CHEMISTRY LETTERS, pp. 2389-2392 1992.

Syntheses and Characterizations of Mono- and Binuclear Ruthenium(II) Compounds with Mercapto Ligands

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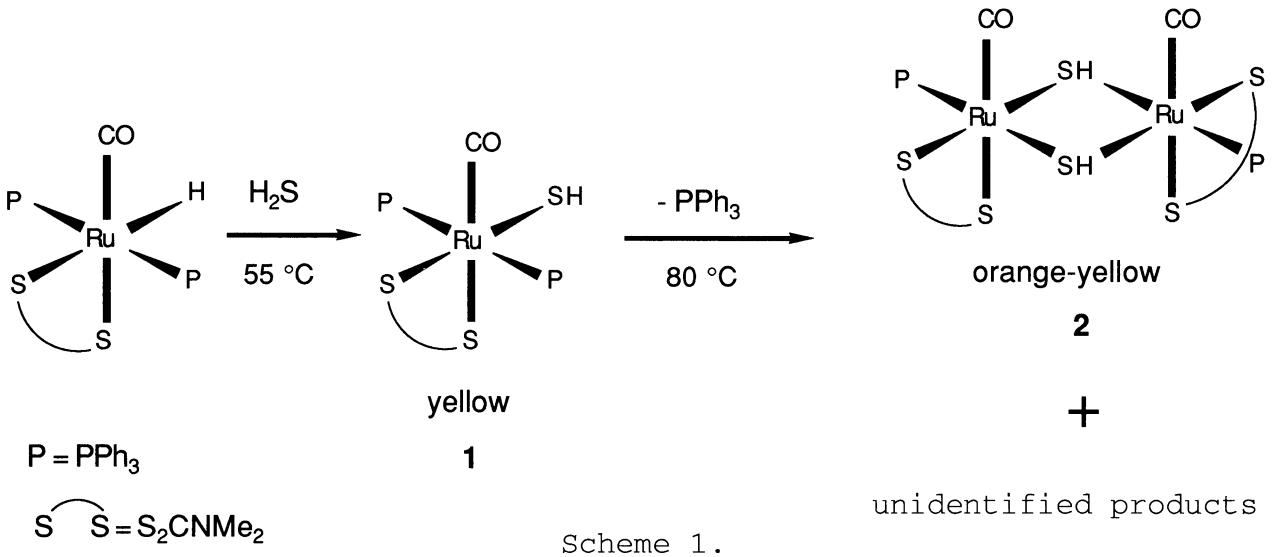
Mono- and binuclear ruthenium compounds with mercapto ligands were stepwise synthesized from hydrogen sulfide and [Ru(II)H(S_2CNMe_2)(CO)(PPh_3)$_2$]. The molecular structures were determined by X-ray crystallography. These compounds are unstable to air.

Transition-metal compounds with H_2S, HS^-, and S^{2-} ligands have received considerable attention, because of both industrial and biological interests.[1] In contrast to the numerous and often stable compounds with S^{2-} ligands, compounds with the HS^- and H_2S ligands are rare and labile, due to the high reactivity of HS^- and H_2S ligands leading to fast consecutive reactions.[1b] Among the previously reported ruthenium HS^- and H_2S compounds, [Ru(II)(SH_2)(PPh_3)'S_4'] ('S_4'$^{2-}$ = 1,2-bis[(2-mercaptophenyl)thio]-ethane(2-))[2] and [($PhMe_2P$)$_3$Ru(II)(μ-SH)$_3$Ru(II)-(SH)(PMe_2Ph)$_2$][3] have recently been characterized for the first time by X-ray crystallography. We succeeded in the stepwise syntheses of a mononuclear ruthenium compound, trans(P)-[Ru(II)(SH)(S_2CNMe_2)(CO)(PPh_3)$_2$] (**1**) and a binuclear ruthenium compound, [Ru(II)(μ-SH)(S_2CNMe_2)(CO)(PPh_3)]$_2$ (**2**). The syntheses, the properties and the crystal structures of these mono- and binuclear ruthenium compounds are reported in this paper.

Compounds **1** and **2** can be stepwise prepared by the reaction of [Ru(II)H(S_2CNMe_2)(CO)(PPh_3)$_2$][4] with H_2S in N_2 as shown in Scheme 1. [RuH(S_2CNMe_2)(CO)(PPh_3)$_2$] (1 g) in 50 cm^3 of benzene reacted with bubbling H_2S at 55 °C for 1 h to produce an orange-yellow solution which was filtered, and 100 cm^3 of ether was added to the filtrate. Yellow powder of **1** was obtained and was recrystallized from dichloromethane/ether to be obtained as yellow crystals in 80% yield.[5] Similarly, [RuH(S_2CNMe_2)(CO)(PPh_3)$_2$] reacted with bubbling H_2S at 80 °C in benzene for 3 h to give **2** and unidentified minor products. Compound **2** was recrystallized from dichloromethane/ether to be obtained as orange-yellow crystals in 70% yield.[6] Compound **2** can also be obtained by refluxing the



Scheme 1.

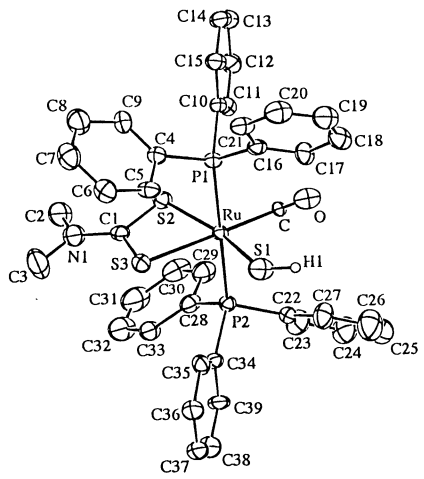


Fig. 1. Structure of **1**.

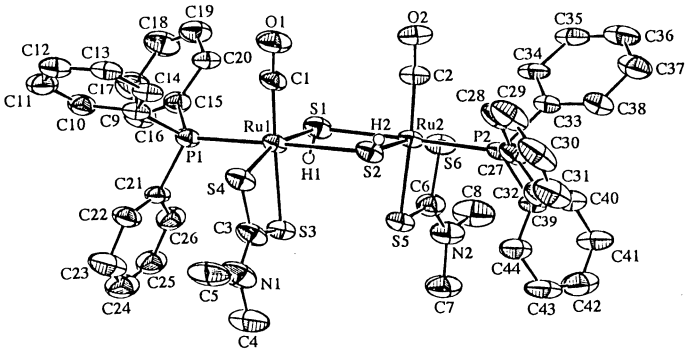


Fig. 2. Structure of **2**.

benzene solution of **1** for 2 h. The reactions can be monitored by silica-gel thin-layer chromatography. These compounds are unstable to air even in solid state. The orange-yellow reaction solution becomes yellowish-brown when it is oxidized.

The molecular structures of **1**[7] and **2**[8] were determined by X-ray crystallography (Figs. 1 and 2). Structures of **1** and **2** could not be well-refined due to poor quality of the crystals and the existence of disordered solvent molecules in the crystal lattices. These solvent molecules are sufficiently separated from the ruthenium compounds and there is no interaction such as hydrogen bondings between them. The PPh_3 groups of **1** are trans to each other and the same trans configuration of the two PPh_3 groups in solution was confirmed by a single singlet signal of $^{31}P\{^1H\}$ NMR

spectrum at 41.1 ppm.[9] The CO asymmetric stretches of **1** are observed at 1936 and 1926 cm^{-1} (KBr). The CO groups of **2** (ν(CO) = 1950 cm^{-1} (KBr)) are coordinated to Ru atoms perpendicularly from the same side of the Ru1Ru2S1S2 plan and the $^{31}P\{^{1}H\}$ NMR spectrum shows a singlet signal at 49.3 ppm. Although some isomers of **2** may exist in the reaction solution, they have not yet been obtained. The results of NMR and IR spectra indicate that the electron density on the ruthenium atom of **1** is slightly larger than that of **2**. The Ru-Ru bond distance (3.672(2) Å) of **2** reveals that there is no metal-metal interaction. The distance is longer than that of the triply bridged compound, $[(PhMe_2P)_3Ru(II)(\mu\text{-}SH)_3Ru(II)(SH)(PMe_2Ph)_2]$ (3.371(3) Å),[3] and is slightly shorter than that of the doubly bridged compound, $[\{Ru(II)(\mu\text{-}SC_6H_5)(bpy)_2\}_2]^{2+}$ (3.785(1), 3.771(1) Å), if compared to other thiolate bridged compounds without metal-metal bonds.[10] The Ru-S_t (terminal, 2.442(4) Å) bond distance of **1** and the Ru-S_b (bridge, 2.423 - 2.481 Å) of **2** are similar to those of $[(PhMe_2P)_3Ru(\mu\text{-}SH)_3Ru(SH)(PMe_2Ph)_2]$ (Ru-S_t, 2.440(7) Å; Ru-S_b, 2.455 - 2.473 Å). The Ru-P distances of **1** and **2** are normal for Ru(II) compounds.

The cyclic voltammetry of **1** and **2** revealed redox waves as follows: **1**, 0.56 V (E_{pa}, irr.), 0.60 V (E_{pc}, irr.) and 0.86 V (E_{pa}, irr.); **2**, 0.56 V (E_{pa}, irr.), ≈1.1 V (E_{pa}, irr.) vs. SCE (irr. = irreversible).[11] The reactivities of **1** and **2** will be reported separately.

References

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4) P. B. Critchlow and S. D. Robinson, *J. Chem. Soc., Dalton*, **1975**, 1367.

5) Satisfactory results of elemental analysis could not be obtained due to the lability of **1**. Anal. Found: C, 58.73; H, 5.10; N, 1.80%. Calcd for $C_{40}H_{37}NOP_2RuS_3$: C, 59.54; H, 4.62; N, 1.74%. ν(CO) = 1936, 1926 cm^{-1}; ν(CN) = 1518 cm^{-1} (KBr).

6) Anal. Found: C, 45.81; H, 4.14; N, 2.44%. Calcd for $C_{45}Cl_2H_{46}N_2O_2P_2Ru_2S_6$: C, 46.03; H, 3.95; N, 2.39%. ν(CO) = 1950 cm^{-1}; ν(CN) = 1518 cm^{-1} (KBr).

7) Crystal data for $[Ru(SH)(S_2CNMe_2)(CO)(PPh_3)_2]\cdot C_2H_5OC_2H_5$ at 23 °C: F.W.

= 881.06, monoclinic, space group $P2_1/c$, a = 10.093(1) Å, b = 19.511(2) Å, c = 21.999(3) Å, β = 96.96(1)°, V = 4300.4(9) Å^3, Z = 4, ρ_{calcd} = 1.36 g cm^{-1}, μ = 6.09 cm^{-1}. A total of 8135 reflections were collected in the range of $4° < 2\theta < 50°$ (±h, k, l) on a Rigaku automatic four cycle diffractometer, AFC-5R. The programs SHELXS 76 and 86 were used for data reduction and structure refinement of **1** and **2**. Of these 6292 were unique, and 3784 with $F_o > 4.00\sigma(F_o)$ were used in the structure solution. R(F) = 0.076, $R(F_w)$ = 0.070 ($w = 1/(\sigma(F)^2 + 0.000991F^2)$). All non-hydrogen atoms except those of diethyl ether were anisotropically refined. Non-hydrogen atoms of diethyl ether were isotropically refined. The positions of the SH hydrogen atoms were located by difference Fourier synthesis in the final step and were not refined. Selected bond distances (Å) and angles (deg): Ru-S1, 2.442(4); Ru-S2, 2.441(3); Ru-S3, 2.477(3); Ru-P1, 2.374(3); Ru-P2, 2.389(3); Ru-C, 1.983(13); C-O, 0.885(13); S2-Ru-S3, 70.4(1); S1-Ru-S2, 165.2(1). The CO group could not be well refined, so the Ru-C distance seems too long and the C-O distance too short for the value of ν(CO).

8) Crystal data for $[Ru(\mu\text{-}SH)(S_2CNMe_2)(CO)(PPh_3)]_2 \cdot CH_2Cl_2$ at 23 °C: F.W. = 1174.23, triclinic, space group $P\bar{1}$, a = 14.833(3) Å, b = 16.420(3) Å, c = 13.225(2) Å, α = 119.97(1)°, β = 97.00(2)°, γ = 63.78(1)°, V = 2676.1(9) Å^3, Z = 2, ρ_{calcd} = 1.44 g cm^{-1}, μ = 9.57 cm^{-1}. A total of 9922 reflections were collected in the range of $4° < 2\theta < 50°$ (±h, -k, ±l). Of these 8030 were unique, and 5349 with $F_o > 5.00\sigma(F_o)$ were used in the structure solution. R(F) = 0.067, $R(F_w)$ = 0.077 ($w = 1/(\sigma(F)^2 + 0.005098F^2)$). All non-hydrogen atoms except dichloromethane were anisotropically refined. Non-hydrogen atoms of dichloromethane were isotropically refined. The positions of the SH hydrogen atoms were located by difference Fourier synthesis in the final step and were not refined. The selected bond distances (Å) and angles (deg): Ru1-Ru2, 3.672(2); Ru1-S1, 2.423(4); Ru1-S2, 2.481(4); Ru2-S1, 2.452(4); Ru2-S2, 2.426(4); Ru1-P1, 2.333(4); Ru2-P2, 2.336(4); Ru1-S3, 2.479(3); Ru1-S4, 2.419(4); Ru2-S5, 2.478(3); Ru2-S6, 2.422(4); Ru1-C1, 1.861(12); Ru2-C2, 1.842(11); S1-Ru1-S2, 82.4(1); S1-Ru2-S2, 82.9(1).

9) NMR spectra were measured in CD_2Cl_2 (85% H_3PO_4 as the external standard).

10) Two kinds of $[\{Ru(\mu\text{-}SC_6H_5)(bpy)_2\}_2]^{2+}$ exist in the unit cell. M. A. Greaney, C. L. Coyle, M. A. Harmer, and E. I. Stiefel, *Inorg. Chem.*, **28**, 912 (1989).

11) Scan rate, 100 mV s^{-1}; in CH_2Cl_2-0.2 mol dm^{-3} n-Bu_4NClO_4; working electrode, Pt plate; counter electrode, Pt wire; $F_c^{0/+}$ = 0.50 V vs. SCE, $E_{pa} - E_{pc}$ = 200 mV (F_c = ferrocene).

(Received August 24, 1992)