Communications to the Editor

A Tetrahedral Anionic Rhenium Carbonyl Hydride: $[H_6Re_4(CO)_{12}{}^{2-}]$[1]

Sir:

Through reduction of and simultaneous CO cleavage from $Re_2(CO)_{10}$, a number of polynuclear carbonyl anions and hydrides have been isolated containing rhenium tetracarbonyl groups ($Re_4(CO)_{16}{}^{2-}$,[2] $H_2Re_3(CO)_{12}{}^{-}$,[3] $H_3Re_2(CO)_{12}$[4]) or a combination of this group with pentacarbonyl groups ($HRe_3(CO)_{14}$).[5] We have now isolated a member of a rhenium *tri*carbonyl series, $[(C_6H_5)_4As^+]_2[H_6Re_4(CO)_{12}{}^{2-}]$ (I), after prolonged heating and more extensive CO cleavage from $Re_2(CO)_{10}$.

Dirhenium decacarbonyl (5.1 g, 7.7 mmoles) was refluxed overnight in tetrahydrofuran in the presence of an excess (33 mmoles) of sodium borohydride. The red solution was then stirred at room temperature for several days, during which time slow gas evolution occurred accompanied by decoloration of the solution to light red-orange and precipitation of a light orange to yellow gel. The supernatant liquid was decanted and the gel extracted with tetrahydrofuran (THF). To the extract, a solution of tetraphenylarsonium chloride in ethanol was added; cooling of this mixture at $-5°$ for 2 days yielded 0.5 g of light yellow parallelopiped crystals of I.[6]

Compound I is soluble in acetone, THF, methylene chloride, and acetonitrile. Conductivity measurements in acetonitrile show that the compound is a 2:1 electrolyte. The H^1 nmr spectrum in acetone shows a sharp peak at τ 27.4 due to Re–H and a sharp singlet at τ 2.20 due to the hydrogen atoms of $(C_6H_5)_4As^+$ (relative intensity $5.94 \pm 0.25{:}40.0$, respectively).

Compound I crystallizes as yellow needles in the centrosymmetric space group $P2_1/n$ ($C_{2h}{}^5$; no. 14) with $a = 11.384$ Å, $b = 11.501$ Å, $c = 22.674$ Å, $\beta = 90.0°$, and $V = 2968$ Å^3. The observed density ($\rho_{\text{obsd}} = 2.07 \pm 0.01$ g cm^{-3}) indicates two molecules per unit cell ($\rho_{\text{obsd}} = 2.079$ g cm^{-3} for $M = 1852$, $Z = 2$).

Complete sets of X-ray diffraction data ($\sin\theta_{\max} = 0.38$; Mo Kα radiation) were collected for b and c mountings of the complex using a Supper-Pace Buerger automated diffractometer. All data were corrected for absorption ($\mu = 98.55$ cm^{-1}). Following unsuccessful attempts to interpret the subsequent Patterson synthesis, the structure was solved by direct methods.[7] Sayre's relationships[8] were applied to 187 selected reflections with $E > 1.4$.[9] Of the eight possible combinations of phase for the three starting reflections, one set achieved internal consistency in two iteration cycles with a consistency index, $C = 0.928$.[10] An E-map based on these phases showed eight regions of high electron density disposed (in the form of distorted cube) about each center of symmetry. It immediately became apparent that the crystallographically required center of symmetry in the $[H_6Re_4(CO)_{12}{}^{2-}]$ dianion was merely statistical in nature, there being a random distribution of two tetrahedral arrangements of rhenium atoms (interrelated by a center of symmetry) throughout the crystal. Subsequent Fourier and least-squares refinement techniques have led to the present discrepancy index of $R_F = 14.3\%$ for the 1683 independent nonzero reflections. The molecular configuration is shown in Figure 1. The rhenium atoms define a tetrahedron in which individual rhenium–rhenium distances are 3.145, 3.157, 3.159, 3.163, 3.165, 3.173 Å (average = 3.160 Å,

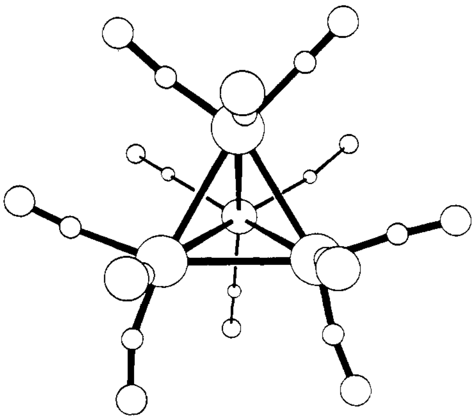

Figure 1. The stereochemistry of the $[H_6Re_4(CO)_{12}{}^{2-}]$ ion. The six hydride ligands were not detected in the crystallographic analysis, but probably bridge each edge of the tetrahedron (see text).

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(1) Work supported by NSF Grants GP-8077 (M. R. C.) and GP-6720 (H. D. K.), and ARPA Contract SD-88 (M. R. C.).

(2) (a) R. Bau, B. Fontal, H. D. Kaesz, and M. R. Churchill, *J. Am. Chem. Soc.*, **89**, 6374 (1967); (b) M. R. Churchill and R. Bau, *Inorg. Chem.*, 7, 2606 (1968).

(3) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Am. Chem. Soc.*, 90, 7135 (1968).

(4) D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *ibid.*, 86, 4841 (1964).

(5) W. Fellmann and H. D. Kaesz, *Inorg. Nucl. Chem. Letters*, **2**, 63 (1966).

(6) *Anal.* Calcd for I: C, 38.9; H, 2.48. Found (Miss Heather King, UCLA): C, 37.9; H, 2.48. Calcd for I: Re, 40.4. Found (Schwartzkopf Microanalytical Laboratories, Woodside, N. Y.): Re, 39.7.

(7) Using a locally modified version of REL (an IBM 7094 program by R. E. Long); see R. E. Long, Ph.D. Dissertation, University of California, Los Angeles, 1965.

(8) D. Sayre, *Acta Cryst.*, **5**, 60 (1942).

(9) $E(hkl)$, the normalized structure factor of the reflection hkl, is defined by

$$E(hkl) - F(hkl)\left[\epsilon^2\sum_{j=1}^{N} f(j,\theta(hkl))\right]^{-1/2}$$

where $F(hkl)$ is the customary structure factor, N is the number of atoms in the unit cell, $f(j,\theta(hkl))$ is the scattering factor of the jth atom at the appropriate Bragg angle (θ) for the reflection hkl, and ϵ is a constant equal to 2 for reflections of the class $0k0$ and $h0l$, equal to 1 for all other reflections.

(10) The consistency index is defined as

$$C = \left\langle |E_A \sum_{A=B+C} E_B E_C| \right\rangle \Big/ \left\langle |E_A| \sum_{A=B+C} [|E_B||E_C| \right\rangle$$

where sums are over all pairs of reflections B and C for which $B + C = A$, and where the angle brackets denote the average over all values of A.

esd ~ 0.007 Å); three terminal carbonyl ligands are bonded to each of the four rhenium atoms.

The 12 oxygen atoms of the $[H_6Re_4(CO)_{12}{}^{2-}]$ anion define a slightly irregular cube-octahedron (see Figure 2) similar to what Wilkes and Dahl found[11] for the carbon atoms in the structure of $Ir_4(CO)_{12}$. Thus, although the final electron-density map shows the disordered anion to be composed of eight "half-rhenium" atoms and 24 "half-carbon" atoms, there are only 12 sites for the oxygen atoms. The disorder of the $[H_6Re_4(CO)_{12}{}^{2-}]$ ions within the $[(C_6H_5)_4As^+]_2[H_6Re_4(CO)_{12}{}^{2-}]$ lattice results from the fact that the external arrangement of oxygen atoms (which, presumably, dictates the packing of the *anions* within the unit cell) is invariant with respect to an inversion of the rhenium atom cluster. This may well prove to be a general structural feature for complexes containing the $M_4(CO)_{12}$ group. The four tetraphenylarsonium ions, however, occupy the general positions for space group $P2_1/n$ and are ordered.

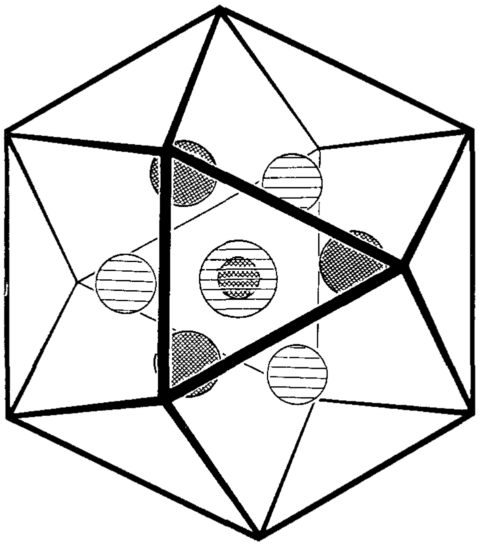

Figure 2. The disordered rhenium tetrahedra inside the cube-octahedral arrangement of oxygen atoms in $[H_6Re_4(CO)_{12}{}^{2-}]$. The oxygen atoms (not shown) occupy the positions at the 12 vertices of the cube-octahedron. Note that this arrangement has approximate O_h symmetry and is invariant with inversion (see text). The eight rhenium "half-atoms" are grouped into the two disordered sets of tetrahedra distinguished here by different shading.

The crystallographic data indicate that the six hydrogen atoms of the anion detected by H^1 nmr must be associated with the six edges of the tetrahedral metal cluster. The observed average Re–Re distance is 3.160 ± 0.007 Å, which is closer to the μ-H-Re–Re distance of 3.177 Å in $[H_3Re_3(CO)_{12}{}^{-}]$[3] than to the nonbridged Re–Re distance of 2.987 Å (av) in $Re_4(CO)_{16}{}^{2-}$,[2] or 3.02 Å in $Re_2(CO)_{10}$,[12] or 3.035 Å in $H_2Re_3(CO)_{12}{}^{-}$.[3] The regularity and consistency of the six rhenium–rhenium distances in the $[H_6Re_4(CO)_{12}{}^{2-}]$ ion, taken with the regular distribution of carbonyl ligands about each metal, precludes the possibility of terminal hydride ligands. A closed valence shell for each of the rhenium atoms and diamagnetism for the anion may then be achieved by an electron-pair bond between each two rhenium atoms as well as a bridging hydrogen atom.[13]

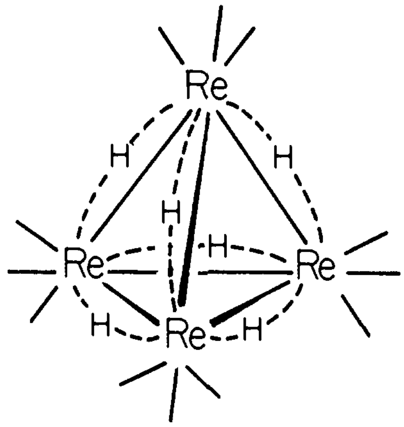

Figure 3. Idealized structure of the $[H_6Re_4(CO)_{12}{}^{2-}]$ ion showing proposed location of the hydrogen atoms; the CO groups have been omitted for clarity.

Two principal absorptions in the carbonyl region of the infrared[14] were observed for acetone solutions of I, 2000 (s) and 1910 (vs) cm^{-1}. In the Raman spectrum[14b] for the neat solid, five maxima were observed: 2030 (m), 1955 (w), 1904 (w, sh), 1889 (vs), and 1875 (w, sh) cm^{-1}. We consider the weak Raman peaks at 1995 and 1904 cm^{-1} to be, within experimental precision, the same modes as give rise to the two strong ir bands. This is what one would expect for an anion of T_d symmetry (A_1, E, F_1 (inactive), two F_2)[15] with a possible slight relaxation of the requirements in the solid state due to near-neighbor interactions.

A sample of $[(C_6H_5)_4As^+]_2[D_6Re_4(CO)_{12}{}^{2-}]$ was prepared from $Re_2(CO)_{10}$ and $NaBD_4$, and its infrared and Raman spectra were compared with those 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. On the other hand, a broad band centered at 1165 cm^{-1} ($\Delta\nu_{1/2} \sim 110$) in the Raman spectrum of the Re–H derivative disappeared in the spectrum of the Re–D derivative and was replaced by a less broad absorption at 832 cm^{-1} ($\Delta\nu_{1/2} \sim 37$ cm^{-1}). Both the ratio of these frequencies (1:1.4) and the change of line width are in good agreement with the assignment to the *bridging* Re–H and *bridging* Re–D stretching motions, respectively, which we have come to recognize as characteristic for this atomic arrangement.[3,16]

The present derivative in a formal sense is a dimer of the recently reported carbonyl hydride anion, $H_3Re_2(CO)_6{}^{-}$,[17] obtained from the reaction of CO with $ReH_9{}^{2-}$. In $H_3Re_2(CO)_6{}^{-}$ a closed valence shell for

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[11] G. R. Wilkes and L. F. Dahl, unpublished; G. R. Wilkes, Ph.D. Dissertation, University of Wisconsin, 1965.

[12] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

[13] Each Re atom of an $Re(CO)_3$ group lacks five electrons to complete its valence shell. In the tetrahedral cluster, it adds three electrons through the formation of σ bonds with the other three Re atoms. Thus the $Re_4(CO)_{12}$ cluster lacks a total of *eight* electrons collectively; in $H_6Re_4(CO)_{12}{}^{2-}$ these are provided by the six H atoms and the net negative charge of two.

[14] (a) Beckman IR-4, LiF prism; (b) Cary Model 81, laser Raman.

[15] R. Bau, Ph.D. Dissertation, University of California, Los Angeles, May 1968, pp 47–60.

[16] (a) J. M. Smith, W. Fellmann, and L. H. Jones, *Inorg. Chem.*, 4, 1361 (1965); (b) R. Bau, J. R. Holmes, and H. D. Kaesz, manuscript in preparation.

[17] A. P. Ginsberg and M. K. Hawkes, *J. Am. Chem. Soc.*, 90, 5930 (1968).

each metal atom may be attained through a rhenium–rhenium triple bond (in addition to the three postulated[17] bridging H atoms). This anion would then be related to our tetranuclear species in a manner analogous to the relation between the N_2 molecule and the P_4 tetrahedron. Compound I and the salt of $H_3Re_2(CO)_6{}^{1-}$ thus represent a common link between these two extreme types of substitution reactions, the substitution of H^- by CO as carried out by Ginsberg and coworkers on $ReH_9{}^{2-}$ and the substitution of H^- for CO on $Re_2(CO)_{10}$ studied by our group.

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Electron Spin Resonance Evidence on the Nature of Trapped Positive Holes in γ-Irradiated 3-Methylpentane Systems at 77°K

Sir:

Production of positive holes in organic glasses by high-energy radiation has been studied extensively by Shida and Hamill[1] by optical methods. They have shown that positive charge resulting from ionization of the matrix can be trapped by suitable scavengers. The optical method, however, does not permit an unequivocal identification of the nature of the positive hole; *i.e.*, it cannot distinguish between species such as a radical cation RH^+, a carbonium ion R^+, a protonated ion $RH_2{}^+$, or a dimeric radical cation such as $(RH)_2{}^+$.

Use of electron spin resonance should provide a method to distinguish between these possible species. To the knowledge of the authors, however, esr studies of positive holes in organic glasses of aliphatic hydrocarbons do not seem to have been very successful.[2]

This report presents the result of an esr study of γ-irradiated 3-methylpentane (3-MP) glasses containing small amounts of tetramethylethylene (TME) which gives direct evidence regarding the nature of the positive hole.

The samples were prepared from purified materials (in some cases with CO_2 added), cooled to liquid nitrogen temperature, and subjected to ^{60}Co γ irradiation at a dose rate of 1.3×10^{18} eV g^{-1} min^{-1}. Esr measurements were carried out with a Model V-4502 Varian spectrometer.

Figure 1a shows the esr spectrum of 3-MP glass containing 0.3 mole % TME and 0.2 mole % CO_2 after irradiation with a dose of 3.9×10^{18} eV g^{-1}. The spectrum can be attributed to three paramagnetic species. The strong central line deviating slightly toward high field from the free-spin value is attributable to $CO_2{}^-$. This assignment is confirmed by the splitting into two lines when $^{13}CO_2$ is used.[3] Furthermore, six lines with an average spacing of 22.5 G may be attributed to the 3-MP radical as suggested in ref 4; they cause the lifting and lowering of the spectrum at low and high fields, respectively. Superimposed on this group is a set of 13 lines equally spaced at 16.7 G; 9 of them can be discerned in Figure 1a. The full set can be obtained at a ten times higher dose and high instrument gain.

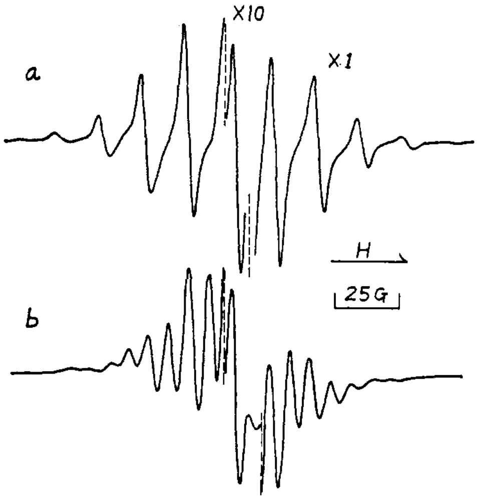

Figure 1. Esr spectra of γ-irradiated 3-MP glasses containing TME and CO_2 at a dose of 3.9×10^{18} eV g^{-1}: (a) 0.3% TME, (b) 10% TME. The central parts of the spectra were recorded at reduced sensitivity.

The intensity ratio of lines 1–3 and 11–13 in the complete set is 0.078:1:5.2 and 5.6:1:0.073.[5] The relative intensities of lines 4–10 cannot be determined accurately because of the superposition of the 3-MP radical spectrum. Nevertheless, the presence of 13 lines and the intensity ratios found for the outer lines agree quite well with a paramagnetic species with 12 equivalent protons, with corresponding ratios of 0.083:1:5.5. . .5.5:1:0.083. The result agrees with what may be expected for a species such as a TME radical ion.

The charge of the ion may be inferred from the following observations. In the presence of CO_2 the 13-line spectrum is stabilized; that is, even after 24 hr its intensity is little changed. In the absence of CO_2 both the trapped electron and the radical-ion signal decay within several minutes; their rate of decay is considerably increased by illumination of the system with infrared light. When a positive charge scavenger is added to the TME–CO_2–3MP system (0.1 mole % N-methyldiphenylamine[6]), the TME radical-ion spectrum

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(1) T. Shida and W. H. Hamill, *J. Am. Chem. Soc.*, **88**, 5376 (1966).

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(3) P. M. Johnson and A. C. Albrecht, *J. Chem. Phys.*, **44**, 1845 (1966).

(4) K. Fueki and Z. Kuri, *J. Am. Chem. Soc.*, **87**, 923 (1965); M. Shirom, R. F. C. Claridge, and J. E. Willard, *J. Chem. Phys.*, **47**, 286 (1967).

(5) The intensity ratios of lines at the low and high field are normalized to the intensities of lines 2 and 12, respectively.

(6) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2369 (1966).