

Pentamethylcyclopentadienyliridium(III) complexes containing tertiary phosphorus chalcogenide ligands: crystal structure of $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\text{PO}(\text{OMe})_2\}\{\eta^2(\text{SPPPh}_2)_2\text{CH}_2\text{-S,S}'\}]\text{BF}_4 \cdot 0.5\text{Me}_2\text{CO}$

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Abstract

Neutral iridium(III) complexes of the unidentate P-donor ligands dppm, dppmS and dppmSe, and cationic complexes with these ligands acting in their bidentate form have been prepared and characterized. Similar cationic complexes with the symmetrical bidentate dichalcogenide ligands dppmS₂ and dppmSe₂ have been described. These compounds react with sodium hydride in tetrahydrofuran or with thallium pyrazolate in dichloromethane to yield the new cationic complexes $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\eta^3(\text{EPPH}_2)_2\text{CH-C,E,E}'\}]^+$ (E = S, Se) in which the anionic methanide dichalcogenide ligand is acting as a tripod ligand with a C,E,E'-donor set. However, the complexes $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}(\eta^2\text{dppmE}_2)]\text{BF}_4$ react with $\text{P}(\text{OMe})_3$ in the presence of TlBF_4 , to give the dicationic compounds $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\text{P}(\text{OMe})_3\}\{\eta^2\text{dppmE}_2\}]\text{BF}_4$. In these complexes, the $\text{P}(\text{OMe})_3$ ligand is transformed into a coordinated $\text{PO}(\text{OMe})_2$ group by reaction with sodium iodide in acetone. The structure of the complex $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\text{PO}(\text{OMe})_2\}\{\eta^2\text{dppmS}_2\text{-S,S}'\}]\text{BF}_4 \cdot 0.5\text{Me}_2\text{CO}$ have been determined by single crystal X-ray diffraction methods.

Keywords: Iridium; Cyclopentadienyl complexes; Tertiary chalcogenides; Phosphonate complexes

1. Introduction

Several derivatives of transition metals with the bis(diphenylphosphine)methane disulphide ligand, $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{Ph}_2$, have been described [1–7]. Recent studies have shown that a methylene proton of the ligand, free or coordinated, can be removed by strong bases to form neutral complexes with the anionic ligand acting as S,S'- or C,S-donor ligand [6–9].

We recently described the synthesis of cationic rhodium(III) and ruthenium(II) complexes containing dichalcogenide ligands derived from 1,2-bis(diphenylphosphine)methane (dppm), of general formula $[(\text{ring})\text{MCl}(\eta^2\text{dppmE}_2\text{-E,E}')^+]$, in which (ring)M = $(\eta^5\text{C}_5\text{Me}_5)\text{Rh}$, $(\eta^6\text{C}_6\text{Me}_6)\text{Ru}$ and $\text{dppmE}_2 = \text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{Ph}_2$, $\text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{P}(\text{Se})\text{Ph}_2$ [10,11]. In these compounds, the methylene protons of the coordinated ligand react with sodium hydride forming a methanide group which displaces the chloride ligand leading to cationic complexes of the type $[(\text{ring})\text{MCl}$

$\{\eta^3(\text{EPPH}_2)_2\text{CH-C,E,E}'\}]^+$, in which the resulting anionic ligands are bound to the metal centre as C,E,E'-tripod ligands.

In this paper we describe the synthesis and characterization of several neutral and cationic pentamethylcyclopentadienyliridium(III) complexes with mono- and dichalcogenide ligands, as well as the reactivity of some of the cationic complexes towards the bases sodium hydride and thallium pyrazolate. The preparation and characterization of the dicationic complexes $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\text{P}(\text{OMe})_3\}\{\eta^2\text{dppmE}_2\text{-E,E}'\}]\text{BF}_4$ and the transformation of the trimethylphosphite group into a coordinated dimethylphosphonate ligand are also described. The molecular structure of the complex $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\text{PO}(\text{OMe})_2\}\{\eta^2\text{dppmS}_2\text{-S,S}'\}]\text{BF}_4 \cdot 0.5\text{Me}_2\text{CO}$, determined by single crystal X-ray diffraction, is also reported. Part of this work has been the subject of a preliminary communication [12].

2. Experimental details

Elemental analyses were made with Heraeus Mikro Standard and Perkin-Elmer 240B microanalysers. In-

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frared spectra were recorded on a Bruker IFS-25 spectrophotometer (over the range 4000–400 cm^{-1}) using KBr pellets. Conductivities were measured in ca. 5×10^{-4} M acetone solution using a WTW LF-521 conductimeter. ^1H (200 MHz), ^{31}P (^1H) (81 MHz) and ^{13}C (^1H) NMR (50 MHz) spectra were recorded on a Bruker AC-200P spectrometer and chemical shifts are reported relative to SiMe_4 and 85% H_3PO_4 in D_2O (positive shifts downfield).

All reactions were carried out by Schlenk techniques under purified nitrogen. Reagent grade solvents were dried, distilled, and stored under a nitrogen atmosphere. The ligands $\text{Ph}_2\text{PCH}_2\text{P}(\text{Se})\text{Ph}_2$ (dppmSe), $\text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{P}(\text{Se})\text{Ph}_2$ (dppmSe₂), $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{Ph}_2$ (dppmS₂) and the starting binuclear complex $[(\eta^5\text{C}_5\text{Me}_5)\text{IrX}(\mu\text{-X})]_2$ (X = Cl, I) were prepared by published procedures [13,14].

3. Preparations of complexes

3.1. $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}_2(\eta^1\text{dppm-P})]$ (1)

A mixture of the binuclear complex $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}(\mu\text{-Cl})]_2$ (120 mg; 0.15 mmol) and the ligand dppm (116 mg; 0.30 mmol) in benzene (30 ml) was boiled under reflux for 2 h. The resulting solution was evaporated to a small volume (5 ml) and the complex crystallized by addition of *n*-hexane. Yield: 202 mg of yellow crystals (86%). Anal. Found: C, 53.80; H, 4.82. $\text{C}_{35}\text{H}_{37}\text{Cl}_2\text{IrP}_2$. Calc.: C, 53.70; H, 4.73%.

3.2. $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}_2(\eta^1\text{dppmE-P})]$ (E = S (2), Se (3))

A mixture of complex 1 (245 mg; 0.31 mmol) with a slight excess of sulphur (11 mg; 0.34 mmol) or grey selenium (27 mg; 0.34 mmol) was boiled under reflux in benzene (30 ml) for 2 h. The resulting solution was evaporated to a small volume (5 ml) and the complex crystallized by addition of *n*-hexane. (2) Yield: 221 mg of yellow crystals (86%). Anal. Found: C, 51.02; H, 4.42. $\text{C}_{35}\text{H}_{37}\text{Cl}_2\text{IrP}_2\text{S}$. Calc.: C, 51.59; H, 4.57%. IR(KBr): $\nu(\text{PS})$, 628 cm^{-1} . (3) Yield: 150 mg of orange-yellow crystals (56%). Anal. Found: C, 48.55; H, 4.60. $\text{C}_{35}\text{H}_{37}\text{Cl}_2\text{IrP}_2\text{Se}$. Calc.: C, 48.79; H, 4.33%. IR(KBr): $\nu(\text{PSe})$, 533 cm^{-1} .

3.3. $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}(\eta^2\text{L})]\text{ClO}_4$ (L = dppm-P, P (4), dppmSe-P, Se (5), dppmS-P, S (6))

The complexes were prepared by two routes. (i) A slurry of $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}(\mu\text{-Cl})]_2$ (80 mg; 0.1 mmol), the ligand dppm (77 mg; 0.2 mmol) or $\text{Ph}_2\text{PCH}_2\text{P}(\text{Se})\text{Ph}_2$ (93 mg; 0.2 mmol), and NaClO_4 (25 mg; 0.2 mmol) in acetone (20 ml) was boiled under reflux for 3 h. The solution obtained was evaporated to dryness and the

solid residue extracted with the minimal amount of chloroform and the complex precipitated by addition of diethyl ether (3) or *n*-hexane (4). (ii) A mixture of complex 2 (200 mg; 0.24 mmol) and NaClO_4 (30 mg; 0.24 mmol) in acetone (30 ml) was boiled under reflux for 3 h. The solution was evaporated to dryness, extracted with chloroform and filtered through Kieselguhr. Orange crystals of the complex were obtained by addition of *n*-hexane. (4) Yellow crystals were obtained from acetone–diethyl ether. Yield: 133 mg (84%). Anal. Found: C, 49.35; H, 4.58. $\text{C}_{35}\text{H}_{37}\text{Cl}_2\text{IrO}_4\text{P}_2$. Calc.: C, 49.62; H, 4.40%. (5) Orange crystals were obtained from chloroform–*n*-hexane. Yield: 270 mg (78%). Anal. Found: C, 45.62; H, 3.94. $\text{C}_{35}\text{H}_{37}\text{Cl}_2\text{IrO}_4\text{P}_2\text{Se}$. Calc.: C, 45.40; H, 4.00%. IR(KBr): $\nu(\text{PSe})$, 530 cm^{-1} . (6) Yield: 209 mg (97%). Anal. Found: C, 47.87; H, 4.22; S, 3.65. $\text{C}_{35}\text{H}_{37}\text{Cl}_2\text{IrO}_4\text{P}_2\text{S}$. Calc.: C, 47.84; H, 4.20; S, 3.55%. IR(KBr): $\nu(\text{PS})$, 576 cm^{-1} .

3.4. $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}(\eta^2\text{L})]\text{ClO}_4$ (L = dppmS₂-S, S' (7a), dppmSe₂-Se, Se' (8a))

A mixture of complex $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}(\mu\text{-Cl})]_2$ (120 mg; 0.15 mmol), the corresponding ligand L (0.30 mmol) and NaClO_4 (37 mg; 0.30 mmol) in acetone (30 ml) was boiled under reflux for 2 h. The solution obtained was evaporated to dryness and the residue was extracted with chloroform (10 ml). The complexes were crystallized by careful addition of *n*-hexane. (7a) Yield: 230 mg of orange crystals (84%). Anal. Found: C, 46.32; H, 4.20; S, 7.04. $\text{C}_{35}\text{H}_{37}\text{Cl}_2\text{IrO}_4\text{P}_2\text{S}_2$. Calc.: C, 46.20; H, 4.10; S, 6.91%. IR(KBr): $\nu(\text{PS})$, 582 cm^{-1} . (8a) Yield: 290 mg of red crystals (96%). Anal. Found: C, 41.77; H, 3.39. $\text{C}_{35}\text{H}_{37}\text{Cl}_2\text{IrO}_4\text{P}_2\text{Se}_2$. Calc.: C, 41.87; H, 3.71%. IR(KBr): $\nu(\text{PSe})$, 524 cm^{-1} .

The analogous tetrafluoroborate complexes $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}(\eta^2\text{L})]\text{BF}_4$, L = dppmS₂-S, S' (7b) and dppmSe₂-Se, Se' (8b), were prepared using TlBF_4 instead NaClO_4 . In this case, the reaction was carried out at room temperature by stirring for 1 h. After filtration the TlCl formed, the acetone solution was concentrated to a small volume and the complexes precipitated by addition of diethyl ether. Red crystals were obtained from acetone–diethyl ether. (7b) Yield: 94%. Anal. Found: C, 46.57; H, 4.34; S, 6.72. $\text{C}_{35}\text{H}_{37}\text{BClF}_4\text{IrP}_2\text{S}_2$. Calc.: C, 46.80; H, 4.15; S, 7.14%. IR(KBr): $\nu(\text{PS})$, 572 cm^{-1} . $\Gamma_{\text{M}} = 131 \text{ cm}^2 \text{ mol}^{-1} \Omega^{-1}$. (8b) Yield: 85%. Anal. Found: C, 42.19; H, 3.74. $\text{C}_{35}\text{H}_{37}\text{BClF}_4\text{IrP}_2\text{Se}_2$. Calc.: C, 42.38; H, 3.76%. IR(KBr): $\nu(\text{PSe})$, 505 cm^{-1} . $\Gamma_{\text{M}} = 127 \text{ cm}^2 \text{ mol}^{-1} \Omega^{-1}$.

3.5. $[(\eta^5\text{C}_5\text{Me}_5)\text{IrI}(\eta^2\text{dppmS}_2\text{-S,S'})]\text{BF}_4$ (9)

A slurry of $[(\eta^5\text{C}_5\text{Me}_5)\text{IrI}(\mu\text{-I})]_2$ (174 mg; 0.15 mmol), the ligand dppmS₂ (135 mg; 0.30 mmol) and TlBF_4 (88 mg; 0.30 mmol) in acetone (20 ml) was

stirred at room temperature for 1 h. The TII formed was filtered off and the solution obtained was evaporated to a small volume. The addition of diethyl ether formed an orange-red solid which was recrystallized from acetone–diethyl ether. (**9**) Yield: 271 mg (83%). Anal. Found: C, 42.00; H, 3.77; S, 6.09. $C_{35}H_{37}BF_4IrP_2S_2$. Calc.: C, 42.48; H, 3.77; S, 6.45%. IR(KBr): $\nu(PS)$, 564 cm^{-1} . $\Gamma_M = 142\text{ cm}^2\text{ mol}^{-1}\ \Omega^{-1}$.

3.6. $[(\eta^5C_5Me_5)Ir\{\eta^3(EPPH_2)_2CH-C,E,E'\}]ClO_4$ ($E = S$ (**10**), Se (**11**))

The complexes were prepared by two routes. (i) The addition of a slight excess of sodium hydride (4.5 mg of 80% dispersion in mineral oil, 0.15 mmol) to a solution of complex **7a** or **8a** (0.15 mmol) in anhydrous tetrahydrofuran (10 ml) produced immediate evolution of hydrogen. The suspension formed was stirred until the evolution of hydrogen ceased and the excess of sodium hydride was filtered off. The resulting solution was evaporated to dryness, and the residue was extracted with dichloromethane (15 ml). The addition of *n*-hexane caused the precipitation of the complexes, which were washed with diethyl ether and dried in vacuo. Yield: about 60%. (ii) A solution of complex **7a** or **8a** (0.1 mmol) in dichloromethane (20 ml) was treated with thallium pyrazolate [15] (27 mg; 0.1 mmol). After stirring for 2 h at room temperature, the mixture was filtered through cellulose to remove the TlCl formed. The solution obtained was evaporated to dryness and the solid residue was extracted with the minimum amount of acetone. Careful addition of diethyl ether and cooling to -20°C , caused the formation of orange crystals. (**10**) Yield: 76 mg (79%). Anal. Found: C, 48.47; H, 4.38; S, 6.91. $C_{35}H_{36}ClIrO_4P_2S_2$. Calc.: C, 48.09; H, 4.12; S, 6.96%. IR(KBr): $\nu(PS)$, 602 cm^{-1} . $\Gamma_M = 114\text{ cm}^2\text{ mol}^{-1}\ \Omega^{-1}$. (**11**) Yield: 74 mg (77%). Anal. Found: C, 43.12; H, 3.79. $C_{35}H_{36}ClIrO_4P_2Se_2$. Calc.: C, 43.39; H, 3.72%. IR(KBr): $\nu(PSe)$, 540 cm^{-1} . $\Gamma_M = 132\text{ cm}^2\text{ mol}^{-1}\ \Omega^{-1}$.

3.7. $[(\eta^5C_5Me_5)Ir\{P(OMe)_3\}\{\eta^2dppmE_2-E,E'\}](BF_4)_2$ ($E = S$ (**12**), Se (**13**))

To a mixture of complex **7b** or **8b** (0.15 mmol) and $TiBF_4$ (44 mg; 0.15 mmol) in acetone (15 ml) was added a slight excess of $P(OMe)_3$ (25 mg; 0.20 mmol). The mixture was stirred at room temperature for 1 h, the thallium chloride formed was filtered off through Kieselguhr and the solution evaporated to a small volume. The careful addition of diethyl ether gave the complexes as yellow crystals. (**12**) Yield: 80 mg (75%). Anal. Found: C, 42.89; H, 4.49; S, 6.29. $C_{38}H_{46}B_2F_8IrO_3P_3S_2$. Calc.: C, 42.51; H, 4.32; S, 5.97%. IR(KBr): $\nu(PS)$, 530 cm^{-1} . $\Gamma_M = 233\text{ cm}^2\text{ mol}^{-1}\ \Omega^{-1}$. (**13**) Yield: 124 mg (88%). Anal. Found: C, 39.74; H,

4.20. $C_{38}H_{46}B_2F_8IrO_3P_3Se_2$. Calc.: C, 39.10; H, 3.97%. IR(KBr): $\nu(PSe)$, 527 cm^{-1} . $\Gamma_M = 271\text{ cm}^2\text{ mol}^{-1}\ \Omega^{-1}$.

3.8. $[(\eta^5C_5Me_5)Ir(PPh_3)\{\eta^2dppmSe_2-Se,Se'\}](BF_4)_2$ (**14**)

To a mixture of complex **8b** (60 mg; 0.06 mmol) and $TiBF_4$ (18 mg; 0.12 mmol) in acetone (15 ml) was added a slight excess of PPh_3 (16 mg; 0.06 mmol). The mixture was stirred at room temperature for 1 h, the thallium chloride formed was filtered off through Kieselguhr and the solution was evaporated to a small volume. The addition of diethyl ether gave the complex as a yellow solid, which was recrystallized from acetone–diethyl ether. Yield: 66 mg (91%). Anal. Found: C, 47.76; H, 4.01. $C_{53}H_{52}B_2F_8IrP_2Se_2$. Calc.: C, 47.39; H, 4.04%. IR(KBr): $\nu(PSe)$, 525 cm^{-1} .

3.9. $[(\eta^5C_5Me_5)Ir\{PO(OMe)_2\}\{\eta^2dppmE_2-E,E'\}]I$ ($E = S$ (**15**), Se (**16**))

A solution of complex **12** or **13** (0.1 mmol) and sodium iodide (0.5 mmol) in acetone (10 ml) was stirred at room temperature for 24 h. The solution was evaporated to dryness and the solid residue was extracted with chloroform (10 ml). The addition of hexane or diethyl ether caused the precipitation of the complexes as orange-yellow crystals. (**15**) Yield: 78 mg (91%). Anal. Found: C, 43.00; H, 4.12; S, 5.96. $C_{37}H_{43}IrO_3P_2S_2$. Calc.: C, 43.92; H, 4.28; S, 6.34%. IR(KBr): $\nu(PS)$, 568; $\nu(PO)$, 1100 and $\delta(PO)$, 585 cm^{-1} . (**16**) Yield: 92 mg (86%). Anal. Found: C, 39.66; H, 3.91. $C_{37}H_{43}IrO_3P_2Se_2$. Calc.: C, 40.19; H, 3.92%. IR(KBr): $\nu(PSe)$, 529; $\nu(PO)$, 1102 and $\delta(PO)$, 580 cm^{-1} .

3.10. $[(\eta^5C_5Me_5)Ir\{PO(OMe)_2\}\{\eta^2(dppmS_2-S,S')\}]BF_4$ (**17**)

The complex was prepared by two routes. (i) A solution of complex **15** (182 mg; 0.18 mmol) in acetone solution (15 ml) was treated with an excess of $TiBF_4$ (74 mg; 0.25 mmol). After stirring for 30 min, the mixture was evaporated to dryness and extracted with chloroform (15 ml). Partial evaporation of solvent and addition of diethyl ether caused the formation of yellow crystals, which were recrystallized from acetone–diethyl ether and dried in vacuo. Yield: 110 mg (63%). (ii) A solution of complex **12** (54 mg; 0.05 mmol) in dichloromethane solution was treated with a large excess of potassium *tert*-butoxide (1 g). After stirring for 8 h, the mixture was filtered and evaporated to a small volume. The addition of *n*-hexane gave a yellow solid. Yield: 18 mg (35%). Anal. Found: C, 46.90; H, 4.40; S, 6.22. $C_{37}H_{43}BF_4IrO_3P_2S_2 \cdot 0.5(CH_3)_2CO$. Calc.: C,

46.20; H, 4.63; S, 6.40%. IR(KBr): $\nu(\text{PS})$, 568 cm^{-1} . $\Gamma_{\text{M}} = 127 \text{ cm}^2 \text{ mol}^{-1} \Omega^{-1}$.

3.11. Crystal structure of $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\text{PO}(\text{OMe})_2\}_2\{\eta^2(\text{dppmS}_2\text{-S,S}')\}]\text{BF}_4 \cdot 0.5\text{Me}_2\text{CO}$ (17)

Suitable crystals were obtained from a slow diffusion of diethyl ether into an acetone solution of the complex. Crystal data and details of measurements and refinements are summarized in Table 1. A list of observed and calculated structure factors, anisotropic thermal parameters, H atom coordinates, bonds lengths and bond angles are available for the authors on request.

4. Results and discussion

The binuclear complex $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}(\mu\text{-Cl})_2]$ reacts with dppm in benzene solution by cleavage of the chlorine bridges to yield the neutral complex $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}_2(\eta^1\text{dppm-P})]$ (1). The uncoordinated P-atom of this complex reacts with elemental sulphur or selenium in refluxing benzene creating the monosulphide or selenide ligands, leading to the complexes $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}_2(\eta^1\text{dppmE-P})]$ (E = S (2), Se (3)).

These complexes were isolated as stable microcrystalline solids. Their spectra in KBr pellets show the characteristic absorptions of the non-coordinated P=S or P=Se group. The ^1H NMR spectra of complex 1 exhibit the expected doublet signal for the C_5Me_5 ring and a doublet of doublets for the methylene protons. For complexes 2 and 3, the CH_2 protons appear as an apparent triplet signal. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show two doublet resonances, where the phosphorus atom bonded to the metal centre (P_{A}) resonate at lower field than the non-coordinated $\text{P}_{\text{B}}(\text{E})$ group. Relevant NMR chemical shifts and coupling constants are listed in Table 2.

When the above reaction was carried out in acetone at reflux temperature, in the presence of NaClO_4 , cationic complexes with the ligands L acting in their bidentate form were obtained, $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}(\eta^2\text{L})]\text{ClO}_4$ (L = dppm (4), dppmSe (5), dppmS (6)). Similarly, the reaction of the symmetrical ligands dppmS₂ and dppmSe₂ with the binuclear starting iridium(III) complex in refluxing acetone, in the presence of NaClO_4 , lead to the formation of the corresponding cationic complexes, $[(\eta^5\text{C}_5\text{Me}_5)\text{IrCl}(\eta^2\text{dppmE}_2\text{-E,E}')]\text{ClO}_4$ (E = S (7a), Se (8a)). However, these reactions can be carried out under mild conditions, using TIBF_4 instead NaClO_4 , with formation of the tetrafluoroborate derivatives, 7b and 8b (Scheme 1).

All cationic compounds were isolated as stable microcrystalline solids and behave as 1:1 electrolytes in acetone solution. In all cases their infrared spectra in KBr show the presence of the uncoordinated anion

(ClO_4^- : ca. 1100, 620 cm^{-1} ; BF_4^- : ca. 1100, 520 cm^{-1}) together with the absorption bands corresponding to the coordinated P=S or P=Se groups. As expected, the $\nu(\text{PE})$ stretching are shifted to lower frequencies ($\nu(\text{PS}) = 564\text{--}582 \text{ cm}^{-1}$; $\nu(\text{PSe}) = 505\text{--}530 \text{ cm}^{-1}$) relative to the free ligand ($\nu(\text{PS})$: 628 cm^{-1} , $\nu(\text{PSe})$: 531 cm^{-1}) [2,16]. Their ^1H NMR spectra in CDCl_3 exhibit the expected resonances to the phenyl groups and the C_5Me_5 ring, together with two doublet of triplets at the range δ 4.3–6.0 ppm corresponding to the non-equivalent methylene protons H_{a} and H_{b} . The proton endo to the chlorine atom is labelled H_{a} and is assigned to the highest field resonance by comparison with the spectra of the similar iodide derivative, $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\eta^2\text{dppmS}_2\text{-S,S}'\}]\text{BF}_4$ (9), which shows no important variation for the lowest field resonance (H_{b}) and a shift for the highest field resonance (H_{a}). These assignments are in accord with those reported for methylene protons of the bis(diphenylphosphine)methane ligand in the platinum(II) complex $[\text{Pt}_2\text{X}_2(\mu\text{-S})(\mu\text{-dppm})_2]$ (X = Cl, Br,

Table 1
Crystal and refinement data for complex $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\text{PO}(\text{OMe})_2\}_2\{\eta^2(\text{SPPH}_2)_2\text{CH}_2\text{-S,S}'\}]\text{BF}_4 \cdot 0.5\text{Me}_2\text{CO}$

Empirical formula	$\text{C}_{37}\text{H}_{43}\text{BF}_4\text{IrO}_3\text{P}_2\text{S}_2 \cdot 0.5(\text{CH}_3)_2\text{CO}$
Colour, habit	orange, prism
Crystal size (mm)	$0.2 \times 0.2 \times 0.4$
Crystal system	monoclinic
Space group	$P2_1/c$
Cell dimensions	
a (Å)	16.485(3)
b (Å)	11.923(3)
c (Å)	22.028(5)
β (°)	95.25(2)
Cell volume (Å ³)	4311.8(17)
Z	4
Formula weight	1000.8
D_{calc} (Mg m^{-3})	1.542
μ ($\text{Mo K } \alpha$) (cm^{-1})	33.38
Diffractometer	Siemens P3/PC
Radiation	$\text{Mo K } \alpha$ ($\lambda = 0.71073$ Å)
Temperature (K)	293
Scan technique	$2\theta - \theta$
Monochromator	highly oriented graphite crystal
Index ranges	$-22 \leq h \leq 22$; $0 \leq k \leq 16$; $0 \leq l \leq 30$
No. reflections measured	11504
No. independent reflections ($R_{\text{int}} = 0.00\%$)	11504
Observed reflections $F > 3.0\sigma(F)$	5745
Absorption correction	DIFABS: min = 0.826, max = 1.151
Refinements system	Siemens SHELXTL PLUS (PC)
Solution	direct methods
No. parameters refined	499
R (%)	3.45
R_w (%)	3.74
Goodness-of-fit	1.18

D) [17]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes with symmetrical ligands (**4,7–9**) show a singlet resonance for the equivalent phosphorus atoms, whilst the spectra of complexes with unsymmetrical ligands (**5,6**) show two doublet resonances, where the P bonded to the metal (P_A) resonates at lower field than the $\text{P}_B = \text{E}$ group.

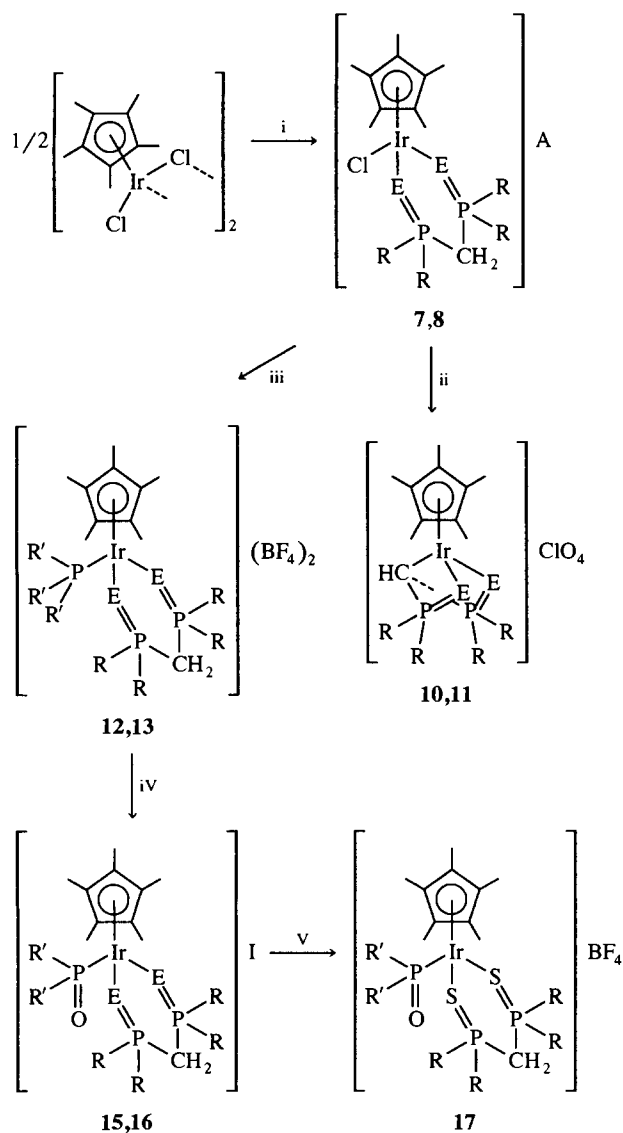
The cationic complexes **7a** and **8a** react with sodium hydride in tetrahydrofuran solution by deprotonation of

the methylene group, yielding new monocationic complexes of general formula $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}(\eta^3(\text{EPPH}_2)_2\text{-CH-C,E,E}')]\text{ClO}_4$ ($\text{E} = \text{S}$ (**10**), Se (**11**)). The coordination mode of the anionic dichalcogenides as C,E,E'-tripod ligands has been recently demonstrated for the similar isoelectronic complexes, $[(\eta^5\text{C}_5\text{Me}_5)\text{Rh}(\eta^3\text{-}(\text{SePPH}_2)_2\text{CH})]\text{ClO}_4$ and $[(\eta^6\text{C}_6\text{Me}_6)\text{Ru}(\eta^3(\text{SPPH}_2)_2\text{-CH})]\text{ClO}_4$, whose crystalline structures have been determined by X-ray diffraction [10,11]. For these com-

Table 2
NMR chemical shifts (δ ppm) and coupling constants (Hz) of iridium(II) complexes ^a

Complex	^1H NMR		$^{31}\text{P}\{^1\text{H}\}$ NMR
	ring	$\text{CH}_2(\text{CH})$	
1	1.4 (d) $^4J(\text{P}_A\text{H}) = 2.3$	3.8 (dd) $^2J(\text{P}_A\text{H}) = 9.5$; $^2J(\text{P}_B\text{H}) = 2.0$	-2.2 (d, P_A), -27.7 (d, P_B) $^2J(\text{P}_A\text{P}_B) = 34.6$
2	1.3 (d) $^4J(\text{P}_A\text{H}) = 2.3$	4.6 (at) $^2J(\text{PH}) = 10.7$	-4.5 (d, P_B), 34.1 (d, P_A) $^2J(\text{P}_A\text{P}_B) = 34$
3	1.3 (d) $^4J(\text{P}_A\text{H}) = 2.3$	4.8 (a) $^2J(\text{PH}) = 10.8$	-3.9 (d, P_B), 23.2 (d, P_A) $^2J(\text{P}_A\text{P}_B) = 33.8$; $^1J(\text{P}_B\text{Se}) = 734$
4	1.8 (t) $^4J(\text{P}_A\text{H}) = 2.8$	4.7 (dt, H_a), 6.3 (dt, H_b) $^2J(\text{PH}_a) = 13$; $^2J(\text{PH}_b) = 9.8$ $^2J(\text{H}_a\text{H}_b) = 15.8$	-39.2 (s)
5	1.7 (d) $^4J(\text{P}_A\text{H}) = 2.5$	4.6 (m, H_a), 4.8 (m, H_b)	17.8 (d, P_A), 33.4 (d, P_BSe) $^2J(\text{P}_A\text{P}_B) = 33.9$; $^1J(\text{P}_B\text{Se}) = 550$
6	1.7 (d) $^4J(\text{P}_A\text{H}) = 2.2$	4.3 (m, H_a), 4.7 (m, H_b)	17.8 (d, P_A), 54.7 (d, P_BS) $^2J(\text{P}_A\text{P}_B) = 28$
7b ^{b,c}	1.9 (s)	5.2 (dt, H_a), 5.7 (dt, H_b) $^2J(\text{PH}_a) = 12$; $^2J(\text{PH}_b) = 17$ $^2J(\text{H}_a\text{H}_b) = 14$	34.1 (s)
8b ^b	1.8 (s)	5.1 (dt, H_a), 6.0 (dt, H_b) $^2J(\text{PH}_a) = 14$; $^2J(\text{PH}_b) = 16$ $^2J(\text{H}_a\text{H}_b) = 14$	14.9 (s) $^1J(\text{PSe}) = 643$; $^3J(\text{P}_B\text{Se}) = 9$
9 ^b	1.9 (s)	4.8 (dt, H_a), 5.8 (dt, H_b) $^2J(\text{PH}_a) = 14$; $^2J(\text{PH}_b) = 14$ $^2J(\text{H}_a\text{H}_b) = 14.5$	32.9 (s)
10 ^d	1.3 (s)	3.7 (s, br)	58.2 (s)
11 ^c	1.3 (s)	4.3 (t) $^2J(\text{PH}) = 2.7$	41.9 (s) $^1J(\text{PSe}) = 488$
12 ^{b,f}	2.0 (d) $^4J(\text{PH}) = 3.7$	5.3 (m, H_a, H_b)	31.0 (m, PS), 73.1 (m, P-OMe)
13 ^{b,g}	2.0 (d) $^4J(\text{PH}) = 3.7$	5.2 (m, H_a), 5.6 (m, H_b)	12.1 (m, PSe), 72.5 (m, P-OMe)
14 ^h	1.61 (d) $^4J(\text{PH}) = 2.4$	3.6 (dt, H_a), 5.7 (dt, H_b) $^2J(\text{PH}_a) = 14$; $^2J(\text{PH}_b) = 14$ $^2J(\text{H}_a\text{H}_b) = 14$	1.1 (t, PPh_3), 9.0 (d, PSe) $^1J(\text{PSe}) = 652$; $^2J(\text{PP}) = 27$
16 ⁱ	1.75 (d) $^4J(\text{PH}) = 2.8$	4.7 (dt, H_a), 7.0 (dt, H_b) $^2J(\text{PH}_a) = 14$; $^2J(\text{PH}_b) = 16$ $^2J(\text{H}_a\text{H}_b) = 14$	32.5 (s, PSe), 59.8 (s, PO) $^1J(\text{PSe}) = 648$
17 ^j	1.79 (d) $^4J(\text{PH}) = 2.8$	5.2 (dt, H_a), 7.0 (dt, H_b) $^2J(\text{PH}_a) = 13$; $^2J(\text{PH}_b) = 18$ $^2J(\text{H}_a\text{H}_b) = 14$	30.7 (s, PS), 39.1 (s, PO)

^a Measured in CDCl_3 at room temperature. Chemical shifts relative to Me_4Si and H_3PO_4 (85%) as external standard. s = singlet, d = doublet, t = triplet, dt = doublet of triplets, at = apparent triplet, m = multiplet. All complexes show multiplets in the region δ 7.4–8.0 ppm corresponding to phenyl groups of the chalcogenide ligands. ^b Acetone- d_6 . ^c $^{13}\text{C}\{^1\text{H}\}$ NMR(CDCl_3): δ 8.9 (s, C_5Me_5), 26.6 [t, CH_2 , $^1J(\text{PC}) = 45.4$ Hz], 91.9 (s, C_5Me_5). ^d $^{13}\text{C}\{^1\text{H}\}$ NMR(CDCl_3): δ -39.9 [t, CH, $^1J(\text{PC}) = 50.5$ Hz], 8.8 (s, C_5Me_5), 89.7 (s, C_5Me_5). ^e $^{13}\text{C}\{^1\text{H}\}$ NMR(CDCl_3): δ -42.0 [t, CH, $^1J(\text{PC}) = 39.8$ Hz], 9.1 (s, C_5Me_5), 89.4 (s, C_5Me_5). ^f ^1H NMR: δ 3.9 [d, $^3J(\text{PH}) = 11.5$ Hz]; $^{13}\text{C}\{^1\text{H}\}$ NMR(DEPT-acetone- d_6): δ 9.3 (s, C_5Me_5), 27.9 [t, CH_2 , $^1J(\text{PC}) = 44.3$ Hz], 56.3 [d, MeOP, $^2J(\text{PC}) = 8.5$ Hz]. ^g ^1H NMR: δ 4.0 [d, $^3J(\text{PH}) = 11.6$ Hz]; $^{13}\text{C}\{^1\text{H}\}$ NMR(CDCl_3): δ 9.5 (s, C_5Me_5), 26.7 [t, CH_2 , $^1J(\text{PC}) = 38.6$ Hz], 56.5 [d, MeOP, $^2J(\text{PC}) = 8.7$ Hz], 101.9 (s, C_5Me_5). ^h Nitromethane- d_3 . ^1H NMR: δ 3.5 [d, $^3J(\text{PH}) = 11.1$ Hz]. ⁱ ^1H NMR: δ 3.3 [d, $^3J(\text{PH}) = 11.1$ Hz]; $^{13}\text{C}\{^1\text{H}\}$ NMR(CDCl_3): δ 8.5 (s, C_5Me_5), 26.0 [t, CH_2 , $^1J(\text{PC}) = 43.0$ Hz], 50.8 (d, MeOP, $^2J(\text{PC}) = 8.0$ Hz), 97 (s, C_5Me_5).



Scheme 1. R = Ph, R' = OMe, E = S, Se; A = ClO₄⁻, BF₄⁻; (i) dp-pmE₂, NaClO₄ or TIBF₄; (ii) NaH-THF or Tlpz-CH₂Cl₂; (iii) P(OMe)₃, TIBF₄; (iv) NaI, Me₂CO; (v) TIBF₄.

pounds the ¹³C{¹H} NMR spectra showed that the formation of the metal-carbon bond produced a strong increase in shielding of the methanide carbon. As expected, the ¹H NMR spectra of complexes **10** and **11** show only one signal for the methanide proton, confirming that the methylene group in the starting complexes undergoes deprotonation and their ¹³C{¹H} NMR spectra show a large increase of shielding of the methanide carbon appearing as a triplet signal in the range δ 40–42 ppm, supporting the proposed formulation. Similar synthetic results were obtained by reaction of the cationic complexes with thallium pyrazolate in dichloromethane solution or with TIBF₄ in acetone solution, in the presence of pyridine. In both cases the chloride ligand is precipitated as TlCl and the pyrazolate anion or pyridine caused the deprotonation of the

chalcogenide ligands. The methanide carbon group formed is bonded to the metal centre, even in the presence of a large excess of pyridine. These cationic

Table 3
Fractional atomic coordinates ($\times 10^4$) and temperature parameters ($\text{\AA}^2 \times 10^3$), with e.s.ds. in parentheses

Atom	x	y	z	U ^a
Ir(1)	2820(1)	-5702(1)	23(1)	39(1)
P(1)	2921(1)	-4177(2)	-585(1)	52(1)
P(2)	1497(1)	-3495(1)	659(1)	40(1)
P(3)	3183(1)	-3858(1)	1344(1)	39(1)
S(1)	1559(1)	-5087(1)	385(1)	49(1)
S(2)	3750(1)	-4837(1)	777(1)	48(1)
O(1)	2898(3)	-3028(4)	-341(2)	68(2)
O(2)	3759(3)	-4374(4)	-903(2)	84(2)
O(3)	2224(4)	-4304(4)	-1139(2)	86(2)
C(1)	3313(4)	-7439(5)	295(3)	50(2)
C(2)	2475(4)	-7513(5)	191(3)	47(2)
C(3)	2250(4)	-7141(5)	-438(3)	54(2)
C(4)	2972(4)	-6899(6)	-707(3)	57(2)
C(5)	3640(4)	-6992(5)	-245(3)	54(2)
C(6)	3805(4)	-7785(6)	880(3)	75(3)
C(7)	1886(4)	-7943(6)	611(3)	68(3)
C(8)	1402(5)	-7207(6)	-755(4)	84(3)
C(9)	3031(6)	-6702(7)	-1376(3)	99(4)
C(10)	4534(4)	-6891(8)	-332(4)	96(4)
C(11)	4011(5)	-3672(9)	-1362(4)	111(4)
C(12)	1908(6)	-3431(8)	-1489(4)	98(4)
C(13)	2477(3)	-2889(5)	941(3)	42(2)
C(14)	1057(4)	-2558(5)	66(3)	45(2)
C(15)	526(4)	-2996(7)	-393(3)	60(2)
C(16)	173(5)	-2305(8)	-847(3)	72(3)
C(17)	318(5)	-1213(9)	-827(4)	83(4)
C(18)	836(6)	-751(8)	-377(5)	107(4)
C(19)	1215(5)	-1439(6)	81(4)	80(3)
C(20)	831(3)	-3421(5)	1267(3)	44(2)
C(21)	724(4)	-2395(6)	1545(3)	64(3)
C(22)	218(5)	-2335(8)	2023(3)	77(3)
C(23)	-160(5)	-3268(9)	2213(3)	80(3)
C(24)	-71(4)	-4274(8)	1935(3)	69(3)
C(25)	435(4)	-4362(6)	1466(3)	56(2)
C(26)	3978(4)	-3044(5)	1749(3)	45(2)
C(27)	4070(4)	-1928(6)	1667(4)	73(3)
C(28)	4736(6)	-1355(7)	1968(5)	99(4)
C(29)	5280(5)	-1933(8)	2348(4)	80(3)
C(30)	5207(5)	-3044(8)	2417(4)	91(4)
C(31)	4557(4)	-3594(7)	2125(3)	77(3)
C(32)	2660(4)	-4583(5)	1907(3)	44(2)
C(33)	2558(4)	-5744(6)	1887(3)	57(2)
C(34)	2148(5)	-6286(6)	2314(3)	72(3)
C(35)	1826(5)	-5676(8)	2765(3)	79(3)
C(36)	1924(5)	-4517(7)	2796(3)	74(3)
C(37)	2338(4)	-3977(6)	2371(3)	56(2)
F(1)	1489(5)	348(8)	1940(5)	226(6)
F(2)	2303(4)	-267(4)	1303(2)	120(3)
F(3)	2768(5)	816(6)	2054(3)	173(4)
F(4)	2383(5)	-977(5)	2193(3)	141(3)
B(1)	2238(7)	9(9)	1890(5)	82(4)
O(1)s	3967(15)	-10339(17)	-996(11)	220(14)
C(1)s	3550(27)	-10209(17)	-547(17)	199(22)
C(2)s	2764(14)	-9719(16)	-699(8)	95(8)
C(3)s	3652(13)	-10558(13)	53(9)	100(8)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{i,j} tensor.

compounds are surprisingly inert in reaction with PPh_3 , P(OMe)_3 , dppm or dppe , and only react with aqueous HCl in acetone solution regenerating the starting complexes.

However, the reaction of the cationic complexes **7b** and **8b** with TIBF_4 in the presence of a slight excess of P(OMe)_3 involves the precipitation of TlCl and the coordination of the ligand with formation of the dicationic complexes $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\text{P(OMe)}_3\}\{\eta^2\text{dppmE}_2\text{-E,E'}\}](\text{BF}_4)_2$ ($\text{E} = \text{S}$ (**12**), Se (**13**)). Their ^1H NMR spectra exhibit the expected methyl proton resonances for the C_5Me_5 ring and for the trimethylphosphite ligand, together with two multiplet resonances for the hydrogen atoms of the methanide group. For the disulphide complex, the methanide protons have a similar chemical shift and the signal appears as a very broad multiplet. The high resolution $^{31}\text{P}\{^1\text{H}\}$ NMR spectra exhibit two unresolved multiplet resonances assigned to the different phosphorus atoms, P(OMe)_3 and $\text{P}=\text{E}$. These results suggest the presence of non-equivalent $\text{P}=\text{E}$ groups, probably owing to a distortion of the coordinated chalcogenide ligand.

In contrast, when the above reaction was carried out with PPh_3 , the corresponding dicationic complex $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\text{PPh}_3\}\{\eta^2\text{dppmSe}_2\text{-Se,Se'}\}](\text{BF}_4)_2$ (**14**) was obtained. In this case, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra

exhibit a triplet signal and a doublet signal at δ 1.1 and 9.0 ppm, assigned to the PPh_3 and $\text{P}=\text{Se}$ groups respectively.

All attempts to deprotonate the coordinated chalcogenide ligand in these compounds (**12–14**) were unsuccessful. Thus, treatment with sodium hydride in tetrahydrofuran gave a mixture of uncharacterized brown solid, and the reaction of complexes **12** and **13** with thallium pyrazolate or potassium *tert*-butoxide in dichloromethane, transform the coordinated trimethylphosphite into a dimethylphosphonate ligand via a Michaelis–Arbuzov-type reaction [18], giving monocationic complexes of formula $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\text{PO(OMe)}_2\}\{\eta^2\text{dppmE}_2\text{-E,E'}\}]\text{BF}_4$, in low yields. When this type of reaction was carried out in acetone using a large excess of sodium iodide, the metathetic exchange of the BF_4^- anion was produced and the corresponding iodide complexes were isolated $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\text{PO(OMe)}_2\}\{\eta^2\text{dppmE}_2\text{-E,E'}\}]\text{I}$ ($\text{E} = \text{S}$ (**15**), Se (**16**)). For these compounds, the phosphorus–phosphorus coupling is not observed and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra exhibit only two singlet resonances, corresponding to PO(OMe)_2 and equivalent $\text{P}=\text{E}$ groups.

The complex **15** reacts with an excess of TIBF_4 in acetone to give in good yield the complex $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\text{PO(OMe)}_2\}\{\eta^2\text{dppmS}_2\text{-S,S'}\}]\text{BF}_4$ (**17**). The structure

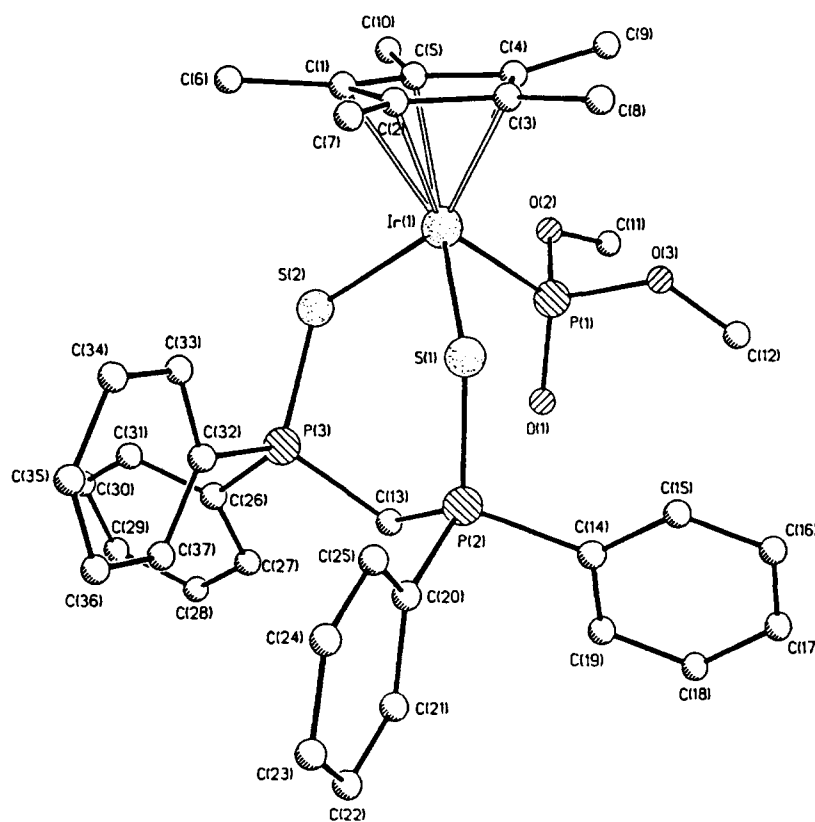


Fig. 1. ORTEP view of the structure of the cationic complex $[(\eta^5\text{C}_5\text{Me}_5)\text{Ir}\{\text{PO(OMe)}_2\}\{\eta^2(\text{SPh}_2)_2\text{CH}_2\text{-S,S'}\}]^+$ showing the atom numbering. Hydrogen atoms have been omitted for clarity.

Table 4

Selected bond lengths (Å) and angles (deg), with e.s.ds. in parentheses

Ir(1)–P(1)	2.273(2)	P(1)–O(1)	1.475(5)
Ir(1)–S(1)	2.408(2)	P(1)–O(2)	1.621(6)
Ir(1)–S(2)	2.389(2)	P(1)–O(3)	1.604(5)
Ir(1)–C(1)	2.284(6)	P(2)–C(13)	1.825(5)
Ir(1)–C(2)	2.272(6)	P(2)–C(14)	1.819(6)
Ir(1)–C(3)	2.164(6)	P(2)–C(20)	1.810(6)
Ir(1)–C(4)	2.181(7)	P(3)–C(13)	1.814(5)
Ir(1)–C(5)	2.164(7)	P(3)–C(26)	1.800(6)
P(2)–C(13)	1.825(5)	P(3)–C(32)	1.796(6)
P(3)–C(13)	1.814(5)	O(2)–C(11)	1.410(1)
P(2)–S(1)	1.998(2)	O(3)–C(12)	1.370(1)
P(3)–S(2)	2.003(2)		
S(1)–Ir(1)–S(2)	99.0(1)	S(2)–P(3)–C(32)	115.5(2)
S(1)–Ir(1)–P(1)	93.6(1)	S(1)–P(2)–C(13)	114.2(2)
S(2)–Ir(1)–P(1)	89.3(1)	S(1)–P(2)–C(14)	113.2(2)
Ir(1)–S(1)–P(2)	117.3(1)	S(1)–P(2)–C(20)	108.7(2)
Ir(1)–S(2)–P(3)	112.3(1)	C(1)–C(2)–C(3)	107.4(6)
Ir(1)–P(1)–O(1)	121.5(2)	C(2)–C(3)–C(4)	107.9(5)
Ir(1)–P(1)–O(2)	104.5(2)	C(3)–C(4)–C(5)	108.1(6)
Ir(1)–P(1)–O(3)	106.3(2)	C(4)–C(5)–C(1)	106.9(6)
S(2)–P(3)–C(13)	112.3(2)	C(5)–C(1)–C(2)	109.2(5)
S(2)–P(3)–C(26)	105.2(2)		

of this complex, established by an X-ray diffraction study, is shown as an ORTEP diagram in Fig. 1. Table 3 and 4 list atomic coordinates and equivalent isotropic thermal parameters of non-H atoms, and relevant bond distances and angles respectively. In the cation, the iridium atom shows a distorted octahedral coordination sphere, commonly referred as a 'three-legged piano stool' configuration, with the centroid of the pentamethylcyclopentadienyl ligand occupying the centre of three octahedral sites, the bis(diphenylphosphine) methylene disulphide ligand bonded to the iridium atom through two sulphur atoms and a dimethylphosphonate group bonded through the phosphorus atom completing the coordination sphere.

The methyl substituents are bent away from the iridium atom and the Ir–C₅Me₅ (centroid) distance is 1.851 Å (individual iridium–carbon distances range from 2.164(7) to 2.284(6) Å) and compares well with those found in other pentamethylcyclopentadienyl iridium complexes [19–22]. The five membered carbocyclic ring involves two shorter bonds C(1)–C(2) and C(3)–C(4) and three larger ones C(2)–C(3), C(4)–C(5) and C(1)–C(5), suggesting some degree of localized 'di- π -olefin' bonding [22,23], although the differences in the bonds lengths are within the accuracy limits.

The Ir–S distances (2.408(2) and 2.388(2) Å) are similar to those found in the thiolate complex [Ir(S₂CNEt₂)₃] (average: 2.370(2) Å) [24]. The P–S (1.998(2) and 2.003(2) Å) and P–C(13) (1.825(5) and 1.814(5) Å) distances of the coordinate bidentate ligand are similar to those found in the related complexes

[Rh(η^4 cod)(η^2 -dppmS₂–S,S')]ClO₄ (P–S: average 1.998(6) Å) [5] and [CuCl(η^2 -dppmS₂–S,S')] (P–S: average 1.973(2); P–C: average 1.816(6) Å) [2]. The Ir–P distance (2.273(2) Å) and the phosphoryl P=O distance (1.475(5) Å) are comparable with those found for the terminal phosphonate ligand in the complex [(η^5 C₅Me₅)Ir(PO(OMe)₂){ μ -PO(OMe)₂}(μ -C₃H₃N₂)-Rh(cod)] (Ir–P: 2.249(2) Å; P=O: 1.486(7) Å) [25]. The P–OMe distances and the P–O–Me angles, however, vary within the usual range [26].

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