Intermediates in the Conversion of $[Os_3(CO)_{11}(PRPh_2)]$ (R = Me or Ph) into $[Os_3(\mu_3\text{-}C_6H_4)(\mu_3\text{-}PR)(CO)_9]$: Crystal and Molecular Structures of $[Os_3(\mu\text{-}H)(\mu_3\text{-}C_6H_4PMePh\text{-}o)(CO)_9]$ and $[Os_3(\mu_3\text{-}C_6H_4PMe\text{-}o)(CO)_{10}]$ *

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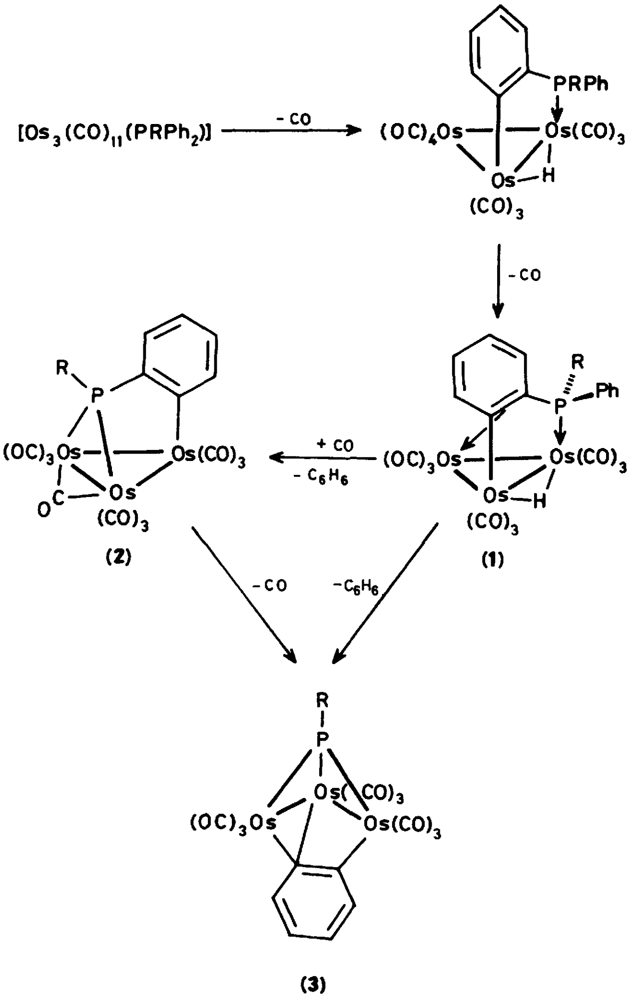
The thermal conversion of $[Os_3(CO)_{11}(PRPh_2)]$ (R = Me or Ph) into $[Os_3(\mu_3\text{-}C_6H_4)(\mu_3\text{-}PR)(CO)_9]$ (**3**) by loss of carbon monoxide, and probably benzene, has been reported. By carrying out the reactions at lower temperatures we have been able to isolate $[Os_3(\mu\text{-}H)(\mu_3\text{-}C_6H_4PMePh)(CO)_9]$ (**1a**) and $[Os_3(\mu_3\text{-}C_6H_4PMe)(CO)_{10}]$ (**2a**) from the methyldiphenylphosphine compound and corresponding derivatives (**1b**) and (**2b**) from the triphenylphosphine derivative. Both (**1**) and (**2**) convert thermally to the $\mu_3\text{-}C_6H_4$ clusters (**3**) and are deduced to be intermediates in the formation of (**3**). The single-crystal *X*-ray structures of (**1a**) and (**2a**) are reported. In (**1a**), $\mu_3\text{-}C_6H_4PMePh\text{-}o$ is a five-electron donor bonded through P to one Os atom, by a σ-Os–C bond to another, and by an η^2 interaction of the C_6H_4 ring to the third. Compound (**2a**) contains the μ_3 ligand $C_6H_4PMe\text{-}o$, as a four-electron donor, and a bridging CO ligand. In the degradation of $PRPh_2$ into the components C_6H_4, PR, and C_6H_6, *ortho*-metallation is the first step, but probably follows an initial loss of CO.

The loss of CO on heating $[Os_3(CO)_{12}]$ to give unsaturated species is followed by the making of Os–Os bonds and the formation of higher clusters such as $[Os_6(CO)_{18}]$.[1] On the other hand, decarbonylation of $[Os_3(CO)_{11}L]$, where L is a tertiary phosphine or arsine, generally leads to bond cleavages (internal oxidative additions) within the ligands L. Two C–H bonds of PMe_3 are cleaved in the formation of $[Os_3H_2(\mu_3\text{-}Me_2PCH)(CO)_9]$ from $[Os_3(CO)_{11}(PMe_3)]$[2] while the corresponding double decarbonylation of $[Os_3(CO)_{11}(PMe_2Ph)]$ leads to one aryl C–H and one aryl C–P cleavage to give $[Os_3H(\mu_3\text{-}C_6H_4)(\mu\text{-}PMe_2)(CO)_9]$ and the PMe_2 group remains intact.[3,4] More extensive breakdown occurs in decarbonylation of the remaining members of the series, $[Os_3(CO)_{11}L]$ (L = $PMePh_2$ or PPh_3), which give $[Os_3(\mu_3\text{-}C_6H_4)(\mu_3\text{-}PR)(CO)_9]$ (R = Me or Ph).[5] Two C–P bonds and an aryl C–H bond are cleaved and, since benzene is probably the by-product, a C–H bond is also formed. These studies on the series $PMe_{3-x}Ph_x$ (x = 0—3) show that aryl C–H cleavage is more favourable than methyl C–H cleavage but it is not clear whether *ortho*-metallation occurs or P–C(aryl) bonds are cleaved in the step immediately following loss of CO from the the PMe_2Ph, $PMePh_2$, or PPh_3 complexes. By isolating and structurally characterising two intermediates in the degradation of $[Os_3(CO)_{11}(PMePh_2)]$ we have mapped out the main features of the route to $[Os_3(\mu_3\text{-}C_6H_4)(\mu_3\text{-}PMe)(CO)_9]$.

Results and Discussion

Synthesis of Compounds.—Evans and co-workers[5] reported that the treatment of $[Os_3(CO)_{11}(PRPh_2)]$ (R = Me, Et, or Ph) in refluxing nonane gave good yields (>70%) of the 'μ_3-benzyne' clusters $[Os_3(\mu_3\text{-}C_6H_4)(\mu_3\text{-}PR)(CO)_9]$ (**3**) as the only isolated products. The *X*-ray structure when R = Et has been



Scheme 1.

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* 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2-μ-hydrido-μ_3-{*o*-[methyl(phenyl)-phosphino]phenyl-$C^1(Os^1)C^{1-2}(Os^3)P(Os^2)$}-*triangulo*-triosmium and 1,2-μ-carbonyl-1,1,1,2,2,2,3,3,3-nonacarbonyl-μ_3-[*o*-(methylphosphido)phenyl-$C^1(Os^3)P(Os^{1,2})$]-*triangulo*-triosmium respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. I.r. and n.m.r. data for compounds (**1**) and (**2**)

Compound	$\nu(CO)^a/cm^{-1}$	^1H N.m.r.^{b}
(**1a**) $[Os_3H(C_6H_4PMePh)(CO)_9]$	2 105w, 2 084s, 2 053s, 2 029vs, 2 016m, 2 010s, 1 999w, 1 983m, 1 970w, 1 955w	8.30 (m) 7.4—6.4 (m) } C_6H_5, C_6H_4 2.60 (d), PMe, J(PH) 7.5 −17.90 (d), OsH, J(PH) 16.6
(**1b**) $[Os_3H(C_6H_4PPh_2)(CO)_9]$	2 105w, 2 083s, 2 053s, 2 028vs, 2 017m, 2 010m (sh), 2 000w, 1 983m, 1 970w, 1 955w	8.20 (m) 7.53—7.15 (m) 6.95—6.60 (m) } C_6H_5, C_6H_4 −17.66 (d), OsH, J(PH) 16.5
(**2a**) $[Os_3(C_6H_4PMe)(CO)_{10}]$	2 095m, 2 056s, 2 045s, 2 027m, 2 007w, 1 994w, 1 988w, 1 839w	8.08 (m) 7.11 (m) } C_6H_4 2.15 (d), PMe, J(PH) 10.7
(**2b**) $[Os_3(C_6H_4PPh)(CO)_{10}]$	2 095m, 2 059s, 2 045s, 2 027m, 2 008w, 1 997m, 1 988w, 1 839w	7.95 (m) 7.64—7.50 (m) 6.86—6.28 (m) } C_6H_5, C_6H_4

[a] Recorded in cyclohexane. [b] Recorded in $CDCl_3$ at 200 MHz at room temperature (δ/p.p.m., J/Hz).

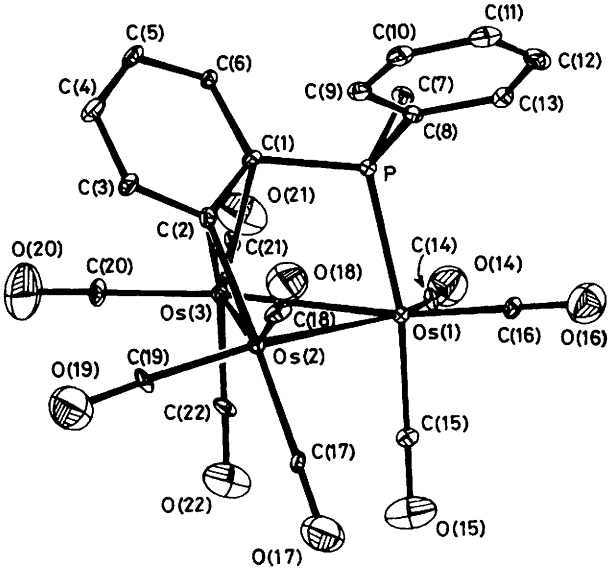
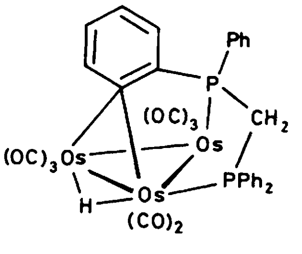
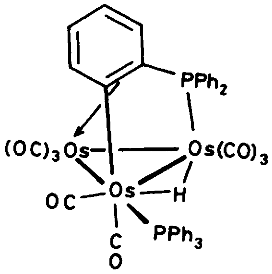


Figure 1. Molecular structure of $[Os_3H(C_6H_4PMePh)(CO)_9]$ (**1a**). Thermal ellipsoids are drawn at the 10% probability level

determined and the C_6H_4 ligand shown to be rather unusually bonded as illustrated as the final product in Scheme 1. It was thought that $PRPh_2$ had fragmented into μ_3-PR, μ_3-C_6H_4, and C_6H_6 although benzene was not established as a product. The route from $[Os_3(CO)_{11}(PRPh_2)]$ to (**3**) almost certainly involves several steps but the report gave no indication of intermediates or other products. We have measured the i.r. spectra of solutions of $[Os_3(CO)_{11}(PRPh_2)]$ (R = Me or Ph) in refluxing heptane over several hours. Although the temperature is more than 50 °C lower, the reaction follows the same course as in refluxing nonane. After *ca.* 30 h the solutions contain almost exclusively clusters (**3**) but over the early stages two other species were detected. The concentration of one compound, (**1**), builds up quickly to a maximum at 3 h and then decreases while another species, (**2**), builds up more slowly and the low concentration achieved after *ca.* 3 h remains constant for many hours before decreasing to zero at *ca.* 30 h. Stopping the reaction after 3 h (or after 1.5 h in refluxing octane) and separating the mixture by t.l.c. gave fairly low yields of $[Os_3H(C_6H_4PRPh)(CO)_9]$ (**1a**; R = Me) and (**1b**; R = Ph), and of $[Os_3(C_6H_4PR)(CO)_{10}]$ (**2a**; R = Me) and (**2b**; R = Ph).



(**4**)



(**5**)

Although complexes (**2**) appear in solution a little after complexes (**1**), it seems surprising perhaps that they contain an extra CO ligand. We suggest that in the loss of C_6H_6 from (**1**) the unsaturated molecule formed is trapped by CO in solution to give (**2**) or isomerises directly by further P–C bond cleavage to (**3**). Because (**2**) contains one more CO ligand than (**1**), it is unlikely that all of compound (**1**) converts to (**3**) *via* (**2**). We have, however, showed in separate experiments that pure (**1**) converts in refluxing octane to (**3**) and that weak i.r. absorptions of (**2**) are observed during the transformation. Likewise pure (**2**) converts directly to (**3**) after 20 min in refluxing nonane.

Compounds (**1**) and (**2**) were characterised initially by i.r. and ^1H n.m.r. spectra (Table 1) which were sufficient to establish (**1**) as $[Os_3H(C_6H_4PRPh)(CO)_x]$ (x = 9 or 10) and (**2**) as $[Os_3(C_6H_4PR)(CO)_x]$ (x = 9 or 10). We could not confidently establish x in each case nor the mode of attachment of ligands to the metal atoms. Hence single-crystal *X*-ray structures were determined for (**1a**) and (**2a**). Compounds (**1b**) and (**2b**) are directly related structurally to these (see spectroscopic data in Table 1).

Structure of Compound (**1a**).—The thermal decarbonylation of $[Os_3(CO)_{10}(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$) gives the *ortho*-metallated compound $[Os_3H(C_6H_4PPhCH_2PPh_2)(CO)_8]$ (**4**) which has been described as unsaturated and reacts with CO to give the corresponding nonacarbonyl of unknown structure.[6] The *ortho*-metallated phenyl group is apparently symmetrically bridging and a one-electron donor. This leaves the cluster with 46 valence electrons as in $[Os_3H_2(CO)_{10}]$. Clusters (**1**) are directly related stoicheiometrically with (**4**) so we determined the crystal structure of (**1a**) to see whether the same type of symmetrically bridging *ortho*-metallated phenyl group is present. The molecular structure of (**1a**) is shown in

Table 2. Fractional atomic co-ordinates (× 10^4) for $[Os_3H(C_6H_4PMePh)(CO)_9]$ (**1a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	6 860(1)	509(1)	8 890.3(4)	C(6)	8 422(13)	754(16)	6 370(13)
Os(2)	3 486.8(4)	−277(1)	7 308(1)	C(7)	9 024(12)	1 819(16)	8 283(14)
Os(3)	7 443(1)	−1 082(1)	7 693(1)	C(8)	7 120(12)	2 773(13)	7 460(13)
P	7 694(3)	1 465(4)	7 894(3)	C(9)	6 627(13)	2 843(16)	6 608(13)
O(14)	8 839(12)	165(13)	10 065(11)	C(10)	6 177(16)	3 864(19)	6 366(16)
O(15)	5 796(13)	−1 111(16)	10 032(12)	C(11)	6 221(17)	4 817(21)	6 876(19)
O(16)	6 176(11)	2 533(14)	9 782(10)	C(12)	6 701(19)	4 669(16)	7 701(20)
O(17)	3 978(12)	−1 067(13)	8 512(14)	C(13)	7 179(15)	3 694(17)	8 029(14)
O(18)	4 166(12)	1 448(14)	6 293(12)	C(14)	8 062(13)	279(14)	9 632(13)
O(19)	4 890(12)	−2 184(15)	6 119(15)	C(15)	6 198(13)	−458(14)	9 585(12)
O(20)	7 609(15)	−2 773(18)	6 296(14)	C(16)	6 421(13)	1 726(15)	9 413(13)
O(21)	9 683(10)	−1 218(14)	8 394(14)	C(17)	4 569(13)	−768(18)	8 070(14)
O(22)	6 765(11)	−2 779(12)	8 922(12)	C(18)	4 637(13)	734(17)	6 740(13)
C(1)	7 648(12)	617(14)	6 923(11)	C(19)	5 148(12)	−1 411(16)	6 586(15)
C(2)	6 718(13)	74(15)	6 583(13)	C(20)	7 506(16)	−2 089(19)	6 800(16)
C(3)	6 625(16)	−128(18)	5 672(13)	C(21)	8 837(11)	−1 148(12)	8 106(11)
C(4)	7 363(15)	29(21)	5 189(15)	C(22)	7 020(13)	−2 106(13)	8 429(15)
C(5)	8 253(15)	471(20)	5 519(15)				

Table 3. Selected structural parameters for $[Os_3H(C_6H_4PMePh)(CO)_9]$ (**1a**)

Bond lengths (Å)

Os(2)–Os(1)	2.991(4)	Os(3)–Os(1)	2.857(4)	C(21)–Os(3)	1.874(16)	C(22)–Os(3)	1.826(22)
Os(3)–Os(2)	2.764(4)	P–Os(1)	2.342(6)	C(1)–P	1.802(20)	C(8)–P	1.842(19)
C(2)–Os(2)	2.154(19)	C(2)–Os(3)	2.319(22)	C(7)–P	1.839(19)	C(2)–C(1)	1.434(24)
C(1)–Os(3)	2.417(18)	C(14)–Os(1)	1.850(20)	C(3)–C(2)	1.416(27)	C(4)–C(3)	1.328(28)
C(15)–Os(1)	1.890(21)	C(16)–Os(1)	1.820(19)	C(5)–C(4)	1.333(29)	C(6)–C(5)	1.346(29)
C(17)–Os(2)	1.907(21)	C(18)–Os(2)	1.810(19)	C(6)–C(1)	1.437(23)		
C(19)–Os(2)	1.790(20)	C(20)–Os(3)	1.855(23)				

Bond angles (°)

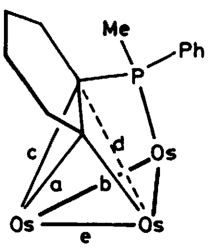
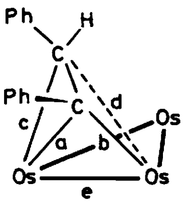
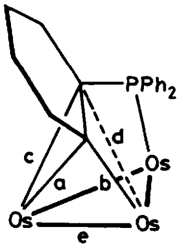
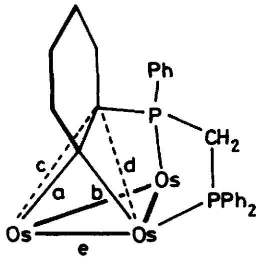
Os(3)–Os(1)–Os(2)	56.3(0)	P–Os(1)–Os(2)	84.7(2)	C(1)–Os(3)–P	35.1(4)	C(2)–Os(3)–P	59.8(5)
P–Os(1)–Os(3)	73.1(2)	C(14)–Os(1)–Os(2)	146.2(5)	C(2)–Os(3)–C(1)	35.2(6)	C(20)–Os(3)–Os(1)	166.5(7)
C(14)–Os(1)–Os(3)	90.5(6)	C(14)–Os(1)–P	92.1(7)	C(20)–Os(3)–Os(2)	102.3(8)	C(20)–Os(3)–P	135.2(8)
C(15)–Os(1)–Os(3)	97.9(7)	C(15)–Os(1)–Os(2)	89.2(6)	C(20)–Os(3)–C(1)	100.2(10)	C(20)–Os(3)–C(2)	84.7(10)
C(16)–Os(1)–Os(2)	115.2(7)	C(15)–Os(1)–P	170.9(6)	C(21)–Os(3)–Os(1)	98.9(6)	C(21)–Os(3)–Os(2)	160.6(4)
C(16)–Os(1)–P	95.9(7)	C(15)–Os(1)–C(14)	89.2(9)	C(21)–Os(3)–P	85.6(6)	C(21)–Os(3)–C(1)	91.7(7)
C(16)–Os(1)–C(14)	98.7(9)	C(16)–Os(1)–Os(3)	166.0(6)	C(21)–Os(3)–C(2)	124.4(8)	C(21)–Os(3)–C(20)	94.5(9)
C(16)–Os(1)–C(15)	92.8(9)	Os(3)–Os(2)–Os(1)	59.4(0)	C(22)–Os(3)–Os(1)	85.6(7)	C(22)–Os(3)–Os(2)	90.7(6)
C(2)–Os(2)–Os(1)	86.6(6)	C(2)–Os(2)–Os(3)	54.6(6)	C(22)–Os(3)–P	130.9(6)	C(22)–Os(3)–C(1)	162.5(7)
C(17)–Os(2)–Os(3)	114.9(8)	C(17)–Os(2)–Os(1)	88.0(7)	C(22)–Os(3)–C(2)	137.8(7)	C(22)–Os(3)–C(20)	93.6(11)
C(17)–Os(2)–C(2)	169.5(8)	C(18)–Os(2)–Os(1)	116.5(8)	C(22)–Os(3)–C(21)	97.8(9)	C(8)–P–Os(1)	117.0(6)
C(18)–Os(2)–Os(3)	148.1(6)	C(18)–Os(2)–C(17)	95.8(10)	C(1)–P–Os(1)	107.4(6)	C(8)–P–C(1)	103.7(9)
C(18)–Os(2)–C(2)	94.7(9)	C(19)–Os(2)–Os(3)	90.4(7)	C(7)–P–Os(1)	114.7(8)	C(8)–P–C(7)	104.3(9)
C(19)–Os(2)–Os(1)	145.6(6)	C(19)–Os(2)–C(2)	88.3(9)	C(7)–P–C(1)	109.1(9)	C(2)–C(1)–Os(3)	68.7(11)
C(19)–Os(2)–C(18)	97.8(11)	Os(2)–Os(3)–Os(1)	64.3(0)	P–C(1)–Os(3)	94.3(8)	C(1)–C(2)–Os(2)	125.4(14)
P–Os(3)–Os(1)	45.8(1)	P–Os(3)–Os(2)	75.7(2)	C(2)–C(1)–P	119.5(13)	Os(3)–C(2)–Os(2)	76.2(7)
C(1)–Os(3)–Os(1)	78.5(5)	C(2)–Os(3)–Os(1)	86.9(5)	C(6)–C(1)–P	118.7(14)	C(1)–C(2)–Os(3)	76.2(11)

Figure 1; fractional atomic co-ordinates are given in Table 2 and selected bond lengths and angles in Table 3.

Broadly the structure of (**1a**) is like that of $[Os_3H(C_6H_4P\text{-}PhCH_2PPh_2)(CO)_8]$ (**4**), except that in (**4**) there is one CO ligand less because it contains two co-ordinated phosphorus atoms. Compound (**1a**) contains three CO ligands at each metal atom, one of which is approximately axial and the other two equatorial. The μ_3 ligand is bonded through P to Os(1) and through the *ortho*-metallated phenyl ring to Os(2) and Os(3). It is very clear that there is not a symmetrical phenyl bridge between Os(2) and Os(3) as indicated for (**4**). Table 4 gives the best picture of this asymmetry and how the bridge relates to that of the vinyl ligand in $[Os_3H(\mu\text{-}\eta^2\text{-}PhC{=}CHPh)(CO)_{10}]$.[7] This was chosen rather than the C_2H_3 compound because the vinyl group adopts the same configuration as in (**4**). There is a σ bond between C(2) and Os(2) and a two-electron-donating η^2 interaction between C(1)–C(2) and Os(3). Overall the μ_3 ligand is a five-electron donor and the molecule is saturated co-ordinatively.

Table 4 also gives data on $[Os_3H(C_6H_4PPh_2)(CO)_8(PPh_3)]$ (**5**) which also appears to have a five-electron-donor ligand ($C_6H_4PPh_2$). The structure was never published in full and only some of the distances are given but its close relation with (**1a**) seems clear. We do not know why some structures adopt symmetrical 'electron-deficient' bridges while others unsymmetrical 'electron-precise' ($\sigma:\eta^2$) bridges but these may be very similar in energy. Vinyl bridges rapidly oscillate. For example, the rapid oscillation of the μ-PhC=CHPh ligand in $[Os_3H(PhC{=}CHPh)(CO)_{10}]$ must occur *via* a symmetrical bridging vinyl.[7] Accordingly one would expect asymmetric $C_6H_4PR_2$ bridges to rapidly oscillate *via* the form with a plane of symmetry which would only be a few kJ mol^{-1} higher in energy. It would be difficult to predict therefore the mode and symmetry of the C_6H_4PRR' bridge.

Table 4. Osmium–carbon bond lengths (Å) in the phenyl and alkenyl bridges in (from left to right) [$Os_3H(C_6H_4PMePh)(CO)_9$] (**1a**), [$Os_3H(PhC{=}CHPh)(CO)_{10}$], [$Os_3H(C_6H_4PPh_2)(CO)_8(PPh_3)$],* and [$Os_3H(C_6H_4PPhCH_2PPh_2)(CO)_8$]

				
a	2.319(22)	2.34(4)	2.34	2.296
b	2.154(19)	2.11(4)	2.16	2.284
c	2.417(18)	2.44(4)		3.151
d	3.206(24)	3.19(4)		3.143
e	2.764(4)	2.820(3)	2.762(2)	2.747
Ref.	This work	7	8	6

* The data omitted for lengths c and d for [$Os_3H(C_6H_4PPh_2)(CO)_8(PPh_3)$] were not given in the original communication [8] and atomic co-ordinates are not apparently unavailable.

Table 5. Fractional atomic co-ordinates ($\times 10^4$) for [$Os_3(C_6H_4PMe)(CO)_{10}$] (**2a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	1 027.4(4)	2 500	8(1)	C(3)	2 777(16)	2 500	−3 657(21)
Os(2)	2 464.4(3)	1 334.7(4)	1 152.9(4)	C(4)	1 877(13)	2 500	−3 703(17)
P	3 208(3)	2 500	−171(4)	C(5)	1 373(15)	2 500	−2 717(18)
O(11)	90(10)	2 500	2 393(12)	C(6)	1 772(11)	2 500	−1 605(14)
O(12)	−178(6)	743(8)	−1 039(9)	C(7)	4 428(13)	2 500	−322(18)
O(21)	1 788(6)	−243(8)	−699(8)	C(11)	449(14)	2 500	1 498(19)
O(22)	1 276(7)	353(10)	3 088(9)	C(12)	283(8)	1 415(11)	−613(11)
O(23)	4 161(7)	74(10)	1 610(13)	C(21)	1 987(9)	396(11)	−40(10)
O(24)	3 199(12)	2 500	3 385(11)	C(22)	1 717(8)	677(11)	2 365(10)
C(1)	2 712(12)	2 500	−1 573(16)	C(23)	3 540(9)	507(12)	1 525(11)
C(2)	3 216(13)	2 500	−2 569(16)	C(24)	2 887(15)	2 500	2 435(17)

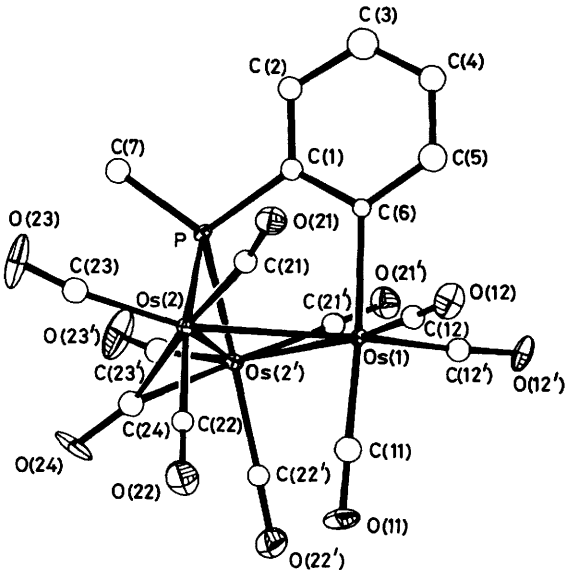


Figure 2. Molecular structure of [$Os_3(C_6H_4PMe)(CO)_{10}$] (**2a**). Thermal ellipsoids are drawn at the 30% probability level

Consistent with (**1a**) containing a five-electron-donating C_6H_4PMePh bridge, the C(17)–Os(2)–C(2) angle is 169.5(8)°, as expected for a *trans* relation between C(17) and C(2). In contrast C(22)–Os(3)–C(2) is 137.8(7); the CO ligand *trans* to the η^2 interaction at Os(3) more closely orientates *trans* to the centre of C(1)–C(2) than to C(1). There are no significant differences in the C–C distances in the C_6 rings to relate to the presence of the η^2 interaction.

It is not immediately obvious where the hydride ligand, which was not located, should be placed. The most obvious position is between Os(2) and Os(3) but the Os(1)–Os(2) edge is significantly longer than Os(1)–Os(3) [2.991(4) compared with 2.857(4) Å] and is associated with much larger Os–Os–CO angles than the Os(1)–Os(3) edge and almost certainly the hydride occupies a bridging site between Os(1) and Os(2).

In the crystal only one of two possible diastereomers is observed; interchange of the Me and Ph groups at P would give the other. ^1H N.m.r. spectra of (**1**) indicate only one diastereomer in solution so that either the one in the crystal is the only one formed or both isomers are in solution but rapidly interconverting. One would expect by analogy with μ-η^2-vinyl ligands that the μ-η^2-phenyl group would rapidly interchange its bonding between Os(2) and Os(3), interconverting diastereomers.

Structure of Compound (**2a**).—The molecular structure of compound (**2a**) is shown in Figure 2; fractional atomic co-ordinates are given in Table 5 and selected bond lengths and angles in Table 6. The molecule has a crystallographic plane of symmetry through Os(1), the C_6H_4PMe ligand, and the μ-CO ligand. The structure is very simple, containing the μ_3 ligand as a four-electron-donating bridge and a μ-CO ligand. Electron-counting requires three Os–Os bonds which are found to be 2.884(4), 2.884(4), and 2.831(4) Å. This μ_3 ligand type has been

Table 6. Structural parameters for $[Os_3(C_6H_4PMe)(CO)_{10}]$ (**2a**)*

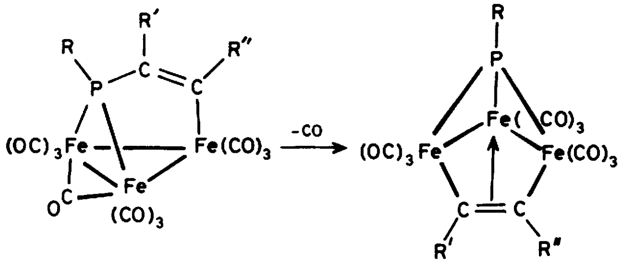
Bond lengths (Å)

Os(2)–Os(1)	2.884(4)	C(6)–Os(1)	2.165(18)	C(1)–P	1.776(20)	C(7)–P	1.824(21)
C(11)–Os(1)	1.920(24)	C(12)–Os(1)	1.865(15)	C(2)–C(1)	1.371(27)	C(6)–C(1)	1.399(23)
P–Os(2)	2.357(5)	C(21)–Os(2)	1.923(15)	C(3)–C(2)	1.414(30)	C(4)–C(3)	1.340(30)
C(22)–Os(2)	1.956(14)	C(23)–Os(2)	1.937(16)	C(5)–C(4)	1.362(28)	C(6)–C(5)	1.412(27)
C(24)–Os(2)	2.141(17)	Os(2)–Os(2′)	2.831(4)				

Bond angles (°)

Os(2′)–Os(1)–Os(2)	58.8(1)	C(6)–Os(1)–Os(2)	90.8(5)	C(23)–Os(2)–Os(2′)	121.3(5)	C(23)–Os(2)–P	93.9(5)
C(11)–Os(1)–Os(2)	85.6(6)	C(11)–Os(1)–C(6)	175.8(7)	C(23)–Os(2)–C(21)	98.9(7)	C(23)–Os(2)–C(22)	95.7(6)
C(12)–Os(1)–Os(2)	105.6(5)	C(12)–Os(1)–C(6)	88.5(6)	C(24)–Os(2)–Os(1)	102.1(5)	C(24)–Os(2)–Os(2′)	48.6(5)
C(12)–Os(1)–C(11)	94.4(7)	C(12′)–Os(1)–Os(2)	164.4(5)	C(24)–Os(2)–P	84.9(6)	C(24)–Os(2)–C(21)	174.0(6)
C(12′)–Os(1)–C(12)	90.0(9)	Os(2′)–Os(2)–Os(1)	60.6(1)	C(24)–Os(2)–C(22)	86.8(7)	C(24)–Os(2)–C(23)	87.0(7)
P–Os(2)–Os(1)	75.9(2)	P–Os(2)–Os(2′)	53.1(2)	Os(2′)–P–Os(2)	73.8(2)	C(1)–P–Os(2)	113.2(6)
C(21)–Os(2)–Os(1)	71.9(5)	C(21)–Os(2)–Os(2′)	126.4(5)	C(7)–P–Os(2)	121.9(6)	C(7)–P–C(1)	109.0(10)
C(21)–Os(2)–P	93.8(5)	C(22)–Os(2)–Os(1)	96.1(5)	C(2)–C(1)–P	122.3(15)	C(6)–C(1)–P	116.0(14)
C(22)–Os(2)–Os(2′)	114.1(5)	C(22)–Os(2)–P	167.0(4)	C(5)–C(6)–Os(1)	124.4(14)	C(1)–C(6)–Os(1)	119.3(13)
C(22)–Os(2)–C(21)	93.4(6)	C(23)–Os(2)–Os(1)	165.5(4)	O(24)–C(24)–Os(2)	138.6(3)	Os(2′)–C(24)–Os(2)	82.8(8)

* Primed atoms are related to those at (*x*, *y*, *z*) by the symmetry operation (*x*, 0.5 − *y*, *z*).



Scheme 2. R = C_6H_4OMe-*p*, R′ = H, R″ = Ph

identified before in the rather more complicated molecule $[Os_3(\mu\text{-}Ph)(\mu\text{-}PPh_2)(\mu_3\text{-}C_6H_4PPh)(CO)_9]$, although in that case the μ_3 ligand does not coincide with a symmetry plane. This compound and $[Os_3H(C_6H_4PPh_2)(CO)_8(PPh_3)]$ (**5**) discussed earlier are two of several products formed in the direct reaction of $[Os_3(CO)_{12}]$ and PPh_3.[8–10] No evidence for compounds (**1b**) and (**2b**) in this direct reaction has been given. Only products containing two P atoms were obtained apart from simple substitution compounds.

Transformation of $[Os_3(CO)_{11}(PRPh_2)]$ (R = Me *or* Ph) via (**1**) *and* (**2**) *into* (**3**).—Scheme 1 represents a summary of our results. We are assuming that the initially formed species on loss of CO is $[Os_3H(C_6H_4PRPh)(CO)_{10}]$ but this complex readily decarbonylates to (**1**) and is not observed. The conversion of compound (**1**) into (**2**) requires the uptake of CO and is unlikely to be the main route to (**3**). There are, however, close analogies to the converson of (**2**) to (**3**). For example, Scheme 2 shows a directly related transformation with P–C bond cleavage leading to the fragments PR and $R'C_2R''$ which occupy triply bridging positions above the below the metal triangle.[11]

The C_6H_4 ligand in (**3**) may be displaced by hydrogenation to give the compounds $[Os_3H_2(PR)(CO)_9]$ (R = Me or Ph). The direct reaction of $[Os_3(CO)_{12}]$ with PH_2Ph has been shown to give $[Os_3H_2(PPh)(CO)_9]$.[12]

Experimental

The monosubstituted clusters $[Os_3(CO)_{11}L]$ (L = PPh_3 or $PMePh_2$) were prepared by reactions of $[Os_3(CO)_{11}(MeCN)]$ in dichloromethane at room temperature with the tertiary phosphine. The PPh_3 cluster (82%) and the $PMePh_2$ cluster (77%) were isolated, after reaction for 3 d, by chromatography on silica. The clusters were characterised by comparison of their spectroscopic data with those reported.[13]

Thermolysis of $[Os_3(CO)_{11}(PPh_3)]$ *in Octane.*—A solution of the PPh_3 compound (0.101 g) in octane (30 cm^3) was heated under nitrogen under reflux for 85 min. Removal of the solvent under reduced pressure and separation by t.l.c. [SiO_2; eluant, dichloromethane–light petroleum (b.p. 30—40 °C) (1:9 v/v)] gave four bands yielding a trace of $[Os_3(CO)_{12}]$, $[Os_3H(C_6H_4PPh_2)(CO)_9]$ (**1b**) (0.021 g), $[Os_3(C_6H_4PPh)(CO)_{10}]$ (**2b**) (0.007 g), and $[Os_3(C_6H_4)(PPh)(CO)_9]$ (**3b**) (0.040 g).

Thermolysis of $[Os_3(CO)_{11}(PMePh_2)]$ *in Octane.*—The $PMePh_2$ compound (0.250 g) was similarly heated in refluxing octane (90 cm^3) under nitrogen for 95 min. Chromatographic work-up as above give six bands of which three gave $[Os_3H(C_6H_4PMePh)(CO)_9]$ (**1a**) (0.011 g), $[Os_3(C_6H_4PMe)(CO)_{10}]$ (**2a**) (0.030 g), and $[Os_3(C_6H_4)(PMe)(CO)_9]$ (**3a**) (*ca.* 1 mg). Similar heating in refluxing heptane gave no reaction after 4 h, while heating in refluxing nonane (80 min) gave only (**3a**) (45%).

Thermolysis of (**1b**) *in Octane.*—Infrared spectra of a solution of $[Os_3H(C_6H_4PPh_2)(CO)_9]$ (**1b**) (0.010 g) in refluxing octane (10 cm^3) were recorded periodically. Absorptions due to clusters (**2a**) and (**3**) were observed.

Thermolysis of (**2a**) *in Nonane.*—Infrared spectra of a solution of $[Os_3(C_6H_4PMe)(CO)_{10}]$ (**2a**) (0.018 g) in refluxing nonane (10 cm^3) showed absorptions of cluster (**3a**) after *ca.* 5 min and the complete conversion to this compound after 20 min.

Hydrogenation of Compound (**3b**).—Hydrogen gas was bubbled for 6.5 h through a refluxing solution of $[Os_3(C_6H_4)(PPh)(CO)_9]$ (**3b**) (0.040 g) in octane (15 cm^3) to give a brown solution. Chromatography on silica [t.l.c.; eluant, light petroleum (b.p. 30—40 °C)] gave six bands of which most were mixtures. The only product isolated pure and characterised was $[Os_3H_2(\mu_3\text{-}PPh)(CO)_9]$, spectroscopically identical with the compound formed by direct reaction of PH_2Ph with $[Os_3(CO)_{12}]$.[12]

Hydrogenation of Compound (**3a**).—Similar treatment of $[Os_3(C_6H_4)(PMe)(CO)_9]$ (0.049 g) in octane (20 cm^3), 4.5 h

Table 7. Crystal data, details of intensity measurements and structure refinement for $[Os_3H(C_6H_4PMePh)(CO)_9]$ (**1a**) and $[Os_3(C_6H_4PMe)(CO)_{10}]$ (**2a**)

Complex	(**1a**)	(**2a**)
Formula	$C_{22}H_{13}O_9Os_3P$	$C_{17}H_7O_{10}Os_3P$
M	1 022.91	972.81
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/a$	*Pnma* (no. 62)
a/Å	13.295(1)	14.880(3)
b/Å	12.152(3)	12.149(8)
c/Å	15.445(1)	11.527(3)
β/°	98.16(1)	
U/Å^3	2 470	2 084
Z	4	4
D_c/g cm^{-3}	2.751	3.101
F(000)	1 840	1 728
Crystal size (mm)	0.38 × 0.25 × 0.10	0.55 × 0.50 × 0.40
μ/cm^{-1}	155.3	184.0
Absorption correction (min., max.)	0.40, 1.00	0.75, 1.00
θ Range	1.5—25.0	1.5—25.0
h, k, l Range	$0\rightarrow15, 0\rightarrow14, -18\rightarrow18$	$0\rightarrow17, 0\rightarrow14, 0\rightarrow13$
Intensity variation	<3%	<3%
Total reflections	4 792	2 115
Unique reflections	4 348	1 926
Significance test	$F_o > 6\sigma(F_o)$	$F_o > 6\sigma(F_o)$
Reflections used in the refinement	3 354	1 534
Refined parameters	319	114
Max. least-squares shift-to-error ratio	0.21	0.08
Min. and max. height in final difference Fourier map, $\Delta\rho$/e Å^{-3}	−0.44, 0.51	−0.14, 0.45
Function minimized	$\Sigma_w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma_w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.0004	0.009
Final R	0.053	0.048
Final R'	0.056	0.053

reflux, gave four bands on chromatography of which only $[Os_3H_2(PMe)(CO)_9]$ was characterised: ν(CO)/cm^{-1} (C_6H_{12}), 2 103w, 2 073s, 2 046s, 2 030m, 2 020m, 2 007s, 1 988m, and 1 975w; ^{1}H n.m.r. ($CDCl_3$), δ −21.35 (Os_3H_2, d, J_{PH} 10.4) and 2.85 (PMe, d, J_{PH} 13.8 Hz).

Crystal Structure Determinations.—Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[14] using a CAD4 diffractometer operating in the ω–2θ scan mode, with monochromated Mo-K_α raidation (λ = 0.710 69 Å). The reflection intensities for both structures were corrected for absorption using the azimuthal-scan method.[15] The relevant experimental data are summarised in Table 7.

The structures were solved by the application of routine heavy-atom methods (SHELX 84[16]), and refined by full-matrix least-squares methods (SHELX 76[17]). The final cycle of refinement for (**1a**) included all hydrogen atoms in their calculated positions (C–H 0.96 Å, U = 0.10 Å^2). All non-hydrogen atoms for this structure were refined with anisotropic thermal coefficients. The final cycle of refinement for (**2a**) included hydrogen atoms for just the six-membered ring. These too were placed into calculated positions (C–H 0.96 Å, U = 0.10 Å^2). For (**2a**) anisotropic refinement was carried out for Os, P, and O atoms. The sources of atomic scattering factors and anomalous scattering parameters are as given in ref. 14. All computations were made on a DEC VAX-11/750 computer.

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