)_3$, −60 °C: 221.7, 213.0, 202.3, 201.7, 199.9, 198.6, 195.9) indicated that **6** is either very unsymmetrical or exists as a mixture of isomers. Attempts to prepare suitable crystals of **6** for X-ray analysis were thwarted by its slow decomposition to a new rhenium complex. In a IR-monitored experiment, freshly isolated **6** was treated with $COCl_2$. The dimer $Re_2(CO)_{10}$ formed (among other products) and was subsequently isolated in 28% yield.



(x)

The reaction of **5** with K(*sec*-$C_4H_9)_3BH$ was analyzed for organic products. No methanol could be detected, but formaldehyde was isolated in 21% yield as its dimedone derivative.[21] When $Re_2(CO)_{10}$ was treated with 3.0 equiv of K(*sec*-$C_4H_9)_3BH$, methanol was isolated in 38% yield as its 3,5-dinitrobenzoate.[22] A separate experiment established that K(*sec*-$C_4H_9)_3BH$ did not react with $K_2[Re_2(CO)_9]$ (**6**).

A sample of **4**·THF was heated at 55 ± 5 °C in THF. It was half-decomposed after ca. 55 h and completely decomposed after 147 h. The disappearance of **4**·THF did not follow a first-order rate law. In the solid state, **4**·THF decomposed over the course of 1 h at 90–100 °C. The orange decomposition residue was extracted with hexanes to give $Re_2(CO)_{10}$ in 39–52% yields. The IR spectrum of the orange hexane-insoluble residue varied from run to run. Attempted recrystallizations of the residue gave oils. No metal hydride products could be detected by ^1H NMR in any of these decomposition experiments. When the decomposition residues (including a run done in the presence of $(C_2H_5)_3B$) were treated with Ph_3SnCl, no $Ph_3SnRe(CO)_5$ formed. When **4**·THF was decomposed at 90–100 °C in vacuo, methanol and formaldehyde assays were negative.

When exposed to fluorescent lighting, **4**·THF underwent photochemical decomposition at somewhat erratic rates. Samples of **4** in THF at 33 ± 3 °C were irradiated at a distance of 5 cm from two 20-W fluorescent lamps. Complete decomposition required anywhere from 3 to 48 h. A metal hydride (^1H NMR, δ −7.10) formed in 42–82% spectroscopic yield. Crude product was precipitated by adding petroleum ether. The IR and ^1H NMR spectra of this material corresponded closely with those reported by Casey and Neumann for $(C_2H_5)_4N^+[$*cis*-$Re_2(CO)_9H]^-$.[15] Hence the structure $Li^+[Re_2(CO)_9H]^-$ was assigned to the photoproduct. A sample of $Li^+[Re_2(CO)_9H]^-$ was heated at 50 °C in THF for 40 h. Analysis by ^1H NMR indicated that ≤5% decomposition took place.

The formyl **4**·THF was treated with H_2 under mild conditions (25 °C, 125 psi, 2 h). It was recovered in >88% yield.

Discussion

A series of three homologous bimetallic formyl complexes, **2**–**4**, have been spectroscopically and chemically characterized. The low-temperature ^{13}C NMR spectrum of **4** (Figure 1) plays an important role in assigning stereochemical structure. It has been previously observed that a temperature decrease can cause the relaxation time of spin $^1/_2$ systems scalar coupled to spin systems with $I > {}^1/_2$ to increase (low-temperature quadrupole decoupling).[23] For ^{185}Re (37% abundance) and ^{187}Re (63% abundance), $I = {}^5/_2$. Hence increased resolution, particularly for the 188.5-ppm resonance, is seen in the ^{13}C NMR spectrum of **4** recorded at −70 °C. Although specific resonances cannot be assigned to individual CO's from our data, only three resonances would be expected if the stereochemistry at the disubstituted rhenium were trans. Therefore **4** must be the cis isomer.

Since homologous manganese and rhenium carbonyl compounds, when attacked by the same nucleophile, commonly afford identical geometric isomers,[24] we favor the formulation of **2** as a cis isomer. The structure of **3** is less certain. The five CO resonances in the ^{13}C NMR spectrum of **3** suggest that, like **4**, **3** has a cis configuration. However, there is no

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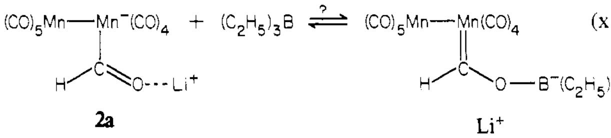
firm criterion for determining whether the formyl ligand is bound to manganese or rhenium. Rhenium complexes are generally more electron rich than manganese complexes[25] and hence less reactive toward nucleophiles.[26] Thus we prefer the structure **3b** (eq vii). However, the product need not reflect the position of initial attack. Fischer et al. found that the sequential treatment of $ReMn(CO)_{10}$ with LiC_6H_5 and $(CH_3)_3O^+BF_4^-$ gave three products: $ReMn(CO)_9(C(OCH_3)C_6H_5)$ (structure unspecified), $Mn_2(CO)_9(C(OCH_3)C_6H_5)$, and $Re_2(CO)_9(C(OCH_3)C_6H_5)$.[27a] Similarly, Casey found that treatment of $(CO)_5MnCH_3$ with $Na^+[Re(CO)_5]^-$ and then CH_3SO_3F gave the *rhenium* carbene *cis*-$(CO)_5MnRe(CO)_4(C(OCH_3)CH_3)$;[27b] the initial adduct was shown to be a *manganese* acyl complex. Since hydride-transfer reactions and the decomposition of **3** give only $ReMn(CO)_{10}$, the integrity of the Re–Mn bond is maintained in eq vii.

The decomposition chemistry of formyl complexes is of intrinsic interest. It is unfortunate that **4**·THF, which can be isolated pure, does not undergo clean thermal decomposition, whereas **2**, which cannot be readily separated from byproduct $(C_2H_5)_3B$, undergoes smooth decomposition as shown in eq iv. Since $(C_2H_5)_3B$ is a good Lewis acid, it might be expected to influence the properties of **2**. A possible associative equilibrium, related to one recently demonstrated with ketone enolates,[28] is depicted in eq xi. This equilibrium should be temperature dependent. Significantly, the formyl ^1H NMR chemical shift of **2** is temperature dependent, whereas that of isolated **4** is not. In samples of **3** and **4** which contain $(C_2H_5)_3B$, the formyl ^1H NMR resonance *is* temperature dependent.


(xi)

2a

7

Collman and Brauman have established that anionic iron acyls of the formula $Na^+[Fe(CO)_4(COR)]^-$ form much tighter ion pairs in THF ($K_D = 0.05 \times 10^5$ M at 25 ± 1 °C) than the corresponding anionic iron alkyls $Na^+[Fe(CO)_4R]^-$ ($K_D = 9.0 \times 10^5$ M).[27] For reactions of the type shown in eq xii,

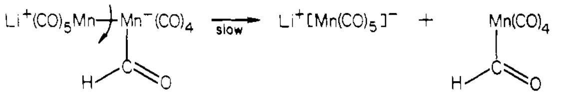
$$M^+[Fe(CO)_4R]^- + R_3P \rightarrow M^+[Fe(CO)_3(R_3P)(COR)]^- \qquad \text{(xii)}$$

rates were much faster when good coordinating counterions were used ($Li^+ > Na^+ >> (Ph_3P)_2N^+$). Rates decreased when cation coordinating agents such as N-methylpyrrolidinone and crown ethers were added. Hence tight ion pairing lowers the activation energy for eq xii. It would be reasonable to assume that the acyl product acquires greater stability from ion pairing than the transition state for its formation. Therefore the microscopic reverse of eq xii should be retarded by tight ion pairing.

Anionic formyl complexes should have ion-pairing properties similar to those of anionic acyl complexes. If the rate-determining step in the decomposition of **2** were to involve the formation of a new anionic species with a higher K_D (less favorable ion pairing or Lewis acid complexation), slower decomposition rates should be observed under conditions where tight ion pairing or Lewis acid complexation to **2** is made more favorable. Hence the slightly slower decomposition of **2** in the presence of excess $(C_2H_5)_3B$ may be due to an increased equilibrium concentration of **7**, in which the formyl oxygen is bound more covalently than in **2**. This Lewis acid stabilization of an anionic formyl complex suggests methods by which metal hydride carbonylation might be induced to proceed in the forward direction. Shriver has recently demonstrated that strong Lewis acids can promote the migration of methyl ligands to coordinated CO.[30]

Any mechanism proposed for the decomposition of manganese formyl **2** must account for several facts. First, the formation of both oxidized ($Mn_2(CO)_{10}$) and reduced ($Li^+[Mn(CO)_5]^-$) products requires a disproportionative mechanism. A manganese–manganese bond-cleavage step is required to generate $Li^+[Mn(CO)_5]^-$, and the decomposition is first order in **2**. The deuterium isotope effect, ca. 1.66, is ambiguous. The C–H bond in **2** is cleaved, but 1.66 is small for a primary isotope effect. On the other hand, 1.66 is large for a secondary isotope effect. However, k_H/k_D values for the departure of X^- from H(D)–CRR′–CR″R‴–X systems range as high as 1.4.[31]

In view of the foregoing, we believe that the α-elimination depicted in eq xiii constitutes a reasonable initial decomposition step. Our present data do not exclude (or provide any evidence for) initial loss of CO from **2**. However, we have unequivocally established that a related anionic compound, the acyl *fac*-$Li^+[Re(CO)_3(PPh_3)(COCH_3)(Br)]^-$, decomposes to *cis*-$Re(CO)_4(PPh_3)(CH_3)$ and LiBr via α-elimination of Br^-.[32] Furthermore, both I^- and $Na^+[Mn(CO)_5]^-$ reversibly attack $(CO)_5MnCH_3$ to form anionic acetyls (e.g., $Na^+[Mn_2(CO)_9(COCH_3)]^-$) which are homologues of **2**.[33] The conversion of $Mn(CO)_5CH_3$ to substituted acetyl manganese tetracarbonyls is well established as proceeding via the coordinatively unsaturated acetyl $Mn(CO)_4(COCH_3)$ (and/or a solvate).[34] Equation xiii therefore has an analogy in the microscopic reverse of these reactions.


(xiii)

2

8

Since no proton-containing intermediates were detected during the decomposition of **2**, coordinatively unsaturated formyl **8** (eq xiii), or some subsequently formed species, must rapidly react with remaining **2** to yield H_2 and the oxidation product $Mn_2(CO)_{10}$. We previously suggested that $HMn(CO)_5$ might function in this capacity.[14a] However, as described above, the independent reaction of $HMn(CO)_5$ with **2** was not rapid and did not give the predicted quantity of H_2. Norton has shown that coordinatively unsaturated $L_nM(COR)$ species are exceptionally reactive toward metal hydrides,[35] so we consider the direct reaction of **8** with **2** to be a plausible alternative.

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The stability trend **4** > **3** > **2** parallels past observations that rhenium forms stronger metal–ligand and metal–metal bonds than manganese.[36] The decomposition products of **3** are similar to those of **2**, so a related decomposition mechanism may be operative.

Surprisingly, the reaction of **3** with $Fe(CO)_5$ shows that **3** is a weaker hydride donor than either **2** or **4**. Thus there must be some synergistic effect of the two metals that makes $ReMn(CO)_{10}$ a better hydride acceptor and/or **3** a poorer hydride donor. Significantly, the formyl $\nu_{C=O}$ for **3**, 1579 cm^{-1}, is at shorter wavelength than that for **2** (1540 cm^{-1}) and **4** (1529 cm^{-1}). Since rhenium complexes are generally more electron rich than their manganese homologues,[25,26] **4** should be a better hydride donor than **2**. However, we were unable to unequivocally show this because **2** decomposed on the time scales needed to establish equilibrium.

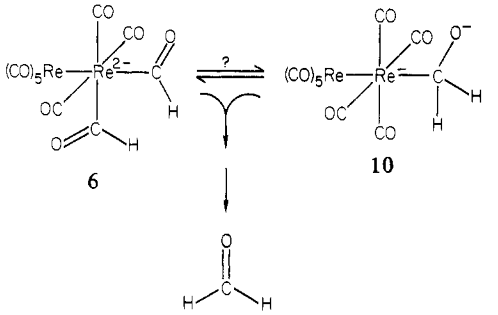
After we discovered that the neutral formyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ underwent a complex hydride-transfer disproportionation process when treated with CH_3SO_3F, CF_3CO_2H, or CF_3SO_3H (without formation of CH_4 or H_2),[16c,d] we reinvestigated the reactions of these electrophiles with **2** and **4**. As indicated, our original results could not be reproduced. On the basis of studies with $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$,[16c,d] we believe it probable that these "harder" electrophiles initially attack the formyl oxygen, forming a carbene ligand that is susceptible to reduction by unreacted formyl. However, we were unable to identify any organometallic products other than $M_2(CO)_{10}$. In contrast, the softer electrophile CH_3I does react with **4** to give CH_4 (ca. 50%). Ketone enolates are a related class of ambident nucleophiles that show differing reactivity toward hard and soft electrophiles.[38] Significantly, acidification of formyls of the type $[Fe(CO)_3(L)(CHO)]^-$ gives formaldehyde and methanol.[2,15] Casey has suggested that this occurs by initial protonation of the formyl oxygen. Methanol has also been reported from the reaction of CF_3CO_2H and the cluster formyl $[Os_3(CO)_{11}(CHO)]^-$.[13a] Geoffroy has found that this reaction also gives the bridging methylidene $Os_3(CO)_{11}(CH_2)$.[13c]

We were unable to completely characterize the thermal decomposition products of **4**. Since $Re_2(CO)_{10}$ is formed, a disproportionative decomposition may be occurring. However, reduced rhenium species $HRe(CO)_5$ and $Li^+[Re(CO)_5]^-$ were not detected. The thermal decarbonylation of **4** would yield $Li^+[Re_2(CO)_9H]^-$, which is stable at 50–60 °C and easily detected by ^1H NMR. Hence CO loss may not be the initial step in the decomposition of **4**. Our inability to detect methanol, formaldehyde, or any organometallic decomposition products other than $Re_2(CO)_{10}$ leaves the fate of the formyl ligand unresolved.

While solutions of **2**, **3**, and **4** each donate hydride toward a variety of electrophiles (eq vi, ix), only reactions involving **4** could be conducted in the absence of trialkylborane. In a previous study utilizing an optically active trialkylborohydride and the prochiral ketone acetophenone, we established that trialkylborane byproducts can participate in hydride-transfer reactions of anionic formyl complexes. Thus, the identity of the hydride donor cannot be precisely stated in reactions involving **2** and **3**. Only with **4** is direct hydride transfer unequivocal. However, the lack of H/D exchange between **2**/$(C_2H_5)_3B$ and $Li(C_2H_5)_3BD$ shows that hydride transfer from **2** to $(C_2H_5)_3B$ is not rapid at −30 °C.

Other workers have also reported hydride-transfer reactions of anionic formyl complexes. Collman and Winter noted that PPN^+-**1** reduced *n*-octyl iodide to octane.[2] Casey and Neumann have described hydride transfers between $(C_2H_5)_4N^+[\textit{cis}\text{-}Re_2(CO)_9(CHO)]^-$ and $[Fe(CO)_3(L)(CHO)]^-$ formyls and their metal carbonyl precursors.[15] We recently reported that *neutral* metal formyl complexes can transfer hydride to metal carbonyl cations.[16e]

Although the rhenium formyl is a hydride donor, it is subject to further hydride attack (eq x). Possible precursors to the formaldehyde produced include species **9** and **10** (eq xiv).



6 **10** (xiv)

Since our original communication, two anionic rhenium bis(formyls) similar to **9** have been characterized.[16a,39] A possible synthesis of $[Re_2(CO)_8(CDO)_2]^{2-}$ (**9**-d_2) has also been claimed.[13d] We suggest that the methanol formed by reaction of $Re_2(CO)_{10}$ with 3 equiv of $K(\textit{sec}\text{-}C_4H_9)_3BH$ is formaldehyde derived. Solutions believed to contain the iridium bis(formyl) $[Ir_4(CO)_{14}(CDO)_2]^{2-}$ have also been observed to give methanol and formaldehyde.[13d]

The inorganic product generated in eq x is formulated as the dianion $K_2[Re_2(CO)_9]$. Since $K(\textit{sec}\text{-}C_4H_9)_3BH$ converts $K^+[Fe(CO)_4(CHO)]^-$ (K^+-**1**) to $K_2[Fe(CO)_4]$, there is good chemical precedent for this transformation.[40] However, our attempts to further characterize this dianion were frustrated by our inability to obtain single crystals or clean reactions upon attempted derivatization.

Conclusion

The chemistry of anionic formyls **2**–**4** is dominated by their hydride-transfer properties. This is a reactivity mode that is not available to anionic acyl complexes. Anionic formyl complexes can be stabilized by the presence of a Lewis acid and can decompose by pathways considerably more complex than simple decarbonylation. These pathways appear to involve hydride transfer from undecomposed formyl to initial decomposition products. Although the formyl ligand in **4** can be reduced to formaldehyde or methanol, the conditions required cannot be considered mild or of particular relevance to CO reduction catalyst mechanisms. Of greater significance than reactions with external reducing agents are, we believe, the disproportionative tendencies of these compounds.[11b,13c,16c,d,39] This seems to us to be a viable, but not widely considered, fate for certain catalyst-bound formyls.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry N_2. Hexane, petroleum ether, and THF were distilled from Na/benzophenone or K/benzophenone.

IR spectra were obtained on a Perkin-Elmer 521 spectrometer. Reaction mixtures were IR monitored with an apparatus previously described.[18] NMR spectra were obtained on Varian A-60, Varian T-60, Bruker WP-200, and Jeol FXQ-90 spectrometers. ^1H NMR spectra were generally referenced to internal $(CH_3)_4Si$ (δ 0.00), *p*-xylene (δ 7.05), THF (δ 3.58), or *p*-di-*tert*-butylbenzene. ^{13}C NMR spectra were referenced to internal $(CH_3)_4Si$ or THF.

Microanalyses were conducted by Galbraith Laboratories. Gas chromatography was performed on a Hewlett-Packard 5720 A

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chromatograph equipped with a 6-ft 10% DC 710 (on Chromosorb W) column.

Starting Materials. $Li(C_2H_5)_3BH$, $K(C_2H_5)_3BH$, $Li(C_2H_5)_3BD$, $K(\textit{sec}\text{-}C_4H_9)_3BH$, and $(C_2H_5)_3B$ were obtained from Aldrich Chemical Co. as 1.0, 1.0, 1.0, 0.5, and 1.0 M THF solutions, respectively. These were standardized prior to mechanistic experiments.

Carbonyls $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Fe(CO)_5$ were purchased from either Pressure or Strem Chemical Co. The mixed dimer $ReMn(CO)_{10}$[41] was prepared by the reaction of $Li^+[Mn(CO)_5]^-$ or $K^+[Mn(CO)_5]^-$ with $(CO)_5ReBr$.[41,42]

Reagents CF_3SO_3H, CF_3CO_2H, CH_3SO_3F, 20% $COCl_2$ in toluene, benzaldehyde, Ph_3SnCl, *n*-octyl iodide, CH_3I, 3,5-dinitrobenzoyl chloride, and dimedone (5,5-dimethyl-1,3-cyclohexanedione) were obtained from common commercial sources and were used without purification.

Preparation of $Li^+[Mn_2(CO)_9(CHO)]^-$ (2). A 5-mm NMR tube was charged with 0.062 g (0.159 mmol) of $Mn_2(CO)_{10}$, 0.30 mL of THF, and 0.0021 g (0.020 mmol) of *p*-xylene. The tube was capped with a septum and cooled to −20 °C (^1H NMR probe temperature). Then 0.160 mL (0.160 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF was added via syringe. Integration of the resulting resonance at δ 13.66 relative to *p*-xylene indicated a 99% yield of **2**.[17] An IR spectrum (Results section) of a similarly prepared solution of **2** was obtained while blowing cold, dry N_2 over the salt windows of the IR sampling device.[18]

Decomposition of 2. Product Analysis. The formyl **2** was prepared by the addition of 0.840 mL (0.840 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF to 0.324 g (0.832 mmol) of $Mn_2(CO)_{10}$ in 20 mL of THF at −20 °C. The mixture was allowed to warm to room temperature and was then stirred for an additional 0.5 h. Then Ph_3SnCl (0.327 g, 0.849 mmol) was added in solid form. The reaction was stirred for 0.5 h, and then solvent was removed by rotary evaporation. The residue was chromatographed on silica gel with 1/3 ethyl acetate/hexane. The initial orange fraction was collected. Then a colorless fraction containing 0.367 g of $Ph_3SnMn(CO)_5$ was obtained. The orange fraction consisted mainly of $Mn_2(CO)_{10}$, but some $Ph_3SnMn(CO)_5$ was also present. The solvent was removed by rotary evaporation, and the residue was dissolved in a minimum of hexane and placed in the freezer for 2 days. A white solid crystallized. The solid was isolated by filtration and vacuum-dried to give 0.005 g of $Ph_3SnMn(CO)_5$. Thus the total yield of $Ph_3SnMn(CO)_5$ was 0.372 g (0.683 mmol, 82%). IR (cm^{-1}, THF): 2090 m, 1995 vs.[18] The solvent was removed from the orange filtrate to give 0.139 g (0.355 mmol, 86%) of $Mn_2(CO)_{10}$.

A second experiment was conducted to measure gas evolution. A 50-mL Schlenk flask was charged with 0.200 g (0.513 mmol) of $Mn_2(CO)_{10}$ and 10 mL of THF. The flask was attached to a Toepler vacuum line and cooled to −78 °C. Then 0.720 mL (0.569 mmol) of 0.79 M $Li(C_2H_5)_3BH$ in THF was added via syringe. The resulting solution was freeze/thaw degassed and then warmed to −40 °C for 10 min and then 24 °C for 1 h. The gas that evolved was collected via the Toepler pump (0.197 mmol, 77%) and was shown by mass spectrometry to be >90% H_2.

To the remaining solution was added 0.196 g (0.509 mmol) of Ph_3SnCl. The solution was stirred overnight, after which time the solvent was removed under vacuum. From the residue, $Mn_2(CO)_{10}$ (0.092 g, 0.236 mmol, 92%) was sublimed. The remaining solid was chromatographed on silica gel in benzene to give 0.195 g (0.359 mmol, 70%) of $Ph_3SnMn(CO)_5$.

Rate Studies. Samples of **2** were prepared in 5-mm septum-capped NMR tubes as described above except that 1,2,4,5-tetrachlorobenzene or *p*-di-*tert*-butylbenzene was used as standard. For rate studies with added $(C_2H_5)_3B$, 1.0 M $(C_2H_5)_3B$ in THF was substituted for a portion of the THF solvent. Concentrations of $(C_2H_5)_3B$ were calculated by assuming that $Mn_2(CO)_{10}$ reacted quantitatively with $Li(C_2H_5)_3BH$ and adding the $(C_2H_5)_3B$ thus liberated to any $(C_2H_5)_3B$ added. Reference 42 tabulates the ln (c_0/c_t) vs. time data obtained. A representative experiment is as follows.

A solution of $Mn_2(CO)_{10}$ (0.047 g, 0.121 mmol) and 1,2,4,5-tetrachlorobenzene (0.0154 g, 0.071 mmol) in 0.50 mL of THF/THF-d_8 was cooled to −78 °C. Then 0.130 mL (0.130 mmol, 1.06 equiv) of 1.0 M $Li(C_2H_5)_3BH$ in THF was added. The sample was inserted into a −40 °C NMR probe, and a ^1H NMR spectrum indicated a 100% yield of **2**. Thus $[\mathbf{2}]_0 = 0.19 \pm 0.02$ M and $[(C_2H_5)_3B] = 0.21 \pm 0.02$ M. The NMR probe was warmed to 15 °C, and the decomposition of **2** was followed through $>3t_{1/2}$.

Rates of decomposition of **2**-d_1 were measured in the absence of an internal standard.

Reaction of 2 with Benzaldehyde. An IR spectrum of 0.186 g (0.477 mmol) of $Mn_2(CO)_{10}$ in 50 mL of THF was taken prior to reaction (2045 s, 2008 vs, 1976 m cm^{-1}). The solution was cooled to −41 °C (CH_3CN/CO_2 bath), and 0.480 mL (0.480 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF was added. The solution was slowly warmed to room temperature. An IR spectrum indicated a 91% yield of $Mn_2(CO)_{10}$ as determined by comparing the intensity of the 2045-cm^{-1} absorption with that prior to the reaction. Dodecane (0.020 mL, 0.088 mmol) was added. The mixture was washed with 50 mL of water and then extracted with 3 × 50 mL of ether and 2 × 50 mL of CH_2Cl_2. The orange layer was dried over $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. Some THF was added to the residue. Analysis by GLC at 130 °C indicated a 66% yield of benzyl alcohol relative to added dodecane.

Reaction of 2 with $Fe(CO)_5$. The formyl **2** was prepared in 90% yield in a NMR tube by the addition of 0.170 mL (0.170 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF to 0.066 g (0.169 mmol) of $Mn_2(CO)_{10}$ and 0.0045 g (0.042 mmol) of *p*-xylene in 0.30 mL of THF at −25 °C. Then $Fe(CO)_5$ (0.025 mL, 0.186 mmol) was added. A ^1H NMR resonance at δ 14.10 (−25 °C) appeared and was assigned to $Li^+[Fe(CO)_4(CHO)]^-$ (Li^+-**1**). Peak integration indicated a 76% yield of Li^+-**1** based upon **2** formed.[17]

In a second experiment, an IR spectrum of a solution of 0.144 g (0.369 mmol) of $Mn_2(CO)_{10}$ in 25 mL of THF was taken prior to reaction with $Li(C_2H_5)_3BH$. Formyl **2** was generated as described above. The solution was then cooled to −78 °C, and 0.050 mL (0.371 mmol) of $Fe(CO)_5$ was added. The reaction was warmed to room temperature, and an IR spectrum was taken. Analysis of the intensity of the 2045-cm^{-1} $Mn_2(CO)_{10}$ absorption indicated a 79% yield. Absorptions at 1933 m, 1907 s, and 1560 m cm^{-1} were assigned to Li^+-**1**. This was confirmed by preparing Li^+-**1** from equimolar quantities of $Fe(CO)_5$ and $Li(C_2H_5)_3BH$.[10b,40] Under these conditions, a 2025-cm^{-1} absorption of Li^+-**1**, previously obscured by $Mn_2(CO)_{10}$, was observed.

Reaction of 2 with $HMn(CO)_5$. The hydride $HMn(CO)_5$ was prepared in 10 mL of THF[43] from 0.107 g (0.274 mmol) of $Mn_2(CO)_{10}$, 0.600 mL (0.600 mmol) of 1.0 M $K(C_2H_5)_3BH$, and 0.050 mL (0.650 mmol) of CF_3CO_2H. Formyl **2** was prepared in 25 mL of THF at −23 °C (CCl_4/CO_2 bath) from 0.201 g (0.516 mmol) of $Mn_2(CO)_{10}$ and 0.520 mL (0.520 mmol) of 1.0 M $Li(C_2H_5)_3BH$. The $HMn(CO)_5$ solution was cooled to −23 °C and transferred via cannula to the formyl solution. The mixture was slowly warmed to room temperature, and 0.222 g (0.576 mmol) of Ph_3SnCl was added. The reaction was stirred for 1 h, and the solvent was then removed by rotary evaporation. The residue was vacuum sublimed at 60 °C to give 0.138 g (0.354 mmol, 69%) of $Mn_2(CO)_{10}$. The remaining white residue that did not sublime was eluted through a silica gel column with 10/90 ethyl acetate/hexane. Thus obtained was 0.293 g (0.538 mmol, 99%) of $Ph_3SnMn(CO)_5$.

A 50-mL Schlenk flask was attached to a Toepler vacuum line and cooled to −23 °C. It was charged with $Mn_2(CO)_{10}$ (0.205 g, 0.526 mmol) and 0.550 mL (0.550 mmol, 1.04 equiv) of 1.0 M $Li(C_2H_5)_3BH$ in THF. After 10 min, 0.140 g (0.713 mmol, 1.35 equiv) of $HMn(CO)_5$ was distilled into the flask. The mixture was stirred for 1 h at −23 °C and was then frozen (−196 °C) to enable collection of the evolved gas (0.044 mmol). The reaction was warmed to −23 °C for another hour, after which another 0.056 mmol of gas was collected. The reaction was warmed to 25 °C for 1 h, and another 0.083 mmol of gas was collected. A mass spectrum of the gas (0.183 mmol total) showed it to be >90% H_2.

Reaction of 2 with CH_3SO_3F. A Schlenk flask containing 0.396 g (1.016 mmol) of $Mn_2(CO)_{10}$ in 20 mL of THF was attached to a gas buret. The system was flushed with N_2. The flask was cooled with a CCl_4/CO_2 bath (−23 °C), and 1.00 mL (1.00 mmol) of $Li(C_2H_5)_3BH$ was added via a septum attached to the side arm of the flask. The reaction was stirred for 15 min, and 0.090 mL (1.00 mmol) of CH_3SO_3F was added. There was no change in gas volume. The

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mixture was slowly warmed to room temperature and then cooled back to −23 °C. Again there was no net change in volume. The solution was warmed to room temperature, and the solvent was removed by rotary evaporation. The residue was chromatographed on silica gel with 10/90 ethyl acetate/hexane. Thus obtained was 0.327 g (82%) of $Mn_2(CO)_{10}$. In multiple experiments, the yield of $Mn_2(CO)_{10}$ ranged from 72 to 82%.

Preparation of $Li^+[ReMn(CO)_9(CHO)]^-$ (3). To 0.033 g (0.063 mmol) of $ReMn(CO)_{10}$ and 0.0086 g (0.045 mmol) of *p*-di-*tert*-butylbenzene in 0.60 mL of THF in a 5-mm NMR tube at −20 °C (NMR probe temperature) was added 0.065 mL (0.065 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF. A ^1H NMR resonance appeared at δ 14.30, and integration indicated a 98% yield of 3 relative to the standard. IR and ^{13}C NMR data: Results section.

Decomposition of 3. Decomposition rates of 3 were measured as described above for 2. Product analysis was conducted as follows.

Formyl 3 was prepared at room temperature by the addition of 0.470 mL (0.470 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF to 0.243 g (0.466 mmol) of $ReMn(CO)_{10}$ in 20 mL of THF. An IR spectrum indicated a clean conversion to 3. The mixture was stirred overnight, after which time an IR spectrum indicated that 3 had completely decomposed. Absorptions were present at 2008 m, 1961 s br, 1884 m, and 1854 m cm^{-1}. The solvent was removed by rotary evaporation. The residue was sublimed at 50–55 °C under vacuum. Thus collected was 0.116 g (0.223 mmol, 48%) of $ReMn(CO)_{10}$. IR (cm^{-1}, hexane): 2057 m, 2018 s, 1977 s.[41] In other similar experiments, yields of $ReMn(CO)_{10}$ ranged from 42 to 48%.

In a second experiment, 3 was prepared by the addition of 0.460 mL (0.460 mmol) of $Li(C_2H_5)_3BH$ to 0.240 g (0.461 mmol) of $ReMn(CO)_{10}$ in 20 mL of THF at −78 °C. The solution was slowly warmed to room temperature and then stirred for 5 h. The solution was then cooled to −78 °C, and 0.349 g (0.906 mmol) of Ph_3SnCl was added. The reaction was warmed to room temperature, and the solvent was removed by rotary evaporation. The residue was chromatographed on silica gel with 5/95 ethyl acetate/hexane. A yellow band was collected, and the solvent was removed by rotary evaporation. The residue was sublimed at 50 °C to give 0.093 g (0.178 mmol, 39%) of $ReMn(CO)_{10}$. The remaining white solid was dissolved in hot hexane and placed in the freezer overnight. Thus obtained was 0.134 g of white crystals. The IR spectrum of this material contained absorptions at 2115 w, 2095 m, 2013 m, 2004 s, and 2046 m cm^{-1}. This is assigned to be a mixture of $Ph_3SnRe(CO)_5$ (IR (cm^{-1}, lit.,[44] cyclohexane): 2114, 2012, 2003) and $Ph_3SnMn(CO)_5$ (IR (cm^{-1}, lit.,[44] cyclohexane): 2093, 2002). The absorption at 2046 cm^{-1} arises from an unidentified product. Comparison of the intensities of the bands at 2115 and 2095 cm^{-1} with authentic samples of $Ph_3SnRe(CO)_5$ and $Ph_3SnMn(CO)_5$ enabled an estimation of the yields of these species as 7% and 28%, respectively.

Reaction of 3 with Benzaldehyde. The formyl 3 was generated at −78 °C in a 5-mm NMR tube by the addition of 0.090 mL of 1.0 M $Li(C_2H_5)_3BH$ in THF to 0.047 g (0.090 mmol) of $ReMn(CO)_{10}$ and 0.0108 g (0.050 mmol) of 1,2,4,5-tetrachlorobenzene in 0.50 mL of THF/THF-d_8. The sample was warmed to −30 °C, and ^1H NMR analysis showed a 78% yield of 3. The solution was cooled to −78 °C, and benzaldehyde (0.012 mL, 0.110 mmol) was added via syringe. The probe was warmed to −30 °C, and after 5 min, a ^1H NMR spectrum was recorded. Only 0.027 mmol of benzaldehyde remained, and 3 had been consumed. The reaction was quenched with aqueous THF, and $C_6H_5CH_2Si(CH_3)_3$ standard (0.0100 g, 0.061 mmol) was added. Analysis by GLC indicated that benzyl alcohol was present in 100% yield based upon 3. IR analysis of a similar experiment showed a 58% yield of $ReMn(CO)_{10}$.

Reaction of 3 with $Fe(CO)_5$. A 5-mm NMR tube was charged with 0.0063 g (0.033 mmol) of *p*-di-*tert*-butylbenzene, 0.059 g (0.113 mmol) of $ReMn(CO)_{10}$, and 0.30 mL of THF. The mixture was cooled to −78 °C, and 0.110 mL (0.110 mmol) of 1.0 M $Li(C_2H_5)_3BH$ was added. A ^1H NMR spectrum was taken at −32 °C and indicated a 84% yield of 3. The sample was cooled back to −78 °C, and 0.015 mL (0.110 mmol) of $Fe(CO)_5$ was added. A ^1H NMR spectrum at −32 °C showed that no reaction had occurred. The mixture was warmed to room temperature and rapidly returned to −32 °C. A ^1H NMR spectrum showed only 3 (δ 14.37, 0.100 mmol, 91%). The solution was warmed to room temperature for 1 h. A ^1H NMR spectrum at ambient probe temperature showed some Li^+-1 (δ 14.73, 0.013 mmol, 13%) and some remaining 3 (δ 15.20, 0.024 mmol, 22%).

Preparation of $Li^+[cis\text{-}Re_2(CO)_9(CHO)]^-$ (4). To 1.039 g (1.593 mmol) of $Re_2(CO)_{10}$ in 15 mL of THF was added 1.60 mL (1.59 mmol) of 1.0 M $Li(C_2H_5)_3BH$ in THF. The rection was stirred for 5 min, and the volatiles were removed under vacuum. The yellow residue was washed with petroleum ether (bp 30–60 °C) and vacuum-dried overnight to yield 0.860 g (1.175 mmol, 74%) of 4 as a THF monosolvate. Reprecipitation of 4·THF could be achieved from ether/petroleum ether. Anal. Calcd. for $C_{14}H_9LiO_{11}Re$ (4·THF): C, 22.95; H, 1.24; Li, 0.95; Re, 50.84. Found with reprecipitated 4·THF: C, 22.76; H, 1.30; Li, 1.07. Found prior to reprecipitation: Re, 50.61.

A 5-mm NMR tube was charged with 0.30 mL of $CDCl_3$, 0.0084 g (0.044 mmol) of *p*-di-*tert*-butylbenzene, and 0.059 g (0.081 mmol) of reprecipitated 4·THF. Decomposition of 4 occurred, and integration of the THF ^1H NMR resonances relative to the standard showed 0.93 ± 0.06 equiv of THF to be present. Identical results were obtained with 4·THF that has not been reprecipitated.

Additional data on 4·THF: mp 80–90 °C dec., sealed capillary; IR and ^1H NMR in the Results section. ^{13}C NMR (ppm, 50 MHz, THF-d_8, 0.02 M $Cr(acac)_3$, −70 °C): 284.2, 203.0, 199.5, 198.7, 193.8, 188.5; (same sample at 0 °C) 284.8, 202.8, 199.0, 198.8, 193.6, 188.4; (same sample at 30 °C) 285.1, 202.6, 198.8, 193.5 (Figure 1).

Reaction of 4·THF with Benzaldehyde. To 0.155 g (0.212 mmol) of 4·THF in 10 mL of THF was added 0.025 mL (0.240 mmol) of benzaldehyde and then 0.50 mL of THF. The orange solution was stirred for 1 h. Water (20 mL) was then added, and the mixture was extracted with 10 mL of ether. The ether was dried over Na_2SO_4, and tetradecane standard (0.030 mL, 0.110 mmol) was added. Analysis by GLC showed 0.156 mmol (74%) of benzyl alcohol. The solvent was removed, and the residue was dissolved in a minimum of ether. Hexane (10 mL) was added, and the solution was placed in the freezer overnight. The dimer $Re_2(CO)_{10}$ crystallized and was collected by filtration and vacuum-dried (0.138 g, 0.212 mmol, 100%).

Reaction of 4·THF with $Fe(CO)_5$. To 0.188 g (0.257 mmol) of 4·THF in 10 mL of THF was added 0.035 mL (0.260 mmol) of $Fe(CO)_5$. An IR spectrum showed bands at 1933 m, 1901 s, and 1553 m cm^{-1} corresponding to Li^+-1 (vide supra). The solvent was removed by rotary evaporation, and the residue was extracted with 3 × 20 mL of hexane. The hexane was pumped off to give 0.151 g (0.232 mmol, 90%) of $Re_2(CO)_{10}$. IR (cm^{-1}, hexane): 2072 s, 2014 s, 1975 s. In a second experiment, 0.050 mL (0.371 mmol) of $Fe(CO)_5$ was added to 0.061 g (0.083 mmol) of 4·THF and 0.0052 g (0.027 mmol) of *p*-di-*tert*-butylbenzene in 0.30 mL of THF. A ^1H NMR spectrum at ambient probe temperature showed a resonance at δ 14.52, which was attributed to Li^+-1. A 72% yield relative to the standard was calculated.

Reaction of 4·THF with *n*-Octyl Iodide. A sample of 4·THF (0.204 g, 0.279 mmol) in 1.0 mL of THF was cooled to −78 °C, and 0.060 mL (0.330 mmol) of *n*-octyl iodide was added. The orange solution was kept at −78 °C for 22 h and then warmed to room temperature. After the addition of 0.020 mL (0.100 mmol) of decane, the solution was analyzed by GLC. Octane (0.190 mmol) was present in 68% yield based upon 4·THF. Unreacted *n*-octyl iodide (0.160 mmol) was also found. The orange solution was chromatographed on silica gel with 10/90 ethyl acetate/hexane. Thus obtained was 0.105 g (0.161 mmol, 58%) of $Re_2(CO)_{10}$.

Reaction of 4·THF with Methyl Iodide. A 25-mL flask was charged with 0.173 g (0.236 mmol) of 4·THF and 5 mL of THF. A second flask was charged with 0.100 mL (1.605 mmol) of CH_3I and 2 mL of THF. Both flasks were attached to a Toepler pump vacuum manifold and were degassed. The solution of 4 was cooled to −196 °C, and the CH_3I solution was distilled into it. The resulting solution was stirred for 1 h at 25 °C and was then refrozen to collect the evolved gas with the Toepler pump. A total of 0.249 mmol of gas (1.03 equiv) was collected. Mass spectral comparison of this gas to a standard CH_4/CO sample showed it to be a (45 ± 5)/(55 ± 5) CH_4/CO mixture. The remaining yellow-orange solution was analyzed by IR and found to contain $Re_2(CO)_{10}$ (2074 m, 2012 s, 1983 m cm^{-1}) and another species (1980 s br, 1941 m, 1900 m cm^{-1}). Solvent removal and silica gel chromatography gave 0.070 g (0.107 mmol, 47%) of $Re_2(CO)_{10}$.

Reactions of 4·THF with CF_3SO_3H, CF_3CO_2H, and CH_3SO_3F. Lengthy descriptions of the negative results obtained in these ex-

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periments are compiled in ref 42a.

Preparation of $K^+[Re_2(CO)_9(CHO)]^-$ (5). A 5-mm NMR tube was charged with 0.0097 g (0.051 mmol) of *p*-di-*tert*-butylbenzene, 0.104 g (0.160 mmol) of $Re_2(CO)_{10}$, and 0.30 mL of THF. To this mixture was added 0.310 mL (0.155 mmol) of 0.5 M $K(sec\text{-}C_4H_9)_3BH$ in THF. A ^1H NMR spectrum indicated an 86% yield of **5** (δ 16.08). IR spectrum: Results section.

Preparation of $K_2[Re_2(CO)_9]$ (6). To 2.059 g (3.158 mmol) of $Re_2(CO)_{10}$ in 15 mL of THF was added 13 mL (6.50 mmol) of 0.5 M $K(sec\text{-}C_4H_9)_3BH$ in THF. The reaction was stirred for 0.5 h, and the solvent was then removed under vacuum. The resulting orange-yellow solid was washed with hexane and vacuum-dried to give 2.020 g (2.870 mmol, 91%) of **6**. The product was precipitated from THF/hexane; mp 120–140 °C dec. IR and ^{13}C NMR: Results section. Anal. Calcd for $C_9K_2O_9Re_2$: C, 15.38; K, 11.13; Re, 53.00. Found: C, 15.42, 14.95; K, 11.42, 11.57; Re, 53.12, 52.93.

Reaction of 6 with $COCl_2$. To 0.169 g (0.241 mmol) of **6** in 15 mL of THF at −78 °C was added 0.20 mL (0.30 mmol) of 20% $COCl_2$ in toluene. The solution was slowly warmed to room temperature and then stirred for an additional hour. The resulting yellow solution showed IR absorptions at 2098 w, 2070 m, 2008 s, 1970 sh, and 1920 s cm^{-1}. The solvent was removed by rotary evaporation, and the residue was passed through a silica gel column with 10/90 ethyl acetate/hexane. Thus isolated was 0.044 g (0.067 mmol, 28%) of $Re_2(CO)_{10}$.

Reaction of 5 with 1 equiv of $K(sec\text{-}C_4H_9)_3BH$. Organic Product Analysis. To 0.559 g (0.857 mmol) of $Re_2(CO)_{10}$ in 20 mL of THF was added 3.40 mL (1.70 mmol) of 0.5 M $K(sec\text{-}C_4H_9)_3BH$ in THF. After 0.5 h, the solvent was removed by vacuum distillation. To the resulting residue was added 20 mL of water, 3 mL of methanol, and 0.5 mL of glacial acetic acid. This mixture was refluxed for 0.5 h and then cooled. Dimedone (0.250 g, 1.78 mmol) dissolved in a minimum of water was added. The solution was filtered, and 1.0 g of NaCl was added. The formaldehyde derivative formed over a 12-h period and was collected by filtration and vacuum-dried at 65 °C (0.053 g, 0.180 mmol, 21%). The ^1H NMR spectrum and TLC R_f value of this material were identical with those of an authentic sample prepared from aqueous formaldehyde.[21]

To 0.471 g (0.723 mmol) of $Re_2(CO)_{10}$ in 20 mL of THF was added 3.0 mL (1.50 mmol) of 0.5 M $K(sec\text{-}C_4H_9)_3BH$ in THF. The reaction was stirred for 1 h. The solvent was vacuum distilled, and the residue was washed with 2 × 25 mL of hexane. If the reduction product $CH_3OB(sec\text{-}C_4H_9)$ had formed,[45] it would have been in the hexane washes. The hexane was treated with 0.10 mL (1.3 mmol) of CF_3CO_2H and was vacuum distilled. To the distillate was added 0.40 g (1.7 mmol) of 3,5-dinitrobenzoyl chloride and 25 mL of THF. The mixture was refluxed overnight. Silica gel TLC comparison with an authentic sample showed methyl 3,5-dinitrobenzoate to be absent.

To 1.026 g (1.574 mmol) of $Re_2(CO)_{10}$ in 25 mL of THF was added 7.0 mL (3.50 mmol) of 0.5 M $K(sec\text{-}C_4H_9)_3BH$ in THF. The reaction was stirred for 0.5 h. Then 1.0 g (4.3 mmol) of 3,5-dinitrobenzoyl chloride was added, and the solution was refluxed for 2 h. Silica gel TLC of the resulting black solution showed the absence of methyl 3,5-dinitrobenzoate.

Reaction of 5 with 2 equiv of $K(sec\text{-}C_4H_9)_3BH$. Methanol Analysis. To 0.590 g (0.905 mmol) of $Re_2(CO)_{10}$ in 20 mL of THF was added 5.50 mL (2.75 mmol) of 0.5 M $K(sec\text{-}C_4H_9)_3BH$ in THF. After 0.5 h, 0.080 mL (0.910 mmol) of CF_3SO_3H was added and the volatiles were vacuum distilled. The distillate was treated with 0.40 g (1.70 mmol) of 3,5-dinitrobenzoyl chloride and then refluxed overnight. The solvent was removed, and the residue was chromatographed on silica gel with 10/90 ethyl acetate/hexane to give 0.079 g (0.035 mmol, 38%) of methyl 3,5-dinitrobenzoate, mp 92–96 °C. The ^1H NMR spectrum was identical with that of an authentic sample.

Decomposition of 4·THF. A 5-mm NMR tube was charged with 0.064 g (0.087 mmol) of **4**·THF, 0.0175 g (0.092 mmol) of *p*-di-*tert*-butylbenzene, and 0.40 mL of THF. The sample was placed in a 55 ± 2 °C oil bath, and the decomposition was monitored by ^1H NMR. Rate data are compiled elsewhere.[42a] After complete decomposition (147 h) IR $\nu_{C≡O}$ bonds at 2071 s, 2012 s, 1962 s, and 1872 m cm^{-1} were present.

A 50-mL round-bottom flask was charged with 1.769 g (2.416 mmol) of **4**·THF. The flask was evacuated and heated in a 90 °C oil bath for 1 h. The sample was cooled, and the resulting orange solid was extracted with 100 mL of hexane. A ^1H NMR spectrum of the remaining orange solid contained no resonances from δ 0 to −33. IR (cm^{-1}, THF): 1969 m, 1880 m. The solvent was removed from the hexane extract by rotary evaporation. The resulting white solid was vacuum-dried to give 0.733 g (1.125 mmol, 47%) of $Re_2(CO)_{10}$. IR (cm^{-1}, hexane): 2072 s, 2014 s, 1975 s. A similar decomposition gave an orange residue with IR absorptions at (THF) 1997 m and 1873 m cm^{-1} and a 39% yield of $Re_2(CO)_{10}$. Extensive attempts to crystallize the orange residue (THF/hexane; ether/petroleum ether) gave oils.

A sample of **4**·THF (0.840 g, 1.147 mmol) was decomposed at 95–100 °C as described above, and a formaldehyde assay was conducted as follows.[21] The sample was cooled to room temperature, and 20 mL of water, 3 mL of methanol, and 0.5 mL of glacial acetic acid were added. This mixture was refluxed for 0.5 h and then stirred at room temperature overnight. The reaction mixture was filtered, and 0.20 g (1.4 mmol) of dimedone in a minimum amount of water was added. Then 1.0 g of NaCl and 0.5 mL of glacial acetic acid were added. No formaldehyde derivative precipitated over the course of 2 days at room temperature.

A sample of **4**·THF (0.230 g, 0.314 mmol) was decomposed at 90 °C as described above, and a methanol assay was conducted as follows. The sample was cooled to room temperature, and 10 mL of THF and 0.23 g (1.0 mmol) of 3,5-dinitrobenzoyl chloride were added. This mixture was refluxed overnight. Silica gel TLC comparison with an authentic sample showed methyl 3,5-dinitrobenzoate to be absent.

A 50-mL round-bottom flask was charged with 0.286 g (0.391 mmol) of **4**·THF and attached to the vacuum manifold of a Toepler pump. The flask was evacuated and heated to 85–90 °C with an oil bath for 0.5 h. The dimer $Re_2(CO)_{10}$ sublimed to the sides of the flask. The flask was cooled to −196 °C and opened to the Toepler pump. No gas had evolved.

An evacuated flask containing 0.333 g (0.454 mmol) of **4**·THF was heated for 1 h in a 94–95 °C oil bath. The flask was cooled, and 10 mL of THF and 0.190 g (0.493 mmol) of Ph_3SnCl were added to the orange residue. This mixture was stirred for 1 h. Silica gel TLC showed the presence of $Re_2(CO)_{10}$, but $Ph_3SnRe(CO)_5$ was absent.

Photolysis of 4·THF. A NMR tube was charged with 0.062 g (0.084 mmol) of **4**·THF, 0.0089 g (0.047 mmol) of *p*-di-*tert*-butylbenzene, and 0.60 mL of THF. The solution was placed ca. 5 cm from two 20-W fluorescent lamps and photolyzed at 33 ± 3 °C for 23 h. A ^1H NMR spectrum (δ −7.10) showed that 0.069 mmol (82%) of $Li^+[Re_2(CO)_9H]^-$ was present. Then 10 mL of 30–60 °C petroleum ether was added. This precipitated a yellow paste, which was then washed with 3 × 10 mL of petroleum ether and vacuum-dried. IR (cm^{-1}, THF): 2083 vw, 2030 w, 2010 m, 1985 sh, 1966 s, 1923 m, 1884 m; lit.[15] $(C_2H_5)_4N^+[cis\text{-}Re_2(CO)_9H]^-$ (cm^{-1}, KBr) 2078 vw, 2028 m, 1972 s, 1924 w-m, 1888 m. ^1H NMR (δ, THF): −7.10.

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