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The Pyrolysis of Isonitrile Substituted Derivatives of Triosmium Dodecacarbonyl

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SUMMARY

The pyrolysis of the isonitrile substituted complexes $Os_3(CO)_{12-x}(CNR)_x$ ($R = Bu^t$, $x = 1,2$) in refluxing octane has been studied. From these pyrolysis reactions and from the reaction of $Os_3(CO)_{12}$ with Bu^tNC in refluxing octane the series of hexanuclear complexes $Os_6(CO)_{18-x}(CNBu^t)_x$ ($x = 1$-5) has been isolated. The pyrolysis of $Os_3(CO)_{11}(CNBu^n)$ also leads to the formation of higher nuclearity clusters and evidence is presented that one product of the reaction is $Os_6(CO)_{17}(CNBu^n)_2$. Possible structures for these isonitrile substituted hexanuclear complexes are discussed in the light of the known structures of $Os_6(CO)_{16}(CNBu^t)_2$ and $Os_6(CO)_{18}(CNC_6H_4Me)_2$.

INTRODUCTION

The pyrolysis of $Os_3(CO)_{12}$ at elevated temperatures (210-260°C) leads to the formation of polynuclear osmium carbonyl species based on 5-8 osmium atoms, and represents the only known synthetic route to many of these higher nuclearity clusters [1].

In the presence of water the course of the reaction is modified, and hydridocarbonyl complexes containing up to seven metal atoms are obtained [2]. It might have been expected that the pyrolysis of $Os_3(CO)_{12}$ derivatives of the type $Os_3(CO)_{12-x}L_x$ (L = 2-electron donor ligand) would also lead to the formation of higher nuclearity clusters but in general this is not the case. Instead reactions involving modifications of one or more of the ligands L, usually with the loss of at least one CO group, are the most common outcome of such pyrolyses. Thus, for example, $Os_3(CO)_{11}(PR_3)$ (R = Me, Et) undergoes a hydrogen abstraction reaction on refluxing in nonane (b.p., 151°C) to give $H_2Os_3(R_2PCR')(CO)_9$ (R = Me, R' = H; R = Et, R' = Me) [3]. The reactions at elevated temperature of $Os_3(CO)_{12}$ with other 2-electron donor ligands such as Ph_3P [4], $PhNH_2$ [5] and C_5H_5N [6], all give products in which the ligands are present in a modified form, but do not lead to the formation of higher nuclearity cluster. The pyrolysis of $Os_3(CO)_{11}[P(OMe)_3]$ at 210°C does lead to a number of pentanuclear clusters and of the several products of this reaction the complexes $Os_5(CO)_{15}(POMe)$ [7], $HOs_5(CO)_{14}[OP(OMe)_2]C$ [8] and $HOs_5C[OP(OMe)OP(OMe)_2]$ [9] have had their crystal structures determined by X-ray analysis. It will be seen that all these products also contain at least one $(MeO)_3P$ ligand in a modified form. No higher nuclearity clusters in which such modification of the ligand has not taken place were isolated.

In a preliminary communication we reported that the reaction of $Os_3(CO)_{12}$ in refluxing heptane solution with isonitrile ligands gives the substituted complexes $Os_3(CO)_{12-x}(CNR)_x$ (x = 1-4) [10]. It was shown that these isonitrile substituted derivatives undergo pyrolysis to give higher nuclearity clusters at much lower temperatures (125°C in refluxing octane) than are needed to pyrolyse $Os_3(CO)_{11}P(OMe)_3$ or $Os_3(CO)_{12}$ itself. At these lower temperatures, and using Bu^tNC as the ligand, pyrolysis leads exclusively to hexanuclear complexes of the type $Os_6(CO)_{18-x}(CNBu^t)_x$ (x = 1-5). No products involving modification of any of the ligands are formed. In this paper a full account of these pyrolysis reactions is presented.

RESULTS AND DISCUSSION

The complex $Os_3(CO)_{11}(CNBu^t)$ on refluxing in dry octane for 16 h. under a nitrogen atmosphere gives a mixture which was shown by t.l.c. to consist of some unchanged starting material and approximately equal amounts of two brown products. These were identified as $Os_6(CO)_{16}(CNBu^t)_2$ and $Os_6(CO)_{15}(CNBu^t)_3$ by mass spectroscopy (prominent molecular ion peaks were observed) and by microanalysis (Table 1). The disubstituted derivative was further characterised by a crystal structure determination using X-ray analysis [11]. Pyrolysis of $Os_3(CO)_{10}(CNBu^t)_2$ in a similar fashion led to the production of approximately equal quantities of $Os_6(CO)_{15}(CNBu^t)_3$ and $Os_6(CO)_{14}(CNBu^t)_4$. The overall product yield for both of these reactions was _ca_. 60% and was not increased by refluxing for a longer period. Even after 36 h. the composition of the reaction mixtures was essentially unchanged, suggesting that an equilibrium position had been reached. The course of the reaction was also unaffected by either the concentration of the reactant or by the pyrolysis temperature. Below 125°C, however, the reaction occurred much more slowly, whilst in refluxing decalin considerable decomposition to osmium metal took place.

Pyrolysis of $Os_3(CO)_{12-x}(CNBu^t)_x$ (x = 1 or 2) did not give the monosubstituted derivative $Os_6(CO)_{17}(CNBu^t)$ as a product, but this complex was produced on refluxing $Os_3(CO)_{12}$ itself with two mole equivalents of Bu^tNC in octane. By this means a mixture containing the complete range of complexes $Os_6(CO)_{18-x}(CNBu^t)_x$ (x = 1-5) was obtained. To some extent the relative proportions of these products could be controlled by varying the initial concentration of Bu^tNC, but ratios of Bu^tNC to $Os_3(CO)_{12}$ higher that 2:1 led to extensive decomposition, and this limited our ability to produce more highly substituted clusters. Indeed only trace quantities of $Os_6(CO)_{13}(CNBu^t)_5$ were ever obtained, and characterisation of this complex is based on mass

TABLE 1

ANALYTICAL DATA FOR ISONITRILE SUBSTITUTED Os_6 CLUSTERS

Cluster	Analysis (Found(Calcd.)(%))		
	C	H	H
$Os_6(CO)_{17}(CNBu^t)$	16.5 (15.6)	0.73 (0.53)	0.98 (0.82)
$Os_6(CO)_{16}(CNBu^t)_2$	18.5 (17.8)	1.90 (1.03)	1.69 (1.60)
$Os_6(CO)_{15}(CNBu^t)_3$	19.92 (19.89)	0.75 (1.49)	2.00 (2.32)
$Os_6(CO)_{14}(CNBu^t)_4$	22.3 (21.9)	2.02 (1.93)	3.00 (3.00)
$Os_6(CO)_{17}(CNBu^n)_2$	18.8 (18.1)	1.86 (1.00)	1.64 (1.56)

TABLE 2

IR and 'H n.m.r. DATA FOR $Os_6(CO)_{18-x}(CNBu^t)_x$ COMPLEXES

Complex	IR[a]			'H n.m.r.
	Solvent	ν(RNC)	ν(CO)	δ[b]
$Os_6(CO)_{17}(CNBu^t)$	CH_2Cl_2	2187m	2091m,2066sh,2058vs,2038vs,2027vs.	1.54
$Os_6(CO)_{16}(CNBu^t)_2$	C_6H_{12}	2169m	2078w,2066m,2050sh,2036s,2026vs,2016sh,1986sh,1961m,1942w,1920w.	1.51
$Os_6(CO)_{15}(CNBu^t)_3$	C_6H_{12}	2162m	2067w,2055w,2043m,2020vs,2015sh,2000sh,1981m,1963w.	1.49
$Os_6(CO)_{14}(CNBu^t)_4$	CH_2Cl_2	2198sh 2171m 2138sh	2063sh,2027s,2006s,1988m,1943w.	1.47
$Os_6(CO)_{13}(CNBu^t)_5$	C_6H_6	2189m 2158m	2081m,2046sh,2041s,2028s,2018sh,1993m,1985m,1977w.	

[a] In cm^{-1} [b] In CD_2Cl_2. δ in ppm relative to TMS

spectroscopy alone although an i.r. spectrum was also recorded (Table 2).

The skeletal electron count for the complexes $Os_6(CO)_{18-x}(CNBu^t)_x$ is the same as for $Os_6(CO)_{18}$ itself, and it is therefore not unexpected that the crystal structure determination carried out on $Os_6(CO)_{16}(CNBu^t)_2$ [11] reveals that the metal atom skeleton present in $Os_6(CO)_{18}$ [12] is preserved in the disubstituted derivative (Figure 1). The structure of $Os_6(CO)_{17}(CNBu^t)$ is not known but seems almost certain to be derived from that of the disubstituted complex by replacing one $CNBu^t$ ligand with a CO group. In $Os_6(CO)_{18}$ there are three pairs of equivalent osmium atoms which may be distinguished by the number of other osmium atoms (3, 4 and 5) to which each atom in the pair is bonded [12]. Since in the disubstituted derivative the Bu^tNC ligands are

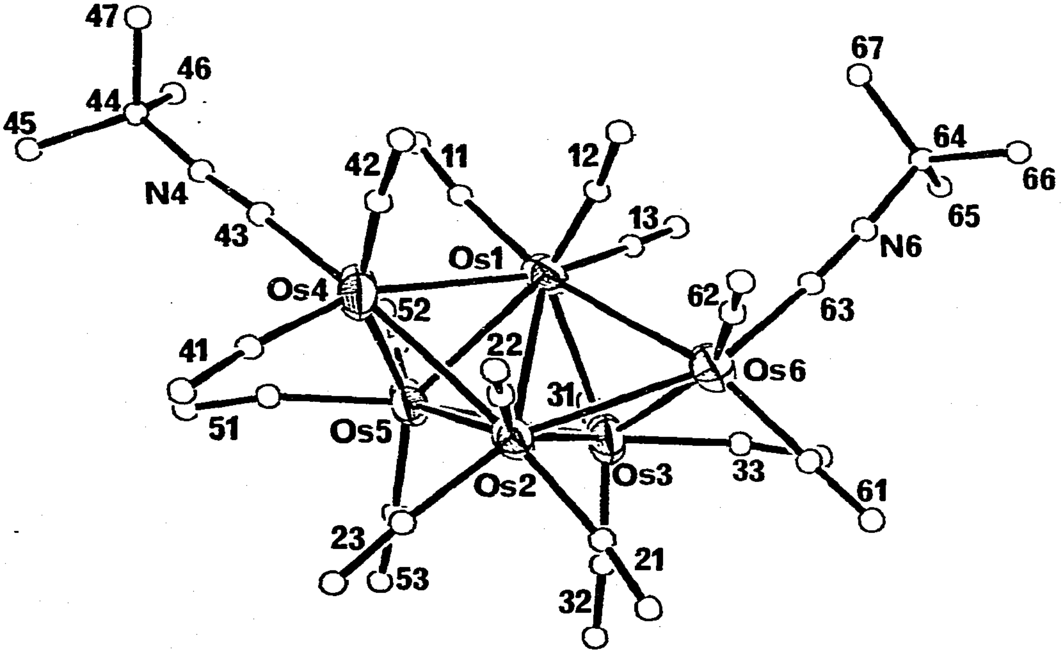

FIGURE 1 The molecular structure of $Os_6(CO)_{16}(CNBu^t)_2$.

attached to the osmium atoms associated with three metal-metal bonds it seems most probable that in the tri- and tetra-substituted derivatives the additional substituents bond to the osmium atoms associated with 4 metal-metal bonds. This implies that the Bu^tNC ligands in the tri- and tetra-substituted derivatives are not all equivalent, but the 'H n.m.r. of the substituted complexes revealed only one signal due to the methyl protons in each case (Table 2). It seems most probable that this is because the chemical shift differences between the different types of methyl groups are too small to be resolved, although the possibility that the molecules are fluxional in solution cannot be eliminated on this basis. It is noteworthy, however, that in $Os_6(CO)_{18}$ itself ^{13}C n.m.r. spectroscopy reveals that there is no interchange of CO ligands between metal atoms on the n.m.r. timescale [13].

The solution infrared spectra of the Bu^tNC substituted complexes (Table 2) show no bands which may be attributed to bridging CO or CNR ligands. In no case does the number of bands in the terminal region due to $\nu(CO)$ or $\nu(CNR)$ require the existence of more than one isomer in solution to be postulated. On the other hand the bands are broad and tend to overlap so that this possibility cannot be ruled out.

The substituted derivatives $Os_6(CO)_{18-x}(CNBu^t)_x$ are much more difficult to reduce than the parent carbonyl complex. Thus, whereas $Os_6(CO)_{18}$ is readily reduced to $[Os_6(CO)_{18}]^{2-}$ even by $Bu_4{}^nNI$ [14], the substituted derivatives are unaffected by this reagent nor by a variety of other stronger reducing agents such as NaH, $NaBH_4$ or $LiAlH_4$. This may be a reflection of the better σ-donor and poorer π-acceptor properties of Bu^tNC as a ligand compared to CO, which presumably increases the electron density on the cluster thereby reducing its tendency to accept further electrons.

The pyrolysis of $Os_3(CO)_{11}(CNBu^n)$ [10] under similar conditions to those used for $Os_3(CO)_{11}(CNBu^t)$ gave a mixture which was separated into three brown products using t.l.c. The product which moved fastest on the t.l.c. plate gave a mass spectrum with a molecular ion peak at $^m/_e$ 1784, the isotope pattern of which was characteristic of six osmium atoms. The only reasonable formulation for this compound would seem to be $Os_6(CO)_{17}(CNBu^n)_2$. This compound, formally a derivative of the unknown $Os_6(CO)_{19}$ is interesting in view of the synthesis of $Os_6(CO)_{18}(CNC_6H_4Me)_2$ from $Os_6(CO)_{18}$ and MeC_6H_4NC [15]. In this latter complex an X-ray crystal structure determination reveals that one isonitrile ligand acts as a 4-electron donor and the other as a 2-electron donor ligand [11]. The complex therefore has an electron count 6 in excess of that for $Os_6(CO)_{18}$, and this is reflected in the metal atom skeleton which has only 9 Os-Os bonds as opposed to the 12 which are present in $Os_6(CO)_{18}$ itself [12]. On this basis the metal atom skeleton in $Os_6(CO)_{17}(CNBu^n)_2$ could have from 9 to 11 metal-metal bonds depending on whether the isonitrile ligands act as 2- or 4-electron donors. On the other hand a summation of electron according to the Wade approach [16] (assuming the Bu^nNC ligands act as 2-electron donors) indicates that there are sevel electron pairs available for skeletal bonding in $Os_6(CO)_{17}(CNBu^n)_2$. This is consistent either with an octahedron of metal atoms (with 12 Os-Os bonds) as found in $[HOs_6(CO)_{18}]^-$ [17] or with a capped sqaure-based pyramid (also with 12 Os-Os bonds) as found in $H_2Os_6(CO)_{18}$ [17]. The large number of $\nu(CO)$ bands seen in the infrared spectrum of the complex in hexane solution (Table 2) suggests that the molecule has a low symmetry. A relatively broad band at 2109 cm^{-1} may be assigned to ν(RNC) of a terminal $CNBu^n$ group and, in addition, there is a band at 1630 cm^{-1} which is not found in any of the simple substituted derivatives. It is, however, at an appropriate frequency for ν(RNC) of an isonitrile ligand acting as a 4-electron donor. In the i.r. spectrum of $Ni_4(CNBu^t)_7$, for example, there are two bands at 1610 and 1605 cm^{-1} which have been attributed to this stretching mode [18]. This suggests that the structure of $Os_6(CO)_{17}(CNBu^n)_2$ may be related to that of $Os_6(CO)_{18}(CNC_6H_4Me)_2$, with one additional metal-metal bond being present. Unfortunately, crystals of the quality required for an X-ray determination could not be obtained.

The other two products of the reaction of $Os_3(CO)_{12}$ with Bu^nNC were difficult to characterise, since they decomposed slowly on silica. One product gave a mass spectrum with a molecular ion peak at $^m/_e$ 1812 corresponding to the formulation $Os_6(CO)_{18}(CNBu^n)_2$, and is probably analoguous to $Os_6(CO)_{18}(CNC_6H_4Me)_2$ [11]. The other complex formed in the reaction had peaks in its mass spectrum with an isotope pattern which suggested that it was an Os_7 cluster, but neither this complex nor $Os_6(CO)_{18}(CNBu^n)_2$ could be obtained free from impurities and were not characterised further.

The reactions between $Os_3(CO)_{12}$ and aryl isocyanides (p-$MeOC_6H_4NC$ and PhNC) in refluxing octane were also briefly investigated. However, chromatography of the reaction mixture showed that as many as twenty products had been formed. The behaviour of some of these complexes on the t.l.c. plates together with mass spectroscopic data indicated that higher nuclearity clusters had been formed, in contrast to the outcome of reactions with aryl phosphines [4]. However, in view of the complexity of the reaction and the low yields of all the products (together with the difficulties experienced in the separation procedures) these reactions were not investigated in detail.

EXPERIMENTAL

(a) Pyrolysis of $Os_3(CO)_{11}(CNBu^t)$

$Os_3(CO)_{11}(CNBu^t)$ (0.01g, 0.01 mmol) was refluxed in dry octane (40 cm^3) under N_2 for 16 h. The mixture was chromatographed on silica-coated t.l.c. plates using a 3:1 hexane:acetone mixture as eluant. In addition to a fast moving yellow band due to unreacted $Os_3(CO)_{11}(CNBu^t)$ two slow moving brown bands developed. These were scraped off the plates, extracted with CH_2Cl_2 and evaporated to dryness. The compounds were recrystallised from acetone/hexane. The faster moving of the two brown bands was then characterised as $Os_6(CO)_{16}(CNBu^t)_2$ and the slower moving band as $Os_6(CO)_{15}(CNBu^t)_3$. The pyrolysis of $Os_3(CO)_{10}(CNBu^t)_2$ was carried out similarly.

(b) Reaction of $Os_3(CO)_{12}$ with Bu^tNC in n-octane

$Os_3(CO)_{12}$ (0.30g, 0.33 mmol) was refluxed with Bu^tNC (0.03g, 0.36 mmol) in octane (50 cm^3) for 3 h. An additional 0.03g of Bu^tNC was then added and the mixture was refluxed for a further 12 h. The complexes $Os_6(CO)_{18-x}(CNBu^t)_x$ (x = 1-5) were then separated by the procedure described above. The more highly substituted the complex the slower it moved on the t.l.c. plate.

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