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Carbon-13 Nuclear Magnetic Resonance Studies of $[Os_6(CO)_{18}]$†

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Summary The bicapped tetrahedral arrangement of osmium atoms in $[Os_6(CO)_{18}]$ persists in solution up to 100 °C; in the temperature range -123 to $+100$ °C three fluxional processes corresponding to localised CO scrambling are observed.

The polynuclear hexaosmium carbonyl $[Os_6(CO)_{18}]$, which is prepared by the pyrolysis of dodecacarbonyltriosmium,[1] has been shown[2] by single crystal X-ray analysis to possess a bicapped tetrahedral structure with three terminal carbonyl groups per osmium atom. This structure may best be rationalised in terms of the Wade electron counting scheme.[1b,3] Of interest in this structure is the presence of three different pairs of osmium atoms [Os(1), Os(2),

and Os(3)]. These differ both in their co-ordination number [Os(1), 6-co-ordinated; Os(2), 7-co-ordinated; and Os(3), 8-co-ordinated] and the electron density which must be associated with them. We have been able to demonstrate from ^{13}C n.m.r. spectroscopic examination that the bicapped tetrahedral geometry is maintained in solution and further, although CO site exchange takes place readily in the temperature region -123 to $+100$ °C, it occurs in a localised fashion about individual osmium atoms and no evidence for CO migration over the Os_6 cluster (*via* CO-bridged intermediates) has been found. This places the activation energy of any bridge–terminal CO exchange for this molecule in excess of 70 kJ mol^{-1}. In studies of CO lability in carbonyl clusters, the assumption is often made

† No reprints available.

that the geometry of the metal polyhedral unit is maintained. This work confirms that the bicapped tetrahedral geometry of the Os_6 cluster is maintained up to 100 °C and that any rearrangement of this geometry [e.g., bicapped tetrahedron → octahedron (O_h)] requires an activation energy in excess of 70 kJ mol⁻¹. The ¹³C n.m.r. spectra recorded for $[Os_6(CO)_{18}]$ over the temperature range −123 to +100 °C are shown in Figure 1. These were obtained for enriched samples (¹³CO, ca. 60%) which were prepared from enriched $[Os_3(CO)_{12}]$ {$[Os_6(CO)_{18}]$ does not easily undergo CO exchange with ¹³CO} in toluene, $CDCl_3$, and $CHFCl_2$ using an XL-100-15 spectrometer operating at 25·2 MHz in the Fourier transform mode and in the presence of the paramagnetic relaxation reagent $[Cr(acac)_3]$.
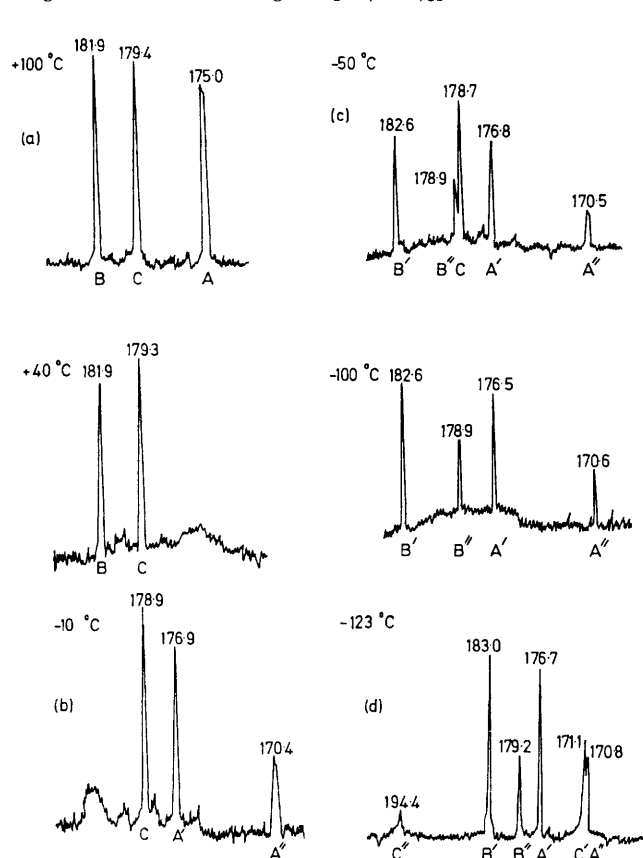
(B′ and B″, Figure 1c). Finally, in the temperature region −100 to −123 °C signal C shows similar broadening and separation phenomena, eventually at −123 °C leading to the overall spectrum shown in Figure 1d which consists of three sets of signals (A′ and A″), (B′ and B″), and (C′ and C″) (−123 °C was the lowest temperature attainable; C′ and C″ had not fully sharpened at this temperature). This spectrum is totally consistent with the known geometry of the carbonyl in which the three different osmium atoms are associated with three CO ligands of types α and β.‡ The temperature dependence of this spectrum may be readily understood in terms of carbonyl scrambling involving independent site exchange about each type of osmium atom.
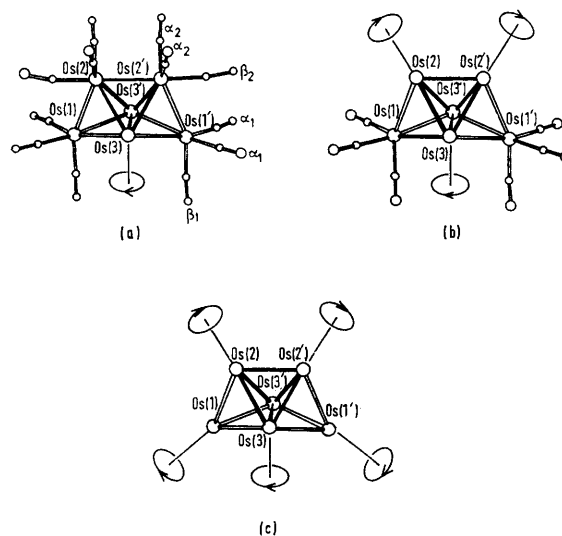

FIGURE 1. ¹³C n.m.r. spectra of $[Os_6(CO)_{18}]$ in the CO region at various temperatures; shifts are relative to Me_4Si.

FIGURE 2. Probable fluxional processes in $[Os_6(CO)_{18}]$.

These phenomena are represented in Figure 2. It is apparent that (a) at ca. −50 °C two sets of carbonyls, viz those associated with Os(3) and Os(3′), undergo exchange about each individual Os, (b) at +40 °C four sets of carbonyls [those associated with Os(3) and Os(3′), and Os(2) and Os(2′)] are exchanging about each metal, and finally (c) at +100 °C all sets of carbonyls undergo localised site exchange. The wide variation in the energy required for this scrambling is shown in the range of $\Delta G^{\ddagger}$ values calculated from the spectra ($\Delta G_A^{\ddagger}$ 61, $\Delta G_B^{\ddagger}$ 53, and $\Delta G_C^{\ddagger}$ 31 kJ mol⁻¹).§ It is of interest to speculate on the reasons why CO migration does not readily occur within this cluster. It may merely reflect the Os–Os distances within the Os_6 framework. Certainly CO bridges are not commonly observed in osmium complexes and, although CO scrambling occurs in $[Os_3(CO)_{12}]$, there is no evidence that this involves migration from one metal atom to another.[4] Alternatively, it may be argued that since the formation of CO bridges necessarily involves an increase in co-ordination number about the metal atom by at least one, for any bridged

The spectrum at +100 °C (Figure 1a) is simple, consisting of three equal intensity singlets A, B, and C. On cooling to +40 °C signal A broadens and at −10 °C separates out into two well resolved peaks of relative intensity 2:1 (A′ and A″, Figure 1b). At about the same temperature signal B begins to broaden and at −50 °C also separates into two well resolved peaks of relative intensity 2:1

‡ ¹³C–¹³C coupling was observable (J ca. 8 Hz, and not ca. 77 Hz as previously reported[4]).

§ For monomeric 7- and 8-co-ordinate species activation energies are low in comparison to those observed with 6-co-ordinate complexes. On this basis it is tempting to associate the values of 31 kJ mol⁻¹ and 53 kJ mol⁻¹ with rearrangement about osmium atoms with the highest co-ordination number [i.e., Os(3), Os(3′), Os(2), and Os(2′)] and that of 61 kJ mol⁻¹ with rearrangement about Os(1) and Os(1′). However, it should be remembered that these energy differences may reflect a change in the $\Delta S^{\ddagger}$ term rather than the $\Delta H^{\ddagger}$ term in the energy equation.

intermediate unreasonably high co-ordination numbers [7, Os(1); 8, Os(2); and 9, Os(3)] would be required.

On reduction with, *e.g.*, activated zinc, $[Os_6(CO)_{18}]$ is quantitatively converted into the dianion $[Os_6(CO)_{18}]^{2-}$, whose i.r. and ^{13}C n.m.r. spectra [δ (CD_2Cl_2) 195·0 at 25·2 MHz, −113 to 0 °C] indicates that it possesses an octahedral (O_h) arrangement of osmium atoms. This is in agreement with Wade's theory which predicts an O_h arrange-

ment for 86-electron species and which has been observed in *e.g.*, $[Rh_6(CO)_{16}]$.

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