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Substituted Butenylindium Generated by Transmetalation of Cyclopropylmethylstannane with Indium Iodide: Synthesis and Characterization of Monobutenylindium

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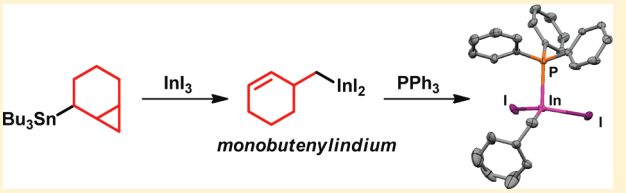
Supporting Information

ABSTRACT: Transmetalation between substituted cyclopropylmethylstannanes and indium iodide provided the corresponding mono- and dibutenylindium species. The bulky substituent on a cyclopropyl ring selectively afforded the monobutenylindium species, which allowed the isolation and X-ray structural analysis of the monobutenylindium complex. In an investigation of the generated substituted butenylindium species, we found that indium halide interacted with the less sterically hindered carbon−carbon bond of the cyclopropyl ring during transmetalation. In addition, we examined the radical coupling reactions of substituted butenylindium species with an α-iodoester. The distribution of the cyclopropylmethylated and alkene products was evidence that the reactions were remarkably affected by the steric effect of the substituents of the butenylindium species, which retarded the cyclization of the radical intermediate.



INTRODUCTION

Organoindium compounds are recognized as an important class of organometallic reagents in organic synthesis because of their characteristics: ease of handling, moisture stability, excellent functional group tolerance, etc.[1] In particular, allylic indiums have been widely used for carbon−carbon bond formations such as the allylation of carbonyl compounds.[1,2] In addition, various types of other organoindium compounds (alkenyl, alkynyl, aryl, etc.) are also applicable to transition-metal-catalyzed cross-coupling reactions.[3] Although the synthetic applications of organoindium compounds have been extensively studied, the structure of the active species is virtually unknown, and the nature of most organoindiums is still undefined.[2f,4] To solve these problems, our group has recently studied organoindium compounds such as alkenylindium[5] (2-carbon unit) and allylindium[6] (3-carbon unit). In addition, the higher homologue, the butenylindium (4-carbon unit) species, was investigated for radical and ionic reactivity, particularly dibutenylindium.[7,8] However, the more basic monobutenyl derivative has not been investigated.[9] Herein, we focus on the synthesis of the monobutenylindium species. Fortunately, the employment of substituted cyclopropylmethylstannanes selectively afforded the monobutenylindium species, as determined by NMR spectroscopy and X-ray structural analysis (Scheme 1). A monobutenylindium species had not previously been isolated, while our group has previously reported the isolation of monobutenylgallium.[8] Furthermore, the radical coupling between the substituted butenylindium species with an α-iodoester elucidated the importance of steric hindrance and the β-effect of indium.

RESULTS AND DISCUSSION

Initially, the reaction of 2,2-dimethylcyclopropylmethyltributylstannane (**1a**) and phenyl 2-iodoacetate (**2**) was conducted to investigate the effect of indium sources and solvents, in which the generation of the butenylindium species was followed by a reaction with **2** (Table 1). The treatment of $InCl_3$ in toluene under open air conditions resulted in a low yield, and unreacted stannane **1a** was recovered (entry 1). This result indicates that the transmetalation between $InCl_3$ and **1a** was not effective. When using $InBr_3$, stannane **1a** was completely consumed, and the yield of the desired product **3a** was improved by as much as 56% (entry 2). Finally, InI_3 was found to be the best choice to afford **3a** (entry 3).[10] In the presence of a radical inhibitor, the coupling reaction was inhibited, indicating that the reaction proceeds in a radical manner (entry 4). The reaction performed in hexane gave a slightly lower yield than that in toluene (entries 3 and 5). Coordinating solvents significantly suppressed the reactions (entries 6−8). Notably, no transmetalation proceeded in THF. Gratifyingly, the addition of a catalytic amount of Et_3B as a radical initiator drastically improved the yield to 94% (entry 9). The reaction in the absence of InI_3 did not give the coupling product (entry 10).

To confirm the generation of the butenylindium species, the transmetalation between **1a** and InI_3 was monitored by ^1H NMR spectroscopy (Figure 1). The mixture of **1a** and InI_3 (**1a**/InI_3 = 1:1) in toluene-d_8 immediately produced a single product (**4a**) with a doublet of doublet signal at δ 5.74 for the internal olefin

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Scheme 1. Synthesis of Monobutenylindium Species by Transmetalation between Substituted Cyclopropylmethylstannanes and InI_3

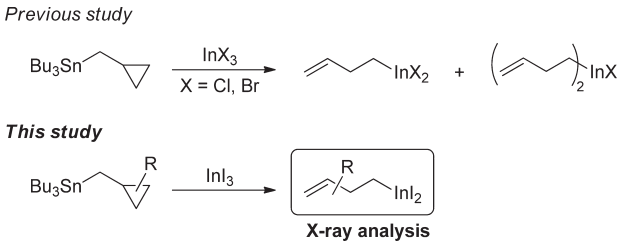
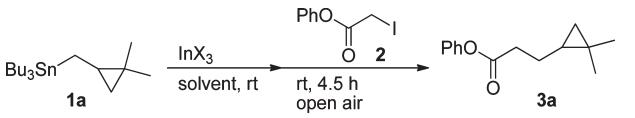


Table 1. Effect of Indium Sources and Solvents[a]



entry	InX_3	solvent	yield/%[b]	recovery of **1a**/%[b]
1	$InCl_3$	toluene	25	44
2	$InBr_3$	toluene	56	0
3	InI_3	toluene	64	0
4[c]	InI_3	toluene	0	6
5	InI_3	hexane	54	0
6	InI_3	Et_2O	14	12
7	InI_3	MeCN	0	40
8	InI_3	THF	0	95
9[d]	InI_3	toluene	94	0
10[d]	none	toluene	0	89

[a] Using 1.5 mmol of **1a**, 1.0 mmol of **2**, and 0.75 mmol of indium halide. [b] Determined by ^{1}H NMR. [c] Galvinoxyl (0.1 mmol) was added. [d] Et_3B (0.1 mmol) was added, and the reaction was carried out under N_2.

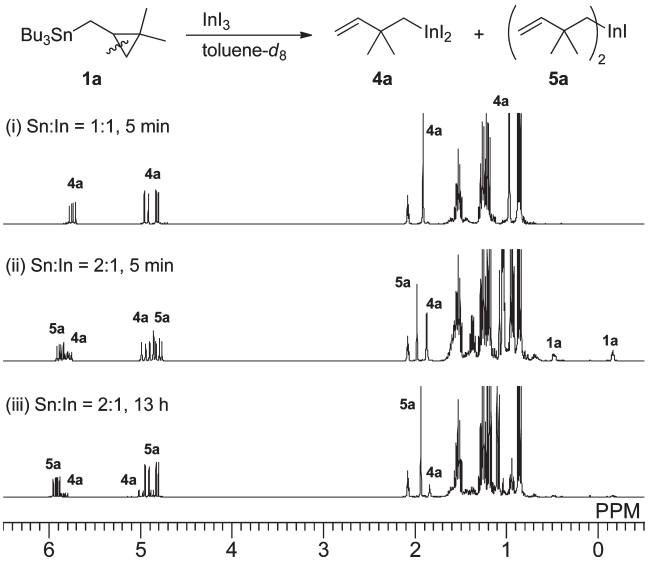
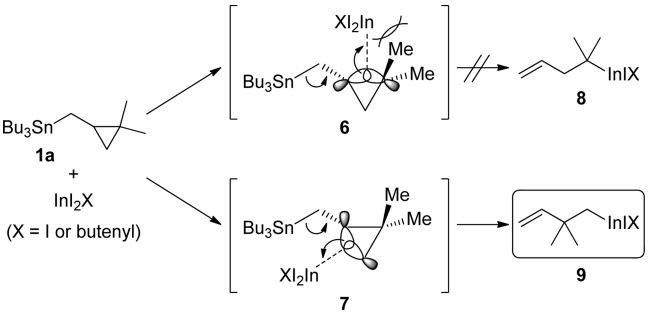


Figure 1. ^{1}H NMR spectra of the reaction mixture of **1a** and InI_3 with (i) 1:1 (5 min), (ii) 2:1 (5 min), and (iii) 2:1 (13 h) ratios in toluene-d_8.

Scheme 2. Plausible Mechanism for Transmetalation between 1a and Indium Iodide



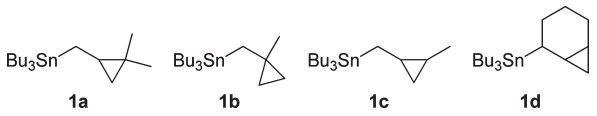
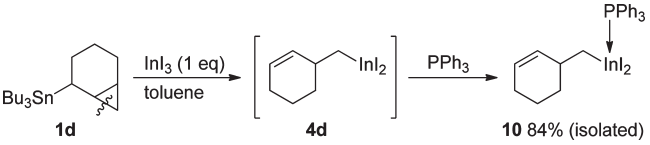


Figure 2. Substituted cyclopropylmethylstannanes.

Scheme 3. Isolation of 2-Cyclohexen-1-ylmethylindium Diiodide−PPh_3 Complex 10



proton, two doublets at δ 4.94 and 4.82 for terminal olefin protons, a singlet at δ 1.91 for methylene protons, and a singlet at δ 0.98 for methyl protons (Figure 1i). **4a** was most certainly a monobutenylindium diiodide, because using two equivalents of **1a** provided two types of butenylindium species, perhaps mono-**4a** and dibutenylindium **5a**, with a small amount of starting material **1a** remaining (Figure 1ii). After the reaction mixture was stirred for a long enough period (13 h), stannane **1a** was almost consumed, and dibutenylindium **5a** was preferentially observed (Figure 1iii). These results show that the first transmetalation between **1a** and InI_3, giving monobutenylindium **4a**, was quite fast, while the second transmetalation, giving dibutenylindium **5a**, was relatively slow probably because of the steric hindrance between butenyl substituents on the indium atom. This is the reason for the selective synthesis of monobutenylindium **4a** from equimolar amounts of **1a** and InI_3. This tendency is quite different from the transmetalation of nonsubstituted cyclopropylmethylstannane and $InBr_3$, in which the dibutenylindium was readily generated even before the complete consumption of the starting stannane.[7]

An investigation into the structure of the generated butenylindium **4a** (**5a**) provided some insight into the mechanism of transmetalation. For efficient transmetalation, the π-Lewis acidity of indium halide provides an important interaction with the carbon−carbon bond of the cyclopropyl ring, which has a much higher p character than a normal carbon−carbon σ bond.[11] Since butenylindium **4a** (**5a**) has two methyl groups at the β-position, the selective ring cleavage takes place at the less hindered carbon−carbon bond of **1a** (**6** vs **7**) to produce butenylindium **9**, rather than **8**, as shown in Scheme 2. This proposed mechanism is

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supported by the fact that InI_3, which is a softer Lewis acid by comparison with either $InCl_3$ or $InBr_3$, gave the best results (see Table 1). In addition, suppression of the transmetalation in coordinating solvents by lowering the Lewis acidity of indium halide can be explained.

Next, to confirm the generation of a monobutenylindium species, isolation by complex formation was attempted using various combinations of stannanes (**1a**−**d**) (Figure 2) and phosphine ligands.[7,8] Although some stable complexes were isolated, only the combination of stannane **1d** and PPh_3 gave a colorless single crystal that was suitable for X-ray structural analysis (Scheme 3).[12,13]

The ORTEP drawing of 2-cyclohexen-1-ylmethylindium diiodide−PPh_3 complex **10** is shown in Figure 3.[14] As far as can be ascertained, this is the first example of the X-ray structural analysis of a monobutenylindium species.[15] The coordination of one PPh_3 constructed a distorted tetrahedral structure with a four-coordinated indium center. In this complex, there was no intermolecular interaction through bridging by halogen atoms. The In1−C1 length at 2.165(9) Å was slightly shorter than the sum of the individual covalent radii (d_{In-C} = 2.18 Å).[16]

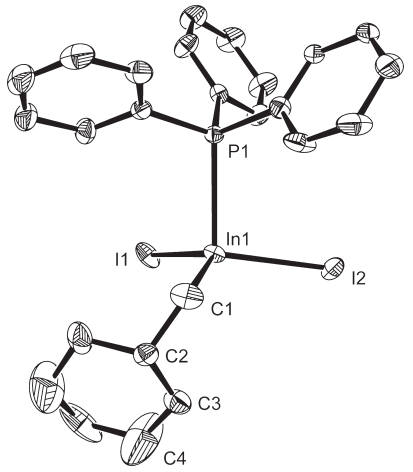


Figure 3. ORTEP drawing of 2-cyclohexen-1-ylmethylindium diiodide−PPh_3 complex **10** (30% thermal ellipsoids; all hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): In1−C1 = 2.165(9), In1−I1 = 2.7189(8), In1−I2 = 2.7252(8), In1−P1 = 2.6341(14), C1−C2 = 1.484(11), C2−C3 = 1.51(10), C3−C4 = 1.33(2); I1−In1−I2 = 107.00(3), I1−In1−C1 = 124.8(3), I2−In1−C1 = 116.5(3), P1−In1−C1 = 106.03(18).

Scheme 4. Plausible Reaction Mechanism

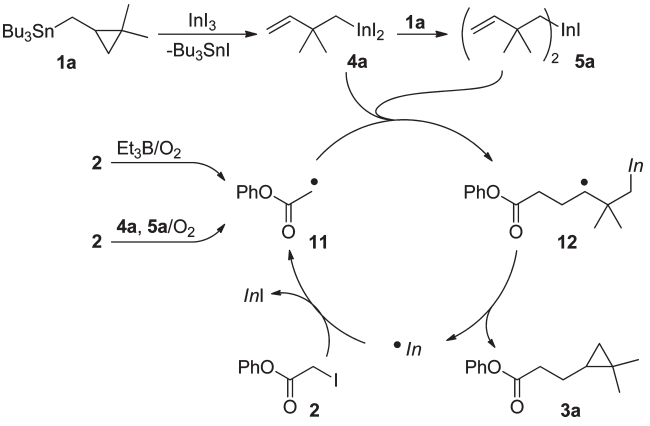
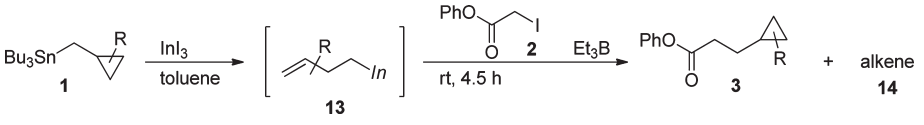


Table 2. Reactions of Cyclopropylmethylstannanes 1 with Iodoester 2[a]



entry	stannane **1**	butenylindium **13**	product **3**	alkene **14**	**3**/**14**[b]	yield/ %[c]
1	Bu$_3$Sn **1a**	In **13a**	PhO O **3a**	n.d. **14a**	**3a**/**14a** (100/0)	81 (94)
2	Bu$_3$Sn **1b**	In **13b**	PhO O **3b**	PhO O **14b**	**3b**/**14b** (32/68)	72 (86)
3[d,e]	Bu$_3$Sn **1c**	In **13c**	PhO O **3c**	PhO O **14c**	**3c**/**14c** (80/20)	45 (56)
4[d]	Bu$_3$Sn **1e**	In **13e**	PhO O **3e**	PhO O **14e**	**3e**/**14e** (93/7)	77 (98)
5[d,e]	Bu$_3$Sn **1d**	In **13d**	n.d.	n.d.		0

[a] Using 1.5 mmol of **1**, 1.0 mmol of **2**, 0.75 mmol of InI_3, and 0.1 mmol of Et_3B. [b] Determined by ^1H NMR. [c] Isolated yields (combined yields of **3** and **14**). Values in parentheses are NMR-determined yields. [d] Et_3B was not added. [e] Open air.

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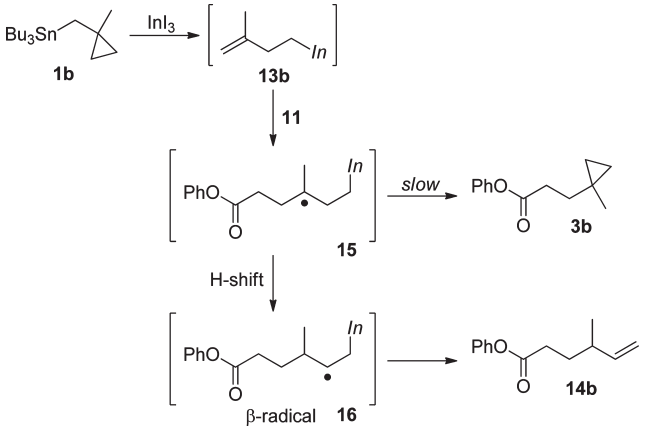
Scheme 5. Plausible Mechanism for Alkene Formation



The In−C bond is comparable to a previously reported one in the dibutenylindium complex.[7] The C3−C4 length of 1.33(2) Å indicates a double bond. Bond lengths of In1−I1 (2.7189(8) Å), In1−I2 (2.7252(8) Å), and In1−P1 (2.6341(14) Å) and bond angles between substituents at the indium atom were reasonable and were comparable to those reported for the InI_3−PPh_3 complex.[17]

Scheme 4 shows a plausible mechanism for the radical coupling reaction of a butenylindium species with iodoester **2**. First, monobutenylindium **4a** is generated from the transmetalation between stannane **1a** and InI_3, and further transmetalation partly provides dibutenylindium **5a**. The radical initiation step may be different from the case of an unsubstituted butenylindium species,[7] because the present case needs the addition of Et_3B (see Table 1). Therefore, two possibilities are proposed: (i) radical species **11** is generated from **2** assisted by Et_3B with O_2; or (ii) butenylindium **4a** or **5a** works as a radical initiator in the presence of a small amount of O_2 (or O_2/Et_3B), and the resultant radical species abstracts the iodo radical from **2** to produce the corresponding radical **11**. The trap of **11** by the butenylindium species is followed by the cyclization of **12** into cyclopropyl product **3a** along with an indium radical (other butenyl group and/or ligands are omitted on In). Finally, the generated indium radical abstracts the iodine from **2** to regenerate **11**.

In order to investigate the reactivity of the substituted butenylindium species for radical coupling, the reactions of various cyclopropylmethylstannanes **1** and iodoester **2** mediated by InI_3 were conducted, as shown in Table 2. The corresponding cyclopropylmethylated product **3a** was afforded in high yield with no byproduct (entry 1) when using 2,2-dimethylbutenylindium **13a** from **1a**. Other stannanes **1b**, **1c**, and **1e** gave varying amounts of olefins. Among them, **1b**, which generates 3-methylbutenylindium by transmetalation, gave the alkene product **14b** predominantly (**3b**/**14b** = 32/68) (entry 2).[18] This is probably because the cyclization of intermediate **15** is disturbed by the steric hindrance of the tertiary radical (Scheme 5). In addition, the β-effect of indium stabilizes radical intermediate **16** to accelerate the isomerization from **15** to **16** through H-shift to give alkene **14b**.[8,19] Scheme 5 would also be a reasonable explanation for why mono- and nonsubstituted cyclopropylmethylstannanes **1c** and **1e** gave moderate (20%) and small (7%) selectivities of alkenes **14c** and **14e** along with major products of desired cyclopropyls **3c** and **3e**, respectively (entries 3 and 4).[20] No β-hydrogen for an H-shift in intermediate **12** (Scheme 4) is perhaps the reason there was no alkene formation from dimethyl-substituted stannane **1a** (entry 1). Unfortunately, the reaction of cyclic butenylindium **13d** did not proceed due to steric hindrance at the reaction site (entry 5).

CONCLUSION

In conclusion, we have reported the facile preparation of substituted butenylindium species from substituted cyclopropylmethylstannanes and InI_3. The selective generation of monobutenylindium species was also confirmed by NMR spectroscopy and X-ray structural analysis. In transmetalation, the π-Lewis acidity of indium halide and the steric hindrance of the cyclopropyl ring are important factors for the effective and selective synthesis of monobutenylindium species. Substituted butenylindium species easily coupled with an iodoester to give the corresponding cyclopropane products and alkenes. The results of this radical coupling revealed a dependence on the substituent for the change in reactivity of the butenylindium species.

ASSOCIATED CONTENT

Supporting Information. Experimental details, characterization data, and CIF of **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) For recent reviews, see: (a) Nair, V.; Ros, S.; Jayan, C. N.; Pillai, B. S. *Tetrahedron* **2004**, *60*, 1959–1982. (b) Augé, J.; Lubin-Germain, N.; Uziel, J. *Synthesis* **2007**, 1739–1764. (c) Yadav, J. S.; Antony, A.; George, J.; Subba Reddy, B. V. *Eur. J. Org. Chem.* **2010**, 591–605.

(2) For selected reviews, see: (a) Podlech, J.; Maier, T. C. *Synthesis* **2003**, 633–655. (b) Paquette, L. A. *Synthesis* **2003**, 765–774. (c) Kumar, S.; Kaur, P.; Kumar, V. *Curr. Org. Chem.* **2005**, *9*, 1205–1235. (d) Kargbo, R. B.; Cook, G. R. *Curr. Org. Chem.* **2007**, *11*, 1287–1309. For selected recent papers, see:(e) Haddad, T. D.; Hirayama, L. C.; Singaram, B. *J. Org. Chem.* **2010**, *75*, 642–649. (f) Schneider, U.; Dao, H. T.; Kobayashi, S. *Org. Lett.* **2010**, *12*, 2488–2491. (g) Kim, J. S.; Jang, D. O. *J. Am. Chem. Soc.* **2010**, *132*, 12168–12169. (h) Min, Q.-Q.; He, C.-Y.; Zhou, H.; Zhang, X. *Chem. Commun.* **2010**, *46*, 8029–8031. (i) Nowrouzi, F.; Janetzko, J.; Batey, R. A. *Org. Lett.* **2010**, *12*, 5490–5493.

(3) For selected papers, see: (a) Pérez, I.; Pérez Sestelo, J.; Maestro, M. A.; Mouriño, A.; Sarandeses, L. A. *J. Org. Chem.* **1998**, *63*, 10074–10076. (b) Pérez, I.; Pérez Sestelo, J.; Sarandeses, L. A. *Org. Lett.* **1999**, *1*, 1267–1269. (c) Pérez, I.; Pérez Sestelo, J.; Sarandeses,

L. A. *J. Am. Chem. Soc.* **2001**, *123*, 4155–4160. (d) Rodríguez, D.; Pérez Sestelo, J.; Sarandeses, L. A. *J. Org. Chem.* **2003**, *68*, 2518–2520. (e) Pena, M. A.; Pérez Sestelo, J.; Sarandeses, L. A. *Synthesis* **2003**, 780–784. (f) Rodríguez, D.; Pérez Sestelo, J.; Sarandeses, L. A. *J. Org. Chem.* **2004**, *69*, 8136–8139. (g) Riveiros, R.; Rodríguez, D.; Pérez Sestelo, J.; Sarandeses, L. A. *Org. Lett.* **2006**, *8*, 1403–1406. (h) Riveiros, R.; Pérez Sestelo, J.; Sarandeses, L. A. *Synthesis* **2007**, 3595–3598. (i) Caeiro, J.; Pérez Sestelo, J.; Sarandeses, L. A. *Chem.—Eur. J.* **2008**, *14*, 741–746. (j) Riveiros, R.; Saya, L.; Pérez Sestelo, J.; Sarandeses, L. A. *Eur. J. Org. Chem.* **2008**, 1959–1966. (k) Takami, K.; Yorimitsu, H.; Shinokubo, H.; Matsubara, S.; Oshima, K. *Org. Lett.* **2001**, *3*, 1997–1999. (l) Takami, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2002**, *4*, 2993–2995. (m) Chen, Y.-H.; Knochel, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 7648–7651. (n) Chen, Y.-H.; Sun, M.; Knochel, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2236–2239. (o) Papoian, V.; Minehan, T. *J. Org. Chem.* **2008**, *73*, 7376–7379. (p) Chupak, L. S.; Wolkowski, J. P.; Chantigny, Y. A. *J. Org. Chem.* **2009**, *74*, 1388–1390. (q) Lee, P. H.; Sung, S.-Y.; Lee, K. *Org. Lett.* **2001**, *3*, 3201–3204. (r) Lee, K.; Lee, J.; Lee, P. H. *J. Org. Chem.* **2002**, *67*, 8265–8268. (s) Lee, K.; Seomoon, D.; Lee, P. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3901–3903. (t) Lee, P. H.; Lee, S. W.; Lee, K. *Org. Lett.* **2003**, *5*, 1103–1106. (u) Lee, P. H.; Lee, S. W.; Seomoon, D. *Org. Lett.* **2003**, *5*, 4963–4966. (v) Lee, S. W.; Lee, K.; Seomoon, D.; Kim, S.; Kim, H.; Kim, H.; Shim, E.; Lee, M.; Lee, S.; Kim, M.; Lee, P. H. *J. Org. Chem.* **2004**, *69*, 4852–4855. (w) Lee, P. H.; Seomoon, D.; Lee, K.; Kim, S.; Kim, H.; Kim, H.; Shim, E.; Lee, M.; Lee, S.; Lim, M.; Sridhar, M. *Adv. Synth. Catal.* **2004**, *346*, 1641–1645. (x) Lee, P. H.; Seomoon, D.; Lee, K.; Kim, H. *Chem.—Eur. J.* **2007**, *13*, 5197–5206. (y) Shen, Z. L.; Goh, K. K. K.; Yang, Y. S.; Lai, Y. C.; Wong, C. H. A.; Cheong, H. L.; Loh, T. P. *Angew. Chem., Int. Ed.* **2011**, *50*, 511–514. (z) Hayashi, N.; Hirokawa, Y.; Shibata, I.; Yasuda, M.; Baba, A. *Org. Biomol. Chem.* **2008**, *6*, 1949–1954. A halogen substitution reaction using alkylindium species toward haloalkenes:(aa) Nomura, R.; Miyazaki, S.-i.; Matsuda, H. *J. Am. Chem. Soc.* **1992**, *114*, 2738–2740.

(4) Allylindium: (a) Araki, S.; Ito, H.; Butsugan, Y. *J. Org. Chem.* **1988**, *53*, 1831–1833. (b) Chan, T. H.; Yang, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3228–3229. (c) Koszinowski, K. *J. Am. Chem. Soc.* **2010**, *132*, 6032–6040. Propargylindium:(d) Miao, W.; Chung, L. W.; Wu, Y.-D.; Chan, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 13326–13334. (e) Xu, B.; Mashuta, M. S.; Hammond, G. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 7265–7267. (f) Xu, B.; Hammond, G. B. *Chem.—Eur. J* **2008**, *14*, 10029–10035. Indium enolate:(g) Babu, S. A.; Yasuda, M.; Shibata, I.; Baba, A. *Org. Lett.* **2004**, *6*, 4475–4478. (h) Babu, S. A.; Yasuda, M.; Shibata, I.; Baba, A. *J. Org. Chem.* **2005**, *70*, 10408–10419. Indium homoenolate:(i) Shen., Z. L.; Goh, K. K. K.; Cheong, H. L.; Wong, C. H. A.; Lai, Y. C.; Yang, Y. S.; Loh, T. P. *J. Am. Chem. Soc.* **2010**, *132*, 15852–15855. Alkylindium, see ref 3y.

(5) Nishimoto, Y.; Moritoh, R.; Yasuda, M.; Baba, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 5462–5471.

(6) (a) Yasuda, M.; Haga, M.; Baba, A. *Organometallics* **2009**, *28*, 1998–2000. (b) Yasuda, M.; Haga, M.; Baba, A. *Eur. J. Org. Chem.* **2009**, 5513–5517. (c) Yasuda, M.; Haga, M.; Nagaoka, Y.; Baba, A. *Eur. J. Org. Chem.* **2010**, 5359–5363.

(7) Yasuda, M.; Kiyokawa, K.; Osaki, K.; Baba, A. *Organometallics* **2009**, *28*, 132–139.

(8) Kiyokawa, K.; Yasuda, M.; Baba, A. *Org. Lett.* **2010**, *12*, 1520–1523.

(9) The coupling reaction of holocarbonyls and butenylindium from butenyl Grignard reagent and indium halide was reported: Usugi, S.; Tsuritani, T.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 841–845.

(10) The reactions using $BF_3 \cdot OEt_2$ or $AlCl_3$ instead of InI_3 did not give the product **3a** at all.

(11) Wong, H. N. C.; Hon, M.-Y.; Tse, C. W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165–198.

(12) The reaction of **1b** or **1c** with InI_3 (**1**/InI_3 = 1:1) in toluene gave monobutenylindium along with a small amount of dibutenylindium. The second transmetalation could be relatively fast because the steric hindrance of substituents of **1b** (**1c**) are smaller than those of **1a** and **1d**.

(13) The generation of **4d** as a single product was observed by NMR spectroscopy.

(14) The data obtained from the measurement was good, and the analysis was completed to optimize the structure. Although some level A alerts still remain, this structure should be justified because of the excellent level of the data and structure refinement.

(15) Monoalkylindiums from the reaction of alkenes, $InBr_3$, and ketene silyl acetals were isolated: Nishimoto, Y.; Ueda, H.; Inamoto, Y.; Yasuda, M.; Baba, A. *Org. Lett.* **2010**, *12*, 3390–3393.

(16) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832–2838.

(17) Brown, M. A.; Tuck, D. G.; Wells, E. J. *Can. J. Chem.* **1996**, *74*, 1535–1549.

(18) The reaction of **1b** with **2** was examined at 0 °C and gave the products in 86% yield and ratio of **3b**/**14b** = 37/63. This result indicates that the ratio of **3**/**14** does not depend on a reaction temperature.

(19) (a) Sakurai, H.; Imai, T.; Hosomi, A. *Tetrahedron Lett.* **1977**, *18*, 4045–4048. (b) Sugawara, M.; Yoshida, J. *Tetrahedron* **2000**, *56*, 4683–4689. (c) Ogasawara, M.; Okada, A.; Murakami, H.; Watanabe, S.; Ge, Y.; Takahashi, T. *Org. Let.* **2009**, *11*, 4240–4243.

(20) We assume that butenylindiums **13a**—**c** with substituents are relatively stable to oxygen, so a radical initiator (Et_3B) or an open air condition is required in a radical initiation step to facilitate an efficient reaction. On the contrary, because nonsubstituted **13e** easily generates a radical species (not fully determined) assisted by oxygen, an additional radical initiator is not required.