

Preliminary communication

PHOTOCHEMISTRY OF TRANSITION-METAL POLYHYDRIDES: DIMERIZATION OF $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$ FOLLOWING PHOTODISSOCIATION OF DIHYDROGEN

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Summary

UV (254 nm) photolysis of OsH_4P_3 ($\text{P} \equiv \text{PMe}_2\text{Ph}$) proceeds, by photodissociation of H_2 , to give the transient OsH_2P_3 . This species exchanges deuterium with C_6D_6 , reacts with phosphine to give *cis*- H_2OsP_4 , and with OsH_xP_3 to give $\text{Os}_2\text{H}_2(\mu\text{-H})_2\text{P}_6$, whose structure was determined by X-ray diffraction. This Os=Os dimer participates in a unique reversible (25°C) phosphine dissociation equilibrium to produce $\text{Os}_2\text{H}_4\text{P}_5$, containing an Os≡Os bond. A structural analog of this dimer was produced by acidolysis of $\text{Os}_2\text{H}_4\text{P}_6$ to give $\text{Os}_2\text{H}_3\text{P}_6^+$, which X-ray diffraction reveals to have a $\text{P}_3\text{Os}(\mu\text{-H})_3\text{OsP}_3^+$ structure.

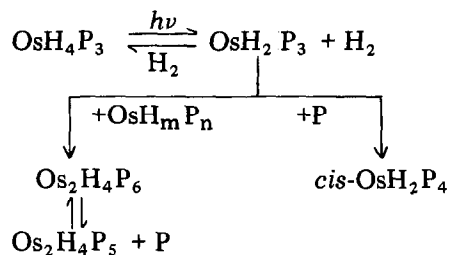
We [1] and others [2] have remarked on the atypical reactivity pattern (eq. 1) of ReH_5P_3 ($\text{P} \equiv \text{PMe}_2\text{Ph}$), as contrasted to other transition metal



polyhydrides, which undergo photodissociation of H_2 [3]. We have also suggested that photocondensation of polyhydride monomers may be a general route to polyhydride oligomers [1]. We report here on the photochemistry of OsH_4P_3 [4,5], including the first observation of a unique equilibrium in which ligand addition/loss competes with Os≡Os bond breaking/making. Few examples exist of multiple bonding involving osmium [6,7].

Photolysis [8] of ~0.1 M benzene or THF solutions of OsH_4P_3 leads to a rather complex array of products (Scheme 1) which are best detected by ^{31}P NMR. Conversion of a saturated THF solution (0.4 ml) is nearly com-

plete in 6 h. Only small amounts of free PMe_2Ph are detected, consistent with the co-production of the phosphine-rich product $\text{cis-OsH}_2\text{P}_4$ [4]. A



SCHEME 1

major ($\sim 50\%$ yield) product has ^{31}P resonances at 0.6 ppm (intensity 1) and -26.7 ppm (intensity 2); these resonances are slightly broadened ($\Delta\nu_{1/2} \sim 15$ Hz and 10 Hz, respectively), but show no resolvable structure. This compound has only very low solubility in nonreactive solvents, and red crystals are deposited from photolyzed solutions. The results of a crystal structure determination [9] (Fig. 1) reveal the product to be $\text{Os}_2(\mu\text{-H})_2\text{H}_2\text{P}_6$, with a *fac*- OsH_3P_3 geometry at each metal center [10]. A metal-metal double bond, influenced by the presence of two bridging hydrogens, is required if

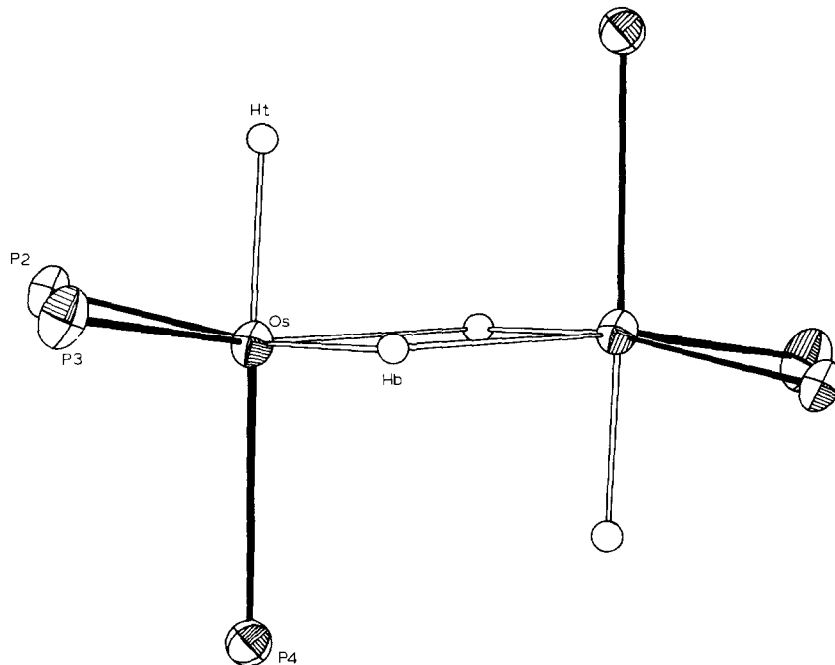


Fig. 1. The inner coordination sphere of $\text{Os}_2\text{H}_4(\text{PMe}_2\text{Ph})_6$. The molecule resides on a crystallographic center of symmetry. Bond lengths (Å): Os—Os 2.818(1), Os—P(2) 2.261(3), Os—P(3) 2.257(3), Os—P(4) 2.340(3), Os—H_t = 1.61(9), Os—H_b = 1.59(10), Os—H_l = 2.18(10). Selected bond angles (°): P(4)—Os—P(2) 100.2(1), P(4)—Os—P(3) 94.5(1), P(2)—Os—P(3) 94.4(1), H_t—Os—P(4) 172(3), H_t—Os—P(2) 87(3), H_t—Os—P(3) 81(3), H_t—Os—H_b 89(4), Os—H_b—Os 96(5).

the osmium centers are to achieve an 18-electron count. The Os=Os bond length, 2.818(1) Å, is virtually identical to the distance of an analogous Ru=Ru bond (2.811(4) Å) [11].

In contrast to the situation with ReH_5P_3 [1,2], evidence points to reductive elimination of H_2 as the primary photochemical event for OsH_4P_3 . Thus, no photodimerization occurs if a benzene solution of OsH_4P_3 is irradiated in the presence of three equivalents of PMe_2Ph ; instead, *cis*- OsH_2P_4 is the only product in such an experiment. This is consistent with phosphine scavenging of a primary photoproduct of formula OsH_2P_3 , a reactivity pattern which partially (vide infra) explains the formation of *cis*- OsH_2P_4 when pure OsH_4P_3 is photolyzed in solution. Moreover, photolysis under 65 atm H_2 completely halts all the conversions shown in Scheme 1. The 16-electron transient OsH_2P_3 also effects exchange of metal-bound hydrogen with C_6D_6 during photolysis experiments; 90% of the Os—H has become Os—D after 1 h of irradiation.

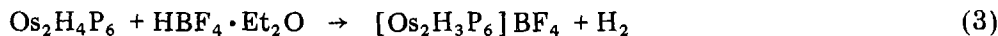
The production of OsH_2P_4 even in the absence of added PMe_2Ph raises the question of the source of this ligand; there are no insoluble "decomposition products" in this reaction. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum [12] of photolyzed solutions also shows a product with an A_2X_3 phosphorus spin system (J 5 Hz). Each of these phosphorus resonances becomes a doublet (apparent $J(\text{P-H}) \approx 20$ Hz) of multiplets when proton decoupling is limited to the region downfield of TMS; hydride ligands are therefore present in this complex. Three separate efforts to crystallize this complex gave crystals which were shown by cell constant measurements to be $\text{Os}_2\text{H}_4\text{P}_6$. This A_2X_3 compound can be converted cleanly and completely to $\text{Os}_2\text{H}_4\text{P}_6$ by treatment of the mixture of photolysis products with free PMe_2Ph . If this solution is then evaporated to dryness and held at ~ 0.02 mmHg for 12 h to pump off the liquid phosphine, the sample dissolves to give a ^{31}P spectrum in which the A_2X_3 pattern again accompanies the resonances of $\text{Os}_2\text{H}_4\text{P}_6$. This is consistent with the occurrence of the equilibrium in eq. 2. The effect of entropy on the equilibrium



can also be demonstrated. A saturated benzene solution containing only $\text{Os}_2\text{H}_4\text{P}_6$, $\text{Os}_2\text{H}_4\text{P}_5$ and the equilibrium stoichiometry of free P at 25°C was heated to 80°C in an NMR probe; prompt recording of the ^{31}P NMR spectrum at 80°C showed only $\text{Os}_2\text{H}_4\text{P}_5$ and (in increased amounts) free P. The ^{31}P NMR spectrum of this solution, recorded immediately upon returning the probe and sample to 25°C showed some growth of $\text{Os}_2\text{H}_4\text{P}_6$; after 24 h, the original equilibrium concentrations had been restored. Low temperature ^{31}P NMR spectra show little change in concentration from the nearly equal amounts of $\text{Os}_2\text{H}_4\text{P}_6$ and $\text{Os}_2\text{H}_4\text{P}_5$ found at 25°C , due to the slow rate of equilibration below 25°C .

Reaction 2 is the first case of reversible addition/elimination (25°C) of a two-electron ligand to a polyhydride accompanied by a double/triple metal—metal bond conversion. In two double/single bond conversions reported earlier [13,14], ligand addition converts a bridging hydride to a terminal position. In the absence of definitive spectroscopic or diffraction evidence for the struc-

ture of $\text{Os}_2\text{H}_4\text{P}_5$, we have explored indirect methods. We have synthesized, according to eq. 3, a complex of stoichiometry related to $\text{Os}_2\text{H}_4\text{P}_5$. The



crystal structure [15] of the cation in this salt (Fig. 2) shows face-sharing octahedra, with an Os/Os distance (2.558(1) Å), sufficiently shorter than that in $\text{Os}_2\text{H}_4\text{P}_6$ to indicate the $\text{Os}\equiv\text{Os}$ triple bond needed to give a 36 valence electron count to the cation. The observation of a ^3P doublet [16] when only the $\mu\text{-H}$ ligands are allowed to couple indicates that internal rotation of the $\text{Os}_2\text{H}_3\text{P}_6$ skeleton is not rapid at room temperature.

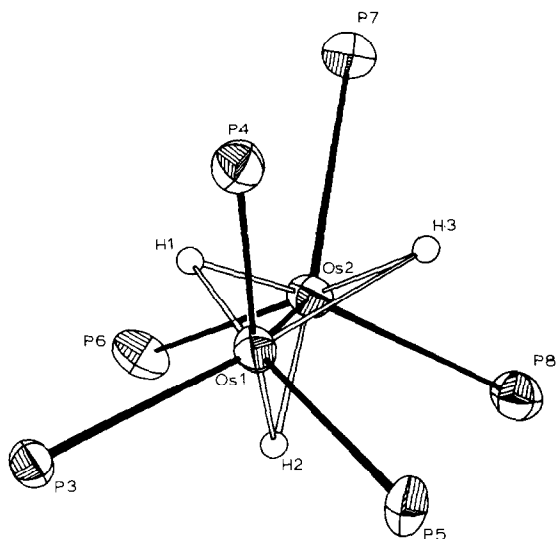
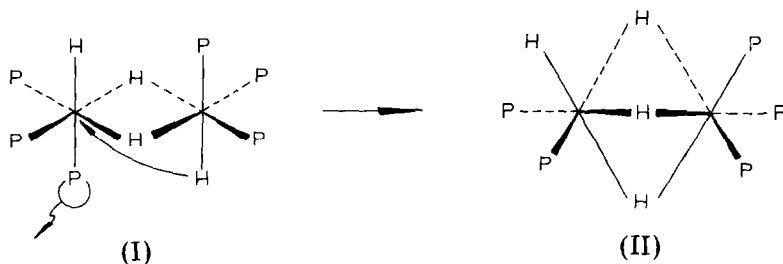


Fig. 2. The inner coordination sphere of $\text{Os}_2\text{H}_3(\text{PMe}_2\text{Ph})_6^+$. Bond lengths (Å): Os(1)—Os(2) 2.558(1), Os—P (average) 2.291(4), Os—H (average) 1.75(11). P—Os—P angles average 93.4(1)° and transoid P—Os—H angles average 165(3)°. Os(1)—($\mu\text{-H}$)—Os(2) (average) 95(5)°, H—Os—H (average) 72(5)°.

We suggest that $\text{Os}_2\text{H}_4\text{P}_5$, a formal analog of $\text{Os}_2\text{H}_3\text{P}_6^+$ (replace H^- by P in the former), has a structure (II) derived from that of the isoelectronic cation.



The 5 Hz coupling constant in the A_2X_3 pattern is assigned as averaged end-to-end $\text{P}_\text{A}-\text{P}_\text{X}$ coupling under conditions where an intramolecular process averages the three phosphorus nuclei of the OsP_3 group.

Photocondensation of fragments derived from OsH_4P_3 occurs by reductive

elimination of H₂ and cannot be achieved by thermal methods [17]. It is selective in producing dimers and not higher clusters (e.g. Os₄H₄P₁₂), and it thus provides access to a substantial array of Os–Os multiple bonds. The neutral ligand dissociation and accompanying Os=Os → Os≡Os transformation of eq. 2 may provide applications in stoichiometric or catalytic substrate modification.

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- 3 G.L. Geoffroy, and M.S. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, 1979, Chapter 7.
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- 5 Low temperature proton NMR (two equally intense hydride resonances, -8.9 and -9.78 at 361 MHz) and ³¹P{¹H}NMR (2/1 broad signals at -30.5 and -33.1 at 146 MHz) both at -120°C in toluene-*d*₈ / CF₂Cl₂, are consistent with a pentagonal bipyramidal solution structure, with two axial and one equatorial phosphine. This structure was found in the solid state by neutron diffraction: D.W. Hart, R. Bau, and T.F. Koetzle, *J. Am. Chem. Soc.*, **99** (1977) 7557.
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- 8 The lowest energy electronic absorption of OsH₄P₃ (λ_{max} 282 nm, $\epsilon = 5400$) necessitates the use of quartz glassware. Irradiations were carried out with medium pressure mercury lamps. Dinitrogen does not interfere.
- 9 Crystallographic data (-165°C): *a* 11.809(5), *b* 18.355(9), *c* 12.494(6) Å, β 116.64(2)°, *V* 2420.5 Å³, *Z* = 2 in space group *P*2₁/*a*; *R*(*F*) 4.7%, *R*_w(*F*) 4.1% for 2613 observed ($F_o > 2.33 \sigma(F_o)$) and absorption-corrected reflections using anisotropic temperature factors for all non-hydrogen atoms. All hydrogens were refined isotropically. For full details, request Molecular Structure Center Report No. 82004 from the Chemistry Library, Indiana University.
- 10 ¹H NMR (360 MHz at 23°C in toluene-*d*₈): In addition to aromatic resonances, δ 1.70 (br. s., int. 1, PMe), δ 1.48 (br. s., int. 2, PMe), -13.6 (br. multiplet) ppm.
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- 12 40.5 MHz ³¹P{¹H} NMR spectrum in toluene-*d*₈: δ -14.7 (q, *J* 5 Hz), -19.0 (t, *J* 5 Hz) ppm; 360 MHz ¹H NMR: in addition to aromatic resonances, 1.88 (two overlapping doublets, 12H, CH₃), 1.47 (d, *J* 7 Hz, 18H, CH₃), -8.95 (br. apparent doublet, Os–H).
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- 15 Crystallographic data (-165°C) for [Os₂H₃(PMe₂Ph)₆]Cl·2.8CH₂Cl₂: *a* 18.393(8), *b* 16.172(6), *c* 20.872(8) Å, β 105.05(2)°, *V* 5995.6 Å³, *Z* = 4 in space group *P*2₁/*n*; *R*(*F*) 4.9%, *R*_w(*F*) 4.6% for 4288 observed ($F_o > 2.33 \sigma(F_o)$) and absorption-corrected reflections using anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms of the cation except H(1) were refined isotropically; H(1) refined towards a residual near Os(1) and the coordinates of H(1) were therefore taken from a final difference Fourier. For full details, request Molecular Structure Center Report No. 82005 from the Chemistry Library, Indiana University.
- 16 Centered at -21.9 ppm with apparent ²J(P–H) 16 Hz. 360 MHz ¹H NMR (23°C in CD₂Cl₂): aromatic resonances plus δ 1.62 (br s, CH₃), -9.45 (v br s, Os–H) ppm.
- 17 Note that OsH₄P₃ does not react with added P at 25°C. After 20 h at 100°C, *cis*-OsH₂P₄ is produced. Note also that a benzene solution of OsH₄P₃ held at 100°C for 24 h shows (³¹P NMR) no trace of any reaction.