Journal of Organometallic Chemistry, 228 (1982) 135—138
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

REACTIONS OF $[Os_3H_2(CO)_{10}]$ AND $[Os_3H(CO)_{11}]^-$ WITH $[N_3SiMe_3]$ AND THE FORMATION OF $[Os_3H(CO)_{10}(\mu\text{-}NHPh)]$ USING $[Os_3(CO)_{11}(NCMe)]$; X-RAY CRYSTAL STRUCTURES OF $[Os_3(\mu\text{-}H)(CO)_{10}(\eta\text{-}N_3H_2)]$ AND $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHSiMe_3)]$

BRIAN F.G. JOHNSON, JACK LEWIS *, PAUL R. RAITHBY, and STEPHEN W. SANKEY
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)

(Received October 5th, 1981)

Summary

Reaction of the cluster $[Os_3H_2(CO)_{10}]$ with (N_3SiMe_3) yields the triazenido species $[Os_3(\mu\text{-}H)(CO)_{10}(\eta\text{-}N_3H_2)]$ (I) which, upon reflux, loses N_2 to give $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NH_2)]$ (II); the capped species $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)]$ may be obtained by reaction of $[Os_3(CO)_{11}(NCMe)]$ with NH_2Ph and subsequent pyrolysis of the high yield product $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHPh)]$; with $[Os_3H(CO)_{11}]^-$ trimethylsilylazide yields $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHSiMe_3)]$ (III); the structures of I and III have been confirmed by single-crystal X-ray analyses.

Although the reactions of triosmium clusters with small molecules containing unsaturated carbon—carbon bonds have been extensively investigated [1], there has been less interest in the reactions between clusters and molecules containing unsaturated nitrogen—nitrogen bonds. Reactions of triosmium clusters with diazo compounds have produced a variety of products [2], and it has been suggested that species of the type $[Os_3H_2(CO)_9(\mu_3\text{-}NR)]$ (R = Ph [3], Me [4]) may be an entry into a dehydrogenation/hydrogenation cycle [5] similar to that observed for $[Fe_3H_2(CO)_9(\mu_3\text{-}NEt)]$ [6]. We now report the reactions of the clusters $[Os_3H_2(CO)_{10}]$ and $[Os_3H(CO)_{11}]^-$ with the unsaturated molecule (N_3SiMe_3), and the results of dehydrogenation reactions on the products.

Reaction of $[Os_3H_2(CO)_{10}]$ with (N_3SiMe_3) in hexane for 24 h leads to the formation of $[Os_3(\mu\text{-}H)(CO)_{10}(\eta\text{-}N_3H_2)]$ (I). The product was purified by TLC (yield 25%) and obtained as orange crystals from hexane. The complex was characterised by spectroscopic studies (Table 1) and the overall molecular structure established by an X-ray analysis *.

---

* Crystal data for I: $C_{10}H_3N_3O_{10}Os_3$, $M = 895.75$, triclinic, space group $P\bar{1}$, a 7.867(3), b 9.113(3), c 14.000(5) Å, α 90.68(2), β 100.37(2), γ 118.80(2)°, U 859.5 Å^3, $Z = 2$, D_c 3.46 g cm^{-3}; μ(Mo-K_α) 221.7 cm^{-1}. Structure refined to $R = 0.050$ ($R_w = 0.047$) for 3056 unique observed diffractometer data (Os, O, N, C anisotropic).

0022-328X/82/0000—0000/$02.75

TABLE 1

SPECTROSCOPIC DATA FOR I, AND III

Compound	Mass spectrum (m/e) [a]	IR ν(CO) (cm^{-1})		
[$Os_3(\mu$-H)(CO)$_{10}(\eta$-$N_3H_2)$] (I)	901	2109(m),	2006(vs),	2059(vs),
		2044(w),	2023(vs),	2013(s),
		2006(w),	1998(m),	1987(w)
[$Os_3(\mu$-H)(CO)$_{10}(\mu$-NHSiMe$_3$)] (III)	946	2109(m),	2069(vs),	2056(vs),
		2020(vs),	2016(vs),	2002(sh, w),
		1997(s),	1985(m),	1980(w),
		1952(vw)		
		1255(s)	(Me$_3$Si)	

[a] For ^{192}Os.

The molecular structure of I is illustrated in Fig. 1, which includes some important bond parameters. The overall geometry may be considered as derived from that of [$Os_3(CO)_{12}$] [7] by the replacement of two adjacent *cis* axial carbonyls by the symmetrically chelating triazenido ligand. The introduction of this group is accompanied by the lengthening of the bridged Os(2)—Os(3) edge by ca. 0.03 Å over the other two Os—Os edges in the complex. Although neither the hydride or the protons bonded to N(1) and N(2) were directly located in the structure determination their presence is indicated by the ^{1}H NMR data; τ

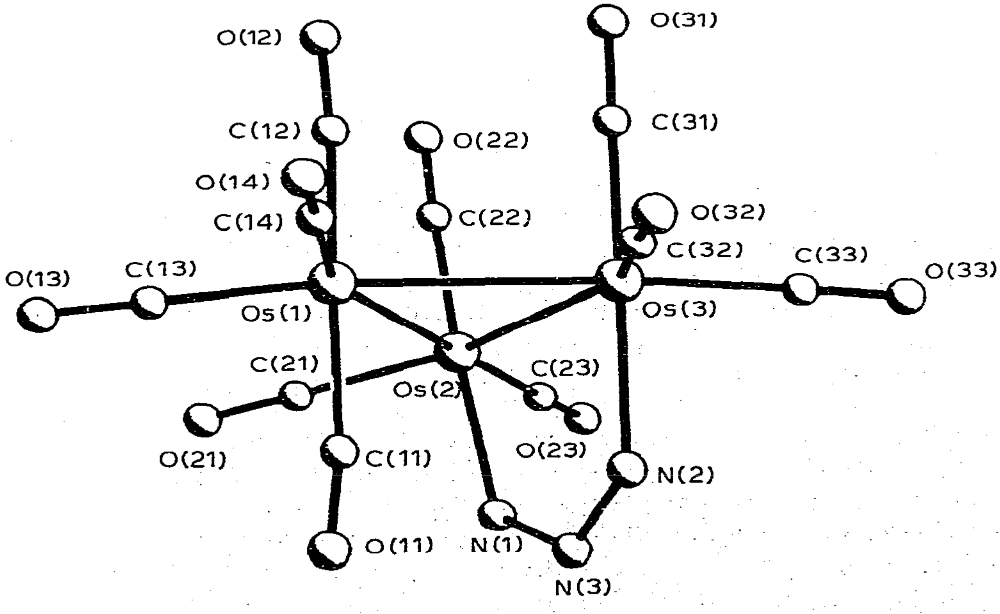

Fig. 1. The molecular structure of [$Os_3(\mu$-H)(CO)$_{10}(\mu$-$N_3H_2)$] (I), including the atom numbering scheme. Bond lengths: Os(1)—Os(2), 2.884(2); Os(1)—Os(3), 2.893(2); Os(2)—Os(3), 2.923(2); Os(1)—N(1), 2.12(2); Os(3)—N(2), 2.13(2); N(1)—N(3), 1.32(2); N(2)—N(3), 1.32(2) Å; bond angles: N(1)—N(3)—N(2), 118(1)°.

1.48 (s,br) (N—H), τ 23.23(s) (Os—H—Os). The equatorial carbonyl groups C(23)O(23) and C(33)O(33) bend away from the long Os(2)—Os(3) edge which suggests that the hydride sits in this "hole" in the ligand polyhedron, bridging the Os(2)—Os(3) edge and lying in the plane of the Os_3 triangle. The Os(2)N(1)-N(3)N(2)Os(3) unit is planar and makes an angle of 83.5(3)° with the Os_3 plane. The geometry of the triazenido ligand is similar to that found in the substituted triazenido complexes $[Cu(MeN_3Me)]_4$ [8] and $[Os_3H(CO)_{10}(HN_3Ph)]$ [9], and there have been no previous reports of the parent (HN_3H) ligand coordinated in metallo-organic complexes. I is not fluxional on the NMR time scale.

The pyrolysis of I in octane for 0.75 h leads to the quantitative formation of the known complex $[Os_3H(CO)_{10}NH_2]$ (II) [10] with loss of N_2. This is in marked contrast to the substituted triazenido complexes $[Os_3H(CO)_{10}(HN_3R)]$ (R = Ph, n-Bu, CH_2Ph, cyclo-C_6H_{11}) which are converted to $[Os_3H_2(CO)_9(\mu_3\text{-}NR)]$ [9]. This capped species may also be prepared by the pyrolysis of $[Os_3H(CO)_{10}\text{-}\mu\text{-}NHPh]$ which can be prepared quantitatively by the action of $PhNH_2$ on $[Os_3(CO)_{11}(NCMe)]$.

The action of (N_3SiMe_3) on $[Os_3H(CO)_{11}]^-$ in CH_2Cl_2 gave a yellow solution

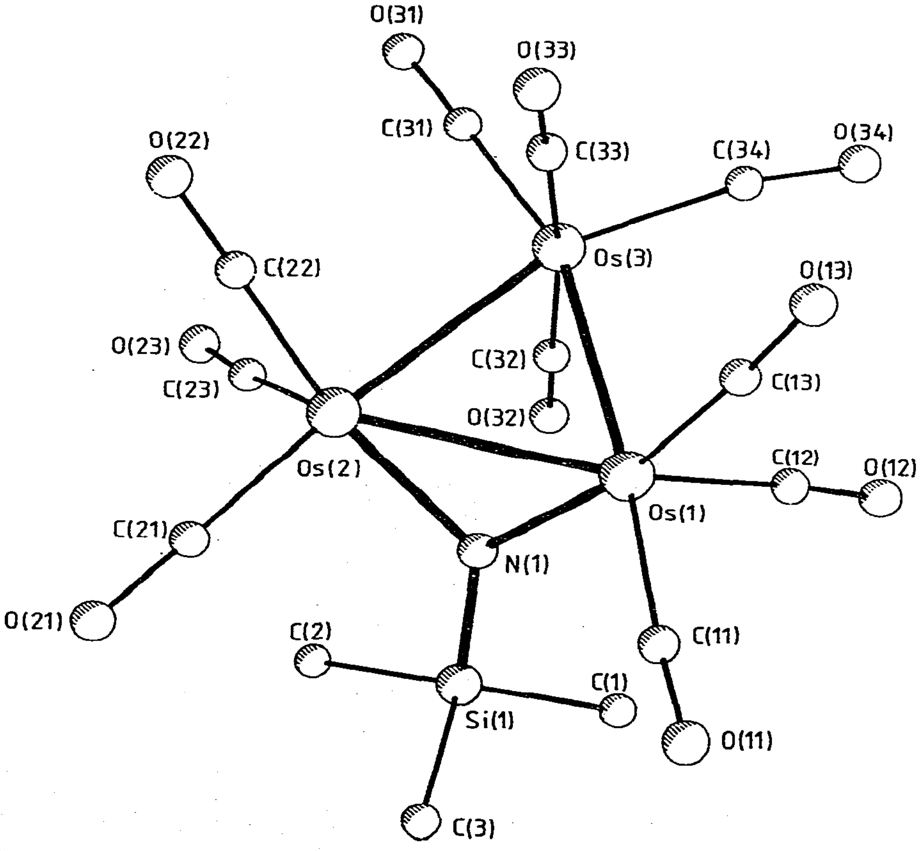

Fig. 2. The molecular structure of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHSiMe_3)]$ (III), including the atom numbering scheme. Bond lengths: Os(1)—Os(2), 2.803(1); Os(1)—Os(3), 2.823(1); Os(2)—Os(3), 2.825(1); Os(1)—N(1), 2.104(14); Os(2)—N(1), 2.129(15); N(1)—Si(1), 1.66(2) Å; bond angles: Os(1)—N(1)—Os(2), 82.9(6); Os(1)—N(1)—Si(1), 135.1(8); Os(2)—N(1)—Si(1), 135.6(8)°. (Supplementary data are available from the authors).

after 24 h, the resultant solid was purified by TLC (hexane) and the major product was characterised as $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHSiMe_3)]$(III) by spectroscopic (Table) and crystallographic techniques *.

The molecular structure of III is shown in Fig. 2, which also includes some important bond parameters. The geometry resembles that of a large number of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}X)]$ type complexes where X is a ligand in which the bridgehead atom is a first row element [11]. The shortest edge of the metal triangle, Os(1)—Os(2) is bridged by the μ-$NHSiMe_3$ ligand, and the Os—N distances and the Os—N—Os angle are similar to the values of 2.154 Å (mean) and 81.6(2)°, respectively, found for $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHSO_2C_6H_4Me)]$ [12], where the bridgehead N atom is also formally sp^3 hybridized. Although neither the N bonded proton nor the hydride were located directly in the structure of III their presence is indicated by ^1H NMR signals at τ 9.107(s,br) (N—H) and τ 22.489(2) (Os—H—Os), while the signal at τ 8.719 is assignable to the $Si(CH_3)_3$ protons. From the distribution of the carbonyl ligands around the Os(1)—Os(2) bond the hydride is also thought to bridge this edge.

Unlike the Fe and Ru analogues III does not readily dehydrogenate to give complexes of the type $[M_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NSiMe_3)]$ which has been fully characterised for M = Fe [13]. There is no reaction between $[Os_3(CO)_{12}]$ and $[N_3SiMe_3]$ in refluxing heptane.

We thank the S.R.C. for financial support.

References

1 A.J. Deeming and M. Underhill, J. Chem. Soc., Dalton Trans., (1974) 1415; E.G. Bryan, B.F.G. Johnson, and J. Lewis, J. Chem. Soc., Dalton Trans., (1977) 1328; M. Tachikawa and J.R. Shapley, J. Organometal. Chem., 124 (1977) C19.

2 R.B. Calvert and J.R. Shapley, J. Am. Chem. Soc., 99 (1977) 5225; 100 (1978) 6544; 7726; J.B. Keister and J.R. Shapley, ibid., 98 (1976) 1056; K. Burgess, B.F.G. Johnson, J. Lewis, and P.R. Raithby, J. Chem. Soc., Dalton Trans., in the press.

3 C.C. Yin and A.J. Deeming, J. Chem. Soc., Dalton Trans., (1974) 1013.

4 Y.C. Lin, C.B. Knobler, and H.D. Kaesz, J. Am. Chem. Soc., 103 (1981) 1216.

5 Y.C. Lin, C.B. Knobler, and H.D. Kaesz, J. Organometal. Chem., 213 (1981) C41.

6 M.A. Andrews and H.D. Kaesz, J. Am. Chem. Soc., 101 (1979) 7255.

7 M.R. Churchill and B.G. De Boer, Inorg. Chem., 16 (1977) 878.

8 J.E. O'Connor, G.A. Janusonis, and E.R. Covey, J. Chem. Soc., Chem. Commun., (1968) 445.

9 K. Burgess, B.F.G. Johnson, J. Lewis, and P.R. Raithby, in preparation.

10 E.G. Bryan, B.F.G. Johnson, and J. Lewis, J. Chem. Soc. Dalton Trans., (1977) 1328.

11 P.R. Raithby, in B.F.G. Johnson (Ed.), Transition Metal Clusters, John Wiley & Sons Ltd., 1980.

12 M.R. Churchill, F.J. Hollander, J.R. Shapley, and J.B. Keister, Inorg. Chem., 19 (1980) 1272.

13 B.L. Barnett and C. Kruger, Angew. Chem. Int. Ed., 10 (1971) 910.

---

* Crystal data for III: $C_{13}H_{11}NO_{10}Os_3Si$, M = 939.92, monoclinic, space group $P2_1/c$, a 17.557(5), b 9.095(4), c 13.503(5) Å, β 90.65(2)°, U 2156.03 Å^3, Z = 4, D_c 2.90 g cm^{-3}; μ(Mo-K_α) 177.27 cm^{-1}. Structure refined to R = 0.054 (R_w = 0.053) for 2765 unique observed diffractometer data (Os, Si, O, N, C anisotropic, methyl H common isotropic).