The Chemistry of the Electron Rich Metallothiol $CpRu(PPh_3)_2SH$. The Interplay of SH, SH_2, and S_2 Ligands.

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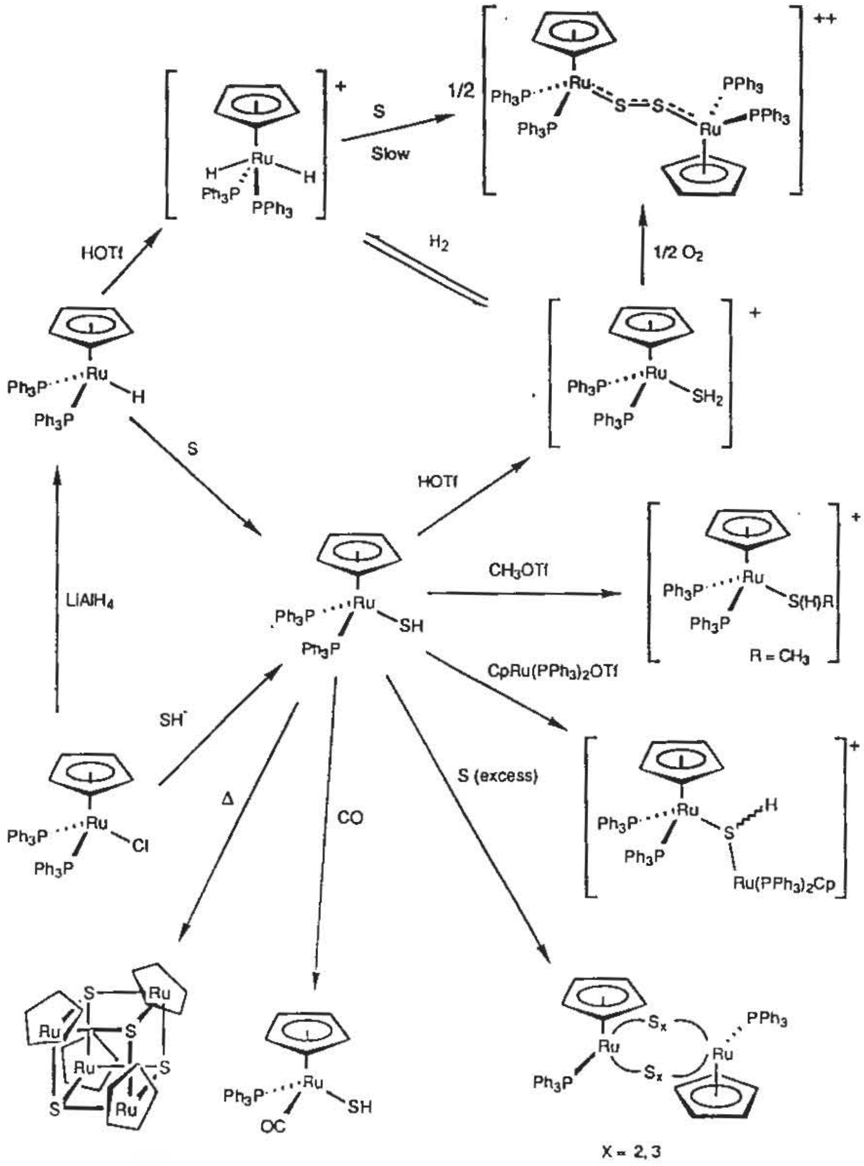
The hydrosulfide (-SH) functionality recurs throughout sulfur chemistry, and organic thiols are of immense importance in biological catalysis and organic synthesis [1,2]. The chemistry of metallothiols has been of interest due to the role of surface M-SH groups in metal sulfide hydrodesulfurization (HDS) catalysts. Our interest in ruthenium thiol compounds was also stimulated by the catalytic properties of RuS_2 [3,4].

In an effort to understand the reactivity of the ruthenium hydrosulfide functionality, we synthesized and characterized $CpRu(PPh_3)_2SH$ (1). The electron rich nature of $CpRu(PPh_3)_2SH$ is reflected in its reactivity. It easily undergoes protonation and alkylation to form H_2S and RSH complexes (Scheme). The H_2S complex is labile, and with hydrogen rapidly establishes an equilibrium with the dihydride complex $[CpRu(PPh_3)_2H_2]OTf$ [5]. In contrast to the unreactive parent chloride, $CpRu(PPh_3)_2Cl$, 1 undergoes complete monocarbonylation to $CpRu(PPh_3)(CO)SH$.



Most interestingly, 1 undergoes a two-electron oxidation to the bridging persulfide complex $[CpRu(PPh_3)_2]_2(\mu-S_2)^{2+}$ (2) [6]. In contrast, most metallothiols have been found to follow organic precedent and undergo net one-electron/metal oxidations. Well documented examples include the oxidation of $(MeCp)_2Ti(SH)_2$ by I_2 [7] and of $Cp_2Mo(SH)_2$ by S_8 [8]. Furthermore, the oxidation of 1 is promoted by acids whereas the oxidation of organic thiols is inhibited by acids.

The structural and electrochemical properties of the persulfide complex 2 are conveniently discussed in terms of a qualitative molecular orbital model wherein the frontier orbitals of the Ru_2S_2 core are treated as a trans-butadiene-like π-network. According to our analysis, the persulfide ligand serves as powerful π-donor to the ruthenium centers. The persulfide complex 2 can be easily reduced to the monocation **2r** but the electrically neutral analogue is too reducing to be isolated.

The oxidation of the ruthenium thiol 1 to the persulfide complex 2 occurs in two steps: coupling of the sulfur ligands followed by dehydrogenation. Our results definitely suggest that the oxidation of 1 does not involve the intermediacy of the thioruthenyl complex "$[CpRu(PPh_3)_2S]^+$". An attempt to generate this species from $CpRu(PPh_3)_2OTf$ by treatment with the sulfur transfer reagent thiirane resulted instead the first thiirane complex $[CpRu(PPh_3)_2(SC_2H_4)]^+$ [9]. This thiirane complex is an analogue of the extremely unstable episulfonium salts, i.e., $RSC_2H_4^+$ [10].

$CpRu(PPh_3)_2SH$ reacts with sulfur to give two ruthenium polysulfides, cyclo-$[CpRu(PPh_3)]_2S_x$ (x = 4,6) [11]. The structure of $[(MeCp)Ru(PPh_3)]_2S_6$ consists of a bicyclic Ru_2S_6 core with short Ru-S bonds. These metal sulfur multiple bonds induce a transannular bonding, similar to that in S_8^{2+}. The structure of $[(MeCp)Ru(PPh_3)]_2S_4$ suggests that there is a delocalized π-network, and accordingly it shows rich electrochemistry.

Thermolysis of 1 in toluene resulted in formation of the phosphine free 68 electron cuboidal cluster $(MeCp)_4Ru_4S_4$ [12]. The solid state structure of this complex reveals a distorted cubane core with two Ru-Ru bonds. The electron rich nature of this cubane is reflected in its electrochemistry, since it undergoes a reversible two-electron oxidation.

In summary, $CpRu(PPh_3)_2SH$ is the precursor of a series of organometallic ruthenium-sulfur compounds. Furthermore, the oxidation of 1 to the persulfide complex 2 clearly establishes the 2e/Ru stoichiometry.

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