# Diastereoselective Protonation, Substitution and Addition Reactions at Pseudotetrahedral Rhenium Complexes

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Dedicated to Professor Dr. R. Tacke on the occasion of his 60th birthday

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The chiral N,P ligand P(Me)(Ph)[8-(2-methylquinolinyl)] (3) was synthesized and separated into its enantiomers via diastereomeric palladium complexes. The reactions of 3 and  $(R_{\rm P})$ -3 with [CpRe(CO)(NO)(NCMe)]BF<sub>4</sub> (7) gave the [CpRe(CO)(NO){P(Me)(Ph)diastereomeric complexes  $(C_{10}H_8N)$ ]BF<sub>4</sub> [8 and  $(R_{Re}, S_P/S_{Re}, S_P)$ -8], which, upon borohydride reduction, yielded the corresponding methyl complexes  $[CpRe(NO){P(Me)(Ph)(C_{10}H_8N)}(CH_3)]$  [9 and  $(R_{Re}, S_P/N)$  $S_{\text{Re}}S_{\text{P}}$ -9]. Treatment of 9 with HBF<sub>4</sub> under carefully controlled conditions gave the diastereomerically pure chelates  $[CpRe(NO){P(Me)(Ph)(C_{10}H_8N)}]BF_4$  $[(R_{\rm Re}, S_{\rm P}/S_{\rm Re}, R_{\rm P})-10,$  $(R_{\rm Re'}R_{\rm P}/S_{\rm Re'}S_{\rm P})$ -10 and  $(R_{\rm Re'}S_{\rm P})$ -10]. The chelate ring was opened with NaSH to produce the hydrosulfido complexes  $[CpRe(NO){P(Me)(Ph)(C_{10}H_8N)}(SH)]$  $[(R_{\rm Re}, S_{\rm P}/S_{\rm Re}, R_{\rm P})-11,$ 

## Introduction

The activation of prochiral unsaturated substrates by chiral, enantiomerically pure transition metal Lewis acids is a promising and often highly efficient strategy for enantioselective synthesis.<sup>[1]</sup> The chirality may be based either on the coordination geometry around the metal atom itself ("metal-based chirality") - prominent examples are the pseudotetrahedral half-sandwich complexes [CpMn- $(CO)(NO)(PPh_3)]$ <sup>[2]</sup> [CpFe(CO)(PPh\_3)(COCH\_3)]<sup>[3]</sup> and  $[CpRe(NO)(PPh_3)(CH_3)]^{[4]}$  – or may be added through the use of chiral ligands ("ligand-based chirality") as exemplified by the pioneering work of Knowles,<sup>[5]</sup> Noyori,<sup>[6]</sup> and Sharpless<sup>[7]</sup> on enantioselective catalysis. The two concepts have been combined in order to study the often facile epimerization at the metal center<sup>[8–10]</sup> and hopefully overcome the problems associated with it with regard to asymmetric synthesis and catalysis.<sup>[10]</sup>

Recently, we have found a kinetically controlled, highly efficient chirality transfer between an amine-functionalized phosphane ligand and the metal center (Scheme 1).<sup>[11]</sup>

 $(R_{\text{Rer}}R_{\text{P}}/S_{\text{Rer}}S_{\text{P}})$ -11 and  $(R_{\text{Rer}}S_{\text{P}})$ -11]. Each step in this sequence proceeded with retention of configuration at rhenium. Complex 11 underwent acid-promoted condensation thioaldehyde with aldehydes to give complexes  $[CpRe(NO){P(Me)(Ph)(C_{10}H_8N)}(S=CHR)]BF_4$  (12a-d, R = Ph, Me,  $4-C_6H_4OMe$ ,  $C_6F_5$ ). The addition of nucleophiles X<sup>-</sup> to **12a** gave rhenium-coordinated  $\alpha$ -chiral thiolate complexes  $[CpRe(NO){P(Me)(Ph)(C_{10}H_8N)}{SC(H)(Ph)(X)}]$  (13a-e, X = acac, PhCH<sub>2</sub>S, EtS, tBuS, CN) with 42-89% de. The thiolate can readily be cleaved from the rhenium complex by a methylation/chelate ring-closure strategy. The stereochemistry of the entire reaction sequence was corroborated for each step by X-ray crystallography.

The high diastereoselectivity is rooted in the intramolecular proton transfer from the dimethylamino sidearm of the chiral phosphane ligand to rhenium, which is much faster for the *unlike* diastereomer. Thus, starting from the mixture  $(R_{\text{Rev}}S_{\text{P}}/S_{\text{Rev}}S_{\text{P}})$ -1 the two enantiomerically pure diastereomers  $(R_{\text{Rev}}S_{\text{P}})$ -2 and  $(S_{\text{Rev}}S_{\text{P}})$ -2 were obtained in 99% *ee* and 93% *de*.<sup>[11]</sup> A considerable drawback of compounds 2 is their inertness in ligand-substitution reactions. The five-membered chelate ring could be opened only with NaCN under quite forcing conditions.<sup>[12]</sup> We now report on a similar system which is reactive enough to be further elaborated.

## Results

#### Phosphane Synthesis and Enantiomer Separation

The synthesis of the new chiral phosphane **3** by nucleophilic substitution (Scheme 2) follows well-established methods.<sup>[13,14]</sup>

Phosphane **3** is a yellow, slightly air-sensitive crystalline solid with the expected NMR spectroscopic data, e.g. a doublet at  $\delta = 1.76$  ppm for the PCH<sub>3</sub> group, a singlet at  $\delta = 2.70$  for the ArylCH<sub>3</sub> group, and a <sup>31</sup>P signal at  $\delta = -33.8$  ppm.



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like-2 (87%, 93% de)

Scheme 1.



of  $(S_{\rm P}S_{\rm C})$ -5 was determined crystallographically in order to assign the configuration at phosphorus. The salt crystallized from acetone in the triclinic space group *P*1 with two independent formula units and one molecule of acetone in the unit cell. A view of one of the cations is shown in Figure 1.



We have made several attempts to devise an enantioselective synthesis for **3**. Thus  $(S_P)$ -(Ph)(Me)(H<sub>3</sub>B)PH<sup>[15]</sup> was deprotonated at -78 °C with butyllithium and added to 2methyl-8-chloroquinoline, but failed to react at this temperature. Higher temperatures would have led to racemization of the borane-protected lithium phosphide reagent.<sup>[15]</sup> The reverse strategy, Br/Li exchange on 2-methyl-8-bromoquinoline<sup>[16]</sup> followed by reaction with various chlorophosphanes such as (Ph)(Me)PCl, PhPCl<sub>2</sub>, or (Et<sub>2</sub>N)<sub>2</sub>PCl never gave any tractable results.

 $(R_{\rm P})$ -3 was finally obtained with 99% *ee* via diastereomeric palladium complexes as reported by Wild et al. for the similar 8-(methylphenylphosphanyl)quinoline.<sup>[14]</sup> Reaction of the dimeric Pd complex ( $S_{\rm C}$ )-4 with phosphane 3 followed by addition of NH<sub>4</sub>PF<sub>6</sub> gave complex 5 as a mixture of diastereomers in high yield (Scheme 3).



Scheme 3.

Slow crystallization of  $(R_{\rm P},S_{\rm C}/S_{\rm P},S_{\rm C})$ -5 from boiling 2butanone gave a 54% crop of  $(S_{\rm P},S_{\rm C})$ -5 which after recrystallization was obtained with 99% *de*. The structure



Figure 1. Structure of the cation of  $(S_{\rm P}S_{\rm C})$ -5, hydrogen atoms were omitted for clarity. Thermal ellipsoids drawn at 50% level. Space group *P*1; selected distances [pm] and angles [°] (standard deviations in parentheses): Pd(1)–P(1) 221.74(6), Pd(1)–N(1) 223.7(2), Pd(1)–N(2) 216.8(2), Pd(1)–C(40) 199.9(3), P(1)–Pd(1)–N(1) 80.23(5), P(1)–Pd(1)–N(2) 169.58(6), P(1)–Pd(1)–C(40) 95.33(7), N(1)–Pd(1)–N(2) 103.69(8), N(1)–Pd(1)–C(40) 174.09(9), N(2)–Pd(1)–C(40) 80.04(9).

As expected, the structure is very similar to that of the  $(S_{\rm P}R_{\rm C})$  diastereomer of the analogous complex of 8-(methylphenylphosphanyl)quinoline.<sup>[14]</sup> The two cations in the unit cell differ somewhat with regard to the geometry around the Pd atom. While the one shown in Figure 1 is almost perfectly planar, the other one is folded with a trans angle P–Pd–N of 156.2°. Inspection of the unit cell diagram shows that this is caused by packing forces within the crystal.

 $(R_{\rm P})$ -3 was cleaved from  $(S_{\rm P}S_{\rm C})$ -5 by treatment with ethylenediamine, and the ethylenediamine palladium complex  $(S_{\rm C})$ -6 converted back to (S)-4 by reaction with 2 M aqueous HCl (Scheme 4).



Scheme 4.

#### Synthesis of Diastereomeric Rhenium Complexes

The acetonitrile complex [CpRe(CO)(NO)(NCMe)]BF<sub>4</sub> (7) is a perfectly suited starting material for the synthesis of chiral half-sandwich rhenium complexes.<sup>[17–19]</sup> Fusing 7 together with a slight excess of racemic 3 under vacuum and without solvent gave a high yield of racemic 8. Similarly, diastereomeric ( $R_{Res}$ , $S_P$ / $S_{Res}$ , $S_P$ )-8 was obtained from the reaction of 7 and ( $R_P$ )-3 with > 98% *ee* (determined by <sup>1</sup>H NMR spectroscopy in the presence of Eu(tfc)<sub>3</sub>). In this case the temperature should not exceed 90 °C to keep the phosphane from racemizing (Scheme 5).



Scheme 5.

The structure of racemic **8** was determined crystallographically. The compound crystallized in the space group  $P2_1/c$  with the CO and NO ligands disordered. A view of the cation is shown in Figure 2. Interatomic distances and angles are very similar to those of analogous complexes.<sup>[4,18]</sup>

Borohydride reduction of the carbonyl ligand<sup>[17]</sup> gave the methyl complexes **9** and  $(R_{\text{Re}}, S_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -**9**, respectively (Scheme 6). The success of the reaction is immediately evident from the disappearance of the CO stretching absorption in the infrared spectrum and new doublets in the <sup>1</sup>H and <sup>13</sup>C NMR spectra typical of a Re–CH<sub>3</sub> group.

By crystallization from toluene/pentane, **9** was partially separated into  $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -**9** (87% *de*) and  $(R_{\text{Re}}, S_{\text{P}}/S_{\text{Re}}, R_{\text{P}})$ -**9** (72% *de*).  $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -**9** crystallized in the triclinic space group  $P\bar{1}$ , a view of the molecule is shown in Figure 3.



Figure 2. Structure of the cation of **8**, hydrogen atoms were omitted for clarity. Thermal ellipsoids drawn at 50% level. C(1) and N(1) are disordered and were labeled arbitrarily. Space group  $P_{2_1}/c$ ; selected distances [pm] and angles [°] (standard deviations in parentheses): Re(1)–P(1) 241.41(11), Re(1)–C(1) 185.6(4), Re(1)–N(1) 184.8(4), P(1)–Re(1)–C(1) 93.16(12), P(1)–Re(1)–N(1) 91.72(12), C(1)–Re(1)–N(1) 92.46(16).



Scheme 6.



Figure 3. Structure of the compound ( $R_{Rc}$ , $R_P/S_{Rc}$ , $S_P$ )-9, hydrogen atoms were omitted for clarity. Thermal ellipsoids drawn at 50% level. Space group  $P\overline{1}$ ; selected distances [pm] and angles [°] (standard deviations in parentheses): Re(1)–P(1) 235.12(14), Re(1)–C(1) 227.2(8), Re(1)–N(1) 174.3(5), N(1)–O(1) 121.0(7), P(1)–Re(1)–C(1) 84.1(2), P(1)–Re(1)–N(1) 92.8(2), C(1)–Re(1)–N(1) 94.0(3).

A sample of  $(R_{\text{Res}}S_{\text{P}}/S_{\text{Res}},R_{\text{P}})$ -9 (72% *de*) was treated at -78 °C with 0.86 equiv. HBF<sub>4</sub>, i.e. just enough to protonate the faster reacting<sup>[11]</sup> *unlike* diastereomer. The ionic product  $(R_{\text{Res}}S_{\text{P}}/S_{\text{Res}},R_{\text{P}})$ -10 was crystallized by addition of diethyl ether and thus easily separated from residual  $(R_{\text{Res}},R_{\text{P}}/S_{\text{Res}},R_{\text{P}})$ -9 (Scheme 7).



(R<sub>Re</sub>, S<sub>P</sub>/S<sub>Re</sub>, R<sub>P</sub>)-9 (72% de)

 $(R_{\rm Re}, S_{\rm P}/S_{\rm Re}, R_{\rm P})$ -10 (74%, 97% de)

Scheme 7.

Similarly, a trace of HBF<sub>4</sub> was added to a sample of  $(R_{\text{Rev}}R_{\text{P}}/S_{\text{Rev}}S_{\text{P}})$ -9 (87% *de*) to convert the residual *unlike* diastereomer into the ring-closed ionic complex which was precipitated and discarded. The supernatant was then treated with more acid yielding  $(R_{\text{Rev}}R_{\text{P}}/S_{\text{Rev}}S_{\text{P}})$ -10 with 94% *de*. The relative configuration of both diastereomers was assigned on the basis of <sup>1</sup>H-<sup>1</sup>H NOESY spectra: Both isomers gave strong crosspeaks between the Cp signal and the resonance of the CH<sub>3</sub> group on the quinoline ring. For  $(R_{\text{Rev}}S_{\text{P}}/S_{\text{Rev}}R_{\text{P}})$ -10, additional crosspeaks connected the Cp signal with the PCH<sub>3</sub> signal, while for  $(R_{\text{Rev}}R_{\text{P}}/S_{\text{Rev}}S_{\text{P}})$ -10 a correlation was observed between the Cp ring and the *ortho* protons of the PC<sub>6</sub>H<sub>5</sub> group. This assignment was finally corroborated by an X-ray structure determination of  $(R_{\text{Rev}}R_{\text{P}}/S_{\text{Rev}}S_{\text{P}})$ -10 (Figure 4).

By the two-step process outlined above a sample of nonracemic  $(R_{\text{Re}}, S_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -9 was finally converted into  $(R_{\text{Re}}, S_{\text{P}})$ -10 (71% de) and  $(S_{\text{Re}}, S_{\text{P}})$ -10 (92% de) (Scheme 8). For the success of this reaction it is very important that the amount of acid in the first step is carefully controlled.

Ring opening with the strong, soft nucleophile  $SH^-$  proceeds smoothly and stereospecifically at 0 °C (Scheme 9).

The lower yield of enantiomerically pure  $(S_{\text{Re}}, S_{\text{P}})$ -11 is mainly due to its good solubility in pentane which is responsible for losses during workup. The presence of the Re– SH group reveals itself through a doublet (J = 13.5 Hz) in the <sup>1</sup>H NMR spectrum near  $\delta = 0.2$ . A structure determi-



Figure 4. Structure of the cation of  $(R_{Re}, R_P/S_{Re}, S_P)$ -10, hydrogen atoms were omitted for clarity. Thermal ellipsoids drawn at 50% level. Space group *C2/c*; selected distances [pm] and angles [°] (standard deviations in parentheses): Re(1)–P(1) 231.50(9), Re(1)–N(1) 176.4(3), Re(1)–N(2) 218.9(3), N(1)–O(1) 119.6(4), P(1)–Re(1)–N(1) 92.59(10), P(1)–Re(1)–N(2) 81.12(8), N(1)–Re(1)–N(2) 96.68(13).



Scheme 9.

nation of the  $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -diastereomer was carried out as an unambiguous proof of the relative configuration at rhenium and phosphorus (Figure 5).

Not unexpectedly, the structure is very similar to that of the methyl complex ( $R_{\text{Re}}$ , $R_{\text{P}}/S_{\text{Re}}$ , $S_{\text{P}}$ )-9 (Figure 3). One noteworthy difference is the large angle S(1)–Re(1)–N(1). This is a common feature of all complexes [CpRe(NO)(PR'<sub>3</sub>)(SR)],



(S<sub>Re</sub>,S<sub>P</sub>)-10 (81%, 92% de)

Scheme 8.





Figure 5. Structure of the compound  $(R_{\text{Rev}}R_{\text{P}}/S_{\text{Rev}}S_{\text{P}})$ -11, hydrogen atoms were omitted for clarity. Thermal ellipsoids drawn at 50% level. Space group  $P\overline{1}$ ; selected distances [pm] and angles [°] (standard deviations in parentheses): Re(1)–P(1) 237.11(15), Re(1)–S(1) 239.1(2), Re(1)–N(1) 179.6(6), N(1)–O(1) 115.0(8), P(1)–Re(1)–S(1) 83.76(6), P(1)–Re(1)–N(1) 91.8(2), S(1)–Re(1)–N(1) 98.5(2).

which is caused by an antibonding interaction between the strongly  $\pi$ -donating SR ligand and the HOMO-1 of the [CpRe(NO)(PR'<sub>3</sub>)] complex fragment.<sup>[19–21]</sup>

Condensation reactions with a number of aldehydes were carried out on both diastereomers of **11**. The desired thioaldehyde complexes **12** were formed in high yields and, as expected, with retention of configuration at rhenium (Scheme 10).



Scheme 10.

As indicated in Scheme 10, the thioaldehyde complexes 12 exist as rapidly equilibrating mixtures of  $\eta^1$  and  $\eta^2$  isomers. This can easily be inferred from the appearance of two well separated NO stretching vibrations in the infrared spectra. The ratio of the isomers depends on the group R and the relative configuration at rhenium and phosphorus. Thus, both diastereomers of 12b and the like diastereomers of 12c and 12d are essentially pure  $\eta^2$  isomers, both diastereomers of 12a contain smaller fractions of the  $\eta^1$  isomers, and the unlike diastereomers of 12c and 12d are roughly equimolar mixtures of both forms.

A structure determination of  $(R_{\text{Re}}, S_{\text{P}}/S_{\text{Re}}, R_{\text{P}})$ -12c was undertaken, the major concern again being the relative configuration at rhenium and phosphorus. A view of the cation is shown in Figure 6.



Figure 6. Structure of the cation of  $(R_{Res}S_P/S_{Res}R_P)$ -12c, hydrogen atoms were omitted for clarity. Thermal ellipsoids drawn at 50% level. Space group P2(1)/n; selected distances [pm] and angles [°] (standard deviations in parentheses): Re(1)–S(1) 239.12(14), Re(1)–C(50) 223.2(5), S(1)–C(50) 173.1(6), Re(1)–P(1) 243.22(14), Re(1)–N(1) 176.0(5), N(1)–O(1) 117.4(7), S(1)–Re(1)–C(50) 43.80(15), P(1)–Re(1)–S(1) 79.80(5), P(1)–Re(1)–C(50) 121.45(15), P(1)–Re(1)–N(1) 90.42(17).

As expected, the structure is very similar to that of  $[CpRe(NO)(PPh_3)(\eta^2-S=CHPh)]BF_4$ .<sup>[22]</sup> The S(1)-C(50) bond is almost parallel to the Re(1)-P(1) bond such as to maximize the interaction between the HOMO of the  $[CpRe(NO)(PR_3)]^+$  complex fragment and the  $\pi^*$  orbital of the thiocarbonyl group.<sup>[4]</sup> This interaction results in a lengthening of the S(1)-C(50) bond in comparison with 2,4,6-tri(*tert*-butyl)thiobenzaldehyde (160.2 pm)<sup>[23]</sup> or  $[CpRu(dppe)(\eta^1-S=CHC_6H_4OMe)]PF_6$  (162.7 pm).<sup>[24]</sup> The aryl group is located *anti* to the Cp ligand such that the configurations at rhenium and carbon are the same.

#### **Diastereoselective Addition of Nucleophiles**

As a first test of the asymmetric induction between rhenium and the thioaldehyde ligand we chose the addition of various nucleophiles  $X^-$  to both diastereomers of **12a** (Scheme 11).

The addition products were isolated in satisfactory yields. The diastereoselectivity of the addition was only moderate. A crystal of the major isomer of  $(R_{\text{Res}}R_{\text{P}}/S_{\text{Res}}S_{\text{P}})$ -13d was investigated by X-ray crystallography. The compound crystallizes in the triclinic space group  $P\overline{1}$  with two molecules in the unit cell which are related by a center of inversion. One of them is shown in Figure 7.

The geometry around the rhenium atom is almost identical to that of  $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -11, including the typically large angle S(1)–Re(1)–N(1). The angles at C(50) are close to tetrahedral with the relative configuration at this atom the same as at Re(1) and P(1).

The enantiomerically enriched addition product  $(S_{\text{Re}}, S_{\text{Ps}}, S_{\text{C}})$ -13b was finally chosen to explore ways to cleave the thiolate ligand from the rhenium complex. Initial experiments to achieve this by protonation with CF<sub>3</sub>COOH or HBF<sub>4</sub> failed. Methylation however worked well. Monitoring the reaction by NMR spectroscopy indicated that a thioether complex was involved as an intermediate. Upon



Scheme 11.



Figure 7. Structure of the compound ( $R_{Res}R_{P_s}R_C/S_{Res}S_{P_s}S_C$ )-13d, hydrogen atoms were omitted for clarity. Thermal ellipsoids drawn at 50% level. Space group *P*1; selected distances [pm] and angles [°] (standard deviations in parentheses): Re(1)–P(1) 236.10(9), Re(1)–S(1) 238.53(9), Re(1)–N(1) 175.4(3), N(1)–O(1) 119.6(4), S(1)–C(50) 184.8(4), S(2)–C(50) 181.8(4), P(1)–Re(1)–S(1) 86.51(3), P(1)–Re(1)–N(1) 89.4(1), S(1)–Re(1)–N(1) 99.0(1), S(1)–C(50)–S(2) 104.5(2).



Scheme 12.

## Discussion

The present study was undertaken with several goals in mind: (i) to establish a broader applicability of the diastereoselective proton transfer from base-functionalized phosphane ligands to metal centers,<sup>[11]</sup> (ii) to investigate the stereochemical course of chelate ring-opening and -closing reactions, and (iii) to find out whether the presence of an additional stereogenic center might influence the diastereoselectivity of nucleophilic addition reactions to unsaturated ligands. In order to arrive at unambiguous conclusions we decided to carry the entire reaction sequence through with both diastereomers and track the stereochemical course of each step by X-ray crystallography.

Horner-type phosphanes PR<sup>1</sup>R<sup>2</sup>R<sup>3</sup> are configurationally stable at temperatures below 100 °C.<sup>[25]</sup> Thus the reactivity of the acetonitrile complex 7 is just sufficient not to jeopardize the stereochemical outcome of the substitution reaction described in Scheme 5. As expected the two spectroscopically distinguishable diastereomers of 8 are formed with 0% de, and any attempt to separate them by crystallization or chromatography is thwarted by the similarity of the CO and NO ligands. By contrast, the two diastereomeric methyl complexes 9 have sufficiently different solubilities to be at least partially separated by crystallization. It should be mentioned here that the success of the CO to methyl reduction (Scheme 6) cannot be taken for granted. In fact, attempts to reduce complexes analogous to 8 with the ligands P(Me)(Ph)(8-quinolinyl), P(Me)(Ph)(2pyridyl) or P(Me)(Ph)(CH<sub>2</sub>NMe<sub>2</sub>) gave intractable mixtures which contained little if any of the desired methyl complexes.<sup>[12]</sup>

As we have pointed out in our previous communication,<sup>[11]</sup> the striking diastereoselectivity of the proton transfer/methane elimination reaction of Scheme 6 and 7 rests on a number of well-established facts: (i) The basicity of electron-rich transition metal complexes is similar to or even exceeds that of organic nitrogen bases;<sup>[26]</sup> (ii) the rate of proton transfer to the metal ("kinetic basicity") is, however, smaller by several orders of magnitude;<sup>[27,28]</sup> (iii) acid induced methyl cleavage involves metal protonation at a site cis to CH<sub>3</sub> followed by reductive elimination.<sup>[29,30]</sup> As a result, a metal complex bearing an amine function on the side arm of one of the ligands will first be protonated at nitrogen followed by intramolecular H<sup>+</sup> transfer to the metal.<sup>[31]</sup> This situation is graphically illustrated in Scheme 13.

Here, K(N) and K(M) represent the (roughly similar) basicities of the nitrogen and metal centers, respectively, and the various  $k_x(N)$  and  $k_x(M)$  are the corresponding rate constants of proton transfer to nitrogen or metal, with  $k_x(N) >> k_x(M)$ . In the absence of a basic solvent a substoichiometric amount of acid HA will be rapidly and completely consumed by the formation of the *N*-protonated spe-



Scheme 13.

cies. In a dilute solution, the entropy-favored intramolecular proton transfer ( $k_i$  step) will be much faster than the *inter*molecular reprotonation of the conjugate base A- followed by direct metal protonation. As the reductive elimination of methane from rhenium is rapid even at low temperatures<sup>[30,31]</sup> (i.e.  $k_{el} >> k_{-i}$ ) it follows that the intramolecular proton transfer from nitrogen to rhenium is the rate-determining step. A clue as to how this step could bring about a high diastereoselectivity comes from an inspection of the structure of the cation of  $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -10 (Figure 4). In this slower formed diastereomer the phenyl group at phosphorus eclipses the cyclopentadienyl ligand on rhenium, whereas in the rapidly formed  $(R_{Res}S_P/S_{Res}R_P)$ -diastereomer the phenyl group eclipses the svelte NO ligand (see also the structure determinations of both diastereomers of  $2^{[11]}$ ). Because the geometry of the transition state of the proton transfer from N to Re approaches that of the final product, it seems safe to assume that this repulsive interaction is responsible for slowing down the proton transfer within the  $(R_{\rm Re}, R_{\rm P}/S_{\rm Re}, S_{\rm P})$  diastereomer (Scheme 14).

The opening of the chelate ring by the attacking nucleophile SH<sup>-</sup> proceeds with retention of configuration at the rhenium center (Scheme 9). It is tempting to ascribe this outcome to the configurational stability of the pyramidal Lewis acid intermediate [CpRe(NO)(PR3)]+.[9] However, it has already been pointed out by Gladysz et al. that substitution reactions of half-sandwich rhenium complexes  $[CpRe(NO)(PPh_3)(L^1)]^+$  proceed by an associative mechanism with a bent-nitrosyl intermediate [CpRe(N- $O(PPh_3)(L^1)(L^2)$ <sup>+</sup>. The observed retention of configuration was tentatively explained as the result of steric repulsions which cause the entering ligand  $L^2$  to attack from a direction anti to the bulky PPh3 ligand.<sup>[32]</sup> For the case presented here this explanation is not quite satisfying. Inspection of a space-filling model of the cation of  $(R_{\rm Re}, R_{\rm P})$  $S_{\text{Re}}S_{\text{P}}$ )-10 shows that for such a mechanism both possible sites of attack are similarly shielded. Furthermore, for the opposite diastereomer  $(R_{\text{Re}}, S_{\text{P}}/S_{\text{Re}}, R_{\text{P}})$ -10, where the Ph and Me groups at phosphorus have exchanged positions, the interstice between NO and phosphorus is even more protected. Thus, if the selectivity were mainly determined by steric interactions we would have to expect (i) a generally lower diastereoselectivity, and (ii) that both diastereomers of 10 would ring-open with significantly different selectivities, which is clearly not the case. We are left to conclude that the origin of the high stereoselectivity of the substitution at rhenium is still an open question.

The synthesis of the thioaldehyde complexes **12a–d** by acid-promoted condensation of the Re–SH complex **11** with aldehydes is straightforward and also more reliable than the alternative H<sup>-</sup>-abstraction from the corresponding benzyl-thiolate complexes.<sup>[33,34]</sup> In addition, it is also more convenient as it is based on a common rhenium complex as starting material. **12a–d** exist in solution as mixtures of  $\eta^1(S)$ 



Scheme 14. For the sake of clarity, only species with  $(R_{\rm Re})$ -configuration are shown.

and  $\eta^2$ (S=C) bonded isomers. This is a quite common phenomenon and has been observed not only for rhenium complexes of thioaldehydes<sup>[33,34]</sup> but also for similar complexes of aldehydes, ketones and imines.<sup>[35-37]</sup> Such a situation is detrimental with regard to the stereoselectivity of addition to the coordinated  $\pi$  ligand, as there are three competing pathways: backside attack at the  $\eta^2$ (S=C) isomer and attack on both enantiofaces of the  $\eta^1(S)$ -bonded thioaldehyde (see Scheme 11). Gladysz et al. have pointed out that both pathways may favor, if to different extents, the same diastereomer of the addition products.<sup>[35,38]</sup> With diastereoselectivities up to 89% this hope was at least partially fulfilled. From the fact that the diastereoselectivity of the addition to carbon is similar for both diastereomers of 12a we conclude that the configuration at phosphorus is only of minor importance for the outcome of the reaction.

As a guide for further development we briefly explored ways to remove the newly formed ligand from rhenium. Methylation transforms the anionic ligand into a neutral one, which, like in many other cases,<sup>[39–42]</sup> is only weakly bound. The thioacetal ligand is then given off under mild conditions while the chelate ring is closed with high stereo-selectivity. The two products are easily separated on the basis of their different solubilities (Scheme 12), allowing also the rhenium chelate to be isolated and recycled.

## **Experimental Section**

General: All experiments were carried out in Schlenk tubes under nitrogen using suitably purified solvents. IR: Bruker IFS 25. <sup>1</sup>H NMR: Bruker AMX 400, Bruker Avance 500, Jeol JNM-LA 300,  $\delta$  values relative to TMS. <sup>13</sup>C NMR: Bruker AMX 400, Bruker Avance 500, Jeol JNM-LA 300,  $\delta$  values relative to TMS, assignments were routinely checked by DEPT procedures. In some cases the <sup>13</sup>C NMR signals of quaternary carbon atoms were too weak to be detected. <sup>31</sup>P NMR: Bruker AMX 400, Bruker Avance 500, Jeol JNM-LA 300,  $\delta$  values relative to 85% H<sub>3</sub>PO<sub>4</sub>. Elemental analyses: Analytical Laboratory of the Institut für Anorganische Chemie. BF<sub>4</sub><sup>-</sup> salts occasionally give low carbon values due to trace formation of fluorocarbon compounds which escape detection. Spectroscopic and analytical data are listed as Supporting Information HPLC: Daicel Chiralcel OD-H column (4.6×250 mm), Jasco pump, gradient unit and multi-wavelength detector. X-ray structures: Bruker SMART APEX CCD. The following starting materials were obtained as described in the literature: [CpRe-(CO)(NO)(NCMe)]BF<sub>4</sub> (7),<sup>[17]</sup> NaSH,<sup>[43]</sup> PH(Me)(Ph),<sup>[44]</sup> [(S<sub>C</sub>)-4].<sup>[14]</sup> Acetylacetone and the thiols were converted into their sodium salts by adding a stoichiometric amount of sodium metal to solutions in ethanol, followed by evaporation to dryness. All other reagents were used as purchased.

**P(Me)(Ph)[8-(2-methylquinolinyl)] (3):** A solution of 2.5 M *tert*-butyllithium in hexane (8.5 mL, 13.6 mmol) was added to a solution of PH(Me)(Ph) (1.45 g, 12.4 mmol) in THF (15 mL). The resulting red solution was added at -78 °C to a solution of 2-methyl-8-chloroquinoline (2.97 g, 16.7 mmol) in THF (10 mL). After stirring for 1.5 h at -78 °C and 2 h at 20 °C water (40 mL) was added. The resulting slurry was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4×20 mL) and the combined organic phases dried with MgSO<sub>4</sub>. The solvent was removed under vacuum and the brownish-yellow residue recrystallized from methanol at -30 °C; yield 2.18 g (67%) light yellow crystals.

( $S_{P_5}S_C$ )-[Pd(Me<sub>2</sub>NC<sub>12</sub>H<sub>10</sub>)(P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N))]PF<sub>6</sub> [( $S_{P_5}S_C$ )-5]: Compound 3 (7.93 g, 30.0 mmol) was added at 20 °C to a suspension of ( $S_C$ )-4 (10.2 g, 14.9 mmol) in methanol (120 mL). After stirring for 1.5 h at this temperature, some colorless precipitate had formed which was removed by filtration through a 0.45- $\mu$  membrane filter. A solution of NH<sub>4</sub>PF<sub>6</sub> (9.80 g, 60.0 mmol) in water (20 mL) was added to the filtrate whereupon the product began to crystallize. More water (250 mL) was added with stirring, the voluminous precipitate was filtered off, washed with water, water/ methanol (1:1), and finally with diethyl ether, and dried under vacuum; yield 19.8 g (93%) colorless crystalline powder. This material was dissolved in a just sufficient amount of boiling 2-butanone and the solution allowed to slowly cool to ambient temperature. The precipitate was collected and recrystallized from 2-butanone; yield 5.7 g (54%) yellow crystals.

( $R_P$ )-P(Me)(Ph)[8-(2-methylquinolinyl)] [( $R_P$ )-3]: Ethylenediamine (1.35 g, 22.4 mmol) and diethyl ether (100 mL) were added to a solution of [( $S_P,S_C$ )-5] (3.20 g, 4.48 mmol) in dichloromethane (90 mL). The mixture was stirred for 1 h at 20 °C, the colorless precipitate filtered off, washed with diethyl ether, and dried. This material was identified spectroscopically (<sup>1</sup>H, <sup>31</sup>P NMR) as ( $S_C$ )-6,<sup>[14]</sup> yield 2.10 g (90%). The filtrate was taken to dryness and the residue taken up in diethyl ether (60 mL) and water (20 mL). The ether phase was collected, the aqueous phase extracted with diethyl ether (2 × 20 mL), and the combined organic phases dried with MgSO<sub>4</sub>. Evaporation gave a colorless solid; yield 0.95 g (83%), spectroscopically (<sup>1</sup>H, <sup>31</sup>P NMR) identical with racemic 3. <sup>1</sup>H NMR in the presence of the chiral shift reagent (–)-1-(9-anthryl)-2,2,2-trifluoroethanol gave an *ee* of 99%.

 $(S_{\rm C})$ -[(PdCl(Me<sub>2</sub>NC<sub>12</sub>H<sub>10</sub>))<sub>2</sub>] [( $S_{\rm C}$ )-4]: 2 N aqueous HCl (30 mL, 60 mmol) was added to a suspension of ( $S_{\rm C}$ )-6 (7.60 g, 14.7 mmol) in methanol (180 mL). After 10 min a yellow solid had formed which was filtered off, washed with methanol, and dried under vacuum; yield 4.87 g (97%), spectroscopically (<sup>1</sup>H NMR) identified as ( $S_{\rm C}$ )-4.<sup>[14]</sup>

[CpRe(CO)(NO){P(Me)(Ph)( $C_{10}H_8$ N)}]BF<sub>4</sub> (8): [CpRe(CO)(NO)-(NCMe)]BF<sub>4</sub> (7) (0.60 g, 1.37 mmol) and 3 (0.52 g, 1.96 mmol) were fused together for 4 h at 90 °C under vacuum. After cooling to 20 °C the mixture was taken up in THF (9 mL) and stirred until a yellow solid had formed. This was filtered off, washed with diethyl ether, and dried; yield 0.81 g (90%), yellow crystalline solid; m.p. 167 °C.

 $(R_{\text{Re}},S_{\text{P}}/S_{\text{Re}},S_{\text{P}})$ -[CpRe(CO)(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}]BF<sub>4</sub> [ $(R_{\text{Re}},S_{\text{P}}/S_{\text{Re}},S_{\text{P}})$ -8]: This compound was obtained as described above from 7 (1.90 g, 4.34 mmol) and ( $R_{\text{P}}$ )-3 (1.30 g, 4.90 mmol); yield 2.50 g (87%), spectroscopically identical with 8. <sup>1</sup>H NMR in the presence of the chiral shift reagent tris[(trifluoromethyl-hydroxymethylene)-(–)-camphorato]europium gave an *ee* of 98%.

**[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}(CH<sub>3</sub>)]** (9): NaBH<sub>4</sub> (0.14 g, 3.75 mmol) was added to a suspension of carbonyl complex **8** (0.71 g, 1.07 mmol) in THF (5 mL). The mixture was stirred for 3 h at 20 °C and the solvents evaporated to dryness. The residue was dissolved in toluene (15 mL) and filtered through a layer of celite. The filtrate was concentrated to 8 mL and stored at -30 °C whereupon brick-red crystals of ( $R_{\rm Re}R_{\rm P}/S_{\rm Re},S_{\rm P}$ )-9 formed. The supernatant was syringed off and the crystals washed with pentane and dried; yield 0.26 g (85%) red crystalline solid, 87% *de* (<sup>1</sup>H NMR).

The supernatant was concentrated to 4 mL and pentane (15 mL) added to precipitate the orange-colored ( $R_{\text{Rev}}S_{\text{P}}/S_{\text{Rev}}R_{\text{P}}$ )-9; yield 0.13 g (43%), orange crystalline solid, 72% *de* (<sup>1</sup>H NMR).



 $(R_{\text{Rev}}S_{\text{P}}/S_{\text{Rev}}S_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}(CH<sub>3</sub>)] [ $(R_{\text{Rev}}S_{\text{P}}/S_{\text{Rev}}S_{\text{P}})$ -9]: NaBH<sub>4</sub> (0.39 g, 10.3 mmol) was added at -78 °C to a suspension of  $(R_{\text{Rev}}S_{\text{P}}/S_{\text{Rev}}S_{\text{P}})$ -8 (1.95 g, 2.95 mmol) in THF (40 mL). The mixture was stirred and warmed to 20 °C over a period of 4 h. The solvent was removed under vacuum and the residue dissolved in toluene (25 mL) and filtered through a layer of celite. The filtrate was taken to dryness leaving a red solid; yield 1.60 g (96%), spectroscopically identical with 9. This material was used in the next step without further purification.

( $R_{\text{Rev}}S_{\text{P}}/S_{\text{Rev}}R_{\text{P}}$ )-[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}]BF<sub>4</sub> [( $R_{\text{Rev}}S_{\text{P}}/S_{\text{Rev}}R_{\text{P}}$ )-10]: A solution of 54% HBF<sub>4</sub> in diethyl ether (26 µL, 0.19 mmol) was added to a solution of ( $R_{\text{Rev}}S_{\text{P}}/S_{\text{Rev}}R_{\text{P}}$ )-9 (127 mg, 0.23 mmol, 72% *de*) in dichloromethane (5 mL) at -78 °C . The mixture was warmed to 20 °C and diethyl ether (15 mL) added. A precipitate formed which was collected by filtration, washed with pentane, and dried under vacuum; yield 105 mg (74%), orange crystalline solid, 97% *de* (<sup>1</sup>H NMR); m.p. 83 °C.

( $R_{\rm Re}, R_P/S_{\rm Re}, S_P$ )-[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}]BF<sub>4</sub> [( $R_{\rm Re}, R_P/S_{\rm Re}, S_P$ )-10]: A solution of 54% HBF<sub>4</sub> in diethyl ether (8 µL, 0.06 mmol) was added to a solution of ( $R_{\rm Re}, R_P/S_{\rm Re}, S_P$ )-9 (255 mg, 0.454 mmol, 87% *de*) in dichloromethane (10 mL) at -78 °C. The mixture was warmed to 20 °C and diethyl ether (20 mL) added. An orange precipitate of ( $R_{\rm Re}, S_P/S_{\rm Re}, R_P$ )-10 formed which was filtered off and discarded. The filtrate was evaporated to dryness and the residue treated with 54% HBF<sub>4</sub> (55 µL, 0.40 mmol) and worked up as described above for ( $R_{\rm Re}, S_P/S_{\rm Re}, R_P$ )-10; yield 195 mg (68%), orange crystalline solid, 94% *de* (<sup>1</sup>H NMR); m.p. 194 °C.

( $R_{\text{Rer}}S_{\text{P}}$ )-[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}]BF<sub>4</sub> [( $R_{\text{Rer}}S_{\text{P}}$ )-10]: A solution of 54% HBF<sub>4</sub> in diethyl ether (195 µL, 1.42 mmol) was added to a solution of ( $R_{\text{Rer}}S_{\text{P}}/S_{\text{Rer}}S_{\text{P}}$ )-9 (1.60 g, 2.84 mmol) in dichloromethane (25 mL) at -78 °C The mixture was warmed to 20 °C, concentrated to 12 mL, and diethyl ether (40 mL) added. A dark orange precipitate formed which was collected by filtration, washed with diethyl ether and pentane, and dried under vacuum; yield 0.77 g (82%), brownish-red crystalline powder, 71% *de* (<sup>1</sup>H NMR). The product is spectroscopically identical with ( $R_{\text{Rer}}S_{\text{P}}/S_{\text{Rer}}R_{\text{P}}$ )-10.

 $(S_{\text{Re}},S_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}]BF<sub>4</sub> [( $S_{\text{Re}},S_{\text{P}}$ )-10]: The filtrate of the previous step was evaporated to dryness, redissolved in dichloromethane, treated with HBF<sub>4</sub> (240 µL, 1.76 mmol) and worked up as described above; yield 0.76 g (81%), red crystalline powder, 92% *de* (<sup>1</sup>H NMR). The product is spectroscopically identical with ( $R_{\text{Re}},R_{\text{P}}/S_{\text{Re}},S_{\text{P}}$ )-10.

 $(R_{\text{Rer}}S_{\text{P}}/S_{\text{Rer}}R_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N){(SH)] [( $R_{\text{Rer}}S_{\text{P}}/S_{\text{Rer}}R_{\text{P}}$ )-11]: NaSH (60 mg, 1.06 mmol) was added at 0 °C to a suspension of  $(R_{\text{Rer}}S_{\text{P}}/S_{\text{Rer}}R_{\text{P}})$ -10 (0.50 g, 0.79 mmol) in THF (15 mL) and ethanol (1 mL). The mixture was warmed to 20 °C, stirred for 2 h, and the solvents evaporated to dryness. The residue was dissolved in benzene, filtered through Celite, and the filtrate evaporated to 2 mL. Addition of pentane (20 mL) induced the product to crystallize, which was filtered off, washed with pentane, and dried; yield 0.32 g (70%), brown powder, 96% *de* (<sup>1</sup>H NMR); m.p. 92 °C.

 $(R_{\text{Rer}}R_P/S_{\text{Rer}}S_P)$ -[CpRe(NO){P(Me)(Ph)(C\_{10}H\_8N)}(SH)] [( $R_{\text{Rer}}R_P/S_{\text{Rer}}S_P$ )-11]: This compound was prepared as above from  $(R_{\text{Rer}}R_P/S_{\text{Rer}}S_P)$ -10; yield 0.45 g (92%), ochre powder, 94% *de* (<sup>1</sup>H NMR); m.p. 60 °C.

 $(S_{\text{Re}}, S_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}(SH)] [( $S_{\text{Re}}, S_{\text{P}}$ )-11]: This compound was prepared as above from ( $S_{\text{Re}}, S_{\text{P}}$ )-10 (0.76 g, 1.20 mmol) and NaSH (0.14 g, 2.40 mmol); yield 0.38 g (55%), yellow powder, 98% *de* (<sup>1</sup>H NMR). The product is spectroscopically identical with ( $R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}}$ )-11.

 $(R_{\text{Re}},S_P/S_{\text{Re}},R_P)$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}(S=CHPh)]BF<sub>4</sub> [ $(R_{\text{Re}},S_P/S_{\text{Re}},R_P)$ -12a]:  $(R_{\text{Re}},S_P/S_{\text{Re}},R_P)$ -11 (1.21 g, 2.09 mmol), benzaldehyde (2.22 g, 20.9 mmol), MgSO<sub>4</sub> (0.50 g, 4.16 mmol), THF (10 mL) and 54% HBF<sub>4</sub> in diethyl ether (0.61 mL, 4.66 mmol) were combined and stirred for 10 min at 20 °C. Basic alumina (0.50 g) was added to absorb excess acid, the solids were filtered off and rinsed with acetone (2 × 5 mL) and the combined filtrate taken to dryness. The residue was recrystallized from THF (2 mL)/diethyl ether (20 mL); yield 1.48 g (91%), yellow powder, 95% *de* (<sup>1</sup>H NMR); m.p. 197 °C.

 $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}(S=CHPh)]BF<sub>4</sub> [ $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -12a]: This compound was prepared as above from  $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -11 (1.69 g, 2.91 mmol), benzaldehyde (3.10 g, 29.2 mmol), MgSO<sub>4</sub> (0.70 g, 5.82 mmol) and 54% HBF<sub>4</sub> (0.85 mL, 6.50 mmol); yield 1.81 g (82%), yellow powder, 92% *de* (<sup>1</sup>H NMR); m.p. 207 °C.

 $(S_{\text{Re}},S_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}(S=CHPh)]BF<sub>4</sub> [ $(S_{\text{Re}},S_{\text{P}})$ -12a]: This compound was prepared as above from  $(S_{\text{Re}},S_{\text{P}})$ -11 (0.38 g, 0.65 mmol), benzaldehyde (0.69 g, 6.50 mmol), MgSO<sub>4</sub> (0.15 g, 1.25 mmol) and 54% HBF<sub>4</sub> (0.19 mL, 2.40 mmol); yield 0.36 g (73%), yellow powder, 95% *de* (<sup>1</sup>H NMR). The product is spectroscopically identical with  $(R_{\text{Re}},R_{\text{P}}/S_{\text{Re}},S_{\text{P}})$ -12a.

**[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}(S=CHR)]BF<sub>4</sub> (12b-d):** Common protocol: The respective diastereomer of **11** (120 mg, 0.207 mmol), aldehyde (2.00 mmol), MgSO<sub>4</sub> (80 mg, 0.66 mmol), THF (5 mL) and 54% HBF<sub>4</sub> in diethyl ether (70  $\mu$ L, 0.51 mmol) were combined and stirred for 10 min at 20 °C. Basic alumina (100 mg) was added to absorb excess acid. The supernatant was syringed off, the solution was filtered through a nylon syringe filter (0.45  $\mu$ ) and the filtrate taken to dryness. The residue was recrystallized from THF (1 mL)/diethyl ether (10 mL).

 $(R_{\text{Re}}, S_{\text{P}}/S_{\text{Re}}, R_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C\_{10}H\_8N)}(S=CHMe)]BF<sub>4</sub> [ $(R_{\text{Re}}, S_{\text{P}}/S_{\text{Re}}, R_{\text{P}})$ -12b]: Yield 109 mg (76%), ochre powder, 95% de (<sup>1</sup>H NMR); m.p. 195 °C.

 $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}(S=CHMe)]BF<sub>4</sub> [( $R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}}$ )-12b]: Yield 112 mg (78%), yellow powder, 96% *de* (<sup>1</sup>H NMR); m.p. 185 °C.

 $(R_{\text{Re}}, S_{\text{P}}/S_{\text{Re}}, R_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}(S=CHC<sub>6</sub>H<sub>4</sub>OMe)-]BF<sub>4</sub> [( $R_{\text{Re}}, S_{\text{P}}/S_{\text{Re}}, R_{\text{P}}$ )-12c]: Yield 128 mg (79%), yellow powder, 88% *de* (<sup>1</sup>H NMR); m.p. 103 °C.

 $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}(S=CHC<sub>6</sub>H<sub>4</sub>-OMe)]BF<sub>4</sub> [( $R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}}$ )-12c]: Yield 132 mg (81%), yellow powder, 96% *de* (<sup>1</sup>H NMR); m.p. 195 °C.

 $(R_{Re},S_P/S_{Re},R_P)$ -[CpRe(NO){P(Me)(Ph)(C\_{10}H\_8N)}(S=CHC\_6F\_5)]BF\_4 [ $(R_{Re},S_P/S_{Re},R_P)$ -12d]: Yield 157 mg (86%), yellow powder, 94% *de* (<sup>1</sup>H NMR); m.p. 132 °C.

 $(R_{\text{Re}}, R_P / S_{\text{Re}}, S_P)$ -[CpRe(NO){P(Me)(Ph)(C\_{10}H\_8N)}(S=CHC\_6F\_5)]BF\_4 [ $(R_{\text{Re}}, R_P / S_{\text{Re}}, S_P)$ -12d]: Yield 163 mg (86%), yellow powder, 97% de (<sup>1</sup>H NMR); m.p. 116 °C.

**[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}{SC(H)(Ph)(X)}] (13a–e):** Common protocol: The respective sodium salt NaX was added at –78 °C to a suspension of ( $R_{\text{Re}},S_{\text{P}}/S_{\text{Re}},R_{\text{P}}$ )-12a or ( $R_{\text{Re}},R_{\text{P}}/S_{\text{Re}},S_{\text{P}}$ )-12a (150 mg, 0.20 mmol) in toluene (2 mL). The mixture was stirred for 12 h and allowed to slowly reach room temperature. A solid was removed by syringe filtration (0.2 µ), the filter was rinsed with toluene (3 mL) and the clear solution concentrated under vacuum to 1 mL. Pentane (10 mL) was slowly added at –78 °C which caused the product to crystallize. The supernatant was syringed off and the residue washed with pentane (3 × 3 mL) and dried.  $(R_{\text{Re}}, S_{\text{P}}/S_{\text{Re}}, R_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}{SC(H)(Ph)(acac)}] [( $R_{\text{Re}}, S_{\text{P}}/S_{\text{Re}}, R_{\text{P}}$ )-13a]: Yield 118 mg (77%), yellow powder, 70% *de* (<sup>1</sup>H NMR); m.p. 167 °C.  $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}{SC(H)(Ph)(acac)}] [( $R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}}$ )-13a]: Yield 90 mg (59%), yellow powder, 53% *de* (<sup>1</sup>H NMR); m.p. 165 °C.

Table 1. Details of the	e structure determinations	of compounds 5,	8, 9	<b>)</b> , <b>10</b> , <b>1</b> 1	, 12c and	13d.
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	5.0.5acetone	8	9	10·CHCl <sub>3</sub>
Empirical formula	C325H35F6N2O05P2Pd	C <sub>23</sub> H <sub>21</sub> BF <sub>4</sub> N <sub>2</sub> O <sub>2</sub> PRe	C <sub>23</sub> H <sub>24</sub> N <sub>2</sub> OPRe	C <sub>23</sub> H <sub>22</sub> BCl <sub>3</sub> F <sub>4</sub> N <sub>2</sub> OPRe
Formula mass	743.97	661.40	561.61	752.76
Crystal color/habit	yellow prism	yellow plate	red block	orange block
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 1	$P2_1/c$	<i>P</i> 1	C2/c
a [A]	11.6022(4)	8.891(2)	9.277(3)	23.0316(16)
b [A]	12.0416(5)	24.452(5)	10.025(3)	14.2414(10)
	13.3622(5)	10.651(2)	13.613(4)	18.9208(13)
$a \begin{bmatrix} c \end{bmatrix}$	83.283(2)	90	/0.323(6)	90
p [ ]	70.367(2)	94.910(4)	80.924(6)	120.395(1)
/ [ ] V [Å <sup>3</sup> ]	1607 77(11)	2307 1(9)	1176 6(6)	5342.2(6)
$\Theta$ [°]	1.67-26.03	2.09-26.11	2.18-26.14	1.76-26.09
h	-14 to 14	-10 to 10	-11 to 11	-28 to 28
k	-14 to 14	-30 to 30	-12 to 12	-17 to 17
l	-15 to 16	-13 to 13	-16 to 16	-23 to 23
Ζ	2	4	2	8
$\mu$ (Mo- $K_{\alpha}$ ) [mm <sup>-1</sup> ]	0.739	5.393	5.246	4.958
Crystal size [mm]	$0.54 \times 0.36 \times 0.19$	$0.15 \times 0.10 \times 0.03$	$0.23 \times 0.19 \times 0.16$	$0.24 \times 0.11 \times 0.10$
$D_{\text{calcd.}} [\text{g cm}^{-1}]$	1.537	1.904	1.585	1.872
T [K]	100(2)	173(2)	173(2)	173(2)
Reflections collected	43516	26041	16410	3/589
Independent reflections	11804	456/	4666	5292
Parameter $P \left[ I > 2 \sigma(I) \right]$	/95 0.0218	329	220	527 0.0255
$R_1 [I > 20(I)]$ $R_2 (overall)$	0.0218	0.0282	0.0373	0.0233
$R_2 \left[ I > 2\sigma(I) \right]$	0.0478	0.0661	0.0894	0.0582
$R_2$ (overall)	0.0482	0.0676	0.0902	0.0599
Absolute structure parameter	-0.012(9)			
Diff. peak/hole [e Å <sup>-3</sup> ]	0.318/-0.514	1.811/-0.459	4.023/-1.677	1.331/-0.972
CCDC	749532	749533	749534	749535
	11.0.5C <sub>6</sub> H <sub>6</sub>	12c•0.50Et <sub>2</sub>	13d	
Empirical formula	11.0.5C <sub>6</sub> H <sub>6</sub> C <sub>25</sub> H <sub>25</sub> N <sub>2</sub> OPReS	<b>12c</b> •0.5OEt <sub>2</sub> C <sub>32</sub> H <sub>34</sub> BF <sub>4</sub> N <sub>2</sub> O <sub>2.5</sub> PReS	<b>13d</b> C <sub>33</sub> H <sub>36</sub> N <sub>2</sub> OPReS <sub>2</sub>	
Empirical formula Formula mass	11.0.5C <sub>6</sub> H <sub>6</sub> C <sub>25</sub> H <sub>25</sub> N <sub>2</sub> OPReS 618.70	<b>12c</b> ·0.50Et <sub>2</sub> C <sub>32</sub> H <sub>34</sub> BF <sub>4</sub> N <sub>2</sub> O <sub>2.5</sub> PReS 822.69	<b>13d</b> C <sub>33</sub> H <sub>36</sub> N <sub>2</sub> OPReS <sub>2</sub> 757.93	
Empirical formula Formula mass Crystal color/habit	$11 \cdot 0.5C_6H_6$ $C_{25}H_{25}N_2OPReS$ 618.70 orange plate	<b>12c</b> ·0.5OEt <sub>2</sub> C <sub>32</sub> H <sub>34</sub> BF <sub>4</sub> N <sub>2</sub> O <sub>2.5</sub> PReS 822.69 yellow block	<b>13d</b> C <sub>33</sub> H <sub>36</sub> N <sub>2</sub> OPReS <sub>2</sub> 757.93 brown plate	
Empirical formula Formula mass Crystal color/habit Crystal system	$11.0.5C_6H_6$ $C_{25}H_{25}N_2OPReS$ 618.70 orange plate triclinic $P\overline{P}$	12c·0.5OEt <sub>2</sub> C <sub>32</sub> H <sub>34</sub> BF <sub>4</sub> N <sub>2</sub> O <sub>2.5</sub> PReS 822.69 yellow block monoclinic	<b>13d</b> C <sub>33</sub> H <sub>36</sub> N <sub>2</sub> OPReS <sub>2</sub> 757.93 brown plate triclinic	
Empirical formula Formula mass Crystal color/habit Crystal system Space group	$11.0.5C_6H_6$ $C_{25}H_{25}N_2OPReS$ 618.70 orange plate triclinic $P\overline{I}$ 0.280(2)	<b>12c</b> $0.5OEt_2$ C <sub>32</sub> H <sub>34</sub> BF <sub>4</sub> N <sub>2</sub> O <sub>2.5</sub> PReS 822.69 yellow block monoclinic $P2_1/n$ 11 0107(2)	<b>13d</b> $C_{33}H_{36}N_2OPReS_2$ 757.93 brown plate triclinic $P\overline{1}$ 0.5895(15)	
Empirical formula Formula mass Crystal color/habit Crystal system Space group <i>a</i> [Å] b [Å]	$11.0.5C_6H_6$ $C_{25}H_{25}N_2OPReS$ 618.70 orange plate triclinic $P\overline{1}$ 9.280(3) 10.248(4)	<b>12c</b> $0.5OEt_2$ C <sub>32</sub> H <sub>34</sub> BF <sub>4</sub> N <sub>2</sub> O <sub>2.5</sub> PReS 822.69 yellow block monoclinic <i>P</i> 2 <sub>1</sub> / <i>n</i> 11.9197(3) 14.3281(3)	13d $C_{33}H_{36}N_2OPReS_2$ 757.93 brown plate triclinic $P\overline{1}$ 9.5885(15) 12.839(2)	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å]	$\frac{11 \cdot 0.5 C_6 H_6}{C_{25} H_{25} N_2 OPReS}$ 618.70 orange plate triclinic <i>P</i> I 9.280(3) 10.248(4) 13.668(5)	<b>12c</b> $0.5OEt_2$ C <sub>32</sub> H <sub>34</sub> BF <sub>4</sub> N <sub>2</sub> O <sub>2.5</sub> PReS 822.69 yellow block monoclinic <i>P</i> 2 <sub>1</sub> / <i>n</i> 11.9197(3) 14.3281(3) 19.008(4)	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] b [Å] c [Å] a [°]	$\begin{array}{c} 11 \cdot 0.5 C_{6} H_{6} \\ \hline C_{25} H_{25} N_{2} OPReS \\ 618.70 \\ orange plate \\ triclinic \\ P\overline{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \end{array}$	$\begin{array}{c} \textbf{12c} 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] b [Å] c [Å] a [°] b [°]	$\begin{array}{c} 11\text{-}0.5\text{C}_{6}\text{H}_{6} \\ \hline C_{25}\text{H}_{25}\text{N}_{2}\text{OPReS} \\ 618.70 \\ \text{orange plate} \\ \text{triclinic} \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \end{array}$	$\begin{array}{c} \textbf{12c} 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)	
Empirical formula Formula mass Crystal color/habit Crystal system Space group $a [\AA]$ $b [\AA]$ $c [\AA]$ $a [^{\Lambda}]$ $c [\AA]$ $a [^{\Omega}]$ $\beta [^{\Omega}]$ $\gamma [^{\Omega}]$	$\begin{array}{c} 11\text{-}0.5\text{C}_{6}\text{H}_{6} \\ \hline \text{C}_{25}\text{H}_{25}\text{N}_{2}\text{OPReS} \\ 618.70 \\ \text{orange plate} \\ \text{triclinic} \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \end{array}$	$\begin{array}{c} \textbf{12c} 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93           brown plate           triclinic $P\overline{1}$ 9.5885(15)           12.839(2)           14.116(2)           74.461(2)           72.009(2)           87.221(2)	
Empirical formula Formula mass Crystal color/habit Crystal system Space group $a [\AA]$ $b [\AA]$ $c [\AA]$ $a [^{A}]$ $c [\AA]$ $a [^{O}]$ $\beta [^{O}]$ $\gamma [^{O}]$ $V [\AA^{3}]$	$\begin{array}{c} 11\text{-}0.5\text{C}_{6}\text{H}_{6} \\ \hline \\ \text{C}_{25}\text{H}_{25}\text{N}_{2}\text{OPReS} \\ 618.70 \\ \text{orange plate} \\ \text{triclinic} \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \end{array}$	$\begin{array}{c} \textbf{12c} 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93           brown plate           triclinic $P\overline{1}$ 9.5885(15)           12.839(2)           14.116(2)           74.461(2)           72.009(2)           87.221(2)           1591.4(4)	
Empirical formula Formula mass Crystal color/habit Crystal system Space group $a [\AA]$ $b [\AA]$ $c [\AA]$ $a [^{A}]$ $a [^{O}]$ $\beta [^{O}]$ $\gamma [^{O}]$ $V [\AA^{3}]$ $\Theta [^{O}]$	$\begin{array}{c} 11\text{-}0.5\text{C}_6\text{H}_6 \\ \\ \text{C}_{25}\text{H}_{25}\text{N}_2\text{OPReS} \\ 618.70 \\ \text{orange plate} \\ \text{triclinic} \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \end{array}$	$\begin{array}{c} \textbf{12c} 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93           brown plate           triclinic $P\overline{1}$ 9.5885(15)           12.839(2)           14.116(2)           74.461(2)           72.009(2)           87.221(2)           1591.4(4)           1.95–26.02	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h	$\begin{array}{c} 11 \text{-} 0.5 \text{C}_6 \text{H}_6 \\ \hline \text{C}_{25} \text{H}_{25} \text{N}_2 \text{OPReS} \\ 618.70 \\ \text{orange plate} \\ \text{triclinic} \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \text{ to } 12 \\ 12 \\ 12 \\ 12 \\ 12 \\ 12 \\ 12 \\ 12$	$\begin{array}{c} \textbf{12c} 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h	$\begin{array}{c} 11 \cdot 0.5 C_{6} H_{6} \\ \hline C_{25} H_{25} N_{2} OPReS \\ 618.70 \\ orange plate \\ triclinic \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \ to \ 12 \\ -13 \ to \ 13 \\ 10.248(4) \\ 13.668(5) \\ 1195.2(7) \\ 1105.2(7) \\ 1105.2(7) \\ 1105.2(7) \\ 1105.2(7) \\ 1105.2(7) \\ 1105.2(7) \\ 1105.2(7) \\ 1105.2(7) \\ 1105.2(7) \\ 1105.2(7) \\ 1105.2(7) \\ 1105.2(7) \\ 1105.2(7) \\ 11$	$\begin{array}{c} \textbf{12c} 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ -17 \text{ to } 17 \\ 02 \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h	$\begin{array}{c} 11 \cdot 0.5 C_6 H_6 \\ \hline C_{25} H_{25} N_2 OPReS \\ 618.70 \\ orange plate \\ triclinic \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \text{ to } 12 \\ -13 \text{ to } 13 \\ -18 \text{ to } 18 \\ 2 \end{array}$	$\begin{array}{c} \textbf{12c} \text{-}0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ -17 \text{ to } 17 \\ -23 \text{ to } 23 \\ 4 \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15         -17 to 17	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h k l Z v(Ma K) [mm-1]	$\begin{array}{c} 11\text{-}0.5\text{C}_6\text{H}_6\\ \hline \\ \text{C}_{25}\text{H}_{25}\text{N}_2\text{OPReS}\\ 618.70\\ \text{orange plate}\\ \text{triclinic}\\ P\bar{1}\\ 9.280(3)\\ 10.248(4)\\ 13.668(5)\\ 68.784(6)\\ 86.103(7)\\ 80.555(6)\\ 1195.2(7)\\ 2.16\text{-}28.36\\ -12\ \text{to}\ 12\\ -13\ \text{to}\ 13\\ -18\ \text{to}\ 18\\ 2\\ 5.257\\ \end{array}$	$\begin{array}{c} \textbf{12c} \cdot 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ -17 \text{ to } 17 \\ -23 \text{ to } 23 \\ 4 \\ 2.080 \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15         -17 to 17         2         4.028	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h k l Z $\mu$ (Mo- $K_a$ ) [mm <sup>-1</sup> ] Crystal size [mm]	$\begin{array}{c} 11 \cdot 0.5 C_6 H_6 \\ \hline C_{25} H_{25} N_2 OPReS \\ 618.70 \\ orange plate \\ triclinic \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \text{ to } 12 \\ -13 \text{ to } 13 \\ -18 \text{ to } 18 \\ 2 \\ 5.257 \\ 0.23 \times 0.20 \times 0.08 \end{array}$	12c $\cdot 0.5OEt_2$ $C_{32}H_{34}BF_4N_2O_{2.5}PReS$ 822.69         yellow block         monoclinic $P2_1/n$ 11.9197(3)         14.3281(3)         19.0098(4)         90         100.465(1)         90         3192.62(12)         1.79–26.08         -14 to 14         -17 to 17         -23 to 23         4         3.980         0.39 × 0.17 × 0.16	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15         -17 to 17         2         4.028         0.31 × 0.24 × 0.16	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h k l Z $\mu$ (Mo- $K_{\alpha}$ ) [mm <sup>-1</sup> ] Crystal size [mm] $D \rightarrow [gcm^{-1}]$	$\begin{array}{c} 11 \cdot 0.5 C_6 H_6 \\ \hline C_{25} H_{25} N_2 OPReS \\ 618.70 \\ orange plate \\ triclinic \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \text{ to } 12 \\ -13 \text{ to } 13 \\ -18 \text{ to } 18 \\ 2 \\ 5.257 \\ 0.23 \times 0.20 \times 0.08 \\ 1.719 \end{array}$	$\begin{array}{c} \textbf{12c} 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ -17 \text{ to } 17 \\ -23 \text{ to } 23 \\ 4 \\ 3.980 \\ 0.39 \times 0.17 \times 0.16 \\ 1.712 \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15         -17 to 17         2         4.028         0.31 × 0.24 × 0.16         1.582	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h k l Z $\mu$ (Mo- $K_{\alpha}$ ) [mm <sup>-1</sup> ] Crystal size [mm] $D_{calcd.} [gcm^{-1}]$	$\begin{array}{c} 11 \cdot 0.5 C_6 H_6 \\ \hline C_{25} H_{25} N_2 OPReS \\ 618.70 \\ orange plate \\ triclinic \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \ to \ 12 \\ -13 \ to \ 13 \\ -18 \ to \ 18 \\ 2 \\ 5.257 \\ 0.23 \times 0.20 \times 0.08 \\ 1.719 \\ 173(2) \end{array}$	$\begin{array}{c} \textbf{12c} \cdot 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ -17 \text{ to } 17 \\ -23 \text{ to } 23 \\ 4 \\ 3.980 \\ 0.39 \times 0.17 \times 0.16 \\ 1.712 \\ 173(2) \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15         -17 to 17         2         4.028         0.31 × 0.24 × 0.16         1.582         173(2)	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h k l Z $\mu$ (Mo- $K_{\alpha}$ ) [mm <sup>-1</sup> ] Crystal size [mm] $D_{calcd.}$ [gcm <sup>-1</sup> ] T [K] Reflections collected	$\begin{array}{c} 11\text{-}0.5\text{C}_6\text{H}_6 \\ \hline \\ \text{C}_{25}\text{H}_{25}\text{N}_2\text{OPReS} \\ 618.70 \\ \text{orange plate} \\ \text{triclinic} \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \text{ to } 12 \\ -13 \text{ to } 13 \\ -18 \text{ to } 18 \\ 2 \\ 5.257 \\ 0.23 \times 0.20 \times 0.08 \\ 1.719 \\ 173(2) \\ 32134 \end{array}$	$\begin{array}{c} \textbf{12c} \text{-}0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ -17 \text{ to } 17 \\ -23 \text{ to } 23 \\ 4 \\ 3.980 \\ 0.39 \times 0.17 \times 0.16 \\ 1.712 \\ 173(2) \\ 50639 \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15         -17 to 17         2         4.028         0.31 × 0.24 × 0.16         1.582         173(2)         32718	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h k l Z $\mu$ (Mo- $K_{\alpha}$ ) [mm <sup>-1</sup> ] Crystal size [mm] $D_{calcd.}$ [gcm <sup>-1</sup> ] T [K] Reflections collected Independent reflections	$\begin{array}{c} 11\text{-}0.5\text{C}_6\text{H}_6 \\ \hline \\ \text{C}_{25}\text{H}_{25}\text{N}_2\text{OPReS} \\ 618.70 \\ \text{orange plate} \\ \text{triclinic} \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \text{ to } 12 \\ -13 \text{ to } 13 \\ -18 \text{ to } 18 \\ 2 \\ 5.257 \\ 0.23 \times 0.20 \times 0.08 \\ 1.719 \\ 173(2) \\ 32134 \\ 5946 \end{array}$	$\begin{array}{c} \textbf{12c} \text{-}0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ -17 \text{ to } 17 \\ -23 \text{ to } 23 \\ 4 \\ 3.980 \\ 0.39 \times 0.17 \times 0.16 \\ 1.712 \\ 173(2) \\ 50639 \\ 6283 \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15         -17 to 17         2         4.028         0.31 × 0.24 × 0.16         1.582         173(2)         32718         6264	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h k l Z $\mu$ (Mo- $K_{\alpha}$ ) [mm <sup>-1</sup> ] Crystal size [mm] $D_{calcd.}$ [gcm <sup>-1</sup> ] T [K] Reflections collected Independent reflections Parameter	$\begin{array}{c} 11 \text{-}0.5\text{C}_6\text{H}_6 \\ \hline \\ \text{C}_{25}\text{H}_{25}\text{N}_2\text{OPReS} \\ 618.70 \\ \text{orange plate} \\ \text{triclinic} \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \text{ to } 12 \\ -13 \text{ to } 13 \\ -18 \text{ to } 18 \\ 2 \\ 5.257 \\ 0.23 \times 0.20 \times 0.08 \\ 1.719 \\ 173(2) \\ 32134 \\ 5946 \\ 246 \end{array}$	$\begin{array}{c} \textbf{12c} \text{-}0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ -17 \text{ to } 17 \\ -23 \text{ to } 23 \\ 4 \\ 3.980 \\ 0.39 \times 0.17 \times 0.16 \\ 1.712 \\ 173(2) \\ 50639 \\ 6283 \\ 378 \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15         -17 to 17         2         4.028         0.31 × 0.24 × 0.16         1.582         173(2)         327118         6264         354	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h k l Z $\mu$ (Mo- $K_{\alpha}$ ) [mm <sup>-1</sup> ] Crystal size [mm] $D_{calcd.}$ [gcm <sup>-1</sup> ] T [K] Reflections collected Independent reflections Parameter $R_1 [I > 2\sigma(I)]$	$\begin{array}{c} 11 \text{-} 0.5 \text{C}_6 \text{H}_6 \\ \hline \text{C}_{25} \text{H}_{25} \text{N}_2 \text{OPReS} \\ 618.70 \\ \text{orange plate} \\ \text{triclinic} \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \text{ to } 12 \\ -13 \text{ to } 13 \\ -18 \text{ to } 18 \\ 2 \\ 5.257 \\ 0.23 \times 0.20 \times 0.08 \\ 1.719 \\ 173(2) \\ 32134 \\ 5946 \\ 246 \\ 0.0430 \\ \end{array}$	$\begin{array}{c} \textbf{12c} 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ -17 \text{ to } 17 \\ -23 \text{ to } 23 \\ 4 \\ 3.980 \\ 0.39 \times 0.17 \times 0.16 \\ 1.712 \\ 173(2) \\ 50639 \\ 6283 \\ 378 \\ 0.0397 \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15         -17 to 17         2         4.028         0.31 × 0.24 × 0.16         1.582         173(2)         327118         6264         354         0.0249	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h k l Z $\mu$ (Mo- $K_a$ ) [mm <sup>-1</sup> ] Crystal size [mm] $D_{calcd.}$ [g cm <sup>-1</sup> ] T [K] Reflections collected Independent reflections Parameter $R_1 [I > 2\sigma(I)]$ $R_1$ (overall)	$\begin{array}{c} 11\text{-}0.5\text{C}_6\text{H}_6 \\ \hline \\ \text{C}_{25}\text{H}_{25}\text{N}_2\text{OPReS} \\ 618.70 \\ \text{orange plate} \\ \text{triclinic} \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \text{ to } 12 \\ -13 \text{ to } 13 \\ -18 \text{ to } 18 \\ 2 \\ 5.257 \\ 0.23 \times 0.20 \times 0.08 \\ 1.719 \\ 173(2) \\ 32134 \\ 5946 \\ 246 \\ 0.0430 \\ 0.0463 \\ \end{array}$	$\begin{array}{c} \textbf{12c} 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ -17 \text{ to } 17 \\ -23 \text{ to } 23 \\ 4 \\ 3.980 \\ 0.39 \times 0.17 \times 0.16 \\ 1.712 \\ 173(2) \\ 50639 \\ 6283 \\ 378 \\ 0.0397 \\ 0.0417 \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15         -17 to 17         2         4.028         0.31 × 0.24 × 0.16         1.582         173(2)         327118         6264         354         0.0249         0.0267	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h k l Z $\mu$ (Mo- $K_{\alpha}$ ) [mm <sup>-1</sup> ] Crystal size [mm] $D_{calcd.}$ [gcm <sup>-1</sup> ] T [K] Reflections collected Independent reflections Parameter $R_1 [I > 2\sigma(I)]$ $R_1$ (overall) $R_2 [I > 2\sigma(I)]$	$\begin{array}{c} 11 \text{-}0.5\text{C}_6\text{H}_6 \\ \hline \\ \text{C}_{25}\text{H}_{25}\text{N}_2\text{OPReS} \\ 618.70 \\ \text{orange plate} \\ \text{triclinic} \\ P\bar{1} \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \text{ to } 12 \\ -13 \text{ to } 13 \\ -18 \text{ to } 18 \\ 2 \\ 5.257 \\ 0.23 \times 0.20 \times 0.08 \\ 1.719 \\ 173(2) \\ 32134 \\ 5946 \\ 246 \\ 0.0430 \\ 0.0463 \\ 0.1084 \\ \end{array}$	$\begin{array}{c} \textbf{12c} 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ -17 \text{ to } 17 \\ -23 \text{ to } 23 \\ 4 \\ 3.980 \\ 0.39 \times 0.17 \times 0.16 \\ 1.712 \\ 173(2) \\ 50639 \\ 6283 \\ 378 \\ 0.0397 \\ 0.0417 \\ 0.1083 \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15         -17 to 17         2         4.028         0.31 × 0.24 × 0.16         1.582         173(2)         32718         6264         354         0.0249         0.0267         0.0637	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ $\Theta [°]$ h k l Z $\mu$ (Mo- $K_a$ ) [mm <sup>-1</sup> ] Crystal size [mm] $D_{calcd.}$ [g cm <sup>-1</sup> ] T [K] Reflections collected Independent reflections Parameter $R_1 [I > 2\sigma(I)]$ $R_2$ (overall) $R_2$ (overall)	$\begin{array}{c} 11\text{-}0.5\text{C}_6\text{H}_6 \\ \hline C_{25}\text{H}_{25}\text{N}_2\text{OPReS} \\ 618.70 \\ \text{orange plate} \\ \text{triclinic} \\ PI \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \text{ to } 12 \\ -13 \text{ to } 13 \\ -18 \text{ to } 18 \\ 2 \\ 5.257 \\ 0.23 \times 0.20 \times 0.08 \\ 1.719 \\ 173(2) \\ 32134 \\ 5946 \\ 246 \\ 0.0430 \\ 0.0463 \\ 0.1084 \\ 0.1106 \\ \end{array}$	$\begin{array}{c} \textbf{12c} 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ -17 \text{ to } 17 \\ -23 \text{ to } 23 \\ 4 \\ 3.980 \\ 0.39 \times 0.17 \times 0.16 \\ 1.712 \\ 173(2) \\ 50639 \\ 6283 \\ 378 \\ 0.0397 \\ 0.0417 \\ 0.1083 \\ 0.1099 \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93           brown plate           triclinic $P\overline{1}$ 9.5885(15)           12.839(2)           14.116(2)           74.461(2)           72.009(2)           87.221(2)           1591.4(4)           1.95–26.02           -11 to 11           -15 to 15           -17 to 17           2           4.028           0.31 × 0.24 × 0.16           1.582           173(2)           327118           6264           354           0.0249           0.0267           0.0637           0.0647	
Empirical formula Formula mass Crystal color/habit Crystal system Space group $a$ [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] $\Theta$ [°] h k l Z $\mu$ (Mo- $K_{\alpha}$ ) [mm <sup>-1</sup> ] Crystal size [mm] $D_{calcd.}$ [gcm <sup>-1</sup> ] T [K] Reflections collected Independent reflections Parameter $R_1$ [ $I \ge 2\sigma(I)$ ] $R_1$ (overall) $R_2$ (overall) Absolute structure parameter	$\begin{array}{c} 11\text{-}0.5\text{C}_6\text{H}_6 \\ \text{C}_{25}\text{H}_{25}\text{N}_2\text{OPReS} \\ 618.70 \\ \text{orange plate} \\ \text{triclinic} \\ PI \\ 9.280(3) \\ 10.248(4) \\ 13.668(5) \\ 68.784(6) \\ 86.103(7) \\ 80.555(6) \\ 1195.2(7) \\ 2.16-28.36 \\ -12 \text{ to } 12 \\ -13 \text{ to } 13 \\ -18 \text{ to } 18 \\ 2 \\ 5.257 \\ 0.23 \times 0.20 \times 0.08 \\ 1.719 \\ 173(2) \\ 32134 \\ 5946 \\ 246 \\ 0.0430 \\ 0.0463 \\ 0.1084 \\ 0.1106 \\ 2.7024 \times 170 \end{array}$	12c $\cdot 0.5OEt_2$ $C_{32}H_{34}BF_4N_2O_{2.5}PReS$ 822.69         yellow block         monoclinic $P2_1/n$ 11.9197(3)         14.3281(3)         19.0098(4)         90         100.465(1)         90         3192.62(12)         1.79–26.08         -14 to 14         -17 to 17         -23 to 23         4         3.980         0.39 × 0.17 × 0.16         1.712         173(2)         50639         6283         378         0.0397         0.0417         0.1083         0.1099	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15         -17 to 17         2         4.028         0.31 × 0.24 × 0.16         1.582         173(2)         327118         6264         354         0.0249         0.0267         0.0637         0.0647	
Empirical formula Formula mass Crystal color/habit Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] $\Theta$ [°] h k l Z $\mu$ (Mo- $K_{\alpha}$ ) [mm <sup>-1</sup> ] Crystal size [mm] $D_{calcd.}$ [gcm <sup>-1</sup> ] T [K] Reflections collected Independent reflections Parameter $R_1$ [ $I > 2\sigma(I)$ ] $R_1$ (overall) $R_2$ ( $I > 2\sigma(I)$ ] $R_2$ (overall) Absolute structure parameter Diff. peak/hole [e Å <sup>-3</sup> ] CCDC	$11.0.5C_6H_6$ $C_{25}H_{25}N_2OPReS$ $618.70$ orange plate         triclinic $PI$ $9.280(3)$ $10.248(4)$ $13.668(5)$ $68.784(6)$ $86.103(7)$ $80.555(6)$ $1195.2(7)$ $2.16-28.36$ $-12$ to $12$ $-13$ to $13$ $-18$ to $18$ $2$ $5.257$ $0.23 \times 0.20 \times 0.08$ $1.719$ $173(2)$ $32134$ $5946$ $246$ $0.0430$ $0.0463$ $0.1084$ $0.1106$	$\begin{array}{c} \textbf{12c} 0.5\text{OEt}_2 \\ \hline C_{32}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_{2.5}\text{PReS} \\ 822.69 \\ \text{yellow block} \\ \text{monoclinic} \\ P2_1/n \\ 11.9197(3) \\ 14.3281(3) \\ 19.0098(4) \\ 90 \\ 100.465(1) \\ 90 \\ 100.465(1) \\ 90 \\ 3192.62(12) \\ 1.79-26.08 \\ -14 \text{ to } 14 \\ -17 \text{ to } 17 \\ -23 \text{ to } 23 \\ 4 \\ 3.980 \\ 0.39 \times 0.17 \times 0.16 \\ 1.712 \\ 173(2) \\ 50639 \\ 6283 \\ 378 \\ 0.0397 \\ 0.0417 \\ 0.1083 \\ 0.1099 \\ \hline 3.757/-2.203 \\ 749537 \\ \end{array}$	13d $C_{33}H_{36}N_2OPReS_2$ 757.93         brown plate         triclinic $P\overline{1}$ 9.5885(15)         12.839(2)         14.116(2)         74.461(2)         72.009(2)         87.221(2)         1591.4(4)         1.95–26.02         -11 to 11         -15 to 15         -17 to 17         2         4.028         0.31 × 0.24 × 0.16         1.582         173(2)         327118         6264         354         0.0249         0.0267         0.0637         0.0647         1.786/-1.029	

 $(R_{Re}, S_P/S_{Re}, R_P)$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}{SC(H)(Ph)-(SCH<sub>2</sub>Ph)}] [( $R_{Re}, S_P/S_{Re}, R_P$ )-13b]: Yield 115 mg (73%), ochre powder, 65% *de* (<sup>1</sup>H NMR); m.p. 122 °C.

 $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}{SC(H)(Ph)-(SCH<sub>2</sub>Ph)}] [( $R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}}$ )-13b]: Yield 123 mg (78%), ochre powder, 89% *de* (<sup>1</sup>H NMR); m.p. 121 °C.

 $(S_{\text{Re}}, S_{\text{P}}, S_{\text{C}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}{SC(H)(Ph)(SCH<sub>2</sub>Ph)}] [( $S_{\text{Re}}, S_{\text{P}}, S_{\text{C}}$ )-13b]: Yield 103 mg (65%), yellow powder, 70% *de* (<sup>1</sup>H NMR). The product is spectroscopically (<sup>1</sup>H, <sup>31</sup>P NMR) identical with ( $R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}}$ )-13b.

 $(R_{Re},S_P/S_{Re},R_P)$ -[CpRe(NO){P(Me)(Ph)(C\_{10}H\_8N)}{SC(H)(Ph)(SEt)}] [ $(R_{Re},S_P/S_{Re},R_P)$ -13c]: Yield 95 mg (65%), ochre powder, 60% *de* (<sup>1</sup>H NMR); m.p. 166 °C.

 $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}{SC(H)(Ph)(SEt)}] [ $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -13c]: Yield 90 mg (62%), ochre powder, 79% de (<sup>1</sup>H NMR); m.p. 40 °C.

 $(R_{\text{Re}}, S_{\text{P}}/S_{\text{Re}}, R_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}{SC(H)(Ph)(StBu)}] [( $R_{\text{Re}}, S_{\text{P}}/S_{\text{Re}}, R_{\text{P}}$ )-13d]: Yield 108 mg (71%), ochre powder, 42% *de* (<sup>1</sup>H NMR); m.p. 52 °C.

 $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}{SC(H)(Ph)(SrBu)}] [ $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -13d]: Yield 114 mg (75%), ochre powder, 46% *de* (<sup>1</sup>H NMR); m.p. 87 °C.

 $(R_{Re},S_P/S_{Re},R_P)$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}{SC(H)(Ph)(CN)}] [( $R_{Re},S_P/S_{Re},R_P$ )-13e]: Yield 137 mg (94%), yellow crystalline solid, 83% *de* (<sup>1</sup>H NMR); m.p. 199 °C.

 $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -[CpRe(NO){P(Me)(Ph)(C<sub>10</sub>H<sub>8</sub>N)}{SC(H)(Ph)(CN)}] [ $(R_{\text{Re}}, R_{\text{P}}/S_{\text{Re}}, S_{\text{P}})$ -13e]: Yield 102 mg (70%), ochre crystalline solid, 79% de (<sup>1</sup>H NMR); m.p. 49 °C.

(*S*)-PhCH<sub>2</sub>SC(H)(Ph)(SMe) [(*S*)-14]: Methyl iodide (16  $\mu$ L, 0.26 mmol) was added at -40 °C to a solution of ( $S_{Res}S_{B}S_{C}$ )-13b (200 mg, 0.25 mmol) in acetonitrile (12 mL). The mixture was warmed to room temperature overnight. The solution was concentrated to 2 mL and extracted with pentane (4 × 10 mL). The acetonitrile fraction was evaporated to dryness, the residue recrystallized from dichloromethane (2 mL)/diethyl ether (5 mL), washed with diethyl ether, and dried; yield 120 mg (65%), orange crystalline solid, identified by NMR as ( $S_{Res}S_{P}$ )-10a, the iodide analog of ( $S_{Res}S_{P}$ )-10, 69% *de*. The combined pentane fractions were evaporated to dryness and the residue chromatographed over silica with hexane/ethyl acetate, 20:1 as eluent; yield 24 mg (37%), colorless oil, spectroscopically identical with an authentic racemic sample.<sup>[45]</sup> HPLC over a chiral column (Daicel Chiralcel OD-H) with hexane/2-propanol, 98:2 as eluent gave an *ee* of 52%.

**X-ray Structure Determinations:** Single crystals were bonded to a glass fiber with frozen perfluorinated polyether oil in each case. A Bruker Smart Apex CCD instrument was used for data collection (graphite monochromator, Mo- $K_{\alpha}$  radiation,  $\lambda = 0.71073$  Å). The structures were solved using Patterson methods and refined with full-matrix least-squares against  $F^2$  (SHELXS-97).<sup>[46]</sup> Hydrogen atoms were included in their calculated positions and refined using a riding model. The details of the measurement are summarized in Table 1. CCDC numbers given in Table 1 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

**Supporting Information** (see also footnote on the first page of this article): Spectroscopic and analytical data of the new compounds.



- [3] S. G. Davies, Aldrichimica Acta 1990, 23, 31-37.
- [4] J. A. Gladysz, B. J. Boone, Angew. Chem. 1997, 109, 566–602; Angew. Chem. Int. Ed. Engl. 1997, 36, 550–583.
- [5] W. S. Knowles, Angew. Chem. 2002, 114, 2096–2107; Angew. Chem. Int. Ed. 2002, 41, 1998–2007, and references therein.
- [6] R. Noyori, Angew. Chem. 2002, 114, 2108–2123; Angew. Chem. Int. Ed. 2002, 41, 2008–2022, and references therein.
- [7] K. B. Sharpless, Angew. Chem. 2002, 114, 2126–2135; Angew. Chem. Int. Ed. 2002, 41, 2024–2032, and references therein.
- [8] H. Brunner, T. Zwack, Organometallics 2000, 19, 2423–2426.
- [9] T. R. Ward, O. Schafer, C. Daul, P. Hofmann, Organometallics 1997, 16, 3207–3215.
- [10] V. Alezra, G. Bernardinelli, C. Corminboeuf, U. Frey, E. P. Kündig, A. E. Merbach, C. M. Saudan, F. Viton, J. Weber, J. Am. Chem. Soc. 2004, 126, 4843–4853, and references therein.
- [11] F. Bock, F. Fischer, W. A. Schenk, J. Am. Chem. Soc. 2006, 128, 68–69.
- [12] F. Bock, Dissertation, University of Würzburg, 2007.
- [13] K. Issleib, M. Haftendorn, Z. Anorg. Allg. Chem. 1970, 376, 79– 86.
- [14] D. G. Allen, G. M. McLaughlin, G. B. Robertson, W. L. Steffen, G. Salem, S. B. Wild, *Inorg. Chem.* **1982**, *21*, 1007–1014.
- [15] B. Wolfe, T. Livinghouse, J. Org. Chem. 2001, 66, 1514-1516.
- [16] D. Sirbu, G. Consiglio, S. Gischig, J. Organomet. Chem. 2006, 691, 1143–1150.
- [17] F. Agbossou, E. J. O'Connor, C. M. Garner, N. Q. Méndez, J. M. Fernández, A. T. Patton, J. A. Ramsden, J. A. Gladysz, *Inorg. Synth.* 1992, 29, 211–225.
- [18] S. Dilsky, W. A. Schenk, Eur. J. Inorg. Chem. 2004, 4859-4870.
- [19] N. Burzlaff, M. Hagel, W. A. Schenk, Z. Naturforsch., Teil B 1998, 53, 893–899.
- [20] N. Burzlaff, W. A. Schenk, Eur. J. Inorg. Chem. 1998, 2055-2061.
- [21] M. A. Cranswick, N. E. Gruhn, O. Oorhles-Steele, K. R. Ruddick, N. Burzlaff, W. A. Schenk, D. L. Lichtenberger, *Inorg. Chim. Acta* 2008, 361, 1122–1133.
- [22] W. A. Schenk, N. Burzlaff, H. Burzlaff, Z. Naturforsch., Teil B 1994, 49, 1633–1639.
- [23] A. Ishii, T. Ishida, N. Kumon, N. Fukuda, H. Oyama, N. Inamoto, F. Iwasaki, R. Okazaki, *Bull. Chem. Soc. Jpn.* 1996, 69, 709– 717.
- [24] W. A. Schenk, T. Stur, E. Dombrowski, Inorg. Chem. 1992, 31, 723–724.
- [25] L. Horner, Pure Appl. Chem. 1980, 52, 843-858.
- [26] H. Werner, Angew. Chem. 1983, 95, 932–954; Angew. Chem. Int. Ed. Engl. 1983, 22, 927–949.
- [27] R. F. Jordan, J. Norton, J. Am. Chem. Soc. 1982, 104, 1255-1263.
- [28] C. Creutz, N. Sutin, J. Am. Chem. Soc. 1988, 110, 2418-2427.
- [29] J. H. Merrifield, J. M. Fernandez, W. E. Buhro, J. A. Gladysz, *Inorg. Chem.* **1984**, 23, 4022–4029.
- [30] J. M. Fernandez, J. A. Gladysz, Organometallics 1989, 8, 207-219.
- [31] M. A. Esteruelas, A. M. López, E. Oñate, E. Royo, *Inorg. Chem.* 2005, 44, 4094–4103.
- [32] M. A. Dewey, Y. Zhou, Y. Liu, J. A. Gladysz, Organometallics 1993, 12, 3924–3932.
- [33] N. Burzlaff, W. A. Schenk, Eur. J. Inorg. Chem. 1999, 1435-1443.
- [34] S. Dilsky, W. A. Schenk, Z. Naturforsch., Teil B 2004, 59, 1093– 1102.
- [35] D. M. Dalton, C. M. Garner, J. M. Fernández, J. A. Gladysz, J. Org. Chem. 1991, 56, 6823–6829.
- [36] N. Q. Mendez, J. W. Seyler, A. M. Arif, J. A. Gladysz, J. Am. Chem. Soc. 1993, 115, 2323–2334.
- [37] G. A. Stark, J. A. Gladysz, Inorg. Chem. 1996, 35, 5509-5513.
- [38] D. M. Dalton, J. M. Fernández, K. Emerson, R. D. Larsen, A. M. Arif, J. A. Gladysz, J. Am. Chem. Soc. 1990, 112, 9198–9212.
- [39] W. A. Schenk, J. Bezler, Eur. J. Inorg. Chem. 1998, 605-611.
- [40] W. A. Schenk, J. Kümmel, I. Reuther, N. Burzlaff, A. Wuzik, O. Schupp, G. Bringmann, *Eur. J. Inorg. Chem.* **1999**, 1745–1756.

<sup>[1]</sup> Handbook of Lewis Acids – Application in Organic Synthesis (Ed.: H. Yamamoto), Wiley-VCH, Weinheim, **2000**.

- [41] W. A. Schenk, J. Bezler, N. Burzlaff, M. Hagel, B. Steinmetz, Eur. J. Inorg. Chem. 2000, 287–297.
- [42] W. A. Schenk, N. Kuhnert, Z. Naturforsch., Teil B 2000, 55, 527– 535.
- [43] F. Fehér, in: Handbuch der Präparativen Anorganischen Chemie (Ed.: G. Brauer), Enke, Stuttgart, 1960, pp. 325–326.
- [44] W. Wolfsberger, Chem.-Ztg. 1986, 112, 450-452.
- [45] K.-H. Geiß, D. Seebach, B. Seuring, Chem. Ber. 1977, 110, 1833– 1851.
- [46] G. M. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112–122. Received: October 16, 2009

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