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Systematic Study of the Stereoelectronic Properties of Trifluoromethylated Triarylphosphines and the Correlation of their Behaviour as Ligands in the Rh-Catalysed Hydroformylation

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In loving memory of Dr. Julio Real

The stereoelectronic properties of a series of trifluoromethylated aromatic phosphines have been studied using different approaches. The σ-donating capability has been evaluated by nuclear magnetic resonance (NMR) spectroscopy of the selenide derivatives and the protonated form of the different trifluoromethylated phosphines. The coupling constants between phosphorous and selenium ($^1J_{SeP}$) and phosphorous and hydrogen ($^1J_{HP}$) can be predicted by empirical equations and correlate the basicity of the phosphines with the number and relative position of trifluoromethyl groups. In contrast, the π-acceptor character of the ligands has been evaluated by measuring the frequency of the CO vibration in the infrared (IR) spectra of the corresponding Vaska type iridium complexes ($[IrCl(CO)(PAr_3)_2]$, PAr_3 = triarylphosphine). Moreover, the correlation between the electronic properties and the performance of these phosphines as ligands in the rhodium-catalysed hydroformylation of 1-octene has been established. Phosphines with the lowest basicity, that are those with the highest number of trifluoromethyl groups, gave rise to more active catalytic systems.

Introduction

The stereoelectronic properties of phosphines can be easily tuned by using different substituents on the phosphorus atom, which make them highly versatile ligands. Therefore, phosphines have become one of the most important ligands in coordination chemistry and, particularly, in homogenous catalysis. Trifluoromethylated triarylphosphines have been widely used as ligands in different catalytic transformations showing improved catalytic activity and selectivity.[1] The electron-withdrawing effect of the trifluoromethyl groups on the aromatic rings of the phosphines decreases the basicity of the ligand and, as a result, also the electron density provided to the metal centre. Consequently, the rate of the different steps of a given catalytic cycle might change, affecting the activity and selectivity of the reaction.

Two contributors are normally considered when referring to the electronic properties of phosphines as ligands: the σ-donor (σ-basicity) and the π-acceptor (π-acidity) character. The σ-donation ability of a phosphine is related to its capability to donate the lone pair of the P atom to, for instance, coordinate a metal atom or to bond a heteroatom, such as oxygen or selenium. Phosphines substituted with electron-donating groups (*i.e.* alkylphosphines) behave as strong bases and thus have a marked σ-donating behaviour. The same reasoning applies to phosphines substituted with electron-withdrawing groups, which are weaker σ-donating ligands. Direct spin-spin coupling constant in organophosphorus selenides has been reported as a simple and straightforward manner to evaluate the σ-donation ability of phosphorus ligands.[2-4] Allen and Taylor observed that the value of the $^1J_{PSe}$ in phosphine selenides increased when introducing electro-withdrawing groups bonded to the phosphorus atom.[2] These observations were attributed to an increase in the *s* character of the phosphorus lone pair in agreement with Bent's rule.[5] The opposite effect was reported with electron-donating or bulky substituents. X-ray diffraction structures of some phosphine selenides have shown shorter P–Se distances in trifluoromethylated triarylphosphines with respect to triphenylphosphine.[6] Moreover, good correlation between the $^1J_{PSe}$ in phosphine selenides and the P–Se distance or the Brønsted basicity of the corresponding phosphines has been reported[3,4]. Deviation of this trend, though, was observed in phosphines containing bulky substituents. Another strategy to measure the σ-donation capability of a phosphine is the coupling constant between the phosphorous and the proton of protonated phosphines by NMR spectroscopy. For this technique, quantitative protonation of the phosphines is required. In this sense, Pestovsky *et al.*[7] reported full protonation of arylphosphines in 1.5 M solutions of CF_3SO_3H in H_2O/CH_3CN. Complete protonation of phosphines in sulfuric acid, fluorosulfuric acid or trifluoroacetic acid has also been reported in the literature with similar values of $^1J_{PH}$ for triphenylphosphine.[8] Correlation between the magnitude of the one-bond H-P coupling constant ($^1J_{HP}$) and the basicity of

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protonated phosphines and phosphites has been previously reported, showing larger values of the $^1J_{HP}$ when decreasing the basicity of the phosphorus ligands.

In coordination chemistry, the π-acidity character of phosphines is related to the ability of these ligands to accept electron density from the metal atom. Although still a matter of research,[9] it has been generally accepted that such electron-backdonation takes place from the *d*-orbitals of the metal centre to the empty σ*-orbitals of the phosphorus ligand, which are of π-symmetry as the *d* metal orbital involved.[10,11]

Tolman studied the electron donor-acceptor properties of different phosphorus ligands measuring the carbonyl A_1 stretching frequency of $Ni(CO)_3L$ complexes in CH_2Cl_2.[12] In analogy with the Ni-carbonyl complexes of Tolman, Vaska-type complexes can also be used to determine the σ/π-bonding characteristics of phosphines.[13] Vaska's compound is the name given to *trans*-carbonylchlorobis(triphenylphosphine)iridium(I), (*trans*-[Ir(CO)Cl(PPh_3)$_2$]). Although it was firstly reported by Angoletta,[14] its composition was correctly elucidated by Vaska and DiLuzio two years later.[15] Currently, Vaska-type complexes are considered those with the general formula *trans*-[M(CO)X$(L)_2$], where M can be either Rh or Ir, X is an halogen or pseudohalogen and L refers to a neutral ligand.[13]

The reaction of hydroformylation, which consists in the addition of equimolar amounts of H_2 and CO (syngas) to olefins to form aldehydes, is one of the most employed homogeneous catalytic processes at industrial level. Trivalent phosphorus compounds are, by far, the most used ligands in the Rh-catalysed hydroformylation. A variety of phosphorus ligands have been described in the literature, especially phosphines or phosphites, either monodentate or chelating.[16,17] The positive effect of using triarylphosphines containing electron-withdrawing groups, such as trifluoromethyls, has been widely acknowledged for monophosphines as well as for diphosphines.[18,19,20] Although the rate-determining step in the rhodium-phosphine-catalysed hydroformylation strongly depends on the reaction conditions, it has been generally accepted that under standard conditions the rate of the reaction is determined in the first stages of the catalytic cycle. This includes the dissociation of CO, the coordination of the alkene substrate and the migratory insertion of the olefin into the Rh–H bond.[21,22] Gleich and Hutter showed that the olefin coordination becomes thermodynamically more favourable when decreasing the basicity of the phosphine ligand,[22] which would explain the enhanced performance of the hydroformylation with the electron poor trifluoromethylated phosphines. The π-accepting features of these ligands would also decrease the back-donation of the rhodium to CO ligand, thus weakening the Rh-CO bond and facilitating the CO dissociation.

In this work, a broad family of triarylphosphines containing trifluoromethyl groups has been synthesised, Figure 1. In order to cover a wide range of substitution pattern, five novel

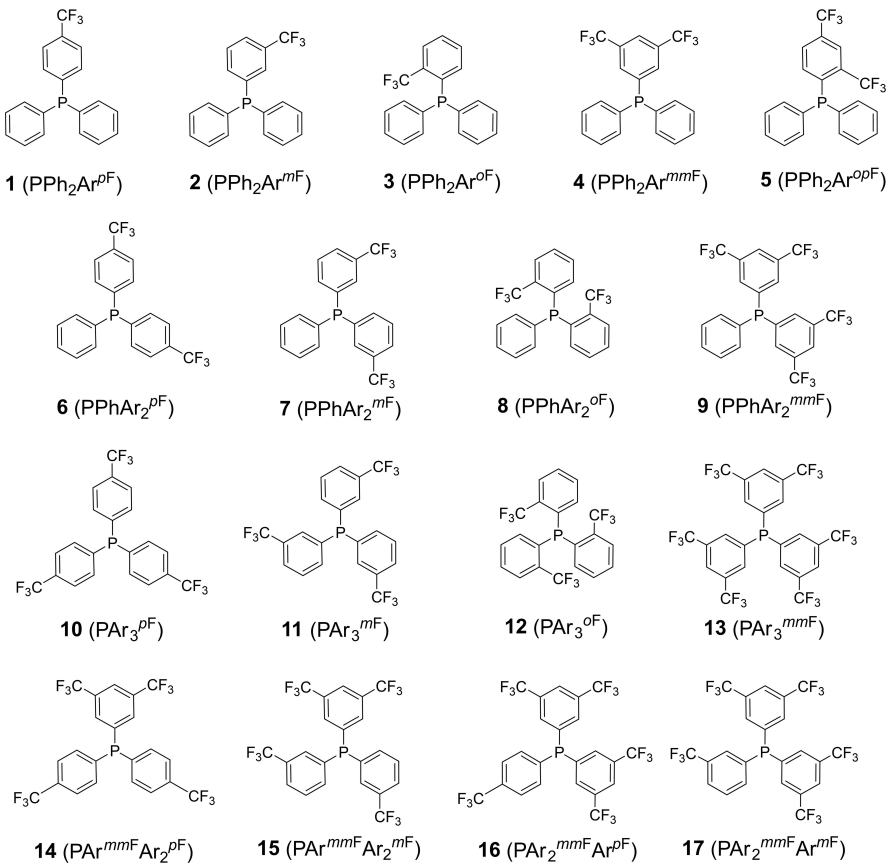


Figure 1. Trifluoromethylated phosphines synthesised in this work.

trifluoromethylated phosphines have been designed and synthesised (phosphines **5**, **14**, **15**, **16** and **17** in Figure 1). The effect produced by the number and relative position of the trifluoromethyls in the stereoelectronic properties of the ligands have been studied by ^{31}P NMR of the selenides derivatives and the protonated phosphines. These experiments have been further compared to the υ(CO) stretching by FTIR of the corresponding iridium Vaska's complexes. Finally, the electronic properties have been correlated with the catalytic performance of the Rh/phosphine-catalysed hydroformylation reaction.

Results and Discussion

Synthesis of the trifluoromethylated phosphines

The phosphines prepared in this work (Figure 1) have been designed to cover all the possible monosubstitution patterns (*ortho*: Ar^{oF}, *meta*: Ar^{mF} and *para*: Ar^{pF}). Moreover, different phosphines containing aromatic rings with double substitution (*meta-meta*: Ar^{mmF} and *ortho-para*: Ar^{opF}) and the combination of two different patterns (*meta-meta* with *meta* and *meta-meta* with *para*) have also been prepared. This way, the number and the relative position of the electronwithdrawing trifluoromethyl groups will be correlated with the stereoelectronic properties of the phosphine ligands.

All the trifluoromethylated phosphines have been synthesised by the corresponding reaction of the Grignard reagent or organolithium derivative with phosphorous trichloride, or aromatic chlorophosphines.[23,24] The Grignard reagent or the organolithium derivative, prepared from the corresponding trifluoromethylated bromo-aryl derivative with Mg or *n*-BuLi, respectively, was reacted with a solution of PCl_3, or the corresponding arylchlorophosphine, in ethereal solvent, to yield the trifluoromethylated triarylphosphine. It is important to mention that, while the Grignard reagent was used to prepare most of these phosphines, this type of reagents cannot be applied to the bulkier *ortho*-substituted ones. In this case, the phosphines are efficiently prepared through the organolithium derivative.

While phosphines **1**–**4** and **6**–**13** were previously reported in the literature, as far as we are concern, phosphines **5**, **14**, **15**, **16** and **17** are firstly described in this paper. Phosphine **5** was prepared from the reaction between the organolithium trifluoromethylated derivative and chlordiphenylphosphine. The new heteroleptic phosphines **14**–**17** were synthesised from the reaction between the corresponding chloro- or dichloro-trifluoromethylphenylphosphine with the Grignard trifluoromethylbenzene reagents. Two trifluoromethylated chlorophosphines were therefore prepared using PCl_3 as a trivalent phosphorus precursor and the corresponding Grignard reagents, which were added in a sequential way. The high reactivity of PCl_3 requires the protection of chlorine groups as *N,N*-diethylphosphoramidous dichloride, Et_2NPCl_2, and *N,N,N′,N′*-tetraethylphosphoro-diamidous chloride, $(Et_2N)_2PCl$. These compounds were used to selectively form the trifluoromethylated chlorophosphines after reaction with the corresponding Grignard reagent followed by P–N cleavage.[25]

The characterization of the phosphines was carried out by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{19}F and ^{31}P), high resolution mass spectrometry (HR-MS) and elemental analysis (C and H) and is collected in the experimental section and the supporting information (**S1**)

Crystals of good quality for single-crystal X-ray diffraction of phosphine PAr^{mmF}Ar$_2^{pF}$ **14** were obtained by slow precipitation in CH_2Cl_2. ORTEP diagram and some selected distances and angles are shown in Figure 2. Helix-like arrangement of the phosphine is observed in **14**, as expected for a triarylphosphine. Values of P–C distances and C–P-C angles were also found within the expected values.

Study of the electronic properties of the trifluoromethylated phosphines

The σ-basicity and the π-acidity contributions of the trifluoromethylated phosphines presented above have been evaluated by the preparation and characterization of different derivatives: phosphine selenides and protonated phosphines (phosphonium ions) for the σ-basicity and the Vaska-type Ir(I) complexes for the evaluation of the σ-basicity and π-acidity.

σ-Donating character: phosphine selenides and phosphonium ions. The σ-donation ability of the phosphines was evaluated by measuring the $^1J_{PSe}$ coupling in the ^{77}Se (s = 1/2, 7.63% natural abundance) isotopomer of the corresponding phosphine selenides. Given that the P–Se bond has a single-bond character and has little double-bond contribution,[26] it can be considered that the phosphine selenide coupling constant is directly related to the σ-donor ability of the ligand. Therefore, the selenide derivatives of the phosphines presented in this work were synthesised using a straightforward methodology. An excess of selenium black was added to 0.01 M solutions of the different phosphines in deuterated chloroform and stirred for 15 h at room temperature under inert atmosphere. The excess of selenium was filtered off and the products were

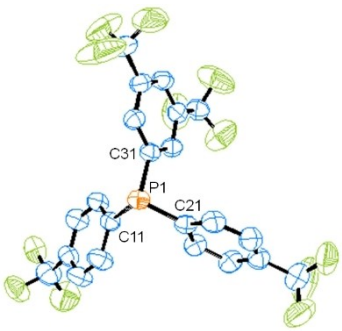


Figure 2. ORTEP plot (ellipsoid at 50% probability) of **14**. Only one orientation of the disordered CF_3 groups is drawn. Aromatic H atoms omitted for clarity. Distances (Å): *P(1)-C(11)* = 1.834(3), *P(1)-C(21)* = 1.834(3), *P(1)-C(31)* = 1.836(3). Angles(°): *C(11)-P(1)-C(21)* = 101.9(1), *C(11)-P(1)-C(31)* = 102.3(1), *C(21)-P(1)-C(31)* = 100.9(1).

analysed by $^{31}P\{^{1}H\}$. Alternatively, for the *ortho*-substituted phosphines (**3**, **5** and **8**), stirring at 50 °C was preferred to obtain the selenide quantitatively. The triply *o*-substituted phosphine **12** did not afford the corresponding selenide under the essayed conditions. The steric hindrance around the P atom produced by the three trifluoromethyl groups is thought to be responsible for the inertness of this phosphine towards the formation of the selenide. Figure 3 shows the $^{31}P\{^{1}H\}$ NMR spectrum of the selenide of the homoleptic phosphine **13**, as a representative example, where it is possible to observe the doublet arising from the coupling between ^{77}Se and ^{31}P.

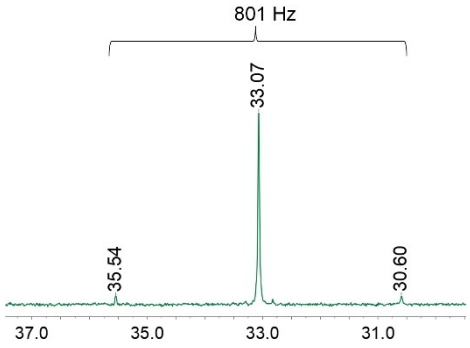


Figure 3. $^{31}P\{^{1}H\}$ (161.98 MHz) NMR spectrum of the selenide of phosphine **13** in $CDCl_3$. δ in ppm. $^{1}J_{SeP} = 801$ Hz

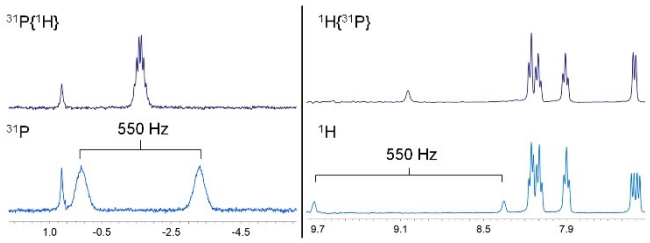


Figure 4. Left- ^{31}P and $^{31}P\{^{1}H\}$ (161.98 MHz) NMR spectra of phosphine **12** (0.05 M) in H_2SO_4 conc. Signals relative to a solution of NH_4PF_6 (0.08 g/ml in D_2O) used as internal standard. Singlet indicated as * correspond to the partial degradation of the internal standard. **Right**- ^{1}H and $^{1}H\{^{31}P\}$ (400.13 Hz) NMR spectra of **12** (0.05 M) in H_2SO_4 conc.

Table 1. Values of $^{1}J_{PSe}$ and $^{1}J_{HP}$ (Hz) for the corresponding selenides and phosphonium ions, respectively, of the trifluoromethylated triarylphosphines

Number of CF_3	Ligand	Selenide $^{1}J_{PSe}$ [a]	Phosphonium $^{1}J_{HP}$ [b]
0	PPh_3 [c]	731 (731)	503 (503)
	1 (PPh_2Ar^{pF})	742 (743)	510 (512)
1	**2** (PPh_2Ar^{mF})	742 (743)	512 (512)
	3 (PPh_2Ar^{oF})	753 (754)	521 (519)
	4 (PPh_2Ar^{mmF})	755 (755)	520 (521)
	5 (PPh_2Ar^{opF})	765 (766)	529 (528)
2	**6** ($PPhAr_2^{pF}$)	753 (755)	519 (521)
	7 ($PPhAr_2^{mF}$)	756 (755)	520 (521)
	8 ($PPhAr_2^{oF}$)	755 (777)	538 (535)
	10 (PAr_3^{pF})	766 (767)	527 (530)
3	**11** (PAr_3^{mF})	767 (767)	528 (530)
	12 (PAr_3^{oF})	-	550 (551)[c]
	9 ($PPhAr_2^{mmF}$)	779 (779)	537 (539)
4	**14** ($PAr^{mmF}Ar_2^{pF}$)	778 (779)	536 (539)
	15 ($PAr^{mmF}Ar_2^{mF}$)	781 (779)	538 (539)
5	**16** ($PAr_2^{mmF}Ar^{pF}$)	791 (791)	546 (548)
	17 ($PAr_2^{mmF}Ar^{mF}$)	791 (791)	545 (548)
6	**13** (PAr_3^{mmF})	801 (803)	555 (557)

[a] Values obtained from the $^{31}P\{^{1}H\}$ in $CDCl_3$. See text for more details. [b] Values obtained from the ^{31}P NMR in conc. H_2SO_4. See text for more details. [c] Determined from ^{1}H NMR spectra. In brackets, calculated values from Eq. (1) and Eq. (2).

The protonated form of the full set of the trifluoromethylated phosphines was prepared by dissolving 0.1 mmol of the corresponding phosphine in 2 ml of concentrated sulfuric acid. This time, the triply *ortho*-substituted phosphine **12** was also reactive. Hydrogen, being a considerably smaller atom than selenium, is able to bond the sterically hindered phosphorus atom of this phosphine. Figure 4 shows the comparison of the ^{31}P and the ^{1}H NMR spectra of the protonated form of phosphine **12**. Clear protonation of the phosphine with $^{1}J_{HP} =$ 550 Hz was observed. Due to the broadness of the signal in the ^{31}P NMR produced by the coupling to hydrogen and fluorine atoms, fine measurement of the coupling constant was obtained from the ^{1}H NMR spectra.

Values of $^{1}J_{PSe}$ of the selenides together with the $^{1}J_{HP}$ of the phosphoniums are collected in Table 1. Both $^{1}J_{PSe}$ and $^{1}J_{HP}$ are cumulative in the whole series of the investigated phosphines and follow the same trend: the higher the number of trifluoromethyl groups, the greater the value of the coupling constants.

Equations correlating the values of both $^{1}J_{PSe}$ and $^{1}J_{HP}$ with the number and position of the trifluormethyl groups were empirically developed, Eq. (1) and Eq. (2) respectively.

$$^{1}J_{SeP} = 731 + 12(m/p) + 22(o) \quad (1)$$

$$^{1}J_{HP} = 503 + 9(m/p) + 16(o) \quad (2)$$

were (m/p) are the number of trifluoromethyl groups in *meta*- or *para*-positions and (o) are those groups in *ortho*-positions.

The selenide of the non-trifluoromethylated triphenylphosphine showed a $^{1}J_{SeP}$ of 731 Hz (Table 1). The addition of one trifluoromethyl group in either *meta* or *para* position produced an increase of 12 Hz. In contrast, the effect of the groups in *ortho* position was larger, increasing the coupling constant in about 22 Hz. While the experimental $^{1}J_{PSe}$ for the *ortho*-monosubstituted phosphine **3** and the *ortho*,*para*-substituted phosphine **5** fitted Eq. (1), a large difference between the experimental value and the calculated one was observed for the *ortho*-disubstituted phosphine **8** (755 *vs* 777). This means that the two trifluoromethyl groups in phosphine **8**, because of steric grounds, force a longer Se–P distance than the one expected for pure electronic effects.

The $^{1}J_{HP}$ of the protonated form of triphenylphosphine was 503 Hz. In this case, one trifluoromethyl in *meta* or *para* position increased 9 Hz the coupling constant, while those groups in *ortho* positions added 18 Hz. Good agreement was found between all the experimental values and those calculated using the empirical Eq. (2). Even the bulkiest *ortho*-trisubstituted

phosphine **12** matched the calculated value with a small deviation.

Finally, excellent correlation was found between the magnitude of the $^1J_{PSe}$ in the selenide and the $^1J_{HP}$ of the corresponding phosphonium ions, with exception of the bis-*ortho*-substituted phosphine **8**, Figure 5.

σ/π-bonding character: Vaska-type Ir (I) complexes. Stretching frequencies of coordinated CO ligands in metal complexes is a common and simple probe to study the σ/π-bonding behaviour of phosphines. The increased π-acidity of phosphorus ligands substituted with more electron-withdrawing groups is clearly observed by displacement of the CO frequency to higher values. Electron-backdonation from the metal centre to these acidic phosphorus ligands is increased as a result of their π-acceptor ability. This effect reduces the electron density on the metal centre and, as a consequence, decreases the back-donation to the CO ligand, resulting in a shorter (stronger) C–O distance, and hence in higher carbonyl frequencies.

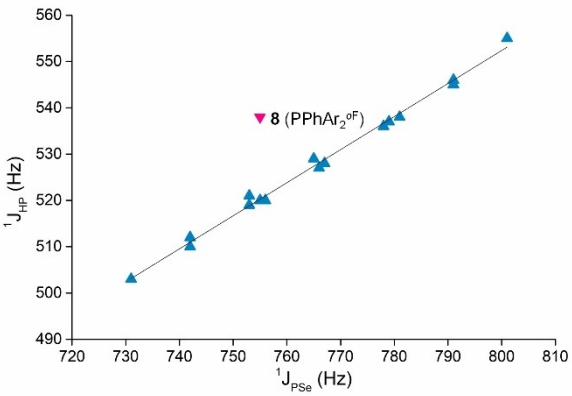


Figure 5. Correlation between the $^1J_{PSe}$ and the $^1J_{HP}$ of the trifluoromethylated phosphines

Vaska's analogue complexes of the formula *trans*-[Ir(CO)Cl(L)$_2$] with the trifluoromethylated phosphines were prepared following the synthetic procedure previously described in our group.[27] Also the Vaska's compound (*trans*-[Ir(CO)Cl(PPh$_3$)$_2$]) was prepared for comparison purposes. Vaska-type complexes of all the trifluoromethylated phosphines were successfully prepared with exception of the *ortho*-substituted phosphine **12** which did not coordinate the metal and the *bis-meta*-substituted phosphines **7** and **15** which could not be purified by precipitation in diethyl ether, *n*-hexane, methanol, water or combinations of them.

The IR spectra of the complexes were registered in CH_2Cl_2 solution and as solid (ATR-FTIR). Table 2 shows the CO frequencies for each of the complexes.

The values of the CO vibration in solution showed good correlation with the number of trifluoromethyl groups in the phosphines. As expected, when the number of trifluoromethyls is increased, the CO frequencies are shifted to higher wavenumbers as a result of a lower σ-donor ability and greater π-acceptor character of the phosphine ligand. Exception to this trend was observed in the Vaska complex of the *ortho*-substituted phosphine **3**, which showed lower CO frequency than PPh_3. A plausible reasoning to this abnormal value could arise from long-range intramolecular interactions between the *ortho*-trifluoromethyl groups and the metal centre. These interactions would provide extra electron density to the metal, thus increasing the backdonation to the CO ligand. This hypothesis was further supported by the single-crystal X-ray structure of the Ir-Vaska complex of phosphine **3**. Figure 6 shows the ORTEP representation of the [IrCl(CO)(PPh$_2$Ar^{oF})$_2$] complex, together with the most relevant bond distances and angles. The X-ray structure shows a slightly distorted square planar geometry of the Ir(I) atom with two phosphine ligands in *trans*-disposition and Cl and CO ligands in the remaining coordinative positions. Distances and angles were found within

Table 2. Carbonyl stretching IR frequencies (cm^{-1}) of the Vaska-type complexes *trans*-[Ir(CO)Cl(L)$_2$]

Number of CF_3	Ligand	CH_2Cl_2[a]	Solid (ATR-FTIR)[b]
0	PPh_3	1964	1949
	1 (PPh$_2$Ar^{pF})	1967	1957
1	**2** (PPh$_2$Ar^{mF})	1968	1950
	3 (PPh$_2$Ar^{oF})	1962	1950
	4 (PPh$_2$Ar^{mmF})	1972	1961
	5 (PPh$_2$Ar^{opF})	1965	1955
2	**6** (PPhAr$_2^{pF}$)	1971	1963
	7 (PPhAr$_2^{mF}$)	- [c]	- [c]
	8 (PPhAr$_2^{oF}$)	1969	1967
	10 (PAr$_3^{pF}$)	1975	1974
3	**11** (PAr$_3^{mF}$)	1976	1982
	12 (PAr$_3^{oF}$)	- [d]	- [d]
	9 (PPhAr$_2^{mmF}$)	1979	1989
4	**14** (PAr^{mmF}Ar$_2^{pF}$)	1979	1972
	15 (PAr^{mmF}Ar$_2^{mF}$)	- [c]	- [c]
5	**16** (PAr$_2^{mmF}$Ar^{pF})	1983	1973
	17 (PAr$_2^{mmF}$Ar^{mF})	1983	1988
6	**13** (PAr$_3^{mmF}$)	1986	1979

[a] IR spectra registered in CH_2Cl_2. [b] IR spectra registered as solid compounds. [c] The complex could not be isolated. [d] The ligand did not coordinate.

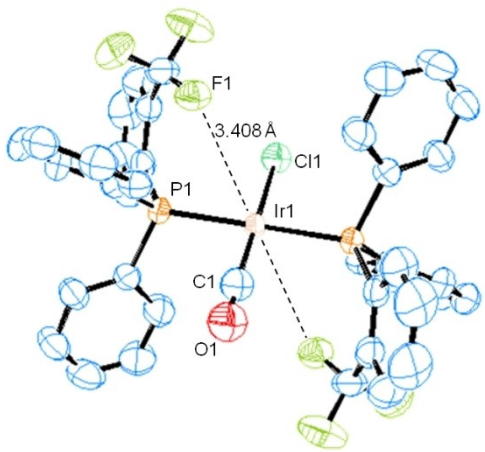


Figure 6. ORTEP plot (ellipsoid at 50% probability) of Ir–Vaska complex of the *ortho*-substituted phosphine **3** [IrCl(CO)(PPh$_2$Ar^{oF})$_2$]. Only one orientation of the CO/Cl groups are shown for simplicity. Distances(Å): *Ir(1)-P(1)* = 2.318(1), *Ir(1)-Cl(1)* = 2.390(6), *Ir(1)-C(1)* = 1.778(18), *C(1)-O(1)* = 1.038(21), *Ir(1)…F(1)* = 3.408(4). Angles(°): *P(1)-Ir(1)-Cl(1)* = 88.4(1), *P(1)-Ir(1)-C(1)* = 92.3(5), *Ir(1)-C(1)-O(1)* = 173.7(6).

the reported values of this sort of complexes.[28] Most interestingly, the structure shows that the geometry of the trifluoromethyl groups at the complex allows the intramolecular coordination of one fluorine atom of the trifluoromethyl group of each phosphine ligands to the iridium, at a distance of 3.408 Å. This observation is in agreement with the low CO frequency observed in the Vaska complex of phosphine **3**. Because of the electron donation of the fluorine with the metal centre, the estimation of the basicity of the phosphine **3**, and most probably also of the other *ortho*-substituted phosphines, using the Vaska complexes should be carefully considered. In these cases, the values of CO frequencies obtained by IR would be a combination of the electron-withdrawing effect of the trifluoromethyl groups and the long-distance donor effect of a fluorine atom of these groups.

No significant differences were found in the CO frequencies of the Ir-Vaska complexes of the *para*- and the *meta*-isomers in solution. However, the CO frequencies in solid (ATR-FTIR) do not follow the same tendency and greater differences between the *para*- and the *meta*-isomers were found. These observations might be tentatively attributed to intermolecular long-distance F–Ir contacts in the solid structures.

Figure 7 shows the graphical representation of the CO vibration frequencies of the Vaska's complexes in solution *versus* the number of trifluoromethyl groups of the phosphines. Clearly, as in the case of the selenides and the protonated phosphines, there is a linear relationship between the frequency of the carbonyl in the IR spectra and the number of trifluoromethyl groups in the phosphines. The frequency increases with the number of trifluoromethyls due to the increase in the acidity of the phosphines. Exception to this trend was found in those phosphines containing only one trifluoromethyl group in *ortho* position, phosphines **3** and **5**, and can be explained by the F–Ir long-range coordination observed in the X-ray structure of **3**.

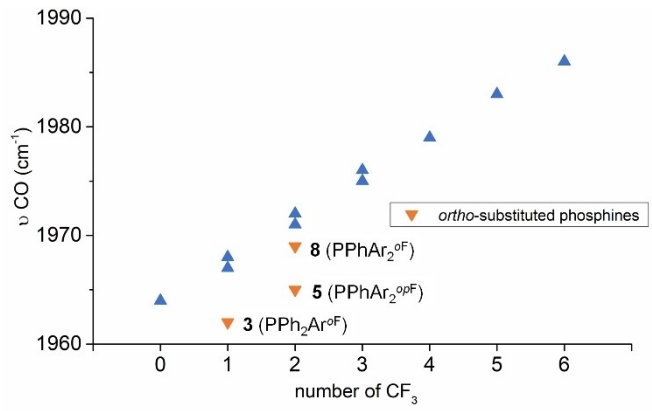


Figure 7. CO vibration frequencies of the Vaska's *trans*-[Ir(CO)Cl(L)$_2$] complexes of the trifluoromethylated phosphines in CH_2Cl_2 solution *vs* the number of trifluoromethyl groups of the phosphines.

Performance of the phosphines as ligands in the Rh-catalysed hydroformylation

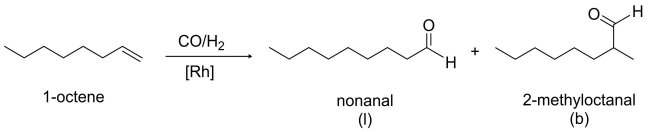
To correlate the stereoelectronic properties with the performance of the trifluoromethylated phosphines in catalysis, the ligands were tested in the Rh-catalysed hydroformylation of 1-octene, Scheme 1. Two possible aldehyde products, branched (2-methyloctanal, **b**) and linear (nonanal, **l**), can be formed. Furthermore, under the reaction conditions, the isomerisation and/or hydrogenation of the substrate can take place, giving yield to internal alkenes and octane, respectively.

All the ligands were tested using the same conditions. The reactions were performed using [Rh(acac)(CO)$_2$] as catalyst precursor and 5 equivalents of the corresponding phosphine. The active catalytic species were formed *in situ* in the autoclave using 16 bar of syngas at 80 °C, before the addition of the substrate. The reactions were carried out at 80 °C and 20 bar of syngas (H_2:CO, 1:1) for 2 h and the consumption of the gas was monitored to determine the reaction rate. Finally, the distribution of the different products was determined by GC.

The catalytic results are shown in Table 3 and Figure 8. As expected, the performance of the catalytic reactions was affected by the nature of the trifluoromethylated phosphines. Conversions above 98% were obtained after 2 h for all the reactions using the trifluoromethylated phosphines. The catalytic system using the *ortho*-substituted phosphines gave poor results in the hydroformylation of 1-octene, with low chemoselectivity towards aldehydes. High concentration of internal alkenes, coming from the isomerization of the substrate, was observed (Table S2) leading also to low regioselectivities. These results indicate a low coordination ability of these ligands, especially when increasing the number of trifluoromethyl groups, since the values are comparable to those of the reaction carried out without phosphine ligand.

Excluding the *ortho*-substituted phosphines, a smooth drop in the chemoselectivity was observed when increasing the number of trifluoromethyl groups, see Figure 8. However, regioselectivities within 70–73% were observed for all these phosphines without a significant trend.

Importantly, the rate of the reaction, measured as the TOF at 50% of conversion in aldehydes, is affected not only by the number of trifluoromethyl groups in the phosphines but also by the relative position of these groups. As clearly observed in Figure 8, *meta*- and *para*-substituted phosphines provided faster reaction rates when increasing the number of trifluoromethyl groups. Interestingly for the same number of trifluoromethyls, *para*-substituted phosphines showed lower reaction rates than the *meta*-substituted ones, *i.e.* **1** *vs* **2**, **6** *vs* **7**, **10** *vs* **11**. Moreover, when using the *meta*-substituted phos-



Scheme 1. Formation of linear (l) and branched (b) aldehydes from 1-octene

Table 3. Rhodium-catalysed hydroformylation of 1-octene with the trifluoromethylated phosphines.[a]

CF_3 groups	Ligand	Conv.[b] [%]	Chemosel.[c] [%]	Regiosel.[d] [%]	TOF 50%[e] [min^{-1}]
	no ligand	98.4	33.9	53.2	-
0	PPh_3	92.5	98.1	72.9	21.0
	1 (PPh_2Ar^{pF})	98.3	96.0	72.7	23.0
1	**2** (PPh_2Ar^{mF})	98.8	97.7	73.0	36.6
	3 (PPh_2Ar^{oF})	98.5	62.7	65.1	14.3
	4 (PPh_2Ar^{mmF})	98.6	96.3	73.0	42.7
	5 (PPh_2Ar^{opF})	98.2	47.3	60.8	4.5
2	**6** ($PPhAr_2^{pF}$)	98.8	97.0	72.3	33.9
	7 ($PPhAr_2^{mF}$)	98.8	97.1	72.9	49.7
	8 ($PPhAr_2^{oF}$)	98.0	37.0	54.4	-
	10 (PAr_3^{pF})	99.1	96.4	70.7	49.0
3	**11** (PAr_3^{mF})	98.9	95.0	72.0	58.9
	12 (PAr_3^{oF})	98.2	34.2	55.7	-
	9 ($PPhAr_2^{mmF}$)	98.7	91.4	72.9	56.6
4	**14** ($PAr^{mmF}Ar_2^{pF}$)	99.0	94.3	71.1	53.7
	15 ($PAr^{mmF}Ar_2^{mF}$)	98.8	91.9	71.9	69.1
5	**16** ($PAr_2^{mmF}Ar^{pF}$)	98.8	89.6	71.2	54.8
	17 ($PAr_2^{mmF}Ar^{mF}$)	98.8	88.6	71.1	71.5
6	**13** (PAr_3^{mmF})	98.9	84.6	67.4	81.4

[a] Conditions: 20 bar $CO:H_2$ (1:1), 80 °C, 2 h of reaction, [1-octene]/[Rh] = 2500, [L]/[Rh] = 5, [Rh] = 0.65 mM. solvent: toluene, *n*-decane 0.17 M as internal standard. Stirring rate 700 rpm. Catalyst preformation: 16 bar $CO:H_2$ (1:1), 80 °C, 30 min. [b] Conversion of 1-octene: (mmol of converted substrate/mmol of starting substrate) × 100. [c] Chemoselectivity towards aldehydes: (mmol of aldehydes/mmol of converted substrate) × 100. [d] Regioselectivity towards linear aldehyde: (mmol of linear aldehyde/mmol of aldehydes) × 100. [e] TOF at 50% of conversion in aldehydes

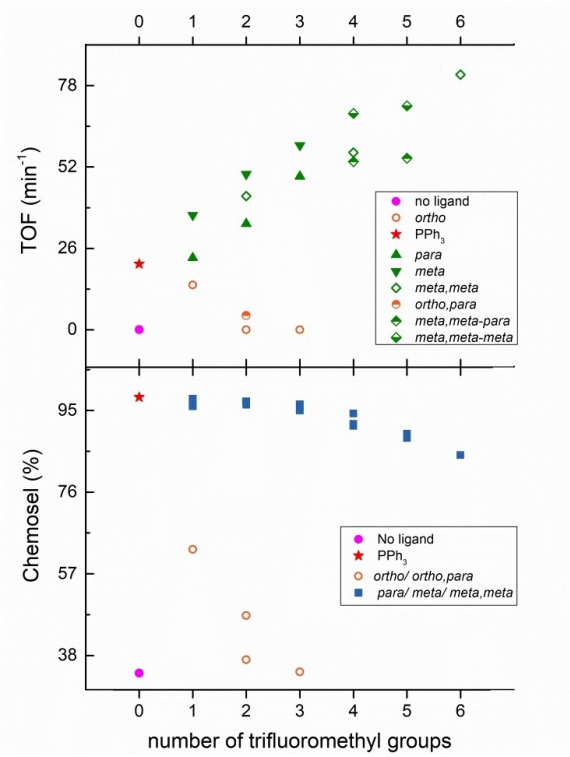


Figure 8. Reaction rate (TOF) and chemoselectivity of the Rh-catalysed hydroformylation of 1-octene *vs* the number of trifluoromethyl groups of the phosphine ligands.

phines, higher values of TOF were observed compared to the *meta-meta*-substituted phosphines with the same number of trifluoromethyls, *i.e.* **4** *vs* **7**, **9** *vs* **15**. Therefore, for the same number of trifluoromethyl groups, their location in different rings has a positive effect in the TOF. These catalytic results contrast to the previous experiments performed for the evaluation of the stereoelectronic properties in which no clear difference between *meta*- and *para*-isomers was observed.

Conclusion

The trifluoromethyl substituents in the aromatic rings of triarylphosphines were found to dramatically affect the stereoelectronic properties of this type of ligands. The σ-donating ability of the phosphines has been evaluated by NMR spectroscopy of the selenide derivatives and the phosphonium ions and was found to be inversely proportional to the number of trifluoromethyl groups. Moreover, the *ortho*-trifluoromethyl groups have a higher influence on the donating properties than the *meta* and *para*-trifluoromethyls. Based on the linear trend observed with the phosphines synthesised in this work, it is possible to predict the σ-donating ability of a given trifluoromethylated phosphine by knowing the position and the number of the trifluoromethyl groups.

The π-accepting ability of the phosphines is also clearly affected by the number and the position of the trifluoromethyl groups, as it was observed through the CO stretching frequency of the corresponding iridium Vaska-type complexes. The π-accepting ability increases with the number of trifluoromethyl groups of the phosphines, except for the *ortho*-substituted phosphines due to a long distance interaction of the fluorine atoms with the metal centre.

The performance of the phosphine in the Rh-catalysed hydroformylation of 1-octene has been correlated with the stereoelectronic properties of the ligands. Higher reaction rates were achieved with the phosphines with lower σ-donating ability and higher π-accepting character, in agreement with the most accepted hydroformylation mechanism. Poor catalytic

results were obtained with the *ortho*-substituted phosphines due to low coordination behaviour of these ligands.

Experimental Section

General Methods

Unless otherwise mentioned, all the synthetic manipulations were performed under nitrogen atmosphere using standard Schlenk techniques. Solvents and liquid reagents were deoxygenated by bubbling nitrogen for 10–15 minutes.

General chemical reagents and solvents were purchased from commercial suppliers which include Sigma-Aldrich, Scharlab and Acros Organics. Trifluoromethylated compounds were purchased from Fluorochem and transition metal compounds were purchased from Alfa Aesar. All the chemicals were used without further purification, unless otherwise specified.

The nuclear magnetic resonance spectra were recorded at the *Servei de Ressonància Magnètica Nuclear* at the UAB on a Bruker Avance III 400 spectrometer (400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C, 376.50 MHz for ^{19}F and 161.98 MHz for ^{31}P). Chemical shifts in ^{1}H and ^{13}C NMR are relative to the signal of the solvent.[29] Chemical shifts in ^{31}P NMR spectra are relative to 85 % H_3PO_4 (0.0 ppm), used as external standard. Chemicals shifts in ^{19}F NMR spectra are relative to flurobenzene (−113.15 ppm with respect to $CFCl_3$). HR-MS analyses were performed at the *Servei d'Anàlisi Química* at UAB in a Bruker microTOF spectrometer coupled to an Apollo II electrospray source (ESI). Elemental analyses were performed at the *Servei d'Anàlisi Química* at UAB in a Thermo Fisher Scientific Flash EA 2000 CHNS. IR spectra recorded in solution were performed in a Perkin Elmer 2000 IR-FT spectrometer. Solid ATR-FTIR spectra were recorded in a Bruker IR Tensor 27 spectrometer equipped with an ATR Specac Golden Gate single reflexion diamond ATR system. Single-crystal XRD data were collected on a Bruker SMART-APEX diffractometer using Mo Kα radiation at the *Servei de Difracció de Raigs X* at the UAB.

Deposition Numbers 2023479 (for [IrCl(CO)(PPh_2Ar^{oF})$_2$]) and 2023480 (for phosphine $PAr^{mmF}Ar_2^{pF}$, **14**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Conversions and selectivities of the Rh-catalysed hydroformylation of 1-octene were obtained by GC with an Agilent 6850 chromatograph equipped with a FID detector, an Agilent 7683B injector and an Agilent HP5 column (25 m long, 0.20 mm ID and 0.33 μm film thickness). For compound identification an Agilent Technologies 6850 chromatograph equipped with an Agilent Technologies 5975 C VL MSD mass spectrometer detector and an Agilent HP5-MS column (30 m long, 0.32 mm ID and 0.5 μm film thickness) were employed.

Synthesis and characterization of trifluoromethylated phosphines

Phosphines from **1** to **4** and from **6** to **13** were prepared according to previously reported methodologies. Detailed information about the synthesis and characterization of these compounds together with the chlorophosphine intermediates can be found in the supporting information. Warning: the organolithium and the Grignard reagents used for the preparation of the phosphines should be carefully handled due to their pyrophoric nature.

(2,4-bis(trifluoromethyl)phenyl)diphenylphosphine (5): 20.1 ml of *n*-butyllithium (2.5 M in hexanes, 50.3 mmol) was added dropwise to a solution of 1-bromo-2,4-bis(trifluoromethyl)benzene (50 mmol) in 50 ml of anhydrous diethyl ether at 0 °C. Quantitative addition was ensured with two portions of 10 ml of diethyl ether. After complete addition, the resulting orange solution was stirred for 30 min at 0 °C. At this same temperature, a solution of chlorodiphenylphosphine (45 mmol) in 30 ml of dry Et_2O was added dropwise. The reaction mixture was stirred for 3 hours at room temperature. Then the orange suspension obtained was cooled down in an ice bath before the addition of 80 ml of 10 % aqueous HCl. The orange organic phase was separated and the aqueous phase was extracted three times with 30 ml of Et_2O. The organic fractions were combined and dried over anhydrous $MgSO_4$. After filtration, the solvent was vacuum evaporated to obtain an orange solid which was purified through flash column in silica gel (CH_2Cl_2:hexanes, 1:1). Pale yellow solid. Yield 12.1 g (67 %) ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.99 (*bs*, 1H, $H_{C3}\{C_6H_3(CF_3)_2\}$); 7.67 (*bd*, 1H, $H_{C5}\{C_6H_3(CF_3)_2\}$, $^{3}J_{HH}$ = 8.1 Hz); 7.42–7.33 (m, 6H, H_{C3}-$H_{C4}\{C_6H_5\}$); 7.27 (*bd*, 1H, $H_{C6}\{C_6H_3(CF_3)_2\}$, $^{3}J_{HH}$ = 8.1 Hz) 7.26–7.20 (m, 4H, $H_{C2}\{C_6H_5\}$). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$). δ 142.48 (d, $C_1\{C_6H_3(CF_3)_2\}$, $^{1}J_{CP}$ = 33.8 Hz); 136.81 (*bs*, $C_6\{C_6H_3(CF_3)_2\}$; 135.63 (qd, $C_2\{C_6H_3(CF_3)_2\}$, $^{2}J_{CF}$ = 30.8 Hz, $^{2}J_{CP}$ = 25.0 Hz); 135.46 (d, $C_1\{C_6H_5\}$, $^{1}J_{CP}$ = 11.9 Hz); 133.93 (d, $C_2\{C_6H_5\}$, $^{2}J_{CP}$ = 20.7 Hz); 131.32 (q, $C_4\{C_6H_3(CF_3)_2\}$, $^{2}J_{CF}$ = 33.5 Hz); 129.50 (s, $C_4\{C_6H_5\}$); 128.97 (d, $C_3\{C_6H_5\}$, $^{3}J_{CP}$ = 7.0 Hz); 128.25 (m, $C_5\{C_6H_3(CF_3)_2\}$); 123.72 (q, C{*o*-CF_3}, $^{1}J_{CF}$ = 275.20 Hz); 123.57 (sept, $C_3\{C_6H_3(CF_3)_2\}$, $^{3}J_{CF}$ = 3.8 Hz); 123.45 (q, C{*p*-CF_3}, $^{1}J_{CF}$ = 272.2 Hz); ^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$) δ −10.46 (q, $^{4}J_{FP}$ = 52.5 Hz). ^{19}F{^{1}H} NMR (235.39 MHz, $CDCl_3$) δ −57.41 (d, F_{oCF3}, $^{4}J_{FP}$ = 52.5 Hz); −63.09 (s, F_{pCF3}). HR-MS (ESI$^+$ *m/z*) [M + H]$^+$: calculated for $[C_{20}H_{13}F_6P]^+$ 399.07; found 399.0735.

(3,5-bis(trifluoromethyl)phenyl)bis(4-(trifluoromethyl)phenyl) phosphine (14) and (3,5-bis(trifluoromethyl)phenyl)bis(3-(trifluoromethyl)phenyl)phosphine (15): The corresponding trifluoromethylated bromobenzene derivative (13.9 mmol) was dissolved in 7.5 ml of anhydrous diethyl ether and added dropwise to a suspension of magnesium chips (16.9 mmol) in 20 ml of anhydrous diethyl ether. After refluxing the reaction mixture for 2 hours, it was cooled down to room temperature. The excess of Mg was filtered off and the solution containing the Grignard derivative was cooled down to 0 °C. The solution of the Grignard derivative was then added dropwise to a solution of (3,5-bis (trifluoromethyl)phenyl)dichlorophosphine (7.0 mmol) in 7.5 ml of anhydrous diethyl ether and cooled in an ice bath. The resulting orange suspension was stirred overnight at room temperature. After that time, the reaction mixture was cooled down to 0 °C (ice bath) and 10 ml of 10 % aqueous HCl were added. The organic layer was separated and the aqueous phase was extracted three times with 10 ml of diethyl ether. The organic fractions were combined and dried over $MgSO_4$. Filtration and evaporation of the solvent gave an orange-brown solid which was further purified through flash silica column (CH_2Cl_2:hexanes, 7:3).

(14): pale orange solid. 1.9 g (51 %) ^{1}H NMR (400.13 MHz, $CDCl_3$), δ 7.91 (s, 1H, $H_{C4}\{C_6H_3(CF_3)_2\}$); 7.73 (d, 2H, $H_{C2}\{C_6H_3(CF_3)_2\}$, $^{3}J_{HP}$ = 6.2 Hz); 7.67 (d, 4H, $H_{C3}\{C_6H_3CF_3\}$, $^{3}J_{HH}$ = 7.6 Hz); 7.42 (*pseudo*-t, 3H, $H_{C2}\{C_6H_4CF_3\}$, $^{3}J_{HP}$ = $^{3}J_{HH}$ = 7.6 Hz). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$), δ 139.70 (d, $C_1\{C_6H_3(CF_3)_2\}$, $^{1}J_{CP}$ = 19.0 Hz); 139.33 (*bd*, $C_1\{C_6H_4CF_3\}$, $^{1}J_{CP}$ = 14.0 Hz); 134.13 (d, $C_2\{C_6H_4CF_3\}$, $^{2}J_{CP}$ = 21.1 Hz); 133.5 (*bd*, $C_2\{C_6H_3(CF_3)_2\}$, $^{2}J_{CP}$ = 21.0 Hz); 132.5 (qd, $C_3\{C_6H_3(CF_3)_2\}$, $^{2}J_{CF}$ = 33.5 Hz, $^{2}J_{CP}$ = 6.0 Hz); 132.24 (q, $C_4\{C_6H_4CF_3\}$, $^{2}J_{CF}$ = 32.8 Hz); 126.12 (m, $C_3\{C_6H_4CF_3\}$, $^{3}J_{CP}$ = 7.5 Hz, $^{3}J_{CF}$ = 3.8 Hz); 123.89 (q, $CF_3\{C_6H_4CF_3\}$, $^{1}J_{CF}$ = 272.6 Hz); 123.64 (sept, $C_4\{C_6H_3(CF_3)_2\}$, $^{3}J_{CF}$ = 3.6 Hz); 123.17 (q, $CF_3\{C_6H_3(CF_3)_2\}$, $^{1}J_{CF}$ = 272.6 Hz). ^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$), δ −4.62 (s). ^{19}F{^{1}H} NMR (376.50 MHz, $CDCl_3$), δ −62.07 (s, 6F, $CF_3\{C_6H_3(CF_3)_2\}$); −62.17 (s, 6F, $CF_3\{C_6H_4CF_3\}$). HR-MS (ESI$^+$ *m/z*) [M +

H]$^+$: calculated for $[C_{22}H_{12}F_{12}P]^+$ 535.0480; found 535.0491. Elemental analysis: calculated for $C_{22}H_{11}F_{12}P$: C, 49.46; H, 2.08; found: C, 49.94; H, 2.19.

(15): yellow oil. 2.4 g (63% yield). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ 7.90 (s, 1H, $H_{C4}\{C_6H_3(CF_3)_2\}$); 7.71 (d, 4H, $H_{C2}\{C_6H_3(CF_3)_2\}$-$H_{C4}\{C_6H_4CF_3\}$); 7.65 (d, 2H, $H_{C2}\{C_6H_4CF_3\}$, $^3J_{HP}$ = 8.1 Hz); 7.57 (t, 2H, $H_{C5}\{C_6H_4CF_3\}$, $^3J_{HH}$ = 7.8 Hz); 7.45 (*pseudo*-t, 2H, $H_{C6}\{C_6H_4CF_3\}$, $^3J_{HH}$ = $^3J_{HP}$ = 7.8 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$), δ 140.0 (d, $C_1\{C_6H_3(CF_3)_2\}$, $^1J_{CP}$ = 18.1 Hz); 136.85 (*b*d, $C_6\{C_6H_4CF_3\}$, $^2J_{CP}$ = 16.0 Hz); 136.06 (d, $C_1\{C_6H_4CF_3\}$, $^1J_{CP}$ = 13.7 Hz); 133.25 (*b*d, $C_2\{C_6H_3(CF_3)_2\}$, $^2J_{CP}$ = 20.4 Hz); 132.42 (qd, $C_3\{C_6H_3(CF_3)_2\}$, $^2J_{CF}$ = 34.3 Hz, $^2J_{CP}$ = 6.4 Hz); 131.89 (qd, $C_3\{C_6H_4CF_3\}$, $^2J_{CF}$ = 32.6 Hz, $^3J_{CP}$ = 8.7 Hz); 130.70 (dq, $C_2\{C_6H_4CF_3\}$, $^2J_{CP}$ = 26.4 Hz, $^3J_{CF}$ = 3.7 Hz); 129.93 (d, $C_5\{C_6H_4CF_3\}$, $^3J_{CP}$ = 5.8 Hz); 127.10 (q, $C_4\{C_6H_4CF_3\}$, $^3J_{CF}$ = 3.7 Hz); 123.83 (q, $CF_3\{C_6H_4CF_3\}$, $^1J_{CF}$ = 272.4 Hz); 123.50 (sept, $C_4\{C_6H_3(CF_3)_2\}$, $^3J_{CF}$ = 3.8 Hz); 123.17 (q, $CF_3\{C_6H_3(CF_3)_2\}$, $^1J_{CF}$ = 272.8 Hz). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$), δ −3.92 (s). $^{19}F\{^1H\}$ NMR (376.50 MHz, $CDCl_3$), δ −62.21 (*b*s, 6F, CF_3); −62.33 (*b*s, 6F, CF_3). HR-MS (ESI$^+$ *m/z*) $[M+H]^+$: calculated for $[C_{22}H_{12}F_{12}P]^+$ 535.0480; found 535.0489. Elemental analysis: calculated for $C_{22}H_{11}F_{12}P$: C, 49.46; H, 2.08; found: C, 50.30; H, 2.11.

Bis(3,5-bis(trifluoromethyl)phenyl)(4-(trifluoromethyl)phenyl) phosphine (16) and bis(3,5-bis(trifluoromethyl)phenyl)(3-(trifluoromethyl)phenyl)phosphine (17): A solution of the corresponding trifluoromethylated bromobenzene (16.4 mmol) in 10 ml of anhydrous diethylether was added dropwise to a suspension of Mg (19.8 mmol) in 20 ml of anhydrous diethyl ether. The mixture was then refluxed for 1.5 h and, after cooling down to room temperature, excess magnesium was filtered off. The solution containing the corresponding Grignard reagent was then added to a cold solution (ice bath) of bis(3,5-bis(trifluoromethyl)phenyl) chlorophosphine (16.7 mmol) dissolved in 30 ml of anhydrous diethyl ether. The resulting orange suspension was stirred overnight at room temperature. The reaction mixture was then cooled down in an ice bath and 70 ml of 10% aqueous HCl were added. The organic layer was separated and the aqueous phase was extracted three times with 30 ml of Et_2O. The organic fractions were combined and dried over $MgSO_4$. Filtration and evaporation of the solvent gave a brown oil which was further purified through flash silica column (CH_2Cl_2:hexanes, 7:3).

(16): orange solid. 6.3 g (63% yield). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ 7.95 (s, 2H, $H_{C4}\{C_6H_3(CF_3)_2\}$); 7.73 (m, 6H, $H_{C2}\{C_6H_3(CF_3)_2\}$-$H_{C3}\{C_6H_3CF_3\}$); 7.43 (*pseudo*-t, 2H, $H_{C2}\{C_6H_4CF_3\}$, $^3J_{HP}$ = $^3J_{HH}$ = 7.9 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$), δ 138.68 (d, $C_1\{C_6H_3(CF_3)_2\}$, $^1J_{CP}$ = 17.1 Hz); 138.22 (*b*d, $C_1\{C_6H_4CF_3\}$, $^1J_{CP}$ = 15.1 Hz); 134.24 (d, $C_2\{C_6H_4CF_3\}$, $^2J_{CP}$ = 21.1 Hz); 133.5 (*b*d, $C_2\{C_6H_3(CF_3)_2\}$, $^2J_{CP}$ = 22.1 Hz); 132.82 (qd, $C_3\{C_6H_3(CF_3)_2\}$, $^2J_{CF}$ = 33.8 Hz, $^2J_{CP}$ = 6.5 Hz); 132.82 (q, $C_4\{C_6H_4CF_3\}$, $^2J_{CF}$ = 33.8 Hz); 126.46 (m, $C_3\{C_6H_4CF_3\}$, $^3J_{CP}$ = 7.1 Hz, $^3J_{CF}$ = 3.5 Hz); 124.09 (sept, $C_4\{C_6H_3(CF_3)_2\}$, $^3J_{CF}$ = 3.6 Hz); 123.79 (q, $CF_3\{C_6H_4CF_3\}$, $^1J_{CF}$ = 272.1 Hz); 123.06 (q, $CF_3\{C_6H_3(CF_3)_2\}$, $^1J_{CF}$ = 272.7 Hz). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$), δ −3.91 (s). $^{19}F\{^1H\}$ NMR (376.50 MHz, $CDCl_3$), δ −62.27 (s, 12F, $CF_3\{C_6H_3(CF_3)_2\}$); −62.35 (s, 3F, $CF_3\{C_6H_4CF_3\}$). HR-MS (ESI$^+$ *m/z*) $[M+H]^+$: calculated for $[C_{23}H_{11}F_{15}P]^+$ 603.0353; found 603.0358. Elemental analysis: calculated for $C_{23}H_{10}F_{15}P$: C, 45.87; H, 1.67; found: C, 46.32; H, 1.77.

(17): yellow oil. 7.6 g (76% yield. ^{1}H NMR (400.13 MHz, $CDCl_3$), δ 7.94 (s, 2H, $H_{C4}\{C_6H_3(CF_3)_2\}$); 7.76 (d, 4H, $H_{C4}\{C_6H_4CF_3\}$, $^3J_{HH}$ = 7.8 Hz); 7.72 (d, 4H, $H_{C2}\{C_6H_3(CF_3)_2\}$, $^3J_{HP}$ = 6.5 Hz); 7.68 (d, 1H, $H_{C2}\{C_6H_4CF_3\}$, $^3J_{HP}$ = 6.5 Hz); 7.61 (t, 1H, $H_{C5}\{C_6H_4CF_3\}$, $^3J_{HH}$ = 7.8 Hz); 7.45 (*pseudo*-t, 1H, $H_{C6}\{C_6H_4CF_3\}$, $^3J_{HH}$ = $^3J_{HP}$ = 7.8 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$), δ 138.72 (d, $C_1\{C_6H_3(CF_3)_2\}$, $^1J_{CP}$ = 17.9 Hz); 136.79 (*b*d, $C_6\{C_6H_4CF_3\}$, $^2J_{CP}$ = 15.4 Hz); 134.84 (d, $C_1\{C_6H_4CF_3\}$, $^1J_{CP}$ = 13.4 Hz); 133.30 (*b*d, $C_2\{C_6H_3(CF_3)_2\}$, $^2J_{CP}$ = 21.3 Hz); 132.76 (qd, $C_3\{C_6H_3(CF_3)_2\}$, $^2J_{CF}$ = 33.7 Hz, $^2J_{CP}$ = 6.4 Hz); 132.20 (qd, $C_3\{C_6H_4CF_3\}$, $^2J_{CF}$ = 32.6 Hz, $^3J_{CP}$ = 9.1 Hz); 130.92 (dq, $C_2\{C_6H_4CF_3\}$, $^2J_{CP}$ = 28.3 Hz, $^3J_{CF}$ = 3.9 Hz); 130.29 (d, $C_5\{C_6H_4CF_3\}$, $^3J_{CP}$ = 5.8 Hz); 127.68 (q, $C_4\{C_6H_4CF_3\}$, $^3J_{CF}$ = 3.6 Hz); 124.01 (sept, $C_4\{C_6H_3(CF_3)_2\}$, $^3J_{CF}$ = 3.8 Hz); 123.65 (q, $CF_3\{C_6H_4CF_3\}$, $^1J_{CF}$ = 272.5 Hz); 123.00 (q, $CF_3\{C_6H_3(CF_3)_2\}$, $^1J_{CF}$ = 273.1 Hz).). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$), δ −3.83 (s). $^{19}F\{^1H\}$ NMR (376.50 MHz, $CDCl_3$), δ −63.04 (*b*s, 3F, $CF_3\{C_6H_4CF_3\}$); −62.33 (*b*s, 12F, $CF_3\{C_6H_3(CF_3)_2\}$). HR-MS (ESI$^+$ *m/z*) $[M+H]^+$: calculated for $[C_{23}H_{11}F_{15}P]^+$ 603.0353; found 603.0371. Elemental analysis: calculated for $C_{23}H_{10}F_{15}P$: C, 45.87; H, 1.67; found: C, 45.86; H, 1.66.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Trifluoromethyl · Phosphines · Stereoelectronic properties · Selenide derivatives · Hydroformylation

[1] a) T. Vogler, A. Studer, *Org. Lett.* **2008**, *10*, 129; b) S. Ng, C. Y. Ho, T. F. Jamison, *J. Am. Chem. Soc.* **2006**, *128*, 11513; c) M. McConville, O. Saidi, J. Blacker, J. Xiao, *J. Org. Chem.* **2009**, *74*, 2692; d) K. Itami, T. Kamei, J. Yoshide, *J. Am. Chem. Soc.* **2001**, *123*, 8773; e) A. C. J. Koeken, M. C. A. van Vliet, L. J. P. van den Roeke, B. J. Deelma, J. T. F. Keurentjes, *Adv. Synth. Catal.* **2008**, *350*, 179; f) D. R. Palo, C. Erkey, *Organometallics* **2000**, *19*, 81; g) T. Davis, C. Erkey, *Ind. Eng. Chem. Res.* **2000**, *39*, 3671; h) S. Fujita, S. Fujisawa, B. M. Bhanage, M. Arai, *Tetrahedron Lett.* **2004**, *45*, 1307; i) A. S. Chan, EP0102341 (B1). **1984**, Montsanto Co; j) D. Peral, D. Herrera, J. Real, T. Flor, J. C. Bayón, *Catal. Sci. Technol.* **2016**, *6*, 800–808.
[2] a) D. W. Allen, B. F. Taylor, *J. Chem. Soc. Dalton Trans.* **1982**, 51; b) D. W. Allen, L. A. March, I. W. Nowell, *J. Chem. Soc. Dalton Trans.* **1984**, 483.
[3] J. Malito, E. C. Alyeat, *Phosphorus Sulfur Silicon Relat. Elem.* **1990**, *54*, 95.
[4] U. Beckmann, D. Süslüyan, P. C. Kunz, *Phosphorus Sulfur Silicon Relat. Elem.* **2011**, *186*, 2061.
[5] H. A. Bent, *Chem. Rev.* **1961**, *61*, 275.
[6] J. A. S. Howell, N. Fey, J. D. Lovatt, P. C. Yates, P. McArdle, D. Cunningham, E. Sadeh, H. E. Gottlieb, Z. Goldschmidt, M. B. Hursthouse, M. B. Light, *J. Chem. Soc. Dalton Trans.* **1999**, 3015.
[7] O. Pestovsky, A. Shuff, A. Bakac, *Organometallics* **2006**, *25*, 2894.
[8] a) G. A. Olah, C. W. McFarland, *J. Org. Chem.* **1969**, *34*, 1832; b) W. McFarlane, R. F. M. White, *J. Chem. Soc. D.* **1969**, 744; c) T. Allman, R. G. Goel, *Can. J. Chem.* **1982**, *60*, 716.
[9] a) T. Leyssens, D. Peeters, A. G. Orpen, J. N. Harvey, *New J. Chem.* **2005**, *29*, 1424; b) T. Leyssens, D. Peeters, A. G. Orpen, J. N. Harvey, *Organometallics* **2007**, *26*, 2637; c) N. Fey, A. G. Orpen, J. N. Harvey, *Coord. Chem. Rev.* **2009**, *253*, 704.
[10] S. X. Xiao, W. C. Trogler, D. E. Ellis, Z. Berkovitch-Yellin, *J. Am. Chem. Soc.* **1983**, *105*, 7033.
[11] a) D. S. Marynick, *J. Am. Chem. Soc.* **1984**, *106*, 4064; b) A. G. Orpen, N. G. Connelly, *J. Chem. Soc. Chem. Commun.* **1985**, 1310; c) J. A. Tossell, J. H. Moore, J. C. Giordan, *Inorg. Chem.* **1985**, *24*, 1100; d) A. G. Orpen, N. G. Connelly, *Organometallics* **1990**, *9*, 1206.
[12] a) C. A. Tolman, *J. Am. Chem. Soc.* **1970**, *92*, 2953; b) C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313.
[13] a) A. Roodt, S. Otto, G. Steyl, *Coord. Chem. Rev.* **2003**, *245*, 121; b) S. Otto, A. Roodt, *Inorg. Chim. Acta* **2004**, *357*, 1.
[14] M. Angoletta, *Gazz. Chim. Ital.* **1959**, *89*, 2359.
[15] a) L. Vaska, J. W. DiLuzio, *J. Am. Chem. Soc.* **1961**, 2784; b) R. U. Kirss, *Bull. Hist. Chem.* **2013**, *38*, 52.
[16] R. Franke, D. Selent, S. Börner, *Chem. Rev.* **2012**, *112*, 5675.
[17] a) P. W. N. M. van Leeuwen in *Rhodium Catalyzed Hydroformylation* (Eds.: P. W. N. M. van Leeuwen, C. Claver), Kluwer Academic Publishers,

Dordrecht, **2000**; pp. 1–14; b) P. W. N. M. van Leeuwen, Z. Freixa in *Comprehensive Organometallic Chemistry III. From Fundamentals to Applications*; (Eds.: D. M. P. Mingos, R. H. Cabtree); Elsevier Ltd, **2007**; pp. 237–265.
[18] L. A. van Der Veen, M. D. K. Boele, F. R. Bregman, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, H. Schenk, C. Bo, *J. Am. Chem. Soc.* **1998**, *120*, 11616.
[19] J. Unruh, J. R. Christenson, *J. Mol. Catal.* **1982**, *14*, 19.
[20] U. Nettekoven, P. C. J. Kamer, M. Wildhalm, P. W. N. M. van Leeuwen, *Organometallics* **2000**, *19*, 4596.
[21] a) P. W. N. M. van Leeuwen, C. P. Casey, G. T. Whiteker in *Rhodium Catalyzed Hydroformylation*; (Eds.: P. W. N. M. van Leeuwen, C. Claver) Kluwer Academic Publishers, Dordrecht, **2000**, pp. 69–72; b) M. Sparta, K. J. Børve, V. R. Jensen, *J. Am. Chem. Soc.* **2007**, *129*, 8487; c) S. Aguado-Ullate, J. A. Baker, V. González-González, C. Müller, J. D. Hirst, J. J. Carbó, *Catal. Sci. Technol.* **2014**, *4*, 979; d) I. Jacobs, B. de Bruin, J. N. H. Reek, *ChemCatChem* **2015**, *7*, 1708; e) E. Zuidema, L. Escorihuela, T. Eichelsheim, J. J. Carbó, C. Bo, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Chem. Eur. J.* **2008**, *14*, 1843.
[22] D. Gleich, J. Hutter, *Chem. Eur. J.* **2004**, *10*, 2435.
[23] D. G. Gilheany, C. M. Mitchell, in *The Chemistry of Organophosphorus Compounds*; (Eds.: F. R. Hartley) John Wiley & Sons, Inc.: Hoboken, NJ, USA, **1990**; pp 154–158.
[24] a) G. R. Miller, A. W. Yankowsky, S. O. Grim, *J. Chem. Phys.* **1969**, *51*, 3185–3190; b) K. C. Eapen, C. Tamborski, *J. Fluorine Chem.* **1980**, *15*, 239–243; c) J. Jeschke, M. Korb, T. Rüffer, C. Gäbler, H. Lang, *Adv. Synth. Catal.* **2015**, *357*, 4069.
[25] a) A. L. Casalnuovo, T. V. RajanBaby, T. A. Ayers, T. H. Warren, *J. Am. Chem. Soc.* **1994**, *116*, 9869; b) C. M. Whitaker, K. L. Kott, R. J. McMahon, *J. Org. Chem.* **1995**, *60*, 3499; c) J. R. Klaehn, D. R. Peterman, M. K. Harrup, R. D. Tillotson, T. A. Luther, J. D. Law, L. M. Daniels, *Inorg. Chim. Acta* **2008**, *361*, 2522; d) P. M. Holstein, M. Vogler, P. Larini, G. Pilet, E. Clot, O. Baudoin, *ACS Catal.* **2015**, *5*, 4300.
[26] a) W. McFarlane, D. S. Rycroft, *J. Chem. Soc. Dalton Trans.* **1973**, 2162; b) S. O. Grim, E. D. Walton, *Inorg. Chem.* **1980**, *19*, 1982.
[27] D. Peral, *Triarilfosfines Sulfonades Trifluorometilades. Aplicacions en Processos Catalítics*. Ph.D. Thesis. Universitat Autònoma de Barcelona, **2013**.
[28] a) M. R. Churchill, J. C. Fettinger, B. J. Rappoli, J. D. Atwood, *Acta Crystallogr.* **1987**, *C43*, 1697; b) M. R. Churchill, J. C. Fettinger, L. A. Buttrey, M. D. Barkan, J. S. Thompson, *J. Organomet. Chem.* **1988**, *340*, 257; c) C. Corcoran, J. Fawcett, S. Friedrichs, J. H. Holloway, E. G. Hope, D. R. Russell, G. C. Saunders, A. M. Stuart, *J. Chem. Dalton Trans.* **2000**, 161.
[29] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176.

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