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Pd-catalyzed desulfonylative homocoupling of arenesulfonyl chlorides in the presence of hexamethyldisilane forming biaryls

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Abstract—Arenesulfonyl chlorides undergo desulfonylative homo-coupling upon heating with hexamethyldisilane in the presence of Pd_2(dibenzylideneacetone)$_3$·$CHCl_3$ as a precatalyst to afford biaryls. Diaryl sulfides are occasionally formed as byproducts.

Transition metal-catalyzed homocoupling of organic halides have been well studied by using various reducing agents.[1] The reaction of organic halides with disilanes, potential reducing agents, however, does not furnish homocoupling, but proceeds to a different direction affording corresponding organosilanes with concomitant formation of halosilanes.[2] Aroyl chlorides are also known to react with hexamethyldisilane, affording aroylsilanes and/or arylsilanes via decarbonylative silylation.[3] In the reactions of aroyl chlorides with hexamethyldisilane, formation of homocoupling or decarbonylative homocoupling products such as benzil, benzophenone, and/or biphenyl derivatives has never been observed. On the other hand, transition-metal-catalyzed reactions of sulfonyl chlorides involving desulfonylation, triggered by the pioneering work by Kamigata, Kasahara and Miura, have been revisited in exploration of further synthetic applications of the readily available and highly reactive sulfonyl chlorides.[4]

While we were working on the chemistry of disilanes with various acid chlorides, inclusive of sulfonyl chlorides, we came across desulfonylative homocoupling of arenesulfonyl chlorides, leading to biaryl formation, which will be reported in this letter.[5]

$$\underset{\mathbf{1}}{2ArSO_2Cl} + Me_3SiSiMe_3 \xrightarrow{\text{Pd cat.}} \underset{\mathbf{2}}{Ar\text{-}Ar} + 2SO_2 + 2SiClMe_3$$

Table 1 summarizes trial experiments under different conditions using several palladium complexes for the reaction of *p*-fluorobenzenesulfonyl chloride (**1a**) forming 4,4′-difluorobiphenyl (**2a**), occasionally along with di(4-fluorophenyl) sulfide (**3a**) and other byproducts.

As for the catalytic performance, $Pd_2(dba)_3·CHCl_3$ appears to be the catalyst of choice. When the reaction was effected by $PdCl_2(PhCN)_2$ (entries 4 and 8), a large quantity of **3a** (vide infra) was formed. Note that these reactions catalyzed by $Pd_2(dba)_3·CHCl_3$ gave *p*-chlorofluorobenzene as a byproduct due to the simple desulfonylation reaction.[6] Palladium catalyst systems having phosphorus ligands were also less selective and/or less active, in particular when PPh_3 was used (entries 5, 6, 9 and 10). However, the use of PPh_3 suppressed the extensive formation of **3a** at the expense of the activity (entries 8 and 9). The formation of **3a** was also suppressed further by lowering the temperature in the presence of $P(OEt)_3$ (entry 10). The solvent effect was also briefly examined under otherwise the same conditions as in entry 10. Ethers and chlorobenzene furnished nearly the same results (entries 11–13). In *N*-methylpyrrolidone, the reaction was slow (entry 14). In octane, the catalyst in situ generated by mixing $PdCl_2(PhCN)_2$ and $P(OEt)_3$ deposited to form an insoluble pale yellow oily paste material and the reaction did not proceed at all. Other metal species like palladium black, $Ni(cod)_2$ and $NiCl_2(PPh_3)_2$ were totally inactive. The experiments of entries 1–3 reveal that the reaction works better when an excess of disilane was used although the stoichiometry requires a **1a**:disilane ratio of 2:1; thus, the use of only 0.5 equiv of disilane reduced the yield of **2a** (entry 2) as compared with entry 1. However, the use

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Keywords: Homogeneous catalysis; Palladium; Sulfonyl chloride; Desulfonylation.

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Table 1. Reaction of *p*-fluorobenzenesulfonyl chloride with hexamethyldisilane[a]

Entry	Precatalyst (mol %)	Ligand (equiv/Pd)	Si_2Me_6 (equiv/**1a**)	Temp. (°C)	Time (h)	**1a** conv (%)	**2a** yield (%)	**3a** yield (%)	Ar_2SO_2 yield (%)	Ar_2S_2 yield (%)	ArCl yield (%)
1	$Pd_2(dba)_3 \cdot CHCl_3$ (3)	—	1	140	3	100	86	6	Trace	1	nd
2	$Pd_2(dba)_3 \cdot CHCl_3$ (3)	—	0.5	140	3	97	51	nd	nd	nd	nd
3	$Pd_2(dba)_3 \cdot CHCl_3$ (3)	—	4	140	3	100	83	nd	nd	nd	nd
4	$PdCl_2(PhCN)_2$ (3)	—	1	140	3	82	22	33	Trace	Trace	10
5	$Pd_2(dba)_3 \cdot CHCl_3$ (3)	$P(OEt)_3$ (2)	1	140	3	100	72	16	1	Trace	nd
6	$Pd_2(dba)_3 \cdot CHCl_3$ (3)	PPh_3 (2)	1	140	3	57	49	3	2	Trace	nd
7	$Pd(PPh_3)_4$ (3)	—	1	140	3	40	0	0	0	4	0
8	$PdCl_2(PhCN)_2$ (5)	—	1	140	3	100	32	40	1	Trace	15
9	$PdCl_2(PhCN)_2$ (5)	PPh_3 (2)	1	140	3	86	55	8	4	Trace	nd
10[b]	$PdCl_2(PhCN)_2$ (5)	$P(OEt)_3$ (2)	1	110	24	95	82	8	Trace	1	nd
11[c]	$PdCl_2(PhCN)_2$ (5)	$P(OEt)_3$ (2)	1	110	24	84	69	4	Trace	0	0
12[d]	$PdCl_2(PhCN)_2$ (5)	$P(OEt)_3$ (2)	1	110	24	100	80	9	Trace	1	0
13[e]	$PdCl_2(PhCN)_2$ (5)	$P(OEt)_3$ (2)	1	110	24	96	83	10	1	0	0
14[f]	$PdCl_2(PhCN)_2$ (5)	$P(OEt)_3$ (2)	1	110	24	49	37	5	1	1	0

[a] Unless otherwise specified, the reaction was carried out using **1a** (1.0 mmol), hexamethyldisilane (1.0 mmol), and ethylbenzene (1.0 mL) at 140 °C for 3 h. The yields of **2a** and other byproducts were determined by ^{19}F NMR spectroscopy.

[b] The reaction was run in toluene.

[c] The reaction was run in cyclopentyl methyl ether.

[d] The reaction was run in anisole.

[e] The reaction was run in chlorobenzene.

[f] The reaction was run in *N*-methylpyrrolidone.

of a large excess did not improve the yield of **2a** further (entry 3). Besides hexamethyldisilane, we attempted to use other disilanes such as 1,1,2,2-tetramethyldisilane, 1,1,2,2-tetramethyl-1,2-dichlorodisilane and hexachlorodisilane. However, none of these induced the coupling reaction at all.

After these initial trials, 4,4′-dimethylbiphenyl (**2b**) was synthesized by the following standard procedure: A mixture of $Pd_2(dba)_3 \cdot CHCl_3$ (15.5 mg, 1.5×10^{-2} mmol), *p*-toluenesulfonyl chloride (**1b**) (190.2 mg, 1.0 mmol), ethylbenzene (1.0 mL), hexamethyldisilane (0.125 mL, 1.0 mmol) and tetradecane (19.7 mg, internal standard for GC analysis) placed in a 20 mL Schlenk tube was stirred at 140 °C for 3 h. After GC analysis of the resulting mixture, volatiles were removed under a reduced pressure. The residue was subjected to silica-gel column chromatography (hexane/Et_2O = 1:1) to afford **2b** as a colorless solid. (71.0 mg, 0.39 mmol, 78% yield).

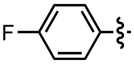
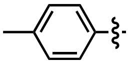
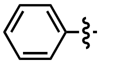
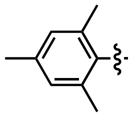
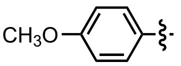
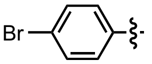
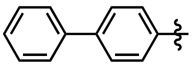
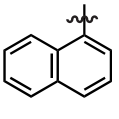
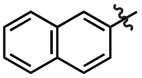
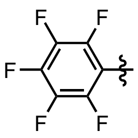
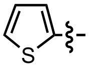
The standard procedure works well with other aromatic sulfonyl chlorides as summarized in Table 2. The electronic nature of the substituent on the aromatic ring does not affect the reactivity significantly. Although palladium complexes can promote dehalogenative silylation,[3] the reaction of *p*-bromobenzenesulfonyl chloride (entry 6) formed only a trace of the corresponding silylated biphenyl (*m*/*z* 298, M^+). Sulfonyl chlorides having sterically demanding substituents react more slowly (entries 4 and 8). In these reactions, the catalyst appears to be deactivated rapidly as visualized by the formation of metallic materials. Accordingly, the yield is not significantly improved by extension of the reaction time as far as the phosphorus-ligand-free catalyst is concerned. Perfluorobenzenesulfonyl chloride, which is envisioned to react via stable perfluorophenylpalladium intermediate[7] (vide infra), also reacted normally to afford the corresponding biphenyl (entry 10). On the other hand, aliphatic sulfonyl chloride does not afford the corresponding desulfonylated homo-dimer; the reaction of octanesulfonyl chloride under the same conditions revealed 9% conversion of the sulfonyl chloride forming 1-octene (via desulfonylation and β-hydrogen elimination) in 4%.

The desulfonylative homocoupling is envisioned to proceed via the sequence of events depicted in Scheme 1, which comprises oxidative addition of S–Cl bond of an arenesulfonyl chloride giving **4** (path a), desulfonylation forming arylpalladium species **5** (path b), its disproportionation to diarylpalladium and dichloropalladium species **6** and **7** (path c), and reductive elimination giving biaryl **2** and palladium(0) species (path d).

The oxidative addition of sulfonyl chloride has been postulated in various reactions starting with sulfonyl chlorides. However, arenesulfonyl-metal species isolated through oxidative addition of arenesulfonyl chlorides are known only for iridium[6,8] and platinum.[9,10] For palladium, not only S–Cl but also Ar–S bond cleavage has been considered to proceed in the oxidative addition.[4l,m,n] We have found that the oxidative addition of benzenesulfonyl chloride with $Pd(PPh_3)_4$ proceeds rapidly at room temperature to allow isolation of $(PhSO_2)PdCl(PPh_3)_2$ (**4**: Ar=Ph) in 10 min in a near quantitative yield.[11,12]

The sulfonylpalladium complex does not undergo desulfonylation at room temperature nor at 60 °C (monitored by ^{31}P NMR spectroscopy for 2 h). However, it does extrude SO_2 at 90 °C as evidenced by the following experiment. Thus, the starting sulfonyl complex, when dissolved in toluene-d_8, displayed a ^{31}P NMR signal at 23.85 ppm, which shifted to 23.68 ppm upon heating to 90 °C. This signal was diminishing over 90 min at

Table 2. Reaction of sulfonyl chlorides with hexamethyldisilane[a]

Entry	Sulfonyl chloride **1**, Ar=	GC yield of biaryl **2** (%)[b]
1	**1a** 	86[c]
2	**1b** 	83 (78)
3	**1c** 	79
4	**1d** 	26[d]
5	**1e** 	79
6	**1f** 	74
7	**1g** 	63
8	**1h** 	41[d]
9	**1i** 	59 (53)
10	**1j** 	61
11	**1k** 	65

[a] Unless otherwise specified, the reaction was carried out using **1** (1.0 mmol), hexamethyldisilane (1.0 mmol), and ethylbenzene (1.0 mL) in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (3 mol %) at 140 °C for 3 h.

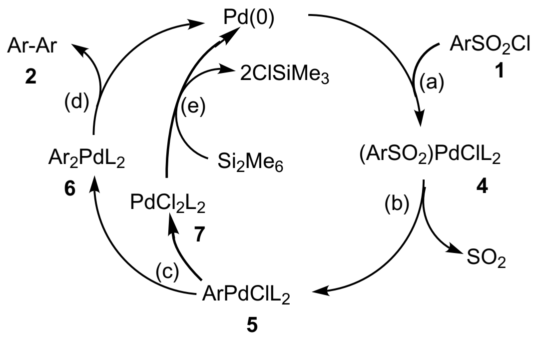
[b] The figures in parentheses are isolated yield.

[c] The yield was determined by ^{19}F NMR spectroscopy.

[d] The yield was determined by ^{1}H NMR spectroscopy.

the temperature to develop a distinctly separated new signal at 24.31 ppm, which shifted, upon cooling to room temperature, to 24.10 ppm, assignable to $PhPdCl(PPh_3)_2$ (**5**: Ar=Ph).[13]

As for path c, the disproportionation forming diaryl- and dichloropalladium species **6** and **7**, we do not have any conclusive evidence. However, the process has been proposed to proceed in homocoupling of organic halides,[14] and relevant mechanistic study on the organic group exchange between two palladium species has also been abundantly documented.[15] In view of these precedents, it is reasonable to assume the disproportionation being involved in the present catalysis. The resulting diarylpalladium species then undergoes reductive elimination affording the biaryl product and the active species is regenerated. Dichloropalladium counterpart is also converted to the active species by reduction with hexamethyldisilane, which is evidenced by the quantitative formation of Me_3SiCl (^{29}Si NMR −30.1 ppm, $CDCl_3$) upon treatment of $PdCl_2(PhCN)_2$ with hexamethyldisilane.



Scheme 1. A plausible mechanism.

To reinforce the mechanistic proposal, we examined the reaction of $(PhSO_2)PdCl(PPh_3)_2$ with hexamethyldisilane (10 equiv relative to Pd complex) at 140 °C for 1 h. Albeit in a low yield (6%), biphenyl was indeed detected by GC analysis, along with trimethylsilylbenzene and diphenyl sulfide. The treatment of $C_6F_5PdCl(PPh_3)_2$ with hexamethyldisilane (1.0 equiv relative to the Pd complex) at 110 °C for 2 h formed only trimethylsilylpentafluorobenzene in 11% yield while another similar reaction run at 140 °C gave decafluorobiphenyl in 13%. Although the yields are low, these results support the disproportionation takes place at a rather high temperature, for example, 140 °C. At 110 °C, however, disilane appears to react with C_6F_5–Pd species before the disproportionation has taken place.

Somewhat puzzling observation that merits further consideration is the formation of sulfide byproduct **3**, encountered, in particular, when the reaction was effected in the presence of $PdCl_2(PhCN)_2$. ^{1}H NMR analysis of the reaction mixture of $PdCl_2(PhCN)_2$-catalyzed reaction (entry 8, Table 1) has revealed the formation of Me_3SiCl (0.762 mmol), the quantity of which agrees fairly well with the total quantity of **2a** and **3a** (0.72 mmol). The analysis also showed the presence of $(Me_3Si)_2O$ (0.41 mmol). If we assume that **3a** has come from reduction of an SO_2 unit, the formation of $(Me_3Si)_2O$ is reasonable although oxygen balance is not satisfactory. Sulfones are occasionally found to be formed as a byproduct in the present catalysis. However, attempted reduction (140 °C, 13 h) of diphenyl sulfone with hexamethyldisilane (2 equiv) in either the presence or absence of $PdCl_2(PhCN)_2$ failed, although the reaction in the presence of $PdCl_2(PPh_3)_2$ slightly formed diphenyl sulfide (6%). At the moment, we are unable to identify the origin of the sulfide formation. Not only sulfone but also other intermediate species having an SO_2 unit may participate in the formation of sulfide.

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