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Triethylborane-Mediated Hydrogallation and Hydroindation: Novel Access to Organogalliums and Organoindiums

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Hydrogallation of carbon−carbon multiple bonds proceeds in the presence of triethylborane as a radical initiator. Several functionalities do not interfere with this reaction. Resulting alkenyl- and alkylgallium species can be trapped by several electrophiles. Highly regioselective radical addition of an indium hydride reagent to alkynes is also achieved. Various functionalities are tolerant under the reaction conditions. The reaction proceeds with complete anti stereoselectivity. Alkenylindiums obtained via hydroindation can be employed for the following cross-coupling reaction with aryl halides in one pot.

Introduction

Hydroboration and hydroalumination are reliable ways to reduce carbon−carbon multiple bonds.[1] In addition, alkenyl- and alkylmetals formed via hydrometalation are versatile reagents which can be utilized in various reactions. However, hydroboration and hydroalumination usually proceed in a syn fashion. For instance, hydroboration of alkynes always provides (*E*)-alkenylboranes selectively. Preparation of (*Z*)-alkenylboranes from alkynes needs several steps.[2] Moreover, it is necessary to protect functionalities such as hydroxy and carboxy groups before performing hydroboration. Operationally simple methods which are widely adaptable for the preparation of various (*Z*)-alkenylmetals from alkynes are limited. In the meantime, gallium[3−5] and indium[6] hydride reagents were not well-investigated. Herein we wish to report triethylborane-mediated[7] hydrogallation and hydroindation reactions of carbon−carbon multiple bonds.

Results and Discussion

Hydrogallation of Alkynes. The gallium hydride reagent ($HGaCl_2$) was prepared by mixing a hexane solution of gallium trichloride (1.0 M, 1.5 mL, 1.5 mmol) and a toluene solution of Red-Al (2.0 M, 0.375 mL, 0.75 mmol) in THF at 0 °C (Scheme 1).[8] To the solution were added 1-dodecyne (1.0 mmol) and triethylborane (0.20 mmol). After 4 h, the reaction was quenched with 1.0 M HCl. Silica gel column purification provided 1-dodecene in 84% yield. An addition of 1.0 M DCl/D_2O instead of hydrochloric acid to the reaction mixture afforded 1-deuterio-1-dodecene in 84% yield as a mixture of stereoisomers ($E/Z = 80/20$). The choice of DIBAL-H as a reducing

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[1] (a) Pelter, A.; Smith, K.; Brown H. C. *Borane Reagents*; Academic Press: London, UK, 1988. (b) Seyden-Penne, J. *Reductions by the Alumino- and Borohydrides in Organic Synthesis*; VCH: New York, 1991. (c) *Comprehensive Organic Chemistry*; Pergamon Press: New York, 1979; Vol. 8.

[2] (a) Brown, H. C.; Imai, T. *Organometallics* **1984**, *3*, 1392−1395. (b) Negishi, E.; Williams, R. M.; Lew, G.; Yoshida, T. *J. Organomet. Chem*. **1975**, *92*, C4−C6. (c) Campbell, J. B., Jr.; Molander, G. A. *J. Organomet. Chem*. **1978**, *156*, 71−79. (d) Srebnik, M.; Bhat, N. G.; Brown, H. C. *Tetrahedron Lett*. **1988**, *29*, 2635−2638. (e) Deloux, L.; Srebnik, M. *J. Org. Chem*. **1994**, *59*, 6871−6873. (f) Takahashi, K.; Takagi, J.; Ishiyama, T.; Miyaura, N. *Chem. Lett*. **2000**, 126−127.

[3] Reduction of alkynes with gallium hydride compounds was reported. Ohshita, J.; Schmidbaur, H. *J. Organomet. Chem*. **1993**, *453*, 7−12.

[4] Reduction of organic halides and carbonyl compounds with $MGaH_4$ (M = Li, Na, K) was reported. (a) Schmidba, H.; Findeiss, W.; Gast, E. *Angew. Chem., Int. Ed. Engl*. **1965**, *4*, 152. (b) Choi, J. H.; Yun, J. H.; Hwang, B. K.; Baek, D. J. *Bull. Korean Chem. Soc*. **1997**, *18*, 541−542. (c) Kim, J. S.; Choi, J. H.; Kim, H. D.; Yun, J. H.; Joo, C. Y.; Baek, D. J. *Bull. Korean Chem. Soc*. **1999**, *20*, 237−240. (d) Choi, J. H.; Yoon, Y. G. *Bull. Korean Chem. Soc*. **1995**, *16*, 469−470. (e) Choi, J. H.; Oh, Y. J. *Bull. Korean Chem. Soc*. **1995**, *16*, 474−475. (f) Choi, J. H.; Yoon, M. Y.; Yun, J. H.; Chung, D. W. *Bull. Korean Chem. Soc*. **1995**, *16*, 416−421. Review on gallium hydrides: (g) Barron, A. R.; MacInnes, A. N. In *Encyclopedia of Inorganic Chemistry*, King, R. B., Ed.; John Wiley & Sons: Chichester, UK, 1994; Vol. 3, p 1249.

[5] Triethylborane-mediated radical reduction of organic halides with the gallium hydride reagent was reported. Mikami, S.; Fujita, K.; Nakamura, T.; Yorimitsu, H.; Shinokubo, H.; Matsubara, S.; Oshima, K. *Org. Lett*. **2001**, *3*, 1853−1855.

[6] (a) Wiberg, E.; Schmidt, M. *Z. Naturforsch*. **1957**, *12b*, 54−58. (b) Yamada, M.; Tanaka, K.; Araki, S.; Butsugan, Y. *Tetrahedron Lett*. **1995**, *36*, 3169−3172. (c) Takami, K.; Yorimitsu, H.; Oshima, K. *Org. Lett*. **2002**, *4*, 2993−2995. (d) Miyai, T.; Inoue, K.; Yasuda, M.; Shibata, I.; Baba, A. *Tetrahedron Lett*. **1998**, *39*, 1929−1932. (e) Inoue, K.; Yasuda, M.; Shibata, I.; Baba, A. *Tetrahedron Lett*. **2000**, *41*, 113−116. (f) Inoue, K.; Shibata, I.; Baba, A. *Tetrahedron Lett*. **2001**, *42*, 4661−4663. (g) Inoue, K.; Sawada, A.; Shibata, I.; Baba, A. *J. Am. Chem. Soc*. **2002**, *124*, 906−907. (h) Inoue, K.; Ishida, T.; Shibata, I.; Baba, A. *Adv. Synth. Catal*. **2002**, *344*, 283−287. (i) Ranu, B. C.; Samanta, S. *Tetrahedron Lett*. **2002**, *43*, 7405−7407.

[7] (a) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc*. **1987**, *109*, 2547−2548. (b) Oshima, K.; Utimoto, K. *J. Synth. Org. Chem., Jpn*. **1989**, *47*, 40−52. (c) Yorimitsu, H.; Oshima, K. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Chapter 1.2. (d) Ollivier, C.; Renaud, P. *Chem. Rev*. **2001**, *101*, 3415−3434.

[8] We have not succeeded in obtaining the spectral evidence of $HGaCl_2$ at this stage. See also ref 13.

10.1021/jo0344790 CCC: $25.00

SCHEME 1

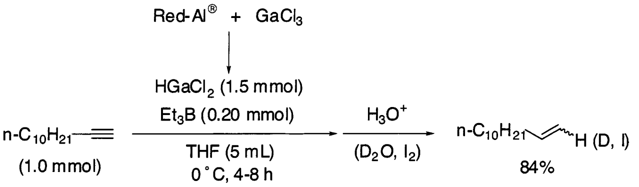
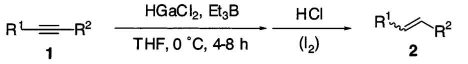
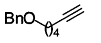
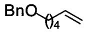
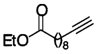
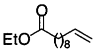
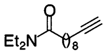
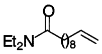
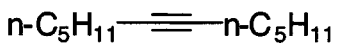
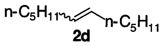
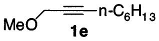
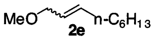
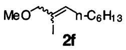
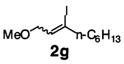
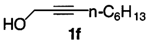
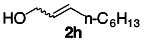
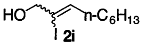


TABLE 1. Hydrogallation of Alkynes[a]



Entry	1	HGaCl$_2$ /equiv	2	Yield/%[b]
1	 **1a**	1.5	 **2a**	76
2	 **1b**	1.5	 **2b**	74
3	 **1c**	1.5	 **2c**	89
4	 **1d**	2.0	 **2d**	90 (59/41)
5	 **1e**	2.0	 **2e**	75 (87/13)
6[c]	**1 e**	2.0	 **2f**  **2g**	76 (**2f**/**2g** = 82/18)
7	 **1f**	3.0	 **2h**	69 (92/8)
8[c]	**1 f**	3.0	 **2i**	51

[a] Alkyne (1.0 mmol), Et$_3$B (0.20 mmol), and THF (5 mL) were used. [b] Isolated yields. *E*/*Z* ratios are in parentheses. [c] Reaction was quenched with iodine.

agent instead of Red-Al provided 1-deuterio-1-dodecene (84% yield) with a slightly lower selectivity (*E*/*Z* = 77/23). Without triethylborane, the reaction did not proceed at all. In addition, a catalytic amount of TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) inhibited the reaction completely. These results strongly suggest that the reaction proceeds via a radical mechanism.

Various alkynes can be employed in this hydrogallation reaction. The results are summarized in Table 1. It is noteworthy that functional groups such as ether and ester moieties did not interfere with the triethylborane-induced reduction, whereas hydroalumination often requires the absence of such coordinating groups. Hydrogallation of internal alkynes also proceeded smoothly, although the products were obtained as a mixture of *E*/*Z* isomers.

To clarify the reaction course, the reaction of 1-dodecyne with the gallium hydride was investigated in detail. We found that the stereochemical outcome of the product heavily depended on the reaction time. Quenching the reaction with 1.0 M DCl/D$_2$O after 2.5 h provided 1-deuterio-1-dodecene in 55% yield as a mixture of stereoisomers (*E*/*Z* = 28/72). The *E*/*Z* ratios of 1-deuterio-1-dodecene varied depending on the reaction time, and the ratios were *E*/*Z* = 56/44 at 3.0 h (61% yield) and *E*/*Z* = 80/20 at 4.0 h (84% yield). The change of the *E*/*Z* ratios suggests that the reaction initially provides (*Z*)-alkenylgallium, which then isomerizes to its (*E*)-isomer. A plausible mechanism is depicted in Scheme 2. A gallium radical ($^{\bullet}GaCl_2$), generated by the action of an ethyl radical on HGaCl$_2$, adds to 1-alkyne to afford alkenyl radical **3**. Radical **3** isomerizes into **4**. Hydrogen donation to **3** rather than to **4** is kinetically preferred because radical **3** is more accessible for gallium hydride as depicted in drawing **A**, thereby yielding (*Z*)-alkenylgallium **5** as a major product at the initial stage of the reaction. Isomerization into the (*E*)-alkenylgallium compound proceeds via a gallium radical addition−elimination sequence:[9] An addition of the gallium radical to (*Z*)-alkenylgallium **5** provides a dimetallic radical species **7** or **8**. Rotation around the Cα−Cβ bond followed by elimination of the gallium radical enables conversion into the more thermodynamically stable (*E*)-alkenylgallium species **6**.

Cross-Coupling Reaction of Aryl Halides with Alkenylgalliums Prepared via Hydrogallation of Alkynes. Next, we tried to employ the alkenylgalliums provided via hydrogallation for the following cross-coupling reaction[10] in one pot (Scheme 3). HGaCl$_2$ (3.0 mmol) prepared as aforementioned was treated with 1-dodecyne (1.5 mmol) and triethylborane (0.30 mmol) to prepare an alkenylgallium species. After removal of THF by reducing pressure, DMSO (5 mL), 3-iodoanisole (1.0 mmol), and palladium catalyst[11] were sequentially added. Heating the resulting mixture at 80 °C for 4 h afforded the cross-coupling products **9a** (*E*/*Z* = 66/34, 31% yield) and **10a** (18% yield). Not only 3-iodoanisole but also 3-iodophenol could be employed in this cross-coupling reaction.

Hydrogallation of Alkenes. The radical addition of HGaCl$_2$ to 1-alkenes proceeded similarly to yield alkylgallium species (Scheme 4). In contrast to the case with alkynes, hydrolysis of the resultant alkylgallium compounds required forcing reaction conditions. After hydrogallation of 1-dodecene, an excess of methyllithium (9.0 equiv) was added to the reaction mixture. Subsequent exposure to concentrated hydrochloric acid (37 wt %) for 1 h provided dodecane in 85% yield. On the other hand, the reaction of an internal alkene, such as 6-dodecene, provided none of hydrogallation products.

Hydrogallation of allenes provided allylic gallium compounds. The addition of the gallium radical mainly occurred at the terminal carbon (Scheme 5). Diene **11** was obtained as a byproduct via dimerization of an allylic radical generated by the attack of the gallium radical at the 2 position. The allylic gallium reagent prepared by this method reacted with electrophiles, such as D$_2$O and benzaldehyde, to provide the corresponding products in moderate yields.[12]

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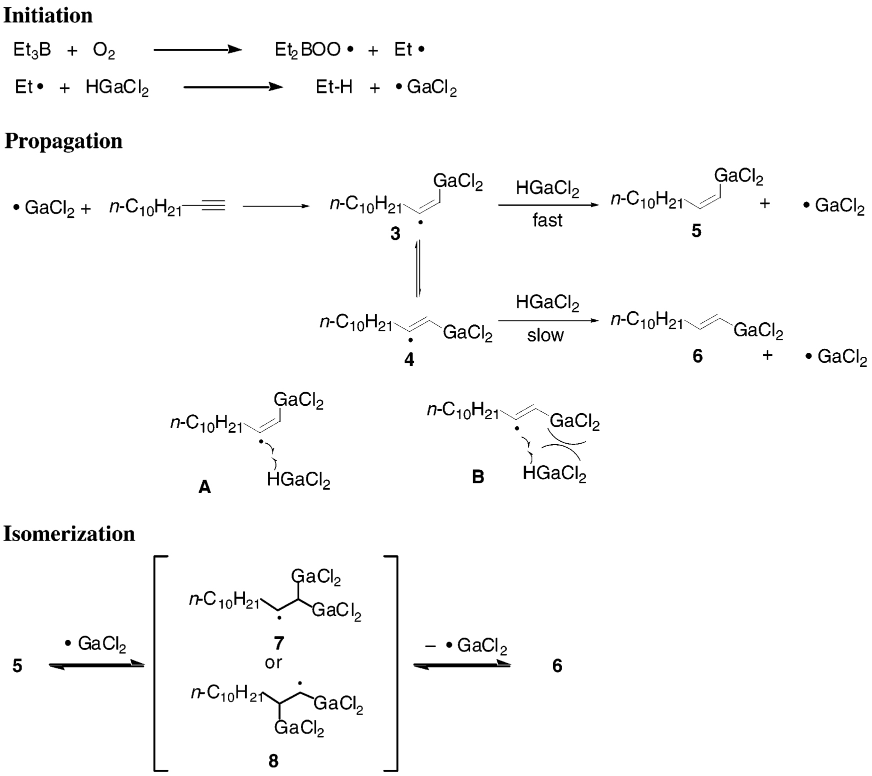
(9) The same isomerization reaction of alkenyl germanes has been reported. Ichinose, Y.; Nozaki, K.; Wakamatsu, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 3709−3712.

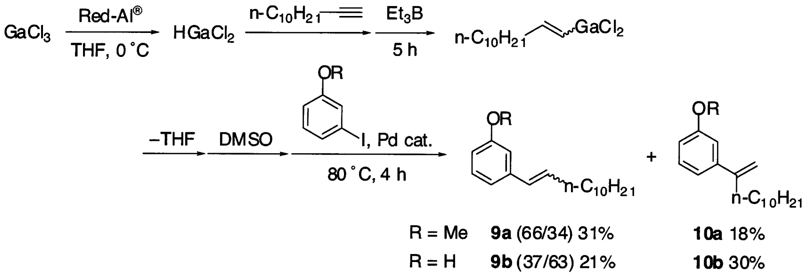
(10) Mikami, S.; Yorimitsu, H.; Oshima, K. *Synlett* **2002**, *7*, 1137−1139.

(11) The palladium catalyst was prepared from Pd$_2$(dba)$_3$·CHCl$_3$ (0.010 mmol) and tri-*o*-tolylphosphine (0.040 mmol) in DMSO (1 mL) in another reaction flask under an argon atmosphere.

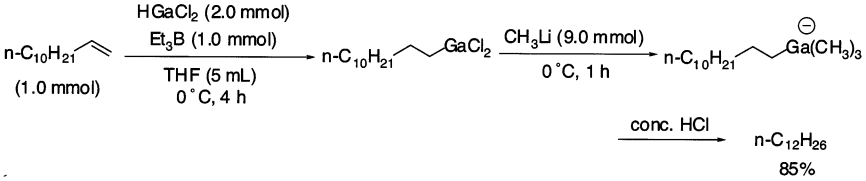
SCHEME 2



SCHEME 3



SCHEME 4



Hydroindation of Alkynes. Treatment of $InCl_3$ (1.35 mmol) in THF with DIBAL-H (1.30 mmol) at 0 °C yielded dichloroindium hydride ($HInCl_2$).[13] To the solution were sequentially added at −78 °C 1-dodecyne (1.0 mmol) and a catalytic amount of triethylborane (0.20 mmol) as a radical initiator. The resulting solution was stirred for 2.5 h at the same temperature. Acidic workup followed by silica gel column purification provided 1-dodecene almost quantitatively (Scheme 6). Hydroindation of 1-dodecyne proceeded in an anti fashion to yield (*Z*)-1-dodecenylindium. Quenching with 1.0 M DCl/D_2O yielded (*Z*)-1-deuterio-1-dodecene exclusively (96%D, $E/Z < 1/99$). Iodolysis of the reaction mixture also afforded the corresponding (*Z*)-isomer selectively[14] in 92% yield. Using Red-Al in place of DIBAL-H resulted in a much lower

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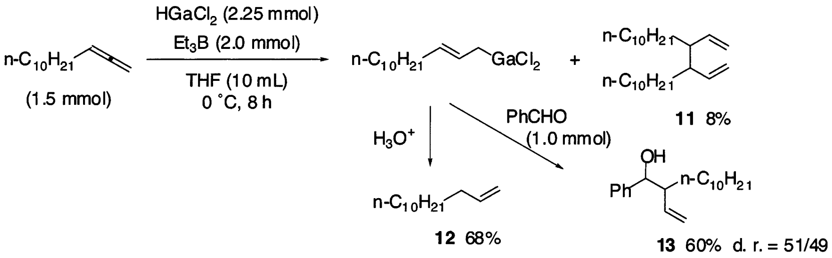
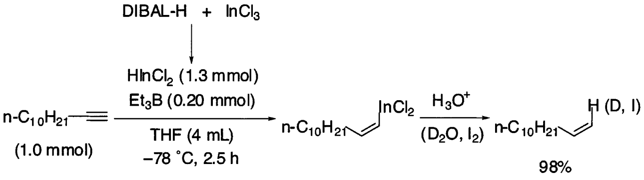
[12] Reactions of allylic gallium species were reported. (a) Han, Y.; Huang, Y.-Z. *Tetrahedron Lett.* **1994**, *35*, 9433−9434. (b) Han, Y.; Chi, Z.; Huang, Y.-Z. *Synth. Commun.* **1999**, *29*, 1287−1296. (c) Araki, S.; Ito, H.; Butsugan, Y. *Appl. Organomet. Chem.* **1988**, *2*, 475−478. (d) Tsuji, T.; Usugi, S.; Yorimitsu, H.; Shinokubo, H.; Matsubara, S.; Oshima, K. *Chem. Lett.* **2002**, 2−3.

[13] ^1H NMR measurements revealed the formation of $HInCl_2$. The hydride attached to the aluminum of DIBAL-H appeared at δ 3.8 ppm (broad) in THF-d_8. A new broad signal (δ 6.8 ppm) was observed after treatment of $InCl_3$ with DIBAL-H. Baba reported that the hydride of $HInCl_2$, prepared from $InCl_3$ and *n*-Bu_3SnH, appeared at δ 6.5 ppm. See: Miyai, T.; Inoue, K.; Yasuda, M.; Shibata, I.; Baba, A. *Tetrahedron Lett.* **1998**, *39*, 1929−1932. However, Baba's $HInCl_2$ did not add to alkynes. The reason for the different reactivity is not clear. Diisobutylaluminum chloride might coordinate to $HInCl_2$, thereby changing the reactivity.

SCHEME 5



SCHEME 6



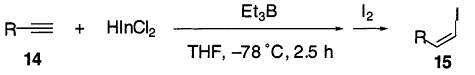
yield (11% yield, E/Z < 1/99). When the reaction was performed without triethylborane, 1-dodecene was produced in only 34% yield.[15] Furthermore, TEMPO inhibited the reaction (0.20 equiv, 48% yield; 0.40 equiv, 10% yield). These observations suggest that the reaction involves a radical mechanism.

We assume that the reaction proceeds via a radical addition of indium hydride reagent across a carbon–carbon triple bond.[16] (Z)-Alkenylidium dichloride that is initially formed does not isomerize to the (E)-isomer, because of the very low reactivity of dichloroindium radical toward the alkenylindium.[17] If the second addition of the indium radical occurs, isomerization of (Z)-alkenylindium compound into its thermodynamically stable (E)-form proceeds via the diindium species.

A variety of alkynes were subjected to the hydroindation reaction and following iodolysis (Table 2). Noteworthy is the fact that many functionalities including hydroxy, carbonyl, and carboxy groups did not interfere with the reaction (entries 3–7). The hydroindation proceeded much faster at the alkynyl moiety than at the alkenyl group to yield iodo diene **15g** selectively starting from enyne **14g** (entry 8). An addition to phenylacetylene yielded a mixture of E/Z isomers with slightly lower selectivity (7/93, entry 9). None of the desired product was obtained in the reaction of trimethylsilylacetylene.

Interestingly, treatment of enyne **16** with $HInCl_2$ and Et_3B at 25 °C afforded the corresponding cyclized product **17** in 30% yield (Scheme 7). The formation of **17** strongly suggests that this hydroindation reaction proceeds in a radical mechanism. Namely, a radical addition of the indium-centered radical to the alkyne moiety of **16** produces vinyl radical **18**. Radical cyclization of **18** yields methylenecyclopentane **19**. Hydride abstraction from dichloroindium hydride followed by acidic workup affords **17**.

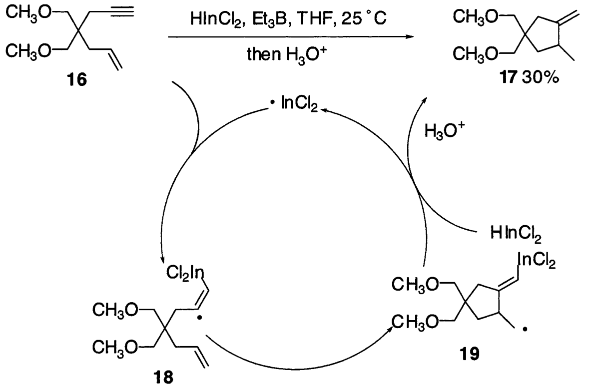
TABLE 2. Hydroindation of Alkynes Followed by Iodolysis[a]



entry	14	R	15	yield/%	E/Z [b]
1	**14a**	$PhCH_2O(CH_2)_3$	**15a**	79	1/99
2[c]	**14a**	$PhCH_2O(CH_2)_3$	**15a**	91	2/98
3	**14b**	$EtOOC(CH_2)_6$	**15b**	99	<1/99
4	**14c**	$HO(CH_2)_4$	**15c**	78	<1/99
5	**14d**	$HOCH_2$	**15d**	57	<1/99
6	**14e**	n-$C_4H_9CO(CH_2)_6$	**15e**	73	<1/99
7	**14f**	$HOOC(CH_2)_6$	**15f**	98	3/97
8	**14g**	$CH_2{=}CH(CH_2)_8$	**15g**	74	1/99
9[c]	**14h**	Ph	**15h**	99	7/93

[a] Alkyne (1.0 mmol), $HInCl_2$ (1.3 mmol), and Et_3B (0.20 mmol) were used. [b] Determined by ^1H NMR. [c] The reaction was performed at −40 °C.

SCHEME 7



Cross-Coupling Reaction of Aryl Halides with Alkenylindiums Prepared via Hydroindation. Increasing attention has been paid to the cross-coupling reaction of organic halides with organoindiums.[18] However, most organoindium reagents were prepared from indium trichloride and the corresponding organolithium or -magnesium reagents. With the protocol to prepare alkenylindiums in hand, we investigated the cross-coupling reaction of aryl halides with alkenylindiums in one pot. After optimization of the reaction conditions, a DMI (1,3-dimethylimidazolidin-2-one)/THF mixed solvent system proved to be effective in obtaining the coupling

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[14] The hydroindation reaction at 0, −10, and −40 °C yielded a mixture of stereoisomers (E/Z = 20/80, 6/94, and 3/97, respectively) after iodolysis.

[15] Indium hydride spontaneously induces the radical reaction. See ref 16. Moreover, some organoaluminum compounds can initiate a radical reaction. See: Chakraborty, A.; Marek, I. *Chem. Commun.* **1999**, 2375–2376.

[16] Reduction of organic halides via a radical process was recently reported. Inoue, K.; Sawada, A.; Shibata, I.; Baba, A. *J. Am. Chem. Soc.* **2002**, *124*, 906–907.

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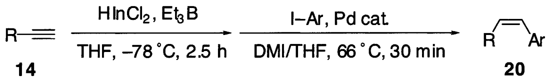
TABLE 3. One-Pot Hydroindation/Cross-Coupling Reaction[a]



14 **20**

entry	**14**	R	Ar	**20**	yield/%	*E*/*Z*[b]
1	**14i**	n-C_6H_{13}	Ph	**20a**	94	5/95
2	**14i**	n-C_6H_{13}	C_6H_4-2-NO_2	**20b**	98	5/95
3	**14i**	n-C_6H_{13}	C_6H_4-4-NO_2	**20c**	99	5/95
4	**14i**	n-C_6H_{13}	C_6H_4-2-CO_2-n-C_4H_9	**20d**	91	5/95
5	**14i**	n-C_6H_{13}	C_6H_4-3-OCH_3	**20e**	89	5/95[c]
6	**14i**	n-C_6H_{13}	2-pyridyl	**20f**	75	3/97[c]
7	**14i**	n-C_6H_{13}	C_6H_4-4-CH_3	**20g**	68	4/96
8	**14i**	n-C_6H_{13}	C_6H_4-3-OH	**20h**	46	1/99
9	**14b**	$C_2H_5OOC(CH_2)_6$	Ph	**20i**	92	3/97
10	**14b**	$C_2H_5OOC(CH_2)_6$	C_6H_4-4-NO_2	**20j**	99	5/95
11	**14j**	$TBSO(CH_2)_3$[d]	Ph	**20k**	70	2/98
12	**14j**	$TBSO(CH_2)_3$[d]	C_6H_4-4-NO_2	**20l**	90	5/95
13	**14c**	$HO(CH_2)_4$	C_6H_4-4-NO_2	**20m**	99	2/98
14	**14c**	$HO(CH_2)_4$	C_6H_4-3-OCH_3	**20n**	99	3/97[c]
15	**14c**	$HO(CH_2)_4$	C_6H_4-3-OH	**20o**	36	3/97[c]
16	**14a**	$PhCH_2O(CH_2)_3$	C_6H_4-3-OCH_3	**20p**	91	20/80[e]
17	**14k**	$PhCH_2OCH_2$	C_6H_4-3-OCH_3	**20q**	78	11/89[e]

[a] Alkyne (1.3 mmol), $InCl_3$ (1.55 mmol), DIBAL-H (1.50 mmol), Et_3B (0.20 mmol), aryl iodide (1.0 mmol), and Pd cat. (0.50 mol %) were used. [b] Determined by ^1H NMR. [c] Hydroindation was performed at −40 °C. [d] TBS = t-$BuMe_2Si$. [e] Hydroindation was performed at 0 °C.

products. DMI (3 mL) was added to a THF solution of the (*Z*)-1-octenylindium reagent (1.3 mmol) prepared via hydroindation as aforementioned. An addition of iodobenzene (1.0 mmol) and palladium−trifurylphosphine complex (0.50 mol %)[19] followed by heating the whole mixture at 66 °C for 30 min afforded β-hexylstyrene (**20a**, $E/Z = 5/95$) in 94% yield. Various combinations of alkynes and aryl iodides were examined as listed in Table 3. High stereoselectivity was accomplished in all cases. Namely, the cross-coupling reaction process retained the stereochemistry of the alkenylindiums. Several functional groups both in alkynes and in aryl iodides were compatible in this one-pot reaction. In particular, coupling of 5-hexyn-1-ol with 3-iodoanisole represents the usefulness of the present strategy (entry 14).

Conclusion

We have revealed novel reactivities of gallium and indium hydride reagents. The gallium hydride reagent undergoes a facile addition to alkynes and alkenes. The reaction tolerates the existence of various functional groups. Organogallium species obtained with the present protocol can be trapped with some electrophiles. Triethylborane-induced hydroindation of alkynes proceeds in an anti manner to afford the corresponding (*Z*)-alkenylindium species. This method allows us to employ unprotected alkynes as (*Z*)-alkenylmetal precursors and to synthesize functionalized (*Z*)-alkenyl iodides and (*Z*)-arylalkenes in a one-pot operation with high stereoselectivity.

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Supporting Information Available: General procedures and spectral data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The palladium catalyst was prepared from $Pd_2(dba)_3{\cdot}CHCl_3$ (0.0025 mmol) and $P(2\text{-furyl})_3$ (0.015 mmol) in THF (1.0 mL) in another reaction flask under an argon atmosphere.