Diastereomeric Halfsandwich Rhenium Complexes Containing Hemilabile Phosphane Ligands[‡]

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Dedicated to Professor Johann Weis on the occasion of his 60th birthday

Keywords: Rhenium / Chiral complexes / Chiral P ligands / Hemilabile P ligands / Sandwich complexes

The syntheses and some typical reactions of diastereomeric rhenium complexes $[CpRe(NO)(CO)\{P(Ph)(R)(R')\}]BF_4$ (R = Me, Ph; R′ = 2-C_6H_4OMe, $CH_2C_4H_3S$, $CH_2C_4H_7O$) (**3a**–**e**) are described. Reduction of the carbonyl ligand with $NaBH_4$ in THF gave the corresponding methyl complexes $[CpRe(NO)\{P(Ph)(R)(R')\}(CH_3)]$ (**4a**–**e**). Acid treatment of the methyl complexes leads to liberation of methane and coordination of the additional donor site of the potentially bidentate phosphane ligand. Of the chelate complexes **5a**–**e**, those with R′ = 2-C_6H_4OMe (**5a**, **d**) decomposed in solution at room temperature. In donor solvents, the chelate ring opens giving the stable solvated complexes $[CpRe(NO)\{P(Ph)(R)(R')\}](solvent)]BF_4$ (solvent = CH_3CN, THF) (**6b**–**e**, **7d**). The new compounds are thus suitable starting materials for the syntheses of diastereomeric rhenium complexes $[CpRe(NO)\{P(Ph)(R)(R')\}(L)]BF_4$.

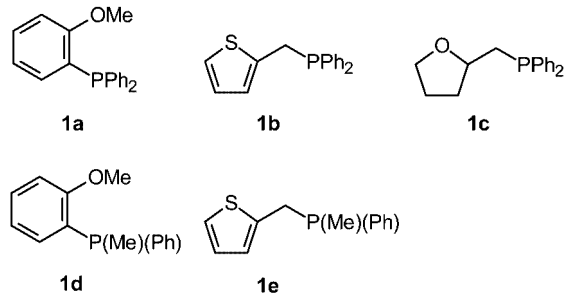
Introduction

Since the first successful enantiomer separation of the pseudotetrahedral *at-metal* chiral complex $[CpMn(CO)(NO)(PPh_3)]PF_6$ by Brunner,[1] a large variety of different *at-metal* chiral, kinetically stable or labile complexes has been synthesised. Some of them have been of synthetic interest, e.g. (R_{Fe})-$[CpFe(CO)(PPh_3)\{C(O)Me\}]$ which has been used, inter alia, in the total synthesis of Captopril.[2,3] Other complexes of this type were investigated as potential catalysts[2] and the chiral Lewis acidic rhenium complex $[CpRe(NO)(PPh_3)]^+$ has been studied in great detail by Gladysz et al.[4,5] We have recently extended this work to thiolate and thioaldehyde complexes of $[CpRe(NO)(PPh_3)]^+$ and its congeners $[CpRe(NO)\{P(OPh)_3\}]^+$ and $[CpRe(NO)\{P(iPr)_3\}]^+$.[6–9] By introducing a second stereogenic centre at the phosphane ligand, higher selectivities in reactions at coordinated ligands might be achieved. Moreover, by introducing a second donor atom into the phosphane, a hemilabile[10,11] ligand can be created which should serve to stabilise reactive intermediates.

Results

Phosphane Synthesis

The hemilabile ligands which are central to this study are shown in Scheme 1.



Scheme 1

The prototypic **1a** is commercially available, whereas **1b** was obtained by a slight modification of a known[12] synthesis as follows. Cleavage of PPh_3 with lithium in THF and alkylation of the resultant lithium diphenylphosphide with 2-(chloromethyl)thiophene gave **1b** in 87% yield. *C*-chiral racemic **1c** has been obtained previously via a similar approach.[13] Cleavage of bis(2-anisyl)phenylphosphane with sodium in liquid ammonia followed by alkylation with methyl iodide gave the *P*-chiral racemic ether phosphane ligand **1d**[14] in 63% yield. Deprotonation of methylphenylphosphane with butyllithium in THF followed by alky-

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lation with 2-(chloromethyl)thiophene gave *P*-chiral **1e** (73%).

The phosphanes **1a**, **1b** and **1d** are colourless solids which are readily soluble in most organic solvents. They can be recrystallised from alcohols or saturated hydrocarbons and may be handled in air for short periods of time. Compound **1c** had been reported as a waxy solid, whereas the phosphane **1e** is a colourless, air-sensitive oil with an unpleasant odour. The ^{31}P NMR signals are shifted to high field as the number of alkyl substituents increases. The methylene group of **1e** can be observed as an ABX system with $^{2}J_{H,H} = 14.4$ Hz and $^{2}J_{P,H} = 3.6$ Hz.

Crystal and Molecular Structure of 1b·BH_3

Compound **1b** was converted into its borane adduct by treatment with BH_3·SMe_2 in THF. Recrystallisation from ethanol/hexane gave crystals suitable for a single-crystal X-ray structure determination (Figure 1).

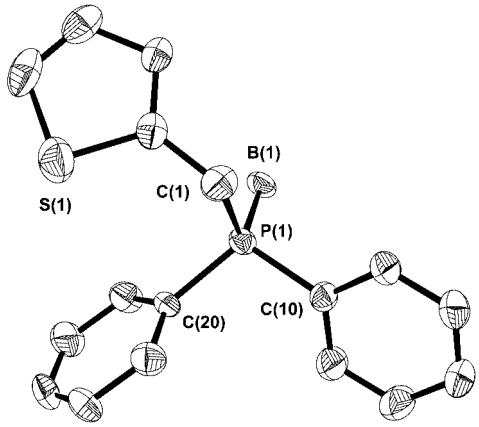
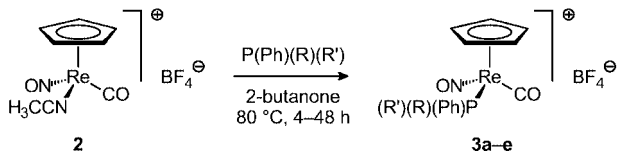


Figure 1. Molecular structure of $PPh_2(CH_2C_4H_3S)$·BH_3 (**1b**·BH_3), hydrogen atoms omitted for clarity. Space group $Pna2_1$; selected distances [pm] and angles (°) (standard deviations in parentheses): P(1)−B(1) 190.4(4), P(1)−C(1) 182.9(3), P(1)−C(10) 181.2(3), P(1)−C(20) 180.6(3); C(1)−P(1)−B(1) 111.98(19), C(10)−P(1)−B(1) 110.52(17), C(20)−P(1)−B(1) 117.02(17), C(1)−P(1)−C(10) 105.82(16), C(1)−P(1)−C(20) 104.13(17), C(10)−P(1)−C(20) 106.58(15)

As expected, the BH_3 group is bound to phosphorus rather than to the sulfur atom of the thiophene moiety. The P−B and P−C bond lengths are in agreement with those of similar borane adducts.[15,16] The angles at the tetrahedral phosphorus atom are slightly distorted reflecting the low electronegativity of the BH_3 substituent.

Carbonyl Complexes

The chiral racemic rhenium complex $[CpRe(CO)(NO)(NCCH_3)]BF_4$ (**2**) was the common starting material for the following syntheses and is readily accessible from $[Re_2(CO)_{10}]$ in three steps.[4] The acetonitrile ligand is known to be easily replaceable by phosphanes[7,17,18] and this methodology was also successful with the phosphanes **1a**−**e** [Equation (1)].



(1)

R \ R'	2-C_6H_4OMe	$CH_2C_4H_3S$	$CH_2C_4H_7O$
Ph	**3a** (85%)	**3b** (83%)	**3c** (95%)
Me	**3d** (62%)	**3e** (76%)	

Compounds **3d** and **3e** were obtained as 1:1 mixtures of diastereoisomers, i.e. Re−P bond formation proceeds without diastereoselectivity. All new complexes $[CpRe(CO)(NO)(PR_3)]BF_4$ (**3a**−**e**) are yellow to yellow-brown air-stable solids (e.g. **3d** melts in air without decomposition). While **3c** is soluble in THF, **3b** and **3d** are insoluble in THF and **3e** is insoluble even in acetone. Due to the stereogenic metal centre, the PCH_2-protons in **3b** can be observed as an ABX system with $^{2}J_{H,H} = 15$ Hz and $^{2}J_{P,H} = 10$ Hz. Diastereomeric **3e** exhibits two such sets of signals. The ^{31}P NMR signals are shifted 25 to 30 ppm downfield compared with the free ligand. The CO and NO stretching frequencies appear in the ranges expected for cationic complexes of this kind.

Crystal and Molecular Structures of 3a, 3b and 3d−AlF_4

Three of the new complexes were investigated by X-ray diffraction. Figure 2−4 show views of the cations.

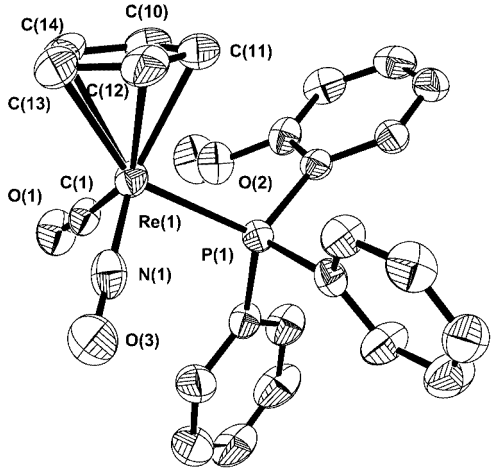


Figure 2. Structure of the cation of $[CpRe(CO)(NO)\{PPh_2(2\text{-}C_6H_4OMe)\}]BF_4$ (**3a**), hydrogen atoms omitted for clarity. Space group $P2_1/c$; selected distances [pm] and angles (°) (standard deviations in parentheses): Re(1)−C(10) 228.2(7), Re(1)−C(11) 229.7(6), Re(1)−C(12) 231.8(6), Re(1)−C(13) 229.9(6), Re(1)−C(14) 229.9(7), Re(1)−C(1) 191.6(6), Re(1)−N(1) 180.1(6), Re(1)−P(1) 239.26(14); Re(1)−C(1)−O(1) 175.1(6), Re(1)−N(1)−O(3) 178.8(5), N(1)−Re(1)−C(1) 97.2(3), P(1)−Re(1)−N(1) 91.37(17), P(1)−Re(1)−C(1) 88.32(18)

Due to the similar sizes of the CO and NO ligands these two groups are usually disordered.[19] Since the extent of this disorder is variable, the apparent Re−C and Re−N bond lengths can vary from their normal values as in **3a** to

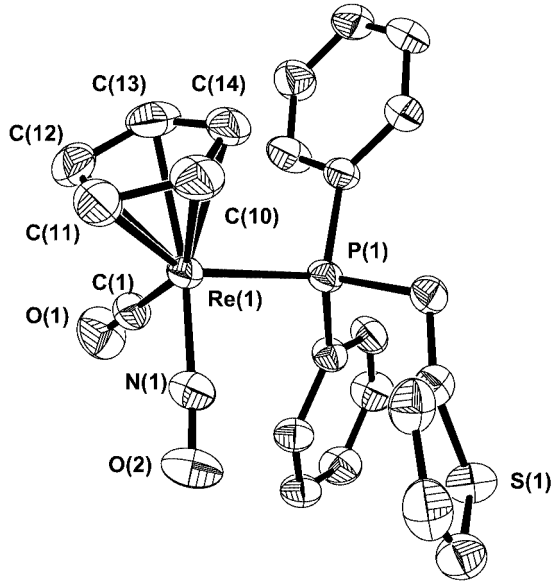


Figure 3. Structure of the cation of [CpRe(CO)(NO){PPh_2-($CH_2C_4H_3S$)}]BF_4 (**3b**), hydrogen atoms omitted for clarity. Space group $P\bar{1}$; selected distances [pm] and angles (°) (standard deviations in parentheses): Re(1)−C(10) 231.4(5), Re(1)−C(11) 227.8(6), Re(1)−C(12) 227.1(6), Re(1)−C(13) 228.1(6), Re(1)−C(14) 231.5(5), Re(1)−C(1) 188.4(5), Re(1)−N(1) 182.6(4), Re(1)−P(1) 239.05(12); Re(1)−C(1)−O(1) 179.7(5), Re(1)−N(1)−O(2) 175.7(4), N(1)−Re(1)−C(1) 92.4(2), P(1)−Re(1)−N(1) 95.56(14), P(1)−Re(1)−C(1) 89.70(16)

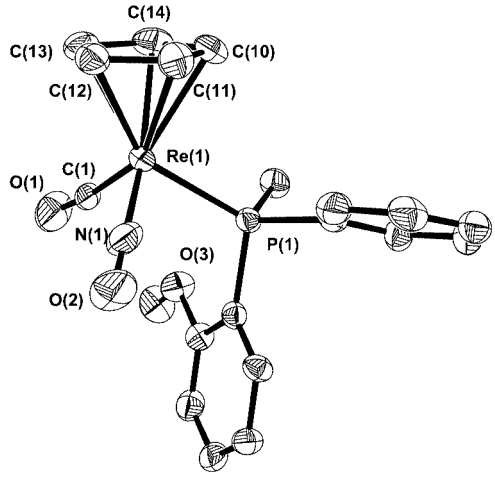


Figure 4. Structure of the cation of [CpRe(CO)(NO){P(Ph)(Me)(2-C_6H_4OMe)}]AlF_4 (**3d-AlF$_4$**), hydrogen atoms omitted for clarity. Space group $P2_1/n$; selected distances [pm] and angles (°) (standard deviations in parentheses): Re(1)−C(10) 231.7(7), Re(1)−C(11) 229.3(7), Re(1)−C(12) 227.7(7), Re(1)−C(13) 229.4(7), Re(1)−C(14) 227.5(7), Re(1)−C(1) 186.2(6), Re(1)−N(1) 183.3(7), Re(1)−P(1) 239.65(17); Re(1)−C(1)−O(1) 173.1(7), Re(1)−N(1)−O(2)−176.3(8), N(1)−Re(1)−C(1) 95.8(3), P(1)−Re(1)−N(1) 89.6(2), P(1)−Re(1)−C(1) 91.1(2)

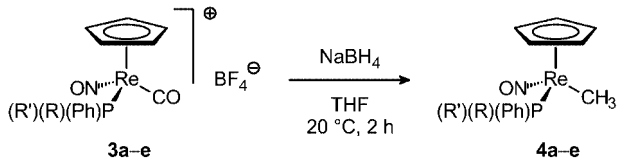
almost equal values as in **3d**. The topological similarity of the CO and NO ligands also thwarted any attempts to separate the diastereoisomers of **3c**−**e** by crystallisation. Moreover, the disorder makes it impossible to determine the relative configuration of the cation of **3d**−**AlF$_4$**.

Neither the NO ligands are bent nor are the cyclopentadienyl ligands slipped in any of the three structures. The rhenium atoms are octahedrally surrounded with the cyclopentadienyl ligand serving as a six-electron donor. In **3a** and **3d**−**AlF$_4$**, the N(1)−Re(1)−C(1) angles are significantly larger [97.2(3)° and 95.8(3)°, respectively] than in **3b** [92.4(2)°]. As the structure of the prototypic $[CpRe(CO)(NO)(PPh_3)]^+$ reveals the same widened N(1)−Re(1)−C(1) angle [95.5(5)°],[20] we have to conclude that the angle in **3b** is abnormally small. This is surprising since the phosphorus ligands of this study all have similar steric and electronic properties.

The surprising appearance of AlF_4^- as a counterion in the structure of **3d**−**AlF$_4$** was traced back to an impurity in the $[NO]BF_4$ which was used in the synthesis of [CpRe-(CO)(NO)($NCCH_3$)]BF_4 (**2**).

Methyl Complexes

The hydride reduction of a Re−CO group has already been described by Gladysz,[4,17] Casey,[21] Graham[22] and our group.[7] The new methyl complexes **4a**−**e** were obtained in the same way in good yields as orange or orange-red solids [Equation (2)].



(2)

R \ R'	2-C_6H_4OMe	$CH_2C_4H_3S$	$CH_2C_4H_7O$
Ph	**4a** (87%)	**4b** (75%)	**4c** (82%)
Me	**4d** (82%)	**4e** (81%)	

Complexes **4a**−**e** are readily soluble in common organic solvents except aliphatic hydrocarbons. This again makes a separation of the diastereomeric complexes **4c**−**e** difficult. Nevertheless, a diastereomeric excess of 35% was achieved during the workup of **4e**. This helped in the assignment of the spectroscopic data of the two diastereoisomers. Characteristic spectroscopic features for all methyl complexes are the low frequency of the NO stretching vibration and the high-field shift of the Re−CH_3 resonance in ^{13}C NMR spectroscopy. Furthermore, the phosphorus resonances are shifted downfield compared with those of the cationic starting materials.

Crystal and Molecular Structure of 4d

Crystals of the *unlike* isomer (R_{Re},S_P/S_{Re},R_P)-**4d** suitable for X-ray diffraction were grown at −30 °C by layering a toluene solution of the diastereomeric mixture with petroleum ether. A comparison of this structure with those of similar alkyl complexes (e.g. [CpRe(NO){P(*i*Pr)$_3$}(CH_3)][7]

and [CpRe(NO)(PPh_3)(CH_2Ph)][23]) did not reveal any significant differences (Figure 5).

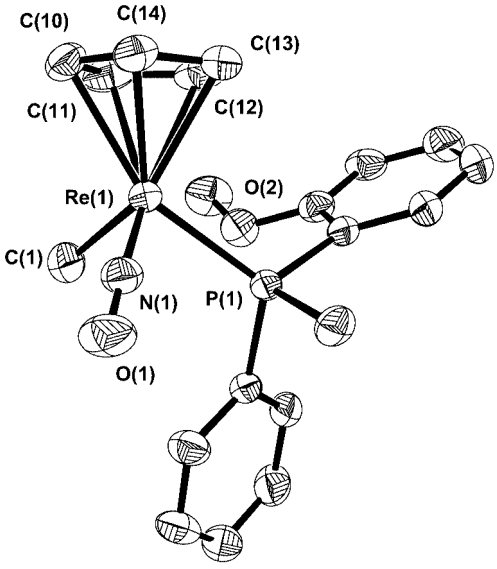
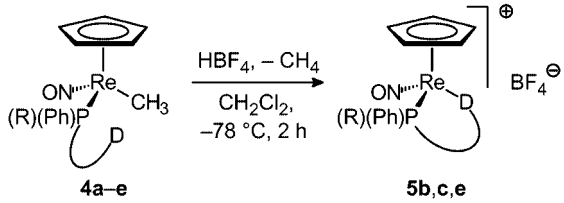


Figure 5. Molecular structure of (R_{Re},S_P/S_{Re},R_P) [CpRe(NO){P(Ph)(Me)(2-C_6H_4OMe)}(CH_3)] (**4d**), hydrogen atoms omitted for clarity. Space group *P*1; selected distances [pm] and angles (°) (standard deviations in parentheses): Re(1)−C(10) 228.4(4), Re(1)−C(11) 234.0(4), Re(1)−C(12) 233.6(4), Re(1)−C(13) 225.7(4), Re(1)−C(14) 222.8(4), Re(1)−C(1) 214.1(4), Re(1)−N(1) 175.6(3), Re(1)−P(1) 234.30(9); Re(1)−N(1)−O(1) 177.9(3), N(1)−Re(1)−C(1) 95.55(18), P(1)−Re(1)−N(1) 88.89(11), P(1)−Re(1)−C(1) 90.24(12)

The P(1)−Re(1) bond in **4d** is 3 pm shorter than in [CpRe(NO){P(*i*Pr)$_3$}(CH_3)] and even 2 pm shorter than in [CpRe(NO)(PPh_3)(CH_2Ph)], reflecting the smaller size of the phosphane ligand. Moreover, the C(1)−Re(1) distance is remarkably shorter [214.1(4) pm] than in [CpRe(NO){P(*i*Pr)$_3$}(CH_3)] [218.2(5)].[7] The cyclopentadienyl ligand is slightly slipped such that the two carbon atoms which are approximately *trans* to the strongly π-accepting NO ligand have moved about 8 pm away from the rhenium atom. As in [CpRe(NO){P(*i*Pr)$_3$}(CH_3)] and [CpRe(NO)(PPh_3)(CH_2Ph)], the N(1)−Re(1)−C(1) angle is widened [95.55(18)°], although the NO and CH_3 ligands are the smallest substituents.

Chelate Ring Closure

It is known that methylrhenium complexes liberate methane when treated with acids.[5,24,25] In the absence of donors, the solvent dichloromethane stabilises the resultant 16 valence electron complex. The CH_2Cl_2 complex thus obtained served as a starting material for a variety of compounds,[5] although it tends to undergo side reactions[6,26] and to decompose above −20 °C.[24,26] The phosphane ligands in this study offer donor functionalities (e.g. oxygen or sulfur), which should serve to stabilise the complex by intramolecular coordination. When the methyl complexes were treated with HBF_4 in dichloromethane, three complexes with chelate structures could be isolated, namely **5b**, **5c** and **5e** [Equation (3)].



(3)

R \ D	2-C_6H_4OMe	$CH_2C_4H_3S$	$CH_2C_4H_7O$
Ph	dec	**5b** (86%)	**5c** (99%)
Me	dec	**5e** (91%)	

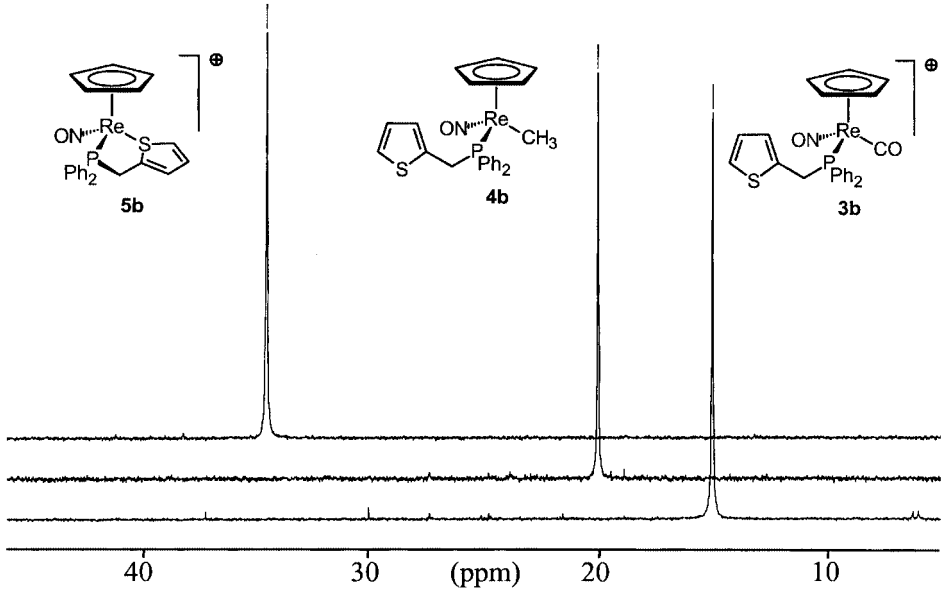
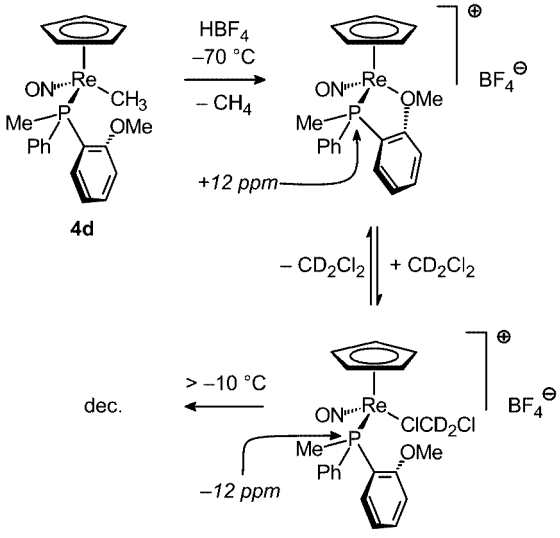


Figure 6. ^{31}P NMR spectra of the complexes [CpRe(NO){PPh_2($CH_2C_4H_3S$)}(X)]Y; X = CO, Y = BF_4 **3b**, X = CH_3, Y = −**4b**, X = −, Y = BF_4 **5b**

Attempts to obtain ring-closed products from the anisyl-substituted phosphane complexes **4a** and **4d** were only partially successful (see below). Two different samples of **4e** with 0 and 34% *de*, respectively, were employed in this reaction in order to gain some insight into the stereochemistry of the demethylation step. In both cases the *de* was retained in the product **5e**.

Although no crystals suitable for X-ray diffraction could be grown, the ring closure can be unambiguously inferred from ^{31}P NMR spectroscopic data. It is known that in chelate complexes the phosphorus chemical shift depends on the ring size. For five-membered rings, an additional 20−30 ppm downfield shift is typical.[27,28] The ^{31}P NMR spectra of **5b**, **5c** and **5e** exhibit this feature, an example is shown in Figure 6. The NO stretching frequency was found in the typical range for cationic ether[29] or thioether[6,30,31] complexes of the general formula $[CpRe(NO)(PR_3)(L)]^+$. All other spectroscopic data are also in agreement with a cationic structure.

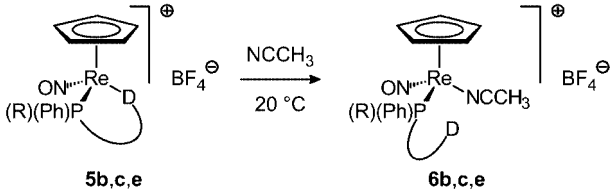
The reaction of **4d** with HBF_4 was investigated by low-temperature NMR spectroscopy. The phosphorus spectrum at −50 °C shows, aside from the expected downfield signals of two diastereomeric ring-closed complexes, a second pair of signals belonging to a cationic, ring-opened complex. Raising the temperature to 20 °C led to a decrease of the downfield signals and an increase of the upfield signals. Continued measurements at 20 °C revealed a slow decrease of both signal sets and, after 24 h, none of the signals could be observed any more. This can be interpreted in terms of a low stability of the ring-closed complex. At temperatures around −30 °C, there seems to be an equilibrium between ring-closed and ring-opened species, were the dichloromethane solvent acts as a ligand. The dichloromethane complex slowly decomposes at temperatures above −20 °C and is removed from the equilibrium which eventually leads to complete decomposition (Scheme 2). Nevertheless, this process is slowed down by the hemilabile ligand, compared with the rapid decomposition of $[CpRe(NO)(PPh_3)(ClCH_2Cl)]BF_4$.[24]



Scheme 2

Stabilitiy of the Ring-Closed Complexes and Preparation of Solvated Complexes

In the acid-promoted ring closure reactions of **5c** and **5e**, no diastereoselectivity was observed thus so far ruling out the possibility of a kinetic diastereoisomeric enrichment. If the diastereomeric complexes differ in energy, a thermodynamic enrichment might be possible. To check this, complexes **5b**, **5c** and **5e** were dissolved in polar solvents (e.g. THF, acetone or acetonitrile at 20 °C or reflux) and the mixtures analysed by ^{31}P NMR spectroscopy. While the acetone solutions did not show any enrichment or decomposition even after being heated to reflux for 24 h, a small diastereomeric enrichment was observed for **5e** in THF. Due to the different solubility of the diastereomers, only a suspension of **5e** in THF could be obtained with one diastereomer preferentially dissolved. The extraction of **5e** with THF led to a *de* of 60%, allowing the assignment of the spectroscopic data to the respective isomers. Upon dissolving the complexes in acetonitrile, new upfield signals in the ^{31}P NMR spectra appeared immediately. After 4 h, only the upfield signals remained. NMR and IR spectroscopic analyses suggested a ring-opening with the acetonitrile occupying the vacated coordination site as shown for **6b**, **6c** and **6e** [Equation (4)].



(4)

R \ D	$CH_2C_4H_3S$	$CH_2C_4H_7O$
Ph	**6b** (90%)	**6c** (82%)
Me	**6e** (93%)	

Crystal and Molecular Structure of 6e

The compositions of the acetonitrile complexes were corroborated by X-ray crystallography. Suitable crystals of the *unlike* diastereomer (R_{Re},S_P/S_{Re},R_P)-$[CpRe(NO)\{P(Ph)(Me)(CH_2C_4H_3S)\}(NCCH_3)]BF_4$ (**6e**) were obtained at 20 °C by layering a THF solution of the diastereomeric mixture with hexane. Figure 7 shows a view of the cation.

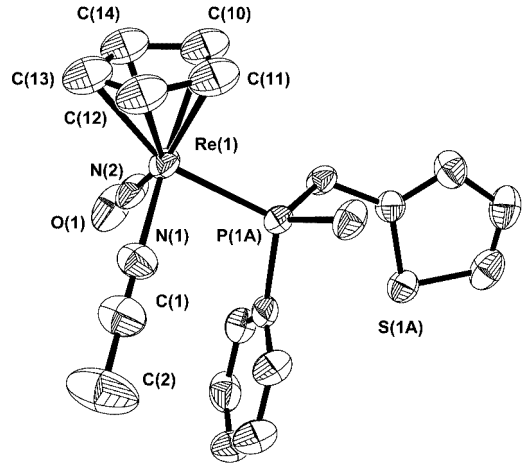
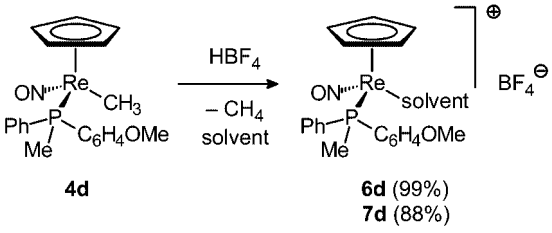


Figure 7. Structure of the cation of (R_{Re},S_P/S_{Re},R_P)-[CpRe(NO){P(Ph)(Me)($CH_2C_4H_3S$)}($NCCH_3$)]BF_4 (**6e**), hydrogen atoms omitted for clarity. Space group $P2_1/c$; selected distances [pm] and angles (°) (standard deviations in parentheses): Re(1)−C(10) 222.3(8), Re(1)−C(11) 228.3(8), Re(1)−C(12) 231.9(8), Re(1)−C(13) 226.9(7), Re(1)−C(14) 221.6(8), Re(1)−N(1) 205.5(6), Re(1)−N(2) 176.0(6), Re(1)−P(1A) 236.3(2); Re(1)−N(2)−O(1) 178.9(5), Re(1)−N(1)−C(1) 176.9(6), N(1)−C(1)−C(2) 178.6(8), N(1)−Re(1)−N(2) 96.9(2), P(1A)−Re(1)−N(1) 85.03(17), P(1A)−Re(1)−N(2) 92.86(18)

The cyclopentadienyl moiety is again slightly slipped such that the two carbon atoms *trans* to the NO ligand have moved away from the rhenium atom. The nitrosyl and nitrile ligands are perfectly linear and the N(1)−Re(1)−N(2) angle is in the typical range. This is somewhat in contrast to the structure of (S_{Re},S_C)-[CpRe(NO)(PPh_3){NCCH-(Ph)CH_2CH_3}]PF_6 where a significantly bent nitrile ligand and a widened N(1)−Re(1)−N(2) angle were observed.[32]

The refinement of the structure of **6e** indicated some disorder which revealed the presence, in the crystal, of ca. 10% of the *like* isomer. This is related to the predominating *unlike* isomer through a reflection of the phosphane ligand at a mirror plane which bisects the N(1)−Re(1)−N(2) angle and passes through the centre of the cyclopentadienyl ring, the rhenium atom and two carbon atoms of the thiophene ring (Figure 8).

Treatment of the methyl complex **4d** with HBF_4 either in a mixture of dichloromethane and acetonitrile or in pure THF gave the cationic solvated complexes **6d** and **7d** without any decomposition. Complex **7d** could be isolated with a *de* of 30% [Equation (5)].



(5)

solvent = CH_3CN (**6d**), THF (**7d**)

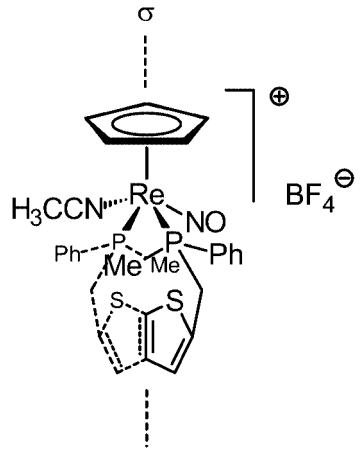


Figure 8. Disorder in the structure of *unlike*-**6e**; the phosphane ligand is reflected along an imaginary mirror plane which contains the Cp centre, the rhenium atom and two carbon atoms of the thiophene moiety giving rise to the *like* diastereoisomer

Crystal and Molecular Structure of 7d

The structure of the *like* isomer of the THF complex **7d** was determined by X-ray diffraction. Figure 9 shows the cation.

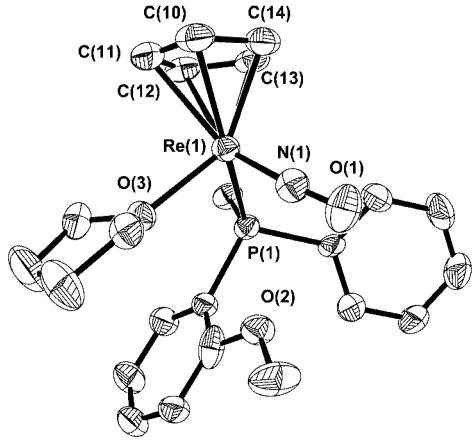


Figure 9. Structure of the cation of (S_{Re},S_P/R_{Re},R_P)-[CpRe(NO){P(Ph)(Me)(2-C_6H_4OMe)}(THF)]BF_4 (**7d**), hydrogen atoms omitted for clarity. Space group $P2_1/c$; selected distances [pm] and angles (°) (standard deviations in parentheses): Re(1)−C(10) 228.9(8), Re(1)−C(11) 235.0(8), Re(1)−C(12) 230.6(8), Re(1)−C(13) 220.8(7), Re(1)−C(14) 217.7(8), Re(1)−N(1) 174.9(7), Re(1)−O(3) 214.6(5), Re(1)−P(1) 238.64(18); Re(1)−N(1)−O(1) 176.0(7), N(1)−Re(1)−O(3) 96.9(3), P(1)−Re(1)−N(1) 90.8(2), P(1)−Re(1)−O(3) 87.60(14)

As for the methyl complex **4d** and the acetonitrile complex **6e** the cyclopentadienyl ligand is slipped, the difference between the longest and the shortest Re−C distances being 17 pm. Once again, the angle between the smallest ligands THF and NO is widened [96.9(3)°]. Since this widening has been observed for all N−Re−X angles in all structures discussed herein, the origin of this distortion must be electronic in nature.

All acetonitrile complexes were isolated in high yields as yellow or brown solids. Except for [CpRe(NO){P(Ph)(Me)($CH_2C_4H_7O$)}($NCCH_3$)]BF_4 (**6c**), the compounds are stable in acetone and even in dichloromethane solution, whereas **6c** decomposes rapidly in both solvents.

The formation of the THF complex **7d** deserves some comment. It implies that the superior donor ability of THF compared with the aryl methoxy group overrides the entropy effect of the five-membered chelate ring.

Discussion

It was the goal of this work to prepare diastereomeric rhenium complexes which contain stereogenic centres both at the metal and the phosphane ligand. Furthermore, the phosphanes bear a donor function (e.g. oxygen or sulfur) to allow intramolecular stabilisation of reactive intermediates. Five such hemilabile phosphanes were investigated. Adapting published methods, the phosphanes could be coordinated successfully to the rhenium complexes.

The phosphanes **1a** and **1d** which contain an *ortho*-anisyl group as a potential donor did not give stable chelate complexes. Although low temperature NMR experiments revealed that at −50 °C the intramolecularly stabilised complex [CpRe(NO){P(Ph)(Me)(2-C_6H_4OMe)}]BF_4 (**5d**) is formed, the ring opens at temperatures above −30 °C giving rise to another cationic complex, probably the dichloromethane adduct which itself decomposes at temperatures above −10 °C. The oxygen of the anisyl group is even less efficient as a donor than THF. On the other hand, ring closure was observed with the phosphanes **1b**, **1c** and **1e**. In these cases, neither THF nor acetone are strong enough donors to break the Re−O or Re−S bonds, while acetonitrile opens the rings irreversibly. As yet, no complete separation of the diastereoisomers could be achieved either during the formation of the ring-closed complexes or by fractional crystallisation (except for **4e**, **5e** and **7d**). On the other hand, once a sample enriched in one diastereomer is employed, then the degree of enrichment is carried over to the next step. This is in line with earlier observations that substitution reactions at half-sandwich complexes of rhenium proceed with retention of configuration.[33,34]

Conclusions

Diastereomeric rhenium complexes containing a stereogenic metal centre and a chiral phosphane ligand are readily accessible. Furthermore, if the phosphanes contain a second donor atom, e.g. oxygen or sulfur, chelate ring closure can occur. The stability of the chelate ring can be tuned by an appropriate choice of donor function. Further modifications of the system are necessary to give access to diastereomerically pure complexes.

Experimental Section

All experiments were carried out in Schlenk tubes under 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 were routinely checked by DEPT procedures. In some cases the ^{13}C NMR signals of quaternary carbon atoms were too weak to be detected. The ^{1}H and ^{13}C NMR signals of the phenyl groups attached to phosphorus are very similar for all compounds and have therefore been omitted from the lists of spectroscopic 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. BF_4^- salts occasionally give low carbon values due to trace formation of fluorocarbon compounds which escape detection. GC-MS: Fisons Instruments Trio-1000. The following starting materials were obtained as described in the literature: 2-(chloromethyl)thiophene,[35] $PPh_2(CH_2C_4H_7O)$ (**1c**),[13] $PPh(2\text{-}C_6H_4OMe)_2$,[36] PPh(Me)(H)[37] and [CpRe(CO)(NO)($NCCH_3$)]BF_4 (**2**).[4] All other reagents were used as purchased.

$PPh_2(CH_2C_4H_3S)$ (1b): This compound has been obtained previously via Li reduction of Ph_2PCl.[12] However, no yields or physical data were given. We found the following synthesis to be more convenient. A solution of $LiPPh_2$, prepared from PPh_3 (8.00 g, 30.5 mmol) and excess lithium in THF (50 mL), was treated with NH_4Cl (1.45 g, 27.1 mmol) to quench LiPh. Freshly distilled 2-(chloromethyl)thiophene (5.00 g, 37.7 mmol) was added dropwise to the red solution at 20 °C. After stirring for 1 h at 20 °C, water (15 mL) was added. The organic layer was separated, the aqueous phase extracted four times with diethyl ether (50 mL) and the combined organic phases dried with $MgSO_4$. The solvent was removed under vacuum and the colourless residue purified by recrystallisation from methanol or by column chromatography over silica (20 cm, petroleum ether/diethyl ether, 1:2). Yield 7.50 g (87%), white solid, m.p. 50 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 3.53 (s, br, 2 H, PCH_2), 6.60 (m, 1 H, thiophene *H*), 6.74 (m, 1 H, thiophene *H*), 6.96 (m, 1 H, thiophene *H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 30.0 (d, $^1J_{P,C}$ = 15 Hz, P*C*H_2), 123.7 (d, $^4J_{P,C}$ = 3 Hz, thiophene *C*H), 125.7 (d, $^3J_{P,C}$ = 7 Hz, thiophene *C*H), 126.8 (d, $^4J_{P,C}$ = 1 Hz, thiophene *C*H), 139.8 (d, $^2J_{P,C}$ = 11 Hz, PCH_2*C*) ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ = −10.7 (s) ppm. $C_{17}H_{15}PS$ (282.35): calcd. C 72.32, H 5.35, S 11.36; found C 72.10, H 5.54, S 10.87.

P(Me)(Ph)(2-C_6H_4OMe) (1d): The preparation of **1d** starting from $PPh(2\text{-}C_6H_4OMe)_2$ was briefly mentioned in the literature, but no details were given.[14] To a solution of sodium (4.00 g, 174 mmol) in liquid ammonia (400 mL) was added $PPh(2\text{-}C_6H_4OMe)_2$ (28.0 g, 86.9 mmol) and the mixture kept at −78 °C for 6 h. NH_4Cl (4.50 g, 84.1 mmol) was then added followed by the dropwise addition of MeI (6.00 mL, 13.7 g, 96.5 mmol). The ammonia was evaporated overnight, the remaining pasty solid was washed twice with water (50 mL) and distilled (kugelrohr, oven temperature 180 °C). The colourless distillate solidified upon cooling to 20 °C. Yield 12.5 g (63%) (ref.[14] 56%), white solid, m.p. 46 °C (ref.[38] 46−47 °C). The NMR spectroscopic data were consistent with those given in ref.[38].

P(Ph)(Me)($CH_2C_4H_3S$) (1e): P(Ph)(Me)(H) (2.52 g, 20.3 mmol) was dissolved in THF (10 mL) and deprotonated with BuLi (8.5 mL 2.5 M, 21.3 mmol) at −78 °C. The orange solution thus obtained was slowly added to a cooled (−78 °C) solution of freshly distilled 2-(chloromethyl)thiophene (2.69 g, 20.3 mmol) in THF (10 mL). The mixture was warmed to 20 °C overnight, water (3 mL) was added, the organic layer was separated and the aqueous layer extracted three times with diethyl ether (20 mL). The combined extracts were dried with $MgSO_4$, the solvent removed and the residue distilled under vacuum. Yield 3.26 g (73%), colourless

oil, b.p. 100−113 °C/0.1 mbar. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 1.03 (d, $^2J_{P,H}$ = 4.1 Hz, 3 H, PCH_3), 2.88, 3.00 (ABX system, $^2J_{H,H}$ = 14.4, $^2J_{P,H}$ = 3.6 Hz, 2 H, PCH_2), 6.51 (m, 1 H, thiophene *H*), 6.65 (m, 1 H, thiophene *H*), 6.73 (m, 1 H, thiophene *H*) ppm. ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = 10.7 (d, $^1J_{P,C}$ = 17 Hz, P*C*H$_3$), 32.3 (d, $^1J_{P,C}$ = 17 Hz, P*C*H$_2$), 123.5 (d, $^4J_{P,C}$ = 3 Hz, thiophene *C*H), 125.4 (d, $^3J_{P,C}$ = 6 Hz, thiophene *C*H), 126.9 (d, $^4J_{P,C}$ = 1 Hz, thiophene *C*H), 140.2 (d, $^2J_{P,C}$ = 6 Hz, PCH$_2$*C*). ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = −29.9 (s) ppm. MS: *m*/*z* (%) = 222 (1) [^{34}S-M$^+$], 221 (3) [M + H]$^+$, 220 (25) [M$^+$], 219 (11) [M − H]$^+$, 97 (100) [$CH_2C_4H_3S^+$]. $C_{12}H_{13}PS$ (220.27).

[CpRe(CO)(NO)(PPh$_2$(2-C$_6$H$_4$OMe))]BF$_4$ (3a): A solution of acetonitrile complex **2** (500 mg, 1.14 mmol) and phosphane **1a** (500 mg, 1.71 mmol) in 2-butanone (10 mL) was heated to reflux for 48 h. Acetone (10 mL) was added, the mixture filtered through silica gel and the silica layer washed twice with acetone (10 mL). The combined filtrate was evaporated to dryness and the residue recrystallised from acetone/diethyl ether. Yield 665 mg (85%), yellow-brown crystalline solid, m.p. 199 °C (dec.). ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 3.74 (s, 3 H, OCH_3), 5.79 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 56.1 (s, O*C*H$_3$), 94.7 (s, *C*$_5$H$_5$), 194.9 (d, $^2J_{P,C}$ = 10 Hz, *C*O) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 0.9 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2029 (CO), 1763 (NO) cm^{-1}. $C_{25}H_{22}BF_4NO_3PRe$ (688.44): calcd. C 43.62, H 3.22, N 2.03; found C 44.03, H 3.48, N 2.00.

[CpRe(CO)(NO){PPh$_2$(CH$_2$C$_4$H$_3$S)}]BF$_4$ (3b): A solution of acetonitrile complex **2** (615 mg, 1.41 mmol) and phosphane **1b** (500 mg, 1.77 mmol) in 2-butanone (15 mL) was heated to reflux for 48 h. Acetone (10 mL) was added, the mixture filtered through silica gel and the silica layer washed twice with acetone (8 mL). The combined filtrate was evaporated to dryness and the residue recrystallised twice from dichloromethane/diethyl ether and finally washed with petroleum ether. Yield 840 mg (83%), yellow crystalline solid, m.p. 106 °C (dec.). ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 4.41, 4.51 (ABX system, $^2J_{H,H}$ = 15.0 Hz, $^2J_{P,H}$ = 10.4 Hz, 2 H, PCH_2), 5.74 (s, 5 H, C_5H_5), 6.64 (m, 1 H, thiophene *H*), 6.87 (m, 1 H, thiophene *H*), 7.17 (m, 1 H, thiophene *H*) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 35.1 (d, $^1J_{P,C}$ = 35 Hz, P*C*H$_2$), 94.4 (s, *C*$_5$H$_5$), 126.9 (d, $^4J_{P,C}$ = 4 Hz, thiophene *C*H), 127.7 (d, $^4J_{P,C}$ = 3 Hz, thiophene *C*H), 129.7 (d, $^3J_{P,C}$ = 7 Hz, thiophene *C*H), 132.5 (d, $^2J_{P,C}$ = 6 Hz, PCH$_2$*C*), 194.7 (d, $^2J_{P,C}$ = 9 Hz, *C*O) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 14.6 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2016 (CO), 1767 (NO) cm^{-1}. $C_{23}H_{20}BF_4NO_2PReS\cdot(C_2H_5)_2O$ (715.53): calcd. C 41.97, H 3.52, N 1.96, S 4.48; found C 41.47, H 3.30, N 1.96, S 4.57.

[CpRe(CO)(NO){PPh$_2$(CH$_2$C$_4$H$_7$O)}]BF$_4$ (3c): A solution of acetonitrile complex **2** (1.00 g, 2.29 mmol) and phosphane **1c** (0.88 g, 3.26 mmol) in 2-butanone (20 mL) was heated to reflux for 48 h. Acetone (20 mL) was added, the mixture filtered through silica gel and the silica layer washed twice with acetone (10 mL). The combined filtrate was evaporated to dryness and the residue washed with diethyl ether. Yield 1.45 g (95%), yellow crystalline solid, m.p. 156 °C (dec.). Both diastereomers: ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 1.60−2.11 (m, 8 H, CH_2CH_2), 2.92−3.19 (m, 4 H, PCH_2), 3.53−3.85 (m, 6 H, CH_2OCH), 5.77 (d, $^3J_{P,H}$ = 0.4 Hz, 5 H, C_5H_5), 5.78 (d, $^3J_{P,H}$ = 0.4 Hz, 5 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 25.1 (s, *C*H$_2$), 25.2 (s, *C*H$_2$), 33.5 (d, $^3J_{P,C}$ = 12 Hz, *C*H$_2$), 33.6 (d, $^3J_{P,C}$ = 12 Hz, *C*H$_2$), 37.9 (d, $^1J_{P,C}$ = 37 Hz, P*C*H$_2$), 38.3 (d, $^1J_{P,C}$ = 37 Hz, P*C*H$_2$), 68.3 (s, O*C*H$_2$), 68.4 (s, O*C*H$_2$), 74.2 (d, $^2J_{P,C}$ = 3 Hz, O*C*H), 74.5 (d, $^2J_{P,C}$ = 3 Hz, O*C*H), 94.3 (s, *C*$_5$H$_5$), 195.4 (d, $^2J_{P,C}$ = 8 Hz, *C*O), 195.5 (d, $^2J_{P,C}$ = 8 Hz, *C*O) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 2.6 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2019 (CO), 1763 (NO) cm^{-1}. $C_{23}H_{24}BF_4NO_3PRe$ (666.43): calcd. C 41.45, H 3.63, N 2.10; found C 41.34, H 3.88, N 1.90.

[CpRe(CO)(NO){P(Ph)(Me)(2-C$_6$H$_4$OMe)}]BF$_4$ (3d): A solution of acetonitrile complex **2** (1.00 g, 2.29 mmol) and phosphane **1d** (1.00 g, 4.34 mmol) in 2-butanone (20 mL) was heated to reflux for 30 h. Acetone (20 mL) was added, the mixture filtered through silica gel and the silica layer washed twice with acetone (10 mL). The solvent was removed under vacuum and the oily residue dissolved in THF (10 mL). Upon stirring, a yellow solid separated which was collected by filtration and washed repeatedly with THF until the washings remained almost colourless. Yield 0.88 g (62%), bright yellow crystalline solid, m.p. 134 °C. Both diastereomers: ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 2.46 (d, $^2J_{P,H}$ = 10.4 Hz, 3 H, PCH_3), 2.52 (d, $^2J_{P,H}$ = 10.4 Hz, 3 H, PCH_3), 3.73 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 5.82 (s, 10 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 20.3 (d, $^1J_{P,C}$ = 42 Hz, P*C*H$_3$), 20.4 (d, $^1J_{P,C}$ = 42 Hz, P*C*H$_3$), 56.0 (s, O*C*H$_3$), 56.2 (s, O*C*H$_3$), 94.2 (s, *C*$_5$H$_5$), 94.2 (s, *C*$_5$H$_5$), 195.2 (d, $^2J_{P,C}$ = 9 Hz, *C*O), 195.8 (d, $^2J_{P,C}$ = 9 Hz, *C*O) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = −15.0 (s), −13.0 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2021 (CO), 1763 (NO) cm^{-1}. $C_{20}H_{20}BF_4NO_3PRe$ (626.37): calcd. C 38.35, H 3.22, N 2.24; found C 38.60, H 3.35, N 2.22.

[CpRe(CO)(NO){P(Ph)(Me)(CH$_2$C$_4$H$_3$S)}]BF$_4$ (3e): A solution of acetonitrile complex **2** (600 mg, 1.37 mmol) and phosphane **1e** (400 mg, 1.82 mmol) in 2-butanone (15 mL) was heated to reflux for 4 h. Upon cooling, a yellow precipitate formed. Diethyl ether (15 mL) was added and the solid was collected by filtration and washed with THF. Yield 640 mg (76%), yellow crystalline solid, m.p. 233 °C. Both diastereomers: ^{1}H NMR (400 MHz, CD_3CN, 20 °C): δ = 2.19 (d, $^2J_{P,H}$ = 10.4 Hz, 3 H, PCH_3), 2.19 (d, $^2J_{P,H}$ = 10.4 Hz, 3 H, PCH_3), 4.04, 4.13 (ABX system, $^2J_{H,H}$ = 15.7, $^2J_{P,H}$ = 9.3 Hz, 2 H, PCH_2), 4.07, 4.11 (ABX system, $^2J_{H,H}$ = 15.4, $^2J_{P,H}$ = 10.0 Hz, 2 H, PCH_2), 5.88 (d, $^3J_{P,H}$ = 0.6 Hz, 5 H, C_5H_5), 5.90 (d, $^3J_{P,H}$ = 0.6 Hz, 5 H, C_5H_5), 6.80 (m, 2 H, thiophene *H*), 6.93 (m, 2 H, thiophene *H*), 7.27 (m, 2 H, thiophene *H*) ppm. ^{13}C NMR (100 MHz, CD_3CN, 20 °C): δ = 16.1 (d, $^1J_{P,C}$ = 40 Hz, P*C*H$_3$), 16.2 (d, $^1J_{P,C}$ = 40 Hz, P*C*H$_3$), 35.2 (d, $^1J_{P,C}$ = 34 Hz, P*C*H$_2$), 35.4 (d, $^1J_{P,C}$ = 34 Hz, P*C*H$_2$), 94.7 (d, $^2J_{P,C}$ = 1 Hz. *C*$_5$H$_5$), 94.8 (d, $^2J_{P,C}$ = 1 Hz. *C*$_5$H$_5$), 127.1 (d, 4$J_{P,C}$ = 4 Hz, thiophene *C*H), 127.1 (d, 4$J_{P,C}$ = 4 Hz, thiophene *C*H), 128.3 (d, 4$J_{P,C}$ = 4 Hz, thiophene *C*H), 128.3 (d, 4$J_{P,C}$ = 4 Hz, thiophene *C*H), 129.7 (d, 3$J_{P,C}$ = 7 Hz, thiophene *C*H), 129.8 (d, 3$J_{P,C}$ = 7 Hz, thiophene *C*H), 134.1 (d, $^2J_{P,C}$ = 10 Hz, PCH$_2$*C*), 134.2 (d, $^2J_{P,C}$ = 10 Hz, PCH$_2$*C*), 195.9 (d, $^2J_{P,C}$ = 7 Hz, *C*O), 195.9 (d, $^2J_{P,C}$ = 7 Hz, *C*O) ppm. ^{31}P NMR (162 MHz, CD_3CN, 20 °C): δ = −6.4 (s), −5.5 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 2016 (CO), 1763 (NO) cm^{-1}. $C_{18}H_{18}BF_4NO_2PReS$ (616.40): calcd. C 35.07, H 2.94, N 2.27, S 5.20; found C 34.83, H 2.92, N 2.30, S 5.09.

[CpRe(NO){PPh$_2$(2-C$_6$H$_4$OMe)}(CH$_3$)] (4a): To a suspension of carbonyl complex **3a** (300 mg, 0.44 mmol) in THF (15 mL) was added $NaBH_4$ (50 mg, 1.32 mmol). The colour of the mixture changed from brown to red and a gas was evolved. After 2 h, the solution was evaporated to dryness, the residue dissolved in benzene (15 mL), filtered through silica gel and the silica washed with benzene. The clear, orange filtrate was evaporated to 1 mL and the product precipitated upon addition of petroleum ether and storing overnight at −30 °C. Yield 220 mg (87%), orange crystalline solid, m.p. 55 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 1.45 (d, $^3J_{P,H}$ = 6.4 Hz, 3 H, ReCH_3), 3.05 (s, 3 H, OCH_3), 4.61 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = −35.7 (d, $^2J_{P,C}$ = 7 Hz, Re*C*H$_3$), 55.0 (s, O*C*H$_3$), 89.6 (d, $^2J_{P,C}$ = 2 Hz, *C*$_5$H$_5$)

ppm. ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = 21.4 (s) ppm. IR (THF): $\tilde{\nu}$ = 1637 (NO) cm^{-1}. $C_{25}H_{25}NO_2PRe$ (588.66): calcd. C 51.01, H 4.28, N 2.38; found C 50.86, H 4.37, N 2.27.

[CpRe(NO){PPh$_2$(CH$_2$C$_4$H$_3$S)}(CH$_3$)] (4b): To a suspension of carbonyl complex **3b** (270 mg, 0.40 mmol) in THF (15 mL) was added $NaBH_4$ (50 mg, 1.32 mmol). The colour of the mixture changed from brown to red and a gas was evolved. After 2 h, the solution was evaporated to dryness, the residue dissolved in benzene (20 mL), filtered through silica gel and celite and the filter aid washed with benzene. The solvent was removed under vacuum and the residue dissolved in boiling hexane (40 mL). The solution was filtered hot over celite and the solvents evaporated to 10 mL. The initial crystallisation was completed by storing the mixture overnight at −30 °C. Yield 174 mg (76%), orange crystalline solid, m.p. 86 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 1.42 (d, $^3J_{P,H}$ = 5.8 Hz, 3 H, ReCH_3] 3.95, 4.01 (ABX system, $^2J_{H,H}$ = 15.0, $^2J_{P,H}$ = 9.0 Hz, 2 H, PCH_2), 4.50 (s, 5 H, C_5H_5), 6.46 (m, 1 H, thiophene *H*), 6.54 (m, 1 H, thiophene *H*), 6.64 (m, 1 H, thiophene *H*) ppm. ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = −38.7 (d, $^2J_{P,C}$ = 8 Hz, ReCH$_3$), 32.9 (d, $^1J_{P,C}$ = 29 Hz, PCH$_2$), 89.0 (d, $^2J_{P,C}$ = 2 Hz. C_5H_5), 124.4 (d, $^4J_{P,C}$ = 3 Hz, thiophene *C*H), 126.8 (d, $^4J_{P,C}$ = 2 Hz, thiophene *C*H), 136.7 (d, $^2J_{P,C}$ = 6 Hz, PCH$_2$*C*) ppm. ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = 19.7 (s) ppm. IR (THF): $\tilde{\nu}$ = 1634 (NO) cm^{-1}. $C_{23}H_{23}NOPReS$ (578.69): calcd. C 47.74, H 4.01, N 2.42, S 5.54; found C 48.17, H 4.18, N 2.32, S 5.60.

[CpRe(NO){PPh$_2$(CH$_2$C$_4$H$_7$O)}(CH$_3$)] (4c): To a solution of carbonyl complex **3c** (390 mg, 0.59 mmol) in THF (20 mL) was added $NaBH_4$ (70 mg, 1.85 mmol) at −78 °C. After 30 min at that temperature, the mixture was allowed to warm to 20 °C which was accompanied by gas evolution. The mixture was filtered through silica gel and the silica washed with THF. After evaporation of the solvent, the residue was dissolved in benzene (20 mL), the solution filtered through celite and the solvents evaporated again. The residue was finally recrystallised at −78 °C from toluene (2 mL) and hexane (10 mL). Yield 265 mg (80%), orange powder, m.p. 40 °C. Both diastereomers: ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 0.66−0.97 (m, 2 H, CH_2), 1.03−1.44 (m, 4 H, CH_2), 1.49 (d, $^3J_{P,H}$ = 5.5 Hz, 3 H, ReCH_3), 1.52 (d, $^3J_{P,H}$ = 5.6 Hz, 3 H, ReCH_3), 2.53−2.88 (m, 2 H, CH_2), 3.22−3.64 (m, 4 H, CH_2), 4.13−4.41 (m, 2 H, C*H*), 4.49 (s, 5 H, C_5H_5), 4.61 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = −39.8 (d, $^2J_{P,C}$ = 7 Hz, Re*C*H$_3$), −38.6 (d, $^2J_{P,C}$ = 7 Hz, Re*C*H$_3$), 25.9 (s, *C*H$_2$), 26.2 (s, *C*H$_2$), 32.7 (d, $^3J_{P,C}$ = 3 Hz, *C*H$_2$), 32.9 (d, $^3J_{P,C}$ = 8 Hz, *C*H$_2$), 37.5 (d, $^1J_{P,C}$ = 31 Hz, P*C*H$_2$), 39.2 (d, $^1J_{P,C}$ = 35 Hz, P*C*H$_2$), 67.0 (s, O*C*H$_2$), 67.4 (s, O*C*H$_2$), 76.3 (d, $^2J_{P,C}$ = 7 Hz, O*C*H), 77.0 (d, $^2J_{P,C}$ = 2 Hz, O*C*H), 89.2 (d, $^2J_{P,C}$ = 2 Hz. C_5H_5), 89.3 (d, $^2J_{P,C}$ = 2 Hz. C_5H_5) ppm. ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = 8.1 (s), 11.1 (s) ppm. IR (THF): $\tilde{\nu}$ = 1632 (NO) cm^{-1}. $C_{23}H_{27}NO_2PRe$ (588.65): calcd. C 48.75, H 4.80, N 2.47; found C 48.56, H 4.70, N 2.36.

[CpRe(NO){P(Ph)(Me)(2-C$_6$H$_4$OMe}](CH$_3$)] (4d): To a suspension of carbonyl complex **3d** (500 mg, 0.80 mmol) in THF (15 mL) was added $NaBH_4$ (95 mg, 2.50 mmol). The colour of the mixture changed from brown to red and a gas was evolved. After 2 h, the reaction was worked up as described for **4b**. Yield 344 mg (82%), orange-red crystalline powder, m.p. 206 °C (dec.). Both diastereomers: ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 1.25 (d, $^3J_{P,H}$ = 6.2 Hz, 3 H, ReCH_3), 1.26 (d, $^3J_{P,H}$ = 6.4 Hz, 3 H, ReCH_3), 1.97 (d, $^2J_{P,H}$ = 8.8 Hz, 3 H, PCH_3), 1.99 (d, $^2J_{P,H}$ = 9.1 Hz, 3 H, PCH_3), 2.89 (s, 3 H, OCH_3), 3.02 (s, 3 H, OCH_3), 4.65 (s, 5 H, C_5H_5), 4.71 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = −38.7 (d, $^2J_{P,C}$ = 6 Hz, Re*C*H$_3$), −38.7 (d, $^2J_{P,C}$ = 6 Hz, Re*C*H$_3$), 15.9 (d, $^1J_{P,C}$ = 35 Hz, P*C*H$_3$), 16.5 (d, $^1J_{P,C}$ = 35 Hz, P*C*H$_3$), 54.7 (s, O*C*H$_3$), 55.0 (s, O*C*H$_3$), 88.5 (d, $^2J_{P,C}$ = 2 Hz, C_5H_5), 88.7 (d, $^2J_{P,C}$ = 2 Hz, C_5H_5]) ppm. ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = −1.2 (s), 0.5 (s) ppm. IR (THF): $\tilde{\nu}$ = 1636 (NO) cm^{-1}. $C_{20}H_{23}NO_2PRe$ (526.59): calcd. C 45.62, H 4.40, N 2.66; found C 45.95, H 4.50, N 2.62.

[CpRe(NO){P(Ph)(Me)(CH$_2$C$_4$H$_3$S)}(CH$_3$)] (4e): To a suspension of carbonyl complex **3e** (350 mg, 0.57 mmol) in THF (15 mL) was added $NaBH_4$ (65 mg, 1.72 mmol). The mixture turned red and a gas was evolved. After 2 h, the reaction was worked up as described for **4a**. Yield 237 mg (81%), orange crystalline powder, m.p. 67 °C. Recrystallisation from hot petroleum ether gave a sample enriched in one diastereomer. Major (68%) diastereomer: ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 1.12 (d, $^3J_{P,H}$ = 6.2 Hz, 3 H, ReCH_3), 1.44 (d, $^2J_{P,H}$ = 8.6 Hz, 3 H, PCH_3), 3.47, 3.61 (ABX system, $^2J_{H,H}$ = 15.0, $^2J_{P,H}$ = 8.6 Hz, 2 H, PCH_2), 4.52 (s, 5 H, C_5H_5), 6.40 (m, 1 H, thiophene *H*), 6.57 (m, 1 H, thiophene *H*), 6.64 (m, 1 H, thiophene *H*) ppm. ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = −39.3 (d, $^2J_{P,C}$ = 7 Hz, Re*C*H$_3$), 15.1 (d, $^1J_{P,C}$ = 36 Hz, P*C*H$_3$), 33.7 (d, $^1J_{P,C}$ = 30 Hz, P*C*H$_2$), 87.9 (d, $^2J_{P,C}$ = 2 Hz. C_5H_5), 124.2 (d, $^4J_{P,C}$ = 3 Hz, thiophene *C*H), 126.8 (d, $^4J_{P,C}$ = 2 Hz, thiophene *C*H), 127.5 (d, $^3J_{P,C}$ = 5 Hz, thiophene *C*H), 137.2 (d, $^2J_{P,C}$ = 8 Hz, PCH$_2$*C*) ppm. ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = −0.9 (s) ppm. Minor (32%) diastereomer: ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 1.22 (d, $^3J_{P,H}$ = 6.1 Hz, 3 H, ReCH_3), 1.40 (d, $^2J_{P,H}$ = 8.6 Hz, 3 H, PCH_3), 3.67, 3.69 (ABX system, $^2J_{H,H}$ = 15.7, $^2J_{P,H}$ = 7.5 Hz, 2 H, PCH_2), 4.54 (s, 5 H, C_5H_5), 6.23 (m, 1 H, thiophene *H*), 6.53 (m, 1 H, thiophene *H*), 6.62 (m, 1 H, thiophene *H*) ppm. ^{13}C NMR (100 MHz, C_6D_6, 20 °C): δ = −40.2 (d, $^2J_{P,C}$ = 7 Hz, Re*C*H$_3$), 11.2 (d, $^1J_{P,C}$ = 32 Hz, P*C*H$_3$), 33.2 (d, $^1J_{P,C}$ = 30 Hz, P*C*H$_2$), 88.0 (d, $^2J_{P,C}$ = 2 Hz. C_5H_5), 124.3 (d, $^4J_{P,C}$ = 3 Hz, thiophene *C*H), 126.7 (d, $^4J_{P,C}$ = 3 Hz, thiophene *C*H), 127.3 (d, $^3J_{P,C}$ = 5 Hz, thiophene *C*H), 136.9 (d, $^2J_{P,C}$ = 10 Hz, PCH$_2$*C*) ppm. ^{31}P NMR (162 MHz, C_6D_6, 20 °C): δ = −4.0 (s) ppm. Both diastereomers: IR (THF): $\tilde{\nu}$ = 1631 (NO) cm^{-1}. $C_{18}H_{21}NOPReS$ (516.62): calcd. C 41.85, H 4.10, N 2.71, S 6.21; found C 42.00, H 4.09, N 2.67, S 5.84.

Chelate Complexes 5b−e: At −78 °C, HBF_4 in diethyl ether (150 µL, ca. 1.50 mmol) was added to a solution of the respective methyl complex (0.38 mmol) in dichloromethane (10 mL). Gas evolution and a change of colour from red to brown was observed. After 1 h, the temperature was raised to 20 °C and the solvents were evaporated to 2 mL. The product, which was precipitated by addition of diethyl ether, was filtered off and washed with diethyl ether and petroleum ether.

[CpRe(NO)(κPPh$_2$(CH$_2$C$_4$H$_3$κS))]BF$_4$ (5b): Yield 212 mg (86%), yellow crystalline solid, m.p. 218 °C (dec.). ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 3.64, 4.01 (ABMX system, $^2J_{H,H}$ = 16.2, $^2J_{P,H}$ = 11.2, $^4J_{H,H}$ = 1.2 Hz, 2 H, PCH_2), 5.49 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 27.7 (d, $^1J_{P,C}$ = 32 Hz, P*C*H$_2$), 91.8 (d, $^2J_{P,C}$ = 1 Hz, C_5H_5), 132.0 (d, $^4J_{P,C}$ = 3 Hz, thiophene *C*H), 133.2 (d, $^4J_{P,C}$ = 3 Hz, thiophene *C*H), 134.9 (d, $^3J_{P,C}$ = 3 Hz, thiophene *C*H), 161.4 (d, $^2J_{P,C}$ = 3 Hz, PCH$_2$*C*) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 34.5 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1722 (NO) cm^{-1}. $C_{22}H_{20}BF_4NOPReS$ (650.46): calcd. C 40.62, H 3.10, N 2.15, S 4.93; found C 39.67, H 3.27, N 2.02, S 4.68.

[CpRe(NO){κPPh$_2$(CH$_2$C$_4$H$_7$κO)}]BF$_4$ (5c): Yield 243 mg (99%), brownish solid, m.p. 182 °C (dec.). Both diastereomers: ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 1.90−2.04 (m, 1 H, CH_2), 2.05−2.49 (m, 9 H, CH_2), 2.73−2.89 (m, 2 H, CH_2), 4.06−4.18

(m, 1 H, C*H*), 4.27−4.33 (m, 1 H, C*H*), 4.35−4.54 (m, 4 H, PCH_2), 5.49 (s, 5 H, C_5H_5), 5.52 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 28.2 (s, *C*H_2), 28.5 (s, *C*H_2), 29.7 (d, $^3J_{P,C}$ = 11 Hz, *C*H_2), 31.6 (d, $^3J_{P,C}$ = 10 Hz, *C*H_2), 31.8 (d, $^1J_{P,C}$ = 28 Hz, P*C*H_2), 35.8 (d, $^1J_{P,C}$ = 27 Hz, P*C*H_2), 88.7 (s, O*C*H_2), 89.7 (s, O*C*H_2), 90.8 (d, $^2J_{P,C}$ = 2 Hz, C_5H_5), 91.1 (d, $^2J_{P,C}$ = 2 Hz, C_5H_5), 95.8 (s, O*C*H), 97.9 (s, O*C*H) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 35.3 (s), 37.5 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1690 (NO) cm^{-1}. $C_{22}H_{24}BF_4NO_2PRe$ (638.42): calcd. C 41.39, H 3.79, N 2.19; found C 41.09, H 3.93, N 1.97.

[CpRe(NO){κP(Ph)(Me)(CH$_2$C$_4$H$_3$κS)}]BF$_4$ (5e): Yield 204 mg (91%), yellow crystalline powder, m.p. 69 °C (dec.). Careful extraction with THF gave a sample enriched in one diastereomer. Major diastereomer: ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 2.19 (d, $^2J_{P,H}$ = 10.2 Hz, 3 H, PCH_3), 3.06−3.63 (m, 2 H, PCH_2), 5.45 (d, $^3J_{P,H}$ = 0.3 Hz, 5 H, C_5H_5). ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 14.7 (d, $^1J_{P,C}$ = 39 Hz, P*C*H$_3$), 26.3 (d, $^1J_{P,C}$ = 32 Hz, P*C*H$_2$), 91.6 (s, C_5H_5), 161.5 (d, $^2J_{P,C}$ = 2 Hz, PCH$_2$*C*). ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 11.3 (s) ppm. Minor diastereomer: ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 2.21 (d, $^2J_{P,H}$ = 10.0 Hz, 3 H, PCH_3), 3.06−3.63 (m, 2 H, PCH_2), 5.83 (d, $^3J_{P,H}$ = 0.2 Hz, 5 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 18.1 (d, $^1J_{P,C}$ = 36 Hz, P*C*H$_3$), 26.5 (d, $^1J_{P,C}$ = 33 Hz, P*C*H$_2$), 90.7 (s, C_5H_5), 163.0 (s, PCH$_2$*C*) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 15.6 (s) ppm. Both diastereomers: IR (CH_2Cl_2): $\tilde{\nu}$ = 1718 (NO) cm^{-1}. $C_{17}H_{18}BF_4NOPReS$ (588.39): calcd. C 34.70, H 3.08, N 2.38, S 5.45; found C 34.62, H 3.36, N 2.28, S 5.19.

Acetonitrile Complexes 6b−e: A solution of the respective chelate complex (0.20 mmol) in acetonitrile (5 mL) was kept for 24 h at 20 °C. The solvents were evaporated to dryness and the product recrystallised from dichloromethane/diethyl ether.

[CpRe(NO){PPh$_2$(CH$_2$C$_4$H$_3$S)}(NCCH$_3$)]BF$_4$ (6b): Yield 125 mg 90%), yellow crystalline solid, m.p. 232 °C (dec.). ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 2.63 (d, $^5J_{P,H}$ = 1.2 Hz, 3 H, NCCH_3), 4.31, 4.46 (ABX system, $^2J_{H,H}$ = 15.1, $^2J_{P,H}$ = 10.1 Hz, 2 H, PCH_2), 5.40 (s, 5 H, C_5H_5), 6.72 (m, 1 H, thiophene *H*), 6.87 (m, 1 H, thiophene *H*), 7.13 (m, 1 H, thiophene *H*) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 4.9 (s, NC*C*H$_3$), 33.0 (d, $^1J_{P,C}$ = 33 Hz, P*C*H$_2$), 91.9 (s, C_5H_5), 126.0 (d, $^4J_{P,C}$ = 4 Hz, thiophene *C*H), 127.4 (d, $^4J_{P,C}$ = 3 Hz, thiophene *C*H), 129.4 (d, $^3J_{P,C}$ = 7 Hz, thiophene *C*H), 134.5 (d, $^2J_{P,C}$ = 4 Hz, PCH$_2$*C*), 141.3 (s, N*C*CH$_3$) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 9.2 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1705 (NO) cm^{-1}. $C_{24}H_{23}BF_4N_2OPReS$ (691.51): calcd. C 41.69, H 3.35, N 4.05, S 4.64; found C 40.65, H 3.54, N 3.67, S 4.48.

[CpRe(NO){PPh$_2$(CH$_2$C$_4$H$_7$O)}(NCCH$_3$)]BF$_4$ (6c): Yield 112 mg (82%), yellow-brown solid, m.p. 139 °C (dec.). Both diastereomers: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20 °C): δ = 1.66−2.17 (m, 6 H, CH_2), 2.89 (d, $^5J_{P,H}$ = 1.2 Hz, 3 H, NCCH_3), 2.95 (d, $^5J_{P,H}$ = 1.2 Hz, 3 H, NCCH_3), 2.86−3.10 (m, 4 H, PCH_2), 3.14−3.29 (m, 2 H, CH_2), 3.50−3.58 (m, 2 H, CH_2), 3.65−3.75 (m, 2 H, CH_2), 3.95−4.05 (m, 2 H, C*H*), 5.70 (s, 5 H, C_5H_5), 5.75 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone, 20 °C): δ = 4.5 (s, NC*C*H$_3$), 4.5 (s, NC*C*H$_3$), 25.9 (s, *C*H$_2$), 25.9 (s, *C*H$_2$), 33.6 (d, $^3J_{P,C}$ = 10 Hz, *C*H$_2$), 33.7 (d, $^3J_{P,C}$ = 10 Hz, *C*H$_2$), 37.0 (d, $^1J_{P,C}$ = 34 Hz, P*C*H$_2$), 37.4 (d, $^1J_{P,C}$ = 35 Hz, P*C*H$_2$), 68.1 (s, O*C*H$_2$), 68.2 (s, O*C*H$_2$), 75.9 (s, O*C*H), 76.4 (s, O*C*H), 92.7 (d, $^2J_{P,C}$ = 1 Hz, C_5H_5), 92.8 (d, $^2J_{P,C}$ = 1 Hz, C_5H_5) ppm, N*C*CH$_3$ not observed. ^{31}P NMR (162 MHz, [D$_6$]acetone, 20 °C): δ = 1.9 (s), 2.7 (s) ppm. IR (CH_3CN): $\tilde{\nu}$ = 1702 (NO) cm^{-1}. $C_{24}H_{27}BF_4N_2O_2PRe$ (679.48): calcd. C 42.42, H 4.01, N 4.12; found. C 41.96, H 4.03, N 3.97.

[CpRe(NO){P(Ph)(Me)(CH$_2$C$_4$H$_3$S)}(NCCH$_3$)]BF$_4$ (6e): Yield 117 mg (93%), dark yellow crystalline solid, m.p. 114 °C. Both diastereomers: ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 2.04 (d, $^2J_{P,H}$ = 9.5 Hz, 3 H, PCH_3), 2.04 (d, $^2J_{P,H}$ = 9.6 Hz, 3 H, PCH_3), 2.42 (d, $^5J_{P,H}$ = 1.3 Hz, 3 H, NCCH_3), 2.80 (d, $^5J_{P,H}$ = 1.3 Hz, 3 H, NCCH_3), 3.95 (m, 4 H, PCH_2), 5.44 (s, 5 H, C_5H_5), 5.53 (s, 5 H, C_5H_5), 6.74 (m, 1 H, thiophene *H*), 6.82 (m, 1 H, thiophene *H*), 6.90 (m, 1 H, thiophene *H*), 6.96 (m, 1 H, thiophene *H*), 7.15 (m, 1 H, thiophene *H*), 7.23 (m, 1 H, thiophene *H*) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 4.3 (s, NC*C*H$_3$), 5.1 (s, NC*C*H$_3$), 13.3 (d, $^1J_{P,C}$ = 37 Hz, P*C*H$_3$), 13.5 (d, $^1J_{P,C}$ = 37 Hz, P*C*H$_3$), 33.2 (d, $^1J_{P,C}$ = 31 Hz, P*C*H$_2$), 33.8 (d, $^1J_{P,C}$ = 35 Hz, P*C*H$_2$), 91.1 (d, $^2J_{P,C}$ = 1 Hz, C_5H_5), 91.4 (d, $^2J_{P,C}$ = 1 Hz, C_5H_5), 125.7 (d, $4J_{P,C}$ = 4 Hz, thiophene *C*H), 125.9 (d, $4J_{P,C}$ = 4 Hz, thiophene *C*H), 127.5 (d, $^4J_{P,C}$ = 3 Hz, thiophene *C*H), 127.7 (d, $^4J_{P,C}$ = 3 Hz, thiophene *C*H), 128.7 (d, $^3J_{P,C}$ = 7 Hz, thiophene *C*H), 128.7 (d, $^3J_{P,C}$ = 7 Hz, thiophene *C*H), 134.2 (d, $^2J_{P,C}$ = 10 Hz, PCH$_2$*C*), 134.5 (d, $^2J_{P,C}$ = 8 Hz, PCH$_2$*C*), 139.7 (s, N*C*CH$_3$), 140.8 (s, N*C*CH$_3$) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = −11.8 (s), −6.9 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1699 (NO) cm^{-1}. $C_{19}H_{21}BF_4N_2OPReS$ (629.44): calcd. C 36.26, H 3.36, N 4.45, S 5.09; found. C 36.16, H 3.50, N 4.29, S 4.93.

[CpRe(NO){P(Ph)(Me)(2-C$_6$H$_4$OMe)}(NCCH$_3$)]BF$_4$ (6d): To a cold (−78 °C) solution of methyl complex **4d** (65 mg, 0.12 mmol) in dichloromethane (3 mL) and acetonitrile (1 mL) was added ethereal HBF_4 (25 μL, ca. 0.25 mmol). The mixture was kept cold for 1 h and was then allowed to warm to room temperature. The solvent was removed under vacuum, the residue dissolved in dichloromethane (1 mL) and the product precipitated by the addition of diethyl ether. Yield 78 mg (99%), yellow crystalline solid, m.p. 183 °C (dec.). Both diastereomers: ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 2.24 (d, $^2J_{P,H}$ = 9.5 Hz, 3 H, PCH_3), 2.36 (d, $^2J_{P,H}$ = 9.8 Hz, 3 H, PCH_3), 2.42 (d, $^5J_{P,H}$ = 1.5 Hz, 3 H, NCCH_3), 2.63 (d, $^5J_{P,H}$ = 1.4 Hz, 3 H, NCCH_3), 3.59 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 5.57 (s, 5 H, C_5H_5), 5.60 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 4.0 (s, NC*C*H$_3$), 4.5 (s, NC*C*H$_3$), 16.8 (d, $^1J_{P,C}$ = 38 Hz, P*C*H$_3$), 18.9 (d, $^1J_{P,C}$ = 39 Hz, P*C*H$_3$), 56.0 (s, O*C*H$_3$), 56.0 (s, O*C*H$_3$), 91.3 (d, $^2J_{P,C}$ = 1 Hz, C_5H_5), 91.7 (d, $^2J_{P,C}$ = 1 Hz, C_5H_5), 139.5 (s, N*C*CH$_3$), 140.2 (s, N*C*CH$_3$) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = −12.1 (s), −11.2 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1705 (NO) cm^{-1}. $C_{21}H_{23}BF_4N_2O_2PRe$ (639.41): calcd. C 39.45, H 3.63, N 4.38; found C 38.26, H 3.95, N 4.06.

[CpRe(NO){P(Ph)(Me)(2-C$_6$H$_4$OMe)}(THF)]BF$_4$ (7d): To a cold (−78 °C) solution of methyl complex **4d** (210 mg, 0.40 mmol) in THF (20 mL) was added ethereal HBF_4 (100 μL, ca. 1.0 mmol). The mixture was kept cold for 1 h and was then warmed to room temperature. The solvents were evaporated to 10 mL and the product precipitated upon the addition of diethyl ether. Yield 235 mg (88%) pink powder, m.p. 88 °C (dec.). Major diastereomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20 °C): δ = 1.72−1.82 (m, 4 H, CH_2), 2.41 (d, $^2J_{P,H}$ = 9.4 Hz, 3 H, PCH_3), 3.56−3.65 (m, 4 H, OCH_2), 3.63 (s, 3 H, OCH_3), 5.97 (s, 5 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone, 20 °C): δ = 18.4 (d, $^1J_{P,C}$ = 39 Hz, P*C*H$_3$), 26.1 (s, *C*H$_2$), 56.0 (s, O*C*H$_3$), 68.0 (s, O*C*H$_2$), 92.5 (d, $^2J_{P,C}$ = 1 Hz, C_5H_5) ppm. ^{31}P NMR (162 MHz, [D$_6$]acetone, 20 °C): δ = −6.2 (s) ppm. Minor diastereomer: ^{1}H NMR (400 MHz, [D$_6$]acetone, 20 °C): δ = 1.55−1.62 (m, 4 H, CH_2), 2.47 (d, $^2J_{P,H}$ = 10.1 Hz, 3 H, PCH_3), 3.35−3.42 (m, 4 H, OCH_2), 3.72 (s, 3 H, OCH_3), 5.90 (s 5 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone, 20 °C): δ = 16.3 (d, $^1J_{P,C}$ = 38 Hz, P*C*H$_3$), 27.4 (s, *C*H$_2$), 56.1 (s, O*C*H$_3$), 71.1 (s, O*C*H$_2$), 93.2 (d, $^2J_{P,C}$ = 1 Hz, C_5H_5) ppm. ^{31}P NMR (162 MHz,

Table 1. Details of the structure determinations of compounds **1b**·BH_3, **3a**, **3b**, **3d**−**AlF_4**, **4d**, **6e** and **7d**·CH_2Cl_2

	1b·BH_3	**3a**	**3b**	**3d**−**AlF_4**	**4d**	**6e**	**7d**·CH_2Cl_2
Empirical formula	$C_{14}H_{18}BOP$	$C_{25}H_{22}BF_4NO_3Pre$	$C_{23}H_{20}BF_4NO_2PReS$	$C_{20}H_{20}AlF_4NO_3PRe$	$C_{20}H_{23}NO_2PRe$	$C_{19}H_{21}BF_4N_2OPReS$	$C_{24}H_{30}BClF_4NO_3PRe$
Formula mass	244.06	688.42	678.44	642.52	526.56	629.42	755.40
Crystal colour/habit	colourless plate	yellow block	yellow block	yellow block	red block	yellow plate	red prism
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	10.5951(8)	16.1437(13)	9.954(2)	11.1876(7)	9.0940(8)	11.1343(10)	9.920(3)
b (Å)	9.6350(8)	8.9379(7)	10.401(2)	13.8896(9)	10.2778(9)	9.7129(9)	18.071(5)
c (Å)	15.7090(12)	19.4659(16)	12.264(3)	14.3243(9)	12.2877(10)	20.4158(19)	16.858(5)
α (°)	90	90	79.742(3)	90	66.838(1)	90	90
β (°)	90	114.265(1)	75.758(3)	107.106(1)	83.946(1)	90.767(2)	106.823(4)
γ (°)	90	90	77.036(3)	90	64.057(1)	90	90
V (Å^3)	1603.6(2)	2560.6(4)	1189.1(5)	2127.4(2)	946.42(14)	2207.7(4)	2892.8(15)
Θ (°)	2.48−28.27	2.30−26.44	2.45−28.24	2.04−28.23	1.81−28.25	2.32−28.27	1.69−28.11
h	−13 to 13	−20 to 18	−13 to 12	−14 to 14	−12 to 12	−14 to 14	−13 to 13
k	−12 to 12	−11 to 11	−13 to 13	−17 to 18	−13 to 13	−12 to 12	−23 to 23
l	−19 to 20	−23 to 24	−16 to 16	−18 to 18	−16 to 16	−26 to 26	−22 to 22
Z	4	4	2	4	2	4	4
μ(Mo-K_α) (mm^{-1})	0.288	4.865	5.318	5.886	6.517	5.718	4.493
Crystal size (mm)	0.20 × 0.10 × 0.05	0.25 × 0.20 × 0.15	0.20 × 0.20 × 0.15	0.20 × 0.20 × 0.15	0.15 × 0.15 × 0.10	0.15 × 0.10 × 0.05	0.15 × 0.15 × 0.10
$D_{calcd.}$ (g·cm^{-3})	1.227	1.786	1.895	2.006	1.848	1.894	1.734
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
Reflections collected	15200	20004	26949	35350	21707	48267	60709
Independent reflections	3600	5212	5489	5991	4397	5262	6827
Parameter	183	308	289	282	229	299	346
R_1 [$I > 2\sigma(I)$]	0.0617	0.0394	0.0352	0.0474	0.0244	0.0418	0.0492
R_1 (overall)	0.0646	0.0482	0.0357	0.0490	0.0260	0.0538	0.0542
wR_2 [$I > 2\sigma(I)$]	0.1449	0.1037	0.0898	0.1022	0.0581	0.0968	0.1164
wR_2 (overall)	0.1496	0.1084	0.0900	0.1037	0.0585	0.1010	0.1180
Diff. peak/hole (e·Å^{-3})	0.482/−0.342	1.994/−1.678	1.564/−1.850	2.163/−1.798	3.488/−1.133	1.781/−1.276	2.097/−3.014
CCDC	242558	242219	242220	242221	242222	242223	242224

[D_6]acetone, 20 °C): δ = −5.8 (s) ppm. Both diastereomers: IR (CH_2Cl_2): $\tilde{\nu}$ = 1701 (NO) cm^{-1}. $C_{23}H_{28}BF_4NO_3PRe$ (670.47): calcd. C 41.20, H 4.21, N 2.09; found C 40.49, H 4.18, N 2.00.

X-ray Structure Determinations: Single crystals of **1b**·BH_3, **3a**, **3b**, **3d**−**AlF_4**, **4d**, **6e** and **7d**·CH_2Cl_2 were bonded to a glass fibre with frozen hydrocarbon oil in each case. A Bruker Smart Apex CCD instrument was used for data collection (graphite monochromator, Mo-K_α radiation, λ = 0.71073 Å). The structures were solved using Patterson methods and refined with full-matrix least-squares against F^2 (SHELXS-97).[39] Hydrogen atoms were included in their calculated positions and refined using a riding model. The details of the measurements are summarised in Table 1. Further data may be obtained from the Cambridge Crystallographic Data Centre. CCDC-242558 (for **1b**·BH_3), -242219 (for **3a**), -242220 (for **3b**), -242221 (for **3d**−**AlF_4**), -242222 (for **4d**), -242223 (for **6e**) and -242224 (for **7d**·CH_2Cl_2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

[1] H. Brunner, *Angew. Chem.* **1969**, *81*, 395−396; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 382.
[2] H. Brunner, *Angew. Chem.* **1999**, *111*, 1248−1263; *Angew. Chem. Int. Ed.* **1999**, *38*, 1194−1208.
[3] S. G. Davies, *Aldrichimica Acta* **1990**, *23*, 31−37.
[4] 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.
[5] J. A. Gladysz, B. J. Boone, *Angew. Chem.* **1997**, *109*, 566−602; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 551−583.
[6] W. A. Schenk, N. Burzlaff, H. Burzlaff, *Z. Naturforsch., Teil B* **1994**, *49*, 1633−1639.
[7] N. Burzlaff, M. Hagel, W. A. Schenk, *Z. Naturforsch., Teil B* **1998**, *53*, 893−899.
[8] N. Burzlaff, W. A. Schenk, *Eur. J. Inorg. Chem.* **1998**, 2055−2061.
[9] N. Burzlaff, W. A. Schenk, *Eur. J. Inorg. Chem.* **1999**, 1435−1443.
[10] A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27−110.
[11] C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Progr. Inorg. Chem.* **1999**, *48*, 233−350.
[12] D. W. Allen, S. J. Grayson, I. Harness, B. G. Hutley, I. W. Mowat, *J. Chem. Soc., Perkin Trans. 2* **1973**, 1912−1915.
[13] E. Lindner, H. Rauleder, C. Scheytt, H. A. Mayer, W. Hiller, R. Fawzi, P. Wenger, *Z. Naturforsch., Teil B* **1984**, *39*, 632−642.
[14] K. Burgess, M. J. Ohlmeyer, K. H. Whitmire, *Organometallics* **1992**, *11*, 3588−3600.
[15] S. Jugé, M. Stephan, R. Merdès, J. P. Genet, S. Halut-Desportes, *J. Chem. Soc., Chem. Commun.* **1993**, 531−533.
[16] A. J. Rippert, A. Linden, H.-J. Hansen, *Helv. Chim. Acta* **2000**, *83*, 311−321.
[17] W. Tam, G.-Y. Lin, W.-K. Wong, W. A. Kiel, V. K. Wong, J. A. Gladysz, *J. Am. Chem. Soc.* **1982**, *104*, 141−152.
[18] W. Mohr, G. A. Stark, H. Jiao, J. A. Gladysz, *Eur. J. Inorg. Chem.* **2001**, 925−933.
[19] G. W. Stowell, R. R. Whittle, C. M. Whaley, D. P. White, *Organometallics* **2001**, *20*, 1050−1052.

[20] A. J. Amoroso, A. M. Arif, J. A. Gladysz, *Bull. Soc. Chim. Fr.* **1997**, *134*, 793−799.
[21] C. P. Casey, M. A. Andrews, D. R. McAlister, J. E. Rinz, *J. Am. Chem. Soc.* **1980**, *102*, 1927−1933.
[22] J. R. Sweet, W. A. G. Graham, *J. Am. Chem. Soc.* **1982**, *104*, 2811−2815.
[23] J. H. Merrifield, C. E. Strouse, J. A. Gladysz, *Organometallics* **1982**, *1*, 1204−1211.
[24] J. M. Fernández, J. A. Gladysz, *Organometallics* **1989**, *8*, 207−219.
[25] M. A. Dewey, Y. Zhou, Y. Liu, J. A. Gladysz, *Organometallics* **1993**, *12*, 3924−3932.
[26] J. J. Kowalczyk, S. K. Agbossou, J. A. Gladysz, *J. Organomet. Chem.* **1990**, *397*, 333−346.
[27] P. E. Garrou, *Chem. Rev.* **1981**, *81*, 229−266.
[28] B. de Klerk-Engels, J. H. Groen, K. Vrieze, A. Möckel, E. Lindner, K. Goubitz, *Inorg. Chim. Acta* **1992**, *195*, 237−243.
[29] S. K. Agbossou, J. M. Fernández, J. A. Gladysz, *Inorg. Chem.* **1990**, *29*, 476−480.
[30] N. Q. Méndez, A. M. Arif, J. A. Gladysz, *Organometallics* **1991**, *10*, 2199−2209.
[31] M. Otto, B. J. Boone, A. M. Arif, J. A. Gladysz, *J. Chem. Soc., Dalton Trans.* **2001**, 1218−1229.
[32] J. H. Merrifield, G.-Y. Lin, W. A. Kiel, J. A. Gladysz, *J. Am. Chem. Soc.* **1983**, *105*, 5811−5819.
[33] J. H. Merrifield, J. H. Fernández, W. E. Buhro, J. A. Gladysz, *Inorg. Chem.* **1984**, *23*, 4022−4029.
[34] J. H. Fernández, J. A. Gladysz, *Inorg. Chem.* **1986**, *25*, 2672−2674.
[35] W. A. Archer, R. Cook, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1983**, 813−819.
[36] W. E. McEwen, W.-I. Shiau, Y.-I. Yeh, D. N. Schulz, R. U. Pagilagan, J. B. Levy, C. Symmes Jr., G. O. Nelson, I. Granoth, *J. Am. Chem. Soc.* **1975**, *97*, 1787−1794.
[37] W. Wolfsberger, *Chemiker-Zeitung* **1988**, *112*, 379−381.
[38] D. Magiera, J. Omelanczuk, K. Dziuba, K. M. Pietrusiewicz, H. Duddeck, *Organometallics* **2003**, *22*, 2426−2471.
[39] G. M. Sheldrick, *SHELX-97, Programs for Crystal Structure Analysis*, University of Göttingen, Göttingen, Germany, **1997**.

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