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A 2-iridafuran from reaction between a 1-iridaindene and methyl propiolate

Anja Bierstedt, George R. Clark, Warren R. Roper *, L. James Wright *

Department of Chemistry, The University of Auckland, Private Bag 92019, 23 Symonds Street, Auckland 1020, New Zealand

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Abstract

The coordinatively unsaturated 1-iridaindene, $Ir[C_8H_5(Ph\text{-}3)]Cl(PPh_3)_2$ has a labile chloride ligand and is easily converted to the corresponding iodide, $Ir[C_8H_5(Ph\text{-}3)]I(PPh_3)_2$ (**1**) by reaction with NaI. When $Ir[C_8H_5(Ph\text{-}3)]I(PPh_3)_2$ (**1**) is treated with methyl propiolate a reactive five-coordinate complex with both a diphenylvinyl ligand from ring-opening of the 1-iridaindene, and a 3-methoxy-3-oxoprop-1-ynyl ligand from deprotonation of methyl propiolate, is first produced. Reaction of this complex with aqueous HCl generates the 2-iridafuran, $Ir[OC_3H(CH{=}CPh_2\text{-}3)(OMe\text{-}5)]ClI(PPh_3)_2$ (**2**) probably from initial protonation at the β-carbon of the 3-methoxy-3-oxoprop-1-ynyl ligand to form a vinylidene ligand and subsequent migration of the diphenylvinyl ligand to the α-carbon of this ligand accompanied by oxygen coordination to iridium. Similar treatment of **1** with methyl propiolate followed by aqueous HI gives the corresponding complex, $Ir[OC_3H(CH{=}CPh_2\text{-}3)(OMe\text{-}5)]I_2(PPh_3)_2$ (**3**). The X-ray crystal structures of **2** and **3** together with NMR spectroscopic data confirm the 2-metallafuran structures of these complexes.

Keywords: Iridafuran; Iridaindene; Iridium; X-ray crystal structure

1. Introduction

Aromatic metallacycles continue to be the subject of extensive investigation. While metallabenzenes are an obvious focus of attention there is also interest in metallaheteroaromatic molecules [1]. This group includes the five-membered ring compounds, the metallafurans, metallathiophenes and metallapyrroles. While examples of metallathiophenes [2,3] and metallapyrroles [4] are quite scarce, there are numerous examples of metallafurans [5] involving metals across the transition series. By metallafurans we understand molecules with the five-membered ring connectivity shown in Chart 1, although in the literature such compounds have been variously referred to as chelated vinyl ketone complexes or oxametallacyclopentadiene complexes as well as metallafurans. The extent to which these compounds exhibit aromatic character varies, but aromaticity is well established for some [5] using the criteria of ring planarity, bond delocalization from structural data, NMR chemical shifts, and the observation of electrophilic substitution reactions. There is a very extensive literature relating to these compounds and they have been prepared in a great variety of ways. The principal routes are depicted in Chart 1 and we discuss these methods with representative but necessarily selective references. The most common synthesis is from insertion of an alkyne into the M—C bond of a metal-acyl complex (Method 1, Chart 1) [6]. Insertion of an alkyne bearing an ester function into a metal—X bond offers another well-documented route (Method 2, Chart 1) [7]. An early and very direct approach involves C—H oxidative addition of an alkene bearing an ester or related function to a low oxidation state metal center (Method 3, Chart 1) [8]. Oxidation of a metallacyclobutadiene is a further route to metallafurans (Method 4, Chart 1) [9]. Closely related to this is the oxidation of a cationic

* Corresponding authors. Tel.: +64 9 373 7999x88320; fax: +64 9 373 7422.
E-mail addresses: w.roper@auckland.ac.nz (W.R. Roper), lj.wright@auckland.ac.nz (L.J. Wright).

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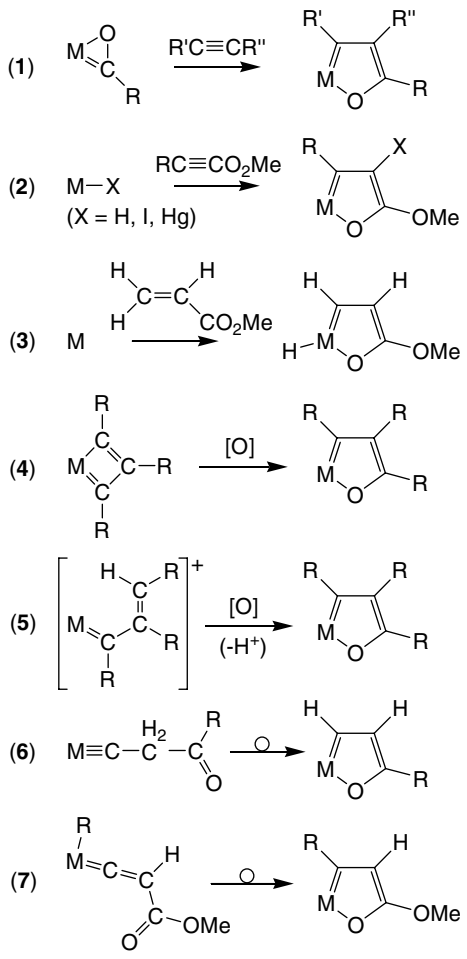


Chart 1. Major synthetic routes to metallafurans.

vinylcarbene complex (Method 5, Chart 1) [10]. In one instance a carbyne complex bearing a keto-function rearranges to a metallafuran (Method 6, Chart 1) [11]. Further rather special approaches include the reaction between an iridium ketene complex and an alkyne [12], and the reaction of a ruthenium vinylidene complex with silver acetylide where the acetylide bears a methyl ester function [13].

While exploring the attempted insertion of a vinylidene ligand into the five-membered ring of an iridaindene we discovered that methyl propiolate opened the iridaindene ring and upon the addition of acid a migratory insertion reaction ensued, generating an iridafuran (Method 7, Chart 1).

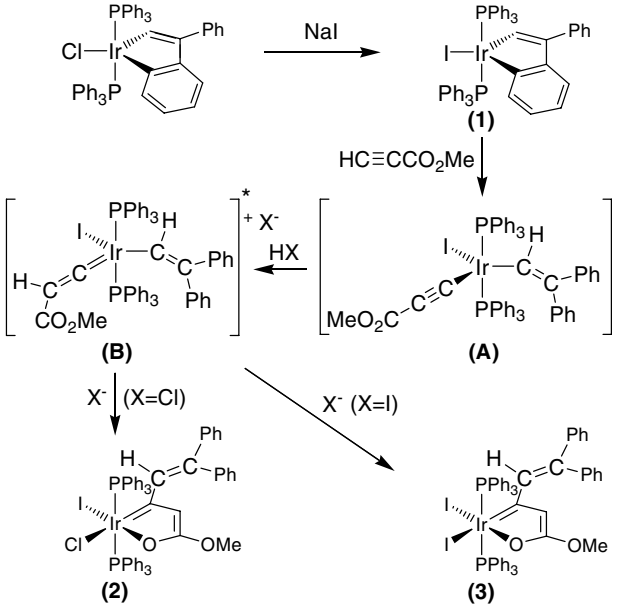
Herein, we report (i) the reaction between $Ir[C_8H_5(Ph\text{-}3)]I(PPh_3)_2$ (**1**) and methyl propiolate to form a reactive five-coordinate complex containing both a diphenylvinyl ligand from ring-opening of the 1-iridaindene, and a 3-methoxy-3-oxoprop-1-ynyl ligand from deprotonation of methyl propiolate, (ii) the reaction of this complex with either HCl or HI to give either the 2-iridafuran, $Ir[OC_3H(CH{=}CPh_2\text{-}3)(OMe\text{-}5)]ClI(PPh_3)_2$ (**2**) or the corresponding di-iodide, $Ir[OC_3H(CH{=}CPh_2\text{-}3)(OMe\text{-}5)]I_2(PPh_3)_2$ (**3**), and (iii) the crystal structure determinations of complexes **2** and **3.**

2. Results and discussion

2.1. The reaction between the iridaindene, $Ir[C_8H_5(Ph\text{-}3)]I(PPh_3)_2$ (1), and methyl propiolate

The chloride derivative of the iridaindene, $Ir[C_8H_5(Ph\text{-}3)]Cl(PPh_3)_2$, was originally prepared from the reaction between $IrCl(CS)(PPh_3)_2$ and $Hg(CH{=}CPh_2)_2$, in 20% yield [3]. A superior method of preparation is the reaction between $IrHCl_2(PPh_3)_3$ and $Hg(CH{=}CPh_2)_2$ which proceeds in 66% yield. This procedure is described in Section 4.2 of this paper. Because of the convenience of increased solubility, we have preferred to work with the iodide derivative of the iridaindene, $Ir[C_8H_5(Ph\text{-}3)]I(PPh_3)_2$ (**1**), and this is easily prepared from the chloride by treatment with NaI as shown in Scheme 1. Spectroscopic data for complexes **1**, **2**, and **3** are collected in Section 4. The ^{13}C and ^{31}P NMR chemical shifts for **1** are very close to those observed for $Ir[C_8H_5(Ph\text{-}3)]Cl(PPh_3)_2$ [3].

When a solution of **1** in dichloromethane with a large excess of methyl propiolate is heated under reflux the color of the solution changes from red to orange-yellow. Removal of all volatiles gives a yellow-brown product which could not be fully purified but which we formulate as the five coordinate acetylide, vinyl complex of iridium(III), $Ir(C{\equiv}CCO_2Me)(CH{=}CPh_2)I(PPh_3)_2$ (**A**) (see Scheme 1). This formulation is based on the following spectroscopic data and upon the product formed on reaction with CO. In the IR spectrum of **A** there is a strong band at 2112 cm^{-1} which is assigned to the terminal acetylide ligand ($\nu C{\equiv}C$), and another at 1681 cm^{-1} assigned to the methyl ester function of this acetylide ligand. In the ^1H NMR spectrum of **A** a singlet at 3.49 ppm is assigned to the methyl group of the ester and aromatic protons are seen in an envelope at 6.61–7.68 ppm. The unique



Scheme 1. Synthesis of iridafurans **2** and **3**.

diphenylvinyl proton is seen as an unresolved multiplet at 7.88 ppm and integral ratios for all these signals are appropriate. The ^{13}C NMR spectrum of **A** is particularly diagnostic of the presence of both the acetylide ligand and the diphenylvinyl ligand. In addition to the methyl carbon resonance at 51.5 ppm the iridium-bound carbon of the acetylide ligand is seen as a triplet at 72.1 ppm ($J_{PC} = 14.64$ Hz), and the other acetylide carbon is also seen as a triplet at 97.8 ppm ($J_{PC} = 3.39$ Hz). The ^{31}P NMR spectrum of **A** shows a singlet at −7.69 ppm. Finally, very convincing evidence for the formulation of **A** is that reaction with CO instantly forms the coordinatively saturated yellow complex, Ir(C≡CCO_2Me)(CH=CPh_2)I(CO)(PPh_3)$_2$ in good yield. This complex has been fully characterized including by X-ray crystal structure determination. The full experimental details for Ir(C≡CCO_2Me)(CH=CPh_2)I(CO)(PPh_3)$_2$, and its further reactions, will be described in a separate paper.

There is precedent for the ring-opening of a metallacyclopentadiene through reaction with an acetylene. An (η^2-acetato)bis(triphenylphosphine)iridacyclopentadiene reacts with alkynes with ring-opening of the five-membered metallacycle to give (alkynyl)(but-1,3-dien-1-yl)(η^2-acetato)bis-(triphenylphosphine)iridium(III) complexes [14]. This is closely related to the ring-opening reaction which we observe in Scheme 1 and it may be significant that our iridaindene, **1**, is coordinatively unsaturated and that the (η^2-acetato)bis(triphenylphosphine)iridacyclopentadiene is also potentially coordinatively unsaturated through opening of the chelated acetate ligand. We have not observed any similar reactions with coordinatively saturated iridaindenes derived from complex **1**, e.g., the carbonyl adduct, Ir[C_8H_5(Ph-3)]I(CO)(PPh_3)$_2$.

2.2. The reactions of Ir(C≡CCO_2Me)(CH=CPh_2)I(PPh_3)$_2$ (A) with either HCl or HI to form either Ir[OC_3H(CH=CPh_2-3)(OMe-5)]ClI(PPh_3)$_2$ (2) or Ir[OC_3H(CH=CPh_2-3)(OMe-5)]I_2(PPh_3)$_2$ (3), and the crystal structures of 2 and 3

When concentrated aqueous HCl or HI is added to a dichloromethane solution of **A** prepared as described above and the reaction mixture heated under reflux, the iridafuran complexes, either Ir[OC_3H(CH=CPh_2-3)(OMe-5)]ClI-(PPh_3)$_2$ (**2**) or Ir[OC_3H(CH=CPh_2-3)(OMe-5)]I_2(PPh_3)$_2$ (**3**), are formed in good yield (see Scheme 1). A reasonable rationalization of these transformations is that complex **A** is initially protonated at the β-carbon atom of the acetylide ligand so forming the cationic vinylidene complex **B**. This is a well-established route to vinylidene complexes [15]. A subsequent migratory insertion reaction, involving movement of the diphenylvinyl ligand to the α-carbon atom of the vinylidene ligand, will be favored for **B** because of its cationic nature. Finally, ring closure by bond formation between iridium and the carbonyl oxygen of the methyl ester substituent, together with coordination of a halide produces the observed red-orange iridafurans, **2** and **3**. This process is summarized in Method 7, Chart 1. Closely related to this preparative method is the result described by Bruce et al. [13] where the ester function resides on the migrating group rather than being a substituent on the vinylidene ligand.

The ^{1}H NMR spectra of **2** and **3** show the proton of the diphenylvinyl group on ring position 3 (see Chart 2 for ring numbering scheme of the 2-iridafurans) at 7.55 and 7.63 ppm, respectively; the proton on ring position 4 at 5.04 and 4.94 ppm, respectively; and the protons of the methoxy substituent on ring position 5 at 2.66 and 2.55 ppm, respectively. The ^{13}C NMR spectrum of **2** shows the carbons of the diphenylvinyl group on ring position 3 at 137.1 (*C*H) and 143.5 (*C*Ph_2) ppm and the corresponding resonances for **3** appear at 135.9 (*C*H) and 143.4 (*C*Ph_2) ppm. The signal for the carbon at ring position 3 is a triplet at 180.3 ppm ($^2J_{PC} = 6.7$ Hz), in compound **2** and the corresponding triplet signal for **3** is at 179.9 ppm ($^2J_{PC} = 6.7$ Hz). These low-field chemical shifts together with the significant coupling to phosphorus suggest a degree of multiple bonding between iridium and the carbon at position 3 (see valence bond structures **C** and **D** in Chart 2), consistent with the description of these compounds as 2-iridafurans. The signals for the carbons at ring positions 4 and 5 are singlets at 119.6 and 188.5 ppm, respectively, in compound **2** and the corresponding signals for **3** are at 119.1 and 190.3 ppm. The ^{31}P NMR spectra of **2** and **3** show the phosphorus resonances as singlets at −18.44 and −25.10 ppm, respectively.

The molecular geometries of **2** and **3** are shown in Figs. 1 and 2, respectively. Crystal data pertaining to these structures are presented in Table 1. Selected bond lengths and angles for **2** and **3** are collected in Table 2. There are two independent molecules in each of the structures. The molecules differ mostly in the orientations of the phenyl rings of the diphenylvinyl substituents, and only one arrangement is shown in each of the figures. In each structure the two triphenylphosphine ligands are located mutually *trans* and the two halide ligands are located mutually *cis*. The structure confirms the presence of a planar five-membered ring incorporating iridium, oxygen, and three carbon atoms, i.e., a 2-iridafuran. The structure of **2** reveals that the introduced chloride ligand (from HCl), takes the position *trans* to carbon. There is a significant difference in the Ir—halogen distances depending upon whether the halogen is located *trans* to oxygen or carbon. For **2**, where chloride is located *trans* to carbon, Ir—ClA is 2.4602(16) and

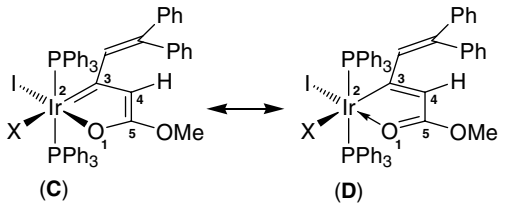


Chart 2. Valence bond structures, **C** and **D**, for the new 2-iridafurans, Ir[OC_3H(CH=CPh_2-3)(OMe-5)]ClI(PPh_3)$_2$ (**2**) and Ir[OC_3H(CH=CPh_2-3)(OMe-5)]I_2(PPh_3)$_2$ (**3**) and the ring numbering scheme for naming of the compounds and the NMR discussion.

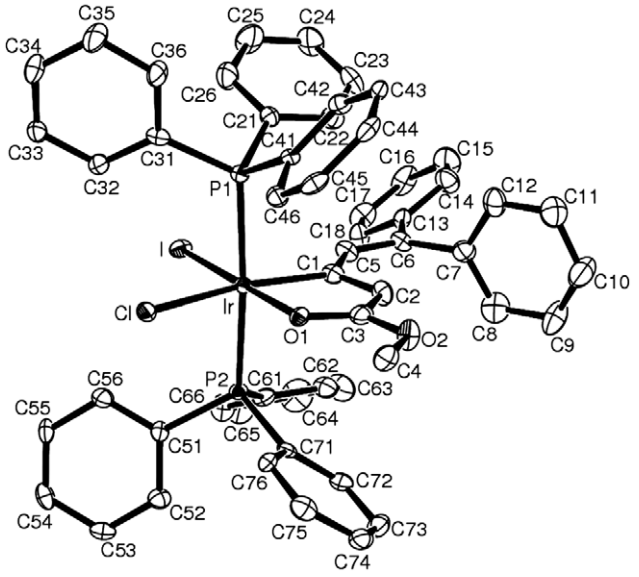


Fig. 1. The molecular geometry of molecule A of Ir[OC_3H(CH=CPh_2-3)(OMe-5)]ClI(PPh_3)$_2$ (**2**) showing the atom labeling and atoms as 50% probability displacement ellipsoids [23]. N.B. the crystallographic atom numbering scheme differs from that given in Chart 1.

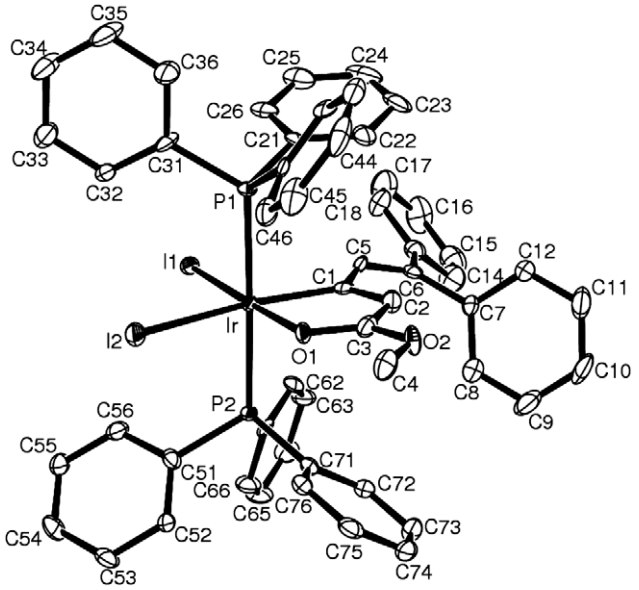


Fig. 2. The molecular geometry of molecule A of Ir[OC_3H(CH=CPh_2-3)(OMe-5)]I_2(PPh_3)$_2$ (**3**) showing the atom labeling and atoms as 50% probability displacement ellipsoids [23]. N.B. the crystallographic atom numbering scheme differs from that given in Chart 1.

Ir—ClB is 2.4755(15) Å. These values are longer than the average for 572 recorded observations for Ir—Cl bonds in 6-coordinate iridium (2.4046 with a SD of 0.066 Å, Cambridge Crystallographic Data Base). For **3**, the iodide located *trans* to carbon has the longer Ir—I bond at Ir—I(2A), 2.7563(5), Ir—I(2B), 2.7764(5) Å compared to the iodide *trans* to oxygen at Ir—I(1A), 2.6639(5), Ir—I(1B), 2.6668(5) Å. These values can be compared with the average for 123 recorded observations for Ir—I bonds in 6-coordinate iridium (2.7564 with a SD of 0.060 Å, Cambridge Crystallographic Data Base). It is interesting that Ir—I distance *trans* to oxygen is at the short end of the observed range. The observed Ir—C distances are: Ir—C(1A), 2.040(6); Ir—C(1B), 2.035(6) in **2** and Ir—C(1A), 2.057(7); Ir—C(1B), 2.051(6) in **3**. All of these distances are considerably shorter than expected for an Ir—C single bond which has an average of 2.1255 with a SD of 0.0560 Å (247 observations, Cambridge Crystallographic Data Base). They are also closely comparable to those values reported for other iridafurans [5,12]. There is also evidence for bond equalization in the observed iridafuran ring C—C distances (see Table 2). Thus the structural data and the NMR spectroscopic data discussed above are all consistent with contributions to the bonding from the two valence bond structures **C** and **D** in Chart 2.

Table 1
Data collection and processing parameters for **2** and **3**

	2	**3**
Formula	$C_{54}H_{45}ClIIrO_2P_2$	$C_{54}H_{45}I_2IrO_2P_2$
Molecular weight	1142.39	1233.84
Crystal system	Monoclinic	Monoclinic
Space group	*Pc*	*C2/c*
a (Å)	18.6340(2)	74.7537(1)
b (Å)	12.3538(2)	12.4000(1)
c (Å)	20.1672(2)	20.0369(1)
β (°)	102.322(1)	93.882(2)
V (Å^3)	4535.56(10)	18,530.51(15)
T (K)	86(2)	83(2)
Z	4	16
D_{calc} (g cm^{-3})	1.673	1.769
F(000)	2248	9568
μ (mm^{-1})	3.796	4.325
Crystal size (mm)	0.24 × 0.24 × 0.20	0.20 × 0.20 × 0.20
$2\theta_{min,max}$ (°)	1.65, 26.42	1.64, 26.49
Reflections collected	26,693	109,225
Independent reflections (R_{int})	14,619 (0.0265)	19,050 (0.0519)
$T_{min,max}$	0.4627, 0.5173	0.3624, 0.5847
Goodness-of-fit on F^2	1.097	1.031
R, wR_2 (observed data)	0.0244, 0.0540	0.0464, 0.0991
R, wR_2 (all data)	0.0261, 0.0550	0.0677, 0.1071

$R = \sum\|F_o| - |F_c\|/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

3. Conclusions

It has been demonstrated that the coordinatively unsaturated iridaindene, **1**, undergoes a reaction with methyl propiolate in which the five-membered metallacyclic ring is opened to a diphenylvinyl ligand (through protonation) accompanied by coordination of a 3-methoxy-3-oxoprop-1-ynyl ligand (from deprotonation of methyl propiolate). This unexpected product reacts further with acids by initial protonation of the β-carbon of the alkynyl ligand to give a coordinated vinylidene ligand, followed by migration of the diphenylvinyl ligand to the α-carbon of the vinylidene ligand together with coordination of the ester carbonyl oxygen to give the 2-iridafurans, Ir[OC_3H(CH=CPh_2-3)-(OMe-5)]ClI(PPh_3)$_2$ (**2**) and Ir[OC_3H(CH=CPh_2-3)(OMe-5)]I_2(PPh_3)$_2$ (**3**). Spectroscopic and structural data for **2** and **3** support the 2-iridafuran formulations.

Table 2
Selected bond lengths (Å) and angles (°) for **2** and **3**

2		**3**	
Bond lengths			
IrA—C(1A)	2.040(6)	Ir(1A)—C(1A)	2.057(7)
IrA—O(1A)	2.086(4)	Ir(1A)—O(1A)	2.097(4)
IrA—P(2A)	2.3606(13)	Ir(1A)—P(1A)	2.3688(17)
IrA—P(1A)	2.3720(14)	Ir(1A)—P(2A)	2.3739(16)
IrA—ClA	2.4602(16)	Ir(1A)—I(1A)	2.6639(5)
IrA—IA	2.6636(4)	Ir(1A)—I(2A)	2.7563(5)
O(A)—C(3A)	1.261(8)	O(1A)—C(3A)	1.263(7)
C(1A)—C(2A)	1.394(9)	C(1A)—C(2A)	1.375(9)
C(1A)—C(5A)	1.465(9)	C(1A)—C(5A)	1.452(9)
C(2A)—C(3A)	1.421(9)	C(2A)—C(3A)	1.427(9)
C(5A)—C(6A)	1.350(9)	C(5A)—C(6A)	1.359(9)
IrB—C(1B)	2.035(6)	Ir(1B)—C(1B)	2.051(6)
IrB—O(1B)	2.079(4)	Ir(1B)—O(1B)	2.088(4)
IrB—P(1B)	2.3690(13)	Ir(1B)—P(1B)	2.3709(16)
IrB—P(2B)	2.3909(13)	Ir(1B)—P(2B)	2.3780(16)
IrB—ClB	2.4755(15)	Ir(1B)—I(1B)	2.6668(5)
IrB—IB	2.6598(4)	Ir(1B)—I(2B)	2.7764(5)
O(1B)—C(3B)	1.251(7)	O(1B)—C(3B)	1.262(7)
C(1B)—C(2B)	1.357(8)	C(1B)—C(2B)	1.373(9)
C(1B)—C(5B)	1.475(8)	C(1B)—C(5B)	1.440(9)
C(2B)—C(3B)	1.436(8)	C(2B)—C(3B)	1.436(9)
C(5B)—C(6B)	1.353(8)	C(5B)—C(6B)	1.352(8)
Bond angles			
C(3A)—O(1A)—IrA	112.0(4)	C(3A)—O(1A)—Ir(1A)	111.4(4)
C(2A)—C(1A)—C(5A)	121.8(6)	C(2A)—C(1A)—C(5A)	122.2(6)
C(2A)—C(1A)—IrA	111.5(4)	C(2A)—C(1A)—Ir(1A)	112.1(5)
C(5A)—C(1A)—IrA	126.7(5)	C(5A)—C(1A)—Ir(1A)	125.7(5)
C(1A)—C(2A)—C(3A)	115.1(6)	C(1A)—C(2A)—C(3A)	114.9(6)
O(1A)—C(3A)—O(2A)	120.6(6)	O(1A)—C(3A)—O(2A)	120.0(6)
O(1A)—C(3A)—C(2A)	120.8(6)	O(1A)—C(3A)—C(2A)	121.5(6)
O(2A)—C(3A)—C(2A)	118.6(6)	O(2A)—C(3A)—C(2A)	118.5(6)
C(6A)—C(5A)—C(1A)	129.5(6)	C(6A)—C(5A)—C(1A)	129.5(7)
C(5A)—C(6A)—C(13A)	120.0(6)	C(5A)—C(6A)—C(7A)	123.9(7)
C(5A)—C(6A)—C(7A)	124.2(6)	C(5A)—C(6A)—C(13A)	119.6(6)
C(13A)—C(6A)—C(7A)	115.8(6)	C(7A)—C(6A)—C(13A)	116.5(6)
C(3B)—O(1B)—IrB	112.2(4)	C(3B)—O(1B)—Ir(1B)	112.5(4)
C(2B)—C(1B)—C(5B)	121.9(5)	C(2B)—C(1B)—C(5B)	121.9(6)
C(2B)—C(1B)—IrB	113.4(4)	C(2B)—C(1B)—Ir(1B)	112.3(5)
C(5B)—C(1B)—IrB	124.7(4)	C(5B)—C(1B)—Ir(1B)	125.8(5)
C(1B)—C(2B)—C(3B)	113.9(5)	C(1B)—C(2B)—C(3B)	115.0(6)
O(1B)—C(3B)—O(2B)	120.5(5)	O(1B)—C(3B)—O(2B)	121.4(6)
O(1B)—C(3B)—C(2B)	120.9(5)	O(1B)—C(3B)—C(2B)	120.3(6)
O(2B)—C(3B)—C(2B)	118.6(5)	O(2B)—C(3B)—C(2B)	118.3(6)
C(6B)—C(5B)—C(1B)	128.6(6)	C(6B)—C(5B)—C(1B)	130.7(6)
C(5B)—C(6B)—C(13B)	121.3(6)	C(5B)—C(6B)—C(7B)	122.9(6)
C(5B)—C(6B)—C(7B)	122.7(6)	C(5B)—C(6B)—C(13B)	121.6(6)
C(13B)—C(6B)—C(7B)	115.9(5)	C(7B)—C(6B)—C(13B)	115.4(6)

4. Experimental

4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [16]. The compound $Ir[C_8H_5$-(Ph-3)]$Cl(PPh_3)_2$ was prepared either by the literature method [3] or by the improved preparation described in Section 4.2, below. $IrHCl_2(PPh_3)_3$ [17] and $Hg(CH{=}CPh_2)_2$ [18] were prepared according to the reported procedures.

Infrared spectra (4000–400 cm^{-1}) were recorded as Nujol mulls between KBr plates on a Perkin–Elmer Paragon 1000 spectrometer. NMR spectra were obtained on either a Bruker DRX 400 or a Bruker Avance 300 at 25 °C. For the Bruker DRX 400, ^1H, ^{13}C and ^{31}P NMR spectra were obtained operating at 400.1 (^1H), 100.6 (^{13}C) and 162.0 (^{31}P) MHz, respectively. For the Bruker Avance 300, ^1H, ^{13}C, and ^{31}P NMR spectra were obtained operating at 300.13 (^1H), 75.48 (^{13}C) MHz, and 121.50 (^{31}P) MHz, respectively. Resonances are quoted in ppm and ^1H NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for $CHCl_3$). ^{13}C NMR spectra were referenced to $CDCl_3$ (77.00 ppm), and ^{31}P NMR spectra to 85%

orthophosphoric acid (0.00 ppm) as an external standard. Mass spectra were recorded using the fast atom bombardment technique with a Varian VG 70-SE mass spectrometer. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

4.2. Improved preparation of $Ir[C_8H_5(Ph\text{-}3)]Cl(PPh_3)_2$

A solution of $IrHCl_2(PPh_3)_3$ (1.015 g, 1.00 mmol) and $Hg(CH{=}CPh_2)_2$ (670 mg, 1.20 mmol) in dry benzene (20 mL) was heated under reflux for 4 h. The reaction mixture was then filtered through Celite to remove the precipitated material and the Celite washed with benzene. The solvent was removed under vacuum and the product purified by recrystallisation from dichloromethane/ethanol to give pure $Ir[C_8H_5(Ph\text{-}3)]Cl(PPh_3)_2$ as an orange solid (614 mg, 66%). The spectral properties of this material were identical to those published previously [3].

4.3. Preparation of $Ir[C_8H_5(Ph\text{-}3)]I(PPh_3)_2$ (**1**)

To a solution of $Ir[C_8H_5(Ph\text{-}3)]Cl(PPh_3)_2$ (2.145 g, 2.31 mmol) in dichloromethane (50 mL) was added a solution of NaI (3.46 g, 23.1 mmol) in ethanol (20 mL) and water (0.5 mL). The reaction mixture was stirred for 2.5 h. The resulting dark-red solution was dried with Na_2SO_4, filtered and the solvent removed under vacuum. Recrystallisation of the residue from dichloromethane/ethanol gave pure **1** as a red crystalline solid (2.07 g, 88%). *m/z* 1022.1301 and 1020.1275; $C_{50}H_{40}I^{193}IrP_2$ and $C_{50}H_{40}I^{191}IrP_2$ requires 1022.1279 and 1020.1256, respectively. Anal. Calc. for $C_{50}H_{40}IIrP_2$: C, 58.77; H, 3.95. Found: C, 58.58; H, 3.96%. IR (cm^{-1}): 1185(w), 1156(w), 1092(m), 768(m), 742(m), 729(m), 693(s), 512(s). ^1H NMR ($CDCl_3$, δ): 6.06–7.37 (m, 40H, multiplet signals not individually assigned from PPh_3, iridaindeneH, and Ph substituent on iridaindene). ^{13}C NMR ($CDCl_3$, δ): 127.5 (t′ [16], $^{2,4}J_{CP} = 10.1$ Hz, *o*-C_6H_5P), 129.8 (s, *p*-C_6H_5P), 130.6 (t′, $^{1,3}J_{CP} = 55.6$ Hz, *i*-C_6H_5P), 135.1 (t′, $^{3,5}J_{CP} = 10.8$ Hz, *m*-C_6H_5P); singlet signals all CH, not individually assigned, at 121.8, 122.0, 123.6, 125.4, 127.1, 127.3, from C's of iridaindene six-membered ring and Ph substituent on iridaindene; 131.4 (t, $^2J_{CP} = 8.3$ Hz, iridaindene *C*2H), 139.0 (s, quat. C, unassigned), 142.4 (t, $^2J_{CP} = 6.8$ Hz, iridaindene *C*Ir), 154.1 (t, $^2J_{CP} = 3.4$ Hz, quat. C, unassigned), 154.9 (s, quat. C, unassigned). ^{31}P NMR ($CDCl_3$, δ): 23.17 (s).

4.4. Preparation of $Ir[OC_3H(CH{=}CPh_2\text{-}3)\text{-}(OMe\text{-}5)]ClI(PPh_3)_2$ (**2**)

$Ir[C_8H_5(Ph\text{-}3)]I(PPh_3)_2$ (**1**) (102 mg, 0.1 mmol) was dissolved in dry dichloromethane (5 mL) which was degassed by repeated freeze-pump-thaw cycles. This solution was then heated to reflux and methyl propiolate (84 mg, 10.0 mmol) added. The colour of the reaction mixture changed slowly from red to orange-yellow. After 15 min, conc. HCl (0.2 mL) was added dropwise to the reaction mixture and heating under reflux continued for 90 min. After cooling to room temperature solid $NaHCO_3$ was added to neutralize the excess acid. This mixture was filtered through Celite and dried over $MgSO_4$. The solvent was removed from this dried solution under vacuum. The resulting red oil was purified by chromatography on silica gel using dichloromethane as eluent. The red-orange band was collected and the solid obtained from this was recrystallised from CH_2Cl_2/ethanol to give pure **2** as a red-orange microcrystalline solid (84 mg, 74%). *m/z* 1142.12391; $C_{54}H_{45}{}^{35}Cl I^{193}IrO_2P_2$ requires 1142.12575. Anal. Calc. for $C_{54}H_{45}ClIrO_2P_2$: C, 56.77; H, 3.97. Found: C, 56.62; H, 3.91%. IR (cm^{-1}): 1714(w), 1548(m), 1262(m), 1188(m), 1157(w), 1091(s), 1029(w), 820(w), 746(m), 697(s). ^1H NMR (see ring-numbering scheme in Chart 1) ($CDCl_3$, δ): 2.66 (s, 3H, OCH_3), 5.04 (s, 1H, *H*(4)), 6.11–7.26 (m, 28H, $CH_{aromatic}$), 7.55 (s, 1H, $CH{=}CPh_2$), 7.94–8.00 (m, 12H, $CH_{aromatic}$). ^{13}C NMR ($CDCl_3$, δ): 53.4 (s, OCH_3), 119.6 (s, *C*(4)), 127.3 (t′, $^{2,4}J_{CP} = 9.2$ Hz, *o*-C_6H_5P), 127.7, 127.9, 128.2, 128.3 (s, aromatic C's of the diphenylvinyl group), 129.8 (s, *p*-C_6H_5P), 130.3 (t′, $^{1,3}J_{CP} = 53.2$ Hz, *i*-C_6H_5P), 135.7 (t′, $^{3,5}J_{CP} = 9.0$ Hz, *m*-C_6H_5P), 137.1 (s, *C*H=CPh_2), 139.9 (s (quat.), *ipso*-C of the diphenylvinyl group), 141.1 (s (quat.), *ipso*-C of the diphenylvinyl group), 143.5 (s, =*C*Ph_2), 180.3 (t, $^2J_{PC} = 6.7$ Hz, *C*3), 188.5 (s, *C*5). ^{31}P NMR ($CDCl_3$, δ): −18.44 (s).

4.5. Preparation of $Ir[OC_3H(CH{=}CPh_2\text{-}3)\text{-}(OMe\text{-}5)]I_2(PPh_3)_2$ (**3**)

$Ir[C_8H_5(Ph\text{-}3)]I(PPh_3)_2$ (**1**) (102 mg, 0.1 mmol) was dissolved in dry dichloromethane (5 mL) which was degassed by repeated freeze-pump-thaw cycles. This solution was then heated to reflux and methyl propiolate (84 mg, 10.0 mmol) added. The colour of the reaction mixture changed slowly from red to orange-yellow. After 15 min, 55% HI (0.2 mL) was added dropwise to the reaction mixture and heating under reflux continued for 30 min. After cooling to room temperature solid $NaHCO_3$ was added to neutralize the excess acid. This mixture was filtered through Celite, and dried over $MgSO_4$. The solvent was removed from this dried solution under vacuum. The resulting red oil was purified by chromatography on silica gel using dichloromethane/hexane (1:1) as eluent. The red-orange band was collected and the solid obtained from this was recrystallised from CH_2Cl_2/ethanol to give pure **3** as a red-orange microcrystalline solid (61 mg, 50%). *m/z*, 1105.15470 and 1107.15434; $C_{54}H_{45}{}^{35}I^{191}IrO_2P_2$ requires 1105.15456 $[M-I]^+$ and $C_{54}H_{45}{}^{35}I^{193}IrO_2P_2$ requires 1107.15690 $[M-I]^+$. Anal. Calc. for $C_{54}H_{45}I_2IrO_2P_2$: C, 52.56; H, 3.68. Found: C, 52.33; H, 3.82%. IR (cm^{-1}): 1549(s), 1261(m), 1205(m), 1086(s), 1037(s), 747(m), 722(m), 692(s). ^1H NMR (see ring-numbering scheme in Chart 1) ($CDCl_3$, δ): 2.55 (s, 3H, OCH_3), 4.94 (s, 1H, *H*(4)), 6.11–7.28 (m, 28H, $CH_{aromatic}$), 7.63 (s, 1H, $CH{=}CPh_2$), 7.99 (m, 12H, $CH_{aromatic}$). ^{13}C NMR ($CDCl_3$, δ): 53.4

(s, OCH_3), 119.1 (s, *C*(4)), 127.2 (t′, $^{2,4}J_{CP} = 9.8$ Hz, *o*-C_6H_5P), 127.4, 127.7, 128.0, 128.2, 128.3 (s, aromatic C's of the diphenylvinyl group), 129.8 (s, *p*-C_6H_5P), 130.8 (s very br, *i*-C_6H_5P), 136.1 (s br, *m*-C_6H_5P), 135.9 (s, *C*H=CPh$_2$), 140.0 (s (quat.), *ipso*-C of the diphenylvinyl group), 141.1 (s (quat.), *ipso*-C of the diphenylvinyl group), 143.4 (s, =*C*Ph$_2$), 179.9 (t, $^2J_{PC} = 6.7$ Hz, *C*3), 190.3 (s, *C*5). ^{31}P NMR ($CDCl_3$, δ): −25.10 (s).

4.6. X-ray crystal structure determinations for complexes 2 and 3

X-ray intensities were recorded on a Siemens SMART diffractometer with a CCD area detector using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 86 or 83 K. Data were integrated and corrected for Lorentz and polarisation effects using SAINT [19]. Semi-empirical absorption corrections were applied based on equivalent reflections using SADABS [20]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using programs SHELXS97 [21] and SHELXL97 [22]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using ORTEP-III [23]. Both crystals contain two crystallographically independent molecules which differ in the orientation of the phenyl rings due to crystal packing effects. Crystal data and refinement details for both structures are given in Table 1.

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Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 299550 and 299551, respectively. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.035.

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