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Highly efficient enantioselective catalysis in supercritical carbon dioxide using the perfluoroalkyl-substituted ligand (*R*,*S*)-3-H^{2}F^6-BINAPHOS

Giancarlo Franciò, Klaus Wittmann, Walter Leitner *

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

Abstract

Perfluoroalkyl-substitution of the aryl groups in the BINAPHOS skeleton was achieved using a synthetic strategy based on the Cu(I)-catalyzed cross coupling of arylmagnesium bromide and $F(CF_2)_6(CH_2)_2I$. The rhodium complexes of the new ligand (*R*,*S*)-3-H^{2}F^6–BINAPHOS (**10**) exhibited spectroscopic properties and reactivities similar to those of the unsubstituted parent compounds. The substitution provided a high affinity of the ligand and its complexes for $scCO_2$ allowing the development of ecologically benign protocols for catalytic asymmetric synthesis and even the spectroscopic detection of catalytically active intermediates. Using this new system, a large variety of substrates were hydroformylated in $scCO_2$ with rates and enantioselectivities comparable to those of the parent system in benzene solution. At the same time, the CO_2-philic substitution pattern resulted in a significantly higher regioselectivity towards the desired chiral aldehydes. Preliminary results indicated for the first time also a remarkable potential of BINAPHOS-derived ligands for asymmetric hydrogenation reactions. The possibility to develop new work-up schemes for product purification and/or catalyst immobilisation based on $scCO_2$ as the only medium for catalysis and extraction (CESS process) was experimentally verified using a rhodium catalyst containing **10**.

Keywords: Homogeneous catalysis; Enantioselective hydroformylation; Enantioselective hydrogenation; Supercritical carbon dioxide; Fluorinated ligands

1. Introduction

Supercritical carbon dioxide ($scCO_2$) has recently received considerable attention as a reaction medium with unique properties for chemical reactions and especially for metal-catalyzed processes [1,2]. The high miscibility of $scCO_2$ with many reaction gases can help to avoid mass transport limitations which are frequently encountered in gas–liquid phase reactions. Further beneficial effects may arise from direct interaction of CO_2 with catalytically active metal centers. The high compressibility of supercritical solvents offers density as an additional process parameter for catalysis opening a wide range of fascinating applications. Of course, the most obvious advantage of the use of $scCO_2$ is the replacement of potentially hazardous organic solvents such as benzene, methylene chloride, diethyl-ether etc. with environmentally benign and toxicologically harmless carbon dioxide. Working beyond the critical temperature of CO_2 provides the attractive option to use the same medium for synthesis, isolation and purification of the product by exploiting the extractive properties of $scCO_2$. Purification by selective extraction with supercritical fluids (SFE) is well established in various technical processes, with decaffeination of green coffee beans being just the most prominent application [3]. Most recently, the successful utilization of $scCO_2$ to separate and recycle homogeneous transition metal catalysts from reaction products has been demonstrated for the first time in our group [4–6]. We refer to such

* Corresponding author. Tel.: +49-208-3062500; fax: +49-208-3062993.

E-mail address: leitner@mpi-muelheim.mpg.de (W. Leitner).

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integrated processes in homogeneous catalysis as catalysis and extraction using supercritical solutions (CESS)-processes.

Nowhere is the consideration of ecological and toxicological issues more important than in the synthesis of biologically active fine chemicals like pharmaceuticals, food additives, agrochemicals, or cosmetics. Many of these materials are chiral and the two mirror images often exhibit different physiological properties. Hence, there is an increasing demand for efficient and ecologically benign methodologies to synthesize such compounds in enantiomerically pure or at least in non-racemic form. Enantioselective homogeneous catalysis using chiral transition metal catalysts has emerged as one of the most attractive approaches in asymmetric synthesis but usually involves the use of large quantities of organic solvents [7]. Clearly, there is a huge potential for the application of $scCO_2$ as a reaction medium for such processes, which has been barely explored up to now.

Several promising examples of asymmetric catalysis in $scCO_2$ were reported during the last 5 years including the hydrogenation of C=C [8–10] and C=N double bonds [6], the epoxidation [11] and the cyclopropanation of alkenes [12], and the nickel-catalyzed hydrovinylation of styrenes [13]. In contrast, asymmetric hydroformylation in $scCO_2$ has remained elusive until recently. Rhodium-catalyzed asymmetric hydroformylation is of great current interest providing for example viable routes to important anti-inflammatory drugs like ibuprofen or naproxen [14]. The chiral phosphine–phosphite ligand (*R*,*S*)-BINAPHOS is known to allow outstanding levels of enantiocontrol in this reaction, but the established protocols require application of ecological and toxicological hazardous organic solvents, in particular benzene [15]. Initial attempts to replace these solvents and to use the ligand (*R*,*S*)-BINAPHOS directly in compressed CO_2 gave preparatively unsatisfactory results [16]. Detailed control experiments revealed that the poor solubility of the chiral ligand and of its rhodium complexes in the supercritical phase was the limiting factor [16a].

As initially shown using the substituent $F(CF_2)_6$-$(CH_2)_2$ (H^2F^6) [17], perfluorinated groups can act as solubilizers for aryl phosphines making the corresponding metal complexes sufficiently 'CO_2-philic' for catalysis in many cases [5,10,18,19]. Based on these findings, we have set out to synthesize the perfluoroalkyl-substituted ligand (*R*,*S*)-3-H^2F^6-BINAPHOS (**10**). Although the fluorine content of **10** is considerable lower than that of most ligands typically used in this medium (Fig. 1), we were confident that this new ligand would provide sufficient solubility for enantioselective catalysis in $scCO_2$. Preliminary studies confirmed that the new ligand **10** formed soluble and efficient catalyst for the hydroformylation of vinylarenes in compressed (liquid or supercritical) CO_2 [20].

In the present contribution, we report details of the synthesis of **10** and its application in asymmetric hydroformylation and hydrogenation reactions. The solution structure of a rhodium hydrido carbonyl complex of **10** relevant to catalysis was elucidated in $scCO_2$ using

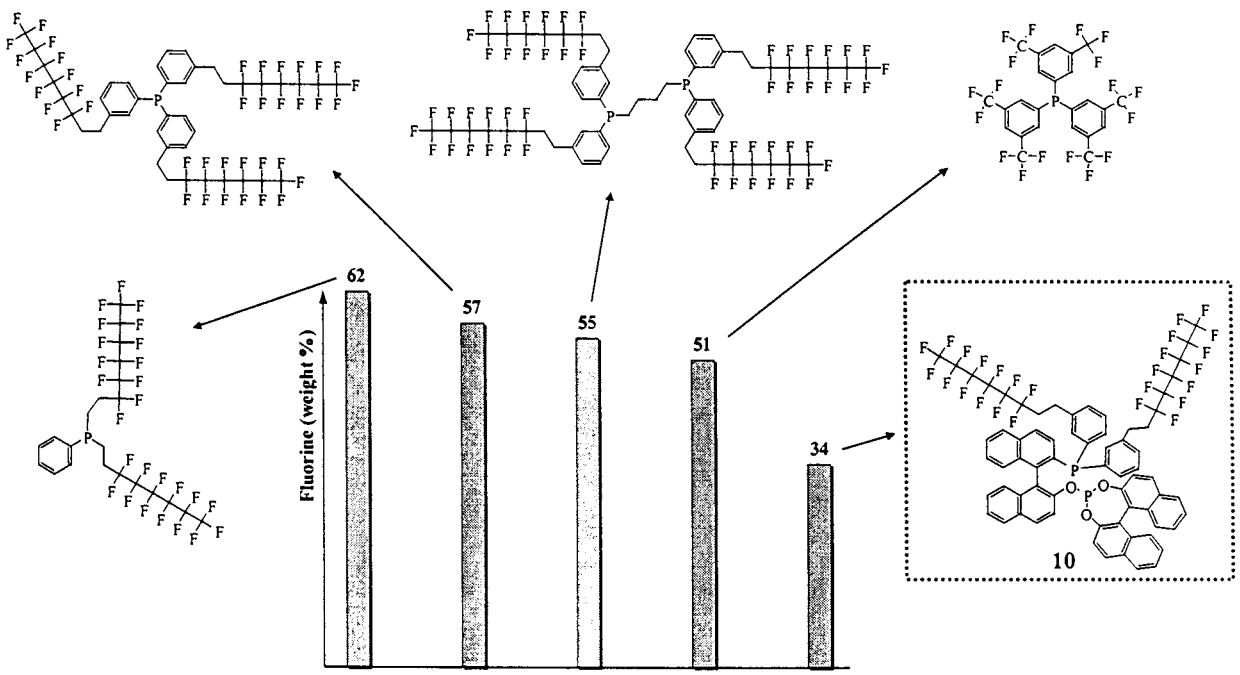
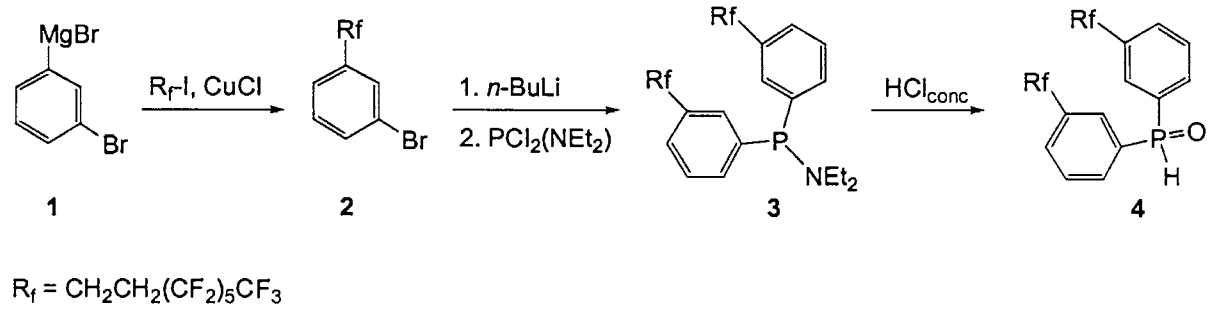
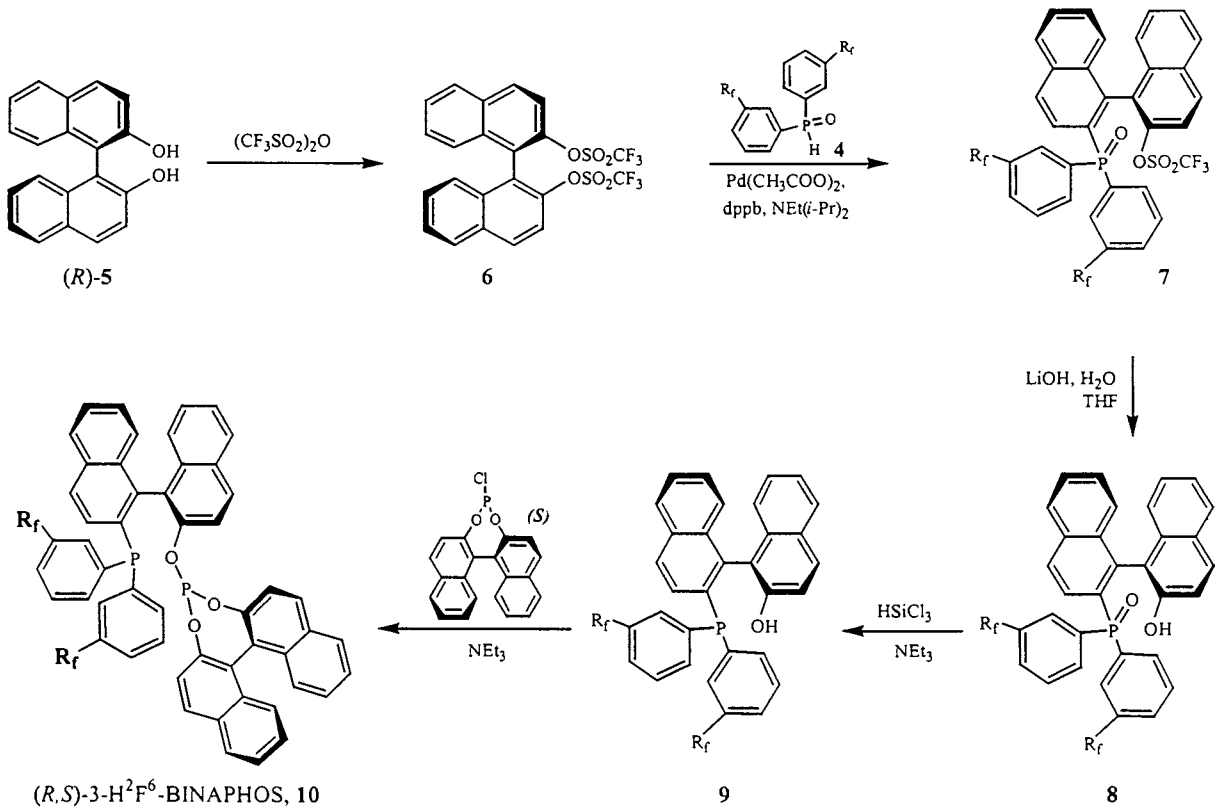


Fig. 1. Fluorine content (wt.%) in 'CO_2-philic' ligands.



Scheme 1.



Scheme 2.

high-pressure NMR spectroscopy. Furthermore, we describe the utilization of the tuneable solvent properties of CO_2 for product purification and catalyst recycling with this system.

2. Results and discussion

2.1. Synthesis of (R,S)-3-H^2F^6–BINAPHOS (10)

The synthesis of (*R*,*S*)-3-H^2F^6–BINAPHOS (**10**) follows a reaction sequence that is largely adapted from the synthesis of (*R*,*S*)-BINAPHOS [15], although some steps needed significant changes of the reaction conditions (Scheme 2). The key step of this sequence is the selective mono-substitution of the bistriflate of binaphthol **6** with a diaryl-phosphineoxide through a palladium-catalyzed C–P coupling reaction. We decided to use this step for the introduction of the perfluoroalkyl chains via the diaryl-phosphineoxide (**4**). The key intermediate **4** is readily available from simple starting materials in good yield using the synthetic strategy shown in Scheme 1.

Copper-catalysed reaction of $F(CF_2)_6(CH_2)_2I$ with the Grignard reagent **1** obtained from *meta*-dibromobenzene provided the perfluoroalkyl-substituted arylbromide **2** [17,21]. Lithiation with *n*-BuLi and reaction with dichloro-diethylamino-phosphine produced the diaryl-diamino-phosphine (**3**) that was not isolated but hydrolized directly to obtain the desired phosphine-ox-

ide (**4**). As with the parent phenyl derivative, the Pd-catalyzed coupling of **4** with **6** occurred very selectively, although higher temperatures and larger catalyst and base loadings were required to obtain the mono-substitued intermediate **7** in excellent yield [22]. Hydrolysis with lithium hydroxide in aqueous THF and subsequent reduction with trichlorosilane afforded the corresponding phosphine-alcohol (**9**). The synthesis was completed by the reaction of **9** with the chlorophosphite derived from *S*-binaphthol. The overall yield for the desired product (*R*,*S*)-3-H^2F^6–BINAPHOS (**10**) based upon **6** was 42%.

2.2. Synthesis and high pressure NMR investigation of catalyst precursors

The complex [{(*R*,*S*)-3-H^2F^6–BINAPHOS}Rh(acac)] (**11**) was synthesized by adding equimolar amounts of ligand **10** to [Rh(acac)$(CO)_2$] in THF solution at −60°C according to an established procedure [23]. The spectroscopic data of **11** and the non-fluorinated parent complex (Table 1) are virtually identical even for the ^{103}Rh nucleus, which is known to provide a very sensitive probe for variations in the steric and electronic properties of coordinating ligands [24]. For example, the difference of 23 ppm in the ^{103}Rh spectrum of complexes derived from the chelating ligands dppe and (3-H^2F^6)-dppe (Table 1, entry 1 and 2) indicates a small but significant electron donating effect of the four perfluoroalkyl chains. In contrast, ^{103}Rh-NMR spectroscopy appears not to be sensitive enough to reflect this electronic change in the case of **11**, where only two chains are introduced compared to the parent compound (Table 1, entry 3 and 4) [25].

Despite the increasing number of successful applications of phosphine complexes as catalysts in $scCO_2$, the direct spectroscopic detection of catalytically active species has not yet been reported for this class of compounds under supercritial conditions [26]. Therefore the reaction of **11** with synthesis gas (20 bar) in $scCO_2$ was investigated by high pressure NMR using a 5 mm tube made from single crystal sapphire [27]. This study revealed clean formation of the five-coordinated hydrido carbonyl complex [H$(CO)_2$Rh(**10**)] (**12**) which was readily identified on the basis of its ^{31}P{^{1}H}- and ^{1}H-NMR data (Fig. 2, Table 2). As for the parent BINAPHOS complex, this species can be expected to enter directly into the catalytic cycle by dissociation of one of the carbonyl ligands [15].

In general, the NMR data of five-coordinated **12** in $scCO_2$ are very similar to those of the unsubstituted parent complex in benzene (Table 2), albeit some differences are observed for example in the coupling constants J_{PH}. It is interesting to note that these data of complex **12** are in fact more similar to the corresponding (*R*,*S*)-BIPHEMPHOS complex, which gives regioselectivities similar to **10** and higher than (*R*,*S*)-BINAPHOS in the hydroformylation of vinylarenes (see Section 2.3). The detection of the hydride signal of **12** is quite remarkable because it indicates that

Table 1
Comparison of NMR data for Rh-complexes containing chelating aryl phosphines substituted with polyfluoroalkylchains and their unsubstituted parent compounds (acac = acetylacetonate; hfacac = hexafluoroacetylacetonate)

Entry	Compounds	δ (P^B) (ppm)	δ (P^A) (ppm)	J_{RhP_B} (Hz)	J_{RhP_A} (Hz)	$J_{P_BP_A}$ (Hz)	δ (^{103}Rh) (ppm)
1	[(dppe)Rh(hfacac)] [a]	72.1		196			438
2	[{(3-H^2F^6)-dppe}Rh(hfacac) [b]	71.8		196			461
3	[{(*R*,*S*)-BINAPHOS}Rh(acac)] [c]	49.3	162.2	175	332	84	273
4	[(**10**)Rh(acac)], **11**	49.6	161.9	175	330	84	271

[a] Ref. [23].
[b] Ref. [17].
[c] Ref. [15].

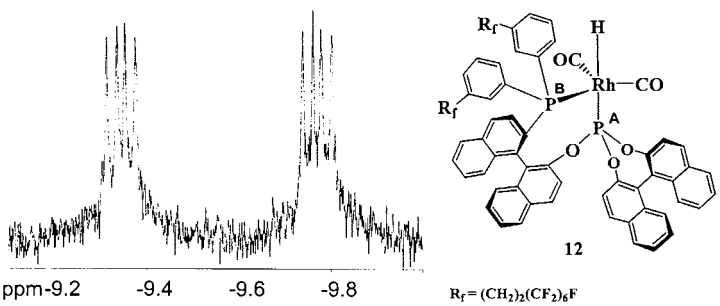
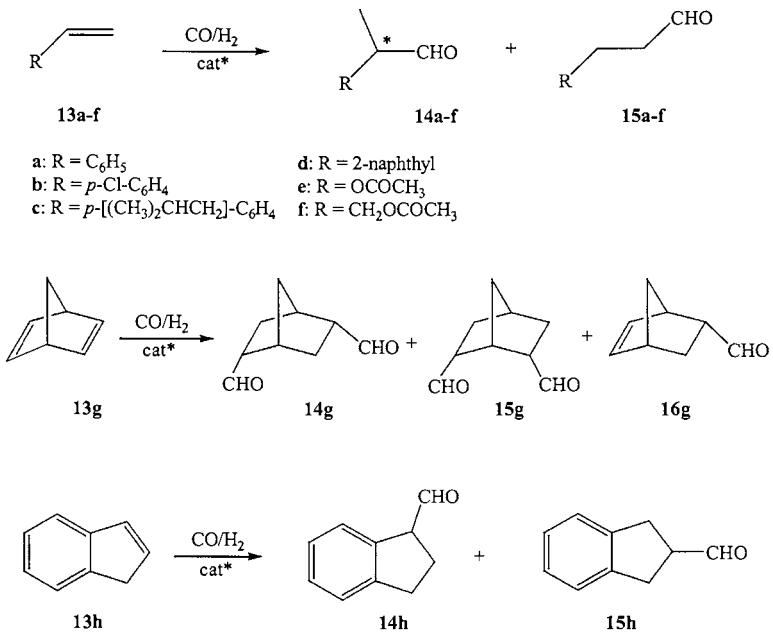


Fig. 2. The hydride region of the ^{1}H-NMR spectrum of **12** obtained in $scCO_2$.

Table 2
NMR data of the complexes $[H(CO)_2Rh(ligand\text{-}P^A,P^B)]$

Ligand-P^A,P^B	Phosphine			Phosphite				Hydride	
	δ (P^B) (ppm)	J (P^BH) (Hz)	J (RhP^B) (Hz)	δ (P^A) (ppm)	J (P^AH) (Hz)	J (RhP^A) (Hz)	J (P^AP^B) (Hz)	δ (^1H) (ppm)	J (RhH) (Hz)
(*R*,*S*)-BINAPHOS [a]	26.9	23	119	184.9	160	182	40	−8.85	9.8
3-H^2F^6-(*R*,*S*)-BINAPHOS [b]	28.0	16	124	183.6	170	181	38	−9.56	9.2
(*R*,*S*)-BIPHEMPHOS [a]	25.0	17	120	183.5	173	177	43	−8.85	8.7

[a] Ref. [15]; solvent C_6D_6.
[b] $T = 40$°C; solvent CO_2–THF-d_8.



Scheme 3.

there is no measurable interaction of CO_2 with the rhodium hydride bond even under high pressure of CO_2. This lack of reactivity of **12** towards CO_2 is in sharp contrast to the situation observed with the isoelectronic complex $[\{Ph_2P(CH_2)_3PPh_2\}_2RhH]$, which inserts CO_2 to give the corresponding formate complex even at ambient pressure [28]. The formation of phosphine rhodium hydride intermediates that do not interact with CO_2 was recently also inferred for enantioselective hydrogenation in $scCO_2$ using indirect mechanistic tools [10].

*2.3. Rhodium-catalyzed asymmetric hydroformylation and hydrogenation using (R,S)-3-H^2F^6-BINAPHOS (**10**) in sCO_2*

Our initial results using **10** as a ligand for catalysis in $scCO_2$ revealed that this system allows for the first time highly enantioselective and regioselective hydroformylation of vinylarenes in $scCO_2$ [20]. The results summarized in Table 3 demonstrate that this conclusion is valid for a broad range of substrates as depicted in Scheme 3.

The catalytic system was conveniently prepared in situ by mixing THF solutions of the complex $[Rh(acac)(CO)_2]$ and the ligand **10** in a window-equipped high pressure reactor. A ratio of **10**/Rh = 2:1 was found to be sufficient to ensure maximum values of enantioselectivity, whereas 4:1 is typically required with the parent BINAPHOS ligand. After stirring the combined THF solutions for ca. 5 min, the organic solvent was evaporated and the substrate was introduced followed by synthesis gas and CO_2 (see Section 4 for details). The final reaction temperature was reached within less than 15 min, ensuring that no significant conversion occurred before temperature equilibration.

Table 3
Rhodium-catalysed asymmetric hydroformylation of substrates **9a–h**

Entry	Substrate (mmol)	S/Rh	L/Rh	d (CO_2) (g ml^{-1})	T (°C)	$p_{H_2/CO}$ (bar)	p_{tot} (bar)	t (h)	Conversion (%)	TOF [a] (h^{-1})	**14**/**15** (%)	ee (%)
1	**13a** (2.0)	1000	2	0.60	60	60	242	16	97.6	61	93.0/7.0	92.0 (*R*)
2	**13a** (4.0)	2000	2	– [b]	60	100	–	17	>99	>118	92.7/7.3	90.6 (*R*)
3	**13a** (4.0)	2000	3	0.68	40	40	178	66	75.4	23	94.8/5.2	93.6 (*R*)
4	**13b** (2.0)	1000	2	0.58	40	40	150	15	89.0	59	91.9/8.1	88.4 (–)
5	**13c** (2.0)	1000	2	0.53	40	40	146	16	>99	>63	95.5/4.5	90.1 (*R*)
6	**13d** (4.0) [c]	2000	2	0.76	45	40	205	16	>99	>125	92.3/7.7 [d]	77.7 (–) [d]
7	**13d** (0.65)	2000	2	0.83	45	40	220	64	68.1	21	90.5/9.5	79.2 (–)
8	**13e** (4.0)	2000	2	0.69	60	60	255	41	72.9	36	92.3/7.7	95.4 (*S*)
9	**13e** (4.0)	2000	2	– [b]	60	60	–	50	>99	>40	91.7/8.3	90.6 (*S*)
10	**13f** (4.0)	2000	2	0.71	42	60	231	41	19.8	10	68.7/31.3	77.4 (n.d.)
11	**13f** (4.0)	2000	2.5	0.74	62	60	286	41	>99	>49	75.1/24.9	26.2 (n.d.)
12	**13g** (4.0)	2000	2	0.69	40	40	171	14	66.9 [e]	96	41.1/58.9	20.6 (n.d.)
13	**13h** (4.0)	2000	2.2	0.78	50	40	212	108	7.2	1.3	94.4/5.6	85.4 (–)
14	**13h** (1.0)	500	2.5	0.61	80	45	240	40	40.0	5	91.9/8.1	25.6 (–)

[a] Average value over total reaction time.
[b] Solvent = benzene.
[c] Two-phase-reaction.
[d] Determined for the combined reactor contents of two runs, see Section 2.4 for details.
[e] **16g**/(**14g**+**15g**) = 30/70, ee of **16g** < 1%.

With the notable exception of 2-vinylnaphtalene (**13d**, see Section 2.4), fully homogeneous reaction mixtures were observed during hydroformylation under the standard conditions of Table 3. Typically, carbon dioxide densities were adjusted to $d(CO_2) > 0.55$ g ml^{-1} at reaction temperatures $T = 40–60$°C (critical density $d_c(CO_2) = 0.47$ g ml^{-1} at $T_c = 31$°C), with initial pressures of synthesis gas at room temperature ranging from 40 to 60 bar. For the vinyl arenes **13a–d** the reaction rates and selectivties of the homogeneous catalyst **10**–Rh system in $scCO_2$ compare well to those of the BINAPHOS-derived catalyst in benzene. In the case of styrene (**13a**), the phase behaviour was found to have little influence on the regio- and enantioselectivity [20] and the high selectivties are retained also in benzene solution (Table 3, entry 1 and 2). Similarly, the overall selectivities during hydroformylation of **13d** were largely independent of the number of phases, although the rate was of course lower at the much lower concentrations required for single phase conditions (Table 3, entry 6 and 7). The homogeneous hydroformylation of vinylacetate (**13e**), however, represents an example where the use of $scCO_2$ as a solvent improves the enantioselectivity significantly as compared to benzene (Table 3, entry 8 and 9). Acetic acid 1-methyl-2-oxo-ethyl ester (**14e**) was obtained in $scCO_2$ with excellent regioselectivity and an ee > 95%, the highest ee ever obtained with this substrate [29].

The homogeneous hydroformylation of acetic acid allyl ester (**13f**) proceeded also smoothly in $scCO_2$ at 60°C, but with a disappointingly low ee (Table 3, entry 11). Lowering the reaction temperature to 42°C lead to a dramatic increase in enantioselectivity, but the reaction rate decreased strongly at the same time (Table 3, entry 10). A similar influence of the reaction temperature was observed with indene **13h** (Table 3, entry 13 and 14), which confirmed to be a difficult substrate for hydroformylation in $scCO_2$ just like in conventional solvents [14,29].

We also attempted to use the novel catalytic system for desymmetrization of the norbornadiene skeleton (**13g**) by asymmetric hydroformylation. A 30/70 mixture of mono- and bis-hydroformylated products was formed under standard reaction conditions in a single homogeneous phase (Table 3, entry 12). The first hydroformylation proceeds with virtually no enantio-discrimination (ee of **16g** < 1%) and the diastereoselectivity of the second hydroformylation is also very small, yielding a mixture of *meso*-product **15g** and chiral product **14g** of 59:41. Nevertheless, the bis-aldehyde **14g** was obtained with an ee of 20.6%, indicating that a significant enantio-discrimination occurs during formation of the chiral bis-hydroformylated product.

The regioselectivities in favor of the branched chiral aldehydes using perfluoroalkyl-substituted **10** as a ligand for rhodium-catalyzed enantioselective hydroformylation in $scCO_2$ are significantly higher than those achieved with unsubstituted BINAPHOS in benzene where comparable data are available [29]. In previous work, it has been unambiguously shown that the regioselectivity of hydroformylation reactions using ligand-free cobalt [26a,30] or rhodium [5] catalysts can be affected by changing the reaction medium from liquid organic solvents to $scCO_2$. On the other hand, the regioselectivity of hydroformylation using ligand-modified catalysts is also highly sensitive to very subtle structural variations of the phosphines [31]. As mentioned above, the increase in regioselectivity with **10** was found to be independent of the phase behavior and remained pertinent also in conventional hydroformylation solvents such as benzene (Table 3) [20]. The higher regioselectivities must therefore be attributed to the substitution pattern of the CO_2-philic ligand. Although steric effects cannot be ruled out at this point [32], the increase in selectivity can be fully rationalized on basis of a small electron-donating effect of the $(CH_2)_2(CF_6)_2F$ substituent (see Section 2.2), applying the recent model of Casey and coworkers [31b]. Since the PAr_2 units of **10** and BINAPHOS occupy an equatorial position in the five-coordinate hydrido carbonyl intermediate, the higher preference for the formation of the branched aldehydes **10** is in accord with a slightly more electron-rich nature of this donor group in **10** as compared to the unmodified BINAPHOS ligand.

Although the BINAPHOS-ligand has found a number of highly interesting applications in asymmetric catalysis, there are currently no reports in literature about the use of this ligand system in hydrogenation reactions [33]. This may not be surprising, as it is often assumed that different design principles are required for chelating ligands to be highly efficient in either rhodium-catalyzed asymmetric hydroformylation or hydrogenation. Our recent experience with the C_1-symmetric phosphine–phosphoramidite ligand QUINAPHOS [34] indicated that this paradigm may be less restricting than anticipated and prompted us to explore the potential of ligand **10** also for hydrogenation reactions in $scCO_2$. We were very pleased to find that addition of 1.1 equivalents of ligand **10** to the cationic rhodium complex $[Rh(cod)_2]BF_4$ formed an active hydrogenation catalyst that gave very high levels of enantiocontrol in the asymmetric hydrogenation of 2-acetamido methyl acrylate (**17a**) and dimethyl itaconate (**17b**) in compressed CO_2 as a solvent (Table 4). In contrast to previous systems [6,8,10] no exchange of the BF_4 anion was necessary to obtain a highly efficient asymmetric hydrogenation catalyst based on **10** under these conditions.

Hydrogenation of the dehydroamino acid **17a** (Table 4, entry 1) occurred in a biphasic system containing a liquid phase and a gas phase. The formation of the liquid phase at temperatures below the melting point of **17a** (m.p. 52–54°C) can be rationalized using the same arguments as for **13d** (Section 2.4) [36]. The alanine derivative **18a** was formed in quantitative yield with an ee of 97.2% in favor of the *R* enantiomer. In the hydrogenation of dimethyl itaconate (**17b**) in $scCO_2$ (Table 4, entry 2) the reaction mixture was initially opaque but became transparent and homogenous after a few minutes. The ee under these conditions was slightly lower than using the same catalytic system in CH_2Cl_2 at lower temperatures (Table 4, entry 3). These preliminary results underline the broad utility of the BINAPHOS skeleton in asymmetric catalysis and its general compatibility with the use of compressed CO_2 as a solvent.

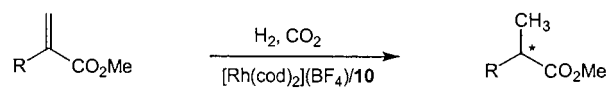
*2.4. Combination of catalysis and extraction using supercritical solutions (CESS process): product purification and catalyst recycling in rhodium-catalyzed hydroformylation using (R,S)-3-H²F⁶-BINAPHOS (**10**)*

Among the various potential benefits often discussed for the use of $scCO_2$ in homogeneous catalysis, the development of 'solventless' syntheses including novel work-up and purification procedures is particularly attractive from a practical point of view [4–6,13,35]. This may be especially useful for high-boiling products, where distillation is either impracticable or puts too much thermal stress on sensitive catalysts. The extractive properties of $scCO_2$ [3] have an interesting potential for enhanced protocols for product purification and catalyst immobilization in enantioselective hydroformylation using rhodium catalysts of (*R*,*S*)-3-H^2F^6-BINAPHOS (**10**).

In contrast to all other substrates, 2-vinyl-naphthalene (**13d**) did not form a homogeneous reaction mixture under typical hydroformylation conditions, but this did not prevent efficient catalysis with **10**/Rh. Although the reaction temperature was held just around or even below the melting points of the organic components, a clear liquid phase was present rather than a viscous melt or a solid at the bottom of the reactor. The formation of the liquid phase results from melting point depression caused by the solubility of CO_2 in the organic compounds. This effect has been utilized recently for solventless hydroformylation of **13d** using subcritical CO_2 and a non-chiral rhodium catalyst [36]. Subcritical CO_2 cannot dissolve substrates or catalysts and its only role is to provide a liquid phase at low temperatures in this case. Under our reaction conditions however, the high density $scCO_2$ phase in the upper part of the reactor can be expected to dissolve at least parts of the reaction components [37]. Indeed, two different crops of product could be isolated when the work-up of the reaction mixture was carried out carefully. Upon cooling the reactor to 0°C before venting, visual inspection of the reactor content showed that the liquid phase on the bottom solidified and at the same time a white solid precipitated from the supernatant CO_2 phase, completely covering the walls and the lid inside the autoclave. After venting and opening the reactor, the two materials could be mechanically separated (bottom layer/precipitate = ca. 3:1 by weight) and analyzed individually. Both layers were found to contain exclusively the two aldehydes **14d** and **15d** as organic products and the enantiomeric excess of **14d** was identical within experimental error in both samples. However, the precipitate showed a significant and reproducible enrichment in favor of the branched chiral aldehyde (**14d**/**15d** = 98.0:2.0) as compared to the bottom layer (**14d**/**15d** = 90.9:9.1).

The enrichment with chiral product in the upper phase results from the preferential solubility of the branched aldehyde over the linear product in supercritical carbon dioxide [38], as demonstrated unambiguously by a control experiment. In this experiment, a sample (420 mg) with the composition **14d**/**15d** = 90.9:9.1 was placed in the autoclave, pressurized with CO_2 ($d = 0.83$ g ml^{-1}), and heated to 45°C for 5 min.

Table 4
Enantioselective hydrogenation of **17a** and **17b**



17a: R=NH(CO)Me
17b: R=CH_2CO_2Me
18a
18b

Entry	Substrate	Solvent	*d* (CO_2) (g cm^{-3})	*T* (°C)	pH_2 (bar)	*t* (h)	Conversion (%)	ee (%)
1	**17a**	CO_2	0.74	40	30	16	>99	97.2 (*R*)
2	**17b**	CO_2	0.74	40	30	16	>99	96.6 (*S*)
3	**17b**	CH_2Cl_2		23	30	24	>99	99.4 (*S*)

Table 5
Rhodium-catalysed asymmetric hydroformylation of styrene (**13a**) applying the CESS process

Run	S/Rh	T (°C)	$P_{H_2/CO}$ (bar)	t (h)	CO_2 for extraction [a]			Conversion [b] (%)	Regioselectivity (%)	ee (%)	Rh leaching (ppm)
					T (°C)	p (bar)	V (l)				
1	1000	55	19	17	63	94	200	82.6	90.9	86.6	0.97
2	1000	55	34	15	60	100	170	97.4	92.0	90.4	0.78
3	2000	50	40	65	61	105	270	99.9	92.2	90.2	0.45
4	1500	54	40	15	61	103	200	92.4	91.2	82.1	0.36
5	1400	55	38	15	59	107	128	95.5	91.5	77.6	1.94
6	3000	40	61	114	60	115	213	98.6	92.9	66.4	0.95
7	1500	50	50	16	60	104	173	95.1	91.4	70.2	0.41
8 [c]	1000			41				89.4	92.4	88.2	

[a] Flow-rate about 1 l min^{-1}, all volumes at ambient conditions.
[b] Quantitative recovery.
[c] One additional equivalent of ligand was added.

Then the autoclave was cooled down to 0°C and vented, whereby the same formation of two different product phases was observed as described above. The amount and composition of the two materials proved also largely identical to the products from the catalytic reaction (bottom layer: 270 mg, **14d**/**15d** = 90.0:10.0; precipitate: 120 mg, **14d**/**15d** = 96.0:4.0). This finding demonstrates nicely the potential for the use of $scCO_2$ not only as solvent during catalysis, but also as medium for subsequent purification processes of the reaction products.

The density-tuneable solvent capacity of $scCO_2$ provides also the possibility to separate and recycle the rhodium catalyst based on **10** in active and selective form as demonstrated for the enantioselective hydroformylation of styrene **13a**. After each run, the reaction mixture was cooled to room temperature and CO_2 was vented partly to reduce the density of the solvent. The mixture was then re-heated, resulting in a two-phase system consisting of a liquid phase and a compressed gas phase. As judged from the coloration, the metal-containing species were contained preferentially in the liquid phase, but the organic products can be expected to distribute significantly between both phases (vide supra). The reactor was now purged from the bottom with CO_2 at constant temperature and pressure, stripping away the products and leaving behind the catalyst for subsequent use.

Eight successive runs were performed according to this procedure, using **13a** under standard conditions and intervened by the extraction step and by reactants charging (Table 5). No apparent loss in selectivity or activity occurred up to the third run. The next three runs saw a slow decrease in enantioselectivity, but regioselectivity and conversion remained uniformly high. Even under these not-optimised simple experimental conditions, the CESS-procedure allowed quantitative recovery of the solvent-free reaction product with a Rh content ranging from 0.36 to 1.94 ppm as determined from atomic absorption measurements. Moreover, the **10**–Rh system was still active after a total catalytic turnover of more than 12 000 TON/Rh, albeit with a moderate decrease in selectivity. The decrease in enantiomeric excess of **14a** may be attributed at least partly to racemization of the product under the experimental conditions [16a], as indicated by the exceptionally low ee resulting from the long contact time chosen in run six. The initial high level of enantioselectivity could be restored by adding only one additional equivalent of ligand in the last run.

3. Conclusions

The results of the present paper illustrate the remarkable potential of supercritical carbon dioxide ($scCO_2$) as a reaction medium for asymmetric synthesis using chiral organometallic catalysts under environmentally benign conditions. As shown here for the BINAPHOS framework, well established and highly efficient ligand systems containing PAr_2 donor groups can be readily adjusted to this non-conventional solvent by modification with perfluoroalkyl substituents whereby the synthetic effort to assemble the chiral ligand framework is largely similar to that of the parent compound. The new ligand (*R*,*S*)-3-H^2F^6-BINAPHOS forms highly efficient enantioselective rhodium catalyst for hydroformylation and (as shown for the first time for BINAPHOS-derivatives) also for hydrogenation.

Choosing the $F(CF_2)_6(CH_2)_2$ group as the CO_2-philic solubilizers results only in a small structural modification of the donor group, but this may still induce a measurable change in selectivity during the complex framework of the catalytic cycle. On the other hand, there is mechanistic evidence emerging from this paper and a related study [10] that the solvent CO_2 does not

interfere directly with the catalytic cycle in hydroformylation and hydrogenation reactions using chiral rhodium–phosphine catalysts. In view of the high reactivity of many metal hydrides towards CO_2 [39], which is manifested not the least in efficient catalytic systems for hydrogenation of $scCO_2$ itself [40], this inert behavior is still somewhat unexpected and may not be universal.

Even in the absence of any chemical interaction, the physico-chemical properties of $scCO_2$ can provide a number of potential benefits for enantioselective catalysis. Using asymmetric hydroformylation with a rhodium catalysts based on **10** as a model reaction, we have laid particular emphasis on its simultaneous use as a medium for reaction and work-up in the present study. We were able to confirm that the selective and density-dependent solubility properties of $scCO_2$ can lead to enrichment of the desired chiral regioisomer in the product stream and can also be used to separate and recycle the precious catalyst in active and selective form. Even with simple equipment and in non-optimised batch-wise operation, remarkable separation efficiency was observed and rhodium contamination of the product could be limited to below 1 ppm. More sophisticated work-up schemes including continuous processes can be readily envisaged and seem highly promising on basis of the present developments.

4. Experimental

4.1. General

Caution: working with highly compressed gases must be carried out only using suitable equipment and under appropriate safety precautions.

All manipulations involving air- and moisture-sensitive compounds were carried out using standard Schlenk techniques under argon. Solvents and olefins were dried, purified, and degassed according to literature protocols and stored under argon. The gases CO/H_2 (1:1), argon (99.995%), and CO_2 (99.9995%) were purchased from Messer Griesheim. Compounds 1-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octyl)-benzene [21], (*R*)-2,2′-bis[trifluoromethanesulfonyl)oxi]-1,1′-binaphthalene (**6**) [41], and (*S*)-4-chloro-3,5-dioxa-4-phospha-cyclohepta[2,1-a;3,4-a′]dinaphthalene [42] were synthesized according to literature procedures. All other compounds are commercially available and were used without further purification. NMR spectra were recorded on Bruker AC 200, AMX 300, ARX 400, and AMX 600 spectrometers. Chemical shifts are given in ppm relative to Me_4Si (^1H, ^{13}C), 85% H_3PO_4 (^{31}P), or $CFCl_3$ (^{19}F) as external standard. The ^{103}Rh shifts are given relative to $\Xi(^{103}Rh) = 3.16$ MHz and were reproducible within 1 ppm [23]. Electron ionization (70 eV) mass spectra were recorded on a Finnigan MAT 95 instrument. GC measurements were carried out on Carlo Erba 5300 and Hewlett–Packard 5890 instruments. Optical rotations were measured on a JASCO DIP-360 spectometer. Rhodium content was determined by atomic absorption spectroscopy (AAS).

4.2. General procedure for the rhodium-catalyzed hydroformylation of olefins in $scCO_2$

Hydroformylation experiments were carried out in a window-equipped stainless-steel high-pressure reactor ($V = 10$ ml). The reactor was charged under an atmosphere of argon with complex [Rh(acac)$(CO)_2$] (1×10^2 μl, 0.02 M in THF) and the appropriate amount of ligand **10** to adjust the desired ratio of **10**/Rh. After stirring the reaction mixture for 5 min, the solvent was removed in vacuo and then the substrate (typically 2–4 mmol) was introduced under an atmosphere of argon. The reactor was pressurised with a 1:1 mixture of CO and H_2 and then filled with a weighed amount of CO_2 by means of a compressor. The reaction mixture was heated and stirred with a PTFE stirring bar for the desired reaction time. After cooling to 0°C, the reactor was carefully vented. The reaction mixture was collected by extraction of the reactor content with benzene-d_6 and analyzed both by ^1H-NMR spectroscopy and, after filtration through a short path of silica, by GC analysis in order to determine conversion and regioselectivity. The enantiomeric excess of the branched aldehydes **14a**–**h** was determined by GC analysis using a diethyl-*tert*-butylsilyl-β-cyclodextrin capillary column (IVADEX 7).

4.3. Hydroformylation of styrene in $scCO_2$ combined with product extraction (CESS process)

After performing the catalysis, the reaction vessel ($V = 100$ ml) was cooled down to room temperature (r.t.) and slowly depressurized until a CO_2 density of about 0.3 g ml^{-1} was reached, at which point the vessel was warmed again to about 60°C ($p \cong 100$ bar). Fresh CO_2 was pumped into the vessel by means of a compressor through a needle valve located at the bottom of the vessel and product-enriched CO_2 was released with similar flow rate from a valve located on the top of the vessel through a cold trap, keeping the pressure constant during the extraction. The extraction was carried out until no more liquid phase was visually detectable and in all cases, quantitative recovery of the product mixture was achieved. After the extraction was completed, the autoclave was filled again with fresh substrate, pressurized with synthesis gas and then filled with CO_2 until a total pressure at reaction temperature of 198 ± 1 bar was obtained.

4.4. General procedure for hydrogenation experiments in $scCO_2$

The hydrogenation experiments were performed in the same reactor (V = 10 ml) using a similar procedure as that employed for the hydroformylation experiments. In this case the catalyst was formed in situ from $[Rh(cod)_2]BF_4$ (1×10^2 μl, 0.02 M in CH_2Cl_2) and the ligand **10** (1×10^2 μl, 0.022 M in CH_2Cl_2). After stirring the catalyst solution for 5 min, the solvent was removed in vacuo and then the substrate (2 mmol) was introduced under an atmosphere of argon. The reactor was pressurized with H_2 and then filled with a weighed amount of CO_2 by means of a compressor. The reaction mixture was heated and stirred with a PTFE stirring bar for 16 h. After cooling to 0°C, the reactor was carefully vented. The reaction mixture was collected by extraction of the reactor content with toluene, filtered through a short path of silica, and analyzed by GC. The enantiomeric excess was determined by GC analysis using a β-cyclodextrin and a trifluoroacetyl γ-cyclodextrin capillary column for **18a** and for **18b**, respectively.

4.5. Synthesis of bis-[3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octyl)-phenyl]-phosphinoxide (4)

A pentane solution of *n*-BuLi (21 ml, 1.7 M) was added dropwise at −25°C to a solution of 1-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,8 - tridecafluoro - octyl) - benzene (18.0 g, 3.6×10^{-3} mol) in diethyl-ether (200 ml). The mixture was warmed up to 0°C and stirred for 30 min at this temperature. Diethylamino–dichlorophosphine (2.6 ml, 0.017 mol) was added at −40°C via syringe to the resulting intensive yellow solution and then the reaction mixture was slowly allowed to warm to r.t., whereby large amounts of precipitate (presumably LiCl) were formed. After 2 h, a ^{31}P-{^1H}-NMR (THF-d_8–diethyl-ether) spectrum of the supernatant reaction mixture showed only one peak ($\delta = 62.6$ s) corresponding to bis-[3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octyl)-phenyl]-diethyl-amino-phosphine (**3**). The reaction mixture was then treated with 5 ml of HCl_{conc} under vigorous stirring. The organic phase was separated, washed with saturated NaCl solution (2 × 20 ml) and saturated $NaHCO_3$ solution (2 × 20 ml), and then dried over $MgSO_4$. The solvents were removed under reduced pressure leading to a pale yellow oil. Spectroscopically pure product was obtained by crystallization from pentane as a colorless microcrystalline compound (yield: 64%).

^{31}P-{^1H}-NMR ($CDCl_3$): $\delta = 21.3$ (s). ^1H-NMR (CD_2Cl_2): $\delta = 7.94$ (d, $^1J_{PH} = 482.6$ Hz, 1H, P–H), 7.57–7.32 (m, 8H, Ar–H), 2.94–2.83 (m, 4H, CH_2), 2.43–2.20 (m, 4H, CH_2). ^{19}F-{^1H}-NMR (CD_2Cl_2): $\delta = -81.5$ (m, 3F, CF_3), −114.9 (m, 2F, CF_2), −122.2 (m, 2F, CF_2), −123.2 (s broad, 2F, CF_2), −123.8 (s, 2F, CF_2), −126.6 (m, 2F, CF_2). MS (EI): m/z 894.

4.6. Synthesis of (R)-trifluoro-methanesulfonic acid 2′-{bis-[3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octyl)-phenyl]-phosphinoyl}-[1,1′]binaphthalenyl-2-yl ester (7)

Palladium diacetate (150 mg, 0.67 mmol), 1,3-bis-(diphenylphosphino)-propane (290 mg, 0.68 mmol), (*R*)-**6** (2.295 g, 4.17 mmol), and **4** (7.5 g, 8.35 mmol) were placed in a Schlenk tube together with dimethylsulfoxide (25 ml) and diisopropylethylamine (15 ml). The reaction mixture was heated to 120°C for 12 h. After cooling to r.t., the reaction mixture was concentrated under vacuo to obtain a dark red residue. The residue was solubilized in ethylacetate and washed twice with saturated Na_2CO_3 solution. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by chromatography on silica (hexane–ethylacetate 3:1). Yield: 91% (white solid).

^{31}P-{^1H}-NMR ($CDCl_3$): $\delta = 28.2$ (s). ^1H-NMR ($CDCl_3$): $\delta = 8.03$–7.80 (m, 4H, Ar–H), 7.66–7.52 (m, 2H, Ar–H), 7.46–7.19 (m, 11H, Ar–H), 7.11–7.03 (m, 2H, Ar–H), 6.88 (m, 1H, Ar–H), 2.83–2.71 (m, 4H, CH_2), 2.36–2.07 (m, 4H, CH_2). ^{19}F-{^1H}-NMR ($CDCl_3$): $\delta = -75.3$ (s, 3F, $OS(O_2)CF_3$), −81.1 (m, 6F, CF_3), −114.8 (m, 4F, CF_2), −122.1 (m, 4F, CF_2), −123.1 (m, 4F, CF_2), −123.7 (s, 4F, CF_2), −126.4 (m, 4F, CF_2). LCMS (ESIpos): 1295 [M + H].

4.7. Synthesis of (R)-2′-{bis-[3-(3,3,4,4,5,5,6,6,7,7,-8,8,8-tridecafluoro-octyl)-phenyl]-phosphinoyl}-[1,1′]-binaphthalenyl-2-ol (8)

A saturated LiOH solution (30 ml) was added to a solution of **7** (4.8 g, 3.7 mmol) in THF (30 ml) and the resulting biphasic mixture was stirred vigorously overnight. The reaction mixture was acidified (pH 2) with concentrated HCl, extracted with ethylacetate (2 × 40 ml), dried over $MgSO_4$, and concentrated under reduced pressure. The resulting pale yellow solid was purified by chromatography on silica (hexane–ethylacetate 2:1). Yield: 69% (white solid).

^{31}P-{^1H}-NMR ($CDCl_3$): $\delta = 30.4$ (s). ^1H-NMR ($CDCl_3$): $\delta = 7.94$–7.80 (m, 3H, Ar–H), 7.74 (m, 1H, Ar–H), 7.59 (m, 1H, Ar–H), 7.56–7.32 (m, 6H, Ar–H), 7.22–6.99 (m, 5H, Ar–H), 6.90 (m, 1H, Ar–H), 6.71–6.59 (m, 2H, Ar–H), 6.40 (m, 1H, Ar–H), 3.04–2.93 (m, 2H, CH_2), 2.56–2.26 (m, 4H, CH_2), 2.17–1.92 (m, 2H, CH_2).

^{19}F-{^1H}-NMR ($CDCl_3$): $\delta = -81.1$ (m, 3F, CF_3), −114.6 (m, 1F, CF_2), −114.9 (m, 1F, CF_2), −122.1 (m, 2F, CF_2), −123.1 (m, 2F, CF_2), −123.6 (m, 2F, CF_2), −126.3 (m, 2F, CF_2). LCMS (ESIpos): 1163 [M + H].

*4.8. Synthesis of (R)-2′-{bis-[3-(3,3,4,4,5,5,6,6,7,7,-8,8,8-tridecafluoro-octyl)-phenyl]-phosphanyl}-[1,1′]-binaphthalenyl-2-ol (**9**)*

Trichlorosilane (1.92 ml, 0.014 mol) and triethylamine (2.8 ml) was added to a solution of **8** (2.03 g, 0.02 mol) in toluene (40 ml) at 0°C. The reaction mixture was heated at 100°C for 12 h. After cooling to r.t., the reaction mixture was quenched with degassed 2 N NaOH (1 ml). The organic phase was filtered through a path of Celite and $MgSO_4$, and then concentrated under reduced pressure to give **9** as a white solid. Yield: 61%.

^{31}P-{^{1}H}-NMR (C_6D_6): $\delta = -12.7$ (s). ^{1}H-NMR (C_6D_6): $\delta = 8.00–7.28$ (m, 10H, Ar–H), 7.22–6.60 (m, 10H, Ar–H), 2.80–2.63 (m, 2H, CH_2), 2.57–2.42 (m, 2H, CH_2), 2.29–1.80 (m, 4H, CH_2). LCMS (ESIpos): 1147 [M + H].

*4.9. Synthesis of 4-(2′-{bis-[3-(3,3,4,4,5,5,-6,6,7,7,8,8,8-tridecafluoro-octyl)-phenyl]-phosphanyl}-[1,1′]-(R)-binaphthalenyl-2-yloxy)-3,5-dioxa-4-phospha-cyclohepta[2,1-a;3,4-a′]-(S)-dinaphthalene, 3-H^{2}F^6-(R,S)-BINAPHOS (**10**)*

A solution of **9** (2.0 g, 1.74 mmol) and triethylamine (1.2 ml, 8.6 mmol) in toluene (20 ml) was added dropwise at 0°C to a solution of (*S*)-4-chloro-3,5-dioxa-4-phospha-cyclohepta[2,1-a;3,4-a′]dinaphthalene (0.611 g, 1.74 mmol) in toluene (10 ml). The reaction mixture was stirred overnight at r.t., filtered off, and concentrated under reduced pressure. The residue was extracted with pentane to obtain the pure title compound. Yield: 99% (white solid).

^{31}P-{^{1}H}-NMR (243.0 MHz, C_6D_6): $\delta = 146.5$ (d, $J_{PP'} = 27.8$ Hz), -13.3 (d). ^{1}H-NMR (600.2 MHz, C_6D_6): $\delta = 7.88–6.38$ (m, 32H, Ar–H), 2.41–2.34 (m, 4H, CH_2), 1.95–1.79 (m, 4H, CH_2). ^{13}C-NMR (150.9 MHz, C_6D_6): $\delta = 148.20$ (d, $J_{P(1)C} = 4.2$ Hz, arom *C*), 148.06 (dd, $J_{P(1)C} = 8.2$, $J_{P(2)C} = 1.8$ Hz, arom *C*), 147.69 (d, $J_{P(1)C} = 2.5$ Hz, arom *C*), 141.71 (d, $J_{P(2)C} = 34.3$ Hz, arom *C*), 139.26 (d, $J_{P(2)C} = 5.6$ Hz, arom *C*), 138.96 (s, arom *C*), 138.94 (d, $J_{P(2)C} = 25.1$ Hz, arom *C*), 137.82 (d, $J_{P(2)C} = 14.6$ Hz, arom *C*), 137.01 (d, $J_{P(2)C} = 12.1$ Hz, arom *C*), 134.91 (d, $J_{P(2)C} = 31.9$ Hz, arom *C*H), 134.85 (d, $J_{P(2)C} = 2.4$ Hz, arom *C*), 134.28 (s, arom *C*), 134.06 (d, $J_{P(2)C} = 7.0$ Hz, arom *C*), 133.36 (s, arom *C*), 133.11 (d, $J_{P(2)C} = 19.2$ Hz, arom *C*H), 132.91 (s, arom *C*), 132.69 (d, $J_{P(2)C} = 11.5$ Hz, arom *C*H), 132.04 (s, arom *C*), 131.92 (d, $J_{P(2)C} = 17.5$ Hz, arom *C*H), 131.62 (s, arom *C*), 131.19 (s, arom *C*), 130.66 (s, arom *C*H), 130.47 (s, arom *C*H), 130.41 (s, arom *C*H), 129.64 (s, arom *C*H), 129.03 (d, $J_{P(2)C} = 5.5$ Hz, arom *C*H), 128.89 (d, $J_{P(2)C} = 4.7$ Hz, arom *C*H), 128.81 (s, arom *C*H), 128.76 (s, arom *C*H), 128.61 (s, arom *C*H), 128.51 (s, arom *C*H), 130.41 (s, arom *C*H), 128.28 (s, arom *C*H), 128.21 (s, arom *C*H), 127.41 (d, $J_{P(2)C} = 2.0$ Hz, arom *C*H), 127.38 (s, arom *C*H), 127.27 (s, arom *C*H), 127.24 (s, arom *C*H), 127.16 (s, arom *C*H), 126.69 (s, arom *C*H), 126.59 (s, arom *C*H), 126.44 (s, arom *C*H), 126.34 (s, arom *C*H), 125.29 (s, arom *C*H), 125.01 (s, arom *C*H), 124.88 (s, arom *C*H), 123.35 (d, $J_{P(1)C} = 1.7$ Hz, arom *C*), 121.98 (s, arom *C*H), 121.85 (s, arom *C*H), 120.98 (d, $J_{P(1)C} = 8.6$ Hz, arom *C*H), 120.55–106.75 (m, CF_x), 32.51 (t, $J_{FC} = 22.0$ Hz, $CH_2CH_2CF_2$), 32.31 (t, $J_{FC} = 21.9$ Hz, $CH_2CH_2CF_2$), 26.27 (s, $CH_2CH_2CF_2$), 26.12 (s, $CH_2CH_2CF_2$). ^{19}F-{^{1}H}-NMR (282.4 MHz, $CDCl_3$): $\delta = -81.3$ (m, 6F, CF_3), -114.6 (m, 4F, CF_2), -122.1 (m, 4F, CF_2), -123.1 (m, 4F, CF_2), -123.5 (m, 2F, CF_2), -123.7 (m, 2F, CF_2), -126.4 (m, 4F, CF_2). LCMS (ESIpos): 1461 [M + H]. $[\alpha]_D^{20} = +177°$ (ca. 1.0, toluene).

*4.10. Synthesis of the complex [Rh(**10**)(acac)] (**11**)*

A pre-cooled solution of the ligand **10** (146 mg, 0.1 mmol) in THF (10 ml) was added to a solution of [Rh(acac)(CO)$_2$] (25.8 mg, 0.1 mmol) in THF (10 ml) at -78°C. After 30 min at -78°C, the reaction mixture was slowly allowed to warm to r.t. and then stirred for further 60 min. The reaction mixture was concentrated to a volume of about 2 ml and pentane was added (20 ml) to form a bright-yellow precipitate that was collected and washed with pentane (10 ml). Yield 98%.

^{31}P-{^{1}H}-NMR (C_6D_6): $\delta = 161.9$ (dd, $J_{PP'} = 84$, $J_{RhP} = 330$ Hz), 49.6 (dd, $J_{RhP'} = 175$ Hz). ^{1}H-NMR (C_6D_6): $\delta = 8.18–6.58$ (m, 32H, Ar–H), 5.26 (s, 1H, CH), 2.81–2.63 (m, 2H, CH_2), 2.52–1.68 (m, 6H, CH_2), 2.18 (s, 3H, CH_3), 1.34 (s, 3H, CH_3). ^{103}Rh-NMR (C_6D_6): $\delta = 271$.

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