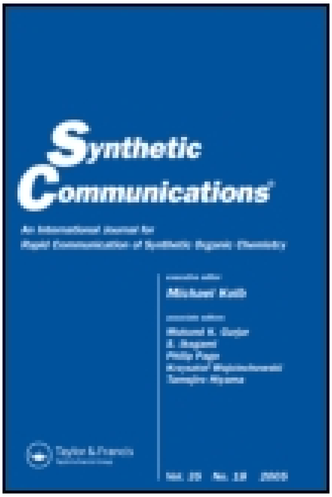

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SILICA-SUPPORTED PHOSPHINE PALLADIUM(0) COMPLEX CATALYZED PHENYLATION OF ACID CHLORIDES AND ARYL IODIDES BY SODIUM TETRAPHENYLBORATE

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ABSTRACT: In the presence of a catalytic amount of silica-supported phosphine palladium(0) complex, sodium tetraphenylborate ($NaBPh_4$) reacts with acid chlorides under mild conditions to give the corresponding phenyl ketones in 57-80% yields; it also reacts with aryl iodides to afford the corresponding biaryls in 75-84% yields.

The palladium catalyzed cross-coupling of organoboranes such as boronic acids, boronates, and trialkylboranes with organic electrophiles in the presence of base is known as the Suzuki reaction[1]. These coupling reactions can tolerate many functional groups and are utilized extensively in the synthesis of natural products. The cross-coupling reactions using the reusable palladium catalysts, such as Pd/C and a polymer-bound palladium catalyst were reported[2,3].

Sodium tetraphenylborate ($NaBPh_4$) is a stable, non-toxic and commercially available phenylating agent and has been used for forming σ-phenyl complexes of various transition metals by the transfer of a phenyl group from boron to met-

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als[4-8]. The formation of carbon – carbon bond through phenyl transfer from $NaBPh_4$ has also been reported[9-11]. From the viewpoint of organic synthesis, several recent reports on its use in palladium catalyzed reactions are interesting; i. e. the phenyl substitution of allylic acetates[12] and chlorides[13] giving the corresponding allylbenzenes, synthesis of diaryl substituted norbornanes and norbornenes[14], phenyl ketones[15] as well as biaryls[16]. It is well – known that zero – valent palladium complexes show unique reactivity in these palladium catalyzed phenylation reaction and tetrakis(triphenylphosphine)palladium(0) is a highly efficient catalyst. However, it is very difficult to use the palladium(0) complex as a practical catalyst because of its instability to air and moisture, and because of difficulties in the separation from a reaction mixture. These difficulties might be overcome by using a polymeric palladium(0) complex which is more stable than a comparable soluble palladium(0) complex. Polymer – supported transition metal complexes are currently attracting great interest because they have advantages of both homogeneous and heterogeneous catalyzed processes. Andersson and coworkers indicated that polymeric catalyst tend to be more efficient in the Heck reaction[17]. However, to our knowledge, no phenylation reaction of organic halides catalyzed by polymeric palladium catalyst has been reported. Recently we prepared a silica – supported phosphine palladium(0) complex ("Si" – P – Pd(0)) from poly – γ – (diphenylphosphino)propylsiloxane("Si" – P) and palladium chloride in acetone, followed by the reduction with hydrazine hydrate in ethanol. In this article we describe its catalytic properties in phenylation reaction of acid chlorides and aryl iodides by $NaBPh_4$.

Treatment of $NaBPh_4$ (1.05mmol) with benzoyl chloride (1mmol) in tetrahydrofuran (THF; 10mL) at 40℃ for 48h in the presence of a catalytic amount of "Si" – P – Pd(0) (3mol%) afforded benzophenone in 78% yield.

When $Pd(PPh_3)_4$ was used as catalyst, benzophenone was obtained in 85% yield. The catalytic activity is slightly lower than that of $Pd(PPh_3)_4$, but the "Si" – P – Pd(0) can be recovered by filtration from reaction mixture. The catalytic activity of the recovered catalyst was tested for phenylation of benzoyl chloride for two recycles and it was found that the yield of benzophenone decreased by 6% and 12% in each recycle, respectively. We applied the reaction to various acid chlorides in THF as solvent (eqn. (1)), typical results are summarized in Table 1.

$$RCOCl + NaBPh_4 \xrightarrow[\text{THF, 40°C}]{\text{"Si" - P - Pd(0)}} RCOPh \qquad (1)$$

The reaction proceeded smoothly with aromatic chlorides. Both strongly electron withdrawing and supplying substituents could be present and the phenylation of O – substituted benzoyl chloride also proceeded smoothly. However, strongly electron supplying substituent such as methoxy group decreased the reactivity of benzoyl chloride. The reactivity of aliphatic acid chlorides were poor and only trace products were obtained. Phenyl ketones all showed strong IR bands at about 1660 cm^{-1} and their ^1H NMR spectra are consistent with the proposed structures.

Synthesis of biaryls is very significant because of their uses as important organic intermediates. Symmetrical biaryls are usually prepared by Ullmann reaction at high temperatures in the presence of Cu powder[18]. Unsymmetrical biaryls could be prepared by the nickel or palladium catalyzed reaction of arylzinc derivatives with aryl halides[19]. In the presence of a catalytic amount of "Si" – P – Pd(0) (3mol%), treatment of $NaBPh_4$(1.05mmol) with iodobenzene(1mmol) in DMF (7mL) at 90°C for 12h gave diphenyl in 84% yield. The reaction is suitable for a variety of functional groups. We applied the reaction into various aryl iodides in DMF as solvent (eqn. (2)), typical results are also summarized in Table 1.

Table 1 Phenylation of organic halides with $NaBPh_4$ catalyzed by a silica-supported phosphine palladium(0) complex[a]

Organic halide	Temp. (℃)	Time (h)	MP (℃)	Lit. MP (℃)	Yield[b] (%)
PhCOCl	40	48	25-26	26[20]	78
$4-ClC_6H_4COCl$	40	48	75-76	75-76[21]	80
$4-CH_3OC_6H_4COCl$	40	48	58-60	58[22]	57
$2-ClC_6H_4COCl$	40	48	42-44	45[23]	74
$4-NO_2C_6H_4COCl$	40	48	136-137	135-136[24]	73
$4-CH_3C_6H_4COCl$	40	48	55-56	57[20]	71
PhI	90	12	69-70	70[25]	84
$4-ClC_6H_4I$	90	12	75-77	77.2[26]	82
$4-CH_3OC_6H_4I$	90	12	87-88	90-91[27]	74
$4-NO_2C_6H_4I$	90	12	112-113	113[28]	78
$4-CH_3OCOC_6H_4I$	90	12	115-116	115-116[29]	84
$4-CH_3C_6H_4I$	90	12	46-47	47.5[30]	75

[a] All reactions were carried out with 1mmol of organic halides, 1.05mmol of $NaBPh_4$, and 0.03mmol of "Si"-P-Pd(0) in THF (10mL) or DMF (7mL). [b] Isolated yield was based on the organic halide.

$$ArI + NaBPh_4 \xrightarrow[\text{DMF, 90℃}]{\text{"Si"} - P - Pd(0)} Ar - Ph \qquad (2)$$

Substituent effects in aryl iodides did not appear to be so significant, both strongly electron supplying and withdrawing substituents could be present. The phenylation reaction of substituted iodobenzenes proceeded smoothly at 90℃ and unsymmetrical biaryls were obtained in good yields. The phenylation reactions of aryl bromides under the same conditions were very slow and only trace products were obtained.

The present method for preparing unsymmetrical biaryls has advantages of readily available starting materials, simple and practical procedures, mild reaction conditions and good yields.

EXPERIMENTAL

Melting points were uncorrected. IR spectra were obtained on a Shimadzu IR – 435 instrument. ^{1}H NMR spectra were obtained on a JEOL FX – 90Q (90MHz) instrument with Me_4Si as an internal standard in CCl_4 or $CDCl_3$ as solvent. All solvents were dried and distilled prior to use.

Preparation of "Si" – P

A mixture of fume silica(6.0g) and γ – chloropropyltriethoxysilane(5.0g) in toluene(140mL) was stirred at 120℃ for 24h. Distilled water(20mL) and 10% hydrochloric acid(0.2mL) were added and the mixture was refluxed for another 48h. After being cooled to room temperature, the mixture was filtered, washed with distilled water(4 × 50mL) and dried under vacuum. The resulting white powder was stirred with 1,1,1,3,3,3 – hexamethyldisilazane(10mL) in toluene (80mL) at 100℃ for 48h. The mixture was allowed to cool and filtered, washed with toluene(3 × 20mL), acetone(3 × 20mL) and dried under vacuum to give 7.0g of poly – γ – chloropropylsiloxane("Si" – Cl). The chlorine content was 7.24wt%.

To a 100mL tetrahydrofuran solution of lithiodiphenylphosphine(0.15M) was added "Si" – Cl(6.0g) and the mixture was refluxed under nitrogen for 30h. After being cooled to room temperature, 2 – chloro – 2 – methylpropane(2mL) was added and the mixture was stirred at room temperature for 2h. The mixture was filtered, washed with ethanol(3 × 30mL), distilled water(5 × 40mL) and dried under vacuum to give 6.5g of poly – γ – (diphenylphosphino)propylsiloxane ("Si" – P). The phosphine content was 4.37wt%.

Preparation of "Si" – P – Pd(0)

To a solution of $PdCl_2$ (0.15g) in acetone (40mL) was added "Si" – P (2.05g). The mixture was refluxed under nitrogen for 48h. The yellow solid was filtered, washed with acetone (3 × 30mL), then stirred with hydrazine hydrate (1.50g, 30mmol) and EtOH(20mL) at 30℃ under nitrogen for 3h. The resulting product was filtered, washed with EtOH(4 × 30mL) and Et_2O(2 × 30mL) and dried under vacuum to give 1.86g of the dark – green polymeric palladium(0) complex. The palladium content was 3.20wt% and the phosphine content was 3.45wt%.

Benzophenone; typical procedure for phenylation of acid chlorides

A mixture of $NaBPh_4$(0.359g, 1.05mmol), benzoyl chloride(0.141g, 1mmol), and "Si" – P – Pd(0)(0.10g, 0.03mmol) in THF(10mL) was stirred under nitrogen at 40℃ for 48h. The "Si" – P – Pd(0) was separated from the mixture by filtration, washed with distilled H_2O(2 × 10mL), EtOH(3 × 10mL) and Et_2O(3 × 10mL) and reused in the next run. The filtrate was poured into a saturated aqueous NaCl solution(100mL) and extracted with methylene chloride (2 × 50mL). The extracts was washed with water, dried over $MgSO_4$. After evaporation of the solution, the residue was purified by preparative TLC on silica gel (petroleum : ethyl acetate = 7 : 1) to give 0.142g of benzophenone(78% yield).

Diphenyl; typical procedure for phenylation of aryl iodides

A mixture of $NaBPh_4$(0.359g, 1.05mmol), iodobenzene(0.204g, 1mmol), and "Si" – P – Pd(0)(0.10g, 0.03mmol) in DMF(7mL) was stirred under nitrogen at 90℃ for 12h. After being cooled to room temperature, the mixture was filtered and the filtrate was poured into a saturated aqueous NaCl solution

(100mL) and extracted with methylene chloride(2 × 50mL). The extracts was washed with water, dried over $MgSO_4$. After evaporation of the solution, the residue was purified by preparative TLC on silica gel (light petroleum) to give 0.130g of diphenyl(84% yield).

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