Catalysis Science & Technology

Accepted Manuscript

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ARTICLE

Strong π-Acceptor Sulfonated Phosphines in Biphasic Rhodium catalyzed Hydroformylation of Polar Alkenes

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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A new series of sulfonated triarylphosphines with strong π-acceptor character were synthesized by direct sulfonation of trifluoromethylated neutral phosphines. Due to the deactivating character of the trifluoromethyl group, high oleum concentration and the use of boric acid to prevent phosphines to be oxidized were required for the sulfonation step. The new sulfonated phosphines are water soluble and more inert toward oxidation than classical sulfonated phosphines. The use of these trifluoromethylated and sulfonated phosphines as ligands in the biphasic hydroformylation of vinyl acetate and allyl cyanide increases the rate of the reaction up to 4 times, compared to the results obtained with the non-trifluoromethylated counterparts, TPPMS, TPPDS and TPPTS. Moreover, it is possible to recycle the catalyst without a significant loss of the system activity.

Introduction

Phosphines are one of the most widely used ligands in transition metal-based homogeneous catalysis. The most interesting feature of these trivalent phosphorous compounds relies on the fact that their stereoelectronic properties can be readily modified by changing their substituents. This is a key factor in order to optimize a given catalyzed transformation. A remarkable application of this concept is the development of water soluble phosphines for biphasic catalytic reactions. In these processes, the metal catalyst remains in the aqueous phase, while the substrate and the products remain in another phase, facilitating their separation from the catalyst by simple decantation. This allows the recycling of the latter, paralleling the advantages of a heterogeneous process, without losing the characteristic selectivity of molecular catalysts. Some biphasic catalytic processes of this type, based on water soluble phosphines, have been implemented in the industry, such as the production of Vitamin A and E intermediates via a carbon-carbon coupling reaction,[1] the hydrodimerization of butadiene developed by *Kuraray* for the production of 1-octanol and nonadiol,[2] or the synthesis of 2-cyano-4'-methylbiphenyl, a key pharmaceutical intermediate, via Suzuki coupling reaction developed by *Hoechst*.[3] However, the most important biphasic process that currently operates in the industry is the *Ruhrchemie-Rhône Poulenc Process* for the hydroformylation of propene and *n*-butene.[4] The process uses the sodium salt of the trisulfonated triphenylphosphine (Na_3TPPTS) that makes the resulting rhodium catalyst highly water soluble. The process has been operating since 1984 and produces more than 800000 tonnes of *n*-butanal per year in five plants.[5]

The modification of the stereoelectronic properties of triarylphosphines is also a classic strategy to optimize catalytic processes. In particular, the presence of electron withdrawing substituents in the phosphine, such as trifluoromethyl groups, decreases the electron density on the phosphorous atom. This results in a reduction of the σ-donating capability of the phosphine and in an increase of their π-backbonding ability, when compared with the non-trifluoromethylated equivalents. As a result of these effects, changes in the rate of one or more steps comprised in a catalytic cycle can be achieved. For instance, triarylphosphines with trifluoromethyl groups have been proven to increase the activity and the selectivity of different catalytic transformations such as carbon-carbon coupling reactions[6] or different carbonylations.[7]

Only two arylic phosphines with sulfonated and fluorinated groups have been so far described in the literature. Fell *et al.* reported the sulfonation of tris(*p*-fluorophenyl)phosphine obtaining a mixture composed mainly of the corresponding disulfonated ligand, with 6% of the trisulfonated derivative, after more than two weeks reaction. This mixture of ligands was essayed in the rhodium catalyzed biphasic hydroformylation of 1-hexene achieving higher regioselectivities than with Na_3TPPTS, , at low phosphine/Rh ratios.[8] Nevertheless, phosphines with fluorine atoms directly bonded to the rings must be far less acidic than trifluoromethyl substituted arylphosphines.[9] Along this line, Bakos *et al.* described the synthesis of a trifluoromethylated and sulfonated phosphine, by sulfonation of the (*p*-anisyl)bis(*p*-trifluoromethylphenyl)phosphine. The Rh complex of this ligand was successfully essayed in the thermoregulated monophasic/biphasic hydrogenation of cinnamic aldehyde. However, the presence of the methoxy substituent, required for preparing this ligand, should decrease the π-acidity of this phosphine.[10]

In the present work, we report the synthesis of a new series of phosphines containing no other substituents than sulfonated and trifluoromethylated groups (Figure 1).

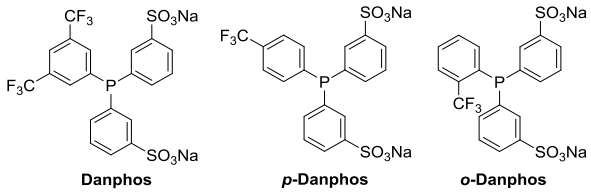


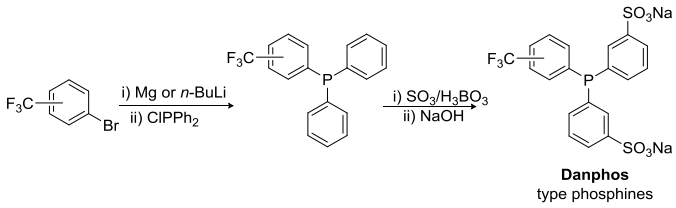
Figure 1. Danphos type phosphines

We have investigated the effect of the trifluoromethyl groups in the biphasic rhodium catalyzed hydroformylation of two different substrates, vinyl acetate and allyl cyanide. Both substrates yield attractive synthetic intermediates containing two different functional groups.

Results and Discussion

Sulfonated and Trifluoromethylated Phosphines

Danphos ligands were synthesized by means of sulfonation of a neutral trifluoromethylated triarylphosphine. The starting diphenylarylphosphines were prepared by the reaction of chlorodiphenylphosphine and the corresponding trifluoromethylated organometallic derivative (Scheme 1). Because of the deactivating effect of the trifluoromethyl groups, only monosulfonated or disulfonated phosphines can be obtained by the reaction of the diphenylarylphosphines with oleum.



Scheme 1. Synthesis of Danphos type phosphines

When standard conditions for the synthesis of TPPTS and other sulfonated phosphines[11] were applied to (trifluoromethylphenyl)diphenylphosphines, phosphine oxides were obtained instead of the desired sulfonated products. It was necessary to use a large excess of SO_3, in the form of 65% oleum, and 4-5 equivalents of boric acid in order to prepare Danphos derivatives. As it has been previously reported,[12] H_3BO_3 in oleum generates a strong acid that assures the protonation of these weakly basic phosphines. In optimized conditions, the reaction progress can be monitored by analyzing an aliquot of the reaction mixture by $^{31}P\{^1H\}$ NMR in a mixture of D_2O and methanol. This mixture dissolves both the starting phosphines and the mono- and disulfonated products. Once the disulfonated product is the only product observed by NMR, the reaction is quenched by pouring the reaction mixture into deoxygenated water/ice slush. Purification of the phosphines from their oxides was carried out by a pH selective biphasic extraction of the tri-*n*-octylammonium salts into a toluene phase.[13] The pH values for the extractions of the different products were determined by $^{31}P\{^1H\}$ NMR, using a mixture of the phosphines with their corresponding oxides. Details of the optimized purification in each case are described in the experimental part. With this procedure, the sodium salts of the sulfonated phosphines were obtained with purities higher than 95%, being the corresponding oxides the only impurities observed.

Aerial Oxidation of Danphos type phosphines

Ligand stability is an important feature in order to achieve an industrial feasible catalytic process, since the price of the ligands can represent a significant part of the overall cost. Moreover, when catalyst recycling is required, the ligand robustness is an important attribute to preserve the activity of the catalyst after different cycles, taking into account the extraction and separation processes. In the case of phosphines, the main drawback associated with the ligand stability arises from their ease oxidation.

In order to study the inertness towards aerial oxidation, solutions of the phosphines ($5 \cdot 10^{-2}$ M) in water were prepared and kept in open air under vigorous stirring for nearly 600 h. Aliquots were periodically analyzed by $^{31}P\{^1H\}$ NMR in order to quantify the percentage of phosphine oxide formed (Figure 2).

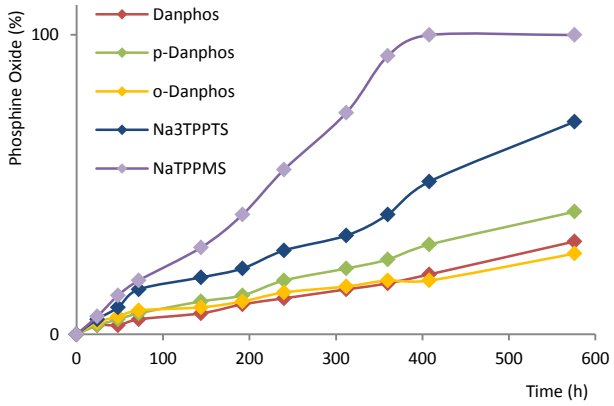


Figure 2. Oxidation of sulfonated phosphines in water.

As expected, the presence of trifluoromethyl groups in Danphos type phosphines increases their robustness against aerial oxidation, when compared with NaTPPMS or Na_3TPPTS. After 600 hours of stirring, the Danphos type phosphines solutions showed oxide percentages between 30 and 40%, while the non trifluoromethylated phosphines, NaTPPMS and Na_3TPPTS, were completely oxidized or oxidized up to 70%, respectively. It is important to note that sulfonate groups also increase the resistance of phosphines towards oxidation, but they do it in lesser extent than trifluoromethyl groups.

Electronic Properties of the Phosphines. Selenide Derivatives

There is a good correlation between the ^{31}P-^{77}Se coupling constant of selenide derivatives of phosphines and their electronic properties.[14] The σ-donating ability of the sulfonated phosphines was measured by means of the ^{31}P-^{77}Se coupling constant of the selenide derivatives in the $^{31}P\{^1H\}$ NMR spectra. The coupling constant increases as the σ-donating ability of the phosphines decreases, because of the shorter distance between the phosphorous and the selenium atoms.

The selenide derivatives of Danphos type phosphines and non-trifluoromethylated phosphines were synthesized by the reaction

of the sulfonated ligands with an excess of black selenium in methanol.

The coupling constants obtained in the $^{31}P\{^{1}H\}$ NMR spectra for all the Danphos type phosphines were higher than those obtained for the corresponding non-trifluoromethylated phosphines, indicating a lower σ-donating ability of the trifluoromethylated ligands (Figure 3).

The presence of sulfonated groups has the same electronic effect than the trifluoromethyl groups, but to lesser extent. In this way, the trisulfonated triphenylphosphines have a smaller σ-donating ability than the disulfonated and the monosulfonated phosphines.

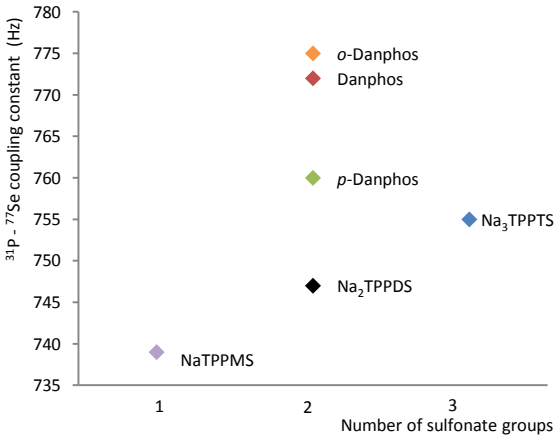


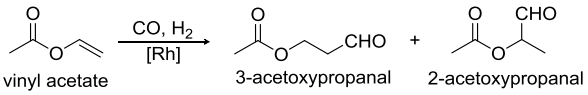
Figure 3. ^{31}P-^{77}Se coupling constants of the selenide derivatives of the sulfonated phosphines determined by $^{31}P\{^{1}H\}$ NMR.

The expected correlation between the σ-donating ability of the phosphines and their inertness against aerial oxidation can be seen by comparing Figures 2 and 3. Danphos type phosphines, which are less σ-donating than the non-trifluoromethylated ligands, are less susceptible to air oxidation.

It is important to note that the position of the trifluoromethyl groups in the ligand structure has an important effect in the σ-donating ability of the phosphines. According to the values of the ^{31}P-^{77}Se coupling constants, as well as the measured resistance to the aerial oxidation, *o*-Danphos is a less σ-donating ligand than *p*-Danphos and Danphos, although these two ligands have the same or double number of trifluoromethyl substituents respectively. It is believed that the close proximity of the *orto*-trifluoromethyl group drains more electronic density from the phosphorus atom than in the case of the *para* or *meta* derivatives, although steric effects cannot be excluded.

Vinyl Acetate Biphasic Hydroformylation with Sulfonated Phosphines

The products obtained from the hydroformylation of vinyl acetate (Scheme 2) have been widely used as synthetic intermediates in industry.[15] In particular, 3-acetoxypropanal is employed to synthesize 1,3-propanediol, a monomer used in the industry of polyurethanes, adhesives and resins. The branched aldehyde 2-acetoxypropanal is an intermediate to produce 1,2-propanediol, broadly employed as an antifreezing agent.



Scheme 2. Hydroformylation of Vinyl Acetate

First, the biphasic hydroformylation of vinyl acetate was carried out using a sulfonated phosphine/Rh molar ratio equal to 4. The rhodium catalytic precursor and the corresponding phosphine were dissolved in 2 mL of water and the substrate (2500 equivalents) was dissolved in 6 mL of toluene. Both solutions were transferred into a reactor equipped with a mechanical stirrer, and the reactor was fed with *syngas* from a reservoir fitted with a pressure transducer in order to graph the gas consumption, which is correlated with the reaction rate.

The reactions were kept at 80ºC for 16 hours with a constant pressure of 30 bar of $CO:H_2$ (1:1). After that time, the two phases were separated and the aqueous phase was re-extracted with diethyl ether in order to collect all the products formed. The combination of organic phases was analyzed by GC-FID (Table 1).

All the reactions were completely regioselective towards the formation of the branched aldehyde, 2-acetoxypropanal. The chemoselectivity was around 90%, but *o*-Danphos only reached 82%. The only byproduct observed was ethyl acetate arising from the hydrogenation of the substrate. Conversions obtained with the trifluoromethylated phosphines were higher than with NaTPPMS, except in the case of *o*-Danphos.

Table 1. Vinyl acetate biphasic hydroformylation with sulfonated phosphines using [L]/[Rh] = 4 [a] [b]

Entry	Ligand (L)	Conv.[c] (%)	Chemo.[d] (%)	TOF[e] (min^{-1})
1	NaTPPMS	62	94	2.2
2	Danphos	78	92	7.6
3	*p*-Danphos	92	89	13
4	*o*-Danphos	58	82	1.5

[a] Conditions: $1.71 \cdot 10^{-2}$ mmol $[Rh(acac)(CO)_2]$, $6.84 \cdot 10^{-2}$ mmol ligand, 43.4 mmol vinyl acetate, 6 ml toluene, 2 ml H_2O, 80 ºC, 30 bar $CO:H_2$ (1:1), 0.2 ml of *n*-dodecane, 16h.
[b] The reactions were completely regioselective towards the branched aldehyde.
[c] Conversion: (substrate converted/total substrate)·100
[d] Chemoselectivity towards aldehyde formation
[e] TOF determined from the slope of the conversion curve at 50% conversion.

The rate of the hydroformylation reaction was drastically affected by the presence of trifluoromethyl groups, as it can be observed in the TOF values of Table 1, obtained when 50% of the substrate was converted. Danphos and *p*-Danphos increased the TOF by almost 4 and 6 times respectively when compared to NaTPPMS,

while *o*-Danphos showed a similar rate to the non-trifluoromethylated ligand. The steric hindrance of the trifluoromethyl group in *orto* position decreases both the conversion and the rate of the vinyl acetate hydroformylation.

It is accepted that the rate determining step of rhodium-phosphine catalyzed hydroformylation is the substrate coordination to the metal centre, which comprises the dissociation of a CO ligand.[16] An increase of the backdonating ability of the phosphine decreases the bond strength between the rhodium and the CO ligand, favoring substrate coordination. This is the reason why the hydroformylation rate is increased with poor electron-donating phosphines.[17,18]

Experiments using 20 equivalents of phosphine (Table 2) and 5 mL of water were performed in order to test the catalyst recycling. The large excess of ligand would assure the complete formation of a water-soluble rhodium complex, minimizing catalyst leaching into the organic phase during the extraction processes. Again, in these conditions, the reaction was regioselective towards the formation of the branched aldehyde for all the ligands essayed. However, the chemoselectivity of the reactions was not complete because of the formation of some ethyl acetate. The large ligand excess gave rise to an inactive catalytic system both with NaTPPMS and the disulfonated phosphine Na_2TPPDS (Table 2, entries 5 and 6). Na_3TPPTS and *o*-Danphos showed similar conversions after 8 h reaction time, but the former is more chemoselective than the fluorinated phosphine (Table 2, entries 7 and 10). With Danphos and *p*-Danphos ligands, high activities were achieved after 3 and 5 hours, respectively. In particular, the rate achieved with the Danphos catalytic system is four times higher than that of Na_3TPPTS (compare TOF in entries 7 and 8 in Table 2).

Table 2. Vinyl acetate biphasic hydroformylation with sulfonated phosphines using [L]/[Rh] = 20 [a] [b]

Entry	Ligand (L)	Time (h)	Conv.[c] (%)	Chemo.[d] (%)	TOF[e] (min^{-1})
5	NaTPPMS	8	1	100	-
6	Na_2TPPDS	24	6	72	-
7	Na_3TPPTS	8	58	71	3.6
8	Danphos	3	79	89	15
9	*p*-Danphos	5	87	79	7.8
10	*o*-Danphos	8	70	57	3.0

[a]Conditions: $1.71 \cdot 10^{-2}$ mmol [Rh(acac)$(CO)_2$], 0.342 mmol ligand, 43.4 mmol vinyl acetate, 3 ml toluene, 5 ml H_2O, 80 ºC, 30 bar CO:H_2 (1:1), 0.2 ml of *n*-dodecane.
[b] The reactions were completely regioselective towards the branched aldehyde.
[c] Conversion: (substrate converted/total substrate)·100
[d] Chemoselectivity towards aldehyde formation
[e] TOF determined from the slope of the conversion curve at 50% conversion.

The recycling experiments were carried out with Danphos and *p*-Danphos. After the first run, the reactor was depressurized and while under *syn-gas* atmosphere diethyl ether was added in order to extract the products. The organic phase was siphoned out of the reactor and the extraction process was repeated twice. Finally, a new charge of fresh substrate was introduced and the temperature and the pressure were set to the reaction values.

Both ligands allowed the recycling of the catalyst up to 4 runs without significant changes in conversion (Table 3). In contrast, the reaction rates resulted substantially modified among the different runs. For Danphos the TOF at 50% conversion in the second run duplicates the one obtained in the first run (entries 11, 12, Table 3). This result can be explained by the presence of aldehydes that remained in the aqueous phase during the extraction process performed after the first run. The presence of aldehydes in the aqueous phase during the second run increases the substrate solubility. Therefore the reaction is run at higher substrate concentration in the aqueous phase, raising the reaction rate. From the second run on, the decrease observed in TOF values could be explained due to the loss of catalyst in tiny colored aqueous droplets observed in the organic phase. These arise from the difficulty to ensure a perfect phase separation inside the reactor because of the small volumes used. As a matter of fact, an inductively coupled plasma optical emission spectrometry analysis (ICP-OES) of the combined organic phases showed that the content of rhodium was below 9 µg, corresponding to less than 0.2% of the initial rhodium. Undoubtedly, a scale-up should reduce such losses, further increasing catalyst recovery.

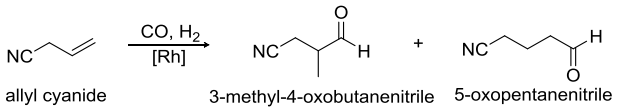
Table 3. Recycling Experiments of Vinyl Acetate biphasic hydroformylation with Danphos and *p*-Danphos using [L]/[Rh] = 20 [a] [b]

Entry	Ligand	Run	Conv.[c] (%)	Chemo.[d] (%)	TOF[e] (min^{-1})
11	Danphos	1	79	89	15
12		2	80	89	33
13		3	82	86	25
14		4	75	90	14
15	*p*-Danphos	1	87	79	7.8
16		2	82	72	7.8
17		3	87	71	13
18		4	83	78	8.4

[a]Conditions: $1.71 \cdot 10^{-2}$ mmol [Rh(acac)$(CO)_2$], 0.342 mmol ligand, 43.4 mmol vinyl acetate, 3 ml toluene, 5 ml H_2O, 80 ºC, 30 bar CO:H_2 (1:1), 0.2 ml of *n*-dodecane.
[b] The reactions were completely regioselective towards the branched aldehyde.
[c] Conversion: (substrate converted/total substrate)·100 after 3 h for Danphos and 5 h for *p*-Danphos.
[d] Chemoselectivity towards aldehyde formation
[e] TOF determined from the slope of the conversion curve at 50% conversion.

Allyl Cyanide Biphasic Hydroformylation with Sulfonated Phosphines

Danphos type phosphines were also used as ligands for the biphasic hydroformyltion of allyl cyanide (Scheme 3). The products obtained from this reaction have been employed to produce intermediates for the synthesis of valuable biological molecules.[19]



Scheme 3. Hydroformylation of Allyl Cyanide.

The same catalytic system employed for vinyl acetate was used for the biphasic hydroformylation of allyl cyanide. The results obtained with Danphos and *p*-Danphos compared with those of the non-trifluoromethylated phosphines are collected in Table 4.

The hydroformylation of allyl cyanide was completely chemoselective. However, the regioselectivity with all the sulfonated phosphines essayed was around 60% towards the branched aldehyde. Only the two aldehydes in Scheme 3 were observed. Not even traces of the α-aldehyde, 2-ethyl-3-oxopropanenitrile, arising from the tandem isomerization/hydroformylation reaction, were detected.

As in the case of vinyl acetate, non-trifluoromethylated phosphines are less active than Danphos and *p*-Danphos phosphines, being again Danphos the one showing the highest rate.

Table 4. Allyl Cyanide biphasic hydroformylation with sulfonated phosphines using [L]/[Rh] = 20 [a] [b]

Entry	Ligand	Conv.[c] (%)	Regio.[d] (%)	TOF [e] (min^{-1})
19	Na_2TPPDS	3	60	-
20	Na_3TPPTS	28	61	-
21	Danphos[f]	95	59	21
22	*p*-Danphos	68	59	7.1

[a]Conditions: $1.71 \cdot 10^{-2}$ mmol [Rh(acac)$(CO)_2$], 0.342 mmol ligand, 43.4 mmol allyl cyanide, 3 ml toluene, 5 ml H_2O, 80 ºC, 30 bar CO:H_2 (1:1), 0.2 ml of *n*-dodecane, 4h.
[b] The reactions were completely chemoselective towards aldehyde formation.
[c] Conversion: (substrate converted/total substrate)·100
[d] Regioselectivity towards the branched aldehyde.
[e] TOF determined from the slope of the conversion curve at 50% conversion.
[f] 3 hours.

Recycling experiments were also performed using the same procedure employed for vinyl acetate. As it can be observed in Table 5, the conversion and the rate of the system decrease with the number of experiments performed, due to some loss of catalyst in the manipulation during the extraction process, as described above.

Table 5. Recycling Experiments of Allyl Cyanide Biphasic Hydroformylation with Danphos and *p*-Danphos using [L]/[Rh] = 20 [a] [b]

Entry	Ligand	Run	Conv.[c] (%)	Regio.[d] (%)	TOF[e] (min^{-1})
23	Danphos	1	95	59	20.9
24		2	87	60	18.6
25		3	84	61	13.5
26		4	85	60	13.0
27	*p*-Danphos	1	68	59	7.1
28		2	57	60	5.8
29		3	58	61	5.6
30		4	49	62	5.1

[a]Conditions: $1.71 \cdot 10^{-2}$ mmol [Rh(acac)$(CO)_2$], 0.342 mmol ligand, 43.4 mmol allyl cyanide, 3 ml toluene, 5 ml H_2O, 80 ºC, 30 bar CO:H_2 (1:1), 0.2 ml of *n*-dodecane.
[b] The reactions were completely chemoselective towards aldehyde formation.
[c] Conversion: (substrate converted/total substrate)·100 after 3 h for Danphos and 4 h for *p*-Danphos.
[d] Regioselectivity towards the branched aldehyde.
[e] TOF determined from the slope of the conversion curve at 50% conversion.

Conclusion

A new family of disulfonated phosphines (Danphos series) was synthesized by a direct sulfonation of neutral trifluoromethylated phosphines by using a large excess of oleum and boric acid to prevent phosphine oxidation. All the synthesized phosphines are water-soluble and show higher aerial oxidation inertness than the non-trifluoromethylated sulfonated ligands, namely NaTPPMS, Na_2TPPDS and Na_3TPPTS.
Danphos type phosphines show a less σ-donating ability than their equivalent non-trifluoromethylated phosphines, as it has been demonstrated by the ^{31}P-^{77}Se coupling constant of the selenide derivatives determined by $^{31}P\{^1H\}$ NMR.
Finally, the water soluble recyclable Rh-Danphos catalyst shows a remarkably high rate in the hydroformylation of vinyl acetate and allyl cyanide, in particular when compared with Na_3TPPTS or other sulfonated and non-trifluoromethylated phosphines.

Experimental Section

General Procedure and Reagents

All manipulations were performed under inert atmosphere using Schlenk techniques. NaTPPMS was synthesized following the methodology described by Joo[20]and Na_2TPPDS was prepared as described by Williams.[21] Diethyl ether and toluene were distilled over sodium/benzophenone when required. The rest of reagents were from commercial origin and they were used without further purification. NMR spectra were acquired on a Bruker Avance II

400 MHz or a Bruker AC-250 spectrometers and were referenced with the residual solvent signal (^{1}H), external H_3PO_4 (^{31}P) and external fluorobenzene (^{19}F). Standard abbreviations for NMR spectral multiplicities are used in this section. Elemental analyses (Flash EA 2000 CHNS Thermo Fisher Scientific instrument) and electrospray mass spectra (Bruker microTOF mass spectrometer with ESI Apolo II) were carried out by the staff of the Analytical Services of Universitat Autònoma de Barcelona. Hydroformylation reactions were performed in a Parr 4598 reactor equipped with a mechanical stirrer.

The neutral trifluoromethylated aryldiphenylphosphines were previously described in the literature.[22] However, a slightly modified procedure was used in this work. This is described below, together with the full NMR characterization.

(3,5-Bis(trifluoromethyl)phenyl)diphenylphosphine and (*p*-trifluoromethylphenyl)diphenylphosphine

(3,5-bis(trifluoromethyl)bromobenzene or *p*-trifluoromethylbromobenzene (50.0 mmol) was dissolved in diethyl ether (50 mL) and was added drop wise over a suspension of magnesium (75.0 mmol) in diethyl ether (80 mL), keeping the temperature at 0ºC. Once the addition was completed, the mixture was refluxed for 4 hours and the excess of magnesium was filtered off with the aid of a cannula. Chlorodiphenylphosphine (47.5 mmol) in diethyl ether (20 mL) was added drop wise over the Grignard reagent and the mixture was again refluxed for 4 hours. Then HCl(aq) (10%, 65 mL) was added to the reaction mixture, and the phases were separated. The organic phase was washed with water (50 mL) and dried with $MgSO_4$. The solvent was removed *in vacuo* and the product was purified by column chromatography using silica as stationary phase and a mixture of CH_2Cl_2:hexane (1:1) as mobile phase.

(3,5-Bis(trifluoromethyl)phenyl)diphenylphosphine: yield 15.1 g (80%). ^{1}H NMR (250.16 MHz, $CDCl_3$) δ 7.84 (s, 1H, $H_{C4}\{C_6H_3(CF_3)_2\}$); 7.72 (d, 2H, $H_{C2}\{C_6H_3(CF_3)_2\}$, $^3J_{HP}$ = 6.2 Hz); 7.46-7.29 (m, 10H, H_{C2}-H_{C3}-$H_{C4}\{C_6H_5\}$). ^{13}C{^{1}H} NMR (90.55 MHz, $CDCl_3$) δ 142.12 (d, $C_1\{C_6H_3(CF_3)_2\}$, $^1J_{CP}$ = 18.7 Hz); 134.91 (d, $C_1\{C_6H_5\}$, $^1J_{CP}$ = 10.5 Hz); 133.86 (d, $C_2\{C_6H_5\}$, $^2J_{CP}$ = 20.3 Hz); 132.99 (br d, $C_2\{C_6H_3(CF_3)_2\}$, $^2J_{CP}$ = 19.4 Hz); 131.69 (qd, $C_3\{C_6H_3(CF_3)_2\}$, $^2J_{CF}$ = 33.2 Hz, $^3J_{CP}$ = 5.7 Hz); 129.72 (s, $C_4\{C_6H_5\}$); 129.02 (d, $C_3\{C_6H_5\}$, $^3J_{CP}$ = 7.4 Hz); 123.22 (q, $C\{CF_3\}$, $^1J_{CF}$ = 273.0 Hz); 122.38 (m, $C_4\{C_6H_3(CF_3)_2\}$). ^{31}P{^{1}H} NMR (101.27 MHz, $CDCl_3$) δ -3.91 (s). ^{19}F{^{1}H} NMR (235.39 MHz, $CDCl_3$) δ -60.74 (s).

(*p*-Trifluoromethylphenyl)diphenylphosphine: yield 11.3 g (72%). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.57 (br d, 2H, $H_{C3}\{C_6H_4CF_3\}$, $^3J_{HH}$ = 8.0 Hz); 7.41-7.29 (m, 12H, $H_{C2}\{C_6H_4CF_3\}$, H_{C2}-H_{C3}-$H_{C4}\{C_6H_5\}$). ^{13}C{^{1}H} NMR (90.55 MHz, $CDCl_3$) δ 143.01 (d, $C_1\{C_6H_4CF_3\}$, $^1J_{CP}$ = 14.8 Hz); 136.16 (d, $C_1\{C_6H_5\}$, $^1J_{CP}$ = 10.6 Hz); 134.05 (d, $C_2\{C_6H_5\}$, $^2J_{CP}$ = 20.0 Hz); 133.69 (d, $C_2\{C_6H_4CF_3\}$, $^2J_{CP}$ = 19.0 Hz); 130.61 (q, $C_4\{C_6H_4CF_3\}$, $^2J_{CF}$ = 32.4 Hz); 129.36 (s, $C_4\{C_6H_5\}$); 128.88 (d, $C_3\{C_6H_5\}$, $^3J_{CP}$ = 7.2 Hz); 125.33 (dq, $C_3\{C_6H_4CF_3\}$, $^3J_{CP}$ = 6.4 Hz - $^3J_{CF}$ = 3.6 Hz); 124.23 (q, $C\{CF_3\}$, $^1J_{CF}$ = 272.3 Hz). ^{31}P{^{1}H} NMR (101.27 MHz, $CDCl_3$) δ - 4.96 (s). ^{19}F{^{1}H} NMR (235.39 MHz, $CDCl_3$) δ -60.58 (s).

(*o*-Trifluoromethylphenyl)diphenylphosphine

n-BuLi 2.5 M in hexane (20.1 mL, 50.3 mmol) was added drop wise over a solution of *o*-trifluoromethylbromobenzene (50.0 mmol) in diethyl ether (70 mL). The mixture was stirred for one hour before the slow addition of chlorodiphenylphosphine (45.0 mmol) dissolved in diethyl ether (20 mL). The reaction mixture was stirred for 3 hours and mixed with HCl(aq) (10%, 80 mL). The phases were separated and the organic phase was washed with water (50 mL). The solvent was removed *in vacuo* and the product was purified by column chromatography using silica as stationary phase and a mixture of CH_2Cl_2:hexane (1:1) as mobile phase. Yield 9.7 g (65%). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.75-7.70 (m, 1H, $H_{C3}\{C_6H_4CF_3\}$); 7.43-7.35 (m, 2H, H_{C4}-$H_{C5}\{C_6H_4CF_3\}$); 7.33-7.26 (m, 6H, H_{C3}-$H_{C4}\{C_6H_5\}$); 7.26-7.19 (m, 4H, $H_{C2}\{C_6H_5\}$); 7.17-7.13 (m, 1H, $H_{C6}\{C_6H_4CF_3\}$). ^{13}C{^{1}H} NMR (90.55 MHz, $CDCl_3$) δ 136.78 (d, $C_1\{C_6H_4CF_3\}$, $^1J_{CP}$ = 29.5 Hz); 136.58 (br d, $C_1\{C_6H_5\}$, $^1J_{CP}$ = 11.7 Hz); 136.22 (d, $C_6\{C_6H_4CF_3\}$, $^2J_{CP}$ = 1.7 Hz); 134.93 (qd, $C_2\{C_6H_4CF_3\}$, $^2J_{CF}$ = 30.1 Hz - $^2J_{CP}$ = 25.4 Hz); 133.81 (d, $C_2\{C_6H_5\}$, $^2J_{CP}$ = 20.4 Hz); 131.73 (s, $C_5\{C_6H_4CF_3\}$); 129.08 (s, $C_4\{C_6H_5\}$); 128.97 (s, $C_4\{C_6H_4CF_3\}$); 128.70 (d, $C_3\{C_6H_5\}$, $^3J_{CP}$ = 6.8 Hz); 126.52 (m, $C_3\{C_6H_4CF_3\}$); 124.50 (q, $C\{CF_3\}$, $^1J_{CF}$ = 275.4 Hz). ^{31}P{^{1}H} NMR (145.78 MHz, $CDCl_3$) δ -9.65 (q, $^4J_{PF}$ = 53.2 Hz). ^{19}F{^{1}H} NMR (235.39 MHz, $CDCl_3$) δ -54.69 (d, $^4J_{FP}$ = 53.2 Hz).

General Procedure for the Synthesis of Danphos type Phosphines

Danphos type phosphines have been licensed and are currently available from Strem Chemicals, Inc.[23]

The appropriate phosphine (35.0 mmol), namely (3,5-bis(trifluoromethyl)phenyl)diphenylphosphine for Danphos, (*p*-trifluoromethylphenyl)diphenylphosphine for *p*-Danphos, and (*o*-trifluoromethylphenyl)diphenylphosphine for *o*-Danphos, was placed into a 250 mL three necked flask, equipped with a pressure-compensated addition funnel and a vacuum/nitrogen connection. At the same time, 140-175 mmol of boric acid (see Table 6) were dissolved into 100 mL of concentrated sulfuric acid (95% w/w) and the solution was transferred into the pressure-compensated addition funnel. Nitrogen was bubbled through the acid solution by using a Pasteur pipette for 15 min. The three necked flask was then placed in an ice bath, and the boric acid solution was slowly added over the neutral phosphine keeping the temperature of the solution below 10ºC, while the mixture was continuously stirred. Once the phosphine was completely dissolved, the addition funnel was charged with 130-150 mL (Table 6) of fuming sulfuric acid (oleum 65% in SO_3) and this was

added drop wise over the phosphine and boric acid solution during a period of 2 h, while the reaction temperature was kept below 10º C.

Table 6. Equivalents of reagents used for each aryldiphenylphosphine and approximate reaction time of the sulfonation step

Ligand	H_3BO_3 (eq.)	SO_3 (eq.)	Time[a] (h)
p-Danphos	5	70	4[b]
Danphos	4	70	16
o-Danphos	4	60	16

[a] Time includes the 2 hours of the oleum addition.
[b] In this case careful control of the reaction time is required, since *p*-Danphos further reacts with oleum.

Once the addition of oleum was completed, the reaction was allowed to reach room temperature and then aliquots were taken at different times and analyzed by $^{31}P\{^1H\}$ NMR (using a mixture of D_2O and methanol) to monitor the reaction progress. Once the disulfonated phosphines were the only products observed in the $^{31}P\{^1H\}$ NMR spectra, the reaction was quenched carefully adding the acid mixture into a 2 L reactor containing a mixture of water and ice prepared by freezing 500 mL of deoxygenated water with liquid nitrogen. The reaction mixture was cooled in an ice bath, and then a deoxygenated solution of NaOH (*ca.* 50 w/w) was slowly added over the solution with continuous stirring until it reaches a pH of 1. To the resulting solution, tri-*n*-octylamine (2.7 equivalents) dissolved in toluene (150 mL) was then added. The pH of the aqueous solution was raised to 3, by the subsequent addition of a NaOH solution (*ca.* 50 w/w). At this point, the phases were separated and the organic phase containing the tri-*n*-octylammonium salt of the disulfonated phosphine and some impurities, including some phosphine oxide, was transferred into a three necked flask. In order to purify the phosphine from its oxides and other colored impurities, a deoxygenated aqueous solution of NaOH (*ca.* 5 wt %) was added to the organic phase until a pH of 6.5 was reached. The phases were separated and the aqueous phase, containing most of the phosphine oxide, was discarded. The desired disulfonated phosphine was extracted from the organic phase to the aqueous phase by the subsequent addition of deoxygenated aqueous solution of NaOH (*ca.* 5 wt %) until a pH of 8 was reached. The phases were again separated and the organic phase was discarded. Water from the aqueous phase was evaporated *in vacuo* to a fine white powder. The phosphine was purified from traces of the starting phosphine and the ammonium salt and the hemisalt of the sulfonated phosphine by refluxing the crude material with toluene overnight (impurities were dissolved in the toluene). The sodium salt of the phosphine was filtered and dried in vacuum to yield a product with at least 95% purity.

***p*-Danphos:** yield: 15.3 g (82%). ^1H NMR (400.13 MHz, D_2O) δ 7.83 (d, 2H, $H_{C6}\{C_6H_4SO_3Na\}$, $^3J_{HH}$ = 7.7 Hz); 7.76 (br d, 2H, $H_{C2}\{C_6H_4SO_3Na\}$, $^3J_{HP}$ = 7.8 Hz); 7.53 (br d, 2H, $H_{C3}\{C_6H_4CF_3\}$, $^3J_{HH}$ = 8.2 Hz); 7.40 (br t, 2H, $H_{C5}\{C_6H_4SO_3Na\}$, $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$ = 7.7 Hz); 7.31-7.28 (m, 4H, $H_{C4}\{C_6H_4SO_3Na\}$, $H_{C2}\{C_6H_4CF_3\}$). $^{13}C\{^1H\}$ NMR (100.61 MHz, D_2O) δ 143.1 (d, $C_1\{C_6H_4SO_3Na\}$, $^3J_{CP}$ = 7.3 Hz); 140.2 (d, $C_1\{C_6H_4CF_3\}$, $^1J_{CP}$ = 12.7 Hz); 136.2 (d, $C_4\{C_6H_4SO_3Na\}$, $^2J_{CP}$ = 18.5 Hz); 136.1 (d, $C_3\{C_6H_4SO_3Na\}$, $^1J_{CP}$ = 11.0 Hz); 133.5 (d, $C_2\{C_6H_4CF_3\}$, $^2J_{CP}$ = 19.0 Hz); 130.3 (q, $C_4\{C_6H_4CF_3\}$, $^2J_{CF}$ = 32.1 Hz); 130.2 (d, $C_2\{C_6H_4SO_3Na\}$, $^2J_{CP}$ = 22.4 Hz); 129.5 (d, $C_5\{C_6H_4SO_3Na\}$, $^3J_{CP}$ = 6.6 Hz); 126.5 (s, $C_6\{C_6H_4SO_3Na\}$); 125.4 (m, $C_3\{C_6H_4CF_3\}$); 123.9 (q, $C\{CF_3\}$, $^1J_{CF}$ = 272.4 Hz). $^{31}P\{^1H\}$ NMR (161.98 MHz, D_2O) δ - 6.3 (s). $^{19}F\{^1H\}$ NMR (376.50 MHz, D_2O) δ -61.1 (s). HR-MS (ESI-MS): *m/z* = 243.9888 calculated for $C_{19}H_{12}F_3O_6PS_2$, found for $[M\text{-}2Na^+]/2$ = 243.9884. Anal. calcd. for $C_{19}H_{12}F_3Na_2O_6PS_2\cdot 2H_2O$ (%): C 40.01, H 2.83, S 11.24; found: C 39.99, H 2.70, S 10.84.

Danphos: yield: 19.4 g (92%). ^1H NMR (400.13 MHz, D_2O) δ 7.97 (s, 1H, $H_{C4}\{C_6H_3(CF_3)_2\}$); 7.84 (d, 2H, $H_{C6}\{C_6H_4SO_3Na\}$, $^3J_{HP}$ = 7.7 Hz); 7.80-7.78 (m, 4H, $H_{C2}\{C_6H_3(CF_3)_2\}$, $H_{C2}\{C_6H_4SO_3Na\}$); 7.43 (t, 2H, $H_{C5}\{C_6H_4SO_3Na\}$, $^3J_{HH}$ = 7.6 Hz); 7.36 (t, 2H, $H_{C4}\{C_6H_4SO_3Na\}$, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.6 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz, D_2O) δ 143.3 (d, $C_1\{C_6H_4SO_3Na\}$, $^3J_{CP}$ = 7.3 Hz); 139.2 (d, $C_1\{C_6H_3(CF_3)_2\}$, $^1J_{CP}$ = 16.0 Hz); 136.1 (d, $C_3\{C_6H_4SO_3Na\}$, $^1J_{CP}$ = 19.5 Hz); 135.4 (d, $C_4\{C_6H_4SO_3Na\}$, $^2J_{CP}$ = 12.1 Hz); 133.2 (br d, $C_2\{C_6H_3(CF_3)_2\}$, $^2J_{CP}$ = 20.2 Hz); 131.2 (qd, $C_3\{C_6H_3(CF_3)_2\}$, $^2J_{CF}$ = 33.2 Hz, $^3J_{CP}$ = 6.6 Hz); 130.3 (d, $C_2\{C_6H_4SO_3Na\}$, $^2J_{CP}$ = 23.6 Hz); 129.6 (d, $C_5\{C_6H_4SO_3Na\}$, $^3J_{CP}$ = 6.4 Hz); 126.8 (s, $C_6\{C_6H_4SO_3Na\}$); 123.4 (m, $C_4\{C_6H_3(CF_3)_2\}$); 123.0 (q, $C\{CF_3\}$, $^1J_{CF}$ = 273.0 Hz). $^{31}P\{^1H\}$ NMR (161.98 MHz, D_2O) δ -5.5 (s). $^{19}F\{^1H\}$ NMR (376.50 MHz, D_2O) δ - 63.0 (s). HR-MS (ESI –MS): *m/z* = 277.9825 calculated for $C_{20}H_{11}F_6O_6PS_2$, found for $[M\text{-}2Na^+]/2$ = 277.9833. Anal. calcd. for $C_{20}H_{11}F_6Na_2O_6PS_2\cdot H_2O$ (%): C 38.72, H 2.11, S 10.34; found: C 38.38, H 2.01, S 10.21.

***o*-Danphos:** yield: 15.5 g (83%). ^1H NMR (400.13 MHz, D_2O) δ 7.81 (d, 2H, $H_{C6}\{C_6H_4SO_3Na\}$, $^3J_{HH}$ = 8.0 Hz); 7.70-7.66 (m, 3H, $H_{C3}\{C_6H_4CF_3\}$, $H_{C2}\{C_6H_4SO_3Na\}$); 7.41-7.37 (m, 2H, H_{C4}-$H_{C5}\{C_6H_4CF_3\}$); 7.33 (br t, 2H, $H_{C5}\{C_6H_4SO_3Na\}$, $^3J_{HH}$ = 7.8 Hz); 7.21 (br t, 2H, $H_{C4}\{C_6H_4SO_3Na\}$, $^3J_{HH}$ = 7.8 Hz, $^3J_{HP}$ = 7.8 Hz); 7.11 (m, 1H, $H_{C6}\{C_6H_4CF_3\}$). $^{13}C\{^1H\}$ NMR (100.61 MHz, D_2O) δ 143.1 (d, $C_1\{C_6H_4SO_3Na\}$, $^3J_{CP}$ = 6.6 Hz); 136.2-135.2 (m, C_3-$C_4\{C_6H_4SO_3Na\}$, $C_6\{C_6H_4CF_3\}$); 133.7 (qd, $C_2\{C_6H_4CF_3\}$, $^2J_{CF}$ = 30.2 Hz, $^2J_{CP}$ = 25.9 Hz); 133.1 (d, $C_1\{C_6H_4CF_3\}$, $^1J_{CP}$ = 23.6 Hz); 132.3 (s, $C_5\{C_6H_4CF_3\}$); 130.0 (s, $C_4\{C_6H_4CF_3\}$); 129.9 (d, $C_2\{C_6H_4SO_3Na\}$, $^2J_{CP}$ = 23.1 Hz); 129.4 (d, $C_5\{C_6H_4SO_3Na\}$, $^3J_{CP}$ = 7.2 Hz); 126.6 (m, $C_3\{C_6H_4CF_3\}$); 126.4 (s, $C_6\{C_6H_4SO_3Na\}$); 124.2 (q, $C\{CF_3\}$, $^1J_{CF}$ = 274.3 Hz). $^{31}P\{^1H\}$ NMR (161.98 MHz, D_2O) δ - 11.2 (q, $^4J_{PF}$ = 52.4 Hz). $^{19}F\{^1H\}$ NMR (376.50 MHz, D_2O) δ - 56.4 (d, $^4J_{FP}$ = 52.4 Hz). HR-MS (ESI-MS): *m/z* = 510.9668 calculated for $C_{19}H_{12}F_3O_6PS_2Na$, found for $[M\text{-}Na^+]$ = 510.9669. Anal. calcd. for $C_{19}H_{12}F_3Na_2O_6PS_2\cdot 2H_2O$ (%): C 40.01, H 2.83, S 11.24; found: C 40.20, H 2.67, S 10.95.

General Procedure for the synthesis of the selenide derivatives

0.10 mmol of the corresponding phosphine were dissolved in 1 mL of methanol-d_4. 0.15 mmol of black selenium (1.5 equivalents) were added and the mixture was stirred for 2 hours at 40ºC. The excess of selenium was filtered off, and the selenide derivative solutions were analyzed by $^{31}P\{^1H\}$ NMR.

Danphos selenide: $^{31}P\{^1H\}$ NMR(101.27 MHz, $CDCl_3$) δ 33.0, $^1J_{PSe}$ = 772 Hz.

***p*-Danphos selenide:** $^{31}P\{^1H\}$ NMR(101.27 MHz, $CDCl_3$) δ 32.7, $^1J_{PSe}$ = 760 Hz.

***o*-Danphos selenide:** $^{31}P\{^1H\}$ NMR(101.27 MHz, $CDCl_3$) δ 34.9, $^1J_{PSe}$ = 775 Hz, $^4J_{PF}$ = 3 Hz.

NaTPPMS selenide: $^{31}P\{^{1}H\}$ NMR(101.27 MHz, $CDCl_3$) δ 33.0, $^{1}J_{PSe}$ = 739 Hz.

Na_2TPPDS selenide: $^{31}P\{^{1}H\}$ NMR(101.27 MHz, $CDCl_3$) δ 33.1, $^{1}J_{PSe}$ = 747 Hz.

Na_3TPPTS selenide: $^{31}P\{^{1}H\}$ NMR(101.27 MHz, $CDCl_3$) δ 33.0, $^{1}J_{PSe}$ = 755 Hz.

General Procedure for the Biphasic Hydroformylation reactions

$1.71 \cdot 10^{-2}$ mmol of [Rh(acac)$(CO)_2$] and 0.342 mmol of sulfonated phosphine were dissolved in 5 ml of deoxygenated water. At the same time, 43.4 mmol of substrate (vinyl acetate or allyl cyanide) and 0.2 ml of *n*-dodecane, used as internal standard, were dissolved in 3 ml of toluene. Both solutions were injected into the reactor, which was previously under *vacuum* for 30 minutes. The autoclave was pressurized with 30 bar of *syngas* ($CO:H_2$ 1:1), heated to 80º C and the mechanical stirring was kept at 700 rpm. The pressure fall over time was monitorized by a transductor connected to the reservoir.

One Run Experiments

At the end of the reaction, the reactor was cooled down to room temperature and it was depressurized. The reaction mixture was transferred to a separation funnel and 5 ml of diethyl ether were added. The phases were separated and the extraction process was repeated twice. Finally the organic phases were injected in the GC-FID in order to quantify the results.

Recycling Experiments

At the end of the reaction, the autoclave was cooled down to room temperature and it was depressurized. 5 ml of diethyl ether were introduced into the reactor, the phases were vigorously stirred and the organic phase was siphoned out of the reactor. The extraction process was repeated twice with 5 ml of diethyl ether and three more times with 5 ml of toluene, to reestablish the initial conditions. Finally a new charge of fresh substrate was introduced for the next run.

Acknowledgements

We thank Matgas 2000 A.I.E. for the use of the autoclave for the hydroformylation reactions under a lease. D.P. and D.H. thank Universitat Autònoma de Barcelona for their PIF scholarship.

Notes and references

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Electronic Supplementary Information (ESI) available: ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR as well as HRMS and IR spectra of Danphos type phosphines are included in the supplementary information. $^{31}P\{^{1}H\}$ NMR spectra of the selenide derivatives are also included. The reaction profiles of the vinyl acetate and allyl cyanide biphasic hydroformylation are also provided. See DOI: 10.1039/b000000x/

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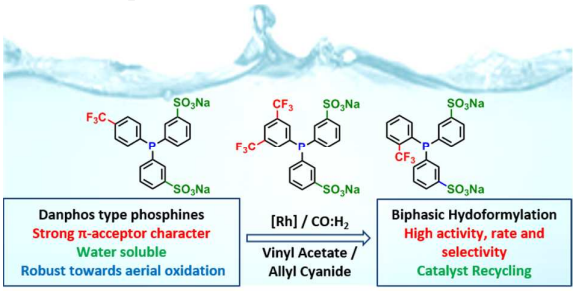
Colour Graphic:



Text:

Triflouromethylated and sulfonated triarylphosphines are remarkable resistant toward oxidation and very active for the biphasic hydroformylation of polar alkenes.