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A novel reaction of $Os_6(CO)_{18}$ with Me_3NO; isolation and NMR study of the new hexaosmium cluster anion $[HOs_6(CO)_{17}]^-$

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Abstract

In the absence of a ligand and in non-coordinating solvents, $Os_6(CO)_{18}$ reacts with 2 equivalents of R_3NO (R = Me, Et) to give the new hexaosmium cluster $[HOs_6(CO)_{17}]^-$. Variable temperature ^1H and ^{13}C NMR and ^2D NMR techniques have been used to investigate the structure of this anion and its dynamic behaviour in solution. The mechanism of the novel reaction is discussed.

Extensive use has been made of trialkylamine oxides as decarbonylating agents for activation of transition metal carbonyl clusters towards substitution [1–3]. The reaction is thought [1] to result in replacement of CO by a NMe_3 ligand, however, the Me_3N-substituted derivatives can seldom be isolated. The decarbonylation reaction is often carried out in the presence of acetonitrile or a ligand L (e.g. L = PR_3, PR_2H) and the MeCN- or L-substituted product isolated directly. Thus the reaction of $Os_6(CO)_{18}$ with n equivalents of Me_3NO in CH_2Cl_2/MeCN solution produces $Os_6(CO)_{18-n}(MeCN)_n$ ($n = 1, 2$) [3]. Recently we have been investigating the reaction of $Os_6(CO)_{18}$ with Me_3NO in the absence of a ligand and in non-coordinating solvents and have found that, with 2 equivalents of Me_3NO, the previously unknown hexanuclear anion, $[HOs_6(CO)_{17}]^+$, is produced in high yield. In this report, we present a detailed NMR study of $[HOs_6(CO)_{17}]^-$, on the basis of which a solution structure for this anion is suggested. A possible mechanism for the novel Me_3NO reaction is also discussed.

The reaction of $Os_6(CO)_{18}$ with two equivalents of Me_3NO is very rapid at room temperature and produces the red-brown $[HOs_6(CO)_{17}]^-$ (**1**) in almost quantitative yield. Compound **1** is air-stable and can be isolated by thin layer chromatography or by precipitation as the $[N(PPh_3)_2]^+$ salt. The anions has not been characterised structurally but, being isoelectronic to $Os_6(CO)_{18}$, is suggested to have a structure based on a bicapped tetrahedron of osmium atoms [4]. The 400 MHz ^1H NMR spectrum of **1** at room temperature shows a very broad hydride signal at δ −9.9 which resolves to a sharp singlet on cooling to 260 K. This signal shows two ^{187}Os satellites (J 31.7, 48.3 Hz) indicating that the hydride is in a bridging position

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between two inequivalent osmium atoms. On heating to 340 K, an up-field shift of the hydride signal to δ -10.4 is observed and above this temperature the signal begins to sharpen again. On cooling to room temperature again, this shift is completely reversed. These observations could be explained in terms of an intramolecular isomerisation process, involving exchange of the hydride ligand between different bridging sites on the cluster. The two hydride signals observed would then correspond to two different isomers of $[HOs_6(CO)_{17}]PPN$ which exist in a highly temperature-dependent equilibrium so that only one isomer is present in detectable concentration at each of the high and low temperature limits. However, dynamic processes involving a carbonyl rearrangement or a structural transformation would also be consistent with the variable temperature ^1H NMR data.

To obtain further structural information, a variable temperature study of the ^{13}C NMR spectrum of $[HOs_6(CO)_{17}]PPN$ has been carried out using a ^{13}CO enriched sample (~ 30%) [5*]. The room temperature ^{13}C NMR spectrum shows six broad resonances between 176 and 194 ppm (see Fig. 1a). On cooling to 250 K, signal E broadens, collapses and, at 230 K, separates into three signals of equal intensity. Signal D similarly collapses and separates into two signals of relative intensity 1 : 2 on cooling to 210 K. At 190 K, signal F is resolved into two signals in the ratio 1 : 2 so the ^{13}C spectrum shows ten sharp carbonyl signals, three of which are split into doublets by coupling to the hydride ligand (see Fig. 1). The carbonyl arrangement shown in Fig. 2, based on that observed for $Os_6(CO)_{18}$ [4], with Os(2) as the unique osmium atom having only two CO ligands, is consistent with the low temperature limiting spectrum. The position of the hydride, bridging Os(1) and Os(2), is inferred from the observed $^{13}C-^1H$ couplings (a *trans* coupling to carbonyl 1a and *cis* couplings to the equivalent carbonyls 1b,c and 2a,b) and from the overall symmetry of the carbonyl arrangement. The assignments of resonances to the carbonyls on osmiums 3, 4 and 5 are made on the basis of the exchange processes observed and are not unambiguous. The dynamic behaviour of **1** between 210 and 290 K, which results in the averaging of three sets of signals, is consistent with a localised exchange of carbonyls between different sites on three inequivalent osmium centres, analogous to that reported for $Os_6(CO)_{18}$ [6]. Thus in the room temperature spectrum, signals D, E and F correspond to the average carbonyl environments on osmiums 4, 3 and 5.

The considerable broadening of the signals A, B and C in the room temperature spectrum of **1** suggested that further exchange processes were occurring at this temperature so a two-dimensional ^{13}C NOE(NOESY) experiment was carried out. This NMR method has been useful for both the detection and quantification of CO exchange phenomena in triosmium and triruthenium clusters [7] and, in our work, has been successfully applied to the examination of chemical exchange in several hexaosmium systems. The result of the NOESY experiment carried out on **1** at 290 K is shown in Fig. 3; assuming that there are no direct $^{13}C-^{13}C$ dipolar interactions [8*], the cross peaks in the ^2D spectrum can be attributed to exchange between the interconnected sites, so the experiment indicates that exchange occurs between all sites on the cluster. This total CO scrambling is surprisingly facile considering that, in $Os_6(CO)_{18}$, no carbonyl migration between osmium atoms is observed even at

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* Reference number with asterisk indicates a note in the list of references.

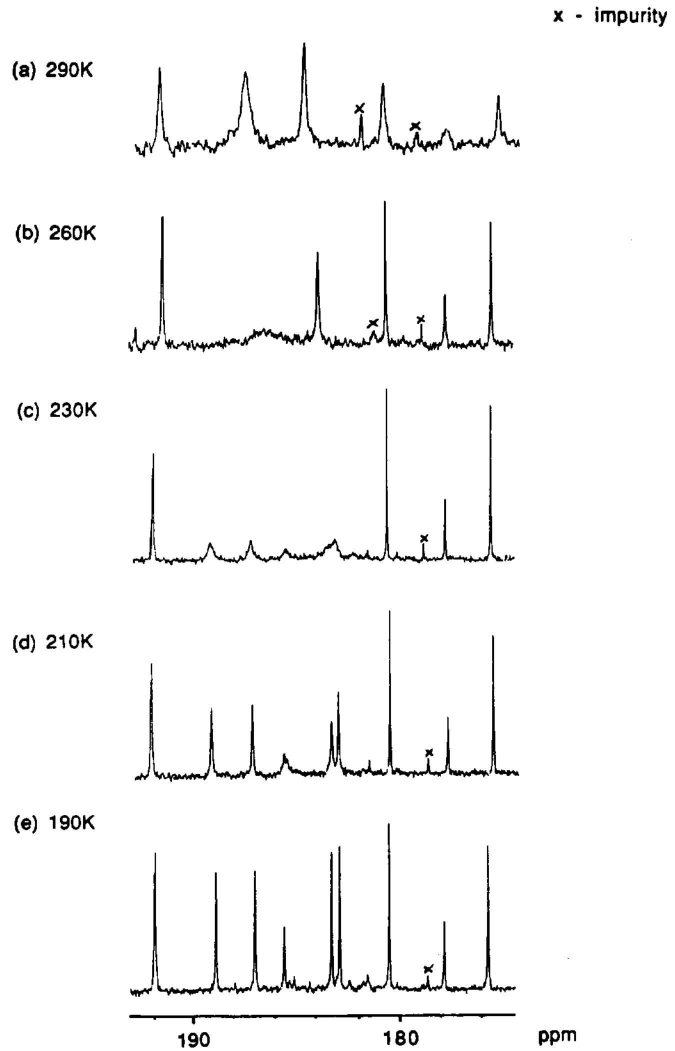


Fig. 1. 400 MHz $^{13}C\{^1H\}$ NMR spectra of $[HOs_6(CO)_{17}]PPN$(in CD_2Cl_2) over the temperature range 290 to 190 K.

360 K [6,9*]. It is likely that the CO scrambling in $[HOs_6(CO)_{17}]^-$ is facilitated by the presence of the vacant coordination site. Scrambling of all carbonyl sites could be achieved by stepwise migration of a carbonyl from a saturated osmium centre to that with the vacant site, resulting in effective movement of the vacant site over the cluster, this would also be consistent with the variable temperature ^1H NMR data. Tertiary phosphine-substituted derivatives of $[HOs_6(CO)_{17}]^-$ are now being studied in an attempt to obtain further information about the fluxional processes occurring in (1).

A mechanism for the formation of $[HOs_6(CO)_{17}]^-$ from $Os_6(CO)_{18}$ and Me_3NO, based on a C–H activation of a coordinated Me_3N group in the amine-substituted derivative $Os_6(CO)_{17}NMe_3$, is proposed (see Scheme 1). Elimination of the amine

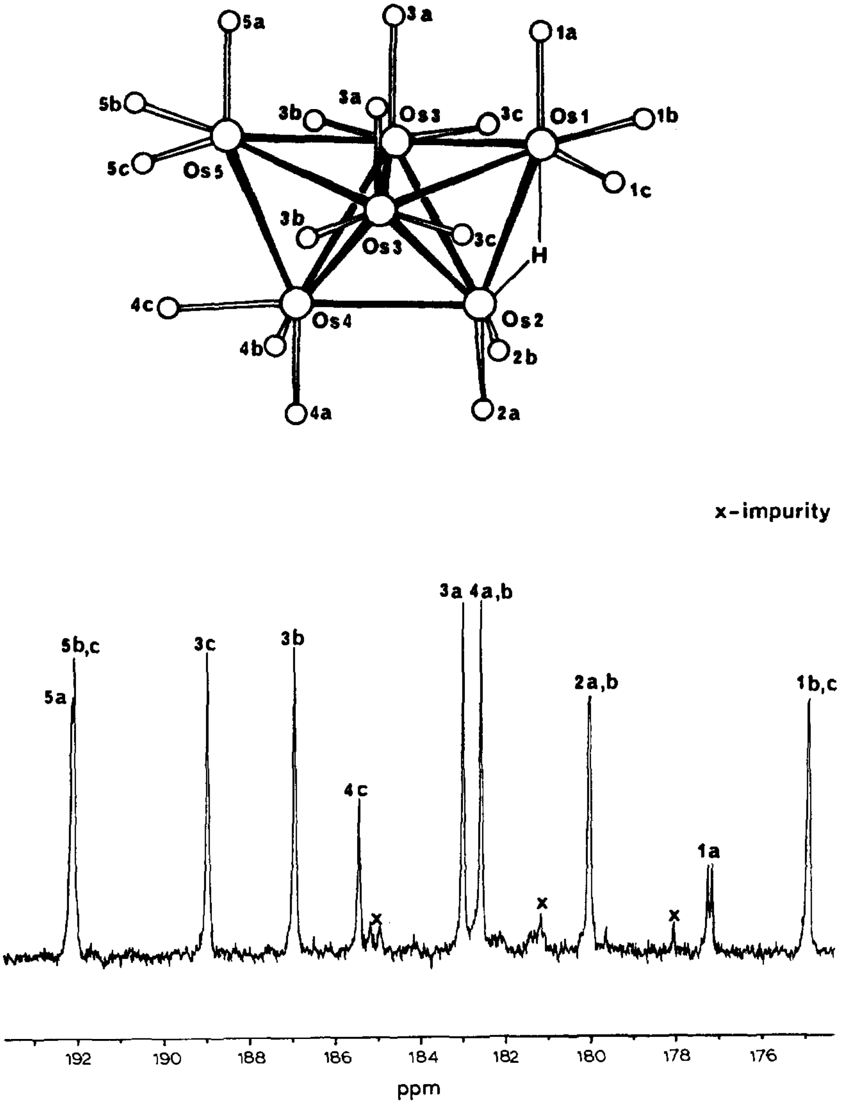


Fig. 2. Proposed solution structure for $[HOs_6(CO)_{17}]PPN$ and a possible assignment of the CO signals in the low temperature ^{13}C spectrum to the different carbonyl environments in this structure.

ligand as an iminium ion would result in formation of the observed cluster product. There are several precedents for such dehydrogenation of amines by osmium clusters in trinuclear systems although these reactions generally require more vigorous conditions [10]. Evidence in support of this proposal has been obtained from the investigation of the reaction of $Os_6(cO)_{18}$ with Et_3NO, which is entirely analogous to that with Me_3NO. This reaction was carried out in CD_2Cl_2 in an NMR tube and signals attributable to the iminium cation $[Et_2N{=}CHCH_3]^+$ were observed in the ^1H NMR spectrum of the reaction mixture [11].

Being isoelectronic to $Os_6(CO)_{18}$, $[HOs_6(CO)_{17}]^-$ may be expected to undergo similar reactions and this has been confirmed in our preliminary investigations of

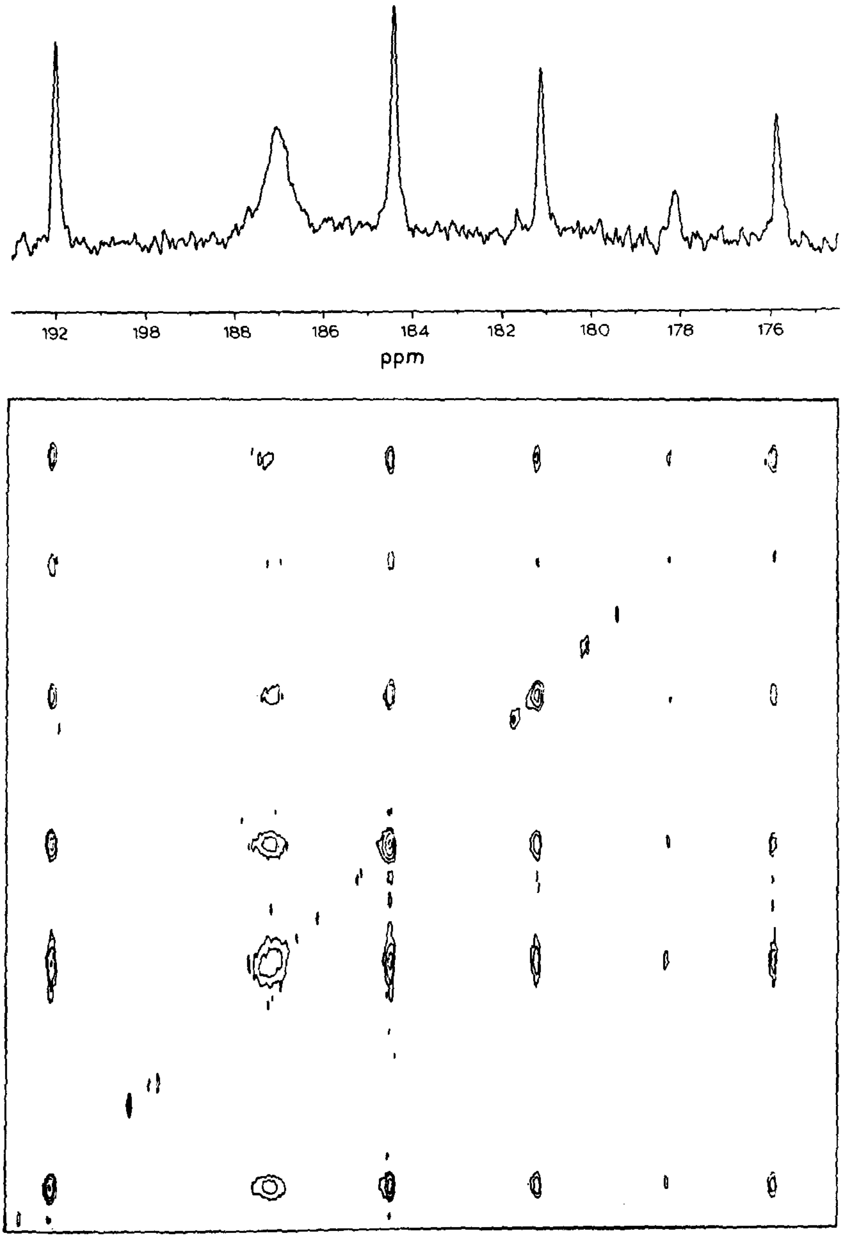
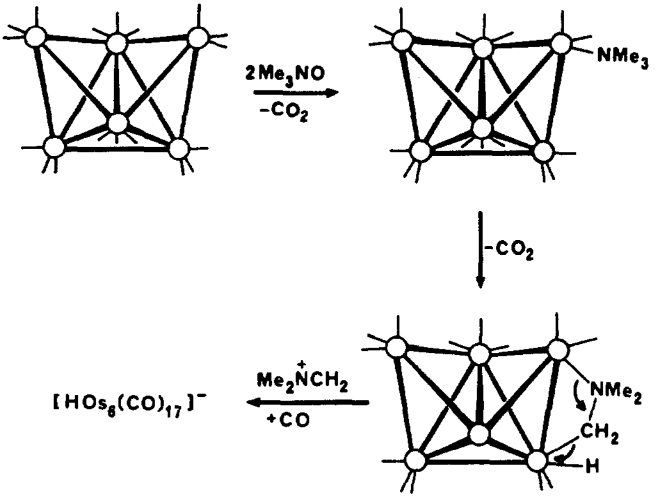


Fig. 3. Contour plot of the ^{13}C NOESY ^2D NMR spectrum of $[HOs_6(CO)_{17}]PPN$ at 290 K using a mixing time of 0.2 s.

the reactivity of (**1**). For example, **1** is susceptible to reduction, treatment with sodium benzophenone ketal in THF producing the trianion $[HOs_6(CO)_{17}]^{3-}$ which is isoelectronic with $[Os_6(CO)_{18}]^{2-}$. Of particular interest are the reactions of **1** with nucleophiles such as CO and tertiary phosphines; **1** is expected to show enhanced activity towards nucleophilc attack, relative to $Os_6(CO)_{18}$, due to the presence of the



Scheme 1. Proposed mechanism for the reaction of $Os_6(CO)_{18}$ with R_3NO (R=Me, Et).

vacant coordination site. The generality of the trialkylamine oxide reaction for the activation of osmium carbonyl clusters and their derivatives is also being tested.

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