EurJIC European Journal of Inorganic Chemistry

FULL PAPER

DOI: 10.1002/ejic.201200693

Asymmetric Transfer Hydrogenation of Ketones Catalyzed by Rhenium Complexes with Chiral Ferrocenylphosphane Ligands

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Keywords: Asymmetric synthesis / Homogeneous catalysis / Hydrogen transfer / Rhenium / Phosphane ligands

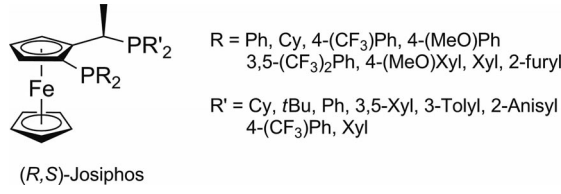
We have prepared a series of new rhenium complexes containing chiral ferrocenyldiphosphane ligands of the Josiphos family, starting from commercially available rhenium sources. These new Re^{V} oxido and nitrido complexes, several of which have been characterized by X-ray crystallography, are air- and moisture-stable and are active catalysts in the asymmetric transfer hydrogenation of ketones using 2-propanol as the hydrogen source in the presence of substoichiometric amounts of triethylamine (TEA). The reaction proceeds cleanly with good to excellent yields (50–99 %) but with moderate enantioselectivity (up to 58 % *ee*). A mechanism not involving hydridic species is proposed.

Introduction

In the search for new, more versatile, more environmentally friendly or greener chemical processes, transfer hydrogenation reactions are a possible attractive alternative to classical reductions with molecular hydrogen because of their high selectivity, mild reaction conditions and operational simplicity.[1] Depending on the nature of the metal and the ligands used, the mechanism of these processes can be classified in two main classes: direct H transfer or a metal-templated, hydride-mediated process.[1b] The most popular hydrogen sources are 2-propanol,[2] formic acid[3] and the azeotropic formic acid/triethylamine mixture.[4] The metal complexes used to catalyze these transformations are limited to Rh,[2–3,5] Ru,[4,6] Ir,[5,7] Ni,[8] and more recently Os[9] and Fe.[10] The ligands used in asymmetric transfer hydrogenation feature different architectures and donor atoms including oxygen, sulfur, nitrogen and phosphorus in different combinations and in bi-, tri- and tetradentate fashions.[1b]

Probably due to its scarcity,[11] the coordination chemistry of rhenium remains relatively underdeveloped as compared to that of other transition metals. Nevertheless, in the last decade this element has gained growing popularity as a catalyst in different processes.[12] As Re is less expensive than Rh or Ir and due to its unique chemistry,[13] Re-catalyzed reactions are an interesting field of exploration. In the field of Re-catalyzed asymmetric synthesis, the pioneering work of Toste on the enantioselective hydrosilylation of ketones and imines[14] and that of Kwong on the asymmetric cyclopropanation of alkenes[15] using chiral Re^{V} and Re^{I} catalysts stand alone. Other important achievements in the Re-catalyzed reduction of carbonyl groups have been reported by Abu-Omar[16] and Royo.[17]

An important class of ligands used in those kinds of transformations are bi-, tri- or tetradentate ferrocenylphosphanes,[6b,18] which were moderately successful until Baratta and coworkers reported outstanding results [(enantioselectivity and turnover numbers (TONs)][9,19] by using Josiphos ligands (Figure 1), some of the most successful in asymmetric catalysis and hence one of the so called "privileged ligands".[20] They have been widely used in several applications both in academia and in industry.[20b]



(*R*,*S*)-Josiphos

Figure 1. General structure of Josiphos ligands. R and R′ substituents presented here account for the commercially available ligands (Solvias AG) though some other new combinations are presented in this work (vide infra). A new class of Josiphos ligands stereogenic at the phosphorus atoms has been recently developed in our group.[21]

Here, we report the synthesis and characterization of a series of new Re^{V} oxido and nitrido complexes with chiral bidentate ferrocenylphosphane ligands of the Josiphos family, and their successful use as catalysts for the asymmetric transfer hydrogenation of ketones. A plausible reaction mechanism is also proposed.

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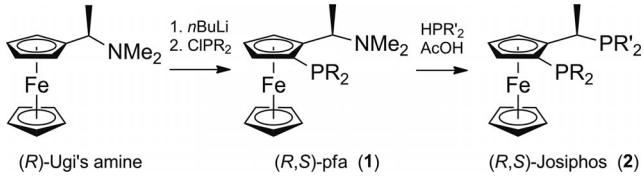
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201200693.

Results and Discussion

Ligand Synthesis

Ferrocenyldiphosphane ligands of the Josiphos family were synthesized by using a slight modification of the reported procedure.[22] The common precursor in all cases was the commercially available (*R*)-Ugi's amine,[23] which in a first step was selectively *ortho*-lithiated and the resulting ferrocenyllithium derivative was allowed to react with the corresponding secondary chlorophosphane to give the (*R*,*S*)-pfa (phosphanylferrocenylamine) intermediate **1**. The dimethylamino moiety was then substituted by the corresponding secondary phosphane with retention of configuration[24] to give the desired Josiphos ligand **2** (Scheme 1). For this study only the "classic" Josiphos (R = Ph, R′ = Cy, **2a**) and the noncommercially available analogues were synthesized. All other ferrocenyldiphosphane ligands were obtained from Solvias AG.



Scheme 1. General procedure for the synthesis of Josiphos ligands.

Table 1. Complexes of the type [$ReOX_3$(Josiphos)] (**3**).

3	R	R′	X	Yield [%]
a	Ph	Cy	Cl	94
b	Cy	Ph	Cl	78
c	Ph	adamantyl	Cl	85
d	Ph	3,5-$(Me)_2$Ph	Cl	71
e	Cy	Cy	Cl	73
f	Ph	*t*Bu	Cl	97
g	Cy	*t*Bu	Cl	85
h	Cy	3,5-$(CF_3)_2$Ph	Cl	16
i	Cy	3,5-$(Me)_2$Ph	Cl	>99
j	*t*Bu	Ph	Cl	72
k	Ph	Cy	Br	97

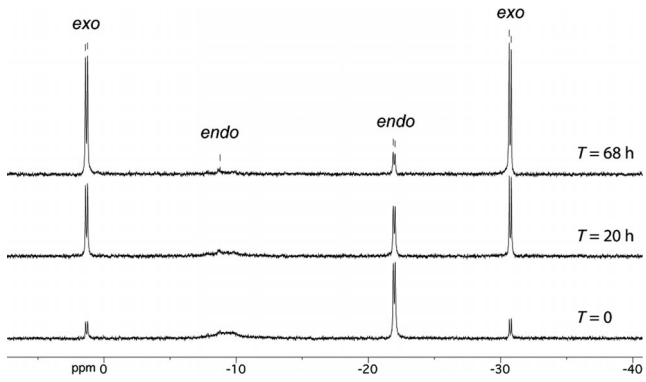


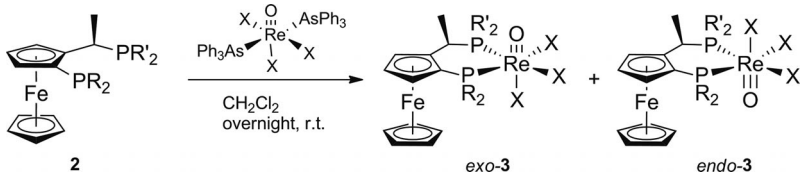
Figure 2. Time-dependent ^{31}P NMR (101.2 MHz, r.t., $CDCl_3$) spectra for complex **3d**.

Synthesis and Characterization of Complexes

The parent oxidotrihalobis(triphenylarsane)rhenium(V) complexes, *mer*-[$ReOX_3(AsPh_3)_2$] (X = Cl, Br), were synthesized by following the reported procedures[25] but using $KReO_4$ instead of $HReO_4$ as the starting material. They reacted readily with Josiphos ligands in CH_2Cl_2 at room temperature to give the corresponding *fac*-[$ReOX_3$(Josiphos)] complexes (**3**, Table 1) in a procedure analogous to the one reported by Parr.[26] As depicted in Scheme 2, the coordination of the chiral diphosphane ligands to the rhenium centre gives a mixture of two isomeric products, *endo*-**3** and *exo*-**3**. This was confirmed by X-ray diffraction (see below). It was observed that upon ligand substitution on *mer*-[$ReOX_3(AsPh_3)_2$], the *endo* isomer is produced first (kinetic product). However, this species slowly isomerizes in solution to the more stable *exo* isomer (thermodynamic product) (Figure 2). The lability of the P–Re bonds in the *endo* complex is evidenced in the ^{31}P NMR spectra by its broad peaks, as a consequence of this dynamic behaviour.

All complexes were obtained in good yields except **3h**, which contains trifluoromethylated substituents at phosphorus. This compromises not only the donor and coordinating abilities of the ligand due to its electron-withdrawing properties, but also confers additional steric demand. The complexes are solids stable to air and moisture that can be stored for several months at room temperature without apparent decomposition. They decompose slowly in solution (in non-degassed solvents) to give oxidation products (see below).

X-ray quality single crystals of *exo*-**3a**, *exo*-**3e**, *exo*-**3i**, *endo*-**3f** and **3g** (both isomers) were obtained by slow diffusion of *n*-hexane, ethyl ether or benzene into a solution of the corresponding compounds in dichloromethane or chloroform (for the X-ray structures of *exo*-**3e** and *exo*-**3i** see the Supporting Information). The crystal structure of *exo*-**3a** is presented in Figure 3. The geometry around the Re centre is a distorted octahedron with a *fac–cis* configuration. One of the main features of the structure is the small O–Re–Cl_{trans} angle of 170.46(12) Å with the oxygen atom



Scheme 2. General procedure for the synthesis of Re oxido complexes.

bent towards the bidentate ligand as reported for other Re^{V} diphosphane monooxido complexes.[26–27] This is due to electronic repulsion between the Re–O moiety and the negatively charged chloride ligands.[27b] The short Re–O bond length [1.685(4) Å] is in good agreement with those for other complexes of this kind[28] and is better described as a triple bond (one σ bond and two π bonds), as it is clearly shorter than a double bond, which has a theoretical length of 1.86 Å.[27a,29] The reason for the increased bond order is the overlap of both p_x and p_y oxygen orbitals with the rhenium d_{xz} and d_{yz} orbitals (*z* axis through the Re–O bond). The two d electrons would then occupy the nonbonding d_{xy} orbital,[28] which explains the observed diamagnetism of the complexes.[29]

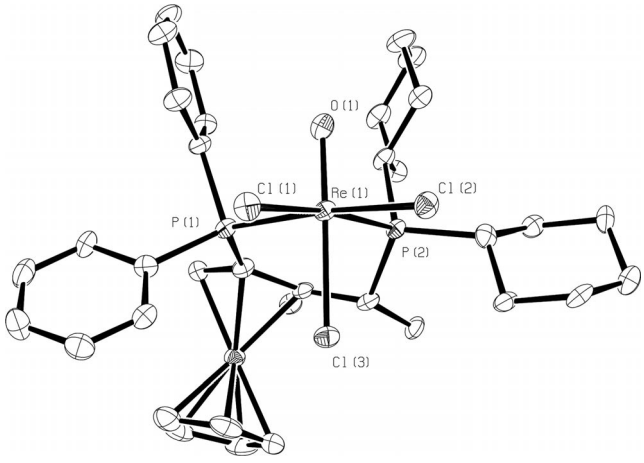


Figure 3. ORTEP III drawing of complex *exo*-**3a**·(CD_2Cl_2)·(C_6H_6). Solvent molecules are omitted for clarity. Ellipsoids at 50% probability. Relevant distances [Å] and angles [°]: Re–P(1) 2.4604(13), Re–P(2) 2.4875(12), Re–O 1.685(4), Re–Cl(1) 2.4024(12), Re–Cl(2) 2.3972(13), Re–Cl(3) 2.4143(13), P(1)–Re–P(2) 89.05(4), O–Re–Cl(3) 170.46(12).

In the case of complex **3g**, both *endo* and *exo* isomers crystallize together in a one to one ratio in the asymmetric unit (Figure 4). The superposition of both structures shows that they are indeed very similar, and both have the same conformation in the six-membered ring formed by the metal and the chelating ligand. The only important differences are in the conformation of the cyclohexyl rings and in the O–Re–Cl_{trans} angle; the *endo* isomer has a more pronounced deviation from linearity and, hence, a more congested steric situation (see Figure 5). Taking this observation into account, the decrease of steric congestion could be the driving force for the observed isomerization process.

An attempt to crystallize the tribromo complex **3k** under noninert conditions gave as a result the oxidation product [$ReOBr_4$(**2a**(κ*O*-$OPPh_2$))] (**4**, Figure 6), in which the neutral rhenium(VI) $ReOBr_4$ moiety is coordinated with the monooxidized form of the Josiphos ligand. Rhenium(VI) complexes are rare and often very reactive.[30] In this case, the Re^{VI} centre is stabilized by the strongly bonded oxido group [Re–O 1.612(7) Å] and the weakly bonded phosphanyloxide ligand [Re–O 2.127(7) Å]. The mechanism of formation of **4** is still unclear but considering the fact that the $[Re^{V}O]^{+3}$ core is a redox-active unit and could serve as an oxido-transfer agent,[31] it is likely that the oxidation of the phosphane ligand occurs by intramolecular oxygen transfer rather than by O_2 in solution.

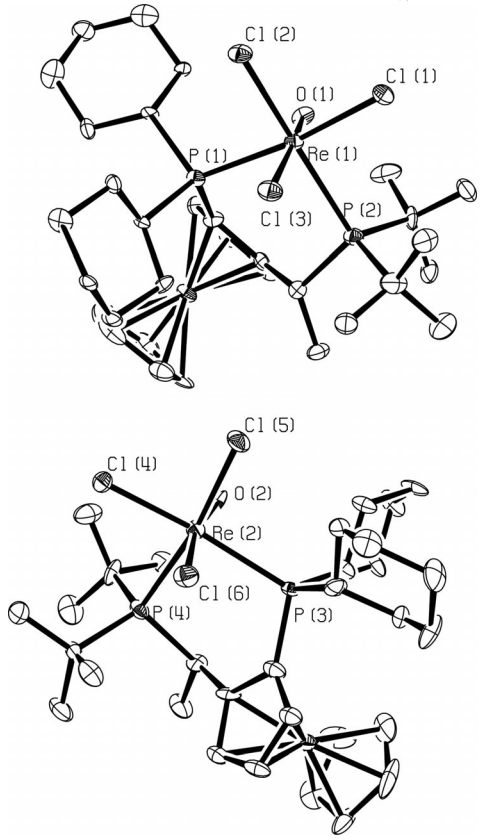


Figure 4. ORTEP III drawing of complex **3g**. Ellipsoids at 50% probability. The asymmetric unit consists of both *endo* (down) and *exo* (up) isomers. Relevant distances [Å] and angles [°]: *exo* isomer Re(1)–P(1) 2.493(3), Re(1)–P(2) 2.578(3), Re(1)–O(1) 1.707(8), Re–Cl(1) 2.393(3), Re–Cl(2) 2.395(3), Re–Cl(3) 2.385(3), P(1)–Re(1)–P(2) 95.63(10), O(1)–Re(1)–Cl(3) 171.1(3); *endo* isomer Re(2)–P(3) 2.458(3), Re(2)–P(4) 2.579(3), Re(2)–O(2) 1.751(8), Re(2)–Cl(4) 2.363(3), Re(2)–Cl(5) 2.414(3), P(3)–Re(2)–P(4) 95.13(9), O(2)–Re(2)–Cl(6) 167.0(3).

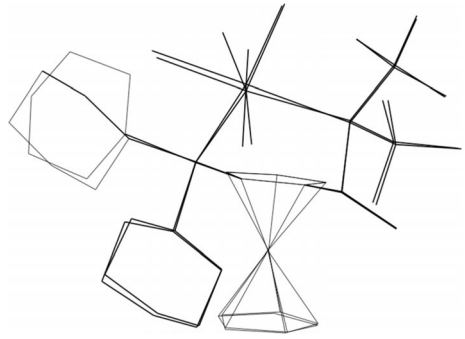


Figure 5. MacMoMo drawing of the superimposed crystal structures of both *endo*-**3g** and *exo*-**3g**.

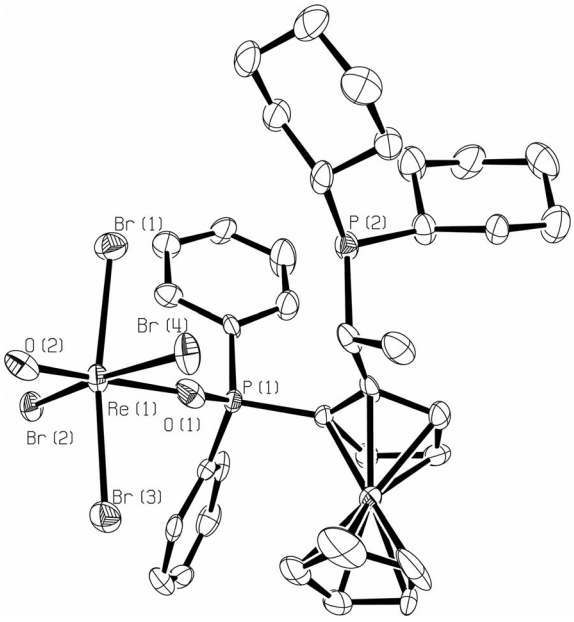
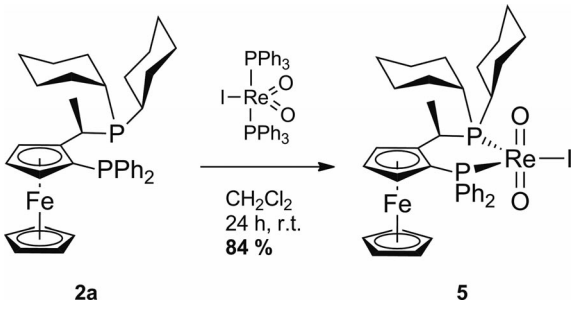


Figure 6. ORTEP III drawing of **4**·(CD_2Cl_2). Solvent molecules are omitted for clarity. Ellipsoids at 50% probability. Relevant distances [Å] and angles [°]: Re–O(1) 2.127(7), Re–O(2) 1.612(7), P(1)–O(1) 1.522(7), O(1)–Re–O(2) 178.0(3).

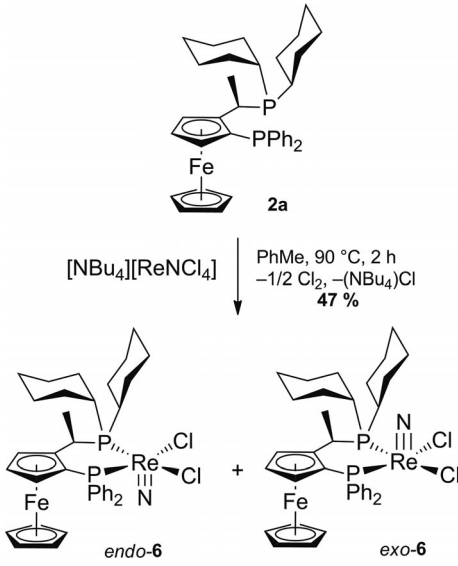
The dioxido derivative [ReO_2I(**2a**)] (**5**) was synthesized in an analogous procedure by simple ligand substitution of the parent complex [$ReO_2I(PPh_3)_2$] with the bidentate ligand at room temperature in dichloromethane (Scheme 3). The elemental analysis of the resulting paramagnetic compound confirms the proposed stoichiometry with the two oxido ligands in a *trans* configuration due to the required *cis* chelation of the biphosphane ligand.



Scheme 3. Procedure for the synthesis of **5**.

The nitrido complex [$ReNCl_2$(**2a**)] (**6**) was synthesized from [NBu_4][$ReNCl_4$] and the biphosphane ligand by adapting the procedure reported by Duatti[32] (Scheme 4). It was also obtained as a mixture of the *endo* and *exo* isomers, and upon crystallization single crystals of *endo*-**6** were obtained, the structure of which was confirmed by single crystal X-ray analysis (Figure 7).

Complex *endo*-**6** exhibits a distorted square pyramidal geometry around the Re centre with the nitrido ligand in the apical position. The rhenium atom is displaced 0.447 Å from the mean plane P(1)–P(2)–Cl(1)–Cl(2) towards the nitrido ligand as previously reported for other rhenium nitrido complexes with chelating diphosphanes.[32]



Scheme 4. Procedure for the synthesis of **6**.

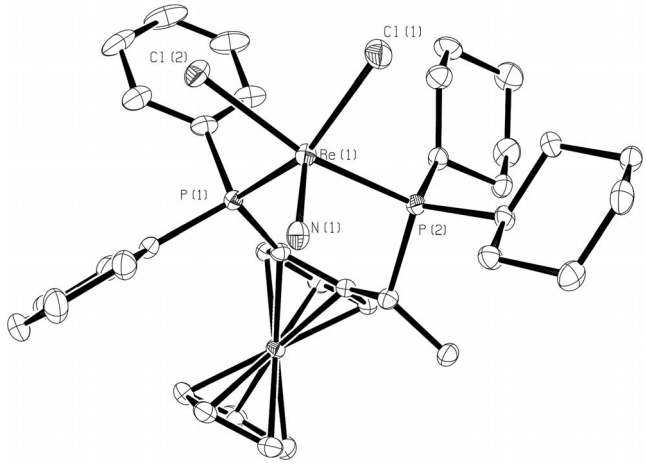


Figure 7. ORTEP III drawing of *endo*-**6**·(CD_2Cl_2). Solvent molecules are omitted for clarity. Ellipsoids at 50% probability. Relevant distances [Å] and angles [°]: Re–P(1) 2.3985(9), Re–P(2) 2.4152(9), Re–N 1.679(3), Re–Cl(1) 2.3879(9), Re–Cl(2) 2.4107(8), P(1)–Re–P(2) 91.45(3).

Rhenium-Catalyzed Transfer Hydrogenation of Ketones

With the Re complexes in hand, their catalytic activity in the transfer hydrogenation of ketones was tested using acetophenone as the model substrate. In a typical procedure, a certain amount of catalyst (ca. 1 mol-%) was dissolved in dry 2-propanol under an argon atmosphere along with one equivalent of acetophenone. Then a base was added (ca. 10 mol-%) and the mixture was heated overnight. For optimization of the conditions, complex **3a** and other Re^V complexes were used as catalysts (Table 2).

Table 2. Result for the transfer hydrogenation of acetophenone under different reaction conditions.

Entry[a]	Catalyst	Base	Time [h]	Temp. [°C]	Yield [%][b]	*ee*[c] [%]
1	**3a**		12	80	0	–
2	**3a**	K_2CO_3[d]	12	80	50	11 (*S*)
3	**3a**	K_2CO_3[d]	48	80	99	*rac*
4	**3a**	*i*PrONa	21	80	67	*rac*
5	**3a**	(*i*Pr)$_2$NEt	20	80	76	17 (*S*)
6	**3a**	NEt_3	24	80	83 (75)	17 (*S*)
7	**3a**	NEt_3	48	25	0	–
8	**3a**	NEt_3	48	40	(46)	19 (*S*)
9[e]	[$ReOCl_2$(Binap)]	NEt_3	20	80	15	*rac*
10[f]	[$ReOCl_2(PPh_3)_2$]	NEt_3	20	80	0	–
11	**3a** (in situ)	NEt_3	20	80	92	14 (*S*)

[a] Reaction conditions: conc. of substrate 0.4 M; ca. 1 mol-% of catalyst; 8 mol-% of base. [b] Calculated by integration of the peaks in the ^{1}H NMR spectra. Numbers in brackets correspond to isolated yields. [c] Determined by using chiral HPLC (see Exp. Section). [d] Excess (ca. 20-fold). [e] *S*-Binap was used. Complex synthesized as reported previously.[26] [f] Synthesized as reported previously.[33]

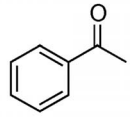
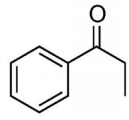
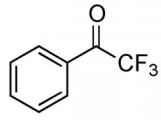
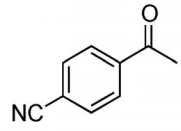
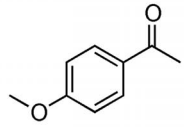
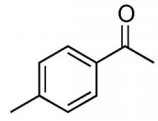
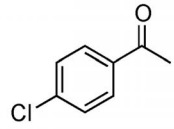
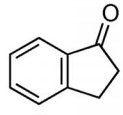
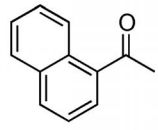
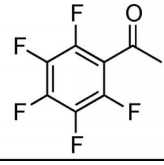
The addition of a base proved crucial because a lack of it (Table 2, Entry 1) resulted in no product formation. When potassium carbonate was used (Table 2, Entries 2 and 3), good conversion was obtained but with a loss of enantioselectivity. The same effect was observed with the addition of sodium isopropoxide (Table 2, Entry 4). This could be due to decomposition of the complex to generate different active species that do not contain the chiral ligand. When triethylamine (TEA) was used instead, moderate enantioselectivities were obtained. The same selectivity was observed when bulkier diisopropylethylamine was added, however with lower yield (Table 2, Entry 5). The reaction temperature also had a dramatic effect on the reaction yield. When the reaction was run at 25 °C (Table 2, Entry 7) no conversion was observed. At 40 °C, a yield of only 46% was obtained after two days, whereas at 80 °C a yield of 80% was obtained (Table 2, Entry 6). When other Re^V complexes were used as catalysts, namely *mer*-[$ReOCl_3(PPh_3)_2$] and *fac*-[$ReOCl_3$(*S*-Binap)], the results were not satisfactory; no conversion was obtained with the former (Table 2, Entry 10) and low conversion and no selectivity with the latter (Table 2, Entry 9). When the catalyst was synthesized in situ, by mixing equimolar amounts of *mer*-[$ReOX_3(AsPh_3)_2$] and the Josiphos ligand in 2-propanol prior to the addition of the ketone, similar results were ob-

Table 3. Results for the transfer hydrogenation of acetophenone catalyzed by rhenium(V) complexes with Josiphos ligands.

Entry[a]	Cat.	Yield [%][b]	*ee*[c] [%]	Entry[a]	Cat.	Yield [%][b]	*ee*[c] [%]
1	**3b**	96	37 (*R*)	10	3i[e]	67	52 (*R*)
2	**3b**[d]	96	37 (*R*)	11	3j	4	23 (*S*)
3	**3c**	79 (35)	8 (*S*)	12	3k	95	15 (*S*)
4	**3d**	50 (31)	12 (*R*)	13	3k[f]	49	20 (*S*)
5	**3e**	97 (85)	10 (*R*)	14	5	97	11 (*S*)
6	**3f**	92	19 (*R*)	15	5[f]	25	20 (*S*)
7	**3g**	89	30 (*R*)	16	5[d]	93	11 (*S*)
8	**3h**	70	55 (*R*)	17	6	88	15 (*R*)
9	**3h**[d]	97	43 (*R*)	18	6[f]	6	15 (*R*)

[a] Reaction conditions: conc. of substrate 0.4 M; ca. 1 mol-% of catalyst; 8 mol-% of TEA; 80 °C, 20 h. [b] Calculated by integration of the peaks in the ^{1}H NMR spectra. Numbers in parentheses correspond to isolated yields. [c] Determined by using chiral HPLC (see Exp. Section). [d] Made in situ. [e] 14 h. [f] 40 °C.

Table 4. Results for the transfer hydrogenation of ketones using complex **3h** as catalyst.

Entry[a]	Ketone	Yield (%)[b]	*ee*[c] (%)
1		97	43 (*R*)
2		89	50 (*R*)
3		>99	19 (*S*)
4		30	58 (*R*)
5		91	44 (*R*)
6		94	27
7		98	55
8		75	0
9		99	53 (*R*)
10		>99	46

[a] Reaction conditions: concentration of substrate 0.4 M; catalyst prepared in situ, 1 mol-% of ligand and 1 mol-% of [$ReOCl_3(AsPh_3)_2$]; ca. 20 mol-% of TEA; 80 °C, 20 h. [b] Calculated by integration of the peaks in the ^{1}H NMR spectra. [c] Determined by using chiral HPLC (see Exp. Section).

tained as when the isolated complex was used (Table 2, Entry 11). Having selected the best conditions for the asymmetric transfer hydrogenation of acetophenone with complex **3a** (Table 2, entry 6), we assessed the catalytic performance of the Re^{V} complexes prepared previously. The results are summarized in Table 3.

In general, good to excellent yields were obtained for the Re-catalyzed transfer hydrogenation of acetophenone with the different complexes. The only exception was for complex **3j** (Table 3, Entry 11) probably because of the steric hindrance imparted by the bis-*tert*-butylphosphane moiety on the ferrocene. It is important to note that in spite of the fact that all complexes have the same chirality (R,S_P), the stereochemical outcome of the reaction changes depending on the nature and relative position of the organic residues on the P atoms. Complex **3a** (R = Ph, R′ = Cy) gives preferentially the *S* isomer (17% *ee*, Table 2, Entry 6), whereas its "inverted" analogue **3b** (R = Cy, R′ = Ph) gives an excess of the *R* isomer (37% *ee*, Table 3, Entry 1). The same effect was observed for **3f** and **3j** (Table 3, Entries 6 and 11). In terms of selectivity, the best results were obtained for those complexes with R = Cy (Table 3, Entries 1, 7, 8 and 10), which preferentially produce the *R* isomer. The same sense of induction was obtained with complex **3e** (R, R′ = Cy), although with lower *ee* (Table 3, Entry 5). The best results were obtained with complex **3h** (Table 3, Entries 8 and 9), which was then selected for screening with different ketones (Table 4). For these reactions, the catalyst was generated in situ as it showed similar selectivity and higher yield than the isolated complex.

For all of the substrates tested, the reaction proceeded cleanly and in general with good to excellent yields. The only exception was for 4-cyanophenyl methyl ketone (Table 4, Entry 4), probably because coordination of the cyano moiety to the metal centre hampers the reactivity of the catalyst. Conversely, the same substrate gave the highest enantioselectivity, most likely because of steric factors.

Mechanistic Aspects

Transfer hydrogenation (TH) of ketones has been shown to proceed by different pathways, which depend heavily on the metal, ligands and reaction conditions.[1a,1c] As this is the first report using a rhenium catalyst in this kind of reaction, no prediction can be made concerning their preferred modus operandi. Nevertheless, having assessed the geometry, reactivity and coordination behaviour of our Re^{V} complexes, a plausible reaction pathway may be proposed (vide infra).

After completion of the TH of acetophenone in 2-propanol using complex *exo*-**3a**, a very stable rhenium-isopropoxide complex, [$ReOCl_2$(*i*PrO)(**2a**)] (**7**), was isolated and characterized. The X-ray structure of **7** is presented in Figure 8. Complex **7** exhibits a slightly distorted octahedral geometry containing a *trans*-oxido-alkoxido unit typical for this kind of complex.[27a,34] The Re–oxido distance [1.727(7) Å] is longer than that in the parent complex *exo*-**3a** but still shows significant triple bond character. The Re–O(alkoxido) distance [1.875(6) Å] suggests strong π-donation so it can be regarded as a double bond. Another remarkable structural feature of **7** is the inverted configuration relative to the parent complex *exo*-**3a**, with the terminal oxido ligand in the *endo* position.

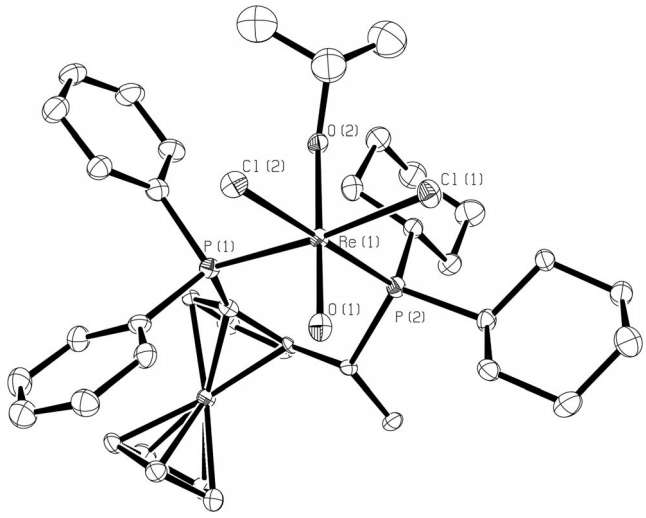


Figure 8. ORTEPIII drawing of **7**. Ellipsoids at 50% probability. Relevant distances [Å] and angles [°]: Re–P(1) 2.458(3), Re–P(2) 2.457(3), Re–O(1) 1.727(7), Re–O(2) 1.875(6), Re–Cl(1) 2.456(2), ReCl(2) 2.477(3), P(1)–Re–P(2) 92.29(9), O(1)–Re–O(2) 178.4(3).

Metal alkoxide complexes are common intermediates in transfer hydrogenation reactions, namely those that proceed either through an inner-sphere monohydridic route or through a Meerwein–Ponndorf–Verley type hydrogen transfer.[1c] These complexes are rather stable and have been proposed to serve simply as inactive catalyst reservoirs in Ru-catalyzed TH[35] or as the resting state of the catalyst in Rh-catalyzed TH.[36] The fact that the isolated alkoxy intermediate **7** still contains two equatorial chloride ligands suggest that the mechanism does not proceed through a metal hydride pathway. As observed by Bäckvall and coworkers for the $RuCl_2(PPh_3)_3$-catalyzed TH,[37] successive alkoxide displacement/β-elimination reactions lead to the formation of metal-dihydride species in basic media; in our case, this has not been observed. Taking these observations into account, the reaction mechanism depicted in Figure 9 is proposed.

The first step of the mechanism is the dissociation of a phosphane ligand in **3**, to allow the coordination of the incoming alcohol. The assumption that the Josiphos ligand could alternate between monodentate and bidentate is supported by the observed thermal isomerization of the complexes (vide supra) and by the fact that the alkoxido complex **7** exhibits an inverted configuration compared with the parent complex *exo*-**3a**. Of the two phosphorus donors of the bidentate Josiphos ligand, the one which is more likely to dissociate first is the less electron-rich and hence the weaker σ donor. For complex **3a** this will be the one directly attached to the ferrocene core, whereas for **3h** the one bear-

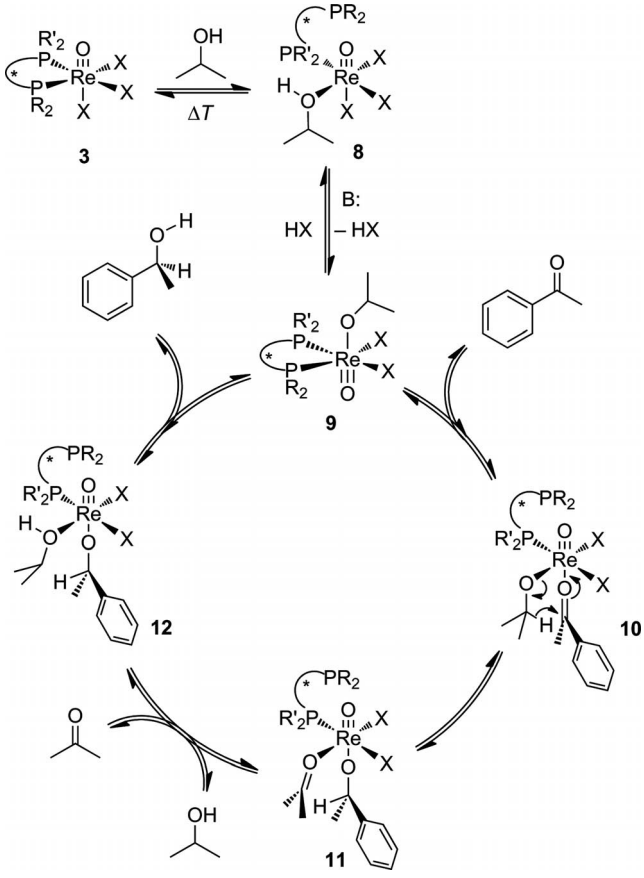


Figure 9. Proposed mechanism for the transfer hydrogenation of acetophenone catalyzed by **3**.

ing the trifluoromethyl substituents shall be more prone to dissociate. The resulting alcohol complex **8** eliminates HX with the aid of the added base to give the alkoxido complex **9**. Upon coordination of the ketone (complex **10**), a direct hydrogen transfer from the coordinated alkoxide to the ketone takes place. This bears a strong resemblance to the mechanism found for TH with Ir-COD (COD = 1,5-cyclooctadiene) derivatives.[38] The resulting complex **11** releases an acetone molecule upon coordination of another alcohol ligand and this complex (**12**) undergoes intramolecular proton exchange and dissociation of the reduced ketone to regenerate metal alkoxide **9**. The central role of the latter is not only supported by its isolation in the form of the specific compound **7**, but more importantly by the fact that the use of either **3a** or **7** as catalysts precursors give essentially identical results, both in terms of activity and selectivity.

The stereochemical outcome of the reaction is believed to depend heavily on steric factors (as the proposed mechanism depicts). However, considering that several factors (solvation, dispersion, steric and electrostatic interactions) have been reported to determine the degree of enantioselectivity,[1c] a definite conclusion cannot be drawn.

Conclusions

We have developed an asymmetric transfer hydrogenation reaction of ketones using new rhenium(V) complexes with chiral bidentate ferrocenylphosphane ligands. The reaction uses 2-propanol as a solvent and as the sole hydrogen source, and requires the addition of substoichiometric amounts of a base. The reaction is clean and gives generally good to excellent yields (up to >99%), although the enantioselectivity is still moderate (up to 58%). The new rhenium(V) complexes are bench stable and easy to handle. An alkoxido complex was isolated after completion of the reaction with catalyst *exo*-**3a**. Based on this, and considering the previously proposed reaction pathways, a plausible reaction mechanism was proposed, in which the reduction occurs by direct hydrogen transfer between the simultaneously coordinated alkoxy and ketone substrate. To the best of our knowledge, this is the first example of a transfer hydrogenation reaction catalyzed by rhenium complexes.

Experimental Section

General Methods: All the reactions were carried out under an inert argon atmosphere using standard Schlenk techniques. Solvents were distilled and dried prior to utilization by using reported procedures.[39] All commercially available reagents were used as received without further purification. (*R*)-[1-(dimethylamino)ethyl]-ferrocene (Ugi's amine) was kindly provided by SOLVIAS AG as the tartrate salt. The ligand precursors dimethyl{(*R*)-1-[(*S*)-2-(diphenylphosphanyl)ferrocenyl]ethyl}amine (**1a**) and dimethyl{(*R*)-1-[(*S*)-2-(dicyclohexylphosphanyl)ferrocenyl]ethyl}amine (1b) were synthesized as described previously.[40] The Josiphos ligand (*R*)-1-[(S_P)-2-(diphenylphosphanyl)ferrocenyl]ethyldicyclohexylphosphane (**2a**) was prepared as previously reported.[22] The ligands (*R*)-1-[(S_P)-2-(dicyclohexyphosphanyl)ferrocenylethyl]diphenylphosphane (**2b**), (*R*)-1-[(S_P)-2-(diphenylphosphanyl)ferrocenyl]ethyldi-(3,5-xylyl)phosphane (**2d**), (*R*)-1-[(S_P)-2-(dicyclohexylphosphanyl)-ferrocenyl]ethyldicyclohexylphosphane (**2e**), (*R*)-1-[(S_P)-2-(diphenylphosphanyl)ferrocenyl]ethyldi-*tert*-butylphosphane (**2f**), (*R*)-1-[(S_P)-2-(dicyclohexylphosphanyl)ferrocenyl]ethyldi-*tert*-butylphosphane (**2g**) and (*R*)-1-[(S_P)-2-(di-*tert*-butylphosphanyl)ferrocenyl]ethyldiphenylphosphane (**2j**) were purchased from Aldrich (Solvias Chiral Ligands Kit) and used as received. The parent rhenium complexes $[ReOCl_3(AsPh_3)_2]$ (X = Cl, Br)[25] and $[NBu_4][ReNCl_4]$[41] were synthesized by following literature procedures. NMR Spectra were recorded with Bruker Avance DPX300 and DPX250 instruments. The chemical shifts are reported in parts per million (ppm). ^1H and ^{13}C NMR shifts are referenced to TMS and calibrated with the residual solvent peak; ^{31}P shifts are relative to H_3PO_4 (85%) as an external reference. Coupling constants *J* are given in Hz. HR ESI-MS and MALDI-MS measurements were performed by the MS service of the Laboratorium für Organische Chemie der ETH Zürich. Values are given as *m*/*z*. Elemental analyses were performed by the microelemental analysis service of the Laboratorium für Organische Chemie der ETH Zürich. FTIR measurements were performed with a Perkin–Elmer Spectrum BX Series spectrometer with solid state samples by using an ATR Golden Gate sampling accessory. HPLC was performed with Agilent Series 1100 or HP 1050 instruments equipped with a UV diode array detector (DAD); flow in mL/min, eluent (hexane/IPrOH-ratio) are given in each case; columns: Chiralcel OD-H, OB, AD-H (4.6 × 250 mm, particle 5 μm) or Chiralcel OJ (4.6 × 250 mm, particle 10 μm). X-ray structural measurements were performed with a Siemens CCD diffractometer (Siemens SMART PLAT-

FORM, with CCD detector, graphite monochromator, Mo-K_α radiation). Data were collected using the program SMART. Integration was performed with SAINT. Structure solution (direct methods) was accomplished with SHELXTL 97. CCDC-869344 (for **3a**), -869345 (for **3d**), -869346 (for **3e**), -869347 (for **3f**), -869348 (for **3g**), -869349 (for **3i**), -869353 (for **4**), -869350 (for **6**) and -869351 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Method for the Synthesis of (*R*,*S*)-pfa (1): In an oven-dried Schlenk tube, (*R*)-[1-(dimethylamino)ethyl]ferrocene (Ugi's amine) (1 equiv.) was dissolved in dry diethyl ether (to a concentration of 1–2 M), and this solution cooled to –78 °C. To this solution *tert*-butyllithium (1.6 M) in pentane (1.2 equiv.) was added dropwise with a syringe. The reaction mixture was stirred at this temperature for 30 min. Then the cooling bath was removed to allow the mixture to warm to room temperature. It was stirred for a further 60 min leading to the formation of a red-orange precipitate. The same amount of ether used before was added and the mixture was stirred for another 60 min giving a clear solution. The solution was cooled again to –78 °C and the corresponding secondary phosphane chloride (1.1 equiv.) was added dropwise with a syringe. The reaction was warmed to room temperature overnight. To the resulting orange suspension a saturated solution of Na_2CO_3 was added slowly to quench the reaction. The biphasic mixture was separated in a separatory funnel and the organic phase was washed with water and brine and dried with $MgSO_4$, then filtered and concentrated to dryness in vacuo to give a sticky orange solid. The crude product was purified by either column chromatography or by recrystallization to give pure **1** as an orange solid.

Dimethyl{(*R*)-1-[(*S*)-2-(diphenylphosphanyl)ferrocenyl]ethyl}amine (1a):[40] From Ugi's amine (4.024 g, 15.652 mmol, 1 equiv.), *tert*-butyllithium (12 mL, 1.6 M in pentane, 19.2 mmol, 1.2 equiv.) and chlorodiphenylphosphane (3 mL, 16.652 mmol, 1.1 equiv.), according to the general method. Recrystallized at –20 °C from a saturated dichloromethane/hexane solution to give orange crystals; yield 5.133 g (74%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.66 (m, 2 H, Ph), 7.48–7.39 (m, 3 H), 7.27 (m, 5 H), 4.45 (s, 1 H, *H*Cp), 4.32 (t, *J* = 2.3 Hz, 1 H, *H*Cp), 4.23 (ddd, *J* = 13.2, 6.4, 2.3 Hz, 1 H, *H*CMe), 4.02 (s, 5 H, Cp), 3.93 (s, 1 H, *H*Cp), 1.84 (s, 6 H, N*Me*), 1.34 (d, *J* = 6.7 Hz, 3 H, HC*Me*) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = –22.82 (s) ppm.

Dimethyl{(*R*)-1-[(*S*)-2-(dicyclohexylphosphanyl)ferrocenyl]ethyl}-amine (1b):[40] From Ugi's amine (1.821 g, 7.08 mmol, 1 equiv.), *tert*-butyllithium (5.4 mL, 1.6 M in pentane, 8.5 mmol, 1.2 equiv.) and chlorodicyclohexylphosphane (1.8 mL, 8.15 mmol, 1.1 equiv.) according to the general method. Flash chromatography through silica, eluted with a mixture of *n*-hexane/ethyl acetate, 5:1. Recrystallized at –20 °C from a saturated ethanol solution to give an orange powder; yield 1.896 g (59%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 4.28 (s, 1 H, *H*Cp), 4.24 (t, *J* = 2.1 Hz, 1 H, *H*Cp), 4.10 (s, 1 H, *H*Cp), 4.05 (s, 5 H, Cp), 3.98 (m, 1 H, *H*CMe), 2.34 (br. s, Cy), 2.09 (br. s, Cy), 2.00 (br. s, Cy), 1.84 (br. s, Cy), 1.68 (m, Cy), 1.48–1.33 (m, Cy), 1.28 (d, *J* = 6.7 Hz, 3 H, Me), 1.23–1.01 (m, Cy) ppm. ^{31}P NMR (121 MHz, CD_2Cl_2): δ = –11.84 (s) ppm.

General Method for the Synthesis of Josiphos Ligands 2: In an oven-dried Schlenk tube, **1** (1 equiv.) was dissolved in degassed glacial acetic acid (to a concentration of 0.5–1 M). To this solution, the corresponding secondary phosphane (1.1 equiv.) was added, and the mixture was stirred at 80 °C for three hours. The solvent and volatiles were removed in vacuo to give an orange sticky solid. It was dissolved in dichloromethane and washed successively with a saturated Na_2CO_3 solution, brine and water, dried with $MgSO_4$ and filtered. It was concentrated to dryness with a rotary evaporator to give the crude product. The crude product was purified either by column chromatography or by recrystallization to give pure **2** as an orange solid.

(*R*)-1-[(S_P)-2-(Diphenylphosphanyl)ferrocenyl]ethyldicyclohexylphosphane (2a):[22] From **1a** (1.394 g, 3.1614 mmol, 1 equiv.) and dicyclohexylphosphane (0.7 mL, 3.4597 mmol, 1.1 equiv.) according to the general procedure. Recrystallized from a saturated dichloromethane solution at –20 °C to give orange crystals; yield: 1.813 g (96%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.73–7.58 (m, 2 H, Ph), 7.46–7.33 (m, 3 H, Ph), 7.16 (d, *J* = 3.2 Hz, 5 H, Ph), 4.36 (s, 1 H, *H*Cp), 4.32 (t, *J* = 2.2 Hz, 1 H, *H*Cp), 4.07 (s, 1 H, *H*Cp), 3.79 (s, 5 H, Cp), 3.30 (dd, *J* = 7.0, 2.0 Hz, 1 H, *H*CMe), 1.77 (br. s, Cy), 1.70 (br. s, Cy), 1.63 (br. s, Cy), 1.59 (dd, *J* = 7.2, 4.7 Hz, 3 H, Me), 1.55–1.43 (m, Cy), 1.35–0.91 (m, Cy) ppm. ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 15.46 (d, *J* = 37.6 Hz), –25.76 (d, *J* = 37.6 Hz) ppm.

(*R*)-1-[(S_P)-2-(Dicyclohexylphosphanyl)ferrocenyl]ethyldiadamantylphosphane (2c): According to the general method, from **1a** (500.6 mg, 1.13 mmol, 1 equiv.), bisadamantylphosphane[42] (412.8 mg, 1.36 mmol, 1.2 equiv.) and with the addition of trifluoroacetic acid (0.08 mL). Purified by flash chromatography in silica eluted with a mixture of *c*-hexane/ethanol, 10:1, to give an orange powder; yield 268.3 mg (34%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.67–7.57 (m, 2 H, Ph), 7.40–7.31 (m, 3 H, Ph), 7.26–7.12 (m, 5 H, Ph), 4.43 (d, *J* = 1.2 Hz, 1 H, *H*Cp), 4.23 (t, *J* = 2.3 Hz, 1 H, *H*Cp), 4.01–3.95 (m, 1 H, *H*Cp), 3.81 (s, 5 H, Cp), 3.43 (dt, *J* = 7.0, 5.5 Hz, 1 H, *H*CMe), 2.00 (br. s, adamantyl), 1.93 (dd, *J* = 7.2, 3.0 Hz, 3 H, Me), 1.79 (br. s, adamantyl), 1.73 (br. s, adamantyl), 1.64 (br. s, adamantyl) ppm. ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 143.22 (dd, *J* = 8.0, 1.7 Hz), 140.96 (dd, *J* = 12.2, 5.3 Hz), 136.45 (d, *J* = 23.4 Hz), 133.50 (dd, *J* = 16.7, 3.0 Hz), 129.21 (s), 128.27 (d, *J* = 8.0 Hz), 127.58 (d, *J* = 6.0 Hz), 127.11 (s), 103.45 (dd, *J* = 25.1, 24.4 Hz), 74.93 (dd, *J* = 12.3, 4.3 Hz), 72.17 (dd, *J* = 5.0, 0.9 Hz), 70.92 (dd, *J* = 4.4, 2.5 Hz), 69.97 (s), 68.67 (s), 42.96 (dd, *J* = 11.0, 3.0 Hz), 42.52 (d, *J* = 12.0 Hz), 40.19 (d, *J* = 2.8 Hz), 39.84 (s), 39.62 (d, *J* = 2.7 Hz), 39.35 (s), 37.63 (s), 29.88–29.29 (m), 19.10 (s) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = 49.79 (d, *J* = 54.1 Hz), –26.35 (d, *J* = 54.1 Hz) ppm. HRMS (MALDI): calcd. for $[M + H]^+$ 699.2967; found 699.2973.

(*R*)-1-[(S_P)-2-(Dicyclohexylphosphanyl)ferrocenyl]ethyldi[3,5-bis-(trifluoromethyl)phenyl]phosphane (2h): From **1b** (106.6 mg, 0.235 mmol, 1 equiv.) and bis[3,5-bis(trifluoromethyl)phenyl]phosphane[43] (111 mg, 0.242 mmol, 1 equiv.) according to the general procedure. Purified by recrystallization from methanol at –20 °C, to give an orange powder; yield 141 mg (69%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.97 (s, Ph), 7.93 (s, Ph), 7.85 (s, Ph), 7.80 (s, Ph), 7.71 (s, Ph), 7.69 (s, Ph), 4.30 (s, Cp, minor conformer), 4.22 (s, 5 H, Cp, major conformer), 4.12 (s, *H*Cp), 4.07 (s, *H*Cp), 3.93 (br. s, 1 H, *H*CMe), 3.64 (s, *H*Cp), 2.66–2.52 (m, Cy), 2.44 (dd, *J* = 16.5, 8.8 Hz, Cy), 2.22 (d, *J* = 8.5 Hz, Cy), 1.90 (br. s, Cy), 1.84–1.68 (m, Cy), 1.53 (dd, *J* = 37.7, 22.3 Hz, Cy), 1.43–1.32 (m, 3 H, Me), 1.28 (d, *J* = 7.6 Hz, Cy), 1.19 (d, *J* = 16.4 Hz, Cy), 1.01–0.70 (m, Cy) ppm. ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 135.94 (dd, *J* = 21.8, 2.8 Hz), 132.16 (dd, *J* = 19.0, 3.6 Hz), 131.78 (d, *J* = 3.1 Hz), 131.45 (d, *J* = 7.0 Hz), 125.99 (d, *J* = 5.7 Hz), 124.17 (s), 122.46 (s), 121.65 (d, *J* = 5.6 Hz), 95.93 (dd, *J* = 23.1, 18.5 Hz), 72.97 (s), 70.70 (s), 70.62 (s), 70.05 (s), 69.20 (s), 67.94 (s), 38.26 (s), 35.55 (s), 33.90 (s), 32.03 (s), 30.63 (d, *J* = 10.2 Hz), 30.40 (s), 30.24 (s), 29.92 (s), 28.88 (s), 28.61 (s), 28.03 (s), 27.87 (s), 27.67 (d, *J* =

11.3 Hz), 26.88 (d, J = 8.0 Hz), 17.50 (s) ppm. ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 11.96 (s, minor conformer), 8.31 (br. s, major conformer), –11.77 (s, minor conformer), –16.16 (br. s, major conformer) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2): δ = –63.24 (d, J = 28.9 Hz, minor conformer), –63.34 (d, J = 26.5 Hz, major conformer) ppm. HRMS (MALDI): calcd. for $[M + H]^+$ 867.1836; found 867.1826.

(*R*)-1-[(*S*$_P$)-2-(Dicyclohexylphosphanyl)ferrocenyl]ethyldi(3,5-xylyl)phosphane (2i): From **1b** (200.7 mg, 0.443 mmol, 1 equiv.) and bis(3,5-xylyl)phosphane (120 μL, 0.529 mmol, 1.2 equiv.) according to the general procedure. Purified by flash chromatography in silica eluted with a mixture of *n*-hexane/ethyl acetate, 20:1 and 5% of TEA, to give an orange powder; yield 155 mg, 95% purity (53%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.00 (s, 1 H, Xyl), 6.98 (s, 2 H, Xyl), 6.95 (s, 2 H, Xyl), 6.89 (s, 1 H, Xyl), 4.19 (s, 2 H, *H*Cp), 4.16 (s, 5 H, Cp), 3.89 (s, 1 H, *H*Cp), 3.52 (ddd, J = 13.8, 6.9, 3.5 Hz, 1 H, *H*CMe), 2.27, [s, 6 H, *Me*(Xyl)], 2.26, [s, 6 H, *Me*(Xyl)], 1.87 (br. s, Cy), 1.70 (dd, J = 24.2, 15.9 Hz, 3 H, HC*Me*), 1.40 (m, Cy), 1.28 (br. s, Cy), 1.14 (br. s, Cy), 0.89 (br. s, Cy) ppm. ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 138.97 (d, J = 18.1 Hz), 138.06 (d, J = 5.0 Hz), 137.67 (d, J = 7.8 Hz), 136.27 (d, J = 19.9 Hz), 133.70 (d, J = 21.1 Hz), 131.20 (s), 130.02 (d, J = 16.0 Hz), 129.69 (s), 99.25 (dd, J = 22.4, 19.4 Hz), 78.94 (dd, J = 22.5, 3.3 Hz), 71.70 (s), 69.71 (s), 69.17 (dd, J = 9.7, 3.9 Hz), 68.07 (s), 37.34 (d, J = 13.0 Hz), 35.91 (dd, J = 12.3, 3.5 Hz), 33.82 (d, J = 22.6 Hz), 32.15 (dd, J = 13.5, 3.5 Hz), 31.60 (d, J = 13.9 Hz), 30.49 (d, J = 4.4 Hz), 28.77 (d, J = 14.9 Hz), 27.86 (d, J = 9.9 Hz), 27.09 (d, J = 4.9 Hz), 21.61 (d, J = 6.9 Hz), 19.84 (t, J = 3.9 Hz) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = 3.66 (d, J = 8.4 Hz), –14.61 (d, J = 7.6 Hz) ppm. HRMS (MALDI): calcd. for $[M + H]^+$ 651.2967; found 651.2968.

General Method for the Synthesis of Complexes 3: In an oven-dried Schlenk tube, $[ReOCl_3(AsPh_3)_2]$ (X = Cl, Br)[25] (1 equiv.) and the corresponding Josiphos ligand **2** were dissolved in dry dichloromethane (to a concentration of ca. 0.1 M). The mixture was then stirred at room temperature for 3–12 h. It was then concentrated in vacuo to a fourth of its original volume, and to the resulting brown solution *n*-hexane was added (two or three times the initial volume) to precipitate a brown solid. This was decanted and washed thoroughly with hexane and finally with ethyl ether. The product was then dried in vacuo and purified (when necessary) by recrystallization.

$[ReOCl_3$(2a)] (3a): From $[ReOCl_3(AsPh_3)_2]$ (298.5 mg, 0.324 mmol, 1 equiv.) and **2a** (194.3 mg, 0.327 mmol, 1 equiv.) according to the general method to give a brown-green solid; yield 274 mg (94%). X-ray quality crystals were obtained by layering a saturated dichloromethane solution with benzene. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 8.28–8.10 (m, 2 H, Ph), 7.57 (m, 3 H, Ph), 7.50–7.37 (m, 2 H, Ph), 7.27 (m, 3 H, Ph), 4.90 (s, 1 H, *H*Cp), 4.60 (d, J = 7.6 Hz, 1 H, *H*Cp), 3.73 (s, 5 H, Cp), 3.41 (s, 1 H, *H*Cp), 2.52 (br. s, 1 H, *H*CMe), 2.07 (dd, J = 12.0, 7.4 Hz, 3 H, Me), 2.00–1.74 (m, Cy), 1.74–1.31 (m, Cy), 1.22 (s, Cy), 1.05–0.80 (m, Cy), 0.74–0.44 (m, Cy) ppm. ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 141.28 (d, J = 53.5 Hz), 135.98 (d, J = 8.4 Hz), 133.67 (d, J = 61.3 Hz), 132.63 (d, J = 8.9 Hz), 131.97 (d, J = 2.6 Hz), 130.88 (d, J = 2.4 Hz), 128.37 (d, J = 10.6 Hz), 128.02 (d, J = 10.1 Hz), 92.78 (d, J = 15.5 Hz), 76.47 (d, J = 2.8 Hz), 72.44 (d, J = 7.7 Hz), 71.97 (s), 71.33 (d, J = 6.5 Hz), 39.86 (d, J = 19.2 Hz), 37.67 (d, J = 19.1 Hz), 31.04 (d, J = 21.7 Hz), 29.91 (s), 29.80 (s), 28.68 (d, J = 8.7 Hz), 28.17 (s), 27.84 (s), 27.42 (s), 27.23 (s), 26.80 (s), 26.28 (s), 17.54 (d, J = 6.7 Hz) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = 3.06 (d, J = 15.5 Hz), –34.81 (d, J = 15.6 Hz) ppm. HRMS (MALDI): calcd. for $[M – Cl]^+$) 867.1133, found 867.1138. $C_{36}H_{44}Cl_3FeOP_2Re$ (903.10): calcd. C 47.88, H 4.91, P 6.86; found C 48.15, H 4.93, P 6.82.

$[ReOCl_3$(2b)] (3b): From $[ReOCl_3(AsPh_3)_2]$ (37.7 mg, 0.041 mmol, 1 equiv.) and **2b** (25.9 mg, 0.043 mmol, 1 equiv.) according to the general method to give a brown solid; yield 29 mg (78%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.84 (s, Ph), 7.74 (s, Ph), 7.73–7.60 (m, Ph), 7.53 (br. s, Ph), 7.41 (d, J = 6.9 Hz, Ph), 7.37–7.18 (m, Ph), 4.90 (s, 1 H, *H*Cp), 4.74 (s, 1 H, *H*Cp), 4.69 (s, 1 H, *H*Cp), 4.56 (s, 1 H, *endo*), *H*Cp, 4.38 (s, 5 H, Cp, *exo*), 4.34 (s, 5 H, *endo*), 4.04–3.81 (m, 1 H, *H*CMe), 3.40 (s, Cy), 3.17 (q, J = 12.2 Hz, Cy), 2.76 (dd, J = 24.5, 11.9 Hz, Cy), 2.48 (d, J = 28.1 Hz, Cy), 2.20–1.99 (m, Cy), 1.98–1.77 (m, Cy), 1.69 (dd, J = 12.7, 6.9 Hz, 3 H, Me), 1.62–1.33 (m, Cy), 1.33–1.07 (m, Cy), 0.94–0.76 (m, Cy) ppm. ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 135.21 (d, J = 6.9 Hz), 134.27 (d, J = 7.2 Hz), 132.02 (d, J = 2.1 Hz), 131.59 (d, J = 3.1 Hz), 129.09 (d, J = 9.2 Hz), 127.85 (d, J = 10.3 Hz), 91.32–90.61 (m), 75.61 (d, J = 4.4 Hz), 71.64 (s), 70.68 (s), 70.38 (d, J = 6.5 Hz), 40.91 (d, J = 23.2 Hz), 38.28 (d, J = 22.2 Hz), 30.22 (s), 29.23 (s), 29.07 (s), 28.74 (s), 28.34 (s), 27.85 (s), 27.73–27.09 (m), 26.77 (s), 26.09 (s), 16.72 (d, J = 6.4 Hz) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = 1.43 (br. s, *endo*), –2.86 (d, J = 13.4 Hz, *exo*), –12.19 (br. s, *exo*), –19.89 (br. s, *endo*) ppm. HRMS (MALDI): calcd. for $[M – Cl]^+$ 867.1134, found 867.1128.

$[ReOCl_3$(2c)] (3c): From $[ReOCl_3(AsPh_3)_2]$ (122 mg, 0.132 mmol, 1 equiv.) and **2c** (99 mg, 0.142 mmol, 1.1 equiv.) according to the general method to give a brown solid; yield 113 mg (85%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 8.43–8.28 (m, Ph), 8.28–8.13 (m, Ph), 8.02 (dd, J = 18.7, 10.2 Hz, Ph), 7.71–7.39 (m, Ph), 7.34 (t, J = 9.0 Hz, Ph), 5.21 (dd, J = 10.9, 7.6 Hz, *H*CMe), 4.86 (s, *H*Cp), 4.78 (s, *H*Cp), 4.75–4.67 (m, *H*Cp), 4.57 (s, *H*Cp), 4.47 (s, *H*Cp), 4.40 (s, *H*Cp), 4.36 (s, Cp), 4.33 (s, *H*Cp), 3.78 (s, Cp), 3.49 (s, adamantyl), 2.97 (br. s, adamantyl), 2.70 (br. s, adamantyl), 2.49 (br. s, adamantyl), 2.38 (dd, J = 9.1, 7.2 Hz, Me), 2.33 (br. s, adamantyl), 2.29 (br. s, adamantyl), 2.19 (br. s, adamantyl), 2.07 (d, J = 8.1 Hz, adamantyl), 1.96 (br. s, adamantyl), 1.88 (br. s, adamantyl), 1.80 (br. s, adamantyl), 1.75 (br. s, adamantyl), 1.69 (br. s, adamantyl), 1.65 (br. s, adamantyl), 1.52 (br. s, adamantyl), 1.46 (br. s, adamantyl), 1.39 (br. s, adamantyl), 1.34 (br. s, adamantyl), 1.26 (br. s, adamantyl), 0.73 (br. s, adamantyl) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = 26.88 (d, J = 11.3 Hz, *exo*), 8.50 (d, J = 14.4 Hz, *endo*), –28.08 (d, J = 11.5 Hz, *exo*), –32.99 (d, J = 14.5 Hz, *endo*) ppm. HRMS (MALDI): calcd. for $[M – Cl]^+$ 971.1761; found 971.1739.

$[ReOCl_3$(2d)] (3d): From $[ReOCl_3(AsPh_3)_2]$ (61 mg, 0.066 mmol, 1 equiv.) and **2d** (43 mg, 0.067 mmol, 1 equiv.) according to the general method to give a brown solid; yield 54 mg (71%). The obtained *endo* isomer isomerizes slowly in solution at room temperature to give the *exo* isomer. X-ray quality crystals of *exo*-**3d** were obtained by layering a saturated chloroform solution with *n*-hexane. *endo* isomer: ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 8.18–8.02 (m, Ar), 7.66 (dd, J = 11.0, 7.2 Hz, Ar), 7.58–7.38 (m, Ar), 7.32 (m, Ar), 7.06 (s, 1 H, Xyl), 6.97 (s, 1 H, Xyl), 4.78 (s, 1 H, *H*Cp), 4.60 (t, J = 2.4 Hz, 1 H, *H*Cp), 4.22 (s, 1 H, *H*Cp), 4.19 (m, *H*CMe), 3.79 (s, 5 H, Cp), 2.30 [s, 6 H, *Me*(Xyl)], 2.22 [s, 6 H, *Me*(Xyl)], 1.49 (dd, J = 13.1, 7.2 Hz, 3 H, HC*Me*) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = –9.27 (br. s), –22.00 (d, J = 14.8 Hz) ppm. HRMS (MALDI): calcd. for $[M – Cl]^+$ 911.0821; found 911.0820. *exo* isomer: ^{13}C NMR (63 MHz, $CDCl_3$): δ = 140.46 (s), 139.59 (s), 137.51 (d, J = 8.2 Hz), 137.34 (d, J = 7.4 Hz), 135.56 (d, J = 8.4 Hz), 134.81 (s), 133.37 (s), 132.80 (s), 132.28 (d, J = 8.2 Hz), 131.94 (d, J = 9.5 Hz), 131.62 (d, J = 7.4 Hz), 130.01 (s), 129.42 (s), 128.63 (s), 128.03 (d, J = 11.1 Hz), 127.27 (d, J = 11.1 Hz), 92.54 (dd, J

= 17.6, 3.5 Hz), 77.30 (s), 75.99–75.72 (m), 73.70 (s), 72.77 (s), 71.54 (s), 70.99 (s), 70.23 (d, J = 6.9 Hz), 32.70 (d, J = 29.9 Hz), 21.70 (s), 21.29 (s), 15.28 (dd, J = 4.9, 1.7 Hz) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 1.33 (d, J = 15.7 Hz), –30.73 (d, J = 15.9 Hz) ppm.

[$ReOCl_3$(2e)] (3e): From [$ReOCl_3(AsPh_3)_2$] (67 mg, 0.073 mmol, 1 equiv.) and **2e** (45 mg, 0.074 mmol, 1 equiv.) according to the general method to give a brown powder; yield 48 mg (73%). X-ray quality crystals were obtained by layering a saturated dichloromethane solution with ethyl ether. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 4.74 (s, 1 H, *H*Cp), 4.55 (s, 1 H, *H*Cp), 4.46 (s, 1 H, *H*Cp), 4.30 (s, 5 H, Cp), 3.50 (s, 1 H, Cy), 3.01 (s, 1 H, Cy), 2.80 [q, J = 13.3 Hz, 1 H, *H*C(Me)], 2.48 (s, 2 H, Cy), 2.30 (d, J = 9.4 Hz, 1 H, Cy), 2.10 (d, J = 7.4 Hz, 3 H), 2.05 (d, J = 7.4 Hz, 3 H), 1.85 (m, Cy), 1.53 (m, Cy), 1.39 (m, Cy), 1.25–0.97 (m, Cy), 0.85 (m, Cy) ppm. ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 91.75 (br. s), 71.27 (s), 70.50 (s), 70.39 (s), 70.09 (s), 70.00 (s), 40.53 (d, J = 16.8 Hz), 36.94 (d, J = 23.3 Hz), 32.17 (d, J = 34.6 Hz), 30.02 (d, J = 5.5 Hz), 29.71 (d, J = 7.1 Hz), 28.96 (s), 28.89–28.38 (m), 27.98 (d, J = 9.6 Hz), 27.69 (d, J = 2.9 Hz), 27.50 (d, J = 1.8 Hz), 26.74 (d, J = 4.1 Hz), 26.55 (d, J = 4.4 Hz) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = 6.19 (d, J = 13.4 Hz), –27.57 (d, J = 13.7 Hz) ppm. HRMS (MALDI): calcd. for $[M - Cl]^+$ 879.20849; found 879.2065.

[$ReOCl_3$(2f)] (3f): From [$ReOCl_3(AsPh_3)_2$] (49.1 mg, 0.053 mmol, 1 equiv.) and **2f** (31.5 mg, 0.058 mmol, 1.1 equiv.) according to the general method to give a brown powder; yield 44 mg (97%). X-ray quality crystals of *endo*-**3f** were obtained by layering a saturated chloroform solution of the isomer mixture with *n*-hexane. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46–8.32 (m, Ph), 8.25–8.13 (m, Ph), 8.13–7.96 (m, Ph), 7.85 (d, J = 7.4 Hz, Ph), 7.80–7.71 (m, Ph), 7.64 (t, J = 7.3 Hz, Ph), 7.45 (br. s, Ph), 7.33 (br. s, Ph), 5.38 (dt, J = 12.9, 6.9 Hz, 1 H, *H*CMe), 4.79 (s, 1 H, *H*Cp), 4.70 (s, 1 H, *H*Cp), 4.66 (s, 1 H, *H*Cp), 4.44 (s, 1 H, *H*Cp), 4.33 [s, 5 H, Cp (*exo*)], 4.09 (s, 1 H, *H*Cp), 3.87 (dt, J = 17.0, 7.2 Hz, 1 H, *H*CMe), 3.76 [s, 5 H, Cp (*endo*)], 3.56 (s, 1 H, *H*Cp), 2.29 [dd, J = 9.2, 7.5 Hz, 3 H, HC*Me* (*exo*)], 2.19 [dd, J = 9.9, 7.6 Hz, 3 H, HC*Me* (*endo*)], 1.56 [s, 9 H, *Me*(*t*Bu) (*exo*)], 1.51 [s, 9 H, *Me*(*t*Bu) (*exo*)], 1.15 [s, 9 H, *Me*(*t*Bu) (*endo*)], 1.10 [s, 9 H, *Me*(*t*Bu) (*endo*)] ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 138.05 (d, J = 50.0 Hz), 136.08 (d, J = 8.4 Hz), 135.20 (d, J = 8.1 Hz), 135.05 (d, J = 47.5 Hz), 133.80 (s), 133.39 (d, J = 8.9 Hz), 132.98 (d, J = 10.4 Hz), 132.36 (s), 131.46 (d, J = 2.6 Hz), 131.20 (s), 130.69 (d, J = 2.3 Hz), 130.51 (s), 130.17 (s), 128.74 (s), 128.55 (s), 128.11 (d, J = 4.5 Hz), 127.97 (s), 127.89 (d, J = 2.4 Hz), 127.69 (d, J = 1.5 Hz), 127.51 (d, J = 1.0 Hz), 93.62 (s), 82.11 (s), 77.36 (s), 75.91 (s), 75.70 (d, J = 6.6 Hz), 72.22 (s), 71.67 (s), 71.06 (d, J = 8.1 Hz), 70.63 (s), 69.92 (d, J = 7.8 Hz), 45.33 (d, J = 8.9 Hz), 44.02 (d, J = 6.5 Hz), 43.24 (d, J = 9.7 Hz), 41.55 (d, J = 10.4 Hz), 39.04 (d, J = 10.0 Hz), 33.19 (s), 32.11 (s), 30.52 (s), 19.71 (s), 18.67 (s) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 27.61 (d, J = 12.0 Hz, *exo*), 23.14 (d, J = 14.6 Hz, *endo*), –27.55 (d, J = 11.9 Hz, *exo*), –33.81 (d, J = 14.7 Hz, *endo*) ppm. HRMS (MALDI): calcd. for $[M - Cl]^+$ 815.0820; found 815.0826.

[$ReOCl_3$(2g)] (3g): From [$ReOCl_3(AsPh_3)_2$] (49 mg, 0.053 mmol, 1 equiv.) and **2g** (32 mg, 0.058 mmol, 1.1 equiv.) according to the general method to give a brown solid; yield 39 mg (85%). X-ray quality crystals were obtained by layering a saturated dichloromethane solution with *n*-hexane. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 4.71 (s, 1 H, *H*Cp), 4.65 (s, 1 H, *H*Cp), 4.63 (s, 1 H, *H*Cp), 4.59 (s, 1 H, *H*Cp), 4.56 (s, 1 H, *H*Cp), 4.50 (s, 1 H, *H*Cp), 4.37 (s, 5 H, Cp), 4.32 (s, 5 H, Cp), 3.82 (dt, J = 13.2, 5.5 Hz, 1 H, *H*CMe), 3.64–3.41 (m, 1 H, *H*CMe), 3.09 (br. s, Cy), 2.99–2.50 (m, Cy), 2.44 (br. s, Cy), 2.25 (dd, J = 10.0, 7.2 Hz, HC*Me*), 2.16 (dd, J = 9.9, 7.2 Hz, HC*Me*), 1.94 (br. s, Cy), 1.79 (br. s, Cy), 1.75 (br. s, Cy), 1.53 (d, J = 12.2 Hz, *t*Bu), 1.41 (d, J = 13.3 Hz, *t*Bu), 1.33–1.16 (m, *t*Bu), 0.94–0.81 (m, Cy) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = 24.89 (s), 23.61 (d, J = 10.4 Hz), –23.29 (s), –37.56 (s) ppm. HRMS (MALDI): calcd. for $[M - 2Cl]^+$ 792.2077; found 792.2085; calcd. for $[M - Cl]^+$ 827.1759; found 827.1758.

[$ReOCl_3$(2h)] (3h): From [$ReOCl_3(AsPh_3)_2$] (25 mg, 0.027 mmol, 1 equiv.) and **2h** (25 mg, 0.029 mmol, 1.1 equiv.) according to the general method to give a brown powder; yield 5.3 mg (16%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.22 (d, J = 8.4 Hz, Ar), 8.13 (d, J = 7.4 Hz, Ar), 7.98 (br. s, Ar), 7.61 (br. s, Ar), 4.99 (s, 1 H, *H*Cp), 4.78 (d, J = 8.5 Hz, 1 H, *H*Cp), 4.64 (s, 1 H, *H*Cp), 4.58 (s, 1 H, *H*Cp), 4.41 (s, 5 H, Cp), 4.40 (s, 5 H, Cp), 4.30 (d, J = 8.8 Hz, 1 H, *H*Cp), 4.25 (s, 1 H, *H*Cp), 3.95–3.83 (m, 1 H, *H*CMe), 3.48 (m, 1 H, *H*CMe), 2.90 (d, J = 12.1 Hz, Cy), 2.82 (br. s, Cy), 2.57 (br. s, Cy), 2.34 (br. s, Cy), 2.12 (br. s, Cy), 2.07–1.78 (m, Cy), 1.70 (dd, J = 13.2, 6.7 Hz, 3 H, Me), 1.64 (dd, J = 13.8, 7.0 Hz, 3 H, Me), 1.53 (br. s, Cy), 1.47–1.20 (m, Cy), 0.92–0.83 (m, 1 H, Cy) ppm. ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 2.71 (s), –4.26 (s), –10.27 (s), –18.27 (s) ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –63.30 (s), –63.43 (s), –63.46 (s), –63.47 (s) ppm. HRMS (MALDI): calcd. for $[M - Cl]^+$ 1139.0629; found 1139.0646.

[$ReOCl_3$(2i)] (3i): From [$ReOCl_3(AsPh_3)_2$] (61.8 mg, 0.067 mmol, 1 equiv.) and **2i** (44.9 mg, 0.069 mmol, 1 equiv.) according to the general method to give a brown solid; yield 65 mg (>99%). X-ray quality crystals were obtained by layering a saturated dichloromethane solution with *n*-hexane. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.39 (s, 1 H, Xyl), 7.35 (s, 1 H, Xyl), 7.17 (s, 1 H, Xyl), 6.98 (s, 1 H, Xyl), 6.94 (s, 1 H, Xyl), 4.61 (br. s, 1 H, *H*CMe), 4.54 (br. s, 2 H, *H*Cp), 4.35 (s, 1 H, *H*Cp), 4.33 (s, 5 H, Cp), 3.12 (dd, J = 22.8, 11.6 Hz, 1 H, Cy), 2.88 (br. s, 1 H, Cy), 2.72 (d, J = 11.4 Hz, 1 H, Cy), 2.35 [s, 6 H, *Me*(Xyl)], 2.13 [s, 6 H, *Me*(Xyl)], 2.08 (d, J = 8.9 Hz, Cy), 1.97–1.67 (m, Cy), 1.57 (dd, J = 13.3, 7.1 Hz, 3 H, HC*Me*), 1.49–1.13 (m, Cy), 1.13–0.71 (m, Cy), 0.38 (br. s, Cy) ppm. ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 137.95 (s), 137.79 (s), 137.61 (s), 133.39 (d, J = 2.0 Hz), 133.35 (d, J = 1.4 Hz), 133.09 (d, J = 7.5 Hz), 132.48 (d, J = 6.6 Hz), 129.96 (s), 129.13 (s), 91.34 (s), 76.44 (s), 71.62 (s), 70.27 (d, J = 5.8 Hz), 42.62 (d, J = 27.5 Hz), 34.33 (d, J = 28.2 Hz), 30.05 (d, J = 3.3 Hz), 28.99 (s), 28.81 (s), 28.50 (s), 28.06 (s), 27.89 (s), 27.65 (s), 27.46 (s), 27.01 (d, J = 2.0 Hz), 26.90 (d, J = 1.3 Hz), 26.33 (s), 21.87 (s), 21.37 (s), 15.66 (d, J = 5.3 Hz) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = 1.45 (br. s), –20.41 (br. s) ppm. HRMS (MALDI): calcd. for $[M - Cl]^+$ 923.1777; found 923.1776; calcd. for $[M + Na]^+$ calcd: 981.1341; found 981.1340.

[$ReOCl_3$(2j)] (3j): From [$ReOCl_3(AsPh_3)_2$] (47 mg, 0.051 mmol, 1 equiv.) and **2j** (30.6 mg, 0.056 mmol, 1.1 equiv.) according to the general method to give a brown solid; yield 31.4 mg (72%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.91–7.21 (m, Ph), 5.08 (s, 1 H, *H*Cp), 5.00 (dd, J = 15.4, 7.4 Hz, 1 H, *H*CMe), 4.84 (s, 1 H, *H*Cp), 4.76 (s, 1 H, *H*Cp), 4.28 (s, 5 H, Cp), 2.07 (s, 9 H, *t*Bu), 2.02 (s, 9 H, *t*Bu), 1.64 (dd, J = 13.2, 7.3 Hz, 3 H, HC*Me*) ppm. ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 134.95 (d, J = 7.3 Hz), 134.60 (d, J = 7.1 Hz), 131.98 (d, J = 2.6 Hz), 131.63 (d, J = 2.9 Hz), 128.63 (d, J = 3.8 Hz), 128.47 (d, J = 4.6 Hz), 90.82 (dd, J = 12.7, 5.1 Hz), 78.61 (s), 76.32 (d, J = 29.0 Hz), 72.75 (s), 71.57 (s), 71.18 (d, J = 5.3 Hz), 45.21 (d, J = 16.8 Hz), 43.71 (d, J = 16.6 Hz), 34.50 (d, J = 28.7 Hz), 32.76 (s), 31.05 (s), 16.66 (d, J = 6.1 Hz) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = 18.12 (d, J = 12.8 Hz), 2.97 (d, J = 13.2 Hz), –8.18 (d, J = 13.3 Hz), –8.69 (d, J = 13.0 Hz) ppm. HRMS (MALDI): calcd. for $[M - Cl]^+$ 815.0820; found 815.0816.

[ReOBr$_3$(2k)] (3k): From [ReOBr$_3$(AsPh$_3$)$_2$] (138.7 mg, 0.131 mmol, 1 equiv.) and **2a** (82.6 mg, 0.139 mmol, 1 equiv.) according to the general method to give a greenish-brown solid; yield 132 mg (97%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 8.31 (dd, J = 16.7, 8.7 Hz, Ph), 8.15–7.97 (m, Ph), 7.64–7.52 (m, Ph), 7.48 (s, Ph), 7.35 (br. s, Ph), 7.34 (s, Ph), 7.26 (m, Ph), 5.29–5.13 (m, 1 H, *H*CMe), 4.94 (s, 1 H, *H*Cp), 4.74 (s, 1 H, *H*Cp), 4.65–4.59 (m, 1 H, *H*Cp), 4.56 (d, J = 1.9 Hz, 1 H, *H*Cp), 4.47 (s, 1 H, *H*Cp), 4.27 (s, 5 H, Cp), 4.25 (s, 1 H, *H*Cp), 3.78 (s, 5 H, Cp), 3.72–3.49 (m, 1 H, *H*Cp), 2.82–2.58 (m, Cy), 2.44–2.22 (m, Cy), 2.13 (dd, J = 12.2, 7.5 Hz, 3 H, Me), 2.05 (dd, J = 12.0, 8.4 Hz, 3 H, Me), 1.98–1.46 (m, Cy), 1.42 (d, J = 8.6 Hz, Cy), 1.34–0.83 (m, Cy), 0.82–0.60 (m, Cy), 0.58–0.33 (m, Cy) ppm. ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 142.13 (d, J = 52.8 Hz), 136.28 (d, J = 8.0 Hz), 135.93 (d, J = 8.2 Hz), 135.70 (d, J = 9.7 Hz), 133.24 (d, J = 61.4 Hz), 133.09 (d, J = 9.9 Hz), 132.31 (d, J = 8.6 Hz), 131.94 (d, J = 2.6 Hz), 131.78 (s), 131.29 (s), 130.75 (d, J = 2.1 Hz), 128.23 (s), 128.05 (s), 127.94 (s), 127.83 (d, J = 5.7 Hz), 92.10 (dd, J = 17.8, 2.3 Hz), 91.13 (d, J = 14.4 Hz), 76.83 (d, J = 7.2 Hz), 76.36 (d, J = 2.4 Hz), 73.03 (d, J = 5.7 Hz), 72.67 (d, J = 9.0 Hz), 71.95 (s), 71.85 (s), 71.63 (s), 71.47–71.23 (m), 71.03 (s), 70.15 (d, J = 8.9 Hz), 65.92 (s), 41.54 (d, J = 19.7 Hz), 38.74 (d, J = 18.5 Hz), 36.69 (d, J = 16.3 Hz), 32.69 (d, J = 22.8 Hz), 31.00 (d, J = 5.4 Hz), 30.67 (d, J = 4.0 Hz), 30.42 (d, J = 4.1 Hz), 30.25 (s), 28.61 (s), 28.41 (d, J = 6.7 Hz), 28.15 (s), 27.99 (s), 27.86 (s), 27.64 (s), 27.50 (s), 27.22 (s), 27.04 (s), 26.92 (s), 26.72 (s), 26.60 (s), 26.50 (s), 26.18 (s), 26.08 (s), 18.21 (d, J = 6.8 Hz), 17.31 (s) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = –0.56 (s, *endo*), –3.73 (d, J = 14.8 Hz, *exo*), –29.68 (s, *endo*), –43.80 (d, J = 14.7 Hz, *exo*) ppm. HRMS (MALDI): calcd. for [M – Br]$^+$ 957.0110; found 957.0088.

[ReO$_2$I(2a)] (5): In a nitrogen-filled glove-box, **2a** (116.2 mg, 0.195 mmol, 1.1 equiv.) and [ReO$_2$I(PPh$_3$)$_2$] (154 mg, 0.177 mmol, 1 equiv.) were dissolved in dichloromethane (3 mL). The resulting deep dark red solution was stirred at room temperature overnight. To this solution *n*-hexane was added until the precipitation of an orange solid occurred. The crude product was decanted, washed thoroughly with *n*-hexane and ethyl ether and dried in vacuo to afford an orange-brown paramagnetic powder; yield 140 mg (84%). HRMS (MALDI): calcd. for [M – I]$^+$ 813.1720; found 813.1750. FTIR (neat): $\tilde{\nu}$ = 3052.48, 2923.36, 2848.79, 1433.99, 1559.78, 1096.27, 908.60, 790.73, 744.09, 692.46 cm^{-1}. $C_{36}H_{44}FeIO_2P_2Re$ (939.64): calcd. C 46.02, H 4.72, P 6.59; found C 45.85, H 4.92, P 6.44.

[ReNCl$_2$(2a)] (6): In an oven-dried Schlenk tube, **2a** (59.3 mg, 0.099 mmol, 1 equiv.) and [NBu$_4$][ReNCl$_4$][41] (52.8 mg) were dissolved in dry toluene (5 mL). The orange solution was stirred at 90 °C for two hours to give a dark brown solution. It was then allowed to cool to room temperature and *n*-hexane (10 mL) was added with a syringe leading to the precipitation of a brown solid. The solid was decanted and washed with *n*-hexane (3 × 10 mL) and dried in vacuo to give a green-brown solid. The crude product was dissolved in dichloromethane, filtered through celite and concentrated to dryness to give the product as a greenish-black solid; yield 40.2 mg (47%). X-ray quality crystals (*endo* isomer) were obtained by recrystallization from a saturated dichloromethane/*n*-hexane solution at –20 °C. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 8.16 (dd, J = 12.1, 7.7 Hz, 2 H, Ph), 7.65 (dd, J = 15.0, 6.9 Hz, 5 H, Ph), 7.35 (dt, J = 13.2, 6.5 Hz, 3 H, Ph), 4.82 (s, 1 H, *H*Cp), 4.60 (s, 1 H, *H*Cp), 4.45 (s, 1 H, *H*Cp), 4.11–3.95 (m, 1 H, *H*CMe), 3.68 (s, 5 H, Cp), 3.05 (dd, J = 24.2, 11.9 Hz, 1 H, Cy), 2.78 (dd, J = 24.9, 12.2 Hz, 1 H, Cy), 2.28 (m, Cy), 1.94 (m, Cy), 1.73 (dd, J = 11.8, 7.5 Hz, 3 H, Me), 1.36–1.20 (m, Cy), 1.14 (m, Cy), 1.00–0.77 (m, Cy), 0.24 (m, Cy), 0.08 (br. s, Cy) ppm. ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 135.07 (d, J = 11.3 Hz), 134.29 (d, J = 9.2 Hz), 134.18 (d, J = 61.2 Hz), 131.32 (d, J = 2.8 Hz), 131.18 (d, J = 2.0 Hz), 129.95 (d, J = 51.6 Hz), 128.63 (d, J = 7.3 Hz), 128.46 (d, J = 9.0 Hz), 92.36 (d, J = 17.0 Hz), 75.26 (s), 72.33 (s), 70.60 (d, J = 15.3 Hz), 68.30 (s), 43.47 (d, J = 28.2 Hz), 36.27 (d, J = 21.0 Hz), 33.97 (d, J = 23.9 Hz), 30.94 (s), 29.15 (s), 28.84 (s), 28.13 (s), 27.47–25.80 (m), 25.18 (s), 24.84 (s), 23.35 (s), 16.03 (s) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = 31.37 (d, J = 11.9 Hz), 15.82 (d, J = 12.0 Hz) ppm.

General Procedure for the Catalytic Transfer Hydrogenation of Ketones: In an oven-dried Young–Schlenk tube, the corresponding amount of catalyst (ca. 1 mol-%) was dissolved in dry 2-propanol at room temperature. When the catalyst was synthesized in situ, the ferrocenyl ligand and the corresponding rhenium precursor were mixed in a 1:1 ratio (ca. 1 mol-% each). To this solution 1 equiv. of the ketone substrate was added (final concentration ca. 0.4 M). Then an excess of TEA (8–20%) was added and the system was heated for 20–24 h at 80 °C. The mixture was then allowed to cool to room temperature, and the solvent and volatiles are removed in vacuo. *n*-Hexane was then added, and the solution was filtered through a plug of silica, eluted with *n*-hexane and concentrated in a rotary evaporator to give the crude product. The yields were determined by integration of ^{1}H NMR signals using a 90° pulse width of 3.33 μs and a relaxation delay between scans of 3 s. The *ee* was measured by using chiral HPLC. In every case the absolute configuration of the product was determined by comparison of the retention time with that of an authentic sample of a pure enantiomer (see Supporting Information).

Isolation of the Rhenium-Alkoxy Intermediate [ReOCl$_2$(*i*PrO)(2a)] (7): After the extraction of the transfer-hydrogenation product with *n*-hexane, the remaining insoluble orange solid was dried in vacuo, dissolved in dichloromethane, and this solution was filtered through a plug of silica and eluted with the same solvent. The solution was concentrated to dryness to give the product as a light orange powder. X-ray quality crystals were obtained by layering a saturated dichloromethane solution with *n*-hexane. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.16 (s, 2 H, Ph), 7.87–7.69 (m, 2 H, Ph), 7.52 (s, 3 H, Ph), 7.41–7.22 (m, 3 H, Ph), 4.76 (s, 1 H, *H*Cp), 4.71 (s, 1 H, *H*Cp), 4.64 (s, 1 H, *H*Cp), 3.83–3.66 [m, 1 H, *H*C(Me)$_2$], 3.56 (s, 5 H, Cp), 3.27 (dd, J = 12.1, 5.8 Hz, 1 H, *H*CMe), 3.18 (dd, J = 24.4, 11.9 Hz, 1 H, Cy), 2.85 (s, 1 H, Cy), 2.63 (dd, J = 22.9, 12.3 Hz, 1 H, Cy), 2.11–1.94 (m, Cy), 1.89 (dd, J = 10.2, 7.6 Hz, 3 H, HC*Me*), 1.75 (br. s, Cy), 1.55 (br. s, Cy), 1.49–1.32 (m, Cy), 1.19–0.99 (m, Cy), 0.85 (dd, J = 24.3, 11.8 Hz, Cy), 0.66 (s, Cy), 0.61 [d, J = 6.0 Hz, 3 H, HC(*Me*)$_2$], 0.05 [d, J = 6.0 Hz, 3 H, HC(*Me*)$_2$] ppm. ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 137.94 (d, J = 58.8 Hz), 135.84 (d, J = 9.3 Hz), 135.33 (d, J = 8.8 Hz), 133.80 (d, J = 55.9 Hz), 131.49 (d, J = 2.5 Hz), 130.98 (d, J = 2.4 Hz), 128.31 (d, J = 10.5 Hz), 127.91 (d, J = 10.3 Hz), 93.63 (d, J = 19.0 Hz), 76.21 (d, J = 2.0 Hz), 75.49 (s), 71.38 (s), 70.86 (s), 70.71 (s), 37.66 (d, J = 20.5 Hz), 36.92 (d, J = 21.4 Hz), 36.02 (d, J = 19.5 Hz), 29.99 (s), 29.06 (d, J = 6.0 Hz), 28.24 (s), 28.09 (d, J = 3.9 Hz), 27.81 (s), 27.64 (s), 27.46 (s), 27.14 (s), 26.44 (d, J = 6.6 Hz), 25.92 (s), 23.24 (s), 22.52 (s), 17.32 (d, J = 5.4 Hz) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = 15.03 (br. s), –11.44 (d, J = 12.7 Hz) ppm. HRMS (MALDI): calcd. for [M – Cl]$^+$ 891.1949; found 891.193.

Supporting Information (see footnote on the first page of this article): Spectroscopic and analytical characterization data (NMR, MS, elemental analyses) for ligands and complexes, summary of crystallographic data, and characterization data for products of transfer hydrogenation reactions.

Acknowledgments

This work was supported by ETH Zürich and the Swiss National Science Foundation. We thank P. Battaglia for the synthesis of ligand **2c**, Dr. G. Santiso-Quiñones for the X-ray analysis of **3f**, L. Hendriks for some experimental work, Dr. J. Welch for useful discussions and advice and B. Pugin from Solvias AG for the useful advice and for providing the ligand precursor Ugi's amine.

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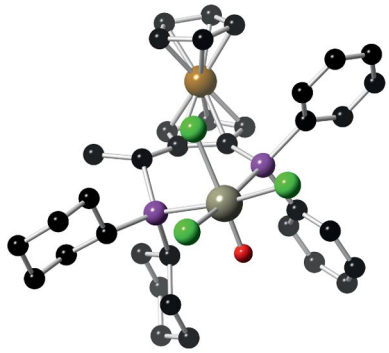
Received: June 24, 2012
Published Online: ■

EurJIC European Journal of Inorganic Chemistry

Rhenium Catalysis

A series of new rhenium complexes containing chiral ferrocenyldiphosphane ligands of the Josiphos family was prepared. The complexes are active catalysts in the asymmetric transfer hydrogenation of ketones using 2-propanol as the hydrogen source and in the presence of triethylamine, thus representing the first example of Re catalysts for this kind of transformation.



Keywords: Asymmetric synthesis / Homogeneous catalysis / Hydrogen transfer / Rhenium / Phosphane ligands

