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Novel α-fluorinated cyclic phosphite and phosphinite ligands and their Rh-complexes as suitable catalysts in hydroformylation

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Abstract

Asymmetrical cyclic phosphite and phosphinite ligands of a novel type bearing either trifluoromethyl or pentafluorophenyl group were synthesized using >PCl or >PN< species and racemic fluorinated alcohols. The P-ligands were converted to complexes of $Rh^{III}(L)(Cp^*)Cl_2$ type (where L = phosphite or phosphinite) and, in two instances, their stereostructures were evaluated by X-ray analysis. These complexes along with in situ systems, formed from $Rh(CO)_2$(acac) precursor and the corresponding ligand, were tested in the hydroformylation of styrene. Both systems provided excellent hydroformylation activities at 100 °C. Using the Rh^I in situ systems, moderate and high regioselectivities towards the branched aldehyde (2-phenyl-propanal) were obtained at 100 and 40 °C, respectively.

Keywords: Cyclic phosphite- and phosphinite ligands; Rhodium complexes; Stereostructure; Homogeneous catalysis; Hydroformylation

1. Introduction

Hydroformylation is probably one of the most detailed investigated homogeneous catalytic reaction. Since the discovery of Roelen in 1938, hundreds of cobalt, rhodium and platinum complexes have been tested as catalysts in the hydroformylation of a great variety of olefins. Both the hydroformylation of simple substrates like propene and the asymmetric hydroformylation (e.g., that of vinylaromatics) hold an enormous potential in synthesis [1]. To find an appropriate balance of chemo-, regio and enantioselectivities, as well as a satisfactory catalytic activity, the search for efficient hydroformylation catalysts still remains a challenge.

Naturally, the most important variable in a homogeneous catalytic system is the ligand itself. Transition metal catalysts applying ligands with phosphorus donors are used almost exclusively [2]. Although mostly mono- and ditertiary phosphines are used, phospholes have also been thoroughly investigated during the systematic structural variation of the ligands [3]. Many examples

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are known where insignificant changes in the structure of the ligand resulted in profound change of the catalytic activity.

In recent years, the interest was shifted from σ-donor phosphines to π-acceptor phosphites and amidophosphites. This is connected with the ease of their synthesis, their high stability, absence of oxidation-sensitive P–C bonds in the molecule and higher stability of the corresponding metal complexes. Although the number of such examples is less than those of phosphines, several applications have been described [4]. Most of the papers published up till now on rhodium–phosphite catalysed hydroformylation reactions involve triphenylphosphite [5], trialkylphosphite (trimethylphosphite [6] and tricyclohexylphosphite [7]) ligands. There are several catalytic systems containing sterically bulky phosphites like 2-*t*-butyl-phenyl derivatives [8] or other 2-substituted aryl derivatives [9]. In this respect, most of the recent publications are devoted to the application of Rh–phosphite catalytic systems [10].

The application of chiral heterobidentate phosphine–phosphite derivatives (e.g., BINAPHOS [11] and its analogues [12]) with various rhodium precursors proved to be a real breakthrough in enantioselective hydroformylation of styrene providing enantiomeric excesses (e.e-s) of practical importance. Diphosphite analogues of the corresponding chiral diphosphines (BINAP [13], CHIRAPHOS [14], BDPP [15]) were also tested in enantioselective hydroformylations. Chiral diphosphites of novel type possessing 2,2-dimethyl-dioxolane ring were also used in the enantioselective hydroformylation of styrene [16]. A review devoted to the advances in Rh-catalyzed asymmetric hydroformylation using phosphite ligands of different types has been published recently [17].

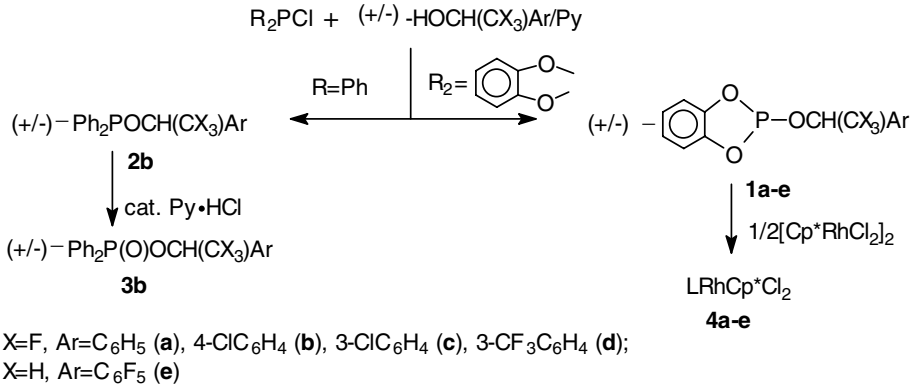
On the other hand, fluorinated ligands also find application in the field of catalysis and are of high interest in fluorous biphasic catalysis (FBC) [18]. For this purpose, the fluorine containing 'pony-tails' are introduced in a variety of known ligands and to reduce the cost and to simplify the introduction procedure, mostly short 'pony-tails' are used nowadays. Till now, the most studied and applied strategy has been focused on the development of monodentate fluorinated phosphines. They were used in hydroformylation [19], hydroboration [20], cross-coupling reactions [21] and in other processes. Regarding fluorine-containing phosphite ligands, a series of symmetrical tris(polyfluoroalkyl)phosphites was synthesized and their Ni complexes were tested in the cyclodimerization of isoprene [22]. Only the Ni complex with $P[OCH(CF_3)_2]_3$ having α-CF_3 groups on the secondary carbon atom was found to demonstrate a surprisingly high activity and selectivity in contrast to complexes with ligands based on primary polyfluoroalkanoles [22,23].

As a part of our continuing efforts regarding the systematic variation of ligands in rhodium-catalysed reactions, our studies were extended to asymmetrical cyclic phosphites with benzoanellation possessing a trifluoromethyl or pentafluorophenyl moiety in α-position. In the present paper, the synthesis of novel P-ligands, their use in the preparation of rhodium complexes, as well as the test of the complexes in hydroformylation reaction are discussed.

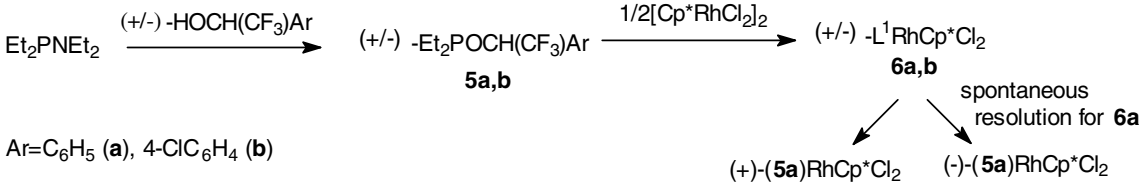
2. Results and discussion

2.1. Synthesis of the ligands and Rh^{III} complexes thereof

In order to obtain the ligands, phosphorylation of the racemic fluorinated alcohols either by P-chlorides ('chloride' method), or by amides ('amide' method) of the corresponding phosphorus(III) acids may be applied in principle. We found that the 'chloride' methodology could be successfully applied only for ligands **1a**–**e** with the 1,3,2-benzodioxaphospholene moiety that are not sensitive towards oxidation (Scheme 1). In contrast, phosphinites are very sensitive towards oxidation, especially in



Scheme 1.



Scheme 2.

solutions. Thus, using the 'chloride' methodology, phosphorylation of the diphenyl- or diethylchlorophosphine is accompanied by partial oxidation even under protective atmosphere of argon apparently catalyzed by the pyridine hydrochloride formed. Moreover, the typical isolation procedure in the reaction of diphenylchlorophosphine with $4\text{-ClC}_6\text{H}_4\text{CH(CF}_3\text{)OH}$ afforded the corresponding phosphinate **3b** instead of phosphinite **2b**.

To overcome this problem, the substitution of diethylamino moiety of the phosphorus atom for the corresponding residue of the racemic alcohol may be used. The interaction proceeds at an elevated temperature in the absence of any solvent according the procedure described by us earlier for **5a** [24] (Scheme 2). The other diethylphosphinite ligand **5b** was obtained similarly by the 'amide' procedure in nearly quantitative yield (see Tables 1,2).

Ligands **1a–e** and **5a,b** appeared as sharp singlets in the ^{31}P NMR spectra at *ca.* 126 or 154 ppm, respectively. The trifluoromethyl group resonates at 0.0–0.9 ppm (either as a singlet or as a doublet with a $^4J_{PF}$ coupling constants up to 6.2 Hz) in the ^{19}F NMR spectra. In the ^{1}H and ^{13}C NMR spectra of the compounds, the signals of the protons and skeletal carbon atoms can be found in the typical regions in agreement with the suggested structure.

Interaction of the ligands **1a–e** and **5a,b** with dimeric (pentamethylcyclopentadienyl)rhodium dichloride in CH_2Cl_2 solution resulted in the corresponding complexes **4a–e** and **6a,b**, respectively. They have been obtained as dark red crystalline compounds incorporating chlorinated hydrocarbons. In some cases, the solvates were disrupted by heating the complexes in vacuo to afford the solvent-free forms as orange-red powders. In the ^{31}P NMR spectra, the cyclic phosphite (**4a–e**) and the diethylphosphinite complexes (**6a,b**) were characterized by δ_P chemical shifts appearing at *ca.* 135 and 155 ppm, respectively. Sharp doublets with characteristic coupling constant ($^1J_{PRh}$) ranging between 241 and 246 Hz for **4a–e** and 155.5–156.5 Hz for **6a,b** were observed. It should be noted that the values of chemical shifts for the complexes are rather close to those of the corresponding P-ligands (**1a–c** and **5a,b**) (the $\Delta\delta$ is *ca.* 10 and about 2 ppm, respectively) that may be in accord with rather weak coordination bonds.

Single crystal X-ray analysis was carried out for representative Rh^{III} complexes bearing either a 1,3,2-benzodioxaphospholene moiety, or two ethyl substituents on the phosphorus atom, namely for **4d** and **6a**, respectively. The X-ray analysis carried out for complex **4d** revealed that it crystallizes as a solvate with one molecule of CH_2Cl_2 (Fig. 1). The complex **4d** crystallizes as racemate (space group $Pca2_1$). The phosphorus atom in **4d** is

Table 1
Yields and elemental analyses of **1a–e 3b**, **5b** and Rh^{III} complexes **4a–e**, **6b**

Compound	Yield (%)[a]	m.p. (°C)	Found (calcd.) (%)		Formula
			C	H	
1a	100(88)	Oil	53.28(53.52)	3.20(3.21)	$C_{14}H_{10}F_3O_3P$
1b	93[b]	Oil	–	–	–
1c	97(80)	49–50(hexane)	48.56(48.23)	2.74(2.60)	$C_{14}H_9ClF_3O_3P$
1d	96(61)	42–43(hexane)	47.22(47.14)	2.30(2.37)	$C_{15}H_9F_6O_3P$
1e	100(78)	57–59(hexane)	48.01(48.02)	2.31(2.30)	$C_{14}H_8F_5O_3P$
3b	90(68)	60	58.59(58.48)	3.71(3.68)	$C_{20}H_{15}ClF_3O_2P$
4a	73(58)	96–97	44.02(44.20)	3.90(3.94)	$C_{24}H_{25}Cl_2F_3O_3PRh \cdot 0.5CH_2Cl_2$
4b	87(62)	108–109	42.68(42.90)	3.74(3.64)	$C_{24}H_{24}Cl_3F_3O_3PRh \cdot 0.5CH_2Cl_2$
4c	92(63)	77–78	43.76(43.83)	3.81(3.68)	$C_{24}H_{24}Cl_3F_3O_3PRh \cdot$
4d	100(53)	105–107	40.21(40.23)	3.22(3.38)	$C_{25}H_{24}Cl_2F_6O_3PRh \cdot CH_2Cl_2$
4e	100(67)	162–163	43.61(43.73)	3.54(3.52)	$C_{24}H_{23}Cl_2F_5O_3PRh$
5b	100(96)	100–102/0.1	43.54(43.58)	4.68(4.57)	$C_{12}H_{15}ClF_3OPS$[c]
6b	100(84)	145–146	43.18(43.12)	5.76(4.96)	$C_{22}H_{35}Cl_3F_3OPRh \cdot$

[a] The yield according to NMR data, in brackets the yield of isolated analytically pure compound.
[b] It was used for complexation without further purification.
[c] Analytical data for thione derivative $Et_2P(S)OCH(CF_3)C_6H_4$-Cl-4 purified by column chromatography (silica gel, hexane:acetone 100:3).

Table 2
Selected ^{31}P, ^{19}F, ^{1}H and ^{13}C NMR parameters for compounds obtained

Compound	NMR spectra: ppm, J Hz, $CDCl_3$							
	^{31}P	^{19}F	^{1}H		^{13}C			
	δ_p ($^{1}J_{P-Rh}$)	δ_{CF3} d ($^{4}J_{P-F}$) or s	δ_{OCH} dq ($^{3}J_{P-H}/^{3}J_{H-F}$)	$C^{*}_{p}d(^{1}J_{C^{*}_{p}-p})$	δ_{OCH} dq ($^{2}J_{P-C}/^{2}J_{C-F}$)	δ_{CF3}dq ($^{3}J_{P-C}/^{1}J_{C-F}$)	$\delta_{POCHC(Ar)}$c	$\delta_{POC(Ar)}$ d ($^{2}J_{P-C}$)
1a	127.09	0.29(1.2)	4.94(8.4/6.4)	–	73.77(2.1/33.6)	122.76(3.8/281.1)	131.78	145.00(7.5) 144.43(7.6)
1b	126.54	–2.27	4.85–4.91	–	–	–	–	–
1c	126.13	0.34	4.84–4.89 m	–	–	–	–	–
1d	125.57	0.19(6.1)[a]	4.96(7.6/6.4)	–	73.02 q $^{2}J_{C-F}$ = 34.4	122.35(3.8/281.4)	132.90	144.82(7.4) 144.17(7.6)
1e	125.52	[b]	5.27m[c] ($^{3}J_{P-H}$ = 6.8)	–	63.60 s	22.27 s	115.20 dt ($^{2}J_{P-C}$ = 3.1; $^{3}J_{C-F}$ = 13.6)	145.20 (7.7) 145.05 (7.9)
2b	125.07	0.55 (6.18)	–	–	–	–	–	–
3b	36.42	1.25	5.63–5.70 m	–	–	–	–	
4a	136.56 d (246.2)	1.25	5.71(8.8/6.0)	1.78(6.4)	76.42 q $^{2}J_{C-F}$ = 35.6	112.43 (6.6/47.8)	135.83	145.39(8.1) 145.62(7.7)
4b	135.92 d (244.5)	1.07	5.94(8.8/6.4)	1.74(6.4)	–	–	–	–
4c	135.51d(243.6)	1.29	5.91–5.97 m	1.74(6.6)				
4d	135.93 d (244.0)	1.21[a]	6.18(7.6/6.4)	1.74(6.8)	–	–	–	–
4e	134.94 d (241.3)	[b]	5.99 ($^{3}J_{P-H}$ = 7.1) apparent qv	1.76(6.7)	–	–	–	–
5a	157.94	0.83(5.25)	4.92–5.01 m	–				
5b	159.04	0.39(5.1)	4.88(8.9/6.9)	–				
6a	153.50(156.5)	2.60	5.72–5.78 m	1.62(3.6)				
6b	155.05(155.5)	–	5.75–5.82 m	1.63(3.6)				

[a] δ (3-CF_3-Ar): **1d** 14,97 s; **4d** 15,13 s.
[b] δ (C$_6F_5$) **1e**: −80,48 to −80,70 (m, *p*-F), −68,64 to −68,80 (m, *o*-F), −88,01 to −88,26 (m, *m*-F); **4e**: −83,92 to −84,11 (m, *p*-F), −76,08 to −76,25 (m, *o*-F), −63,64 to −63,79 (m, *m*-F).
[c] δ (CH_3-CH) 1,55 d $^{3}J_{H-H}$ = 6,8 Hz.

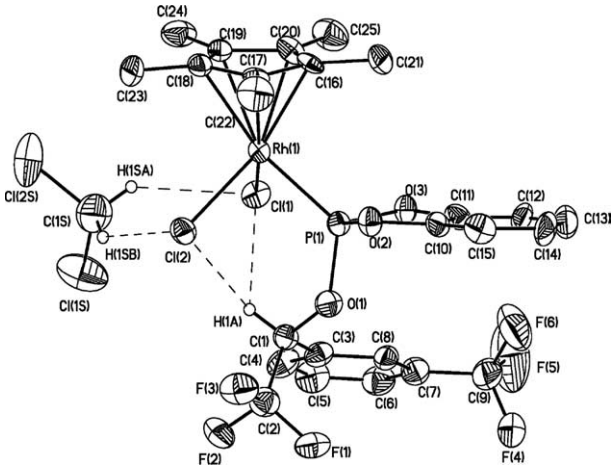


Fig. 1. Perspective view of **4d** with the representation of atoms by the thermal ellipsoids at 50% probability level. The selected bond lengths (Å): Rh(1)–P(1) 2.259(1), Rh(1)–Cl(1) 2.440(1), Rh(1)–Cl(2) 2.439(1), Rh(1)–Cp_{cent} 1.855(6), P(1)–O(1) 1.627(3), P(1)–O(2) 1.655(4), P(1)–O(3) 1.654(4), O(1)–C(1) 1.442(5), O(2)–C(10) 1.424(7), O(3)–C(11) 1.410(7); Bond angles (°): P(1)–Rh(1)–Cl(2) 89.48(6), P(1)–Rh(1)–Cl(1) 87.44(6), Cl(2)–Rh(1)–Cl(1) 94.82(5), O(1)–P(1)–O(3) 104.1(2), O(1)–P(1)–O(2) 98.2(2), O(3)–P(1)–O(2) 96.07(15), O(1)–P(1)–Rh(1) 122.15(12), O(3)–P(1)–Rh(1) 115.35(15), O(2)–P(1)–Rh(1) 116.69(16), C(1)–O(1)–P(1) 126.3(3).

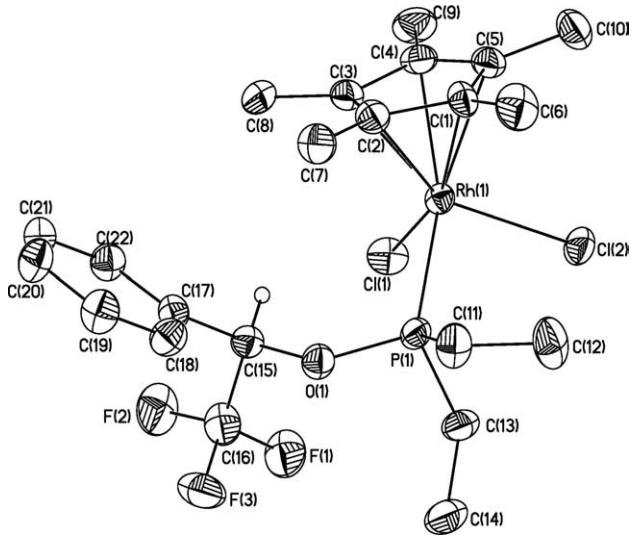


Fig. 2. Perspective view for the one of two independent molecules in complex **6a** with the representation of atoms by the thermal ellipsoids at 50% probability level.

characterized by a distorted P-pyramid with angles for O(1)P(1)O(2) and O(1)P(1)O(3) reduced up to 96.1(1)–98.2(2)° and with an increased angle for Rh(1)P(1)O(1) (122.1(1)°). The dioxaphospholene ring possesses an envelope conformation with a deviation of the P(1) atom by 0.25 Å. The benzodioxaphospholene ring is almost coplanar with the Cp* ligand with an angle of 8°.

The analysis of intramolecular contacts have revealed that the rather acidic hydrogen atom at C(1) participates in the bifurcated $RhCl_2\cdots H$ contact with Cl···H distances equal to 2.69 and 2.62 Å (for Cl(1) and Cl(2) atom, respectively). It should be noted that from geometrical point of view these contacts are comparable with the intermolecular H···Cl ones (2.55–2.68 Å) formed with a solvate CH_2Cl_2 molecule. Therefore, it is suggested that the mutual disposition of $RhCl_2$ and $C(CF_3)(C_6H_4CF_3)$ fragments is controlled not only by anomeric interactions of the O(1) electron lone pairs with Rh(1)–P(1) and P(1)–O(2)/P(1)–O(3) antibonding orbitals, but by intramolecular Cl···H contacts as well.

The X-ray analysis of **6a** reported earlier in our preliminary communication [24] has revealed that it crystallizes in the chiral space group ($P2_12_12_1$) giving the enantiopure crystals ($[\alpha]_{20}^{D} \sim 900^{\circ}$ (*c* 1, $CHCl_3$)) (Fig. 2). Therefore, the crystallization of the **6a** leads to the spontaneous resolution of enantiomers and using further the latter as seeds may allow obtaining the chiral catalyst from a racemic solution. In this study of catalytic activity, the racemic compound was, however, used. It should be noted that the exchange of two electron-releasing ethyl groups in **6a** for the electron-withdrawing 1,3,2-benzdioxaphospholene moiety, as it is in **4d**, resulted in the shortening of the Rh–P bond (2.284(1) versus 2.259(1) Å) and the P–O(1) bond (1.641(3) versus 1.627(3) Å), as well as the elongation of the Rh–Cl bonds (2.404(1) versus 2.440(1) Å).

In a similar manner, the interaction of phosphite **1a** with $Rh(CO)_2(acac)$ resulted in the formation of Rh(L)(CO)(acac) complex (L = **1a**) that was characterized by its ^{31}P NMR spectra (δ_P 126.1, $J_{P-Rh(I)}$ = 241.0 Hz). Comparing with the Rh^{III} complex containing the same ligand (**4a**), the smaller δ_P shift may suggest a weaker coordination bond with Rh^{I}. This complex is stable in solution under argon, but decomposed during the isolation attempted.

2.2. Hydroformylation in the presence of rhodium–phosphite catalysts

Styrene as the model substrate was reacted with CO/H_2 (1/1) at 40 or 100 °C at 100 bar in the presence of $Rh(L)(Cp^*)Cl_2$ **4a**,**c**–**e**, **6a** (where L represents **1a, c**–**e** and **5a**, respectively) 'preformed' or rhodium–L in situ catalysts (Fig. 3) The phosphorus ligands applied differ significantly both in electronic and in steric properties. It is worth noting, that the Taft constants (σ_I) for CF_3 and C_6F_5 groups are 0.32–0.41 [25] and 0.31 [26], respectively, so ligands **1a** and **1e** are rather similar both from electronic and steric point of view.

In addition to the formation of the two formyl regioisomers, 2-phenyl-propanal (**A**) and 3-phenyl-propanal (**B**), that of ethylbenzene (**C**) arising from hydrogenation was also expected (Scheme 3).

All 'preformed' catalysts (**4a**, **4d**, **4e** and **6a**) were active at 100 °C under the given conditions. Practically

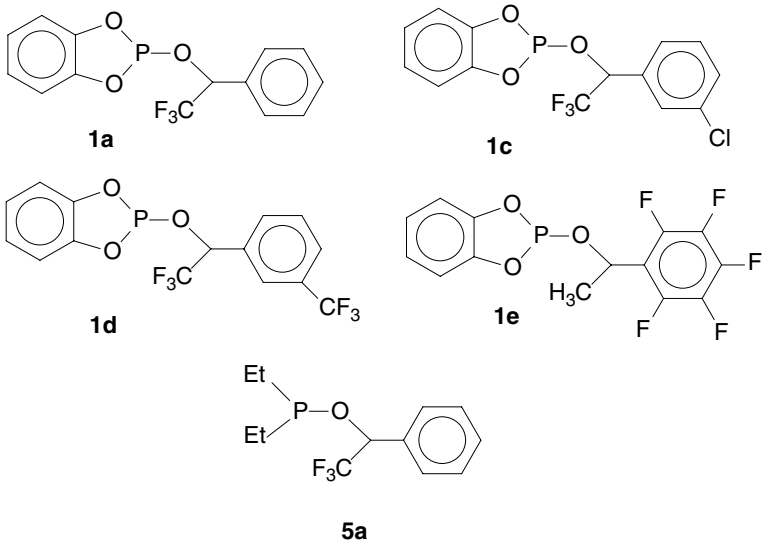
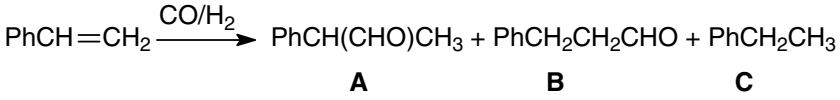


Fig. 3. Ligands used for catalytic experiments either in 'preformed' or in in situ systems.



Scheme 3.

complete conversions have been obtained in most cases in up to 3 h (i.e., TOF values up to 2000) except for the diethylphosphinite derived catalyst **6a**. Decreased activity was observed with the complex of phosphinite ligand having donor ethyl groups at the phosphorus atom (**6a**). The reaction was highly chemoselective towards the formation of aldehydes. (The chemoselectivity of the hydro- formylation was higher than 96% in all cases.) The regioselectivities towards **A** fall in the range of 44–54%, i.e., nearly a 1:1 mixture of branched (**A**) and linear (**B**) aldehydes has been obtained.

Contrary to the results obtained with the 'preformed' catalysts, the in situ formed rhodium catalysts proved to be active even at 40 °C. At elevated reaction times (up to 72 h) the hydroformylation resulted in practically complete conversions both with **1a** and **1d** (Table 3).

Excellent chemoselectivities (above 98%) have been obtained in all cases both at 40 and 100 °C except for the 3-chlorophenyl ligand **1c** at 40 °C (79%). The chemoselectivities are higher than those obtained with preformed catalysts and varied from 98% to 100%.

The regioselectivities show strong temperature dependence. At 40 °C, the branched aldehyde **A** predominated that was formed in excellent regioselectivities (95% in all three cases). The regioselectivities observed at 100 °C show a good agreement with those detected with preformed systems involving **1a**. Slightly higher branched selectivity (60%) has been obtained with **1d**.

According to a generally accepted mechanism, the low activity of the 'preformed' catalysts at 40 °C can be interpreted as follows: (i) The reduction of the Rh^{III} precursor to Rh^{I} species, needed for the complexation of

Table 3
Hydroformylation of styrene in the presence of in situ catalysts formed from $Rh(CO)_2(acac)$ and 2L (L = **1a**, **1c** and **1d**)[a]

Run	Ligand	Temperature (°C)	R. time (h)	Conv.[b] (%)	R_C[c] (%)	R_{br}[d] (%)	TOF (h^{-1})
1	**1a**	40	72	100	100	95.8	>55
2	**1a**	100	2	100	97.9	56.9	>2000
3	**1d**	40	72	100	100	95.4	>55
4	**1d**	100	2	100	98.5	60.3	>2000
5	**1c**	40	72	47.5	79.4	95.1	>26
6	**1c**	100	2	100	98.1	57.3	>2000

[a] Reaction conditions: p = 100 bar ($CO:H_2$ = 1:1); [Rh]/[styrene] = 1/4000; solvent: toluene.
[b] Determined by GC.
[c] Chemoselectivity (**A** + **B**)/(**A** + **B** + **C**) × 100.
[d] Regioselectivity towards branched aldehyde **A**/(**A** + **B**) × 100.

olefin and carbon monoxide, as well as oxidative addition of hydrogen (which is probably the slowest step in the whole process [14]), is difficult at low temperature. (ii) Although the Rh(L)(Cp^*)HCl complex formed in hydrogenolysis should release hydrogen chloride in reductive elimination in order to form a coordinatively unsaturated complex containing soft Rh^I centre. In the absence of a base it is not a facile reaction. The $Rh(L)^*(Cp)H_nCl_{2-n}$ ($n = 1,2$) type Rh^{III} complexes are not ready to activate the olefin even if a vacant coordination site is available.

The increased activity of the in situ system formed from $Rh(CO)_2(acac)$ precursor and the corresponding phosphite ligand is due to the facile formation of Rh^I catalytic intermediates. The $Rh(L)_2(CO)(H)$ key-intermediate is easily available in the in situ system and could be formed even at low temperature [27]. Furthermore, an alternative catalytic route involving the direct formation of catalytically active 'P-ligand-free' hydridocarbonyl-rhodium species cannot be excluded.

Considering the ligands used in in situ systems, there is a sharp difference between the 3-chlorophenyl-containing (**1c**) and the other two phosphites (**1a** and **1d**) at 40 °C. Namely, the chemoselectivity towards hydroformylation is definitely lower in the presence of **1c**, accompanied by the decrease in catalytic activity. Therefore, different species have to be operative in hydroformylation and further intermediates have to be involved in the catalytic cycle. The activation of the aryl-chloro bond by Rh^I species (even in small extent) might be resulted in the formation of rhodium-chloro species. Substantially, there are two possibilities for the formation of catalytically active species: (i) hydrogenolysis of the Rh–Cl bond yielded monohydrido-rhodium species, (ii) activation of dihydrogen in oxidative addition results in Rh^{III} species containing $Rh(H)_2Cl$ moiety which should undergo reductive elimination by loosing HCl (facile elimination in the presence of an amine but not in the absence of that).

In conclusion, we obtained a series of novel fluorinated phosphite P-ligands and their Rh^{III} complexes. Representative examples of the prepared complexes or in situ systems formed from $Rh(CO)_2(acac)$ precursor and the corresponding P-ligand have been tested in the hydroformylation of styrene demonstrating high catalytic activity.

3. Experimental

3.1. General

All reactions were conducted under an inert atmosphere of dry argon by using Schlenk glassware and vacuum line techniques. Solvents were freshly distilled from standard drying agents. Toluene was distilled under argon from sodium in the presence of benzophenone. Styrene was freshly distilled before use. The NMR spectra were recorded on a 'Bruker AMX-400′ spectrometer in $CDCl_3$ solutions using residual proton signal or the characteristic ^{13}C chemical shift of the deutero solvent as an internal standard (^1H or ^{13}C, respectively) and 85% H_3PO_4 (^{31}P) as an external standard. The ^{19}F chemical shifts were determined with trifluoroacetic acid (δ ^{19}F 76.53 ppm) as an external standard. GLC analyses were carried out with a HP-5890/II gas chromatograph using a 15 m HP-5 column (temperature program: initial temperature: 200 °C (2 min), rate: 10 °C/min, final temperature: 300 °C).

The starting 1-(2,3,4,5,6-pentafluorophenyl)-1-ethanol was purchased from Aldrich and used in synthesis without purification. α-Trifluoromethylbenzyl alcohols were synthesised by reduction of the corresponding ketones according the procedure developed by us earlier [28]. 2-chloro-1,3,2-benzodioxaphospholene was obtained by known procedure [29]. For the synthesis of ligand **5a** and its Rh^{III} complex **6a**, see [24].

3.2. Synthesis of the P-ligands

3.2.1. 2-(2,2,2-Trifluoro-1-phenylethoxy)-1,3,2-benzodioxaphospholene *1a*

To a cooled (−5° to 0°) solution of the equimolar mixture of pyridine (0.65 g, 8.2 mmol) and (±)-2,2,2-trifluoro-1-phenyl-1-ethanol (1.44 g, 8.2 mmol) in a mixture solvent (hexane:ether; 4:1; 100 ml), under argon and with stirring, 2-chloro-1,3,2-benzodioxaphosphole (1.43 g, 8.2 mmol) was added dropwise at the same temperature over 0.5 h. The mixture was allowed to warm to room temperature and stirred for additional 3 h. The precipitate was filtered off under argon, washed with Et_2O (2×30 ml) and discarded. The filtrate was evaporated in vacuo yielding crude ligand **1a** as an oil (2.56 g), in a purity of *ca.* 98% according ^{31}P and ^1H NMR. For purification, hexane (10 ml) was added to the crude oil and the mixture was chilled to −20 °C. After decanting the hexane phase and concentration in vacuo, **1a** was isolated in a pure form as colourless oil (2.27 g, 88%).

2-[1-(4-Chlorophenyl)-2,2,2-trifluoroethoxy]-1,3,2-benzodioxaphospholene **1b,** 2-[1-(3-chlorophenyl)-2,2,2-trifluoroethoxy]-1,3,2-benzodioxaphospholene **1c,** 2-[2,2,2-trifluoro-1-[3-(trifluoromethyl)phenyl]ethoxy]-1,3,2-benzodioxaphospholene **1d,** and 2-[1-(2,3,4,5,6-pentafluorophenyl)ethoxy]-1,3,2-benzodioxaphospholene **1e** were obtained similarly. All of the ligands were purified as above. Table 1 shows the yields, melting points and analytical data the ligands **1a**–**e** obtained, NMR data are summarized in Table 2. In principle, the crude products may be used in the complexation reactions without further purification.

3.2.2. 2-[2,2,2-Trifluoro-1-(4-chlorophenylethyl)] diethylphosphinite **5b**

Equimolar mixture of diethyl-(*N*,*N*-diethylamino)-phosphinite (1.10 g, 6.84 mmol) and (±)-2,2,2-trifluoro-1-(4-chlorophenyl)ethanol (1.44 g, 6.84 mmol) was feed into the distillation flask that was heated up to 155 °C and maintained under these conditions over 45 min. During that time, the diethylamine formed distilled off. The residue was distilled in vacuo yielding 1.75 g (86%) of **5b**; b.p. 100–102 °C/0.5 torr. Analytical data were obtained for the corresponding sulphide derivative obtained by the addition of sulphur to the compound in benzene solution after purification by column chromatography (see Tables 1 and 2).

3.3. Synthesis of the (π-pentamethylcyclopentadienyl)(phosphite)-or(phosphinite)rhodium dichlorides **4a–e**, **6b** (typical procedure)

The solution of $[RhCp^*Cl_2]_2$ (128 mg, 0.207 mmol) in 3 ml of CH_2Cl_2 was added to a solution of either phosphite **1a–e** or phosphinite **5b** (0.407 mmol) in 7 ml of CH_2Cl_2. After stirring the immediately formed red solution for 1 h at room temperature, the solvent was evaporated in vacuo up to the volume of *ca*. 0.5 ml and then about 4 ml of pentane was added. The crystal precipitated (dark red prisms) was filtered off and dried in vacuo to afford the desired complexes (Tables 1 and 2).

3.4. X-ray crystallography

Crystals of **4d** suitable for X-ray diffraction were grown by slow evaporation of CH_2Cl_2 from the solution of the complex. At 120 K crystals of **4d** ($C_{26}H_{26}Cl_4F_6O_3PRh$) are orthorhombic, space group $Pca2_1$, $a = 23.347(8)$, $b = 10.913(4)$, $c = 12.383(4)$ Å, $V = 3155(2)$ Å^3, $Z = 4$, $M = 776.15$, $d_{calc} = 1.634$ g cm^{-3}, μ(Mo Kα) = 9.93 m^{-1}, $F(000) = 1552$. Intensities of 33209 reflections were measured with a Smart 1000 CCD diffractometer at 120 K (λ(Mo Kα) = 0.71072 Å, $2\theta < 58°$), and 8319 independent reflections ($R_{int} = 0.0550$) were used in the further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The refinement converged to $wR_2 = 0.0935$ and GOF = 1.062 for all independent reflections ($R_1 = 0.0468$ was calculated against F for 6330 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL PLUS 5.0 [30]. Crystallographic data (excluding structure factors) for the structure of **4d** have been deposited to the Cambridge Crystallographic Data Centre; No. CCDC-262146. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax: (internat.) +44-1223/336-033; deposit@ccdc.cam.ac.uk).

3.5. Hydroformylation experiments

In a typical experiment a solution of 0.00625 mmol of preformed catalyst **4a**,**d**,**e**, or **6a** in 7.5 ml toluene containing 2.6 ml (25 mmol) of styrene was transferred under argon into a 20 ml stainless steel autoclave. (In case of the in situ catalysts 1.6 mg (0.00625 mmol) $Rh(CO)_2(acac)$ precursor and 0.0125 mmol of **1a** (or **1c** or **1d**) were dissolved in 7.5 ml toluene, 25 mmol styrene was added and the homogeneous solution was transferred under argon into a stainless steel autoclave.) The reaction vessel was pressurized to 100 bar total pressure ($CO/H_2 = 1/1$) and placed in an oil bath and the mixture was stirred with a magnetic stirrer for the appropriate reaction time. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analysed by GC.

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