Enantioselective Organic Syntheses Using Chiral Transition Metal Complexes, 8[+] Chiral Rhenium Complexes of Functionalized Thioaldehydes

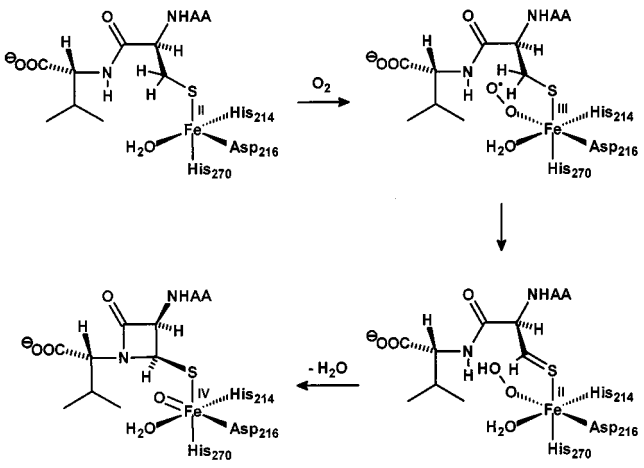
Nicolai Burzlaff[a] and Wolfdieter A. Schenk*[a]

Dedicated to Professor Helmut Werner on the occasion of his 65th birthday

Keywords: Captopril / Cysteine / Rhenium / S ligands / Thioaldehydes

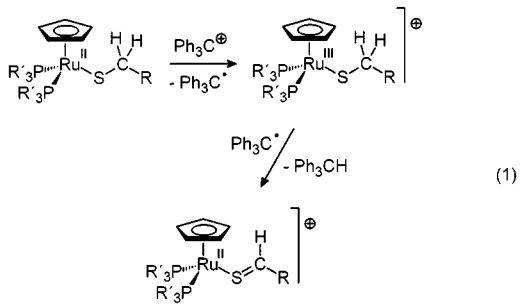
Chiral racemic rhenium thioaldehyde complexes [CpRe(NO)(PPh$_3$)(η^2-S=CHR)]PF$_6$ (**2a–g**) bearing functionalized aliphatic groups R [R = CH$_2$Ph (**a**), COOEt (**b**), CH$_2$COOMe (**c**), CH$_2$C(O)NHCH$_2$Ph (**d**), (*R*)-CH(NC$_8$H$_4$O$_2$)COOMe (**e**), (*S*,*S*)-CH(Me)C(O)NC$_4$H$_7$COOMe (**f**), C$_4$H$_3$O (**g**)] have been obtained by hydride abstraction from the corresponding thiolate complexes [CpRe(NO)(PPh$_3$)(SCH$_2$R)] (**1a–g**). With the exception of **2b**, only single stereoisomers with *like* configurations at rhenium and the thioaldehyde carbon atom were obtained. In some cases, the corresponding sulfinate complexes [CpRe(NO)(PPh$_3$)(SO$_2$CH$_2$R)] (**3d–f**) were formed as by-products. The analogous toluenesulfinate complex [CpRe(NO)(PPh$_3$){SO$_2$(4-C$_6$H$_4$CH$_3$)}] (**3a**) has been prepared from [CpRe(NO)(PPh$_3$)(THF)]BF$_4$ (**8**), and the structure of **3e** has been determined by X-ray crystallography. The use of phosphorus ligands other than PPh$_3$ was briefly explored with the synthesis of [CpRe(NO)(PR′$_3$)(η^2-S=CHR)]PF$_6$ (**5a–d**) [R′ = OPh, R = Ph (**a**), 4-C$_6$H$_4$Cl (**b**), R′ = *i*Pr, R = Ph (**c**), H (**d**)]. Nucleophilic addition of NaSMe to [CpRe(NO)(PPh$_3$){η^2-S=CH(4-C$_6$H$_4$OMe)}]PF$_6$ (**5e**) gave the dithioacetal complex [CpRe(NO)(PPh$_3$){SCH(SMe)(4-C$_6$H$_4$OMe)}] (**9**) in high yield and with low diastereoselectivity. Diels–Alder additions of **5a**, **e** with 2,3-dimethylbutadiene and 2,3-dimethoxybutadiene gave complexes of cyclic thioethers (**10a–c**). From the relative rates of reaction (**5a** >> **5e**) and the low diastereoselectivity, it was concluded that the cycloadditions as well as the nucleophilic addition proceed via the linkage isomers [CpRe(NO)(PR′$_3$)(η^1-S=CHR)]PF$_6$.

The central step of penicillin biosynthesis leading to the formation of the β-lactam ring is initiated by a hydrogen atom abstraction from the α position of an iron(III)-coordinated cysteine moiety. The thioaldehyde intermediate thus formed undergoes nucleophilic attack by the deprotonated amide group of the cysteine[2] (Scheme 1).



Scheme 1. Hydride abstraction and ring closure steps of penicillin biosynthesis[2]

We have in the past reported a similar and very efficient synthesis of ruthenium thioaldehyde complexes from the corresponding thiolates and triphenylcarbenium salts.[3] Mechanistically, this reaction proceeds through a one-electron oxidation of Ru^{II} to Ru^{III}, followed by hydrogen atom abstraction (Equation 1).[4]



For ruthenium, this synthesis appears to be limited to complexes of aromatic thioaldehydes. However, the same reaction carried out on rhenium thiolates of the type [CpRe(NO)(PPh$_3$)(SCH$_2$R)] also gave the corresponding thioaldehyde complexes with R = H, CH$_3$.[5] We report herein on an extension of this methodology to complexes of aliphatic thioaldehydes, particularly those bearing functional groups on the side chain.

Complexes of aliphatic thioaldehydes have hitherto attracted only limited attention. Cobalt and rhodium thioacetaldehyde complexes have been synthesized either by nucleophilic substitution of α-(bromoethyl) complexes or by

[+] Part 7: Ref.[1]

[a] Institut für Anorganische Chemie der Universität, Am Hubland, D-97074 Würzburg, Germany
Fax: (internat.) + 49(0)931/888-4605
E-mail: wolfdieter.schenk@mail.uni-wuerzburg.de

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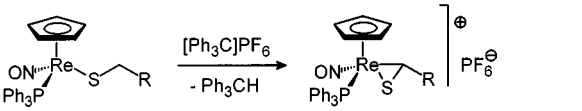
hydrogenation of a thioketene complex.[6][7] A phenylthioacetaldehyde complex of ruthenium has been obtained by H_2S addition to the corresponding vinylidene complex.[8] Thioaldehyde complexes of titanium and zirconium are generally accessible by intramolecular methane elimination from $[L_nM(CH_3)(SCH_2R)]$ complexes[9][10] or simply by α-deprotonation of thiolate ligands.[11] Complexes of η^4-coordinated unsaturated thioaldehydes have been obtained by metal-induced ring-opening of thietes.[12] However, in none of these cases have any substrates bearing functional groups on the side chain been involved.

Results

Synthesis of Thioaldehyde Complexes

Treatment of the thiolate complexes **1a**−**c**[1] with triphenylcarbenium hexafluorophosphate at −70°C as described previously[5] gave the expected thioaldehyde complexes **2a**−**c** in fair to good yields (Equation 2).



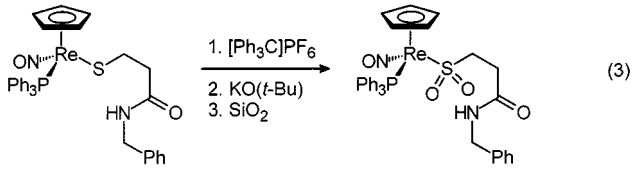
(2)

1a - c

R: CH_2Ph (**a**), C(O)OEt (**b**), $CH_2C(O)OMe$ (**c**)

2a (81%)
2b (76%)
2c (58%)

The method has its limitations, however. Similar reactions with R = $CH{=}CH_2$, CH_2NHAc, or $CH_2C(O)NHCH_2Ph$ gave inseparable mixtures of products, among which the expected thioaldehyde complexes could only be identified spectroscopically. In one such case, base hydrolysis of the reaction mixture led to the formation of the corresponding sulfinate complex **3d** along with some starting material **1d** (Equation 3).

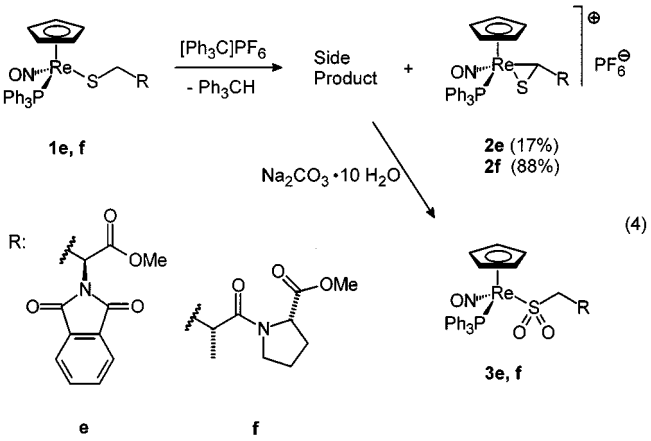


(3)

1d **3d** (25%)

Similarly, the thiolate complexes derived from the methyl esters of (*R*)-*N*-phthaloylcysteine (**1e**) and *N*-[(*S*)-3-mercapto-2-methylpropionyl]-(*S*)-proline (Captopril) (**1f**) gave the corresponding thioaldehyde complexes in poor (**2e**) and good yields (**2f**). The formation of side products became more pronounced at low temperature; their hydrolysis again gave the sulfinate complexes **3e**, **f** (Equation 4), which could be isolated by chromatography.

The new thioaldehyde complexes were obtained as brownish-yellow microcrystalline materials, which were found to be soluble only in polar organic solvents such as dichloromethane or acetone. A dominant feature of their



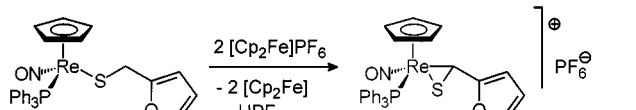
(4)

1e, f **2e** (17%) **2f** (88%) **3e, f**

e **f**

infrared spectra, besides the absorptions of the ester and amide groups, is an intense NO stretching absorption around 1750 cm^{-1}. In the ^1H- and ^{13}C-NMR spectra, the thioformyl group gives resonances near $\delta(^1H) = 6$ and $\delta(^{13}C) = 45$, which confirms the $\eta^2(C,S)$-coordination of the thioaldehyde ligand.[5] For this coordination mode, the existence of diastereoisomers with *syn* and *anti* arrangements of the Cp ligand and the substituent at the thioformyl group can be expected. For **2b**, two isomers in an 80:20 ratio were indeed found, whereas **2a** and **2c** were obtained as single diastereoisomers. Low-temperature NMR spectra did not reveal any dynamic phenomena down to −60°C. The complexes **1e**, **f**, which contain enantiomerically pure thiolate ligands, were employed in this synthesis as diastereomeric mixtures with opposing configurations at rhenium. As a consequence, **2e**, **f** were obtained as 1:1 mixtures of diastereoisomers. The same reaction carried out on diastereomerically pure (R_{Re},R_C)-**1e**[1] gave **2e** as a single isomer, indicating that the hydride abstraction proceeds with retention of configuration at rhenium.

Treatment of the (2-furyl)methylthiolate complex **1g** with triphenylcarbenium hexafluorophosphate gave only an intractable, dark-purple mixture. As noted previously, the dehydrogenation of thiolate complexes may in some cases be brought about using ferrocenium hexafluorophosphate as a one-electron oxidant.[4] Using this method we obtained the expected (2-furyl)methanethial complex **2g** in acceptable yield as a single diastereoisomer (Equation 5).



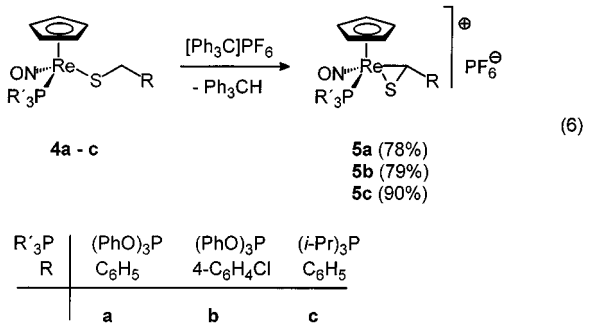
(5)

1g **2g** (41%)

Again, **2g** was obtained as a yellow crystalline compound and its spectroscopic properties were very similar to those of the analogous thiobenzaldehyde complex.[5]

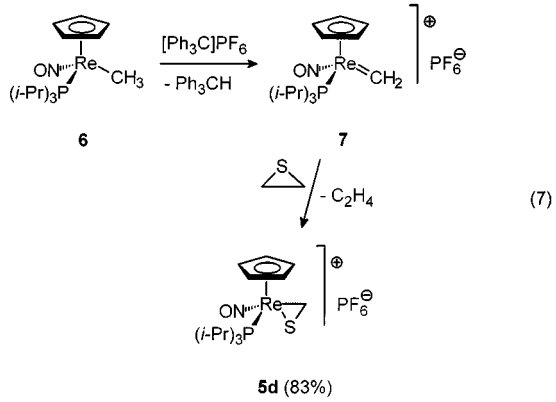
The use of other rhenium complexes with different steric and electronic properties was investigated briefly. The triphenylphosphite complexes **4a**, **b** and the triisopropylphosphane complex **4c**[13] reacted cleanly with triphenylcarbenium hexafluorophosphate, giving good yields of the corre-

sponding thiobenzaldehyde complexes **5a**−**c**, again as single diastereoisomers (Equation 6).



(6)

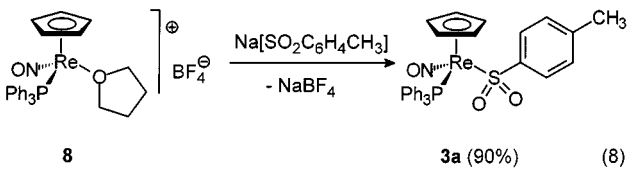
Finally, the thioformaldehyde complex **5d** was obtained from the methyl complex **6** by a reaction sequence closely analogous to the synthesis of $[CpRe(NO)(PPh_3)(S{=}CH_2)]PF_6$ originally reported by Gladysz[14] (Equation 7).



(7)

The thioaldehyde complexes **5a**−**d** are spectroscopically very similar to their triphenylphosphane analogues. The variation of the electron density at rhenium is apparent from the shift of ν(NO) to higher frequencies for L = $P(OPh)_3$ and, for L = $P(iPr)_3$ in particular, from the 5 ppm upfield shift of the ^{13}C resonance of the thiocarbonyl carbon atom.

Since rhenium sulfinate complexes $[CpRe(NO)(PPh_3)(SO_2R)]$ have not been described previously, we decided to prepare an authentic example by a ligand substitution reaction (Equation 8).



(8)

Complexes **3a**, **d**−**f** were obtained as light-yellow materials and were found to be readily soluble in dichloromethane and chloroform. Their infrared spectra show an intense ν(NO) absorption around 1700 cm^{-1} and two medium-intensity bands at 1150−1180 and 1038−1055 cm^{-1} due to $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$. A further characteristic feature of sulfinate complexes is a low field ^{13}C-NMR signal[15] due to the α-carbon atom, which is found at δ = 157 for **3a** and at δ = 70 for **3d**.

Crystal and Molecular Structure of 3e

The identity of the sulfinate complexes was finally confirmed by an X-ray structure determination of the cysteine derivative **3e**. The compound crystallized as an acetone solvate in the centrosymmetric space group $P\bar{1}$, which indicates that racemization of the cysteine-derived ligand must have occurred en route to **3e**. Indeed, the sample of **1e** used in this reaction had been obtained under sufficiently alkaline conditions (NaOEt/HOEt) to effect racemization at the α carbon atom.[1] Figure 1 shows a view of the molecule in its (*S*,*S*) configuration.

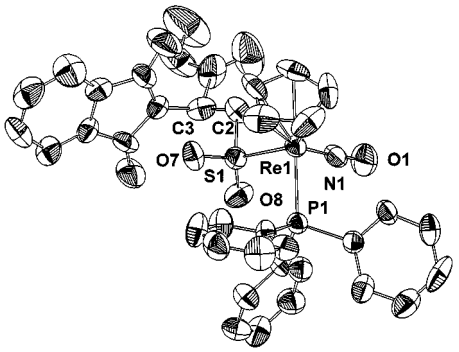


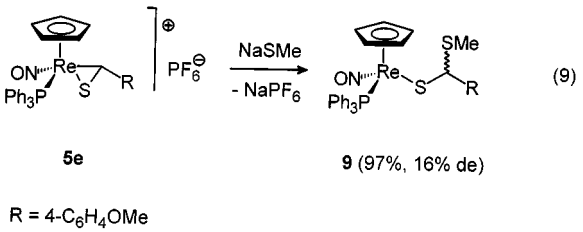
Figure 1. Molecular structure $[CpRe(NO)(PPh_3)\{SO_2CH_2CH(NC_8H_4O_2)COOMe\}]$ (**3e**). Selected distances [pm] and angles [°] (standard deviations in parentheses): Re(1)−S(1) 235.8(4), Re(1)−P(1) 236.8(4), Re(1)−N(1) 174(2), N(1)−O(1) 121(2), S(1)−C(2) 178(2), S(1)−O(7) 146.3(11), S(1)−O(8) 145.3(11),; S(1)−Re(1)−P(1) 92.82(14), S(1)−Re(1)−N(1) 94.2(4), P(1)−Re(1)−N(1) 90.9(4), Re(1)−S(1)−C(2) 103.4(5), Re(1)−S(1)−O(7) 111.2(4), Re(1)−S(1)−O(8) 117.8(5), O(7)−S(1)−O(8) 114.4(7); P(1)−Re(1)−S(1)−C(2) 161.5(12).

It is interesting to compare the molecular dimensions of **3e** with those of the starting thiolate complex **1e**.[1] All relevant bond lengths except those involving the sulfur atom are the same within one standard deviation. The S−Re and S−C bonds in **3e** are 4 pm shorter due to the contraction of the valence orbitals at the sulfur atom resulting from the increase of the formal oxidation state and the attachment of two highly electronegative oxygen atoms, respectively. The most conspicuous difference between the structures of **1e** and **3e** concerns the bond angles at rhenium. In **1e**, the angle S−Re−N is widened to 102.35(11)°.[1] A similar distortion has been found in other thiolate complexes, e.g. $[CpRe(NO)(PPh_3)\{SCH(Ph)(2\text{-}C_6H_4Me)\}]$ [101.3(2)°][16] and $[CpRe(NO)\{P(iPr)_3\}(SCH_3)]$ [102.2(4)°].[13] In **3e**, however, the N−Re−S angle [94.2(4)°] is close to the value of a regular octahedron, despite the fact that a sulfinate ligand is sterically more demanding than a thiolate group.

Reactions of Thioaldehyde Complexes

Typical reactions of transition metal thioaldehyde complexes include nucleophilic additions and [2+4]-cycload-

ditions.[17–19] We have found previously that thiolates add rapidly to cationic η^1-thioaldehyde complexes of ruthenium.[4] In a similar experiment, **5e**[5] was treated with sodium methylthiolate in acetone. An almost quantitative yield of the dithioacetal complex **9** was isolated as a mixture of two diastereoisomers (Equation 9).



(9)

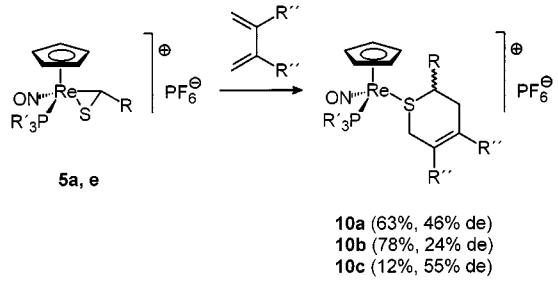
5e

9 (97%, 16% de)

R = 4-C_6H_4OMe

Complex **9** was obtained as a yellow oil and was found to be soluble in most common organic solvents. The spectroscopic properties of **9** are very similar to those of other thiolate complexes of the type [CpRe(NO)(PPh_3)(SR)].[1] Particularly characteristic is an intense ν(NO) absorption at ca. 1650 cm^{-1} and, in the ^{13}C-NMR spectrum, two low field signals due to the α carbon at sulfur in the two diastereoisomers, 1 ppm apart and split into doublets through coupling with phosphorus.

The complexes were next subjected to Diels–Alder-type additions with 2,3-dimethylbutadiene and 2,3-dimethoxybutadiene (Equation 10).



5a, e

10a (63%, 46% de)
10b (78%, 24% de)
10c (12%, 55% de)

R′$_3$P	$(PhO)_3P$	$(PhO)_3P$	Ph_3P
R	C_6H_5	C_6H_5	4-C_6H_4OMe
R′′	CH_3	OCH_3	CH_3
	5a	**5a**	**5e**
	10a	**10b**	**10c**

(10)

The triphenylphosphane complex **5e** reacted sluggishly; even after 5 d at room temperature the isolated yield of the adduct **10c** was only 12%. In contrast, the triphenylphosphite complex **5a** gave good yields of the cycloaddition products **10a**, **b** in less than 1 h. Again, the diastereoselectivity was disappointingly low. **10a–c** were obtained as yellow crystalline solids. In the ^{1}H-NMR spectra, some of the signals of the minor diastereoisomers of **10a**, **b** are broadened due to slightly hindered inversion at sulfur.[20][21] In this regard, **10a**, **b** are quite similar to the analogous cycloadducts of the ruthenium thioaldehyde complexes reported previously.[4]

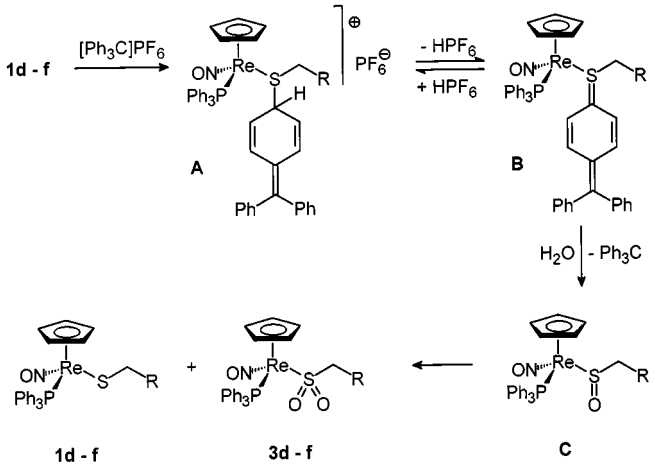
Discussion

There is a striking similarity between the synthesis of thioaldehyde complexes through β-hydride abstraction discovered in this laboratory (Equation 1)[3][4] and the formation of the thioaldehyde intermediate in penicillin biosynthesis (Scheme 1).[2] Both involve the coordination of a thiolate group to a d^6 transition metal complex followed by a one-electron oxidation to give the corresponding d^5 system, and H atom abstraction from the carbon atom in the position β to the metal. In view of this, it seemed a worthwhile undertaking to extend our investigations to thioaldehyde complexes derived from cysteine and other functionalized thiolates. Reactivity studies would then perhaps provide a deeper insight into the inner workings of isopenicillin N synthase (IPNS).

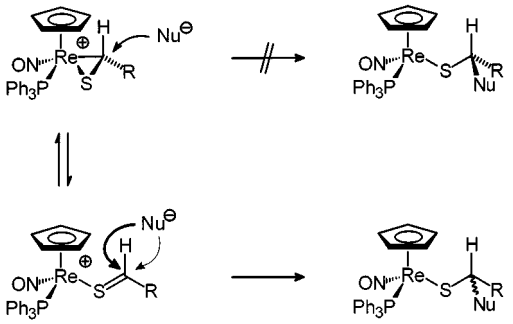
The coordination of prochiral alkenes and heteroalkenes to the chiral Lewis acid $[CpRe(NO)(PPh_3)]^+$ is, in general, accompanied by a high degree of diastereoselectivity.[22] For purely steric reasons, an *anti* arrangement of the Cp ring at rhenium and the substituent R is preferred. This is apparently also true for thiobenzaldehydes[5] and the aliphatic thioaldehydes forming the basis of this study. In the case of the thioacetaldehyde complex [CpRe(NO)(PPh_3)(S=$CHCH_3$)]PF_6, we have been able to detect the minor (*RS*,*SR*)-diastereoisomer by low-temperature NMR.[5] The equilibration of the diastereoisomers proceeds via the corresponding η^1-(*S*) isomers, which can often be observed separately,[23][24] e.g. in the case of the similar ruthenium complexes [$CpRu(PMe_3)_2$(S=CHR)]PF_6.[4] This is in contrast to the thioformaldehyde complexes [CpRe(NO)(PPh_3)(S=CH_2)]PF_6[14] and **5d**, as well as the ester derivative **2b**, which are static at room temperature. The energy of the π* level of the C=S double bond, which is raised by +I substituents and lowered by −M substituents, obviously determines the activation energy for the $\eta^2 \rightarrow \eta^1 \rightarrow \eta^2$ rearrangement.

Although in general the hydride abstraction with triphenylcarbenium salts gave good results, it was not always devoid of side reactions. Thus, starting from the thiolate complexes **1d–f**, the ^{31}P-NMR spectra of the crude reaction mixtures invariably featured a prominent signal at δ = 11, which is typical of thioether complexes [CpRe(NO)(PPh_3)(SRR′)]PF_6.[5] Attempted isolation of these byproducts led to further decomposition, which, after workup under basic conditions, ultimately resulted in the formation of the sulfinate complexes **3d–f** (Equation 3, 4). A likely explanation for this course of events is summarized in Scheme 2.

Electrophilic attack by the trityl cation gives an unstable thioether complex **A**. Under basic conditions, provided for example by chromatography on silica, **A** is deprotonated to give a resonance-stabilized metallated sulfur ylide **B**, which, in turn, is hydrolyzed to a sulfenate complex **C**. Transition metal sulfenate complexes remain a rare and little-understood class of compounds.[25] While there are some examples of quite stable complexes,[25–27] others seem to have a pronounced tendency to undergo a redistribution of their oxygen atoms.[28] Such a disproportionation would ulti-



Scheme 2. Formation of sulfinate side products **3d**−**f**



Scheme 3. Stereochemical course of nucleophilic attack at the carbon atom

mately produce the observed sulfinate complexes **3d**−**f** along with the starting compounds **1d**−**f**.

A comparison of spectroscopic and structural data of the sulfinate complex **3e** and the corresponding thiolate **1e**[1] reveals further insights into the bonding in low-valent transition metal thiolate complexes. The importance of antibonding interactions between the p-type lone pairs at sulfur and the occupied d orbitals at the metal has been stressed repeatedly.[29][30] In sulfinate complexes such as **3e** the sulfur electrons are no longer available for such π interactions. As a consequence, the electron density at rhenium is lowered compared to that in **1e**, which is most obvious from a 50 cm^{-1} hypsochromic shift of ν(NO). Furthermore, the N−Re−S angle, which in **1e** is widened to more than 102° to minimize antibonding,[13] is now lowered again to 94°. Thus, in hindsight the structure of **3e** offers additional proof of our contention that bond angles in low-valent transition metal thiolate complexes are influenced by π-antibonding interactions to a similar extent as bond lengths and dihedral angles.[29]

The disappointingly low diastereoselectivity of the nucleophilic addition (Equation 9) deserves some comment. If this reaction were analogous to the addition of nucleophiles to coordinated alkenes,[31][32] i.e. backside attack by Nu^- accompanied by cleavage of the metal−carbon bond, then the diastereoselectivity should somehow reflect the high diastereoisomer ratio of the starting thioaldehyde complexes. If, on the other hand, the η^2-thioaldehyde complexes described here are in rapid equilibrium with their η^1-isomers − such equilibria have been observed in many other cases, including the closely related ruthenium complexes $[CpRu(PR'_3)_2(S{=}CHR)]$[4] − then a much lower asymmetric induction would be expected (Scheme 3).

In the Diels−Alder addition (Equation 10), the less stable but more reactive η^1-isomers also play a decisive role. We have seen previously that with decreasing electron donation from the supporting phosphane ligands, the isomer ratio shifts in favor of the η^1 form.[4] As a consequence, the triphenylphosphite complex **5a** reacts with dienes much more rapidly than the triphenylphosphane complex **5e** does. The diastereoselectivity, on the other hand, is again too low to be synthetically useful.

Conclusions

We have demonstrated herein that the synthesis of thioaldehyde complexes through β-hydride abstraction can be extended to aliphatic thioaldehydes, and that it tolerates ester and amide functionalities. In particular, the successful synthesis of the cysteine-derived thioaldehyde complex **2e** offers additional proof of the mechanism of penicillin biosynthesis proposed by Baldwin.[2] Nucleophilic additions and cycloadditions at the C=S function proceed via the more reactive η^1 linkage isomers. In order to achieve high diastereoselectivities in these reactions, it will be necessary to employ less electron-donating and sterically more demanding phosphorus ligands.

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 quaternary 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 phenyl groups are unremarkable 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$_3$)(SR)] (**1a**−**g**),[1] [CpRe(NO)(PR′$_3$)(SR)] (**4a**−**c**),[13] [CpRe(NO)(PPh$_3$){η^2-S=CH(4-C_6H_4OMe)}]PF_6 (**5e**),[5] [CpRe(NO){P(*i*Pr)$_3$}(CH_3)] (**6**),[13] [CpRe(NO)(PPh$_3$)(OC_4H_8)]BF_4 (**8**),[33] sodium methylthiolate.[34] All other reagents were used as purchased.

[CpRe(NO)(PPh$_3$)(η^2-S=CHCH$_2$Ph)]PF_6 (2a): At −70°C, a solution of $[Ph_3C]PF_6$ (66 mg, 0.17 mmol) in dichloromethane (5 mL) was added to a solution of **1a** (102 mg, 0.15 mmol) in the same solvent (10 mL). The mixture was allowed to warm to 20°C and then concentrated in vacuo to a volume of 2 mL. Addition of diethyl ether led to precipitation of the product, which was filtered off, washed with diethyl ether, and dried in vacuo. Yield 100 mg (81%); m.p. 108°C. − ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C):

δ = 3.03 [dd, ^2J(H,H) = 13.8 Hz, ^3J(H,H) = 9.6 Hz, 1 H, CH_2], 3.93 [dd, ^2J(H,H) = 13.8 Hz, ^3J(H,H) = 3.0 Hz, 1 H, CH_2], 6.00 [ddd, ^3J(H,H) = 9.6 Hz, ^3J(H,H) = 3.6 Hz, ^3J(P,H) = 2.0 Hz, 1 H, SCH], 6.33 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 48.5 (s, SCH_2), 54.0 (s, SCH), 101.4 (s, C_5H_5). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 6.9 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1744 cm^{-1} (NO). − $C_{31}H_{28}F_6NOP_2ReS$ (824.8): calcd. C 45.14, H 3.42, N 1.70, S 3.89; found C 44.97, H 3.63, N 1.71, S 3.84.

[CpRe(NO)(PPh$_3$)(η^2-S=CHCOOEt)]PF$_6$ (2b): This compound was prepared analogously from **1b**. Yield 92 mg (76%), m.p. 212°C (dec.). − Major diastereoisomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 1.27 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 4.21, 4.26 [q of AB systems, ^2J(H,H) = 10.9 Hz, ^3J(H,H) = 7.1 Hz, 2 H, OCH_2], 5.87 [d, ^3J(P,H) = 1.2 Hz, 1 H, SCH], 6.51 [d, ^3J(P,H) = 0.9 Hz, 5 H, C_5H_5]. − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 14.8 (s, CH_3), 39.9 (s, SCH), 62.2 (s, OCH_2), 102.3 (s, C_5H_5), 171.8 (s, C=O). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 8.0 (s). − Minor diastereoisomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 1.36 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 4.37, 4.39 [q of AB systems, ^2J(H,H) = 4.1 Hz, ^3J(H,H) = 7.1 Hz, 2 H, OCH_2], 5.08 [d, ^3J(P,H) = 1.7 Hz, 1 H, SCH], 6.23 [d, ^3J(P,H) = 0.8 Hz, 5 H, C_5H_5]. − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 14.6 (s, CH_3), 43.7 (s, SCH), 62.9 (s, OCH_2), 103.4 (s, C_5H_5), 174.9 (s, C=O). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 6.2 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1764 (NO), 1719 cm^{-1} (COOR). − $C_{27}H_{26}F_6NO_3P_2ReS$ (806.7): calcd. C 40.20, H 3.25, N 1.74, S 3.97; found C 40.52, H 3.46, N 1.69, S 4.02.

[CpRe(NO)(PPh$_3$)(η^2-S=CHCH$_2$COOMe)]PF$_6$ (2c): This compound was prepared analogously from **1c**. The purple-black crude product was suspended in acetone and stirred for 24 h. **2c** was precipitated from the filtered solution by adding diethyl ether. Yield 70 mg (58%), m.p. 100°C. − ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 3.19, 3.56 [d of AB systems, ^2J(H,H) = 17.0 Hz, ^3J(H,H) = 6.4 Hz, ^3J(H,H) = 5.6 Hz, 2 H, CH_2], 3.70 (s, 3 H, OCH_3), 5.88 (br. t, 1 H, SCH), 6.34 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 45.5 (s, SCH), 52.3 (s, OCH_3), 69.3 (s, CH_2), 101.7 (s, C_5H_5), 172.8 (s, C=O). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 6.8 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1744 cm^{-1} (NO). − $C_{27}H_{26}F_6NO_3P_2ReS$ (806.7): calcd. C 40.20, H 3.25, N 1.74, S 3.97; found C 40.46, H 3.45, N 1.81, S 4.07.

[CpRe(NO)(PPh$_3$){η^2-S=CHCH(NC$_8$H$_4$O$_2$)COOMe}]PF$_6$ (2e): This compound was prepared from a 1:1 diastereomeric mixture of (R_{Re},R_C/S_{Re},R_C)-**1e**.[1] The dark-brown crude product was suspended in acetone and stirred for 24 h. After evaporation of the solvent to dryness, the residue was washed with benzene and treated again with acetone as above. Crystallization from dichloromethane/diethyl ether/pentane finally gave pure **2e**. Yield 24 mg (17%), m.p. 117°C. − (R_{Re},R_C,R_C)-Diastereoisomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 3.83 (s, 3 H, OCH_3), 4.81 [d, ^3J(H,H) = 9.6 Hz, 1 H, CH], 6.30 [dd, ^3J(H,H) = 9.2 Hz, ^3J(P,H) = 1.8 Hz, 1 H, SCH], 6.52 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 46.3 (s, SCH), 53.9 (s, OCH_3), 68.3 (s, CH), 102.7 (s, C_5H_5), 167.3 (s, C=O), 168.0 (s, C=O). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 7.3 (s). − (S_{Re},S_C,R_C)-Diastereoisomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 3.79 (s, 3 H, OCH_3), 4.62 [d, ^3J(H,H) = 10.0 Hz, 1 H, CH], 6.45 [dd, ^3J(H,H) = 9.6 Hz, ^3J(P,H) = 2.0 Hz, 1 H, SCH], 6.34 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 45.7 (s, SCH), 53.8 (s, OCH_3), 69.2 (s, CH), 102.3 (s, C_5H_5), 167.9 (s, C=O), 168.7 (s, C=O). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 7.0 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1778 (CO), 1748 (NO), 1722 cm^{-1} (CO). − $C_{35}H_{29}F_6N_2O_5P_2ReS$ (951.8): calcd. C 44.17, H 3.07, N 2.94, S 3.37; found C 43.67, H 3.43, N 2.91, S 3.43.

Using the same procedure, diastereomerically pure (R_{Re},R_C,R_C)-**2e** was obtained from pure (R_{Re},R_C)-**1e**.

[CpRe(NO)(PPh$_3$){SO$_2$CH$_2$CH(NC$_8$H$_4$O$_2$)COOMe}] (3e): This compound was isolated as a 1:1 mixture of diastereoisomers from the combined benzene extracts by partial evaporation and precipitation with pentane. A complete separation from **2e** and traces of unidentified decomposition products could not be achieved. However, the compound was fully characterized by X-ray crystallography. − Both diastereoisomers: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 3.70 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 3.68−3.80 (m, 1 H, CH_2), 3.88−4.01 (m, 2 H, CH_2), 4.16−4.24 (m, 1 H, CH_2), 5.34 (s, 5 H, C_5H_5), 5.38 (s, 5 H, C_5H_5), 5.53−5.57 (m, 2 H, CH). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 47.2 (s, CH), 47.6 (s, CH), 53.1 (s, OCH_3), 53.1 (s, OCH_3), 66.3 (s, CH_2), 68.0 (s, CH_2), 93.9 (s, C_5H_5), 93.9 (s, C_5H_5), 167.3 (s, C=O), 167.4 (s, C=O), 169.0 (s, C=O), 169.2 (s, C=O). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 13.3 (s), 13.8 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1778 (CO), 1748 (COOR), 1722 (CO), 1700 cm^{-1} (NO).

[CpRe(NO)(PPh$_3$){η^2-S=CHCH(Me)C(O)NC$_4$H$_7$COOMe}]PF$_6$ (2f): This compound was prepared as a 1:1 mixture of diastereoisomers from (R_{Re},S_C,S_C/S_{Re},S_C,S_C)-**1f**[1] and [Ph$_3$C]PF$_6$ at 20°C. Yield 121 mg (88%), m.p. 72°C (dec.). − Both diastereoisomers: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 1.43 [d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 1.57 [d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 1.90−2.20 (m, 2 × 2 H, CH_2), 2.72 [dq, ^3J(H,H) = 9.6 Hz, ^3J(H,H) = 6.8 Hz, 1 H, CH], 2.77 [dq, ^3J(H,H) = 9.6 Hz, ^3J(H,H) = 6.8 Hz, 1 H, CH], 3.65 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 4.20−4.46 (m, 2 × 2 H, CH_2), 5.61 (m, 1 H, CH), 5.83 (m, 1 H, CH), 5.82 [dd, ^3J(H,H) = 9.4 Hz, ^3J(P,H) = 2.0 Hz, 1 H, SCH], 5.90 [dd, ^3J(H,H) = 9.6 Hz, ^3J(P,H) = 2.2 Hz, 1 H, SCH], 6.31 [d, ^3J(P,H) = 0.4 Hz, 5 H, C_5H_5], 6.47 [d, ^3J(P,H) = 0.8 Hz, 5 H, C_5H_5]. − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 18.2 (s, CH_3), 25.3 (s, CH_2), 25.4 (s, CH_2), 25.9 (s, CH_3), 29.2 (s, CH_2), 29.3 (s, CH_2), 47.8 (s, CH_2), 47.8 (s, CH_2), 50.0 (s, SCH), 52.1 (s, OCH_3), 52.2 (s, OCH_3), 52.7 (s, SCH), 55.9 (s, CH), 56.5 (s, CH), 59.4 (s, CH), 59.6 (s, CH), 101.6 (s, C_5H_5), 101.9 (s, C_5H_5), 173.0 (s, C=O), 173.1 (s, C=O), 173.4 (s, C=O), 175.4 (s, C=O). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 6.8 (s), 7.2 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1747 (NO), 1641 cm^{-1} (CO). − $C_{33}H_{35}F_6N_2O_4P_2ReS$ (917.9): calcd. C 43.18, H 3.84, N 3.05, S 3.49; found C 42.89, H 4.09, N 2.90, S 3.40.

[CpRe(NO)(PPh$_3$){SO$_2$CH$_2$CH(Me)C(O)NC$_4$H$_7$COOMe}] (3f): Treatment of **1f** with [Ph$_3$C]PF$_6$ at −70°C gave a mixture of compounds, which was hydrolyzed with an excess of $Na_2CO_3 \cdot 10\,H_2O$ in THF. After concentration to dryness, the residue was dissolved in dichloromethane and chromatographed by passage through a short (20 cm) silica column with dichloromethane/acetone, 2:1, as eluent. The yellow band containing **3f** was concentrated to dryness and the residue was recrystallized from dichloromethane/pentane. Yield 41 mg (34%), m.p. 190°C (dec.). − Both diastereoisomers: ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.09 [d, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.25 [d, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.80−2.20 (m, 2 × 4 H, CH_2), 2.95 [dd, ^2J(H,H) = 13.2 Hz, ^3J(H,H) = 2.8 Hz, 1 H, SO_2CH_2], 3.06 [dd, ^2J(H,H) = 13.4 Hz, ^3J(H,H) = 4.2 Hz, 1 H, SO_2CH_2], 3.14 (m, 1 H, CH), 3.29 (m, 1 H, CH), 3.50−3.60 (m, 2 H, CH_2), 3.65 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 3.78 (m, 2 H, CH_2), 3.81 [dd, ^2J(H,H) = 13.2 Hz, ^3J(H,H) = 6.8 Hz, 1 H, SO_2CH_2], 3.89 [dd, ^2J(H,H) = 12.8 Hz, ^3J(H,H) = 8.8 Hz, 1 H, SO_2CH_2], 4.43 [dd, ^3J(H,H) = 8.8 Hz, ^3J(H,H) = 4.4 Hz, 1 H, CH], 4.51 [dd, ^3J(H,H) = 8.8 Hz, ^3J(H,H) = 4.4 Hz, 1 H, CH],

5.33 (s, 5 H, C_5H_5), 5.34 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 17.8 (s, CH_3), 18.2 (s, CH_3), 24.7 (s, CH_2), 24.8 (s, CH_2), 29.0 (s, CH_2), 29.0 (s, CH_2), 31.8 (s, CH), 33.8 (s, CH), 46.8 (s, CH_2), 46.8 (s, CH_2), 51.9 (s, OCH_3), 52.0 (s, OCH_3), 58.6 (s, CH), 58.9 (s, CH), 73.9 (s, SO_2CH_2), 75.3 (s, SO_2CH_2), 93.8 (s, C_5H_5), 94.0 (s, C_5H_5), 173.0 (s, C=O), 173.1 (s, C=O), 174.0 (s, C=O), 174.6 (s, C=O). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 14.0 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1747 (COOR), 1699 (NO), 1645 ($CONR_2$), 1177 (SO), 1045 cm^{-1} (SO). − $C_{33}H_{36}N_2O_6PReS$ (805.9): calcd. C 49.18, H 4.50, N 3.48, S 3.98; found C 48.85, H 4.59, N 3.20, S 3.74.

[CpRe(NO)(PPh$_3$){SO$_2$CH$_2$CH$_2$C(O)NHCH$_2$Ph}] (3d): Treatment of **1d** (111 mg, 0.15 mmol) with $[Ph_3C]PF_6$ (66 mg, 0.17 mmol) at −70°C as described above for **2a** gave a mixture of compounds, which was solvolyzed with an excess of KO(*t*Bu) in THF. After concentration to dryness, the residue was dissolved in dichloromethane and chromatographed by passage through a short (20 cm) silica column with dichloromethane/acetone, 4:1, as eluent. A first eluted yellow band was found to contain **1d** and some unidentified material. A second, light-yellow band containing **3d** was concentrated to dryness and the residue was recrystallized from dichloromethane/pentane. Yield 29 mg (25%), m.p. 55°C. − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 2.67 [t, ^3J(H,H) = 6.0 Hz, 2 H, CH_2], 3.44 [t, ^3J(H,H) = 6.4 Hz, 2 H, CH_2], 4.20 [t, ^3J(H,H) = 5.6 Hz, 1 H, NH], 4.37 [d, ^3J(H,H) = 5.2 Hz, 2 H, NCH_2], 5.33 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 30.0 (s, CH_2), 43.4 (s, CH_2), 67.6 (s, SCH_2), 93.7 (s, C_5H_5), 171.8 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 13.6 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1693 (NO), 1152 (SO), 1038 cm^{-1} (SO). − $C_{33}H_{32}N_2O_4PReS$ (769.9): calcd. C 51.48, H 4.19, N 3.64, S 4.16; found C 50.77, H 4.61, N 3.54, S 4.27.

[CpRe(NO)(PPh$_3$)(η^2-S=CHC$_4$H$_3$O)]PF$_6$ (2g): A solution of **1g** (111 mg, 0.17 mmol) and $[Cp_2Fe]PF_6$ (0.52 g, 1.57 mmol) in acetone (20 mL) was stirred for 2 d at 20°C. The mixture was then concentrated to dryness and the residue was dissolved in dichloromethane and chromatographed on a short (20 cm) silica column with dichloromethane/acetone, 10:1, as eluent. The first eluted bright-yellow band was found to contain ferrocene. A second, brownish-yellow band containing **2g** was concentrated to dryness and the residue was recrystallized from dichloromethane/diethyl ether. Yield 56 mg (41%), m.p. 88°C (dec.). − ^{1}H NMR (400 MHz, CD_3CN, 20°C): δ = 6.41 (s, 5 H, C_5H_5), 6.51 [dd, ^3J(H,H) = 3.2 Hz, ^3J(H,H) = 1.6 Hz, 1 H, CH], 6.56 [d, ^3J(H,H) = 3.2 Hz, 1 H, CH], 6.80 (s, 1 H, SCH), 7.41 [d, ^3J(H,H) = 1.2 Hz, 1 H, CH]. − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 42.0 (s, SCH), 101.8 (s, C_5H_5), 110.2 (s, CH), 111.7 (s, CH), 144.0 (s, OCH), 157.7 (s, OC). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 7.9 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1751 cm^{-1} (NO). − $C_{28}H_{24}F_6NO_2P_2ReS$ (800.7): calcd. C 42.00, H 3.02, N 1.75, S 4.00; found C 41.76, H 3.23, N 1.74, S 4.01.

[CpRe(NO){P(OPh)$_3$}(η^2-S=CHPh)]PF$_6$ (5a): This compound was prepared as described above for **2a**. Yield 100 mg (78%), m.p. 228°C (dec.). − ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 6.59 (s, 5 H, C_5H_5), 6.99 (s, 1 H, SCH). − ^{13}C NMR (100 MHz, CD_3NO_2, 20°C): δ = 53.5 (s, SCH), 100.8 (s, C_5H_5). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 77.0 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1767 cm^{-1} (NO). − $C_{30}H_{26}F_6NO_4P_2ReS$ (858.7): calcd. C 41.96, H 3.05, N 1.63, S 3.73; found C 41.76, H 2.83, N 1.65, S 3.85.

[CpRe(NO){P(OPh)$_3$}{η^2-S=CH(4-C$_6$H$_4$Cl)}]PF$_6$ (5b): This compound was prepared analogously to **2a**. Yield 106 mg (79%), m.p. 110°C (dec.). − ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 6.58 (s, 5 H, C_5H_5), 6.92 (s, 1 H, SCH). − ^{13}C NMR (100 MHz, CD_3NO_2, 20°C): δ = 51.7 (s, SCH), 100.9 (s, C_5H_5). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 76.7 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1767 cm^{-1} (NO). − $C_{30}H_{25}ClF_6NO_4P_2ReS$ (893.2): calcd. C 40.34, H 2.82, N 1.57, S 3.59; found C 40.33, H 2.94, N 1.59, S 3.79.

[CpRe(NO){P(*i*Pr)$_3$}(η^2-S=CHPh)]PF$_6$ (5c): This compound was prepared analogously to **2a**. Yield 96 mg (90%), m.p. 150°C (dec.). − ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 1.44 [dd, ^3J(P,H) = 15.6 Hz, ^3J(H,H) = 7.2 Hz, 9 H, CH_3], 1.48 [dd, ^3J(P,H) = 16.4 Hz, ^3J(H,H) = 7.2 Hz, 9 H, CH_3], 3.25 [dsept, ^2J(P,H) = 9.6 Hz, ^3J(H,H) = 7.2 Hz, 3 H, CH], 6.72 (s, 5 H, C_5H_5), 6.89 (s, 1 H, SCH). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 20.1 [d, ^2J(P,C) = 2 Hz, CH_3], 20.3 [d, ^2J(P,C) = 2 Hz, CH_3], 31.4 [d, ^1J(P,C) = 28 Hz, CH], 45.9 (s, SCH), 100.3 (s, C_5H_5). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 22.2 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1740 cm^{-1} (NO). − $C_{21}H_{32}F_6NOP_2ReS$ (708.7): calcd. C 35.59, H 4.55, N 1.98, S 4.52; found C 35.51, H 4.58, N 1.94, S 4.58.

[CpRe(NO){P(*i*Pr)$_3$}(η^2-S=CH$_2$)]PF$_6$ (5d): To a solution of **6** (105 mg, 0.23 mmol) in dichloromethane (5 mL) at −70°C was added $[Ph_3C]PF_6$ (90 mg, 0.23 mmol). The mixture was stirred at this temperature for 30 min. Thiirane (20 μL, 0.33 mmol) was then added and the mixture was allowed to warm to 20°C. It was then concentrated in vacuo to a volume of 1 mL. Addition of diethyl ether led to precipitation of the product, which was filtered off and dried in vacuo. Yield 121 mg (83%), m.p. 188°C (dec.). − ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 1.35 [dd, ^3J(P,H) = 15.6 Hz, ^3J(H,H) = 7.2 Hz, 9 H, CH_3], 1.45 [dd, ^3J(P,H) = 14.8 Hz, ^3J(H,H) = 7.2 Hz, 9 H, CH_3], 3.13 [dsept, ^2J(P,H) = 9.6 Hz, ^3J(H,H) = 7.2 Hz, 3 H, CH], 3.30 [dd, ^3J(P,H) = 1.2 Hz, ^2J(H,H) = 1.2 Hz, 1 H, SCH], 4.84 [dd, ^3J(P,H) = 1.2 Hz, ^2J(H,H) = 1.2 Hz, 1 H, SCH], 6.61 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 20.0 [d, ^2J(P,C) = 3 Hz, CH_3], 20.3 [d, ^2J(P,C) = 2 Hz, CH_3], 25.2 (s, SCH), 30.7 [d, ^1J(P,C) = 28 Hz, CH], 99.5 (s, C_5H_5). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 22.7 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1744 cm^{-1} (NO). − $C_{15}H_{28}F_6NOP_2ReS$ (632.6): calcd. C 28.48, H 4.46, N 2.21, S 5.07; found C 28.77, H 4.45, N 2.14, S 5.31.

[CpRe(NO)(PPh$_3$){SO$_2$(4-C$_6$H$_4$Me)}] (3a): A solution of **8** (281 mg, 0.40 mmol) and $NaSO_2(4\text{-}C_6H_4Me) \cdot H_2O$ (157 mg, 0.80 mmol) in THF (20 mL) and ethanol (20 mL) was stirred for 1 h at 20°C. The mixture was then concentrated to dryness and the residue was extracted with benzene. After filtration through Celite, the benzene was partially evaporated and the product was precipitated by adding pentane. Yield 252 mg (90%), m.p. 214°C (dec). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 2.28 (s, 3 H, CH_3), 5.04 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 21.1 (s, CH_3), 94.0 (s, C_5H_5). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 13.8 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1695 (NO), 1182 (SO), 1054 cm^{-1} (SO). − $C_{30}H_{27}NO_3PReS$ (698.8): calcd. C 51.56, H 3.89, N 2.00, S 4.59; found C 51.33, H 3.98, N 1.99, S 4.47.

[CpRe(NO)(PPh$_3$){SCH(SMe)(4-C$_6$H$_4$OMe)}] (9): To a solution of **5e** (69 mg, 0.08 mmol) in acetone (6 mL) at −50°C was added NaSMe (20 mg, 0.29 mmol). The mixture was allowed to warm to 20°C and then concentrated to dryness. The yellow residue was redissolved in THF and chromatographed by passage through a short (20 cm) silica column with THF/diethyl ether, 2:1, as eluent. A first yellow band was collected, the solvents were evaporated, and the residue was recrystallized at low temperature from dichloromethane/pentane. Owing to its semi-solid nature, the product could not be rigorously freed of solvent. Yield 57 mg (97%). − Major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 2.12 (s, 3 H, SCH_3), 3.77 (s, 3 H, OCH_3), 4.73 (s, 1 H, CH), 4.93

(s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 17.0 (s, SCH_3), 55.3 (s, OCH_3), 65.1 [d, ^3J(P,C) = 8 Hz, CH], 90.9 (s, C_5H_5). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 19.3 (s). − Minor diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 2.00 (s, 3 H, SCH_3), 3.78 (s, 3 H, OCH_3), 4.71 (s, 1 H, CH), 5.10 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 16.7 (s, SCH_3), 55.3 (s, OCH_3), 64.2 [d, ^3J(P,C) = 8 Hz, CH], 91.3 (s, C_5H_5). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 19.0 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1653 cm^{-1} (NO).

[CpRe(NO){P(OPh)$_3$}(SC$_5$H$_5$PhMe$_2$)]PF$_6$ (10a): A solution of **5a** (117 mg, 0.14 mmol) and 2,3-dimethylbutadiene (275 μL, 2.34 mmol) in dichloromethane (15 mL) was kept at 20°C. The orange colour of the starting material faded gradually. After 4 h, the mixture was concentrated to dryness. ^{1}H-NMR analysis of the crude residue indicated complete conversion with 46% *de*. Recrystallization from dichloromethane/pentane gave analytically pure **10a**. Yield 80 mg (63%), m.p. 226°C (dec.). − Major diastereoisomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 1.81 (s, 3 H, CH_3), 1.85 (s, 3 H, CH_3), 2.85, 2.92 [d of AB systems, ^2J(H,H) = 18.6 Hz, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 2.8 Hz, 2 H, CH_2], 3.81, 4.27 [AB system, ^2J(H,H) = 16.4 Hz, 2 H, SCH_2], 4.40 [dd, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 5.2 Hz, 1 H, CH], 5.08 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 19.6 (s, CH_3), 19.8 (s, CH_3), 38.1 (s, CH_2), 44.2 (s, CH_2), 58.0 (s, CH), 92.6 (s, C_5H_5), 123.3 (s, C=C), 128.8 (s, C=C). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 105.5 (s). − Minor diastereoisomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 1.75 (s, 3 H, CH_3), 1.79 (s, 3 H, CH_3), 2.69 (m, 2 H, CH_2), 3.54, 3.92 [AB system, ^2J(H,H) = 17.4 Hz, 2 H, SCH_2], 4.40 (m, 1 H, CH), 5.52 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 19.3 (s, CH_3), 20.0 (s, CH_3), 40.1 (s, CH_2), 46.9 (s, CH_2), 56.9 (s, CH), 93.2 (s, C_5H_5), 123.3 (s, C=C), 129.2 (s, C=C). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 104.3 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1733 cm^{-1} (NO). − $C_{36}H_{36}F_6NO_4P_2ReS$ (940.9): calcd. C 45.96, H 3.86, N 1.49, S 3.41; found C 46.16, H 3.67, N 1.48, S 3.32.

[CpRe(NO){P(OPh)$_3$}{SC$_5$H$_5$Ph(OMe)$_2$}]PF$_6$ (10b): This compound was prepared analogously from **5a** (143 mg, 0.17 mmol) and 2,3-dimethoxybutadiene (210 μL, 1.75 mmol). The orange colour of the starting material faded within 15 min. ^{1}H-NMR analysis of the crude product indicated complete conversion with 24% *de*. Yield 127 mg (78%), m.p. 83°C (dec.). − Major diastereoisomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 3.09, 3.17 [d of AB systems, ^2J(H,H) = 17.9 Hz, ^3J(H,H) = 8.5 Hz, ^3J(H,H) = 4.9 Hz, 2 H, CH_2], 3.68 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.90, 4.54 [AB system, ^2J(H,H) = 15.0 Hz, 2 H, SCH_2], 4.57 [dd, ^3J(H,H) = 8.6 Hz, ^3J(H,H) = 4.9 Hz, 1 H, CH], 5.08 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 34.0 (s, CH_2), 40.7 (s, CH_2), 58.1 (s, OCH_3), 58.8 (s, CH), 59.3 (s, OCH_3), 92.7 (s, C_5H_5), 135.7 (s, C=C), 138.5 (s, C=C). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 104.5 (s). − Minor diastereoisomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 2.88 (m, 2 H, CH_2), 3.65 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 3.95−4.10 (m, 2 H, SCH_2), 4.54 (m, 1 H, CH), 5.57 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 35.6 (s, CH_2), 42.0 (s, CH_2), 57.1 (s, CH), 58.1 (s, OCH_3), 59.3 (s, OCH_3), 93.3 (s, C_5H_5), 136.4 (s, C=C), 138.4 (s, C=C). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 103.7 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1735 cm^{-1} (NO). − $C_{36}H_{36}F_6NO_6P_2ReS$ (972.9): calcd. C 44.44, H 3.73, N 1.44, S 3.30; found C 44.45, H 3.68, N 1.29, S 3.00.

[CpRe(NO)(PPh$_3$){SC$_5$H$_5$Me$_2$(4-C$_6$H$_4$OMe)}]PF$_6$ (10c): A solution of **5e** (146 mg, 0.17 mmol) and 2,3-dimethylbutadiene (0.60 mL, 5.30 mmol) in acetone (4 mL) was kept for 5 d at 20°C. The mixture was then concentrated to dryness and the crude product was chromatographed by passage through a short (20 cm) silica column using dichloromethane/acetone, 20:1, as eluent. A first yellow band was found to contain the product, while the second consisted of unchanged **5e**. Both were collected and worked-up by evaporation of the solvents and recrystallization of the residues from dichloromethane/diethyl ether. Yield 20 mg (12%), m.p. 125°C (dec.). − Major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.33 (s, 3 H, CH_3), 1.64 (s, 3 H, CH_3), 2.47 [d, ^2J(H,H) = 15.6 Hz, 1 H, SCH_2], 2.60 [d, ^2J(H,H) = 18.2 Hz, 1 H, CH_2], 2.82 (m, 1 H, CH_2), 2.89 [d, ^2J(H,H) = 16.9 Hz, 1 H, SCH_2], 3.85 (s, 3 H, OCH_3), 4.00 [dd, ^3J(H,H) = 9.8 Hz, ^3J(H,H) = 4.3 Hz, 1 H, CH], 4.96 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 19.2 (s, CH_3), 19.7 (s, CH_3), 39.6 (s, CH_2), 44.2 (s, CH_2), 55.6 (s, OCH_3), 57.4 (s, CH), 92.8 (s, C_5H_5), 122.0 (s, C=C), 128.3 (s, C=C). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 12.1 (s). − Minor diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.39 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 2.06 [d, ^2J(H,H) = 14.7 Hz, 1 H, SCH_2], 2.60 (m, 1 H, CH_2), 3.53 [d, ^2J(H,H) = 15.7 Hz, 1 H, CH_2], 3.81 (s, 3 H, OCH_3), 4.04 (m, 1 H, CH), 5.23 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 19.0 (s, CH_3), 19.7 (s, CH_3), 55.4 (s, OCH_3), 57.7 (s, CH), 92.5 (s, C_5H_5), 123.1 (s, C=C), 127.8 (s, C=C). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 11.4 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1712 cm^{-1} (NO). − $C_{37}H_{38}F_6NO_2P_2ReS$ (922.9): calcd. C 48.15, H 4.15, N 1.52; found C 47.82, H 3.82, N 1.84.

X-ray Structure Determination of [CpRe(NO)(PPh$_3$){SO$_2$CH$_2$CH(NC$_8$H$_4$O$_2$)COOMe}] · [D$_6$]acetone (3e · [D$_6$]acetone): $C_{35}H_{30}N_2O_7PReS \cdot C_3D_6O$: molecular mass 904.0, crystal size 0.3 × 0.15 × 0.05 mm, obtained from a saturated [D$_6$]acetone solution; triclinic crystal system, space group $P\bar{1}$ (No. 2), a = 8.4564(4), b = 13.229(2), c = 18.647(3) Å, α = 102.036(14)°, β = 93.63(2)°, γ = 102.69(2)°; V = 1977.1(10) Å^3, Z = 2, d_{calcd} = 1.519 g cm^{-3}; μ(Mo-K_α) = 1.82 cm^{-1}. Data were collected at 293 K in the range 2° < θ < 23° from one-half of the reflection sphere (Enraf−Nonius CAD4 diffractometer, graphite monochromator, Mo-K_α radiation, λ = 0.70930 Å). Of the 5926 measured reflections, 5485 were symmetry-independent and 3044 were classified as observed [$I_O > 2\sigma(I_O)$]. An empirical absorption correction based on the counts of 4 reflections was applied. The structure was solved by the Patterson method by using the program package SHELXS-86[35] with hydrogen atoms included in their calculated positions. Refinement using the program package SHELXL-93[36] gave R_1 = 0.066, wR_2 = 0.121. The 5 highest maxima of a final difference Fourier map were below 0.895 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 CSD-408460.

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