Some Benzyne Complexes of Osmium Derived from Dimethylphenylphosphine or Dimethylphenylarsine

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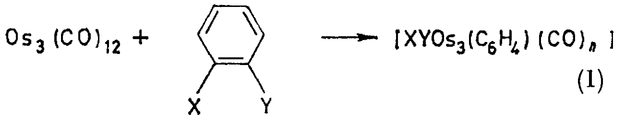
The complexes $[Os_3(CO)_{11}(EMe_2Ph)]$ or $[Os_3(CO)_{10}(EMe_2Ph)_2]$ (E = P or As) on heating give C_6H_4-bridged complexes $[HOs_3(C_6H_4)(EMe_2)(CO)_9]$, $[HOs_3(C_6H_4)(PMe_2)(PMe_2Ph)(CO)_8]$, $[Os_3(C_6H_4)(EMe_2)_2(CO)_7]$, and $[HOs_3(Me_2PC_6H_4C_6H_3)(PMe_2)(CO)_8]$. When E = As, dimeric complexes containing bridging C_6H_4 are also obtained. Structures and mechanisms of the fluxional behaviour of these complexes are discussed in the light of n.m.r. spectra.

In a recent study nine products were shown to be formed in the reaction of the complex $Os_3(CO)_{12}$ with PPh_3.[1-3] Three of these products are simple substitution complexes of the type $[Os_3(CO)_{12-x}(PPh_3)_x]$ ($x = 1, 2,$ or 3), but the others are of novel types as shown by X-ray structural analysis.[1,2] Their formation occurs *via* C–H and C–P bond-cleavage and C–C bond-formation reactions which are probably of an intracluster nature. Several interesting metal–ligand interactions, such as a phenyl group bridging two osmium atoms and a benzyne (*ortho*-phenylene) group bridging three osmium atoms, have been established in these derivatives. Similar reactivity has also been reported for ruthenium complexes.[4]

In this paper we describe some extensions of this work using PMe_2Ph and $AsMe_2Ph$ as ligands. It was hoped that a reduction in the number of phenyl groups to one per ligand would reduce the number of products, but more importantly would simplify n.m.r. studies. N.m.r. spectra of the PPh_3 derivatives in the aromatic region were too complicated to be readily interpreted,[3] whereas the complexes described here give simple spectra providing useful structural information. The results of a study of fluxional behaviour of some C_6H_4 complexes were reported in outline earlier[5] but are fully reported here. In our studies we have prepared C_6H_4 complexes of triosmium starting with three different types of aryl compound, dimethylphenylphosphine or -arsine, *o*-phenylenebis(dimethylarsine) (diars),[6] and benzene.[7] Thus we have now established the general reaction (1) and inherent stability of the $Os_3(C_6H_4)$ framework.



(1)

where $X = Y = H, n = 9$
$X = Y = AsMe_2, n = 7$
$X = H, Y = PMe_2$ or $AsMe_2, n = 9$

RESULTS AND DISCUSSION

Substitution Reactions of $Os_3(CO)_{12}$.—In the earlier study[3] the complex $Os_3(CO)_{12}$ was treated with PPh_3 (2 mol equivalents per Os_3) at 413 K to give directly a number of derivatives and a similar range of complexes was formed by heating $[Os_3(CO)_{10}(PPh_3)_2]$. In our work we prepared simple substitution derivatives $[Os_3(CO)_{12-x}(EMe_2Ph)_x]$ ($x = 1, 2,$ or 3; E = P or As) under milder conditions (toluene at 383 K), separating these on alumina prior to separate treatment at higher temperatures to give further products. I.r. spectra of the substitution derivatives (see Table 2) showed them to be isostructural with analogous complexes with other tertiary phosphine ligands (for examples

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[1] C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *J.C.S. Chem. Comm.*, 1972, 87.

[2] G. J. Gainsford, J. M. Guss, P. R. Ireland, R. Mason, C. W. Bradford, and R. S. Nyholm, *J. Organometallic Chem.*, 1972, **40**, C70.

[3] C. W. Bradford and R. S. Nyholm, *J.C.S. Dalton*, 1973, 529.

[4] M. I. Bruce, G. Shaw, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 2094.

[5] A. J. Deeming, R. S. Nyholm, and M. Underhill, *J.C.S. Chem. Comm.*, 1972, 224.

[6] A. J. Deeming and R. E. Kimber, unpublished work.

[7] A. J. Deeming and M. Underhill, *J. Organometallic Chem.*, 1972, **42**, C60.

see refs. 3 and 8). The single n.m.r. absorptions (singlet for E = As, doublet for E = P) for the methyl groups in each complex shows the apparent equivalence of the ligands when more than one is co-ordinated in a cluster (Table 3).

TABLE 1

Products from reactions and some associated data. Calculated elemental analytical data given in parentheses next to the found percentages

Starting materials	Refluxing solvent and time of reflux	Products	Yield (%)	Colour	M.p. (T/K)	C	H	P	O
$Os_3(CO)_{12}$ + PMe_2Ph	C_6H_5Me (5 h)	$[Os_3(CO)_{11}(PMe_2Ph)]$	25	Yellow	367—370	22·55(22·45)	1·05(1·1)	3·15(3·05)	
		$[Os_3(CO)_{10}(PMe_2Ph)_2]$	32	Red	424—425	28·05(27·7)	1·9(1·95)	5·35(5·5)	
		$(Os_3(CO)_9(PMe_2Ph)_3]$	17	Orange	430—432	32·3(32·05)	2·6(2·7)	7·4(7·5)	
$Os_3(CO)_{12}$ + $AsMe_2Ph$	C_6H_5Me (5 h)	$[Os_3(CO)_{11}(AsMe_2Ph)]$	15	Yellow	372—374	21·6(21·5)	1·0(1·05)		16·6(16·6)
		$[Os_3(CO)_{10}(AsMe_2Ph)_2]$	32	Orange	383—386	25·85(25·7)	1·95(1·85)		13·05(13·15)
		$[Os_3(CO)_9(AsMe_2Ph)_3]$	4	Orange	422—424	28·65(28·95)	2·5(2·45)		10·8(10·5)
$[Os_3(CO)_{11}(PMe_2Ph)]$	Nonane (1 h)	$[HOs_3(C_6H_4)(PMe_2)(CO)_9]$	27	Yellow	423 (decomp.)	21·2(21·2)	1·1(1·5)	3·2(3·2)	15·15(15·0)
		Starting complex	39						
$[Os_3(CO)_{11}(AsMe_2Ph)]$	Nonane (80 min)	$[HOs_3(C_6H_4)(AsMe_2)(CO)_9]$	15	Yellow	424—426	20·95(20·95)	1·3(0·95)		
		$[HOs_2(C_6H_4)(AsMe_2)(CO)_6]$	8	V. pale yellow	*				
$[Os_3(CO)_{10}(PMe_2Ph)_2]$	Nonane (10 h)	$[Os_3(C_6H_4)(PMe_2)_2(CO)_7]$	17	Red	463 (decomp.)	21·45(21·2)	1·75(1·65)	6·6(6·4)	11·5(11·6)
		$[HOs_3(Me_2PC_6H_4C_6H_3)(PMe_2)(CO)_8]$	9	Red	443 (decomp.)	27·0(26·95)	1·9(1·9)	5·7(5·8)	12·1(12·25)
$[Os_3(CO)_{10}(PMe_2Ph)_2]$	Octane (17 h)	$[HOs_3(C_6H_4)(PMe_2)(CO)_8(PMe_2Ph)]$	16	Orange	433 (decomp.)	26·75(26·5)	2·1(2·05)	5·9(5·7)	13·1(13·25)
$[Os_3(CO)_{10}(AsMe_2Ph)_2]$	Nonane (7h)	$[Os_3(C_6H_4)(AsMe_2)_2(CO)_7]$	16	Red	363—367	19·75(19·4)	1·75(1·55)		
		$[HOs_3(C_6H_4)(AsMe_2)(CO)_9]$	30	Yellow					
$[Os_3(CO)_{10}(AsMe_2Ph)_2]$	Heptane (sealed tube, 423 K, 6 h)	$[HOs_2(C_6H_4)(AsMe_2)(CO)_6]$	4	V. pale yellow	*				
		$[Os_2(C_6H_4)(AsMe_2)_2(CO)_6]$	4	V. pale yellow	*				
		$[HOs_3(C_6H_4)(AsMe_2)(CO)_9]$	8						
		$[Os_3(C_6H_4)(AsMe_2)_2(CO)_7]$	12						

* Obtained as oils.

TABLE 2

I.r. data (cm^{-1}) around 2 000 cm^{-1} recorded in cyclo hexane solution

Complex	ν(CO)
$[Os_3(CO)_{11}(PMe_2Ph)]$	2 105m, 2 052s, 2 031s, 2 018vs, 2 000m, 1 986m, 1 972m, 1 968m, 1 955w
$[Os_3(CO)_{11}(AsMe_2Ph)]$	2 106m, 2 054s, 2 033s, 2 022vs, 2 002m, 1 990m, 1 973m, 1 955w
$[Os_3(CO)_{10}(PMe_2Ph)_2]$	2 084m, 2 026s, 2 009sh, 2 002vs, 1 963s, 1 946m, 1 934sh
$[Os_3(CO)_{10}(AsMe_2Ph)_2]$	2 086m, 2 027s, 2 012s, 2 004vs, 1 961s, 1 957sh, 1 941w
$[Os_3(CO)_9(PMe_2Ph)_3]$	1 985s, 1 975vs, 1 935s, 1 919m
$[Os_3(CO)_9(AsMe_2Ph)_3]$	1 994s, 1 977vs, 1 934s, 1 920s
$[HOs_3(C_6H_4)(PMe_2)(CO)_9]$	2 090w, 2 070vs, 2 041s, 2 031vw, 2 014vw, 2 009s, 2 001m, 1 985w, 1 978w, 1 966w
$[HOs_3(C_6H_4)(AsMe_2)(CO)_9]$	2 092m, 2 071s, 2 043s, 2 011s, 2 003s, 1 987m, 1 977m, 1 969m
$[Os_3(C_6H_4)(PMe_2)_2(CO)_7]$	2 055m, 2 009s, 1 996vs, 1 988m, 1 970vw, 1 953s, 1 938m
$[Os_3(C_6H_4))AsMe_2)_2(CO)_7]$	2 053m, 2 008s, 1 996s, 1 988sh, 1 952s, 1 937m
$[HOs_3(C_6H_4)(PMe_2)(CO)_8(PMe_2Ph)]$	2 082s, 2 072vw, 2 049vw, 2 040vs, 2 014vs, 1 999s, 1 980vw, 1 971sh, 1 968m, 1 959vw, 1 945m, 1 941sh
$[HOs_3(Me_2PC_6H_4C_6H_3)(PMe_2)(CO)_8]$	2 069s, 2 031vs, 2 029sh, 2 021vw, 1 998vs, 1 967sh, 1 964s, 1 949m
$[Os_2(PMe_2C_6H_4)(PMe_2)(CO)_6]$	2 069s, 2 034vs, 2 025sh, 1 998s, 1 975sh, 1 971s, 1 957s
$[Os_2(C_6H_4)(AsMe_2)_2(CO)_6]$	2 065s, 2 036w, 2 030w, 2 002s, 1 989s, 1 965w
$[HOs_3(C_6H_4)(AsMe_2)(CO)_6]$	2 093m, 2 076s, 2 018s, 2 004s

Pyrolysis of the Substituted Complexes.—On heating these simple substituted complexes, either under reflux in n-octane (398 K) or n-nonane (423 K), certain derivatives were obtained, each of which was characterised as a C_6H_4 or a substituted C_6H_4 complex (see Table 1). The low to moderate yields partly reflect the extensive chromatography required to isolate pure samples. We have drawn the following conclusions from these reactions.

(*a*) Generally cleavage of both the *ortho*-C–H and the C–P or C–As bonds occurs, with no species being obtained as a result of C–H cleavage alone as was the case with PPh_3.

(*b*) In the reactions of the complexes $[Os_3(CO)_{11}(PMe_2Ph)]$ and $[Os_3(CO)_{10}(PMe_2Ph)_2]$ only products containing all of the original phosphorus atoms were obtained and only on prolonged heating did $[Os_3(CO)_{11}(PMe_2Ph)]$ give some $[Os_3(C_6H_4)(PMe_2)_2(CO)_7]$ with associated decomposition. In contrast the complexes $[Os_3(CO)_{10}(AsMe_2Ph)_2]$ and $[Os_3(CO)_9(AsMe_2Ph)_3]$ gave significant yields of products with one less As per cluster than that initially present. A possibility is that a ligand dissociates from the co-ordinatively saturated starting materials before activation of an *ortho*-C–H bond can occur; this is believed to be the first step in the reaction.[1,3] In the case of the PMe_2Ph complexes a CO group may initially dissociate, whereas $AsMe_2Ph$ is more weakly bound than the phosphine and can dissociate in competition with CO.

$$[Os_3(CO)_{12-x}(PMe_2Ph)_x] \xrightarrow{-CO} [Os_3(CO)_{11-x}(PMe_2Ph)_x] \longrightarrow \text{products} \quad (2)$$

$$[Os_3(CO)_{12-x}(AsMe_2Ph)_x] \xrightarrow{-AsMe_2Ph} [Os_3(CO)_{12-x}(AsMe_2Ph)_{x-1}] \longrightarrow \text{products} \quad (3)$$

(*c*) No evidence for dimeric derivatives was obtained in pyrolysis of the PMe_2Ph complexes, whereas low yields of dimeric species were obtained from the $AsMe_2Ph$

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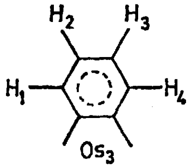
[8] A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 897.

TABLE 3

N.m.r. data, recorded in $CDCl_3$ at 100 MHz unless stated



Complex	T/K	τ	Assignment	Coupling const. (J/Hz), *etc.*
$[Os_3(CO)_{11}(PMe_2Ph)]$	309	7·78d	Me	J(P–H) 10
		2·50m	Ph	
$[Os_3(CO)_{11}(AsMe_2Ph)]$	300	8·00s	Mc	
		2·45s	Ph	
$[Os_3(CO)_{10}(PMe_2Ph)]$	309	7·85d	Me	J(P–H) 10
		2·50m	Ph	
$[Os_3(CO)_{10}(AsMe_2Ph)_2]$	300	8·00s	Me	
		2·45s	Ph	
$[Os_3(CO)_9(PMe_2Ph)_3]$	309	7·73d	Me	J(P–H) 10
		2·50m	Ph	
$[Os_3(CO)_9(AsMe_2Ph)_3]$	300	8·20s	Mc	
		2·60m	Ph	
$[Os_3(C_6H_4)(PMe_2)_2(CO)_7]$	213	8·21t	Me	$\lvert J(P_1{-}H) + J(P_2{-}H)\rvert$ 8·5
		7·63t	Me	$\lvert J(P_1{-}H) + J(P_2{-}H)\rvert$ 8·5
		3·34m	H_2,H_3	Approx. quintet
		2·72d	H_4	$J(H_4{-}H_3)$ 7
		2·43d	H_1	$J(H_1{-}H_2)$ 7
	333	8·21t	Me	
		7·63t	Me	
		3·38m	H_2,H_3	Symmetrical AA′XX′ pattern
		2·62m	H_1,H_4	
$[Os_3(C_6H_4)(AsMe_2)_2(CO)_7]$	183	8·49s	Me	
		7·88s	Me	
		3·50q	H_2,H_3	Approx. quintet
		2·66d	H_4	$J(H_3{-}H_4)$ 7
		2·86d	H_1	$J(H_1{-}H_2)$ 7
	333	8·49s	Me	
		7·88s	Me	
		3·51m	H_2,H_3	Symmetrical AA′XX′ pattern
		2·77m	H_1,H_4	
$[HOs_3(C_6H_4)(PMc_2)(CO)_9]$ *	213	27·01d	Os–H	J(P–H) 8
		8·41d	Me	J(P–H) 9
		7·79d	Me	J(P–H) 9
		3·33t	H_2	$J(H_2{-}H_3)$ 6·3
		2·96t	H_3	
		1·45d	H_4	$J(H_4{-}H_3)$ 8·3
		0·99d	H_1	$J(H_1{-}H_2)$ 8·3
	333	26·90d	Os–H	
		8·43d	Me	
		7·82d	Me	
		3·11m	H_2,H_3	Symmetrical AA′XX′ pattern
		1·26m	H_1,H_4	
$[HOs_3(C_6H_4)(AsMe_2)(CO)_9]$ *	223	27·00s	Os–H	
		8·64s	Me	
		8·05s	Me	
		3·20t	H_2	$J(H_2{-}H_3)$ 6
		2·90t	H_3	
		0·88d	H_4	$J(H_4{-}H_3)$ 8
		1·35d	H_1	$J(H_1{-}H_2)$ 8
	365	27·00s	Os–H	
		8·64s	Me	
		8·05s	Me	
		3·20m	H_2,H_3	Symmetrical AA′XX′ spectrum
		1·16m	H_1,H_4	
$[HOs_3(C_6H_4)(PMe_2)(CO)_8(PMe_2Ph)]$	333	26·09t	Os–H	J(P–H) 12
		8·50d	P*Me*$_2$	J(P–H) 8
		8·36d		J(P–H) 8
		7·64d	P*Me*$_2$Ph	J(P–H) 10
		3·31m	H_2,H_3	Symmetrical AA′XX′ spectrum
		1·32m	H_1,H_4	
		2·53m	C_6H_5	
$[HOs_3(Me_2PC_6H_4C_6H_3)(PMe_2)(CO)_8]$ †	300	25·41q	Os–H	J(P–H) 10, 8
		8·32q	Me	J(P–H) 8·5, 1·3
		7·94q	Me	J(P–H) 8·3, 2·5
		7·92q	Me	J(P–H) 8·3, 1·5
		7·69q	Me	J(P–H 8·0, 3·0
		3·00t	$C_6H_3C_6H_4$	Four signals are equivalent to 7 hydrogen atoms
		2·79d		
		2·50s		
		2·32m		

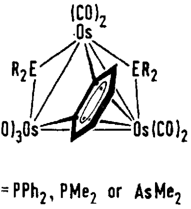
TABLE 3 (*Continued*)

Complex	T/K	τ	Assignment	Coupling const. (J/Hz), *etc.*
$[HOs_3(C_6H_4)(AsMe_2)(CO)_6]$ ‡	273	25·63s	Os–H	
		8·96s	Me	
		8·06s	Me	
		3·46m	H_2,H_3	Symmetrical AA′XX′ pattern
		3·12m	H_1,H_4	
$[Os_2(C_6H_4)(AsMe_2)_2(CO)]$ ‡	273	8·71s	Me	
		7·85s	Me	
		3·24m	H_2,H_3	Symmetrical AA′XX′ pattern
		2·12m	H_1,H_4	
$[Os_2(PMe_2C_6H_4)(PMe_2)(CO)_6]$	300	8·90d	Me	J(P–H) 11
		8·23d	Me	J(P–H) 9
		8·13d	Me	J (P–H) 9
		7·77d	Me	J(P–H) 10
		3·02m	C_6H_4	3 Relative intensities
		1·80m		1

* Assignments of aryl hydrogen signals were made by complete spin decoupling, for example, on irradiation at H_2 frequency the H_1 signal became a singlet. † Recorded at 220 MHz. ‡ Computer of average transients (c.a.t.) technique required to get acceptable spectrum.

complexes. These dimers (see Tables) were obtained in such low yields that they were only characterised by mass, i.r., and n.m.r. spectroscopy [using c.a.t. (computer of average transients) techniques] and not by elemental analysis. Although the $[Ru_3(C_6H_4)(PPh_2)_2(CO)_7]$ was isolated from a similar reaction, dimers were the main derivatives of $Ru_3(CO)_{12}$.[4]

Structures and Fluxional Behaviour of the Complexes $[Os_3(C_6H_4)(EMe_2)_2(CO)_7]$ (E = As or P).—Each of the C_6H_4 complexes we have prepared showed an AA′XX′ spectrum for this ligand in the ^1H n.m.r. spectrum at 333 K but, whereas the dimeric species were non-fluxional, the trimeric complexes showed temperature variation of the spectrum to give ABXY patterns at low temperatures. We were only able to resolve clearly four of the expected ten lines of each branch of the AA′XX′ spectra and so we did not determine coupling constants. We will consider the complexes $[Os_3(C_6H_4)(EMe_2)_2(CO)_7]$ (E = As or P) as examples for discussion since they can be compared directly with $[Os_3(C_6H_4)(PPh_2)_2(CO)_7]$ which has been shown by an *X*-ray study to have structure (I).[1] All three complexes have almost identical i.r. spectra in solution (CCl_4 for PPh_2 complex[3] or C_6H_{12} for our complexes) around 2 000 cm^{-1}, and since the solid-state and solution spectra of $[Os_3(C_6H_4)(PPh_2)_2(CO)_7]$ are quite similar it is probable that structure (I) persists in solution. Thus we assume that the EMe_2 complexes also have structure (I) in solution.



(I)

The ^1H n.m.r. spectrum for EMe_2 complexes of this structure should show four different Me signals and four different aryl hydrogen signals. However, at room temperature only four signals were observed. Figure 1 shows ^1H n.m.r. spectra for the complex with E = As. The spectrum is consistent with symmetrically *ortho*-disubstituted benzene and with equivalent EMe_2 groups but with non-equivalent methyls on each group. The two 1 : 2 : 1 triplet patterns for the methyl signals of the PMe_2 complex demonstrate strong

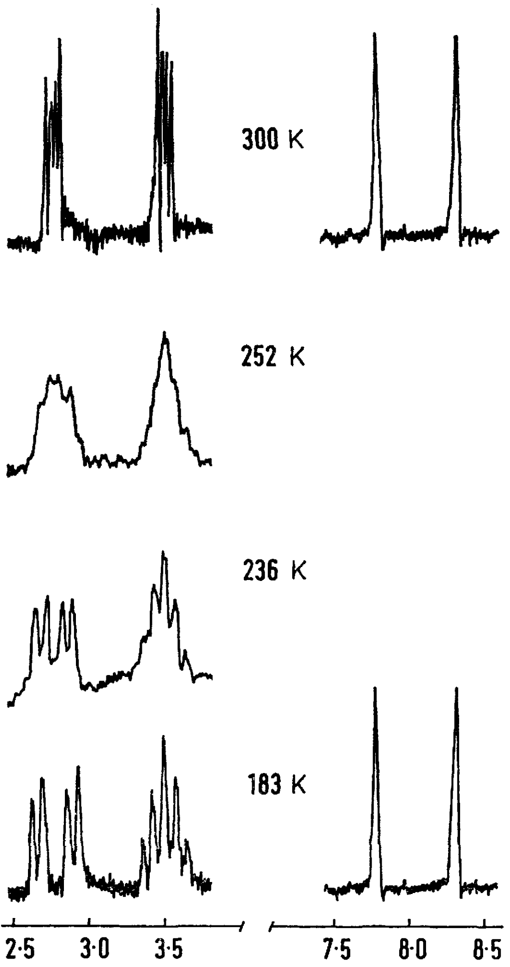
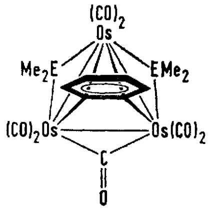


FIGURE 1 ^1H N.m.r. spectra of the complex $[Os_3(C_6H_4)(AsMe_2)_2(CO)_7]$ in CS_2

^{31}P–^{31}P coupling as in the complex $[Fe_2(PMe_2)_2(CO)_6]$.[9] Although these spectra are in themselves consistent with structure (II) of C_s symmetry, the apparent plane of symmetry is due to fluxional behaviour. Thus an ABXY spectrum was obtained for the C_6H_4 signals below the coalescence temperature [$T_c = 278$ K, $\Delta G^‡(T_c) = 58{\cdot}0$ kJ mol^{-1} (E = P) and $T_c = 248$ K, $\Delta G^‡(T_c) = 51{\cdot}3$ kJ mol^{-1} (E = As)], in agreement with frozen-out structure (I). However, even on cooling to 213 K for the PMe_2 complex (in $CDCl_3$) and to 153 K for the $AsMe_2$ complex (in CCl_2F_2) there was no sign of the coalescence temperature being reached for the Me signals to give signals due to the expected four non-equivalent methyl groups of the frozen-out structure (I). This might suggest that the EMe_2 groups exchange more rapidly than the C_6H_4 hydrogens. The following observations are also relevant to the mechanism of the process(es) occurring.



(II)

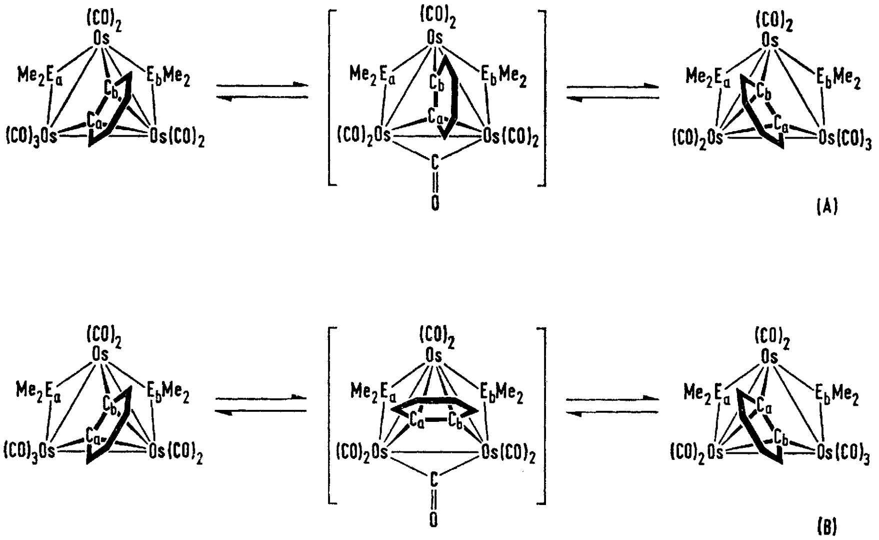


FIGURE 2 Mechanisms of fluxional behaviour of the complex $[Os_3(C_6H_4)(EMe_2)(CO)_7]$: (A), E_a–E_b exchange without C_a–C_b exchange; (B), E_a–E_b exchange with C_a–C_b exchange

(*a*) Even at high temperatures (333 K) separate signals for the Me groups of each EMe_2 bridge were observed and thus the methyl groups on the C_6H_4 side of the Os_3 ring do not exchange with those on the other. It is probable that a mechanism involving transfer of EMe_2 bridges around the Os_3 ring would lead to complete exchange of the methyl groups and hence we believe that these bridges remain intact. The observed process(es) must therefore involve C_6H_4 movement with respect to the metal ring.

(*b*) The proton-decoupled ^{31}P n.m.r. spectrum of the PMe_2 complex showed a sharp singlet at 308 K at $-132{\cdot}7$ p.p.m. with respect to 85% H_3PO_4,[10] that is, the PMe_2 bridges are effectively equivalent at this temperature. At 163 K this signal had broadened to a width of 200 Hz but, since lower temperatures could not be used, the limiting low-temperature AB quartet expected for structure (I) was not obtained. It is possible, but improbable, that the broadening is due to increased viscosity, but whether it is due to this or to slowing down of the process leading to PMe_2–PMe_2 exchange we can regard 163 K as an upper limit for the coalescence temperature. Taking 200 Hz as the limiting chemical shift between ^{31}P signals, we obtained $\Delta G^‡ \leqslant 31$ kJ mol^{-1}. The value of $\Delta G^‡$ is not very sensitive to the precise value chosen for the chemical-shift separation, for example, a shift of 50 Hz gives $\Delta G^‡ = 33$ kJ mol^{-1}, and so we conclude that PMe_2–PMe_2 exchange occurs by a considerably more rapid process than that giving exchange of C_6H_4 hydrogen atoms.

Thus two processes are required to explain these data and the minimum movements of atoms are illustrated in Figure 2. Process (A) gives EMe_2 exchange without exchange of C_a with C_b, while process (B), which is slower, gives exchange of C_a with C_b and of E_a with E_b. A combination of these processes leads to complete rotation of the C_6H_4 ligand with respect to the metal triangle. Each process is associated with a CO transfer and has an intermediate or transition state of C_s symmetry as shown in Figure 2. Rapid CO transfer between metal atoms in clusters is well substantiated in other systems.[11] Moreover, in the ground state the

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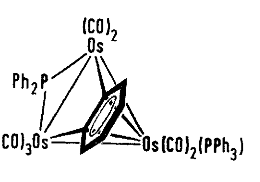
[9] R. G. Hayter, *Inorg. Chem.*, 1964, **3**, 711.

[10] B. E. Mann, personal communication.

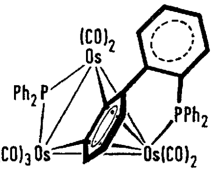
[11] F. A. Cotton, L. Kruczynski, B. L. Shapiro, and L. F. Johnson, *J. Amer. Chem. Soc.*, 1972, **94**, 6191.

plane of the organic ring is about 69° to the plane of the metal atoms (based on the isostructural PPh_2 complex [1]) and *must* be vertical in the transition state or intermediate, and therefore the organic ring must 'flip' as well as rotate during these processes. Thus, although the processes are very rapid, considerable rearrangement is involved.

Other Trimeric Complexes.—We have also isolated the hydrido-complexes $[HOs_3(C_6H_4)(EMe_2)(CO)_9]$ (E = P or As) and $[HOs_3(C_6H_4)(PMe_2)(CO)_8(PMe_2Ph)]$ which all belong to the same class of complex. These complexes contrast remarkably with $[HOs_3(C_6H_4)(PPh_2)(CO)_7(PPh_3)]$ derived from PPh_3 which seemingly differs in the CO content. Similarly in a complex we have prepared containing coupled arene rings there is an extra carbonyl group compared with the PPh_3 derivative. Thus for the complexes $[HOs_3(C_6H_4)(PR_2)(PR_2Ph)(CO)_n]$ and $[HOs_3(R_2PC_6H_4C_6H_3)(PR_2)(CO)_n]$ when R = Me, $n = 8$, but when R = Ph, $n = 7$. The derivatives with R = Ph were shown by *X*-ray studies [1,2] to have structures (III) and (IV) and the CO content was clearly established in this way. The anomaly is not simply due to inaccuracies in determining the number of carbonyl groups. All of our complexes (R = Me) except $[HOs_3(Me_2PC_6H_4C_6H_3)(PMe_2)(CO)_8]$ clearly showed parent ions in their mass spectra and also oxygen analyses have confirmed these formulations. The complex $[HOs_3(Me_2PC_6H_4C_6H_3)(PMe_2)(CO)_8]$ showed the highest mass ion in the mass spectrum as $m/e = M - 28$,* but we prefer to formulate it as the octa- rather than the hepta-carbonyl on the basis of analytical data (see Table 1). Absorption patterns around 2 000 cm^{-1} are very sensitive in detecting isostructural relations in complexes of this type, for example, replacement of PMe_2 by $AsMe_2$ or PPh_2 hardly affects this region of the spectrum for complexes $[Os_3(C_6H_4)(ER_2)_2(CO)_7]$. The strong dissimilarity of the i.r. spectra of our hydrido-complexes with those of the PPh_3 derivative shows that they are not isostructural.



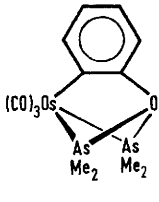
(III)



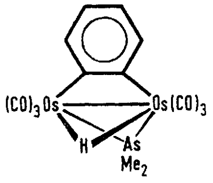
(IV)

One reasonable explanation we can provide for the above differences is that C_6H_4 can act either as a two- or a four-electron donor to the metal atoms, that is, it can be equivalent to one or two CO groups. Thus in the complexes $[HOs_3(C_6H_4)(EMe_2)(CO)_9]$ (E = P or As) it is a two-electron donor, whereas it is a four-electron donor in $[Os_3(C_6H_4)(EMe_2)_2(CO)_7]$. Yet the form of the n.m.r. spectra and the variations with temperature of these different complexes are almost identical. For the hydrido-complexes coalescence temperatures for the C_6H_4 signals are 277 K $[\Delta G^{\ddagger}(T_c) = 56{\cdot}8$ kJ mol^{-1} (E = P)] and 273 K $[\Delta G^{\ddagger}(T_c) = 56{\cdot}0$ kJ mol^{-1} (E = As)]. Similar fluxional behaviour was observed for the complex $HOs_3(C_6H_4)(PMe_2)(CO)_8(PMe_2Ph)]$ but the coalescence temperature was not determined. These results suggest that only minor changes in the nature of the C_6H_4–metal interaction are required to change the number of electrons donated. Three structural determinations of C_6H_4 complexes of the four-electron donor type have shown tilts of $69 \pm 3°$ between the planes of the metal and the aromatic ring,[1,2] and one reasonable description is of the ring forming σ-bonds to two metal atoms and donating through the π-system to the third. It is possible that an increase of this angle to approximately 90° leads to reduction or elimination of this donation. A crystal-structure determination of an apparently two-electron donor C_6H_4 system might resolve the problem.

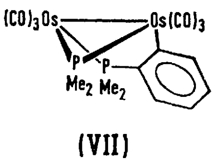
Dimeric Complexes.—Two dimeric complexes, $[Os_2(C_6H_4)(AsMe_2)_2(CO)_6]$ and $[HOs_2(C_6H_4)(AsMe_2)(CO)_6]$, were formed in very low yield in the pyrolysis of $[Os_3(CO)_{10}(AsMe_2Ph)_2]$ while the latter was also formed from $[Os_3(CO)_{11}(AsMe_2Ph)]$. These species were characterised by i.r. and mass spectrometry and they showed temperature-invarient AA'XX' n.m.r. spectra. Accordingly we assign structures (V) and (VI) to these complexes. A doubly bridging C_6H_4 group reported for nickel, $[Ni_2(C_6H_4)_2(PEt_3)_4]$, has a similar n.m.r. spectrum.[12] No dimeric complexes were isolated from pyrolyses of the PMe_2Ph complexes, but on bubbling CO through a nonane solution of $[Os_3(C_6H_4)(PMe_2)_2(CO)_7]$ heated under reflux a mixture was obtained from which we isolated $[Os_2(PMe_2)(PMe_2C_6H_4)(CO)_6]$, (VII).



(V)



(VI)



(VII)

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* Where *M* is the mass of the complex as formulated.

[12] J. E. Dobson, R. G. Miller, and J. P. Wiggen, *J. Amer. Chem. Soc.*, 1971, **93**, 554.

This formulation is preferred to $[Os_2(C_6H_4)(PMe_2)_2(CO)_6]$, analogous to the $AsMe_2$ complex, because of the four Me signals and complex C_6H_4 signals in the n.m.r. spectrum. In this reaction with CO a phosphorus–carbon bond is reformed by a process that might be described as PMe_2 insertion into an osmium–carbon bond.

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen, although the products were stable in air at room temperature and were isolated in air. Specific reaction conditions are given in Table 1.

Preparation of Substitution Products.—Typically $Os_3(CO)_{12}$ was heated in toluene under reflux with PMe_2Ph or $AsMe_2Ph$ (3 mol equiv. per Os_3) for *ca.* 5 h. After removal of solvent under vacuum the residual red oil was chromatographed on an alumina column to give three bands corresponding to the mono-, di-, and tri-substituted complexes.

Pyrolysis Reactions.—A solution of the substituted complex in octane or nonane was heated under reflux to give a red solution. The solvent was removed under vacuum and the residual oil was separated by use of column chromatography on alumina and/or preparative t.l.c. on silica.

Mass spectra were recorded on an A.E.I. MS12 spectrometer and the pyrolysis products all showed parent molecular ions in significant abundance, except $[HOs_3(Me_2PC_6H_4C_6H_3)(PMe_2)(CO)_8]$ (see Discussion section). Dimeric- and trimeric ions showed the expected isotopic distribution patterns. I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer and were calibrated against water-vapour absorptions (error ±2 cm^{-1}). ^{31}P N.m.r. spectra were measured [10] on a Bruker HFX-90 spectrometer operating in the continuous-wave mode. CH_2Cl_2, containing 10% CF_3Ph to provide field–frequency lock, was used as solvent and spectra were recorded with complete ^1H-decoupling. ^1H N.m.r. spectra were recorded on a Varian HA/100 spectrometer and assignment of the C_6H_4 signals made by spin decoupling. At room temperature or above single irradiation at the coalesced signal due to H_2 and H_3 gave a singlet for the H_1 and H_4 resonance. Below coalescence, simultaneous irradiation at the two absorption frequencies of the H_2 and H_3 protons, using two Wigan Decade oscillators, gave a singlet each for the H_1 and H_4 signals. We obtained Arrhenius data from these decoupled spectra by matching experimental with computer-simulated spectra, but we feel that these data are unreliable due to line-shape distortion under decoupling conditions. Accordingly we have simply reported approximate $\Delta G^‡$ values at coalescence temperatures. Coalescence temperatures are given for the non-decoupled spectra but are not very different from those obtained from coalescence of the H_1 and H_4 singlets under decoupling conditions.

We would like to acknowledge the help of the late Professor Sir R. S. Nyholm, under whose guidance this work was started, Dr. Brian E. Mann, for helpful discussions as well as for the ^{31}P spectra, I. Russell for technical assistance, the S.R.C., for research studentships (to M. U. and R. E. K.), and Johnson, Matthey Ltd. for a loan of OsO_4.

[3/1304 *Received, 20th June,* 1973]