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The Preparation and ^{13}C nmr Spectra of some Trinuclear Osmium Complexes Containing an O-Alkylated Carbonyl Group.

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SUMMARY

The new osmium clusters $[HOs_3(CO)_9(CNBu^t)(COR)]$ (R = Me or Et) and $[HOs_3(CO)_9(CNBu^t)(COMe)]$ have been prepared via the alkylation of $[HOs_3(CO)_{11}]^-$. These clusters contain an O-alkylated carbonyl group and are structurally different from the isomeric bridging acyl complexes $[HOs_3(CO)_{10}(COR)]$ which have been reported previously. The two isomers do not interconvert even at elevated temperatures.

The ^{13}C nmr spectra of the new complexes are reported together with the ^{13}C spectrum of the analogous iron complex $[HFe_3(CO)_{10}(COMe)]$. Alkyl group 'flipping' and polytopal rearrangement of the $M(CO)_4$ and $M(CO)_3$ units are observed for M = Os and Fe but there is no scrambling of CO groups between metal centres on the nmr timescale.

INTRODUCTION

The protonation of polynuclear metal carbonyl complexes invariably leads to the formation of metal hydrogen bonds rather than to attack at the oxygen atom of a carbonyl group.[1,2] On the other hand Lewis acids such as AlR_3 normally bond to metal carbonyl clusters through the oxygen atom of a bridging carbonyl group and can induce the formation of such bridging groups where these are not present initially.[3]

The methylation of metal carbonyl complexes using methylating agents such as $[(CH_3)_3O]BF_4$ has been far less thoroughly studied than protonation. In principle such methylation could lead either to the formation of bonds from the methyl group to the metal atoms or to a carbonyl oxygen atom. The methylation of $[Fe_3(CO)_{11}]^{2-}$ with CH_3SO_3F leads to the formation of $[Fe_3(CO)_{11}CH_3]^-$ which, on protonation, gives $[HFe_3(CO)_{11}CH_3 \cdot H_2O]$. An X-ray study of this complex reveals that it contains a $COCH_3$ group bridging between two metal atoms.[4] On the other hand, treatment of $[H_2Os_3(CO)_{10}]$ with CH_2N_2 leads initially to the formation of $[H(CH_3)Os_3(CO)_{10}]$ in which the methyl group bridges two osmium atoms.[5]

The above experiments indicate that the outcome of methylating polynuclear carbonyl anions is uncertain. In the case of $[HOs_3(CO)_{11}]^-$ either methylation of a carbonyl oxygen to give $[HOs_3(CO)_{10}(COMe)]$ or of a metal-metal bond (with CO loss as in the protonation of $[HOs_3(CO)_{11}]^-$)[6] to give $[H(CH_3)Os_3(CO)_{10}]$ both seem possible. In addition, the preparation of $[HOs_3(COMe)(CO)_{10}]$ from the reaction of $Os_3(CO)_{12}$ with aldehydes has been previously reported and in this complex a bridging acyl group is present.[7] In the present context this ligand can be formally regarded as a bridging carbonyl group in which the carbonyl carbon atom has been methylated. In view of these interesting possibilities we have investigated the alkylation of $[HOs_3(CO)_{11}]^-$.

RESULTS AND DISCUSSION

A Preparation and structural characterisation

The reaction of $[Et_4N][HOs_3(CO)_{11}]$ with an excess of $MeSO_3F$

T A B L E 1

IR^a AND ^1H nmr^b DATA

Compound	$\nu(CO)$, cm^{-1}	δ M-H	δ CH_3	Other ^1H resonances
I $[HOs_3(CO)_{10}(COMe)]$	2106m,2064s,2056s,2023s,2009s, 1997s,1990sh,1979m.	-16.2	4.6	
II $[HOs_3(CO)_{10}COEt]$	2105m,2062s,2055s,2022s,2007s, 1994s,1989sh,1977m.	-16.2	1.66 (t,J(HH)7Hz)	CH_2, 4.68 (q,J(HH)7Hz)
$[HFe_3(CO)_{10}COMe]^c$	2095w,2048vs,2036vs,2015vs, 2005sh,1999m,1989sh,1977m.	-18.2	4.23	
III $[HOs_3(CO)_9(CNBu^t)(COMe)]$	2085m,2049s,2004m,1989m,1979s, 1960m (νCNR, 2120m).	-16.3	4.4	Bu^t, 1.55
$[HOs_3(CO)_{10}(CO)Me]^d$		-13.9 ($CDCl_3$)	2.2 ($CDCl_3$)	

[a] In hexane solution [b] In CD_2Cl_2 solution except where indicated δ (ppm) relative to TMS [c] Ref 4 [d] Ref 7

at rt. gives an immediate colour change from red to yellow and, on removal of excess $MeSO_3F$, the complex $[HOs_3(CO)_{10}(COMe)]$, I, is obtained. It can be purified by sublimation. $[HOs_3(CO)_{10}(COEt]$ II, was prepared similarly using $[Et_3O]BF_4$. The complexes are soluble in most organic solvents and their formulae were confirmed by the observation of molecular ion peaks in their mass spectra and by microanalysis. The structure of the complexes $[HOs_3(CO)_{10}(COR)]$ was initially deduced from the similarity of the 'H nmr and IR spectroscopic data (Table 1) to those obtained for $[HFe_3(CO)_{10}(COMe)]$. In addition to the ν(CO) bonds reported in Table 1, all three osmium complexes show a broad band at *ca* 1680 cm^{-1} which may be assigned as being principally due to ν(CO) of the COR ligand. Subsequently, a crystal structure determination by X-ray analysis on the isocyanide substituted derivative $[HOs_3(CO)_9(CNBu^t)COMe]$, III, has confirmed that these complexes contain O-alkylated bridging carbonyl groups.[8] Thus the methylated complex $[HOs_3(CO)_{10}(COMe)]$ described here is an isomer of the bridging acyl complex prepared earlier by Deeming.[7] It has not proved possible to interconvert these isomers by heating. Deeming found that traces of the bridging acyl complex could be produced by heating the complex $[HOs_3(CO)_{10}(OCHCH_2)]$ (a third isomer of I) to 358K in cyclohexane for 65 hours but reported no trace of I. Similarly, we find that heating I in toluene solution to 423K gives no traces of either of its two known isomers even after several hours at this temperature.

The reaction between $[HOs_3(CO)_{11}]^-$ and $MeSO_3F$ led to small quantities of a second complex which was identified as $[HOs_3(CO)_{10}(O_2CMe)]$ from its mass spectrum and the identity of its infrared and 'H nmr spectrum with those previously reported for this complex.[9] This impurity arises from protonation by HSO_3F (present in the $MeSO_3F$) of the anion $[Os_3(CO)_{11}C(O)OMe]^-$ formed by the attack of RO^- on $Os_3(CO)_{12}$ in methanolic KOH. In accord with this the complex $[HOs_3(CO)_{10}O_2CEt]$ was formed as the by-product when the reaction was carried out in ethanolic KOH using $MeSO_3F$ as the methylating agent. CO loss must also take place on protonation.

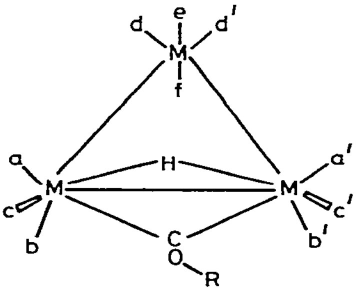
III is prepared from I by treatment of I with an equimolar quantity of Bu^tNC in hexane. The ^{13}C nmr spectrum of III (vide infra) and the results of the X-ray analysis reveal that the Bu^tNC ligand occupies an axial position on the Os atom which is not involved with the bridging ligands and that it is on the opposite side of the metal atom triangle to that occupied by the COMe group. Such axial substitution is commonly found in derivatives of the type $Os_3(CO)_{12-x}(CNR)_x$[10] in contrast to all reported phosphine derivatives of $Os_3(CO)_{12}$ where the substituents occupy equatorial positions.[11]

B ^{13}C nmr Spectra

(i) $[HOs_3(CO)_{10}(COR)]$ (R = Me, Et)

These molecules have no symmetry and hence all the carbonyl groups (for which an identification scheme is given in the Figure) should give rise to separate ^{13}C signals. The spectra

Figure 1



Key to ^{13}C nmr assignments for $[HM_3(CO)_{10}(COR)]$ (M = Fe, Os)

TABLE 2

^{13}C nmr DATA[a]

Compound	Temperature	δ ppm[b]	Relative Intensity	Assignment[c]	J(^{13}C-^{1}H)[d]
[$HOs_3(CO)_{10}(COMe)$]	193K	180.6	1	e	
		179.1	1	f	
		178.7) 178.6)	2	aa'	
		175.4) 174.6)	2	dd'	
		174.5) 173.9)	2	cc'	9.3
		169.4) 168.7)	2	bb'	
		352.2	1	$\underline{\text{C}}$OMe	
[$HOs_3(CO)_{10}(COEt)$]	193K	181.2	1	e	
		179.7	1	f	
		179.3	2	aa'	
		176.0) 175.2)	2	dd'	
		175.0) 174.4)	2	cc'	9.3
		170.0) 169.3)	2	bb'	
		349.7	1	$\underline{\text{C}}$OEt	
[$HOs_3(CO)_9(CNBu^t)(COMe)$]	273K	180.9	1		
		179.7	2		
		176.4	2		
		174.6	2		
		168.4	2		
[$HFe_3(CO)_{10}(COMe)$]	161K	215.8	1	e	
		214.1	1	f	
		212.7	2	aa'	
		210.2	2	cc'	3.6
		207.3	2	dd'	
		204.1	2	bb'	5.3

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[a] In CH_2Cl_2 solution [b] Proton decoupled spectra [c] See figure for key to assignments [d] In Hz

of the two complexes at 193K are, as expected, very similar and are given in Table 2 together with assignments. The alkylated carbonyl resonance occurs at ca 350 ppm downfield from TMS.

The resonances due to a and a' are already beginning to coalesce at 193K for R = Me and are not resolvable for R = Et. On warming the samples the resonances due to c and c' then b and b' and finally d and d' progressively collapse and at ca 303K single resonances are observed for all these pairs of signals. This coalescence is clearly due to flipping of the alkyl group and the increasing coalescence temperature merely reflects the increasing chemical shift difference between the two signals of each pair.

Two distinct mechanisms have been proposed to explain this type of rearrangement. Either rotation about the carbon-oxygen bond or inversion at oxygen involving a linear COR intermediate may occur. Both mechanisms are found in related organic compounds containing this group although which mechanism operates in specific cases is a matter of some controversy.[12] Cotton has considered this problem in relation to binuclear transition metal complexes containing bridging CNR groups and suggests that inversion at nitrogen is more likely than rotation round the C-N bond in view of the very short C-N bond length, which indicates a high C-N bond order.[13] The C-O bond length of the COMe ligand in $[HOs_3(CO)_9(CNBu^t)COMe]$[8] is 1.27Å indicating considerable multiple bond character and this suggests that here too inversion at oxygen via a linear transition state is the more likely process. An approximate value of $\Delta G^{\ddagger}$ may be calculated from the coalescence temperatures and values of 57kJ mol^{-} for $[HOs_3(CO)_{10}COEt]$ and 56kJ mol^{-1} for $[HOs_3(CO)_{10}COMe]$ are obtained. These may be compared with the value of ca 40kJ mol^{-1}

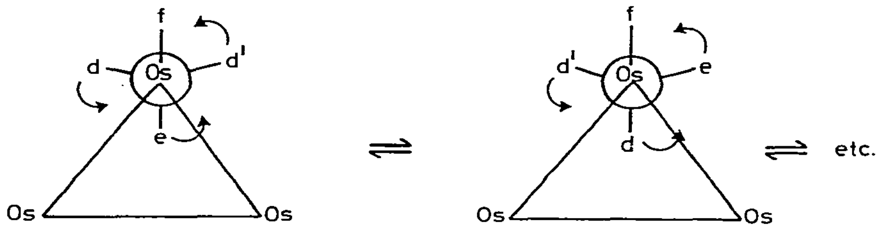
obtained for flipping of the R groupsof the bridging CNR ligands in the complex $[(\eta\text{-}C_5H_5)Fe(CO)(CNR)]_2$.[13]

The only ^{13}C resonances which are not expected to be affected by flipping of the R group are those due to carbonyl groups e and f. The assignment of the two lowest field resonances to these groups is made on this basis. The fluxional process which begins above 333K involves these and one other pair of resonances. The only reasonable choice for the latter is dd' and it is on the basis of this observation that the assignment of dd' is based. Coalescence of the three signals takes place at ca 363K and a single sharp resonance is observed at 403K. The process which is occurring can only be the polytopal rearrangement of an $Os(CO)_4$ group. Such a process has been postulated previously for many trinuclear cluster compounds; the principal experimental evidence on which this postulate is based is the line broadening which has been observed in various other $[HOs_3(CO)_{10}X]$ species.[9] However, it is believed that this is the first case in which this process can be confirmed by the observation of the averaged, coalesced resonance.

In the case of $[HOs_3(CO)_{10}COEt]$, the coalescence of the four ^{13}C resonances (d, d', e and f) due to the carbonyl groups of the $Os(CO)_4$ group clearly occurs as a two-step process. At 353 K d, d' and e have collapsed but f is still sharp and only begins to broaden on raising the temperature by ca 10 K. This observation may be accounted for if it is assumed that the scrambling of d, d' and e takes place initially by a trigonal twist mechanism[14] about one axis as shown in Figure 2.

Having assigned dd', e and f the remaining resonances are assigned according to the magnitude of the difference in chemical shift of the pairs nn' (n = a,b,c). The smallest difference would be expected for aa' and the largest for cc', the latter

Figure 2



The trigonal twist mechanism for partial CO scrambling in $[HOs_3(CO)_{10}COEt]$

being the only pair to show 'H coupling [J('H-^{13}C), 9.3Hz]. On this basis, since aa' occurs at lower field than cc', the lower of the two resonances belonging to the axial carbonyls is assigned to e.

A final scrambling process begins at ca 443 K when the resonances due to aa', bb' and cc' collapse, presumably due to polytopal rearrangement of the $Os(CO)_3$ groups. That such a rearrangement can take place in Os_3 clusters has been conclusively demonstrated by experiments involving the stereospecific exchange of ^{13}CO in complexes of the type $[Os_3(CO)_{10}X_2]$.[15]

(ii) $[HOs_3(CO)_9(CNBu^t)(COMe)]$

The ^{13}C nmr spectrum of this complex shows five resonances at 273 K (Table 2) of relative intensity 1:2:2:2:2 as expected if the COMe group is flipping at this temperature. On progressively cooling to 193 K the resonances at δ179.7 and δ168.4 ppm collapse and then reappear as resonances at δ180.0, 179.6, 169.3 and 169.1 ppm. The intensity of each of these four resonances is approximately half that of each of the original two resonances relative to other unchanged peaks in the spectrum. For two of the carbonyl pairs the coalescence temperature is not reached at 193K which was the lowest temperature at which the spectrum was recorded. The 273K spectrum remains unchanged up to 343K. Above this temperature decomposition takes place.

(iii) [$HFe_3(CO)_{10}(COMe)$]

At 161K six resonances are seen of relative intensity 1:1:2:2:2:2 The enrichment of this complex was accomplished by stirring unenriched [$HFe_3(CO)_{10}(COMe)$] in CH_2Cl_2 under a ^{13}CO atmosphere whereas the osmium complexes were prepared from enriched $Os_3(CO)_1$ The failure to observe the $\underline{C}OMe$ resonance for the iron complex, even at 161K, indicates that the $\underline{C}OMe$ carbon atom is not enriched and implies that alkyl migration between CO groups does not take place at an appreciable rate. The ^{13}C spectrum at 265K shows that flipping of the alkyl group is fast on the nmr timescale at this temperature and suggests that $\Delta G^{\ddagger}$ is probably lower than for the osmium complex, although this is not certain in the absence of the low temperature limiting spectrum.

When proton decoupling is not applied the resonance at δ212.7 ppm loses intensity and broadens, while the resonances at δ210.2 and 204.1 ppm show resolvable $'H-^{13}C$ coupling of 3.6 and 5.3Hz respectively. The assignments given in Table 2 are consistent with this coupling pattern and similar to those made for [$HOs_3(CO)_{10}(COR)$] except that the relative positions of cc' and dd' are changed. On warming the sample above 161K the resonances due to dd', e and f, broaden and by 243K these have collapsed, indicating polytopal rearrangement of the $Fe(CO)_4$ group. The averaged resonance is seen at δ209.8 ppm (toluene solution, 343K). At 273K broadening of the remaining resonances aa', bb' and cc' commences, these having collapsed by 308K presumably due to polytopal rearrangement of the $Fe(CO)_3$ groups. The complex decomposes above 343K and the averaged resonance due to this process could not be seen.

EXPERIMENTAL

^{13}C nmr spectra of isotopically enriched samples were recorded on a Varian XL100 FT spectrometer (^{13}C, 25.2 MHz). Above 223K 0.07 mol dm^{-3} tris(pentane-2,4-dionato)chromium(III) was added as a shiftless relaxation agent. Chemical shifts are quoted as positive downfield of TMS ($\delta = 0$) having been measured relative to the solvent as an internal secondary standard.

Preparations

(i) $[HOs_3(CO)_{10}(COMe)]$(I)

A sample of $[Os_3(CO)_{12}]$ (0.25g, 0.11 mmol) was reacted with an excess of 1 molar methanolic KOH (25 cm^3) to give the red anion $[HOs_3(CO)_{11}]^-$.[16] This was isolated as its Et_4N^+ salt by addition of a saturated aqueous solution of $[Et_4N]Br$ and filtration of the product. A 0.25g sample of $[Et_4N][HOs_3(CO)_{11}]$ was treated with an excess (ca 1 cm^3) of $MeSO_3F$ under a nitrogen atmosphere. There was an immediate colour change from red to yellow and after five minutes the excess $MeSO_3F$ was distilled off in vacuo. The residue was transferred to a sublimation apparatus and pure $[HOs_3(CO)_{10}(COMe)]$ (yield: ca 50%) was sublimed off (353K, 0.1 mm Hg). (Anal Found: C, 15.68; H, 0.89. $C_{12}H_4O_{11}Os_3$ calcd: C, 16.09; H, 0.45%).

(ii) $[HOs_3(CO)_{10}(COEt)]$(II)

This complex was prepared similarly to $[HOs_3(CO)_{10}(COMe)]$ using a suspension of $[Et_3O]BF_4$ (0.5g) in hexane (5 cm^3) as the alkylating agent (Yield ca 40%. Anal Found: C, 17.53, H, 0.75. $C_{13}H_6O_{11}Os_3$ calcd: C, 17.75; H, 0.68%).

(iii) $[HOs_3(CO)_9(CNBu^t)(COMe)]$(III)

A sample of $[HOs_3(CO)_{10}COMe]$ (0.1g, 0.11 mmol) in hexane (10 cm^3) was refluxed with an equimolar quantity of Bu^tNC for 8 hours. Cooling the solution to 273K gave yellow crystals which were recrystallised from hexane. (Yield ca 70%. Anal Found: C, 20.66; H, 1.59. $C_{16}H_{13}NO_{10}Os_3$ calcd: C, 20.22; H, 1.37%).

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