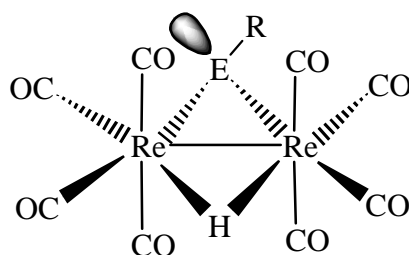


Selective syntheses, structures and reactivity of hydrido chalcogenido bridged rheniumcarbonyl complexes

Functional compounds are required for methodical preparative routes to metal cluster compounds. Such precursor complexes are e.g. hydrido chalcogenido bridged dirhenium carbonyl complexes.

This Ph. D. thesis describes several selective syntheses to build these complexes. The complex $\text{Re}_2(\text{CO})_8(\text{NCMe})_2$ reacted with thiols RSH or selenol RSeH (R = organic group), respectively, by oxidative addition in toluene at 80°C to give hydrido chalcogenido bridged dirhenium complexes of the general formula $\text{Re}_2(\mu\text{-H})(\mu\text{-ER})(\text{CO})_8$ ($\text{E} = \text{S}, \text{Se}$; R = organic group) in 60% to 80% yield. The analogous tellurium compound was formed by the reaction of $\text{Re}_2(\mu\text{-H})(\mu\text{-Cl})(\text{CO})_8$ with NaTePh in 83% yield.



Scheme 1: Hydrido chalcogenido bridged dirhenium carbonyl complexes $\text{Re}_2(\mu\text{-H})(\mu\text{-SR})(\text{CO})_8$

The reactivities of these complexes were exemplarily analyzed for the hydrido sulfido bridged rhenium carbonyl complexes with respect to a) CO-ligand substitution, b) $\mu\text{-H}$ -Ligand (metalation) and c) expansion via the sulfido bridge.

CO substitution by other ligands L gave only axial and diaxial substituted compounds. Depending on the sterical demand of L a permanent inversion of the sulfido bridge is observed for monosubstituted compounds. In $\text{Re}_2(\mu\text{-H})(\mu\text{-SNph})(\text{CO})_7(\text{NCMe})$ this dynamic process was analyzed by ^1H -2D-EXSY NMR spectroscopy. In order to demonstrate the acidity of the $\mu\text{-H}$ ligand $\text{Re}_2(\mu\text{-H})(\mu\text{-SR})(\text{CO})_8$ was deprotonated and reacted with ClMPPH_3 ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) to give the novel heteronuclear cluster complexes $\text{Re}_2(\mu\text{-MPPH}_3)(\mu\text{-SR})(\text{CO})_8$. Finally novel sulfur centred spirocyclic cluster complexes e.g. $[\text{Re}_2(\mu\text{-H})(\text{CO})_8(\mu_4\text{-S})]_2\text{Fe}_2(\text{CO})_6$ were synthesized by reaction of $\text{Re}_2(\mu\text{-H})(\mu\text{-SH})(\text{CO})_8$ and reactive metal carbonyl complexes.