Interconversion of μ_2-Phenolato and μ_3-Oxodienediyl Ligands in Triosmium Clusters: *X*-Ray Crystal Structure of 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2:2,3-di-μ-hydrido-(μ_3-3-benzyl-2-oxocyclohexa-3,5-diene-1,1-diyl-1,2-C^1-3-*O*)-*triangulo*-triosmium(3*Os*–*Os*)

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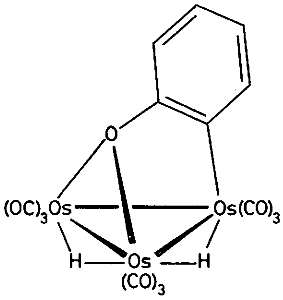
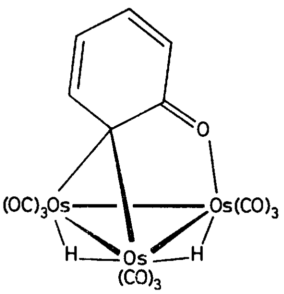
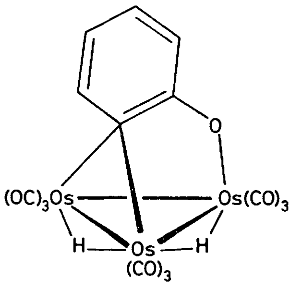
Summary The *X*-ray crystal structure of $[Os_3(CO)_9H_2(\mu_3\text{-}OC_6H_3CH_2Ph)]$, derived from $[Os_3(CO)_{12}]$ and 2-benzylphenol, shows the complex to contain what is best considered as the non-aromatic μ_3-3-benzyl-2-oxocyclohexa-3,5-diene-1,1-diyl ligand and, although we have found no ligand reactivity consistent with this, the ^{13}C n.m.r. spectra of the unsubstituted $[Os_3(CO)_{10}H_2(\mu_3\text{-}OC_6H_4)]$ and the related $[Os_3(CO)_{10}H_2(\mu_3\text{-}NHC_6H_4)]$ are inconsistent with aromatic descriptions for the carbon rings of both compounds.



(2a)

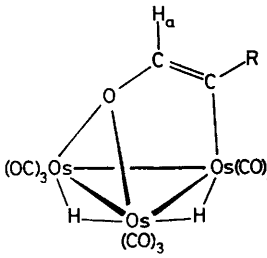


(2b)

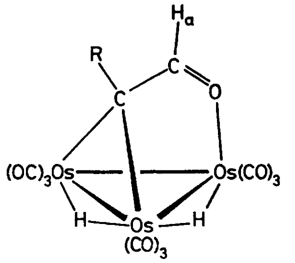


(2c)

Phenol reacts with $[Os_3(CO)_{12}]$ to give the μ_2-phenolato complex $[Os_3(CO)_{10}H(\mu_2\text{-}OPh)]$ (**1**) which loses CO on thermolysis at 150 °C in refluxing nonane to give $[Os_3(CO)_9H_2(OC_6H_4)]$ (**2**) formed by transfer of a hydrogen atom from the 2-position of the benzene ring to the metal atoms.[1] Compound (**2**) was characterised by i.r., ^1H n.m.r., and mass spectra and elemental analysis and we proposed structure (**2a**) containing the 2-metallated μ_3-OC_6H_4 ligand and retaining the *O*-bridge as in (**1**). We have since shown that direct reaction of $[Os_3(CO)_{12}]$ with phenol at 170—185 °C gives $[Os_3(CO)_{10}(\mu_2\text{-}OPh)_2]$ (**3**) as well as (**1**) and (**2**) and that 2-isopropyl- or 2-benzyl-phenol gives the substituted analogue of (**2**). Two methyl doublets are obtained in the ^1H n.m.r. spectrum (< 10 °C) of the Me_2CH-substituted compound consistent with there being no plane of symmetry though the C_6 ring (the expected AB quartet for the $PhCH_2$ derivative is unresolved). This would support the asymmetric hydride arrangement as shown in (**2a**). We have noted the close spectral similarity between (**2**) and complexes $[Os_3(CO)_9H_2(RC{\cdot}CH{\cdot}O)]$ (**4**)[2] and suggested structure (**4a**) for these related to our proposed structure (**2a**). However, a low field ^1H n.m.r. shift for H_a (δ 10—11·6 p.p.m. depending on R) would be anomalous for structure (**4a**) but would be expected for the formyl description (**4b**). An *X*-ray analysis of the benzyl-substituted derivative of (**2**) $[Os_3(CO)_9H_2(OC_6H_3CH_2Ph\text{-}3)]$ was undertaken to resolve doubts about the structure of (**2**) presented by this observation.



(4a)



(4b)

Crystal data: $C_{22}H_{12}O_{10}Os_3$, $M = 1006{\cdot}9$, monoclinic, $a = 8{\cdot}814(2)$, $b = 10{\cdot}830(2)$, $c = 25{\cdot}69(3)$ Å, $\beta = 92{\cdot}81(2)^\circ$, $U = 2450$ Å^3, $Z = 4$, $D_c = 2{\cdot}72$, $\mu(\text{Mo-}K_\alpha) = 149{\cdot}4\ \text{cm}^{-1}$, space group $P2_1/c$. Intensity data were recorded using a Nonius CAD4 diffractometer with Mo-K_α radiation. Of the 5337 intensities recorded, 4275 satisfied the criterion $I > 1{\cdot}5\sigma(I)$. The structure was solved by direct methods (3 Os atoms), developed *via* successive electron density synthesis and refined by least-squares. The final *R* value is 0·0515 (all atoms anisotropic, data corrected for absorption).†

The molecular structure is shown in the Figure. The cluster contains the μ_3-$OC_6H_3CH_2Ph$ ligand as expected but a carbon rather than an oxygen atom is bridging so that bonding description (**2b**) or (**2c**) is appropriate and not (**2a**) as originally proposed. The metal-bonded hydride ligands were not located but are best positioned as bridging Os-1–Os-2 and Os-2–Os-3 on the basis of commonly employed criteria. Thus metal–metal bond lengths and Os–Os–C (equatorial CO) angles are larger for these Os–Os interactions than for the Os-1–Os-3 interaction. The Os-2–Os-3 length of 2·79 Å is shorter than that for Os-1–Os-2 because the bond lengthening effect of the bridging hydride is counteracted by an opposite effect of the Os_2C ring as found in related molecules.[3] Neglecting the asymmetry resulting from the hydride positions there is an approximate plane of symmetry coincident with the plane of the C_6 ring. Considering the aromatic description (**2c**) with 'electron-deficient' Os–C bonding as found for the μ_2-Ph ligand in $[Os_3(CO)_8(PPh_2)(PPhC_6H_4)(Ph)]$,[4] the ligand plane is orthogonal to the carbon bridged Os–Os axis in both compounds and the Os–C(phenyl)–Os angle of 85° corresponds with the angle of 77° in our compound. However, the 2-oxocyclohexa-3,5-diene-1,1-diyl description for the ligand (**2b**) is supported by the C–O bond length of 1·29 Å and the distribution of C–C distances in the C_6 ring.

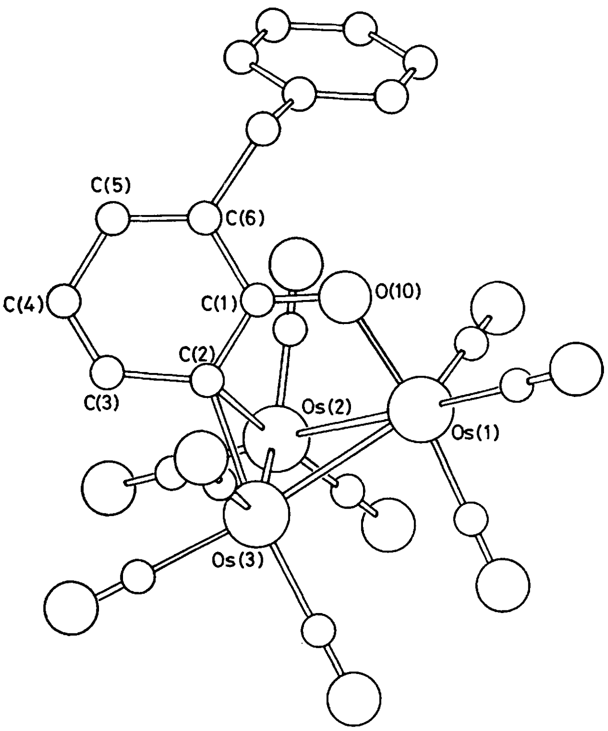


FIGURE. A single molecule of $[Os_3(CO)_9H_2(OC_6H_3CH_2Ph)]$. Some important bond lengths are: Os(1)–Os(2), 2·949(1); Os(1)–Os(3), 2·785(1); Os(2)–Os(3), 2·786(1); Os(1)–O(10), 2·09(1); O(10)–C(1), 1·28(1); C(1)–C(2), 1·44(2); C(2)–C(3), 1·52(2); C(3)–C(4), 1·28(2); C(4)–C(5), 1·45(2); C(5)–C(6), 1·36(2); C(6)–C(1), 1·44(2); Os(2)–C(2), 2·21(1); Os(3)–C(2), 2·24(1) Å

Hoping to establish whether the compound reacts as (**2b**) or (**2c**) we attempted to displace the ketonic function from Os-3 by reaction of (**2**) with CO (atmospheric pressure, in a sealed glass tube in nonane at 146 °C) but this did not give $[Os_3(CO)_{10}H_2(\mu_2\text{-}C_6H_4O)]$, analogous to $[Os_3(CO)_{10}H_2(\mu_2\text{-}CH_2)]$,[5] but rather its oxygen-bonded isomer (**1**). Attempts to distinguish (**2b**) from (**2c**) by adding the dienophile $Fe(CO)_3$ or the trienophile $Mo(CO)_3$ to (**2**) by reaction with the appropriate precursors $[Fe(CO)_3\{(PhCH{:}CH)_2CO\}]$ or $[Mo(CO)_3(MeCN)_3]$ were unsuccessful, the precursors decomposing while leaving (**2**) unchanged. A similar lack of reactivity was found with the dienophile maleic anhydride ($CDCl_3$ solution, 70 °C, 9 h).

Carbon-13 n.m.r. data for (**2**) show quite large downfield shifts for the ring carbon atoms compared with (**3**) [δ(downfield from Me_4Si; $CDCl_3$): compound (**3**): 169·62 (C-1), 117·98 (C-2,C-6), 129·78 (C-3,C-5), and 122·38 (C-4), and compound (**2**): 178·29, 174·98 (C-1,C-2), 166·07 (C-6), 138·61 (C-4), 124·13 (C-3), and 116·53 (C-5) p.p.m. (probable assignments)]. It is not possible to use these data in any simple way to differentiate (**2b**) from (**2c**). The nitrogen

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

analogue of (**2**), $[Os_3(CO)_9H_2(HNC_6H_4)]$,[6] gives smaller downfield shifts on *ortho*-metallation [δ(downfield from Me_4Si; $CDCl_3$): 178·08, 176·61 (C-1,C-2), 144·12 (C-6), 123·49, 122·03 (C-4,C-5), and 114·00 (C-3) p.p.m.]. The sensitivity of the C-4 and C-6 shifts to replacement of O by NH is very much greater than that expected for an aromatic system and possibly indicates that the relative contributions of forms such as (**2b**) and (**2c**) changes or indeed that there is a complete change of structure on making this replacement.

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