

Preliminary communication

**The preparation and X-ray crystal structure
 of $[\text{Ru}(\text{SC}_6\text{F}_5)_2\{\text{P}(\text{C}_6\text{H}_5)_2(\text{H}_4\text{C}_6\text{H}-2)\}_2]$**

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Abstract

The complex $[\text{Ru}(\text{SC}_6\text{F}_5)_2(\text{PPh}_3)_2]$ has been prepared from $[\text{RuCl}_2(\text{PPh}_3)_3]$ and $[\text{Pb}(\text{SC}_6\text{F}_5)_2]$ and shown by X-rays to have a pseudo-octahedral structure apparently with two Ru–H–C interactions. It reacts with CO to give $[\text{Ru}(\text{SC}_6\text{F}_5)_2(\text{CO})_2(\text{PPh}_3)_2]$.

The chemistry of ruthenium is prominent in the area of C–H bond activation [1] and in the formation of unsaturated complexes which have potential as, or act as, catalysts in hydrogenation, Fischer–Tropsch reactions etc. [2]. Prominent among catalytically active compounds are those of the PPh_3 ligand whose bulk aids the formation of unsaturated complexes such as $[\text{RuCl}_2(\text{PPh}_3)_3]$ [3]. During the course of our studies of metal-thiolate complexes [4] we have found that the bulky thiolate ligand SC_6F_5^- is particularly effective in creating potentially unsaturated centres and here we report the formation of the mononuclear complex $[\text{Ru}(\text{SC}_6\text{F}_5)_2(\text{PPh}_3)_2]$, in which the unsaturated ruthenium centre interacts with two aromatic C–H bonds, revealed by X-ray crystallography as discussed below.

Treatment of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with $[\text{Pb}(\text{SC}_6\text{F}_5)_2]$ in acetone gave purple, very air-sensitive crystals analysing as $[\text{Ru}(\text{SC}_6\text{F}_5)_2(\text{PPh}_3)_2]$ (A). This complex is an analogue of the series $\{[\text{RuX}_2\text{L}_2]_2\}$ [5] (X = H or halogen, L = PPh_3 or AsPh_3) but unlike these dimers, A is a monomer, presumably a consequence of the bulk of the thiolate and phosphine ligands.

This has been confirmed by an X-ray diffraction study which has shown (Fig. 1) a greatly distorted octahedral coordination of two mutually *trans* thiolate ligands, two *cis* phosphine ligands, and two rather weaker ('agostic') $\text{Ru} \cdots \text{H}$ interactions

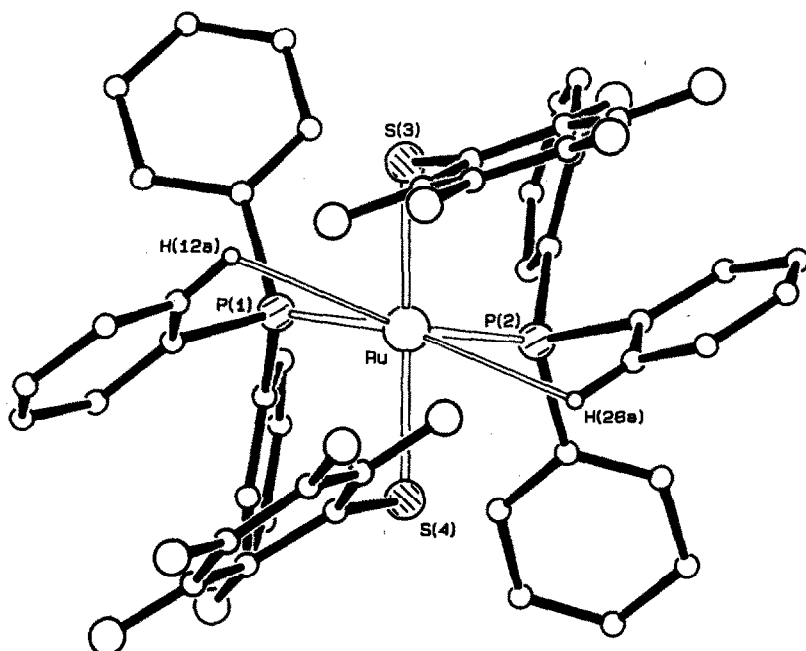


Fig. 1. View of the complex $[\text{Ru}(\text{SC}_6\text{F}_5)_2(\text{PPh}_3)_2]$, down an axis of pseudo-two-fold symmetry. Selected bond dimensions: Ru–P(1) 2.213(5), Ru–P(2) 2.215(4), Ru–S(3) 2.334(5), Ru–S(4) 2.333(4), Ru–H(12a) 2.86, Ru–H(26a) 2.80 Å, P(1)–Ru–P(2) 106.2(2), P(1)–Ru–H(12a) 64.2, P(2)–Ru–H(26a) 66.9, H(12a)–Ru–H(26a) 126.4, S(3)–Ru–S(4) 157.8(2)°. Note: the H atoms are in idealised positions with respect to their phenyl rings.

involving *ortho*-hydrogen atoms of a phenyl of each of the phosphine ligands*. The next nearest atoms to the metal atom are a pair of fluorine atoms, but with Ru...F at 3.73 and 3.34 Å we do not consider these F atoms to be bonded to the Ru, but instead involved in the tight packing of ligands. The Ru–P–C angles in the chelating rings are, at ca. 103°, much reduced from the other Ru–P–C angles (116.9–122.6°) and indicate the strains required to achieve the agostic bonding.

Interactions of this type have been observed for $[\text{RuHCl}(\text{PPh}_3)_3]$ [6], $[\text{RuCl}_2(\text{PPh}_3)_3]$ [3] and the cation $[\text{Rh}(\text{PPh}_3)_3]^+$ [7]; formation of these may be considered to be a first step in an *ortho*-metallation reaction, which is also common in this area of coordination chemistry.

It is significant also that a C–F–Ru interaction has been observed in the ruthenium(III) complex $[\text{Ru}(\text{SC}_6\text{F}_5)_2\{\text{SC}_6\text{F}_4(\text{F}-2)\}(\text{PMe}_2\text{Ph})_2]$ [8], but such an interaction has not occurred in the ruthenium(II) complex reported here. Evidently the greater electrophilicity of the ruthenium(III) centre is necessary to allow interaction with fluoride.

Complex A reacts with CO in tetrahydrofuran or acetone to give yellow $[\text{Ru}(\text{SC}_6\text{F}_5)_2(\text{CO})_2(\text{PPh}_3)_2]$ ($\nu(\text{CO})$, 2048, 1990 cm^{-1} , KBr) but does not react with

* A table of atomic coordinates and a full list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

cyclooctadiene. As might be expected for such an essentially unsaturated molecule, A is active in hydrogenation and Fischer–Tropsch reactions which will be reported at a later date.

Crystal data. $[\text{Ru}(\text{PPh}_3)_2(\text{SC}_6\text{F}_5)_2]$, $\text{C}_{48}\text{H}_{30}\text{F}_{10}\text{P}_2\text{RuS}_2$, $M = 1023.9$. Monoclinic, $C2/c$ (no. 15), a 24.030(7), b 13.402(5), c 29.184(10) Å. β 107.34(3)°, V 8971.4 Å³. $Z = 8$, $F(000) = 4112$, $\mu(\text{Mo-K}\alpha)$ 5.8 cm⁻¹, $D_c = 1.516$ g cm⁻³.

Crystals are purple-coloured plates; the one chosen for diffractometer measurements was ca. 0.12 × 0.24 × 0.48 mm, mounted on a glass fibre and coated in epoxy resin. Photographic examination showed sharp diffraction spots, but a limited range of θ for measureable intensities. Indeed, on our Enraf–Nonius CAD4 diffractometer (with monochromated Mo-radiation), intensity measurements could usefully be made only to $\theta_{\text{max}} 17^\circ$. Accurate cell dimensions were refined from the goniometer settings of 25 reflections having $10 < \theta < 11^\circ$.

During processing of the data, corrections were made for Lorentz-polarisation effects and to ensure no negative net intensities. 2605 unique reflections were then read into the SHELX program system [9] for structure determination and refinement.

The coordinates of the Ru atom were calculated from a Patterson map, and the remaining non-hydrogen atoms were located in electron-density and difference Fourier maps. Hydrogen atoms were introduced in idealized positions. With the limited dataset, only the Ru, P, S and F atoms were refined anisotropically; the H atoms were set to ride on their bonded C atoms.

Refinement was concluded at $R = 0.080$, $R_w = 0.071$ for 2135 reflections (all those with $I > \sigma(I)$) weighted $w = (\sigma(F^2) + 0.00102F^2)^{-1}$. Scattering factors for C, H, F, P, Ru and S atoms were from ref. 10.

All computations were made on the VAX11/750 computer at the Glasshouse Crops Research Institute, Littlehampton, with programs described in ref. 11.

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