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New Efficient Methods for the Synthesis and *In-Situ* Preparation of Ruthenium(II) Complexes of Atropisomeric Diphosphines and Their Application in Asymmetric Catalytic Hydrogenations

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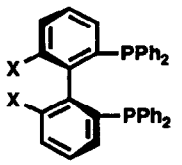
Abstract: A new synthetically useful method for the synthesis of the diphosphine ruthenium dicarboxylato complexes (P–P)Ru(O_2CR)$_2$ (R = CF_3 and CH_3) is presented, which uses the easily accessible complex (COD)$_2$Ru$_2$(μ-O_2CCF_3)$_4$ as starting material. This complex as well as (COD)Ru(η^2-O_2CCH_3)$_2$ and (COD)$_2$Ru$_2$Cl$_4$($NCCH_3$) have been shown to be suitable precursor complexes for the *in-situ* preparation of ruthenium(II) dicarboxylato and dichloro complexes of atropisomeric diphosphines, respectively. The high efficacy of the preformed and *in-situ* generated ruthenium complexes as precatalysts is demonstrated in asymmetric hydrogenations of allylic alcohols, enamides, and a β-keto ester.

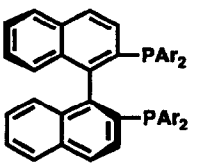
Ruthenium(II) dicarboxylato complexes derived from atropisomeric diphosphines such as BINAP have found wide application as precatalysts in asymmetric hydrogenations of a variety of substrates such as allylic alcohols, β-keto esters, α,β-unsaturated carboxylic acids, and enamides.[1]

Although a detailed procedure for the preparation of the ruthenium dicarboxylato complexes (BINAP)Ru(O_2CR)$_2$ (R = CH_3, Bu^t) has been reported,[2] we found the preparation of pure samples of these complexes to be troublesome following the pathway via the chloro-bridged dimeric complex (P-P)$_2$Ru$_2$Cl$_4$(NEt_3).[3] Furthermore, treatment of the diacetato complex with trifluoroacetic acid proved to be an unsatisfactory method for the synthesis of the corresponding bis(trifluoroacetato) complex both in respect to purity and handling of the isolated material. Similar unsatisfactory results have been obtained with the parent 6,6'-dimethyl- and 6,6'-dimethoxy-substituted atropisomeric diphosphines in the biphenyl series, BIPHEMP [4] and MeO-BIPHEP,[5] respectively.

In order to overcome these preparative difficulties, we have focused our efforts on the development of new and practical high-yield routes to dicarboxylato ruthenium complexes of atropisomeric diphosphines. The

starting point of our investigations was the previously reported dinuclear complex $(COD)_2Ru_2(O_2CCF_3)_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-}OH_2)$,[6a] which was shown by Singleton et al. to react with phosphines with substitution of the COD ligands to give mono or dinuclear ruthenium complexes.[6a] Since the dimeric core remained intact even with the basic monophosphine PMe_2Ph,[6b] we hoped the dimer would react analogously with the less basic atropisomeric bis(triaryl)phosphines.





a X = Me **BIPHEMP** **c** Ar = Ph **BINAP**

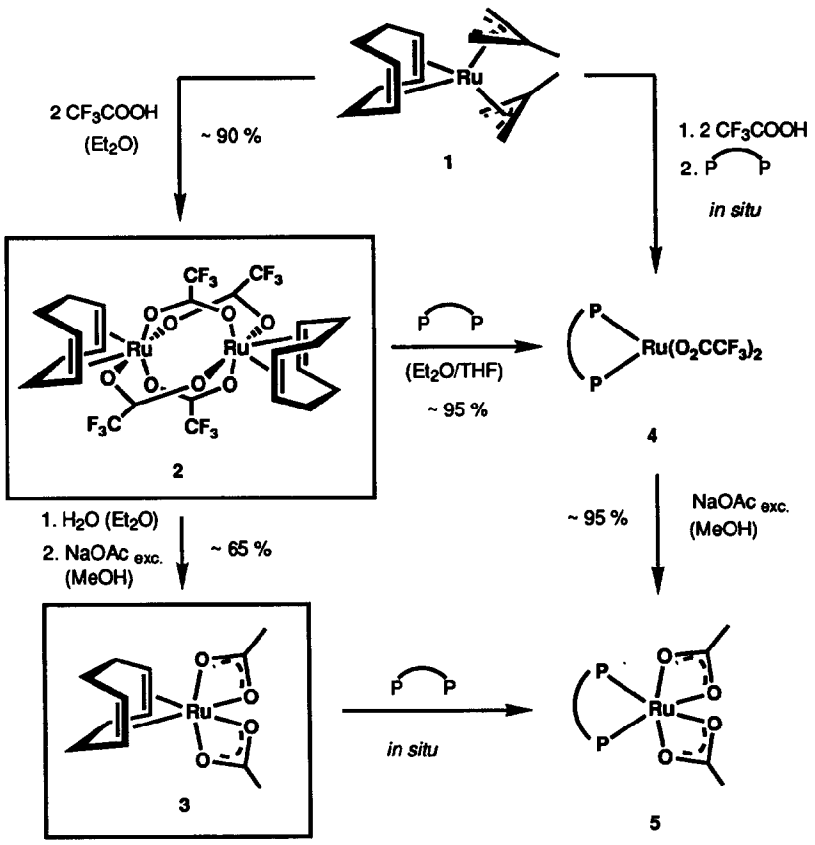
b X = OMe **MeO-BIPHEP** **d** Ar = p-Tol **p-Tol-BINAP**

((*S*)-diphosphines depicted)

Surprisingly, when trying to prepare the Singleton complex by reaction of $(COD)Ru(\eta^3\text{-methallyl})_2$ (**1**) with trifluoroacetic acid,[6a] we obtained the H_2O-free complex $(COD)_2Ru_2(\mu\text{-}O_2CCF_3)_4$ (**2**) in 90 % yield (see Scheme). The dimeric structure of complex **2** has been deduced from ^1H- and ^{13}C-NMR data (see Experimental) by comparison with those of $(COD)Ru(\eta^2\text{-}O_2CCH_3)_2$ (**3**), which has been obtained in moderate yield (65 %) upon sequential reaction of **2** with H_2O, and then an excess of sodium acetate in methanol (Scheme). In contrast to **3**, the bis(trifluoroacetato) complex **2** proved to be extremely sensitive towards H_2O: upon addition of 1 drop of H_2O to a $CDCl_3$ solution of **2**, the signals of **2** were replaced by those assignable to the H_2O-bridged dimeric complex.[7]

In all cases studied so far, the COD ligands in **2** were readily displaced in Et_2O/THF at 40 °C by atropisomeric diphosphines to afford the corresponding *pure* bis(trifluoroacetato) complexes $(P\text{–}P)Ru(O_2CCF_3)_2$ (**4a - d**) in high yield (see Scheme). In principle, ^1H- and ^{31}P-NMR cannot distinguish between mono- or dinuclear structures for **4a - d**. The interpretation of the ^1H- and ^{31}P-NMR spectra of **4a - d** is compounded by the extreme sensitivity of these complexes even towards traces of H_2O in $CDCl_3$. Depending upon the concentration of these complexes in $CDCl_3$, a varying amount of H_2O-containing species could always be detected. Moreover, the ^1H- and ^{31}P-NMR spectra are complicated by the fact that, except for **4a**, at least *two* H_2O-complexes are formed as indicated by the characteristic resonances of the H_2O-protons between δ 11.3 - 12.4 ppm and the observed AB-systems of the phosphorus atoms. Characteristic NMR data of the isolated complexes **4a - d** are listed in Table 1.

Scheme



The presumed structure of the major and in the case of **4a** sole H_2O-containing dimeric complex (cf.[6b]) is shown below.

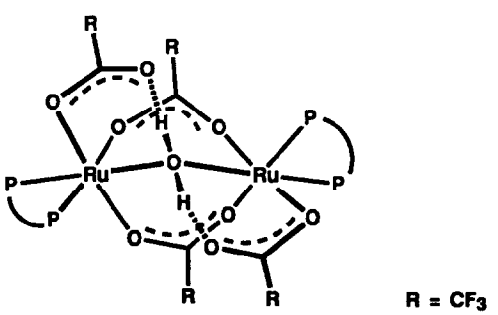


Table 1. Selected ^1H- and ^{31}P-NMR Data of Complexes (*S*)-**4a-d** in $CDCl_3$

Complex	^1H (250 MHz) [a]		^{31}P (101.26 MHz) [a]
	δ (H_2O)	δ (6,6'-substituents)	δ (P)
(*S*)-**4a** [b]		1.22 (*s*, 2 aromat. CH_3) [c]	59.1 (*s*) [c]
	11.31 (*s*) [d]	1.35 and 1.06 [d]	55.2 (*d*, J = 49.0) and 49.8 (*d*, J = 49.0) [d]
		(2 *s*, 2 aromat. CH_3)	
(*S*)-**4b**	11.34 (*s*) [d]	3.45 and 3.40 [d]	54.4 (*s*) [d]
		(2 *s*, 2 aromat. OCH_3)	
	12.14 (*s*)	[f]	62.2 (*d*, J = 49.4) and 53.2 (*d*, J =49.4)
(*S*)-**4c**			60.4 (*s*) [c]
	11.43 [d]		54.4 (*d*, J = 47.4) and 51.4 (*d*, J = 47.4) [d]
	12.37		64.0 (*d*, J = 48.0) and 54.3 (*d*, J = 48.0)
(*S*)-**4d** [e]	11.42 [d]		71.9 (*d*, J = 49.5) and 20.4 (*d*, J = 49.5) [d]
	12.21		52.8 (*d*, J = 47.4) and 51.1 (*d*, J = 47.4)
			62.5 (*d*, J = 48.0) and 53.0 (*d*, J = 48.0)

[a] δ in ppm, coupling constants J in Hz; resonances of aromatic H have been omitted for the sake of simplicity. [b] ^1H (270 MHz), ^{31}P (162.0 MHz). [c] Assigned to (P–P)$Ru(O_2CCF_3)_2$. [d] Assigned to major isomer (P–P)$_2Ru(\mu\text{-}O_2CCF_3)_2(O_2CCF_3)_2(\mu\text{-}H_2O)$. [e] The CH_3 protons of the p-tolyl substituents give rise to several singlets at δ ~ 1.7 - ~ 2.5. [f] Protons cannot be unequivocally assigned due to the low intensity of the corresponding signals.

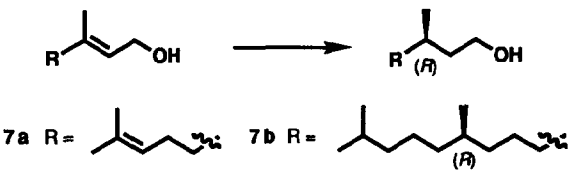
Interestingly, when 1 drop of CD_3OD was added to the $CDCl_3$ solutions of complexes **4a - d**, the resonances corresponding to the H_2O-containing species disappear, and only *one* singlet is observed in the ^{31}P-NMR spectra (see Experimental), thus indicating the equivalence of both phosphorus atoms in the diphosphine ligand. This is also reflected in the ^1H-NMR spectra where the protons of the 6,6'-dimethyl- and 6,6'-dimethoxy- substituents of **4a** and **4b** appear as a singlet, and those of the para-methyl groups of **4d** as two singlets in accordance with the formation of C_2-symmetrical complexes, presumably (P–P)$_2Ru_2(\mu\text{-}O_2CCF_3)_4$, (P–P)$Ru(\eta^2\text{-}O_2CCF_3)_2$, or (P–P)$Ru(\eta^1\text{-}O_2CCF_3)_2(CD_3OD)_2$.

Complexes **4a - d** could be cleanly converted in excellent yield into the corresponding diacetato complexes **5a - d** upon treatment with an excess of sodium acetate in methanol (40 °C, 2 h) (cf.[8a]); after extraction of the complexes into CH_2Cl_2 no further purification steps were necessary to obtain pure samples of **5a - d**.

Thus a convenient access to the dicarboxylato complexes of type **4** and **5** has been developed. The mild reaction conditions, the virtually quantitative yields, and the high purity of the products of this new route seemed ideally suited for the *in-situ* preparation of the dicarboxylato ruthenium complexes. To date, to the best

of our knowledge, such an *in-situ* method is lacking, whereas in rhodium catalyzed asymmetric reactions this methodology is well-established, because of the availability of suitable precursor complexes such as $[(COD)_2Rh]X$ (X = noncoordinating anion) and $[(COD)RhX]_2$ (X = halogen or O_2CCF_3 [9a]) and their smooth and quantitative reaction with diphosphines. The trifluoroacetato-bridged rhodium dimer can be considered to be the rhodium(I) analogue of our ruthenium(II) complex **2** and has been successfully used in the asymmetric hydrogenation of ketopantoyl lactone where it proved to be superior to the corresponding chloro-bridged dimer in the presence of BPPM type ligands.[9b] In order to simplify the *in-situ* procedure, we modified the conditions employed for the preparation of the precatalysts **4** and **5** in such a way that the exchange of COD by diphosphine was carried out in the solvent or solvent mixture of the subsequent hydrogenation.

Table 2. Asymmetric Hydrogenation of Allylic Alcohols



Entry	Substrate	Catalyst [a]	S/C[b]	% Conversion 1 h	% Conversion 24 h	% e.e. (*R*) [c]
1	**7a**	**2** + (*S*)-pTol-BINAP	12 000	99	100	97.5
2	**7a**	((*S*)-pTol-BINAP)Ru(O_2CCF_3)$_2$	12 000	100		97.7
3	**7a**	**2** + (*S*)-BIPHEMP	12 000	34	100	98.1
4	**7a**	((*S*)-BIPHEMP)Ru(O_2CCF_3)$_2$	12 000	100		98.2
5	**7a**	**3** + (*S*)-BIPHEMP	4 000	15	66	95.8
6	**7a**	((*S*)-BIPHEMP)Ru(O_2CCH_3)$_2$	4 000	99	100	96.4
7	**7b**	**2** + (*S*)-BIPHEMP	50 000	80	100	98.5 [d]
8	**7b**	((*S*)-BIPHEMP)Ru(O_2CCF_3)$_2$	50 000	95	100	98.5 [d]
9	**7b**	((*S*)-MeO-BIPHEP)Ru(O_2CCF_3)$_2$	50 000	99	100	98.7 [d]
10	**7b**	**2** + (*S*)-BINAP	16 000	80	100	96.0 [d]
11	**7b**	((*S*)-BINAP)Ru(O_2CCF_3)$_2$	50 000	98	100	97.9 [d]
12	**7b**	**2** + (*S*)-pTol-BINAP	50 000	99	100	96.9 [d]
13	**7b**	**1** + CF_3COOH + (*S*)-pTol-BINAP	50 000	99	100	97.0 [d]
14	**7b**	((*S*)-pTol-BINAP)Ru(O_2CCF_3)$_2$	50 000	99	100	97.5 [d]

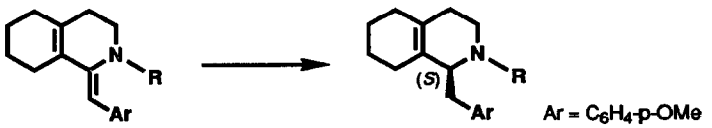
[a] Hydrogenation conditions: MeOH (c = 20 %), 20 - 25 °C, 60 bar. [b] Substrate/Catalyst mole ratio. [c] GC analysis of the diastereomeric esters prepared with Trolox™ methyl ether.[10] [d] The e.e.-value refers to C(3).

The preformed complexes **4** and **5** and the corresponding *in-situ* generated precatalysts were tested in asymmetric hydrogenations of various substrates.

The results obtained in the asymmetric hydrogenation of geraniol (**7a**)[11] and (2*E*,7*R*)-tetrahydrofarnesol (**7b**)[11] are listed in Table 2. It should be noted that the *in-situ* catalysts were prepared according to a general procedure (see Experimental) which was not optimized for every diphosphine. As a consequence, the activity and the enantioselectivity of the *in-situ* catalysts did in some cases not fully match those of the preformed complexes. Interestingly, ((*S*)-p-Tol-BINAP)Ru(O_2CCF_3)$_2$ (**4d**) exhibited the same excellent performance *in situ* as the preformed complex (Entries 1 and 12). This was also true for the even more simply generated complex **4d** (Entry 13).

In the asymmetric hydrogenation of the (*Z*)-enamides **8a**[12] and **8b**, various ruthenium complexes of (*S*)-BIPHEMP have been investigated. The results are compiled in Table 3.

Table 3. Asymmetric Hydrogenation of (*Z*)-Enamides



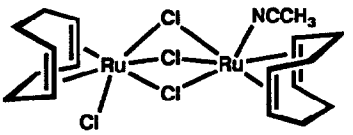
8a R = CHO
8b R = Ac

Entry	Substrate	Catalyst [a]	% Conversion 5 h	% Conversion 24 h	% e.e. (*S*) [c]
1	**8a**	**3** + (*S*)-BIPHEMP [b]	52	93	97.0
2	**8a**	((*S*)-BIPHEMP)Ru(O_2CCH_3)$_2$ [b]	90	99	98.2
3	**8a**	**6** + (*S*)-BIPHEMP	85	94	95.9
4	**8a**	**2** + (*S*)-BIPHEMP	85	94	96.7
5	**8a**	((*S*)-BIPHEMP)Ru(O_2CCF_3)$_2$	50	99	98.2
6	**8b**	**2** + (*S*)-BIPHEMP	98	100	97.3
7	**8b**	((*S*)-BIPHEMP)Ru(O_2CCF_3)$_2$	100		98.0

[a] Hydrogenation conditions: S/C = 1000, MeOH/CH_2Cl_2 5:1 (v/v; c = 1.5 %), 100 °C, 60 bar. [b] Hydrogenation in methanol. [c] Determination of the e.e.: 1) Hydrolysis with excess of anhydrous KOH in diethylene glycol, 190 °C, 18 h; 2) (-)-camphanoyl chloride/DMAP, pyridine; 3) GC analysis.

According to Noyori *et al.*,[12] hydrogenation of (*Z*)-enamide **8a** in the presence of as much as 0.5 mol% of complex **4d** was sluggish (100 bar, 30 °C, 100 h; 97 % e.e.). Remarkably, we achieved complete hydrogena-

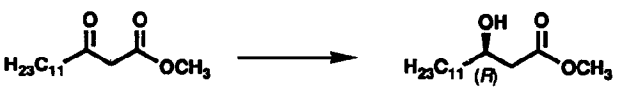
tion of **8a** with trifluoroacetato complex **4a** or acetato complex **5a** in 24 h at 100 °C/60 bar and without loss of enantioselectivity (Table 3, Entries 2, 5). The corresponding *in-situ* catalysts turned out to be slightly less active. This was also true for the corresponding dichloro complex prepared *in situ* from the known chloro-bridged precursor **6**[13] and (*S*)-BIPHEMP. Excellent results were also obtained in the hydrogenation of **8b** with either preformed or *in-situ* generated **4a**.



6

So far, $[(BINAP)_2Ru_2Cl_4]NEt_3$[3] and the well-defined cationic complexes of the type $[(\eta^6\text{-arene})Ru(P\text{–}P)Cl]X$ (P–P = BINAP[14], BIPHEMP[8b]) and $[(BIPHEMP)_3Ru_3(\mu^3\text{-}Cl)_2(\mu^2\text{-}Cl)_3]X$[8b] are the only ruthenium chloro complexes that have been successfully used in highly enantioselective hydrogenations.

Table 4. Hydrogenation of β-Keto Ester **9**



9

Entry	Catalyst [a]	% Conversion 1 h	% Conversion 20 h	% e.e. (*R*) [c]
1	**6** + (*R*)-BINAP	26	99	95.8
2	**6** + (*R*)-pTol-BINAP	31	93	94.8
3	**6** + (*R*)-MeO-BIPHEP	29	97	97.1
4	**6** + (*R*)-BIPHEMP	31	99	97.3
5	((*R*)-BIPHEMP)$Ru(O_2CCH_3)_2$ + 2 HCl [b]	75	99	97.0

[a] Hydrogenation conditions: S/C = 50 000, MeOH/CH_2Cl_2 96:4 (v/v; c = 20 %), 80 °C, 35 bar. [b] A solution of 2 molequiv. of anhydrous HCl in MeOH was added to a solution of the ruthenium complex in CH_2Cl_2, and the catalyst solution was stirred for 1 h. [c] GC analysis of the diastereomeric esters prepared with Trolox™ methyl ether.[10]

Surprisingly, the use of precursor complex **6** for the synthesis of chiral ruthenium diphosphine complexes has not yet been reported. In our hands this complex proved to be extremely useful for the convenient and

efficient screening of diphosphines in the hydrogenation of β-keto ester **9** (Table 4.; cf.[15]). Instead of generating the precatalyst having the stoichiometry (P–P)$RuCl_2$ from **4a - d** by the ligand exchange method[15] (see Table 4, footnote [b]), **6** can simply be treated with the respective diphosphine (see Experimental) to afford catalysts having only slightly lower activity (Entries 1 - 4). Relatively short reaction times with substrate/catalyst ratios of up to 50 000 could be achieved with all catalysts.

EXPERIMENTAL

All manipulations were carried out routinely under an argon atmosphere using Schlenk techniques or in a glove box. All solvents were dried before use and destilled under argon; trifluoroacetic acid was destilled from phosphorus pentoxide under argon. (COD)Ru(η^3-methallyl)$_2$[16] and $(COD)_2Ru_2Cl_4(NCCH_3)$[13] were synthesized according to the published methods.

^{1}H-NMR at 250 MHz (Bruker AC 250E) and 270 MHz (Bruker HX-270): chemical shifts in ppm (δ) with TMS as internal standard; ^{13}C-NMR at 100.62 MHz (Bruker AM 400): chemical shifts in ppm (δ) with TMS as internal standard; ^{31}P-NMR at 101.26 MHz (Bruker AC 250E) and 202.46 MHz (Bruker AM 500): chemical shifts in ppm (δ) with 85 % H_3PO_4 as external standard. δ values of protons refer to aromat. H unless otherwise specified.

Synthesis of (η^4-Cycloocta-1,5-diene)tetrakis(μ-trifluoroacetato)ruthenium(II) (2)

A solution of 8.9 g (27.86 mmol) of (COD)Ru(η^3-methallyl)$_2$ (**1**) in 90 ml of diethylether is treated dropwise with 4.3 ml (56.2 mmol) of trifluoroacetic acid and stirred for 1 h at r.t. to give an orange solution. The solution is evaporated to dryness and the yellow residue stirred in 10 ml of diethylether at - 5 °C. The dark brown supernatant is decanted and the remaining solid dried *in vacuo* to give a yellow powder. Yield: 11.0 g (90.7 %) **2**.

Anal.calc. for $C_{24}H_{24}F_{12}O_8Ru_2$ (870.56): C 33.11, H 2.78, F 26.19; found: C 33.23, H 2.86, F 25.68.

^{1}H-NMR (250 MHz, $CDCl_3$): 4.05 (br. *s*, 8 olefin. H), 2.55 (*m*, 8 aliphat. H), 2.12 (*m*, 8 aliphat. H).

$^{13}C\{^1H\}$-NMR (100.62 MHz, $CDCl_3$): 91.6 (=CH-), 28.1 ($-CH_2-$).

Synthesis of Di(η^2-acetato)(η^4-cycloocta-1,5-diene)ruthenium(II) (3)

A suspension of 2.58 g (2.90 mmol) of $(COD)_2Ru_2(O_2CCF_3)_4$ (**2**) in 20 ml of methanol is treated with ca. 0.06 ml (3.3 mmol) of H_2O and stirred for 5 min. 2.38 g (29.0 mmol) of sodium acetate is added and the mixture stirred for 1 h at 40 °C. The solvent is removed and the residue extracted with 20 ml of dichloromethane. After filtration, the resulting brown filtrate is evaporated to dryness and the remaining solid washed with small portions of pentane/diethylether (5/1 v/v) to give 1.24 g (65.4 %) **2** as yellow powder.

Anal. calc. for $C_{12}H_{18}O_4Ru$ (327.34): C 44.03, H 5.54; found: C 43.90, H 5.73.

^{1}H-NMR (250 MHz, $CDCl_3$): 4.68 (*m*, 2 =CH-), 3.25 (*m*, 2 =CH-), 2.41 - 1.95 (*m*, 4 -CH_2-), 2.07 (*s*, 2 CH_3). $^{13}C\{^1H\}$-NMR(100.62 MHz, $CDCl_3$): 89.15 and 84.54 (=CH-), 31.28 and 27.00 (-CH_2-), 23.83 (O_2CCH_3).

General Procedure for the Synthesis of (P–P)Ru(O_2CCF_3)$_2$ (4a - d)

A solution of 2.0 g (2.3 mmol) of complex 1 and 4.60 mmol of the diphosphine in 30 ml of diethylether and 10 ml of tetrahydrofuran is stirred for 16 h at 40 °C. The resulting orange solution is evaporated to dryness and the residue stirred in 10 ml of diethylether to give an orange suspension. The supernatant is decanted and the remaining solid washed with pentane (2 * 15 ml) and dried *in vacuo* to afford an orange-yellow powder. Yield: 94 - 97 % **4a - d**.

Bis(trifluoroacetato)[(*S*)-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)]ruthenium(II) ((*S*)-**4a**):
Anal. calc. for $C_{42}H_{32}F_6O_4P_2Ru$ (877.22): C 57.47, H 3.67; found: C 57.15, H 4.06.
^{1}H-NMR (270 MHz, $CDCl_3$/1 drop of CD_3OD): 7.72 (*m*, 2 H), 7.58 (*m*, 4 H), 7.48 - 7.31 (*m*, 6 H), 7.27 - 7.17 (*m*, 6 H), 7.09 - 6.97 (*m*, 6 H), 6.77 (*d*, J = 7.8, 2 H), 1.17 (*s*, 2 aromat. CH_3).
$^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$/1 drop of CD_3OD): 57.85 (*s*).

Bis(trifluoroacetato)[(*R*)-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)]ruthenium(II) ((*R*)-**4a**):
Anal. calc. for $C_{42}H_{32}F_6O_4P_2Ru$ (877.22): C 57.47, H 3.67; found: C 57.36, H 4.25.
^{1}H-NMR and $^{31}P\{^1H\}$-NMR identical with those of (*S*)-**4a**.

Bis(trifluoroacetato)[(S)-(6,6'-dimethoxylbiphenyl-2,2'-diyl)bis(diphenylphosphine)]ruthenium(II) ((*S*)-**4b**):
Anal. calc. for $C_{42}H_{32}F_6O_6P_2Ru$ (909.72): C 55.45, H 3.55; found: C 55.88, H 4.08.
^{1}H-NMR (250 MHz, $CDCl_3$/1 drop of CD_3OD): 7.58 - 7.26 (*m*, 14 H), 7.20 (*t*, J = 7.4, 2 H), 7.05 (*t*, J = 7.5, 4 H), 6.97 (*m*, 4 H), 6.43 (~ *dd*, J = 8.2, 1.9, 2 H), 3.44 (*s*, 2 OCH_3).
$^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$/1 drop of CD_3OD): 58.3 (*s*).

Bis(trifluoroacetato)[(*S*)-(1,1'-binaphthyl-2,2'-diyl)bis(diphenylphosphine)]ruthenium(II) ((*S*)-**4c**):
Anal. calc. for $C_{48}H_{32}F_6O_6P_2Ru$ (949.79): C 60.70, H 3.40; found: C 60.52, H 3.88.
^{1}H-NMR (250 MHz, $CDCl_3$/1 drop of CD_3OD): 7.90 (*m*, 2 H), 7.77 - 7.29 (*m*, 14 H), 7.24 (*t*, J = 7.8, 2 H), 7.04 (*m*, 4 H), 6.82 (*t*, J = 7.0, 2 H), 6.62 (*t*, J = 6.9, 2 H), 6.50 (*t*, J = 7.4, 4 H), 6.38 (*d*, J = 8.6, 2 H).
$^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$/1 drop of CD_3OD): 57.3 (*s*).

Bis(trifluoroacetato)[(*S*)-(1,1'-binaphthyl-2,2'-diyl)bis(di-p-tolylphenylphosphine)]ruthenium(II) ((*S*)-**4d**):
Anal. calc. for $C_{52}H_{40}F_6O_4P_2Ru$ (1005.89): C 62.09, H 4.01; found: C 62.52, H 4.23.
^{1}H-NMR (250 MHz, $CDCl_3$/1 drop of CD_3OD): 7.96 (*m*, 2 H), 7.67 - 7.52 (*m*, 8 H), 7.40 - 7.18 (*m*, 6 H), 6.90 - 6.74 (*m*, 6 H), 6.27 (*m*, 6 H), 2.38 and 1.85 (2 *s*, 4 aromat. CH_3).
$^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$/1 drop of CD_3OD): 55.2 (*s*).

General Procedure for the Synthesis of (P–P)Ru(O_2CCH_3)$_2$ (5a - d)

A suspension of 3.19 mmol of complex **4a - d** and 2.62 g (31.9 mmol) of sodium acetate in 25 ml of methanol is stirred for 2 h at 40 °C. The solvent is removed and the residue extracted with 50 ml of dichloromethane. After filtration, the resulting orange filtrate is evaporated to dryness and the remaining solid stirred with 10 ml of diethylether. The supernatant is decanted and the remaining solid washed with 5 ml of pentane to give a yellow powder. Yield: 95 - 98 % **5a - d.**

Di(η^2-acetato)[(*S*)-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)]ruthenium(II) ((*S*)-(**5a**):
Anal. calc. for $C_{42}H_{38}O_4P_2Ru$ (769.78): C 65.53, H 4.98; found: C 64.69, H 5.37.
^{1}H-NMR (250 MHz, $CDCl_3$): 7.73 (*m*, 4 H), 7.43 (*m*, 6 H), 7.24 (*m*, 8 H), 7.07 (*dd*, J = 7.2, 7.2, 4 H), 6.86 (*t*, J = 7.6, 2 H), 6.62 (*d*, J = 7.4, 2 H), 1.73 (*s*, 2 O_2CCH_3), 1.33 (*s*, 2 aromat. CH_3).
$^{31}P\{^1H\}$-NMR (202.46 MHz, $CDCl_3$): 65.4 (*s*).

Di(η^2-acetato)[(*R*)-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)]ruthenium(II) ((*R*)-(**5a**):
Anal. calc. for $C_{42}H_{38}O_4P_2Ru$ (769.78): C 65.53, H 4.98; found: C 64.86, H 5.20.
^{1}H-NMR and $^{31}P\{^1H\}$-NMR identical with those of (*S*)-**5a.**

Di(η^2-acetato)[(*S*)-(6,6'-dimethoxylbiphenyl-2,2'-diyl)bis(diphenylphosphine)]ruthenium(II) ((*S*)-(**5b**):
Anal. calc. for $C_{42}H_{38}O_6P_2Ru$ (801.78): C 62.92, H 4.78; found: C 62.96, H 5.18.
^{1}H-NMR (250 MHz, $CDCl_3$): 7.75 (*m*, 4 H), 7.47 - 7.25 (*m*, 10 H), 7.19 (*t*, J = 7.4, 2 H), 7.02 (*t*, J = 7.3, 4 H), 6.82 (*t*, J = 7.9, 2 H), 6.68 (*m*, 2 H), 6.19 (*d*, J = 8.1, 2 H), 3.34 (*s*, 2 OCH_3), 1.84 (*s*, 2 O_2CCH_3).
$^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$): 63.9 (*s*).

Di(η^2-acetato)[(*S*)-(1,1'-binaphthyl-2,2'-diyl)bis(diphenylphosphine)]ruthenium(II) ((*S*)-**5c**):
Anal. calc. for $C_{48}H_{38}O_4P_2Ru$ (841.85): C 68.48, H 4.55; found: C 69.40, H 5.03.
^{1}H-NMR (250 MHz, $CDCl_3$): 7.84 (*m*, 4 H), 7.46 (*m*, 12 H), 7.20 (*ddd*, J = 8.0, 6.8, 1.1, 2 H), 7.10 (*m*, 4 H), 6.88 (*ddd*, J = 8.5, 6.8, 1.3, 2 H), 6.62 (*d*, J = 8.6, 2 H), 6.51 (*m*, 6 H), 1.80 (*s*, 2 O_2CCH_3).
$^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$): 65.2 (*s*).

Di(η^2-acetato)[(*S*)-(1,1'-binaphthyl-2,2'-diyl)bis(di-p-tolylphosphine)]ruthenium(II) ((*S*)-**5d**):
^{1}H-NMR (250 MHz, $CDCl_3$): 7.73 (*m*, 4 H), 7.57 - 7.44 (*m*, 6 H), 7.27 - 7.17 (*m*, 6 H), 6.98 - 6.82 (*m*, 6 H), 6.57 (*d*, J = 8.5, 2 H), 6.28 (*d*, J = 7.6, 4 H), 2.38 and 1.83 (2 *s*, 4 aromat. CH_3), 1.77 (*s*, 2 O_2CCH_3).
$^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$): 63.8 (*s*).

General Procedure for the *In-Situ* Preparation of the Catalysts

In a glove box (argon, <1 ppm oxygen), a solution of the chiral ligand (0.01 - 0.1 mmol) in 20 - 100 ml of methanol or dichloromethane was added to a solution of the stoichiometric amount of the metal complex in 20 ml of methanol (**1** + 2 molequiv. of CF_3COOH, **2**, or **3**) or dichloromethane (**6**). The resulting catalyst solution was stirred at r.t. for 90 min. (**6**) or overnight (**1** + 2 molequiv. of CF_3COOH, **2**, or **3**).

General Procedure for the Hydrogenations

In a glove box (argon, <1 ppm oxygen), a 500 ml stainless steel autoclave equipped with a magnetically driven stirrer was charged successively with the substrate, the solvent, the catalyst solution, and 10 bar of argon. Before connecting the autoclave to the hydrogen source (99.9999 %), the lines were carefully flushed with hydrogen. The argon was replaced by three cycles of pressurizing with 20 bar of hydrogen and venting. The hydrogenations were run under the conditions given in Tables 2 - 4.

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[8] a) Other high-yield procedures for the synthesis of *pure* samples of (P–P)Ru(O_2CCH_3)$_2$ have been developed and exemplified for P–P = BIPHEMP and MeO-BIPHEP by starting from (η^6-p-cymene)-Ru(O_2CCH_3)$_2$ [5a] and [(η^6-p-cymene)$RuCl_2$]$_2$ [8b], respectively; b) B. Heiser, E. Broger, Y. Crameri, P. Schönholzer, R. Schmid, 7th International Symposium on Homogeneous Catalysis, Lyon, September 1990, Abstract P-103.

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