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

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Reaction of the complex [CpRe(NO)(CO)₂]BF₄ with triisopropylphosphine gives the chiral CO substitution product [CpRe(NO){P(i-Pr)₃}(CO)]BF₄. The corresponding triphenylphosphite complex [CpRe(NO){P(OPh)₃}(CO)]BF₄ may be obtained by oxidative CO removal. Reduction of the remaining CO ligand with NaBH₄ furnishes the corresponding methyl complexes [CpRe(NO)(L)(CH₃)]. The structure of [CpRe(NO){P(i-Pr)₃}(CH₃)] was determined: triclinic space group P¯1 (No. 2), a = 8.442(4), b = 9.582(5), c = 11.820(8) Å, α = 81.81(4), β = 87.18(4), γ = 63.87(5)°, Z = 2. Reaction of the methyl complexes with HBF₄ in the presence of thiols gives, after chromatographic workup, the thiolate derivatives [CpRe(NO)(L)(SR)] (L = CO, P(OPh)₃, P(i-Pr)₃, R = CH₂Ph, CH₂(4-C₆H₄Cl), CH₂(4-C₆H₄OMe), CH₃, C₂H₅).

The structure of [CpRe(NO){P(i-Pr)₃}(SCH₃)] was determined: monoclinic space group P2₁ (No. 3), a = 7.0515(7), b = 17.3469(10), c = 7.9727(7) Å, β = 114.021(7)°, Z = 2. In both structures, a significant opening of the angle N-Re-X (X = C, S) suggests that antibonding interactions between orbitals of the ligand X and the second-highest MO of the [CpRe(NO)(L)] complex fragment are avoided.

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