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Reactions of coordinated phosphorus trichloride, phenylphosphonous dichloride, 1-phenyl-3,4-dimethylphosphole and mesitylphosphine in osmium(II) complexes

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Abstract

Substitution of a single labile triphenylphosphine ligand in $OsHCl(CO)(PPh_3)_3$ by PCl_3, PCl_2Ph, $Ph\overline{PCHCMeCMeC}H$ or PH_2(mesityl) [mesityl = 2,4,6-trimethylphenyl] gives complexes with the new ligand *trans* to the hydride ligand and mutually *cis* to the two triphenylphosphine ligands. The PCl_3 and PCl_2Ph complexes undergo slow substitution reactions at phosphorus, at temperatures > 50 °C, with the nucleophiles methoxide, toluidine and hydride. The hydride ligand is readily cleaved either by acetonitrile solutions of aqueous perchloric acid, to give cationic acetonitrile containing complexes or by chlorine, to give neutral dichloride complexes. In all but one instance the products are isolated as mixtures of isomeric complexes with *trans* triphenylphosphine ligands. An exception to this dominant stereochemistry is observed for the complex containing the bulky mesitylphosphine ligand, $OsHCl(PH_2mesityl)(CO)(PPh_3)_2$ for which the product of the hydride cleavage and subsequent carbonylation reaction consists of an almost equal mixture of isomers of $[OsCl(PH_2mesityl)(CO)_2(PPh_3)_2]ClO_4$ with *cis* and *trans* triphenylphosphine ligands. The structure of one of these isomers, with a mesitylphosphine *trans* to triphenylphosphine, has been determined by X-ray crystallography.

Introduction

The modification of suitably funtionalized phosphorus(III) ligands within the coordination sphere of a transition metal has allowed for the preparation of complexes with phosphorus ligands such as HP=S, PH_2OR and PHIPh which are unknown as unbound species [1–3]. Complexes of phosphorus(III) halides have proved particulary useful for the addition of up to three nucleophiles to phosphorus [4]. On the other hand, complexes of phosphine and primary phosphines are useful for the addition of electrophiles to the phosphorus lone pair in an oxidation usually followed by deprotonation of a P–H bond [5]. In addition to these approaches the modification of coordinated phospholes [6], elemental phosphorus [7] and phosphorus oxides and sulfides [8] have provided a variety of phosphorus donor ligands.

In prior work we have reported the chemistry of complexes of phosphine and phenylphosphine which have served as precursors to phosphido $L_nM(PH_2)$ and phenylphosphido $L_nM(PHPh)$ complexes [3,5]. In this paper we describe related work with PCl_3, PCl_2Ph, 1-phenyl 3,4-dimethylphosphole and mesitylphosphine.

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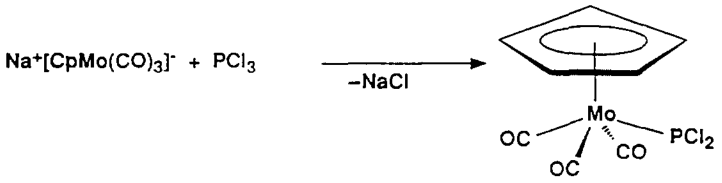
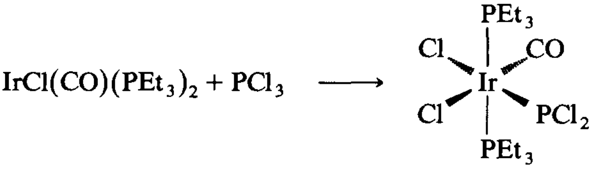
Results and discussion

The most widely exploited functionalized phosphorus ligands are those with phosphorus–chlorine bonds [9]. PCl_3 undergoes nucleophilic attack by organotransition metal anions such as $[Fe(CO)_4]^{-2}$ [10], and $[CpMo(CO)_3]^-$ [11], equation 1,



(1)

or by oxidative addition to complexes of low valent platinum group metals such as $IrCl(CO)L_2$ [12], equation 2, giving L_nMPCl_2 complexes.



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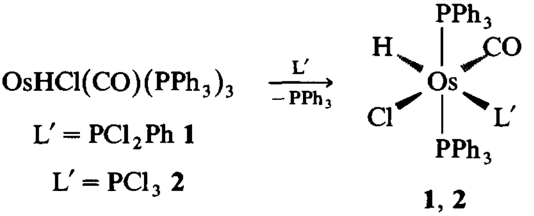
Although a small number of PCl_3 and PCl_2Ph complexes have been prepared [9] the systematic chemistry of the coordinated ligands remains relatively undeveloped [4].

Osmium complexes of PCl_3 and PCl_2Ph

Stable osmium(II) complexes of phosphorus trichloride and phenylphosphonous dichloride are readily prepared by substitution for a single labile triphenylphosphine ligand in $OsHCl(CO)(PPh_3)_3$, equation 3.



(3)

The ligand substitution reaction represented in equation 3 is driven by the relative steric demands of the two phosphorus ligands as has been shown by our work [3,5] and by the previous work by Shaw [13] for the related ruthenium complexes. The complexes **1** and **2** are isolated as air-stable diamagnetic colourless solids. The IR and NMR data listed in Tables 1, 2, and 3 illustrate the great affinity the $OsHCl(CO)(PPh_3)_2$ fragment has for these ligands. In particular, the very large coupling constant between the *trans* hydride and the phosphorus of PCl_3 in **2**, $^2J_{HP} = 291$ Hz, is more than 100 Hz greater than the value found for the PCl_2Ph complex **1** and much greater than the normal range for this coupling (80–100 Hz). In addition, the frequency of the carbonyl stretching band in **2**, 1967 cm^{-1}, is 20 cm^{-1} higher than in the related complexes of $OsHCl(CO)(L')(PPh_3)_2$ presented in

Table 1

Infrared spectroscopic data for new compounds [a]

Complex	ν(CO)	ν(Os-H)	Other bands
OsHCl(PCl$_2$Ph)(CO)(PPh$_3$)$_2$ (1)	1952 1912cs [b]	2030m	803m, δ(Os–H); 284w, ν(OsCl) 464s, 443s, ν(P–Cl)
OsHCl(PCl$_3$)(CO)(PPh$_3$)$_2$ (2)	1967	2069cs 2033m	786m, δ(Os–H); 304m, ν(Os–Cl) 482vs, ν(P–Cl)
trans-OsHCl(P[OMe]$_2$Ph)(CO)(PPh$_3$)$_2$ (3)	1943 1909cs 1897cs	2002m	1047s, 1011s, ν(P–OMe) 778m, δ(Os–H); 275w, ν(Os–Cl)
OsHCl(PCl[NH-*p*-tolyl]Ph)(CO)(PPh$_3$)$_2$ (4)	1936	2012w	3218br, ν(N–H); 1598w, 1499m, 1275m 930m, 810m
OsCl$_2$(PCl$_2$Ph)(CO)(PPh$_3$)$_2$ (5)	1994 1927w		501m, 462m, ν(P–Cl)
cis-OsHCl(P[OMe]$_2$Ph)(CO)(PPh$_3$)$_2$ (6)	1921	2080m	1056m, 1014s, ν(P–OMe) 798w, 784m, δ(Os–H)
OsCl$_2$[P(OMe)$_2$Ph](CO)(PPh$_3$)$_2$ (7)	1966 1918w 1930cs 1900cs		1052s, 1008s, ν(P–OMe)
[OsCl(PCl[NH-*p*-tolyl]Ph)(CO)(NCCH$_3$)-(PPh$_3$)$_2$]ClO$_4$ (8)	1989br		1511m, 1283m, 1225w, 946w, 811w
OsCl$_2$(PCl$_3$)(CO)(PPh$_3$)$_2$ (9)	1995 1958m		519vs, ν(P–Cl)
OsCl$_2$[P(OMe)$_3$](CO)(PPh$_3$)$_2$ (10)	1971 1930m		1058s, 1039s, ν(P–OMe)
OsHCl(DMP)(CO)(PPh$_3$)$_2$ (11)	1912 1897cs	2086m 2024w	811w, 804w, 790m 278m, ν(Os–Cl)
[OsCl(DMP)(NCCH$_3$)(CO)(PPh$_3$)$_2$]ClO$_4$ (12)	1953br		813m; 297w, ν(Os–Cl)
OsCl$_2$(DMP)(CO)(PPh$_3$)$_2$ (13)	1958 1897		1523w, 1065m, 802s 294w, 270w, ν(Os–Cl)
OsCl(N$_3$)(DMP)(CO)(PPh$_3$)$_2$ (14)	1950 1913m 1896cs		2042s, 2005w, ν(N$_3$) 802m.
OsHCl(PH$_2$mesityl)(CO)(PPh$_3$)$_2$ (15)	1919	1998m	2315w, ν(P–H); 923m, δ(P–H) 1604w, 851m; 284w, ν(Os–Cl)
[OsCl(PH$_2$mesityl)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ (16) As a mixture of isomers	2067 1992		906s, δ(P–H); 306w, ν(Os–Cl) 1603w, 854m

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[a] In cm^{-1}, all carbonyl bands strong unless specified otherwise. Spectra recorded as nujol mulls between KBr or CsI discs and calibrated with polystyrene; s = strong, m = medium, w = weak, sh = shoulder, (s) = dichloromethane solution spectrum. cs = crystal splitting band. [b] Multiple (CO) bands are attributed to solid-state splitting.

Table 2

^{1}H NMR spectroscopic data for new compounds [a]

Compound		^{1}H NMR data
$\mathrm{OsHCl(PCl_2Ph)(CO)(PPh_3)_2}$		$-5.3(\mathrm{dt},{}^2J_{HP}=194,22,1,\mathrm{Os}\text{-}H)$
(1)		$5.3(\mathrm{s},1/2,\mathrm{C}H_2\mathrm{Cl_2})$
$\mathrm{OsHCl(PCl_3)(CO)(PPh_3)_2}$		$-5.68\mathrm{dt},{}^2J_{HP}=289.3,21.9,1,\mathrm{Os}\text{-}H)$
(2)		
trans-$\mathrm{OsHCl(P[OMe]_2Ph)(CO)(PPh_3)_2}$		$-5.5(\mathrm{dt},{}^2J_{HP}=116,21.1,1,\mathrm{Os}\text{-}H)$
(3)		$3.3(\mathrm{d},{}^3J_{HP}=10.4,6,\mathrm{POC}H_3)$
$\mathrm{OsHCl(PCl[NH}$-*p*-$\mathrm{tolyl]Ph)(CO)(PPh_3)_2}$		$-5.23(\mathrm{dt},{}^2J_{HP}=123.2,23.1,\mathrm{Os}\text{-}H)$
(4)		$2.25(\mathrm{s},3,\mathrm{C_6H_4C}H_3)$
		$6.73(\mathrm{d}{}^2J_{HH}=8.16,2,\mathrm{C_6}H_4)$
		$6.95(\mathrm{d},{}^2J_{HH}=8.16,2,\mathrm{C_6}H_4)$
cis-$\mathrm{OsHCl(P[OMe]_2Ph)(CO)(PPh_3)_2}$		$-7.14(\mathrm{ddd},{}^2J_{HP}=84.4,25.8,18.6,1,\mathrm{Os}\text{-}H)$
(6)		$3.48(\mathrm{d},{}^3J_{HP}=11.8,3,\mathrm{POC}H_3)$
		$3.48(\mathrm{d},{}^2J_{HP}=11.4,3,\mathrm{POC}H_3)$
$\mathrm{OsCl_2[P(OMe)_2Ph](CO)(PPh_3)_2}$		$3.4(\mathrm{d},{}^3J_{HP}=11,6,\mathrm{POC}H_3)$
(7)		
$\mathrm{[OsCl(PCl[NH}$-*p*-$\mathrm{tolyl]Ph)(CO)(NCCH_3)(PPh_3)_2]ClO_4}$		
(8)		
Isomers I, II	I	$1.53(\mathrm{s},3,\mathrm{C}H_3\mathrm{CN})$
		$2.3(\mathrm{s},3,\mathrm{C_6H_4C}H_3)$
	II	$2.01(\mathrm{s},3,\mathrm{C}H_3\mathrm{CN})$
		$2.25(\mathrm{s},3,\mathrm{C_6H_5C}H_3)$
$\mathrm{OsCl_2[P(OMe)_3](CO)(PPh_3)_2}$		$3.2(\mathrm{d},{}^3J_{HP}=11,9,\mathrm{POC}H_3)$
(10)		
$\mathrm{OsHCl(DMP)(CO)(PPh_3)_2}$		$-5.7(\mathrm{dt},{}^2J_{HP}=74.4,21,1,\mathrm{Os}\text{-}H)$
(11)		$1.8(\mathrm{s},6,\mathrm{C}H_3)$
$\mathrm{OsHCl(PH_2mesityl)(CO)(PPh_3)_2}$ [b]		$-5.82(\mathrm{dt},{}^2J_{HP}=95.9,21.1,1,\mathrm{Os}\text{-}H)$
(15)		$1.94(\mathrm{s},6,[2,6\text{-}\mathrm{C}H_3])$
		$2.24(\mathrm{s},3,[4\text{-}\mathrm{C}H_3])$
		$5.10(\mathrm{dt},{}^1J_{HP}=340.9,{}^3J_{HP}=3.4,2,\mathrm{P}H_2)$
		$6.63(\mathrm{d},{}^4J_{HP}=1.83,2,\mathrm{C_6}H_2\mathrm{Me_3})$
$\mathrm{[OsCl(PH_2mesityl)(CO)_2(PPh_3)_2]ClO_4}$		$1.98(\mathrm{s},6,[2,6\text{-}\mathrm{C}H_3])$
(16)		$2.21(\mathrm{s},3,[4\text{-}\mathrm{C}H_3])$
trans-$\mathrm{PPh_3}$ isomer		$5.55(\mathrm{dt},2,\mathrm{P}H_2\mathrm{mesityl})$
		$6.64(\mathrm{d},{}^4J_{HP}=3.4,2,\mathrm{C_6}H_2\mathrm{Me_3})$
cis-$\mathrm{PPh_3}$ isomer		$2.25(\mathrm{s},3,[4\text{-}\mathrm{C}H_3])$
		$2.41(\mathrm{s},6,[2,6\text{-}\mathrm{C}H_3])$
		$4.81(\mathrm{dm}{}^1J_{HP}=421.3,1,\mathrm{P}H)$
		$5.36(\mathrm{dm},{}^1J_{HP}=423.4,1,\mathrm{P}H)$
		$6.9(\mathrm{d},{}^4J_{HP}=3.5,2,\mathrm{C_6}H_2\mathrm{Me_3})$

[a] As $\mathrm{CDCl_3}$ solutions at 21 °C. Proton chemical shifts (δ) are given in ppm with respect to tetramethylsilane. Shifts of triphenylphosphine protons are not included. [b] Two bond coupling constants for hydride ligands (${}^2J_{HP}$) are listed as H–$P\mathrm{H_2}$ coupling first and H–$P\mathrm{Ph_3}$ second.

Table 1. These spectroscopic results illustrate the enhanced π-accepting character and compactness of $\mathrm{PCl_3}$.

The complexes **1** and **2** are relatively inert towards nucleophilic attack at the phosphorus and either one can be recrystallized unchanged from methanol or ethanol at room temperature. Nucleophilic chloride substitution at the phosphorus with alkoxide requires **1** and **2** to be heated to moderate temperatures (> 50 °C) in the presence of base. An example of this reaction is the formation of the dimethyl

Table 3

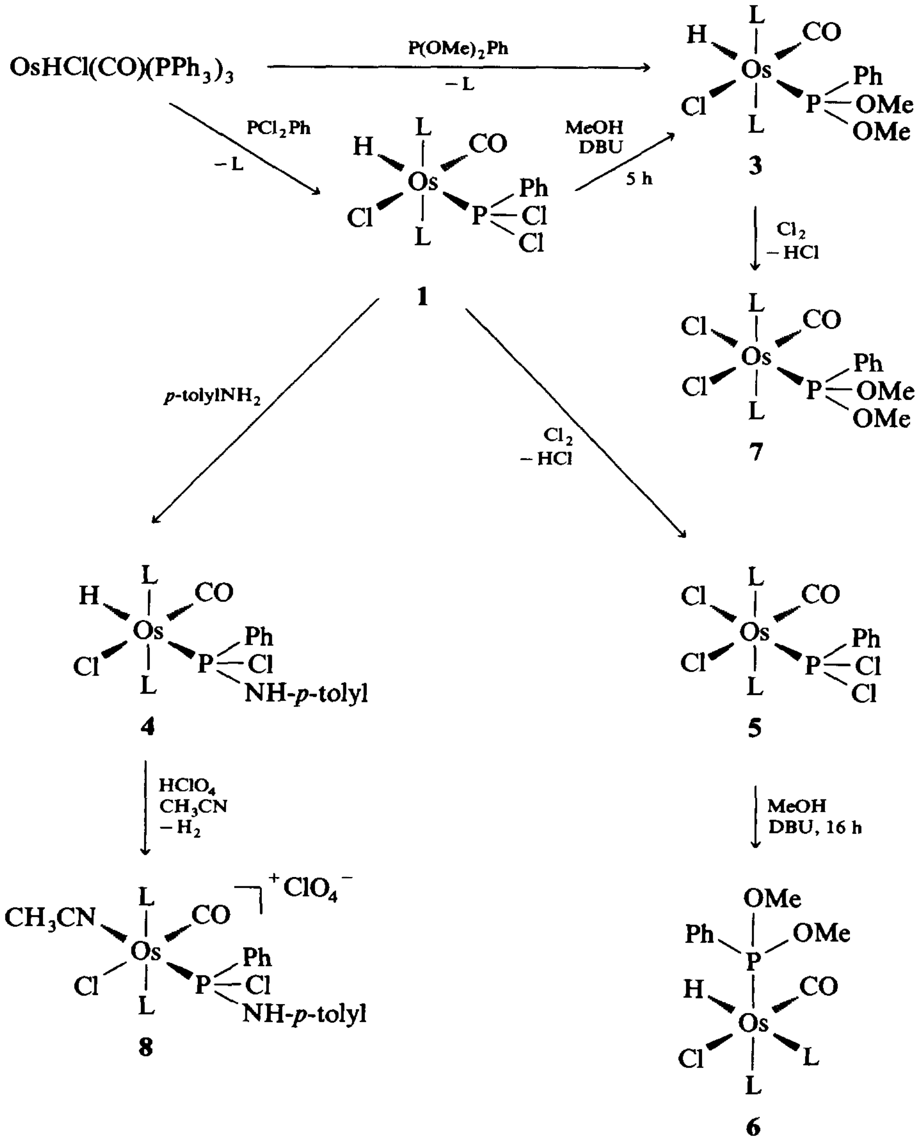
^{31}P NMR spectroscopic data for new compounds [a]

Compound		^{31}P NMR data
OsHCl(PCl$_3$)(CO)(PPh$_3$)$_2$		85.3(t,$^2J_{HP}$ = 15.1,PCl$_3$)
(2)		6.0(d,$^2J_{HP}$ = 15.1,PPh$_3$)
OsHCl(PCl[NH-p-tolyl]Ph)(CO)(PPh$_3$)$_2$		70.9(d,$^2J_{PP}$ = 24.9,PCl(NHR)Ph)
(4)		5.8(dd,$^2J_{PP}$ = 252.3,24.7,PPh$_3$)
		−0.8(d,$^2J_{PP}$ = 252.1,PPh$_3$)
cis-OsHCl(P[OMe]$_2$Ph)(CO)(PPh$_3$)$_2$		124.2(dd,$^2J_{PP}$ = 338.5,40.9,P(OMe)$_2$Ph)
(6)		3.3(dd,$^2J_{PP}$ = 337.5,16.5,PPh$_3$)
		−7.7(dd,$^2J_{PP}$ = 40.8,16.5,PPh$_3$)
[OsCl(PCl[NH-p-tolyl]Ph)(CO)(NCCH$_3$)(PPh$_3$)$_2$]ClO$_4$		
(8)		
Isomers I, II	I	49.0(dd,$^2J_{PP}$ = 13.4,22.7,PCl(NHR)Ph)
		−10.4(dd,$^2J_{PP}$ = 263.6,23.2,PPh$_3$)
		−21.7(dd,$^2J_{PP}$ = 263.3,13.1,PPh$_3$)
	II	53.3(dd,$^2J_{PP}$ = 21.3,8.0,PCl(NHR)Ph)
		−12.4(dd,$^2J_{PP}$ = 305.5,21.7,PPh$_3$)
		−22.2(dd,$^2J_{PP}$ = 305.4,8.2,PPh$_3$)
[OsCl(PH$_2$mesityl)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$		−103.3(t,$^2J_{PP}$ = 23.5,PH$_2$mesityl)
(16)		−19.3(d,$^2J_{PP}$ = 23.4,PPh$_3$)
trans-PPh$_3$ isomer		
cis-PPh$_3$ isomer		−93.2(dd,$^2J_{PP}$ = 263.8,17.7,PH$_2$)
		−15.9(dd,$^2J_{PP}$ = 281.5,23.8,PPh$_3$)
		−16.61(m,PPh$_3$)

[a] As CDCl$_3$ solutions at 21° C. Phosphorus shifts are given in ppm with respect to external 85% H$_3$PO$_4$.

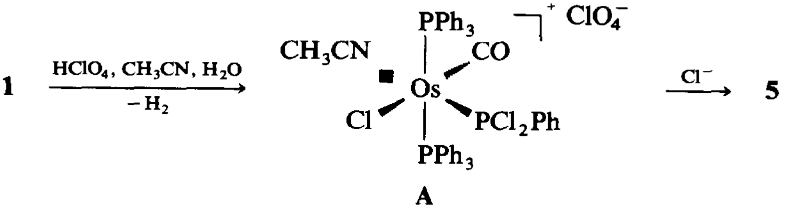
phenylphosphonite complex, **3**, when **1** is heated under reflux in a benzene/methanol solution for five hours in the presence of DBU (Scheme 1). Under these conditions both chlorides can be exchanged for an alkoxide, but when **1** is treated with excess *p*-toluidine in benzene at reflux only a single chloride is substituted. The product from this latter reaction is the phenylphosphonous chloride(*p*-tolylamide) complex, **4**. While part of this difference in reactivity may be due to the lower basicity of toluidine compared to DBU, another factor could be the reduced susceptibility of the phosphorus in **4** towards further substitution because of a π-interaction between the nitrogen and the phosphorus.

The susceptibility of the phosphorus–chloride bond to nucleophilic substitution is increased when the overall complex is positively charged. Cationic complexes are readily derived from **1** and **4** by treating dichloromethane solutions of these compounds with aqueous perchloric acid in the presence acetonitrile. In each case there is an instant evolution of gas but the products isolated from these two reactions differ markedly. In the case of **4** a stable, crystalline, cationic complex, **8**, can be isolated in good yield. On the other hand, a mixture of cationic and neutral complexes result in the first instance from the reaction involving **1**. Further recrystallization of this mixture gives the neutral complex OsCl$_2$(PCl$_2$Ph)(CO)(PPh$_3$)$_2$, **5**, in poor (< 30%) yield as a mixture of isomers with *cis* and *trans* chloride ligands. The most likely origin of the second metal-bound chloride is from hydrolysis of the cationic phenylphosphonous dichloride complex, **A**. The low yield of **5** and, more importantly, the presence of *two* chlorides in the product indicate



Scheme 1. Reactions of $OsHCl(PCl_2Ph)(CO)(PPh_3)_2$. $L = PPh_3$ (N.B. **5** and **7** are prepared as a mixture of isomers with *cis* and *trans* chloride ligands.)

that even under these mild conditions, room temperature and acid conditions, the phenylphosphonous dichloride ligand in **A** is very susceptible to nucleophilic attack.

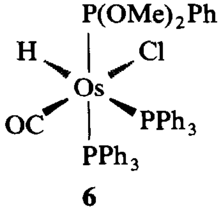


Deliberate attempts to hydrolyze $OsHCl(PCl_2Ph)(CO)(PPh_3)_2$ with wet THF at reflux in the presence of base failed to give tractable products with any discernible phosphoryl stretching activity $\nu(P{=}O)$, in the IR spectrum.

The dichloride complex **5** is best prepared, as a mixture of isomers with *cis* and *trans* chlorides, by direct chlorination of the hydride complex, **1**, with a solution of chlorine in carbon tetrachloride. The presence of isomers is indicated by the infrared spectrum which contains two carbonyl stretching bands. As judged from the intensity of these bands the ratio of isomers from this reaction is almost the same as that obtained when **1** is treated with aqueous perchloric acid and acetonitrile. This suggests that three may be a common intermediate or mechanism in these hydride cleavage reactions.

Methanolysis of **5** as a mixture of isomers results in the formation of **6**, an isomer of $OsHCl[P(OMe)_2Ph](CO)(PPh_3)_2$, **3**, as in equation 4.

$$\underset{\mathbf{5}}{OsCl_2(PCl_2Ph)(CO)(PPh_3)_2} \xrightarrow[16\ h,\ \Delta]{MeOH,\ DBU} \tag{4}$$

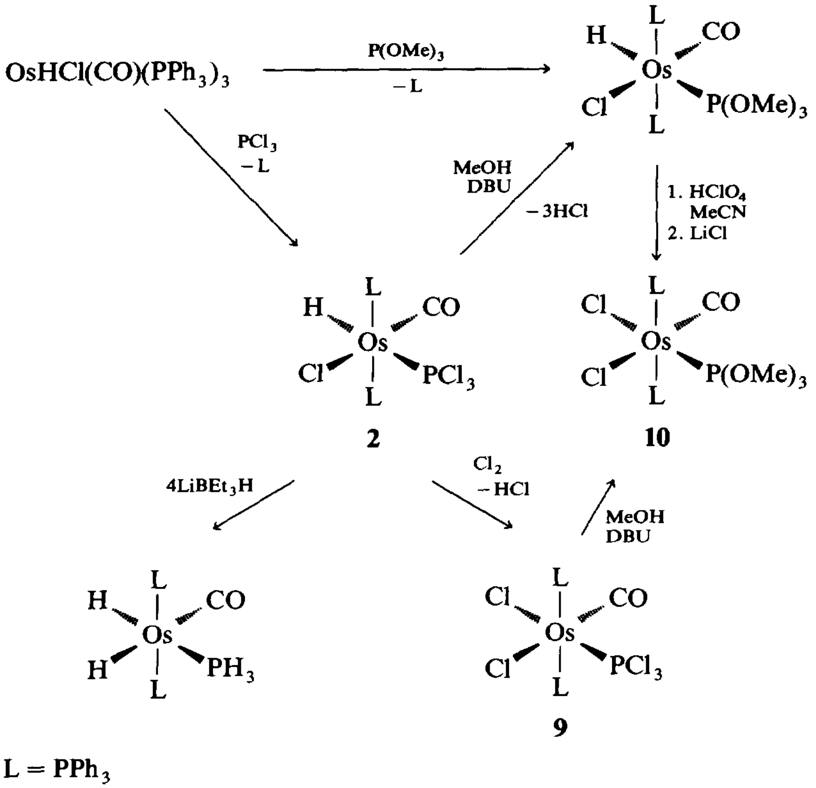


6

The structure assigned to **6** is based on the ^{31}P NMR spectrum, which indicates three inequivalent phosphorus ligands with a strong *trans* coupling constant ($^2J_{PP} =$ 338.5 Hz) between a triphenylphosphine and the dimethyl phenylphosphonite. The ^1H NMR has a hydride resonance that is coupled to three inequivalent phosphorus nuclei and the diastereotopic methyl groups appear as two doublets. The isomer with *trans* triphenylphosphine ligands, **3**, results from either direct substitution of dimethyl phenylphosphonite into $OsHCl(CO)(PPh_3)_3$ or by methanolysis of **1** (Scheme 1). There is no evidence that **3** and **6** interconvert on heating even after prolonged periods at reflux in benzene. Nor does $OsCl_2[P(OMe)_2Ph](CO)(PPh_3)_2$, **7**, isomerize or reduce to **6**, when it is heated in the same solvent mixture, and for the same period of time, as was used in the preparation of **6**. These experiments illustrate the kinetic inertness of the Os(II) centre in these complexes and highlight the specificity of the processes involved in the transformation shown in equation 4.

The chemistry of the phosphorus trichloride complex $OsHCl(PCl_3)(CO)(PPh_3)_2$, **2**, is outlined in Scheme 2. Many aspects of the chemistry of this compound are similar to that of the phenylphosphonous dichloride complex **1** discussed above. However, **2** does not react with *p*-toluidine under the same conditions as were employed in the preparation of **4**. Methanolysis of $OsCl_2(PCl_3)(CO)(PPh_3)_2$, **9**, results in $OsCl_2[P(OMe)_3](CO)(PPh_3)_2$, **10**, which, unlike the reaction of its phenylphosphonous dichloride analogue, equation 4, retains the initial geometry with mutually *trans* triphenylphosphine ligands. Lithium triethylborohydride reduces the coordinated phosphorus trichloride in **2** to phosphine and also replaces the metal bound chloride with hydride to give $OsH_2(PH_3)(CO)(PPh_3)_2$, in 60% yield. This same product is also obtained in better yield, and higher purity, by reduction of $OsHCl(PH_3)(CO)(PPh_3)_2$ with $LiBEt_3H$ [5].

Several factors suggest that these nucleophilic substitution reactions occur within the coordination sphere of the metal. Although ligand dissociation, followed by



Scheme 2. Reactions of $OsHCl(PCl_3)(CO)(PPh_3)_2$. (N.B. **9** and **10** are prepared as a mixture of isomers with *cis* and *trans* chloride ligands.)

nucleophilic attack and recoordination, could lead to the same products in the case of the reaction between toluidine and **1**, a phenylphosphonous di(toluamide) complex would be the expected product. The observed product, **4**, contains only a single toluamide substituent and suggests that this reaction occurred within the coordination sphere of the metal.

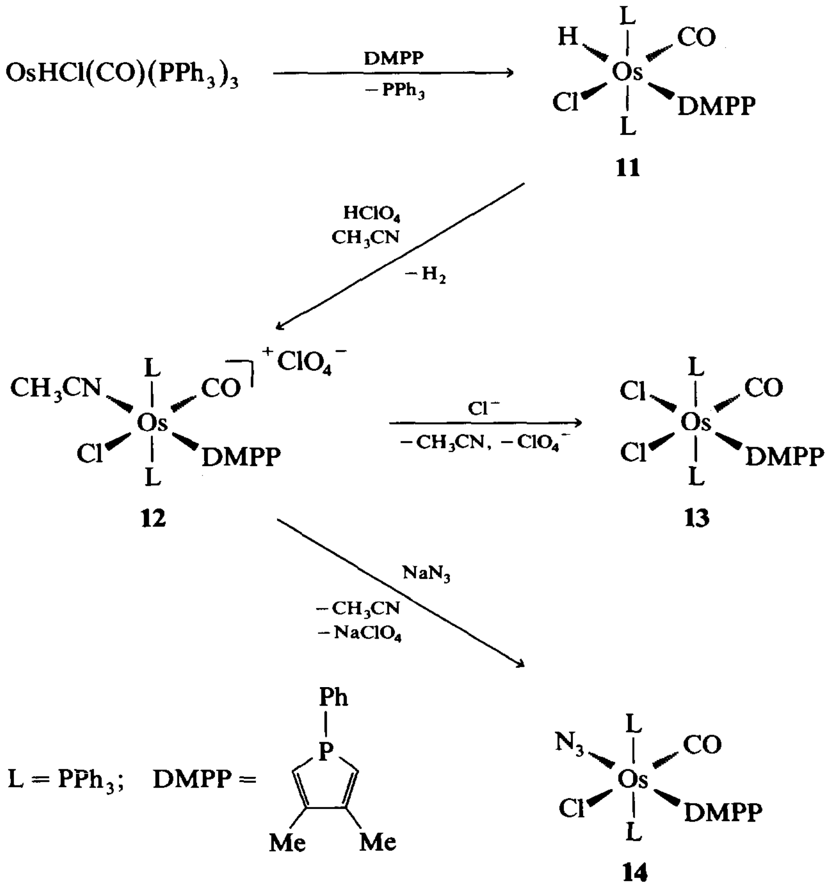
Further studies are needed to resolve these mechanistic details.

Phosphole complexes of osmium

The phosphole ligand has a remarkably diverse coordination chemistry [6] with examples of μ_2-, η^1-, η^2-, η^4- and bridging complexes having been characterized. Substitution of 1-phenyl 3,4-dimethylphosphole (DMPP) for the labile triphenylphosphine in $OsHCl(CO)(PPh_3)_3$ gives $OsHCl(DMPP)(CO)(PPh_3)_2$, **11**, in high yield (Scheme 3). As detailed in the experimental section this complex can be derivatized with acetonitrile solutions of aqueous perchloric acid, to cleave the hydride ligand, followed by substitution with chloride and azide to give the complexes **12–14**. The resulting neutral and cationic phosphole complexes were than treated with dieneophiles such as *N*-phenylmaleimide and dimethylacetylene dicarboxylate to test for Diels–Alder cyclo-addition reactivity. Under a variety of reaction conditions there was either no reaction between the DMPP complexes and dimethylacetylene dicarboxylate, or only intractable products were obtained. If the expected Diels–Alder reaction leads to a 7-phosphanorbornadiene ligand the steric bulk of this tertiary phosphine may increase its lability, or, even though mild conditions are employed in these preparations, the ligand may cyclo-revert to generate reactive terminal phosphinidene complexes.

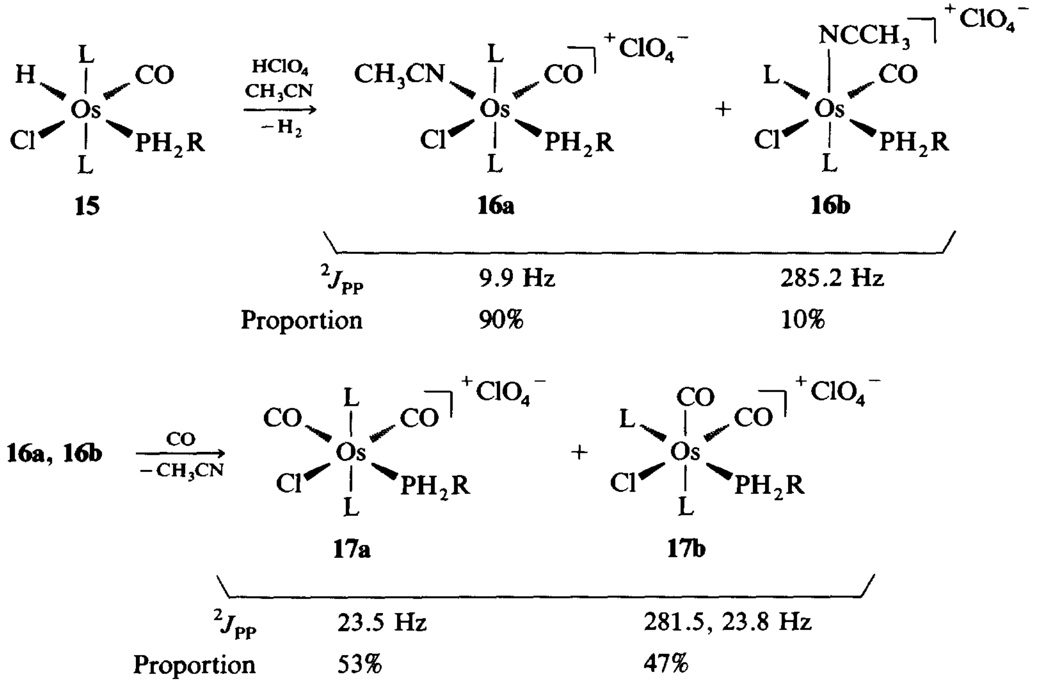
Mesitylphosphine complexes

The recent isolation of compounds with double bonds involving second row, main group elements highlights the importance of kinetic stabilization of these substances by sterically demanding substituents. Thus, may of the phospha-alkenes and diphosphenes that have recently been prepared have substituents such as mesityl, 2,4,6-tri(t-butyl)C_6H_2– and $(SiMe_3)_2CH$–. Since kinetic stabilization is also expected to be important in the preparation of a terminal phosphinidene complex, the coordination chemistry of mesitylphoshine was explored. In these complexes the



(N.B. **12** is formed along with a minor amount of another isomer and **13** is formed together with the isomer having *trans* Cl ligands.)

Scheme 3. 1-Phenyl 3,4-dimethylphosphole complexes of osmium.



	16a	16b
$^2J_{PP}$	9.9 Hz	285.2 Hz
Proportion	90%	10%

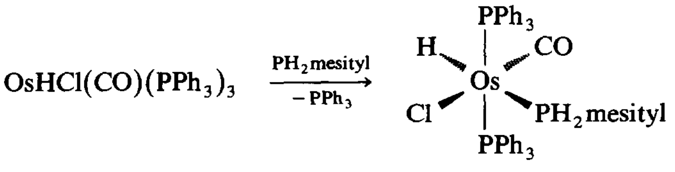
	17a	17b
$^2J_{PP}$	23.5 Hz	281.5, 23.8 Hz
Proportion	53%	47%

L = PPh_3, R = mesityl

Scheme 4. Mesitylphosphine complexes.

phosphorus is surrounded not only by the bulk of the $L_nOs(PPh_3)_2$ fragment but also by the mesityl substituent.

Mesitylphosphine is readily introduced into $OsHCl(CO)(PPh_3)_3$ with reaction conditions similar to those used in the preparation of the phenylphosphine complex $OsHCl(PH_2Ph)(CO)(PPh_3)_2$ [5]. The resulting complex $OsHCl(PH_2mesityl)(CO)(PPh_3)_2$, **15**, also undergoes reaction with aqueous perchloric acid in acetonitrile but here the similarity to the chemistry of the phenylphosphine complex ends. Acid cleavage of the hydride-metal bond introduces a different form of isomerism: the



15

minor isomer (about 10%) has *cis* triphenylphosphine ligands, while the major isomer has the usual *trans* configuration for these two ligands (Scheme 4). All other examples of this reaction which we have studied give isomeric mixtures, but the isomers always have *trans* triphenylphosphine ligands. Carbonylation of this mixture gives the dicarbonyl cation as a pair of isomers, with *cis* and *trans* tirphenylphosphine ligands, in almost equal proportions.

Subsequent ^{31}P and ^{1}H NMR studies of these molecules confirmed the assigned

Table 4

Bond lengths (Å) for $[OsCl(PH_2mesityl)(CO)_2(PPh_3)_2]ClO_4$

Os–Cl(1)	2.431(8)	P(3)–C(71)	1.80(3)
Os–P(1)	2.468(7)	O(1)–C(1)	1.16(3)
Os–P(2)	2.497(7)	O(2)–C(2)	1.06(3)
Os–P(3)	2.391(8)	C(71)–C(72)	1.43(4)
Os–C(1)	1.88(3)	C(71)–C(76)	1.38(4)
Os–C(2)	1.90(3)	C(72)–C(73)	1.39(5)
P(1)–C(11)	1.82(3)	C(72)–C(77)	1.53(5)
P(1)–C(21)	1.83(3)	C(73)–C(74)	1.37(5)
P(1)–C(31)	1.82(3)	C(74)–C(75)	1.39(5)
P(2)–C(41)	1.84(3)	C(74)–C(78)	1.56(5)
P(2)–C(51)	1.83(3)	C(75)–C(76)	1.43(5)
P(2)–C(61)	1.84(3)	C(76)–C(79)	1.52(5)

geometries. Attempts to grow crystals of the dicarbonyl complex resulted in obvious mixtures of crystals with two distinct morphologies. One type of crystal was particularly well suited for an X-ray diffraction study as they grew as large, well formed prisms. An ORTEP view of **17b** is depicted in Fig. 1 and bond length, bond angle and atomic positional parameters are collected in Tables 4, 5, and 6 respectively.

The geometry of the unexpected isomer contains *cis* triphenylphosphine ligands with the mesitylphosphine *trans* to one of these. The three coplanar (sum of $P(x)–Os–P(y) = 357°$) phosphorus ligands distort the coordination geometry at the osmium ($P(1)–Os–P(2) = 102.6(1)°$) away from the almost ideal octahedral geometry seen for many Os(II) complexes. Of the three metal–phosphorus bond lengths present, the bond to the mesitylphosphine is the shortest while the bond to the triphenylphosphine *trans* to the carbonyl ligand is the longest.

Before the complexity of this mixture had been ascertained by structural and NMR methods as detailed above, some reactions of these cationic mesitylphoshine complexes were explored. Deep green solutions result when benzene suspensions of $[OsCl(PH_2mesityl)(CO)_2(PPh_3)_2]ClO_4$ are treated with base. Tractable products could not be recovered from this solution and the original deprotonation reaction is

Table 5

Bond angles (°) for $[OsCl(PH_2mesityl)(CO)_2(PPh_3)_2]ClO_4$

Cl(1)–Os–P(1)	94.2(3)	P(3)–Os–C(1)	86.1(8)
Cl(1)–Os–P(2)	87.2(3)	P(3)–Os–C(2)	94.1(9)
Cl(1)–Os–P(3)	83.7(3)	C(1)–Os–C(2)	91.5(12)
Cl(1)–Os–C(1)	89.9(8)	Os–P(1)–C(11)	114.8(9)
Cl(1)–Os–C(2)	177.3(9)	Os–P(1)–C(21)	107.4(9)
P(1)–Os–P(2)	102.7(2)	Os–P(1)–C(31)	120.3(9)
P(1)–Os–P(3)	170.4(3)	Os–P(2)–C(41)	114.1(9)
P(1)–Os–C(1)	84.6(8)	Os–P(2)–C(51)	111.5(10)
P(1)–Os–C(2)	88.3(9)	Os–P(2)–C(61)	118.4(10)
P(2)–Os–P(3)	86.6(3)	Os–P(3)–C(71)	117.0(11)
P(2)–Os–C(1)	172.3(8)	Os–C(1)–O(1)	178(3)
P(2)–Os–C(2)	91.2(9)	Os–C(2)–O(2)	176(3)

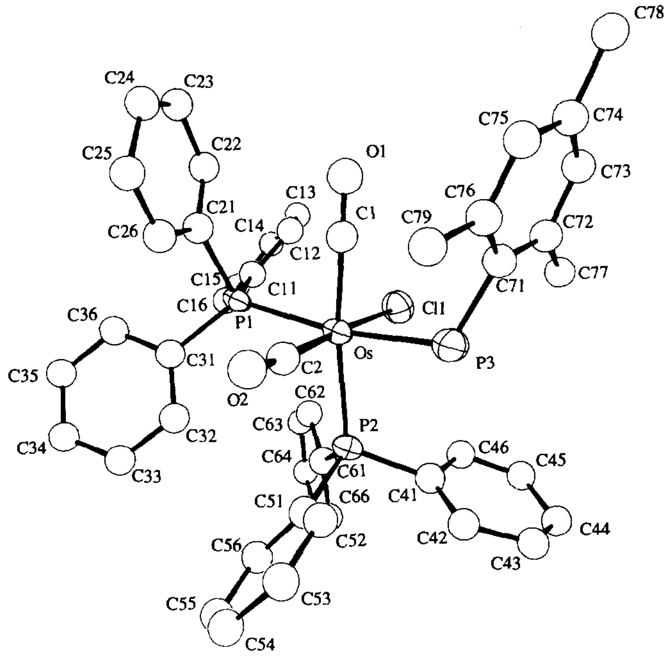


Fig. 1. Geometry and atomic numbering for $[OsCl(PH_2mesityl)(CO)_2(PPh_3)_2]^+$.

not reversible; addition of perchloric acid to the green solution gave a purple-coloured solution from which starting material could not be isolated. Both of these observations stand in contrast with the reversible deprotonation of $[OsCl(PH_2Ph)(CO)_2(PPh_3)_2]ClO_4$ to give the pale yellow crystalline phenylphosphido complex $OsCl(PHPh)(CO)_2(PPh_3)_2$ [3]. The coloured species in these reactions remain unidentified.

Experimental

Standard Schlenk techniques [14] were used for the preparation, handling and purification of all moisture- and oxygen-sensitive materials. Solvents were purified as follows: benzene, toluene, THF, n-hexane and diethyl ether were distilled under nitrogen from sodium/benzophenone; dichloromethane, chloroform and acetonitrile were distilled under nitrogen from calcium hydride; ethanol was distilled from magnesium ethoxide [15].

Routine recrystallizations were carried out by dissolving the sample in an excess of a low boiling-point solvent and an equivalent quantity of a higher boiling-point solvent, in which the compound was insoluble, was added. Crystallization was achieved under reduced pressure using a rotary evaporator. Some compounds were purified by column chromatography on silica (Riedel de Haen Kieselgel S) or neutral alumina [15].

New compounds were characterized by IR, ^1H and ^{31}P NMR and by elemental analysis. Analytical data were obtained from the Microanalytical Laboratory, Uni-

Table 6

Atomic positions for [OsCl)PH$_2$mesityl)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$

Atom	*x*	*y*	*z*
Os	0.3694(5)	0.10807(1)	0.34705(4)
P(1)	0.0344(3)	0.11609(8)	0.5254(2)
P(2)	0.1518(3)	0.16873(9)	0.3072(2)
P(3)	0.0314(4)	0.08919(11)	0.1787(3)
Cl(1)	0.2706(4)	0.07895(10)	0.3789(3)
Cl(b)	−0.2477(5)	0.14795(15)	−0.0831(4)
O(b1)	−0.1082(18)	0.1615(5)	−0.0601(12)
O(b2)	−0.283(3)	0.1427(9)	0.020(2)
O(b3)	−0.256(4)	0.1084(13)	−0.120(3)
O(b4)	−0.331(3)	0.1712(10)	−0.148(3)
O(c2)	−0.281(4)	0.1458(10)	−0.199(3)
O(c3)	−0.354(4)	0.1733(11)	−0.058(3)
O(c4)	−0.289(5)	0.1111(14)	−0.059(4)
O(1)	−0.0889(10)	0.0296(3)	0.3726(7)
O(2)	−0.2482(10)	0.1426(3)	0.3012(7)
C(1)	−0.0434(12)	0.0597(4)	0.3616(9)
C(2)	−0.1442(15)	0.1316(4)	0.3162(10)
C(11)	0.1902(12)	0.0977(3)	0.6109(8)
C(12)	0.2705(14)	0.1217(4)	0.6864(10)
C(13)	0.3921(16)	0.1091(5)	0.7494(11)
C(14)	0.4302(17)	0.0702(5)	0.7414(12)
C(15)	0.3525(15)	0.0448(4)	0.6699(11)
C(16)	0.2305(13)	0.0604(4)	0.6014(10)
C(21)	−0.1132(12)	0.0878(4)	0.5508(9)
C(22)	−0.0921(14)	0.0525(4)	0.6007(10)
C(23)	−0.2125(16)	0.0291(4)	0.6071(11)
C(24)	−0.3443(17)	0.0419(5)	0.5630(12)
C(25)	−0.3661(17)	0.0777(5)	0.5201(12)
C(26)	−0.2478(15)	0.1010(4)	0.5141(10)
C(31)	−0.0062(12)	0.1626(3)	0.5728(9)
C(32)	−0.0108(13)	0.1951(4)	0.5149(10)
C(33)	−0.0477(15)	0.2307(4)	0.5507(11)
C(34)	−0.0756(14)	0.2337(4)	0.6455(10)
C(35)	−0.0719(15)	0.2017(4)	0.7041(11)
C(36)	−0.0375(15)	0.1641(4)	0.6689(10)
C(41)	0.2385(12)	0.1647(3)	0.2005(9)
C(42)	0.1733(14)	0.1769(4)	0.1054(10)
C(43)	0.2439(15)	0.1719(4)	0.0251(10)
C(44)	0.3758(16)	0.1566(4)	0.0418(11)
C(45)	0.4403(16)	0.1436(5)	0.1371(11)
C(46)	0.3732(14)	0.1477(4)	0.2180(10)
C(51)	0.0221(13)	0.2072(4)	0.2701(9)
C(52)	−0.0941(15)	0.1990(4)	0.1936(10)
C(53)	−0.2053(17)	0.2271(5)	0.1600(13)
C(54)	−0.1895(18)	0.2624(5)	0.2112(13)
C(55)	−0.0761(17)	0.2717(5)	0.2836(12)
C(56)	0.0352(15)	0.2441(4)	0.3152(11)
C(61)	0.2984(13)	0.1885(4)	0.4012(9)
C(62)	0.3616(16)	0.2222(4)	0.3776(11)
C(63)	0.4803(17)	0.2366(5)	0.4466(12)
C(64)	0.5427(17)	0.2144(5)	0.5326(13)
C(65)	0.4745(14)	0.1809(4)	0.5525(10)
C(66)	0.3530(13)	0.1672(4)	0.4851(9)

Table 6 (contintued)

Atom	x	y	z
C(71)	−0.0142(14)	0.0398(4)	0.1463(10)
C(72)	0.0957(16)	0.0126(4)	0.1420(11)
C(73)	0.0591(16)	−0.0258(5)	0.1266(11)
C(74)	−0.0790(16)	−0.0374(5)	0.1152(11)
C(75)	−0.1884(15)	−0.0119(4)	0.1168(11)
C(76)	−0.1529(17)	0.0279(5)	0.1350(11)
C(77)	0.2518(17)	0.0232(5)	0.1540(12)
C(78)	−0.1178(19)	−0.0809(6)	0.0985(14)
C(79)	−0.2760(16)	0.0553(5)	0.1335(11)

versity of Otago. IR spectra were measured on a Perkin–Elmer 597 spectrometer either as a Nujol or a Kel-F mull between NaCl, KBr or CsI plates, or as a dichloromethane solution between KBr plates. ^{1}H NMR spectra were recorded on either a Varian EM 360L or a Bruker AM400 spectrometer. ^{13}C, ^{31}P and ^{77}Se NMR spectra were measured on a Bruker AM400 and referenced to tetramethylsilane, 85% orthophosphoric acid and dimethylselenide respectively. Melting points (uncorrected) were measured on a Reichert hot-stage microscope.

$OsHCl(PCl_2Ph)(CO)(PPh_3)_2$ (1)

$OsHCl(CO)(PPh_3)_3$, 0.65 g, and a threefold excess of phenylphosphonous dichloride (about 0.2 mL) were heated together at reflux in 10 mL benzene for $2\frac{1}{2}$ h. After 10 min at reflux temperature a clear, colourless solution had formed. After a further 5 min at reflux a white precipitate began to form and the mass of this increased over the next hour. This mixture was then cooled and n-hexane (70 mL) was added. Filtration, followed by successive washes with diethylether and n-hexane gave 0.52 g (87% yield) of white crystals, m.p. 215 °C. An analytical sample of this sparingly soluble material was recrystallized from dichloromethane/ethanol. Anal. (as $\frac{1}{2}$ dichloromethane solvate as confirmed by ^{1}H NMR) Found: C, 52.51; H, 4.54. $C_{43}H_{36}Cl_3OOsP_3 \cdot \frac{1}{2}CH_2Cl_2$ calcd.: C, 52.21; H, 3.73%.

$OsHCl(PCl_3)(CO)(PPh_3)_2$ (2)

$OsHCl(CO)(PPh_3)_3$, 0.25 g, was suspended in 10 mL dry benzene and treated with a threefold excess of phosphorus trichloride (0.7 mmole, 0.099 g, 0.066 mL). This mixture was heated at reflux for 2 h. Within 10 min of the beginning of reflux a clear, colourless solution formed. After cooling, the benzene and excess phosphorus trichloride were removed in vacuo. The colourless gummy residue was recrystallized from dichloromethane/ethanol to give 0.21 g of white plates, m.p. 176 °C. Anal. Found: C, 48.43; H, 3.95. $C_{37}H_{31}Cl_4OOsP_3$ calcd.: C, 48.48; H, 3.42%.

trans-*$OsHCl[P(OMe)_2Ph](CO)(PPh_3)_2$ (3)*

Method A. $OsHCl(PCl_2Ph)(CO)(PPh_3)_2$ (1), 0.09 g, was heated at reflux in 20 mL 1 : 1 THF/methanol for 12 h in the presence of 0.1 mL DBU. After cooling this mixture all solvents were removed under vacuum and the residue was recrystallized from dichloromethane/ethanol to give 0.04 g, 45%, of fine needles m.p. 215 °C.

Method B. $OsHCl(CO)(PPh_3)_3$, 0.22 g, and excess *O,O*-dimethyl phenylphosphonite (about 0.2 mL) were heated together in 20 mL benzene for 2.5 h. This solution was cooled and the solvent was removed in vacuo. Recrystallization of the residue from dichloromethane/ethanol gave 0.19 g, of colourless needles (95%). Anal. Found: C, 56.89 H, 5.11. $C_{45}H_{42}ClO_3OsP_3$ calcd.: C, 56.92; H, 4.47%.

$OsHCl[PCl(NH$-p-$tolyl)Ph](CO)(PPh_3)_2$ (4)

$OsHCl(PCl_2Ph)(CO)(PPh_3)_2$ (1), 0.25 g, and *p*-toluidine (0.07 g, 1.3 equiv.) were heated together in 10 mL benzene for 3h. During this period a small quantity of colourless solid formed. The mixture was then cooled and the solvent was removed in vacuo. The gummy residue was then recrystallized from dichloromethane/ethanol to give, after filtration and washes with ethanol and n-hexane, 0.24 g (89% yield) m.p. 163° C. Anal. Found: C, 58.21; H, 4.53; N, 1.30. $C_{50}H_{54}Cl_2NOOsP_3$ calcd.: C, 58.36; H, 4.32; N, 1.36%.

$OsCl_2(PCl_2Ph)(CO)(PPh_3)_2$ (5)

$OsHCl(PCl_2Ph)(CO)(PPh_3)_2$ (1), 0.1 g, in 10 mL dry dichloromethane was treated with 0.5 mL of a 3 *M* solution of chlorine in carbon tetrachloride (about 15 fold excess) and left standing for 1 day. During this period a fine precipitate of product formed. Ethanol was added (about 30 mL) and the dichloromethane was removed in vacuo. After filtration and washes with ethanol and n-hexane the yield was 0.11 g (100%) m.p. 216° C. Anal. Found: C, 52.12; H. 3.69. $C_{43}H_{35}Cl_4OOsP_3$ calcd.: C, 51.44; H, 3.61%. This sparingly soluble compound is also the by-product of the hydrolysis of the cation which was produced by hydride–osmium bond cleavage (with aqueous perchloric acid in acetonitrile) and chloride substitution, of $OsHCl(PCl_2Ph)(CO)(PPh_3)_2$.

cis-*$OsHCl[P(OMe)_2Ph](CO)(PPh_3)_2$ (6)*

$OsCl_2(PCl_2Ph)(CO)(PPh_3)_2$ (5), 0.07 g, was suspended in 5 mL each of dry THF and methanol and 0.1 mL of DBU was added. This mixture was heated at reflux for 16 h and then all solvents were removed in vacuo. Recrystallization of the resulting residue form dichloromethane/ethanol gave 0.05 g, 71%, m.p. 172° C. Anal. Found: C, 56.48; H, 4.72. $C_{45}H_{42}ClO_3OsP_3$ calcd.: C, 56.92; H, 4.47%.

$OsCl_2[P(OMe)_2Ph](CO)(PPh_3)_2$ (7)

$OsHCl[P(OMe)_2Ph](CO)(PPh_3)_2$ (3) was treated by the same two step method as was used for the preparation of $OsCl_2[P(OMe)_3](CO)(PPh_3)_2$ (**10**) (Method A). From 0.15 g of **1** 0.16 g of **7** was prepared in an overall yield of 98%. The product was sparingly soluble and crystallized from dichloromethane/ethanol as white needles m.p. 233° C. Anal. Found: C, 54.98; H, 4.58. $C_{45}H_{41}Cl_2O_3OsP_3$ calcd.: C, 54.93; H, 4.21%.

$[OsCl[PClPh(NH$-p-$tolyl)](NCCH_3)(CO)(PPh_3)_2]ClO_4$ (8)

$OsHCl[PClPh(NH$-*p*-$tolyl)](CO)(PPh_3)_2$ (4), 0.106 g, was treated with aqueous perchloric acid (0.05 mL) in a 1 : 1 solution of dichloromethane/acetonitrile. After 1 h the solvent was removed in vacuo and dichloromethane/ethanol/isopropanol was used to recrystallize the tan residue to give 0.101 g (84%) of colourless plates m.p. 152° C (dec). Anal. Found: C, 53.75; H, 4.65; N, 2.28. $C_{52}H_{46}Cl_3N_2O_5OsP_3$ calcd.: C, 53.45; H, 3.98; N, 2.40%.

$OsCl_2(PCl_3)(CO)(PPh_3)_2$ (9)

$OsHCl(PCl_3)(CO)(PPh_3)_2$ (**2**), 0.1 g, in 10 mL dry dichloromethane was treated with 1 mL of a *3* M chlorine solution in carbon tetrachloride. After 12 h all solvents were removed in vacuo and the residue was recrystallized from dichloromethane/ethanol to give 0.1 g (96%) of product m.p. 205 ° C. Anal. Found: C, 47.06; H, 3.78. $C_{37}H_{30}Cl_5OOsP_3$ calcd.: C, 46.73; H, 3.19%.

$OsCl_2[P(OMe)_3](CO)(PPh_3)_2$ (10)

Method A. $OsHCl[P(OMe)_3](CO)(PPh_3)_2$ [16], 0.06 g, was dissolved in 10 mL dichloromethane and treated with a solution of 10 mL acetonitrile and 0.1 mL aqueous perchloric acid. Vigorous hydrogen evolution ceased within 10 min. After 1 h all solvents were removed and the thick viscous residue was recrystallized from dichloromethane/ethanol/isopropanol to give 0.05 g of $[OsCl[P(OMe)_3](NCCH_3)(CO)(PPh_3)_2]ClO_4$. This product was spectroscopically characterized and was used for the next step which involved dissolving in 10 mL dichloromethane solution and adding a 20 mL solution of 0.08 g lithium chloride in ethanol. Within 10 min a white precipitate formed. After 4 h the dichloromethane was removed in vacuo and the white product filtered and washed with water, ethanol and n-hexane. Overall yield from the hydride complex was 65%, 0.04 g, m.p. 234 ° C. Anal. Found: C, 50.73; H, 4.11. $C_{40}H_{39}Cl_2O_4OsP_3$ calcd.: C, 51.23; H, 4.20%.

Method B. $OsCl_2(PCl_3)(CO)(PPh_3)_2$ (**9**), 0.08 g, was heated at reflux for 24 h in 20 mL of a 1 : 1 solution of THF and methanol in the presence of a drop of DBU. This solution was then cooled and, after an equal volume of ethanol was added, the dichloromethane was removed in vacuo to give 0.06 g of product. This was identified by spectroscopic means and by comparison with a sample prepared by Method A.

$OsHCl(DMPP)(CO)(PPh_3)_2$ (11)

$OsHCl(CO)(PPh_3)_3$, 0.5 g, 0.48 mmole, in 20 mL warm benzene was treated with a two fold excess of 1-phenyl 3,4-dimethylphosphole(DMPP). This mixture was heated at reflux for 1½ h and then cooled and the benzene was removed in vacuo. The white residue was recrystallized from dichloromethane/ethanol to give 0.43 g, 92%, of colourless cubes, m.p. 183 ° C. This product was characterized spectroscopically (Tables 1, 2, and 3).

$[OsCl(DMPP)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (12)

$OsHCl(DMPP)(CO)(PPh_3)_2$, 0.25 g, was treated with 0.2 mL aqueous perchloric acid in 40 mL of a 1 : 1 solution of dichloromethane/acetonitrile. Hydrogen evolution began instantly but proceeded relatively slowly. After 2 h the solvent was removed and the colourless gum recrystallized from dichloromethane/ethanol/isopropanol to give 0.24 g (87%) of large colourless cubes m.p. 143 ° C. Anal. Found: C, 55.42; H, 4.95; N, 1.23. $C_{51}H_{46}Cl_2NO_5OsP_3$ calcd.: C, 55.33; H, 4.20; N, 1.27%.

$OsCl_2(DMPP)(CO)(PPh_3)_2$ (13)

$[OsCl(DMPP)(NCCH_3)(CO)(PPh_3)_2]ClO_4$, 0.2 g, and 0.05 g of lithium chloride were dissolved in 10 mL 1 : 1 dichloromethane/ethanol. Within 10 min a cloudiness developed and this became a substantial precipitate over a two hour period. Additional ethanol was added and the dichloromethane was removed in vacuo.

Filtration, followed by successive washes with water, ethanol and n-hexane, yielded 0.19 g, 98%, of fine colourless needles m.p. 197 ° C. Anal. Found: C, 59.29; H, 5.28. $C_{49}H_{43}Cl_2OOsP_3$ calcd.: C, 58.74; H, 4.33%.

$Os(N_3)Cl(DMPP)(CO)(PPh_3)_2$ (14)

$[OsCl(DMPP)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (0.4 g) was treated as for the dichloride complex above except that 0.1 g of sodium azide was used instead of lithium chloride. After 1 h the dichloromethane was removed in vacuo and the product, 0.35 g cream-coloured needles, 91%, was recovered by filtration and successive washes with water, ethanol and n-hexane. M.p. 163 ° C. Anal. Found: C, 58.12; H, 4.92; N, 4.01. $C_{49}H_{43}ClN_3OOsP_3$ calcd.: C, 58.42; H, 4.36; N, 4.16%.

$OsHCl(PH_2mesityl)(CO)(PPh_3)_2$ (15)

$OsHCl(CO)(PPh_3)_3$, 0.52 g, and 1.5 equivalents of mesitylphosphine [17] (0.11 g, 0.75 mmole) were heated at reflux under nitrogen in 20 mL oxygen-free benzene for 30 min. The colourless solution was cooled and concentrated to an oil by removal of the solvents in vacuo. This residue was recrystallized from dichloromethane/ethanol to give 0.45 g (96%) of colourless crystals m.p. 181 ° C (dec). Anal. (as $\frac{3}{4}$ dichloromethane solvate as confirmed by ^1H NMR) Found: C, 56.35; H, 5.85. $C_{46}H_{44}ClOOsP_3 \cdot \frac{3}{4}CH_2Cl_2$ calcd.: C, 56.53; H, 4.57%.

$[OsCl(PH_2mestiyl)(CO)_2(PPh_3)_2]ClO_4$ (17a and 17b)

This was prepared as a mixture of isomers in two steps from $OsHCl(PH_2$ $mesityl)(CO)(PPh_3)_2$ as follows. $OsCl(PH_2mesityl)(CO)(PPH_3)_2$, 1 g, in 20 mL dichloromethane was treated with a 20 mL acetonitrile solution of 0.5 mL aqueous perchloric acid. This mixture was stirred 2 h and then all the solvents were removed in vacuo to give a colourless oil. This residue was recrystallized from dichloromethane/ethanol/isopropanol to give 0.9 g (81%). In the second step this mixture was carbonylated in 20 mL dichloromethane contained in a Fischer–Porter bottle (500 mL) at 200 kPa, 25 ° C, for 12 h. After release of the CO pressure, ethanol was added and a white solid (0.46 g, 77% yield from $OsHCl(PH_2mesityl)(CO)(PPh_3)_2$) was recovered by concentration of the solution in vacuo. M.p. 173 ° C. Anal. Found: C, 53.94; H, 4.45. $C_{47}H_{43}Cl_2O_6OsP_3$ calcd.: C, 53.36; H, 4.10%. Crystals of **17b**, suitable for an X-ray diffraction study were grown from dichloromethane/ethanol.

Crystal structure determination

Crystal data. $C_{47}H_{43}ClO_2OsP_3.ClO_4$, **17b**, $M = 1057.88$ monoclinic, space group $P2_1/n$ (No. 14, alternative setting), $a = 9.674(1)$, $b = 34.756(5)$, $c = 13.720(1)$ Å, $\beta = 102.19(1)°$, $V = 4509.3(9)$ Å^3, $Z = 4$, ρ(calcd) = 1.558 g cm^{-3}, $T = 292 \pm 1$ K, $F(000) = 2032$, $\lambda = 0.71069$ Å, Zr filtered Mo-K_α radiation, μ(Mo-K_α) = 32.69 cm^{-1}, crystals grown from dichloromethane/ethanol.

Intensity data collection. Enraf–Nonius CAD4 diffractometer, ω–2θ scans, scan width = $0.80 + 0.35 \tan \theta$ to θ max 24°. No decline in intensity standards, data collected for $-12 \leq h \leq 0$, $-40 \leq k \leq 0$, $-16 \leq l \leq 16$ comprised 7649 measurements. Lorentz and polarization factors applied, and absorption corrections (from psi scan data [18]) with max. and min. transmission 1.000 and 0.853 respectively; after averaging ($R = 0.044$) there remained 6274 unique reflections of which 4495 had $F^2 > 3\sigma(F^2)$.

Structure solution and refinement. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares. Computations were carried out using SHELX [19]. Atomic scattering factors and dispersion corrections were from standard listings [20]. The function minimised was $\Sigma w \| F_o | - | F_c \|^2$, with $w \propto 1/[\sigma^2(F_o) + gF_o^2]$. The perchlorate anion adopts two possible orientations in the crystal (by rotation about the Cl(B)–O(B1) bond) with almost equal probability for each arrangement (refined occupancies 0.51, 0.49). No attempt was made to locate hydrogen atoms. The osmium, chlorine and phosphorus atoms were assigned anisotropic thermal parameters. Final R and $R_w (= \Sigma w \| F_o | - | F_c \|^2 / \Sigma w | F_o |^2)$ and the weighting parameter g were 0.052, 0.050 and 2.34×10^{-4} respectively. Final atomic positions are listed in Table 6. Supplementary data comprising atomic thermal parameters, bond lengths involving phenyl rings, and observed and calculated structure factor listings are available on request from the authors (G.R.C.).

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References

1 D.S. Bohle, C.E.F. Rickard and W.R. Roper, Angew. Chem., Int. Ed. Engl., 100 (1988) 308; Angew. Chem., 27 (1988) 302.

2 F. Mercier and F. Mathey, J. Chem. Soc., Chem. Commun., 1984, 782.

3 D.S. Bohle, T.C. Jones, C.E.F. Rickard and W.R. Roper, Organometallics., 5 (1986) 1612; D.S. Bohle and W.R. Roper, J. Organomet. Chem., 273 (1984) C4.

4 C.S. Kraihanzel and C.M. Bartish, J. Am. Chem. Soc., 94 (1972) 3572; J. Organomet. Chem., 43 (1972) 343.

5 D.S. Bohle, G.R. Clark, C.E.F. Rickard, W.R. Roper and M.J. Taylor, J. Organomet. Chem., 348 (1988) 385.

6 F. Mathey, J. Fischer and J. Nelson, Structure and Bonding, 55 (1983) 153.

7 O.J. Scherer, Angew. Chem., Int. Ed. Engl., 24 (1985) 924; Angew. Chem., 97 (1985) 905.

8 J.G. Riess, in Rings, Clusters and Polymers of the Main Group Elements, A.C.S. Symposium Series 232 (1983) 17: P.T. Wood and J.D. Woollins, Transition Met. Chem., 11 (1986) 358.

9 O. Stelzer, Top. in Phosphor. Chem., 9 (1977) 1.

10 R.B. King, F.-J. Wu and E.M. Holt, J. Am. Chem. Soc., 109 (1987) 7764.

11 W. Malisch, R. Maisch, I.J. Colquhoun and W.J. McFarlane, J. Organomet. Chem., 220 (1981) C1. See also W. Malisch and R. Alsmann, Angew. Chem., Int. Ed. Engl., 15 (1976) 769.

12 E.A.V. Ebsworth, R.O. Gould, N.T. McManus, N.J. Pilkington and D.W.H. Rankin, J. Chem. Soc., Dalton Trans., (1984) 2561.

13 P.G. Douglas and B.L. Shaw, J. Chem. Soc. (A), (1970) 1556.

14 D.F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw-Hill, 1969.

15 D.D. Perrin, W.L.F. Armarego and D.R. Perrin, Purification of Laboratory Chemicals, Second Edition, Pergamon, Oxford, 1980, p. 249.

16 K.R. Grundy, Ph.D. Thesis, University of Auckland, 1975.

17 W.C. Davies, J. Chem. Soc., (1935) 462; T. Oshikawa and Yamashita, Chem. Ind., (1985) 126.

18 A.C. North, D.C., Phillips and F.S. Mathews, Acta Crystallogr. A, 24 (1968) 351.

19 SHELX-76, Program for Crystal Structure Determination, G.M. Sheldrick, Univ. of Cambridge, England, 1976.

20 International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.