NJC

Cite this: *New J. Chem.*, 2011, **35**, 2488–2495

www.rsc.org/njc

PAPER

Fluoride catalyzed P–aryl-coupling—a mild approach to functionalized arylphosphines†

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Received (in Montpellier, France) 27th May 2011, Accepted 11th July 2011
DOI: 10.1039/c1nj20448c

Functionalized triaryl- and diarylalkylphosphines are accessible in high yields following a mild fluoride catalyzed phosphorous–carbon coupling protocol starting from fluoroarenes and silylated phosphines. The reaction requires a minimum of solvent and can be applied to the synthesis of several functionalized phosphines on a kilogram scale without problems. In contrast to the phosphine synthesis in a superbasic medium, there is no salt formation during the reaction which simplifies the work-up process.

Introduction

Phosphines are the most common ligands in homogeneous catalysis with electron-rich transition metals. They are applied in a broad variety of different catalytic reactions, a series of them being of industrial relevance such as hydroformylations,[1] hydrogenations,[2] hydrocyanations,[3] cross-coupling reactions,[2a] C–C-couplings,[2c,4] hydrosilations,[2b] Diels–Alder reactions,[5] or polymerisations.[6] Therefore it is not surprising that the development of phosphine chemistry has received wide interest over the last decades, especially for application in enantioselective catalysis.[7] Phosphine ligands determine not only the activity and the selectivity but also the physical properties of the catalysts. Prime examples for this are the water soluble sulfonated arylphosphines initially developed by Kuntz *et al.* in the 1980s.[8]

The central phosphorous–carbon bonds of phosphines are usually formed by reacting either (a) a carbon centered electrophile (*e.g.* RX) with a phosphorous nucleophile ($M_yPR'_{3-y}$, y = 1–3) or (b) a carbon nucleophile (MR) with a phosphorous based electrophile ($X_yPR'_{3-y}$, y = 1–3). Following the second method, metalated carbon compounds react with phosphorous halides generally without any problems. The solely limitation consists in the incompatibility of functional groups within R and R′ towards the organometallic reagent, narrowing the scope of accessible products.

In contrast, the gradual formation of multiple phosphorous–carbon bonds in one reaction batch is difficult if metalated phosphines are employed. Due to their high sensitivity against water and oxygen, these compounds are not easily accessible. Deprotonation of phosphines of the type H_yPR_{3-y} (y = 1–3) using organometallic reagents, mostly *n*-butyllithium, is probably the best way to build up phosphorous–carbon bonds with phosphorous nucleophiles. Alternatively, phosphides can be generated *in situ* from phosphines in a superbasic medium such as DMSO/KOH.[9] Using an aryl compound as the carbon electrophile, the well-known reactivity of S_NAr-reactions can be observed: aryl fluorides turn out to be the most reactive aryl-X components and electron-withdrawing substituents considerably increase the reactivity of the aryl halide. This type of reaction was intensively investigated in the last 20 years, mainly by Stelzer *et al.*[9] It opens up access to a variety of different phosphine ligands. Water-soluble phosphines of industrial relevance such as *p*-TPPTS (sodium triphenylphosphine trisulfonate, 4,4′,4′′-phosphinidynetris(benzenesulfonic acid)) can be synthesized without protection of the sulfonic acid sites. However, the scope of reactants is limited by the aggressive superbasic medium. The reaction demands considerable amounts of solvent and the commonly used, highly toxic and gaseous phosphine (PH_3) makes dosing difficult. Additionally, its application affords rigorous security measures.

Results and discussion

We recently published so far unknown triarylphosphines bearing pyrazolyl- and pyrimidinyl groups at the aryl substituents,[10] obtained *via* classical synthetic routes using protecting group strategies. The aim of further investigations was to reduce the number of synthetic steps significantly along with increasing the yield. Additionally, the formation of the phosphorous–carbon bonds had to take place under mild

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† Electronic supplementary information (ESI) available: NMR and IR spectra, X-ray structure analyses. CCDC 827385 ((2-cyanophenyl)-diphenylphosphine) (**3h**) and 827386 (4-(diphenylphosphino)benzoic acid). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1nj20448c

conditions for the given substitution pattern. We herein present a generally applicable method for the formation of phosphorous–aryl bonds, where aryl fluorides react with silylphosphines under fluoride catalysis.

Trialkylsilyl groups are often applied as protecting groups in organic synthesis and as organometallic reagents to transfer *e.g.* alkinyl groups under mild catalytic reaction conditions.[11] This method has been widely used for the formation of conjugated polyines.[12] Normally, R_3Si-protecting groups can be easily cleaved by fluoride ions in a polar solvent. For the fluoride catalyzed phosphorous–carbon coupling we made use of silylated phosphines of the type $Ph_{3-x}P(SiMe_3)_x$ (x = 1–3)[13] which were already used as precursors for the formation of new phosphorous–carbon bonds. As an example, diphenyl(trimethylsilyl)phosphine reacts with aryl iodides to give the corresponding aryldiphenylphosphines in the presence of a palladium catalyst.[14] Furthermore, silylated phosphines can be coupled with non-aromatic compounds under palladium,[15] nickel,[16] or diazaphospholene catalysis,[17] with activated vinyl chlorides to give vinyl phosphines[13e] and even uncatalyzed with acid chlorides to yield acyl-substituted phosphines.[18] Moreover, silylated phosphines undergo additions to the C═O-, C═N- and C═S-bonds of aldehydes, imines and thiocarbonyls.[19]

There are just a few reports on the application of silylated phosphines for the formation of phosphorous–carbon bonds. Recently, Rieger *et al.* reported the reaction of tBu_2PSiMe_3 with the extremely electron-poor $B(C_6F_5)_3$ leading to tBu_2P-C_6F_4-$B(C_6F_5)_2$.[20] The reactivity described therein has earlier been documented by Grobe *et al.* who reacted highly electron-rich dialkylsilylphosphines $(Alk)_2PSiMe_3$ with electron-poor fluoro(hetero)arenes.[21] However, here high reaction temperatures are required and no functional groups at the arenes other than fluoride, chloride or CF_3 have been reported. The reaction times are long and the amount of substrate that was used was in the range of 0.1–1.0 g. The authors did not mention whether the addition of excess of fluoride would enhance the reaction rates.

To the best of our knowledge, the fluoride catalyzed reaction of silylated phosphines with electron-deficient aryl fluorides to arylphosphines (Scheme 1) has not been described yet.[22]

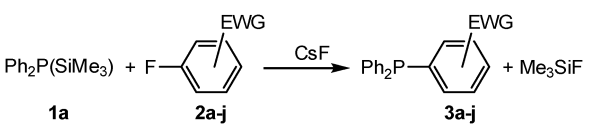
Crucial for the success of this reaction are (a) a high affinity of the silylated phosphine to fluorine and (b) a high reactivity of the fluoroaromatic compound. If this is the case, an adequate amount of fluoride ions is permanently available for the generation of further phosphide ions. Control experiments performed in the absence of fluoride or an oxygen base (see later) gave no conversion at all. For most of our experiments diphenyl(trimethylsilyl)phosphine (**1a**), easy accessible in large quantities from triphenylphosphine, was used,[13a–c] but phenylbis(trimethylsilyl)- (**1b**)[13b,d,e] and tris(trimethylsilyl)-phosphine (**1c**)[13f–k] were examined too. DFT-calculations (Gaussian98W,[23] B3LYP/6-311G*[24,25]) to determine the NBO charge density on phosphorous atoms of the corresponding mono-desilylated anions diphenylphosphide ($\mathbf{1a}^{-1}$: +0.127), phenyl(trimethylsilyl)phosphide ($\mathbf{1b}^{-1}$: −0.348) and bis(trimethylsilyl)phosphide ($\mathbf{1c}^{-1}$: −0.870) show an increasing stabilization of the anions along with a decreasing grade of silylation, reflecting in an increasing reactivity towards fluoride mediated desilylation in the order **1a** > **1b** > **1c**.

All electron-withdrawing functionalized fluoroaromatic compounds are worthwhile considering, excluding aryl fluorides with acidic protons (*e.g.* primary and secondary amides) or with an oxidizing effect (*e.g.* fluoronitrobenzene). We propose the mechanism shown in Scheme 2 for this reaction: fluoride ions generate reactive phosphide anions which undergo nucleophilic substitution at the fluoroarene, again liberating fluoride ions. Depending on the reactivity of the phosphide and the fluoroarene substrate, the amount of catalyst required and the reaction conditions may vary.

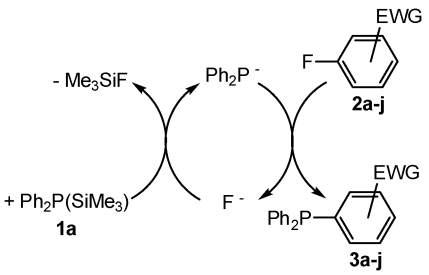
To optimize the reaction conditions we used (*E*)-3-(*N*,*N*-dimethylamino)-1-(4′-fluorophenyl)-prop-2-en-1-one (**2b**) as a model compound, wherein the carbonyl substituent has only a minor activating effect due to the electron-donating dimethylamino group.

Within this work we screened several fluoride ion sources and CsF proved to be the most suitable one. However, a high excess of CsF often leads to poorer results. Probably, the rapid release of large quantities of phosphide goes along with an increased formation of by-products.[26] The optimal, normally significantly substoichiometric amount of fluoride ions depends on the reactivity of the fluoroaromatic compound used and of the silylated phosphine as well as on the morphology of the CsF. We could demonstrate that not only CsF but also catalytic amounts of hydroxides and alcoholates, *e.g.* NaOH and NaOMe, are able to initiate the reaction. The fluoride ions, liberated in the course of the reaction, are responsible for the turnover. We also examined $(n\text{Bu})_4NF$ as a fluoride source. However, the yields are poorer with this catalyst, since this compound is difficult to dry, leading to partial hydrolysis of the silylated phosphines.

Especially polar aprotic solvents such as NMP, DMSO and DMF, well dissolving CsF, have proved to be the most suitable reaction media. An analogue solvent dependence is well known from the phosphorous–aryl coupling in the superbasic medium.[9a] The amount of solvent can be reduced considerably since no further salt load is formed within the fluoride catalyzed variant. For the reference system **2b** the amount of solvent could be reduced to less than 0.2 mL DMF



Scheme 1 Fluoride catalyzed P–C-coupling.



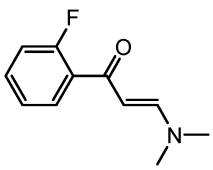
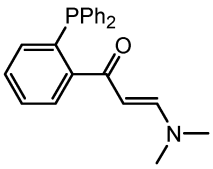
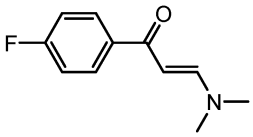
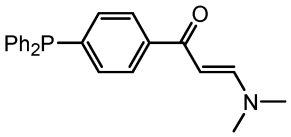
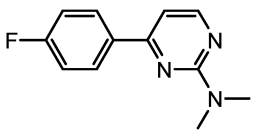
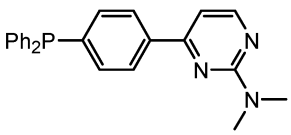
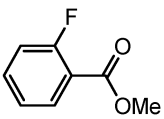
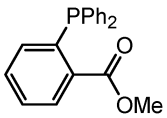
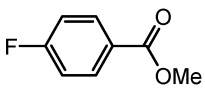
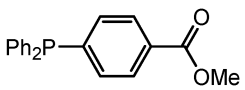
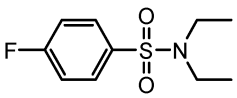
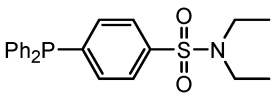
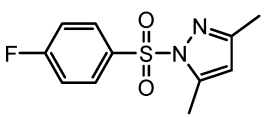
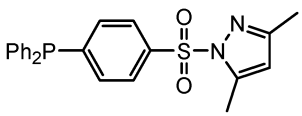
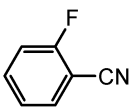
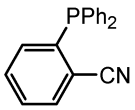
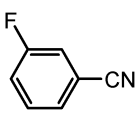
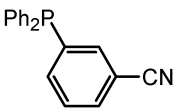
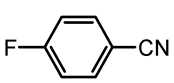
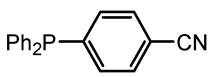
Scheme 2 Proposed mechanism of the fluoride catalyzed P–C-coupling.

per mmol of the fluoroaromatic compound and the amount of catalyst to less than 1 mol% of CsF.

At reaction temperatures above 120 °C an increased formation of by-products is observed. Therefore, a temperature of 80 °C has proved to be most suitable for the reaction of **1a** with less reactive fluoroaromatic compounds. Electron-deficient aryl fluorides react in the presence of CsF as a catalyst within a few minutes at room temperature. The conversion of highly reactive aryl fluorides requires cooling.

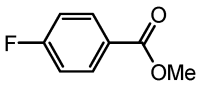
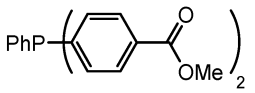
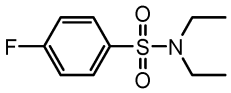
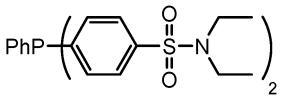
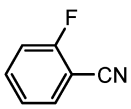
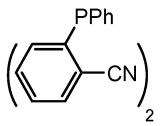
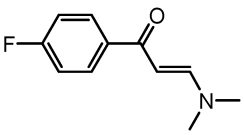
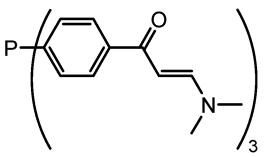
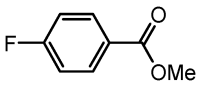
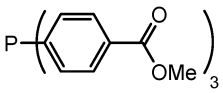
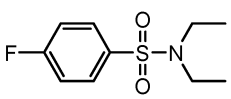
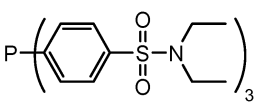
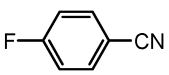
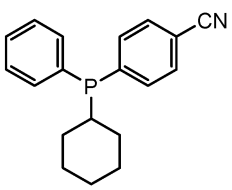
Different batches of CsF can show a varying reactivity. However, additional drying of CsF in the vacuum at 150 °C leads to an increased reactivity. Residual moisture can be excluded as a reason for this behavior, since the hydrolysis of **1a** to diphenylphosphine in the presence of commercial CsF is not observed. We assume that the morphology of the CsF changes during heating. A strong increase of activity could be achieved by dissolving CsF in water, removing the solvent and drying at 150 °C. A voluminous solid results whereby the

Table 1 Fluoride catalyzed coupling of diphenyl(trimethylsilyl)phosphine (**1a**) with aryl fluorides

Aryl fluoride		CsF/mol%	T/°C	t/min	Product		Yield (%)
2a		126	RT	2880	**3a**		95[a]
2b		20	80	60	**3b**		94[b]
2c		10	RT	1440	**3c**		74[b]
2d		50	RT	60	**3d**		81[b]
2e		20	RT	50	**3e**		92[b]
2f		50	RT	5	**3f**		99[b]
2g		32	−12	75	**3g**		90[b]
2h		50	RT	10	**3h**		94[b]
2i		21	RT	20	**3i**		97[b]
2j		17	RT	10	**3j**		80[b]

[a] Yield determined by ^{31}P and/or ^{1}H NMR. [b] Isolated yield.

Table 2 Fluoride catalyzed coupling of phenylbis(trimethylsilyl)phosphine (**1b**), tris(trimethylsilyl)phosphine (**1c**) and cyclohexylphenyl-(trimethylsilyl)phosphine (**1d**) with different aryl fluorides

Phosphine	Aryl fluoride		CsF/mol%	T/°C	t/min	Product		Yield[a] (%)
1b	**2e**		50	RT	10	**3k**		81
1b	**2f**		100	RT	10	**3l**		93
1b	**2h**		47	RT	10	**3m**		80
1c	**2b**		44	100	240	**3n**		97
1c	**2e**		50	RT	360	**3o**		94
1c	**2f**		297	RT	360	**3p**		94
1d	**2j**		30	60	1200	**3q**		72

[a] Isolated yield.

reaction of **1a** with **2f** at room temperature is already finished after 5 minutes.

The fluoride catalyzed reactions of diphenyl(trimethylsilyl)-phosphine (**1a**) with aryl fluorides (**2a–j**) to give functionalized aryldiphenylphosphines (**3a–j**) are summarized in Table 1. The reactions with phenylbis(trimethylsilyl)phosphine (**1b**) and tris(trimethylsilyl)phosphine (**1c**) are presented in Table 2. Corresponding to the variable activity of substituted aryl-fluorides in S_NAr-reactions, the reactivity of the substrates increases with decreasing electron density of the aryl ring. *Meta*-functionalized aryl fluorides can only react when strongly electron-withdrawing substituents are present, the *para*-functionalized substrates showed the following order in reactivity: C(O)CH=CH–NMe_2 < C(O)OMe < SO_2NR_2, CN. For steric reasons *ortho*-functionalized aryl fluorides exhibit lower reactivities than the corresponding *para*-functionalized derivatives. Especially in multiple functionalizations with phenylbis(trimethylsilyl)- (**1b**) and tris(trimethylsilyl)phosphine (**1c**) huge differences in reactivity can be observed. As an example, the synthesis of tri-*ortho*-functionalized triarylphosphines is not possible due to the steric hindrance. However, a complete functionalization can always be observed in the reactions of **1b** or **1c** with activated *para*-substituted aryl fluorides. This behavior seems understandable, considering the fact that a decreasing grade of silylation goes along with an increasing reactivity against phosphorous–silicon bond cleavage of the trimethylsilylphosphines. Therefore, in the reaction control by ^{31}P-NMR-spectroscopy no intermediates of the type $(Me_3Si)_2PAr$ or $(Me_3Si)PAr_2$ could be detected. Using 2- or 4-fluoroacetophenone as a substrate, the formation of diphenylphosphine as a by-product in the reaction with diphenyl(trimethylsilyl)phosphine (**1a**) can always be observed. The acidity of the acetyl protons is probably high enough that the intermediary formed PPh_2^--ions react as a base with the substrate and are therefore no longer available for the phosphorous–carbon coupling. As an example of a sulfonic acid derivative, the reaction of *N*,*N*-diethyl-4-fluorobenzene-sulfonamide (**2f**) shows excellent yields. Sulfonic acid esters cannot be converted with this method, instead oxidation of the phosphorous is observed. This also applies to

4-fluorobenzenesulfonic acid pyrazolide, whereas the sterically demanding substituted 1-(4′-fluorobenzenesulfonic acid)-3,5-dimethylpyrazolide (**2g**) yields the desired phosphine in 89%.

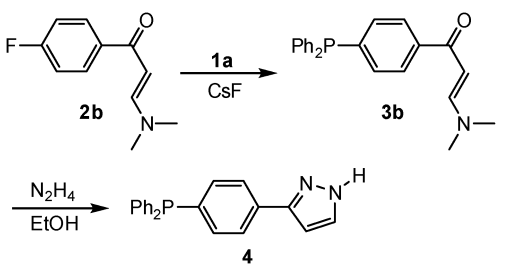
The progress of the reaction can be monitored without any problems by the intensively red-orange color of the phosphide anions: as soon as the color of the solution brightens, the reaction is finished. The work-up of the reactions is done by extraction with CH_2Cl_2/H_2O or $CH_2Cl_2/HCl_{aq.}$. The herein presented method for the formation of phosphorous–carbon bonds can be run at a kilogram scale without problems. This way, approximately 1 kg of the coupling product $Ph_2PC_6H_4C(O)CH{=}CHNMe_2$ (**3b**) could be obtained based on around 600 g of **2b** and 800 g of **1a**, using only 600 mL of DMF as a solvent.

In some cases the phosphorous–carbon coupling and the follow-up reaction of the functional groups could be performed without any work-up of the intermediates. As an example, **2b** is directly converted into the corresponding pyrazole derivative **4** (Scheme 3).

Fluoride catalyzed P–C bond formation provides access to a broad variety of functionalized aryl phosphines, including chelating systems, which we are presently investigating for application in catalysis. *Para*-functionalized phosphines obtained by this route have already been successfully applied for grafting "single-site" catalysts onto inorganic supports.[27] We recently have extended this methodology to fluoride catalyzed N–C bond formation.[28]

Recrystallization of (2-cyanophenyl)diphenylphosphine (**3h**) and 4-(diphenylphosphino)benzoic acid, the latter obtained by hydrolysis of the corresponding methyl ester **3e**, gave single crystals suitable for X-ray structure analysis. The molecular structures of these compounds are presented in Fig. 1.

Substitution of one or both phenyl groups in diphenyl-(trimethylsilyl)phosphines (**1a**) by an alkyl group will lead to the more electron-rich alkylphenyl(trimethylsilyl)- or dialkyl-(trimethylsilyl)phosphines. To prove the applicability of the fluoride catalyzed P–C coupling for such substrates, we used cyclohexylphenyl(trimethylsilyl)phosphine (**1d**)[13b] as the model system. Compared to **1a** the substitution of the phenyl group against a cyclohexyl unit will lead to an increase of steric hindrance at the phosphorous centre in **1d**. Additionally, the electronic conditions will change: DFT-calculations of the NBO charge density on the phosphorous atoms of the desilylated anions cyclohexylphenylphosphide ($\mathbf{1d}^{-1}$: +0.053) and dicyclohexylphosphide (Cy_2P^{-1}: −0.187) show that the generation of these anions from their trimethylsilylated precursors should be almost as simple as for compound **1a**. It is



Scheme 3 One-pot fluoride catalyzed P–C-coupling with follow-up reaction.

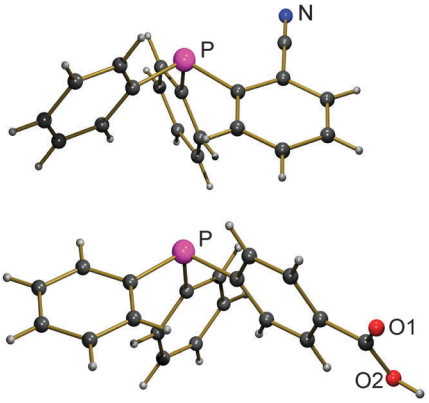
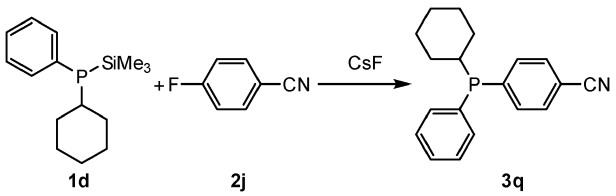


Fig. 1 Molecular structures of (2-cyanophenyl)diphenylphosphine (**3h**) and 4-(diphenylphosphino)benzoic acid in the solid state (for further details on structural analysis see ESI†).



Scheme 4 Fluoride catalyzed P–C-coupling with an alkylaryltrimethylsilyl phosphine.

therefore not surprising that the fluoride catalyzed coupling of **1d** with 4-fluorobenzonitrile (**2j**) results in the formation of the corresponding cyano-functionalized alkyldiarylphosphine **3q** without any problems (Scheme 4, Table 2).

Conclusions

Fluoride catalyzed phosphorous–carbon bond formation opens up access to a broad variety of interesting functionalized aryl phosphine structures. The reaction can be performed under very mild reaction conditions in a minimum of organic solvent and without salt formation, which simplifies the work-up process. Up-scaling of these syntheses to the formation about one kilogram of the desired product is possible without problems.

Experimental section

General remarks

Reactions were performed under a nitrogen atmosphere in flame-dried glassware using standard Schlenk techniques. Unless otherwise stated, chemicals and solvents are commercially available and were used without further purification. Solvents had to be degassed prior to use. CsF was activated by dissolving in water, removing the solvent and drying at 150 °C. Diphenyl(trimethylsilyl)phosphine (**1a**), phenylbis(trimethylsilyl)-phosphine (**1b**) and tris(trimethylsilyl)phosphine (**1c**) were synthesized following literature procedures.[13] NMR spectra were obtained on Bruker DPX 200, DPX-400 or Bruker Avance 600 systems using $CDCl_3$ as a solvent, with proton (200 MHz, 400 MHz or 600 MHz), carbon (50 MHz, 101 MHz or 151 MHz) and phosphorous resonances (81 MHz, 162 MHz or 243 MHz).

We here present four examples of fluoride catalyzed P–C couplings, further procedures are deposited in the ESI† to this article.

Syntheses

Large-scale synthesis of (*E*)-[2-((3′-*N*,*N*-dimethylamino)prop-2′-en-1′-onyl)phenyl]diphenylphosphine (3a). In a flame-dried, nitrogen flushed three-necked flask CsF (176 g, 1.16 mol) was suspended in dry DMF (700 mL) and (*E*)-3-(*N*,*N*-dimethylamino)-1-(2′-fluorophenyl)prop-2-en-1-one (**2a**) (178 g, 921.23 mmol) was added. After dropwise addition of diphenyl(trimethylsilyl)phosphine (**1a**) (238 mL, 929.45 mmol), the reaction mixture was stirred for 48 h at room temperature. The mixture was diluted with H_2O (800 mL) and CH_2Cl_2 (800 mL), the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layers were washed with H_2O (3 × 400 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The product was obtained as a yellow solid (314 g, 95%). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 2.69 + 2.94 (2 s, 6H, H-10$_E$, H-11$_E$), 5.40 (d, $^3J_{HH}$ = 12.6 Hz, 1H, H-8$_E$), 7.04 (dd, $^3J_{HP}$ = 3.3 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, H-2$_E$), 7.26–7.34 (m, 12H, H-2$_{Ph}$, H-3$_{Ph}$, H-4$_{Ph}$, H-3$_E$, H-4$_E$), 7.38 (ddd, $^4J_{HP}$ = 1.2 Hz, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.5, 1H, H-5$_E$), 7.64 (m, 1H, H-9$_E$) ppm. ^{13}C-NMR ($CDCl_3$, 100.62 MHz): δ = 36.51 + 44.38 (s, 6C, C-10$_E$, C-11$_E$), 95.89 (s, 1C, C-8$_E$), 127.10 (d, $^3J_{CP}$ = 5.5 Hz, 1C, C-5$_E$), 127.76 (s, 2C, C-4$_{Ph}$), 127.82 (d, $^3J_{CP}$ = 6.5 Hz, 4C, C-3$_{Ph}$), 128.03 (s, 1C, C-4$_E$), 128.83 (s, 1C, C-3$_E$), 133.15 (d, $^2J_{CP}$ = 19.4 Hz, 4C, C-2$_{Ph}$), 134.17 (s, 1C, C-1$_E$), 135.55 (d, $^2J_{CP}$ = 19.4 Hz, 1C, C-2$_E$), 138.40 (d, $^1J_{CP}$ = 11.1 Hz, 2C, C-1$_{Ph}$), 146.94 (d, $^2J_{CP}$ = 25.9 Hz, 4C, C-6$_E$), 154.28 (s, 1C, C-9$_E$), 190.91 (s, 1C, C-7$_E$) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = −8.8 (s) ppm.

[4-(Methoxycarbonyl)phenyl]diphenylphosphine (3e). In a procedure similar to the one discussed above, 4-fluorobenzoic acid methyl ester (**2e**) (6.50 mL, 50.18 mmol), diphenyl-(trimethylsilyl)phosphine (**1a**) (13.40 mL, 52.33 mmol) and CsF (1.54 g, 10.14 mmol) in dry DMF (24.00 mL) were reacted. The reaction mixture was stirred for 50 min at room temperature. The product was obtained as a colourless solid (14.83 g, 92%). ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 3.91 (s, 3H, H-6$_B$), 7.30–7.39 (m, 12H, H-2$_{Ph}$, H-3$_{Ph}$, H-4$_{Ph}$, H-2$_B$), 7.98 (dd, $^4J_{HP}$ = 1.4 Hz, $^3J_{HH}$ = 8.3 Hz, 2H, H-3$_B$) ppm. ^{13}C-NMR ($CDCl_3$, 50.33 MHz): δ = 52.1 (s, 1C, C-6$_B$), 128.6 (d, $^3J_{CP}$ = 7.2 Hz, 4 C, C-3$_{Ph}$), 129.1 (s, 2C, C-4$_{Ph}$) 129.2 (d, $^3J_{CP}$ = 6.4 Hz, 2C, C-3$_B$), 130.0 (s, 1C, C-4$_B$), 133.1 (d, $^2J_{CP}$ = 18.8 Hz, 2C, C-2$_B$), 133.9 (d, $^2J_{CP}$ = 20.0 Hz, 4C, C-2$_{Ph}$), 136.11 (d, $^1J_{CP}$ = 0.6 Hz, 2C, C-1$_{Ph}$), 144.0 (d, $^1J_{CP}$ = 14.4 Hz, 1C, C-1$_B$), 166.8 (s, 1C, C-5$_B$) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = −3.6 (s) ppm.

One-pot P–C-coupling with follow-up functionalization, synthesis of [4-(pyrazol-3′-yl)phenyl]diphenylphosphine (4). In a flame-dried, nitrogen flushed Schlenk tube CsF (0.36 g, 2.37 mmol) was suspended in dry DMF (4.70 mL) and (*E*)-3-(*N*,*N*-dimethylamino)-1-(4′-fluorophenyl)prop-2-en-1-one (**2b**) (4.61 g, 23.86 mmol) was added. After dropwise addition of diphenyl(trimethylsilyl)phosphine (**1a**) (7.10 mL, 23.80 mmol), the reaction mixture was stirred for 10 min at 100 °C. Then hydrazine monohydrate (3.50 mL, 72.01 mmol) and ethanol (10.00 mL) were added and the reaction mixture was refluxed for 15 h. The work-up corresponds to the procedure presented above, the product was obtained as a yellow solid (6.33 g, 81%). ^{1}H-NMR ($CDCl_3$, 200.13 MHz): δ = 6.65 (d, $^3J_{HH}$ = 2.3 Hz, 1H, H-6$_P$), 7.34–7.46 (m, 12H, H-2$_{Ph}$, H-3$_{Ph}$, H-4$_{Ph}$, H-2$_P$,), 7.63 (d, $^3J_{HH}$ = 2.2 Hz, 1H, H-7$_P$), 7.78 (d, $^3J_{HH}$ = 7.1 Hz, 2H, H-3$_P$) ppm. ^{13}C-NMR ($CDCl_3$, 100.61 MHz): δ = 102.8 (s, 1C, C-6$_P$), 125.7 (d, $^3J_{CP}$ = 6.9 Hz, 2C, C-3$_P$), 128.5 (d, $^3J_{CP}$ = 7.0 Hz, 4C, C-3$_{Ph}$), 128.7 (s, 2C, C-4$_{Ph}$), 132.1 (s, 1C, C-7$_P$), 132.6 (s, 4C, C-4$_P$), 133.7 (d, $^3J_{CP}$ = 19.5 Hz, 1C, C-2$_{Ph}$), 134.1 (d, $^3J_{CP}$ = 19.5 Hz, 2C, C-2$_P$), 137.0 (d, $^3J_{CP}$ = 11.9 Hz, 2C, C-1$_{Ph}$), 137.10 (d, $^3J_{CP}$ = 11.2 Hz, 1C, C-1$_P$), 148.9 (s, 1C, C-5$_P$) ppm. ^{31}P-NMR ($CDCl_3$, 91.01 MHz): δ = −4.4 (s) ppm.

(4-Cyanophenyl)cyclohexylphenylphosphine (3q). In a flame-dried, nitrogen flushed three-necked flask CsF (497 mg, 3.27 mmol) was suspended in dry DMF (15 mL) and stirred for 30 min at room temperature. 4-Fluorobenzonitrile (**2j**) (1.31 g, 10.81 mmol) was added and the reaction mixture was stirred for further 10 min at room temperature. After addition of cyclohexylphenyl(trimethylsilyl)phosphine (**1d**) (2.83 g, 10.70 mmol), the reaction mixture was stirred for 20 h at 60 °C and the solvent was removed *in vacuo*. The residue was diluted with aqueous NH_4Cl (50 mL) and CH_2Cl_2 (50 mL), the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with H_2O (3 × 20 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The product was obtained as a yellow-brown oil (2.25 g, 72%). ^{1}H-NMR ($CDCl_3$, 600.13 MHz): δ = 1.14–1.34 (m, 5H, H$_{cy}$), 1.65–1.79 (m, 5H, H$_{cy}$), 2.17–2.23 (m, 1H, H$_{cy}$), 7.36–7.37 (m, 3H, H$_{ar}$), 7.43–7.46 (m, 2H, H$_{ar}$), 7.50–7.53 (m, 2H, H$_{ar}$), 7.57–7.58 (m, 2H, H$_{ar}$) ppm. ^{13}C-NMR ($CDCl_3$, 150.92 MHz): δ = 26.3 (s, C-8$_{Cy}$), 26.9 (d, $^3J_{CP}$ = 12.5 Hz, 2C, C-7$_{Cy}$), 29.4 (d, $^2J_{CP}$ = 12.5 Hz, C-6$_{Cy}$), 29.8 (d, $^2J_{CP}$ = 16.6 Hz, C-6$_{Cy}$), 35.4 (d, $^1J_{CP}$ = 11.1 Hz, C-5$_{Cy}$), 111.9 (s, C-12$_{Ph}$), 118.9 (s, C-13$_{Ph}$), 128.7 (d, $^3J_{CP}$ = 6.9 Hz, 2C, C-3$_{Ph}$), 129.5 (s, C-4$_{Ph}$), 131.7 (d, $^3J_{CP}$ = 5.6 Hz, 2C, C-11$_{Ph}$), 133.7 (d, $^2J_{CP}$ = 18.0 Hz, 2C, C-10$_{Ph}$), 134.2 (d, $^2J_{CP}$ = 20.8 Hz, 2C, C-2$_{Ph}$), 135.3 (d, $^1J_{CP}$ = 13.9 Hz, C-1$_{Ph}$), 145.2 (d, $^1J_{CP}$ = 20.8 Hz, C-9$_{Ph}$) ppm. ^{31}P-NMR ($CDCl_3$, 161.98 MHz): δ = −2.1 (s) ppm.

X-Ray structure analyses. Crystal data and refinement parameters are collected in Table 3. The structures were solved using a direct method (SIR92[29]), and completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures.[30] Semi-empirical absorption correction from equivalents (Multiscan)[31] was carried out for the structural elucidation of (2-cyanophenyl)diphenylphosphine (**3h**), while for 4-(diphenylphosphino)benzoic acid no absorption correction has been performed. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms positions were calculated in ideal positions (riding model) except the hydrogen atom H2O in 4-(diphenylphosphino)benzoic acid, which is bound to the oxygen atom O_2, was located in the difference Fourier synthesis, and was

Table 3 Crystallographic data for (2-cyanophenyl)di-phenylphosphine (**3h**) and 4-(diphenylphosphino)benzoic acid

Compound	(2-Cyanophenyl)-diphenylphosphine	4-(Diphenylphosphino)-benzoic acid
Formula	$C_{19}H_{14}NP$	$C_{19}H_{15}O_2P$
Formula weight	287.28	306.28
T/K	150(2)	150(2)
Wavelength/Å	1.54184 (Cu Kα)	1.54184 (Cu Ká)
Crystal size/mm	0.26 × 0.18 × 0.08	0.24 × 0.22 × 0.18
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	8.4168(5)	7.8941(2)
b/Å	9.9909(8)	28.6950(7)
c/Å	10.6003(9)	7.0857(2)
α/°	107.361(7)	90
β/°	104.961(6)	97.221(3)
γ/°	107.851(6)	90
V/Å^3	747.45(12)	1592.33(7)
Z	2	4
$\rho_{calc.}$/g cm^{-3}	1.276	1.278
μ (Cu Kα)/mm^1	1.544	1.559
θ-range/°	5.10/62.62	5.86/62.68
Index ranges	$-9 \le h \le 9$ $-10 \le k \le 11$ $-12 \le l \le 11$	$-9 \le h \le 8$ $-33 \le k \le 33$ $-7 \le l \le 8$
Reflns. collected	6228	13 185
Unique reflns.	2349 R_{int} = 0.0334	2504 R_{int} = 0.0997
Absorption correction	Semi-empirical from equivalents (multiscan)	None
Data/restraints/param.	2349/0/190	2504/1/202
GOF on F^2	0.979	1.123
Final R indices $[I > 2\sigma(I)]^a$	R_1 = 0.0321 wR_2 = 0.0859	R_1 = 0.0415 wR_2 = 0.1164
R indices[a] (All data)	R_1 = 0.0388 wR_2 = 0.0881	R_1 = 0.0490 wR_2 = 0.1303
$\Delta\rho_{max}$/min (e Å^{-3})	0.233/−0.247	0.266/−0.389

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

refined semi-freely with the help of a distance restraint, while constraining its U-value to 1.2 times the $U(eq)$ value of O_2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 827385 ((2-cyanophenyl)diphenylphosphine) (**3h**) and CCDC 827386 (4-(diphenylphosphino)-benzoic acid).

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