Rhodium– and Iridium–Perfluorophenylthiolato Complexes: the X-Ray Structures of $[(C_5Me_5)Ir(SC_6F_4H)_2]$ and $[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3][(C_5Me_5)Rh(SC_6F_5)_3]$ and Evidence for Novel Equilibria in Solution

Juventino J. Garcia,[a] **Hugo Torrens,**[a] **Harry Adams,**[b] **Neil A. Bailey**[b] **and Peter M. Maitlis**[b]

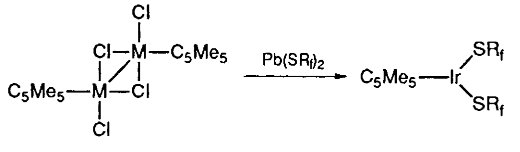
[a] *Departamento de Quimica Inorganica, Facultad de Quimica, Universidad Nacional Autonoma de Mexico, 04510 Mexico DF*

[b] *Department of Chemistry, The University, Sheffield S3 7HF, UK*

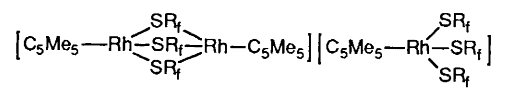
Reaction of $[(C_5Me_5M)_2(\mu\text{-}Cl)_2Cl_2]$ (M = Rh, Ir) with $[Pb(SR_f)_2]$ gave covalent $[(C_5Me_5)Ir(SR_f)_2]$ ($R_f = C_6F_4H$, **2b-F$_4$**), and ionic $[(C_5Me_5)_2Rh_2(\mu\text{-}SR_f)_3][(C_5Me_5)Rh(SR_f)_3]$ ($R_f = C_6F_5$, **2a-F$_5$**), characterised by single crystal X-ray determinations; NMR spectra of **2b-F$_4$** and its analogues are compatible with a retention of the solid state structure in solution for iridium, while those of **2a-F$_5$** and its analogues indicate that the rhodium complexes participate in equilibria: $3[(C_5Me_5)_2Rh(SR_f)_2] \rightleftharpoons [(C_5Me_5)_2Rh_2(\mu\text{-}SR_f)_3][(C_5Me_5)Rh(SR_f)_3]$.

Ligand substitution reactions on pentamethylcyclopendienyl-rhodium and -iridium complexes[1] are of considerable importance, especially in view of the utility of these complexes for many types of reaction.[2] For the simplest ligands, the halides, such studies are quite difficult since there is no convenient spectroscopic property which can easily be monitored. We have therefore turned to complexes with the pseudo-halides, SR_f (R_f = polyfluorophenyl),[3] which can more easily lend themselves to examination.[4] Thiolato complexes of rhodium and iridium have attracted wide interest, most recently in connection with their reactivity towards organic substrates.[5] We find that such rhodium complexes exhibit complicated equilibria in solution but that the corresponding iridium complexes are very much less labile.

Reaction of the chloro-complexes **1** (**a**, M = Rh; **b**, M = Ir) with two equivalents per M of the perfluorophenylthio-lead



1 **2b – F$_4$**, R$_f$ = C$_6$F$_4$H



3a – F$_5$, R$_f$ = C$_6$F$_5$

salts in chloroform solution, afforded complexes of the basic formula '$C_5Me_5M(SR_f)_2$', and lead chloride, which precipitated [eqn. (1)].

$$1/2[(C_5Me_5)_2M_2(\mu\text{-}Cl)_2Cl_2] + [Pb(SR_f)_2] \rightarrow \text{'}C_5Me_5M(SR_f)_2\text{'} + PbCl_2\downarrow \quad (1)$$

1, M = Rh or Ir

The actual structures adopted by '$C_5Me_5M(SR_f)_2$' depend on (*i*) the metal, (*ii*) the solvent, and (*iii*) the precise nature of R$_f$, and of any other counter-ions present, though this has not yet been investigated in detail.

Thus, for example, the deep-green iridium complex **2b-F$_4$** obtained from reaction of **1b** and $Pb(SC_6F_4H)_2$ (bis-2,3,5,6-tetrafluorophenylthiolatolead), has been shown by a single crystal X-ray determination† (Fig. 1) to be a 'covalent' monomer, $[(\eta^5\text{-}C_5Me_5)Ir(SC_6F_4H)_2]$ with formally five-coordinate Ir [intramolecular, Ir–S 2.323(4), 2.274(4) Å; the shortest intermolecular Ir–S is 6.00 Å to a translationally related molecule]. The SC_6F_4H ligands are angled at S (113°) and lie so that one is in an 'axial', the other in an 'equatorial' site, relative to the C$_5$ plane.

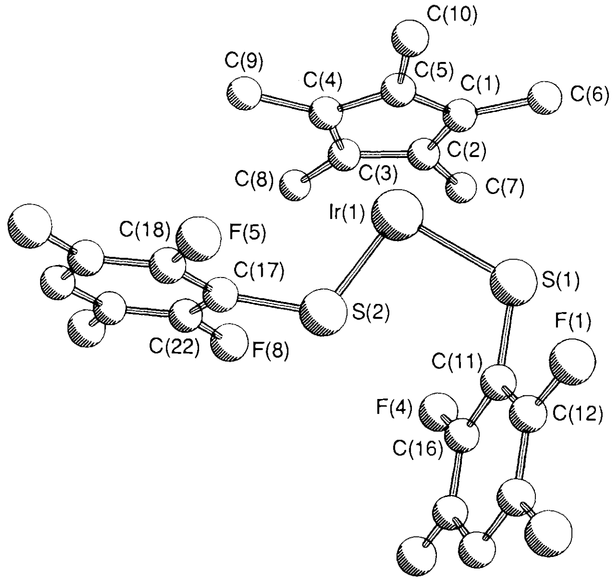


Fig. 1 View of the X-ray crystal structure of $[(\eta^5\text{-}C_5Me_5)Ir(SC_6F_4H)_2]$ **2b-F$_4$**

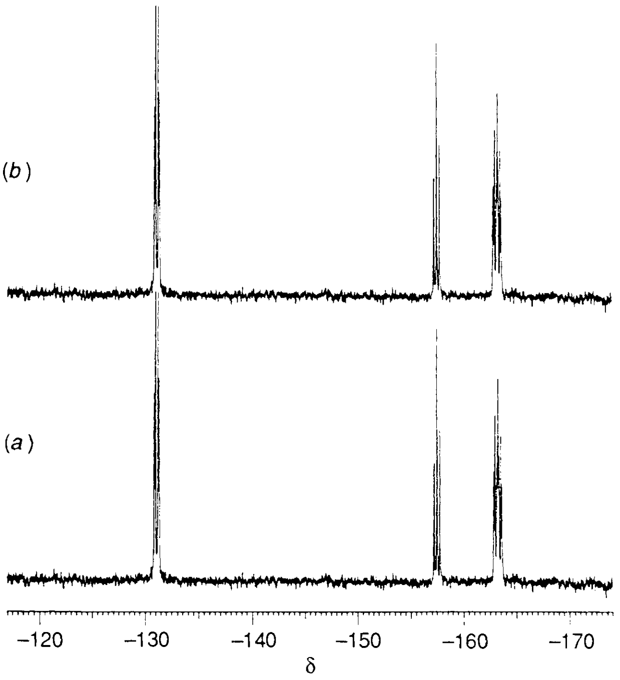


Fig. 2 ^{19}F NMR spectra of $[(\eta^5\text{-}C_5Me_5)Ir(SC_6F_5)_2]$ **2b-F$_5$** in (*a*) toluene and (*b*) acetone

The NMR spectra of complex **2b-F$_4$** in solution (toluene, acetone or nitromethane) are fully consistent with this structure; in particular the ^{19}F NMR shows just two bands, as δ −131.4 and −140.0, corresponding to a single set of *o*- and *m*-Fs. The complex is also essentially non-conducting in acetone solution (12 ohm^{-1} cm^2 mol^{-1}‡). Preliminary X-ray data on the pentafluorophenyl analogue **2b-F$_5$**, as well as the NMR spectra [Fig. 2, ^{19}F resonances, δ −132.6 (m, *o*-F), −159.4 (t, *p*-F) and −164.0 (m, *m*-F)] and the very low

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† *Crystal data* for $[(\eta^5\text{-}C_5Me_5)Ir(SC_6F_4H)_2]$ **2b-F$_4$**, $C_{22}H_{17}F_8IrS_2$, M = 689.69, triclinic, a = 8.248(6), b = 11.213(12), c = 14.203(20) Å, α = 107.63(9), β = 93.65(9), γ = 107.51(7)°, U = 1176(2) Å^3; D_c = 1.948 g cm^{-3}, Z = 2, space group $P\bar{1}(C_i^1$, No. 2), MoKα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 58.92 cm^{-1}, F(000) = 659.85. Three dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 4-circle diffractometer by the ω-scan method. The 3471 independent reflections for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 8 azimuthal scans (minimum and maximum transmission coefficients, 0.065 and 0.111). The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least-squares methods. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final R 0.0521, with allowance for the thermal anisotropy of all non-hydrogen atoms; unit weights gave satisfactory convergence. Complex scattering factors were taken from ref. 7 and from the program package SHELXTL as implemented on the Data General Nova 3 computer.

Crystal data for $[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3][(C_5Me_5)Rh(SC_6F_5)_3]\cdot 0.5PhMe$ **3a-F$_5$**, $C_{69.5}H_{49}F_{30}Rh_3S_6$, M = 1955.20, monoclinic, a = 18.00(6), b = 16.256(25), c = 26.73(7) Å, β = 103.68(22)°, U = 7600(32) Å^3; D_c = 1.709 g cm^{-3}, Z = 4, space group $P2_1/c$ (C_{2h}^5, no. 14), Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 9.03 cm^{-1}, F(000) = 3867.65. Three dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 40°$ on a Nicolet R3 4-circle diffractometer by the ω-scan method. The 3359 independent reflections for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 8 azimuthal scans (minimum and maximum transmission coefficients 0.532 and 0.612). The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least-squares methods. In view of the somewhat limited quality and quantity of the X-ray data extensive geometric constraints were applied to the cyclic fragments during refinement. Refinement converged at a final R 0.1330, with allowance for the thermal anisotropy of Rh, F and S atoms; unit weights gave satisfactory convergence. Complex scattering factors were taken from ref. 7 and from the program package SHELXTL as implemented on the Data General Nova 3 computer.

Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, Issue No. 1.

‡ All conductivities measured in acetone at a concentration of 10^{-3} mol dm^{-3}.

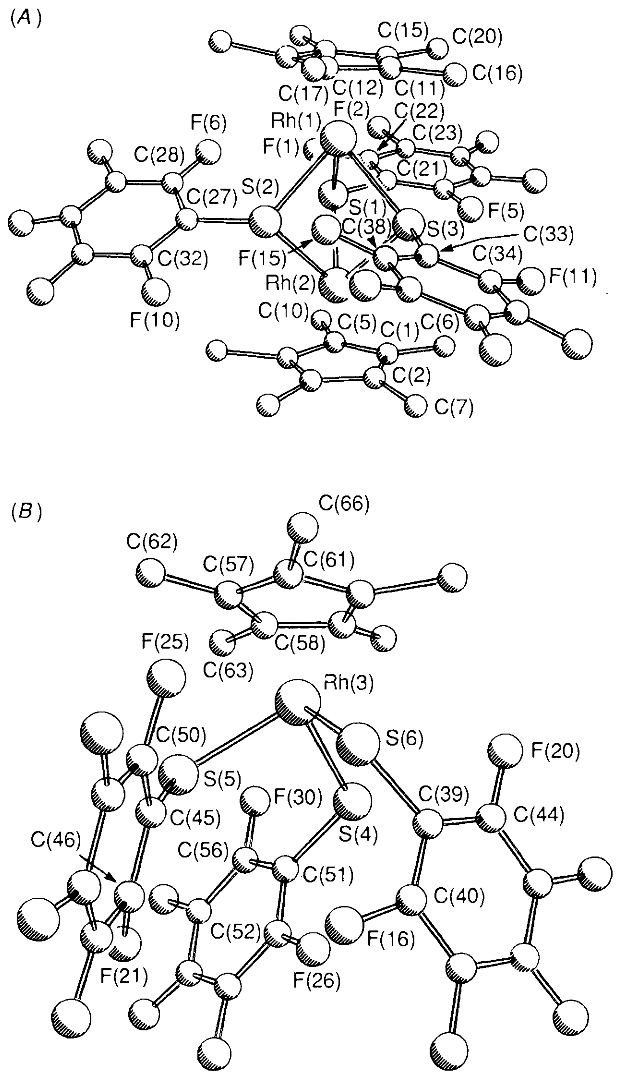

Fig. 3 View of the X-ray crystal structure of $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3][(\eta^5\text{-}C_5Me_5)Rh(SC_6F_5)_3]$ **3a-F$_5$**; (*A*) the cation, and (*B*) the anion

conductivity in acetone (15 ohm^{-1} cm^2 mol^{-1}‡) are consistent with this complex adopting the same structure as **2b-F$_4$**. There is no evidence for the presence of other forms, either, in more polar solvents.

By contrast, the rhodium complex **1a** reacted with $Pb(SC_6F_5)_2$ to give the deep-green *ionic* complex, $[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3][(C_5Me_5)Rh(SC_6F_5)_3]$ **3a-F$_5$** according to the single crystal X-ray determination† (Fig. 3). In this structure the cation has two C_5Me_5Rh units bridged by three SC_6F_5 ligands [Rh-μ-S (av.) 2.440(13) Å; ∠SRhS 76–80°] with equatorially splayed C_6F_5s and pyramidal bridging Ss. In the anion the three terminal SC_6F_5 ligands 'hang down' from the C_5Me_5Rh [Rh-S(av.) 2.414(15) Å; ∠SRhS 91–95°]. In both ions the SR_f ligands adopt very approximate C_3 symmetry with respect to the rhodiums.

The solution behaviour of complex **3a-F$_5$** depends strongly on the solvent. In a very polar solvent such as methanol the NMR spectra (Fig. 4) are consistent with the X-ray structure. Thus, for example, the ^{19}F NMR shows each of the *o*-, *m*- and *p*-Fs as a pair of multiplets of approximately equal intensity [δ −128.0, −132.75, *o*-F; −161.6, −166.0, *m*-F; and −153.3, −161.6, *p*-F], as would be expected for the structure of **3a-F$_5$** if it is retained in solution. The ^{19}F NMR spectrum in toluene, in sharp contrast, shows just three resonances [δ −134.2, *o*-F; −167.0, *m*-F; and −161.8, *p*-F], very similar to that of the iridium complex **2b-F$_5$** [δ −131.1, *o*-F; −163.2, *m*-F; and −157.4, *p*-F], and to which the 'covalent' five-coordinate structure has been assigned. Solvents of intermediate polarity such as acetone show resonances for **3a-F$_5$** characteristic of both the 'covalent' and the 'ionic' forms (ratio 60 : 40) and show an appreciable conductivity (90 ohm^{-1} cm^2 mol^{-1}), but which is lower than that normally associated with 1 : 1 electrolytes (100–140 ohm^{-1} cm^2 mol^{-1}).[6]

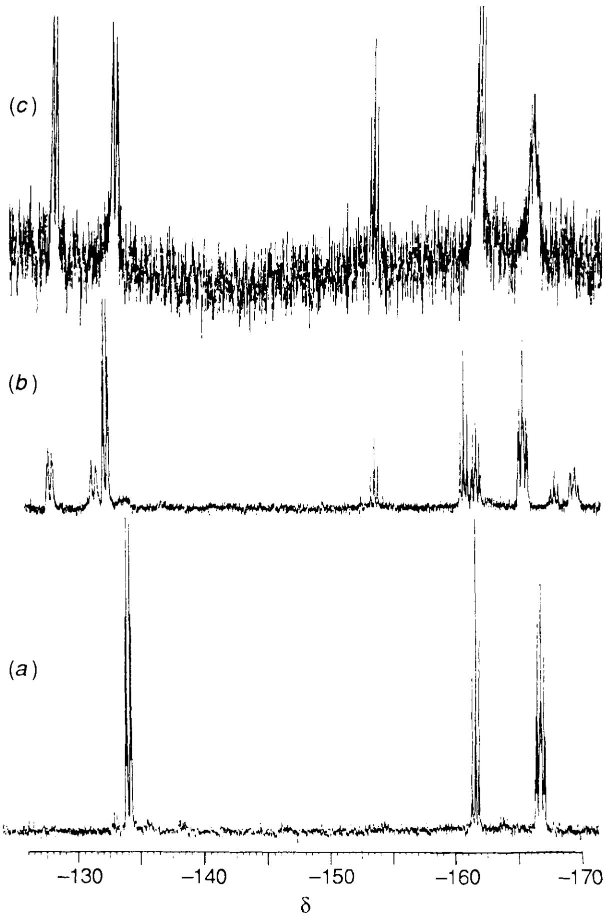

Fig. 4 ^{19}F NMR spectra of $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3][(\eta^5\text{-}C_5Me_5)Rh(SC_6F_5)_3]$ **3a-F$_5$** in (*a*) toluene, (*b*) acetone and (*c*) methanol

The rhodium complex **3a-F$_4$** from **1a** and $Pb(SC_6F_4H)_2$ behaves in exactly the same way as **3a-F$_5$**, and shows the covalent form in toluene and both forms (ratio 1 : 1) in acetone. Thus, the form which the molecule adopts in solutions is determined chiefly by the metal, and we conclude that such rhodium complexes are very labile and participate in the equilibrium (2), while the iridium analogues are substantially inert.

$$3[(C_5Me_5)Rh(SR_f)_2] \rightleftharpoons [(C_5Me_5)_2Rh_2(\mu\text{-}SR_f)_3][(C_5Me_5)Rh(SR_f)_3] \quad (2)$$

This agrees with qualitative observations on the halides; thus, for example, the rhodium chloro-complex **1a** forms the cationic $[(C_5Me_5)_2M_2(\mu\text{-}Cl)_3]^+$ much more easily than the analogous iridium complex.[8]

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