

Isomeric Conformations in a Pentaco-ordinated Ruthenium Compound; Crystal and Molecular Structures of the Orange and Violet Isomers of $(\text{Ph}_3\text{P})_2[(\text{CF}_3)_2\text{C}_2\text{S}_2]\text{Ru}(\text{CO})$

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Summary The molecular conformations of two square pyramidal species, one violet the other orange, both of composition $(\text{Ph}_3\text{P})_2[(\text{CF}_3)_2\text{C}_2\text{S}_2]\text{Ru}(\text{CO})$ are described.

THEORETICAL studies of preferential isomeric conformation in the case of pentaco-ordination favour the trigonal bipyramid,^{1,2} although the predicted energy difference is small (about 3 to 5 kcal mol⁻¹). A recent review³ states that "... pentaco-ordinate substances are, in general, remarkably free of isomeric conformations, ...". We report the crystal and molecular structures of two Ru complexes of the same composition which co-exist in solution and which can be isolated in pure crystalline form. In both cases the co-ordination around the central atom is square pyramidal and the data available thus far⁴ show no evidence of a trigonal bipyramidal species.

Crystal data: Violet form, $a = 22.394(8)$, $b = 19.107(6)$, $c = 17.480(5)$ Å; $D_m = 1.56(2)$, $D_c = 1.56$ g cm⁻³, for $Z = 8$, space group $Pbca$. Data were collected with a diffractometer using Mo- K_α radiation. The discrepancy index, $R(F)$, is 0.060. Orange form; $a = 10.147(3)$, $b = 10.081(4)$, $c = 38.627(9)$ Å, $\beta = 102.27(3)^\circ$; $D_m = 1.50(2)$, $D_c = 1.49$ g cm⁻³ for $Z = 4$, space group $P2_1/c$. Diffractometer data were recorded with Cu- K_α radiation, final $R(F)$ is 0.047. Both sets of data were corrected for absorption and both structures were solved by the heavy-atom method and refined by standard least-squares techniques. Most of the important bond distances appear in the Figure and a selection of bond angles is given in the Table.

TABLE. Bond angles ($^\circ$) in the co-ordination sphere

	Violet	Orange
P(1)-Ru-P(2)	105.2(1)	100.8(1)
P(1)-Ru-S(1)	162.3(1)	85.8(1)
P(1)-Ru-S(2)	88.3(1)	168.7(1)
P(1)-Ru-C	89.6(3)	89.3(2)
P(2)-Ru-S(1)	92.5(1)	150.6(1)
P(2)-Ru-S(2)	111.8(1)	84.0(1)
P(2)-Ru-C	94.3(3)	92.2(2)
S(1)-Ru-S(2)	86.5(3)	85.1(1)
S(1)-Ru-C	87.5(3)	116.7(2)
S(2)-Ru-C	153.2(3)	100.8(2)
Ru-C-O	171.8(9)	173.8(6)

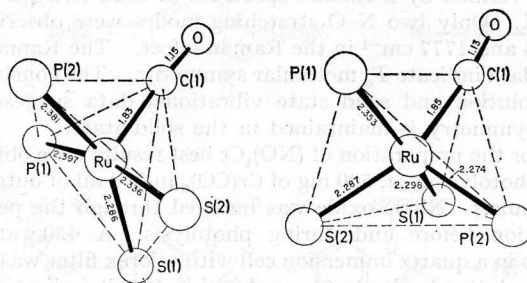


FIGURE. Distances characterizing the pentaco-ordinate arrangement of the ligands around the Ru species found in the orange (left) and the violet isomers (right). The standard deviations in the bond lengths are: Ru-P and Ru-S bonds 0.003 Å; other bonds 0.010 Å.

The following comments summarize the results: solution studies⁴ indicate that the orange form is the favoured isomer; the violet form can be obtained only under very specific conditions⁴ and even then the orange isomer is present in the solution and as orange crystalline material. Only a single molecular species is found in each type of crystal. If there are any other species (*i.e.*, trigonal bipyramidal) in solution their lifetimes must be very short and attempts to obtain other crystalline forms have, so far, failed. There are very small differences in the bonding parameters obtained for the orange and violet species; the small differences in the Ru-S, Ru-P and Ru-C distances could be due to changes in steric hindrance between the two phosphines. However, due to the conformational changes electronic effects could also contribute. This is being

studied by Mössbauer spectroscopy.⁵ If steric hindrance effects are of significant magnitude to be responsible for the changes, it is interesting to note that the most hindered (potentially) form is the orange, which apparently is also the preferred one. The height of the metal above the plane of the basal ligands is essentially the same (0.34 *vs.* 0.35 Å for the orange and violet forms, respectively). The Ru-C-O angle is not significantly affected by exchanging from the axial (orange) to the equatorial (violet) position and the differences in bond lengths in this fragment are minor.

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⁵ M. L. Good, personal communication.