Triosmium Clusters derived from Benzylamine and Benzyl Alcohol: Formation of a μ_3-*o*-Phenylene Complex in the Conversion of Benzyl Alcohol into Benzene †

By **Kazi A. Azam, Candido Choo Yin,** and **Antony J. Deeming,*** Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ

Benzylamine reacts (125 °C) with $[Os_3(CO)_{12}]$ to give mainly the μ-carbamoyl complex $[Os_3(CO)_{10}H\{\mu\text{-}OCN(CH_2Ph)H\}]$ together with small amounts of $[Os_3(CO)_{10}H\{\mu\text{-}N(CH_2Ph)H\}]$ which may also be obtained by decarbonylation of the first product. The complex $[Os_3(CO)_{10}(C_8H_{14})_2]$ gives (60—70 °C) the same products, but with the benzylamido-complex predominating. It is probable, but not established, that these derivatives are involved in the $[Os_3(CO)_{12}]$-catalysed carbonylation of benzylamine to $(PhCH_2NH)_2CO$. The analogue of only one of these, $[Os_3(CO)_{10}H(\mu\text{-}OCH_2Ph)]$, is formed from benzyl alcohol, and thermolysis of nonane solutions of this derivative at 146 °C in sealed glass tubes gives C_6H_6, PhCHO, $[Os_3(CO)_{12}]$, and $[Os_4(CO)_{12}H_4]$ only; related products are obtained from the 4-methyl-substituted analogue, while $[Os_3(CO)_{10}H(\mu\text{-}OCMePhH)]$ gives only PhCOMe as an organic product. A possible scheme for these degradations is discussed in terms of the intermediates $[Os_3(CO)_9H_2(\mu\text{-}OCH_2C_6H_4)]$ and $[Os_3(CO)_9H_2(\mu_3\text{-}C_6H_4)]$ which have been isolated from reaction solutions flushed with N_2. The complex $[Os_3(CO)_9H_2(\mu_3\text{-}C_6H_3Me\text{-}4)]$ is formed from both isomers $[Os_3(CO)_{10}H(OCH_2C_6H_4Me\text{-}2 \text{ or } \text{-}4)]$. Interconversions and structures (based on spectroscopic evidence) of the above complexes are described.

SINCE in much of its chemistry the *triangulo*-cluster of dodecacarbonyltriosmium remains intact, ligand transformations within the cluster may be conveniently studied. Hydrogen-transfer reactions of μ- and μ_3-ligands in Os_3 clusters have particularly interested us. Thus phenol [1] and aniline [2] add oxidatively to $[Os_3(CO)_{12}]$ to give $[Os_3(CO)_{10}H(\mu\text{-}XPh)]$ ($X = O$ or NH) initially which give $[Os_3(CO)_9H_2(\mu_3\text{-}XC_6H_4)]$ by further loss of CO and a second oxidative addition with C–H bond cleavage at a carbon β to the heteroatom. Benzylamine and benzyl alcohol, having no β-hydrogens, could metallate at the α-carbon (as does pyridine [3]) or at the γ-carbon to give a μ-chelating ligand (as does 2-phenylpropan-2-ol [1]). Our present results show that $PhCH_2OH$ and $N(CH_2Ph)H_2$ behave rather differently to each other with $[Os_3(CO)_{12}]$ (unlike aniline and phenol) and only for benzyl alcohol were α- and γ-C–H cleavages identified. Some aspects of this work have been communicated previously.[4]

RESULTS AND DISCUSSION

Benzylamine.—Although the overall conversion of $[Os_3(CO)_{12}]$ into $[Os_3(CO)_{10}H\{N(CH_2Ph)H\}]$ (2) is formally an oxidative addition, we have evidence that this occurs by an initial nucleophilic attack of the amine at co-ordinated CO [reaction (1)]. Only after decarbonylation of the carbamoyl ligand so generated [reaction (2)] does the stoicheiometry correspond to a simple oxidative addition. Complex (1) is the main product on treating $[Os_3(CO)_{12}]$ with benzylamine at 125 °C with only small quantities of (2) produced, the best yields of (1) being obtained under a CO atmosphere. The use of a CO atmosphere might imply that (1) is formed from (2), but (2) does not react with CO to give (1) and certainly not under the conditions of the preparation, whereas the reverse transformation occurs on thermolysis at 150 °C, on treatment of (1) with an excess of benzylamine, or even on treatment with CO, at similar

$$[Os_3(CO)_{12}] + N(CH_2Ph)H_2 \longrightarrow [Os_3(CO)_{10}H\{OCN(CH_2Ph)H\}] + CO \quad (1)$$

$$[Os_3(CO)_{10}H\{OCN(CH_2Ph)H\}] \longrightarrow [Os_3(CO)_{10}H\{N(CH_2Ph)H\}] + CO \quad (2)$$

temperatures but much more slowly in this case. We have found that in many reactions of $[Os_3(CO)_{12}]$ an atmosphere of CO reduces the rate of reaction while helping to reduce decomposition, and this could be its role in improving the yield of (1) in the reaction of $[Os_3(CO)_{12}]$ with $N(CH_2Ph)H_2$.

The cyclo-octene ligands in $[Os_3(CO)_{10}(C_8H_{14})_2]$ [5] are readily replaced and so the complex has been used as a precursor to $Os_3(CO)_{10}$ adducts. We have shown that this complex reacts at 60—70 °C with benzylamine to give mainly (2) but also a little (1). From this it seems likely that (1) is formed from $[Os_3(CO)_{12}]$ by direct nucleophilic addition of benzylamine at a carbonyl of $[Os_3(CO)_x]$ ($x = 10$—12), or by rearrangement of the initially formed substitution product $[Os_3(CO)_{11}\{N(CH_2Ph)H_2\}]$. Once two CO groups have been removed a direct oxidative addition is favoured and (2) predominates. As in other cases, CO displacement is the limiting step in this chemistry.

Complexes containing amino- and carbamoyl ligands are key intermediates in the catalytic carbonylation of

$$2N(CH_2Ph)H_2 + CO \longrightarrow (PhCH_2NH)_2CO + 2H \quad (3)$$

amines to give substituted ureas [6] and $[Os_3(CO)_{12}]$ does indeed slowly catalyse reaction (3). We have obtained

---

† No reprints available.

[1] K. A. Azam, A. J. Deeming, R. E. Kimber, and P. R. Shukla, *J.C.S. Dalton*, 1976, 1853.

[2] C. Choo Yin and A. J. Deeming, *J.C.S. Dalton*, 1974, 1013.

[3] C. Choo Yin and A. J. Deeming, *J.C.S. Dalton*, 1975, 2091.

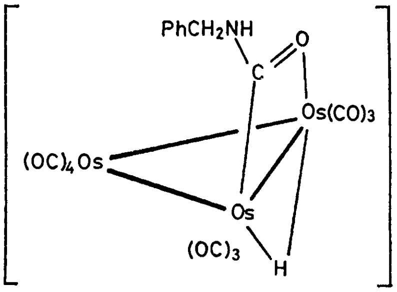
[4] K. A. Azam and A. J. Deeming, *J.C.S. Chem. Comm.*, 1977, 472.

[5] M. Tachikawa and J. R. Shapley, *J. Organometallic Chem.*, 1977, **124**, C19.

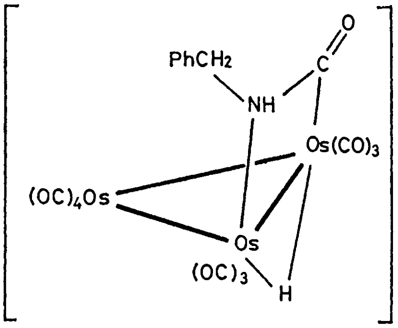
[6] A. Rosenthal and I. Wender, 'Organic Synthesis *via* Metal Carbonyls,' eds. I. Wender and P. Pino, Interscience, 1968, vol. 1, pp. 405—466.

dibenzylurea (26 mol per mol catalyst) by treating benzylamine with CO in octane with $[Os_3(CO)_{12}]$ as catalyst (see Experimental section). Although we have not established whether (1) or (2) is actually involved in this reaction, this does seem likely.

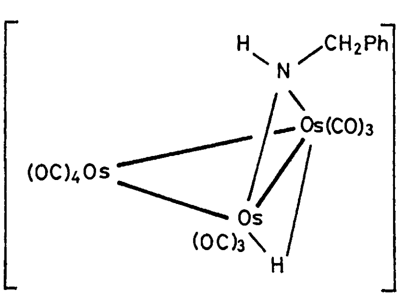
We were unable to examine in detail the thermal reactions of complexes (1) and (2) expected to lead to C–H cleavage because of lack of material and complexity of degradation products. For example, (2) in refluxing nonane under N_2 for 5 h gave a complex mixture as indicated by the ν(CO) spectrum and plate chromatography; a 16% recovery of (2) was all we achieved.



(1a)

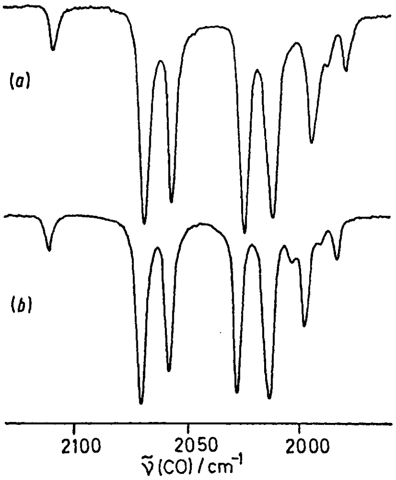


(1b)



(2)

Structures of (1) *and* (2).—Both complexes gave parent molecular ions in their mass spectra and the fragmentation pattern for (2) corresponds closely to that of (1) once one CO group has been lost. The most intense ions correspond to loss of CO groups and H_2 to give eventually a residual $[Os_3(C_7H_7N)]^+$ ion. The strong overall similarity of the ν(CO) spectra of (1) and (2) with that of $[Os_3(CO)_{10}H(NPhH)]$[2] confirms that both should be formulated as $[Os_3(CO)_{10}H(\mu\text{-}X)]$ [$X = N(CH_2Ph)H$ or $OCN(CH_2Ph)H$], but the carbamoyl complex may have structure (1a) or (1b). The ^1H n.m.r. spectrum of (1) contains ABX signals for the $OCN(CH_2Ph)H$ protons with a 0.34 p.p.m. shift between the CH_2 signals consistent with no plane of symmetry through the O–C–N group of atoms. The carbonyl ν(CO) absorption at 1 505 cm^{-1} (cyclohexane solution) is only consistent with (1b) if some electronic effects specific to a bridge of this sort allows CO bond weakening compared with uncomplexed organic amides, whereas this is the expected wavenumber for (1a). For example,[4] the μ-acyl complexes $[Os_3(CO)_{10}H(\mu\text{-}OCR)]$ have ν(CO) at *ca.* 1 500 cm^{-1} and similar wavenumbers are found for $[Fe_2(CO)_6(\mu\text{-}AsMe_2)(\mu\text{-}OCNMe_2)]$[7] which has been structurally characterised by *X*-ray diffraction to have a μ-carbamoyl group as in (1a). The close similarity of the total ν(CO) spectrum of (1) and of $[Os_3(CO)_{10}H(OCC_5H_{11})]$ and other μ-acyl complexes (Figure) confirms that they are isostructural with respect to metal co-ordination. It is surprising that the CH_2 signals are so separated since these hydrogen atoms are well removed from any permanent asymmetry, inversion at N should be rapid, and asymmetry results ultimately from the arrangement of the Os_3CO core.



Infrared spectra at *ca.* 2 000 cm^{-1} of the complexes $[Os_3(CO)_{10}H(OCR)]$ [$R = N(CH_2Ph)H$ (*a*) and $n\text{-}C_5H_{11}$ (*b*) [4]]

Benzyl Alcohol.—The analogue of (1) was not observed as a product of the reaction of benzyl alcohol and $[Os_3(CO)_{12}]$, the only significant product being $[Os_3(CO)_{10}H(OCH_2Ph)]$ (3).[1] Whether or not the analogue of (1) is formed but rapidly decarbonylates is unknown, but the alcohol is probably too weakly nucleophilic to add to CO. Decarbonylation of (3) gives products derived by bond cleavage within the benzyloxo-ligand. Complex (3) in nonane in an n.m.r. tube sealed under N_2 was heated at 146 °C for an extended period. The slow conversion of the $\mu\text{-}OCH_2Ph$ ligand into C_6H_6 and PhCHO (with no other organic products) was observed; $[Os_3(CO)_{12}]$ and $[Os_4(CO)_{12}H_4]$ are the only metal carbonyls produced. Believing that the bond cleavages within the benzyloxo-ligand to give C_6H_6 and PhCHO would require an initial displacement of CO from the metal and that in a sealed tube this CO remains avail-

---

[7] E. Keller, A. Trenkle, and H. Vahrenkamp, *Chem. Ber.*, 1977, **110**, 441.

able, we thermolysed (3) in refluxing nonane under a flow of N_2 to remove CO. The ν(CO) spectrum of the reaction solution showed the presence of two species, other than (3) and the carbonyl products above, which we isolated and characterised as $[Os_3(CO)_9H_2(OCH_2C_6H_4)]$ (4) and $[Os_3(CO)_9H_2(C_6H_4)]$ (5). Complex (4) is [(3) − CO] and (5) is [(3) − H_2 − 2CO] and was previously obtained from $[Os_3(CO)_{12}]$ and benzene directly[8] or from benzaldehyde indirectly[4] *via* decarbonylation of $[Os_3(CO)_{10}H(OCPh)]$. The formation and structure of (4) are closely related to those of $[Os_3(CO)_9H_2(OCMe_2C_6H_4)]$ obtained from $[Os_3(CO)_{10}H(OCMe_2Ph)]$, itself derived from 2-phenylpropan-2-ol and $[Os_3(CO)_{12}]$.[1] This dimethyl analogue of (4) has considerably more thermal stability than (4) which is converted into (5) at 150 °C (see Scheme). We have been able to build up this Scheme as shown by carrying out most of the steps individually (those marked *) as described in the Experimental section. The complete conversion of the μ-OCH_2Ph ligand [of (3)] into C_6H_6 and PhCHO in a sealed-tube thermolysis may then be rationalised if CO is present to displace benzene from (5), but when CO is removed by flushing with N_2 intermediates may be isolated. There is, however, no evidence that the Scheme provides the exclusive path to these products. The conversion of (4) into (5) is the least easily understood step. This could involve direct extrusion of CH_2O from (4), or the separate loss of H_2 and CO, which is intuitively more attractive, but an alternative is that

Analytical and spectroscopic data

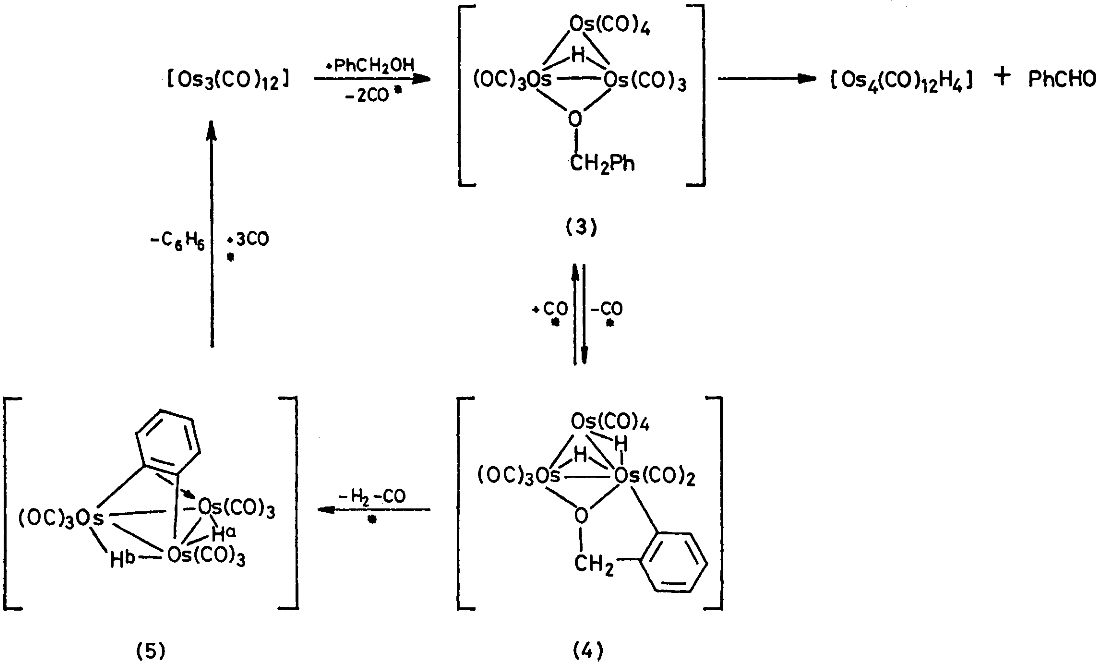
	Analyses[a] (%)			I.r. spectra[b]	^{1}H N.m.r. spectra[c]			
Complex	C	H	N	[ν(CO)]/cm^{-1}		Relative in-tensity	Assignment	J/Hz
(1) $[Os_3(CO)_{10}H\{OCN(CH_2Ph)H\}]$[d]	22.1	1.05	1.55[e]	2 108w, 2 068s,	7.25 (m)	5	C_6H_5	
	(21.95)	(0.9)	(1.4)	2 056s, 2 024s,	6.11 (br)	1	NH^c	$J(H^a$–$H^c)$ 5.50
				2 011s, 1 994m,	4.46 (dd)	1	CH^aH^b	$J(H^b$–$H^c)$ 4.75
				1 987w, 1 979w,	4.12 (dd)	1		$J(H^a$–$H^b)$ 14.85
				1 505w	−14.25 (s)	1	OsH	
(2) $[Os_3(CO)_{10}H\{N(CH_2Ph)H\}]$[f]	21.3	1.1	1.6[g]	2 105w, 2 067s,	7.32 (m)	5	C_6H_5	
	(21.3)	(0.95)	(1.45)	2 052s, 2 022s,	4.54 (br)	1	NH^a	
				2 004s, 1 991s,	4.00 (d)	2	$CH^b{}_2$	$J(H^a$–$H^b)$ 8.0
				1 981w, 1 976w	−14.95 (d)	1	OsH^c	$J(H^a$–$H^c)$ 3.0
(3) $[Os_3(CO)_{10}H(OCH_2Ph)]$[h]	21.6	0.75		2 110w, 2 072vs,	7.36 (m)	5	C_6H_5	
	(21.3)	(0.85)		2 059s, 2 032vs,	4.60 (s)	2	CH_2	
				2 018 (sh), 2 006w,	−12.42 (s)	1	OsH	
				2 000s, 1 988m				
(6) $[Os_3(CO)_{10}H(OCH_2C_6H_4Me$-$4)]$[h]	22.7	0.75		2 110w, 2 072s,	7.17 (m)	4	C_6H_4	
	(22.2)	(0.85)		2 060s, 2 024vs,	4.53 (s)	2	CH_2	
				2 020 (sh), 1 999s,	2.33 (s)	3	CH_3	
				1 988m, 1 982w	−12.5 (s)	1	OsH	
(7) $[Os_3(CO)_{10}H(OCH_2C_6H_4Me$-$2)]$[h]	22.25	1.0		2 111w, 2 073s,	7.20 (m)	4	C_6H_4	
	(22.2)	(1.05)		2 060s, 2 042vs,	4.68 (s)	2	CH_2	
				2 020 (sh), 1 999s,	2.22 (s)	3	CH_3	
				1 988m, 1 983w	−12.33 (s)	1	OsH	
(14) $[Os_3(CO)_{10}H(OC_6H_3Me_2$-$2,6)]$[h,i]				2 111w, 2 073s,	7.27 (m)	3	C_6H_3	
				2 060s, 2 024vs,	2.15 (s)	6	CH_3	
				2 019 (sh), 2 007w,	−12.48 (s)	1	OsH	
				2 000s, 1 989m,				
				1 984w				
(4) $[Os_3(CO)_9H_2(OCH_2C_6H_4)]$[j]	21.15	1.15		2 129m, 2 082s,	7.77 (dd)	1	H^1	$J(H^1$–$H^2)$ 7.0
	(20.65)	(0.85)		2 055 (sh), 2 050s,	7.02 (m)	3	H^2-H^4	$J(H^1$–$H^3)$ 2.2
				2 037s, 2 011m,	5.33 (d)	1		
				1 998m, 1 965s	4.66 (d)	1	CH^aH^b	$J(H^a$–$H^b)$ 14.6
					−12.24 (d)	1	OsH^c	$J(H^c$–$H^d)$ 1.0
					−15.56 (d)	1	OsH^d	
(8) $[Os_3(CO)_9H_2(OCH_2C_6H_3Me)]$[k]				2 129m, 2 081s,				
				2 054 (sh), 2 049s,				
				2 036s, 2 009m,				
				1 998m, 1 964s				
(9) $[Os_3(CO)_9H_2(OCH_2C_6H_3Me)]$				2 129m, 2 081s,				
				2 055 (sh), 2 050s,				
				2 037s, 2 010m,				
				1 997m, 1 964s				
(10) $[Os_3(CO)_9H_2(C_6H_3Me$-$4)]$	21.15	0.9		2 110m, 2 082s,	7.78 (d)	1	H^4	$J(H^3$–$H^4)$ 8.0
	(21.0)	(0.9)		2 057s, 2 036s,	7.65 (d)	1	H^1	$J(H^3$–$H^1)$ 2.0
				2 025s, 2 009s,	6.66 (dd)	1	H^3	
				1 998m, 1 984m	2.30 (s)	3	CH_3	
					−18.93	2	OsH	

[a] Calculated figures are given in parentheses. [b] Recorded in cyclohexane solution; ±1 cm^{-1}. [c] Recorded at 100 MHz and 27 °C in $CDCl_3$ unless stated otherwise. [d] ν(NH) at 3 405 cm^{-1} (C_4Cl_6) mull); ν(CO) (organic) at 1 497 and 1 517 cm^{-1} (Nujol). [e] O, 17.5 (17.85%). [f] ν(NH) at 3 375 cm^{-1} (C_4Cl_6 mull). [g] O, 16.9 (16.7%). [h] N.m.r. recorded at 60 MHz at 35 °C. [i] Insufficient material to obtain analytically pure sample. [j] Very similar ν(CO) spectrum to those previously reported[1] for the corresponding $OCMe_2C_6H_4$ and $OCHMeC_6H_4$ complexes; the latter, $[Os_3(CO)_9H_2(OCHMeC_6H_4)]$ has now been obtained fairly pure [C, 22.15 (21.6); H, 1.3 (1.05%)]. [k] From 4-methylbenzyl alcohol; trace amounts of a brown solid characterised by ν(CO) only. [l] From 2-methylbenzyl alcohol; trace amounts of a brown solid characterised by ν(CO) only.

---

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

(4) is not on the direct path to C_6H_6 at all. A simple conversion into (5) as implied in the Scheme is not favoured since $[Os_4(CO)_{12}H_4]$ is formed as well as (5) when (4) is pyrolysed. It could be that PhCHO (free or co-ordinated) is formed at some stage from which the C_6H_4 ligand is generated. Benzaldehyde does react with $[Os_3(CO)_{12}]$ to give (5)[4] so that this is not unreasonable.



SCHEME Reactions marked with an asterisk were observed individually

The complexes $[Os_3(CO)_{10}H(OCH_2C_6H_3Me)]$ (6) and (7), derived from 4- and 2-methylbenzyl alcohol respectively, also undergo degradation corresponding to (3)—(5) (Scheme), but give the same isomer of $[Os_3(CO)_9H_2(C_6H_3Me)]$ (10). Complexes (8) and (9), both analogous to (4), are assumed to be isomers, but their very low yields allowed only the i.r. spectra to be recorded, which as expected are indistinguishable. Hydrogen-1 n.m.r. spectroscopy of (10) (see Table) shows coupling for the three arene signals which is only consistent with the structure shown. We do not know how the rearrangement to form this isomer from 2-methylbenzyl alcohol took place, but a direct loss of H_2 and CO [(4) to (5) Scheme] would give different isomers. Possibly isomerism–scrambling occurs for the final product by reaction (4), with (10) being the most

$$[Os_3(CO)_9H_2(C_6H_3Me\text{-}3)] \rightleftharpoons [Os_3(CO)_9H(C_6H_4Me\text{-}3)] \rightleftharpoons [Os_3(CO)_9H_2(C_6H_3Me\text{-}4)] \quad (4)$$

stable isomer. This is reminiscent of the tautomeric equilibrium between $[Os_3(CO)_{10}H(Me)]$ and $[Os_3(CO)_{10}H_2(CH_2)]$, one being co-ordinatively unsaturated the other saturated.[9] A similar reversible transfer of hydrogen atoms between ligand and metal was observed with $[Os_3(CO)_9H(MeC{:}C{:}CH_2)]$ (11) which isomerises thermally to $[Os_3(CO)_9H(MeC\cdot CH\cdot CH)]$ (12).[10] In order to establish which hydrogen atom(s) migrated in this transformation we prepared $[Os_3(CO)_9D(MeC{:}C{:}CH_2)]$ (>95% D at metal) by treatment of (11) with neat CF_3CO_2D followed by CD_3COCD_3. Thermolysis of a $[^2H_8]$toluene solution of this at 162 °C in a sealed tube gave scrambling within this isomer faster than isomerisation, probably by equilibrium (5) involving the co-ordinatively unsaturated but-2-yne complex.[11]

No benzyne complex (or free benzene) is formed by sealed tube thermolysis of $[Os_3(CO)_{10}H(OCHMePh)]$ (13); PhCOMe is the only significant organic product.

$$[Os_3(CO)_9H(MeC{:}C{:}CH_2)] \rightleftharpoons [Os_3(CO)_9(MeC{:}CMe)] \quad (5)$$

The ^1H n.m.r. spectrum of (5) has been reported to contain AA'BB' signals for the apparently symmetrical C_6H_4 group and a two-hydrogen hydride singlet. Analogy with related alkyne complexes seemed to indicate the asymmetric structure shown in the Scheme. We have confirmed that the apparent plane of symmetry is due to time-averaging. The spectrum of (5) in $CDCl_3$ is essentially unchanged down to −60 °C, but a solution in OMe_2 shows hydride-signal broadening at lower temperatures with two signals of *ca.* 50 Hz width at −140 °C [δ −17.0 and −20.9 p.p.m.; $T_c = -120 \pm 10$ °C; $\Delta G^{\ddagger}(T_c) = 28 \pm 2$ kJ mol^{-1}]. The upper signal (δ 6.87 p.p.m.) of the AA'BB' signals broadens on cooling from −130 to −140 °C with little correspond-

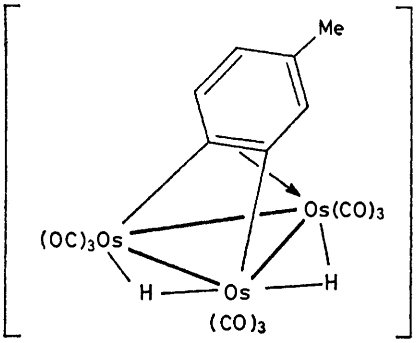
---

[9] R. B. Calvert and J. R. Shapley, *J. Amer. Chem. Soc.*, 1977, **99**, 5225.

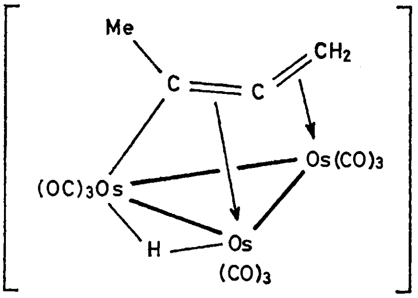
[10] A. J. Deeming, S. Hasso, and M. Underhill, *J.C.S. Dalton*, 1975, 1614.

[11] A. J. Deeming and S. Hasso, unpublished work.

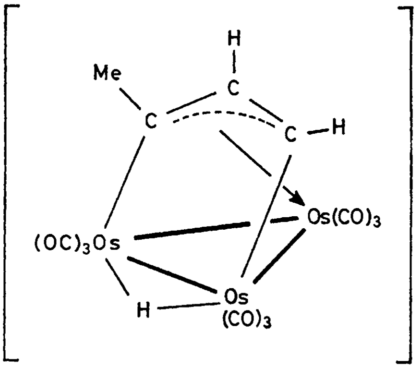
ing change for the lower signal (δ 7.11 p.p.m.). This is presumably the onset of the freezing-out of these signals to give the expected ABCD set. Hydride exchange presumably occurs more slowly than C_6H_4 exchange, the latter occurring by rapid H^a transfer to the vacant edge of the Os_3 triangle. Although this is unconfirmed here, this behaviour is supported by related observations on alkyne analogues of (5).[8,12-14]



(10)



(11)



(12)

Although γ-metallation of 2,6-dimethylphenol with $[Os_3(CO)_{12}]$ was attempted, only $[Os_3(CO)_{10}H(OC_6H_3Me_2\text{-}2,6)]$ (14) could be obtained.

EXPERIMENTAL

All the reactions were carried out under nitrogen, carbon monoxide, or *in vacuo* but separations were performed in air. The products all gave parent molecular ions in their mass spectra with qualitatively the correct isotopic patterns and the expected fragmentation behaviour, for example the successive loss of CO ligands.

Reactions of Benzylamine with $[Os_3(CO)_{12}]$. (*a*) *Preparation of complexes.* Carbon monoxide was bubbled through a refluxing solution of benzylamine (2 cm³) and $[Os_3(CO)_{12}]$ (0.203 g) in octane (23 cm³) for 3.5 h. After removal of the octane and excess of amine under reduced pressure the residue was separated by preparative t.l.c. (silica) eluting with light petroleum (b.p. 40—60 °C)–chloroform mixtures (up to 7% v/v chloroform for a reasonable separation). Two yellow bands gave 2,3-μ-N-*benzylcarbamoyl*-1,1,1,1,2,2,2,3,3,3-*decacarbonyl*-2,3-μ-*hydrido*-triangulo-*triosmium* (1) (0.139 g, 63%) and 2,3-μ-*benzylamido*-1,1,1,2,2,2,3,3,3-*decacarbonyl*-2,3-μ-*hydrido*-triangulo-*triosmium* (2) (0.013 g, 6%) both as yellow crystals, m.p. 158—161 and 157—159 °C respectively. A similar reaction for 7 h gave an improved yield of (2) (16%) at the expense of (1), while the reaction under N_2 gave lower yields; $[Os_3(CO)_{12}]$ (0.230 g) gave (2) (2.5%) and (1) (9%).

(*b*) *Catalytic formation of* 1,3-*dibenzylurea.* The complex $[Os_3(CO)_{12}]$ (0.154 g), benzylamine (10 cm³), and octane (25 cm³) were heated at 150 °C under CO (45 atm, 4.56 MPa) for 6 h. After removal of solvent and excess of benzylamine under reduced pressure, distillation of the residue (100 °C, *ca.* 0.1 mmHg) * gave a pale yellow oily distillate. Continuous extraction of this with heptane (60 cm³) gave white crystals of 1,3-dibenzylurea {1.1 g, 26 mol per mol $[Os_3(CO)_{12}]$}, m.p. 164.5—165.5 °C. The urea was fully characterised by elemental analysis, and ¹H n.m.r., i.r., and mass spectra.

Reaction of Benzylamine with $[Os_3(CO)_{10}(C_8H_{14})_2]$.—Benzylamine (0.05 cm³) was added to a solution of the bis(cyclo-octene) complex (0.018 g) in cyclo-octene (0.5 cm³) and cyclohexane (10 cm³). No reaction occurred at room temperature but after 2 h at 60—70 °C removal of the solvent under reduced pressure and chromatography on silica gave (1) (0.002 g) and (2) (0.007 g).

Reactions of Complex (1).—(*a*) *Thermolysis.* Complex (1) (0.052 g) in $[^2H_8]$toluene (0.75 cm³) was degassed and sealed *in vacuo* in an n.m.r. tube. The ¹H n.m.r. spectrum (δ −10 to −20 p.p.m.) was recorded periodically while heating at 150 °C for 47 h. The hydride signal due to (1) decreased and one due to (2) was observed. Work-up involving t.l.c. (silica) gave starting material (0.003 g, 6%), $[Os_3(CO)_{12}]$ (0.012 g, 25%), and complex (2) (0.007 g, 14%). A similar treatment but with added benzylamine (five-fold excess), heating for 48 h at 140 °C gave $[Os_3(CO)_{12}]$ (11%), starting complex (17%), and (2) (31%).

(*b*) *With hydrogen.* Hydrogen at atmospheric pressure was bubbled rapidly through a solution of (1) (0.100 g) in refluxing decane (25 cm³) for 1 h; no reaction was observed in refluxing octane (3.5 h). Separation by t.l.c. gave (2) (0.017 g, 18%).

(*c*) *With carbon monoxide.* Carbon monoxide was bubbled through a refluxing solution of complex (1) (0.019 g) in nonane for 4 h. No reaction was observed and even after 44 h under reflux (under CO but not with the gas flowing) starting material (74%) was recovered with only trace amounts of (2).

Thermolysis of $[Os_3(CO)_{10}H(OCH_2Ph)]$ (3).—(*a*) *In an open vessel.* A solution of (3) (0.170 g), prepared as described previously,[1] in nonane (50 cm³) was heated under reflux for 9 h under a flow of N_2 to remove any displaced CO. After leaving the resulting solution to stand (overnight, 20 °C), the white crystals of $[Os_4(CO)_{12}H_4]$ (0.025

---

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[12] W. G. Jackson, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1977, **139**, 125.

[13] J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Organometallic Chem.*, 1975, **97**, C16.

[14] A. J. Deeming, *J. Organometallic Chem.*, 1978, **150**, 123.

g, 15%) which deposited were filtered off. The residue from the filtrate, after removal of the solvent under reduced pressure, gave by t.l.c. (silica) eluting with light petroleum–toluene (98 : 2 v/v) a purple band of $[Os_3(CO)_{10}H_2]$ (traces) and a yellow band yielding crystals of 1,1,1,2,2,2,3,3,3-nonacarbonyl-1,2;2,3-di-μ-hydrido-μ_3-*o*-phenylene-*triangulo*-triosmium (0.021 g, 12%), having identical i.r., ^{1}H n.m.r., and mass spectra to those of the complex obtained from benzene and $[Os_3(CO)_{12}]$. When a similar reaction was carried out, monitoring the i.r. spectrum of the nonane solution, $[Os_3(CO)_9H_2(OCH_2C_6H_4)]$ (4) was detected. Small quantities of *complex* (4) were isolated from a similar reaction in refluxing octane under N_2 for 3 h, which also gave (5) (23%) and trace amounts of $[Os_3(CO)_{10}H_2]$ and $[Os_4(CO)_{12}H_4]$.

(*b*) *In a sealed tube.* Complex (3) (0.058 g) and nonane (0.5 cm^3) were sealed under N_2 in an n.m.r. tube and heated at 146 °C. New n.m.r. absorptions appeared due to benzaldehyde (unambiguous assignment) and benzene (possible assignment), the only organic products, and after 23 d only a little starting material remained while the mol ratio C_6H_6 : PhCHO was 2.4 : 1. G.l.c. analysis of the final solution confirmed these products, and the metal residue was shown to be a mixture of $[Os_3(CO)_{12}]$ and $[Os_4(CO)_{12}H_4]$. T.l.c. analysis showed that $[Os_3(CO)_9H_2(X)]$ ($X = C_6H_4$ or $OCH_2C_6H_4$) were not present.

Reaction of Complex (5) *with Carbon Monoxide.*—The complex (0.014 g) was sealed in an n.m.r. tube in nonane (0.5 cm^3) saturated with CO and heated at 146 °C. The ^{1}H n.m.r. spectrum showed that after 18 h too little starting material remained to be detected with benzene (δ 7.25 p.p.m.) as the only organic product. Benzene (*ca.* 51%) was confirmed by g.l.c. analysis and the yellow insoluble residue was identified as $[Os_3(CO)_{12}]$ (*ca.* 49%).

Reaction of Complex (4) *with Carbon Monoxide.*—Carbon monoxide was bubbled through a refluxing solution of (4) (0.005 g) in octane for 6.5 h. Normal work-up and t.l.c. gave (3), i.r. and mass spectral identification, as the only observed product.

Thermolysis of Complex (4).—A solution of (4) (0.005 g) in nonane (5 cm^3) was heated under reflux under N_2 for 1 h. Treatment as above gave (5) and $[Os_4(CO)_{12}H_4]$ in quantities difficult to determine with any accuracy.

Reaction of $[Os_3(CO)_{12}]$ *with* 4-*Methylbenzyl Alcohol.*—A solution of $[Os_3(CO)_{12}]$ (0.436 g) and freshly sublimed 4-methylbenzyl alcohol (0.42 g) in xylene (125 cm^3) was heated under reflux under N_2 for 11 h. The cooled solution was decanted from crystals of $[Os_3(CO)_{12}]$ (0.197 g) and solvent, and unchanged alcohol was removed to give an oil which on t.l.c. yielded $[Os_3(CO)_{10}H(OCH_2C_6H_4Me\text{-}4)]$ (6) as yellow *crystals* (0.071 g, 30%) and a trace amount of $[Os_3(CO)_9H_2(OCH_2C_6H_3Me)]$ (8) as a brown *solid*. A similar treatment of $[Os_3(CO)_{12}]$ with 2-methylbenzyl alcohol gave *complexes* (7) (18%) and (9) (trace).

Thermolysis of Complex (6).—A solution of (6) (0.047 g) in nonane (50 cm^3) was heated under reflux for 6 h and chromatographic work-up gave 1,1,1,2,2,2,3,3,3-*nonacarbonyl*-1,2;2,3-*di*-μ-*hydrido*-μ_3-4-*methyl*-o-*phenylene*-triangulo-*triosmium* (10) (0.009 g, 19%). Similar treatment of complex (7) (0.900 g) in refluxing nonane (50 cm^3) (8 h) also gave (10) (15%) as yellow crystals.

Thermolysis of Complex (6) *in a Sealed Tube.*—Complex (6) (0.040 g) in nonane (0.55 cm^3) in a sealed n.m.r. tube under N_2 was heated at 146 °C for 60 d. Signals due to (6) were gradually replaced by those of toluene and $4\text{-}MeC_6H_4CHO$. G.l.c. estimation of these compounds gave toluene (56%) and $4\text{-}MeC_6H_4CHO$ (17%) while $[Os_3(CO)_{12}]$ and $[Os_4(CO)_{12}H_4]$ were identified as products as well as minor unidentified metal carbonyls.

Thermolysis of $[Os_3(CO)_{10}H(OCHMePh)]$ (13).—(*a*) *In an open vessel.* A solution of (13) (0.105 g) in nonane (30 cm^3) was heated under reflux under N_2 for 4 h. Chromatography of the residue after removal of the solvent gave starting material (0.030 g), $[Os_3(CO)_9H_2(OCHMeC_6H_4)]$ [1] (0.020 g, 27%), and trace amounts of $[Os_3(CO)_{10}H_2]$.

(*b*) *In a sealed tube.* A solution of (13) (0.064 g) in nonane (0.5 cm^3) in an n.m.r. tube sealed under N_2 was heated at 146 °C. Over 45 d signals due to (13) disappeared with the appearance of new signals due to PhCOMe as the major organic product, the identity of which was later confirmed by g.l.c. Other minor organic products were not identified, but methane, acetaldehyde, and benzene were not formed; $[Os_3(CO)_{12}]$ and $[Os_4(CO)_{12}H_4]$ were the main metal carbonyl products.

Reaction of $[Os_3(CO)_{12}]$ *with* 2,6-*Dimethylphenol.*—A solution of $[Os_3(CO)_{12}]$ (0.467 g) and $2,6\text{-}Me_2C_6H_3OH$ (0.309 g) in xylene (100 cm^3) was heated under reflux under N_2 for 22 h. Work-up involving chromatography (silica) gave $[Os_3(CO)_{10}H(OC_6H_3Me_2\text{-}2,6)]$ (14) as an impure yellow *solid* (0.005 g). None of the other chromatographic bands was identified.

We thank the Association of Commonwealth Universities for the award of a scholarship (to K. A. A.), the S.R.C. for the award of a studentship (to C. C. Y.), and Johnson, Matthey Ltd. for a generous loan of osmium tetraoxide.

[8/024 *Received, 6th January,* 1978]