Substitution Reactions on Triosmium Clusters of the Type $[Os_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$[X = NHMe, O_2CR, C_5H_4N, or OC(NHMe); R = H, Me, or Ph]

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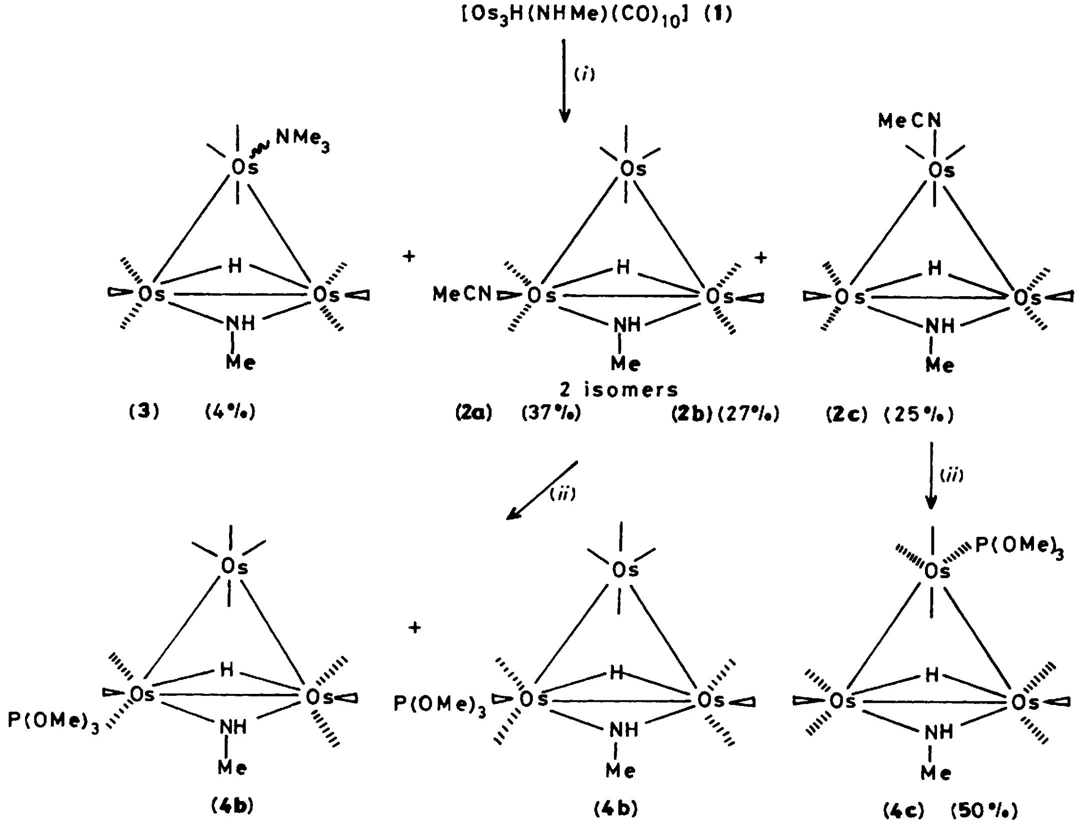
The reaction of $[Os_3H(NHMe)(CO)_{10}]$ with Me_3NO in solvents containing acetonitrile produces three isomers of the acetonitrile derivative $[Os_3H(NHMe)(CO)_9(MeCN)]$, (**2a**)—(**2c**), together with a trace of $[Os_3H(NHMe)(CO)_9(NMe_3)]$. The acetonitrile derivatives all react with $P(OMe)_3$ to give isomers of $[Os_3H(NHMe)(CO)_9\{P(OMe)_3\}]$. Prolonged reaction of (**2c**) with $P(OMe)_3$ results in two isomers of the disubstituted complex $[Os_3H(NHMe)(CO)_8\{P(OMe)_3\}_2]$. Reaction of Me_3NO with compounds of the type $[Os_3H(\mu\text{-}X)(CO)_{10}]$, where X is one of the bidentate ligands O_2CR (R = H, Me, or Ph), C_5H_4N, or O=C(NHMe), results in the formation of the trimethylamine derivatives $[Os_3H(X)(CO)_9(NMe_3)]$. These compounds react with $P(OMe)_3$ to form $[Os_3H(X)(CO)_9\{P(OMe)_3\}]$. All the products were characterised by i.r., ^1H n.m.r., and mass spectroscopy and structural assignments made.

In the preceding papers we have used[1,2] the formation of acetonitrile and phosphite derivatives of $[Os_3H(X)(CO)_{10}]$ as a means of investigating the different co-ordination sites within the molecule. We now extend this study from where the bridgehead atom of the group X is a Group 7 atom (X = Cl, Br, or I)[2] or a Group 6 atom (X = OR or SR)[1] to where the bridgehead atom is a Group 5 atom (X = NHMe). Preliminary results for compounds where X is a bidentate bridging ligand are also given.

Results and Discussion

The reaction of $[Os_3H(NHMe)(CO)_{10}]$ (**1**) with Me_3NO in CH_2Cl_2–MeCN produces three isomers of the acetonitrile derivative $[Os_3H(NHMe)(CO)_9(MeCN)]$ [(**2a**)—(**2c**)] and the complex $[Os_3H(NHMe)(CO)_9(NMe_3)]$ (**3**) (see Scheme). In this way, reaction is similar to the reaction of $[Os_3H(SMe)(CO)_{10}]$ with Me_3NO under the same conditions.[1] However, in the latter case two isomers with the acetonitrile ligand attached to the unique osmium atom were formed and



Scheme. Substitution reaction of $[Os_3H(NHMe)(CO)_{10}]$ (**1**); (*i*) Me_3NO in CH_2Cl_2–MeCN; (*ii*) $P(OMe)_3$

Table 1. Infrared (cyclohexane) and mass spectrometric data for the new compounds

Compound	$\tilde{\nu}$(CO)/cm^{-1}	*m*/*e*
(3) $[Os_3H(NHMe)(CO)_9(NMe_3)]$	2 081w, 2 047s, 2 021s, 2 011s, 1 997s, 1 972, 1 942m, 1 923w	—
(2c) $[Os_3H(NHMe)(CO)_9(MeCN)]$	2 047s, 2 021s, 1 984s, 1 972s, 1 955m	900
(2b) $[Os_3H(NHMe)(CO)_9(MeCN)]$	2 086m, 2 043s, 2 011vs, 2 003ms, 1 987m, 1 980m, 1 966m, 1 955m, 1 945m	900
(2a) $[Os_3H(NHMe)(CO)_9(MeCN)]$	2 091m, 2 049s, 2 013s, 2 003s, 1 995s, 1 978ms, 1 970ms, 1 943m	—
(4c) $[Os_3H(NHMe)(CO)_9\{P(OMe)_3\}]$	2 084w, 2 056s, 2 021m, 1 999s, 1 979m, 1 964w, 1 947w	983
(4a) $[Os_3H(NHMe)(CO)_9\{P(OMe)_3\}]$	2 088m, 2 047s, 2 011s, 1 992ms, 1 981ms, 1 971ms, 1 947m	983
(4b) $[Os_3H(NHMe)(CO)_9\{P(OMe)_3\}]$	2 088m, 2 047s, 2 010m (sh), 2 008s, 1 993ms, 1 980ms, 1 975ms, 1 957ms	983
(5b) $[Os_3H(NHMe)(CO)_8\{P(OMe)_3\}_2]$	2 068m, 2 023s, 1 995s, 1 990s, 1 968m, 1 953m, 1 943m, 1 938mw (sh)	1 079
(5a) $[Os_3H(NHMe)(CO)_8\{P(OMe)_3\}_2]$	2 068m, 2 023s, 1 995s, 1 965m, 1 962m, 1 953m, 1 943m	1 079
(1) $[Os_3H(NHMe)(CO)_{10}]$	2 104mw, 2 065s, 2 051s, 2 020s, 2 003s, 1 991s, 1 979m, 1 953vw, br	887
$[Os_3H\{O{=}C(NHMe)\}(CO)_9(NMe_3)]$	2 094m, 2 050s, 2 015s, 2 006s, 1 995s, 1 977m, 1 967m, 1 927m	946
(6) $[Os_3H(O_2CH)(CO)_9(NMe_3)]$	2 103m, 2 062s, 2 022s, 2 015s, 2 004s, 1 995m, 1 983m, 1 980m (sh), 1 934m	933
(7) $[Os_3H(O_2CMe)(CO)_9(NMe_3)]$	2 101mw, 2 060ms, 2 021s, 2 013s, 2 001s, 1 993m, 1 980m, 1 978m (sh), 1 932	947
(8) $[Os_3H(O_2CPh)(CO)_9(NMe_3)]$	2 101m, 2 060s, 2 019vs, 2 014s, 2 003s, 1 992m, 1 992m, 1 980m, br, 1 931m	1 009
(12) $[Os_3H(C_5H_4N)(CO)_9(NMe_3)]$	2 093m, 2 048s, 2 015s, 2 007s, 1 993s, 1 975m, 1 968m, 1 928m	—
(15) $[Os_3H\{O{=}C(NHMe)\}(CO)_9\{P(OMe)_3\}]$	2 091m, 2 049s, 2 022m, 2 011s, 1 998s, 1 989m, 1 980m, 1 967m, 1 955m	1 011
(9) $[Os_3H(O_2CH)(CO)_9\{P(OMe)_3\}]$	2 099m, 2 059s, 2 029ms, 2 025ms, 2 017s, 2 001s, 1 980m, 1 970vw, 1 960vw	998
(10) $[Os_3H(O_2CMe)(CO)_9\{P(OMe)_3\}]$	2 099m, 2 058s, 2 020ms, 2 023ms, 2 016s, 1 999s, 1 978m, 1 968vw, 1 958vw	1 012
(11) $[Os_3H(O_2CPh)(CO)_9\{P(OMe)_3\}]$	2 099m, 2 058s, 2 028ms, br, 2 016s, 2 003s, 1 978m, 1 966vw, 1 958vw	1 074
(14) $[Os_3H(C_5H_4N)(CO)_9\{P(OMe)_3\}]$	2 090m, 2 047s, 2 021ms, 2 018ms, 2 010s, 1 999s, 1 989mw, 1 977mw, 1 968m	1 031

Table 2. ^1H N.m.r. data for compounds containing a (μ-NHMe) group (δ/p.p.m. relative to $SiMe_4$, *J* values in Hz, $CDCl_3$ solvent)

Compound	NH (br, 1 H)	NMe (d, 3 H)		MeCN(s, 3 H) or $P(OMe)_3$ (d, 9 H)		Metal–Hydride (d, 1 H)	
	δ	δ	J_{HH}	δ	J_{PH}	δ	J_{HH}
(1) $[Os_3H(NHMe)(CO)_{10}]$	3.99	3.34	6.2	—		−14.82 J_{OsH} 34	2.8
(2c) $[Os_3H(NHMe)(CO)_9(MeCN)]$	4.15	3.39	6.1	2.54		−14.02	2.7
(2b) $[Os_3H(NHMe)(CO)_9(MeCN)]$	4.22	3.41	6.2	2.68		−19.48 (s)	—
(2a) $[Os_3H(NHMe)(CO)_9(MeCN)]$	3.67	2.90	5.2	2.48		−13.59	2.4
(3) $[Os_3H(NHMe)(CO)_9(NMe_3)]$	3.71	3.33	6.1	*		−14.28	2.2
(4c) $[Os_3H(NHMe)(CO)_9\{P(OMe)_3\}]$	4.00	3.33	6.0	3.64	12.3	−14.59 (t) J_{PH} 3.0	3.0
(4a) $[Os_3H(NHMe)(CO)_9\{P(OMe)_3\}]$	*ca.* 3.86	3.24	6.1	3.78	12.5	−14.99 (dd) J_{PH} 55	2.4
(4b) $[Os_3H(NHMe)(CO)_9\{P(OMe)_3\}]$	3.92	3.05	6.2	3.70	11.9	−15.04 (dd) J_{PH} 7.5	3.0
(5a) $[Os_3H(NHMe)(CO)_8\{P(OMe)_3\}_2]$	3.98	3.24	5.9	3.75 3.59	11.4 12.3	−14.94 (dt) J_{PH} 2.2 J_{PH} 56.5	2.2
(5b) $[Os_3H(NHMe)(CO)_8\{P(OMe)_3\}_2]$	4.07	3.03	6.3	3.68 3.62	11.9 12.3	−14.87 (m)	

* NMe_3: δ 3.23 (s, 9 H).

only one with the ligand attached to the bridgehead osmium atoms. The new compounds were characterised as far as possible by comparison of i.r. spectra with those for the compounds produced in the $[Os_3H(SMe)(CO)_{10}]$ system. ^1H N.m.r. and i.r. spectroscopic data are summarised in Tables 1 and 2.

Compound **(3)** was difficult to obtain pure and is formed in low yield and so characterisation was difficult. The ^1H n.m.r. spectrum of **(3)** showed peaks at δ 3.71 (br, 1 H), 3.33 (d, 3 H, J_{HH} 6.1), 3.23 (s, 9 H), and −14.28 (d, 1 H, J_{HH} 2.2 Hz), which were assigned to the NH, NMe, NMe_3, and metal–hydride groups respectively {*cf.* δ 3.04 for NMe_3 in $[Os_3H(Cl)(CO)_9(NMe_3)]$[2]}. Compound **(2c)** was identified by comparison of i.r. spectra as having the same structure as the isomer of the analogous $[Os_3H(SMe)(CO)_9(MeCN)]$ derivative. Unfortunately, the exact stereochemistry of this compound is still in doubt but it is proposed that the acetonitrile ligand is bound axially on the unique osmium

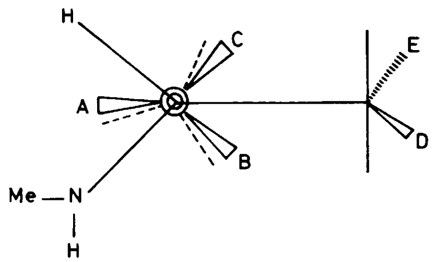


Figure 1. Projection of $[Os_3H(NHMe)(CO)_{10}]$ (**1**) along the osmium–osmium bridgehead bond showing various co-ordination sites for the phosphite ligands in $[Os_3H(NHMe)(CO)_8\{P(OMe)_3\}_2]$ (**5a**) and (**5b**)

atom and is on the same side of the Os_3 triangle as the bridging hydride.

It is the formation of the isomers (**2a**) and (**2b**) in this reaction that is of particular interest. Compound (**2a**) decomposes slowly in the absence of MeCN, whereas (**2b**) is reasonably stable. These compounds have similar i.r. spectra, and display the same pattern to other $[Os_3H(X)(CO)_9L]$ (L = MeCN or NMe_3) species where the ligand L is attached to one of the bridgehead osmium atoms.[1,2] ^1H N.m.r. spectroscopy reveals that the metal–hydride resonance for (**2a**) occurs at δ -13.59 (d, 1 H), whereas, that for (**2b**) is at δ -19.48 (s). From work previously reported[1,2] it has been observed that for compounds with the acetonitrile ligand co-ordinated to one of the bridgehead osmium atoms, the resonance for the bridging hydride is 1—2 p.p.m. downfield from that of the parent compound $[Os_3H(X)(CO)_{10}]$. Therefore, isomer (**2a**) appears to fit into this category while (**2b**) does not. The metal–hydride resonance for $[Os_3H(NHMe)(CO)_{10}]$ (**1**) is at δ -14.82 p.p.m. It is therefore proposed that isomer (**2a**) has the acetonitrile ligand co-ordinated *trans* to the bridging hydride (as seen for some phosphorus donor ligands in the preceding paper[1]).

All three acetonitrile derivatives (**2a**)—(**2c**) react with $P(OMe)_3$ to form the various phosphite derivatives (**4a**)—(**4c**) (yields 50—70%) (Scheme). Compound (**2a**) reacts at room temperature to produce compound (**4a**) in 70% yield with only trace amounts of (**4b**) while the thermal reaction of (**2b**) results in a 41% yield of (**4b**) and 26% of (**4a**). These two species were found to interconvert in solution to give (**4a**) as the major equilibrium species (60:40) by ^1H n.m.r. The isolation of isomers (**4b**) and (**4a**) as separate pure compounds confirms the assignment of spectroscopic data for the related isomers of $[Os_3H(OR)(CO)_9\{P(OMe)_3\}]$ and $[Os_3H(SR)(CO)_9\{P(OMe)_3\}]$[1] (R = Me, Et, or Ph) where separation was not achieved.

Care had to be taken in the reaction of (**2c**) with $P(OMe)_3$, as it was found that further substitution of carbonyl ligands by phosphite could occur. Prolonged heating gave two compounds [(**5a**) and (**5b**)] of formula $[Os_3H(NHMe)(CO)_8\{P(OMe)_3\}_2]$, as determined by mass spectroscopy. It was also found that (**4c**) reacts further with $P(OMe)_3$ to give (**5a**) and (**5b**). ^1H N.m.r. spectroscopy of (**5a**) revealed that the bridging hydride resonance consisted of a doublet of triplets with $J_{PH} = 56.5$ and $J_{PH} = J_{HH} = 2.2$ Hz[*] while for (**5b**) it was a multiplet of width 8 Hz. The two compounds were found to interconvert in solution to give a *ca.* 50:50 equilibrium mixture. These data are consistent with (**5a**) and (**5b**) having one phosphite attached to one of the bridgehead osmium atoms with the other co-ordinated to the unique osmium atom.

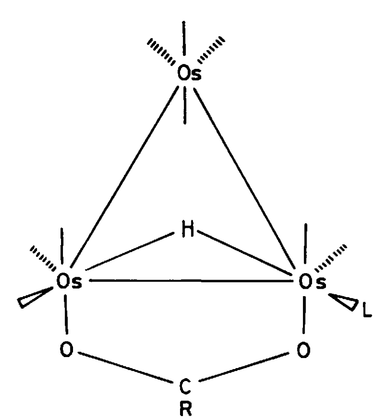


Figure 2. Structure of $[Os_3H(O_2CR)(CO)_{10}]$ (L = CO) and proposed structures for $[Os_3H(O_2CR)(CO)_9(NMe_3)]$ (L = NMe_3) and $[Os_3H(O_2CR)(CO)_9\{P(OMe)_3\}]$ [L = $P(OMe)_3$]

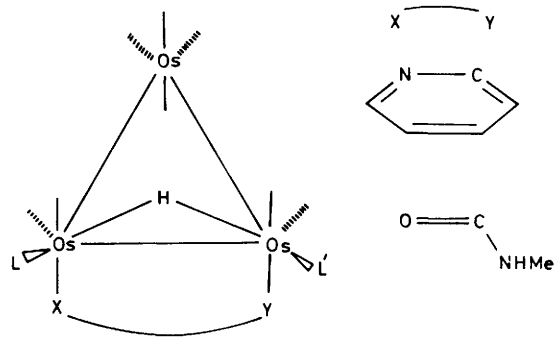


Figure 3. Structures of $[Os_3H(C_5H_4N)(CO)_{10}]$ and $[Os_3H\{O=C(NHMe)\}(CO)_{10}]$ showing the two possible co-ordination sites L and L′ for the trimethylamine and trimethyl phosphite derivatives

The ^1H n.m.r. evidence indicates that compound (**5a**) has the $P(OMe)_3$ ligand in position B (see Figure 1) on the bridgehead osmium atom while (**5b**) has this ligand in position A. It is believed that the phosphite ligand will co-ordinate in an equatorial site on the unique osmium atom, and so for compound (**5b**) both positions D and E are available giving rise to the complicated spectrum. For compound (**5a**) it is thought that position D will not be favoured due to steric hindrance from the phosphite ligand at position B.

The compounds $[Os_3H(O_2CR)(CO)_{10}]$ (R = H, Me, or Ph) (Figure 2) react swiftly with Me_3NO in CH_2Cl_2 to produce the yellow compounds $[Os_3H(O_2CR)(CO)_9(NMe_3)]$ [R = H (**6**), Me (**7**), or Ph (**8**)]. In all cases it was found that the addition of one equivalent of Me_3NO did not result in complete conversion to the trimethylamine derivative. Traces of starting material were always left, and addition of excess Me_3NO resulted in decomposition. It was found that addition of *ca.* 0.75 equivalents of Me_3NO, followed by separation of the starting material from the product resulted in the lowest amount of decomposition. The starting material could then be recycled to increase the yield. Infrared spectroscopic evidence (Table 1) suggests that (**6**), (**7**), and (**8**) have structures similar to those compounds with the MeCN or NMe_3 ligand attached to one of the bridgehead osmium atoms.[1,2]

Reaction of (**6**)—(**8**) with $P(OMe)_3$ occurs at elevated temperature (10 min reflux in cyclohexane) to give high yields of the phosphite derivatives $[Os_3H(O_2CR)(CO)_9\{P(OMe)_3\}]$ [R = H (**9**), Me (**10**), or Ph (**11**)]. The magnitude of the phosphorus–hydrogen coupling constants for the metal–hydride resonances (*ca.* 10 Hz) indicates that the phosphite ligand is attached to one of the bridgehead osmium atoms, and lies in an equatorial site *cis* to the bridging hydride.

For the compounds $[Os_3H(C_5H_4N)(CO)_{10}]$ and $[Os_3H-$

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[*] Spectra were run on a 100 and 250 MHz spectrometer with decoupling.

Table 3. ^1H n.m.r. data for $[Os_3H(X)(CO)_9L]$ (X = bidentate bridging ligand) (δ/p.p.m. relative to $SiMe_4$, J values in Hz, $CDCl_3$ solvent)

Compound	Metal–Hydride (s, 1 H)		NMe_3 (s, 9 H)	$P(OMe)_3$ (d, 9 H)		Others
	δ	J_{PH}	δ	δ	J_{PH}	
(6) $[Os_3H(O_2CH)(CO)_9(NMe_3)]$	−9.38		3.11			8.07 (s, 1 H)
(9) $[Os_3H(O_2CH)(CO)_9\{P(OMe)_3\}]$	−10.57	12.2		3.83	11.4	7.47 (d, 1 H) J_{PH} 1.9
(7) $[Os_3H(O_2CMe)(CO)_9(NMe_3)]$	−9.35		3.09			2.06 (s, 3 H)
(10) $[Os_3H(O_2CMe)(CO)_9\{P(OMe)_3\}]$	−10.56	12.2		3.79	9.2	1.91 (s, 3 H)
(8) $[Os_3H(O_2CPh)(CO)_9(NMe_3)]$	−9.13		3.12			7.85 (m, 2 H) 7.36 (m, 3 H)
(11) $[Os_3H(O_2CPh)(CO)_9\{P(OMe)_3\}]$	−10.34	12.2		3.77	12.1	7.66 (m, 2 H) 7.31 (m, 3 H)
(15) $[Os_3H\{O{=}C(NHMe)\}(CO)_9\{P(OMe)_3\}]$	−14.37	9.7		3.73	12.1	2.64 (d, 3 H) J_{HH} 4.9 5.78 (br, 1 H)
(12) $[Os_3H(C_5H_4N)(CO)_9(NMe_3)]$*	−13.25		2.83			8.27 (d, 1 H) J_{HH} 5.0 7.52 (d, 1 H) J_{HH} 6.8 7.23 (dd, 1 H) J_{HH} 6.8, 9.6 6.83 (m, 1 H)
(14) $[Os_3H(C_5H_4N)(CO)_9\{P(OMe)_3\}]$*	−15.04	10.1		3.57	12.2	8.03 (d, 1 H) J_{HH} 6.0 7.16 (m, 2 H) 6.60 (m, 1 H)

* Recorded in CD_2Cl_2.

Table 4. Analytical data

Compound	Found (%)			Calc. (%)		
	C	H	N	C	H	N
(2b) $[Os_3H(NHMe)(CO)_9(MeCN)]$	16.30	1.35	2.55	16.10	0.90	3.15
(2c) $[Os_3H(NHMe)(CO)_9(MeCN)]$	16.70	1.35	3.05	16.10	0.90	3.15
(4) $[Os_3H(NHMe)(CO)_9\{P(OMe)_3\}]$	15.90	1.35	1.35	15.95	1.45	1.45
$[Os_3H\{O{=}C(NHMe)\}(CO)_{10}]$	15.60	0.55	1.45	15.85	0.55	1.55
(13) $[Os_3H\{O{=}C(NHMe)\}(CO)_9(NMe_3)]$	18.45	1.55	2.60	17.90	1.50	3.00
(7) $[Os_3H(O_2CMe)(CO)_9(NMe_3)]$	17.90	1.50	1.20	17.85	1.40	1.50
(9) $[Os_3H(O_2CH)(CO)_9\{P(OMe)_3\}]$	15.95	1.15	—	15.75	1.10	—
(14) $[Os_3H(C_5H_4N)(CO)_9\{P(OMe)_3\}]$	20.10	1.40	1.75	19.90	1.35	1.35

$\{O{=}C(NHMe)\}(CO)_{10}]$, containing asymmetric bidentate ligands, reaction with Me_3NO in CH_2Cl_2 produces moderate yields of the compounds $[Os_3H(C_5H_4N)(CO)_9(NMe_3)]$ **(12)** and $[Os_3H\{O{=}C(NHMe)\}(CO)_9(NMe_3)]$ **(13)** respectively. I.r. spectroscopy indicates that the trimethylamine ligand is attached to one of the bridgehead osmium atoms and ^1H n.m.r. spectroscopic evidence suggests that only one of the two possible isomers is present in each case (Figure 3). However, on the basis of the above data it was not possible to tell which isomer was present.

Compounds **(12)** and **(13)** react with $P(OMe)_3$ to produce $[Os_3H(C_5H_4N)(CO)_9\{P(OMe)_3\}]$ **(14)** and $[Os_3H\{O{=}C(NHMe)\}(CO)_9\{P(OMe)_3\}]$ **(15)** respectively. Again, i.r. and ^1H n.m.r. (Table 3) spectroscopy suggested that only one of the two possible isomers are present and that the phosphite ligand is co-ordinated to one of the bridgehead osmium atoms, lying in the equatorial plane *cis* to the bridging hydride. However, there is no indication as to which isomer is formed.

Experimental

The compound $[Os_3H(C_5H_4N)(CO)_{10}]$ was prepared by the literature method,[3] and the compounds $[Os_3H(O_2CR)(CO)_{10}]$ (R = H, Me, or Ph) prepared by a modification of the literature synthesis, using $[Os_3(CO)_{10}(MeCN)_2]$ instead of $[Os_3(CO)_{10}(C_6H_8)]$ as the starting material.[4] Analytical data for the new compounds are given in Table 4.

Preparation of $[Os_3H\{O{=}C(NHMe)\}(CO)_{10}]$.—$[Os_3(CO)_{11}(MeCN)]$[3] (93 mg) was dissolved in CH_2Cl_2 (60 cm^3). Nitrogen was bubbled through this solution for 10 min before bubbling methylamine gas through for 5 min. The solvent was then removed and the residue chromatographed (t.l.c.) using CH_2Cl_2–hexane (1:1.14 v/v) as eluant. Yield: 60 mg (65%).

Preparation of $[Os_3H(NHMe)(CO)_{10}]$ **(1)**.—$[Os_3H(Cl)(CO)_{10}]$[3] (108 mg) was dissolved in cyclohexane (30 cm^3), and with methylamine gas bubbling through the reaction mixture, the solvent was brought to reflux for 10 min. $[Os_3H(NHMe)(CO)_{10}]$ was isolated as the major product by t.l.c. using hexane as eluant. Yield: 74 mg (67%).

Reaction of $[Os_3H(NHMe)(CO)_{10}]$ *with* Me_3NO.—$[Os_3H(NHMe)(CO)_{10}]$ (47 mg) was dissolved in CH_2Cl_2 (20 cm^3) with MeCN (2 cm^3) added. To this, Me_3NO (4.5 mg) was added, and the reaction mixture stirred for *ca.* 30 min, with the reaction being monitored by spot t.l.c. After filtration through silica the solvent was removed *in vacuo* and the residue chromatographed using CH$_2$Cl$_2$–hexane (1:4 v/v) as eluant. Compounds isolated, in order of decreasing R_f, were [Os$_3$H(NHMe)(CO)$_{10}$] (**1**) (2 mg), [Os$_3$H(NHMe)(CO)$_9$ (NMe$_3$)] (**3**) (2 mg, 4%), [Os$_3$H(NHMe)(CO)$_9$(MeCN)] (**2c**) (12 mg, 25%), [Os$_3$H(NHMe)(CO)$_9$(MeCN)] (**2b**) (13 mg, 27%), and [Os$_3$H(NHMe)(CO)$_9$(MeCN)] (**2a**) (18 mg, 37%).

Reaction of [Os$_3$H(NHMe)(CO)$_9$(MeCN)] (**2a**)—(**2c**) *with* P(OMe)$_3$.—(*a*) [Os$_3$H(NHMe)(CO)$_9$(MeCN)] (**2a**) (13 mg) was dissolved in cyclohexane (10 cm^3), and 1 drop of P(OMe)$_3$ was added. The solution instantaneously changed colour from a light yellow to a darker yellow. The solvent was removed and the product isolated by t.l.c. using CH$_2$Cl$_2$–hexane (1:4 v/v) as eluant. Yield of [Os$_3$H(NHMe)(CO)$_9${P(OMe)$_3$}] (**4a**) 11 mg (70%). There was a small quantity of the compound [Os$_3$H(NHMe)(CO)$_9${P(OMe)$_3$}] (**4b**) eluting just in front of (**4a**).

(*b*) The reaction of (**2b**) with P(OMe)$_3$ was carried out in the same way as for (**2a**) but refluxing in cyclohexane for 20 min was required before the reaction was complete. Isolation of the products by t.l.c. using CH$_2$Cl$_2$–hexane (1:25 v/v) gave [Os$_3$H(NHMe)(CO)$_9${P(OMe)$_3$}] (**4b**) (41%) and [Os$_3$H(NHMe)(CO)$_9${P(OMe)$_3$}] (**4a**) (26%).

(*c*) The reaction of (**2c**) with P(OMe)$_3$ was carried out in the same manner as (*b*) above, with frequent monitoring by i.r. spectroscopy. Prolonged heating results in the formation of the disubstituted phosphite derivatives [Os$_3$H(NHMe)(CO)$_8${P(OMe)$_3$}$_2$] (**5a**) and (**5b**). With care up to 50% yields of [Os$_3$H(NHMe)(CO)$_9${P(OMe)$_3$}] (**4c**) were obtained, whereas on prolonged heating the combined yield of (**5a**) and (**5b**) was 75%. The compounds produced were separated by chromatography using ethyl acetate–hexane (1:4 v/v) as eluant.

Preparation of [Os$_3$H(O$_2$CR)(CO)$_9$(NMe$_3$)] [R = H (**6**), Me (**7**), *or* Ph (**8**)].—In each case [Os$_3$H(O$_2$CR)(CO)$_{10}$] was dissolved in CH$_2$Cl$_2$ and 0.75 molar equivalents of Me$_3$NO added. The reaction mixture was stirred for 10 min, and then the solvent was removed *in vacuo*. Chromatography [CH$_2$Cl$_2$–hexane (1:3 v/v)] resulted in the separation of the faster eluting starting material from the product. The starting material was then recycled to increase the quantity of the trimethylamine derivative obtained. Yields: (**6**) 70%, (**7**) 70%, and (**8**) 55%.

Reaction of [Os$_3$H(O$_2$CR)(CO)$_9$(NMe$_3$)] *with* P(OMe)$_3$.—A quantity of [Os$_3$H(O$_2$CR)(CO)$_9$(NMe$_3$)] was added to cyclohexane with 1 drop of P(OMe)$_3$. The reaction mixture was refluxed for *ca.* 10 min and the solvent removed *in vacuo*. Chromatography using CH$_2$Cl$_2$–hexane as the eluant was used to isolate the compounds [Os$_3$H(O$_2$CR)(CO)$_9${P(OMe)$_3$}] as the major products. Yields: R = H (**9**) 80%, R = Me (**10**) 80%, R = (**11**) 95%.

Preparation of [Os$_3$H(C$_5$H$_4$N)(CO)$_9$(NMe$_3$)] (**12**) *and* [Os$_3$H(C$_5$H$_4$N)(CO)$_9${P(OMe)$_3$}] (**14**).—(*a*) To [Os$_3$H(C$_5$H$_4$N)(CO)$_{10}$] (35 mg) dissolved in CH$_2$Cl$_2$ (25 cm^3), Me$_3$NO (*ca.* 1 equivalent) was added over a period of 15 min until no starting material remained (as indicated by spot t.l.c.). The reaction mixture was filtered through silica, and the solvent removed *in vacuo*. The residue was chromatographed using CH$_2$Cl$_2$–hexane (30:70) as eluant to yield compound (**12**) as the major product (yield: 18 mg, 50%). A thick line of decomposition products remained at the bottom of the plates, and the compound showed signs of decomposing as it eluted.

(*b*) The phosphite derivative (**14**) was prepared by synthesising (**12**) as before, and reacting it with P(OMe)$_3$ before isolation. To the residue, achieved by the removal of the solvent from the reaction mixture, CH$_2$Cl$_2$ (20 cm^3) containing 1 drop of P(OMe)$_3$ was added. This was stirred for 5 min and then the product was isolated by t.l.c. using CH$_2$Cl$_2$–hexane (30:70) as eluant. [Os$_3$H(C$_5$H$_4$N)(CO)$_{10}$] (20 mg) gave 14 mg (64%) of (**14**).

Preparation of [Os$_3$H{O=C(NHMe)}(CO)$_9$L][L = NMe$_3$ (**13**) *or* P(OMe)$_3$ (**15**)].—(*a*) [Os$_3$H{O=C(NHMe)}(CO)$_{10}$] (20 mg) was dissolved in CH$_2$Cl$_2$ (20 cm^3) and Me$_3$NO added until no starting material remained (as monitored by i.r. spectroscopy). The solvent was removed under vacuum and the residue chromatographed using CH$_2$Cl$_2$–hexane (1:1 v/v) as eluant. The product, (**13**), was isolated as the only eluting band. Yield: 13 mg (63%).

(*b*) [Os$_3$H{O=C(NHMe)}(CO)$_9$(NMe$_3$)] was added to cyclohexane (15 cm^3) and 1 drop of P(OMe)$_3$ was added. The reaction mixture was heated slightly to dissolve (**13**), whereupon i.r. spectroscopy indicated that reaction had occurred. Removal of solvent and chromatography, using CH$_2$Cl$_2$–hexane (1:1 v/v) as eluant, resulted in the isolation of [Os$_3$H{O=C(NHMe)}(CO)$_9${P(OMe)$_3$}] (**15**). Yield: 14.5 mg (90%).

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