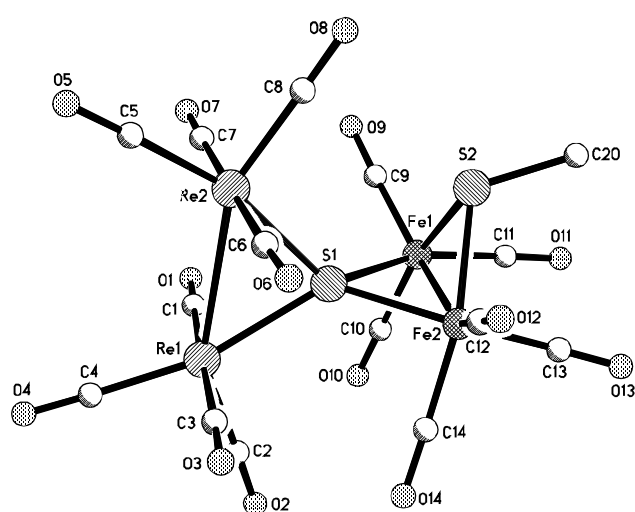


Synthesis of heteronuclear chalcogen centred spirocyclic transition metal carbonyl complexes

Abstract

The aim of this thesis was the directed synthesis of formerly inaccessible heteronuclear chalcogen centred spirocyclic transition metal carbonyl complexes. In order to reach this objective the novel complex $\text{Re}_2(\mu\text{-H})(\mu\text{-SeH})(\text{CO})_8$ was prepared from the reaction of $\text{Re}_2(\mu\text{-H})(\mu\text{-Cl})(\text{CO})_8$ with NaSeH . Its SeH-oxidative addition to $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ gave the spirocyclic compound $(\text{CO})_8(\mu\text{-H})\text{Re}_2(\mu_4\text{-Se})\text{Os}_3(\mu\text{-H})(\text{CO})_{10}$. The novel heteronuclear complexes $(\text{CO})_8(\mu\text{-H})\text{Re}_2(\mu_4\text{-S})\text{Fe}_2(\mu\text{-SR})(\text{CO})_6$ (fig.) and $(\text{CO})_{10}(\mu\text{-H})\text{Os}_3(\mu_4\text{-S})\text{Fe}_2(\mu\text{-SR})(\text{CO})_6$ ($\text{R} = \text{Me}, \text{Ph}$) were analogously synthesised by SH-oxidative addition of $\text{Fe}_2(\mu\text{-SH})(\mu\text{-SR})(\text{CO})_6$ ($\text{R} = \text{Me}, \text{Ph}$) to $\text{Re}_2(\text{CO})_8(\text{NCMe})_2$ or $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$, respectively. The preparative method described above was expanded by reacting $[\text{Re}_2(\mu\text{-PCy}_2)(\text{CO})_8]^-$ to $\text{Fe}_2(\mu\text{-E}_2)(\text{CO})_6$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$). The



resulting anionic intermediates $[(\text{CO})_8(\mu\text{-PCy}_2)\text{Re}_2(\mu_4\text{-E})\text{Fe}_2(\mu\text{-E})(\text{CO})_6]^-$ were trapped with MeI giving the complexes $(\text{CO})_8(\mu\text{-PCy}_2)\text{Re}_2(\mu_4\text{-E})\text{Fe}_2(\mu\text{-EMe})(\text{CO})_6$. Oxidative coupling of the anionic precursor complexes gave the respective dichalcogenides $[(\text{CO})_8(\mu\text{-PCy}_2)\text{Re}_2(\mu_4\text{-E})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-E}_2)$. For $\text{E} = \text{S}$ the precursor complex could be protonated by CF_3COOH yielding $(\text{CO})_8(\mu\text{-PCy}_2)\text{Re}_2(\mu_4\text{-S})\text{Fe}_2(\mu\text{-SH})(\text{CO})_6$.

Its expansion by SH-oxidative addition to $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ resulted in the formation of $(\text{CO})_8(\mu\text{-PCy}_2)\text{Re}_2(\mu_4\text{-S})\text{Fe}_2(\text{CO})_6(\mu_3\text{-S})\text{Os}_3(\mu\text{-H})(\text{CO})_{10}$. The combination of the preparative methods described above was achieved in the reaction of $[(\text{CO})_{10}\text{Os}_3(\mu_4\text{-S})\text{Fe}_2(\mu\text{-SR})(\text{CO})_6]^-$ ($\text{R} = \text{Me}, \text{Ph}$) with $\text{Fe}_2(\mu\text{-E}_2)(\text{CO})_6$ ($\text{E} = \text{Se}, \text{Te}$). This synthetic approach gave double spirocyclic complexes of the type $(\text{CO})_6(\mu\text{-SR})\text{Fe}_2(\mu_4\text{-S})\text{Os}_3(\text{CO})_{10}(\mu_4\text{-E})\text{Fe}_2(\mu\text{-EMe})(\text{CO})_6$. The molecular structures show helical chirality.