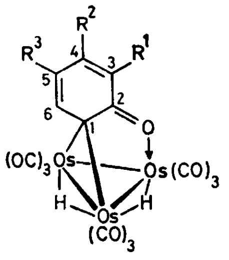
ortho-Metallation Products of Phenol and Aniline with Dodecacarbonyltriosmium. *X*-Ray Crystal Structure of $[Os_3H_2(CO)_9(NHC_6H_3F)]$ †

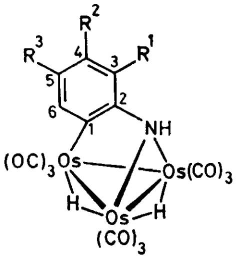
By **Kazi A. Azam, Antony J. Deeming,*** and **Ian P. Rothwell,** Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ
Michael B. Hursthouse* and **J. D. Julius Backer-Dirks,** Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

Comparisons have been made between ^1H and ^{13}C n.m.r. data for complexes $[Os_3H_2(CO)_9(C_6H_4X)]$ (X = O or NH) derived from $[Os_3(CO)_{12}]$ and phenol and aniline respectively, and substituted derivatives of these. These comparisons show that the substituted phenol derivatives all form an isostructural series containing cyclohexadienone ligands as in the previously determined *X*-ray structure of the 2-benzylphenol derivative. In contrast, the aniline derivatives form another isostructural series which contains aromatic ligands. This was confirmed by a single-crystal *X*-ray structure determination for the title compound $[Os_3H_2(CO)_9(NHC_6H_3F)]$ formed from 4-fluoroaniline. The crystals are monoclinic, space group $P2_1/c$, $a = 8.630(3)$, $b = 8.957(1)$, $c = 26.070(3)$ Å, $\beta = 97.99(2)°$, and $Z = 4$. The structure was refined to $R = 0.055$ for 4 003 observed reflections. The ligand NHC_6H_3F bridges two osmium atoms by an amido-group and is bound to the third osmium atom by a σ-Os–C bond at the *ortho*-position; overall it is a four-electron donor. As well as $[Os_3H_2(CO)_9\{C_6H_3(OH)O\text{-}p\}]$, quinol gave the compound $[Os_6H_3(CO)_{19}(C_6H_3O_2)]$ which contains two triangular Os_3 clusters linked by the organic ligand through the oxygen atoms.

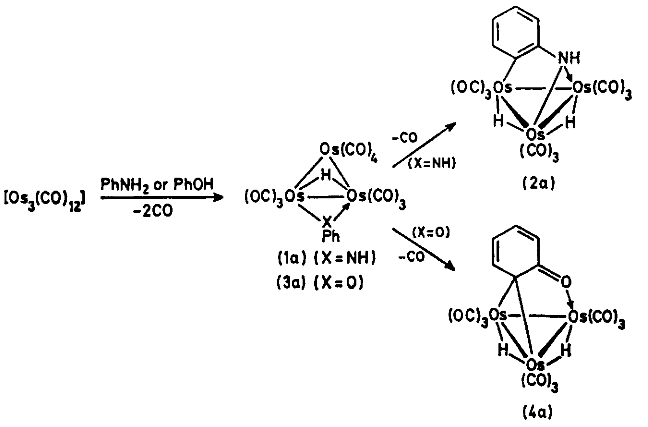
A FEW years ago we reported that aniline reacts with $[Os_3(CO)_{12}]$ to give initially $[Os_3H(CO)_{10}(NHPh)]$ (1a), which decarbonylates to give $[Os_3H_2(CO)_9(C_6H_4NH)]$ complex (2a) (Scheme).[1] Compound (2a) may be regarded as a double oxidative-addition product, the second oxidative addition being an *ortho*-metallation. Later, we reported complexes $[Os_3H(CO)_{10}(OPh)]$ (3a) and $[Os_3H_2(CO)_9(C_6H_4O)]$ (4a) derived similarly from phenol.[2] Complex (4a) is related to (2a) by an isoelectronic replacement of NH by O, and we originally believed compounds (4a) and (2a) to be isostructural. Later, the structure of (4a) became doubtful because of very strong analogies with complexes derived from ketens and aldehydes.[3] The doubts were confirmed by the *X*-ray structure of the compound (4f), corresponding to (4a) but derived from 2-benzylphenol, which clearly showed that a carbon rather than an oxygen atom of the μ_3-ligand was bridging. The phenol molecule had been trapped in its dienone form. Consequently our proposed structure for (2a) needed re-examination and we have now carried out a detailed ^{13}C n.m.r. study of these compounds and an *X*-ray structure determination of complex (2d) derived from 4-fluoroaniline. Our results now clearly establish that phenol and substituted phenols give compounds of type (4) while aniline and substituted anilines give compounds of type (2).



	R^1	R^2	R^3
(4a)	H	H	H
(4b)	Me	Me	H
(4c)	Me	H	Me
(4d)	H	H	F
(4e)	H	H	OH
(4f)	$PhCH_2$	H	H
(4g)	Me_2CH	H	H



	R^1	R^2	R^3
(2a)	H	H	H
(2d)	H	H	F



SCHEME

RESULTS

Phenol Derivatives.—The complexes (4b—g) were synthesised from substituted phenols by direct reaction with $[Os_3(CO)_{12}]$ in essentially the same manner as with phenol,[1] and in certain cases the intermediates $[Os_3H(CO)_{10}(OC_6H_2R^1R^2R^3)]$ (3a) ($R^1 = R^2 = R^3 = H$), (3d) ($R^1 = R^2 = H$; $R^3 = F$), and (3e) ($R^1 = R^2 = H$; $R^3 = OH$) were also isolated (see Experimental section and Table 1). The ν(CO)

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† Nonacarbonyl-(μ_3-5-fluoro-2-iminophenyl)-di-μ-hydrido-*tri-angulo*-triosmium.

TABLE 1

Infrared spectrum and analytical data

Compound	ν(CO) [a]/cm^{-1}	Analysis [b]/%	
		C	H
(2a) [c]	2 118s, 2 084s, 2 058s, 2 043s, 2 033s, 2 012s, 1 996s, 1 984m, 1 980s		
(2d) [c]	2 118s, 2 085s, 2 054s, 2 044s, 2 034s, 2 013s, 1 997s, 1 987m, 1 981s		
(3d)	2 113w, 2 074vs, 2 064m, 2 036w, 2 026vs, 2 008m, 1 992w, 1 988w	20.00 (19.95)	0.50 (0.50)
(3e)	2 112w, 2 072vs, 2 064m, 2 036w, 2 025vs, 2 006m, 1 991w, 1 986w	20.00 (20.00)	0.60 (0.65)
(4a) [d]	2 112m, 2 086s, 2 058s, 2 035s, 2 028s, 2 014m, 2 003s, 1 998w, 1 981m		
(4b)	2 110m, 2 083vs, 2 053vs, 2 030s, 2 024s, 2 011m, 2 000s, 1 984w, 1 978m	22.00 (21.60)	1.05 (1.05)
(4c)	2 110m, 2 084vs, 2 056vs, 2 033s, 2 025s, 2 012m, 2 000s, 1 985w, 1 979m	21.65 (21.60)	1.00 (1.05)
(4d)	2 113m, 2 086vs, 2 058vs, 2 036s, 2 030s, 2 015m, 2 004s, 1 988w, 1 982m	19.40 (19.25)	0.40 (0.55)
(4e)	2 110m, 2 084vs, 2 056vs, 2 034s, 2 025s, 2 013m, 2 002s, 1 986w, 1 980m	19.35 (19.30)	0.55 (0.65)
(4f)	2 112m, 2 086vs, 2 057vs, 2 035s, 2 028s, 2 013m, 2 003s, 1 987sh, 1 980m	26.55 (26.25)	1.20 (1.20)
(4g)	2 112m, 2 086vs, 2 057vs, 2 034s, 2 027s, 2 013m, 2 002s, 1 987sh, 1 980m	22.65 (22.55)	1.20 (1.25)
(5)	2 114w,[e] 2 110m,[f] 2 086vs,[f] 2 074vs,[e] 2 063s,[e] 2 057s,[f] 2 037m,[e,f] 2 024vs,[e] 2 015m,[f] 2 004s,[e,f] 1 992m,[e] 1 989m,[e,f] 1 981m [f]		

[a] Measured in cyclohexane solution. [b] Calculated figures in parentheses. [c] See ref. 1. [d] See ref. 2. [e] Peaks assigned to $Os_3H(CO)_{10}$ group. [f] Peaks assigned to $Os_2H_2(CO)_9$ group.

TABLE 2

Hydrogen-1 n.m.r. data

Compound	Chemical shifts [a]				
	3-H or R	4-H or Me	5-H or Me	6-H	Os-H
(2a) [b]	6.51m	6.51m	6.51m	7.49dd (3.2, 5.1)	−14.03s −14.47s
(2d) [c]	6.56dd (8.6, 5.2)	6.18m		7.15dd (2.8, 8.6)	−14.39s
(4a) [d]	6.42d	7.69ddd	6.04ddd	7.24dd	−11.66d −14.06d (1.5)
(4b)	1.97s	1.86s	5.89d (8.7)	7.00d (8.7)	−11.77d −14.14d (1.8)
(4c)	2.01s	7.38s (br)	2.04s	6.81s (br)	−11.68d −14.00d (1.8)
(4d)	6.40dd (10.0, 4.5)	7.59ddd (10.0, 3.5, 7.9)		6.86dd (3.5, 9.0)	−11.41d −13.85d (1.9)
(4e) [c]	6.41d (9.5)	7.59dd (9.5, 3.0)		6.75d (3.0)	−11.44d −13.67d (1.6)
(4f)	3.72s 6.2m	6.2m	6.00t (6.4)	7.54d (6.4)	−11.90d −14.76d (2.0)
(4g)	3.00m 0.96d (7.2)	7.15dd (8.0, 1.8)	6.02t (8.0)	7.54dd (8.0, 1.8)	−11.66d −14.02d (2.0)
(3d)	6.87dd (9.5, 7.3)			6.40dd (9.5, 4.3)	−12.13s
(3e)	6.64 (9.0)			6.35d (9.0)	−12.21s
(5)	6.34d (9.0)	7.07dd (9.0, 3.5)		6.33d (3.5)	−12.24s −11.41d −13.77d (1.8)

[a] Recorded in $CDCl_3$ at 27 °C; low temperatures for hydride doublets; coupling (Hz) in parentheses, those to F last. [b] Hydride signals at −50 °C (see ref. 1). [c] In $(CD_3)_2CO$. [d] Ref. 2; J_{34} 7.0, J_{35} 1.8, J_{45} 8.5, J_{46} 1.5, J_{56} 7.5 Hz.

absorptions for complexes (4) are all extremely similar both in intensities and frequencies, which can only mean that they are of the same structural type as found for (4f) by *X*-ray diffraction (Figure 1).[3] Of course, structure (A) (Figure 2) can be ruled out, but it is not so immediately clear whether the bonding description (B) or (C) is most appropriate. The possibility of an electron-deficient phenyl bridge as in (C) is indicated by the structure of $[Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)]$, for example.[4] However, bond length considerations totally support the dienone description (B). Thus there is an alternation of bond lengths around the diene part of the ring, one C–C bond of the ring is essentially single (1.52 Å) and the C–O length (1.28 Å) indicates a multiple bond.

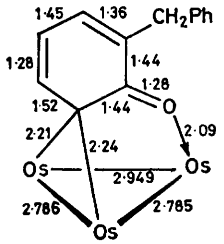
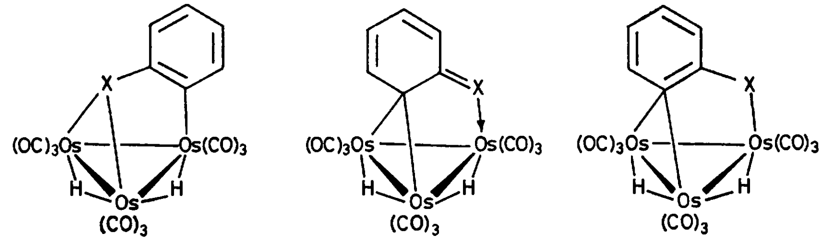


FIGURE 1 Main features of the structure of $[Os_3H_2(CO)_9\{C_6H_3(CH_2Ph)O\}]$ (4f) (standard deviations: Os–Os 0.001, Os–C and Os–O 0.01, C–C 0.01 Å)



(A) (B) (C)

FIGURE 2 Structures considered for compounds (2) (X = NH) and (4) (X = O)

We have collected ^1H and ^{13}C n.m.r. data for complexes (4) hoping to derive criteria for assigning structure (Tables 2 and 3). The ^{13}C spectral assignments for compound (4a) were made by considering the chemical shifts brought about by methyl substitution in forming (4b) and (4c), together with the loss in intensity for the ring-carbon signals when H is replaced by Me as a substituent. Two weak signals at low field for each compound (4) were assigned to C^1 and C^2 but we could not tell which was which. We did not assign metal ^{13}CO signals for (4) but those for the phenoxo-complexes (3) are given in Table 3 and agree essentially with those for other complexes of type $[Os_3(CO)_{10}(\mu\text{-X})(\mu\text{-Y})]$.[5]

Aniline Derivatives.—Compound (2d) derived from 4-fluoroaniline was synthesised [1] and data compared with the unsubstituted compound (2a) and the phenol analogues (4a) and (4d). It is quite clear that the ^1H and ^{13}C n.m.r. data for (2a) and (4a) and for (2d) and (4d) do not correspond. Most significantly, the influence of the introduced fluoro-substituent is quite different in each case. The usual ^{13}C shifts on replacing a hydrogen atom at C^5 by a fluorine atom in simple substituted benzenes are given in Table 4. Fluorine substitution in compound (2a) gives the shifts expected for an aromatic ring, with those of the two *ortho*-carbons (positions 4 and 6) approximately the same. On the other hand, F-substitution in (4a) gives quite different shifts at the two *ortho*-positions. These substitution shifts more than anything else suggest that, while the μ_3-C_6H_4O ligand has essentially localised double and single bonds, the μ_3-C_6H_4NH ligand remains aromatic.

To confirm this conclusion, a single-crystal *X*-ray structure determination of an aniline derivative was carried out.

TABLE 3

Carbon-13 n.m.r. data [a]

Compound	Ring-carbon shifts [b]						CO ligand shifts [c]
	1	2	3	4	5	6	
(2a)	{178.1	176.6}	114.0	{122.0	123.5}	144.1	
(2d) [d]	{178.5	173.5} (1.4)	114.8 (8.1)	108.8 (23.1)	158.5 (243.5)	130.3 (18.7)	
(4a)	{178.3	175.0}	124.1	138.6	116.5	166.1	
(4b) [d]	{176.6	176.0}	130.9	148.4	120.3	162.8	
(4c) [d]	{176.2	175.9}	132.9	141.1	124.8	161.9	
(4d) [d]	*e*	*e*	125.2 (7.5)	129.7 (27.7)	*e*	145.0 (15.1)	
(3a)	165.9	120.2	129.9	122.0	129.9	120.2	181.3(1), 179.9(1), 175.6(2), 175.1(2), 174.1(2), 171.1(2)
(3d)	162.9	121.0 (8.0)	116.2 (23.4)	158.3 (239.7)	116.2 (23.4)	121.0 (8.0)	182.1(1), 180.4(1), 176.1(2), 175.4(2), 174.5(2), 171.7(2)
(3e)	161.4	120.3	116.0	150.6	116.0	120.3	181.6(1), 180.0(1), 175.8(2), 175.1(2), 174.1(2), 171.4(2)
(6) [f]	169.6	118.0	129.8	122.4	129.8	118.0	180.8(2), 178.9(4), 176.9(2), 171.0(2)

[a] Recorded in $CDCl_3$ unless stated otherwise. [b] Values in braces indicate that precise assignment was not made; *J*(FC) (Hz) in parentheses. [c] Number of carbon atoms given in parentheses; recorded in presence of $[Cr(acac)_3]$ (acac = acetylacetonate). [d] Recorded in CD_2Cl_2. [e] Not assigned. [f] $[Os_3(CO)_{10}(OPh)_2]$, formed as a by-product in the reaction of phenol with $[Os_3(CO)_{12}]$, and included for comparison with (3a).

Compounds (2) are of the same structural type since the ν(CO) spectra (at *ca.* 2 000 cm^{-1}) are virtually identical and since (2d) gave better crystals this was chosen for study.

TABLE 4

Carbon-13 n.m.r. shifts on substituting H by F in compounds (2a), (3a), and (4a) [a]

Compound (solvent)	*ipso*	*ortho*	*meta*	*para*
Substituted benzenes [b] (CCl_4)	+34.8	−12.9	+1.4	−4.5
(2d) ($CDCl_3$)	+35.0	−13.2, −13.8	+0.8, +0.4	−3.2
	{+36.5	−14.7, −13.8	+0.8, +0.4	−3.2 } [c]
(3d) ($CDCl_3$)	+36.3	−13.7	+0.8	−3.0
(4d) ($CDCl_3$)	*d*	−9.0, −21.1	+1.1, *d*	*d*

[a] Positive values are downfield shifts. [b] See ref. 6. [c] Figures in braces are based on another less likely assignment of C^4 and C^5 for (2a). [d] Not assigned.

The molecular structure is shown in Figure 3 and the atomic co-ordinates in Table 5; bond lengths and bond angles are given in Tables 6 and 7 respectively. Supplementary Publication No. SUP 23014 (19 pp.) * contains tables of anisotropic temperature factors and observed and calculated structure factors.

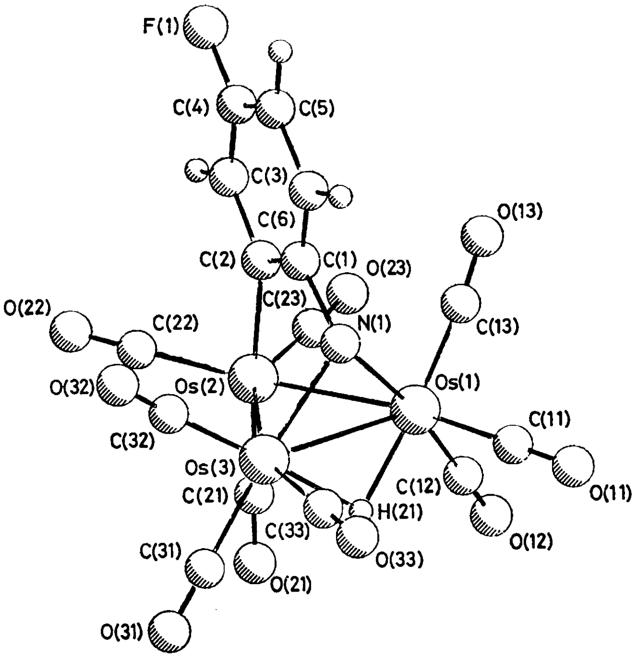
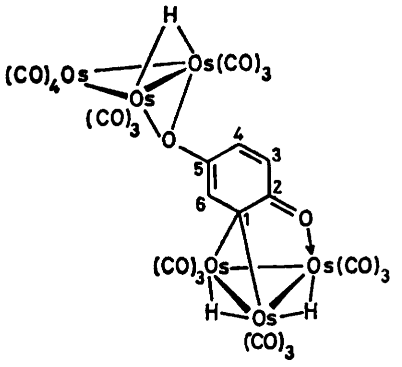


FIGURE 3 Molecular structure of $[Os_3H_2(CO)_9(NHC_6H_3F)]$ (2d). The hydrogen atom H(21) located experimentally has been included

The overall features of the structure are consistent with arrangement (A) in Figure 2. The nitrogen atom is almost equidistant from Os(1) and Os(3) while the C_6 ring is σ-bonded through C(2) to Os(2). The ring is clearly aromatic with C–C distances in the range 1.35(2)—1.42(2) Å which contrasts with the wider range, 1.28(1)—1.52(1) Å, for the C_6 ring in compound (4f), Figure 1. There is an approximate mirror plane through the $Os_3(NC_6H_3F)$ group of atoms, except that bond Os(2)–Os(3) (2.996 Å) is longer than Os(1)–Os(2) (2.810 Å). This asymmetry is attributed largely to the hydride ligand positions. One of the two hydride ligands appeared in the later stages of the analysis and although there is considerable uncertainty in its position, it is clearly shown to bridge Os(1) and Os(3) on the opposite side of the Os_3 ring to N(1). The Os(3)–H and Os(1)–H lengths of 1.9(1) and 1.8(1) Å are not significantly different. The other hydride ligand (the observed diamagnetism, and ^1H n.m.r. spectra require there to be two hydrido-ligands) is deduced to be bridging Os(2) and Os(3). The Os(2)–Os(3) bond is significantly longer than the Os(1)–Os(2) bond and the Os–Os–C(carbonyl) angles associated with it are also larger. The four such angles for Os(2)–Os(3) that would be affected by the presence of a bridging hydride are 98.1, 108.9, 90.7, and 115.3° compared with the corresponding angles of 94.3, 90.1, 92.1, and 90.8° that are associated with Os(1)–Os(2). More space is created for the hydride by opening up these angles and since the two larger angles (108.9 and 115.3°) are for carbonyl groups on the same side of the Os_3 triangle as the organic ligand we assume the bridging hydride lies close to the plane of the metal atoms rather than much below this plane as does the other hydride ligand.

Quinol Complexes.—Quinol gave complexes (3e) and (4e) quite analogous to the corresponding phenol derivatives. However, an additional yellow band was obtained on t.l.c. of the product mixture from $[Os_3(CO)_{12}]$ and quinol. We initially thought this was a mixture of a deca- and a nonacarbonyl of type (3) and (4) since the i.r. spectrum around 2 000 cm^{-1} can be almost exactly reproduced by a combination of a spectrum of (3e) with that of (4e) (Table 1). The easy movement of the band on the t.l.c. plate (SiO_2) indicated the lack of free OH groups and careful division of the band into fractions failed to give any separation. We conclude that it is the single pure complex $[Os_6H_3(CO)_{19}(C_6H_3O_2)]$ (5). The ^1H n.m.r. spectrum is also totally consistent with this, showing three equal intensity hydride signals (δ −11.41 d, −12.24 s, −13.77 d) which compare with the hydride signals for (3e) (δ −12.21 s) and (4e) (δ −11.44 d and −13.67 d). In (5) as well as in (4e) the sharp hydride doublets observed below −20 °C give broad signals at 35 °C. We presume that (5) is formed by the OH group of complex (4e) reacting with $[Os_3(CO)_{12}]$ present in the reaction mixture, and by doing so successfully competes with the excess of quinol also present. No evidence for



(5)

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 5

Atomic co-ordinates (× 10^4) for (2d), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Os(1)	7 231(1)	4 938(1)	1 102
Os(2)	6 078(1)	2 101(1)	1 311
Os(3)	9 013(1)	2 509(1)	833
N(1)	9 257(10)	3 854(10)	1 505(3)
F(1)	8 287(12)	1 581(11)	3 396(3)
C(1)	9 029(14)	3 185(12)	1 999(4)
C(2)	7 628(13)	2 405(11)	2 011(4)
C(3)	7 440(15)	1 864(14)	2 506(4)
C(4)	8 527(18)	2 107(14)	2 933(5)
C(5)	9 854(17)	2 869(15)	2 901(5)
C(6)	10 114(16)	3 435(14)	2 413(4)
C(11)	8 274(17)	6 672(14)	883(4)
C(12)	5 339(15)	5 572(15)	704(5)
C(13)	6 602(15)	5 683(15)	1 721(5)
C(21)	4 847(17)	1 978(16)	627(6)
C(22)	5 655(20)	99(16)	1 503(7)
C(23)	4 415(17)	2 970(15)	1 601(6)
C(31)	8 386(16)	1 419(17)	200(6)
C(32)	10 517(17)	1 033(17)	1 117(5)
C(33)	10 527(16)	3 622(18)	535(5)
O(11)	8 815(14)	7 732(11)	742(4)
O(12)	4 200(12)	5 942(14)	466(4)
O(13)	6 279(13)	6 042(12)	2 117(4)
O(21)	4 180(14)	1 915(14)	226(5)
O(22)	5 332(16)	−1 043(13)	1 621(6)
O(23)	3 441(13)	3 498(14)	1 799(5)
O(31)	8 079(15)	777(16)	−167(5)
O(32)	11 471(14)	251(12)	1 296(4)
O(33)	11 441(14)	4 274(17)	363(4)
H(3)	6 399(15)	1 235(14)	2 551(4)
H(5)	10 704(17)	3 046(15)	3 240(5)
H(6)	11 163(16)	4 057(14)	2 374(4)
H(21)	7 688(111)	4 026(111)	512(34)

$[Os_6H_2(CO)_{20}(C_6H_4O_2)]$, which is not *ortho*-metallated, and $[Os_6H_4(CO)_{18}(C_4H_2O_2)]$, which is doubly *ortho*-metallated, was found. Complex (5) does not decarbonylate under the same conditions as (3e) since the double bonds are in the wrong positions to allow $Os_3(CO)_9$ groups to be attached on each side of the C_6 ring.

DISCUSSION

While the replacement of O in complexes (4) by NH leads to the adoption of quite a different structure, the various other substitutions we have carried out at carbon have no such effect. The relative tendencies of O and NH to bridge osmium atoms seem to control the selection of structure, the most stable one being adopted in each case.

TABLE 6

Bond lengths (Å) in (2d)

Os(2)–Os(1)	2.810(4)	C(1)–N(1)	1.459(14)
Os(3)–Os(1)	2.808(4)	C(4)–F(1)	1.337(14)
N(1)–Os(1)	2.143(11)	C(2)–C(1)	1.400(17)
C(11)–Os(1)	1.921(16)	C(6)–C(1)	1.345(16)
C(12)–Os(1)	1.895(14)	C(3)–C(2)	1.410(15)
C(13)–Os(1)	1.895(15)	C(4)–C(3)	1.370(19)
H(21)–Os(1)	1.831(96)	C(5)–C(4)	1.347(21)
Os(3)–Os(2)	2.996(4)	C(6)–C(5)	1.415(18)
C(2)–Os(2)	2.125(13)	O(11)–C(11)	1.141(16)
C(21)–Os(2)	1.947(17)	O(12)–C(12)	1.138(15)
C(22)–Os(2)	1.910(17)	O(13)–C(13)	1.152(16)
C(23)–Os(2)	1.881(17)	O(21)–C(21)	1.123(17)
N(1)–Os(3)	2.112(10)	O(22)–C(22)	1.115(18)
C(31)–Os(3)	1.929(16)	O(23)–C(23)	1.148(18)
C(32)–Os(3)	1.927(17)	O(31)–C(31)	1.117(16)
C(33)–Os(3)	1.894(16)	O(32)–C(32)	1.130(17)
H(21)–Os(3)	1.894(96)	O(33)–C(33)	1.124(17)

We hoped to study the dynamic nature of complexes (4) by introducing benzyl and isopropyl substituents. The asymmetry resulting from hydride locations [asymmetry apparent in the solid-state structures of (4f) and (2d)] should render the $PhCH_2$ and $(CH_3)_2CH$ hydrogen atoms diastereotopic. However, we observed a ^1H n.m.r. singlet for the methylene group over a range of temperatures. The $(CH_3)_2CH$ hydrogens of (4g) do give two doublets between +10 and −30 °C, but the separation is only 0.01 p.p.m. at +10 °C and is not resolved above this. Most likely these groups are too far removed from the cluster to be sensitive enough probes for asymmetry. Hydride exchange occurs in all complexes (4) at rates essentially insensitive to the ring substituents since all show similarly broad hydride signals at 30 °C which sharpen into doublets at lower temperatures. The hydride exchange mechanism is not known but, as well as a hydride shift between metal-bridging sites, movement of the μ_3-ligand is an alternative mechanism. Thus the interconversion of the aromatic form (A) and the non-aromatic form (B) (Figure 2) would lead to ligand rotation which would of course lead to hydride exchange. It is unfortunate that we have not yet

TABLE 7

Bond angles (°) in (2d)

Os(3)–Os(1)–Os(2)	64.4(1)	C(32)–Os(3)–Os(2)	108.6(5)
N(1)–Os(1)–Os(2)	77.4(3)	C(33)–Os(3)–Os(2)	155.0(5)
C(11)–Os(1)–Os(2)	169.1(4)	H(21)–Os(3)–Os(2)	77.2(31)
C(12)–Os(1)–Os(2)	94.3(5)	C(31)–Os(3)–N(1)	169.1(5)
C(13)–Os(1)–Os(2)	90.1(5)	C(32)–Os(3)–N(1)	95.1(5)
H(21)–Os(1)–Os(2)	83.3(32)	C(33)–Os(3)–N(1)	92.6(6)
N(1)–Os(1)–Os(3)	48.2(2)	H(21)–Os(3)–N(1)	86.7(29)
C(11)–Os(1)–Os(3)	104.9(5)	C(32)–Os(3)–C(31)	94.3(7)
C(12)–Os(1)–Os(3)	123.7(5)	C(33)–Os(3)–C(31)	92.4(7)
C(13)–Os(1)–Os(3)	135.8(4)	H(21)–Os(3)–C(31)	84.5(29)
H(21)–Os(1)–Os(3)	41.9(29)	C(33)–Os(3)–C(32)	93.0(7)
C(11)–Os(1)–N(1)	97.3(6)	H(21)–Os(3)–C(32)	174.2(30)
C(12)–Os(1)–N(1)	170.4(5)	H(21)–Os(3)–C(33)	81.4(32)
C(13)–Os(1)–N(1)	93.0(5)	Os(3)–N(1)–Os(1)	82.6(4)
H(21)–Os(1)–N(1)	87.3(30)	C(1)–N(1)–Os(1)	114.7(8)
C(12)–Os(1)–C(11)	90.0(6)	C(1)–N(1)–Os(3)	119.2(8)
C(13)–Os(1)–C(11)	99.8(6)	C(2)–C(1)–N(1)	116.5(10)
H(21)–Os(1)–C(11)	87.0(32)	C(6)–C(1)–N(1)	118.4(11)
C(13)–Os(1)–C(12)	91.9(7)	C(6)–C(1)–C(2)	125.0(12)
H(21)–Os(1)–C(12)	86.8(30)	C(1)–C(2)–Os(2)	119.2(9)
H(21)–Os(1)–C(13)	173.1(31)	C(3)–C(2)–Os(2)	127.1(10)
Os(3)–Os(2)–Os(1)	57.7(1)	C(3)–C(2)–C(1)	113.6(11)
C(2)–Os(2)–Os(1)	81.5(4)	H(3)–C(3)–C(2)	118.8(8)
C(21)–Os(2)–Os(1)	92.1(5)	C(4)–C(3)–C(2)	122.5(13)
C(22)–Os(2)–Os(1)	170.2(5)	H(3)–C(3)–C(4)	118.7(9)
C(23)–Os(2)–Os(1)	90.8(5)	C(3)–C(4)–F(1)	120.2(14)
C(2)–Os(2)–Os(3)	82.7(4)	C(5)–C(4)–F(1)	118.4(14)
C(21)–Os(2)–Os(3)	90.7(5)	C(5)–C(4)–C(3)	121.4(13)
C(22)–Os(2)–Os(3)	115.3(6)	H(5)–C(5)–C(4)	120.6(9)
C(23)–Os(2)–Os(3)	148.5(4)	C(6)–C(5)–C(4)	118.8(13)
C(21)–Os(2)–C(2)	172.6(5)	H(5)–C(5)–C(6)	120.6(9)
C(22)–Os(2)–C(2)	90.9(7)	C(5)–C(6)–C(1)	118.8(14)
C(23)–Os(2)–C(2)	91.5(6)	H(6)–C(6)–C(1)	120.6(8)
C(22)–Os(2)–C(21)	95.0(8)	H(6)–C(6)–C(5)	120.7(9)
C(23)–Os(2)–C(21)	92.4(7)	O(11)–C(11)–Os(1)	176.2(13)
C(23)–Os(2)–C(22)	95.7(8)	O(12)–C(12)–Os(1)	179.5(10)
Os(2)–Os(3)–Os(1)	57.8(1)	O(13)–C(13)–Os(1)	174.7(11)
N(1)–Os(3)–Os(1)	49.2(2)	O(21)–C(21)–Os(2)	177.8(14)
C(31)–Os(3)–Os(1)	120.5(5)	O(22)–C(22)–Os(2)	176.2(16)
C(32)–Os(3)–Os(1)	143.0(3)	O(23)–C(23)–Os(2)	176.9(14)
C(33)–Os(3)–Os(1)	97.3(6)	O(31)–C(31)–Os(3)	177.5(13)
H(21)–Os(3)–Os(1)	40.2(28)	O(32)–C(32)–Os(3)	175.0(13)
N(1)–Os(3)–Os(2)	73.6(3)	O(33)–C(33)–Os(3)	179.1(13)
C(31)–Os(3)–Os(2)	98.1(5)	Os(3)–H(21)–Os(1)	97.8(41)

confirmed that this is the mechanism because activation energies would give a direct estimate of the maximum energy differences between structures (A) and (B). Incidentally, the hydride ^{1}H n.m.r. signals of $[Os_3H_2(CO)_9(C_6H_8O)]$, the tetrahydro-form of (4a) derived from cyclohexanone,[7] are sharply resolved doublets even at 30 °C. The slower exchange rate in this case would result from the form analogous to (A) having no aromatic stabilisation. We hope to carry out experiments to test these ideas.

EXPERIMENTAL

Syntheses.—Complexes (4a), (2a), and (2d) were prepared as described earlier.[1,2] Complexes (3) and (4) were obtained as air-stable yellow crystals by direct reaction of approximately equal masses of $[Os_3(CO)_{12}]$ and the appropriate substituted phenol in refluxing nonane or xylene. A good yield of the decacarbonyl complex (3d) (80%) was obtained after 6.5 h in refluxing nonane together with a little (4e) which increased in yield on refluxing for longer. Treatment of $[Os_3(CO)_{12}]$ (0.25 g) with quinol (0.5 g) in refluxing nonane for 4.5 h gave mainly (3e) (72%) with a little (4e) and (5). More (4e) was obtained from (3e) by extended reflux in nonane. Complexes (4b) (60%) and (4c) (75%) were obtained from refluxing nonane after 11 and 8 h respectively. Complexes (4f) (26%) and (4g) (28%) were obtained after 13 and 16 h respectively in refluxing xylene. Reactions were carried out under nitrogen but work-up, in particular t.l.c. (SiO_2) separations, were carried out in air.

X-*Ray Structure Determination of* $[Os_3H_2(CO)_9(NHC_6H_3F)]$ (2d).—*Crystal data*. $C_{15}H_6FNO_9Os_3$, $M = 933.81$, Monoclinic, $a = 8.630(3)$ $b = 8.957(1)$, $c = 26.070(3)$ Å, $\beta = 97.99(2)°$, $U = 1\,995.5$ Å^3, space group $P2_1/c$, $D_m > 2.96$ g cm^{-3}, $Z = 4$, $D_c = 3.11$ g cm^{-3}, $F(000) = 1\,647.74$, μ(Mo-K_α) = 183.61 cm^{-1}.

Data collection. CAD4 Diffractometer, ω—2θ scan, ω scan width = 0.8 + 0.15 tan θ, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), $1.50 < \theta < 30.0°$, $h, k, \pm l$; crystal morphology and size: $\{0\ \bar{1}\ 2\}$ 0.0625, $\{0\ 2\ \bar{5}\}$ 0.0625, $\{0\ \bar{1}\ \bar{1}\}$ 0.1125, $\{0\ 1\ 2\}$ 0.1125, $\{\bar{1}\ 0\ 2\}$ 0.225, $\{1\ 0\ \bar{2}\}$ 0.225 mm (distances from the volume centre to the face). Total unique data = 5 758, observed = 4 003 $[I > 3\sigma(I)]$, absorption correction applied.

Structure solution and refinement. Direct methods (Os positions) + difference syntheses; all non-H atoms anisotropic, H atoms on ring fixed in idealised positions; weighting scheme $w = 1/\{\sigma^2(F_o) + 0.0004\,F_o{}^2\}$: $R = 0.055$, $R' = 0.0445$. Programs, computers, and scattering factors were as in ref. 8.

We thank the S.R.C. and the Association of Commonwealth Universities for studentships (to I. P. R. and K. A. A.) and for other support and Johnson Matthey Ltd. for a loan of OsO_4.

[1/223 *Received*, 11*th February*, 1981]

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