The Initial Reaction of $Os_3(CO)_{12}$ with Halogens

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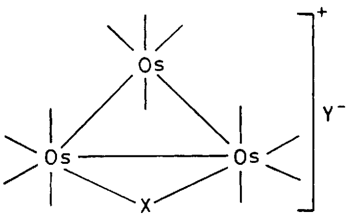
The reaction of $Os_3(CO)_{12}$ with chlorine or bromine yields as the first observed product *ax,eq*-$Os_3(CO)_{12}(X)_2$ (X = Cl or Br) whereas the corresponding reaction with iodine gives $[Os_3(CO)_{12}(I)][I_3]$.

The reaction of $Os_3(CO)_{12}$ with halogens (X_2; X = Cl, Br, I) yields as the first product $Os_3(CO)_{12}(X)_2$.[1] These derivatives were originally thought to have a linear XOs_3X arrangement of atoms, but the crystal structure of $Os_3(CO)_{12}(I)_2$ revealed a linear Os_3 chain with the iodine ligands in *cis* positions to this chain on different terminal osmium atoms [*i.e.*, (**3c**)].[2] We recently recorded[3] the ^{13}C NMR spectrum of $Os_3(CO)_{12}(I)_2$ and were surprised to find that as prepared by the literature method the product had far more resonances than that expected for the structure (**3c**). This prompted an investiga-

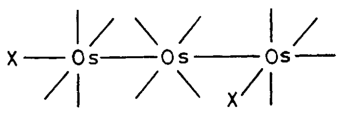
Table 1. ^{13}C NMR and IR spectroscopic data for the halogeno-osmium derivatives.

	δ(CO)[a]	ν(CO)[b]
(1a)[c]	179.6(4), 175.8(2), 168.8(2), 167.0(2), 156.8(2)	2139.5(s), 2099.5(s), 2082(vs), 2055.5(m), 2023(w)
(1c)	174.9(2), 172.2(4), 166.0(2), 164.2(2), 154.8(2)	2133(s), 2097(s), 2077(vs), 2053(m), 2022(w)
(1d)[d]	177.4(2), 174.9(4), 168.6(2), 166.1(2), 157.4(2)	2134(s), 2097(s), 2077(vs), 2051.5(m), 2020.5(w)
(2a)	184.0(4), 177.5(2), 175.8(4), 168.5(1), 161.5(1)	2153(vw), 2124(m), 2082(w,sh), 2063(s), 2039.5(s), 1998(w)
(2b)	184.2(4), 175.4(2), 175.1(4), 168.0(1), 160.3(1)	2151(vw), 2122.5(m), 2081(w,sh), 2061.5(s), 2039.5(s), 1998.5(w)
(2c)[e]	(185.0) (174.4)	
(3a)	184.4(4), 178.7(4), 169.1(2), 161.7(2)	2150(vw), 2120(s), 2062.5(vs,br.), 2030.5(s), 2002.5(w)
(3b)	185.0(4), 176.3(4), 168.6(2), 160.4(2)	2148.5(vw), 2118.5(s), 2061.5(vs,br.), 2030.5(s), 2001.5(w)
(3c)	186.3(4), 172.8(4), 167.0(2), 158.8(2)	2144(w), 2114(s), 2085(vw), 2059(vs,br.), 2029.5(s), 2000(w)

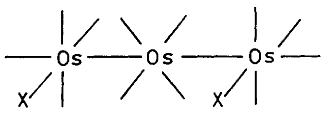
[a] Spectra in CH_2Cl_2/CD_2Cl_2 (4:1) at −30 °C unless otherwise indicated. [b] Spectra in CH_2Cl_2. [c] Ambient temperature. [d] [$^2H_6$]-Acetone, ambient temperature. [e] Tentative assignment, see text; spectrum of $Os_3(CO)_{12}$ under the same conditions: δ 182.9, 170.7.



(1) a; X = Cl, Y = $SbCl_6$
c; X = I, Y = I_3
d; X = I, Y = PF_6



(2) a; X = Cl
b; X = Br
c; X = I



(3) a; X = Cl
b; X = Br
c; X = I

tion of the initial reaction of $Os_3(CO)_{12}$ with halogens which has revealed that it is much more complicated than has been suspected previously.

Dropwise addition of a saturated solution of Cl_2 in CH_2Cl_2 to a solution of $Os_3(CO)_{12}$ in CH_2Cl_2 at −30 °C caused an immediate colour change from yellow to colourless. Nitrogen was bubbled through the solution to remove excess chlorine and hexane was added to afford a white solid that analysed as $Os_3(CO)_{12}(Cl)_2$ **(2a)**. When the reaction was monitored by ^{13}C NMR spectroscopy [^{13}CO-enriched $Os_3(CO)_{12}$; CH_2Cl_2/CD_2Cl_2, 4:1 solution], the spectrum of the reaction mixture, taken as soon as possible after the addition of Cl_2, revealed five major signals (Figure 1; Table 1) in the ratio 4:2:4:1:1. When the sample was allowed to stand at room temperature these signals disappeared over three hours whilst the weak signals observed in the initial spectrum grew in intensity. The 2:2:1:1 pattern for the latter signals is that expected for the known diequatorial isomer of $Os_3(CO)_{12}(Cl)_2$ **(3a)**. We attribute the major resonances in the initial spectrum as due to

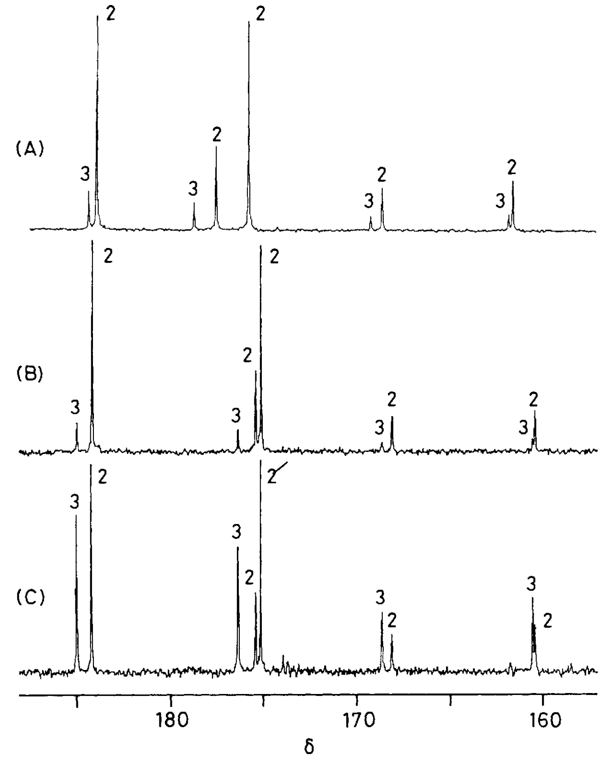


Figure 1. ^{13}C NMR spectra of the reaction of $Os_3(CO)_{12}$ with halogens. Spectrum (A): initial spectrum of the reaction of $Os_3(CO)_{12}$ with Cl_2. Spectrum (B): initial spectrum of the reaction of $Os_3(CO)_{12}$ with Br_2. Spectrum (C): spectrum after the sample [$Os_3(CO)_{12}/Br_2$ reaction] had been allowed to stand at room temperature for 1 h. [All spectra: ^{13}CO-enriched $Os_3(CO)_{12}$, CH_2Cl_2/CD_2Cl_2, 4:1, −30 °C, 100.6 MHz operating frequency.]

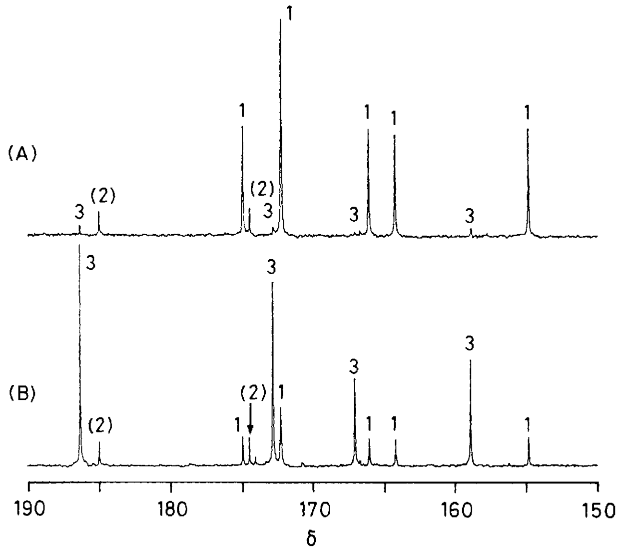


Figure 2. ^{13}C NMR spectra of the reaction of $Os_3(CO)_{12}$ with I_2. Spectrum (A): initial spectrum. Spectrum (B): spectrum after sample had been allowed to stand at room temperature for 1 h (conditions as given in Figure 1).

the axial, equatorial isomer of $Os_3(CO)_{12}(Cl)_2$ [*i.e.*, (**2a**)].† The reaction of $Os_3(CO)_{12}$ with Br_2 was similar (Figure 1, Table 1) except that the isomerisation of (**2b**) to (**3b**) appeared somewhat slower than the isomerisation of (**2a**) to (**3a**). The isomerisations may also be conveniently monitored by IR spectroscopy (Table 1).

The reaction of I_2 in CH_2Cl_2 with $Os_3(CO)_{12}$ in CH_2Cl_2 at −30 °C gave, on addition of hexane, a red–brown product (**1c**). The product analysed as $Os_3(CO)_{12}I_4$, and a 2:1 I_2 : $Os_3(CO)_{12}$ molar ratio was necessary for the reaction to go to completion. The IR spectrum of (**1c**) (CO-stretching region) is markedly different from that of (**2a**) and (**2b**) (Table 1). When the reaction was monitored by ^{13}C NMR spectroscopy, with conditions as described above, the initial spectrum also consisted of five intense signals but in a ratio of 1:2:1:1:1 (Figure 2). On this evidence we formulate the initial product in this case as the ionic derivative $[Os_3(CO)_{12}(I)][I_3]$ [*i.e.*, (**1c**)]. The ^{13}C NMR spectrum of (**1c**) has the same pattern as that reported for $[Os_3(CO)_{12}(H)][PF_6]$.[4]

In solution (**1c**) also completely rearranged over about 3 h to give eq,eq-$Os_3(CO)_{12}(I)_2$ (**3c**) as monitored by both ^{13}C NMR and IR spectroscopy (Figure 2, Table 1).

Further evidence for the ionic formulation of (**1c**) came from the metathesis of the complex in CH_2Cl_2 at −78 °C with NH_4PF_6 in tetrahydrofuran to give $[Os_3(CO)_{12}(I)][PF_6]$ (**1d**). This complex did not rearrange in solution but the ^{13}C NMR and IR spectra in the carbonyl region were virtually identical to those of (**1c**) except for shifts due to the different solvents employed for the NMR spectra [(**1d**) is only sparingly soluble in CH_2Cl_2]. We have also found that treatment of (**3a**) in CH_2Cl_2 at −78 °C with $SbCl_5$ gives a product, the spectroscopic properties of which indicate it is $[Os_3(CO)_{12}(Cl)][SbCl_6]$ (**1a**) (Table 1).‡

Two weak resonances at δ 185.0 and 174.4 [that are not due to $Os_3(CO)_{12}$] were observed when the conversion of (**1c**) to (**3c**) was followed by ^{13}C NMR spectroscopy (Figure 2). These peaks were observed throughout the conversion but disappeared when the reaction was complete. These resonances may be due to the two strongest resonances of (**2c**) (they appear in the positions expected for these resonances). This suggests that the formation of *eq,eq*-$Os_3(CO)_{12}(I)_2$ (**3c**) proceeds *via* the ionic intermediate (**1c**) and then the axial, equatorial isomer (**2c**). It appears likely that the corresponding reaction of $Os_3(CO)_{12}$ with Cl_2 (and Br_2) proceeds by a similar pathway but the lifetime of the ionic intermediate is too short to be detected by the techniques employed in this study.

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† We believe some of the diequatorial isomer (**3a**) is formed in the initial reaction since the isomerisation of (**2a**) to (**3a**) would be negligible at −30 °C.

‡ Mononuclear osmium carbonyl complexes are known to give ionic intermediates on halogenation.[5]