Journal of Organometallic Chemistry, 149 (1978) C43—C46

Preliminary communication

ISOCYANIDE SUBSTITUTION IN OCTADECACARBONYL HEXAOSMIUM*

COLIN R. EADY, PAUL D. GAVENS, BRIAN F.G. JOHNSON, JACK LEWIS*, MARIA CARLOTTA MALATESTA, MARTIN J. MAYS, A. GUY ORPEN, A. VALENTINA RIVERA, GEORGE M. SHELDRICK,
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)
and MICHAEL B. HURSTHOUSE
Queen Mary College, Mile End Road, London E1 4NS (Great Britain)

(Received January 25th, 1978)

Summary

The crystal structures of the two isocyanide substituted hexaosmium clusters, $Os_6(CO)_{18}(CNC_6H_4Me)_2$ and $Os_6(CO)_{16}(CNCMe_3)_2$ are reported. The former involves both a triple bridging and a terminal isonitrile group whilst the latter is related to the parent carbonyl $Os_6(CO)_{18}$. The molecular structures are discussed in terms of electronic inequivalences within the metal cluster framework.

Isocyanides behave as good π-acceptor groups, and stabilise metals in low oxidation states in a manner similar to carbon monoxide. We have studied the replacement of carbon monoxide in octadecacarbonyl hexaosmium by isocyanide [1] and the production of hexaosmium cluster units from thermolysis of isocyanide substituted triosmium carbonyl species [2]. The structures of two of these reaction products have been determined and illustrate different bonding modes both in the metal cluster unit and the coordinated isocyanide moiety.

Reaction of $Os_6(CO)_{18}$ with *p*-tolyl isocyanide leads to the addition of two moles of the isocyanide to give $Os_6(CO)_{18}(CNC_6H_4CH_3)_2$. The ^1H NMR spectrum of the compound indicates two different environments for the isocyanide groups. The detailed structure was elucidated by X-ray diffraction and is shown in Fig. 1. As anticipated from the stoichiometry of the compound, a major change has occurred in the structure of the metal framework, with three of the Os—Os bonds of the parent carbonyl $Os_6(CO)_{18}$ being ruptured, the six electrons required to accomplish this being provided by the two isocyanide groups.

---

* No reprints available.

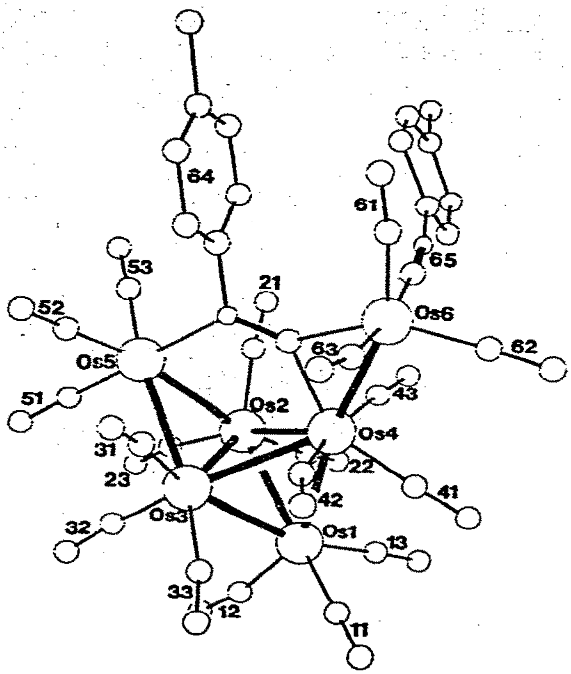

Fig. 1. The molecule of $Os_6(CO)_{15}(CNC_6H_4CH_3)_2$; the E.C. values are —1 [Os(1) and Os(5)], 0 [Os(2), Os(3) and Os(6)] and +1 [Os(4) and N(64)].

The terminal isocyanide donates two electrons to the cluster unit whilts the bridging isocyanide contributes four electrons.

For the bridging isocyanide, the atoms Os(5), N(64), C(64), Os(6), and Os(4) are approximately coplanar, with the bonds from the nitrogen and carbon to the metal atoms being consistent with single bond distances, implying sp^2 hybrid bonds at the N(64) and C(64) atoms. A four electron triply-bridging isocyanide has previously been reported in the complex $Ni(CNCMe_3)_7$ [3], whilst in the complex $(Me_3CNC)_6Pt_3$ [4], the bridging isocyanide involves an alternative mode of bonding of a two electron bridge between two metal centres.

One of the products of pyrolysis of the triosmium cluster $Os_3(CO)_{11}(CNCMe_3)$ is a related compound $Os_6(CO)_{16}(CNCMe_3)_2$. The X-ray structure of this compound shows that the metal framework of the parent $Os_6(CO)_{18}$ has been maintained, with replacement of two of the carbonyls with terminal isocyanide groups. The substitution of the carbonyls at Os(4) and Os(6) shown in Fig. 2 slightly lengthen the mean Os—Os distance to these atoms whilst the mean Os—Os distance of the central tetrahedron of osmium atoms is the same as in the parent carbonyl, $Os_6(CO)_{18}$.

The two structures emphasise that in these osmium clusters the stereochemistry of the cluster unit is sensitive to the number of electrons donated, and also involves the metal atom in a variety of stereochemical environments within the same molecule. As with the hexaosmium cluster $Os_6(CO)_{18}$, in order to maintain the E.A.N. rule at each metal centre, two-electron donor bonds must be invoked between certain pairs of osmium atoms; the formation of such bonds will lead to a highly polar electron distribution within the metal framework

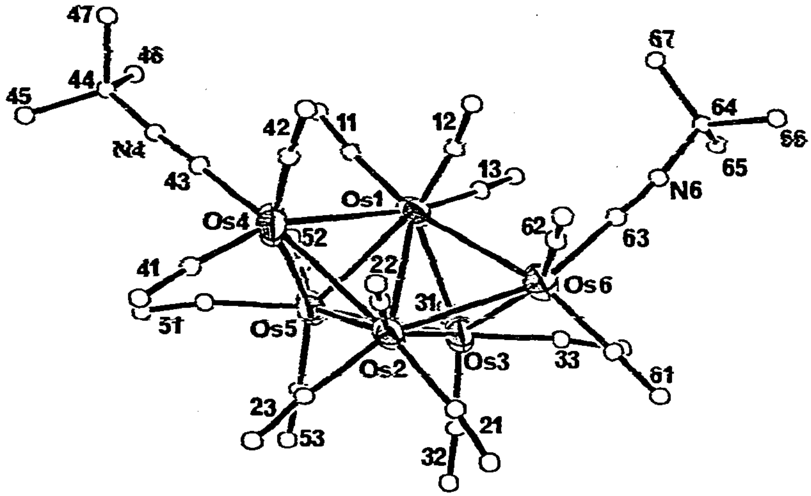

Fig. 2. The molecule of $Os_6(CO)_{16}(CN\ t\text{-}Bu)_2$; the E.C. values are —1 [Os(4) and Os(6)], 0 [Os(3) and Os(5)] and +1 [Os(1) and Os(2)].

that must influence both the reactivity of the cluster and reflect in the bonding modes of both the metal—metal bonds and the carbonyl group to the metal centres. For each osmium atom to obey the E.A.N. rule each metal centre requires ten electrons. We can calculate a 'formal oxidation state' for each metal centre, by subtracting 10 from the sum of the total number of metal—metal bonds formed (each metal contributing one electron per bond) and twice the number of terminal carbonyl or isocyanide ligands (as two electron donors) bonding to the metal. We feel that it may be more appropriate to term this number the 'electron connectivity' (E.C.) as indicative of the number of electron pairs involved. The actual charge distribution will reflect the relatively complex interactions present in these molecules, and may not correlate with the E.C. values given in Tables 1 and 2 and the legends to Fig. 1 and 2. However, the E.C. values should indicate the trends to be anticipated in any property associated with charge distribution.

Thus, as pointed out by Mason, Thomas and Mingos [5] for the $Os_6(CO)_{18}$ molecule, in the structure of the two molecules reported here the shortest Os—

TABLE 1

INCIPIENT CARBONYL BRIDGES IN $Os_6(CO)_{16}(CNC_6H_4CH_3)_2$ [a]

Atoms and E.C. values	d(Os—Os) (Å)	<(Os—C—O) (deg)	d(C••Os) (Å)
Os(4) [+1] —C(42)•••Os(3) [0]	2.868(5)	162.7(3.2)	2.70(4)
Os(4) [+1] —C(43)•••Os(2) [0]	2.891(5)	174.0(3.0)	2.84(4)
Os(4) [+1] —C(41)•••Os(1) [—1]	2.862(5)	172.7(4.0)	2.87(4)
Os(2) [0] —C(21)•••Os(5) [—1]	2.864(5)	170.8(3.5)	2.89(4)
Os(3) [0] —C(31)•••Os(5) [—1]	2.891(5)	168.8(4.0)	2.90(4)
Os(2) [0] —C(22)•••Os(1) [—1]	2.779(5)	169.1(2.7)	2.91(4)
Os(3) [0] —C(33)•••Os(1) [—1]	2.778(5)	170.3(3.3)	2.99(4)

[a] There are no incipient bridges across Os(2) [0]—Os(3) [0] 2.727(5) and Os(4) [1]—Os(6) [0] 2.847(5) Å.

TABLE 2

INCIPIENT CARBONYL BRIDGES IN $Os_6(CO)_{16}(CN\text{-}t\text{-}Bu)_2$ [a]

Atoms and E.C. values	d(Os—Os) (Å)	<(Os—C—O) (deg)	d(C··Os) (Å)
Os(5) [0] —C(51)···Os(4) [−1]	2.820(3)	167.6(2.8)	2.74(3)
Os(3) [0] —C(33)···Os(6) [−1]	2.842(3)	171.7(2.7)	2.78(3)
Os(2) [+1] —C(21)···Os(6) [−1]	2.775(3)	170.7(1.6)	2.87(3)
Os(1) [+1] —C(11)···Os(4) [−1]	2.781(3)	172.2(1.8)	2.91(3)
Os(2) [+1] —C(23)···Os(5) [0]	2.788(3)	174.5(3.2)	2.94(3)
Os(1) [+1] —C(12)···Os(6) [−1]	2.860(4)	171.6(2.0)	2.97(3)
Os(1) [+1] —C(13)···Os(3) [0]	2.787(3)	176.8(2.6)	2.99(3)
Os(2) [+1] —C(22)···Os(4) [−1]	2.861(3)	177.1(2.2)	3.01(3)

[a] There are no incipient bridges across Os(1) [+1]—Os(2) [+1] 2.784(3), Os(1) [+1]—Os(5) [0] 2.797(3) and Os(2) [+1]—Os(3) [0] 2.800(2) Å.

Os bond links atoms with the same value of the electron connectivity. As would also follow from Cotton's discussion on 'semi-bridging' carbonyl groups, incipient bridge bonding by carbonyl groups would be expected for metals of different electron connectivity. Tables 1 and 2 summarise the evidence for such bonding interaction as indicated by deviations of Os—C—O groups from linearity and the short metal····C distances observed. The major bonding of this type occurs with metal atoms of different E.C., and always takes the form of an incipient bond between a terminal carbonyl on the metal of a higher E.C. and the metal atom of lower E.C.

Although the isonitrile ligands impose overall C_s symmetry in $Os_6(CO)_{16}(CN\text{-}t\text{-}Bu)_2$, the Os—Os bond lengths show an appreciable C_2 distortion from idealised C_{2v} structure. The C_2 arrangement appears to suffer less carbonyl—carbonyl repulsion than the C_s structure; it appears that the Os—Os distances are able to undergo relative large changes (± 0.06 Å in this instance) to accommodate such interactions.

References

1 C.R. Eady, B.F.G. Johnson, J. Lewis and M.C. Malatesta, unpublished results.
2 M.J. Mays and P.D. Gavens, J. Organometal. Chem., 124 (1977) C37.
3 V.W. Day, R.O. Day, J.S. Kristoff, F.J. Hirsekorn and E.L. Muetterties, J. Amer. Chem. Soc., 97 (1975) 2571.
4 M. Green, J.A.K. Howard, M. Murray, J.L. Spencer and F.G.A. Stone, J. Chem. Soc. Dalton, (1977) 1509.
5 R. Mason, K.M. Thomas and D.P.M. Mingos, J. Amer. Chem. Soc., 95 (1973) 3802.