ChemComm

Diphenylphosphinophenolate: a ligand for the palladium-catalysed silylation of aryl halides activating simultaneously both palladium and silicon

Eiji Shirakawa,*[a] Takuya Kurahashi,[b] Hiroto Yoshida[b] and Tamejiro Hiyama*[b]

[a] *Graduate School of Materials Science, Japan Advanced Institute of Science and Technology, Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan. E-mail: shira@jaist.ac.jp*

[b] *Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto, 606-8501, Japan. E-mail: thiyama@NPC05.kuic.kyoto-u.ac.jp*

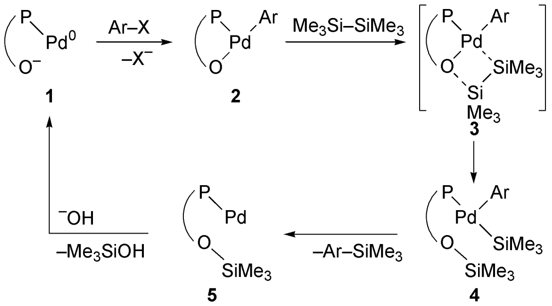
Received (in Cambridge, UK) 31st July 2000, Accepted 25th August 2000
First published as an Advance Article on the web 18th September 2000

Diphenylphosphinophenolate was found to be an effective ligand for the palladium-catalysed silylation of aryl halides, activating not only palladium but also silicon of a disilane, where aryl bromides and iodides having such substituents as methyl, methoxy, amino, ethoxycarbonyl, trifluoromethyl, formyl or phenyl are applicable to the reaction with hexamethyldisilane to give the corresponding trimethylsilylarenes.

The transition metal-catalysed silylation of aryl halides with disilanes should be one of the most straightforward and economical ways to arylsilanes,[1,2] which are versatile synthetic precursors especially for the palladium-catalysed cross-coupling reaction with organic electrophiles.[3] Although there have been many reports on the palladium-catalysed silylation using triphenylphosphine as a ligand,[1] the reaction requires drastic conditions to obtain arylsilanes in acceptable yields. Low reaction rate is ascribed to the low reactivity of a disilane toward a Pd(II) complex that is generated by oxidative addition of an aryl halide to a Pd(0) complex. In order to accelerate the rate-determining transmetalation step, two routes are possible in terms of electronic balance: one is to make the palladium(II) more electron-deficient and the other is to increase the electron density of the nucleophile. Ligands play significant roles for the former but not for the latter.

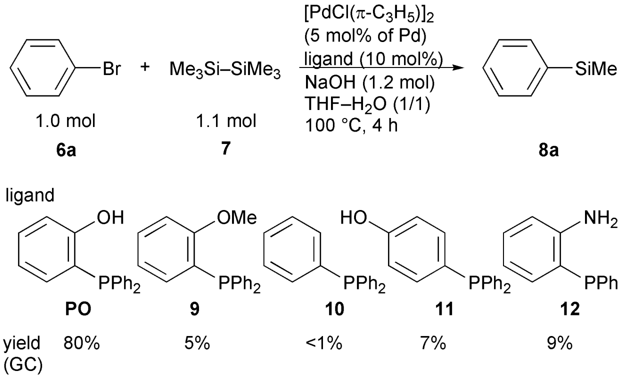
We envisaged that a phosphine having a phenolate group should not only serve as a bidentate ligand for palladium but also activate directly an incoming silyl nucleophile. Thus, in the palladium-catalysed silylation of aryl halides with disilanes, we considered that the phenolate anion in the ligand could coordinate to the silicon atom of a disilane and enhance its nucleophilicity in the transmetalation step in the catalytic cycle that we assumed to be working (Scheme 1). Here we report that a palladium complex coordinated by 2-(diphenylphosphino)-phenolate (PO)[4] efficiently catalyses the silylation of aryl halides using hexamethyldisilane.

We first compared the PO ligand in efficiency with other phosphines in the palladium-catalysed reaction of bromobenzene (**6a**) with hexamethyldisilane (**7**) (Scheme 2). Thus, **6a** (1.0 mol) was treated with **7** (1.1 mol) in the presence of a 1 : 2 mixture of $[PdCl(\pi\text{-}C_3H_5)]_2$–PO (5 mol% of Pd) and sodium hydroxide (1.2 mol) in a 1 : 1 mixture of THF and H_2O at 100 °C for 4 h to give trimethylsilylbenzene (**8a**) in 80% yield. Reduction of the amount of sodium hydroxide (0.1 mol, 9%; 0 mol, 0%), masking the hydroxy group of PO as **9**, or use of triphenylphosphine (**10**) in lieu of PO decisively reduced the yield, implying the significance of the phenolate moiety, whereas inefficiency of *p*-hydroxy derivative **11** revealed the importance of the *o*-phenolate anionic functionality. Aminophosphine **12** also was ineffective. These results clearly demonstrate that the catalytic cycle depicted in Scheme 1 is working smoothly with the Pd–PO catalyst.



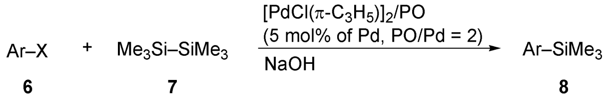
The oxygen atom may coordinate on palladium in complex **1**, **4** and **5**.

Scheme 1



Scheme 2

The applicability of the catalytic system was proved by trimethylsilylation of various aryl bromides and iodides (Scheme 3 and Table 1). Trimethylsilylbenzene and 4-trimethylsilyltoluene were obtained in high yields from bromobenzene and 4-bromotoluene, respectively (Table 1, entries 1 and 2). Although an electron-donating substituent like methoxy or amino on the aryl bromide decreased the yield, as was the case with a triphenylphosphine ligand,[1a] use of a 1 : 1 mixture of toluene and H_2O as the solvent in combination with 10 mol% tetrabutylammonium bromide afforded the corresponding arylsilanes in yields over 90% (entries 3–6). The toluene/H_2O/Bu_4NBr system was effective also for the silylation of an aryl bromide having an ester moiety, preventing ester hydrolysis during the reaction (entries 7 and 8). Other aryl bromides with various substituents gave the corresponding arylsilanes in good yields (entries 9–12). Dibromo- or tribromobenzene also reacted smoothly to give bis(trimethylsilyl)- or tris(trimethylsilyl)benzene, respectively (entries 13 and 14). Aryl iodides also were found to be good substrates for this silylation reaction (entries 15–17). This is noteworthy, as iodobenzene is recorded not to react at all with a Pd–Ph_3P catalyst, the low efficiency of



Scheme 3

DOI: 10.1039/b006165o

Table 1 Palladium-catalysed silylation of aryl halides with hexamethyldisilane

Entry	Aryl halide **6**	Conditions[a]	Amount of **8** (mol)	Yield[b] (%)
1[c]	PhBr	A	1.1	88
2	$\text{4-MeC}_6\text{H}_4\text{Br}$	A	2.5	82
3	$\text{4-MeOC}_6\text{H}_4\text{Br}$	A	2.5	73
4	$\text{4-MeOC}_6\text{H}_4\text{Br}$	B	2.5	91
5	$\text{4-NH}_2\text{C}_6\text{H}_4\text{Br}$	A	2.5	50
6	$\text{4-NH}_2\text{C}_6\text{H}_4\text{Br}$	B	2.5	92
7	$\text{4-EtOCOC}_6\text{H}_4\text{Br}$	A	2.5	23
8	$\text{4-EtOCOC}_6\text{H}_4\text{Br}$	B	2.5	87
9	$\text{4-CF}_3\text{C}_6\text{H}_4\text{Br}$	A	2.5	70
10	$\text{4-HCOC}_6\text{H}_4\text{Br}$	A	1.1	65
11	$\text{4-PhC}_6\text{H}_4\text{Br}$	A	2.5	80
12	2-NaphthBr	A	2.5	64
13	$\text{C}_6\text{H}_4\text{Br}_2\text{-1,4}$	A	5.0	81
14	$\text{C}_6\text{H}_3\text{Br}_3\text{-1,3,5}$	A	7.5	81
15	PhI	A[c]	1.1	83
16	$\text{4-MeOC}_6\text{H}_4\text{I}$	A	2.5	76
17	$\text{4-CF}_3\text{C}_6\text{H}_4\text{I}$	A	2.5	70

[a] The reaction was carried out at 100 °C for 24 h using an aryl halide (0.40 mmol), hexamethyldisilane and sodium hydroxide (0.48 mmol) in the presence of $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$ (0.01 mmol) and PO (0.04 mmol). A: THF(1 ml)–H_2O(1 ml); B: tetrabutylammonium bromide(0.04 mmol), toluene(1 ml)–H_2O(1 ml). [b] Isolated yields based on aryl halide are given. [c] The reaction was completed in 10 h.

the catalyst being attributed to the inertness of the oxidative adduct $\text{PhPdI(Ph}_3\text{P)}_2$.[1a,5] In our case the oxidative adduct **2** lacks a halide ligand which explains the results that the Pd–PO catalyst is free from the influence of the kind of halide.

In conclusion, we have demonstrated that a palladium catalyst coordinated by phosphinophenolate is efficient for the silylation of aryl halides using hexamethyldisilane. The protocol using a ligand that activates a transition metal and an incoming nucleophile simultaneously should be applicable to various transition metal-catalysed reactions. Studies on the details of the mechanism as well as application of the protocol are in progress in our laboratories.

Notes and references

1 (*a*) H. Matsumoto, S. Nagashima, K. Yoshihiro and Y. Nagai, *J. Organomet. Chem.*, 1975, **85**, C1; (*b*) D. Azarian, S. S. Dua, C. Eaborn and D. R. M. Walton, *J. Organomet. Chem.*, 1976, **117**, C55; (*c*) H. Matsumoto, K. Yoshihiro, S. Nagashima, H. Watanabe and Y. Nagai, *J. Organomet. Chem.*, 1977, **128**, 409; (*d*) C. Eaborn, R. W. Griffiths and A. Pidcock, *J. Organomet. Chem.*, 1982, **225**, 331; (*e*) Y. Hatanaka and T. Hiyama, *Tetrahedron Lett.*, 1987, **28**, 4715.

2 The palladium-catalysed decarbonylative silylation of arenecarbonyl halides also affords arylsilanes: (*a*) J. D. Rich, *J. Am. Chem. Soc.*, 1989, **111**, 5886; (*b*) J. D. Rich and T. E. Krafft, *Organometallics*, 1990, **9**, 2040; (*c*) T. E. Krafft, J. D. Rich and P. J. McDermott, *J. Org. Chem.*, 1990, **55**, 5430.

3 T. Hiyama, in *Metal-catalyzed Cross-coupling Reactions*, ed. F. Diederich and P. J. Stang, Wiley-VCH, Weinheim, 1998, ch. 10, pp. 421–453 and references therein.

4 Although there have been many reports on PO as a ligand for various transition metals, no report appeared concerning direct activation of a reaction partner for the transition metal. For Pd–PO complexes, see: H. D. Empsall, B. L. Shaw and B. L. Turtle, *J. Chem. Soc., Dalton Trans.*, 1976, 1500.

5 Aryl iodides react with **7** in the presence of $\text{Pd(PPh}_3)_4$ and TASF $(\text{Et}_2\text{N})_3\text{S}^+\text{F}_2\text{Si}^-\text{Me}_3$, see ref. 1(*e*).