Journal of Organometallic Chemistry, 291 (1985) 221–229
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ACTIVATION OF THE CARBON-NITROGEN TRIPLE BOND OF BENZONITRILE IN THE PRESENCE OF TRIOSMIUM CLUSTERS AND ACETIC ACID. CRYSTAL STRUCTURE OF $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}O_2CCH_3)$, A PRODUCT OF THE REACTION

P. MICHELIN LAUSAROT, G.A. VAGLIO, M. VALLE

Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino (Italy)

A. TIRIPICCHIO, M. TIRIPICCHIO CAMELLINI

Istituto di Chimica Generale ed Inorganica, Università di Parma, Via Massimo d'Azeglio 85, 43100 Parma (Italy)

and P. GARIBOLDI

Laboratorio di Chimica Organica della Facoltà di Scienze, Università di Milano, Via Venezian 21, 20133 Milano (Italy)

(Received February 19th, 1985)

Summary

The activation of the CN triple bond of benzonitrile in the presence of acetic acid and of $Os_3(CO)_{12}$ or $H_2Os_3(CO)_{10}$ has been studied. When $Os_3(CO)_{12}$ reacts with PhCN and acetic acid in refluxing n-octane the three main products are $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}O_2CCH_3)$ (I), $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-N=CHPh})$ (II) and $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHCH}_2\text{Ph})$ (III); II and III are analogues of $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-N=CHPh})$ and $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-NHCH}_2\text{Ph})$ obtained from PhCN, $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$, and acetic acid. In contrast to the reaction with ruthenium clusters, $Os_3(CO)_{12}$ and $H_2Os_3(CO)_{10}$ also give the adduct $Os_3(CO)_{10}(CH_3COOH)$ (I). The structure of I has been fully elucidated by X-ray diffraction. Crystals of I are monoclinic, space group $P2_1/m$, with unit cell parameters a 7.858(6), b 12.542(8), c 9.867(6) Å, β 109.92(2)°, $Z = 2$. In I an edge of the triangular cluster of osmium atoms is doubly bridged by a hydride and an acetate ligand. Ten terminal carbonyl groups are bonded to the metal atoms.

Introduction

Recently $Ru_3(CO)_{12}$ has been shown to activate the CN triple bond of benzonitrile (PhCN), leading to formation of $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-N=CHPh})$ in the presence of either molecular hydrogen [1,2] or acetic acid [1]. Further hydrogenation of the nitrile to give $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-NHCH}_2Ph)$ has been achieved only by use of acetic acid, which seems to be essential, under mild conditions [3].

With the aim of further investigating the rôle of the acetic acid in the activation of organic nitriles with metal clusters, we have studied the compounds formed, when $Os_3(CO)_{12}$ or $H_2Os_3(CO)_{10}$ are treated with benzonitrile and acetic acid under various conditions. Previously the hydrogenation of the CN triple bond by osmium clusters had been reported only for the case of the formally electronically unsaturated $H_2Os_3(CO)_{10}$ with the activated nitrile CF_3CN [4–6], and no hydrogen transfer to benzonitrile in the presence of $H_2Os_3(CO)_{10}$ had been reported [7].

Results and discussion

As reported in Schemes 1 and 2, both $Os_3(CO)_{12}$ and $H_2Os_3(CO)_{10}$, in refluxing n-octane, give complexes which contain PhCN (L) as ligand, hydrogenated to various extents.

In the presence of acetic acid the major products are three complexes of molecular formula $Os_3(CO)_{10}(CH_3COOH)$ (I), $Os_3(CO)_{10}(L + 2H)$ (II) and $Os_3(CO)_{10}(L + 4H)$ (III), in addition to hydrides such as $H_2Os_4(CO)_{13}$. Infrared and proton nuclear magnetic resonance data for these compounds are shown in Table 1.

The ^1H NMR spectrum of compound I exhibits a one proton hydride singlet at τ 20.48 and a three proton singlet at τ 8.06 (CH_3) and its mass spectrum shows the molecular ion at *m/z* 916 and stepwise loss of ten carbonyl groups.

The ^1H NMR spectrum of complex II shows a hydride signal at τ 24.68 as a doublet (*J* 0.9 Hz); decoupling shows that the signal is long-range coupled with a one proton doublet at τ 1.62 (not exchangeable with D_2O) which can be assigned to the =CH proton. A multiplet at τ 2.38–2.66 can be assigned to the five benzene protons. The mass spectrum shows the molecular ion at *m/z* 961 and fragment ions due to the progressive loss of ten carbonyl groups.

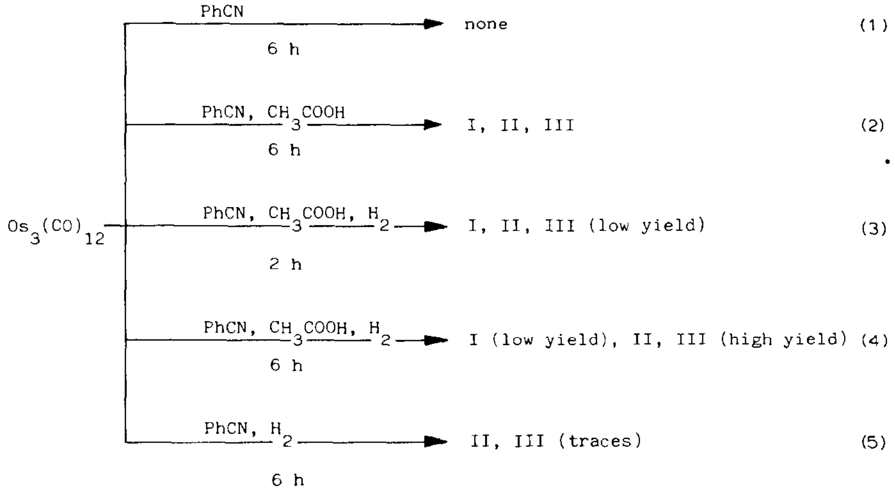
Compound III gives a proton NMR spectrum showing a hydride signal at τ 24.29 as a doublet (*J* 2.7 Hz), a two proton doublet at τ 5.99 (*J* 7.8 Hz) assigned to the benzylic CH_2, a one proton broad signal at τ 5.42 due to NH (exchangeable with

TABLE 1

IR AND ^1H NMR DATA

Complex	ν(CO) [a](cm^{-1})	Chemical shift [b](τ)
I	2113w, 2076vs, 2064s, 2029vs, 2014s, 1989w, 1986w	8.06s(3H), 20.48s(1H)
II	2105w, 2067vs, 2056s, 2021vs, 2012s, 1997s, 1982w	1.62d(1H), 2.38–2.66m(5H) 24.68d(1H)
III	2104w, 2067vs, 2051s, 2021vs, 2003s, 1991s, 1981w, 1978(sh)w	2.6–2.8m(5H), 5.42br(1H) 5.99d(2H), 24.29d(1H)

[a] Solvent n-hexane. [b] Solvent $CDCl_3$.

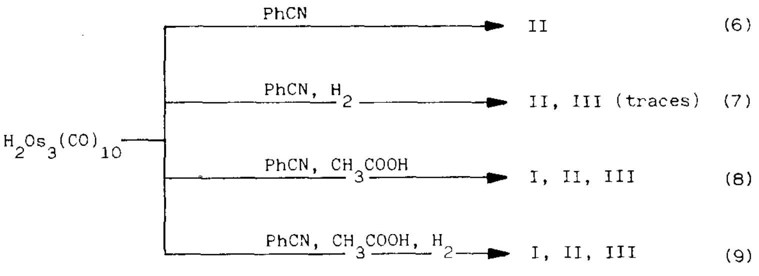


SCHEME 1. Conditions for the synthesis of I, II and III from $Os_3(CO)_{12}$.

D_2O), and a multiplet at τ 2.6–2.8 due to the five benzene protons. Upon decoupling of the NH proton both doublets collapse to singlets, showing the presence of a CH_2–NH–Os–H linkage. The mass spectrum shows the molecular ion at *m/z* 963 and stepwise loss of ten carbonyl groups.

On the basis of the spectroscopic data, II and III must have analogous structures to (μ-H)$Ru_3(CO)_{10}$(μ-N=CHPh) and (μ-H)$Ru_3(CO)_{10}$(μ-NH-CH_2-Ph), previously described [1,3]. Compound I, the analogue of which was not found as a stable product from the reactions of $Ru_3(CO)_{12}$, PhCN and acetic acid, has been characterized by X-ray diffraction analysis.

The structure of I is shown in Fig. 1 together with the atomic numbering scheme. Selected bond distances and angles in it are listed in Table 2. The complex consists of a (nearly equilateral) isosceles triangle of osmium atoms (the Os–Os bonds are 2.857(2) and 2.875(3) Å) with the slightly longer side symmetrically bridged diequatorially by a hydride ligand (the Os–H distances are 1.80 Å) and diaxially by an acetate anion. The complex has crystallographic imposed C_s-*m* symmetry, with the mirror perpendicular to the plane of the metal atoms and passing through the Os(2) atom and the midpoint of the Os(1)–Os(1′) edge. The hydride ligand is slightly displaced (0.24 Å) from the osmium plane, in a direction away from the acetate



SCHEME 2. Conditions for the synthesis of I, II and III from $H_2Os_3(CO)_{10}$.

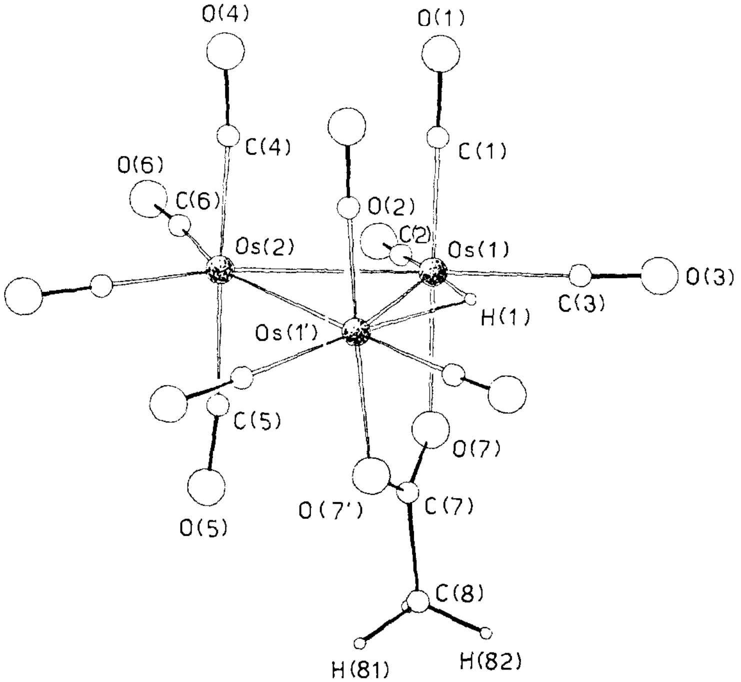


Fig. 1. View of the complex $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}O_2CCH)_3$ with the atomic numbering scheme.

group. The dihedral angle between the Os(1)–H(1)–Os(1′) and the metal triangle planes is 167°. Four terminal carbonyl groups are bonded to the Os atom non involved in the bridges (two of them are approximately equatorial with respect to the cluster plane, and two occupy approximately axial positions), while three terminal carbonyl groups are bonded to the other two Os atoms (two are equatorial and one is axial). The acetate ligand interacts with the Os atoms through the two oxygen atoms of the carboxylate group (the Os–O bonds are 2.13(1) Å) and shows an expected geometry, with a O–C–O angle of 127.6(7)° and C–O bonds of 1.25(2) Å, in the normal range for delocalized carboxylate anions. The C(7), C(8), O(7), O(7′) atoms of the acetate anion are coplanar, with the Os(1) and Os(1′) atoms deviating from that plane by 0.17 Å. The mean plane through Os(1), Os(1′), C(7), O(7) and O(7′), bent by 7.3° from the acetate plane, is almost perpendicular to the plane of the metal atoms, the dihedral angle between them being 97.0°.

The structure of I is closely comparable, as expected, with that of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}O_2CH)$ [8], in which a formate ligand is present. The located hydride ligand in I confirms the assignment of a nearly equatorial position, bridging the slightly longer side of the cluster in the formate derivative (average Os–Os bond in two independent complexes 2.909(10) Å, compared with 2.875(5) Å for the non bridged Os–Os bonds). The bonding and the orientation of the formate ligand with respect to the cluster are very similar (the Os–O bonds in the range 2.152(9)–2.175(9) Å are a little longer than in I, while the average O–C–O angle and C–O bonds, 127.8(14)° and 1.251(14) Å, are equal).

A slight increase of the Os–Os bond length in the side bridged by a hydride ligand and by a O_2C–R moiety has been noted also in the triosmium fragment of the

TABLE 2

SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Os(1)-Os(1′)	2.875(3)	C(7)-O(7)	1.25(2)
Os(1)-Os(2)	2.857(2)	C(7)-C(8)	1.52(4)
Os(1)-C(1)	1.83(2)	O(1)-C(1)	1.16(2)
Os(1)-C(2)	1.88(2)	O(2)-C(2)	1.18(2)
Os(1)-C(3)	1.97(2)	O(3)-C(3)	1.06(2)
Os(1)-O(7)	2.13(1)	O(4)-C(4)	1.18(4)
Os(2)-C(4)	1.90(3)	O(5)-C(5)	1.18(4)
Os(2)-C)5)	1.90(4)	O(6)-C(6)	1.18(3)
Os(2)-C(6)	1.85(2)		
Os(1)-Os(2)-Os(1′)	60.4(1)	C(6)-Os(2)-Os(1)	97.5(7)
Os(2)-Os(1)-Os(1′)	59.8(1)	O(7)-Os(1)-Os(1′)	81.4(3)
C(1)-Os(1)-C(2)	93.0(7)	O(7)-Os(1)-C(2)	89.0(6)
C(1)-Os(1)-C(3)	90.9(8)	O(7)-Os(1)-C(3)	88.0(6)
C(2)-Os(1)-C(3)	94.3(7)	O(7)-Os(1)-C(1)	177.8(6)
C(1)-Os(1)-Os(2)	89.7(5)	O(7)-Os(1)-Os(2)	91.4(4)
C(1)-Os(1)-Os(1′)	97.5(4)	Os(1)-O(7)-C(7)	124.5(7)
C(2)-Os(1)-Os(2)	87.2(5)	O(7)-C(7)-O(7′)	127.6(7)
C(2)-Os(1)-Os(1′)	145.1(5)	O(7)-C(7)-C(8)	116.1(5)
C(3)-Os(1)-Os(2)	178.4(5)	Os(1)-C(1)-Os(1)	176 (1)
C(3)-Os(1)-Os(1′)	118.6(5)	Os(1)-C(2)-O(2)	178 (1)
C(4)-Os(2)-C(5)	177.2(13)	Os(1)-C(3)-O(3)	177 (2)
C(4)-Os(2)-C(6)	89.8(6)	Os(2)-C(4)-O(4)	175 (2)
C(5)-Os(2)-C(6)	91.9(6)	Os(2)-C(5)-O(5)	173 (3)
C(4)-Os(2)-Os(1)	90.6(1)	Os(2)-C(6)-O(6)	177 (2)
C(5)-Os(2)-Os(1)	87.0(1)		

[a] The primed atoms are related to the unprimed ones by the transformation: x, $\frac{1}{2}-y$, z.

$[(\mu\text{-H})Os_3(CO)_{10}(O_2C)Os_6(CO)_{17}]^-$ anion [9], the only other example reported to our knowledge of a O_2C-R group bonded to a hydridotriosmium cluster (Os–Os distance in the bridged side 2.895(7) Å, Os–Os distances in the other two sides 2.864(7) and 2.875(7) Å).

It is relevant to take note of two dinuclear osmium complexes containing a double acetate bridge: in $Os_2(CO)_6(\mu\text{-}O_2CCH_3)_2$ [10] there is a short Os–Os distance (2.731(2) Å, average value for two independent molecules) with average Os–O bonds of 2.076(6) Å; in $Os_2(\mu\text{-O})(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ [11], the Os–Os distance is very long, even though it is bridged by two acetate groups and by an oxide ligand (Os–Os distance: 3.440(2) Å, with Os–O bonds of 2.083(9) and 2.118(9) Å).

The structure determined for I confirms the suggested structure for $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}O_2CCH_3)$, previously obtained through reactions of acetic acid and $Os_3(CO)_{10}(C_6H_8)$ [12].

From Scheme 1 it can be seen that reaction of $Os_3(CO)_{12}$ and PhCN alone (eq. 1) does not lead to the formation of II and III, but gives very small amounts of other unidentified compounds. If the reaction is carried out in the presence of acetic acid (eq. 2) the main product is I, but II and III are also formed. The yields of II and III are increased when the reaction between $Os_3(CO)_{12}$, PhCN and acetic acid is carried out in a stream of hydrogen (eq. 3 and 4). Under these experimental conditions the amount of I decreases with time and that of III increases. This suggests that III is formed through I. However I does not react with PhCN, in the presence of acetic acid and/or H_2, to give III, but instead decomposes.

It must be pointed out that in all the experiments in which hydrogen is bubbled through the solution (eq. 3–5), $Os_3(CO)_{12}$ is partially converted into $H_2Os_3(CO)_{10}$, well known to be a very reactive compound [7,12]. This hydride is one of the products of the reaction of $Os_3(CO)_{12}$ and PhCN in the presence of H_2, and it also leads to II and trace amounts of III (eq. 7, Scheme 2). It was therefore of interest to investigate the reactions of $H_2Os_3(CO)_{10}$ with PhCN under various experimental conditions (Scheme 2).

Only II is formed from $H_2Os_3(CO)_{12}$ and PhCN alone (eq. 6), whilst I, II and III are obtained when acetic acid is also present (eq. 8). Besides II, traces of III are also formed when $H_2Os_3(CO)_{10}$ is treated with benzonitrile in the presence of H_2 (eq. 7), this behaviour being analogous to that of $Os_3(CO)_{12}$ with PhCN and H_2. In both cases extensive breakdown of the clusters takes place.

The isolation of I has allowed us to prove that it is not an intermediate leading to II and III. However, its stability is one of the drawbacks of the use of acetic acid with triosmium clusters, because the formation of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}O_2CCH_3)$ (I) represents a side reaction which lowers the yields of II and III. A corresponding stable compound was not isolated from the systems containing $Ru_3(CO)_{12}$, PhCN and acetic acid [1,3]. So far no other acid has been found to promote the hydrogenation of the CN triple bond of PhCN in the presence of $Os_3(CO)_{12}$ or $Ru_3(CO)_{12}$.

Even though acetic acid plays an important rôle in the hydrogenation of the CN triple bond of PhCN in the presence of $Os_3(CO)_{12}$, the results do not show that it is essential as has been shown to be the case for $Ru_3(CO)_{12}$ [1,3]. The reactivity of $H_2Os_3(CO)_{10}$, which is always one of the reaction products in the presence of H_2, is much higher than that of $H_4Ru_4(CO)_{12}$, and it is likely that II and traces of III resulting from reaction 5 (Scheme 1) are produced as a consequence of the conversion of $Os_3(CO)_{12}$ to $H_2Os_3(CO)_{10}$.

It must be emphasized that the use of the acetic acid in activation of the CN triple bond of organic nitriles, in the presence of $Ru_3(CO)_{12}$ [1,3] and $Os_3(CO)_{12}$, provides an interesting alternative to previously available syntheses of substituted clusters, which can be time consuming and give low yields.

Experimental

$Os_3(CO)_{12}$ was purchased from Strem, $H_2Os_3(CO)_{10}$ was prepared from $Os_3(CO)_{12}$ and H_2 in refluxing n-octane [13–15]. Kieselgel PF (254–366), glacial acetic acid and benzonitrile (analytical grade) were from Merck. Hydrogen and nitrogen, from SIAD, were dried before use. Solvents (analytical grade from C. Erba) were redistilled, and dried over molecular sieves.

Mass spectra were recorded on a double focusing Kratos MS 80 operating with direct inlet system. IR spectra were recorded on a Perkin–Elmer 580B spectrophotometer. ^1H NMR spectra were recorded with $CDCl_3$ solutions on a Varian XL-200 spectrometer at 200.057 MHz. A 5000 Hz sweep width was used with a digital resolution of 0.156 Hz/point. The internal reference was TMS.

(a) Reaction of PhCN and glacial acetic acid with $Os_3(CO)_{12}$. In a typical experiment a mixture of 0.132 mmol of $Os_3(CO)_{12}$, 0.96 mmol of PhCN and 1.74 mmol of glacial acetic acid in 100 ml of n-octane under a stream of N_2 was stirred

for 15 min. The solution was heated under reflux for 6 h (except when otherwise specified) and then cooled under N_2. Separation of the products was by TLC on Kieselgel plates using a 19/1 light petroleum/diethyl ether mixture as eluent. Under these conditions II and III were not resolved, but they gave separate bands upon rechromatography on Kieselgel with light petroleum as eluent. Compounds I, II and III were crystallised from n-hexane at $-10°C$.

(b) Reaction of PhCN and glacial acetic acid with $Os_3(CO)_{12}$ *under a stream of hydrogen.* Experimental conditions were as described in (a) except that H_2 was bubbled through the refluxing solution.

(c) Reaction of PhCN with $Os_3(CO)_{12}$. The reaction was carried out as described in (a) except that glacial acetic acid was omitted.

(d) Reaction of PhCN with $Os_3(CO)_{12}$ *under a stream of* H_2. Experimental conditions were as in (c) except that H_2 was bubbled through the refluxing solution.

(e) Reaction of PhCN, glacial acetic acid and $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}O_2CCH_3)$. A mixture of 0.130 mmol of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}O_2CCH_3)$, 1.74 mmol of glacial acetic acid and 0.96 mmol of PhCN in 100 ml of n-octane was stirred under a stream of N_2 for 15 min. The solution was then refluxed for 6 h under a stream of H_2. TLC showed that neither II nor III was formed, and that extensive decomposition of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}O_2CCH_3)$ had taken place.

(f) Reactions of PhCN with $H_2Os_3(CO)_{10}$. Reactions of PhCN with $H_2Os_3(CO)_{10}$ were carried out as described for the corresponding reactions with $Os_3(CO)_{12}$ in (a), (b), (c) and (d), except that solutions were refluxed for 2 h.

X-Ray data collection, structure determination and refinement of I

A yellow prismatic crystal of approximate dimensions 0.23 × 0.33 × 0.40 mm was selected and mounted on a Siemens AED single-crystal diffractometer. Unit cell parameters were obtained by least-squares refinement of the θ values of 25 carefully centered reflections chosen from diverse regions of the reciprocal space. Intensity data were collected at 295 K with θ in the range 3–28° ($\theta/2\theta$ scan) using the niobium-filtered Mo-K_α radiation. Of 2290 independent measured reflections, 1484, having $I \geqslant 2\theta(I)$, were used for the analysis. Corrections were applied for Lorentz, polarization, and absorption effects (for the absorption effect the maximum and minimum transmission factor values were 1.2612 and 0.7680) [16].

Crystal data: $C_{12}H_4O_{12}Os_3$, $M = 910.76$, monoclinic, a 7.858(6), b 12.542(8), c 9.867(6) Å, β 109.92(2)°, V 914(1) Å^3, $Z = 2$, D_c 3.308 g cm^{-3}, $F(000) = 800$, space group $P2_1/m$, μ(Mo-K_α) 208.86 cm^{-1}.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares using the SHELX system of computer programs [17] with first isotropic and then anisotropic thermal parameters for all the non hydrogen atoms. The hydrogen atoms were clearly located in a ΔF map, not refined, but introduced in the final structure factor calculations. The atomic scattering factors used, corrected for the anomalous dispersion of the Os atoms, were taken from literature [18]. The function minimized in the least-squares calculations was $\Sigma w[\Delta F]^2$; unit weights were chosen in the first stages of the refinement, then weights were applied according to $w = K[\sigma^2(F_0) + gF_0{}^2]$ with $K = 0.867$ and $g = 0.005$. Final R and R_w values 0.040 and 0.053, respectively. Final atomic coordinates for the non hydrogen and hydrogen atoms are given in Table 3 and 4 respectively. Thermal parameters and a list of observed and calculated structure

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) WITH e.s.d.'s IN PARENTHESES FOR THE NON HYDROGEN ATOMS

Atom	x/a	y/b	z/c
Os(1)	670(1)	1354(1)	2243(1)
Os(2)	3998(1)	2500	3377(1)
O(1)	602(19)	1099(9)	5236(12)
O(2)	2992(19)	−632(10)	2420(16)
O(3)	−2942(18)	218(14)	1038(18)
O(4)	3812(27)	2500	6444(18)
O(5)	4334(26)	2500	362(21)
O(6)	6564(21)	621(14)	4112(18)
O(7)	602(18)	1608(9)	89(11)
C(1)	648(22)	1164(11)	4079(18)
C(2)	2073(20)	124(13)	2327(17)
C(3)	−1665(27)	601(14)	1436(18)
C(4)	3791(27)	2500	5238(30)
C(5)	4078(40)	2500	1475(38)
C(6)	5524(23)	1334(18)	3889(21)
C(7)	485(31)	2500	−494(23)
C(8)	329(49)	2500	−2071(30)

TABLE 4

FRACTIONAL COORDINATES ($\times 10^4$) FOR THE HYDROGEN ATOMS

Atom	x/a	y/b	z/c
H(1)	−789	2500	1993
H(81)	−948	2500	−2778
H(82)	1005	1779	−2266

factors may be obtained from the authors on request.

All calculations were carried out on the CYBER 76 computer of the Centro di Calcolo Elettronico dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Acknowledgement

This work was partially financed by the Italian CNR.

References

1 P. Michelin Lausarot, M. Turini, G.A. Vaglio, M. Valle, A. Tiripicchio, M. Tiripicchio Camellini and P. Gariboldi, J. Organomet. Chem., 273 (1984) 239.
2 W. Bernhardt and H. Vahrenkamp, Angew. Chem. Int. Ed. Engl., 23 (1984) 381.
3 P. Michelin Lausarot, G.A. Vaglio, M. Valle, A. Tiripicchio and M. Tiripicchio Camellini, J. Chem. Soc. Chem. Comm., (1983) 1391.
4 R.D. Adams, D.A. Katahira and L.W. Yang, J. Organomet. Chem., 219 (1981) 85.
5 Z. Dawoodi, M.J. Mays and P.R. Raithby, J. Organomet. Chem., 219 (1981) 103.
6 Z. Dawoodi, M.J. Mays, K. Henrick, J. Chem. Soc. Dalton, (1984) 433.

7 A.J. Deeming and S. Hasso, J. Organomet. Chem., 114 (1976) 313.
8 J.R. Shapley, G.M.S. George, M.R. Churchill and F.J. Hollander, Inorg. Chem., 21 (1982) 3295.
9 J.J. Grey and G.M. Sheldrick, Acta Cryst., B, 34 (1978) 1718.
10 G. Bullitt and F.A. Cotton, Inorg. Chim. Acta, 5 (1971) 406.
11 J.E. Armstrong, W.R. Robinson and R.A. Walton, J. Chem. Soc. Chem. Comm., (1981) 1120.
12 E.G. Bryan, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton, (1977) 1328.
13 J.R. Shapley, J.B. Keister, M.R. Churchill and B.G. DeBoer, J. Am. Chem. Soc., 97 (1975) 4145.
14 H.D. Kaesz, S.A.R. Knox, J.W. Koepke and R.B. Saillant, J. Chem. Soc. Chem. Comm., (1971) 477.
15 S.A.R. Knox, J.W. Koepke, M.A. Andrews and H.D. Kaesz, J. Am. Chem. Soc., 97 (1975) 3942.
16 Absorption corrections following N. Walker and D. Stuart, Acta Cryst., A39 (1983) 158, and using the program ASSORB written by F. Ugozzoli, University of Parma.
17 G.M. Sheldrick, System of computing programs, University of Cambridge, 1976.
18 International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.