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1,2,3-Triphenylphosphirene derivatives of the iridium carbonyl clusters $[HIr_4(CO)_9L(\mu\text{-}PPh_2)]$ (L = CO, PPh_3) resulting from substitution, insertion and hydrometallation processes †

Peter B. Hitchcock,[a] John F. Nixon,*[a] Maria D. Vargas *[b] and Cláudio M. Ziglio[b]

[a] *School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UK BN1 9QJ*
[b] *Instituto de Química, Universidade Estadual de Campinas, CP 6154, Campinas, 13083-970, SP, Brazil*

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1,2,3-Triphenylphosphirene reacts with $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ **1**, at room temperature, to afford $[Ir_4(CO)_8(\mu_3\text{-}\eta^2\text{-}PhPCPh{=}CPh)(\mu\text{-}PhPCPh{=}CHPh)(\mu\text{-}PPh_2)]$ **2** which contains the phosphametallacycle (μ_3-η^2-PhPCPh=CPh) and the phosphidoalkenyl (μ-PhPCPh=CHPh) ligands arising from insertion and hydrometallation processes respectively. In contrast, the PPh_3 derivative of **1**, $[HIr_4(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ **3**, reacts selectively at room temperature with the phosphirene to give only CO substitution products, $[HIr_4(CO)_{9-n}(PPh_3)(\eta^1\text{-}PhPCPh{=}CPh)_n(\mu\text{-}PPh_2)]$ (n = 1, **4** and 2, **5**) which are the first carbonyl cluster compounds containing intact η^1-ligated phosphirene rings. High yield conversion of compound **4** into the phosphametallacycle species $[HIr_4(CO)_7(PPh_3)(\mu_3\text{-}\eta^2\text{-}PhPCPh{=}CPh)(\mu\text{-}PPh_2)]$ **6** is achieved under mild thermolytic conditions. An insight into the mechanism of formation of **2** was given by the reaction of the phosphirene ring with the anion $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ **1a** derived from **1**, followed by protonation, which gave $[HIr_4(CO)_8(\mu_3\text{-}\eta^2\text{-}PhPCPh{=}CPh)(\mu\text{-}PPh_2)]$ **7**, which is analogous to **6** with a CO ligand replacing PPh_3. Quantitative conversion of the hydride phosphametallacycle **7** into the labile phosphidoalkenyl cluster $[Ir_4(CO)_{11}(\mu\text{-}PhPCPh{=}CHPh)(\mu\text{-}PPh_2)]$ **8** is easily achieved in the presence of CO (1 atm, RT, 2 h), as a result of the reductive elimination of a C–H group. Compound **8** undergoes facile CO dissociation and co-ordination of the phosphidoalkenyl C=C bond to the metal centre to produce $[Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}PhPCPh{=}CHPh)(\mu\text{-}PPh_2)]$ **9**. The molecular structures of compounds **2**, **4**, **6** and **9** were established by X-ray diffraction studies and the structures of all compounds in solution were investigated by a combination of ^1H and $^{31}P\{^1H\}$ NMR studies.

Introduction

The chemistry of phosphirene and phosphirane ring systems has been reviewed[1,2] and also, more recently, discussed together with other phosphorus containing heterocycles.[3] Our previous studies have established that a single transition metal–ligand fragment can either co-ordinate to the phosphorus lone-pair electrons of the phosphirene or insert into one of the ring P–C bonds *via* a transient η^2-(P–C) complex. Complexes have been synthesised directly in the co-ordination sphere of metals or made from the preformed heterocycle.[4–7] Palladium catalysed alkyne insertions of phosphirenes ligated to $[W(CO)_5]$ are known[8,9] and CO can also be incorporated into the ring of phosphirene complexes[10] albeit at high temperature. These reactions no doubt involve transient four-membered metallacycles and, in support of this, several 14-electron fragments of the type ML_2 (M = Ni, Pt) readily insert into the P–C bonds of phosphirenes and phosphiranes under mild conditions.[11–14]

In contrast, studies of the interaction of these rings with carbonyl cluster compounds are scarce. To our knowledge, only the thermolytic reaction of $[Ru_3(CO)_{12}]$ with the 1,2,3-triphenylphosphirene ring has been reported to date, from which known $[Ru_4(CO)_{11}(\mu_4\text{-}PPh)(\mu_3\text{-}\eta^2\text{-}PhCCPh)]$ and $[Ru_3(CO)_8(\mu_3\text{-}\eta^6\text{-}C_4Ph_6P_2)]$ were obtained, the latter as the result of the opening of two rings and head-to-tail coupling through a P–C bond.[15] The nature of the various steps involved in the formation of these compounds is unknown and mechanistic investigations would probably be hampered by the harsh conditions of this reaction. In view of the many possible ways in which unsaturated molecules can interact with cluster compounds and undergo further transformations, we were interested to investigate the reaction of 1,2,3-triphenylphosphirene with the labile cluster $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ **1**, which is known to undergo facile substitution of up to two CO ligands by a range of phosphines.[16] Although **1** does not react with alkynes and alkenes,[17] phosphines containing unsaturated fragments, such as $Ph_2PC{\equiv}CPh$, can interact further with **1** to yield μ_4-η^3-Ph_2PCCPh containing species and products resulting from P–C bond activation,[18,19] further hydrometallation[20] or P–C bond formation.[21] We report herein our systematic studies of the reactions of this hydrido-phosphido cluster **1** and of its tuned derivatives $[HIr_4(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ **3** and $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ **1a** with 1,2,3-triphenylphosphirene which yielded novel: (i) η^1-phosphirene clusters as the result of CO substitution, (ii) μ_3-η^2-PhPCPh=CPh phosphametallacycle clusters, *via* the opening of a co-ordinated ring, and (iii) phosphidoalkenyl clusters containing the μ-PhPCPh=CHPh or μ_3-η^3-PhPCPh=CHPh groups arising from hydrometallation and further interaction of the C=C bond.

Results and discussion

Reaction of $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ 1 with 1,2,3-triphenylphosphirene

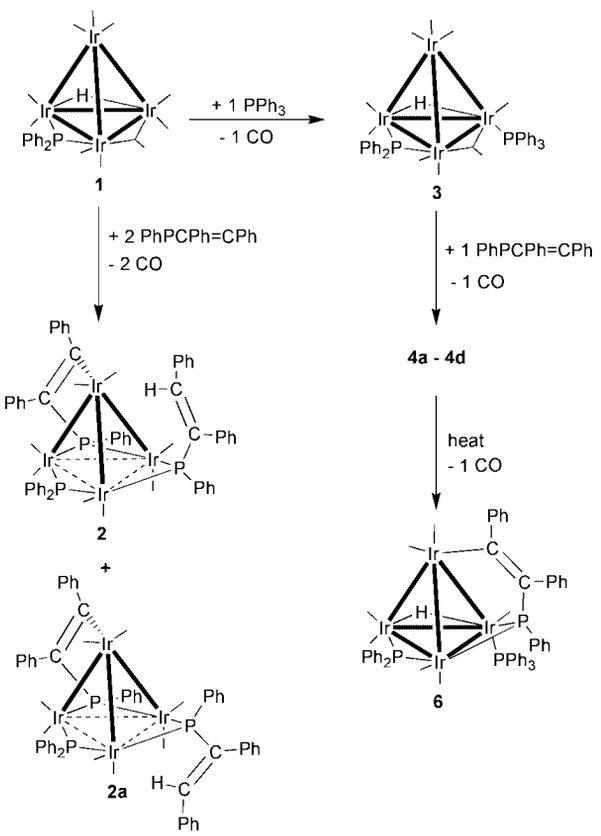
Treatment of equimolar amounts of the orange compound $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ **1** with 1,2,3-triphenylphosphirene in toluene at room temperature afforded, after 4 h, two dark-red

† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b003002n/

Table 1 ^{1}H and ^{31}P{^{1}H} NMR data[a] for $[Ir_4(CO)_8(\mu_3\text{-}\eta^2\text{-PhPCPh=CPh})(\mu\text{-PhPCPh=CHPh})(\mu\text{-PPh}_2)]$ **2**, **2a**, $[HIr_4(CO)_8(PPh_3)(\eta^1\text{-PhPCPh=CPh})(\mu\text{-PPh}_2)]$ **4a**–**4d**, $[HIr_4(CO)_7(PPh_3)(\mu_3\text{-}\eta^2\text{-PhPCPh=CPh})(\mu\text{-PPh}_2)]$ **6**, $[HIr_4(CO)_8(\mu_3\text{-}\eta^2\text{-PhPCPh=CPh})(\mu\text{-PPh}_2)]$ **7**, $[Ir_4(CO)_{11}(\mu\text{-PhPCPh=CHPh})(\mu\text{-PPh}_2)]$ **8** and $[Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-PhPCPh=CHPh})(\mu\text{-PPh}_2)]$ **9**

Compound	^{31}P{^{1}H} NMR (δ, J/Hz)	^{1}H NMR (δ, J/Hz)
2	2.8 (dd, $J_{P\text{-}P}$ 139, 129), −16.2 (dd, $J_{P\text{-}P}$ 139, 130), −40.2 (dd, $J_{P\text{-}P}$ 129, 130)	6.0–7.0 (m)
2a	4.0 (br), −10.8 (dd, $J_{P\text{-}P}$ 142, 130), −38.0 (t, $J_{P\text{-}P}$ 130)	6.0–7.0 (m), 8.2 (d, $J_{H\text{-}P}$ 21)
2a[b]	5.5 (dd, $J_{P\text{-}P}$ 130, 142), −13.0 (dd, $J_{P\text{-}P}$ 127, 142), −39.8 (dd, $J_{P\text{-}P}$ 127, 130); −4.2 (dd, $J_{P\text{-}P}$ 132, 138), −14.1 (dd, $J_{P\text{-}P}$ 127, 138), −38.2 (dd, $J_{P\text{-}P}$ 127, 132)	6.0–7.0 (m), 8.2 (d, $J_{H\text{-}P}$ 21)
4a–**4d**	273.7 (s), −5.9 (s), −203.1 (s), **4a**; 271.6 (s), 1.7 (s), −201.7 (s), **4b**; 257.6 (s), 0.5 (s), −153.9 (s), **4c**; 255.4 (s), 1.1 (s), −165.0 (s), **4d**	6.0–7.5 (m), −11.1 (d, $J_{H\text{-}P}$ 55), −11.3 (d, $J_{H\text{-}P}$ 55), −11.4 (d, $J_{H\text{-}P}$ 53), −11.7 (d, $J_{H\text{-}P}$ 50)
6	189.6 (dd, $J_{P\text{-}P}$ 176, 8), 154.0 (dd, $J_{P\text{-}P}$ 176, 4), 5.3 (dd)	6.4–7.8 (m), −9.3 (ddd, $J_{H\text{-}P}$ 35, 27, 8)
7	195.1 (d, $J_{P\text{-}P}$ 185), 167.8 (d)	6.5–8.0 (m), −11.1 (dd, $J_{H\text{-}P}$ 32, 29)
8[c]	21.2 (d, $J_{P\text{-}P}$ 219), −88.6 (d)	6.5–8.0 (m), 7.6 (d, $J_{H\text{-}P}$ 21)
9[c]	66.9 (d, $J_{P\text{-}P}$ 197), −73.5 (d)	6.5–8.0 (m), 6.3 (d, $J_{H\text{-}P}$ 21)

[a] Measured in $CDCl_3$ at room temperature unless otherwise stated. [b] Measured in CD_2Cl_2 at −50 °C. [c] Measured in C_6D_6.



Scheme 1

products, **2** and **2a**, in about 15 and 10% yield, respectively, in addition to unreacted **1** and other minor species which were not characterised. When compound **1** was treated with two equivalents (or a slight excess) of 1,2,3-triphenylphosphirene, **2** and **2a** were obtained in about 20 and 13%, respectively. Because compounds **2** and **2a** run very closely on the TLC plates (silica or alumina) with a variety of solvent systems, **2** was always isolated along with small quantities of **2a**, although **2a** was separated efficiently. Both species were fully characterised by spectroscopic methods and in the case of compound **2**, also by a single-crystal X-ray diffraction study. Spectroscopic data revealed that **2** and **2a** are isomers of formula $[Ir_4(CO)_8(\mu_3\text{-}\eta^2\text{-PhPCPh=CPh})(\mu\text{-PhPCPh=CHPh})(\mu\text{-PPh}_2)]$.

The ^{31}P{^{1}H} NMR spectrum of compound **2** in $CDCl_3$, at room temperature, exhibits three doublet of doublet resonances at δ 2.8 (dd, $J_{P\text{-}P}$ 139, 129 Hz), −16.2 (dd, $J_{P\text{-}P}$ 139, 130 Hz) and −40.2 (dd, $J_{P\text{-}P}$ 129, 130 Hz) (Table 1), indicating the presence of two phosphirene groups, in addition to a PPh_2 group. The three phosphorus resonances appear at higher frequency than expected for a η^1-phosphirene ligand,[5,7] suggesting that the two phosphirene groups had undergone ring opening to give two new phosphido ligands. Additionally the large magnitude of the $J_{P\text{-}P}$ couplings observed for the three phosphorus nuclei indicated that the phosphido ligands are located *trans* to each other, which is coherent with both these groups bridging the edges of a triangular face. The low frequency of the three phosphorus resonances strongly indicated that the metal atoms bridged by the phosphido groups are not involved in effective M–M bonds.[22]

The ^{1}H NMR spectrum of **2** in $CDCl_3$, at room temperature, shows no resonance in the hydride region, down to δ −30, which suggested that the hydride ligand had migrated to one of the phosphirene groups to afford the new phosphorus–carbon ligand PhPCPh=CHPh containing a phosphaalkenyl moiety (see Scheme 1). The resonance of the alkenyl hydrogen was not detected possibly being obscured by the phenyl hydrogen resonances at δ 6.0–7.5.

In order to establish unequivocally the structure of **2** a single-crystal diffraction study was undertaken. A perspective view of **2** is shown in Fig. 1, together with the labelling scheme. Relevant structural parameters are listed in Table 2. There are two independent molecules of **2** (A and B) present in the asymmetric unit which are enantiomeric isomers. The structure of the two molecules each consists of a distorted tetrahedron array of Ir, with the elongated base edges [mean A 3.091(2) and B 3.097(2) Å, compared with base to apex edges, A 2.768(2) and B 2.766(2) Å] spanned by a PPh_2 [Ir(2)–Ir(3) A 3.137(2) and B 3.124(2) Å] and PhPCPh=CHPh [Ir(1)–Ir(3) A 3.152(2) and B 3.170(2) Å] phosphido groups, both acting as three-electron donors, and by the four-electron donor phosphido fragment PhPCPh=CPh [Ir(1)–Ir(2) A 3.002(2) and B 2.978(2) Å], which bridges symmetrically the Ir(1)···Ir(2) edge [Ir(1)–P(3) A 2.310(8), B 2.315(8) and Ir(2)–P(3) A 2.307(8), B 2.316(8) Å] and also interacts with apex Ir(4) *via* a carbon atom [Ir(4)–C(10) A 2.17(3) and B 2.12(3) Å]. C(9) and C(10) are essentially sp^2 hybridised [C(9)–C(10) A 1.41(4), B 1.34(4) Å, P(3)–C(9)–C(10) A 116(2), B 115(2)°]. The hydrogen atom of the PhPCPh=CHPh group has not been located but the bond lengths and angles in the alkenyl moiety [C(59)–C(60) A 1.36(4), B 1.37(4) Å and P(1)–C(59)–C(60) A and B 115(2)°, C(59)–C(60)–C(41) A and B 130(3)°] are in accord with sp^2 hybridised carbon atoms. The Ir_3P_3 fragment is essentially coplanar which accounts for the large $^{2}J_{P\text{-}P}$ coupling constants ($^{2}J_{P\text{-}P}$ = 139, 130 and 129 Hz) observed in the ^{31}P{^{1}H} NMR spectrum of **2** (see Table 1). Compound **2** also bears two terminal CO ligands on each metal atom which are essentially linear. The compound is therefore formally a 62e system, the long average base Ir–Ir bonds reflecting the presence of the two extra electrons over the expected 60e tetrahedral structure. A similar trend has been previously observed for the triangular 50e cluster $[Ir_3(\mu\text{-PPh}_2)_3(CO)_5(Bu^tNC)_2]$ [mean Ir–Ir 3.235(2) Å].[23,24]

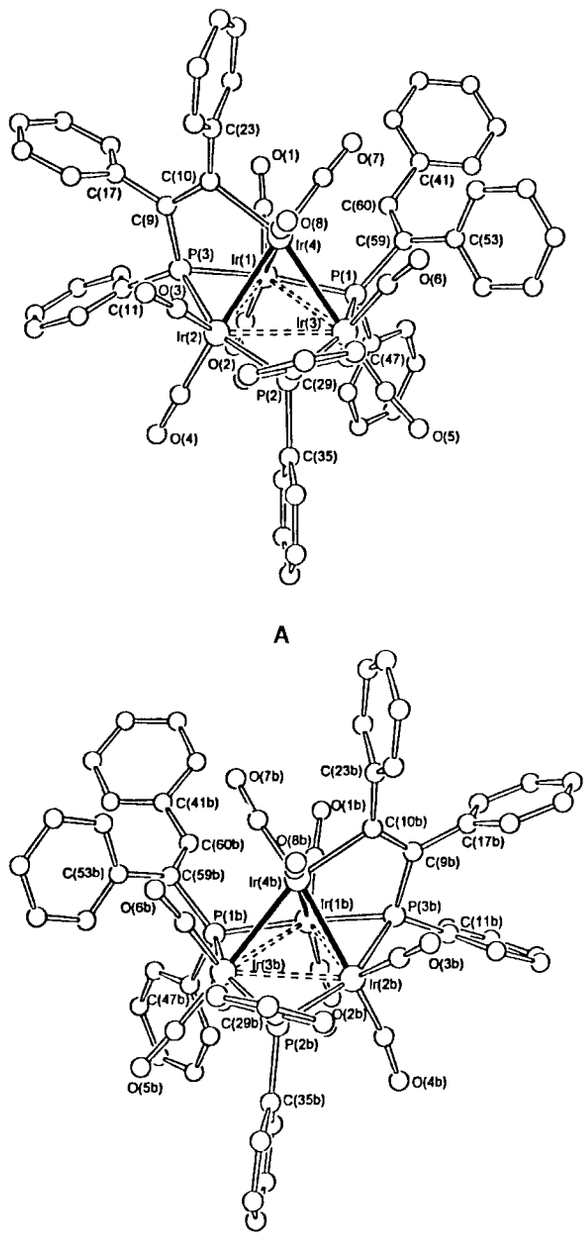


Fig. 1 Molecular structure of $[Ir_4(CO)_8(\mu_3\text{-}\eta^2\text{-PhPCPh=CPh})(\mu\text{-PhPCPh=CHPh})(\mu\text{-}PPh_2)]$ **2** (isomers A and B).

The similarity of the ^1H and $^{31}P\{^1H\}$ NMR and infrared spectra of **2** and **2a** (see Experimental section and Table 1) indicates that they possess very similar structures. The $^{31}P\{^1H\}$ NMR spectrum of **2a** in $CDCl_3$, at room temperature, consists of a very broad resonance at δ 4.0 and two sharp resonances at δ −10.8 (dd, $J_{P\text{-}P}$ 142, 130 Hz) and −38.0 (t, $J_{P\text{-}P}$ 130 Hz). The ^1H NMR spectrum of **2a** shows no hydride signal down to δ −30, suggesting that this compound has undergone the same type of ligand rearrangement observed in **2**. Moreover, in this case, a doublet assigned to an alkenyl hydrogen was observed at δ 8.2 (d, $J_{H\text{-}P}$ 21 Hz), confirming the presence of the phosphidoalkenyl ligand in **2a**. The fact that the alkenyl hydrogen resonance of **2a** appears at higher frequency to that of the isomer **2** suggests that these compounds differ with respect to the orientation of the phosphidoalkenyl ligand on the cluster frameworks of **2** and **2a**. The proposed structure of compound **2a** is shown in Scheme 1.

When a CD_2Cl_2 solution of **2a** was cooled to −50 °C the phosphorus resonances in the $^{31}P\{^1H\}$ NMR spectrum split into two groups of three signals at δ 5.5 (dd, $J_{P\text{-}P}$ 130, 142 Hz), −13.0 (dd, $J_{P\text{-}P}$ 127, 142 Hz) and −39.8 (dd, $J_{P\text{-}P}$ 127, 130 Hz), and δ −4.2 (dd, $J_{P\text{-}P}$ 132, 138 Hz), −14.1 (dd, $J_{P\text{-}P}$ 127, 138 Hz) and −38.2 (dd, $J_{P\text{-}P}$ 127, 132 Hz), respectively, suggesting that compound **2a** exists in solution as a mixture of two isomers which interconvert at room temperature. The two groups of signals show similar patterns indicating that the two compounds have very similar structures. It is therefore proposed that the two isomers differ only with respect to the orientation of the alkenyl group, and that they interconvert *via* its rotation around the P–C phosphidoalkenyl bond (see Scheme 1). It is interesting that the $^{31}P\{^1H\}$ NMR spectrum of compound **2** remained unchanged down to −60 °C. Therefore, either the alkenyl group in **2** does not rotate, *i.e.* the compound exists in only one form, or rotation of this group in **2** is less constrained by the other ligands than in **2a** and only the average structure of the isomers is seen in the NMR time scale.

Treatment of compound **1** with 1,2,3-triphenylphosphirene failed to lead to the product resulting from the incorporation of only one phosphirene ring, even when the reaction was carried out at low temperature (−30 °C) in CH_2Cl_2, instead of THF, and with slow addition of a dilute solution of the phosphirene (1 equivalent) to the cluster solution. We have shown previously,[16,19] however, that cluster **1** reacts with one equivalent of a variety of phosphines $L = P(C_6H_4X\text{-}4)_3$, X = OMe, Me, H, Cl and F and $Ph_2PC{\equiv}CPh$ to afford mono-substituted compounds in excellent yields and that bis-substitution products are only obtained in the presence of an excess of L. Selective formation of $[HIr_4(CO)_9L(\mu\text{-}PPh_2)]$ is consistent with the fact that an increase in the cluster electron density, as the result of the substitution of a CO group for a better σ-donor and worse π-acceptor ligand, enhances the metal back donation to the remaining CO groups, making the second CO substitution less favourable. Furthermore, nucleophilic attack would also be less favourable due to both electronic and steric reasons. The phosphirene ring possesses much lower basicity and smaller cone angle in comparison with most phosphines and both factors are probably responsible for the low selectivity of its reaction with compound **1**. Hence, in an attempt to isolate derivatives of **1** containing a single intact phosphirene ring, and possibly obtain an insight into the mechanism of formation of **2** and **2a**, the reactions of 1,2,3-triphenylphosphirene with $[HIr_4(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ **3** and the anionic cluster $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ **1a**, which are less labile than **1**, were investigated and these are discussed below.

Reaction of $[HIr_4(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ 3 with 1,2,3-triphenylphosphirene

The red compound $[HIr_4(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ **3** reacted with 1,2,3-triphenylphosphirene, in toluene at room temperature, to give, after 3 h, $[HIr_4(CO)_8(PPh_3)(\eta^1\text{-PhPCPh=CPh})(\mu\text{-}PPh_2)]$ **4** in *ca.* 60% yield (see Scheme 1), in addition to the bis-substituted species $[HIr_4(CO)_7(PPh_3)(\eta^1\text{-PhPCPh=CPh})_2(\mu\text{-}PPh_2)]$ **5**, in 10% yield, identified on the basis of its IR spectrum. Compound **4** was formulated and fully characterised on the basis of analytical and spectroscopic data (see Experimental section and Table 1).

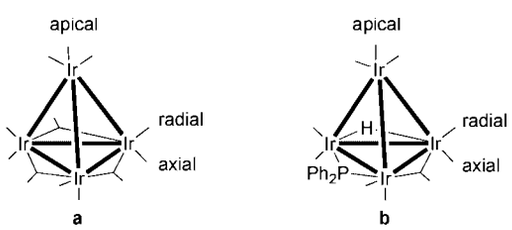
The ^1H and $^{31}P\{^1H\}$ NMR spectra of **4** established the presence of four isomers (**4a**–**4d**) in solution, in approximate ratios **4a**:**4b**:**4c**:**4d** ≈5:1:1.5:2. The $^{31}P\{^1H\}$ NMR spectrum of the **4a**–**4d** mixture comprises four groups of three singlets at δ 273.7, −5.9 and −203.1 (**4a**), δ 271.6, 1.7 and −201.7 (**4b**), δ 257.6, 0.5 and −153.9 (**4c**), δ 255.4, 1.1 and −165.0 (**4d**). In each case, the two highest frequency resonances were assigned to the $\mu\text{-}PPh_2$ and PPh_3 groups, by comparison with the respective chemical shifts of the precursor **3** (δ_{PPh_2} 276.2 and δ_{PPh_3} 0.42). The lowest frequency resonances were attributed to the single phosphirene ligand in each isomer. The fact that the phosphirene phosphorus resonance appeared at low frequency

Table 2 Selected intramolecular distances (Å) and angles (°) for compound **2**

	A	B		A	B
Ir(1)–Ir(2)	3.002(2)	2.978(2)	P(1)–C(59)	1.81(3)	1.84(3)
Ir(1)–Ir(3)	3.152(2)	3.170(2)	C(59)–C(60)	1.36(4)	1.37(4)
Ir(1)–Ir(4)	2.731(2)	2.734(2)	C(60)–C(41)	1.53(3)	1.43(3)
Ir(2)–Ir(3)	3.137(2)	3.124(2)	C(59)–C(53)	1.47(3)	1.48(3)
Ir(2)–Ir(4)	2.738(2)	2.736(2)	P(2)–C(29)	1.76(2)	1.80(2)
Ir(3)–Ir(4)	2.839(2)	2.736(2)	P(2)–C(35)	1.82(2)	1.79(2)
Ir(1)–P(1)	2.356(8)	2.346(8)	P(3)–C(9)	1.74(3)	1.77(3)
Ir(3)–P(1)	2.306(8)	2.319(8)	C(9)–C(10)	1.41(4)	1.34(4)
Ir(2)–P(2)	2.353(8)	2.362(8)	C(9)–C(17)	1.50(3)	1.50(3)
Ir(3)–P(2)	2.327(8)	2.323(8)	C(10)–C(23)	1.41(3)	1.45(3)
Ir(1)–P(3)	2.310(8)	2.315(8)	C(10)–Ir(4)	2.17(3)	2.12(3)
Ir(2)–P(3)	2.307(8)	2.316(8)	P(3)–C(11)	1.80(2)	1.77(2)
Ir(1)–P(1)–Ir(3)	85.1(2)	85.6(3)	P(1)–Ir(1)–P(3)	155.7(3)	155.4(3)
Ir(2)–P(2)–Ir(3)	84.2(3)	83.6(3)	P(2)–Ir(2)–P(3)	156.7(3)	157.8(3)
Ir(1)–P(3)–Ir(2)	81.1(3)	80.0(3)	P(1)–Ir(3)–P(2)	149.6(3)	148.4(3)
Ir(1)–P(1)–C(59)	120.3(9)	119.7(9)	Ir(2)–P(3)–C(9)	113(1)	111(1)
C(47)–P(1)–C(59)	103(1)	103(1)	P(3)–C(9)–C(10)	116(2)	115(2)
P(1)–C(59)–C(60)	115(2)	115(2)	P(3)–C(9)–C(17)	125(2)	122(2)
P(1)–C(59)–C(53)	120(2)	120(2)	C(9)–C(10)–C(23)	129(3)	127(3)
C(59)–C(60)–C(41)	130(3)	130(3)	C(9)–C(10)–Ir(4)	112(2)	115(2)
C(29)–P(2)–C(35)	105(1)	104(1)	C(23)–C(10)–Ir(4)	119(2)	118(2)

in the four isomers suggested that the ring remains intact and thus acts as an η^1 ligand. The ^{1}H NMR spectrum confirmed the presence of the hydride ligand in all isomers: δ −11.1 (d, $J_{H\text{-}P}$ 55 Hz), −11.3 (d, $J_{H\text{-}P}$ 55 Hz), −11.4 (d, $J_{H\text{-}P}$ 53 Hz) and −11.7 (d, $J_{H\text{-}P}$ 50 Hz). The similarity between the NMR data of the four isomers indicated that their structures differ only with respect to the position of the incoming phosphirene ligand.

^{31}P NMR data of phosphine derivatives of iridium carbonyl clusters have been used to assign the co-ordination site of the P-donor ligand,[25] and a similar correlation was used herein to assign the positions of the η^1-phosphirene ligand in the four isomers **4a**–**4d**. This assignment is based on the observation that in the ^{31}P NMR spectra of reported phosphine derivatives of $[Ir_4(CO)_{12}]$, the co-ordination chemical shifts of the ligands, $\Delta\delta$ ($\delta_{\text{co-ordinated}} - \delta_{\text{free ligand}}$), decrease in the sequence radial > axial ≈ apical (see Scheme 2a).[25] Isomers **4a** and **4b** present



Scheme 2

negative $\Delta\delta$ values for the co-ordinated phosphirene (−12.7 and −10.7 ppm, respectively), which suggested that the rings occupy axial or apical positions (see Scheme 2b). Considering that apical substitution was established unequivocally by an X-ray diffraction study of one of these isomers (Fig. 2) that contains the phosphirene ligand directed towards the tetrahedron face that bears a bridging hydride ligand, the two isomers probably differ with respect to the position of the phosphirene ligand on the apical iridium atom (see Scheme 3). It is thus proposed that the isomer, whose structure was not determined in the solid state, possesses the phosphirene ligand pointed towards the tetrahedron face that bears a bridging CO, for steric reasons, rather than the face containing the bulky PPh_2 group. Furthermore, the large $\Delta\delta$ values of **4c** and **4d** (37.1 and 26.0 ppm) suggest that the phosphirene ligands occupy radial positions in these two isomers (see Scheme 3). Because of the bulky PPh_3 group, it is proposed that the phosphirene ligand

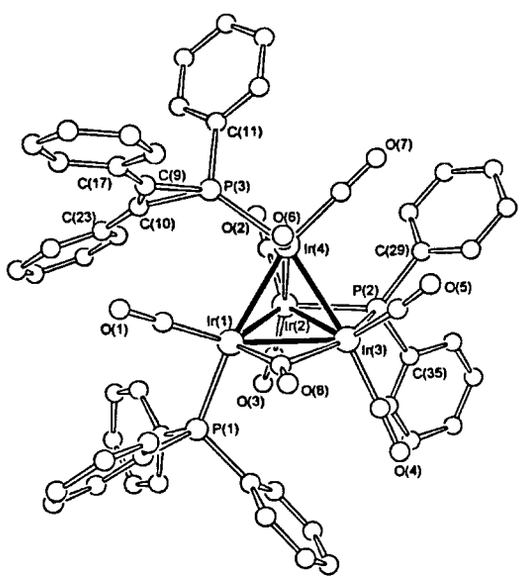
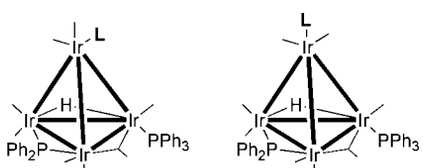
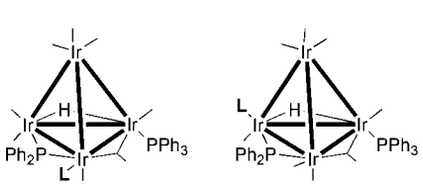
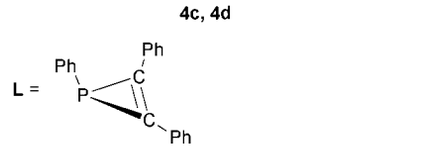


Fig. 2 Molecular structure of $[HIr_4(CO)_8(\eta^1\text{-PhPCPh=CPh})(PPh_3)(\mu\text{-}PPh_2)]$ **4**.







Scheme 3

Table 3 Selected intramolecular distances (Å) and angles (°) for compounds **4** and **6**

	4	**6**		**4**	**6**
Ir(1)–Ir(2)	2.798(1)	2.915(2)	Ir(1)–C(8)	1.89(3)	
Ir(1)–Ir(3)	2.753(1)	2.736(2)	Ir(3)–C(8)	2.24(2)	
Ir(1)–Ir(4)	2.704(1)	2.675(2)	P(2)–C(29)	1.814(1)	1.812(1)
Ir(2)–Ir(3)	2.804(1)	2.875(2)	P(2)–C(35)	1.830(1)	1.840(1)
Ir(2)–Ir(4)	2.727(1)	2.720(2)	P(3)–C(9)	1.74(2)	1.78(3)
Ir(3)–Ir(4)	2.720(1)	2.736(2)	P(3)–C(10)	1.77(2)	
Ir(1)–P(1)	2.331(6)	2.360(9)	C(9)–C(10)	1.30(3)	1.32(4)
Ir(2)–P(2)	2.291(5)	2.340(9)	C(9)–C(17)	1.48(2)	1.54(3)
Ir(3)–P(2)	2.308(5)	2.285(9)	C(10)–C(23)	1.44(2)	1.39(3)
Ir(1)–P(3)		2.250(8)	C(10)–Ir(4)		2.17(3)
Ir(2)–P(3)		2.348(9)	P(3)–C(11)	1.88(2)	1.81(1)
Ir(4)–P(3)	2.319(6)				
P(1)–Ir(1)–Ir(4)	166.5(1)	166.3(2)	P(3)–C(9)–C(17)	142.6(1)	120(2)
P(1)–Ir(1)–Ir(3)	111.1(1)	105.7(2)	P(3)–C(10)–C(23)	146.4(1)	
P(1)–Ir(1)–C(1)	91.7(6)	98.0(1)	C(9)–C(10)–C(23)	146(2)	130(3)
Ir(2)–P(2)–Ir(3)	75.1(1)	76.9(3)	C(10)–C(9)–C(17)	148(2)	122(3)
C(29)–P(2)–C(35)	101.8(7)	102.4(1)	Ir(1)–P(3)–C(9)		113.3(1)
P(3)–Ir(4)–Ir(3)	154.0(1)		Ir(2)–P(3)–C(9)		107.8(1)
Ir(4)–P(3)–C(11)	124.8(1)		Ir(4)–C(10)–C(23)		117.3(1)
Ir(4)–P(3)–C(9)	125.5(8)		P(1)–Ir(1)–P(3)		112.8(3)
Ir(4)–P(3)–C(10)	130.7(8)		P(2)–Ir(2)–P(3)		154.6(3)
P(3)–C(9)–C(10)	69.5(1)	118(2)	Ir(1)–C(8)–Ir(3)	83.0(1)	
P(3)–C(10)–C(9)	66.9(1)				

in each isomer is bonded to a distinct iridium atom bridged by the PPh_2 group.

A mixture of **4a**–**4d** was crystallised from CH_2Cl_2/hexane, and suitable crystals for X-ray analysis were isolated and later shown to be of either isomers **4a** or **4b**. The molecular structure of this isomer in the solid state is shown in Fig. 2, together with the atomic labelling scheme. Relevant structural parameters are listed in Table 3. The molecule exhibits the same basic ligand arrangement observed for **3**,[16] containing a hydride, phosphido and carbonyl ligands bridging the base edges, the main difference being the presence of a triphenylphosphirene ring in place of a CO ligand on the apical Ir(4) atom. The heterocyclic ring is bonded *via* the phosphorus atom [Ir(4)–P(3) 2.319(6) Å] that is *trans* to Ir(3) [P(3)–Ir(4)–Ir(3) 154.0(1)°] and is oriented over the Ir(1)–Ir(2)–Ir(4) face bridged by the hydride ligand. Co-ordination of the ring to the iridium centre does not result in an increase in the intracyclic C(9)–C(10) bond length [1.30(3) Å in **4** compared to 1.299(3) Å in the free ligand[26]], however a decrease in the mean intracyclic P–C bond lengths was observed from 1.820(3) Å in the free ligand to 1.76(2) Å in **4**. Similar effects have been observed upon co-ordination of triphenylphosphirene to the mononuclear fragments $[PtCl_2(PEt_3)]$[7,12] and $[W(CO)_5]$[26,27] and these changes have been attributed to the suppression of the destabilising interaction between the lone pair at P and the double bond.[27]

The Ir–Ir distances in the Ir_4 tetrahedron in compound **4a** or **4b** are comparable to values reported for the precursor **3**.[16] The three basal edges which are bridged by a carbonyl [Ir(1)–Ir(3) 2.753(1) Å], a hydride which was located with the help of a space filling diagram [Ir(1)–Ir(2) 2.798(1) Å], and a PPh_2 group [Ir(2)–Ir(3) 2.804(1) Å], respectively, are all longer than the three unbridged apex-to-base edges (average 2.717 Å). All seven terminal CO ligands are essentially linear and are distributed, one on Ir(1) and two on each of the other Ir atoms in such a way that all metal atoms obey the 18 electron rule. To our knowledge, this is the first carbonyl cluster with an intact phosphirene ring reported to date.

The contrasting behaviour of the triphenylphosphirene towards co-ordination to clusters **1** and **3** is not easily rationalised. The phosphirene ring opening process is believed to be governed by donation of metal d-electrons into the σ*(PC) antibonding orbital of the phosphirene ligand.[12] Considering that the PPh_3 containing cluster **3** possesses higher metal electron density than **1**, it might be expected that activation of the phosphirene P–C bond in **4a**–**4d** would be far more facile than in an analogous η^1-phosphirene derivative of cluster **1**, but this apparent contradiction can be explained on the basis of kinetics considerations. It is reasonable to assume that this ring opening process in both cluster compounds involves initial CO substitution and co-ordination of the phosphorus lone pair to a metal centre, followed by activation of the P–C bond *via* η^2-co-ordination to an adjacent metal centre. This process would require dissociation of an additional CO group (or alternatively cleavage of a M–M bond) to give a site vacancy for the interaction with the P–C bond. It is thus understandable that the transient CO substituted η^1-phosphirene derivative of cluster **1** would be more labile than **4a**–**4d** with its η^1-phosphirene and PPh_3 ligands, the latter exercising a stabilising effect on the remaining CO ligands. With the aim of inducing CO dissociation and subsequent ring opening process in **4a**–**4d**, the thermal reaction of the isomeric mixture was investigated and is discussed below.

Thermolysis of $[HIr_4(CO)_8(PPh_3)(\eta^1\text{-PhPCPh=CPh})(\mu\text{-}PPh_2)]$ 4a–4d

As anticipated, when the red complexes **4a**–**4d** were heated in toluene at 50 °C for 12 h, a rearrangement occurred to give the green compound $[HIr_4(CO)_7(PPh_3)(\mu_3\text{-}\eta^2\text{-PhPCPh=CPh})(\mu\text{-}PPh_2)]$ **6** in 60% yield, after purification by TLC and crystallisation (see Scheme 1), besides unreacted **4** (10%) and other decomposition products. Compound **6** was fully characterised by spectroscopic methods (see Experimental section and Table 1) and by a single-crystal X-ray diffraction study.

The $^{31}P\{^1H\}$ NMR spectrum of **6** consists of three doublet of doublet patterns at δ 189.6 (dd, $J_{P\text{-}P}$ 176, 8 Hz), 154.0 (dd, $J_{P\text{-}P}$ 176, 4 Hz) and 5.3 (dd), respectively, the high frequency signals being assigned to the PPh_2 group and phosphirene ring and the low frequency signal to the PPh_3 ligand. The large chemical shift change of the phosphirene, from about δ −200 in **4a**–**4d** to δ 189.6 or 154.0 in **6**, in addition to the large $J_{P\text{-}P}$ coupling with the PPh_2 group, confirmed that the intact phosphirene ring had undergone conversion to a η^2-PhPCPh=CPh phosphido ligand coplanar with the PPh_2 group. In contrast with species **2**, **2a**, the ^{31}P NMR data for **6** indicate that the ring opening process did not bring about lengthening

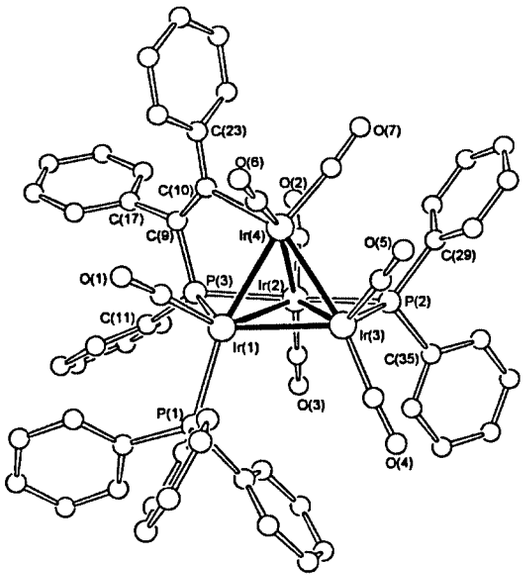


Fig. 3 Molecular structure of $[HIr_4(CO)_7(PPh_3)(\mu_3\text{-}\eta^2\text{-}PhPCPh{=}CPh)(\mu\text{-}PPh_2)]$ **6**.

of the M–M bond between the metal atoms bridged by the phosphido ligands.[22] The ^{1}H NMR spectrum of **6** in $CDCl_3$, at room temperature, shows a resonance at δ −9.3 (ddd, $J_{H\text{-}P}$ 35, 27, 8 Hz) for a hydride ligand. The presence of this hydride ligand suggested that the rearrangement of the phosphirene ring had led to a phosphametallacycle ligand, similar to that in **2**, **2a**, as a result of P–C bond oxidative addition. The large $J_{H\text{-}P}$ couplings between the hydride and the two phosphido phosphorus nuclei, observed in the ^{1}H NMR spectrum, indicated that the three nuclei are located *trans* to each other, possibly in a triangular face of the polyhedron. A structure for compound **6** was thus proposed, as shown in Scheme 1, and was confirmed by a single-crystal X-ray diffraction study.

The molecular structure of **6** in the solid state is shown in Fig. 3, together with the atomic labelling scheme. Relevant structural parameters are shown in Table 3. The structure contains a distorted tetrahedral arrangement of metal atoms [average Ir–Ir 2.772(2) Å] with short base-to-apex edges [average Ir–Ir 2.710(1) Å] and longer base edges bridged by a hydride [Ir(1)–Ir(3) 2.736(2) Å], located with the help of a space filling diagram, a μ-PPh_2 [Ir(2)–Ir(3) 2.875(2) Å] and a PhPCPh=CPh group [Ir(1)–Ir(2) 2.915(2) Å] which also interacts with apical Ir(4) *via* C(10) [Ir(4)–C(10) 2.17(3) Å]. The bond lengths and angles within the phosphametallacycle are comparable to those in compound **2** (see Tables 2 and 3). The Ir_3P_2 fragment deviates only slightly from planarity which explains the large $J_{P1\text{-}P2} = 176$ Hz observed in the ^{31}P NMR spectrum. The PPh_3 ligand is bonded axially to Ir(1), which also bears a terminal CO ligand, while the remaining six CO groups are bonded two to each of the other three Ir atoms. All CO ligands are essentially linear. The cluster contains formally 60 valence electrons, but only two of its metal atoms obey the 18 electron rule. A rather short Ir(1)–Ir(4) distance [2.675(2) Å] suggests that electron density is being redistributed from 19e rich Ir(1) that bears the PPh_3 ligand to the 17e poor apical Ir(4).

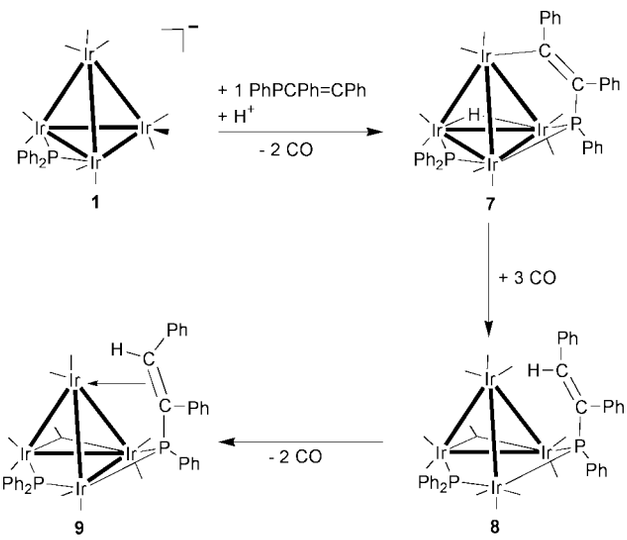
The solid state structure of compound **6** (Fig. 3) is not related straightforwardly to that of its precursor **4** (isomer **4a** or **4b**, Fig. 2, see above), the metallacycle P(3) in **6** being bonded to base Ir(1) and Ir(2) atoms, and the phosphirene P(3) in **4a** or **4b**, to apical Ir(4). However, its formation is readily rationalised from isomers **4c** or/and **4d** in which the phosphirene ring occupies radial positions on base Ir atoms not bonded to PPh_3 (see Scheme 3). Considering that thermolysis of **4a**–**4d** is relatively selective and only gives **6** in good yield, it is proposed that the latter derives from isomers **4c** or/and **4d** and that, under thermolysis conditions, isomers **4a** and **4b** transform into **4c** or/and **4d**, most probably *via* intramolecular migration of the phosphirene ring from an apical to a basal position. It is interesting to note that the thermal reaction of **4a**–**4d** failed to produce a phosphidoalkenyl compound, analogous to species **2**, **2a**, even when the reaction was kept for a long period of time at high temperature.

Reaction of $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ 1a with 1,2,3-triphenylphosphirene

We have reported that the anion $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ is an ideal precursor for the synthesis of mono-substituted phosphine derivatives of **1**, which are obtained in yields above 95%, after an immediate reaction with the desired phosphine and subsequent protonation of the CO substituted monoanion.[16] Even in cases where the phosphine can interact further, *e.g.* $Ph_2PC{\equiv}CPh$,[19] the initial η^1 mono-substituted derivative can be obtained in good yield if the reaction is undertaken at low temperature and in CH_2Cl_2 or toluene, which cannot act as Lewis bases.[28]

Thus, when an equivalent of 1,2,3-triphenylphosphirene was left to react with the purple anion **1a** in toluene, for 4 h, at room temperature, only the red compounds **2** and **2a** were isolated (*ca.* 20 and 13% yields, respectively), after protonation with CF_3COOH. However, when the reaction was carried out at −30 °C the green compound $[HIr_4(CO)_8(\mu_3\text{-}\eta^2\text{-}PhPCPh{=}CPh)(\mu\text{-}PPh_2)]$ **7** was produced in *ca.* 25% yield, after TLC, as well as unreacted **1** (15%). The structure of compound **7** was formulated on the basis of analytical and spectroscopic data and by comparison with ^{1}H and ^{31}P{^{1}H} NMR data of compounds **2**, **2a** and **6** discussed above.

The ^{31}P{^{1}H} NMR spectrum of cluster **7** in $CDCl_3$, at room temperature, comprises two doublets at δ 195.1 ($J_{P\text{-}P}$ 185 Hz) and 167.8, thus confirming the incorporation of a single phosphirene ring into the cluster framework. The large $J_{P\text{-}P}$ coupling between the phosphorus nuclei of **7** provides clear evidence that the phosphirene group underwent a rearrangement to give a bridging ligand coplanar to the PPh_2 group. The high frequency phosphorus resonances support a structure for **7** bearing two phosphido groups bridging metals involved in M–M bonds.[22] The ^{1}H NMR spectrum of **7** in $CDCl_3$, at room temperature, exhibits a hydride resonance at δ −11.1 (dd, $J_{H\text{-}P}$ 32, 29 Hz), indicating that the structure of compound **7** is similar to that of **6** with a phosphametallacycle ligand arising from P–C bond oxidative addition of the phosphirene ring (see Scheme 4). The



Scheme 4

isolation of two analogous compounds which differ only with respect to the presence of a PPh_3 ligand in **6** in place of a CO group in **7** permitted a comparative investigation of their reactions with CO in an attempt to produce the respective phosphidoalkenyl derivatives *via* hydrometallation.

Reaction of $[HIr_4(CO)_8(\mu_3\text{-}\eta^2\text{-PhPCPh=CPh})(\mu\text{-}PPh_2)]$ 7 with CO

The green compound **7** reacts with CO under mild conditions (1 atm, RT and 2 h) to give quantitative yields of a yellow product formulated as $[Ir_4(CO)_{11}(\mu\text{-PhPCPh=CHPh})(\mu\text{-}PPh_2)]$ **8**. Compound **8** is stable in solution in the presence of an atmosphere of CO, but undergoes facile conversion to the cluster $[Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-PhPCPh=CHPh})(\mu\text{-}PPh_2)]$ **9** when the CO is displaced by bubbling argon through the solution, or under vacuum. Compound **8** could not therefore be isolated and was formulated solely on the basis of NMR data, whereas compound **9** was fully characterised on the basis of spectroscopic and analytical data, and its molecular structure was established unequivocally by a single-crystal X-ray diffraction study.

The reaction of compound **7** with CO, in C_6D_6, was monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. The *in situ* $^{31}P\{^1H\}$ NMR spectra showed a shift of the high frequency phosphorus resonances of **7** (δ 195.1 and 167.8) to lower frequencies, δ 21.2 (d, $J_{P\text{-}P}$ 219 Hz) and −88.6 (d), upon conversion into complex **8**. The two phosphorus resonances of **8** lay within the range of chemical shifts observed for compounds in which the phosphido ligands bridge metal atoms which do not interact,[22] as for example in the butterfly clusters $[HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}Ph_2PCCPh)(\mu\text{-}PPh_2)]$ (δ −2.3, Ir···Ir 3.686(1) Å)[20] and $[Ir_4(CO)_8(PCy_3)(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)\text{=}CPh)(\mu\text{-}PPh_2)]$ (δ −60.0, Ir···Ir 3.753 Å),[19] thus suggesting the presence of at least two additional CO ligands over the cluster framework of **8**. The absence of a hydride resonance in the *in situ* ^1H NMR spectrum of **8** and the presence of a doublet at δ 7.6 ($J_{H\text{-}P}$ 21 Hz) indicated that the hydride ligand had migrated to the phosphirene fragment, resulting in a phosphidoalkenyl ligand, possibly as the result of the addition of one CO ligand. Compound **8** was thus proposed to have the structure shown in Scheme 4, containing two elongated edges bridged by the $\mu\text{-}PPh_2$ ligand and the μ-PhPCPh=CHPh phosphido group formed upon reductive elimination of the alkenyl group. The three additional CO ligands are tentatively distributed over the polyhedron in such a way that all Ir atoms obey the 18-electron rule.

The phosphorus resonances of compound **9** appeared as two doublets at δ 66.9 ($J_{P\text{-}P}$ 197 Hz) and −73.5, respectively, in the $^{31}P\{^1H\}$ NMR spectrum obtained in C_6D_6, at room temperature, suggesting that one phosphorus ligand bridges two Ir atoms which are not involved in M–M bonding. The ^1H NMR spectrum of **9** confirmed the presence of a phosphidoalkenyl ligand resulting from the hydrometallation process on the precursor **7**. However, in this case, the alkenyl hydrogen resonance appeared at lower frequency with respect to that of **8**, at δ 6.3 (d, $J_{H\text{-}P}$ 21 Hz), which suggested that conversion of cluster **8** into **9** involved a rearrangement of the phosphidoalkenyl ligand. The shielding effect observed in the alkenyl hydrogen suggested interaction of the olefin group of **9** with a metal centre, as shown in Scheme 4. The proposed structure was confirmed subsequently by a single-crystal X-ray diffraction study.

The molecular structure of **9** in the solid state is shown in Fig. 4, together with the labelling scheme, and relevant bond distances and angles are listed in Table 4. The metal framework of **9** can be described as a butterfly whose wings are spanned by a slightly asymmetric 3e donor PPh_2 ligand [Ir(2)–P(2) 2.3423(18) and Ir(3)–P(2) 2.3539(18) Å]. The Ir–Ir bond lengths range from 2.7305(3) to 2.8752(4) Å, the longest bond

Table 4 Selected intramolecular distances (Å) and angles (°) for compound **9**

Ir(1)–Ir(2)	2.7305(4)	Ir(3)–P(2)	2.3539(18)
Ir(1)–Ir(3)	2.8752(4)	Ir(4)–C(10)	2.319(6)
Ir(1)–Ir(4)	2.7889(4)	Ir(4)–C(11)	2.324(6)
Ir(2)···Ir(3)	3.598(4)	P(1)–C(10)	1.798(7)
Ir(2)–Ir(4)	2.7620(4)	C(10)–C(11)	1.405(9)
Ir(3)–Ir(4)	2.8002(4)	P(1)–C(12)	1.833(9)
Ir(1)–P(1)	2.3117(17)	P(2)–C(30)	1.829(7)
Ir(2)–P(1)	2.2856(17)	P(2)–C(36)	1.829(7)
Ir(2)–P(2)	2.3423(18)		
C(10)–P(1)–Ir(1)	111.9(2)	Ir(2)–P(2)–Ir(3)	100.01(6)
C(10)–P(1)–Ir(2)	110.9(2)	Ir(2)–P(1)–Ir(1)	72.87(5)
C(11)–C(10)–C(18)	121.7(6)	P(1)–Ir(2)–P(2)	136.71(6)
C(11)–C(10)–P(1)	119.3(5)	Ir(2)–Ir(1)–Ir(3)	79.807(10)
P(1)–C(10)–Ir(4)	82.3(2)	Ir(3)–C(7)–Ir(1)	86.5(3)
C(10)–C(11)–C(24)	129.0(6)	C(2)–Ir(1)–C(1)	100.7(3)
C(10)–C(11)–Ir(4)	72.2(3)	C(4)–Ir(2)–C(3)	100.3(3)

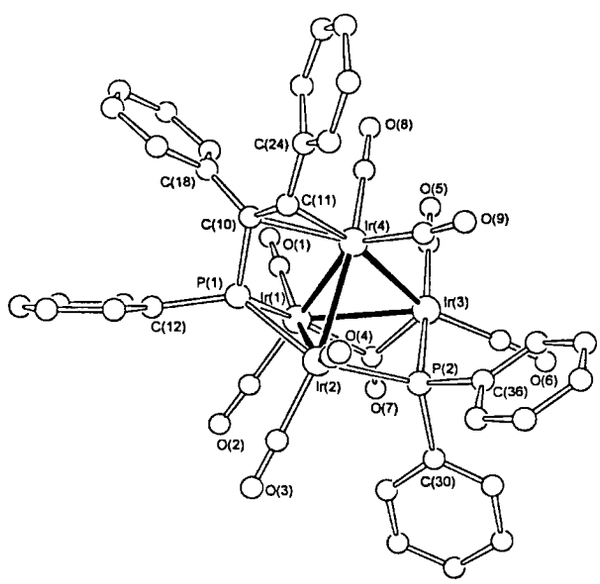


Fig. 4 Molecular structure of $[Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-PhPCPh=CHPh})(\mu\text{-}PPh_2)]$ **9**.

corresponding to a hinge to apex vector of the butterfly [Ir(1)–Ir(3) 2.8752(4) Å] which is bridged by a CO ligand. The phosphidoalkenyl ligand interacts with the Ir(1)–Ir(2)–Ir(4) face, *via* the phosphorus atom, in an asymmetric manner [Ir(1)–P(1) 2.3117(17) and Ir(2)–P(1) 2.2856(17) Å], and *via* the alkene [–C(Ph)=C(H)Ph] moiety which is π-bonded to the Ir(4) atom [Ir(4)–C(10) 2.319(6) and Ir(4)–C(11) 2.324(6) Å] and thus formally donates 5 electrons to the metal frame. As the result of this π-interaction, elongation of the C(10)–C(11) bond is observed to 1.405(9) Å from 1.36(4) A, 1.37(4) Å B [C(59)–C(60)] in compound **2** which contains the same phosphidoalkenyl ligand, except that it does not involve any π-interaction as in **9**. The eight remaining CO ligands are essentially linear and are distributed two on each Ir atom. The 62 electron species **9** obeys the Wade rule and the 18 electron rule at each metal centre. Compound **9** is the first Ir_4 carbonyl cluster bearing a co-ordinated mono-olefin whose structure has been established by an X-ray analysis study, although the molecular structures of a few diolefin containing $[Ir_4(CO)_{12}]$ derivatives, *e.g.* $[Ir_4(CO)_9L(2,3\text{-}\eta:5,6\text{-}\eta\text{-nbd})]$ (L = PPh_3 and PMe_2Ph)[29] and $[Ir_4(CO)_{10}(cod)]$[30] have been reported.

The structures of **9** and $[Ir_4(CO)_8(PCy_3)(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)\text{=}CPh)(\mu\text{-}PPh_2)]$[19] are closely related, with the PPh_2 group bridging Ir atoms that do not interact [3.598(4) and 3.753(1)

Å, respectively], the main difference being the nature of the ligand that caps one of the butterfly wings, a μ-phosphido–π-alkenyl ligand in the case of compound **9**, and an η^1-phosphino–π-σ-alkenyl ligand in the other case. Both ligands are anionic and therefore the average formal oxidation state of the metal atoms in the two clusters is $+\frac{1}{2}$. These two factors explain the similarity of the chemical shift values observed for the PPh_2 phosphorus nuclei in the two compounds, δ −73.5 and −60.0 for cluster **9** and for the other cluster, respectively.

Although as anticipated the phosphametallacycle containing cluster **7** reacted smoothly with CO, to give compound **8** containing a phosphidoalkenyl ligand, the phosphametallacycle of the PPh_3 containing cluster **6** did not undergo a similar hydrometallation process upon reaction with CO under the same conditions. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture indicated formation of a number of hydride containing products with PPh_3, μ-PPh_2 and μ_3-PhPCPh=CPh phosphorus chemical shifts ranging from δ *ca.* 170 to about −70. These data suggest that addition of CO might have led to the opening of the cluster frame and possibly to the migration of the PPh_3 ligand, resulting in a number of similar hydride products. The PPh_3 ligand is therefore responsible for the stability of the "oxidative addition product" **6** (with respect to C–H reductive elimination), which in the presence of CO, only undergoes metal framework opening, as a result of CO addition. In contrast, compound **7**, with a less electron density rich metal frame, undergoes facile reductive elimination of the hydride and μ_3-PhPCPh=CPh ligands, induced by the addition of CO.

Conclusions

We have identified several possible steps involved in the interaction and activation of 1,2,3-triphenylphosphirene in the co-ordination sphere of cluster **1** and its derivatives. In a similar fashion to some mononuclear complexes (*viz*. $M(CO)_6$ M = Mo, W), the first step seems to involve η^1 interaction *via* the P atom of the heterocycle upon CO substitution. The stability of the resulting complex containing the intact phosphirene L seems to depend on the ease with which an additional free co-ordination site on the cluster is generated, *via* CO dissociation or M–M bond cleavage. In this context, whereas complexes $[M(CO)_5L]$ are stable, further transformation of the phosphirene after co-ordination to **1** is unavoidable, but we isolated a compound containing an intact phosphirene ring with cluster **3**, the less labile PPh_3 mono-substituted derivative of **1**. As in the case of labile mononuclear complexes, P–C bond activation occurs, but because the activated phosphirene can interact further with the cluster compound, formation of a phosphidometallacycle results, rather than the simple metallacycle being formed in the co-ordination sphere of mononuclear species. As both clusters **1** and **3** contain a hydride ligand, hydrometallation of the activated phosphirene is the next possible step, which however has not yet been observed in mononuclear complexes. We have found that the process, which leads to the formation of a μ-phosphidoalkenyl ligand, is extremely sensitive to the metal frame electronic density. Indeed, only in the case of the phosphirene derivative of cluster **1**, C–H reductive elimination occurs, driven by CO addition, whereas in the case of the derivative of cluster **3**, the presence of the good σ-donor and poor π-acceptor PPh_3 ligand stabilises the oxidative addition phosphidometallacycle species against hydrometallation. Finally, the next possible step, *i.e.* interaction of the olefin moiety of the μ-phosphidoalkenyl ligand, was also observed, upon CO substitution.

Experimental

Tetrairidium dodecarbonyl (Strem Chemicals), tetrabutylammonium bromide (Aldrich), silver hexafluoroantimonate (Aldrich), diphenylphosphine, triphenylphosphine and trifluoroacetic acid (Merck) were used as purchased; DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, Aldrich) was distilled before use. All solvents were freshly distilled and degassed before use. The compounds $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ **1** and $[HIr_4(CO)_9(PPh_3)(\mu\text{-}PPh_2)]$ **3**, were prepared by published methods.[16] 1,2,3-Triphenylphosphirene was obtained from F. Mathey.[26] The progress of the reactions was monitored by analytical TLC (precoated plates, silica gel F254, 0.25 mm thick; Merck), IR and $^{31}P\{^1H\}$ NMR spectroscopy. The separation and purification of the reaction products were carried out by preparative TLC (2 mm thick glass plates 20 × 20 cm, silica gel GF 254; Fluka). The reactions and manipulations were performed in typical Schlenk systems, under an inert atmosphere of argon. All Ir_4-clusters were stored under an inert atmosphere to avoid the decomposition observed in some compounds which were stored for a long time in the solid state.

Infrared spectra were recorded on a Bomem (FT-IR Michelson) spectrophotometer between 2200 and 1600 cm^{-1} (ν_{CO}), $^{31}P\{^1H\}$ and ^1H NMR spectra on a Bruker AC 300P spectrometer using, as references, 85% H_3PO_4 (external) for the former and $SiMe_4$ for the other nuclei.

Preparation of $[Ir_4(CO)_8(\mu_3\text{-}\eta^2\text{-}PhPCPh{=}CPh)(\mu\text{-}\eta^1\text{-}PhPCPh{=}CHPh)(\mu\text{-}PPh_2)]$ 2, 2a

Method 1. To an orange solution of compound **1** (100 mg, 0.081 mmol), in toluene (20 cm^3), at room temperature, a solution of 1,2,3-triphenylphosphirene (23 mg, 0.081 mmol), in toluene (10 cm^3), was added slowly, using a dropping funnel (about 1 h) and the mixture was left stirring for 4 h. The solvent was evaporated and the mixture separated by TLC with CH_2Cl_2/hexane (2 : 3) to yield unreacted **1** (10 mg, 10%), the isomers **2** (11 mg, 15%) and **2a** (7 mg, 10%), and some decomposition products (Found: C, 41.8; H, 2.5. $C_{60}H_{41}O_8P_3Ir_4\cdot0.35C_6H_{14}$ (**2**, **2a**·$0.35C_6H_{14}$) requires C, 41.8; H, 2.4%); ν_{max}/cm^{-1} (CO) **2** 2061w, 2039vs, 2032vs, 2007s, 1996s, 1952 (br) (hexane); **2a** 2058w, 2038vs, 2011vs, 2001 (sh), 1970vw, 1951 (br) (hexane). Crystals of **2** for the X-ray study were obtained from CH_2Cl_2/hexane at 20 °C over a period of 12 h.

Method 2. DBU (12 μl) was added to a solution of **1** (100 mg, 0.081 mmol) in toluene (20 cm^3), under quick stirring, at room temperature. After stirring for 15 min, a solution of 1,2,3-triphenylphosphirene (46 mg, 0.162 mmol) in toluene (10 cm^3) was added to the mixture which was left stirring for 4 h, after which time CF_3COOH (6 μl) was added. The solvent was evaporated under vacuum, and the mixture separated by TLC as described above to yield **2** (15 mg, 20%) and **2a** (10 mg, 13%), besides some decomposition products.

Preparation of $[HIr_4(CO)_8(PPh_3)(\eta^1\text{-}PhPCPh{=}CPh)(\mu\text{-}PPh_2)]$ 4 and $[HIr_4(CO)_7(PPh_3)(\eta^1\text{-}PhPCPh{=}CPh)_2(\mu\text{-}PPh_2)]$ 5

A solution of 1,2,3-triphenylphosphirene (19 mg, 0.068 mmol) in toluene (10 cm^3) was added slowly to a red solution of compound **3** (100 mg, 0.068 mmol), in toluene (20 cm^3) at room temperature, and the mixture left stirring for 3 h. The solvent was evaporated and the mixture separated by TLC with CH_2Cl_2/hexane (2 : 3) to yield unreacted **3** (10 mg, 10%), **4** (76 mg, 60%), **5** (20 mg, 10%) and some decomposition products. Compound **4** was recrystallised from CH_2Cl_2/hexane to give red microcrystals (Found: C, 44.5; H, 3.5. $C_{58}H_{41}O_8P_3Ir_4\cdot2.0C_6H_{14}$ (**4**·$2.0C_6H_{14}$) requires C, 44.2; H, 3.7%); ν_{max}/cm^{-1} (CO) **4** 2054m, 2044m, 2020vs, 1979s, 1806 (br) (hexane); **5** 2019m, 2001vs, 1981s, 1967vs, 1800 (br) (hexane). Crystals of **4a** or **4b** for the X-ray study were obtained from CH_2Cl_2/hexane at 20 °C over a period of 12 h.

Table 5 Crystallographic data for compounds **2**, **4**, **6** and **9**

	2	**4**	**6**	**9**
Formula	$C_{60}H_{41}Ir_4O_8P_3$	$C_{58}H_{41}Ir_4O_8P_3$	$C_{57}H_{41}Ir_4O_7P_3$	$C_{41}H_{26}Ir_4O_9P_2$
M	1751.6	1727.6	1699.6	1493.4
T/K	293	293	293	293
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	22.206(4)	12.575(4)	15.174(6)	12.2575(3)
b/Å	17.563(2)	20.875(5)	20.952(5)	18.6562(4)
c/Å	35.748(5)	21.202(5)	17.733(6)	19.2753(6)
β/°	100.08(2)	103.35(2)	109.27(3)	107.346(2)
U/Å^3	13727(4)	5415(3)	5322(3)	4207.4(2)
Z	8	4	4	4
D_c/g cm^{-3}	1.70	2.12	2.12	2.36
μ/mm^{-1}	7.85	9.94	10.11	12.74
Independent reflections (R_{int})	19075 (0.0754)	6628 (0.0835)	6485 (0.0887)	7386 (0.079)
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.086, 0.187	0.059, 0.131	0.079, 0.131	0.034, 0.068
(all data)	0.197, 0.251	0.098, 0.151	0.180, 0.166	0.051, 0.074

Preparation of $[HIr_4(CO)_7(PPh_3)(\mu_3\text{-}\eta^2\text{-}PhPCPh{=}CPh)(\mu\text{-}PPh_2)]$ 6

A red solution of compound **4** (80 mg, 0,047 mmol) in toluene (20 cm^3) was heated at 50 °C for 12 h. The solvent was evaporated and the mixture separated by TLC with CH_2Cl_2/hexane (2:3) to yield unreacted **4** (8 mg, 10%), **6** (47 mg, 60%), and some decomposition products. Compound **6** was recrystallised from CH_2Cl_2/hexane to give dark green microcrystals (Found: C, 44.2; H, 3.3. $C_{57}H_{41}O_7P_3Ir_4{\cdot}2.0C_6H_{14}$ (**6**$\cdot$2.0C_6H_{14}) requires C, 44.3; H, 3.7%); ν_{max}/cm^{-1} (CO) **6** 2040m, 2020vs, 2007s, 1985s (hexane). Crystals for the X-ray study were obtained from the same solvent system at 20 °C over a period of 24 h.

Preparation of $[HIr_4(CO)_8(\mu_3\text{-}\eta^2\text{-}PhPCPh{=}CPh)(\mu\text{-}PPh_2)]$ 7

DBU (12 μl) was added at room temperature to an orange solution of **1** (100 mg, 0.081 mmol), in toluene (20 cm^3), under quick stirring. After further stirring for 15 min the red mixture was cooled to −30 °C and a solution of 1,2,3-triphenylphosphirene (23 mg, 0.081 mmol) in toluene (10 cm^3) was added. The mixture was left stirring for 3 h, after which time CF_3COOH (6 μl) was added. The solvent was evaporated under vacuum, and the mixture separated by TLC with CH_2Cl_2/hexane (2:3) to yield unreacted **1** (15 mg, 15%), **7** (30 mg, 25%), and some decomposition products. Compound **7** was recrystallised from CH_2Cl_2/hexane to give dark green microcrystals (Found: C, 34.1; H, 2.2. $C_{40}H_{26}O_8P_2Ir_4{\cdot}0.5C_6H_{14}$ (**7**$\cdot$0.5C_6H_{14}) requires C, 34.2; H, 2.2%); ν_{max}/cm^{-1} (CO) **7** 2061m, 2035vs, 2020s, 2003s, 1980w (hexane).

Preparation of $[Ir_4(CO)_{11}(\mu\text{-}\eta^1\text{-}PhPCPh{=}CHPh)(\mu\text{-}PPh_2)]$ 8 and $[Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}PhPCPh{=}CHPh)(\mu\text{-}PPh_2)]$ 9

Carbon monoxide was bubbled continuously for 2 h through a green stirred solution of compound **7** (40 mg, 0.027 mmol) in toluene (20 cm^3), at room temperature, to give the labile **8**. Bubbling argon through the fresh yellow solution of **8**, for 4 h, gave compound **9** (36 mg, 90%), which was recrystallised from CH_2Cl_2/hexane to give yellow microcrystals (Found: C, 33.8; H, 2.2. $C_{41}H_{26}O_9P_2Ir_4{\cdot}0.35C_6H_{14}$ (**9**$\cdot$0.35C_6H_{14}) requires C, 33.9; H, 2.1%); ν_{max}/cm^{-1} (CO) **9** 2081s, 2073s, 2034vs, 2007s, 1988s, 1973m, 1961m, 1861 (br) (hexane). The progress of the two reactions was monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. A solution of **7** in C_6D_6 was transferred to a 5 mm NMR tube and carbon monoxide was bubbled slowly, at room temperature. At regular intervals the NMR tube was placed into the NMR probe and the spectra were recorded. After the total conversion to the product **8**, argon was bubbled through the solution and the final spectra were recorded containing only the compound **9**. Crystals for the X-ray study were obtained from CH_2Cl_2/hexane at 20 °C over a period of 24 h.

Crystal structure determinations of 2, 4, 6 and 9

Data were collected at 293 K on an Enraf-Nonius CAD4 diffractometer. Crystal and refinement details are given in Table 5. Non-H atoms were located by heavy atom methods and the structures refined using SHELXS-86[31] and refined on F^2 with all reflections using SHELXS-93.[31] Hydrogen atoms were included in rigid mode.

CCDC reference number 186/2036.

See http://www.rsc.org/suppdata/dt/b0/b003002n/ for crystallographic files in .cif format.

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