A C–F–Ru Interaction in a Complex: Preparation and *X*-Ray Structure of $[Ru\{SC_6F_4(F\text{-}2)\}(SC_6F_5)_2(PMe_2Ph)_2]$

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Treatment of $[RuCl_3(PMe_2Ph)_3]$ with $Pb(SC_6F_5)_2$ in acetone gives $[Ru\{SC_6F_4(F\text{-}2)\}(SC_6F_5)_2(PMe_2Ph)_2]$ whose *X*-ray structure shows a C–F–Ru interaction.

As part of our programme of investigation of sulphur ligands at metal sites,[1] we have examined the reactions of $[MX_3(PR_3)_3]$ (M = Ru or Os, X = Cl or Br, PR_3 = PMe_2Ph, PEt_2Ph, $PMePh_2$, or $PEtPh_2$) with thiolate reagents, in particular $[Pb(SC_6F_5)_2]$.

Treatment of $[MCl_3(PR_3)_3]$ with $[Pb(SC_6F_5)_2]$ in acetone at reflux gives a smooth reaction with precipitation of $PbCl_2$, and the compounds $[M(SC_6F_5)_3(PR_3)_2]$ have been isolated in high yield as paramagnetic green (M = Ru) or purple (M = Os) crystals.

The crystal structure† of one example of this series, $[Ru\{SC_6F_4(F\text{-}2)\}(SC_6F_5)_2(PMe_2Ph)_2]$ ($\mu_{\mathrm{eff.}}$ = 1.9 μ_B; e.s.r. rhombic signal, *g* values *ca.* 2.13, 2.09, and 2.00 in frozen CH_2Cl_2) has been determined as shown in Figure 1, which includes selected bond distances and angles. The important feature of this structure is the interaction of a 2-fluorine of one SC_6F_5 ligand with the metal to create an S–F chelate ligand,

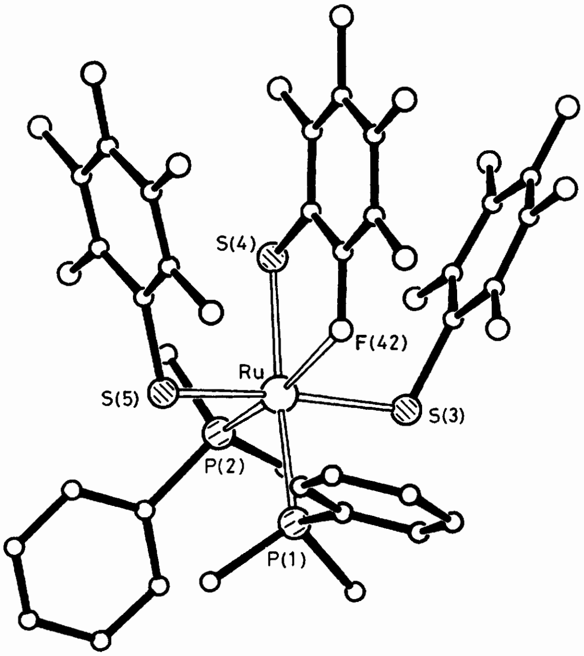

Figure 1. Structure of $[Ru\{SC_6F_4(F\text{-}2)\}(SC_6F_5)_2(PMe_2Ph)_2]$. Principal bond dimensions (Å and °): Ru–F(42) 2.489(6), Ru–S(3) 2.321(3), Ru–S(4) 2.419(3), Ru–S(5) 2.323(3), Ru–P(1) 2.364(3), Ru–P(2) 2.280(3), C(42)–F(42) 1.349(14); S(4)–Ru–F(42) 76.4(2), S(3)–Ru–F(42) 85.0(1), S(5)–Ru–F(42) 87.0(1), S(4)–Ru–P(2) 94.1(1), P(1)–Ru–F(42) 95.1(2), P(2)–Ru–P(1) 94.4(1).

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† *Crystal data:* $[Ru\{SC_6F_4(F\text{-}2)\}(SC_6F_5)_2(PMe_2Ph)_2]$, *i.e.* $C_{34}H_{22}F_{15}P_2RuS_3$, M = 974.7, orthorhombic, space group *Pbca* (No. 61), a = 18.110(4), b = 18.063(3), c = 22.858(8) Å, U = 7477.3 Å^3, Z = 8, D_c = 1.732 g cm^{-3}, $F(000)$ = 3864, $\mu(\text{Mo-}K_\alpha)$ = 7.6 cm^{-1}, $\lambda(\text{Mo-}K_{\bar{\alpha}})$ = 0.71069 Å. The crystals are small, very dark green, square prisms. One, *ca.* 0.10 × 0.12 × 0.36 mm was mounted on a glass fibre and, suspected of being slightly air-sensitive, was coated in epoxy resin. After photographic examination, accurate cell dimensions were refined from the goniometer settings of 25 reflections having θ *ca.* 10° on an Enraf-Nonius CAD4 diffractometer (using monochromated Mo-radiation). Diffraction intensities were recorded to $\theta_{\mathrm{max.}}$ = 20°, beyond which there were few observable reflections. Corrections were made for Lorentz and polarisation effects, and to ensure no negative intensities; no deterioration or absorption corrections were considered necessary. 3473 unique reflections were entered into the SHELX program system[7] for structure determination (by the heavy atom method) and refinement (by large-block-matrix least-squares methods). At convergence, R = 0.081, R_w = 0.054 for 2664 reflections (with $I > \sigma_I$) weighted $w = \sigma_F^{-2}$. (For the 1807 reflections with $I > 2\sigma_I$, R = 0.044, R_w = 0.036). Hydrogen atoms were included in idealised positions (the methyl group H-atoms in staggered arrangements), and their parameters were set to ride on those of their bonded C-atoms. Scattering factors for neutral atoms were used.[8] Computer programs, as listed in reference 9, were adapted for, and run on, a VAX-11/750 machine at G.C.R.I., Littlehampton. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

thus achieving six-co-ordination in an approximately octahedral arrangement. The Ru–F distance of 2.489(6) Å [*cf.* calc. 2.7 Å for F (van der Waals' radius) + Ru (atomic radius)][2] implies a moderate bond strength for the interaction, which is to our knowledge the first characterised example of a fluorine attached to carbon interacting with a metal (an 'agostic' C–F).[3] Two Ir–X–C (X = Br or I) interactions have been structurally characterised.[4]

A further feature of this structure is that the C_6F_5 groups of S(3) and S(5) are eclipsed about the S · · · S vector; they are thus aligned with the central chelating ligand to form, as close as possible, a stacked pattern.

Ruthenium–H–C interactions are known in complexes: for example the compound $[RuCl_2(PPh_3)_3]$ completes octahedral co-ordination at the metal by interaction of a 2-hydrogen of a phenyl group.[5] Treatment of this complex with $[Pb(SC_6F_5)_2]$ gives $[Ru(SC_6F_5)_2(PPh_3)_2]$ which has two such C–H–Ru interactions giving octahedral co-ordination (*X*-ray structure).[6]

We find that the compounds $[\overline{M\{SC_6F_4(F}\text{-}2)\}(SC_6F_5)_2(PR_3)_2]$ have a potentially rich chemistry. For example, they react with CO to give adducts and in the presence of zinc these are reduced to give *trans*-$[M(SC_6F_5)_2(CO)_2(PR_3)_2]$. These and other products of reactions with small molecules will be described in detail at a later date.

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