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Phosphine (PH_3) complexes of ruthenium, osmium and iridium as precursors of terminal phosphido (PH_2) complexes and the crystal structure of $[Os(\mu_2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2 \cdot (C_2H_2Cl_4)_4$

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Abstract

Stable phosphine complexes $MHCl(PH_3)(CO)(PPh_3)_2$ (M = Os, **1a**, M = Ru, **1b**) and $IrHXCl(PH_3)(PPh_3)_2$ (X = H, **2**, X = Cl, **3**) have been prepared by substitution of phosphine for a labile triphenylphosphine in tris(triphenylphosphine) precursors. Strong acids (e.g. aqueous $HClO_4$ in CH_3CN) cleave the hydride–metal bonds in **1a,1b** to give $[MCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**9a,9b**) as a mixture of isomeric complexes. The ligands Cl^-, PMe_3, and CO can be substituted for the labile acetonitrile in **9a** to give $OsCl_2(PH_3)(CO)(PPh_3)_2$ (**12**) $[OsCl(PH_3)(PMe_3)(CO)(PPh_3)_2]ClO_4$ (**10**) and $[OsCl(PH_3)(CO)_2(PPh_3)_2]ClO_4$ (**11**), respectively. Base deprotonates **10** and **11** to give stable isolable terminal phosphido complexes $OsCl(PH_2)L(CO)(PPh_3)_2$ (L = CO, **14**, L = PMe_3, **15**), but when **9a** is deprotonated, acetonitrile is also lost and a dimeric complex $[Os(\mu_2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2$ (**13**) is formed. The colourless crystals of **13** are triclinic with space group $P\bar{1}$, a 14.101(4), b 15.091(5), c 11.708(5) Å, α 96.68(3), β 91.71(3), γ 63.92(2)°, $Z = 1$, $V = 2222.0$ Å^3. The final refinement gave $R = 0.0589$, $R_w = 0.0603$ for 4865 observed reflections. Phosphine oxidatively adds to $Os(CO)_2(PPh_2)_3$ to give the stable hydride-phosphido-complex, $OsH(PH_2)(CO)_2(PPh_3)_2$ (**19**).

Introduction

Apart from cyclopentadienyl and its derivatives, tertiary phosphines constitute the largest, and most diverse, class of ligands in organometallic chemistry [1]. It is significant then that the coordination chemistry of the parent species, phosphine, PH_3, is particularly undeveloped. Since the first report by Fischer in 1968 of an organometallic phosphine complex [2], a variety of simple early transition metal carbonyl phosphine complexes have been prepared [3]. However, apart from several nickel(0) complexes [4], phosphine complexes of the later transition metals are

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restricted to examples of iridium(I) species at low temperature [5] and to two iridium(III) complexes. There is a general perception that phosphine is a poor σ-donor and π-acceptor [5], and consequently a labile, weakly binding, ligand. However, phosphine is extremely compact (cone angle θ 87°) [6]. Although the metal–phosphorus bond in phosphine complexes may be weaker than for related tertiary phosphine ligands, the kinetic consequences of such low steric demand can be very important at congested metal centres.

The general reactivity patterns of coordinated phosphine are poorly understood. Several observations [7] suggest that there is increased acidity of the PH group, but this has been neither measured experimentally nor exploited synthetically. Indeed, one way to view this potentially rich area of chemistry is that coordinated phosphine has a trifunctional phosphorus centre. To utilize this functionality the first step is proton abstraction to give terminal phosphido complexes such as **B** and **D** in equations 1 and 2. Isolation of **B** and **D** will largely be determined by the extent to

$$\underset{\textbf{(A)}}{L_nM\text{–}PH_3} \rightarrow \underset{\textbf{(B)}}{L_nM\text{–}PH_2^-} + H^+ \quad (1)$$

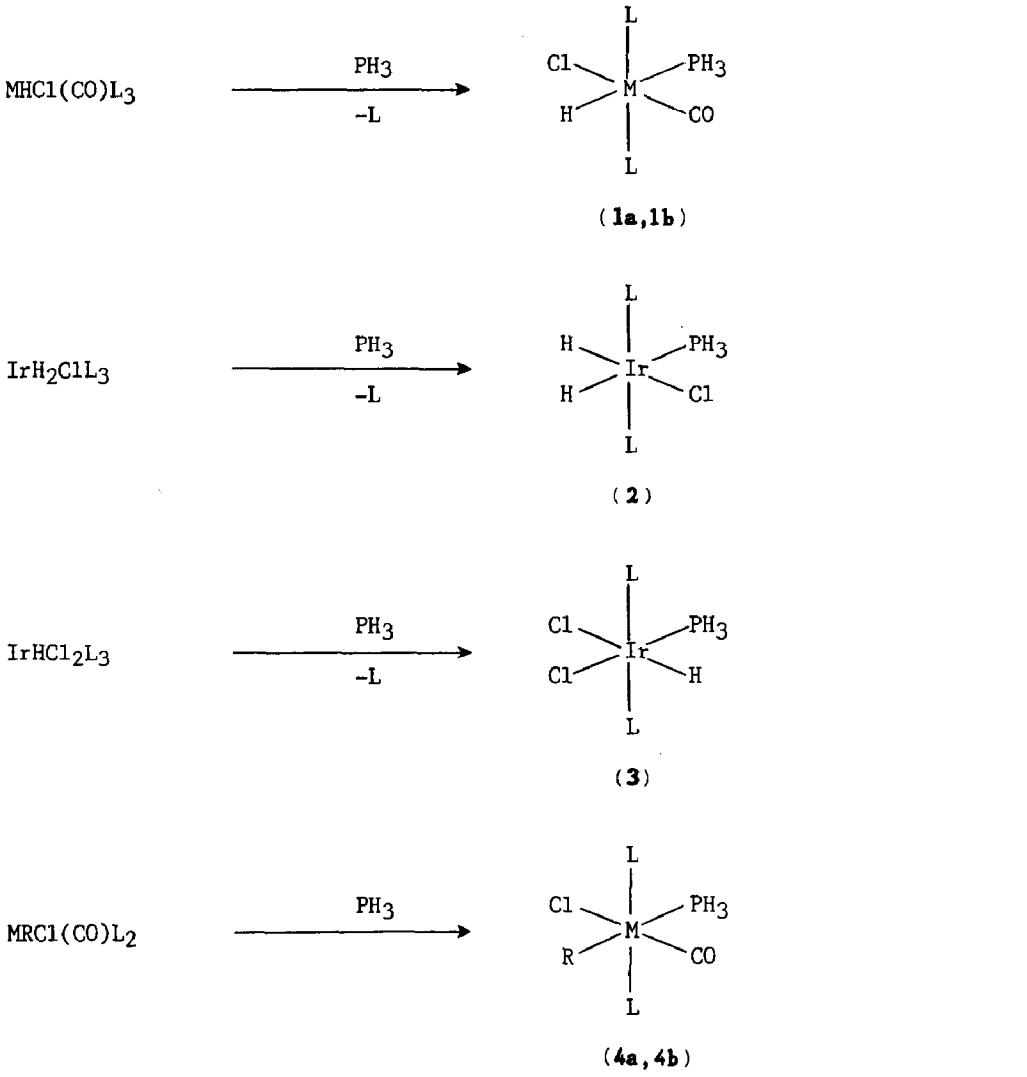
$$\underset{\textbf{(C)}}{[L_nM\text{–}PH_3]^+} \rightarrow \underset{\textbf{(D)}}{L_nM\text{–}PH_2} + H^+ \quad (2)$$

which oligomerization is prevented. Steric bulk provided by other ligands, such as triphenylphosphine in the examples below, kinetically stabilizes complexes like **B** and **D**. In this paper we report: (a) the facile synthesis of isolable ruthenium, osmium and iridium phosphine complexes; (b) high yield synthetic paths to complexes **A** and **C**; (c) deprotonation reactions of such complexes which yield isolable species like **D** or dimers of it; and (d) the structural characterization of one such dimer $[Os(\mu_2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2$. Some of these results have been communicated before [8].

Results and discussion

Phosphine is readily introduced into the coordination sphere of suitable ruthenium, osmium and iridium complexes (Scheme 1). These preparations can be divided into two broad classes: as in **1–3** where phosphine substitutes for a single labile triphenylphosphine; or by coordination of phosphine to a coordinatively unsaturated complex to give **4**. Each product **1–4** is isolated as an air stable, crystalline, colourless compound. Since steric effects [6,9] dominate such substitution reactions, replacement of triphenylphosphine (cone angle θ 145°) by a very compact phosphine (cone angle θ 87°) is complete within 10 min in benzene at reflux. Although phosphine coordinates readily in the preparation of **4a,4b**, triphenylphosphine does not add to these coordinatively unsaturated complexes [10]. Coordination of phosphine in **4a,4b** is rapid and complete in less than a minute at room temperature. Even though excess phosphine is used in the preparation of **1–4**, multiple substitution is not found under the conditions employed.

The geometry of the new phosphine complexes is firmly established by ^1H and ^{31}P NMR spectroscopy. Hydrogen–phosphorus and phosphorus–phosphorus coupling constants confirm the relative geometries of the hydride, phosphine and triphenylphosphine ligands in **1–3**. Thus in **1a** a *trans*-arrangement of hydride and



Scheme 1. Synthesis of phosphine complexes. L = PPh_3; **a**: M = Os, R = *p*-tolyl; **(b)** M = Ru, R = Ph.

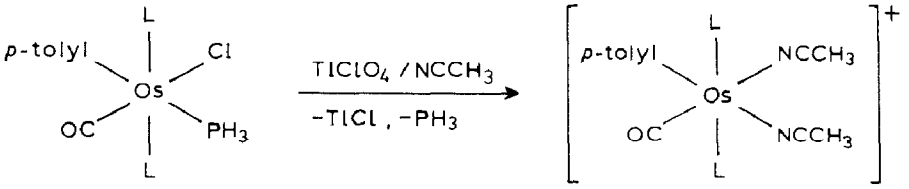
phosphine ligands is indicated by the magnitude of the phosphorus hydrogen coupling (^2J(HP) 105.7 Hz) while in **3** this coupling constant (^2J(HP) 19.63 Hz) indicates a *cis* geometry for these two ligands. It is significant that only a single geometry is found in the product of these substitution reactions. In contrast with the reaction described below there is no evidence for isomerism.

Reactions of phosphine complexes

Three general reaction types can be envisaged for the phosphine complexes **1–4**: (A) Metallation of, or proton abstraction from, the phosphine; (B) Chloride abstraction with silver(I) or thallium(I) salts; (C) Hydride cleavage with acids or electrophiles. Each of these types is discussed below in that order with an emphasis on the particularly useful products derived by (C).

Recent work indicates that lithium [11], mercury(II) [12], and silver(I) [12] readily metallate phosphine or primary phosphine ligands. In certain cases phosphine protons are also sufficiently acidic for phosphido complexes to be formed when phosphine complexes are treated with strong alkali [13]. Possibly because of the degree of functionality present at the metal in **1–4**, direct proton abstraction from these compounds does not lead to tractable products. In the deprotonation reactions which are described below there is only a single example of the reaction of a neutral complex that leads to tractable product (the dimer **13**, Scheme 3). Thus, strategies such as (B) and (C) have been employed on **1–4** to give cationic phosphine complexes.

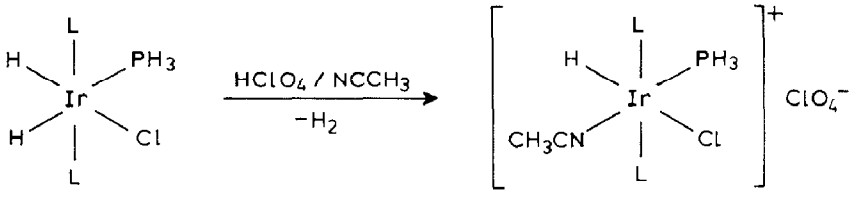
Silver(I) salts rapidly react with the labile chloride ligands in **3** and **4** to produce a silver chloride precipitate. However, in competition with this reaction is one, possibly involving metallation by silver of the phosphine, which leads to the production of a silver mirror. Products recovered from these reactions are devoid of ν(PH) and δ(PH) activity in the infrared spectrum. Solutions of thallium perchlorate in acetonitrile also lead to net chloride abstraction from **4a**. However the final product (eq. 3) recovered from this reaction, the bis-acetonitrile complex [Os(*p*-tolyl)$(NCCH_3)_2(CO)(PPh_3)_2]ClO_4$, results from loss of both chloride and phosphine.



(3)

(**4a**)

Many acids cleave a hydride ligand in compounds **1a,1b** and **2** but not in **3**. Of the two hydrides present in **2** the hydride *trans* to the phosphine is cleaved rapidly with aqueous perchloric acid/acetonitrile solutions to give **5** (eq. 4).

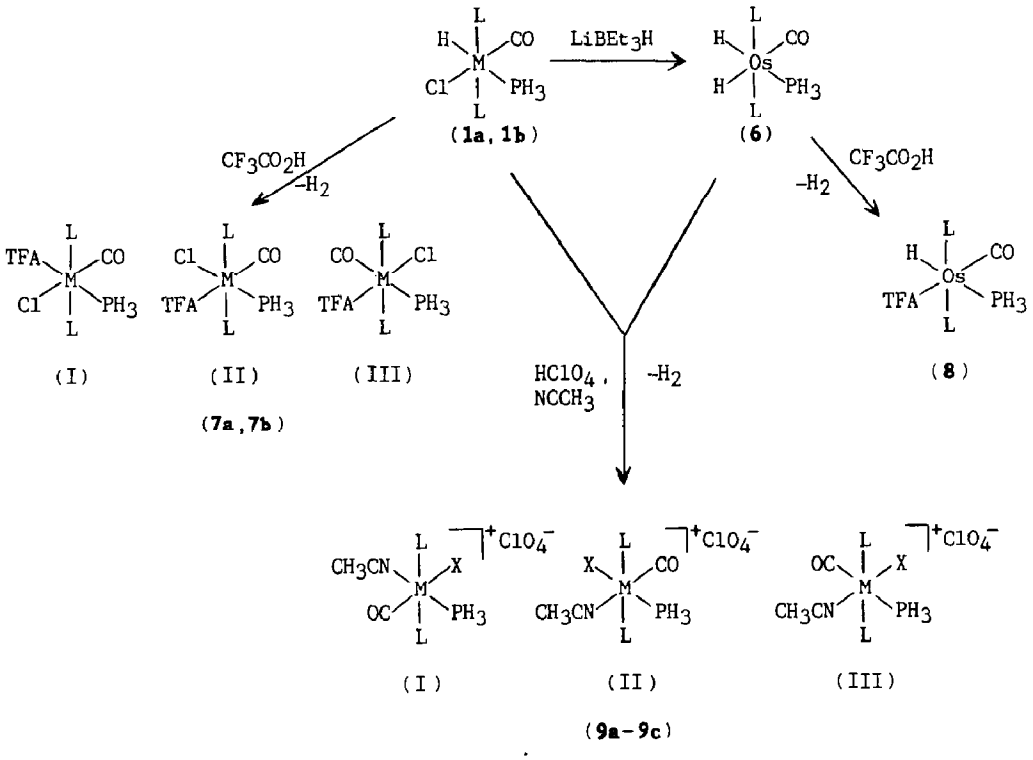


(4)

(**2**) (**5**)

The geometry assigned to **5** is based on ^{1}H NMR data (Table 9). As outlined in Scheme 2 the hydride cleavage reactions of **1a,1b** and **6** (M = Os) lead to tractable stable phosphine complexes. Acetonitrile solutions of aqueous perchloric acid produce mixtures of isomeric cationic complexes formulated as **9** I–III. With trifluoroacetic acid neutral trifluoroacetate complexes **7a,7b** and **8** result.

The three isomeric complexes **9a** I–III correspond to all three possible isomers with mutually *trans*-triphenylphosphine ligands (Scheme 2) as determined by ^{1}H and ^{31}P NMR. Only two isomers are produced when **1b** (M = Ru) or **6** (M = Os, X = H) are treated in this manner. In the last case (X = H) **9c** the relative geometries of the hydride and phosphorus ligands is firmly established by NMR.



Scheme 2. Hydride cleavage reactions of phosphine complexes. X = H, Cl; L = PPh_3; TFA = trifluoroacetate; a: M = Os, X = Cl; b: M = Ru, X = Cl; c: M = Os, X = H.

However the absolute geometries of isomers I–III, that is, the positions of the carbon monoxide, acetonitrile and chloride ligands in **9a,9b** cannot be ascertained from these data. In one case **9a** (M = Os, X = Cl) it is possible to obtain crystals of the individual isomers I–III and to physically separate them. By using ^1H NMR with these samples it is possible to show that I–III do not interconvert on the time

Table 1

Isomer distributions from hydride cleavage reactions

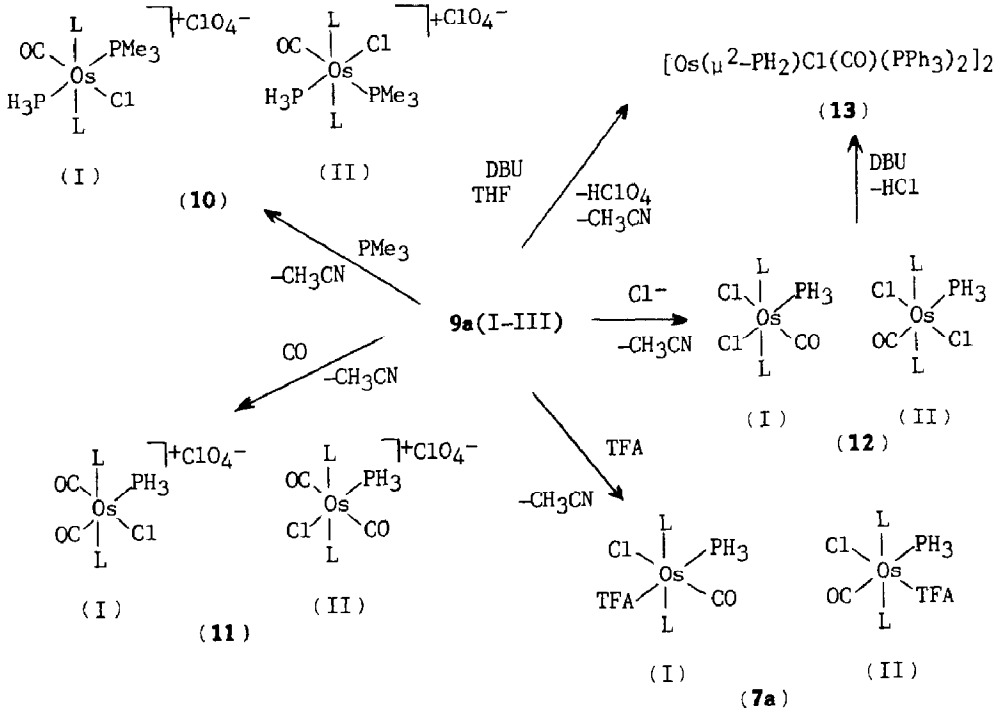
Perchloric acid in acetonitrile			
	9a	**9b**	**9c**
	M = Os, X = Cl	M = Ru, X = Cl	M = Os, X = H
% of total I	54	84	82
% of total II	32	16	18
% of total III	14		
Trifluoroacetic acid			
	7a	**7b**	**8**
	M = Os, X = Cl	M = Ru, X = Cl	M = Os, X = H
% of total I	63	47	100
% of total II	22	42	
% of total III	15	11	

scale (about 2 h) of the preparation and work up and that all of the peaks in the spectrum of the mixture can be accounted for. Unfortunately it has not been possible to grow crystals suitable for X-ray diffraction and thus to confirm the absolute geometries of I–III. For the major isomer of **9a** I, the carbon monoxide resonance in the ^{13}C spectrum is an overlapping doublet of triplets (δ(CO) 181.53 ppm, ^{2}J(CP) 9.9, 10.1 Hz) which indicates a *cis* geometry of the phosphine and carbon monoxide. Substitution reactions, outlined in the next section, suggest that I, with the introduced acetonitrile *trans* to phosphine, is the major product.

The neutral trifluoroacetate complexes **7a,7b,8** which result when **1a,1b** and **6** are treated with trifluoroacetic acid differ markedly in respect of their distribution of isomers. In the case of **8**, a single isomer, with hydride *trans* to phosphine (^{2}J(HP) 102.9 Hz), is produced, while from **7a,7b** a number of isomers is formed (Scheme 2 and Table 1). The ratios of isomers produced in these reactions are determined by integration of the phosphine resonances in the ^{1}H NMR.

Reactions of cationic complexes

Introduction of a labile acetonitrile ligand into the coordination sphere of **9** opens up the possibility of substituting a variety of neutral and anionic ligands into **9** (Scheme 3). The conditions which are required for these substitution reactions vary markedly: with trimethylphosphine substitution is complete within minutes at room temperature while carbon monoxide requires forcing conditions (16 h, 60 °C, 80 psi) to effect complete substitution of the acetonitrile. Each of the products of these reactions, **10** I,II and **11** I,II is a pair of isomers produced in approximately the same ratio (Table 2). The conditions employed for the carbonylation of **9a** are



Scheme 3. Reactions of $[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**9a**). L = PPh_3, TFA = trifluoroacetate.

Table 2

Isomer distribution of substitution reactions of L′ into $[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$

	L′	PMe_3 **10**	CO **11**	$CF_3CO_2^-$ **7a**	Cl^- **12**
% of total	I	75	71	71	[a]
% of total	II	25	29	–	
% of total	III	–	–	29	[a]

[a] See text.

more vigorous than those (8 h, 25°C, 40 psi) which are required for $[OsCl(PH_2Ph)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ [14]. This suggests that the *trans* effect of phosphine is less than that of phenylphosphine and that the reaction proceeds by a dissociative mechanism. Attempts to substitute *p*-tolyl isocyanide for the acetonitrile in **9a** fail to give tractable compounds. This is in contrast with the above phenylphosphine complex which reacts readily with *p*-tolylisocyanide to give $[OsCl(PH_2Ph)(CNR)(CO)(PPh_3)_2]ClO_4$. Of the three expected isomers which could be formed in the reaction of trimethylphosphine and **9a** only two are detected by NMR spectroscopy.

In an attempt to ascertain whether there is kinetic or thermodynamic control of the substitution reactions to give the trimethylphosphine complex **10** a variety of conditions were employed for its preparation. As judged by the intensities of the carbonyl stretching bands in the infrared spectrum, conducting the substitution reactions at −78°C produces the same ratio of isomers (3/1) as at room temperature. This ratio is also preserved after a 6 h reflux of **10** I,II in dichloromethane. Little interconversion seems to be occurring under these conditions. Thus it is likely that the origin of I and II is from the isomerism present in **9a**.

As depicted in Scheme 3, trifluoroacetate and chloride substitute for the acetonitrile in **9a** to give the neutral phosphine complexes **7a** and **12**, respectively. The compound **7a** can also be produced directly from $OsHCl(PH_3)(CO)(PPh_3)_2$ and trifluoroacetic acid but the isomeric distribution of the two products is very different (Table 3). The 3/1 ratio of the two products from the substitution reaction **9a** to **7a** (Scheme 3) is very close to that seen in the substitution reactions of carbon monoxide and trimethylphosphine. This is surprising considering how very different the ligands are in terms of basicity and π-acceptor character. Because of the insolubility of the dichloride complex **12** it is not possible to measure the isomeric ratio for this product, but the large difference in the carbonyl stretching bands in the infrared spectrum of **12** (Table 7) clearly indicates the presence of two isomers, which can only be with the two chloride ligands *cis* as in **12**I or *trans* as in **12**II. The ruthenium analogue of **9a**, $[RuCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**9b**), carbony-

Table 3

Isomer ratios for the formation of $OsCl(O_2CCF_3)(PH_3)(CO)(PPh_3)_2$ (**7a**)

	I	II	III
Hydride cleavage with CF_3CO_2H	63	22	15
$CF_3CO_2^-$ substitution into **9a**	71	–	29

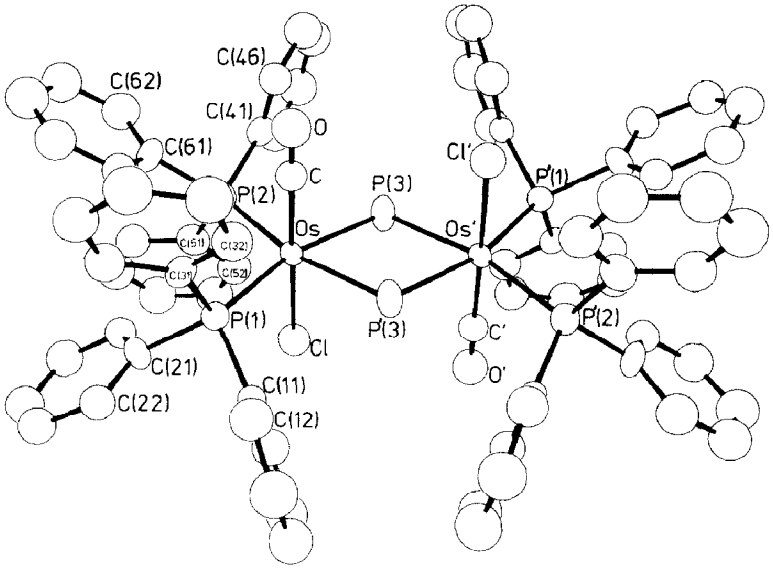


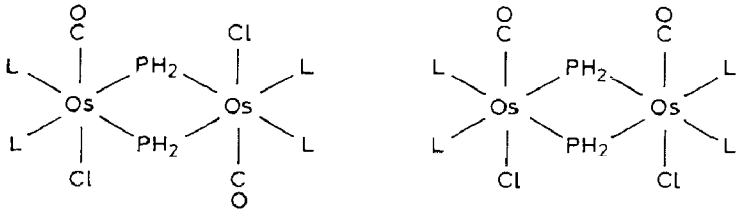
Fig. 1. Inner coordination sphere of $[Os(\mu_2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2$ (**13**).

lates under less forcing conditions to give only a single isomer of $[RuCl(PH_3)(CO)_2(PPh_3)_2]ClO_4$ (**16**) in high yield.

*Deprotonation reactions of $[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**9a**)*

At room temperature solutions and suspensions of **9a** rapidly react with base (DBU) to give slightly yellow solutions. At this point attempts to isolate products from the reaction fail; only amorphous powders with extremely broad ν(CO) bands in the infrared spectrum are isolated. However, if a tetrahydrofuran suspension of **9a** and DBU is heated under reflux a white crystalline solid rapidly forms. Recrystallization of this product from dichloromethane/ethanol gives a pure, poorly soluble, neutral complex. A phosphido ligand is indicated by the strong PH activity (ν(PH) 2298, 2280 cm^{-1}: δ(PH) 820 cm^{-1}) present in the infrared spectrum. An X-ray diffraction study (Fig. 1) revealed the dimeric nature of **13**. Deprotonation of the neutral phosphine complex **12** with base (DBU) in tetrahydrofuran at reflux also affords **13** albeit in lower yields.

Raman spectroscopic studies of crystalline samples of **13** reveal four bands in the phosphorus–hydrogen stretching region at least two of which are also infrared active (Table 7). This observation eliminates the centrosymmetric *trans* structure (I) on its own and our interpretation is that **13** is an isomeric mixture of *trans*-I (C_{2h}) and *cis*-II (C_{2v}) forms. This isomerism is also present in solution as the ^{31}P NMR



spectra of **13** have two distinct sets of bridging phosphido and triphenylphosphine resonances with similar chemical shifts and coupling constants. These are attributable to the presence of the two isomers I and II.

X-ray crystallographic study of $[Os(\mu_2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2$

To confirm the dimeric nature of **13** a single crystal X-ray diffraction study was performed. The bond length and bond angle data are presented in Tables 4 and 5 respectively and in Table 6 the final atomic positions are collected.

As depicted in Fig. 1 the geometry at each metal is octahedral with *cis*-triphenylphosphine ligands each *trans* to a bridging phosphido ligand. Complete disorder of the axial chloride and carbon monoxide ligands suggests that the isomeric forms of **13**, I and II have co-crystallized together. This result is supported by the above-mentioned vibrational studies. One particular geometry, with a *trans* configuration **13** I, is depicted in Fig. 1.

The osmium–phosphorus bond lengths to the bridging phosphorus atoms (Os–P(3) 2.396(3), Os–P′(3) 2.401(3) Å) are significantly shorter than those to the triphenylphosphine ligands (Os–P(2) 2.425(3), Os–P(1) 2.423(3) Å). Figure 2 depicts the in-plane geometry of the metal and phosphorus ligands. Attempts to locate the hydrogen atoms of the bridging phosphido groups by Fourier difference methods have failed. Steric effects are probably responsible for this *cis*-triphenylphosphine

Table 4

Interatomic distances (Å) for $[Os(\mu_2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2 \cdot (C_2H_2Cl_4)_4$

Os–P(1)	2.423(3)	Os–Cl(1)	2.44 [a]
Os–P(2)	2.425(3)	Os–C(1)	1.90 [a]
Os–P(3)	2.396(3)	C(1)–O(1)	1.10 [a]
Os–P′(3)	2.401(3)		
P(1)–C(11)	1.853(13)	P(2)–C(41)	1.858(14)
P(1)–C(21)	1.852(12)	P(2)–C(51)	1.849(14)
P(1)–C(31)	1.844(12)	P(2)–C(61)	1.837(14)

Bond lengths for $CHCl_2CHCl_2$ solvate

C(71)–C(72)	1.35(3)	C(81)–C(82)	1.41(3)
C(71)–Cl(6)	1.78(2)	C(81)–Cl(7)	1.79(3)
C(71)–Cl(4)	1.82(2)	C(81)–Cl(8)	1.81(3)
C(72)–Cl(3)	1.94(3)	C(82)–Cl(9)	1.79(3)
C(72)–Cl(5)	1.76(3)	C(82)–Cl(10)	1.84(3)

Bond lengths for triphenylphosphine phenyl rings

	i					
	1	2	3	4	5	6
C(*i*1)–C(*i*2)	1.42(2)	1.39(2)	1.40(2)	1.38(2)	1.40(2)	1.45(2)
C(*i*1)–C(*i*6)	1.41(2)	1.39(2)	1.40(2)	1.39(2)	1.39(2)	1.39(2)
C(*i*2)–C(*i*3)	1.43(2)	1.43(2)	1.45(2)	1.41(2)	1.39(2)	1.41(2)
C(*i*3)–C(*i*4)	1.39(2)	1.32(2)	1.37(2)	1.36(2)	1.39(2)	1.37(2)
C(*i*4)–C(*i*5)	1.37(3)	1.42(2)	1.36(2)	1.36(2)	1.37(2)	1.41(2)
C(*i*5)–C(*i*6)	1.37(2)	1.44(2)	1.45(2)	1.42(2)	1.44(2)	1.41(2)

[a] Atoms not refined.

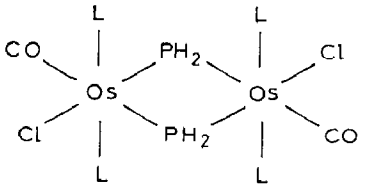
Table 5

Interatomic angles (°) for $[Os(\mu_2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2 \cdot (C_2H_2Cl_4)_4$

Angles involving osmium			
P(1)–Os–P(2)	105.3(1)	P(2)–Os–Cl(1)	90.4(1)
P(1)–Os–P(3)	163.7(1)	P(2)–Os–C(1)	87.0(1)
P(1)–Os–P′(3)	90.4(1)	P(3)–Os–Cl(1)	87.4(1)
P(2)–Os–P(3)	91.0(1)	P(3)–Os–C(1)	89.1(1)
P(2)–Os–P′(3)	164.2(2)	P′(3)–Os–C(1)	91.6(2)
P(3)–Os–P′(3)	73.3(2)	P′(3)–Os–Cl(1)	89.9(2)
P(1)–Os–Cl(1)	91.1(1)	Cl(1)–Os–C(1)	175.6 [a]
P(1)–Os–C(1)	93.0(1)		
Os–P(3)–Os′	106.67(3)	Os–C(1)–O(1)	180 [a]
Selected angles for triphenylphosphine ligands			
Os–P(1)–C(11)	115.1(4)	Os–P(2)–C(41)	113.9(5)
Os–P(1)–C(21)	121.7(4)	Os–P(2)–C(51)	117.0(5)
Os–P(1)–C(31)	116.3(4)	Os–P(2)–C(61)	119.4(5)
C(11)–P(1)–C(21)	96.3(6)	C(41)–P(2)–2C(51)	102.7(6)
C(21)–P(1)–C(31)	102.4(7)	C(51)–P(2)–C(61)	102.2(6)
C(11)–P(1)–C(31)	101.5(6)	C(41)–P(2)–C(61)	98.7(6)

[a] Atoms not refined.

geometry being preferred rather than the alternative geometry with *trans*-triphenylphosphines:



Formation of a stable dimeric complex like **13** is surprising and unusual in this chemistry. The ^{31}P NMR spectrum indicates that the solid state geometry is preserved in solution as there is strong coupling between triphenylphosphine and phosphido phosphorus nuclei (^2J(PP) 195 Hz). Other acetonitrile containing cations such as **9b** (M = Ru) or **9c** (M = Os, X = H) also react with DBU but dimeric species cannot be isolated even after prolonged heating at reflux in tetrahydrofuran. If there are large substituents on the phosphorus, dimeric complexes do not form; $[OsCl(PH_2Ph)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ [14] reacts rapidly with DBU but even after prolonged reflux in tetrahydrofuran dimeric complexes cannot be isolated.

Other bridging phosphido dimeric and trimeric compounds, $[(OC)_4Mn(\mu_2\text{-}PH)]_n$, $n = 2,3$, have been prepared from Me_3SiPH_2 and $(OC)_5MnCl$ [15]. These bridging phosphido ligands can be halogenated with CX_4, X = Cl, Br, I to give $[(OC)_4Mn(\mu_2\text{-}PX_2]_2$ and $[(OC)_4Mn(\mu_2\text{-}PCl_2)]_3$. A similar reactivity pattern for **13** is not observed. Even after a 4 h reflux in carbon tetrachloride **13** is recovered unchanged. Halide abstraction with silver tetrafluoroborate was also attempted to functionalize either the metal or the phosphorus, no reaction was observed even after **13** and $AgBF_4$ were heated at reflux overnight in acetonitrile.

(*Continued on p. 401*)

Table 6

Atomic positions for $[Os(\mu_2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2 \cdot (CHCl_2CHCl_2)_4$

Atom	x	y	z
Os	0.1407(0)	0.4428(0)	0.5586(0)
P(1)	0.2232(3)	0.5273(3)	0.6829(3)
P(2)	0.2373(3)	0.2719(3)	0.5230(3)
P(3)	0.0194(3)	0.4060(3)	0.4377(3)
Cl(1)	0.2016	0.4831	0.3877
Cl(2)	0.0783	0.3921	0.7201
C(1)	0.1881	0.4742	0.4255
C(2)	0.0921	0.4033	0.6843
O(1)	0.2155	0.4924	0.3485
O(2)	0.0640	0.3805	0.7571
C(11)	0.1697(9)	0.6625(9)	0.6742(11)
C(12)	0.1324(13)	0.7325(13)	0.7739(14)
C(13)	0.1061(15)	0.8337(14)	0.7612(16)
C(14)	0.1215(14)	0.8599(13)	0.6560(15)
C(15)	0.1599(13)	0.7909(13)	0.5612(15)
C(16)	0.1806(12)	0.6942(12)	0.5690(13)
C(21)	0.3639(10)	0.4990(11)	0.6636(11)
C(22)	0.4030(11)	0.5612(11)	0.7220(12)
C(23)	0.5130(12)	0.5329(12)	0.7086(13)
C(24)	0.5755(13)	0.4550(13)	0.6380(14)
C(25)	0.5384(12)	0.3905(12)	0.5748(14)
C(26)	0.4281(11)	0.4153(10)	0.5907(12)
C(31)	0.2121(10)	0.5242(10)	0.8388(10)
C(32)	0.1113(12)	0.5559(12)	0.8873(13)
C(33)	0.0954(14)	0.5562(13)	1.0088(15)
C(34)	0.1855(14)	0.5184(14)	1.0716(16)
C(35)	0.2854(13)	0.4836(13)	1.0279(15)
C(36)	0.3008(12)	0.4874(12)	0.9074(13)
C(41)	0.2191(10)	0.1821(9)	0.4759(12)
C(42)	0.2346(12)	0.1337(12)	0.3659(14)
C(43)	0.1966(15)	0.0619(14)	0.3385(16)
C(44)	0.1391(15)	0.0465(14)	0.4179(16)
C(45)	0.1186(14)	0.0967(14)	0.5249(16)
C(46)	0.1608(11)	0.1655(11)	0.5576(12)
C(51)	0.3756(11)	0.2437(11)	0.4107(13)
C(52)	0.3441(13)	0.2688(12)	0.2997(14)
C(53)	0.4187(15)	0.2457(15)	0.2127(16)
C(54)	0.5251(16)	0.1971(15)	0.2366(17)
C(55)	0.5602(15)	0.1732(15)	0.3443(17)
C(56)	0.4825(13)	0.1958(12)	0.4336(14)
C(61)	0.3531(10)	0.2104(10)	0.6426(12)
C(62)	0.4121(14)	0.1034(13)	0.6313(15)
C(63)	0.4782(14)	0.0586(14)	0.7213(16)
C(64)	0.4890(15)	0.1175(15)	0.8145(17)
C(65)	0.4273(13)	0.2212(13)	0.8307(15)
C(66)	0.3606(11)	0.2669(11)	0.7414(12)
C(71)	0.2435(19)	0.1207(18)	0.9056(20)
C(72)	0.1501(20)	0.1939(19)	0.9457(21)
Cl(3)	0.1915(6)	0.2946(5)	1.0143(6)
Cl(4)	0.2008(6)	0.0327(5)	0.8298(6)
Cl(5)	0.0846(6)	0.1706(6)	1.0561(7)
Cl(6)	0.3371(5)	0.0656(6)	1.0119(6)
C(81)	0.1773(22)	0.7653(21)	0.1196(23)

Table 6 (continued)

Atom	x	y	z
C(82)	0.2836(20)	0.7237(18)	0.1526(21)
Cl(7)	0.1044(6)	0.7649(7)	0.2417(6)
Cl(8)	0.1298(10)	0.8913(7)	0.0859(9)
Cl(9)	0.3133(5)	0.7994(5)	0.2629(5)
Cl(10)	0.3622(9)	0.7079(10)	0.0224(7)

Table 7

Infrared spectroscopic data [a,b]

Complex		ν(CO) [c]	ν(PH)	δ(PH)	Other bands [d]
$OsHCl(PH_3)(CO)(PPh_3)_2$	**(1a)**	1942s 1908(s)	2362w 2331m	1030s 1016s	2030m, ν(Os–H) 822w, δ(Os–H) 283w, ν(Os–Cl)
$RuHCl(PH_3)(CO)(PPh_3)_2$	**(1b)**	1951s 1922s 1830s	2370w 2321m	1013s 1000s	1976m, ν(Ru–H) 798w, δ(Ru–H) 284w, ν(Ru–Cl)
$IrH_2Cl(PH_3)(PPh_3)_2$	**(2)**		2348w	1019s	2242m,2079m, ν(Ir–H) 861w,846w,801w, δ(Ir–H)
$IrHCl_2(PH_3)(PPh_3)_2$	**(3)**		2385w 2363w 2341w	1032s 1013s	2177m, ν(Ir–H) 802m, δ(Ir–H) 294w, 253w, ν(Ir–Cl)
Os(*p*-tolyl)$Cl(PH_3)(CO)$-$(PPh_3)_2$	**(4a)**	1910s	2337w 2319w	1017m	804m,793m, (tolyl) 282m, ν(Os–Cl)
$Ru(Ph)Cl(PH_3)(CO)(PPh_3)_2$	**(4b)**	1924s	2336w	1010s 1000s	291m, ν(Ru–Cl)
$[IrHCl(PH_3)(NCCH_3)$-$(PPh_3)_2]ClO_4$	**(5)**		2340w	1035s	
$OsH_2(PH_3)(CO)(PPh_3)_2$	**(6)**	1972s 1956s 1931m	2322m	1048s	2011sh,1851s, ν(Os–H) 840w,809w,790w, δ(Os–H)
$OsCl(TFA)(PH_3)(CO)(PPh_3)_2$	**(7a)**	1982m 1960s 1929sh	2393w 2357w	1040m	1691s, $\nu(O_2CCF_3)$ 1210s,1140m, ν(C–F)
$RuCl(TFA)(PH_3)(CO)(PPh_3)_2$	**(7b)**	1995s 1967m	2360w	1018s	1690s, $\nu(O_2CCF_3)$ 1205s,1132s, ν(C–F)
$OsH(TFA)(PH_3)(CO)(PPh_3)_2$	**(8)**	1946s 1916s 1927(s)	2363m	1027s 1019m	2050m, ν(Os–H) 1691s,1667s, $\nu(O_2CCF_3)$ 1201s,1139s, ν(C–F) 792w, δ(Os–H) 1680(s), $\nu(O_2CCF_3)$
$[OsCl(PH_3)(NCCH_3)(CO)$ $(PPh_3)_2]ClO_4$ all isomers I–IIII	**(9a)**	1963s	2377w	1036s	283w, ν(Os–Cl)
$[RuCl(PH_3)(NCCH_3)(CO)$ $(PPh_3)_2]ClO_4$ both isomers I,II	**(9b)**	1976s		1020m	283w, ν(Ru–Cl)
$[OsH(PH_3)(NCCH_3)(CO)$ $(PPh_3)_2]ClO_4$ both isomers I,II	**(9c)**	1972s 1949s	2370w	1021s	2103w, ν(Os–H)
$[OsCl(PH_3)(PMe_3)(CO)$ $(PPh_3)_2]ClO_4$ both isomers I,II	**(10)**	1963s 1945m 1966(s) 1942(s)	2370w		957s,864s, ρ(P–Me) 295w,285w, ν(Os–Cl)
$[OsCl(PH_3)(CO)_2(PPh_3)_2]ClO_4$ both isomers I,II	**(11)**	2063s 2004s	2290w	1039m 1001m 934w	298w, ν(Os–Cl)

Table 7 (continued)

Complex		ν(CO) [c]	ν(PH)	δ(PH)	Other bands [d]
$OsCl_2(PH_3)(CO)(PPh_3)_2$ both isomers I,II	(12)	1987s 1922s 1940(s)	2360w	1035s	293w,271w, ν(Os–Cl)
$[Os(\mu_2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2$	(13)	1923s	2300m 2284s	804s	2355m,2336w,2298s, 2284m, ν(PH) Raman 1928m, ν(CO) bands 286s, ν(Os–Cl)
$OsCl(PH_2)(CO)_2(PPh_3)_2$	(14)	2028s 1962s 1956m 2023(s) 1958(s)	2285m 2250m	1190w	293w, ν(Os–Cl)
$OsCl(PH_2)(PMe_3)(CO)(PPh_3)_2$	(15)	1927s 1916s 1889m 1927(s) 1894(s)	2281m 2260m		956s, ρ(P–Me) 263w, ν(Os–Cl)
$[RuCl(PH_3)(CO)_2(PPh_3)_2]ClO_4$	(16)	2063s 2009s	–	998m 986m 952w	302w, ν(Ru–Cl)
$RuCl(PH_2)(CO)_2(PPh_3)_2$	(17)	2033s 1978s	2284m 2252m	1192w	286w, ν(Ru–Cl)
$[OsH(PH_3)(CO)_2(PPh_3)_2]ClO_4$	(18)	2061s 2011s 1954s	2370w	1019s	806w, δ(Os–H)
$OsH(PH_2)(CO)_2(PPh_3)_2$	(19)	2023s 1978s 1940m 1907s	2296m 2280m	–	815w, δ(Os–H)
$[OsCl(PH_2Ph)(CN\text{-}p\text{-}tolyl)(CO)(PPh_3)_2]ClO_4$		1999s		840w 802m	2168m, ν(CNR) 292w, ν(Os–Cl)

[a] In cm^{-1}. Spectra recorded as a nujol mull between KBr or CsI discs and calibrated with polystyrene. [b] s, strong; m, medium; w, weak; sh, shoulder; (s) dichloromethane solution spectrum. [c] Multiple ν(CO) bands are attributed to solid-state splitting. [d] Absorbtions due to triphenylphosphine not given. TFA = trifluoroacetate in complexes 7 and 8.

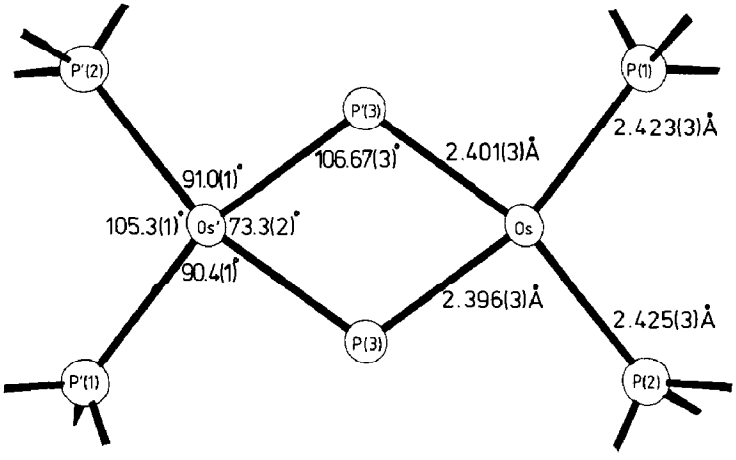


Fig. 2. View of plane containing the metal and phosphorus atoms in $[Os(\mu_2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2$.

Table 8

NMR spectroscopic data for new compounds [a]

Compound	^{1}H NMR Data				^{31}P NMR Data		
	$\delta(PH_n)$	$^1J(HP)$	$^3J(HP)$	Other [c]	$\delta(PH_n)$	$\delta(PPh_3)$	$^2J(PP)$
$OsHCl(PH_3)(CO)(PPh_3)_2$ **(1a)**	3.15	330.1	3.8	−4.77(dt,^2J(HP) 105.7,18.9,1, Os−*H*)	−146.7	9.8	11.0
$RuHCl(PH_3)(CO)(PPh_3)_2$ **(1b)**	2.89	310.6	3.9	−5.12(dt,^2J(HP) 132.3,18.2,1, Ru−*H*)	−136.0	41.2	17.3
$IrH_2Cl(PH_3)(PPh_3)_2$ **(2)**	2.74	332.3	5.0	−8.73(dtd,^2J(HP) 153.7,16.2, ^2J(HH) 5.1,1,*H*-Ir-$(PH_3)_{trans}$) −21.96(ddt,^2J(HP) 13.1,14.3, ^2J(HH) 5.1,1,*H*-Ir-$(PH_3)_{cis}$)	−149.1	11.8	15.7
$IrHCl_2(PH_3)(PPh_3)_2$ **(3)**	2.73	390.3	4.6	−20.07(td,^2J(HP) 19.6,12.6,1, Ir-*H*)	−119.5	−4.1	15.8
Os(*p*-tolyl)$Cl(PH_3)(CO)(PPh_3)_2$ **(4a)**	3.10	335.7	3.25	2.15(s,3,$C_6H_4CH_3$); 6.52(d,^3J(HH) 7.6,2,$CH_3C_6H_4$)	−142.5	−8.93	10
$Ru(Ph)Cl(PH_3)(CO)(PPh_3)_2$ **(4b)**	2.72	318.6	2.9		−129.4	24.5	16.7
$[IrHCl(PH_3)(NCCH_3)(PPh_3)_2]ClO_4$ **(5)**	2.95	410.6	4.5	−19.46(dt,^2J(HP) 22.7,11.6,1, Ir-*H*)1.92(s,3,CH_3CN)	−129.5	1.52	17.2
$OsH_2(PH_3)(CO)(PPh_3)_2$ **(6)**	2.82	326.2	4.6	−8.24(dtd,^2J(HP) 69.9,21.5, ^2J(HH) 4.7,1,*H*-Os-$(PH_3)_{trans}$) −8.74(ddt,^2J(HP) 24.8,22.4, ^2J(HH) = 4.7,1,*H*-Os-$(PH_3)_{cis}$)	−166.2	25.1	12.4
$OsCl(TFA)(PH_3)(CO)(PPh_3)_2$	I 2.98	391.1	2.6		I −125.8	−3.85	12.3
(7a)	II 2.82	382.3	2.7		II −118.6	−10.15	12.8
isomers I–III	III 3.74	376.0	3.4		III −130.0	−6.24	15.7
$RuCl(TFA)(PH_3)(CO)(PPh_3)_2$	I 2.72	381.6	3.1		I −90.1	22.1	24.5
(7b)	II 2.66	374.0	3.2		II −83.5	19.3	25.0
isomers I–III	III 3.41	367.6	4.1		III −87.1	21.5	30.0
$OsH(TFA)(PH_3)(CO)(PPh_3)_2$ **(8)**	3.12	341.1	3.6	−4.11(dt,^2J(HP) 102.9,19.0,1, *H*-Os)	−150.0	17.9	10.3
$[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$	I 3.39	399.7	3.2	1.6(s,3,CH_3CN)	I −131.7	−1.4	11.9

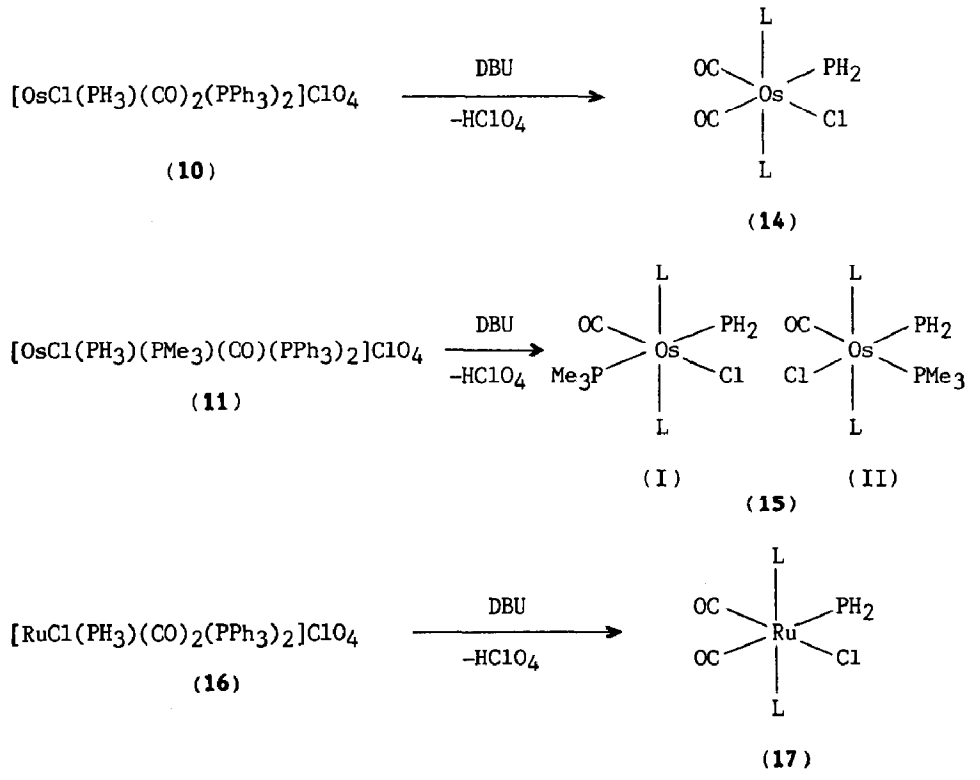
(9a)	II	3.75	393.1	4.7	1.9(s,3,CH_3CN)	II	−128.1	−8.8	18.2
isomers I–III	III	3.46	398.1	3.2		III	−127.1	5.7	12.7
[RuCl(PH_3)(NCCH_3)(CO)(PPh_3)$_2$]ClO_4	I	3.24	390.7	3.7	1.67(s,3,CH_3CN)	I	−94.4	26.4	25.4
(9b)	II	3.33	385.9	4.4	1.81(s,3,CH_3CN)	II	−92.2	28.5	23.2
isomers I,II									
[OsH(PH_3)(NCCH_3)(CO)(PPh_3)$_2$]ClO_4	I	3.01	367.0	6.7	−15.31(tdd,^2J(HP) 28.6,12.9, ^3J(HH) 3.4,1, *H*-Os)	I	−147.5	10.8	27.7
(9c)						II	−158.6	14.5	14.0
isomers I,II					1.94(s,3,CH_3CN)				
	II	3.50	352.8	4.1	−6.38(dt,^2J(HP) 79.9,17.2,2,1, *H*-Os)1.42(s,3,CH_3CN)				
[OsCl(PH_3)(PMe_3)(CO)(PPh_3)$_2$]ClO_4	I	2.80	757.3	3.3	1.49(dt,^3J(HP) 9.5, ^4J(HP) 2.0,9,P(CH_3)$_3$)	I	−122.3(dt,^2J(PP) 257.8(PH_3–PMe_3), ^2J(PP) 24.6(PH_3–PPh_3), PH_3) −48.9(dt,^2J(PP) 21.8(PMe_3–PPh_3), PMe_3) −14.7(dt, PPh_3)		
(10)									
isomer I,II									
	II	3.59	383.0	5.6	2.2(dt,^2J(PH) 9.5,^4J(HP) 2.2,9, P(CH_3)$_3$)				
[OsCl(PH_3)(CO)$_2$(PPh_3)$_2$]ClO_4	I	3.34	415.9	2.9		I	−121.9	−15.6	26
(11)	II	3.83	404.7			II	−136.9	−11.1	9.6
both isomers I,II									
$OsCl_2$(PH_3)(CO)(PPh_3)$_2$	I	2.82	332.2	2.7		I	−118.9	−9.9	12.9
(12)	II [b]								
both isomers I,II									
[Os(μ_2-PH_2)Cl(CO)(PPh_3)$_2$]$_2$						I	−225.4	0.9	196.6
(13)						II	−229.2	1.2	195.2
OsCl(PH_2)(CO)$_2$(PPh_3)$_2$		0.87	175.3	10.5			−211.7	−10.8	–
(14)									
OsCl(PH_2)(PMe_3)(CO)(PPh_3)$_2$	0.70(dtd,^1J(HP) 179.6,^3J(H-PMe_3) 10.3, ^3J(H-PPh_3) 4.8,2,PH_2) 1.18(d,^2J(HP) 8.6,9(P(CH_3)$_3$)					−189.2(d,^2J(PP) 68(PH_2-PMe_3), PH_2) −54.8(dt,^2J(PP) 12.8(PMe_3-PPh_3), PMe_3) −4.2(d,PPh_3)			
(15)									
[RuCl(PH_3)(CO)$_2$(PPh_3)$_2$]ClO_4		3.78	393.7	6.0			−100.5	17.0	35.2
(16)									
RuCl(PH_2)(CO)$_2$(PPh_3)$_2$							−188.4	22.5	6
(17)									

continued

Table 8 (continued)

Compound	^{1}H NMR Data				^{31}P NMR Data		
	$\delta(PH_n)$	$^1J(HP)$	$^3J(HP)$	Other [c]	$\delta(PH_n)$	$\delta(PPh_3)$	$^2J(PP)$
$[OsH(PH_3)(CO)_2(PPh_3)_2]ClO_4$ **(18)**	I 3.29	392.9	7.0	−7.67(dtq,^2J(HP) 31.2,15.9, ^3J(HH) 5.0,1, *H*-Os-$(PH_3)_{cis}$)	I −151.5	6.0	28
	II 3.56	372.3	4.2	−7.94(dt,^2J(HP) 44.3,14.1,1, *H*-Os-$(PH_3)_{trans}$)	II −155.9	17.2	12.9
$OsH(PH_2)(CO)_2(PPh_3)_2$ **(19)**	−0.02	185.6	–	−7.00(td,^2J(H−PPh_3) 20.5, 6.6,1,Os-*H*) ^2J(H−PH_2)	−241.0	8.5	–
$[OsCl(PH_2Ph)(CN\text{-}p\text{-}tolyl)(CO)(PPh_3)_2]ClO_4$	5.38	387	7.2	2.35(s,3,CH_3) 6.27(d,^3J(HH) 8.4,2,CH_{ortho}) 7.30(d,^3J(HH) 8.4,2,CH_{meta})	−28.0(t,^2J(PP) 20,PH_2Ph) −15.2(d,^2J(PP) 20,PPh_3)		

[a] As chloroform solutions at 21°C. Proton chemical shifts (δ) are given in ppm with respect to tetramethylsilane and for phosphorus with respect to external 85% H_3PO_4. Coupling constants in Hz. [b] Too insoluble to measure spectrum. [c] Two bond coupling constants for hydride ligands (^2J(HP)) are listed as H−PH_2 coupling first and the H−PPh_3 second.



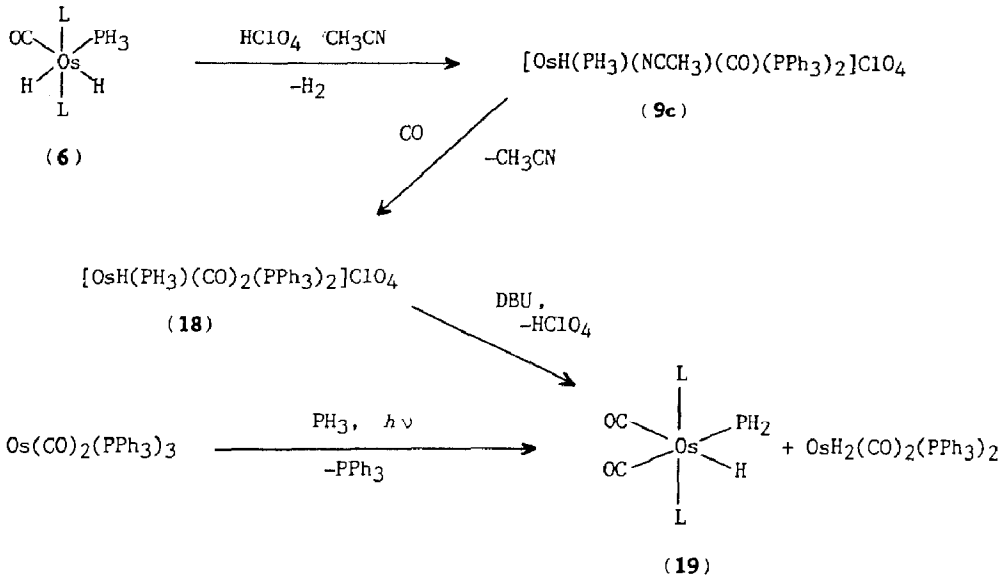
Scheme 4. Synthesis of terminal phosphido complexes.

Terminal phosphido complexes

Loss of the labile acetonitrile in **9a** leads to a coordinatively unsaturated complex which can dimerize to give **13**. If there is a complete, and non-labile coordination sphere, as is the case in **10** and **11**, then the dimerization reaction would be blocked. Indeed, if either of these cationic complexes is treated with DBU at room temperature, terminal phosphido complexes result (Scheme 4). The isolated monomeric species, **14, 15** and **17** are air stable, sparingly soluble, crystalline compounds. The general spectroscopic characteristics of these compounds includes sharp and moderately strong ν(P–H) in the infrared spectrum and in the ^{31}P NMR the phosphido resonance is shifted upfield (Table 8). There is reduced phosphorus–hydrogen one bond coupling (^1J(HP) 172–179 Hz) and an upfield shift in the phosphido resonance in the ^{1}H NMR. NMR experiments on these terminal phosphido complexes are complicated by the presence of moisture. If rigorously dried solvents or anhydrous conditions for the preparation of **14, 15** and **17** are not used then only an average of the signals for the protonated and unprotonated environment is seen. The deprotonation reactions outlined in Scheme 4 are reversible and addition of perchloric acid regenerates the phosphine complexes **10, 11** and **16**. In a subsequent paper the general chemistry of the synthetically useful **14, 15** and **17** will be described. It will be shown that a variety of electrophiles attack the phosphorus to yield a wide range of derivatives.

Hydride phosphine complexes

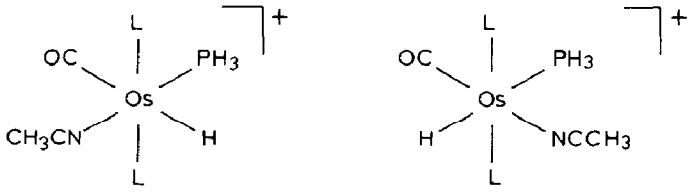
Reaction of $OsHCl(PH_3)(CO)(PPh_3)_2$ (**1a**) with lithium triethylborohydride re-



Scheme 5. Synthesis of $OsH(PH_2)(CO)_2(PPh_3)_2$.

sults in excellent yields of the dihydride complex $OsH_2(PH_3)(CO)(PPh_3)_2$ (**6**) (Scheme 2). If the ruthenium analogue **1b** is treated with this reagent under the same conditions the only product which is recovered is $RuH_2(CO)(PPh_3)_3$ in low yield. If the same three steps that were used in the preparation of the terminal phosphido complex **14** from **1a** are applied to **6** it is possible to prepare a hydrido phosphido complex **19** (Scheme 5), i.e., hydride cleavage, carbonylation and deprotonation convert **6** to **19** in 30% yield.

Hydride cleavage of **6** with either perchloric acid or trifluoroacetic acid is more stereospecific than for the chloride analogue **1a**. As depicted in Scheme 2 trifluoroacetic acid results in only a single isomer, **8**, with a hydride *trans* to a phosphine (^2J(HP) 102.9 Hz). No other isomers or intermediate products can be detected when this reaction is monitored by proton NMR. With aqueous acetonitrile/perchloric acid mixtures only two isomers are produces (ratio 4.6/1). Proton NMR allows for unambiguous assignment of the geometry of **9c** as I and II.



Carbonylation of **9c** with similar pressures, temperatures and solvents as used for **9c** required longer times (24 vs. 16 h). Similar differences in the rates of substitution for acetonitrile in $[OsX(PH_2Ph)(CO)(NCCH_3)(PPh_3)_2]ClO_4$ have been attributed to the differences in the steric demands of the hydride and chloride ligands [14]. Deprotonation of **18** with DBU allows for the isolation of the hydride phosphido complex **19** as an air-stable, colourless, crystalline compound. Since the overall yield

of **19** from **1a** is only 30% a more efficient route to **19** was needed if its chemistry was to be developed. Formally **19** is the result of oxidative-addition of phosphine to the $Os(CO)_2(PPh_3)_2$ fragment. This also proves to be a synthetically viable reaction as photolysis of $Os(CO)_2(PPh_3)_3$, which generates $Os(CO)_2(PPh_3)_2$ [16], in the presence of excess phosphine results in **19** in 81% yield. The other product of this reaction, $OsH_2(CO)_2(PPh_3)_2$, can be separated from **19** by chromatography as described in the experimental section. Primary phosphines such as phenylphosphine [14] and mesitylphosphine react with $Os(CO)_2(PPh_3)_3$ with photolysis to give solely the dihydride $OsH_2(CO)_2(PPh_3)_2$. The possible phosphorus byproducts from these reactions $[RP]_n$, cyclopolyphosphines, have not been detected but are known as byproducts of many reactions of simple trivalent phosphorus substrates and transition metal compounds [17].

Experimental

General techniques and instrumentation for this work has been detailed in prior papers [14]. Phosphine was generated from the pyrolysis of phosphorous acid [18] and reactions with it were performed under nitrogen using standard Schlenk techniques. The resulting phosphine complexes, and the cations derived from them, are all air-stable and can be handled in the open. Terminal phosphido complexes are air-stable solids but are slightly sensitive to air in solution. The NMR results were obtained on a Bruker AM400.

*$OsHCl(PH_3)(CO)(PPh_3)_2$ (**1a**)*

$OsHCl(CO)(PPh_3)_3$, 5.0 g, 4.8 mmol, was suspended in 20 ml oxygen-free benzene under a nitrogen in a 200 ml Schlenk tube. An excess of phosphine was introduced into the space above the solvent and the suspension was stirred for 10 min. Then heated gently under reflux. During this period the starting material dissolved and a clear colourless solution formed. This was cooled and the residual phosphine was flushed out of the apparatus with nitrogen. The benzene was removed and the white residue recrystallized from dichloromethane/ethanol to give large white crystals of product (4.45 g, 95%) after filtration and washes with ethanol and n-hexane. M.p. 178–180 °C as hexagonal prisms. Anal. (as 3/4 dichloromethane solvate as confirmed by ^1H NMR.) Found: C, 51.76; H, 4.22. $C_{37}H_{34}ClOOsP_3 \cdot 3/4CH_2Cl_2$ calcd.: C, 51.70; H, 4.09%.

*$RuHCl(PH_3)(CO)(PPh_3)_2$ (**1b**)*

$RuHCl(CO)(PPh_3)_3$, 6 g, 6.3 mmol, was treated with phosphine as in **1a**. The mixture was cooled, the benzene removed in vacuo, and the grey residue purified by column chromatography on Florisil (3 cm × 10 cm column) using dichloromethane to elute a faint yellow band. Light yellow crystals of **1b** were recovered by recrystallization from dichloromethane/ethanol to give 4.1 g, 90%. Two further recrystallizations from dichloromethane/ethanol were required for an analytically pure sample. M.p. 152 °C, white plates. Anal. (as 1/4 dichloromethane solvate as confirmed by ^1H NMR.) Found: C, 60.14; H, 4.82. $C_{37}H_{34}ClOP_3Ru \cdot 1/4CH_2Cl_2$ calcd.: C, 60.02; H, 4.67%.

$IrH_2Cl(PH_3)(PPh_3)_2$ (2)

$IrH_2Cl(PPh_3)_3$, 0.34 g, 0.33 mmol, was dissolved in 20 ml oxygen-free benzene and excess phosphine gas introduced into the space above the solution. The mixture was stirred at room temperature for 10 min brought to a gentle reflux for 5 min and then cooled to room temperature. The phosphine and benzene were removed in vacuo, and the residue was recrystallized from dichloromethane/ethanol filtered off, washed several times with ethanol and n-hexane to give 0.25 g (90%) of sparkling white crystals. M.p. 179–181°C. Anal. (as a dichloromethane solvate, as confirmed by ^{1}H NMR.) Found: C, 49.93; H, 4.21. $C_{36}H_{35}ClIrP_3 \cdot CH_2Cl_2$ calcd.: C, 50.89; H, 4.28%.

$IrHCl_2(PH_3)(PPh_3)_2$ (3)

$IrHCl_2(PPh_3)_3$, 0.5 g, 0.48 mmol, was suspended in 20 ml benzene and phosphine gas introduced. A colourless solution was obtained after gentle heating to reflux. After 20 min the solution was cooled and stripped of solvent and the residue recrystallized from dichloromethane/ethanol to give 0.38 g, 96% of white rods. M.p. 190–192°C. Anal. Found: C, 52.56; H, 4.14. $C_{36}H_{34}Cl_2IrP_3$ calcd.: C, 52.55; H, 4.17%.

$OsCl(p\text{-tolyl})(PH_3)(CO)(PPh_3)_2$ (4a)

$OsCl(p\text{-tolyl})(CO)(PPh_3)_2$ [10], 0.32 g, 0.37 mmol, was suspended in 30 ml benzene under nitrogen, and phosphine was introduced into the space above the solution. The suspension was heated for 5 min to give a slightly yellow solution. This was allowed to cool and the remaining phosphine was flushed from the flask. After removal of the solvent the residue was purified by column chromatography on a 10 cm silica column with dichloromethane as eluant. The colourless product was recrystallized from dichloromethane/ethanol as white needles. M.p. 224–226°C, 0.28 g, 83%. Anal. (as $\frac{1}{2}$ dichloromethane solvate from ^{1}H NMR) Found: C, 56.37; H, 4.82. $C_{44}H_{40}ClOOsP_3 \cdot \frac{1}{2}CH_2Cl$ calcd.: C, 56.50; H, 4.38%.

$RuCl(Ph)(PH_3)(CO)(PPh_3)_2$ (4b)

$RuCl(Ph)(CO)(PPh_3)_2$ [10], 0.73 g, 0.91 mmol was suspended in 10 ml benzene under nitrogen. Phosphine was introduced and the red solid rapidly dissolved to give a slight green solution. After 5 min the residual phosphine was flushed out and the benzene removed in vacuo. White crystals (0.74 g, 97%) were obtained by recrystallization from dichloromethane/ethanol. M.p. 197–199°C. Anal. Found: C, 64.30; H, 5.21. $C_{43}H_{38}ClOP_3Ru$ calcd.: C, 64.53; H, 4.80%.

$[IrHCl(PH_3)(NCCH_3)(PPh_3)_2]ClO_4$ (5)

A solution of $IrH_2Cl(PH_3)(PPh_3)_2$ (**2**), 0.13 g, 0.16 mmol in 20 ml dichloromethane was treated with a solution of 0.2 ml of 60% aqueous perchloric acid in 20 ml of acetonitrile. Rapid hydrogen gas evolution ceased within minutes and the resulting colourless solution was allowed to stir for a further 20 min. All volatile solvents were stripped off and oily residue recrystallized from dichloromethane/ethanol/isopropanol to give 0.13 g (85% yield) of colourless product. Attempts to recrystallize this led to rapid decomposition, and it was characterized spectroscopically (see Tables 7 and 8).

$OsH_2(PH_3)(CO)(PPh_3)_2$ (6)

A solution of $OsHCl(PH_3)(CO)(PPh_3)_2$ (**1a**) 1.007 g, 1.2 mmol in 40 ml THF was treated with 2.5 equivalents of lithium triethylborohydride (2.5 ml of 1*M* THF solution). The mixture was stirred for 4 h at room temperature during which it became slightly yellow. An excess of ethanol was added to destroy residual lithium triethylborohydride and all solvents were then removed in vacuo. The oily residue was recrystallized with dichloromethane/ethanol to give 0.87 g (93% yield) of white needles. M.p. 170–173°C (dec.). Anal. Found: C, 56.38; H, 4.84. $C_{37}H_{35}OOsP_3$ calcd.: C, 57.06; H, 4.54%.

$OsCl(\eta^1\text{-}OC[O]CF_3)(PH_3)(CO)(PPh_3)_2$ (7a)

Method A. A solution of $OsHCl(PH_3)(CO)(PPh_3)_2$ (**1a**) 0.1 g, 0.12 mmol in 10 ml of dichloromethane was treated with 1 ml of trifluoroacetic acid. Hydrogen evolution ceased within 3 min. After 1 h the mixture was evaporated to dryness and the residue recrystallized from dichloromethane/ethanol to give 0.1 g (88% yield). M.p. 204–210°C (needles). Spectroscopic data for this complex are included in Tables 7 and 8.

Method B. A solution of $[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**9a**) 0.1 g, 0.11 mmol in 10 ml of dichloromethane was treated with a solution of 0.4 g, 3 mmol of sodium trifluoroacetate in 20 ml of ethanol. A fine solid gradually formed during 2 h and the dichloromethane was then removed in vacuo to give crystals 0.089 g, (92% yield) of **7a**.

$RuCl(\eta^1\text{-}OC[O]CF_3)(PH_3)(CO)(PPh_3)_2$ (7b)

$RuHCl(PH_3)(CO)(PPh_3)_2$ (**1b**) 0.14 g, 0.19 mmol, was treated with 0.25 ml of trifluoroacetic acid in 10 ml dichloromethane. Hydrogen evolution ceased within 10 min and after 2 h the mixture was worked up as in Method A for **7a**. The product was 0.1 g (62%) of white solid. Spectroscopic data are presented in Tables 7 and 8.

$OsH(\eta^1\text{-}OC[O]CF_3)(PH_3)(CO)(PPh_3)_2$ (8)

$OsH_2(PH_3)(CO)(PPh_3)_2$ (**6**) 0.06 g, 0.077 mmol, in 10 ml dry dichloromethane was treated with a 2.5 excess of trifluoroacetic acid (0.22 g, 0.015 ml, 0.19 mmol) and the mixture was stirred for 1 h at room temperature. Hydrogen evolution was slow but steady. After 1 h the volatile species were removed in vacuo. Two recrystallizations from dichloromethane/ethanol gave 0.058 g (85% yield) as white plates. M.p. 161–163°C (dec.). Anal. Found C, 52.40; H, 4.50. $C_{39}H_{34}F_3O_3OsP_3$ calcd.: C, 52.58; H, 3.85%.

$[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (9a)

To a solution of $OsHCl(PH_3)(CO)(PPh_3)_2$ (**1a**) 0.45 g, 0.55 mmol in 10 ml of dichloromethane was added a solution of 0.4 ml of 60% aqueous perchloric acid in 20 ml acetonitrile. After 2 h stirring at room temperature the solvents were removed and the oil recrystallized from dichloromethane/ethanol/isopropanol to yield 0.45 g, 85% of colourless cubes. M.p. 168–170°C. Anal. Found: C, 48.99; H, 4.06; N, 1.38. $C_{39}H_{36}Cl_2NO_5OsP_3$ calcd.: C, 49.16; H, 3.82; N, 1.47%.

$[RuCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (9b)

$RuHCl(PH_3)(CO)(PPh_3)_2$ (**1b**), 0.2 g was treated as described for **4a**. Recrystallization from dichloromethane/ethanol/isopropanol gave 0.26 g, 93% of white

cubes. M.p. 145–149 °C. Anal. Found: C, 54.04; H, 4.90; N, 1.27. $C_{39}H_{36}Cl_2NO_5P_3Ru$ calcd.: C, 54.23; H, 4.21; N, 1.62%.

$[OsH(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (9c)

$OsH_2(PH_3)(CO)(PPh_3)_2$ (**6**) 0.2 g, 0.26 mmol in 20 ml of dichloromethane was treated with a solution of 0.2 ml of 60% aqueous perchloric acid and 10 ml of acetonitrile. Vigorous hydrogen gas evolution ceased within 15 min. After 2 h all solvents were removed in vacuo and the colourless residue recrystallized from dichloromethane/ethanol/isopropanol to give 0.2 g (85% yield) of colourless product. M.p. 164–166 °C. Anal. Found: C, 51.00; H, 4.45; N, 1.51%. $C_{39}H_{37}ClNO_5OsP_3$ calcd.: C, 51.01; H, 4.07; N, 1.52%.

$[OsCl(PH_3)(PMe_3)(CO)(PPh_3)_2]ClO_4$ (10)

$[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**9a**), 0.3 g, was suspended in 10 ml THF and a two-fold excess of trimethylphosphine (2.2 ml of 0.29 *M* benzene solution) was added. This resulted in rapid dissolution of the starting material to give a colourless solution from which some white crystals of product separated within 5 min. This mixture was stirred for a further 30 min. and then ethanol was added and the product recrystallized by removing the THF in vacuo. Filtration, followed by washes with ethanol and n-hexane led to 0.31 g (99%) of white needles. M.p. 133–135 °C. Anal. Found: C, 48.55; H, 5.05. $C_{40}H_{42}Cl_2O_5OsP_4$ calcd.: C, 48.63; H, 4.29%.

$[OsCl(PH_3)(CO)_2(PPh_3)_2]ClO_4$ (11)

$[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**9a**), 5.41 g, 5.68 mmol, was dissolved in 30 ml chloroform and carbonylated (300 kPa, 70 °C, 12 h). During carbonylation some of the product crystallized out as a white precipitate. The suspension was then cooled and recrystallized with ethanol to give 5.21 g (98%) of product **11**. M.p. 178–180 °C. Anal. Found: C, 48.81; H, 3.91. $C_{38}H_{33}Cl_2O_6OsP_3$ calcd.: C, 48.57; H, 3.55%.

$OsCl_2(PH_3)(CO)(PPh_3)_2$ (12)

To a solution of $[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**9a**) in 25 ml of dichloromethane was added a solution of 0.1 g lithium chloride in 10 ml of ethanol. The mixture was stirred overnight during which a white precipitate of product formed. The dichloromethane was removed in vacuo and the residue washed with ethanol, water, ethanol and finally n-hexane to leave 0.34 g (76%) of product. M.p. 238–240 °C. Anal. (as $\frac{1}{2}$ dichloromethane solvate from ^1H NMR). Found: C, 50.06; H, 5.01. $C_{37}H_{33}Cl_2OOsP_3 \cdot \frac{1}{2}CH_2Cl_2$ calcd.: C, 50.59; H, 3.86%.

$[Os(\mu_2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2$ (13)

Method A. A mixture of $OsCl_2(PH_3)(CO)(PPh_3)_2$ (**12**) 0.1 g and 0.03 g of 45% NaH (as a paraffin dispersion) in THF was heated under reflux in THF for 12 h then cooled. The THF was removed in vacuo and ethanol (~ 20 ml) added to destroy the residual sodium hydride. The mixture was then completely dissolved by addition of dichloromethane and the product crystallized out by concentration of this mixture in vacuo. The first recrystallization gives 0.03 g, 31%, and this was made analytically pure by two further recrystallizations from dichloromethane/

ethanol. M.p. 273°C (as white cubes). Anal. Found: C, 54.80; H, 4.70. $C_{74}H_{64}Cl_2O_2Os_2P_6$ calcd.: C, 54.78; H, 3.98%. Crystals suitable for X-ray diffraction were grown from dichloromethane/1,1,2,2-tetrachloroethane.

Method B. $[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**9a**), 0.2 g, was suspended in 10 ml of dry THF and 0.1 ml of DBU was added to give a yellow solution and a slight oily precipitate. The mixture was heated under reflux for 8 h to give an almost colourless solution with a copious precipitate. The mixture was cooled the THF removed in vacuo, and the residue recrystallized from dichloromethane/ethanol as above to give 0.12 g, 70% of **13**.

*$OsCl(PH_2)(CO)_2(PPh_3)_2$ (**14**)*

$[OsCl(PH_3)(CO)_2(PPh_3)_2]ClO_4$ (**11**), 0.53 g, was suspended in 20 ml ethanol and 0.11 ml (1.5 equivalent) of DBU was added. The suspension was stirred for a 1 h during which the solid changed from a pure white to a very pale yellow. This solid was filtered off, and washed with methanol, ethanol, and n-hexane; the yield was 0.42 g (89%). For most purposes this product was sufficiently pure, but an analytical sample was obtained by recrystallization from dichloromethane/ethanol. M.p. 224–226°C. Anal. Found 53.93; H, 5.05. $C_{38}H_{32}ClO_2OsP_3$ calcd.: C, 54.38; H, 3.85%.

*$OsCl(PH_2)(PMe_3)(CO)(PPh_3)_2$ (**15**)*

$[OsCl(PH_3)(PMe_3)(CO)(PPh_3)_2]ClO_4$ (**10**), 0.1 g, was suspended in dry benzene under nitrogen and 0.05 ml of DBU added. The white suspended solid dissolved rapidly to give a light yellow solution. After 5 min this was concentrated to ~ 2 ml and ~ 20 ml of ethanol was added. The white solid which separated was washed with ethanol and n-hexane. The remaining traces of DBU and DBU · $HClO_4$ were then removed by recrystallization from dichloromethane/ethanol to give 0.08 g (89%) of light yellow plates. M.p. 113–118°C. Anal. (as $\frac{1}{2}$ dichloromethane solvate as confirmed by ^1H NMR). Found: C, 53.11; H, 5.23. $C_{40}H_{41}ClOOsP_4 \cdot \frac{1}{2}CH_2Cl_2$ calcd.: C, 52.96; H, 4.56%.

*$[RuCl(PH)_3)(CO)_2(PPh_3)_2]ClO_4$ (**16**)*

$[RuCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (***9b***), 0.24 g was dissolved in 50 ml of dichloromethane and carbonylated in a 200 ml Fischer–Porter bottle at 200 kPa, 60°C, 16 h. Two recrystallizations of the product from dichloromethane/ethanol gave a white solid (0.22 g, 94%, M.p. 154°C (dec)). Anal. Found: C, 54.18; H, 4.27. $C_{38}H_{33}Cl_2O_6P_3Ru$ calcd.: C, 53.65; H, 3.92%.

*$RuCl(PH_2)(CO)_2(PPh_3)_2$ (**17**)*

$[RuCl(PH_3)(CO)_2(PPh_3)_2]ClO_4$ (**16**), 0.4 g, 0.47 mmol, was suspended in dry ethanol under nitrogen, DBU, 0.1 ml, was added and the suspension stirred for 1 h. The light yellow solid formed was filtered off and washed with ethanol and n-hexane, to give 0.34 g, 96%, M.p. 183–185°C. This complex reacts with halogenated solvents and an analytical sample was obtained by recrystallization from THF/ethanol under nitrogen. Anal. Found: C, 60.39; H, 4.68. $C_{38}H_{32}ClO_2P_3Ru$ calcd.: C, 60.84; H, 4.31%.

$[OsH(PH_3)(CO)_2(PPh_3)_2]ClO_4$ (18)

$[OsH(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**9c**), 0.2 g, was carbonylated at 50 °C. 430 kPa (50 psi) for 24 h in dichloromethane. Ethanol was then added and the white product (0.18 g, 91%) crystallized out. M.p. 178–181 °C. Anal. Found: C, 50.61; H, 4.24, $C_{38}H_{34}ClO_6OsP_3$ calcd.: C, 50.41; H, 3.79%.

$OsH(PH_2)(CO)_2(PPh_3)_2$ (19)

Method A. $[OsH(PH_3)(CO)_2(PPh_3)_2]ClO_4$ (**18**), 0.1 g, was suspended in 5 ml dry THF and treated with 0.05 ml DBU to give a yellow solution. Ethanol (20 ml) was added and the solution concentrated in vacuo, to give 0.03 g, 34% of a slight yellow solid. M.p. 191 °C (plates). Anal. Found: C, 54.56; H, 4.69. $C_{38}H_{33}O_2OsP_3$ Calcd: C, 54.57; H, 4.05%.

Method B. $Os(CO)_2(PPh_3)_3$ [20], 0.6, was suspended in 15 ml rigorously degassed benzene in a 200 ml Schlenk tube. An excess of phosphine was then introduced and allowed to dissolve in the benzene for 10 min. The yellow suspension cooled in an ice-bath, was irradiated with a quartz-halogen sun lamp. After 45 min the resulting colourless solution was stripped of excess phosphine and benzene under vacuum. The resulting residue, which smelled strongly of phosphorus hydrides species, was then recrystallized from dichloromethane/ethanol to give a 0.46 g (98%) of a mixture of **19** and $OsH_2(CO)_2(PPh_3)_2$.

Purification: The product was converted into **18** by treatment with perchloric acid (~ 0.1 ml) in 10 ml of (1/1) ethanol/dichloromethane. The solvents were removed and the residue dissolved in dichloromethane and placed on a 5 cm × 3 cm column of neutral alumina. The neutral $OsH_2(CO)_2(PPh_3)_2$ was eluted first with 100 ml dichloromethane, and recrystallized from ethanol. Acetone (200 ml) was used to elute a mixture of **18** and **19**. The acetone was removed and the pale yellow residue recrystallized from dichloromethane/ethanol in the presence of 0.1 ml of DBU to give 0.35 g **19** in an overall yield of 75% from $Os(CO)_2(PPh_3)_3$.

$[OsCl(PH_2Ph)(CN\text{-}p\text{-}tolyl)(CO)(PPh_3)_2]ClO_4$

$[OsCl(PH_2Ph)(NCCH_3)(CO)(PPh_3)_2]CO_4$ (**14**), 0.7 g, and 0.1 g (1.25 equivalents) of *p*-tolylisocyanide were stirred together for 10 h in 20 ml dichloromethane at room temperature. Ethanol (20 ml) and isopropanol (10 ml) were added and the mixture concentrated. The white crystalline product was filtered off and washed with n-hexane to give 0.72 g, 96%, of product. M.p. 136 °C. Anal. Found: C, 55.28; H, 4.72; N, 1.06. $C_{51}H_{44}Cl_2NO_5OsP_3$ calcd.: C, 55.43; H, 4.02; N, 1.27%.

X-ray crystal study of $[Os(\mu_2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2$ (13)

Crystal data: $[Os(\mu_2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2 \cdot (Cl_2CHCHCl_2)_4$ $C_{74}H_{64}Cl_2O_2OsP_6 \cdot 4(C_2H_2Cl_4)$, $M = 2092.3$. Colourless prisms, triclinic, space group $P\bar{1}$, a 14.101(4), b 15.091(5), c 11.708(5) Å, α 96.68(3), β 91.71(3), γ 63.92(2)°, $Z = 1$, d(calcd) 1.56 g cm^{-3}, V 2222.0 Å^3, $F(000) = 1052.0$, monochromated Mo-K_α, radiation of λ 0.71069 Å, μ(Mo-K_α) 69.6 cm^{-1}.

Data were collected at 298 ± 1 °C on a CAD-4 diffractometer from a crystal of dimensions of 0.26 × 0.13 × 0.05 mm which was bounded by the faces {010}, {001}, {110}. By a $2\theta/\omega$ scan, 6894 reflections [4865 > 2.5 $\sigma(I_0)$] were collected in the 2θ range 4–50°. Absorption corrections were applied by the empirical azimuthal method [19], with the maximum and minimum correction factors being 0.9991 and

0.8898 respectively. Positions for the osmium, phosphorus and carbon atoms were located by conventional Patterson and Fourier difference methods. At this stage ($R = 0.1297$) chloride carbonyl disorder was apparent and half weighted positions for carbon, oxygen and chlorine atoms were included but refined no further. Four tetrachloroethane solvate molecules were also located at this point. After two further full matrix least squares refinement cycles, with the osmium and phosphorus atoms refined anisotropically, the final residuals were $R = 0.0589$, $R_w = 0.0603$.

Tables of thermal parameters and observed and calculated structure factors may be obtained from the authors.

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