tion,[1-3] *i.e.*, the 2β-OH group. The enormous shift for the quaternary C-19 methyl group, which shifts from δ 1.03 to 7.85, is in accord with its spatial proximity, *i.e.*, 1,3 diaxial to the 2β-hydroxyl function.[3] Of further interest is the increased resolution of the methylene–methine envelope which is now spread over an area more than twice as wide as that in the normal spectrum, *i.e.*, from δ 1.25 to 4.20. The observed shift of this whole region to lower field indicates that *every* proton in **1** is significantly shifted, even ring D protons, the furthest of which is greater than 10 Å removed from the 2β-OH function. These observations are not unexpected since sizable paramagnetic shifts are expected for protons as far away as 27 Å from the site of coordination.[3]

Information regarding assignments for ring B and C protons can be obtained from closer scrutiny of the methylene–methine envelope (δ 1.0–5.0) at 220 MHz. The 220-MHz spectrum of this region together with proton assignments, most of which are tentative, are shown in Figure 1C. Irradiation of $H_{5\alpha}$ (δ 5.63) in the 100-MHz spectrum of **1** (see Figure 1B) causes the quartet of doublets on the low-field side of the methylene envelope (δ 4.00) to collapse to a triplet of doublets. This signal was assigned accordingly to $H_{6\beta}$. Saturation of $H_{6\beta}$ causes a collapse in what appeared to be a triplet of doublets centered at δ 2.60 at 100 MHz (see Figure 1B), but which, from the 220-MHz spectrum, is shown to be a quartet of doublets (see Figure 1C) and is thus assigned to $H_{7\alpha}$ axial. The remaining signals in the δ 2.5–4.5 region of the 220-MHz spectrum of **1** were tentatively assigned on the basis of their observed signal multiplicities and the expected dependence of their chemical shift on the distance of their location from the site of coordination. Thus, since $H_{11\alpha}$, $H_{6\alpha}$, and $H_{7\beta}$ are the only three protons (except for ring A protons) in the approximate vicinity of the 2β-hydroxyl function that can give rise to a doublet of quartet signal, the lowest field doublet of quartets (δ 3.75) is assigned to $H_{11\alpha}$, since[4] $R \simeq$ 4.4 Å, the highest field doublet of quartets (δ 2.90) is assigned to $H_{7\beta}$, since $R \simeq$ 6.3 Å, and the intermediately situated quartet of doublets (δ 3.50), partially overlapped by the tentatively assigned $H_{11\beta}$ signal, is assigned to $H_{6\alpha}$, since $R \simeq$ 5.3 Å. The remaining protons in this region were assigned in similar fashion.

It is apparent that shifts induced by Eu(DPM)$_3$ can give valuable insight not only into the structure of ring A, but also rings B and C even though only one OH function is present in the compound. We have also investigated the effects of Eu(DPM)$_3$ on a number of ring D hydroxy steroids and have found that all protons in both the C and D rings can be unambiguously assigned in a majority of cases. This method therefore offers a new and simple approach to ring D conformational analysis in steroids, since the magnitude of vicinal couplings between various D-ring protons can be simply related to dihedral angles through the Karplus relationship.[5]

The potential of shifts induced by Eu(DPM)$_3$ for the study of structurally complex triterpenes is illustrated by the spectra of friedelan-3β-ol (**2**) (10 mg, 0.23 × 10^{-4} mol). The normal spectrum of **2** (CDCl$_3$), shown in Figure 2A, is practically devoid of information with all eight methyl signals residing in a very narrow region to high field (δ 0.4–1.2). The addition of Eu(DPM)$_3$ (17 mg, 0.24 × 10^{-4} mol) results in a spectrum spread over more than 20 ppm and reveals a multitude of signals which are assigned, as shown in Figures 2B and 2C, by methods similar to those described for 1. In these spectra, all ring A protons (except $H_{3\alpha}$ which is farther than 20 ppm distant from TMS) and two ring B protons ($H_{6\alpha}$ and $H_{6\beta}$) are clearly in evidence. Further, all methyl signals are now separated distinctly from each other, with two, namely the tertiary 4-CH$_3$ (δ 8.67) and the quaternary 5-CH$_3$ (δ 8.42), suffering the most significant shifts to lower field in accordance with their spatial proximity to the site of coordination.[1-3] The remaining methyl singlets were assigned such that the order of their appearance from low to high field corresponds to the magnitude of their separation from the 3β-OH function.

In the large variety of hydroxy steroids we have studied to date, the most significant, although not serious, broadening effects have been recorded for protons close to the site of coordination. We interpret this broadening to originate from a direct electron–proton dipole–dipole interaction[6,7] between unpaired metal electrons and nearby protons.

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[3] P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734 (1970).

[4] As in the accompanying communication, *R* represents the vector distance from the proton(s) in question to the hydroxyl oxygen atom. Values for *R* were measured from Dreiding models.

[5] M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963); M. Karplus, *J. Chem. Phys.*, 30, 11 (1959).

[6] The contribution to T_1 resulting from the dipole–dipole interaction of an unpaired electron and a proton is given by[7] $1/T_1 = h^2\gamma_e^2\gamma_p^2\tau/r^6$, where τ is the correlation time for random molecular rotation, r is the distance between the nuclear and electron dipoles, and other signals have their usual significance.

[7] A. Abragam, "The Principle of Nuclear Magnetism," Oxford University Press, London, 1961, p 264; N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, 73, 679 (1948).

[8] (a) Address correspondence to this author. (b) Public Health Service Predoctoral Fellow, 1969.

Paul V. Demarco,[8a] Thomas K. Elzey
Lilly Research Laboratories, Eli Lilly and Company
Indianapolis, Indiana 46206

R. Burton Lewis,[8b] Ernest Wenkert
Department of Chemistry, Indiana University
Bloomington, Indiana 47401

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Preparation and Properties of $H_4Re_4(CO)_{12}$, an Unsaturated Polynuclear Carbonyl Hydride Cluster[1]

Sir:

During a study of the thermal cleavage of metal cluster compounds we have observed, while heating $H_3Re_3(CO)_{12}$ to 190° in hydrocarbon solution, a deep red coloration through which we have identified a new polynuclear tricarbonyl hydride of rhenium.

Decalin (60 ml, cis-trans, degassed and dried over Na) containing $H_3Re_3(CO)_{12}$[2] (0.51 g, 0.57 mmol) is heated under nitrogen at reflux for 0.5 hr. Uncon-

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[2] D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **86**, 4841 (1964).

Table I. Parent Ion Multiplet in the Mass Spectrum of $H_4Re_4(CO)_{12}$[a]

m/e	1080	1081	1082	1083	1084	1085	1086	1087	1088	1089
Rel intensity[b]										
obsd	6.7	2.8	34.0	6.7	82.1	12.8	90.1	14.5	41.3	6.7
calcd[c]	5.0	0.7	33.5	5.0	85.2	12.6	96.5	14.2	40.9	6.0

[a] AEI MS9 spectrometer; inlet probe at 120°; ionizing current, 70 eV. [b] Arbitrary scale, mm ± 0.5. [c] For the isotopic distribution in the title compound, assuming no loss of hydrogen during ionization. The calculated spectrum was normalized to the observed spectrum by equalization of total intensity.

verted starting material is precipitated by cooling to 0°. After filtration, benzene (3 ml, dried and redistilled) is slowly added to the solution, precipitating 0.1 g of a deep red powder, I. A mass spectrum of I showed, among other features, a parent multiplet (Table I) in agreement with the formula $H_4Re_4(CO)_{12}$.[3] Additional multiplets were observed indicating loss of 12 CO groups and 4 H atoms. The intensity patterns of lower multiplets showed increasingly marked departure from the isotopic pattern shown in Table I owing to simultaneous loss of H during ionization and fragmentation.

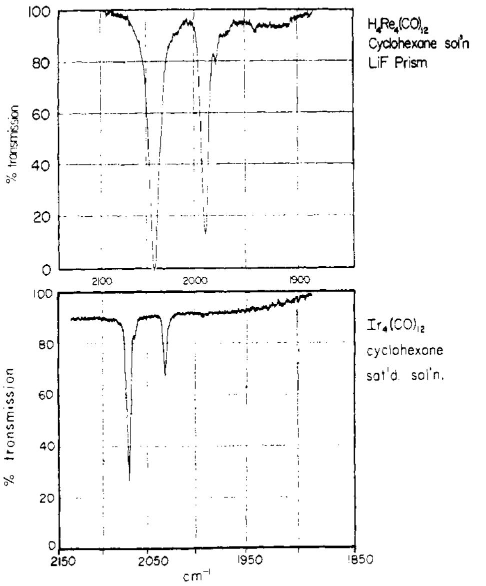
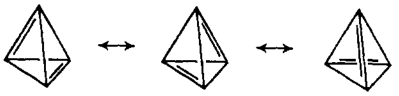


Figure 1. Infrared absorptions in the carbonyl stretching region for $H_4Re_4(CO)_{12}$ and $Ir_4(CO)_{12}$,[4b] in cyclohexane solution; Beckman IR 4 spectrophotometer equipped with LiF prism.

The ^1H nmr of I in CCl_4 solution showed a single resonance at τ 15.08 (TMS internal standard) together with resonances of the hydrocarbon of crystallization. Two principal absorptions occur in the carbonyl stretching region, Figure 1, in the infrared spectrum of I. These data suggest that I is a molecule of high symmetry, most likely resembling $Ir_4(CO)_{12}$[4] which also has a two-peak pattern in the carbonyl region of similar relative intensities.[4b] A sample of $D_4Re_4(CO)_{12}$ was prepared from $D_3Re_3(CO)_{12}$[2] and its infrared spectrum compared with that of I. No bands characteristic of a terminal Re–H (*ca.* 1800–2200 cm⁻¹) or a terminal Re–D (*ca.* 1250–1550 cm⁻¹) were observed, indicating a bridging position for hydrogen (discussed below).

An electron count suggests that the cluster is unsaturated. If we assume that each rhenium is receiving one electron from each of three metal–metal bonds, six electrons from three CO groups, and one electron from a hydrogen atom, each metal would be short one electron of a closed valence shell. To account for the diamagnetism[5] and the high symmetry of the complex, one is led to draw double bonds between pairs of Re atoms and to assume resonance between three equivalent canonical structures by analogy to the Kekulé structures of benzene.



However, a description of the bonding should also account for the placement of the hydrogen atoms. Structural studies on polynuclear carbonyl hydrides indicate[6] that bridging hydrogen affects mainly metal–metal bond distances, with little perturbation of the coordination geometry of other atoms around the metal. We have carried out a qualitative molecular orbital treatment considering first the bonding of the metal cluster and carbonyl groups in an arrangement similar to that found in the tetrahedral dodecacarbonyl clusters of $Ir_4(CO)_{12}$[4a] and $H_6Re_4(CO)_{12}^{2-}$.[6a] A consideration of positions of suitable overlaps will then assist in the placement of the hydrogen atoms. Within the cluster orbitals it is difficult to identify the usual σ and π separations because these are strongly mixed under T_d symmetry. However, it is clear that molecular orbitals of A_1 and T_2 symmetry arising principally from combinations of metal d orbitals will be localized over the faces, which can overlap with the orbitals of a tetrahedral array of hydrogen 1s orbitals, grouped into the same two symmetry species. Thus triply bridging hydrogen atoms located over the faces of the tetrahedron (the most likely position as indicated by the overall symmetry and the absence of terminal metal–hydrogen stretching modes) can be accommodated through the molecular orbital treatment. The highest occupied MO is required to be filled, in accord with the diamagnetism[5] of the complex. Through the addition of four electrons (*via* two hydride ions; see below) I is related to the known $H_6Re_4(CO)_{12}^{2-}$ ion.[6b] In

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(3) The material appears to crystallize as a solvate. *Anal.* Calcd for $H_4Re_4(CO)_{12}\cdot C_{10}H_{18}$: C, 21.59; H, 1.81. Found (Heather King, UCLA): C, 22.99; H, 1.60. When the red powder is dissolved in cyclohexane and reprecipitated with benzene, the product is a cyclohexane solvate. *Anal.* Calcd for $H_4Re_4(CO)_{12}\cdot C_6H_{12}$: C, 18.49; H, 1.38. Found: C, 18.84; H, 1.39.

(4) (a) G. R. Wilkes and L. F. Dahl, unpublished; G. R. Wilkes, Ph.D. Dissertation, University of Wisconsin, 1965; (b) R. Bau, D. Hendrickson, and H. D. Kaesz, unpublished; R. Bau, Ph.D. Dissertation, University of California, Los Angeles, 1968.

(5) Magnetic susceptibility measurements in a Faraday balance yielded a very low positive molar susceptibility, as expected for a diamagnetic metal carbonyl cluster; see discussion in ref 2.

(6) (a) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Amer. Chem. Soc.*, 90, 7135 (1968); (b) H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *ibid.*, 91, 1021 (1969); (c) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Commun.*, 458 (1970).

this case, it is believed that the hydrogen atoms are located over the edges, where, according to the symmetry classifications, orbitals principally from the metal of A_1, E, and T_2 species would be available for bonding to the six-hydrogen atom array whose orbitals are grouped in those same symmetry species.

The chemical reactions of I illustrate its unsaturated nature. Contact with any substance with well-developed donor power, including solvents such as ether and acetonitrile as well as the usual ligands such as CO or phosphines in hydrocarbon solution, brings about reaction at room temperature, in some cases, instantly. Most of these lead to degradation of the tetrahedral cluster. The reaction with CO yields $H_3Re_3(CO)_{12}$ and $HRe(CO)_5$ as the principal products. Use of isotopically labeled CO gives labeled products which, in the case of $H_3Re_3(CO)_{12}$, could assist in assigning the carbonyl modes and which, in turn, could indicate whether the substitution was stereospecific or not.

Treatment of I in cyclohexane solution in a heterogeneous reaction with $NaBH_4$ results in a very slow reaction in which the red color and all traces of I are observed to disappear from the hydrocarbon solvent. Removal of the cyclohexane and addition of acetone reveals (by ir) the spectrum of the $H_6Re_4(CO)_{12}{}^{2-}$ ion (2000 and 1910 cm^{-1}), a saturated compound previously isolated from the reduction of $Re_2(CO)_{10}$ with $NaBH_4$.

(7) (a) Address correspondence to this author; (b) publication no. 2651.

Roger Saillant, Gail Barcelo, Herbert Kaesz[7a]
Department of Chemistry,[7b] *University of California*
Los Angeles, California 90024
Received June 29, 1970

Chemiluminescent Reactions of Iron and Nickel Carbonyls with Ozone

Sir:

While checking for possible interferences in the chemiluminescent detection of NO, spurious light emission was observed in the region of 5000–6500 Å when carbon monoxide was mixed with ozonized oxygen in a flow reactor. The light emission could be greatly reduced by passing the carbon monoxide over asbestos at 200° or through a Dry Ice trap. In the latter case, intense orange light was observed as the trap was warmed. Thus, the emission is not directly from carbon monoxide but is due to an impurity. A spectrum of this emission showed broad maxima at 5650, 5900, and 6200 Å, with some vibrational structure. From published spectra,[1] the luminescence observed here was identified as FeO emission with a small contribution from NiO. In addition, deposits of iron and nickel oxides were found on the reactor walls. These results clearly indicate that carbonyl impurities, commonly present when carbon monoxide is stored in steel tanks, are responsible for the light emission. This was further confirmed with $Fe(CO)_5$ and $Ni(CO)_4$ samples. Emission of FeO and NiO has been observed previously in high-temperature flames[1] and in O-atom reaction of the carbonyls,[2] but no study of chemiluminescence in ozonolysis has been reported.

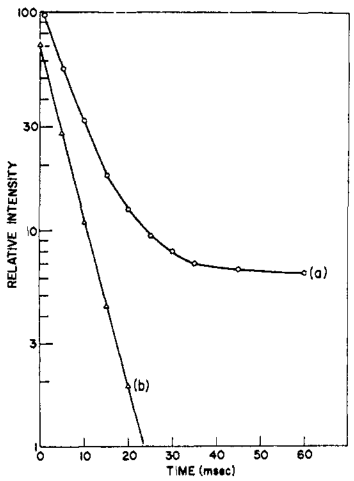

Figure 1. (a) Light emission from carbonyl containing carbon monoxide. (b) Light emission from $Fe(CO)_5$.

The kinetics and mechanism of the chemiluminescent reactions were studied by measuring the emission intensity as a function of reaction time and reactant concentration. Ozone was determined from the decay rate of the NO_2* emission from the well-known reaction $NO + O_3 \rightarrow NO_2^* + O_2$. When carbon monoxide containing both iron and nickel carbonyl was treated with a large excess of ozone, the intensity of the unresolved spectrum showed an initial first-order decay followed by a very flat tail (Figure 1a). However, from the distinct spectral distribution of the two reaction zones, iron oxide was found to be responsible for the exponential decay while nickel oxide gives rise to the tail. This kinetic behavior of FeO and NiO emission was confirmed with pure samples as described below.

The orange FeO emission from the reaction of pure iron carbonyl in excess ozone followed first-order decay (Figure 1b) with a lifetime given by the relation $\tau = (k[O_3])^{-1}$, where $k = 1 \times 10^{-13}$ cc/(molecule sec). The lifetime was also shown to be independent of carbonyl concentration under the conditions used here. These results indicate that the light emission is closely coupled to the primary reaction of ozone with iron carbonyl. The reaction must be at least 58 kcal exothermic to provide energy for light emission of FeO at 5000 Å.

The NiO emission was observed with pure nickel carbonyl and ozone only in the presence of carbon monoxide. Since the light extends the entire length (50 cm) of the flow reactor with very little decay, kinetic measurements could not be made. With only ozone and nickel carbonyl, a black deposit indicates that a nonluminous reaction occurs under these conditions. The NiO emission can then be generated by adding carbonyl-free CO well downstream. This shows that a nickel-containing species produced in the nonluminous reaction travels some distance before it reacts with carbon monoxide to yield NiO chemiluminescence. The most likely species is ground-state NiO, which can be easily reduced by carbon monoxide. The reaction of ozone with nickel atoms is exothermic by 76

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(1) R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," Wiley, New York, N. Y., 1963.

(2) W. R. Brennen, Ph.D. Thesis, Harvard University, 1964.