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Iridium–fluorobenzenethiolato complexes: crystal structures of $[Ir(SC_6F_5)(CO)(PPh_3)_2]$, $[Ir_3(\mu-SC_6F_5)_3(\mu-CO)(CO)_4(PPh_3)_2]$ and $[Ir(SC_6F_5)(\eta-O_2)(CO)(PPh_3)_2]$

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Abstract

Iridium-fluorobenzenetiolate complexes of general formula $[Ir(SR_F)(CO)(PPh_3)_2]$, $(R_F=C_6F_5$ **1a**, C_6HF_4 -4 **1b**, C_6H_4F -4 **1c**, and $C_6H_4CH_3$ -2 **1d**), were prepared by methatetical reactions with $Tl(SR_F)$ or HSR_F . The unexpected trimetallic compound $[Ir3(\mu-SC_6F_5)_3(\mu-CO)(CO)_4(PPh_3)_2]$ **2** was also isolated when $R_F=C_6F_5$. Oxidative addition of fluorothiols to the corresponding Ir(I) precursors, afforded the compounds $[Ir(H)(Cl)(SR_F)(CO)(PPh_3)_2]$ $(R_F=C_6F_5$ **3a**, C_6HF_4 -4 **3b** and C_6H_4F -4 **3c**) and $[Ir(H)(SR_F)_2(CO)(PPh_3)_2]$ $(R_F=C_6F_5$ **4a**, C_6HF_4 -4 **4b** and C_6H_4F -4 **4c**). Irreversible oxygen uptake by compounds **1** gives rise to the oxo-derivatives $[Ir(SR_F)(O_2)(CO)(PPh_3)_2]$ **1a**, $[Ir_3(\mu-SC_6F_5)_3(\mu-CO)(CO)_4(PPh_3)_2]$ **2** and $[Ir(SC_6F_5)(\pi^2-O_2)(CO)(PPh_3)_2]$ **3a** were determined by X-ray diffraction crystallography. Compound **2** contains an asymmetrical Ir_3S_3 ring with one iridium-iridium bond (2.665(1)Å) doubly bridged by CO and $(C_6F_5S)^-$. (© 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorothiolato; Iridium; Dioxygen; X-ray

A great amount of attention has been paid to the synthesis, characterisation and study of thiolate-containing bi or polynuclear complexes of the platinum group metals. Such complexes have rendered interesting, sometimes unique, examples of mixed oxidation states [1], unusual geometries [2-8], agostic bonds [9,10], neutral-ionic equibrium [11], etc. This class of compounds are also relevant models to study co-operative effects between metals in processes like conventional [12] or stereo-selective catalysis [13,14]. On the other hand, interest on monometallic thiolate derivatives has grown steadily over recent years due to the role that they probably play in processes such as the activation of small molecules [15,16], metal-catalysed carbon-sulfur bond cleavage and formation [17-27], desulfurization of thio-compounds [28-37], etc. Following our interest in fluorinated thiolate derivatives of transition metals [38-40], we have studied a series of iridium compounds, including mono- and

1. Experimental

All reactions were routinely performed under dry, oxygen-free dinitrogen atmospheres, using standard Schlenk-tube techniques. Solvents were dried and degassed using published techniques [41], stored over molecular sieves and distilled under nitrogen prior to use. Thin layer chromatography (TLC) (Merck, 5X7.5cm² Kieselgel 60

bimetallic complexes, bearing R_FS^- ligands with $R_F=$ C₆F₅, C₆HF₄-4 and C₆H₄F-4. In this paper results regarding the compounds $[Ir(SR_F)(CO)(PPh_3)],$ $[Ir(H)(Cl)(SR_{\rm F})(CO)(PPh_3)],$ $[Ir(H)(SR_F)_2(CO)(PPh_3)]$ and $[Ir(SR_F)(O_2)(CO)(PPh_3)]$ are discussed as well as crystal and molecular structures the X-ray of $[Ir(SC_6F_5)(CO)(PPh_3)_2], [Ir_3(\mu-SC_6F_5)_3(\mu-CO)(CO)_4 (PPh_3)_2$ and $[Ir(SC_6F_5)(\eta^2-O_2)(CO)(PPh_3)]$. A part of this work has been the subject of a preliminary communication [1].

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 F_{254}) was used when possible to monitor the progress of the reaction under study.

Literature methods were used for the synthesis of $[(Ir(\mu-SC_6F_5)(CO)_2)_2]$ [1], Pb(SC₆F₅)₂ [42], and TlSC₆F₅ [42]. All other chemicals were commercial products used as received without further purification.

All metal complexes were collected on sintered-glass frits and washed with the appropriate solvents before being dried in a stream of nitrogen.

Complexes were characterised by infrared spectra recorded over the 4000–200 cm⁻¹ range on a Perkin–Elmer 1330 with a Data Station 1300 using samples mulled in Nujol between KBr plates or as CsI pellets. Data are expressed in wavenumbers (cm⁻¹) with relative intensities (s=strong, m=medium, w=weak)

¹H, spectra were obtained on a Bruker ACP 200 (200.13 MHz) spectrometer in the deuterated solvent. ¹⁹F, spectra were measured with a SDS-360 MHz operating at 282.23 MHz, by Spectral Data Services Inc. (Illinois USA). ³¹P-{¹H}, spectra were obtained on a Bruker ACP 200 spectrometer operating at 81.01 MHz. Chemical shifts are relative to internal TMS δ =0 (¹H), external CFCl₃ δ =0 (¹⁹F) and external 85% H₂PO₄ δ =0 (³¹P) with downfield values reported positive. A standard variable-temperature unit was used to control the probe and it was checked periodically by thermocouple to ensure temperature readings were within ±1°C.

Elemental analyses were determined by Galbraith Labs. Inc., USA.

FAB spectra were obtained on a JEOL SX102 mass spectrometer operated at an accelerating voltage of 10 KV. Samples were desorbed from nitrobenzyl alcohol matrix using 3KeV xenon atoms. Mass measurements in FAB are performed at 3000 resolution using magnetic field scans and the matrix ions as the reference material, or electric field scans with the sample peak bracketed by two (polyethylene glycol or cesium iodide) reference ions.

Preparation of complexes **1** *to* **5**. Since synthetic experimental set-up were relatively similar for each class of compounds, only a representative example of each type is described as follows.

 $[Ir(SC_6HF_4-4)(CO)(PPh_3)_2]$ Α solution 1b. of $Tl(SC_6HF_4-4)$, (0.195g, 0.505 mmol) in acetone (15 ml) was added dropwise to $(IrCl(CO)(PPh_3)_2)$ (0.39g, 0.5 mmol) dissolved in 20 ml of acetone. The mixture rapidly turns yellow while a white solid precipitates off. The yellow solution was stirred for 1 h. TlCl was filtered off and the solution concentrated to ca. 5 ml under vacuum. Slow evaporation of the solvent renders yellow crystals of $[Ir(SC_6HF_4-4)(CO)(PPh_3)_2]$ **1b**. Anal. Found: C, 55.5; H, 3.4. C₄₃H₃₁F₄IrOP₂S. Calc.: C, 55.7; H, 3.4. Yield 91%. IR ν (CO) 1965.4 cm⁻¹. ¹H NMR: 6.49, SC₆HF₄; ¹⁹F NMR: -128.5 F_{o} , -139.4 F_{m} ; ³¹P NMR: 24.98. MS (m/e) Found: 925, Calc: 925.

 $[Ir(SC_6H_4F-4)(CO)(PPh_3)_2]$ **1c**. Yellow. Anal. Found: C, 59.9; H, 4.3. C₄₃H₃₄FIrOP₂S. Calc: C, 59.2; H, 3.9. Yield 89%. IR ν (CO) 1992.1 cm⁻¹. ¹H NMR: 6.73, SC₆H₄F-4; ¹⁹F NMR: -117.3 Fp; ³¹P NMR: 27.36. MS (*m/e*) Found: 871, Calc: 871.

[$Ir(SC_6H_4Me-2)(CO)(PPh_3)_2$] **1d**. Yellow. Anal. Found: C, 60.8; H, 3.7. C₄₄H₃₇IrOP₂S. Calc.: C, 60.9; H, 4.3. Yield 90%. IR ν (CO) 1948.0 cm⁻¹. ¹H NMR: 6.43, 2.82 SC₆H₄Me-2; ³¹P NMR: 26.22. MS (*m*/*e*) Found: 868, Calc.: 868.

 $[Ir_3(SC_6F_5)3(CO)5(PPh_3)_2]$ **2**. A solution of P(C₆H₅)₃, (0.2g, 1.0 mmol) in acetone (15 ml) was added dropwise to [{Ir(SC₆F₅)(CO)₂}2] (0.44g, 0.5 mmol) dissolved in 20 ml of acetone. The solution rapidly turned yellow and it was stirred for 1 h. The solution was concentrated to *ca*. 5 mL under vacuum. Toluene (5mL) was added and the solution keep at *ca*. 0°C for 24 h. Two distinct crystalline products separated, yellow crystals corresponding to compound (Ir(SC₆F₅)(CO)(PPh₃)₂] **1a** and reddish crystals of (Ir₃(SC₆F₅)₃(CO)5(PPh₃)₂] **2**.

[*IrH*(*Cl*)(*SC*₆*HF*₄-4)(*CO*)(*PPh*₃)₂] **3b**. A solution of HSC_6HF_4 -4, (0.095g, 0.5 mmol) in acetone (15 mL) was added dropwise to a suspension of (*IrCl*(*CO*)(*PPh*₃)₂] (0.40g, 0.5 mmol) in 20 mL of acetone. The suspension mixture rapidly turns white and it was magnetically stirred for 1 hour. After concentrating to *ca*. 5 mL under vacuum it was filtered off to separate [*IrH*(*Cl*)(*SC*₆*HF*₄-4)(*CO*)(*PPh*₃)₂] **3b**. Anal. Found: C, 53.4; H, 3.2. $C_{43}H_{32}CIF_4IrOP_2S$. Calc.: C, 53.7; H, 3.4. Yield 78%. IR ((CO) 2024.0; ν (MH) 2218.0 cm⁻¹. ¹H NMR: -14.7 M-H, J(H-P)=11.3; 6.7, SC₆HF₄-4; ¹⁹F NMR: -127.8 F_o, -138.6 F_m; ³¹P NMR: -7.7. MS (*m*/*e*) Found: 962, Calc.: 962.

[*IrH*(*Cl*)(*SC*₆*H*₄*F*-4)(*CO*)(*PPh*₃)₂] **3c**. White. Anal. Found: C, 57.0; H, 3.9. $C_{43}H_{35}ClFIrOP_2S$. Calc.: C, 56.9; H, 3.9. Yield 84%. IR ν (CO) 2025.6; ν (MH) 2218.7 cm⁻¹. ¹H NMR: -16.15, MH, J(H-P)=12; 6.10, SC₆H₄F-4; ¹⁹F NMR: -119.0, F_p; ³¹P NMR: -13.99. MS (m/e) Found: 908, Calc.: 908.

[*IrH*(*SC*₆*HF*₄-*4*)₂(*CO*)(*PPh*₃)₂] **4b**. A solution of HSC_6HF_4 -4, (0.097g, 0.5 mmol) in acetone (15 mL) was added dropwise to a suspension of (*Ir*(*SC*₆*HF*₄-4)(*CO*)(*PPh*₃)₂] (0.47g, 0.5 mmol) in 20 mL of acetone. The suspension mixture rapidly turns white and it was magnetically stirred for 1 h. After concentrating to ca. 5 mL under vacuum it was filtered off to separate (*IrH*(*SC*₆*HF*₄-4)₂(*CO*)(*PPh*₃)₂] **4b**. White. Anal. Found: C, 52.8; H, 2.8. C₄₉H₃₃F₈*IrOP*₂S₂. Calc.: C, 53.1; H, 3.0. Yield 82%. IR ν (CO) 2059.0; ν (MH) 2225.0 cm⁻¹. ¹H NMR: -14.9 M-H, J(H-P)=9.1; 6.65, SC₆*HF*₄-4; ¹⁹F NMR: -128.5 F_o, -139.6 F_m; ³¹P NMR: -6.9. MS (*m/e*) Found: 1108, Calc.: 1108.

[*IrH*(SC_6H_4F -4)₂(*CO*)(*PPh*₃)₂] **4c**. White. Anal. Found: C, 58.7; H, 3.5. $C_{49}H_{39}F_2IrOP_2S_2$. Calc.: C, 58.9; H, 3.9. Yield 87%. IR ν (CO) 2220.0; ν (MH) 2045.0 cm⁻¹. ¹H NMR: -15.7, MH, J(H-P)=10.9; 6.12, SC₆H₄F-4; ¹⁹F NMR: -122.3, F_p ; ³¹P NMR: -8.45. MS (m/e) Found: 1000, Calc.: 1000. [$Ir(SC_6HF_4-4)(O_2)(CO)(PPh_3)_2$] **5b**. Dry oxygen was bubbled through a solution of [$Ir(SC_6HF_4-4)(CO)(PPh_3)_2$] (0.46g, 0.5 mmol) in 20 mL of acetone. The solution turns yellow and after ca. 1 hour it concentrated to ca. 5 mL under vacuum. Slow evaporation of this solution renders ($Ir(SC_6HF_4-4)(O_2)(CO)(PPh_3)_2$] **5b**. Yellow. Anal. Found: C, 54.6; H, 3.5. $C_{43}H_{31}F_4IrO_3P_2S$. Calc.: C, 53.9; H, 3.3. Yield 76%. IR ((CO) 1988.9; $\nu(O_2)$ 848.5 cm⁻¹. ¹H NMR: 6.72, SC_6HF_4 -4; ¹⁹F NMR: -126.6 F_o , -137.7 F_m ; ³¹P NMR: 6.71. MS (m/e) Found: 957, Calc.: 957.

 $[Ir(SC_{6}H_{4}F-4)(O_{2})(CO)(PPh_{3})_{2}]$ **5**c. Yellow. Anal. Found: C, 57.1; H, 3.8. $C_{43}H_{34}FIrO_{3}P_{2}S$. Calc.: C, 57.1; H, 3.8. Yield 87%. IR ((CO) 1988.0; ((O_{2}) 850.0 cm⁻¹.¹H

Table 1

Crystallographic data, data collection and structure refinement

NMR: 6.10, SC₆H₄F-4; ¹⁹F NMR: -118.4, Fp; ³¹P NMR: 2.93. MS (m/e) Found: 903, Calc.: 903.

[$Ir(SC_6H_4Me-2)(O_2)(CO)(PPh_3)_2$] **1d**. Yellow. Anal. Found: C, 59.9; H, 4.4. $C_{44}H_{37}IrO_3P_2S$. Calc.: C, 58.7; H, 4.1. Yield 85%. IR ν (CO) 1994.0, ν (O₂) 848.0 cm⁻¹. ¹H NMR: 6.42, 2.31, SC₆H₄Me-2; ³¹P NMR: 1.01. MS (m/e) Found: 900, Calc.: 900.

Single-Crystal X-Ray Structure Analysis. Details on crystallographic data, data collection and structure refinement for compounds **1a**, **2** and **5a** are listed in Table 1. Due to the low quality of crystals the Ψ -scan technique gave no clear corrections and DIFABS was used as an alternative.

Compound	1a	2	5a	
Crystal data				
Empirical formula	$C_{43}H_{30}OSF_5P_2Ir$	$C_{59}H_{30}O_5S_3F_{15}P_2Ir_3$	$C_{43}H_{30}O_{3}SF_{5}P_{2}Ir$	
Molecular weight	943.43	1838.65	975.93	
Space group	Monoclinic, $P_2 1/n$	Monoclinic, $P_2 1/a$	Triclinic, P1	
Unit cell	Least-squares	Lease-squares	Least-squares	
determination	fit from 25	fit from 100	fit from 100	
	reflexions	reflexions	reflexions	
	$(4 < 2\theta < 45^{\circ})$	$(4 < 2\theta < 46^{\circ})$	$(4 < 2\theta < 43^{\circ})$	
Crystal size mm	$0.4 \times 0.4 \times 0.3$	$0.38 \times 0.24 \times 0.21$	$0.28 \times 0.21 \times 0.20$	
a. Å	12.082(3)	16.229(1)	19.141(5)	
b. Å	15.473(3)	30.817(4)	11.817(2)	
c. Å	20.048(7)	12.758(1)	9.885(1)	
α deg	90.0	90.0	68.57(1)	
B deg	92,97(2)	112,18(1)	108.99(1)	
γ deg	90.0	90.0	110.54(2)	
$V Å^3$	3743(2)	5908(1)	1898 5(7)	
Z	4	4	2	
$a \text{ gcm}^{-3}$	1.67	2.0669	1.7072	
F(000)	1856	2720	960	
μ , cm ⁻¹	37.48	69.64	37.01	
Experimental data				
Four circle	CAD4-Enraf-Nonius	Philips PW 1100	Philips PW 1100	
Diffractometer		Bisecting geometry	Bisecting geometry	
Radiation	ΜοΚα	ΜοΚα	ΜοΚα	
	$(\lambda = 0.71069 \text{\AA})$	$(\lambda = 0.71069 \text{\AA})$	$(\lambda = 0.71069 \text{\AA})$	
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	
θ limits, deg	1-25	2-22	2-25	
Data collected	7040	7290	6746	
Unique data used	4143	5806	5340	
1	$(Fo)^2 > 3\sigma(Fo)^2$	$(I \ge 2\sigma(I))$	$(I > 3\sigma(I))$	
Range of hkl	-14/14; 0/18; 0/23	-19/19, 0/37, 0/15	-22/22, -14/14, 0/12	
Solution and refinement				
Solution	Direct methods	Direct methods	Direct methods	
Refinement	L.s. on Fobs	L.s. on Fobs	L.s. on Fobs	
H atoms	Calculated	Calculated	Calculated	
Absorption correction	DIFABS [43]	DIFABS [43]	DIFABS [43]	
	1.19-0.88	1.39-0.75	2.004-0.656	
R^{a}	0.032	0.058	0.106	
R_{w}^{b}	0.035	0.084	0.131	
Goodness of fit, s	1.57	0.364	0.653	
No. of variables	571	775	871	
$\Delta \rho \max (e/Å^3)$	0.74	1.60	5.84	

 ${}^{a}R = \Sigma ||F_{o}| - |Fc|| / \Sigma |F_{o}|. {}^{b}R_{w} = [\Sigma w (|F_{o}| - |Fc|)^{2} / \Sigma w |F_{o}|^{2}]^{1/2}.$

[Ir(SC₆F₅)(CO)(PPh₃)₂] **1a**. An absorption correction following the DIFABS procedure [43] was applied to isotropically refined data. Maximum and minimum absorption factors 1.19 and 0.88 respectively. The positions of the hydrogen atoms were calculated geometrically and introduced in the refinement with all parameters fixed. A Chebychev Polynomial weighting scheme (w= (weight)*(1-($\Delta F/6/*(F)$)**2)**2) was used. Final R and Rw values 0.032 and 0.035. All calculations were carried out using CRYSTALS [50,52].

[Ir₃(SC₆F₅)₃(CO)5(PPh₃)₂] **2**. An absorption correction following the DIFABS procedure [43] was applied to isotropically refined data. Maximum and minimum absorption factors 1.39 and 0.75 respectively. The positions of the hydrogen atoms were calculated geometrically and introduced in the refinement with all parameters fixed. An empirical weighting scheme of type $w=w_1 \cdot w_2$, $w_1=1/\sigma_1^2$; $w_2=1/\sigma_2^2$; $\sigma_1=a+b|F_o|$, $\sigma_2^2=c+d\sin\theta/\lambda$ was applied, the *a*, *b*, *c* and *d* coefficients being those to eliminate trends in $<\Delta^2 F>$ vs. $<\Delta|F_o|>$ and $<\sin\theta/\lambda>$. Final R value 0.058. Computer and programs: VAX 11/750, DIRDIF [44], XRAY80 [45], DIFABS [43], PARST [46]. Anomalous dispersion and scattering factors International Tables for X-ray Crystallography [47].

 $[Ir(SC_6H_5)(O_2)(CO)(PPh_3)_2]$ **5a**. An absorption correction following the DIFABS procedure [43] was applied to isotropically refined data; maximum and minimum absorption factors 2.004 and 0.656 respectively. The temperature factor of the C atom of the carbonyl group was fixed all along the refinement process as it became negative. The Ir-C1 coordinates were fixed along with its thermal parameter. The positions of the hydrogen atoms were calculated geometrically and introduced in the refinement with all parameters fixed. An empirical weighting scheme, as

described for compound **2**, was applied in order to give no trends in $<\Delta^2 F >$ vs. $<|F_o|>$ and $<\sin\theta/\lambda>$.The final difference map showed two large peaks (5.84 and 5.43 e Å⁻³) in the neighbourhood of the Ir atom. Final R and Rw values 0.106 and 0.131. Computer and programs: VAX 11/750, SIR92 [48], XRAY80, DIFABS, PESOS [49], PARST and CRYSTALS [50]. Anomalous dispersion and scattering factors: International Tables for X-ray Crystallography [47].

2. Results and discussion

Analytical and other physical properties of the compounds prepared, NMR parameters as well as $\nu(C\equiv O)$, $\nu(O=O)$ and $\nu(M-H)$ frequencies are given in the experimental section. In general, other infrared frequencies are consistent with the given formula but have been omitted since they are of limited value to the following discussion.

Reaction of $[{\rm Ir}(\mu-{\rm SC}_6{\rm F}_5)({\rm CO})_2]^2]$ with triphenylphosphine. Addition of triphenylphosphine to a solution of the sulfur-bridged dinuclear d⁸ metal complex $[{\rm Ir}(\mu-{\rm SC}_6{\rm F}_5)({\rm CO})_2]^2]$ in acetone at room temperature, rapidly yields a clear pale-yellow solution, from which a mixture of two kinds of crystals was obtained. Owing to their lability in solution, spectroscopic studies of this mixture gave rise to conflicting results and therefore, the crystals were analysed by X-ray diffraction techniques. The resulting complexes from this reaction are *trans*- $[{\rm Ir}({\rm SC}_6{\rm F}_5)({\rm CO})({\rm PPh}_3)_2]$ **1a** and $[{\rm Ir}_3({\rm SC}_6{\rm F}_5)_3({\rm CO})_5-({\rm PPh}_3)_2]$ (Scheme 1).

Trans-[Ir(SC₆F₅)(CO)(PPh₃)₂] **1a** has been obtained previously from the metathetical reaction of *trans*-



Scheme 1.

 $[Ir(Cl)(CO)(PPh_3)_2]$ with $Tl(SC_6F_5)$ [51] which is a general method to prepare Vaska's type complexes [16]. From this reaction we found no traces of the trinuclear compound **2**.

Figs. 1 and 2 show perspective views of the molecular structures of complexes **1a** and **2**, respectively, indicating the atom numbering scheme.

Selected bond distances and angles for complexes **1a** and **2** are listed in Tables 2 and 3, Torsion angles involving the central ring of $[Ir_3(\mu-SC_6F_5)_3(\mu-CO)(CO)_4(PPh_3)_2]$ **2** are collected in Table 4.

The molecule of *trans*-[Ir(SC₆F₅)(CO)(PPh₃)₂] **1a** shows, as expected, a substantially planar arrangement around the metallic centre. Both iridium–phosphorus distances are practically equal (2.305(2) and 2.315(2)Å). The C₆F₅ ring aligns itself parallel to a C₆H₅ ring from a neighbouring intramolecular triphenylphosphine. This is a fact that is often encountered in SC₆F₅ bearing compounds and it probably results from packing effects. In solution, NMR data are consistent with rapid rotation of the pentafluorophenyl ring.

The structure of the complex $[Ir_3(\mu-SC_6F_5)_3(\mu-CO)(CO)4(PPh_3)_2]$ **2** has a basic skeleton formed by three iridium atoms bridged by three SC₆F₅ groups. Atoms Ir1,

Ir2, S2, Ir3 and S3 are roughly coplanar; S1 and C19 (bridging CO) that form the flaps of the envelope, are respectively below (-1.916\AA) and above (0.358\AA) this plane. Two iridium atoms (Ir1 and Ir2) are formally pentacoordinated, sharing a bridging carbonyl ligand. Each of these iridium atoms are bonded to a terminal carbonyl ligand and to a triphenylphosphine ligand. Iridium1iridium2 is the shortest intermetallic distance $(2.665(4)\text{\AA})$ and it suggests a metal-metal bond; which is in agreement with the electron counting. This distance is slightly shorter than those found in previously reported trinuclear complexes [2-8]. It also shows significant differences when compared with the other two iridium-iridium distances, both larger than 3.5Å. Iridium-sulphur distances on this fragment are also significantly different (Ir1-S1 2.37(1), Ir1-S3 2.54(1) and Ir2-S1 2.39(1), Ir2-S2 2.58(1)Å). The third iridium atom has a square planar arrangement with cis carbonyls (1.77(3) and 1.85(4)Å) and two essentially equal iridium-sulphur distances (Ir3-S2 2.36(1) and Ir3-S3 2.37(1)Å). Both angles around sulfur atoms are quite different, Ir1-S1-Ir2 angle is 68.10 consistent with the shorter distance, and the related Ir2-S1 and Ir1-S1 distances are 2.39(1) and 2.37(1)Å respectively, but the Ir1-S3-Ir3 angle is 123.5°, and Ir1-S3 is 2.54(1)Å. While



Fig. 1. ORTEP [27] view of the molecular structure of trans- $[Ir(SC_6F_5)(CO)(PPh_3)_2]$ 1a showing the atomic numbering.



Fig. 2. ORTEP [27] view of the molecular structure of $[Ir_3((-SC_6F_5)_3(\mu-CO)(CO)4(PPh_3)_2]$ 2 showing the atomic numbering.

the Ir2–S2–Ir3 angle is 126.2° and the Ir2–S2 distance is 2.58(1)Å. Clearly, angles around S1 indicate a tetrahedral environment, as is usually observed in thiolate derivatives [2–8]. However, those around S2 and S3 indicate an unusual planar structure. These data are in agreement with previous results found for the crown-like complex [Ir₃(μ -S-*t*-Bu)₃(μ -CO)(CO)4(PMe₃)₂] reported previously [2–8].

Rearrangement of metal complexes to derivatives of

1 4010 2								
Selected	bond	distances	(Å) and	angles (°)	with	standard	deviations	for
complex	trans	Ir(SC ₆ F ₅)(CO)(P	$[Ph_{3})_{2}]$				

Ir1-S1	2.382(2)	S1-Ir1-P1	83.44(7)
Ir1-P1	2.315(2)	S1-Ir1-P2	96.89(7)
Ir1-P2	2.305(2)	P1-Ir1-P2	176.87(7)
Ir1-C1	1.799(8)	S1-Ir1-C1	173.0(3)
S1-C1	1.761(8)	P1-Ir1-C1	89.5(3)
C1-O1	1.157(9)	P2-Ir1-C1	90.2(3)
P1-C*	1.826	S1-C1-C2	122.3(7)
P2-C*	1.823	Ir1-C1-O1	178.0(8)

*Average length.

Table 2

higher nuclearity promoted by PPh_3 has been previously observed for several systems [53]. Unfortunately no evidence regarding the mechanism leading to **2** could be gained from the experimental outcome of this reaction

Table 3

Selected bond distances (Å) and angles (°) with standard deviations for complex $[Ir_3(\mu-SC_6F_5)_3(\mu-CO)(CO)_4(PPh_3)_2]$

1 . 3.	0 3/3 (1) /	/4 3/24	
Ir1-Ir2	2.665(1)	\$1-Ir1-\$3	81.2(2)
Ir1-Ir3	4.323(2)	S1-Ir2-S2	86.4(2)
Ir2-Ir3	4.406(1)	S2-Ir3-S3	92.5(2)
Ir1-S1	2.37(1)	S3-Ir3-C22	89(1)
Ir1-S3	2.54(1)	S3-Ir3-C23	175(1)
Ir2-S1	2.39(1)	S2-Ir3-C23	92(1)
Ir2-S2	2.58(1)	S2-Ir3-C22	178(1)
Ir3-S2	2.36(1)	S1-Ir2-C21	161(1)
Ir3-S3	2.37(1)	S1-Ir2-C19	86(1)
Ir1-C19	2.07(3)	Ir1-S1-Ir2	68.1(2)
Ir1-P1	2.36(1)	Ir2-S2-Ir3	126.2(3)
Ir2-P2	2.34(1)	Ir1-S3-Ir3	123.5(3)
Ir3-C22	1.77(3)	Ir1-C19-Ir2	80(1)
Ir3-C23	1.85(4)	Ir2-C19-O19	139(2)

Table 4 Torsion angles (°) involving the central ring of $[Ir_3(\mu-SC_6F_5)_3(\mu-CO)(CO)_4(PPh_2)_2]$

-115(1)
149.4(4)
-18(2)
47(1)
-62.7(3)
-43(1)
109.3(2)
32(2)
-47(1)
-99.2(2)
43(1)
-36(1)
43.0(3)
2.9(3)
6.6(4)

although the formation of this trinuclear complex may be rationalised following the pathway suggested by Poilblanc et al. [2-8] involving five co-ordinated species or through tetra-co-ordinated complexes as shown on the following diagram.



Reactions of trans-[Ir(Cl)(CO)(PPh₃)₂] with Tl(SR_F). Reactions of trans-[Ir(Cl)(CO)(PPh₃)₂] with Tl(SR_F) (R_F=C₆F₅, C₆HF₄-4, C₆H₄F-4 or C₆H₄Me-2) in acetone at room temperature yield yellow solutions, together with white precipitate of thallium chloride. From these solutions, the complexes trans-[Ir(SC₆F₅)(CO)(PPh₃)₂] **1a**, trans-[Ir(SC₆HF₄-4)(CO)(PPh₃)₂] **1b**, trans-[Ir(SC₆H₄F-4)(CO)(PPh₃)₂] **1c** or trans-[Ir(SC₆H₄Me-2)(CO)(PPh₃)₂] 1d were isolated under dry, oxygen-free-nitrogen as yellow crystalline solids.

The ³¹P NMR spectra of compounds **1a–d** show single resonances (δ =25.19, 24.98, 27.36 and 26.22 ppm respectively) arising from magnetically equivalent phosphine ligands in a *trans* arrangement.

FAB mass spectrometry of compounds 1a-d show the expected molecular ions-listed on Table 1-with a decomposition patterns suggesting the consecutive loss of CO, PPh₃ and the fluorinated thiolate substituents.

Reactions of trans- $[Ir(Cl)(CO)(PPh_3)_2]$ with HSR_F .

Addition of the thiols HSR_{F} ($\text{R}_{\text{F}}=\text{C}_{6}\text{F}_{5}$, $\text{C}_{6}\text{HF}_{4}\text{-4}$ or $\text{C}_{6}\text{H}_{4}\text{F}\text{-4}$) to a suspension of trans-[Ir(Cl)(CO)(PPh_{3})_{2}] in toluene at room temperature yields an off-white precipitate of the complexes [IrH(Cl)(SC_{6}\text{F}_{5})(CO)(PPh_{3})_{2}] **3a**, [IrH(Cl)(SC_{6}\text{HF}_{4}\text{-4})(CO)(PPh_{3})_{2}] **3b** or [IrH(Cl)-(SC_{6}\text{H}_{4}\text{F}\text{-4})(CO)(PPh_{3})_{2}] **3c**.

The ¹⁹F{-¹H} NMR spectra of $[Ir(H)(Cl)(SC_6F_5)-(CO)(PPh_3)_2]$ **3a** show three complex absorptions corresponding to *ortho*-($\delta = -127.75$ ppm), *metha*-($\delta = -162.75$ ppm) and *para*-($\delta = -160.65$ ppm) fluorine atoms (A₂B₂C magnetic system) with the expected 2:2:1 relative ratio.

The ³¹P NMR spectra show a broad signal centred at $\delta = -7.2$ ppm, whereas ¹H NMR spectra show the expected multiplet on the phenyl region (PPh₃) and two triplets arising from hydride-phosphorus coupling on two different isomers. The relative populations of these isomers depends on reaction conditions. Obtained as described here, their relative ratio is *ca.* 1:9, with $\delta = -14.99$ ppm, ²J_{H-P}=8.19 Hz and $\delta = -15.51$ ppm, ²J_{H-P}=7.46 Hz respectively.

NMR magnetic couplings suggest that both observed isomers bear equivalent phosphine ligands. There are three possible isomers on which such an equivalence is found: trans-H-Ir-SR_F, trans-H-Ir-Cl and trans-H-Ir-CO.

Considering the relative similarities of ¹H NMR parameters ($\Delta \delta = 0.6$ ppm and $\Delta^2 J_{H-P} = 0.3$ Hz) it seems likely that those isomers with chloride ions or the pseudohalogen (SC₆F₅)⁻ both on the same relative position *trans* to the H⁻ ligand, are the more reasonable structures to rationalise the experimental observations. On the other hand, a δ value around -15 ppm in the ¹H spectra of these complexes is consistent with the hydrido ligand being *trans* to a ligand of low *trans*-influence such as Cl⁻ or SR⁻ [54–56].

It has been suggested [51] that compounds **1a** and **3a** establish the equilibrium shown in reaction 1.

$[IrH(Cl)(SC_6F_5)(CO)(PPh_3)_2] \biguplus [Ir(SC_6F_5)(CO)(PPh_3)_2] + HCl$

However, attempts to reductively eliminate HCl from 1a-by treatment with KOH, NEt₃ etcetera-have all been unsuccessful. The reductive elimination of HCl from chloro hydrido transition metal complexes has been recently reviewed [57]. It is now well established that reductive elimination under biphasic or phase transfer catalysis conditions is a more suitable and accurate experimental method. Indeed, HCl elimination is cleanly accomplished by treating $[IrH(Cl)(SC_6F_5)(CO)(PPh_3)_2]$ **3a** under phase transfer conditions (toluene, 60% KOH-18-crown-6), yielding trans- $[Ir(SC_6F_5)(CO)(PPh_3)_2]$ 1a. On the other dechlorinate hand, attempts to $[IrH(Cl)(SC_6F_5) (CO)(PPh_3)_2$ 3a in order to yield cationic complexes, as shown in reaction 2, have also failed to yield the desired products.

 $[IrH(Cl)(SC_6F_5)(CO)(PPh_3)_2] + MX \longrightarrow [IrH(SC_6F_5)(CO)(PPh_3)_2]^{+}X^{+} MCl$

 $MX = NaBPh_4$, $AgNO_3$, etc.

Reactions of **3a** with chloro abstracting reagents *i.e.* $NaBPh_4$ or $AgNO_3$ result in mixtures of ill-defined products with loss of carbon monoxide or thiolate ion.

FAB mass spectrometry of compounds 3a-c show the expected molecular ions and a decomposition pattern with consecutive loss of CO, PPh₃ and SR_F.

Reactions of trans-[Ir(SR_F)(CO)(PPh₃)₂] with HSR_F. Reactions of trans-[Ir(SR_F)(CO)(PPh₃)₂] **1a**-**c** with their corresponding thiols, HSR_F (R_F=C₆F₅, C₆HF₄-4 or C₆H₄F-4), in toluene suspensions, at room temperature, yield the complexes [IrH(SC₆F₅)₂(CO)(PPh₃)₂] **4a**, [IrH(SC₆HF₄-4)₂(CO)(PPh₃)₂] **4b** or [IrH(SC₆H₄F-4)₂(CO)(PPh₃)₂] **4c**. Under the reaction conditions used in this work, compounds **4a**-**c**, are obtained as one of the two possible isomers bearing mutually trans triphenylphosphine ligands. Thus ³¹P NMR spectra show a single absorptions at $\delta = -6.4$ **4a**, -6.9 **4b** and -8.45 **4c** ppm.

¹⁹F{-¹H} NMR spectra of $[IrH(SC_6F_5)_2$ -The $(CO)(PPh_3)_2$ 4a show the expected pattern due to *ortho*-, metha- and para-fluorine substituents (A2B2C magnetic system) from two non-equivalent C_6F_5 rings at $\delta_0 =$ -134.2, -133.8; $\delta_{\rm m} = -167.3$, -168.1 and $\delta_{\rm p} = -161.2$ ppm. In addition to absorptions due to the phenyl rings, ¹H NMR spectra show a triplet at $\delta = -14.8$ ppm with ${}^{2}J_{P-H} =$ 9.7 Hz. Similarly, ${}^{19}F\{-{}^{1}H\}$ NMR spectra of $[IrH(SC_6HF_4-4)_2(CO)(PPh_3)_2]$ **4b** show an absorption pattern due to ortho- and metha-fluorine substituents from two non-equivalent SC₆HF₄-4 rings at $\delta = -128.5$, $\delta = -$ 128.9 and $\delta = -139.6$, $\delta = -139.7$ ppm. Besides absorptions due to the phenyl rings, ¹H NMR spectra of 4b show two triplets of triplets (AX₂Y₂ system) for the para-H at $\delta_{\rm p} = 6.45$ ppm and a triplet due to the hydride ion at $\delta = -14.9$ ppm with a H-P coupling constant. ²J_{P-H}=9.1 Hz. Finally $[IrH(SC_6H_4F-4)_2(CO)(PPh_3)_2]$ 4c shows 19 F{ $-^{1}$ H} NMR spectra consisting of two absorptions due to para-fluorine substituents from two non-equivalent



Fig. 3. ORTEP [27] view of the molecular structure of $[Ir(SC_6F_5)(O_2)(CO)(PPh_3)_2]$ 5a with thermal ellipsoids at 50% probability level. H atoms have been omitted for sake of clarity.

Table 5 Selected bond distances (Å) and angles (°) with standard deviations for complex $[Ir(SC_6F_5)(O_2)(CO)(PPh_3)_2]$

Ir1–P1	2.376(4)	O2-Ir1-O3	41.2(8)
Ir1-P2	2.382(5)	C1-Ir1-O3	158.9(5)
Ir1-S1	2.407(7)	C1-Ir1-O2	118.0(5)
Ir1-C1	1.69(0)	S1-Ir1-O3	106.4(6)
Ir1-O2	2.02(3)	S1-Ir1-O2	147.0(6)
Ir1-O3	2.02(2)	Ir1-O2-O3	69(1)
02–03	1.42(3)	Ir1-O3-O2	70(1)

 SC_6H_4F -4 rings $\delta_p = -122.3$ and -122.4 ppm. ¹H spectra of **4c** show absorptions due to the C₆H5 and SC₆H₄F-4 rings and a triplet due to the hydride ion at $\delta = -15.7$ ppm with a H-P coupling constant ²J_{P-H} = 10.9 Hz.

As with all compounds of these series, FAB mass spectrometry of compounds $4\mathbf{a}-\mathbf{c}$ show the expected molecular ions and a decomposition patterns reflecting loss of CO, PPh₃ and the thiolate ligand.

Dioxygen uptake on trans- $[Ir(SR)(CO)(PPh_3)_2]$ derivatives. Exposed to the air, solutions of trans- $[Ir-(SR_F)(CO)(PPh_3)_2]$ **1a–d** react with molecular oxygen giving rise to the $[Ir(SR_F)(O_2)(CO)(PPh_3)_2]$ (R=C₆F₅, **5a**, C₆HF₄-4 **5b**, C₆H₄F-4 **5c**, or C₆H₄Me-2 **5d**) complexes.

Raman spectra of *trans*-[Ir(SC₆F₅)(CO)(PPh₃)₂] **1a** and [Ir(SC₆F₅)(O₂)(CO)(PPh₃)₂] **5a** are identical on the region 2000–600 cm⁻¹ region. Additional, not assigned, absorptions are observed however at 552.4 cm⁻¹ for **1a** and at 526.5, 482.3, 434.9 and 327.9 cm⁻¹ for **5a**.

The crystal and molecular structure of complex 5a has been determined by X-ray diffraction methods. Fig. 3 shows a perspective view of this molecule indicating the atom numbering scheme. Table 5 collects selected bond distances and angles of complex 5a.

The phenyl rings attached to P and S atoms present a rather bad geometry as well as large standard deviations owing to the poor quality of diffraction data (as it is also reflected in the relatively high values of R factors).

The phosphine ligands are trans to each other whereas the O_2 moiety shows the symmetrical side-on arrangement expected for a peroxo compound. The co-ordination may be described as trigonal-bipyramid with the diatomic molecule π -bonded at equatorial positions. However, a distorted octahedral assignment equally tenable

Variable temperature ${}^{19}F\{-{}^{1}H\}$ NMR experiments show that uptake of molecular oxygen by $[Ir(SC_6F_5)(CO)(PPh_3)_2]$ **1a** is not a reversible process. A linear relation between ln(intensity) and the reaction time, indicates that the conversion of **1a** to **5a** by oxygen uptake is a first order reaction with an activation energy Ea= 24.54 Kcalmol⁻¹.

Supplementary Material Available

Tables of Crystal and intensity measurement data,

positional parameters of calculated hydrogen atoms, anisotropic thermal parameters, and bond distances and angles. Ordering information is given on any current masthead page.

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