Preparation of Two Isomers of $[Ru(S_2CH)(PMe_2Ph)_4]PF_6$ and the Characterisation of the Purple One as a Five-co-ordinate Ruthenium(II) Salt Containing a Phosphonium Adduct of a Dithioformato Ligand. The *X*-Ray Crystal Structure of $[Ru\{S_2C(H)PMe_2Ph\}(PMe_2Ph)_3]PF_6$

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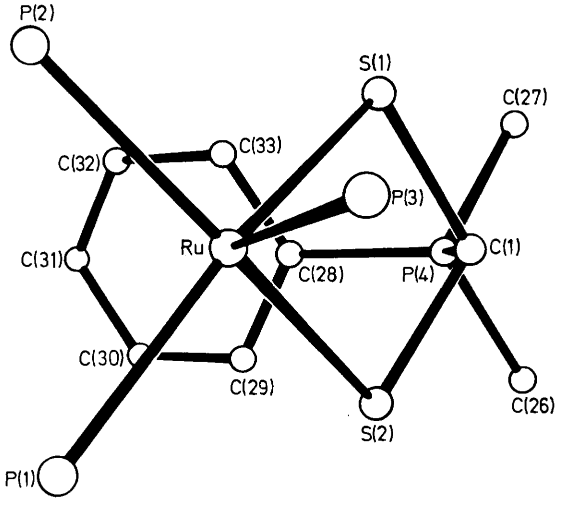
Summary The purple salt $[Ru\{S_2C(H)PMe_2Ph\}(PMe_2Ph)_3]PF_6$, shown by *X*-ray analysis to contain a phosphonium-betaine group, and formed by a sterically-controlled rearrangement of the orange dithioformato complex $[Ru(S_2CH)(PMe_2Ph)_4]PF_6$, undergoes a reverse rearrangement during substitution reactions with $P(OMe)_3$.

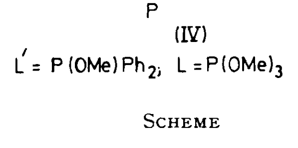
WE have synthesised the orange dithioformato complex $[Ru(S_2CH)(PMe_2Ph)_4]PF_6$ (I) from the reaction between CS_2 and $[RuH(PMe_2Ph)_5]PF_6$,[1] and found that (I) underwent a rearrangement in boiling methanol to give a purple compound (II), which is isomeric with (I). The ^1H n.m.r. spectrum of (II) in CD_2Cl_2 contained a singlet at τ 3·75 (1H), a doublet (J 13 Hz) at τ 7·95 (6H), and a partial triplet at τ 8·47 (18H). The triplet is characteristic of three 'virtually coupled' PMe_2Ph groups arranged facially. The coupling of 13 Hz in the doublet is similar to that found[2] in the sulphide of PMe_2Ph, while the unique hydrogen resonance at 3·75 is much higher than that expected for a dithioformato group.[3] The ^{13}C n.m.r. spectrum, obtained from a $^{13}CS_2$ enriched sample of (II), showed that the dithioformato C atom was coupled to a single ^1H nucleus and to one ^{31}P atom and suggested that the C-H bond of the S_2CH^- group had remained intact and that a phosphine ligand was attached in some way to the dithioformato group. The crystal structure was solved to determine the exact configuration of (II).



FIGURE

Crystal data: $[Ru\{S_2C(H)PMe_2Ph\}(PMe_2Ph)_3]PF_6$, forms dark purple crystals which are triclinic, space group $P\bar{1}$, $a = 11{\cdot}28$, $b = 11{\cdot}76$, $c = 15{\cdot}79$ ($\pm 0{\cdot}01$) Å, $\alpha = 99{\cdot}9$, $\beta = 102{\cdot}6$, $\gamma = 87{\cdot}8$ ($\pm 0{\cdot}1°$); $U = 2014$ Å^3, $Z = 2$, $D_m = 1{\cdot}44$ g cm^{-3}, $D_c = 1{\cdot}45$ g cm^{-3}. Intensity data were collected on a Philips four-circle diffractometer with graphite-monochromated Mo-K_α radiation to $\theta = 20°$; 2960 reflections were judged to be observed. The structure was solved by Patterson and Fourier methods and was refined by block-diagonal least-squares (Ru, five P and two S atoms anisotropic) to $R = 0{\cdot}07$.

The co-ordination geometry of the ruthenium atom is distorted square pyramidal. Three phosphine ligands are arranged facially and the two S atoms complete the base of the pyramid. The fourth phosphine group is bonded to the dithioformato carbon atom as a phosphonium ion, which is evident from the four effectively identical P–C bond lengths ($1{\cdot}80 \pm 0{\cdot}02$ Å) and the C–P–C angles ($110 \pm 2°$). The plane of the phenyl ring faces towards the basal plane of the square pyramid (see Figure; Ru $\cdots\cdots$ phenyl ring is *ca.* 5 Å) and effectively protects the vacant (octahedral) site since (II) is stable in air and inert to addition reactions with MeCN, pyridine and amines. The distortion in the basal plane of the pyramid is large; P(1)–Ru–S(1) 161°, P(2)–Ru–S(2) 152° with the ligands bent towards the vacant site. Bond lengths are: Ru–S(1) 2·37, Ru–S(2) 2·37, Ru–P(1) 2·31, Ru–P(2) 2·28, Ru–P(3) 2·20, C(1)–S 1·82 and 1·83 Å. The bond to P(3) is among the shortest Ru–P bonds recorded so far in this class of compound and may be contrasted to the long Ru–P bond of 2·48 Å to the unique P atom *trans* to the H atom in $[RuH(PMe_2Ph)_5]^+$.[4] The bond angles S(1)–C–S(2) 105°, S(1)–C–P(4) 112°, and S(2)–C–P(4) 111° show that the C atom of the



L′ = P(OMe)Ph$_2$; L = P(OMe)$_3$

SCHEME

CS_2 is sp^3 hybridised and therefore we conclude that the H atom is attached to this carbon atom which is consistent with the n.m.r. results. These angles may be compared[5] with the angles S–C–S 111°, and S–C–P 118 and 131° found in $[Ir(S_2CPPh_3)(CO)(PPh_3)_2]^+$ for the zwitterionic ligand $Ph_3P^+CS_2^-$ in which the CS_2 carbon atom is sp^2 hybridized.

It is evident that the ready isomerisation of (I) to (II) is controlled by the magnitude of the strain energy caused by the short non-bonded contacts between the four phosphine groups bonded to the Ru atom in (I). Chemical evidence shows that, under sterically favourable conditions, the PMe_2Ph group can be transferred back onto the Ru atom. Thus, substitution reactions of (II) with a small ligand, L = $P(OMe)_3$, yield the yellow octahedral complex $[Ru(S_2CH)(PMe_2Ph)_2L_2]PF_6$ (III), whilst with the larger phosphinite, L′ = $P(OMe)Ph_2$, the purple salt $[Ru\{S_2C(H)\text{-}PMe_2Ph\}(PMe_2Ph)L'_2]PF_6$ (IV) is obtained. The reaction of (IV) with $P(OMe)_3$ then produced (III), thus demonstrating that the migration of the PMe_2Ph ligand from Ru to C is reversible.

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