

# Diastereomeric Halfsandwich Rhenium Complexes Containing Thiolate and Thioaldehyde Ligands [1]

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Z. Naturforsch. **59b**, 1093 – 1102 (2004); received July 22, 2004

The reaction of diastereomeric methyl rhenium complexes [CpRe(NO)(NMDPP)(CH<sub>3</sub>)] (NMDPP = neomenthyl-diphenylphosphine) and [CpRe(NO)(PAMP)(CH<sub>3</sub>)] (PAMP = phenyl-2-anisyl-methylphosphine) with thiols in the presence of HBF<sub>4</sub> gave thiolate complexes [CpRe(NO)(NMDPP)(SCH<sub>2</sub>Ph)] and [CpRe(NO)(PAMP)(SCH<sub>2</sub>R)] (R = Ph, 4-C<sub>6</sub>H<sub>4</sub>Cl, 4-C<sub>6</sub>H<sub>4</sub>OMe, 2-C<sub>4</sub>H<sub>3</sub>O, CH<sub>3</sub>, CH=CH<sub>2</sub>). Treatment of [CpRe(NO)(PAMP)(THF)]BF<sub>4</sub> with the thiols and Na<sub>2</sub>CO<sub>3</sub> gave the same compounds under neutral conditions. Similarly, the reaction of the chelate complex {CpRe(NO)[κP(Ph)(Me)(CH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>κS)]}BF<sub>4</sub> with thiols and NaOEt yielded the ring-opened products {CpRe(NO)[P(Ph)(Me)(CH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>S)](SCH<sub>2</sub>R)} (R = Ph, 4-C<sub>6</sub>H<sub>4</sub>Cl, 4-C<sub>6</sub>H<sub>4</sub>OMe). One of the benzylic hydrogen atoms can be abstracted with [Ph<sub>3</sub>C]BF<sub>4</sub> to give the diastereomeric thiobenzaldehyde complexes [CpRe(NO)(PAMP)(S=CHR)]BF<sub>4</sub> (R = Ph, 4-C<sub>6</sub>H<sub>4</sub>Cl, 4-C<sub>6</sub>H<sub>4</sub>OMe) and {CpRe(NO)[P(Ph)(Me)(CH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>S)](S=CHPh)}BF<sub>4</sub>. In these products, the thioformyl group is predominantly  $\eta^2(C,S)$  coordinated to rhenium, but in a few cases the corresponding  $\eta^1(S)$  isomers were also detected by IR and NMR spectroscopy.

*Key words:* Rhenium, Chiral Complexes, Chiral P Ligands, Thiolate Complexes,  
Thioaldehyde Complexes