The Preparation, Characterisation, and some Reactions of $[Os_3H(X)(CO)_9(NMe_3)]$ (X = Cl, Br, or I)

Evert J. Ditzel, Brian E. Hanson, Brian F. G. Johnson, and Jack Lewis *
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The clusters $[Os_3H(X)(CO)_{10}]$ (X = Cl, Br, or I) react with trimethylamine oxide to produce the complexes $[Os_3H(X)(CO)_9(NMe_3)]$. The trimethylamine ligand of these compounds is readily displaced by $P(OMe)_3$ to give $[Os_3H(X)(CO)_9\{P(OMe)_3\}]$. The compound $[Os_3H(Cl)(CO)_9(NMe_3)]$ also reacts with ethylene, phenylacetylene, and PPh_3 to give $[Os_3H(Cl)(CO)_9(C_2H_4)]$, $[Os_3Cl(CO)_{10}(CHCHPh)]$, or $[Os_3H(Cl)(CO)_9(PPh_3)]$ respectively. The compound $[Os_3H(Cl)(CO)_8(PPh_3)_2]$ can also be prepared by the reaction of $[Os_3H(Cl)(CO)_{10}]$ with 2.5 equivalents of Me_3NO followed by PPh_3. All the products were characterised by i.r. and ^1H n.m.r. spectroscopy, and structural assignments made.

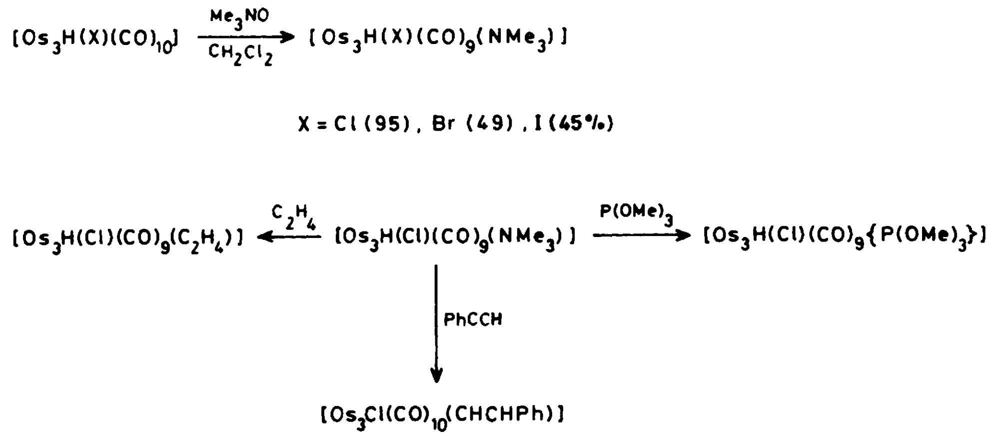
Our interest in the substitution chemistry of triosmium clusters utilizing trimethylamine oxide as a decarbonylating reagent has led us to an investigation of the reaction of Me_3NO with the compounds $[Os_3H(X)(CO)_{10}]$. A previous study[1] on the reaction of $[Os_3(CO)_{10}(NO)_2]$ with Me_3NO showed that the trimethylamine co-ordinated preferentially to the osmium cluster even when the reaction was performed in the presence of phosphines. In this paper we now report the preparation of $[Os_3H(X)(CO)_9(NMe_3)]$ from the reaction of $[Os_3H(X)(CO)_{10}]$ (X = Cl, Br, or I) with Me_3NO. The reactivity of these compounds towards substitution of the NMe_3 ligand is investigated.

Results and Discussion

Dichloromethane solutions of $[Os_3H(X)(CO)_{10}]$ (X = Cl, Br, or I) react with Me_3NO to produce good yields of $[Os_3H(X)(CO)_9(NMe_3)]$ [X = Cl (**1**), Br (**2**), or I (**3**)] (see Scheme). In general the reactions {which were monitored by i.r. spectroscopy following the disappearance of the bands [ν(CO)] due to the starting material} required slightly more than a stoicheiometric amount of Me_3NO. All products were obtained as moderately air-stable yellow solids. The ^1H n.m.r. spectra of these compounds show, in addition to the high-field metal–hydride singlets, resonances at δ 3.04 (**1**), 3.07 (**2**), or 3.15 (**3**). These may be assigned to the co-ordinated trimethylamine ligand {*cf.* δ 3.25 for $[Os_3H_2(CO)_9(NMe_3)]$[2] and δ 3.23 for $[Os_3H_2(CO)_8(\mu_3\text{-}S)(NMe_3)]$[3–5]}.

The reaction of $[Os_3H(Cl)(CO)_{10}]$ with Me_3NO in a mixed dichloromethane–acetonitrile solvent was attempted in an effort to make an analogous acetonitrile derivative. However, although i.r. spectroscopy and spot chromatography of the reaction mixture indicated a product other than (**1**), the compound was too unstable to be isolated. The compound appeared to require the presence of some free acetonitrile for stability.

The reaction of compound (**3**) with $P(OMe)_3$ in CH_2Cl_2, and compounds (**1**) and (**2**) with $P(OMe)_3$ in refluxing CH_2Cl_2 results in the formation of the compounds $[Os_3H(X)(CO)_9\{P(OMe)_3\}]$ [X = Cl (**4**), Br (**5**), or I(**6**)] in good yields (69, 90, and 90% respectively). The i.r. and n.m.r. spectroscopic data for these compounds are summarised in Table 1. The ^1H n.m.r. metal–hydride resonances exhibit phosphorus–hydrogen coupling constants of the order of 7 Hz. This would suggest that the phosphite ligand is co-ordinated to one of the bridgehead osmium atoms. A comparison with data for structurally characterised compounds of a related nature[4] suggests that the phosphite ligand lies in the equatorial plane (Figure 1). Comparison of the i.r. data for compounds (**1**)—(**3**) with those for compounds (**4**)—(**6**) suggests that the trimethylamine derivatives have the same gross structure as the phosphite derivatives (*i.e.* the NMe_3 ligand is co-ordinated to one of the bridgehead osmium atoms). It is not certain that the ligands are in the same stereochemical arrangement although the solid-state structure of $[Os_3(CO)_9(NO)_2(NMe_3)]$[1] leads us to suggest that the NMe_3 ligand also is in the plane of the Os_3 triangle.



Scheme.

Table 1. Spectroscopic data for the new compounds

Compound	$\tilde{\nu}(CO)^{a}/cm^{-1}$	^{1}H n.m.r.^{b} (δ/p.p.m.)	Mass spectrum m/e^{c}
(**1**) $[Os_3H(Cl)(CO)_9(NMe_3)]$	2 104m, 2 061s, 2 021vs, 2 006s, 1 998m, 1 987m, 1 981w, 1 938m	3.04 (s, 9 H) −11.81 (s, 1 H)	925
(**2**) $[Os_3H(Br)(CO)_9(NMe_3)]$	2 103m, 2 061s, 2 020vs, 2 005s, 1 997ms, 1 986m, 1 980w, 1 937m	3.07 (s, 9 H) −12.50 (s, 1 H)	968
(**3**) $[Os_3H(I)(CO)_9(NMe_3)]$	2 102m, 2 060s, 2 019vs, 2 004s, 1 996ms, 1 985m, 1 980w (sh), 1 935m	3.15 (s, 9 H) −13.63 (s, 1 H)	984^{d}
(**4**) $[Os_3H(Cl)(CO)_9\{P(OMe)_3\}]$	2 101m, 2 061vs, 2 024s, 2 015vs, 2 009m (sh), 1 988m, 1 980m, 1 968w	3.70 (d, 9 H, J_{PH} 12.0) −14.24 (d, 1 H, J_{PH} 7.9)	990
(**5**) $[Os_3H(Br)(CO)_9\{P(OMe)_3\}]$	2 100m, 2 069vs, 2 025s, 2 015vs, 2 008m (sh), 1 986m, 1 979m, 1 964w	3.69 (d, 9 H, J_{PH} 12.0) −15.09 (d, 1 H, J_{PH} 7.0)	1 033
(**6**) $[Os_3H(I)(CO)_9\{P(OMe)_3\}]$	2 098m, 2 058vs, 2 024s, 2 015vs, 2 010s (sh), 2 003m, 1 985m, 1 980m, 1 963w	3.68 (d, 9 H, J_{PH} 12.2) −16.58 (d, 1 H, J_{PH} 7.2)	1 080
(**7**) $[Os_3H(Cl)(CO)_9(PPh_3)]$	2 098ms, 2 060s, 2 020s, 2 014s br, 2 005m (sh), 1 986m, 1 979m, 1 958m	−13.27 (d, 1 H, J_{PH} 6.9)	—
(**8**) $[Os_3H(Cl)(CO)_9(C_2H_4)]$	2 105m, 2 068s, 2 033m, 2 025vs, 2 012w, 2 008w, 1 993w, 1 986w, 1 967m	3.46 (m, 4 H) −13.99 (s, 1 H)	894
(**9**) $[Os_3Cl(CO)_{10}(CHCHPh)]$	2 104m, 2 068s, 2 056m, 2 018s, 2 007s, 1 999m, 1 990w, 1 984w, 1 976m	7.41 (m, 5 H) 6.83 (d, 1 H, J_{HH} 16.1) 6.36 (d, 1 H)	996
(**10**) $[Os_3H(Cl)(CO)_8(PPh_3)_2]$	2 079s, 2 015vs, 2 008s, 2 002vs, 1 958mw, 1 947m	7.24 (m, 30 H) −12.71 (t, 1 H, J_{PH} 6.7)	

[a] Recorded in cyclohexane. [b] Recorded in CD_2Cl_2; J values in Hz. [c] Molecular ions based on ^{192}Os and ^{37}Cl. [d] Corresponds to $[Os_3H(I)(CO)_{10}]$ produced by decomposition.

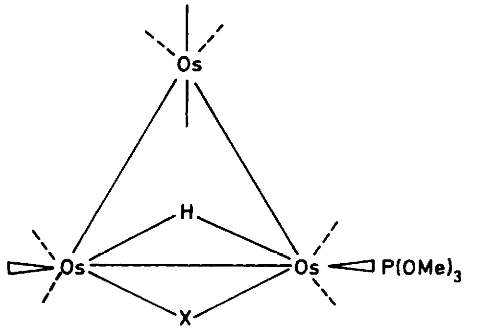


Figure 1. Proposed structure of $[Os_3H(X)(CO)_9\{P(OMe)_3\}]$

Compound (**1**) also reacts readily with PPh_3 to give $[Os_3H(Cl)(CO)_9(PPh_3)]$ (**7**) in 55% yield. This compound has spectroscopic data similar to compounds (**4**)—(**6**) above but different from those of a previously prepared compound of formula $[Os_3H(Cl)(CO)_9(PPh_3)]$.[5,6] This isomer of (**7**) is believed to have the phosphine co-ordinated to the unique osmium atom as opposed to one of the bridgehead osmium atoms.

Ethylene reacts with compound (**1**) to produce a compound of stoicheiometry $[Os_3H(Cl)(CO)_9(C_2H_4)]$ (**8**). Compound (**8**), therefore, represents a rare example of ethylene bonded to a single osmium atom in an osmium cluster {other examples being $[Os_3(CO)_{11}(C_2H_4)]$[6] and $[Os_3H_2(CO)_8(\mu_3\text{-}S)(C_2H_4)]$[7]}. In each case the ethylene co-ordinates by displacing a weakly-bound ligand, either acetonitrile or trimethylamine.

It is well known that olefins bonded in a Dewar-Chatt fashion to a metal atom rotate rapidly.[8,9] For this reason, only a single resonance was observed for ethylene in $[Os_3(CO)_{11}(C_2H_4)]$[6] and $[Os_3H_2(CO)_8(\mu_3\text{-}S)(C_2H_4)]$.[7] In (**8**), however, rapid rotation will not result in the equivalence of all the protons in C_2H_4 due to the asymmetric character of the $Os_3H(Cl)$ framework. Instead an AA′BB′ spin pattern is expected and obtained. Figure 2 shows the variable-temperature ^{1}H n.m.r. spectra for (**8**) in the olefin and hydride region. As the temperature is lowered the complex spin pattern broadens. Coalescence occurs near −90 °C. A limiting spectrum could not be reached.

The olefin complexes $[Os_3(CO)_{11}(C_2H_4)]$[6] and $[Os_3H(CO)_8(\mu_3\text{-}S)(C_2H_4)]$[7] undergo thermal reactions in which C–H bond cleavage occurs giving $[Os_3H(CO)_{10}(CHCH_2)]$ and $[Os_3H(CO)_8(\mu_3\text{-}S)(CHCH_2)]$ respectively. The ethylene compound isolated in this study, however, does not show similar behaviour. Thermal reaction of (**8**) simply produces $[Os_3H(Cl)(CO)_{10}]$ plus an unidentified residue.

The reaction of phenylacetylene with (1) does not lead to simple substitution of the amine by the alkyne. Hydride migration occurs and CO is apparently picked up from *in situ* decomposition to give $[Os_3Cl(CO)_{10}(CHCHPh)]$ (**9**). Interestingly, (**9**) cannot be prepared directly from $[Os_3H(Cl)(CO)_{10}]$ and phenylacetylene. In refluxing benzene there was no reaction between these molecules after 16 h. A proposed structure for (**9**) is shown in Figure 3.

In the preparation of $[Os_3H(Cl)(CO)_9(PPh_3)]$ (**7**), a minor product was isolated which was identified as $[Os_3H(Cl)(CO)_8(PPh_3)_2]$ (**10**) on the basis of elemental analysis and ^{1}H n.m.r. and i.r. spectroscopic data. It was possible to prepare this compound in a higher yield *via* a direct synthesis. It was found that taking $[Os_3H(Cl)(CO)_{10}]$ in a mixed CH_2Cl_2–MeCN solvent and adding 2.5 molar equivalents of Me_3NO followed by 2 equivalents of triphenylphosphine resulted in a 59% yield of (**10**). ^{1}H N.m.r. spectroscopy showed a multiplet at δ 7.24 due to the phenyl protons and a triplet at δ −12.71 (J_{PH} = 6.7 Hz). The triplet was attributed to a bridging metal–hydride which is coupled to two equivalent phosphorus nuclei. The structure shown in Figure 4 is consistent with these spectroscopic data.

The electronic and steric factors which influence the most favoured site for a particular ligand are not easy to separate. For the binary carbonyl $[Os_3(CO)_{12}]$ an investigation of steric factors[10] shows that there is less steric strain for substitution in an equatorial site than in an axial one. Consideration of Os–C

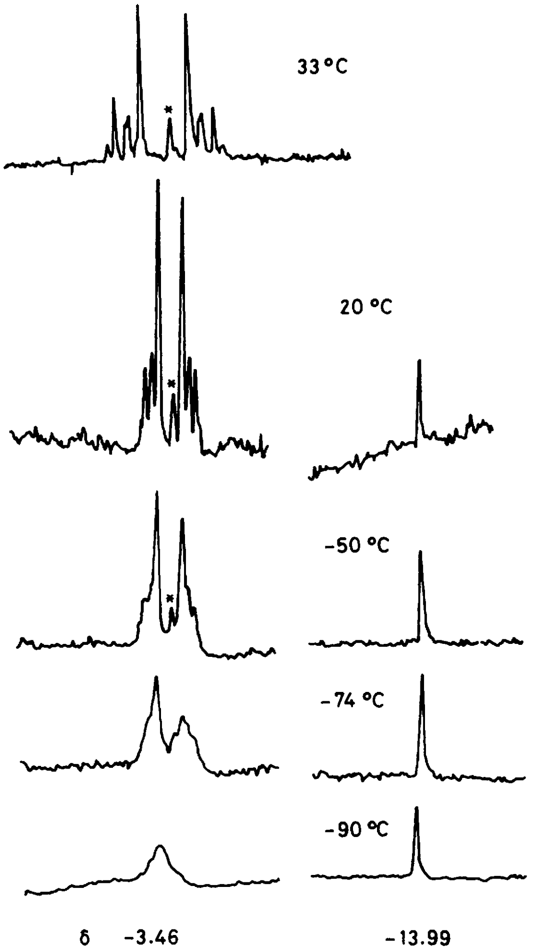


Figure 2. Variable-temperature ^1H n.m.r. for $[Os_3H(Cl)(CO)_9(C_2H_4)]$ (**8**) in the olefin and hydride regions. The spectrum at 33 °C was recorded on an expanded scale and the asterisked peak is due to an unknown impurity present in all samples

bond lengths, in the solid-state structure of $[Os_3(CO)_{12}]$,[11] suggests that for the equatorial carbonyl ligands there is more bonding between the metal and the carbon. Thus, the equatorial carbonyl ligands have shorter Os–C bond lengths (1.912 Å) than the axial ligands (1.946 Å).

A combination of these two effects means that bulky ligands and/or ligands capable of π-acid behaviour comparable to that of CO are likely to favour the equatorial site, while small non-acceptor ligands will adopt axial positions. This generalisation should remain true for ligands co-ordinated around the unique osmium in a cluster of the type $[Os_3H(X)(CO)_{10}]$ (where X is a three-electron donor). However, the situation is changed for the co-ordination sites around the bridgehead osmium atoms.

An investigation of *X*-ray analyses for compounds of the type $[Os_3H(X)(CO)_{10}]$[12] leads to the following observations. (*a*) The Os–C bond lengths *trans* to the unique osmium atom are the longest. (*b*) Of the two pseudo-axial ligands (B and C in Figure 5) the carbonyl ligands *trans* to the bridging X group are the 'most axial'. This would tend to suggest that, on the basis of electronic effects alone, ligands with weaker π-acid strength than CO, *e.g.* $P(OMe)_3$ or NMe_3, should co-ordinate in the equatorial site (A). The compounds reported in this paper appear to fit in this category, however, in the following papers[13] we report some phosphine and phosphite derivatives that do not.

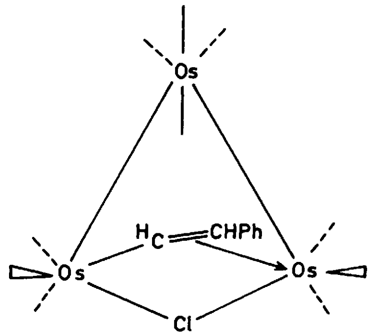


Figure 3. Proposed structure of $[Os_3Cl(CO)_{10}(CHCHPh)]$ (**9**)

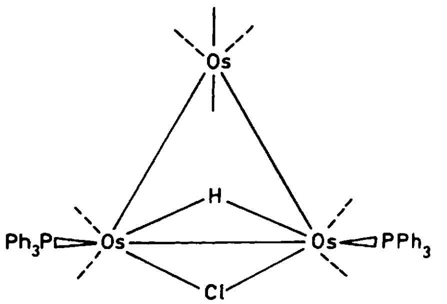


Figure 4. Proposed structure for $[Os_3H(Cl)(CO)_8(PPh_3)_2]$ (**10**)

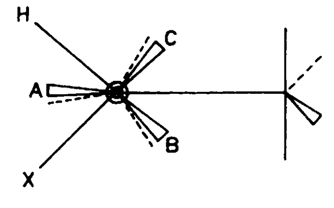


Figure 5. Projection of $[Os_3H(X)(CO)_{10}]$ along the osmium–osmium bridgehead bond

Experimental

None of the compounds reported here is oxygen sensitive but all reactions were carried out under an atmosphere of dry nitrogen to exclude moisture. Products were separated in the air by thin layer chromatography (t.l.c.) with plates coated with 0.25 mm of Merck Kieselgel 60 F_{254}. All solvents were dried over appropriate reagents and distilled prior to use. ^1H N.m.r. spectra were obtained on a Varian XL-100 Fourier-transform spectrometer. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer in the range 2 150—1 600 cm^{-1}. Mass spectra were obtained on an AE-I MS12 spectrometer with *ca.* 70 eV (112×10^{-19} J) ionising potential at 50—200 °C.

The compounds $[Os_3H(X)(CO)_{10}]$ (X = Cl, Br, or I) were prepared by literature methods.[6] Water was removed from trimethylamine oxide dihydrate (Aldrich Chemicals Ltd.) by use of a Dean-Stark apparatus with benzene as a solvent. Elemental analyses for compounds (**1**), (**5**), (**7**), and (**10**) are given in Table 2.

Preparation of $[Os_3H(X)(CO)_9(NMe_3)]$ (X = Cl, Br, *or* I).—$[Os_3H(Cl)(CO)_{10}]$ (52 mg, 0.058 mmol) was dissolved in CH_2Cl_2 (25 cm^3) and Me_3NO (5 mg, 0.065 mmol) added. The reaction mixture was stirred for 15 min with monitoring by i.r. spectroscopy and spot t.l.c. More Me_3NO was added if

Table 2. Microanalytical data

	Found (%)			Calc. (%)		
Compound	C	H	N	C	H	N
(**1**) $[Os_3H(Cl)(CO)_9(NMe_3)]$	16.35	1.30	1.20	15.70	1.10	1.55
(**5**) $[Os_3H(Br)(CO)_9\{P(OMe)_3\}]$	14.75	1.50	—	14.00	1.00	—
(**7**) $[Os_3H(Cl)(CO)_9(PPh_3)]$	29.55	1.75	—	28.90	1.45	—
(**10**) $[Os_3H(Cl)(CO)_8(PPh_3)_2]$	38.90	2.90	—	38.75	2.30	—

required, otherwise the reaction mixture was filtered through a short (*ca.* 5 cm) silica column to remove any excess Me_3NO. The solvent was removed *in vacuo* and $[Os_3H(Cl)(CO)_9(NMe_3)]$ isolated using t.l.c. [CH_2Cl_2–hexane (1:3 v/v) as eluant]. Yield: 51 mg, 0.057 mmol, 95%. The compounds $[Os_3H(X)(CO)_9(NMe_3)]$ (X = Br or I) were prepared in a similar manner with yields of 49 and 45% respectively.

Preparation of $[Os_3H(X)(CO)_9\{P(OMe)_3\}]$ (X = Cl, Br, *or* I).—$[Os_3H(Cl)(CO)_9(NMe_3)]$ (25 mg, 0.028 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and two drops of $P(OMe)_3$ added. The reaction mixture was refluxed for 30 min and then the solvent removed under vacuum. The residue was chromatographed using CH_2Cl_2–hexane (1:3 v/v) as eluant to isolate the product, $[Os_3H(Cl)(CO)_9\{P(OMe)_3\}]$, as the fastest moving band. Yield: 18.5 mg, 0.019 mmol (69%). The compounds with X = Br or I were prepared (in 90% yield) in the same manner except that the formation of $[Os_3H(I)(CO)_9\{P(OMe)_3\}]$ did not require the elevated temperatures. It was often convenient to perform these preparations in a one-pot synthesis from $[Os_3H(X)(CO)_{10}]$ using the impure solid trimethylamine derivatives.

Preparation of $[Os_3H(Cl)(CO)_9(PPh_3)]$.—The reaction was carried out as for the phosphite derivative above except that the reaction was done at room temperature with stirring for 2—3 h. Preparative t.l.c. using CH_2Cl_2–hexane (1:3 v/v) as eluant separated the faster eluting compound $[Os_3H(Cl)(CO)_9(PPh_3)]$ (yield 55%) from $[Os_3H(Cl)(CO)_8(PPh_3)_2]$ (yield 10%).

Reaction of $[Os_3H(Cl)(CO)_9(NMe_3)]$ *with* C_2H_4.—$[Os_3H(Cl)(CO)_9(NMe_3)]$ (20 mg, 0.022 mmol) was dissolved in CH_2Cl_2 (40 cm^3) and placed under a static pressure [*ca.* 1.2 atm (*ca.* 121 590 N m^{-2})] of ethylene at room temperature. A reaction followed by ^1H n.m.r. showed the reaction to go to completion over a period of 24 h. Preparative t.l.c. using cyclohexane as eluant was best performed under a blanketing atmosphere of C_2H_4. The product obtained corresponded to $[Os_3H(Cl)(CO)_9(C_2H_4)]$.

Preparation of $[Os_3Cl(CO)_{10}(CHCHPh)]$.—To $[Os_3H(Cl)(CO)_9(NMe_3)]$ (40 mg, 0.044 mmol) in CH_2Cl_2 (80 cm^3) was added $PhC{\equiv}CH$ (0.1 cm^3). This solution was allowed to stand for 24 h at room temperature. Work-up by t.l.c. [cyclohexane–CH_2Cl_2 (3:1 v/v) as eluant] yielded $[Os_3Cl(CO)_{10}(CHCHPh)]$. Yield: 13 mg, 0.013 mmol, 30%. A large amount of material did not move in neat CH_2Cl_2 and was left uncharacterised.

Preparation of $[Os_3H(Cl)(CO)_8(PPh_3)_2]$.—$[Os_3H(Cl)(CO)_{10}]$ (27 mg, 0.030 mmol) was dissolved in CH_2Cl_2 (10 cm^3) containing MeCN (0.5 cm^3). Me_3NO (5 mg, 0.065 mmol) was added and the reaction mixture stirred for 15 min. Then two equivalents of PPh_3 (16 mg, 0.061 mmol) were added. The solution gradually changed colour from yellow to orange, and after 1 h the solvent was removed *in vacuo*. Thin layer chromatography using CH_2Cl_2–hexane (3:1 v/v) as eluant gave four bands with the compound of highest R_f being $[Os_3H(Cl)(CO)_9(PPh_3)]$ (6.5 mg, 0.006 mmol, 20%). The orange compound of third highest R_f was the desired product (23.5 mg, 0.017 mmol, 59%). The other two compounds were not identified.

Reaction of $[Os_3H(Cl)(CO)_{10}]$ *with* Me_3NO *in* MeCN.—$[Os_3H(Cl)(CO)_{10}]$ (20 mg, 0.022 mmol) was dissolved in MeCN (6 cm^3) containing CH_2Cl_2 (2 cm^3). Me_3NO (2 mg, 0.028 mmol) was added and the reaction stirred for 10 min. Spot t.l.c. at this stage showed the absence of starting material and the presence of a compound of lower R_f than $[Os_3H(Cl)(CO)_9(NMe_3)]$. Attempts to isolate this compound were not successful.

Acknowledgements

We thank the S.E.R.C. for financial support and the N.S.F. for a National Needs Postdoctoral Fellowship (to B. E. H.). E. J. D. is thankful to the Royal Commission for the Exhibition of 1851 and the New Zealand University Grants Committee for a Studentship.

References

1 B. F. G. Johnson, J. Lewis, P. R. Raithby, and C. Zuccaro, *J. Chem. Soc., Chem. Commun.*, 1979, 916.

2 J. Banford, Ph.D. Thesis, University of Cambridge, 1982.

3 B. F. G. Johnson, J. Lewis, and D. Pippard *J. Organomet. Chem.*, 1978, **160**, 263.

4 See, for example, R. D. Adams, N. M. Golembeski, and J. P. Selegue, *Inorg. Chem.*, 1981, **20**, 1242; R. D. Adams, D. A. Katahira, and Li-Wu Yong, *J. Organomet. Chem.*, 1981, **219**, 85.

5 D. A. Pippard, Ph.D. Thesis, University of Cambridge, 1978.

6 B. F. G. Johnson, J. Lewis, and D. A. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407.

7 B. F. G. Johnson, J. Lewis, and D. A. Pippard, *J. Chem. Soc., Chem. Commun.*, 1978, 551; B. F. G. Johnson, J. Lewis, and D. A. Pippard, *J. Organomet. Chem.*, 1981, **213**, 249.

8 L. Kruczynski, L. K. K. Lishingman, and J. Takats, *J. Am. Chem. Soc.*, 1974, **96**, 4006; S. T. Wilson, M. J. Colville, J. R. Shapley, and J. P. Osborn, *ibid.*, p. 4038.

9 B. F. G. Johnson and J. A. Segal, *J. Chem. Soc., Chem. Commun.*, 1972, 1312; C. E. Holloway, G. Mulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 1969, 53.

10 B. F. G. Johnson and P. Holland, unpublished work; P. D. Gavens, Ph.D. Thesis, University of Cambridge, 1979.

11 M. R. Churchill and D. G. DeBoer, *Inorg. Chem.*, 1977, **16**, 878.

12 See, for example, M. R. Churchill and R. A. Lashewycz, *Inorg. Chem.*, 1979, **18**; M. R. Churchill and H. J. Wasserman, *ibid.*, 1980, **19**, 2391; V. F. Allen, J. R. Mason, and P. B. Hitchcock, *J. Organomet. Chem.*, 1977, **140**, 297.

13 E. J. Ditzel, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, following paper; *ibid.*, p. 1293.

Received 13*th February* 1986; *Paper* 6/316