

Scheme 2.

Na_2PdCl_4 and $\text{P}(t\text{-Bu})_3$ generate a good catalyst for the Sonogashira cross-coupling of aryl chlorides and terminal alkynes. In our case (entries 5 and 6) the yield of 1-(4-methylphenyl)-2-phenylacetylene never surpassed 11%. Exchanging Na_2PdCl_4 for $\text{Pd}(\text{OAc})_2$ led to worse results (entry 7). In the presence of $[(\pi\text{-allyl})\text{PdCl}]_2$ and $\text{P}(t\text{-Bu})_3$ (4:15 mol %) cross-coupling occurred with a yield of 30%, together with a 59% yield of the product of homocoupling of phenylacetylene (entry 8). Similar results were obtained with $\text{Pd}_2(\text{dba})_3/\text{P}(t\text{-Bu})_3$ (entries 10–12, 20 and 21). As the later system is less expensive than $[(\pi\text{-allyl})\text{PdCl}]_2/\text{P}(t\text{-Bu})_3$ we continued our exploration with it. We varied the base (entries 11–18)

and the amount of co-catalyst CuI (entries 10 and 11, 19–21) and found that CuI is necessary for the cross-coupling and that K_2CO_3 is a better base than Et_3N as it improves the competition between the desired cross-coupling and undesired homocoupling reactions. We have also explored the role of diaminocarbene ligands generated by α -elimination from salts **5**–**7** (Scheme 3). But, as seen from Table 1 (entries 22–24), this led to no cross-coupling at all! With phosphines other than $\text{P}(t\text{-Bu})_3$, the yield of product of cross-coupling remained very poor (entries 9, 25–27). We have also examined the role of the solvent and have found that THF is far better than toluene and acetonitrile.

The best conditions found for the desulfurative cross-coupling of TsCl and phenylacetylene were then applied to other substrates (Table 2) including sulfonyl chlorides with electron-rich or electron-poor aromatic systems, and various terminal alkynes. As expected, yields of cross-coupling products **3** increased when using an excess of alkynes **2**, as it compensates for the competitive

Table 1. Screening for Pd-catalyst, co-ligands and bases.^[a]

Entry	Catalyst (mol %)	Co-ligand (mol %)	Base	CuI (mol %)	Yield [%] of	
					3	4 ^[b]
1	$\text{PdCl}_2(\text{PhCN})_2$ (5)	–	Et_3N	5	ca.10	78
2	$\text{PdCl}_2(\text{PhCN})_2$ (5)	–	K_2CO_3	5	<6	62
3	$\text{PdCl}_2(\text{PhCN})_2$ (5)	$\text{P}(t\text{-Bu})_3$ (10)	Et_3N	5	25	62
4	$\text{PdCl}_2(\text{PhCN})_2$ (5)	$\text{P}(t\text{-Bu})_3$ (10)	K_2CO_3	5	28	60
5	Na_2PdCl_4 (7)	$\text{P}(t\text{-Bu})_3$ (15)	Et_3N	10	<5	30
6	Na_2PdCl_4 (7)	$\text{P}(t\text{-Bu})_3$ (15)	Et_3N	10	11	13 ^[c]
7	$\text{Pd}(\text{OAc})_2$ (7)	$\text{P}(t\text{-Bu})_3$ (15)	Et_3N	10	8	25
8	$[(\pi\text{-allyl})\text{PdCl}]_2$ (4)	$\text{P}(t\text{-Bu})_3$ (15)	Et_3N	10	30	59
9	Pd_2dba_3 (3)	PPh_3 (10)	Et_3N	5	<9	43
10	Pd_2dba_3 (3)	$\text{P}(t\text{-Bu})_3$ (10)	Et_3N	10	25	68
11	Pd_2dba_3 (3)	$\text{P}(t\text{-Bu})_3$ (10)	K_2CO_3	5	28	35
12	Pd_2dba_3 (3)	$\text{P}(t\text{-Bu})_3$ (10)	K_2CO_3	10	30	50
13	Pd_2dba_3 (3)	$\text{P}(t\text{-Bu})_3$ (10)	Na_2CO_3	10	9	22
14	Pd_2dba_3 (3)	$\text{P}(t\text{-Bu})_3$ (10)	Li_2CO_3	10	<8	34
15	Pd_2dba_3 (3)	$\text{P}(t\text{-Bu})_3$ (10)	DABCO	10	4	45
16	Pd_2dba_3 (3)	$\text{P}(t\text{-Bu})_3$ (10)	DBU	10	6	24
17	Pd_2dba_3 (3)	$\text{P}(t\text{-Bu})_3$ (10)	$\text{EtN}(i\text{-Pr})_2$	10	10	60
18	Pd_2dba_3 (3)	$\text{P}(t\text{-Bu})_3$ (10)	– ^[d]	10	<10	50
19	Pd_2dba_3 (3)	$\text{P}(t\text{-Bu})_3$ (10)	Et_3N	–	3	60
20	Pd_2dba_3 (3)	$\text{P}(t\text{-Bu})_3$ (10)	Et_3N	15	29	60 ^[e]
21	Pd_2dba_3 (3)	$\text{P}(t\text{-Bu})_3$ (10)	K_2CO_3	15	30	45 ^e
22	$[(\pi\text{-allyl})\text{PdCl}]_2$ (3)	5 (10)	Et_3N	10	0	<40
23	Pd_2dba_3 (3)	6 (10)	K_2CO_3	10	0	<16
24	Pd_2dba_3 (3)	7 (10)	K_2CO_3	10	0	<2
25	Pd_2dba_3 (3)	8 (10)	Et_3N	10	<13	40
26	Pd_2dba_3 (3)	9 (10)	Et_3N	10	<10	40
27	Pd_2dba_3 (3)	10 (10)	Et_3N	10	<15	27

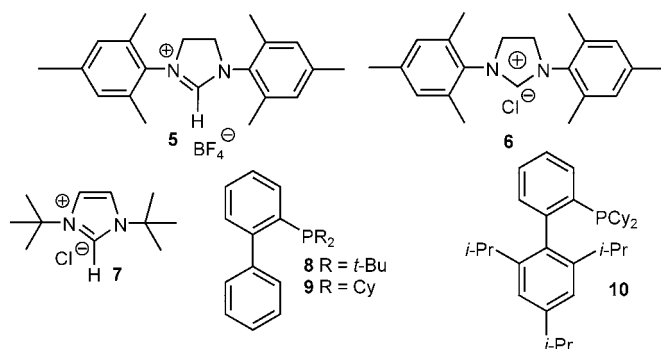
^[a] All experiments in boiling THF (unless noted), 0.15–0.2 molar, 1:1.3 mixtures of TsCl and $\text{PhC}\equiv\text{CH}$, 5–20 h (until disappearance of TsCl by TLC, yields of **3** based on TsCl after flash chromatography on silica gel.

^[b] Yields based on phenylacetylene.

^[c] In toluene.

^[d] *N*-Methylmorpholine.

^[e] Same reaction but in MeCN at 65 °C, 10 h, the yield in **3** was <5% (ca. 70% **4**).



Scheme 3. Co-ligand precursors and co-ligands.

homocoupling reactions. Recently Ho et al.^[22] found that homocoupling of alkynes can be retarded under argon atmosphere diluted with H₂. In our case (Table 2, entry 1) a 1:1 mixture of Ar/H₂ led to slightly better results. Phase-transfer catalysts such as Bu₄NBr or Bu₄NCl did not improve the yields in products **3**. This contrasts with several reports^[16,21,23] stating that these ammonium salts can induce better yield in Heck-type reactions. In one case (Table 2, entry 6) 40 mol % of MeN(oct)₃Cl led to a lower yield of product of cross-coupling than in the absence of the phase-transfer catalyst.

At least two possible mechanisms can be operative for our desulfitative Sonogashira–Hagihara cross-coupling reactions. In one of them, the palladium catalyst L₂Pd⁽⁰⁾ undergoes oxidative addition into the S–Cl bond of the arenesulfonyl chloride. A fast desulfitation occurs with the formation of an ArPdL₂Cl species that reacts, as in

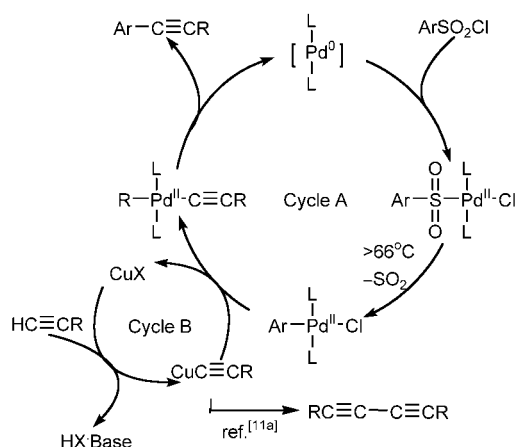


Figure 1. Probable catalytic cycle for the desulfitative Sonogashira–Hagihara cross-coupling of arenesulfonyl chlorides and terminal alkynes.

the usual Sonogashira–Hagihara reaction, with the alkynylcopper intermediate (CuC≡CR); then reductive elimination produces ArC≡CR and the initial catalyst L₂Pd⁽⁰⁾ (Figure 1). An alternative mechanism is to invoke an oxidative addition of the latter catalyst into the C–S bond of the ArSO₂Cl reagent, followed by desulfitation.

Conclusion

Arenesulfonyl chlorides undergo desulfitative Stille, carbonylative Stille, Suzuki–Miyaura and Heck–Mizor

Table 2. Sonogashira–Hagihara desulfitative cross-coupling of arenesulfonyl chlorides **1** and terminal alkynes **2** by using Pd₂dba₃/P(*t*-Bu)₃/CuI.^[a]

Entry	Ar in ArSO ₂ Cl (1)	R in HC≡CR (2)	Yield [%] in ArC≡CR (3) based on 1 using	
			1.3 equivs. of 2 ^[b]	2 equivs. of 2 ^[c]
1	4-methylphenyl	phenyl	30 [34] ^[d]	40
2	4-methylphenyl	<i>t</i> -butyl	45	60
3	4-methylphenyl	1-hexyl	50	63
4	1-naphthyl	<i>t</i> -butyl	55 [52] ^[e] [38] ^[f]	65
5	1-naphthyl	1-hexyl	57 [40] ^[e]	72
6	1-naphthyl	1-hexyl	57 ^[g] [28] ^[h] [57] ^[i]	–
7	1-naphthyl	tri(isopropyl)silyl	35 [50] ^[d]	60
8	4-fluorophenyl	1-hexyl	40 [43] ^[d]	52
9	4-nitrophenyl	tri(isopropyl)silyl	41	59
10	3-cyanophenyl	1-hexyl	–	52
11	3-cyanophenyl	<i>t</i> -butyl	–	50

^[a] See details in Experimental Section.

^[b] Yields of purified products, after flash chromatography.

^[c] Yields were determined through gas chromatography.

^[d] 1:1 Ar/H₂ atmosphere.

^[e] Et₃N instead of K₂CO₃.

^[f] 5 instead of 15 mol % of CuI.

^[g] 4 mol % [(π -allyl)PdCl]₂ and 15 mol % P(*t*-Bu)₃ instead of the usual conditions.

^[h] With MeN(Oct)₃Cl (40 mol %).

^[i] Slow addition of HC≡CR, 2–4 h.

oki cross-coupling reactions. We have shown in this paper that they can also be cross-coupled with terminal alkynes. The best catalyst found so far for the desulfitative Sonogashira–Hagihara cross-coupling reactions is $\text{Pd}_2(\text{dba})_3/\text{P}(t\text{-Bu})_3/\text{CuI}$ using K_2CO_3 as base, and boiling THF as medium. Competition of the homocoupling of the acetylene cannot be avoided, but its effect on the yields of products of cross-coupling can be reduced by slow addition of 2 equivalents of the alkyne to the reaction mixture.

Experimental Section

General Remarks

Unless stated otherwise, reactions were conducted in flame-dried glassware under a vacuum. THF was distilled before use from sodium and benzophenone. Catalysts and ligands were purchased from Strem Chemical, Inc. All commercially available reagents were used without further purification. Solvents after reactions and extraction were evaporated in a rotary evaporator under vacuum (solvents were removed by cooling at -20°C , in the case of low boiling point or low molecular mass products). TLC for reaction monitoring was performed on 60 F_{254} (Merck) with detection by UV light and charring with KMnO_4 . ^1H and ^{13}C NMR spectra were recorded by using a Bruker DPX-400 or Bruker ARX-400 spectrometer at 400 MHz and 100.6 MHz, respectively, and are reported relative to Me_4Si ($\delta=0.0$) or to the solvents residual ^1H -signal (CDCl_3 , $\delta_{\text{H}}=7.27$). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (J in hertz) and integration. Data for ^{13}C NMR spectra reported in terms of chemical shift. IR spectra were recorded on a Perkin-Elmer 1420 spectrometer and are reported in frequency of absorption (cm^{-1}). HRMS (MALDI-TOF) mass spectra were taken on a Kratos Analytical Instruments system.

Typical Experimental Procedure for Desulfitative Sonogashira–Hagihara Cross-Coupling Reactions (Table 2)

A round-bottom flask was dried under vacuum, and to the flask were added the corresponding arenesulfonyl chloride (1.00 mmol), Pd_2dba_3 (0.03 mmol), CuI (0.15 mmol) and also an internal standard (4,4'-dimethyldiphenyl, 0.25 mmol) under a nitrogen atmosphere (glove-box). The flask was connected to a vacuum line and filled with Ar (three times), then THF (4 mL) was added under Ar. Next, $\text{P}(t\text{-Bu})_3$ [0.1 mmol, $\text{P}(t\text{-Bu})_3$ sold by Strem Chemicals in a Sure/Seal bottle as a 10 wt % solution in hexane], K_2CO_3 (2.5 mmol) or Et_3N (2.5 mmol, in 1 mL of THF), were added in that order. The alkyne (1.3 to 2.0 mmol) was added *via* a syringe under reflux and the mixture stirred for 5–10 h. After cooling to 20°C , the mixture was diluted with Et_2O and washed with H_2O . The aqueous layer was extracted again with Et_2O (3 times). The combined organic phases were dried (MgSO_4), filtered, and concentrated under reduced pressure (solvents were removed under reflux and cooling to -20°C in the case of low boiling point or low

molecular mass products). The residue was analyzed by gas chromatography or/and purified by flash chromatography on silica gel.

1-(4-Methylphenyl)-2-phenylacetylene (Table 2, entry 1): ^{241}H NMR (CDCl_3): $\delta=7.44$ (d, 2H, $J=8.0$ Hz, ArH), 7.41–7.33 (m, 5H, ArH), 7.17 (d, 2H, $J=8.0$ Hz, ArH), 2.38 (s, 3H, CH_3).

1-(4-Methylphenyl)-2-*t*-butylacetylene (Table 2, entry 2): ^{251}H NMR (CDCl_3): $\delta=7.24$ (d, 2H, $J=7.7$ Hz, ArH), 7.09 (d, 2H, $J=7.7$ Hz, ArH), 2.43 (s, 3H, CH_3), 1.39 [s, 9H, $\text{C}(\text{CH}_3)_3$].

1-(4-Methylphenyl)-2-hexylacetylene (Table 2, entry 3): ^{261}H NMR (CDCl_3): $\delta=7.24$ (d, 2H, $J=7.7$ Hz, ArH), 7.09 (d, 2H, $J=7.7$ Hz, ArH), 2.60 (t, 2H, $J=7.0$ Hz, CH_2), 1.74 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 1.4 (m, 4H, $2 \times \text{CH}_2$), 0.96 (t, 3H, $J=7.0$ Hz, CH_3).

1-(*t*-But-1-yn-1-yl)naphthalene (Table 2, entry 4): ^{271}H NMR (CDCl_3): $\delta=8.35$ (d, 1H, $J=8.6$ Hz, ArH), 7.85 (d, 1H, $J=8.0$ Hz, ArH), 7.79 (d, 1H, $J=8.0$ Hz, ArH), 7.54 (m, 1H, ArH), 7.64 (d, 1H, $J=7.4$ Hz, ArH), 7.42 (t, 1H, $J=8.0$ Hz, ArH), 7.3 (m, 1H, ArH), 1.47 [s, 9H, 7.0, $\text{C}(\text{CH}_3)_3$].

1-(Oct-1-yn-1-yl)naphthalene (Table 2, entry 5): ^{281}H NMR (CDCl_3): $\delta=8.38$ (d, 1H, $J=8.3$ Hz, ArH), 7.86 (d, 1H, $J=7.7$ Hz, ArH), 7.80 (d, 1H, $J=8.3$ Hz, ArH), 7.65 (d, 1H, $J=7.0$ Hz, ArH), 7.56 (m, 2H, ArH), 7.42 (t, 1H, $J=7.3$ Hz, ArH), 2.60 (t, 2H, $J=7.0$ Hz, CH_2), 1.74 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 1.4 (m, 4H, $2 \times \text{CH}_2$), 0.96 (t, 3H, $J=7.0$ Hz, CH_3).

1-(1-Naphthyl)-2-(triisopropylsilyl)acetylene (Table 2, entry 7): R_f : 0.42 (pentane); oil; IR (film): $\nu=2942, 2890, 2864, 2152, 1462, 1392, 1074, 1014, 996, 881, 798, 772, 736$ cm^{-1} ; ^1H NMR (CDCl_3): $\delta=8.42$ (d, 1H, $J=8.3$ Hz, ArH), 7.85 (t, 2H, $J=8.8$ Hz, ArH), 7.75 (d, 1H, $J=7.4$ Hz, ArH), 7.61 (t, 1H, $J=7.7$ Hz, ArH), 7.54 (t, 1H, $J=7.7$ Hz, ArH), 7.44 (t, 1H, $J=7.7$ Hz, ArH), 1.23 [m, 21H, $3 \times \text{CH}(\text{CH}_3)_2$]; ^{13}C NMR: $\delta=133.5, 133.1, 131.0, 128.8, 128.3, 126.8, 126.4, 126.3, 125.2, 121.2, 104.9, 95.8, 18.8, 11.4$; MS: m/z (rel. int.) = 308 (M^+ , 43), 265 (67), 237 (17), 223 (43), 209 (58), 195 (100), 179 (32), 165 (22), 105 (23), 85 (8); HRMS (MALDI-TOF): calcd. for $\text{C}_{21}\text{H}_{28}\text{Si}$: 308.1960; found: 308.1967.

1-(4-Fluorophenyl)-2-hexylacetylene (Table 2, entry 8): R_f : 0.39 (pentane); oil; IR (film): $\nu=2955, 2938, 2858, 2352, 1601, 1507, 1465, 1427, 1230, 835$ cm^{-1} ; ^1H NMR (CDCl_3): $\delta=7.38$ (td, 2H, $J=8.6, 3.2$ Hz, ArH), 6.99 (t, 2H, $J=8.6$ Hz, ArH), 2.40 (t, 2H, $J=7.0$ Hz, CH_2), 1.53 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 1.3 (m, 4H, $2 \times \text{CH}_2$), 0.91 (t, 3H, $J=7.0$ Hz, CH_3); ^{13}C NMR: $\delta=162.4, 133.7, 117.8, 115.7, 90.5, 79.8, 31.7, 28.9, 28.7, 22.9, 19.6, 14.4$; MS: m/z (rel. int.) = 204 (M^+ , 5), 189 (11), 147 (16), 133 (37), 119 (24), 105 (51), 91 (100), 79 (84); HRMS (MALDI-TOF): calcd. for $[\text{C}_{14}\text{H}_{17}\text{F} + \text{K}]^+$: 243.0951; found: 243.0959.

1-(4-Nitrophenyl)-2-(triisopropylsilyl)acetylene (Table 2, entry 9): ^{291}H NMR (CDCl_3): $\delta=8.20$ (d, 2H, $J=8.9$ Hz, ArH), 7.63 (d, 2H, $J=8.9$ Hz, ArH), 1.15–1.13 [m, 21H, $3 \times \text{CH}(\text{CH}_3)_2$].

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