Journal of Organometallic Chemistry, 368 (1989) 269–275
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09855

Synthesis, characterization, and X-ray crystal structure of $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-Te})$

H.-Thomas Schacht, Anne K. Powell and Heinrich Vahrenkamp *
Institut für Anorganische und Analytische Chemie, Albert-Ludwigs-Universität, D-7800 Freiburg, Alberstr. 21 (F.R.G.)

Makoto Koike, Heinz-Josef Kneuper, and John R. Shapley *,
School of Chemical Sciences, University of Illinois, Urbana, Illinois, 61801 (U.S.A.)

(Received December 27th, 1988)

Abstract

The compound $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-Te})$ has been prepared from $Os_3(CO)_{10}(NCCH_3)_2$ and H_2Te, and its structure has been determined by X-ray crystallography.

Introduction

There is considerable current interest in metal carbonyl clusters incorporating main group elements [1]. Osmium and ruthenium carbonyl clusters with sulfide ligands have attracted particular attention [2], but relatively little work has been carried out on complexes of the heavier congeners. Thus the complexes $(\mu\text{-H})_2M_3(CO)_9(\mu_3\text{-S})$ (M = Os [3]; M = Ru [4]) have been extensively examined in respect of structure, ligand mobility, and some reactions. On the other hand the complexes $(\mu\text{-H})_2M_3(CO)_9(\mu_3\text{-E})$ (M = Os, E = Se [5]; M = Ru, E = Se or Te [6]) have been characterized only spectroscopically, and $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-Te})$ has not been mentioned previously. In this paper we describe the synthesis, characterization, and X-ray crystal structure of $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-Te})$.

Experimental

General

All manipulations were performed under N_2 by standard Schlenk techniques. THF was distilled from a solution of sodium benzophenone ketyl prior to use. Al_2Te_3 was obtained from Cerac Inc. and used without further purification. $Os_3(CO)_{10}(NCCH_3)_2$ was prepared by a published method [7]. The H_2Te was generated as described previously [8].

0022-328X/89/$03.50

^1H NMR spectra were recorded on a General Electric QE-300 or GE-500 spectrometer; chemical shifts were referenced to the solvent resonance. Infrared spectra were recorded on a Perkin–Elmer 1750 FT-IR spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois. Field desorption mass spectra were obtained on a Varian-MAT 731 mass spectrometer in the Mass Spectrometry Laboratory of the School of Chemical Sciences. The crystallographic data set was obtained with a Nonius CAD-4 diffractometer in Freiburg.

Synthesis of $(\mu\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}Te)$

Solid Al_2Te_3 (600 mg) was added in portions during 3 h to 6 *M* hydrochloric acid (20 ml) at room temperature. The H_2Te generated was carried in a N_2 stream through $CaCl_2$ and P_2O_5 drying traps and into a hot (60 °C) solution of $Os_3(CO)_{10}(NCCH_3)_2$ (52.9 mg, 0.057 mmol) in THF (40 ml). The solvent was then removed under reduced pressure and the residue separated by preparative TLC on silica gel. Elution with dichloromethane/n-hexane (30/70) gave two yellow bands. The one with the larger R_f value was extracted with dichloromethane and recrystallized from hot n-hexane. This gave 44.3 mg (0.047 mmol, 82%) of yellow crystals. M.p. 163 °C. Anal. Found: C, 11.46; H, 0.25. $C_9H_2O_9Os_3Te$ calcd.: C, 11.35; H, 0.21%. ^1H NMR ($CDCl_3$) δ −21.69, $^2J(^1H\text{-}^{125}Te)$ 19.4 Hz. MS (field desorption; ^{192}Os, ^{130}Te) $m/z = 960$ (M^+). IR (cyclohexane): $\nu(CO)$, 2112(w), 2081(s), 2054(vs), 2031(s), 2009(s), 1996(m), 1989(w), 1953(vw) cm^{-1}. The second band was found to consist largely of $HOs_3(CO)_{10}(\mu\text{-}OH)$. This product was obtained in considerably lower yields if the H_2Te was not rigorously dried. In an alternative procedure, H_2Te was generated from 6 *M* aqueous H_2SO_4 and dried with $MgSO_4$ and P_2O_5, with comparable results.

X-Ray crystallographic study

A crystal of the size 0.20 × 0.19 × 0.05 mm was obtained from h-hexane: space group $C2/c$, $Z = 8$, a 2120.3(4), b 1412.5(4), c 1302.7(3) pm, β 124.86(2)°, V 3.201 nm^3, $d_{calc.}$ 3.95 gcm^{-3}, Mo-K_α radiation, μ 245.4 cm^{-1}, 2θ 2–42°. The structure was solved after an empirical absorption correction [9] with Patterson methods using Sheldrick's programs [10] and Keller's program for plotting [11]. Using 1279 reflexions with $I \geq 4\ \sigma(I)$ and applying anisotropic refinement for the Os and Te atoms a final R value of 0.062 (unit weights) was achieved with maxima of +2.8 and −2.6 e/Å^3 in the final difference Fourier map. Table 1 lists the atomic parameters. All structural and experimental details have been deposited [12*].

Results and discussion

Synthesis and characterization of $(\mu\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}Te)$ *(1)*

Complex **1** is formed straightforwardly from the reaction of H_2Te with the "lightly stabilized" complex $Os_3(CO)_{10}(NCCH_3)_2$. The reaction mixture must be heated in order to facilitate elimination of one equivalent of carbon monoxide and must be reasonably dilute in order to avoid trapping of the carbon monoxide by the

---

* Reference number with asterisk indicates a note in the list of references.

Table 1

Atomic parameters for **1**

Atom	x	y	z	U_{eq}
Os1	0.3161(1)	0.3765(2)	0.2546(2)	0.037(1)
Os2	0.3591(1)	0.3404(2)	0.4984(2)	0.037(1)
Os3	0.4304(1)	0.2245(2)	0.4018(2)	0.037(1)
Te	0.2818(2)	0.2140(3)	0.3142(4)	0.041(2)
C10	0.370(3)	0.496(4)	0.307(5)	0.03(1)
O10	0.401(3)	0.564(4)	0.318(5)	0.08(1)
C11	0.223(3)	0.432(4)	0.205(5)	0.04(2)
O11	0.160(3)	0.460(3)	0.161(4)	0.06(1)
C12	0.286(3)	0.352(4)	0.084(5)	0.04(1)
O12	0.272(3)	0.364(3)	−0.014(5)	0.07(1)
C20	0.413(3)	0.448(4)	0.567(5)	0.04(2)
O20	0.446(3)	0.527(4)	0.605(5)	0.08(2)
C21	0.272(3)	0.391(4)	0.472(5)	0.03(1)
O21	0.216(2)	0.426(3)	0.457(4)	0.06(1)
C22	0.387(3)	0.272(4)	0.638(5)	0.03(1)
O22	0.407(2)	0.233(3)	0.731(4)	0.06(1)
C30	0.533(4)	0.264(4)	0.465(6)	0.05(2)
O30	0.595(3)	0.274(3)	0.494(4)	0.07(1)
C31	0.456(3)	0.123(5)	0.513(6)	0.05(2)
O31	0.474(3)	0.060(3)	0.577(4)	0.07(1)
C32	0.416(3)	0.146(4)	0.275(5)	0.03(1)
O32	0.409(2)	0.102(3)	0.187(4)	0.06(1)

starting material. It is necessary to exclude moisture rigorously since the reaction with H_2O to form $HOs_3(CO)_{10}(\mu\text{-}OH)$ appears to be favoured over the interaction with H_2Te to form **1**.

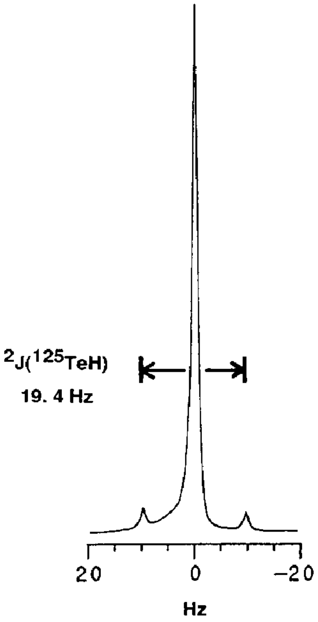

Fig. 1. Hydride region ^1H NMR spectrum of $(\mu\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}Te)$.

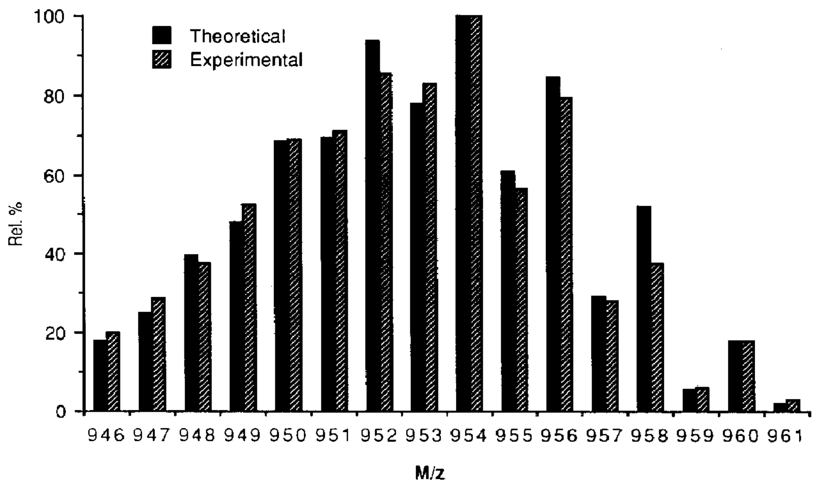

Fig. 2. Comparison of observed and calculated isotope patterns for $[H_2Os_3(CO)_9Te]^+$. For all Os = ^{192}Os and Te = ^{130}Te, $m/z = 960$.

The ^{1}H NMR signal observed for **1** shows evidence for ^{1}H-^{125}Te coupling as shown in Fig. 1. The satellite intensities were found to represent 6.5% of the total signal, which agrees satisfactorily with the natural abundance of ^{125}Te of 7% [13].

The field desorption mass spectrum of **1** shows a clean molecular ion. Figure 2 presents a comparison of the observed and calculated isotope patterns for the ion $[H_2Os_3(CO)_9Te]^+$. The agreement is very good, demonstrating that the cluster is not susceptible to hydrogen loss upon ionization in the mass spectrometer.

Molecular structure

The X-ray analysis showed that $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-Te})$ (**1**) consists of symmetrical molecules with a non-crystallographic mirror plane perpendicular to the Os_3 plane passing through the Te atom and the midpoint of the Os(1)–Os(2) bond. Figure 3 shows the numbering scheme, and Fig. 4 indicates the molecular symmetry.

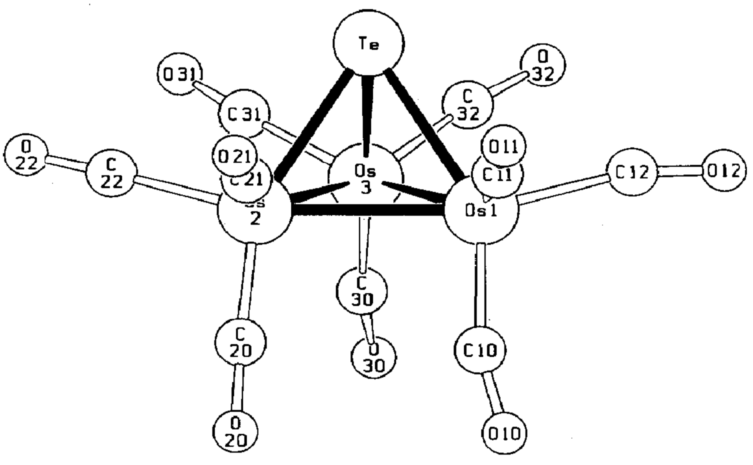

Fig. 3. Molecular configuration and atom labeling for $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-Te})$.

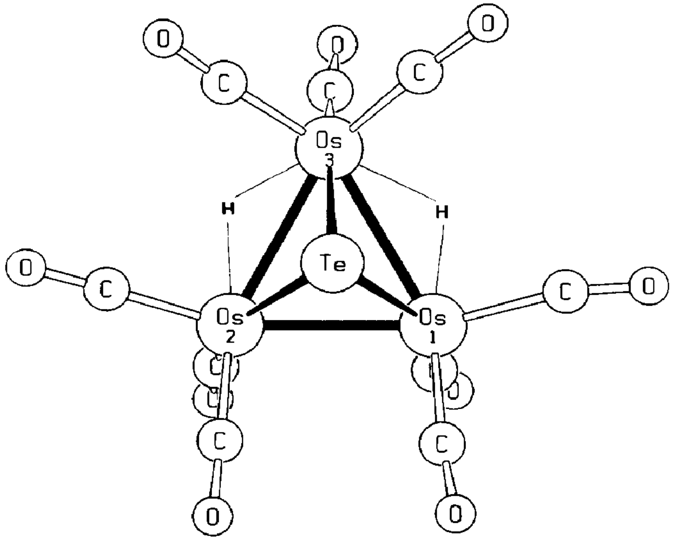

Fig. 4. Top view of the molecule of $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-Te})$ including the assumed hydride positions.

The positions of the two hydride ligands, which could not be obtained from the X-ray data, become obvious from the disposition of the CO ligands and the Os–Os bond lengths. As usual [14] there are distinct openings in the ligand sphere and a lengthening of the metal–metal bonds where the hydride ligands are accomodated. For **1** this is the case at the Os(1)–Os(3) and Os(2)–Os(3) bonds, and on the side of the Os_3 triangle opposite to the μ_3-Te ligand. Figure 4 indicates this by including the H atoms in positions which are equivalent to those obtained by neutron diffraction for $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-S})$ [3c].

The bond lengths in the heavy atom core of **1** are within the normal range, as can be seen from Table 2. The Os–Te bonds, for which there is no precedent are, on the average, 267 pm long. When compared with the Os–S bond lengths in $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-S})$ (**2**) (239 pm av.), this corresponds roughly to the difference in covalent radii of sulfur (104 pm) and tellurium (137 pm). As a consequence of the rather long Os–Te bonds the angles at tellurium are rather small, and the smallest of these, Os(1)–Te–Os(2) 63.5(1)°, when compared to the two others (67.1(1)° and 67.9(1)°), again reflects the relative shortness of the Os(1)–Os(2) bond.

Of the series of compounds $H_2M_3(CO)_9(\mu_3\text{-E})$ (M = Ru, Os; E = S, Se, Te) two others have been structurally characterized, namely $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-S})$ (**2**) [3c] and $(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-S})$ (**3**) [4c]. Table 3 compares the M_3E core bond lengths of the three clusters **1**–**3**. In all three cases the hydride bridged metal–metal bonds are 12–16 pm longer than the non-bridged ones. Differences due to the replacement of Os for Ru are insignificant, cf. the M–M and M–S bonds. Thus the only major

Table 2

Important bond lengths in **1** (pm)

Os1–Os2	280.4(3)	Os1–Te	265.4(5)
Os1–Os3	297.4(3)	Os2–Te	267.1(5)
Os2–Os3	295.4(3)	Os3–Te	267.4(5)

Table 3

Bond length comparisons for $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-Te})$ (**1**), $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-S})$ (**2**), and $(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-S})$ (**3**),

bond	**1**	**2**	**3**
M–M non-bridged	280	276	276
M–M H-bridged (av.)	296	291	288
M–(μ_3-E) (av.)	266	239	236

difference between **1**, **2**, and **3** lies in the elongation of the M_3E pyramid in **1** due to the large tellurium atom. The similarity of **1** and **2** is maintained in their solid state structures, the compounds being isomorphous and isostructural.

Conclusions

The cluster $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-Te})$ completes the series of compounds $H_2M_3(CO)_9(\mu_3\text{-E})$ for M = Ru, Os, and E = S, Se, Te. It has been obtained in very good yield, and fully characterized by ^1H NMR and mass spectrometry and X-ray diffraction. It is now available for comparative chemical investigations, among which studies of the Brönsted acidity, of insertions into the metal–hydrogen bonds, and of catalytic properties seem attractive.

Acknowledgements

This research was supported at the University of Illinois in part by NSF Grant CHE 84-07233 to J.R.S. and in part by NATO Grant No. 917/83 jointly to H.V. and J.R.S. M.K. is indebted to Sankei Scholarship and the University of Illinois for fellowship support. Work in Freiburg was also supported in part by NATO grant No. 917/83 and by the Fonds der Chemischen Industrie.

References

1 K.H. Whitmire, J. Coord. Chem., 17 (1988) 95.
2 R.D. Adams, Polyhedron, 4 (1985) 2003.
3 (a) A.J. Deeming and M. Underhill, J. Organomet. Chem., 42 (1972) C60; (b) A. Forster, B.F.G. Johnson, J. Lewis and T.W. Matheson, ibid., 104 (1976) 225; (c) B.F.G. Johnson, J. Lewis, D.A. Pippard, P.R. Raithby, G.M. Sheldrick, and K.D. Rouse, J. Chem. Soc., Dalton Trans., (1979) 616; (d) B.F.G. Johnson, J. Lewis and D.A. Pippard, J. Organomet. Chem., 213 (1981) 249; (e) B.F.G. Johnson, R.L. Kelly, J. Lewis and J.R. Thornback, ibid., 190 (1980) C91; (f) R.D. Adams, D.F. Foust and P. Mathur, Organometallics, 2 (1980) 990.
4 (a) A.J. Deeming, R. Ettore, B.F.G. Johnson and J. Lewis, J. Chem. Soc. A, (1971) 1797; (b) E. Sappa, O. Gambino and G. Getini, J. Organomet. Chem., 35 (1972) 375; (c) R.D. Adams and D.A. Katahira, Organometallics, 1 (1982) 53; (d) R.D. Adams and D. Männig and B.E. Segmüller, ibid., 2 (1983) 149.
5 R.D. Adams and I.T. Horváth, Inorg. Chem., 23 (1984) 4718.
6 B.F.G. Johnson, J. Lewis, P.G. Lodge, and P.R. Raithby, J. Chem. Soc., Chem. Commun., (1979) 719.
7 B.F.G. Johnson, J. Lewis, and D.A. Pippard, J. Chem. Soc., Dalton Trans., (1981) 407.
8 W.A. Herrmann, C. Hecht, E. Herdtweck, and H.J. Kneuper, Angew. Chem., 99 (1987) 158; Angew. Chem. Int. Ed. Engl., 26 (1987) 132.
9 N. Walker and D. Stuart, Acta Cryst. A, 39 (1983) 19.
10 Programs of the SHELX system: G.M. Sheldrick, Universität Göttingen, 1986.
11 Program SCHAKAL, E. Keller, Universität Freiburg, 1987.

12 Further details of the structure determination can be obtained from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD 53467, the authors and the journal citation.

13 C. Brevard and P. Granger, Handbook of High Resolution Multicuclear NMR, Wiley, New York, 1981.

14 A.P. Humphries and H.D. Kaesz, Prog. Inorg. Chem., 25 (1979) 145.