Metallation of Hydroxy-aryl and -alkyl Compounds by Reaction with Dodecacarbonyl-*triangulo*-triosmium †

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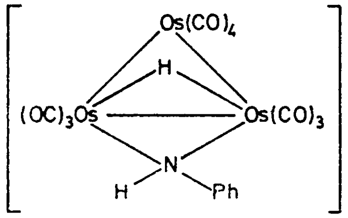
Various organic hydroxy-compounds ROH react with $[Os_3(CO)_{12}]$ at 140 °C to give species of type $[Os(CO)_{10}H(OR)]$ (R = Ph, 2-naphthyl, $CHMe_2$, CH_2Ph, CHMePh, or CMe_2Ph), some of which convert at higher temperatures into the dihydrides $[Os_3(CO)_9H_2(X)]$, the second metal hydride being derived from R. Where hydrogen-atom transfer is from the β-carbon atom, compounds containing the triply bridged ligand X ($X = OC_6H_4$, $2\text{-}OC_{10}H_6$, $1\text{-}OC_{10}H_6$, or $OC_6H_3OH\text{-}o$) are formed, whereas γ-carbon–hydrogen bond cleavage gives species with X bridging two osmium atoms and forming a five-membered chelate ring with one of them ($X = OCMe_2C_6H_4$, $OCHMeC_6H_4$, or $1\text{-}OC_{10}H_6$). The spectroscopic evidence for these conclusions is discussed.

LEWIS and his co-workers[1,2] reported the formation of hydridomethoxo- and dimethoxo-derivatives of $[Os_3(CO)_{12}]$, (I), of formula $[Os_3X(CO)_{10}(OMe)]$ (X = H or OMe). These were isolated in low yield from the reaction between osmium tetraoxide and carbon monoxide in methanol which gave mainly compound (I) as the desired product. These methoxo-compounds were probably formed by reaction of methanol with (I). Related SR compounds may be prepared from thiols,[2] and the formation of $[Os_3(CO)_{10}H(OH)]$ from (I) and water is, of course, related.[3] Hydrogen sulphide reacts with (I) to give $[Os_3(CO)_9H_2(S)]$ directly.[4] The related hydride $[Os_3(CO)_{10}H(NPhH)]$, (II), is readily formed from aniline and (I), and this converts into the *ortho*-metallated derivative $[Os_3(CO)_9H_2(NHC_6H_4)]$, (III).[5] At higher temperatures hydrogen transfer leads to the isomer $[Os_3(CO)_9H_2(NPh)]$, (IV). In these and other examples[6,7] the successive transfer of hydrogen atoms from ligand to metal has been observed, and we will describe in this paper similar transformations of the alkoxo-compounds $[Os_3(CO)_{10}H(OR)]$, most of which were newly prepared by ourselves. Internal metallations generally give five-membered chelate rings, but in polynuclear metal systems metallation can take place at carbon atoms α or β to the heteroatom to form bridges rather than chelates. We have shown in this work that where only γ metallation is feasible chelate rings are formed even in polynuclear systems. There are more sites accessible for metallation in cluster compounds than in mononuclear compounds.



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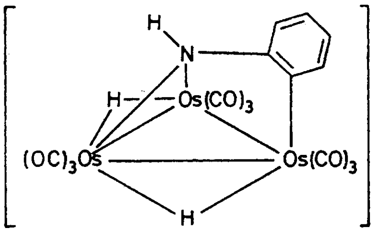

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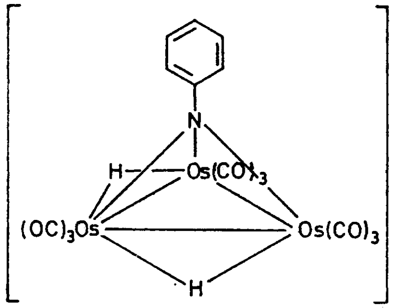

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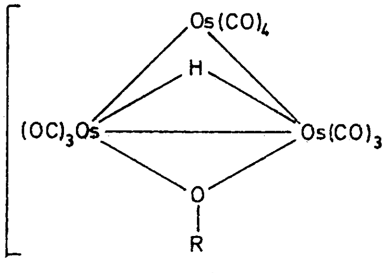
RESULTS AND DISCUSSION

Decacarbonyl Compounds.—The initial reaction of ROH with compound (I) appears to be transfer of hydrogen from oxygen to osmium and in many cases compounds of type $[Os_3(CO)_{10}H(OR)]$, (V; R = Me,[1] Ph, 2-naphthyl, $CHMe_2$, CH_2Ph, CHMePh, or CMe_2Ph), were isolated. In certain cases (R = 1-naphthyl or 2-hydroxyphenyl) further loss of carbon monoxide with hydrogen transfer from carbon occurred so that decacarbonyls were not observed. Compounds of type (V) all have very similar spectra at *ca.* 2 000 cm^{-1} and hence all have structures related to that of $[Os_3(CO)_{10}H(OMe)]$, the crystal structure



(V)

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† No reprints available.

[1] B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc.* (*A*), 1968, 2859.

[2] G. R. Crooks, B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc.* (*A*), 1969, 797.

[3] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1973, **57**, C84.

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

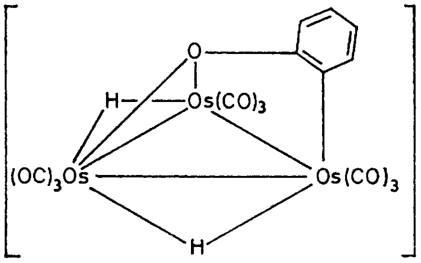
[5] A. J. Deeming and C. Choo Yin, *J.C.S. Dalton*, 1974, 1013.

[6] A. J. Deeming and M. Underhill, *J.C.S. Dalton*, 1973, 2727.

[7] A. J. Deeming, S. Hasso, and M. Underhill, *J. Organometallic Chem.*, 1974, **80**, C53; *J.C.S. Dalton*, 1975, 1614.

of which is known.[8] The group R could adopt one of two positions at the ψ-tetrahedral oxygen atom, but the most favourable of these for subsequent metallation to occur should be readily accessible.

Dihydrido-compounds derived from Compounds (V; R = aryl).—As in the formation of $[Os_3(C{:}CH_2)(CO)_9H_2]$ from $[Os_3(CH{:}CH_2)(CO)_{10}H]$[7] and of compound (III) from (II),[5] we found that compound (V; R = Ph) readily loses a CO ligand in refluxing nonane to give the nonacarbonyl $[Os_3(CO)_9H_2(OC_6H_4)]$, (VI), which was characterised by elemental analysis, mass, infrared, and ^1H n.m.r. spectra. The removal of the *ortho*-hydrogen is unambiguously confirmed by the ^1H n.m.r. spectrum (Figure 1), all four ring protons giving separate signals and enabling nuclear spin–spin coupling analysis by double resonance. The two protons bound to osmium gave separate broad signals at 27 °C which coalesced at higher temperatures, and the kinetic data for hydride exchange in these and other dihydrido-compounds, such as (III), will be discussed elsewhere.



(VI)

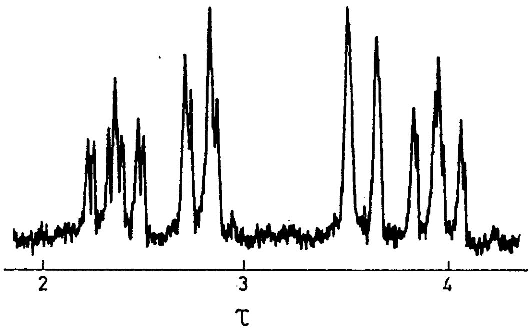
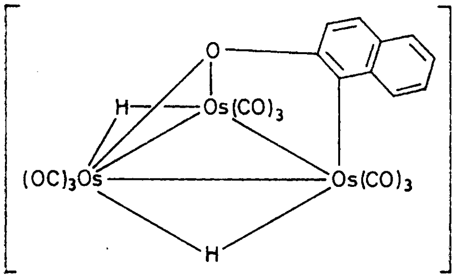


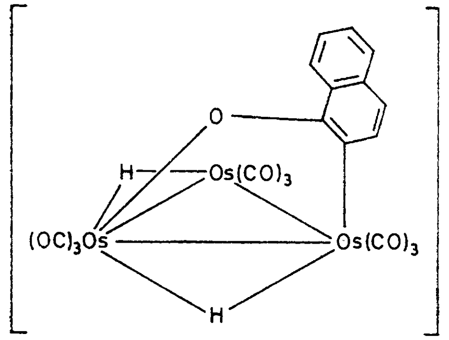
FIGURE 1 Hydrogen-1 n.m.r. spectrum for the OC_6H_4 ligand of compound (VI)

The 2-naphthyl derivative (V; R = $2\text{-}C_{10}H_7$) similarly gave *ortho*-metallation in refluxing nonane, exclusively at the 1-position with no detectable formation of the 3-metallated isomer. The product $[Os_3(CO)_9H_2(OC_{10}H_6)]$, (VII), is spectroscopically analogous to compound (VI) and showed two sharp hydride signals at low temperatures only. The site of metallation is confirmed by n.m.r.; notably there was an AB quartet (τ 1.97 and 3.55) due to the two remaining hydrogens of the metallated ring.

With 1-naphthol no intermediate decacarbonyl of type (V) was isolated or even detected by i.r. spectroscopy when the course of the reaction was monitored in this way. Instead the reaction proceeded smoothly to the nonacarbonyl stage and two isomers of $[Os_3(CO)_9H_2(OC_{10}H_6)]$ were isolated, only one, (VIII), being analogous to compound (VI). Compounds (VI)—(VIII) have very similar ν(CO) absorptions, and hydride ligand exchange in (VIII) leads to broad signals at room temperature as with the other compounds. The ^1H n.m.r. confirms *ortho*-metallation.

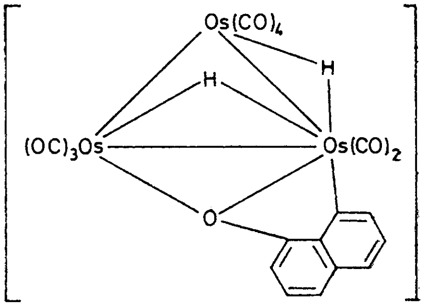


(VII)



(VIII)

The other isomer formed from 1-naphthol is interesting since it is quite different structurally from compound (VI) with metallation having occurred at the carbon atom γ rather than β to the oxygen atom (established by ^1H n.m.r.). We propose that this isomer, compound (IX) has a 4,3,2-carbonyl distribution with a five-membered chelate ring rather than the more usual 3,3,3-carbonyl distribution with a triply bridged organic ligand as in structure (X), although our evidence for this is indirect. We have now examined many compounds $[Os_3(CO)_9H_2(X)]$ of the latter type and their ν(CO) absorptions are all of a similar pattern, although not as closely compar-



(IX)

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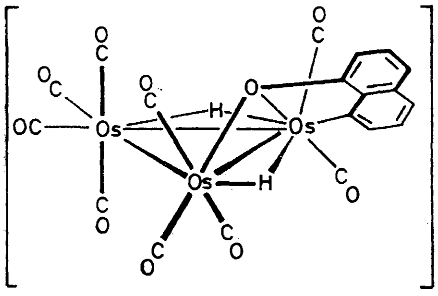
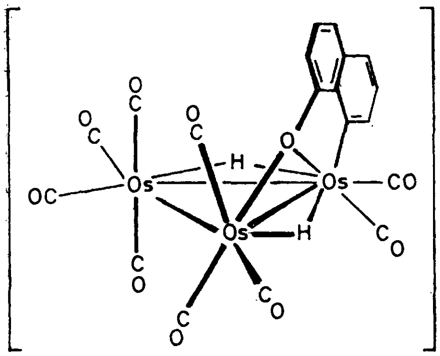
[8] R. Mason, *Pure Appl. Chem.*, 1973, **33**, 513; R. Mason and D. M. P. Mingos, *J. Organometallic Chem.*, 1973, **50**, 53.

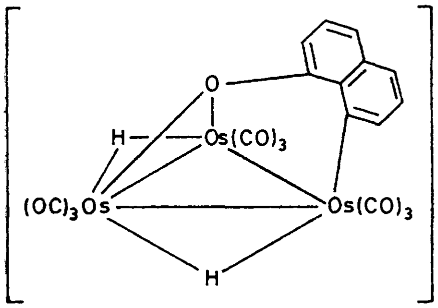
able as those of compounds (VI)—(VIII). Figure 2 shows a few spectra [(*a*)—(*d*)] of species with 3,3,3-carbonyl distributions and a triply bridged ligand X. The spectrum (*e*) of compound (IX) is sufficiently different to conclude qualitatively that it has a different metal carbonyl arrangement. The lack of hydride-exchange effects in the ^{1}H n.m.r. also supports a 4,3,2-carbonyl distribution. Up to 100 °C there were two sharply resolved hydride signals; thermal decomposition (rapid at 145 °C) prevented the use of higher temperatures. Hydride exchange in $[Os_3(C{:}CH_2)(CO)_9H_2]$ involves hydrogen-atom transfer between filled and vacant bridging sites between metal atoms,[9,10] which is facile for a 3,3,3-distribution where transfer would lead to a form of similar or identical energy. For a compound with a 4,3,2-carbonyl distribution a hydride migration from one bridging site to another is likely to produce a significantly less stable molecule preventing dynamic behaviour. We have no direct evidence for hydride positions but those displayed are reasonable. A compound of structure (X) would contain very strained six-membered rings, whereas a much less strained five-membered ring is formed if metallation occurs at an osmium atom already bound to the oxygen atom to give structure (IX). The carbon may be bound to osmium at an equatorial site, structure (IXa), or axial site, structure (IXb), but we have no evidence to determine the configuration.



(IXa)



(IXb)



(X)

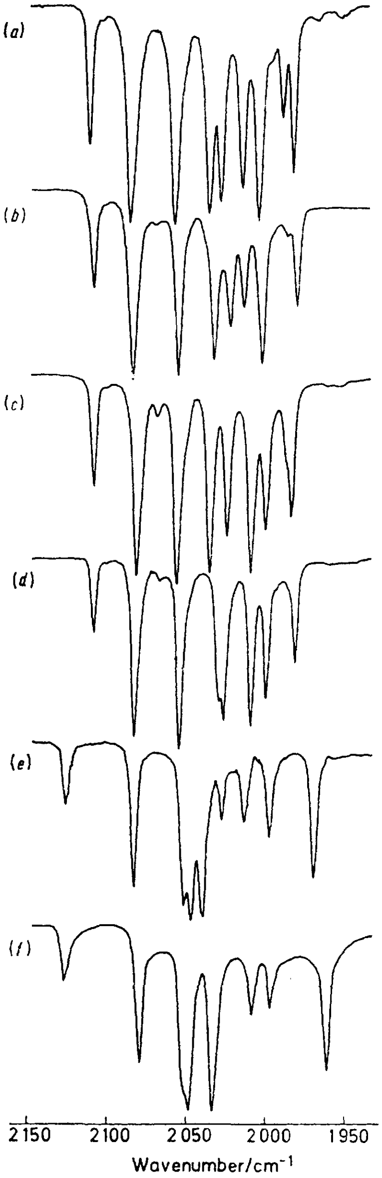


FIGURE 2 Spectra due to ν(CO) absorptions of cyclohexane solutions of compounds of type $[Os_3X(CO)_9H_2]$. Compounds with a 3,3,3-CO distribution at the metal atoms: (*a*), X = OC_6H_4, (VI); (*b*), X = $OC_{10}H_6$, (VII); (*c*), X = C_6H_4 (derived from benzene [9]); (*d*), X = NHC_4H_2 (derived from pyrrole [15]). Compounds with a 4,3,2-CO distribution: (*e*), X = $OC_{10}H_6$, (IX); (*f*), X = $OMe_2C_6H_4$, (XI)

Attempting to prepare other molecules with this type of structure we treated 2-phenylpropan-2-ol, $PhCMe_2OH$,

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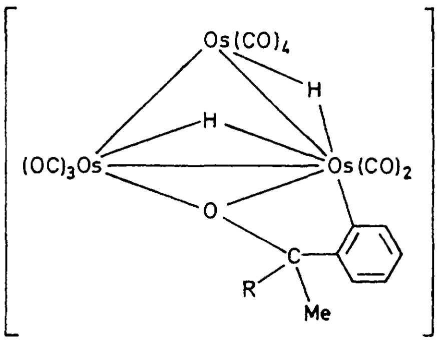
[9] A. J. Deeming and M. Underhill, *J.C.S. Dalton*, 1974, 1415.

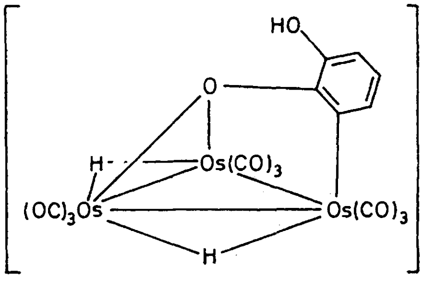
[10] W. G. Jackson, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1975, **90**, C13.

with $[Os_3(CO)_{12}]$ and obtained directly a nonacarbonyl $[Os_3(CO)_9H_2(OCMe_2C_6H_4)]$, (XI). This compound has carbonyl absorptions quite similar to those of (IX), see Figure 2; it is non-fluxional and has non-equivalent Me groups. These are all consistent with the structure shown. A structurally equivalent derivative $[Os_3(CO)_9H_2(OCHMeC_6H_4)]$, (XII), was obtained from 1-phenylethanol in very low yield. Its ν(CO) absorptions are very similar to those of (XI) and the ^1H n.m.r. spectrum confirms *ortho*-metallation. Although there is some evidence[11] that an analogous species from benzyl alcohol is formed in very low concentration on heating compound (V; R = CH_2Ph) at 150 °C in nonane, there are various other species formed such as benzaldehyde, benzene, $[Os_3(C_6H_4)(CO)_9H_2]$, $[Os_3(CO)_{10}H_2]$, and $[Os_4(CO)_{12}H_4]$ which may result from metallation at both α- and γ-carbon atoms. Formation of chelate rings by *ortho*-metallation would be more favourable with 2-phenylpropan-2-ol than with benzyl alcohol, not only because of other sites of attack with the latter but because of the *gem*-dimethyl effect.[12] We are studying the benzyl alcohol reaction further as an example of α metallation.



(XI) R = Me
(XII) R = H

2,6-Dimethylphenol might also have given a γ-metallated compound but we were unable to isolate any tractable derivatives of $[Os_3(CO)_{12}]$. *ortho*-Dihydroxybenzene (catechol) could also form five-membered chelate rings incorporating both oxygen atoms, but the only complex we could isolate from its reaction with $[Os_3(CO)_{12}]$ was $[Os_3(CO)_9H_2(OC_6H_3OH\text{-}o)]$, (XIII). We were unable to obtain this compound completely pure, but its very similar carbonyl i.r. spectrum to that of (VI) and other spectroscopic data (see Table) leave no doubt that the structure is as shown. Presumably this compound was formed *via* $[Os_3(CO)_{10}H(OC_6H_4OH\text{-}o)]$, a compound of type (V), with the second hydrogen being transferred from the *ortho*-carbon rather than the *ortho*-hydroxy-group. There was no evidence for the formation of $[Os_3(CO)_9H_2(o\text{-}O_2C_6H_4)]$.



(XIII)

Cationic Trihydrido-compounds derived by Protonation.—Protonation of the nonacarbonyl derivatives of phenol and naphthols, compounds (VI), (VIII), and (IX), also supports the structures as discussed above. In general compounds of type $[Os_3X(CO)_9H_2]$ react with trifluoroacetic acid or sulphuric acid to give $[Os_3X(CO)_9H_3]^+$. Where X = S, the three hydride nuclei are equivalent,[13] which is consistent with the trihydride having C_{3v} symmetry, but where X = $C{:}CH_2$[14] or NHC_6H_4, compound (III),[15] the trihydrido-cations show two hydride signals (intensity ratio = 1 : 2) in the ^1H n.m.r. spectrum. This is consistent in each case with protonation at the Os–Os bond not already bridged by hydrogen atoms so that where X = $C{:}CH_2$ or NHC_6H_4 a plane of symmetry has been gained. Compound (VI) is much less reactive towards acid but nevertheless dissolved in neat CF_3CO_2H to give mainly unchanged compound together with some trihydride which, after several days, increased to *ca.* 60% of the whole. The product $[Os_3(CO)_9H_3(OC_6H_4)]^+$ showed two hydride signals at 27 °C at τ 23.96 (intensity 1) and 25.36 (intensity 2) consistent with a compound with a plane of symmetry. As expected compound (VIII) also reacted in neat CF_3CO_2H to give a trihydrido-cation with a very similar spectrum: τ 23.28 (intensity 1) and 25.48 (intensity 2). These results are in good agreement with the structures shown for compounds (III) and (VIII) with retention of the basic structure on protonation. Compound (IX) also reacted with CF_3CO_2H but, instead of a trihydride, a dihydride of unknown formulation was formed [τ 20.24, doublet, intensity 1; τ 24.04, doublet, intensity 1; J(HH) 1.7 Hz]. The simple protonation at the metal as with compounds (III) and (VIII) has not occurred and probably relates to structural differences.

EXPERIMENTAL

All the reactions were carried out under N_2 or in sealed evacuated vessels. Separations on silica (E. Merck, HF_{254}, type 60) were carried out in air. All the new compounds, except (XIII), gave good mass spectra showing the parent molecular ion with qualitatively the expected isotopic distribution patterns and fragment ions which predominantly result from the loss of CO and H_2.

*Reactions of Hydroxy-compounds with Dodecacarbonyl-*triangulo*-triosmium,* (I).—*Phenol.* A solution of $[Os_3(CO)_{12}]$, (I) (0.575 g), and phenol (1.47 g) in xylene (130 cm^3) was heated under reflux for 10 h. The solvent was removed under reduced pressure and the resulting yellow oil was

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[11] K. A. Azam and A. J. Deeming, unpublished work.

[12] B. L. Shaw, *J. Amer. Chem. Soc.*, 1975, **97**, 3856 and refs. therein.

[13] A. J. Deeming, R. Ettorre, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1971, 1797.

[14] A. J. Deeming, S. Hasso, M. Underhill, A. J. Canty, B. F. G. Johnson, W. G. Jackson, J. Lewis, and T. W. Matheson, *J.C.S. Chem. Comm.*, 1974, 807.

[15] C. Choo Yin, A. J. Deeming, and R. E. Kimber, unpublished work.

Analytical and spectroscopic data

Complex	Analyses[a] (%)		I.r. spectra,[b] $\tilde{\nu}$(CO)/cm^{-1}	N.m.r. spectra[c]			
	C	H		τ	Relative intensity	Assignment	J/Hz
$[Os_3(CO)_{10}H(OPh)]$	20.35	0.95	2 112w, 2 073s,	3.0 (m)	3	H^3—H^5	
(V; R = Ph)	(20.35)	(0.65)	2 064ms, 2 034w,	3.57 (d)	2	H^2, H^6	4.0
			2 025vs, 2 007ms,	22.20 (s)	1	OsH	
			1 991w (sh), 1 986mw				
$[Os_3(CO)_{10}H(OC_{10}H_7)]$	24.25	0.85	2 112m, 2 073vs,	2.2—2.9 (m)	*ca.* 5	H^4—H^8	
(V; R = 2-naphthyl)	(24.15)	(0.8)	2 064s, 2 037m,	3.27 (m)	2	H^1, H^3	
			2 025vs, 2 007s,	21.97 (s)	1	OsH	
			1 991m, 1 987m				
$[Os_3(CO)_{10}H(OCH_2Ph)]$	21.6	0.75	2 110w, 2 072vs,	2.64 (m)	5	Ph	
(V; R = CH_2Ph)	(21.3)	(0.85)	2 059s, 2 023vs,	5.40 (s)	2	CH_2	
			2 018 (sh), 2 006w,	22.42 (s)	1	OsH	
			2 000s, 1 988m,				
			1 983w				
$[Os_3(CO)_{10}H(OCHMePh)]$	22.7	1.05	2 112m, 2 072vs,	2.70 (m)		Ph	
(V; R = CHMePh)	(22.2)	(1.05)	2 059s, 2 023vs,	6.43 (q)	1	$C\mathit{H}(CH_3)$	6.5
			2 019s, 2 007w,	8.55 (d)	3	$CH(C\mathit{H}_3)$	
			2 000s, 1 996 (sh),	22.67 (s)	1	OsH	
			1 989m, 1 948w				
$[Os_3(CO)_{10}H(OCMe_2Ph)]$ [d]			2 111w, 2 072s,				
(V; R = CMe_2Ph)			2 059ms, 2 024vs,				
			2 019 (sh), 2 007w, (sh),				
			2 000ms, 1 996w (sh),				
			1 989m, 1 984w (sh)				
$[Os_3(CO)_{10}H(OCHMe_2)]$			2 110w, 2 070s,	8.84 (d)	6	Me	J(Me–H) 7
(V; R = $CHMe_2$)			2 059ms, 2 023vs,	7.30 (sp)	1	$OC\mathit{H}$	
			2 004w (sh), 1 998ms,	22.84 (s)	1	$Os\mathit{H}$	
			1 988m, 1 982mw				
$[Os_3(CO)_9H_2(OC_6H_4)]$	19.7	0.80	2 112m, 2 086s,	2.31 (ddd)	1	H^5	$J(H^4$–$H^5)$ 8.5
(VI)	(19.65)	(0.65)	2 058s, 2 036 (sh),	2.76 (dd)	1	H^3	$J(H^5$–$H^6)$ 7.0
			2 030vs, 2 015m,	3.58 (d)	1	H^6	$J(H^3$–$H^4)$ 7.5
			2 004ms, 1 988m,	3.96 (ddd)	1	H^4	$J(H^3$–$H^5)$ 1.5
			1 981m	21.66 (d) [e]	1	OsH_a	$J(H^4$–$H^6)$ 1.8
				24.06 (d) [e]	1	OsH_b	$J(H_a$–$H_b)$ 1.5
$[Os_3(CO)_9H_2(OC_{10}H_6)]$	24.05	1.05	2 108m, 2 083vs,	1.94 (d)	1	H^4	$J(H^4$–$H^3)$ 9.5
(VII)	(23.6)	(0.85)	2 055vs, 2 032s,	2.58 (m)	*ca.* 4	H^5–H^8	
			2 022m, 2 013m,	3.52 (d)	1	H^3	
			2 002s, 1 988w,	20.69 (d) [e]	1	OsH_a	$J(H_a$–$H_b)$ 1.5
			1 980m	23.34 (d) [e]	1	OsH_b	
$[Os_3(CO)_9H_2(OC_{10}H_6)]$	24.0	0.85	2 108m, 2 083vs,	1.84 (m)	1		
(VIII)	(23.6)	(0.85)	2 055vs, 2 032m,	2.24 (m)	1	H^5—H^8	
			2 025m, 2 012m,	2.54 (m)	2		
			1 998s, 1 980m	3.14 (d)	1	H^3, H^4	$J(H^3$–$H^4)$ 8.2
				3.73 (d)	1		
				21.54 (d) [e]	1	OsH_a	$J(H_a$–$H_b)$ 1.5
				23.80 (d) [e]	1	OsH_b	
$[Os_3(CO)_9H_2(OC_{10}H_6)]$	24.1	0.90	2 126m, 2 085vs,	2.12 (dd)	1		J 2,2 7.5
(IX)	(23.6)	(0.85)	2 054vs, 2 048vs,	2.5—3.0 (m)	*ca.* 4	H^2—H^7	
			2 042vs, 2 030m,	3.16 (dd)	1		J 3.3, 7.4
			2 015m, 1 998m,	21.05 (s)	1	OsH_a	
			1 972m	24.82 (s)	1	OsH_b	
$[Os_3(CO)_9H_2(OCMe_2C_6H_4)]$	23.25	1.40	2 128m, 2 080s,	2.22 (m)	1	H^3—H^6	
(XI)	(22.25)	(1.25)	2 052 (sh), 2 050s,	3.00 (m)	3		
			2 034s, 2 009m,	8.43 (s)	3	CH_3	
			1 998m, 1 963s	8.59 (s)	3	CH_3	
				22.57 (s)	*ca.* 1	OsH_a	
				25.72 (s)	*ca.* 1	OsH_b	
$[Os_3(CO)_9H_2(OCHMeC_6H_4)]$ [f]			2 129m, 2 081s,	2.20 (m)	1	H^3—H^6	
(XII)			2 053 (sh), 2 047s,	2.95 (m)	3		
			2 035s, 2 009m,	5.27 (q)	1	$C\mathit{H}Me$ [g]	
			1 999m, 1 965s	22.12 (d)	*ca.* 1	OsH_a	$J(H_a$–$H_b)$ 1.2
				25.60 (d)	*ca.* 1	OsH_b	
$[Os_3(CO)_9H_2(OC_6H_3OH)]$ [f]			2 113m, 2 087s,	2.84 (d)	1		J 8.0
(XIII)			2 059s, 2 037ms,	3.28 (d)	1	Ring protons	J 8.0
			2 030ms, 2 016ms,	4.02 (t)	1		J 8.0
			2 005s, 1 990mw,	4.38 (s)	1	OH	
			1 983m	21.15 (s)	1	OsH_a	
				24.02 (s)	1	OsH_b	

[a] Calculated figures are given in parentheses. [b] Recorded in cyclohexane solution; ±1 cm^{-1}. [c] Recorded at 100 MHz at 27 °C in $CDCl_3$ unless stated otherwise; s = singlet, t = triplet, q = quartet, sp = septet, m = multiplet. [d] Characterised by i.r. and mass spectra only. [e] Signals were broad at room temperature, sharpening and resolving at *ca.* –60 °C into doublets. [f] Characterised by i.r., n.m.r., and mass spectra only. [g] The Me doublet expected at τ 8.6 was obscured by absorptions due to hydrocarbon impurities.

chromatographed on silica (preparative layer chromatography) to give 1,1,1,1,2,2,2,3,3,3-*decacarbonyl*-2,3-μ-*hydrido*-2,3-μ-*phenoxo*-triangulo-*triosmium*, $[Os_3(CO)_{10}H(OPh)]$, (V; R = Ph), as yellow crystals (0.275 g, 48%).

Naphth-1-*ol*. A solution of (I) (0.233 g) and recrystallised naphth-1-ol (1.45 g) in sodium-dried xylene (75 cm^3) was heated under reflux for 8.5 h. After removal of the solvent under reduced pressure the brown residue was extracted with toluene and chromatographed on a silica column. A yellow band eluted with toluene was rechromatographed on silica plates eluting slowly with pentane–toluene (5 : 1 v/v). After eluting five times two yellow bands were obtained which gave yellow crystals identified as $[Os_3(CO)_9H_2(OC_{10}H_6)]$, (VIII) (0.023 g, 9%), and its isomer, (IX) (0.086 g, 38%).

Naphth-2-*ol*. A solution of (I) (0.253 g) and recrystallised naphth-2-ol (2.0 g) in sodium-dried xylene (85 cm^3) was heated under reflux for 1.5 h. After removal of the solvent under reduced pressure, chromatography of the residue on a silica column (eluant, toluene) gave a yellow band giving yellow crystals (yield of crude product 0.203 g, 81%). Recrystallisation from dichloromethane–pentane gave $[Os_3(CO)_{10}H(OC_{10}H_7)]$, (V; R = naphth-2-yl), as yellow needles with the same ν(CO) spectrum as that of the crude product.

Benzyl alcohol. A solution of (I) (0.271 g) in xylene (37 cm^3) and benzyl alcohol (13 cm^3) was heated under reflux for 13 h. The solvent and alcohol were removed under reduced pressure and the residue was chromatographed on plates (silica) eluting with light petroleum–toluene (9 : 1 v/v) to give a broad band which gave $[Os_3(CO)_{10}H(OCH_2Ph)]$, (V; R = benzyl), as yellow crystals (0.147 g, 54%).

Methanol. A suspension of (I) (0.408 g) in methanol (35 cm^3) was placed in a glass-lined steel autoclave, degassed, sealed *in vacuo*, and heated at 160—170 °C for 19 h. After cooling, the solution was decanted from unchanged (I) which was retreated with methanol as above. After removal of solvent from the combined methanolic solutions, chromatography of the residual oil on silica gave $[Os_3(CO)_{10}H(OMe)]$ (0.040 g, 10%) and $[Os_3(CO)_{10}(OMe)_2]$ (0.054 g, 13%), spectroscopically identical to previously reported compounds.[1]

Propan-2-*ol*. Compound (I) (0.335 g) and propan-2-ol (30 cm^3) were sealed *in vacuo* in a glass-lined steel autoclave (capacity 100 cm^3) and heated at 145—155 °C for 17 h. After cooling, the solution was decanted from unchanged (I) which was treated twice more with fresh propan-2-ol as above. Preparative layer chromatography (silica) of the propan-2-ol soluble fractions gave $[Os_3(CO)_{10}H(OCHMe_2)]$, (V; R = $CHMe_2$), as yellow crystals (0.155 g, 46%).

1-*Phenylethanol*. A solution of (I) (0.405 g) and 1-phenylethanol (10 cm^3) in xylene (150 cm^3) was heated under reflux for 6 h. After cooling, precipitated (I) was separated and treated as above with fresh alcohol (3 cm^3). After one further treatment the combined reaction mixtures were evaporated and the residue chromatographed on a silica column eluting with toluene. The yellow band was rechromatographed on plates (silica) to give an oil $[Os_3(CO)_{10}H(OCHMePh)]$, (V; R = CHMePh) (0.071 g, 18%), which eventually gave yellow crystals from pentane. Another very minor band was identified as the nonacarbonyl $[Os_3(CO)_9H_2(OCHMeC_6H_4)]$, (XII), as off-white crystals (0.007 g, 2%); however, this was not obtained sufficiently pure for elemental analysis.

2-*Phenylpropan*-2-*ol*. A solution of (I) (0.41 g) and freshly sublimed $PhCMe_2OH$ (0.88 g) in xylene (150 cm^3) was heated under reflux for 8 h and the mixture allowed to cool to room temperature overnight. The solution was decanted from unchanged crystals of (I) which was treated twice more with fresh alcohol as above. The solvent was removed from the combined reaction mixtures and a solution of the residue in diethyl ether was thoroughly washed with water and the solvent removed. Chromatography of the residue (silica plates) gave as the major band compound (XI), $[Os_3(CO)_9H_2(OCMe_2C_6H_4)]$, as off-white crystals (0.026 g, 7%) from pentane. A minor band gave trace quantities of compound (V; R = CMe_2Ph), $[Os_3(CO)_{10}H(OCMe_2Ph)]$, which was characterised by its i.r. and mass spectra only.

ortho-*Dihydroxybenzene*. A solution of (I) (0.316 g) and $C_6H_4(OH\text{-}o)_2$ (1.5 g) in xylene (125 cm^3) was heated under reflux for 12 h. The solvent was removed under reduced pressure, silica and water were added to the resulting oil, and the mixture was shaken for 14 h. The silica was filtered off and dried *in vacuo* and the organometallic component extracted with chloroform. Preparative layer chromatography gave two distinct bands, one of which was identified as $[Os_3(CO)_9H_2(OC_6H_3OH\text{-}o)]$, (XIII), as yellow crystals (0.020 g, 7%).

Action of refluxing Solvents on Decacarbonyl Compounds.—(V; R = Ph). A solution of $[Os_3(CO)_{10}H(OPh)]$ (0.275 g) in n-nonane (100 cm^3) was heated under reflux for 9 h. The solvent was removed under reduced pressure and the residual oil chromatographed (silica) to give $[Os_3(CO)_9H_2(OC_6H_4)]$, (VI), as yellow crystals (0.126 g, 48%).

(V; R = 2-*Naphthyl*). A solution of $[Os_3(CO)_{10}H(OC_{10}H_7)]$ (0.10 g) in nonane (60 cm^3) was heated under reflux for 6.5 h. The brown solution was filtered to remove some brown deposit and, after removal of solvent under reduced pressure, the residue was chromatographed on silica plates using light petroleum–toluene (5 : 1 v/v) as eluant. Two yellow bands gave crystals identified as compound (VII), $[Os_3(CO)_9H_2(OC_{10}H_6)]$ (45%), and starting material (11%).

We thank Johnson, Matthey Ltd. for their generous loan of OsO_4, the S.R.C. for a research studentship (to R. E. K.), the Association of Commonwealth Universities for a Commonwealth Scholarship (to K. A. A.), and the British Council for support (to P. R. S.).

[6/149 *Received, 23rd January*, 1976]