Optically Active Transition-Metal Complexes, 8[+]

Transition-Metal Complexes of the Optically Active Cyclopentadienyl Ligand PinCp*: Crystal Structure of (S_{Re})-(η^5-PinCp*)Re(NO)(PPh_3)[$CONHCH(CH_3)C_{10}H_7$]

Albrecht Salzer,*[a] Annegret Hosang,[a] Jutta Knuppertz,[a] and Ulli Englert[a]

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

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The synthesis of (η^5-PinCp*)Re($CO)_3$ [PinCp* = tetramethyl(pinanyl)cyclopentadienyl] is described. Successive substitution of two CO ligands by NO^+ and PPh_3 generates a 1:1 diastereomeric mixture of chiral-at-metal [(S_{Re})/(R_{Re})-(PinCp*)Re(CO)(NO)(PPh_3)]BF_4. The diastereomers are converted with sodium methoxide into the derivative "esters" (S_{Re})/(R_{Re})-(PinCp*)Re($COOCH_3$)(NO)(PPh_3), and then with (+)-(*R*)-(1-naphthylethyl)amine to the "amides" (S_{Re})/(R_{Re})-(PinCp*)Re(NO)(PPh_3)[$CONHCH(CH_3)C_{10}H_7$] [(S_{Re})/(R_{Re}) = 1:1]. Fractional crystallisation separates the (S_{Re}) isomer with an optical purity of > 98%. The latter compound has been characterized by X-ray structure analysis. By treating the (S_{Re})-amide with CF_3CO_2H and $NaBF_4$, (S_{Re})-(PinCp*)Re(CH_3)(NO)(PPh_3) can be generated. Protolysis of this compound with HBF_4/Et_2O in CD_2Cl_2 at –78 °C leads to the solvent-stabilized complex (S_{Re})-[(PinCp*)Re(NO)(PPh_3)($ClCD_2Cl$)]$^+BF_4^-$. The thermal and configurational stability of this chiral Lewis acid is investigated at various temperatures. The syntheses of [PinCp*$RhCl_2]_2$, PinCp*$TiCl_3$ and PinCp*$M(CO)_2$(NO) (M = Mo, W) are also described. Starting with PinCp*$M(CO)_2$(NO), the relatively stable 16-VE complexes PinCp*MCl_2(NO) and PinCp*$W(CH_2SiMe_3)_2$(NO) are synthesized.

Introduction

Chiral Lewis acids, derived from transition-metal complexes, play an increasingly important role in enantioselective organic synthesis.[1–4] Both their thermal as well as their configurational stability are essential for their application as catalysts in asymmetric synthesis. While Gladysz et al.[4] have investigated the stability of the chiral-at-metal Lewis acid (S_{Re})-[(η^5-C_5H_5)Re(NO)(PPh_3)($ClCD_2Cl$)]$^+$ BF_4^-, our group has studied the behaviour of a chiral Lewis acid incorporating an optically active cyclopentadienyl ligand, namely (S_{Re})-[(η^5-PCp)Re(NO)(PPh_3)-($ClCD_2Cl$)]$^+$-BF_4^- (PCp = "pinene-fused cyclopentadienyl").[5][6] Gladysz determined the configurational stability of (S_{Re})-[(η^5-C_5H_5)Re(NO)(PPh_3)($ClCD_2Cl$)]$^+BF_4^-$ by either investigating the optical purity of the decomposition products formed after warming above −20°C, or by analysing the products generated when nucleophiles are added at low temperatures. The configurational stability of (S_{Re})-[(η^5-PCp)Re(NO)(PPh_3)($ClCD_2Cl$)]$^+BF_4^-$, on the other hand, was determined by low-temperature ^{31}P-NMR spectrocopy, where the optically active cyclopentadienyl ligand served as an internal spectroscopic probe of diastereomeric purity. Both systems show no inversion of configuration at the stereogenic metal centre up to their decomposition points at −20°C.

Recently, Gladysz et al.[7] have extended their studies to the peralkylated derivative (S_{Re})-[(η^5-C_5Me_5)Re(NO)-(PPh_3)($ClCD_2Cl$)]$^+BF_4^-$, under the assumption that peralkylated ligands should enhance the thermal and configurational stability of the chiral Lewis acid by either shielding the central metal atom through the bulk of the ligand, or by stabilizing the cationic centre through the electron-donating effect of the five alkyl groups. Surprisingly, they found that decomposition of (S_{Re})-(η^5-C_5Me_5)Re(NO)(PPh_3)-($ClCD_2Cl$)]$^+BF_4^-$ seems to occur even below −35°C. They also noticed that products formed by addition of nucleophiles at lower temperatures were only recovered with a maximum enantiomeric purity of 90%. Because spectroscopic methods for directly determining the conformational stability of enantiomers are limited, Gladysz et al. were not able to fully rationalize their observations.

As our previous work[6] had shown that the fate of a stereogenic metal centre could be easily monitored by low-temperature NMR spectroscopy when an optically active cyclopentadienyl ligand is present, we also investigated the synthesis and stability of a chiral Lewis acid derived from a peralkylated, optically active ligand such as PinCp* [PinCp* = tetramethyl(pinenyl)cyclopentadienyl], a ligand that has been first introduced by Lai et al.[8] This ligand, like PCp used by us before, should serve as an internal chiral probe to directly determine the stability of peralkylated derivatives of Gladysz' chiral Lewis acids. We also wanted

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[a] Institut für Anorganische Chemie, RWTH Aachen, D-52056 Aachen, Germany
Fax: (internat.) + 49-(0)241/888-8288
E-mail: albrecht.salzer@ac.rwth-aachen.de

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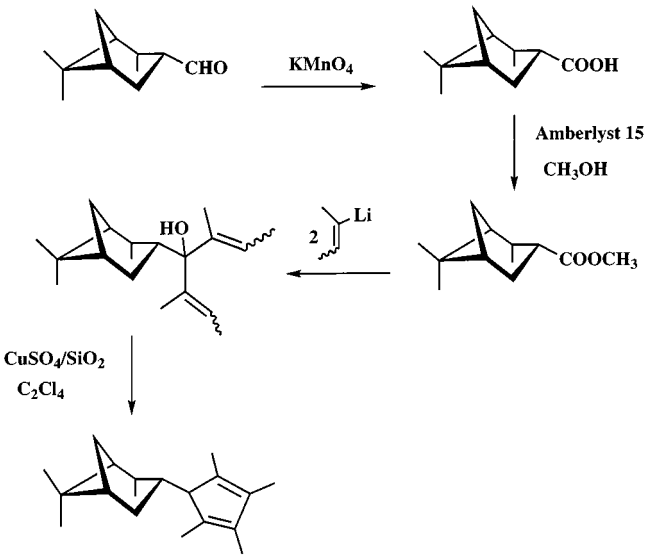
to show that this ligand could be universally used as a chiral replacement for Cp* by incorporating it into a series of other organometallic compounds.

Results and Discussion

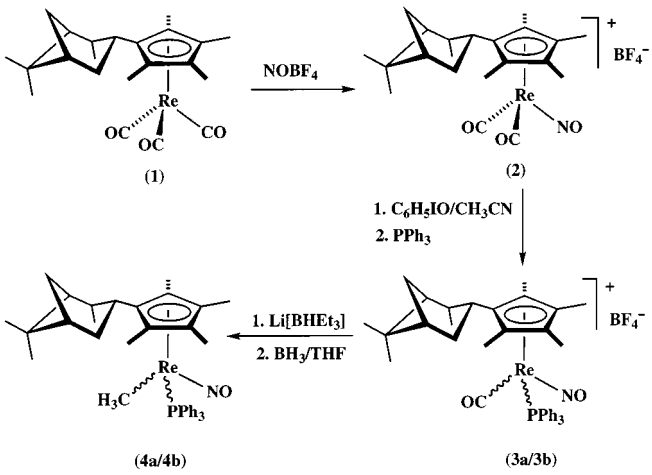
1. Synthesis of a Diastereomeric Mixture of (S_{Re})/(R_{Re})-(η^5-PinCp*)Re(CH_3)(NO)(PPh_3)

The ligand PinCp* was prepared from optically active (+)-pinanaldehyde,[9] which was oxidized to the (+)-carboxylic acid and then converted in several steps into a peralkylated cyclopentadiene ligand, as described by Lai for the other enantiomer[8] (Scheme 1).



Scheme 1

Following the same method as before,[6] (η^5-PinCp*)-Re($CO)_3$ (**1**) was synthesized in good yield by reaction of [Re($CO)_3$($THF)_2$]Cl with PinCp*Li in THF (Scheme 2). Because the peralkylated ligand has homotopic faces, only one product is generated and no separation step is required. In line with the work of Gladysz et al.,[10] the tricarbonyl complex was treated with freshly prepared $NOBF_4$ in CH_2Cl_2 at 0°C to form [(η^5-PinCp*)Re($CO)_2$(NO)]$^+$ (**2**) as yellow crystals after workup. The two diastereotopic CO groups could now be distinguished in the ^{13}C-NMR spectrum as two singlets. Because PPh_3 is less π-accepting than CO, the second CO ligand could not be substituted directly. In a first step, one of the CO groups had to be oxidized with iodosobenzene in acetonitrile. The intermediate acetonitrile complex was then treated with an excess of PPh_3 to give a diastereomeric mixture of (S_{Re})/(R_{Re})-[(η^5-PinCp*)-Re(CO)(NO)(PPh_3)]$^+BF_4^-$ (**3a/3b**), which was obtained in excellent yield and purity. The IR spectrum contains two bands for the CO and NO ligands. The ^{1}H- and ^{13}C-NMR spectra each have two sets of signals due to the two diastereomers. The signals of the diastereomeric CO ligands are quite interesting, because they appear as two doublets at δ = 202, each with a coupling constant of 8.3 Hz. There was, unexpectedly, only one signal for both diastereomers in the ^{31}P-NMR spectrum, both in [D_6]acetone and in [D_3]nitromethane.



Scheme 2

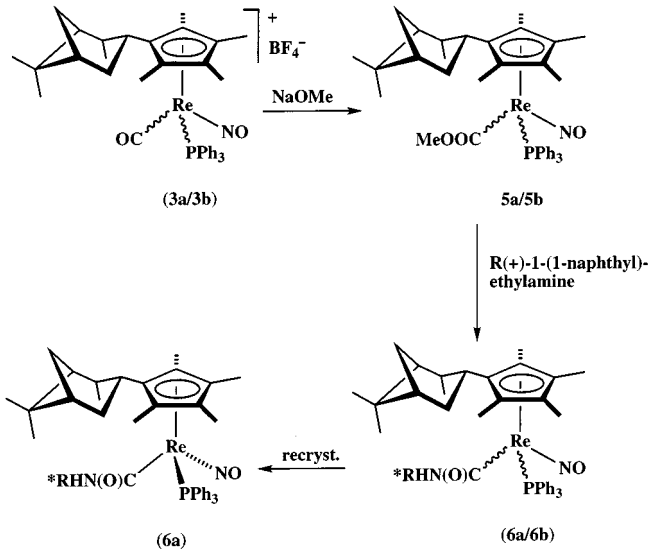
The reduction of the CO ligand to a methyl group was achieved in a two-step reaction with Li(C_2H_5)BH_3 and BH_3·THF.[11] After workup, (S_{Re})/(R_{Re})-(η^5-PinCp*)-Re(CH_3)(NO)(PPh_3) (**4a/4b**) was obtained as a red powder. The IR spectrum had one characteristic band for the NO ligand, while the ^{1}H- and ^{13}C-NMR spectra again contained two sets of signals for the two diastereomers. In the ^{1}H-NMR spectrum, the four methyl groups of the five-membered ring and the three methyl groups of the pinanyl part of each diastereomer overlapped. These signals therefore cannot be assigned unambiguously. Two signals, one at δ = 25.7 and one at δ = 23.4, appeared in the ^{31}P-NMR spectrum of the diastereomeric complexes. Because one of these signals is sharp and the other one is broad, it appears as if one of the two diastereomers is undergoing hindered ligand rotation. Measurements at low temperature confirmed that the broadened signal disappears below 0°C; two new signals, at a 3.5:1 ratio, appeared below −25°C. The sharp signal for the other diastereomer is retained throughout this experiment. That the original spectrum was observed again after the NMR sample was warmed up, confirms that hindered ligand rotation is a likely explanation for this phenomenon. It is interesting, but not yet explained why the two diastereomers should show such disparate behaviour and which type of rotation is involved.

The two signals of **4a/4b** appeared in a ratio of 1:1 in the ^{31}P-NMR spectrum, at room temp. The optically active PinCp* ligand therefore caused no asymmetric induction at the rhenium stereogenic centre. A reason for this may be the high temperature required for the substitution of the second CO group.

2. Resolution of Optically Active (S_{Re})-(PinCp*)Re(CH_3)(NO)(PPh_3) (4a)

Usually, mixtures of diastereomers can be separated by fractional crystallization or by chromatography. In our case, fractional crystallization was not possible because of the poor crystallinity of the mixture of (S_{Re})/(R_{Re})-(η^5-PinCp*)-Re(CH_3)(NO)(PPh_3). Also, no solvent mixture could be found to separate the diastereomers by preparative MPLC. We therefore followed the route of Gladysz et al. for the separation of (S_{Re})/(R_{Re})-(η^5-C_5Me_5)Re(CH_3)(NO)(PPh_3)[7] by using a suitable derivative.

The starting material for the separation was the complex (S_{Re})/(R_{Re})-[(η^5-PinCp*)Re(CO)(NO)(PPh_3)]$^+BF_4^-$ (**3a/3b**), which was treated with sodium methoxide in methanol to give the methyl ester (S_{Re})/(R_{Re})-[(η^5-PinCp*)Re(COOMe)(NO)(PPh_3) (**5a/5b**) in excellent yield (Scheme 3). The ^{31}P-NMR spectrum contained two sharp singlets in a ratio of 1:1. We could determine the ratio of the two diastereomers by using the two singlets of the methoxy groups at $\delta = 3$ in the ^{1}H-NMR spectrum. The CO groups appear in the ^{13}C-NMR spectrum as two doublets at $\delta = 203$ and 202, with $J_{C-P} = 13.8$ Hz.



Scheme 3

The methyl ester complexes were then treated with commercially available (+)-(*R*)-(1-naphthyl)ethylamine in CH_2Cl_2 to obtain the amide complexes **6a/6b**. The solvent was evaporated and the residual orange oil was stirred in *n*-hexane. An orange solid separated, which was collected by filtration, and recrystallized from benzene/*n*-hexane as crystals of one single diastereomer in an optical purity of > 98%, as determined by ^{1}H- and ^{31}P-NMR spectra (Scheme 3).

This less soluble diastereomer was identified by a crystal-structure determination to be (S_{Re})-(η^5-PinCp*)Re(NO)(PPh_3)[CONHCH(CH_3)$C_{10}H_7$] (**6a**) (Figure 1). These observations agree with Gladysz′ findings for (η^5-C_5Me_5)Re(NO)(PPh_3)[CONHCH(CH_3)$C_{10}H_7$], where the symmetrical products (S_{Re},S_{amid}) and (R_{Re},R_{amid}) were also more soluble than the mixed products (S_{Re},R_{amid}) and (R_{Re},S_{amid}).[7] The pinanyl substituent in **6a** adopts a conformation in which the methyl group points away from the metal centre and the dimethylmethylene bridge lies parallel to the plane of the cyclopentadienyl ring. This is very similar to the stereochemistry found in Lai′s molybdenum compound.[8]

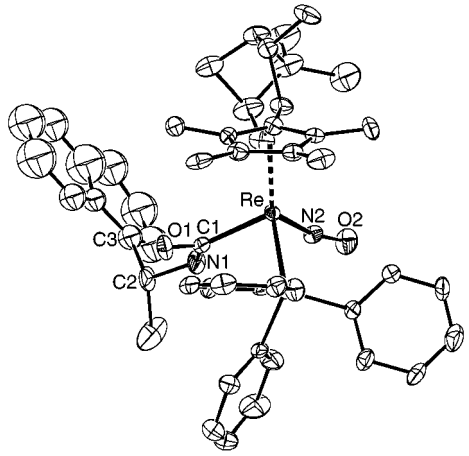


Figure 1. Crystal structure of (S_{Re})-(η^5-PinCp*)Re(NO)(PPh_3)-[CONHCH(CH_3)$C_{10}H_7$] (**6a**)

The enantiomerically pure amide was treated with trifluoroacetic acid at 0°C, which recovered the cationic, optically pure carbonyl complex, which was then isolated as the tetrafluoroborate salt (S_{Re})-[(η^5-PinCp*)Re(CO)-NO(PPh_3)]$^+BF_4^-$ (**3a**). By following this procedure with the other diastereomer, recovered by concentration of the mother liquor of the resolution step, the (R_{Re})-carbonyl complex could also be obtained in 80% optical purity. The reduction of pure **3a** to the methyl complex **4a** was carried out as described above for the diastereomeric mixture. The ^{31}P-NMR spectrum of (S_{Re})-(η^5-PinCp*)Re(CH_3)(NO)-(PPh_3) (**4a**) shows the broadened signal of the diastereomer undergoing hindered rotation. This signal, upon cooling, underwent the same changes as described before.

3. Formation and Stability of the Diastereomeric Mixture of (S_{Re})/(R_{Re})-[(η^5-PinCp*)-Re(NO)(PPh_3)($ClCD_2Cl$)]$^+BF_4^-$ (7a/7b) and Its Optically Pure (S_{Re}) Isomer

The chiral Lewis acid (S_{Re})/(R_{Re})-[(η^5-PinCp*)-Re(NO)(PPh_3)($ClCD_2Cl$)]$^+BF_4^-$ (**7a/7b**) was generated as described before.[5][12] The diastereomers were dissolved in CD_2Cl_2 in an NMR tube and treated with HBF_4 at −78°C. The ^{31}P-NMR spectrum, measured directly after shaking the reaction mixture, had three sharp signals of different intensity at $\delta = 14$, assignable to the two diastereomeric cations where one cation is a mixture of two rotamers. Additional signals appeared at $\delta = 15$ and 11 and seem to be decomposition products. When the solution was warmed, one of the three signals of the chiral Lewis acid remained unchanged, while the two others became broad. This behav-

iour is similar to that of the diastereomeric mixture of the complex (S_{Re})/(R_{Re})-[(η^5-PinCp*)Re(CH_3)(NO)(PPh_3) described above. Warming to −20°C resulted in a rapid decrease in the intensity of the three signals and a concomitant growth of the signals at δ = 11 and 15. The signal at δ = 11 appeared as two singlets in a ratio of 1:1, one of them sharp, the other one broadened.

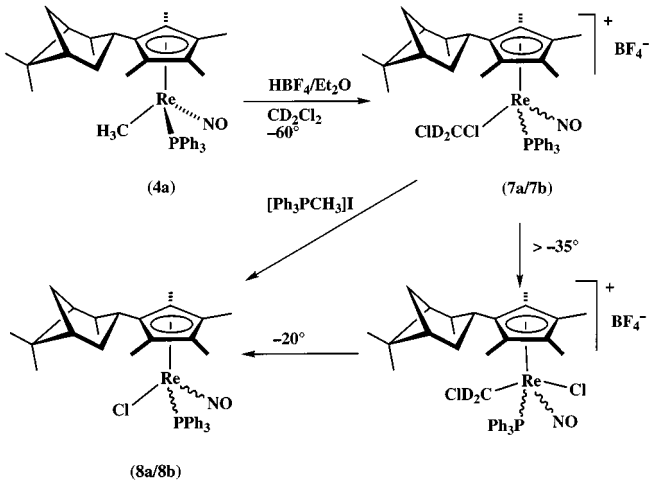
We then repeated the same experiment with optically pure (S_{Re})-[(η^5-PinCp*)Re(CH_3)(NO)(PPh_3). We expected to see only the two signals of the (S_{Re}) isomer, but surprisingly we also immediately observed the third signal due to the second diastereomer. This indicates that inversion at the metal centre starts taking place directly after mixing the compounds at −80°C. A noticeable amount of decomposition products was also observed at this temperature. At −60°C, the two diastereomers approached a ratio of 1:1, which was reached at −40°C. At −20°C, the cation had completely disappeared and the two signals at δ = 11 were again apparent as one sharp and one broadened signal. The IR spectrum of the reaction mixture, measured at room temperature, contained two NO signals, one at 1746 cm^{-1}, and one at 1641 cm^{-1}; they are assigned to the main decomposition products at δ = 11 and 15.

These results clearly show that the chiral Lewis acid (S_{Re})-[(η^5-PinCp*)Re(NO)(PPh_3)($ClCD_2Cl$)]$^+BF_4^-$ has an extremely low configurational stability. Even at −80°C, a small amount of the inversion product can be detected and at −40°C complete inversion has occurred. These conclusions could be drawn solely on the basis of low-temperature ^{31}P-NMR spectroscopy and they confirm the results obtained by Gladysz et al. for the Cp* complex. Gladysz′ observations, that the optically purity of the Lewis acid diminishes on reaction with another nucleophile can now be explained: Inversion at the metal centre already starts occurring shortly before the CD_2Cl_2 ligand is exchanged for a new nucleophile.

To find an explanation for the thermal and configurational instability of the complex [(η^5-Cp*)-Re(NO)(PPh_3)($ClCD_2Cl$)]$^+BF_4^-$, Gladysz et al. examined the products formed on warming the solution. They found that oxidative addition of the dichloromethane fragment takes place to give the cationic complex [(η^5-PinCp*)-Re(NO)(PPh_3)(CD_2Cl)Cl]$^+BF_4^-$. This Re^{III} species gives rise to a singlet at δ = 11 in its ^{31}P-NMR spectrum and an NO band at 1739 cm^{-1} in its IR spectrum. It was rationalized that the electron-rich permethylated complex confers stability to this unexpected Re^{III} species; this favours the formation of a higher oxidation species, which, contrary to expectations, lowers the stability of the chiral Lewis acid.

As we also saw two signals at δ = 11 in the ^{31}P-NMR spectra and a signal at 1746 cm^{-1} in the IR spectra, we tried to isolate [(η^5-PinCp*)Re(NO)(PPh_3)(CD_2Cl)Cl]$^+$-BF_4^- by dissolving the dried residue of the NMR sample in a small amount of THF and precipitating it with ether. A solid appeared, which dissolved again after being stirred for a short time. If this precipitate was in fact the Re^{III} species, of which we are sure, it must be quite unstable in the case of the PinCp* complex.

The chiral Lewis acid decomposition products whose signals were observed at δ = 15 appeared to be more stable. By comparing[12][13] the ^{31}P-NMR and IR data of the analogous PCp and Cp* complexes, we deduced this species to be a diastereomeric mixture of (S_{Re})/(R_{Re})-(η^5-PinCp*)-ReCl(NO)(PPh_3) (**8a/8b**). This could have formed directly by nucleophilic substitution of the stabilizing solvent molecule by a chloride anion, available from a small amount of DCl in the solvent. On the other hand, it could have formed by loss of CD_2Cl^+ from the Re^{III} species. We favour the second pathway because the signal at 1746 cm^{-1} disappears in favour of the signal at 1641 cm^{-1} (Scheme 4).



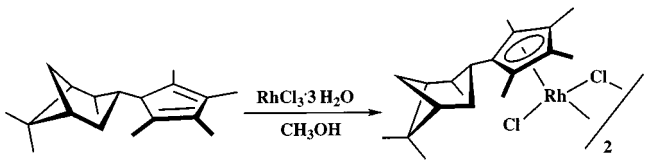
Scheme 4

To confirm this, we synthesized the chloride complex independently, following the route that Gladysz used for the Cp* complex.[13] After formation of the chiral Lewis acid, methyltriphenylphosphonium iodide was added. The solution turned red and the product could be identified by IR, ^{1}H-, ^{13}C-, ^{31}P-NMR, and MS data to be the expected chloride species (**8a/8b**). The IR and ^{31}P-NMR signals were identical to those of the previous NMR experiments. The ^{31}P-NMR spectrum of **8a/8b** contained a sharp and a broad signal. The broadened signal disappeared upon cooling below 0°C and two new signals appeared upon further cooling. The sharp signal does not change during this time. The same behaviour was previously observed for (S_{Re})/(R_{Re})-[(η^5-PinCp*)Re(CH_3)(NO)(PPh_3). Again, a hindered ligand rotation associated most likely with the bulky PinCp* ligand occurs within the (S_{Re}) isomer, but not in the case of the (R_{Re}) isomer. It remains unclear why this phenomenon should so persistently be restricted to only one of the two diastereomers.

4. Synthesis of Other Metal Complexes of the Chiral Cyclopentadienyl Ligand PinCp*

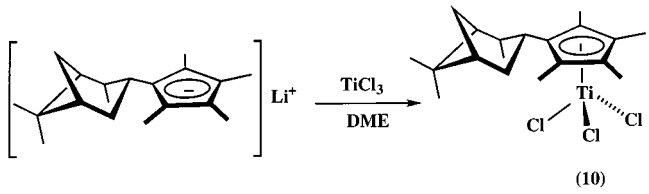
As rhodium complexes with a chiral cyclopentadienyl ligand are known to be useful in asymmetric hydrogenations,[14] we also synthesized a corresponding PinCp* complex. We prepared [PinCp*$RhCl_2$]$_2$ (**9**) by heating

$RhCl_3 \cdot 3H_2O$ and PinCp*H in methanol under reflux for a few days (Scheme 5). After the solvent was evaporated, a red solid was collected in reasonable yields, which was characterized by ^1H- and ^{13}C-NMR spectroscopy and elemental analysis. We are currently trying to perform these experiments in the presence of zeolites to prepare a corresponding "ship-in-the-bottle" complex and to test **9** as a catalyst precursor in enantioselective hydrogenation.



Scheme 5

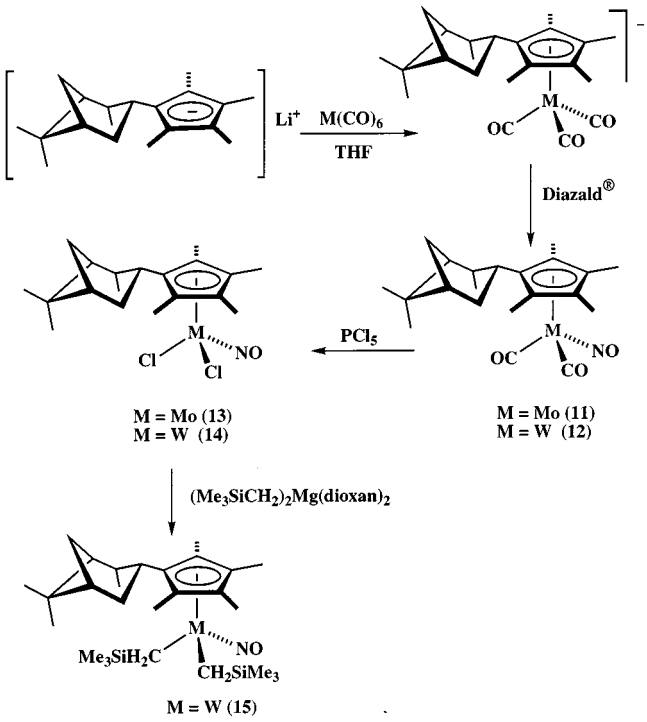
Chiral cyclopentadienyl ligands are also often attached to early transition metals like Ti, Zr, and Hf.[15] Such complexes may be efficient Ziegler-Natta polymerization catalysts, or catalyse enantioselective synthesis. We prepared the complex (PinCp*)$TiCl_3$ (**10**) by treating $TiCl_3 \cdot 3THF$ with PinCp*Li in DME under reflux.[16] After workup, a red solid was isolated and characterized by ^1H- and ^{13}C-NMR and MS data to be PinCp*$TiCl_3$. Extraction of the remaining solid with CCl_4 did not lead to the isolation of the expected doubly substituted product (PinCp*)$_2TiCl_2$. The reaction with PinCp* therefore takes a different route from that with Cp*, where Cp*$_2TiCl_2$ is the major product under the same reaction conditions (Scheme 6).



Scheme 6

Legdzins et al. have prepared many complexes with the 14-VE backbone Cp′M(NO) [M = Mo, W; Cp′ = C_5H_5 or C_5Me_5].[17] Their aim was to synthesize stable 16-VE complexes of the type Cp′M(NO)(R)(R′), where the alkyl or aryl substituents could be equivalent or different from each other. To synthesize such a complex with the chiral ligand PinCp* we followed the procedure published for Cp*.[18] [(η^5-PinCp*)M$(CO)_3$]$^-$ was synthesized by treating $M(CO)_6$ with PinCp*Li in THF. The anion was then directly converted into the neutral, coordinatively saturated complexes (η^5-PinCp*)M$(CO)_2$(NO) (**11**,**12**) without further purification by treating the tricarbonyl complex with Diazald. The product was purified by sublimation and excess Diazald was separated by column chromatography (hexane/ether, 4:1). The reaction of the nitrosyl complexes with PCl_5 in ether yielded the 16-VE complexes (PinCp*)MCl_2(NO) (**13**,**14**) as poorly soluble, green solids (Scheme 7).

The nitrosyl dichloride complex was alkylated with $(Me_3SiCH_2)_2Mg \cdot (dioxane)_2$ at very low temperatures.[19] As the Cp* tungsten complex was more stable than the corresponding molybdenum compounds,[20] we restricted our investigations to the former. The NO group of the dialkylated product (PinCp*)W(NO)$(CH_2SiMe_3)_2$ (**15**) has an IR absorption at 1582 cm^{-1} which agrees with a weakening of the N−O bond as found by Legdzins et al. in crystal structures. The ^1H- and ^{13}C-NMR spectra contain two signals for the diastereotopic $SiMe_3$ groups. The compound does not appear to be as stable in solution as the corresponding Cp* complex, but it can be stored at room temperature as a solid. We could also obtain a monoalkylated product as a red oil by using only half an equivalent of the magnesium reagent and strict temperature control, but this product was too unstable to be isolated and fully characterized in analytically pure form.



Scheme 7

We also tried to generate a new stereogenic centre at the metal atom by a thermal or photochemical substitution of one of the CO groups in (PinCp*)W$(CO)_2$(NO). Brunner[21] had reported an efficient substitution of PPh_3 for CO to generate the complex CpMo(CO)(NO)(PPh_3) in refluxing toluene. He obtained quantitative yields, while another group[22] claimed that this substitution does not take place even at very high temperatures. We treated (PinCp*)Mo$(CO)_2$(NO) with PPh_3 in refluxing toluene over several hours. No substitution could be observed, which may be either because the PinCp* ligand is more electron-donating or because of steric hindrance. A photochemical ligand exchange also did not occur by irradiation in toluene, where after one hour the starting material had completely decomposed.

PinCpH* also reacts with carbonyliron and -ruthenium complexes to form dimeric carbonyl complexes. These will be described elsewhere.

Conclusion

The optically active peralkylated ligand PinCp*H can be introduced into a series of metal complexes of titanium, molybdenum, tungsten, rhenium and rhodium. In most cases, these new complexes have properties similar to those of the corresponding Cp* complexes. The PinCp* ligand can serve as an internal spectroscopic probe for the configurational stability of the chiral-at-metal Lewis acid [PinCp*ReNO(PPh_3)($ClCD_2Cl$)]$^+$.

Experimental Section

General Remarks: All experiments were performed under purified nitrogen using standard vacuum-line and Schlenk-tube techniques. Diethyl ether and THF were distilled from sodium benzophenone ketyl. Acetonitrile and dichloromethane were distilled from calcium hydride. Dimethoxyethane (DME) and *n*-hexane were dried with molecular sieves. [$Re(CO)_3(THF)_2$]Cl,[23] $NOBF_4$,[24] iodosobenzene,[25] [$(Me_3Si)CH_2Mg$]·(dioxane)$_2$[26] and PinCp*[8] were prepared as described in the literature. (+)-3-Formylpinane was a gift from BASF. − Infrared spectra were recorded with a Perkin−Elmer 1750 FT spectrophotometer as solutions in *n*-hexane, CH_2Cl_2, or DME in NaCl cells. − NMR spectra were recorded with either a Varian VXR 300 or a Varian Unity 500 spectrometer in $CDCl_3$ or C_6D_6 unless otherwise stated. ^{1}H- and ^{13}C-NMR spectra were referenced to tetramethylsilane (TMS) or from internal solvent peaks; ^{31}P-NMR spectra were referenced to H_3PO_4 (external). All ^{13}C- and ^{31}P-NMR data are of proton-decoupled (broadband) spectra.

(+)-(1*S*,2*S*,3*S*,5*R*)-Pinane-3-carboxylic Acid: (+)-3-Formylpinane (49.8 g, 0.30 mol) was dissolved in acetone and treated slowly with a cold saturated aqueous solution of $KMnO_4$ (31.6 g, 0.2 mol). The solution was stirred for 2 h at room temperature and the precipitate of MnO_2 was filtered off with a Buchner funnel, and through Celite/cotton wool. The solution was treated with solid KOH to an approximate pH value of 12 and extracted 3 times with ether. After acidification with concd. HCl, the aqueous solution was again extracted 3 times with ether. The organic phases were combined and dried with $MgSO_4$. The solvent was evaporated under reduced pressure in a rotary evaporator, leaving a pale-yellow oil, yield 52.8 g (0.29 mol, 98%). This product was used for the further synthesis of PinCp*.[8]

[(η^5-PinCp*)Re(CO)$_3$ (1): PinCp*H (5.16 g, 20.0 mmol) was dissolved in 80 mL of THF and cooled to −78°C. *n*BuLi (1.6 M in hexane, 20 mmol, 12.5 mL) was added by syringe while the solution was stirred. The mixture was allowed to warm to room temperature and was then refluxed for 14 h. PinCp*Li precipitated as a white solid. The solvent was removed by vacuum distillation and the product was washed twice with 100 mL of *n*-hexane. The white solid was dissolved in 50 mL of THF, cooled to 0°C, and a solution of 20.0 mmol of [$Re(CO)_3(THF)_2$]Cl in THF was added dropwise. The solution was then refluxed for 12 h and, after cooling to room temperature, the solvent was removed by vacuum distillation. The residue was extracted with hot *n*-hexane and filtered hot through Celite. After concentrating the solution, the product precipitated at −30°C as an off-white solid; yield: 10.00 g (19.0 mmol, 95%). − IR (*n*-hexane): $\tilde{\nu}_{(CO)}$ = 2014 (s), 1923 (s) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 2.94 (q, J_{H-H} = 9.5 Hz, 1 H, H-4), 2.38 (m, 1 H), 2.27 (s, 3 H, C_5Me_4), 2.21 (s, 3 H, C_5Me_4), 2.17 (d, J_{H-H} = 7.3 Hz, 6 H, C_5Me_4), 2.08 (m, 3 H, H-9), 1.90 (t, J_{H-H} = 5.5 Hz, 2 H), 1.26 (s, 3 H, H-9), 1.19 (s, 1 H), 1.16 (s, 3 H, H-8), 1.02 (d, J_{H-H} = 7.0 Hz, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 198.1 (CO), 105.5, 100.9, 98.4, 96.9 (C_5Me_4), 49.2 (C-5), 43.2 (C-1), 39.42, 34.4 (C-2/6/10), 39.1 (br., C-3), 33.9 (C-4), 28.7, 23.5 (C-8/9), 21.2 (C-7), 12.0, 10.9, 10.8 (C_5Me_4). − $C_{22}H_{29}O_3Re$ (527.66): calcd. C 50.08, H 5.54; found C 50.08, H 5.52.

[(η^5-PinCp*)Re(CO)$_2$(NO)]$^+$BF$_4^-$ (2): Compound **1** (2.30 g, 4.36 mmol) was dissolved in 100 mL of CH_2Cl_2 and cooled to 0°C. Freshly prepared $NOBF_4$ (0.79 g, 6.77 mmol) was added in small portions and CO started to evolve immediately. After 3 h of stirring, the solution was poured into 300 mL of diethyl ether and a light yellow precipitate formed. The solid was collected by filtration and washed with diethyl ether. Recrystallisation from CH_2Cl_2/*n*-hexane gave a yellow compound **2**; yield: 2.63 g (4.27 mmol, 98%). − IR (hexane): $\tilde{\nu}_{(CO)}$ = 2093 (s), 2040 (s); $\tilde{\nu}_{(NO)}$ = 1799 (m) cm^{-1}. − ^{1}H NMR ([D$_6$]acetone): δ = 3.37 (q, *J* = 9.5 Hz, 1 H, H-4), 2.64 (s, 3 H, C_5Me_4), 2.57 (s, 3 H, C_5Me_4), 2.50 (d, J_{H-H} = 2.8 Hz, 6 H, 2∞ C_5Me_4), 2.47 (m, 1 H), 2.35 (m, 2 H), 2.12 (m, 1 H), 1.99 (m, 2 H), 1.30 (s, 3 H, H-9), 1.28 (s, 1 H), 1.22 (s, 3 H, H-8), 1.12 (d, J_{H-H} = 7.0 Hz, 3 H, H-7). − ^{13}C NMR ([D$_6$]acetone): δ = 187.0, 186.9 (CO), 112.1, 109.2 (C_5Me_4), 49.9 (C-5), 43.8 (C-1/3), 40.1, 38.3, 34.9 (C-2/6/10), 35.2 (C-4), 29.0, 23.7 (C-8/9), 21.4 (C-7), 11.9, 11.7, 10.5, 10.3 (C_5Me_4). − $C_{21}H_{29}BF_4NO_3Re$ (616.47): calcd. C 40.91, H 4.74, N 2.27; found C 40.56, H 2.25, N 2.25.

(*S*$_{Re}$)/(*R*$_{Re}$)-[(η^5-PinCp*)Re(CO)(NO)(PPh_3)]$^+$BF$_4^-$ (3a/3b): The nitrosyl complex **2** (2.56 g, 4.16 mmol) was dissolved in 50 mL of acetonitrile and freshly prepared iodosobenzene (1.05 g, 4.78 mmol) was added at 0°C. CO_2 evolution started immediately and the solution was stirred until the solid had dissolved (about 1.5 h). The solution was filtered through 2 cm of silica gel and after evaporation of the solvent (*S*$_{Re}$)/(*R*$_{Re}$)-[(η^5-PinCp*)Re(CH_3CN)(NO)(PPh_3)]$^+$BF$_4^-$ was obtained as a brown oil. − IR (CH_3CN): $\tilde{\nu}_{(CO)}$ = 2010 (s), $\tilde{\nu}_{(NO)}$ = 1743 cm^{-1}. − The oil was dissolved in 2-butanone and PPh_3 (1.33 g, 5.09 mmol) was added in small portions while stirring. The dark-brown mixture was refluxed for 12 h and the solvent was removed afterwards by vacuum distillation. The residue was recrystallized from acetone/Et_2O; yield of yellow **3a/3b**: 3.18 g (3.74 mol, 90%). − IR (CH_2Cl_2): $\tilde{\nu}_{(CO)}$ = 2005 (s), $\tilde{\nu}_{(NO)}$ = 1747 (s) cm^{-1}. − ^{1}H NMR ([D$_6$]acetone): δ = 7.70−7.50 (m, 30 H, PPh_3), 3.45 (q, J_{H-H} = 9.46 Hz, 1 H, H-4), 3.40 (q, J_{H-H} = 7.02, 1 H, H-4′), 2.85 (s, 3 H), 2.50 (s, 3 H), 2.46 (m, 1 H), 2.38 (m, 3 H), 2.31 (s, 3 H), 2.27 (s, 3 H), 2.16 (m, 3 H), 2.00 (m, 2 H), 1.86 (s, 3 H), 1.71 (s, 3 H), 1.51 (s, 3 H), 1.33(s, 1 H), 1.30 (m, 6 H), 1.27 (s, 3 H), 1.24 (s, 3 H), 1.12 (m, 6 H). − ^{13}C NMR ([D$_6$]acetone): δ = 201.8 (d, J_{C-P} = 12.6 Hz, CO), 201.4 (d, J_{C-P} = 12.6 Hz, CO′), 134.3 (d, J_{C-P} = 11.4 Hz, C-b), 134.1 (d, J_{C-P} = 11.4 Hz, C-b′), 133.3 (dd, J_{C-P} = 6.6 Hz, C-d/d′), 131.2 (d, J_{C-P} = 12.6 Hz, C-a/a′), 130.7 (d, J_{C-P} = 11.4 Hz, C-c), 130.6 (d, J_{C-P} = 11.4 Hz, C-c′), 115.5, 114.7, 109.7, 107.5, 106.0 (C_5Me_4), 50.2 (C-5/5′), 44.4 (br. s, C-3/3′), 43.9, 43.7 (C-1/1′), 40.2, 40.1 (C-10/10′), 37.8, 36.3 (C-4/4′), 35.9, 35.6, 34.9 (C-2/2′/6/6′), 29.4, 29.0, 23.9, 23.7 (C-8/8′/9/9′), 21.8, 21.7 (C-7/7′), 15.1, 11.8, 11.6, 10.2, 10.0, 9.8, 9.4 (C_5Me_4). − ^{31}P NMR ([D$_6$]acetone): δ = 12.9. − $C_{38}H_{44}BF_4NOPRe$ (834.71): calcd. C 53.65, H 5.21, N 1.65; found C 52.98, H 5.22, N 1.64.

(*S*$_{Re}$)/(*R*$_{Re}$)-(η^5-PinCp*)Re(CH_3)(NO)(PPh_3) (4a/4b): The diastereomeric mixture of **3** (1.56 g, 1.83 mmol) was suspended in 50 mL of THF and 3.7 mL of Li(C_2H_5)$_3$BH in THF (1 M in THF, 3.7 mmol) was injected. The precipitate dissolved slowly, while the colour of the solution became honey-brown. Then 9.2 mL of 0.776 M BH_3·THF in THF (7 mmol) was added. H_2 evolution occurred immediately and the solution was stirred for 30 min. The

solvent was then removed and the residue extracted with toluene and passed through a short silica gel column. The solvent was evaporated to give complex **4a/4b** as a red powder; yield 1.31 g (1.74 mmol, 95%). − IR (hexane): $\nu_{(NO)}$ = 1634 (s) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.50−7.32 (m, 30 H, PPh_3), 3.22 (q, J_{H-H} = 9.46 Hz, 1 H, H-4), 3.13 (q, J_{H-H} = 9.46 Hz, 1 H, H-4′), 2.38 (m, 2 H), 2.28 (m, 2 H), 2.21 (m, 2 H), 2.06 (s, 3 H), 2.00(m, 1 H), 1.90 (m, 4 H), 1.82 (s, 3 H), 1.80 (s, 3 H), 1.53(s, 3 H), 1.50 (s, 3 H), 1.29−1.23 (6 s, 18 H), 1.11 (d, J_{H-H} = 7.02 Hz, 3 H), 1.06 (d, J_{H-H} = 7.02 Hz, 3 H), 0.84 (d, J_{H-P} = 7.02, 3 H, Re−Me), 0.79 (d, J_{H-P} = 7.02 Hz, 3 H, Re−Me′), 0.68 (s, 3 H), 0.5 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 136.4, 136.0 (d, J_{C-P} = 47.7 Hz, C-a), 136.0, 135.6 (d, 47.7 Hz, C-a′), 134.08, 134.01 (d, J_{C-P} = 9.8 Hz, C-b), 134.04, 133.96 (d, 10.4 Hz, C-b′), 129.5 (C-d/d′), 128.1, 128.0 (C-c/c′), 107.5, 105.9, 103.7, 103.6, 100.4, 96.6, 95.6, 94.7 (C_5Me_4), 49.6, 49.5 (C-5/5′), 43.8 (br., C-3/3′), 43.2, 43.1 (C-1/1′), 39.6, 39.5 (C-10/10′), 35.7, 35.4, 34.8, 34.6,34.4 (C-4/4′/2/2′/6/6′), 28.9, 23.6, 23.5 (C-8/8′/9/9′), 21.6, 21.5 (C-7/7′), 11.9,11.8, 10.8, 10.7, 10.6, 7.6, 7.3 (C_5Me_4), −22.7 (d, J_{C-P} 7.0 Hz, Re−Me), −24.7 (d, J_{C-P} = 7.2 Hz, Re−Me). − ^{31}P NMR (C_6D_6): δ = 25.7 (br.), 23.4. − $C_{38}H_{47}NOPRe$ (750.92): calcd. C 60.78, H 6.31, N 1.87; found C 59.96, H 6.33, N 1.87

(S_{Re})/(R_{Re})-(η⁵-PinCp*)Re(COOCH₃)(NO)(PPh₃) (5a/5b): The diastereomeric mixture of **3a/3b** (1.04 g, 1.23 mmol) was dissolved in 30 mL of dichloromethane and 2.7 mL of 4.37 M sodium methoxide in MeOH (10.68 mmol) was added while stirring. The progress of the reaction was monitored by IR spectroscopy. After the disappearance of the starting material, the solvent was removed. The residue was extracted with hot *n*-hexane, filtered and concentrated. Slow cooling gave a yellow precipitate which was purified by washing with a small amount of *n*-hexane. Yield of **5a/5b**: 1.15 g (1.14 mmol, 93%). − IR (CH_2Cl_2): $\tilde{\nu}_{(NO)}$ = 1646 (s), $\tilde{\nu}_{(COOMe)}$ = 1576 (m) cm^{-1}. − IR (MeOH): $\tilde{\nu}_{(NO)}$ = 1663 (s), $\tilde{\nu}_{(COOMe)}$ = 1550 (m) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.47 (m, 12 H, PPh_3), 7.36(m, 18 H, PPh_3), 3.27 (q, J_{H-H} = 9.46 Hz, 1 H, H-4), 3.17 (q, J_{H-H} = 9.46 Hz, 1 H, H-4′), 3.03 (s, 3 H, OCH_3), 2.98 (s, 3 H, OCH_3), 2.36 (m, 3 H), 2.25 (s, 4 H), 2.16 (s, 2 H), 2.07 (m, 3 H), 1.97 (s, 1 H), 1.91 (m, 2 H), 1.87 (s, 6 H), 1.72 (s, 3 H), 1.47 (s, 2 H), 1.31 (s, 2 H), 1.29 (s, 1 H), 1.28 (s, 3 H), 1.24 (s, 6 H), 1.21 (m, 1 H), 1.16 (s, 9 H), 1.08 (d, J_{H-H} = 7.02 Hz, 3 H), 1.02 (d, J_{H-H} = 7.02 Hz, 3 H), 0.95 (d, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 203.2 (d, J_{C-P} = 13.7 Hz, CO), 202.6 (d, J_{C-P} = 13.7 Hz, CO), 135.0 (d, J_{C-P} = 25 Hz, C-a), 134.6 (d, J_{C-P} = 25 Hz, C-a′), 134.2, 134.1 (d, J_{C-P} = 3.8 Hz, C-b), 134.1, 134.0 (d, J_{C-P} = 3.8 Hz, C-b′), 130.0, 129.9 (C-d/d′), 128.1, 128.0 (C-c/c′), 111.2, 110.6, 104.5, 104.1, 100.1, 100.0 (C_5Me_4), 49.7, 49.5, 49.4, 49.1 (C-5/5′/OCH_3/OCH_3′), 44.5, 44.1 (br., C-3/3′), 43.3, 43.2 (C-1/1′), 39.6, 39.5 (C-10/10′), 36.5, 35.4 (C-4/4′), 34.8, 34.7, 34.4, 34.3 (C-2/2′/6/6′), 28.8, 28.7, 23.6, 23.4 (C-8/8′/9/9′), 21.7, 21.6 (C-7/7′), 11.9, 11.8, 11.6, 11.1, 10.9, 9.9, 8.9, 8.7 (C_5Me_4/C_5Me_4′). − ^{31}P NMR ($CDCl_3$): δ = 18.7, 18.1. − $C_{39}H_{47}NO_3PRe$ (794.97): calcd. C 58.92, H 5.96, N 1.76; found C 58.88, H 5.89, N 1.74.

(S_{Re})/(R_{Re})-(η⁵-PinCp*)Re(NO)(PPh₃)[CONHCH(CH₃)C₁₀H₇] (6a/6b): Compound **5a/5b** (1.02 g, 1.28 mmol) was dissolved in 30 mL of CH_2Cl_2 and (+)-(*R*)-1-(1-naphthyl)ethylamine (0.42 mL, 2.56 mmol) was added dropwise via a syringe. The solution was stirred at room temperature until the reaction was completed (reaction monitoring by IR spectroscopy). The solvent was then removed and the oily residue was stirred in *n*-hexane until a yellow precipitate formed. The solid was collected by filtration and recrystallized from CH_2Cl_2/*n*-hexane. After a few days, orange crystals of (S_{Re})-(η⁵-PinCp*)Re(NO)(PPh_3)[CONHCH(CH_3)$C_{10}H_7$] (**6a**) had formed. Yield: 0.35 g (0.38 mmol, 60%) of optical purity: > 98% *de*. − IR (CH_2Cl_2): $\tilde{\nu}_{(NO)}$ = 1624 (s), $\tilde{\nu}_{(CO)}$ = 1533 (m) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 8.16 (d, J_{H-H} = 7.32 Hz, 1 H), 7.78 (d, J_{H-H} = 7.94 Hz, 1 H), 7.67 (dd, J_{H-H} = 1.83 Hz, J<inf'H−H</INF' = 6.91 Hz, 1 H), 7.55 (t, J_{H-H} = 8.55 Hz, 6 H, H-b), 7.39 (m, 13 H, H-c/d/naphthyl), 5.76 (quint, J_{H-H} = 6.87 Hz, 1 H, NCH), 5.26 (s, 1 H, NH), 3.08 (q, J<inf'H&NDASH;H</INF' = 9.36 Hz, 1 H, H-4), 2.17 (t, J_{H-H} = 7.48 Hz, 2 H), 2.10 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3), 1.89 (m, 1 H), 1.78 (t, J_{H-H} = 5.56 Hz, 1 H), 1.52 (s, 3 H, CH_3), 1.43 (s, 1 H), 1.26 (s, 1 H), 1.18 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3), 0.95 (s, 3 H, CH_3), 0.84 (d, J_{H-H} = 6.41, 1 H), 0.78 (d, J_{H-H} = 6.71 Hz, 3 H, $NCCH_3$). − ^{13}C NMR ($CDCl_3$): δ = 199.5 (d, J_{H-H} = 11.6 Hz, CO), 141.4 (C-Naph1), 134.2 (C-NCH), 133.9 (C-a PPh_3), 131.3 (C-Naph8/9), 139.8, 128.3, 128.2, 128.1 (d, J_{H-H} = 9.8 Hz), 127.1, 125.7, 125.3, 125.2, 124.5, 122.2 (CH-Naph, PPh_3), 111.7, 101.1, 98.6 (C_5Me_4), 49.3 (C-5), 43.9, 42.9 (C-3/NaphCH_3), 43.5 (C-1), 39.3, 34.8, 34.4 (C-2/6/10), 35.0 (C-4), 28.8, 23.4 (C-8/9), 20.3 (C-7), 12.0, 11.5, 10.2, 8.1 (C_5Me_4). − ^{31}P NMR ($CDCl_3$): δ = 19.5. − $C_{50}H_{46}O_2N_2PRe$ (924.10): calcd. C 64.29, H 6.04, N 3.00; found C 64.19, H 6.11, N 3.04.

(S_{Re})-(η⁵-PinCp*)Re(NO)(PPh_3)(CH_3) (4a): The optically pure amide **6a** (0.34 g, 0.36 mmol) was dissolved in 5 mL of dichloromethane and CF_3COOH (68.0 mL, 0.90 mmol) was added dropwise at 0 °C. The solution was stirred at this temperature for 10 min; the orange colour changed to yellow. The solvent was removed and the residue was dissolved in 5 mL of MeOH. Then $NaBF_4$ (0.075 g, 0.72 mmol), dissolved in 2 mL of water, was added dropwise. An additional 6 mL of water was then added and a yellow precipitate formed. Stirring was continued for 15 min, the solid was collected by filtation and dried in vacuo. Yield of **3a** (S_{Re})-[(η⁵-PinCp*)-Re(CO)(NO)(PPh_3)]$^+BF_4^-$: 0.30 g (0.36 mmol, 99%). − ^{13}C NMR ([D_6]acetone): δ = 206.0 (CO), 134.3, 134.1 (d, J_{C-P} = 11.5 Hz, C-b), 133.3 (C-d), 131.5 (C-a), 130.7, 130.5 (d, J_{C-P} = 11.4 Hz, C-c), 116.9, 116.1, 110.2, 107.6, 106.3 (C_5Me_4), 50.4 (C-5), 44.3 (br., C-3), 43.9 (C-1), 40.2 (C-10), 36.5 (C-4), 36.0, 35.0 (C-2/6), 38.9, 23.9 (C-8/9), 21.8 (C-7), 12.3, 11.7, 10.1, 9.6 (C_5Me_4). − The yellow precipitate of **3a** was dissolved in 20 mL of THF and 0.71 mL of Li[(C_3H_5)$_3$BH] in THF (1 M in THF, 0.71 mmol) was added. After 20 min of stirring, 1.25 mL of BH3·THF (0.94 M in THF, 1.34 mmol) was added dropwise. While the solution was stirred for 30 min, it turned red. The solvent was removed in vacuo, the residue taken up in toluene and passed through 3 cm of silica gel. After evaporating the solvent in vacuo, the red solid was recrystallized from *n*-hexane. Yield of **4a**: 0.26 g (0.34 mmol, 95%). − IR (*n*-hexane): nu tilde$_{(NO)}$ = 1634 (s) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.50−7.32 (m, 15 H, PPh_3), 3.22 (q, J_{H-H} = 9.46 Hz, 1 H, H-4), 2.38 (m, 1 H), 2.28 (m, 1 H), 2.21 (m, 1 H), 2.06 (s, 1 H), 2.00 (m, 1 H), 1.90 (m, 1 H), 1.82 (s, 3 H), 1.50 (s, 3 H), 1.29 (s, 3 H), 1.23 (s, 3 H), 1.06 (d, J_{H-H} = 7.02 Hz, 3 H), 0.84 (d, J_{H-P} = 7.02, 3 H, ReMe), 0.5 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 136.4, 136.1 (d, J_{C-P} = 47.6 Hz, C-a), 134.1, 134.0 (d, J_{C-P} = 10.4 Hz, C-b), 129.6 (C-d), 128.1, 128.0 (d, J_{C-P} = 9.8 Hz, C-c), 96.6, 94.7 (C_5Me_4), 49.6 (C-5), 43.6 (br., C3), 43.1 (C-1), 39.6 (C-10), 35.4 (C-4), 34.9, 34.4 (C-2/6), 28.0, 23.6 (C-8/9), 21.6 (C-7), 11.8, 10.8, 10.6, 7.3 (C_5Me_4), 22.7, −22.8 (d, J_{C-P} = 6.5 Hz, ReCH_3). − ^{31}P NMR ($CDCl_3$): δ = 24.8 (br.) (25 °C); 25.4 (br.), 23.1 (br.) (−20 °C); 25.5, 23.1 (−50 °C). − $C_{38}H_{47}NOPRe$ (750.92): calcd. C 60.78, H 6.31, N 1.87; found C 60.82, 6.38, N 1.85.

(S_{Re})/(R_{Re})-[(η⁵-PinCp*)Re(NO)(PPh_3)($ClCD_2Cl$)]$^+BF_4^-$ (7a/7b) (NMR Experiment): A 5-mm NMR tube was filled with a solution of **4a/4b** (60.0 mg, 0.08 mmol) in 0.7 mL of CD_2Cl_2. The NMR tube was cooled to −78 °C and 11 μL of HBF_4·Et_2O (54% in Et_2O, 0.081 mmol) was added by syringe. The tube was sealed, shaken

quickly and a ^{31}P-NMR spectrum was measured at −80°C immediately. − ^{31}P NMR (CD_2Cl_2): δ = 14.7, 14.3, 14.2 (−80°C); 14.6, 14.1, 14.0 (−60°C); 14.5 (v br.), 14.0, (br.), 13.9 (−40°C); 13.9 (v br.), 13.8 (−20°C).

(S_{Re})-[(η^5-PinCp*)Re(NO)(PPh_3)($ClCD_2Cl$)]$^+BF_4^-$ (7a) (NMR Experiment): Optically pure **4a** was treated the same way as the diastereomeric mixture. − ^{31}P NMR (CD_2Cl_2): δ = 14.7, 14.3 (−80°C); 14.6, 14.1 (−60°C); 14.5 (v br.), 14.0, (br.) (−40°C); 13.9 (v br.) (−20°C).

(S_{Re})/(R_{Re})-(η^5-PinCp*)ReCl(NO)(PPh_3) (8a/8b): Complexes **4a/4b** (60 mg, 0.08 mmol) were dissolved in 10 mL of CH_2Cl_2 and cooled to −78°C. 11.8 µL HBF_4·Et_2O (54% in Et_2O, 0.087 mmol) was added by syringe and the mixture was stirred at this temperature for 10 min. Then $[Ph_3PCH_3]^+I^-$ (39.5 mg, 0.098 mmol) was added and the cooling bath was removed. The solution was warmed to room temperature, passed through 3 cm of silica gel and dried. Yield of a red solid **8a/8b**: 49.3 mg (0.06 mmol, 80%). − IR (CH_2Cl_2) $\tilde{\nu}_{(NO)}$ = 1641 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 7.60−7.52 (m, 6 H, H-b), 7.37 (m, 9 H, H-c/d), 3.14 (q, J_{H-H} = 9.46 Hz, 1 H, H-4), 3.06 (q, J_{H-H} = 9.46 Hz, 1 H, H-4′), 2.49 (m, 1 H), 2.34 (m, 2 H), 2.29 (m, 1 H), 2.20 (m, 2 H), 2.05 (m, 4 H), 1.96 (s, 1 H), 1.92 (m, 1 H), 1.89 (m, 2 H), 1.75 (s, 3 H), 1.73 (s, 3 H), 1.65 (s, 3 H), 1.3 (s, 3 H), 1.28−1.16 (6s, 18 H), 1.14 (d, J_{H-H} = 6.7 Hz, 3 H), 1.11 (d, 7.0 Hz, 3 H), 0.85 (m, 3 H), 0.78 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 134.32, 134.24 (d, J_{C-P} = 10.4 Hz, C-b), 134.29, 134.21 (d, J_{C-P} = 9.9 Hz, C-b′), 130.0 (C-d/d′), 128.3, 128.2 (C-c/c′), 115.9, 115.5, 107.9, 105.3, 103.8, 97.3, 95.7, 93.2, 90.7 (C_5Me_4), 49.5, 49.3 (C-5/5′), 43.3 (br., C-3/3′), 43.0, 42.9 (C-1/1′), 39.5 (C-10/10′), 36.4, 34.7, 34.5, 34.3 (C-2/2′/6/6′), 34.9 (C-4/4′), 28.8, 28.7, 23.5, 23.4 (C-8/8′/9/9′), 21.6, 21.4 (C-7/7′), 12.1, 11.6, 11.4, 10.9, 10.7, 10.6, 8.4, 7.0 (C_5Me_4/C_5Me_4′). − ^{31}P NMR ($CDCl_3$): δ = 17.0 (br.), 15.2 (25°C); 17.5 (v br.), 15.4 (0°C); 18.1 (br.), 16.3 (v. br.), 15.5 (−25°C); 18.4, 16.6, 15.6 (−50°C). − MS (EI); *m*/*z* (%): 771 (10) [M$^+$].

[(η^5-PinCp*)$_2$$RhCl_2$]$_2$ (9): PinCp*H (2.00 g, 7.70 mmol) was dissolved in 50 mL of methanol and Rh_3·$3H_2O$ (0.96 g, 37.4% Rh, 3.50 mmol) was added. The light red solution was refluxed for 5 d and the solvent was concentrated to 10 mL afterwards. Storage at 5°C for several hours gave a red solid, which was filtered, washed with diethyl ether and dried. Compound **9** can be recrystallized from CH_2Cl_2/Et_2O. Yield of the red solid **9**: 1.52 g (1.76 mmol, 50%). − ^{1}H NMR ($CDCl_3$): δ = 2.82 (q, J_{H-H} = 9.46 Hz, 1 H, H-4), 2.49 (m, 1 H), 2.35 (m, 1 H), 2.06 (m, 2 H), 1.90 (m, 2 H), 1.83 (s, 3 H), 1.80 (s, 3 H), 1.65 (s, 3 H), 1.61 (s, 3 H), 1.24 (s, 3 H), 1.14 (s, 3 H), 0.95 (d, J_{H-H} = 10.1 Hz), 0.98 (d, J_{H-H} = 6.7 Hz). − ^{13}C NMR ($CDCl_3$): δ = 100.1, 98.2, 96.3, 93.1, 90.8 (C_5Me_4), 48.8 (C-5), 42.2 (C-1), 41.3 (br., C-3), 39.6, 34.3 (C-2/6), 32.7 (C-4), 32.5 (C-10), 28.8, 23.5 (C-8/9), 21.6 (C-7), 11.6, 11.1, 10.0, 9.2 (C_5Me_4). − $C_{38}H_{58}Cl_4Rh_2$ (862.5): calcd.: C 52.92, H 6.78; found C 53.41, H 6.75.

(η^5-PinCp*)$TiCl_3$ (10): PinCp*Li (0.86 g, 3.46 mmol) was dissolved in DME and $TiCl_3$·3THF (0.43 g, 1.15 mmol) was added at −78°C. The solution was warmed to room temp. and refluxed for 2 d. Concd. HCl (2.7 mL) was added carefully at −30°C, followed by 10 mL of chloroform. The layers were separated and the organic layer was dried with $NaSO_4$. The solvent was removed and the nearly dry residue was transferred to a Soxhlet extractor. The extraction was performed with pentane saturated with HCl gas. The red solution, obtained after 30 min, was dried and a red solid was obtained. Yield of the red solid **10**: 0.13 g (0.32 mmol, 28%). − ^{1}H NMR ($CDCl_3$): δ = 3.63 (q, J_{H-H} = 9.46 Hz, 1 H, H-4), 2.67 (s, 3 H), 2.47 (s, 3 H), 2.46 (s, 3 H), 2.43−2.34 (m, 1 H), 2.27 (s, 3 H), 2.22−2.17 (m, 1 H), 2.13 (m, 1 H), 1.90 (m, 1 H), 1.80 (m, 1 H), 1.28 (s, 3 H), 1.26 (m, 2 H), 1.23 (s, 3 H), 0.95 (d, J_{H-H} = 7.02 Hz, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 148.8, 141.2, 137.9, 137.1, 134.3 (C_5Me_4), 49.4 (C-5), 43.8 (br., C-3), 42.6 (C-1), 39.6 (C-10), 37.6 (C-4), 34.4, 33.5 (C-2/6), 28.8, 23.5 (C-8/9), 21.7 (C-7), 16.6, 15.6, 15.2, 14.0 C_5Me_4). − MS (EI): *m*/*z* (%): 375 (7) [M$^+$ − Cl], 256 (80) [PinCp*$^+$]. − $C_{19}H_{29}Cl_2Ti$ (411.7): calcd.: C 55.43, H 7.10; found C 56.18, H 7.21.

(η^5-PinCp*)$Mo(CO)_2(NO)$ (11): PinCp*Li (3.54 g, 13.41 mmol) was dissolved in THF and, after addition of $Mo(CO)_6$ (3.33 g; 13.41 mmol), the reaction mixture was heated under reflux for 12 h. After cooling the solution, Diazald (2.7 g, 12.60 mmol), dissolved in 10 mL of THF, was added dropwise, so that the temperature did not exceed room temp. Stirring was continued for 3 h, with a continuous slight flow of nitrogen over the solution. The solvent was distilled off and the residue was sublimed at 140°C and 10^{-3} bar. The sublimed product was then purified by chromatography (Al_2O_3; hexane/ether, 4:1) to give red crystals after evaporation of the solvent. Yield: 3.60 g (8.19 mmol, 65%). − IR (hexane): $\tilde{\nu}_{(CO)}$ = 2004 (s), 1930 (s), $\tilde{\nu}_{(NO)}$ = 1667 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 3.03 (q, J_{H-H} = 9.77 Hz, 1 H, H-4), 2.37 (m, 1 H) 2.17 (s,3 h), 2.12 (m, 3 H), 2.07 (s, 3 H), 2.03 (s, 3 H), 2.03 (s, 3 H), 1.85 (m, 2 H), 1.26 (s, 3 H), 1.21 (m, 1 H), 1.17 (s, 3 H) 1.02 (d, J_{H-H} = 7.02 Hz, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 230.7, 230.6 (CO), 114.8, 108.2, 106.0, 105.1 (C_5Me_4), 49.2 (C-5), (43.5 (br., C-3) 43.1 (C-1) 39.5 (C-2/6), 38.0 (C-10), 34.5 (C-4), 28.8, 23.5 (C-8,9), 21.5 (C-7), 12.1, 12.0, 10.9, 10.8 (C_5Me_4). − $C_{21}H_{29}NO_3Mo$ (439.4): calcd.: C 57.40, H 6.65, N 3.19; found: C 57.62, H 6.72, N 3.15.

(η^5-PinCp*)$W(CO)_2NO$ (12): (η^5-PinCp*)$W(CO)_2NO$ (**12**) was prepared in a similar way to **11** from PinCp*Li (3.00 g 11.40 mmol) and $W(CO)_6$ (4.05 g, 11.50 mmol) after 5 d of reflux. Diazald (2.44 g, 11.4 mmol) was added as before. Yield: 3.61 g (6.84 mmol, 60%), red crystals. − IR (hexane): $\tilde{\nu}_{(CO)}$ = 1995 (s), 1918 (s), $\tilde{\nu}_{(NO)}$ = 1661 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 3.03 (q, J_{H-H} = 9.2 Hz, 1 H, H-4), 2.35 (m, 1 H) 2.27 (s, 3 H), 2.18 (s, 3 H), 2.14 (s, 3 H), 2.10 (s, 3 H), 1.89 (m, 2 H), 1.25 (s, 3 H), 1.19 (m, 1 H), 1.16 (s, 3 H) 0.99 (d, J_{H-H} = 7.0 Hz, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 222.4 (2CO), 113.4, 106.4, 104.6, 104.0 (C_5Me_4), 49.4 (C-5), (43.4 (C-3) 43.2 (C-1) 39.4 (C-10))34.8 (C-2/6), 34.5 (C-4), 28.8, 23.4 (C-8,9), 21.1 (C-7), 11.8, 10.7, 10.6 (C_5Me_4). − $C_{21}H_{29}NO_3W$ (527.31): calcd.: C 47.83, H 5.54, N 2.66; found C 48.51, H 5.61, N 2.70.

(η^5-PinCp*)$MoCl_2(NO)$ (13): Compound **11** (0.85 g, 1.94 mmol) was dissolved in ether and treated slowly at 0°C with solid PCl_5 (0.40 g, 1.94 mmol). Stirring was continued for 12 h at room temp.; the solution turned a vivid green with a green solid precipitate. After addition of 30 mL of hexane, the volume was reduced to 10 mL under vacuum. The green solid was filtered, washed with a small amount of cold ether and dried. Yield 0.75 g (1.65 mmol, 85%). − IR (THF): $\tilde{\nu}_{(CO)}$ = 1660 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 3.13 (q, J_{H-H} = 9.46 Hz, 1 H, H-4), 2.38 (m, 1 H), 2.23 (s, 3 H), 2.19 (m, 3 H), 2.10 (s, 3 H), 2.06 (m, 3 H) 1.95 (s, 3 H) 1.86 (m, 2 H), 1.26 (s, 3 H), 1.18 (m, 1 H) 1.14 (s, 3 H) 1.00 (d, J_{H-H} = 7.02 Hz), 3 H). − ^{13}C NMR ($CDCl_3$): δ = 127.0, 125.8, 124.6, 119.1 (C_5Me_4), 49.2 (C-5), 43.1 (br., C-3) 42.4 (C-1), 39.5, 34.5 (C-2/6), 34.9 (C-4). 33.2 (C-10) 28.8, 23.4 (C-8/9), 21.8 (C-7), 12.9, 12.6, 10.7, 10.3 (C_5Me_4). − MS: *m*/*z* (%): 455 (20) [M$^+$], 425 (95) [M$^+$ − NO], 385 (25) [M$^+$ − 2 Cl]. − $C_{19}H_{29}Cl_2NOMo$ (454.27): calcd.: C 48.88, H 6.60; found C 48.63, H 6.49.

(η^5-PinCp*)$WCl_2(NO)$ (14): Compound **12** (1.07 g, 2.03 mmol) was dissolved in ether and was treated slowly at 0°C with solid PCl_5 (0.42 g, 2.03 mmol). Reaction and workup as above. Yield

0.95 g(1.75 mmol, 86%). − IR (THF): $\tilde{\nu}_{(CO)}$ = 1632 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 3.15 (q, J_{H-H} = 9.53 Hz, 1 H, H-4), 2.42 (s, 3 H), 2.25 (s, 3 H), 2.21 (s, 3 H), 2.15 (m, 2 H), 2.04 (m, 3 H) 2.02−1.78 (m, 4 H) 1.86 (m, 2 H), 1.26 (s, 3 H), 1.21 (m, 1 H) 1.16 (s, 3 H) 1.00 (d, J_{H-H} = 7.02 Hz, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 124.2, 123.2, 119.3, 117.3 (C_5Me_4), 49.9 (C-5), 43.4 (br., C-3) 43.1 (C-1), 39.9, 35.5 (C-2/6), 34.4 (C-4). 33.2 (C-10) 29.0, 23.6 (C-8/9), 21.8 (C-7), 12.5, 12.3, 10.8, 10.3 (C_5Me_4). − MS: *m*/*z* (%): 543 (40) [M^+], 490 (70) [M^+ − Cl, − NO], 385 (30) [M^+ − 2 Cl, − NO]. − $C_{19}H_{29}Cl_2NOW$ (542.18): calcd.: C 40.78, H 5.51; found C 40.52, H 5.39.

(η⁵-PinCp*)W(CH_2SiMe_3)$_2$NO (15): Compound **14** (346.9 mg, 0.64 mmol) and [$(CH_3)_3Si(CH_2)_2Mg$]·(dioxan)$_2$ (246.1 mg, 0.64 mmol) were mixed as solids in a Schlenk tube. After cooling to −196°C, 20 mL of THF was slowly condensed into the tube under vacuum. After waiting for 10 min, the Schlenk tube was transferred into a Dewar cooled to −78°C. The temperature was allowed to rise to −50°C and kept at this temperature for 12 h. The solution assumed a deep purple colour. The solvent was evaporated at 0°C, the residue taken up in cold ether and filtered at −20°C through Celite. A purple residue was obtained after evaporating the solvent at 0°C, yield 315.9 mg (0.51 mmol, 80%). − IR (hexane): $\tilde{\nu}_{(CO)}$ = 1582 (s) cm^{-1}. − ^1H NMR (C_6D_6): δ = 3.03 (q, J_{H-H} = 9.15 Hz, 1 H, H-4), 2.28 (m, 2 H), 2.13 (m, 1 H), 1.90 (s, 3 H), 1.82 (s, 3 H), 1.78 (m, 1 H), 1.71 (d, J_{H-H} = 11.58, 1 H, H-a1), 1.68 (S, 3 H), 1.66 (d, J_{H-H} = 11.29 Hz, 1 H, H-b1), 1.49 (s, 3 H), 1.33−1.22 (m, 2 H), 1.17 (s, 3 H), 1.10 (m, 1 H), 1.08 (s, 3 H), 0.93 (d, J_{H-H} = 7.01 Hz, 3 H), 0.38 (2 s, 18 H, $SiMe_3$), −1.21 (d, J_{H-H} = 11.29 Hz, 1 H, H-b2), −1.29 (d, J_{H-H} = 11.58 Hz, 1 H, H-a2). − ^{13}C NMR (C_6H_6): δ = 119.2, 117.2, 113.6, 112.2 (C_5Me_4), 65.2, 63.4, (2 × C-11), 49.6 (C-5), 43.0 (br., C-3), 42.8 (C-1), 39.5, 35.0 (C-2/6), 34.9 (C-4), 30.1 (C-10), 28.9, 23.5 (C-8/9) 21.8 (C-7), 14.3, 12.0, 9.7, 9.5 (C_5Me_4), 1.41, 1.37 ($SiMe_3$). − $C_{27}H_{51}NOSi_2W$ (645.72): calcd. C 49.28, H 8.11; found C 49.64, H 8.23.

X-ray Crystallographic Study: (S_{Re})-[(η⁵-PinCp*)Re(COOMe)NO-(PPh_3) (**5a**) crystallizes in the orthorhombic space group $P2_12_12_1$ (no. 19). Crystal data: $C_{50}H_{56}N_2O_2PRe$, formula mass 934.19 g mol^{-1}, *a* = 11.522(5), *b* = 18.789(2), *c* = 20.116(6) Å, *V* = 4355(2) $Å^3$, *Z* = 4, $d_{calcd.}$ = 1.425 g cm^{-3}, μ(Mo-K_α) = 29.02 cm^{-1}, *F*(000) = 1904. Intensity data were collected at 203 K on an orange rod of approximate dimensions 0.47 × 0.18 × 0.15 mm with an ENRAF-Nonius CAD4 diffractometer in the ω mode up to θ_{max} = 26°. A total of 11726 reflections were corrected for Lorentz and polarization effects and for absorption (numerical by Gaussian integration;[28] min. transmission 0.5339, max. transmission 0.6826). After averaging symmetry-equivalent data, the structure was solved[29] by Patterson and subsequent Fourier difference synthesis. Full-matrix least-squares refinement on *F*[29] of 428 variables for 7010 independent observations with $I > 1.0\ \sigma(I)$ converged at *R* = 0.057, R_w = 0.058 [$w^{-1} = \sigma^2(F_o)$], *GOF* = 1.338. During refinement the naphtyl moiety was treated as a rigid group, all other non-hydrogen atoms were assigned anisotropic displacement parameters, and hydrogen atoms were included as riding in calculated positions [C−H = 0.98 Å, U_{iso}(H) = 1.3 U_{eq}(C)]. A final Fourier difference synthesis showed a residual electron density of ca. 3 $eÅ^{-3}$ in the region of the disordered naphtyl moiety. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data centre as supplementary publication no. CCDC-114499. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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