PERKIN 1

Pd(0)–Cu(I)-catalyzed cross-coupling of alkynylsilanes with triarylantimony(V) diacetates

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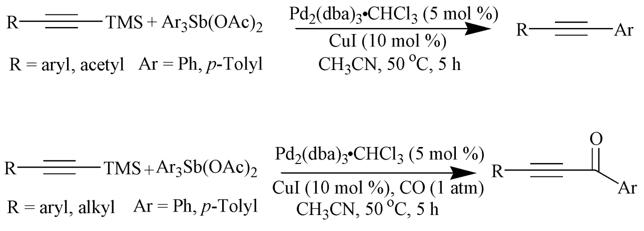
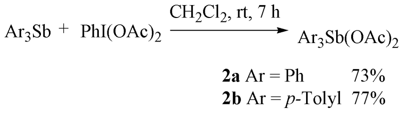
Treatment of alkynylsilanes with triarylantimony diacetates in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%) and CuI (10 mol%) in CH_3CN at 50 °C for 5 h afforded aryl-substituted alkynes in good yield. Alternatively, direct carbonylative coupling of triarylantimony diacetates with alkynylsilanes was accomplished under atmospheric pressure of carbon monoxide.

The palladium-catalyzed cross-coupling reaction of terminal alkynes with aryl or vinyl halides in the presence of a Pd(0)–Cu(I) co-catalyst system, known as Sonogashira and Hagihara coupling,[1] has been widely utilized as a practical synthetic method for carbon–carbon bond formation in organic synthesis. In synthesis, for the introduction of appropriate functionalities, a terminal alkyne moiety is often protected with a trimethylsilyl group. Thus the direct coupling of alkynylsilanes should be more accessible. There have only been a few reports of such direct coupling reactions of alkynylsilanes with aryl halides; in the presence of fluoride ion by Hiyama *et al.*[2] or under basic conditions by Rossi[3] and Huang[4] and their co-workers. Recently Hiyama *et al.*[5] reported a copper(I)-salt mediated direct Pd(0)-cross coupling reaction of alkynylsilanes with triflates in the presence of CuCl in DMF. Nagasaka *et al.*[6] also reported the direct silver-promoted cross-coupling of alkynylsilanes with aryl iodides to form aryl-substituted alkynes. Alternatively, in order to synthesize alkynyl ketones CuCl-catalyzed reaction of alkynylsilanes and acyl halides by one-pot desilylation–coupling was reported by Hosomi *et al.*[7]. We have investigated the use of triarylantimony(V) diacetates[8] in palladium-catalyzed cross-coupling reactions; here we wish to report the direct palladium-catalyzed cross-coupling and carbonylative cross-coupling of alkynylsilanes with triarylantimony diacetates to afford the aryl-substituted alkynes and alkynyl ketones (Scheme 1).[9]



Scheme 1

Triarylantimony(V) diacetates **2a**[10] and **2b**[11] were prepared by reaction of triarylantimony(III) with $PhI(OAc)_2$ by stirring in CH_2Cl_2 at room temperature for 7 h (Scheme 2).

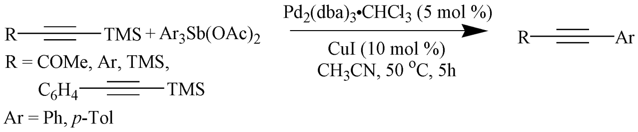


Scheme 2

Results and discussion

1 Pd(0)–Cu(I)-catalyzed cross-coupling of alkynylsilanes with organoantimony(V) compounds

The results of the palladium–copper catalyzed cross-coupling of alkynylsilanes with triarylantimony diacetates are summarized in Scheme 3 and Table 1.



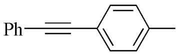
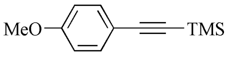
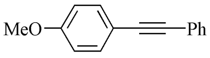
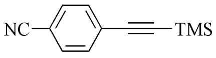
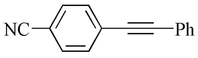
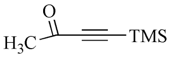
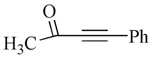
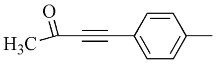
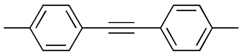
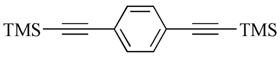
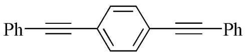
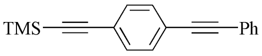
Scheme 3

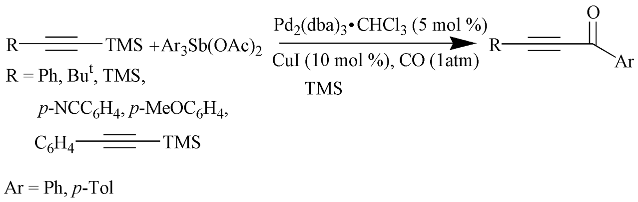
The (phenylethynyl)trimethylsilane (**1a**) reacted with triphenylantimony diacetate (**2a**) in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%) and CuI (10 mol%) in CH_3CN at 50 °C for 5 h to afford 1,2-diphenylacetylene (**3a**) in 81% yield (entry 1 in Table 1). No homocoupling reaction of alkynylsilanes[12] was observed using $Ar_3Sb(OAc)_2$. The addition of CuI is critical and improved the yield. Of the catalysts ($Pd_2(dba)_3{\cdot}CHCl_3$, $PdCl_2$, $(\pi\text{-allyl})_2Pd_2Cl_2$, $Pd_2(dba)_3$, $PdCl_2(PhCN)_2$) tested, $Pd_2(dba)_3{\cdot}CHCl_3$ was the best choice. Among the solvents (DMF, CH_3CN, toluene and DME) tested, CH_3CN was the most suitable at 50 °C. Under the same conditions the reaction of **1a** with tri-*p*-tolylantimony diacetate (**2b**) gave 1-phenyl-2-*p*-tolylacetylene (**3b**[13a]) in 80% yield (entry 2). For the aryl-substituted silanes **1b** and **1c**, triphenylantimony diacetate (**2a**) was successfully coupled to give **3c**[12c] and **3d**[13b] under the same conditions in 73 and 70% yields, respectively (entries 3 and 4). The acetyl-substituted ethynylsilane **1d** was treated with **2a** and **2b** to provide **3e** and **3f** in 85 and 82% yields, respectively (entries 5 and 6). When the 1,2-bis(trimethylsilyl)ethyne (**1e**) was reacted with **2a** and **2b**, the disubstituted acetylene **3a** and **3g**[13c] were afforded in 80 and 77% yields, respectively (entries 7 and 8). Finally for the 1,4-bis(trimethylsilanylethynyl)benzene (**1f**), disubstituted product **3h**[13d] was obtained using $Pd_2(dba)_3{\cdot}CHCl_3$ as a catalyst (entry 9). However, when $PdCl_2$ was employed as a catalyst, the mono-substituted product **3i**[13e] was afforded in 42% yield (entry 10).

2 Pd(0)–Cu(I)-catalyzed carbonylative cross-coupling of alkynylsilanes with organoantimony(V) compounds

This coupling was extended to carbonylative cross-coupling of silanes with antimony(V) compounds. The results are summarized in Scheme 4 and Table 2.

Table 1 Pd(0)–Cu(I)-catalyzed cross-coupling of alkynylsilanes with triarylantimony diacetates

Entry	Silanes	Triarylantimony diacetates	Product	Yield (%)
1	Ph—≡—TMS **1a**	$Ph_3Sb(OAc)_2$ **2a**	Ph—≡—Ph **3a**	81
2	**1a**	(p-Tol)$_3Sb(OAc)_2$ **2b**	 **3b**	80
3	 **1b**	**2a**	 **3c**	73
4	 **1c**	**2a**	 **3d**	70
5	 **1d**	**2a**	 **3e**	85
6	**1d**	**2b**	 **3f**	82
7	TMS—≡—TMS **1e**	**2a**	Ph—≡—Ph **3a**	77
8	**1e**	**2b**	 **3g**	80
9	 **1f**	**2a**	 **3h**	75
10	**1f**	**2a**	 **3i**	42



Scheme 4

(3,3-Dimethylbut-1-ynyl)trimethylsilane (**1g**) was treated with triphenylantimony diacetate (**2a**) in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%) and CuI (10 mol%) under atmospheric pressure of carbon monoxide in CH_3CN to give ynone **4e**[13f] in 80% yield (entry 6 in Table 2). Under the same conditions phenylethynylsilane (**1a**) reacted with **2a** to afford benzoyl substituted alkynone **4a**[13g] in 62% yield (entry 1). For the substituted arylethynylsilanes **1b** and **1c**, the reactions with triphenylantimony diacetate (**2a**) provided the carbonylated coupled products **4b**[13h] and **4c** in 65 and 68% yields, respectively (entries 2 and 3). The bis-silyl substituted **1e** and **1f** were readily coupled with **2a** to afford the mono carbonylated silanes **4a** and **4d** in 66 and 58% yields, respectively (entries 4 and 5). This method was also applied to p-tolyl substituted antimony diacetate **2b**. The alkynylsilanes **1g** and **1b** were subjected to carbonylative cross-coupling to afford ynones **4f** and **4g** in 77 and 81% yields, respectively (entries 7 and 8). To the best of our knowledge this is the first direct Pd(0)-catalyzed carbonylative cross-coupling of alkynylsilanes without deprotection of a silyl group.

In considering the plausible mechanism for carbonylative cross-coupling, the palladium complex **A** is generated by oxidative addition of the Ar–Sb bond of triarylantimony(V) diacetate onto Pd(0) followed by carbonylation. Alternatively, the alkynyl group is transferred from alkynylsilane to copper to form alkynylcopper **B**. The alkynyl group in **B** migrates from copper to palladium to furnish intermediate **C** which is subjected to reductive elimination to give the direct coupled product, regenerating Pd(0) and Cu(I) as a catalyst (Scheme 5).[14]

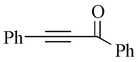
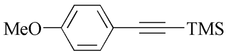
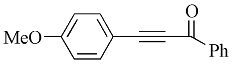
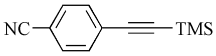
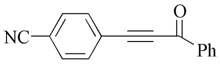
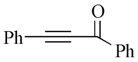
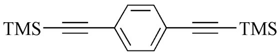
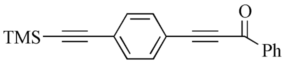
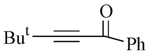
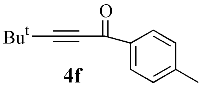
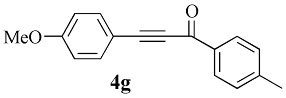
In conclusion triarylantimony(V) diacetates were prepared conveniently and cross-coupling and carbonylative cross-coupling of triarylantimony(V) derivatives with alkynylsilanes were achieved in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%) and CuI (10 mol%), at 50 °C at atmospheric pressure of carbon monoxide for the carbonylative cross-coupling.

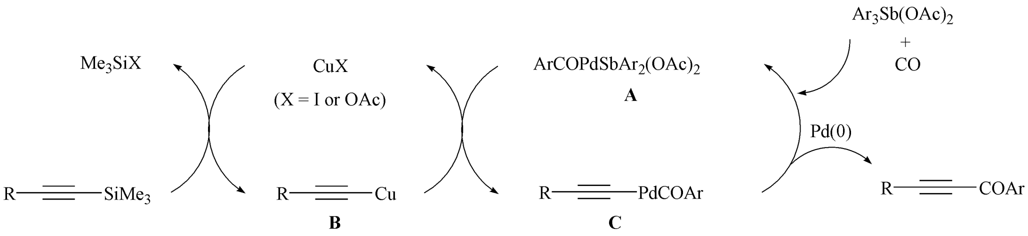
Experimental

Typical procedure for the preparation of triarylantimony(V) diacetate

A mixture of triarylantimony (2.0 mmol) and (diacetoxyiodo)-benzene diacetate (2.2 mmol) in dichloromethane (20 mL) was stirred at room temperature for 7 h. The solvent was concentrated under reduced pressure to a small volume. A mixture of diethyl ether–pentane was added and the solution was kept overnight at −15 °C. The solid was filtered and recrystallized from a mixture of dichloromethane and pentane.

Table 2 Pd(0)–Cu(I)-catalyzed carbonylative cross-coupling of alkynylsilanes with triarylantimony diacetates

Entry	Silanes	Triarylantimony diacetates	Product	Yieid (%)
1	Ph—≡—TMS **1a**	$Ph_3Sb(OAc)_2$ **2a**	 $PhC\equiv CC(O)Ph$ **4a**	62
2	 **1b**	**2a**	 **4b**	65
3	 **1c**	**2a**	 **4c**	68
4	TMS—≡—TMS **1e**	**2a**	 $PhC\equiv CC(O)Ph$ **4a**	66
5	 **1f**	**2a**	 **4d**	58
6	Bu^t—≡—TMS **1g**	**2a**	 $Bu^tC\equiv CC(O)Ph$ **4e**	80
7	**1g**	$(p\text{-Tol})_3Sb(OAc)_2$ **2b**	 **4f**	77
8	**1b**	**2b**	 **4g**	80



Scheme 5

Triphenylantimony(V) diacetate (**2a**): mp 210–212 °C (lit.[15] 208–209 °C); δ_H 1.83 (s, 6H), 7.48 (m, 9H), 7.99 (m, 6H).

Tri(*p*-tolyl)antimony(V) diacetate (**2b**): mp 157–159 °C; δ_H 1.82 (s, 6H), 2.39 (s, 9H), 7.27 (d, 6H, J = 8 Hz), 7.86 (d, 6H, J = 8 Hz).

Typical procedure for the cross-coupling of alkynylsilanes with organoantimony(V) compounds

Diphenylacetylene (3a). To a mixture of triphenylantimony diacetate (**2a**) (412 mg, 1.00 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (112 mg, 5 mol%) and CuI (19 mg, 10 mol%) was added (phenylethynyl)trimethylsilane (**1a**) (169 mg, 1.00 mmol) under N_2 charged at 50 °C in CH_3CN (20 mL). The reaction mixture was stirred at 50 °C for 5 h, extracted with ether (20 mL × 3), and washed with water (20 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (hexanes, R_f = 0.48) to afford the coupled product diphenylacetylene (**3a**) (144 mg, 81%); δ_H (500 MHz; $CDCl_3$) 7.26 (m, 2H), 7.36 (m, 4 H), 7.54 (m, 4 H); ν_{max} (KBr)/ cm^{-1} 3063, 1600, 1499, 1070, 755; *m*/*z* 178 (100), 176, 152, 89, 88, 76.

Compounds **3b–3i** were prepared following the above procedures using the appropriate starting material.

1-Phenylethynyl-4-methylbenzene (3b). Hexanes, R_f = 0.40; δ_H (500 MHz; $CDCl_3$) 2.37 (s, 3 H), 7.17 (d, 1 H, J = 7.8 Hz), 7.34 (m, 3 H), 7.42 (m, 2 H), 7.53 (m, 2 H); ν_{max} (KBr)/cm^{-1} 3084, 2964, 1612, 1480, 1372, 695; *m*/*z* 192 (100), 191, 189, 165, 115.

1-Methoxy-4-(phenylethynyl)benzene (3c). EtOAc–hexanes 1 : 10, R_f = 0.52; δ_H (500 MHz; $CDCl_3$) 3.83 (s, 3 H), 6.89 (dd, 1 H, J = 4.2, 2.0 Hz), 7.33 (m, 3 H), 7.51 (m, 4 H); ν_{max} (KBr)/ cm^{-1} 3080, 2958, 1617, 1405; *m*/*z* 208, 207 (100), 193 (49), 165 (52).

4-Phenylethynylbenzonitrile (3d). EtOAc–hexanes 1 : 30, R_f = 0.33; δ_H (500 MHz; $CDCl_3$) 7.37 (m, 3 H), 7.50 (m, 2 H), 7.62 (m, 4 H); *m*/*z* 204 (11), 103 (100), 156 (10), 88 (11).

4-Phenylbut-3-yn-2-one (3e). EtOAc–hexanes 1 : 10, R_f = 0.48; δ_H (500 MHz; $CDCl_3$) 2.45 (s, 3 H), 7.38 (m, 2 H), 7.45 (m, 1 H), 7.56 (m, 2 H); ν_{max} (KBr)/cm^{-1} 3054, 2865, 1680, 1456.

4-(4-Methylbenzene)but-3-yn-2-one (3f). EtOAc–hexanes 1 : 10, R_f = 0.47; δ_H (500 MHz; $CDCl_3$) 2.38 (s, 3 H), 2.45 (s, 3 H), 7.19 (d, 2 H, J = 9.9 Hz), 7.47 (dd, 2 H, J = 9.9, 2.1 Hz);

δ_C (125 MHz; $CDCl_3$) 200.9, 157.9, 150.5, 137.6, 137.2, 130.0, 128.7, 30.1, 21.9; ν_{max} (KBr)/cm^{-1} 3054, 2865, 1680,1456; *m*/*z* 158 (27), 143 (100), 115 (13), 89 (9); HRMS for $C_{11}H_{10}O$ calcd: 158.0732, found: 158.0728.

Bis(4-methylphenyl)acetylene (3g). Hexanes, $R_f = 0.38$; δ_H (500 MHz; $CDCl_3$) 2.36 (s, 3 H), 7.24 (d, 2 H, $J = 8.0$ Hz), 7.50 (d, 2 H, $J = 8.0$ Hz); ν_{max} (KBr)/cm^{-1} 3080, 2964, 1609, 1480, 1377; *m*/*z* 207 (10), 106 (100), 189 (15), 102 (10), 101 (11), 89 (14).

1,4-Bis(phenylethynyl)benzene (3h). Hexanes, $R_f = 0.27$; δ_H (500 MHz; $CDCl_3$) 7.45 (m, 3 H), 7.58 (m, 4 H); *m*/*z* 278 (100), 139 (28), 126 (9).

Trimethyl[4-(phenylethynyl)phenylethynyl]silane (3i). Hexanes, $R_f = 0.29$; δ_H (500 MHz; $CDCl_3$) 0.12 (s, 9 H), 7.32 (m, 3 H), 7.49 (m, 4 H), 7.52 (m, 2 H); *m*/*z* 274 (13), 273 (55), 260 (22), 259 (100), 130 (17).

Typical procedure for the carbonylative cross-coupling of alkynylsilanes with organoantimony(V) compounds

3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-one (4b). To a mixture of triphenylantimony diacetate (**2a**) (412 mg, 1.00 mmol), $Pd_2(dba)_3\cdot CHCl_3$ (112 mg, 5 mol%) and CuI (19 mg, 10 mol%) was added (4-methoxyphenylethynyl)trimethylsilane (**1b**) (168 mg, 1.00 mmol) under atmospheric pressure of CO at 50 °C in CH_3CN (20 mL). The reaction mixture was stirred at 50 °C for 5 h, extracted with ether (20 mL × 3), and washed with water (20 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc–hexanes 1 : 10, $R_f = 0.19$) to afford the coupled product 3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one (**4b**) (118 mg, 65%); δ_H (500 MHz; $CDCl_3$) 3.89 (s, 3 H), 6.98 (m, 2 H), 7.41 (m, 2 H), 7.45 (m, 1 H), 7.66 (m, 2 H), 8.19 (m, 2 H); ν_{max} (KBr)/cm^{-1} 3055, 2200, 1632, 1264; *m*/*z* 237, 236, 208, 193, 165, 159 (100), 144.

Compounds **4a**,**c**–**g** were prepared following the above procedures using the appropriate starting material.

1,3-Diphenylprop-2-yn-1-one (4a). EtOAc–hexanes 1 : 10, $R_f = 0.34$; δ_H (500 MHz; $CDCl_3$) 7.41 (m, 2 H), 7.48 (m, 1 H), 7.52 (m, 1 H), 7.62 (m, 1 H), 7.68 (m, 1 H), 8.22 (m, 2 H); ν_{max} (KBr)/cm^{-1} 3055, 2200, 1641; *m*/*z* 206 (95), 178 (100), 129 (94).

4-(3-Oxo-3-phenylprop-1-ynyl)benzonitrile (4c). EtOAc–hexanes 1 : 7, $R_f = 0.34$; δ_H (500 MHz; $CDCl_3$) 7.36–7.82 (m, 7 H), 8.19 (m, 2 H); δ_C (125 MHz; $CDCl_3$) 174.9, 134.0, 132.1, 130.8, 130.6, 129.9, 127.2, 126.4, 122.5, 115.4, 111.6, 87.1; *m*/*z* 235 (15), 234 (99), 233 (100), 105 (14), 191 (12), 128 (29), 103 (82), 91 (23), 77 (33); ν_{max} (KBr)/cm^{-1} 3056, 2987, 2305, 2205, 1644; HRMS for $C_{16}H_9NO$ calcd: 231.0684, found:231.0681.

1-Phenyl-3-(4-trimethylsilanylethynylphenyl)prop-2-yn-1-one (4d). EtOAc–hexanes 1 : 10, $R_f = 0.43$; δ_H (500 MHz; $CDCl_3$) 0.22 (s, 9 H), 7.58 (m, 2 H), 7.62 (m, 2 H), 7.74 (m, 1 H), 7.80 (m, 2 H), 8.18 (m, 2 H); δ_C (125 MHz; $CDCl_3$) 178.5, 137.5, 134.9, 133.5, 132.8, 130.3, 129.5, 126.4, 120.6, 104.7, 98.9, 92.9, 88.9, 0.5; ν_{max} (KBr)/cm^{-1} 3055, 2987, 2199, 1641, 1423, 1265, 744; HRMS for $C_{20}H_{18}OSi$ calcd: 302.1127, found: 302.1123.

4,4-Dimethyl-1-phenylpent-2-yn-1-one (4e). EtOAc–hexanes 1 : 10, $R_f = 0.41$; δ_H (500 MHz; $CDCl_3$) 1.34 (s, 9 H), 7.61 (m, 2 H), 7.73 (m, 1 H), 8.05 (m, 2 H); *m*/*z* 186 (10), 143 (34), 128 (23), 105 (100), 77 (19).

4,4-Dimethyl-1-(*p*-tolyl)pent-2-yn-1-one (4f). EtOAc–hexanes 1 : 10, $R_f = 0.47$; δ_H (500 MHz; $CDCl_3$) 1.56 (s, 9 H), 2.42 (s, 3 H), 7.27 (m, 2 H), 7.69 (m, 2 H), 8.00 (m, 2 H); δ_C (125 MHz; $CDCl_3$) 178.8, 145.5, 135.5, 130.3, 129.9, 104.1, 78.9, 30.9, 28.7, 22.5; ν_{max} (KBr)/cm^{-1} 3055, 2888, 1706, 1450; HRMS for $C_{14}H_{16}O$ calcd: 200.1201, found: 200.1203.

3-(4-Methoxyphenyl)-1-(*p*-tolyl)prop-2-yn-1-one (4g). EtOAc–hexanes 1 : 10, $R_f = 0.16$; δ_H (500 MHz; $CDCl_3$) 2.45 (s, 3 H), 3.89 (s, 3 H), 6.98 (m, 2 H), 7.41 (m, 2 H), 7.45 (m, 1 H), 7.66 (m, 2 H), 8.19 (m, 2 H); δ_C (125 MHz; $CDCl_3$) 178.5, 162.3, 145.7, 135.5, 130.3, 130.0, 129.7, 115.1, 112.7, 94.5, 87.6, 56.1, 22.5; ν_{max} (KBr)/cm^{-1} 3055, 2963, 2200, 1632, 1264; HRMS for $C_{17}H_{14}O_2$ calcd: 250.0994, found: 250.0988.

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