Supporting Information

Manuscript: Dialkyl(di)thiophosphate complexes of ruthenium(II)

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The X-ray crystal structure of 8

The alcohol hydrogen atom bonded to O(13) in the structure of **8** was located from a ΔF map and refined freely subject to an O–H distance restraint of 0.900 Å with an s.u. of 0.001 Å. This hydrogen atom is involved in an intramolecular O–H···π hydrogen bond to the C(59)-based phenyl ring with an H···centroid separation of *ca*. 2.54 Å and an O–H···centroid angle of *ca*. 168°, the H···centroid vector being inclined by *ca*. 81° to the ring plane. The included dichloromethane molecule was found to be disordered. Four orientations were identified of *ca*. 39, 26, 20 and 15% occupancy, their geometries optimised, the thermal parameters of adjacent atoms restrained to be similar, and all of the atoms were refined isotropically.

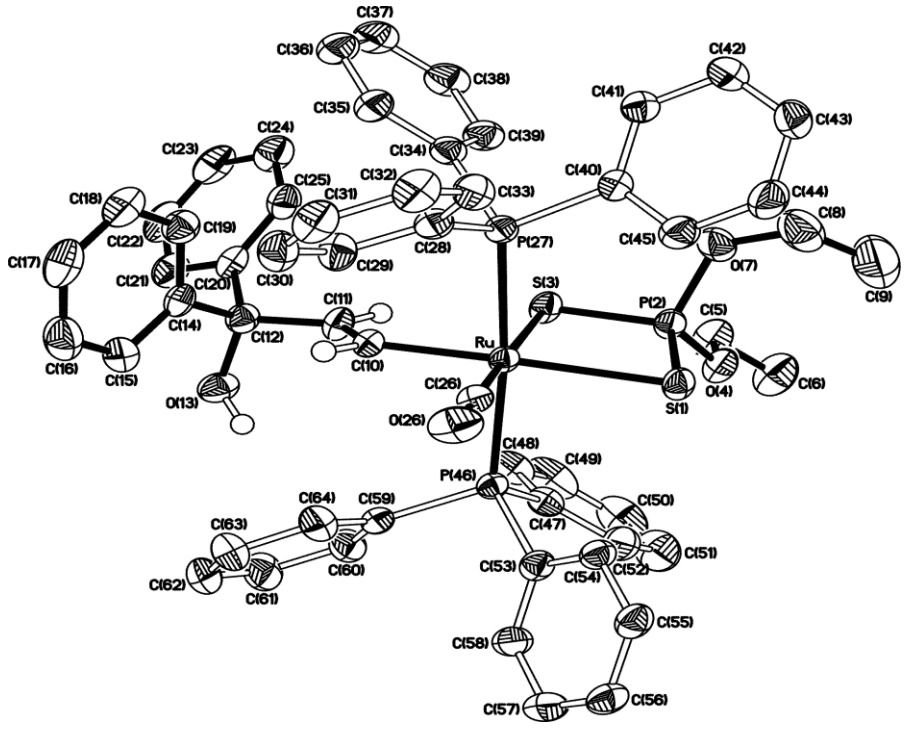
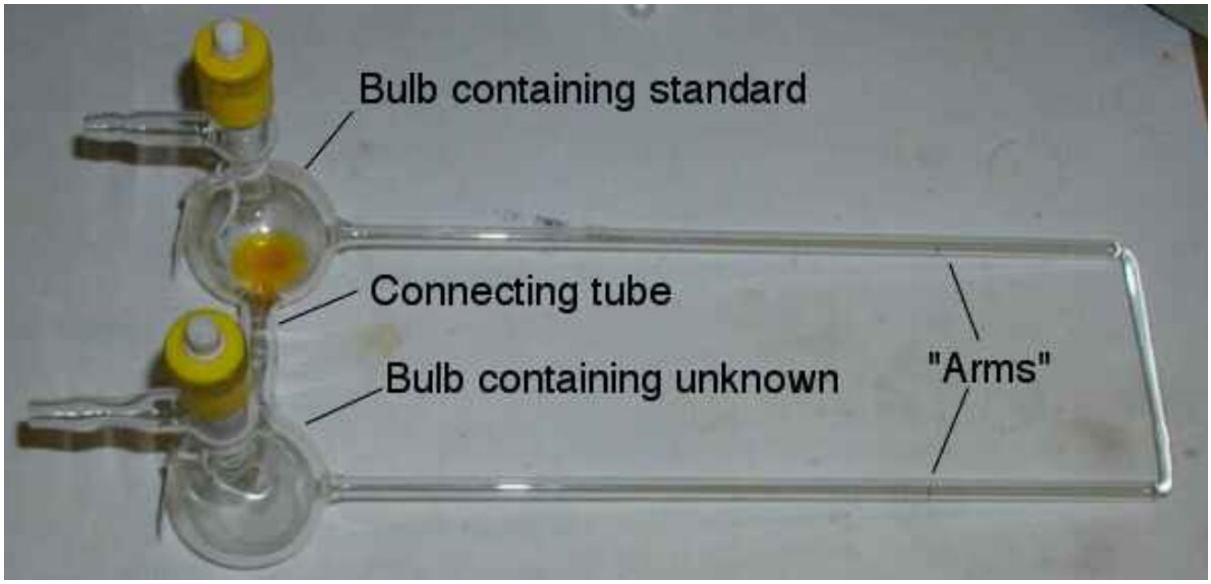


Fig. S1 The molecular structure of **8** (50% probability ellipsoids).

The Signer apparatus for molecular weight determination

The apparatus is shown below. Similar masses (10 mg) of the complex to be examined ('unknown') and a standard are weighed (to 4 decimal places) and dissolved, separately, in dichloromethane (~2-3 mL). These solutions are introduced to the separate bulbs of the apparatus and the taps closed. One valve is then attached to the Schlenk line and a very slight vacuum created. The apparatus is placed in a warm place and is left undisturbed while the vapour pressures equilibrate through the glass frit connecting the bulbs. To make the measurement, the apparatus is rotated so that the solvent fills the arms and the heights from the sealed end in both arms are determined. The heights of the solvent in the two arms will be proportional to the volume of solution. Readings are taken over a two day period until the measurements stabilise.



Ferrocene (M_w = 186.03) is typically used as a standard, however, the standard should ideally have a similar molecular weight to the unknown being determined. For this reason, Vaska's complex (M_w =780.25) was used for the determinations in this work. The stability of the standard in CD_2Cl_2 was confirmed by ^{31}P NMR spectroscopy over a period of days.

The molecular weight is then given by:

$$M_x = \frac{(m_x)(M_s)(h_s)}{(m_s)(h_x)}$$

Where:

M_x and M_s are the molar masses of the unknown and of the standard.

m_x and m_s are the masses of the unknown and of the standard used in the experiment.

h_x and h_s are the heights of the unknown and standard solutions in the arms.

References:

R. Signer, *Annalen*, 1930, **478**, 246.

E. P. Clark, *Ind. Eng. Chem., Anal. Ed.*, 1941, **13**, 820.