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).

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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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[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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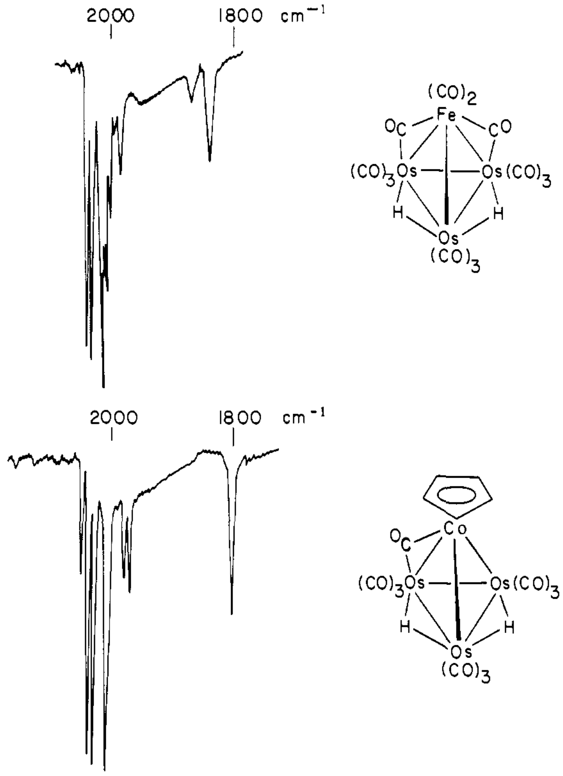

Figure 1. Infrared spectra and proposed structures of $H_2FeOs_3(CO)_{13}$ and $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$.

The classical valence bond representation of $H_2Os_3(CO)_{10}$ implies the presence of an osmium–osmium double bond. In an operative sense, the proposed intermediate, $H_2Os_3(CO)_{10}[Fe(CO)_4]$, can be likened to an $Fe(CO)_4$–olefin complex (eq 3).

$$Fe_2(CO)_9 + H_2Os(CO)_{10} \rightarrow Fe(CO)_5 + H_2Os_3(CO)_{10}[Fe(CO)_4] \rightarrow H_2FeOs_3(CO)_{13} + CO \quad (3)$$

Reaction pathways 1 and 2, especially the latter, afford significantly improved yields over earlier preparations of $H_2FeOs_3(CO)_{13}$. This cluster was reported as a side product isolated in 6% yield from the reaction between $H_2Os(CO)_4$ and $Fe_2(CO)_9$.[10] A later report[5] revealed that the reaction between the electron-precise cluster $Os_3(CO)_{12}$ and $Fe(CO)_4^{2-}$ followed by protonation gives $H_2FeOs_3(CO)_{13}$ in 9% yield.

In view of the success of reaction 2 as a high-yield pathway to an iron–osmium cluster, we extended this general procedure to the preparation of a new cobalt–osmium cluster via the displacement reaction 4.

$$(\eta^5\text{-}C_5H_5)Co(CO)_2 + H_2Os_3(CO)_{10} \rightarrow H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10} + 2CO \quad (4)$$

An excess of $(\pi^5\text{-}C_5H_5)Co(CO)_2$ will slowly react at 90 °C with $H_2Os_3(CO)_{10}$ in toluene to yield the new cluster $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$ in 60% yield. This compound is isolatable by column chromatography (silica gel 80:20 hexane/benzene) as an air-stable black-green solid. Its mass spectrum exhibits a high-mass cutoff at *m/e* 982, and the relative intensity distributions of the parent-ion cluster and those fragments due to loss of CO are in good agreement with the calculated intensity values for a three-osmium system.[11] High-resolution mass measurement on the *m/e* 982 ion confirms an elemental composition of $^1H_7{}^{12}C_{15}{}^{16}O_{10}{}^{59}Co^{192}Os_3$ (obsd 981.8223; calcd 981.8207).

The infrared spectrum of $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$ in cyclohexane consists of the following bands in the carbonyl stretching region: 2095 (m), 2068 (vs), 2050 (vs), 2012 (vs), 2000 (sh), 1977 (m), 1968 (m), 1800 (s) cm^{-1}. On the basis of comparison of infrared spectra, Geoffroy and Gladfelter[5] assign a tetrahedral structure of $H_2FeOs_3(CO)_{13}$ analogous to the crystallographically established tetrahedral structure of $H_2FeRu_3(CO)_{13}$.[12] Variable temperature ^{13}C NMR spectra of $H_2FeOs_3(CO)_{13}$ are fully consistent with spectra reported[5] for $H_2FeRu_3(CO)_{13}$. In Figure 1, the infrared spectrum and structure of $H_2FeOs_3(CO)_{13}$ are compared with the infrared spectrum and our proposed structure of $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$. The bridging carbonyl regions of these spectra differ significantly. In the case of $H_2FeOs_3(CO)_{13}$, two bands are observed at 1875 and 1848 cm^{-1} which Geoffroy and Gladfelter[5] attribute to symmetric and asymmetric stretching of the two equivalent bridging CO groups. The single, sharp bridging CO band at 1800 cm^{-1} in the infrared spectrum of $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$ is consistent with the presence of only one bridging CO ligand in this molecule.

In addition to one sharp resonance of intensity five at τ 4.53, due to the cyclopentadienyl hydrogens, the low-temperature (−80 °C) 90-MHz ^1H NMR spectrum of $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$ reveals the presence of two distinct bridging hydrogen resonances at τ 27.17 and τ 30.89. This observation permits distinction between the proposed structure and one in which the positions of hydrogens generate a cluster structure with apparent C_s symmetry. As the temperature is raised, the hydride resonances broaden and at 22 °C coalesce into one weak broad peak centered at τ 29.03. The cyclopentadienyl resonance is temperature independent. The ^{13}C NMR spectrum at −80 °C $\{^1H\}$ shows one bridge carbonyl and nine nonequivalent terminal carbonyls.

A new pentanuclear iron–osmium cluster, $H_2Fe_2Os_3(CO)_{16}$, has been isolated in low yield (<2%) from reaction 1. The low-resolution mass spectrum of this material exhibits a cutoff at *m/e* 1138 while high-resolution mass measurements confirm an elemental composition of $^1H_2{}^{12}C_{16}{}^{16}O_{16}{}^{56}Fe_2{}^{192}Os_3$ (calcd 1137.6877; obsd 1137.6897). Its infrared spectrum contains bands only in the terminal carbonyl region at 2086 (vs), 2070 (vs), 2062 (vs), 2040 (w), 2030 (s), 2005 (m), and 1983 (w) cm^{-1}. The room-temperature 90-MHz ^1H NMR spectrum of $H_2Fe_2Os_3(CO)_{16}$ consists of a single resonance at τ 31.4. Work is currently directed towards improving the yield of this pentanuclear compound.

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General Methodology for *cis*-Hydroisoquinoline Synthesis: Synthesis of Reserpine[1]

Sir:

Reserpine (**1**) has figured prominently during the last 3 decades as a compound of considerable medicinal importance, due largely to its extensive use in the treatment of hypertension and mental disorders.[2] Its isolation from the roots of the tropical shrub

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