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S-H Stretching Frequencies in Ruthenium Mercaptan Complexes and the Crystal and Molecular Structures of [CpRu(PPh₃)₂(s-C₄H

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The S-H Stretching Frequencies in Ruthenium Mercaptan Complexes and the Crystal and Molecular Structures of

$[\text{CpRu}(\text{PPh}_3)_2(\text{s-C}_4\text{H}_9\text{SH})]\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$ and $[\text{CpRu}(\text{PPh}_3)_2(\text{i-C}_4\text{H}_9\text{SH})]\text{BF}_4 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$.

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The S-H IR stretching frequency appears as a weak absorption between 2600 and 2400 cm^{-1} . With the advent of Fourier Transform Infrared spectrophotometers, the researcher is better able to observe this resonance. To examine the effect of coordination on the S-H stretching frequencies of organic thiols, we have prepared a series of Ru-mercaptan complexes of the general formula $[\text{CpRu}(\text{PPh}_3)_2(\text{RSH})]\text{BF}_4$, where R = n-propyl, isopropyl, - $\text{CH}_2\text{CH}_2\text{SH}$, n-butyl, isobutyl, and s-butyl. The crystal structures of the s-butyl- and isobutylthiol complexes, $[\text{CpRu}(\text{PPh}_3)_2(\text{s-C}_4\text{H}_9\text{SH})]\text{BF}_4$ and $[\text{CpRu}(\text{PPh}_3)_2(\text{i-C}_4\text{H}_9\text{SH})]\text{BF}_4$ will also be presented.

The general synthesis of the $[\text{CpRu}(\text{PPh}_3)_2(\text{RSH})]\text{BF}_4$ complexes follows. A 0.2120 g (0.29 mmol) sample of $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ was dissolved in 30 mL of CH_2Cl_2 and 5 mL of the thiol was added. In a darkened room, excess (0.1 g, 0.5 mmol) AgBF_4 was added to the solution while stirring. After 15 min., the solution was concentrated to dryness under vacuum. The yellow material was dissolved in 20 mL of CH_2Cl_2 and the solution was filtered through Celite (Aldrich Chemical Company, cat. no. 16,743-6). The filtrate was concentrated to dryness, and the residue after recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexanes}$ gave a yellow microcrystalline product.

The Ru-mercaptan complexes are moisture sensitive, even in the solid state. All six compounds were characterized by single crystal X-ray diffraction studies. The isopropyl and ethanedithiol complexes were crystallographically disordered and were characterized by elemental analysis and ^1H NMR, respectively. The n-butyl compound gave poor quality crystals, but refinement showed atom connectivity in the complex ($R = 0.13$).

The structure of the $[\text{CpRu}(\text{PPh}_3)_2(\text{s-C}_4\text{H}_9\text{SH})]\text{BF}_4$, **1**, complex was determined by X-ray diffraction techniques: triclinic space group $P\bar{1}$, $a = 13.229$ (3), $b = 13.213$ (8), $c = 14.717$ (6) Å, $\alpha = 66.87$ (4), $\beta = 84.24$ (3), $\gamma = 69.86$ (4)°, $Z = 2$, $R = 0.048$, $R_w = 0.061$. The $[\text{CpRu}(\text{PPh}_3)_2(\text{i-C}_4\text{H}_9\text{SH})]\text{BF}_4$, **2**, complex crystallized in the triclinic space group $P\bar{1}$, $a = 14.029$ (6), $b = 14.323$ (8), $c = 12.245$ (4) Å, $\alpha =$

69.43 (3), $\beta = 84.35$ (3), $\gamma = 98.23$ (4)°, $Z = 2$, $R = 0.049$, $R_w = 0.077$.

Crystals of **1** were grown by the slow diffusion of hexane into a CH_2Cl_2 solution of **1**. Data were collected on a Snytex P3 automated diffractometer (Mo $K\alpha 1$, $\lambda = 0.71069$ Å) using a variable scan rate and a Θ - 2Θ scan mode to a maximum 2Θ value of 60.0° . Data were corrected for Lorentz, polarization, absorption and background effects. Observed reflections (4302, $I.3.0\sigma(I)$) were used for the solution of the heavy atom positions by direct methods. Refinement of scale factor, positional and anisotropic thermal parameters for all atoms was carried out to convergence. Disorder of the BF_4 group became apparent and was accounted for with one fluorine atom in a full occupancy position and the six others in 50% occupancy positions. The 50% occupancy of the CH_2Cl_2 group was estimated from temperature parameters. Hydrogen atoms of the cyclopentadienyl ring and the CH and CH_2 groups of the isobutyl substituent were located from a difference Fourier synthesis. Phenyl hydrogen atoms were placed in positions calculated using idealized geometry and a C-H distance of 0.97 Å. Hydrogens of the methyl groups and of the methylene chloride were not located. Final cycles of least squares refinement were completed with anisotropic thermal parameters for all atoms, leading to a final agreement factor, $R = 0.049$, ($R = \sum |F_o| - |F_c| / \sum |F_o|$). In the final stages of refinement a weight of $1/\sigma(F)^2$ was used. $R_w = 0.077$.

Crystals of **2** were grown by the slow diffusion of pentane into a CH_2Cl_2 solution of **2**. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo $K\alpha$ radiation. A linear correction factor was applied to the data to account for the decay. Data were collected using the ω - 2Θ scan technique to a maximum 2Θ value of 40.0° . The data were corrected for Lorentz and polarization effects and an analytical absorption correction was applied.

The structure was solved by direct methods and

refined by full matrix least-squares. The final cycle of the full matrix least-squares refinement was based on 3294 observed reflections ($I > 3.00 \sigma(I)$) and 467 parameters and converged with $R = 0.048$, $R_w = 0.061$. The hydrogen atoms were constrained to idealized positions ($C-H = 0.95 \text{ \AA}$) except for the H atom attached to the S, which is reported at a position indicated on a difference map, however the peak height of the position was comparable to the general noise level on the final difference map. The position is supported however by the reasonable bond angles it generates. The overall quality of the final refinement was negatively effected by three regions of disorder: the BF_4 anion, which was modeled by one F of occupancy factor 1.00, three at 0.75 and three at 0.25; the solvent molecule which exhibited large thermal motion; and the butyl group, the terminal C atoms also showing large thermal motion (this could explain the short C44-C45 distance of 1.13 \AA). The atoms of these three regions were refined with isotropic thermal factors, while all other non-hydrogen atoms were refined anisotropically.

The dechlorination of $CpRu(PPh_3)_2Cl$ with $AgBF_4$ in the presence of the organic thiol leads to the formation of moisture sensitive, yellow products in moderate to good yields. In all cases, the IR spectrum shows a change in the S-H stretch from the free (unbound) mercaptan to the coordinated mercaptan (Table 1). The ν_{SH} stretch for the $Cr(CO)_5(t\text{-butylSH})$ compound has been assigned to a peak at 2555 cm^{-1} (Darensbourg et al., 1990). The change in the S-H stretching frequency appears to be a function of steric bulk; the smaller straight-chain R groups, n-propyl and $-CH_2CH_2SH$, show a smaller change in frequency than the larger t-butyl, phenethyl and benzyl R groups. Conroy-Lewis and Simpson (1991) have prepared two Ru-t-butyl mercaptan complexes, $[CpRu(dppm)(t\text{-}C_4H_9SH)]PF_6$ and $[CpRu(PPh_3)(t\text{-}C_4H_9NC)(t\text{-}C_4H_9SH)]PF_6$. The S-H stretch was too weak to be observed in the dppm complex. In $[CpRu(PPh_3)(t\text{-}C_4H_9NC)(t\text{-}C_4H_9SH)]PF_6$, the ν_{SH} is 2544 cm^{-1} .

The structures of 1 and 2 show the Ru atom bound to the Cp, two P atoms of the PPh_3 ligands and the S of the isobutyl mercaptan (Fig. 1) or s-butyl mercaptan (Fig. 2). The Ru-S distances of $2.375(2)$ in 1 and $2.379(2) \text{ \AA}$ in 2 are similar to the Ru-S distance of $2.377(2) \text{ \AA}$ in $[CpRu(PPh_3)_2(n\text{-}C_3H_7SH)]BF_4$ (Amarasekera and Rauchfuss, 1989) but considerably shorter than the Ru-S distance of $2.396(2) \text{ \AA}$ in $[CpRu(PPh_3)_2(t\text{-}C_4H_9SH)]BF_4$ (Minick et al., 1993). The structure of $[CpRu(dppm)(t\text{-}C_4H_9SH)]PF_6$ shows a Ru-S distance of 2.371 \AA (Conroy-Lewis and Simpson, 1991). The S-H distance in 2 is 1.376 \AA . This is considerably longer than the same distance in $[CpRu(PPh_3)_2(n\text{-}C_3H_7SH)]BF_4$ (Amarasekera and Rauchfuss, 1989) and $[CpRu(PPh_3)_2(t\text{-}C_4H_9SH)]BF_4$ (Minick et al., in press) (1.25 and $1.289(2) \text{ \AA}$, respectively). The S-H distance in $Cr(CO)_5(t\text{-}butylSH)$ is $1.2(1) \text{ \AA}$

(Darensbourg et al., 1990).

Table 1. S-H Stretching Frequencies, ν , (cm^{-1}) and Force Constants, k , (mdynes/\AA)^a showing change upon coordination of thiols to $CpRu(PPh_3)_2^+$.

Mercaptan	Free	k	Bound	k
n-propyl	2560	3.773	2525	3.671
isopropyl	2558	3.767	2514	3.639
edt	2552	3.750	2519 (2568)	3.653 (3.797)
benzyl	2566	3.791	2512	3.633
phenethyl	2568	3.797	2515	3.642
n-butyl	2562	3.779	2517	3.648
isobutyl	2564	3.785	2515	3.642
s-butyl	2560	3.773	2512	3.633
t-butyl	2558	3.767	2504	3.610
$Cr(CO)_5(t\text{-}BuSH)$			2555 ^b	3.759
$[CpRu(PPh_3)(t\text{-}C_4H_9NC)(t\text{-}BuSH)]PF_6$			2544 ^c	3.726
$[CpRu(dppe)(phetSH)]BF_4$			2517	3.648

a) $\Delta E = (h/2\pi)(k/\mu)^{1/2}$, $\mu = 1.6227 \times 10^{-27} \text{ kg}$

b) Darensbourg, et al., 1990

c) Conroy-Lewis and Simpson, 1991

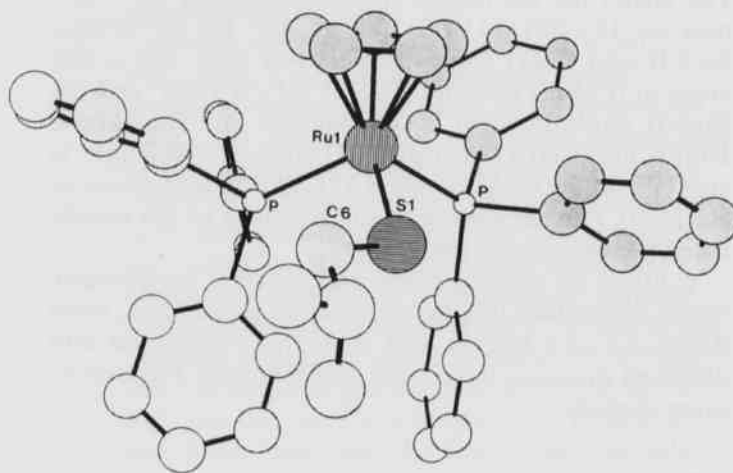


Fig. 1. Structure of the cation of $[CpRu(PPh_3)_2(i\text{-}C_4H_9SH)]BF_4 \cdot 1/2CH_2Cl_2$ showing coordination of $i\text{-}C_4H_9SH$. Selected bond distances (Å) and angles ($^\circ$): Ru1-S1 $2.375(2)$, S1-C6 $1.82(1)$, C6-S1-Ru1 $113.6(3)$.

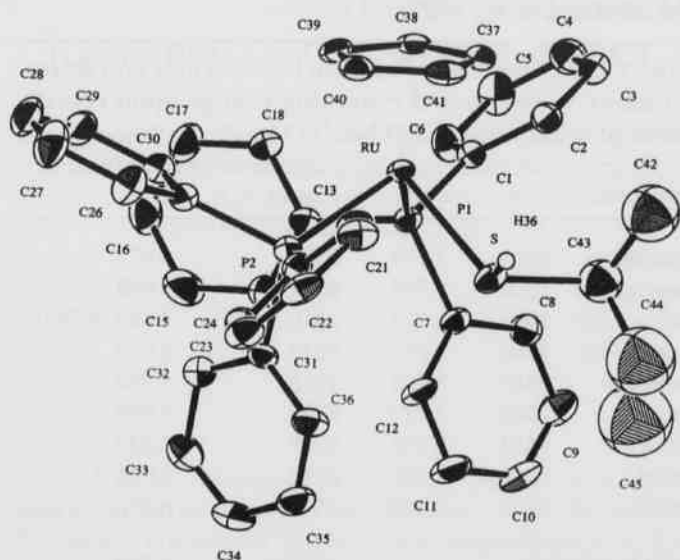


Fig. 2. Structure of $[\text{CpRu}(\text{PPh}_3)_2(\text{s-C}_4\text{H}_9\text{SH})]\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$ showing cation atom labeling scheme. Selected bond distances (Å) and angles ($^\circ$): Ru-S 2.379(2), S-C43 1.83(1), S-H36 1.376, C43-S-Ru 118.2(4), Ru-S-H36 106.37, C43-S-H36 98.24.

The angles about the S atom in 2 are 106.37° for Ru-S-H36, 98.24° for C43-S-H36 and $118.2(4)^\circ$ for Ru-S-C43. The angles for the $[\text{CpRu}(\text{PPh}_3)_2(\text{t-C}_4\text{H}_9\text{SH})]\text{BF}_4$ complex are $125.7(3)$, $111.7(1)$ and $91.9(3)^\circ$ for the C-S-Ru, Ru-S-H and C-S-H angles respectively [17]. The C-S-H angle in $[\text{CpRu}(\text{PPh}_3)_2(\text{n-C}_3\text{H}_7\text{SH})]\text{BF}_4$ is $99(3)^\circ$ and the Ru-S-H angle is $97(3)^\circ$ (Amarasekera and Rauchfuss, 1989). For $\text{Cr}(\text{CO})_5(\text{t-butylSH})$, the Cr-S-H angle is $106(1)^\circ$ and the Cr-S-C angle is $121.3(2)^\circ$ (Darensbourg et al., 1990). Further studies of the reactivity of the coordinated mercaptans are under way.

A listing of atomic coordinates, general temperature factor expressions (U), hydrogen atom coordinates, bond distances and angles and tables of calculated and observed structure factors are available from the authors upon request.

Acknowledgements

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Literature Cited

- Amarasekera, J. and T.B. Rauchfuss. 1989. Interconversion of persulfido, sulfur hydride, and hydride ligands coordinated to $\text{CpRu}(\text{PPh}_3)_2^+$ *Inorg. Chem.* 28:3875-3883.
- Conroy-Lewis, F.M. and S.J. Simpson. 1991. Molecular mercaptan (thiol) complexes: The synthesis of the tert-butylthiol complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Bu}^t\text{NC})(\text{Bu}^t\text{SH})]\text{PF}_6$ and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppm})(\text{Bu}^t\text{SH})]\text{PF}_6$ and the x-ray single crystal structure of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppm})(\text{Bu}^t\text{SH})]\text{PF}_6$ [dppm = bis(diphenylphosphino)methane]. *J. Chem. Soc., Chem. Commun.* 388-389.
- Darensbourg, M.Y., E.M. Longridge, V. Payne, J. Reibenspies, C.G. Riordan, J.J. Springs and J.C. Calabrese. 1990. Isolation of chromium(0) thols: Molecular structure of $(\text{Bu}^t\text{SH})\text{Cr}(\text{CO})_5$. *Inorg. Chem.* 29:2721-2726.
- Minick, D., J.W. Crump, M. Draganjac and A.W. Cordes. 1993. Crystal and molecular structure of $[\text{CpRu}(\text{PPh}_3)_2(\text{t-C}_4\text{H}_9\text{SH})]\text{BF}_4$. *J. Cryst. Spec. Res.*, 23:629-632.