

Optically active transition-metal complexes II. [☆]
Rhenium complexes with the optically active cyclopentadienyl ligand
PCp: X-ray structures of the *exo* and *endo* isomers of PCpRe(CO)₃
and of the derivative PCpReNO(CH₃)PPh₃

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Abstract

The synthesis of the optically active *exo* and *endo* isomers of PCpRe(CO)₃ [PCp = 'pinene-fused cyclopentadienyl'] is described. The yield and relative ratio of the two isomers is strongly dependent on solvent, temperature and the various starting materials Re(CO)₃L₂X [X = Cl, L = CO, THF, pyridine, CH₃CN, DME] as well as the derivative MPCp [M = Li, Tl] used. Both isomers have been characterized by crystal structure analyses. The *exo* isomer undergoes a sequence of ligand substitutions to give the 'chiral-at-rhenium' derivatives [PCpReNO(CO)PPh₃]⁺BF₄⁻ and PCpReNO(CH₃)PPh₃ as a 1 : 1 inseparable mixture of diastereomers. The latter compound has also been characterized by an X-ray structure analysis with both diastereomers occupying unique positions in the crystal lattice.

Keywords: Optically active ligands; Rhenium; Cyclopentadienyl; Crystal structure; NMR spectroscopy; IR spectroscopy

1. Introduction

During the past 15 years the chemistry of the chiral, substitution-labile dichloromethane complex [(η^5 -Cp)Re(NO)(PPh₃)(ClCH₂Cl)]⁺BF₄⁻ has been extensively studied by Gladysz and coworkers [1–17]. The complex serves as a functional equivalent of the chiral, 16-valence-electron Lewis acid [(η^5 -Cp)Re(NO)(PPh₃)]⁺ and has been the object of considerable mechanistic investigation. Generated by protolysis of the methyl complex (η^5 -Cp)Re(NO)(PPh₃)(CH₃) with HBF₄ · Et₂O in dichloromethane at –78°C, the complex exhibits overall retention at rhenium after reaction with various neutral donor ligands [4,5]. However, starting from racemic (η^5 -Cp)Re(NO)(PPh₃)(CH₃) and prochiral nucleophiles L, two diastereomeric racemates can be ultimately obtained as the corresponding Lewis base

adducts [(η^5 -Cp)Re(NO)(PPh₃)(L)]⁺BF₄⁻. Although diastereoselectivity was high in many cases, especially after equilibration at 95°C in chlorobenzene [17], employment of a rhenium complex with an optically active cyclopentadienyl ligand as the starting material could provide higher degrees of binding selectivities, even at ambient temperature. Furthermore, mechanistic studies, such as those of equilibration processes, would be facilitated, as they could now be executed by NMR analysis (preferably ³¹P NMR), all possible isomers being diastereomers.

The optically active pinane-related cyclopentadienyl ligand, (1*R*,8*R*)-(–)-9,9-dimethyltricyclo[6.1.1.0^{2,6}]-deca-2,5-dienyl (PCp⁻; Fig. 1), initially synthesized by Paquette et al. [18], represents a promising tool in the synthesis and characterization of chiral transition metal complexes.

Derived from (1*R*,8*R*)-(–)-nopol, a compound of the 'chiral pool', the optically pure diene PCpH can be prepared from relatively cheap starting materials in good overall yields [19,20]. As the chiral dienyl ligand PCp⁻ possesses two non-equivalent π surfaces, it can

[☆] For Part I, see Ref. [20]. Dedicated to Prof. Dr. P. Paetzold on the occasion of his 60th birthday.

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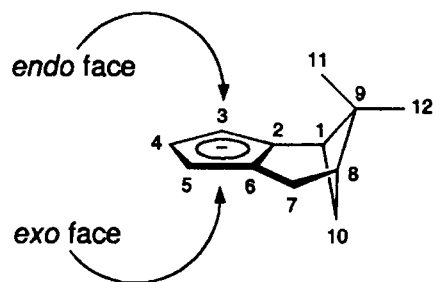


Fig. 1. The PCp⁻ anion and its numbering scheme.

be stereoselectively complexed by Ti^{IV}, Fe⁰ and Ru⁰ reagents. LiPCp reacts with Ti^{IV} reagents with high π -facial selectivity, which inverts with variation of temperature [21,22]. Treatment of PCpH, however, with Fe(CO)₅ or Ru₃(CO)₁₂ in the presence of the hydrogen acceptor norbornene affords the isostructural complexes [PCpM(CO)₂]₂ (M = Fe, Ru), in which the metal is coordinated exclusively to the sterically less hindered *exo* face of PCp [18,23,24].

The aim of our research was to investigate whether diastereomerically pure rhenium tricarbonyl complexes PCpRe(CO)₃ could be prepared from this ligand by face-selective complexation and to find out in which way diastereomers, generated by substitution of ligands to create a chiral pseudo-tetrahedral environment at the rhenium centre, could be separated. In addition to that, we hoped to gain better insight into those organometallic reaction mechanisms that are not easily deducible from reactions of racemic mixtures.

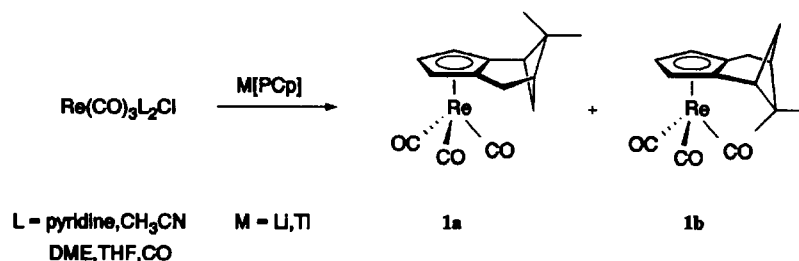
2. Results and discussion

2.1. Syntheses and investigations of the π -facially selective formation of *exo*- and *endo*-(η^5 -PCp)Re(CO)₃ (**1a** and **1b**)

In our initial attempts at synthesizing (η^5 -PCp)Re(CO)₃ by general literature methods [25], starting from Re(CO)₅Cl and TIPCp in *n*-hexane, toluene, THF or Et₂O, we always obtained mixtures of *exo*-(η^5 -PCp)Re(CO)₃ (**1a**) and *endo*-(η^5 -PCp)Re(CO)₃ (**1b**) in

modest yields (about 50%) with low diastereomeric excesses of **1a** (*de*: 30%–36%) (Scheme 1).

Variation of temperature produced no significant difference in the π -facial selectivity of the reaction, but the yield decreased from 50% at 25°C to 35% at -78°C. One of the main hindrances to increasing the yield is the competitive homolysis of the Re–C σ -bond of the (η^1 -PCp)Re(CO)₅ intermediate, which is formed directly after substitution of chloride by the PCp anion [26]. This intermediate, instead of losing two CO ligands and forming the final product (η^5 -PCp)Re(CO)₃, decomposes by homolysis of the Re–C σ -bond and generation of radical products, some of which recombine to give Re₂(CO)₁₀ as a side-product. Therefore, employment of [Re(CO)₃(THF)Cl]₂ as a precursor, with labile THF ligands which can readily be displaced, should facilitate the overall process and suppress homolysis [27–30]. Indeed, treatment of [Re(CO)₃(THF)Cl]₂ with TIPCp in THF at 0°C increased the yield to 85%. Unfortunately, the diastereomeric excess of **1a** decreased to 4%. Similar experiments, performed at various temperatures and utilizing LiPCp instead of TIPCp, failed to produce any enhancement. While suppressing the homolysis of the Re–C σ -bond, and giving yields of product similar to the unsubstituted Cp ligand [25], this method failed to show any significant diastereoselectivity. We assumed that stereochemical control of the complexation of the PCp⁻ anion should only be possible if *monomeric* rhenium starting materials with bulky ligands are employed. We therefore attempted to achieve better results by employment of stable *monomeric* complexes like Re(CO)₃L₂Cl (L = pyridine, CH₃CN, DME), where the two ligands L are bulkier than CO which might favour π -facial selectivity. With L = pyridine [31] and CH₃CN [32], diastereomeric excesses indeed increased to 80%; yields however decreased to 35%. As the N-containing ligands, pyridine and CH₃CN, are bound much more strongly to rhenium in Re(CO)₃L₂Cl than CO, homolysis of the Re–C σ -bond in (η^1 -PCp)Re(CO)₃L₂ became again a competitive reaction. The use of L = DME seemed to afford a compromise, for both good yields and modest diastereomeric excess could be achieved. Surprisingly, reversal of π -facial selectivity occurred in the case of L =



Scheme 1.

Table 1
Ratios and yields of **1a** and **1b**

L	M	Yield (%)	1a/1b
pyridine	Li	40	33:67
pyridine	Tl	35	90:10
CH ₃ CN	Li	35	80:20
CH ₃ CN	Tl	40	55:45
DME	Li	76	64:36
DME	Tl	80	37:63
THF	Li	75	53:47
THF	Tl	85	52:48
CO	Li	45	65:35
CO	Tl	50	68:32

pyridine and DME, depending on whether LiPCp or TlPCp was employed. In no case did we discover any reversal of selectivity with variation of temperature, as described by Paquette and coworkers [22,33,34]. Best results were obtained when the reactions were performed at 0°C. Yields and ratios of **1a/1b** are listed for all reactions at 0°C in Table 1.

Diastereomeric excesses were determined by integration of the ¹H NMR peaks assigned to the methyl groups of **1a** (δ : 1.40 and 0.72 ppm) and **1b** (δ : 1.35 and 1.17 ppm). The chemical shifts of these resonances show a larger difference $\Delta\delta$ for **1a** than for **1b**, as a result of differential diamagnetic anisotropy effects of the Cp ring-current. Furthermore, **1a** and **1b** exhibit the same IR absorptions in the carbonyl region and cannot therefore be distinguished by IR spectroscopy. ¹³C NMR spectra of both **1a** and **1b** show only one single resonance for the CO ligands with identical chemical shifts for **1a** and **1b**.

Separation of **1a** and **1b** has so far only been achieved by fractional crystallization in n-hexane at -30°C, producing colourless crystalline needles as single crystals. Both diastereomers were structurally characterized by single-crystal X-ray diffraction (Section 2.4).

2.2. Preparation of R_{Re},S_{Re} -*exo*-(η^5 -PCp)Re(NO)-(PPh₃)CH₃ (**5a**, **5b**)

In line with the work of Gladysz et al. [35], *exo*-(η^5 -PCp)Re(CO)₃ (**1a**) was treated with freshly prepared

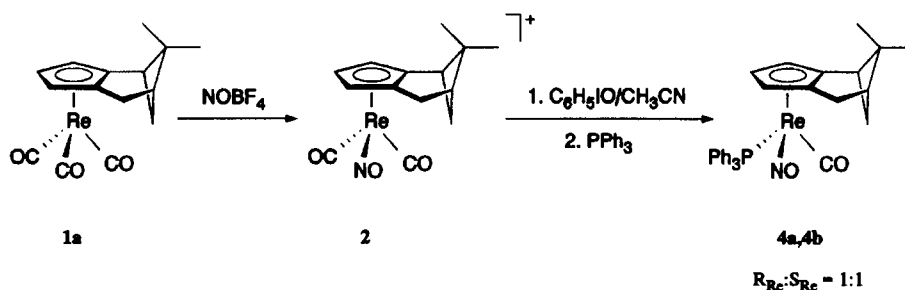
NOBF₄ in CH₂Cl₂ at 0°C to provide *exo*-[(η^5 -PCp)Re(NO)(CO)₂]⁺BF₄⁻ (**2**) as a yellow solid in excellent yield after work-up (Scheme 2). The ¹³C NMR spectrum of **2** exhibits two resonances at 182.5 and 182.3 ppm assigned to its two diastereotopic CO ligands.

Treatment of **2** in CH₃CN with iodobenzene as a mild oxidizing agent resulted in the smooth formation of R_{Re},S_{Re} -*exo*-[(η^5 -PCp)Re(NO)(CO)(NCCH₃)]⁺BF₄⁻ (**3a**, **3b**) [2,35]. The course of the reaction can easily be monitored by IR. After removal of solvent, crude **3a** + **3b** was refluxed in 2-butanone with excess of PPh₃ to afford the desired product R_{Re},S_{Re} -*exo*-[(η^5 -PCp)Re(NO)(CO)(PPh₃)]⁺BF₄⁻ (**4a**, **4b**) in good overall yield (Scheme 2). ¹H and ³¹P NMR analysis of **4a** + **4b** indicated that the ratio of diastereomers R_{Re}/S_{Re} , owing to the newly generated chiral centre at rhenium, was about 1:1. Reduction of **4a** + **4b** could readily be performed in THF by addition of NaBH₄ at ambient temperature. Purification by chromatography and subsequent crystallization from a hot saturated n-hexane solution, which was slowly cooled to room temperature, provided red single crystals of R_{Re},S_{Re} -*exo*-(η^5 -PCp)Re(NO)(PPh₃)(CH₃) (**5a**, **5b**) in 80% yield (Scheme 3).

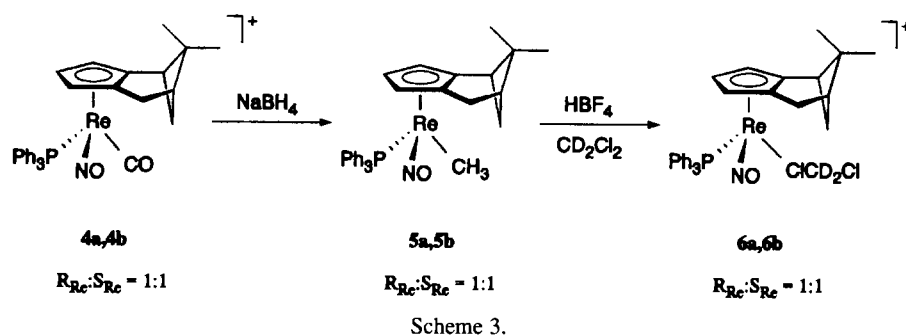
The ratio of diastereomers $R_{Re}/S_{Re} = 1:1$ was again determined by ³¹P and ¹H NMR spectra. The X-ray structure of **5a**, **5b** shows that both diastereomers cocrystallize in a 1:1 ratio (Section 2.4). Fractional crystallization is therefore not a suitable method for separation of the diastereomers in this case.

2.3. Formation and stability of R_{Re},S_{Re} -[*exo*-(η^5 -PCp)Re(NO)(PPh₃)(ClCD₂Cl)]⁺BF₄⁻ (**6a**, **6b**)

According to Gladysz et al., methyl rhenium complexes such as **5a** or **5b** can readily be converted to chiral, pyramidal, solvent-stabilized Lewis acids, which are of stable configuration in dichloromethane or chlorobenzene at low temperatures [5]. If treated with HBF₄·Et₂O in CD₂Cl₂ at -78°C, **5a**, **5b** were converted into R_{Re},S_{Re} -*exo*-[(η^5 -PCp)Re(NO)(PPh₃)-(ClCD₂Cl)]⁺BF₄⁻ (**6a**, **6b**) (Scheme 3). This reaction



Scheme 2.



was performed in an NMR tube and immediately analyzed by ^{31}P NMR spectroscopy at -80°C . Two resonance peaks (δ : 13.4 and 11.9 ppm) due to two diastereomers (ratio of integration: $R_{\text{Re}}/S_{\text{Re}} \sim 1:1$) were observed. On stepwise warming to -20°C , ^{31}P NMR spectra showed only two resonances, which shifted slightly to higher field, over the entire temperature range. Above -20°C decomposition of **6a** and **6b** occurred. The relative stability of the 16-valence-electron cations (**6a**, **6b**) in CD_2Cl_2 to -20°C suggested that CD_2Cl_2 acts as a weakly coordinating ligand to the metal centre. In order to answer the question of whether decomposition or inversion of **6a**, **6b** occurs faster in a variation-of-temperature NMR experiment, it would be necessary to separate the two diastereomers **5a** and **5b** and investigate only one of them after protolysis as described above. We currently cannot distinguish whether **6a** and **6b** are configurationally stable over the whole temperature range, or whether a slow equilibration between the R_{Re} and S_{Re} isomer takes place. Our present efforts are therefore focused on preparing pure optically active **5a** or **5b** in good overall yield.

2.4. X-ray structures of **1a**, **1b**, **5a** and **5b**

Complex **1a** has the appearance of a normal cyclopentadienyl half-sandwich transition metal complex (Fig. 2). The angles (O)C–Re–C(O) deviate only slightly from 90° and confirm the octahedral coordination at the rhenium atom. The dihedral angle between the PCp π -plane and the plane defined by the three carbon atoms of the CO ligands is 2.0° and is thus hardly significant. This is in contrast to the observations on related pentamethylcyclopentadienyl complexes of the diolefin ligand nopadiene [20] and methylnopadienyl [36], where a pronounced tilt of the two ligand planes was observed, most likely due to repulsion between the methylene bridge of the pinene unit and the second ring ligand. This difference may be due to the fact that the three carbonyl ligands have a considerably smaller cone angle than a pentamethylcyclopentadienyl ring.

The Re–C distances to the cyclopentadienyl ring vary within the limits 2.301 and 2.359 Å. As expected, the Re–C bond lengths for the three CO ligands are all identical. Surprisingly the X-ray structure of diastereomer **1b** exhibits no significant differences in its appearance apart from the inverse aliphatic pinene part of

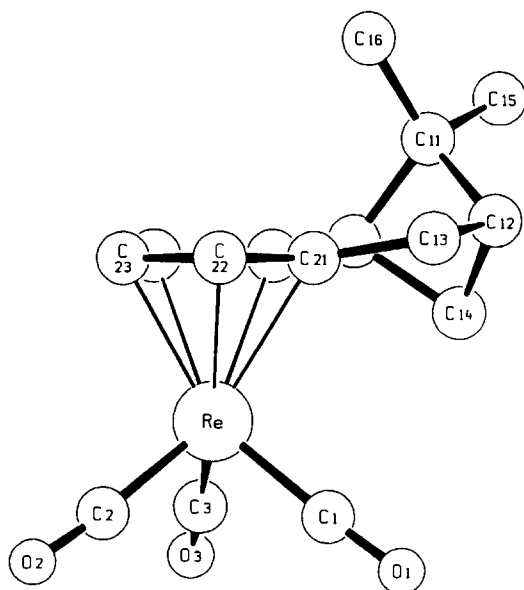


Fig. 2. Molecular structure and crystallographic numbering scheme for *exo*-PCpRe(CO)₃ (**1a**).

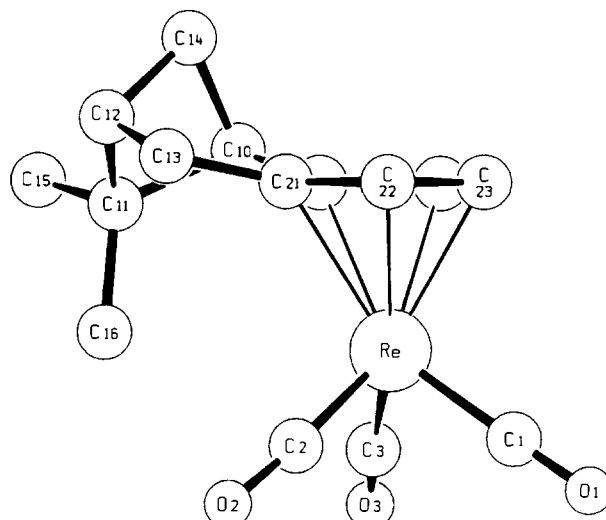


Fig. 3. Molecular structure and crystallographic numbering scheme for *endo*-PCpRe(CO)₃ (**1b**).

the PCp ligand (Fig. 3). The angle between the PCp π -plane and the plane defined by the carbon atoms of the carbonyl ligands is 2.6° and differs slightly from that of **1a**. Apparently the three CO ligands can avoid steric interaction with the methyl groups by rotation (turnstile mechanism). In solution, however, the system is dynamic and only one NMR resonance assigned to the CO ligands can be observed in the ^{13}C NMR spectrum at ambient temperatures. The (O)C–Re–C(O) angles vary within the limits 86° and 92° , and the Re–C

distances to the cyclopentadienylring range from 2.28 \AA to 2.37 \AA .

For the complexes **5a** and **5b**, we find the rare case that both diastereomers cocrystallize in a ratio of 1 : 1 in the unit cell (Fig. 4). The solid-state structure analysis shows the orientation of the bulky PPh_3 group as far as possible away from the sterically demanding pinene part of the PCp ligand [Fig. 5 shows the situation for the R_{Re} isomer (**5a**)]. The exchange of the position of the small NO and methyl ligand, which are well shielded below

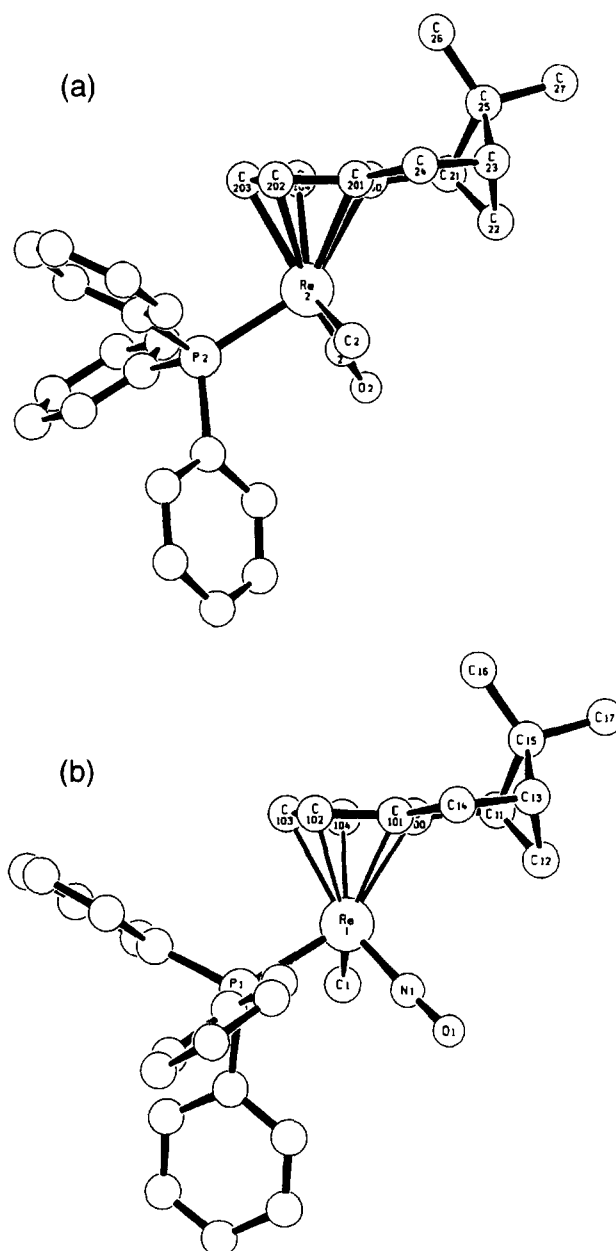
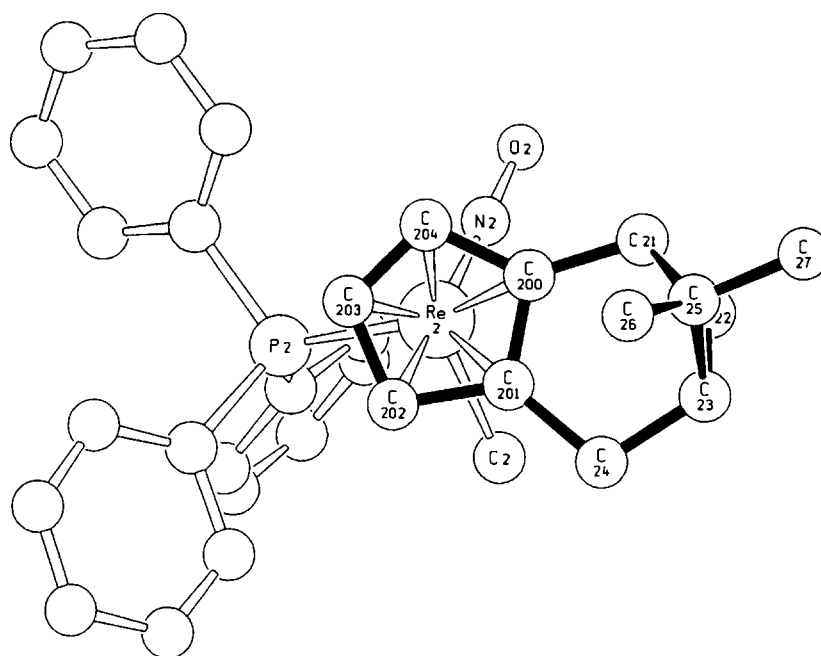


Fig. 4. Molecular structures and crystallographic numbering schemes for $R_{\text{Re}}\text{-exo-PCpRe}(\text{NO})(\text{CH}_3)(\text{PPh}_3)$ (**5a**) and $S_{\text{Re}}\text{-exo-PCpRe}(\text{NO})(\text{CH}_3)(\text{PPh}_3)$ (**5b**).

Fig. 5. Top view for R_{Re} -*exo*-PCpRe(NO)(CH₃)(PPh₃) (**5a**).

the π -plane, does not appear to have any great influence on the overall geometry of the complexes, which is largely dominated by the bulkier ligands PPh₃ and PCp.

The Re–N and Re–CH₃ distances are significantly longer for the S_{Re} (**5b**) than for the R_{Re} diastereomer (**5a**). For **5a**, bond angles at the metal centre deviate to

Table 2
Summary of crystal data and details of the intensity collection and refinement for **1a**, **1b** and **5a/5b**

	1a	1b	5a/5b
Empirical formula	C ₁₅ H ₁₅ O ₃ Re	C ₁₅ H ₁₅ O ₃ Re	C ₃₁ H ₃₃ NOPRe
Molecular weight (g mol ⁻¹)	429.49	429.49	652.79
Colour, habit	colourless parallelepiped	colourless needles	red parallelepiped
Crystal size (mm ³)	0.8 × 0.5 × 0.2	0.1 × 0.1 × 0.5	0.2 × 0.2 × 0.15
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)	<i>P</i> 2 ₁ (No. 4)	<i>P</i> 2 ₁ (No. 4)
<i>a</i> (Å)	7.109(2)	7.039(8)	9.074(1)
<i>b</i> (Å)	12.019(3)	9.156(8)	18.168(3)
<i>c</i> (Å)	16.128(4)	10.894(9)	16.159(2)
β (°)		92.20(9)	90.09(1)
<i>V</i> (Å ³)	1378.0(6)	702.0(1)	2664.0(1)
<i>Z</i>	4	2	4
Density (calc.) (g cm ⁻³)	2.070	2.035	1.628
<i>F</i> (000)	816	408	1296
Monochromator	graphite	graphite	graphite
Absorption coefficient, μ (cm ⁻¹)	89.38	87.85	25.21
Radiation, λ (Å)	Mo K α (0.71073)	Mo K α (0.71073)	Ag K α (0.56087)
Temp. (K)	200	253	293
Scan mode (2 θ range) (°)	ω (4–58)	ω (6–50)	ω -2 θ (0–48)
No. of unique rflns.	2096	2316	10213
<i>N</i> _o (No. of obsd. rflns.)	2054 (<i>F</i> > 6.0 σ (<i>F</i>))	1934 (<i>I</i> > 2.5 σ (<i>I</i>))	5619 (<i>I</i> > 2.0 σ (<i>I</i>))
<i>N</i> _p (No. of params. refined)	173	171	630
Weighting scheme		$w^{-1} = \sigma^2(F_o)$	
<i>R</i>	0.032	0.043	0.043
<i>R</i> _w	0.044	0.052	0.047
Residual fluctuation			
in final DF map (e Å ⁻³)	2.2	3.4	3.3

Table 3
Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) of *exo*-PCpRe(CO)₃ (**1a**) with estimated standard deviations in parentheses

Atom	x	y	z	U_{eq}^a
Re	0.8882(1)	0.7799(1)	0.2083(1)	0.016(1)
O1	1.1601(15)	0.6396(7)	0.3142(6)	0.034(3)
O2	1.0164(20)	0.6783(9)	0.0440(6)	0.058(4)
O3	1.1846(14)	0.9641(7)	0.1902(6)	0.038(3)
C1	1.0600(18)	0.6932(9)	0.2725(7)	0.022(3)
C2	0.9752(20)	0.7147(10)	0.1070(7)	0.032(4)
C3	1.0751(16)	0.8925(8)	0.1974(7)	0.021(3)
C10	0.7085(16)	0.9568(8)	0.3564(6)	0.016(3)
C11	0.5507(17)	0.9310(9)	0.4241(7)	0.018(3)
C12	0.6749(18)	0.8289(9)	0.4522(6)	0.022(3)
C13	0.6394(18)	0.7274(8)	0.3946(7)	0.024(3)
C14	0.8479(17)	0.8994(9)	0.4186(7)	0.022(3)
C15	0.5468(21)	1.0207(9)	0.4912(7)	0.030(4)
C16	0.3495(17)	0.9112(10)	0.3927(8)	0.026(3)
C20	0.6705(17)	0.8805(7)	0.2864(7)	0.017(3)
C21	0.6423(16)	0.7646(7)	0.3058(6)	0.017(3)
C22	0.5832(18)	0.7112(10)	0.2306(8)	0.030(4)
C23	0.5793(18)	0.7904(9)	0.1663(8)	0.029(4)
C24	0.6316(17)	0.8979(9)	0.2000(7)	0.021(3)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as one-third of the trace of the orthogonalized U tensor.

a greater degree from an octahedral coordination. Summaries of crystal data, selected bond lengths and angles for **1a**, **1b**, **5a** and **5b** are listed in Table 2–8.

Table 4
Selected bond lengths (\AA) and angles ($^\circ$) of *exo*-PCpRe(CO)₃ (**1a**) with estimated standard deviations in parentheses

<i>Bond lengths</i>			
Re—C1	1.909(12)	C10—C20	1.479(14)
Re—C2	1.915(12)	C11—C12	1.579(16)
Re—C3	1.905(11)	C11—C15	1.527(16)
Re—C20	2.334(11)	C11—C16	1.536(17)
Re—C21	2.359(11)	C12—C13	1.554(15)
Re—C22	2.348(13)	C12—C14	1.588(17)
Re—C23	2.301(13)	C13—C21	1.501(15)
Re—C24	2.314(12)	C20—C21	1.443(13)
O1—C1	1.173(15)	C20—C24	1.436(16)
O2—C2	1.144(16)	C21—C22	1.435(16)
O3—C3	1.167(14)	C22—C23	1.407(17)
C10—C11	1.596(16)	C23—C24	1.450(16)
C10—C14	1.570(15)		
<i>Bond angles</i>			
C1—Re—C2	91.9(5)	C14—C10—C20	109.3(8)
C1—Re—C3	89.5(5)	C10—C11—C12	87.3(8)
C2—Re—C3	89.3(5)	C10—C11—C15	111.1(9)
C10—C20—C21	117.3(9)	C10—C11—C16	117.3(9)
C10—C20—C24	133.3(8)	C12—C11—C15	110.8(9)
C13—C21—C20	119.8(9)	C12—C11—C16	119.7(9)
C13—C21—C22	132.0(9)	C15—C11—C16	109.1(10)
Re—C1—O1	177.4(11)	C11—C12—C13	110.4(9)
Re—C2—O2	175.4(13)	C11—C12—C14	85.5(8)
Re—C3—O3	177.6(10)	C13—C12—C14	109.9(9)
C20—C21—C22	106.8(9)	C12—C13—C21	109.5(8)
C11—C10—C14	85.5(8)	C10—C14—C12	87.9(8)
C11—C10—C20	105.9(9)	Re—C20—C10	127.7(8)

3. Experimental details

3.1. General

All reactions and manipulations were performed under nitrogen by use of standard vacuum line and Schlenk tube techniques. All solvents were degassed before use. Diethyl ether was distilled from sodium benzophenone ketyl. Acetonitrile and dichloromethane were distilled from calcium hydride. Dimethoxyethane (DME) and n-hexane were dried over molecular sieves. Unless otherwise indicated, all commercially available reagents were used as received. Column chromatography was performed on Grade II (activated) silica gel (Merck Kieselgel 60). For organometallic complexes, all chromatography was carried out under nitrogen. n-Butyllithium (1.6 M in n-hexane) (Aldrich) and 2-butanone (Fluka) were used as supplied. NOBF_4 [37], $\text{Re}(\text{CO})_5\text{Cl}$ [38–41], iodosylbenzene [42,43] and PCpH [19,20] were prepared as described in the literature. Infrared spectra were recorded on a Perkin-Elmer 1750 Fourier-transform spectrophotometer as solutions in n-hexane, dichloromethane or DME using NaCl cells. NMR spectra were recorded on either a Varian VXR 300 or a Varian Unity 500 spectrometer in CDCl_3 or C_6D_6 solutions unless otherwise stated. ^1H and ^{13}C NMR spectra were referenced to tetramethylsilane (TMS) using internal solvent peaks; ^{31}P NMR spectra were refer-

Table 5

Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for *endo*-PCpRe(CO)₃ (**1b**) with estimated standard deviations in parentheses

Atom	x	y	z	U_{eq}^a
Re	0.04153(4)	0.000	0.39596(3)	0.03315(9)
O1	-0.131(1)	-0.021(2)	0.6484(7)	0.066(3)
O2	-0.262(1)	0.236(1)	0.326(1)	0.068(3)
O3	-0.212(1)	-0.237(1)	0.301(1)	0.065(3)
C1	-0.068(1)	-0.014(3)	0.552(1)	0.045(3)
C2	-0.145(2)	0.145(2)	0.359(1)	0.043(3)
C3	-0.122(2)	-0.149(1)	0.330(1)	0.031(3)
C10	0.329(1)	-0.095(1)	0.139(1)	0.032(3)
C11	0.204(1)	-0.005(3)	0.0388(9)	0.040(2)
C12	0.341(2)	0.120(2)	0.065(1)	0.040(3)
C13	0.292(2)	0.209(2)	0.180(1)	0.044(3)
C14	0.497(1)	0.005(4)	0.1024(9)	0.045(3)
C15	0.223(2)	-0.074(2)	-0.086(1)	0.049(4)
C16	-0.010(1)	0.010(2)	0.0533(9)	0.047(3)
C20	0.298(1)	-0.042(1)	0.265(1)	0.029(3)
C21	0.287(1)	0.106(1)	0.2854(8)	0.029(3)
C22	0.314(2)	0.133(1)	0.419(1)	0.033(3)
C23	0.344(1)	-0.003(3)	0.478(1)	0.058(3)
C24	0.333(2)	-0.117(2)	0.379(1)	0.044(3)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as one-third of the trace of the orthogonalized U tensor.

enced to H_3PO_4 (external). All ^{13}C and ^{31}P NMR data are given in terms of the proton-decoupled (broad-band) spectra.

In the crystal structure determinations of **1a**, **1b**, **5a** and **5b**, the data collection was performed on a Siemens 3m/V diffractometer (**1a**) and on an ENRAF Nonius

Table 6

Selected bond lengths (\AA) and angles ($^\circ$) of *endo*-PCpRe(CO)₃ (**1b**) with estimated standard deviations in parentheses

<i>Bond lengths</i>			
Re—C1	1.90(1)	C10—C20	1.48(2)
Re—C2	1.90(3)	C11—C12	1.52(3)
Re—C3	1.91(2)	C11—C15	1.51(2)
Re—C20	2.37(1)	C11—C16	1.52(1)
Re—C21	2.35(1)	C12—C13	1.54(2)
Re—C22	2.28(2)	C12—C14	1.57(4)
Re—C23	2.28(1)	C13—C21	1.48(2)
Re—C24	2.33(2)	C20—C21	1.38(2)
O1—C1	1.15(2)	C20—C24	1.43(2)
O2—C2	1.22(3)	C21—C22	1.48(2)
O3—C3	1.07(3)2	C22—C23	1.41(4)
C10—C11	1.60(2)	C23—C24	1.50(3)
C10—C14	1056(3)		
<i>Bond angles</i>			
C1—Re—C2	86.(1)	C14—C10—C20	101.(1)
C1—Re—C3	92.(1)	C10—C11—C12	86.(1)
C2—Re—C3	91.2(5)	C10—C11—C15	109.(2)
C10—C20—C21	119.(1)	C10—C11—C16	120.(1)
C10—C20—C24	128.(1)	C12—C11—C15	114.(1)
C13—C21—C20	120.(1)	C12—C11—C16	123.(2)
C13—C21—C22	130.(2)	C15—C11—C16	105.(1)
Re—C1—O1	179.(1)	C11—C12—C13	113.(1)
Re—C2—O2	175.(2)	C11—C12—C14	89.(2)
Re—C3—O3	176.(2)	C13—C12—C14	109.(1)
C20—C21—C22	108.(2)	C12—C13—C21	108.(1)
C11—C10—C14	86.(1)	C10—C14—C12	85.9(9)
C11—C10—C20	112.(1)	Re—C20—C10	139.(1)

CAD4 diffractometer (**1b** and **5a/5b**). Crystal data, data collection parameters and refinement parameters are given in Table 2. The structures were solved by direct methods and refined on structure factors with the Siemens SHELXTL-PLUS (**1a**) and the SDP program system (**1b** and **5a/5b**).

3.2. Preparations

3.2.1. Preparation of *exo*- and *endo*-(η^5 -PCp)Re(CO)₃- (**1a** and **1b**)

PCpH (0.82 g, 5.1 mmol) was dissolved in 30 ml of Et₂O and cooled to 0°C. While stirring 3.2 ml (5.1 mmol) of ⁿBuLi (1.6 M in hexane) were added via a syringe. The mixture was then refluxed for 2.5 h. LiPCp precipitated as a white solid. The solvent was removed by vacuum distillation and the product was taken up in 25 ml of DME.

To 1.8 g (5.0 mmol) of Re(CO)₅Cl were added 100 ml of DME and the suspension refluxed for 4 h. Re(CO)₅Cl dissolved and CO gas evolved. The solution was then cooled to 0°C and, while stirring, 5.1 mmol of LiPCp in 25 ml of DME were added dropwise over a period of 15 min. The mixture was stirred for further 10 min at 0°C and then refluxed for 1 h. After cooling, the solvent was removed by vacuum distillation and the residue extracted with n-hexane and filtered. Chromatography over silica gel (1.5 × 15 cm) in n-hexane and evaporation of the solvent afforded a pale brown solid as the crude product; yield of **1a** + **1b**, 1.6 g (3.8 mmol, 76%) with **1a**/**1b** = 64 : 36.

Purification and separation of the two isomers was achieved by dissolving the crude product in n-hexane. The complex *exo*-(η^5 -PCp)Re(CO)₃ (**1a**) was separated by fractional crystallization at -30°C. Colourless crystalline needles of **1a** precipitated as single crystals after 3 d and these were filtered off and dried under vacuum; yield 0.72 g of **1a** (34%). After repeated crystallizations and reductions of the solvent volume, the mother liquid contained only *endo*-(η^5 -PCp)Re(CO)₃ (**1b**), of which colourless crystalline needles were obtained as single crystals at -30°C after 5 d.

Compound **1a**: IR (n-hexane)(cm⁻¹): 2023; 1932. ¹H NMR (500 MHz, CDCl₃) δ : 5.16 (t, *J* = 2.8 Hz, 1H); 5.08 (dd, *J* = 2.8, 1.5 Hz, 1H); 5.04 (br, 1H); 2.90 (dd, *J* = 16.2, 3.1 Hz, 1H); 2.77 (m, 2H); 2.53 (t, *J* = 5.5 Hz, 1H); 2.23 (m, 1H); 1.49 (d, *J* = 10.1 Hz, 1H); 1.40 (s, 3H, CH₃); 0.72 (s, 3H, CH₃) ppm. ¹³C NMR (125 MHz, CDCl₃) δ : 195.6; 120.4; 103.2; 83.2; 79.4; 77.0; 41.8; 41.1; 40.6; 38.4; 26.6; 26.4; 21.9 ppm. Anal. Found: C, 42.52; H, 3.62%. C₁₅H₁₅O₃Re Calc.: C, 41.95; H, 3.52%.

Compound **1b**: IR (hexane)(cm⁻¹): 2023; 1931: ¹H NMR (500 MHz, CDCl₃) δ : 5.23 (t, *J* = 2.8, 1H); 4.97 (br, 1H); 4.78 (dd, *J* = 2.8, 1.5 Hz, 1H); 2.80 (m, 2H); 2.75 (dd, *J* = 16.5, 3.4 Hz, 1H); 2.64 (t, *J* = 5.0 Hz,

1H); 2.22 (m, 1H); 1.35 (s, 3H, CH₃); 1.17 (s, 3H, CH₃); 1.09 (d, *J* = 9.8 Hz, 1H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ : 195.6; 118.6; 104.3; 85.5; 77.3; 73.6; 41.4; 41.1; 39.7; 36.5; 27.3; 26.6; 22.5 ppm.

3.2.2. Preparation of *exo*-[(η^5 -PCp)Re(NO)(CO)₂]⁺BF₄⁻ (**2**)

Compound **1a** (2.49 g, 5.80 mmol) was dissolved in 45 ml of dichloromethane and kept at 0°C by means of an ice bath. While stirring, 0.93 g (7.98 mmol) of freshly prepared NOBF₄ were added slowly. The solution turned yellow and gas evolved. The mixture was stirred for 20 h while the ice bath was allowed to warm up. The solvent was then removed and the residue extracted with acetone and filtered. The filtrate was concentrated and ethyl ether added to precipitate the yellow product, which was collected by filtration, washed with ether and dried; yield of **2**, 2.94 g (5.67 mmol, 98%).

Compound **2**: IR (CH₂Cl₂)(cm⁻¹): 2109; 2052; 1799. ¹H NMR (500 MHz, CD₂Cl₂) δ : 6.26 (t, *J* = 2.8 Hz, 1H); 6.03 (br, 1H); 6.00 (dd, *J* = 2.8, 1.5 Hz, 1H); 3.15 (dd, *J* = 17.7, 1.8 Hz, 1H); 3.02 (m, 2H); 2.87 (t, *J* = 5.3 Hz, 1H); 2.43 (m, 1H); 1.49 (s, 3H, CH₃); 1.08 (d, *J* = 11.0 Hz, 1H); 0.83 (s, 3H, CH₃) ppm. ¹³C NMR (125 MHz, CD₂Cl₂) δ : 182.5; 182.3; 131.6; 114.5; 93.1; 89.5; 87.9; 42.0; 41.4; 41.3; 38.4; 27.0; 26.3; 22.2 ppm. Anal. Found: C, 32.22; H, 2.93; N, 2.67%. C₁₄H₁₅BF₄NO₃Re Calc.: C, 32.44; H, 2.92; N, 2.7%.

3.2.3. Preparation of *R*_{Re},*S*_{Re}-*exo*-[(η^5 -PCp)Re(NO)(CO)(PPh₃)]⁺BF₄⁻ (**4a**, **4b**)

Compound **2** (2.84 g, 5.48 mmol) was dissolved in 100 ml of acetonitrile and the solution kept at 0°C by means of an ice bath. While stirring, 1.32 g (6.0 mmol) of freshly prepared iodobenzene were added slowly. The suspension was stirred for 20 h while gradually being brought to room temperature. The progress of the reaction was monitored by IR spectroscopy. Evaporation of the solvent afforded an orange solid of crude *R*_{Re},*S*_{Re}-*exo*-[(η^5 -PCp)Re(NO)(CO)(NCCH₃)]⁺BF₄⁻ (**3a**, **3b**); yield of **3a** + **3b**, 2.82 g (5.32 mmol, 97%). This solid was taken up in 120 ml of 2-butanone and 2.87 g (10.96 mmol) of PPh₃ were added. The solution was refluxed with stirring for 4 h. After cooling, the solvent was removed by vacuum distillation. The residue was washed with diethyl ether and purified by recrystallization from acetone/diethyl ether to give light yellow needles of *R*_{Re},*S*_{Re}-*exo*-[(η^5 -PCp)Re(NO)(CO)(PPh₃)]⁺BF₄⁻ (**4a**, **4b**) with the ratio of diastereomers *R*_{Re}/*S*_{Re} = 1 : 1; yield of **4a** + **4b**, 3.13 g (4.17 mmol, 76%).

Compounds **3a** + **3b**: IR (CH₂Cl₂)(cm⁻¹): 2020; 1756. IR (CH₃CN)(cm⁻¹): 2022; 1756.

Compounds **4a** + **4b**: IR (CH₂Cl₂)(cm⁻¹): 2015; 1753. IR (THF)(cm⁻¹): 2011; 1746. ¹H NMR (500

Table 7

Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) of $R_{\text{Re}}, S_{\text{Re}}\text{-exo-PCpRe(NO)(PPh}_3\text{)(CH}_3\text{)}$ (5a, 5b) with estimated standard deviations in parentheses

Atom	x	y	z	U_{eq}^a
Re1	0.02008(5)	0.562	0.78609(3)	0.0389(1)
Re(2)	-0.05151(5)	0.54317(3)	0.29282(3)	0.03241(9)
P1	0.2234(3)	0.6308(2)	0.8278(2)	0.0324(7)
P2	-0.2414(3)	0.6214(2)	0.3329(2)	0.0297(7)
O1	-0.031(1)	0.5025(7)	0.9556(6)	0.080(4)
O2	0.015(1)	0.4900(8)	0.4619(7)	0.085(4)
N1	-0.011(1)	0.5283(6)	0.8888(7)	0.048(3)
N2	-0.012(1)	0.5146(6)	0.3931(7)	0.044(3)
C1	-0.114(2)	0.6605(9)	0.798(1)	0.070(5)
C2	0.088(1)	0.6354(8)	0.2860(9)	0.054(4)
C11	-0.265(1)	0.4543(8)	0.7064(9)	0.051(4)
C12	-0.261(2)	0.4181(9)	0.7917(9)	0.058(4)
C13	-0.171(2)	0.3564(7)	0.752(1)	0.059(4)
C14	-0.008(2)	0.3765(8)	0.751(1)	0.060(4)
C15	-0.252(2)	0.3766(9)	0.667(1)	0.063(4)
C16	-0.169(2)	0.3661(9)	0.587(1)	0.068(5)
C17	-0.394(2)	0.335(1)	0.663(1)	0.082(5)
C21	0.178(2)	0.4022(8)	0.235(1)	0.060(4)
C22	0.298(2)	0.456(1)	0.253(1)	0.066(5)
C23	0.313(1)	0.4697(8)	0.1624(9)	0.053(4)
C24	0.200(1)	0.5251(6)	0.1305(9)	0.050(4)
C25	0.257(2)	0.3876(9)	0.1490(9)	0.055(4)
C26	0.166(2)	0.3693(9)	0.0737(9)	0.061(4)
C27	0.384(2)	0.333(1)	0.158(1)	0.079(5)
C100	-0.119(1)	0.4928(7)	0.6921(8)	0.042(3)
C101	0.009(1)	0.4534(7)	0.7168(8)	0.043(3)
C102	0.134(2)	0.4957(9)	0.6893(9)	0.057(4)
C103	0.081(2)	0.5590(9)	0.6500(8)	0.073(4)
C104	-0.065(2)	0.5597(9)	0.6523(8)	0.073(4)
C110	0.370(1)	0.5821(7)	0.8830(7)	0.038(3)
C111	0.366(2)	0.5058(8)	0.898(1)	0.066(5)
C112	0.471(2)	0.4711(9)	0.940(1)	0.087(6)
C113	0.592(2)	0.5104(9)	0.972(1)	0.076(5)
C114	0.604(2)	0.587(1)	0.959(1)	0.072(5)
C115	0.495(1)	0.6202(8)	0.919(1)	0.056(4)
C120	0.316(1)	0.6764(7)	0.7451(8)	0.041(3)
C121	0.242(2)	0.7308(7)	0.7001(9)	0.048(4)
C122	0.302(2)	0.7664(8)	0.6327(9)	0.064(5)
C123	0.441(2)	0.747(1)	0.609(1)	0.086(6)
C124	0.518(2)	0.693(1)	0.649(1)	0.077(5)
C125	0.453(2)	0.6570(9)	0.7173(9)	0.057(4)
C130	0.192(1)	0.7040(7)	0.9044(8)	0.039(3)
C131	0.243(1)	0.7755(8)	0.8952(9)	0.050(4)
C132	0.215(2)	0.8277(8)	0.956(1)	0.071(5)
C133	0.152(2)	0.8063(8)	1.0279(9)	0.060(4)
C134	0.097(2)	0.735(1)	1.036(1)	0.065(5)
C135	0.121(2)	0.6843(8)	0.9771(8)	0.049(4)
C200	0.041(1)	0.4441(6)	0.2179(8)	0.041(3)
C201	0.051(1)	0.5064(7)	0.1694(7)	0.038(3)
C202	-0.095(2)	0.537(1)	0.1535(9)	0.066(4)
C203	-0.191(2)	0.4890(8)	0.1939(9)	0.059(4)
C204	-0.113(2)	0.4340(8)	0.230(1)	0.061(4)
C210	-0.394(1)	0.5789(6)	0.3895(6)	0.033(3)
C211	-0.391(1)	0.5058(7)	0.406(1)	0.053(4)
C212	-0.507(2)	0.4727(8)	0.449(1)	0.073(5)
C213	-0.623(1)	0.5159(9)	0.476(1)	0.064(4)
C214	-0.626(2)	0.5886(9)	0.461(1)	0.069(5)
C215	-0.507(2)	0.6203(8)	0.417(1)	0.056(4)
C220	-0.329(1)	0.6684(7)	0.2438(8)	0.038(3)
C221	-0.243(1)	0.7178(8)	0.1983(8)	0.047(4)
C222	-0.300(2)	0.7536(9)	0.132(1)	0.060(4)

Table 7 (continued)

Atom	x	y	z	U_{eq}^a
C223	-0.442(2)	0.7403(9)	0.105(1)	0.066(5)
C224	-0.522(2)	0.691(1)	0.148(1)	0.072(5)
C225	-0.471(2)	0.6551(8)	0.216(1)	0.057(4)
C230	0.199(1)	0.6960(7)	0.4055(7)	0.033(3)
C231	-0.255(1)	0.7684(7)	0.3967(8)	0.041(3)
C232	-0.224(2)	0.8194(9)	0.459(1)	0.069(5)
C233	-0.146(2)	0.8039(8)	0.5288(9)	0.055(4)
C234	-0.094(2)	0.7343(9)	0.5351(9)	0.067(5)
C235	-0.113(2)	0.6805(7)	0.4764(9)	0.052(4)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as one-third of the trace of the orthogonalized U tensor.

Table 8

Selected bond lengths (Å) and angles (°) of R_{Re}, S_{Re} -*exo*-PCpRe(NO)(PPh₃)₂CH₃ (**5a**, **5b**) with estimated standard deviations in parentheses

<i>Bond lengths</i>			
Re1—P1	2.330(3)	C200—C201	1.38(2)
Re1—N1	1.79(1)	C200—C204	1.43(2)
Re1—C1	2.18(2)	C201—C202	1.46(2)
Re1—C100	2.34(1)	C202—C203	1.40(2)
Re1—C101	2.27(1)	C203—C204	1.36(2)
Re1—C102	2.23(1)	C11—C12	1.53(2)
Re1—C103	2.27(1)	C11—C15	1.55(2)
Re1—C104	2.29(1)	C11—C100	1.52(2)
Re2—P2	2.327(3)	C12—C13	1.53(2)
Re2—N2	1.74(1)	C13—C14	1.52(2)
Re2—C2	2.10(1)	C13—C15	1.60(2)
Re2—C200	2.33(1)	C14—C101	1.51(2)
Re2—C201	2.30(1)	C15—C16	1.51(2)
Re2—C202	2.29(1)	C15—C17	1.50(2)
Re2—C203	2.26(1)	C21—C22	1.49(2)
Re2—C204	2.29(1)	C21—C25	1.59(2)
O1—N1	1.19(1)	C21—C200	1.48(2)
O2—N2	1.22(1)	C22—C23	1.49(2)
C100—C101	1.42(2)	C23—C24	1.52(2)
C100—C104	1.46(2)	C23—C25	1.59(2)
C101—C102	1.44(2)	C24—C201	1.53(2)
C102—C103	1.40(2)	C25—C26	1.51(2)
C103—C104	1.33(2)	C25—C27	1.53(2)
<i>Bond angles</i>			
P1—Re1—N1	92.3(3)	C14—C101—C100	119.(1)
P1—Re1—C1	88.3(4)	C14—C101—C102	134.(1)
P2—Re2—N2	94.3(3)	C15—C11—C100	107.(1)
P2—Re2—C2	88.4(4)	C16—C15—C17	109.(1)
N1—Re1—C1	96.0(6)	C202—C203—C204	110.(1)
N2—Re2—C2	99.4(5)	C21—C22—C23	89.(1)
Re1—N1—O1	177(1)	C21—C25—C23	82.5(9)
Re2—N2—O2	176.(1)	C21—C25—C26	120.(1)
C101—C102—C103	108.(1)	C21—C25—C27	111.(1)
C11—C12—C13	87(1)	C21—C200—C201	118.(1)
C11—C15—C13	84(1)	C21—C200—C204	137.(1)
C11—C15—C16	121.(1)	C22—C21—C25	87.(1)
C11—C15—C17	114.(1)	C22—C21—C200	108.(1)
C11—C100—C101	116.(1)	C22—C23—C24	112.(1)
C11—C100—C104	138.(1)	C22—C23—C25	87.(1)
C12—C11—C15	89.(1)	C23—C24—C201	108.(1)
C12—C11—C100	108.(1)	C23—C25—C26	120.(1)
C12—C13—C14	110.(1)	C23—C25—C27	111.(1)
C12—C13—C15	87.(1)	C24—C23—C25	111.(1)
C13—C14—C101	109.(1)	C24—C201—C200	118.(1)
C13—C15—C16	118.(1)	C24—C201—C202	130.(1)
C13—C15—C17	108.(1)	C25—C21—C200	107.(1)
C14—C13—C15	113.(1)	C26—C25—C27	110.(1)

MHz, acetone- d_6) δ : 7.67 (m, 18H, Ph); 7.50 (m, 12H, Ph); 6.29 (br, 1H); 6.19 (m, 1H); 5.68 (br, 1H); 5.61 (m, 1H); 5.42 (m, 1H); 5.37 (m, 1H); 3.26–2.83 (m, 8H); 2.40 (m, 2H); 1.48 (s, 3H, CH₃); 1.46 (s, 3H, CH₃); 1.38 (d, $J = 10.4$ Hz, 1H); 1.35 (d, $J = 10.4$ Hz, 1H); 0.81 (s, 3H, CH₃); 0.80 (s, 3H, CH₃) ppm. ¹³C NMR (125 MHz, acetone- d_6) δ : 198.1; 197.9; 134.0; 133.9; 133.1; 132.1; 131.6; 130.6; 130.5; 129.2; 128.0; 113.5; 111.8; 96.3; 95.3; 93.9; 93.0; 87.4; 85.5; 42.1; 41.9; 41.8; 41.5; 39.0; 37.0; 27.2; 27.0; 26.6; 26.5; 22.2; 22.1 ppm. ³¹P NMR (202 MHz, acetone- d_6) δ : 11.5; 11.3 ppm. Anal. Found: C, 49.43; H, 3.96; N, 1.84%. C₃₁H₃₀BF₄NO₂Pre Calc.: C, 49.48; H, 4.02; N, 1.86%.

3.2.4. Preparation of R_{Re}, S_{Re} -exo-(η^5 -PCp)Re(NO)-(PPh₃)(CH₃) (5a, 5b)

Compounds **4a** + **4b** (1.16 g, 1.54 mmol) were dissolved in 100 ml of THF. While stirring, 0.175 g (4.63 mmol) NaBH₄ were added. The solution was stirred for 3 h at room temperature. The solvent was removed under reduced pressure, the residue extracted with toluene and filtered. Chromatography over silica gel (1.5 × 20 cm) in toluene and evaporation of the solvent afforded an orange solid. This was dissolved in hot n-hexane and the solution gradually cooled to room temperature. Red single crystals precipitated which were filtered off and dried under oil pump vacuum; yield of **5a** + **5b**, 0.80 g (1.23 mmol, 80%) with the ratio of diastereomers $R_{Re}/S_{Re} = 1:1$.

Compounds **5a** + **5b**: IR (THF)(cm⁻¹): 1631. IR (CH₂Cl₂)(cm⁻¹): 1613. ¹H NMR (500 MHz, CD₂Cl₂) δ : 7.40 (m, 30H, 6 × Ph); 5.21 (br, 1H); 5.19 (dd, $J = 2.8, 1.5$ Hz, 1H); 4.33 (m, 1H); 4.03 (dd, $J = 2.8, 1.5$ Hz, 1H); 3.63 (m, 1H); 3.24 (br, 1H); 2.87–2.56 (m, 8H); 2.24 (m, 2H); 1.62 (d, $J = 9.8$ Hz, 1H); 1.56 (d, $J = 10.1$ Hz, 1H); 1.43 (s, 3H, CH₃); 1.42 (s, 3H, CH₃); 0.99 (d, $J = 5.8$ Hz, 3H, CH₃); 0.94 (d, $J = 6.1$ Hz, 3H, CH₃); 0.82 (s, 3H, CH₃); 0.79 (s, 3H, CH₃) ppm. ¹³C NMR (125 MHz, CD₂Cl₂) δ : 137.4; 137.0; 134.1; 134.0; 130.1; 128.6; 128.5; 118.7; 118.6; 104.8; 101.6; 91.3; 88.4; 87.8; 86.8; 83.4; 83.3; 42.4; 42.3; 41.6; 41.4; 41.3; 37.1; 35.4; 30.1; 27.3; 27.0; 26.7; 25.3; 22.0; -27.9; -35.7 ppm. ³¹P NMR (202 MHz, CD₂Cl₂) δ : 27.5; 26.9 ppm. Anal. Found: C, 56.85; H, 5.16; N, 2.21%. C₃₁H₃₃NOPRe Calc.: C, 57.04; H, 5.10; N, 2.15%.

3.2.5. Preparation of R_{Re}, S_{Re} -exo-[(η^5 -PCp)Re(NO)-(PPh₃)(ClCD₂Cl)]⁺BF₄⁻ (6a, 6b)

(NMR experiment): A 5-mm NMR tube was charged with 0.061 g (0.094 mmol) of **5a** + **5b** and 0.50 ml of CD₂Cl₂. The tube was cooled to -78°C and HBF₄·Et₂O (12.9 μ l, 0.094 mmol) was added via a syringe. The tube was shaken and placed in a -80°C NMR probe. ³¹P NMR spectra at various temperatures were recorded.

Compounds **6a** + **6b**: ³¹P NMR (202 MHz, CD₂Cl₂) δ : 13.4; 11.9 ppm.

4. Supplementary material

Further details of the crystal structure investigation (complete listings of crystal and refinement data, bond lengths and angles, H-atom coordinates, thermal parameters (U) and structure factors) are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen.

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