Available online at www.sciencedirect.com

Journal of Organometallic Chemistry 690 (2005) 972–981

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

A 2-iridathiophene from reaction between $IrCl(CS)(PPh_3)_2$ and $Hg(CH{=}CHPh)_2$

Guo-Liang Lu, Warren R. Roper *, L. James Wright *, George R. Clark

Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand

Received 31 August 2004; accepted 20 October 2004

Abstract

The thiocarbonyl analogue of Vaska's compound is produced in high yield by first treating $IrCl(CO)(PPh_3)_2$ with CS_2 and methyl triflate to give $[Ir(\kappa^2\text{-}C[S]SMe)Cl(CO)(PPh_3)_2]CF_3SO_3$ (**1**), secondly, reacting **1** with $NaBH_4$ to give $IrHCl(C[S]SMe)(CO)(PPh_3)_2$ (**2**), and finally heating **2** to induce elimination of both MeSH and CO to produce $IrCl(CS)(PPh_3)_2$ (**3**). When $IrCl(CS)(PPh_3)_2$ is treated with $Hg(CH{=}CHPh)_2$ the novel 2-iridathiophene, $Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HCl(PPh_3)_2$ (**4**) is produced. The X-ray crystal structure of the iodo-derivative of **4**, $Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HI(PPh_3)_2$ (**5**) confirms the unusual 2-metallathiophene structure. Treatment of $IrCl(CS)(PPh_3)_2$ with $Hg(CH{=}CPh_2)_2$ produces both a coordinatively unsaturated 1-iridaindene, $Ir[C_8H_5(Ph\text{-}3)]Cl(PPh_3)_2$ (**6**) and a chelated dithiocarboxylate complex, $Ir(\kappa^2\text{-}S_2CCH{=}CPh_2)Cl(CH{=}CPh_2)(PPh_3)_2$ (**7**). X-ray crystal structure determinations for **6** and **7** are reported.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Iridathiophene; Iridium; X-ray crystal structure; Thiocarbonyl ligand

1. Introduction

Since the report of the first metallabenzene in 1982 [1], this novel class of compounds has grown to include stable examples incorporating all three third-row platinum group metals (Os [2], Ir [3], Pt [4]) as well as a fused ring metalla-aromatic in the form of an iridanaphthalene [5]. There are even examples of related isometallabenzenes [6], metallabenzynes [7], and of other metalla-heteroaromatic molecules, e.g., a group of iridathiophenes [8] and a group of metallafurans [9].

In the original osmabenzene synthesis, the OsC_5 ring was assembled from two ethyne molecules and a single carbon atom from a thiocarbonyl ligand already resident on the osmium in the starting material, $Os(CS)(CO)(PPh_3)_3$. Two pathways can be envisaged for this reaction. The first involves initial formation of an osmacyclobutenthione ring, from combination of CS with one ethyne molecule, followed by ring expansion through reaction with a second ethyne to give an osmacyclohexadienthione and finally aromatization of this osmacyclohexadienthione through coordination of sulfur to osmium. There is precedent for the first step of this pathway in that reaction between $Os(CS)(CO)(PPh_3)_3$ and diphenylacetylene produces a complex with an osmacyclobutenthione ring [10]. The second pathway would involve initial formation of an osmacyclopentadiene from combination of two ethyne molecules on the osmium followed by ring expansion through insertion of the thiocarbonyl ligand into this five-membered ring. Either pathway depends for its success on the readiness with which the thiocarbonyl ligand undergoes insertion reactions. In related work, we have demonstrated that the thiocarbonyl ligand will insert into Os–H [11], Os–C [12], Os–Si [13], and Os–B [14] bonds. With the exception of the Os–C example,

---

* Corresponding authors. Tel: +64 9 373 7999x8320; fax: +64 9 373 7422.

E-mail address: w.roper@auckland.ac.nz (W.R. Roper).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.10.050

insertion of a carbonyl ligand into these bonds, has not been observed.

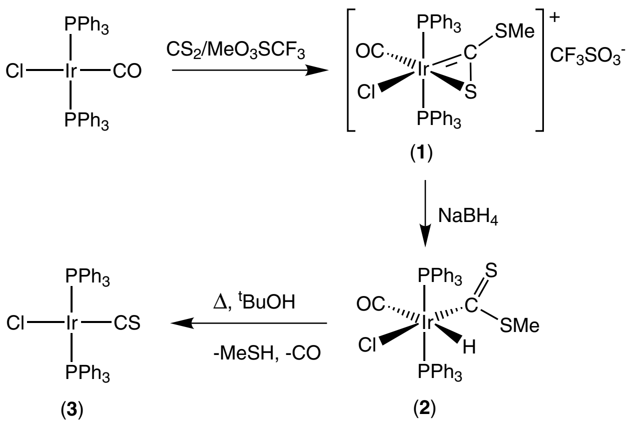
We have discovered that reaction between $OsCl(NO)(PPh_3)_3$ and $Hg(CH{=}CHPh)_2$ leads, among other products, to the hydrido 1-osmaindene complex, $Os(C_8H_6)H(NO)(PPh_3)_2$, presumably through cyclometallation of an introduced CH=CHPh ligand [15]. We were therefore led to examine the reaction between $IrCl(CS)(PPh_3)_2$ and $Hg(CH{=}CHPh)_2$ in the expectation that any iridaindene formed might insert the thiocarbonyl ligand thus producing an iridanaphthalene. In fact, this did not happen but, nevertheless, unexpected and interesting products were formed.

Herein, we report: (i) full experimental details for the high-yield conversion of $IrCl(CO)(PPh_3)_2$ to $IrCl(CS)(PPh_3)_2$ (**3**) via the intermediates $[Ir(\kappa^2\text{-}C[S]SMe)Cl(CO)(PPh_3)_2]CF_3SO_3$ (**1**) and $IrHCl(C[S]SMe)(CO)(PPh_3)_2$ (**2**), (ii) the reaction of **3** with $Hg(CH{=}CHPh)_2$ which leads to the hydrido 2-iridathiophene, $Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HCl(PPh_3)_2$ (**4**), (iii) the conversion of **4** to the iodide analogue, $Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HI(PPh_3)_2$ (**5**), (iv) the reaction of **3** with $Hg(CH{=}CPh_2)_2$ which leads to a mixture of the 1-iridaindene, $Ir[C_8H_5(Ph\text{-}3)]Cl(PPh_3)_2$ (**6**) and the dithiocarboxylate complex, $Ir(\kappa^2\text{-}S_2CCH{=}CPh_2)Cl(CH{=}CPh_2)(PPh_3)_2$ (**7**), and (iii) the crystal structure determinations of complexes **5**–**7**.

2. Results and discussion

2.1. High-yield conversion of $IrCl(CO)(PPh_3)_2$ to $IrCl(CS)(PPh_3)_2$

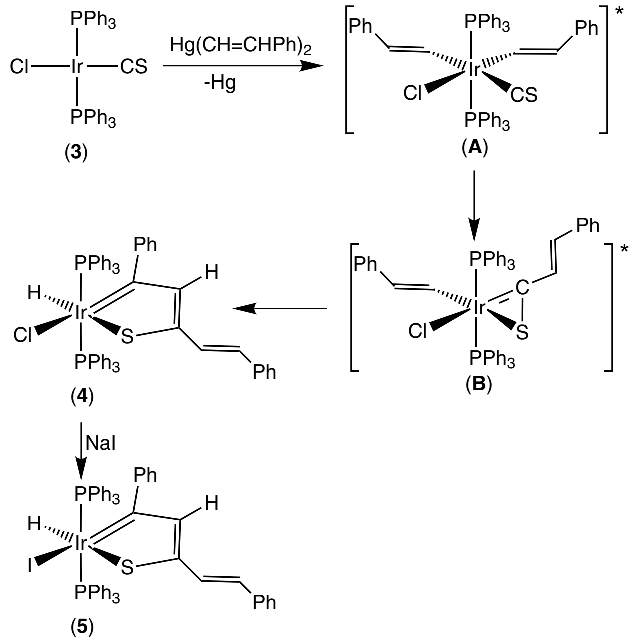
As depicted in Scheme 1, and has been reported, briefly, in an earlier publication [16], when $IrCl(CO)(PPh_3)_2$ is dissolved in CS_2 (so forming $Ir(\kappa^2\text{-}CS_2)Cl(CO)(PPh_3)_2$) and then treated with methyl triflate, methylation occurs at the unbound sulfur and the methyldithioester-containing cation is formed as the triflate salt, $[Ir(\kappa^2\text{-}C[S]SMe)Cl(CO)(PPh_3)_2]CF_3SO_3$ (**1**). Complex **1** is a pale yellow solid formed in almost quantitative yield. The IR spectrum shows $\nu(CO)$ at 2038 cm^{-1}. In the ^1H NMR spectrum, there is a signal at 2.19 ppm associated with the dithioester methyl group and in the ^{13}C NMR spectrum a signal at 30.7 ppm is also associated with this group. The iridium-bound carbon of the dithioester group appears as a triplet at 239.7 ppm ($^2J_{CP} = 3.9$ Hz) and the carbonyl carbon appears as a triplet at 168.8 ppm ($^2J_{CP} = 8.3$ Hz). The mutually *trans* arrangement of the two triphenylphosphine ligands is indicated by the appearance of virtual triplet signals for the carbons of these ligands and by the singlet resonance in the ^{31}P NMR spectrum at -2.50 ppm. Treatment of this salt with sodium borohydride introduces an hydride ligand so forming in high yield the neutral, orange-pink, monodentate methyldithioester-containing complex, $IrHCl(C[S]SMe)(CO)(PPh_3)_2$ (**2**). The IR spectrum of **2** shows $\nu(CO)$ at 2036 cm^{-1} and there is a further medium absorption at 985 cm^{-1} associated with the monodentate dithioester function. In the ^1H NMR spectrum, there is a triplet signal at -11.91 ppm ($^2J_{HP} = 14.0$ Hz) associated with the hydride ligand. The triplet coupling indicates that the two triphenylphosphine ligands remain mutually *trans* as depicted to Scheme 1. In the ^{13}C NMR spectrum, the methyl carbon resonance is at 20.8 ppm and the iridium-bound carbon of the dithioester group appears as a broad signal at 288.7 ppm and the carbonyl carbon appears as a triplet at 161.4 ppm ($^2J_{CP} = 8.0$ Hz). There is a singlet resonance in the ^{31}P NMR spectrum at -1.46 ppm. Heating complex **2** in *t*-butanol results in the elimination of MeSH and the loss of CO to give in quantitative yield, the previously reported [17], orange, iridium(I) thiocarbonyl complex, $IrCl(CS)(PPh_3)_2$ (**3**). The distinctive $\nu(CS)$ for **3** at 1332 cm^{-1} and all other spectroscopic features were concordant with literature values.



Scheme 1. Synthesis of $IrCl(CS)(PPh_3)_2$ (**3**).

2.2. Reaction between $IrCl(CS)(PPh_3)_2$ and $Hg(CH{=}CHPh)_2$ leading to the hydrido-2-iridathiophene, $Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HCl(PPh_3)_2$ (4), and the crystal structure of $Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HI(PPh_3)_2$ (5)

As shown in Scheme 2, complex **3** reacts rapidly with $Hg(CH{=}CHPh)_2$ in benzene under reflux with deposition of elemental mercury and formation, in high yield, the green-black crystalline hydrido-2-iridathiophene, $Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HCl(PPh_3)_2$ (**4**). This formula is written assuming the 2-metallathiophene structure with the numbers following the substituents Ph and CH=CHPh indicating the ring positions of these substituents (the numbering system is given in Chart 1). There is proof of this structure in the X-ray crystal



Scheme 2. Reaction between $IrCl(CS)(PPh_3)_2$ and $Hg(CH{=}CHPh)_2$. *Compounds **A** and **B** are postulated intermediates, not characterised.

structure determination of the iodide derivative of **4** (compound **5**) to be described below. Related iridathiophene complexes have been described previously from introduction to iridium of the thiapentadienide ion and subsequent systematic modification of this ligand [8a,8b]. That the same ring system is assembled in the work described in this paper from a CS ligand and two styryl fragments is testimony to the stability of this aromatic metallacycle. Remarkably, the iridathiophene described by Bleeke could be treated with excess bromine, without damaging the ring, to bring about electrophilic substitution (bromination) of the iridathiophene (see compound depicted in Chart 1) [8b].

There is precedent for the reaction of $IrCl(CO)(PPh_3)_2$ with organomercury compounds, for example, the reaction with $Hg(C{\equiv}CPh)_2$ leads to the simple oxidative addition product, $Ir[Hg(C{\equiv}CPh)](C{\equiv}CPh)Cl(CO)(PPh_3)_2$ [18]. This compound resists thermal elimination of mercury. In the reaction sequence described in Scheme 2, involving $IrCl(CS)(PPh_3)_2$ rather than $IrCl(CO)(PPh_3)_2$, it is likely that the initial product is also the oxidative addition product, $Ir[Hg\ (CH{=}CHPh)](CH{=}CHPh)Cl(CS)(PPh_3)_2$, but this must undergo further reactions, rapidly. One possibility is that mercury is eliminated [19] to give compound **A** in Scheme 2 which in turn undergoes rapid migratory insertion of the CS ligand to give compound **B** [12]. β-Hydrogen elimination from **B** would give both $PhC{\equiv}CH$ (perhaps retained in the coordination sphere) and the Ir–H bond observed in the product **4**. Combination of the $PhC{\equiv}CH$ with the κ^2-vinylthioacyl ligand in **B** could lead to the observed product $Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HCl(PPh_3)_2$ (**4**). Other pathways can be envisaged but whatever steps occur the overall reaction is clean and high yielding.

The IR spectrum of **4** shows $\nu(IrH)$ at 2195 cm^{-1}. In the ^1H NMR spectrum, there is a triplet signal at -11.11 ppm ($^2J_{HP} = 14.0$ Hz) associated with the hydride ligand. The triplet coupling indicates that the two triphenylphosphine ligands remain mutually *trans* as depicted in Scheme 2. In the ^{13}C NMR spectrum, the 2-iridathiophene ring carbons appear at 222.9 (C3), 144.9 (C4), and 209.8 (C5) ppm (following the ring numbering system given in Chart 1). The low-field resonance for C3 is consistent with a carbene-like character for the Ir–C bond. These chemical shifts correspond closely with the values found for Bleeke's related iridathiophene complexes depicted in Chart 1 where the ring carbons have been renumbered from the original publications to match the numbering scheme we are using. For the

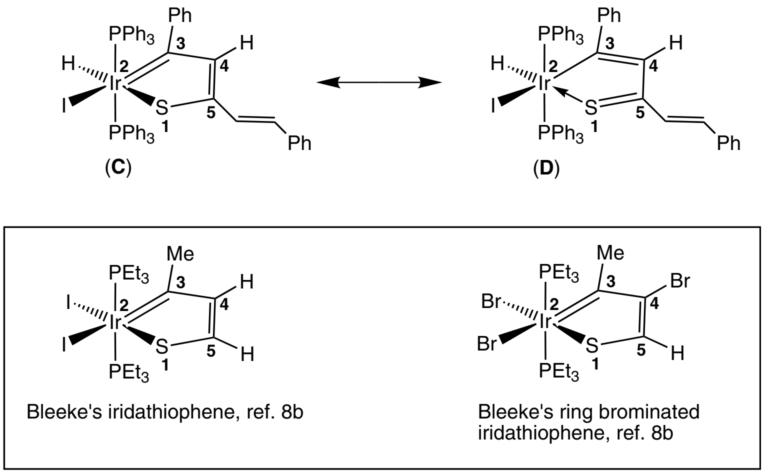


Chart 1. Ring numbering scheme and valence bond structures for the new 2-iridathiophene, $Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HI(PPh_3)_2$ (**5**), and other related iridathiophenes.

non-brominated iridathiophene, the C3, C4 and C5 chemical shifts are 235.3, 150.3 and 205.1 ppm, respectively, and for the brominated iridathiophene the corresponding chemical shifts are 222.4, 129.2 and 201.5 ppm [8b].

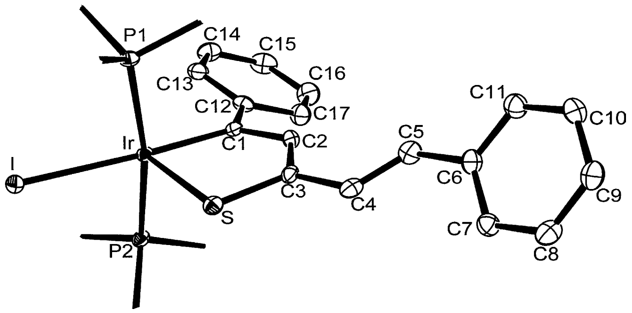


Fig. 1. The molecular geometry and atomic numbering scheme for Ir[SC_3H(Ph-3)(CH=CHPh-5)]HI($(PPh_3)_2$) (**5**) (for clarity, phenyl rings on the triphenylphosphine ligands are not shown). N.B. the crystallographic numbering scheme differs from that given in Chart 1.

Crystals of **4** suitable for X-ray study could not be obtained. However, the lability of the chloride ligand allowed replacement of the chloride by iodide forming Ir[SC_3H(Ph-3)(CH=CHPh-5)]HI($(PPh_3)_2$) (**5**) and suitable crystals of **5** were easily obtained. The spectroscopic properties of **5** are closely similar to those of **4**. The IR spectrum of **5** shows ν(IrH) at 2221 cm^{-1} and in the ^1H NMR spectrum there is a triplet signal at −11.95 ppm ($^2J_{HP}$ = 16.0 Hz) associated with the hydride ligand. In the ^{13}C NMR spectrum, the 2-iridathiophene ring carbons appear at 225.0 (C3), 144.6 (C4), and 211.7 (C5) ppm (following the ring numbering system given in Chart 1). The molecular geometry of **5** is shown in Fig. 1. Crystal data pertaining to this structure and other structures reported in this paper are presented in Table 1. Selected bond lengths and angles for **5** are collected in Table 2. The two triphenylphosphine ligands are located mutually *trans* and the hydride ligand is *trans* to S. The Ir–C distance is 2.018(3) Å, a value intermediate between the values for iridium–carbon single and double bonds as also indicated by the low-field ^{13}C NMR chemical shift discussed above. The Ir–S distance is 2.4048(7) Å, only slightly longer than the value found for the Ir–S bond in the cationic iridathiophene (2.383(3) Å) [8b], which also has a hydride ligand *trans* to S. The defining feature of the 2-iridathiophene ring is the move towards equalization of the ring C–C bond distances. Using the numbering system in Chart 1, C3–C4 is 1.384(4) and C4–C5 is 1.403(4) Å. Similar equalization of these distances is seen in the iridathiophene structures reported by Bleeke, 1.362(15) and 1.399(16) Å in the cationic iridathiophene [8b], 1.362(19) and 1.370(22) Å in the brominated iridathiophene [8b]. The combined structural and spectroscopic data for **5** suggests electron delocalization within the five-membered metallacycle and that it is appropriate to consider contributions to the bonding from both valence bond structures **C** and **D** in Chart 1.

Table 1
Data collection and processing parameters for **5**–**7**

Compound	**5**	**6**	**7**
Empirical formula	$C_{53}H_{44}IIrP_2S$	$C_{50}H_{40}ClIrP_2 \cdot 2CH_2Cl_2$	$C_{65}H_{52}ClIrP_2S_2$
Molecular weight	1093.98	1100.26	1186.78
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	*Pbca*	$P2_1/n$
a (Å)	11.7400(2)	11.0556(2)	14.8861(4)
b (Å)	17.4351(3)	23.3614(3)	18.9695(5)
c (Å)	21.2830(3)	35.3358(3)	18.5187(5)
α (°)	90.0	90.0	90.0
β (°)	94.3560(10)	90.0	91.738(1)
γ (°)	90.0	90.0	90.0
V (Å)^3	4 343.79(12)	9 126.3(2)	5 226.9(2)
Z	4	8	4
D_{calc} (g cm^{-3})	1.673	1.602	1.508
F(0 0 0)	2 152	4 384	2 392
μ (mm^{-1})	3.943	3.325	2.789
Crystal size (mm)	0.36 × 0.20 × 0.12	0.22 × 0.10 × 0.10	0.42 × 0.32 × 0.20
θ (Min–max) (°)	1.92–27.23	1.74–25.76	1.54–27.09
Independent reflections ($I > 2\sigma(I)$)	9545, R_{int} 0.0299	8735 R_{int} 0.0597	10,528 R_{int} 0.0139
T(min,max)	0.331, 0.649	0.528, 0.732	0.366, 0.572
Goodness-of-fit on F^2	1.062	1.221	1.077
R, wR_2(observed data)	0.0246, 0.0573	0.0704, 0.1274	0.0179, 0.0417
R, wR_2(all data)	0.0308, 0.0605	0.1049, 0.1389	0.0212, 0.0433

$^aR = \sum \|F_o| - |F_c\|/\Sigma|F_o|.wR_2 = \{\sum[(w(F)_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for **5**

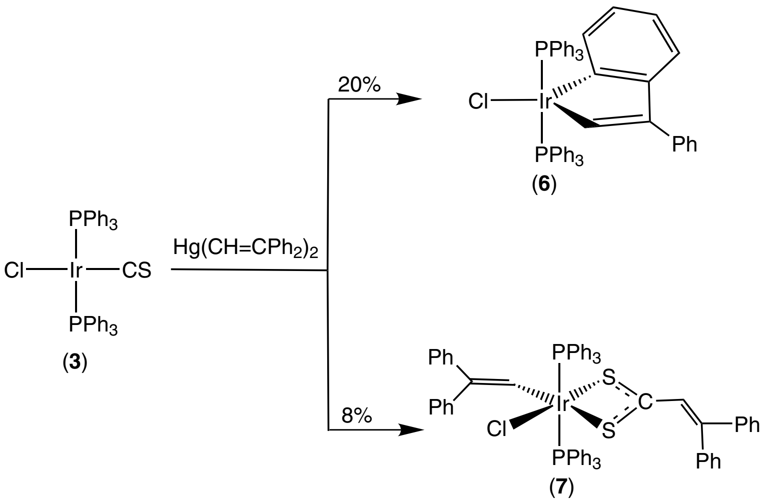
Bond lengths	
Ir–I	2.7589(2)
Ir–S	2.4048(7)
Ir–P1	2.3482(7)
Ir–P2	2.3209(7)
Ir–C1	2.018(3)
S–C3	1.687(3)
C1–C2	1.384(4)
C1–C12	1.487(4)
C2–C3	1.403(4)
C3–C4	1.459(4)
C4–C5	1.326(4)
C5–C6	1.460(4)
Bond angles	
I–Ir–S	99.03(2)
I–Ir–P1	84.91(2)
I–Ir–P2	88.46(2)
I–Ir–C1	177.12(8)
P1–Ir–P2	169.43(3)
S–Ir–C1	83.04(8)
Ir–C1–C2	118.0(2)
C1–C2–C3	121.4(3)
S–C3–C2	118.5(2)
S–C3–C4	116.8(2)
C3–C4–C5	125.2(3)
C4–C5–C6	124.2(3)

*2.3. Reaction between $IrCl(CS)(PPh_3)_2$ and $Hg(CH{=}CPh_2)_2$ leading to a mixture of the 1-iridaindene, $Ir[C_8H_5(Ph\text{-}3)]Cl(PPh_3)_2$ (**6**) and the dithiocarboxylate complex, $Ir(\kappa^2\text{-}S_2CCH{=}CPh_2)Cl(CH{=}CPh_2)(PPh_3)_2$ (**7**), and the crystal structure determinations of these complexes*

The reaction between $IrCl(CS)(PPh_3)_2$ and $Hg(CH{=}CHPh)_2$, as detailed above in Section 2.2, did not lead to an iridanaphthalene which had been our original aim as discussed Section 1. Instead, the reaction pathway led to a molecule with an Ir–H bond (complex **4**) and a reasonable explanation for the presence of the hydride ligand is that it arose from a β-hydrogen elimination reaction of the styryl ligand. Accordingly, the reaction of $IrCl(CS)(PPh_3)_2$ with $Hg(CH{=}CPh_2)_2$, in which there is no β-hydrogen in the vinyl group, was explored. An added advantage of $Hg(CH{=}CPh_2)_2$ is that regardless of the orientation about the carbon–carbon double bond in the resulting iridium-bound vinyl ligand, there will always be a phenyl group in a position appropriate for *ortho*-metalation. There are several reports of such *ortho*-metalation reactions leading to metallaindene complexes, e.g., [20]. As depicted in Scheme 3, this reaction does lead to a 1-iridaindene, the orange complex, $Ir[C_8H_5(Ph\text{-}3)]Cl(PPh_3)_2$ (**6**), (in only 20% yield) but surprisingly this compound no longer incorporates a CS ligand. Complete loss of a CS ligand is very unusual and a clue as to the fate of this ligand is provided by a second product isolated from this reaction (in only 8% yield) which has two S atoms in a dithiocarboxylate ligand, the dark-red complex, $Ir(\kappa^2\text{-}S_2CCH{=}CPh_2)Cl(CH{=}CPh_2)(PPh_3)_2$ (**7**). In view of the low yields of the isolated products and their complex and unexpected nature, we do not feel that it is useful to speculate on the details of the reaction pathway. Nevertheless, complexes **6** and **7** have both been fully characterised including by crystal structure determination.

In the ^1H NMR spectrum of **6**, there is an unresolved triplet at 7.42 ppm assigned to the iridium-bound CH, and in the ^{13}C NMR spectrum, triplet resonances at 131.6 ppm ($^2J_{CP} = 8.1$ Hz) and 141.8 ppm ($^2J_{CP} = 6.5$ Hz) are assigned to the two iridium-bound carbon atoms, IrCH and IrC, respectively. An interesting feature of complex **6** is that it is coordinatively unsaturated. In a future publication, we will report on the further reactions of this compound.

The molecular geometry of **6** is shown in Fig. 2. Selected bond lengths and angles for **6** are collected in Table 3. The two triphenylphosphine ligands are again



Scheme 3. Reaction between $IrCl(CS)(PPh_3)_2$ and $Hg(CH{=}CPh_2)_2$.

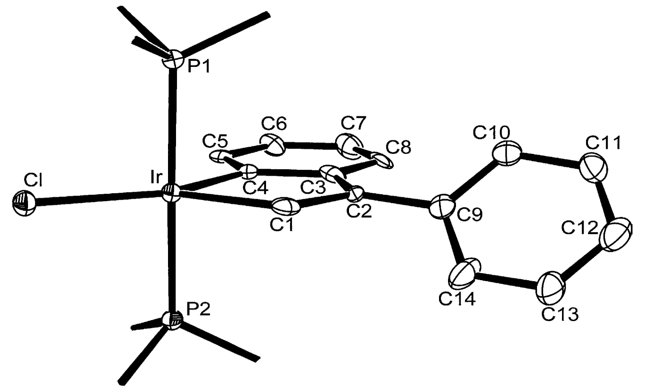


Fig. 2. The molecular geometry and atomic numbering scheme for Ir[C_8H_5(Ph-3)]Cl(PPh_3)$_2$ (**6**) (for clarity, phenyl rings on the triphenylphosphine ligands are not shown).

Table 3
Selected bond lengths (Å) and angles (°) for **6**

Bond lengths	
Ir–Cl	2.402(2)
Ir–P1	2.336(2)
Ir–P2	2.330(2)
Ir–C1	1.982(10)
Ir–C4	2.004(10)
C1–C2	1.344(13)
C2–C3	1.457(14)
C2–C9	1.475(13)
C3–C4	1.427(14)
Bond angles	
Cl–Ir–P1	91.19(8)
Cl–Ir–P2	90.70(8)
Cl–Ir–C1	136.7(3)
Cl–Ir–C4	147.2(3)
P1–Ir–P2	176.61(9)
C1–Ir–C4	76.1(4)
Ir–C1–C2	122.9(8)
C1–C2–C3	111.3(9)
C1–C2–C9	123.3(9)
C2–C3–C4	111.0(9)
Ir–C4–C3	118.7(7)

located mutually *trans* with Ir–P distances of 2.336(2) and 2.330(2) Å. The Ir–Cl distance is 2.402(2) Å and this is close to the average for 65 recorded observations for Ir–Cl bonds in five-coordinate iridium (2.3851 with a SD of 0.0382 Å, Cambridge Crystallographic DataBase). The Ir–CH distance is 1.982(10) Å and the other Ir–C distance is 2.004(10) Å. These values are less than would be expected for single bonds, which is consistent with some degree of multiple bond character, although the five-coordinate nature of **6** will also be influencing these distances. There is, however, little evidence for any delocalization within the five-membered ring since C1–C2 (see Fig. 2) is 1.344(13) Å, whereas C2–C3 is 1.457(14) and C3–C4 is 1.427(14) Å.

The minor product of the reaction depicted in Scheme 3, is the dark-red, dithiocarboxylate complex, Ir(κ^2-S_2CCH=CPh_2)Cl(CH=CPh_2)(PPh_3)$_2$ (**7**). One can speculate that the dithiocarboxylate ligand arises in some way from intermolecular S atom abstraction from the CS ligand by a thioacyl ligand. In the ^{1}H NMR spectrum of **7**, a triplet signal at 8.52 ppm ($^3J_{HP}$ = 3.2 Hz) is assigned to the proton of the iridium-bound vinyl group and a singlet signal at 5.61 ppm is assigned to the proton of the vinyl substituent on the dithiocarboxylate ligand. In the ^{13}C NMR spectrum, a triplet signal at 142.6 ppm ($^2J_{CP}$ = 3.2 Hz) is assigned to the iridium-bound carbon and another triplet at 235.3 ($^3J_{CP}$ = 3.6 Hz) is assigned to the dithiocarboxylate carbon.

The molecular geometry of **7** is shown in Fig. 3. Selected bond lengths and angles for **7** are collected in Table 4. The two triphenylphosphine ligands are again

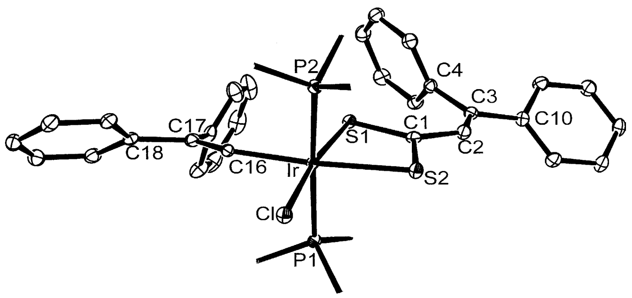


Fig. 3. The molecular geometry and indicative atomic numbering scheme for Ir(κ^2-S_2CCH=CPh_2)Cl(CH=CPh_2)(PPh_3)$_2$ (**7**) (for clarity, phenyl rings on the triphenylphosphine ligands are not shown). Numbering of the illustrated phenyl rings is, clockwise around the rings, C4–C9, C10–C15, C18–C23 and C24–C29.

Table 4
Selected bond lengths (Å) and angles (°) for **7**

Bond lengths	
Ir–Cl	2.4392(4)
Ir–S1	2.3350(4)
Ir–S2	2.4604(5)
Ir–P1	2.3745(5)
Ir–P2	2.3566(5)
Ir–C16	2.081(2)
S1–C1	1.694(2)
S2–C1	1.709(2)
C1–C2	1.4559(3)
C2–C3	1.355(3)
C16–C17	1.351(3)
Bond angles	
Cl–Ir–S1	172.64(1)
Cl–Ir–S2	101.33(1)
Cl–Ir–P1	87.32(2)
Cl–Ir–P2	89.09(2)
Cl–Ir–C16	85.40(5)
P1–Ir–P2	175.08(2)
S1–Ir–S2	71.41(1)
S1–Ir–C16	101.89(5)
S2–Ir–C16	173.19(5)
Ir–S1–C1	91.13(6)
Ir–S2–C1	86.61(7)
S1–C1–S2	110.78(11)
C1–C2–C3	130.3(2)
Ir–C16–C17	140.16(14)

located mutually *trans* with Ir–P distances of 2.3566(5) and 2.3745(5) Å. The Ir–Cl distance is 2.4392(4) Å, slightly longer than the average for 496 recorded observations for Ir–Cl bonds in six-coordinate iridium (2.4087 with a SD of 0.0669 Å, Cambridge Crystallographic DataBase). The Ir–C distance is 2.081(2) Å. This and all other features of the iridium-bound diphenylvinyl group are unremarkable. The attachment of the dithiocarboxylate is unsymmetrical with the longer Ir–S distance (2.4604(5) Å) *trans* to the diphenylvinyl ligand and the shorter Ir–S distance (2.3350(4) Å) *trans* to chloride. Presumably, this is a reflection of the relative *trans* influences of the carbon donor and the chloride. Similar observations have frequently been made for related dithiocarbamate complexes [21].

3. Conclusions

It has been demonstrated that the introduction of 2-phenylvinyl ligands to $IrCl(CS)(PPh_3)_2$, through reaction with $Hg(CH{=}CHPh)_2$, leads to the assembly of a 2-iridathiophene through ligand combination of CS and two 2-phenylvinyl fragments. The initial hydride-containing 2-iridathiophene, $Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HCl(PPh_3)_2$ (**4**) is readily converted to $Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HI(PPh_3)_2$ (**5**) and spectroscopic data for both and the crystal structure of **5** confirm the 2-iridathiophene formulation. By using $Hg(CH{=}CPh_2)_2$ instead of $Hg(CH{=}CHPh)_2$ in the reaction with $IrCl(CS)(PPh_3)_2$, the absence of a β-hydrogen diverts the reaction away from 2-iridathiophene formation and produces, in low yield, the coordinatively unsaturated 1-iridaindene, $Ir[C_8H_5(Ph\text{-}3)]Cl(PPh_3)_2$ (**6**), which no longer retains a CS ligand, and the chelated dithiocarboxylate complex, $Ir(\kappa^2\text{-}S_2CCH{=}CPh_2)Cl(CH{=}CPh_2)(PPh_3)_2$ (**7**).

4. Experimental

4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [22]. The compounds $IrCl(CO)(PPh_3)_2$ [23], $Hg(CH{=}CHPh)_2$ [24,25], and $Hg(CH{=}CPh_2)_2$ [25,26], were prepared by the literature methods.

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. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

4.2. Preparation of $[Ir(\kappa^2\text{-}C[S]SMe)Cl(CO)(PPh_3)_2]CF_3SO_3$ (*1*)

$IrCl(CO)(PPh_3)_2$ (2.00 g, 2.56 mmol) was stirred in CS_2 (50 mL) until fully dissolved. Methyl triflate (1.25 mL, 11.0 mmol) was added and the resulting solution stirred for 4 h to afford a pale yellow suspension. Benzene (50 mL) was added to complete precipitation and the pale yellow solid collected by filtration (CAUTION: filtrate will contain unreacted methyl triflate). The solid was recrystallised from dichloromethane/benzene to give pure **1** as an off-white microcrystalline solid (2.58 g, 94 %). The ^1H NMR spectrum shows the presence of benzene of solvation (2/3 of a molecule of benzene per molecule of complex), consistent with the elemental analysis. Anal. Calc. for $C_{40}H_{33}ClF_3IrO_4P_2S_3 \cdot 2/3C_6H_6$: C, 49.21; H, 3.60. Found: C, 49.22; H, 3.60%. IR (cm^{-1}): 2038s ν(CO); 1272s, 1261s, 1153s, 1030s. ^1H NMR ($CDCl_3$, δ): 2.19 (s, 3H, CS_2Me), 7.47–7.70 (m, 30H, PPh_3). ^{13}C NMR ($CDCl_3$, δ): 30.7 (s, CS_2Me), 125.9 (t′ [22], $^{1,3}J_{CP} = 59.8$ Hz, $i\text{-}C_6H_5$), 129.3 (t′, $^{2,4}J_{CP} = 11.0$ Hz, $o\text{-}C_6H_5$), 132.6 (s, $p\text{-}C_6H_5$), 134.3 (t′, $^{3,5}J_{CP} = 10.8$ Hz, $m\text{-}C_6H_5$), 168.8 (t, $^2J_{CP} = 8.3$ Hz, CO), 239.7 (t, $^2J_{CP} = 3.9$ Hz, CS_2Me). ^{31}P NMR ($CDCl_3$, δ): −2.50 (s, PPh_3).

4.3. Preparation of $IrHCl(C[S]SMe)(CO)(PPh_3)_2$ (*2*)

In a Schlenk tube, $[Ir(\kappa^2\text{-}C[S]SMe)Cl(CO)(PPh_3)_2]CF_3SO_3$ (**1**) (2.50 g, 2.45 mmol) was suspended in ethanol (20 mL) and treated with a solution of sodium borohydride (0.50 g, 13.2 mmol) in ethanol (10 mL). The solution was stirred for 15 min to produce an orange-pink solid which was collected by filtration. This was recrystallised from dichloromethane/ethanol to afford pure **2** as pink crystals (1.62 g, 76%). Anal. Calc. for $C_{39}H_{34}ClIrOP_2S_2$: C, 53.69; H, 3.93. Found: C, 53.69, H, 4.01%. IR (cm^{-1}): 2036s ν(CO), 985m (CS_2Me). ^1H NMR ($CDCl_3$, δ): −11.91 (t, 1H, $^2J_{HP} = 14.0$ Hz, IrH) 1.94 (s, 3H, CS_2Me), 7.32–7.75 (m, 30H, PPh_3). ^{13}C NMR ($CDCl_3$, δ): 20.8 (s, Me), 127.8 (t′, $^{2,4}J_{CP} = 10.0$ Hz, $o\text{-}C_6H_5$) 129.7 (t′, $^{1,3}J_{CP} = 58.4$ Hz, $i\text{-}C_6H_5$), 130.7 (s, $p\text{-}C_6H_5$), 134.7 (t′, $^{3,5}J_{CP} = 10.0$ Hz, $m\text{-}C_6H_5$), 161.4 (t, $^2J_{CP} = 8.0$ Hz, CO), 288.7 (m, CS_2Me). ^{31}P NMR ($CDCl_3$, δ): −1.46 (s, PPh_3).

4.4. Preparation of $IrCl(CS)(PPh_3)_2$ (**3**)

$IrHCl(C[S]SMe)(CO)(PPh_3)_2$ (**2**) (1.60 g, 1.83 mmol) was suspended in *t*-butanol (40 mL) and heated under reflux for 11 h with a slow stream of nitrogen passing through the suspension. The resulting yellow-orange suspension was filtered to give an orange solid which was recrystallised from dichloromethane/ethanol to give pure **3** as orange crystals (1.40 g, 95.8%). Characterization was by comparison with literature spectroscopic data [17].

4.5. Preparation of $Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HCl(PPh_3)_2$ (**4**)

A suspension of $IrCl(CS)(PPh_3)_2$ (0.127 g, 0.16 mmol) and $Hg(CH{=}CHPh)_2$ (0.072 g, 0.18 mmol) in benzene (20 mL) was heated under reflux for 5 min to give a dark red solution with a precipitate of elemental mercury. The mercury was removed by filtration through Celite and all volatiles then removed from the filtrate under reduced pressure. The residue was taken up in CH_2Cl_2 and purified by column chromatography on silica gel using first a mixture of CH_2Cl_2 and hexane (v/v = 1:1), and then pure CH_2Cl_2 as eluents. The major brown band from the CH_2Cl_2 eluent was collected, and the isolated solid recrystallised from CH_2Cl_2/EtOH/heptane to give pure **4** as greenish black crystals (0.120 g, 75%). Anal. Calc. for $C_{53}H_{44}ClIrP_2S0.\ 5CH_2Cl_2$: C, 61.49; H, 4.34. Found: C, 61.61; H, 4.46%. IR (cm^{-1}): 2195, ν(IrH). ^1H NMR ($CDCl_3$, δ): −11.11 (t, 1H, $^2J_{PH} = 14.0$ Hz, Ir*H*), 6.76–7.54, (m, 43H, multiplet signals not individually assigned from PPh_3, H, Ph, and styryl substituents on iridathiophene). ^{13}C NMR ($CDCl_3$, δ): 127.3 (t′, $^{2,4}J_{CP} = 10.0$ Hz, *o*-C_6H_5P), 129.6 (s, *p*-C_6H_5P), 132.4 (t′, $^{1,3}J_{CP} = 55.4$ Hz, *i*-C_6H_5P), 134.6 (t′, $^{3,5}J_{CP} = 10.0$ Hz, *m*-C_6H_5P); singlet signals all CH, not individually assigned, at 126.5, 127.8, 128.8, 129.4, 129.7, 130.1, 136.8, from Ph, and styryl substituents on iridathiophene; 135.9 (s, quat., tentatively assigned as quaternary carbon from bound styryl phenyl), 144.9 (s, tert., *C*4), 150.4 (s, quat., tentatively assigned as quaternary carbon from phenyl substituent on ring C3), 209.8 (t, coupling unresolved, quat., ring *C*5), 222.9 (t, coupling unresolved, quat., ring *C*3). ^{31}P NMR ($CDCl_3$, δ): 6.27 (s).

4.6. Preparation of $Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HI(PPh_3)_2$ (**5**)

$Ir[SC_3H(Ph\text{-}3)(CH{=}CHPh\text{-}5)]HCl(PPh_3)_2$ (0.100 g, 0.10 mmol) dissolved in CH_2Cl_2 (10 mL) and NaI (0.075 g, 0.5 mmol) dissolved in a mixture of EtOH (10 mL) and water (0.5 mL) were combined. After stirring for 16 h all the volatiles were removed under reduced pressure. The residue was extracted with CH_2Cl_2 and the extract concentrated and purified by chromatography using a silica gel column and eluting with a mixture of CH_2Cl_2/hexane (3:2). The dark brown band was collected and from this was obtained pure **5** (0.098 g, 90%). Anal. Calc. for $C_{53}H_{44}IIrP_2S$: C, 58.19; H, 4.05. Found: C, 58.24; H, 4.14%. IR (cm^{-1}): 2221w, ν(IrH). ^1H NMR ($CDCl_3$, δ): −11.95 (t, 1H, $^2J_{PH} = 16.0$ Hz, Ir*H*), 6.79–7.54, (m, 43H, multiplet signals not individually assigned from PPh_3, H, Ph, and styryl substituents on iridathiophene). ^{13}C NMR ($CDCl_3$, δ): 127.1 (t′, $^{2,4}J_{CP} = 10.0$ Hz, *o*-C_6H_5P), 129.6 (s, *p*-C_6H_5P), 133.0 (t′, $^{1,3}J_{CP} = 55.4$ Hz, *i*-C_6H_5P), 134.9 (t′, $^{3,5}J_{CP} = 10.0$ Hz, *m*-C_6H_5P); singlet signals all CH, not individually assigned, at 126.6, 127.9, 128.8, 129.0, 130.3, 135.8 from Ph, and styryl substituents on iridathiophene; 137.4 (s, quat., tentatively assigned as quaternary carbon from bound styryl phenyl), 144.6 (s, tert., *C*4), 150.0 (s, quat., tentatively assigned as quaternary carbon from phenyl substituent on ring *C*3), 211.7 (t, coupling unresolved, quat., ring *C*5), 225.0 (t, coupling unresolved, quat., ring *C*3). ^{31}P NMR ($CDCl_3$, δ): −1.22 (s).

4.7. Preparation of $Ir[C_8H_5(Ph\text{-}3)]Cl(PPh_3)_2$ (**6**)

A mixture of $IrCl(CS)(PPh_3)_2$ (0.240 g, 0.30 mmol) and $Hg(CH{=}CPh_2)_2$ (0.198 g, 0.33 mmol) in benzene (30 mL) was heated under reflux for 2 h to give a dark reddish brown solution with a precipitate of elemental mercury. After filtering through Celite to remove the mercury, the solvent was removed under reduced pressure. The crude product was dissolved in CH_2Cl_2 and subjected to column chromatography on silica gel eluting with CH_2Cl_2 and hexane (v/v = 1:1). The dark brown band was collected and the isolated solid recrystallised from CH_2Cl_2 and EtOH to give pure **6** as an orange solid (0.056 g, 20%) and the filtrate from the recrystallization was reserved for treatment as described in Section 4.8 below. The bulk sample of **6**, when recrystallised as above and dried over P_2O_5 under vacuum, returned elemental analysis figures consistent with the sample being unsolvated. However, the single crystal chosen for X-ray analysis was grown at room temperature over several days from CH_2Cl_2/EtOH and proved to be a 1:1 CH_2Cl_2 solvate (see Table 1). Anal. Calc. for $C_{50}H_{40}ClIrP_2$: C, 64.54; H, 4.33. Found: C, 64.54; H, 4.39%. ^1H NMR ($CDCl_3$, δ): 6.10–7.36, (m, 39H, multiplet signals not individually assigned from PPh_3, iridaindeneH, and Ph substituent on iridaindene); 7.42 (unresolved triplet, 1H, iridaindene C2*H*). ^{13}C NMR ($CDCl_3$, δ): 127.8 (t′, $^{2,4}J_{CP} = 10.0$ Hz, *o*-C_6H_5P), 129.7 (t′, $^{1,3}J_{CP} = 54.4$ Hz, *i*-C_6H_5P), 129.9 (s, *p*-C_6H_5P), 134.7 (t′, $^{3,5}J_{CP} = 10.0$ Hz, *m*-C_6H_5P); singlet signals all CH, not individually assigned, at 121.5, 122.2, 123.1, 125.3, 127.1, 127.2, 132.1, from C's of iridaindene six-membered ring and Ph substituent on iridaindene;

131.6 (t, $^{2}J_{CP}$ = 8.1 Hz, iridaindene *C*2H), 139.7 (s, quat. C, unassigned), 141.8 (t, $^{2}J_{CP}$ = 6.5 Hz, iridaindene *C*Ir), 154.6 (unresolved triplet, quat. C, unassigned), 156.4 (s, quat. C, unassigned). ^{31}P NMR ($CDCl_3$, δ): 24.33 (s).

4.8. Preparation of $Ir(\kappa^2\text{-}S_2CCHCPh_2)Cl(CH{=}CPh_2)(PPh_3)_2$ *(7)*

The solvent was removed from the filtrate left in the recrystallization step described in Section 4.7. The resulting residue was recrystallised from CH_2Cl_2 and heptane to give pure **7** as a dark red solid (0.028 g, 8%). The bulk sample of **7**, when recrystallised as above and dried over P_2O_5 under vacuum, returned elemental analysis figures consistent with the sample retaining 0.25 molecules of CH_2Cl_2 of solvation. The ^{1}H NMR of this analytical sample confirmed the presence of CH_2Cl_2 in an approximately 0.25:1 ratio with the complex. However, the single crystal of **7** chosen for X-ray analysis was grown at room temperature over several days from CH_2Cl_2/heptane and proved to be unsolvated (see Table 1). Anal. Calc. for $C_{65}H_{52}ClIrP_2S_2 \cdot 0.25CH_2Cl_2$: C, 64.87; H, 4.38; S, 5.31. Found: C, 64.79; H, 4.32; S, 5.20%. ^{1}H NMR ($CDCl_3$, δ): 5.61 (s, 1H, S_2CC*H*=), 6.24–7.49 (m, 50H, multiplet signals not individually assigned from PPh_3, and the four Ph substituents on vinyl groups); 8.52 (t, $^{3}J_{HP}$ = 3.2 Hz, 1H, IrC*H*=). ^{13}C NMR ($CDCl_3$, δ): 127.0 (t′, $^{2,4}J_{CP}$ = 10.2 Hz, *o*-C_6H_5P), 130.1 (t′, $^{1,3}J_{CP}$ = 54.0 Hz, *i*-C_6H_5P), 129.5 (s, *p*-C_6H_5P), 135.3 (t′, $^{3,5}J_{CP}$ = 10.2 Hz, *m*-C_6H_5P); singlet signals all CH, not individually assigned, at 123.7, 125.3, 125.9, 126.7, 127.3, 128.0, 128.0, 128.1, 128.2, 129.0, 129.8, 131.0, 134.8 from PPh_3, and the four Ph substituents on vinyl groups; 137.1 (s, quat. C, unassigned), 141.2 (s, quat. C, unassigned), 142.6 (t, $^{2}J_{CP}$ = 3.2 Hz, Ir*C*H=), 143.1 (s, quat. C, unassigned), 146.8 (s, quat. C, unassigned), 235.3 (t, $^{3}J_{CP}$ = 3.6 Hz, S_2*C*). ^{31}P NMR ($CDCl_3$, 121.5MHz): −6.62 (s).

4.9. X-ray crystal structure determinations for complexes ***5–7***

Data were collected on a Siemens SMART CCD diffractometer at 83 K with graphite-monochromated Mo Kα radiation (λ 0.71073 Å) using ω scans. The data were corrected for Lorentz and polarization effects and absorption corrections were applied using symmetry-related measurements [27]. Structures were solved using SHELXS [28] and refined by full-matrix least squares using SHELXL [29]. Anisotropic thermal parameters were refined for all non-hydrogen atoms except one partially-disordered dichloromethane molecule of crystallization in **6**. Hydrogen atoms were included in calculated positions and allowed to ride on their carrier atom. Crystal data and refinement details for all three structures are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for **5**, **6**, and **7** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 245794, 245795 and 245796 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 www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Marsden Fund administered by the Royal Society of NZ for supporting this work. We also thank Dr. K.G. Town for performing some of the original work on the preparation of $IrCl(CS)(PPh_3)_2$.

References

[1] G.P. Elliott, W.R. Roper, J.M. Waters, J. Chem. Soc., Chem. Commun. (1982) 811.

[2] (a) G.P. Elliott, N.M. McAuley, W.R. Roper, Inorg. Synth. 26 (1989) 184;
(b) C.E.F. Rickard, W.R. Roper, S.D. Woodgate, L.J. Wright, J. Organomet. Chem. 623 (2001) 109;
(c) C.E.F. Rickard, W.R. Roper, S.D. Woodgate, L.J. Wright, Angew. Chem., Int. Ed. Engl. 39 (2000) 750.

[3] (a) J.R. Bleeke, Acc. Chem. Res. 24 (1991) 271;
(b) J.R. Bleeke, Chem. Rev. 101 (2001) 1205.

[4] (a) V. Jacob, T.J.R. Weakley, M.M. Haley, Angew. Chem. Int. Ed. 41 (2002) 3470;
(b) C.W. Landorf, V. Jacob, T.J.R. Weakley, M.M. Haley, Organometallics 23 (2004) 1174.

[5] M. Paneque, C.M. Posadas, M.L. Poveda, N. Rendón, V. Salazar, E. Oñate, K. Mereiter, J. Am. Chem. Soc. 125 (2003) 9898.

[6] P. Barrio, M.A. Estruelas, E. Oñate, J. Am. Chem. Soc. 126 (2004) 1946.

[7] T.B. Wen, Z.Y. Zhou, G. Jia, Angew. Chem. Int. Ed. 40 (2001) 1951.

[8] (a) J.R. Bleeke, M.F. Ortwerth, M.Y. Chiang, Organometallics 12 (1993) 985;
(b) J.R. Bleeke, M.F. Ortwerth, A.M. Rohde, Organometallics 14 (1995) 2813.

[9] (a) P. DeShong, D.R. Sidler, P.J. Rybczynski, G.A. Slough, A.L. Rheingold, J. Am. Chem. Soc. 110 (1988) 2575;
(b) C.A. Rusik, M.A. Collins, A.S. Gamble, T.L. Tonker, J.L. Templeton, J. Am. Chem. Soc. 111 (1989) 2550;
(c) K.E. Garrett, J.B. Sheridan, D.B. Pourreau, W.C. Feng, G.L. Geoffroy, D.L. Staley, A.L. Rheingold, J. Am. Chem. Soc. 111 (1989) 8383;
(d) D.S. Frohnapfel, P.S. White, J.L. Templeton, Organometallics 19 (2000) 1497;

(e) D.B. Grotjahn, J.M. Hoerter, J.L. Hubbard, J. Am. Chem. Soc. 126 (2004) 8866.

[10] G.P. Elliott, W.R. Roper, J. Organomet. Chem. 250 (1983) C5.

[11] (a) T.J. Collins, W.R. Roper, J. Chem. Soc., Chem. Commun. (1976) 1044;
(b) W.R. Roper, K.G. Town, J. Chem. Soc., Chem. Commun. (1977) 781.

[12] G.R. Clark, T.J. Collins, K. Marsden, W.R. Roper, J. Organomet. Chem. 157 (1978) C23.

[13] C.E.F. Rickard, W.R. Roper, D.M. Salter, L.J. Wright, Organometallics 11 (1992) 3931.

[14] G.J. Irvine, M.J.G. Lesley, T.B. Marder, N.C. Norman, C.R. Rice, E.G. Robins, W.R. Roper, G.R. Whittell, L.J. Wright, Chem. Rev. 98 (1998) 2685.

[15] C.E.F. Rickard, W.R. Roper, S.D. Woodgate, L.J. Wright, unpublished work.

[16] T.J. Collins, W.R. Roper, K.G. Town, J. Organomet. Chem. 121 (1976) C41.

[17] (a) M. Yagupsky, G. Wilkinson, J. Chem. Soc. (A) (1968) 2813;
(b) M. Kubota, C.R. Carey, J. Organomet. Chem. 29 (1970) 491.

[18] J.P. Collman, J.W. Kang, J. Am. Chem. Soc. 89 (1967) 844.

[19] V.I. Sokolov, O.A. Reutov, Coord. Chem. Rev. 27 (1978) 89.

[20] H. Werner, R. Weinand, W. Knaup, K. Peters, H.G. von Schnering, Organometallics 10 (1991) 3967.

[21] W.-H. Kwok, G.-L. Lu, C.E.F. Rickard, W.R. Roper, L.J. Wright, J. Organomet. Chem. 689 (2004) 2979.

[22] S.M. Maddock, C.E.F. Rickard, W.R. Roper, L.J. Wright, Organometallics 15 (1996) 1793.

[23] K. Vrietze, J.P. Collman, C.T. Sears Jr., M. Kubota, Inorg. Synth. 11 (1968) 101.

[24] G.F. Wright, J. Org. Chem. 1 (1936) 457.

[25] M.G. Moloney, J.T. Pinhey, J. Chem. Soc., Perkin Trans. 1 (1988) 2847.

[26] V.I. Sokolov, V.V. Bashilov, O.A. Reutov, J. Organomet. Chem. 162 (1978) 271.

[27] R.H. Blessing, Acta Crystallogr., Sect. A 51 (1995) 33.

[28] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.

[29] G.M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.