

sp^3 -hybridized head atoms C8 and C8' of the ring linkage to a bicyclo system. This is also the main reason for the two connected phthalocyaninato units not being planar. The whole ligand is an anion with three negative charges.

The C—N distances reflect the interruption of the conjugation. The bonds at the head atom C8 average 1.476 Å, and this is close to the expected value for a single bond between sp^3 - and sp^2 -hybridized atoms. They adjoin shorter bonds of about 1.285 Å which represent double bonds. The other C—N distances have intermediate values of 1.323 to 1.441 Å, being typical for a conjugated C—N system.

The coordination of the Nb atom is completed by one chloro ligand to a monocapped trigonal prism. The Cl, Nb and the atom N4 lie on a twofold axis. The complex therefore has the symmetry C_2 .

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Structure of (μ -Acetato- $1\kappa O:2\kappa O'$)-nonacarbonyl- $1\kappa^3 C,2\kappa^3 C,3\kappa^3 C$ - μ -hydrido-(triphenylphosphine- $3\kappa P$)-triangulo-triosmium($3Os-Os$) Cyclohexane Solvate

BY MICHAEL WEBSTER, ANDREW C. STREET, JOHN EVANS* AND VALENTIN D. ALEXIEV

Department of Chemistry, The University, Southampton SO9 5NH, England

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Abstract. $[\text{Os}_3(\text{C}_2\text{H}_3\text{O}_2)(\text{H})(\text{CO})_9\{\text{P}(\text{C}_6\text{H}_5)_3\}].\text{C}_6\text{H}_{12}$, $M_r = 1229.14$, triclinic, $P\bar{1}$, $a = 13.869$ (3), $b = 14.763$ (4), $c = 10.818$ (4) Å, $\alpha = 109.45$ (4), $\beta = 82.27$ (3), $\gamma = 117.83$ (2)°, $V = 1846.4$ Å³, $Z = 2$, $D_x = 2.210$, $D_m = 2.22$ (7) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 103.8$ cm⁻¹, $F(000) = 1144$, room temperature, $R = 0.038$ for 4841 unique observed reflections [$F > 3\sigma(F)$]. The triangular cluster has the shortest Os—Os edge (2.753 Å) bridged by a bidentate acetate ligand which adopts axial sites. The PPh_3 ligand is in an equatorial site on the Os not involved with the acetate bridge. The hydride ligand was not located directly and is considered to be along the longest Os—Os bond (3.041 Å), *cis* to the phosphine ligand.

Introduction. In the course of characterizing tethered clusters formed by the reaction of $\text{Os}_3\text{H}_2(\text{CO})_{10}$ with a phosphinated silica ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}$) using EXAFS (Cook, 1985) and ³¹P CP-MAS NMR techniques (Alexiev, Clayden, Cook, Dobson, Evans, & Smith, 1986), it became evident that one of the

References

- BARNHART, G. & SKILES, B. F. (1956). US patent 2,722,284.
 BAUMANN, F., BIENERT, B., RÖSCH, G., VOLLMANN, H. & WOLF, W. (1956). *Angew. Chem.* **68**, 133–150.
 FRENZ, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.
 GINGL, F. & STRÄHLE, J. (1988). *Z. Naturforsch. Teil B*, **43**, 445–448.
 GINGL, F. & STRÄHLE, J. (1989). *Z. Naturforsch. Teil B*, **44**, 110–116.
International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2A. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 MUETTERTIES, E. L. & WRIGHT, C. M. (1967). *Q. Rev. Chem. Soc.* **21**, 109–194.
 PERKINS, M. A. & WHELEN, M. S. (1957). US patent 2,782,207.
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ of Göttingen, Federal Republic of Germany.

isomers of the complex $[\text{Os}_3\text{H}(\text{CO})_9(\text{O}_2\text{CCH}_3)(\text{PPh}_3)]$ exhibited spectroscopic properties which closely matched those of the surface species. Three isomers are formed by the reaction of $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{PPh}_3)]$ with acetic acid, and two of them could be characterized as having hydride and acetate bridges spanning the same Os—Os edge, with one of these metal centres bearing the phosphine substituent. The third isomer, which proved to be the best spectroscopic model for the surface species, evidently had a different ligand disposition and was therefore characterized by X-ray diffraction.

Experimental. The title compound was prepared from the room temperature reaction of $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{PPh}_3)]$ dissolved in the minimum of CH_2Cl_2 with excess acetic acid for 48 h and the products separated by TLC on alumina-coated plates using *n*-hexane/ CH_2Cl_2 (19:1 v/v) as eluant (Alexiev, 1987). Air-stable yellow crystals were obtained from cyclohexane solution and mounted in thin-walled glass capillaries. Preliminary photographic X-ray examination established the crystal system and cell dimensions, and the density was measured by flo-

* Author to whom correspondence should be addressed.

Table 1. Atomic coordinates and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

| | x | y | z | U |
|-------|-------------|--------------|--------------|------------|
| Os(1) | 0.67416 (3) | 0.47793 (3) | 0.75332 (4) | 33.5 (1)* |
| Os(2) | 0.65973 (3) | 0.25871 (3) | 0.71775 (4) | 41.9 (1)* |
| Os(3) | 0.48271 (3) | 0.27591 (3) | 0.66013 (4) | 40.8 (1)* |
| P | 0.8532 (2) | 0.6197 (2) | 0.8107 (2) | 34.7 (9)* |
| C(1) | 0.7006 (8) | 0.4656 (8) | 0.5705 (10) | 42.9 (23) |
| O(1) | 0.7147 (6) | 0.4655 (6) | 0.4623 (8) | 61.3 (20) |
| C(2) | 0.6008 (8) | 0.5590 (8) | 0.7553 (10) | 47.4 (25) |
| O(2) | 0.5543 (7) | 0.6060 (7) | 0.7543 (8) | 69.5 (23) |
| C(3) | 0.6340 (8) | 0.4834 (8) | 0.9308 (10) | 42.6 (23) |
| O(3) | 0.6112 (7) | 0.4905 (7) | 1.0402 (8) | 65.8 (22) |
| C(4) | 0.7960 (10) | 0.2588 (10) | 0.7329 (12) | 59.6 (30) |
| O(4) | 0.8748 (8) | 0.2541 (8) | 0.7447 (10) | 87.6 (28) |
| C(5) | 0.5705 (10) | 0.1111 (10) | 0.6746 (12) | 61.5 (30) |
| O(5) | 0.5114 (9) | 0.0186 (9) | 0.6496 (10) | 90.5 (29) |
| C(6) | 0.6293 (9) | 0.2685 (9) | 0.8912 (12) | 57.5 (29) |
| O(6) | 0.6119 (7) | 0.2772 (8) | 1.0018 (9) | 79.2 (26) |
| C(7) | 0.3769 (11) | 0.1319 (11) | 0.6058 (13) | 66.4 (33) |
| O(7) | 0.3059 (9) | 0.0437 (9) | 0.5718 (10) | 94.8 (31) |
| C(8) | 0.4281 (8) | 0.2925 (9) | 0.8283 (11) | 47.8 (25) |
| O(8) | 0.3946 (6) | 0.2995 (7) | 0.9332 (8) | 63.0 (21) |
| C(9) | 0.4054 (10) | 0.3348 (10) | 0.6093 (12) | 59.3 (29) |
| O(9) | 0.3597 (9) | 0.3740 (9) | 0.5827 (11) | 100.9 (32) |
| O(10) | 0.6952 (6) | 0.2449 (6) | 0.5162 (7) | 51.5 (18) |
| O(11) | 0.5470 (6) | 0.2484 (6) | 0.4663 (7) | 48.1 (17) |
| C(10) | 0.6323 (9) | 0.2395 (9) | 0.4365 (11) | 49.2 (25) |
| C(11) | 0.6637 (11) | 0.2194 (12) | 0.2973 (12) | 74.6 (36) |
| C(21) | 0.8690 (6) | 0.7147 (5) | 0.9756 (5) | 42.2 (23) |
| C(22) | 0.8564 (6) | 0.6765 (5) | 1.0816 (5) | 49.6 (25) |
| C(23) | 0.8623 (6) | 0.7439 (5) | 1.2094 (5) | 66.4 (32) |
| C(24) | 0.8810 (6) | 0.8494 (5) | 1.2312 (5) | 69.4 (34) |
| C(25) | 0.8936 (6) | 0.8876 (5) | 1.1253 (5) | 67.6 (33) |
| C(26) | 0.8876 (6) | 0.8202 (5) | 0.9974 (5) | 56.6 (28) |
| C(31) | 0.9132 (5) | 0.7071 (5) | 0.7064 (6) | 40.6 (22) |
| C(32) | 1.0255 (5) | 0.7533 (5) | 0.6880 (6) | 57.3 (28) |
| C(33) | 1.0715 (5) | 0.8227 (5) | 0.6119 (6) | 74.8 (36) |
| C(34) | 1.0053 (5) | 0.8461 (5) | 0.5542 (6) | 63.5 (31) |
| C(35) | 0.8929 (5) | 0.7999 (5) | 0.5726 (6) | 64.7 (31) |
| C(36) | 0.8469 (5) | 0.7305 (5) | 0.6487 (6) | 48.7 (25) |
| C(41) | 0.9564 (5) | 0.5732 (5) | 0.8028 (6) | 39.4 (22) |
| C(42) | 1.0328 (5) | 0.6148 (5) | 0.9036 (6) | 53.3 (27) |
| C(43) | 1.1145 (5) | 0.5822 (5) | 0.8868 (6) | 65.0 (32) |
| C(44) | 1.1199 (5) | 0.5081 (5) | 0.7692 (6) | 64.9 (32) |
| C(45) | 1.0435 (5) | 0.4665 (5) | 0.6684 (6) | 55.8 (28) |
| C(46) | 0.9618 (5) | 0.4991 (5) | 0.6852 (6) | 49.1 (25) |
| C(51) | 0.2181 (19) | 0.0037 (19) | 0.2342 (23) | 140 (7) |
| C(52) | 0.1785 (23) | -0.0724 (23) | 0.1038 (28) | 178 (10) |
| C(53) | 0.2306 (21) | -0.0592 (21) | -0.0142 (26) | 167 (9) |
| C(54) | 0.3369 (21) | 0.0411 (21) | -0.0130 (26) | 156 (8) |
| C(55) | 0.3804 (29) | 0.1076 (28) | 0.1207 (33) | 244 (15) |
| C(56) | 0.3244 (19) | 0.1050 (19) | 0.2375 (24) | 148 (8) |

Table 2. Selected distances (\AA) and angles ($^\circ$)

| | | | |
|-------------------|---------------|------------------|---------------|
| Os(1)—Os(2) | 3.041 (1) | Os(2)—O(10) | 2.132 (7) |
| Os(2)—Os(3) | 2.753 (1) | Os(3)—O(11) | 2.151 (7) |
| Os(3)—Os(1) | 2.878 (1) | C(10)—O(10) | 1.27 (1) |
| P—Os(1) | 2.373 (2) | C(10)—O(11) | 1.24 (1) |
| P—C(21) | 1.830 (5) | C(10)—C(11) | 1.48 (2) |
| P—C(31) | 1.830 (5) | C—C (fixed) | 1.395 |
| P—C(41) | 1.835 (5) | C—H (fixed) | 0.95 |
| Os—C | min. 1.84 (1) | max. 1.92 (1) | mean 1.88 (3) |
| C—O (carbonyl) | min. 1.15 (1) | max. 1.18 (2) | mean 1.16 (1) |
| Os—C—O | min. 174 (1) | max. 178 (1) | |
| Os(1)—Os(2)—Os(3) | 59.3 (1) | P—Os(1)—Os(2) | 112.6 (1) |
| Os(2)—Os(3)—Os(1) | 65.3 (1) | P—Os(1)—Os(3) | 166.8 (1) |
| Os(3)—Os(1)—Os(2) | 55.4 (1) | C(21)—P—C(31) | 103.3 (3) |
| Os(1)—P—C(21) | 114.9 (2) | C(31)—P—C(41) | 101.0 (3) |
| Os(1)—P—C(31) | 116.9 (2) | C(41)—P—C(21) | 105.2 (3) |
| Os(1)—P—C(41) | 113.8 (2) | O(11)—Os(3)—C(7) | 87.5 (4) |
| O(10)—Os(2)—C(4) | 86.9 (4) | O(11)—Os(3)—C(8) | 176.4 (4) |
| O(10)—Os(2)—C(5) | 90.7 (4) | O(11)—Os(3)—C(9) | 89.4 (4) |
| O(10)—Os(2)—C(6) | 179.0 (4) | | |

available in *SHELX76* (Sheldrick, 1976); subsequent structure-factor and electron-density syntheses located the remaining non-H atoms of the cluster and solvent molecule. Phenyl C atoms were treated as a rigid group [$d(\text{C—C}) = 1.395 \text{ \AA}$], and the geometry of the cyclohexane moiety was constrained during refinement. Later electron-density maps gave evidence for some of the phenyl H atoms and these, along with the methyl H atoms, were introduced in geometrically calculated positions [$d(\text{C—H}) = 0.95 \text{ \AA}$] with a common refined temperature factor. The hydride atom was not located in this structure. Full-matrix least-squares refinement minimizing $\sum w(\Delta F)^2$ converged to $R = 0.038$ {189 parameters, 4841 reflections, anisotropic (Os,P) and isotropic (O,C,H) atoms, $w = 1/[\sigma^2(F) + 0.0005F^2]$, max. $\Delta/\sigma = 0.4$, $wR = 0.044$, $S = 1.35$, with all unique data $R = 0.065$, $wR = 0.047$ }. The residual electron density was in the range 1.5 to -1.0 e \AA^{-3} with the largest peaks close to the Os atoms. Scattering factors for neutral atoms and anomalous-dispersion corrections were taken from *SHELX76* (Sheldrick, 1976) and *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101) (Os only). All calculations were carried out using *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965) on an IBM3090 computer. The final atomic coordinates are given in Table 1 and selected molecular geometry is presented in Table 2.*

Discussion. The structure of the discrete molecule is shown in Fig. 1. The triphenylphosphine ligand is in an equatorial site on Os(1), with the P atom lying in the Os_3 plane, as observed for $\text{Os}_3\text{H}_2(\text{CO})_9(\text{PPh}_3)$

* Lists of structure factors, anisotropic thermal parameters, calculated H-atom positions and complete geometric details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53038 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

*Equivalent isotropic temperature factor from anisotropic atom, defined as $U_{\text{eq}} = \text{one third of the trace of the orthogonalized } U_j \text{ tensor.}$

tation ($\text{CCl}_4/\text{CHBr}_3$). The variability in density is presumably due to solvent loss. Accurate cell dimensions were obtained from 25 centred reflections ($9.1 < \theta < 14.4^\circ$) using an Enraf-Nonius CAD-4 diffractometer fitted with graphite monochromator and Mo radiation. The intensities of 6491 unique reflections were recorded (ω - 2θ scan, $1.5 < \theta < 25^\circ$; $h - 16$ to 16 ; $k - 17$ to 17 ; $l 0$ to 12) using a crystal of dimensions $0.4 \times 0.1 \times 0.15 \text{ mm}$. The three standard reflections showed small variations with time which were allowed for in the data-reduction program. An empirical ψ -scan absorption correction was applied to the data ($T_{\text{min}} = 0.645$, $T_{\text{max}} = 0.994$) and 4841 reflections with $F > 3\sigma(F)$ were used in the analysis. The normalized structure factor statistics favoured the centrosymmetric space group $P\bar{1}$ and the subsequent analysis confirmed this. The Os atoms were located using the direct methods strategy (*EEES*)

(Benfield, Johnson, Lewis, Raithby, Zuccaro & Henrick, 1979). The acetate group bridges Os(2) and Os(3), each of which also bears three CO ligands (two equatorial and one axial). The acetate ligand adopts an axial site on each of its coordination positions [O(10)—Os(2)—C(6) 179.0(4) and O(11)—Os(3)—C(8) 176.4(4)°] and bridges the shortest of the Os—Os bonds [2.753(1) Å]. This contrasts with the structures of Os₃H(S₂CH)(CO)₁₀ (Adams & Selegue, 1980) and Os₃H(O₂CH)(CO)₁₀ (Shapley, St. George, Churchill & Hollander, 1982), where the hydride and bidentate ligand both bridge the same longest edge of the triosmium unit. Rather, the similarity is with the phosphine-substituted cluster Os₃H(S₂CH)(CO)₉(PMe₂Ph) (Adams & Selegue, 1980), where the analogous distance with the larger donor atoms is elongated to 2.854 Å. The intermediate Os—Os bond length (2.878 Å) is similar to the non-bridged metal-metal bonds in Os₃H(O₂CH)(CO)₁₀.

The hydride position was not located directly in the X-ray analysis, but examination of the angles subtended in the equatorial plane is consistent with it residing along the longest Os—Os bond, *i.e.* Os(1)—Os(2) [3.041(1) Å], as observed by Adams & Selegue (1980) for Os₃H(S₂CH)(CO)₉(PMe₂Ph). For example, the Os(2)—Os(1)—P and Os(1)—Os(2)—C(4) angles, at 112.6(1) and 115.2(4)° respectively, are substantially larger than the corresponding angles relating to the Os(1)—Os(3) bond: Os(3)—Os(1)—C(2) 92.8(3), Os(1)—Os(3)—C(9) 95.1(4)°. This location for the hydride is supported by the ¹H NMR spectrum at room temperature of the complex in CDCl₃ solution: δ 7.4*m* (15H, PPh₃), 1.6*s* (3H, Me) and -12.6*d* (1H, ²J_{PH} 13Hz, Os—H—Os). This value of *J*(P—H) is

typical of a *cisoid* ligand disposition at a common coordination centre. The ¹³C NMR spectrum at 215 K is entirely consistent with the molecular structure being unchanged on dissolution: δ 192.5*q* (³J_{CH} 7Hz, O₂CMe), 186.2*dd* (*J*_{PC} 8Hz, *J*_{CH} 3Hz), 184.9*dd* (*J*_{PC} 6Hz, *J*_{CH} 3Hz), 182.4*s*, 182.3*s* (2C), 180.6*d* (*J*_{CH} 5Hz), 178.1*d* (*J*_{CH} 11Hz), 177.7*s* and 177.5*d* (*J*_{CH} 6Hz). Clearly, with the exception of one accidental degeneracy at 182.3, all of the carbonyl groups are inequivalent, and two are coupled to both ³¹P and ¹H, indicating that the hydride is bonded to the PPh₃-substituted Os centre.

It appears from this study, and that of Adams & Selegue (1980), that substitution of a phosphine into an Os₃H(E₂CR)(CO)₁₀ cluster (*E* = O or S) causes the hydride to migrate from the edge shared with the (dithio)carboxylate (E₂CR) bridge, to an unbridged one, and being *cis* to the phosphine group. It seems likely that the PR₃ unit renders its bonded Os centre more electron rich than the other metals in the cluster. This then preferentially binds the hydride ligand. The other two isomers of the title compound have the phosphine on one of the bridged Os atoms, and in that case the hydride can maintain its proximity to the phosphine while still in the original shared bridge site. The preference for bridging hydrides to adopt sites near strong-donor ligands has been related to the 'electron-deficient' nature of three-centre-two-electron bonds, such as these Os—H—Os units (Adams & Selegue, 1980). This study extends the scope of that observation.

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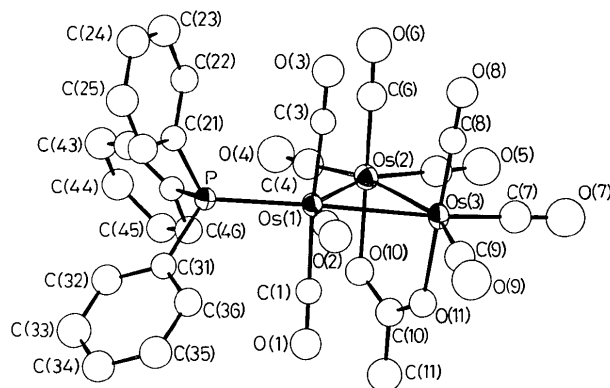


Fig. 1. View of the discrete molecule showing the atom-numbering scheme. The atom surfaces are drawn at the 40% probability level and H atoms are omitted for clarity.

References

- ADAMS, R. D. & SELEGUE, J. P. (1980). *J. Organomet. Chem.* **195**, 223–238.
- ALEXIEV, V. D. (1987). PhD Thesis, Univ. of Southampton, England.
- ALEXIEV, V. D., CLAYDEN, N. J., COOK, S. L., DOBSON, C. M., EVANS, J. & SMITH, D. J. (1986). *J. Chem. Soc. Chem. Commun.* pp. 938–941.
- BENFIELD, R. E., JOHNSON, B. F. G., LEWIS, J., RAITHY, P. R., ZUCCARO, C. & HENRICK, J. (1979). *Acta Cryst.* **B35**, 2210–2212.
- COOK, S. L. (1985). PhD Thesis, Univ. of Southampton, England.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- SHAPLEY, J. R., ST., GEORGE, G. M., CHURCHILL, M. R. & HOLLANDER, F. J. (1982). *Inorg. Chem.* **21**, 3295–3303.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.