Synthetic Methods

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Palladium-Catalyzed Bromoalkynylation of C–C Double Bonds: Ring-Structure-Dependent Synthesis of 7-Alkynyl Norbornanes and Cyclobutenyl Halides**

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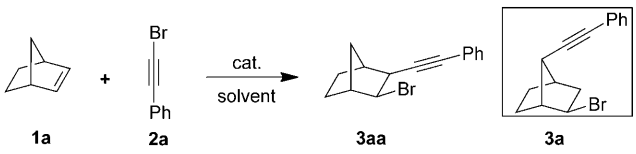
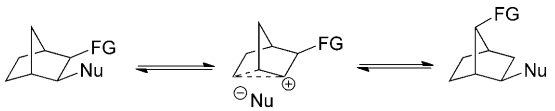
The development of efficient and sustainable procedures for the synthesis of complex molecules is an important task in modern organic chemistry. The direct cleavage of an alkynyl–halogen bond followed by the reconnection of both the alkynyl and halogen ions with the two carbon atoms of an unsaturated carbon–carbon bond provides ready access to highly functionalized products from simple alkynes with excellent atom economy.[1] We previously achieved highly regio- and stereoselective bromoalkynylation of internal alkynes for the synthesis of conjugated *cis*-bromoalkenynes.[2] Subsequent research on this subject revealed a further use of bromoalkynes in complex molecule synthesis.

Norbornene derivatives are an appealing group of organic molecules that are convenient starting materials for the synthesis of polymers, solar-energy-storage materials, and bioactive products.[3] In addition, their strained structure and high potential to coordinate to transition metals, as well as their possible industrial applications have attracted considerable research interest.[4] Thus, we decided to react phenylethynyl bromide (**2a**) with norbornene (**1a**), expecting to obtain 2-bromo-3-(2-phenylethynyl)bicyclo[2.2.1]heptane (**3aa**; Scheme 1). However, when using the previously optimized conditions,[2] we did not detect the formation of **3aa**, instead we obtained 2-bromo-7-(2-phenylethynyl)-bicyclo[2.2.1]heptane (**3a**) in excellent yield, as confirmed by ^{1}H NMR spectroscopy. This unexpected result attracted our interest, since, to the best of our knowledge, no example of a direct 7-alkynyl bromonorbornane formation has been reported.

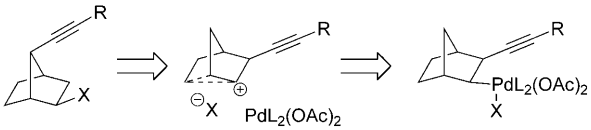


Scheme 1. Bromoalkynylation of norbornene (**1a**) with phenylethynyl bromide (**2a**).

From previous reports,[5] we realized that after the formation of the nonclassical "norbornonium" cation, the C-7 functionalization can be achieved through a nucleophile rearrangement (Scheme 2). Our success in synthesizing C-7-functionalized norbornyl alkynes proved the compatibility of this cation with the aforementioned alkynylation reaction conditions (see retrosynthesis in Scheme 3). The resulting products, which were formed with high selectivity, are not otherwise easily accessible and can find potential applications in both synthetic and materials chemistry.[6]



Scheme 2. Rearrangement of a functional group by nucleophile dissociation.



Scheme 3. Retrosynthesis of a 7-alkynyl halonorbornane via a "non-classical" cation by Pd dissociation. L = CH_3CN.

The scope of the C-7 functionalization reaction was examined for several haloalkynes and norbornene-derivatives (Scheme 4 and Table 1). Both electron-rich and electron-poor phenylethynyl bromides were reacted with 2-norbornene (**1a**) to give the corresponding alkynylation products **3a**–**3k** in good to excellent yields (Table 1, entries 1–11). The reaction tolerated a variety of substituents including Cl, Br, F, NO_2, and OMe groups, and substituents at the *ortho* position of the benzyl group did not affect the yield of the reaction (Table 1, entries 2 and 7). 5-Substituted 2-norbornene **1b** (mixture of *endo* and *exo*) was also successfully converted to 2,5,7-substituted norbornanes **3l**–**3p** in good yields with no obvious inversion of configuration compared to the corresponding starting materials (Table 1, entries 12–16). The reaction showed no regioselectivity when 5-vinyl-2-norbornene **1c** and polycyclic norbonene **1d** were used as the substrates

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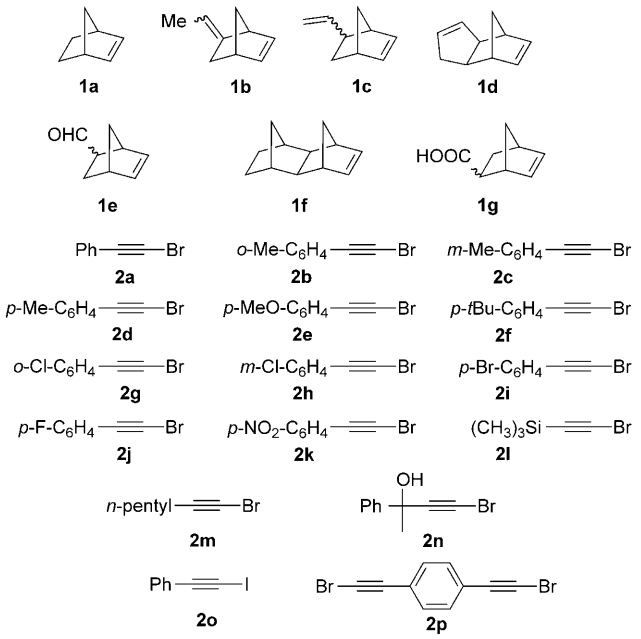


Scheme 4. Norbornene derivatives and haloalkynes. Substrates **1b**, **1c**, **1e**, and **1g** are mixtures of *endo* and *exo* isomers (see the Supporting Information).

(Table 1, entries 17 and 18). On the other hand, the carbonyl substituent in norbornene **1e** led to an obvious selectivity for 2,5,7-substituted norbornane **3s** (Table 1, entry 19). To our surprise, the use of 4-bromo-2-phenylbut-3-yn-2-ol (**2n**) resulted in the formation of the dehydration product **3w** in 67% yield (Table 1, entry 23). Trimethylsilylethynyl bromide (**2l**) also added onto norbornene to afford 2-bromo-7-alkynylnorbornane **3u** in good yield (Table 1, entry 21), thus showing the mildness and robustness of our method.[7] Alkyl alkynyl bromides such as *n*-pentyl bromide (**2m**) can also undergo this transformation in good yields (Table 1, entry 22). In this case, simple filtration through a silica gel plug was sufficient to remove the residual catalyst and provide product **3v**. Interestingly, the use of 1,4-bis(2-bromoethynyl)benzene (**2p**) resulted in the formation of the corresponding diyne product **3z** as white crystals in 73% yield (Table 1, entry 26). The molecular structure of **3z** was established by X-ray crystallography (Figure 1), which enabled us to confirm the reaction nature as a 2,7-addition process. We also extended this reaction to phenylethynyl iodide (**2o**) and found that the

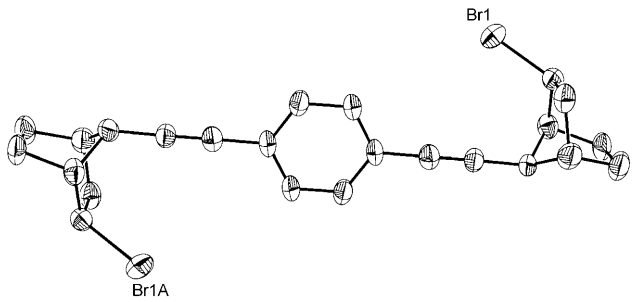
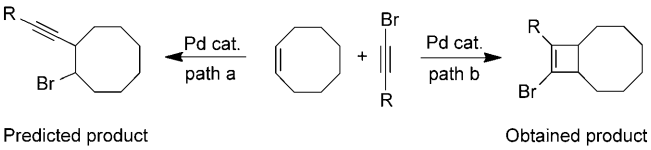


Figure 1. X-ray crystal structure of **3z**. Thermal ellipsoids set at 50% probability.

iodoalkynylation took place to give **3y** in excellent yields (Table 1, entry 25). The use of norbornenoic acid **1g** resulted in the exclusive formation of the 3-alkynyl derivative **3x** (Table 1, entry 24), thus indicating that the nucleophilic attack occurred prior to the rearrangement.[8] Unfortunately, the reaction of haloalkynes with open-chain alkenes, such as 4-octene, only afforded a mixture of products, and the reaction was unsuccessful with terminal alkenes.

The reaction between a bromoalkyne and cyclooctene is equally interesting, since the latter is more flexible compared to the strained norbornene derivatives. We predicted that the reaction should lead to a 2-propynyl bromide derivative (Scheme 5, path a). However, when the reaction was per-



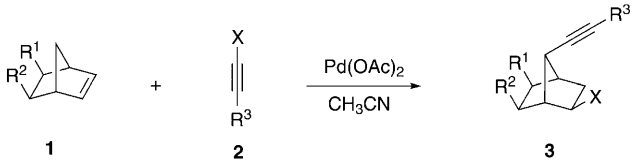
Scheme 5. Bromoalkynylation of cyclooctene.

formed under conditions similar to those described above, we found that this reaction resulted in the formation of a four-membered ring by a [2+2] cycloaddition reaction (Scheme 5, path b). To the best of our knowledge, the [2+2] cycloaddition of alkynes and monocyclic alkenes continues to represent a challenge.[9] This approach represents another utilization of haloalkynes for carbocycle formations that employ palladium catalysis.

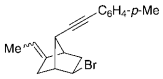
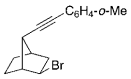
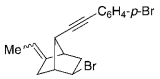
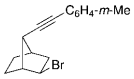
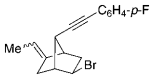
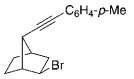
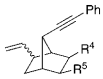
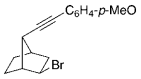
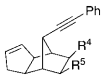
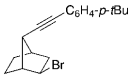
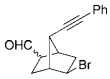
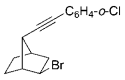
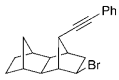
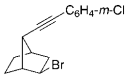
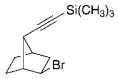
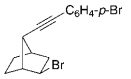
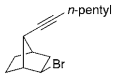
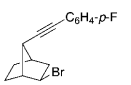
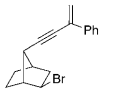
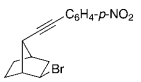
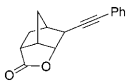
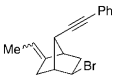
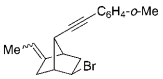
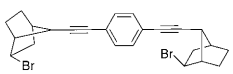
As shown in Scheme 6, aromatic alkynyl bromides with either electron-donating or electron-withdrawing groups attached to the benzene rings were able to smoothly undergo a [2+2] cycloaddition with cyclooctene, and generated the corresponding products in moderate to good yields. The reaction tolerated a variety of substituents including Cl, Br, F, and OMe groups. The steric hindrance associated with the alkynyl bromide also affected the yield of the reaction, as the introduction of an *o*-trifluoromethyl group onto the alkynyl bromide lowered the conversion of the haloalkyne (Scheme 6, **5o**). We also extended this reaction to phenylethynyl iodide (**2o**) and found that the [2+2] cycloaddition took place to give **5n** in good yield. Other alkenes such as cycloheptene were also subjected to this reaction, however, the yields decreased and the main products were inseparable from Alder–ene by-products.[9e] Furthermore, it was found that reactions with cyclododecene were completely ineffective. These observations indicate that the ring size of the alkene plays a major role in the formation of the desired product. Finally, the reaction of bromoalkyne **2e** with cyclopentene under typical palladium-catalyzed cross-coupling conditions gave enynes **6a** and **6b** in 87% yield, thus suggesting that the reaction involves the insertion of the alkene to an alkynyl palladium species rather than a palladium cyclopentene intermediate (Scheme 7a).[9]

To demonstrate the synthetic utility of cyclobutenyl bromide, we showed that the Pd/Cu-catalyzed coupling of **5b** with phenylacetylene gave enyne **7a** in 71% yield.

Table 1: Addition of haloalkynes to norbornene derivatives.[a]



1 **2** **3**

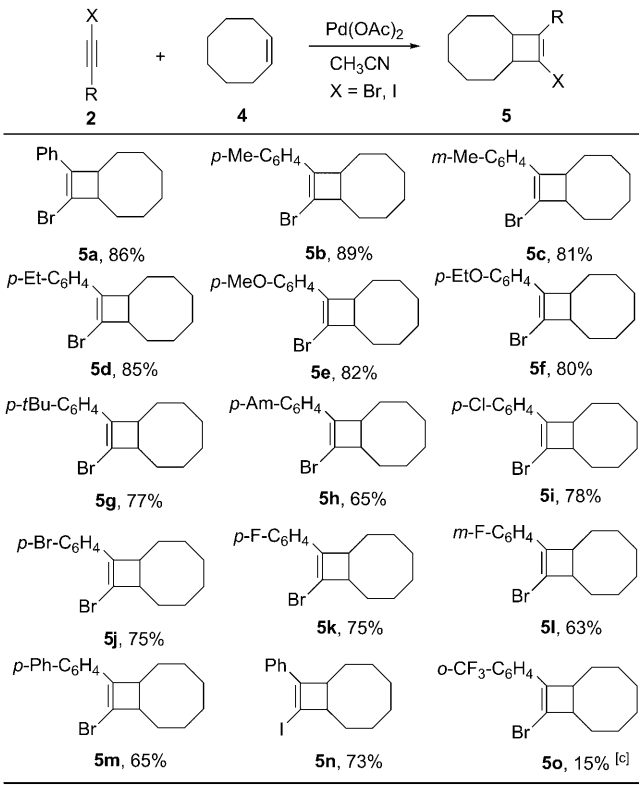
Entry	Alkene	Haloalkyne	Product	Yield [%][b]	Entry	Alkene	Haloalkyne	Product	Yield [%][b]
1	**1a**	**2a**	 **3a**	95	14	**1b**	**2d**	 **3n**	87
2	**1a**	**2b**	 **3b**	89	15	**1b**	**2i**	 **3o**	78
3	**1a**	**2c**	 **3c**	91	16	**1b**	**2j**	 **3p**	65
4	**1a**	**2d**	 **3d**	92	17	**1c**	**2a**	 **3q′**: $R^4=H$, $R^5=Br$ **3q″**: $R^4=Br$, $R^5=H$	87,[c] 1:1
5	**1a**	**2e**	 **3e**	96	18	**1d**	**2a**	 **3r′**: $R^4=H$, $R^5=Br$ **3r″**: $R^4=Br$, $R^5=H$	84,[c] 1:1
6	**1a**	**2f**	 **3f**	95	19	**1e**	**2a**	 **3s**	68[d]
7	**1a**	**2g**	 **3g**	81	20	**1f**	**2a**	 **3t**	87
8	**1a**	**2h**	 **3h**	85	21	**1a**	**2l**	 **3u**	82
9	**1a**	**2i**	 **3i**	84	22	**1a**	**2m**	 **3v**	91,[e] 1:1
10	**1a**	**2j**	 **3j**	83	23	**1a**	**2n**	 **3w**	67,[e] 4:1
11	**1a**	**2k**	 **3k**	83	24	**1g**	**2a**	 **3x**	95
12	**1b**	**2a**	 **3l**	85	25	**1a**	**2o**	 **3y**	91
13	**1b**	**2b**	 **3m**	83	26	**1a**	**2p**	 **3z**	73[f]

[a] Reaction conditions: $Pd(OAc)_2$ (5 mol%), alkene (1.3 mmol), haloalkyne (1.0 mmol), CH_3CN, 35 °C, 8–12 h. [b] Yields of isolated products. Some products contained 3–5% of an unidentified isomer that could not be removed by preparative TLC on silica gel or by column chromatography (see the Supporting Information). [c] The ratio of regioisomers was estimated by ^1H NMR analysis or GC-MS of the crude product. [d] *exo*/*endo* = 1:3. [e] Minor regioisomers were 2-bromo-3-alkynyl-norbornane derivatives. [f] The reaction was carried out with 3 equivalents of the alkene.

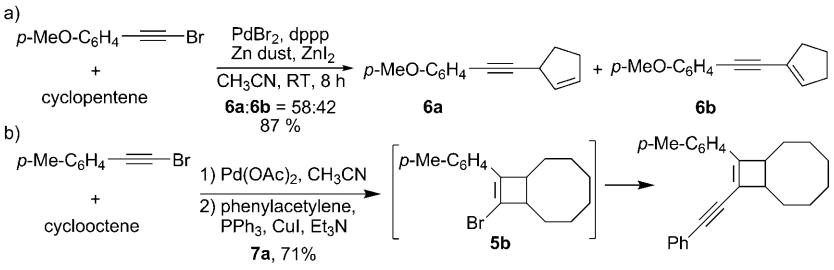
Compound **7a** is difficult to obtain through the direct cycloaddition between a diyne and a cycloalkene (Scheme 7b). The molecular structure of complex **7a** was established by X-ray crystallography (see the Supporting Information).

As shown in Scheme 8 for the reaction of bromoalkynes, the structures of the products depend on the employed cyclic alkenes. Norbornenes, which have strained structures, afforded noncrowded products, whereas the flexible cyclooctene led to strained four-membered-ring products. More interesting is that the cleavage of chemical bonds also depends on the cyclic alkenes. Although this distinct reactivity has not been thoroughly understood, it seems that the ring structure or ring constraints result in the formation of different products.

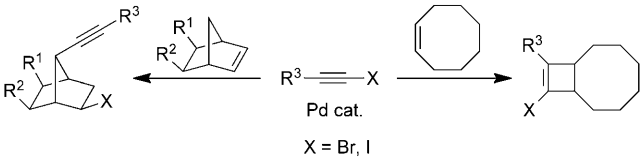
As the bromoalkynylation process involves several bond-forming and -migrating steps, it is currently difficult to make strong mechanistic implications. A pathway that involves a "bridging" palladium center seems most likely based on the stereoselective formation of *cis*-norbornyl products



Scheme 6. Cycloaddition of haloalkynes to cyclooctene. Reaction conditions: $Pd(OAc)_2$ (5 mol%), **2** (1.0 mmol), **4** (1.3 mmol), CH_3CN, 35 °C, 12–15 h. Yields of isolated products are reported. [a] GC-MS and NMR reveals the formation of Alder–ene products as inseparable mixtures.[9e] *p*-Am = *n*-pentyl.

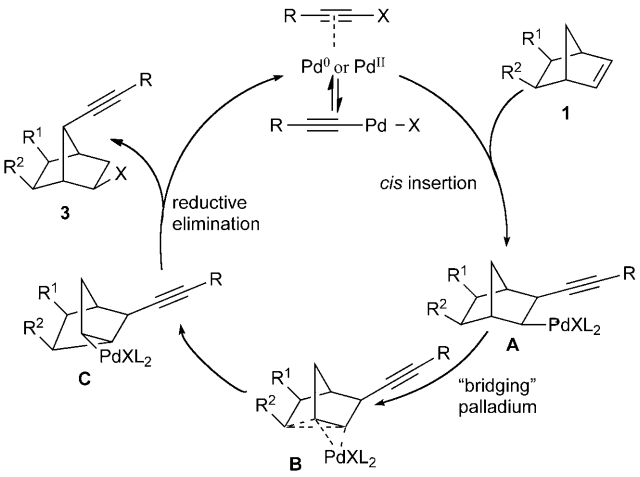


Scheme 7. Heck and Sonogashira cross-coupling reactions. dppp = 1,3-bis(diphenylphosphino)propane.



Scheme 8. Products from reactions of bromoalkynes with cyclooctene (flexible) and norbornene (strained).

(Scheme 9). At least two mechanisms involving Pd^0/Pd^{II} and Pd^{II}/Pd^{IV} can be envisaged.[10,11] We believe that this reaction is initialized by an oxidative addition of the Pd^0 or Pd^{II}



Scheme 9. Proposed mechanism for the bromoalkynylation reaction.

complex to the haloalkyne to form a high-valent alkyne–palladium species. The *cis*-alkynyl palladium intermediate **A** is then formed by the addition of the alkyne–palladium intermediate to the alkene. Subsequently, the "bridging" palladium complex **B** is generated, and the palladium is delivered to the bridgehead carbon on the same side as the incoming alkyne. Thus, the alkyl palladium halide intermediate **C** is formed with high stereoselectivity. A subsequent reductive elimination of **C** generates brominated product **3** and the active catalyst species.[12]

In conclusion, we have successfully developed a ring-structure-dependent synthesis of 7-alkynyl norbornanes and cyclobutenyl halides that occurs by the palladium-catalyzed bromoalkynylation of C–C double bonds. The reaction conditions are extremely mild and tolerate various functional groups. These novel processes not only represent the first examples of bromoalkynylation reactions of alkenes, but also afford 7-alkynyl norbornane products and cyclobutenyl bromides selectively with excellent atom economy. Current efforts are aimed at further elucidating the detailed reaction mechanism and applying these novel methods to the synthesis of complex and highly-functionalized molecules.

Experimental Section

Typical procedure for the reaction of phenylethynyl bromide and norbornene (Table 1, **3a**): $Pd(OAc)_2$ (12 mg, 0.05 mmol), CH_3CN (2 mL), NBE (122 mg, 1.3 mmol), and phenylethynyl bromide (180 mg, 1 mmol) were added successively to a Schlenk tube. After stirring for 10 h at 35 °C, the solution was filtered though a small amount of silica gel. The residue was purified by preparative TLC on silica gel (*n*-hexane) to furnish **3a** (260 mg, 95%) as a pale-yellow oil. IR (KBr): $\nu_{max} = 3051, 2965, 2874, 2226, 1597, 1489, 1444, 983, 757, 692\ cm^{-1}$; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.44–7.47$ (m, 2H), 7.25–7.28 (m, 3H), 3.96 (q, $J = 4.8$ Hz, 1H), 2.73(d, $J = 4.4$ Hz, 1H), 2.62–

2.66 (m, 2H), 2.47 (t, $J = 4.0$ Hz, 1H), 2.18 (q, $J = 8.0$ Hz, 1H), 1.58–1.68 (m, 2H), 1.15–1.28 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 131.2$, 131.2, 128.0, 128.0, 127.5, 123.9, 89.2, 84.4, 50.4, 49.7, 43.9, 42.7, 39.9, 29.4, 26.8 ppm; HRMS EI (m/z): calcd for $C_{15}H_{15}Br$, 274.0357; found, 274.0351.

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[1] a) T. Morishita, H. Yoshida, J. Ohshita, *Chem. Commun.* **2010**, *46*, 640 – 642; b) T. Wada, M. Iwasaki, A. Kondoh, H. Yorimitsu, K. Oshima, *Chem. Eur. J.* **2010**, *16*, 10671 – 10674.

[2] Y. Li, X. Liu, H. Jiang, Z. Feng, *Angew. Chem.* **2010**, *122*, 3410 – 3413; *Angew. Chem. Int. Ed.* **2010**, *49*, 3338 – 3341.

[3] For reviews on the application of norbornene derivatives, see: a) A. Martins, B. Mariampillai, M. Lautens, *Top. Curr. Chem.* **2010**, *292*, 1 – 33; b) K. C. Nicolaou, A. Ortiz, H. Zhang, P. Dagneau, A. Lanver, M. P. Jennings, S. Arseniyadis, R. Faraoni, D. E. Lizos, *J. Am. Chem. Soc.* **2010**, *132*, 7138 – 7152; c) Y. Cho, V. Zunic, H. Senboku, M. Olsen, M. Lautens, *J. Am. Chem. Soc.* **2006**, *128*, 6837 – 6846; d) M. A. Kinsella, V. J. Kalish, S. M. Weinreb, *J. Org. Chem.* **1990**, *55*, 105 – 111; e) B. Castagner, J. L. Leighton, *Tetrahedron* **2007**, *63*, 5895 – 5902; f) Y. Yoshida, J. Mohri, S. Ishii, M. Mitani, J. Saita, S. Matsui, H. Makio, T. Nakano, H. Tanaka, M. Onda, Y. Yamamoto, A. Mizuno, T. Fujita, *J. Am. Chem. Soc.* **2004**, *126*, 12023 – 12032; g) J. Holtsclaw, M. Koreeda, *Org. Lett.* **2004**, *6*, 3719 – 3722; h) A. Tsubata, T. Uchiyama, A. Kameyama, T. Nishikubo, *Macromolecules* **1997**, *30*, 5649 – 5654; i) I. Nishimura, A. Kameyama, T. Nishikubo, *Macromolecules* **1998**, *31*, 2789 – 2796; j) M. Waibel, N. Cramer, *Angew. Chem.* **2010**, *122*, 4557 – 4560; *Angew. Chem. Int. Ed.* **2010**, *49*, 4455 – 4458.

[4] a) Q. Liu, H. Duan, X. Luo, Y. Tang, G. Li, R. Huang, A. Lei, *Adv. Synth. Catal.* **2008**, *350*, 1349 – 1354; b) M. Catellani, E. Motti, N. D. Cá, *Acc. Chem. Res.* **2008**, *41*, 1512 – 1522; c) M. Catellani, *Top. Organomet. Chem.* **2005**, *14*, 21 – 53; d) D. A. Candito, M. Lautens, *Org. Lett.* **2010**, *12*, 3312 – 3315.

[5] a) W. C. Baird, Jr., *J. Org. Chem.* **1966**, *31*, 2411 – 2414; b) F. Chauvet, A. Heumann, B. Waegell, *J. Org. Chem.* **1987**, *52*, 1916 – 1922; c) D. D. Gültekin, Y. Taşkesenligil, A. Daştan, M. Balci, *Tetrahedron Lett.* **2008**, *64*, 4377 – 4383; d) L. F. Lourie, Y. A. Serguchev, G. V. Shevchenko, M. V. Ponomarenko, A. N. Chernega, E. B. Rusanov, J. A. K. Howard, *J. Fluorine Chem.* **2006**, *127*, 377 – 385; e) M. Mella, M. Fagnoni, A. Albini, *Org. Biomol. Chem.* **2004**, *2*, 3490 – 3495; f) J. D. Roberts, C. C. Lee, W. H. Saunders, Jr., *J. Am. Chem. Soc.* **1954**, *76*, 4501 – 4510; g) S. Winstein, D. S. Trifan, *J. Am. Chem. Soc.* **1949**, *71*, 2953 – 2953; h) E. M. Arnett, N. Rienta, C. Petro, *J. Am. Chem. Soc.* **1980**, *102*, 398 – 400.

[6] a) P. Fackler, C. Berthold, F. Voss, T. Bach, *J. Am. Chem. Soc.* **2010**, *132*, 15911 – 15913; b) R. C. Larock, D. R. Leach, S. M. Bjorge, *J. Org. Chem.* **1986**, *51*, 5221 – 5226; c) D. G. Lonergan, G. Deslongchamps, *Tetrahedron* **1998**, *54*, 14041 – 14052; d) K. Kohno, K. Nakagawa, T. Yahagi, J. C. Choi, H. Yasuda, T. Sakakura, *J. Am. Chem. Soc.* **2009**, *131*, 2784 – 2785.

[7] a) Y. Takayama, C. Delas, K. Muraoka, F. Sato, *Org. Lett.* **2003**, *5*, 365 – 368; b) Y. Nakano, K. Ishizuka, K. Muraoka, H. Ohtani, Y. Takayama, F. Sato, *Org. Lett.* **2004**, *6*, 2373 – 2376; c) M. Kivala, F. Mitzel, C. Boudon, J. P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Chem. Asian J.* **2006**, *1*, 479 – 489.

[8] a) K. C. Nicolaou, S. P. Seitz, W. J. Sipio, J. F. Blount, *J. Am. Chem. Soc.* **1979**, *101*, 3884 – 3893; b) R. M. Trend, Y. K. Ramtohul, B. M. Stoltz, *J. Am. Chem. Soc.* **2005**, *127*, 17778 – 17788; c) L. Zhou, C. K. Tan, X. Jiang, F. Chen, Y. Y. Yeung, *J. Am. Chem. Soc.* **2010**, *132*, 15474 – 15476; d) S. R. Mellegaard, J. A. Tunge, *J. Org. Chem.* **2004**, *69*, 8979 – 8981.

[9] For reviews on [2+2] cycloadditions, see: a) M. Lautens, W. Klute, W. Tam, *Chem. Rev.* **1996**, *96*, 49 – 92; b) K. Villeneuve, N. Riddell, R. W. Jordan, G. C. Tsui, W. Tam, *Org. Lett.* **2004**, *6*, 4543 – 4546; c) A. Allen, K. Villeneuve, N. Cockburn, E. Fatila, N. Riddell, W. Tam, *Eur. J. Org. Chem.* **2008**, 4178 – 4192; d) J. Treutwein, G. Hilt, *Angew. Chem.* **2008**, *120*, 6916 – 6919; *Angew. Chem. Int. Ed.* **2008**, *47*, 6811 – 6813; e) G. Hilt, A. Paul, J. Treutwein, *Org. Lett.* **2010**, *12*, 1536 – 1539; f) V. López-Carrillo, A. M. Echavarren, *J. Am. Chem. Soc.* **2010**, *132*, 9292 – 9294; g) K. C. Chao, D. K. Rayabarapu, C. C. Wang, C. H. Cheng, *J. Org. Chem.* **2001**, *66*, 8804 – 8810; h) D. J. Huang, D. K. Rayabarapu, L. P. Li, T. Sambaiah, C. C. Cheng, *Chem. Eur. J.* **2000**, *6*, 3706 – 3713; i) T. Shibata, K. Takami, A. Kawachi, *Org. Lett.* **2006**, *8*, 1343 – 1345; j) B. M. Fan, X. J. Li, F. Z. Peng, H. B. Zhang, A. S. C. Chan, Z. H. Shao, *Org. Lett.* **2010**, *12*, 304 – 306; k) K. Villeneuve, W. Tam, *Angew. Chem.* **2004**, *116*, 620 – 623; *Angew. Chem. Int. Ed.* **2004**, *43*, 610 – 613; l) N. Riddell, W. Tam, *J. Org. Chem.* **2006**, *71*, 1934 – 1937; m) R. W. Jordan, K, Villeneuve, W. Tam, *J. Org. Chem.* **2006**, *71*, 5830 – 5833; n) N. Cockburn, E. Karimi, W. Tam, *J. Org. Chem.* **2009**, *74*, 5762 – 5765.

[10] For reviews on the oxidative addition of a haloalkyne with low-valent palladium to give an alkynylpalladium(II) intermediate, see: a) W. Shi, Y. Luo, X. Luo, L. Chao, H. Zhang, J. Wang, A. Lei, *J. Am. Chem. Soc.* **2008**, *130*, 14713 – 14720; b) I. V. Seregin, V. Ryabova, V. Gevorgyan, *J. Am. Chem. Soc.* **2007**, *129*, 7742 – 7743.

[11] The insertion of a simple palladium salt into an alkynyl bromide is rare, however, the formation of an alkynylpalladium(IV) complex was achieved with haloalkyne derivatives as oxidative reagents. See: a) S. Nicolai, S. Erard, D. F. González, J. Waser, *Org. Lett.* **2010**, *12*, 384 – 387; b) K. Muñiz, *Angew. Chem.* **2009**, *121*, 9576 – 9588; *Angew. Chem. Int. Ed.* **2009**, *48*, 9412 – 9423; c) A. J. Canty, T. Rodemann, B. W. Skelton, A. H. White, *Organometallics* **2006**, *25*, 3996 – 4001; d) F. Kessler, N. Szesni, K. Põhako, B. Weibert, H. Fischer, *Organometallics* **2009**, *28*, 348 – 354; e) K. M. Gericke, D. I. Chai, N. Bieler, M. Lautens, *Angew. Chem.* **2009**, *121*, 1475 – 1479; *Angew. Chem. Int. Ed.* **2009**, *48*, 1447 – 1451; f) A. S. Dudnik, V. Gevorgyan, *Angew. Chem.* **2010**, *122*, 2140 – 2142; *Angew. Chem. Int. Ed.* **2010**, *49*, 2096 – 2098.

[12] The reductive elimination of aryl halides from Pt^{IV}, Pd^{IV}, Pd^{III}, and Pd^{II} complexes has been demonstrated. See: a) X. Zhao, V. M. Dong, *Angew. Chem.* **2011**, *123*, 962 – 964; *Angew. Chem. Int. Ed.* **2011**, *50*, 932 – 934; b) A. Yahav-Levi, I. Goldberg, A. Vigalok, *J. Am. Chem. Soc.* **2006**, *128*, 8710 – 8711; c) S. R. Whitfield, M. S. Sanford, *J. Am. Chem. Soc.* **2007**, *129*, 15142 – 15143; d) T. Furuya, T. Ritter, *J. Am. Chem. Soc.* **2008**, *130*, 10060 – 10061; e) D. C. Power, T. Ritter, *Nat. Chem.* **2009**, *1*, 302 – 309; f) S. G. Newman, M. Lautens, *J. Am. Chem. Soc.* **2011**, *133*, 1778 – 1780; g) D. Kalyani, M. S. Sanford, *J. Am. Chem. Soc.* **2008**, *130*, 2150 – 2151; h) X. Shen, A. M. Hyde, S. L. Buchwald, *J. Am. Chem. Soc.* **2010**, *132*, 14076 – 14078; i) A. H. Roy, J. F. Hartwig, *J. Am. Chem. Soc.* **2003**, *125*, 13944 – 13945.

