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α-Fluorinated cyclic amidophosphite ligands. Their synthesis, Rh complexes and catalytic activity in the hydroformylation of styrene

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Abstract

The synthetic approaches to cyclic phosphite and amido(diamido)phosphite ligands bearing the residues of electron withdrawing perfluorinated tails at the β-position to the phosphorus atom have been elaborated. Catalytic systems based on rhodium complexes of these ligands formed *in situ* using $Rh(CO)_2(acac)$ as a catalytic precursor demonstrate high activity in the hydroformylation of styrene along with good selectivity in respect to branched aldehyde. Quantum-chemical calculations proved that both the rate of the formation of branched alkyl complex, as well as its reactivity are influenced by the steric and electronic parameters in the same manner.

Keywords: Polyfluorinated cyclic phosphite and amidophosphite ligands; Rhodium complexes; Homogeneous catalysis; Hydroformylation

1. Introduction

Nowadays phosphite or/and amidophosphite ligands attract attention in metal catalysed processes. These compounds possess a series of principal advantages in comparison with σ-donor phosphine ligands [1]. On one hand, they are easily available, as most of them may be obtained via direct one step phosphorylation from a variety of precursors including optically active ones; at the same time, the synthesis of optically active phosphines is more complicated. On the other hand, these compounds are more stable against oxidation due to the absence of P–C bonds in the molecule. This fact is essential in the synthesis of some coordination compounds and in hydroformylations where oxidation of phosphines deems a marked problem. Furthermore, these ligands have pronounced π-acceptor properties allowing the stabilization of low oxidation state of the complexing metals and an increase of its electrophilicity. In general, the introduction of oxygen and/or nitrogen heteroatoms into the first coordination sphere of the phosphorus atom presents a more effective way to adjust the chemical stability, as well as the donor–acceptor and steric properties of the ligand, as compared to the traditional introduction of substituents into the phenyl substituents of PPh_2 moieties typical for most phosphines.

In hydroformylation, being one of the most important homogeneous catalytic industrial processes, small σ-donor ligands was found to retard the reaction while π-acceptor

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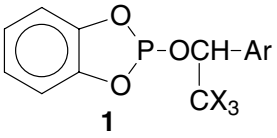
ligands, such as bulky phosphites [2] or phosphabenzenes [3] possessed high catalytic activity for both hydroformylation of internal and terminal olefins. In these cases the enormous catalytic activity was attributed to a monoligand–rhodium complex as a catalytically active species.

Taking into account that fluorinated ligands also find application in the field of catalysis possessing high activity and are of high interest in fluorous biphasic catalysis (FBC) [4], recently [5], we elaborated the synthesis of non-symmetric benzoannulated cyclic phosphites **1** bearing the residue of substituted benzylic alcohols containing fluorine substituents in aliphatic and/or aromatic positions. In this case, electron withdrawing polyfluorinated tails were used to stabilize the phosphorus(III) benzylic esters which otherwise would undergo a rather rapid decomposition [6].

The rhodium complexes of $Rh^{III}(L)(Cp^*)Cl_2$ type or Rh^I complexes formed *in situ* from $Rh(CO)_2(acac)$ precursor and the corresponding ligand proved to be active as catalysts in the hydroformylation of styrene.



1

X=F, Ar=C_6H_5, 3-Cl-C_6H_4, 3-$CF_3C_6H_4$;
X=H, Ar=C_6F_5

Both systems provided excellent hydroformylation activities at 100 °C (TOF values up to 2000) excluding the ligand bearing the *m*-chlorine atom. At this temperature only moderate regioselectivities towards the branched aldehyde (2-phenylpropanal) were, however, observed. Using the Rh^I *in situ* systems, high regioselectivities were observed already at 40 °C, the activity of the catalyst decreased, however, under such conditions and the complete conversion took *ca.* 72 h.

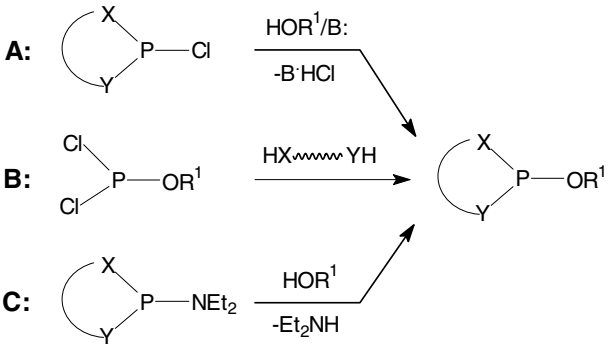
Taking into account that many examples are known where minor modifications in the structure of the ligand resulted in a profound change in of the catalytic activity and/or in the selectivity, it seemed to be interesting to estimate the structure–activity relationship for such ligands varying either the heteroatoms in the first coordination sphere of the phosphorus or the substituents at the α-carbon atom. In this paper, the synthesis and the catalytic activity in the hydroformylation of styrene as well as quantum-chemical estimation of structure–activity relationship, of novel cyclic amidophosphite ligands bearing polyfluorinated tails are reported.

2. Results and discussion

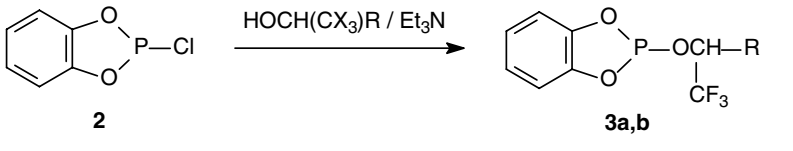
2.1. Synthesis

In principle, two general methodologies can be used to obtain (amido)phosphites. The more common route is based on the so called 'chloride methodology', wherein the corresponding pre-formed cyclic phosphorus(III) acid chloride interacts with the corresponding alcohol in the presence of a base (Scheme 1, path A). The treatment of dichlorophosphites by bisnucleophiles means one variant of this method (Scheme 1, path B). The other route, the so-called "amide" procedure, is based on the interaction of phosphorus(III) acid amides with the desired alcohols (Scheme 1, path C). All the approaches shown in Scheme 1 were used in our work to find the optimum choice for the synthesis of the target molecules.

Thus, to obtain the ligands **1** from easily available 2-chloro-1,3,2-benzodioxaphosphole **2**, the 'chloride method' (pathway **A**) was found to be the best choice [5]. The same approach was used to synthesize their analogues bearing either an alkyl chain or a diethoxyphosphoryl group instead of the aromatic ring adjacent to trifluoromethyl substituent (**3**) (Scheme 2). The original procedure [5a] involved minor modifications (triethylamine was used



Scheme 1.



2 **3a,b**

R=n-C_6H_{13} (**a**), $P(O)(OEt)_2$ (**b**)

Scheme 2.

instead of pyridine and the order of the addition of the reagents was changed (see Section 3)).

Then we switched for the preparation of amidophosphites. As *ortho*-*N*-methylaminophenol can be prepared in only *ca.* 10% yield [7], we used the 'amide' procedure (path C) giving amidophosphites in high yields and purities, applying N-diethylamidophosphite **4** as the starting material for the synthesis of monoamidophosphites **5a–e** (Scheme 3).

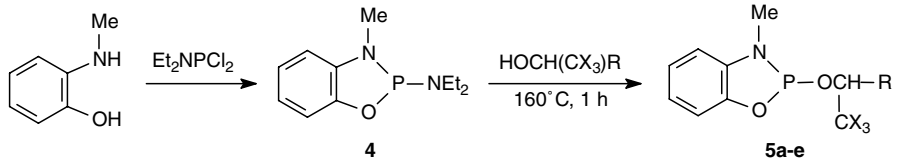
Non-fused amidophosphites **8a–c** and diamidophosphites **9a–c** bearing the *N*-methyl group(s) were synthesized from 2-chloro-3-methyl-1,3,2-oxazaphospholidine **6** or 2-chloro-1,3-dimethyl-1,3,2-diazaphospholidine **7**, respectively (Scheme 4). The compounds (**8a–c** and **9a–c**) were isolated in analytically pure form after the work-up procedure in yields of 82–98%. Note that as amidophosphites **5** and **8** possess a stereogenic phosphorus atom along with the stereogenic carbon atom in the side-chain, they were obtained as a mixture of two diastereomers observed in the ^{31}P NMR spectra as two singlets. The diastereomer **A** having upfield chemical shift in the ^{31}P NMR spectra was usually the major one and the ratio of isomers ranged between 1.3 and 1.5:1. In the ^{1}H and ^{13}C NMR spectra two series of signals corresponding to **A** and **B** diastereomers were observed (see Section 3.2).

This procedure could not be used for the preparation of diamidophosphites bearing sterically hindered substituents (e.g. *i*Pr, *t*Bu, Ph) on the nitrogen atoms, as we failed to obtain the starting cyclic diamidochlorophosphites **10** from phosphorus trichloride and the corresponding *N*,*N*′-dialkyl(aryl)alkylene diamine (Scheme 5).

Even applying low temperatures (−50 °C) and working in diluted solutions, the desired interaction to afford **10** ($n = 2,3$) was accompanied by the formation of linear aminochlorophosphites of type **11** and **12** of oligomeric nature.

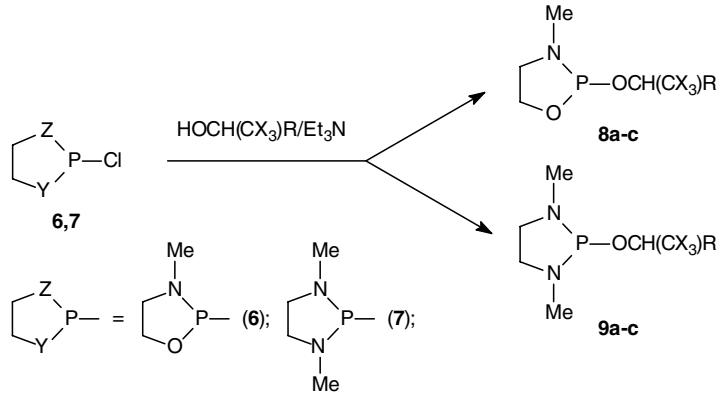
The yields of cyclic products **10** ($n = 2$, 3) estimated by ^{31}P NMR spectra were less than 60% in the case of the substrate with isopropyl group. Moreover, we failed to isolate products **10** by distillation of the crude mixtures, as the linear products underwent disproportionation. The proportion of cyclic chlorophosphites **10** decreased till 20% by increasing the steric hindrance at the nitrogen atoms and by increasing the length of the alkylene bridge in the starting alkylene diamine.

Therefore, during our efforts to obtain cyclic diamidophosphites of the above type, dichlorophosphites **13a**,**b** were obtained first by the reaction of PCl_3 and the corresponding fluorinated alcohols followed by the cyclization with *N*′,*N*-dialkyl(aryl)alkylene diamines (Scheme 6). It should be noted that due to the weak nucleophilicity of fluorinated alcohols, the yields of intermediates **13** obtained by typical procedure were only *ca.* 50%.The use of catalytic amount of 4-dimethylaminopyridine (DMAP)



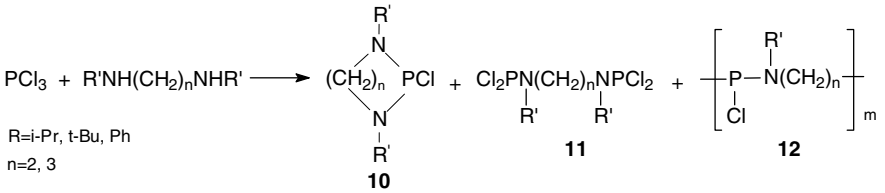
X=F, R= C_6H_5 (**5a**), 3-$CH_3OC_6H_4$ (**5b**); 3-$CF_3C_6H_4$ (**5c**); n-C_6H_{13} (**5d**)
X=H, R=C_6F_5 (**5e**)

Scheme 3.

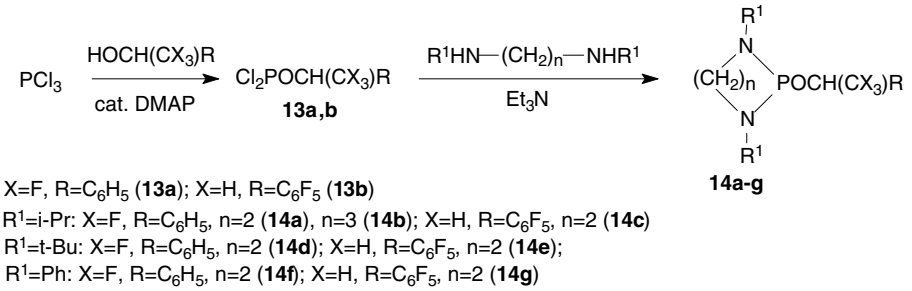


X=F, R=3-$CF_3C_6H_4$ (**8a**), P(O)$(OEt)_2$ (**8b**); X=H, R=C_6F_5 (**8c**)
X=F, R=C_6H_5 (**9a**), P(O)$(OEt)_2$ (**9b**); n-C_6H_{13} (**9c**);

Scheme 4.



Scheme 5.



Scheme 6.

allowed, however, both the increase of the yield up to 77% and the accomplishment of the substitution at room temperature [8]. Applying this approach, diamidophosphites **14** could be obtained in good yields (83–87%, based on **13a**,**b** or *ca.* 60% on the basis of PCl_3).

All compounds were characterized by elemental analysis or MS data, as well as NMR spectroscopy. The stereostructure of ligand **14f** was evaluated by single crystal X-ray analysis. According to the data obtained, diamidophosphite **14f** crystallises as a racemate. The five-membered 1,3,2-diazaphospholidine cycle is characterized by the envelope conformation with the deviation of the C(10) atom by 0.32 Å (Fig. 1). The N(1) and P(1) atoms are pyramidal (sum of bond angles 356° and 299.1°) while in contrary the N(2) arom is planar (sum of bond angles is 359.8°). The Ph rings at both nitrogen atoms of the cycle are almost coplanar with the base of envelope with torsion angles C(12)C(11)N(1)P(1) and C(22)C(17)N(2)P(1) equal to 22.9° and 8.3°, respectively. The phenyl ring C(3)–C(8) in alkoxy group is situated directly above the C(17)–C(22) one with the dihedral angle between the planes of aromatic cycles equal to 20.5° and the shortest C(11)···C(20) contact equal to 3.430(2) Å. Such mutual disposition of these phenyl rings almost screens the acidic hydrogen atom at the chiral C(1) atom and as the consequence, it does not participate in any shortened intermolecular contacts in the crystal of **14f.**

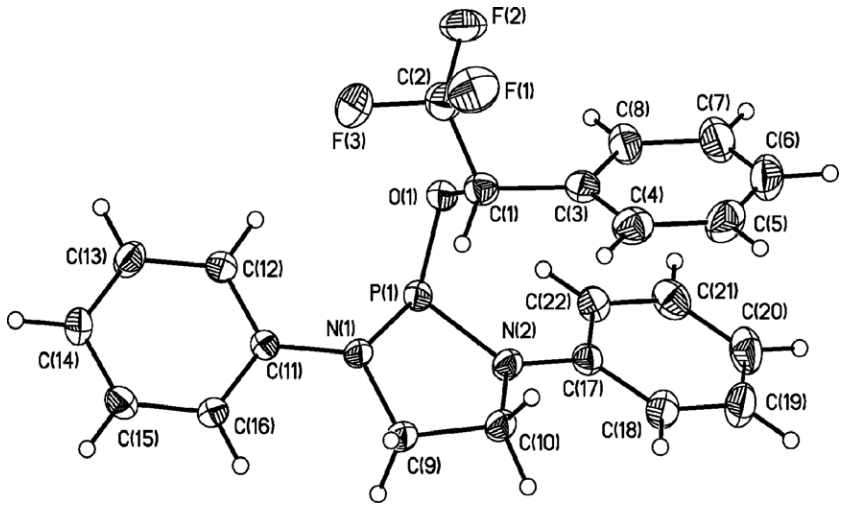
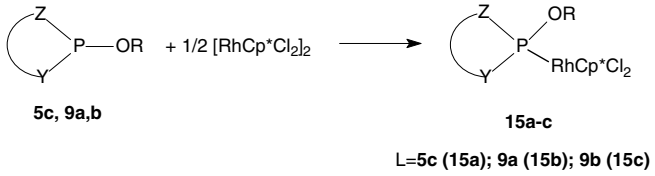


Fig. 1. Perspective view of **14f** with representation of atoms by the thermal ellipsoids at 50% probability level. The selected bond lengths (Å): P(1)–O(1) 1.657(1), P(1)–N(2) 1.693(2), P(1)–N(1) 1.701(2), O(1)–C(1) 1.429(2), N(1)–C(11) 1.410(2), N(1)–C(9) 1.474(2), N(2)–C(17) 1.409(2), N(2)–C(10) 1.461(2); bond angles (°): O(1)–P(1)–N(2) 105.04(8), O(1)–P(1)–N(1) 103.58(8), N(2)–P(1)–N(1) 90.51(8), C(1)–O(1)–P(1) 122.83(12), C(11)–N(1)–C(9) 118.94(16), C(11)–N(1)–P(1) 121.52(13), C(9)–N(1)–P(1) 115.61(12), C(17)–N(2)–C(10) 120.82(15), C(17)–N(2)–P(1) 123.26(14), C(10)–N(2)–P(1) 115.70(12).



Scheme 7.

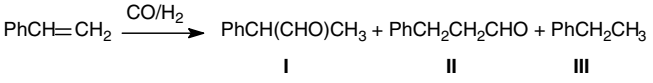
Similar to phosphites **1**, the mono- and the diamidophosphites obtained were suitable *P*-ligands to give the stable Rh(III) complexes as illustrated by the reaction of compounds (**5c**, **9a**,**b**) with dimeric (π-pentamethylcyclopentadienyl)rhodium(III) dichloride (Scheme 7).

According to the X-ray diffraction analysis of the complex **15a** formed by substituted 2,3-dihydro-1,3,2-benzoxazaphosphole **5c** (Fig. 2), the principal geometrical parameters are similar to those in its analogue formed by the similar ligand excluding of dioxaphospholene ring instead of 3-methyl-1,3,2-benzoxazaphospholene ring [5a] with slight decrease of the Rh(1)–P(1) bond up to 2.231(2) Å in comparison to 2.259(1) Å published previously. The phosphorus atom is characterized by the distorted *P*-pyramid with angles for OPO and OPN reduced up to 92.6(4)–106.7(4)° and with increase of the Rh(1)P(1)N(1) angle (124.0(3)°). Furthermore, the X-ray analysis have revealed that **15a** crystallises in the chiral space group *C*2 (the Flack parameter is equal to 0.02(6)) in contrast to the above mentioned complex with dioxaphospholene ring published in [4a] which crystallized as a racemate. Therefore, the complex **15a** presents a conglomerate, which undergoes crystal induced spontaneous resolution to give enantiopure crystals. It should be noted that for (π-pentamethylcyclopentadienyl)(phosphite)rhodium dichlorides $LRhCp^*Cl_2$ the spontaneous resolution was also observed by us earlier in the case of the complex formed by 2,2,2-trifluoro-1-phenylethyl diethylphosphinite ($L = Et_2POCH(CF_3)C_6H_5$) [4b].

2.2. Hydroformylation in the presence of rhodium—fluorine-containing phosphite and amidophosphite in situ catalysts

Styrene as a model substrate was allowed to react with CO/H_2 (1/1) at 40 °C or 100 °C at 100 bar in the presence of rhodium–L *in situ* catalysts formed from $Rh(CO)_2(acac)$ and the corresponding phosphite or amidophosphite ligand (where L represents **3a**, **3b**, **5c**, **5d**, **8a**, **8c**, **14a** and **14b**; for structural formulae see Scheme 2,3,4 and 6) over 2 h. The above phosphorus ligands differ significantly both in electronic and in steric properties (see Section 2.3).

In addition to the formation of the two formyl regioisomers, 2-phenyl-propanal (**I**) and 3-phenyl-propanal (**II**), that of ethylbenzene (**III**) arising from hydrogenation was also expected (Scheme 8).



Scheme 8.

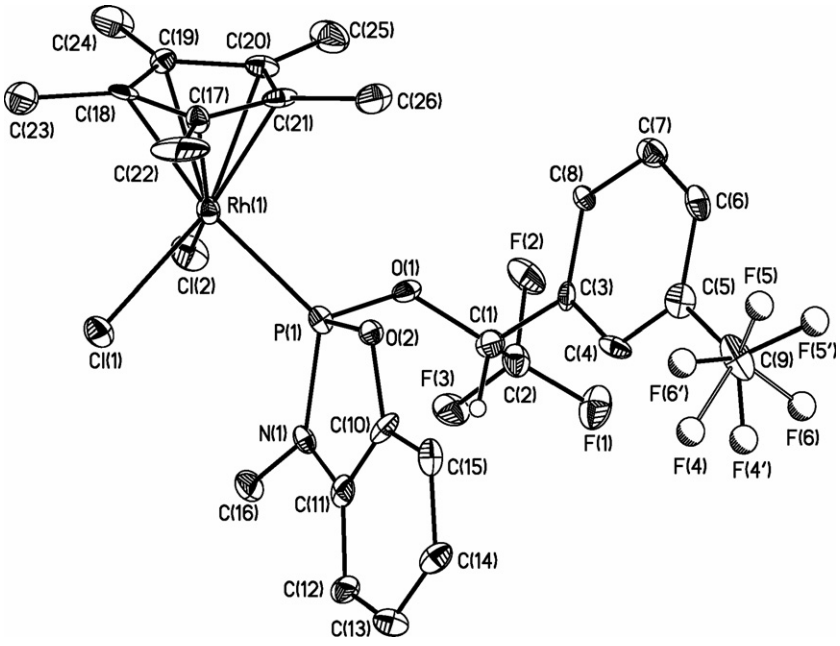


Fig. 2. Perspective view of **15a** with representation of atoms by the thermal ellipsoids at 50% probability level. The fluorine atoms of the disordered CF_3 group are shown by balls. The selected bond lengths (Å): Rh(1)–P(1) 2.231(2), Rh(1)–Cl(2) 2.393(3), Rh(1)–Cl(1) 2.408(3), Rh(1)–Cp*cent 1.815(9), P(1)–O(1) 1.616(6), P(1)–O(2) 1.624(7), P(1)–N(1) 1.688(9); bond angles (°): P(1)–Rh(1)–Cl(2) 89.46(12), P(1)–Rh(1)–Cl(1) 89.08(10), Cl(2)–Rh(1)–Cl(1) 91.40(10), O(1)–P(1)–O(2) 102.2(4), O(1)–P(1)–N(1) 106.7(4), O(2)–P(1)–N(1) 92.6(4), O(1)–P(1)–Rh(1) 110.3(2), O(2)–P(1)–Rh(1) 118.0(3), N(1)–P(1)–Rh(1) 124.0(3).

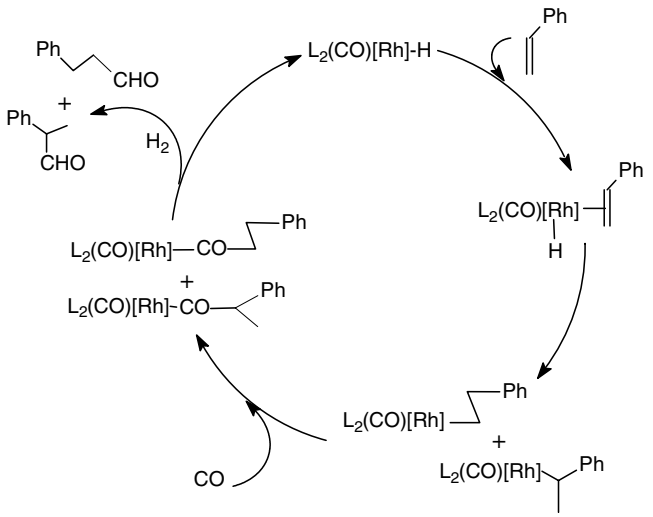
Table 1
Hydroformylation of styrene in the presence of *in situ* catalyst formed from $Rh(acac)(CO)_2$ and L[a]

L	Conv.[b] (%)	R_C[c] (%)	R_{RB}[d] (%)
3a	99	99	87
3b	>99.5	99	90
5c	98	>99.5	91
5d	>99.5	>99.9	90
8a	88	>99.9	87
8c	97	99	89
14a	86	99	81
14b	61	>99.9	77

[a] Reaction conditions: $p = 100$ bar ($CO:H_2 = 1:1$), reaction temperature = 70 °C, r. time = 2 h, Rh:L:styrene = 1:2:500, solvent: toluene.
[b] Determined by GC.
[c] Chemoselectivity = (moles of **I** + moles of **II**)/(moles of **I** + moles of **II** + moles of **III**) × 100.
[d] Regioselectivity = (moles of **I**)/(moles of **I** + moles of **II**) × 100.

All the *in situ* catalysts were active at 70 °C under the given conditions (Table 1). Practically complete conversions have been obtained in 2 h with tris(phosphite) type ligands (**3a**, **3b**) and amidophosphites **5c** and **5d** having fused 1,3,2-benzoxaphospholene or 1,3,2-benzazaphospholene cycles respectively. Decreased activity was observed with the monocyclic ligands **8a**, **14a**,**b** while the ligand **8c** having perfluorophenyl substituent instead of trifluoromethyl group in **8a** still demonstrated 97% conversion. The lowest activity was observed with the diamidophosphite ligand **14b** with six-membered 1,3,2-diazaphosphorine cycle.

The reaction was highly chemoselective towards the formation of aldehydes. Excellent chemoselectivities (higher than 99%, in some cases higher than 99.9%) were obtained in all cases. The regioselectivities towards the branched aldehyde regioisomer (**I**) fall in the range of 77–91%, *i.e.* the branched aldehyde (**I**) predominated over the linear one (**II**). Although the range of regioselectivity was rather narrow, two groups of ligands can be distinguished: the regioselectivities obtained with phosphites and amidophosphites are slightly higher or lower than 90%, those obtained with diamidophosphites (**14a** and **14b**) are typically about 80%.



Scheme 9.

Although the above hydroformylations were not carried out with the aim of clearing-up some mechanistic details, according to a generally accepted mechanism (Scheme 9), some conclusions could be drawn on the basis of the catalytic results.

As expected, the Rh^I precursor provided the $RhH(CO)_n(L)_m$ ($n,m = 1,2$) species by facile substitution of the acac ligand under 'hydroformylation conditions'. Furthermore, the $RhH(CO)(L)_2$ key-intermediate, as well as the corresponding $Rh(alkyl)(CO)(L)_2$ intermediate, formed by styrene insertion, are easily available in the *in situ* system and could be formed even at such a relatively low temperature, as 70 °C. It is worth noting that the formation of the branched alkyl complex (Rh(1-phenylethyl)$(CO)(L)_2$ intermediate) is favoured in the presence of all ligands. From the two major reaction pathways based on this alkyl-intermediate, *i.e.* carbon monoxide insertion followed by hydrogenolysis, as well as direct hydrogenolysis of the Rh-alkyls, the previous one is highly favoured. As a consequence of this, almost the exclusive formation of the aldehydes (**I** and **II**) and only traces of the hydrogenated product (**III**) could be observed in our experiments.

In conclusion, some representative examples of novel fluorinated phosphite and amidophosphite *P*-ligands were tested in the homogeneous catalytic hydroformylation of styrene. The systems demonstrated high catalytic activity, excellent chemoselectivity towards hydroformylation and moderate to high (up to 91%) regioselectivity towards the branched aldehyde. The activity of compounds with fused 1,3,2-benzoxaphospholene or 1,3,2-benzazaphospholene cycles was comparable with that of the most active rhodium–monophosphine catalysts.

2.3. Theoretical studies

Among the numerous examples of phosphite and amidophosphite ligands discussed in this study some have been selected in order to find some correlation between the electronic and steric properties and the activity and regioselectivity in the rhodium-catalyzed hydroformylation of styrene.

The lowest energy conformers of the selected ligands **3a**,**b**, **5c**,**d**, **8a**,**c**, **14a**,**b** optimized at PBE level of theory are depicted in Fig. 3, the electronic and steric data are summarised in Table 2. As the influence of steric effects on organometallic compounds are generally discussed using Tolman's cone angle concept [9], we determined the cone angle (Θ) on all the lowest energy conformers of each ligand. Some electronic properties characteristic for coordination to transition metals were determined using the natural bond orbital (NBO) method [10]. The natural charge (Q_P) describes the charge on the phosphorus atom obtained by natural population analysis, *i.e.* the nuclear charge minus the total electron population. The natural electron

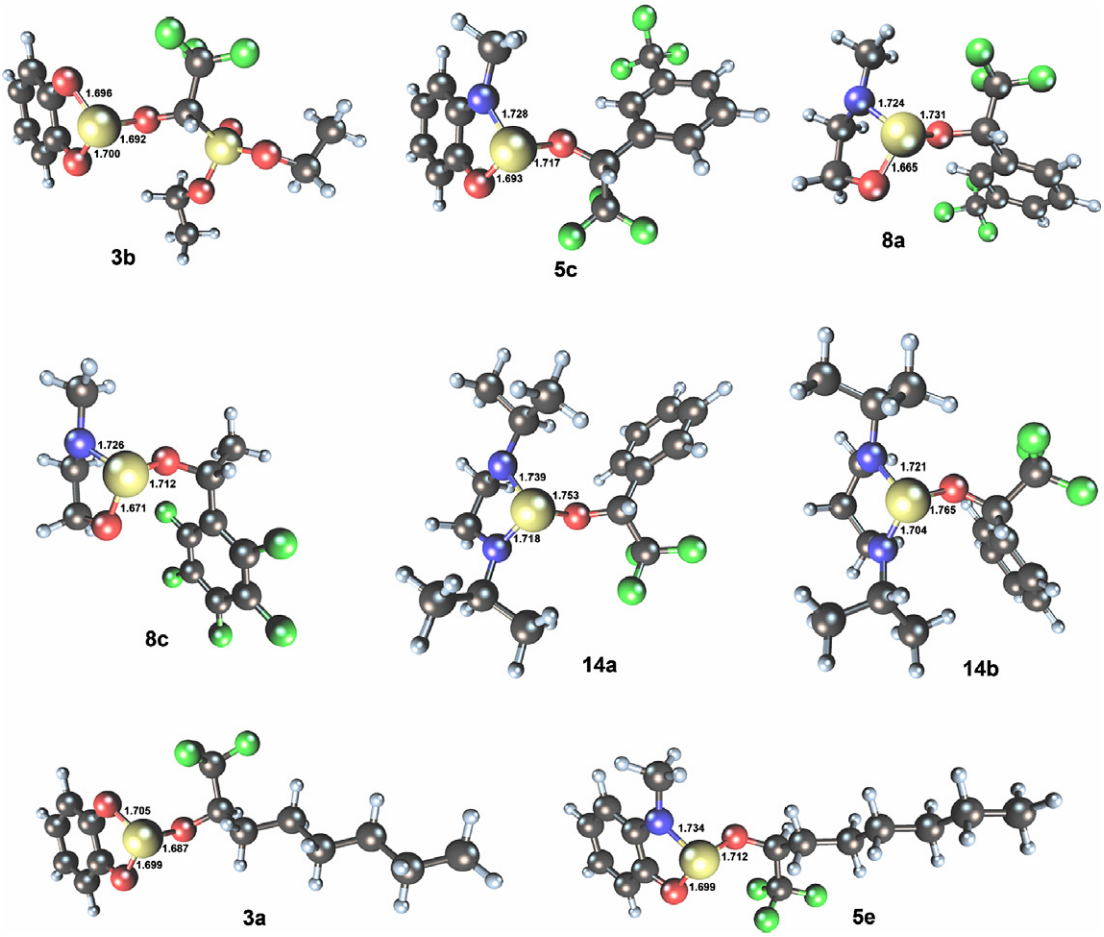


Fig. 3. PBE/6-31G*-optimized structures of ligands selected for hydroformylation experiments. P–O and P–N bond lengths are given in Ångstrom.

Table 2
NBO properties and Tolman's cone angles of ligands selected for catalytic experiments

Ligand	Q_P[a]	NEC (valence)[b]	$NHO_{P,lp}$[c]	Θ (°)
3a	1.505	3S(1.59)3p(1.83)	sp0.39	133
3b	1.522	3S(1.58)3p(1.81)	sp0.40	112
5c	1.447	3S(1.55)3p(1.93)	sp0.46	132
5d	1.436	3S(1.55)3p(1.94)	sp0.45	155
8a	1.451	3S(1.53)3p(1.94)	sp0.49	130
8c	1.451	3S(1.52)3p(1.95)	sp0.49	134
14a	1.344	3S(1.50)3p(2.09)	sp0.55	151
14b	1.369	3S(1.47)3p(2.10)	sp0.60	156

[a] NBO charge on the phosphorus atom.
[b] Natural electronic configuration on phosphorus.
[c] Natural bond orbital hybridization on the phosphorus lone pair.

configuration (NEC) gives the effective valence electron configuration for the phosphorus atom. The lone pair of the phosphorus is composed entirely of a single normalized natural hybrid orbital (NHO).

The role of the cone angle was mainly examined for the ligand pairs **3a**–**3b** and **5c**–**5d**, respectively. Although the electron density is slightly more depleted in case of **5c** and **3b** as compared to **5d** and **3a**, respectively, the electron configuration and the p character of the lone pairs do not show significant difference. The *n*-hexyl group greatly increases, however, the cone angle of the ligands (see **5d** vs. **5c** and **3a** vs. **3b**) thus the slight decrease of regioselectivity may be attributed to steric effect.

The influence of the fused phenyl group may be followed comparing ligands **5c** and **8a**. The more rigid structure of the benzooxazaphospholidinyl group results in slightly elongated P–N and P–O bond length, a lone pair on phosphorus with more s character and also higher catalytic activity and selectivity to the branched aldehyde.

The ring size and hence the ring strain of the cyclic diamidophosphites **14a** and **14b** influences significantly the electronic structure around the phosphorus atom. Both the catalytic activity and the selectivity are dropped when $n = 3$. The more positively charged phosphorus and the lone pair with more p character may be attributed to the larger bite angle and shorter P–N bonds. The P–N bonds of **14b** become more polarized, as the natural charge on nitrogen atoms decrease from −0.783 and −0.798 to −0.787 and −0.802, respectively.

In accordance with the simultaneous change of catalytic activity and branched selectivity, it may be concluded that both the rate of the formation of branched alkyl complex as well as its reactivity are influenced by the steric and electronic parameters in the same manner.

To conclude, the application of a combination of 'chloride' and 'amide' methodologies gives the possibility to obtain a variety of asymmetric cyclic phosphites and amidophosphites bearing the residue of weak nucleophilic fluorinated alcohols in high yields. Catalytic systems based on rhodium complexes of these ligands formed *in situ* demonstrate high activity in the hydroformylation of styrene. According to the 'structure–activity' relationship the more rigid structure of the ligand and the presence of the nitrogen atom at the phosphorus result in higher catalytic activity and selectivity to the branched aldehyde.

3. Experimental

3.1. General

The NMR spectra were recorded on a 'Bruker-DPX-200' and 'Bruker AMX-400' spectrometer in $CDCl_3$ solutions using residual proton signals or the characteristic ^{13}C chemical shift of the deuterated solvent as an internal standard (for ^1H and ^{13}C NMR, respectively) and 85% H_3PO_4 as an external standard (for ^{31}P–{^1H} NMR). The ^{19}F chemical shifts were determined with $CFCl_3$ as an external standard. The mass-spectra (EI) were obtained on a Varian MAT-311A spectrometer at 70 eV.

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 starting 1-(2,3,4,5,6-pentafluorophenyl)-ethanol was purchased from Aldrich and used in synthesis without purification. α-Trifluoromethylbenzyl alcohols were synthesized by the reduction of the corresponding ketones according the procedure developed by us earlier [11]. Diethyl 2,2,2-trifluoro-1-hydroxyethylphosphonate was synthesized by the interaction of trifluoroacetic acid ethyl ester and diethylphosphite by the procedure described in Ref. [12]. 2-Chloro-1,3,2-benzodioxaphosphole **2** was obtained by a known procedure [13]. 2-Chloro-3-methyl-1,3,2-oxazaphospholidine **6** was obtained from phosphorus trichloride and 2-*N*-(methylamino)ethanol as it was described [14], but with minor modifications (solvent: 50 mL of diethyl ether, for 4.81 g (0.035 mol) of PCl_3, 2 h at −50 °C → 2 h at 20 °C) to increase the yield up to 51% (vs. 24%). 2-Chloro-1,3-dimethyl-1,3,2-diazaphospholidine **7** was prepared according to Ref. [15]. Dichlorophosphites **13a**,**b** were obtained according to the catalytical procedure elaborated by us earlier [8].

3.2. Synthesis of the P-ligands

3.2.1. Phosphites *3a,b*

Triethylamine (0.2 g, 2 mmol) was added to a stirred and cooled (−5 to 0 °C) solution of chlorophosphite **2** (0.35 g, 2 mmol) in 30 mL of diethyl ether under argon and the mixture was stirred over additional 5 min. Then the solution of 2 mmol of the corresponding alcohol in 30 mL of diethyl ether was added. The mixture was allowed to warm up to ambient 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*. The residue was treated with 30 mL of pentane and kept at 0 °C overnight. The clear solution was decanted from the precipitate and evaporated under reduced pressure followed by drying (20 °C, 0.1 mm Hg, 2 h) to afford the desired unsymmetric trisphosphites **3a**,**b** as colourless oils.

3.2.2. 2-{[1-(Trifluoromethyl)heptyl]oxy}-1,3,2-benzodioxaphosphole *3a*

Yield 87%, ^{31}P NMR: 133.5; ^{19}F NMR: −78.7 (appeared t, $^3J_{F-H} = {}^4J_{P-F} = 7.5$ Hz); ^1H NMR: 4.2–4.0 (m, CH, 1H); 0.92 (t, $^3J_{H-H} = 6$ Hz, CH_3, 3H); 1.62 (q, $^3J_{H-H} = 6$ Hz, $ICCH_2$, 2H); 1.4–1.2 (m, –$(CH_2)_4$–, 8H); 7.2–7.0 (m, C_6H_4, 4H). ^{13}C NMR: 13.9 (CH_3); 22.4, 24.3; 28.5; 28.9; 31.36; 123.5 (qd, CF_3, $^3J_{P-C} = 3.6$ Hz, $^1J_{C-F} = 276.1$ Hz); 72.6 (dq, CH, $^2J_{C-F} = 31.9$ Hz, $^2J_{P-C} = 6.2$); 111.1 (d, $^3J_{P-C} = 12.7$ Hz), 112.3 (d, $^3J_{P-C} = 1.9$ Hz), 122.0; 123.0 (d, $^4J_{P-C} = 4.4$ Hz), 143.8 (d, $C_{Ar}OP$, $^2J_{P-C} = 3.5$ Hz), 144.8 (d, $C_{Ar}OP$, $^2J_{P-C} = 7.1$ Hz). EI-MS, *m*/*z* 323 $(M+H)^+$.

3.2.3. Diethyl 1-(1,3,2-benzodioxaphosphol-2-yloxy)-2,2,2-trifluoroethylphosphonate *3b*

Yield 91%, ^{31}P NMR: 137.3 (br.s, P^{III}), 10.7 (m, P^{IV}); ^{19}F NMR: −72.15 (dd, $^3J_{F-H} = 7.5$ Hz, $^4J_{P-F} = 13$ Hz); ^1H NMR: 4.6–4.4 (m, CH, 1H); 4.4–4.1 (m, OCH_2, 4H); 1.35 (t, $^3J_{H-H} = 6$ Hz, CH_3, 6H); 7.25–7.0 (m, C_6H_4, 4H). ^{13}C NMR; 15.8 and 15.9 (both d, CH_3, $^3J_{P-C} = 5.1$ Hz); 64.0 and 64.1 (both d, $POCH_2$, $^2J_{P-C} = 21.1$ Hz); 68.2 (dqd, $^1J_{P(IV)-C} = 168.0$ Hz, $^2J_{P(III)-C} = 8.8$ Hz, $^2J_{C-F} = 34.3$ Hz); 112.4 (d, $^3J_{P-C} = 2.1$); 121.6 (qdd, $^2J_{P(IV)-C} = 5.1$ Hz, $^3J_{P(III)-C} = 5.1$ Hz, $^1J_{C-F} = 280.0$ Hz); 123.0; 144.1 (d, $C_{Ar}OP$, $^2J_{P-C} = 6.0$ Hz), 144.2 (d, $C_{Ar}OP$, $^2J_{P-C} = 5.8$ Hz). Anal. Calc. for $C_{12}H_{15}F_3O_6P_2$: C, 38.52, H, 4.04; P, 16.55. Found: C, 38.46; H, 4.14; P, 16.39%.

3.2.4. Amidophosphites *5a–e*

3.2.4.1. N,N-Diethyl-3-methyl-1,3,2-benzoxazaphosphol-2(3H)-amine 4. To a cooled (−10 °C) solution of diethylamidodichlorophosphite (4.39 g, 0.0252 mol) in diethyl ether (100 mL) the mixture of *N*-methyl-o-aminophenol (3.1 g, 0.0252 mol) and triethylamine (5.09 g. 0.0504 mol) in 100 mL of Et_2O was added. The mixture was allowed to warm up to room temperature and stirred for 2 h. Then, the precipitate was filtered off, the solvent was evaporated and the residue was distilled in vacuum to give 3.58 g (63%) of amidophosphite **4**, b.p. 160–162 °C (15 mm Hg); ^{31}P NMR: 133.0. ^1H NMR: 1.01 (t, 6H, $^3J_{H-H} = 6$ Hz), 2.6–2.9 (m, 4H, PCH_2), 2.97 (d, 3H, CH_3–N, $^3J_{P-H} = 10$ Hz), 6.5–7.2 (m, 4H, Ar).

*3.2.5. General procedure for amidophosphites **5a–e***

The mixture of diamidophosphite **4** (0.45 g, 2 mmol) and equimolar amount of the corresponding alcohol was measured in a flask, mixed thoroughly to form a homogeneous solution and heated to 160 °C using an oil bath. After 15–20 min, the formation of diethylamine was complete. The bath was removed and the flask was cooled to 100 °C and kept at this temperature in vacuum over 1 h to give the desired product in a purity of 99% according NMR data.

*3.2.6. 3-Methyl-2-(2,2,2-trifluoro-1-phenylethoxy)-2,3-dihydro-1,3,2-benzoxazaphosphole **5a***

Yield 92%, ^{31}P NMR: 129.0 (**A**), 131.0 (**B**) (both br.s, **A**:**B** = 1.5:1); ^{19}F NMR: −76.9 (appeared t, $^{3}J_{F-H} = {}^{4}J_{P-F} = 5{,}6$ Hz); ^{1}H NMR: 2.51 and 3.21 (both d, 3H, CH_3N, $^{3}J_{P-H} = 12$ Hz); 4.40–4.61 (m, 1H, CH); 6.42–7.51 (m, 9H, Ar). ^{13}C NMR: 27.0 (**A**) (d, NCH_3, $^{2}J_{P-C} = 19.7$ Hz), 27.6 (**B**) (d, NCH_3, $^{2}J_{P-C} = 20.4$ Hz); 73.0 (**A**) (q, CH, $^{2}J_{C-F} = 32.8$ Hz), 73.1 (**B**) (q, CH, $^{2}J_{C-F} = 32.8$ Hz); 107.3 (**B**), 107.9 (**A**); 108.3 (**B**) (d, $J = 4.8$ Hz), 109.0 (**A**) (d, $J = 12.1$ Hz); 111.0 (**A**), 111.6 (**B**); 119.1 (**A**), 119.2 (**B**); 119.8 (**A**), 120.1 (**B**); 122.75; 123.0 (q, CF_3, $^{1}J_{C-F} = 280.1$ Hz); 123.1 (qd, CF_3, $^{3}J_{P-C} = 2.2$ Hz, $^{1}J_{C-F} = 280.0$ Hz); 127.4, 128.1 (**B**); 128.3 (**A**), 129.3; 132.8 (**B**), 133.0 (**A**) (both s, C_{Ar}CH); 135.1 (d, C_{Ar}NMe (**A**), $^{2}J_{P-C} = 2.9$ Hz), 135.7 (d, C_{Ar}NMe (**B**), $^{2}J_{P-C} = 2.9$ Hz), 148.7 (**B**) (d, C_{Ar}OP, $^{2}J_{P-C} = 11.7$ Hz), 149.6 (**A**) (d, C_{Ar}OP, $^{2}J_{P-C} = 11.6$ Hz). Anal. Calc. for $C_{15}H_{13}F_3NO_2P$: C, 55.05, H, 4.00. Found: C, 54.70; H, 4.36%.

*3.2.7. 3-Methyl-2-[2,2,2-trifluoro-1-(3-methoxyphenyl)ethoxy]-2,3-dihydro-1,3,2-benzoxazaphosphole **5b***

Yield 90%, ^{31}P NMR: 123.9 (**A**), 125.7 (**B**) (both br.s, **A**:**B** = 1.3:1); ^{19}F NMR: −77.84 (appeared t, $^{3}J_{F-H} = {}^{4}J_{P-F} = 7{,}5$ Hz); ^{1}H NMR: 2.56 and 3.21 (both d, 3H, CH_3N, $^{3}J_{P-H} = 8$ Hz); 3.76, 3.77 (both s, 3H, ICH_3); 4.45–4.63 (m, 1H, CH); 6.45–7.25 (m, 8H, Ar). ^{13}C NMR: 27.1 (**A**) (d, NCH_3, $^{2}J_{P-C} = 19.2$ Hz), 27.7 (**B**) (d, NCH_3, $^{2}J_{P-C} = 20.1$ Hz); 55.0 (OCH_3); 73.0 (q, CH, $^{2}J_{C-F} = 32.9$ Hz); 107.3 (**A**), 107.8 (**B**); 108.7 (**A**) (d, $J = 5.2$ Hz), 109.0 (**B**) (d, $J = 9.1$ Hz); 111.0 (**B**), 111.6 (**A**), 112.5 (**A**), 112.9 (**B**); 115.3; 119.2 (**A**) (d, $^{3}J_{P-C} = 16.2$ Hz), 119.7 (B) (d, $^{3}J_{P-C} = 8.1$ Hz), 122.7 (d, $J_{P-C} = 6.0$ Hz); 123.1 (qd, CF_3, $^{3}J_{P-C} = 10.4$ Hz, $^{1}J_{C-F} = 279.0$ Hz); 135.2 (**B**) and 135.7 (**A**) (C_{Ar}NMe); 134.2 (d, $^{3}J_{P-C} = 16.9$ Hz); 148.7 (**A**) (d, C_{Ar}OP, $^{2}J_{P-C} = 12.1$ Hz); 149.5 (**B**) (d, C_{Ar}OP, $^{2}J_{P-C} = 11.2$ Hz); 159.16 (**B**) (s, C_{Ar}OMe), 159.22(**A**) (s, C_{Ar}OMe). EI-MS, *m*/*z* 358 $(M+H)^+$.

*3.2.8. 3-Methyl-2-{2,2,2-trifluoro-1-[3-(trifluoromethyl)phenyl]ethoxy}-2,3-dihydro-1,3,2-benzoxazaphosphole **5c***

Yield 95%, ^{31}P NMR: 124.0 (**A**), 124.5 (**B**) (both m, **A**:**B** = 1.3:1); ^{19}F NMR: −63,5 (br.s, 3-CF_3Ar), −78.13 (appeared t, $CH(CF_3)$, $^{3}J_{F-H} = {}^{4}J_{P-F} = 7{,}5$ Hz); ^{1}H NMR: 2.57 and 3.25 (both d, 3H, CH_3N, $^{3}J_{P-H} = 10$ Hz); 4.53, 4.66 (both dq, 1H, CH, $^{3}J_{F-H} = 6$ Hz, $^{3}J_{P-H} = 2$ Hz); 6.35–7.72 (m, 8H, Ar). ^{13}C NMR: 27.8 (d, NCH_3, $^{2}J_{P-C} = 19.7$ Hz); 72.5 (dq, CH, $^{2}J_{C-F} = 32.8$ Hz, $^{2}J_{P-C} = 3.7$ Hz); 107.4; 111.6; 119.6; 124.5 ($^{3}J_{P-C} = 3.2$ Hz); 122.8 (q, CH–CF_3, $^{1}J_{C-F} = 280.0$ Hz); 123.6 (q, ArCF_3, $^{1}J_{C-F} = 271.0$ Hz); 126.2 ($^{3}J_{P-C} = 3.8$ Hz), 128.8, 130.5 (q, $C_{Ar}CF_3$, $^{2}J_{C-F} = 32.1$ Hz); 130.7, 135.5 (d, C_{Ar}NMe, $^{2}J_{P-C} = 2.9$ Hz); 148.4 (d, C_{Ar}OP, $^{2}J_{P-C} = 11.7$ Hz). Anal. Calc. for $C_{16}H_{12}F_6NO_2P$: C, 48.62, H, 3.06; N, 3.54. Found: C, 48.67; H, 3.04; N, 3.67%.

*3.2.9. 3-Methyl-2-{[1-(trifluoromethyl)heptyl]oxy}-2,3-dihydro-1,3,2-benzoxazaphosphole **5d***

Yield 95%, ^{31}P NMR: 127.8 (**A**, br.s), 139.0 (**B**, m) (**A**:**B** = 1.3:1); ^{19}F NMR: −78.96 (dd, $^{3}J_{F-H} = 6.0$ Hz, $^{4}J_{P-F} = 2.1$ Hz), −79.37 (dd, $^{3}J_{F-H} = 7.5$ Hz, $^{4}J_{P-F} = 7.1$ Hz); ^{1}H NMR: 0.92 (t, 3H, CH_3-C, $^{3}J_{H-H} = 6.1$ Hz), 1.4–1.2 (m, 8H, –$(CH_2)_4$–); 1.57 (q, 2H, OCH_2, $^{3}J_{H-H} = 6.2$ Hz), 3.16 and 3.18 (both d, 3H, CH_3N, $^{3}J_{P-H} = 10$ Hz); 3.65–3.80 and 4.10–4.25 (both m, 1H, CH); 6.90–6.75, 7.00–7.10 (m, 4H, Ar). ^{13}C NMR: 13.9 (CH_3); 22.4 and 22.5; 24.37; 27.6 (d, NCH_3, $^{2}J_{P-C} = 19.1$ Hz), 28.0 (d, NCH_3, $^{2}J_{P-C} = 20.7$ Hz); 28.0 (**A**) (d, NCH_3, $^{2}J_{P-C} = 20.4$ Hz); 28.5 and 28.7; 29.0 and 29.4; 31.4 (d, $^{3}J_{P-C} = 3.0$ Hz); 71.7 (q, CH, $^{2}J_{C-F} = 30.6$ Hz), 71.9 (q, CH, $^{2}J_{C-F} = 31.4$ Hz); 107.6, 108.0; 111.4, 111.7; 118.8, 119.0 (d, $^{3}J_{P-C} = 5.3$ Hz); 122.6, 122.7; 124.1 (dq, CF_3, $^{1}J_{C-F} = 274.0$ Hz, $^{3}J_{P-C} = 13.1$ Hz); 135.8, 135.4 (C_{Ar}NMe); 148.7 (d, C_{Ar}OP, $^{2}J_{P-C} = 10.7$ Hz), 149.1 (d, C_{Ar}OP, $^{2}J_{P-C} = 11.5$ Hz). Anal. Calc. for $C_{15}H_{21}F_3NO_2P$: C, 53.73; H, 6.31; N 4.18. Found: C, 53.62; H, 6.31; N, 4.30%.

*3.2.10. 3-Methyl-2-[1-(pentafluorophenyl)ethoxy]-2,3-dihydro-1,3,2-benzoxazaphosphole **5e***

Yield 95%, ^{31}P NMR: 123.3 (**A**), 124.6 (**B**) (both m, **A**:**B** = 1.15:1); ^{19}F NMR: 143.5 (m, *o*-F), 156.6 (m, *p*−F), 163.0 (m, *m*-F); ^{1}H NMR: 1.50 and 1.52 (both d, 3H, CH_3, $^{3}J_{H-H} = 8$ Hz); 2.90 and 3.21 (both d, 3H, CH_3N, $^{3}J_{P-H} = 10$ Hz); 5.01 (appeared quintet, 1H, CH, $^{3}J_{H-H} = {}^{3}J_{P-H} = 8$ Hz); 6.50–7.12 (m, 4h, Ph). ^{13}C NMR: 22.3 (CH_3CH), 27.5 (**B**) (d, NCH_3, $^{2}J_{P-C} = 19.6$ Hz), 28.0 (**A**) (d, NCH_3, $^{2}J_{P-C} = 20.4$ Hz); 62.4 (OCH); 107.0 (**B**), 107.4 (**A**); 108.7 (**B**) (d, $J = 4.6$ Hz), 109.0 (**A**) (d, $^{3}J_{P-C} = 11.0$ Hz); 110.7 (**A**), 111.2 (**B**); 118.9 (**A**), 119.0 (**A**); 119.8 (**A**), 120.1 (**B**); 122.5 (**A**), 122.6 (**B**); 149.1 (d, C_{Ar}OP, $^{2}J_{P-C} = 11.6$ Hz); 135.8 (C_{Ar}NMe); 138.37 (br); 139.2 (br); 141.7 (br); 143.2 (br); 145.4 (br); 149.1 (d, C_{Ar}OP, $^{2}J_{P-C} = 11.6$ Hz). Anal. Calc. for $C_{15}H_{11}F_5NO_2P$: C, 49.60, H, 3.86; N, 3.86. Found: C, 49.61; H, 3.86; N, 3.97%.

*3.2.11. Amidophosphites **8a–c**, **9a–c** (general procedure)*

Triethylamine (0.2 g, 2 mmol) was added to a stirred and cooled (−5 to 0 °C) solution of chlorophosphite **6** (0.28 g, 2 mmol) for compounds **8a–c** or to that of chlorophosphite **7** (0.3 g, 2 mmol) for compounds **9a–c** in 30 mL

of diethyl ether under argon and the mixture was stirred for additional 5 min. Then the solution of 2 mmol of the corresponding alcohol in 30 mL of diethyl ether was added. The mixture was allowed to warm up to ambient 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*. The residue was treated with 30 mL of pentane and kept at 0 °C overnight. The clear solution was decanted from the precipitate and evaporated under reduced pressure followed by drying (20 °C, 0.1 mm Hg, 2 h) to afford the desired amidophosphites (**8a**–**c**, **9a**–**c**) as a colourless oils.

3.2.12. 3-Methyl-2-{2,2,2-trifluoro-1-[3-(trifluoromethyl)phenyl]ethoxy}-1,3,2-oxazaphospholidine **8a**

Yield 90%. ^{31}P NMR: 142.1 (**A**), 143.7 (**B**) (both br.s, **A**:**B** = 1:1.3); ^{19}F NMR: −63.5 (br.s, CF_3Ar), −77,9 and −78,2 (both br.s, CF_3CH, **A** and **B**); ^{1}H NMR: 2.72 and 2.64 (d, 3H, CH_3N, $^3J_{P-H} = 12$ Hz); 2.95–3.30 (m, 2H, CH_2N); 5.18–5.35 (m, 1H, CH); 3.45–4.12 (m, 2H, CH_2O). ^{13}C NMR: 30.5 (d, CH_3N, $^2J_{P-C} = 20.4$ Hz), 30.6 (d, CH_3N, $^2J_{P-C} = 21.9$ Hz); 48.4 (d, CH_2N, $^2J_{P-C} = 5.8$ Hz), 48.7 (d, CH_2N, $^2J_{P-C} = 5.1$ Hz); 69.0 (d, CH_2O, $^2J_{P-C} = 9.5$ Hz), 69.1 (d, CH_2O, $^2J_{P-C} = 10.2$ Hz); 71.7 (dq, CH, $^2J_{C-F} = 32.8$ Hz, $^2J_{P-C} = 13.1$ Hz), 72.1 (dq, CH, $^2J_{C-F} = 32.8$ Hz, $^2J_{P-C} = 15.3$); 123.5 (dq, $CHCF_3$, $^1J_{C-F} = 283.1$ Hz, $^3J_{P-C} = 7.3$ Hz); 124.3 (m); 124.8 (q, Ar-CF_3, $^1J_{C-F} = 269.2$ Hz); 125.9 (m); 128.75; 128.83; 130.6 (d, OCH–C_{Ar}, $^3J_{P-C} = 7.3$ Hz); 130.9 (br); 135.2; 135.3. Anal. Calc. for $C_{12}H_{12}F_6NO_2P$: C, 41.51; H, 3.48; N, 4.03. Found: C, 41.04; H, 3.53; N, 3.90%.

3.2.13. Diethyl 2,2,2-trifluoro-1-[(3-methyl-1,3,2-oxazaphospholidin-2-yl)oxy]ethylphosphonate **8b**

Yield 85%. ^{31}P NMR: 13.5 (m, P^{IV}), 147.2 (br.s, P^{III}); ^{19}F NMR: −72.07 and −72.45 (both m); ^{1}H NMR: 1.37 (t, 6H, CH_3C, $^3J_{H-H} = 6$ Hz), 2.76 and 2.80 (both d, 3H, NCH_3, $^3J_{P-H} = 12$ Hz); 3.00–3.25 (m, 2H, NCH_2); 4.45–4.65 (m, CH, 1H); 4.10–4.50 (m, OCH_2, 6H). ^{13}C NMR: 15.6 (d, CH_3CH_2OP, $^3J_{P-C} = 5.5$ Hz), 15.7 (d, CH_3CH_2OP, $^3J_{P-C} = 5.5$ Hz); 30.2 (d, CH_3N, $^2J_{P-C} = 19.7$ Hz), 30.6 (d, CH_3N, $^2J_{P-C} = 20.4$ Hz); 47.8 (d, CH_2N, $^2J_{P-C} = 5.8$ Hz), 48.2 (d, CH_2N, $^2J_{P-C} = 5.8$ Hz); 62.9, 63.0, 63.2, 63.4 (all d, CH_3CH_2OP, $^2J_{P-C} = 6.6$ Hz); 66.6 and 68.2 (both m, OCH); 68.5, 68.7 (both d, $P^{III}OCH_2$, $^2J_{P-C} = 10.2$ Hz), 122.3 (q of m, $CHCF_3$, $^1J_{C-F} = 282.0$ Hz). EI-MS, *m*/*z* 340 $(M+H)^+$.

3.2.14. 3-Methyl-2-[1-(pentafluorophenyl)ethoxy]-1,3,2-oxazaphospholidine **8c**

Yield 82%. ^{31}P NMR: 141.0 and 140.7 (overlapping m); ^{19}F NMR: 143.4 (m, *o*-F_{Ar}), 156.2 (m, *p*-F_{Ar}), 162.8 (m, *m*-F_{Ar}); ^{1}H NMR: 1.61 (d, 3H, CH_3CH, $^3J_{H-H} = 6$ Hz); 2.63 and 2.70 (both d, 3 H, NCH_3, $^3J_{P-H} = 10$ Hz); 2.90–3.24 (m, 2H, NCH_2); 4.10–4.54 (m, OCH_2, 2H); 5.35–5.50 (m, 1H, OCH). ^{13}C NMR: 22.2 (br., CH_3); 30.9 (d, CH_3N, $^2J_{P-C} = 15.3$ Hz), 31.1 (d, CH_3N, $^2J_{P-C} = 15.4$ Hz); 48.8 (d, CH_2N, $^2J_{P-C} = 5.1$ Hz), 48.9 (d, CH_2N, $^2J_{P-C} = 5.1$ Hz); 66.4 (d, OCH, $^2J_{P-C} = 5.8$ Hz), 66.7 (d, OCH, $^2J_{P-C} = 5.8$ Hz); 68.7 (d, OCH_2, $^2J_{P-C} = 5.8$ Hz), 130.6 (br), 135.8 (br.m), 136.0 (br.m), 138.5 (br.m), 143.1 (br.m), 145.7 (br.m). Anal. Calc. for $C_{11}H_{11}F_5NO_2P$: C, 41.92; H, 3.52; N, 4.44. Found: C, 41.48; H, 3.65; N, 4.42%.

3.2.15. 1,3-Dimethyl-2-(2,2,2-trifluoro-1-phenylethoxy)-1,3,2-diazaphospholidine **9a**

Yield 88%. ^{31}P NMR: 132.4 (br.s); ^{19}F NMR: −77.11 (dd, $^3J_{F-H} = 7.0$ Hz, $^4J_{P-F} = 4.1$ Hz); ^{1}H NMR: 2.46 and 2.57 (both d, 6H, CH_3N, $^3J_{P-H} = 12.2$ Hz); 3.00–3.35 (m, 4H, CH_2N); 5.12 (appeared quintet, 1H, CH, $^3J_{P-H} = {}^3J_{P-H} = 7.0$ Hz,); 7.35–7.51 (m, 5H, Ph). ^{13}C NMR: 33.0 (d, CH_3N, $^2J_{P-C} = 22.6$ Hz), 33.4 (d, CH_3N, $^2J_{P-C} = 24.8$ Hz); 52.1 (d, CH_2N, $^2J_{P-C} = 10.9$ Hz), 52.5 (d, CH_2N, $^2J_{P-C} = 10.2$ Hz); 72.1 (qd, CH, $^2J_{C-F} = 31.3$ Hz, $^2J_{P-C} = 7.3$ Hz); 124.1 (qd, $CHCF_3$, $^1J_{C-F} = 280.1$ Hz, $^3J_{P-C} = 3.6$ Hz);127.6 (*o*-C_{Ar}), 128.0 (*m*-C_{Ar}), 128.7 (*p*-C_{Ar}), 134.7 (*ipso*-C_{Ar}). EI-MS, *m*/*z* 293 $(M+H)^+$.

3.2.16. Diethyl 1-[(1,3-dimethyl-1,3,2-diazaphospholidin-2-yl)oxy]-2,2,2-trifluoroethylphosphonate **9b**

Yield 96%. ^{31}P NMR: 14.3 (m, P^{IV}), 144.9 (br.s, P^{III}); ^{19}F NMR: −72.11 (dd, $^3J_{F-H} = 8.0$ Hz, $^4J_{P-F} = 7.5$ Hz); ^{1}H NMR: 1.35 (t, 6H, CH_3C, $^3J_{H-H} = 6.1$ Hz); 2.71 and 2.77 (both d, 6H, CH_3N, $^3J_{P-H} = 12.1$ Hz); 3.05–3.35 (m, 4H, CH_2N); 4.11–4.40 (m, 4H, CH_2O), 4.53 (dq, 1H, CH, $^3J_{F-H} = 8.0$ Hz, $^2J_{P-H} = 20.1$ Hz). ^{13}C NMR: 16.0 (d, CH_3CH_2OP, $^3J_{P-C} = 5.3$ Hz), 33.5 (d, CH_3N, $^2J_{P-C} = 22.8$ Hz), 33.8 (d, CH_3N, $^2J_{P-C} = 24.3$ Hz); 52.2 (d, CH_2N, $^2J_{P-C} = 9.9$ Hz), 52.3 (d, CH_2N, $^2J_{P-C} = 9.9$ Hz); 63.1 (d, $P(O)OCH_2$, $^2J_{P-C} = 6.8$ Hz), 63.2 (d, $P(O)OCH_2$, $^2J_{P-C} = 6.9$ Hz); 68.2 (dqd, OCH, $^2J_{D(III)-C} = 13.7$ Hz, $^2J_{C-F} = 32.7$ Hz, $^1J_{P(IV)-C} = 170.3$ Hz); 122.9 (qd, $CHCF_3$, $^1J_{C-F} = 281.1$ Hz, $^3J_{P-C} = 8.1$ Hz). Anal. Calc. for $C_{10}H_{21}F_3N_2O_4P_2$: C, 34.10; H, 6.01; P, 17.59. Found: C, 33.98; H, 6.00; P, 16.99%.

3.2.17. 1,3-Dimethyl-2-{[1-(trifluoromethyl)heptyl]oxy}-1,3,2-diazaphospholidine **9c**

Yield 98%. ^{31}P NMR: 141.3 (br.s); ^{19}F NMR: −78.2 (appeared t, $^3J_{F-H} = {}^4J_{P-F} = 7.5$ Hz); ^{1}H NMR: 0.90 (t, 3H,CH_3C, $^3J_{H-H} = 6.2$ Hz); 1.15–1.25 (m, 8H, –$(CH_2)_4$–); 1.60–1.75 (m, 2H, OCH_2); 2.71 and 2.75 (d, 6H, CH_3N, $^3J_{P-H} = 14.2$ Hz); 3.00–3.15 and 3.25–3.35 (m, 4H, CH_2N); 4.00–4.25 (m, 1H, CH). ^{13}C NMR: 13.7 (CH_3); 22.3, 24.6, 28.7, 29.8, 31.5 ($(CH_2)_5$); 33.7 (d, CH_3N, $^2J_{P-C} = 21.9$ Hz), 34.2 (d, CH_3N, $^2J_{P-C} = 24.8$ Hz); 52.4 (d, CH_2N, $^2J_{P-C} = 9.5$ Hz), 52.5 (d, CH_2N, $^2J_{P-C} = 9.5$ Hz); 71.1 (qd, CH, $^2J_{C-F} = 29.9$ Hz, $^2J_{P-C} = 17.5$ Hz);

125.0 (qd, CHCF$_3$, $^1J_{C-F} = 280.1$ Hz, $^3J_{P-C} = 2.9$ Hz). EI-MS, *m/z* 301 $(M+H)^+$.

3.2.18. Diamidophosphites **14a–g** (general procedure)

A mixture of 2 mmol of the corresponding diamine and 4 mmol of triethylamine in 30 mL of ether was added to a cooled (0 °C) solution of a dichlorophosphite (2 mmol) **13a**,**b** in 30 mL of ether. The mixture was allowed to warm up to room temperature and stirred for 2 h. Then the precipitate formed was filtered off, washed by an additional amount of ether (2 × 15 mL). The combined filtrate was evaporated to dryness, pentane was added to the residue and kept at 0 °C overnight. The clear pentane solution was decanted, evaporated and the residue dried in vacuum (2 h, 40 °C) to yield the desired diamidophosphite. Compounds **14g**,**f** were recrystallized from hexane.

3.2.19. 1,3-Diisopropyl-2-(2,2,2-trifluoro-1-phenylethoxy)-1,3,2-diazaphospholidine **14a**

Yield 87% (oil), ^{31}P NMR: 129.3; ^{19}F–{^{1}H} NMR: −77.8; ^{1}H NMR: 1.02, 1.03, 1.04, 1.16 (all d, 4 × 3H, CH$_3$ (*i*-Pr), $^3J_{H-H} = 6.0$ Hz); 3.01–3.32 (m, 6H, CH$_2$N + CHN); 5.15 (dq, 1H, CH, $^3J_{F-H} = 8.0$ Hz, $^3J_{P-H} = 2.1$ Hz); 7.25–7.51 (m, 5H, Ph). ^{13}C NMR: 21.5 (d, CH$_3$, $^3J_{P-C} = 7.3$ Hz); 21.8 (d, CH$_3$, $^3J_{P-C} = 9.5$ Hz); 21.9 (d, CH$_3$, $^3J_{P-C} = 8.8$ Hz); 22.1 (d, CH$_3$, $^3J_{P-C} = 9.5$ Hz); 45.0 (d, CH$_2$N, $^2J_{P-C} = 9.5$ Hz), 45.2 (d, CH$_2$N, $^2J_{P-C} = 9.5$ Hz); 47.1 (d, CHN, $^2J_{P-C} = 10.2$ Hz), 47.3 (d, CH$_2$N, $^2J_{P-C} = 12.4$ Hz); 72.3 (qd, OCH, $^2J_{C-F} = 30.6$ Hz, $^2J_{P-C} = 10.2$); 124.2 (qd, CF$_3$, $^1J_{C-F} = 281.0$ Hz, $^3J_{P-C} = 4.4$ Hz); 125.7, 127.8. 128.7, 135.1 (*ipso*-C_{Ar}). EI-MS, *m/z* 349 $(M+H)^+$. Anal. Calc. for $C_{16}H_{24}F_3N_2OP$: C 55.17, H 6.94. Found: C 55.41; H 6.82%.

3.2.20. 1,3-Diisopropyl-2-(2,2,2-trifluoro-1-phenylethoxy)hexahydro-1,3,2-diazaphosphorine **14b**

Yield 84% (oil); ^{31}P NMR: 129.9; ^{19}F NMR: −78.3; ^{1}H NMR: 0.79, 1.00, 1.15, 1.20 (all d, 4 × 3H, CH$_3$ (*i*-Pr), $^3J_{H-H} = 6.0$ Hz); 2.51–3.5 (m, 8H, CH$_2$CH$_2$N + CHN); 4.92 (dq, 1H, CH, $^3J_{F-H} = 8.0$ Hz, $^3J_{P-H} = 2.0$ Hz); 7.25–7.75 (m, 5H, Ph). ^{13}C NMR: 20.6 (d, CH$_3$, $^3J_{P-C} = 10.9$ Hz); 20.7 (d, CH$_3$, $^3J_{P-C} = 10.9$ Hz); 21.8 (d, CH$_3$, $^3J_{P-C} = 10.2$ Hz); 22.1 (d, CH$_3$, $^3J_{P-C} = 8.8$ Hz); 26.8 (NCH$_2$*C*H$_2$-CH$_2$N); 37.6 (d, CH$_2$N, $^2J_{P-C} = 5.1$ Hz), 38.2 (d, CH$_2$N, $^2J_{P-C} = 5.8$ Hz); 51.5 (d, CHN, $^2J_{P-C} = 8.0$ Hz), 51.9 (d, CH$_2$N, $^2J_{P-C} = 12.4$ Hz); 72.8 (qd, OCH, $^2J_{C-F} = 31.4$ Hz, $^2J_{P-C} = 14.6$); 124.4 (qd, CHCF$_3$, $^1J_{C-F} = 280.7$ Hz, $^3J_{P-C} = 7.3$ Hz); 127.8, 127.9. 128.6, 135.2 (*ipso*-C_{Ar}). EI-MS, *m/z* 363 $(M+H)^+$.

3.2.21. 1,3-Diisopropyl-2-[1-(pentafluorophenyl)ethoxy]-1,3,2-diazaphospholidine **14c**

Yield 80% (oil), ^{31}P NMR: 125.0; ^{19}F NMR: −143.2 (m, *o*-F), −157.2 (m, *p*-F), −163.2 (m, *m*-F); ^{1}H NMR: 1.10, 1.11, 1.12, 1.13 (all d, 4 × 3H, CH$_3$ (*i*-Pr), $^3J_{H-H} = 6.0$ Hz); 1.56 (d, 3H, CH$_3$, $^3J_{H-H} = 6.0$ Hz), 3.02–3.40 (m, 6H, CH$_2$N + CHN); 5.39 (dq, 1H, CH, $^3J_{H-H} = 6.0$ Hz, $^3J_{P-H} = 2.0$ Hz). ^{13}C NMR: 21.8 (d, NCH*C*H$_3$, $^3J_{P-H} = 8.8$ Hz); 21.9 (d, NCH*C*H$_3$, $^3J_{P-C} = 8.8$ Hz); 22.0 (d, NCH*C*H$_3$, $^3J_{P-C} = 10.2$ Hz); 22.1 (d, NCH*C*H$_3$, $^3J_{P-C} = 10.2$ Hz); 22.6 (br., OCH*C*H$_3$); 45.4 (d, CH$_2$N, $^2J_{P-C} = 5.1$ Hz), 45.5 (d, CH$_2$N, $^2J_{P-C} = 5.1$ Hz); 47.4 (d, CHN, $^2J_{P-C} = 14.6$ Hz); 47.7 (d, CHN, $^2J_{P-C} = 13.9$ Hz); 61.2 (d, OCH, $^2J_{P-C} = 10.2$); 135.8 (m); 138.6 (m); 141.6 (m); 143.1 (m); 145.6 (m). EI-MS, *m/z* 385 $(M+H)^+$.

3.2.22. 1,3-Di(tert-butyl)-2-(2,2,2-trifluoro-1-phenylethoxy)-1,3,2-diazaphospholidine **14d**

Yield 84%, m.p. 47–48 °C, ^{31}P NMR: 123.9; ^{19}F NMR: −76,9; ^{1}H NMR: 1.12, 1.15 (two s, 2 × 9H, CH$_3$); 3.00–3.35 (m, 4H, CH$_2$N); 5.14 (dq, 1H, CH, $^3J_{F-H} = 8.0$ Hz, $^3J_{P-H} = 2.0$ Hz); 7.30–7.52 (m, 5H, Ph). ^{13}C NMR: 29.1 (d, NC*C*H$_3$, $^3J_{P-C} = 10.9$ Hz); 29.3 (d, NC*C*H$_3$, $^3J_{P-C} = 10.9$ Hz); 44.8 (d, CH$_2$N, $^2J_{P-C} = 8.8$ Hz); 45.2 (d, CH$_2$N, $^2J_{P-C} = 8.8$ Hz); 52.2 (d, N*C*(CH$_3$)$_3$, $^2J_{P-C} = 6.7$ Hz); 52.3 (d, N*C*(CH$_3$)$_3$, $^2J_{P-C} = 3.4$ Hz); 72.0 (qd, OCH, $^2J_{C-F} = 30.6$ Hz, $^2J_{P-C} = 6.6$ Hz); 124.4 (qd, CF$_3$, $^1J_{C-F} = 281.0$ Hz, $^3J_{P-C} = 5.1$ Hz); 127.9 (*o*-C_{Ar}), 128.3 (*m*-C_{Ar}), 128.7 (*p*-C_{Ar}), 135.5 (*ipso*-C_{Ar}). EI-MS, *m/z* 377 $(M+H)^+$.

3.2.23. 1,3-Di(tert-butyl)-2-[1-(pentafluorophenyl)ethoxy]-1,3,2-diazaphospholidine **14e**

Yield 86%, m.p. 43–45 °C, ^{31}P NMR: 120.0; ^{19}F NMR: −143.0 (m, *o*-F), −157.5 (m, *p*-F), −163.4 (m, *m*-F); ^{1}H NMR: 1.17, 1.22 (two s, 2 × 9H, CH$_3$); 1.56 (d, 3H, CH$_3$, $^3J_{H-H} = 6.1$ Hz); 3.25–3.40 (m, 4H, CH$_2$N); 5.45 (dq, 1H, CH, $^3J_{H-H} = 6.1$ Hz, $^3J_{P-H} = 4.1$ Hz). ^{13}C NMR: 22.8 (br., OCH*C*H$_3$); 29.1 (d, NC*C*H$_3$, $^3J_{P-C} = 10.7$ Hz); 29.3 (d, NC*C*H$_3$, $^3J_{P-C} = 10.6$ Hz); 45.0 (d, CH$_2$N, $^2J_{P-C} = 9.1$ Hz); 45.3 (d, CH$_2$N, $^2J_{P-C} = 9.1$ Hz); 52.0 (d, N*C*(CH$_3$)$_3$, $^2J_{P-C} = 4.6$ Hz); 52.2 (d, N*C*(CH$_3$)$_3$, $^2J_{P-C} = 3.8$ Hz); 60.6 (d, OCH, $^2J_{P-C} = 8.6$ Hz); 136.1 (m); 138.5 (m); 141.1 (m) 143.3 (m); 145.7 (m). EI-MS, *m/z* 413 $(M+H)^+$.

3.2.24. 1,3-Diphenyl-2-(2,2,2-trifluoro-1-phenylethoxy)-1,3,2-diazaphospholidine **14f**

Yield 83%, m.p. 119–120 °C; ^{31}P NMR: 107.2; ^{19}F–{^{1}H} NMR: −77.7; ^{1}H NMR: 3.45–3.91 (m, 4H, CH$_2$N); 5.04 (dq, 1H, CH, $^3J_{F-H} = 7.5$ Hz, $^3J_{P-H} = 2.1$ Hz); 6.30–7.00, 7.05–7.25 (m, 15H, Ph). ^{13}C NMR: 45.6 (d, CH$_2$N, $^2J_{P-C} = 10.2$ Hz); 47.2 (d, CH$_2$N, $^2J_{P-C} = 9.5$ Hz); 72.8 (q, OCH, $^2J_{C-F} = 32.1$ Hz); 123.6 (qd, CF$_3$, $^1J_{C-F} = 279.3$ Hz, $^3J_{P-C} = 5.1$ Hz); 127.5, 127.9, 128.9, 129.1, 132.7; 143.9 (*ipso*-C_{Ar}N, $^2J_{P-C} = 16.8$ Hz); 144.2 (*ipso*-C_{Ar}N, $^2J_{P-C} = 18.9$ Hz). Anal. Calc. for $C_{22}H_{20}F_3N_2OP$: C, 63.46, H, 4.84; N, 6.73. Found: C, 63.49; H, 4.83; N, 6.60%.

3.2.25. 2-[1-(Pentafluorophenyl)ethoxy]-1,3-diphenyl-1,3,2-diazaphospholidine **14g**

Yield 75%, m.p. 107–108 °C, ^{31}P NMR: 108.0; ^{19}F NMR: −144.0 (m, *o*-F), −157.0 (m, *p*-F), −163.0 (m,

m-F); ^{1}H NMR: 1.48 (d, 3H, CH_3, $^3J_{H-H} = 6.2$ Hz), 3.62–3.91 (m, 4H, CH_2N); 5.38 (dq, 1H, CH, $^3J_{H-H} = 6.2$ Hz, $^3J_{P-H} = 2.1$ Hz); 6.25–7.02, 7.10–7.40 (m, 10H, Ph). ^{13}C NMR: 22.3 ($OCHCH_3$); 62.6 (OCH); 46.8 (d, CH_2N, $^2J_{P-C} = 9.4$ Hz); 114.3 (d, $^4J_{P-C} = 1.9$ Hz); 115.6 (d, $^4J_{P-C} = 1.8$ Hz); 119.9; 120.4; 129.1 (d, $^3J_{P-C} = 25.2$ Hz); 129.5; 135.7 (m); 138.6 (m); 141.9 (m) 142.4 (m); 144.3 (*ipso*-$C_{Ar}N$, $^2J_{P-C} = 16.6$ Hz); 144.5 (*ipso*-$C_{Ar}N$, $^2J_{P-C} = 16.3$ Hz). EI-MS, *m*/*z* 452 $(M+H)^+$.

3.3. Synthesis of the (π-pentamethylcyclopentadienyl)-(amidophosphite)rhodium dichlorides **15a–c** (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 the corresponding (amido)phosphite (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-orange) was filtered off and dried *in vacuo* to afford the desired complexes.

Compound **15a**. Yield 86%, m.p. 202–203 °C, ^{31}P NMR: 130.38 (d, $^1J_{P-Rh} = 229.2$ Hz); ^{19}F–{^{1}H} NMR: −62.63 (s, 3F, $CF_3C_6H_4$,), −76.23 (s, 3F, CF_3CH); ^{1}H NMR: 1.69 (d, 15H, CH_3 in Cp^*, $J = 6.0$ Hz); 3.12 (d, 3H, CH_3N, $^3J_{P-H} = 10.0$ Hz); 5.69, 5.78 (both dq, 1H, CH, $^3J_{F-H} = 6.1$ Hz, $^3J_{P-H} = 3.2$ Hz); 6.71 (d, 1H, Ar, $^3J_{H-H} = 7.7$); 6.80–6.87 (m, 2H, Ar); 7.02 (t, 1H, Ar, $^3J_{H-H} = 7.7$ Hz); 7.35–7.45 (m, 3H, Ar); 7.60 (d, 1H, Ar, $^3J_{H-H} = 7.2$ Hz). Anal. Calc. for $C_{26}H_{27}Cl_2F_6NO_2PRh$: C, 44.34, H, 3.86. Found: C, 44.36; H, 3.91%.

Compound **15b**. Yield 89%, m.p. 223–224 °C, ^{31}P NMR: 116.48 (d, $^1J_{P-Rh} = 196.8$ Hz); ^{19}F–{^{1}H} NMR: −76.08; ^{1}H NMR: 1.58 (d, 15H, CH_3 in Cp^*, $J = 4.9$ Hz); 2.39 (br.d, 3H, CH_3N, $^3J_{P-H} = 10.6$ Hz); 2.64 (br., 3H, CH_3N); 3.24–3.38 (m, 4H, CH_2N); 6.01 (br., 1H, CH); 7.30–7.32, 7.43–7.47 (both m, 3H + 2H, Ph). Anal. Calc. for $C_{22}H_{31}Cl_2F_3N_2OPRh$: C, 43.95, H, 5.20; N, 4.66. Found: C, 44.12; H, 5.09; N, 4.77%.

Compound **15c**. Yield 83%, m.p. 139–140 °C, ^{31}P NMR: 11.72 (s, P^{IV}), 116.59 (d, P^{III}, $^1J_{P-Rh} = 218.2$ Hz); ^{19}F–{^{1}H} NMR: −69.3; ^{1}H NMR: 1.31 (t, 6H,CH_3C, $^3J_{H-H} = 5.2$ Hz); 1.61 (d, 15H, CH_3 in Cp^*, $J = 3.8$ Hz); 2.83 and 2.86 (both d, 6H, CH_3N, $^3J_{P-H} = 11.4$ Hz); 3.27–3.35 and 3.42–3.57 (both m, 2H + 2H, CH_2N); 4.18-4.28 (m, 4H, CH_2O), 5.17 (br., 1H, CH). Anal. Calc. for $C_{20}H_{36}Cl_2F_3N_2O_4P_2Rh$: C, 36.33, H, 5.49; N, 4.24. Found: C, 36.17; H, 5.56; N, 3.98%.

3.4. X-ray crystallography

Crystals of **14f** and **15a** suitable for X-ray diffraction were grown up by slow evaporation of solutions of the compounds in CH_2Cl_2. X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector, using graphite monochromated Mo Kα radiation (λl = 0.71073 Å, ω-scans) at 120 K (Table 3). Low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. Reflection intensities were integrated using SAINT software [16] and absorption correction was applied semi-empirically using SADABS program [17]. The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. The analysis of difference Fourier synthesis has revealed that one of CF_3 groups in complex **15a** is disordered by two positions which were refined with equal occupancies in anisotropic approximation. The positions of hydrogen atoms were calculated from geometrical point of view. Crystal data and structure refinement parameters for **14f** and **15a** are given in Table 3. All calculations were performed using the SHELXTL software [18].

Table 3
Crystal data and structure refinement parameters for **14f** and **15a**

Compound	**14f**	**15a**
Empirical formula	$C_{22}H_{20}F_3N_2OP$	$C_{26}H_{27}Cl_2F_6NO_2PRh$
Formula weight	416.37	704.27
Temperature (K)	120	120
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2$
a (Å)	6.3451(10)	15.052(2)
b (Å)	10.0166(16)	8.9471(11)
c (Å)	15.513(3)	22.443(3)
α (°)	88.911(5)	
β (°)	88.667(5)	108.234(5)
γ (°)	83.709(5)	
V (Å^3)	979.6(3)	2870.7(7)
Z (Z')	2(1)	4(1)
F(000)	432	1416
D_{calc} (g cm^{-1})	1.412	1.630
Linear absorption, μ (cm^{-1})	1.84	9.01
T_{min}/T_{max}	0.9572/0.9765	0.7145/0.9153
Flack parameter	–	0.02(6)
Scan type	ω	ω
θ Range (°)	1.91–27.5	1.91–27.50
Completeness of dataset (%)	99.4	99.3
Reflections measured	7697	8802
Independent reflections	4474 [$R_{int} = 0.0317$]	5302 [$R_{int} = 0.0515$]
Observed reflections [$I > 2\sigma(I)$]	2849	3272
Parameters	262	368
Final $R(F_{hkl})$: R_1	0.0457	0.0578
wR_2	0.0995	0.1021
Goodness-of-fit value	0.957	0.999
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.417, −0.283	1.052, −0.926

The crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC-614283 for **14f** and CCDC-614284 for **15a**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

3.5. Hydroformylation experiments

In a typical experiment 1.6 mg (0.00625 mmol) of $Rh(CO)_2(acac)$ precursor and 0.0125 mmol of ligand were dissolved in 1.5 mL toluene, 3.125 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 by $CO/H_2 = 1/1$ 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 analysed immediately by GC.

3.6. Computational details

Full geometry optimizations have been performed at the density functional level of theory without any symmetry constraints using the Gaussian 03 suite of programs [19] and the 6-31G* basis set [20]. The stationary points were characterized by frequency calculations in order to verify that the minima have zero imaginary frequency. The NBO analyses were carried out on the stationary points using the NBO 3.1 program [10] as implemented in Gaussian. For all the calculations the gradient-corrected exchange functional developed by Perdew, Burke and Ernzerhof was utilized in combination with a correlation functional also developed by the same authors [21] and denoted as PBE. The initial structures for geometry optimizations were obtained by Monte Carlo conformational analyses using the Spartan '04 program package [22] and the MMFF force field. In order to determine the Tolman's cone angles [9] the STERIC program [23] was used.

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