

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE
OF (η^5 -PENTAMETHYLCYCLOPENTADIENYL){BIS(PENTAFLUOROPHENYL)THIOMETHYLPHENYL
PHOSPHINE- κ_2S,P }CHLOROIRIDIUM(III) TETRAFLUOROBORATER.M. Bellabarba^{1,2}, M. Nieuwenhuyzen¹, G.C. Saunders³¹The School of Chemistry, Queen's University Belfast, David Keir Building, Belfast, BT9 5BA, United Kingdom²Current address: Sasol Technology (UK) Ltd, Purdie Building, North Haugh, St Andrews, KY16 9ST, United Kingdom³Department of Chemistry, The University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand

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The salt (η^5 -pentamethylcyclopentadienyl){bis(pentafluorophenyl)thiomethylphenylphosphine- κ_2S,P }chloroiridium(III) tetrafluoroborate, $[(\eta^5-C_5Me_5)IrCl\{\kappa_2S,P-(C_6F_5)_2PC_6H_4SMe-2\}]BF_4$, crystallizes as a conglomerate in the orthorhombic crystal system in space group $P2_12_12_1$ with unit cell parameters $a = 9.9621(9)$ Å, $b = 16.7793(15)$ Å, $c = 18.5040(16)$ Å, $V = 3093.1(5)$ Å³, $Z = 4$, $d_{calc} = 2.014$ g·cm⁻³. The structure of the S_{Ir} , S_S stereoisomer reveals three-legged piano stool geometry about Ir, with Cp*—Ir, Ir—P, Ir—S and Ir—Cl distances of 1.847(5), 2.2791(14), 2.3451(13) and 2.3840(12) Å respectively.

Keywords: conglomerate, η^5 -pentamethylcyclopentadienyl, iridium, X-ray structure.

Intramolecular dehydrofluorinative coupling of pentamethylcyclopentadienyl and phosphines bearing polyfluoroaryl substituents occurs readily in cationic complexes of rhodium [1, 2] and iridium [2, 3], especially in cases where the phosphine moiety is a component of a chelating ligand. A number of the products are chiral, with some crystallizing as conglomerates, for example the salts comprising cations of tethered ligands $[\{\eta^5,\kappa P,\kappa P-C_5Me_4CH_2-2-C_5F_3N-4-P(C_6F_5)CH_2CH_2PPh_2\} \cdot RhCl][BF_4]$ [4] and $[\{\eta^5,\kappa P-C_5Me_4CH_2-2-C_6F_4P(C_6F_5)CH_2P(C_6F_5)_2\}RhCl_2]$ [5]. Here we report the structure of an iridium complex, $[(\eta^5-C_5Me_5)IrCl\{\kappa P,\kappa S-(C_6F_5)_2PC_6H_4SMe-2\}]BF_4$ (**1**), which undergoes intramolecular dehydrofluorinative coupling [3], and which also crystallizes as a conglomerate.

Experimental. Crystals of compound **1** [3] were grown from dichloromethane. Diffraction data of a single crystal were collected at 153(2) K on a Bruker SMART diffractometer using the SAINT-NT [6] software with graphite-monochromated MoK_α radiation. Crystallographic and refinement data are given in Table 1. Lorentz and polarization corrections were applied. Empirical absorption corrections were applied using SADABS [8]. The structure was solved using direct methods and refined with the programme package SHELXTL [9]. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were added, and idealized positions and a riding model with fixed thermal parameters (U_{ij} $1.2U_{eq}$ for the atom to which they are bonded (1.5 for CH₃)) were used for subsequent refinements. The function minimized was $\sum[w(|F_0|^2 - |F_c|^2)]$. CCDC 221314 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

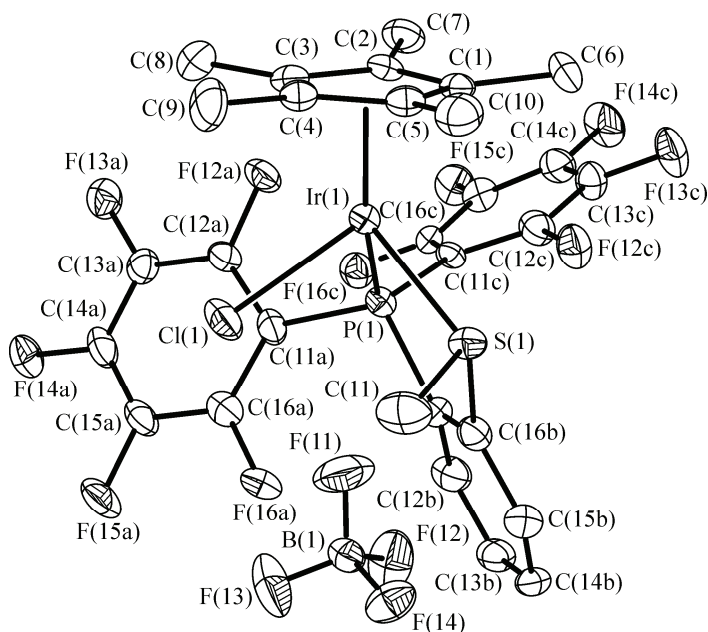
Table 1

Crystallographic data and refinement parameters for compound 1

Parameter	Value
Empirical formula	C ₂₉ H ₂₂ BClF ₁₄ IrPS
Molecular mass	937.96
Wavelength, Å	0.71073
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> , <i>b</i> , <i>c</i> , Å	9.9621(9), 16.7793(15), 18.5040(16)
<i>V</i> , Å ³ ; <i>Z</i>	3093.1(5); 4
<i>d</i> _{calc} , g·cm ⁻³	2.014
μ , mm ⁻¹	4.629
<i>F</i> (000)	1808
Crystal size, mm	0.36×0.28×0.24
θ data collection range, deg.	1.64—25.00
Intervals of reflection indices	-11 ≤ <i>h</i> ≤ 11, -19 ≤ <i>k</i> ≤ 19, -22 ≤ <i>l</i> ≤ 22
Measured / Independent reflections	24995 / 5418 [<i>R</i> (int) = 0.0459]
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	5130
Parameters	439
Goodness of fit on <i>F</i> ² , <i>S</i>	0.959
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0276, <i>wR</i> ₂ = 0.0532
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0301, <i>wR</i> ₂ = 0.0542
Weighting scheme	$w^{-1} = [\sigma^2 F_0 ^2 + (0.0280 \times \{ F_0 ^2 + 2 F_c ^2\}/3)^2]$
Residual electron density (max / min), e/Å ⁻³	-0.630 / 0.846
Flack parameter [7]	-0.022(5)

Results and discussion. Salt 1 crystallized as a conglomerate in the non-centrosymmetric space group *P*2₁2₁2₁. The structure of the *S*_{Ir}, *S*_S stereoisomer was determined (Fig. 1). The cation shows the expected three-legged piano stool geometry about the iridium atom, which is a stereogenic centre. The

Fig. 1. Molecular structure of the *S*_{Ir}, *S*_S stereoisomer of salt 1



sulphur atom is also a stereogenic centre, and as for [$\{\eta^5, \kappa P, \kappa S-C_5Me_4CH_2C_6F_4-2-P(C_6F_5)C_6H_4SMe-2\}RhCl]BF_4$, **2**, [1] the methyl substituent of the sulphur atom is *syn* to the chlorine atom, presumably for steric reasons. (The Cl—M—S—C(Me) torsion angle is $-34.7(2)^\circ$ for **1** *cf* $3.1(2)^\circ$ for **2**.) The same conformation is adopted in solution [3].

The Cp*—Ir, Ir—P and Ir—Cl distances of 1.847(5), 2.2791(14) and 2.3840(12) Å respectively lie within the ranges of those reported for complexes of formulation $[(\eta^5-C_5Me_5)IrCl(PS)]^{0/1+}$ [10–13]. The Ir—S distance is shorter, being closest to those of the neutral complexes $[(\eta^5-C_5Me_5)IrCl(\kappa_2S, P-L)]$ L = 1-PPh₂-2-S-1,2-dicarba-*closo*-carborane (2.3529(12) Å) [12] and L = 3-PPri₂-2-S-indene (2.3566(9) Å) [13]. The angles at iridium are within the ranges of those reported for $[(\eta^5-C_5Me_5)IrCl(PS)]^{0/1+}$, except for Cp*—Ir—P ($136.7(2)^\circ$), which is slightly larger.

There is a significant distortion of the pentamethylcyclopentadienyl ring from C₅ symmetry about the Ir—C₅(centroid) axis. The data suggest slight ring slippage from cyclopentadienyl to 'η³, η²-enylene' coordination [14, 15] with C(2) the centre of the allyl functionality. The ene functionality is approximately *trans* to the phosphorus atom (the P—Ir—Cp*—ene(centre) torsion angle is $177.8(2)^\circ$), which exerts a greater *trans* influence than chloride or thiolate. The ene Ir—C(4) and Ir—C(5) distances of 2.240(5) and 2.246(5) Å respectively are longer than the three enyl Ir—C distances, which lie in the range 2.199(5) to 2.227(5) Å. Consistent with this the C(4)—C(5) distance of 1.418(7) is significantly shorter than the other C—C bond distances, which lie in the range 1.434(7) to 1.472(8) Å. However, the internal ring C—C—C angles are virtually identical, lying in the range $107.4(5)$ to $108.6(5)^\circ$.

The structural parameters of the (C₆F₅)₂PC₆H₄SMe-2 ligand of complex **1** are similar to the relevant parameters of complex **2** [1]. In particular the respective P—C, S—C, C—F and the C—C distances are identical within experimental error with the exception of the PC—CCH₂ distance of **2**, 1.424(7) Å, which is longer than the PC—C(ArF) distances of **1** and **2** (1.383(5) to 1.396(7) Å). A similar lengthening of the PC—C bond is observed on going from $[(\eta^5-C_5Me_5)RhCl\{\kappa P, \kappa P-(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2\}]^+$ to $[\{\eta^5, \kappa P, \kappa P-C_5Me_4CH_2C_6F_4-2-P(C_6F_5)C_2H_4P(C_6F_5)_2\}RhCl]^+$ [1]. The angles at phosphorus are similar for the two complexes, but the M—S—C angles are slightly larger for **2**. The P—C—C, S—C—C, C—S—C and C—C—C angles of the C₆H₄ moiety of **1** are identical to those of **2**. The C—C—C angles of the C₆F₅ rings of **1** are similar to those of **2**. For both complexes the C—C(P)—C angles are *ca.* 115° and the C(P)—C—C angles greater than 120° . For the C₆F₄ moiety of **2** the C—C(P)—C angle is similarly small ($117.0(4)^\circ$) and the C(P)—C(F)—C angle large ($123.2(4)^\circ$), but the C(P)—C(C)—C angle is $118.2(4)^\circ$. There is one larger and one smaller P—C—C angle for each C₆F₅ ring of **1** and **2** ($124.4(3)$ and $120.3(3)^\circ$), and likewise for the C₆F₄ moiety of **2** ($122.8(3)$ and $120.2(3)^\circ$), but the difference in **2** is less pronounced than in **1**, indicative of less steric crowding.

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