Enantioselective Organic Syntheses Using Chiral Transition Metal Complexes, 7[◇]

Synthesis of Chiral Rhenium Complexes Containing Functionalized Thiolate Ligands

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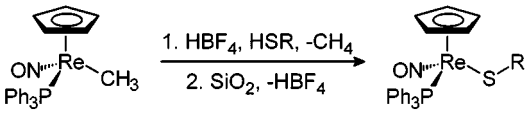
Chiral racemic rhenium thiolate complexes [CpRe(NO)(PPh_3)(SR)] were obtained under either acidic or basic conditions. Thus, when [CpRe(NO)(PPh_3)(CH_3)] (**1**) was treated with etheral HBF_4 and HSR the thiolate complexes [CpRe(NO)(PPh_3)(SR)] [SR = SCH_2(2-furyl) (**2**), SCH_2C(O)OEt (**3**)] were obtained after chromatographic workup. Ligand exchange reactions between [CpRe(NO)(PPh_3)(OC_4H_8)]BF_4 (**4**) and sodium thiolates yielded analogous complexes with SR = SH (**5**), SCH_2CH_2Ph (**6**), $SCH_2CH{=}CH_2$ (**7**). SR groups which tolerate strongly alkaline conditions may be introduced by treatment of **4** with HSR in the presence of sodium ethoxide as demonstrated by the high-yield synthesis of **2** as well as of complexes with SR = SCH_2CH_2NHAc (**8**), $SCH_2CH_2C(O)OH$ (**9**). A milder synthesis using hydrated sodium carbonate as a base provided **8** and compounds with SR = $SCH_2CH_2C(O)OMe$ (**10**), $SCH_2CH_2C(O)NHCH_2Ph$ (**11**) in high yields. Using similar methods, thiolate complexes of (*R*)-*N*-acetylcysteine (**13**), its methyl ester (**14**), (*R*)-*N*-phthaloylcysteine (**16**), and *N*-[(*S*)-3-mercapto-2-methylpropionyl]-*S*-proline (Captopril) (**17**) were obtained as diastereomeric pairs. The formation of **13** was preceded by the O-bonded isomer **12** which slowly rearranges in solution. **13** can be converted under acidic conditions into its methyl (**14**) or ethyl (**15**) esters. The diastereomers of **16** were separated by crystallization, and the structure of the (*R,R*)-isomer **16a** determined.

Thiolate ligands have some remarkable properties which are exploited by nature in a number of important metalloenzymes.[2] SR groups being soft donors bind strongly to most of the transition metal ions. Due to their high polarizability and π-donor capacity,[3] they are able to stabilize various oxidation states of the metal and to promote the formation of clusters[2][4] which can function as electron reservoirs for redox processes. Enzymatic reactions which lead to the transformation of coordinated thiolate ligands seem to be comparatively rare. One of the few prominent examples is the penicillin biosynthesis[5] whose first step involves the oxidative dehydrogenation of an iron-coordinated, cysteine-containing tripeptide to a thioaldehyde intermediate.[6] We have recently described a similar oxidative route for the synthesis of stable thioaldehyde complexes of ruthenium[7][8] and rhenium.[9] In order to further exploit the characteristic reactivity of coordinated thioaldehydes in nucleophilic additions and cycloadditions[8][10][11][12] we decided to investigate thiolate complexes bearing various functional groups on the SR ligand.

Results

Achiral Thiolates

Two synthetic strategies were chosen in which the rhenium–sulfur bond is formed under either acidic[8] or basic conditions. Treatment of the racemic methylrhenium complex **1**[13] with a twofold excess of etheral HBF_4 and 2-(mercaptomethyl)furan or ethyl mercaptoacetate followed by chromatography over silica gave the corresponding rhenium thiolate complexes **2** and **3** in fair to good yields (Eq. 1).



(1)

1 **2** (52%) **3** (94%)

SR: SCH_2(2-furyl) (**2**), SCH_2C(O)OEt (**3**)

Since the strongly acidic conditions of this route may not be compatible with a number of functional groups, a synthesis based on a nucleophilic substitution at rhenium was sought. The tetrahydrofuran complex [CpRe(NO)(PPh_3)(OC_4H_8)]BF_4 (**4**) which is easily obtained through acid cleavage of **1**[14] seemed to be an appropriate starting material. Although **4** was noted to be labile[14] it has found only sporadic use in ligand exchange reactions.[15] When **4** was treated with isolated sodium thiolates in THF/ethanol, the corresponding thiolate complexes **5–7** were formed in good

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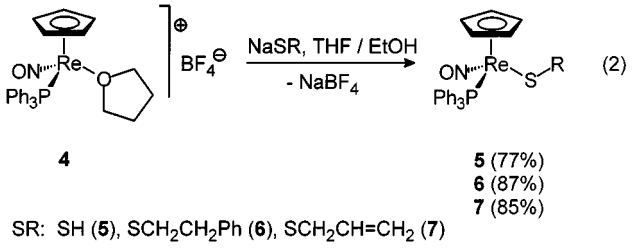
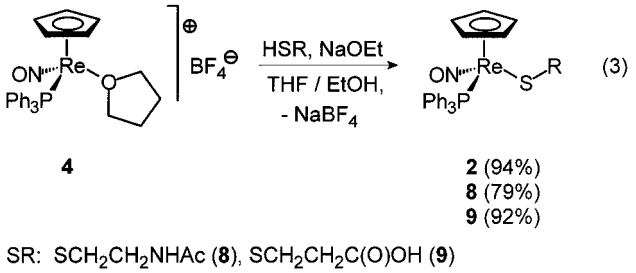
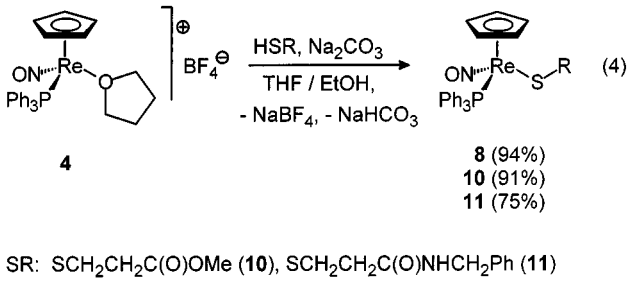
yields (Eq. 2). The thiolate anions may also be generated in situ from thiol and sodium ethoxide. This was demonstrated by the high-yield synthesis of **2**, **8**, and **9** (Eq. 3).





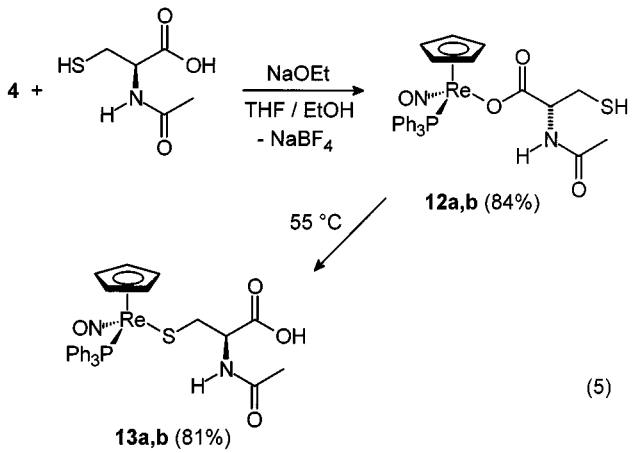
The use of ethoxide as a base may, however, cause problems when chiral thiolates are to be employed which would racemize under strongly alkaline conditions. Hydrated sodium carbonate, which finds some use in peptide syntheses,[16] was expected to be mild enough to circumvent this obstacle. Indeed, simple stirring of a mixture of **4**, $Na_2CO_3 \cdot 10\ H_2O$, and a thiol produced the expected thiolate complexes **8**, **10**, and **11** in high purity and yield (Eq. 4).

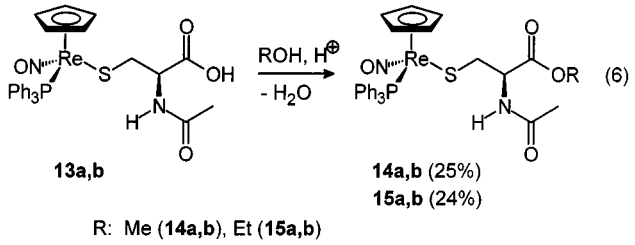


The new thiolate complexes are yellow, slightly air-sensitive crystalline solids which are more or less readily soluble in all common organic solvents. Typical spectroscopic features include low NO stretching frequencies in the infrared spectra which hint at the high donor ability of the SR ligand. In the ^1H NMR spectra, all methylene protons of the SR group are diastereotopic; those in α position give widely separated signals which are easily analyzed. The SH complex **5** exhibits a high-field signal at $\delta = 0.09$ which is split into a doublet due to coupling with phosphorus. In the ^{13}C-NMR spectra the α carbon signal is shifted by approximately 15 ppm to lower field compared to the uncoordinated thiol, and split into a doublet due to coupling with phosphorus. In cases of doubt such as **7–11** this serves as unambiguous proof that the SR ligand is indeed coordinated through the sulfur atom.

Chiral, Enantiomerically Pure Thiolates

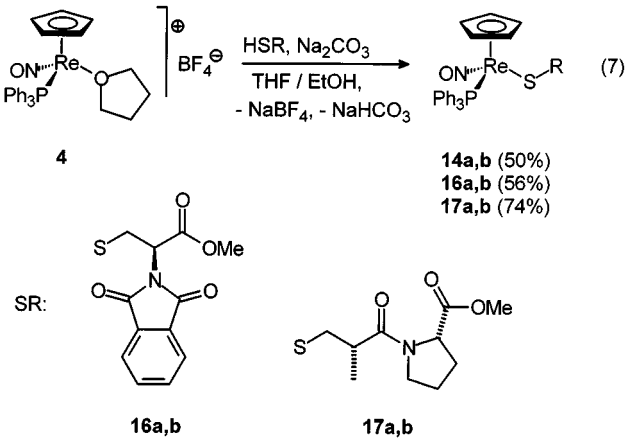
Reaction of the THF complex **4** with (*R*)-*N*-acetylcysteine and sodium ethoxide initially gave the orange-brown carboxylate complex **12a**, **b** as a 1:1 mixture of diastereoisomers. Upon prolonged storage in solution or refluxing in acetone, **12a**, **b** converts almost quantitatively into the yellow S-bonded isomer **13a**, **b** (Eq. 5) which, after one crystallization, was obtained in 17% de. Conversely, solutions of **13a**, **b** revert back to an equilibrium mixture containing approximately 5% **12a**, **b**.





For a further elaboration of the thiolate side chain it may be desirable to have the carboxylate group protected as ester. To this end, the diastereomeric complexes **13a**, **b** were treated with alcohol and acid (Eq. 6). This reaction was also intended to be an additional test of the stability of the rhenium complex. The expected esters **14a**, **b** and **15a**, **b** were indeed obtained, albeit in less than satisfactory yields. Spectroscopic analysis of the crude reaction mixtures indicated that the losses were primarily due to the chromatographic workup which was necessary to remove the acid, rather than destruction of the rhenium complex. Obviously it is advisable to convert amino acids to their esters before coordinating them to the transition metal. Thus, **4** was reacted with the methyl esters of (*R*)-*N*-acetylcysteine, (*R*)-*N*-phthaloylcysteine, and *N*-[(*S*)-3-mercapto-2-methylpropionyl]-*S*-proline in the presence of sodium carbonate (Eq. 7). The three products were isolated as 1:1 mixtures of diastereoisomers. **17a**, **b** was partially enriched by crystalliza-

tion to 15% de while diastereomerically pure **16a** crystallized from an acetone solution.



The physical properties of the diastereomeric thiolate complexes **13a**,**b**–**17a**,**b** closely resemble those of the other members of this series. As expected, they give double sets of signals in their ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra. Coordination to rhenium via the sulfur atom is unequivocally inferred from the large coupling of the α carbon with the phosphorus atom. This clearly distinguishes **13a**, **b** from their carboxylate-bound isomers **12a**, **b** whose ^{13}C-NMR spectra exhibit doublet resonances for the carboxylate carbon atom.

Crystal and Molecular Structure of 16a

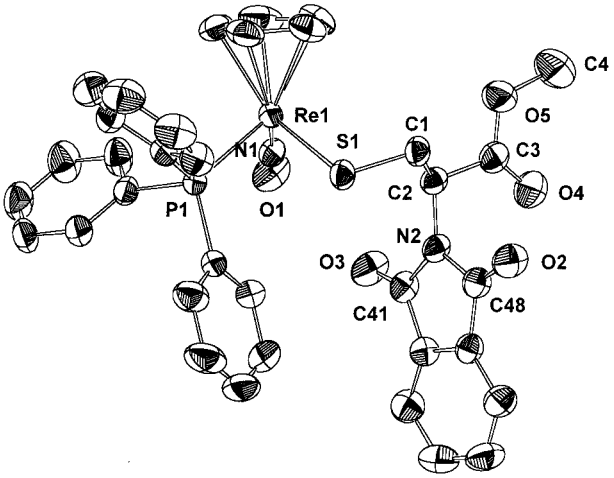
From an acetone solution of **16a**, **b** diastereomerically pure **16a** was obtained by slow crystallization. A suitable single crystal was analyzed by X-ray diffraction. It belonged to the enantiomorphic space group $P2_1$ which immediately showed that it is an enantiomerically pure compound. The stereocenters at both rhenium and carbon have the (*R*) configuration (Figure 1) which is in line with the Flack parameter. Bond distances and angles are well within the normal range for complexes of the type [CpRe(NO)(PPh_3)(SR)].[17][18]

The angle S–Re–N(1) [102.35(11)°] is surprisingly large for both **16a** and the (diarylmethyl)thiolate complex investigated by Gladysz.[18] As there are not any obvious steric interactions between the NO and SR ligands, the driving force of this distortion must be electronic in origin.[1] Also of note is the transoid arrangement of the groups at rhenium and sulfur [dihedral angle P–Re–S–C(1) = 167.4°] which simultaneously minimizes steric interactions as well as the repulsion between the lone pairs at sulfur and the HOMO of the [CpRe(NO)(PPh_3)] complex fragment.[1]

Discussion

This work was aimed at the synthesis of chiral racemic rhenium thiolate complexes [CpRe(NO)(PPh_3)(SR)]. Three routes proceeding under acidic, basic, or close to neutral

Figure 1. Molecular structure (*R*,*R*)-[CpRe(NO)(PPh_3)($SCH_2CH(NC_8H_4O_2)COOMe$)] (**16a**) (without H atoms)[a]



[a] Selected distances [pm] and angles[°] (standard deviations in parentheses): Re(1)–S(1) 239.45(10), Re(1)–P(1) 235.44(12), Re(1)–N(1) 176.3(4), N(1)–O(1) 119.7(5), S(1)–C(1) 182.2(5), S(1)–Re(1)–P(1) 87.31(6), S(1)–Re(1)–N(1) 102.35(11), P(1)–Re(1)–N(1) 92.80(13), Re(1)–S(1)–C(1) 106.2(2), P(1)–Re(1)–S(1)–C(1) 167.4(2).

conditions were developed in order to ensure tolerance for a range of functional groups. Acid cleavage of the methyl complex **1** produces the solvent-stabilized 16-electron species $[CpRe(NO)(PPh_3)]^+$ which immediately picks up any stronger Lewis base present in the solution.[19] The thiol complexes [CpRe(NO)(PPh_3)(HSR)]BF_4 thus formed eliminate HBF_4 simply upon chromatography over silica.[9] This route produces thiolate complexes in good yields but is limited of course to SR groups which tolerate strongly acidic conditions.

Gladysz et al., in their seminal work on chiral rhenium complexes,[20] made extensive use of the dichloromethane complex [CpRe(NO)(PPh_3)($ClCH_2Cl$)]BF_4[21] in ligand exchange reactions. With the strongly nucleophilic thiolate ions this compound, in addition to ligand exchange, undergoes nucleophilic substitution at carbon which leads to the formation of (chloromethyl)thioether complexes in sizeable quantities.[9] The tetrahydrofuran complex **4** whose synthesis[14] can easily be scaled up to multigram quantities, finally proved to be the starting material of choice.

For potentially ambidentate ligands such as allyl thiolate or the anions of cysteine and its derivatives, coordination through sulfur is favored thermodynamically. Nevertheless, for cysteine itself, which under the conditions of equation 5 exists in solution in its doubly deprotonated form, the carboxylate isomer is formed as the kinetic product. A similar observation was not made in the case of the 3-mercaptopropionic acid complex **9** (Eq. 3), due probably to the absence of bulky groups around the sulfur atom. Bond formation between the chiral rhenium complex and the various SR ligands was not expected to be accompanied by kinetic resolution. Nevertheless it is gratifying that partial or even full diastereomer separation could easily be effected by simple crystallization.

Conclusions

It has been shown here that the chiral Lewis acid $[CpRe(NO)(PPh_3)]^+$ can be efficiently connected to simple thiolates as well as those derived from biologically relevant molecules such as the amino acid (*R*)-cysteine or *N*-[(*S*)-3-mercapto-2-methylpropionyl]-*S*-proline, an ACE (*angiotensin converting enzyme*) inhibitor which under the brand name "Captopril" is used as an antihypertension drug. Apart from the more classical use of the rhenium complex fragment as a protective group for the thiolate function and a chiral auxiliary[20] for stereoselective addition reactions, one can also envisage that compounds such as **13–17** might find uses as specific "organometallic markers" in biochemistry[22] or as carriers of heavy atoms for protein crystallography.[23]

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Experimental Section

All experiments were carried out in Schlenk tubes under an atmosphere of nitrogen using suitably purified solvents. – IR: Perkin-Elmer 283, Bruker IFS 25. – ^{1}H NMR: Bruker AMX 400, δ values relative to TMS. – ^{13}C NMR: Bruker AMX 400, δ values relative to TMS; assignments were routinely checked by DEPT; in some cases the ^{13}C-NMR signals of quarternary carbon atoms were too weak to be detected. – ^{31}P NMR: Bruker AMX 400, δ values relative to 85% H_3PO_4. The ^{1}H- and ^{13}C-NMR signals of the PPh_3 ligand are very similar for all compounds and have therefore been omitted from the lists of spectral data. – Elemental analyses: Analytical Laboratory of the Institut für Anorganische Chemie. The following starting materials were obtained as described in the literature: $[CpRe(NO)(PPh_3)(CH_3)]$ (**1**),[13] $[CpRe(NO)(PPh_3)(OC_4H_8)]BF_4$ (**4**),[14] NaSH,[24] other sodium thiolates,[25] $HSCH_2CH_2C(O)NHCH_2Ph$,[26] (*R*)-*N*-phthaloylcysteine.[16] All other reagents were used as purchased.

[CpRe(NO)(PPh$_3$)(SCH$_2$C$_4$H$_3$O)] (**2**): To a solution of **1** (225 mg, 0.40 mmol) and 2-(mercaptomethyl)furan (115 mg, 1.00 mmol) in toluene (15 ml) was added at –70 °C a solution of HBF_4 in diethyl ether (1.00 mmol). The mixture was allowed to warm up to 20 °C, and all volatiles were removed under vacuum. The semi-solid residue was chromatographed with THF/ether over a short silica column and further purified by crystallization from dichloromethane/pentane. Yield 137 mg (52%), m.p. 153 °C. – ^{1}H NMR (400 MHz, [D$_6$]acetone, 20 °C): δ = 3.73, 3.77 [AB system, ^2J(H,H) = 14.2 Hz, 2 H; SCH_2], 5.28 (s, 5 H; C_5H_5), 6.13 [dd, ^3J(H,H) = 3.2 Hz, ^4J(H,H) = 0.8 Hz, 1 H; CH], 6.28 [dd, ^3J(H,H) = 3.1 Hz, ^3J(H,H) = 1.9 Hz, 1 H; CH], 7.36 [dd, ^3J(H,H) = 1.8 Hz, ^4J(H,H) = 0.9 Hz, 1 H; CH]. – ^{13}C NMR (100 MHz, [D$_6$]acetone, 20 °C): δ = 39.4 [d, ^3J(P,C) = 9 Hz; SCH_2], 92.3 (s; C_5H_5), 106.2 (s; CH), 111.1 (s; CH), 141.2 (s; CH), 158.9 (s; CH). – ^{31}P NMR (162 MHz, [D$_6$]acetone, 20 °C): δ = 19.6 (s). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1654 (NO), 1606 cm^{-1} (C=C). – $C_{28}H_{25}NO_2PReS$ (656.8) calcd C 51.21, H 3.84, N 2.13, S 4.88; found C 50.90, H 3.88, N 1.98, S 5.16.

[CpRe(NO)(PPh$_3$)(SCH$_2$C(O)OEt)] (**3**): This compound was prepared analogously from **1** and ethyl mercaptoacetate. Yield 149 mg (94%), m.p. 106 °C. – ^{1}H NMR (400 MHz, [D$_6$]acetone, 20 °C): δ = 1.24 [t, ^3J(H,H) = 7.1 Hz, 3 H; CH_3], 3.07, 3.45 [AB system, ^2J(H,H) = 12.1 Hz, 2 H; SCH_2], 4.07, 4.12 [AB system of quartets, ^2J(H,H) = 10.8 Hz, ^3J(H,H) = 7.1 Hz, 2 H; OCH_2], 5.35 (s, 5 H; C_5H_5). – ^{13}C NMR (100 MHz, [D$_6$]acetone, 20 °C): δ = 14.5 (s; CH_3), 43.6 [d, ^3J(P,C) = 9 Hz; SCH_2], 60.6 (s; OCH_2), 92.6 (s; C_5H_5), 174.0 (s; CO). – ^{31}P NMR (162 MHz, [D$_6$]acetone, 20 °C): δ = 19.5 (s). – IR (CH_2Cl_2) $\tilde{\nu}$ = 1721 (CO), 1653 cm^{-1} (NO). – $C_{27}H_{27}NO_3PReS$ (662.8) calcd C 48.93, H 4.11, N 2.11, S 4.84; found C 48.91, H 4.01, N 1.97, S 5.08.

[CpRe(NO)(PPh$_3$)(SH)] (**5**): A solution of **4** (281 mg, 0.40 mmol) and NaSH (28 mg, 0.50 mmol) in THF (20 ml) and ethanol (20 ml) was stirred 1 h at 20 °C. The mixture was taken to dryness, and the residue dissolved in benzene and filtered over Celite. The filtrate was partially evaporated and the product precipitated by adding pentane. Yield 178 mg (77%), m.p. 60 °C (dec). – ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 0.09 [d, ^3J(P,H) = 12.6 Hz, 1 H; SH], 4.77 (s, 5 H; C_5H_5). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = 91.4 (s; C_5H_5). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = 23.0 (s). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1655 cm^{-1} (NO). – $C_{23}H_{21}NOPReS$ (567.7) calcd C 47.91, H 3.67, N 2.43, S 5.56; found C 47.91, H 3.75, N 2.25, S 5.41.

[CpRe(NO)(PPh$_3$)(SCH$_2$CH$_2$Ph)] (**6**): This compound was prepared analogously from **4** and sodium 2-phenylethanethiolate. Yield 237 mg (87%), m.p. 168 °C. – ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 2.88–3.34 (m, 4 H; CH_2CH_2), 4.80 (s, 5 H; C_5H_5). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = 42.1 (s; CH_2), 45.1 [d, ^3J(P,C) = 8 Hz; SCH_2], 91.1 (s; C_5H_5). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = 20.2 (s). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1644 cm^{-1} (NO). – $C_{31}H_{29}NOPReS$ (680.8) calcd C 54.69, H 4.29, N 2.06, S 4.71; found C 54.39, H 4.30, N 2.05, S 4.66.

[CpRe(NO)(PPh$_3$)(SCH$_2$CH=CH$_2$)] (**7**): This compound was prepared analogously from **4** and sodium allylthiolate. Yield 210 mg (85%), m.p. 202 °C. – ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 3.02, 3.39 [AB system of doublets, ^2J(H,H) = 13.0 Hz, ^3J(H,H) = 7.2 Hz, 2 H; SCH_2], 4.87 [ddd, ^2J(H,H) = 2.0 Hz, ^3J(H,H) = 9.9 Hz, ^4J(H,H) = 1.0 Hz, 1 H; =CH_2], 4.95 [dd, ^2J(H,H) = 1.9 Hz, ^3J(H,H) = 16.9 Hz, 1 H; =CH_2], (s, 5 H; C_5H_5), 5.87 [ddt, ^3J(H,H) = 16.9 Hz, ^3J(H,H) = 9.8 Hz, ^3J(H,H) = 7.2 Hz, 1 H; =CH] . – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 45.3 [d, ^3J(P,C) = 7 Hz; SCH_2], 91.3 (s; C_5H_5), 113.2 (s; =CH_2), 141.2 (s; =CH). – ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ = 19.0 (s). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1645 (NO), 1608 cm^{-1} (C=C). – $C_{26}H_{25}NOPReS$ (616.7) calcd C 50.64, H 4.09, N 2.27, S 5.20; found C 50.99, H 4.31, N 2.20, S 4.50.

[CpRe(NO)(PPh$_3$)(SCH$_2$C$_4$H$_3$O)] (**2**): To a solution of **4** (281 mg, 0.40 mmol) and 2-(mercaptomethyl)furan (57 mg, 0.50 mmol) in THF (20 ml) and ethanol (20 ml) was added at 20 °C a solution of sodium ethoxide in ethanol (0.50 mmol). After 1 h the mixture was taken to dryness, and the residue dissolved in benzene and filtered over Celite. The filtrate was partially evaporated and the product precipitated by adding pentane. Yield 257 mg (94%).

[CpRe(NO)(PPh$_3$)(SCH$_2$CH$_2$NHAc)] (**8**): This compound was prepared analogously from **4** and *N*-acetylcysteamine. Yield 209 mg (79%), m.p. 154 °C. – ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 1.71 (s, 3 H; CH_3), 2.48 (m, 1 H; CH_2), 2.96 (m, 1 H; CH_2), 3.37 (m, 1 H; SCH_2), 3.95 (m, 1 H; SCH_2), 4.87 (s, 5 H; C_5H_5), 5.77 (s, br, 1 H; NH). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = 23.2 (s; CH_3), 40.3 [d, ^3J(P,C) = 8 Hz; SCH_2], 43.3 (s; CH_2), 91.5 (s; C_5H_5), 168.9 (s; CO). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = 20.2 (s). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1650 (NO), 1513 cm^{-1} (CONH). – $C_{27}H_{28}N_2O_2PReS$ (661.8) calcd C 49.00, H 4.26, N 2.23, S 4.85; found C 49.14, H 4.51, N 3.98, S 4.65.

[CpRe(NO)(PPh$_3$)(SCH$_2$CH$_2$COOH)] (**9**): This compound was prepared analogously from **4** and 3-mercaptopropionic acid. Yield 239 mg (92%), m.p. 205 °C (dec). – ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 2.56 (m, 1 H; CH_2), 2.27–2.89 (m, 2 H; CH_2), 3.09 (m, 1 H; CH_2), 4.77 (s, 5 H; C_5H_5). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = 37.5 [d, ^3J(P,C) = 8 Hz; SCH_2], 39.6 (s; CH_2), 91.2 (s; C_5H_5), 177.8 (s; CO). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = 19.5 (s). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1742 (COOH), 1661 cm^{-1} (NO). – $C_{26}H_{25}NO_3PReS$ (648.7) calcd C 48.14, H 3.88, N 2.16, S 4.94; found C 48.23, H 3.95, N 2.01, S 4.77.

[CpRe(NO)(PPh$_3$)(OCOCH(NHAc)CH$_2$SH)] (**12a**, **b**): This compound was prepared analogously from **4** and (*R*)-*N*-acetylcysteine. Yield 237 mg (84%), orange-brown crystalline solid, dec. 57 °C. – Both diastereoisomers: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20 °C): δ = 1.33 [t, ^3J(H,H) = 8.5 Hz, 1 H; SH], 1.40 [dd, ^3J(H,H) = 9.0 Hz, ^3J(H,H) = 7.8 Hz, 1 H; SH], 1.78 (s, 3 H; CH_3), 1.84 (s, 3 H; CH_3), 2.39, 2.56 [AB system of dd, ^2J(H,H) = 13.3 Hz, ^3J(H,H) = 8.9 Hz, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 4.8 Hz, ^3J(H,H) = 4.0 Hz, 2 H; SCH_2], 2.39, 2.66 [AB system of dd, ^2J(H,H) = 13.3 Hz, ^3J(H,H) = 8.9 Hz, ^3J(H,H) = 7.2 Hz, ^3J(H,H) = 4.8 Hz, ^3J(H,H) = 4.2 Hz, 2 H; SCH_2], 4.10 [dt, ^3J(H,H) = 6.4 Hz, ^3J(H,H) = 4.3 Hz, 1 H; CH], 4.18 [dt, ^3J(H,H) = 6.6 Hz, ^3J(H,H) = 4.5 Hz, 1 H; CH], 5.40 (s, 2 × 5 H; C_5H_5), 6.62 [d, ^3J(H,H) = 6.1 Hz, 1 H; NH], 6.69 [d, ^3J(H,H) = 5.7 Hz, 1 H; NH]. – ^{13}C NMR (100 MHz, [D$_6$]acetone, 20 °C): δ = 22.9 (s; CH_3), 23.0 (s; CH_3), 27.8 (s; SCH_2), 27.9 (s; SCH_2), 55.1 (s; CH), 55.3 (s; CH), 91.9 (s; C_5H_5), 169.1 (s; HNCO), 177.2 [d, ^3J(P,C) = 3 Hz, COORe], 177.3 [d, ^3J(P,C) = 2 Hz, COORe]. – ^{31}P NMR (162 MHz, [D$_6$]acetone, 20 °C): δ = 21.2 (s), 21.4 (s). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1674 cm^{-1} (NO). – $C_{28}H_{28}N_2O_4PReS$ (705.8) calcd C 47.65, H 4.00, N 3.97, S 4.54; found C 47.52, H 4.00, N 3.65, S 4.46.

[CpRe(NO)(PPh$_3$)(SCH$_2$CH(NHAc)COOH)] (**13a**, **b**): The material from the above reaction was dissolved in acetone and stirred for 3 d at 20 °C. The product was isolated by evaporation and crystallization from benzene/pentane. NMR analysis revealed **13a**, **b** in 17% de and some residual **12a,b** which does not disappear even after refluxing. Yield 229 mg (81%, based on **4)**, dec. 216 °C. – Major diastereoisomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20 °C): δ = 1.96 (s, 3 H; CH_3), 2.76, 3.07 [AB system of d, ^2J(H,H) = 13.1 Hz, ^3J(H,H) = 8.1 Hz, ^3J(H,H) = 4.2 Hz, 2 H; SCH_2], 4.44 [dd, ^3J(H,H) = 8.1 Hz, ^3J(H,H) = 4.2 Hz, 1 H; CH], 5.35 (s, 5 H; C_5H_5), NH and OH signals not detected. – ^{13}C NMR (100 MHz, [D$_6$]acetone, 20 °C): δ = 22.8 (s; CH_3), 43.0 [d, ^3J(P,C) = 8 Hz; SCH_2], 56.4 (s; CH), 92.5 [d, ^2J(P,C) = 1 Hz; C_5H_5], 170.4 (s; HNCO), 173.1 (s; COOH). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = 19.4 (s). – Minor diastereoisomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20 °C): δ = 1.97 (s, 3 H; CH_3), 2.71, 2.86 [AB system of d, ^2J(H,H) = 12.8 Hz, ^3J(H,H) = 9.3 Hz, ^3J(H,H) = 5.5 Hz, 2 H; SCH_2), 4.60 (dd, ^3J(H,H) = 9.3 Hz, ^3J(H,H) = 5.6 Hz, 1 H; CH], 5.45 (s, 5 H; C_5H_5), NH and OH signals not detected. – ^{13}C NMR (100 MHz, [D$_6$]acetone, 20 °C): δ = 22.8 (s; CH_3), 41.7 (d, ^3J(P,C) = 8 Hz; SCH_2), 55.6 (s; CH), 92.8 (s; C_5H_5), 169.9 (s; HNCO), 172.9 (s; COOH). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = 19.3 (s). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1749 (COOH), 1657 (NO), 1607 cm^{-1} (CONH).

[CpRe(NO)(PPh$_3$)(SCH$_2$CH(NHAc)COOMe)] (**14a**, **b**): To a solution of **13a**, **b** (200 mg, 0.28 mmol) in methanol (10 ml) a few droplets of HBF_4 (54% in ether) were added. The mixture was stirred 3 d at 20 °C. After evaporation to dryness the residue was chromatographed over silica using THF/ether as an eluent. The product zone was evaporated and the residue recrystallized from dichloromethane/pentane. Yield 50 mg (25%), dec. 163 °C. – Both diastereoisomers ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.98 (s, 3 H; CH_3), 2.02 (s, 3 H; CH_3), 2.67 [dd, ^2J(H,H) = 13.6 Hz, ^3J(H,H) = 3.6 Hz, 1 H; SCH_2], 2.86 [dd, ^2J(H,H) = 13.2 Hz, ^3J(H,H) = 6.0 Hz, 1 H; SCH_2], 3.21–3.27 (m, 2 H; SCH_2), 3.67 (s, 3 H; OCH_3), 3.76 (s, 3 H; OCH_3), 4.58–4.64 (m; 2 × 1 H; CH), 5.19 (s, 5 H; C_5H_5), 5.22 (s, 5 H; C_5H_5), 6.44 [d, ^3J(H,H) = 7.2 Hz, 1 H; NH], 6.74 [d, ^3J(H,H) = 5.6 Hz, 1 H; NH]. – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 23.0 (s; CH_3), 23.2 (s; CH_3), 42.0 [d, ^3J(P,C) = 8 Hz ; SCH_2], 45.0 [d, ^3J(P,C) = 8 Hz; SCH_2], 52.1 (s; OCH_3), 52.3 (s; OCH_3), 54.7 (s; CH), 55.3 (s; CH), 91.5 [d, ^2J(P,C) = 1 Hz; C_5H_5], 91.6 (s; C_5H_5), 169.8, 170.1, 172.1, 172.2 (s; HNCO and COOMe). – ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ = 18.6 (s), 18.7 (s). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1748 (COOMe), 1651 cm^{-1} (NO). – $C_{29}H_{30}N_2O_4PReS$ (719.8) calcd C 48.39, H 4.20, N 3.89, S 4.45; found C 48.32, H 4.12, N 3.75, S 4.32.

[CpRe(NO)(PPh$_3$)(SCH$_2$CH(NHAc)COOEt)] (**15a**, **b**): This compound was prepared analogously by refluxing a solution of **13a**, **b** (200 mg, 0.28 mmol) in ethanol (10 ml) in the presence of HBF_4. Yield 49 mg (24%), 19% de (by NMR), dec. 197 °C. – Major diastereoisomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20 °C): δ = 1.24 [t, ^3J(H,H) = 7.1 Hz, 3 H; CH_3], 1.92 (s, 3 H; CH_3), 2.75 [dd, ^2J(H,H) = 13.3 Hz, ^3J(H,H) = 6.9 Hz, 1 H; SCH_2], 2.99–3.06 (m, 1 H; SCH_2), 4.15 [q, ^3J(H,H) = 7.2 Hz, 2 H; OCH_2], 4.53 [dt, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 6.6 Hz, 1 H; CH], 5.35 (s, 5 H; C_5H_5), 7.01 [d, ^3J(H,H) = 7.0 Hz, 1 H; NH]. – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 14.2 (s; CH_3), 23.2 (s; CH_3), 45.2 [d, ^3J(P,C) = 8 Hz ; SCH_2], 55.0 (s; CH), 61.3 (s; OCH_2), 91.6 (s; C_5H_5), 169.9, 170.7 (s; HNCO and COOEt). – ^{31}P NMR (162 MHz, [D$_6$]acetone, 20 °C): δ = 19.4 (s). – Minor diastereoisomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20 °C): δ = 1.19 [t, ^3J(H,H) = 7.1 Hz, 3 H; CH_3], 1.93 (s, 3 H; CH_3), 2.71 [dd, ^2J(H,H) = 13.2 Hz, ^3J(H,H) = 4.1 Hz, 1 H; SCH_2], 2.99–3.06 (m, 1 H; SCH_2), 4.09 [q, ^3J(H,H) = 7.0 Hz, 2 H; OCH_2], 4.43 (m, 1 H; CH), 5.35 (s, 5 H; C_5H_5), 6.90 [d, ^3J(H,H) = 5.5 Hz, 1 H; NH]. – ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 14.2 (s; CH_3), 23.0 (s; CH_3), 42.0 [d, ^3J(P,C) = 11 Hz ; SCH_2], 55.3 (s; CH), 61.0 (s; OCH_2), 91.6 (s; C_5H_5), 170.2, 171.6 (s; HNCO and COOEt). – ^{31}P NMR (162 MHz, [D$_6$]acetone, 20 °C): δ = 18.9 (s). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1748 (COOMe), 1651 cm^{-1} (NO). – $C_{30}H_{32}N_2O_4PReS$ (733.8) calcd C 49.10, H 4.40, N 3.82, S 4.37; found C 49.54, H 4.95, N 3.46, S 4.20.

[CpRe(NO)(PPh$_3$)(SCH$_2$CH$_2$NHAc)] (**8**): A suspension of $Na_2CO_3 \cdot 10\ H_2O$ (286 mg, 1.00 mmol) and *N*-acetylcysteamine (60 mg, 0.50 mmol) in THF (40 ml) was stirred 1 h at 20 °C. To this, a solution of **4** (281 mg, 0.40 mmol) in THF (20 ml) and ethanol (20 ml) was added and the mixture stirred again for 1 h. All volatiles were then removed under vacuum, the residue dissolved in benzene and filtered over Celite, and the product precipitated by adding pentane. Yield 249 mg (94%).

[CpRe(NO)(PPh$_3$)(SCH$_2$CH$_2$COOMe)] (**10**): This compound was prepared analogously from **4** and ethyl (3-mercapto)propionate. Yield 241 mg (91%), dec. 69 °C (dec). – ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 2.74–2.82 (m, 1 H; CH_2), 2.93 (m, 2 H; CH_2), 3.24–3.33 (m, 1 H; CH_2), 3.37 (s, 3 H; OCH_3), 4.83 (s, 5 H; C_5H_5). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = 38.1 [d, ^3J(P,C) = 8 Hz; SCH_2], 40.1 (s; CH_2), 50.9 (s; OCH_3), 91.3 (s; C_5H_5), 173.3 (s; CO). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = 20.0 (s). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1736 (COOMe), 1646 cm^{-1} (NO). – $C_{27}H_{27}NO_3PReS$ (662.8) calcd C 48.93, H 4.11, N 2.11, S 4.84; found C 49.16, H 4.16, N 2.07, S 4.59.

[CpRe(NO)(PPh$_3$)(SCH$_2$CH$_2$C(O)NHCH$_2$Ph)] (**11**): This compound was prepared analogously from **4** and (3-mercaptopropionyl)benzylamine. Yield 221 mg (75%), m.p. 39 °C. – ^{1}H NMR (400 MHz, [D$_6$]acetone, 20 °C): δ = 2.39–2.47 (m, 1 H; CH$_2$), 2.51–2.65 (m, 2 H; CH$_2$), 2.90–2.97 (m, 1 H; CH$_2$), 4.40 [d, ^3J(H,H) = 5.6 Hz, 2 H; NCH$_2$], 5.30 (s, 5 H; C$_5$H$_5$), 7.60 [t, ^3J(H,H) = 5.6 Hz, 1 H; NH]. – ^{13}C NMR (100 MHz, [D$_6$]acetone, 20 °C): δ = 38.3 [d, ^3J(P,C) = 8 Hz; SCH$_2$], 42.1 (s; CH$_2$), 43.2 (s; CH$_2$), 92.5 (s; C$_5$H$_5$), 173.0 (s; CO). – ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 19.5 (s). – IR (CH$_2$Cl$_2$) nu(tilde) = 1654 cm^{-1} (NO). – C$_{33}$H$_{32}$N$_2$O$_2$PReS (737.9) calcd C 53.72, H 4.37, N 3.80, S 4.35; found C 53.76, H 4.64, N 3.77, S 4.67.

*[CpRe(NO)(PPh$_3$)(SCH$_2$CH(NC$_8$H$_4$O$_2$)*COOMe)] (**16a**, **b**): (*R*)-*N*-Phthaloylcysteine (200 mg, 0.80 mmol) was dissolved in ether (15 ml) and treated at 20 °C with a slight excess of diazomethane. After 15 min all volatiles were removed under vacuum and the residue treated with hydrated sodium carbonate and **4** as described above. After chromatography over silica using dichloromethane/acetone (10©lon1) as an eluent and subsequent crystallization from benzene/pentane the product was isolated as a 1:1 mixture of diastereoisomers. Yield 181 mg (56%), dec. 214 °C. From a concentrated solution in acetone the pure (*R*,*R*) form separates as orange crystals. – (*R*,*R*) Diastereoisomer **16a**: ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 3.05 [dd, ^2J(H,H) = 13.6 Hz, ^3J(H,H) = 3.6 Hz, 1 H; SCH$_2$], 3.72 (s, 3 H; OCH$_3$), 3.89 [ddd, ^2J(H,H) = 13.6 Hz, ^3J(H,H) = 11.6 Hz, ^4J(P,H) = 1.0 Hz, 1 H; SCH$_2$], 5.21 [dd, ^3J(H,H) = 11.6 Hz, ^3J(H,H) = 3.6 Hz, 1 H; CH], 5.22 (s, 5 H; C$_5$H$_5$). – ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 41.2 [d, ^3J(P,C) = 9 Hz ; SCH$_2$], 52.6 (s; OCH$_3$), 56.2 (s; CH), 91.5 (s; C$_5$H$_5$), 167.5, 170.2 (s; CO). – ^{31}P NMR (162 MHz, CDCl$_3$, 20°C): δ = 18.9 (s). – (*S*,*R*) Diastereoisomer **16b**: ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 3.35 [dd, ^2J(H,H) = 13.2 Hz, ^3J(H,H) = 11.2 Hz, 1 H; SCH$_2$], 3.68 [dd, ^2J(H,H) = 13.2 Hz, ^3J(H,H) = 4.8 Hz,, 1 H; SCH$_2$], 3.69 (s, 3 H; OCH$_3$), 4.98 [dd, ^3J(H,H) = 11.0 Hz, ^3J(H,H) = 4.6 Hz, 1 H; CH], 5.19 (s, 5 H; C$_5$H$_5$). – ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 41.8 [d, ^3J(P,C) = 9 Hz ; SCH$_2$], 52.5 (s; OCH$_3$), 56.3 (s; CH), 91.5 (s; C$_5$H$_5$), 167.9, 169.5 (s; CO). – ^{31}P NMR (162 MHz, CDCl$_3$, 20 °C): δ = 19.0 (s). – IR (CH$_2$Cl$_2$): ν̃ = 1777, 1720 (phthalimide), 1743 (COOMe), 1649 cm^{-1} (NO). – C$_{35}$H$_{30}$N$_2$O$_5$PReS (807.9) calcd C 52.04, H 3.74, N 3.47, S 3.97; found C 51.74, H 4.00, N 3.37, S 3.97.

[CpRe(NO)(PPh$_3$)(SCH$_2$CH(Me)C(O)NC$_4$H$_7$COOMe)] (**17a**, **b**): *N*-[(*S*)-3-mercapto-2-methylpropionyl]-*S*-proline (174 mg, 0.80 mmol) was converted to its methyl ester and reacted with **4** as described above. After chromatography over silica using dichloromethane/acetone (4:1) as an eluent and subsequent crystallization from benzene/pentane the product was isolated as a 1:1 mixture of diastereoisomers. Yield 229 mg (74%), m.p. 162 °C. A further crystallization from benzene/pentane yielded a sample with 15% de. – Major diastereoisomer: ^{1}H NMR (400 MHz, C$_6$D$_6$, 20 °C): δ = 1.19–1.40 (m, 2 H; CH$_2$), 1.32 [d, ^3J(H,H) = 6.8 Hz, 3 H; CH$_3$], 1.45–1.70 (m, 3 H; CH$_2$, and CH), 2.83 (m, 1 H; CH$_2$), 2.92 [dd, ^3J(H,H) = 11.6 Hz, ^3J(H,H) = 4.0 Hz, 1 H; CH$_2$], 3.34 (s, 3 H; OCH$_3$), 3.45–3.55 (m, 2 H; CH$_2$), 4.64 [t, ^3J(H,H) = 5.6 Hz, 1 H; CH], 4.95 (s, 5 H; C$_5$H$_5$). – ^{13}C NMR (100 MHz, C$_6$D$_6$, 20 °C): δ = 18.6 (s; CH$_3$), 24.9 (s; CH$_2$), 29.2 (s; CH$_2$), 43.4 (s; CH), 46.9 (s; CH$_2$), 49.0 [d, ^3J(P,C) = 8 Hz ; SCH$_2$], 51.4 (s; OCH$_3$), 58.9 (s; CH), 91.7 (s; C$_5$H$_5$), 173.2, 175.0 (s; CO). – ^{31}P NMR (162 MHz, C$_6$D$_6$, 20 °C): δ = 21.0 (s). – Minor diastereoisomer: ^{1}H NMR (400 MHz, C$_6$D$_6$, 20 °C): δ = 1.19–1.40 (m, 2 H; CH$_2$), 1.50 [d, ^3J(H,H) = 6.8 Hz, 3 H; CH$_3$], 1.45–1.70 (m, 2 H; CH$_2$), 1.77–1.85 (m, 1 H; CH), 2.99 (m, 1 H; CH$_2$), 3.20–3.27 (m, 1 H; CH$_2$), 3.37 (s, 3 H; OCH$_3$), 3.61–3.69 (m, 2 H; CH$_2$), 4.80 [dd, ^3J(H,H) = 8.6 Hz, ^3J(H,H) = 4.2 Hz, 1 H; CH], 4.88 (s, 5 H; C$_5$H$_5$). – ^{13}C NMR (100 MHz, C$_6$D$_6$, 20 °C): δ = 17.6 (s; CH$_3$), 25.0 (s; CH$_2$), 29.3 (s; CH$_2$), 43.4 (s; CH), 47.0 (s; CH$_2$), 47.1 [d, ^3J(P,C) = 8 Hz; SCH$_2$], 51.4 (s; OCH$_3$), 59.1 (s; CH), 91.7 (s; C$_5$H$_5$), 173.3, 175.1 (s; CO). – ^{31}P NMR (162 MHz, C$_6$D$_6$, 20 °C): δ = 20.3 (s). – IR (CH$_2$Cl$_2$): ν̃ = 1744 (COOMe), 1633 cm^{-1} (NO). – C$_{33}$H$_{36}$N$_2$O$_4$PReS (773.9) calcd C 51.22, H 4.69, N 3.62, S 4.14; found C 50.93, H 4.48, N 3.56, S 4.10.

X-Ray Structure Determination of (R,R)-[CpRe(NO)(PPh$_3$)-(SCH$_2$CH(NC$_8$H$_4$O$_2$)COOMe)] (**16a**): C$_{35}$H$_{30}$N$_2$O$_5$PReS, molecular mass 807.9, crystal size 0.6 × 0.3 × 0.1 mm, obtained from a saturated acetone solution; monoclinic crystal system, space group $P2_1$ (No. 4), a = 8.594(2), b = 17.566(4), c = 10.801(3) Å, β = 95.269(12)°; V = 1623.8(7) Å^3, Z = 2, d_{calcd} = 1.652 g cm^{-3}; μ(Mo-*K*α) = 2.05 cm^{-1}. Data were collected at 293 K in the range 2° < Θ < 27° from one fourth of the reflection sphere (Enraf-Nonius CAD4 diffractometer, graphite monochromator, Mo-*K*α radiation, λ = 0.70930 Å). Of the 3877 measured reflections 3641 were symmetry-independent and 3456 classified as observed [$I_O > 2\sigma(I_O)$]. The structure was solved by the Patterson method by using the program package SHELXS 86[27] with hydrogen atoms included in their calculated positions. Refinement using the program package SHELXL 93[28] gave R_1 = 0.017, wR_2 = 0.040, Flack parameter©lon –0.002(6). The 5 highest maxima of a final difference Fourier map were below 0.28 e Å^{-3}. Further details of the structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number 408461.

[1] N. Burzlaff, M. Hagel, W. A. Schenk, *Z. Naturforsch., B* **1998**, *53*, 893–899.
[2] E. Block, J. Zubieta in *Advances in Sulfur Chemistry* (Ed.: E. Block), JAI Press, London, **1994**, pp. 133–193.
[3] M. T. Ashby, *Comments Inorg. Chem.* **1990**, *10*, 297–313.
[4] B. Krebs, G. Henkel, *Angew. Chem.* **1991**, *103*, 785–804; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 769–788.
[5] J. E. Baldwin, M. Bradley, *Chem. Rev.* **1990**, *90*, 1079–1088.
[6] P. L. Roach, I. J. Clifton, C. M. H. Hensgens, N. Shibata, C. J. Schofield, J. Hajdu, J. E. Baldwin, *Nature* **1997**, *387*, 827–830.
[7] W. A. Schenk, T. Stur, E. Dombrowski, *Inorg. Chem.* **1992**, *31*, 723–724.
[8] W. A. Schenk, T. Stur, E. Dombrowski, *J. Organomet. Chem.* **1994**, *472*, 257–273.
[9] W. A. Schenk, N. Burzlaff, H. Burzlaff, *Z. Naturforsch. B* **1994**, *49*, 1633–1639.
[10] H. Fischer, U. Gerbing, K. Treier, J. Hofmann, *Chem. Ber.* **1990**, *123*, 725–732.
[11] H. Fischer, C. Kalbas, U. Gerbing, *J. Chem. Soc. Chem. Commun.* **1992**, 563–564.
[12] H. Fischer, A. Ruchay, R. Stumpf, C. Kalbas, *J. Organomet. Chem.* **1993**, *459*, 249–255.
[13] W. Tam, G. Y. Lin, W. K. Wong, W. A. Kiel, V. K. Wong, J. A. Gladysz, *J. Am. Chem. Soc.* **1982**, *104*, 141–152.
[14] S. K. Agbossou, J. M. Fernandez, J. A. Gladysz, *Inorg. Chem.* **1990**, *29*, 476–480.
[15] S. K. Agbossou, C. Roger, A. Igau, J. A. Gladysz, *Inorg. Chem.* **1992**, *31*, 419–424.
[16] S. Wolfe, J. C. Godfrey, C. T. Holdrege, Y. G. Perron, *Can. J. Chem.* **1968**, *46*, 2549–2559.
[17] P. C. Cagle, A. M. Arif, J. A. Gladysz, *J. Am. Chem. Soc.* **1994**, *116*, 3655–3656.
[18] P. C. Cagle, O. Meyer, D. Vichard, K. Weickhardt, A. M. Arif, J. A. Gladysz, *Organometallics* **1996**, *15*, 194–204.
[19] J. J. Kowalczyk, S. K. Agbossou, J. A. Gladysz, *J. Organomet. Chem.* **1990**, *397*, 333–346.
[20] J. A. Gladysz, B. J. Boone, *Angew. Chem.* **1997**, *109*, 566–602; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 550–583.
[21] J. M. Fernandez, J. A. Gladysz, *Organometallics* **1989**, *8*, 207–219.
[22] G. Jaouen, A. Vessieres, I. S. Butler, *Acc. Chem. Res.* **1993**, *26*, 361–369.

[23] C. Giacovazzo, H. L. Monaco, D. Viterbo, F. Scordari, G. Gilli, G. Zanotti, M. Catti, *Fundamentals of Crystallography*, Oxford University Press, Oxford, **1992**, pp. 538–541.
[24] R. E. Eibeck, *Inorg. Synth.* **1963**, *7*, 128–131.
[25] A. Schöberl, A. Wagner in *Methoden der Organischen Chemie (Houbel-Weyl)*, 4th Edition, Vol. 9, Thieme, Stuttgart, **1955**, p. 45.
[26] T. Kametani, K. Kigasawa, M. Hiiragi, N. Wagatsuma, T. Kohagizawa, H. Inoue, *Heterocycles* **1978**, *9*, 831–840.
[27] G. M. Sheldrick, *SHELXS 86, Program for Crystal Structure Solution*, Universität Göttingen, Germany, **1986**.
[28] G. M. Sheldrick, *SHELXL 93, Program for Crystal Structure Refinement*, Universität Göttingen, Germany, **1993**.
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