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A Palladium/Perfluoroalkylated Pyridine Catalyst for Sonogashira Reaction of Aryl Bromides and Chlorides in a Fluorous Biphasic System

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Palladium perfluorooctanesulfonate [$Pd(OPf)_2$] catalyses the highly efficient Sonogashira reaction of aryl bromides and chlorides in the presence of a catalytic amount of perfluoroalkylated pyridine as a ligand in a fluorous biphasic system (FBS) composed of toluene and perfluorodecalin. The reaction can be performed under phosphane-, copper- and DMF-free conditions in an air atmosphere. By simple separation of the fluorous phase containing palladium/perfluoroalkylated pyridine catalyst, the reaction can be repeated several times.

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 cocatalyst.[6] However, these solvents have high boiling points, which make them difficult to be removed after completion of the reaction. Furthermore, oxidative homocoupling of acetylenes (Glaser-type reaction) cannot be avoided in copper-mediated reactions,[7] in which diaryldiacetylene byproducts 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 aqueous media,[10] reaction in microemulsion,[11] polymer-[12]and zeolite-supported[13] catalytic reaction system, phase-transfer catalytic reaction conditions,[14] various copper-free conditions,[8,9,15–17] use of a variety of promoters,[18] such as Zn, Mg and Sn and the use of microwave irradiation.[19] The use of a fluorous biphasic system (FBS) as a phase-separation and catalyst immobilization technique has also been developed for the catalytic coupling reaction.[20] Transition-metal-catalyzed reactions in an FBS have become one of the most important methods for facile catalyst separation from the reaction mixture and recycling of the catalyst since FBS was introduced by Horváth and Rábai in 1994.[21] Traditional palladium-catalyzed Sonogashira reactions often require relatively large amounts of catalysts, which have to be removed from the reaction product. Perfluoro-labelled Pd complexes offer a solution to this problem since the perfluoro-labelled catalysts are soluble in fluorous solvents and can be separated from the organic product very easily by liquid–liquid extractions.[22] However, the previous studies of the Sonogashira reaction under fluorous biphasic conditions were related to phosphane palladium catalysts.[22] It is known that catalysts containing phosphane ligands are unstable.[22,23] Therefore, the development of phosphane-free and recyclable palladium catalysts having high activity and good stability is a topic of enormous importance. In the reported copper-free palladium catalyst systems, in order to achieve the satisfactory yield either aryl iodides or aryl bromides bearing electron-withdrawing substituents, were employed.[15] Quire recently, Hua reported the Sonogashira reaction of electron-rich aryl bromides with terminal alkynes using $PdCl_2(PPh_3)_2$ as a catalyst and DMF as a solvent.[16] Hell and coworkers prepared a Pd/MgLa mixed oxide as an efficient catalyst for the Sonogashira reaction of activated chlorides in DMF.[17]

As part of our studies to explore the utility of transition metal perflates catalyzed reactions in fluorous solvents,[24] we decided to investigate the application of a novel fluorous palladium catalyst, palladium(II) perfluorooctanesulfonate [$Pd(OSO_2R_{f8})_2$, $R_{f8} = (CF_2)_7CF_3$, $Pd(OPf)_2$] with a perfluoroalkylated pyridine ligand **1** [pyridine-3-carbaldehyde bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)acetal], for Sonogashira reaction of bromides and chlorides in FBS. The coupling process can be performed under copper- and DMF-free conditions in an air atmosphere. The fluorous palladium catalyst and perfluoroalkylated

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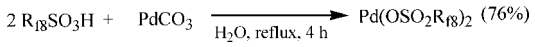
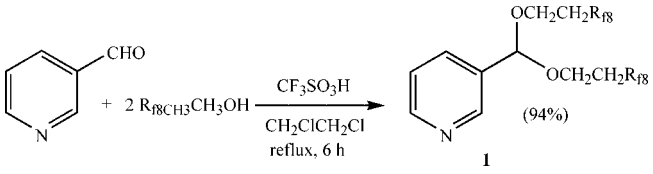
pyridine are stable and easy to prepare. The fluorous phase containing the active palladium species is easily separated and can be reused several times without a significant loss of catalytic activity.

Results and Discussion

We prepared $Pd(OPf)_2$ from palladium carbonate ($PdCO_3$) by stirring it with heptadecafluorooctanesulfonic acid ($R_{f8}SO_3H$, PfOH) (Scheme 1), and perfluorinated pyridine **1** according the method described by Uemura (Scheme 2).[25] $Pd(OPf)_2$ and **1** were very soluble in perfluorodecalin ($C_{10}F_{18}$), perfluoromethylcyclohexane ($CF_3C_6F_{11}$) and perfluorotoluene ($CF_3C_6F_5$). Compound **1** also showed significant solubility in ether, THF, $CHCl_3$ and CH_2Cl_2. However, **1** always appeared to be less soluble in toluene, hexane and octane. $Pd(OPf)_2$ showed almost no solubility in traditional organic solvents such as methanol, CH_3CN, CH_2Cl_2 and toluene.



Scheme 1.



Scheme 2.

Quantitative data on fluorous phase affinities were sought. The perfluorodecalin/toluene partition coefficients were determined by GC or ICP according to a previously reported method.[26,27] These reflect *relative* as opposed to *absolute* solubilities and are summarized in Table 1. In pyridine ligand, two R_{f8} pony tails give high fluorous phase affinities (coefficients 99.8:0.2), allowing essentially quantitative recovery. $Pd(OPf)_2$ was retained in the fluorous phase quantitatively, with the coefficients being >99.9:<0.1.

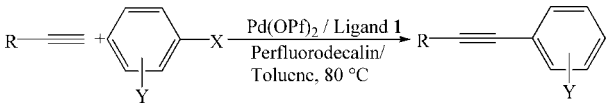
Table 1. Partition Coefficients (24 °C).

Analyte	Perfluorodecalin/toluene
1	99.8:0.2[a]
$Pd(OPf)_2$	>99.9:<0.1[b]

[a] Detected by GC. [b] Detected by ICP.

The Sonogashira reaction of bromobenzene with phenylacetylene in an FBS composed of toluene and perfluorodecalin ($C_{10}F_{18}$) at 80 °C was firstly examined. In a typical experiment, the catalyst and ligand were added to a mixture of perfluorodecalin and toluene, then a slight excess of the acetylene (1.2 equiv.) and a solution of the aryl halide in toluene and NEt_3 was added. The reaction mixture was stirred at 80 °C. The course of the reaction was followed by GC. Thus, in the reaction of bromobenzene with phenylacetylene in the presence of $Pd(OPf)_2$ and ligand **1**, the coupling product was obtained in 96% GC yield after 4 h (Table 2, Entry 1). No byproducts were observed, diaryldiacetylenes, which are the most common byproducts that are observed in the reaction with a copper salt cocatalyst were not detected by GC. Compared with the reported copper-free methods, our procedure produces better yields in shorter reaction times.[6,15–17]

Table 2. Sonogashira reaction of aryl bromides and chlorides in FBS.[a]



Entry	X	Y	R	Time [h]	Yield [%][b]
1	Br	H	Ph	4	96 (92)
2	Br	H	n-C_5H_{11}	5	95
3	Br	H	n-C_6H_{13}	5	92 (89)
4	Br	H	CH_3OCO	6	84
5	Br	4-CH_3CO	Ph	2	97 (94)
6	Br	2-CH_3CO	Ph	2	94
7	Br	4-NO_2	Ph	2	97
8	Br	4-CF_3	Ph	2	96
9	Br	3-CF_3	Ph	3	94
10	Br	3-CHO	Ph	2.5	95 (91)
11	Br	4-F	Ph	3	91
12	Br	4-CH_3	Ph	8	89
13	Br	4-CH_3O	Ph	10	83 (80)
14	Br	2-CH_3O	Ph	10	85
15	Cl	H	Ph	16	68
16	Cl	H	Ph	18	70[c]
17	Cl	4-CH_3CO	Ph	12	85 (83)
18	Cl	3-CH_3CO	Ph	12	79
19	Cl	2-CH_3CO	Ph	12	84
20	Cl	4-CHO	Ph	12	88 (84)
21	Cl	3-CHO	Ph	12	81 (80)
22	Cl	2-CHO	Ph	12	84
23	Cl	4-CF_3	Ph	12	85
24	Cl	4-NO_2	Ph	10	87
25	Cl	2-NO_2	Ph	10	85
26	Cl	4-CH_3	Ph	32	55 (50)
27	Cl	4-CH_3O	Ph	32	41

[a] Reaction conditions: halobenzene (10 mmol), acetylene (12 mmol), ligand **1** (0.2 mmol), $Pd(OPf)_2$ (0.05 mmol), fluorous solvent (4 mL), toluene (2 mL), NEt_3 (15 mmol), 80 °C. [b] GC yield based on halobenzene. Numbers in parentheses are isolated yields. [c] 0.06 mmol of $Pd(OPf)_2$ and 0.24 mmol of ligand **1** were used.

The efforts were directed to the study of recycling such a catalytic system using the reaction of bromobenzene with phenylacetylene. We found that, upon heating at 80 °C, the organic phase (upper toluene layer containing bromobenzene and NEt_3) is miscible with the fluorous phase [bottom perfluorodecalin layer containing $Pd(OPf)_2$ and ligand **1**] and the coupling reaction became a monophasic reaction. After completion of the reaction, the toluene (upper phase) was colourless, suggesting that palladium-**1** complex could dissolve in the fluorous phase. In addition, there is no formation of palladium black in the fluorous phase. The separated fluorous phase could be reused for the next reaction without any specific treatment and the work up procedure of recycling was accomplished by simple phase separation.

In order to analyze and quantify the catalyst recovery, the reaction rates (= activity) at cycles 1, 3 and 5 were compared. The representative results are shown in Figure 1. It was found that there was almost no difference in the formation rate of the Sonogashira product at cycles 1, 3 and 5 within a 4 h reaction time, which indicated that there was not only no loss of the catalyst but also no depression of catalytic activity during the recycling. Thus, it can be deduced that >99% of the catalyst should still remain in the fluorous phase even after the fourth cycle. It is important to study the leaching problem in these catalyst recycling systems. On the basis of ^{19}F NMR spectroscopic data, no loss of $Pd(OPf)_2$ to the organic phases can be detected. Only trace amounts of ligand **1** (<0.1%) and perfluorodecalin were found by GC–MS in separated organic layer. In fact, we also investigated the exact amount of palladium and ligand **1** in the recovered fluorous phase by ICP and GC, finding that >99.7% of palladium and 99.8% of ligand **1** were retained in perfluorodecalin. This result suggests the robustness of the catalytic system for recycled use.

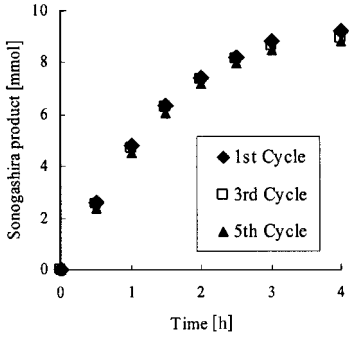


Figure 1. Sonogshira reaction of bromobenzene with phenylacetylene in FBS at different cycles.

We then screened other phosphane-free palladium catalysts for the coupling of bromobenzene with phenylacetylene under the reaction conditions of $Pd(OPf)_2$ in the presence of ligand **1** in FBS and found that $Pd(OAc)_2$, $PdCl_2$, $PdCO_3$ and $PdCl_2(MeCN)_2$ showed low catalytic activity to afford diphenylacetylene in 46, 35, 10 and 12% GC yields, respectively. When the less reactive acetylene, 1-heptyne (Table 2, Entry 2) and 1-octyne (Table 2, Entry 3) were used, the coupling product was produced efficiently. The reaction of an electron-poor alkyne such as methyl propiolate gave 84% GC yield (Table 2, Entry 4).

Thus, the coupling reaction catalyzed by $Pd(OPf)_2$–**1** complex was extended to chlorobenzene, under the above reaction conditions. Although the reaction became slower, chlorobenzene gave 68% of diphenylacetylene after 16 h (Table 2, Entry 15). Increasing catalyst loading did not improve the yield significantly (Table 2, Entry 16). The effect of substituents was also examined in this reaction. The results are summarized in Table 2. Aryl bromides (Table 2, Entries 5–14) and electron deficient aryl chlorides (Table 2, Entries 17–25) with aryl alkynes gave the corresponding aryl-substituted acetylenes in good-to-excellent yields. Notably, 91% GC yield was obtained in the reaction of *p*-fluorobromobenzene with phenylacetylene (Table 2, Entry 11). The less active electron-rich *p*-methylbromobenzene (Table 2, Entry 12) and *p*-methoxybromobenzene (Table 2, Entries 13–14) produced lower yields. The aryl chlorides with electron donating groups such as *p*-methyl (Table 2, Entry 26) and *p*-methoxy (Table 2, Entry 27) afforded the coupling products in 55 and 41% yields, respectively, after 32 h. Steric effects did not influence the yield significantly; for example, in the reaction of *o*-bromo- (Table 2, Entry 6) or *o*-chloroacetophenone (Table 2, Entry 19) with phenylacetylene, the corresponding coupled products were obtained in 94 and 84% yields, respectively.

Conclusions

The fluorous biphasic system of a combination of $Pd(OPf)_2$ and perfluoroalkylated pyridine **1** showed a high catalytic activity for Sonogashira coupling reaction of aryl bomides and activated chlorides. The advantages of our catalytic system over others are: the reaction can be performed under phosphane-, copper- and DMF- free conditions in an air atmosphere (1), the fluorous palladium catalyst and perfluoroalkylated pyridine are easily accessible and stable to atmosphere (2), the fluorous phase containing palladium/perfluoroalkylated pyridine catalyst is easily separated and can be reused several times without a significant loss of yield of reaction (3).

Experimental Section

$Pd(OPf)_2$: Heptadecafluorooctanesulfonic acid ($R_{f8}SO_3H$) was commercially obtained from ARCOS Co. 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 heated at reflux with stirring for 4 h. The resulting gelatin-like solid was collected, washed and dried at 160 °C for 24 h in vacuo 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. ^{19}F NMR (500 MHz, $CF_3C_6H_5$): δ = –126.2, –121.2, –114.2, –81.4. IR (KBr): $\tilde{\nu}$ = 1230 (CF_3), 1148 (CF_2), 1080 (SO_2), 1061 (SO_2), 752 (S–O), 640 (C–S) cm^{-1}. $C_{16}F_{34}O_6PdS_2$ (1104.6): calcd. C 17.38, Pd 9.63; found C 17.29, Pd 9.61.

Typical Procedure for Sonogashira Reaction in an FBS: To a mixture of $Pd(OPf)_2$ (0.055 g, 0.05 mmol) and toluene (2 mL) in a glass tube was added ligand **1** (0.204 mg, 0.2 mmol) under vigorous stirring. After a few minutes, perfluorodecalin (4 mL), bromobenzene (1.58 g, 10 mmol) and NEt_3 (2.1 mL, 15 mmol) were introduced into the glass tube, and then phenylacetylene (1.24 g, 12 mmol) in toluene (2 mL) was added. After stirring at 80 °C for 4 h, the mixture was cooled with an ice bath. Then, the fluorous layer on the bottom was separated for the next reaction. The reaction mixture (organic phase) was diluted with water (5 mL) and extracted with hexane (2 × 10 mL). The combined organic extracts were dried with Na_2SO_4 and *p*-xylene (1.06 g, 10 mmol) was added as an 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 (cyclohexane) to give diphenylacetylene as a white solid (1.67 g, 92%).

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