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Structures of Heptadecacarbonyl(triphenylphosphine)hexaosmium(0) and Hexadecacarbonylbis(triphenylphosphine)hexaosmium(0)

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Abstract. $[\text{Os}_6(\text{CO})_{17}\{\text{P}(\text{C}_6\text{H}_5)_3\}]$ (I), $M_r = 1879.47$, triclinic, $P\bar{1}$, $a = 9.122$ (4), $b = 14.542$ (7), $c = 16.569$ (7) Å, $\alpha = 74.07$ (4), $\beta = 87.10$ (3), $\gamma = 71.83$ (3)°, $V = 2006.6$ Å³, $Z = 2$, $D_x = 3.11$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 19.02$ mm⁻¹, $F(000) = 1700$, $T = 290$ K, $R = 0.038$ for 5896 reflections. $[\text{Os}_6(\text{CO})_{16}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ (II), $M_r = 2113.9$, monoclinic, $C2/c$, $a = 17.472$ (4), $b = 18.064$ (2), $c = 17.688$ (3) Å, $\beta = 104.29$ (2)°, $V = 5409.0$ Å³, $Z = 4$, $D_x = 2.60$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 14.18$ mm⁻¹, $F(000) = 3824$, $T = 296$ K, $R = 0.039$ for 4895 reflections. The six Os atoms, in both (I) and (II), define a bicapped tetrahedron closely related to that in the parent carbonyl, $\text{Os}_6(\text{CO})_{18}$. The triphenylphosphine ligands are terminally bound to one, in (I), or both, in (II), of the capping Os atoms, and in each case the Os–P vector lies approximately *trans* to the longest Os–Os bond [2.998 (4) Å in (I) and 2.943 (1) Å in (II)]. Two terminal carbonyl groups are also bound to these metal atoms, while the other metal atoms are each coordinated to three carbonyl groups. In (I) the Os atoms and carbonyl groups are also linked by a network of incipient bridge bonds, a feature which is also observed in (II).

Introduction. The introduction of the labile acetonitrile ligand into triosmium cluster carbonyls greatly enhances their reactivity under mild reaction conditions. The

clusters $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ and $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ have become important as starting materials in a wide variety of cluster reactions (Johnson, Lewis & Pippard, 1981; Tachikawa & Shapley, 1977; Deeming, Ghatak, Owen & Peters, 1982; Mayr, Lin, Boag & Kaesz, 1982). It has recently been found possible to activate higher nuclearity osmium clusters with acetonitrile in a similar manner to the trinuclear systems (Gómez-Sal, Johnson, Kamarudin, Lewis & Raithby, 1985). In this paper we report the reaction of the activated complexes $\text{Os}_6(\text{CO})_{18-n}(\text{NCCH}_3)_n$, $n = 1, 2$, with triphenylphosphine to afford the clusters $\text{Os}_6(\text{CO})_{17}[\text{P}(\text{C}_6\text{H}_5)_3]$ (I) and $\text{Os}_6(\text{CO})_{16}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ (II), the X-ray crystal structures of which have been determined.

Experimental. (I) Reaction of $\text{Os}_6(\text{CO})_{18}$ with slight excess of $(\text{CH}_3)_3\text{NO}$ (1.1 equivalents) in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ at 195 K affords the complex $\text{Os}_6(\text{CO})_{17}(\text{NCCH}_3)$. This product is used *in situ* in the reaction with triphenylphosphine (1 equivalent) to give $\text{Os}_6(\text{CO})_{17}[\text{P}(\text{C}_6\text{H}_5)_3]$ as the major product. Purification and recrystallization from CH_2Cl_2 , black block-shaped single crystals obtained. Synthesis of (II) is similar to that of (I) except that two equivalents of $(\text{CH}_3)_3\text{NO}$ are used to generate the complex $\text{Os}_6(\text{CO})_{16}(\text{NCCH}_3)_2$, which is then reacted with an excess of triphenylphosphine to give $\text{Os}_6(\text{CO})_{16}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ in 25% yield. After purification, dark brown long brick-shaped single

crystals obtained from slow evaporation of ethyl acetate solution.

(I) Crystal 0.186 × 0.342 × 0.418 mm; Stoe-Siemens AED diffractometer; unit-cell parameters refined from 2θ values of 56 reflections centred at ±ω (15 < 2θ < 25°); 7552 reflections with 5 < 2θ < 50° (*hkl* range: *h* 0–10, *k* –17–17, *l* –19–19); profile analysis (Clegg, 1981); no significant variations for three standard reflections; numerical absorption correction with crystal bounded by planes (010), (010), (001), (001̄), (011), (011), (100) and (100), relative transmission factors 0.0808–0.0134. 7060 unique reflections (*R*_{int} = 0.0169), 5896 with *F* > 5σ(*F*). Structure solved by automatic direct methods (Os atoms) and difference Fourier syntheses; blocked-cascade refinement on *F*; *w*⁻¹ = σ²(*F*) + 0.001*F*². Anisotropic thermal parameters for Os, P and O, phenyl groups as rigid hexagons with C–C = 1.395, C–H = 1.08 Å on external C–C–C angle bisectors, H atoms with common isotropic temperature factor. Scattering factors including anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). 313 parameters, *R* = 0.038, *wR* = 0.042; max. (shift/e.s.d.) = 0.08; largest peak in final difference map = 2.7 e Å⁻³, largest trough = –1.5 e Å⁻³; program: modified version of *SHELX76* (Sheldrick, 1976).

(II) Crystal 0.05 × 0.07 × 0.25 mm; Enraf-Nonius CAD-4 diffractometer; unit-cell parameters from 25 reflections in range 19 < 2θ < 33°; 4895 unique reflections with 2 < 2θ < 50° (*hkl* range: *h* 0–22, *k* 0–22, *l* –22–22); no significant variations for three standard reflections; empirical absorption correction applied based on ψ scans for 8 reflections with varying 2θ values (Cromer & Liberman, 1970), transmission coefficients 0.8276–0.9999. 3468 unique reflections with *I* > 3σ(*I*). Structure solved by automatic direct methods (Os atoms) and difference Fourier syntheses; full-matrix least-squares refinement on *F*, *w* = 4*F*_o²/σ²(*F*_o²). Anisotropic thermal parameters for Os and P atoms. Scattering factors as for (I). 173 parameters, *R* = 0.039, *wR* = 0.046; max. (shift/e.s.d.) = 0.51; largest peak in final difference map = 2.1 e Å⁻³; program: *Enraf-Nonius Structure Determination Package, SDP-plus* (Frenz, 1982).

Discussion. Atomic coordinates for (I) are given in Table 1, and those for (II) in Table 2, while associated bond lengths and angles for the two structures are presented in Tables 3 and 4, respectively.* The structure of Os₆(CO)₁₇{P(C₆H₅)₃} (I) is illustrated in Fig. 1 and that of Os₆(CO)₁₆{P(C₆H₅)₃}₂ (II) in Fig. 2.

* Lists of structure factors, anisotropic thermal parameters, complete lists of bond parameter data and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42561 (59 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The overall geometry of the Os₆ bicapped tetrahedra in the title compounds resembles that in the parent binary carbonyl, Os₆(CO)₁₈ (Mason, Thomas & Mingos, 1973), and the bis(butyl isocyanide) derivative, Os₆(CO)₁₆(CNBu)₂ (Orpen & Sheldrick, 1978). The presence of the phosphine ligands, however, destroys the idealized C_{2v} symmetry of the parent carbonyl reducing it to C_s symmetry in (I) and to C₂ in (II).

While each of the six metal atoms has three ligand groups bonded to it, the number of connections to other metal atoms varies from atom to atom. Os(1) and Os(4) in (I) and Os(1) and Os(1') in (II) are bonded to five other Os atoms, and in terms of simple electron-counting rules these metals have 19 electrons each. Os(2) and Os(3) in (I) and Os(2) and Os(2') in (II) are bonded to four other metal atoms and each have 18 electrons associated with them. Os(5) and Os(6) in (I) and Os(3) and Os(3') in (II) are bonded to only three other metal atoms and formally have 17 electrons each. Except for the phosphine-substituted metals, Os(5) in (I) and Os(3) and Os(3') in (II), the bond lengths within the metal framework follow the same trends as in other bicapped tetrahedral structures. The shortest Os–Os distance in the structures, 2.743 (4) Å in (I) and 2.769 (1) Å in (II), is between the two 18-electron Os atoms, and is similar to the value of 2.732 (1) Å in Os₆(CO)₁₈ (Mason, Thomas & Mingos, 1973) and 2.754 (3) Å in Os₆(CO)₁₆(CNBu)₂ (Orpen & Sheldrick, 1978). The bond lengths to Os(6) in (I) and Os(3) in (II) show the same variations as for the capping Os atoms in Os₆(CO)₁₆(CNBu)₂, where the Os–Os range is 2.775 (3)–2.861 (3) Å. The replacement of a carbonyl or an isocyanide group by a phosphine ligand has little effect on the two Os–Os bonds which are pseudo *cis* to the Os–P vector. However, the Os–Os distances which are *trans* to the Os–P vector, Os(1)–Os(5) in (I) and Os(3)–Os(1') in (II), are *ca* 0.14 and 0.08 Å longer, respectively, than the equivalent bond in the isocyanide complex, 2.860 (4) Å. The Os–Os bond lengthening is consistent with the poorer π-acceptor properties of the phosphine when compared with that of the carbonyl group. A similar lengthening effect has been observed in the 'raft' cluster Os₆(CO)₁₇[P(OCH₃)₃]₄ where the Os–Os bonds *trans* to Os–P vectors are also *ca* 0.04 Å longer than those *trans* to Os–C(carbonyl) vectors (Goudsmit, Johnson, Lewis, Raithby & Whitmire, 1982).

In both the title complexes and in Os₆(CO)₁₆(CNBu)₂ (Orpen & Sheldrick, 1978), replacement of a carbonyl by a phosphine or isocyanide group, respectively, occurs at a formally electron-deficient metal centre, a capping Os atom. This position is also the one which would cause least steric congestion in replacing a carbonyl ligand by a bulkier group. This site of replacement probably reflects the better σ-donor properties of a phosphine compared to a carbonyl by formally placing greater electron density on the

electron-deficient metal. The Os—P bond lengths, 2.363 (5) Å in (I) and 2.368 (2) Å in (II), are similar to the value of 2.370 (2) Å found for the Os—P distance in Os₃H₂(CO)₁₀[P(C₆H₅)₃] (Churchill & DeBoer, 1977) where the Os—P bond is *trans* to a long Os—Os bond, 2.917 (1) Å.

The distribution of the ligands around the phosphine-substituted capping Os atom, Os(5) in (I) and Os(3) and Os(3') in (II), differs slightly from that in the isocyanide-substituted cluster Os₆(CO)₁₆(CNBu^t)₂ (Orpen & Sheldrick, 1978). In the latter complex the *trans*

Os—Os—C(isocyanide) angles lie in the range 153–159°, while in (I) the *trans* Os—Os—P angle deviates from linearity by only *ca* 10° and by only *ca* 6° in (II).

In both (I) and (II) a network of incipient bridging carbonyl ligands is observed, similar to that reported for Os₆(CO)₁₆(CNBu^t)₂ (Eady, Gavens, Johnson, Lewis, Malatesta, Mays, Orpen, Rivera, Sheldrick & Hursthouse, 1978). Incipient carbonyl bridge bonding is usually observed between metal atoms in different formal oxidation states (different formal electron counts). A carbonyl group which is formally bonded to an 'electron-rich' metal bends towards an adjacent 'electron-poor' metal. This 'interaction' is characterized by relatively short Os...C contacts and deviations from linearity of the carbonyl group. The dimensions of the incipient bridging carbonyls in (I) and (II) are presented in Table 5. In structure (I) the shortest contacts are between Os(3) (18 electrons) and Os(5) (17 electrons), and Os(2) (18e) and Os(6) (17e). The carbonyl groups C(11)O(11), C(13)O(13), C(42)O(42) and C(43)O(43) are each involved in bridges to two metal atoms, so that the Os(1) and Os(4) atoms (19e) interact with both the formally 18- and 17-electron Os atoms. The carbonyls C(12)O(12) and C(41)O(41) show weak interactions with single Os atoms. There are also two

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$) for Os₆(CO)₁₇[P(C₆H₅)₃] (I)

$U_{eq} = \frac{1}{3}$ (trace of the orthogonalized U_{ij} matrix).

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Os(1)	6417 (1)	3348 (1)	2476 (1)	25 (1)
Os(2)	7626 (1)	4978 (1)	2022 (1)	30 (1)
Os(3)	8620 (1)	3449 (1)	1260 (1)	29 (1)
Os(4)	9442 (1)	3100 (1)	2963 (1)	27 (1)
Os(5)	9084 (1)	1536 (1)	2418 (1)	26 (1)
Os(6)	6891 (1)	4233 (1)	3694 (1)	40 (1)
P(1)	11315 (4)	288 (2)	2187 (2)	26 (2)
C(101)	12998 (8)	-119 (6)	2901 (5)	28 (3)
C(102)	12822 (8)	47 (6)	3696 (5)	29 (3)
C(103)	14073 (8)	-350 (6)	4273 (5)	41 (3)
C(104)	15501 (8)	-912 (6)	4055 (5)	53 (4)
C(105)	15677 (8)	-1078 (6)	3260 (5)	60 (5)
C(106)	14426 (8)	-682 (6)	2683 (5)	66 (5)
C(111)	11073 (11)	-946 (7)	2260 (5)	32 (3)
C(112)	11781 (11)	-1537 (7)	1728 (5)	43 (4)
C(113)	11659 (11)	-2501 (7)	1868 (5)	60 (5)
C(114)	10828 (11)	-2872 (7)	2540 (5)	45 (4)
C(115)	10120 (11)	-2280 (7)	3072 (5)	55 (4)
C(116)	10242 (11)	-1317 (7)	2931 (5)	49 (4)
C(121)	12074 (11)	641 (8)	1146 (6)	30 (3)
C(122)	13315 (11)	1026 (8)	1025 (6)	52 (4)
C(123)	13800 (11)	1358 (8)	215 (6)	62 (5)
C(124)	13044 (11)	1304 (8)	-474 (6)	60 (5)
C(125)	11803 (11)	919 (8)	-353 (6)	58 (4)
C(126)	11318 (11)	588 (8)	457 (6)	43 (3)
C(11)	5673 (15)	2974 (9)	1594 (8)	28 (3)
O(11)	5095 (11)	2772 (8)	1094 (6)	42 (6)
C(12)	5773 (15)	2374 (9)	3339 (8)	31 (3)
O(12)	5262 (14)	1867 (9)	3814 (8)	61 (7)
C(13)	4546 (17)	4416 (10)	2337 (9)	37 (3)
O(13)	3327 (12)	4999 (8)	2236 (8)	50 (7)
C(21)	7353 (18)	5946 (11)	2631 (10)	45 (4)
O(21)	7147 (22)	6652 (9)	2852 (10)	105 (11)
C(22)	9245 (16)	5416 (10)	1436 (9)	36 (3)
O(22)	10268 (15)	5697 (9)	1129 (8)	68 (8)
C(23)	5990 (17)	5884 (11)	12659 (10)	40 (3)
O(23)	5014 (15)	6421 (8)	850 (8)	54 (7)
C(31)	8503 (16)	2461 (10)	718 (9)	35 (3)
O(31)	8302 (13)	2050 (7)	256 (6)	47 (6)
C(32)	7351 (15)	4408 (9)	353 (8)	30 (3)
O(32)	6614 (13)	4951 (8)	-245 (6)	45 (6)
C(33)	10501 (17)	3547 (10)	812 (9)	38 (3)
O(33)	11688 (12)	3603 (8)	514 (8)	53 (7)
C(41)	9720 (18)	2266 (11)	4123 (10)	45 (4)
O(41)	10036 (17)	1804 (8)	4782 (7)	61 (8)
C(42)	11442 (17)	2447 (10)	2598 (9)	36 (3)
O(42)	12683 (12)	2203 (8)	2426 (7)	45 (6)
C(43)	10353 (19)	4036 (12)	3233 (11)	50 (4)
O(43)	10942 (13)	4499 (8)	3442 (8)	67 (8)
C(51)	8859 (16)	788 (10)	3512 (9)	34 (3)
O(51)	8671 (14)	360 (7)	4150 (6)	47 (6)
C(52)	7939 (16)	902 (10)	2008 (9)	37 (3)
O(52)	7184 (12)	516 (8)	1761 (8)	54 (7)
C(61)	6605 (19)	3282 (12)	4619 (11)	49 (4)
O(61)	6414 (23)	2654 (12)	5205 (9)	111 (12)
C(62)	4982 (21)	5100 (13)	3797 (11)	54 (4)
O(62)	3746 (16)	5647 (11)	3837 (10)	84 (10)
C(63)	7845 (24)	4712 (15)	4382 (13)	68 (5)
O(63)	8404 (22)	5056 (15)	4791 (11)	149 (15)

Table 2. Atomic coordinates (Os $\times 10^5$; others $\times 10^4$) and equivalent isotropic thermal parameters (\AA^2) for Os₆(CO)₁₆[P(C₆H₅)₃]₂ (II)

$U_{eq} = \frac{1}{3}$ (trace of the orthogonalized U_{ij} matrix).

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Os(1)	4004 (3)	54194 (3)	69071 (3)	2.156 (9)
Os(2)	7040 (3)	65324 (3)	80701 (3)	2.490 (10)
Os(3)	12883 (3)	50602 (3)	83916 (3)	2.320 (10)
P(1)	2664 (2)	4876 (2)	8577 (2)	2.67 (7)
C(111)	3325 (8)	5677 (7)	8862 (7)	3.0 (3)
C(112)	4032 (9)	5635 (9)	9451 (9)	4.7 (3)
C(113)	4540 (10)	6210 (10)	9600 (10)	5.2 (4)
C(114)	4350 (10)	6840 (10)	9180 (10)	5.8 (4)
C(115)	3700 (10)	6910 (10)	8590 (10)	6.8 (5)
C(116)	3171 (9)	6320 (8)	8438 (9)	4.2 (3)
C(121)	3025 (7)	4187 (7)	9335 (7)	2.8 (2)
C(122)	3190 (9)	3472 (8)	9161 (8)	3.8 (3)
C(123)	3400 (10)	2936 (9)	9737 (9)	4.8 (3)
C(124)	3450 (10)	3130 (10)	10490 (10)	5.8 (4)
C(125)	3320 (10)	3820 (9)	10690 (9)	4.8 (3)
C(126)	3107 (9)	4357 (8)	10123 (8)	3.8 (3)
C(131)	2962 (8)	4492 (7)	7727 (7)	3.0 (3)
C(132)	3690 (10)	4650 (10)	7610 (10)	5.2 (4)
C(133)	3890 (10)	4380 (10)	6940 (10)	7.3 (5)
C(134)	3380 (10)	3930 (10)	6430 (10)	5.2 (4)
C(135)	2690 (9)	3775 (9)	6535 (9)	4.8 (3)
C(136)	2455 (8)	4055 (8)	7195 (8)	3.7 (3)
C(11)	416 (8)	4422 (7)	6631 (8)	3.3 (3)
O(11)	461 (6)	3805 (6)	6449 (8)	4.4 (3)
C(12)	-94 (9)	5819 (8)	9097 (8)	4.0 (3)
O(12)	-29 (7)	6076 (7)	9731 (7)	5.8 (3)
C(13)	-1463 (7)	5603 (7)	8118 (7)	2.7 (2)
O(13)	-2054 (6)	5750 (5)	8230 (6)	4.0 (2)
C(21)	270 (10)	7345 (9)	8463 (9)	4.6 (3)
O(21)	-22 (7)	7878 (7)	8687 (7)	6.3 (3)
C(22)	1510 (10)	6507 (9)	9017 (9)	4.5 (3)
O(22)	1990 (7)	6597 (6)	9598 (7)	5.5 (3)
C(23)	1351 (8)	7062 (7)	7568 (7)	3.0 (2)
O(23)	1751 (7)	7387 (6)	7262 (6)	5.5 (3)
C(31)	1409 (8)	4992 (7)	9446 (8)	3.5 (3)
O(31)	1411 (7)	4969 (6)	10118 (7)	5.5 (3)
C(32)	1201 (7)	4059 (7)	8314 (7)	2.7 (2)
O(32)	1126 (6)	3413 (6)	8255 (6)	4.9 (2)

Table 3. Bond lengths (Å) and interbond angles (°) for

Os ₆ (CO) ₁₇ {P(C ₆ H ₅) ₃ } (I)			
Os(1)—Os(2)	2.824 (4)	Os(1)—Os(3)	2.781 (4)
Os(1)—Os(4)	2.800 (4)	Os(1)—Os(5)	2.998 (4)
Os(1)—Os(6)	2.788 (4)	Os(1)—C(11)	1.911 (17)
Os(1)—C(12)	1.928 (15)	Os(1)—C(13)	1.889 (14)
Os(2)—Os(3)	2.743 (4)	Os(2)—Os(4)	2.782 (4)
Os(2)—Os(6)	2.814 (4)	Os(2)—C(21)	1.897 (20)
Os(2)—C(22)	1.905 (17)	Os(2)—C(23)	1.895 (15)
Os(3)—Os(4)	2.823 (4)	Os(3)—Os(5)	2.833 (4)
Os(3)—C(31)	1.923 (19)	Os(3)—C(32)	1.888 (13)
Os(3)—C(33)	1.865 (3)	Os(4)—Os(5)	2.777 (4)
Os(4)—Os(6)	2.831 (4)	Os(4)—C(41)	1.951 (17)
Os(4)—C(42)	1.929 (16)	Os(4)—C(43)	1.954 (23)
Os(5)—P(1)	2.363 (5)	Os(5)—C(51)	1.878 (15)
Os(5)—C(52)	1.848 (20)	Os(6)—C(61)	1.830 (18)
Os(6)—C(62)	1.835 (18)	Os(6)—C(63)	1.860 (28)
P(1)—C(101)	1.827 (11)	P(1)—C(111)	1.847 (13)
P(1)—C(121)	1.826 (12)	C(11)—O(11)	1.151 (21)
C(12)—O(12)	1.114 (19)	C(13)—O(13)	1.157 (16)
C(21)—O(21)	1.141 (25)	C(22)—O(22)	1.171 (22)
C(23)—O(23)	1.100 (18)	C(31)—O(31)	1.143 (22)
C(32)—O(32)	1.167 (16)	C(33)—O(33)	1.177 (16)
C(41)—O(41)	1.112 (19)	C(42)—O(42)	1.123 (19)
C(43)—O(43)	1.112 (27)	C(51)—O(51)	1.106 (18)
C(52)—O(52)	1.164 (23)	C(61)—O(61)	1.185 (23)
C(62)—O(62)	1.171 (22)	C(63)—O(63)	1.160 (36)

Os(2)—Os(1)—Os(3)	58.6 (2)	Os(2)—Os(1)—Os(4)	59.3 (2)
Os(3)—Os(1)—Os(4)	60.8 (2)	Os(2)—Os(1)—Os(5)	105.2 (2)
Os(3)—Os(1)—Os(5)	58.6 (2)	Os(4)—Os(1)—Os(5)	57.1 (2)
Os(2)—Os(1)—Os(6)	60.2 (2)	Os(3)—Os(1)—Os(6)	110.0 (2)
Os(4)—Os(1)—Os(6)	60.9 (2)	Os(5)—Os(1)—Os(6)	112.2 (2)
Os(2)—Os(1)—C(11)	117.8 (5)	Os(3)—Os(1)—C(11)	76.0 (5)
Os(4)—Os(1)—C(11)	130.2 (4)	Os(4)—Os(1)—C(13)	122.8 (5)
Os(5)—Os(1)—C(11)	80.3 (4)	Os(6)—Os(1)—C(11)	167.4 (3)
Os(2)—Os(1)—C(12)	149.2 (5)	Os(3)—Os(1)—C(12)	140.6 (4)
Os(4)—Os(1)—C(12)	104.9 (5)	Os(5)—Os(1)—C(12)	82.5 (5)
Os(6)—Os(1)—C(12)	89.2 (6)	C(11)—Os(1)—C(12)	92.7 (7)
Os(2)—Os(1)—C(13)	81.1 (6)	Os(3)—Os(1)—C(13)	119.2 (5)
Os(5)—Os(1)—C(13)	167.9 (5)	Os(6)—Os(1)—C(13)	79.9 (6)
C(11)—Os(1)—C(13)	87.6 (7)	C(12)—Os(1)—C(13)	97.5 (7)
Os(1)—Os(2)—Os(3)	59.9 (2)	Os(1)—Os(2)—Os(4)	59.9 (2)
Os(3)—Os(2)—Os(4)	61.5 (2)	Os(1)—Os(2)—Os(6)	59.3 (2)
Os(3)—Os(2)—Os(6)	110.3 (2)	Os(4)—Os(2)—Os(6)	60.8 (2)
Os(1)—Os(2)—C(21)	124.5 (6)	Os(3)—Os(2)—C(21)	168.5 (5)
Os(4)—Os(2)—C(21)	110.3 (5)	Os(6)—Os(2)—C(21)	68.8 (6)
Os(1)—Os(2)—C(22)	143.2 (4)	Os(3)—Os(2)—C(22)	84.1 (6)
Os(4)—Os(2)—C(22)	97.6 (4)	Os(6)—Os(2)—C(22)	138.1 (5)
C(21)—Os(2)—C(22)	89.4 (8)	Os(1)—Os(2)—C(23)	97.2 (6)
Os(3)—Os(2)—C(23)	100.5 (6)	Os(4)—Os(2)—C(23)	155.4 (6)
Os(6)—Os(2)—C(23)	117.5 (6)	C(21)—Os(2)—C(23)	89.6 (8)
C(22)—Os(2)—C(23)	96.8 (7)	Os(1)—Os(3)—Os(2)	61.5 (2)
Os(1)—Os(3)—Os(4)	59.9 (2)	Os(2)—Os(3)—Os(4)	60.1 (2)
Os(1)—Os(3)—Os(5)	64.5 (2)	Os(2)—Os(3)—Os(5)	112.1 (2)
Os(4)—Os(3)—Os(5)	58.8 (2)	Os(1)—Os(3)—C(31)	102.4 (5)
Os(2)—Os(3)—C(31)	158.6 (4)	Os(4)—Os(3)—C(31)	126.6 (5)
Os(5)—Os(3)—C(31)	68.1 (5)	Os(1)—Os(3)—C(32)	99.4 (5)
Os(2)—Os(3)—C(32)	83.1 (5)	Os(4)—Os(3)—C(32)	142.7 (4)
Os(5)—Os(3)—C(32)	144.0 (5)	Os(1)—Os(3)—C(33)	157.0 (5)
Os(2)—Os(3)—C(33)	104.7 (6)	Os(4)—Os(3)—C(33)	97.6 (5)
Os(5)—Os(3)—C(33)	109.5 (9)	C(31)—Os(3)—C(32)	86.0 (7)
C(31)—Os(3)—C(33)	94.8 (2)	C(32)—Os(3)—C(33)	96.5 (2)
Os(1)—Os(4)—Os(2)	60.8 (2)	Os(1)—Os(4)—Os(3)	59.3 (2)
Os(2)—Os(4)—Os(3)	58.6 (2)	Os(1)—Os(4)—Os(5)	65.0 (2)
Os(2)—Os(4)—Os(5)	112.6 (2)	Os(3)—Os(4)—Os(5)	60.8 (2)
Os(1)—Os(4)—Os(6)	59.4 (2)	Os(2)—Os(4)—Os(6)	60.2 (2)
Os(3)—Os(4)—Os(6)	107.5 (2)	Os(5)—Os(4)—Os(6)	117.9 (2)
Os(1)—Os(4)—C(41)	105.2 (6)	Os(2)—Os(4)—C(41)	139.2 (5)
Os(3)—Os(4)—C(41)	150.8 (6)	Os(5)—Os(4)—C(41)	90.6 (7)
Os(6)—Os(4)—C(41)	79.5 (5)	Os(1)—Os(4)—C(42)	133.3 (5)
Os(2)—Os(4)—C(42)	121.1 (5)	Os(3)—Os(4)—C(42)	81.8 (5)
Os(5)—Os(4)—C(42)	74.3 (6)	Os(6)—Os(4)—C(42)	167.1 (5)
C(41)—Os(4)—C(42)	96.7 (7)	Os(1)—Os(4)—C(43)	131.1 (4)
Os(2)—Os(4)—C(43)	76.2 (5)	Os(3)—Os(4)—C(43)	117.0 (6)
Os(5)—Os(4)—C(43)	161.9 (5)	Os(6)—Os(4)—C(43)	80.2 (6)
C(41)—Os(4)—C(43)	92.0 (8)	C(42)—Os(4)—C(43)	87.6 (8)
Os(1)—Os(5)—Os(3)	56.9 (2)	Os(1)—Os(5)—Os(4)	57.9 (2)
Os(3)—Os(5)—Os(4)	60.4 (2)	Os(1)—Os(5)—P(1)	170.7 (1)
Os(3)—Os(5)—P(1)	113.8 (2)	Os(4)—Os(5)—P(1)	118.7 (2)
Os(1)—Os(5)—C(51)	94.9 (5)	Os(3)—Os(5)—C(51)	148.1 (4)
Os(4)—Os(5)—C(51)	93.1 (6)	P(1)—Os(5)—C(51)	94.0 (5)
Os(1)—Os(5)—C(52)	95.7 (5)	Os(3)—Os(5)—C(52)	106.9 (5)
Os(4)—Os(5)—C(52)	153.5 (4)	P(1)—Os(5)—C(52)	87.4 (5)
C(51)—Os(5)—C(52)	89.1 (8)	Os(1)—Os(6)—Os(2)	60.5 (2)
Os(1)—Os(6)—Os(4)	59.8 (2)	Os(2)—Os(6)—Os(4)	59.1 (2)
Os(1)—Os(6)—C(61)	97.8 (7)	Os(2)—Os(6)—C(61)	155.9 (6)

Table 3 (cont.)

Os(4)—Os(6)—C(61)	102.1 (6)	Os(1)—Os(6)—C(62)	104.4 (8)
Os(2)—Os(6)—C(62)	104.1 (6)	Os(4)—Os(6)—C(62)	160.4 (6)
C(61)—Os(6)—C(62)	90.9 (8)	Os(1)—Os(6)—C(63)	161.5 (6)
Os(2)—Os(6)—C(63)	108.4 (7)	Os(4)—Os(6)—C(63)	102.2 (7)
C(61)—Os(6)—C(63)	89.4 (10)	C(62)—Os(6)—C(63)	92.4 (10)
Os(5)—P(1)—C(101)	118.6 (4)	Os(5)—P(1)—C(111)	115.7 (4)
C(101)—P(1)—C(111)	99.5 (5)	Os(5)—P(1)—C(121)	113.0 (4)
C(101)—P(1)—C(121)	104.0 (5)	C(111)—P(1)—C(121)	104.0 (6)
P(1)—C(101)—C(102)	119.9 (4)	P(1)—C(101)—C(106)	119.8 (4)
P(1)—C(111)—C(112)	123.3 (4)	P(1)—C(111)—C(116)	116.5 (4)
P(1)—C(121)—C(122)	121.2 (5)	P(1)—C(121)—C(126)	118.5 (5)
Os(1)—C(11)—O(11)	173.8 (11)	Os(1)—C(12)—O(12)	173.4 (11)
Os(1)—C(13)—O(13)	172.7 (15)	Os(2)—C(21)—O(21)	167.2 (13)
Os(2)—C(22)—O(22)	175.1 (15)	Os(2)—C(23)—O(23)	177.4 (15)
Os(3)—C(31)—O(31)	165.4 (10)	Os(3)—C(32)—O(32)	174.9 (12)
Os(3)—C(33)—O(33)	178.1 (15)	Os(4)—C(41)—O(41)	172.2 (17)
Os(4)—C(42)—O(42)	167.0 (16)	Os(4)—C(43)—O(43)	173.8 (13)
Os(5)—C(51)—O(51)	177.4 (13)	Os(5)—C(52)—O(52)	178.1 (13)
Os(6)—C(61)—O(61)	178.4 (18)	Os(6)—C(62)—O(62)	177.6 (17)
Os(6)—C(63)—O(63)	176.9 (15)		

Table 4. Bond lengths (Å) and interbond angles (°) for Os₆(CO)₁₆{P(C₆H₅)₃}₂ (II)

Os(1)—Os(1')	2.794 (1)	Os(1)—Os(2)	2.819 (1)
Os(1)—Os(2')	2.781 (1)	Os(1)—Os(3)	2.781 (1)
Os(2)—Os(3)	2.943 (1)	Os(2)—Os(2')	2.769 (1)
Os(1)—C(12)	1.862 (14)	Os(1)—C(11)	1.886 (13)
Os(2)—C(21)	1.867 (16)	Os(1)—C(13)	1.894 (12)
Os(2)—C(23)	1.865 (13)	Os(2)—C(22)	1.905 (16)
Os(3)—C(31)	1.828 (14)	Os(3)—P(1)	2.368 (3)
P(1)—C(111)	1.842 (13)	Os(3)—C(32)	1.817 (12)
P(1)—C(131)	1.844 (12)	P(1)—C(121)	1.824 (12)
C(12)—O(12)	1.192 (16)	C(11)—O(11)	1.169 (15)
C(21)—O(21)	1.199 (17)	C(13)—O(13)	1.130 (14)
C(23)—O(23)	1.147 (14)	C(22)—O(22)	1.165 (17)
C(32)—O(32)	1.177 (14)	C(31)—O(31)	1.188 (16)
Os(1')—Os(1)—Os(2)	59.40 (1)	Os(1')—Os(1)—Os(2')	60.74 (2)
Os(1')—Os(1)—Os(3)	63.72 (2)	Os(1')—Os(1)—Os(3')	57.93 (2)
Os(1')—Os(1)—C(11)	103.6 (4)	Os(1')—Os(1)—C(12)	129.6 (4)
Os(1')—Os(1)—C(13)	133.9 (4)	Os(2)—Os(1)—Os(2')	59.28 (2)
Os(2)—Os(1)—Os(3)	61.30 (2)	Os(2)—Os(1)—Os(3')	106.91 (2)
Os(2)—Os(1)—C(11)	149.2 (4)	Os(2)—Os(1)—C(12)	112.8 (4)
Os(2)—Os(1)—C(13)	83.7 (4)	Os(2')—Os(1)—Os(3)	112.67 (2)
Os(2')—Os(1)—Os(3')	59.76 (2)	Os(2')—Os(1)—C(11)	138.5 (4)
Os(2')—Os(1)—C(12)	72.9 (4)	Os(2')—Os(1)—C(13)	124.7 (4)
Os(3)—Os(1)—Os(3')	114.58 (2)	Os(3)—Os(1)—C(11)	88.4 (4)
Os(3)—Os(1)—C(12)	162.4 (4)	Os(3)—Os(1)—C(13)	74.9 (4)
Os(3')—Os(1)—C(11)	79.2 (4)	Os(3')—Os(1)—C(12)	82.8 (4)
Os(3')—Os(1)—C(13)	168.1 (4)	C(11)—Os(1)—C(12)	97.9 (6)
C(11)—Os(1)—C(13)	94.4 (5)	C(12)—Os(1)—C(13)	88.2 (2)
Os(1)—Os(2)—Os(1')	59.86 (2)	C(12)—Os(1)—C(13)	88.2 (2)
Os(1)—Os(2)—Os(3)	58.70 (2)	Os(1)—Os(2)—C(12)	96.4 (3)
Os(1)—Os(2)—C(21)	143.8 (5)	Os(1)—Os(2)—C(22)	126.1 (4)
Os(1)—Os(2)—C(23)	92.4 (4)	Os(1')—Os(2)—Os(2')	61.04 (2)
Os(1')—Os(2)—Os(3)	62.94 (2)	Os(1')—Os(2)—C(12)	38.6 (3)
Os(1')—Os(2)—C(21)	102.0 (5)	Os(1')—Os(2)—C(22)	109.6 (4)
Os(1')—Os(2)—C(23)	151.5 (4)	Os(2')—Os(2)—Os(3)	110.78 (1)
Os(2')—Os(2)—C(21)	84.2 (5)	Os(2')—Os(2)—C(22)	166.4 (5)
Os(2')—Os(2)—C(23)	100.8 (4)	Os(3)—Os(2)—C(21)	144.8 (5)
Os(3)—Os(2)—C(22)	69.6 (4)	Os(3)—Os(2)—C(23)	110.1 (4)
C(21)—Os(2)—C(22)	88.6 (6)	C(21)—Os(2)—C(23)	97.2 (6)
C(22)—Os(2)—C(23)	91.5 (6)	Os(1)—Os(3)—Os(1')	58.35 (2)
Os(1)—Os(3)—Os(2)	59.99 (2)	Os(1)—Os(3)—P(1)	118.34 (8)
Os(1)—Os(3)—C(31)	151.2 (4)	Os(1)—Os(3)—C(32)	98.6 (4)
Os(1')—Os(3)—Os(2)	57.3 (2)	Os(1')—Os(3)—P(1)	174.4 (8)
Os(1')—Os(3)—C(32)	93.2 (4)	Os(1')—Os(3)—C(32)	98.6 (4)
Os(2)—Os(3)—P(1)	117.34 (8)	Os(2)—Os(3)—C(31)	102.2 (4)
Os(2)—Os(3)—C(32)	153.2 (4)	P(1)—Os(3)—C(31)	89.5 (4)
P(1)—Os(3)—C(32)	86.2 (4)	C(31)—Os(3)—C(32)	89.8 (5)
C(111)—P(1)—C(111)	104.8 (6)	C(111)—P(1)—C(113)	103.6 (6)
C(121)—P(1)—C(113)	103.1 (6)	P(1)—C(111)—C(112)	122 (1)
P(1)—C(111)—C(112)	119 (1)	P(1)—C(121)—C(122)	122 (1)
P(1)—C(121)—C(122)	121 (1)	P(1)—C(131)—C(132)	120 (1)
Os(1)—C(11)—O(11)	176 (1)	Os(1)—C(11)—O(11)	176 (1)
Os(1)—C(13)—O(13)	177 (1)	Os(1)—C(13)—O(13)	176 (1)
Os(2)—C(21)—O(21)	177 (1)	Os(2)—C(22)—O(22)	170 (1)
Os(2)—C(23)—O(23)	180 (1)	Os(3)—C(31)—O(31)	173 (1)
Os(3)—C(32)—O(32)	178 (1)		

short contacts between Os(2) and C(32) and Os(3) and C(22), although both Os(2) and Os(3) formally have 18 electrons each. The carbonyls C(23)O(23) and C(33)-O(33), and those bonded to Os(5) and Os(6) show no short contacts with other metal atoms, and the average Os—C—O angle for those groups is 178 (2)° compared to that of 171 (3)° for the carbonyl groups listed for (I) in Table 5. The incipient bridging carbonyl network in (II) is similar to that in (I) except that the average Os—C—O angle for those groups is marginally higher at 175 (2)°. Again the 17-electron atoms, Os(3) and Os(3'), are involved in a number of contacts with carbonyls from both Os(1) and Os(1') (19e) and Os(2) and Os(2') (18e), but the carbonyls C(31)O(31) and C(32)O(32) do not interact with the other metal atoms. The 18-electron atoms, Os(2) and Os(2'), have short contacts with the carbonyls C(12)O(12) and C(13)O(13) and their symmetry equivalents, bound to the 'electron-rich' Os(1) and Os(1') atoms. There are no incipient bridge bonds to the 19-electron Os(1) and Os(1') atoms themselves.

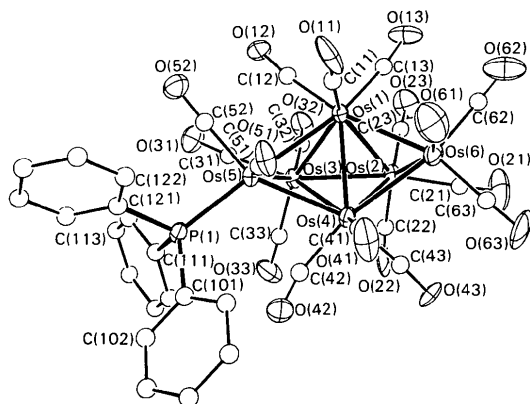


Fig. 1. ORTEP (Johnson, 1976) diagram of $\text{Os}_6(\text{CO})_{17}[\text{P}(\text{C}_6\text{H}_5)_3]$ (I) showing the atom labelling. Thermal motion is depicted as 30% probability ellipsoids.

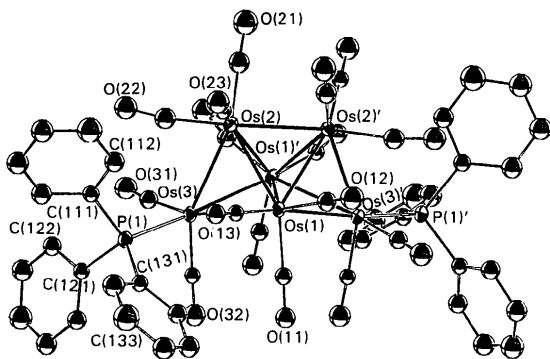


Fig. 2. ORTEP (Johnson, 1976) diagram of $\text{Os}_6(\text{CO})_{16}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ (II) showing the atom labelling. Thermal motion is depicted as 30% probability ellipsoids.

Table 5. Incipient bridging carbonyl group dimensions in $\text{Os}_6(\text{CO})_{17}[\text{P}(\text{C}_6\text{H}_5)_3]$ (I) and $\text{Os}_6(\text{CO})_{16}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ (II)

	Os...C contacts ≤ 3.35 Å	Os—C—O (°)
$\text{Os}_6(\text{CO})_{17}[\text{P}(\text{C}_6\text{H}_5)_3]$ (I)		
Os(5)...C(31)	2.77 (2)	165 (1)
Os(6)...C(21)	2.77 (2)	167 (1)
Os(5)...C(42)	2.92 (2)	167 (2)
Os(6)...C(13)	3.08 (1)	173 (2)
Os(3)...C(11)	2.97 (2)	174 (1)
Os(2)...C(43)	2.99 (2)	174 (1)
Os(3)...C(22)	3.18 (2)	175 (2)
Os(2)...C(13)	3.15 (1)	173 (2)
Os(3)...C(42)	3.18 (2)	167 (2)
Os(2)...C(32)	3.14 (2)	175 (1)
Os(5)...C(11)	3.27 (2)	174 (1)
Os(6)...C(41)	3.13 (2)	173 (2)
Os(5)...C(12)	3.35 (1)	173 (1)
Os(6)...C(43)	3.16 (2)	174 (1)
$\text{Os}_6(\text{CO})_{16}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ (II)		
Os(2)...C(12)	2.86 (1)	177 (1)
Os(2')...C(13)	3.22 (2)	176 (1)
Os(2')...C(21)	3.18 (2)	177 (1)
Os(3)...C(11)	3.32 (2)	176 (1)
Os(3)...C(12)	3.28 (1)	177 (1)
Os(3)...C(22)	2.83 (2)	170 (1)
Os(3')...C(11)	3.18 (2)	176 (1)
Os(3')...C(13)	2.93 (2)	176 (1)

The average Os—C(carbonyl) and C—O distances are 1.89 (3) and 1.15 (3) Å for (I) and 1.87 (3) and 1.17 (2) Å for (II).

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The Structure of 6-(3-Hydroxy-4,5-dimethoxyphenyl)-3,7-dioxabicyclo[3.3.0]octan-2-one

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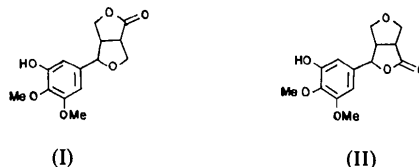
Abstract. C₁₄H₁₆O₆, *M_r* = 208.3, monoclinic, *P*2₁/*c*, *a* = 10.765 (4), *b* = 14.619 (5), *c* = 8.374 (4) Å, β = 98.02 (3)°, *V* = 1305 (2) Å³, *Z* = 4, *D_x* = 1.43 Mg m⁻³, λ(Mo *Kα*) = 0.71073 Å, μ = 0.07 mm⁻¹, *F*(000) = 592, *T* = 296 K, *R* = 0.058 for 807 reflections with *I* > 2σ(*I*). The bond lengths and angles are normal. In the dioxabicyclo group the five-membered rings are in unsymmetrical twist configurations. The dihedral angle between the best least-squares planes through these rings is 75 (1)°. Intermolecular hydrogen bonding occurs between the hydroxy and oxo groups.

Introduction. The term lignana was first introduced by Harworth (1942) to describe products from plants having a carbon skeleton formed by two *n*-propylbenzene moieties linked through their β positions. Later, Gottlieb (1972) proposed a biogenetic definition to include recently discovered structural types resulting from the association of two *n*-propylbenzenic residues, which did not fall into Harworth's structural classification.

During a systematic chemical study of *Ormosia flava* (Ducke) Rudd, family Leguminosae, a white crystalline substance (hereafter named ormosalin) was isolated (melting point 418–420 K) whose infrared, ultraviolet and proton NMR spectra showed characteristic

features of lignanas of the type bicyclo[3.3.0]octanes. Its mass and ¹³C NMR spectra indicated the absence of the second aromatic ring in the system C₆–C₃–C₃–C₆ characteristic of these compounds (Böechat, 1984).

From the spectroscopic and chemical studies (Böechat, 1984), the isomeric structures (I) and (II) were proposed. To discriminate between these two possibilities and to determine the three-dimensional configuration of the molecule a crystal structure determination was undertaken.



Experimental. Prismatic transparent crystals, 0.12 × 0.14 × 0.30 mm, Nonius CAD-4 diffractometer; cell parameters by least squares on setting angles for 17 reflections, 6 < θ < 18°; intensities by ω–2θ scans for ω = (0.80 + 0.35 tanθ)° at ω speed of (1.9–6.7)° min⁻¹ min.–max.; range of *hkl*: –9 < *h* < 9, 0 < *k* < 17, 0 < *l* < 12, θ_{max} = 25°; standard 040, varied ±3% of mean intensity over data collection; 2410 reflections measured, 2285 unique, *R*_{int} = 0.020,