and extending our experiments to include the collisionless regime by increasing fluence and decreasing pressure.

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(5) The Arrhenius parameters shown in eq 2 were estimated using methods described in S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1976.
Similar effects are noted in the IR–laser photolysis of alkyl iodides.

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(7) The average rate of a process i, $\langle k_i(E) \rangle$, can be formulated using a generalized Lindemann model.^{8} The resulting expression depends on the rates of radiative and collisional activation and deactivation, decomposition, laser power, and pulse width. The time evolution of $k_i(E)$ depends on the relative rates of laser pumping, energy pooling, deactivation, and reaction and can be determined using a kinetic master equation. Work in this regard is in progress in our laboratories.

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Mixed-Metal Clusters via Metal Hydride Coupling. New Rhenium–Osmium Clusters and the Crystal Structure of H$_2$Re$_2$Os$_3$(CO)$_{20}$

Sir:

The systematic preparation of metal carbonyl cluster compounds combining two or more different metals is a challenging synthetic problem and is potentially of practical importance in the generation of supported bimetallic catalysts.[1] Heterometallic bond formation via the displacement reaction of a metal carbonyl anion with a metal halide compound is the most predictable of the known procedures.[2] Other methods involving either the copyrolysis of different homometallic

carbonyl units[2,3] or the combination of a metal carbonyl anion and a neutral metal carbonyl[4,5] can be selective but frequently afford a mixture of products. The metal hydride coupling reaction shown in

$$L_nM_xS + HM'L_m \rightarrow L_nM_x \cdots H \cdots M'L_m$$
$$\text{or } L_nM_x(H)M'L_m + S \quad (1)$$
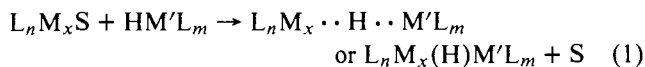
is a relatively unexplored approach to heterometallic cluster compounds.[6] Loss of the two-electron donor ligand S from the metal center M generates a vacant site that may interact with the H–M' bond to form either a stable M$\cdots$H$\cdots$M' three-center two-electron bond (as in HMnRe$_2$(CO)$_{14}$[7]) or new M–H and M–M' bonds (as suggested for formation of H$_2$Os$_2$(CO)$_8$[8]). We have recently shown that the labile derivatives Os$_3$-(CO)$_{12-x}$S$_x$ ($x = 1, 2$; S = cyclooctene or acetonitrile) can be prepared and used for substitution reactions.[9] Combining these derivatives with HRe(CO)$_5$ as in eq 1 has allowed us to prepare the compounds Os$_3$(CO)$_{12-x}$[HRe(CO)$_5$]$_x$ ($x = 1, 2$).

Treatment of the cyclooctene complex Os$_3$(CO)$_{10}$(C$_8$H$_{14}$)$_2$[9] with an excess of HRe(CO)$_5$ in benzene[10] provided a single product, isolated as a yellow solid in 90% yield after thin-layer chromatography. The electron impact mass spectrum of this material is consistent with the formulation H$_2$Re$_2$Os$_3$(CO)$_{20}$.[12] In its ^{1}H NMR spectrum two hydride signals are observed at τ 26.9 and 28.1 (CH$_2$Cl$_2$) with $J_{HH} = 2$ Hz. The ^{13}C {^{1}H} NMR spectrum of the compound, prepared from ^{13}CO-enriched Os$_3$(CO)$_{10}$(C$_8$H$_{14}$)$_2$, displays at 33 °C three singlets of intensity 2 C and four singlets of intensity 1 C.[13] These data are consistent with a structure that retains the basic Os$_3$ triangle of Os$_3$(CO)$_{12}$, but with two rhenium carbonyl groups substituted unsymmetrically for two equatorial carbonyl ligands (cf. Os$_3$(CO)$_{10}$(PEt$_3$)$_2$[14]). The data do not determine whether the rhenium carbonyl groups are bound to the Os$_3$ triangle by Os–H–Re or Os–Re bonds. However, a single-crystal x-ray diffraction study of H$_2$Re$_2$Os$_3$(CO)$_{20}$ has established the latter mode together with the probable positions of the hydrogen ligands as in structure II.

I   II
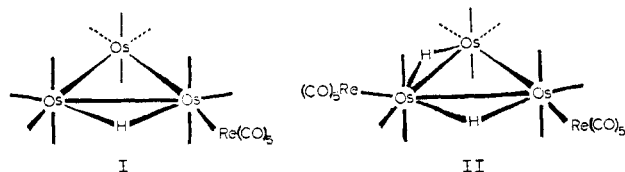
The H$_2$Re$_2$Os$_3$(CO)$_{20}$ molecule crystallizes in the monoclinic space group Cc with $a = 9.248$ (2) Å, $b = 23.010$ (4) Å, $c = 29.665$ (5) Å, $\beta = 104.59$ (1) °, $V = 6109$ (2) Å^3, and π (calcd) = 3.27 g cm^{-3} for $M = 1505$ and $Z = 8$. Diffraction data were collected with a Syntex P2$_1$ automated diffractometer using Mo Kα radiation and an ω-scan technique. Data were corrected for absorption ($\mu = 205$ cm^{-1}); the structure was solved by Patterson methods (which indicated the lower space group Cc, rather than the centrosymmetric $C2/c$) and refined by full-matrix least-squares methods (409 variables; 2764 data in the range 3° < 2θ < 40° with $F > \sigma(F)$) using the Syntex XTL system to final discrepancy indices of $R_F = 4.5\%$ and $R_{wF} = 4.9\%$. All atoms other than hydrogen atoms have been located and refined. Metal atoms were assigned anisotropic thermal parameters, while all other atoms were restricted to isotropic thermal parameters. The crystallographic asymmetric unit consists of two molecules of H$_2$Re$_2$Os$_3$(CO)$_{20}$ related to each other by a (local) pseudoinversion center at a *general* position in the unit cell. The two molecules have identical connectivities and their bond lengths and angles are identical with the limits of experimental error. One such molecule is illustrated in Figure 1.

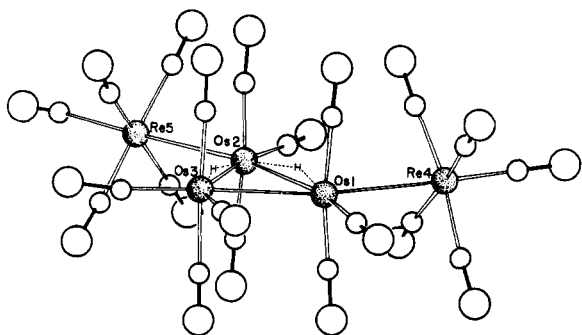The metal core consists of a triangle of osmium atoms with

Figure 1. The $H_2Re_2Os_3(CO)_{20}$ molecule, with the probable positions of the hydride ligands indicated.

a rhenium atom bonded to equatorial sites of two of these atoms. The Os(1)–Os(3) bond lengths in the two independent molecules are 2.876 (3) and 2.876 (3) Å—i.e., closely similar to the Os–Os bond length of 2.877 (3) Å (average) found in $Os_3(CO)_{12}$.[15] In contrast to this, the remaining Os···Os distances are significantly longer, with Os(1)–Os(2) = 3.058 (3) and 3.061 (3) Å and Os(2)–Os(3) = 3.083 (3) and 3.074 (3) Å. We believe that these vectors are bridged by μ_2-hydrido ligands. (In other molecules simple μ_2-hydrido bridged osmium–osmium bond lengths are 2.989 (1) Å for $(\mu_2$-H)(H)-$Os_3(CO)_{11}$[15] and 3.019 (1) Å for $(\mu_2$-H)(H)Os_3-$(CO)_{10}PPh_3$.)[16] The osmium–rhenium bond lengths are normal, with Os(1)–Re(4) = 2.952 (4) and 2.946 (4) Å and Os(2)–Re(5) = 2.982 (3) and 2.975 (3) Å. The angles involving the equatorial rhenium atoms are as follows: ∠Os(2)–Os(1)–Re(4) = 104.1 (1) and 104.0 (1)° and ∠Os(3)–Os(2)–Re(5) = 104.2 (1) and 102.9 (1)°. Each metal atom has a regular coordination geometry, there being three carbonyl ligands associated with Os(1) and Os(2), four for Os(3), five for Re(4) and Re(5).

Treatment of $Os_3(CO)_{12}$ with $Me_3NO\cdot2H_2O$ (1 equiv) in acetonitrile followed by excess $HRe(CO)_5$ in benzene provided a single new product, which was isolated as a yellow solid in ~50% yield after TLC. Spectroscopic data for this material is consistent with the formula $HReOs_3(CO)_{16}$[17] and it is assigned structure **1**. In an attempt to prepare $H_3ReOs_3(CO)_{24}$, $Os_3(CO)_{10}(NCMe)_2$[9] was treated with 1 equiv $Me_3NO\cdot$ $2H_2O/NCMe$[18] and then $HRe(CO)_5$, but the product isolated was $HReOs_3(CO)_{15}$.[19] Similar treatment of $H_2Re_2Os_3(CO)_{20}$ provided $H_2Re_2Os_3(CO)_{19}$. However, subsequent experiments showed that $H_2Re_2Os_3(CO)_{19}$ could be formed by allowing $H_2Re_2Os_3(CO)_{20}$ to react with $Me_3NO\cdot2H_2O/NCMe$ alone; an analogous reaction gave $HReOs_3(CO)_{15}$ from $HReOs_3(CO)_{16}$. The detailed structures of these more condensed clusters remain to be determined. Nevertheless, it is clear that the combination of $HRe(CO)_5$ coupling with Me_3NO decarbonylation provides considerable control of metal–metal bond formation in the Re–Os system. The efficacy of these techniques with other heterometallic combinations is being explored.

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(12) M$^+$, m/e 1512 (^{187}Re, ^{192}Os); (M − xCO)$^+$ (x = 1–13) and (M − HRe-(CO)$_4$ − yCO)$^+$ (y = 0–11) also observed.
(13) ^{13}C NMR (CH_2Cl_2, parts per million downfield from TMS): 193.4 (2 C), 183.8 (2 C), 183.0 (1 C), 177.8 (1 C), 176.2 (2 C), 165.5 (1 C), 163.8 (1 C). No signals for carbonyls attached to rhenium were observed, either at 30 or at −50 °C, suggesting that CO exchange between osmium and rhenium is very slow.
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(17) Mass spectrum: M$^+$, m/e 1212 (^{187}Re, ^{192}Os); also (M − xCO)$^+$ (x = 1–16) and (M − HRe(CO)$_4$ − yCO)$^+$ (y = 1–10). ^{1}H NMR (CH_2Cl_2): τ 28.8. A compound of the same formula, identified by mass spectroscopy, was obtained in an impure state by Knight and Mays.[4]
(18) This treatment is assumed to provide mainly $Os_3(CO)_9(NCMe)_3$, since addition of $PPhMe_2$ to the solution leads to $Os_3(CO)_9(PPhMe_2)_3$. However, the triacetonitrile species has not been isolated.
(19) Mass spectrum: M$^+$, m/e 1184 (^{187}Re, ^{192}Os), and (M − xCO)$^+$ (x = 1–15); also series involving Os_3 and ReOs ions. ^{1}H NMR (CH_2Cl_2): τ 26.8 (s, 1 H vs. $HOs_3(CO)_{10}OMe$ internal standard). IR (C_6H_{12}): ν_{CO} 2114 (vw), 2084 (m), 2058 (m), 2029 (m), 2015 (s), 2002 (s), 1991 (m), 1981 (w), 1971 (m), 1965 (sh), 1932 (w) cm^{-1}. A compound of formula $HReOs_3(CO)_{15}$ was isolated by Knight and Mays;[4] its molecular structure was recently determined to be rhomboidal (M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, **16**, 2493 (1977)). However, $HReOs_3(CO)_{15}$ prepared as described here appears to differ from Knight and Mays' compound in solubility and IR spectrum. We have not yet been able to obtain crystals of our compound suitable for x-ray diffraction.
(20) Mass spectrum: M$^+$, m/e 1484 (^{187}Re, ^{192}Os), and (M − xCO)$^+$ (x = 1–19); also series involving ReOs$_3$, Os$_3$, Re$_2$Os, and Re$_2$ ions. ^{1}H NMR (CH_2Cl_2): τ 25.6 (d, 1 H), 26.0 (d, 1 H); J = 0.8 Hz. IR (C_6H_{12} ν_{CO}): 2107 (m), 2078 (m), 2062 (m), 2051 (m), 2015 (s), 2004 (s), 2000 (s), 1994 (s), 1986 (m), 1976 (s), 1964 (s), 1950 (vw), 1930 (w) cm^{-1}.

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Total Synthesis of *dl*-Lycoramine

Sir:

Lycoramine (**1**) is one of the galanthamine-type alkaloids found in plants of the *Amaryllidaceae*.[1] We now report a total synthesis of *dl*-lycoramine.[2]
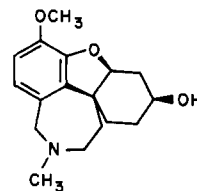
1

The synthesis of **1** features a new benzodihydrofuran ring construction (e.g., A → B → C). In the sequence, heteroatom-directed photoarylation[3] (B → C) establishes the crucial carbon–carbon bond[4] joining an aromatic ring to a quaternary carbon atom located at a ring junction. The photoreaction **5a** → **6** → **7** to be described here is representative of a general