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A Dinuclear Ruthenium Complex with both Terminal and Bridging Mercapto Ligands

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There are currently a number of reports concerning transition metal complexes with SH^- ligands [1] in connection with hydrodesulfurization by heterogeneous catalysis [2] and with biological reactions [3]. However, little is known about ruthenium mercapto complexes [4]. In a previous paper we reported the preparation of $RuH(SH)(PPh_3)_3$ from the reaction of H_2S or S_8 with $RuH_2(PPh_3)_4$ [5]. Here we show that reaction of H_2S with $RuH_2(PMe_2Ph)_4$ gives a new type of dinuclear ruthenium complex $(PhMe_2P)_3Ru(\mu\text{-}SH)_3Ru(SH)(PMe_2Ph)_2$ (**1**) which possesses both terminal and bridging mercapto ligands in its molecule. The characterization reported here of complex **1** is the first X-ray structural determination of the mercapto complex of ruthenium.

Contact of H_2S with toluene solution of $RuH_2(PMe_2Ph)_4$ at 50 °C gives a yellow solid of **1** after 80 h. (44% yield; m.p. 163 °C (dec.); elemental analysis agreed with calculated values).

$$2RuH_2(PMe_2Ph)_4 + 4H_2S \longrightarrow \underset{\mathbf{1}}{(PhMe_2P)_3Ru(\mu\text{-}SH)_3Ru(SH)(PMe_2Ph)_2} + 3PMe_2Ph + 4H_2$$

The presence of coordinated SH groups in **1** are confirmed by an IR band ν(SH) at 2525 cm^{-1}. Complex **1** containing deuterated mercapto ligands, prepared from D_2S and $RuH_2(PMe_2Ph)_4$, shows a reasonably clear ν(SD) band at 1810 cm^{-1}. ^1H NMR spectrum of **1** in toluene-d_8 at room temperature shows three broad peaks at −1.9–−3.2 ppm (δ value) in an integrated ratio of 2:1:1 assignable to four mercaptide hydrogens. CH_3 protons of PMe_2Ph ligands give rise to a complex multiplet.

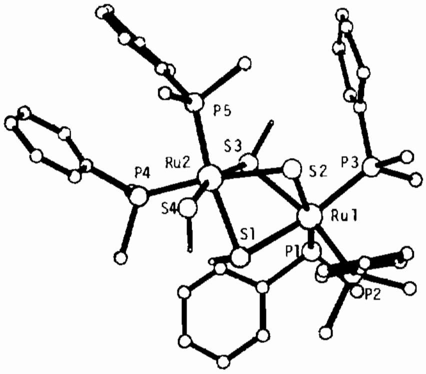

Fig. 1. Molecular structure of $(PhMe_2P)_3Ru(\mu\text{-}SH)_3Ru(SH)(PMe_2Ph)_2$. Three mercapto hydrogens are also shown. Bond lengths (Å): Ru1–S1 2.455(6), Ru1–S2 2.458(6), Ru1–S3 2.473(6), Ru1–P1 2.305(7), Ru1–P2 2.481(6), Ru1–P3 2.310(7), Ru2–S1 2.457(6), Ru2–S2 2.481(6), Ru2–S3 2.420(7), Ru2–S4 2.440(7), Ru2–P4 2.284(6), Ru2–P5 2.272(6), HS1–S1 1.21, HS3–S3 1.37, HS4–S4 1.19(7). Bond angles (°): Ru1–S1–Ru2 86.7(2), Ru1–S2–Ru2 86.1(2), Ru1–S3–Ru2 87.1(2).

In order to establish the molecular structure of **1**, X-ray structure determination was applied to a crystal of **1** containing solvated THF. A perspective drawing of the molecule is given in Fig. 1. The two ruthenium atoms have a distorted octahedral coordination and are linked by three bridging mercapto groups. A terminal mercapto ligand is bonded to Ru2. Remaining coordination sites are occupied by five PMe_2Ph ligands.

The phenyl groups of the three phosphines coordinated to Ru1 are situated in positions close to the bridging mercapto groups, and the plane of each phenyl group faces toward the bridging mercapto group. These structural features suggest the existence of attractive interaction between the SH group and π-electrons of the phenyl group. Probably the mercapto hydrogen interacts with the π-electrons in a manner similar to the common CH/π and OH/π interactions [6, 7], which have usually been observed by means of IR and NMR spectroscopy [8, 9]. Such interactions are regarded as the origin of unusual selectivity of some reactions and the unique structure of some compounds [10, 11]. Actually, the difference map reveals that the hydrogens of the two bridging mercapto groups HS1 and HS3 are located near the phenyl carbon atoms of the phosphine ligands coordinated to Ru1. As illustrated in Fig. 2, the distances of the phenyl planes to the nearest mercapto hydrogen atoms are 2.69 and 2.63 Å, respectively. These distances are small when van der

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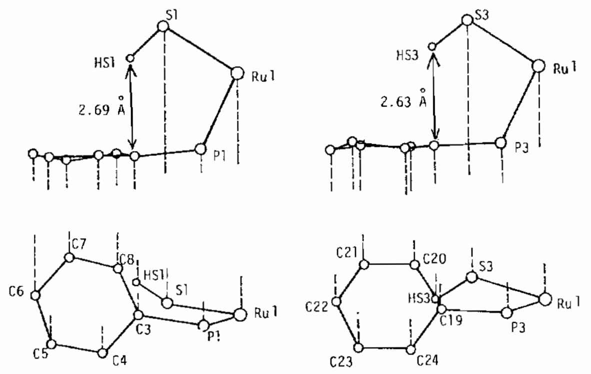

Fig. 2. Geometries of SH/π contacts projected on each phenyl plane (lower figures) and its side view (upper figures).

Waals radii of hydrogen and phenyl carbon atoms are considered.

A similar positional relationship of mercapto ligand and a phenyl plane is observed in the structure of $Rh(SH)(CO)(PPh_3)_2$ [12], although except for unusually short distances between the mercapto hydrogen and phenyl carbons, these structural features are not mentioned in that paper. Short contact distances between the sulfur atom and carbon atoms of phenyl rings are also reported in the structure of $[(ppp)Fe(\mu\text{-}SH)_3Fe(ppp)]^+$ (ppp = bis[2-(diphenylphosphino)ethyl] phenylphosphine) [13]. Presumably in these cases a similar SH/π interaction exists. This suggests that the bondings HS–M–P–Ph (M = Fe, Ru and Rh) satisfy structural demands for SH/π interaction and that the hydrogen of the mercapto ligand in the complexes of transition metal groups 8–10 has an adequate electronic density to form attractive interaction with π-electrons of phenyl groups.

Crystal data for $C_{40}H_{59}P_5S_4Ru_2 \cdot C_4H_8O$ (crystallized from THF–Et_2O at –20 °C) is as follows: orthorhombic, space group $P2_12_12_1$, a = 19.789(1) Å, b = 22.384(1) Å, c = 11.379(1) Å, V = 5040.4(4) Å^3, $Z = 4$, λ(Cu Kα) = 1.54184 Å. The structure was solved by direct method and heavy atom technique and refined by least-squares method to R = 0.083 (R_w = 0.088) for 3025 reflections with $F > 3\sigma(F_o)$, collected on a Rigaku automated four-cycle diffractometer. No absorption correction was made. Anisotropic temperature factors were applied for non-hydrogen atoms. Positions of mercapto hydrogens HS1, HS3 and HS4 are obtained reasonably well from the difference map. Calculated positions were applied to phenyl hydrogens. Positions of the hydrogens were not refined further, but were included in the structure calculations*.

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*Listings of positional and thermal parameters and observed and calculated structural factors are available on request from the authors.