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 RuS₂ [3,4].

In an effort to understand the reactivity of the ruthenium hydrosulfide functionality, we synthesized and characterized CpRu(PPh₃)₂SH (1). The electron rich nature of CpRu(PPh₃)₂SH is reflected in its reactivity. It easily undergoes protonation and alkylation to form H₂S and RSH complexes (Scheme). The H₂S complex is labile, and with hydrogen rapidly establishes an equilibrium with the dihydride complex [CpRu(PPh₃)₂H₂]OTf [5]. In contrast to the unreactive parent chloride, CpRu(PPh₃)₂Cl, 1 undergoes complete monocarbonylation to CpRu(PPh₃)(CO)SH.
Most interestingly, 1 undergoes a two-electron oxidation to the bridging persulfide complex \([\text{CpRu}(\text{PPh}_3)_2(\mu-S_2)]^2+\) (2) [6]. In contrast, most metallo-thiols have been found to follow organic precedent and undergo net one-electron/metal oxidations. Well documented examples include the oxidation of \((\text{MeCp})_2\text{Ti(SH)}_2\) by \(I_2\) [7] and of \(\text{Cp}_2\text{Mo(SH)}_2\) 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 \(\text{Ru}_2S_2\) core are treated as a trans-butadiene-like \(\pi\)-network. According to our analysis, the persulfide ligand serves as powerful \(\pi\)-donor to the ruthenium centers. The persulfide complex 2 can be easily reduced to the monocation 2\(r\) 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 "\([\text{CpRu}(\text{PPh}_3)S]\)". An attempt to generate this species from \(\text{CpRu}(\text{PPh}_3)_2\text{OTf}\) by treatment with the sulfur transfer reagent thiirane resulted instead the first thiirane complex \([\text{CpRu}(\text{PPh}_3)_2(\text{SC}_2\text{H}_4)]^+\) [9]. This thiirane complex is an analogue of the extremely unstable episulfonium salts, i.e., \(\text{RSC}_2\text{H}_4^+\) [10].

\(\text{CpRu(PPh}_3)_2\text{SH}\) reacts with sulfur to give two ruthenium polysulfides, \(\text{cyclo-[CpRu(PPh}_3)_2S}_x\) \((x = 4, 6)\) [11]. The structure of \([[(\text{MeCp})\text{Ru(PPh}_3)]_2S_6\) consists of a bicyclic \(\text{Ru}_2S_6\) core with short Ru-S bonds. These metal sulfur multiple bonds induce a transannular bonding, similar to that in \(S_8\). The structure of \([(\text{MeCp})\text{-Ru(PPh}_3)]_2S_4\) suggests that there is a delocalized \(\pi\)-network, and accordingly it shows rich electrochemistry.

Thermolysis of 1 in toluene resulted in formation of the phosphine free 68 electron cuboidal cluster \((\text{MeCp})_4\text{Ru}_4S_4\) [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, \(\text{CpRu(PPh}_3)_2\text{SH}\) is the precursor of a series of organometallic ruthenium-sulfur compounds. Furthermore, the oxidation of 1 to the persulfide complex 2 clearly establishes the \(2e/\text{Ru}\) stoichiometry.

References


   (b) Pecararo, T. A.; Chianelli, R. R. J. Cat. 1981, 57, 430.


