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OSMIUM-COORDINATED ALKENE AND ALKYNE LIGANDS DERIVED FROM TRIETHYLPHOSPHINE AND DIETHYLPHENYLPHOSPHINE

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Summary

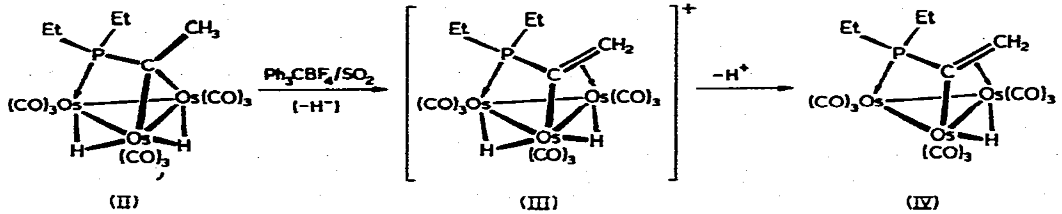
$Os_3(CO)_{11}(PEt_3)$ has been converted into the alkene compound $HOs_3(Et_2PC{=}CH_2)(CO)_9$ and hence by isomerisation into the alkyne compound $HOs_3(PEt_2)(CHCH)(CO)_9$, both of which are fluxional with facile movement of the hydrocarbon ligands with respect to the Os_3 triangle. Thus thermolysis of $Os_3(CO)_{11}(PEt_3)$ gives $H_2Os_3(Et_2PCCH_3)(CO)_9$, which has been dehydrogenated to $HOs_3(Et_2PC{=}CH_2)(CO)_9$ by hydride abstraction from the unique CH_3 followed by deprotonation from the metal. The alkene compound isomerises by a 1,2-hydrogen shift and P—C fission to the alkyne compound $HOs_3(PEt_2)(CHCH)(CO)_9$. $Os_3(CO)_{11}(PEt_2Ph)$ in hydrocarbon solvents at 150°C gives the vinylphosphido-compound $HOs_3(EtPCH{=}CH_2)(CO)_9$ as well as $HOs_3(PEt_2C_6H_4)(CO)_9$ and $HOs_3(PEt_2)(C_6H_4)(CO)_9$.

Introduction

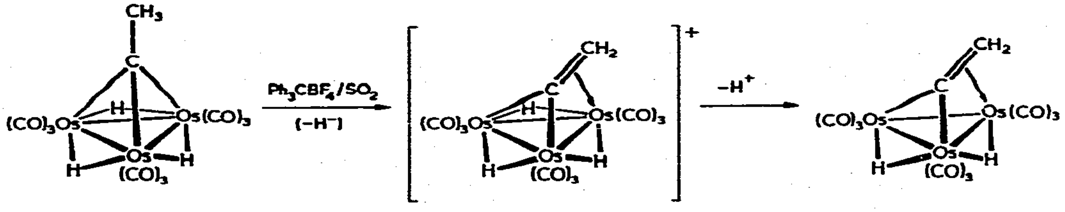
Derivatives of PMe_3 and PEt_3 with $Os_3(CO)_{12}$ resulting from C—H cleavage at the α-carbon atom have been described [1]. For example, PEt_3 reacts with $Os_3(CO)_{12}$ in refluxing toluene (110°C) to give substitution derivatives, $Os_3(CO)_{12-x}(PEt_3)_x$ ($x = 1$, 2 or 3) [2]. The compound $Os_3(CO)_{11}(PEt_3)$ at higher temperatures (refluxing nonane, 150°C) undergoes internal metallation, two hydrogen atoms being transfered, presumably successively, from carbon to osmium with the loss of two CO ligands:

$$\underset{(I)}{Os_3(CO)_{11}(PEt_3)} = \underset{(II)}{H_2Os_3(Et_2PCCH_3)(CO)_9} + 2\ CO$$

Compound II is believed to have the structure shown in Scheme Ia with the organic ligand triply-bridging the osmium atoms. A similar reaction with $Os_3(CO)_{10}(PEt_3)_2$ gives $H_2Os_3(Et_2PCCH_3)(CO)_8(PEt_3)$ which is a PEt_3-substituted derivative



SCHEME Ia



SCHEME Ib

of II. In every case both hydrogen atoms are transfered not only from the same PEt_3 ligand but also from the same carbon atom. Compound II is the starting material for some alkene and alkyne compounds to be described in this paper.

Results and discussion

Dehydrogenation of $H_2Os_3(Et_2PCCH_3)(CO)_9$ (II)

We have noted the series of compounds $H_xOs_3(CCH_x)(CO)_9$ ($x = 1$, 2 or 3) which might be regarded as osmium-substituted derivatives of acetylene, ethylene and ethane respectively [3—6], and a similar series based on II as the saturated form might be possible. In attempting to obtain unsaturated forms it was observed that (II) reacts slowly with Ph_3CBF_4 in liquid SO_2 to give, by hydride ion abstraction from the methyl group, the species $[H_2Os_3(Et_2PCCH_2)(CO)_9]^+$ (III) (Scheme 1a), which was not isolated but identified by its ^1H NMR spectrum (Table 1). A similar conversion of $H_3Os_3(CCH_3)(CO)_9$ to $[H_3Os_3(CCH_2)(CO)_9]^+$ has been achieved (Scheme 1b) [7]. Hydride ion abstraction from a carbon β to the metal is a feature of transition metal systems where the metal—carbon bonding can be modified to accommodate the change, in these cases by forming monoalkene—metal interactions with the positive charge largely located on the metal atoms. Evaporation of the liquid SO_2 and treatment of the residue with methanol lead to deprotonation from the metal to give $HOs_3(Et_2PCCH_2)(CO)_9$ (IV) and $H_2Os_3(CCH_2)(CO)_9$ respectively. The removal of H^- followed by H^+ amounts to dehydrogenation which may be reversed by direct reaction with H_2 (partially and with decomposition for the phosphine derivative).

Compound IV is also formed in very low yield (3%) in the thermolysis of I which gives II as the major product. Attempts to dehydrogenate further by treating $HOs_3(Et_2PCCH_2)(CO)_9$ (IV) with triphenylmethyl tetrafluoroborate as above were unsuccessful so the compound $Os_3(Et_2PC{\equiv}CH)(CO)_9$, which could be imagined as the third member of the series, has not been obtained.

Structure of $HOs_3(Et_2PCCH_2)(CO)_9$ (IV)

The mass spectrum confirmed that two hydrogen atoms had been lost in forming IV from its parent molecule $H_2Os_3(Et_2PCCH_3)(CO)_9$, while the ^1H NMR spectrum (Fig. 1 and Table 1) is totally consistent with its formation as an osmium-substituted derivative of diethylvinylphosphine. As well as the osmium hydride doublet and the ethyl resonances, there are two doublets due to the C_2H_2 moiety. The lack of coupling between these two protons confirms the arrangement $Et_2P{-}C{-}CH_2$ rather than $Et_2{-}CH{-}CH$. The values of $J(H^{31}P)$ show that one proton is *cis* and the other *trans* to the phosphorus atom about the double bond [$J(H_a{}^{31}P) = 17.6$ Hz (*cis*) and $J(H_b{}^{31}P) = 30.8$ Hz (*trans*)]. The ^1H NMR spectrum of the protonated form, (III), shows the same ligand arrangement and nonequivalent metal hydrides. The hydride positions are unknown; those shown in the figures are conjectural (see later). The ligand Et_2PCCH_3 is best regarded as a 4e-donor (as a neutral ligand) so that compound II fits the E.A.N. rule if there are three Os—Os bonds and similarly the ligand Et_2PCCH_2 in III and IV is a 5e-donor.

Compound IV is closely related to the fluxional molecule $HOs_3(CH{=}CH_2)(CO)_{10}$ [6,8,9] for which the hydride position is known and the analogous position for IV is shown in the figures. The $CH{=}CH_2$ ligand rapidly interchanges its bonding between the two bridged metal atoms as shown in Scheme 2b. This process was detected [10] by the coalescence of the ^{13}C NMR signals of corresponding pairs of carbonyl groups on the two bridged osmium atoms. A corresponding process

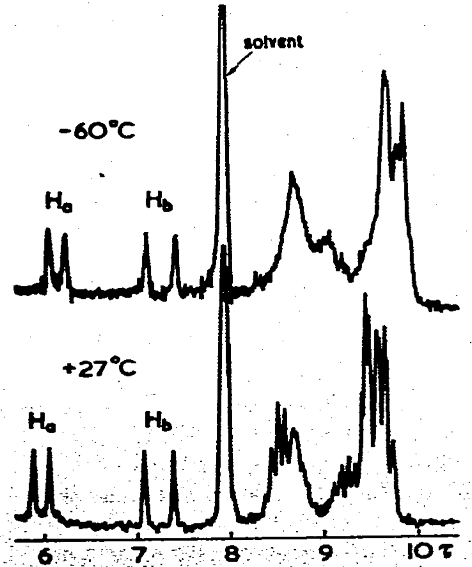
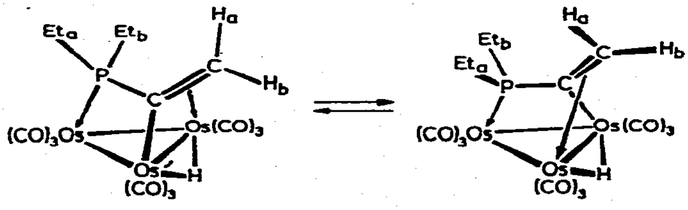
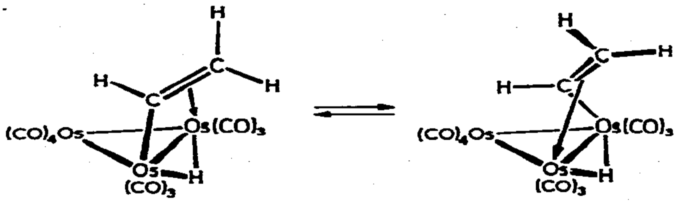


Fig. 1. ^1H NMR spectra for $HOs_3(Et_2PC{=}CH_2)(CO)_9$ (IV), recorded in $C_6D_5CD_3$ (hydride signal omitted).



SCHEME 2a



SCHEME 2b

for IV would lead to exchange of Et_a with Et_b (Scheme 2a). For the static structure all four $C\underline{H}_2CH_3$ are different but for effectively equivalent Et groups at high exchange rates the $C\underline{H}_2CH_3$ protons should give just one *AB* quartet with further coupling, of course, with the $CH_2C\underline{H}_3$ and ^{31}P nuclei. While no attempt was made to sort out this problem, considerable changes in the Et-resonances including broadening take place on cooling from 27 to —60°C, which seemingly result from a reduction in the rate of the process in Scheme 2a on lowering the temperature.

Thermolysis of $HOs_3(Et_2PC{=}CH_2)(CO)_9$ *(IV)*

It has been shown that $HOs_3(CH_3C \cdot C \cdot CH_2)(CO)_9$, a derivative of but-2-yne, undergoes an interesting isomerisation to $HOs_3(CH_3C \cdot CH \cdot CH)(CO)_9$ at 150°C [6]. By analogy with the results of a X-ray study of a very similar ruthenium compound [11], the ligand in the initial isomer is best described as a 5e-donating allenyl group with a σ—Os—C bond and monoalkene bonds to the other osmium atoms. We originally suggested [6] that this isomer contained a 1,2-osmium disubstituted π-allyl ligand but undoubtedly it is better described as shown in Scheme 3b. 1,2-Hydrogen shifts in both the ruthenium [12] and osmium [6] compounds give 1,3-metal disubstituted π-allylic isomers like that in Scheme 3b. The distinct possibility of 1,2-hydrogen shifts of this sort in IV led us to thermolyse this compound at 165—170°C in d^8-toluene in a sealed tube under nitrogen following changes in the ^1H NMR spectrum. Compound V (Scheme 3a) was not observed but the quantitative formation of $HOs_3(PEt_2)(CHCH)(CO)_9$ (VI) indicates that a 1,2-hydrogen shift has occurred but together with P—C bond cleavage. The expected product V might well be an intermediate in the formation of VI as shown in Cheme 3a.

The formulation of VI in this way requires some justification. Its mass spectrum and elemental analysis confirm the stoichiometry and a ^1H NMR doublet

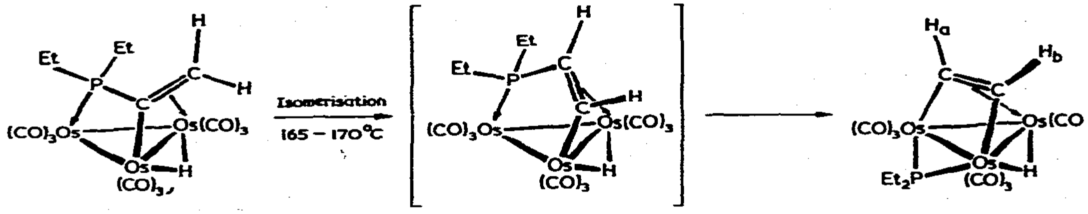
TABLE 1

IR [a] AND ^{1}H NMR DATA [b]

Compound	ν(CO) (cm^{-1})		τ (ppm)	Assignment	J(Hz)
$H_2Os_3(Et_2PCCH_3)(CO)_9$ [c]	2097m	2070s	7.54d	$CC\underline{H}_3$	$J(H^{31}P)$ 18.0
(II) ($CDCl_3$, −59°C)	2045vs	2020s	7.3—8.2	$PC\underline{H}_2CH_3$	
	2007s	2001m	8.84m	$PCH_2C\underline{H}_3$	
	1988m	1979m	25.19d	$Os\underline{H}$	$J(H^{31}P)$ 9.4
	1967m		30.05d	$Os\underline{H}$	$J(H^{31}P)$ 8.0
$[H_2Os_3(Et_2PCCH_aH_b)(CO)_9]^+$ [d]			4.87d	$\underline{H}_a$	$J(H_a{}^{31}P)$ 17.8
(III) (SO_2/Ph_3CBF_4, 27°C)			6.28d	$\underline{H}_b$	$J(H_b{}^{31}P)$ 29.2
			7.5m	$PC\underline{H}_2CH_3$	
			8.7m	$PCH_2C\underline{H}_3$	
			28.95d	$Os\underline{H}$	$J(H^{31}P)$ 5.0
			29.39d	$Os\underline{H}$	$J(H^{31}P)$ 6.9
$HOs_3(Et_2PCCH_aH_b)(CO)_9$	2090s	2059vs	5.38d	$\underline{H}_a$	$J(H_a{}^{31}P)$ 17.6
(IV) ($CDCl_3$, 27°C)	2031vs	2017s	6.94d	$\underline{H}_b$	$J(H_b{}^{31}P)$ 30.8
	1999s	1990s	8.0m	$PC\underline{H}_2CH_3$	
	1978s	1976(sh)	8.95m	$PCH_2C\underline{H}_3$	
	1959m		28.22d	$Os\underline{H}_c$	$J(H_c{}^{31}P)$ 8.3
$HOs_3(PEt_2)(CH_aCH_b)(CO)_9$ [e]	2096w	2073vs	—0.22t	$C\underline{H}_a$ [e]	$J(H_a{}^{31}P)$ 9.0
(VI) ($C_6D_5CD_3$, −30°C)	2047s	2019m	0.66dd	$C\underline{H}_b$ [e]	$J(H_b{}^{31}P)$ 5.8
	2010vs	1994m	8.0—9.8	$PC\underline{H}_2C\underline{H}_3$	$J(H_aH_b)$ 9.0
	1984w	1968m	29.23d	$Os\underline{H}_c$	$J(H_c{}^{31}P)$ 10.8
$HOs_3(PEt_2C_6H_4)(CO)_9$	2085m	2054s	1.74m	C_6H_4	
(VII) ($CDCl_3$, 27°C)	2031vs	2011m	2.67m		
	1989(sh)	1985m	3.04m		
	1980m	1973w	3.29m		
	1958w		6.8—9.8	$PC\underline{H}_2C\underline{H}_3$	
			28.01d	$Os\underline{H}$	$J(H^{31}P)$ 14.5
$HOs_3(PEt_2)(C_6H_4)(CO)_9$	2092w	2071vs	1.04d	C_6H_4 [f]	
(VIII) ($CDCl_3$, −40°C)	2042s	2016m	1.50d		
	2009s	2004m	2.99m		
	1988w	1979w	3.26m		
	1967(sh)	1964w	7.5—9.6	$PC\underline{H}_2C\underline{H}_3$	
			27.02d	$Os\underline{H}$	$J(H^{31}P)$ 9.0
$HOs_3(EtPCH{=}CH_2)(CO)_9$	2089w	2059s	5.17[g]	$\underline{H}_a$	$J(H_aH_c)$ 12.9
(IX) ($CDCl_3$, 27°C)	2034vs	2014s	6.62[h]	$\underline{H}_b$	$J(H_aH_b)$ 8.5
	2001w	1992w	6.97[h]	$\underline{H}_c$	$J(H_bH_c)$ ~0
	1988m	1969w	7.8—9.2	$PC\underline{H}_2C\underline{H}_3$	$J(H_a{}^{31}P)$ 18.5
			29.48d	$Os\underline{H}$	$J(H_b{}^{31}P)$ 33.4
					$J(H_c{}^{31}P)$ 19.7
					$J(H_d{}^{31}P)$ 13.5

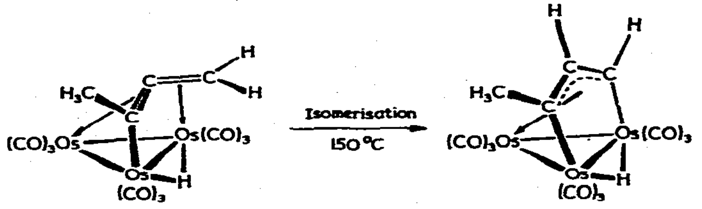
[a] Recorded in cyclohexane; ±1 cm^{-1}. [b] Recorded at 100 MHz at the temperature and in the solvent given. [c] Reference 1; broad $Os\underline{H}$ signal at τ 27.6 ppm at 70°C. [d] Not isolated; identified by comparison of its NMR data with those of IV. [e] At 60°C H_a and H_b signals have coalesced to a doublet at τ 0.03 ppm with $J(H^{31}P)$ = 6.9 Hz. [f] C_6H_4 signals at τ 1.22 and 3.08 ppm at 27°C. [g] 8-line multiplet. [h] 1 : 1 : 1 : 1 quartet.

(^{31}P coupling) at 0.03 τ in $C_6D_5CD_3$ solution at 60°C is at a characteristically low field for a triply-bridging acetylene. For comparison, $H_2Os_3(CHCH)(CO)_9$ has a corresponding signal at 0.69 τ which is close to the average shift of the two peaks observed at —120°C at —0.14 τ and 1.64 τ [13]; above —90°C these peaks have coalesced. As depicted in Scheme 3a the two acetylene hydrogen atoms in VI are also non-equivalent and on cooling the solution this signal broadens and



(IV) (V) (VI)

SCHEME 3a



SCHEME 3b

gives separate signals for H_a and H_b, a 1 : 2 : 1 triplet at −0.22 τ and a 1 : 1 : 1 : 1 quartet at 0.66 τ. The size of coupling to the ^{31}P nucleus for H_a (9.0 Hz) and for H_b (5.8 Hz) is much less than expected for compounds such as IV and V where the P—C bond is intact. In many respects compound VI is closely similar to $HOs_3(PMe_2)(C_6H_4)(CO)_9$ [14] and to $HOs_3(PEt_2)(C_6H_4)(CO)_9$, compound VIII, to be described later in this paper. Significantly all three compounds give very similar ν(CO) absorptions around 2000 cm^{-1}, and all are fluxional, leading to H_a—H_b exchange in VI and a comparable exchange in VIII which results in an *ABXY* spectrum for C_6H_4 at low temperatures converting to an *AA'XX'* spectrum at higher temperatures (Fig. 2). Rates have not been accurately measured but are not very different for the two compounds illustrated. A discussion of mechanism must await structural determinations and further work, but rotation of the C_6H_4 ligand relative to the Os_3 triangle as established for $Os_3(PMe_2)_2(C_6H_4)(CO)_7$ is most likely [14]. It is unnecessary to invoke movement of the ligand CCH_2 in $H_2Os_3(CCH_2)(CO)_9$ to explain the two rapid intramolecular processes [5,15], whereas with alkyne ligands, as in $H_2Os_3(CHCH)(CO)_9$, there is the possibility of facile hydrocarbon movement as with C_6H_4 compounds.

Once there has been an initial activation at a saturated group, ethyl in this case, all subsequent chemistry is centred on this group, so that the sequence of ligand changes has been followed: $PEt_3 \rightarrow PEt_2$—$CHCH_3$ (not observed) → PEt_2—$CCH_3 \rightarrow PEt_2$—$CCH_2 \rightarrow PEt_2 + CHCH$. The PEt_2 part of the original ligand remains intact. The formation of alkyne from alkene ligands has been established in several cases, in particular in the direct reaction of alkenes with triosmium or triruthenium clusters, see the review [16], while here a saturated ligand has been converted through an alkene to an alkyne.

Alkene and benzyne derivatives of PEt_2Ph

Previously we have shown that $Os_3(CO)_{11}(PMe_2Ph)$ degrades to $HOs_3(PMe_2)$-

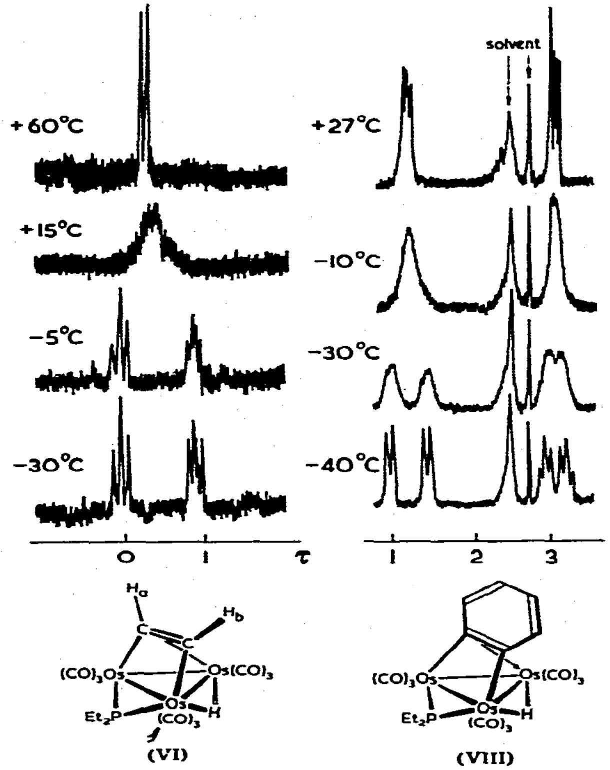
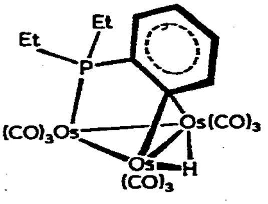


Fig. 2. ^{1}H NMR spectra for the C_2H_2 ligand of VI and the C_6H_4 ligand of VIII recorded in $CDCl_3$.

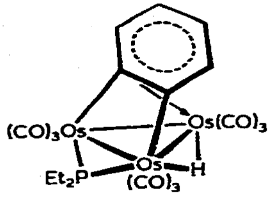
$(C_6H_4)(CO)_9$ with C—H fission at the *ortho*-site of the ring with no reaction at the methyl group [14]. It was expected that $Os_3(CO)_{11}(PEt_2Ph)$ would behave similarly, but treatment of this compound in refluxing nonane gave three main products. Two are *ortho*-metallated arene compounds as expected: $HOs_3(PEt_2C_6H_4)(CO)_9$ (VII) and its isomer $HOs_3(PEt_2)(C_6H_4)(CO)_9$ (VIII), the latter entirely equivalent to the PMe_2 species. The third product $HOs_3(EtPCH{=}CH_2)(CO)_9$ (IX) is generated formally by loss of C_6H_6 and 2 CO. Loss of arene could follow *ortho*-metallation as in the formation of benzene from benzyl alcohol promoted by $Os_3(CO)_{12}$ [17].

It is believed that the structure of IX is as shown. A $EtPCH{=}CH_2$ ligand coordinated through the phosphorus atom and the carbon—carbon double bond is strongly indicated by the ^{1}H NMR spectrum, and as a 5e-donor it satisfies the electronic requirements of the metal atoms. The ν(CO) spectrum as well as the structure of IX are quite similar to those of IV. The $CH{=}CH_2$ group gives ^{1}H NMR signals (τ 5.17, 6.62 and 6.97) with proton—proton and proton—phosphorus coupling entirely consistent with this formulation (Table 1). Spin—spin coupling constants J(HH) and $J(H^{31}P)$ across the double bond are reduced from free vinylphosphine values consistent with alkene coordination as are the chemical shifts above. In an attempt to displace the alkene from the metal to leave the phosphorus coordinated, IX was treated with atmospheric pressure CO in refluxing heptane or nonane for extended periods but to no effect. Indeed IX is thermally very stable and after 2 h at 183°C in nonane in a sealed glass tube most was recovered; products in traces were not studied.

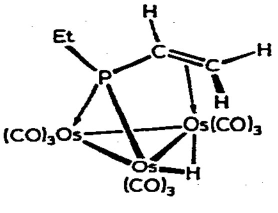
The other products VII and VIII are not of a new type. A series of six derivatives of PPh_3 and $Os_3(CO)_{12}$ has been thoroughly examined structurally [18,19] and shown to contain ligands such as doubly- or triply-bridging $PPh_2C_6H_4$, triply-bridging C_6H_4 and doubly-bridging C_6H_5. Compound VII, $HOs_3(PEt_2C_6H_4)(CO)_9$, may be compared with $HOs_3(PPh_2C_6H_4)(CO)_8(PPh_3)$ which is one of these six and so VII almost certainly contains an osmium-bridging phenyl group as shown. ^1H NMR for all four C_6H_4 protons of VII appear separately even at room temperature unlike those for its isomer VIII. Compound VII is presumably the precursor of VIII, which contains the C_6H_4 ligand showing separate proton signals at low temperature, an *ABXY* spectrum, and an *AA'XX'* spectrum at room temperature and above. Clearly rapid site exchange within the C_6H_4 group is possible for VIII but not VII.



(VII)



(VIII)



(IX)

Conclusion

Our results not only demonstrate the high affinity of Os_3 clusters for alkenes and alkynes, but also show that in cluster chemistry at elevated temperatures (above 100°C) one cannot employ trialkylphosphines, let alone triarylphosphines, as inert ligands simply present to modify the steric and electronic requirements of the metal atoms in their reactions. This has been a traditional role for tertiary phosphines, but it is doubtful whether any ligand could play this role in triosmium chemistry.

Experimental

All reactions at elevated temperatures and those involving free tertiary phosphines were carried out under nitrogen; work-up and separation procedures in air.

Mass spectra

All neutral compounds described in this paper have considerable thermal stability and are volatile so that mass spectra are easily obtained with direct insertion into a source at 100—140°C. Parent molecular ions with the expected isotopic patterns were observed in all cases. Loss of CO is the main mode of fragmentation, but the compounds do show differences. The molecular ion of II is the only one that looses $C_2H_5^{\cdot}$ (29 mass units) rather than C_2H_4 or CO (28 mass units) as the primary fragmentation. Other compounds, IV, VII, VIII and IX successively loose 28 and then 30 mass units (probably CO then CO + H_2 but without accurate mass measurements this has not been confirmed).

Tertiary phosphine-substituted derivatives of $Os_3(CO)_{12}$

To obtain good yields of $Os_3(CO)_{11}L$ the reported method [1,2], which gives mainly $Os_3(CO)_{10}L_2$ and smaller quantities of $Os_3(CO)_{11}L$ and $Os_3(CO)_9L_3$, was modified. A solution of $Os_3(CO)_{12}$ (1.159 g) and PEt_3 (about 0.1 g) in toluene (AR, 80 cm^3) was heated under reflux for 30 min. The solvent was removed under reduced pressure and the residue extracted with toluene (20 cm^3) to leave behind unreacted crystals of $Os_3(CO)_{12}$. These were treated four more times as above so that in total PEt_3 (0.57 g) was used. The combined toluene extracts were chromatographed on a column (alumina) eluting with light petroleum/toluene mixtures to give $Os_3(CO)_{11}(PEt_3)$ (0.782 g), $Os_3(CO)_{10}(PEt_3)_2$ (0.184 g) and $Os_3(CO)_9(PEt_3)_3$ (0.012 g). PEt_2Ph derivatives were prepared similarly. ν(CO) absorptions were as reported [2].

Action of refluxing solvent on $Os_3(CO)_{11}(PEt_3)$

In refluxing nonane $H_2Os_3(Et_2PCCH_3)(CO)_9$ (II) is formed [1]. However, a solution of $Os_3(CO)_{11}(PEt_3)$ (1.165 g) in *o*-xylene (80 cm^3) was heated under reflux for 29.5 h. Removal of the solvent and chromatography on silica columns and plates gave several bands from which were isolated the starting material as orange crystals (0.29 g), $H_2Os_3(Et_2PCCH_3)(CO)_9$ (II) as very pale yellow crystals (0.21 g) [1] and $HOs_3(Et_2PCCH_2)(CO)_9$ (IV) as yellow crystals (0.032 g) (Found: C, 19.6; H, 1.5; P, 3.3. $C_{15}H_{13}O_9Os_3P$ calcd.: C, 19.2; H, 1.4; P, 3.3%).

Dehydrogenation of $H_2Os_3(Et_2PCCH_3)(CO)_9$ (II)

A solution of II (0.063 g) and Ph_3CBF_4 (0.33 g) in liquid SO_2 (1.5 cm^3) in a sealed NMR tube was allowed to stand at room temperature for 3 weeks. The NMR spectrum recorded at intervals showed the slow conversion to III (data in Table 1). The solvent was evaporated and the residue treated with methanol. Removal of the methanol and extraction with pentane gave a yellow solution. Chromatography of the extract on plates (silica) gave $HOs_3(Et_2PCCH_2)(CO)_9$ (IV) as yellow crystals (0.042 g), which was spectroscopically identical to the material obtained in the previous experiment.

Hydrogenation of $HOs_3(Et_2PCCH_2)(CO)_9$ (IV)

Hydrogen was bubbled through a refluxing solution of IV (0.025 g) in decane (25 cm^3). After 1 h there was considerable decomposition but an IR spectrum showed that II was the main component of the mixture. No reaction occurred in refluxing heptane.

Thermolysis of $HOs_3(Et_2PCCH_2)(CO)_9$ (IV)

A solution of IV (0.020 g) in $C_6D_5CD_3$ (0.5 cm^3) containing two drops of benzene as an NMR reference was heated at 165—170°C in an NMR tube sealed under vacuum. After 1.5 h a new hydride species appeared in the NMR spectrum and after 20 h the conversion to this compound was complete. The solvent was removed under vacuum and layer chromatography (silica) gave $HOs_3(PEt_2)(CHCH)(CO)_9$, (VI), as colourless crystals (0.010 g) (Found: C, 18.7; H, 1.3. $C_{15}H_{13}O_9Os_3P$ calcd.: C, 19.2; H, 1.4%).

Action of refluxing nonane on $Os_3(CO)_{11}(PEt_2Ph)$

A solution of this compound (0.694 g) in nonane (80 cm^3) was heated under reflux for 5 h. The orange-brown solution was evaporated to dryness under vacuum and chromatography of the residue on preparative layer plates (silica) eluting with light petroleum gave several bands, three of which gave tractable products: $HOs_3(PEt_2C_6H_4)(CO)_9$ (VII), as yellow crystals (0.028 g) (Found: C, 23.15; H, 1.45; P, 3.1. $C_{19}H_{15}O_9Os_3P$ calcd.: C, 23.1; H, 1.55; P, 3.15%), $HOs_3(PEt_2)(C_6H_4)(CO)_9$ (VIII), as orange crystals (0.210 g) (Found: C, 23.2; H, 1.45; P, 3.25. $C_{19}H_{15}O_9Os_3P$ calcd.: C, 23.1; H, 1.55; P, 3.15%), and $HOs_3(EtPCH{=}CH_2)(CO)_9$ (IX), as yellow crystals (0.238 g) (Found: C, 17.25; H, 1.0; P, 3.55. $C_{13}H_9O_9Os_3P$ calcd.: C, 17.15; H, 1.55; P, 3.4%).

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