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Palladium catalyzed P–C coupling – a powerful tool for the syntheses of hydrophilic phosphines

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Abstract

A new synthetic procedure for the preparation of hydrophilic phosphines based on the palladium catalyzed P–C coupling of mono and multiply functionalized aromatic bromides and iodides with primary and secondary phosphines has been developed. In addition to multiply functionalized anionic phosphines and those bearing electron rich substituents like OH, NH_2 cationic guanidinium type phosphine ligands are accessible by this method in high yields. The novel guanidinium phosphines are readily soluble in water showing a remarkable stability in a wide pH range. They turned out to be quite effective catalyst ligands in Rh catalyzed hydroformylation reactions and Pd catalyzed C–C coupling in two-phase systems and aqueous solutions. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: P–C coupling; Pd catalyzed; Multiply functionalized phosphines

1. Introduction

Since the early work of Kuntz [1] in 1975 there is an evergrowing interest in water soluble and hydrophilic phosphine ligands for application in aqueous organometallic chemistry and homogeneous catalysis in two-phase systems (water, organic solvent) [2]. The biphasic system facilitates separation of the organic product containing phase from the aqueous catalyst phase and permits the catalyst to be recycled. The economic and environmental advantages of this technique are apparent. Although sulfonated phosphines like the trisodium salt of the tri(*m*-sulfophenyl)phosphine (TPPTS, **A**) have been preferably applied in biphasic catalysis [3], alternative hydrophilic phosphine ligands containing COO^- (**B**) [4], NMe_3^+ (**C**) [5](a), PMe_3^+ (**D**) [5](b), OH, polyether and sugar groups [5](c) have been proposed for application in these systems. While for sulfonated aromatic phosphines of the TPPTS-type satisfying synthetic procedures (direct sulfonation of neutral phosphines [6], indirect sulfonation [7]) have been developed, hydrophilic phosphine ligands containing other hydrophilic functional groups are accessible only in low yield multistage syntheses [2,8–10]. By analogy with the palladium catalyzed C–C cross coupling reactions (Heck reactions) [11], which are an extremely useful synthetic tool in organic chemistry, metal catalyzed P(III)–C cross coupling was expected to be applicable as a general phosphorus–carbon bond formation method in ligand syntheses. There are only a very few reports in the literature on the syntheses of phosphine ligands using this methodology. Thus Stille-type coupling of silyl derivatives of primary phosphines $R(H)PSiMe_3$ ($R{=}i$Pr, *t*Bu, CEt_3) with aryl halides X–Ar–Z (X=Br, I, Z=H, Me, Cl, Br, OMe, COOMe, CN) yields secondary phosphines R(H)P–

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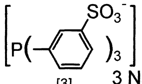
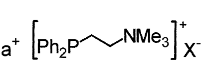
Ar–Z [12]. Arylation of borane protected secondary phosphines may be employed for the syntheses of optically active borane phosphine complexes as shown by Imamoto et al. [13]. The application of the elusive silylphosphines and borane complexes as starting materials limits seriously the preparative scope of these P(III)–C cross coupling reactions, however.



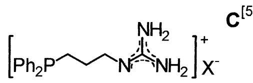
A[3]

$[Ph_2P\text{-}(CH_2)\text{-}COO]^- Na^+$ **B**[4]



C[5a]

$[Ph_2P\text{-}(CH_2)_n\text{-}PMe_3]^+ X^-$ **D**[5b]



E[22]

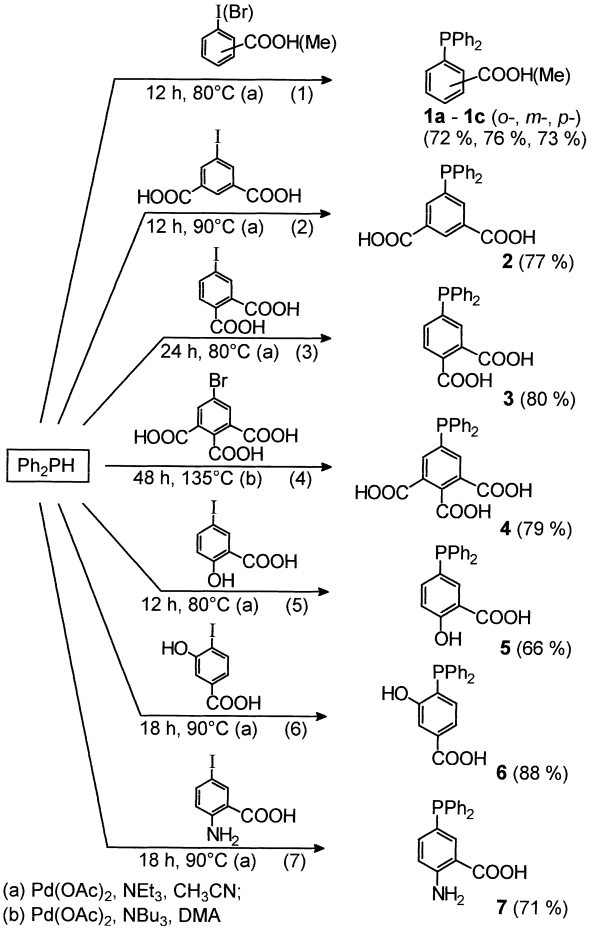
Within a program aimed at the development of new synthetic routes to hydrophilic phosphines for biphasic catalysis our primary interest was directed towards P(III)–C cross coupling reactions between primary or secondary phosphines and multiply functionalized aryl halides bearing polar groups. In order to illustrate the preparative potential of this synthetic strategy we report here the syntheses of some representative hydrophilic phosphines and the application of their transition metal complexes in biphasic and aqueous phase catalysis.

2. Experimental

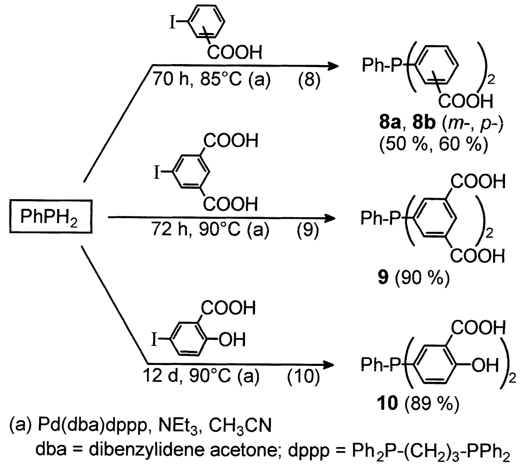
All experiments were carried out under an atmosphere of purified nitrogen or argon in oxygen-free solvents. Ph_2PH [14], $PhPH_2$ [15] and $Pd[Ph_3P]_4$ [16] were prepared according to literature methods. All compounds were characterized by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. The NMR spectra were recorded on a Bruker ARX400 at 400.1, 100.6 or 162.0 MHz, respectively. Mass spectra were run on a Varian MAT 311 A.

2.1. *General procedure for the preparation of carboxylated phosphines using Pd catalyzed P–C coupling reactions [17]*

To a solution of 50.0 mmol of the triethyl ammonium salts of the bromo- or iodobenzoic acid derivatives in 150 ml of acetonitrile or dimethylacetamide, 50.0 mmol of Et_3N or 50.0 mmol of $n$$Bu_3N$ were added. After addition of 0.01–0.02 mmol $Pd(OAc)_2$, $Pd[Ph_3P]_4$ or $Pd_2(dba)_3$ and of 50.0 mmol Ph_2PH or 25.0 mmol $PhPH_2$ the mixtures were heated with stirring to 80–130°C for 12–48 h. The conversion of Ph_2PH or $PhPH_2$ was followed by $^{31}P\{^1H\}$ NMR spectroscopic reaction control. After completion of the reaction the solvent was removed in vacuo. The remaining solids were dissolved in an equivalent amount of 0.1 N NaOH and the solution was washed with three aliquots of 50 ml of Et_2O. On acidifying of the aqueous phase with 3 N HCl the phosphines were precipitated as white to cream-colored solids. For further purification the products could be recrystallized from methanol/water mixtures or CH_2Cl_2. Yields are given in Schemes 1 and 2.



Scheme 1. Pd catalyzed P–C coupling reactions with Ph_2P.



Scheme 2. Pd catalyzed P–C coupling reactions with $PhPH_2$.

2.2. *General procedure for the preparation of guanidinium phosphines using Pd catalyzed P–C coupling reactions [18]*

To 46.0 g (210 mmol) of 3-iodoaniline 100 ml of aqueous HCl (15%) were added. The hydrochloride formed was filtered on a Buchner funnel, recrystallized from water and dried in vacuo (20°C, 0.01 mbar); yield 52.6 g (98%). After addition of 14.36 g (205 mmol) of dimethylcyanamide the mixture was heated to 130°C for 10 min. The product obtained was suspended in 100 ml of water and filtered. To the filtrate KOH solution was added until the solution showed a pH value of 12. It was extracted with three aliquots of 100 ml of dichloromethane and the collected organic phases were dried over magnesium sulfate. After removal of the solvent *N*′-(3-iodophenyl)-*N*,*N*-dimethylguanidine was obtained as a colorless solid.

To the solution of 32.1 g (111.2 mmol) of *N*′-(3-iodophenyl)-*N*,*N*-dimethylguanidine and 6.12 g (55.6 mmol) of $PhPH_2$ in 150 ml of acetonitrile, 0.26 g (0.225 mmol) of $Pd[Ph_3P]_4$ were added. The reaction mixture was heated at reflux for 40 h. Thereafter the solvent was removed in vacuo, phenyl[*bis*-(*N*,*N*-dimethylguanidinium-phenyl)]phosphine diiodide being obtained as cream-colored powder (yield 37.0 g (97%)).

The product gave correct elemental analyses. It was identified by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy [19]. Phenyl[*bis*-3-(guanidinium-phenyl)]-phosphine diiodide, containing the $[–C_6H_4\text{-3-NH–}C(NH_2)_2]^+$ moiety was obtained in an analogous manner.

3. Results and discussion

3.1. *Multifunctional carboxylated phosphine ligands*

Compared with their sulfonated analogs phosphine ligands containing carboxylic acid moieties have been much less investigated as catalyst components. This may at least in part be due to the fact that the synthetic accessibility especially for multifunctional ligands of this type is rather limited with low yield multistage synthetic procedures being required for their preparation. Using Pd catalyzed P–C cross coupling between diphenyl (Ph_2PH) or phenylphosphine ($PhPH_2$) and bromo or iodo derivatives of benzoic, phthalic, isophthalic, salicylic, anthranilic and hemimellitic acid derivatives a series of multiply functionalized phosphine ligands containing carboxylic groups have been obtained in satisfying to high yields. Palladium(II) acetate was mainly employed as a precatalyst in low concentrations ranging from 0.1 to 0.05 mol%. Acetonitrile or dimethylacetamide were used as solvents, triethylamine or tributylamine as bases. Some of the ligands obtained by this synthetic procedure are collected in Schemes 1 and 2 together with experimental details.

A perusal of the results reveals that the substitution pattern in the substrates employed is of no significant influence on the yields in which the phosphine ligands are formed. However, the reaction conditions vary somewhat. This is in sharp contrast to P–C coupling by nucleophilic aromatic phosphination of functionalized fluorobenzene derivatives. This type of reaction which has been used by us for the syntheses of sulfonated [7] and carboxylated [20,21] aromatic phosphines is hampered by the introduction of electron donating substituents like OH or NH_2 in *o*- or *p*-position to fluorine.

For the P–C coupling reactions reported here the bromo derivatives can be employed in some cases instead of the more reactive iodo analogs, more forcing conditions (higher temperatures, longer reaction times) are required, however. This has been shown for the reaction between 3-bromobenzoic acid or bromohemimellitic acid and diphenylphosphine (Scheme 1, Eq. (1) (*ortho*-derivative, methyl ester), Eq. (4); reaction conditions and yields see [17]).

3.2. Guanidinium phosphines

In contrast to the widely studied anionic phosphine ligands, e.g. TPPTS (**A**) [1,2], or $Ph_2P–CH_2–COO^-Na^+$ (**B**) [4] only a very few examples of cationic phosphines have been applied as catalyst ligands in biphasic catalysis so far. Cationic phosphine ligands bearing peripheral guanidinium functions have only very recently been reported [19,22]. The introduction of one of the most basic and hydrophilic group adds pronounced water solubility and anion binding capacity to these ligands. In Pd catalyzed C–C coupling reactions phosphine ligands of this type with rigid spacer groups between the phosphorus atom and the guanidinium function turned out to be superior to those with a flexible alkylene bridging unit (**E** [22]).

Guanidinium phosphines (e.g. **11**, **12**) with *m*-phenylene spacers between phosphorus and the $[NH–C(NH_2)(NR_2)]^+$ substituents are accessible in high yields by palladium catalyzed P–C coupling of *m*-iodophenylguanidines with phenylphosphine (Eqs. (11) and (12)). The *m*-iodophenylguanidines may be obtained by standard synthetic procedures using iodoanilines as starting materials (Eq. (11)). Due to the strongly basic character of the guanidine moiety, the *m*-iodophenylguanidines play a dual function in these P–C coupling reactions acting as electrophiles and bases and no extra base has to be added to the reaction mixtures.

The guanidinium phosphines are readily soluble in water, the aqueous solutions being stable within a pH range of 1–12. Exchange of the counter anions (e.g. I vs. X) may be easily achieved through intermediate preparation of the free guanidine bases by deprotonation of the guanidinium groups with KOH and reprotonation with the corresponding acids HX. The guanidinium phosphines are stable towards molecular oxygen, oxidation being observed only after a long time contact of their solutions with air. A whole series of guanidinium phosphines $\{Ph_{3-n}P[C_6H_4–m–NH–C(NH_2)(NMe_2)]_n\}^{n+}nCl^-$ have been obtained alternatively by a multistage protected group synthesis using the aminophenylphosphines $Ph_{3-n}P(C_6H_4–m–NH_2)_n$ as starting materials [19].

3.3. Hydroxy- and aminophenylphosphines

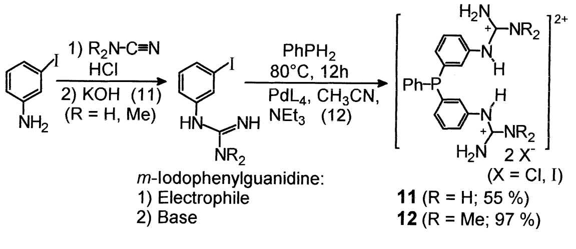
The Pd catalyzed P–C coupling reaction as developed by us has a rather broad synthetic applicability. It is compatible with electron rich substrates like iodophenols or iodoanilines, no protecting groups for the reactive OH or NH_2 functionalities being necessary (Scheme 4). By P–C coupling of primary or secondary phosphines with iodophenols or iodoanilines mono- or bifunctional ligands are obtained in high yields ranging from 62% to 98%. This single step synthesis using commercially available starting materials is superior to the methods reported in the literature [8] for the preparation of these ligands.

The *o*-aminophenylphosphines are of interest as building blocks for chiral mono- and polydentate P, N hydride ligands [23]. The hydroxyphenylphosphines have been used as starting materials for the preparation of triphenylphosphine derivatives with polyether substituents. The solubilities of these ligands (''smart ligands'') in water show inverse temperature dependence. They have therefore been employed in thermoregulated phase transfer catalysis [24].

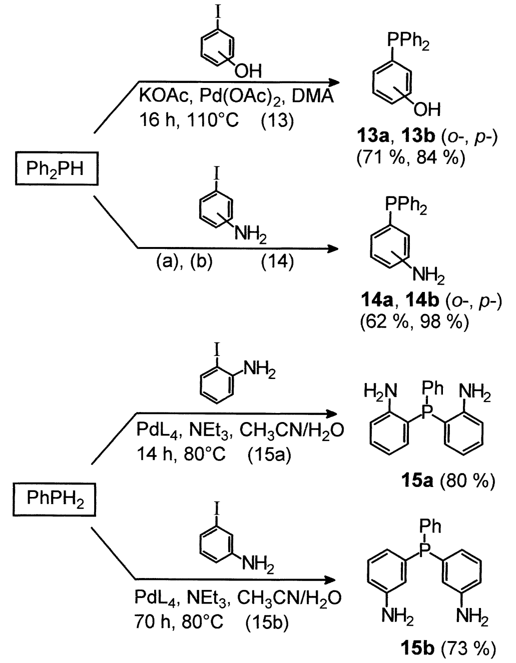
3.4. Effect of catalyst concentration, co-catalysts and reaction control

The P–C bond formation reactions reported in Schemes 1–4 are metal catalyzed. In the absence of the palladium catalysts formed from the precatalysts $Pd(OAc)_2$, $Pd(Ph_3P)_4$ or $Pd_2(dba)_3$ no reaction was observed under the conditions employed in the catalytical processes as indicated by separate experiments. Using the $Pd(OAc)_2$ catalyzed arylation of $PhPH_2$ with $2\text{-}MeOOC–C_6H_4–I$ as prototype reaction it was shown that the reaction rates are increased at higher catalyst concentrations (Fig. 1).

The Pd catalyzed arylation of $PhPH_2$ with functionalized aryl iodides proceeds stepwise, chiral secondary phosphines of type **16** being formed as intermediates (Scheme 5, Eqs. (16) and (17)). This was proven by reaction control using ^{31}P NMR spectroscopy indicating the formation of the secondary phosphines. A representative concentration vs. time



Scheme 3. Syntheses of guanidinium phosphines by Pd catalyzed P–C coupling reactions.

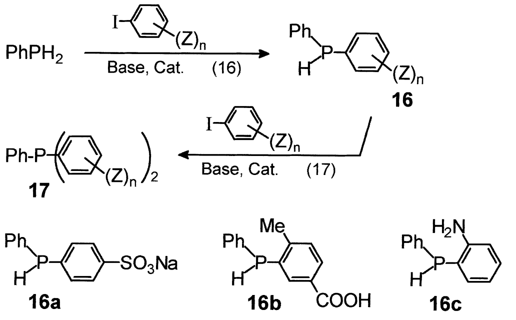


(a) *o*-isomer: PdL$_4$, NEt$_3$, CH$_3$CN/H$_2$O; 34 h, 80°C
(b) *p*-isomer: Pd(OAc)$_2$, KOAc, DMA; 3 h, 130°C

Scheme 4. Syntheses of aminophenyl- and hydroxyphenylphosphines.

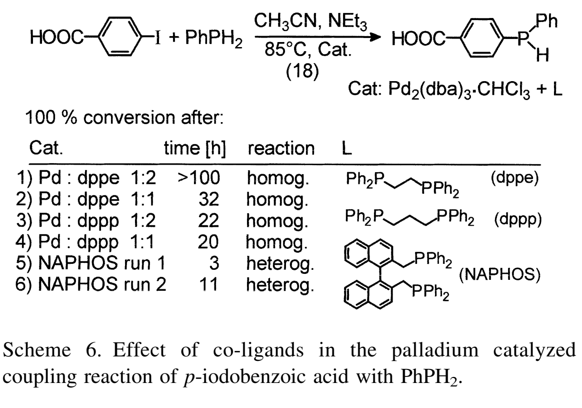
profile is shown in Fig. 2 for the reaction between PhPH$_2$ and I–C$_6$H$_4$–3-NH$_2$. In some cases the secondary phosphines could be isolated, e.g. **16**(**a**)–(**c**), using the appropriate stoichiometry and quenching the reaction mixtures by cooling down to room temperature at a maximum concentration of R(H)P–C$_6$H$_{5-n}$(Z)$_n$ (n=1, 2; Z=substituents).

Decomposition of the catalyst occurred in some cases during the arylation of PhPH$_2$. This was indicated by the precipitation of a black solid and decolorization of the reaction mixtures. The reaction rates dropped down to a low level. Product formation by P–C coupling did not completely stop, however, indicating that a heterogeneous catalytical process might still be effective.



Scheme 5. Stepwise arylation of PhPH$_2$.

Catalyst decomposition could be avoided if ditertiary phosphine ligands are added to the precatalysts mentioned above. The effect of different co-ligands has been studied using the monoarylation of PhPH$_2$ with *p*-iodobenzoic acid as a prototype reaction (Scheme 6, Eq. (18)). NEt$_3$ was used as the base and Pd$_2$(dba)$_3$·CHCl$_3$ as the precatalyst. The best results were obtained with 1,3-*bis*(diphenylphosphino)propane in a 1:1 molar ratio (Pd:ligand) wherein a homogeneous catalyst system was formed (entry 4). Using equimolar amounts of 1,2-*bis*(diphenylphosphino)ethane (Pd:L ratio 1:1) capable of formation of stable five membered chelate ring systems the reaction was much slower, however (entry 2). If this co-ligand was employed in a 1:2 molar ratio the catalytical activity dropped down completely (entry 1). This is



Cat.	time [h]	reaction	L
1) Pd : dppe 1:2	>100	homog.	(dppe)
2) Pd : dppe 1:1	32	homog.	
3) Pd : dppp 1:2	22	homog.	(dppp)
4) Pd : dppp 1:1	20	homog.	
5) NAPHOS run 1	3	heterog.	(NAPHOS)
6) NAPHOS run 2	11	heterog.	

Scheme 6. Effect of co-ligands in the palladium catalyzed coupling reaction of *p*-iodobenzoic acid with PhPH$_2$.

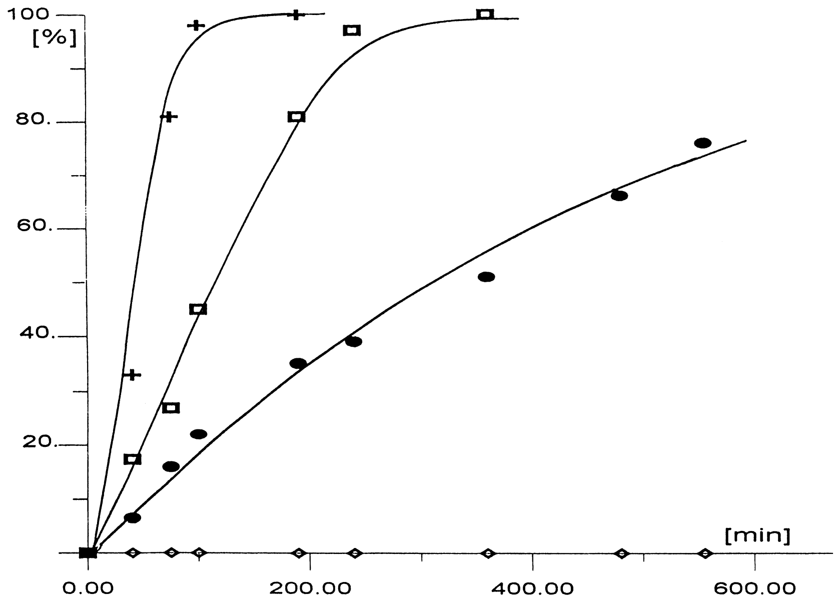


Fig. 1. Dependence of the reaction rate on catalytic concentration for the reaction of $PhPH_2$ with 2-MeOOC–C_6H_4–I: (+) 0.2, (□) 0.1, (●) 0.05 mol% catalyst; (◆) without catalyst (taken from [17]).

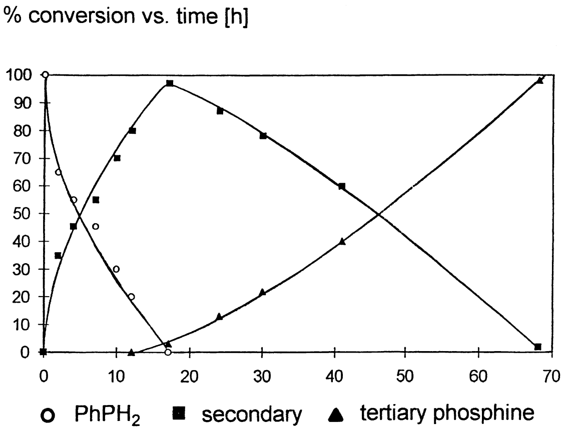


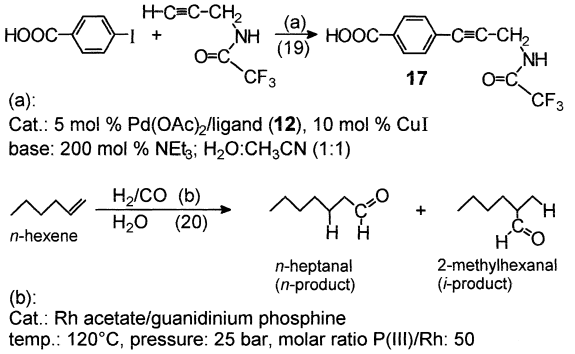
Fig. 2. Conversion vs. time diagram for the reaction of $PhPH_2$ with 3-NH_2–C_6H_4I.

probably due to the formation of a stable chelate complex of composition $Pd(dppe)_2$ which is coordinatively saturated thus showing no catalytical activity. Addition of 2,2′-*bis*(diphenylphosphinomethyl)-1,1′-binaphthalene (NAPHOS) [25] to the precatalyst in the reaction mixtures was accompanied by the formation of a precipitate. The heterogeneous catalytical system still promoted P–C coupling quite effectively, however. Its activity was varying in different runs and the reproducibility of the results was not satisfying (entries 5 and 6, Scheme 6).

3.5. Metal catalyzed C–C coupling reactions using guanidinium phosphines as catalyst ligands

The palladium complexes of the guanidinium phosphines turned out to be quite effective catalysts for Castro–Stephens coupling reactions in aqueous solutions [19]. Thus reaction between *p*-iodobenzoic acid and *N*-(trifluoroacetyl)propargylamine in H_2O/acetonitrile mixtures (50:50–70:30) under very mild conditions gave the coupling product in almost quantitative yields using triethylamine as a base (Scheme 7, Eq. (19)). The palladium catalyst (5 mol%) employed was prepared by mixing palladium acetate with the guanidinium phosphine (e.g. **12**) in a 1:5 molar ratio. Copper(I) iodide promoted these reactions but it was not vital to the success of the C–C bond formation.

Very recently it has been found that the guanidinium phosphines, were more active as ligands in biphasic Rh catalyzed hydroformylation of *n*-hexene compared with the standard ligand TPPTS (Eq. (20)). The ratio



Scheme 7. C–C coupling reactions using guanidinium phosphines as ligands.

of water:organic phase was 2:1, using a syngas pressure of 25 bar at 125°C. The *n*/*i* selectivity obtained with the guanidinium phosphines was, however, somewhat lower than that of TPPTS. Further details on the application of guanidinium phosphines as catalyst ligands in C–C coupling and hydroformylation reactions will be published elsewhere [26].

4. Conclusions

Palladium catalyzed P–C coupling reactions between primary or secondary phosphines and functionalized bromo- or iodobenzenes were shown to be an efficient synthetic route to carboxylated and hydrophilic phosphines in addition to the novel cationic phosphine ligands containing guanidinium groups in their peripheries. No protective groups have to be introduced into the substrates, the reaction being compatible with a variety of functionalities and different solvents including aqueous biphasic systems. Using the appropriate stoichiometry and reaction conditions primary phosphines, e.g. $PhPH_2$, may be partially arylated, chiral secondary phosphines being obtained selectively.

The guanidinium phosphines have shown to be active catalyst ligands in Pd catalyzed C–C coupling reactions and rhodium catalyzed hydroformylation of *n*-hexene.

Acknowledgements

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