Reactions of Dodecacarbonyl-*triangulo*-triosmium with Alkenes and Benzene; Fluxional Behaviour of μ_3-(Ethan-1-yl-2-ylidyne)-di-μ-hydrido-*triangulo*-tris(tricarbonylosmium)(3*Os–Os*)

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Ethylene on reaction with $Os_3(CO)_{12}$ heated under reflux in octane undergoes 1,1-elimination of H_2 to give the ethan-1-yl-2-ylidyne complex $[H_2Os_3(CH_2C)(CO)_9]$, (I), whereas cyclopentene and benzene undergo 1,2-elimination of H_2 to give corresponding cyclopenta-1,2-diylidene and cyclohexa-3,5-dien-1,2-diylidene complexes (II) and (III). Kinetic data are given for intramolecular exchange of the $-CH_2C\leqslant$ hydrogen atoms of complex (I) which is faster than hydride exchange, and mechanisms for these processes are discussed. Diphenyl(*o*-vinylphenyl)phosphine (dpvp) reacts with $Os_3(CO)_{12}$ to give the complex $[H_2Os_3(Ph_2P{\cdot}C_6H_4{\cdot}C_2H)(CO)_8]$, (IV), which is related to the derivatives above.

RECENTLY several reactions of cluster carbonyl complexes have been reported in which carbon–hydrogen bond cleavage occurs with olefins to give metal–carbon and –hydrogen bonds. For example, cyclo-octene (C_8H_{14}) reacts with $M_3(CO)_{12}$ ($M = $ Ru or Os) to give the complex $[H_2M_3(C_8H_{12})(CO)_9]$ [1] and bicyclo[3.2.1]-octa-2,6-diene (C_8H_{10}) reacts with $Ru_3(CO)_{12}$ to give $[H_2Ru_3(C_8H_8)(CO)_9]$.[2] The alkene molecule in each case has been dehydrogenated to give a co-ordinated 'alkyne' bridging three metal atoms *via* one π- and two σ-bonds. Hydrogen transfer to the metal atom has also been reported for reactions of $Ru_3(CO)_{12}$ with hexa-2,4-diene [3] or cyclohexa-1,3-diene [4] to give the complex $[HRu_3(C_6H_9)(CO)_9]$ and with cyclododeca-1,5,9-trienes to give $[HRu_3(C_{12}H_{15})(CO)_9]$.[5] In these complexes the unsaturated ligand bridges three metal atoms *via* one π-allyl and two σ-bonds.

Believing that this type of reactivity is not restricted to complex alkenes, we have examined reactions of $Os_3(CO)_{12}$ with ethylene and cyclopentene, together with the related reaction with benzene. Preliminary reports on some of this work have appeared previously,[6,7] Our interest in this type of behaviour started with attempts to prepare the diphenyl(*o*-vinylphenyl)phosphine (dpvp) derivative, $[Os(CO)_3(dpvp)]$, by reacting this ligand with $Os_3(CO)_{12}$. We obtained instead the complex $[H_2Os_3(Ph_2P{\cdot}C_6H_4{\cdot}C_2H)(CO)_8]$, (IV), which is related to other olefin derivatives described in this paper.

RESULTS AND DISCUSSION

Reaction of $Os_3(CO)_{12}$ *with Ethylene.*—Ethylene was bubbled for 24 h through a refluxing octane solution of $Os_3(CO)_{12}$ and chromatography of the resulting mixture on silica gave a complex of apparent formula $[Os_3(CO)_9(C_2H_4)]$ in moderate yield. The displacement of three CO groups by ethylene suggested that simple substitution had not occurred and indeed the complex gave four n.m.r. signals at room temperature in $CDCl_3$, two singlets at τ 3·90 and 4·43 assigned to a C_2H_2 ligand and two doublets at τ 28·13 and 31·83 due to hydride groups (see Table). Lack of coupling between the organic hydrogen atoms suggested co-ordinated ethan-1-yl-2-ylidyne, $-CH_2C\leqslant$, whereas analogy with previous results on cyclic alkenes [1,2] favoured HC≡CH as the ligand in this molecule. Absorptions due to ν(C–H) at 2 952(sh), 2 921, and 2 848 cm^{-1} are not particularly diagnostic.

A single-crystal *X*-ray study [8] has shown a structure consistent with the formulation $[H_2Os_3(CH_2C)(CO)_9]$

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[1] A. J. Canty, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1972, **43**, C35; A. J. Canty, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1973, 2056.

[2] A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1972, **36**, C43.

[3] M. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone, and M. Valle, *J.C.S. Chem. Comm.*, 1972, 545.

[4] T. H. Whitesides and R. A. Budnik, *J.C.S. Chem. Comm.*, 1973, 87.

[5] M. I. Bruce, M. A. Cairns, A. Cox, M. Green, M. D. H. Smith, and P. Woodward, *Chem. Comm.*, 1970, 735; A. Cox and P. Woodward, *J. Chem. Soc.* (*A*), 1971, 3599; M. I. Bruce, M. A. Cairns, and M. Green, *J.C.S. Dalton*, 1972, 1293.

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

[7] A. J. Deeming and M. Underhill, *J.C.S. Chem. Comm.*, 1973, 277.

[8] R. Baker, personal communication.

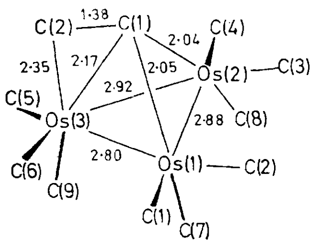
(Figure). One carbon atom is bonded to all three metal atoms while the other is within bonding distance of only one osmium. Consequently we feel that both hydrogen atoms must be located on the latter carbon even though there is no direct evidence for their positions.

Analytical,[a] i.r.,[b] and ^1H n.m.r. data [c] for the new complexes

Complex	C	H	O	P	ν(CO)/cm^{-1}	t/°C	τ	Assignment	J/Hz
$[H_2Os_3(CH_2C)(CO)_9]$ [d]	15·4	0·45	16·8		2 109vw, 2 082vs,	27 [d]	3·90 (s)	C*H*	
	(15·5)	(0·45)	(16·9)		2 059vs, 2 052sh,		4·43 (s)	C*H*	
					2 032s, 2 022s,		28·13 (d)	Os*H*	J (H–H) 1·4
					2 019s, 2 011m,		31·83 (d)	Os*H*	
					1 993, 1 985m				
$[H_2Os_3\{CH(Me)C\}(CO)_9]$ [e]					2 107vw, 2 082vs,	27	1·84 (s)		
					2 058vs,		2·96 (q)	C*H*Me	J (H–H) 5·8
					2 030s, 2 020s,		7·13 (s)		
					2 015s, 2 007m,		7·87 (d)	CH*Me*	J (H–H) 5·8
					1 990vw,		28·30 (s)	Os*H*	
					1983m		31·30 (s)	Os*H*	
$[H_2Os_3(C_5H_6)(CO)_9]$	19·05	0·9	16·05		2 108w, 2 080s,	35	7·23 (t)	C_5H_6	
	(18·9)	(0·9)	(16·15)		2 055vs, 2 031s,		7·85 (m)		
					2 024m, 2 010s,		8·85 (m)		
					1 998m, 1 982m		29·7 (br)	Os*H* [f]	
						−46	27·80 (s)	Os*H*	
							31·83 (s)	Os*H*	
$[H_2Os_3(C_6H_4)(CO)_9]$ [g]	20·3	0·7			2 109m, 2 082s,	27	2·13 (m)	C_6H_4	AA′XX′ pattern
	(20·0)	(0·65)			2 056vs, 2 035s,		3·14 (m)		
					2 025m, 2 010s,		28·96 (s)	Os*H*	
					2 000m, 1 987sh,				
					1 984m				
$[H_2Os_3(Ph_2P{\cdot}C_6H_4{\cdot}C_2H)(CO)_8]$	31·25	1·65		2·8	2 090w, 2 082vs,	27	2·68 (m)	$Ph_2P{\cdot}C_6H_4{\cdot}C_2H$	
	(31·05)	(1·6)		(2·85)	2 065sh,		3·20 (m)		
					2 050vs, 2 031s,		26·8 (d) [h]	Os*H*	J (P–H) 25·4
					2 017w, 2 007s,		30·8 (d) [h]	Os*H*	J (P–H) 10·3
					1 997w, 1 983m,				
					1 970w				

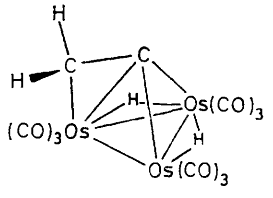
[a] Found (Calc.) in %. [b] Measured in cyclohexane. [c] Recorded in $CDCl_3$ at 100 MHz unless otherwise stated; signal integrations consistent with assignments, including OsH signals. [d] ν(C–H) at 2 952sh, 2 921, and 2 848 cm^{-1} (CCl_4); n.m.r. spectrum, recorded in $CD_3C_6D_5$, varies at higher temperatures as described in Discussion section. [e] Not obtained in pure form; signals at τ 1·84 and 7·13 due to another species (see text). [f] Signal 200 Hz wide gave two sharp singlets at −46 °C. [g] N.m.r. spectrum almost unchanged at −50 °C. [h] Doublets plus unresolved fine structure.

One reasonable description is that two hydrogen atoms on one carbon of the ethylene have been substituted by two osmium atoms, permitting simple mono-olefin type interaction with the third osmium, and the other complexes in this paper could be considered similarly. An acceptable alternative using only σ-osmium–carbon bonds is implied by the nomenclature and structural formulae.

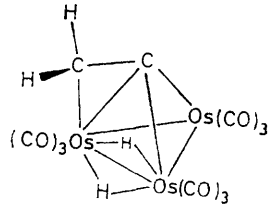


Structure of the complex $[H_2Os_3(CH_2C)(CO)_9]$ showing distances between skeletal atoms [8]

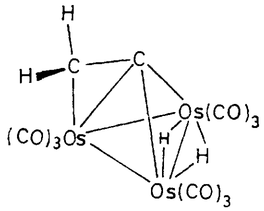
Metal-bonded hydrogen atoms were also not located in the structural study, but some observations are relevant here. All Os–Os bonds are different and the CH_2C ligand is distinctly tilted away from the shortest of these [∠Os(1)–C(1)–C(2), 138; ∠Os(2)–C(1)–C(2), 124°]. The reason for this tilt is only apparent if the hydride ligands are asymmetrically disposed, hence we favour structures (Ia) or (Ib) in preference to (Ic) or (Id). Methods of variable reliability have been used to locate hydride positions in polynuclear carbonyl complexes: [9] nematic-phase n.m.r. spectra; Raman spectra; metal–metal bond lengths; coupling of the hydride nuclei with ^{31}P nuclei of tertiary phosphines; angles between terminal carbonyls and metal–metal bonds; and, for certain lighter transition-metal systems,



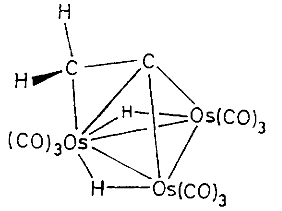
(Ia)



(Ib)



(Ic)



(Id)

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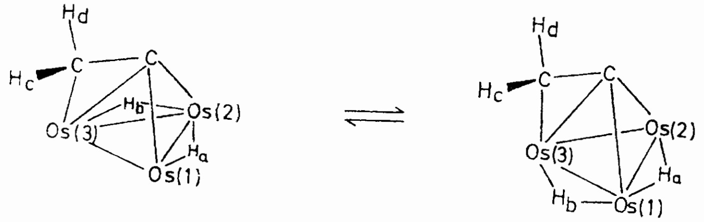
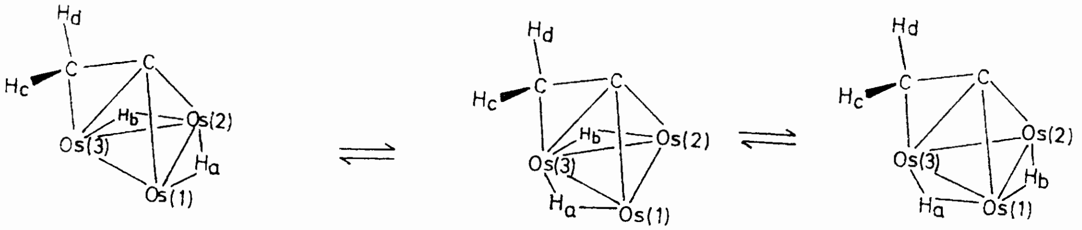
[9] H. D. Kaesz, *Chem. in Britain*, 1973, **9**, 344.

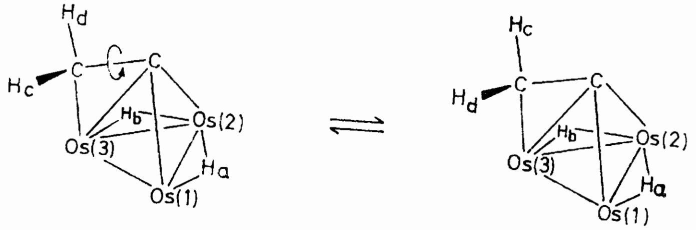
X-ray crystallography. If metal–metal bond lengthening is associated with hydrogen bridging, the complex is of structure (Ia). However, bond shortening has also been found to be associated with hydrogen bridging so this is not an unambiguous criterion. Of the Os–Os–C(carbonyl) angles associated with each metal–metal bond only the four smallest are considered to be sensitive to the presence of a hydride ligand bridging those metal atoms. The four smallest angles are 123 (8), 96 (3), 116 (7), and 100° (2) for Os(1)–Os(2), 122 (8), 97 (4), 111 (9), and 110 (5) for Os(2)–Os(3), and 95 (9), 91 (6), 99 (7), and 95° (1) for Os(1)–Os(3). Numbers in parentheses after each angle refer to carbonyl ligands as labelled in the Figure. Thus from these data it would appear that Os(1)–Os(2) and Os(2)–Os(3) bonds are associated with significantly larger angles than the other bond and probably accommodate the hydrogen atoms as shown in structure (Ia). The appearance of four n.m.r. signals and at least nine ν(CO) absorptions also agrees with the low symmetry of this structure (see Table).



(1)



(2)



(3)

Kinetics and Mechanism of the Fluxional Behaviour of the Complex [$H_2Os_3(CH_2C)(CO)_9$].—The two singlets due to the CH_2C ligand broadened above room temperature and coalesced at 72 °C to a singlet. Rates of exchange were obtained by matching computer-simulated spectra with observed spectra at various temperatures, and gave $E_a = 85{\cdot}3$ kJ mol^{-1}, $\log_{10} A = 15{\cdot}0$, $\Delta H^{\ddagger} = 82{\cdot}4$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 32{\cdot}4$ J K^{-1} mol^{-1}. Above 97 °C the hydride signals also began to broaden but even at 115 °C they were still clearly resolved (half-height width *ca.* 7 Hz). Since we did not obtain spectra at any higher temperature, coalescence was not observed. Applying kinetic data obtained for CH_2C exchange to the hydride signals we calculated a coalescence temperature of 96 °C, and therefore the hydride ligands must exchange at a significantly slower rate than the CH_2C hydrogen atoms. Mechanisms are discussed initially in terms of structure (Ia).

Mechanism (1) involves only hydride migrations from one edge of the metal triangle to a vacant edge. Migration of H_b across the cluster to the vacant site between Os(1) and Os(3) would lead to exchange of H_c with H_d but not of H_a with H_b. At higher temperature the hydride-signal broadening is probably due to the onset of a slower process of mechanism (2). Here migration of H_a to the vacant site, followed by migration of H_a or H_b back into the vacated site between Os(1) and Os(2), would lead to simultaneous exchange of H_a with H_b and of H_c with H_d. A combination of these two processes would explain the observed n.m.r. spectra. Fast processes involving movement of bridging hydride ligands between the edges of transition-metal polyhedra are known, for example, in [$H_4Ru_4(CO)_8\{P(OMe)_3\}_4$].[10] Other possible processes involve movement of the CH_2C ligand with respect to the metal triangle. Mechanism (3) requires rotation about the C–C bond which would lead exclusively to H_c–H_d ex-

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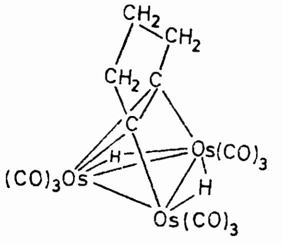
[10] S. A. R. Knox and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1971, **93**, 4594.

change. Presumably this would require $Os(3){-}CH_2C{<}$ bond cleavage. Complete cleavage would leave the C–C bond intact whereas partial cleavage, for example with charge separation to give $[H_2Os_3^{-}({}^{+}CH_2C)(CO)_9]$, is unlikely to be fast and would probably lead to hydride exchange at the same rate as CH_2C hydrogen exchange. Consequently we feel that hydride-migration mechanisms (1) and (2) are the most probable if the complex has structure (Ia). For a complex of structure (Ib) the faster process would probably be interchange of the CH_2 group between the two osmium atoms bridged by hydrogens.

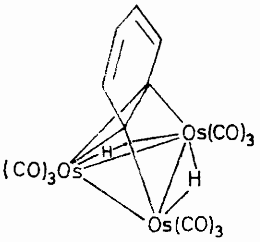
Reaction of $Os_3(CO)_{12}$ *with Cyclopentene*.—The complex $Os_3(CO)_{12}$ in heptane reacted slowly with cyclopentene at 150 °C in a sealed glass tube to give $[H_2Os_3(C_5H_6)(CO)_9]$, (II), which is analogous to the cyclooctene derivative.[1] As expected for cyclic olefins, 1,2-elimination of H_2 from the olefin occurs. At low temperature two hydride singlets were obtained which coalesced at 35 °C with $\Delta G^{\ddagger}$ $(T_c) = 58{\cdot}1$ kJ mol^{-1}. We have no evidence for the hydride positions, nor for the mechanism of fluxional behaviour, but presumably the latter is related to that for the complexes $[H_2M_3(C_8H_{12})(CO)_9]$ for which $\Delta G^{\ddagger}$ (T_c) values are 49·3 (M = Ru) [1] and 70·7 kJ mol^{-1} (M = Os).[1]



(II)

Reaction of $Os_3(CO)_{12}$ *with Propene*.—The complex $Os_3(CO)_{12}$ was treated with propene, as with ethylene, and a similar very pale yellow band on a t.l.c. plate was observed on attempted separation of the product mixture. Unlike the ethylene derivative, however, this band gave an oil which was apparently a mixture of two species which could not be separated even after further chromatography. Spectroscopic evidence indicated that $[H_2Os_3\{CH(Me)C\}(CO)_9]$ was the major component. The i.r. spectrum around 2 000 cm^{-1} was very similar to that of complex (I), and in the n.m.r. spectrum a quartet at τ 2·96 and a doublet at τ 7·87 (J 5·8 Hz) correspond unambiguously to the $-CH(Me)C{<}$ ligand; the expected hydride signals were also apparent. Singlets at τ 1·84 and 7·13, also in the intensity ratio 1 : 3, are probably due to the minor component (20%) of the mixture. It is possible that this species contains the ligand HC–CMe resulting from competitive 1,2-elimination of H_2 from propene, but in the absence of pure materials we were unable to confirm this. Reactions of $Os_3(CO)_{12}$ with *cis*- or *trans*-but-2-ene also gave mixtures which we could not separate. The increased complication of the reactions of propene or butenes may also be due to competitive cleavage of methyl C–H bonds.

Reaction of $Os_3(CO)_{12}$ *with Benzene*.—The reaction with benzene was slower than that with olefins and higher temperatures were required. On heating a benzene solution of $Os_3(CO)_{12}$ in a sealed glass tube at *ca.* 194 °C the yellow solution turned brown after several hours, and after heating for 2 days chromatography yielded variable quantities (very low to 34% conversion) of the yellow crystalline complex, $[H_2Os_3(C_6H_4)(CO)_9]$, (III). Several other brown, purple, or orange products were obtained which were not characterised but are probably the same as obtained by heating $Os_3(CO)_{12}$ in the absence of solvent at similarly high temperatures.[11] The n.m.r. spectrum at 27 °C in $CDCl_3$ showed one hydride singlet and an AA′XX′ spectrum characteristic of an *o*-C_6H_4 group, similar to those for C_6H_4 complexes of triosmium derived from PMe_2Ph or $AsMe_2Ph$. The same spectrum was obtained at −60 °C. The complex may differ from the olefin derivatives by having equivalent hydride ligands, but is much more likely to be of analogous structure with even more rapid hydride exchange. The extremely close similarity of its i.r. spectrum around 2 000 cm^{-1} (see Table) to that of the cyclopentene derivative (II) suggests that they are isostructural apart from the nature of the organic ring. Structures (II) and (III) are reasonable possibilities based on analogies with complex (I). However, other feasible structures have been suggested, which are probably more consistent with effective-atomic-number rule.[1]



(III)

Reaction of $Os_3(CO)_{12}$ *with Diphenyl*(o-*vinylphenyl*)-*phosphine* (dpvp).—The clusters $M_3(CO)_{12}$ (M = Fe or Ru) react with dpvp to give the monomers $[M(CO)_3(dpvp)]$ and $[M(CO)_2(dpvp)_2]$.[12] Reflecting in part the greater strength of trinuclear clusters of osmium, the corresponding reaction with this metal gave a mixture from which only a trinuclear complex could be isolated (19%). The mass spectrum gave a parent ion corresponding to $[Os_3(CO)_8(dpvp)]$, but the n.m.r. spectrum showed this to be a dihydrido-complex (signals integrating for one hydrogen each at τ 26·8 and 30·8).

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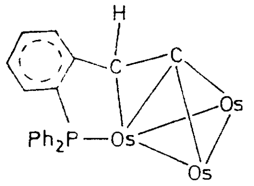
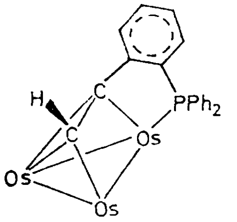
[11] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1972, **37**, C39; R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Amer. Chem. Soc.*, 1973, **95**, 3802.

[12] M. A. Bennett, G. B. Robertson, I. B. Tomkins, and P. O. Whimp, *Chem. Comm.*, 1971, 341.

Since there were no signals due to either a co-ordinated or non-co-ordinated vinyl group, we believe that the complex is $[H_2Os_3(Ph_2P\cdot C_6H_4\cdot C_2H)(CO)_8]$, (IV), with



(IVa)



(IVb)

the remaining olefinic hydrogen signal obscured by signals due to aromatic ring hydrogens. This formulation is preferred to that resulting from *ortho*-C–H bond cleavage as found for other phenylphosphines.[13] However, we have not established whether there is 1,1- or 1,2-elimination of hydrogen to give a skeleton as shown in (IVa) or (IVb) respectively.

1,1- versus 1,2-*Elimination.*—Probable intermediates in double oxidative addition of olefins are hydride–vinyl species of the type $[HOs_3(vinyl)(CO)_{10}]$ resulting from single oxidative additions. In the corresponding reaction with benzene the intermediate would be $[HOs_3Ph(CO)_{10}]$. Differentiation between 1,1- and 1,2-elimination would then depend on the course of the second oxidative addition. If α-hydrogen atoms are present in the vinyl groups, as in those derived from terminal olefins, it appears that these are more readily transferred than β-hydrogens. However, no monohydrido-species were isolated or even detected spectroscopically as intermediates in these reactions to support these ideas. Recently we isolated the complex $[HOs_3(CH{=}CH_2)(CO)_{10}]$ from the almost quantitative reaction of $[H_2Os_3(CO)_{10}]$ with acetylene at room temperature.[14] This vinyl species is indeed a probable intermediate in the ethylene reaction since it rapidly converts to $[H_2Os_3(CH_2C)(CO)_9]$ and $Os_3(CO)_{12}$ when heated under reflux.

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen or the reacting gas but, since none of the products showed sensitivity towards air oxidation, chromatographic separations were carried out in air.

Preparation of μ₃-(*Ethan*-1-*yl*-2-*ylidyne*)-*di*-μ-*hydrido*-triangulo-*tris*(*tricarbonylosmium*)(3Os–Os).—Ethylene was bubbled through $Os_3(CO)_{12}$ (0·53 g) heated under reflux in n-octane (150 cm³) for 24 h. After removal of solvent under reduced pressure the residue was extracted with pentane leaving crystals of unreacted $Os_3(CO)_{12}$. Solvent was removed from the extract to give an oil which was chromatographed on t.l.c. plates (silica) to give a very pale yellow band. The latter yielded $[H_2Os_3(CH_2C)(CO)_9]$, (I), as very pale yellow *crystals* (0·14 g), m.p. 122—124 °C. The unreacted $Os_3(CO)_{12}$ was retreated in a similar manner to give a further crop of complex (I) (total yield 0·26 g, 53%).

Reaction of Dodecacarbonyl-triangulo-*triosmium with Propene.*—Propene was bubbled for 48 h through a n-octane solution of $Os_3(CO)_{12}$ heated under reflux. Similar treatment of the resulting solution to that obtained from ethylene gave a pale yellow band on t.l.c. plates. This band gave an oily mixture shown spectroscopically to contain $[H_2Os_3\{CH(Me)C\}(CO)_9]$ as the major component.

Preparation of μ₃-(*Cyclopenta*-1,2-*diylidene*)-*di*-μ-*hydrido*-triangulo-*tris*(*tricarbonylosmium*)(3Os–Os).— Cyclopentene (25 cm³), $Os_3(CO)_{12}$ (0·44 g), and degassed n-heptane (35 cm³) were heated in a sealed glass tube at 150 °C for 2 weeks. The solution was filtered to remove $Os_3(CO)_{12}$ (0·19 g, 42%) and the filtrate evaporated to give a red oil which gave pale yellow crystals on standing at −13 °C (0·060 g, 24%). These were washed with cold diethyl ether and recrystallised from chloroform–ethanol to give the product as colourless *crystals*, m.p. >130 °C (decomp.).

Preparation of μ₃-(*Cyclohexa*-3,5-*dien*-1,2-*diylidene*)-*di*-μ-*hydrido*-triangulo-*tris*(*tricarbonylosmium*)(3Os–Os).— The complex $Os_3(CO)_{12}$ (0·61 g) in sodium-dried benzene (AnalaR, 60 cm³) was heated in a sealed glass tube at 194 °C for 39 h. After cooling, unreacted $Os_3(CO)_{12}$ (0·38 g) was allowed to crystallise and the remaining solution was evaporated to dryness and separated by t.l.c. (silica) to give $[H_2Os_3(C_6H_4)(CO)_9]$ (0·080 g, 34%) as yellow *crystals*.

Reaction of Diphenyl(o-*vinylphenyl*)*phosphine with* $Os_3(CO)_{12}$.—A solution of $Os_3(CO)_{12}$ (0·96 g) and the tertiary phosphine, dpvp (0·99 g, 3 mol per Os_3), in octane (100 cm³) was heated under reflux under a nitrogen atmosphere for 2 h. The solvent was removed under reduced pressure to give an orange oil which was separated on an alumina column with chloroform–light petroleum (b.p. 40—60 °C) (1 : 9 v/v) as eluant. Two bands were obtained, the first giving $[H_2Os_3(Ph_2P\cdot C_6H_4\cdot C_2H)(CO)_8]$ as yellow *crystals* (0·21 g, 19%), m.p. 230—235 °C. The second band gave a mixture of products which were not identified.

Kinetic Data for the Complex $[H_2Os_3(CH_2C)(CO)_9]$.—Line shapes for CH_2C n.m.r. signals were computed for various rates of coalescence of the two singlets to one singlet. Matching computed line shapes against those observed gave k (s⁻¹) at each temperature (T/K) as follows: 9·0 (318); 24·0 (328); 65·0 (338); 390 (358); 650 (368); 1 350 (378); and 3 500 (388). Activation parameters were obtained from the Arrhenius and Eyring equations in the usual manner. Errors are estimated as ±1·5 kJ mol⁻¹ (activation energy) and ±0·3 ($\log_{10} A$).

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