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

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The reaction of diastereomeric methyl rhenium complexes [CpRe(NO)(NMDPP)(CH_3)] (NMDPP = neomenthyl-diphenylphosphine) and [CpRe(NO)(PAMP)(CH_3)] (PAMP = phenyl-2-anisyl-methylphosphine) with thiols in the presence of HBF_4 gave thiolate complexes [CpRe(NO)(NMDPP)(SCH_2Ph)] and [CpRe(NO)(PAMP)(SCH_2R)] (R = Ph, 4-C_6H_4Cl, 4-C_6H_4OMe, 2-C_4H_3O, CH_3, $CH{=}CH_2$). Treatment of [CpRe(NO)(PAMP)(THF)]BF_4 with the thiols and Na_2CO_3 gave the same compounds under neutral conditions. Similarly, the reaction of the chelate complex {CpRe(NO)[κP(Ph)(Me)($CH_2C_4H_3\kappa$S)]}BF_4 with thiols and NaOEt yielded the ring-opened products {CpRe(NO)[P(Ph)(Me)($CH_2C_4H_3$S)](SCH_2R)} (R = Ph, 4-C_6H_4Cl, 4-C_6H_4OMe). One of the benzylic hydrogen atoms can be abstracted with [Ph_3C]BF_4 to give the diastereomeric thiobenzaldehyde complexes [CpRe(NO)(PAMP)(S=CHR)]BF_4 (R = Ph, 4-C_6H_4Cl, 4-C_6H_4OMe) and {CpRe(NO)[P(Ph)(Me)($CH_2C_4H_3$S)](S=CHPh)}BF_4. 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

Introduction

Thioaldehydes are less stable than their oxo analogues. This difference can be traced back mainly to the weak overlap of the p orbitals of sulfur and carbon. Thioaldehydes are thus more reactive, both towards nucleophiles and electrophiles, and they have a pronounced tendency to oligo- or polymerize [2, 3]. Nevertheless, monomeric thioaldehydes can be stabilized by coordination in a transition metal complex [3]. Although the reactivity of the thioaldehyde function is significantly lowered by coordination, electrophilic or nucleophilic additions as well as cycloadditions are still possible [3].

Aldehydes and thioaldehydes can bind *end-on* through sulfur or oxygen, respectively, or *side-on* through the π system. Occasionally both binding modes coexist in a dynamic equilibrium [3]. In the case of the rhenium cations [CpRe(NO)(PPh_3)(E=CHR)]$^+$, this has been observed for aldehyde complexes [4 – 7] as well as for the analogous thioaldehyde complexes [8]. As a result, reactions with nucleophiles [6, 8, 9] or cycloadditions [9] may proceed with variable diastereoselectivities. The selectivity problem might be alleviated by the introduction of a second stereogenic center. Recently we described the synthesis of diastereomeric rhenium complexes containing stereogenic centers at both the metal and the phosphine ligand [10]. Here we report the synthesis of analogous diastereomeric thiolate and thioaldehyde complexes.

Results and Discussion

Starting materials

Neomenthyl-diphenylphosphine (NMDPP, **1a**), which has a chiral carbon skeleton, and the borane adduct of *P*-stereogenic (*S*)-phenyl-2-anisyl-methylphosphine (*S*-PAMP · BH_3, *S*-**1b** · BH_3) were prepared by published methods [11, 12]. The stereochemical purity of **1a** was checked by ^{31}P NMR spectroscopy as well as by a crystal structure determination of the borane adduct **1a** · BH_3 which was obtained as a side product in one of the reactions described below. Figure 1 shows a view of the molecule.

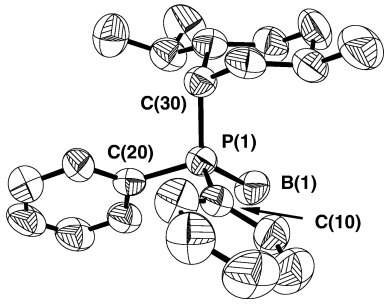


Fig. 1. Molecular structure of NMDPP · BH_3 (**1a** · BH_3), hydrogen atoms omitted for clarity. Space group $I4_1$. Selected bond lengths [pm] and angles [°] (estimated standard deviations in parentheses): P(1)–B(1) 192.6(5), P(1)–C(10) 182.6(4), P(1)–C(20) 180.7(4), P(1)–C(30) 185.0(4); C(10)–P(1)–B(1) 109.1(2), C(20)–P(1)–B(1) 110.0(2), C(30)–P(1)–B(1) 120.3(2), C(10)–P(1)–C(20) 104.13(17), C(10)–P(1)–C(30) 104.04(18), C(20)–P(1)–C(30) 108.02(18).

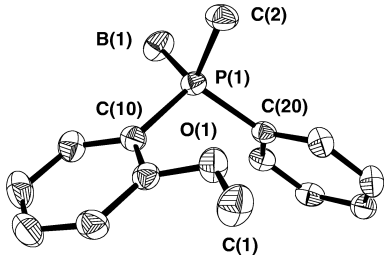
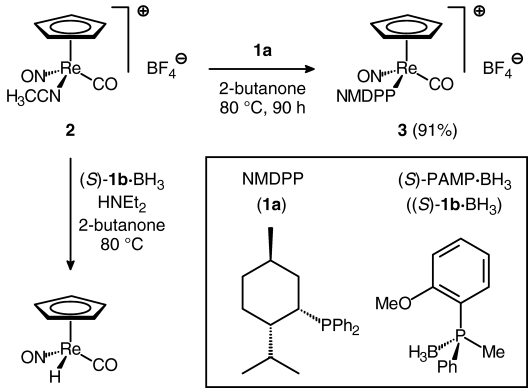


Fig. 2. Molecular structure of *S*-PAMP · BH_3 (*S*-**1b** · BH_3), hydrogen atoms omitted for clarity. Space group $P2_12_12_1$. Selected bond lengths [pm] and angles [°] (estimated standard deviations in parentheses): P(1)–B(1) 190.7(2), P(1)–C(2) 180.24(17), P(1)–C(10) 181.14(15), P(1)–C(20) 181.24(15); C(2)–P(1)–B(1) 110.14(10), C(10)–P(1)–B(1) 112.20(9), C(20)–P(1)–B(1) 112.43(8), C(2)–P(1)–C(10) 108.00(8), C(2)–P(1)–C(20) 106.84(8), C(10)–P(1)–C(20) 106.97(7).

In the case of *S*-**1b** · BH_3, a crystal measuring several millimeters across was selected and a small piece chipped off for X-ray structure determination, while the remainder was used to dertermine the sign (+) of the optical rotation [13]. *S*-**1b** · BH_3 crystallizes in the chiral space group $P2_12_12_1$, which is an additional proof of the stereochemical uniformity of this material. Figure 2 shows a view of the molecule.

For both adducts, all bond lengths were found in the expected range. In particular, the P(1)–B(1) bond is significantly longer than the P(1)–C(sp^3) bonds. A similar difference was found in (R_P)-P(Ph)(Me)[N(Me)CH(Me)CH(Ph)OH] · BH_3, a precursor to (*R*)-**1b** · BH_3, [14] making the assignment of the BH_3 and CH_3 groups of *S*-**1b** · BH_3 unambiguous. The



(1)

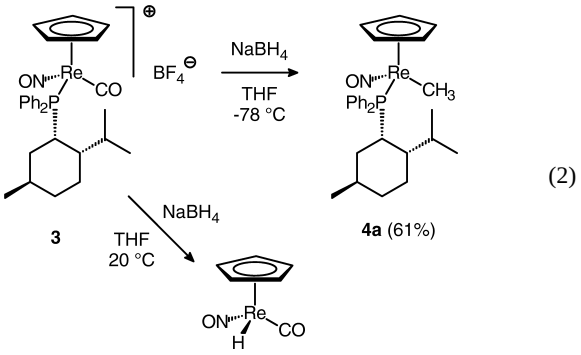
B–P–C angles (109.1 – 120.3° in **1a** · BH_3, 110.1 – 112.4° in *S*-**1b** · BH_3) are significantly larger then the C–P–C angles (104.0 – 108.0° in **1a** · BH_3, 106.8 – 108.0° in *S*-**1b** · BH_3), reflecting the lower electronegativity of boron.

The replacement of the acetonitrile ligand of [CpRe(CO)(NO)($NCCH_3$)]BF_4 (**2**) [15] by phosphines is the common entrance to *at-metal* chiral rhenium complexes. This strategy is also successful for **1a**, although a rather long reaction time is necessary (eq. (1)).

An unexpected problem arose with the use of enantiomerically pure *S*-**1b** · BH_3. The racemic phosphine had already been introduced successfully [10]. However, neither *in situ* removal of the BH_3 group with diethylamine, nor deprotection of the phosphine followed by reaction of the crude mixture with the acetonitrile complex **2** led to the desired phosphine complex. Instead, the hydride complex *rac*-[CpRe(CO)(NO)(H)] [16] was isolated. It appeares that the diethylamine-borane adduct, which we could not separate from the phosphine, had served as a hydride source.

The reduction of the remaining carbonyl group is usually achieved with $NaBH_4$ in dry THF [15, 17 – 20]. In the case of carbonyl complex **3**, a slightly different situation was encountered. Besides reduction, nucleophilic attack at the metal by the hydride reagent occurred, followed by loss of the phosphine ligand. The ratio of the two reaction pathways is temperature-dependent. At −78 °C CO reduction is favored while at 20 °C PR_3 substitution takes place exclusively (eq. (2)). With other reducing reagents only the hydride complex could be isolated.

The phosphine **1a** and its borane adduct (**1a** · BH_3) are side products in addition to $NaBF_4$ and THF · BH_3



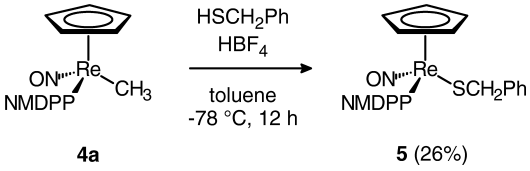
(2)

which are formed in both reactions. The hydride complex was readily identified by its IR spectrum and by the hydride signal in its ^{1}H NMR spectrum. Free **1a** and **1a** · BH_3 were detected by their ^{31}P NMR signals. Attempts made to purify the methyl complex **4a** by column chromatography were unsuccessful. Efforts to separate the complex mixture of products by crystallisation led to the isolation of a crystal of **1a** · BH_3 suitable for X-ray structure determination (see above).

Recently, Gladysz and coworkers described similar problems with the reduction of {CpRe(CO)(NO)[P(4-$C_6H_4CF_3)_3$]}BF_4. In that instance, reaction with $NaBH_4$ led to an inseparable mixture of the neutral complexes {CpRe(NO)[P(4-$C_6H_4CF_3)_3$](CH_3)} and {CpRe(NO)[P(4-$C_6H_4CF_3)_3$](H)} [21]. Similarly, the course of the reduction of the iron complexes [$Cp^*Fe(CO)_2(PR_3)$]PF_6 (R = Me, *n*-Bu, Ph) with $NaBH_4$ was found to be temperature dependent. At low temperatures the methyl complexes [$Cp^*Fe(CO)(PR_3)(CH_3)$] were produced, while at 20 °C only the hydride complex [$Cp^*Fe(CO)_2$(H)] was formed [22]. Obviously, the loss of the phosphine ligand is a common problem in this type of reaction.

Thiolate complexes

In previous studies we explored several ways to prepare halfsandwich rhenium thiolate complexes of the type [CpRe(NO)(PR_3)(SCH_2R')]. Key intermediates were the methyl complexes [CpRe(NO)(PR_3)(CH_3)] (R = Ph, *i*-Pr, OPh) and the THF complex [CpRe(NO)(PPh_3)(THF)]BF_4 [20, 23, 24]. Methyl complex **4a**, although obtained only in an impure form, could be converted into the benzyl thiolate complex **5** by reaction with benzylthiol and acid at low temperature (eq. (3)). Similarly, the racemic PAMP complex **4b** [10] upon reaction with



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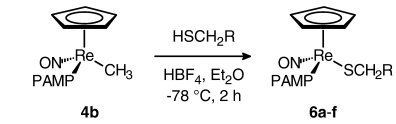
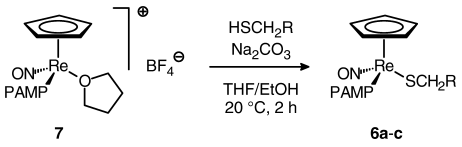


(4)

R	C_6H_5	4-C_6H_4Cl	4-C_6H_4OMe	2-C_4H_3O	CH_3	$CH{=}CH_2$
	6a (87%)	**6b** (70%)	**6c** (68%)	**6d** (84%)	**6e** (73%)	**6f** (74%)



(5)

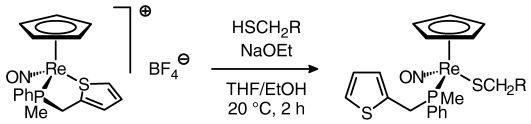
R	C_6H_5	4-C_6H_4Cl	4-C_6H_4OMe
	6a (61%)	**6b** (74%)	**6c** (69%)

a series of thiols under acidic conditions gave the thiolate complexes **6a**–**f** in good yields (eq. (4)).

All thiolate complexes are fairly air-stable, yellow or yellow-orange crystalline powders. They are soluble in most organic solvents except alkanes. Even in chlorinated solvents, the complexes do not decompose after several hours. A characteristic feature of their IR spectra is the low NO stretching frequency, attesting to the high σ- and π-donor abilities of the thiolate ligands. The NMR spectra reveal the presence of two diastereoisomers in almost equimolar amounts as judged by the intensity of the Cp signals. The diastereotopic SCH_2 protons give rise to AB-systems with a ^2J(H,H) coupling between 12 and 15 Hz. In the ^{13}C NMR spectra the SCH_2 signals are split into doublets due to a sizable ^3J(P,C) coupling which indicates that the dihedral angle C–S–Re–P in these complexes is close to 180° [20, 24].

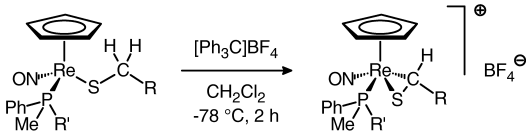
The strongly acidic conditions of the reaction described above limit this method to thiols not bearing acid-sensitive functional groups. As an alternative, the THF complex **7** can be used as a starting material. Thus the reaction of **7** with thiols in the presence of Na_2CO_3 gave the thiolate complexes **6a**–**c** also in good yields (eq. (5)).

The products were identical with those obtained from the methyl complex **4b**, the yields were nearly the same in both cases. Thus, thiolate complexes of the



(6)

R	C_6H_5	4-C_6H_4Cl	4-C_6H_4OMe
	9a (70%)	**9b** (53%)	**9c** (70%)



(7)

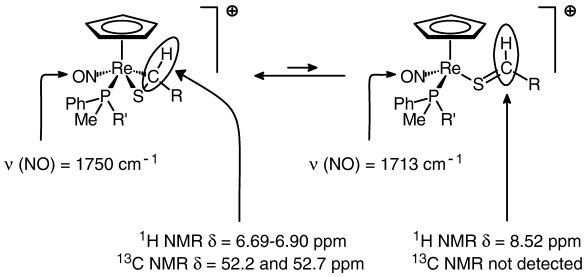
R' \ R	C_6H_5	4-C_6H_4Cl	4-C_6H_4OMe
2-C_6H_4OMe	**10a** (98%)	**10b** (80%)	**10c** (96%)
2-C_4H_3S	**11** (98%)		

general formula [CpRe(NO)(PAMP)(SCH_2R)] can be prepared under either acidic or mildly basic conditions.

The intramolecularly stabilized complex {CpRe(NO)[κP(Ph)(Me)($CH_2C_4H_3$κS)]}BF_4 (**8**) is still another useful starting material. We have demonstrated recently that the hemilabile chelate ring can be opened in acetonitrile solution to give the acetonitrile complex {CpRe(NO)[P(Ph)(Me)($CH_2C_4H_3S$)]($NCCH_3$)}BF_4 [10]. Similarly, treatment of **8** with sodium thiolates gave the neutral thiolate complexes **9a – c** (eq. (6)) in satisfactory yields as equimolar mixtures of diastereoisomers.

Physical properties and spectroscopic data of **9a – c** are very similar to those of the other benzylthiolate complexes. In their ^{1}H NMR spectra, in addition to the AB system of the SCH_2 group, an ABX-system with a ^2J(H,H) coupling of 15 Hz and ^2J(P,H) couplings of 9 Hz is found. In the case of **9b** both spin systems seriously overlap making a complete assignment impossible.

It is noteworthy that when diastereomerically enriched **8** [10] was used in the reaction, **9a** and **9b** were obtained with approximately the same degree of enrichment. **9c**, on the other hand, could only be isolated as a 1:1 mixture of diastereoisomers. However, since no epimerisation at rhenium occurs for **9a** and **9b**, we may safely assume that the loss of the diastereomeric excess in the case of **9c** is an artefact of the workup procedure.



Scheme 1. The hapticity equilibrium of the thioaldehyde complexes **10a – c**.

Halfsandwich thiolate complexes of ruthenium and rhenium, when reacted with a hydride abstraction reagent, are cleanly converted to the corresponding thioaldehyde complexes [9, 23 – 27]. Thus, treatment of the thiolate complexes **6a-c** and **9a** with $[Ph_3C]BF_4$ resulted in a formal hydride abstraction, giving rise to the thiobenzaldehyde complexes **10a-c** and **11** (eq. (7)).

While the thiobenzaldehyde complexes **10a – c** are reddish-brown or purple crystalline solids, complex **11** is a yellow powder. All complexes are readily soluble in polar organic solvents and are stable in solution for several days. The high value of the NO stretching frequency and the ^{1}H and ^{13}C NMR signals of the coordinated thioformyl group are in agreement with a predominant *side-on* coordination mode as shown in eq. (7). However, a shoulder in the IR spectrum of **9b** at lower frequency and a broad ^{13}C NMR signal for the S=C(H)R carbon as well as two sets of S=C(H)R protons in the ^{1}H NMR spectra of **9c** reveal a dynamic behaviour of the thiobenzaldehyde ligand in solution (Scheme 1).

This type of rapid hapticity change is well known for thioaldehyde complexes [3] including those of ruthenium [26, 27] and rhenium [9]. For the analogous aldehyde complexes {CpRe(NO)(PPh_3)[O=C(H)R]}$^+$ Gladysz *et al.* have shown that the equilibrium of the *side-on* and *end-on* coordinated species depends on the electronic nature of the organic group R [4 – 7]. In the present case only one set of signals for the *side-on* coordinated thioformyl group could be detected. This implies that the thioaldehyde is coordinated to the chiral Lewis acid [CpRe(NO)(PPh_3)]$^+$ with high diastereoselectivity [28]. Scheme 1 shows the most probable configuration with the sulfur atom *cis* to phosphorus and the thioformyl hydrogen atom pointing towards the cyclopentadienyl ring. This structure is completely analogous to that of {CpRe(NO)(PPh_3)[S=C(H)Ph]}PF_6

which has been determined by X-ray diffraction [23].

Conclusions

This work was aimed at the synthesis of diastereomeric rhenium thiolate complexes [CpRe(NO)(P*)(SCH_2R)], where P* represents a chiral phosphine ligand. Besides the C-chiral neomenthyldiphenylphosphine (NMDPP, **1a**), the P-chiral racemic phenyl-2-anisyl-methylphosphine (PAMP) and phenyl-methyl-(2-thienylmethyl)phosphine were employed. While the synthesis of thiolate complexes [CpRe(NO)(NMDPP)(SCH_2R)] suffered from problems with the starting methyl complex **4a**, the methyl complex [CpRe(NO)(PAMP)(CH_3)] (**4b**), the THF complex [CpRe(NO)(PAMP)(THF)]BF_4 (**7**), and the intramolecularly stabilized complex {CpRe(NO)[κP(Ph)(Me)($CH_2C_4H_3$κS)]}BF_4 (**8**) served well as starting materials. Thus a range of synthetic conditions (acidic, neutral, or basic) are available enabling the introduction of functionalized thiolate ligands bearing acid- or base-sensitive groups.

Hydride abstraction from the benzylic position led to the formation of the corresponding thiobenzaldehyde complexes in nearly quantitative yields. IR and NMR spectroscopic data reveal a *side-on* coordination of the thioaldehyde ligand with one predominant configuration where the sulfur and phosphorus atoms are *cis* and the thioaldehyde hydrogen atom is positioned *syn* to the cyclopentadienyl ring. In some instances a second isomer with an *end-on* bound thioaldehyde ligand could be observed in solution by IR and NMR spectroscopy. Further work will be necessary to exploit this particular situation for diastereoselective reactions at the coordinated thioformyl group.

Experimental Section

All experiments were carried out in Schlenk tubes under an atmosphere of nitrogen using suitably purified solvents. – IR: Bruker IFS 25. – ^{1}H NMR: Bruker AMX 400, Jeol JNM-LA 300, δ values relative to TMS. – ^{13}C NMR: Bruker AMX 400, Jeol JNM-LA 300, δ values relative to TMS, assignments routinely checked by DEPT spectra. In some cases the ^{13}C NMR signals of quarternary carbon atoms were too weak to be detected. The ^{1}H and ^{13}C NMR signals of the aryl groups attached to phosphorus are very similar for all compounds and have therefore been omitted from the lists of spectral data. – ^{31}P NMR: Bruker AMX 400, Jeol JNM-LA 300, δ values relative to 85% H_3PO_4. – Elemental analyses: Analytical Laboratory of the Institut für Anorganische Chemie. – The following starting materials were obtained as described in the literature: NMDPP (**1a**) [11], (*S*)-PAMP · BH_3 (*S*-**1b** · BH_3) [12], [CpRe(CO)(NO)($NCCH_3$)]BF_4 (**2**) [15], [CpRe(NO)(PAMP)(CH_3)] (**4b**) [10], [CpRe(NO)(PAMP)(THF)]BF_4 (**7**) [10], and {CpRe(NO)[κP(Ph)(Me)($CH_2C_4H_3$κS)]}BF_4 (**8**) [10]. All other reagents were used as purchased.

*[CpRe(CO)(NO)(NMDPP)]BF_4 (**3**)*

A solution of [CpRe(CO)(NO)($NCCH_3$)]BF_4 (**2**) (830 mg, 1.90 mmol) and NMDPP (**1a**) (800 mg, 2.47 mmol) in 2-butanone (12 ml) was heated under reflux for 90 h. All volatiles were removed under vacuum, and the residue purified by column chromatography over silica gel (20 cm) using acetone/petroleum ether (50/70) 3:1 as eluent. Yield 1.25 g (91%), yellow crystalline solid.

M. p. 199 °C (dec). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2013 (CO), 1760 (NO) cm^{-1}. – ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: δ = 0.29 (d, *J* = 6.8 Hz, 3 H, Me), 0.37 (d, *J* = 6.8 Hz, 3 H, Me), 0.81 (d, *J* = 6.8 Hz, 3 H, Me), 0.90 (d, *J* = 6.7 Hz, 3 H, Me), 1.10 (d, *J* = 7.6 Hz, 3 H, Me), 1.16 (d, *J* = 7.6 Hz, 3 H, Me), 1.24 – 1.39 (m, 2 H), 1.63 – 1.90 (m, 12 H), 1.97 – 2.28 (m, 4 H), 3.25 – 3.50 (m, 2 H, Ph_2PCH), 5.58 (s, 5 H, C_5H_5), 5.65 (s, 5 H, C_5H_5). – ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: δ = 17.2, 17.2, 19.2, 19.6 (all Me), 20.4 – 20.8 (m, CH_2), 23.1 (CH), 23.3 (CH), 27.5 (d, *J* = 9 Hz, CH), 27.6 (d, *J* = 9 Hz, CH), 28.0 – 28.3 (m, CH_2), 30.6 (d, *J* = 4 Hz, CH), 30.8 (d, *J* = 4 Hz, CH), 39.0 (d, *J* = 31 Hz, Ph_2PCH), 40.6 – 41.4 (m, CH_2), 42.0 (d, *J* = 30 Hz, Ph_2PCH), 94.3 (C_5H_5), 94.5 (C_5H_5), 196.7 (d, *J* = 7 Hz, CO), 197.4 (d, *J* = 7 Hz, CO). – ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: δ = 15.7, 16.1. – $C_{28}H_{34}BF_4NO_2PRe$ (720.56): calcd. C 46.67, H 4.76, N 1.94; found C 46.48, H 5.07, N 2.09.

*[CpRe(NO)(NMDPP)(CH_3)] (**4a**)*

To a cold (−78 °C) solution of **3** (650 mg, 0.90 mmol) in THF (15 ml) and diethyl ether (5 ml) $NaBH_4$ (100 mg, 2.63 mmol) was added. The dark-brown suspension was stirred and allowed to warm to 20 °C overnight. The red mixture was filtered over silica gel and the residue washed with THF. The combined filtrates were evaporated to dryness, and the residue extracted three times with hexane (30 ml). The extract was filtered over celite and concentrated to 3 ml. Upon cooling to −78 °C an orange-red precipitate formed. The supernatant was removed by syringe and the solid dried under vacuum. The product mixture was found by NMR to contain NMDPP (**1a**), NMDPP · BH_3 (**1a** · BH_3), [CpRe(NO)(NMDPP)(CH_3)] (**4a**) and [CpRe(CO)(NO)(H)], which could not be separated any further. Yield 340 mg, orange-red solid.

IR (THF): $\tilde{\nu} = 1632$ (NO) cm^{-1}. – ^1H NMR (400 MHz, C_6D_6, 20 °C), both diastereomers: $\delta = 4.40$ (s, 5 H, C_5H_5), 4.51 (s, 5 H, C_5H_5). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C), both diastereomers: $\delta = -37.0$ (d, $J = 7$ Hz, ReMe), −34.5 (d, $J = 7$ Hz, ReMe), 89.2 (C_5H_5), 89.9 (C_5H_5). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C), both diastereomers: $\delta = 17.9$, 20.8. – $C_{28}H_{37}NOPRe$ (620.78).

*[CpRe(NO)(NMDPP)(SCH_2Ph)] (**5**)*

A sample of **3** (360 mg, 0.500 mmol) was reduced with $NaBH_4$ (60 mg, 1.58 mmol) to **4a** as described above. The orange-red product mixture was taken up in toluene (10 ml), cooled to −78 °C, and mercaptomethylbenzene (150 μl, 158 mg, 1.27 mmol) was added, followed by etheral HBF_4 (100 μl, 1.00 mmol). The mixture was allowed to warm to 20 °C overnight, and worked up by column chromatography over silica gel (20 cm) using diethyl ether/petroleum ether (50/70) 1:2 as eluent. The orange-red fraction was collected and the solvent removed under vacuum. The residue was dissolved in hexane (3 ml), and the product was precipitated by cooling to −78 °C. Yield 95 mg (26%), orange solid.

M. p. 135 °C (dec). – IR (hexane): $\tilde{\nu} = 1655$ (NO) cm^{-1}. – ^1H NMR (400 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 0.38$ (d, $J = 7.0$ Hz, 3 H, Me), 0.50 (d, $J = 6.7$ Hz, 3 H, Me), 0.82 – 2.05 (m, 18 H), 3.11 – 3.24 (m, 1 H, Ph_2PCH), 3.48 – 3.62 (m, 1 H, Ph_2PCH), 3.91, 4.19 (AB-system, $J =$ 12.9 Hz, 2 H, SCH_2), 4.03 (s, br, 2 H, SCH_2), 4.53 (s, 5 H, C_5H_5), 4.59 (s, 5 H, C_5H_5). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 17.8$ (Me), 20.6 – 20.9 (m, CH_2 and Me), 24.4 (Me), 24.5 (Me), 28.8 – 29.5 (m, CH and CH_2), 30.0, 30.2, 31.5, 31.5, 34.2, 34.4, 38.7 (all CH), 39.6 (d, $J = 26$ Hz, Ph_2PCH), 47.0 (d, $J = 6$ Hz, SCH_2), 48.0 (d, $J = 6$ Hz, SCH_2), 91.3 (C_5H_5). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 14.8$, 15.1. – $C_{34}H_{41}NOPReS$ (728.95): calcd. C 56.02, H 5.67, N 1.92, S 4.40; found C 55.16, H 5.76, N 1.83, S 4.51.

*[CpRe(NO)(PAMP)(SCH_2R)] (**6a** – **f**) from methyl complex* **4b**

To a cold (−78 °C) solution of [CpRe(NO)(PAMP)(CH_3)] (**4b**) (190 mg, 0.36 mmol) in diethyl ether (10 ml) the corresponding thiol (1.00 mmol) and, after 5 min, etheral HBF_4 (25 μl, *ca.* 0.25 mmol) were added. The mixture was kept cold for 1 h and then slowly warmed to 20 °C. After 1 h, the solvent was removed under vacuum, and the residue suspended in benzene (10 ml) and triethylamine (0.5 ml). The mixture was filtered over silica gel, the residue washed with benzene, and the clear filtrate evaporated to a volume of 1 ml. The product was precipitated by adding hexane (10 ml) and cooling to −30 °C overnight.

6a: Yield 200 mg (87%), orange-yellow crystalline powder. – M. p. 165 °C (dec). – IR (CH_2Cl_2): $\tilde{\nu} = 1641$ (NO) cm^{-1}. – ^1H NMR (400 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 2.19$ (d, $J = 9.7$ Hz, 3 H, PMe), 2.36 (d, $J = 10.3$ Hz, 3 H, PMe), 2.89 (s, 3 H, OMe), 2.90 (s, 3 H, OMe), 3.99, 4.17 (AB-system, $J = 12.6$ Hz, 2 H, SCH_2), 3.99, 4.18 (AB-system, $J = 12.6$ Hz, 2 H, SCH_2), 4.78 (s, 5 H, C_5H_5), 4.81 (s, 5 H, C_5H_5). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 15.4$ (d, $J = 38$ Hz, PMe), 17.1 (d, $J = 37$ Hz, PMe), 47.5 (d, $J = 8$ Hz, SCH_2), 47.6 (d, $J = 8$ Hz, SCH_2), 54.8 (OMe), 54.8 (OMe), 90.4 (C_5H_5), 90.4 (C_5H_5). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = -7.1$, −2.9. – $C_{26}H_{27}NO_2PReS$ (634.74): calcd. C 49.20, H 4.29, N 2.21, S 5.05; found C 49.29, H 4.36, N 2.14, S 4.82.

6b: Yield 170 mg (70%), orange-yellow crystalline powder. – M. p. 143 °C (dec). – IR (CH_2Cl_2): $\tilde{\nu} = 1642$ (NO) cm^{-1}. – ^1H NMR (400 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 2.17$ (d, $J = 9.7$ Hz, 3 H, PMe), 2.33 (d, $J = 10.0$ Hz, 3 H, PMe), 2.90 (s, 3 H, OMe), 2.90 (s, 3 H, OMe), 3.84, 3.93 (AB-system, $J = 12.6$ Hz, 2 H, SCH_2), 3.84, 3.94 (AB-system, $J = 12.6$ Hz, 2 H, SCH_2), 4.76 (s, 5 H, C_5H_5), 4.79 (s, 5 H, C_5H_5). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 15.4$ (d, $J = 38$ Hz, PMe), 17.1 (d, $J = 37$ Hz, PMe), 46.8 (d, $J = 9$ Hz, SCH_2), 46.9 (d, $J = 8$ Hz, SCH_2), 54.8 (OMe), 54.8 (OMe), 90.3 (C_5H_5), 90.4 (C_5H_5). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = -7.3$, −3.2. – $C_{26}H_{26}ClNO_2PReS$ (669.20): calcd. C 46.67, H 3.92, N 2.09, S 4.79; found C 47.13, H 4.16, N 2.02, S 4.53.

6c: Yield 162 mg (68%), orange-yellow crystalline powder. – M. p. 124 °C (dec). – IR (CH_2Cl_2): $\tilde{\nu} = 1639$ (NO) cm^{-1}. – ^1H NMR (400 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 2.22$ (d, $J = 9.6$ Hz, 3 H, PMe), 2.39 (d, $J = 10.0$ Hz, 3 H, PMe), 2.91 (s, 3 H, OMe), 2.92 (s, 3 H, OMe), 3.34 (s, 6 H, OMe), 3.99, 4.18 (AB-system, $J =$ 12.7 Hz, 2 H, SCH_2), 3.99, 4.18 (AB-system, $J = 12.7$ Hz, 2 H, SCH_2), 4.81 (s, 5 H, C_5H_5), 4.84 (s, 5 H, C_5H_5). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 15.4$ (d, $J = 38$ Hz, PMe), 17.2 (d, $J = 38$ Hz, PMe), 46.9 (d, $J = 8$ Hz, SCH_2), 47.0 (d, $J = 7$ Hz, SCH_2), 54.7, 54.8, 54.8 (all OMe), 90.4 (d, $J = 1$ Hz, C_5H_5), 90.4 (d, $J = 1$ Hz, C_5H_5). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = -7.0$, −2.8. – $C_{27}H_{29}NO_3PReS$ (664.77): calcd. C 48.78, H 4.40, N 2.11, S 4.82; found C 49.68, H 4.70, N 2.07, S 4.73.

6d: Yield 190 mg (84%), orange-yellow crystalline powder. – M. p. 50 °C (dec). – IR (CH_2Cl_2): $\tilde{\nu} = 1643$ (NO) cm^{-1}. – ^1H NMR (400 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 2.18$ (d, $J = 9.6$ Hz, 3 H, PMe), 2.33 (d, $J = 10.0$ Hz, 3 H, PMe), 2.90 (s, 3 H, OMe), 2.92 (s, 3 H, OMe), 4.02, 4.15 (AB-system, $J = 14.2$ Hz, 2 H, SCH_2), 4.02, 4.16 (AB-system, $J = 14.2$ Hz, 2 H, SCH_2), 4.82 (s, 5 H, C_5H_5), 4.85 (s, 5 H, C_5H_5). – ^{13}C NMR

(100 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 15.6$ (d, $J = 38$ Hz, PMe), 17.2 (d, $J = 37$ Hz, PMe), 39.2 (d, $J = 8$ Hz, SCH_2), 39.3 (d, $J = 8$ Hz, SCH_2), 54.8 (OMe), 54.9 (OMe), 90.5 (d, $J = 1$ Hz, C_5H_5), 90.6 (d, $J = 1$ Hz, C_5H_5), 106.1, 110.9, 140.6, 140.6 (all furyl-CH), 158.8 (s, SCH_2C), 158.8 (s, SCH_2C). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = -7.1, -3.1$. – $C_{24}H_{25}NO_3PReS$ (624.71): calcd. C 46.14, H 4.03, N 2.24, S 5.13; found C 46.76, H 4.27, N 2.15, S 5.80.

6e: Yield 152 mg (73%), orange-yellow crystalline powder. – M. p. 186 °C (dec). – IR (CH_2Cl_2): $\tilde{\nu} = 1638$ (NO) cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 1.60$ (t, $J = 7.3$ Hz, 6 H, SCH_2Me), 2.33 (d, $J = 9.7$ Hz, 3 H, PMe), 2.39 (d, $J = 10.0$ Hz, 3H, PMe), 3.02, 3.30 (AB-system of q, $J = 12.2$ Hz, 7.3 Hz, 2 H, SCH_2Me), 3.02, 3.30 (AB-system of q, J(H,H) = 12.2 Hz, 7.3 Hz, 2 H, SCH_2Me), 2.91 (s, 3 H, OMe), 2.94 (s, 3 H, OMe), 4.83 (s, 5 H, C_5H_5), 4.86 (s, 5 H, C_5H_5). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 15.5$ (d, $J = 38$ Hz, PMe), 17.2 (d, $J = 37$ Hz, PMe), 20.7 (SCH_2Me), 20.7 (SCH_2Me), 36.7 (d, $J = 9$ Hz, SCH_2Me), 36.7 (d, $J = 9$ Hz, SCH_2Me), 54.8 (OMe), 54.9 (OMe), 90.4 (d, $J = 1$ Hz, C_5H_5), 90.5 (d, $J = 1$ Hz, C_5H_5). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = -6.9, -2.9$. – $C_{21}H_{25}NO_2PReS$ (572.68): calcd. C 44.04, H 4.40, N 2.45, S 5.60; found C 43.99, H 4.43, N 2.36, S 4.84.

6f: Yield 156 mg (74%), yellow crystalline powder. – M. p. 62 °C (dec). – IR (CH_2Cl_2): $\tilde{\nu} = 1640$ (NO) cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 2.20$ (d, $J = 9.6$ Hz, 3 H, PMe), 2.36 (d, $J = 10.0$ Hz, 3 H, PMe), 2.91 (s, 3 H, OMe), 2.93 (s, 3 H, OMe), 3.03 – 3.71 (m, 4 H, $SCH_2CH{=}CH_2$), 4.85 (s, 5 H, C_5H_5), 4.88 (s, 5 H, C_5H_5), 4.95 – 5.58 (m, 4 H, $SCH_2CH{=}CH_2$), the remaining vinyl signal was hidden in the aryl region. – ^{13}C NMR (100 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 15.5$ (d, $J = 37$ Hz, PMe), 17.3 (d, J(P,C) = 37 Hz, PMe), 46.3 ($SCH_2CH{=}CH_2$), 46.3 ($SCH_2CH{=}CH_2$), 54.8 (OMe), 54.9 (OMe), 90.5 (d, J(P,C) = 2 Hz, C_5H_5), 90.5 (d, J(P,C) = 1 Hz, C_5H_5), 113.0 ($SCH_2CH = CH_2$), 113.0 ($SCH_2CH = CH_2$), 142.2 ($SCH_2CH = CH_2$), 142.2 ($SCH_2CH = CH_2$). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = -6.9, -2.9$. – $C_{22}H_{25}NO_2PReS$ (584.69): calcd. C 45.19, H 4.31, N 2.40, S 5.48; found C 45.24, H 4.34, N 2.15, S 5.99.

*[CpRe(NO)(PAMP)(SCH_2R)] (**6a** – **c**) from THF complex **7***

To a suspension of [CpRe(NO)(PAMP)(THF)]BF_4 (**7**) (90 mg, 0.13 mmol) in THF (5 ml) and ethanol (1 ml), the respective thiol (0.40 mmol) and Na_2CO_3 (53 mg, 0.50 mmol) were added. The mixture was stirred for 90 min at 20 °C, and a colour change from pink to brown was observed. The solvent was removed under vacuum and the residue extracted with benzene (5 ml). After filtration over silica, the solvent was evaporated again, and the solid residue washed with petroleum ether.

6a: Yield 52 mg (64%), orange-yellow crystalline powder, identical by m. p. and spectra with the material obtained from **4b**.

6b: Yield 66 mg (75%), orange-yellow crystalline powder, identical by m. p. and spectra with the material obtained from **4b**.

6c: Yield 61 mg (70%), orange-yellow crystalline powder, identical by m. p. and spectra with the material obtained from **4b**.

*{CpRe(NO)[P(Ph)(Me)($CH_2C_4H_3S$)](SCH_2R)} (**9a** – **c**)*

A thiolate solution, prepared from sodium (10 mg, 0.43 mmol), thiol (0.40 mmol) and ethanol (2 ml), was added to a suspension of {CpRe(NO)[κP(Ph)(Me)($CH_2C_4H_3$κS)]}BF_4 (**8**) (147 mg, 0.25 mmol) in THF (10 ml). While the mixture was stirred at 20 °C it turned into a clear solution. All volatiles were removed under vacuum, the residue taken up in benzene (20 ml) and filtered over celite. The filtrate was taken to dryness, the residue dissolved in dichloromethane (2 ml), and hexane (20 ml) was added. The product precipitated by concentrating the solution to 10 ml.

9a: Yield 110 mg (70%), orange-yellow crystalline powder. – M. p. 38 °C. – IR (THF): $\tilde{\nu} = 1647$ (NO) cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6, 20 °C), major diastereoisomer: $\delta = 1.70$ (d, $J = 9.4$ Hz, 3 H, PMe), 4.16, 4.18 (ABX-system, $J = 15.3$, 9.0 Hz, 2 H, PCH_2), 4.31, 4.46 (AB-system, $J = 11.5$ Hz, 2 H, SCH_2), 4.62 (s, 5 H, C_5H_5), 6.36 – 6.41, 6.48 – 6.53, 6.55 – 6.60 (all m, 1 H, thiophene-H); minor diastereoisomer: $\delta = 1.44$ (d, $J = 9.1$ Hz, 3 H, PMe), 4.09, 4.56 (ABX-system, $J = 15.4$, 8.4 Hz, 2 H, PCH_2), 4.28, 4.49 (AB-system, $J = 11.7$ Hz, 2 H, SCH_2), 4.64 (s, 5 H, C_5H_5), 6.25 – 6.29, 6.48 – 6.53, 6.55 – 6.60 (all m, 1 H, thiophene-H). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C), major diastereoisomer: $\delta = 15.9$ (d, $J = 41$ Hz, PMe), 30.4 (d, $J = 28$ Hz, PCH_2), 47.3 (d, $J = 8$ Hz, SCH_2), 89.9 (d, $J = 1$ Hz, C_5H_5); minor diastereoisomer: $\delta = 12.1$ (d, $J = 34$ Hz, PMe), 31.7 (d, $J = 30$ Hz, PCH_2), 46.9 (d, $J = 8$ Hz, SCH_2), 89.6 (d, $J = 1$ Hz, C_5H_5). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C), major diastereoisomer: $\delta = -6.4$; minor diastereoisomer: $\delta = -6.5$. – $C_{24}H_{25}NOPReS_2$ (624.78): calcd. C 46.14, H 4.03, N 2.24, S 10.26; found C 46.70, H 4.53, N 1.98, S 9.88.

9b: Yield 87 mg (53%), yellow crystalline powder. – M. p. 70 °C (dec). – IR (THF): $\tilde{\nu} = 1648$ (NO) cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6, 20 °C), major diastereoisomer: $\delta = 1.67$ (d, $J = 9.5$ Hz, 3 H, PMe), 3.72 – 4.23 (m, 4 H, PCH_2 and SCH_2), 4.60 (s, 5 H, C_5H_5), 6.34. – 6.40, 6.45 – 6.54, 6.56 – 6.62 (all m, 1 H, thiophene-H); minor diastereoisomer: $\delta = 1.43$ (d, $J = 9.2$ Hz, 3 H, PMe), 3.72 –

4.23 (m, 4 H, PCH_2 and SCH_2), 4.62 (s, 5 H, C_5H_5), 6.24 – 6.28, 6.45 – 6.54, 6.56 – 6.62 (all m, 1 H, thiophene-H). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C), major diastereoisomer: $\delta = 15.8$ (d, $J = 41$ Hz, PMe), 30.5 (d, $J = 28$ Hz, PCH_2), 46.6 (d, $J = 8$ Hz, SCH_2), 89.9 (d, $J = 1$ Hz, C_5H_5); minor diastereoisomer: $\delta = 12.1$ (d, $J = 35$ Hz, PMe), 31.7 (d, $J = 30$ Hz, PCH_2), 46.2 (d, $J = 8$ Hz, SCH_2), 89.6 (d, $J = 1$ Hz, C_5H_5). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C), major diastereoisomer: $\delta = -6.5$; minor diastereoisomer: $\delta = -6.7$. - $C_{24}H_{24}ClNOPReS_2$ (659.23): calcd. C 43.73, H 3.67, N 2.12, S 9.73; found C 42.54, H 3.70, N 2.09, S 9.47.

9c: Yield 115 mg (70%), yellow crystalline powder. – M. p. 126 (dec). – IR (THF): $\tilde{\nu} = 1646$ (NO) cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 1.46$ (d, $J = 9.1$ Hz, 3 H, PMe), 1.72 (d, $J = 9.4$ Hz, 3 H, PMe), 3.34 (s, 6 H, OMe), 3.80, 4.28 (ABX-system, $J = 15.4$, 8.2 Hz, 2 H, PCH_2), 3.87, 3.90 (ABX-system, $J = 15.4$, 9.0 Hz, 2 H, PCH_2), 3.98, 4.16 (AB-system, $J = 12.7$ Hz, 2 H, SCH_2), 4.00, 4.19 (AB-system, $J = 12.8$ Hz, 2 H, SCH_2), 4.65 (s, 5 H, C_5H_5), 4.67 (s, 5 H, C_5H_5), 6.26 – 6.30 (m, 1 H, thiophene-H), 6.38 – 6.42 (m, 1 H, thiophene-H), 6.48 – 6.54 (m, 2 H, thiophene-H), 6.56 – 6.60 (m, 2 H, thiophene-H). – ^{13}C NMR (100 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = 12.1$ (d, $J = 35$ Hz, PMe), 15.9 (d, $J = 41$ Hz, PMe), 30.5 (d, $J = 28$ Hz, PCH_2), 31.7 (d, $J = 30$ Hz, PCH_2), 46.3 (d, $J = 8$ Hz, SCH_2), 46.6 (d, $J = 8$ Hz, SCH_2), 54.8 (OMe), 89.6 (d, $J = 1$ Hz, C_5H_5), 89.9 (d, $J = 1$ Hz, C_5H_5). – ^{31}P NMR (162 MHz, C_6D_6, 20 °C), both diastereoisomers: $\delta = -6.4$, -6.4. – $C_{25}H_{27}NO_2PReS_2$ (654.81): calcd. C 45.86, H 4.16, N 2.14, S 9.79; found C 45.09, H 4.11, N 2.00, S 9.94.

*[CpRe(NO)(PR$_3$)(η^2-S=C(H)Ar)]BF$_4$ (**10a** – **c**, **11**)*

At −78 °C, a solution of $[Ph_3C]BF_4$ (92 mg, 0.25 mmol) in dichloromethane (3 ml) was added to a solution of the thiolate complex (0.20 mmol) in the same solvent (5 ml). The mixture was stirred for 1 h at −78 °C and allowed to warm to 20 °C over a period of 1 h. The solution was concentrated to 1 ml and the product precipitated by addition of diethyl ether.

10a: Yield 140 mg (98%), reddish-brown powder. – M. p. 88 °C (dec). – IR (CH_2Cl_2): $\tilde{\nu} = 1750$ (NO) cm^{-1}. – ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: $\delta = 2.61$ (d, $J = 10.7$ Hz, 3 H, PMe), 2.65 (d, $J = 11.3$ Hz, 3 H, PMe), 3.61 (s, 3 H, OMe), 3.87 (s, 3 H, OMe), 5.93 (d, $J = 1.0$ Hz, 5 H, C_5H_5), 5.97 (d, $J = 0.9$ Hz, 5 H, C_5H_5), 6.69 – 6.79 (m, 3 H, S=C(*H*)Ph and aryl-H). – ^{13}C NMR (75.5 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: $\delta = 15.4$ (d, $J = 45$ Hz, PMe), 18.1 (d, $J = 44$ Hz, PMe), 51.4 (S=*C*(H)Ph), 51.9 (S=*C*(H)Ph), 56.3 (OMe), 56.5 (OMe), 99.5 (C_5H_5), 100.2 (C_5H_5). – ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: $\delta = -12.3$, -10.0. – $C_{26}H_{26}BF_4NO_2PReS$ (720.55): calcd. C 43.34, H 3.64, N 1.94, S 4.45; found C 43.04, H 3.81, N 1.86, S 3.91.

Table 1. Details of the structure determinations of compounds **1a** · BH_3 and *S*-**1b** · BH_3.

	1a•BH_3	*S*-**1b**•BH_3
Empirical formula	$C_{22}H_{32}BP$	$C_{14}H_{18}BOPe$
Formula mass	338.28	244.06
Crystal colour/habit	colourless block	colourless block
Crystal system	tetragonal	orthorhombic
Space group	$I4_1$	$P2_12_12_1$
a [Å]	17.9001(18)	8.9113(7)
b [Å]	17.9001(18)	11.6424(9)
c [Å]	26.396(4)	13.3465(10)
α [°]	90	90
β [°]	90	90
γ[°]	90	90
V [Å^3]	8457.7(17)	1384.68(18)
Θ [°]	1.37 – 25.45	2.32 – 28.27
h	−21 to 20	−11 to 11
k	−21 to 13	−15 to 15
l	−30 to 31	−17 to 17
Z	16	4
μ(Mo-K_α) [mm^{-1}]	0.130	0.179
Crystal size [mm]	0.20 × 0.10 × 0.10	0.25 × 0.20 × 0.20
$D_{calcd.}$ [gcm^{-3}]	1.063	1.171
T [K]	173(2)	173(2)
Reflections coll.	22083	31616
Indep. reflections	7676	3295
Parameters	463	157
$R_1(I > 2\sigma(I))$	0.0507	0.0356
R_1 (overall)	0.1040	0.0359
$wR_2(I > 2\sigma(I))$	0.0995	0.0888
wR_2 (overall)	0.1153	0.0891
Flack parameter [30]	0.15(10)	0.02(8)
Diff. peak/hole [eÅ^{-3}]	0.242/ − 0.134	0.316/ − 0.203
CCDC	245425	242218

10b: Yield 121 mg (80%), purple powder. – M. p. 84 °C (dec). – IR (CH_2Cl_2): $\tilde{\nu} = 1750$ (NO), 1713 (NO) cm^{-1}. – ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: $\delta = 2.60$ (d, $J = 9.8$ Hz, 3 H, PMe), 2.64 (d, $J = 10.4$ Hz, 3 H, PMe), 3.61 (s, 3 H, OMe), 3.87 (s, 3 H, OMe), 5.95 (d, $J = 1.1$ Hz, 5 H, C_5H_5), 5.99 (d, $J = 0.9$ Hz, 5 H, C_5H_5), 6.64 – 6.80 (m, 3 H, S=C(*H*)Ar and aryl-H). – ^{13}C NMR (75.5 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: $\delta = 15.5$ (d, $J = 45$ Hz, PMe), 18.1 (d, $J = 44$ Hz, PMe), 49.9 (S=*C*(H)Ar), 50.5 (S=*C*(H)Ar), 56.3 (OMe), 56.6 (OMe), 99.7 (C_5H_5), 100.4 (C_5H_5). – ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: $\delta = -12.3$, -10.0. – $C_{26}H_{25}BClF_4NO_2PReS$ (754.99): calcd. C 41.36, H 3.34, N 1.86, S 4.25; found C 40.53, H 3.63, N 1.96, S 3.73.

10c: Yield 144 mg (96%), reddish-brown powder. – M. p. 180 °C (dec). – IR (CH_2Cl_2): $\tilde{\nu} = 1748$ (NO) cm^{-1}. – ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: $\delta = 2.60$ (d, $J = 10.6$ Hz, 3 H, PMe), 2.65 (d, $J =$

11.3 Hz, 3 H, PMe), 3.61, 3.79, 3.81, 3.87 (all s, 3 H, OMe), 5.90 (s, 5 H, C_5H_5), 5.94 (s, 5 H, C_5H_5), 6.69 – 6.91 (m, 7 H, S=C(*H*)Ar and aryl-H), 8.52 (s, br, S=C(*H*)Ar). – ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: $\delta = 15.4$ (d, $J = 44$ Hz, PMe), 18.0 (d, $J = 45$ Hz, PMe), 52.2 (br, S=*C*(H)Ar), 52.7 (br, S=*C*(H)Ar), 55.7, 55.7, 56.3, 56.5 (all O*Me*), 99.4 (C_5H_5), 100.1 (C_5H_5). – ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: $\delta = -12.5$, -10.1. – $C_{27}H_{28}BF_4NO_3PReS$ (750.58): calcd. C 43.21, H 3.76, N 1.87, S 4.27; found C 42.97, H 4.13, N 1.88, S 3.89.

11: Yield 140 mg (98%), yellow powder. – M. p. 50 °C (dec). – IR (CH_2Cl_2): $\tilde{\nu} = 1739$ (NO) cm^{-1}. – ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: $\delta = 2.29$ (d, $J = 10.4$ Hz, 3 H, PMe), 2.34 (d, $J = 10.5$ Hz, 3 H, PMe), 4.07, 4.56 (ABX-system, $J = 16.5$, 8.7 Hz, 2 H, PCH_2), 4.17, 4.42 (ABX-system, $J = 15.8$, 8.1 Hz, 2 H, PCH_2), 5.94 (d, $J = 0.9$ Hz, 5 H, C_5H_5), 6.09 (d, $J = 0.9$ Hz, 5 H, C_5H_5), 6.60 (d, $J = 1.1$ Hz, 1 H, S=C(*H*)Ph), 6.67 (d, $J = 1.0$ Hz, 1 H, S=C(*H*)Ph). – ^{13}C NMR (75.5 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: $\delta = 10.8$ (d, $J = 43$ Hz, PMe), 12.8 (d, $J =$ 43 Hz, PMe), 32.0 (d, $J = 35$ Hz, PCH_2), 32.6 (d, $J = 37$ Hz, PCH_2), 51.5 (S=*C*(H)Ph), 51.6 (S=*C*(H)Ph), 99.8 (C_5H_5), 100.0 (C_5H_5). – ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C), both diastereoisomers: $\delta = -11.3$, -9.8. – $C_{24}H_{24}BF_4NOPReS_2$ (710.57): calcd. C 40.57, H 3.40, N 1.97, S 9.03; no satisfactory elemental analysis obtained.

X-ray structure determinations

Single crystals of **1a** · BH_3 and *S*-**1b** · BH_3 were sealed to a glass fibre with frozen hydrocarbon oil. A Bruker Smart Apex CCD instrument was used for data collection (graphite monochromator, Mo-K_α radiation, $\lambda = 0.71073$ Å). The structures were solved using Patterson methods and refined with full-matrix least squares against F^2 (SHELXS-97) [29]. Hydrogen atoms were included in their calculated positions and refined in a riding model. The details of the measurements are summarized in Table 1. Further data may be obtained from the Cambridge Crystallographic Data Centre. **1a** · BH_3: CCDC 245425, *S*-**1b** · BH_3: CCDC 242218. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

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