Carbon–Hydrogen Cleavage Reactions of Some Trimethyl- and Triethylphosphine Complexes of Osmium

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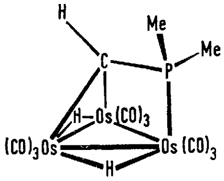
A new type of metallation reaction is reported in which the complexes $Os_3(CO)_{11}(PR_3)$ or $Os_3(CO)_{10}(PR_3)_2$ (R = Me or Et) on heating in refluxing n-nonane give the derivatives $H_2Os_3(R_2PCX)(CO)_9$ or $H_2Os_3(R_2PCX)(CO)_8(PR_3)$ where X = H or Me. The ligands R_2PCX bridge the three metal atoms and the nonacarbonyl complexes show rapid exchange between hydrides as well as between R-groups. Isomerism observed for $H_2Os_3(Me_2PCH)(CO)_8(PMe_3)$ is probably due to the PMe_3 occupying different co-ordination positions.

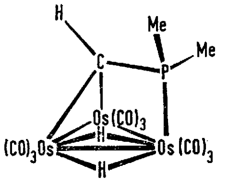
CARBON–HYDROGEN cleavage in a substituent of a tertiary phosphine co-ordinated to a transition metal commonly occurs to form a metal–carbon bonded system. Generally it is aryl[1] or benzylic[2] carbon–hydrogen bonds that are cleaved. Alkyl substituents on tertiary phosphines have been activated in a few cases[3,4] but there is only one report as far as we are aware of the activation of a methyl group bonded to phosphorus. Chatt and Davidson[5] have reported a tautomerism between $Ru(Me_2PCH_2CH_2PMe_2)_2$ and $HRu(CH_2PMeCH_2CH_2PMe_2)(Me_2PCH_2CH_2PMe_2)$ in which there is an internal oxidative addition reaction of Ru^0 to give a Ru^{II} complex. Here we report that controlled pyrolyses of $Os_3(CO)_{11}(PMe_3)$ and of $Os_3(CO)_{10}(PMe_3)_2$ in high boiling hydrocarbon solvents give dihydrido-complexes containing the fragment Me_2PCH bridging the three metal atoms. Thus dehydrogenation of just one of the methyl groups has occurred. The formulations and structures of products are based primarily on mass spectral and n.m.r. evidence. Corresponding PEt_3-complexes have also been examined to establish whether hydrogens at the α- or the β-carbons are activated. Results show that dehydrogenation occurs at the α-methylene group to give the ligand Et_2PCMe. The relationship between these results and those on other dehydrogenation reactions will be discussed in this paper.

Trimethylphosphine Complexes.—New complexes of type $Os_3(CO)_{12-x}(PMe_3)_x$ (x = 1—3) were prepared by heating $Os_3(CO)_{12}$ with PMe_3 (3 mol. equivalents) in toluene at 383 K in a sealed glass tube. A mixture of the three compounds was readily separated on alumina and spectral data given in Tables 1 and 2 agree with those for related complexes[6-9] and will not be discussed further.

On heating $Os_3(CO)_{11}(PMe_3)$ in refluxing nonane for several hours there is a ready conversion to a complex of apparent formula $Os_3(CO)_9(PMe_3)$ as given by its mass spectrum and elemental analysis. The very pale yellow crystals are sufficiently volatile to be sublimed without decomposition and the parent ion is very clearly established, while the n.m.r. spectrum gives five signals at 213 K in the intensity ratio 1 : 3 : 3 : 1 : 1, two of which are assigned to non-equivalent metal hydrides. On the basis of this we formulate the complex as $H_2Os_3(Me_2PCH)(CO)_9$ with structure (I) or (II). The basic interaction between the Me_2PCH group and the metal atoms is almost certainly as shown, with σ-osmium–carbon bonds to two osmium atoms with a donor interaction between the P-atom and the third. This is reminiscent of the interactions found in the vinylidene complex which we reported recently,[10] the *X*-ray determined structure of which[11] shows similar metal–ligand interactions.



(I)



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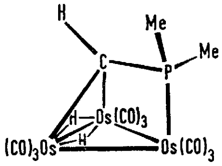

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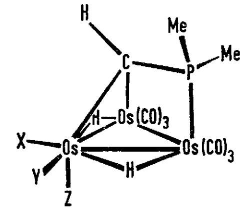

(IV)

As in all these dihydrido-complexes, direct evidence for the hydride positions is not available, but as with the vinylidene complex $H_2Os_3(CCH_2)(CO)_9$, the Me_2PCH ligand is bonded asymmetrically with non-equivalent methyl groups (see Table 2 for n.m.r. data). Thus we suggest hydride-positions as in (I) or (II), but intuitively favour the single bridges as in (I). Structure (III) is perhaps more easily accommodated by the 18-electron rule but is inconsistent with n.m.r. data. Structures with terminal hydrides are possible on our evidence but

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TABLE 1

I.r. and analytical data for the complexes [a]

Complex	M.p./K	C	H	P	ν(CO)/cm⁻¹				
$Os_3(CO)_{11}(PMe_3)$	393—396	18·1(17·6)	1·15(1·15)	2·95(3·25)	2107w	2054m	2031m	2019s	2001vw
					1988w	1972w	1967sh	1958vw	1939w
$Os_3(CO)_{10}(PMe_3)_2$	464—467	19·45(19·2)	1·8(1·8)	6·3(6·2)	2084w	2024m	2007m	2000s	1961m
					1942w	1937sh			
$Os_3(CO)_9(PMe_3)_3$	493 decomp.	20·85(20·6)	2·6(2·6)	8·85(8·85)	1987m	1976s	1932m	1920m	
$H_2Os_3(Me_2PCH)(CO)_9$	387 decomp.	16·25(16·05)	1·05(1·0)	3·8(3·45)	2100m	2072s	2046vs	2021s	2010s
					2003m	1989m	1980m	1969w	
$H_2Os_3(Et_2PCMe)(CO)_9$	450 decomp.	19·5(19·15)	1·6(1·6)	3·65(3·3)	2097m	2070s	2045vs	2020s	2007s
					2001m	1988m	1979m	1967m	
$H_2Os_3(Me_2PCH)(CO)_8(PMe_3)$ [a]	386—390	17·9(17·75)	1·85(1·9)	6·4(6·55)(A)	2072m	2038vs	2023s	2018sh*	1998w*
					1991s	1982s	1968s	1956m	1950w*
				(B)	2074s	2035vs	2022sh*	2018s	1998w
					1990w*	1979m	1968w*	1955m	1949m
$H_2Os_3(Et_2PCMe)(CO)_8(PEt_3)$	371—375	23·35(23·3)	2·9(2·95)	6·15(6·0)	2068m	2036vs	2018s	1989s	1979m
					1965s	1960sh	1951w		

[a] Found percentages given with calculated figures in parentheses. I.r. data for cyclohexane solutions calibrated against water vapour absorptions (±2 cm⁻¹). [b] I.r. data for mixtures enriched in isomers (A) or (B). Asterisks indicate bands due to the other isomer.

TABLE 2

N.m.r. data for new complexes in $CDCl_3$ solution

Complex	Temp./K	Frequency/MHz	τ [a]	Assignment	J(PH)/Hz
$Os_3(CO)_{11}(PMe_3)$	308	60	8·10(d)	Me	9·8
$Os_3(CO)_{10}(PMe_3)_2$	308	60	8·13(d)	Me	9·8
$Os_3(CO)_9(PMe_3)_3$	308	60	8·18(d)	Me	9·8
$H_2Os_3(Me_2PCH)(CO)_9$	308	60	5·58 [b]	CH	2·8
			8·09(d)	Me	9·2
			27·79br	OsH	
	202	100	5·59br	CH	
			7·95(d)	Me	10·0
			8·18(d)	Me	9·0
			25·75(d)	OsH	10·8
			30·08(d)	OsH	6·2
$H_2Os_3(Et_2PCMe)(CO)_9$	343	100	7·54(d)	CMe	18·0
			7·3—8·2(m) [c]	$CH_2\mathrm{CH}_3$	
			8·84(m)	CH_2CH_3	
			27·6br	OsH	
	214	100	7·52(d)	CMe	18·0
			7·1—8·2(m) [c]	$CH_2\mathrm{CH}_3$	
			8·83(m)	CH_2CH_3	
			25·19(d)	OsH	9·4
			30·05(d)	OsH	8·0
$H_2Os_3(Me_2PCH)(CO)_8(PMe_3)$	300	100	5·52(m)	$\mathrm{C}H$	
(isomer A)	293	220	8·00(d)	PMe	9·4
			8·12(d)	PMe_3	9·5
			8·20(d)	PMe	9·3
	300	100	25·68(t)	OsH	11·2
			30·44(dd)	OsH	12·0, 8·0
$H_2Os_3(Me_2PCH)(CO)_8(PMe_3)$	300	100	6·24(dm)	$\mathrm{C}H$	12·0
(isomer B)	293	220	8·01(d)	PMe	9·5
			8·26(d)	PMe	9·1
			8·32(d)	PMe_3	10·6
	300	100	26·06(t)	OsH	11·2
			29·25(dd)	OsH	24·7, 8·9
$H_2Os_3(Et_2PCMe)(CO)_8(PEt_3)$	308	60	7·46(dd)	CMe	20·4, 4·0
			8·06(m)	$CH_2\mathrm{CH}_3$	
			8·84(m)	CH_2CH_3	
			25·30(t)	OsH	10·0
			30·75(dd)	OsH	9·0, 11·0

[a] d, Doublet; q, quintet; t, triplet; dd, doublet of doublets; dm, doublet of multiplets; m, multiplet. [b] A 1 : 2 : 2 : 2 : 1 quintet interpreted as two overlapping 1 : 2 : 1 triplets, J(PH) 2·8, J(HH) 1·4 Hz. [c] Two CH_2-multiplets are apparent in this chemical shift range possibly due to their non-equivalence at all temperatures.

we have chosen not to consider these because all evidence in analogous systems seems to point to bridging hydrides.

The complex $H_2Os_3(Me_2PCH)(CO)_9$ is, however, fluxional and at room temperature the two Me-doublets have coalesced to a single doublet and the hydride signals have broadened to give a single resonance of 100 Hz width which sharpens at higher temperatures. The molecule by this process has effectively gained a plane of symmetry. There is considerable similarity between this behaviour and that of the vinylidene complex $H_2Os_3(CCH_2)(CO)_9$.[10] The kinetics and mechanism of the process are at present being investigated.

The appearance of the $Me_2PC\mathit{H}$ signal in the n.m.r. spectrum is of interest in that at room temperature it appears as a quintet of approximate intensity ratio 1 : 2 : 2 : 2 : 1 which we interpret as a doublet of triplets due to coupling to the ^{31}P nucleus and equal coupling to the hydride ligands. The line separation is only 1·4 Hz and similar splitting cannot be resolved in the hydride signals. Below room temperature the fine structure disappears and reappears below 223 K as a triplet pattern. At high temperatures the Me_2PCH couples equally to both hydride nuclei as a result of their rapid exchange.

The pyrolysis of $Os_3(CO)_{10}(PMe_3)_2$ gave a PMe_3-substituted derivative of the above complex which exists as isomers (A) and (B). The isomeric mixture of this product, $H_2Os_3(Me_2PCH)(CO)_8(PMe_3)$, can be separated into two close but clearly resolved bands on silica using preparative t.l.c. plates, but by the time each band had been extracted and the isomers examined spectroscopically they were no longer isomerically pure. Each was obtained in *ca.* 80—90% isomeric purity and solutions enriched in either isomer gave the same equilibrium mixture [isomer (A) : isomer (B) = 1·42 : 1·00] within a few days at room temperature. Each isomer, albeit contaminated with the other, gave the same mass spectrum and the same elemental analysis. The predicted six methyl doublets in the n.m.r. spectrum of the equilibrium mixture of non-fluxional isomers were resolved at 220 MHz (see Figure 1). For each isomer similar coupling patterns were observed for the hydride-signals, and thus we believe that these ligands are similarly positioned, structure (IV), and that the isomerism is a result of the PMe_3-ligand occupying different co-ordination sites on the same metal atom (X, Y, or Z).

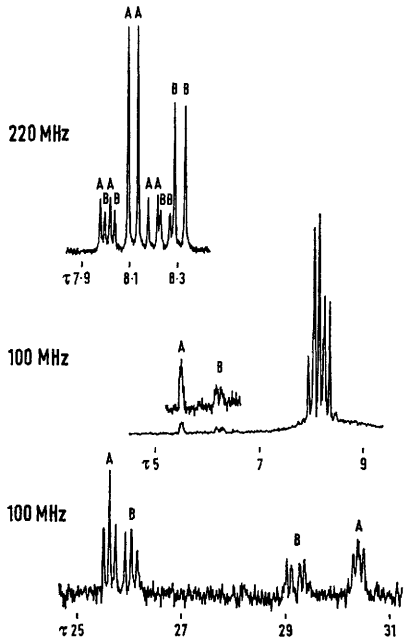

FIGURE 1 ^1H N.m.r. spectrum of $H_2Os_3(Me_2PCH)(CO)_8(PMe_3)$

The most notable difference between these isomers is the coupling between the *CH* proton and the ^{31}P nucleus of the PMe_3 ligand, $J(PH) < 3$ Hz (isomer A) and $J(PH)$ 12·0 Hz (isomer B). Unfortunately there is no criterion for interpreting this difference in terms of co-ordination site of the PMe_3 ligand. The isomerisation might involve dissociation of CO or PMe_3. However, the isomers are indefinitely inert towards substitution at room temperature even in the presence of a very large excess of tertiary phosphine where any dissociation would likely lead to substitution. This very limited evidence supports an intramolecular mechanism for the isomerisation.

Since these molecules are non-fluxional with hydride signals being sharp at normal temperatures, it is probable that the electronic effect of the PMe_3 ligand makes one arrangement of hydrides much more favourable energetically than any other, so that migration of hydrides around the cluster cannot readily occur.

Triethylphosphine Complexes.—Although there is the possibility of activation of hydrogens at the β-carbon, we have evidence for only α-carbon–hydrogen cleavage and the PEt_3 system is directly analogous to the PMe_3 complexes described above. For example $Os_3(CO)_{11}(PEt_3)$ gives $H_2Os_3(Et_2PCMe)(CO)_9$ on pyrolysis and this complex is similar in most respects to $H_2Os_3(Me_2PCH)(CO)_9$. They show very similar i.r. spectra *ca.* 2000 cm^{-1} and they both show two hydride doublets in the low temperature n.m.r. spectra, which broaden and coalesce at higher temperatures. Similarly, $Os_3(CO)_{10}(PEt_3)_2$ gives $H_2Os_3(Et_2PCMe)(CO)_8(PEt_3)$ which exists in only one isomeric form corresponding to isomer (A) of $H_2Os_3(Me_2PCH)(CO)_8(PMe_3)$. In both PEt_3 derivatives the unique Me-groups give clearly assigned n.m.r. signals, a doublet [$J(PH)$ 18·0 Hz] for $H_2Os_3(Et_2PCMe)(CO)_9$ and a doublet of doublets [$J(PH)$ 20·0 and 4·0 Hz] for $H_2Os_3(Et_2PCMe)(CO)_8(PEt_3)$. The smaller coupling constant is due to coupling to $^{31}PEt_3$.

These results unambiguously show activation of the α-group, which is surprising. With complexes containing one metal atom five-membered ring formation is favoured.[4] In this work the PEt_3 ligand could either react with the metal to which it is co-ordinated or, more likely, with an adjacent one. In either case the β-CH_3 group lies much closer to the metal than the α-CH_2 and hence we believe there are electronic rather than steric reasons for α-activation.

Dehydrogenation of Organic Molecules by Reaction with $Os_3(CO)_{12}$.—The reactions described here are related to those between $Os_3(CO)_{12}$ and a variety of molecules of type H_2X to give the products $H_2Os_3X(CO)_9$ where H_2X = ethylene,[10,12] benzene,[12] hydrogen sulphide,[12] cyclopentene,[13] bicyclo[3,2,1]octa-2,6-diene,[14] cyclooctene,[15] or p-X-$C_6H_4NH_2$ (X = H, Me, or F).[16] It is very likely that intermediates of form $HOs_3(HX)(CO)_{10}$ are involved and these have been isolated in the case of

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[16] A. J. Deeming and C. Choo Yin, unpublished results.

the *p*-substituted anilines.[14] In all cases the molecules H_2X in displacing three carbonyl groups must have provided six electrons for metal–ligand bonding. Cleavage of the two H–X bonds has effectively provided four electrons and the other electrons are donated either from a lone-pair on the heteroatom or from a filled π-orbital on the ligand and Figure 2 illustrates how this is achieved for the compounds listed above.

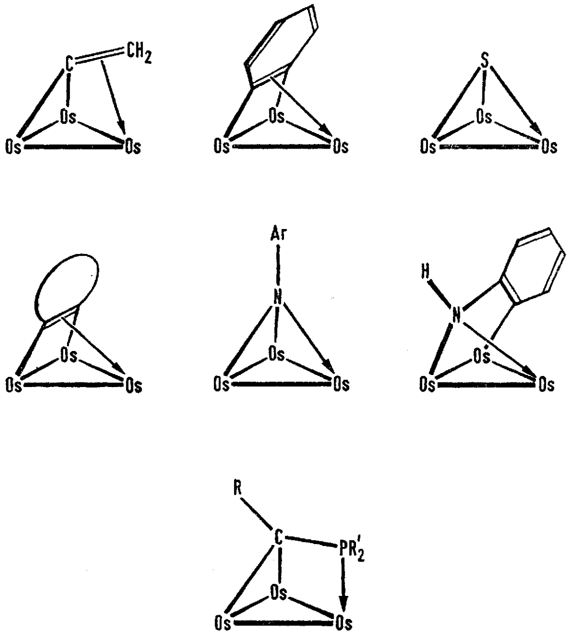

FIGURE 2 Interactions between Os_3 and X in the molecules $H_2Os_3X(CO)_9$ derived from H_2X

EXPERIMENTAL

All reactions were carried out under nitrogen but as the products were thermally and air stable isolation procedures were carried out in air.

Reaction of Dodecacarbonyltriosmium with Trimethylphosphine.—Trimethylphosphine (0·62 g) was distilled into a glass tube containing $Os_3(CO)_{12}$ (2·25 g) and degassed toluene (90 ml) and the tube sealed under vacuum. After heating at 383—393 K for 10 h the cold solution was filtered and the solvent removed under reduced pressure. The residual red oil was chromatographed on an alumina column eluting with pentane–toluene to give three bands which after removal of solvent yielded $Os_3(CO)_{11}(PMe_3)$ as yellow crystals (0·10 g, 5%), $Os_3(CO)_{10}(PMe_3)_2$ as red crystals (0·49 g, 22%), and $Os_3(CO)_9(PMe_3)_3$ as orange crystals (0·27 g, 11%).

The corresponding PEt_3 complexes were prepared as described previously.[7]

Pyrolyses in Refluxing n-Nonane.—After refluxing solutions of the complexes $Os_3(CO)_{12-x}(PR_3)_x$ (x = 1 or 2, R = Me or Et) in nonane (0·1 g per 50 ml) for several hours, the solvent was removed under reduced pressure and products isolated by separation of the resulting mixture on an alumina column or preparative t.l.c. silica plates. Other components in the mixtures were not isolated.

$Os_3(CO)_{11}(PMe_3)$. Reflux for 5 h gave $H_2Os_3(Me_2PCH)(CO)_9$ as pale yellow crystals (60%).

$Os_3(CO)_{10}(PMe_3)_2$. Reflux for 5 h gave an oil which on silica plates eluting with 5—10% ether in pentane gave two clearly resolved bands corresponding to two isomers of $H_2Os_3(Me_2PCH)(CO)_8(PMe_3)$. Isomer (A) gave pale yellow crystals (44%) and isomer (B) pale yellow crystals (31%) but spectroscopic evidence showed that they were not isomerically pure.

$Os_3(CO)_{11}(PEt_3)$. Reflux for 15 h gave $H_2Os_3(Et_2PCMe)(CO)_9$ as pale yellow crystals (32%).

$Os_3(CO)_{10}(PEt_3)_2$. Reflux for 9 h gave $H_2Os_3(Et_2PCMe)(CO)_8(PEt_3)$ as yellow crystals (58%).

All the dihydrido-derivatives showed parent molecular ions in the mass spectra.

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