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Investigations into the hydrogenation of diolefins and prochiral olefins employing the "Daniphos"-type ligands †

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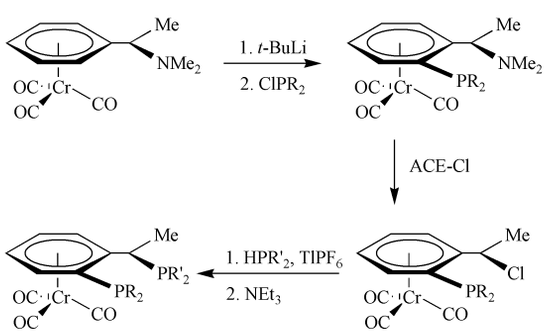
A number of enantiopure, planar chiral diphosphines of the Daniphos-type have been synthesized in good chemical yields and excellent stereochemical outcome according to a modular, straightforward synthetic method based on an arene–chromium–tricarbonyl scaffold. They were readily converted to their rhodium complexes, two of which have been characterized by X-ray crystallography. Their catalytic performance has been assessed by carrying out hydrogenations of dienes and prochiral olefins, taking the Josiphos ligand as a reference system for comparison. Interesting influences of the substitution patterns and solvents were found. Reaction rates of the hydrogenations of diolefins were also found to be strongly dependent on the respective substituents.

Introduction

In organometallic chemistry, transition metal mediated catalysis is one of the fastest growing fields. Herein the choice of the appropriate ligand, especially in asymmetric variation, is of crucial importance. To optimize catalytic performance, ligands of "modular structure" have attracted appreciable attention in recent years.[1] This structural feature allows for changing the ligand′s electronic and steric properties through a wide range by means of a simple, universal synthetic protocol. This allows the use of a general ligand type for several catalytic reactions and "fine tuning" the ligand for a specific reaction.

More recently a new strategy has been established by one of us[2] for the synthesis of optically active bifunctional arene–chromium–tricarbonyl complexes bearing elements of central as well as planar chirality (Scheme 1). Some of these had already been applied to homogeneous enantioselective catalysis like hydrovinylation, hydrogenation, hydroamination and allylic sulfonation.[2]



Scheme 1

Here we present the results of some investigations into the hydrogenation of dienes and prochiral olefins employing some diphosphines based on the aforementioned structure.

Results and discussion

Enantiomerically pure diphosphines **1**–**4** (see Table 1)‡ have been prepared according to the general procedure outlined in Scheme 1 in good overall yields from 29–79%. Starting from

Table 1 Ligands employed in this investigation

Compound	R	R′	Overall yield (%)
1	Ph	Ph	73
2	Ph	*t*-Bu	69
3	Ph	Cy	79
4	Cy	Ph	29

η^6-[(*R*)-(phenylethyl)dimethylamine]Cr(CO)$_3$ the first donor function is introduced diastereospecifically by directed *ortho* metalation (DOM)[3] and subsequent quenching with the appropriate chlorophosphine. This reaction step is almost quantitive (96–98% isolated yield). The dimethylamino group is then replaced under retention of configuration for a chloro substituent by reaction with 1-chloroethyl chloroformate (ACE-Cl) in high yield (87–90%).[2] Finally another nucleophilic substitution in the α-position that also proceeds under retention[2] leads to the desired diphosphines with yields of 78–83% for compounds **1**–**3**. Only for complex **4** a lower yield of 34% has been achieved.

These diphosphines were complexed to [(NBD)Rh]$^+$ and [(COD)Rh]$^+$ fragments by literature-known methods,[4] yielding the [(NBD)Rh(PP*)]BF_4 complexes **5**–**8** from compounds **1**–**4** and [(COD)Rh(PP*)]BF_4 complex **9** from diphosphine **3**. As expected, due to the C_1-symmetry of the ligands, all Rh-complexes showed a typical set of resonances in the ^{31}P-NMR spectrum: a doublet of doublets around 50 ppm for the α-P-atom and another doublet of doublets at about 25 ppm for the *ortho*-P-atom, revealing characteristic Rh–P and P–P coupling constants, *e.g.* for complex **9** $J_{RhP} = 148$ Hz and $J_{PP} = 35$ Hz, respectively.

A single-crystal X-ray structural analysis of [(NBD)-Rh(PPh_2/PCy_2)]BF_4 **7** and [(NBD)Rh(PCy_2/PPh_2)]BF_4 **8** established the structures of the complexes as Fig. 1 and 2 show along with the selected bond lengths and intramolecular angles (Tables 2 and 3). It should be noted that both compounds feature the R and R′ substituents in an inverse manner with respect to the α- and *ortho*-position (*vide infra*).

The deviation from the square-planar towards a tetrahedral coordination sphere is characteristic. The dihedral angles between the planes defined by P,Rh,P and MP1,Rh,MP2 (the midpoints of the double bonds) are 12.3(1)° for 7 and 6.5(1)° for

† Dedicated to the memory of Professor Noel McAuliffe.

‡ For convenience, in the following the ligands are denoted as "PX_2/PY_2", PX_2 meaning the *ortho*-group and PY_2 the group in the α-chain.

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Table 2 Selected distances (Å) and angles (°) for **7**

Rh1–P1	2.293(2)	Rh1–P2	2.311(2)
Rh1–MP1[a]	2.093(6)	Rh1–MP2[a]	2.082(6)
Rh1–C36	2.199(6)	Rh1–C39	2.196(7)
Rh1–C37	2.208(6)	Rh1–C40	2.184(6)
P1–C1	1.849(6)	P2–C7	1.892(7)
P1–C12	1.835(7)	P2–C24	1.850(7)
P1–C18	1.804(7)	P2–C30	1.834(7)
⟨Cr1–C(C_6H_4 ring)⟩	2.221(7)	⟨Cr1–C(CO)⟩	1.828(9)
P1–Rh1–P2	90.7(1)	MP1–Rh1–MP2[a]	69.0(1)
P1–Rh1– MP1[a]	99.7(1)	P2–Rh1– MP2[a]	101.6(1)
C9–Cr1–C10	88.6(3)	C10–Cr1–C11	89.9(3)
C11–Cr1–C9	88.9(6)		

[a] MP1 and MP2 denote the midpoints of the olefinic bonds C36–C37 and C39–C40, respectively.

Table 3 Selected distances (Å) and angles (°) for **8**

Rh1–P1	2.355(2)	Rh1–P2	2.266(2)
Rh1–MP1[a]	2.140(6)	Rh1–MP2[a]	2.067(6)
Rh1–C36	2.254(6)	Rh1–C39	2.175(6)
Rh1–C37	2.237(6)	Rh1–C40	2.177(6)
P1–C1	1.867(6)	P2–C7	1.871(6)
P1–C12	1.848(6)	P2–C24	1.810(6)
P1–C18	1.853(6)	P2–C30	1.872(6)
⟨Cr1–C(C_6H_4 ring)⟩	2.226(7)	⟨Cr1–C(CO)⟩	1.826(9)
P1–Rh1–P2	92.4(1)	MP1–Rh1–MP2[a]	68.8(1)
P1–Rh1– MP1[a]	103.5(1)	P2–Rh1– MP2[a]	95.6(1)
C9–Cr1–C10	87.3(3)	C10–Cr1–C11	87.6(3)
C11–Cr1–C9	89.4(6)		

[a] MP1 and MP2 denote the midpoints of the olefinic bonds C36–C37 and C39–C40, respectively.

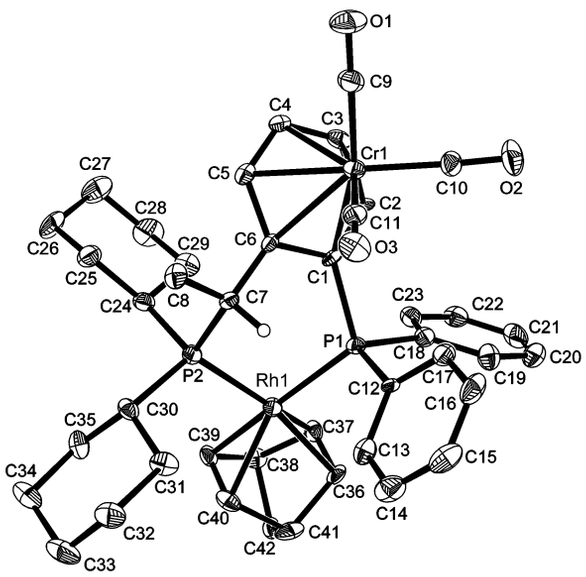


Fig. 1 Molecular structure of $[(NBD)Rh(PPh_2/PCy_2)]^+$ **7** (ORTEP, 30% thermal ellipsoids). All hydrogens except for the asymmetric carbon atom have been omitted for clarity.

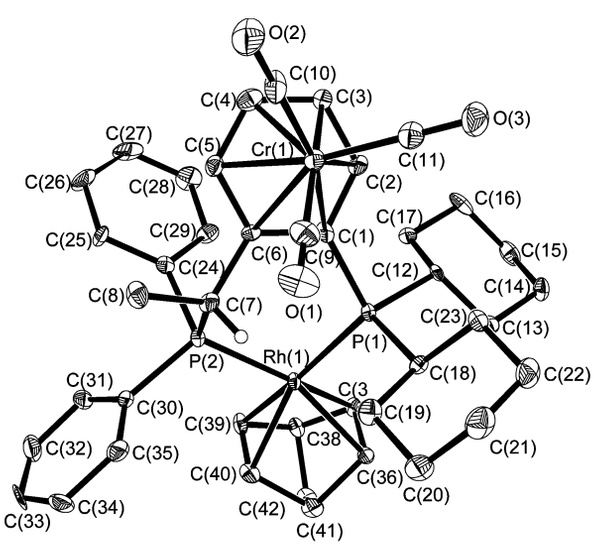


Fig. 2 Molecular structure of $[(NBD)Rh(PCy_2/PPh_2)]^+$ **8** (ORTEP, 30% thermal ellipsoids). All hydrogens except for the asymmetric carbon atom have been omitted for clarity.

8, thus the latter are in the same range as for Josiphos (6.9°)[5] which exhibits the same substituent pattern (in the form of $[(NBD)Rh(Josiphos)]BF_4 \cdot 2CH_2Cl_2$). Another difference in the structure parameters of **7** and **8** is found in the phosphorus–rhodium bond lengths. While in **7** the P–Rh bond lengths are almost equal (Table 2) (see Josiphos: 2.300 and 2.330(3) Å), in **8** clearly different P–Rh bond lengths are found (Table 3).

Nevertheless the bond lengths are in the expected range. A description of the conformation of the chelate rings is possible by selected torsion angles (Table 4). In order to account for a possible conformational change due to the complexation to rhodium a structure-related ligand (PPh_2/PPh_2)[6] was included into the discussion.

As the values in Table 4 show, there are no significant differences in the torsion angles at the relatively rigid side chain containing C7 and P2. Thus, neither change takes place in the conformation due to complexation of the ligand to rhodium, nor are substantial differences found between the two complexes of the Daniphos and the Josiphos class.

The situation is different for the phosphorus atom directly bound to the arene. While in the free ligand this phosphorus atom lies in the plane of the corresponding rings, P1 is 0.35 Å in **7** and 0.45 Å in **8** as well as 0.41 Å in Josiphos above the ring plane. For **3** and **4** only a rotation of 4 and 21° around the arene–P bond (Table 4) is necessary to coordinate to form **7** and **8**, contrary to Josiphos, where a rotation of 44° is required.[5]

Catalytic applications

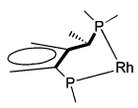
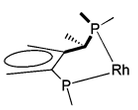
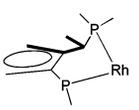
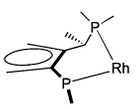
Diolefin hydrogenation. In most experiments of rhodium-catalysed asymmetric hydrogenations the catalysts are, for reasons of easier handling, used in form of their diolefin (COD or NBD) complexes like [(diene)M(PP*)]X or $[(diene)_2M]X$ in presence of the PP* ligand (with $X = BF_4^-$ for instance). Earlier investigations[7] have shown that this proceeding has some drawbacks on the hydrogenation of the prochiral substrate, as it leads to an induction period in the reaction, due to parallel hydrogenation of both the diene and the substrate, especially when COD derivatives are used. This might even leave a certain percentage of the catalysts unused.

To assess this effect for the present type of complexes some preliminary experiments have been carried out. The NBD complexes **5**–**8** have been subjected to the hydrogenation of NBD solutions (at ambient hydrogen pressure, 1 bar) in order to find out the rate constant of the reaction.[8] In case of the COD derivative **9** some ^{31}P-NMR experiments have been done.

NBD. For the hydrogenations of norbornadiene, 1 mmol solutions of NBD have been employed (see Experimental section for details).

Fig. 3 shows a clear gradation in activity dependent on the substituent in the α-chain. The aromatic derivative $[(NBD)Rh(PPh_2/PPh_2)]BF_4$ **5** (graph E) proved to be considerably slower than its aliphatic counterparts $[(NBD)Rh\{(PPh_2/P(t\text{-}Bu)_2\}]BF_4$ **6** and $[(NBD)Rh(PPh_2/PCy_2)]BF_4$ **7** (graphs C and D). For these complexes there is also a clear selectivity visible for the hydrogenation of the first (NBD to NBE) and second (NBE to NBA) double bond of the diene. The former is represented by the first (linear) part of the curves, the latter by

Table 4 Comparison of characteristic torsion angles (°)

	Compound				
	(PPh_2/PPh_2)[6]	**7**	**8**	Josiphos (Rh–complex)[5]	Josiphos (ligand)[5]
	−67	−70	−71	−69	−70
	−81	−55	−50	−56	−64
	−19	−24	−22	−15	−24
	−121	−117	−100	−101	−145

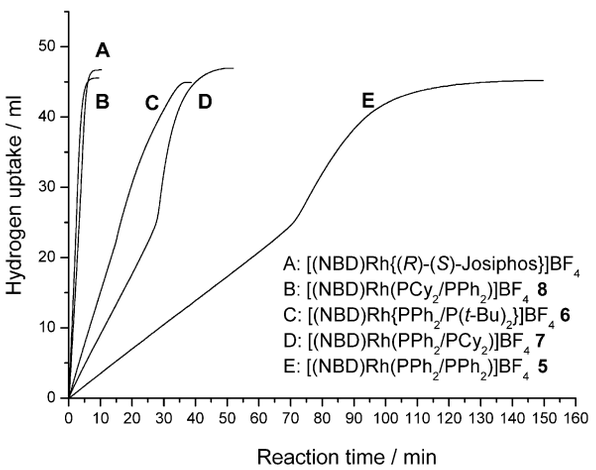
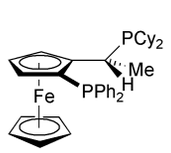


Fig. 3 Hydrogen consumption curves of the hydrogenation of NBD solutions for the examined compounds (1 bar hydrogen pressure).

the second part. This effect is quite often found and can be explained with the smaller equilibrium constant of the NBE complex compared to that of the NBD complex (chelate effect), which prevents a sufficient complexation of the monoene necessary for hydrogenation, provided that the concentration of the diene is large enough.

In Table 5 the calculated pseudo-rate constants k_{obs} (obs = observed; the values still contain the solubility of hydrogen under the experimental conditions) for all measured compounds are given. As can be seen, the ferrocene known as "Josiphos" (see sketch) is faster than the aforementioned chromium complexes. Also a distinction between the activity for the hydrogenation of the double bonds can no longer be observed (graph A). But surprisingly, $[(NBD)Rh(PCy_2/PPh_2)]BF_4$ **8**, isomeric to **7** in which the α- and *ortho* donor groups are exchanged, is the fastest among all the compounds examined (graph B). This complex also gave some unexpected results in the hydrogenation of prochiral olefins (see below).



Changing the solvent from methanol to THF has no great effect on the reaction, although in MeOH the reactions run

Table 5 Rate constants for the hydrogenation of NBD in MeOH and THF

Ligand PP*	k_{obs}[a]/min^{-1}	Solvent
$PPh_2/P(t\text{-}Bu)_2$ **2**	7.03	MeOH
	6.07	MeOH
	5.65	THF
PPh_2/PCy_2 **3**	3.60	MeOH
	3.59	MeOH
	4.82	THF
PPh_2/PPh_2 **1**	1.47	MeOH
	1.41	MeOH
	0.72	THF
(*R*)-(*S*)-Josiphos	31.4	MeOH
	37.3	MeOH
PCy_2/PPh_2 **4**	42.3	MeOH
	42.98	MeOH
	24.2	THF
	30.1	THF

[a] The respective experiments for confirmation have been carried out employing different batches of catalysts, solvents and diolefin solutions, therefore the slight deviations can be explained.

slightly faster except for **7**. But the reaction rates remain comparable and especially the ranking of the compounds remains unchanged.

In summary it can be stated that the hydrogenation of NBD is fast and the prehydrogenation of the precursor is completed in the range of minutes. With regard to the time taken for the hydrogenation of the substrate itself (hours) and taking the effort of the prehydrogenation of the precatalyst in advance of the actual reaction into account, the latter seemed unnecessary to us (see also Fig 5).

COD. To get a measure of the reactivity of the COD ligand towards hydrogenation in our system, we carried out some preliminary NMR experiments. Therefore 0.01 mmol of $[(COD)Rh(PPh_2/PCy_2)]BF_4$ **9** was placed in an NMR tube, dissolved in 0.7 ml CD_3OD, treated with hydrogen and the reaction was monitored *via* ^{31}P-NMR spectroscopy. In between the relatively short times necessary for recording the spectra the solution was shaken. Fig. 4 shows the decrease of the COD complex over time.

From the graph a $t_{1/2}$-value of about 30 minutes can be deduced, which means that a conversion of 98.5% (which is equivalent to six times $t_{1/2}$) of the starting material is achieved after approximately 180 minutes. This is extremely slow compared to the NBD complexes and confirms the general picture

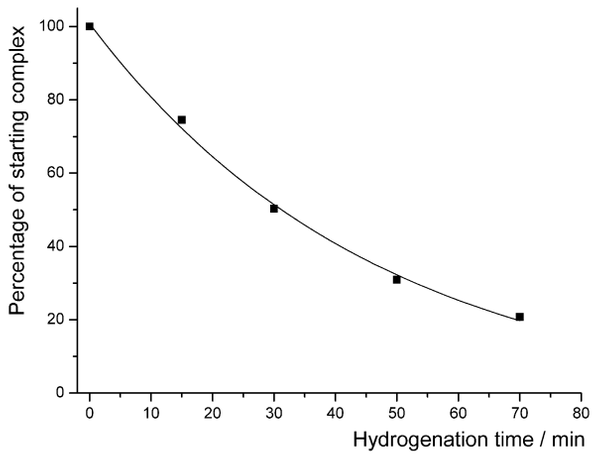


Fig. 4 Hydrogenation of $[(COD)Rh(PPh_2/PCy_2)]BF_4$ **9**.

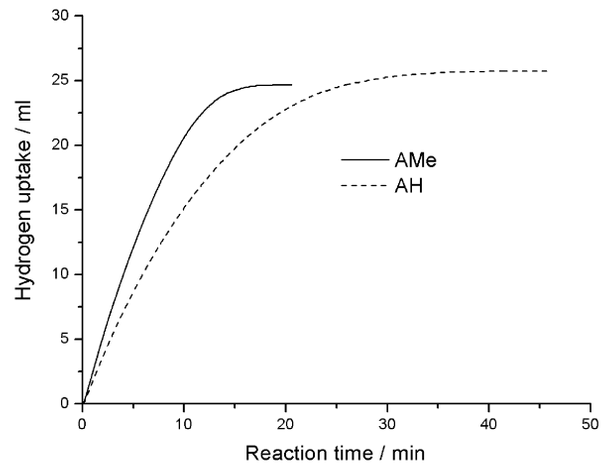


Fig. 5 Hydrogenation of AMe and AH with $[(NBD)Rh(PPh_2/PCy_2)]BF_4$ **7**.

of greater reactivity of norbornadiene Rh-complexes compared to their cyclooctadiene analogues. As a consequence no further experiments involving the COD derivatives have been carried out. Yet it has to be mentioned that after complete conversion of cyclooctadiene, the presumed solvent complex $[(PPh_2/PCy_2)Rh(CD_3OD)_2]^+$ has been observed by ^{31}P NMR spectroscopy at a chemical shift of $\delta = 90.45$ and 57.20 ppm, which is congruent with the species that has been found invariably after catalytic experiments employing the NBD complexes.

Hydrogenation of prochiral olefins

In addition to diolefins prochiral olefins have also been subjected to hydrogenation experiments at ambient hydrogen pressure (1 bar). We chose the standard substrates *N*-acetamido cinnamic acid (AH) and its methyl ester (AMe). Fig. 5 gives an example for the hydrogen consumption curves recorded, comparing the hydrogenation of AH and AMe with complex **7** in THF. Table 6 summarizes the results.

The *ee* values range from very low (2.4%) to moderate (81.5%). For reasons of comparison we have also done an experiment with (*R*)-(*S*)-Josiphos[7] as a ligand (entry 14). The result of 80.8% *ee* is comparable to that of our analogous chromium complex **3** with 81.5%.

From Table 6 the dramatic effects can be studied that occur when changing the particular R-groups on the donor functions as well as the solvent. For example interchanging the phosphorus side chains in the α- and *ortho*-positions in complexes $[(NBD)Rh(PPh_2/PCy_2)]BF_4$ **7** and $[(NBD)Rh(PPh_2/PCy_2)]BF_4$ **8** – while leaving the stereochemistry in the ligand backbone itself untouched – leads to the opposite configuration of the product (81.5 % *ee* (*R*) *vs*. 31.1% *ee* (*S*), entries 4 and 5).

We were interested to examine if such an effect would also be observed in case of the *t*-Bu derivative **2**. Unfortunately repeated attempts to synthesize a $P(t\text{-}Bu)_2/PPh_2$ complex failed. Obviously the $P(t\text{-}Bu)_2$ group is too bulky to be introduced at the *ortho* position and a "spacer" like the α-chain is required. In this context it is worth mentioning that the use of the ligand $P(i\text{Pr})_2/PPh_2$ in the hydrogenation of the pterine ring of folic acid leads to the opposite diastereomer in contrast to all other derivatives we tested in this reaction, which all exhibit a $P(aryl)_2/P(alkyl)_2$-substitution pattern.[9] Obviously the distribution of the aryl and alkyl side chains plays a crucial role in these very ligands. Although some "inverse" Josiphos ligands are known as well, to the best of our knowledge an effect like this has not been observed before.[10] Currently we are focusing on the synthesis of other complementary $P(alkyl)_2/P(aryl)_2$–$P(aryl)_2/P(alkyl)_2$ ligand combinations to pursue our studies on this effect.

Another striking effect is the poor enantioselectivity on changing from cyclohexyl to *t*-butyl substituents on the α-phosphorus (entriės 6–9). In THF there is almost no stereochemical discrimination present. When taking DMF as solvent instead of THF, the *ee* value rises to 40.7% and again the configuration of the product is changed from *S* to *R*.

Throughout all our investigations a high dependency on the solvent was found. It can be deduced from the hydrogen consumption curves for the conversion of prochiral olefins that the equilibrium is preferably on the side of the solvent complex;[11] this might give a hint on the crucial role the solvent plays in hydrogenations employing the type of ligands in question.

Experimental

All manipulations were carried out under nitrogen using Schlenk techniques. Solvents were dried and deoxygenated by standard procedures. Chromatography was carried out with Merck alumina 90. NMR spectra were recorded on a Varian Mercury 200 (^1H: 200 MHz, ^{13}C: 50 MHz, ^{31}P: 81 MHz) and a Varian Unity 500 (^1H: 500 MHz, ^{13}C: 125 MHz, ^{31}P: 202 MHz) at ambient temperature. IR spectra were recorded on a Perkin-Elmer FT-IR model 1720 X spectrometer. Mass spectra were obtained with a Finnigan MAT 95 spectrometer, using CI (isobutane as reactant gas) and SIMS recording techniques for the chromium and rhodium complexes respectively.

General procedure A

To a stirred solution of η^6-[(*R*)-(phenylethyl)dimethylamine]-$Cr(CO)_3$ in dry diethyl ether 1.2 equivalents of *t*-BuLi (1.7 molar solution in hexane) were added dropwise by means of a syringe pump over a period of one hour at a temperature of −80 °C. The reaction mixture was allowed to stir for another hour. Afterwards the precipitated lithiated complex was dissolved by slowly adding 20 ml of THF. The electrophile (1.2 eq., dissolved in approx. 20 ml of Et_2O) was then added with a syringe pump in one hour. After warming to ambient temperature, LiCl was filtered off and the solvent was removed *in vacuo*.

General procedure B

To a stirred solution of the chromium complex (1 eq.) in dry THF, four equivalents of 1-chloroethyl chloroformate were added at −40 °C. The solution was allowed to warm to ambient temperature by stirring overnight and then evaporated. The residue was redissolved in Et_2O, filtered and then evaporated to dryness under high vacuum.

General procedure C

To a stirred solution of the chloride-substituted chromium complex (1 eq.) in dry acetone (20 ml / mmol) was added

Table 6 Results of the hydrogenations of AMe and AH (1 mmol substrate, 0.01 mmol catalyst)

Entry	Ligand PP*	Substrate	Solvent	Conversion (%)	*ee*[a] (%)	Configuration of product
1	PPh_2/PCy_2 **3**	AMe	MeOH	80	60.7	*R*
2	PPh_2/PCy_2 **3**	AH	MeOH	100	53.7	*R*
3	PPh_2/PCy_2 **3**	AMe	THF	100	81.5	*R*
4	PPh_2/PCy_2 **3**	AH	THF	100	66.2	*R*
5	PCy_2/PPh_2 **4**	AH	THF	100	31.1	*S*
6	$PPh_2/P(t\text{-}Bu)_2$ **2**	AMe	MeOH	34	2.4	*S*
7	$PPh_2/P(t\text{-}Bu)_2$ **2**	AME	THF	98	7	*S*
8	$PPh_2/P(t\text{-}Bu)_2$ **2**	AH	THF	99.3	6.7	*S*
9	$PPh_2/P(t\text{-}Bu)_2$ **2**	AH	DMF	84.1	40.7	*R*
10	PPh_2/PPh_2 **1**	AMe	MeOH	16	5.8	*R*
11	PPh_2/PPh_2 **1**	AMe	THF	19	10.3	*R*
12	PPh_2/PPh_2 **1**	AH	DMF	5.4	23.9	*S*
13	PPh_2/PPh_2 **1**	AH	THF	26.1	29	*S*
14	(*R*)-(*S*)-Josiphos	AMe	MeOH	100	80.8	*R*

[a] Measured on the crude product, GC with a chiral column: XE 60-L-valine *t*-butylamide, 165 °C.

1 equivalent of the nucleophile. Subsequently, 1 equivalent of $TlPF_6$, dissolved in an appropriate volume of acetone, was added dropwise over a period of one hour with a syringe pump. The reaction mixture was stirred overnight at ambient temperature, quenched by adding NEt_3, filtered and finally evaporated.

General procedure D

In a Schlenk flask 1 equivalent of $[(NBD)RhCl]_2$ or $[(COD)RhCl]_2$, respectively, and 2 equivalents of $AgBF_4$ were dissolved in 10 ml THF and the solution was stirred vigorously for 30 minutes at ambient temperature. The precipitated AgCl was filtered off employing a syringe equipped with a filter needle and the clear liquid dripped into a solution of 1 equivalent of the diphosphine in 5 ml THF. After stirring for 10 minutes, the product $[(diene)Rh(PP^*)]BF_4$ was precipitated by adding Et_2O. The etheral solution was discarded and the solid dried *in vacuo*.

$[\eta^6\text{-}(R,R)\text{-}\{(NMe_2)CHMe\}C_6H_4PPh_2]Cr(CO)_3$

$[\eta^6\text{-}(R,R)\text{-}\{(NMe_2)CHMe\}C_6H_4PPh_2]Cr(CO)_3$ was prepared from $[\eta^6\text{-}(R)\text{-}\alpha\text{-}(phenylethyl)dimethylamine]Cr(CO)_3$(2.3 g, 8.07 mmol), *t*-BuLi (5.69 ml, 9.68 mmol) and chlorodiphenylphosphine (2.13 g, 9.68 mmol) according to general method A. It was purified by column chromatography on alumina [eluent: first pentane, then Et_2O]. Yield: 3.83 g (7.96 mmol, 98%). IR ($CHCl_3$): ν_{max} 1979, 1902 (CO) cm^{-1}. ^{31}P NMR (200 MHz, C_6D_6): δ = −14.66 ppm. ^1H NMR (200 MHz, C_6D_6): δ = 7.56–7.06 (m, 10H, ar-*H*(PPh_2)), 4.87 (dtr, 1H, *J* = 6.1 Hz, J_{PH} = 1.2 Hz, ar-*H*), 4.66 (tr, 1H, *J* = 6.4 Hz, ar-*H*), 4.55 (quin, 1H, *J* = 6.5 Hz, NMe_2CHMe), 4.45 (dd, 1H, *J* = 6.4 Hz, J_{PH} = 3.4 Hz, ar-*H*), 4.22 (td, 1H, *J* = 6.4 Hz, J_{PH} = 0.9 Hz, ar-*H*), 1.51 (s, 6H, NMe_2), 0.75 (d, 3H, *J* = 7.6 Hz, NMe_2CHMe) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 233.00 (*C*O), 138.68 (d, J_{CP} = 5.5 Hz, ar-*ipso*C(PPh_2)), 137.48 (d, J_{CP} = 15.3 Hz, ar-*ipso*C(PPh_2)), 135.16–128.82 (10C, ar-*C*(PPh_2)), 120.19 (d, J_{CP} = 19.7 Hz, ar-*ipso*C), 106.14 (d, J_{CP} = 25.2 Hz, ar-*ipso*C), 100.45 (d, J_{CP} = 3.8 Hz, ar-*C*), 94.10 (ar-*C*), 89.46 (ar-*C*), 87.74 (d, J_{CP} = 3.9 Hz, ar-*C*), 58.80 (d, J_{CP} = 14.3 Hz, NMe_2CHMe), 37.77 (NMe_2), 5.68 (NMe_2CHMe) ppm. Anal. Calcd. for $C_{25}H_{24}O_3PNCr$: H: 5.15, C: 63.97. Found: H: 5.27, C: 64.94%.

$[\eta^6\text{-}(R,R)\text{-}\{(NMe_2)CHMe\}C_6H_4PCy_2]Cr(CO)_3$

$[\eta^6\text{-}(R,R)\text{-}\{(NMe_2)CHMe\}C_6H_4PCy_2]Cr(CO)_3$ was prepared from $[\eta^6\text{-}(R)\text{-}\alpha\text{-}(phenylethyl)dimethylamine]Cr(CO)_3$ (2.5 g, 8.77 mmol), *t*-BuLi (6.19 ml, 10.53 mmol) and chlorodicyclohexylphosphine (2.45 g, 10.53 mmol) according to general method A. It was purified by column chromatography on alumina [eluent: first pentane, then Et_2O]. Yield: 4.07 g (8.46 mmol, 96%). IR ($CHCl_3$): ν_{max} 1968, 1894 (CO) cm^{-1}. ^{31}P NMR (200 MHz, C_6D_6): δ = −6.60 ppm.^1H NMR (500 MHz, C_6D_6): δ = 5.04 (dd, 1H, *J* = 6.1 Hz, J_{HP} = 0.9 Hz, ar-*H*), 4.77 (tr, 1H, *J* = 6.5 Hz, ar-*H*), 4.53 (mbr, 2H, ar-*H* and NMe_2CHMe), 4.36 (tr, 1H, *J* = 7.0 Hz, ar-*H*), 1.93 (s, 6H, NMe_2CHMe), 1.79–1.56 (mbr, 11H, *Cy*), 1.38–1.01 (mbr, 11H, *Cy*), 0.83 (d, 3H, *J* = 7.1 Hz, NMe_2CHMe) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 233.34 (*C*O), 117.95 (d, J_{CP} = 20.0 Hz, ar-*ipso*C), 108.59 (d, J_{CP} = 38.3 Hz, ar-*ipso*C), 97.03 (d, J_{CP} = 3.9 Hz, ar-C), 93.66, 89.89, 89.31 (ar-*C*), 57.98 (d, J_{CP} = 18.9 Hz, NMe_2CHMe), 38.86 (NMe_2CHMe), 38.46 (d, J_{CP} = 16.7 Hz, *ipso*CCy), 33.78 (d, J_{CP} = 22.8 Hz, *ipso*CCy), 33.11–26.77 (10C, *Cy*), 5.82 (d, J_{CP} = 5.0 Hz, NMe_2CHMe) ppm. Anal. Calcd. for $C_{25}H_{36}O_3PNCr$: H: 7.54, C: 62.36. Found: H: 7.69, C: 61.59%.

$[\eta^6\text{-}(R,R)\text{-}\{(Cl)CHMe\}C_6H_4PPh_2]Cr(CO)_3$

$[\eta^6\text{-}(R,R)\text{-}\{(Cl)CHMe\}C_6H_4PPh_2]Cr(CO)_3$ was prepared from $[\eta^6\text{-}(R,R)\text{-}\{(NMe_2)CHMe\}C_6H_4PPh_2]Cr(CO)_3$ (8.18 g, 17.42 mmol) and 1-chloroethyl chloroformate (9.97 g, 69.70 mmol) according to general method B. By repeated recrystallization from dichloromethane/pentane the pure product was obtained. Yield: 7.22 (15.68 mmol, 90%). IR ($CHCl_3$): ν_{max} 1970, 1902 (CO) cm^{-1}.^{31}P NMR (200 MHz, C_6D_6) δ = −20.58 ppm. ^1H NMR (500 MHz, C_6D_6) δ = 7.51 (brtr, 2H, ar-*H*(PPh_2)), 7.32 (m, 2H, ar-*H*(PPh_2)), 7.15–7.03 (m, 6H, ar-*H*(PPh_2)), 5.94 (dq, 1H, *J* = 9.5 Hz, *J* = 6.5 Hz, ClC*H*Me), 4.66 (d, 1H, *J* = 6.5 Hz, ar-*H*), 4.62 (dd, 1H, *J* = 3 Hz, *J* = 6.5 Hz, ar-*H*), 4.51 (tr, 1H, *J* = 6.4 Hz, ar-*H*), 4.22 (tr, 1H, *J* = 6.5 Hz, ar-*H*), 1.43 (d, 3H, *J* = 6.5 Hz, ClCH*Me*) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 232.23 (CO), 135.98 (d, $^1J_{CP}$ = 8 Hz, ar-*ipso*C(PPh_2)), 134.95 (d, $^1J_{CP}$ = 12.5 Hz, ar-*ipso*C(PPh_2)), 135.03–128.73 (10C, ar-*C*(PPh_2), 117.35 (d, $^1J_{CP}$ = 22 Hz, ar-*ipso*C), 103.92 (d, $^1J_{CP}$ = 25 Hz, ar-*ipso*C), 97.72 (d, J_{CP} = 2.5 Hz, ar-*C*), 93.87, 90.85 (ar-*C*), 87.99 (d, J_{CP} = 3 Hz, ar-*C*), 54.50 (d, $^4J_{CP}$ = 29 Hz, Cl*C*HMe), 23.00 (ClCH*Me*) ppm. Anal. Calcd. for $C_{23}H_{18}O_3PClCr$: H: 3.94, C: 59.95. Found: H: 4.05, C: 60.16%.

$[\eta^6\text{-}(R,R)\text{-}\{(Cl)CHMe\}C_6H_4PCy_2]Cr(CO)_3$

$[\eta^6\text{-}(R,R)\text{-}\{(Cl)CHMe\}C_6H_4PCy_2]Cr(CO)_3$ was prepared from $[\eta^6\text{-}(R,R)\text{-}\{(NMe_2)CHMe\}C_6H_4Cy_2]Cr(CO)_3$ (3.60 g, 7.48 mmol) and 1-chloroethyl chloroformate (4.28 g, 29.92 mmol) according to general method B. No further purification was necessary. Yield: 3.10 (6.56 mmol, 87%). IR ($CHCl_3$): ν_{max} 1972, 1899 (CO) cm^{-1}. ^{31}P NMR (200 MHz, $CDCl_3$): δ = −12.92 ppm. ^1H NMR (200 MHz, $CDCl_3$): δ = 5.75 (dd, 1H, *J* = 9.8 Hz, *J* = 7.1 Hz, ClC*H*Me), 5.50 (m, ar-*H*), 5.47 (m, ar-*H*), 5.42 (m, ar-*H*), 5.31 (m, ar-*H*), 1.88–1.64 (mbr, 14H, *Cy* and ClCH*Me*), 1.44–1.15 (mbr, 11H, *Cy*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 231.89 (*C*O), 116.13 (d, J_{CP} = 20.6 Hz, ar-*ipso*C), 105.91 (d, J_{CP} = 35.7 Hz, ar-*ipso*C), 95.73 (ar-*C*), 93.42 (ar-*C*), 90.81 (ar-*C*), 89.05 (d, *J* = 2.8 Hz, ar-*C*), 54.46 (d, J_{CP} = 31.1 Hz, Cl*C*HMe), 36.62 (d, J_{CP} = 10.7 Hz, *Cy*), 34.65 (d, J_{CP} = 16.5 Hz, *Cy*), 32.19–24.20 (11C, *Cy* and ClCH*Me*) ppm.

[η⁶-(*R,R*)-{(PPh$_2$)CHMe}C$_6$H$_4$PPh$_2$]Cr(CO)$_3$ 1

1 was prepared from [η⁶-(*R,R*)-{ClCHMe}C$_6$H$_4$PPh$_2$]Cr(CO)$_3$ (0.94 g, 2.04 mmol), diphenylphosphine (0.379 g, 2.04 mmol) and TlPF$_6$ (0.676 g, 1.94 mmol) according to general method C. Yield: 1.02 g (1.67 mmol, 83%). IR ($CHCl_3$): ν_{max} 1969, 1900 (CO) cm^{-1}. ^{31}P NMR (200 MHz, $CDCl_3$): δ = 7.88 (d, J_{PP} = 20.1 Hz, α-P), −19,99 (d, J_{PP} = 20.1 Hz, *ortho*-P) ppm. ^{1}H NMR (500 MHz, C_6D_6): δ = 7.67 (trm, *ortho*- or α-ar-*H*(PPh$_2$)), 7.43 (trm, *ortho*- or α-ar-*H*(PPh$_2$)), 7.24–6.95 (m, *ortho*- or α-ar-*H*PPh$_2$)), 5.03–4.96 (m, 2H, ar-*H* and PPh$_2$C*H*Me), 4.50 (tr, 1H, *J* = 6.5 Hz, ar-*H*), 4.22 (trd, 1H, *J* = 6.5 Hz, *J* = 0.9 Hz, ar-*H*), 4.11 (ddtr, 1H, *J* = 6.5, J_{HP} = 3.5 Hz, *J* = 0.5 Hz ar-*H*), 1.28 (dd, 3H, *J* = 6.5 Hz, J_{HP} = 4.5 Hz, PPh$_2$CH*Me*) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 232.84 (*C*O), 136.80 (d, J_{CP} = 19 Hz, *ortho*- or α-ar-*ipso*C(PPh$_2$)), 136.30–128.29 (*ortho*- and α-ar-C(PPh$_2$)), 123.34 (dd, J_{CP} = 22 Hz, J_{CP} = 22 Hz, ar-*ipso*C), 103.89 (dd, J_{CP} = 19.2 Hz, J_{CP} = 3.5 Hz, ar-*ipso*C), 99.31, 94.11, 89.70 (ar-*C*), 88.75 (dd, J_{CP} = 4 Hz, J_{CP} = 4 Hz, ar-*C*), 33.78 (dd, J_{CP} = 24.5 Hz, J_{CP} = 24.5 Hz, PPh$_2$*C*HMe), 15.02 (PPh$_2$CH*Me*) ppm. Anal. Calcd. for $C_{35}H_{28}O_3P_2Cr$: H: 4.62, C: 68.85. Found: H: 4.69, C: 68.12%.

[η⁶-(*R,R*)-{(P*t*-Bu$_2$)CHMe}C$_6$H$_4$PPh$_2$]Cr(CO)$_3$ 2

2 was prepared from [η⁶-(*R,R*)-{ClCHMe}C$_6$H$_4$PPh$_2$]Cr(CO)$_3$ (1.04 g, 2.26 mmol), di-*tert*-butylphosphine (0.330 g, 2.26 mmol) and TlPF$_6$ (0.788 g, 2.26 mmol) according to general method C. It was purified by column chromatography on alumina [eluent: first pentane, then Et$_2$O]. Yield: 1.01 g (1.77 mmol, 78%). IR ($CHCl_3$): ν_{max} 1983, 1924 (CO) cm^{-1}. ^{31}P NMR (200 MHz, $CDCl_3$): δ = 48.79 (d, J_{PP} = 69.2 Hz, α-P), −21.80 (d, J_{PP} = 67.8 Hz, *ortho*-P) ppm. ^{1}H NMR (500 MHz, C_6D_6): δ = 7.63 (trm, 2H, ar-*H*(PPh$_2$)), 7.37 (trm, 2H, ar-*H*(PPh$_2$)), 7.15 (m, 6H, ar-*H*(PPh$_2$)), 5.16 (trd, 1H, *J* = 6 Hz, *J* = 1 Hz, ar-*H*), 4.71 (tr, 1H, *J* = 6.5 Hz, ar-*H*), 4.55 (dd, 1H, *J* = 6.5 Hz, J_{HP} = 3.5 Hz, ar-*H*), 4.47 (dqd, 1H, *J* = 7 Hz, J_{HP} = 7 Hz, J_{HP} = 1Hz, P*t*-Bu$_2$C*H*Me), 4.23 (trd, 1H, *J* = 6 Hz, *J* = 1 Hz, ar-*H*), 1.51 (dd, 3H, *J* = 7 Hz, J_{HP} = 2.5 Hz, P*t*-Bu$_2$–CH*Me*), 1.21 (d, 9H, J_{HP} = 10.5 Hz, C*Me*$_3$), 0.86 (d, 9H, J_{HP} = 11 Hz, C*Me*$_3$) ppm. ^{13}C NMR (125 MHz, C_6D_6), δ = 233.00 (*C*O), 139.57 (dd, J_{CP} = 5 Hz, J_{CP} = 4.5 Hz, ar-*ipso*C(PPh$_2$)), 138.36 (dd, J_{CP} = 15.5 Hz, J_{CP} = 9 Hz, ar-*ipso*C(PPh$_2$)), 135.59–128.19 (10C, ar-*C*(PPh$_2$)), 127.09 (dd, J_{CP} = 22 Hz, J_{CP} =20 Hz, ar-*ipso*C), 103.57 (dd, J_{CP} = 25 Hz, J_{CP} = 3.5 Hz, ar-*ipso*C), 101.69 (d, J_{CP} = 2.7 Hz, ar-*C*), 94.69 (ar-*C*), 89.15 (d, J_{CP} = 2 Hz, ar-*C*), 88.68 (dd, J_{CP} = 3.5 Hz, J_{CP} = 2.5 Hz, ar-*C*), 35.21 (dd, J_{CP} = 38 Hz, J_{CP} = 15.5 Hz, P*t*-Bu$_2$*C*HMe), 35.09 (dd, J_{CP} = 35.5 Hz, J_{CP} = 3.5 Hz, *C*Me$_3$), 34.56 (d, J_{CP} = 32 Hz, *C*Me$_3$), 32.16 (d, J_{CP} = 14 Hz, C*Me*$_3$), 31.57 (dd, J_{CP} = 13 Hz, J_{CP} = 4 Hz, C*Me*$_3$), 15.09 (P*t*-Bu$_2$CH*Me*)) ppm. Anal. Calcd. for $C_{31}H_{36}O_3P_2Cr$: H: 6.36, C: 65.26. Found: H: 6.51, C: 64.59%.

[η⁶-(*R,R*)-{(PCy$_2$)CHMe}C$_6$H$_4$PPh$_2$]Cr(CO)$_3$ 3

3 was prepared from [η⁶-(*R,R*)-{ClCHMe}C$_6$H$_4$PPh$_2$]Cr(CO)$_3$ (1.04 g, 2.26 mmol), dicyclohexylphosphine (0.448 g, 2.26 mmol) and TlPF$_6$ (0.788 g, 2.26 mmol) according to general method C. It was purified by column chromatography on alumina [eluent: first pentane, then Et$_2$O]. Yield: 1.25 g (2.01 mmol, 89%). IR ($CHCl_3$): ν_{max} 1975, 1905 (CO) cm^{-1}. ^{31}P NMR (200 MHz, $CDCl_3$): δ = 15.12 (d, J_{PP} = 45.8 Hz, α-P), −21.21 (d, J_{PP} = 45.8 Hz, *ortho*-P) ppm. ^{1}H NMR (500 MHz, C_6D_6): δ = 7.64 (brtr, 2H, ar-*H*(PPh$_2$)), 7.39 (tr, 2H, *J* = 7.5 Hz, ar-*H*(PPh$_2$)), 7.13–7.04 (m, 6H, ar-*H*(PPh$_2$)), 5.08 (d, 1H, *J* = 6.5 Hz, ar-*H*), 4.72 (tr, 1H, *J* = 6.5 Hz, ar-*H*), 4.58 (dd, 1H, *J* = 6 Hz, J_{HP} = 3.5 Hz, ar-*H*), 4.31 (trd, 1H, *J* = 7.5 Hz, J_{HP} = 7.5 Hz, PCyC*H*Me), 4.21 (tr, 1H, *J* = 6.5 Hz, ar-*H*), 1.82–1.40 (m, 11H, *Cy*$_2$), 1.33 (dd, 3H, *J* =7 Hz, J_{CP} = 3.5 Hz, PCy$_2$-CH*Me*), 1.19–1.00 (m, 11H, P*Cy*$_2$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 232.93 (*C*O), 138.66 (dd, J_{CP} = 6.5 Hz, J_{CP} = 3 Hz, ar-*ipso*C(PPh$_2$)), 137.88 (dd, J_{CP} = 14.5 Hz, J_{CP} = 4.5 Hz, ar-*ipso*C(PPh$_2$)), 135.45–127.91 (10C, ar-*C*(PPh$_2$)), 126.50 (dd, J_{CP} = 22.5 Hz, J_{CP} = 19 Hz, ar-*ipso*C), 103.32 (dd, J_{CP} = 24 Hz, J_{CP} = 3 Hz, ar-*ipso*C), 100.89, 94.73, 89.12 (ar-*C*), 87.69 (d, J_{CP} = 3.5 Hz, ar-*C*), 33.81 (d, J_{CP} = 23.5 Hz, *Cy*), 33.50 (d, $^1J_{CP}$ =21.5 Hz, *Cy*), 32.19 (d, J_{CP} = 26.5 Hz, J_{CP} = 21 Hz, PCy$_2$-*C*HMe), 31.54 (d, J_{CP} = 19 Hz, *Cy*), 31.68 (dd, $^1J_{CP}$ = 25 Hz, J_{CP} = 2 Hz, *Cy*), 30.36 (d, J_{CP} = 7.5 Hz, *Cy*), 26.99 (d, J_{CP} = 11.5 Hz, *Cy*), 26.64 (2C, *Cy*), 14.37 (PCy$_2$CH*Me*) ppm. Anal. Calcd. for $C_{31}H_{36}O_3P_2Cr$: H: 6.48, C: 67.52. Found: H: 6.53, C: 67.40%.

[η⁶-(*R,R*)-{(PPh$_2$)CHMe}C$_6$H$_4$PCy$_2$]Cr(CO)$_3$ 4

4 was prepared from [η⁶-(*R,R*)-{ClCHMe}C$_6$H$_4$PCy$_2$]Cr(CO)$_3$ (3.10 g, 6.56 mmol), diphenylphosphine (1.220 g, 6.56 mmol) and TlPF$_6$ (2.289 g, 6.56 mmol) according to general method C. It was purified by column chromatography on alumina [eluent: first pentane, then Et$_2$O–pentane: 2 : 1]. Yield: 1.39 g (2.23 mmol, 34%). IR ($CDCl_3$): ν_{max} 1965, 1892 (CO) cm^{-1}. ^{31}P NMR (200 MHz, $CDCl_3$): δ = 8.35 (d, J_{PP} = 25.6 Hz, α-P), −14.35 (d, J_{PP} = 23.8 Hz, *ortho*-P) ppm. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.45–7.27 (m, 10H, ar-*H*(PPh$_2$)), 5.56 (d, *J* = 6.3 Hz, 1H, ar-*H*), 5.21 (m, 2H, ar-*H*), 4.48 (m, 1H, PPh$_2$C*H*Me), 4.34 (d, *J* = 3.4 Hz, 1H, ar-*H*), 1.96–1.16 (m, 22H, P*Cy*$_2$), 0.86 (t, *J* = 6.4 Hz, 3H, PPh$_2$CH*Me*) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 233.36 (*C*O), 137.67 (d, J_{CP} = 19.2 Hz, ar-*ipso*C(PPh$_2$)), 136.55 (d, J_{CP} = 23 Hz, ar-*C*), 133.51 (d, J_{CP} = 5.3 Hz, ar-*ipso*C(PPh$_2$)), 122.46 (d, J_{CP} = 21.1 Hz, ar-*ipso*C), 107.56 (d, J_{CP} = 36.5 Hz, ar-*ipso*C), 131.56 (d, J_{CP} = 15.3 Hz, ar-*C*), 130.20 (ar-*C*), 128.68 (d, J_{CP} = 3.9 Hz, ar-*C*), 128.33 (d, J_{CP} = 7.7 Hz, ar-*C*), 127.87 (d, J_{CP} = 5.0 Hz, ar-*C*), 98.03 (ar-*C*), 89.93 (ar-*C*), 77.53 (ar-*C*), 37.14 (d, J_{CP} = 17.3 Hz, *ipso*C*Cy*), 36.28 (dd, J_{CP} = 14.4 Hz, J_{CP} = 5.7 Hz, *ipso*C*Cy*), 33.31 (PPh$_2$*C*HMe), 33.13–26.50 (10C, C*Cy*), 16.06 PPh$_2$CH*Me*) ppm. Anal. Calcd. for $C_{31}H_{36}O_3P_2Cr$: H: 6.48, C: 67.52. Found: H: 6.55, C: 67.32%.

[(NBD)Rh(PPh$_2$/PPh$_2$)]BF$_4$ 5

5 was prepared from [η⁶-(*R,R*)-{(PPh$_2$)CHMe}C$_6$H$_4$PPh$_2$]-Cr(CO)$_3$**1** (0.105 g, 0.171 mmol), [(NBD)RhCl]$_2$ (0.040 g, 0.086 mmol) and $AgBF_4$ (0.033 g, 0.171 mmol) according to general method D. Yield: 0.138 g (0.155 mmol, 90%). ^{31}P NMR (200 MHz, $CDCl_3$): δ = 54.42 (dd, J_{PP} = 43.9 Hz, J_{PRh} = 159.3 Hz, α-P), 27.56 (dd, J_{PP} = 44.6 Hz, J_{PRh} = 154.7 Hz, *ortho*-P) ppm. MS (SIMS): *m*/*z* (rel. int.) = 86.9 (100) $[BF_4]^-$, 804.7 (5.5) $[(NBD)Rh(PPh_2/PPh_2)]^+$.

[(NBD)Rh(PPh$_2$/P*t*-Bu$_2$)]BF$_4$ 6

6 was prepared from [η⁶-(*R,R*)-{(P*t*-Bu$_2$)CHMe}C$_6$H$_4$PPh$_2$]-Cr(CO)$_3$ **2** (0.109 g, 0.191 mmol), [(NBD)RhCl]$_2$ (0.044 g, 0.096 mmol) and $AgBF_4$ (0.037 g, 0.191 mmol) according to general method D. Yield: 0.155 g (0.182 mmol, 95%). ^{31}P NMR (200 MHz, $CDCl_3$): δ = 72.74 (dd, J_{PP} = 34.8 Hz, J_{PRh} = 150.2 Hz, α-P), 26.81 (dd, J_{PP} = 34.8 Hz, J_{PRh} = 159.3 Hz, *ortho*-P) ppm. MS (SIMS): *m*/*z* (rel. int.) = 86.9 (100) $[BF_4]^-$, 764.8 (4.6) $[(NBD)Rh(PPh_2/Pt\text{-}Bu_2)]^+$.

[(NBD)Rh(PPh$_2$/PCy$_2$)]BF$_4$ 7

7 was prepared from [η⁶-(*R,R*)-{(PCy$_2$)CHMe}C$_6$H$_4$PPh$_2$]-Cr(CO)$_3$ **3** (0.106 g, 0.170 mmol), [(NBD)RhCl]$_2$ (0.039 g, 0.085 mmol) and $AgBF_4$ (0.033 g, 0.170 mmol) according to general method D. Yield: 0.121 g (0.134 mmol, 79%). ^{31}P NMR (200 MHz, $CDCl_3$): δ = 51.30 (dd, J_{PP} = 40.3 Hz, J_{PRh} = 153.8 Hz, α-P), 27.87 (dd, J_{PP} = 40.3 Hz, J_{PRh} = 157.5 Hz, *ortho*-P) ppm. MS (SIMS): *m*/*z* (rel. int.) = 86.9 (100) $[BF_4]^-$, 816.9 (100) $[(NBD)Rh(PPh_2/PCy_2)]^+$.

Table 7 Experimental X-ray diffraction parameters and crystal data

	$[(NBD)Rh(PPh_2/PCy_2)]BF_4 \cdot CH_3OH$	$[(NBD)Rh(PCy_2/PPh_2)]BF_4$
Empirical formula	$C_{43}H_{52}BCrF_4O_4P_2Rh$	$C_{42}H_{48}BCrF_4O_3P_2Rh$
Formula weight	936.51	904.46
Crystal size/mm	0.5 × 0.3 × 0.2	0.4 × 0.3 × 0.3
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12$
a/Å	12.214(2)	19.748(4)
b/Å	16.428(3)	21.086(4)
c/Å	21.749(4)	9.499(2)
V/Å^3	4364.0(15)	3955.4(14)
D_{calc}/Mg m^{-3}	1.425	1.519
Z	4	4
μ(Mo-Kα)/mm^{-1}	0.757	0.831
F(000)	1928	1856
T/K	200	200
Reflections collected	16101	16923
Independent reflections	4472	4893
Observed reflections	3690	4093
Refined parameters	505	487
$R1$ ($2\sigma(I)$)	0.0347	0.0345
$R1$ (all data)	0.0468	0.0445
$wR2$ (all data)	0.0639	0.0660
Goodness of fit	0.940	0.911
Largest difference peak and hole/e Å^3)	0.411/–0.365	0.483/–0.488

$[(NBD)Rh(PCy_2/PPh_2)]BF_4$ 8

8 was prepared from $[\eta^6$-(R,R)-$\{(PPh_2)CHMe\}C_6H_4PCy_2]$-$Cr(CO)_3$ **4** (0.250 g, 0.410 mmol), $[(NBD)RhCl]_2$ (0.092 g, 0.200 mmol) and $AgBF_4$ (0.078 g, 0.410 mmol) according to general method D. Yield: 0.210 g (0.230 mmol, 58%). ^{31}P NMR (200 MHz, $CDCl_3$): δ = 56.32 (dd, J_{PP} = 41.1 Hz, J_{PRh} = 162.1 Hz, α-P), 26.15 (dd, J_{PP} = 39.4 Hz, J_{PRh} = 147.4 Hz, *ortho*-P) ppm. MS (SIMS): m/z (rel. int.) = 86.9 (100) $[BF_4]^-$, 817.8 (7.4) $[(NBD)Rh(PCy_2/PPh_2)]^+$.

$[(COD)Rh(PPh_2/PCy_2)]BF_4$ 9

9 was prepared from $[\eta^6$-(R,R)-$\{(PCy_2)CHMe\}C_6H_4PPh_2]$-$Cr(CO)_3$ **3** (0.266 g, 0.428 mmol), $[(COD)RhCl]_2$ (0.105 g, 0.214 mmol) and $AgBF_4$ (0.083 g, 0.428 mmol) according to general method D. Yield: 0.276 g (0.300 mmol, 70%). ^{31}P NMR (200 MHz, $CDCl_3$): δ = 49.32 (dd, J_{PP} = 33.9 Hz, J_{PRh} = 150.2 Hz, α-P), 24.16 (dd, J_{PP} = 34.8 Hz, J_{PRh} = 148.3 Hz, *ortho*-P) ppm.

Hydrogenation reactions (typical procedure)

In a reaction vessel are placed 1 mmol of substrate and 0.01 mmol of catalyst. It is connected to the main apparatus, equipped with an automatic gas-measuring device, and purged of oxygen by applying high vacuum and argon consecutively five times. The whole apparatus is thermostated to 25 °C. 15 ml of solvent are added *via* a burette and the reaction mixture is set under hydrogen by quickly applying vacuum and hydrogen consecutively three times. It is compensated for ambient pressure and the measurement is started.

X-Ray structure determinations on 7 and 8

Diffraction data were collected on a STOE-IPDS diffractometer at −73 °C using graphite monochromated Mo-Kα radiation. The structures were solved by direct methods (SHELXS-97)[12] and refined by full matrix least squares techniques against F^2 (SHELXL-97).[13] A internal STOE-IPDS program (DECAY) was used for the absorption correction. No transmission coefficients are specified. The intensities are corrected according to a diagram which represents the mean reflection intensity of an image as a function of the exposure number. For each image a factor is calculated. XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in theoretical positions and were refined using a riding model.

Selected crystal data and details of the structure solutions are summarised in Table 7. Single crystals of complexes $[(NBD)Rh(PPh_2/PCy_2)]BF_4$ **7** and $[(NBD)Rh(PCy_2/PPh_2)]BF_4$ **8** suitable for X-ray diffraction studies were obtained by recrystallization from methanol, mounted in inert oil and transferred to the cold gas stream of the diffractometer.

CCDC reference numbers 195664 (**7**) and 195665 (**8**).

See http://www.rsc.org/suppdata/dt/b2/b212095j/ for crystallographic data in CIF or other electronic format.

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