PART I. REACTIONS OF THE ORGANOIRON SULFANES, \( \mu-S_x \)(Fe\(\text{Cp}(\text{CO})_2 \))_2 (x=3,4) INCLUDING A NOVEL METHOD FOR THE SYNTHESIS OF NEW ORGANOIRON THIOCARBOXYLATEDS, Fe\(\text{Cp}(\text{CO})_2 \)SCOR.

PART II. REACTIONS OF METAL CARBONYLS M(CO)\(_6\) (M=Cr, Mo, W) WITH LITHIUM TRIETHYL BOROHYDRIDE, Li\((\text{C}_2\text{H}_5)\)_3BH.

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ABSTRACT

The research described in this thesis is divided into two parts. In part I the reactivities of the organoiron sulfanes, \((\mu-S_X)_2[Fe\,Cp(CO)]_2\) \((X=3,4)\) were studied by carrying out the reaction of the trisulfanes \((X=3)\) with \(Fe_2(CO)_9\), the photolysis of the tetrasulfane \((X=4)\), and the reaction of the tri- and tetrasulfanes with acid chlorides, \(R\text{COCl}\), as electrophiles. The reaction of trisulfane with \(Fe_2(CO)_9\) gave mainly the stable sulfide cluster, \(Fe_3(CO)_9S_2\). In this reaction \(Fe_2(CO)_9\) abstracted sulfur atoms from the irontrisulfane which contains a reactive bridging "S-S-S" group.

The photolysis of the ironpentasulfane produced green dimeric sulfide complex, \(Fe_2(Cp)_2(CO)(S_2)_2\). This complex, in solution exists in cis-trans isomeric forms. The equilibrium concentration of the two isomers depends on the polarity of the solvent. The relative concentration of cis-isomer increases as the polarity of the solvent increases. It was also found that the green sulfide complex thermally converts into two structurally related brown complexes, \(Fe_2(Cp)_2(S_2)_2\), upon losing the CO ligand.

The reactions of the iron sulfanes \((X=3,4)\) with the acid chlorides, \(R\text{COCl}\), \((R=2-C\text{H}_3C\text{H}_2\text{CH}_2,\,2-C\text{H}_3\text{COOC}\text{H}_2,\,3,5-(NO_2)_2C\text{H}_3)\) at room temperature, produced the new s-bonded monothiocabxylate complexes, \(Fe\,Cp(CO)_2SCOR\), in moderate yield. The
reactivity of the organoiron sulfanes toward acid chlorides as electrophiles was attributed to the reactivity of the sulfur atoms as electron donor in the bridging \( S_x \) (\( x=3,4 \)) group. These reactions provide a novel and convenient route to the new \( S \)-bonded monothiocarboxylate complexes, \( \text{Fe} \:\text{Cp(CO)}_2\text{SCOR} \).

Part II describes the reaction of the metal carbonyls \( \text{M(CO)}_6 \) (\( \text{M} = \text{Cr, Mo, and W} \)) with \( \text{Li(C}_2\text{H}_5)_3\text{BH} \). In this reaction the mononuclear hydride, \( \text{HCr(CO)}_5^- \) and the bridging hydride, \( (\mu-\text{H})[\text{Cr(CO)}_5^-]_2 \) were identified in solution. The \( (\mu-\text{H})[(\text{M(CO)}_5^-)_2 \) (\( \text{M} = \text{Mo and W} \)) were also identified in solution. No evidence for the formation of the formyl complexes was observed.