cally.[9] Our observations have important theoretical consequences, and the details will be discussed elsewhere. The purpose of the present note is only to present the lifetimes which should be useful in studying the photochemistry of SO_2 in the atmosphere.

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A Quadruply Hydrogen-Bridged Metal–Metal Bond. The Neutron Diffraction Analysis of $H_8Re_2(PEt_2Ph)_4$

Sir:

While investigating the chemistry of rhenium polyhydride complexes of the type H_7ReL_2 (L = tertiary phosphine), Chatt and Coffey noticed in 1969 that these unusual compounds often decomposed in solution to give a red crystalline product which they formulated as $[H_xReL_2]_2$.[1] This product was called a rhenium agnohydride complex because of the unknown number of hydrogen atoms in the molecule. In this communication we report an x-ray and neutron diffraction analysis of the structure of this compound (with L = PEt_2Ph), which gives a value of $x = 4$, or eight hydrogen atoms per dimeric unit. We also discovered in this compound the unprecedented feature of a metal–metal bond (formally a triple bond) bridged by *four* hydrogen atoms.

$H_8Re_2(PEt_2Ph)_4$ [octahydridotetrakis(diethylphenylphosphine)dirhenium(IV)] was prepared in the manner of Chatt and Coffey[1] and recrystallized as deep-red bricks from *n*-hexane. A small crystal was selected for x-ray analysis and larger ones were grown for neutron diffraction work. The compound crystallizes in the monoclinic space group $C2/c$, with $a = 23.309$ (7), $b = 12.353$ (4), $c = 19.634$ (6) Å, $\beta = 129.38$ (1)°, $Z = 4$, $\rho(\text{calcd}) = 1.59$ g cm^{-3}, $\rho(\text{obsd}) = 1.60$ g cm^{-3}. X-ray data were collected at room temperature on a Nonius CAD-3 diffractometer with Mo Kα radiation up to a $(\sin\theta/\lambda)$ limit of 0.54 Å^{-1}. The x-ray analysis yielded the positions of all the nonhydrogen atoms in the molecule, and revealed the skeleton of the molecule as a planar, ethylene-like Re_2P_4 fragment with a rather short Re–Re distance [2.538 (4) Å]. The final agreement factors for the x-ray data are $R_F = 0.053$ and $R_{wF} = 0.057$ for 2367 reflections with $I > 2\sigma$; $R_F = 0.061$ and $R_{wF} = 0.061$ for all data (2557 reflections).[2]

The subsequent neutron diffraction analysis was carried out on a crystal of volume 5.0 mm^3 at the Brookhaven high flux beam reactor.[3a,b] Data were collected up to a $(\sin\theta/\lambda)$ limit of 0.62 Å^{-1} with neutrons of wavelength 1.1598 Å. Because of the lower temperature used in the neutron data collection (80.0 ± 0.5 K), the unit cell is slightly smaller than that found in the x-ray study: $a = 23.137$ (7), $b = 12.276$ (4), $c = 19.438$ (5) Å, $\beta = 129.51$ (2)°. The Re, P, and C positions derived from the x-ray analysis were used to phase the neutron data, and a subsequent difference-Fourier synthesis revealed the positions of the hydrogen atoms in the molecule. After full-matrix least-squares refinement (in which the parameters were divided into two blocks),[3c] the final agreement factors[2] stand at $R_{F^2} = 0.117$ and $R_{wF^2} = 0.098$ for all data (3565 reflections); $R_F = 0.086$ and $R_{wF} = 0.049$ for data with $I > 2\sigma$ (2729 reflections). The observation/parameter ratio for all data is 6.9.

Table I. Selected Distances and Angles in $H_8Re_2(PEt_2Ph)_4$[a]

Distances (in Å)			
Re–Re′	2.538 (4)	H(3)⋯H(4)	3.005 (8)
Re–P(1)	2.336 (4)	Re–P(2)	2.333 (5)
Re–H(1)	1.882 (7)	Re–H(2)	1.885 (7)
Re–H(1)′	1.862 (7)	Re–H(2)′	1.883 (8)
Re–H(3)	1.682 (7)	Re–H(4)	1.656 (6)
H(1)⋯H(2)	2.042 (8)	H(1)⋯H(2)′	1.870 (8)
H(1)⋯H(3)	2.323 (11)	H(2)⋯H(3)	2.317 (11)
H(1)′⋯H(4)	2.280 (10)	H(2)′⋯H(4)	2.333 (11)
H(1)⋯H(1)′	2.752 (8)	H(2)⋯H(2)′	2.785 (8)
Angles (in Degrees)			
Re′–Re–P(1)	129.2 (1)	Re′–Re–H(3)	115.4 (3)
Re′–Re–P(2)	128.0 (1)	Re′–Re–H(4)	116.3 (3)
P(1)–Re–P(2)	102.7 (2)	H(3)–Re–H(4)	128.3 (4)
H(1)–Re–H(1)′	94.6 (3)	H(2)–Re–H(2)′	95.3 (3)
H(1)–Re–H(2)	65.6 (3)	H(1)–Re–H(2)′	59.6 (3)
Re–H(1)–Re′	85.4 (3)	Re–H(2)–Re′	84.7 (3)
H(1)⋯H(2)⋯H(1)′	89.3 (3)	H(2)⋯H(1)⋯H(2)′	90.7 (3)

[a] The values in this table are those derived from the neutron diffraction analysis. For comparison, some corresponding x-ray values are Re–Re′ = 2.530 (1), Re–P(1) = 2.340 (5), Re–P(2) = 2.327 (5) Å, Re′–Re–P(1) = 129.6 (2), Re′–Re–P(2) = 127.7 (1), P(1)–Re–P(2) = 102.6 (2)°.

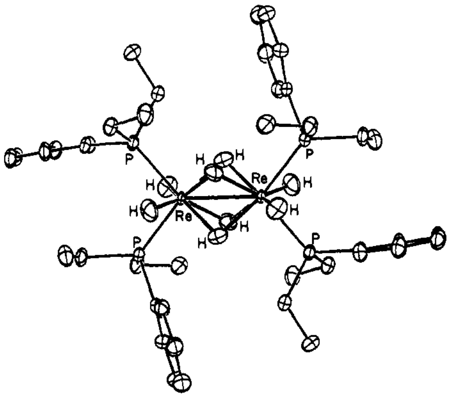

Figure 1. The molecular geometry of $H_8Re_2(PEt_2Ph)_4$, with the hydrogen atoms of the ethyl and phenyl groups removed for clarity. Thermal ellipsoids correspond to 50% probability.

The molecular geometry is depicted in Figures 1 and 2, and selected distances and angles are given in Table I. A crystallographic center of symmetry situated mid-way between the Re atoms relates the two halves of the molecule to each other. The core of the molecule consists of four bridging hydrogen atoms tightly clustered around the rhenium-rhenium bond, at an average distance of 1.38 Å from the center of this bond. These four hydrogen atoms define a distorted square, with one side ~9% longer than the other [2.042 (8), 1.870 (8) Å]. The quartet of hydrogen atoms is essentially normal to the Re–Re bond and is required to be planar by crystallographic symmetry. The other four hydrogen atoms are terminal, with two on each metal. The terminal H_2P_2 units and the bridging H_4

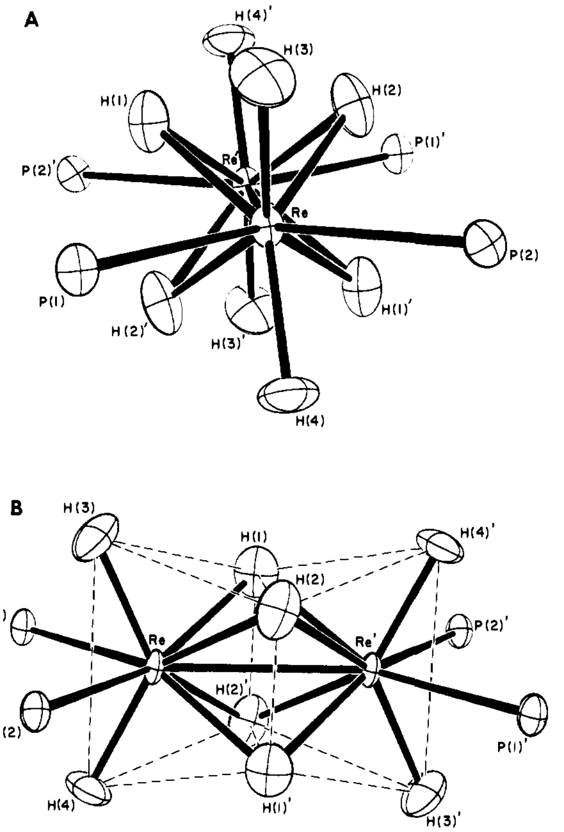

Figure 2. A (top): a view of the $H_8Re_2P_4$ core of the molecule looking roughly along the Re–Re axis, showing the mutually staggered arrangement between the terminal H_2P_2 units and the square formed by the quartet of bridging hydrogen atoms; the slightly longer H(1)···H(2) distance, as compared with the H(1)···H(2)′ distance, is evident in this diagram. B (bottom): another view of the $H_8Re_2P_4$ core, this time showing the outlines of the distorted trigonal prisms formed by the hydrogen atoms (dotted lines); a crystallographic center of symmetry is situated at the center of the molecule. In both A and B, thermal ellipsoids correspond to 40% probability.

group are in a mutually staggered arrangement (Figure 2A), so that the H_6P_2 coordination about each Re is roughly square antiprismatic (the terminal H_2P_2 group is, however, distinctly nonplanar). Alternatively, the coordination about Re may be envisaged as a distorted tricapped trigonal prism, with six hydrogen atoms defining a highly distorted prism, the sides of which are capped by the Re–Re and Re–P bonds (Figure 2B). Thus, the eight hydride ligands in the molecule can be pictured as two trigonal prisms sharing a common square face. Interestingly, the H_4Re_2 core of the molecule is almost octahedral, with the Re–H distances [average = 1.878 (7) Å] roughly equal to the H···H distances [average = 1.956 (8) Å].

From electron-counting considerations, the Re–Re bond can be termed formally a triple bond. Indeed, the Re–Re distance in $H_8Re_2(PEt_2Ph)_4$ [2.538 (4) Å] is intermediate between that of the classic quadruply bonded anion $[Re_2Cl_8]^{2-}$ [2.241 (7) Å][4] and the formally double-bonded compound $H_2Re_2(CO)_8$ [2.896 (3) Å].[5] The bonding in $H_8Re_2(PEt_2Ph)_4$ can thus loosely be described as a quadruply protonated metal–metal triple bond.[6] It is as though the four lobes that comprise the pair of mutually perpendicular π bonds were all protonated.[8] The general form of the central $H_2P_2Re(\mu_2\text{-}H)_4ReP_2H_2$ unit is somewhat suggestive of the structures of $Li_4Cr_2(CH_3)_8 \cdot 4THF$[9a] and $Li_4Mo_2(CH_3)_8 \cdot 4THF$,[9b] in which a metal–metal quadruple bond is surrounded by a ring of four lithium atoms.[10]

The terminal Re–H distances in $H_8Re_2(PEt_2Ph)_4$ [average 1.669 (7) Å] agree very well with those found in $[ReH_9]^{2-}$ [1.68 (1) Å][11] and are 0.21 Å shorter than the bridging Re–H distances [average 1.878 (7) Å]. The lengthening of M–H distances from the terminal to the bridging mode by amounts ranging from 0.1 to 0.2 Å has been noticed before,[12] but this is the first time that an accurate direct comparison could be made within the same molecule. The shortest intramolecular H···H contact distance [H(1)···H(2)′ = 1.870 (8) Å] is comparable to similar minimum H···H contacts in K_2ReH_9 [1.872 (15) Å],[11] $H_4Os(PMe_2Ph)_3$ [1.840 (6) Å],[13] and $H_3Ta(C_5H_5)_2$ [1.847 (8) Å].[14] These values are probably close to the limit beyond which nonbonding hydrogen atoms cannot be further compressed.

In addition to the quadruply protonated M≡M bond found here $[M(\mu_2\text{-}H)_4M]$, there are several known cases of triply protonated M≡M bonds $[M(\mu_2\text{-}H)_3M]$, such as $[(OC)_3Re(H)_3Re(CO)_3]^-$,[15] $[(Me_5C_5)Ir(H)_3Ir(C_5Me_5)]^+$,[16] $[(as_3)Co(H)_3Co(as_3)]^+$ [$(as_3) = CH_3C(CH_2AsPh_2)_3$],[17] and related compounds. The structure of $[(Me_5C_5)Ir(H)_3Ir(C_5Me_5)]^+[BF_4]^-$ has recently been investigated by us with neutron diffraction techniques.[18] It is interesting to note that the H···H nonbonding separations between bridging hydrogen atoms in these molecules are longer than they are in $H_8Re_2(PEt_2Ph)_4$: for example, 2.14 Å in $[(Me_5C_5)Ir(H)_3Ir(C_5Me_5)]^+$,[18] 2.1 Å in $[(as_3)Co(H)_3Co(as_3)]^+$,[17] and 2.2 Å in $[(OC)_4W(H)_2W(CO)_4]^{2-}$,[7] the latter being a $[M(\mu_2\text{-}H)_2M]$ system. It is evident that the shortness of the H···H contacts found in $H_8Re_2(PEt_2Ph)_4$ is a simple geometric consequence of packing four hydrogen atoms around a metal–metal bond, rather than three or two.

In their original paper, Chatt and Coffey reported that the ^1H NMR spectrum of the agnohydride, in the high-field region, consisted of a symmetrical quintet, indicating that the hydride ligands are equivalent on the NMR time scale and are being influenced equally by the four ^{31}P nuclei.[1] They explained this observation by invoking a metal–metal bond and coupling of the phosphorus nuclei. We have remeasured the ^1H NMR spectrum of $H_8Re_2(PEt_2Ph)_4$[19] and note a number of interesting observations. Firstly, the high-field resonance (τ 16.59) is indeed a quintet with $J_{P\text{-}H}$ = 9.28 Hz. Careful integration of the hydride resonance vs. the $-CH_2-$ and CH_3-resonances is consistent with eight hydride ligands per molecule (calcd for $H:CH_2:CH_3$, 1:2:3; obsd for $H:CH_2:CH_3$, 1:2.1:3.2). Secondly, a preliminary variable-temperature study of the ^1H NMR indicates that the molecule is fluxional with all hydride ligands rapidly equilibrating at room temperature. On cooling below 0 °C, the symmetrical hydride quintet begins to broaden. We have not, as yet, observed a "frozen-out" spectrum, but are planning to perform a thorough variable-temperature ^1H and ^{31}P NMR study of $H_8Re_2(PEt_2Ph)_4$.

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Supplementary Material Available. A listing of atomic parameters (2 pages) and structure factor tables (6 pages). Ordering information is given on any current masthead page.

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(18) Neutron diffraction analysis of $[(Me_5C_5)Ir(H)_3Ir(C_5Me_5)]^+[BF_4]^-$ preliminary results: unit cell monoclinic, space group $P2_1/c$, a = 10.423, b = 20.222, c = 11.174 Å, β = 108.35°. The H atoms are essentially arranged in an equilateral triangle surrounding the metal–metal bond. Average distances and angles in the H_3Ir_2 core of the molecule are Ir–Ir = 2.455, Ir–H = 1.75, H···H = 2.14 Å, H–Ir–H = 75.8, Ir–H–Ir = 89.6°. R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzle, unpublished results (data collected at T = 80 K).
(19) The ^1H NMR spectrum was measured on a Varian XL-100 spectrometer operating at 100.1 MHz in the Fourier-transform mode, with benzene-d_6 as solvent (chemical shifts are reported relative to external TMS): τ 16.59 (quintet, J_{P-H} = 9.28 Hz, 8 H), 8.95 (d of t, $^3J_{P-H}$ = 15.17 Hz, J_{H-H} = 7.46 Hz, 24 H), 8.12 (m, 16 H), 2.31 (m, 20 H). The four sets of resonances correspond to the hydridic, methyl, methylene, and phenyl hydrogen atoms respectively.
(20) Alfred P. Sloan Fellow, 1974–1976; NIH Research Career Development Awardee, 1975–1980.
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Structure of $[Pt(en)(5'\text{-}CMP)]_2 \cdot 2H_2O$. An Example of Direct Platinum–Phosphate Bonding

Sir:

The cross-linking of DNA by platinum has been suggested as a likely mechanism[1,2] for the anti-tumor activity of *cis*-$Pt(NH_3)_2Cl_2$, $Pt(en)Cl_2$, and related platinum complexes.[4,5] Covalent attachment of a platinum fragment to DNA could take place at a variety of sites on a double-stranded nucleic acid. In particular, there appears to be a distinct correlation between Pt-binding ability and the G + C content of a polynucleotide.[6] Although most investigators have favored the bases as the primary sites of Pt-DNA bonding, it has been suspected that the phosphate groups on the polynucleotide backbone may also play a part in stabilizing the Pt-DNA complex.[7] In this communication we report the existence of direct platinum–phosphate bonding in the structure of $[Pt(en)(5'\text{-}CMP)]_2 \cdot 2H_2O$ (en = ethylenediamine; 5′-CMP = 5′-cytidine monophosphate).

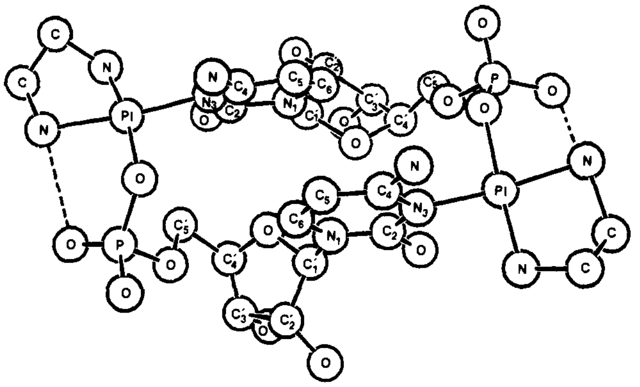

Figure 1. The molecular geometry of $[Pt(en)(5'\text{-}CMP)]_2$.

$[Pt(en)(5'\text{-}CMP)]_2$ was prepared by treating a solution of $Pt(en)Cl_2$ with 2 mol of $AgNO_3$,[8,9] filtering off silver chloride, and adding an equivalent amount of $Na_2(5'\text{-}CMP)$. After the mixture (pH 6–7) was allowed to stand at room temperature for ~2 weeks, it was passed through Sephadex G-10 to separate the product from low molecular weight species such as unreacted starting material. Vapor diffusion of the resulting solution against methanol produces tiny prismatic crystals of the product. Crystals of $[Pt(en)(5'\text{-}CMP)]_2 \cdot 2H_2O$ are monoclinic (space group $P2_1$), with a = 15.059 (9), b = 11.674 (7), c = 12.353 (21) Å, β = 94.23 (9)°, Z = 2. Data were collected on a Nonius CAD-3 automated diffractometer with Mo Kα radiation up to a 2θ limit of 45°. The structure was solved by heavy atom methods and refined to an R factor of 9.0% for 1200 nonzero reflections.[10,11]

The molecular plot of the dimeric molecule is shown in Figure 1. The CMP ligands are linked in a head-to-tail fashion by two bridging Pt(en) fragments, such that each Pt atom is bonded to the N_3 atom of one nucleotide and to a phosphate oxygen of the other. The cytosine rings within each dimer are positioned somewhat parallel to each other (angle between planes = 16°) at a distance of 3.51 Å apart. Average distances and angles in the molecule are as follows: Pt–O = 1.97, Pt–N_3 = 2.06; Pt–N(en) = 1.97 Å; O–Pt–N_3 = 90.4, N_3–Pt–N(en) = 95.6 and 174.7; O–Pt–N(en) = 88.2 and 174.2, N(en)–Pt–N(en) = 86.0°. The ribose sugar rings are in the C_2'-endo configuration, and the conformations about the glycosidic bonds are anti.[12] A strong hydrogen bond is found between a phosphate oxygen and an ethylenediamine nitrogen at a distance of 2.75 Å, so that in effect each phosphate group forms a hydrogen-bonded chelate about platinum:

$$\underbrace{\mathrm{P{-}O \cdots H_2N(en){-}Pt{-}O}}$$

Distances from Pt to the carbonyl oxygen at C_2 and the amino nitrogen at C_4 are 2.99 and 3.16 Å, respectively. The two water molecules of crystallization are hydrogen bonded to a phosphate group and to a carbonyl oxygen of one of the CMP ligands.

The structure of $[Pt(en)(5'\text{-}CMP)]_2$ described here represents the first example of a platinum-CMP complex isolated and structurally characterized.[13] Platinum-phosphate bonding had not been previously found in a platinum nucleotide com-