Substituted Osmium Clusters containing Labile Ligands. The Preparation, Characterisation, and some Reactions of $[Os_3H(OR)(CO)_9(MeCN)]$ (R = H, Me, Et, or Ph) and the Isomers of $[Os_3H(SR)(CO)_9(MeCN)]$ (R = Me, Et, or Ph); the Crystal and Molecular Structure of $[Os_3H(SPh)(CO)_9(PEt_3)]$ †

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The compounds $[Os_3H(ER)(CO)_{10}]$ (E = O, R = H, Me, Et, or Ph; E = S, R = Me, Et, or Ph) react with Me_3NO in MeCN to produce the acetonitrile derivatives $[Os_3H(ER)(CO)_9(MeCN)]$. For ER = OR there is only one such compound formed which has the acetonitrile ligand attached to one of the bridgehead osmium atoms. These clusters react with $P(OMe)_3$ to form two isomers of the compounds $[Os_3H(OR)(CO)_9\{P(OMe)_3\}]$, both of which have the phosphite ligands co-ordinated to one of the bridgehead osmium atoms. For the case ER = SR three isomers of the acetonitrile derivative are formed, two with the acetonitrile ligand attached to the unique osmium atom and one as in the alkoxy case. These isomers react with phosphorus donor ligands to produce isomers of the compounds $[Os_3H(SR)(CO)_9(PR'_3)]$, where the phosphorus donor ligand is bound to the same osmium atom as the acetonitrile in the starting material. The compounds $[Os_3H(OR)(CO)_8\{P(OMe)_3\}_2]$ were prepared from reaction of $[Os_3H(OR)(CO)_{10}]$ with 2.2 equivalents of Me_3NO followed by $P(OMe)_3$. All the products have been characterised by i.r. and ^1H n.m.r. spectroscopy and structural assignments made. The structure of $[Os_3H(SPh)(CO)_9(PEt_3)]$ was confirmed by *X*-ray analysis and shown to consist of a triangle of Os atoms with one edge bridged by both a hydride and a phenylthiolato ligand. The triethylphosphine ligand occupies a 'pseudo' axial site on one of the Os atoms involved in bridge bonds. The nine carbonyl groups all occupy terminal co-ordination sites.

For $[Os_3(CO)_{12}]$ the statement (based on a consideration of steric and electronic effects) that on substitution two-electron donor ligands that are bulky and/or capable of acid behaviour comparable to that of CO are likely to bond in equatorial sites, while small non-π-acceptor ligands will adopt axial positions appears to hold true. That is the $P(OMe)_3$ ligand occupies an equatorial site in $[Os_3(CO)_{11}\{P(OMe)_3\}]$ [1] while the MeCN ligand takes up an axial site in $[Os_3(CO)_{11}(MeCN)]$ [2] from the reactions of type (1) (L = NMe_3 or MeCN, L′ = PR'_3, X = halogen) reported previously [3] and extended in this paper. We are now able to report the results of an investigation of the possible co-ordination sites on a class of substituted clusters.

$$[Os_3H(X)(CO)_{10}] \xrightarrow{Me_3NO} [Os_3H(X)(CO)_9L] \xrightarrow{L'} [Os_3H(X)(CO)_9L'] \quad (1)$$

Results and Discussion

The compounds $[Os_3H(OR)(CO)_{10}]$ (R = H, Me, Et, or Ph) react with trimethylamine oxide (Me_3NO) in acetonitrile, or dichloromethane solutions containing acetonitrile, to produce 50—70% yields of the compounds $[Os_3H(OR)(CO)_9(MeCN)]$ [R = H (**1**), Me (**2**), Et (**3**), or Ph (**4**)], equation (2).

$$[Os_3H(OR)(CO)_{10}] + Me_3NO \xrightarrow{MeCN} [Os_3H(OR)(CO)_9(MeCN)] \quad (2)$$

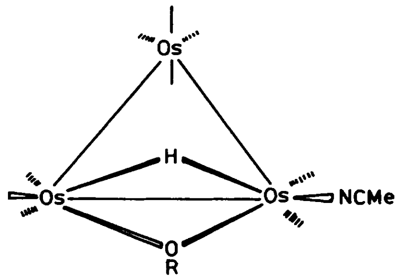

Figure 1. Proposed structure for $[Os_3H(OR)(CO)_9(MeCN)]$ (**1**)—(**4**)

These yellow complexes can be isolated as moderately air-stable solids which decompose in solution. In the case of (**1**) and (**4**) this decomposition is rapid in most solvents unless acetonitrile is also present.

The ^1H n.m.r., i.r., and microanalytical data are summarised in Tables 1, 2, and 3 respectively. The i.r. spectra are similar to that of $[Os_3H(Cl)(CO)_9(NMe_3)]$,[3] suggesting that these compounds have a similar structure (Figure 1). The instability of complex (**1**) in solution made it difficult to obtain a ^1H n.m.r. spectrum. In $CDCl_3$, (**1**) decomposed over a period of 0.5 h to give a brown intractable solid plus some $[Os_3H(OR)(CO)_{10}]$. A spectrum obtained from this decomposing solution was compared with one obtained from the compound dissolved in CD_2Cl_2 containing three drops of CD_3CN. Peaks at approximately δ −11.54 (s) and 0.02 (s) were common to both. The CD_2Cl_2–CD_3CN spectrum showed a resonance at δ 1.97 (s) as compared with that of δ 2.45 (s) in $CDCl_3$. The value of δ 1.97 is consistent with free acetonitrile in $CDCl_3$, whereas δ 2.45 is consistent with a co-ordinated MeCN ligand. The peaks at δ −11.54 and 0.02 were assigned to the metal–hydride and

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† 1,1,1,2,2,3,3,3-Nonacarbonyl-1,2-μ-hydrido-1,2-μ-phenylthio-2-triethylphosphine-*triangulo*-triosmium.

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

Table 1. I.r. and mass spectroscopic data for new compounds derived from $[Os_3H(OR)(CO)_{10}]$

Compound	ν(CO) (cyclohexane)/cm^{-1}	*m/e*[a]
(1) $[Os_3H(OH)(CO)_9(MeCN)]$	2 097mw, 2 057s, 2 020s, 2 011s br, 1 988m, 1 979m, 1 976m (sh), 1 946m	—
(2) $[Os_3H(OMe)(CO)_9(MeCN)]$	2 099m, 2 055s, 2 018vs, 2 013s, 2 005s, 1 990w, 1 979m, 1 973m, 1 945mw	—
(3) $[Os_3H(OEt)(CO)_9(MeCN)]$	2 099m, 2 055s, 2 017vs, 2 005s, 1 987w, 1 979m, 1 973m, 1 945mw	—
(4) $[Os_3H(OPh)(CO)_9(MeCN)]$	2 102m, 2 060s, 2 021vs, 2 018s (sh), 2 008s, 1 995w, 1 985m, 1 979m, 1 949m	—
(5) $[Os_3H(OH)(CO)_9\{P(OMe)_3\}]$[b]	2 097mw, 2 056s, 2 021ms, 2 012s, 1 992w, 1 981m, 1 974m, 1 960w	970
(6) $[Os_3H(OMe)(CO)_9\{P(OMe)_3\}]$	2 095m, 2 054s, 2 020ms, 2 010s, 1 991m, 1 980m, 1 973m, 1 960w	984
(7) $[Os_3H(OEt)(CO)_9\{P(OMe)_3\}]$	2 094m, 2 053s, 2 019ms, 2 009s, 1 990m, 1 979m, 1 972m, 1 960w	998
(8) $[Os_3H(OPh)(CO)_9\{P(OMe)_3\}]$	2 097m, 2 058s, 2 021ms, 2 011s, 1 996m, 1 985mw, 1 977m, 1 961w	1 046
(9) $[Os_3H(OH)(CO)_8\{P(OMe)_3\}_2]$[c]	2 079m, 2 013s (sh), 2 010s, 1 997s (sh), 1 995s, 1 966m, 1 950m, 1 939m	1 066
(10) $[Os_3H(OMe)(CO)_8\{P(OMe)_3\}_2]$	2 075m, 2 011s, 1 993s (sh), 1 990s, 1 963m, 1 956m, 1 943m (sh), 1 940m	1 080
(11a) $[Os_3H(OPh)(CO)_8\{P(OMe)_3\}_2]$	2 077m, 2 014s, 1 997ms (sh), 1 992ms, 1 966m, 1 950m (sh), 1 947m	1 142
(11b) $[Os_3H(OPh)(CO)_8\{P(OMe)_3\}_2]$	2 080m, 2 016s br, 1 999s, 1 968m, 1 953m	1 142

[a] For ^{192}Os. [b] ν(OH) at 3 564w cm^{-1}. [c] ν(OH) at 3 542w cm^{-1}.

Table 2. ^1H N.m.r. data for new acetonitrile derivatives (δ/p.p.m. relative to $SiMe_4$; *J* in Hz); recorded in $CDCl_3$ unless otherwise stated

Compound	Metal–hydride (s, 1 H)	Co-ordinated acetonitrile (s, 2 H)	Others
(1) $[Os_3H(OH)(CO)_9(MeCN)]$	−11.54	2.45	0.02 (s, 1 H)
(2) $[Os_3H(OMe)(CO)_9(MeCN)]$	−11.32	2.47	3.70 (s, 3 H)
(3) $[Os_3H(OEt)(CO)_9(MeCN)]$	−11.33	2.43	3.47 (m, 2 H), 1.12 (t, 3 H, J_{HH} 7)
(12) $[Os_3H(SMe)(CO)_9(MeCN)]$	−15.71	2.47	2.00 (s, 3 H)
(15) $[Os_3H(SEt)(CO)_9(MeCN)]$	−15.84	2.46	2.08 (s, 2 H), 1.27 (t, 3 H, J_{HH} 7.5)
(16) $[Os_3H(SEt)(CO)_9(MeCN)]$	−16.63	2.56	2.46 (q, 2 H), 1.25 (t, 3 H, J_{HH} 7.2)
(17) $[Os_3H(SEt)(CO)_9(MeCN)]$	−16.43	2.56	2.47 (q, 2 H), 1.26 (t, 3 H, J_{HH} 6.1)
(18) $[Os_3H(SPh)(CO)_9(MeCN)]$[a]	−15.75	1.82	7.26 (m, 5 H)
(19) $[Os_3H(SPh)(CO)_9(MeCN)]$	−16.28	2.58	7.30 (m, 5 H)
(20) $[Os_3H(SMe)(CO)_9(NMe_3)]$[b]	−16.82		2.46 (s, 3 H)

[a] Recorded in CD_2Cl_2. [b] $\delta(NMe_3)$ = 3.20 (s, 9 H).

Table 3. Microanalytical data for the new complexes

	Found (%)			Calc. (%)		
Compound	C	H	N	C	H	N
(2) $[Os_3H(OMe)(CO)_9(MeCN)]$	15.95	0.85	1.30	16.10	0.80	1.55
(7) $[Os_3H(OEt)(CO)_9\{P(OMe)_3\}]$	18.05	1.55	—	16.95	1.50	—
(9) $[Os_3H(OH)(CO)_8\{P(OMe)_3\}_2]$	15.75	1.90	—	15.45	1.85	—
(12) $[Os_3H(SMe)(CO)_9(MeCN)]$	16.50	1.05	1.45	15.80	0.75	1.55
(16) $[Os_3H(SEt)(CO)_9(MeCN)]$	17.15	1.05	1.25	16.85	1.00	1.50
(19) $[Os_3H(SPh)(CO)_9(MeCN)]$	20.80	1.05	0.70	20.95	0.95	1.45
(21) $[Os_3H(SMe)(CO)_9\{P(OMe)_3\}]$	17.20	1.55	—	15.70	1.30	—

hydroxide respectively. The parent compound $[Os_3H(OH)(CO)_{10}]$ shows similar resonances at δ −12.75 and 0.20.[4] No suitable spectrum, however, could be obtained for $[Os_3H(OPh)(CO)_9(MeCN)]$ **(4)**. The chemical shifts for the methyl groups of the co-ordinated acetonitrile ligands are similar to those reported previously in the clusters $[Os_3(CO)_{11}(MeCN)]$ (δ 2.74)[5] and $[Os_3H_2(CO)_8(\mu_3\text{-}S)(MeCN)]$ (δ 2.52).[6]

Compounds **(1)**—**(4)** react with $P(OMe)_3$ to produce the complexes $[Os_3H(OR)(CO)_9\{P(OMe)_3\}]$ [R = H **(5)**, Me **(6)**, Et **(7)**, or Ph **(8)**]. Again, comparison of i.r. spectra with that of $[Os_3H(Cl)(CO)_9\{P(OMe)_3\}]$[4] suggests that these compounds have a similar structure (Figure 2). However, the ^1H n.m.r. spectra for **(6)**, **(7)**, and **(8)** indicate that a slightly more complex situation exists. Instead of the expected doublet in the phosphite region there were two doublets, and four peaks were observed in the high-field metal–hydride region. The nature of the spectra indicated that more than one compound was present. However, it was not possible to separate them.

By recording the n.m.r. spectra on instruments operating at different fields (100 or 250 and 400 MHz), it was revealed that the four high-field signals were in fact two doublets, with coupling constants of *ca.* 10 and 55 Hz. Consideration of all the spectroscopic data led to the proposal that two geometric isomers of **(6)**—**(8)** are possible. Both have the phosphite ligand attached to one of the bridgehead osmium atoms. In one case the ligand occupies the equatorial site lying in the plane of the Os_3 triangle while in the other the ligand takes the place of a carbonyl *trans* to the bridging hydride (positions A and B respectively in Figure 3). The previously prepared compound $[Os_3H(OH)(CO)_9(PMe_2Ph)]$[7] has J_{PH} 8.7 Hz for the metal–hydride n.m.r. resonance. The solid-state structure for this compound reveals that the phosphine ligand is attached to one of the bridgehead osmium atoms, and is lying in the equatorial plane.

Reaction of $[Os_3H(OR)(CO)_{10}]$ (R = H, Me, or Ph) with 2.2 mol equivalents of Me_3NO in MeCN, followed by the addition of $P(OMe)_3$ produces the complexes $[Os_3H(OR)(CO)_8\{P(OMe)_3\}_2]$ [R = H (**9**), Me (**10**), or Ph (**11a**) and (**11b**)]. Careful examination of the i.r. spectra revealed that while the patterns were similar to that of $[Os_3H(Cl)(CO)_8(PPh_3)_2]$,[7] the pattern for (**9**) and (**11b**) was distinct from that of (**10**) and (**11a**). ^1H N.m.r. data revealed that the high-field metal–hydride signal for (**9**) and (**11b**) was a triplet (J_{PH} *ca.* 8 Hz) with one doublet in the region expected for $P(OMe)_3$ ligands. On the other hand (**10**) and (**11a**) exhibited metal–hydride signals that were doublet of doublets (J_{PH} *ca.* 8 and 65 Hz). Structures consistent with these spectroscopic data are shown in Figure 4. Compounds (**11a**) and (**11b**) slowly interconvert in solution to produce a 60:40 (**11a**):(**11b**) equilibrium mixture of the two isomers. An interesting comparison may be made between complex (**9**) and $[Os_3H(OH)(CO)_8(dppm)]$[8] (dppm = $Ph_2PCH_2PPh_2$). In the latter complex the phosphorus donor atoms of the bidentate ligand are co-ordinated to the bridgehead Os atoms, and both lie in the plane of the Os_3 triangle. The ^1H n.m.r. data for these two complexes are similar, the triplet signals for the hydroxide and hydride ligands in $[Os_3H(OH)(CO)_8(dppm)]$ occurring at δ 4.3 and −11.68, respectively.

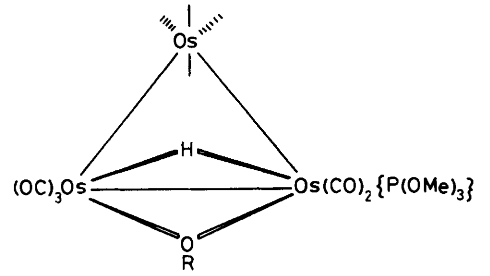


Figure 2. Structure of $[Os_3H(OR)(CO)_9\{P(OMe)_3\}]$ (**5**)—(**8**). For the stereochemical positioning of the phosphite ligand in the isomers refer to the text and Figure 3

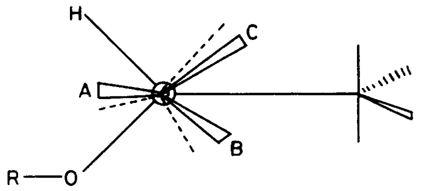
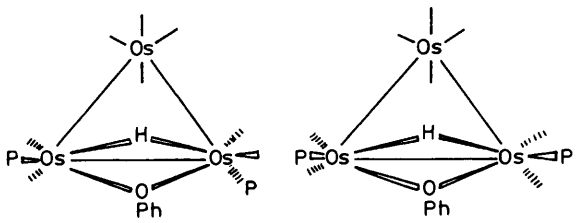


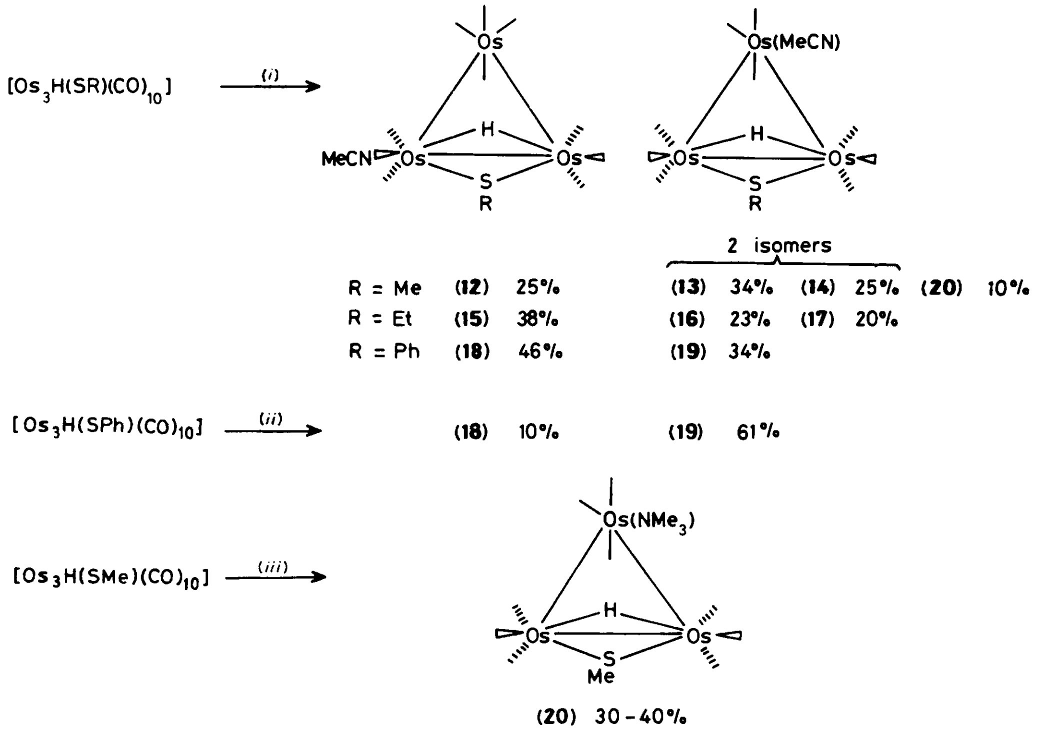
Figure 3. Projection of the molecule $[Os_3H(OR)(CO)_{10}]$ along the bridgehead osmium osmium bond

The reaction of compounds $[Os_3H(SR)(CO)_{10}]$ (R = Me, Et, or Ph) with Me_3NO, and the products obtained are summarised in the Scheme. The i.r. and n.m.r. spectroscopic data for the new compounds are presented in Tables 2, 4, and 5. Compounds (**13**) and (**14**) have been prepared previously using



(*a*) (*b*)

Figure 4. Probable structures for the isomers of $[Os_3H(OPh)(CO)_8\{P(OMe)_3\}_2]$: (*a*) compound (**11a**), (*b*) compound (**11b**)



Scheme. Reactions of $[Os_3H(SR)(CO)_{10}]$ with Me_3NO. (*i*) Me_3NO in MeCN–CH_2Cl_2 (1:10), (*ii*) Me_3NO in MeCN, (*iii*) Me_3NO in CH_2Cl_2. The exact stereochemistry of the two isomers is not known; however, it is thought that it is an 'axial up–axial down' type of isomerism

Table 4. I.r. and mass spectroscopic data for new compounds derived from $[Os_3H(SR)(CO)_{10}]$

Compound		ν(CO) (cyclohexane)/cm^{-1}	*m/e*
(20)	$[Os_3H(SMe)(CO)_9(NMe_3)]$	2 084mw, 2 050s, 2 023s, 2 003s, 1 983s, 1 976s, 1 948ms, 1 943ms	935
	$[Os_3H(SEt)(CO)_9(NMe_3)]$	2 084ms, 2 050s, 2 023s, 2 003s, 1 982s, 1 978s (sh), 1 948ms, 1 943ms	—
	$[Os_3H(SPh)(CO)_9(NMe_3)]$	2 085m, 2 051s, 2 024s, 2 003s, 1 987s, 1 976s, 1 948ms, 1 944ms	—
Compounds with MeCN or $P(OMe)_3$ on the unique osmium atom			
(16)	$[Os_3H(SEt)(CO)_9(MeCN)]$	2 080w, 2 050s, 2 032s, 1 990s, 1 981s, 1 972s, 1 959m	931
(17)	$[Os_3H(SEt)(CO)_9(MeCN)]$	2 083w, 2 050s, 2 030s, 2 000s, 1 989m, 1 980s, 1 959w	931
(19)	$[Os_3H(SPh)(CO)_9(MeCN)]$	2 080w, 2 052s, 2 034s, 1 992s, 1 983s, 1 974m, 1 961m	—
(21)	$[Os_3H(SMe)(CO)_9\{P(OMe)_3\}]$	2 087w, 2 057s, 2 031m, 2 005s, 1 986s, 1 966mw (sh), 1 964m	1 000
(22)	$[Os_3H(SEt)(CO)_9\{P(OMe)_3\}]$	2 087w, 2 057s, 2 032m, 2 005s, 1 985s, 1 968mw, 1 964m	1 014
Compounds with MeCN or $P(OMe)_3$ on one of the bridghead osmium atoms			
(12)	$[Os_3H(SMe)(CO)_9(MeCN)]$	2 098m, 2 054s, 2 016vs, 2 005s, 1 991w, 1 981m, 1 975m, 1 950m	—
(15)	$[Os_3H(SEt)(CO)_9(MeCN)]$	2 098m, 2 054s, 2 016s, 2 005s, 1 991w, 1 981m, 1 974m, 1 950m	—
(18)	$[Os_3H(SPh)(CO)_9(MeCN)]$	2 100m, 2 056ms, 2 018vs, 2 006ms, 1 993m, 1 983m, 1 977m, 1 951m	—
(23)	$[Os_3H(SMe)(CO)_9\{P(OMe)_3\}]$	2 095ms, 2 053s, 2 019s, 2 012s, 2 006s, 1 991m, 1 981m, 1 975ms, 1 953w	1 000
(24)	$[Os_3H(SEt)(CO)_9\{P(OMe)_3\}]$	2 095ms, 2 053s, 2 020s, 2 012s, 2 006s br, 1 991m, 1 981m, 1 975ms, 1 953m	1 014
(25)	$[Os_3H(SPh)(CO)_9\{P(OMe)_3\}]$	2 095ms, 2 055s, 2 020s, 2 005s, 1 994m, 1 984m, 1 977ms, 1 955m	1 062
(28)	$[Os_3H(SPh)(CO)_9(PPh_3)]$	2 094ms, 2 054s, 2 017s, 2 006s, 1 993m, 1 981m, 1 976m, 1 958m	1 200
Compounds previously prepared by an alternative method			
(13)	$[Os_3H(SMe)(CO)_9(MeCN)]$	2 080w, 2 051s, 2 032s, 1 990s, 1 981s, 1 973m, 1 960mw	917
(14)	$[Os_3H(SMe)(CO)_9(MeCN)]$	2 082w, 2 050s, 2 030s, 2 000s, 1 989m, 1 979s, 1 958w	917
(26)	$[Os_3H(SPh)(CO)_9(PMe_2Ph)]$	2 090m, 2 051s, 2 014vs, 1 997s br, 1 965m, 1 947ms br	1 076
(27)	$[Os_3H(SPh)(CO)_9(PEt_3)]$	2 090m, 2 051s, 2 013s, 1 996s, 1 993m (sh), 1 968m, 1 941m	1 056

an alternative method.[6] Compounds (**16**), (**17**), and (**19**) were therefore characterised and classified by comparison of i.r. spectra. It should be noted that while for R = Ph only one isomer (**19**) exists, the pairs of isomers (**13**), (**14**), and (**16**), (**17**) slowly interconvert in solution producing 70:30 equilibrium mixtures with (**13**) and (**16**) predominating.

The ^1H n.m.r. spectrum of (**18**) did not show a peak in the normal co-ordinated acetonitrile region (*ca.* δ 2—3) but showed a peak at δ 1.82 (s) which had an integrated intensity of 3 with respect to the phenyl resonances. When CD_3CN was added this peak completely disappeared, to be replaced by a large peak due to free MeCN. This implied that the peak at δ 1.82 was due to the co-ordinated MeCN ligand. It is believed that the reason why the resonance has shifted upfield with respect to free acetonitrile, as opposed to the normal downfield shift, is that the methyl protons are being shielded as a result of the anisotropy of the ring current of the phenyl group.

Compound (**20**) was characterised as $[Os_3H(SMe)(CO)_9(NMe_3)]$ on the basis of i.r., n.m.r., and mass spectroscopy. The i.r. spectrum indicated the presence of two compounds, and had a very similar pattern to the pair of isomers (**13**) and (**14**). The ^1H n.m.r. spectrum showed peaks at δ 3.20 (s) and 2.46 (s) in the ratio 3:1. These are assignable to the NMe_3 and SMe ligands respectively. It was possible to obtain up to a 40% yield of this compound by carrying out the reaction in the absence of acetonitrile (Scheme). Further evidence for the structure shown in this Scheme is the fact that (**20**) reacts with PPh_3 to give the known compound $[Os_3H(SMe)(CO)_9(PPh_3)]$.[9] This has the phosphine ligand attached to the unique osmium atom. It is interesting to note that the reaction of the compounds $[Os_3H(OR)(CO)_{10}]$ with Me_3NO in the absence of MeCN gives only decomposition products.

It is thought that the difference in reactivities and products formed in the reactions between $[Os_3H(OR)(CO)_{10}]$ and $[Os_3H(SR)(CO)_{10}]$ with Me_3NO is due to the ability of the SR group to act either as a five-electron donor μ_3-capping group or a three-electron donor μ-bridging ligand. This has been demonstrated[9] in the reactions (3) (L = C_2H_4, CO, PPr^i_3 or MeCN). Consequently attack of Me_3NO on $[Os_3H(SR)(CO)_{10}]$ may involve a $\mu_3 \longrightarrow \mu$ change in the transition state. The corresponding range of co-ordination modes has so far not been observed from compounds derived from $[Os_3H(OR)(CO)_{10}]$. Solvent interaction is also important in these reactions as is shown by the change in isomer distribution for the reaction of $[Os_3H(SPh)(CO)_{10}]$ when changing from CH_2Cl_2–MeCN to neat MeCN solution.

$$[Os_3H(\mu_3\text{-}SR)(CO)_9] + L \longrightarrow [Os_3H(\mu\text{-}SR)(CO)_9L] \quad (3)$$

The compounds (**13**), (**14**) and (**16**), (**17**) react with $P(OMe)_3$ upon gentle warming in cyclohexane to give the complexes $[Os_3H(SR)(CO)_9\{P(OMe)_3\}]$ [R = Me (**21**) or Et (**22**)] respectively, both of the isomers giving the same phosphite derivative in each case. These compounds are thought to have the phosphite ligand bound in an equatorial site to the unique osmium atom (Figure 5). The related compound $[Os_3H(SCHPh_2)(CO)_9(PEt_3)]$[10] has been shown to have this configuration. The ^1H n.m.r. spectra of (**21**) and (**22**) (100 and 250 MHz) show the metal–hydride as a doublet (J_{PH} *ca.* 3 Hz). A $^3J_{PH}$ coupling of a similar magnitude has previously been observed for the compound $[Os_3H_2(CO)_{10}\{P(OPh)_3\}]$.[11]

Structural isomers of the above phosphite derivatives are produced when compounds (**12**), (**15**), and (**18**) react with $P(OMe)_3$. The complexes $[Os_3H(SR)(CO)_9\{P(OMe)_3\}]$ [R = Me (**23**), Et (**24**), or Ph (**25**)] are all produced in high yield and have i.r. spectral data similar to those of $[Os_3H(OR)(CO)_9\{P(OMe)_3\}]$ (**6**)—(**8**), indicating a similar structure (Figure 2). ^1H N.m.r. spectroscopy revealed the existence of the geometric isomers for these compounds similar to those for compounds (**6**), (**7**), and (**8**). The coupling constants $^2J_{PH}$ were of the order 49 and 9 Hz. For (**23**) and (**24**) the predominant isomer is the one with the phosphite ligand bound *trans* to the bridging hydride. This contrasts the situation for the isomers of (**6**)—(**8**) where the equatorial site on one of the bridgehead osmium atoms was the preferred co-ordination site.

The thermal reaction of $[Os_3H(SPh)(CO)_{10}]$ with various

Table 5. ^{1}H N.m.r. data for compounds with the phosphorus donor ligand attached to one of the bridgehead osmium atoms (δ/p.p.m. relative to $SiMe_4$; J in Hz)

Compound[a]		Metal–hydride (d)		Phosphite (d, 9 H)		Average ratio A:B	Others
		δ	J_{PH}	δ	J_{PH}		
(5) $[Os_3H(OH)(CO)_9\{P(OMe)_3\}]$	A	−13.12	8.6	3.76	12.1	100% A	0.29 (d, 1 H, J_{PH} 7.3)
(6) $[Os_3H(OMe)(CO)_9\{P(OMe)_3\}]$	B	−12.67	58	3.80	10.5	2:1	4.01 (s, 3 H)
	A	−12.55	7.9	3.74	8.3		
(7) $[Os_3H(OEt)(CO)_9\{P(OMe)_3\}]$	B	−12.79	58	3.78	11.4	2:1	3.25 (m, 2 H), 1.00 (t, 3 H, J_{HH} 7.1)
	A	−12.65	7.0	3.75	11.7		
(8) $[Os_3H(OPh)(CO)_9\{P(OMe)_3\}]$	B	−12.25	59	3.71	11.1	8:1	6.34 (d, 2 H, J_{HH} 8.3)
	A	−12.24	8.4	3.54	11.1		6.74 (t, 1 H, J_{HH} 6.4) 7.09 (m, 2 H)
(23) $[Os_3H(SMe)(CO)_9\{P(OMe)_3\}]$	B	−17.35	50	3.75	9.9	3:2	2.38, 2.17 (s, 3 H)
	A	−17.52	7.5	3.69	10.1		
(24) $[Os_3H(SEt)(CO)_9\{P(OMe)_3\}]$	B	−17.47	49	3.76	11.1	4:3	2.29 (m, 2 H), 1.26 (t, 3 H)
	A	−17.62	7.5	3.68	12.1		1.23 (t, 3 H, J_{HH} 7.2)
(25)[b] $[Os_3H(SPh)(CO)_9\{P(OMe)_3\}]$	B	−17.16	48	3.69	12.1	1:4	7.33 (s, 5 H)
	A	−17.23	8.7	3.43	12.2		
(26) $[Os_3H(SPh)(CO)_9(PMe_2Ph)]$	B	−16.70	26	–	–	100% B	7.19 (m, 5 H) 7.35 (m, 5 H) 2.26 (d, 6 H, J_{PH} 10)
(27) $[Os_3H(SPh)(CO)_9(PEt_3)]$	B	−16.69	26	–	–	100% B	7.26 (m, 5 H) 2.17 (s, 2 H) 0.99 (dt, 3 H, J_{PH} 16.4, J_{HH} 7.9)
(28) $[Os_3H(SPh)(CO)_9(PPh_3)]$	A	−16.16	5.8	–	–	100% A	7.35, 6.71 unresolved

Other new phosphine derivatives

Compound	Metal–hydride (1 H)	$P(OMe)_3$		Others
		δ	J_{PH}	
(9) $[Os_3H(OH)(CO)_8\{P(OMe)_3\}_2]$	−12.95 (t, J_{PH} 9)	3.67	12.2 (18 H)	−0.01 (d, 1 H, J_{PH} 6)
(10) $[Os_3H(OMe)(CO)_8\{P(OMe)_3\}_2]$	−12.82 (dd, J_{PH} 8, J_{PH} 65)	3.78	12.1 (9 H)	3.79 (3 H)[c]
		3.47	12.0 (9 H)	6.65 (t, 1 H, J_{HH} 7.2) 7.04 (m, 2 H)
(11) $[Os_3H(OPh)(CO)_8\{P(OMe)_3\}_2]$	−11.60 (t, J_{PH} 8.6)	3.63	12.0 (18 H)	6.27 6.63 (unresolved, 5 H)
		3.67		7.02
(21) $[Os_3H(SMe)(CO)_9\{P(OMe)_3\}]$	−17.14 (d, $^3J_{PH}$ 3.4)	3.66	12.2 (9 H)	2.43 (s, 3 H)
(22) $[Os_3H(SEt)(CO)_9\{P(OMe)_3\}]$	−17.30 (d, $^3J_{PH}$ 2.5)		12.2 (9 H)	2.36 (q, 2 H) 1.25 (t, 3 H, J_{HH} 7.2)

[a] A = $P(OMe)_3$ in the equatorial plane, B = $P(OMe)_3$ *trans* to the bridging hydride. [b] Recorded in CD_2Cl_2. [c] Tentative assignment based on spectra run at 100 and 400 MHz.

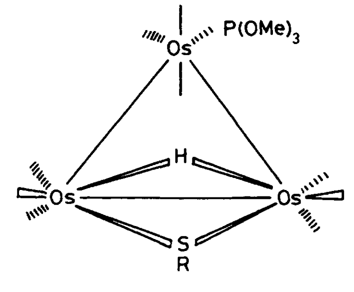


Figure 5. Proposed structure for $[Os_3H(SR)(CO)_9\{P(OMe)_3\}]$ **(21)** and **(22)**

phosphines has previously been described.[12] Of the mono-substituted derivatives formed, it was found that the compound $[Os_3H(SPh)(CO)_9(PMe_2Ph)]$ **(26)** exists as two isomers with phosphorus to hydrogen coupling constants of 6.5 and 28.5 Hz. Only one isomer of $[Os_3H(SPh)(CO)_9(PEt_3)]$ **(27)** was formed with $^2J_{PH}$ 26 Hz. From this it would seem likely that here the phosphine ligands are bound to one of the unique osmium atoms lying either in the equatorial plane ($^2J_{PH}$ *ca.* 6 Hz) or *trans* to the bridging hydride. The compounds **(26)** and **(27)** are formed in high yield by the reaction of the acetonitrile derivative **(18)** with the appropriate phosphine. In both cases the only geometric isomer observed was the one with $^2J_{PH}$ *ca.* 26 Hz. Interestingly PPh_3 reacts with **(18)** to produce $[Os_3H(SPh)(CO)_9(PPh_3)]$ **(28)** in only one isomeric form but with $^2J_{PH}$ 5.8 Hz.

Crystals of $[Os_3H(SPh)(CO)_9(PEt_3)]$ **(27)** suitable for an *X*-ray crystallographic study were obtained, and an investigation was undertaken in order to establish the ligand arrangement. The structure of **(27)** is shown in Figure 6, and associated bond parameters are presented in Table 6. The crystal structure consists of discrete molecules of **(27)** separated by normal van der Waals distances.

The molecular structure of $[Os_3H(SPh)(CO)_9(PEt_3)]$ **(27)** consists of an irregular Os_3 triangle, one edge of which is bridged by both a phenylthiolato group and a hydride. The third Os atom, Os(2), is co-ordinated to four terminal carbonyl groups, two in axial and two in equatorial sites. Of the two Os atoms co-ordinated by the two bridging groups, Os(1) is also co-ordinated to three terminal carbonyls, one in an equatorial site and two in 'pseudo axial' sites. The other metal atom, Os(3), is bonded to an equatorial carbonyl, one 'pseudo axial' carbonyl,

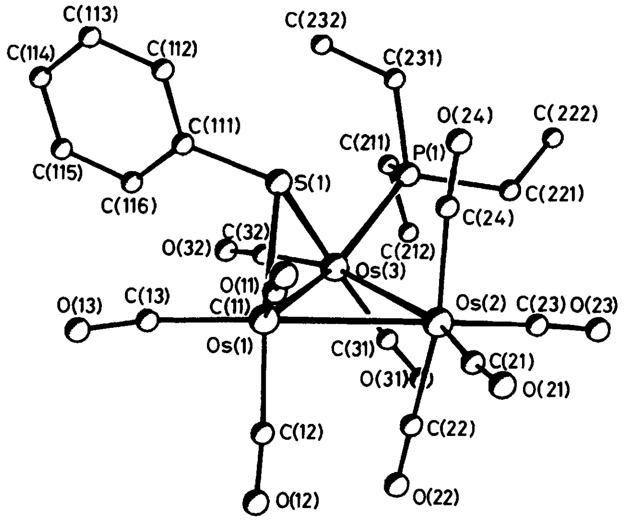


Figure 6. The molecular structure of [$Os_3H(SPh)(CO)_9(PEt_3)$] (**27**) showing the atom-numbering scheme. Hydrogen atoms have been omitted for clarity

and a 'pseudo axial' triethylphosphine which lies on the same side of the Os_3 triangle as the thiolato group. The distances of the S(1) and P(1) atoms from the plane of the Os_3 triangle are 1.88 and 1.31 Å, respectively, and the dihedral angle between the Os(1)Os(2)Os(3) and Os(1)Os(3)S(1) planes is 105.3°.

The bridged Os(1)–Os(3) distance of 2.883(1) Å is marginally longer than the range of values [2.841(3)—2.871(1) Å] found in other Os_2(μ-H)(μ-SR) systems,[13] although μ-SR groups have been found to span much longer metal–metal separations [3.791(1) Å] in Os_2(μ-X)(μ-SR) systems, where X is a ligand other than hydrogen.[14] In (**27**) the thiolato group forms a symmetrical bridge and the Os–S bond lengths [average 2.426(4) Å] are slightly longer than the range of values [2.402(6)—2.419(4) Å] found in related complexes;[13] the Os–S–Os angles do not show significant differences within this series of examples. The S(1)–C(111) bond length and S(1)–C(111)–C angles do not deviate significantly from the expected values, and the plane of the phenyl ring makes angles of 77.7 and 90.5° with the Os(1)Os(2)Os(3) and Os(1)Os(3)S(1) planes.

The bridging hydride was not located directly, but its position spanning the Os(1)–Os(3) edge is consistent with bending back of the *cis* carbonyls [average *cis* Os–Os–C 115(3)°]. The average *cis* Os–Os–C angle for the other Os–Os edges is 89(6)°.

The two unbridged Os–Os edges differ by *ca.* 0.04 Å, but the average value of 2.88(2) Å is not significantly different from the average value for the Os–Os bonds [2.877(3) Å] in [$Os_3(CO)_{12}$].[15] The longer Os(2)–Os(3) bond has the 'pseudo axial' phosphine *cis* to it and the increase in length may be consistent with the greater steric bulk of this group. A similar trend has been observed in the structure of [$Os_3(CO)_{11}\{P(OMe)_3\}$] where the phosphine occupies an equatorial site.[1]

The Os(3)–P(1) bond length [2.346(4) Å] is similar to the values of 2.361(2) and 2.329(2) Å for the related bonds in [$Os_3H_2(CO)_9(PPh_3)$][16] and [$Os_3H(OH)(CO)_9(PMe_2Ph)$],[8] respectively. The bond parameters within the triethylphosphine ligand are not significantly different from the idealised values. It is the co-ordination site of the phosphine ligand which is of interest in this case. The 'pseudo axial' site of a monophosphine ligand has not been previously structurally characterised in triosmium chemistry; however, an axial site is occupied by a phosphorus donor atom in [$Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4$-*o*$\}$].[17] In the structure of (**27**) the phosphine is approximately *trans* to the bridging hydride, but the Os(1)–Os(3)–P(1) angle is somewhat more obtuse than the equivalent Os(3)–Os(1)–C(11) angle which indicates less of a deviation from the Os_3 equatorial plane.

Table 6. Selected bond lengths (Å) and angles (°) for [$Os_3H(SPh)(CO)_9(PEt_3)$] (**27**)

Os(1)–Os(2)	2.862(1)	Os(2)–Os(3)	2.901(1)
Os(1)–Os(3)	2.883(1)	Os(1)–S(1)	2.425(4)
Os(3)–P(1)	2.346(4)	Os(3)–S(1)	2.426(4)
Os(1)–C(11)	1.903(15)	Os(2)–C(21)	1.941(20)
Os(1)–C(12)	1.885(16)	Os(2)–C(22)	1.930(16)
Os(1)–C(13)	1.911(16)	Os(2)–C(23)	1.904(16)
Os(3)–C(31)	1.863(14)	Os(2)–C(24)	1.962(17)
Os(3)–C(32)	1.878(14)		

Os(3)–Os(1)–Os(2)	60.6(1)	Os(3)–Os(2)–Os(1)	60.0(1)
S(1)–Os(1)–Os(2)	83.9(1)	C(21)–Os(2)–Os(1)	97.1(5)
S(1)–Os(1)–Os(3)	53.5(1)	C(21)–Os(2)–Os(3)	156.9(5)
C(11)–Os(1)–Os(2)	90.1(5)	C(22)–Os(2)–Os(1)	80.8(4)
C(11)–Os(1)–Os(3)	135.6(4)	C(22)–Os(2)–Os(3)	84.4(4)
C(11)–Os(1)–S(1)	93.6(5)	C(22)–Os(2)–C(21)	95.5(7)
C(12)–Os(1)–Os(2)	90.8(4)	C(23)–Os(2)–Os(1)	160.0(5)
C(12)–Os(1)–Os(3)	118.4(5)	C(23)–Os(2)–Os(3)	101.4(5)
C(12)–Os(1)–S(1)	171.8(5)	C(23)–Os(2)–C(21)	101.7(7)
C(12)–Os(1)–C(11)	92.6(7)	C(24)–Os(2)–Os(1)	91.0(4)
C(13)–Os(1)–Os(3)	112.5(5)	C(24)–Os(2)–Os(3)	85.1(4)
C(13)–Os(1)–S(1)	95.1(5)	C(24)–Os(2)–C(21)	92.9(7)
C(13)–Os(1)–C(11)	97.8(7)	C(24)–Os(2)–C(22)	169.0(6)
C(13)–Os(1)–C(12)	89.3(6)	C(24)–Os(2)–C(23)	94.9(7)
Os(2)–Os(3)–Os(1)	59.3(1)	Os(1)–S(1)–Os(1)	72.9(1)
S(1)–Os(3)–Os(1)	53.5(1)	C(111)–S(1)–Os(1)	109.4(4)
S(1)–Os(3)–Os(2)	83.1(1)	C(111)–S(1)–Os(3)	116.2(4)
P(1)–Os(3)–Os(1)	143.1(1)	P(1)–Os(3)–Os(2)	102.3(1)
P(1)–Os(3)–S(1)	95.2(1)	C(31)–Os(3)–Os(1)	115.3(4)
C(31)–Os(3)–Os(2)	81.9(5)	C(31)–Os(3)–S(1)	164.7(5)
C(31)–Os(3)–P(1)	90.7(4)	C(32)–Os(3)–Os(1)	112.2(5)
C(32)–Os(3)–Os(2)	167.3(5)	C(32)–Os(3)–S(1)	99.3(5)
C(32)–Os(3)–P(1)	89.9(5)	C(32)–Os(3)–C(31)	94.8(7)

The relatively high estimated standard deviations on the Os–C(carbonyl) and C–O distances precludes an accurate assessment of the bonding of the carbonyl groups, but the general trends in Os–C bond distances follow those expected for good π-acceptor ligands.

It has been noted previously[3] that, of the two 'pseudo axial' carbonyl ligands attached to the bridgehead osmium atoms in [$Os_3H(X)(CO)_{10}$], the carbonyl ligands *trans* to the X group are the 'most axial.' It is believed that for substituted clusters derived from [$Os_3(CO)_{12}$], the major reason for bulky ligands to bond equatorially is the axial ligand–axial ligand interaction across the metal triangle. It is thought that it is for this reason that substitution in the site *trans* to the bridging X group in [$Os_3H(X)(CO)_{10}$] is not seen. Why there is a deviation away from co-ordination in the equatorial site is not yet clear, but it seems to be due to a subtle balancing of electronic and steric effects.

Experimental

The compounds [$Os_3H(OPh)(CO)_{10}$],[18] [$Os_3H(OEt)(CO)_{10}$],[18] [$Os_3H(SEt)(CO)_{10}$],[19] and [$Os_3H(SPh)(CO)_{10}$][19] were prepared by their respective literature methods. [$Os_3H(OMe)(CO)_{10}$] and [$Os_3H(SMe)(CO)_{10}$] were prepared by direct reaction of MeOH and HSMe with [$Os_3(CO)_{10}(MeCN)_2$].[5] [$Os_3H(OH)(CO)_{10}$] was prepared by reaction of [$Os_3(CO)_{10}(MeCN)_2$] with refluxing wet diethyl ether.

Preparation of [$Os_3H(OR)(CO)_9(MeCN)$] [R = H (**1**), Me (**2**), Et (**3**), *or* Ph (**4**)].—[$Os_3H(OH)(CO)_{10}$] (23 mg, 0.027

mmol) was dissolved in MeCN (5 cm^3) and a solution of Me_3NO in MeCN (*ca.* 2 mg cm^{-3}) was added slowly. The reaction mixture was stirred for *ca.* 0.5 h, with monitoring by spot t.l.c., until all of the starting material was consumed. Chromatography on thin-layer silica plates using MeCN–CH_2Cl_2–hexane (5:30:55) as eluant isolated the acetonitrile derivative (**1**) as the major product. Yield: 16 mg, 0.018 mmol, 65%. The preparation of the compounds with R = Me, Et, or Ph was carried out in a similiar manner with the following exception. For R = Me or Et the eluant used for chromatography was CH_2Cl_2–hexane (30:70). In all cases similar results were obtained if CH_2Cl_2–MeCN (10:1) was used as the reaction solvent. Filtration of the reaction mixture through silica before removal of the solvent normally resulted in less decomposition. This procedure removes any excess Me_3NO. Average yields: $[Os_3H(OMe)(CO)_9(MeCN)]$ (**2**) (*ca.* 50%), $[Os_3H(OEt)(CO)_9(MeCN)]$ (**3**) (*ca.* 65%), and $[Os_3H(OPh)(CO)_9(MeCN)]$ (**4**) (*ca.* 55%).

Preparation of $[Os_3H(OR)(CO)_9\{P(OMe)_3\}]$ [R = H (**5**), Me (**6**), Et (**7**), *or* Ph (**8**)].—In all cases, a quantity of $[Os_3H(OR)(CO)_9(MeCN)]$ was dissolved in CH_2Cl_2 containing a small amount of MeCN. The solution was stirred briefly after the addition of 1—2 drops of $P(OMe)_3$ and the solvent then removed under vacuum. Isolation by t.l.c. using CH_2Cl_2–hexane (30:70) as eluant gave $[Os_3H(OR)(CO)_9\{P(OMe)_3\}]$ as a major product. Yields: R = H (90), Me (70), Et (70), or Ph (85%).

Preparation of $[Os_3H(OR)(CO)_8\{P(OMe)_3\}_2]$ [R = H (**9**), Me (**10**), *or* Ph (**11a**) *and* (**11b**)].—$[Os_3H(OH)(CO)_{10}]$ (20 mg, 0.023 mmol) was dissolved in MeCN, and Me_3NO (4 mg, 0.053 mmol) was added. The solution was stirred for 20 min and then filtered through silica. To this two drops of $P(OMe)_3$ were added and the solvent was then removed *in vacuo*. The product, (**9**), was isolated by t.l.c. using CH_2Cl_2–hexane (35:65) as eluant. Yield: 14.4 mg, 0.013 mmol, 59%. $[Os_3H(OMe)(CO)_8\{P(OMe)_3\}_2]$ (**10**) was prepared in a similar manner. Yield: 50%. For $[Os_3H(OPh)(CO)_8\{P(OMe)_3\}_2]$ (**11**) chromatography resulted in the separation of the two geometrical isomers (**11a**) and (**11b**). Compound (**11a**) (with the larger R_f value) was produced in 30% yield, while (**11b**) was produced in 25% yield.

Preparation of $[Os_3H(SR)(CO)_9(MeCN)]$ [R = Me (**12**)—(**14**), Et (**15**)—(**17**), *or* Ph (**18**), (**19**)].—$[Os_3H(SMe)(CO)_{10}]$ (70 mg, 0.078 mmol) was dissolved in CH_2Cl_2–MeCN (10:1, 20 cm^3) and Me_3NO (7 mg, 0.093 mmol) was added. The reaction mixture was stirred for *ca.* 30 min with the progress of the reaction being monitored by spot t.l.c. On completion, the solution was filtered through silica and the solvent removed *in vacuo*. The products, which were isolated by t.l.c. using CH_2Cl_2–hexane (30:70) as eluant, were (in order of decreasing R_f) $[Os_3H(SMe)(CO)_9(NMe_3)]$ (**20**) (7.5 mg, 0.080 mmol) (10%), $[Os_3H(SMe)(CO)_9(MeCN)]$ (**13**) (26 mg, 0.026 mmol) (34%), $[Os_3H(SMe)(CO)_9(MeCN)]$ (**14**) (19 mg, 0.021 mmol) (25%), and $[Os_3H(SMe)(CO)_9(MeCN)]$ (**12**) (20 mg, 0.021 mmol) (25%). The reactions for $[Os_3H(SEt)(CO)_{10}]$ and $[Os_3H(SPh)(CO)_{10}]$ were carried out in a similar manner (compounds are reported in order of decreasing R_f). $[Os_3H(SEt)(CO)_{10}]$ (106 mg, 0.116 mmol) gave (**16**) (25 mg, 0.027 mmol) (23%), (**17**) (22 mg, 0.024 mmol) (20%), and (**15**) (41 mg, 0.044 mmol) (38%). $[Os_3H(SPh)(CO)_{10}]$ (60 mg, 0.063 mmol) gave (**19**) (21 mg, 0.022 mmol) (34%) and (**18**) (28 mg, 0.029 mmol) (46%). Only trace amounts of the trimethylamine derivatives analogous to (**20**) were formed.

Preparation of $[Os_3H(SMe)(CO)_9(NMe_3)]$ (**20**).—The preparation is the same as above except neat CH_2Cl_2 is used as the solvent. Yields of 30—40% of (**20**) were obtained along with the return of some starting material plus decomposition products.

Table 7. Atomic co-ordinates (× 10^4) for $[Os_3H(SPh)(CO)_9(PEt_3)]$ (**27**)

Atom	X/a	Y/b	Z/c
Os(1)	9 166(1)	740(1)	1 803(1)
Os(2)	8 910(1)	765(1)	3 577(1)
Os(3)	7 094(1)	131(1)	2 435(1)
S(1)	8 515(3)	−881(3)	1 900(2)
P(1)	6 281(3)	−1 065(3)	3 216(2)
C(11)	10 686(12)	398(12)	2 000(10)
O(11)	11 588(10)	208(11)	2 141(9)
C(12)	9 497(15)	2 047(12)	1 815(9)
O(12)	9 716(11)	2 822(8)	1 765(8)
C(13)	9 122(15)	762(11)	602(10)
O(13)	9 140(13)	880(10)	−118(8)
C(21)	10 408(17)	1 171(12)	3 916(10)
O(21)	11 238(11)	1 378(12)	4 187(10)
C(22)	8 359(13)	2 019(12)	3 298(9)
O(22)	8 048(10)	2 766(9)	3 142(8)
C(23)	8 213(15)	805(13)	4 617(10)
O(23)	7 883(13)	867(11)	5 276(9)
C(24)	9 302(14)	−583(12)	3 663(9)
O(24)	9 557(12)	−1 332(9)	3 775(8)
C(31)	6 327(12)	1 057(10)	3 000(10)
O(31)	5 822(10)	1 581(9)	3 381(7)
C(32)	5 978(12)	−28(12)	1 572(9)
O(32)	5 263(11)	−82(11)	1 090(9)
C(111)	8 233(9)	−1 346(8)	866(6)
C(112)	8 751(9)	−2 203(8)	695(6)
C(113)	8 587(9)	−2 618(8)	−98(6)
C(114)	7 905(9)	−2 176(8)	−719(6)
C(115)	7 387(9)	−1 319(8)	−548(6)
C(116)	7 551(9)	−904(8)	245(6)
C(211)	4 760(13)	−1 250(13)	2 970(11)
C(212)	4 054(16)	−348(15)	3 202(17)
C(221)	6 399(17)	−869(12)	4 366(9)
C(222)	5 690(21)	−1 584(17)	4 873(13)
C(231)	6 857(16)	−2 252(12)	3 074(12)
C(232)	6 591(15)	−2 716(14)	2 250(13)

Reaction of $[Os_3H(SPh)(CO)_{10}]$ *with* Me_3NO *in* MeCN.—When the above reaction is carried out using only MeCN as the solvent the products are formed in a different ratio. In a typical reaction $[Os_3H(SPh)(CO)_{10}]$ (40 mg, 0.042 mmol) gave (**19**) (7 mg, 0.007 mmol) (12%) and (**18**) (25 mg, 0.026 mmol) (60%).

Reaction of $[Os_3H(SR)(CO)_9(MeCN)]$ *with* $P(OMe)_3$.—*Class* (a). *Acetonitrile ligand co-ordinated to one of the bridgehead osmium atoms: compounds* (**12**), (**15**), and (**18**). In each case a quantity of the acetonitrile derivative was dissolved in dichloromethane and 1—2 drops of $P(OMe)_3$ was added. The reaction mixture was stirred for 2—3 min and the solvent then removed *in vacuo*. Chromatography using CH_2Cl_2–hexane (30:70) as eluant isolated the phosphite derivatives as the major products. Yields: $[Os_3H(SMe)(CO)_9\{P(OMe)_3\}]$ (**23**) (88%), $[Os_3H(SEt)(CO)_9\{P(OMe)_3\}]$ (**24**) (70%), and $[Os_3H(SPh)(CO)_9\{P(OMe)_3\}]$ (**25**) (73%).

Class (b). *Acetonitrile ligand co-ordinated to the unique osmium atom: compounds* (**13**), (**14**), *and* (**16**), (**17**). In each case the two isomers produced the same phosphite derivative. Approximately 20 mg of the acetonitrile derivative were taken in 20 cm^3 cyclohexane and one drop of $P(OMe)_3$ added. The reaction mixture was then heated (*ca.* 50 °C) for 5—10 min with the reaction being monitored by i.r. spectroscopy. On completion, the solvent was removed and the residue chromatographed using CH_2Cl_2–hexane (30:70) as eluant. Yields:

$[Os_3H(SMe)(CO)_9\{P(OMe)_3\}]$ (**21**) (60—70%) and $[Os_3H(SEt)(CO)_9\{P(OMe)_3\}]$ (**22**) (75%).

Reactions of $[Os_3H(SPh)(CO)_9(MeCN)]$ (**18**) with PEt_3, PPh_3, or PMe_2Ph were carried out as for class (a) above to produce $[Os_3H(SPh)(CO)_9(PEt_3)]$ (**27**) (90%), $[Os_3H(SPh)(CO)_9(PPh_3)]$ (**28**) (70%), and $[Os_3H(SPh)(CO)_9(PMe_2Ph)]$ (**26**) (70%) respectively.

Crystal-structure Determination of $[Os_3H(SPh)(CO)_9(PEt_3)]$ (**27**).—Yellow crystals were obtained by slow evaporation of a pentane solution.

Crystal data. $C_{21}H_{21}O_9Os_3PS$, M = 1 051.01, monoclinic, a = 12.062(3), b = 14.101(3), c = 15.935(3) Å, β = 93.52(2)°, U = 2 705.2 Å^3 (from 2θ values of 56 centred reflections), T = 291 K, graphite-monochromated Mo-K_α radiation, λ = 0.710 69 Å, space group $P2_1/a$ (alt. $P2_1/c$, no. 14), Z = 4, D_c = 2.58 g cm^{-3}, $F(000)$ = 1 912. Yellow rectangular blocks; crystal size 0.266 × 0.266 × 0.247 mm; μ(Mo-K_α) = 142.16 cm^{-1}.

Data collection and processing.[20] Stoe-Siemens AED diffractometer, $5 < 2\theta < 50°$; $\pm h$, $+k$, $\pm l$: on-line profile fitting;[21] empirical absorption correction based on azimuthal scan measurements for 6 sets of equivalent reflections (transmission factors 0.030—0.006); no significant variation in intensity for three standard reflections. 10 378 Data, 4 765 unique (merging R = 0.072), 2 968 with $F > 5\sigma(F)$.

Structure analysis and refinement. Direct methods (Os atoms) followed by Fourier-difference syntheses. Full-matrix least-squares refinement with anisotropic Os, P, S, and carbonyl C and O atoms. Phenyl ring refined as a rigid body with C–C 1.395 Å. Phenyl and ethyl H atoms in calculated positions with one, overall, refined U_{iso} [0.082(13) Å^2]. The weighting scheme $w = 3.028/[\sigma^2(F_o) + 0.001 F_o^2]$ with $\sigma(F_o)$ from counting statistics gave reasonable agreement analyses. Final R and R' values are 0.053, 0.056. Programs and computers used and sources of scattering factors are given in ref. 20. Final atomic co-ordinates are presented in Table 7.

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