Journal of Fluorine Chemistry 129 (2008) 1124–1128

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Short communication

Polymer-supported palladium perfluorooctanesulfonate [$Pd(OPf)_2$]: A recyclable and ligand-free palladium catalyst for copper-free Sonogashira coupling reaction in water under aerobic conditions

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ARTICLE INFO

Article history:
Received 2 June 2008
Received in revised form 30 July 2008
Accepted 30 July 2008
Available online 7 August 2008

Keywords:
Sonogashira reaction
Palladium perfluorooctanesulfonate
Amberlyst A-21
Supported palladium catalyst

ABSTRACT

Amberlyst A-21, a kind of well-known and cheap polymeric material, was treated with palladium perfluorooctanesulfonate [$Pd(OPf)_2$] giving a reagent with a palladium loading of 1.94 (wt%). The polymer-supported fluorous palladium catalyzes the highly efficient Sonogashira coupling reaction in water. The reactions can be performed under copper- and ligand-free conditions in an air atmosphere. The palladium catalyst is easily separated and can be reused several times without a significant loss of catalytic activity.

1. Introduction

The Sonogashira cross-coupling reaction, discovered in the mid seventies is a powerful method for C–C bond formation [1]. It can be used in the synthesis of a variety of compounds [2], including heterocycles [3], several natural products and pharmaceuticals [4]. Besides natural products, oligomers and polymers have also been prepared via the Sonogashira reaction [5]. Traditionally, the reaction is carried out in aprotic, polar solvents such as DMF and DMAC, with a complex palladium catalyst in conjunction with CuX (X = Cl, Br, I) as a co-catalyst [6]. However, these solvents have high boiling points, which make them difficult to be removed after reaction. Furthermore, oxidative homocoupling of acetylenes (Glaser-type reaction) cannot be avoided in copper-mediated reaction [7], in which by-products (diaryldiacetylenes) are generally difficult to separate from the desired products and copper acetylide is a potentially explosive reagent [8].

In recent years numerous modifications have been reported for the Sonogashira coupling procedure, such as reaction in ionic liquids [9], reaction in microemulsion [10], zeolite-supported reaction system [11], fluorous biphasic system (FBS) using fluorous palladium catalysts [12], phase-transfer catalytic reaction conditions [13], various copper-free conditions [8,9,14–16], use of a variety of promoters [17], such as Zn, Mg, Sn, and the use of microwave irradiation [18].

From the standpoint of environmentally benign organic synthesis, the development of highly active and easily reusable immobilized catalysts and the use of water instead of organic compounds as solvent are of great interest to chemists [19–21]. To date, numerous accomplishments on polymer-supported catalysts suggest that the polymer-supported catalytic system is a promising alternative [22]. On the other hand, the use of aqueous media in organic reactions have become popular because water based synthetic processes are inherently safer (water is non-toxic and nonflammable) as well as inexpensive [23–25]. Ideally, the catalytic synthesis is efficiently performed in water, and the catalyst can be easily separated from the reaction mixture by simple filtration. Quite recently, a variety of aqueous catalytic systems [26] and polymer-supported palladium catalysts [27] for the Sonogashira cross-coupling reaction have been reported. However, to the best of our knowledge, example of ligand-free palladium catalyst catalyzed the Sonogashira reaction in pure water was very limited [28].

In our previous research on palladium-catalyzed reactions, we reported palladium perfluorooctanesulfonate [$Pd(OPf)_2$] as an efficient catalyst for the Sonogashira [29], Heck [30] and Suzuki [31] cross-coupling reactions in the presence of perfluoroalkylated-pyridine ligands in fluorous biphasic system. However, the use of fluorous solvent in such catalytic system has prompted various concerns, the major of which involve cost, solvent leaching,

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doi:10.1016/j.jfluchem.2008.07.022

and environmental persistence [32]. Additionally synthesis of perfluoroalkylated-pyridine ligands is achieved by using expensive perfluoroalkylated alcohol [29–31,33]. Taking these into consideration, we decided to concentrate on developing a supported-$Pd(OPf)_2$ catalytic system which is highly active and stable for the Sonogashira reaction. Our goal was to find out a new catalyst system effective in the absence of fluorous solvent under aerobic, copper- and ligand-free conditions and recyclable in water as a reaction medium. In this paper, we develop a practical protocol for the copper-free Sonogashira coupling of aryl iodides, bromides and chlorides with terminal alkynes in water under aerobic conditions with the Amberlyst A-21 supported $Pd(OPf)_2$ as a catalyst.

2. Experimental

2.1. General remarks

^1H NMR and ^{13}C NMR spectra were characterized with a Bruker Advance RX300 spectrometer. GC analyse was performed on a Saturn 2000GC/MS instrument. IR spectra were recorded on a Bomen MB154S infrared analyzer. Elemental analyses were performed on a Yanagimoto MT3CHN recorder. Inductively coupled plasma (ICP) spectra were measured on an Ultima2C apparatus. Amberlyst A-21 was commercially obtained from Weide Chemical Co. of Tianjin. Heptadecafluorooctanesulfonic acid ($R_{f8}SO_3H$) was commercially obtained from ARCOS Co. Amberlyst A-21 was dried at 80 °C in vacuum for 24 h before being used. Other commercially available reagents were used without further purification.

2.2. Preparation of $Pd(OPf)_2$

A mixture of a solution of $R_{f8}SO_3H$ (1.23 g, 2.5 mmol) in water (5 ml) and palladium carbonate (0.17 g, 1.0 mmol) was refluxed with stirring for 4 h. The resulting gelatin-like solid was collected, washed and dried at 160 °C for 24 h in vacuum to give a brown solid (0.84 g, 76%), which does not have a clear melting point up to 500 °C, but shrinks around 330 °C and 410 °C. IR (KBr) υ1 230 (CF_3), 1 148 (CF_2), 1 080 (SO_2), 1 061 (SO_2), 752 (S–O) and 640 (C–S) cm^{-1}. $C_{16}F_{34}O_6PdS_2$: calcd. C 17.38, Pd 9.63; found C 17.29, Pd 9.61. ^{19}F NMR ($CF_3C_6H_5$): δ −126.2, −121.2, −114.2, −81.4.

2.3. Preparation of Amberlyst A-21-$Pd(OPf)_2$

A mixture of $Pd(OPf)_2$ (2 g) and Amberlyst A-21 (8 g) in acetone (100 ml) was refluxed with stirring for 24 h. The mixture was allowed to stand at room temperature for *ca.* 2 h without stirring. Then the deposit was separated and washed with water (20 ml 3×) and toluene (20 ml 2×). The isolated solids was dried at 80 °C for 24 h in vacuum to give a gray solid (9.92 g). The solid contained 1.94% Pd by weight based on the ICP analysis. Other phosphine-free palladium catalysts supported on Amberlyst A-21 were prepared according to the similar method.

2.4. Typical procedure for the Sonogashira reaction with Amberlyst A-21-$Pd(OPf)_2$

Iodobenzene (2.04 g, 10 mmol) was added to a mixture of Amberlyst A-21-$Pd(OPf)_2$ (0.55 g, 1 mol% Pd) and water (10 ml) in a glass flask under vigorous stirring. After *ca.* 5 min, phenylacetylene (1.24 g, 12 mmol) and NEt_3 (2.1 ml, 15 mmol) were introduced into the glass tube. After stirring at 80 °C for 1 h, the reaction mixture was cooled and diluted with water (10 ml) and toluene (15 ml). When the filtration was finished, the filtrate was extracted with hexane (2 × 10 ml). The combined organic extracts were dried over Na_2SO_4 and *p*-xylene (1.06 g, 10 mmol) was added as internal standard for GC analysis. After GC and GC/MS analyses, the solvents and volatiles were removed under vacuum, and then the residue was subjected to column chromatography on SiO_2 with cyclohexane as eluent to give diphenylacetylene as white solid (1.71 g, 94%). The isolated product was analysed by ^1H NMR and ^{13}C NMR and compared with authentic samples.

Diphenylacetylene: A white solid; mp: 58–60 °C (lit. 59–61 °C); ^1H NMR (300 MHz, TMS, $CDCl_3$) δ 7.45 (m, 4H), 7.23 (m, 6H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 89.4, 123.5, 128.2, 128.4, 131.5; MS (EI) *m*/*z* 178 (M^+).

4-Methyldiphenylacetylene: A white solid; mp: 67–68 °C (lit. 69–70 °C); ^1H NMR (300 MHz, TMS, $CDCl_3$) δ 7.45 (m, 2H), 7.36 (d, 2H), 7.27 (m, 3H), 7.11 (d, 2H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 88.6, 89.4, 120.1, 123.5, 128.2, 129.1, 131.4, 138.3; MS (EI) *m*/*z* 192 (M^+).

2-Methyldiphenylacetylene: A colorless liquid; ^1H NMR (300 MHz, TMS, $CDCl_3$) δ 7.41 (m, 3H), 7.22 (m, 3H), 7.09 (m, 3H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 88.7, 89.5, 120.1, 123.6, 128.3, 129.1, 131.3, 138.2; MS (EI) *m*/*z* 192 (M^+).

4-Methoxydiphenylacetylene: A yellowish solid; mp: 60–62 °C (lit. 62–63 °C); ^1H NMR (300 MHz, TMS, $CDCl_3$) δ 7.49 (m, 4H), 7.22 (m, 3H), 6.78 (d, 2H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 55.9, 93.0, 115.0, 128.4, 128.5, 132.4, 133.2, 160.5; MS (EI) *m*/*z* 208 (M^+).

2-Methoxydiphenylacetylene: A yellowish liquid; ^1H NMR (300 MHz, TMS, $CDCl_3$) δ 7.45 (m, 3H), 7.23 (m, 3H), 7.06 (m, 1H), 6.72 (m, 2H), 3.73 (s, 3H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 55.4, 92.9, 112.1, 128.4, 128.5, 132.4, 133.3, 163.4; MS (EI) *m*/*z* 208 (M^+).

4-Nitrodiphenylacetylene: A yellowish solid; mp: 118–120 °C (lit. 119–120 °C); ^1H NMR (300 MHz, TMS, $CDCl_3$) δ 8.14 (d, 2H), 7.61 (d, 2H), 7.47 (m, 2H), 7.28 (m, 3H), 7.11 (d, 2H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 87.6, 94.7, 122.1, 123.5, 128.4, 129.3, 130.2, 131.7, 132.3, 146.9; MS (EI) *m*/*z* 223 (M^+).

1-Phenyl-1-heptyne: A colorless liquid; ^1H NMR (300 MHz, TMS, $CDCl_3$) δ 7.41 (d, 2H), 7.24 (m, 1H), 7.23 (m, 2H), 2.05 (m, 2H), 1.45 (m, 2H), 1.31 (m, 4H), 0.98 (m, 3H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 14.2, 18.8, 21.9, 28.7, 30.6, 78.7, 100.1, 122.8, 128.4, 128.5, 132.3; MS (EI) *m*/*z* 172 (M^+).

1-Phenyl-1-octyne: A colorless liquid; ^1H NMR (300 MHz, TMS, $CDCl_3$) δ 7.40 (d, 2H), 7.24 (m, 1H), 7.22 (m, 2H), 2.06 (m, 2H), 1.46 (m, 2H), 1.31 (m, 6H), 0.96 (m, 3H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 14.1, 18.7, 22.7, 28.3, 31.0, 78.8, 100.1, 122.8, 128.3, 128.5, 132.4; MS (EI) *m*/*z* 186 (M^+).

1-Phenyl-1-methoxycarboxyl-acetylene: A colorless liquid; ^1H NMR (300 MHz, TMS, $CDCl_3$) δ 7.42 (d, 2H), 7.23 (m, 1H), 7.22 (m, 2H), 3.68 (s, 3H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 50.8, 82.3, 88.7, 122.6, 128.4, 128.5, 132.3; MS (EI) *m*/*z* 160 (M^+).

4-Acetyldiphenylacetylene: A white solid; mp: 98–101 °C (lit. 99–102 °C); ^1H NMR (300 MHz, TMS, $CDCl_3$) δ 7.94 (m, 2H), 7.62 (m, 2H), 7.56 (m, 2H), 7.37 (m, 3H), 2.62 (s, 3H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 26.6, 88.5, 92.7, 122.5, 128.1, 128.3, 128.8, 131.7, 136.1, 197.2; MS (EI) *m*/*z* 220 (M^+).

2-Acetyldiphenylacetylene: A yellowish liquid; ^1H NMR (300 MHz, TMS, $CDCl_3$) δ 7.95 (m, 2H), 7.64 (m, 2H), 7.58 (m, 2H), 7.39 (m, 3H), 2.62 (s, 3H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 26.5, 88.7, 92.7, 122.4, 128.1, 128.3, 128.5, 128.8, 131.7, 136.2, 197.3; MS (EI) *m*/*z* 220 (M^+).

4-Trifluoromethyldiphenylacetylene: A white solid; mp: 103–105 °C (lit. 104–106 °C); ^1H NMR (300 MHz, TMS, $CDCl_3$) δ 7.58 (m, 2H), 7.54 (m, 4H), 7.32 (m, 3H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 87.9, 91.8, 122.6, 125.3, 125.4, 127.1, 128.3, 128.8, 131.7, 131.8; MS (EI) *m*/*z* 246 (M^+).

2-Trifluoromethyldiphenylacetylene: A colorless liquid; ^1H NMR (300 MHz, TMS, $CDCl_3$) δ 7.59 (m, 2H), 7.55 (m, 4H), 7.31 (m, 3H);

^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 87.7, 92.0, 122.5, 125.3, 125.5, 127.3, 128.2, 128.8, 131.7, 131.9; MS (EI) m/z 246 (M^+).

4-Fluorodiphenylacetylene: A white solid; mp: 109–111 °C (lit. 108–111 °C); ^{1}H NMR (300 MHz, TMS, $CDCl_3$) δ 7.47 (d, 2H), 7.44 (d, 2H), 7.22 (m, 2H), 7.20 (m, 1H), 6.94 (d, 2H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 92.9, 115.1, 118.4, 122.7, 128.4, 128.5, 133.9, 162.6; MS (EI) m/z 196 (M^+).

Diphenylacetylene-4-carboxaldehyde: A white solid; mp: 94–95 °C (lit. 96.5 °C); ^{1}H NMR (300 MHz, TMS, $CDCl_3$) δ 9.87 (s, 1H), 7.78 (d, 2H), 7.65 (d, 2H), 7.46 (d, 2H), 7.23 (m, 2H), 7.19 (m, 1H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 92.9, 122.8, 128.4, 128.5, 129.6, 132.3, 136.7, 191.1; MS (EI) m/z 206 (M^+).

Diphenylacetylene-3-carboxaldehyde: A yellowish solid; mp: 47 °C (lit. 48 °C); ^{1}H NMR (300 MHz, TMS, $CDCl_3$) δ 9.88 (s, 1H), 8.01 (s, 1H), 7.74 (m, 2H), 7.46 (d, 2H), 7.41 (m, 1H), 7.22 (m, 2H), 7.20 (m, 1H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 92.9, 122.7, 123.2, 128.4, 128.5, 128.9, 133.4, 136.5, 138.1, 191.0; MS (EI) m/z 206 (M^+).

Diphenylacetylene-2-carboxaldehyde: A yellowish liquid; ^{1}H NMR (300 MHz, TMS, $CDCl_3$) δ 10.21 (s, 1H), 7.77 (d, 1H), 7.64 (d, 1H), 7.50 (m, 1H), 7.46 (d, 2H), 7.39 (m, 1H), 7.21 (m, 2H), 7.19 (m, 1H); ^{13}C NMR (75 MHz, TMS, $CDCl_3$) δ 92.9, 122.7, 128.4, 128.5, 129.0, 132.3, 134.2, 137.0, 191.1; MS (EI) m/z 206 (M^+).

2.5. Typical procedure for catalyst recycling

After the reaction as described above, the mixture was allowed to stand for *ca.* 30 min without stirring at room temperature, and then filtered. The solids were washed with water (5 ml 2×). The catalyst isolated was dried at 80 °C for 24 h in vacuum. The resulting catalyst was ready for further runs: that is, iodobenzene (10 mmol), phenylacetylene (12 mmol), and NEt_3 (15 mmol) in water (10 ml) was added to the recycled catalyst and the mixture was stirred at 80 °C.

3. Results and discussion

We prepared $Pd(OPf)_2$ from palladium carbonate ($PdCO_3$) by stirring it with heptadecafluorooctanesulfonic acid ($R_{f8}SO_3H$) (Scheme 1) [29–31]. To select our catalytic system, we took into account that the palladium catalyst has to be fixed onto a polymer, possibly by chelation. Because recent developments in our group on the polymeric material Amberlyst A-21 provide a new possible candidate for a solid support for immobilization of ytterbium perfluorooctanesulfonate [$Yb(OPf)_3$] catalyst [34], we selected to test the activity of $Pd(OPf)_2$ on Amberlyst A-21. This well-known polymer is a dimethylaminomethyl-grafted polystyrene and thus bears an amine group that can act as a chelatant [35]. The Amberlyst A-21-$Pd(OPf)_2$ can be conveniently prepared by stirring $Pd(OPf)_2$ and Amberlyst A-21 in acetone at elevated temperature (Scheme 2). After filtration and washing, the catalyst was dried and the content of palladium confirmed by weight and analysis.

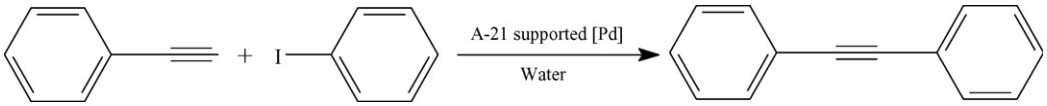
$$2\,R_{f8}SO_3H + PdCO_3 \xrightarrow[H_2O,\ \text{reflux, 4 h}]{} Pd(OSO_2R_{f8})_2\ (76\%)$$

Scheme 1. Preparation of $Pd(OPf)_2$.

The Sonogashira reaction of iodobenzene with phenylacetylene in water at 80 °C was firstly examined (Table 1). In a typical experiment, the catalyst added to a solution of aryl halide in water, then a slight excess of the acetylene (1.2 equiv.) and NEt_3 as a base were added. The reaction mixture was stirred at 80 °C. The course of the reaction was followed by GC. Thus, in the reaction of iodobenzene with phenylacetylene in the presence of Amberlyst A-21-$Pd(OPf)_2$, the coupling product was obtained in 98% GC yield after 1 h. No by-products were observed, diaryldiacetylenes, which are the most common by-products observed in the reaction with a copper salt co-catalyst were not detected by GC.

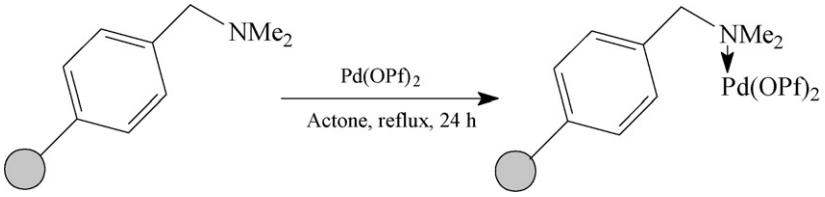
The efforts were directed to the study of recycling of such catalytic system using the reaction of iodobenzene with phenylacetylene. After stirring at 80 °C for 1 h, the reaction mixture was extracted with hexane. The separated supported palladium catalyst could be reused for the next reaction after washing and drying. The reaction of iodobenzene with phenylacetylene under the conditions mentioned above were run for five consecutive cycles respectively, furnishing the corresponding diphenylacetylene with 98, 98, 96, 96, 95% GC yields. No noticeable loss of activity was observed as noted by yield. There were no significant differences between the IR spectra of the initial and recovered fluorous catalyst which may indicate that the supported fluorous palladium catalyst was recovered unaltered after the coupling process had taken place. To better gauge the extent of catalyst recovery, the leaching problem in these catalyst recycling systems was studied. In each iteration, the catalyst from the reaction

Table 1
Sonogashira reaction of iodobenzene and phenylacetylene in water[a]



Entry[b]	[Pd]	Time (h)	Yield (%)[c]
1	$Pd(OPf)_2$	1	98 (94)
1a	$Pd(OPf)_2$	1	98
1b	$Pd(OPf)_2$	1	96
1c	$Pd(OPf)_2$	1	96
1d	$Pd(OPf)_2$	1	95
2	$PdCl_2$	1.5	96 (91)
2a	$PdCl_2$	1.5	83
2b	$PdCl_2$	2	60
3	$Pd(OAc)_2$	2	95 (91)
3a	$Pd(OAc)_2$	3	76
3b	$Pd(OAc)_2$	4	43
4	$PdCO_3$	2	72 (69)
5	$PdCl_2(MeCN)_2$	3	64 (62)

[a] The reaction condition: iodobenzene, 10 mmol; phenylacetylene, 12 mmol; [Pd], 1 mol%; NEt_3, 15 mmol; H_2O, 10 ml; 80 °C.
[b] Entries a, b and c correspond to the 1st, 2nd and 3rd recycling of the catalyst, respectively.
[c] GC yield based on halobenzene. Numbers in parentheses are isolated yields.



Scheme 2. Preparation of Amberlyst A-21-Pd(OPf)$_2$.

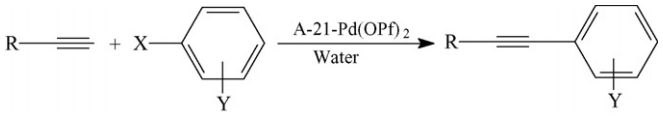
Table 2
Recycling of the catalyst in Sonogashira reaction of iodobenzene and phenylacetylene

Cycle	1	2	3	4	5
Pd leaching (ppm)	3.6	5.1	6.0	8.4	11.6
Conversion (%)	100	100	100	100	100

mixture was filtered off, washed and reused without any precautions against exposure to the air. As is shown in Table 2, palladium leaching from the catalyst is negligible with each cycle. In all of the five cycles, the reaction was completed in 1 h. The results demonstrate the Amberlyst A-21-Pd(OPf)$_2$ catalyst may have practical utility.

We then screened other phosphine-free palladium catalysts supported on Amberlyst A-21 for the reaction of iodobenzene with phenylacetylene in water. It was found that supported $PdCl_2$ and $Pd(OAc)_2$ catalysts had similarly high activity for the reaction with a quantitative conversion to the coupling product at 80 °C over 1.5 and 2 h, respectively. However, an obvious decrease in conversion was observed in the recycle of catalysts. In the case of $PdCO_3$ and $PdCl_2(MeCN)_2$, only a moderate conversion was realized. It is noteworthy that the same coupling reaction was tried using other Sonogashira reaction conditions (such as $PdCl_2(PPh_3)_2$/CuI/Et_3N or $Pd(PPh_3)_4$/CuI/Et_3N, and only trace amounts of the desired product were obtained. From these observations it was revealed that Pd(OPf)$_2$ is the best choice as supported catalyst for our purpose to construct a recyclable catalytic system in water for the Sonogashira reaction. The robustness of the catalyst for recycle use may partly be attributed to that this transition metal perflates is stable in aqueous conditions [36].

Table 3
Sonogashira reactions in the presence of Amberlyst A-21-Pd(OPf)$_2$ in water[a]



Entry	X	Y	R	Time (h)	Yield (%)[b]
1	I	4-CH_3	Ph	1	95 (93)
2	I	2-CH_3	Ph	1	96 (95)
3	I	4-CH_3O	Ph	1.5	93 (90)
4	I	4-NO_2	Ph	0.5	98 (94)
5	I	H	n-C_5H_{11}	2	92 (88)
6	I	H	n-C_6H_{13}	2	90 (87)
7	I	H	CH_3OCO	3.5	83 (81)
8	Br	H	Ph	6	92 (88)
9	Br	4-CH_3CO	Ph	6	95 (92)
10	Br	2-CH_3CO	Ph	6	92 (89)
11	Br	4-NO_2	Ph	5	94 (93)
12	Br	4-CF_3	Ph	5	91 (89)
13	Br	3-CF_3	Ph	5	90 (88)
14	Br	3-CHO	Ph	4.5	95 (91)
15	Br	4-F	Ph	6	89 (85)
16	Br	4-CH_3	Ph	8	84 (82)
17	Br	4-CH_3O	Ph	10	81 (78)
18	Br	2-CH_3O	Ph	10	83 (81)
19	Cl	4-CH_3CO	Ph	16	75 (73)
20	Cl	2-CH_3CO	Ph	16	74 (73)
21	Cl	4-CHO	Ph	18	79 (75)
22	Cl	2-CHO	Ph	18	75 (70)

[a] The reaction condition: halobenzene, 10 mmol; acetylene, 12 mmol; A-21-Pd(OPf)$_2$, 1 mol%; NEt_3, 15 mmol; H_2O, 10 ml; 80 °C.
[b] GC yield based on halobenzene. Numbers in parentheses are isolated yields.

To examine the scope for this coupling reaction, a variety of terminal acetylenes were coupled with different phenyl iodides, bromides and chlorides, and good to excellent results were obtained (Table 3). Phenyl iodides containing electron-donating and electron-withdrawing groups readily coupled with phenylacetylene in rather short time (Table 3, entries 1–4). When the less reactive acetylene, 1-heptyne (Table 3, entry 5) and 1-octyne (Table 3, entry 6) were used, the coupling product was produced efficiently. The reaction of electron-poor alkyne such as propiolic acid methyl ester gave 83% GC yield (Table 3, entry 7). Thus, the coupling reaction was extended to bromobenzene under the above reaction conditions. Although the reaction became slower, bromobenzene gave 92% of diphenylacetylene after 6 h (Table 3, entry 8). The effect of substituents was also examined in this reaction (Table 3, entries 9–18). The less active electron-rich bromotoluene (Table 3, entry 16) and bromoanisole (Table 3, entries 17 and 18) produced a lower yield. Notably, 89% GC yield was obtained in the reaction of *p*-fluorobromobenzne with phenylacetylene (Table 3, entry 15). Steric effects did not influence the yield significantly, for example, in the reaction of *o*- and *p*-bromoacetophenone with phenylacetylene the corresponding coupled products were obtained in 92% and 95% yields, respectively (Table 3, entries 9 and 10). The reaction also showed excellent functional group tolerance as was evident from the successful coupling of *o*- and *p*-chloroacetophenone (Table 3, entries 19 and 20), or *o*- and *p*-chlorobenzaldehyde with phenylacetylene (Table 3, entries 21 and 22).

4. Conclusion

In conclusion, Amberlyst A-21-Pd(OPf)$_2$ was found to be an interesting and highly efficient catalyst for the Sonogashira cross-coupling reactions. The reactions can be carried out under ligand- and copper-free conditions in an air atmosphere. The catalyst performed is easily separated and can be reused several times without a noticeable change in activity. Further investigations of more favourable strategy and conditions for recycle of Pd(OPf)$_2$, as well as synthetic applications, are currently in progress and will be reported in due course.

Acknowledgments

We thank the Nature and Science Foundation of Jiangsu Province (BK2007592) and the National Defense Committee of Science and Technology of China (40406020301) for financial support.

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