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The reactivity of an iridaphosphirene complex, [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$], Cy = cyclohexyl, toward electrophiles

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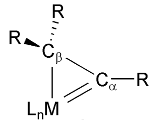
The reactivity of an iridaphosphirene complex, [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$], Cy = cyclohexyl, toward a variety of electrophiles has been examined and in all cases reactivity occurs at the phosphorus centre within the three membered ring. Reaction with several protic reagents has led to the formation of the iridaphosphirenium salts, [Ir{=C(Bu^t)-P(H)(Cy)}(CO)(PPh$_3$)$_2$]X, X = BF$_4^-$, CF$_3$SO$_3^-$ or CF$_3$CO$_2^-$, two of which have been crystallographically characterised. Though thermally stable in the solid state, in dichloromethane solutions these rearrange *via* 1,2-hydrogen migrations over seven days to give the Ir(I)–η^1-phosphaalkene complexes, [Ir(CO)(PPh$_3$)$_2${η^1-P(Cy)=C(H)(Bu^t)}]X, one of which (X = BF$_4^-$) has been crystallographically characterised. The reactions of [Ir{=C(Bu^t)P(Cy)}(CO)(PPh$_3$)$_2$] with MeI, S and Se have also been investigated and found to give the complexes, [Ir{=C(Bu^t)P(Me)(Cy)}(CO)(PPh$_3$)$_2$]I and [Ir{=C(Bu^t)P(=E)(Cy)}(CO)(PPh$_3$)$_2$] E = S or Se, the former two of which have been structurally authenticated.

Introduction

The last five years has seen a steady increase in the interest surrounding transition metal η^2–3e$^-$ vinyl complexes.[1] This has largely arisen from the fact that they undergo a variety of useful reactions with nucleophiles and electrophiles, isomerisations to η^3-allyl and carbene complexes, in addition to electron transfer reactions. With regards to the structure and bonding exhibited by the vast majority of these complexes, Casey *et al.* have made the convincing argument that they should be considered as metallacyclopropene complexes, **1**, rather than η^2-vinyl complexes, **2**.[2] This is based on structural evidence, *viz.* shortness of the M–C$_\alpha$ bond and the fact that the M–C$_\alpha$–R fragment is often almost perpendicular to the R–C$_\beta$–R fragment; spectroscopic evidence, *viz.* the C$_\alpha$ centre resonates at very low field and the C$_\beta$ centre at much higher field in the ^{13}C NMR spectra of these complexes; and theoretical evidence, *viz.* the results of DFT studies. It must be said, however, that a small number of complexes have been reported which contain close to planar vinyl ligands that are weakly η^2-coordinated to the metal centre.[3]

In our laboratory we have recently been examining the analogy between the phosphavinyl, –C(R)=P(R), and vinyl fragments and have found that the former can behave very differently to their vinyl counterparts within the coordination sphere of main group elements. These differences largely revolve around the facility by which coordinated phosphavinyl ligands can intramolecularly couple to give a variety of organometallic cage and heterocyclic compounds.[4–8] An examination of the chemistry of transition metal–phosphavinyl complexes has not proven as fruitful due to the fact that the various accessible oxidation states of many transition metals often lead to oxidative coupling of the phosphavinyl fragment to give phosphorus containing heterocycles.[9]

One success we have had is with the reaction of the phosphavinyl Grignard reagent, [CyP=C(Bu^t)MgCl(OEt$_2$)] Cy = cyclohexyl, with Vaska's compound, [IrCl(CO)(PPh$_3$)$_2$], which affords the iridaphosphirene complex, [Ir{=C(Bu^t)P(Cy)}(CO)-(PPh$_3$)$_2$] **3**, in good yield.[10] Structural and spectroscopic studies of this compound have shown that it has more in common with the metallocyclopropene formulation of its hydrocarbon analogues than the η^2-vinyl bonding description. Data to support this include a CPCC torsion angle of 77.9° within the phosphavinyl ligand and a very low field resonance for the iridium bound carbon centre, C$_\alpha$, at 331.5 ppm in its ^{13}C NMR spectrum. In addition, when **3** is treated with CO an η^1-phosphavinyl complex does not result but instead PPh$_3$ displacement occurs to give [Ir{=C(Bu^t)P(Cy)}(CO)$_2$(PPh$_3$)]. Interestingly, this complex is not stable in solution and decomposes to give a number of products which include the novel oxo-η^3-phosphaallyl complex, **4**, which is formed *via* a C–C coupling of one carbonyl ligand with the phosphavinyl fragment. Considering the novelty of this reaction and the analogy between **3** and metallocyclopropenes it seemed worthy to explore the further reactivity of **3**. The results of its reactions with a variety of electrophiles are reported herein.



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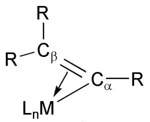

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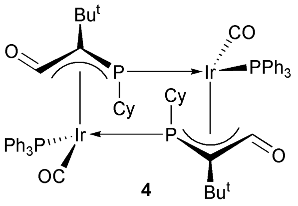

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Results and discussion

Treatment of metallocyclopropenes, **1**, with protic reagents can lead to protonation of the metal, C$_\alpha$ or C$_\beta$ sites depending on the metal and/or vinyl substituents employed.[1] If an analogy is drawn with **3**, its reaction with protic reagents, HX, could potentially lead to protonation at (i) the metal centre to give a η^1-phosphavinyl complex, [Ir^{III}{η^1-C(Bu^t)=P(Cy)}(CO)HX-(PPh$_3$)$_2$], (ii) the C$_\alpha$ centre to give a phosphaalkene complex, [Ir^I(CO)(PPh$_3$)$_2${η^1-P(Cy)=C(H)(Bu^t)}]X or (iii) the phosphavinyl P-centre to give a λ^5-iridaphosphirenium complex, [[Ir{=C(Bu^t)P(H)(Cy)}(CO)(PPh$_3$)$_2$]X, X = anion. To investigate these possibilities the reaction of **3** with several acids has been investigated and in all cases moderate yields of the iridaphosphirenium salts, **5**, resulted (Scheme 1).

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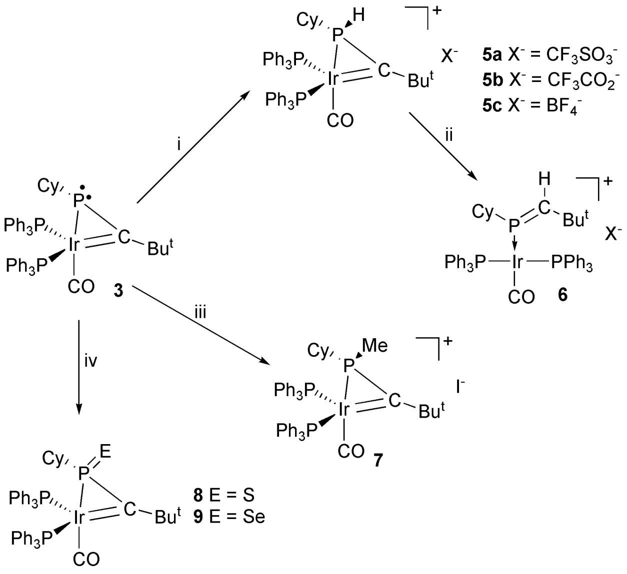

Scheme 1 *Reagents and conditions:* (i), HX, Et_2O; (ii), 7 days, CH_2Cl_2; (iii), MeI, THF; (iv), E, toluene.

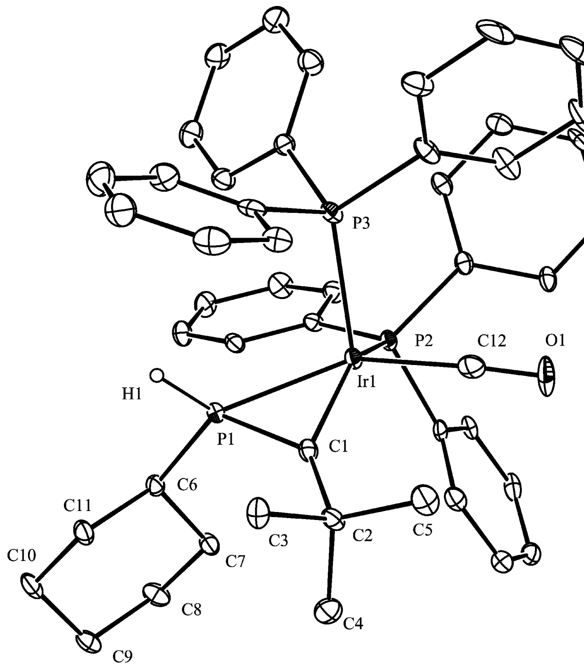

Fig. 1 Structure of the cationic component of compound **5a**. Selected bond lengths (Å) and angles (°): Ir(1)–C(1) 1.934(8), Ir(1)–P(1) 2.3186(19), Ir(1)–P(2) 2.384(2), Ir(1)–P(3) 2.347(2), Ir(1)–C(12) 1.873(9), P(1)–C(1) 1.735(8), P(1)–H(1) 1.31(7), P(1)–C(6) 1.828(8), C(12)–O(1) 1.169(10), C(1)–C(2) 1.512(11), C(12)–Ir(1)–C(1) 100.0(3), C(12)–Ir(1)–P(1) 147.1(2), C(1)–Ir(1)–P(1) 47.1(2), C(12)–Ir(1)–P(3) 98.8(3), C(1)–Ir(1)–P(3) 119.8(2), P(1)–Ir(1)–P(3) 100.27(7), C(12)–Ir(1)–P(2) 88.4(3), C(1)–Ir(1)–P(2) 138.3(2), P(1)–Ir(1)–P(2) 114.81(7), P(3)–Ir(1)–P(2) 98.67(7), C(1)–P(1)–C(6) 119.5(4), C(1)–P(1)–Ir(1) 54.7(3), C(2)–C(1)–P(1) 138.1(6), P(1)–C(1)–Ir(1) 78.2(3).

These proved to be thermally stable in the solid state and all exist as ion separated salts. As a result, the spectroscopic data for the three complexes are similar. Most informative of these come from their $^{31}P\{^1H\}$ NMR spectra which display high field virtual triplet resonances (*ca.* −140 ppm) which lie *ca.* 20 ppm to lower field of the iridaphosphirene resonance in **3**, as would be expected upon protonation of the heterocyclic phosphorus centre. In addition, the IR spectra of **5** revealed shifts to higher frequency (*ca.* 50 cm^{-1}) for the CO stretching absorptions in these complexes compared to that in **3** (1954 cm^{-1}). This, again, is not surprising considering that in the former complexes the CO ligands are associated with cationic moieties.

X-ray crystal structure analyses of **5a** and **5b** were carried out and in both the geometry of the phosphirenium moiety is very similar and thus only the structure of the cation of **5a** is depicted in Fig. 1. It is noteworthy, however, that **5b** crystallised with one molecule each of toluene and CF_3CO_2H per asymmetric unit. In addition, the structures of both cations are strikingly similar to that of their neutral precursor, **3**. The iridium centre of **5a** can be considered as having a heavily distorted trigonal bipyramidal geometry with the carbonyl ligand and P(1) taking up the axial sites and C(1), P(2) and P(3) in the equatorial positions. The P(1)–C(1) interaction [1.734(8) Å] is short for a single P–C bond but not significantly shorter than the corresponding bond in **3**, [1.753(13) Å]. In addition, the Ir(1)–C(1) distance [1.934(8) Å] is longer than in **3** [1.918(14) Å] but still in the normal region for localised Ir–C double bonds,[11] whilst the P(1)–Ir(1) bond length [2.3186(19) Å] is significantly shorter than the analogous distance in **3** [2.442(3) Å]. This difference can be explained by the electron poor nature of the phosphirenium phosphorus centre in cationic **5a** relative to the phosphirene phosphorus centre in neutral **3**. The fact that the C(6)P(1)C(1)C(2) torsion angle is 63.6° confirms that **5a** should be considered as an iridaphosphirenium complex rather than a protonated η^2-phosphavinyl complex. Very similar geometrical trends have been observed in metallacyclopropene complexes, **1**, which theoretical studies suggest arise from a degree of isolobality between the C_2 fragment of the 3-membered ring and $4e^-$ donor alkyne ligands.[2]

Although **5a**–**c** are thermally very stable in the solid state, in dichloromethane solutions they are less so and quantitatively and irreversibly rearrange *via* 1,2-hydrogen migrations to give the cationic Ir(I)–phosphaalkene complexes, **6** (Scheme 1), over one week. It is noteworthy that similar but reversible 1,2-hydrogen shifts between the two carbon centres in metallocyclopropenes, *e.g.* [Cp*Re(CO)$_2${=C(H)(Ph)C(*o*-tolyl)}], have been observed.[2] In addition, and in a related fashion to the formation of the phosphaalkene complexes, **6**, protonation of metallocyclopropenes can occur at the C_α centre which leads to the formation of free alkenes.[12] In order to generate the free phosphaalkene, CyP=C(H)(Bu^t), from **6**, X = BF_4^-, CO gas was passed through a dichloromethane solution of the phosphaalkene complex over five minutes. An examination of the $^{31}P\{^1H\}$ NMR spectrum of the product mixture revealed that the known phosphaalkene[13] had been quantitatively displaced from the cation of **6**, as evidenced by the appearance of a singlet resonance at 255 ppm. The by-product in this reaction was found to be the previously reported compound, $[Ir(CO)_3(PPh_3)_2][BF_4]$.[14]

The spectroscopic data for **6**, X = BF_4^-, are consistent with its proposed structure. Of note is its $^{31}P\{^1H\}$ NMR spectrum which displays an AB_2 pattern, the doublet signal of which (δ 15.4 ppm) corresponds to the chemically equivalent PPh_3 ligands whilst the triplet signal occurs at low field (δ 222.4 ppm) in the normal region for η^1-coordinated phosphaalkenes. The coupling between the two signals (51 Hz) suggests a *cis*-relationship between the phosphaalkene and the two phosphine ligands.

The structure of the cationic component of **6**, X = BF_4^-, is depicted in Fig. 2. The molecule sits on a crystallographic mirror plane which contains the phosphaalkene ligand and thus its cyclohexyl substituent is necessarily disordered. There are no close contacts between the cation and the BF_4 anion, and the $16e^-$ iridium centre has a slightly distorted square planar geometry. Both the P(1) and C(1) centres have trigonal planar geometries and the distance between these centres [1.607(14) Å] is normal for a localised P–C double bond.[11]

The reactivity of **3** toward a number of other electrophiles was examined with similar results to its protonation. Its treatment with MeI did not lead to oxidative addition to the iridium centre but methylation of the phosphorus centre in the 3-membered ring to give **7** in high yield (Scheme 1). Similarly,

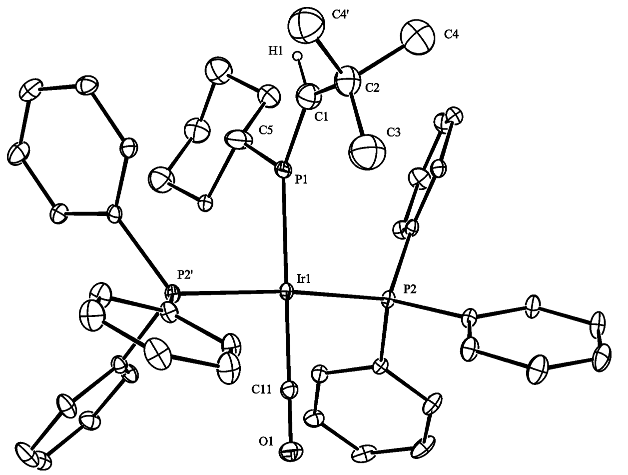

Fig. 2 Structure of cationic component of compound **6**. Selected bond lengths (Å) and angles (°): Ir(1)–P(1) 2.328(3), Ir(1)–C(11) 1.859(9), Ir(1)–P(2) 2.3365(15), P(1)–C(1) 1.607(14), P(1)–C(5) 1.998(18), C(1)–C(2) 1.408(19), C(11)–Ir(1)–P(1) 179.7(3), C(11)–Ir(1)–P(2) 87.81(4), P(1)–Ir(1)–P(2) 92.20(4), P(2)–Ir(1)–P(2′) 173.22(7), C(1)–P(1)–Ir(1) 139.0(6), C(5)–P(1)–Ir(1) 116.2(4), P(1)–C(1)–C(2) 131.4(13).

its reaction with either elemental sulfur or selenium leads to oxidation of the same phosphorus centre to give **8** and **9** respectively. It is worth noting that **7** is indefinitely stable in solution and therefore does not undergo a 1,2-methyl migration similar to the 1,2-hydrogen migrations that occur for **5a**–**c**.

The $^{31}P\{^1H\}$ NMR spectra of **7**–**9** all show virtual triplet resonances corresponding to the metallophosphirene phosphorus centres at significantly lower field (**7** δ −125.5 ppm, **8** δ −86.1 ppm, **9** δ −117.4 ppm) than the related resonances seen for both **3** and **5**. This observation reflects the relatively electron poor nature of the phosphorus centres in the former compounds. In addition, the ^{13}C NMR spectra of **7**–**9** display low field signals (**7** δ 330.4 ppm, **8** δ 371.3 ppm, **9** δ 341.2 ppm) corresponding to the carbon centres double bonded to iridium.

The structure of the cation of **7** and the molecular structure of **8** (Fig. 3 and 4) both show geometries at the iridium centre similar to those in **3** and **5**. Moreover, their P(1)–C(1) bond lengths [**7** 1.738(5) Å, **8** 1.746(6) Å] and Ir(1)–C(1) distances [**7** 1.932(4) Å, **8** 1.945(6) Å] are close to those in **3** and **5** and their Ir(1)–P(1) interactions [**7** 2.3280(11) Å, **8** 2.3552(17) Å] are comparable to those in **5** but significantly shorter than in **3**, as would be expected. Finally, the P(1)–S(1) distance in **8** [1.992(2) Å] is in the normal range for double bonds between these two elements.[11]

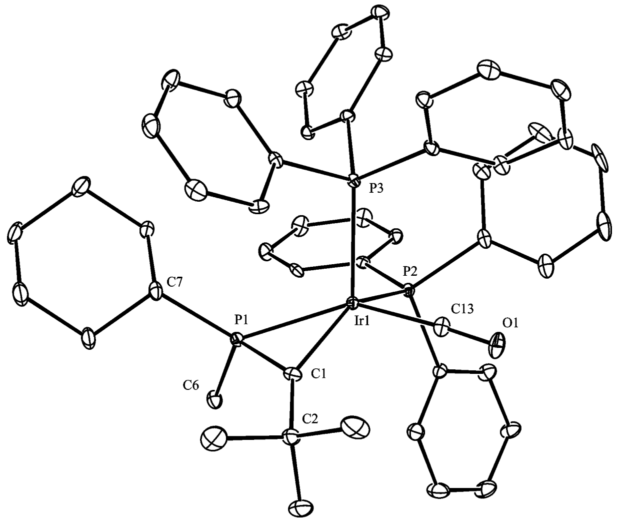

Fig. 3 Structure of cationic component of compound **7**. Selected bond lengths (Å) and angles (°): Ir(1)–C(1) 1.932(4), Ir(1)–P(1) 2.3280(11), Ir(1)–P(2) 2.3903(11), Ir(1)–P(3) 2.3630(13), Ir(1)–C(13) 1.888(5), P(1)–C(1) 1.738(5), P(1)–C(6) 1.821(5), P(1)–C(7) 1.845(5), C(13)–O(1) 1.138(5), C(1)–C(2) 1.521(6), C(13)–Ir(1)–C(1) 98.7(2), C(13)–Ir(1)–P(1) 144.71(15), C(1)–Ir(1)–P(1) 47.03(14), C(13)–Ir(1)–P(3) 96.16(15), C(1)–Ir(1)–P(3) 122.96(13), P(1)–Ir(1)–P(3) 109.44(4), C(13)–Ir(1)–P(2) 89.11(14), C(1)–Ir(1)–P(2) 137.78(13), P(1)–Ir(1)–P(2) 110.64(4), P(3)–Ir(1)–P(2) 96.97(4), C(1)–P(1)–C(6) 115.0(2), C(1)–P(1)–C(7) 119.7(2), C(1)–P(1)–Ir(1) 54.43(15), C(2)–C(1)–P(1) 137.7(4), P(1)–C(1)–Ir(1) 78.54(18).

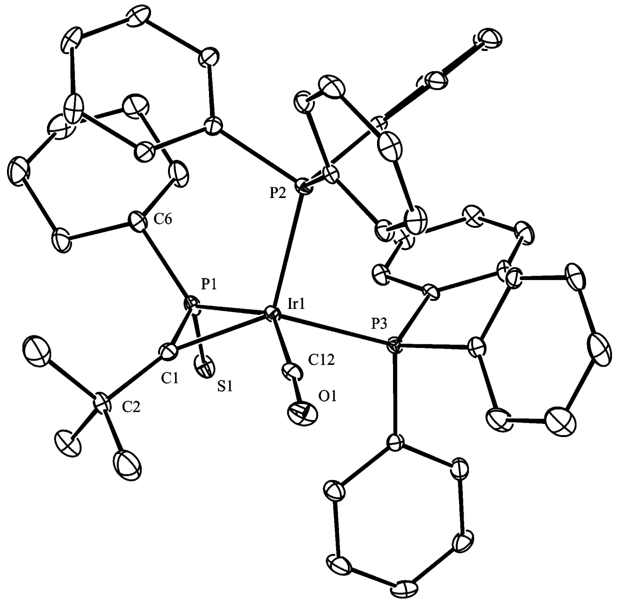

Fig. 4 Molecular structure of compound **8**. Selected bond lengths (Å) and angles (°): Ir(1)–C(1) 1.945(6), Ir(1)–P(1) 2.3552(17), Ir(1)–P(2) 2.3486(16), Ir(1)–P(3) 2.3692(17), Ir(1)–C(12) 1.899(7), P(1)–C(1) 1.746(6), P(1)–S(1) 1.992(2), P(1)–C(6) 1.843(7), C(12)–O(1) 1.145(8), C(1)–C(2) 1.503(8), C(12)–Ir(1)–C(1) 98.4(3), C(12)–Ir(1)–P(1) 143.75(19), C(1)–Ir(1)–P(1) 46.71(19), C(12)–Ir(1)–P(3) 92.3(2), C(1)–Ir(1)–P(3) 133.50(18), P(1)–Ir(1)–P(3) 105.73(6), C(12)–Ir(1)–P(2) 97.26(19), C(1)–Ir(1)–P(2) 125.14(19), P(1)–Ir(1)–P(2) 110.73(6), P(3)–Ir(1)–P(2) 97.79(6), C(1)–P(1)–C(6) 114.6(3), C(1)–P(1)–S(1) 118.5(2), C(6)–P(1)–S(1) 110.7(2), C(1)–P(1)–Ir(1) 54.2(2), C(2)–C(1)–P(1) 137.0(5), P(1)–C(1)–Ir(1) 79.1(3).

Conclusions

In conclusion, the reactivity of an iridaphosphirene complex, **3**, toward a variety of electrophiles has been investigated. In all cases reaction occurs at the phosphorus centre of the 3-membered ring and not the metal centre. The protonated complexes, **5a**–**c**, slowly undergo irreversible 1,2-hydrogen shifts to yield cationic iridium(I)–phosphaalkene complexes from which the phosphaalkene can be liberated by treatment with CO. A number of analogies between the structure, bonding and reactivity of **3** and those of metallocyclopropene complexes have been identified and discussed.

Experimental

General remarks

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon or dinitrogen. The solvents diethyl ether, THF, toluene and hexane were distilled over either potassium or Na/K alloy then freeze/thaw degassed prior to use. Dichloromethane was distilled from CaH_2. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on either Bruker DPX400 or Jeol Eclipse 300 spectrometers in deuterated solvents and were referenced to the residual ^1H or ^{13}C resonances of the solvent used (^1H and ^{13}C NMR) or external 85% H_3PO_4, 0.0 ppm (^{31}P NMR). ^{13}C NMR spectra of all compounds were complicated by overlapping multiplets in the aliphatic and aromatic regions and these signals could not be confidently assigned. The resonances due to the Ir=C carbon centre were too weak to be observed in **5**. Mass spectra

Table 1 Crystal data for compounds **5a**, **5b**·C_7H_8·CF_3CO_2H, **6**·Et_2O, **7** and **8**·$2C_7H_8$

	5a	**5b**·C_7H_8·CF_3CO_2H	**6**·Et_2O	**7**	**8**·$2C_7H_8$
Chemical formula	$C_{49}H_{51}F_3IrO_4P_3S$	$C_{59}H_{60}F_6IrO_5P_3$	$C_{52}H_{61}BF_4IrO_2P_3$	$C_{49}H_{53}IIrOP_3$	$C_{62}H_{66}IrOP_3S$
Fw	1078.07	1248.18	1089.93	1069.92	1144.32
Crystal system	Monoclinic	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$Pnma$	$P2_12_12_1$	$P2_1/c$
a/Å	16.616(3)	10.767(2)	19.183(4)	14.369(3)	12.675(3)
b/Å	15.143(3)	14.326(3)	16.407(3)	15.828(3)	37.548(8)
c/Å	18.633(4)	18.809(4)	15.806(3)	19.492(4)	12.036(2)
α/°	90	76.13(3)	90	90	90
β/°	97.30(3)	84.30(3)	90	90	111.17(3)
γ/°	90	84.07(3)	90	90	90
V/Å^3	4650.4(16)	2793.2(10)	4974.7(17)	4433.1(15)	5341.6(18)
Z	4	2	4	4	4
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
μ(Mo-Kα)/mm^{-1}	3.07	2.54	2.83	3.85	2.67
Reflections collected	59497	43499	85374	47718	70879
Unique reflections (R_{int})	8076 (0.1318)	10961 (0.0957)	5892 (0.03977)	10064 (0.0621)	9740 (0.1108)
R_1 ($I > 2\sigma(I)$)	0.0560	0.0542	0.0547	0.0293	0.0475
wR'_2 (all data)	0.1096	0.1404	0.1258	0.0594	0.1051

were recorded using a VG Fisons Platform II instrument under APCI (atmospheric pressure chemical ionisation) conditions. FAB mass spectra were obtained from the EPSRC Mass Spectrometry Service, Swansea University. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. The microanalysis was obtained from the Warwick Microanalytical Service. Where reproducible micro-analyses could not be obtained the NMR spectra of the samples suggested their purity was greater than 95%. The starting material, compound **3** was prepared by the literature procedure.[10] All other reagents were used as received.

[Ir{=C(Bu^t)P(H)(Cy)}(CO)(PPh$_3$)$_2$][CF$_3$SO$_3$] 5a

To a solution of **3** (0.10 g, 0.11 mmol) in diethyl ether (10 cm^3) at −78 °C was added HSO_3CF_3 (0.12 mmol) in diethyl ether (5 cm^3) over 5 min. The resulting solution was warmed to room temperature, stirred for 4 h after which time volatiles were removed *in vacuo*. The residue was washed with hexane, dissolved in CH_2Cl_2 (*ca.* 1 cm^3) and layered with hexane to afford orange prisms of **5a** overnight. (0.06 g, 52%), m.p. 183–185 °C; NMR: ^{1}H (400 MHz, CD_2Cl_2, 300 K) δ 0.70–2.03 (m, 11H, Cy), 1.52 (s, 9H, Bu^t), 7.02–7.53 (m, 30H, ArH), PH resonance not observed; ^{31}P{^{1}H} (121.7 MHz, CD_2Cl_2, 300 K) δ −142.7 (v.t. (virtual triplet), Ir=CP, $^2J_{PP}$ = 32 Hz), 8.0 (v.t., PPh$_3$, $^2J_{PP}$ = 32 Hz), 9.6 (v.t., PPh$_3$, $^2J_{PP}$ = 32 Hz); IR (Nujol, ν/cm^{-1}) 2003 (s, CO str.), 2350 (m, PH str.); MS FAB (Noba matrix): *m*/*z*: 900 [M$^+$ − (CO + CF_3SO_3), 70%].

[Ir{=C(Bu^t)P(H)(Cy)}(CO)(PPh$_3$)$_2$][X] X = CF$_3$CO$_2$ 5b, BF$_4$ 5c

Compounds **5b** and **5c** were prepared in a similar fashion to **5a**.

5b: (yield 60%), m.p. 73–75 °C; NMR: ^{1}H (400 MHz, C_7D_8, 300 K) δ 0.70–2.03 (m, 11H, Cy), 1.47 (s, 9H, Bu^t), 7.02–7.87 (m, 30H, ArH), PH resonance not observed; ^{31}P{^{1}H} (121.7 MHz, C_7D_8, 300 K) δ −139.2 (v.t., Ir=CP, $^2J_{PP}$ = 32 Hz), 5.70 (v.t., PPh$_3$, $^2J_{PP}$ = 32 Hz), 13.2 (v.t., PPh$_3$, $^2J_{PP}$ = 32 Hz); IR (Nujol, ν/cm^{-1}) 2013 (s, CO str.), 2340 (m, PH str.); MS FAB (Noba matrix): *m*/*z*: 930 [M$^+$ – CF_3CO_2 100%].

5c: (yield 50%), m.p. 169–171 °C; NMR: ^{1}H (400 MHz, CD_2Cl_2, 300 K) δ 0.79–1.87 (m, 11H, Cy), 1.53 (s, 9H, Bu^t), 6.99–7.67 (m, 30H, ArH), PH resonance not observed; ^{31}P{^{1}H} (121.7 MHz, CD_2Cl_2, 300 K) δ −142.9 (v.t., Ir=CP, $^2J_{PP}$ = 32 Hz), 8.20 (v.t., PPh$_3$, $^2J_{PP}$ = 32 Hz), 9.43 (v.t., PPh$_3$, $^2J_{PP}$ = 32 Hz); IR (Nujol, ν/cm^{-1}) 2014 (s, CO str.), 2370 (m, PH str.); MS FAB (Noba matrix): *m*/*z*: 930 [M$^+$ − BF$_4$, 25%].

[Ir(CO)(PPh$_3$)$_2${η^1-P(Cy)=C(H)(Bu^t)}][BF$_4$] 6

A solution of **5c** (0.030 g, 0.03 mmol) in CH_2Cl_2 (2 cm^3) was allowed to stand at 25 °C for 7 days after which time it was layered with hexane (10 cm^3) to yield orange prisms of **6** overnight. (0.028 g, 93%), m.p. 183–185 °C; NMR: ^{1}H (400 MHz, CD_2Cl_2, 300 K) δ 0.70–2.04 (m, 11H, Cy), 0.82 (s, 9H, Bu^t), 7.23–7.58 (m, 30H, ArH), 7.65 (d, 1H, P=CH, $^2J_{PH}$ = 23 Hz); ^{31}P{^{1}H} (121.7 MHz, CD_2Cl_2, 300 K) δ 15.2 (d, 2 PPh$_3$, $^2J_{PP}$ = 51 Hz), 222.4 (t, P=C, $^2J_{PP}$ = 51 Hz); IR (Nujol, ν/cm^{-1}) 2006 (s, CO str.); MS FAB (Noba matrix): *m*/*z*: 745 [Ir(CO)(PPh$_3$)$_2$$^+$, 40%], 715 [Ir(PPh$_3$)$_2$$^+$, 55%], 263 [PPh$_3H^+$, 100%].

[Ir{=C(Bu^t)P(Me)(Cy)}(CO)(PPh$_3$)$_2$]I 7

To a solution of **3** (0.10 g, 0.11 mmol) in THF (10 cm^3) at −78 °C was added MeI (0.12 mmol) in THF (5 cm^3) over 5 min. The resulting solution was warmed to room temperature, stirred for 4 h after which time volatiles were removed *in vacuo*. The residue was washed with hexane, dissolved in CH_2Cl_2 (*ca.* 1 cm^3) and layered with hexane to afford red prisms of **7** overnight. (0.075g, 70%), m.p. 216–218 °C; NMR: ^{1}H (400 MHz, C_6D_6, 300 K) δ 0.85–2.08 (m, 11H, Cy), 1.18 (d, 3H, PMe, $^2J_{PH}$ = 12 Hz), 1.53 (s, 9H, Bu^t), 6.99–7.46 (m, 30H, ArH); ^{13}C (101.6 MHz, CD_2Cl_2, 300 K) δ 178.3 (m, CO), 330.4 (m, Ir=C); ^{31}P{^{1}H} (121.7 MHz, CD_2Cl_2, 300 K) δ −121.4 (v.t., Ir=CP, $^2J_{PP}$ = 31 Hz), 4.8 (v.t., PPh$_3$, $^2J_{PP}$ = 31 Hz), 8.9 (v.t., PPh$_3$, $^2J_{PP}$ = 31 Hz); IR (Nujol, ν/cm^{-1}) 1992 (s, CO str.); MS FAB (Noba matrix): *m*/*z*: 944 [M$^+$ − I, 12%], 650 [M$^+$ − (I + CO), 100%]; Acc. mass ES$^+$: calc. for [M$^+$ − I] 943.2948, found 943.2942; elemental analysis, found: C 54.03, H 5.01, $C_{49}H_{53}IIrOP_3$ requires C 55.00, H 4.99.

[Ir{=C(Bu^t)P(=S)(Cy)}(CO)(PPh$_3$)$_2$] 8

A solution of **3** (0.10 g, 0.11 mmol) in toluene (10 cm^3) was added to a suspension of sulfur (0.15 mmol) in toluene (10 cm^3) at 25 °C and the resulting solution stirred for 3 h. Concentration of this solution *in vacuo* to *ca.* 5 cm^3 and cooling overnight to −30 °C afforded red prisms of **8**. (0.074g, 72%), m.p. 104–106 °C; NMR: ^{1}H (400 MHz, C_6D_6, 300 K) δ 0.66–2.38 (m, 11H, Cy), 1.82 (s, 9H, Bu^t), 7.29–7.78 (m, 30H, ArH); ^{13}C (101.6 MHz, CD_2Cl_2, 300 K) δ 183.3 (m, CO), 371.3 (m, Ir=C); ^{31}P{^{1}H} (121.7 MHz, CD_2Cl_2, 300 K) δ −86.1 (v.t., Ir=CP, $^2J_{PP}$ = 27 Hz), 9.1 (v.t., PPh$_3$, $^2J_{PP}$ = 27 Hz), 13.5 (v.t., PPh$_3$, $^2J_{PP}$ = 27 Hz); IR (Nujol, ν/cm^{-1}) 1983 (s, CO str.); MS APCI: *m*/*z*: 961 [MH$^+$, 100%], 263 [PPh$_3$H$^+$, 75%].

[Ir{=C(Bu^t)P(=Se)(Cy)}(CO)(PPh$_3$)$_2$] 9

To a solution of **3** (0.10 g, 0.11 mmol) in toluene (10 cm^3) at 25 °C was added selenium powder (0.15 mmol). The resulting suspension was stirred for 3 h and filtered. Concentration of the filtrate *in vacuo* to *ca.* 5 cm^3 and cooling overnight to −30 °C afforded black prisms of **9**. (0.044g, 40%), m.p. 95–97 °C; NMR: ^{1}H (400 MHz, C_6D_6, 300 K) δ 0.60–2.32 (m, 11H, Cy), 1.86 (s, 9H, Bu^t), 7.00–7.95 (m, 30H, ArH); ^{13}C (101.6 MHz, CD_2Cl_2, 300 K) δ 189.8 (m, CO), 341.2 (m, Ir=C); ^{31}P{^{1}H} (121.7 MHz, CD_2Cl_2, 300 K) δ −117.4 (v.t., Ir=CP, $^2J_{PP}$ = 28 Hz, $^1J_{SeP}$ = 653 Hz), 7.1 (v.t., PPh_3, $^2J_{PP}$ = 27 Hz), 14.5 (v.t., PPh_3, $^2J_{PP}$ = 27 Hz); IR (Nujol, ν/cm^{-1}) 1974 (s, CO str.); MS APCI: m/z: 1008 [MH$^+$, 100%].

Structure determinations

Crystals of **5a**, **5b**·$CF_3CO_2H·C_7H_8$, **6**·Et_2O, **7** and **8**·$2C_7H_8$ suitable for X-ray structure determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97 [15]) using all unique data. Crystal data, details of data collections and refinements are given in Table 1. The molecular structures of the complexes are depicted in Fig. 1–4 and show ellipsoids at the 30% probability level.

CCDC reference numbers 208255–208259.

See http://www.rsc.org/suppdata/dt/b3/b304076n/ for crystallographic data in CIF or other electronic format.

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