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Synthesis and X-ray Structure of an H_2S Complex, $RuCl_2$(P-N)(P(*p*-tolyl)$_3$)(SH_2) (P-N = *o*-(Diphenylphosphino)-*N*,*N*-dimethylaniline)

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The interaction of transition metal complexes with H_2S continues to attract attention. Such chemistry is of relevance in the biological sulfur cycle, in the formation of ores, in hydrodesulfurization catalysis, and in the use of H_2S as a source of H_2 and elemental sulfur (or organosulfur compounds). Literature dealing with these topics is plentiful and can be traced through recent references.[1,2] However, isolation and characterization of metal complexes containing H_2S remain challenging,[2,3] as such species tend to undergo oxidative addition reactions to give products with SH ligands or bridged or terminal sulfide,[4] and only recently has an H_2S complex been characterized crystallographically.[2] This was the structure reported by Sellmann *et al.* of the Ru(II)-complex $Ru(SH_2)(PPh_3)$('S_4')·THF ('S_4' = 1,2-bis[(2-mercaptophenyl)thio]ethane(2−)) formed by the reaction of the polymeric complex $[Ru(PPh_3)('S_4')]_x$ with liquid H_2S at −70 °C; the reaction with H_2S gas at room temperature in THF resulted in a mixture of the bridging sulfide complex $[(\mu\text{-}S_2)\{Ru(PPh_3)('S_4')\}_2]$ and other uncharacterized products depicting the more typical reactivity of H_2S with transition metal complexes.[2]

We report here the synthesis, isolation, and spectroscopic and X-ray structural characterization of a Ru(II)−H_2S complex, $RuCl_2(P\text{-}N)(PR_3)(SH_2)$, **2b**, where P-N is *o*-(diphenylphosphino)-*N,N*-dimethylaniline and R = *p*-tolyl (eq 1); spectroscopic evidence for complex **2a** is also presented. To our knowledge, this is the first example of a structurally characterized transition metal−H_2S complex formed under ambient conditions.

$$\begin{array}{ccc} \mathrm{RuCl_2(P\text{-}N)(PR_3)} & \underset{\mathrm{Ar}}{\overset{\mathrm{H_2S}}{\rightleftharpoons}} & \mathrm{RuCl_2(P\text{-}N)(PR_3)(SH_2)} \\ \mathbf{1a},\ \mathrm{R = Ph} & & \mathbf{2a},\ \mathrm{R = Ph} \\ \mathbf{1b},\ \mathrm{R} = p\text{-tolyl} & & \mathbf{2b},\ \mathrm{R} = p\text{-tolyl} \end{array} \qquad (1)$$

Experimental procedures were carried out under N_2 or Ar using standard Schlenk techniques. Reagent grade C_6H_6, hexanes, and THF were distilled from Na/benzoquinone under N_2 and were deoxygenated by freeze−thaw−pump cycles prior to use; $CDCl_3$ (Merck Frosst Canada) was dried over activated molecular sieves (Fisher 4A) and stored under Ar. Purified H_2S (Matheson) was used as supplied. The precursors, 5-coordinate complexes **1a**,**b**, were made as described previously.[5] Solution NMR spectra were recorded on a Varian XL300 spectrometer (121.4 Mhz for $^{31}P\{^1H\}$) using TMS or PPh_3 (δ_P −5.59 in $CDCl_3$ vs 85% H_3PO_4) as external references, with positive shifts implying lower fields; δ_P shifts are reported relative to the H_3PO_4. IR spectra (Nujol mulls between KBr plates) were recorded on a Bomem MB-102 FT spectrometer.

Note that H_2S is extremely toxic and all experimentation involving this reagent should be carried out in a well-ventilated fume hood!

For the preparations of $RuCl_2(o\text{-}Ph_2PC_6H_4NMe_2)(PR_3)(SH_2)$ (R = Ph, 2a; R = *p*-tolyl, 2b), H_2S gas (2 mL) was injected into a solution of $RuCl_2(P\text{-}N)(PR_3)$ (**1a** or **1b**, 0.06 mmol) in C_6H_6 (1 mL). Hexanes (10 mL) were added to the resultant red solution under Ar, and the mixture was stirred for 15 min. The yellow product (**2a** or **2b**) was filtered off and dried under vacuum overnight (95% yield). Complex **2b** was also prepared in 100% yield by reacting 0.03 mmol of powdered, solid **1b** with H_2S gas (1 atm) at ∼20 °C; the initally green solid turned yellow within 1 min, and the mixture was "stirred" for a further 2 h. Acceptable elemental analysis was obtained only for **2b**. Anal. Calcd for $C_{41}H_{43}Cl_2NP_2SRu$: C, 60.37; H, 5.31; N, 1.72; S, 3.93. Found: C, 60.62; H, 5.33; N, 1.67; S, 4.25. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C, under 1 atm H_2S) [δ_A, δ_X (^2J Hz)]: **2a**, 48.91, 42.82 (30.1); **2b**, 50.31, 40.91 (30.3). ^1H NMR ($CDCl_3$, 293 K, under 1 atm H_2S). **2a**, δ 1.05 (br, 2H, Ru−S*H₂*), 2.97 (s, 3H, N−Me), 3.66 (s, 3H, N−Me), 6.50−8.40 (m, 26H, aromatic); **2b**, δ 0.95 (br, 2H, Ru−SH_2), 2.15 (s, 9H, Me of *p*-tolyl), 3.05 (s, 3H, N−Me), 3.41 (s, 3H, N−Me), 6.35−8.10 (m, 26H, aromatic). Each spectrum also shows a singlet at δ 0.75 due to free H_2S. Red-brown crystals of **2b** were grown by layering a THF solution of the complex with hexanes.

Crystallographic data for $RuCl_2(o\text{-}Ph_2PC_6H_4NMe_2)[P(p\text{-}tolyl)_3](SH_2)$ (**2b**) are given in Table 1. Measurements were collected on a Rigaku AFC6S diffractometer at 294 K. The final unit-cell parameters were obtained by least-squares analysis on the setting angles for 21 reflections with $2\theta = 10.60-17.20$. The intensities of 3 representative reflections, measured every 200 reflections throughout the data collection, decayed uniformly by 23.7%, and a polynomial correction factor was applied. The structure was solved by conventional heavy atom methods, the coordinates of the Ru atom being determined by the Patterson function and those of the remaining non-hydrogen atoms from a subsequent Fourier synthesis. The asymmetric unit contains a partially occupied water site on a 2-fold axis and a THF solvent site disordered about a 2-fold axis. Only one of the H_2S protons could be located. Solvent hydrogens were not included in the model. Calculations were performed using a TEXSAN/TEXRAY structure analysis package (Molecular

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Table 1. Crystallographic Data

compd	$RuCl_2(o\text{-}Ph_2PC_6H_4NMe_2)[P(p\text{-}MeC_6H_4)_3]\text{-}(SH_2)\cdot 0.5THF\cdot 0.41H_2O$
formula	$C_{43}H_{47.82}O_{0.91}Cl_2NP_2RuS$
fw	859.22
cryst system	tetragonal
space group	$I4_1/a$ (No. 88)
a, Å	20.587(7)
c, Å	38.51(1)
V, Å^3	16322(9)
Z	16
ρ_{calc}, g/cm^3	1.398
T, °C	21
radiation	Mo
μ, cm^{-1}	6.8
R(F)	0.048
$R_w(F)$	0.057

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o^2)]^{1/2}$.

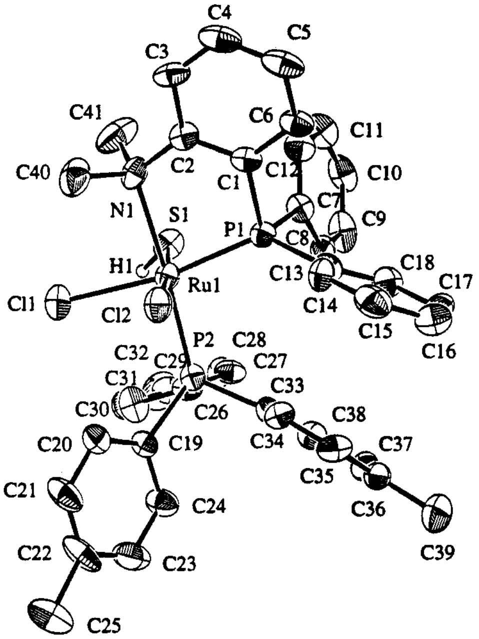

Figure 1. ORTEP plot of **2b** (H atoms omitted for clarity). Thermal ellipsoids for non-hydrogen atoms are drawn at 33% probability.

Structure Corp., 1985). The final *R* and R_w values were 0.048 and 0.057, respectively, for 2365 reflections with $I \geq 2.0\sigma(I)$. Selected bond lengths and bond angles appear in Table 2 (Supporting Information). Complete tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, torsion angles, intermolecular contacts, and least-square planes are included as Supporting Information.

Interaction of the 5-coordinate species $RuCl_2(P\text{-}N)(PR_3)$ (**1**)[5] with 1 atm of H_2S in benzene, $CHCl_3$, or THF solution at 20 °C leads to rapid and quantitative formation of the H_2S species **2**; the reactions are reversible in solution if H_2S is removed by vacuum or by purging the system with Ar (see below). The complexes (**2**) were isolated as air-sensitive, yellow powders by the addition of hexanes and drying under vacuum (95% yield); **2b** was also formed quantitatively by reacting solid **1b** with 1 atm of H_2S at 20 °C, although surprisingly **1a** did not react with H_2S under corresponding conditions.

X-ray analysis of **2b** reveals a close to octahedral geometry around the Ru with *cis*-chlorides and the H_2S *trans* to a chloride (Figure 1). The *trans* bond angles are in the range 170.0–174.6°, and the *cis* angles range from 81.3 to 94.3°. The chelate bite angle P(1)–Ru–N(1) of 81.3° is similar to that found in **1b** (81.81°).[5] Only one H atom of the coordinated H_2S was located in the structure which thus erroneously portrays a Ru(III)–mercapto complex, but the structural parameters, observed diamagnetism, reversible solution behavior, and spectroscopic evidence for coordinated H_2S ligand show the complex to be the Ru(II)–H_2S adduct. The Ru–S bond length of 2.330(4) Å is comparable to that of Sellmann's complex (2.399(5) Å)[2] and is significantly shorter than that of terminal mercapto complexes (average Ru–SH, 2.46 Å).[1c,6] The length of the located S–H bond (1.25 Å) is shorter than that found in gaseous H_2S (1.33 Å)[7] and is in the range reported for Sellmann's complex (average 1.20 Å).[2] The Ru–Cl(1)(trans to phosphorus) (2.469 Å) and Ru–Cl(2)(trans to sulfur) (2.429 Å) distances are typical of those of related Ru(II) complexes[6,8] and are longer than those in the corresponding Ru(III) species, *mer*-$RuCl_3(P\text{-}N)(PPh_3)$: 2.40 Å (trans to phosphorus) and 2.33 Å (for mutually trans chlorines).[9] The stability of the crystals of **2b** is unparalleled; the crystal stability of Sellman's H_2S complex results from intermolecular H-bonds between the H_2S ligand and both a S-atom of the macrocyclic ligand and a THF solvate, the solvent-free complex being labile and not characterizable crystallographically.[2] In **2b**, there are no such stabilizing interactions with the coordinated H_2S.

The ^1H NMR data reveal the coordinated H_2S and strong ν_{SH} IR bands at 2506 and 2476 cm^{-1} (**2a**) and 2495 and 2449 cm^{-1} (**2b**) compare with those of 2410 and 2290 cm^{-1} of Sellman's complex which are lower because of the presence of the S–H···S and S–H···O hydrogen bridges. Unlike previously reported H_2S complexes, **2a**,**b** are fairly stable as solids under Ar and do not lose H_2S under vacuum over 24 h at ambient temperature, but they rapidly decompose to uncharacterized black solids when exposed to air.

In C_6D_6 solution under Ar, **2a,b** reversibly lose H_2S, and integrations of the NMR data yield, for example, a value of ~ 30 M^{-1} at 20 °C for the associative equilibrium constant for the reaction **1b** + H_2S = **2b**.

Species **1** are highly reactive generally toward small molecules; we have reported on the η^2-H_2 and η^1-N_2 derivatives[5] and will report elsewhere on the binding of O_2, CO, H_2O, SO_2, CH_3OH, and C_2H_5SH.[9]

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Supporting Information Available: Table 2 (bond lengths and angles) and tables of crystallographic data, atomic coordinates and equivalent isotropic thermal parameters, hydrogen atom parameters, anisotropic thermal parameters, complete bond lengths and angles, torsion angles, intermolecular contacts, and least-square planes for the structure of **2b** (12 pages). Ordering information is given on any current masthead page.

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