Therefore, we propose that in this first step a hydrazido(2−) complex is formed as an intermediate. The reaction is shown in eq 3. The hydrazido(2−) complex may alternatively form as

$$2Mo(N_2)_2(triphos)(L) + 4HBr \rightarrow 2MoBr_2(NNH_2)(triphos) + 2N_2 + 2L \quad (3)$$

[MoBr(NNH$_2$)(triphos)(L)]Br. So far we have not been able to isolate and characterize this intermediate.

The second, slower step involves further loss of $^1/_2$ of a mol of N$_2$ and formation of ammonia. This latter step appears to be best described as a valence disproportionation involving two [Mo(N-NH$_2$)] units (eq 4). The reaction appears to be at least bimolecular since reducing the volume of solvent at ambient temperature after loss of 1 mol of N$_2$ causes an increase in the rate of evolution of the remaining $^1/_2$ of a mol of N$_2$. The intimate details of this second step remain a mystery at present. However, we do know that there is no scrambling of nitrogen atoms between NN units. This was shown by reacting HBr with **1** that had been partially labeled with dinitrogen-30. Analysis of the total amount of N$_2$ evolved showed *no* increase in the amount of $^{14}N{\equiv}^{15}N$ present over that occurring in the original N$_2$ gas used to prepare labeled complex **1**. This result together with the absence of hydrazine among the products rule out a linear tetrazane-type intermediate.

$$2MoBr_2(NNH_2)(triphos) + 4HBr \rightarrow 2MoBr_3(triphos) + 2NH_4Br + N_2 \quad (4)$$

It is interesting to contrast the ligand arrangement of the three groups of bis(dinitrogen) complexes: Mo(N$_2$)$_2$(dppe)$_2$, Mo(N$_2$)$_2$L$_4$ (where L = PMe$_2$Ph or PMePh$_2$), and **1**. The former complex contains two bidentate tertiary phosphine ligands, and protonolysis stops at the stage where diprotonation has been achieved and the hydrazido(2−) complex formed, e.g., [MoBr(NNH$_2$)(dppe)$_2$]Br. In contrast, the bis(dinitrogen) complexes of molybdenum containing four monodentate phosphine ligands are protonated to varying extents, depending upon the acid and the solvent, with the ultimate product being ammonia (with hydrazine often as a coproduct). Apparent intermediates in the ammonia-forming reaction that have been isolated and characterized for the molybdenum complexes are, e.g., MoBr(NNH)(dppe)$_2$[12] and MoBr$_2$(NNH$_2$)(PMe$_2$Ph)$_3$.[11] It has been proposed that the difference in behavior between these two groups of bis(dinitrogen) complexes rests with the ease with which coordination sites become available during the course of protonolysis together with the nature of the conjugate base of the acid.[2] Complex **1** is a hybrid of these two types. On the one hand, it contains the tridentate ligand which remains coordinated to molybdenum in the molybdenum-containing product while on the other hand it contains a monodentate phosphine which is displaced at some stage during protonolysis.

Further work is in progress to (i) isolate and characterize the proposed intermediate, (ii) elucidate the mechanism of the reaction, (iii) study the tungsten analogue, and (iv) carry out the protonolysis reaction in the presence of a reducing agent in order to regenerate the N$_2$-binding species in situ and hence produce a catalytic cycle.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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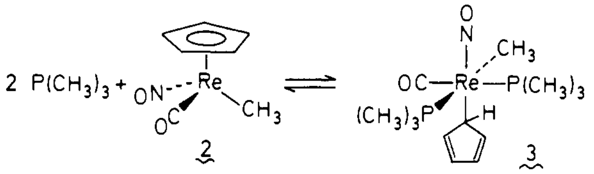
Conversion of an η^5-Cyclopentadienyl-Metal Complex to an η^1-Cyclopentadienyl-Metal Complex upon Addition of Trimethylphosphine

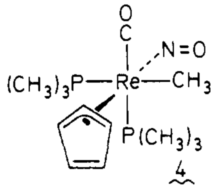
Sir:

We recently reported several synthetic routes to a hydroxymethyl metal compound, (η^5-C$_5$H$_5$)Re(CO)(NO)(CH$_2$OH) (**1**). Hydroxymethyl metal compounds have been suggested as important intermediates in the metal-catalyzed reduction of carbon monoxide[2] but have previously been unavailable for study.[3,4] Pruett has suggested that CO insertion into a Rh–CH$_2$OH species is a likely step in the rhodium cluster catalyzed synthesis of ethylene glycol from CO and H$_2$. In an attempt to find a model for such a CO-insertion process, we have studied the reactions of P(CH$_3$)$_3$ with (η^5-C$_5$H$_5$)Re(CO)(NO)(CH$_2$OH) (**1**) and with (η^5-C$_5$H$_5$)Re(CO)(NO)(CH$_3$) (**2**). We were surprised to find that reaction of P(CH$_3$)$_3$ with **2** does not produce an acetylrhenium complex but instead produces an η^1-cyclopentadienyl bis(phosphine) derivative (**3**).



An equimolar solution of **2** and P(CH$_3$)$_3$ (0.24 M) in acetone-d_6 undergoes a rapid reaction at room temperature. Proton NMR (270 MHz) spectra indicate that 50% of methylrhenium compound **2** (δ 5.80; 0.88) and 95% of the free P(CH$_3$)$_3$ [δ 0.96 (d, J = 2.2 Hz)] are consumed while a new product **3** appears with resonances at δ 5.57 (t, J = 1.5 Hz, 5 H), 1.70 (d, J = 8 Hz, 9 H), 1.49 (d, J = 8.3 Hz, 9 H), and 0.60 (dd, J = 8.3, 2.0 Hz, 3 H). The NMR spectrum thus requires that adduct **3** contain a methyl group which is cis to one P(CH$_3$)$_3$ ligand and trans to another P(CH$_3$)$_3$ ligand. When 2.5 equiv of P(CH$_3$)$_3$ were employed, complete conversion of the red methyl compound **2** to the yellow bis(phosphine) adduct **3** was observed. The reaction of (PCH$_3$)$_3$ with **2** is rapid in THF, acetone, benzene, and hexane. For synthetic purposes, hexane is the solvent of choice since **3** crystallizes from solution as it is formed and drives the equilibrium (vide infra) toward **3**. Reaction of **2** (0.111 g, 0.341 mmol) with P(CH$_3$)$_3$ (1.10 mmol) followed by rapid removal of hexane (0 °C, 10^{-3} mmHg) gave **3** as a yellow solid (0.163 g; 100%). The infrared spectrum (cyclohexane) of **3** has bands at 1994 and 1690 cm^{-1} compared with 1970 and 1715 cm^{-1} for starting material **2**.

The spectroscopic properties of **3** are consistent with either of two different 18-electron formulations: a fluxional η^1-C$_5$H$_5$Re^{I} derivative with a linear nitrosyl unit (**3**) or a fluxional η^3-C$_5$H$_5$Re^{III} derivative[6] with a bent nitrosyl ligand (**4**). Structure **4** seemed



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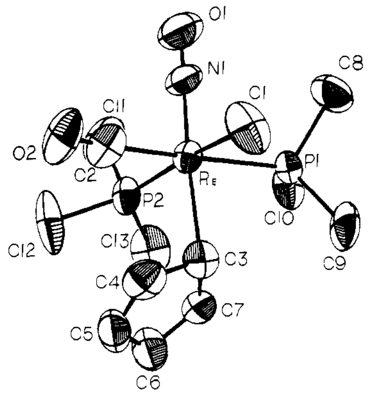

Figure 1. Ortep drawing of $(\eta^1\text{-}C_5H_5)Re(CO)(NO)(CH_3)[P(CH_3)_3]_2$ with 50% thermal ellipsoids.

Table I. Selected Bond Lengths in $(\eta^1\text{-}C_5H_5)Re(CO)(NO)(CH_3)[P(CH_3)_3]_2$ (Å)[a]

Re-P1	2.46	C2-O2	1.11
Re-P2	2.47	N1-O1	1.15
Re-C1	2.26	C3-C4	1.48
Re-C2	2.00	C4-C5	1.36
Re-C3	2.32	C5-C6	1.39
Re-N1	1.80	C6-C7	1.34
Re-C4	3.18	C7-C3	1.44
Re-C7	3.23		

[a] All lengths are 0.01 Å.

Table II. Selected Bond Angles in $(\eta^1\text{-}C_5H_5)Re(CO)(NO)(CH_3)[P(CH_3)_3]_2$ (deg)

P1-Re-P2	98.7	N1-Re-C1	93.9
P1-Re-C1	84.0	N1-Re-C2	92.8
P2-Re-C2	89.5	C3-Re-C1	83.0
C2-Re-C1	87.6	C3-Re-C2	89.3
N1-Re-P1	89.1	Re-N1-O1	179.7
N1-Re-P2	92.4	Re-C2-O2	173.7
C3-Re-P1	88.3		
C3-Re-P2	90.8		

plausible since it could account for the shift of the CO stretch to higher energy due to a change in formal oxidation state from I to III and for the shift of the NO stretch to lower energy due to bending of the nitrosyl ligand. In principle, structures **3** and **4** are distinguishable by NMR if the fluxional isomerization of the η^1- or η^3-C_5H_5 unit could be frozen out at low temperature. However, both the 270-MHz ^1H NMR at −100 °C and the 25-MHz ^{13}C NMR at −95 °C showed equivalence of all cyclopentadienyl protons (δ 5.58) and carbons (δ 114.8).

The X-ray crystal structure of the rhenium complex was determined ($R_1 = 0.041$, $R_2 = 0.057$) to distinguish between structures **3** and **4** and is shown in Figure 1 (Table I and II).[7] The molecule has an η^1-cyclopentadienyl group trans to a linear nitrosyl group and is clearly best formulated as **3**. The increase of the CO stretching frequency upon going from **2** to **3** is still surprising in view of the addition of two strong donor $P(CH_3)_3$ ligands but is evidently due to decreased electron donation from a trans $P(CH_3)_3$ ligand in **3** compared with a trans η^5-C_5H_5 ligand in **2**. The decrease of the NO stretching frequency upon going from **2** to **3** is most likely due to increased electron donation from the trans η^1-C_5H_5 of **3** compared with the trans η^5-C_5H_5 of **2** and from the two added $P(CH_3)_3$ ligands.[8]

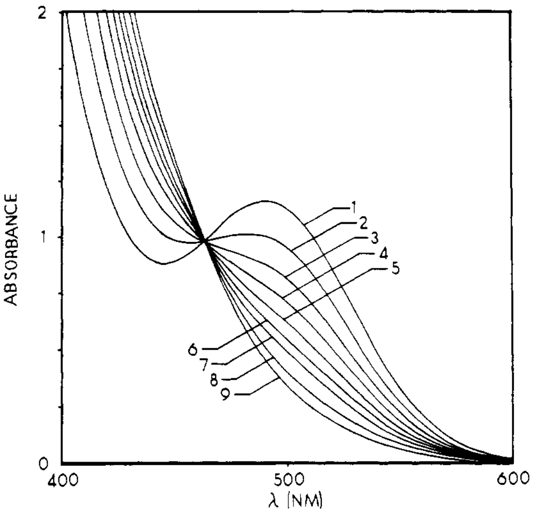

Figure 2. Reaction of **2** (0.013 M) with $P(CH_3)_3$ (0.25 M) in THF at 25 °C. Spectra 1-9 were recorded at 0, 5, 10, 15, 20, 25, 30, 40, and 50 min.

Table III. Observed Rate Constants for the Reaction of $P(CH_3)_3$ with $(\eta^5\text{-}C_5H_5)Re(CO)(NO)(CH_3)$ 0.0121 M in THF at 25.0 °C

$[P(CH_3)_3]$, M	k_{obsd}, s^{-1}	k_2[a], M^{-1} s^{-1}
0.484	1.35×10^{-3}	2.92×10^{-3}
0.242	6.40×10^{-4}	2.79×10^{-3}
0.123	3.35×10^{-4}	2.96×10^{-3}

[a] Corrected for small amounts of consumed $P(CH_3)_3$.

To our knowledge, the reaction of $P(CH_3)_3$ with **2** constitutes the first example of the conversion of an η^5-C_5H_5 system into an isolatable η^1-C_5H_5 complex. In 1957, Fischer suggested CO displacement of an η^5-C_5H_5 unit to an η^1-C_5H_5 unit in the reaction of CO with $(\eta^5\text{-}C_5H_5)_2ReH$ which gave a bis(carbonyl) adduct;[9] however, in 1958, Wilkinson and Green demonstrated by NMR that the reaction product was $(\eta^5\text{-}C_5H_5)Re(CO)_2(\eta^2\text{-}C_5H_6)$.[10] Cross and Wardle reported that $(Et_3P)(\eta^5\text{-}C_5H_5)PdBr$ reacted with PEt_3 to give a small amount of material with a resonance at δ 6.37 which they attributed to $(\eta^1\text{-}C_5H_5)Pd(PEt_3)_2Br$; the major isolated product of the reaction was $[\eta^5\text{-}C_5H_5Pd(PEt_3)_2]^+Br^-$.[11] Ustynyuk et al. found that $(\eta^5\text{-}C_5H_5)_2Ni$ reacts with $P(C_6H_5)_3$ at 50 °C to give a green compound which reverts to starting materials on alumina chromatography; the structure of the green material was suggested to be $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Ni[P(C_6H_5)_3]$.[12] Ligand displacement of η^5-C_5H_5 has also been suggested in a number of other organometallic reactions.[13]

The formation of phosphine adduct **3** is reversible. A 0.018 M solution of **3** in acetone-d_6 liberated phosphine slowly and came to equilibrium within 1 day at room temperature to give a 1.2:1.0:1.7 mixture of **3**:**2**:$P(CH_3)_3$. The complete conversion of **3** back to **2** and $P(CH_3)_3$ was accomplished by allowing a solution of **3** (0.1626 g, 0.341 mmol) in 5 mL of acetone to equilibrate

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(6) The X-ray structure of $(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)W(CO)_2$ has been determined: Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Friedrich, P.; Bejenke, V.; Neugebauer, D. *J. Organomet. Chem.* **1978**, *145*, 329–333. Infrared evidence for $(\eta^3\text{-}C_5H_5)Co(CO)_3$ in a CO matrix at 12 K has been presented: Crichton, O.; Rest, A. J.; Taylor, D. J. *J. Chem Soc., Dalton Trans.* **1980**, 167–173.

(7) A crystal (0.1 × 0.3 × 0.3 mm) obtained by slowly cooling a saturated hexane solution of **3** from +10 to −5 °C over 3 days was mounted on a Syntex $P_{\bar{1}}$ diffractometer (Mo $K\alpha$, graphite monochromater). **3** crystallizes in the monoclinic space group $C2/c$, with unit-cell constants $a = 17.416$ (6), $b = 8.513$ (2), $c = 25.387$ (12) Å; $\beta = 102.10$ (3)°; $Z = 8$ (ρ_{obsd} 1.71 g cm^{-3}, $\rho_{calcd} = 1.72$ g cm^{-3}). 3061 reflections ($2\theta \le 55°$) with intensities $\geq 3\sigma$ were used in structure refinement. The structure was solved by using standard heavy-atom techniques. Final coordinates, anisotropic thermal parameters, and structure factor amplitudes are included in Supplementary Material.

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for 1 h and then removing acetone and $P(CH_3)_3$ slowly under vacuum. Five cycles of this equilibration and $P(CH_3)_3$ removal sequence gave red crystalline **2** (0.1086 g, 98%) which was identified by IR and ^1H NMR spectroscopy.

The rate of reaction of **2** with excess $P(CH_3)_3$ in THF at 25.0 °C was monitored by following the decrease in absorbance at 488 nm (for **2**, ϵ_{488} 84.1 M^{-1} cm^{-1}; for **3**, ϵ_{488} 29.9 M^{-1} cm^{-1}) (Figure 2). The conversion of **2** to **3** followed pseudo-first-order kinetics to >80% reaction. The observed rate constants depended linearly on the phosphine concentration (Table III). The second-order rate constant, corrected for small amounts of consumed $P(CH_3)_3$, was determined to be $(2.89 \pm 0.09) \times 10^{-3}$ M^{-1} s^{-1}. The conversion of a THF solution of **3** to an equilibrium mixture of **3**, **2**, and $P(CH_3)_3$ was monitored by UV at 488 nm. The initial rate constant for disappearance of **3** at 25.0 °C was 3.1×10^{-4} s^{-1}, and the equilibrium constant was 7.10×10^2 M^{-2}.

The kinetic observation of a second-order reaction requires a rate-determining step involving both **2** (or a species in rapid equilibrium with **2**) and $P(CH_3)_3$ followed by rapid coordination of a second $P(CH_3)_3$. The rate-determining step might involve either an associative reaction of $P(CH_3)_3$ with unrearranged **2** or an attack of $P(CH_3)_3$ on a coordinatively unsaturated species which is in rapid equilibrium with **2**. Three possible rearrangements of the ligands on **2** could produce a vacant coordination site: (1) the η^5-C_5H_5 could "slip" to form an η^1- or η^3-C_5H_5 species, (2) the nitrosyl ligand could bend to change the formal oxidation state and electron count of the rhenium center, or (3) the methyl could migrate to the CO ligand to generate a coordinatively unsaturated acetylrhenium intermediate. Only the final possibility seems unlikely since the corresponding hydride, $(\eta^5\text{-}C_5H_5)Re(CO)(NO)H$, reacts with excess $P(CH_3)_3$ at room temperature to give an η^1-C_5H_5 bis(phosphine) hydride complex[14] analogous to **3** and since hydride migration from a metal to CO to form a formyl intermediate has never been observed.[2]

The hydroxymethyl complex $(\eta^5\text{-}C_5H_5)Re(CO)(NO)(CH_2OH)$ (**1**) also reacts with $P(CH_3)_3$ at 25 °C in acetone to produce a similar product, $(\eta^1\text{-}C_5H_5)Re(CO)(NO)(CH_2OH)[P(CH_3)_3]_2$ (**5**) [^1H NMR (acetone-d_6): δ 5.68 (dd, J = 1.5, 1.8 Hz, 5 H), 4.89 (d, J = 5.3 Hz, CH_2OH), 2.86 (br s, OH), 1.73 (d, J = 9 Hz, 9 H), 1.49 (d, J = 7.1 Hz, 9 H); IR (THF) 1979, 1680 cm^{-1}]. **5** is unstable and completely decomposes within 2 h at room temperature.

Methyl complex **2** also reacts with bis(dimethylphosphino)ethane to produce an η^1-C_5H_5 compound, $(\eta^1\text{-}C_5H_5)Re(CO)(NO)(CH_3)[(CH_3)_2P(CH_2)_2P(CH_3)_2]$: ^1H NMR (acetone-d_6) δ 5.47 (t, J = 1.5 Hz, 5 H), 1.65 (dd, J = 7.7, 1.8 Hz, 3 H), 1.68 (d, J = 9.6 Hz, 3 H), 1.63 (d, J = 8.8 Hz, 3 H), 1.53 (d, J = 8.1 Hz, 3 H), 1.51 (d, J = 9.6 Hz, 3 H), 1.0–3.0 (m, 4 H); IR (cyclohexane) 1986, 1687 cm^{-1}.

In contrast to $P(CH_3)_3$, no reaction of tri-*n*-butylphosphine (PBu_3) with **2** in benzene was observed even upon heating for 1 h at 70 °C.[15] At 100 °C, reaction of $(\eta^5\text{-}C_5H_5)Re(CO)(NO)(CH_3)$ (**2**) with 2 equiv of PBu_3 in C_6D_6 gave $(\eta^5\text{-}C_5H_5)Re(NO)(PBu_3)(COCH_3)$ (**6**)[16] (70% isolated yield) and $(\eta^5\text{-}C_5H_5)Re(NO)(PBu_3)(CH_3)$ (**7**)[17] (17% isolated yield).

Acknowledgment. Support from the Division of Basic Energy Sciences of the Department of Energy is gratefully acknowledged.

Supplementary Material Available: Tables of fractional coordinates, anisotropic thermal parameters, and structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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Received April 28, 1980

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[14] For $(\eta^1\text{-}C_5H_5)Re(CO)(NO)(H)[P(CH_3)_3]_2$: ^1H NMR (acetone-d_6) δ 5.54 (t, J = 1.7 Hz, 5 H), 1.79 (d, J = 9.0 Hz, 9 H), 1.64 (d, J = 8.3 Hz, 9 H), 0.08 (dd, J = 56.8, 29.8 Hz). Attempts to isolate this compound by removal of solvent (0 °C, 10^{-2} mmHg) resulted in decomposition to unidentifiable products.

[15] The half-life for formation of 6 from **2** (0.17 M) and PBu_3 (0.35 M) at 90 °C was approximately 5 h.

[16] For **6**: ^1H NMR (C_6D_6) δ 4.97 (s, 5 H), 2.90 (s, 3 H), 1.8–1.5 (m, 6 H), 1.27 (m, 12 H), 0.85 (t, $J.$ = 6.7 Hz, 9 H); IR (THF) 1645, 1561 cm^{-1}; ^{31}P NMR (C_6D_6) δ −6.34 relative to external H_3PO_4. Anal. Calcd for $C_{19}H_{35}NO_2$,PRe: C, 43.33; H, 6.70; N, 2.68. Found: C, 43.63; H, 6.99; N, 2.79.

[17] A mixture of **7** and PBu_3 was isolated by column chromatography. For **6**: ^1H NMR (C_6D_6) δ 4.74 (s, C_5H_5), 1.21 (d, J = 5.2 Hz, $ReCH_3$), 1.62 (m), 1.29 (m), 0.93 (t, J = 6.0 Hz); IR (THF) 1628 cm^{-1}.

[18] NSF National Needs Postdoctoral Fellow, 1979–1980.

Lewis Acid–Base Behavior of $H_2Os_3(CO)_{10}$: Versatile Pathways to Mixed-Metal Clusters

Sir:

Mixed-metal clusters have been prepared from the electronically unsaturated hydridoosmium carbonyl cluster $H_2Os_3(CO)_{10}$ by procedures which exploit its Lewis acid character.[1-4] We find that $H_2Os_3(CO)_{10}$ can also function as an apparent Lewis base. An illustration of the synthetic versatility of $H_2Os_3(CO)_{10}$ is the preparation of $H_2FeOs_3(CO)_{13}$ by two new and different routes: one route in which $H_2Os_3(CO)_{10}$ functions as an apparent Lewis acid and another route in which it functions as an apparent Lewis base (eq 1 and 2).

$$H_2Os_3(CO)_{10} + Fe(CO)_4{}^{2-} \xrightarrow{H^+} H_2FeOs_3(CO)_{13} \text{ 30\% yield} \tag{1}$$

$$H_2Os_3(CO)_{10} + Fe_2(CO)_9 \rightarrow H_2FeOs_3(CO)_{13} \text{ 82\% yield} \tag{2}$$

In reaction 1, the strongly nucleophilic metal carbonylate $K_2Fe(CO)_4$ will react at 0 °C with an equimolar quantity of $H_2Os_3(CO)_{10}$ in THF without evolution of any noncondensable gases to give a clear deep red solution. Removal of the THF solvent and protonation of the resulting anionic material with liquid HCl at −110 °C yields $H_2FeOs_3(CO)_{13}$ in 20–30% yield. The orange cluster was identified on the basis of mass spectral data and its infrared spectrum, which is identical with the previously reported spectrum.[5] The room-temperature ^1H NMR spectrum at 90 MHz consists of one resonance at τ 30.7. This chemical-shift value is in the range expected for metal-edge bridging hydrogen.[6]

Cluster expansion through reaction 1 effectively exploits the Lewis acid character of the triosmium system. The finding of Stone and co-workers[3] that certain electron-rich metal complexes will also add to $H_2Os_3(CO)_{10}$ is another example of this general reactivity pattern which had previously been established for nonmetal electron donors.[7,8]

Reaction 2 is a desirable alternate route to the preparation of $H_2FeOs_3(CO)_{13}$ because it provides a significantly higher yield of product and is technically easier to carry out. A twofold excess of $Fe_2(CO)_9$ reacts at room temperature with a benzene solution of $H_2Os_3(CO)_{10}$ to give $H_2FeOs_3(CO)_{13}$ in 82% yield. In this reaction, the triosmium system can be viewed to be functioning as a Lewis base rather than as a Lewis acid as in the case of reaction 1. Since a Lewis base will displace $Fe(CO)_5$ from $Fe_2(CO)_9$ to give an adduct of $Fe(CO)_4$,[9] it is not unreasonable to propose that the formation of $H_2FeOs_3(CO)_{13}$ by reaction 2 proceeds through an intermediate $H_2Os_3(CO)_{10}Fe(CO)_4$ adduct.

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