

Tuning the Steric and Electronic Properties of Chiral Rhenium Thiolate Complexes [1]

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Reaction of the complex $[\text{CpRe}(\text{NO})(\text{CO})_2]\text{BF}_4$ with triisopropylphosphine gives the chiral CO substitution product $[\text{CpRe}(\text{NO})\{\text{P}(i\text{-Pr})_3\}(\text{CO})]\text{BF}_4$. The corresponding triphenylphosphite complex $[\text{CpRe}(\text{NO})\{\text{P}(\text{OPh})_3\}(\text{CO})]\text{BF}_4$ may be obtained by oxidative CO removal. Reduction of the remaining CO ligand with NaBH_4 furnishes the corresponding methyl complexes $[\text{CpRe}(\text{NO})(\text{L})(\text{CH}_3)]$. The structure of $[\text{CpRe}(\text{NO})\{\text{P}(i\text{-Pr})_3\}(\text{CH}_3)]$ was determined: triclinic space group $\text{P}\bar{1}$ (No. 2), $a = 8.442(4)$, $b = 9.582(5)$, $c = 11.820(8)$ Å, $\alpha = 81.81(4)$, $\beta = 87.18(4)$, $\gamma = 63.87(5)^\circ$, $Z = 2$. Reaction of the methyl complexes with HBF_4 in the presence of thiols gives, after chromatographic workup, the thiolate derivatives $[\text{CpRe}(\text{NO})(\text{L})(\text{SR})]$ ($\text{L} = \text{CO}$, $\text{P}(\text{OPh})_3$, $\text{P}(i\text{-Pr})_3$, $\text{R} = \text{CH}_2\text{Ph}$, $\text{CH}_2(4\text{-C}_6\text{H}_4\text{Cl})$, $\text{CH}_2(4\text{-C}_6\text{H}_4\text{OMe})$, CH_3 , C_2H_5). The structure of $[\text{CpRe}(\text{NO})\{\text{P}(i\text{-Pr})_3\}(\text{SCH}_3)]$ was determined: monoclinic space group $\text{P}2_1$ (No. 3), $a = 7.0515(7)$, $b = 17.3469(10)$, $c = 7.9727(7)$ Å, $\beta = 114.021(7)^\circ$, $Z = 2$. In both structures, a significant opening of the angle N-Re-X ($\text{X} = \text{C}$, S) suggests that antibonding interactions between orbitals of the ligand X and the second-highest MO of the $[\text{CpRe}(\text{NO})(\text{L})]$ complex fragment are avoided.

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