

Acylphosphido and η^2 -phosphaalkenyl complexes of osmium

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Abstract

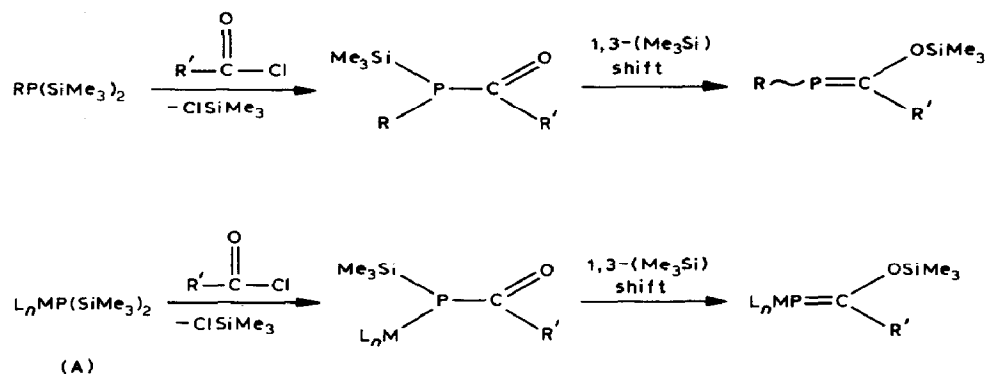
Acylphosphido complexes, $\text{OsCl}[\text{PH}(\text{C}(\text{O})\text{R})](\text{CO})_2(\text{PPh}_3)_2$, ($\text{R} = t\text{-Bu}$, CH_3 , CO_2Et , Ph , $p\text{-C}_6\text{H}_4\text{NO}_2$, CF_3 ; **2a–e**, **3**) are formed when $\text{OsCl}(\text{PH}_2)(\text{CO})_2(\text{PPh}_3)_2$ is treated with the appropriate acid chloride or anhydride. Related complexes, $\text{MX}[\text{PH}(\text{C}(\text{O})\text{CF}_3)](\text{CO})\text{L}'(\text{PPh}_3)_2$, ($\text{M} = \text{Ru}$, $\text{X} = \text{Cl}$, $\text{L}' = \text{CO}$: **7**; $\text{M} = \text{Os}$, $\text{X} = \text{H}$, $\text{L}' = \text{CO}$: **8**; $\text{M} = \text{Os}$, $\text{X} = \text{Cl}$, $\text{L}' = \text{PMe}_3$: **9**) are also prepared from the related PH_2 complexes and trifluoroacetic anhydride. The structure of a representative example of one of these with a pivaloylphosphido ligand, **2a**, has been determined. The pale yellow crystals are triclinic, space group $P\bar{1}$, a 10.691(1), b 12.565(3), c 17.291(2) Å, α 97.39(1), β 103.871(9), γ 102.72(1)° with $Z = 2$ and V 2159 Å³.

When **3** is treated with sodium hydride in THF at reflux for 1.5 h, HCl is lost and a η^2 -phospha-alkenyl complex $\text{Os}(\text{P}=\text{C}(\text{O})\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**10**) is formed. The two-coordinate phosphorus atom in **10** is nucleophilic, and with $\text{Fe}_2(\text{CO})_9$ forms the adduct $\text{Os}[\text{P}(\text{Fe}(\text{CO})_4)=\text{C}(\text{O})\text{CF}_3](\text{CO})_2(\text{PPh}_3)_2$ (**12**), and with methyl iodide gives a methyltrifluoroacylphosphido complex, $\text{OsI}[\text{PMe}(\text{C}(\text{O})\text{CF}_3)](\text{CO})_2(\text{PPh}_3)_2$ (**11b**). Both **10** and **12** have been structurally characterized. Bright orange crystals of **12** crystallize in the monoclinic space group $P2_1/c$, with a 12.168(3), b 18.135(3), c 21.804(3) Å and β 103.11(2)°, $Z = 4$, V 4686 Å³. Complete details of the structure of **10** are also reported. The bonding in **10** and **12** is discussed in terms of two canonical forms, one with phospha-alkene like character, the other with phosphinidene character.

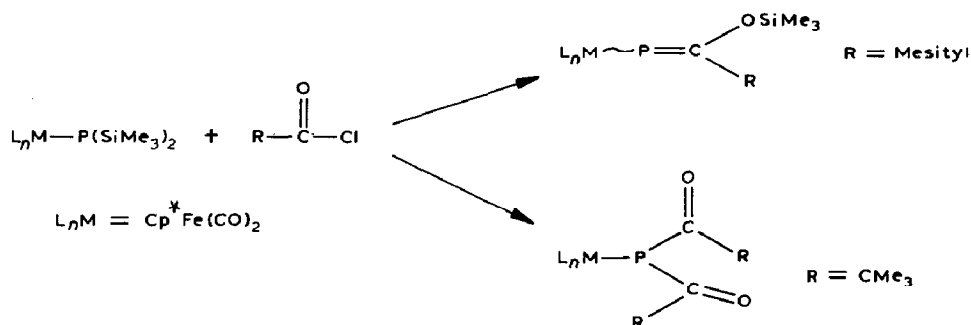
Introduction

Compared with the chemistry of organic amides the chemistry of acylphosphines is very poorly developed. Examples of this class of compounds were first firmly established thirty years ago but interest in these compounds was limited until

recently [1] when silylacylphosphines were found to be precursors for the preparation of phospho-alkenes and phospho-alkynes [2]. These syntheses are thermodynamically driven by the relative weakness of the P-Si bond compared to the Cl-Si and O-Si bonds:



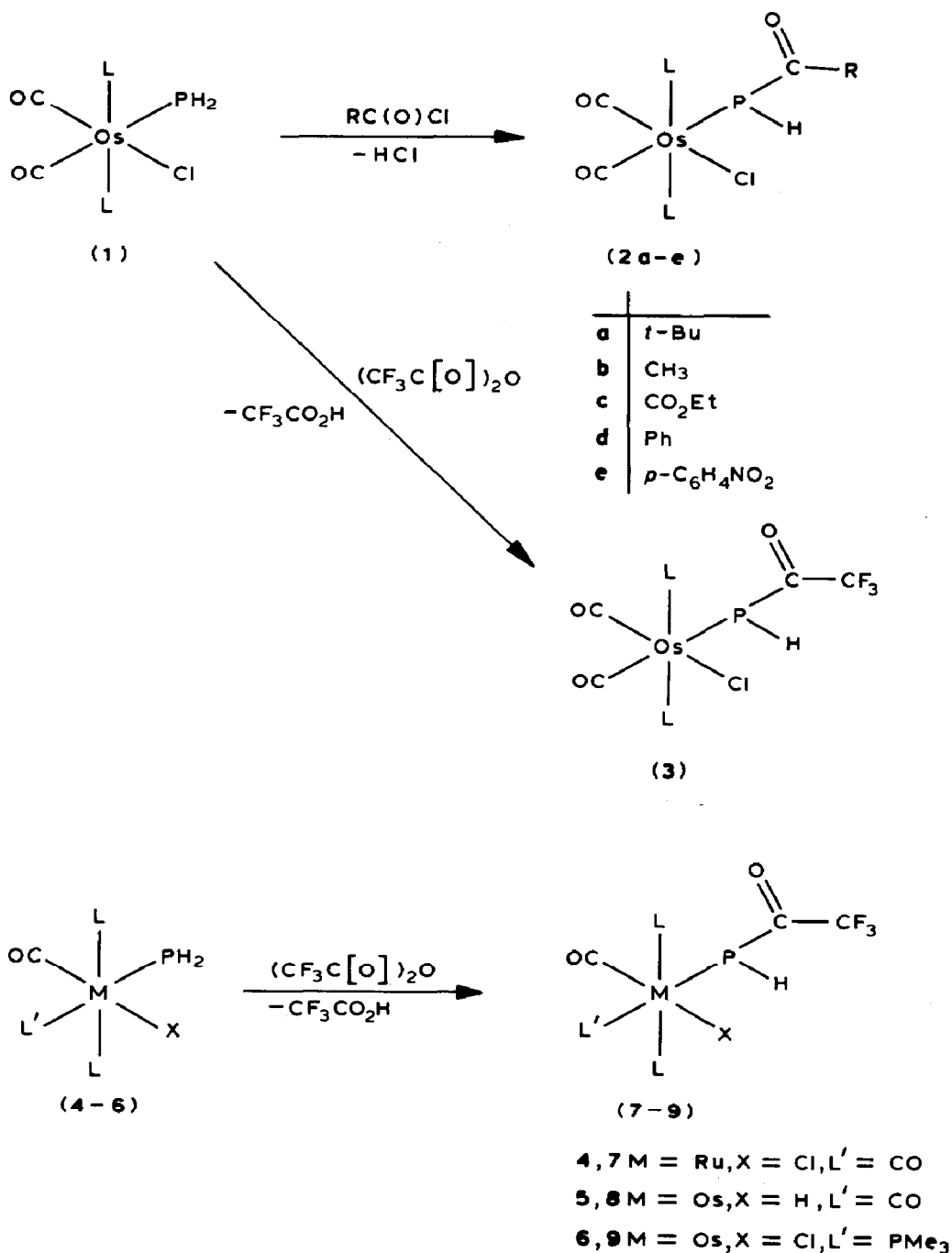
Weber has extended this synthetic strategy to compounds with transition metal substituents, and has found, as in the equation above, that when certain bis(trimethylsilyl)phosphido metal complexes (A) are treated with acid chlorides, metallated phospho-alkenes are formed [4]. In a related reaction, when A is treated with phosphonous dihalides, metalladiphosphenes, $\text{L}_n\text{MP}=\text{PR}$, are formed [5]. However, the utility of this strategy is obviously limited by the availability of the bis(trimethylsilyl)phosphido complex (A) and less obviously by the nature of the acid chloride. For example, the reaction of $\text{Cp}^*\text{Fe}(\text{CO})_2[\text{P}(\text{SiMe}_3)_2]$ and acid chloride where $\text{R} = \text{mesityl}$ results in a phospho-alkene complex, but with pivaloyl chloride, $\text{R} = \text{t-Bu}$, a bis(pivaloyl) complex forms [6]:



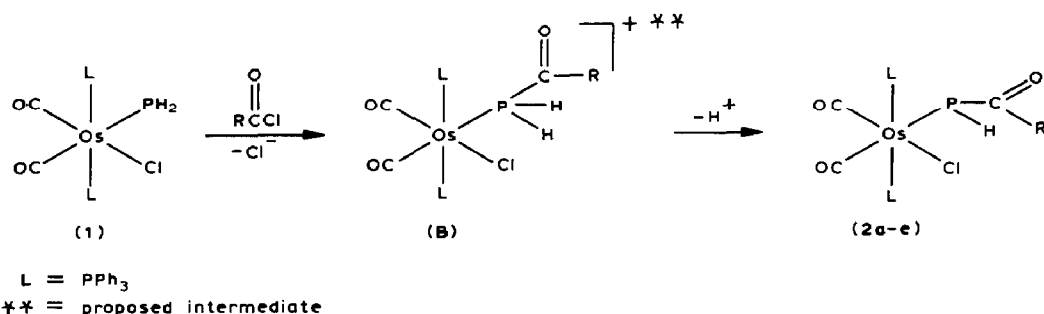
In order to elaborate further the chemistry of metallated phospho-alkene complexes other synthetic routes to these compounds must be developed. We have previously reported [7] the preparation of $\text{Os}(\text{P}=\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (10) with a η^2 -phospho-alkenyl ligand, by dehydrochlorination of $\text{OsCl}[\text{PH}(\text{C}[\text{O}]\text{CF}_3)](\text{CO})_2(\text{PPh}_3)_2$. Herein we report: (1) full details of this preparation and the reactivity of 10; (2) the preparation of new acyl phosphido complexes; (3) the structure of one of these, $\text{OsCl}[\text{PH}(\text{C}[\text{O}]\text{CMe}_3)](\text{CO})_2(\text{PPh}_3)_2$; and (4) the complete structure of $\text{Os}(\text{P}=\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ and its derived η^1 -phosphorus bound iron tetracarbonyl adduct.

Results and discussion

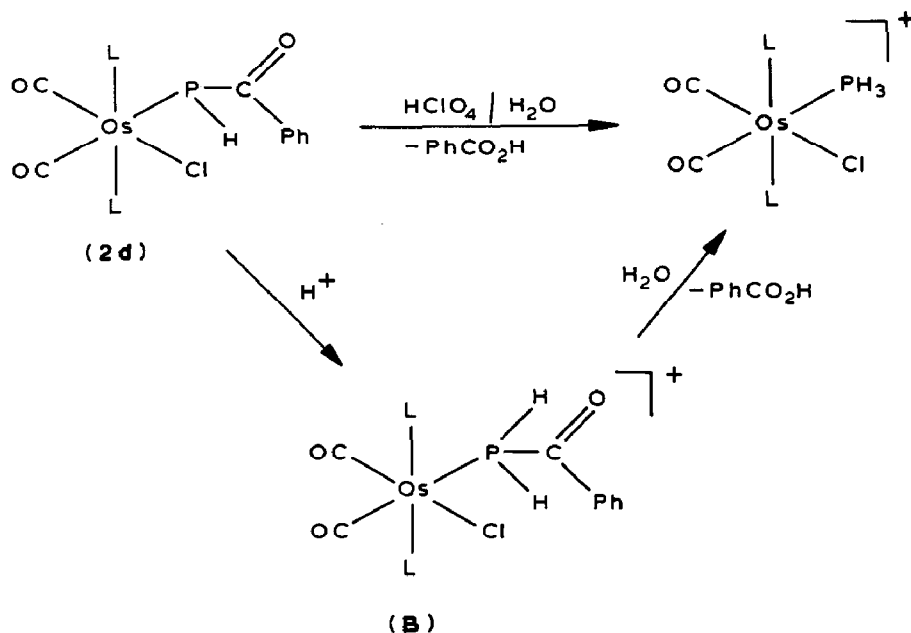
Acid chlorides and anhydrides react rapidly with terminal phosphido complexes **1**, **4**, **5** and **6** to give the neutral acylphosphido complexes **2a-e**, **3**, **7**, and **9** (Scheme 1). Each one of these products is isolated as a neutral, slightly coloured, crystalline



Scheme 1. Preparation of acyl phosphido complexes.

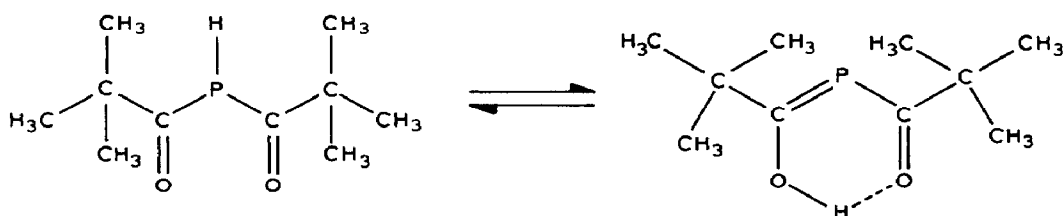


compound. The expected cationic products in this reaction, **B**, are never isolated or observed. Since only very weak Brönsted bases are present in the reaction mixture

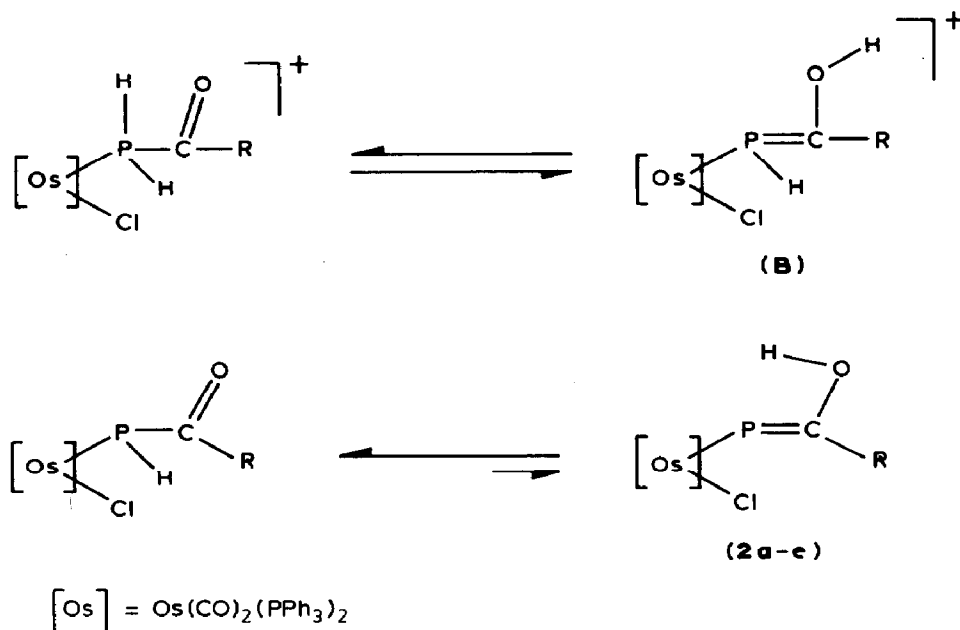


the cationic complex **B** must be very acidic. The original phosphido complex **1** must not act as a base to promote this reaction as **2a-e** are prepared in good yields (63–57%) and there is no evidence for the formation of $[\text{OsCl}(\text{PH}_3)(\text{CO})_2(\text{PPh}_3)_2]^+$ from the protonation of **1**. Attempts to generate a cationic acylphosphine complex like **B**, by treating **2d** with aqueous perchloric acid, results instead in the cationic phosphine complex $[\text{OsCl}(\text{PH}_3)(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$, the synthetic precursor [8] of **1a**. This can be rationalized in terms of an acid catalyzed hydrolysis of the acylphosphido group of **B**. The mild conditions required for this hydrolysis, room temperature for 10 min, contrasts sharply with the forcing conditions required for the hydrolysis of amides [9].

Primary and secondary acylphosphines are known to exhibit keto-enol tautomerism [1]. For example, bis(pivaloyl)phosphine has the enol structure in the solid state but in solution, NMR studies indicate the presence of the keto form [10]:

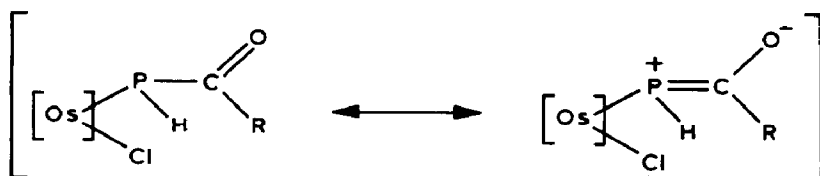


While such a tautomerism is expected to contribute to the acidity of the unobserved cationic monoacylphosphine complex **B** it is unlikely to be important in describing the chemistry of the acylphosphido complexes **2a-e**:



Thus in the solid state **2a-e** have weak, but discernible, phosphorus-hydrogen stretching bands (Table 8) and in the solution IR spectra of **2a-e** there are strong carbonyl stretching bands due to the acylphosphido ligands. In the proton NMR spectra of **2a-e** there is a single resonance due to the phosphorus bound proton which has a relatively strong one bond phosphorus-hydrogen coupling ($^1J(\text{HP})$ 212–258 Hz). These data indicate that any exchange that is occurring is slow on the NMR time scale. There is no evidence for tautomerism in the ^{31}P NMR spectra of **2a-e** as there are only two signals present. These correspond to the coordinated triphenylphosphine, at lower fields, and at higher field that of the acylphosphido ligand.

Two canonical structures can be written to describe the bonding in **2a-e**:



The low frequencies for the carbonyl stretch in the IR spectra for the acylphosphido ligands in **2a-e** suggests that the charge separated structure contributes to the

bonding in **2**. To understand the nature of the bonding in **2** further an X-ray diffraction study of **2a** was performed.

Crystal structure of $\text{OsCl}[\text{PH}(\text{C}[\text{O}]\text{CMe}_3)](\text{CO})_2(\text{PPh}_3)_2 \cdot \text{CHCl}_3$

As depicted in Fig. 1 the overall geometry at the osmium is octahedral with mutually *trans* triphenylphosphine ligands. Experimental data for all three structural studies in this report are collected in Table 1 and the bond length, bond angle, and atomic position data for **2a** are presented in Tables 2, 3 and 4 respectively. The bond lengths and angles at the osmium are similar to those found in other octahedral Os^{II} complexes with the $\text{OsCl}(\text{CO})_2(\text{PPh}_3)_2$ fragment [11]. For the pivaloylphosphido ligand in **2a** the osmium–phosphorus bond length, 2.488(4) Å, and the angle at the phosphorus, $\text{Os}-\text{P}(3)-\text{C}(71) = 109.4(5)^\circ$, are both slightly smaller than those values found for the phenylphosphido ligand (2.523(7) Å and $113.4(6)^\circ$ respectively) in $\text{OsCl}(\text{PPh})(\text{CO})_2(\text{PPh}_3)_2$ [11]. The phosphorus-bound hydrogen was not located with Fourier difference techniques.

Within the pivaloylphosphido ligand there are some surprising trends in bond lengths. Acylphosphines usually have P–C bond lengths that are 0.06 Å longer than the typical value, 1.83 Å, for P–C single bonds [1]. Bis(acyl)phosphines such as $\text{PH}(\text{C}[\text{O}]\text{CMe}_3)_2$, with labile enolizable protons, exhibit solid state structures with shortened P–C bonds (1.77–1.82 Å) and lengthened C–O bonds (1.25–1.29 Å) [1]. Although the high e.s.d. values make interpretation difficult, there is a significant trend in the pivaloylphosphido ligand of **2a** towards the enolate form ($\text{P}(3)-\text{C}(71)$ 1.792(15) and $\text{C}(71)-\text{O}(3)$ 1.258(17) Å). A comparison with the structurally char-

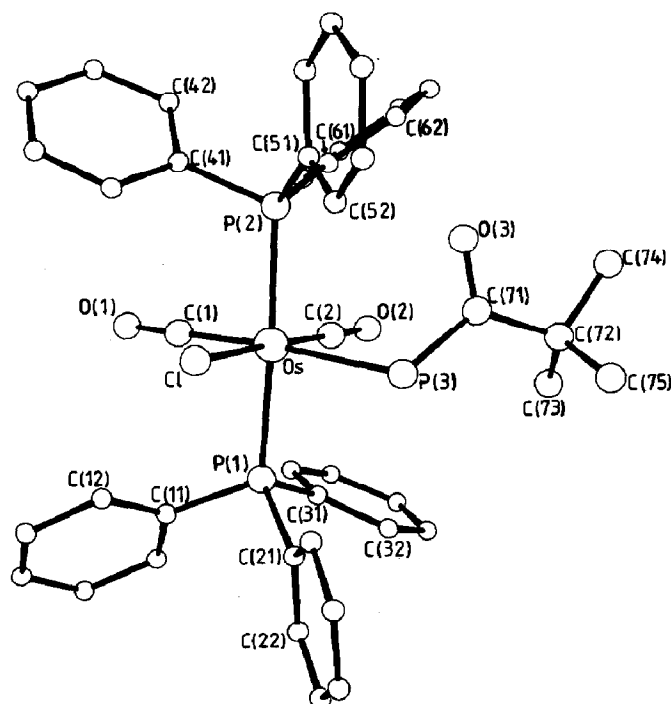


Fig. 1. Structure of $\text{OsCl}[\text{PH}(\text{C}[\text{O}]\text{-t-Bu})](\text{CO})_2(\text{PPh}_3)_2 \cdot \text{CHCl}_3$ (**2a**).

Table 1

Experimental data for the X-ray diffraction studies

	2a	10	12
Crystal data ^a			
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$C 2/c$	$P 2_1/c$
<i>a</i> , Å	10.691(1)	19.555(13)	12.168(3)
<i>b</i> , Å	12.565(3)	13.168(2)	18.135(3)
<i>c</i> , Å	17.291(2)	28.888(13)	21.804(3)
α , °	97.39(1)	—	—
β , °	103.87(1)	103.83(4)	103.11(2)
γ , °	102.71(1)	—	—
<i>V</i> , Å ³	2159.1	7223.0	4686.0
<i>Z</i>	2	8	4
mol. wt.	923.39	898.81	1066.70
ρ (calcd), g cm ⁻³	1.42	1.65	1.51
Collection temperature (°C)	25	-90	25
Measurement of intensity data			
Radiation	Monochromated Mo- K_α (λ 0.71069 Å)		
scan type	ω (crystal)- 2θ (counter)		
2θ range (°)	3-46	3-50	3-46
reflections collected	6563[5181 > 3 σ (<i>I</i>)] ^b	6365[3184 > 3 σ (<i>I</i>)]	4324[2173 > 3 σ (<i>I</i>)]
Absorption coefficient (cm ⁻¹)	34.49	35.63	33.46

^a Unit cell parameters were obtained from a least-squares fit to the setting angles of 25 reflections. ^b Due to crystal decomposition it was necessary to use two separate crystals for data collection. Corrections were made for crystal decomposition and separate scale factors refined for the data from each crystal.

Table 2

Bond lengths for OsCl[PH(C[O]-*t*-Bu)](CO₂)(PPh₃)₂·CHCl₃ (2a) (Å)

Os-P(1)	2.419(3)	Os-Cl(1)	2.461(3)
Os-P(2)	2.439(3)	Os-C(1)	1.879(13)
Os-P(3)	2.488(4)	Os-C(2)	1.836(14)
P(3)-C(71)	1.792(15)	C(1)-O(1)	1.150(15)
C(71)-O(3)	1.258(17)	C(2)-O(2)	1.166(14)
C(71)-C(72)	1.55(2)	P(1)-C(11)	1.801(12)
C(72)-C(73)	1.53(4)	P(1)-C(21)	1.833(12)
C(72)-C(74)	1.57(3)	P(1)-C(31)	1.815(12)
C(72)-C(75)	1.53(3)	P(2)-C(41)	1.815(11)
		P(2)-C(51)	1.824(11)
		P(2)-C(61)	1.804(11)
Bonds in chloroform solvate			
C(81)-Cl(2)	1.75(2)	C(81)-Cl(3)	1.75(2)
C(81)-Cl(4)	1.73(2)		

Bond lengths in triphenylphosphine phenyl rings ^a

	<i>i</i> = 1	2	3	4	5	6
C(<i>i</i> 1)-C(<i>i</i> 2)	1.40	1.41	1.40	1.41	1.40	1.42
C(<i>i</i> 1)-C(<i>i</i> 6)	1.38	1.41	1.40	1.41	1.41	1.42
C(<i>i</i> 2)-C(<i>i</i> 3)	1.45	1.41	1.44	1.42	1.42	1.41
C(<i>i</i> 3)-C(<i>i</i> 4)	1.38	1.39	1.37	1.40	1.38	1.40
C(<i>i</i> 4)-C(<i>i</i> 5)	1.38	1.38	1.38	1.39	1.42	1.38
C(<i>i</i> 5)-C(<i>i</i> 6)	1.44	1.41	1.38	1.42	1.39	1.38

^a The e.s.d. for each of these lengths is 0.02 Å.

Table 3

Bond angles for $\text{OsCl}[\text{PH}(\text{C}(\text{O})\text{-t-Bu})](\text{CO})_2\text{PPh}_3)_2 \cdot \text{CHCl}_3$ (**2a**) ($^\circ$)

<i>Angles at osmium</i>			
P(1)–Os–P(2)	177.6(1)	P(1)–Os–Cl(1)	89.8(1)
P(1)–Os–P(3)	86.8(1)	P(1)–Os–C(1)	88.6(4)
P(2)–Os–P(3)	95.5(1)	P(1)–Os–C(2)	90.7(4)
P(3)–Os–Cl(1)	89.7(1)	P(2)–Os–Cl(1)	89.4(1)
P(3)–Os–C(1)	175.3(4)	P(2)–Os–C(1)	87.1(4)
P(3)–Os–C(2)	84.4(4)	P(2)–Os–C(2)	90.3(4)
Cl(1)–Os–C(1)	91.4(4)	C(1)–Os–C(2)	94.6(6)
Cl(1)–Os–C(2)	170.0(4)		
<i>Angles in pivaloylphosphido ligand</i>			
Os–P(3)–C(71)	109.4(5)	C(71)–C(72)–C(74)	108.5(1.6)
P(3)–C(71)–O(3)	116.7(1.2)	C(71)–C(72)–C(75)	109.6(1.7)
P(3)–C(71)–C(72)	125.1(1.1)	C(73)–C(72)–C(74)	109 (2)
O(3)–C(71)–C(72)	117.3(1.4)	C(73)–C(72)–C(75)	114 (2)
C(71)–C(72)–C(73)	112.0(1.8)	C(74)–C(72)–C(75)	104(2)
<i>Angles in carbon monoxide and triphenylphosphine ligands^a</i>			
Os–C(1)–O(1)	176.4(1.1)	C(21)–P(1)–C(31)	104.8(5)
Os–C(2)–O(2)	178.5(1.2)	Os–P(2)–C(41)	112.7(4)
Os–P(1)–C(11)	116.4(4)	Os–P(2)–C(51)	120.7(4)
Os–P(1)–C(21)	120.9(4)	Os–P(2)–C(61)	112.8(4)
Os–P(1)–C(31)	107.8(4)	C(41)–P(2)–C(51)	99.8(5)
C(11)–P(1)–C(21)	99.7(5)	C(51)–P(2)–C(61)	107.1(5)
C(11)–P(1)–C(31)	105.7(6)	C(41)–P(2)–C(61)	101.4(5)
<i>Bond angles in chloroform solvate</i>			
Cl(2)–C(81)–Cl(3)	110.7(1.0)	Cl(3)–C(81)–Cl(4)	110.3(10)
Cl(2)–C(81)–Cl(4)	110.0(1.0)		

^a Bond angles in phenyl rings not included.

acterized bis(pivaloyl)phosphido ligand in $\text{Cp}^*\text{Ru}(\text{CO})_2[\text{P}(\text{C}(\text{O})\text{CMe}_3)_2]$ [12] also highlights this trend. In the ruthenium complex there are very compact bond angles at the phosphorus (Ru–P–C 105.5° (av.)), lengthened phosphorus–carbon bond lengths (P–C $1.873 \text{ \AA}$ (av.)) and relatively short carbon–oxygen bond lengths (C–O $1.205 \text{ \AA}$ (av.)).

Thus both the spectroscopic and structural results for the acyl phosphido complexes suggest that there may be an interaction between the phosphorus lone pair and the acyl π^* orbital. However recent theoretical results for vinylphosphine indicate that there is very little allylic like interaction of the phosphorus lone pair and the π^* orbital of the carbon–carbon double bond [13]. Another factor that should be noted is that the short metal–phosphorus bond lengths found in **2a** suggests that there is an additional metal–phosphorus interaction, possibly π -back-bonding in character, which delocalizes electron density from the metal d set into the acylphosphido ligand. As the reactions in the next section illustrate, the phosphorus lone pair is not very susceptible to electrophilic attack. This may be another consequence of the delocalization of the phosphorus lone pair.

Reactions of acylphosphido complexes

Not only is the phosphorus in **2a–e** a weak base but it is also a poor nucleophile. Many of the characteristic reactions of pyramidal terminal phosphido complexes

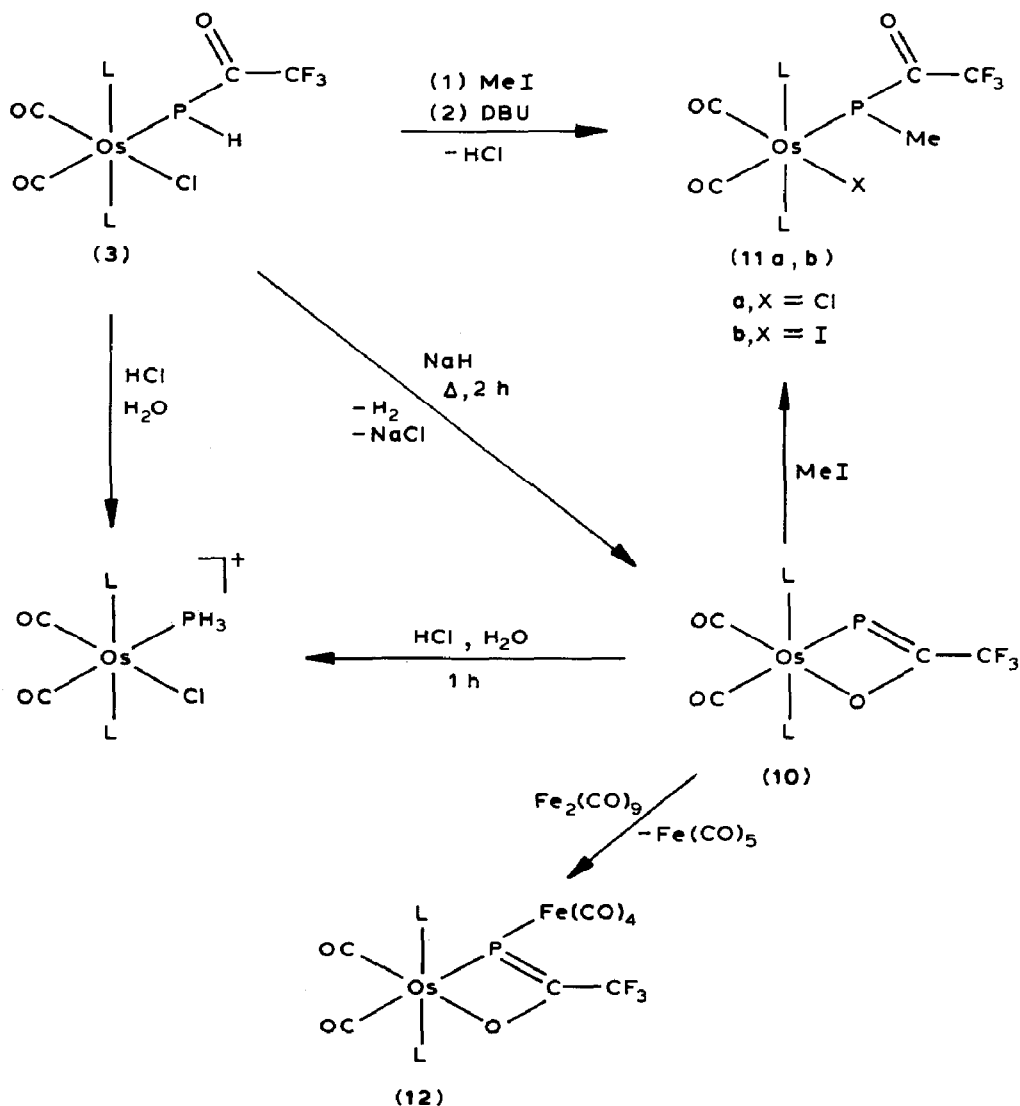
Table 4

Atomic positions for $\text{OsCl}[\text{PH}(\text{C}(\text{O})\text{-t-Bu})](\text{CO})_2(\text{PPh}_3)_2 \cdot \text{CHCl}_3$ (**2a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Os	0.04158(4)	0.24230(4)	0.23332(3)
Cl(1)	−0.1387(3)	0.3373(3)	0.2167(2)
P(1)	−0.1229(3)	0.0647(3)	0.1866(2)
P(2)	0.2050(3)	0.4228(3)	0.0016(2)
P(3)	0.0258(4)	0.2240(3)	0.3725(2)
C(1)	0.0459(12)	0.2436(10)	0.1254(8)
C(2)	0.1761(13)	0.1724(11)	0.2568(8)
O(1)	0.0537(10)	0.2413(8)	0.0601(6)
O(2)	0.2625(9)	0.1294(8)	0.2734(6)
O(3)	0.2709(11)	0.3402(10)	0.4436(7)
C(11)	−0.2161(11)	0.0334(10)	0.0811(7)
C(12)	−0.2775(13)	0.1118(11)	0.0499(9)
C(13)	−0.3651(16)	0.0848(14)	−0.0320(10)
C(14)	−0.3842(16)	−0.0179(14)	−0.0783(10)
C(15)	−0.3278(18)	−0.0976(15)	−0.0476(12)
C(16)	−0.2390(15)	−0.0692(13)	0.0335(10)
C(21)	−0.2601(11)	0.0288(10)	0.2328(7)
C(22)	−0.3396(12)	−0.0814(11)	0.2126(8)
C(23)	−0.4505(14)	−0.1130(12)	0.2432(9)
C(24)	−0.4809(14)	−0.0328(12)	0.2932(9)
C(25)	−0.4062(14)	0.0767(12)	0.3126(9)
C(26)	−0.2938(13)	0.1086(11)	0.2833(9)
C(31)	−0.0361(11)	−0.0434(10)	0.2002(7)
C(32)	−0.0370(13)	−0.1003(11)	0.2644(8)
C(33)	0.0454(15)	−0.1763(13)	0.2763(10)
C(34)	0.1241(15)	−0.1916(13)	0.2259(10)
C(35)	0.1210(15)	−0.1365(13)	0.1618(10)
C(36)	0.0435(13)	−0.0629(11)	0.1492(9)
C(41)	0.2082(11)	0.4976(9)	0.1919(7)
C(42)	0.3289(14)	0.5451(12)	0.1751(9)
C(43)	0.3243(15)	0.6061(13)	0.1114(10)
C(44)	0.2050(14)	0.6232(12)	0.0670(9)
C(45)	0.0871(16)	0.5772(14)	0.0849(11)
C(46)	0.0876(13)	0.5129(12)	0.1467(9)
C(51)	0.1903(11)	0.5310(9)	0.3507(7)
C(52)	0.0866(13)	0.5138(12)	0.3875(9)
C(53)	0.0754(15)	0.6009(13)	0.4444(10)
C(54)	0.1687(14)	0.7020(12)	0.4637(9)
C(55)	0.2733(14)	0.7215(12)	0.4260(9)
C(56)	0.2818(13)	0.6363(11)	0.3690(8)
C(61)	0.3747(11)	0.4118(9)	0.3044(7)
C(62)	0.4658(13)	0.4590(11)	0.3835(8)
C(63)	0.5969(14)	0.4456(12)	0.4013(9)
C(64)	0.6366(14)	0.3834(12)	0.3429(9)
C(65)	0.5480(13)	0.3371(11)	0.2674(8)
C(66)	0.4194(12)	0.3492(10)	0.2472(8)
C(71)	0.1901(15)	0.2487(13)	0.4393(10)
C(72)	0.2326(16)	0.1768(14)	0.5021(10)
C(73)	0.239(3)	0.063(3)	0.461(2)
C(74)	0.375(3)	0.240(2)	0.559(2)
C(75)	0.142(2)	0.170(3)	0.559(2)
C(81)	0.7234(17)	0.5465(15)	0.1373(11)
Cl(2)	0.5817(5)	0.4390(4)	0.0863(3)
Cl(3)	0.7038(7)	0.6129(6)	0.2273(4)
Cl(4)	0.7543(7)	0.6412(6)	0.0752(5)

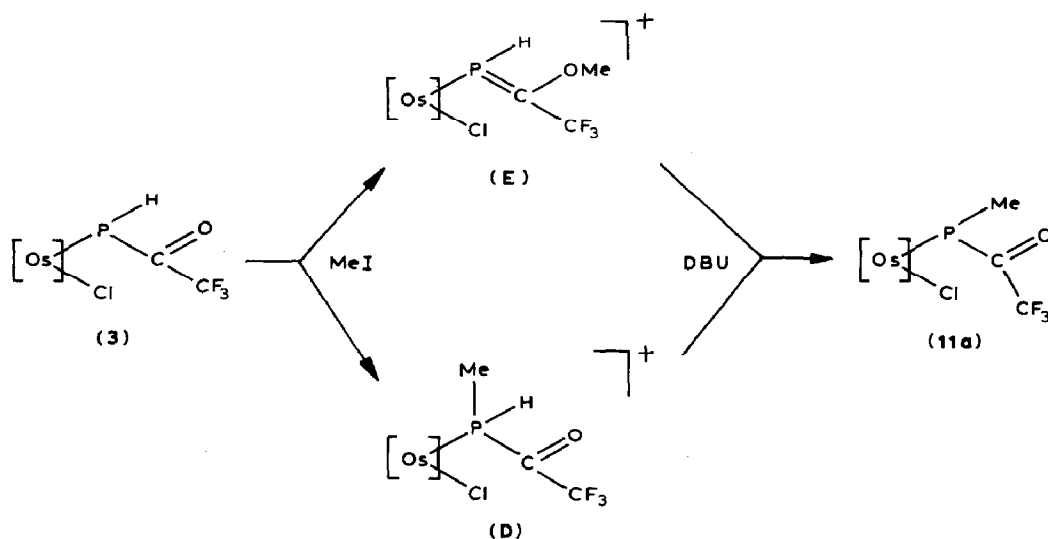
[11] fail to give tractable products, or any reaction at all, with **2a-e**. Thus attempts to add sulphur, with S_8 , gold(I) iodide, with $[N(n-Bu)_4][AuI_2]$, or iron tetracarbonyl, with $Fe_2(CO)_9$, all fail to give the expected products. Even though excess acid chlorides are present in the preparation of **2a-e** there is no indication that multiple acylation occurs to give bis(acyl)phosphido complexes. In the preparations of **3**, **7-9** excess trifluoroacetic anhydride is used but again there is no indication that bis(trifluoroacyl)phosphido complexes result. Attempts to silylate the acyl oxygen with trimethylsilyl-chloride and -triflate, to give in the first instance cationic complexes with the phospho-alkene ligand $HP=C(OSiMe_3)R$, also failed to give any tractable products.

However, there is one important example of electrophilic addition to an acylphosphido ligand. When **3** is treated with excess methyl iodide, and this is immediately followed with an addition of excess 1,8-diazabicyclo[5,4,0]undec-7-ene



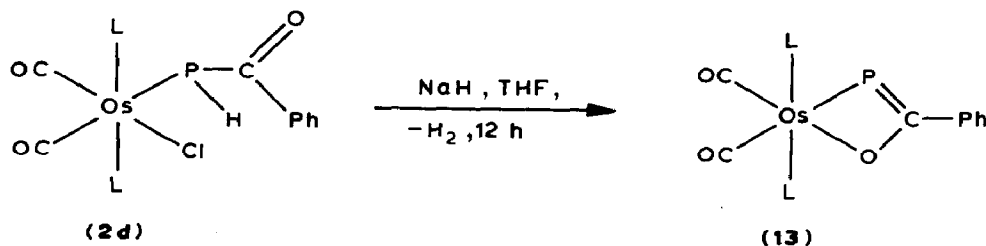
Scheme 2. Reactions of $OsCl[PH(C[O]CF_3)](CO)_2(PPh_3)_2$ and $Os(P=C[O]CF_3)(CO)_2(PPh_3)_2$.

(DBU) a bright yellow solution results from which **11a** can be isolated in 57% yield (Scheme 2). Consistent with this formulation as a methyltrifluoroacylphosphido complex, is the presence of an acyl carbonyl stretch at 1512 cm^{-1} in the infrared spectrum and the two bond coupling constant ($^2J(\text{HP})$ 6.7 Hz) for the methyl resonance in the ^1H NMR spectrum. The initial site of methylation is most likely the phosphorus and this would generate a cationic intermediate such as **D**.



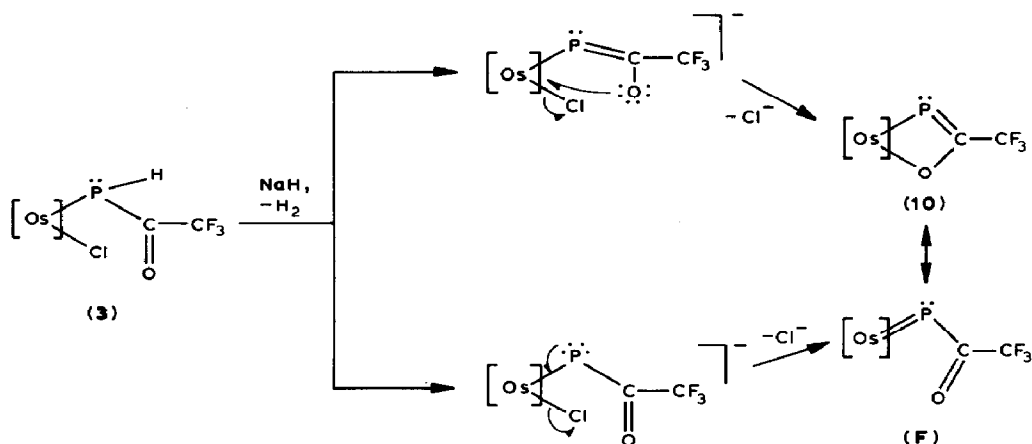
Methylation of the oxygen, to give a cationic phospho-alkene complex **E**, would have to undergo an unusual 1,3-methylshift on deprotonation to produce the observed product, **11a**.

As depicted in Scheme 2 the most interesting reactions of **3** (and also of **2d**) are with bases such as DBU and sodium hydride. These are the only acylphosphido complexes which give tractable products on reaction with base. Even with prolonged heating at reflux in THF with DBU, **2c** is recovered unreacted in good return. Suspensions of sodium hydride and **3** heated in THF at reflux for 90 min result in a pale yellow solution of the phospho-alkene complex **10**. A related phospho-alkene complex, **13**, can be prepared from **2d** with these reagents. However, even with long reaction times and excess base, **13** is always formed as a mixture with unreacted **2d** and decomposition products of **13**. Consequently the characterization of **13** is limited



to the IR spectroscopy of these mixtures. But the phospho-alkene complex **10** is fully characterized by analytical, spectroscopic and structural techniques.

Two plausible mechanisms for the formation of **10** are indicated below. The distinguishing feature of these two paths is the mechanism by which the chloride is lost. Mathey [14] has suggested that an associative substitution of the nucleophilic



oxygen for chloride would lead to ring formation to give **10**. However, in view of the kinetic inertness of Os^{II} towards nucleophilic substitution, a dissociative mechanism, to give a terminal phosphinidene species like **F**, is a more likely way to account for chloride loss. This mechanism is closely related to that proposed to account for loss of chloride from Os^{II} in the OsCl(L')(CO)₂(PPh₃)₂ fragment [15]. As will be shown in the discussion of the structural results **F** is another representation of the bonding in **10**. One feature of the reaction is its limitation to the acylphosphido complexes **2d** and **3**. In the case of **3** the σ -inductive effects of the CF₃ group are probably as important as the π -effects from the acyl ligand in their contribution towards the increased acidity of the phosphorus-bound proton.

Structures of $\text{Os}(\text{P}=\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**10**) and its $\text{Fe}(\text{CO})_4$ adduct (**12**)

As depicted in Figs. 2 and 3 the geometries at the osmium in **10** and its iron tetracarbonyl adduct, $\text{Os}(\text{P}[\text{Fe}(\text{CO})_4]=\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**12**) are very similar. Bond lengths, bond angles and atomic positions are collected for **10** and **12** in Tables 5 & 8, 6 & 9 and 7 & 10 respectively. As the compounds **10** and **12** are so closely related their structures are discussed together here. The preparation of **12** will be detailed in the following section. In both complexes the overall structure associated with the Os(CO)₂(PPh₃)₂ fragments are similar. However there are major differences in the geometries found in the η^2 -phospha-alkene ligand in **10** and the η^2 - μ_2 -phospha-alkene of **12**. These differences are presented in Fig. 4 which is a view of the $\text{OsP}=\text{C}[\text{O}]\text{CF}_3$ ring from along the osmium-triphenylphosphine axis. Dimensions for **10** are indicated by () and for **12** by []. In each case the phosphorus-carbon bond lengths are within the range associated with P=C bonds [16]. The phosphorus-carbon double bonds in **10** and **12** are slightly shorter than that found in the bent phospha-alkene complex $\text{CpFe}(\text{CO})_2(\text{P}=\text{C}(\text{OSiMe}_3)\text{CMe}_3)$ [17] and are similar to those found in the complexes $\text{Cp}^*\text{Mo}(\text{CO})_3(\text{P}=\text{C}(\text{SiMe}_3)_2)$ [18] and $\text{CpMo}(\text{CO})_2(\text{P}=\text{C}(\text{SiMe}_3)_2)$ [19] where the metal-phosphorus-carbon geometries are respectively bent and linear.

In **12** the iron tetracarbonyl group is η^1 -axially bound and forms a very large angle at the phosphorus (Os-P-Fe 153.7(5)°). Since both η^1 - and η^2 -phospha-alkene and diphosphene complexes [20,21] are known it is significant that a η^2 -Fe(CO)₄ adduct, such as **G**, is not formed. There are only two other reported examples of

(Continued on p. 370)

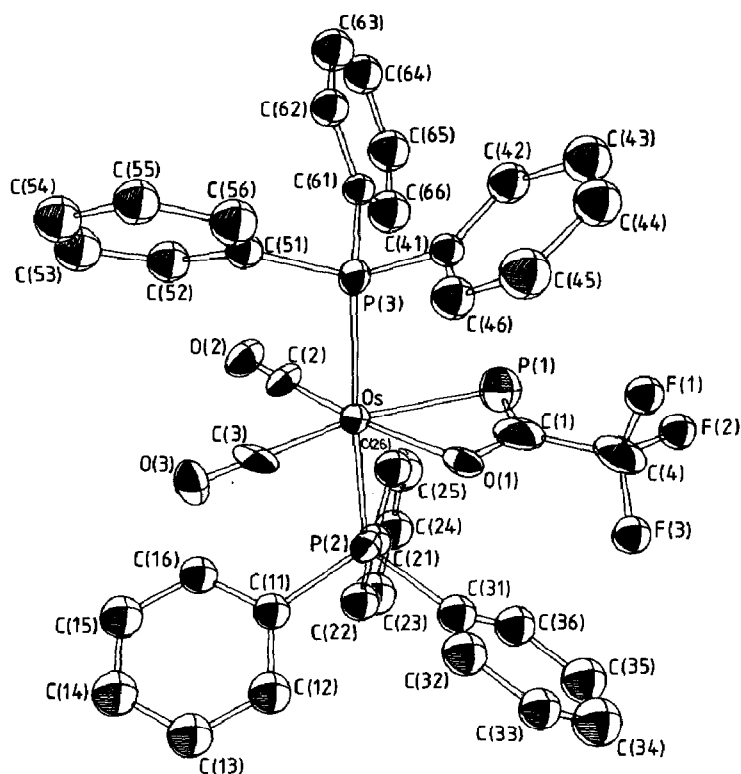


Fig. 2. Structure of $\text{Os}(\text{P}=\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**10**).

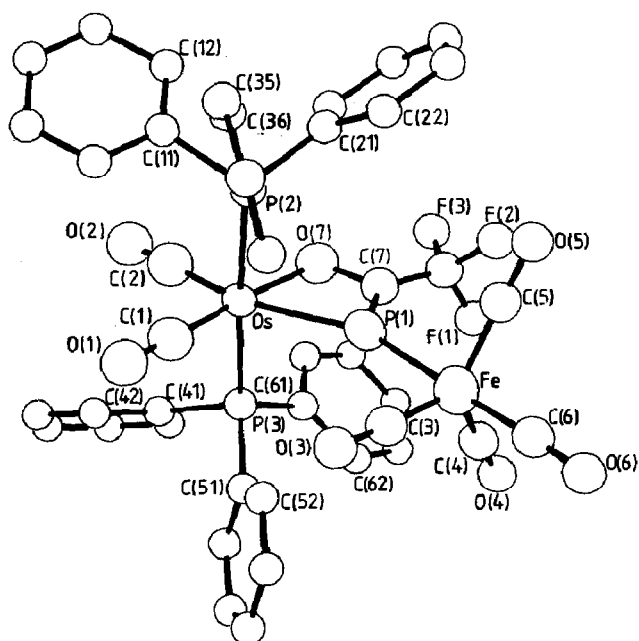


Fig. 3. Structure of $\text{Os}(\text{P}[\text{Fe}(\text{CO})_4]-\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**12**).

Table 5

Bond lengths for $\text{Os}(\text{P}=\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**10**) (Å)

Os–P(1)	2.482(6)	P(1)–C(1)	1.657(24)
Os–P(2)	2.372(6)	C(1)–O(1)	1.246(27)
Os–P(3)	2.360(6)	C(1)–C(4)	1.595(3)
Os–O(1)	2.226(11)	C(4)–F(1)	1.31(3)
Os–C(2)	1.854(21)	C(4)–F(2)	1.22(3)
Os–C(3)	1.897(21)	C(4)–F(3)	1.35(3)
C(2)–O(2)	1.161(25)	C(3)–O(3)	1.133(25)
P(2)–C(11)	1.833(20)	P(3)–C(41)	1.831(18)
P(2)–C(21)	1.849(18)	P(3)–C(51)	1.842(20)
P(2)–C(31)	1.821(17)	P(3)–C(61)	1.798(21)

Bond lengths in triphenylphosphine phenyl rings ^a

	<i>i</i> = 1	2	3	4	5	6
C(<i>i</i> 1)–C(<i>i</i> 2)	1.35	1.36	1.36	1.38	1.36	1.37
C(<i>i</i> 1)–C(<i>i</i> 6)	1.39	1.39	1.38	1.39	1.38	1.45
C(<i>i</i> 2)–C(<i>i</i> 3)	1.40	1.33	1.41	1.40	1.40	1.40
C(<i>i</i> 3)–C(<i>i</i> 4)	1.38	1.35	1.35	1.32	1.37	1.37
C(<i>i</i> 4)–C(<i>i</i> 5)	1.32	1.36	1.38	1.42	1.36	1.33
C(<i>i</i> 5)–C(<i>i</i> 6)	1.41	1.43	1.33	1.39	1.41	1.39

^a The e.s.d. for each of these lengths is 0.03 Å.

Table 6

Bond angles for $\text{Os}(\text{P}=\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**10**) (°)

<i>Angles at osmium</i>			
P(1)–Os–P(2)	88.6(2)	O(1)–Os–C(2)	172.8(7)
P(1)–Os–P(3)	83.8(2)	O(1)–Os–C(3)	96.3(6)
P(1)–Os–O(1)	67.3(4)	O(1)–Os–P(2)	89.8(4)
P(1)–Os–C(2)	105.6(7)	O(1)–Os–P(3)	89.0(4)
P(1)–Os–C(4)	163.5(6)		
C(2)–Os–C(3)	90.9(8)	C(3)–Os–P(2)	93.1(6)
C(2)–Os–P(2)	89.3(8)	C(3)–Os–P(3)	91.5(6)
C(2)–Os–P(3)	91.4(8)	P(2)–Os–P(3)	175.3(2)
<i>Angles in phospho-alkene ligand</i>			
Os–P(1)–C(1)	73.6(8)	C(1)–C(4)–F(1)	113.3(1.9)
Os–O(1)–C(1)	90.8(1.2)	C(1)–C(4)–F(2)	114.4(2.1)
P(1)–C(1)–O(1)	128.2(1.6)	C(1)–C(4)–C(3)	106.6(2.2)
P(1)–C(1)–C(4)	121.3(1.8)	F(1)–C(4)–F(2)	117.8(2.6)
O(1)–C(1)–C(4)	110.4(1.9)	F(2)–C(4)–F(3)	98.8(2.0)
		F(1)–C(4)–F(3)	103.5(2.2)
<i>Angles in carbon monoxide and triphenylphosphine ligands ^a</i>			
Os–C(2)–O(2)	177.1(21)	Os–C(3)–O(3)	179.2(1.8)
Os–P(2)–C(11)	111.4(6)	Os–P(3)–C(41)	111.2(7)
Os–P(2)–C(21)	116.9(7)	Os–P(3)–C(51)	115.4(7)
Os–P(2)–C(31)	115.3(6)	Os–P(3)–C(61)	118.4(7)
C(11)–P(2)–C(21)	101.4(8)	C(41)–P(3)–C(51)	105.5(9)
C(21)–P(2)–C(31)	104.9(8)	C(51)–P(3)–C(61)	102.6(1.0)
C(31)–P(2)–C(11)	105.5(9)	C(61)–P(3)–C(41)	102.2(9)

^a Angles at phenyl ring carbons not included.

Table 7

Atomic positions for $\text{Os}(\text{P}=\text{C}(\text{O})\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ (**10**)

Atom	x	y	z
Os	0.8608(0)	0.1359(1)	0.4013(0)
P(1)	0.8108(4)	0.0907(5)	0.3164(2)
P(2)	0.7685(3)	0.0415(4)	0.4215(2)
P(3)	0.9494(3)	0.2248(4)	0.3748(2)
C(1)	0.7725(11)	0.1987(17)	0.3259(9)
O(1)	0.7822(6)	0.2492(9)	0.3635(4)
C(2)	0.9232(12)	0.0320(16)	0.4260(7)
O(2)	0.9631(8)	−0.0332(10)	0.4395(5)
C(3)	0.8835(10)	0.2048(15)	0.4609(7)
O(3)	0.8970(7)	0.2449(10)	0.4967(5)
C(4)	0.7176(12)	0.2550(18)	0.2838(10)
F(1)	0.7253(11)	0.3537(12)	0.2845(7)
F(2)	0.7073(11)	0.2122(15)	0.2453(4)
F(3)	0.6533(10)	0.2412(17)	0.2925(6)
C(11)	0.7749(10)	0.0449(13)	0.4860(7)
C(12)	0.7233(11)	0.0816(16)	0.5051(8)
C(13)	0.7326(11)	0.0821(15)	0.5549(7)
C(14)	0.7961(11)	0.0523(15)	0.5841(8)
C(15)	0.8469(11)	0.0185(16)	0.5651(8)
C(16)	0.8374(11)	0.0102(15)	0.5153(7)
C(21)	0.7669(9)	−0.0970(13)	0.4102(6)
C(22)	0.7330(10)	−0.1613(13)	0.4342(7)
C(23)	0.7331(11)	−0.2614(16)	0.4270(8)
C(24)	0.7674(11)	−0.3001(15)	0.3954(7)
C(25)	0.8038(12)	−0.2407(17)	0.3709(8)
C(26)	0.8034(11)	−0.1331(18)	0.3778(7)
C(31)	0.6796(9)	0.0849(13)	0.3937(6)
C(32)	0.6336(10)	0.0212(15)	0.3647(7)
C(33)	0.5651(12)	0.0565(16)	0.3437(8)
C(34)	0.5451(10)	0.1500(16)	0.3548(7)
C(35)	0.5922(12)	0.2109(16)	0.3863(8)
C(36)	0.6586(10)	0.1812(14)	0.4036(7)
C(41)	1.0101(10)	0.2889(14)	0.4244(7)
C(42)	1.0451(11)	0.2269(15)	0.4609(7)
C(43)	1.0862(11)	0.2709(16)	0.5023(8)
C(44)	1.0954(11)	0.3706(18)	0.5065(8)
C(45)	1.0587(11)	0.4366(16)	0.4699(8)
C(46)	1.0185(11)	0.3937(15)	0.4280(7)
C(51)	0.9175(11)	0.3246(15)	0.3300(7)
C(52)	0.8838(11)	0.4075(16)	0.3424(8)
C(53)	0.8580(11)	0.4835(15)	0.3088(7)
C(54)	0.8707(13)	0.4764(18)	0.2641(9)
C(55)	0.9048(12)	0.3932(17)	0.2525(8)
C(56)	0.9287(11)	0.3133(16)	0.2849(8)
C(61)	1.0087(10)	0.1532(14)	0.3482(6)
C(62)	1.0714(12)	0.1928(16)	0.3435(8)
C(63)	1.1115(12)	0.1371(20)	0.3182(8)
C(64)	1.0940(12)	0.0402(17)	0.3025(8)
C(65)	1.0363(13)	−0.0025(18)	0.3107(6)
C(66)	0.9912(11)	0.0489(15)	0.3331(8)

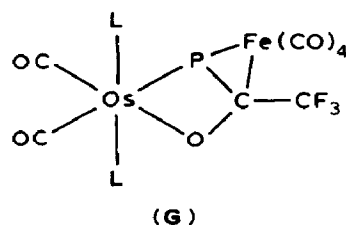
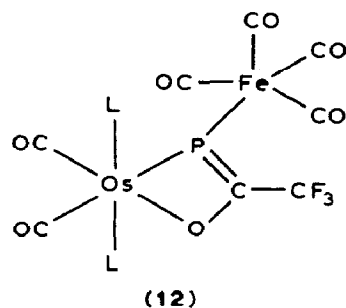
Table 8

Bond lengths for $\text{Os}\{\text{P}\{\text{Fe}(\text{CO})_4\}=\text{C}[\text{O}]\text{CF}_3\}(\text{CO})_2(\text{PPh}_3)_2$ (**12**) (Å)

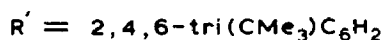
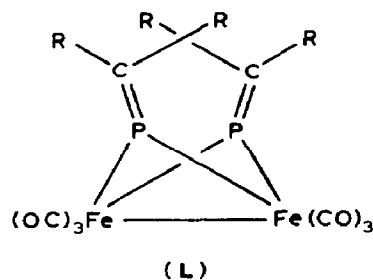
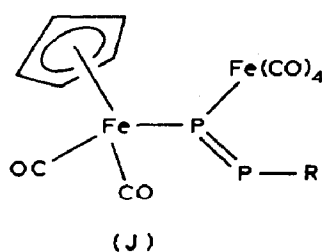
Os–P(1)	2.449(10)	Fe–P(1)	2.295(11)	P(1)–C(7)	1.64(3)
Os–P(2)	2.398(8)	Fe–C(3)	1.74(5)	C(7)–O(7)	1.38(3)
Os–P(3)	2.405(8)	Fe–C(4)	1.74(6)	C(7)–C(8)	1.57(6)
Os–O(7)	2.077(20)	Fe–C(5)	1.74(5)	C(8)–F(1)	1.27(5)
Os–C(1)	1.76(3)	Fe–C(6)	1.69(6)	C(8)–F(2)	1.28(5)
Os–C(2)	1.79(4)			C(8)–F(3)	1.23(5)
C(1)–O(1)	1.23(3)	C(3)–O(3)	1.15(4)	C(5)–O(5)	1.19(5)
C(2)–O(2)	1.17(4)	C(4)–O(4)	1.20(5)	C(6)–O(6)	1.20(6)
P(2)–C(11)	1.87(3)	P(2)–C(31)	1.82(3)	P(3)–C(51)	1.84(3)
P(2)–C(21)	1.81(3)	P(3)–C(41)	1.86(3)	P(3)–C(61)	1.75(3)

Bond lengths in triphenylphosphine phenyl rings

$i =$	1	2	3	4	5	6
C(<i>i</i> 1)–C(<i>i</i> 2)	1.37(4)	1.39(4)	1.38(4)	1.35(4)	1.41(4)	1.49(5)
C(<i>i</i> 2)–C(<i>i</i> 3)	1.52(5)	1.50(5)	1.38(4)	1.41(5)	1.38(5)	1.42(5)
C(<i>i</i> 3)–C(<i>i</i> 4)	1.36(4)	1.36(5)	1.38(5)	1.43(4)	1.39(5)	1.47(5)
C(<i>i</i> 4)–C(<i>i</i> 5)	1.39(4)	1.38(5)	1.44(5)	1.40(4)	1.33(5)	1.36(5)
C(<i>i</i> 5)–C(<i>i</i> 6)	1.41(4)	1.46(5)	1.40(4)	1.43(5)	1.40(5)	1.41(5)
C(<i>i</i> 6)–C(<i>i</i> 1)	1.35(4)	1.31(4)	1.44(4)	1.41(4)	1.44(4)	1.38(4)



structurally characterized complexes with bridging $\mu_2\text{-P}=\text{E}$ ($\text{E} = \text{PR}$, **J** [22]; $\text{E} = \text{CR}_2$, **L** [23]) ligands. In **L** there are very short iron–phosphorus bond lengths and the phospho-alkene bridges and iron–iron bond. An axially bound iron tetracarbonyl group is present in **J** and while the metal–phosphorus bond lengths are similar to those in **12** the metal–phosphorus–metal bond angle in **J** is much smaller than this angle in **12**. Comparison of the structure of **J** with its structurally characterized progenitor, **M**, [5] indicate that there are very few significant changes in *bond angles* or lengths in the iron tetracarbonyl adduct. The large bond angle at the phosphorus



(Continued on p. 373)

Table 9

Bond angles for $\text{Os}[\text{P}\{\text{Fe}(\text{CO})_4\}=\text{C}(\text{O})\text{CF}_3](\text{CO})_2(\text{PPh}_3)_2$ (12) ($^\circ$)*Angles at osmium*

P(1)–Os–P(2)	88.7(3)	O(7)–Os–C(1)	175.2(1.2)
P(1)–Os–P(3)	89.3(3)	O(7)–Os–C(2)	92.5(1.3)
P(1)–Os–O(7)	67.7(6)	O(7)–Os–P(2)	87.3(6)
P(1)–Os–C(1)	107.5(1.1)	O(7)–Os–P(3)	88.7(6)
P(1)–Os–C(2)	160.2(1.2)		
C(1)–Os–C(2)	92.2(1.6)	C(2)–Os–P(2)	88.4(1.2)
C(1)–Os–P(2)	92.3(1.0)	C(2)–Os–P(3)	92.3(1.2)
C(1)–Os–P(3)	91.7(1.0)	P(2)–Os–P(3)	176.0(3)

Angles in phospho-alkene ligand

Os–P(1)–Fe	153.7(5)	C(7)–C(8)–F(1)	108(5)
Os–P(1)–C(7)	78.8(1.2)	C(7)–C(8)–F(2)	109(4)
Os–O(7)–C(7)	99.2(1.8)	C(7)–C(8)–F(3)	114(5)
Fe–P(1)–C(7)	127.3(1.3)	F(1)–C(8)–F(2)	105(5)
P(1)–C(7)–O(7)	114(2)	F(2)–C(8)–F(3)	114(5)
P(1)–C(7)–C(8)	136(3)	F(1)–C(8)–F(3)	107(5)
O(7)–C(7)–C(8)	110(3)		

Angles at iron

P(1)–Fe–C(3)	93.5(1.4)	C(3)–Fe–C(5)	122(2)
P(1)–Fe–C(4)	83.9(1.6)	C(3)–Fe–C(6)	89(2)
P(1)–Fe–C(5)	87.9(1.6)	C(4)–Fe–C(5)	122(2)
P(1)–Fe–C(6)	177.3(1.8)	C(4)–Fe–C(6)	96(2)
C(3)–Fe–C(4)	116(2)	C(5)–Fe–C(6)	90(2)

Angles in carbon monoxide and triphenylphosphine ^a

Os–C(1)–O(1)	178(3)	Os–C(2)–O(2)	175(3)
Fe–C(3)–O(3)	174(4)	Fe–C(4)–O(4)	167(5)
Fe–C(5)–O(5)	170(4)	Fe–C(6)–O(6)	175(5)
Os–P(2)–C(11)	111.4(9)	Os–P(3)–C(41)	112.2(9)
Os–P(2)–C(21)	117.8(1.0)	Os–P(3)–C(51)	117.1(9)
Os–P(2)–C(31)	116.1(1.0)	Os–P(3)–C(61)	115.0(1.1)
C(11)–P(2)–C(21)	103.5(1.4)	C(41)–P(3)–C(51)	101.4(1.2)
C(21)–P(2)–C(31)	103.9(1.4)	C(51)–P(3)–C(61)	104.7(1.5)
C(11)–P(2)–C(31)	102.2(1.4)	C(41)–P(3)–C(61)	105.1(1.5)

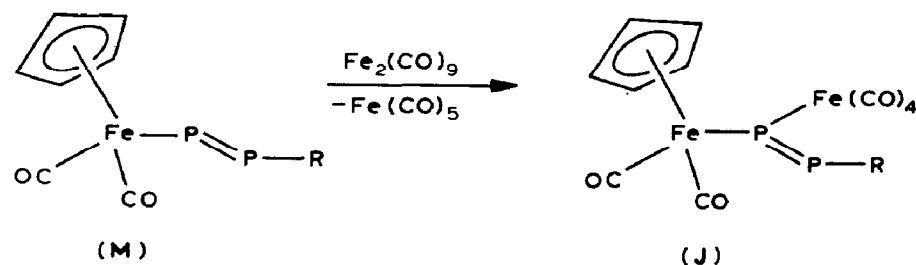
^a Angles at phenyl ring carbons not included.

Table 10

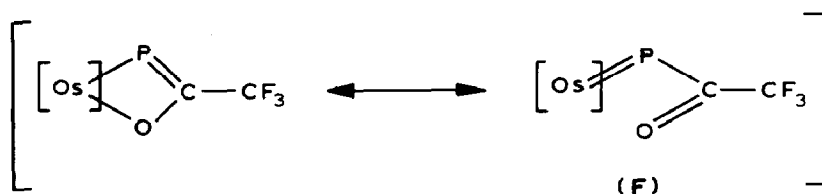
Atomic positions for $\text{Os}[\text{P}(\text{Fe}[\text{CO}]_4)=\text{C}(\text{O})\text{CF}_3](\text{CO})_2(\text{PPh}_3)_2$ (12)

Atom	x	y	z
Os	0.1193(1)	0.1237(1)	0.1472(1)
Fe	0.2009(4)	0.3715(3)	0.1359(3)
P(1)	0.1812(8)	0.2519(5)	0.1661(5)
P(2)	0.3075(7)	0.0918(5)	0.1404(4)
P(3)	-0.0640(7)	0.1585(5)	0.1614(4)
C(7)	0.210(3)	0.219(2)	0.238(2)
O(7)	0.1843(17)	0.1452(12)	0.2420(14)
C(8)	0.260(5)	0.251(3)	0.305(3)
F(1)	0.189(3)	0.295(2)	0.319(1)
F(2)	0.346(3)	0.291(2)	0.303(1)
F(3)	0.279(3)	0.204(2)	0.347(2)
C(1)	0.067(3)	0.113(2)	0.065(2)
O(1)	0.035(2)	0.105(1)	0.008(1)
C(2)	0.096(3)	0.028(2)	0.162(2)
O(2)	0.075(2)	-0.031(2)	0.174(1)
C(3)	0.146(4)	0.353(2)	0.057(2)
O(3)	0.117(3)	0.336(2)	0.005(2)
C(4)	0.103(4)	0.390(2)	0.181(2)
O(4)	0.044(3)	0.417(2)	0.213(2)
C(5)	0.344(4)	0.364(3)	0.170(2)
O(5)	0.444(4)	0.362(2)	0.185(2)
C(6)	0.221(4)	0.460(4)	0.116(3)
O(6)	0.227(3)	0.523(3)	0.100(2)
C(11)	0.323(2)	-0.010(2)	0.130(1)
C(12)	0.393(3)	-0.052(2)	0.174(2)
C(13)	0.399(3)	-0.133(2)	0.158(1)
C(14)	0.330(3)	-0.160(2)	0.105(2)
C(15)	0.256(3)	-0.113(2)	0.066(2)
C(16)	0.251(3)	-0.037(2)	0.078(2)
C(21)	0.422(2)	0.114(2)	0.208(1)
C(22)	0.498(3)	0.168(2)	0.199(2)
C(23)	0.592(3)	0.189(2)	0.253(2)
C(24)	0.598(3)	0.153(2)	0.309(2)
C(25)	0.515(4)	0.105(3)	0.317(2)
C(26)	0.425(3)	0.085(2)	0.263(2)
C(31)	0.355(2)	0.129(2)	0.073(1)
C(32)	0.302(2)	0.187(2)	0.037(1)
C(33)	0.342(3)	0.214(2)	-0.013(2)
C(34)	0.436(3)	0.180(2)	-0.025(2)
C(35)	0.497(3)	0.118(2)	0.008(2)
C(36)	0.452(3)	0.095(2)	0.058(2)
C(41)	-0.163(2)	0.079(2)	0.152(1)
C(42)	-0.181(3)	0.039(2)	0.098(2)
C(43)	-0.248(3)	-0.025(2)	0.093(2)
C(44)	-0.316(3)	-0.039(2)	0.137(2)
C(45)	-0.298(3)	0.007(2)	0.190(2)
C(46)	-0.222(3)	0.069(2)	0.200(2)
C(51)	-0.195(3)	0.225(2)	0.105(2)
C(52)	-0.095(3)	0.265(2)	0.063(2)
C(53)	-0.157(4)	0.314(2)	0.020(2)
C(54)	-0.272(4)	0.320(2)	0.018(2)
C(55)	-0.314(3)	0.279(2)	0.057(2)
C(56)	-0.263(3)	0.230(2)	0.105(2)

Table 10 (continued)

Atom	x	y	z
C(61)	-0.065(3)	0.196(2)	0.235(2)
C(62)	-0.109(3)	0.272(2)	0.240(2)
C(63)	-0.105(3)	0.288(2)	0.304(2)
C(64)	-0.064(3)	0.241(2)	0.359(2)
C(65)	-0.029(4)	0.172(3)	0.350(2)
C(66)	-0.024(3)	0.153(2)	0.288(2)

in **12** is most likely due to steric influences that arise from the nearby triphenylphosphine ligands. However the changes in $\text{OsP}=\text{C}[\text{O}]\text{CF}_3$ ring geometry are only partially understood in these terms. Two canonical descriptions can be drawn to represent the bonding in **10**:



In **10** the very long osmium–oxygen and short carbon–oxygen bond lengths suggest that the contribution by **F** is important, and that, therefore, there is some phosphinidene character in the bonding of **10**. Coordination of $\text{Fe}(\text{CO})_4$ to the phosphorus results in large changes in the bond lengths and angles at the oxygen, on the *other side of the ring*! There are no significant differences in the osmium–phosphorus and phosphorus–carbon bond lengths in the two structures. In **12** there is a much stronger osmium–oxygen interaction and the carbon–oxygen bond length is close to that of a single bond [24]. Possibly because of this stronger osmium–oxygen bond the P–C–O angle decreases by about 14° and the P–C–C angle opens up by an almost equal amount, in both **10** and **12** the O–C–C bond angles are the same. While the steric differences of the coordinated $\text{Fe}(\text{CO})_4$ group in **12** must effect these bond angles the bond lengths to oxygen indicate that the canonical form **F** is important in describing the bonding in the phospho-alkene ligand.

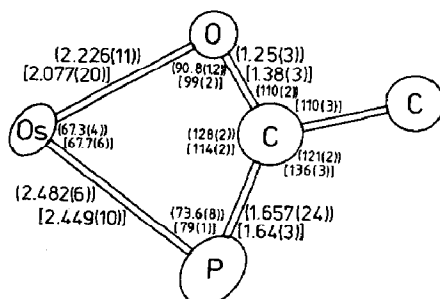


Fig. 4. Bond lengths within the $\text{OsP}=\text{C}[\text{O}]$ ring for **10** () and **12** [].

Reactions of $\text{Os}(\overline{\text{P}=\text{C}[\text{O}]\text{CF}_3})(\text{CO})_2(\text{PPh}_3)_2$ (10)

Like the acylphosphido complexes 2–3 the phosphorus in 10 has diminished nucleophilic character. Methylation of 10 with methyl iodide requires long periods

Table 11

Infrared spectroscopic data ^{a,b}

Complex	Acylphosphido			
	$\nu(\text{CO})$ ^c	$\nu(\text{PH})$	$\nu(\text{C}=\text{O})$	Other bands
$\text{OsCl}[\text{PH}(\text{C}[\text{O}]\text{-t-Bu})](\text{CO})_2(\text{PPh}_3)_2$ (2a)	2040, 1968	2301w	1619m	976w, 887m
$\text{OsCl}[\text{PH}(\text{C}[\text{O}]\text{CH}_3)](\text{CO})_2(\text{PPh}_3)_2$ (2b)	2029, 1967 1938(s)	2302w	1621s	1120m 870w, $\delta(\text{P-H})$ 283w, $\nu(\text{Os-Cl})$
$\text{OsCl}[\text{PH}(\text{C}[\text{O}]\text{OEt})](\text{CO})_2(\text{PPh}_3)_2$ (2c)	2027, 1963	2304w	1665m	1112s, $\nu(\text{O-C})$ 811w, $\delta(\text{P-H})$ 296m, $\nu(\text{Os-H})$
$\text{OsCl}[\text{PH}(\text{C}[\text{O}]\text{Ph})](\text{CO})_2(\text{PPh}_3)_2$ (2d)	2030, 1960	2293w	1573m	1198m; 867, $\delta(\text{P-H})$ 294m, $\nu(\text{Os-Cl})$
$\text{OsCl}[\text{PH}(\text{C}[\text{O}]\text{-p-C}_6\text{H}_4\text{-NO}_2)](\text{CO})_2(\text{PPh}_3)_2$ (2e)	2030, 1967	2292w	1574m	1519s, 1343s, $\nu(\text{NO}_2)$ 1191m; 883w, $\delta(\text{P-H})$ 840m.
$\text{OsCl}[\text{PH}(\text{C}[\text{O}]\text{CF}_3)](\text{CO})_2(\text{PPh}_3)_2$ (3)	2040, 1977 1948(s)	2322w	1630m	1259s, 1182s, 1138s, $\nu(\text{C-F})$ 895m, $\delta(\text{P-H})$
$\text{RuCl}[\text{PH}(\text{C}[\text{O}]\text{CF}_3)](\text{CO})_2(\text{PPh}_3)_2$ (7)	2030, 1995 1962(s)		1629m	1255s, 1202s, 1192s, 1136s, $\nu(\text{C-F})$ 898m, $\delta(\text{P-H})$ 293m, $\nu(\text{Ru-Cl})$
$\text{OsH}[\text{PH}(\text{C}[\text{O}]\text{CF}_3)](\text{CO})_2(\text{PPh}_3)_2$ (8)	2013, 1957	2332	1641m	2058m, $\nu(\text{Os-H})$ 1261s, 1191s, 1146s, $\nu(\text{C-F})$ 828s
$\text{OsCl}[\text{PH}(\text{C}[\text{O}]\text{CF}_3)](\text{CO})(\text{PMe}_3)(\text{PPh}_3)_2$ (9)	1946s, 1903w		1684m	1200s, 1191s, 1182s, 1135s, $\nu(\text{C-F})$ 957m, 858w, 846w, 789w
$\text{Os}(\overline{\text{P}=\text{C}[\text{O}]\text{CF}_3})(\text{CO})_2(\text{PPh}_3)_2$ (10)	2018, 1946 1922(s)			1300s, 1171s, 1161s, $\nu(\text{C-F})$ 1039s, $\nu(\text{C-O})$
$\text{OsCl}[\text{PMe}(\text{C}[\text{O}]\text{CF}_3)](\text{CO})_2(\text{PPh}_3)_2$ (11a)	2041, 1975 1952(s), 1948(s) 1938(s)		1512m	1269s, 1182s, 1129s, $\nu(\text{C-F})$ 991s, $\rho(\text{PMe})$, 895m. 296w, $\nu(\text{Os-Cl})$
$\text{OsI}[\text{PH}(\text{C}[\text{O}]\text{CF}_3)](\text{CO})_2(\text{PPh}_3)_2$ (11b)	2037, 1971 1960(s), 1945(s)		1512m	1267s, 1180s, 1129s, $\nu(\text{C-F})$ 993s, $\rho(\text{PMe})$
$\text{Os}(\overline{\text{P}[\text{Fe}(\text{CO})_4]=\text{C}[\text{O}]\text{CF}_3})(\text{CO})_2(\text{PPh}_3)_2$ (12)	2044sh 2031, 1955 1938, 1916			1314s, 1167s, 1125s, $\nu(\text{C-F})$ 1054s, $\nu(\text{C-O})$

^a In cm^{-1} . Spectra recorded as a Nujol mull between KBr or CsI discs and calibrated with polystyrene.

^b s = strong, m = medium, w = weak, sh = shoulder, (s) = dichloromethane solution spectrum. ^c Multiple $\nu(\text{CO})$ bands are attributed to solid state splitting. ^d Absorptions due to triphenylphosphine not given.

Table 12

NMR spectroscopic data for new compounds (δ in ppm; J in Hz)

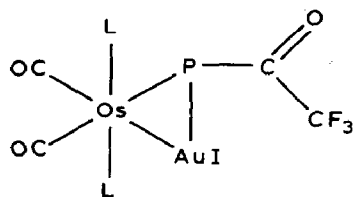
Compound	^1H NMR	^{31}P NMR
$\text{OsCl}[\text{PH}(\text{ClO})\text{-t-Bu}](\text{CO})_2(\text{PPh}_3)_2$	(2a) 0.77(s, 9, $\text{C}(\text{CH}_3)_3$); 3.76(dt, $^1J(\text{HP})$ 220.0, $^3J(\text{HP})$ 12.3, 1, PH)	
$\text{OsCl}[\text{PH}(\text{ClO})\text{CH}_3](\text{CO})_2(\text{PPh}_3)_2$	(2b) 1.79(d, $^3J(\text{HF})$ 44.3, $\text{PC}(\text{O})\text{CH}_3$); 3.08(dt, $^1J(\text{HP})$ 212.1, PH)	
$\text{OsCl}[\text{PH}(\text{ClO})\text{OEt}](\text{CO})_2(\text{PPh}_3)_2$	(2c) 0.89(t, $^3J(\text{HH})$ 7.0, 3, CH_3); 3.04(dt, $^1J(\text{HP})$ 216.0, $^3J(\text{HP})$ 13.1, 1, PH)	
$\text{OsCl}[\text{PH}(\text{ClO})\text{Ph}](\text{CO})_2(\text{PPh}_3)_2$	(2d) 3.66(q, $^3J(\text{HH})$ 7.0, 2, CH_2); 3.95(dt, $^1J(\text{HP})$ 224.0, $^3J(\text{HP})$ 10.5, 1, PH)	-11.6(s, PPh_3) -60.6(s, $\text{PH}[\text{C}(\text{O})\text{Ph}]$) -12.0(s, PPh_3) -52.2(s, $\text{PH}[\text{C}(\text{O})\text{R}]$)
$\text{OsCl}[\text{PH}(\text{ClO})\text{-}p\text{-C}_6\text{H}_4\text{NO}_2](\text{CO})_2(\text{PPh}_3)_2$	(2e) 3.88(dt, $^1J(\text{HP})$ 228.1, $^3J(\text{HP})$ 9.4, 1, PH) 7.52(d, $^3J(\text{HH})$ 8.7, 2, CH-ortho); 8.01(d, $^3J(\text{HH})$ 8.7, 2, CH-meta)	-12.4(d, $^2J(\text{PP})$ 5.0, PPh_3 -75.3(dm, $^2J(\text{PP})$ 5.0, $\text{PH}[\text{C}(\text{O})\text{R}]$) 20.1(dm, $^2J(\text{PP})$ 11.0, PPh_3) -54.3(tq, $^2J(\text{PP})$ 11.0, $^3J(\text{PP})$ 9.4, $\text{PH}[\text{C}(\text{O})\text{CF}_3]$)
$\text{OsCl}[\text{PH}(\text{ClO})\text{CF}_3](\text{CO})_2(\text{PPh}_3)_2$	(3) 3.55(dtq, $^1J(\text{HP})$ 237.9, $^3J(\text{HP})$ 11.6, $^4J(\text{HF})$ 2.0, 1, PH)	
$\text{RuCl}[\text{PH}(\text{ClO})\text{CF}_3](\text{CO})_2(\text{PPh}_3)_2$	(7) 3.44(dtq, $^1J(\text{HP})$ 226.0, $^3J(\text{HP})$ 11.7, $^4J(\text{HF})$ 1.9, 1, PH)	
$\text{OsH}[\text{PH}(\text{ClO})\text{CF}_3](\text{CO})_2(\text{PPh}_3)_2$	(8) -7.02(m, 1, OsH) 2.80(dm, $^1J(\text{HP})$ 258, $^3J(\text{HP})$ 10.0, 1, PH)	
$\text{OsCl}[\text{PH}(\text{ClO})\text{CF}_3](\text{CO})(\text{PMe})_3(\text{PPh}_3)_2$	(9) 1.35(d, $^2J(\text{HP})$ 9.9, $\text{P}(\text{CH}_3)_3$) [4.4-5.4] a (dt, $^1J(\text{HP})$ [220-340] a , $^3J(\text{HP})$ 9.5, 1, PH)	
$\text{Os}(\text{P}=\text{ClO})\text{CF}_3(\text{CO})_2(\text{PPh}_3)_2$	(10)	
$\text{OsCl}[\text{PMe}(\text{ClO})\text{CF}_3](\text{CO})_2(\text{PPh}_3)_2$	(11a) 0.8(dq, $^2J(\text{HP})$ 6.7, $^5J(\text{HF})$ 2.3, $\text{PC}(\text{H}_3)_3$)	13.82(dq, $^2J(\text{PP})$ 11.7, $^5J(\text{PF})$ 4.9, PPh_3); 74.01(tq, $^2J(\text{PP})$ 12.0, $^3J(\text{PF})$ 24.9, $\text{P}=\text{C}$)
$\text{Os}[\text{PH}(\text{ClO})\text{CF}_3](\text{CO})_2(\text{PPh}_3)_2$	(11b) 1.1(dq, $^2J(\text{HP})$ 8, $^5J(\text{HF})$ 2.3, $\text{PC}(\text{H}_3)_3$)	
$\text{Os}[\text{P}(\text{Fe}(\text{CO})_4)_2\text{ClO}]\text{CF}_3(\text{CO})_2(\text{PPh}_3)_2$	(12)	14.03(dq, $^2J(\text{PP})$ 35.5, $^3J(\text{PF})$ 5.2, PPh_3) 43.09(tq, $^2J(\text{PP})$ 35.5, $^3J(\text{PF})$ 21.2, $\text{P}(\text{Fe}(\text{CO})_4)_2\text{ClO}]\text{CF}_3$)

 a Precise chemical shift and coupling constant not observable as one branch obscured by aromatic protons, range of values given instead.

at elevated temperature (1 h, 40 °C). This contrasts with the almost instantaneous methylation of **1**. The product from this reaction, the neutral methyltrifluoroacylphosphido iodide complex (**11b**) is the result of methylation, ring opening and iodide substitution. In formal valence bond terms the reduced nucleophilicity of the phosphorus can be related to the decreased "*p* character" of the lone pair on the sp^2 -hybridized phosphorus.

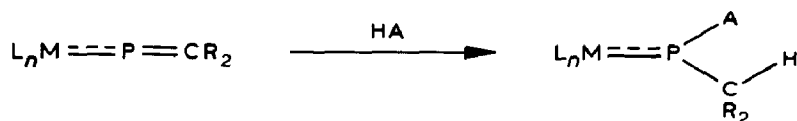
The only product of the reaction of **10** with aqueous hydrochloric acid is $[\text{OsCl}(\text{PH}_3)(\text{CO})_2(\text{PPh}_3)_2]^+$ which is isolated as the perchlorate salt after addition of lithium perchlorate to the reaction mixture during recrystallization. As was suggested for the reaction of **3** with acid this is most likely the result of acid catalyzed hydrolysis. In fact **3** is possibly the product formed in the first instance by addition of HCl to **10**.

Another Lewis acid which adds to the phosphorus is iron tetracarbonyl. This fragment is readily derived from diironnonacarbonyl and upon coordination to the phosphorus in **10** it returns a stable, slightly photolytically sensitive, orange complex **12**. Coordination of $\text{Fe}(\text{CO})_4$ leaves the η^2 -phospha-alkene ligand intact. Gold(I) iodide will also react with **10** to give a neutral complex which correctly analyzes for a simple gold adduct [7]. This fact, and the presence of an acyl carbonyl stretch at 1646 cm^{-1} in the infrared spectrum suggests that this product arises from ring opening and net AuI addition across the phosphorus–osmium bond:

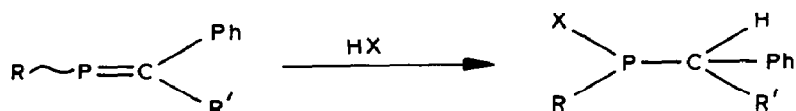


However, subsequent ^{31}P NMR studies indicated that this product is a complex mixture of which this species may be one of three inseparable compounds. It was not possible to grow crystals suitable for an X-ray diffraction study from this mixture. Attempted reactions of **10** with sulphur or trifluoroacetic anhydride both failed to give tractable products.

The reactions of other bent metallaphospha-alkene complexes resemble the reactions of **10**. For example, $\text{CpW}(\text{CO})_3(\text{P}=\text{C}(\text{SiMe}_3)_2)$ is protonated and methylates at the phosphorus [18]. However, linear phospha-alkene complexes react rapidly with protic reagents with a reverse polarity. Thus alcohol ($\text{A} = \text{OMe}$ or OEt), secondary amine ($\text{A} = \text{N}(\text{i-Pr})_2$), and thiol ($\text{A} = \text{SC}_6\text{F}_5$) all add across the carbon–phosphorus double bond so that the carbon is protonated and the nucleophilic fragment adds to the phosphorus [19]:



This reactivity pattern for the phosphorus–carbon double bond is similar to that seen in uncoordinated phospha-alkenes which are known to protonate at the carbon when treated with HA [25]:



As has been suggested [26] for pyramidal phosphido complexes the phosphorus lone pair in the bent metallaphospha-alkene complexes has enhanced nucleophilicity with respect to both the linear and uncoordinated analogues. This distinction in the reactivity patterns associated with distinct geometrical changes at the phosphorus is also found in planar and pyramidal phosphido complexes. Thus when there is a lone pair of electrons at the phosphorus, as in pyramidal phosphido and bent $\text{L}_n\text{MP}=\text{CR}_2$ complexes, there is pronounced nucleophilic character at the phosphorus. However, when these electrons are involved in multiple metal-phosphorus bonding, as in planar phosphido and linear $\text{L}_n\text{MP}=\text{CR}_2$ complexes, then the phosphorus is more susceptible to nucleophilic attack [11]. This structural/reactivity dichotomy may dominate much of the chemistry of low coordination number phosphorus donor ligands. Further studies are under way to elucidate the factors which control these ligand based reactivity patterns.

Experimental

The general techniques and instrumentation used in this work have been described before [8,27]. Acid halides and anhydrides were dried and distilled under nitrogen before use.

General preparation of acyl phosphido complexes (2a-e; 9)

The terminal phosphido complex, [8] either **1**, **4**, **5** or **6**, typically 0.2 g, was suspended in 10 ml dry THF under nitrogen. A two-fold excess of acid chloride or anhydride was then slowly added dropwise over 15 min. During the course of addition the slightly lime coloured suspension gradually dissolved to give pale yellow to deep red coloured solutions. These solutions were stirred for an additional half hour and the THF, and in some cases the volatile carboxylic acids produced, were then removed by vacuum transfer to a cold trap. The residue was left under vacuum for an additional 15–45 min. This dry residue was then dissolved in a minimum dichloromethane and transferred to a round bottom flask, 20 ml ethanol was then added, and the product crystallized by concentrating the solution in vacuo to about 5 ml. The crystalline products were then filtered off and washed successively with ethanol and n-hexane. Special details and any variation from this general technique are listed below for each case.

$\text{OsCl}[\text{PH}(\text{C}[\text{O}]\text{-}t\text{-Bu})](\text{CO})_2(\text{PPh}_3)_2$ (**2a**)

1 (0.223 g, 0.27 mmol) and pivaloyl chloride (0.037 g, 0.038 ml, 0.31 mmol) yield 0.141 g (57%) of the light yellow **2g**. M.p. 132°C as large cubes. Anal. Found: C, 55.53; H, 4.86. $\text{C}_{43}\text{H}_{40}\text{ClO}_3\text{OsP}_3$ calc: C, 55.93; H, 4.38%. Crystals suitable for X-ray diffraction were grown from THF/ethanol.

$\text{OsCl}[\text{PH}(\text{C}[\text{O}]\text{Me})](\text{CO})_2(\text{PPh}_3)_2$ (**2b**)

This was the most sensitive of all of the acyl phosphido complexes described herein. It will react with halogenated solvents and it must be handled in dry

oxygen-free solvents. 0.18 g of **1** was treated with 0.1 ml (1.6-fold excess) of acetyl chloride to give a yellow solution. As above the THF and volatiles were removed in vacuo and the residue redissolved in 2 ml THF. n-Hexane (15 ml) was then added, the suspension concentrated to about 5 ml, and an additional 15 ml n-hexane added. Filtration gave 0.12 g (63%) of light yellow solid. Analytical sample recrystallized from THF/ethanol under nitrogen. M.p. 181–183°C. Anal. Found: C, 54.13; H, 4.17. $C_{40}H_{34}ClO_3OsP_3$ calc: C, 54.51; H, 3.90%. 1H NMR spectrum determined as C_6D_6 solution in dry oxygen free conditions.

OsCl[PH(C[O]OEt)](CO)₂(PPh₃)₂ (2c)

1 (0.36 g, 0.43 mmol) and 0.3 ml ethyl chloroformate were heated at reflux in 20 ml THF for one half hour to give a very faint yellow solution. Work-up as above gave 0.35 g (88%) of needles m.p. 167°C. Anal. Found: C, 53.75; H, 4.30. $C_{41}H_{36}ClO_4OsP_3$ calc: C, 54.03; H, 3.99%.

OsCl[PH(C[O]Ph)](CO)₂(PPh₃)₂ (2d)

1 (0.39 g, 0.47 mmol) and 0.65 g, 0.47 mmol, 0.054 ml of benzoyl chloride treated as above. Work-up gave 0.38 g (86%) of bright yellow rods, m.p. 177°C. Anal. Found: C, 57.66; H, 4.36. $C_{45}H_{36}ClO_3OsP_3$ calc: C, 57.29; H, 3.85%.

OsCl[PH(C[O]-p-C₆H₄NO₂)](CO)₂(PPh₃)₂ (2e)

1 (0.31 g, 0.37 mmol) and 0.09 g of solid *p*-nitrobenzoyl chloride were dissolved in 10 ml THF to give a deep orange-red solution after 3 min. Work-up as above gave 0.22 g (60%) of orange needles, m.p. 181°C. Anal. Found: C, 55.73; H, 4.37; N, 1.32. $C_{45}H_{35}ClNO_5OsP_3$ calc: C, 55.68; H, 3.59; N, 1.42%.

OsCl[PH(C[O]CF₃)](CO)₂(PPh₃)₂ (3)

1 (0.34 g) in 20 ml dry THF was stirred vigorously and trifluoroacetic anhydride (0.085 g, 0.038 ml) was added dropwise *slowly* over 15 min during which the suspension dissolved to give a slightly yellow solution. (If the addition was too rapid the solution turned deep orange and the yield was much lower). This solution was treated as in **2** to yield 0.31 g, 81%, of light yellow needles, m.p. 210°C. Anal. Found: C, 51.53; H, 3.80. $C_{40}H_{31}ClF_3OsO_3P_3$ calc: C, 51.38; H, 3.32%.

RuCl[PH(C[O]CF₃)](CO)₂(PPh₃)₂ (7)

$RuCl(PH_2)(CO)_2(PPh_3)_2$ (**4**) (0.8 g, 1.06 mmol), was suspended in 10 ml THF and 0.42 g, 0.03 ml of trifluoroacetic anhydride was added *slowly* over the course of one half hour. Rapid addition led to unknown deeply coloured products and a dramatic drop in yield. Work-up as above gave 0.6 g (66%) of yellow needles m.p. 185–187°C. Anal. Found: C, 57.51; H, 4.35. $C_{40}H_{31}ClF_3O_3P_3Ru$ calc: C, 56.78; H, 3.70%.

OsH[PH(C[O]CF₃)](CO)₂(PPh₃)₂ (8)

$OsH(PH_2)(CO)_2(PPh_3)_2$ (**5**) (0.14 g, 0.16 mmol), in 10 ml dry THF was treated with excess trifluoroacetic anhydride (0.05 g, 0.039 ml, 1.5-fold excess) to give a bright yellow solution instantly. Work-up as for **3** gave 0.07 g (45%) of **8** as bright yellow rods, m.p. 99°C. Anal. Found: C, 50.72; H, 4.53. $C_{40}H_{32}F_3O_3OsP_3$ calc: C, 50.74; H, 3.51%.

OsCl[PH(C[O]CF₃)](PMe₃)(CO)(PPh₃)₂ (9)

OsCl(PH₂)(PMe₃)(CO)(PPh₃)₂ (**6**) (0.2 g) and trifluoroacetic anhydride (0.2 ml) were treated as in **8** to give a very slightly yellow solution. The solvents were removed and the residue recrystallized from dichloromethane/isopropanol which had been treated with one drop of DBU. The product was washed thoroughly with methanol, ethanol and n-hexane to give 0.09 g of colourless prisms, m.p. 209–211°C. Anal.: Found: C, 51.48; H, 4.40. C₄₂H₄₀ClF₃O₂OsP₄ calc: C, 51.30; H, 4.11%.

Os(P=C[O]CF₃)(CO)₂(PPh₃)₂ (10)

OsCl[PH(C[O]CF₃)](CO)₂(PPh₃)₂ (**3**) (0.34 g) and 0.04 g of sodium hydride (as a 65% dispersion in paraffin) were suspended in 30 ml THF and this mixture was heated at reflux for 1.5 h. During this period the solution became a bright yellow and there was gradual but steady evolution of hydrogen. This mixture was cooled and the excess of sodium hydride was removed by filtration through a celite pad washed thoroughly with dry THF (3 × 10 ml). The THF was then removed in vacuo and the residue redissolved in 20 ml dichloromethane, and 30 ml ethanol was added. Concentration of this mixture gave 0.2 g (89%) of **10** as yellow prisms m.p. 195°C. ¹H NMR indicated a 1/1 dichloromethane solvate present. Anal. Found: C, 49.95; H, 3.69. C₄₀H₃₀F₃O₃OsP₃ · CH₂Cl₂ calc: C, 50.01; H, 3.29%. Crystals suitable for X-ray diffraction were grown from THF/ethanol under nitrogen.

OsCl[PMe(C[O]CF₃)](CO)₂(PPh₃)₂ (11a)

OsCl[PH(C[O]CF₃)](CO)₂(PPh₃)₂ (**3**) 0.25 g, was dissolved in 20 ml dry THF and was treated with excess methyl iodide (0.1 ml). This mixture was stirred 1 min and then excess DBU was immediately added to give the instantaneous formation of a bright yellow solution. All solvents were removed in vacuo to give a yellow oily mass. A minimum of dichloromethane was added to dissolve this residue, an equal volume of ethanol added, and the solution was immediately concentrated to give bright yellow prisms. m.p. 164°C, 0.16 g, 57%. Anal. Found: C, 52.26; H, 4.03. C₄₁H₃₃ClF₃O₃OsP₃ calc: C, 51.87; H, 3.81%.

OsI[PMe(C[O]CF₃)](CO)₂(PPh₃)₂ (11b)

Os(P=C[O]CF₃)(CO)₂(PPh₃)₂ (**10**) (0.2 g, 0.22 mmol), and 0.1 ml of methyl iodide were heated at reflux in 10 ml dichloromethane for 1 h. The resulting bright yellow solution was then cooled and an equal volume of ethanol was added. Concentration in vacuo gave 0.15 g of bright yellow needles m.p. 148°C, 65%. Anal. Found: C, 47.39, H, 3.70. C₄₁H₃₃F₃IO₃OsP₃ calc: C, 47.31; H, 3.20%.

Os(P{Fe(CO)₄}=C[O]CF₃)(CO)₂(PPh₃)₂ (12)

Os(P=C[O]CF₃)(CO)₂(PPh₃)₂ (**10**) (0.05 g, 0.056 mmol), and 0.020 g, 0.056 mmol of freshly prepared diironnonacarbonyl were suspended in 10 ml THF. Within 10 min an orange solution formed. After 1 h the solvent was removed in vacuo and the residue was left under vacuum for a further hour to remove any residual iron pentacarbonyl. The remaining orange gum was dissolved in dichloromethane and 20 ml ethanol was added. Upon concentration, large orange crystals of **12** formed. Filtration followed by washes with ethanol and n-hexane gave 0.06 g (100%) of orange prisms m.p. 199°C. Anal. Found: C, 49.82; H, 3.31. C₄₄H₃₀F₃FeO₇OsP₃ calc: C, 49.54; H, 2.84%. Crystals suitable for X-ray diffraction were grown from toluene/ethanol.

Reaction of 3 and 10 with HCl

These complexes were dissolved in 10 ml dichloromethane and 10 ml ethanol was added. About 0.1 ml of 16 M HCl as an aqueous solution was added. After 1.5 hour lithium perchlorate, about 0.01 g, and 10 ml isopropanol were added. The product $[\text{OsCl}(\text{PH}_3)(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$ was isolated by concentration in vacuo and was identified by comparison of IR spectra with those of a known sample [8].

Crystal structure determinations

Data were collected on a CAD-4 diffractometer for **2a** and **12** at 25°C. Data for **10** were collected at -90°C on a Syntex diffractometer. Crystallographic details are given in Table 1. For **2a** the space group $P\bar{1}$ was assumed and verified by subsequent structure solution while for **10** and **12** the monoclinic space groups $C2/c$ and $P2_1/c$ were determined by systematic absences. The data in each cases were corrected for Lorentz and polarization effects and in the case of **2a** and **12** for decomposition. Absorption corrections were applied by the empirical ψ scan method.

The studies were solved by conventional Patterson and difference Fourier techniques, which determined the co-ordinates of all non-hydrogen atoms. Full-matrix least squares refinement with anisotropic thermal parameters for all atoms except the phenyl carbons converged to $R = 0.060$ ($R_w = 0.062$) for **2a**, $R = 0.071$ ($R_w = 0.064$) for **10**, and $R = 0.070$ ($R_w = 0.075$) for **12**. Final atomic positional parameters are listed in Tables 4, 7 and 10.

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