

Photolytisch induzierte Reaktionen von CpCo(CO)_2 ($\text{Cp} = \text{C}_5\text{H}_5$, $\text{C}_5\text{H}_4\text{Me}$, C_5Me_5 und C_5Ph_5) mit Thiiran zu dinuklearen 1,2-Ethanedithiolato-S-S-Komplexen

Photolytically Induced Reactions of CpCo(CO)_2 ($\text{Cp} = \text{C}_5\text{H}_5$, $\text{C}_5\text{H}_4\text{Me}$, C_5Me_5 and C_5Ph_5)
with Thiirane Yielding Dinuclear 1,2-Ethanedithiolato-S,S Complexes

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The complexes CpCo(CO)_2 ($\text{Cp} = \text{C}_5\text{H}_5$, $\text{C}_5\text{H}_4\text{Me}$, C_5Me_5 and C_5Ph_5) (**1a–d**) react with thiirane $\text{C}_2\text{H}_4\text{S}$ under UV-irradiation in THF to form the dinuclear μ_2 -1,2-ethanedithiolato-S,S complexes $[(\text{CpCo})_2(\mu_2\text{-S}_2\text{C}_2\text{H}_4)]$ (**2a–d**) as main products. Using column chromatography, in case of $\text{Cp} = \text{C}_5\text{H}_5\text{Me}$ also the dimeric complex $[(\text{C}_5\text{H}_4\text{MeCo}(\mu_2\text{-S}_2\text{C}_2\text{H}_4))]_2$ (**3b**), in case of $\text{Cp} = \text{C}_5\text{Ph}_5$ the mixed disulfido-sulfido complex $[(\text{C}_5\text{Ph}_5\text{Co})_2(\mu_2\text{-S}_2)(\mu_2\text{-S})]$ (**4d**) were isolated in small yields. Only **2a** reversibly adds SO_2 gas to form the μ_2 - SO_2 complex $[(\text{C}_5\text{H}_5\text{CoSCH}_2)_2(\mu_2\text{-SO}_2)]$ (**5a**). A bromo ligand bridging the Co atoms can be introduced by the reaction of $[(\text{C}_5\text{Me}_5\text{CoBr}_2)]_2$ (**6c**) with 1,2-ethanedithiol which gives the cationic complex $[(\text{C}_5\text{Me}_5\text{CoSCH}_2)_2(\mu_2\text{-Br})_2\text{CoBr}_4]$ (**7c**). All compounds have been characterized by their IR, ^1H and ^{13}C NMR and MS spectra and compounds **2b–d**, **3b** and **7c** by X-ray structure analyses, which prove the *pseudo* tetrahedral skeleton $(\text{CpCoS})_2$ and the ethane bridge between both sulfur atoms. **3b** shows, however, a new unsymmetrical bonding mode of both dithiolato bridges with $\eta^1\text{-S}$ und $\mu_2\text{-S}$ ligand functions.

Key words: Cyclopentadienylcobalt Complexes, 1,2-Ethanedithiolato-S-S Bridges, Bromo Bridge, Decarbonylation Reaction, X-Ray Data