# Radical Coupling of Iodocarbonyl Compounds with Butenylindium Generated by Transmetalation between Cyclopropylmethylstannane and Indium Halides

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The reaction of cyclopropylmethylstannane **1** with α-iodocarbonyl compounds **2** in the presence of either $InBr_3$ or $InCl_3$ gave the C−C coupling products **3**. Various types of iodocarbonyl compounds such as esters, amides, and ketones were applied to this system to afford the corresponding cyclopropylethyl-substituted carbonyls **3**. Transmetalation between cyclopropylmethylstannane and indium halides afforded butenylindium dihalide and dibutenylindium halide, as confirmed by NMR spectroscopy. The reactivity of dibutenylindium halide was greater than that of monobutenyl species. The active species, dibutenylindium halide, was stabilized by complexation using DPPE, and its structure was analyzed using X-ray crystallography. The solid state of the complex shows a linear structure with a core $(-Cl-In-Cl-In-P-C-C-P-In-)_n$ with five-coordinated indium centers. The reaction between **1** and **2**, mediated by indium halides, proceeded in a radical manner. The *in situ*-generated alkylindium species and a small amount of oxygen, which can be supplied by atmospheric air, initiated the radical reaction.

## Introduction

Cyclopropylmethylstannane has the potential to introduce a cyclopropyl ring to organic molecules through C−C bond formation. Although some examples using cyclopropylmethylstannane were reported by Young, only ring-opening reactions took place with inorganic reagents such as $SO_2$, Brønstead acid, or iodine.[1] The lack of a suitable activation method creates difficulty in the control of cyclopropylmethylstannane for carbon−carbon bond formation. There are some examples of starting from a butenylmetal species instead of a cyclopropylmethyl compound to introduce cyclopropylmethyl groups in organic compounds. For example, there is the reaction of butenylstannane with acetals, acid chlorides, and aldehydes in the presence of Lewis acids to form cyclopropylmethylated products.[2,3] *In situ*-generated butenylgallium, -indium, and -aluminum from butenyl Grignard reagents with metal halides are assumed, and they couple with α-halocarbonyls in the presence of $Et_3B$ as a radical initiator.[4] However, the reaction using cyclopropylmethylstannane for introduction of the cyclopropyl ring through C−C bond formation has never been reported as far as we know.

In this paper, we report a radical coupling of cyclopropylmethylstannane with α-halocarbonyl compounds mediated by indium halides. In this system, no additional radical initiator was required. Effective transmetalation between the stannane and indium halides gives the butenylindium species, as confirmed by NMR spectroscopy and X-ray analysis. The use of the stannane is advantageous because it allows smooth and clean transmetalation, and the byproduct, halostannane, had no effect on the reaction system.

## Results and Discussion

**Reaction of Cyclopropymethylstannane 1 with α-Iodocarbonyl 2a.** The reaction of cyclopropylmethylstannane **1** with phenyl 2-iodoacetate **2a** in the presence of 0.5 equiv of $InBr_3$ gave the corresponding coupling product **3a** in 73% yield in toluene and a nitrogen-flowing flask (Table 1, entry 1). Although a trace amount of the ring-opening product, which was not precisely identified,[5] was observed, the effective introduction of a cyclopropyl group was accomplished. Without additives, there was no reaction (entry 2). Some solvents, such as $Et_2O$ or MeCN, gave lower yields, and no reaction was observed in THF, probably due to strong solvent coordination (entries 4−6). Exposure to air improved the yield of **3a** (entry 7). The other indium halides, $InCl_3$ or $InI_3$, gave lower yields (entries 8 and 9). $GaCl_3$ also gave a high yield of **3a** (entry 10), but $AlCl_3$ afforded phenyl 4-iodohexanoate in 41% yield with a trace amount of **3a** (entry 11). In the reaction using $BF_3 \cdot OEt_2$ as an additive, a low yield of **3a** was obtained and the rearranged species, butenylstannane, was confirmed after the reaction (entry 12).[1] When $ZnCl_2$, $TiCl_4$, $ZrCl_4$, $HfCl_4$, or $SnCl_2$ was used as additive, satisfactory yields were not obtained (entries 13−17). The loading of a catalytic amount of galvinoxyl suppressed the reaction (entry 18), and thus the reaction proceeds via a radical mechanism.

**Investigation of Active Species.** To gain a thorough understanding of the active species, the relationship between the

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(1) (a) Lucke, A. J.; Young, D. J. *J. Org. Chem.* **2005**, *70*, 3579–3583. (b) Lucke, A. J.; Young, D. J. *Tetrahedron Lett.* **1991**, *32*, 807–810.

(2) (a) Sugawara, M.; Yoshida, J. *Chem. Commun.* **1999**, 505–506. (b) Sugawara, M.; Yoshida, J. *Tetrahedron* **2000**, *56*, 4683–4689.

(3) (a) Peterson, D. J.; Robbins, D. *Tetrahedron Lett.* **1972**, *13*, 2135–2138. (b) Peterson, D. J.; Robbins, D.; Hansen, J. R. *J. Organomet. Chem.* **1974**, *73*, 237–250. (c) Herndon, J. W.; Harp, J. J. *Tetrahedron Lett.* **1992**, *33*, 6243–6246. (d) Ueno, Y.; Ohta, M.; Okawara, M. *Tetrahedron Lett.* **1982**, *23*, 2577–2580. (e) Nicolaou, K. C.; Claremon, D. A.; Barnette, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704–3706.

(4) Usugi, S.-i.; Tsuritani, T.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 841–845.

(5) (a) Sakurai, H.; Inai, T.; Hosomi, A. *Tetrahedron Lett.* **1977**, *18*, 4045–4048. (b) Hatanaka, Y.; Kuwajima, I. *Tetrahedron Lett.* **1986**, *27*, 719–722.

10.1021/om8009156 CCC: $40.75 
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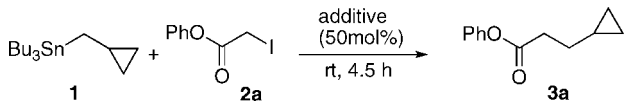
**Table 1. Optimization of Reaction Conditions**[a]




1 2a 3a

| entry | additive | solvent | yield, % |
|---|---|---|---|
| 1 | $InBr_3$ | toluene | 73 |
| 2 | none | toluene | 0 |
| 3 | $InBr_3$ | $CH_2Cl_2$ | 76 |
| 4 | $InBr_3$ | $Et_2O$ | 42 |
| 5 | $InBr_3$ | MeCN | 17 |
| 6 | $InBr_3$ | THF | 0 |
| 7[b] | $InBr_3$ | toluene | 79 |
| 8 | $InCl_3$ | toluene | 50 |
| 9 | $InI_3$ | toluene | 57 |
| 10 | $GaCl_3$ | toluene | 71 |
| 11 | $AlCl_3$ | toluene | <5[c] |
| 12 | $BF_3 \cdot OEt_2$ | toluene | 9 |
| 13 | $ZnCl_2$ | toluene | 0 |
| 14 | $TiCl_4$ | toluene | 13 |
| 15 | $ZrCl_4$ | toluene | 0 |
| 16 | $HfCl_4$ | toluene | 0 |
| 17 | $SnCl_2$ | toluene | 0 |
| 18 | $InBr_3$[d] | toluene | <5 |

[a] All entries were carried out at room temperature in solvent (1 mL) with 1.0 mmol of **1**, 1.0 mmol of **2a**, and 0.5 mmol of additive. [b] Exposure to air (15 min). [c] Phenyl 4-iodohexanoate was formed (41% yield). [d] Addition of galvinoxyl (0.1 mmol).

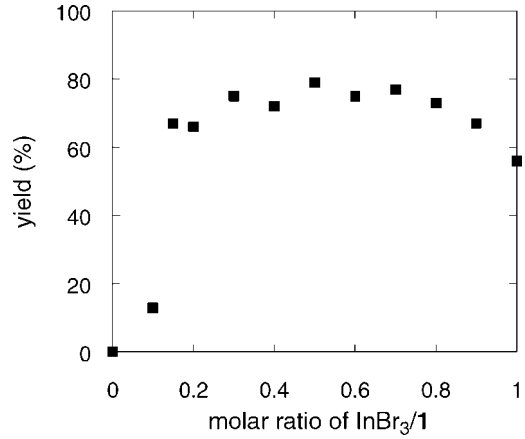



**Figure 1.** Relationship between amount of $InBr_3$ and the yield of **3a** in the reaction of **1** (1 mmol) with **2a** (1 mmol) at rt for 4.5 h.

loading ratio of $InBr_3$/**1** and the product yield was investigated in the reaction of **1** with **2a**, and the results are shown in Figure 1. As the ratio $InBr_3$/**1** increased from 0.1 to 0.5, higher yields of **3a** were obtained, and ca. 0.5 equiv of $InBr_3$ afforded the highest yield. It was curious that ca. 0.3 equiv of $InBr_3$ also gave a relatively high yield, while the yield was reduced when 1.0 equiv of $InBr_3$ was used. These results suggest generation of different active species as a result of varying the ratio of $InBr_3$/**1**.

As confirmation of the conclusion demonstrated by the results in Figure 1, we examined the three types of mixtures of $InBr_3$ and **1** with the ratios of 1/1, 1/2, and 1/3 (= $InBr_3$/**1**) using NMR spectroscopy (Figure 2). The 1/1 mixture of $InBr_3$/**1** gave two types of butenyl-substituted species that were assumed to be butenylindium dibromide **4** and dibutenylindium bromide **5** generated by transmetalation (spectrum a). One species that is reasonable for dibutenylindium bromide **5** was observed when mixed at a ratio of 1/2 ($InBr_3$/**1**) (spectrum b). No other highly substituted species were found from the 1/3 mixture ($InBr_3$/**1**), and only dibutenylindium species **5** and unreacted **1** were

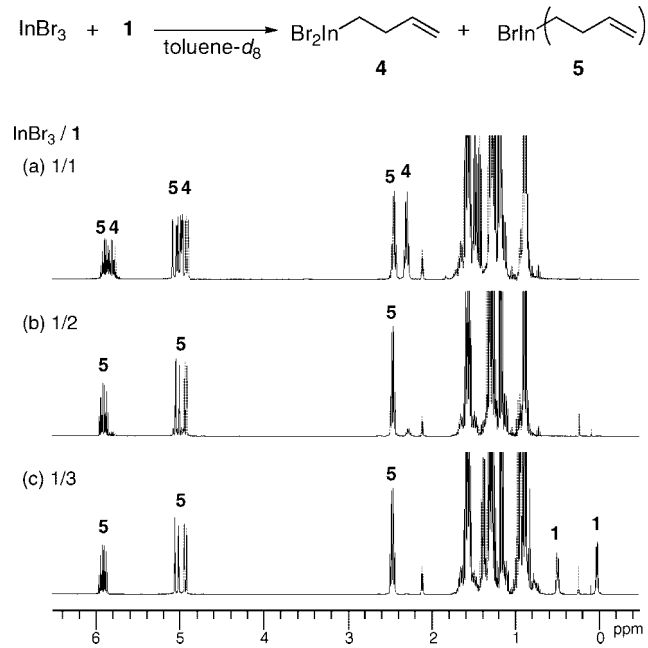



**Figure 2.** $^1H$ NMR spectra of the reaction mixtures of $InBr_3$ and **1** with (a) 1/1, (b) 1/2, and (c) 1/3 ratios in toluene-$d_8$.

observed (spectrum c). The mass spectrum of the 1/2 mixture of $InBr_3$/**1** gave the molecular ion corresponding to the dibutenylindium species [calculated for ($C_8H_{14}In$), 225.0134; found for *m*/*z*, 225.0134]. The dibutenyl species **5** was more reactive than **4**, as evidenced by more rapid consumption of **5** than of **4** when iodoester **2a** was added to a mixture that included both **4** and **5** (see Supporting Information). The amount of **4** remained nearly constant until **5** was completely consumed. Both butenyl groups on **5** were transferred to the product prior to transfer of the butenyl group on **4**. The amount of the monobutenyl species **4** was decreased after **5** had disappeared (see Supporting Information). The result that loading 1.0 equiv of $InBr_3$ resulted in low efficiency, as shown in Figure 1, is consistent with the greater production of the less reactive monosubstituted indium species. Transmetalation of allylic stannane or hydrostannane with indium halides is widely reported,[6,7] but this is the first example where transmetalation of cyclopropylmethylstannane results in a homoallylic building block.[8]

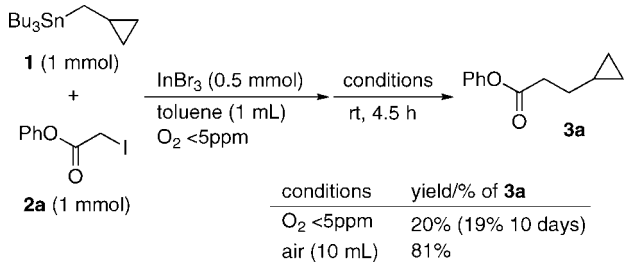
**Reaction Mechanism.** To investigate the effect of air on the coupling reaction shown in Table 1, the $InBr_3$-mediated reaction of **1** with **2a** was performed in a nitrogen-filled glovebox ($O_2$ < 5 ppm), as shown in Scheme 1. The reaction gave **3a** in 20% yield after 4.5 h (19% yield even after 10 days). On the other hand, loading 10 mL of air through a syringe into the mixture of **1**, **2a**, and $InBr_3$ prepared in the glovebox gave **3a** in 81% yield after stirring for 4.5 h. These results suggest that oxygen plays an important role in the generation of radical species like

(6) (a) Yasuda, M.; Miyai, T.; Shibata, I.; Baba, A.; Nomura, R.; Matsuda, H. *Tetrahedron Lett.* **1995**, *36*, 9497–9500. (b) Miyai, T.; Inoue, K.; Yasuda, M.; Baba, A. *Synlett* **1997**, 699–700. (c) Inoue, K.; Shimizu, Y.; Shibata, I.; Baba, A. *Synlett* **2001**, 1659–1661. (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.; Sawada, A.; Shibata, I.; Baba, A. *Tetrahedron Lett.* **2001**, *42*, 4661–4663. (g) Baba, A.; Shibata, I. *Chem. Rec.* **2005**, *5*, 323–335.

(7) Marshall, J. A.; Hinkle, K. W. *J. Org. Chem.* **1995**, *60*, 1920–1921.

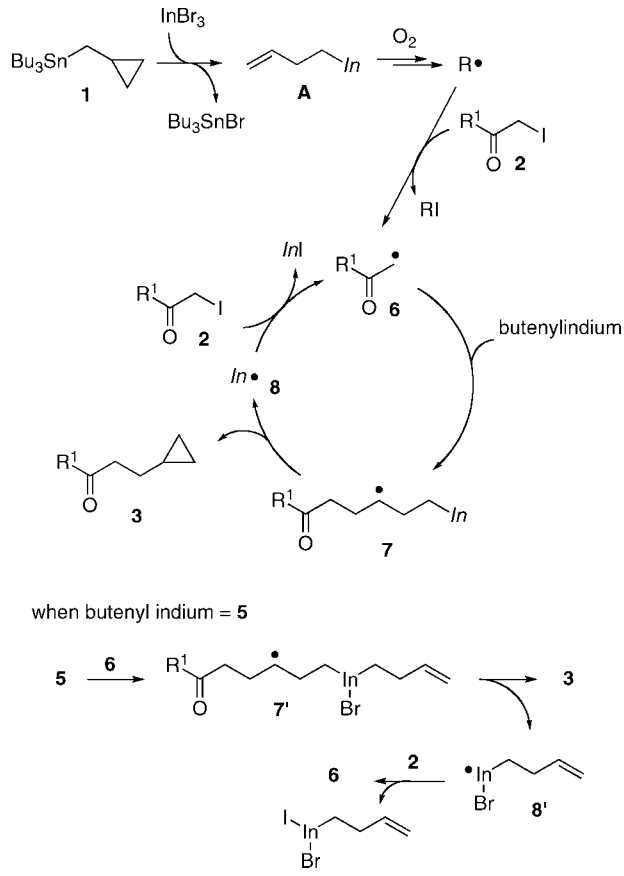
(8) We examined the transmetalation of **1** with $AlCl_3$ but observed only butenylstannane as a rearranged product. $GaCl_3$ gave butenylgallium species in the reaction with **1**, and further studies are now in progress.

**Scheme 1. Effect of Air on the Coupling Reaction**




| conditions | yield/% of **3a** |
|---|---|
| $O_2$ <5ppm | 20% (19% 10 days) |
| air (10 mL) | 81% |

**Scheme 2. Plausible Reaction Mechanism**




the $O_2$−$Et_3B$ system.[9] In our system, use of another radical initiator is not necessary, as exposure to air is sufficient to initiate the coupling reaction. The *in situ*-generated butenylindium species acts as a radical initiator as well as an alkylating reagent. The conventional experimental bench procedure (not in a glovebox) using a nitrogen-flow system may have adequate oxygen to accelerate the reaction system.

A plausible reaction mechanism is shown in Scheme 2. Transmetalation between **1** and $InBr_3$ gives butenylindium species **A** (other butenyl group and/or ligands are omitted on In). Oxygen-assisted radical initiation abstracts iodine from the iodocarbonyl compound **2**.[9] The generated acylmethyl radical **6** is trapped by butenylindium to give the radical species **7**. Species **7** cyclizes with elimination of the indium radical **8**,

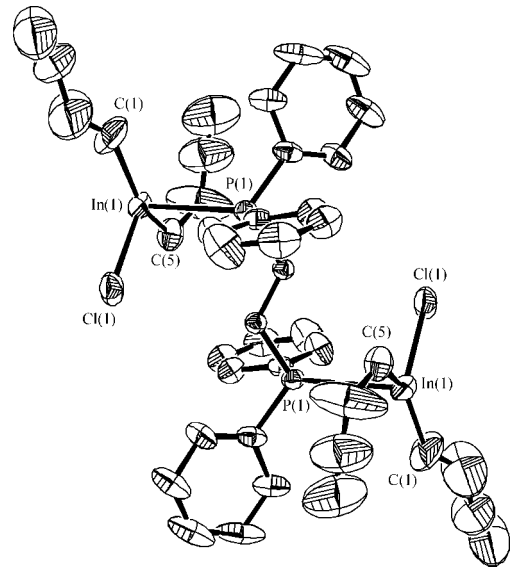
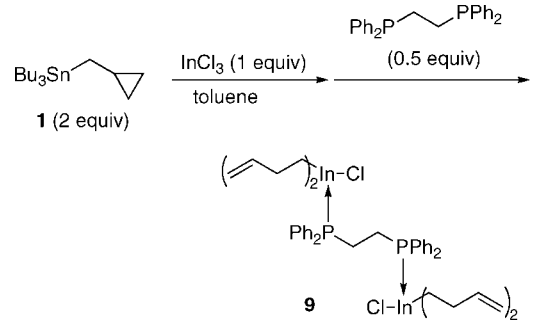



**Figure 3.** ORTEP drawing of molecular structure of dibutenylindium chloride−DPPE complex **9** (all hydrogens are omitted for clarity).

**Scheme 3. Isolation of Butenylindium Species**




which abstracts iodine from **2**, and the acylmethyl radical **6** is regenerated. When the radical species **6** is trapped by dibutenylindium bromide **5**, the resulting indium radical, butenylindium(II) bromide **8′**, is generated via **7′**. The species **8′** abstracts the iodine of **2** to give **6** and butenylbromoindium(III) iodide. Because the formed butenylbromoindium(III) iodide is close to radical **6**, fast coupling between them takes place effectively.[10] This mechanism is consistent with the observation that both butenyl groups on dibutenylindium bromide **5** are preferentially consumed over the butenyl group on **4**. Species **7** could abstract an iodine from **2** to afford an iodinated compound, which then cyclizes into product **3**.[11] However, this mechanism does not explain the rate difference between the butenyl groups on **5** and **4**. Another interesting point is that the byproduct halostannane is not likely to affect the reaction system, and transmetalation starting from tin compounds is quite effective.

**X-ray Analysis of Butenylindium Generated by Transmetalation.** Complexation of the active species in the reaction system by various ligands was examined to prove that butenylindium species were generated using X-ray analysis of

(9) (a) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547–2549. (b) Miura, K.; Ichinose, Y.; Nozaki, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 143–147. (c) Yorimitsu, H.; Nakamura, T.; Shinokubo, H.; Oshima, K.; Omoto, K.; Fujimoto, H. *J. Am. Chem. Soc.* **2000**, *122*, 11041–11047. (d) Ollivier, C.; Renaud, P. *Chem. Rev.* **2001**, *101*, 3415–3434. (e) Yorimitsu, H.; Oshima, K. In *Radicals in Organic Synthesis*; Renaud, P.; Sibi, M. P. Eds.; Wiley-VCH: Weinheim, 2001; Vol. 1, Chapter 1.2.

(10) It might also be explainable that the iodoindium species has a high reactivity toward the carbonyl compound. The halogens on the indium center dramatically affect the reactivity of oxy-functionalized compounds; for example: Nishimoto, Y.; Yasuda, M.; Baba, A. *Org. Lett.* **2007**, *9*, 4931–4934. The iodine might supply high reactivity in this case.

(11) A halogen substitution reaction using alkylindium species toward haloalkenes was reported: Nomura, R.; Miyazaki, S.-i.; Matsuda, H. *J. Am. Chem. Soc.* **1992**, *114*, 2738–2740.

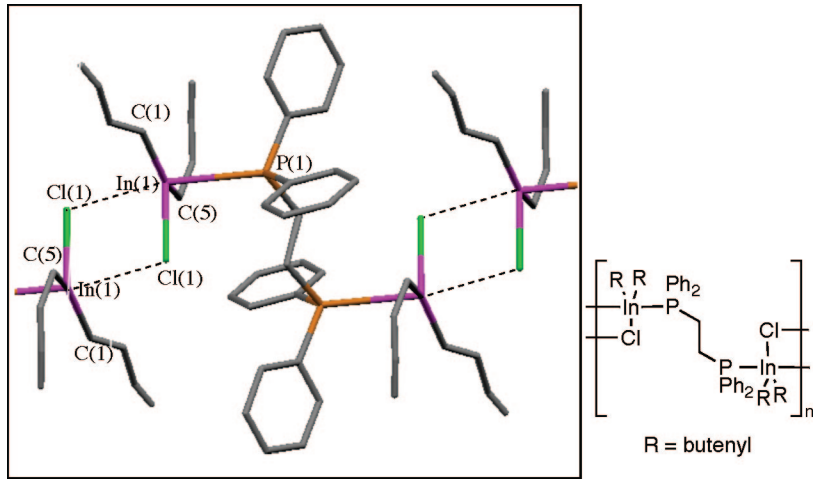



**Figure 4.** Molecular structure and its intermolecular contacts of dibutenylindium chloride−DPPE complex **9** (all hydrogens are omitted for clarity). Selected bond angles (deg) and lengths (Å): C(1)−In(1)−C(5) 146.6(3), C(1)−In(1)−$Cl_{eq}$(1) 106.5(3), C(5)−In(1)−$Cl_{eq}$(1) 105.93(17), P(1)−In(1)−$Cl_{ax}$(1) 169.95(2), P(1)−In(1)−$Cl_{eq}$(1) 88.73(3), In(1)−C(1) 2.145(11), In(1)−C(5) 2.148(6), In(1)−P(1) 2.9264(11), In(1)−$Cl_{eq}$(1) 2.5011(17), In(1)−$Cl_{ax}$(1) 2.9899(13).

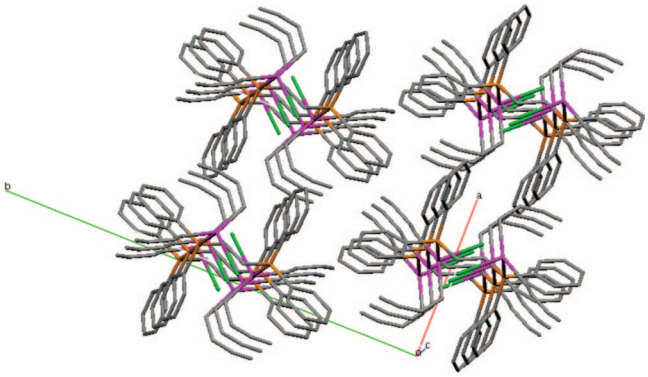


**Figure 5.** Packing structure of dibutenylindium chloride−DPPE complex **9** (all hydrogens are omitted for clarity).

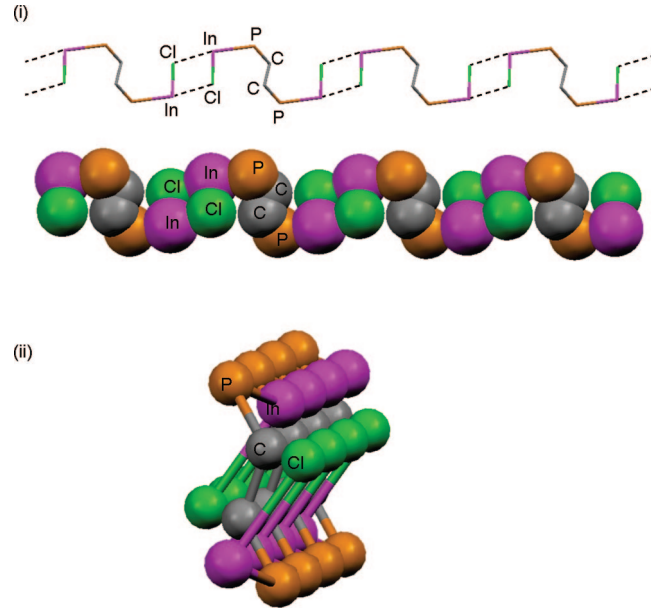



**Figure 6.** Part of a linear shaped structure of dibutenylindium chloride−DPPE complex **9** (In, P, and carbons of DPPE are shown only for clarity). Views along the *a* axis and *c* axis (with a slight deviation) are shown in (i) and (ii), respectively.

isolated compounds. Among various ligands and indium sources employed, DPPE and $InCl_3$ gave a crystal of dibutenylindium complex **9** that was suitable for X-ray analysis, as shown in Scheme 3.

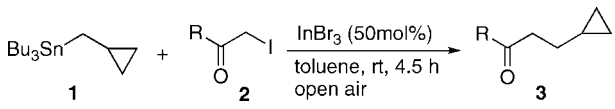
The ORTEP drawing of the indium complex **9** and its intermolecular contacts are shown in Figures 3 and 4. The five-coordinated indium centers had two butenyl groups, a phosphorus in DPPE, and two chlorines. Each chlorine binds two indium centers by bridging.[12] Although DPPE is often used as a bidentate ligand, each phosphine moiety in **9** independently coordinates to different indium centers. The indium center exhibited a distorted trigonal bipyramidal structure with bond angles of C−In−C (146.6°) and C−In−Cl (106.5° and 105.9°), the sum of which was 359°. P−In−Cl exhibited bond angles of 169.95° and 88.73°. The lengths of the two In−C bonds were 2.145 and 2.148 Å. The lengths of the other three bonds around the indium, In−P, In−$Cl_{eq}$, and In−$Cl_{ax}$, were 2.926, 2.501, and 2.990 Å, respectively. This is the first example of X-ray crystallographic analysis of a butenylindium species.

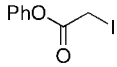
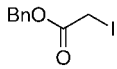
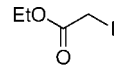
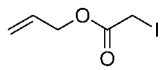
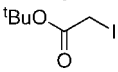
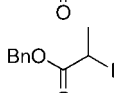
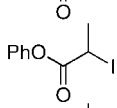
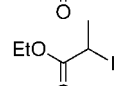
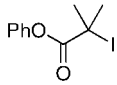
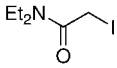
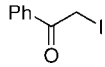
Because two In−Cl moieties interact with each other and the phosphines in DPPE independently coordinate to indium centers, the packing structure is clearly linear with a core (−Cl−In−Cl−In−P−C−C−P−In−)$_n$, as shown in Figures 5 and 6. The unit has a length of ca. 10 Å. The view along the *c* axis of the linear structure exhibits three types of atoms (P, In, Cl) in a linear arrangement at close distances. This arrangement appears promising for new materials, although applications of this compound have not yet been investigated.

**Synthesis of Cyclopropylethyl Carbonyl Compounds 3.** Table 2 shows the scope and limitations of using the reaction system for various substrates. The reactions were carried out with exposure to air through the $CaCl_2$ drying tube. Primary iodoesters **2a**−**d** (entries 1−4) effectively gave the corresponding coupling products, the cyclopropylethyl carbonyl compounds **3a**−**d**. Although the *tert*-butyl ester **2e** gave a low yield, in the absence of air, the yield increased to 53% (entry 5).[13] The coupling also proceeded with secondary substrates **2f**−**h** in moderate to high yields (entries 6−8). A high yield was obtained for the reaction with iodolactone **2i** (entry 9). The reaction with

(12) (a) Schachner, J. A.; Lund, C. L.; Burgess, I. J.; Quail, J. W.; Schatte, G.; Müller, J. *Organometallics* **2008**, *27*, 4703–4710. (b) Schachner, J. A.; Lund, C. L.; Quail, J. W.; Müller, J. *Organometallics* **2005**, *24*, 4483–4488.

**Table 2. Reaction of 1 with α-Iodocarbonyl Compounds 2[a]**




| entry | iodocarbonyl | | yield/ % | (under $N_2$)[c] |
|---|---|---|---|---|
| 1 |  | **2a** | **3a** 79 | (64) |
| 2[b] |  | **2b** | **3b** 71 | (56) |
| 3 |  | **2c** | **3c** 66 | (62) |
| 4 |  | **2d** | **3d** 68 | (50) |
| 5 |  | **2e** | **3e** 11 | (53) |
| 6 |  | **2f** | **3f** 48 | (46) |
| 7 |  | **2g** | **3g** 47 | (79) |
| 8 |  | **2h** | **3h** 65 | (47) |
| 9 |  | **2i** | **3i** 80 | (98) |
| 10 |  | **2j** | **3j** <5 | (<5) |
| 11[b,d] | | | 15 | (30) |
| 12[b,d] |  | **2k** | **3k** 54 | (62) |
| 13 |  | **2l** | **3l** 71 | (67) |

[a] All entries were carried out at room temperature in solvent (1 mL) with 1.0 mmol of **1**, 1.0 mmol of **2**, and 0.5 mmol of $InBr_3$. Tin compound **1** was added to the mixture of **2** and $InBr_3$ in toluene. [b] Iodocarbonyl **2** was added to the mixture of **1** and $InBr_3$ in toluene that had been previously stirred at room temperature for 30 min. [c] Reactions were carried out on the bench using a nitrogen-flowing flask. [d] Reactions were carried out at 100 °C.

the tertiary iodoester **2j** resulted in a low yield (entry 11). Instead of iodoesters, iodoamide **2k** and iodoketone **2l** gave the corresponding products in satisfactory yields (entries 12 and 13). A conventional reaction procedure, which used a nitrogen-flow flask on the bench whereby a very small amount of oxygen was introduced, gave yields that were nearly identical to those obtained under air, although in some cases lower yields were obtained.

## Conclusion

This paper describes the transmetalation of cyclopropylmethylstannane with indium halides to give dibutenylindium halide and butenylindium dihalide. This transmetalation can be applied to the reactions with iodocarbonyls to give coupling products that bear cyclopropyl groups. This reaction does not require a radical initiator. Open air conditions sometimes accelerated the radical reaction pathway. The generated dibutenylindium species was stabilized by a phosphine ligand, and the resulting complex was analyzed using X-ray crystallography. The butenylindium species was used as an alkylating reagent without a radical initiator. Transmetalation starting from the stannane proceeded in an effective and clean manner for the synthesis of interesting cyclopropylated carbonyl compounds.

## Experimental Section

**General Procedures.** IR spectra were recorded as thin films or as solids in KBr pellets on a HORIBA FT-720 spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were obtained with a 400 and 100 MHz spectrometer, respectively, with TMS as internal standard. $^{119}Sn$ NMR spectra were obtained with a 150 MHz spectrometer with $Me_4Sn$ as external standard. Mass spectra were recorded on a JEOL JMS-DS303. All reactions were carried out under nitrogen. Column chromatography was performed on silica gel (Merck C60). Recycle GPC was performed with $CHCl_3$ as the eluent. Bulb-to-bulb distillation (Kugelrohr) was accomplished in a Sibata GTO-250RS at the oven temperature and pressure indicated. Yields were determined by GLC or $^1H$ NMR using internal standards.

**Materials.** Dehydrated toluene, dichloromethane, $Et_2O$, acetonitrile, and THF were purchased and used as obtained. The additives examined in Table 1 were also purchased from commercial sources. Cyclopropylmethylstannane **1** was prepared as previously described.[1a] All iodocarobnyls **2a**−**l** were prepared according to the known method.[14] The spectral data of **2d**,[15] **2e**,[16] **2g**,[17] **2h**,[14] **2i**,[18] **2k**,[19] and **2l**[20] were in excellent agreement with the reported data. The spectral data of **2c** were in an excellent agreement with those obtained for the commercially available product. The synthetic procedure and spectral data of the other iodocarbonyls **2a**, **2b**, **2f**, and **2j** are shown below. All other reagents were commercially available.

**Cyclopropylmethyltributylstannane (1).**[21] To tributyltin methoxide (330 mmol) was added poly(methylhydrosiloxane) (330 mmol), and the mixture was stirred for 8 h at room temperature. The resultant mixture was purified by distillation under reduced pressure to give $Bu_3SnH$ (85.9 g, 89%).[22] To hexachloroacetone (600 mmol) was added triphenylphosphine (110 mmol) at 0 °C, and the suspension was stirred vigorously for 5 min. To the suspension was slowly added 1-cyclopropylmethanol (100 mmol) for 25 min. The mixture was warmed to room temperature and stirred for 3 h before flash distillation to collect a volatile product, chlorocyclopropylmethane (7.9 g, 88%).[1a] To a solution of *n*-butyllithium (1.6 M in hexane, 47 mL) in THF (80 mL) at 0 °C was slowly added diisopropylamine (75 mmol), and the mixture was stirred for 20 min. To the mixture was slowly added $Bu_3SnH$ (75 mmol) for 30 min, and the mixture was stirred for 15 min to generate $Bu_3SnLi$. 1-Chloro-1-cyclopropylmethane (70 mmol) was slowly added to the mixture for 30 min, which was warmed to room temperature. After stirring for 16 h KF(aq) (10%, 200 mL)

(13) The conditions without air employed on the bench might have enough oxygen during the experimental process. A very small amount of oxygen resulted in high efficiency in this case.

(14) Loiseau, F.; Simone, J.-M.; Carcache, D.; Bobal, P.; Neier, R. *Monatsh. Chem.* **2007**, *138*, 121–129.
(15) Curran, D. P.; Tamine, J. *J. Org. Chem.* **1991**, *56*, 2746–2750.
(16) Neu, H.; Kihlbleg, T.; Långström, B. *J. Labelled Compd. Radiopharm.* **1997**, *39*, 509–524.
(17) Kihara, N.; Ollivier, C.; Renaud, P. *Org. Lett.* **1999**, *1*, 1419–1422.
(18) Denmark, S. E.; Yang, S.-M. *J. Am. Chem. Soc.* **2004**, *126*, 12432–12440.
(19) Hlavinka, M. L.; Greco, J. F.; Hagadorn, J. R. *Chem. Commun.* **2005**, 5304–5306.
(20) Yin, G.; Zhou, B.; Meng, X.; Wu, A.; Pan, Y. *Org. Lett.* **2006**, *8*, 2245–2248.
(21) $H^A$ and $H^B$ are defined as hydrogens that are *cis* and *trans* to RC*H*-cyclopropyl, respectively.
(22) Hayashi, K.; Iyoda, J.; Shiihara, I. *J. Organomet. Chem.* **1967**, *10*, 81–94.

was poured into the mixture. EtOAc (200 mL) was added, and the organic layer was washed using saturated NaCl(aq) (200 mL) and $H_2O$ (200 mL). After drying with $MgSO_4$ the solvent was evaporated and the residue was purified by column chromatography (hexane) on silica gel and distillation under reduced pressure to give the product (9.4 g, 37%): bp 78 °C/0.07 mmHg; $^1$H NMR (400 MHz, $CDCl_3$) 1.49 (m, 6H, 2′-$H_2$ × 3), 1.31 (tq, $J$ = 7.2, 7.2 Hz, 6H, 3′-$H_2$ × 3), 0.96−0.69 (m, 18H, 4′-$H_3$ × 3, 1′-$H_2$ × 3, 1-$H_2$ and $SnCH_2CH$), 0.46 (m, 2H, $H^A$ × 2), −0.04 (m, 2H, $H^B$ × 2); $^{13}$C NMR (100 MHz, $CDCl_3$) 29.4 (t, C-2′, d, $^2J_{Sn-C}$ = 19.7 Hz), 27.5 (t, C-3′, d, $^3J_{Sn-C}$ = 52.4 Hz), 15.0 (t, C-1, d, $^1J_{119Sn-C}$ = 307.2, $^1J_{117Sn-C}$ = 293.3 Hz), 13.8 (q, C-4′), 9.2 (d, $SnCH_2CH$, d, $^2J_{Sn-C}$ = 19.7 Hz), 9.0 (t, C-1′, d, $^1J_{119Sn-C}$ = 312.1, $^1J_{117Sn-C}$ = 299.0 Hz), 8.3 (t, two methylene groups in cyclopropyl ring, d, $^3J_{Sn-C}$ = 34.4 Hz); $^{119}$Sn NMR (150 MHz, $CDCl_3$) −15.6; IR (neat) 2958, 2924, 1462 cm$^{-1}$; MS (EI, 70 eV) *m*/*z* 291 (39), 289 (86), 288 (31), 287 (59), 285 (28), 235 (57), 233 (57), 231 (37), 179 (94), 178 (29), 177 (100), 176 (34), 175 (70), 173 (22), 121 (31), 119 (24); HRMS (EI, 70 eV) calcd for ($C_{12}H_{27}{}^{120}Sn$) 291.1135 (M − $CH_2C_3H_5$), found for *m*/*z* 291.1104 and calcd for ($C_{12}H_{25}{}^{120}Sn$) 289.0978 (M − Bu), found for *m*/*z* 289.1048. Anal. Calcd for $C_{16}H_{34}Sn$: C, 55.68; H, 9.93. Found: C, 55.47; H, 9.91.

**Phenyl 2-Iodoacetate (2a).** To a stirred solution of sodium iodide (135 mmol) in acetone (150 mL) was added phenyl bromoacetate (45 mmol). The mixture was stirred for 3 h, and then acetone was evaporated. Ethyl acetate (200 mL) was added, and the organic layer was washed by $Na_2S_2O_3$(aq) (10%, 200 mL) and water (2 × 200 mL) and then dried ($MgSO_4$). The solvent was evaporated and the residue was purified by recrystallization to give the product (10.5 g, 90%): mp 65−67 °C; $^1$H NMR (400 MHz, $CDCl_3$) 7.40 (dd, $J$ = 8.0, 8.0 Hz, 2H, *m*), 7.25 (t, $J$ = 8.0 Hz, 1H, *p*), 7.11 (d, $J$ = 8.0 Hz, 2H, *o*), 3.90 (s, 2H, 2-$H_2$); $^{13}$C NMR (100 MHz, $CDCl_3$) 167.5 (s, C-1), 150.5 (s, C-*i*), 129.5 (d, C-*m*), 126.2 (d, C-*p*), 120.9 (d, C-*o*), −6.0 (t, C-2); IR (KBr) 1736 (C═O) cm$^{-1}$; MS (EI, 70 eV) *m*/*z* 262 ($M^+$, 8), 94 (100); HRMS (EI, 70 eV) calcd for ($C_8H_7IO_2$) 261.9491 ($M^+$), found for *m*/*z* 261.9475. Anal. Calcd for $C_8H_7IO_2$: C, 36.67; H, 2.69; I, 48.43. Found: C, 36.68; H, 2.63; I, 48.70.

**Benzyl 2-Iodoacetate (2b).** To a stirred solution of sodium iodide (30 mmol) in acetone (60 mL) was added benzyl 2-chloroacetate (30 mmol). The mixture was stirred for 3 h, and then acetone was evaporated. Ethyl acetate (200 mL) was added, and the organic layer was washed by $Na_2S_2O_3$(aq) (10%, 100 mL) and water (100 mL × 2) and then dried ($MgSO_4$). The solvent was evaporated, and the residue was purified by distillation under reduced pressure to give the product (6.7 g, 80%): bp 75 °C/0.1 mmHg; $^1$H NMR (400 MHz, $CDCl_3$) 7.40−7.30 (m, 5H, Ar), 5.15 (s, 2H, $C_6H_5CH_2$), 3.71 (s, 2H, 2-$H_2$); $^{13}$C NMR (100 MHz, $CDCl_3$) 168.5 (s, C-1), 135.0 (s, C-*i*), 128.5 (d), 128.4 (d, C-*p*), 128.2, (d), 67.7 (t, $C_6H_5CH_2$), −5.5 (t, C-2); IR (neat) 1732 (C═O) cm$^{-1}$; MS (EI, 70 eV) *m*/*z* 276 ($M^+$, 0.04), 149 ($C_6H_5CH_2OCOCH_2^+$, 89), 107 ($C_6H_5CH_2O^+$, 100), 91 ($C_6H_5CH_2^+$, 90); HRMS (EI, 70 eV) calcd for ($C_9H_9IO_2$) 275.9647 ($M^+$), found for *m*/*z* 275.9655. Anal. Calcd for $C_9H_9IO_2$: C, 39.16; H, 3.29; I, 45.97. Found: C, 39.07; H, 3.16; I, 45.96.

**Benzyl 2-Iodopropanoate (2f).** To a stirred solution of benzyl alcohol (110 mmol) and pyridine (120 mmol) in $CH_2Cl_2$ (80 mL) at 0 °C was slowly added a solution of 2-bromopropionyl bromide (120 mmol) in $CH_2Cl_2$ (20 mL) for 25 min.[23] The mixture was warmed to room temperature, stirred for 12 h, and then quenched by water (200 mL). Chloroform (200 mL) was added, and the organic layer was washed by 1 M HCl aq (200 mL) and saturated $NaHCO_3$(aq) (200 mL) and then dried ($MgSO_4$). The solvent was evaporated, and the residue was purified by distillation under reduced pressure to give the bromoester (24.0 g, 87%), bp 78 °C/0.05 mmHg. The spectral data of the obtained bromoester (benzyl 2-bromopropanoate) were in excellent agreement with the reported data.[24] To a stirred solution of sodium iodide (100 mmol) in acetone (100 mL) was added benzyl 2-bromopropanoate (50 mmol). The mixture was stirred for 8 h, and then the solvent was evaporated. Ethyl acetate (200 mL) was added, and the organic layer was washed by $Na_2S_2O_3$ (aq) (10%, 100 mL) and water (100 mL × 2) and then dried ($MgSO_4$). The solvent was evaporated, and the residue was purified by distillation under reduced pressure to give the product (12.4 g, 82%): bp 84 °C/0.06 mmHg; $^1$H NMR (400 MHz, $CDCl_3$) 7.42−7.30 (m, 5H, Ar), 5.17 (m, 2H, $C_6H_5CH_2$), 4.51 (q, $J$ = 7.2 Hz, 1H, 2-H), 1.97 (d, $J$ = 7.2 Hz, 3H, 3-$H_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) 171.6 (s, C-1), 135.2 (s, *i*), 128.5 (d), 128.4 (d, *p*), 128.2 (d), 67.4 (t, $C_6H_5CH_2$), 23.2 (q, C-3), 12.8 (d, C-2); IR (neat) 1736 (C═O) cm$^{-1}$; MS (CI, 200 eV) *m*/*z* 291 (M + 1, 13), 91 ($C_6H_5CH_2^+$, 100); HRMS (CI, 200 eV) calcd for ($C_{10}H_{12}IO_2$) 290.9882 (M + 1), found for *m*/*z* 290.9894. Anal. Calcd for $C_{10}H_{11}IO_2$: C, 41.40; H, 3.82; I, 43.75. Found: C, 41.63; H, 3.78; I. 43.92.

**Phenyl 2-Iodo-2-methylpropanoate (2j).** To a stirred solution of phenol (110 mmol) and sulfuric acid (95%, 0.3 mL) in toluene (65 mL) was added 2-bromo-2-methylpropionyl bromide (110 mmol). The mixture was heated to reflux for 5 h and then cooled to room temperature and quenched by water (200 mL). Ethyl acetate (200 mL) was added, and the organic layer was washed by KOH(aq) (10%, 200 mL) and water (200 mL) and then dried ($MgSO_4$). The solvent was evaporated, and the residue was purified by distillation under reduced pressure to give the bromoester (21.6 g, 81%), bp 63 °C/0.04 mmHg. The spectral data of the obtained bromoester were in excellent agreement with the reported data.[25] To a stirred solution of sodium iodide (160 mmol) in acetone (80 mL) was added phenyl 2-bromo-2-methylpropanoate (40 mmol). The mixture was heated to reflux for 14 h and then cooled to room temperature, and acetone was evaporated. Ethyl acetate (200 mL) was added, and the organic layer was washed by $Na_2S_2O_3$(aq) (10%, 100 mL) and water (100 mL × 2) and then dried ($MgSO_4$). The solvent was evaporated, and the residue was purified by distillation under reduced pressure to give the product (8.72 g, 75%): bp 100 °C/0.6 mmHg; $^1$H NMR (400 MHz, $CDCl_3$) 7.40 (dd, $J$ = 8.0, 8.0 Hz, 2H, *m*), 7.25 (t, $J$ = 8.0 Hz, 1H, *p*), 7.13 (d, $J$ = 8.0 Hz, 2H, *o*), 2.20 (s, 6H, 3-$H_3$ and 2-Me); $^{13}$C NMR (100 MHz, $CDCl_3$) 171.9 (s, C-1), 150.7 (s, *i*), 129.4 (d, *m*), 126.0 (d, *p*), 120.8 (d, *o*), 33.5 (q, C-3 and 2-Me); IR (neat) 1747 (C═O) cm$^{-1}$; MS (EI, 70 eV) *m*/*z* 290 ($M^+$, 28), 197 ($COC(CH_3)_2I^+$, 48), 169 ($C(CH_3)_2I^+$, 100), 163 ($C_6H_5OCOC(CH_3)_2^+$, 76), 135 (64), 94 (85), 70 ($COC(CH_3)_2^+$, 28), 69 (22), 41 (38); HRMS (EI, 70 eV) calcd for $C_{10}H_{11}IO_2$ 289.9804 ($M^+$), found for *m*/*z* 289.9822. Anal. Calcd for $C_{10}H_{11}IO_2$: C, 41.40; H, 3.82; I, 43.75. Found: C, 41.65; H, 3.68; I, 43.59.

**Procedure for Optimization of Coupling of Cyclopropylmethylstannane 1 and Iodocarbonyls 2 (Table 1).** According to the next paragraph, the reactions were employed under the conditions noted in text.

**General Procedure for $InBr_3$-Mediated Coupling of Cyclopropylmethylstannane 1 and Iodocarbonyls 2 (Table 2).** To a suspension of $InBr_3$ (0.5 mmol) and iodocarbonyls **2** (1 mmol) in toluene (1 mL) was added (cyclopropylmethyl)tributylstannane **1** (1 mmol) with a $CaCl_2$ drying tube that was exposed to air. The reaction mixture was stirred at rt for 4.5 h. The mixture was quenched by addition of $NH_4F$(aq) (10%, 10 mL) and extracted with diethyl ether (3 × 10 mL). The collected organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The procedures used for further purification of the new compounds are shown in the

(23) Kakiya, H.; Nishimae, S.; Shinokubo, H.; Oshima, K. *Tetrahedron* **2001**, *57*, 8807–8815.

(24) DeGraw, J. I.; Christie, P. H.; Kisliuk, R. L.; Gaumont, Y.; Sirotnak, F. M. *J. Med. Chem.* **1990**, *33*, 212–215.

(25) Schick, H.; Ludwig, R.; Kleiner, K.; Kunath, A. *Tetrahedron* **1995**, *51*, 2939–2946.

Product Data section. The reactions under nitrogen were performed using the same operation.

**NMR Study of Transmetalation between 1 and 2 (Figure 2).** Three mixtures with different ratios of $InBr_3$/**1** (= 1/1, 1/2, and 1/3) were prepared in toluene-$d_8$. After mixing for ca. 2 h, the mixtures were transferred into NMR tubes, and the resulting spectra are shown in Figure 2.

**Product Data.** The spectral data of **3e**,[26] **3f**,[4] **3i**,[4] **3k**,[4] and **3l**[4] were in excellent agreement with the reported data. Spectral data for the products **3a**, **3b**, **3c**, **3d**, **3g**, **3h**, and **3j** are shown below.

**Phenyl 3-Cyclopropylpropanoate (3a).**[21] According to the general procedure, this compound was prepared from **1** and **2a** to give the product as a colorless liquid after chromatography (hexane). Further purification was performed by distillation under reduced pressure. Bp 90 °C/0.07 mmHg; $^1$H NMR (400 MHz, $CDCl_3$) 7.38 (dd, $J$ = 8.0, 7.2 Hz, 2H, *m*), 7.22 (t, $J$ = 7.2 Hz, 1H, *p*), 7.08 (d, $J$ = 8.0 Hz, 2H, *o*), 2.66 (t, $J$ = 7.2 Hz, 2H, 2-H$_2$), 1.66 (dt, $J$ = 7.2, 7.2 Hz, 2H, 3-H$_2$), 0.81 (ttt, $J$ = 8.0, 7.2, 5.6 Hz, 1H, $COCH_2CH_2CH$), 0.49 (ddd, $J$ = 8.0, 5.6, 4.8 Hz, 2H, H$^A$ × 2), 0.13 (ddd, $J$ = 5.6, 5.6, 4.8 Hz, 2H, H$^B$ × 2); $^{13}$C NMR (100 MHz, $CDCl_3$) 172.1 (s, C-1), 150.7 (s, C-*i*), 129.3 (d, C-*m*), 125.7 (d, C-*p*), 121.5 (d, C-*o*), 34.5 (t, C-2), 30.0 (t, C-3), 10.4 (d, $COCH_2CH_2CH$), 4.5 (t, two methylene groups in cyclopropyl ring); IR (neat) 1759 (C=O) cm$^{-1}$; MS (EI, 70 eV) *m*/*z* 190 (M$^+$, 37), 97 ($COCH_2CH_2C_3H_5^+$, 34), 94 (100), 69 ($CH_2CH_2C_3H_5^+$, 44), 55 ($CH_2C_3H_5^+$, 24); HRMS (EI, 70 eV) calcd for ($C_{12}H_{14}O_2$) 190.0994 (M$^+$), found for *m*/*z* 190.1000.

**Benzyl 3-Cyclopropylpropanoate (3b).**[21] According to the general procedure, this compound was prepared from **1** and **2b** to give the product as a colorless liquid after chromatography (hexane/EtOAc = 95/5). Further purification was performed by distillation under reduced pressure. Bp 77 °C /0.2 mmHg; $^1$H NMR (400 MHz, $CDCl_3$) 7.41−7.28 (m, 5H, Ar), 5.12 (s, 2H, $C_6H_5CH_2$), 2.46 (t, $J$ = 7.2 Hz, 2H, 2-H$_2$), 1.54 (dt, $J$ = 7.2, 7.2 Hz, 2H, 3-H$_2$), 0.70 (ttt, $J$ = 8.0, 5.6, 7.2 Hz, 1H, $COCH_2CH_2CH$), 0.40 (ddd, $J$ = 8.0, 5.6, 4.0 Hz, 2H, H$^A$ × 2), 0.05 (ddd, $J$ = 5.6, 5.6, 4.0 Hz, 2H, H$^B$ x 2); $^{13}$C NMR (100 MHz, $CDCl_3$) 173.5 (s, C-1), 136.1 (s, C-*i*), 128.5 (d), 128.2 (d), 128.1 (d, C-*p*), 66.1 (t, $C_6H_5CH_2$), 34.4 (t, C-2), 30.4 (t, C-3), 10.4 (d, $COCH_2CH_2CH$), 4.4 (t, two methylene groups in cyclopropyl ring); IR (neat) 1736 (C=O) cm$^{-1}$; MS (EI, 70 eV) *m*/*z* 204 (M$^+$, 0.71), 104 (61), 91 ($C_6H_5CH_2^+$, 100); HRMS (EI, 70 eV) calcd for $C_{13}H_{16}O_2$ 204.1150 (M$^+$), found for *m*/*z* 204.1139. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.52; H, 7.71.

**Ethyl 3-Cyclopropylpropanoate (3c).**[21] According to the general procedure, this compound was prepared from **1** and **2c** to give the product as a colorless liquid after chromatography (hexane/EtOAc = 94/6). Further purification was performed by distillation under reduced pressure. Bp 90 °C/20 mmHg; $^1$H NMR (400 MHz, $CDCl_3$) 4.13 (q, $J$ = 7.2 Hz, 2H, $CH_3CH_2OCO$), 2.39 (t, $J$ = 7.2 Hz, 2H, 2-H$_2$), 1.53 (dt, $J$ = 7.2, 7.2 Hz, 2H, 3-H$_2$), 1.26 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2OCO$), 0.71 (m, 1H, $COCH_2CH_2CH$), 0.43 (ddd, $J$ = 8.0, 5.6, 4.0 Hz, 2H, H$^A$ × 2), 0.05 (m, 2H, H$^B$ × 2); $^{13}$C NMR (100 MHz, $CDCl_3$) 173.7 (s, C-1), 60.1 (t, $CH_3CH_2OCO$), 34.5 (t, C-2), 30.1 (t, C-3), 14.2 (q, $CH_3CH_2OCO$), 10.4 (d, $COCH_2CH_2CH$), 4.3 (t, two methylene groups in cyclopropyl ring); IR (neat) 1739 (C=O) cm$^{-1}$; MS (EI, 70 eV) *m*/*z* 142 (M$^+$, 15), 114 ($CH_3CH_2OCOCH_2CH_2CH^+$, 70), 113 ($OCOCH_2CH_2C_3H_5^+$, 20), 99 ($CH_2OCOCH_2CH_2C_3H_5^+$, 32), 97 ($COCH_2CH_2C_3H_5^+$, 64), 96 (21), 88 (96), 73 ($CH_3CH_2OCO^+$, 42), 71 (27), 70 (32), 69 ($CH_2CH_2C_3H_5^+$, 100), 68 (88), 67 (22), 61 (36), 60 (88), 55($CH_2C_3H_5^+$, 71), 54 (27), 42 (22), 41 ($C_3H_5^+$, 74), 39 (31); HRMS (EI, 70 eV) calcd for ($C_8H_{14}O_2$) 142.0994 (M$^+$), found for *m*/*z* 142.1010.

**Allyl 3-Cyclopropylpropanoate (3d).**[21] According to the general procedure, this compound was prepared from **1** and **2d** to give the product as a colorless liquid after chromatography (hexane/EtOAc = 94/6). Further purification was performed by distillation under reduced pressure. Bp: 120 °C/30 mmHg; $^1$H NMR (400 MHz, $CDCl_3$) 5.93 (ddt, $J$ = 17.6, 10.4, 5.6 Hz, 1H, $CH_2CHCH_2OCO$), 5.32 (ddd, $J$ = 17.6, 3.2, 1.6 Hz, 1H, $CH_2CH{=}CHH$), 5.24 (ddd, $J$ = 10.4, 3.2, 1.6 Hz, 1H, $CH_2CH{=}CHH$), 4.58 (ddd, $J$ = 5.6, 1.6, 1.6 Hz, 2H, $CH_2CHCH_2OCO$), 2.44 (t, $J$ = 7.2 Hz, 2H, 2-H$_2$), 1.63 (dt, $J$ = 7.2, 7.2 Hz, 2H, 3-H$_2$), 0.72 (ttt, $J$ = 8.0, 5.6, 7.2 Hz, 1H, $COCH_2CH_2CH$), 0.43 (ddd, $J$ = 8.0, 5.6, 4.0 Hz, 2H, H$^A$ × 2), 0.06 (ddd, $J$ = 5.6, 5.6, 4.0 Hz, 2H, H$^B$ × 2); $^{13}$C NMR (100 MHz, $CDCl_3$) 173.4 (s, C-1), 132.3 (d, $CH_2CHCH_2OCO$), 118.1 (t, $CH_2CHCH_2OCO$), 65.0 (t, $CH_2CHCH_2OCO$), 34.4 (t, C-2), 30.1 (t, C-3), 10.5 (d, $COCH_2CH_2CH$), 4.4 (t, two methylene groups in cyclopropyl ring); IR (neat) 1739 (C=O), 1651 (C=C) cm$^{-1}$; MS (CI, 200 eV) *m*/*z* 155 (M + 1, 100); HRMS (CI, 200 eV) calcd for ($C_9H_{15}O_2$) 155.1072 (M + 1), found for *m*/*z* 155.1080.

**Phenyl 3-Cyclopropyl-2-methylpropanoate (3g).**[21] According to the general procedure, this compound was prepared from **1** and **2f** to give the product as a colorless liquid after chromatography (hexane/EtOAc = 94/6). Further purification was performed by distillation under reduced pressure. Bp: 95 °C/0.15 mmHg; $^1$H NMR (400 MHz, $CDCl_3$) 7.38 (dd, $J$ = 8.0, 7.2 Hz, 2H, *m*), 7.22 (t, $J$ = 7.2 Hz, 1H, *p*), 7.08 (d, $J$ = 8.0 Hz, 2H, *o*), 2.81 (tq, $J$ = 7.2, 7.2 Hz, 1H, 2-H), 1.69 (ddd, $J$ = 14.4, 7.2, 7.2 Hz, 1H, 3-H*H*), 1.53 (ddd, $J$ = 14.4, 7.2, 7.2 Hz, 1H, 3-H*H*), 1.34 (d, $J$ = 7.2 Hz, 3H, 2-Me), 0.82 (m, 1H, $COCH(CH_3)CH_2CH$), 0.50 (m, 2H, H$^A$ × 2), 0.13 (m, 2H, H$^B$ × 2); $^{13}$C NMR (100 MHz, $CDCl_3$) 175.1 (s, C-1), 150.7 (s, *i*), 129.3 (d, *m*), 125.5 (d, *p*), 121.4 (d, *o*), 40.2 (d, C-2), 38.6 (t, C-3), 16.9 (q, 2-Me), 8.8 (d, $COCH(CH_3)CH_2CH$), 4.6 (t, $COCH(CH_3)CH_2CHC^AH_2$), 4.4 (t, $COCH(CH_3)CH_2CHC^BH_2$); IR (neat) 1759 (C=O) cm$^{-1}$; MS (EI, 70 eV) *m*/*z* 204 (M$^+$, 28), 111 ($COCH(CH_3)CH_2C_3H_5^+$, 54), 94 (88), 83 ($CH(CH_3)CH_2C_3H_5^+$, 70), 55 ($CH_2C_3H_5^+$, 100); HRMS (EI, 70 eV) calcd for ($C_{13}H_{16}O_2$) 204.1150 (M$^+$), found for *m*/*z* 204.1145. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.15; H, 7.74.

**Ethyl 3-Cyclopropyl-2-methylpropanoate (3h).**[21] According to the general procedure, this compound was prepared from **1** and **2h** to give the product as a colorless liquid after chromatography (hexane/EtOAc = 94/6). Further purification was performed by distillation under reduced pressure. Bp: 100 °C/10 mmHg; $^1$H NMR (400 MHz, $CDCl_3$) 4.13 (q, $J$ = 7.2 Hz, 2H, $CH_3CH_2OCO$), 2.53 (tq, $J$ = 7.2, 7.2 Hz, 1H, 2-H), 1.53 (ddd, $J$ = 14.4, 7.2, 7.2 Hz, 1H, 3-H*H*), 1.37 (ddd, $J$ = 14.4, 7.2, 7.2 Hz, 1H, 3-H*H*), 1.26 (t, $J$ = 7.2 Hz, 3H, $CH_3CH_2OCO$), 1.18 (d, $J$ = 7.2 Hz, 3H, 2-Me), 0.69 (m, 1H, $COCH_2CH_2CH$), 0.43 (m, 2H, H$^A$ × 2), 0.04 (m, 2H, H$^B$ × 2); $^{13}$C NMR (100 MHz, $CDCl_3$) 176.8 (s, C-1), 60.1 (t, $CH_3CH_2OCO$), 40.1 (d, C-2), 38.7 (t, C-3), 17.0 (q, 2-Me), 14.2 (q, $CH_3CH_2OCO$), 8.9 (d, $COCH(CH_3)CH_2CH$), 4.5 (t, $COCH(CH_3)CH_2CHC^AH_2$), 4.2 (t, $COCH(CH_3)CH_2CHC^BH_2$); IR (neat) 1736 (C=O) cm$^{-1}$; MS (EI, 70 eV) *m*/*z* 156 (M$^+$, 14), 128 ($CH_3CH_2OCOCH(CH_3)CH_2CH^+$, 70), 102 (65), 87 (36), 83 ($CH(CH_3)CH_2C_3H_5^+$, 48), 74 (100), 55 ($CH_2C_3H_5^+$, 91), 41 ($C_3H_5^+$, 25); HRMS (EI, 70 eV) calcd for ($C_9H_{16}O_2$) 156.1150 (M$^+$), found for *m*/*z* 156.1139.

**Phenyl 3-Cyclopropyl-2,2-dimethylpropanoate (3j).**[21] According to the general procedure, this compound was prepared from **1** and **2j** to give the product as a colorless liquid after chromatography (hexane/EtOAc = 94/6) and recycle GPC. $^1$H NMR (400 MHz, $CDCl_3$) 7.38 (dd, $J$ = 8.0, 7.2 Hz, 2H, *m*), 7.22 (t, $J$ = 7.2 Hz, 1H, *p*), 7.08 (d, $J$ = 8.0 Hz, 2H, *o*), 1.63 (d, $J$ = 7.2 Hz, 2H, 3-H$_2$), 1.36 (s, 6H, 2-Me$_2$), 0.79 (ttt, $J$ = 8.0, 7.2, 4.8 Hz, 1H, $COC(CH_3)_2CH_2CH$), 0.50 (ddd, $J$ = 8.0, 5.6, 4.0 Hz, 2H, H$^A$ × 2), 0.13 (ddd, $J$ = 5.6, 4.8, 4.0 Hz, 2H, H$^B$ × 2); $^{13}$C NMR (100 MHz, $CDCl_3$) 176.5 (s, C-1), 151.0 (s, *i*), 129.3 (d, *m*), 125.5 (d, *p*), 121.4 (d, *o*), 45.4 (t, C-3), 43.4 (s, C-2), 25.3 (q, 2-Me$_2$), 7.0

(26) Orsini, F.; Pelizzoni, F.; Ricca, G. *Tetrahedron* **1984**, *40*, 2781–2787.

(d, $COC(CH_3)_2CH_2CH$), 4.5 (t, two methylene groups in cyclopropyl ring); IR (neat) 1751 (C=O) $cm^{-1}$; MS (EI, 70 eV) *m*/*z* 218 ($M^+$, 3), 125 ($COC(CH_3)_2CH_2C_3H_5^+$, 50), 97 ($C(CH_3)_2CH_2C_3H_5^+$, 84), 96 (28), 94 (84), 81 (30), 55 ($CH_2C_3H_5^+$, 100); HRMS (EI, 70 eV) calcd for ($C_{14}H_{18}O_2$) 218.1307 ($M^+$), found for *m*/*z* 218.1367. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.76; H, 8.29.

**Dibutenylindium Chloride−DPPE Complex (9).** To a suspension of $InCl_3$ (0.5 mmol) in toluene (1 mL) was added (cyclopropylmethyl)tributylstannane (**1**; 1 mmol) at rt. The mixture was stirred for 2 h, and then 1,2-bis(diphenylphosphino)ethane (0.25 mmol) was loaded. The mixture was stirred for 1 h, and then the volatiles were evaporated to give a viscous liquid, which was then washed by hexane to give the product as a white solid (95 mg, 42%). The product was recrystallized from dichloromethane/hexane for X-ray analysis. The data obtained from the measurement was good ($R_{int}$ = 0.056), 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. $^1$H NMR (400 MHz, $CDCl_3$) 7.47−7.31 (m, 20H, Ar), 5.89 (ddt, *J* = 16.8, 9.6, 6.4 Hz, 4H, 3-H × 4), 4.95 (dd, *J* = 16.8, 1.6 Hz, 4H, 4-*H*H × 4), 4.88 (dd, *J* = 9.6, 1.6 Hz, 4H, 4-H*H* × 4), 2.38 (dt, *J* = 7.2, 6.4 Hz, 8H, 2-$H_2$ × 4), 2.36 (m, 4H, P$CH_2CH_2$P), 1.11 (t, *J* = 7.2 Hz, 8H, 1-$H_2$ × 4); $^{13}$C NMR (100 MHz, $CDCl_3$) 142.7 (C-3), 132.8 (*o*, d, $^2J_{P-C}$ = 15.6 Hz), 132.3 (*i*), 130.2 (*p*), 129.0 (*m*, d, $^3J_{P-C}$ = 8.2 Hz), 113.1 (C-4), 30.9 (C-2), 21.9 (P$CH_2CH_2$P, d, $^1J_{P-C}$ = 9.8 Hz), 20.4 (C-1).

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**Supporting Information Available:** Results of NMR experiment of the reaction of varying **2a** and crystallographic data for **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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