Reactions of Acetylene, Methyl- and Phenyl-substituted Acetylenes, and Ethylene with 1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3-di-μ-hydrido-*tri-angulo*-triosmium

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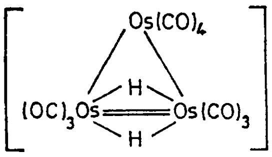
Acetylene and substituted acetylenes react with $[H_2Os_3(CO)_{10}]$ without CO loss at room temperature to give vinyl derivatives of type $[HOs_3(CR^1{:}CHR^2)(CO)_{10}]$ ($R^1 = R^2 =$ H or Ph; $R^1 =$ H, $R^2 =$ Me or Ph), alkenylene complexes $[Os_3(CR^1{:}CR^2)(CO)_{10}]$ ($R^1 = R^2 =$ H or Me; $R^1 =$ H, $R^2 =$ Me), and the phenylethynyl complex $[HOs_3(C_2Ph)(CO)_{10}]$, while other derivatives containing coupled alkynes are formed in low yield, if at all, at room temperature. On heating these complexes in hydrocarbon solvents, hydrogen transfer and CO loss occur to give $[H_2Os_3(C_2R_2)(CO)_9]$ (R = H, Me, or Ph), $[HOs_3(C_2R)(CO)_9]$ (R = H or Me), and $[HOs_3(MeC_3H_2)(CO)_9]$ [in two isomeric forms (A) or (B)]. The dihydrido-complexes may also be prepared by hydrogenation of $[Os_3(CR^1{:}CR^2)(CO)_{10}]$ ($R^1 =$ H or Me, $R^2 =$ Me). Structures are proposed on spectroscopic evidence. The significance of these results to the reactivity of olefins with $Os_3(CO)_{12}$ is discussed.

ALKENES react with dodecacarbonyl-*triangulo*-triosmium with transfer of two hydrogen atoms to the metal leaving the residual organic group X bridging the three osmium atoms in the product $[H_2Os_3X(CO)_9]$.[1,2] One hydrogen atom is removed from each unsaturated carbon in cyclic alkenes, whereas with terminal alkenes both hydrogens may be removed from the terminal carbon as an alternative. We have now treated $[H_2Os_3(CO)_{10}]$, (I), with simple alkynes and obtained decacarbonyl derivatives which convert on heating into nonacarbonyl complexes, some being the same or analogous to those from alkenes. The loss of CO in this conversion occurs with transfer of a hydrogen atom from the organic group to the metal and this is now a general feature of triosmium cluster chemistry. Some of these results have been described in a preliminary form.[3]



(I)

RESULTS AND DISCUSSION

Reaction of Acetylene with $[H_2Os_3(CO)_{10}]$, (I).—Complex (I) in hexane solution reacted smoothly and quantitatively with acetylene (1 atm, room temperature) † to give the bridging vinyl complex $[HOs_3(CH{:}CH_2)(CO)_{10}]$, (II; $R^1 = R^2 =$ H). In this and other reactions of (I) with alkynes *etc.*, at room tem-

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† 1 Atm = 101 325 Pa.

[1] A. J. Deeming and M. Underhill, *J.C.S. Dalton*, 1974, 1415.

[2] A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 145 and refs. therein.

[3] A. J. Deeming, S. Hasso, and M. Underhill, *J. Organometallic Chem.*, 1974, **80**, C53.

Analytical and spectroscopic data

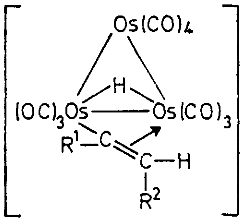
Complex	M.p. (θ_c/°C)	Analyses[a]/%		I.r. spectra[b] ν(CO)/cm^{-1}	N.m.r. spectra[c]			
		C	H		τ	Relative intensities	Assignment[d]	J/Hz
$[HOs_3(CH{:}CH_2)(CO)_{10}]$[e]	108—111	16.6	0.5	2 108w, 2 064vs,	2.42(ddd)	1	H_c	$J(H_bH_c)$ 14.9,
	(decomp.)	(16.4)	(0.45)	2 056s, 2 025vs,				$J(H_cH_d)$ 9.7
				2 016s, 2 012m,	5.02(dt)	1	H_d	$J(H_bH_d)$ 2.2,
				1 997m, 1 988vw,				$J(H_aH_c$ 1.7
				1 983w	6.60(dd)	1	H_b	$J(H_aH_d)$ 2.2,
								$J(H_aH_b)$ *ca.* 0
					29.38(s)	1	OsH_a	
$[HOs_3(CH{:}CHMe)(CO)_{10}]$	155—158	17.5	0.8	2 107w, 2 063vs,	2.95(dd)	1	H_c	$J(H_bH_c)$ 13.5
		(17.4)	(0.7)	2 055s, 2 024vs,	5.60(dq)	1	H_b	$J(H_bMe)$ 5.5
				2 015s, 2 005m,	7.95(d)	3	Me	$J(H_aH_c)$ 2.0
				1 995m, 1 987w,	28.72(d)	1	OsH_a	
				1 981w				
$[HOs_3(CH{:}CHPh)(CO)_{10}]$	106	22.8	1.0	2 104w, 2 063vs,	2.11(dd)	1	H_c	$J(H_bH_c)$ 14.4
		(22.65)	(0.85)	2 053s, 2 023vs,	2.66(m)	5	Ph	$J(H_aH_c)$ 1.7
				2 012s, 2 006s,	4.70(d)	1	H_b	
				1 995m, 1 981w	28.37(d)	1	OsH_a	
$[HOs_3(CPh{:}CHPh)(CO)_{10}]$	95—100	27.9	1.3	2 102w, 2 061vs,	2.88(m,br)	*ca.* 10	2Ph + H_b	
		(27.95)	(1.15)	2 050s, 2 023vs,	25.22(s)	1	OsH_a	
				2 004s, 1 993s,				
				1 981m				
$[HOs_3(C_2Ph)(CO)_{10}]$	98—102	22.85	0.75	2 109w, 2 071vs,	2.63(m)	5	Ph	
		(22.7)	(0.65)	2 060s, 2 024vs,	26.37(s)	1	OsH	
				2 017s, 2 006s,				
				1 981m				
$[Os(CH{:}CH)(CO)_{10}]$	120—124	16.35	0.25	2 102w, 2 063vs,	0.33(s)	*f*	C_2H_2	
		(16.45)	(0.25)	2 058vs, 2 027s,				
				2 010m, 2 002m,				
				1 981vw, 1 954vw,				
				1 851w,br				
$[Os_3(C_4H_4)(CO)_9]$	130—134	18.05	0.55	2 111m, 2 064vs,	1.36(m)	2}	AA′XX′	
		(17.85)	(0.45)	2 037s, 2 031s,	3.02(m)	2}	spectrum	
				2 016s, 2 002s,				
				1 989m, 1 986(sh),				
				1 945m				
$[Os_3(CH{:}CMe)(CO)_{10}]$	95—100	17.55	0.55	2 099m, 2 061vs,	1.12(s)	1	H	
		(17.55)	(0.45)	2 056vs, 2 025s,	7.60(s)	3	Me	
				2 007m, 1 999m,				
				1 848w,br				
$[Os_3(CMe{:}CMe)(CO)_{10}]$	152—156	18.9	0.65	2 098w, 2 057vs,	7.57(s)		Me	
		(18.6)	(0.65)	2 045(sh), 2 022s,				
				2 007m, 1 998m,				
				1 843w,br				
$[Os_3(C_4Me_4CO)(CO)_9]$	108—111	22.8	1.2	2 092m, 2 056vs,	6.71(s)	1	2Me	
		(22.55)	(1.25)	2 049s, 2 021s,	7.63(s)	1	2Me	
				2 006(sh), 1 999m,				
				1 980w, 1 616w				
$[Os_2(C_2Me_4CO)(CO)_6]$[g]		28.85	1.95	2 078m, 2 060s,	6.90(s)	1	2Me	
		26.35	(1.75)	2 008s, 2 004s,	7.94(s)	1	2Me	
				1 697w				
$[H_2Os_3(C{:}CHPh)(CO)_9]$	84—85	22.25	0.95	2 106w, 2 083s,	1.55(s)	1	CH	
		(22.05)	(0.85)	2 059s, 2 029s,	2.79(m,br)	5	Ph	
				2 019s, 2 006m,	27.91(s)	1	OsH	
				1 992w, 1 985w	30.06(s)	1	OsH	
$[H_2Os_3(CH{:}CMe)(CO)_9]$	129—133	17.5	0.85	2 108w, 2 080vs,	2.70(s)	1	CH	
	(sublim.)	(16.55)	(0.7)	2 056vs, 2 031vs,	7.12(s)	3	Me	
				2 025s, 2 010vs,	27.82(s)	1	OsH	
				2 001vs, 1 984m	31.33(s)	1	OsH	
$[H_2Os_3(CMe{:}CMe)(CO)_9]$	108—110	17.9	0.85	2 105w, 2 078vs,	7.20(s)	6	2Me	
	(sublim.)	(17.75)	(0.9)	2 055vs, 2 029vs,	27.28(s)	1	OsH	
				2 020s, 2,008vs	31.85(s)	1	OsH	
				1 998m, 1 981m				
$[H_2Os_3(CPh{:}CPh)(CO)_9]$[g]		30.55	2.15	2 108w, 2 083vs,				
		(27.6)	(1.2)	2 057vs, 2 031vs,				
				2 027s, 2 015vs,				
				2 001m, 1 994w,				
				1 982m				
$[HOs_3(C_2H)(CO)_9]$	170—174	16.0	0.3	2 105w, 2 077s,	4.37(s)	1	CH	
	(sublim.)	(15.55)	(0.25)	2 055s, 2 023s,	33.74(s)	1	OsH	
				2 017s, 1 985m				
$[HOs_3(C_2Me)(CO)_9]$	164—169	16.95	0.6	2 101w, 2 073vs,	6.92(s)	3	Me	
	(sublim.)	(16.7)	(0.45)	2 053vs, 2 022vs,	33.5(s)	1	OsH	
				2 012s, 1 984(sh),				
				1 982m				
$[HOs_3(C_4H_5)(CO)_9]$, isomer (A)		18.25	0.85	2 099m, 2 070vs,	5.84(s)	1	H_a	
		(17.8)	(0.7)	2 045vs, 2 026vs,	7.31(s)	3	Me	

TABLE (*Continued*)

Complex	M.p. (θ_c/°C)	Analyses [a]/% C	Analyses [a]/% H	I.r. spectra, [b] ν(CO)/cm^{-1}	N.m.r. spectra [c] τ	N.m.r. spectra [c] Relative intensities	N.m.r. spectra [c] Assignment [d]	N.m.r. spectra [c] J/Hz
[structure (XIV)]				2 016s, 2 000s,	7.60(s)	1	H_b	
				1 992m, 1 985w,	32.22(s)	1	OsH_c	
				1 978m				
isomer (B)	139—144	18.75	0.95	2 099m, 2 070vs,	1.94(d)	1	H_a	$J(H_aH_b)$ 6.9
[structure (XIII)]		(17.8)	(0.7)	2 050vs, 2 021vs,	2.64(d,br) [h]	1	H_b	
				2 010s, 2 003vs,	7.49(s)	3	Me	
				1 991m, 1 980(sh),	29.17(s,br) [h]	1	OsH_c	
				1 962vw				

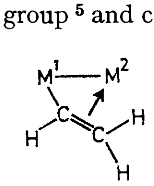
[a] Calculated figures are given in parentheses. [b] Recorded in cyclohexane solution unless stated otherwise. [c] Recorded at 100 MHz and 27 °C in $CDCl_3$ unless stated otherwise; d = doublet, t = triplet, q = quartet, and m = multiplet. [d] For $[H_aOs(CR^1{:}CH_bR^2)(CO)_{10}]$, $R^1 = H_c$ or Ph and $R^2 = H_d$, Me, or Ph. [e] O, 18.3 (18.2)%. [f] Integration against added MeI showed the signal was due to 2 H. [g] Isolated in yields too low for accurate elemental analysis and full characterisation (shown by chromatography to be a single osmium species, mass spectra gave a clear parent molecular ion); probably contaminated with hydrocarbon impurities. [h] The broadness of these peaks is consistent with a small coupling between H_b and H_c as in the ruthenium analogue.

perature no CO is lost and higher temperatures are normally required to give CO dissociation. It seems probable that the reaction with acetylene occurs by direct addition, which is made possible perhaps by the unsaturation present in the dihydrido-complex. A double Os=Os bond was argued to be present in (I) [4] and acetylene addition across this bond might occur before insertion into the Os–H bond. Simple addition compounds of (I) with other small molecules such as CO and tertiary phosphines can be isolated and we are at present examining these.* If the simple adduct $[H_2Os_3(CH{:}CH)(CO)_{10}]$ is initially formed it must readily convert to (II) since it cannot be observed spectroscopically during the reaction.

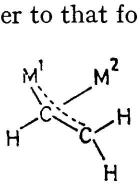


(II)

The vinyl group in (II) is bridging since the wide spread of chemical shifts in its ^1H n.m.r. spectrum (see Table) is rather larger than expected for a simple σ-bonded C_2H_3 group [5] and closer to that found for a C_2H_3 group bound by a σ bond to M^1 and for a monoalkene–metal interaction to M^2 (A).[6] An alternative description of the bonding is shown in (B) and has been preferred for $[Fe_2Br(\mu\text{-}CH{:}CHBr)(CO)_6]$ because of the short M^1–C bond.[7] We have not distinguished these possibilities in our case. A small nuclear coupling between two of the C_2H_3 protons and the metal-bound hydrogen was apparent (see Table) but was not resolved in the hydride signal itself. The complex showed a clear parent molecular ion in its mass spectrum as did all the complexes described in this paper. In (II) all Os–Os bonds are formally single and no further insertion of acetylene was observed at room temperature consistent with Os–Os unsaturation being required for ready insertion.



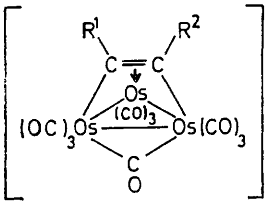
(A)



(B)

Reactions of Substituted Alkynes with Complex (I).—All the alkynes used reacted with purple (I) in hexane solution at room temperature to give orange solutions, but only acetylene gave a single product.

Terminal alkynes. Propyne gave a mixture yielding (II; $R^1 = H$, $R^2 = Me$) and the complex $[Os_3(CH{:}CMe)(CO)_{10}]$, (III; $R^1 = H$, $R^2 = Me$). The former complex is directly analogous to that derived from acetylene and *cis*-addition of Os–H across propyne was established from the value of $J(H_b\text{–}H_c)$ (13.5 Hz) showing that two hydrogen atoms are mutually *trans* about the carbon–carbon double bond. The other product contains a bridging carbonyl group [ν(CO) at 1 848 cm^{-1}]. For electron-counting purposes the group $Os(CO)_3$ is equivalent to $Rh(\eta\text{-}C_5H_5)$ and hence complexes of structure (III) are equivalent to $[Rh_3(C_5H_5)_3(alkyne)(CO)]$ which



(III)

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* *Note added at proof:* Adducts of (I), $[H_2Os_3(CO)_{10}L]$ (L = CO, PPh_3, PMe_2Ph, PhCN, *etc.*), described since we submitted this paper, are believed to contain one terminal and one bridging hydride ligand (A. J. Deeming and S. Hasso, *J. Organometallic Chem.*, 1975, **88**, C21; J. B. Keister and I. R. Shapley, *ibid.*, **85**, C29).

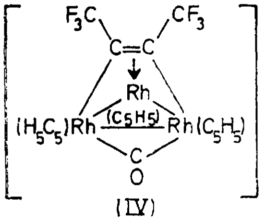
[4] B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc.* (*A*), 1968, 2859; R. Mason and D. M. P. Mingos, *J. Organometallic Chem.*, 1973, **50**, 53.

[5] B. E. Mann, B. L. Shaw, and N. I. Tucker, *Chem. Comm.*, 1970, 1333.

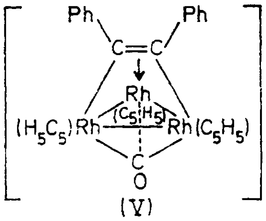
[6] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3600.

[7] C. Kruger, Y. H. Tsay, F. W. Grevels, and E. Koerner von Gustorf, *Israel J. Chem.*, 1972, **10**, 201.

have structures (IV) or (V).[8,9] Structure (IV) with a doubly bridged CO [ν(CO) at 1 810 cm^{-1}] as in (III) is found for hexafluorobut-2-yne while an asymmetrical triply bridged CO [ν(CO) at 1 675 cm^{-1}] occurs for

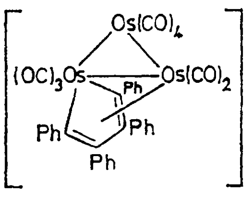


(IV)



(V)

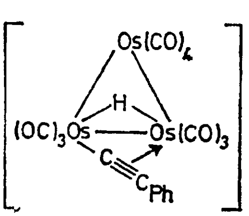
diphenylacetylene. Complex $Os_2(CO)_9$ is the only other osmium species we know to contain a bridging carbonyl group.[10] Probably $[HOs_3(CH{:}CHMe)(CO)_{10}]$ is formed initially and this reacts with more propyne displacing propene to form $[Os_3(CH{:}CMe)(CO)_{10}]$. Indeed, when acetylene was bubbled through a solution of (II; $R^1 = R^2 = H$) in refluxing hexane for 2 h a mixture was obtained containing $[Os_3(CH{:}CH)(CO)_{10}]$, (III; $R^1 = R^2 = H$) (35%), together with other species believed to contain coupled acetylene molecules of which we isolated



(VI)

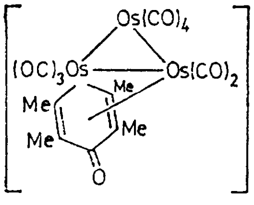
$[Os_3(C_4H_4)(CO)_9]$. Data for the latter (see Table) agree with a structure analogous to (VI) found for $[Os_3(C_4Ph_4)(CO)_9]$.[11]

The other terminal acetylene used, phenylacetylene, behaved like propyne in giving two main derivatives: $[HOs_3(CH{:}CHPh)(CO)_{10}]$, (II; $R^1 = H$, $R^2 = Ph$), formed by *cis* addition to phenylacetylene; and not (III; $R^1 = H$, $R^2 = Ph$) like the acetylene and propyne analogues, but the hydrido-form $[HOs_3(C_2Ph)(CO)_{10}]$. We do not know why the latter is formed or how the phenylacetylide ligand is bonded but some similarities to (II; $R^1 = R^2 = H$), *e.g.* the i.r. spectrum at *ca.* 2 000 cm^{-1}, supports structure (VII).

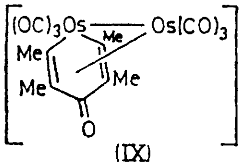


(VII)

Non-terminal acetylenes. Diphenylacetylene with (I) gave $[HOs_3(CPh{:}CHPh)(CO)_{10}]$ among other products. The geometry about the C=C bond is unknown but structure (II) is most probable. But-2-yne did not give an analogous derivative, the main product (50%) being $[Os_3(CMe{:}CMe)(CO)_{10}]$ of structure (III). The other isolated product (17%) contains all ten carbonyl groups but one of these we believe has been incorporated into a metallatetramethylcyclohexadienone ring and we formulate the complex as $[Os_3(C_4Me_4CO)(CO)_9]$. By comparison with $[Os_3(C_4Ph_4)(CO)_9]$, we tentatively put forward structure (VIII) for our complex. Two equal-intensity singlets in the ^1H n.m.r. spectrum (−48 to +30 °C) and ν(CO) at 1 616 cm^{-1} also support this structure. In refluxing heptane the complex breaks down to $[Os_2(C_4Me_4CO)(CO)_6]$ which probably has structure (IX). The iron analogue is known.[12]

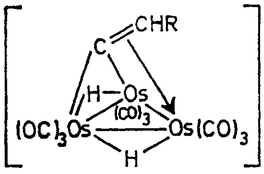


(VIII)



(IX)

Conversion of Deca- into Nona-carbonyl Complexes in refluxing Hydrocarbon Solvents.—Ethylene reacts slowly with $Os_3(CO)_{12}$ in refluxing nonane at 125 °C to give $[H_2Os_3(C{:}CH_2)(CO)_9]$, structure (X; R = H), and we have postulated[1] the intermediate (II; $R^1 = R^2 = H$). If this is correct the latter should convert into (X) at 125 °C. Indeed in 20 min in refluxing octane it was completely converted into (X) (*ca.* 70%) and $Os_3(CO)_{12}$ (*ca.* 30%). Since (II; $R^1 = R^2 = H$) reacts readily with CO to give $Os_3(CO)_{12}$ as the only osmium-containing product, it seems likely that, in the conversion of the deca- into the nona-carbonyl complex, the CO displaced reacts with unchanged decacarbonyl to account for the



(X)

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[8] S. A. Gardner, P. S. Andrews, and M. D. Rausch, *Inorg. Chem.*, 1973, **12**, 2396.

[9] T. Yamamoto, A. R. Garber, G. M. Bodner, L. J. Todd, M. D. Rausch, and S. A. Gardner, *J. Organometallic Chem.*, 1973, **56**, C23.

[10] J. R. Moss and W. A. G. Graham, *Chem. Comm.*, 1970, 835.

[11] G. Ferraris and G. Gervasio, *J.C.S. Dalton*, 1974, 1813.

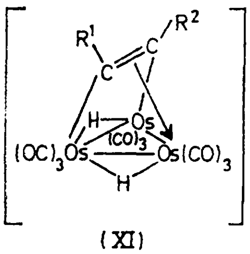
[12] W. Hubel and E. H. Braye, *J. Inorg. Nuclear Chem.*, 1959, **10**, 250.

formation of $Os_3(CO)_{12}$. With no CO lost at all from solution the stoicheiometry would be as in (1).

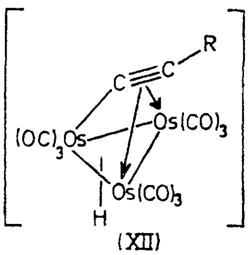
$$3[HOs_3(CH{:}CH_2)(CO)_{10}] \longrightarrow 2[H_2Os_3(C{:}CH_2)(CO)_9] + Os_3(CO)_{12} + C_2H_4 \quad (1)$$

Thus it would appear that in forming (X) from ethylene, the first oxidative addition to give (II; $R^1 = R^2 = H$) is slower than the second. We also have evidence that in this first step loss of CO rather than C–H cleavage is rate limiting. Ethylene reacted with (I) in hexane solution at room temperature over 5 d to give some (II; $R^1 = R^2 = H$).* Probably insertion of ethylene yields $[HOs_3(CH_2CH_3)(CO)_{10}]$ which readily eliminates ethane allowing ethylene to add oxidatively. Whatever the course of this particular reaction, C–H cleavage in ethylene can occur under mild conditions and it is the necessity for CO displacement that prevents reaction of ethylene with $Os_3(CO)_{12}$ at room temperature.

The loss of CO from a decacarbonyl in refluxing hexane (67 °C) or heptane (96 °C) with hydrogen transfer from ligand to metal also occurs for $[HOs_3(CH{:}CHMe)(CO)_{10}]$, $[HOs_3(CH{:}CHPh)(CO)_{10}]$, $[HOs_3(CPh{:}CHPh)(CO)_{10}]$, $[Os_3(CH{:}CMe)(CO)_{10}]$, $[Os_3(CH{:}CH)(CO)_{10}]$, and $[Os_3(CMe{:}CMe)(CO)_{10}]$. The formation of dihydrido-complexes from the substituted vinyl species is relevant to their formation of olefins. We have previously described the reaction of propene with $Os_3(CO)_{12}$ which gives two species forming a single band on a t.l.c. plate.[1] These species are (X; R = Me) and what is believed to be its isomer $[H_2Os_3(CH{:}CMe)(CO)_9]$, (XI; $R^1 = H$, $R^2 = Me$ or $R^1 = Me$, $R^2 = H$). On heating (II; $R^1 = H$, $R^2 = Me$) a similar inseparable mixture was obtained and separated from a small amount of $[HOs_3(C_2Me)(CO)_9]$, (XII) (see later). Whereas propene gave a ratio of complexes (X) : (XI) of *ca.* 3 : 1, the prop-1-enyl complex gave a ratio of *ca.* 5 : 1. Nevertheless it seems that it is the second oxidative-addition step of the alkene reaction that largely if not totally determines the proportion of 1,1- as against 1,2-disubstitution of olefin. Complex (XI; $R^1 = H$, $R^2 = Me$ or $R^1 = Me$, $R^2 = H$) could be prepared isomerically pure by bubbling hydrogen through a refluxing hexane solution of (III; $R^1 = H$, $R^2 = Me$). (The but-2-yne analogue may be similarly prepared.) The species (XI) shows no tendency to isomerise so that the isomeric mixtures of (X) and (XI) from the above reactions are not at equilibrium and the compositions are probably controlled by the relative rates of the hydrogen-transfer reactions.



(XI)

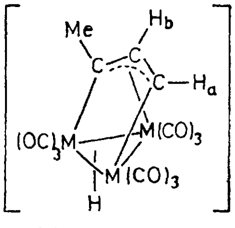


(XII)

In contrast only one isomer of $[H_2Os_3(C{:}CHPh)(CO)_9]$, that of (X), was obtained from a refluxing octane solution of (II; $R^1 = H$, $R^2 = Ph$). Similar treatment of (II; $R^1 = R^2 = Ph$) gave a mixture from which we could only isolate the complex $[H_2Os_2(CPh{:}CPh)(CO)_9]$. This was not fully characterised due to its extremely low yield, but from its mass and i.r. spectra alone it probably has structure (XI). The i.r. spectra at *ca.* 2 000 cm^{-1} for complexes $[H_2Os_3(X)(CO)_9]$ ($X = C_6H_4$ or C_5H_6)[1] derived from benzene and cyclopentene are very similar to those of structure (XI) described here.

Dihydrides are thus formed from monohydridodecacarbonyls by loss of CO and monohydrides are formed from non-hydridic decacarbonyls of structure (III) in a related manner. Thus complexes (III; R = H or Me) give the derivatives (XII) which are directly analogous to several known complexes of ruthenium. The structure of $[HRu_3(C_2Bu^t)(CO)_9]$ has been determined crystallographically but the hydrogen atoms were not located.[13] [Structures (XII)—(XV) are as shown to indicate that the hydride positions are unknown but it seems likely that these are doubly bridging.] The C_2R ligand in (XII) is formally a five-electron donor, and a simple description is that it is σ bonded to one osmium atom while bridging the other two as the alkyne does in $[Co_2(alkyne)(CO)_6]$.

Disubstituted acetylene complexes behave similarly in that (III; $R^1 = R^2 = Me$) also loses CO to give a monohydrido-species. In refluxing heptane $[HOs_3(C_4H_5)(CO)_9]$, isomer (A), is formed which isomerises in $[^2H_8]$toluene in a sealed n.m.r. tube (156 °C) to isomer (B). These isomers apparently differ in the nature of the organic ligand, formally a five-electron donor in each case. Isomer (B) is directly analogous to the ruthenium complex $[HRu_3(C_4H_5)(CO)_9]$ derived from butadiene and $Ru_3(CO)_{12}$.[14] Spectroscopic data, in particular the ^1H n.m.r. spectrum, support structure (XIII) which has been confirmed for several ruthenium complexes by *X*-ray crystallography. The ligand C_4H_5 forms two σ bonds and one η^3-allyl type interaction with



(XIII) M=Ru or Os

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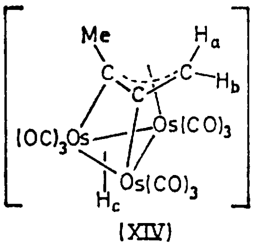
* *Note added at proof*: Formation of (II; $R^1 = R^2 = H$) from (I) and ethylene (I. B. Keister and J. R. Shapley, *J. Organometallic Chem.*, 1975, **85**, C29) and of several of the alkyne derivatives described in this paper (W. G. Jackson, B. F. G. Johnson, J. W. Kellend, J. Lewis, and K. T. Scharpp, *J. Organometallic Chem.*, 1975, **87**, C27; **88**, C17) have been briefly communicated since this paper was submitted.

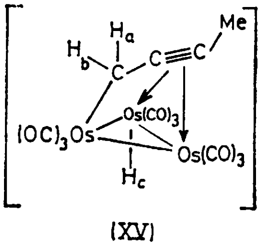
[13] G. Gervasio and G. Ferraris, *Cryst. Struct. Comm.*, 1973, **3**, 447.

[14] O. Gambino, M. Valle, S. Aime, and G. A. Vaglio, *Inorg. Chim. Acta*, 1974, **8**, 71.

the metal triangle and is thus a five-electron donor. In its formation from but-2-yne two hydrogen atoms have been transferred from a Me group, one to the metal and the other to an adjacent carbon. Isomer (A) formed initially may have structure (XIV) or (XV), in which only one hydrogen atom has been transferred. Apart from the Me group there are two magnetic environments for protons on the C_4H_5 ligand (H_a and H_b) and for structure (XV) an asymmetry resulting from the position of H_c would be necessary to account for this. In structure (XIV), however, H_a and H_b are related simply as *anti*- and *syn*-substituents and the lack of coupling between them strongly supports this relation. Hence structures (XIV) and (XIII) proposed for isomers (A) and (B) are related in containing a η^3-allyl group 1,3- and 1,2-disubstituted respectively by osmium atoms. Isomerism, probably of the same origin, has already been noted for $[HRu_3(C_6H_9)(CO)_9]$.[14]



(XIV)



(XV)

Mass Spectra of Complexes.—All complexes described in this paper are sufficiently stable and volatile to give clear parent molecular ions in their mass spectra. The main fragmentations were successive loss of CO groups, characteristic of metal carbonyls, and loss of H_2. The stage at which this latter fragmentation occurs can be related to the hydrogen-transfer reactions already described. For example, nonacarbonyls (X) and (XI) showed no detectable loss of H_2 from the parent ion, but only after the first CO had been lost did loss of H_2 predominate. In contrast decacarbonyls (II) lost H_2 only after two CO groups had been displaced and, presumably, after a deca- is converted into a nonacarbonyl identical fragmentation paths occur. The nonacarbonyls (XII)—(XIV) also lost two CO before H_2 was lost so it may be the number of hydrogen atoms originally attached to the metal atoms that determines at which stage hydrogens are lost. Exceptions are (XII; R = H) and (III; $R^1 = R^2 = H$) which lost hydrogen atoms only after most of the CO ligands had been displaced.

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen or the reacting gas but separations on preparative-layer chromatography plates (silica; E. Merck, HF_{254}, type 60) were carried out in air. The eluant was pentane and the bands were extracted with chloroform unless stated otherwise.

1,1,1,2,2,2,3,3,3-*Decacarbonyl*-2,3-*di*-μ-*hydrido*-tri-angulo-*triosmium* (I).—This was prepared by the method of Kaesz *et al.*[15] After bubbling hydrogen through a refluxing solution of $Os_3(CO)_{12}$ (0.298 g) in octane for 1.5 h, the solvent was removed and the residue passed through a silica column eluting with pentane. A purple band gave (I) as intense purple-black crystals (0.238 g, 75%), used without further purification.

Reactions of Complex (I) *with Alkynes.*—*Acetylene.* (*a*) Acetylene was passed through an alumina column, a trap at −78 °C, and a flask containing a solution of (I) (0.155 g) in hexane (200 cm^3) at 20 °C for 4 h. The stoppered flask was allowed to stand overnight. The purple solution became orange-yellow and the solvent was removed under reduced pressure to give an orange solid which was recrystallised from pentane to give 1,1,1,2,2,2,3,3,3-decacarbonyl-2,3-μ-hydrido-2,3-μ-(η-vinyl)-*triangulo*-triosmium, $[HOs_3(CH{:}CH_2)(CO)_{10}]$ (II; $R^1 = R^2 = H$), as orange *crystals* (0.16 g, 100%).

(*b*) Acetylene was bubbled through a refluxing solution of (II; $R^1 = R^2 = H$) (0.057 g) in hexane (80 cm^3) for 2 h. Layer chromatography after removal of solvent gave 2,3-μ-carbonyl-μ_3-(η-vinylene-*Os*^{1})-*cyclo*-tris(tricarbonylosmium) (3*Os*–*Os*), $[Os_3(CH{:}CH)(CO)_{10}]$ (III; $R^1 = R^2 = H$), as orange *crystals* (0.026 g, 46%) and $[Os_3(C_4H_4)(CO)_9]$ as purple *crystals* (0.0062 g, 11%) together with some starting material. Other products, which increased in number and quantity on extended reaction times, were not characterised.

Propyne. Propyne was bubbled for 2 h through a solution of (I) (0.346 g) in hexane (200 cm^3) at room temperature. After 6 h the solution had become orange-brown with some precipitation. Removal of solvent and chromatography gave two main yellow bands yielding $[Os_3(CH{:}CMe)(CO)_{10}]$, (III; $R^1 = H$, $R^2 = Me$), as orange-brown *crystals* (0.067 g, 19%) and $[HOs_3(CH{:}CHMe)(CO)_{10}]$, (II; $R^1 = H$, $R^2 = Me$), as bright orange *crystals* (0.028 g, 8%).

But-2-*yne.* A solution of but-2-yne (0.5 cm^3, 6.4 mmol) and (I) (0.203 g, 0.238 mmol) in hexane (15 cm^3) became orange after 24 h. Separation as above gave $[Os_3(CMe{:}CMe)(CO)_{10}]$, (III; $R^1 = R^2 = Me$), as orange *crystals* (0.089 g, 41%) and $[Os_3(C_4Me_4CO)(CO)_9]$, (VIII), as orange-pink *crystals* (0.034 g, 15%). There was no evidence for the formation of (II; $R^1 = R^2 = Me$).

Phenylacetylene. A solution of phenylacetylene (0.1 cm^3, 0.91 mmol) and (I) (0.256 g, 0.30 mmol) in hexane (100 cm^3) changed from purple to dark red over 3 d. Separation as above gave several species of which two were characterised as $[HOs_3(CH{:}CHPh)(CO)_{10}]$, (II; $R^1 = H$, $R^2 = Ph$), as yellow *crystals* (0.064 g, 22%) and $[HOs_3(C_2Ph)(CO)_{10}]$, (VII), as yellow *crystals* (0.027 g, 10%).

1,2-*Diphenylacetylene.* A solution of 1,2-diphenylacetylene (0.312 g, 1.75 mmol) and (I) (0.301 g, 0.353 mmol) in hexane (150 cm^3) became orange in 2 d. Separation as above gave $[HOs_3(CPh{:}CHPh)(CO)_{10}]$, (II; $R^1 = R^2 = Ph$), as orange *crystals* (0.110 g, 30%), but other species were not characterised.

Action of Ethylene on Complex (I).—A solution of (I) (0.145 g) in hexane (150 cm^3) saturated with ethylene was allowed to stand at room temperature for 5 d. Plate chromatography of the resulting mixture gave (II; $R^1 = R^2 = H$) (0.0095 g, 7%) and (I) (0.0224 g, 16%).

Reactions of Decacarbonyl Complexes in refluxing Hydrocarbon Solvents.—$[HOs_3(CH{:}CH_2)(CO)_{10}]$. A solution of this complex (0.035 g) in n-heptane (40 cm^3) was heated under reflux for 20 h. After removal of solvent under

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[15] H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Saillant, *Chem. Comm.*, 1971, 477.

reduced pressure, plate chromatography gave the complex $[H_2Os_3(C{:}CH_2)(CO)_9]$, (X; R = H) (0.017 g, 50%), and a mixture of this complex and $Os_3(CO)_{12}$ (0.008 g, 22%). In refluxing octane complete conversion within 30 min into (X) (*ca.* 70%) and $Os_3(CO)_{12}$ (*ca.* 30%) was observed.

$[HOs_3(CH{:}CHMe)(CO)_{10}]$. A solution of this complex (0.021 g) in n-octane (25 cm³) was heated under reflux for 1 h. Layer chromatography gave two main bands, one giving an isomeric mixture of $[H_2Os_3(C{:}CHMe)(CO)_9]$, (X; R = Me), and $[H_2Os_3(CH{:}CMe)(CO)_9]$, (XI; R^1 = H, R = Me), as a pale yellow crystalline solid (0.0098 g, 47%) and the other $[HOs_3(C_2Me)(CO)_9]$, (XII; R = Me), as white *crystals* (0.006 g, 29%).

$[HOs_3(CH{:}CHPh)(CO)_{10}]$. A solution of this complex (0.0257 g) in refluxing n-octane (40 cm³) for 2 h 20 min gave, with work-up as above, $[H_2Os_3(C{:}CHPh)(CO)_9]$, (X; R = Ph) (0.0227 g, 88%), as white *crystals*; $Os_3(CO)_{12}$ detected in solution by i.r. spectroscopy was not isolated.

$[HOs_3(CPh{:}CHPh)(CO)_{10}]$. A similar treatment to that above (1 h 20 min) gave two species, one of which was characterised as $[H_2Os_3(CPhCPh)(CO)_9]$, (XI; $R^1 = R^2$ = Ph), as colourless *crystals* (6%). The other gave a very similar i.r. spectrum at *ca.* 2 000 cm^{-1} but there was insufficient material for full characterisation.

$[Os_3(CH{:}CMe)(CO)_{10}]$. A solution of this complex (0.032 g) in n-hexane (30 cm³) was heated under reflux for 13 h. Separation as above gave (XII; R = Me) as very pale yellow *crystals* (0.0174 g, 54%). After a similar reaction in refluxing n-octane (5 min) the only species observed in solution (i.r.) was (XII).

$[Os_3(CMe{:}CMe)(CO)_{10}]$. A similar treatment of this complex (0.128 g) in n-heptane (70 cm³) (2 h) gave slightly impure $[HOs_3(C_4H_5)(CO)_9]$, isomer (A), as yellow-brown *crystals* (0.104 g, 80%) after initial chromatography. Further chromatography was required to remove a small amount of another complex which remained uncharacterised.

Isomerisation of $[HOs_3(C_4H_5)(CO)_9]$, *Isomer* (A).—A solution of this isomer in $[^2H_8]$toluene in a sealed n.m.r. tube was heated at 156 °C and its spectrum was recorded at intervals. After 5 h, complete conversion to isomer (B) was apparent. Removal of solvent under reduced pressure gave a yellow *oil* which crystallised on treatment with light petroleum (b.p. 40—60 °C).

Action of Carbon Monoxide on $[HOs_3(CH{:}CH_2)(CO)_{10}]$.—Carbon monoxide was bubbled through a refluxing solution of the complex (0.040 g) in n-hexane (50 cm³) for 4 h 20 min. On cooling yellow crystals of $Os_3(CO)_{12}$ (0.031 g, 79%) separated, while the i.r. spectrum of the solution showed starting material still present. Ethylene, although presumed to be formed, was not characterised.

Action of Hydrogen.—On $[HOs_3(CH{:}CH_2)(CO)_{10}]$. Hydrogen was bubbled for 4 h through a refluxing solution of the complex (0.030 g) in n-hexane (40 cm³). Chromatography yielded (I) (0.016 g, 55%) and unchanged starting material (0.004 g, 13%). It was not established whether ethylene or ethane was evolved.

On $[Os_3(CH{:}CMe)(CO)_{10}]$. (*a*) Hydrogen was bubbled for 18 h through a refluxing solution of the complex (0.020 g) in n-hexane (25 cm³). Plate chromatography gave two main bands, one of which gave (XI; R^1 = H, R^2 = Me) as pale yellow crystals (0.009 g, 45%) while the other gave an uncharacterised mixture. (*b*) A similar reaction in refluxing n-heptane (20 min) was shown by the i.r. spectrum to give complete conversion to the complex (XII; R = Me) also formed at this temperature in the absence of hydrogen gas.

On $[Os_3(MeC_2Me)(CO)_{10}]$. Hydrogen was bubbled through a solution of the complex (0.071 g) in refluxing heptane (100 cm³) for 0.5 h. After removal of solvent under reduced pressure, treatment of the residual oil gave (XI; $R^1 = R^2$ = Me) as very pale yellow crystals (0.031 g, 43%).

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