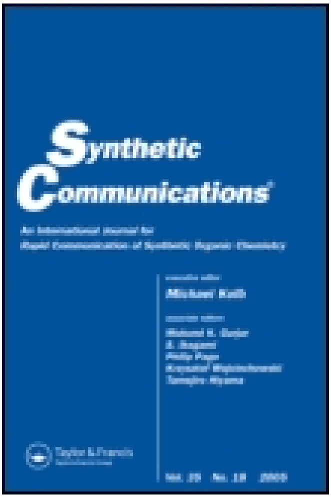

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Amidation of Aryl Halides Catalyzed by Silicasupported Bidentate Phosphine Palladium Complex

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AMIDATION OF ARYL HALIDES CATALYZED BY SILICA-SUPPORTED BIDENTATE PHOSPHINE PALLADIUM COMPLEX

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ABSTRACT: A silica—supported bidentate phosphine palladium complex was prepared from poly—4—oxa—6,7—bis(diphenylphosphino)heptyl siloxane and palladium chloride in acetone. It was an efficient catalyst for the amidation of aryl halides with carbon monoxide and aniline at 1 atm pressure, affording aryl amides.

Carbonylation of aryl halides, in the presence of various nucleophiles and catalyzed by palladium complexes, is a convenient method for the synthesis of various aromatic compounds viz., acids, esters, amides, aldehydes and ketones. In most cases, homogeneous catalysts are used and the reaction conditions, rates, and selectivity are extremely dependent on the nature of both the necleophile and the ligands of palladium in the catalystic species[1-6]. Polymer—supported organotransition metal complexes are currently attracting great interest because they have the advantages of both homogeneous and heterogeneous catalyzed processes, the ease of separation of

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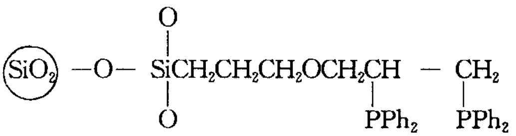
catalyst from the desired reaction products and the ease of recovery of the catalyst are most important. Choudary et al[7] reported polymer—anchored monodentate phosphine palladium with a P/Pd of 0.895 catalyzed carboethoxylation of organic halides in ethanol, but the activity of the catalyst was moderate and decreased gradually during repeated use. Recently we prepared a silica—supported bidentate phosphine palladium complex("Si"—2P—Pd) from poly—4—oxa—6,7—bis(diphenylphosphino)heptyl siloxane ("Si"—2P) and palladium chloride in acetone.



$$\text{SiO}_2\text{—O—}\overset{\text{O}}{\underset{\text{O}}{\text{Si}}}\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\underset{\text{PPh}_2}{\text{CH}} - \underset{\text{PPh}_2}{\text{CH}_2}$$

("Si"—2P)

Here we wish to report its catalytic properties in the amidation of aryl halides with carbon monoxide and aniline at 1 atm pressure.

$$Ar-X+CO+PhNH_2 \xrightarrow[(n-Bu)_3N]{\text{"Si"}-2P-Pd} ArCONHPh$$

The amidation of iodobenzene was carried out at 100°C in the presence of tri—n—butylamine, the amounts of the catalyst have great influence on the amidation of iodobenzene (entries 1—4). When 1.5Mol% palladium complex was used, the amidation of iodobenzene could be accomplished with good yield. The catalytic activity of "Si"—2P—Pd is comparable to that of analogous homogeneous catalyst ($Pd(PPh_3)_2Cl_2$), the catalyst can be separated from product by a simple filtration and can be reused without any noticeable deactivation(entries 4—8). The palladium black was not observed in

Table 1. Amidation of aryl halides with aniline under atmospheric pressure of CO(a)

Entry	Aryl Halides	Mol%Pd	Temp (℃)	Time (h)	Isolated yield(%)	MP (℃)	Lit. MP (℃)
1	C_6H_5I	0.8	100	10	59	160—161	162.5—163[2]
2	C_6H_5I	1.0	100	10	72		
3	C_6H_5I	2.0	100	10	80		
4	C_6H_5I	1.5	100	10	82		
5	C_6H_5I	Recycle—1	100	10	80		
6	C_6H_5I	Recycle—2	100	10	79		
7	C_6H_5I	Recycle—3	100	10	79		
8	C_6H_5I	1.5(b)	100	10	81		
9	4—ClC_6H_4I	1.5	100	10	86	195—196	194—195[8]
10	4—$CH_3OC_6H_4I$	1.5	100	10	77	171—172	173—174[2]
11	C_6H_5Br	1.5	100	10	46		
12	C_6H_5Br	1.5	130	15	68		
13	4—ClC_6H_4Br	1.5	130	15	74		
14	4—$CH_3OC_6H_4Br$	1.5	130	15	63		
15	4—$CH_3C_6H_4Br$	1.5	130	15	66	145—146	146[8]
16	4—$NO_2C_6H_4Br$	1.5	130	15	37	210—211	211—212[2]
17	1—$C_{10}H_7Br$	1.5	130	25	40	160—161	161—163[9]
18	C_6H_5Cl	1.5	130	15	5		

(a)Carried out with 5 mmol of halides, 8mmol of aniline, and 7mmol of tri—n—butylamine. The products in Table—1 were identified by IR and ^{1}H—NMR. (b)Pd $(PPh_3)_2Cl_2$ was used as catalyst.

the products and on the reactor and it was showed that a bidentate phosphine ligand can efficiently prevent the palladium on polymer support from being leached.

This method was applicable to the amidation of various aryl halides with aniline at atmospher of CO(see Table 1). As expected, amidation of aryl iodides is considerably more rapid than that of the corresponding aryl bromides and give aryl amides at 100℃ in good yields. The amidation of aryl bromides were carried out at 130℃ and needed longer time. The reactivity of chlorobenzene was poor. The reactivity of bromobenzenes or iodobenzenes having electron — withdrawing substituents was higher than that of bromobenzenes or iodobenzenes having electron — donating substituents. But, the amidation of 4 — Nitrobromobenzene was an exception. As precedented in the work of Heck[2], the N — phenylamidation of 4 — Nitrobromobenzene was complicated since the reduction of the nitro group catalyzed by palladium also occurred to form an N — phenylurea group from the nitro group, CO, and aniline. The amidation of 1 — bromonaphathane with bulky group was also carried out in moderate yield (entry17)

EXPERIMENTAL

The poly — 4 — oxa — 6, 7 — bis(diphenylphosphino)heptyl siloxane("Si" — 2P) was prepared as described by Lu[10], the phosphine content was 5.14wt%. Melting points were uncorrected. IR spectra were obtained using a Shimadzu IR — 435. ^{1}H — NMR spectra were obtained using a EM — 360L spectrometer in $CDCl_3$.

Preparation of "Si" — 2P — Pd

2.147g (3.559mg atom of P) of "Si" — 2P, 40ml of acetone and 0.210g (1.186mg atom of Pd) of $PdCl_2$ were placed in a three — necked flask (100ml) equipped with a magnetic stirrer bar, a reflux condensor and a gas inlet tube. The mixture was refluxed under nitrogen for 48h. The solid articles became golden in color, the solution became colorless and transparent. The product was filtered, washed by distilled water and acetone and dried in vacuo. The palladium content of the product was 4.66wt%, the phosphine content was 4.34wt% and the P/Pd was 3.20.

Typical Procedure: Synthesis of N—phenylbenzamide.

To a 50ml round—bottomed flask, fitted with a gas inlet tube, a magnetic stirrer bar and a reflux condensor, were placed "Si"—2P—Pd (180mg, 0.075mmol Pd), iodobenzene (1.02g, 5mmol), aniline (0.74g, 8mmol), and tri—n—butylamine (1.29g, 7mmol). The atmosphere was replaced with carbon monoxide and a slow stream of CO was passed into the flask. The mixture was stirred at 100℃ for 10h. The reaction mixture was cooled, dissolved in ether (200ml). The "Si"—2P—Pd was separated from the mixture by filtration, washed with ether and reused in the next run. The ether solution was washed with 20% hydrochloric acid solution (50ml×2) to remove salts and excess amine. The extracts were washed with distilled water (50ml ×3). The ether layer was decolorized with decolorizing carbon, dried with anhydrous magnesium sulfate and filtered. The solid product formed after concentration of the solution was filtered and air—dried to give 0.81g (82% yield) of N—phenylbenzamide.

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