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Preliminary communication

CONVERSION OF $H_2Os_3(\mu_3\text{-}NCH_3)(CO)_9$ TO $Os_4(\mu_3\text{-}NCH_3)(CO)_{12}$; CRYSTAL AND MOLECULAR STRUCTURE OF THE TWO METHYLNITRENE CLUSTER COMPLEXES

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Summary

The complex $H_2Os_3(\mu_3\text{-}NCH_3)(CO)_9$ is converted to $Os_4(\mu_3\text{-}NCH_3)(CO)_{12}$ in decalin at 198°C in 35% yield. Crystal data for the former obtained at –158°C are: orthorhombic, space group *Pmcn*, a 14.113(2), b 6.605(1), c 17.683(4) Å, $Z = 4$, D_c 3.44 g cm^{-3}. The hydrogen atoms are related by symmetry. The position of the unique hydrogen atom has been refined. It is observed asymmetrically bridging (closer to the unique Os atom) the longer edge of the isosceles triosmium triangle. The hydrogen atoms are out of the trimetal plane away from the triply-bridging nitrogen atom.

Crystal data for the tetraosmium complex at 25°C are: monoclinic, space group *C2/c* a 30.818(9), b 8.463(2), c 16.621(2) Å, β 108.90(2)°, $Z = 8$, D_c 3.75 g cm^{-3}. The four osmium atoms form a distorted tetrahedral framework capped by the nitrogen atom of the methylnitrene group on the face containing the three longer Os—Os separations.

The organoimido (or alkylnitrene) group, $=\ddot{N}R$, is an important participant in the chemistry of nitrogen-functionalized organic substrates with transition metal complexes [1]. In cluster complexes the organoimido group tends easily to form the triply-bridging geometry as illustrated by the complexes $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ [2], $Fe_3(\mu_3\text{-}NSiMe_3)(CO)_{10}$ [3], $(\eta^5\text{-}C_5H_5)_3Ni_3(\mu_3\text{-}NPh)$ [4], and $H_2Fe_3(\mu_3\text{-}NR)(CO)_9$, (Ia, R = C_2H_5, and Ib, R = n-C_3H_7) [5]. Complex Ia was shown easily to be dehydrogenated to the alkylidineimido complex $HFe_3(N{=}CHCH_3)(CO)_9$, a reversible process [5].

Osmium analogs of I have been reported: $H_2Os_3(\mu_3\text{-}NR)(CO)_9$ (IIa, R = Ph [6], and IIb, R = CH_3 [7]). Looking to the nitrene complex IIb for an entry into a dehydrogenation/hydrogenation cycle of the kind reported for Ia [5], we further heated complex IIb and found it to be stable in decalin up to around

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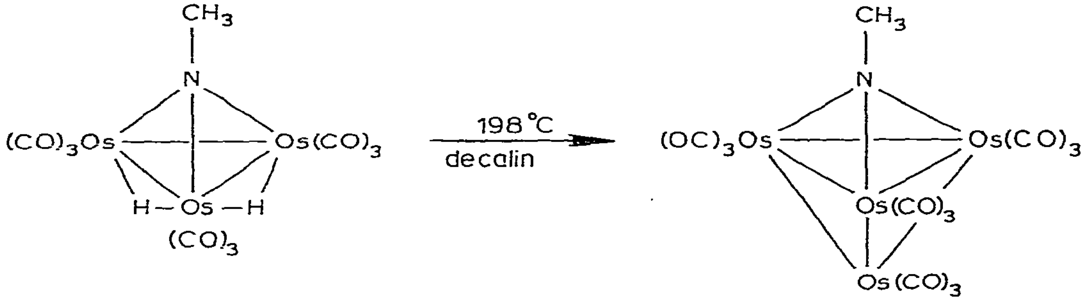
198°C. At that temperature, the trinuclear nitrene complex is converted to the tetraosmium complex III. This transformation may be viewed as loss of H_2 from IIb with subsequent capture of an $Os(CO)_3$ moiety produced through cluster fragmentation (which must also be occurring at these elevated temperatures).



(II b) (III)

Under the Wade-Mingos formalism [8], an $Os(CO)_3$ group is considered to donate 2 electrons to cluster bonding. This transformation may thus be regarded as an isovalent substitution of H_2 by an $Os(CO)_3$ group. At these elevated temperatures, III is relatively stable.

IR and NMR data are listed in Table 1. ^1H NMR spectra of IIb indicate equivalent hydrogen atoms bonded to the metal cluster even at low temperature (–60°C). For III, the mass spectrum indicated a parent molecular ion multiplet whose principal peak was measured at m/e = 1133; this was accompanied hy multiplets of fragments corresponding to successive loss of 12 CO groups. IR spectra in the carbonyl stretching region (Table 1) indicate a high symmetry and imply a methylnitrene group triply bridging on the face of a tetrahedral metal cluster. This would be the first for this class of cluster complexes [9a], parallel to the recent report of a face-bridging μ_3-phenylphosphidotetrairidium cluster complex [9b]. Due to these features and the relative lack of structural information on nitrene cluster complexes [1], structure determination of both new compounds was undertaken.

The ORTEP projections of IIb and III are shown in Fig. 1 and 2, respectively. Selected bond distances are given in Table 2. Nitrogen atoms triply bridging are above their respective Os_3 plane by 1.28(1) and 1.29(2) Å, for IIb and III, respectively [3]. In IIb, the Os—H—Os angle of 95(7)° is close to that of a

TABLE 1

SPECTROSCOPIC PROPERTIES

	$H_2Os_3(\mu_3\text{-}NCH_3)(CO)_9$ (IIb)	$Os_4(\mu_3\text{-}NCH_3)(CO)_{12}$ (III)
ν(CO) (cm^{-1}) in hexane	2112m, 2032s, 2078s, 2032s, 2005s, 1986s, 1974m	2099vw, 2057(sh), 2051vs, 2002s, 1990m
^1H NMR (δ in ppm) in $CDCl_3$	4.69(CH_3) –18.74 (Hydride)	5.91(CH_3)

dihydrido-μ_3-sulphido triosmium complex [10]. Both cluster complexes are electronically saturated [11] with 48 electrons for IIb and 60 electrons for III. If one regards the latter as an electron-precise structure [8a], i.e. a structure with an electron-pair bond along each of the polyhedral edges, this leads to a

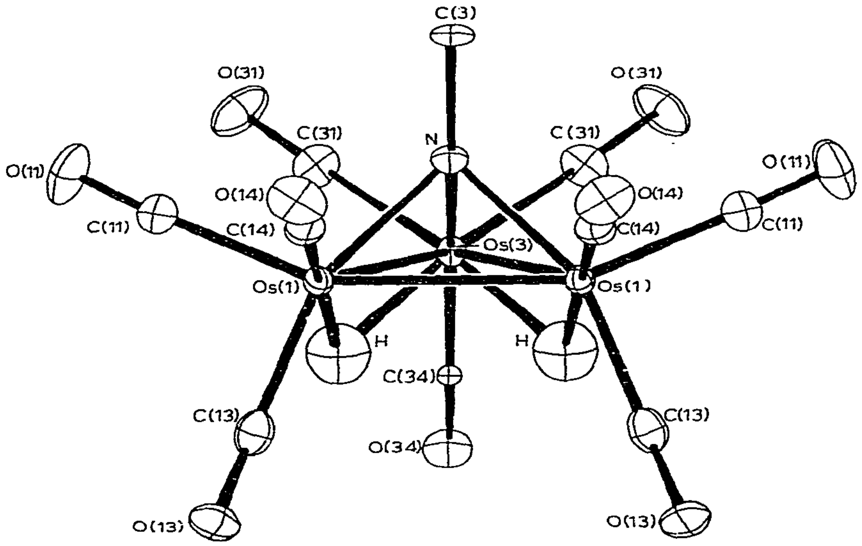


Fig. 1. ORTEP projection of $H_2Os_3(\mu_3\text{-}NCH_3)(CO)_9$. Thermal ellipsoids at 50% probability.

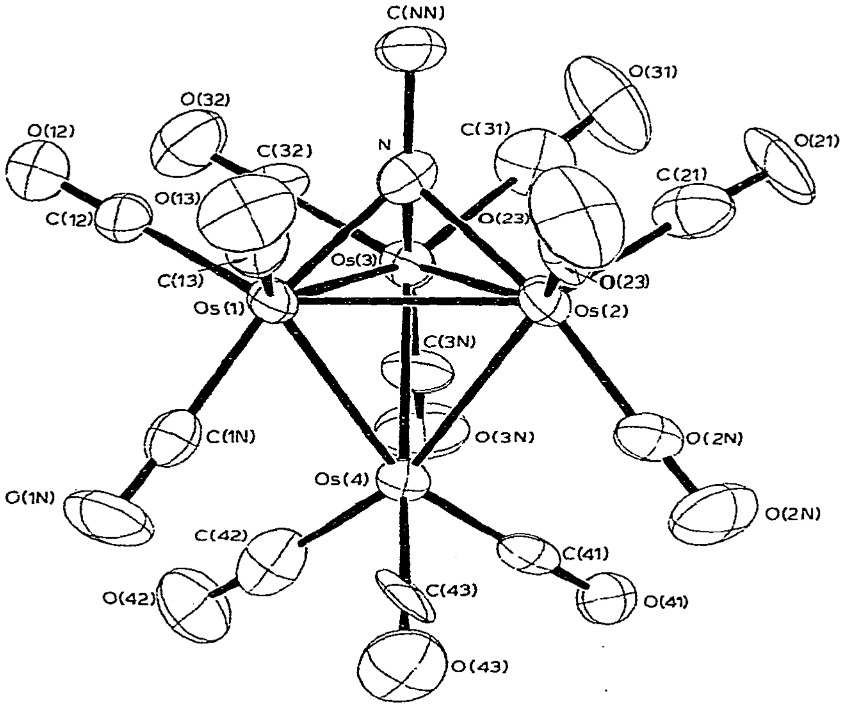


Fig. 2. ORTEP projection of $Os_4(\mu_3\text{-}NCH_3)(CO)_{12}$. Thermal ellipsoid at 50% probability.

TABLE 2

SELECTED BOND DISTANCES (in Å) OF IIb AND III

IIb [a]	Os(1)—Os(3)	2.8612(7)	Os(1)—Os(1)	2.7498(7)
	Os(1)—H	2.1(2)	Os(3)—H	1.7(1)
	Os(1)—N	2.070(8)	Os(3)—N	2.081(14)
	N to Os_3 plane	1.28(1)	N—C(5)	1.46(2)
III	Os(1)—Os(2)	2.835(2)	Os(1)—Os(4)	2.750(1)
	Os(1)—Os(3)	2.826(2)	Os(2)—Os(4)	2.768(2)
	Os(2)—Os(3)	2.831(2)	Os(3)—Os(4)	2.768(2)
	Os(1)—N	2.08(2)	Os(2)—N	2.12(2)
	Os(3)—N	2.05(2)	N—C(Me)	1.48(3)
	N to Os(1)—Os(2)—Os(3) plane			1.29(2)

[a] The molecule lies across the mirror plane of the crystal.

building-up of electron density on the nitrogen-capped triosmium face and electron deficiency at the unique $Os(CO)_3$ group. The metal—metal separations fall into two groups (see Table 2) distinguishing two types of metal—metal interactions in the complex. One may regard the shorter distance separating Os(4) from the other three osmium atoms as a reflection of its tendency to draw electron density from these atoms to counteract electron deficiency which would otherwise develop. Alternately, one may account for the differences in metal—metal separations by the cluster electron pair bonding scheme suggested in the second paragraph above.

By way of reference we may cite the following compounds for comparison of the related atomic separations to the title compounds. For nitrene triply bridging to a triangular cluster face, we cite $Fe_3(\mu_3\text{-}NSiMe_3)(CO)_{10}$ [3]; the separation between N and the Fe_3 plane is 1.21 Å. For comparison of Os—Os distances we may cite $[(Ph_3P)_2N]_2[H_2Os_4(CO)_{12}]$ [12] and $Os_5(CO)_{16}$ [13]. The four unbridged Os—Os distances in the former average to 2.799 Å; there are two hydrogen-bridged bonds at 2.937 and 2.931 Å. In the second derivative, two types of Os—Os separations are observed, three averaging 2.750 Å and two long separations of 2.866 and 2.889 Å.

We are investigating the systematic application of this proposed reaction pathway to the synthesis of mixed metal clusters starting with IIb and suitable carbonyl fragment precursors. We are now in position also to see whether a systematic dehydrogenation cycle can be carried out on the triangular face of a tetrametal cluster complex.

References

1 W.A. Nugent and B.L. Haymore, Coord. Chem. Rev., 31 (1980) 123.
2 R.J. Doedens, Inorg. Chem., 8 (1969) 570.
3 B.L. Barnett, and C. Kruger, Angew. Chem. Intern. Ed., 10 (1971) 910.
4 S. Otsuka, A. Nakamura and T. Yoshida, Inorg. Chem., 7 (1968) 261.
5 M.A. Andrews and H.D. Kaesz, J. Amer. Chem. Soc., 101 (1979) 7255.
6 C.C. Yin and A.J. Deeming, J. Chem. Soc. Dalton, (1974) 1013.
7 Y.C. Lin, C.B. Knobler and H.D. Kaesz, J. Amer. Chem. Soc., 103 (1981) 1216.
8 (a) D.M.P. Mingos, Nature (London) Phys. Sci., 236 (1972) 99; (b) K. Wade, Chem. Ber., 11 (1975) 177; (c) K. Wade, Adv. Inorg. Chem. Radiochem., 18 (1976) 177.
9 (a) P. Chini and B.T. Heaton, Topics in Current Chemistry, 71 (1977) 3; (b) F. Demartin, M. Manassero, M. Sansoni, L. Garlaschelli and U. Sartorelli, J. Organometal. Chem., 204 (1981) C10.

10 B.F.G. Johnson, J. Lewis, D. Pippard, P.R. Raithby, G.M. Sheldrick and K.D. Rouse, J. Chem. Soc. Dalton, (1979) 616.
11 (a) J.W. Lauher, J. Amer. Chem. Soc., 100 (1978) 5305; (b) 101 (1979) 2604.
12 B.F.G. Johnson, J. Lewis, P.R. Raithby, G.M. Sheldrick and G. Suss, J. Organometal. Chem., 162 (1978) 179.
13 B.E. Reichert and G.M. Sheldrick, Acta Cryst., B, 33 (1977) 173.