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The synthesis and crystal structures of the first examples of six-membered inorganic iridacycles containing the $[(Ph_2PE)_2N]^-$ ligand ($E = S$ or Se)

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Abstract

The reaction of the potassium salt of either imidotetraphenyldithiodiphosphinate (L^1) or imidotetraphenyldiselenodiphosphinate (L^2) with $[Cp^*IrCl(\mu\text{-}Cl)]_2$ in THF yields the complexes $Cp^*Ir\{Ph_2P(S)NP(S)Ph_2\text{-}S,S'\}Cl$ (**1**) and $Cp^*Ir\{Ph_2P(Se)NP(Se)Ph_2\text{-}Se,Se'\}Cl$ (**2**), respectively. Compounds **1** and **2** can be further converted into a range of new mononuclear species comprising mixed $[Cp^*,E_3]$ donor sets by metathetic exchange of the chloro ligand for either thiocyanate or selenocyanate. These are the first examples of neutral monomeric Ir(III) complexes which have this ligand set. All compounds were characterised by a combination of NMR spectroscopy (^1H and $^{31}P\{^1H\}$), IR spectroscopy, microanalysis and X-ray crystallography. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structure; Inorganic heterocycle; Iridacycle; NMR spectroscopy; Phosphorus(V) ligands; Pseudo-halides

1. Introduction

Imidotetraaryldichalcogenodiphosphinates of general formula $[(R_2PE)_2N]^-$, where $E = O$, S or Se, have a well-defined coordination chemistry, with examples of simple complexes known for elements from each block of the periodic table [1]. These complexes are usually characterised by their high thermal and chemical stability and their ease of preparation. Complexes of metals with this class of ligand have found applications in catalysis [1e] as NMR shift reagents [1f] and in metal-selective extraction technology [1h]. We report here the use of two such ligands, where $R = Ph$, $E = S$ (L^1) or Se (L^2), to prepare complexes comprising the first examples of the six-membered inorganic iridacycles Ir(EPNPE) ($E = S$, **1** and $E = Se$, **2**).

A search of the chemical literature reveals no neutral monomeric complexes of the type $Cp^*Ir`E'_3$, where $`E'_3$ represents any ligand set which coordinates to the iridium through three sulfurs, three seleniums or a mixture of sulfur and selenium, irrespective of the substitution at the chalcogen. The most closely related compounds are the remarkable series of complexes reported by Herberhold et al. with general formula $[Cp^*Ir(PMe_3)\eta^2\text{-}S_n]$, where $n = 5$, 6 or 7 [2]. The dimeric compounds $[(Cp^*Ir)_2S_8]$ reported by Chen and Angelici [3] and $\{[Cp^*Ir(S^iPr)]_2\eta^2\text{-}S_n\}$ where $n = 2$ or 9 reported by Hidai and co-workers [4] and the cubane-like tetrameric complexes $[Cp^*M(\mu^3\text{-}E)]_4$ ($M = Rh$, Ir, $E = S$, Se) [5] indicated that there may be the possibility of preparing monomeric compounds if the correct ligand set were used. Starting from this premise, compounds **1** and **2** were metathesised with the pseudo-halides thiocyanate and selenocyanate to prepare complexes of general formula $Cp^*Ir`E'_3$ where $`E'_3$ represents ligands with the donor set [S, S′, S″], [S, S′, Se], [Se, Se′, S] or [Se, Se′, Se″].

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Table 1
Analytical and spectroscopic data for **1**–**7**

Compound	^{31}P (ppm) [$^{1}J(^{77}$Se–^{31}P) Hz]	^{1}H(arom) (ppm)	^{1}H(Cp*) (ppm)	C(calc)	H(calc)	N(calc)	ν(CH) Cp* (cm^{-1})	ν(CN) (cm^{-1})	ν(PE) (cm^{-1})	$\nu(P_2N_{asym})$ (cm^{-1})
1	31.0	8.20–6.90	1.34	45.25 (45.20)	4.05 (3.90)	1.45 (1.50)	2914	–	571	1189, 1173, 1104
2	18.3 [572]	8.25–6.86	1.39	45.15 (45.10)	3.75 (3.90)	1.25 (1.55)	2914	–	540	1193, 1174
3	29.3	8.04–7.13	1.43	50.30 (50.40)	4.30 (4.25)	3.45 (3.35)	2912	2101	570	1190, 1178, 1105
4	15.7 [567]	8.05–7.10	1.47	44.95 (45.30)	3.95 (3.80)	3.15 (3.00)	2910	2101	542	1229, 1181, 1153
5	29.0	7.98–7.11	1.46	47.70 (47.70)	3.90 (4.00)	3.40 (3.15)	2913	2107	569	1195, 1177, 1105
6	15.5 [572]	8.05–7.05	1.50	42.85 (43.10)	3.45 (3.65)	2.70 (2.85)	2913	2108	542	1232, 1181
7	29.7	8.10–6.92	1.50	51.65 (52.00)	4.35 (4.45)	1.30 (1.50)	2919	–	567	1181, 1106 [a]

[a] Bands partially obscured by the intense (S=O) stretches associated with the sulfonyl group of the counter ion.

Table 2
Crystal data for **1**–**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_{34}H_{35}ClIrNP_2S_2.CHCl_3$	$C_{34}H_{35}ClIrN_2P_2Se_2.CHCl_3$	$C_{35}H_{35}IrN_2P_2S_3$	$C_{35}H_{35}IrN_2P_2SSe_2$	$C_{35}H_{35}IrN_2P_2S_2Se$	$C_{35}H_{35}IrN_2P_2Se_3$	$C_{41}H_{42}IrNO_3P_2S_3$
Colour	Orange	Orange	Orange	Orange	Red	Orange	Green
Crystal size (mm)	0.36 × 0.4 × 0.4	0.16 × 0.36 × 0.36	0.1 × 0.23 × 0.3	0.03 × 0.06 × 0.13	0.1 × 0.1 × 0.25	0.1 × 0.1 × 0.2	0.06 × 0.1 × 0.25
a (Å)	10.8707(3)	10.91310(10)	11.69110(10)	11.8638(5)	11.7340(10)	11.87670(10)	15.3812(2)
b (Å)	11.8831(3)	12.58110(10)	18.9620(10)	19.0625(9)	19.0872(2)	19.0646(4)	11.8593(2)
c (Å)	17.1741(4)	14.3903(3)	15.84980(10)	16.0809(7)	15.9826(2)	16.1446(3)	22.4774(3)
α (°)	109.6890(10)	75.3620(10)					
β (°)	94.2810(10)	88.740(10)	104.60(10)	105.2790(10)	104.610(10)	105.1900(10)	98.7600(10)
γ (°)	111.8020(10)	80.0790(10)					
Volume (Å^3)	1888.07(8)	1882.57(5)	3400.22(4)	3508.2(3)	3464.00(6)	3527.82(10)	4052.28(10)
System	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
Z	2	2	4	4	4	4	4
Total data	8335	8183	14794	21371	14584	20623	17224
Unique data	5396	5304	4922	8211	4951	8241	5834
R_{int}	0.0284	0.0228	0.0175	0.0744	0.0897	0.1419	0.1832
Absorption correction	None	None	SADABS	Semi-emp. Ψ scans	SADABS	Semi-emp. Ψ scans	Semi-emp. Ψ scans
R	0.0231	0.0264	0.0193	0.0494	0.0395	0.0388	0.0423
R_w	0.0586	0.0632	0.0487	0.0992	0.0802	0.0618	0.0695

Table 3
Selected bond lengths (Å) and angles (°) for **1–7**

	1 (X = Cl, E = S)	**2** (X = Cl, E = Se)	**3** (X = <u>S</u>CN, E = S)	**4** (X = <u>S</u>CN, E = Se)	**5** (X = <u>Se</u>CN, E = S)	**6** (X = <u>Se</u>CN, E = Se)	**7** (X = vacant, E = S)
Bond lengths (Å)							
Ir(1)–X	2.4267(10)	2.4276(13)	2.4073(10)	2.411(2)	2.5209(9)	2.5149(10)	–
Ir(1)–E(1)	2.4133(10)	2.4988(5)	2.4215(9)	2.5048(8)	2.427(2)	2.5065(7)	2.3214(13)
Ir(1)–E(2)	2.4044(11)	2.5209(5)	2.3970(9)	2.5269(9)	2.409(2)	2.5220(8)	2.3148(13)
E(1)–P(1)	2.0295(14)	2.182(2)	2.0218(13)	2.172(2)	2.035(2)	2.171(2)	2.042(2)
P(1)–N(1)	1.601(3)	1.595(4)	1.573(3)	1.586(7)	1.588(6)	1.589(6)	1.595(4)
N(1)–P(2)	1.583(3)	1.592(4)	1.590(3)	1.576(6)	1.589(6)	1.575(6)	1.582(4)
P(2)–E(2)	2.0214(14)	2.1836(14)	2.0130(13)	2.191(2)	2.022(3)	2.186(2)	2.058(2)
Ir(1)–C	2.168(4)–2.190(4)	2.164(5)–2.198(5)	2.143(4)–2.179(4)	2.166(9)–2.210(8)	2.152(8)–2.193(8)	2.167(8)–2.208(9)	2.135(5)–2.187(5)
Bond angles (°)							
X–Ir(1)–E(1)	82.15(3)	83.02(4)	82.24(4)	91.02(7)	81.41(5)	91.40(3)	–
X–Ir(1)–E(2)	85.13(4)	83.58(4)	91.79(4)	82.47(7)	92.02(5)	81.70(3)	–
E(1)–Ir(1)–E(2)	90.36(4)	88.84(2)	101.49(3)	101.77(3)	101.44(6)	101.80(3)	102.30(4)
Ir(1)–E(1)–P(1)	107.98(5)	104.73(4)	109.22(5)	110.29(7)	109.70(9)	110.62(6)	104.82(7)
E(1)–P(1)–N(1)	118.35(13)	118.6(2)	118.10(13)	118.0(3)	118.0(2)	118.2(2)	116.7(2)
P(1)–N(1)–P(2)	133.2(2)	134.1(3)	131.7(2)	133.7(4)	132.2(4)	133.7(4)	125.9(3)
N(1)–P(2)–E(2)	118.91(14)	118.4(2)	118.55(12)	117.4(3)	118.6(2)	117.9(2)	116.8(2)
P(2)–E(2)–Ir(1)	109.02(5)	103.99(4)	111.81(5)	107.47(6)	112.22(9)	107.71(6)	110.82(7)
C–Ir(1)–E(1)	97.29(11)–154.79(12)	96.88(14)–156.42(14)	95.35(13)–157.50(13)	90.3(3)–152.5(3)	94.5(2)–157.1(3)	89.4(2)–151.3(3)	98.2(2)–162.2(2)
C–Ir(1)–E(2)	95.63(12)–157.36(13)	97.69(13)–153.3(2)	90.15(13)–152.71(14)	95.1(3)–157.2(2)	89.4(2)–150.1(4)	95.0(2)–157.0(2)	95.51(14)–152.0(2)
C–Ir(1)–X	92.44(12)–156.97(12)	93.29(14)–130.1(2)	93.50(13)–147.7(2)	94.5(3)–149.0(4)	94.5(2)–151.9(4)	94.8(3)–151.0(3)	–
C–Ir–C	38.2(2)–64.8(2)	37.1(2)–64.4(2)	36.7(2)–63.7(2)	36.3(4)–64.2(3)	36.5(4)–63.6(3)	36.5(3)–63.4(3)	37.5(2)–65.1(2)

2. Experimental

2.1. Materials

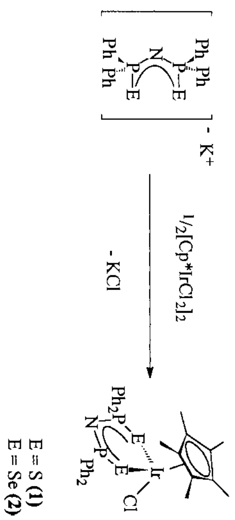
All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. All solvents were distilled prior to use. [Cp*IrCl(μ-Cl)]$_2$ [6] and K[(Ph$_2$PE)$_2$N] (E = S [7] or Se [8]) were prepared according to published procedures. Ag(SCN), Ag(C$_7$H$_7$SO$_3$), NH$_4$(SCN) and K(SeCN) were obtained commercially and used as received.

2.2. Instrumentation

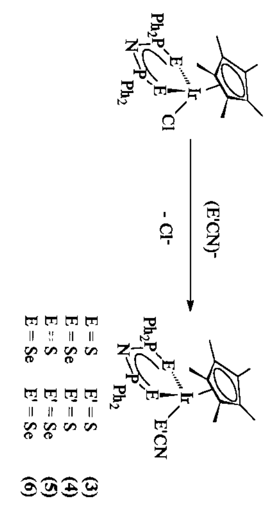
IR spectra were recorded as KBr pellets over the range 4000–200 cm^{-1} using a Perkin–Elmer system 2000 FT spectrometer. The ^{1}H-NMR spectra were recorded on a Bruker AC250 FT spectrometer (250 MHz) with chemical shifts (δ) reported relative to external TMS (see Table 1). The ^{31}P{^{1}H}-NMR spectra were recorded on a Jeol FX90Q spectrometer (36.2 MHz) with chemical shifts (δ) reported relative to external 85% H$_3$PO$_4$; all NMR spectra were recorded in CDCl$_3$ solutions. Elemental analyses were performed using a Perkin–Elmer 2400 CHN elemental analyser by the Loughborough University Microanalytical Service within the Department of Chemistry.

2.3. X-ray crystallography

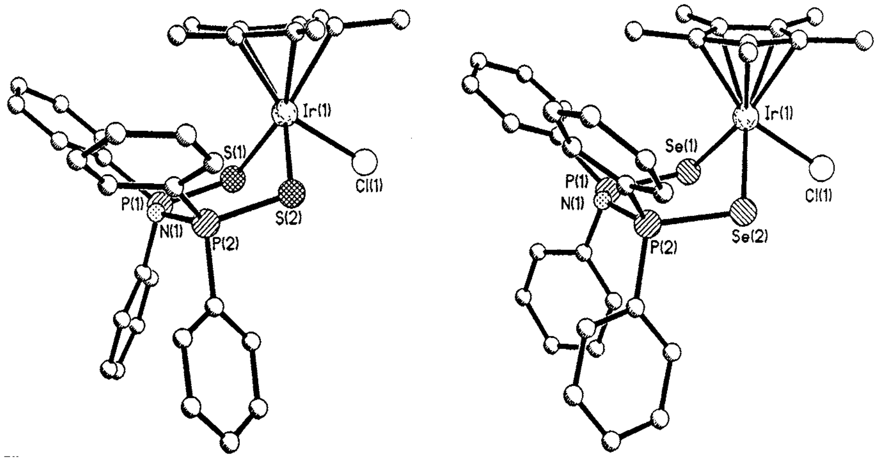
The X-ray crystallographic studies were performed on **1–7** at ambient temperatures using a Siemens SMART diffractometer with graphite-monochromated Mo–K$_α$ radiation (λ = 0.71073 Å) and ω scans. The crystal data, a summary of the data collections and the



Scheme 1. The preparation of **1** and **2**.

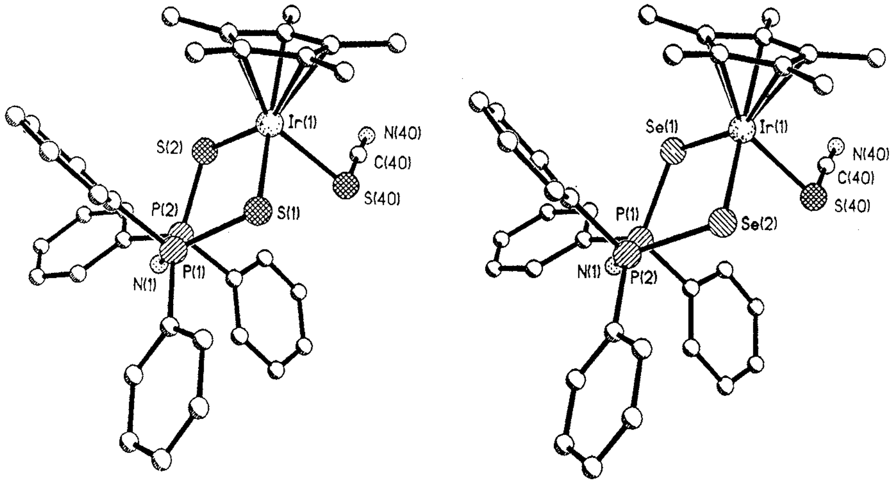


Scheme 2. The preparation of **3–6**.



1 2

Fig. 1. The molecular structures of **1** and **2** (H atoms omitted for clarity, solvate molecule not shown).



3 4

Fig. 2. The molecular structures of **3** and **4** (H atoms omitted for clarity).

structure refinements for these compounds are given in Table 2; selected bond lengths and angles are collected in Table 3. All structures were solved by direct methods and all of the non-hydrogen atoms refined with anisotropic displacement parameters. Refinement was by full-matrix least-squares methods on F^2, calculations were performed using the program SHELXTL-PC [9].

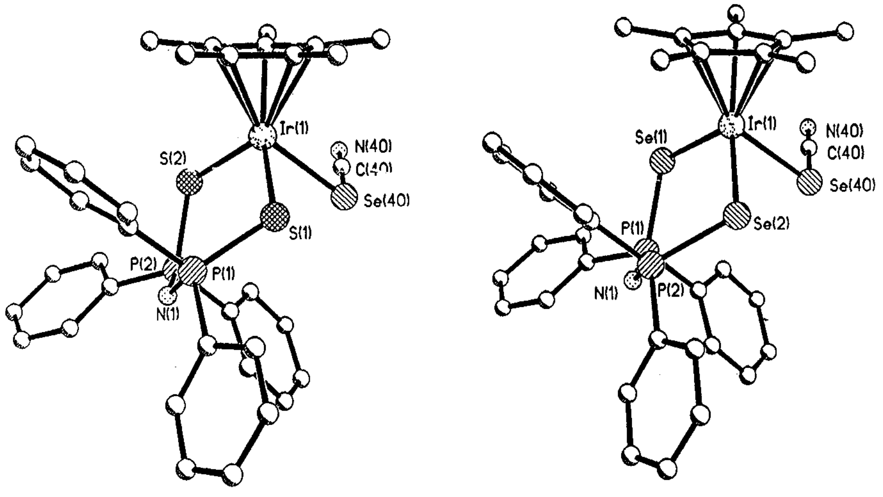
2.4. Preparation of complexes

2.4.1. Ir($C_5(CH_3)_5$)η^2-{$Ph_2P(S)NP(S)Ph_2$-S,S'}Cl (1)

To a solution of [Cp*IrCl(μ-Cl)]$_2$ (0.025 g, 0.031 mmol) in THF (5 ml) was added K[L^1] (0.04 g, 0.068 mmol) as a solid. The solution was stirred at room temperature (r.t.) for 30 min, after which the solvent was removed under reduced pressure. The orange residue was extracted into 2 ml of $CHCl_3$ from which the product was obtained as orange crystals after vapour diffusion of 60:80 petroleum. The product **1** was collected by suction filtration and dried in vacuo. Yield: 0.044 g, 80%.

2.4.2. Ir($C_5(CH_3)_5$)η^2-{$Ph_2P(Se)NP(Se)Ph_2$-Se,Se'}Cl (2)

To a solution of [Cp*IrCl(μ-Cl)]$_2$ (0.031 g, 0.0389 mmol) in THF (5 ml) was added K[L^2] (0.047 g, 0.0808 mmol) as a solid. The solution was stirred at r.t. for 30 min, after which the solvent was removed under reduced pressure. The orange residue was extracted into 4 ml of CH_2Cl_2 and filtered through a Celite pad. The volume was reduced to 1 ml and addition of 60:80 petroleum (10 ml) gave the product **2** as an orange solid which was collected by suction filtration and dried in vacuo. Yield: 0.054 g, 77%.



5 **6**

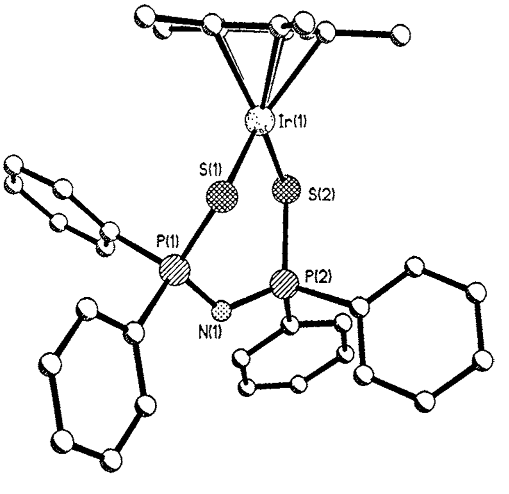
Fig. 3. The molecular structures of **5** and **6** (H atoms omitted for clarity).

2.4.3. *$Ir(C_5(CH_3)_5)\eta^2$-$\{Ph_2P(S)NP(S)Ph_2$-S,S'$\}SCN$ (3)*

To a solution of **1** (0.04 g, 0.049 mmol) in THF (5 ml) was added Ag(SCN) (0.009 g, 0.054 mmol) as a solid. The solution was stirred at r.t. for 30 min, during which time a fine white precipitate formed. The solvent was removed under reduced pressure, and the orange residue was extracted into 2 ml of $CHCl_3$ and filtered through a Celite pad. Vapour diffusion of 60:80 petroleum into this solution gave the product **3** as orange–red crystals. Yield: 0.034 g, 67%.

2.4.4. *$Ir(C_5(CH_3)_5)\eta^2$-$\{Ph_2P(Se)NP(Se)Ph_2$-Se,Se'$\}$ SCN (4)*

To a solution of **2** (0.029 g, 0.032 mmol) in THF (5 ml) was added $NH_4(SCN)$ (0.010 g, 0.131 mmol) as a solid. The solution was stirred at r.t. for 40 h, after which the solvent was removed under reduced pressure. The residue was extracted into 4 ml of CH_2Cl_2 and filtered through a Celite pad. The volume was reduce to 1 ml and addition of 60:80 petroleum (9 ml) gave complex **4**. The solid was collected by suction filtration and dried in vacuo. Yield: 0.021 g, 70%.



7

Fig. 4. The structure of the cation in **7** (H atoms omitted for clarity, anion not shown).

2.4.5. *$Ir(C_5(CH_3)_5)\eta^2$-$\{Ph_2P(S)NP(S)Ph_2$-S,S'$\}SeCN$ (5)*

To a solution of **1** (0.05 g, 0.061 mmol) in THF (5 ml) was added K(SeCN) (0.010 g, 0.068 mmol) as a solid. The solution was stirred at r.t. for 3 h, after which the solvent was removed under reduced pressure. The orange–red residue was extracted into 2 ml of $CHCl_3$ and filtered through a Celite pad. Vapour diffusion of 60:80 petroleum into this solution gave the product **5** as red crystals. Yield: 0.035 g, 64%.

2.4.6. *$Ir(C_5(CH_3)_5)\eta^2$-$\{Ph_2P(Se)NP(Se)Ph_2$-Se,Se'$\}$-SeCN] (6)*

To a solution of **2** (0.029 g, 0.032 mmol) in THF (5 ml) was added K(SeCN) (0.020 g, 0.139 mmol) as a solid. The solution was stirred at r.t. for 24 h, after which the solvent was removed under reduced pressure. The residue was extracted into 4 ml of CH_2Cl_2 and the solution filtered through a Celite pad. The volume was reduced to 1 ml and addition of 60:80 petroleum (10 ml) gave complex **6**, which was collected by suction filtration and dried in vacuo. Yield: 0.026 g, 84%.

2.4.7. *$[Ir(C_5(CH_3)_5)\eta^2$-$\{Ph_2P(S)NP(S)Ph_2S,S'\}]$-$(C_7H_7SO_3)$ (7)*

To a solution of **1** (0.035 g, 0.043 mmol) in THF (5 ml) was added $Ag(C_7H_7SO_3)$ (0.014 g, 0.048 mmol) as a solid. The solution was stirred at r.t. for 30 min, during which time a white precipitate formed and the solution turned a deep green colour. The solvent was removed under reduced pressure and the green residue was extracted into 2 ml of THF. The product was obtained as green–black crystals after slow diffusion of diethyl ether. Yield: 0.029 g, 72%.

3. Results and discussion

The dimeric complex $[Cp^*IrCl(\mu\text{-}Cl)]_2$ reacts with $K[L^1]$ and $K[L^2]$ in THF solution to form the monomeric complexes **1** and **2**, respectively (Scheme 1) using a method similar to that previously reported for the rhodium analogues [1b]. These complexes can be used as the starting point for the preparation of a range of substituted products by exchange of the labile chloro ligand for thiocyanate (**3**, **5**) and selenocyanate (**4**, **6**) ligands, Scheme 2. The products from these reactions are rare examples of monomeric Cp^*IrE_3 complexes, where E_3 represents a three atom donor set of either mixed or single chalcogens as the donor site of a ligand. Analytical data for complexes **1**–**7** are presented in Table 1.

All of the complexes isolated are stable microcrystalline solids with good solubility in common organic solvents. Spectroscopic analysis of **1**–**7** reveals a high degree of similarity in their IR and NMR responses. Further, within the two groups of complexes, those with L^1 (**1**, **3**, **5**, and **7**) and those with L^2 (**2**, **4**, and **6**), the similarities are even more pronounced.

The ^1H-NMR data for **1**–**7** (Table 1) show very little variation in the position of the $(C_5(CH_3)_5)$ resonance (1.34–1.50 ppm), a result that is indicative of the similarity of these complexes, and the resonances due to the aromatic protons are found to be similarly consistent. The $^{31}P\{^1H\}$-NMR data also reflect this congruity with a more pronounced dependence upon whether the ligand is L^1 or L^2 rather than any coherent dependence upon the nature of the monodentate ligand X. For both types of complex, the largest value for the chemical shift is seen for $X = Cl$, but shows very little variation between $X = SCN$ or SeCN. The $^1J(^{77}Se–^{31}P)$ couplings observed for **2**, **4** and **6** are reduced by approximately 100 Hz with respect to the value observed for $K[L^2]$ ($^1J(^{77}Se–^{31}P) = 687$ Hz). This similarity within the two types of complex is continued in the IR data for **1**–**7** where the values of $\nu(PE)$ for **1**, **3**, **5**, **7** vary by only 4 cm^{-1}, and for **2**, **4**, **6** by only 2 cm^{-1}. The $\nu_{asym}(PN)$ values are also strongly convergent, while the $\nu(CN)$ responses indicate that in **3**–**6** the pseudohalide is E-bound.

Crystallographic studies (Tables 2 and 3) reveal structures for **1**–**6** that are very much in keeping with simple predictions, with overall pseudo tetrahedral 'piano-stool' geometries. Both L^1 and L^2 act as chelating ligands through their respective chalcogens, and so adopt a *cis* geometry at the metal centre. For **1** and **2** (Fig. 1) the conformation of the (Ir–E–P–N–P–E) ring is best described as boat like, where the Ir and the N represent the 'bow' and 'stern', whilst in the other structures the ring can be loosely described as puckered (Figs. 2 and 3). Global comparisons of the bond lengths of HL^1 [10] and HL^2 [8] in the solid state with the complexes **1**, **3**, **5** and **2**, **4**, **6**, respectively reveals some distinct trends (Table 3). Most noticeably, the length of the (PE) bond is increased on deprotonation and coordination (between 2.035(2) and 2.013(1) Å in **1**, **3**, **5**, c.f. 1.950(1) and 1.937(1) Å in HL^1; between 2.191(2) and 2.171(2) Å for **2**, **4**, **6**, c.f. 2.101(1) and 2.085(1) Å in HL^2) and the (PN) bond length is reduced (between 1.601(3) and 1.573(3) Å in **1**, **3**, **5**, c.f. 1.683(2) and 1.672(2) Å in HL^1; between 1.595(4) and 1.575(6) Å for **2**, **4**, **6**, c.f. 1.684(4) and 1.678(4) Å in HL^2). These changes can be rationalised in terms of a delocalisation of the charge and bonds within the iridacycle formed, such that the (PE) bond in the complex has far more single-bond character than in the free ligand, and the (PN) bond experiences an effective increase in bond order. The values for the $^1J(^{77}Se–^{31}P)$ coupling constants are smaller than those seen for HL^2, again indicative of a reduction in the (PSe) bond order. The changes in bond lengths are entirely consistent with the changes seen for other complexes of these ligands with transition metals [1b–d,g,8]. For each of these products **1**–**6**, there is a small but seemingly consistent variation in some of the structural parameters, which may indicate that there is at least in the solid state a preponderance of one of the contributing canonical forms rather than a true averaging such as would be expected in a fully delocalised system. The distances [Ir–E(1)] and [Ir–E(2)] vary by up to 10% in some complexes, and there are distinct differences in [P(1)–N(1)], [P(2)–N(1)] and [E(1)–P(1)] [E(2)–P(2)] bond lengths. It is not clear whether this variation is significant and carried through to the solution state or is an artefact of the solid state structure, but it has been cited previously as an indication of incomplete delocalisation within the metallacycle [8].

A similar observation has been made by Valderrama and Contreras in the solid state structure of the cation in the complex $[Cp^*Ir\{PO(OMe)_2\}\{\eta^2\text{-}(SPPh_2)_2CH_2\text{-}S,S']BF_4$ containing the disulfide of bis(diphenylphosphino)methane (dppm) as a ligand [11]. In this case the (P–S) bonds are the same within 0.5%, but in the same complex the (Ir–S) bonds differ by ca. 2%. Since this ligand is entirely symmetrical with no delocalisation, it may well indicate that the asymmetry observed in the bond lengths of **1**–**6** is not a real effect of incomplete delocalisation at all.

The ligands HL^1 and HL^2 have a pronounced similarity to the dichalcogenides of dppm, and the literature for these ligands contains examples of η^2 coordination through both chalcogens [11–13] or, when deprotonated, through a [C, S] donor set [14,15] and even η^3 coordination through a [C, Se, Se′] donor set [16]. Although there are examples of L^1 and L^2 binding metals in a similar fashion, using [N, S] [17] and [N, Se, Se′] donor sets [18], there is no evidence so far to suggest that these different binding modes are available to complexes of Ir(III).

Compound **7** is rather unusual in that after removal of the chloro ligand by reaction with silver *p*-tolylsulfonate, the coordinatively unsaturated cation formed does not under the conditions used readily accept a molecule of solvent as a ligand, nor does it form even a weak interaction with the anion in the solid state (Fig. 4). Further, there is no evidence for any agostic interactions with other areas of the cation or any tendency to dimerise. Instead, the cation rearranges to give a perpendicular arrangement of the Cp* with respect to the plane defined by [Ir–S(1)–S(2)] (90.1°), a similar structural motif to that seen for the related ruthenium complexes reported by Mashima et al. [19]. The ion in **7** is formally 16-electron, which in Ir(I) is usually associated with a square planar geometry, although examples of Ir(III) with this geometry are less well known. Comparison of the crystallographic data obtained for **7** with **1**–**6** shows that in the cation the (Ir–S) bonds are shortened, consistent with the Ir in **7** having a greater Lewis acid character. The angle defined by (P–N–P) is also significantly compressed (125.9(3) in **7** c.f. 131.7(2)–134.1(3)° **1**–**6**) as are both the (S–P–N) angles (116.7(2) and 116.8(2) **7**, c.f. 118.0(2)–118.9(1)° **1**–**6**).

The reaction of **2** with silver *p*-tolylsulphonate yields a green solution and a yellow solid which precipitates from the THF solution. Examination of the solution by $^{31}P\{^1H\}$-NMR showed one major component at δ + 21.9 ppm, in addition to a small amount of unreacted **2**. We tentatively ascribe this major component to a compound analogous to **7**, as $[Cp^*Ir\{Ph_2P(Se)NP(Se)Ph_2\text{–}Se,Se'\}](C_7H_7SO_3)$ (**8**). Isolation of the crude yellow solid by filtration and examination by $^{31}P\{^1H\}$-NMR indicated the presence of a major species at δ + 10.2 ppm and a small amount of **2**. The identity of both species awaits further elucidation and these results will be reported in due course.

4. Conclusions

Imidotetraaryldichalcogenodiphosphinates continue to give rise to complexes that are stable, tractable and readily characterised. These ligands are capable of supporting unusual fragments and stabilising reactive species, and will continue to be the subject of much research.

5. Supplementary material

Data have been deposited in the Cambridge Crystallographic Database as CCDC nos. 118867–72 (compounds **1**–**6**) and CCDC no. 118896 (compound **7**). Copies of this information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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