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Organotransition metal substituted primary phosphines: osmium phosphido (PH_2) complexes

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Abstract

Stable osmium phosphido complexes, $Os(\eta^2\text{-chelate})(PH_2)(CO)(PPh_3)_2$, (chelate = acetate, *N,N*-dimethyldithiocarbamate, acetylacetonate, or nitrite) have been prepared by treating $[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ with sodium acetate, sodium *N,N*-dimethyldithiocarbamate, acetylacetone/DBU, and sodium nitrite/DBU respectively. These and the related phosphido complexes $OsX(PH_2)(CO)_2(PPh_3)_2$, (X = H, Cl, OAc) undergo reactions with the electrophiles H^+, R^+, $Fe(CO)_4$, AuI, S_8, and Se and the products have all been characterised. An X-ray diffraction study has established the structure of $Os(\eta^2\text{-OAc})(PH_2AuI)(CO)(PPh_3)_2 \cdot (CH_2Cl_2)_2$. The preparation of complexes with the unusual methylphosphinite (PH_2OMe) ligand, $M(PH_2OMe)(CO)_2(PPh_3)_2$ (M = Ru, Os) and $[MH(PH_2OMe)(CO)_2(PPh_3)_2]ClO_4$ (M = Ru, Os) and the methylthiophosphinite (PH_2SMe) ligand, $[OsX(PH_2SMe)(CO)_2(PPh_3)_2]ClO_4$, (X = Cl, H) are also described.

Introduction

The terminal PH_2 ligand is the parent of the broad class of three coordinate phosphorus donor ligands in which the phosphorus is singly bonded to two other substituents in addition to the transition metal. This structural definition distinguishes phosphido ligands from other low coordinate phosphorus ligands such as diphosphenes (RP=PR) [1], phospha-alkenes ($RP{=}CR_2$) [2], oxophosphanes (RP=O) [3] and thioxophosphanes (RP=S) [4–7] which have distinct double bonds between phosphorus and other substituents. Phosphido complexes are known [8] to adopt either one of two geometries: (i) a pyramidal geometry as in **A**, where there are a lone pair of electrons localized on the phosphorus, compact metal–phosphorus–atom bond angles, and relatively long metal-phosphorus bond lengths; and (ii) a planar geometry as in **B**, with multiple metal–phosphorus bonding, large metal–phosphorus–atom bond angles, and short metal–phosphorus bond lengths.

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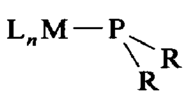
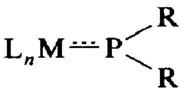


(A)



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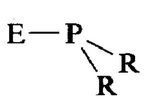
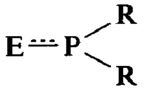
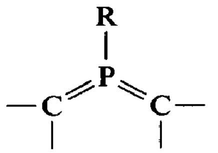


(C)

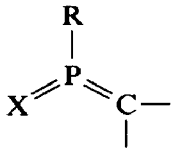


(D)

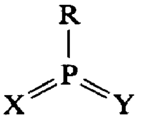
This geometric dichotomy distinguishes organotransition metal substituted phosphines from other substituents which, almost without exception, are confined to the pyramidal geometry **C**. Examples of planar three coordinate phosphorus compounds analogous to **D** are limited [9] to pentavalent species like the bis(methylene)phosphoranes (**E**), metaphosphinates (**F**), metaphosphonates (**G**) and metaphosphates (**H**). Thus, transition metal substituted phosphines, i.e. phosphido complexes, have discernible structural characteristics that separate them from the well known organic analogues, the phosphines.



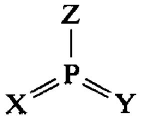
(E)



(F)



(G)



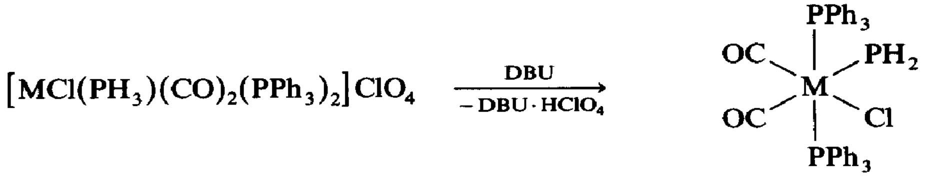
(H)

(X = Y = O, S, Se, NR; Z = OR, NR_2)

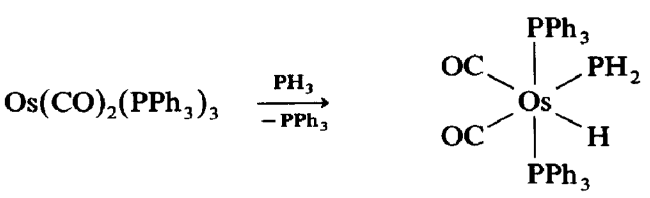
In spite of these differences the best way to systematize the observed reactivity patterns of pyramidal phosphido complexes [8,10] is by comparison with the extensive chemistry of phosphines. In this comparison the terminal PH_2 complexes correspond to primary phosphines. Herein we report: (i) simple high yield preparations of new phosphido complexes $Os(\eta^2\text{-chelate})(PH_2)(CO)(PPh_3)_2$, (chelate = acetate, *N*,*N*-dimethyl dithiocarbamate, acetylacetonate, and nitrite); (ii) reactions of these and the related complexes $OsX(PH_2)(CO)_2(PPH_3)_2$ (X = H, Cl, OAc) with a range of electrophiles, including H^+, R^+, $Fe(CO)_4$, AuI, S_8 and Se; (iii) the structure of one such derivative $Os(\eta^2\text{-OAc})(PH_2AuI)(CO)(PPh_3)_2$ which has an open μ^2-PH_2 ligand; and (iv) the preparation and reactions of complexes with the unusual alkyl phosphinite (PH_2OR) and methyl thiophosphinite (PH_2SMe) ligands.

Preparation of terminal phosphido complexes

In earlier publications [11,12] we described the preparations of terminal phosphido complexes **2a**, **2b** and **3** by either deprotonation of cationic phosphine complexes or (in one case) by oxidative addition of phosphine to $Os(CO)_2(PPh_3)_3$.



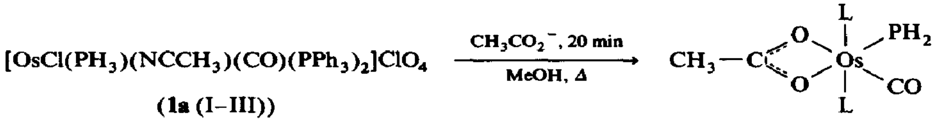
(**2a**: M = Os; **2b**: M = Ru)



(**3a**: M = Os; **3b**: M = Ru)

These preparations make use of either the increased acidity of the phosphorus bound hydrogens in complexes with a net positive charge, or the susceptibility of phosphine towards oxidative addition. Seven complexes containing the PH_2 ligand have been reported before or while this work was in progress [13–17]. In most of these cases the complex is formed by oxidative-addition of phosphine to Ir(I) centers, but there is also a report of the deprotonation of the phosphine in $Cp^*Mn(CO)_2(PH_3)$ with potassium hydride to give an anionic phosphido complex [17].

An additional, and perhaps more useful, method for the preparation of terminal phosphido complexes involves treatment of the acetonitrile containing complex $[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**1a** (I–III)), which is a mixture of three geometric isomers each with mutually *trans*-triphenylphosphine ligands [12], with potential chelating ligands. For example, when methanol suspensions of **1a** (I–III) and an excess of sodium acetate are heated to reflux, the reagents rapidly dissolve and then a yellow crystalline precipitate forms. After 20 min under reflux and subsequent cooling, the bright yellow neutral complex $Os(\eta^2\text{-}O_2CCH_3)(PH_2)(CO)(PPh_3)_2$ (**4a**) can be recovered in 92% yield simply by filtration. This product is formulated as having both a bidentate, or dihapto, acetate ligand and a terminal phosphido ligand:

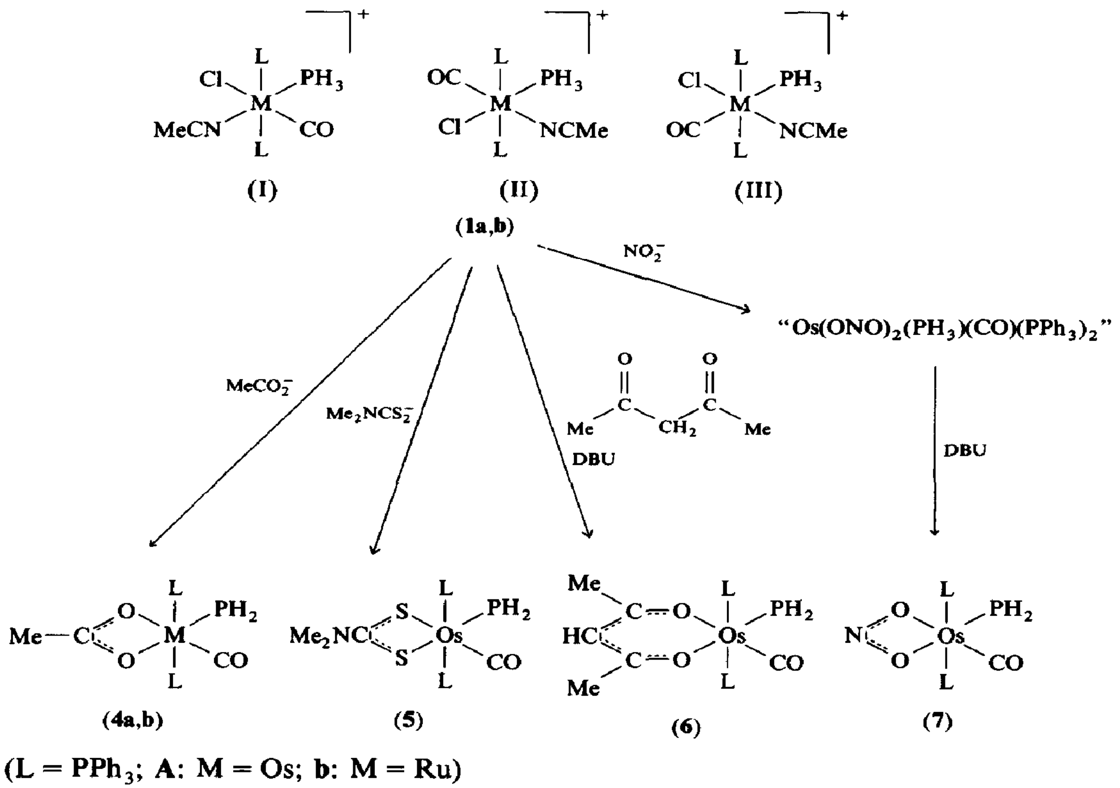


(**1a** (I–III))

(**4a**)

When **1a** (I–III) is treated with sodium *N*,*N*-dimethyl dithiocarbamate under the same conditions as those used for the preparation of **4a**, a tan coloured product, $Os(\eta^2\text{-}S_2CNMe_2)(PH_2)(CO)(PPh_3)_2$ (**5**) is formed in 85% yield. An acetylacetonato complex (**6**) can also be prepared from **1a** (I–III) but the presence of base (DBU) is required to promote this reaction (Scheme 1). Finally, the bright yellow η^2-nitrito complex $Os(\eta^2\text{-}O_2N)(PH_2)(CO)(PPh_3)_2$ (**7**) is formed in a two-step one-pot reaction when **1a** (I–III) is treated first with sodium nitrite and then with base (DBU). It is possible to isolate a colourless solid that analyzes correctly for $Os(ONO)_2(PH_3)(CO)(PPh_3)_2$, after the first step, but both the ^1H and ^{31}P NMR spectra indicate that this solid is a mixture of at least three species, some or all of which may be either linkage or geometrical isomers.

The geometry assigned to **4a** is based on spectroscopic date and on the structure of its gold(I) iodide adduct (which is described later). Two moderately intense bands at 2268 and 2260 cm^{-1} in the phosphorus-hydrogen stretching region of the infrared spectrum of **4a** are due to the presence of a phosphido ligand. The frequencies of these bands, their intensities, and number, as well as the absence of the strong



Scheme 1. Preparation of phosphido complexes with chelating ligands.

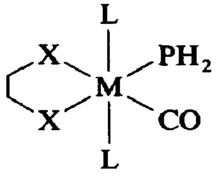
characteristic phosphine deformation band between 1050–1000 cm^{-1} all indicate that **4a** does not contain a phosphine ligand. Also, in the ^{1}H NMR spectrum the phosphorus bound protons are shifted upfield to 0.99 ppm and show diminished one bond phosphorus-hydrogen coupling constants (^1J(HP) 194.5 Hz for **2a**). These features are present in the spectra of **4**–**7**, and confirm the presence of terminal phosphido ligands in each of these compounds.

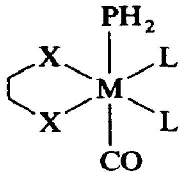
For **4a**, the carboxylate stretching bands (a weak band at 1516 cm^{-1} and a moderately intense band at 1459 cm^{-1}, Δ 57 cm^{-1}) clearly indicate the presence of a dihapto chelating acetate ligand [18]. Another correlation found in these bis(triphenylphosphine)acetato complexes is that the range of proton chemical shifts for the methyl resonance for the η^2-acetato geometry (0.31–0.38 ppm) is significantly upfield from the range (1.21–1.45 ppm) found when this ligand is monodentate.

Infrared data for the dithiocarbamato and acetylacetenato ligands in **5** and **6** also indicate that these ligands are bound as bidentate chelates. In dithiocarbamato complexes the position of the strong C–N stretch is diagnostic of the coordination mode for these ligands [19]; in the infrared spectrum of **6** the presence of strong bands at 1572, 1527 and 936 cm^{-1} is indicative [20] of a delocalized bidentate diketonate ligand [21].

In respect of the nitrite ligand in **7** the infrared data is less informative. Both η^1- and η^2-O bound nitrito [22], and η^1-N bound, nitro, geometries are known. The observed ranges [23] in the N–O stretching frequencies for these structural types are not mutually exclusive [20]. In the infrared spectrum of **7** the strong N–O stretch at 1188 cm^{-1} and a weak band at 1380 cm^{-1} are probably due to a η^2-nitrito geometry.

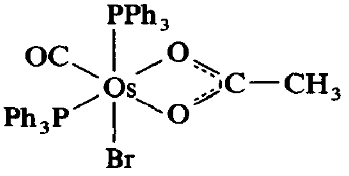
The geometric requirements of bidentate chelate ligands in **4–7**, and the equivalence of the triphenylphosphine ligands (as shown by the equivalence of the triphenylphosphine resonances in the ^{31}P NMR spectrum), constrain the geometries for these complexes to two possibilities, **I**, and **J**:


(I)

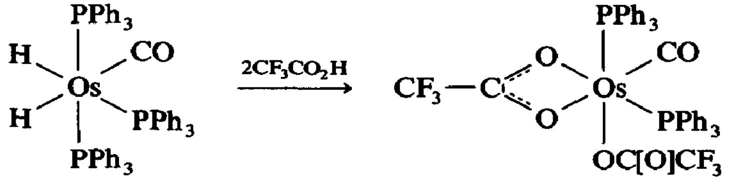

(J)

(X⌒X = chelate)

On steric grounds structure **I** is expected to be more stable. The question of geometry is significant because the structure of the closely related acetate complex $OsBr(\eta^2\text{-}O_2CCH_3)(CO)(PPh_3)_2$ has a distorted octahedral geometry with *cis* triphenylphosphine ligands [24]:



This geometry also corresponds to that suggested [25] to be present in many η^2-acetato complexes formed in hydride cleavage reactions with carboxylic acids:



[26]

However, the NMR evidence for **5** and **6** can not be reconciled with geometry **J**, which has a mirror plane of symmetry orthogonal to the plane defined by the chelate ligand. The presence of this symmetry element would require the methyl groups of the acetylacetonate and *N*,*N*-dimethyl dithiocarbamate ligands to be equivalent. This is not the case, and the ^1H NMR spectra of each of these compounds have two distinct methyl resonances.

The mechanism for conversion of **1a** (I–III) to the phosphido complexes **4–7** involves at least three distinct events: (i) substitution of the anionic chelate for the acetonitrile; (ii) loss of chloride and formation of a chelate ring; and (iii) deprotonation of the phosphine ligand to give a phosphido complex. The following observations suggest that these events probably occur in the above order.

The chemistry of **1a** reveals that a wide range of ligands will replace the acetonitrile [12]. Strong bases, like DBU, are required to deprotonate **1a** while weaker bases such as trimethylphosphine and trifluoroacetate replace the acetonitrile.

Thus, it is unlikely in the case of **4**, **5** and **7** that acetonitrile-containing phosphido complexes are involved in these reactions:

$$[\mathrm{OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2}]^+ \xrightarrow[-\mathrm{H^+}]{\mathrm{CH_3CO_2^-}} \mathrm{OsCl(PH_2)(NCCH_3)(CO)(PPh_3)_2}$$

However, the reaction of **1a** with acetylacetone requires the presence of a strong base, and in this case such phosphido complexes are possible intermediates in these reactions.

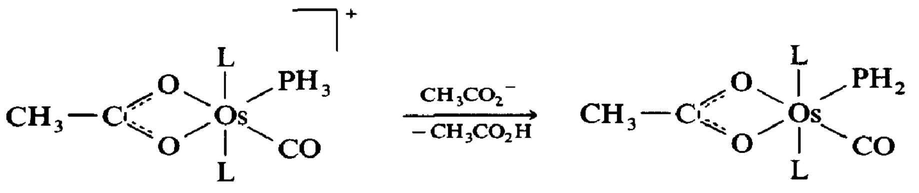
When **1a,b** (I–III) is treated with sodium acetate at room temperature the pale solid recovered is a mixture of two complexes. The major component, which comprises about 60% of the mixture, is the phosphido complex **4a**. The other component is a phosphine complex (ν(P–H) = 2360w cm^{-1}, and δ(P–H) = 1049s cm^{-1}) with a unidentate acetato ligand (ν(C–O)$_a$ = 1595s, ν(C–O)$_s$ = 1376s cm^{-1}, Δ = 219 cm^{-1}). Both of these features suggest that $\mathrm{OsCl(\eta^1\text{-}OC[O]CH_3)(PH_3)(CO)(PPh_3)_2}$ is present. When this mixture is suspended in methanol with sodium acetate and heated under reflux for 20 min, pure **4a** is recovered in 90% yield. Clearly, more forcing conditions are required to transform this intermediate into the final product.

The chelate effect operates here to expel the chloride, and results in the formation of the chelate ring. The total reaction **1a** → **4a** can be written:

$$2\mathrm{CH_3CO_2Na} + \underset{(\mathbf{1a})}{\text{Complex}\cdot\mathrm{HClO_4}} \longrightarrow \underset{(\mathbf{4a})}{\text{Complex}} + \mathrm{NaCl} + \mathrm{NaClO_4} + \mathrm{CH_3CO_2H}$$

As is often found in examples of the chelate effect [27], entropy considerations contribute significantly to the free energy for this reaction since there is a net increase in the number of molecules during the reaction. Other factors that drive the reaction forward include the low solubility of **4a** in methanol compared with that of **1a**, and the expected high solvation energies of the sodium salts and acetic acid in methanol.

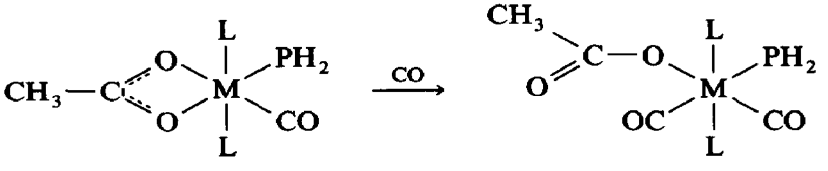
The final step in the reaction is most likely the deprotonation of the cationic phosphine complex **9** to give **2a**. The best base present is the acetate ion, and its involvement in acid-base reactions with **9** demonstrates the remarkable increase in acidity of phosphine protons in the latter. The occurrence of this reaction has been confirmed by treating an independently prepared sample of **9** with sodium acetate to give **4a**.



(9) **(4a)**

Methanol suspensions of sodium formate and sodium trifluoroacetate do not give η^2-chelate complexes analogous to **4**–**7** when they are heated to reflux with **1a** (I–III) in methanol. Instead, use of sodium formate leads to the dihydride complex $\mathrm{OsH_2(PH_3)(CO)(PPh_3)_2}$ in 75% yield, and use of sodium trifluoroacetate leads to a mixture of isomeric trifluoroacetate complexes [12].

Two dicarbonyl phosphido complexes $M(\eta^1\text{-OC[O]CH}_3)(PH_2)(CO)_2(PPh_3)_2$ (**8a,b**) can be prepared by carbonylation of **4a,b**:



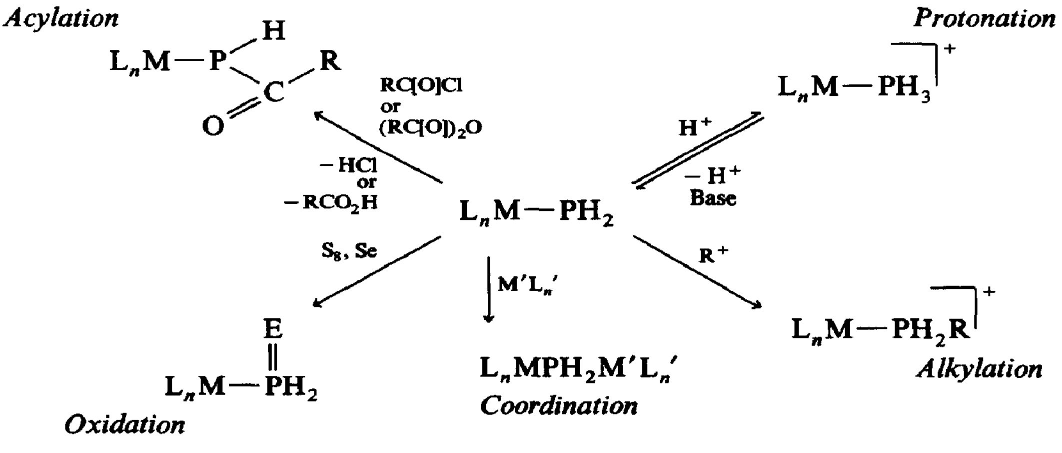
(**4a,b**) (**8a,b**)

(**a**: M = Os; **b**: M = Ru)

These off-white complexes are the acetate analogues of the chloride and hydride species **2a,b** and **3**. Only a single isomer of **8a,b** is produced in these reactions, and the mild conditions employed (25 °C, 50 psi, 20 min) suggest that the terminal PH_2 ligand has a stronger *trans* influence than carbon monoxide.

Reactions of terminal PH_2 complexes

The predominant reactivity pattern for both primary phosphines and organotransition metal PH_2 complexes is addition of electrophiles to phosphorus. There is, however, a major difference in the stability of the products of these reactions. This difference is best illustrated by the sulfide and selenide adducts that are formed by the reaction of these compounds with the respective elements. Primary phosphine sulfides and selenides are only stable when bulky substituents (R = tris(2,4,6-t-butyl)phenyl are present to prevent oligomerization or subsequent addition reactions [28–30], whereas the phosphido sulfide and selenide complexes $[(OsX(PH_2E)(CO)_2(PPh_3)_2]$ (X = Cl, N, OC[O]CH$_3$) are stable tractable species. While there is a certain confusion in the literature [31,32] about the acylation of primary phosphines, terminal phosphido complexes are readily acylated by acid chlorides or anhydrides [11,33]. There is a general increase in the nucleophilicity of transition metal substituted phosphines, and Gladysz has attributed this to a gauche interaction between the phosphorus lone pair and the metal *d* electrons [34,35].

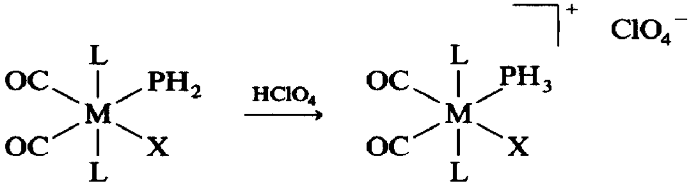


Scheme 2. Generalized nucleophilic reactions of pyramidal $L_nM\text{–}PH_2$ complexes.

Scheme 2 summarizes many of the features observed for the reactions of $OsX(PH_2)(CO)_n(PPh_3)_2$ ($n = 1, 2$; X = H, Cl, η^1-OC[O]CH_3 or η^2-O_2CCH_3). These reactions provide a strong contrast with the emerging reactivity patterns for the planar phosphido(phosphenium) complexes (**B**), which generally react with Lewis bases [36]. Also significant are the differences in the reactivity of the η^2- versus η^1-acetate complexes, which further illustrate the relative ease by which a η^2-acetate is opened with substitution to give a η^1-acetate ligand. 2

Protonation, methylation, and acylation reactions

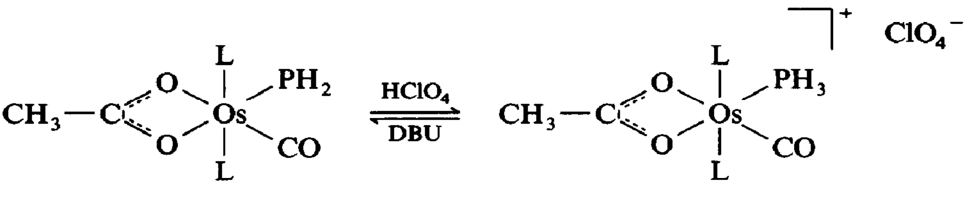
The phosphorus lone pair in **2**–**8** is readily protonated to give cationic phosphine-containing complexes in the first instance. Subsequent reactions with substitution and loss of anionic ligands is possible, and the degree to which these reactions occur depends upon the concentration of the acid, the coördinating ability of the counter ion and the anionic ligand at the osmium. For **2a**,**b** and **3** addition of perchloric acid regenerates the cationic complexes of phosphine which were their original synthetic precursors.



(**2a**,**b**, **3**)

(**2a**: M = Ru, X = Cl;
2b: M = Os, X = Cl;
3: M = Os, X = H)

A similar reversible protonation is also found when the η^2-acetate complex **4a** is treated with a small excess of perchloric acid to give **9**:

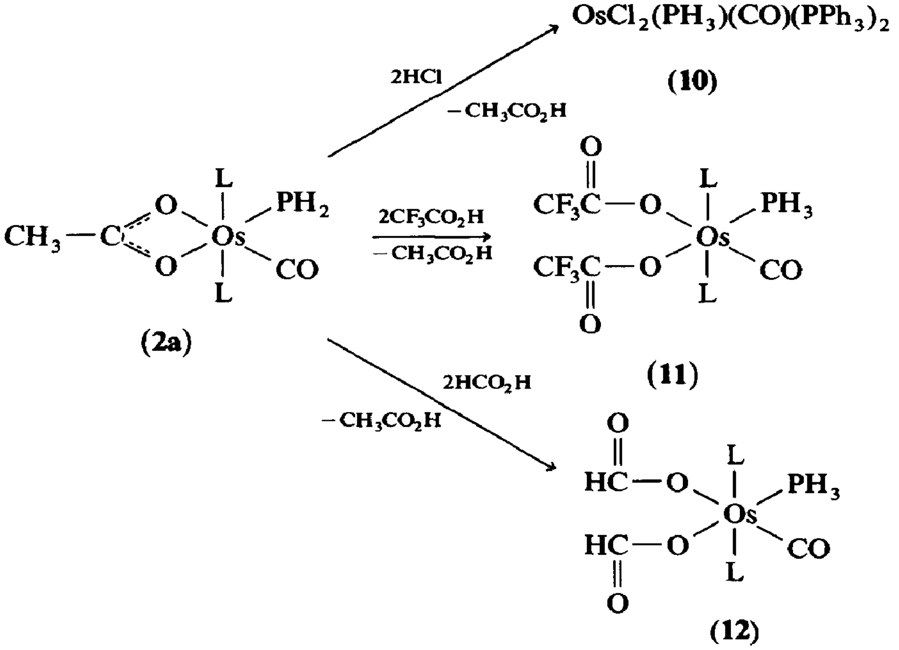


(**4a**) (**9**)

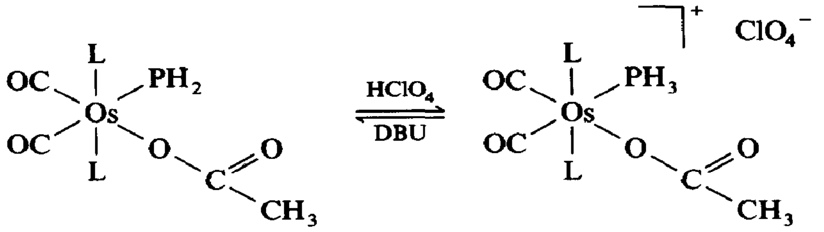
But acids with coordinating anions undergo substitution reactions in which a η^2-acetate is replaced by two conjugate acid units to give the neutral bis-chloride, -trifluoroacetate, and -formate complexes **10**, **11** and **12**.

IR, ^1H and ^{31}P NMR spectroscopy all indicate that **11** and **12** are each produced as a single isomeric species in good yield. The known complex **10** is produced as a pair of isomers, probably with *cis* and *trans* chlorides. Curiously, this mixture is also produced by chloride replacement of the acetonitrile ligand in **1a** (I–III) [12]. As judged by the relative intensities of the ν(CO) bands in the IR, both reactions produce the same relative proportions of isomers for **10**.

The products from the protonation of the dicarbonyl acetato complexes **8a**,**b**

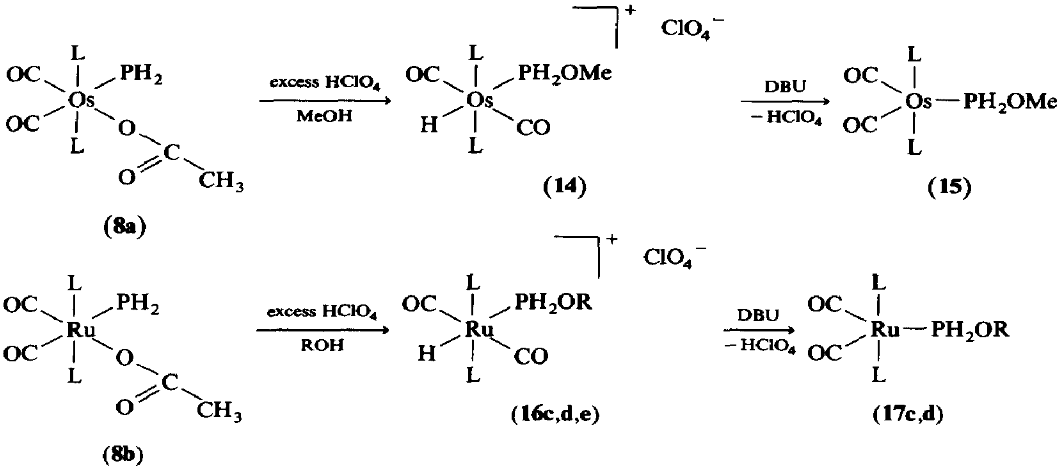


depend upon the concentration of the acid used. Reversible protonation of the phosphorus occurs when **8a** is treated with a small excess of perchloric acid to give **13**:



(**8a**) (**13**)

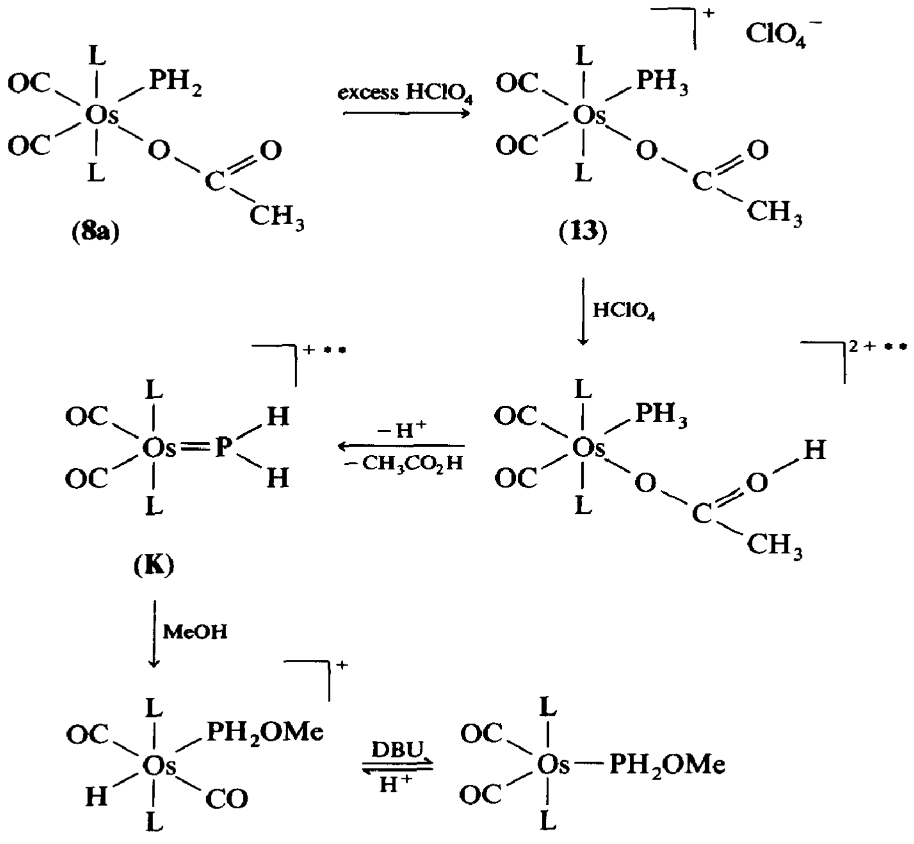
However with an excess of acid and in the presence of alcohol, an unexpected series of irreversible reactions occurs. Since both the reactants and products are colourless there is little perceptible sign of a reaction, but the products isolated do not show carboxylate stretching bands in the infrared spectrum. In addition, these products, which are isolated as perchlorate salts, have a single very intense carbonyl stretch between 2026–2010 cm^{-1}, a weak band between 2102–2094 cm^{-1}, and strong bands between 1003–988 cm^{-1}. These first two features are indicative of *trans* carbonyl ligands, while the strong bands near 1000 cm^{-1} are associated with phosphite stretching modes [37]. Taken together these results suggest that the products are the cationic hydrido complexes **14** and **16c–e** depicted in Scheme 3. Phosphorus and proton NMR evidence reveals that these complexes have hydride ligands (for example the ^1H NMR of **14**: $\delta = -7.97$(dt, $^2J(H\text{-}PH_3) = 47.0$, $^2J(H\text{-}PPh_3) = 14.8$ Hz, 1, Os–*H*)) *trans* to a phosphorus donor and *cis* to two equivalent triphenylphosphine ligands. The identity of the methyl phosphinite ligands in **14** is clear from its downfield chemical shift (^{31}P $\delta = 56.11$ ppm) and from the coupling of this signal to the other phosphorus and hydrogen nuclei.



(L = PPh$_3$; **c**: R = OMe; **d**: R = OEt; **e**: R = O^{i}Pr)

Scheme 3. Preparation and reactions of alkyl phosphinite complexes.

Phosphinous acid and its derivatives are unstable [38], and the only previous report of the stabilization of this fundamental phosphorus species is by coordination

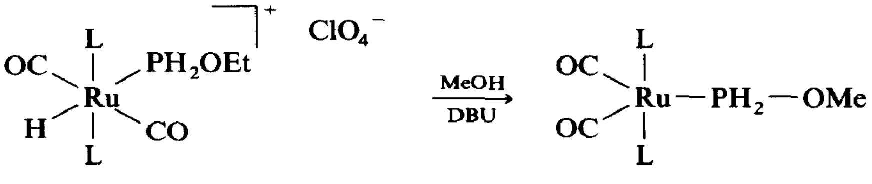


(L = PPh$_3$)

Scheme 4. Mechanism for the formation of alkyl phosphinite complexes. * * Proposed intermediates.

to a tungsten pentacarbonyl fragment [39,40]. The mechanism by which these complexes are prepared is intriguing not only because of the novelty of the products but also because this reaction is an excellent example of acid labilization of the acetate ligand in **8a,b**. Scheme 4 depicts some of the complex series of acid-base equilibria which are possible for **8a,b** in these reactions. Here the protonation of the cationic phosphine complex (**9**) would lead to a cationic planar phosphido species (**K**) which, after loss of acetic acid, could then rapidly add methoxide to give **9**. The final step in the formation of **14** and **16c–e** is the protonation at the metal between the carbon monoxide ligands of the M^0 alkyl phosphinite complexes (**15**, **17c,d**). This site of addition leads to what is probably a kinetic product, the stereochemistry of which is strong evidence for the intermediacy of such M^0 intermediates. Other mechanisms, such as proton abstraction from alcohol, would probably result in a product with a *cis* geometry of the hydride and the alkyl phosphinite ligands. These final reactions are readily reproduced by treating alcohol suspensions of the cationic hydride complexes with base to give the reduced Os^0 complexes **15** and **17c,d**, Scheme 3. These d^8 complexes can be in turn be reprotonated with perchloric acid in methanol to regenerate the cationic precursors **14**, and **16c–e**.

In the preparation of the Ru^0 alkyl phosphinite complexes **17c,d**, alkoxide exchange was observed. An example of this is observed when the cationic ethyl phosphinite complex **16d** is treated with base in methanol to give a Ru^0 complex **17c** that contains a methyl phosphinite ligand:

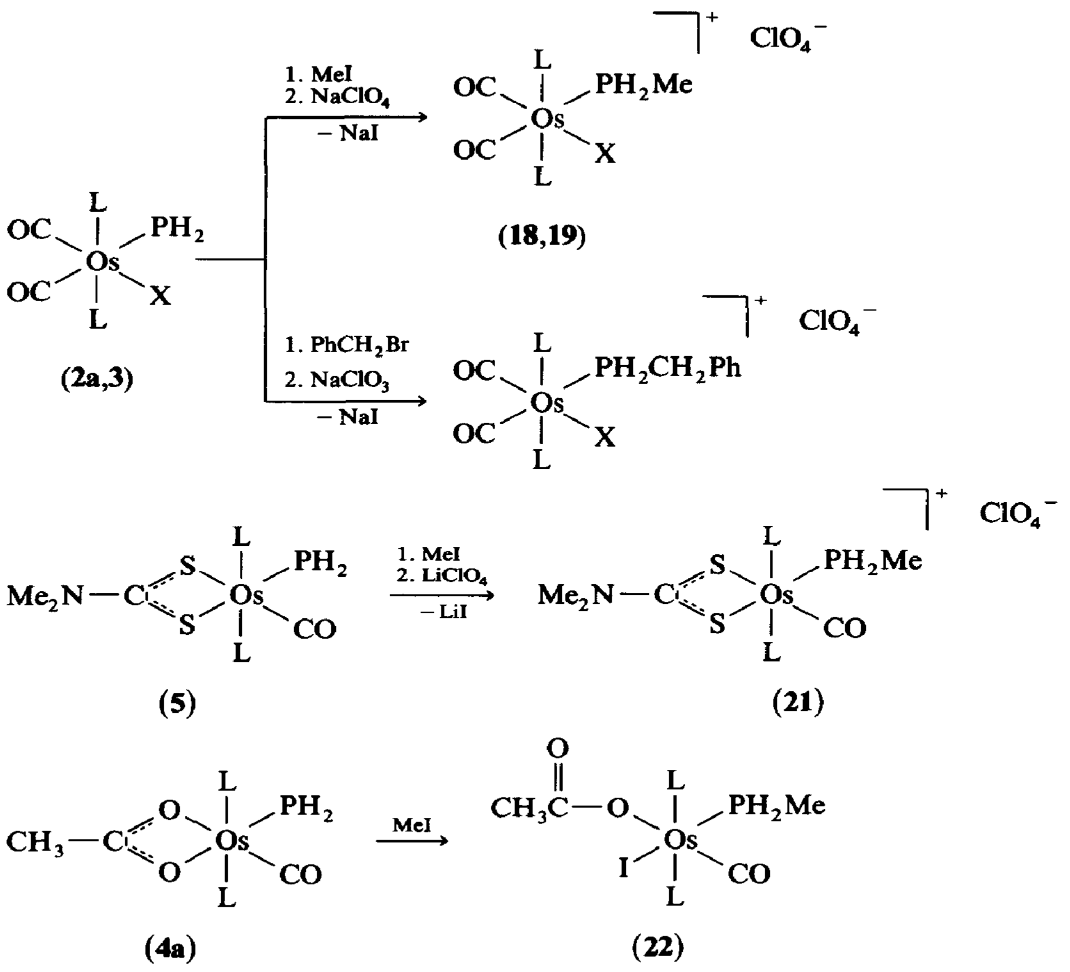


(**16**) (**17**)

It is somewhat surprising that this exchange occurs under basic conditions and not under the acidic conditions encountered in the work-up of complexes **15** and **17c–e**. This is possibly because the exchange involves nucleophilic attack at the phosphorus prior to deprotonation.

Alkylation reactions

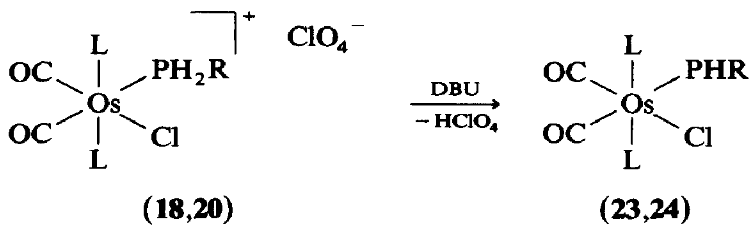
Alkylation of the phosphorus with methyl iodide or benzyl bromide results in the facile formation of complexes with primary phosphine ligands. Examples of these reactions are collected in Scheme 5, and in all but one case the products of these reactions are cationic complexes, which are readily isolated as perchlorate salts in high yield. The exception, the final reaction in Scheme 5, again illustrates the susceptibility of the η^2-acetate ligand in these complexes towards substitution, in this instance by an iodide to give the neutral methylphosphine complex $OsI(OC[O]CH_3)(PH_2Me)(CO)(PPh_3)_2$ (**22**). The structure depicted in Scheme 5 for **22** is based on the expectation that the iodide will replace the oxygen *trans* to the more strongly labilizing methylphosphine ligand. The benzylation reaction is the slowest depicted, and this can be attributed to the combination of increased steric effects and the presence of a poorer leaving group. Methyl or benzylphosphido



(L = PPh$_3$; **2a**,**18**: X = Cl; **3**,**19**: X = H)

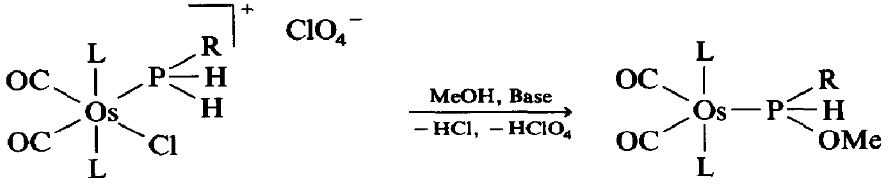
Scheme 5. Alkylation reactions of terminal phosphido complexes.

complexes, (**23**,**24**), can in turn be prepared from **18** and **20** by deprotonation with non-nucleophilic bases such as DBU:



(**18**,**23**: R = Me; **20**,**24**: R = CH$_2$Ph)

The pale yellow complexes **23** and **24** are more air sensitive than the phosphido complexes **4ab**–**7**. Deprotonation of **18** and a closely related t-butyl derivative (**25**) in refluxing methanol, results in net reduction of the osmium with loss of the metal bound chloride and methoxide addition to the phosphorus to give methyl alkylphosphonite Os^0 complexes **26**,**27**:

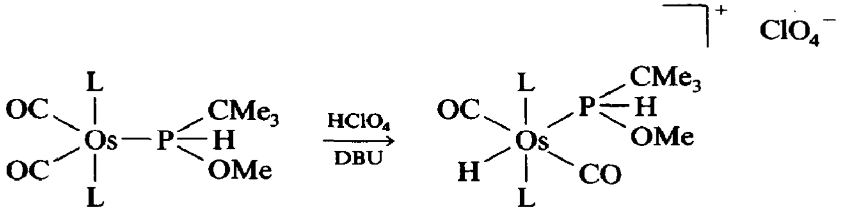


(**18**,**25**) (**26**,**27**)

(**18**,**26**: R = Me; **25**,**27**: R = CMe$_3$)

The mechanism of these reactions has been discussed in detail [10], and a likely intermediate is a cationic planar phosphido complex similar to **K** in Scheme 4. It is significant that the PH$_3$ analogues of **18** and **19** do not react in this manner even upon prolonged (4 h) reflux in methanol. This suggests that intermediates like **K** require some electron-releasing substituents on phosphorus in order that the phosphido ligand geometry can undergo a pyramidal to planar interconversion.

As with the alkylphosphonite complexes **15** and **17c**,**d**, the complex **27** can be reversibly protonated and deprotonated. The product, a hydrido complex with *trans* carbonyl ligands (**28**) is related to the complexes **15** and **17c**,**d** in Scheme 3.



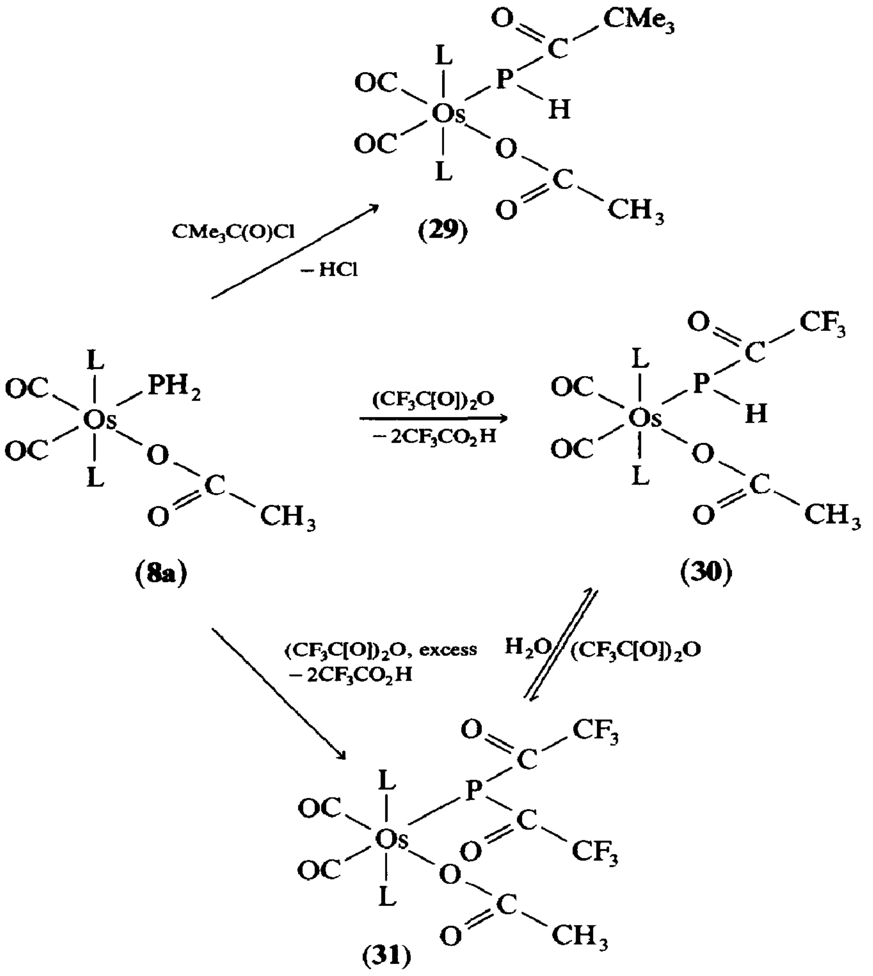
(**27**) (**28**)

Acylation reactions

We have described previously [11,33] the facile acylation of the phosphido ligands in **2a**,**b** and **3** with acid chlorides and anhydrides to give neutral acylphosphido complexes OsX[PH(C[O]R)](CO)$_2$(PPh$_3$)$_2$. Related products can be obtained when **8a** is treated with either pivaloyl chloride or trifluoroacetic anhydride, which rapidly acylate the phosphorus centre to give bright yellow solutions from which the complexes **29** and **30** can be isolated (see reactions on next page).

When **8a** is treated with trifluoroacetic anhydride a new bright orange product (**31**) is formed. From the spectroscopic data (Tables 6–8), in particular the downfield chemical shift of the acylphsophido resonance to 20.01 ppm and the multiplicity of the ^3J(PF) coupling, this material is formulated as a bis(trifluoroacyl)phosphido complex. Formation of a bisacyl species is unusual in this chemistry, and although in the acylation reactions of **2a** and **3** an excess of acid halide is always employed, bis(acyl)phosphido complexes are not formed. A related and structurally characterized bis(pivaloyl)phosphido complex, (η^5-C$_5$Me$_5$)Ru(CO)$_2$[P(C[O]CMe$_3$)$_2$] [41,42] has been prepared by addition of two equivalents of pivaloyl chloride to (η^5-C$_5$Me$_5$)Ru(CO)$_2$[P(SiMe$_3$)$_2$].

Addition of trifluoroacetic anhydride to **30** also results in the formation of **31**. Slow hydrolysis of **31** affords **30**, a reaction which is not observed for mono-

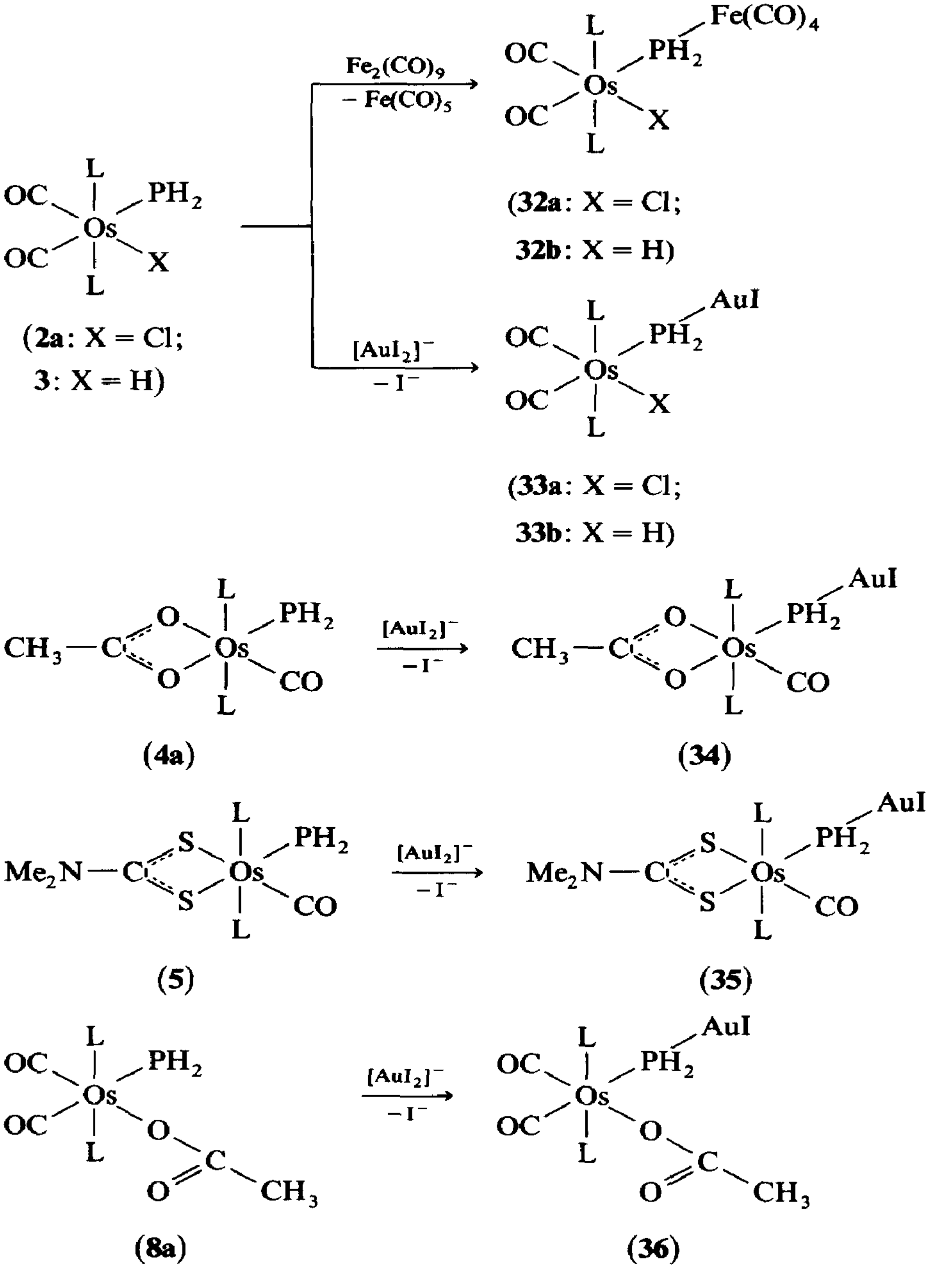


acylphosphido complexes. Moisture slowly hydrolyses the bis(acylphosphido) substituent in **31** to give **30**, containing a trifluoroacylphosphido ligand.

Compared with the chloride in $\mathrm{OsCl(PHC[O]CF_3)(CO)_2(PPh_3)_2}$, the acetate in **30** is more easily displaced to give the metallaphospha-alkene complex $\overline{\mathrm{Os(P{=}C[O}}\mathrm{]CF_3)(CO)_2(PPh_3)_2}$. The reaction of **30** with sodium hydride is rapid and is complete in a shorter time (1 h vs. 1.5 h) and at lower temperatures (ambient conditions vs. THF at reflux) than is the reaction of the chloride analogue with sodium hydride. Since the yield of this product is higher from the reaction of **30** with sodium hydride, this represents an improved method for the preparation of the trifluoromethylmetallaphospha-alkene complex. Given the efficacy of this reaction it may be possible to prepare other examples of this class by using these η^1-acetato complexes.

PH_2 bridging complexes

The fragments gold(I) iodide and iron(0) tetracarbonyl can both be added to the phosphorus lone pair in **2a,3** to give the phosphido bridged binuclear complexes **32a,b** and **33a,b** (Scheme 6). Although the iron tetracarbonyl adducts are photolytically sensitive these compounds are stable in solution and as solids towards atmospheric oxidation. While mercury(II) reagents and silver(I) reagents such as



Scheme 6. PH_2 bridged binuclear complexes.

di(*p*-tolyl)mercury and silver perchlorate readily metallate the P–H bonds in **2a**, and primary phosphines in general [12], the gold(I) reagent does not. The gold(I) iodide fragment can also be added to the phosphido complexes **4a**,**5** and **8a** to give **34**–**36**, respectively.

There is a slight increase in the carbonyl stretching frequency for the bridging complexes compared to the terminally bound ligand (Table 6). Thus coordination of the phosphorus lone pair to a second metal reduces the overall donor ability of the

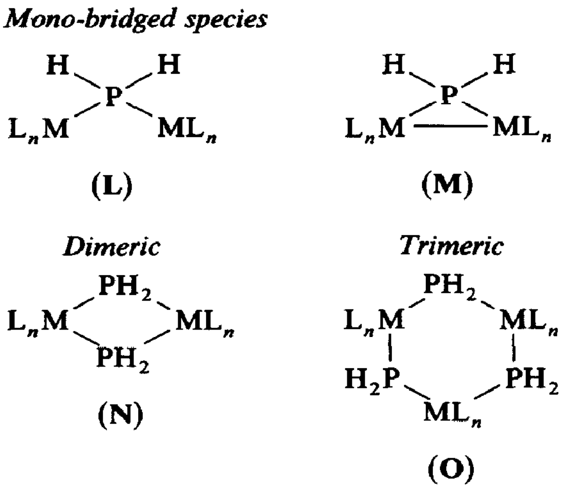


Fig. 1. Types of bridging PH_2 complexes.

phosphido ligand. The infrared characteristics for terminal phosphido complexes, that is a sharp pair of P–H stretching bands with medium intensity between 2285–2260 cm^{-1}, differ markedly from those for the bridging ligand where this band is shifted to higher frequencies (2328–2311 cm^{-1}) and has considerably reduced intensity. Also, the P–H deformation band(s) of terminal phosphido ligands are very weak, while in bridging complexes these are strong bands between 815 and 788 cm^{-1}. In the proton and phosphorus NMR of these compounds there are other relationships between these two types of phosphido ligands: (i) in the ^1H NMR spectra there is a down-field shift in the resonance for the bridging ligand; (ii) the direct one bond ^1J(HP) coupling constants increase to between 306–335 Hz; and (iii) in the ^{31}P NMR spectra there is a downfield shift for the phosphido ligand phosphorus resonance upon coordination of a second metal.

Table 1

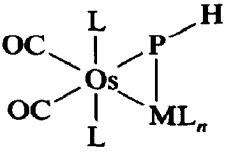
Ranges for spectroscopic data for PH_2 bridged complexes

PH_2 bridge type	Number of examples	$\delta(^{31}P)$	NMR data [a]		IR data (cm^{-1})	
			$\delta(^1H)$	^1J(HP)	ν(P–H)	δ(P–H)
Mono bridged						
No M–M bond						
(L)	32	−62– −179.1	3.8 –2.15	260–349	2301–2342	775–817
M–M bond						
(M)	3	64– 76	4.07–5.14	330–369	*	*
Cyclic						
Dimeric						
(N)	7	−194– −328.5	1.8 –0.6	285–362	*	*
Trimeric						
(O)	2	−108– −131	2.52–2.6	286–295	*	*

[a] Chemical shifts in ppm with respect to 85% phosphoric acid for ^{31}P and tetramethylsilane for ^1H results. ^1J(HP) is in Hertz.

There is currently a wide range of PH_2 bridged complexes [15,16,43–49], and examples are known without (**L**) and with (**M**) metal–metal bonding as well as dimeric (**N**) and trimeric (**O**) species (Fig. 1). The overall ranges for the spectroscopic results for **L**–**O** are shown in Table 1. It can be seen that each type has distinct characteristics for the phosphorus and proton chemical shifts, although these correlations should be considered tentative until additional examples of the species **M** and **O** have been reported. In particular, the formation of the three membered ring, as in **M** and the four membered ring as in **N** are probably responsible for the dramatic variations in the ^{31}P chemical shifts [50].

When any of the complexes **32a,b** or **33a,b** are treated with bases such as DBU or sodium hydride no tractable products can be isolated. While loss of HCl from **32a** or **33a** might return a η^2-μ^2-phosphinidene complex such as that shown below there is no evidence that these are formed or further decompose into other products.

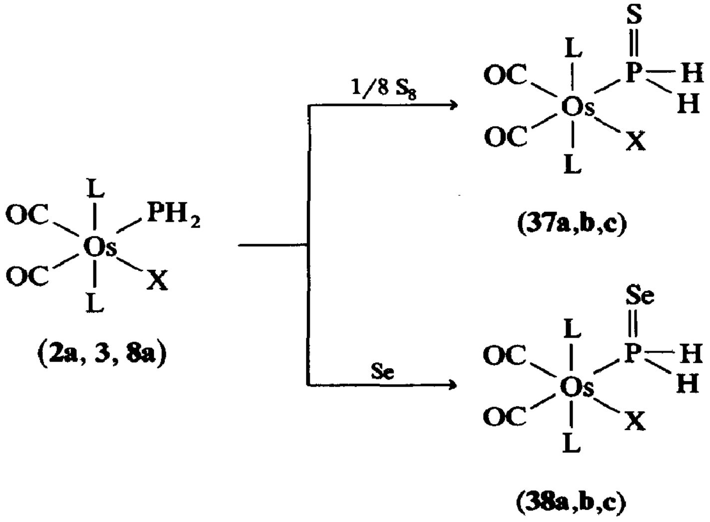


(ML_n = $Fe(CO)_4$, AuI)

Attempts to activate **32a,b** photolytically with ultraviolet radiation in the presence of triphenylphosphine results only in isolation of a low yield of $Fe(CO)_3(PPh_3)_2$.

Sulfur and selenium addition to PH_2 *complexes*

Secondary phosphines [51] and primary phosphines with bulky substituents [30] can be oxidized with one equivalent of sulfur (or oxygen [52]) to give stable phosphine sulfides or oxides. Without the kinetic stabilization of bulky substituents sulfur addition results in a complex series of condensation and elimination reactions [28,29]. With respect to sulfur and selenium addition the terminal phosphido

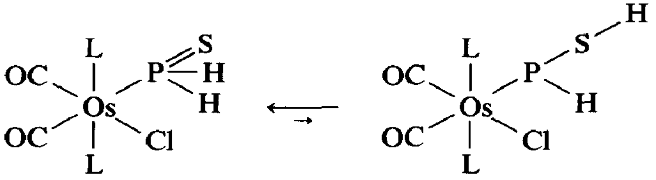


(**a**: X = Cl; **b**: X = H; **c**: X = O_2CCH_3)

Scheme 7. Preparation of organometallic primary phosphine sulphides and selenides.

complexes **2a,b**, **3**, and **8a** behave like primary phosphines with bulky substituents. As is shown in Scheme 7 the products of these reactions are the organometallic primary phosphine sulfides **37a–c** and selenides **38a–c**.

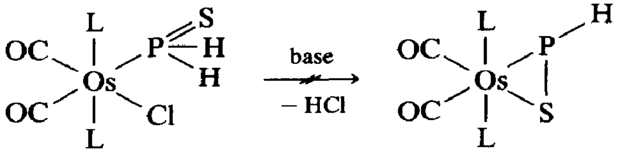
Just as was found for the secondary phosphine sulfides, the thiono form of these phosphido sulfides is more stable than the thio form and the equilibrium below lies well to the left:



(Thiono form) (Thio form)

Spectroscopic data are particularity important in assessing such an equilibrium and in the ^{1}H NMR for **37a** there is a single sharp resonance for the phosphorus bound protons with a large P–H coupling constant $^1J(\mathrm{HP}) = 382$ Hz. The ^{31}P NMR spectrum of **37a** is also very simple and even long acquisition times reveal only two resonances, which are attributable to the triphenylphosphine ligands, $\delta = -7.6$ ppm, and to the phosphido sulfide ligand, $\delta = -42.9$ ppm, $^2J(\mathrm{PP}) = 25.7$ Hz. Both of these results indicate that any exchange due to a thiono $\rightleftharpoons$ thio equilibrium is slow on the NMR time scale and that the concentration of the thio form at any given instant is quite low. Deuterium exchange in the case of **37a** requires several hours before there is a discernible decrease in the intensity of the signals of the phosphorus bound protons. For comparison, under similar conditions, that is in $CDCl_3$ solution at room temperature, complete deuterium exchange requires about 10 min for **37**.

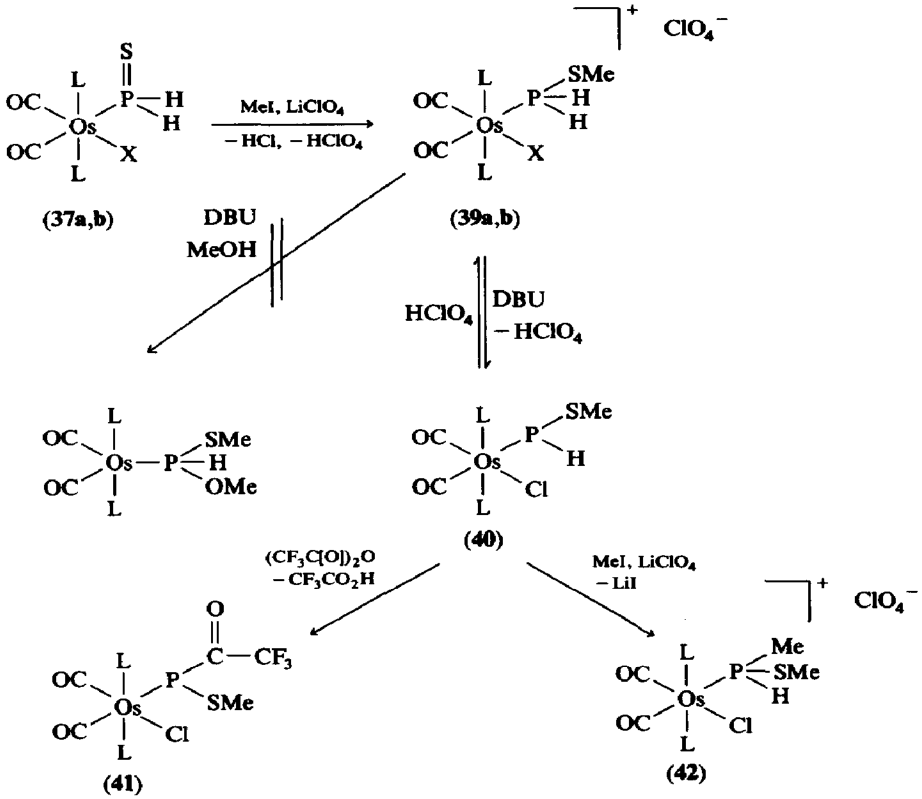
If the thiono $\rightleftharpoons$ thio equilibrium exists in this system then there should be an increase in the kinetic lability of the phosphorus bound protons. However there is, in fact, no increase in the acidity of these protons, and when **37a** is treated with DBU under any conditions it is not possible to isolate products which are solely the result of HCl loss; in other words, a thioxophosphane complex is not formed with this reagent:



(**37a**)

However this complex is readily prepared by alternative methods [53]. While these complexes decompose under basic conditions they are stable towards acid in dry chloroform solutions, and in situ ^{1}H NMR experiments indicate that **37a** can be reversibly protonated and deprotonated at the sulfur.

Methyl iodide reacts rapidly with **37a,b** to give cationic complexes with the coordinated *S*-methyl thiophosphinite ligand, **39a,b**. Alternatively the compounds **39a,b** could be viewed as quasi-phosphonium salts or even as sulfenium salts. Regardless of the semantic distinctions that are used in describing these compounds



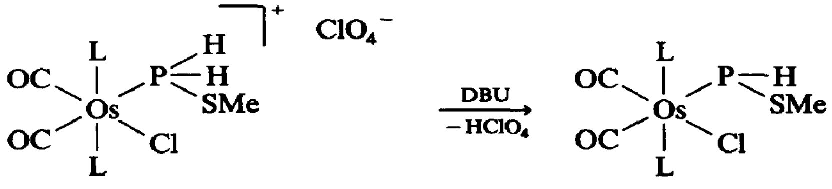
Scheme 8. Derivatives of $OsCl(PH_2S)(CO)_2(PPh_3)_2$.

they are readily isolated as colourless perchlorate salts. These complexes are the basis of the chemistry presented in Scheme 8.

The facility of the methylation reaction is surprising since it is the reverse of the thermodynamically driven Michaelis–Arbuzov rearrangement [54].

The driving force for this rearrangement is the formation of the very strong phosphoryl bond. Since the thiophosphoryl bond is weaker than the phosphoryl bond thiophosphites undergo Michaelis–Arbuzov rearrangements with less facility than the corresponding phosphite. Phosphine oxides can be alkylated with strong alkylating reagents such as trialkyloxonium salts but the resulting phosphonium salts are rapidly dealkylated by nucleophiles such as carboxylates, amines and phenoxides [55]. Although there are no reports of the alkylation of secondary phosphine sulfides there is a recent report of the methylation and reversible protonation of the oxygen in the iron phosphonate complex $Cp(CO)_2FeP(O)(OEt)_2$ [56].

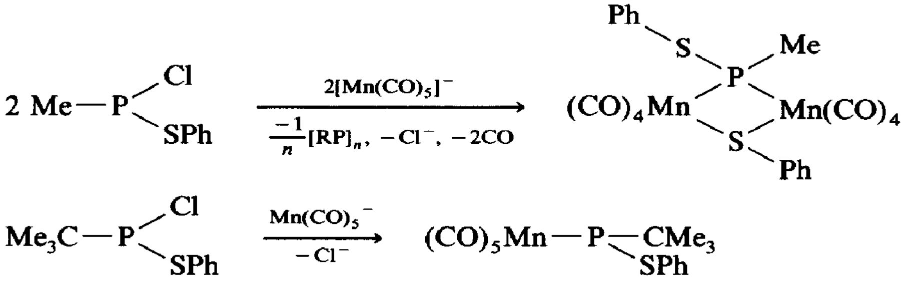
The *S*-methyl thiophosphinite complex **39a** reacts rapidly with base and a single phosphorus bound proton is lost to give a neutral complex **40** with a PHSMe ligand:



(39a) (40)

This air-stable, poorly soluble, light yellow methylthiophosphido complex (**40**) can be directly prepared in a one-pot reaction of the phosphido sulfide complex **37a** with methyliodide and then with DBU.

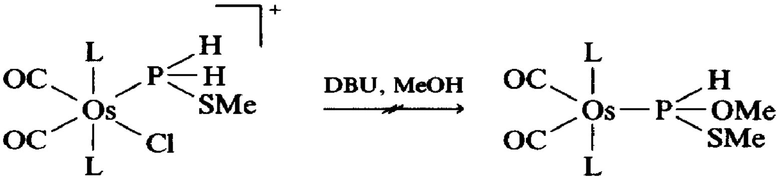
The terminal phosphido complex **40** is unique in that it contains a PHSMe ligand and there are no other related complexes L_nMPHX, with either pyramidal or planar phosphido ligand geometries, where X = OR, SR, NR_2, Cl, Br, or I. In fact the only analogous trivalent phosphine [57] CF_3PHI, is unusual as it does not undergo condensation reactions to give cyclopolyphosphines. The only closely related complexes are a manganese mononuclear complex with the η^1-P(SPh)CMe_3 and a dinuclear compound where PMe(SPh) bridges two metals [58]:



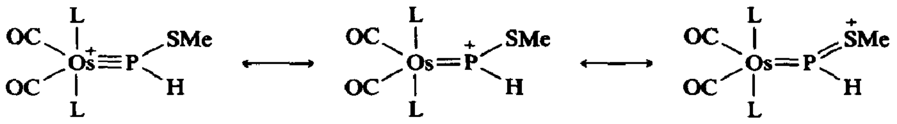
The yield of the binuclear complex is relatively poor, 25%, and the loss of the phosphinidene fragment indicates that this is probably a complex multi-step reaction that may, or may not, involve complexes with terminal PRSPh ligands. There were no reported reactions of $Mn(CO)_5[P(SPh)CMe_3]$.

Spectroscopically, **40** is characterized by a moderately intense low frequency (2244 cm^{-1}) phosphorus-hydrogen stretch and a very weak band of uncertain origin at 876 cm^{-1} in the infrared spectrum. Other bands which might arise from the PHSMe ligand are obscured by the bands due to the triphenylphosphine and carbonyl ligands. In the proton NMR spectrum of **40** the phosphorus bound proton has a relatively small one bond coupling ($^1J(HP) = 167.2$ Hz) and is coupled to two inequivalent triphenylphosphine ligands. As is seen in the ^{31}P NMR of other pyramidal phosphido ligands there are broad singlets for the phosphorus resonances of the triphenylphosphine and the thiomethylphosphido ligands. The triphenylphosphine inequivalence could arise from hindered rotation around the phosphorus–metal bond or very high inversion barriers at the phosphorus.

Non-nucleophilic bases such as DBU do not react with **40** either during its preparation or at reflux in dichloromethane. Basic solutions of methanol or ethanol also do not react with **40** and the cationic PH_2SMe complex **39a** is only deprotonated in basic methanol to give **40**. There is no evidence that zerovalent complexes with the PH(OMe)(SMe) ligand are formed under these conditions:

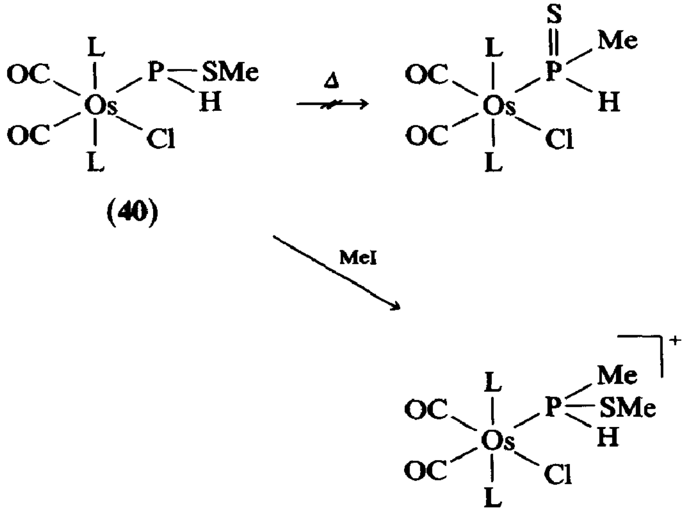


This observation is inconsistent with the expectation that, as in carbene complexes, and planar phosphido complexes, heteroatom substituents should stabilize the planar phosphido intermediates in these reactions:



However the methylthio substituent may also stabilize the pyramidal phosphido geometry and thus increase the energy of the pyramidal to planar interconversion [59].

The methylthiophosphido complex also does not undergo an Arbuzov type rearrangement even when nucleophilic catalysts such as I^- are present. Indeed, with methyl iodide **40** is methylated to give the cationic methylthio-methylphosphine complex **42**. There is no indication that this complex rearranges to the methylphosphido sulfide.



(40)

(42)

This last reaction illustrates that the most important reactivity pattern of **40** involves the nucleophilicity of the phosphorus lone pair. Thus **40** reacts with acid to return a *S*-methyl thiophosphinite complex **39a**, with methyliodide to give the *S*-methyl methylthiophosphinite complex **42**, and with trifluoroacetic anhydride the trifluoroacylphosphido complex **41** (Scheme 8). In this final reaction the acyl substituent increases the acidity of the phosphorus bound proton to such an extent that it is lost even without added base.

DBU also deprotonates the PHMe(SMe) ligand in **42** but the resulting pale yellow solid, presumably with a PMe(SMe) ligand, is relatively reactive and this product was not fully characterized.

X-ray diffraction study of $Os(\eta^2\text{-}O_2CMe)(PH_2AuI)(CO)(PPh_3)_2$ (34)

In order to throw light on the nature of the bonding of the η^2-acetate ligands and of the μ_2-PH_2 bridging ligand in these Os^{II} derivatives the gold(I) iodide adduct $Os(\eta^2\text{-}O_2CMe)(PH_2AuI)(CO)(PPh_3)_2$ (**34**), as a bis(dichloromethane) solvate, was structurally characterized. A fully labelled view of the whole molecule is shown in

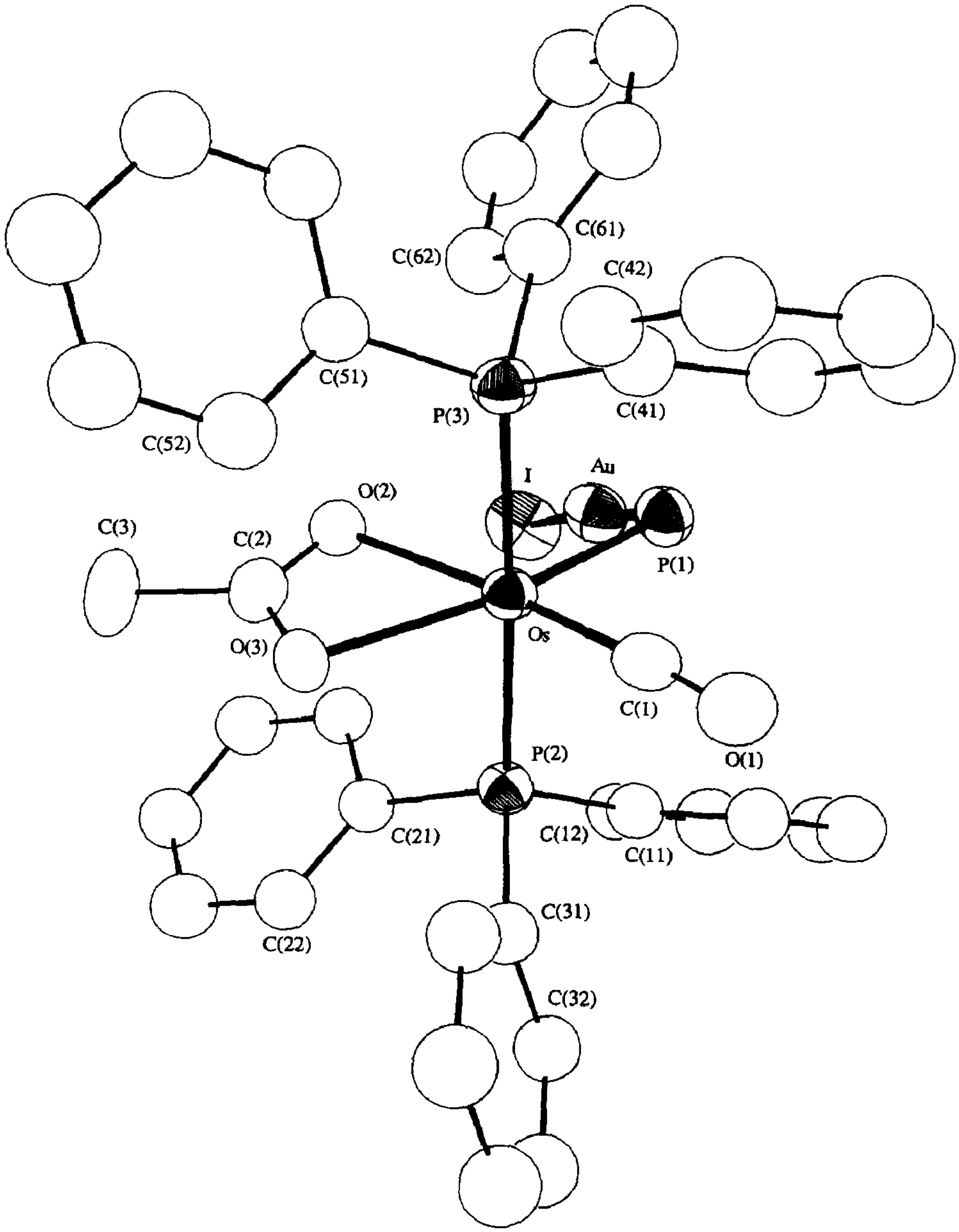


Fig. 2. Molecular structure of $Os(\eta^2\text{-}O_2CCH_3)(PH_2AuI)(CO)(PPh_3)_2$.

Fig. 2 and important bond lengths, bond angles, and atomic positional parameters are collected in Tables 2, 3 and 4 respectively. Overall, the complex has a distorted octahedral geometry at the osmium with mutually *trans* triphenylphosphine ligands. The single phosphido ligand bridges the two metal centres and the short phosphorus–metal bond lengths and compact inter-metal angle at the phosphorus can be partly attributed to the relatively small steric demands of all of the phosphorus substituents. There is a linear geometry at the gold (P(1)–Au–I = 175.3(1)°), and the gold iodide bond length is within the range of values found for gold(I) iodide

Table 2

Interatomic distances (Å) for $Os(\eta^2\text{-}O_2CCH_3)(PH_2AuI)(CO)(PPh_3)_2\cdot(CH_2Cl_2)_2$

Bond lengths involving osmium and gold

Os–P(1)	2.318(2)	Os–O(2)	2.180(6)	Au–P(1)	2.270(3)
Os–P(2)	2.391(2)	Os–O(3)	2.219(6)	Au–I	2.569(1)
Os–P(3)	2.402(2)	Os–C(1)	1.832(10)		

Bond lengths involving acetate and carbonyl ligands

C(2)–O(2)	1.232(11)	C(2)–O(3)	1.296(11)	C(2)–C(3)	1.518(13)
C(1)–O(1)	1.126(11)				

Bond lengths involving the triphenylphosphine ligands

P(2)–C(11)	1.825(9)	P(3)–C(41)	1.805(10)
P(2)–C(21)	1.808(9)	P(3)–C(51)	1.827(9)
P(2)–C(31)	1.831(10)	P(3)–C(61)	1.839(10)

	i					
	1	2	3	4	5	6
C(*i*1)–C(*i*2)	1.39(1)	1.38(1)	1.40(1)	1.41(1)	1.41(1)	1.37(1)
C(*i*1)–C(*i*6)	1.40(1)	1.42(1)	1.39(1)	1.40(1)	1.40(1)	1.41(2)
C(*i*2)–C(*i*3)	1.43(2)	1.42(1)	1.39(1)	1.41(2)	1.40(2)	1.42(2)
C(*i*3)–C(*i*4)	1.38(2)	1.33(2)	1.36(2)	1.39(2)	1.38(2)	1.37(2)
C(*i*4)–C(*i*5)	1.40(2)	1.42(1)	1.40(2)	1.35(2)	1.41(2)	1.41(2)
C(*i*5)–C(*i*6)	1.39(1)	1.38(1)	1.41(2)	1.40(2)	1.40(2)	1.44(2)

Bond lengths for dichloromethane solvate molecules

C(71)–Cl(1)	1.76(2)	C(81)–Cl(3)	1.76(3)
C(71)–Cl(2)	1.76(2)	C(81)–Cl(4)	1.57(3)

Table 3

Bond angles (°) for $Os(\eta^2\text{-}O_2CCH_3)(PH_2AuI)(CO)(PPh_3)_2\cdot(CH_2Cl_2)_2$ (34) [a]

Angles at the metals			
P(1)–Os–P(2)	92.2(1)	P(1)–Os–C(1)	89.4(3)
P(1)–Os–P(3)	91.1(1)	P(1)–Os–O(2)	99.4(2)
P(2)–Os–P(3)	176.7(1)	P(1)–Os–O(3)	156.7(2)
P(3)–Os–C(1)	91.7(3)	P(2)–Os–C(1)	88.0(3)
P(3)–Os–O(2)	87.1(2)	P(2)–Os–O(2)	92.7(2)
P(3)–Os–O(3)	95.8(2)	P(2)–Os–O(3)	81.2(2)
C(1)–Os–O(2)	171.1(3)	O(2)–Os–O(3)	58.9(2)
C(1)–Os–O(3)	112.5(3)	P(1)–Au–I	175.2(1)
Angles within the acetate and carbonyl ligands			
Os–O(2)–C(2)	93.4(6)	O(2)–C(2)–C(3)	123.2(10)
Os–O(3)–C(2)	89.8(5)	Os(3)–C(2)–C(3)	119.0(9)
O(2)–C(2)–O(3)	117.8(8)	Os–C(1)–O(1)	178.1(9)
Angles at the phosphorus atoms			
Os–P(1)–Au	113.5(1)	Os–P(3)–C(41)	114.6(3)
Os–P(2)–C(11)	116.4(3)	Os–P(3)–C(51)	118.9(3)
Os–P(2)–C(21)	113.1(3)	Os–P(3)–C(61)	112.9(3)
Os–P(2)–C(31)	112.8(3)	C(41)–P(3)–C(51)	102.4(4)
C(11)–P(2)–C(21)	105.9(4)	C(41)–P(3)–C(61)	104.1(5)
C(11)–P(2)–C(31)	103.7(4)	C(51)–P(3)–C(61)	102.1(4)
C(21)–P(2)–C(31)	103.7(4)		
Bond angles within dichloromethane solvate molecules			
Cl(1)–C(71)–Cl(2)	108.8(10)	Cl(3)–C(81)–Cl(4)	118.1(20)

[a] Bond angles in phenyl rings not included.

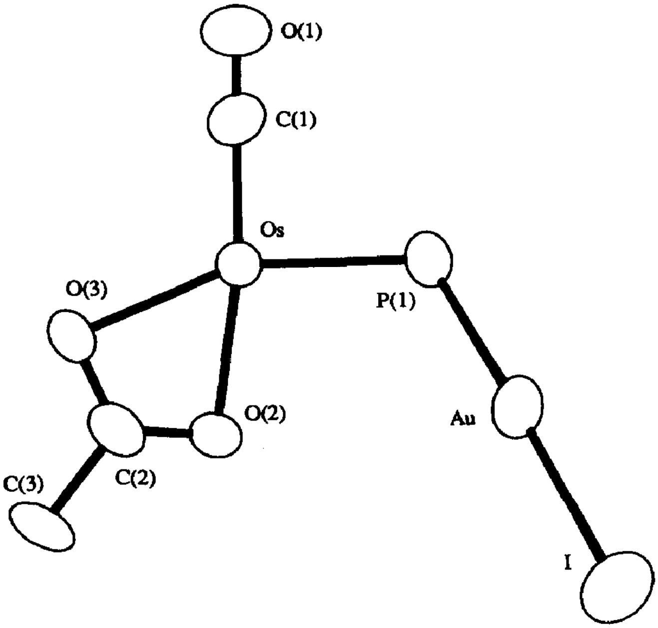


Fig. 3. View along the PPh_3–Os–PPh_3 axis of $Os(\eta^2\text{-}O_2CCH_3)(PH_2AuI)(CO)(PPh_3)_2$.

Table 4

Atomic positions for $Os(\eta^2\text{-}O_2CCH_3)(PH_2AuI)(CO)(PPh_3)_2 \cdot (CH_2Cl_2)_2$ (34)

Atom	x	y	z	Atom	x	y	z
Os	0.24900(2)	0.23110(2)	0.25525(2)	C(34)	0.0309(10)	0.3394(8)	0.5758(8)
Au	0.33557(3)	−0.01097(2)	0.23774(2)	C(35)	0.0512(10)	0.3699(9)	0.4883(8)
I	0.25066(7)	−0.20764(6)	0.19529(6)	C(36)	0.0928(9)	0.3105(7)	0.4269(7)
P(1)	0.3993(2)	0.1624(1)	0.2827(1)	C(41)	0.4456(8)	0.4498(7)	0.1999(7)
P(2)	0.1554(1)	0.1406(1)	0.3664(1)	C(42)	0.4334(9)	0.5419(8)	0.1750(7)
P(3)	0.3346(2)	0.3269(1)	0.1425(1)	C(43)	0.5215(10)	0.6369(9)	0.2225(9)
O(1)	0.3853(6)	0.3987(5)	0.4266(5)	C(44)	0.6199(10)	0.6369(9)	0.2917(9)
O(2)	0.1289(5)	0.1196(4)	0.1261(4)	C(45)	0.6317(11)	0.5494(9)	0.3174(9)
O(3)	0.0678(5)	0.2320(5)	0.1967(4)	C(46)	0.5451(9)	0.4551(8)	0.2716(8)
C(1)	0.3342(8)	0.3559(7)	0.3603(7)	C(51)	0.2383(8)	0.3594(6)	0.0442(6)
C(2)	0.0480(8)	0.1536(7)	0.1285(6)	C(52)	0.1353(9)	0.3752(8)	0.0604(8)
C(3)	−0.0727(9)	0.1078(9)	0.0561(8)	C(53)	0.0614(10)	0.3990(9)	−0.0154(9)
C(11)	0.2436(7)	0.0854(6)	0.4490(6)	C(54)	0.0901(11)	0.4123(9)	−0.1034(9)
C(12)	0.2156(8)	−0.0196(7)	0.4438(7)	C(55)	0.1963(10)	0.4017(9)	−0.1178(9)
C(13)	0.2903(10)	−0.0597(9)	0.5064(9)	C(56)	0.2697(9)	0.3749(7)	−0.0441(7)
C(14)	0.3910(10)	0.0081(9)	0.5716(9)	C(61)	0.4102(8)	0.2603(7)	0.0731(7)
C(15)	0.4186(10)	0.1135(8)	0.5767(8)	C(62)	0.3577(9)	0.1571(8)	0.0372(7)
C(16)	0.3460(8)	0.1532(7)	0.5158(7)	C(63)	0.4105(11)	0.1008(9)	−0.0179(9)
C(21)	0.0204(7)	0.0366(6)	0.3044(6)	C(64)	0.5156(11)	0.1529(10)	−0.0363(9)
C(22)	−0.0873(8)	0.0305(7)	0.3216(7)	C(65)	0.5715(11)	0.2587(10)	−0.0005(9)
C(23)	−0.1911(9)	−0.0517(8)	0.2695(8)	C(66)	0.5182(10)	0.3154(8)	0.0553(8)
C(24)	−0.1846(9)	−0.1251(7)	0.2038(7)	Cl(1)	0.8160(4)	0.4691(3)	0.6926(3)
C(25)	−0.0764(9)	−0.1224(8)	0.1825(7)	Cl(2)	0.7051(5)	0.3503(4)	0.4978(4)
C(26)	0.0247(8)	−0.0422(7)	0.2334(6)	C(71)	0.6819(15)	0.3854(13)	0.6137(13)
C(31)	0.1092(8)	0.2214(7)	0.4501(6)	Cl(3)	0.7068(7)	0.1687(6)	0.2337(6)
C(32)	0.0887(9)	0.1934(8)	0.5384(8)	Cl(4)	0.8264(7)	0.3835(6)	0.2567(6)
C(33)	0.0479(9)	0.2525(8)	0.5990(8)	C(81)	0.8299(27)	0.2721(23)	0.2310(22)

Table 5

Structural parameters for bridging phosphido complexes

Compound	Angle at metal P–M–P (°)	Angle at phosphorus M–P–M (°)	Bond lengths M–P (Å)	Ref.
$[(OC)_4MnPH_2]_2$	76.1	103.9	2.351	64
$[Os(\mu^2\text{-}PH_2)Cl(CO)(PPh_3)_2]_2$	73.3	106.7	2.396, 2.401	12
$[(OC)_4MnPH_2]_3$	89.1	130.1	2.382	64
$[CpNi(PH_2)]_3$	92.3	124.3	2.152	64
$Os(\eta^2\text{-}O_2CCH_3)(PH_2AuI)(CO)(PPh_3)_2$	–	113.5	P–Os 2.320 P–Au 2.268	
$IrHBr(CO)(PEt_3)_2PH_2RuCl_2(\eta^6\text{-Arene})$	–	131.4	P–Ir 2.412 P–Ru 2.367	16
$Cp^*Mn(CO)_2PH_2Fe(CO)_2Cp$	–	127.5	P–Fe 2.291 P–Mn 2.259	17

adducts [60]. The gold–phosphorus bond length is in the range [61] 2.19–2.325 Å found in gold(I) triphenylphosphine complexes, and is longer than that found in $[N(^nBu)_4][Ph_2P(AuBr)_2]$, 2.243(3) Å [62], and in $[2,4,6\text{-}(^tBu)_3C_6H_2PH_2]AuCl$, 2.242(2) Å [68]. The distortion away from ideal octahedral geometry at the osmium is attributable to the small 'bite', typically about 60°, of the bidentate acetate ligand. A second view of this molecule, Fig. 3, along the triphenylphosphine–metal axis, clearly shows that the acetate is bound so that an oxygen atom is not coordinated directly *trans* to the PH_2AuI group. This feature is found in other mononuclear η^2-carboxylate complexes that also contain ligands with strong *trans* influences [63].

In Table 5 the bond angles at the metal and phosphorus in related structurally characterized bridging phosphido complexes are contrasted with that in **34**. The most salient feature in Table 5 is that the inter-metal angle at the phosphorus in **34** is between the values found for the dimeric and trimeric cyclic structures. It is also significantly smaller than that found in the complexes $IrHBr(CO)(PEt_3)_2PH_2$ $RuCl_2(\eta^6\text{-Arene})$ and $Cp^*Mn(CO)_2PH_2Fe(CO)_2Cp$. Both of these features can be attributed to the minimal steric requirements of the gold(I) iodide centre.

Conclusion

The majority of the reactions of $L_nM{-}PH_2$ complexes, namely protonation, alkylation, acylation, coordination and oxidation, are also well known for aliphatic and aromatic primary phosphines. On the other hand, the alcohol addition reactions which afford complexes of alkyl phosphinites parallel the known chemistry of other phosphido complexes. This reaction type is unknown for aliphatic and aromatic primary phosphines. Although no osmium or ruthenium $L_nM{-}PH_2$ complex with a planar phosphorus geometry has been isolated or structurally characterized, the preparation of such a complex should make possible the synthesis of many other unusual adducts that are expected to arise from nucleophilic addition to the phosphorus.

Table 6

Infrared spectroscopic data [a,b,c] for new compounds

Complex	ν(CO)	ν(PH)	δ(PH)	Other bands
Os(η^2-O$_2$CMe)(PH$_2$)(CO)(PPh$_3$)$_2$ **(4a)**	1912	2268m 2260m	1072w	1516w, ν(C–O)$_a$ 1459m, ν(C–O)$_s$
Ru(η^2-O$_2$CMe)(PH$_2$)(CO)(PPh$_3$)$_2$ **(4b)**	1923	2268m	–	1509m, ν(C–O)$_a$ 1450m, ν(C–O)$_s$
Os(η^2-S$_2$CNMe$_2$)(PH$_2$)(CO)(PPh$_3$)$_2$ **(5)**	1901	2232w 2217m	1062w	1516m, ν(C–N) 1380s, 1140m, 1151m, 996, ν(C–S)
Os(η^2-acac)(PH$_2$)(CO)(PPh$_3$)$_2$ **(6)**	1908 1893cs	2250m	1074w	1572s, 1527, 1274m, 936w
Os(η^2-O$_2$N)(PH$_2$)(CO)(PPh$_3$)$_2$ **(7)**	1916	2286m 2259w 2240m	1073w	1313w, ν(N–O)$_a$ 1188m, ν(N–O)$_s$
Os(OC[O]CH$_3$)(PH$_2$)(CO)$_2$(PPh$_3$)$_2$ **(8a)**	2021 1954	2285w 2268m	–	1640s, ν(C–O)$_a$ 1365s, ν(C–O)$_s$
Ru(OC[O]CH$_3$)(PH$_2$)(CO)$_2$(PPh$_3$)$_2$ **(8b)**	2028 1970	2281m 2265m	–	1605s, ν(C–O)$_a$ 1367s, ν(C–O)$_s$
[Os(η^2-O$_2$CMe)(PH$_3$)(CO)(PPh$_3$)$_2$]ClO$_4$ **(9)**	1970	–	1037s	1464s, ν(C–O)$_a$ 1378s, ν(C–O)$_s$
Os(OC[O]CF$_3$)$_2$(PH$_3$)(CO)(PPh$_3$)$_2$ **(11)**	1975	2338w	1042s	1686s, ν(C–O)$_a$ 1410m, ν(C–O)$_s$ 1181s, 1145s, ν(C–F)
Os(OC[O]H)$_2$(PH$_3$)(CO)(PPh$_3$)$_2$ **(12)**	1973cs 1958	2349w	1043s	1619s, 1306m, 1289s 1092m, 780w, 773w
[Os(η^1-OC[O]Me)(PH$_3$)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$	2100cs 2061 1983	2405w	1000s	1630s, ν(C–O)$_a$ 1376s, ν(C–O)$_s$ 1314s
[OsH(PH$_2$OMe)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ **(14)**	2098w 2010	–	–	1001m, 993s, ν(P–OMe) 782m, δ(Os–H)
Os(PH$_2$OMe)(CO)$_2$(PPh$_3$)$_2$ **(15)**	1910 1860	2277w	912w	989s, ν(P–OMe)
[RuH(PH$_2$OMe)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ **(16c)**	2102w 2026s	2319w	–	988s, ν(P–OMe) 779w, δ(Ru–H)
[RuH(PH$_2$OEt)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ **(16d)**	2100w 2022s	2321w	–	1001s, 992s, ν(P–OEt) 924m, δ(P–H)
[RuH(PH$_2$O^{i}Pr)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ **(16e)**	2094w 2017	2340w	882w	951s, 931s, ν(P–OR)
Ru(PH$_2$OMe)(CO)$_2$(PPh$_3$)$_2$ **(17c)**	1958w 1922 1877	2258m	929w	985s, ν(P–OMe)
Ru(PH$_2$OEt)(CO)$_2$(PPh$_3$)$_2$ **(17d)**	1912 1864	2272m 2260m	–	995s, 912s, ν(P–OMe)
[OsCl(PH$_2$Me)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ **(18)**	2064, 2002 1966cs	–	998m 990m	306m, ν(Os–Cl)
[OsH(PH$_2$Me)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ **(19)**	2077, 2040 1961m	–	1001s 989sh	804w, δ(Os–H)
[OsCl(PH$_2$CH$_2$Ph)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ **(20)**	2062, 2007	–	901m	930m, 920m 303w, ν(Os–Cl)
[Os(η^2-S$_2$CNMe$_2$)(PH$_2$Me)(CO)(PPh$_3$)$_2$]ClO$_4$ **(21)**	1933	–	993m	1541m, ν(C–N) 1401m, 1377m
OsI(OC[O]Me)(PH$_2$Me)(CO)(PPh$_3$)$_2$ **(22)**	1941	2340	999m	1590m, ν(C–O)$_a$ 1368m, ν(C–O)$_s$

Table 6 (continued)

Complex	$\nu(CO)$	$\nu(PH)$	$\delta(PH)$	Other bands
$OsCl(PHMe)(CO)_2(PPh_3)_2$ (23)	2017, 1952	2237m	872m	295m, $\nu(Os{-}Cl)$
$OsCl(PHCH_2Ph)(CO)_2(PPh_3)_2$ (24)	2006, 1943	2242m	–	284m, $\nu(Os{-}Cl)$
$[OsCl(PH_2CMe_3)(CO)_2(PPh_3)_2]ClO_4$ (25)	2062, 1999	–	892m 821w	303w, $\nu(Os{-}Cl)$
$Os[PH(OMe)Me](CO)_2(PPh_3)_2$ (26)	1909, 1846	2244w	869m	1031s, 987s 978s, $\nu(P{-}OMe)$
$Os[PH(OMe)(CMe_3)](CO)_2(PPh_3)_2$ (27)	1904, 1852	2252m 2238m	897m	1030m, 961m, 818m, $\nu(P{-}OMe)$
$[OsH[PH(OMe)(CMe_3)](CO)_2(PPh_3)_2]ClO_4$ (28)	2080m, 2057cs 1984, 1962cs	–	916m	1044s, 955m, 916m, 816w, $\nu(P{-}OMe)$ 780m, $\delta(Os{-}H)$
$Os(\eta^1\text{-}OC[O]Me)[PH(C[O]CMe_3)](CO)_2(PPh_3)_2$ (29)	2019 1969cs 1948	2295w	–	1617m, $\nu(C{-}O)$ 1600m, $\nu(C{-}O)_a$ 1380m, $\nu(C{-}O)_s$ 1313m, 872m, 804w
$Os(\eta^1\text{-}OC[O]Me)[PH(C[O]CF_3)](CO)_2(PPh_3)_2$ (30)	2031 1960	2340w	–	1613s, $\nu(C{-}O)$ 1600s, $\nu(C{-}O)_a$ 1373s, $\nu(C{-}O)_s$ 1260s, 1181s, 1137s, $\nu(C{-}F)$ 975m, 872s
$Os(\eta^1\text{-}OC[O]Me)[P(C[O]CF_3)_2](CO)_2(PPh_3)_2$ (31)	2047 1973	–	–	1670m, 1622m, 1598m, $\nu(C{-}O)$ 1332m, 1313m, 1258s, 1204s, 1189s 1157s, 1143s, $\nu(C{-}F)$ 944m, 907m
$OsCl[PH_2Fe(CO)_4](CO)_2(PPh_3)_2$ (32a)	2030, 1975 1949, 1906 1880sh	2326w	815m	302w, $\nu(Os{-}Cl)$
$OsH[PH_2Fe(CO)_4](CO)_2(PPh_3)_2$ (32b)	2043, 2019 2006, 1988w 1954w, 1937 1904br	2311w	863m 812m	776w, $\nu(Os{-}H)$
$OsCl(PHPhFe(CO)_4)(CO)_2(PPh_3)_2$	2037, 1978 1959, 1935 1913	2328	923m 854 838w	–
$OsCl(PH_2AuI)(CO)_2(PPh_3)_2$ (33a)	2049, 1980	–	795m	302w, $\nu(Os{-}Cl)$ 775w
$OsH(PH_2AuI)(CO)_2(PPh_3)_2$ (33b)	2050, 2003	2328w	828w 788m 777m	1940m, $\nu(Os{-}H)$
$Os(\eta^2\text{-}O_2CMe)(PH_2AuI)(CO)(PPh_3)_2$ (34)	1938	2312w	817m 799w	1512w, $\nu(C{-}O)_a$ 1470m, $\nu(C{-}O)_s$
$Os(\eta^2\text{-}S_2CNMe_2)(PH_2AuI)(CO)(PPh_3)_2$ (35)	1919	2301m	795s	1533m, $\nu(C{-}N)$ 1377m, 1161m, 1076m 997w, $\nu(C{-}S)$
$Os(\eta^1\text{-}OC[O]Me)(PH_2AuI)(CO)_2(PPh_3)_2$ (36)	2042 1950	2342w	796m	1623m, $\nu(C{-}O)_a$ 1362s, $N(C{-}O)_s$
$OsCl(PH_2S)(CO)_2(PPh_3)_2$ (37a)	2109w, 2046 1980	2317w	922m 887s	302m, $\nu(Os{-}Cl)$

(continued)

Table 6 (continued)

Complex	ν(CO)	ν(PH)	δ(PH)	Other bands
$OsH(PH_2S)(CO)_2(PPh_3)_2$ (**37b**)	2040, 2003	2296w	908s	1927m, ν(Os–H); 788w, δ(Os–H)
$Os(\eta^2\text{-}OC[O]Me)(PH_2S)(CO)_2(PPh_3)_2$ (**37c**)	2050 1969	2297w 2270w	900s	1621s, $\nu(C–O)_a$ 1369s, $\nu(C–O)_s$ 601m, ν(P=S) [d]
$OsCl(P(S)HPh)(CO)_2(PPh_3)_2$	2047, 1972	2283w	944 916w 844m	601m, ν(P=S)
$OsCl(PH_2Se)(CO)_2(PPh_3)_2$ (**38a**)	2120w, 2048 1981	2312w	889w 853m	
$OsH(PH_2Se)(CO)_2(PPh_3)_2$ (**38b**)	2039, 1998	2299w	881s	1930m, ν(Os–H)
$Os(\eta^1\text{-}OC[O]Me)(PH_2Se)(CO)_2(PPh_3)_2$ (**38b**)	2056 1980	2306w 2292m	865s	1623m, $\nu(C–O)_a$ 1314s, $\nu(C–O)_s$ 594m, ν(P=Se) [d]
$[OsCl(PH_2SMe)(CO)_2(PPh_3)_2]ClO_4$ (**39a**)	2062, 1994	–	863m	
$[OsH(PH_2SMe)(CO)_2(PPh_3)_2]ClO_4$ (**39b**)	2067, 2038	–	883m	1962m, ν(Os–H); 799w, δ(Os–H)
$OsCl(PHSMe)(CO)_2(PPh_3)_2$ (**40**)	2028, 1965 1933cs	2244m	876w	280w, ν(Os–Cl)
$OsCl[P(C[O]CF_3)SMe](CO)_2(PPh_3)_2$ (**41**)	2026, 1979	–	–	1672m, ν(C=O); 1252s, 1190m, 1174m, 1141s, ν(C–F); 915m
$[OsCl(PHMeSMe)(CO)_2(PPh_3)_2]ClO_4$ (**42**)	2063, 1995	–	904m	

[a] In cm^{-1}. Spectra recorded as Nujol mulls between KBr or CsI plates and calibrated with polystyrene. [b] All carbonyl bands are strong unless indicated otherwise, s = strong, m = medium, w = weak, sh = shoulder, (s) = solution spectrum recorded in dichloromethane, cs = crystal splitting band. [c] Bands due to triphenylphosphine ligands not included. [d] ν(P=S) and ν(P=Se) are tentatively assigned.

Experimental

Standard Schlenk techniques were used in the preparation and reactions of the terminal phosphido complexes **2a–8**, for the derivatives of $OsCl(PH_2S)(CO)_2(PPh_3)_2$ (**39–42**) and for the M^0 complexes **15** and **17**. Otherwise the new complexes described here can easily be handled in the open. General instrumental and experimental details have been described previously [10,12,65].

Preparation of new compounds

*$Os(\eta^2\text{-}O_2CCH_3)(PH_2)(CO)(PPh_3)_2$ (**4a**).* A mixture of $[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**1a**: 0.7 g, 0.73 mmol), sodium acetate (1.4 g, 17.1 mmol) and 30 mL methanol was heated under reflux for 20 min, during which the initially colourless suspension formed a slightly yellow solution from which the deep yellow product separated. The flask was subsequently cooled in an ice/salt bath, the solid was filtered off and washed successively with methanol, water, methanol, ethanol and n-hexane. The light yellow product, 0.56 g (92%), was sufficiently pure for most

Table 7

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

Compound	^{1}H NMR data
$Os(\eta^2\text{-}O_2CMe)(PH_2)(CO)(PPh_3)_2$ **(4a)**	0.99(dt, ^1J(HP) = 194.5, ^3J(HP) = 7,2,PH_2) [b] 1.56(s,3,CH_3)
$Ru(\eta^2\text{-}O_2CMe)(PH_2)(CO)(PPh_3)_2$ **(4b)**	0.38(s,3,CH_3) [b] 0.60(dt, ^1J(HP) = 223.2,2,PH_2)
$Os(\eta^2\text{-}S_2CNMe_2)(PH_2)(CO)(PPh_3)_2$ **(5)**	2.12(s,3,CH_3) [b] 2.36(s,3,CH_3)
$Os(\eta^2\text{-acac})(PH_2)(CO)(PPh_3)_2$ **(6)**	1.06(s,3,CH_3) 1.22(s,3,CH_3) 4.22(s,1,CH)
$Os(\eta^2\text{-}O_2N)(PH_2)(CO)(PPh_3)_2$ **(7)**	1.14(dt, ^1J(HP) = 200.5, ^3J(HP) = 9.6,2,PH_2)
$Os(OC[O]Me)(PH_2)(CO)_2(PPh_3)_2$ **(8a)**	0.62(dt, ^1J(HP) = 190, ^3J(HP) = 4.5,2,PH_2) 1.21(s,3,CH_3)
$[Os(\eta^2\text{-}O_2CMe)(PH_3)(CO)(PPh_3)_2]ClO_4$ **(9)**	0.34(s,3,CH_3) 3.80(dt, ^1J(HP) = 404.1, ^3J(HP) = 4.3,3,PH_3)
$Os(OC[O]CF_3)_2(PH_3)(CO)(PPh_3)_2$ **(11)**	3.77(dt, ^1J(HP) = 384.3, ^3J(HP) = 2.9,3,PH_3)
$Os(OC[O]H)_2(PH_3)(CO)(PPh_3)_2$ **(12)**	3.70(dt, ^1J(HP) = 381.2, ^3J(HP) = 3.03,3,PH_3)
$[Os(\eta^1\text{-}OC[O]Me)(PH_3)(CO)_2(PPh_3)_2]ClO_4$ **(13)**	1.35(s,3,CH_3) 4.10(dt, ^1J(HP) = 397.5, ^3J(HP) = 5.9,3,PH_3)
$[OsH(PH_2OMe)(CO)_2(PPh_3)_2]ClO_4$ **(14)**	−7.97(dt, ^2J(H−PH$_2$OMe) = 47.0, ^2J(H−PPh$_3$) = 14.8,1,Os−H) 3.20(d, ^3J(HP) = 13.1,3,POCH_3) 6.51(dt, ^1J(HP) = 386.5, ^3J(HP) = 8.52,2,PH_2)
$Os(PH_2OMe)(CO)_2(PPh_3)_2$ **(15)**	3.06(d, ^2J(HP) = 12.5,3,OCH_3) [b] 6.95(dt, ^1J(HP) = 336.1, ^3J(HP) = 10.2,2,PH_2OMe)
$[RuH(PH_2OMe)(CO)_2(PPh_3)_2]ClO_4$	−6.42(dt, ^2J(H−PH$_2$OR) = 75.2, ^2J(H−PPh$_3$) = 15.4,t,Ru−H) 3.19(d, ^3J(HP) = 12.3,3,OCH_3) 6.30(dt, ^1J(HP) = 362.9, ^3J(HP) = 4.04,2,PH_2OMe)
$[RuH(PH_2OEt)(CO)_2(PPh_3)_2]ClO_4$ **(16d)**	−6.43(dt, ^2J(H−PH$_2$OR) = 74.6, ^2J(H−PPh$_3$) = 15.5,1,Ru−H) 0.89(t, ^3J(HH) = 7.1,3,CH_3) 3.37(dq, ^3J(HP) = 8.7, ^3J(HH) = 7.02,2,OCH_2) 6.43(dt, ^1J(HP) = 362.3, ^3J(HP) = 3.8,2,PH_2)
$[RuH(PH_2O^iPr)(CO)_2(PPh_3)_2]ClO_4$ **(16e)**	−6.40(dt, ^2J(H−PH$_2$OR) = 74.7, ^2J(H−PPh$_3$) = 15.6,1,Ru−H) 0.89(d, ^3J(HH) = 6.2,6,CH_3) 3.51(dm, ^3J(HP) = 10.9,1,CH) 6.37(dt, ^1J(HP) = 361.0, ^3J(HP) = 4.02,2,PH_2OR)
$Ru(PH_2OEt)(CO)_2(PPh_3)_2$ **(17d)**	1.05(t, ^3J(HH) = 82.3,CH_3) [b] 3.24(dq, ^3J(HP) = 8.2, ^3J(HH) = 7.0,2,CH_2) 6.59(dt, ^1J(HP) = 304, ^3J(HP) = 9.4,2,PH_2OEt)
$[OsCl(PH_2Me)(CO)_2(PPh_3)_2]ClO_4$ **(18)**	0.61(dt, ^2J(HP) = 12.2, ^3J(HH) = 6.7,3,PCH_3) 4.82(dm, ^1J(HP) = 396.1,2,PH_2)
$[OsH(PH_2Me)(CO)_2(PPh_3)_2]ClO_4$ **(19)**	−7.36(dt, ^2J(H−PH$_2$CH$_3$) = 28.2, ^2J(H−PPh$_3$) = 16.4,1,Os−H) 0.51(dt, ^2J(HP) = 11.6, ^3J(HP) = 6.4,3,PCH_3) 4.21(dm, ^1J(HP) = 385.0,2,PH_2)
$[Os(\eta^2\text{-}S_2CNMe_2)(PH_2Me)(CO)(PPh_3)_2]ClO_4$ **(21)**	0.96(dt, ^2J(HP) = 11.32, ^2J(HH) = 6.4,3,PCH_3) 2.15(s,3,NCH_3) 2.36(s,3,NCH_3) 4.11(dtq, ^1J(HP) = 379.2, ^3J(HP) = 4.83, ^3J(HH) = 6.4,2,PH_2)

Table 7 (continued)

Compound	^{1}H NMR data
OsI(OC[O]Me)(PH$_2$Me)(CO)(PPh$_3$)$_2$ **(22)**	0.47(dt, ^2J(HP) = 11.0, ^3J(HH) = 6.1,3,PCH_3) 1.41(s,3,CCH_3) 4.09(dtq, ^1J(HP) = 402.9, ^3J(HP) = 5.8, ^3J(HH) = 6.0,2,PH_2)
OsCl(PHMe)(CO)$_2$(PPh$_3$)$_2$ **(23)**	1.1(d, ^2J(HP) = 5,3,CH_3) ^{b}
OsCl(PHCH$_2$Ph)(CO)$_2$(PPh$_3$)$_2$ **(24)**	2.9(dd, ^2J(HP) = 7, ^3J(HH) = 3,2,CH_2) ^{b}
[OsCl(PH$_2$CMe$_3$)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ **(25)**	0.95(d, ^3J(HP) = 16.4,9,CH_3)
Os[PH(OMe)Me](CO)$_2$(PPh$_3$)$_2$ **(26)**	1.1(dd, ^2J(HP) = 6, ^3J(HH) = 6,3,PCH_3) ^{b} 2.8(d, ^3J(HP) = 12.2,3,POCH_3) 7.4(dtq, ^1J(HP) = 325, ^3J(HP) = 9, ^3J(HH) = 6,1,PH)
Os[PH(OMe)(CMe$_3$)](CO)$_2$(PPh$_3$)$_2$ **(27)**	0.8(d, ^3J(HP) = 15.8,9,PCCH_3) ^{b} 2.5(d, ^3J(HP) = 13.2,3,OCH_3) 6.8(dt, ^1J(HP) = 336, ^3J(HP) = 8.4,1,PH)
[OsH[PH(OMe)(CMe$_3$)](CO)$_2$(PPh$_3$)$_2$]ClO$_4$ **(28)**	−10.2(dt, ^2J(H–PH(OMe)R) = 42, ^2J(H–PPh$_3$) = 21,1,Os–H) 1.3(d, ^3J(HP) = 18,9,CCH_3) 3.1(d, ^3J(HP) = 12,3,OCH_3)
Os(η^1-OC[O]Me)[PH(C[O]CMe$_3$)](CO)$_2$(PPh$_3$)$_2$ **(29)**	0.71(s,9,C[CH_3]$_3$) 1.21(s,3,CCH_3) 3.73(dt, ^1J(HP) = 219.1, ^3J(HP) = 12.3,1,PH)
Os(η^1-OC[O]Me)[PH(C[O]CF$_3$)](CO)$_2$(PPh$_3$)$_2$ **(30)**	1.21(s,3,CH_3) 3.58(dq, ^1J(HP) = 238.3, ^3J(HP) = 10.6, ^3J(HF) = 2.12,1,PH)
Os(η^1-OC[O]Me)[P(C[O]CF$_3$)$_2$](CO)$_2$(PPh$_3$)$_2$ **(31)**	1.16(s,3,CH_3)
OsCl[PH$_2$Fe(CO)$_4$](CO)$_2$(PPh$_3$)$_2$ **(32a)**	2.38(dt, ^1J(HP) = 319.2, ^3J(HP) = 10.0,2,PH_2)
OsH[PH$_2$Fe(CO)$_4$](CO)$_2$(PPh$_3$)$_2$ **(32b)**	−6.79(dtt, ^2J(H–PH$_2$Fe) = 16.31, ^2J(H–PPh$_3$) = 18.7, ^3J(HH) = 3.0,1,Os–H) 2.15(dtd, ^1J(HP) = 306.2, ^3J(HP) = 11.9, ^3J(HH) = 2.9,2,PH_2)
OsCl[PHPhFe(CO)$_3$](CO)$_2$(PPh$_3$)$_2$	5.08(ddd, ^1J(HP) = 300.7, ^3J(HP) = 12.0,14.0,1,PHPh)
OsCl(PH$_2$AuI)(CO)$_2$(PPh$_3$)$_2$ **(33a)**	3.10(dt, ^1J(HP) = 335.2, ^3J(HP) = 8.4,2,PH_2)
OsH(PH$_2$AuI)(CO)$_2$(PPh$_3$)$_2$ **(33b)**	−7.03(dtt, ^2J(H–PH$_2$) = 18.3, ^2J(H–PPh$_3$) = 19.2, ^3J(HH) = 3.5,2,PH_2) 2.30(dtd, ^1J(HP) = 330.5, ^3J(HP) = 10.09, ^3J(HH) = 3.5,2,PH_2)
Os(η^2-O$_2$CMe)(PH$_2$AuI)(CO)(PPh$_3$)$_2$ **(34)**	0.31(s,3,CH_3) 2.76(dt, ^1J(HP) = 349.2, ^3J(HP) = 6.5,2,PH_2)
Os(η^2-S$_2$CNMe$_2$)(PH$_2$AuI)(CO)(PPh$_3$)$_2$ **(35)**	2.09(s,3,CH_3) 2.29(s,3,CH_3) 2.86(dt, ^1J(HP) = 333.7, ^3J(HP) = 5.8,2,PH_2)
Os(η^1-OC[O]Me)(PH$_2$AuI)(CO)$_2$(PPh$_3$)$_2$ **(36)**	1.39(s,3,CH_3) 2.90(dt, ^1J(HP) = 329.6, ^3J(HP) = 8.8,2,PH_2)
OsCl(PH$_2$S)(CO)$_2$(PPh$_3$)$_2$ **(37a)**	5.35(dt, ^1J(HP) = 382, $^3J_{HP}$ = 18,2,PH_2)
OsH(PH$_2$S)(CO)$_2$(PPh$_3$)$_2$ **(37b)**	−7.19(dtt, ^2J(H–PPh$_3$) ^2J(H–PH$_2$S) = 22, ^3J(HH) = 2.7,1,Os–H) 5.07(dtd, ^1J(HP) = 372.5, ^3J(HP) = 11.2, ^3J(HH) = 2.4,2,PH_2S)

Table 7 (continued)

Compound	^{1}H NMR data
$Os(\eta^1\text{-}OC[O]Me)(PH_2S)(CO)_2(PPh_3)_2$ (**37c**)	1.44(s,3,CH_3) 5.82(dt, ^1J(HP) = 367.0, ^3J(HP) = 7.9,2,PH_2S)
$OsCl(PH_2Se)(CO)_2(PPh_3)_2$ (**38a**)	4.20(dt, ^1J(HP) = 378.5, ^3J(HP) = 9.0,2,PH_2)
$OsH(PH_2Se)(CO)_2(PPh_3)_2$ (**38b**)	−6.94(dtt, ^2J(H−PH$_2$Se) = 21.7, ^2J(H−PPh$_3$) = 18.9, ^3J(HH) = 2.6,1,Os−H) 3.87(dtd, ^1J(HP) = 368.3, ^3J(HP) = 9.9, ^3J(HH) = 2.6,2,PH_2Se)
$Os(\eta^1\text{-}OC[O]Me)(PH_2Se)(CO)_2(PPh_3)_2$ (**38c**)	1.45(s,3,CH_3) 4.69(dt, ^1J(HP) = 362.2, ^3J(HP) = 7.9,2,PH_2Se)
$[OsCl(PH_2SMe)(CO)_2(PPh_3)_2]ClO_4$ (**39a**)	2.12(d, ^3J(HP) = 11.3,3,SCH_3) 4.45(dt, ^1J(HP) = 422.1, ^3J(HP) = 7.8,2,PH_2)
$[OsH(PH_2SMe)(CO)_2(PPh_3)_2]ClO_4$ (**39b**)	−7.25(dt, ^2J(H−PH$_2$SMe) = 15.5, ^2J(H−PPh$_3$) = 26.8,1,Os−H) 2.01,(d,^3J(HP) = 11.4,3,SCH_3) 5.20(dt, ^1J(HP) = 414.5, ^3J(HP) = 9.5,2,PH_2)
$OsCl(PHSMe)(CO)_2(PPh_3)_2$ (**40**)	1.51(d, ^3J(HP) = 10.9,3,CH_3) 4.06(ddd, ^1J(HP) = 167.7, ^3J(HP) = 15.1, and 10.0,2,PH)
$OsCl[P(C[O]CF_3)SMe](CO)_2(PPh_3)_2$ (**41**)	1.75(d, ^3J(HP) = 13.3,3,PSCH_3)
$[OsCl(PHMeSMe)(CO)_2(PPh_3)_2]ClO_4$ (**42**)	1.19(dd, ^3J(HH) = 5.7, ^2J(HP) = 10.2,3,PCH_3) 2.28(d, ^3J(HP) = 10.9,3,SCH_3) 5.52(dtq, ^1J(HP) = 411.9, ^3J(HP) = 14.3, ^3J(HH) = 5.7,1,PH)

[a] As chloroform solutions at 21° C. Chemical shifts (δ) are given in ppm with respect to tetramethylsilane. [b] Spectrum measured in C_6D_6, signals for the phosphorus bound protons in **23** and **24** not observed. [c] Range for possible shifts and coupling constants. One branch of doublet obscured by triphenylphosphine protons.

uses. A sample for microanalysis was obtained by recrystallization from dichloromethane/ethanol. M.p. 169–171° C. Anal. Found: C, 56.46; H, 4.65. $C_{39}H_{35}O_3OsP_3$ calcd.: C, 56.10; H, 4.23%.

*$Ru(\eta^2\text{-}O_2CCH_3)(PH_2)(CO)(PPh_3)_2$ (**4b**).* A suspension of $[RuCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**1b**: 0.1 g) and sodium acetate (0.3 g) in 30 mL of methanol was stirred at room temperature for 20 min, during which there was a rapid yellowing of the solution followed by separation of deep yellow crystals. To ensure completion of the reaction the suspension was heated to reflux for 2 min and then cooled in an ice/salt bath. The bright yellow product was filtered off and washed successively with methanol, waster, methanol, ethanol and n-hexane. This afforded 0.06 g (75%) of a compound sufficiently pure for most purposes. A sample for microanalysis was obtained by recrystallization from dichloromethane/ethanol. M.p. 177–179° C (dec). Anal. Found: C, 62.61; H, 5.25. $C_{39}H_{35}O_3PRu_3$ calcd.: C, 62.81; H, 4.74%.

*$Os(\eta^2\text{-}S_2CN(CH_3)_2)(PH_2)(CO)(PPh_3)_2$ (**5**).* A mixture of $[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**1a**: 0.1 g), sodium *N,N*-dimethyl dithiocarbamate (0.15 g) and 15 mL of methanol was heated under reflux for 20 min then cooled in an ice/salt bath. The tan precipitate was filtered off and washed successively with water,

Table 8

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

Compound	^{31}P NMR data
Os(η^2-O$_1$CMe)(PH$_2$)(CO)(PPh$_3$)$_2$	−143.2(s, *P*H$_2$) [b]
(4a)	20.5(s, *P*Ph$_3$)
Os(η^2-acac)(PH$_2$)(CO)(PPh$_3$)$_2$	−154.3(s, *P*H$_2$) [b]
(6)	20.5(s, *P*Ph$_3$)
Os(η^2-O$_2$N)(PH$_2$)(CO)(PPh$_3$)$_2$	−145.9(s, *P*H$_2$) [b]
(7)	20.4(s, *P*Ph$_3$)
Os(OC[O]Me)(PH$_2$)(CO)$_2$(PPh$_3$)$_2$	−212.0(s, *P*H$_2$) [b]
(8a)	0.2(s, *P*Ph$_3$)
[Os(η^2-O$_2$CMe)(PH$_3$)(CO)(PPh$_3$)$_2$]ClO$_4$	−129.4(t, ^2J(PP) = 13.5, P*H*$_3$)
(9)	13.2(d, ^2J(PP) = 14.3, *P*Ph$_3$)
Os(OC[O]CF$_3$)$_2$(PH$_3$)(CO)(PPh$_3$)$_2$	−136.0(t, ^2J(PP) = 14.1, *P*H$_3$)
(11)	3.3(d, ^2J(PP) = 14.8, *P*Ph$_3$)
[Os(η^1-OC[O]Me)(PH$_3$)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$	−131.6(t, ^2J(PP) = 27.6, *P*H$_3$)
(13)	−4.5(d, ^2J(PP) = 25.5, *P*Ph$_3$)
[OsH(PH$_2$OMe)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$	2.6(d, ^2J(PP) = 16.1, *P*Ph$_3$)
(14)	56.1(t, ^2J(PP) = 16.2, *P*H$_2$OMe)
Os(PH$_2$OMe)(CO)$_2$(PPh$_3$)$_2$	21.6(d, ^2J(PP) = 23.8, *P*Ph$_3$) [b]
(15)	53.0(t, ^2J(PP) = 23.0, *P*H$_2$OMe)
[RuH(PH$_2$OMe)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$	37.9(d, ^2J(PP) = 24.3, *P*Ph$_3$)
(16c)	89.8(t, ^2J(PP) = 23.7, *P*H$_2$OMe)
[RuH(PH$_2$OEt)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$	38.0(d, ^2J(PP) = 23.9, *P*Ph$_3$)
(16d)	78.8(t, ^2J(PP) = 24, *P*H$_2$OEt)
[RuH(PH$_2$O^{i}Pr)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$	38.1(d, ^2J(PP) = 18, *P*Ph$_3$)
(16e)	70.8(t, ^2J(PP) = 24.1, *P*H$_2$OR)
Ru(PH$_2$OMe)(CO)$_2$(PPh$_3$)$_2$	59.2(d, ^2J(PP) = 45.5, *P*Ph$_3$) [b]
(17c)	89.7(t, ^2J(PP) = 45.4, *P*H$_2$OMe)
Os(η^1-OC[O]Me)[PH(C[O]CF$_3$)](CO)$_2$(PPh$_3$)$_2$	−68.9(dm, ^2J(PP) = 5.1, *P*HC[O]CF$_3$)
(30)	−2.1(d, ^2J(PP) = 4.8, *P*Ph$_3$)
Os(η^1-OC[O]Me)[P(C[O]CF$_3$)$_2$](CO)$_2$(PPh$_3$)$_2$	−4.4(s(br), *P*Ph$_3$)
(31)	20.0(m(br), *P*(C[O]CF$_3$)$_2$)
OsCl(PH$_2$AuI)(CO)$_2$(PPh$_3$)$_2$	−140.0(t, ^2J(PP) = 20.6, *P*H$_2$AuI)
(33a)	−14.0(d, ^2J(PP) = 20.7, *P*Ph$_3$)
OsH(PH$_2$AuI)(CO)$_2$(PPh$_3$)$_2$	−179.1(t, ^2J(PP) = 20.9, *P*H$_2$AuI)
(33b)	6.7(d, ^2J(PP) = 23.7, *P*Ph$_3$)
Os(η^2-O$_2$CMe)(PH$_2$AuI)(CO)(PPh$_3$)$_2$	−131.6(t, ^2J(PP) = 9.7, *P*H$_2$)
(34)	16.0(d, ^2J(PP) = 9.8, *P*Ph$_3$)
Os(η^2-S$_2$CNMe$_2$)(PH$_2$AuI)(CO)(PPh$_3$)$_2$	−149.7(t, ^2J(PP) = 12.3, *P*H$_2$)
(35)	4.8(d, ^2J(PP) = 11.8, *P*Ph$_3$)
Os(η^1-OC[O]Me)(PH$_2$AuI)(CO)$_2$(PPh$_3$)$_2$	−146.1(t, ^2J(PP) = 22.8, *P*H$_2$)
(36)	−2.8(d, ^2J(PP) = 22.5, *P*Ph$_3$)
OsCl(PH$_2$s)(CO)$_2$(PPh$_3$)$_2$	−42.9(t, ^2J(PP) = 25.6, *P*H$_2$S)
(37a)	−7.6(d, ^2J(PP) = 25.6, *P*Ph$_3$)
OsH(PH$_2$S)(CO)$_2$(PPh$_3$)$_2$	−54.75(t, ^2J(PP) = 29.3, *P*H$_2$S)
(37b)	9.68(d, ^2J(PP) = 29, *P*Ph$_3$)
Os(η^1-OC[O]Me)(PH$_2$S)(CO)$_2$(PPh$_3$)$_2$	−56.3(t, ^2J(PP) = 27.7, *P*H$_2$S)
(37c)	−3.5(d, ^2J(PP) = 27.7, *P*Ph$_3$)
OsCl(PH$_2$Se)(CO)$_2$(PPh$_3$)$_2$ [c]	−92.72(t, ^2J(PP) = 24.9, *P*H$_2$Se)
(38a)	−13.63(d, ^2J(PP) = 24.4, *P*Ph$_3$)
OsH(PH$_2$Se)(CO)$_2$(PPh$_3$)$_2$	−128.14(t, ^2J(PP) = 27, *P*H$_2$Se)
(38b)	6.66(d, ^2J(PP) = 27, *P*Ph$_3$)
Os(η^1-OC[O]Me)(PH$_2$Se)(CO)$_2$(PPh$_3$)$_2$ [c]	−99.9(t, ^2J(PP) = 26.7, *P*H$_2$Se)
(38c)	−3.7(d, ^2J(PP) = 26.8, *P*Ph$_3$)

Table 8 (continued)

Compound	^{31}P NMR data
$[OsCl(PH_2SMe)(CO)_2(PPh_3)_2]ClO_4$ **(39a)**	-35.94(t, ^2J(PP) = 23.4, PH$_2$SMe) -14.41(d, ^2J(PP) = 23.8, PPh$_3$)
$[OsH(PH_2SMe)(CO)_2(PPh_3)_2]ClO_4$ **(39b)**	-46.38(t, ^2J(PP) = 27.2, PH$_2$SMe) 2.70(d, ^2J(PP) = 26.0, PPh$_3$)
$OsCl(PHSMe)(CO)_2(PPh_3)_2$ **(40)**	-59.72(s, PHSMe) -11.58(s, PPh$_3$)
$OsCl[P(C[O]CF_3)SMe](CO)_2(PPh_3)_2$ **(41)**	-10.7(m, PPh$_3$) 25.3(dm, ^2J(PP) = 14.2, PSMe)
$[OsCl(PHMeSMe)(CO)_2(PPh_3)_2]ClO_4$ **(42)** **(42)**	-22.01(dd, ^2J(PP) = 22.9, PHCH$_3$(SCH$_3$)) -16.63(d, ^2J(PP) = 23.2, PPh$_3$) -16.23(d, ^2J(PP) = 24.3, PPh$_3$)

[a] As chloroform solutions at 21°C. Proton chemical shifts (δ) are given in ppm with respect to tetramethylsilane and for phosphorus, shifts are given in ppm with respect to external 85% H_3PO_4 and ^{77}Se chemical shifts are with respect to dimethylselenide. [b] Spectrum measured in C_6D_6. [c] ^{77}Se NMR results for **38a**: -364(d, ^1J(PSe) = 517); for **38b**: -412.9(d, ^1J(PSe) = 529.5).

methanol, ethanol and n-hexane to give 0.081 g (85%) of the product, m.p. 178–179°C. For most uses this sample was sufficiently pure but a sample for microanalysis was obtained by recrystallization from dichloromethane/ethanol. Anal. Found: C, 53.56; H, 4.73; N, 1.74. $C_{40}H_{38}NOOsP_3S_2$ calcd.: C, 53.61; H, 4.28; N, 1.56%.

$Os(acac)(PH_2)(CO)(PPh_3)_2$ (6). A mixture of $[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**1a**: 0.1 g), acetylacetone (1 mL), DBU (0.1 mL) and methanol (10 mL) was stirred at room temperature for 48 h to give a bright yellow precipitate. This was filtered off and washed with methanol, ethanol and n-hexane to give 0.09 g (97%) of fine needles. The product can be purified by recrystallization under nitrogen from dichloromethane/ethanol. It was characterized spectroscopically.

$Os(\eta^2\text{-}O_2N)(PH_2)(CO)(PPh_3)_2$ (7). $[OsCl(PH_3)(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (**1a**: 0.12 g), and sodium nitrite (0.3 g) were dissolved in methanol (20 mL) at room temperature. A yellow colour formed briefly but faded rapidly to give an off white precipitate. After 2 h DBU (0.2 mL) was added and the suspension stirred for a further 1 h. The resulting yellow suspension was cooled in an ice/salt bath and then filtered, and the solid washed with water, methanol, ethanol and n-hexane to give 0.09 g (86%) of the product. An analytically pure sample was obtained by recrystallization from dichloromethane/ethanol. M.p. 165–167°C, as bright yellow needles. Anal. Found: C, 53.75; H, 4.37; N, 1.46. $C_{37}H_{32}NO_3OsP_3$ calcd.: C, 54.07; H, 3.93; N, 1.70%.

*$Os(\eta^1\text{-}OC[O]CH_3)(PH_2)(CO)_2(PPh_3)_2$ (**8a**).* A solution of $Os(\eta^2\text{-}O_2CCH_3)(PH_2)(CO)(PPh_3)_2$ (**4a**: 0.1 g) in 5 mL of deoxygenated dichloromethane was exposed to carbon monoxide at 50 psi for 20 min at room temperature, during which the yellow solution gradually became a very pale yellow. Ethanol (10 mL) was added, and concentration in vacuo afforded a colourless product, 0.1 g (95%). This was sufficiently pure for subsequent reactions, but for microanalysis a sample was recrystallized from dichloromethane/ethanol as colourless cubes, m.p. 177–179°C. Anal. Found: C, 55.44; H, 4.71. $C_{40}H_{35}O_4OsP_3$ calcd.: C, 55.68; H, 4.10%.

*$Ru(\eta^1\text{-}OC[O]CH_3)(PH_2)(CO)_2(PPh_3)_2$ (**8b**).* $Ru(\eta^2\text{-}O_2CCH_3)(PH_2)(CO)$-

$(PPh_3)_2$ (**4b**: 0.2 g) was introduced into a Fischer-Porter bottle which contained 10 mL dichloromethane which had been saturated with carbon monoxide. This mixture was immediately repressurized with carbon monoxide to 60 psi and the pressure was maintained for 15 min. To the resulting foul-smelling pale yellow solution was added 20 mL of ethanol, and the product was recrystallized rapidly to give 0.17 g (82%) of yellow needles, m.p. 132–135°C (dec). Anal. Found: C, 61.59; H, 4.96. $C_{40}H_{35}O_4P_3Ru$ calcd.: C, 62.09; H, 4.57%.

$[Os(\eta^2\text{-}O_2CCH_3)(PH_3)(CO)(PPh_3)_2]ClO_4$ (9). A solution of $Os(\eta^2\text{-}O_2CCH_3)(PH_2)(CO)(PPh_3)_2$ (**4a**: 0.1 g) in a mixture of 5 mL of dichloromethane and 5 mL of ethanol was treated with 0.1 mL of aqueous perchloric acid. The yellow colour disappeared immediately. Concentration of the colourless solution, with addition of 10 mL of isopropanol once crystallization had set in, gave colourless needles, 0.11 g (98%). M.p. 169–171°C. Anal. Found: C, 48.05; H, 4.38. $C_{39}H_{36}ClO_7OsP_3$ calcd.: C, 48.52; H, 3.82%. The reverse reaction was accomplished by addition of DBU to dichloromethane/ethanol solutions of **9**, followed by concentration in vacuo.

$OsCl_2(PH_3)(CO)(PPh_3)_2$ (10). A solution of $Os(\eta^2\text{-}O_2CCH_3)(PH_2)(CO)(PPh_3)_2$ (**4a**: 0.05 g) in 10 mL of dichloromethane and treated with 0.05 mL of concentrated hydrochloric acid. Addition of 10 mL of ethanol led to immediate loss of colour and after concentration of the solution in vacuo, colourless crystals of **10** (0.03 g) were obtained. The product was identified by infrared spectroscopy [12].

$Os(OC[O]CF3)_2(PH_3)(CO)(PPh_3)_2$ (11) and $Os(OC[O]H)_2(PH_3)(CO)(PPh_3)_2$ (12). A solution of $Os(\eta^2\text{-}O_2CCH_3)(PH_2)(CO)(PPh_3)_2$ (**4a**: 0.11 g) in 10 mL of dichloromethane was treated with 0.5 mL of trifluoroacetic acid and the resulting colourless solution was stirred for 30 min. Ethanol (20 mL) was added and concentration of the solution in vacuo gave the colourless product (0.11 g (85%)) as flakes, m.p. 191–194°C. Anal. Found: C, 49.71; H, 3.83. $C_{41}H_{33}F_6O_5OsP_3$ calcd.: C, 49.10; H, 3.32%. The bis(formato) complex (**12**) was prepared in the same manner in 70% yield from **4a** and formic acid. Characteristic spectroscopic data are included in Tables 6, 7 and 8.

$[Os(\eta^1\text{-}OC[O]CH_3)(PH_3)(CO)_2(PPh_3)_2]ClO_4$ (13). A solution of $Os(\eta^1\text{-}OC[O]CH_3)(PH_2)(CO)_2(PPh_3)_2$ (**8a**: 0.1 g) in 10 mL of dichloromethane was treated with a drop (ca. 0.05 mL) of aqueous perchloric acid and 10 mL ethanol was added to produce a homogeneous solution. Concentration, and addition of 10 mL of isopropanol after crystallization had set in, afforded 0.09 g (85%) of colourless clusters, m.p. 150–151°C. Anal. Found: C, 50.13; H, 4.64. $C_{40}H_{36}ClO_6OsP_3$ calcd.: C, 49.87; H, 3.77%.

$[OsH(PH_2OMe)(CO)_2(PPh_3)_2]ClO_4$ (14). A solution of $Os(\eta^1\text{-}OC[O]CH_3)(PH_2)(CO)_2(PPh_3)_2$ (**8a**: 0.1 g) in 10 mL dichloromethane was treated with a 20 mL of a methanol solution of 0.2 mL of aqueous perchloric acid. The solution, which remained colourless throughout, was concentrated below 10 mL total volume, 20 mL ethanol was added, and the volume of solvent reduced until crystallization commenced. Isopropanol (10 mL) was then added and the solvent volume again reduced. The solid was filtered off and washed with ethanol, isopropanol, and n-hexane to afforded 0.11 g (100%) of large colourless prisms, m.p. 189–190°C. Anal. Found: C, 49.67; H, 4.49. $C_{39}H_{36}ClO_7OsP_3$ calcd.: C, 50.08; H, 3.89%.

$Os(PH_2OMe)(CO)_2(PPh_3)_2$ (15). An excess of DBU was added to a vigorously stirred suspension of $[OsH(PH_2OMe)(CO)_2(PPh_3)_2]ClO_4$ (**14**: 0.08 g) in 10 mL of dry deoxygenated methanol under nitrogen. A light yellow solution rapidly formed

upon dissolution of the colourless cation, and within 5 min large light yellow crystals separated. The suspension was stirred for a further 1 h at room temperature and then cooled in an ice/salt and filtered. The bright yellow crystals (0.05 g (71%)) were washed successively with methanol, ethanol and n-hexane, m.p. 155–156 °C (dec), yellow plates. Anal. Found: C, 56.10; H, 4.23. $C_{39}H_{35}O_3OsP_3$ calcd.: C, 55.72; H, 4.69%. Treatment of this product with aqueous perchloric acid in dichloromethane/ethanol rapidly regenerated **14**.

$[RuH(PH_2OR)(CO_2)(PPh_3)_2]ClO_4$ (16c,d,e; c, R = Me; d, R = Et; e, R = ^{i}Pr). A solution of $Ru(\eta^1\text{-}OC[O]CH_3)(PH_2)(CO)_2(PPh_3)_2$ (**8b**) in 10 mL of dichloromethane was treated with a solution of the appropriate alcohol and an excess of aqueous perchloric acid (typically 0.5 mL). After addition of 10 mL of ethanol and 10 mL of isopropanol the mixture was concentrated in vacuo.

$[RuH(PH_2OMe)(CO)_2(PPh_3)_2]ClO_4$ (**16c**) was prepared in 92% yield from 0.1 g of **8b** and methanolic perchloric acid, m.p. 167–169 °C, as flat colourless prisms. Anal. Found: C, 55.54; H, 4.98. $C_{39}H_{36}ClO_7P_3Ru$ calcd.: C, 55.35; H, 4.30%.

$[RuH(PH_2OEt)(CO)_2(PPh_3)_2]ClO_4$ (**16d**) was prepared in 96% yield from 0.32 g **8b** and aqueous perchloric acid in ethanol, m.p. 167 °C as clusters of colourless needles. Anal. Found: C, 55.64; H, 4.95. $C_{40}H_{38}ClO_7P_3Ru$ calcd.: C, 55.85; H, 4.46%.

$[RuH(PH_2O^iPr)(CO)_2(PPh_3)_2]ClO_4$ (**16e**) was prepared in 69% yield from 0.23 g **8b** and aqueous perchloric acid in 10 mL isopropanol, m.p. 157–159 °C, as colourless rods. Anal. Found: C, 56.54; H, 4.63. $C_{41}H_{40}ClO_7P_3Ru$ calcd.: C, 56.32; H, 4.62%.

$Ru(PH_2OMe)(CO)_2(PPh_3)_2$ (17c). (a) From $[RuH(PH_2OMe)(CO)_2(PPh_3)_2]ClO_4$ (**16c**): A solution of $[RuH(PH_2OMe)(CO)_2(PPh_3)_2]ClO_4$ (**16c**: 0.21 g) in 10 mL of oxygen-free methanol was treated with 0.2 mL DBU, whereupon the colourless salt rapidly dissolved and a yellow solution was formed and the product crystallized out rapidly. After 1 h at room temperature the product was filtered off and washed with methanol, ethanol and n-hexane to give 0.14 g (78%) of bright yellow needles, m.p. 122–128 °C. Anal. Found: C, 62.12; H, 5.01. $C_{39}H_{35}O_3P_3Ru$ calcd.: C, 62.81; H, 4.74%.

(b) From $[RuH(PH_2OEt)(CO)_2(PPh_3)_2]ClO_4$ (**16d**): To a suspension of $[RuH(PH_2OEt)(CO)_2(PPh_3)_2]ClO_4$ (**16d**: 0.28 g) in 25 mL of oxygen-free methanol was added an excess of DBU. After 90 min the deep yellow suspension was cooled in an ice/salt bath then filtered to give 0.18 g (74%), bright yellow needles of m.p. 122–128 °C.

$Ru(PH_2OEt)(CO)_2(PPh_3)_2)$ (17d). A suspension of $[RuH(PH_2OEt)(CO)_2(PPh_3)_2]ClO_4$ (**16d**: 0.17 g) in 10 mL of oxygen-free ethanol was treated with 0.1 mL of DBU. The starting material dissolved to give a bright yellow solution from which large yellow crystals separated. After 1 h the suspension was cooled in an ice/salt bath and then filtered to give 0.12 g (76%) of yellow prisms, m.p. 148–150 °C. Anal. Found: C, 63.20; H, 4.90. $C_{40}H_{37}O_3P_3Ru$ calcd.: C, 63.23; H, 4.92%.

$[OsCl(PH_2CH_3)(CO)_2(PPh_3)_2]ClO_4$ (18). A suspension of $OsCl(PH_2)(CO)_2(PPh_3)_2$ (**2a**: 0.45 g) in 20 mL of dry THF under nitrogen in a Schlenk tube was treated with an excess of methyl iodide (0.2 mL). During 10 min a clear colourless solution was formed as the starting material dissolved. After 15 min the solvents were removed under high vacuum to leave a colourless oil, which was redissolved in about 10 mL of dichloromethane. An ethanol solution (20 mL) of 0.05 g of sodium

perchlorate was added and the solution concentrated until crystallization began, whereupon 20 mL of isopropanol was added. The product was filtered off and washed with isopropanol and then n-hexane to give 0.51 g (100%) of colourless cubes, m.p. 187 °C (dec). Anal. Found: C, 49.41; H, 4.68. $C_{39}H_{35}Cl_2O_6OsP_3$ calcd.: C, 49.11; H, 3.71%.

$[OsH(PH_2CH_3)(CO)_2(PPh_3)_2]ClO_4$ (19). A mixture of $OsH(PH_2)(CO)_2(PPh_3)_2$ (**3**: 0.14 g), a two-fold excess of methyl iodide (0.34 mmol, 0.049 g, 0.021 mL) and 10 mL of dichloromethane was stirred at room temperature for 20 min. The solvent was then removed in vacuo, ca. 0.02 g of lithium perchlorate was added, and the mixture dissolved in a mixture of 10 mL each of dichloromethane, ethanol, and isopropanol. Concentration in vacuo gave 0.11 g (70%) of colourless needles, m.p. 186 °C. Anal. Found: C, 50.59; H, 4.34. $C_{39}H_{36}ClO_6OsP_3$ calcd.: C, 50.95; H, 3.96%.

$[OsCl(PH_2CH_2Ph)(CO)_2(PPh_3)_2]ClO_4$ (20). A suspension of $OsCl(PH_2)(CO)_2(PPh_3)_2$ (**2a**: 0.1 g) in 10 mL of THF was treated with 0.1 mL of benzyl bromide. The mixture was heated under reflux for 0.5 h until a clear solution was formed, then cooled, and the volatile components were removed in vacuo. The residue was worked up as for **18** to give 0.11 g (90%) of colourless crystals of **20**. Anal. (as 1 : 1 dichloromethane solvate as confirmed by ^1H NMR) Found: C, 49.45; H, 4.19. $C_{45}H_{39}Cl_2O_6OsP_3 \cdot CH_2Cl_2$ calcd.: C, 49.56; H, 3.71%.

$[Os[\eta^2\text{-}S_2CN(CH_3)_2](PH_2CH_3)(CO)(PPh_3)_2]ClO_4$ (21). A solution of $Os[\eta^2\text{-}S_2CN(CH_3)_2](PH_2)(CO)(PPh_3)_2$ (**5**: 0.1 g) in 10 mL of dichloromethane was treated with 0.1 mL of methyl iodide. This mixture was stirred at room temperature for 1 h and the solvent then removed from the colourless solution. The residue was treated with lithium perchlorate (0.01 g) and the mixture dissolved in a mixture of equal volumes of dichloromethane, ethanol, and isopropanol. Crystallization was induced by concentration in vacuo to give 0.08 g (71%) of colourless needles, m.p. 167–168 °C. Anal. Found: C, 48.51; H, 5.58; N, 1.48. $C_{41}H_{41}ClNO_5OsP_3S_2$ calcd.: C, 48.73; H, 4.10; N, 1.39%.

$OsI(\eta^1\text{-}OC[O]CH_3)(PH_2CH_3)(CO)(PPh_3)_2$ (22). A mixture of $Os(\eta^2\text{-}O_2CCH_3)(PH_2)(CO)(PPh_3)_2$ (**4a**: 0.1 g), 0.2 mL of methyl iodide, and 5 mL of THF was stirred for 5 min, and the resulting colourless solution then concentrated in vacuo to leave a gum, which was crystallized from dichloromethane/ethanol to give colourless needles, 0.09 g (77%). Characteristic spectroscopic data for this complex are listed in Tables 6, 7 and 8.

$OsCl(PHCH_3)(CO)_2(PPh_3)_2$ (23). To a suspension of $[OsCl(PH_2CH_3)(CO)_2(PPh_3)_2]ClO_4$ (**18**: 0.1 g) in 10 mL of benzene was added 0.05 mL of DBU. The colourless starting material dissolved instantly to give a slight yellow solution and a muddy oil. After 30 min the solution was concentrated to < 2 mL and 40 mL of n-hexane was added to give a bulky pale yellow precipitate, which was filtered off and washed with ethanol, methanol, ethanol and n-hexane. The yield was 0.076 g (85%) of a product sufficiently pure for most uses. An analytically pure sample was obtained by recrystallization from benzene/n-hexane. M.p. 128 °C. Anal. (as 1/4 benzene solvate as confirmed by ^1H NMR) Found: C, 55.81; H, 4.60. $C_{39}H_{34}ClO_2OsP_3 \cdot \frac{1}{4}C_6H_6$ calcd.: C, 55.73; H, 4.11%.

$OsCl(PHCH_2Ph)(CO)_2(PPh_3)_2$ (24). A suspension of $[OsCl(PH_2CH_2Ph)(CO)_2(PPh_3)_2]ClO_4$ (**20**: 0.3 g) in 10 mL of benzene was treated drop-wise with 0.07 mL of DBU. The colourless starting material gradually dissolved and a yellow solution

and a little oil were formed. After 5 min some of the solvent was evaporated and 30 mL of n-hexane rapidly added to give a fine precipitate, which was filtered off and wash thoroughly with methanol to give 0.11 g, (41%), of a light yellow solid. Characteristic spectroscopic data for this complex are listed in Tables 6, 7 and 8.

$[OsCl(PH_2CMe_3)(CO)_2(PPh_3)_2]ClO_4$ (25). The preparation of this cation was identical in respect of the reagents and the conditions used to that of the closely related phenylphosphine complex $[OsCl(PH_2Ph)(CO)_2(PPh_3)_2]ClO_4$ described previously [65]. It was prepared in three steps from $OsHCl(CO)(PPh_3)_3$ and t-butylphosphine in an overall yield of 73%. This product was recrystallized after the carbonylation from dichloromethane/ethanol/isopropanol, as a flocculent powder, m.p. 151–154 °C. Anal. Found: C, 50.68; H, 4.53. $C_{42}H_{41}Cl_2O_6OsP_3$ calcd.: C, 50.65; H, 4.16%.

$Os[PH(OMe)Me](CO)_2(PPh_3)_2$ (26). A suspension of $[OsCl(PH_2Me)(CO)_2$-$(PPh_3)_2]ClO_4$ (**18**: 0.35 g) in 20 mL of rigorously degassed methanol was heated almost to reflux. An excess of DBU (0.2 mL) was then added, upon which the remaining undissolved starting material went into solution, and the solution rapidly became a bright yellow. After crystals of the product appeared (within the first minute) the heating was discontinued and the mixture cooled in an ice-salt bath to complete the crystallization. The product was then filtered off and washed with methanol, ethanol and n-hexane to give 0.25 g (80%) of bright yellow prisms, m.p. 158 °C. This product was sufficiently pure for most purposes, but it can be recrystallized with difficulty from absolutely oxygen-free benzene/ethanol, as was done for the analytical sample. Anal. (as 1/2 benzene solvate as confirmed by ^1H NMR) Found: C, 58.00; H, 5.26. $C_{40}H_{37}O_3OsP_3 \cdot \frac{1}{2}C_6H_6$ calcd.: C, 58.16; H, 4.55%.

$Os[PH(OMe)(CMe_3)](CO)_2(PPh_3)_2$ (27). A suspension of $[OsCl(PH_2CMe_3)$-$(CO)_2(PPh_3)_2]ClO_4$ (**25**: 0.15 g) in oxygen-free methanol was heated under reflux and treated with an excess of DBU (0.05 mL), upon which the white starting material immediately dissolved to give a bright yellow solution. After 2 min the heating was discontinued and the mixture cooled in an ice-salt bath to complete the crystallization of the bright yellow product, which was filtered off and washed with methanol, ethanol, and n-hexane to give 0.11 g (82%) of yellow prisms, m.p. 156–166 °C. This product was sufficiently pure for the reactions described below, but an analytically pure sample was obtained by recrystallization from benzene/ethanol under nitrogen. Anal. Found: C, 58.95; H, 5.23. $C_{43}H_{41}O_3OsP_3$ calcd.: C, 58.09; H, 4.66%.

$[OsH[PH(OMe)(CMe_3)](CO)_2(PPh_3)_2]ClO_4$ (28). A benzene solution of Os-$[PH(OMe)(CMe_3)](CO)_2(PPh_3)_2$ (**27**: 0.2 g) was treated with a solution of 0.1 mL aqueous perchloric acid in 10 mL of isopropanol, whereupon the colour immediately disappeared. Ethanol (10 mL) was added and the solution concentrated to < 5 mL to afford 0.22 g (99%) of colourless rhombohedrons, m.p. 188–194 °C. Anal. Found: C, 52.31; H, 4.87. $C_{43}H_{44}ClO_7OsP_3$ calcd.: C, 52.09; H, 4.48%.

$Os(\eta^1$-$OC[O]CH_3)(PH[C(O)CMe_3])(CO)_2(PPh_3)_2$ (29). A solution of $Os(\eta^1$-$OC[O]CH_3)(PH_2)(CO)_2(PPh_3)_2$ (**8a**: 0.07 g) in 10 mL of THF under nitrogen was treated with 0.0098 g (0.01 mL) of pivaloyl chloride. There was no perceptible change in the colour of the mixture. The solvent volume was reduced to about 1 mL and then 50 mL of n-hexane was added to precipitate the product (0.06 g (77%)), which was filtered off. The product can be purified by recrystallization from

dichloromethane/ethanol. Characteristic spectroscopic data for the complex are listed in Tables 6, 7 and 8.

$Os(\eta^1\text{-}OC[O]CH_3)(PH[C(O)CF_3])(CO)_2(PPh_3)_2$ *(30)*. A solution of $\mathrm{Os(\eta^1\text{-}OC[O]CH_3)(PH_2)(CO)_2(PPh_3)_2}$ (**8a**: 0.1 g) in 5 mL of THF under nitrogen was treated with 0.027 g (0.022 mL, 1.1 equivalents) of trifluoroacetic anhydride and the resulting yellow solution was stirred for 2 min. Volatile materials were then removed in vacuo. Recrystallization of the residue afforded 0.1 g (90%) of light yellow cubes, m.p. 176–175 °C. Anal. Found: C, 52.04; H, 4.05. $\mathrm{C_{42}H_{34}F_3O_3OsP_3}$ calcd.: C, 52.61; H, 3.58%.

$Os(\eta^1\text{-}OC[O]CH_3)[P(C[O]CF_3)_2](CO)_2(PPh_3)_2$ *(31)*. A solution of $\mathrm{Os(\eta^1\text{-}OC[O]CH_3)(PH_2)(CO)_2(PPh_3)_2}$ (**8a**: 0.1 g) in 10 mL of THF was treated with 0.2 mL of trifluoroacetic anhydride, whereupon the solution immediately turned deep yellow. After 5 min the solvents were removed in vacuo and the residue was recrystallized from dichloromethane/ethanol to give 0.1 g (82%) yellow prisms, m.p. 100 °C (dec). Anal. Found: C, 50.72; H, 3.93. $\mathrm{C_{44}H_{35}F_6O_6OsP}$ calcd.: C, 50.00; H, 4.34%. This compound can also be prepared by treating **30** with an excess of trifluoroacetic anhydride. The isolation procedure is the same as that for **30**.

Reaction of $Os(\eta^1\text{-}OC[O]CH_3)(PH[C(O)CF_3])(CO)_2(PPh_3)_2$ *(30) with sodium hydride.* A suspension in 10 mL of dry THF of $\mathrm{Os(\eta^1\text{-}OC[O]CH_3)(PH[C(O)CF_3])(CO)_2(PPh_3)_2}$ (**30**: 0.11 g) and 0.017 g of sodium hydride as a 45% dispersion in paraffin was stirred at room temperature for 1 h and the unchanged hydride then removed by filtration of the bright yellow solution through Celite. The THF was removed in vacuo and the residue recrystallized from dichloromethane/ethanol to give 0.07 g (81%) of the phosphaalkene complex $\mathrm{\overline{Os(P{=}C[O]}CF_3)(CO)_2(PPh_3)_2}$ as identified by infrared spectroscopy [11,33].

$OsCl(PH_2[Fe(CO)_4])(CO)_2(PPh_3)_2$ *(32a)*. A mixture of $\mathrm{OsCl(PH_2)(CO)_2(PPh_3)_2}$ (**2a**: 0.07 g, 0.08 mmol), 0.036 g of freshly prepared [66] $\mathrm{Fe_2(CO)_9}$ (0.1 mmol, 1.2 equivalents) in 10 mL of THF was stirred under nitrogen. Within 3 min a clear colourless solution had formed and the solids dissolved. Within 10 min a slight brown colour was formed. After 20 min the solvent and the iron pentacarbonyl by-product were removed in vacuo, and the orange/brown residue was recrystallized from dichloromethane/ethanol to give 0.06 g (74%) of yellow prisms, m.p. 184–186 °C (dec). Anal. Found: C, 49.72; H, 3.85. $\mathrm{C_{42}H_{32}ClFeO_6OsP_3}$ calcd.: C, 50.08; H, 3.21%.

$OsH(PH_2[Fe(CO)_4])(CO)_2(PPh_3)_2$ *(32b)*. A suspension of $\mathrm{OsH(PH_2)(CO)_2(PPh_3)_2}$ (**3**: 0.05 g, 0.06 mmol), 0.025 g of freshly prepared $\mathrm{Fe_2(CO)_9}$ (0.068 mmol, 1.1 equivalents) in 10 mL of THF was stirred. The solids rapidly dissolved to give an orange solution, which was stirred for a further 90 min. The volatile materials were then removed in vacuo and the orange residue kept under dynamic vacuum for an additional 30 min and then recrystallized from dichloromethane/ethanol to give 0.04 g (66%) of light yellow plates. Anal. Found: C, 51.60; H, 3.82. $\mathrm{C_{42}H_{33}FeO_6OsP_3}$ calcd.: C, 51.86; H, 3.43%.

$OsCl(PHPh[Fe(CO)_4])(CO)_2(PPh_3)_2$. $\mathrm{OsCl(PHPh)(CO)_2(PPh_3)_2}$ (0.078 g, 0.085 mmol) and 0.031 g of freshly prepared $\mathrm{Fe_2(CO)_9}$ (0.085 mmol) were added to 10 mL of dry oxygen-free THF. The solids dissolved within 30 sec to give an orange solution, which was stirred for a further 30 min. The volatile components were removed under vacuum to leave an orange oil, which was recrystallized form dichloromethane ethanol to give 0.08 g (87%) of bright yellow hexagonal plates, m.p.

149–154 °C (with gas evolution). Anal. Found: C, 53.54; H, 3.83. $C_{48}H_{36}ClFeO_6OsP_3$ calcd.: C, 53.22; H, 3.36%.

OsCl(PH$_2$AuI)(CO)$_2$(PPh$_3$)$_2$ (33a). A solution of $OsCl(PH_2)(CO)_2(PPh_3)_2$ (**2a**: 0.05 g) and 0.041 g of $[N(^nBu)_4][AuI_2]$ [67] in 10 mL of dichloromethane was stirred for 2 h in the open at room temperature. Ethanol (20 mL) was then added to the colourless solution and the mixture concentrated in vacuo to give 0.07 g (100%) of colourless needles, m.p. 152–156 °C. Anal. (as 1/2 dichloromethane solvate, as confirmed by ^1H NMR) Found: C, 38.38; H, 3.40. $C_{38}H_{32}AuClIO_2OsP_3 \cdot \frac{1}{2}CH_2Cl_2$ calcd.: C, 38.35; H, 2.76%.

OsH(PH$_2$AuI)(CO)$_2$(PPh$_3$)$_2$ (33b). $OsH(PH_2)(CO)_2(PPh_3)_2$ (**3**: 0.071 g, 0.088 mmol) and 0.067 h (0.097 mmol) of $[N(^nBu)_4][AuI_2]$ were treated as described for **33a** to give 0.1 g (100%) of colourless cubes, m.p. 219 °C (dec) of **33b**. Anal. Found: C, 40.06; H, 3.65. $C_{38}H_{33}AuIO_2OsP_3$ calcd.: C, 40.43; H, 2.95%.

Os(η^2-O$_2$CCH$_3$)(PH$_2$AuI)(CO)(PPh$_3$)$_2$ (34). $Os(\eta^2\text{-}O_2CCH_3)(PH_2)(CO)(PPh_3)_2$ (**4a**: 0.05 g) and 0.042 g of tetra(n-butyl)ammonium gold(I)diiodide were dissolved in 10 mL of dichloromethane to give immediately a very pale yellow solution. After 10 min, 10 mL of ethanol was added, and the solution was concentrated in vacuo to give large pale yellow prisms, 0.08 g (100%), m.p. 182–185 °C (with decomposition to colloidal gold). Anal. Found: C, 37.76; H, 3.37. $C_{39}H_{35}AuIO_3OsP_3$ calcd.: C, 37.35; H, 2.91%. Crystals suitable for X-ray diffraction were grown from dichloromethane/ethanol.

Os[η^2-S$_2$CN(CH$_3$)$_2$](PH$_2$AuI)(CO)(PPh$_3$)$_2$ (35). A solution of $Os[\eta^2\text{-}S_2CN(CH_3)_2](PH_2)(CO)(PPh_3)_2$ (**5**: 0.02 g) and 0.026 g (0.038 mmol, 1.7 equivalents) of tetra(n-butyl)ammonium gold(I)diiodide in 20 mL of dichloromethane was stirred for 30 min and to the slightly yellow solution was added 20 mL of ethanol. The solution was concentrated to give 0.03 g (100%) of light tan crystals. Characteristic spectroscopic data for this complex are included in Tables 6, 7 and 8.

Os(η^1-OC[O]CH$_3$)(PH$_2$AuI)(CO)$_2$(PPh$_3$)$_2$ (36). A mixture of $Os(\eta^1\text{-}OC[O]CH_3)(PH_2)(CO)_2(PPh_3)_2$ (**8a**: 0.06 g, 0.069 mmol), 0.053 g (0.076 mmol, 1.1 equivalents) of tetra(n-butyl)ammonium gold(I)diiodide, and 10 mL dichloromethane was stirred for 10 min. Work-up as for **34** and **35** gave colourless cubes, 0.08 g (100%), m.p. 140 °C (dec). Anal. Found: C, 40.97; H, 3.73. $C_{40}H_{35}AuIO_4OsP_3$ calcd.: C, 40.48; H, 2.98%.

OsCl(PH$_2$S)(CO)$_2$(PPh$_3$)$_2$ (37a). A mixture of $OsCl(PH_2)(CO)_2(PPh_3)_2$ (**2a**: 0.30 g), 1.15 equivalents of sulphur (0.012 g) and 40 mL of oxygen-free benzene was vigorously stirred under nitrogen for 16 h, during which most of the solids dissolved. Remaining insoluble materials were removed by filtration through a Celite pad (which was washed thoroughly with dichloromethane afterwards), and the solution was then concentrated in vacuo to leave a viscous oil, which was recrystallized from dichloromethane/ethanol to give 0.27 g (86%) of a pale yellow solid, m.p. 168 °C. Anal. (as 1/2 dichloromethane solvate as confirmed by ^1H NMR) Found: C, 50.92; H, 4.58. $C_{38}H_{32}ClO_2OsP_3 \cdot \frac{1}{2}CH_2Cl_2$ calcd.: C, 50.60; H, 3.65%.

OsH(PH$_2$S)(CO)$_2$(PPh$_3$)$_2$ (37b). A mixture of $OsH(PH_2)(CO)_2(PPh_3)_2$ (**3**: 0.072 g), 1.15 equivalents of sulphur (0.033 g) and 10 mL of oxygen-free benzene was stirred for 4 h at room temperature, during which the solution became very slightly yellow. This smelly mixture was then stripped of solvent and the gummy residue recrystallized from dichloromethane/ethanol to give 0.06 g (80%) of colourless plates, m.p. 164–166 °C. Anal. Found: C, 54.59; H, 4.83. $C_{38}H_{33}O_2OsP_3S$ calcd.: C, 54.53; H, 3.98%.

$Os(\eta^1\text{-}OC[O]CH_3)(PH_2S)(CO)_2(PPh_3)_2$ (37c). A solution of $Os(\eta^1\text{-}OC[O]CH_3)(PH_2)(CO)_2(PPh_3)_2$ (**8a**: 0.28 g, 0.32 mmol), and 0.011 g (0.35 mmol, 1.1 equivalents) of sulphur in 20 mL of benzene was stirred for 5 h at room temperature. The resulting smelly pale yellow solution was stripped of benzene and the gummy tar recrystallized from dichloromethane/ethanol to give 0.28 g (98%) of colourless rhombohedrons, m.p. 153–154°C. Anal. Found: C, 53.45; H, 4.65. $C_{40}H_{35}O_4OsP_3S$ calcd.: C, 53.68; H, 3.95%.

$OsCl(P[S]HPh)(CO)_2(PPh_3)_2$. A mixture of $OsCl(PHPh)(CO)_2(PPh_3)_2$ (0.15 g), one equivalent of sulphur (0.0053 g) and 10 mL of oxygen-free benzene was stirred for 11 h to give a colourless solution, which was then concentrated to < 2 mL and 50 mL of n-hexane was added rapidly to give a flocculent precipitate. This very air sensitive material was filtered off and recrystallized from dichloromethane/n-hexane under nitrogen to give 0.11 g (71%) of colourless crystals, m.p. 122–125°C. Anal. Found: C, 55.95; H, 4.36. $C_{44}H_{36}ClO_2OsP_3S$ calcd.: C, 55.78; H, 3.84%.

$OsCl(PH_2Se)(CO)_2(PPh_3)_2$ (38a). A mixture of $OsCl(PH_2)(CO)_2(PPh_3)_2$ (**2a**: 0.079 g, 0.095 mmol), 1.2 equivalents of finely ground selenium powder (0.0089 g) and 30 mL of oxygen-free benzene was vigorously stirred for 16 h to give a pale yellow solution and a small amount of unchanged selenium. The selenium was filtered of on a Celite pad which was then thoroughly washed with dichloromethane. The solvents were removed from the filtrate in vacuo and the smelly residue recrystallized from dichloromethane/ethanol to give 0.07 g (80%) of pale yellow rods, m.p. 153–156°C (dec). Anal. Found: C, 49.94; H, 4.36. $C_{38}H_{32}ClO_2OsP_3Se$ calcd.: C, 49.70; H, 3.52%.

$OsH(PH_2Se)(CO)_2(PPh_3)_2$ (38b). A mixture of $OsH(PH_2)(CO)_2(PPh_3)_2$ (**3**: 0.807 g), 1.1 equivalents of finely ground selenium, (0.087 g, 0.11 mmol) in oxygen-free benzene was stirred for 6 h under nitrogen. The resulting slightly yellow solution was stripped of benzene and the residue recrystallized from dichloromethane/ethanol to give 0.086 g (97%) of the product, which was purified by column chromatography (silica, 5 cm, eluted with 1/1 dichloromethane/acetone) and recrystallized from dichloromethane/ethanol to give 0.05 g (57%) of cream coloured crystals, m.p. 153–156°C. Anal. (as 1/4 dichloromethane solvate as confirmed by ^1H NMR) Found: C, 50.65; H, 4.82. $C_{38}H_{33}O_2OsP_3Se \cdot \frac{1}{4}CH_2Cl_2$ calcd.: C, 50.76; H, 3.74%.

$Os(\eta^1\text{-}OC[O]CH_3)(PH_2Se)(CO)_2(PPh_3)_2$ (38c). A mixture of $Os(\eta^1\text{-}OC[O]CH_3)(PH_2)(CO)_2(PPh_3)_2$ (**8a**: 0.23 g, 0.27 mmol), selenium (0.025 g, 0.32 mmol, 1.2 equivalents) and 50 mL of benzene was stirred vigorously for 12 h at room temperature. The pale yellow solution was filtered through Celite and the Celite pad washed at least three times with dichloromethane to ensure that all soluble products were recovered. The components were then removed from the filtrate in vacuo and the resulting sludge was crystallized from dichloromethane/ethanol to give 0.235 g, (92%) of a product that was sufficiently pure for most purposes. A sample for microanalysis was obtained by two recrystallizations from dichloromethane/ethanol as needles, m.p. 143–145°C. Anal. Found: C, 50.39; H, 4.43. $C_{40}H_{35}O_4OsP_3Se$ calcd.: C, 51.01; H, 3.75%.

$[OsCl(PH_2SMe)(CO)_2(PPh_3)_2]ClO_4$ (39a). A mixture of $OsCl(PH_S)(CO)_2$-$(PPh_3)_2$ (**37a**: 0.427 g), 0.5 mL of methyl iodide, and 20 mL of dichloromethane was stirred in the open for 2 h to give a colourless solution. This was stripped of solvents

and 0.01 g of lithium perchlorate was added, and the mixture was dissolved in a mixture of 10 mL each of dichloromethane and ethanol. Solvents were taken off until crystallization began, 10 mL of isopropanol was added, and the mixture concentrated to about 5 mL. Filtration, followed by a wash with 2 mL isopropanol and then n-hexane gave 0.41 g (85%) of colourless crystals, m.p. 144–146 °C. Anal. (as 1/2 dichloromethane solvate, as confirmed by ^{1}H NMR) Found: C, 46.15; H, 4.00. $C_{39}H_{35}Cl_2O_6OsP_3S \cdot \frac{1}{2}CH_2Cl_2$ calcd.: C, 46.14; H, 3.54%.

$[OsH(PH_2SMe)(CO)_2(PPh_3)_2]ClO_4$ (39b). A solution of $OsH(PH_2S)(CO)_2(PPh_3)_2$ (**37b**: 0.1 g) in 10 mL of dichloromethane was treated with 0.25 mL of methyl iodide and the mixture was stirred for 5 min. The solvents were then removed in vacuo and 0.01 g of lithium perchlorate was added. The mixture was then dissolved in a mixture of 10 mL each of dichloromethane, ethanol, and isopropanol, and the solution concentrated to give colourless crystals, 0.08 g (77%). Characteristic spectroscopic data for this complex are included in Tables 6, 7 and 8.

$OsCl(PHSMe)(CO)_2(PPh_3)_2$ (40). (a) From $[OsCl(PH_2SMe)(CO)_2(PPh_3)_2]ClO_4$ (**39a**): A solution of $[OsCl(PH_2SMe)(CO)_2(PPh_3)_2]ClO_4$ (**39a**: 0.11 g) in 20 mL of dichloromethane was treated with an excess of DBU (0.1 mL) to give a very pale yellow solution. Ethanol (20 mL) was then added and the light yellow product precipitated by concentration of this solution. Filtration and washing with ethanol and n-hexane gave 0.086 g (87%) of product.

(b) From $OsCl(PH_2S)(CO)_2(PPh_3)_2$ (**37a**): A mixture of $OsCl(PH_2S)(CO)_2(PPh_3)_2$ (**37a**: 0.17 g), 0.3 mL of methyl iodide, and dichloromethane (20 mL) was stirred at room temperature for 90 min and the volatile materials were then removed in vacuo. The residual colourless oil was redissolved in a minimum of dichloromethane and 10 mL of ethanol was added. An excess of DBU (0.15 mL) was then added, and the solution immediately became yellow and a fine precipitate rapidly formed. The dichloromethane was then removed under reduced pressure and the residue washed with methanol, ethanol and n-hexane, to give 0.13 g (65%) of **40**, m.p. 173–175 °C, as fine yellow needles. Anal. (as 3/4 dichloromethane solvate as confirmed by ^{1}H NMR) Found: C, 50.31; H, 4.12. $C_{39}H_{34}ClO_2OsP_3S \cdot \frac{3}{4}CH_2Cl_2$ calcd.: C, 50.31; H, 3.78%.

$OsCl[P(C[O]CF_3)SMe](CO)_2(PPh_3)_2$ (41). To a suspension of $OsCl(PHSMe)(CO)_2(PPh_3)_2$ (**40**: 0.1 g) in 10 mL of dry THF, trifluoroacetic anhydride (0.3 mL) was added dropwise, to give a deep yellow solution. The solvent was removed in vacuo to give a deep-yellow residue, which was recrystallized from dichloromethane/ethanol to give 0.06 g (54%) of glittering yellow needles, m.p. 143–145 °C. Anal. Found: C, 50.94; H, 4.26. $C_{41}H_{33}ClF_3O_3OsP_3S$ calcd.: C, 50.18; H, 3.40%.

$[OsCl(PHMeSMe)(CO)_2(PPh_3)_2]ClO_4$ (42). A suspension of $OsCl(PHSMe)(CO)_2(PPh_3)_2$ (**40**: 0.1 g) in 10 mL of dichloromethane was treated with 0.3 mL methyl iodide and the mixture kept at room temperature for 30 min. The colourless solution was then stripped of all volatile materials and 0.05 g of sodium perchlorate was added. The mixture was dissolved in dichloromethane and ethanol and then the solution concentrated. Once crystallization began 10 mL of isopropanol was added, and the solution concentrated further to give 0.085 g, (75%) of colourless crystals, m.p. 174–175 °C. Anal. Found: C, 48.05; H, 3.74. $C_{40}H_{37}Cl_2O_6OsP_3S$ calcd.: C, 48.00; H, 4.28%.

X-ray diffraction study of $Os(\eta^2\text{-}O_2CCH_3)(PH_2AuI)(CO)(PPh_3)_2$ *(34)*

Crystal data. $C_{41}H_{39}AuCl_4IO_3OsP_3$, $M = 1327.8$, triclinic, space group $P\bar{1}$, a 12.320(3), b 13.962(2), c 14.122(4) Å, α 96.76(2), β 101.93(3), γ 107.72(2)°, V 2221.0 Å^3, $Z = 2$, d(calcd) 1.98 g cm^{-3}, $F(000) = 1260$, monochromated Mo-K_α, λ 0.71069Å, μ(Mo-K_α) 74.9 cm^{-1}.

Data were collected at 291 ± 1°C on a CAD-4 diffractometer from a crystal 0.30 × 0.20 × 0.20mm, 8545 reflections being recorded in the 2θ range 2–54° using $2\theta/\omega$ scans. Empirical absorption corrections were applied, the maximum and minimum factors being 0.993 and 0.788 respectively. The structure was solved by conventional Patterson and difference Fourier techniques and refined by full-matrix least-squares. A difference map revealed the presence of two molecules of dichloromethane solvent which were included in the refinement. All atoms except the phenyl carbon and the solvent were allowed to refine anisotropically. Refinement converged to $R = 0.042$, $R_w = 0.046$ for 6413 observed ($I > 3\sigma(I)$) reflections.

Tables of thermal parameters and observed and calculated structure factors are available from the authors.

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