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Stereospecific Exchange of Carbon Monoxide in Clusters of the Type $[Os_3(CO)_{10}X_2]$

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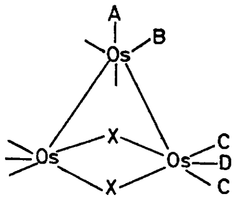
Summary A ^{13}C n.m.r. study of complexes of the type $[Os_3(CO)_{10}X_2]$, where X is a three-electron donor, has shown that stereospecific exchange of labelled carbon monoxide occurs on the non-unique osmium atoms, that a subsequent exchange process distributes this label among the non-equivalent sites on the non-unique osmium atoms, and that carbonyl bridging between different types of osmium atoms does not occur.

ALTHOUGH the potential of ^{13}CO n.m.r. spectroscopy as a structural and mechanistic tool in metal cluster chemistry has recently become apparent,[1] the limited solubility of metal carbonyl cluster compounds, coupled with the low abundance and low sensitivity (relative to ^1H) of the ^{13}C nucleus, often necessitates the use of isotopically enriched samples in the recording of ^{13}CO n.m.r. spectra. A number of discussions of intermolecular carbon monoxide exchange processes have appeared in the literature, which mostly involve dissociative mechanisms and result in the isotopic enrichment being distributed statistically among the non-equivalent sites of the molecule. This statistical distribution is almost always found to occur for both cluster and mononuclear compounds and only in the case of $[Ru(CO)_4(SiCl_3)_2]$[2] has stereospecific exchange of ^{13}CO been previously reported. We have undertaken a ^{13}CO n.m.r. study of some compounds of the type $[Os_3(CO)_{10}X_2]$ (X = Cl, Br, I, and OEt) and have discovered that these compounds have the novel property of exchanging the two pseudo-equatorial carbonyl ligands (D; Figure) while the carbonyl groups A, B, and C do not exchange. The subsequent distribution of isotopically enriched carbon monoxide about the non-unique osmium atoms can be achieved by refluxing the samples in toluene for as short a time as 5 min; however, under these moderate conditions, carbonyl exchange does not occur between different osmium atoms *via* carbonyl bridging.



FIGURE

$[Os_3(CO)_{10}Cl_2]$ was prepared using the published method[3] from $[Os_3(CO)_{12}]$ and ^{13}CO enriched $[Os_3(CO)_{12}]$. The isotopically enriched species $[Os_3(CO)_{10}Cl_2]$ displayed four carbonyl resonances at all temperatures studied (−90 to 95 °C), *viz.*: 182·6, 177·7, 177·0, and 178·3 p.p.m. with an intensity ratio of *ca.* 1:2:1:1. This spectrum is fully consistent with the expected geometry for complexes of this type (Figure). The unenriched sample was stirred at room temperature under ^{13}CO in toluene for 3 days and the resulting compound displayed only one carbonyl resonance at 168·3 p.p.m. showing that carbon monoxide substitution had occurred stereospecifically at positions A, B, or D. The sample was heated to 110 °C in toluene for $<$ 5 min and the ^{13}CO n.m.r. spectrum then consisted of two lines at 177·7 and 168·3 p.p.m. in the intensity ratio *ca.* 2:1. This indicates a distribution of ^{13}CO in the sites C and one of the sites A, B, or D and further heating at 110 °C for up to 1 h did not lead to the statistical distribution of ^{13}CO among the non-equivalent sites in the complex. We have previously shown[4] that for systems of the type $[Os_3(CO)_{10}HX]$, carbonyl scrambling about the *triangulo* osmium unit *via* bridge formation does not occur in this temperature range and we therefore make the following assignments: 182·6 (A/B), 177·7 (C), 177·0 (A/B), and 168·3 (D) p.p.m. and conclude that carbonyl group D undergoes stereospecific exchange and that a thermal rearrangement occurs to give a statistical distribution of ^{13}CO among the non-equivalent sites (C/D) on the non-unique osmium atoms.

The spectra were recorded on a Varian XL 100 spectrometer operating in the Fourier transform mode at 25·2 MHz using $CD_3C_6D_5$ as solvent in the presence of 0·05M $[Cr(acac)_3]$. All chemical shifts are quoted relative to Me_4Si. The investigation of these systems is continuing and preliminary results indicate that these unusual substitution and exchange properties are general to compounds of this type (X = Cl, Br, I, or OEt).

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