Journal of Organometallic Chemistry, 377 (1989) C1–C4
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20345PC

Preliminary communication

Synthesis and crystal structure of $HOs_3(CO)_9(C{\equiv}CSiMe_3)$

Brian F.G. Johnson, Jack Lewis, F.R.S., Magda Monari,
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (U.K.)

Dario Braga and Fabrizia Grepioni
Dipartimento di Chimica 'G. Ciamician', Universitá degli Studi di Bologna, Via Selmi 2,
40126 Bologna (Italy)

(Received March 3rd, 1989)

Abstract

The functionalised cluster $Os_3(CO)_{10}(CH_3CN)_2$ reacts at room temperature with trimethylsilylacetylene to afford the orange derivative $Os_3(CO)_{10}(Me_3SiC_2H)$ which undergoes decarbonylation and hydrogen migration to give the cluster $HOs_3(CO)_9(C{\equiv}CSiMe_3)$, which has been fully characterised by an X-ray diffraction study.

The current interest in multisite cluster-bound acetylene derived ligands [1] depends on the fact that these compounds may be regarded as models for chemisorption of alkynes on transition metal surfaces [2] and for the activation and reduction of the carbon–carbon triple bond [3]. Our interest is in the preparation of linked cluster systems of the type reported by Magnus et al. [4]. We report here the synthesis of a suitable precursor cluster $HOs_3(CO)_9(C{\equiv}CSiMe_3)$ from $Os_3(CO)_{10}$-(Me_3SiC_2H) in refluxing hexane, and its characterisation by an X-ray diffraction study.

Treatment of $Os_3(CO)_{10}(CH_3CN)_2$ (**1**) with an excess of trimethylsilylacetylene in CH_2Cl_2 under N_2 at room temperature for 10 min, followed by TLC (silica gel, eluant hexane) gave a 90% yield of $Os_3(CO)_{10}(Me_3SiC_2H)$ (**2**). This compound was identified primarily from its spectroscopic data: ν(CO) hexane, 2099m, 2059vs, 2056sh, 2023vs, 2008s, 1999s, 1854m cm^{-1}; ^{1}H NMR, $CDCl_3$, δ 10.53s (1H, CH), 0.040s (9H, 3Me). The geometry of compound **2** in which the Me_3SiC_2H ligand is coordinated in a μ_3-η^2($\parallel$) fashion to the Os_3 unit was established from a comparison of its spectroscopic properties with those of analogous $Os_3(\mu_3\text{-}\eta^2\text{-alkyne})(CO)_{10}$ derivatives [5]. The orange derivative **2** is converted within weeks at room temperature in the solid state or within 3 h in refluxing hexane into an off-white compound **3**, which was characterised as $HOs_3(CO)_9(C{\equiv}CSiMe_3)$ (50% yield) after separation

0022-328X/89/$03.50

on TLC plates (silica gel, eluant hexane). Spectroscopic and analytical data for **3**: ν(CO) hexane; 2100w, 2074s, 2052s, 2020vs, 2011s, 1981m, 1949w cm^{-1}; ^{1}H NMR, $CDCl_3$, δ 0.38s (9H, 3Me), -23.70s (1H, Os–H–Os); ^{13}C NMR, $CDCl_3$, δ 1.49 (s, $Si(CH_3)_3$, 48.71 ($C{\equiv}CSiMe_3$), 144.27 ($\mathit{C}{\equiv}CSiMe_3$), 162.37, 169.43, 172.40 (9CO) $M^+ = 921$) are consistent with this formulation. Together with compound **3** a second white fraction was isolated in a 5% yield. The nature of this uncharacterised product which exhibits the same IR band pattern: ν(CO) hexane, 2104w, 2078s, 2056s, 2023vs, 2017s, 1985m, 1952w cm^{-1}, is still under investigation.

Formation of the acetylide cluster **3** from compound **2** occurs with CO loss and concomitant hydrogen transfer to the metal. This mode of reaction is in agreement with the fact that in triosmium cluster chemistry triply bridging alkyne compounds $Os_3(HCCR)(CO)_{10}$ generally undergo thermally decarbonylation with hydrogen migration to the metal to give the nonacarbonyl clusters $HOs_3(CO)_9(C{\equiv}CR)$ in which the acetylenic ligand is coordinated in a μ_3-η^2 ($\perp$) mode [6].

An alternative route to the synthesis of acetylide clusters has been observed in the recently reported preparation of $(\mu_3\text{-}\eta^2\text{-}C{\equiv}CSiMe_3)CoFe_2(CO)_9$ [7]. In this heteronuclear complex, formed unexpectedly from the reaction of $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ with $Co_2(CO)_8$, the acetylide ligand $C{\equiv}CSiMe_3$ is coordinated in a μ_3-η^2($\perp$) mode, as shown by an X-ray crystal structure determination. As we are interested in the further reactions of $HOs_3(CO)_9(C{\equiv}CSiMe_3)$, and bearing in mind the paucity of crystal structures for this class of compounds, which could provide better understanding of the bonding interactions of the alkynes with the metal core, we prepared crystals of **3** suitable for crystal structure determination by crystallization from hexane at $-20\,^\circ$C.

The single crystal X-ray diffraction study * showed that **3** contains (see Fig. 1) an almost equilateral Os triangle (Os–Os bond length range 2.833(1)–2.846(1) Å) with two equatorial and one axial CO ligand bound to each Os atom. The $C{\equiv}CSiMe_3$ ligand is coordinated to all three metal atoms, with the triple bond perpendicular to one Os–Os bond. This bonding fashion is rather unusual among alkyne trimetallic clusters belonging to the sparingly populated class of compounds whose alkyne ligands interact via $1\sigma + 2\pi$ interactions supplying a total of five electrons to the cluster orbitals [1]. Usually the alkyne ligands lie parallel to one triangle edge interacting via $2\sigma + 1\pi$ bonds with the metal atoms [8]. Os–C(alkyne) interactions can be grouped into three distinct sets: the σ-type one, which is short (1.94(1) Å), and two sets of long bonds from the Os–Os axis (2.26(1), 2.23(1) Å for

---

* *Crystal data.* $C_{14}H_{10}O_9Os_3Si$, triclinic, space group $P\bar{1}$, $a = 9.201(2)$, $b = 13.127(2)$, $c = 9.118(2)$ Å, $\alpha = 107.31(3)$, $\beta = 98.57(3)$, $\gamma = 93.18(2)^\circ$, $U = 1033.8$ Å^3, $Z = 2$, $F(000) = 816$, $\mu(MoK_\alpha) = 177.8$ cm^{-1}, θ-range 2.5–25°, final R values 0.033, wR = 0.035 for 2956 out of 3872 independent reflections [$I_0 > 2\sigma(I_0)$]. Absorption correction was applied by the Walker and Stuart method (max. corr. 85%) [12]. Intensity data were collected at room temperature on an Enraf–Nonius CAD4 diffractometer by the ω–2θ method. All non-H atoms were allowed to vibrate anisotropically, a single isotropic thermal parameter was refind for the H atoms (0.14 Å^2). The H atoms were included in calculated positions and refined riding on their respective C atoms. The structure was solved by direct methods; for all calculations the SHELX76 package of programs was used [13]. Full listings of atomic coordinates and bond lengths and angles are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication. Tables of structure factors are available from the authors.

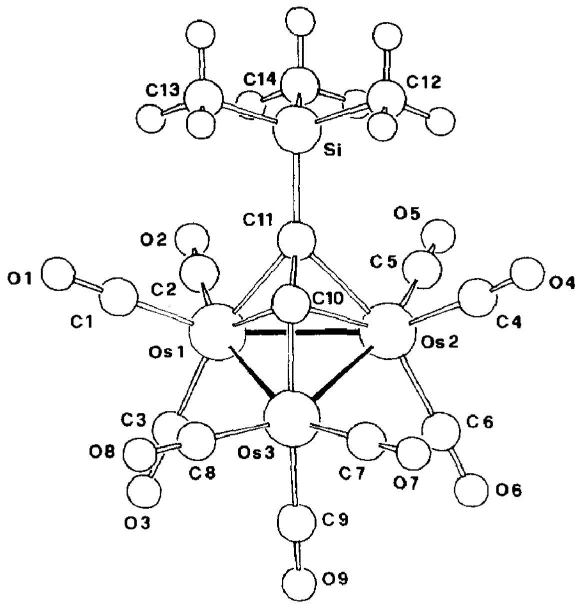

Fig. 1. Molecular structure of $HO_3(CO)_9(C{\equiv}CSiMe_3)$ (3) showing the atom numbering scheme. Important bond lengths (Å) and angles (°): Os1–Os2 2.833(1), Os2–Os3 2.843(1), Os1–Os3 2.846(1), Os1–C10 2.227(8), Os3–C10 1.939(8), Os1–C11 2.258(8), Os2–C10 2.235(8), Os2–C11 2.254(9), C10–C11 1.31(1), C11–Si 1.867(9) Å; C10–C11–Si 140.0(7)°.

the Si- and Os-bonded C atoms, respectively). A similar bonding pattern was observed in the closely related species $HRu_3(CO)_9(C{\equiv}C\text{-}Bu^t)$ [9] (1.947(3), 2.270(3), 2.211(3) Å), in $HOs_3(CO)_9(C{\equiv}CCF_3)$ [10] (1.937(10), 2.266(10), 2.180(10) Å), which also possess μ_3-η^2-($\perp$) alkyne ligands and in the afore-mentioned mixed species $CoFe_2(CO)_9(C{\equiv}CSiMe_3)$ [7] (1.821(4) (Co–C) 2.31(4) and 2.012(4) Å). Bond angles within the SiC≡C system in both 3 and this latter species are in agreement with an overall picture of rather "adapted" μ_3-η^2($\perp$) alkynes (Os–C≡C 154(1), Co–C≡C 158.8(3), C≡C–Si 140(1) and 145.6(3)°, respectively) and are also closely comparable with the values reported for the Os and Ru species mentioned above (Ru: 153.7(2), 141.0(2); Os: 147.5(8), 133.9(3)°).

The C≡C length of 1.31(1) Å also indicates that the bond retains substantial multiple bond character. Direct location of the H-hydride atom was not achieved in the present X-ray study, and the usually observed M–M bond lengthening caused by the presence of a μ_2-H atom was not detected. However, a rather confident positioning of this atom along the alkyne bridged Os(1)–Os(2) bond can be made from a comparison of space filling diagrams (see Fig. 2) which shows a large "niche" along this edge. This attribution is substantiated by the neutron diffraction study of the related species $HRu_3(CO)_9(C{\equiv}CBu^t)$, in which the H atom was observed. We suggest that the H-bridge lengthening effect is compensated and almost cancelled by an effect in the opposite direction due to the special C≡C($\perp$)Os–Os interaction. Interestingly the shortening caused by the alkyne ligand appears to be further enhanced in the species $HOs_3(CO)_9(C{\equiv}CCF_3)$, where the supposedly H-bridged bond is shorter than the unbridged ones (2.828(1), compared with an average of 2.873(1) Å) [10].

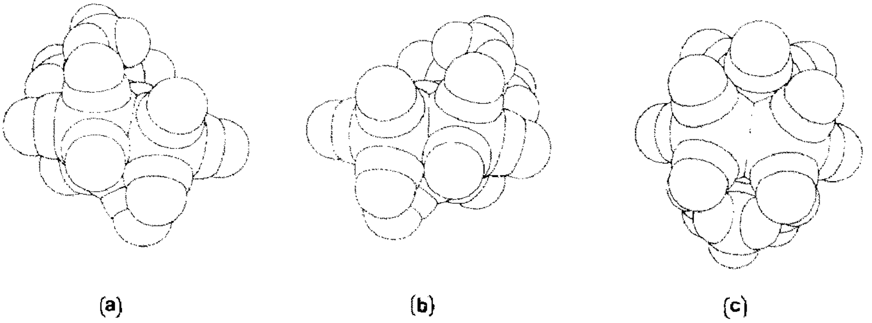
(a) (b) (c)

Fig. 2. Space filling comparison of the three Os–Os edges of 3 showing the "hole" left by H (hydride) atom (C).

The C–Si distances fall in a narrow range (1.840(1)–1.867(1) Å) and agree well with values observed for other systems containing a C-bonded $SiMe_3$ group, such as $Mo_2(C_5H_5)_2(CO)_4(\mu SiMe_3C_2SiMe_3)$ (mean 1.871(5) Å) [11], and $CoFe_2(CO)_9(C{\equiv}CSiMe_3)$ (1.862(4) Å).

Acknowledgements

We thank the E.E.C. for financial support.

References

1 (a) A.J. Carty, Pure Appl. Chem., 54 (1982), 113; (b) E. Sappa, A. Tiripicchio and P. Braunstein, Chem. Rev., 83 (1983) 203.

2 J.E. Parmeter, M.M. Hills and W.H. Weinberg, J. Am. Chem. Soc., 108 (1986) 3563 and refs. therein.

3 (a) E.L. Muetterties, Bull. Soc. Chim. Belg., 85 (1976) 451; (b) ibid. 84 (1975) 253.

4 P. Magnus and D.P. Becker, J. Chem. Soc., Chem. Commun., (1985) 640.

5 R.D. Adams and J.P. Selegue, Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Ch. 33, p. 967.

6 A.J. Deeming, S. Hasso and M. Underhill, J. Chem. Soc., Dalton Trans., (1975) 1614.

7 D. Seiferth, J.B. Hoke, A.L. Rheingold, M. Cowie and A.D. Hunter, Organometallics, 7 (1988) 2163.

8 D. Boccardo, M. Botta, R. Gobetto, D. Osella, A. Tiripicchio, M. Tiripicchio Camellini, J. Chem. Soc., Dalton Trans., (1988) 1249; A.J. Carty, N.J. Taylor, and E. Sappa, Organometallics, 7 (1988) 405.

9 M. Catti, G. Gervasio, and S.A. Mason, J. Chem. Soc., Dalton Trans., (1977) 2260.

10 Z. Dawoodi, M.J. Mays and K. Henrick, J. Chem. Soc., Dalton Trans., (1984) 1769.

11 J.A. Beck, S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 195.

12 N. Walker, D. Stuart, Acta Crystallogr. A, 39 (1983) 158.

13 SHELX76 by G.M. Sheldrick, University of Cambridge, 1976.