Journal of Organometallic Chemistry, 329 (1987) 401–404
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Crystal structure of $Os_3(CO)_9(\mu_2\text{-}H)_2(\mu_3\text{-}C{=}\overline{CCH_2CH_2C}H_2)$

A.S. Batsanov, V.G. Andrianov, Yu.T. Struchkov[*], A.A. Koridze, O.A. Kizas and N.E. Kolobova

Nesmeyanov Institute of Organoelement Compounds, Vavilov St. 28, 117813, Moscow (U.S.S.R.)

(Received January 20th, 1987)

Abstract

An X-ray diffraction study of $Os_3(CO)_9(\mu_2\text{-}H)_2(\mu_3\text{-}C{=}\overline{CCH_2CH_2C}H_2)$ at $-120\,^\circ C$ ($R = 0.039$ for 2227 reflections) has revealed a μ_3-η^2-coordination of the methylenecyclobutane ligand, which bridges one Os–Os bond via a methylidene carbon and is linked to the third Os atom by the C=C bond.

Complex I, $Os_3(CO)_9(\mu_2\text{-}H)_2(\mu_3\text{-}C{=}\overline{CCH_2CH_2C}H_2)$, was obtained by thermal reaction of $Os_3(CO)_{12}$ with methylenecyclobutane [1]. The protonation of I yields the cationic complex $[Os_3H_3(CO)_9(\mu_3\text{-}C{=}\overline{CCH_2CH_2C}H_2)]^+$ (II). In connection with structural investigation of II and other complexes of the $[Os_3H_3(CO)_9(\mu_3\text{-}C{=}CR_2)]^+$ type and their supposed fluxional behaviour in solutions we carried out an X-ray single crystal study of I.

Complex I (see Fig. 1 and Table 1) is a 48-electron (i.e. obeys the EAN rule) triangulo-cluster, structurally similar to $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}C{=}CH_2)$ (III) which has been studied previously [2]. All CO groups are terminal and linear. The methylenecyclobutane ligand is σ-bonded to Os(1) and Os(2) via C(10) and η^2-coordinated to Os(3) by the olefinic C(10)=C(11) bond. The Os(3)C(10)C(11) plane is normal to the mean plane of the olefinic moiety C(14)C(12)C(11)C(10), but the Os(3)–C(10) and Os(3)–C(11) distances of 2.21 and 2.40 Å are very different, this feature is similar to that observed in III (2.17 and 2.35 Å). The C(10)=C(11) bond is tilted away from the Os(1)Os(2)C(10) plane by 19° towards Os(3), while the C(11)C(12)C(14) plane is inclined towards this bond by 28°, on the opposite side. In the 4-membered carbocycle, the C(13) atom is displaced from the plane of the other three atoms by 0.35 Å (on the side opposite to Os(3)).

Hydride ligands in I, as well as in III, were not located in electron density maps. Nevertheless, there is strong evidence that they are μ_2-bridging across the Os(1)–Os(2) and Os(2)–Os(3) bonds. Indeed, hydride bridges are known to exert metal–metal bond elongation, and in I the Os(1)–Os(2) and Os(2)–Os(3) bond lengths of 2.894 and 2.911 are ca. 0.1 Å longer than the Os(1)–Os(3) bond length of 2.783 Å (in III, 2.88, 2.92 and 2.80 Å). Furthermore, Os–Os–CO *cis*-angles,

(*Continued on p. 404*)

0022-328X/87/$03.50

Table 1

Bond distances (Å) and angles (°) in the structure of 1

Os(1)–Os(2)	2.8936(7)	Os(2)–C(10)	2.09(1)	O(5)–C(5)	1.14(2)
Os(1)–Os(3)	2.7831(7)	Os(3)–C(7)	1.89(2)	O(6)–C(6)	1.13(2)
Os(1)–C(1)	1.97(1)	Os(3)–C(8)	1.89(1)	O(7)–C(7)	1.15(2)
Os(1)–C(2)	1.92(2)	Os(3)–C(9)	1.90(2)	O(8)–C(8)	1.15(2)
Os(1)–C(3)	1.91(2)	Os(3)–C(10)	2.21(1)	O(9)–C(9)	1.16(2)
Os(1)–C(10)	2.05(1)	Os(3)–C(11)	2.40(1)	C(10)–C(11)	1.38(2)
Os(2)–Os(3)	2.9109(8)	O(1)–C(1)	1.11(2)	C(11)–C(12)	1.51(2)
Os(2)–C(4)	1.91(2)	O(2)–C(2)	1.15(2)	C(11)–C(14)	1.52(2)
Os(2)–C(5)	1.90(2)	O(3)–C(3)	1.15(2)	C(12)–C(13)	1.57(3)
Os(2)–C(6)	1.97(2)	O(4)–C(4)	1.14(2)	C(13)–C(14)	1.56(3)
Os(2)–Os(1)–Os(3)	61.66(2)	Os(3)–Os(2)–C(5)	143.1(4)	C(8)–Os(3)–C(9)	92.9(7)
Os(2)–Os(1)–C(1)	111.5(4)	Os(3)–Os(2)–C(6)	119.5(4)	C(8)–Os(3)–Q	95.8(7)
Os(2)–Os(1)–C(2)	145.4(5)	Os(3)–Os(2)–C(10)	49.2(4)	C(9)–Os(3)–Q	104.9(7)
Os(2)–Os(1)–C(3)	103.0(5)	C(4)–Os(2)–C(5)	93.4(7)	Os(1)–C(1)–O(1)	178(1)
Os(2)–Os(1)–C(10)	46.3(4)	C(4)–Os(2)–C(6)	95.0(7)	Os(1)–C(2)–O(2)	178(1)
Os(3)–Os(1)–C(1)	106.3(4)	C(4)–Os(2)–C(10)	101.0(6)	Os(1)–C(3)–O(3)	171(2)
Os(3)–Os(1)–C(2)	90.5(5)	C(5)–Os(2)–C(6)	94.5(6)	Os(2)–C(4)–O(4)	178(1)
Os(3)–Os(1)–C(3)	155.4(5)	C(5)–Os(2)–C(10)	94.2(6)	Os(2)–C(5)–O(5)	175(1)
Os(3)–Os(1)–C(10)	51.7(4)	C(6)–Os(2)–C(10)	161.3(6)	Os(2)–C(6)–O(6)	178(1)
C(1)–Os(1)–C(2)	95.1(6)	Os(1)–Os(3)–Os(2)	61.04(2)	Os(3)–C(7)–O(7)	176(1)
C(1)–Os(1)–C(3)	97.1(7)	Os(1)–Os(3)–C(7)	89.8(4)	Os(3)–C(8)–O(8)	177(1)
C(1)–Os(1)–C(10)	152.4(6)	Os(1)–Os(3)–C(8)	96.2(5)	Os(3)–C(9)–O(9)	178(1)
C(2)–Os(1)–C(3)	94.8(7)	Os(1)–Os(3)–C(9)	164.1(5)	Os(1)–C(10)–Os(2)	88.6(5)
C(2)–Os(1)–C(10)	101.0(6)	Os(1)–Os(3)–Q [a]	61.3(4)	Os(1)–C(10)–C(11)	135(1)
C(3)–Os(1)–C(10)	103.7(7)	Os(2)–Os(3)–C(7)	104.8(4)	Os(2)–C(10)–C(11)	130(1)
Os(1)–Os(2)–Os(3)	57.30(2)	Os(2)–Os(3)–C(8)	151.3(5)	C(10)–C(11)–C(12)	126(1)
Os(1)–Os(2)–C(4)	145.4(5)	Os(2)–Os(3)–C(9)	105.9(5)	C(10)–C(11)–C(14)	129(1)
Os(1)–Os(2)–C(5)	96.0(4)	Os(2)–Os(3)–Q	58.9(4)	C(12)–C(11)–C(14)	92(1)
Os(1)–Os(2)–C(6)	117.3(4)	C(7)–Os(3)–C(8)	91.4(6)	C(11)–C(12)–C(13)	88(1)
Os(1)–Os(2)–C(10)	45.2(4)	C(7)–Os(3)–C(9)	103.1(7)	C(12)–C(13)–C(14)	89(1)
Os(3)–Os(2)–C(4)	97.1(5)	C(7)–Os(3)–Q	150.7(7)	C(11)–C(14)–C(13)	88(1)

[a] Q is the midpoint of the C(10)–C(11) bond.

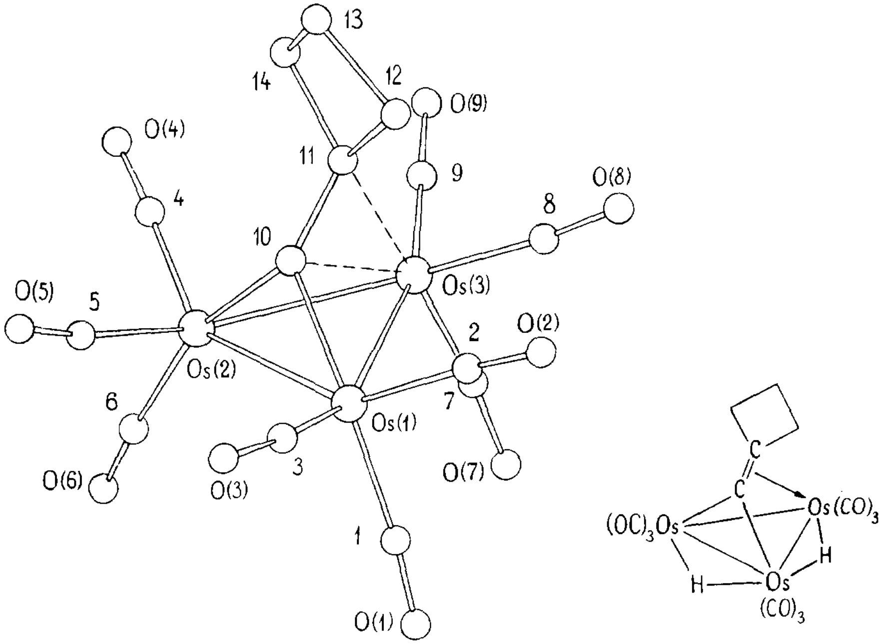

Fig. 1. Molecular structure of I (hydrogen atoms omitted).

Table 2

Atomic coordinates ($\times 10^4$, for Os $\times 10^5$) and B_{eq} for I

Atom	*x*	*y*	*z*	B_{eq} (Å)
Os(1)	14566(6)	24147(4)	8323(3)	1.31(2)
Os(2)	8290(7)	24796(4)	25115(3)	1.33(2)
Os(3)	−15199(6)	18115(4)	13425(3)	1.30(1)
O(1)	3204(14)	379(9)	392(7)	3.0(3)
O(2)	114(13)	2822(10)	−834(6)	2.7(3)
O(3)	4153(14)	3958(11)	597(8)	3.8(3)
O(4)	−1437(14)	3193(12)	3791(7)	3.7(4)
O(5)	3112(14)	4256(10)	2893(7)	3.4(3)
O(6)	2486(14)	798(10)	3553(7)	3.2(3)
O(7)	−665(14)	−441(10)	953(7)	3.4(3)
O(8)	−3225(14)	2067(11)	−245(7)	3.3(3)
O(9)	−4618(14)	1622(13)	2238(8)	4.6(4)
C(1)	2564(17)	1114(12)	536(8)	1.6(3)
C(2)	621(18)	2684(11)	−208(10)	2.1(4)
C(3)	3213(19)	3339(16)	730(11)	3.0(5)
C(4)	−611(18)	2920(14)	3302(9)	2.3(4)
C(5)	2303(17)	3559(13)	2756(8)	1.8(4)
C(6)	1887(17)	1423(12)	3186(9)	1.9(4)
C(7)	−1013(17)	399(12)	1128(8)	1.7(4)
C(8)	−2552(17)	1954(13)	348(9)	2.1(4)
C(9)	−3453(18)	1707(14)	1892(10)	2.6(4)
C(10)	−94(17)	3246(12)	1513(8)	1.8(4)
C(11)	−1564(19)	3692(12)	1388(9)	2.1(4)
C(12)	−2036(19)	4367(13)	686(10)	2.4(4)
C(13)	−2723(29)	5179(14)	1291(10)	2.6(5)
C(14)	−2572(21)	4330(15)	1952(11)	2.9(4)

involving the Os(1)–Os(2) and Os(2)–Os(3) bonds, are wider than those involving the Os(1)–Os(3) bond (average values 107 and 96°) owing to steric repulsion by μ_2-H ligands. The signals of hydride protons in the ^{1}H NMR spectrum of I (two doublets with δ −18.71 and −21.16 ppm) are remarkably non-equivalent [1], which is consistent with a non-symmetric arrangement of hydrides relative to the methylenecyclobutane ligand.

Experimental

X-Ray diffraction intensities were measured with a Syntex $P2_1$ four circle autodiffractometer at −120°C, using graphite monochromated Mo-K_α radiation. All calculations were carried out with an Eclipse S/200 computer using INEXTL programs [3]. Crystal data of I: monoclinic, space group $P2_1/n$, a 8.467(2), b 12.765(3), c 16.889(4) Å, β 90.78(2)°, V 1825.1(7) Å^3, $Z = 4$, $C_{14}H_8O_9Os_3$, d_{calc} 3.24 g cm^{-3}, μ(Mo-K_α) 221.2 cm^{-1}. Least squares anisotropic refinement of all non-hydrogen atoms converged at $R = 0.039$, $R = 0.048$ for 2227 unique absorption corrected (according to the real shape of the crystal [4]) reflections with $I \geqslant 2\sigma$ and $2\theta \leqslant 48°$. The weighting scheme $W^{-1} = \sigma_F^2 + (0.025F_{meas})^2$ was used. Atomic coordinates and $B_{eq} = 1/3\sum_{ij} B_{ij} a_i a_j (a_i a_j)$ are listed in Table 2.

References

1 A.A. Koridze, O.A. Kizas, N.E. Kolobova, P.V. Petrovskii and E.I. Fedin, J. Organomet. Chem., 265 (1984) C33.

2 A.J. Deeming and M. Underhill, J. Chem. Soc., Dalton Trans. (1974) 1415.

3 R.G. Gerr, A.I. Yanovskii and Yu.T. Struchkov, Kristallografiya, 28 (1983) 1029.

4 R.G. Gerr, M.Yu. Antipin, N.G. Furmanova and Yu.T. Struchkov, Kristallografiya, 24 (1979) 951.