

⁽⁸⁾ B. K. Sen and P. B. Sarkar, *Sci. Cult.*, 27, 404 (1961); S. Sen, *Z. Anorg. Allgem. Chem.*, 335, 222 (1965). – ⁽⁹⁾ A. Sergeeva, A. V. Mazera and A. Mazuroki, *Kood. Khim.*, 1, 1681 (1975). – ⁽¹⁰⁾ R. G. Bhattacharyya and P. S. Roy, *Transition Met. Chem.*, 7, 285 (1982); *Ibid.*, *J. Coord. Chem.*, 12, 129 (1982); *Ibid.*, *Indian J. Chem.*, 22A, 111 (1983).

⁽¹¹⁾ R. G. Bhattacharyya, G. P. Bhattacharjee and A. M. Saha, *Transition Met. Chem.*, 8, 255 (1983). – ⁽¹²⁾ S. Glasstone, *Textbook of Physical Chemistry*, Macmillan, London, 1972. – ⁽¹³⁾ K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Interscience, N.Y., 1978. – ⁽¹⁴⁾ L. F. Farnell, R. W. Randall and E. Rosenberg, *Chem. Comm.*, 1078 (1971). – ⁽¹⁵⁾ B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radio Chem.*, 13, 135 (1970). –

⁽¹⁶⁾ P. Schuster, G. Zundel and C. Sandorfy, *The Hydrogen Bond: Recent Developments in Theory and Experiments*, North-Holland Publ. Co., Oxford, p. 1229, 1976. – ⁽¹⁷⁾ P. Schuster, G. Zundel and C. Sandorfy, *J. Chem. Phys.*, 55, 1373 (1971). – ^(18a) S. Jagner and N. G. Vennerberg, *Acta Chem. Scand.*, 32, 3330 (1968); ^(b) P. T. Manoharan and H. L. Hamilton, *Inorg. Chem.*, 2, 1043 (1963); ^(c) A. Tullberg and N. G. Vennerberg, *Acta Chem. Scand.*, 21, 1462 (1967). – ⁽¹⁹⁾ J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, 13, 339 (1974).

¹³C n.m.r. spectrum and the probable isomeric structures of $K_3[Re(NO)(CN)_5] \cdot 2H_2O$ in D_2O solvent.

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Communication

Reactions and Molecular Structure of Di- μ -pentafluorothiolo-tobis-(1,5-cyclooctadiene)dirhodium(I)

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X-ray diffraction studies have shown that Rh_2Cl_2 skeleton in $[\{RhCl(COD)\}_2]^{(1)}$ (COD = 1,5-cyclooctadiene) is planar, whereas it is bent along the Cl–Cl axis in $[\{RhCl(CO)_2\}_2]^{(2)}$ and $[\{RhCl(C_2H_4)_2\}_2]^{(3)}$. It has also been shown that solid state vibrational spectroscopy is a useful tool to distinguish between both structures⁽⁴⁾. This knowledge has led to the assumption that similar compounds with monodentate ligands have bent Rh_2L_2 (L = bridging ligand) rings, whereas those in which chelating ligands are involved, have a coplanar Rh_2L_2 entity^(5, 6).

Several dinuclear transition metal compounds containing the bridging pentafluorothiophenolato-moiety are known^(6, 7). Unfortunately the solid state structures have been resolved only for a limited number of compounds⁽⁷⁾ and, to our knowledge, none of these is a rhodium derivative.

Our interest in dimeric rhodium compounds with bridging $(SC_6F_5)^-$ groups, prompted us to study further the validity of the above-mentioned structural assumption, which should have important implications regarding both chemical and stereoscopic aspects of these species.

The molecular structure and labeling scheme for $[\{Rh(SC_6F_5)(COD)\}_2]$ are shown in Figure 1*.

Two essentially planar $Rh(SC_6F_5)(COD)$ groups intersect at an angle of ca. 117°. With this geometry, the Rh–Rh bond length is 2.955 Å which is, not unexpectedly, outside the range found for similar compounds having a two-electron bond (2.40–2.50 Å)⁽⁸⁾. This distance may be compared with those found in the carbonyl⁽²⁾ (3.31 Å) and the ethylene⁽³⁾ (3.498 Å) compounds, respectively.

Although the structure of $[\{Rh(SC_6F_5)(COD)\}_2]$ is similar to that of $[\{RhCl(CO)_2\}_2]$, there is no evidence of intramolecular interactions such as those present in the chloro-bridged compound, which explain the bending of the Rh_2Cl_2 ring.

Molecular models suggest that steric interactions could induce the adopted structure. Particularly noteworthy are the non-bonded distances between the *ortho*-fluorine and the

* The atomic coordinates and full lists of bond lengths, bond angles and F_o/F_c values have been deposited as supplementary material with the Editor, from whom copies can be obtained on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

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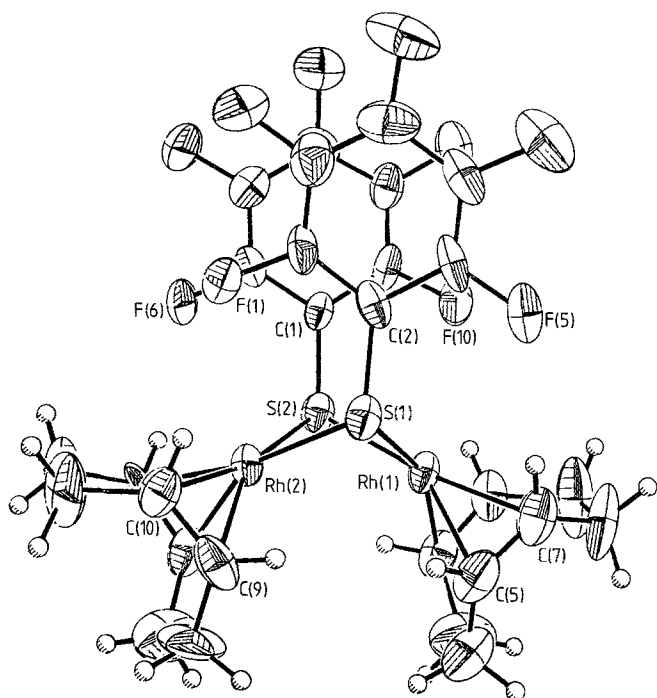
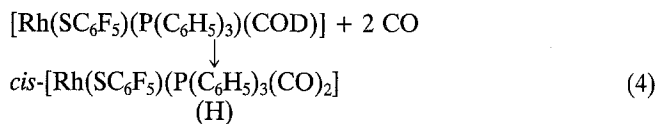
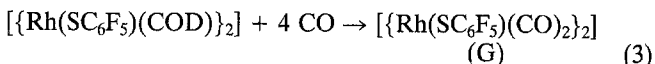
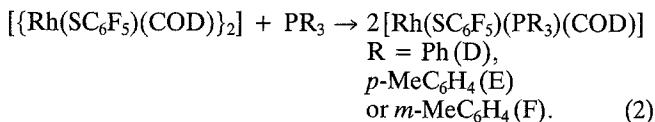
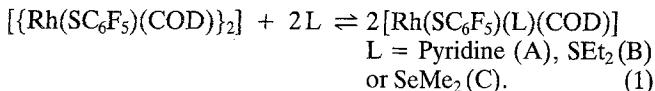


Figure 1. Molecular structure of the title compound. Relevant bond lengths and angles are: Rh1-S1, 2.386; Rh1-S2, 2.420; Rh2-S1, 2.415; Rh2-S2, 2.408, S1-C2, 1.761; S2-C1, 1.748; Rh-C (average), 2.155; S-C (average), 1.755 (Å); Rh1-S1-S2, 89.0; Rh2-S1-S2, 88.6; Rh1-S2-C1, 111.0; Rh2-S2-C1, 107.8; Rh1-S1-C2, 109.3; Rh2-S1-C2, 112.9, S1-Rh2-C9, 87.1 and S2-Rh1-C7, 171.6(°).

upper hydrogen atoms, which point almost directly towards each other [F(5)-H(7), 2.408 Å; F(1)-H(10), 2.597 Å; F(6)-H(8), 2.398 Å and F(10)-H(6), 2.725 Å] and which are all shorter than the sum of the van der Waals radii of hydrogen (1.45 Å) and fluorine (1.60 Å). The pentafluorophenyl rings are practically eclipsed, in a *syn* configuration, with a C(1)-S(2)-S(1)-C(2) torsion angle of *ca.* 1°.

The reactions of $[\{\text{Rh}(\text{SC}_6\text{F}_5)(\text{COD})\}_2]$ with PR_3 (R = Ph, *p*-MeC₆H₄ or *m*-MeC₆H₄), pyridine, CO, SeMe₂ or SET₂ shown in Eqns. (1) to (3), occur with cleavage of the bridge to afford mononuclear, presumably square-planar, compounds.



Pyridine, diethyl sulfide and dimethyl selenide as neat liquids or in a solvent, react with the rhodium complex with a change in the color of the solution (from orange to bright yellow) and a substantial modification of the electronic spectra [Reaction (1)]. The products have not been isolated however, since removal of the solvent leaves behind the unchanged starting rhodium complex.

Reactions (2) and (3) afford the expected products, of which compound (G) has been prepared previously by a different synthetic route⁽⁵⁾. Both reactions, specially when R = Ph, are relevant in relation to catalysis in hydroformylation reactions. It has been suggested⁽⁹⁾ that in this process, the sulphur bridge is unaffected during the catalytic process, in contrast with the behaviour of the chloro-bridged complexes which undergo cleavage upon reaction with carbon monoxide and hydrogen.

Crystal data

$[\{\text{Rh}(\text{SC}_6\text{F}_5)(\text{C}_8\text{H}_{12})\}_2]$. Triclinic, $a = 9.734(6)$ Å, $b = 11.831(12)$ Å, $c = 13.985(19)$ Å, $\alpha 104.59(8)'$, $\beta = 106.58(8)^\circ$, $\gamma = 104.22(7)^\circ$, $F(000) = 734$, space group $P\bar{1}$, $\mu(\text{Mo-K}\alpha) = 13.84 \text{ cm}^{-1}$. A total of 9889 reflections were measured by the ω -scan technique on a Nicolet R3M diffractometer ($2\theta_{\text{max}} = 60^\circ$). No absorption correction was applied. The structure was solved by direct methods (Shelxtl, Rev. 3.0) and refined by full matrix least-squares to an R value of 0.074 for 8000 reflections with $I > 3\sigma(I)$. All non H atoms anisotropic, H atoms fixed at C-H = 0.95 Å with a common B_{iso} .

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References

- (1) J. A. Ibers and R. G. Snyder, *Acta Cryst.*, 15, 923 (1962). - (2) L. F. Dahl, C. Martell and D. L. Wampler, *J. Am. Chem. Soc.*, 83, 1761 (1961). - (3) W. E. Oberhansli and L. F. Dahl, *J. Organometal. Chem.*, 3, 43 (1965). - (4) D. M. Adams and P. J. Chandler, *J. Chem. Soc.*, 588 (1969). - (5) E. S. Bolton, R. Havlin and G. R. Knox, *J. Organometal. Chem.*, 18, 153 (1969). - (6) R. Salcedo and H. Torrens, *Transition Met. Chem.*, 5, 247 (1980). - (7) R. H. Fenn and G. R. Segrott, *J. Chem. Soc.*, (A), 3198 (1970). - (8) F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, 20, 2703 (1981). - (9) P. Kalck, J. M. Frances, P. M. Pfister, F. G. Southern and A. Thorez, *Chem. Comm.*, 510 (1983).

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