17.4 ppm; b) **11**: m.p. 77 °C; $[\alpha]^{D}_{25} = -157.6$ ($c = 1.02$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.12$–4.08 (m, 2H; CH,C*H*H), 3.94 (dd, $J = 12.0$, 5.0 Hz, 1H; C*H*H), 3.76 (s, 3H; CO_2CH_3), 3.28 (s, 3H; OCH_3), 3.26 (s, 3H; OCH_3), 1.32 (s, 3H; CCH_3), 1.27 ppm (s, 3H; CCH_3); ^{13}CNMR (100 MHz, $CDCl_3$): $\delta = 171.0$, 99.6, 98.7, 68.1, 57.7, 51.9, 50.0, 48.2, 17.9, 17.7 ppm; c) **12**: m.p. 77 °C; $[\alpha]^{D}_{25} = -266.5$ ($c = 1.6$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.73$ (s, 1H; CHO), 4.07 (d, $J = 11.6$ Hz, 1H; C*H*H), 3.91–3.86 (m, 1H; C*H*H), 3.77 (d, $J = 4.4$ Hz, 1H; CH), 3.38 (s, 3H; OCH_3), 3.28 (s, 3H; OCH_3), 1.37 (s, 3H; CCH_3), 1.24 ppm (s, 3H; $C(CH_3)$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 201.2$, 99.4, 98.5, 74.6, 55.6, 50.3, 48.2, 17.8, 17.7 ppm.

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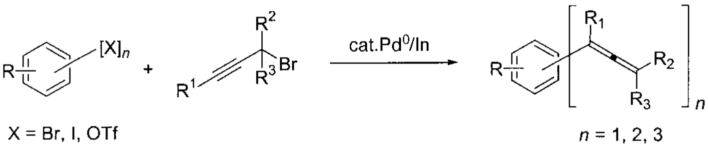
[9] CCDC-186381 to CCDC-186386 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Highly Efficient Catalytic Synthesis of Substituted Allenes Using Indium[**]

Kooyeon Lee, Dong Seomoon, and Phil Ho Lee[*]

Since allenes are versatile building blocks both for organic synthesis[1] and in transition-metal-promoted carbon–carbon bond-forming reactions,[2] development of practical methods for their preparation is of great interest. Allene moieties can be prepared by alkylation of allenylmethyl halides with an appropriate carbanionic species,[1e] by S_N2'-type selective displacement of propargyl alcohol derivatives with organocopper reagents,[1e,3] and by intramolecular regio- and stereoselective reduction of alkynes.[4] The synthesis of allenes by metal-catalyzed cross-coupling reactions is an alternative method;[5] however, some disadvantages are the inconvenient preparation of the reagents, limited substrate scope, and incompatibility of sensitive groups to the reaction conditions.[6] Recently, several reports have described the synthesis of allenes with transition metal complexes.[5] Despite this recent progress a method for the highly efficient and catalytic synthesis of substituted allenes is still needed. We have realized this goal (Scheme 1) as part of our continuing studies directed toward the development of efficient indium-mediated reactions.[7], [8]

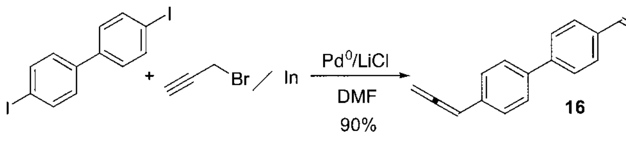
The catalytic activity of several palladium complexes was initially examined in the reaction of 1-iodonaphthalene with allenylindium. The best results were obtained with 4 mol% $[Pd(PPh_3)_4]$ in the presence of 3 equivalents of LiI in DMF at 100 °C under a nitrogen atmosphere (see Experimental Section), and 1-allenylnaphthalene was produced in quantitative yield (98%) with complete regioselectivity (Table 1, entry 1). The allenylindium reagent generated in situ from the reaction of 1 equivalent of indium with 1.5 equivalents of propargyl bromide gave the best results as a coupling partner.[9]



Scheme 1. Palladium-catalyzed cross-coupling reaction mediated by indium. Tf = trifluoromethanesulfonyl.

To demonstrate the efficiency and scope of the present method, we applied this catalytic system to a variety of propargyl halides and organic electrophiles. For the propargyl halides as coupling partners, the presence of various alkyl substituents at the α and γ positions had little effect on either the reaction rate or the product yield (Table 1). Under the optimized conditions, treatment of iodobenzene with 3-bromo-1-phenyl-1-butyne and indium gave selectively trisubstituted allene **2** in 80% yield (entry 2). Varying the electron demand of the substituents on the arene did not diminish the efficiency and selectivity (entries 3, 7–9). It is noteworthy that protection of an oxo group and a hydroxy group on substrates is not necessary, as demonstrated by the reactions of 4-iodoacetophenone (entry 5) and 3-iodophenol (entry 6), respectively. Hetero substituents turned out to be compatible with the reaction conditions (entry 10). The method worked equally well with vinyl halides (entries 11 and 12) and imidoyl bromide (entry 13). Treatment of iodophenylacetylene with allenylindium produced 3-methyl-1-phenyl-3,4-pentadien-1-yne (**14**) in 91% yield (entry 14). In the case of vinyl triflate, the desired product **15** was obtained in 90% yield (entry 15). Surprisingly, no propargylic cross-coupling product is formed in any reactions.

We then applied the present method to polyhalogenated aromatic compounds to obtain polyallenyl-substituted arenes, which can be used effectively in material and polymer sciences. Reaction of 4,4′-diiodobiphenyl with two equivalents of allenylindium produced 4,4′-diallenylbiphenyl **16** in 90% yield [Eq. (1)]. We were pleased to observe that treatment of 1,3,5-tribromobenzene with 1-bromo-2-butyne and indium selectively gave 1,3,5-tri(1′-methylallenyl)benzene (**17**) in 70% yield [Eq. (2)]. On the basis of these results, unsym-



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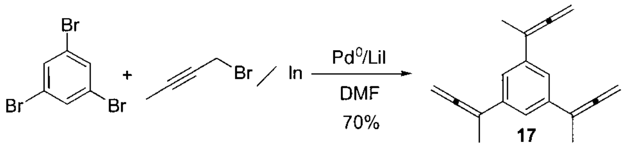

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[*] Prof. Dr. P. H. Lee, K. Lee, D. Seomoon
Department of Chemistry, Kangwon National University
Chunchon 200-701 (Korea)
Fax: (+82)33-253-7582
E-mail: phlee@kangwon.ac.kr

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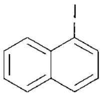
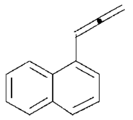
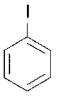
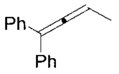
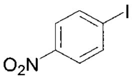
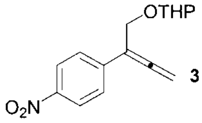
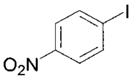
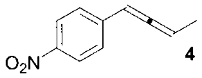
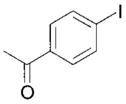
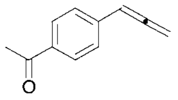
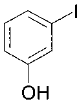
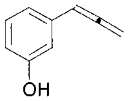
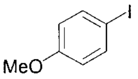
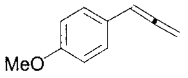
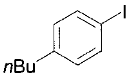
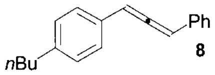
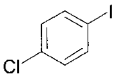
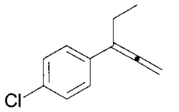
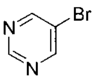
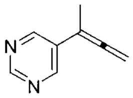
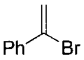
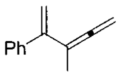
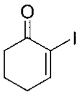
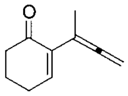
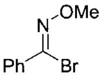
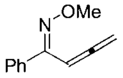
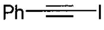
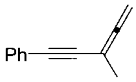
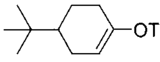
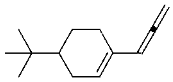
Table 1. Palladium-catalyzed cross-coupling reactions of in-situ-generated allenylindium reagents with organic acceptors.

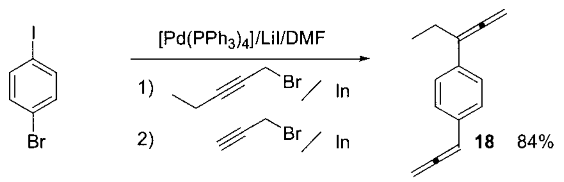
Entry	Acceptor	R^1	R^2	R^3	Product	Yield [%][a]
1		H	H	H	 **1**	98 97[b] 22[c](58)[d] 97[e] 84[f]
2		Ph	Me	H	 **2**	80
3		$THPOCH_2$[g]	H	H	 **3**	91
4		H	H	Me	 **4**	90
5		H	H	H	 **5**	87[b]
6		H	H	H	 **6**	90[b]
7		H	H	H	 **7**	91[b] 66[f]
8		H	H	Ph	 **8**	90
9		Et	H	H	 **9**	96
10		Me	H	H	 **10**	92
11		Me	H	H	 **11**	91
12		Me	H	H	 **12**	90
13		H	H	H	 **13**	86[b]
14		Me	H	H	 **14**	91
15		H	H	H	 **15**	90[b]

[a] Yield of isolated product. The reaction was performed in the presence of 4 mol% $[Pd(PPh_3)_4]$ and 3 equiv LiI in DMF at 100 °C; allenylindium was obtained from the reaction of 1 equiv indium with 1.5 equiv propargyl bromide unless otherwise noted. [b] 3 Equiv LiCl was used. [c] 1 Equiv LiCl was used. [d] Yield of recovered 1-iodonaphthalene. [e] LiBr was used. [f] THF was used as a solvent. [g] THP = tetrahydropyranyl.

metrical bis(allenes) **18** and **19** were prepared chemoselectively and regioselectively in one pot from 4-bromoiodobenzene and 2,5-dibromopyridine in good yields [Eqs. (3) and (4)].

Iodobenzene was treated with 1-bromo-2,7-octadiyne and indium to produce allenyne **20** in 92% yield, which is a useful compound in palladium-catalyzed carbocyclization [Eq. (5)].[2p] Interestingly, the double cross-coupling reaction of two equivalents of ethyl 4-iodobenzoate with one equivalent of 1,10-dibromo-2,8-decadiyne in the presence of indium yielded bis(allene) **21** in 68% yield [Eq. (6)].[2o]

In conclusion, we have demonstrated for the first time that allenylindium reagents generated in situ from the reaction of



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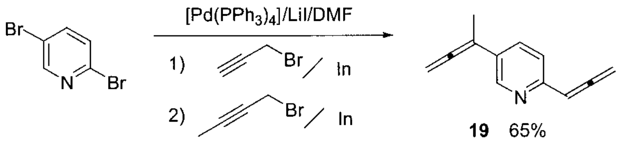

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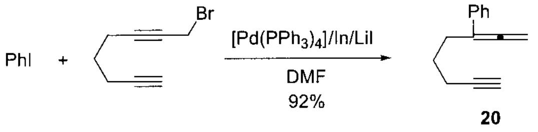

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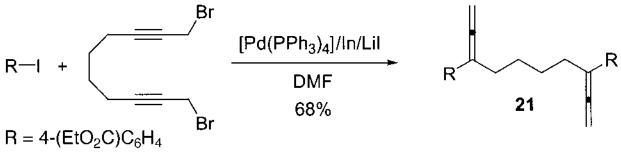

(6)

indium with propargyl bromides can be employed as effective cross-coupling partners in palladium-catalyzed cross-coupling reactions with a variety of organic electrophiles to produce substituted allenes, polyallenes, and unsymmetrical bis(allenes) in excellent yields with complete regioselectivity and chemoselectivity.

Experimental Section

Typical experimental procedure: 1-Iodonaphthalene (127.0 mg, 0.5 mmol) was added at room temperature under a nitrogen atmosphere to a suspension of [Pd(PPh$_3$)$_4$] (23.1 mg, 4 mol %) and lithium iodide (200.8 mg, 1.5 mmol) in DMF (1 mL). After 15 min the allenylindium reagent, which was generated from propargyl bromide (89.2 mg, 0.75 mmol) and indium (57.0 mg, 0.5 mmol) in DMF (1 mL), was added, and the mixture was stirred at 100 °C for 1 h. The reaction mixture was quenched with saturated aqueous NaHCO$_3$. The aqueous layer was extracted with diethyl ether (3 × 20 mL), and the combined organic solvents were washed with water and brine, dried with MgSO$_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with *n*-hexane to give 1-allenylnaphthalene (81.3 mg, 98 %).

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