New Isomers of $[Os_3(CO)_{10}(PMe_2Ph)_2]$ and $[Os_3(CO)_9(PMe_2Ph)_3]$

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The compounds $[Os_3(CO)_{10}(\eta^4\text{-s-}cis\text{-}C_4H_6)]$ (C_4H_6 = buta-1,3-diene), $[Os_3(CO)_{10}(\mu\text{-s-}trans\text{-}C_4H_6)]$, and $[Os_3(CO)_{10}(MeCN)_2]$ react with PMe_2Ph at room temperature to give $[Os_3(CO)_{10}(PMe_2Ph)_2]$ and $[Os_3(CO)_9(PMe_2Ph)_3]$ as mixtures of isomers. The decacarbonyl compound separates on silica into a 1,1- and a 1,2-isomer, which do not interconvert at room temperature, although the 1,2-isomer exists as two rapidly interconverting isomers of C_s and C_{2v} symmetry respectively. Likewise the nonacarbonyl compound separates into non-interconvertible 1,2,3- and 1,1,2-isomers. Carbon-13 and ^{31}P n.m.r. studies have demonstrated specific localised and delocalised CO exchanges and that intramolecular phosphine transfer between metal atoms does not occur. Indeed 1,1-$[Os_3(CO)_{10}(PMe_2Ph)_2]$ gives $[Os_3H(CO)_9(\mu\text{-}Me_2PC_6H_4\text{-}o)(PMe_2Ph)]$ readily in refluxing toluene whereas the 1,2-isomer does not react at this temperature, giving other decarbonylation products above 120 °C.

Thermal reaction of $[Os_3(CO)_{12}]$ with tertiary phosphines (PR_3) in refluxing toluene gives a mixture of the substitution products $[Os_3(CO)_{11}(PR_3)]$, $[Os_3(CO)_{10}(PR_3)_2]$, and $[Os_3(CO)_9(PR_3)_3]$, which may be separated by column chromatography on alumina.[1] Substitution of more than three CO ligands by monophosphines is not possible under these conditions and each osmium atom is substituted by only one equatorially positioned PR_3 ligand. No evidence for the formation of isomers from these reactions has been found, although it was briefly mentioned that $[Os_3(CO)_{10}(MeCN)_2]$ and $[Os_2(CO)_{10}(C_8H_{14})_2]$ (C_8H_{14} = cyclo-octene) react at 25 °C with PR_3 to give $[Os_3(CO)_{10}(PR_3)_2]$ and that $[Os_3(CO)_{10}(PMe_2Ph)_2]$ among other compounds was shown by low-temperature n.m.r. studies to exist in two non-defined isomeric forms.[2] The dynamic behaviour of the compounds $[Os_3(CO)_{11}(PEt_3)]$, $[Os_3(CO)_{10}(PEt_3)_2]$, and $[Os_3(CO)_9(PEt_3)_3]$, formed by direct thermal substitution of $[Os_3(CO)_{12}]$, has been studied by variable-temperature ^{13}C and ^{31}P n.m.r. with no indication of isomers being present.[3] For example, $[Os_3(CO)_{10}(PEt_3)_2]$ shows two ^{31}P n.m.r. absorptions at −60 °C (which have coalesced by 40 °C) and seven CO signals in the ^{13}C n.m.r. spectrum in the intensity ratio 2:2:2:1:1:1:1. These observations are consistent with a C_s structure in which the PEt_3 ligands are equatorially positioned at two osmium atoms in non-equivalent sites.[3] The compound is dynamic in solution with rapid exchange of CO ligands *via* bridging-CO intermediates; total exchange of the CO ligands is observed at high temperatures. Although the non-equivalent PEt_3 ligands exchange, this seems to occur without any Os–P bond cleavage.

Results and Discussion

Synthesis of Compounds.—The syntheses of the compounds $[Os_3(CO)_{12-x}(PMe_2Ph)_x]$ (x = 1, 2, or 3) (**1**)—(**3**) respectively, by direct substitution of $[Os_3(CO)_{12}]$ have been described.[1] In order to introduce more than one PMe_2Ph ligand at an osmium atom, we used PMe_2Ph to displace butadiene from the isomer of $[Os_3(CO)_{10}(\eta^4\text{-}C_4H_6)]$ (C_4H_6 = buta-1,3-diene) (**4**), in which the s-*cis*-diene is co-ordinated at an axial and an equatorial site at one osmium atom.[4] Slow diene displacement occurs over days at room temperature in dichloromethane solution in the dark to give good yields of a new isomer of $[Os_3(CO)_{10}(PMe_2Ph)_2]$, compound 1,1-(**2**), giving orange crystals, as the major product (50%). The i.r. spectrum is quite unlike that of the known 1,2-isomer, 1,2-(**2**), which is formed directly from $[Os_3(CO)_{12}]$ (Table 1). The new isomer was identified as the 1,1-isomer (see section on spectroscopic characterisation). The known isomer 1,2-(**2**) is also produced in small amounts from the reaction of PMe_2Ph with (**4**) as are the known cluster 1,2,3-

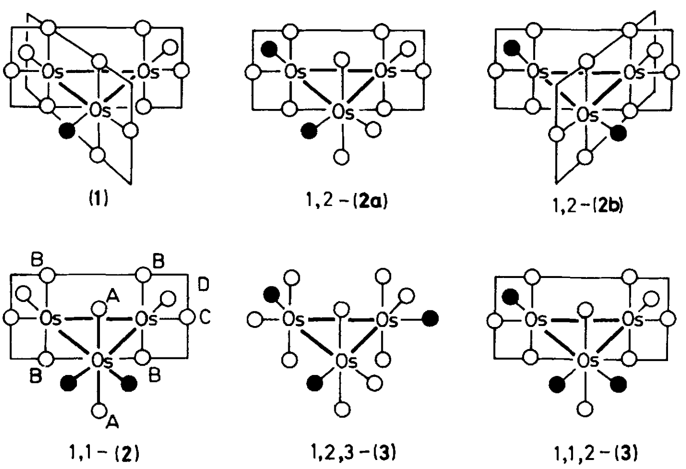
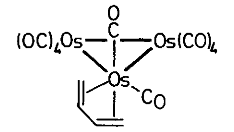


Figure 1. Observed isomers of $[Os_3(CO)_{12-x}(PMe_2Ph)_x]$ (x = 1,2, or 3); ○ = CO, ● = PMe_2Ph. The planes illustrated each contain six CO ligands allowing a 'merry-go-round' mechanism *via* a di-μ-CO bridged intermediate as proposed for $[Os_3(CO)_{12}]$

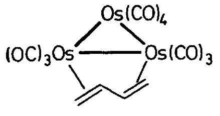
Table 1. Infrared and ^1H and ^{31}P n.m.r. data

Compound	$\nu(CO)^a/cm^{-1}$	$\delta(^1H)^b$	Assignment	J/Hz	$\delta(^{31}P)^b$
$[Os_3(CO)_{10}(PMe_2Ph)_2]$ Isomer 1,1-(**2**)	2 089m, 2 037s, 2 012(sh), 2 003vs, 1 985(sh), 1 979w, 1 957s, 1 912(sh), 1 907w	1.81(d)	Me	9.2	5.01(s)
$[Os_3(CO)_{10}(PMe_2Ph)_2]$ Isomer 1,2-(**2**)	2 084m, 2 026s, 2 009(sh), 2 002vs, 1 963s, 1 946m, 1 934(sh)	2.15(d)^c	Me	9.7	6.77(s)^{d,e} 1.10(s)^{d,e} 4.41(s)^{d,f}
$[Os_3(CO)_9(PMe_2Ph)_3]$ Isomer 1,1,2-(**3**)	2 061w, 2 004s, 1 982s, 1 963m, 1 947m, 1 938m, 1 929m, 1 898w	1.74(d)	Me	9.1	5.7(d)^g
		1.80(d)	Me	9.3	3.6(t)^g
		2.14(d)	Me	9.5	−1.5(d)^g
$[Os_3(CO)_9(PMe_2Ph)_3]$ Isomer 1,2,3-(**3**)	1 988s, 1 974vs, 1 934s, 1 920m	2.27(d)	Me	10	*h*
$[Os_3H(CO)_9(Me_2PC_6H_4\text{-}o)(PMe_2Ph)]$ (**7**)	2 066m, 2 029vs, 2 006vs, 1 975s, 1 959m	8.06(m), 7.14(m), 6.83(m), 6.50(m),	C_6H_4		*h* *h*
		2.15(d),	PMe_2Ph	8.2	
		2.11(d),		8.9	
		1.96(d),	$PMe_2C_6H_4$	8.2	
		0.18(d),		8.1	
		−17.74(dd)	Os_3H	12.0, 18.2	

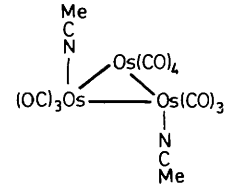
[a] Recorded in cyclohexane. [b] In $CDCl_3$ at 20 °C unless stated otherwise. [c] At −90 °C in CD_2Cl_2, two doublets at 2.09 (J = 9.8) and at 2.07 (J = 9.8 Hz) were observed for the major isomer; the expected doublet for the minor isomer probably underlies these strong doublets. [d] At −60 °C in toluene. [e] Major isomer. [f] Minor isomer. [g] Two equal coupling constants (5 Hz). [h] Not recorded.



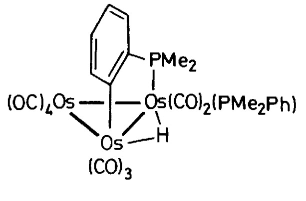
(**4**)



(**5**)



(**6**)



(**7**)

$[Os_3(CO)_9(PMe_2Ph)_3]$ [compound 1,2,3-(**3**)] and a new isomer, 1,1,2-$[Os_3(CO)_9(PMe_2Ph)_3]$ [compound 1,1,2-(**3**)].

We have investigated the nature and yields of these products from the room-temperature reactions of PMe_2Ph with the clusters $[Os_3(CO)_{10}(\eta^4\text{-}s\text{-}cis\text{-}C_4H_6)]$ (**4**), $[Os_3(CO)_{10}(\mu\text{-}s\text{-}trans\text{-}\eta^4\text{-}C_4H_6)]$ (**5**), and $[Os_3(CO)_{10}(MeCN)_2]$ (**6**); Table 2 shows the variation of product distribution. It is evident that there is a considerable measure of product control in that, when the diene is displaced from one metal atom, the 1,1-isomer of compound (**2**) is the major product whereas 1,2-(**2**) predominates when ligand(s) are replaced from two metal atoms as in compounds (**5**) and (**6**).

The two isomers of $[Os_3(CO)_9(PMe_2Ph)_3]$, 1,2,3-(**3**) and 1,1,2-(**3**), produced in small yields from (**4**), (**5**), or (**6**), are not formed by secondary reaction of PMe_2Ph with either isomer of $[Os_3(CO)_{10}(PMe_2Ph)_2]$. We have shown separately that compounds 1,2-(**2**) and 1,1-(**2**) do not react with PMe_2Ph under these conditions. In the cases of the butadiene complexes (**4**) and (**5**), intermediates of type $[Os_3(CO)_{10}(PMe_2Ph)(\eta^2\text{-}C_4H_6)]$ might be formed which decarbonylate at room temperature to give isomers of $[Os_3(CO)_9(PMe_2Ph)(\eta^4\text{-}C_4H_6)]$ subsequently leading to compounds 1,2,3-(**3**) and 1,1,2-(**3**). However, this is not a possible route from $[Os_3(CO)_{10}(MeCN)_2]$ (**6**). How compounds (**3**) are formed is therefore uncertain, even though a knowledge of their mechanism of formation is important to gain an understanding of these substitution reactions.

Spectroscopic Characterisation and Fluxional Behaviour.— The C_{2v} structure of 1,1-(**2**) is apparent from its low-temperature $^{13}C\text{-}\{^1H\}$ n.m.r. spectra (Figure 2) which consist of a triplet and three singlets with relative intensities 2:4:2:2. The triplet [δ 202.1 p.p.m., $^2J(^{13}C^{31}P)$ = 9.5 Hz] is assigned to the axial CO ligands A (Figures 1 and 2) at the same metal atom as the phosphines, to which they are coupled. The remaining singlets at δ 186.7, 179.4, and 170.3 p.p.m. are assigned as shown. The relative assignments of C and D were only made as a consequence of the dynamic behaviour observed in the spectra above −30 °C. The triplet remains unbroadened and well resolved up to 80 °C, so that the axial CO ligands A are not involved in any exchange process. As the temperature increases above −30 °C, the signals of B and C broaden more rapidly than that of D so that at around 50 °C the signals due to B and C are approaching coalescence whilst that of D remains distinct. These observations are consistent with those of Lewis *et al.*[3] on 1,2-$[Os_3(CO)_{10}(PEt_3)_2]$ and $[Os_3(CO)_{11}(PEt_3)]$ for which the fastest carbonyl exchange was identified as a 'merry-go-round' process involving six CO ligands in a plane as shown in Figure 1. This exchange occurs *via* a di-μ-CO intermediate {with a structure like that of $[Fe_3(CO)_{12}]^5$} and $[^{187}Os_3(CO)_{12}]$ seems to behave similarly. In the latter case 'merry-go-round' scrambling can occur over all three planes, resulting in axial–equatorial exchange as well as migration of CO ligands over all three metal atoms.[6] In compound 1,1-(**2**) a 'turnstile' mechanism comes into operation at higher temperatures (> 50 °C) resulting

Table 2. Yields (%) of isomers isolated from the room-temperature reactions of (**4**), (**5**), and (**6**) with PMe_2Ph (3 mol per mol Os_3) in dichloromethane in the dark

		$[Os_3(CO)_{10}(PMe_2Ph)_2]$		$[Os_3(CO)_9(PMe_2Ph)_3]$	
Starting compound	Reaction time/d	1,1-(**2**)	1,2-(**2**)	1,1,2-(**3**)	1,2,3-(**3**)
$[Os_3(CO)_{10}(\eta^4\text{-s-}cis\text{-}C_4H_6)]$ (**4**)	9	50.0	5.7	2.8	2.8
$[Os_3(CO)_{10}(\mu\text{-s-}trans\text{-}C_4H_6)]$ (**5**)	2	6.8	18.8	6.2	7.0
1,2-$[Os_3(CO)_{10}(MeCN)_2]$ (**6**)	2	5.1	60.6	6.7	2.7

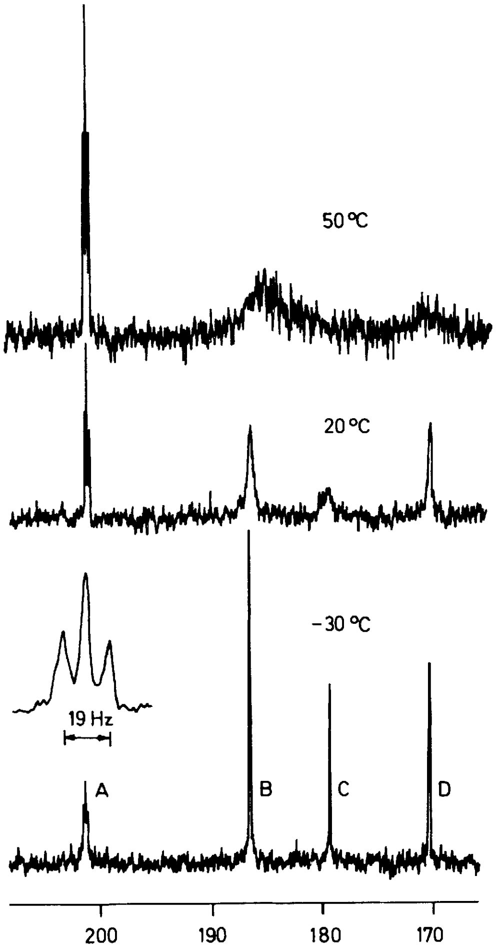


Figure 2. Carbon-13 n.m.r. spectra of $[Os_3(CO)_{10}(PMe_2Ph)_2]$, isomer 1,1-(**2**), recorded in $CDCl_3$ in the presence of $[Cr(acac)_3]$ as a shiftless relaxation agent. The low-field triplet at −30 °C is expanded

in complete B–C–D scrambling although we were unable to observe the spectrum at the high-temperature limit because decarbonylation of 1,1-(**2**) occurs above 100 °C. Note that there are no suitable planes for 'merry-go-round' exchange at the substituted osmium atom of 1,1-(**2**) at whatever sites the PMe_2Ph ligands are positioned so that carbonyl ligands A cannot migrate between osmium atoms.

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of compound 1,2-(**2**) show that it is a mixture of two isomers which are in rapid exchange at room temperature and above and are inseparable chromatographically. The major isomer has non-equivalent phosphorus nuclei whereas these are equivalent in the minor isomer. The likely structures of these isomers are 1,2-(**2a**) and 1,2-(**2b**) respectively (Figure 1) and, although the third possible 1,2-isomer with adjacent equatorial PMe_2Ph ligands cannot be ruled out, this is likely to be significantly higher in energy for steric reasons.

The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of 1,2-(**2**) showed signals due to the major isomer 1,2-(**2a**) [singlets at δ 193.1 (intensity 4, two isochronous signals each of intensity 2), 184.4 (2), 180.1 (1), 177.6 (1), 175.8 (1), 171.4 (1); CD_2Cl_2–CH_2Cl_2 at −90 °C] corresponding to that described for 1,2-$[Os_3(CO)_{10}(PEt_3)_2]$[3] and, although some weak signals in the low-temperature spectrum are attributable to 1,2-(**2b**), no useful information was obtained. Figure 3 shows that at higher temperatures there is interconversion between isomers 1,2-(**2a**) and 1,2-(**2b**) in addition to exchange of the non-equivalent phosphines of isomer 1,2-(**2a**). We have now observed similar 1,2-isomers for various tertiary phosphines and phosphites and we are examining their interconversions. These isomers are probably those alluded to by Tachikawa and Shapley.[2] The major isomer of $[Os_3(CO)_9(PMe_2Ph)_3]$, 1,2,3-(**3**), contains equivalent PMe_2Ph ligands and corresponds to that studied by Lewis and co-workers.[3] The minor isomer is of lower symmetry, contains non-equivalent PMe_2Ph ligands, is identified as 1,1,2-(**3**), and probably has the configuration shown in Figure 1. One ^{31}P nucleus couples to the other two and gives a triplet in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum while the others give doublets. Presumably the PMe_2Ph ligand which shares an osmium atom with another phosphine and is linearly related to the third phosphine across the osmium–osmium bond gives the triplet signal. Too little of the isomer 1,1,2-(**3**) was obtained for a ^{13}C n.m.r. study.

Thermal Decarbonylation of 1,1-$[Os_3(CO)_{10}(PMe_2Ph)_2]$.—Compound 1,1-(**2**) readily undergoes thermal decarbonylation in refluxing toluene to produce after 5 h a mixture of compounds (see Experimental section). The major product is $[Os_3H(CO)_9(\mu\text{-}Me_2PC_6H_4\text{-}o)(PMe_2Ph)]$ (**7**), in which *ortho*-metallation of one phenyl group has occurred with oxidative transfer of a hydrogen atom to the osmium atoms. The hydride ligand gives a ^1H n.m.r. signal (Table 1) showing coupling to two non-equivalent phosphorus nuclei. The structure shown is consistent with data in Table 1, but in view of the μ-aryl moieties established in other systems such as $[Os_3H(CO)_8(\mu_3\text{-}Ph_2PCH_2PPhC_6H_4\text{-}o)]$[7] and $[Os_3(CO)_8(\mu\text{-}Ph)(PPh_2)(PPhC_6H_4\text{-}o)]$,[8] the $Me_2PC_6H_4$ ligand is very possibly triply bridging.

The other products isolated from thermolysis of 1,1-(**2**) were (**1**), 1,2-(**2**), and 1,2,3-(**3**). The formation of these minor products implies competitive dissociation of CO and PMe_2Ph, the former predominating. The build-up of the 1,2-isomer of $[Os_3(CO)_{10}(PMe_2Ph)_2]$ does not imply that this is more thermodynamically stable than 1,1-(**2**) since it is the more inert. Thus, the thermal decarbonylation of compound 1,1-(**2**) contrasts with that of its isomer, 1,2-(**2**), which shows no reaction in refluxing toluene even after 5 h. Thermolysis of the 1,2-isomer at higher temperatures (> 125 °C) has previously been shown to give many products including $[Os_3(CO)_7(\mu_3\text{-}C_6H_4)(PMe_2)_2]$ or $[Os_3H(CO)_8(\mu_3\text{-}C_6H_4)(PMe_2)(PMe_2Ph)]$ depending upon the reflux temperature, but not compound (**7**).[1]

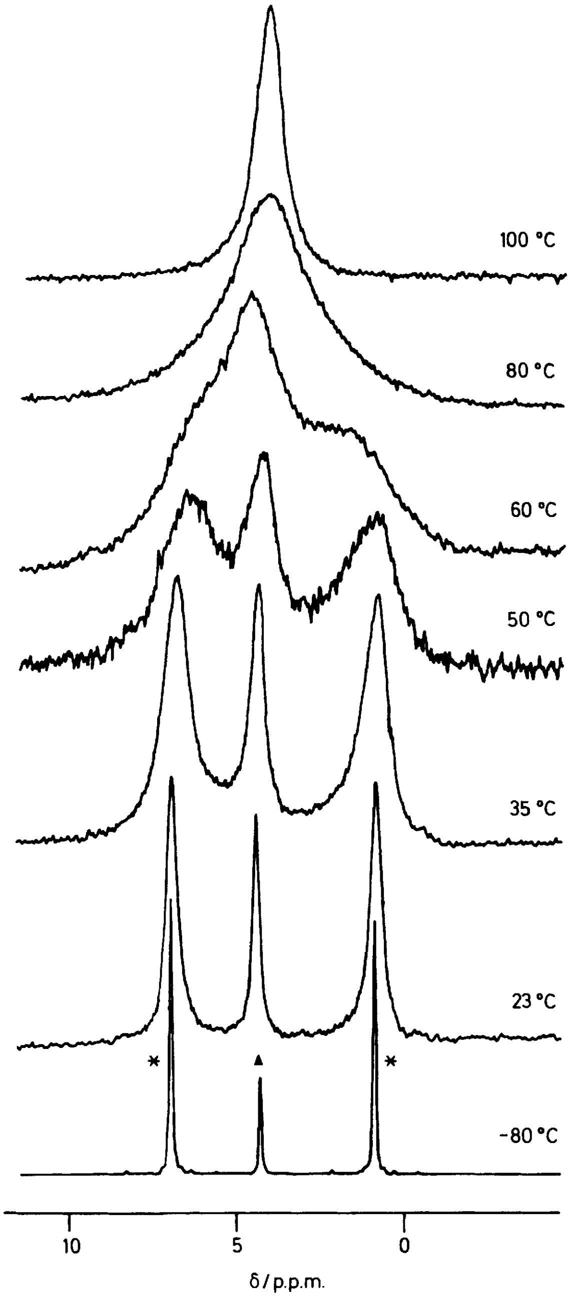


Figure 3. Phosphorus-31 n.m.r. spectra of $[Os_3(CO)_{10}(PMe_2Ph)_2]$, isomers 1,2-(**2a**) (*) and 1,2-(**2b**) (▲) recorded in $CD_3C_6D_5$–$CH_3C_6H_5$ (25% deuteriated compound) and referenced to external H_3PO_4 (85%)

Experimental

N.m.r. spectra were recorded on a Varian XL-200 spectrometer. Phosphorus-31 chemical shifts are relative to external H_3PO_4 (85%). Carbon-13 spectra were obtained at natural abundance for solutions which contained *ca.* 0.05 mol dm^{-3} tris(pentane-2,4-dionato)chromium(III), $[Cr(acac)_3]$, as relaxation agent. The starting materials $[Os_3(CO)_{10}(MeCN)_2]$ (**6**),[9] $[Os_3(CO)_{10}(\eta^4\text{-s-}cis\text{-}C_4H_6)]$ (**4**),[4] and $[Os_3(CO)_{10}(\mu\text{-s-}trans\text{-}\eta^4\text{-}C_4H_6]$ (**5**),[4] were prepared by methods already reported.

Reaction of $[Os_3(CO)_{10}(cis\text{-}\eta^4\text{-}C_4H_6)]$ (**4**) *with Dimethylphenylphosphine.*—A solution of PMe_2Ph (0.257 g, 3 mol per mol Os_3) and compound (**4**) (0.411 g) in dichloromethane (50 cm^3) was allowed to stand at room temperature in the dark under nitrogen for 9 d by which time the i.r. spectrum indicated that no compound (**4**) remained. Removal of the solvent under vacuum followed by chromatographic separation of the residue [t.l.c. (SiO_2); eluant, light petroleum (b.p. 30—40 °C)–dichloromethane (10:2 v/v)] gave in order of elution: $[Os_3(CO)_{10}(PMe_2Ph)_2]$ isomer 1,1-(**2**) (0.256 g, 50%) (Found: C, 27.7; H, 1.9. $C_{26}H_{22}O_{10}Os_3P_2$ requires C, 27.7; H, 2.0%), isomer 1,2-(**2**) (0.029 g, 5.7%), and $[Os_3(CO)_9(PMe_2Ph)_3]$, isomer 1,1,2-(**3**) (0.015 g, 2.8%) (Found: C, 32.4; H, 2.55; P, 7.5. $C_{33}H_{33}O_9Os_3P_3$ requires C, 32.05; H, 2.7; P, 7.5%), and isomer 1,2,3-(**3**) (0.015 g, 2.8%). Compounds 1,2-(**2**) and 1,2,3-(**3**) were characterised by comparison of their spectra with those reported.[1]

Reaction of $[Os_3(CO)_{10}(\mu\text{-s-}trans\text{-}C_4H_6)]$ (**5**) *with Dimethylphenylphosphine.*—A similar reaction to that above using compound (**5**) (0.096 g) and PMe_2Ph (0.058 g, 3 mol per mol Os_3) in dichloromethane (20 cm^3), reacting for 48 h, gave 1,1-(**2**) (0.008 g, 6.8%), 1,2-(**2**) (0.022 g, 18.8%), 1,1,2-(**3**) (0.008 g, 6.2%), and 1,2,3-(**3**) (0.009 g, 7.0%).

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ (**6**) *with Dimethylphenylphosphine.*—A similar reaction using compound (**6**) (0.113 g) and PMe_2Ph (0.051 g, 3 mol per mol Os_3) in dichloromethane (15 cm^3), reacting for 48 h, gave (**1**) (0.013 g, 10.6%) {possibly derived from some $[Os_3(CO)_{11}(MeCN)]$ impurity in compound (**6**)}, 1,1-(**2**) (0.007 g, 5.1%), 1,2-(**2**) (0.083 g, 60.6%), 1,1,2-(**3**) (0.010 g, 6.7%), and 1,2,3-(**3**) (0.004 g, 2.7%).

Reaction of Compound 1,1-(**2**) *with Dimethylphenylphosphine.*—A solution of PMe_2Ph (0.0025 g) and 1,1-(**2**) (0.019 g) in dichloromethane (8 cm^3) was allowed to stand at room temperature in the dark for 48 h. Chromatographic work-up as described above gave a single band, identified as starting material, 1,1-(**2**). A similar treatment of 1,2-(**2**) with PMe_2Ph gave only unchanged starting material.

Thermolysis of $[Os_3(CO)_{10}(PMe_2Ph)_2]$, *Isomer* 1,1-(**2**).—A solution of 1,1-(**2**) (0.163 g) in toluene (15 cm^3) was refluxed under argon for 2 h. Removal of the solvent under vacuum and separation of the residue [t.l.c. (SiO_2); eluant, light petroleum (b.p. 30—40 °C)–dichloromethane (10:3 v/v)] gave in order of elution: (**1**) (0.033 g, 23%), 1,1-(**2**) (0.004 g, 3%), 1,2-(**2**) (0.032 g, 20%), $[Os_3H(CO)_9(Me_2PC_6H_4\text{-}o)(PMe_2Ph)]$ (**7**) (0.047 g, 30%) (Found: C, 26.9; H, 1.9. $C_{25}H_{22}O_9Os_3P_2$ requires C, 27.3; H, 2.0%), and 1,2,3-(**3**) (0.018 g, 10%).

Thermolysis of $[Os_3(CO)_{10}(PMe_2Ph)_2]$, *Isomer* 1,2-(**2**).—A similar treatment of this isomer, but refluxing under nitrogen for 5 h, gave a solution containing only the starting material (i.r. evidence). Thermolysis at higher temperatures (125 °C) has been shown to give $[Os_3(CO)_7(\mu_3\text{-}C_6H_4)(PMe_2)_2]$ among other compounds.[1]

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References

1 A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 1970, 897; A. J. Deeming, R. E. Kimber, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1973, 2589.
2 M. Tachikawa and J. R. Shapley, *J. Organomet. Chem.*, 1977, **124**, C19.
3 B. F. G. Johnson, J. Lewis, B. E. Reichert, and K. T. Schorpp, *J. Chem. Soc., Dalton Trans.*, 1976, 1403.
4 M. Tachikawa, J. R. Shapley, R. C. Haltiwanger, and C. G. Pierpont, *J. Am. Chem. Soc.*, 1976, **98**, 4651; C. G. Pierpont, *Inorg. Chem.*, 1978, **17**, 1976.

5 C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, 1969, **91**, 1351; F. A. Cotton and J. M. Troup, *ibid.*, 1974, **96**, 4155.
6 A. A. Koridze, O. A. Kizas, N. M. Astakhova, P. V. Petrovskii, and Yu. K. Grishin, *J. Chem. Soc., Chem. Commun.*, 1981, 853.
7 J. A. Clucas, D. F. Foster, M. M. Harding, and A. K. Smith, *J. Chem. Soc., Chem. Commun.*, 1984, 949.
8 C. W. Bradford and R. S. Nyholm, *J. Chem. Soc., Dalton Trans.*, 1973, 529 and refs. therein.
9 B. F. G. Johnson, J. Lewis, and D. A. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407.

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