Asymmetric Catalysis

DOI: 10.1002/anie.200906308

Indium(I)-Catalyzed Asymmetric Allylation, Crotylation, and α-Chloroallylation of Hydrazones with Rare Constitutional and High Configurational Selectivities**

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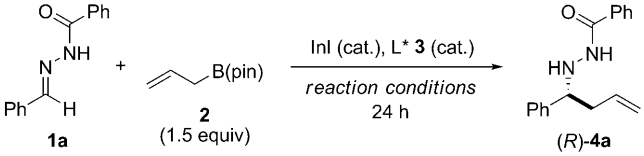
The main group metal indium is appealing for use in catalysis, as indium-based compounds have low toxicity, and are inexpensive, selective, and tolerant toward functional groups.[1,2] Although In^{III} Lewis acids are commonly used in catalysis,[3] In^{I} compounds[4] can display amphiphilic properties depending on the ligands to which they are coordinated, owing to two vacant p orbitals (acid) and a lone pair of electrons (base).[5] Despite this intriguing character, synthesis exploiting In^{I} is rare; more than stoichiometric amounts of In^{I} reagents are generally required in synthetic use.[1,6] In earlier reports,[7] our research group uncovered indium(I)-catalyzed racemic C–C bond formations with allyl boronates. In the course of our studies, NMR spectroscopic analyses revealed the generation of reactive allyl In^{I} species through catalytic B-to-In transmetalation.[7b] Meanwhile, the importance of suitable In^{I} ligation for both structural or physical properties[8] and chemical reactivity[8j,k] has been demonstrated. To the best of our knowledge, however, chiral In^{I} complexes and their catalytic use for asymmetric C–C bond formation are unknown.

Catalytic asymmetric allylation of non-activated imines and their derivatives is challenging,[9] but can provide access to optically enriched homoallyl amine derivatives, which have proved to be useful chiral building blocks for pharmaceutical and agrochemical applications. Most powerful catalytic asymmetric methods have been developed using Sn,[10] Si,[11] B,[12] and in situ prepared indium reagents.[13] Unfortunately, very few catalytic methods were found to be efficient, practical, or general. Herein we report the catalytic use of an unprecedented chiral In^{I} complex for asymmetric C–C bond formations between hydrazones[14] and allyl boronates, which display rare regioselectivity and high configurational selectivities.

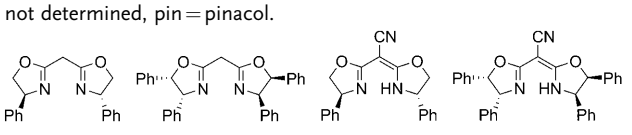
Initial investigations involved ligand screening[15] for the reaction employing acylhydrazone **1a** and allyl boronate **2** in the presence of a catalytic amount of indium(I) iodide[7a–c] (Table 1). Chiral bis(oxazoline) ligands **3a** and **3b** gave the desired product **4a** with promising asymmetric induction; with a catalyst loading of 10 mol% in dichloromethane, **3b** proved to be more efficient than **3a** (Table 1, entries 1 and 2). Although the enantiomeric ratio (e.r.) dropped in toluene, high asymmetric induction was restored in toluene/MeOH

Table 1: Optimization of reaction conditions for asymmetric In^{I} catalysis.



Entry	InI [mol%]	L* **3** (mol%)	Reaction Conditions	Yield [%][a]	e.r.
1	10	**3a** (10)	CH_2Cl_2, RT	40	81:19[b]
2	10	**3b** (10)	CH_2Cl_2, RT	65	86:14
3	10	**3b** (10)	toluene, RT	36	62:38
4	10	**3b** (10)	toluene/MeOH (16:1), RT	89	96:4
5	5	**3b** (5)	toluene/MeOH (16:1), 0°C	quant	98:2
6[c]	5	**3c** (5)	toluene/MeOH (16:1), 0°C	90	97:3[b]
7[c]	5	**3d** (5)	toluene/MeOH (16:1), 0°C	99	98:2
8	5	**3d** (5)	toluene/EtOH (16:1), 0°C	91	98:2
9[d]	5	**3d** (5)	toluene/*i*PrOH (16:1), 0°C	quant	95:5
10[c]	–	**3d** (5)	toluene/MeOH (16:1), 0°C	trace	n.d.
11[c]	5[e]	**3d** (5)	toluene/MeOH (16:1), 0°C	55	89:11

[a] Yield of isolated **4a** after purification on silica gel (PTLC). [b] Use of L* **3a** or **3c**: (*S*)-**4a** was obtained as the major enantiomer. [c] Reaction time was 12 h. [d] Reaction time was 48 h. [e] Use of InI_3 instead of InI. n.d. = not determined, pin = pinacol.



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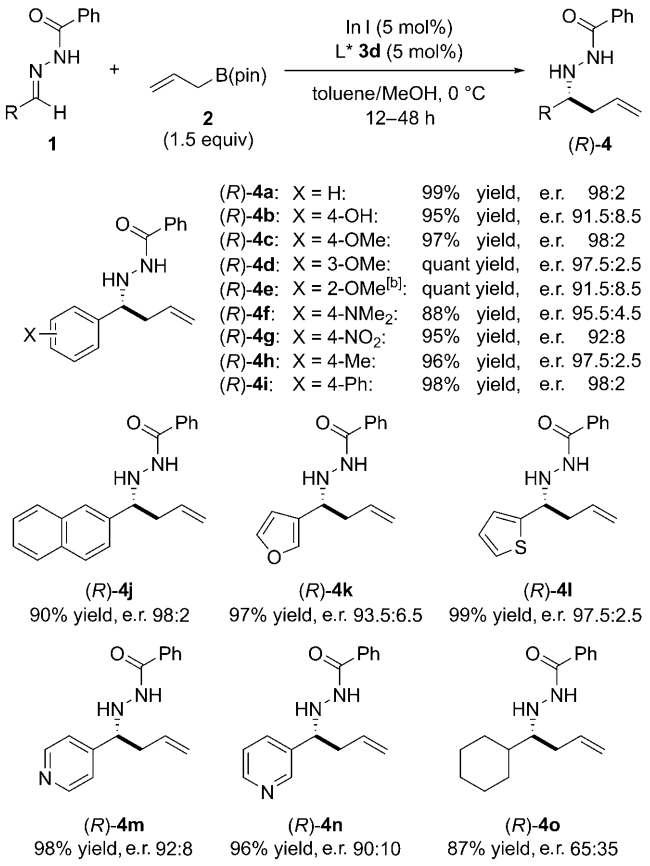
[**] This work was supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS) and the Global COE Program (Chemistry Innovation through Cooperation of Science and Engineering), the University of Tokyo, MEXT, Japan. H.K. gratefully acknowledges the JSPS for a Research Fellowship for Young Scientists.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200906308.

(16:1; Table 1, entries 3 and 4). Further experiments revealed that the use of chiral semicorrin ligands[16] **3c** and **3d** showed a significant rate enhancement compared with **3b**, while maintaining an excellent level of asymmetric induction (e.r. = 98:2; Table 1, entries 5–7). The use of other alcohols did not lead to further improvement (Table 1, entries 8 and 9). Notably, the allylation essentially did not proceed in the absence of InI, and InI_3 proved to be substantially less effective (Table 1, entries 10 and 11).[17]

We consider this asymmetric In^I catalysis for C–C bond formation remarkable for a number of reasons: 1) Contrary to reported reactions of In^I halides with Lewis bases (ligands),[4,5,8] we did not observe disproportionation of In^I.[18] 2) To the best of our knowledge, an enantiomeric ratio of 98:2 for product **4a** is to date the best result for metal-catalyzed asymmetric allylation of aromatic imine derivatives.[19] 3) These findings reveal the critical role of chiral ligands (L*) **3a–d** in stabilizing the labile In^I[4,5,8] and in creating excellent environments for asymmetric induction.

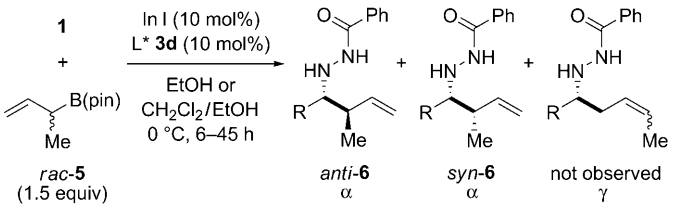
Next, we investigated the scope of hydrazones **1** (Scheme 1). Various aromatic substrates bearing functionalities such as free hydroxy, methoxy, tertiary amino, and nitro groups were allylated in high yields with enantiomeric ratios of up to 98:2. Furthermore, O-, S-, and N-containing heterocycles proved to be excellent substrates with enantiomeric ratios of up to 97.5:2.5. Aliphatic hydrazones such as **1o** (R = cyclohexyl) proved to be less efficient in terms of asymmetric induction.



Scheme 1. Scope for asymmetric indium(I)-catalyzed allylation of **1** with **2**. [a] Yield of (*R*)-**4a–o** isolated after purification on silica gel (PTLC). [b] Reaction temperature was −20 °C.

We then examined indium(I)-catalyzed asymmetric crotylation (Table 2). Initial trials with hydrazone **1a** and α-methylallyl boronate *rac*-**5** under our reported conditions,[7c]

Table 2: Asymmetric indium(I)-catalyzed crotylation of **1** with *rac*-**5**.



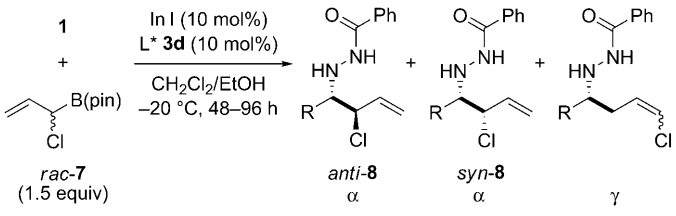
Entry	**1**	α/γ	α-Adduct **6**: R	Yield [%][c]	*anti*-**6**/*syn*-**6**	e.r. (*anti*-**6**)
1	**1a**	>99:1	**6a**: Ph	85	19:1	97:3
2[a]	**1b**	>99:1	**6b**: 4-HOC_6H_4	98	11:1	94:6
3	**1c**	>99:1	**6c**: 4-$MeOC_6H_4$	86	19:1	96.5:3.5
4	**1d**	>99:1	**6d**: 3-$MeOC_6H_4$	90	7:1	94.5:5.5
5[b]	**1h**	>99:1	**6h**: 4-MeC_6H_4	quant	8:1	96:4
6[b]	**1k**	>99:1	**6k**: 3-furyl	98	11:1	96.5:3.5
7	**1l**	>99:1	**6l**: 2-thienyl	quant	15:1	94:6
8	**1p**	>99:1	**6p**: 4-ClC_6H_4	83	17:1	92:8

[a] Use of L* **3c**: the opposite enantiomer was obtained as the major enantiomer. [b] Reaction temperature: −20 °C. [c] Yield of isolated α-adduct **6** after purification on silica gel (PTLC).

in the presence of various chiral ligands, provided the desired product **6a** with disappointing regio-, diastereo-, and enantioselectivites.[15] After extensive experimentation,[15] high α/γ and *anti*/*syn* ratios as well as high asymmetric induction could be obtained with InI and L* **3d** in EtOH (α/γ = >99:1, *anti*/*syn* = 19:1, e.r. = 97:3; Table 2, entry 1). These optimized reaction conditions were applicable to various hydrazones **1**; all aromatic and heteroaromatic substrates tested were converted exclusively into α-adducts **6** in high yields with *anti*/*syn* ratios of up to 19:1 and enantiomeric ratios of up to 96.5:3.5 (Table 2, entries 2–8). The present work constitutes the first systematic crotylation study with a broad variety of imine derivatives; several characteristic features of this asymmetric In^I catalysis are noteworthy: 1) The unusual α selectivity[20] observed with *rac*-**5** contrasts its exclusive γ selectivity in the absence of a catalyst[21a] and under Lewis or Brønsted acid catalysis;[21b,c] this rare α selectivity suggests B-to-In transmetalation prior to C–C bond formation.[22] 2) The use of **5** in racemic form provided enantiomerically enriched *anti*-**6**[15] as the major product; in this context, it is noted that the preparation of α-substituted allyl boronates of type **5** in enantiomerically enriched form is not trivial.[23] 3) This diastereoselective reaction avoids the use of geometrically enriched or pure crotyl reagents, typically required to selectively form products of type **6**. 4) Our catalytic In^I method provides substantially higher regioselectivity and configurational selectivities for product **6a** compared with a recently reported stoichiometric In^0 Barbier procedure.[24]

Next, we employed α-chloroallyl boronate *rac*-**7** (Table 3), which is a rarely used nucleophile that adds in the absence of a

Table 3: Asymmetric indium(I)-catalyzed α-chloroallylation of **1** with *rac*-**7**.

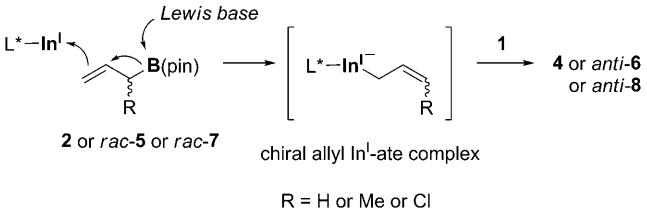


Entry	**1**	α/γ	α-Adduct **8**: R	Yield [%][a]	*anti*-**8**/*syn*-**8**	e.r. (*anti*-**8**)
1	**1a**	49:1	**8a**: Ph	84	99:1	92:8
2	**1j**	99:1	**8j**: 2-naphthyl	71	33:1	90.5:9.5
3	**1l**	>99:1	**8l**: 2-thienyl	89	99:1	93:7

[a] Yield of isolated α-adduct **8** after purification on silica gel (PTLC).

catalyst with γ selectivity to electrophiles.[25] Remarkably, the present asymmetric In^I catalysis proved to be compatible with the reactive allylic C–Cl bond of *rac*-**7**, and almost exclusive α selectivity was observed;[22] α-adducts **8** were formed in good yields with excellent *anti*/*syn* ratios[15] (up to 99:1) and enantiomeric ratios of up to 93:7. These reactions represent rare examples of the catalytic formation of stereogenic centers bearing a chlorine atom with high asymmetric induction, which may lead to new disconnection approaches in the total synthesis of chlorinated natural products.[26] In addition, further synthetic transformations of the unsaturated β-chloroamine unit of **8** may be envisaged with respect to both the chloro functional group and the C=C double bond.

Our attention then turned to the mechanism of this catalytic asymmetric C–C bond formation. InI and the chiral semicorrin ligand L* **3d** (ratio = 1:1) were stirred in toluene/MeOH (16:1) at room temperature for 1 h; through MALDI-TOF MS analysis of this mixture we observed in situ generation of a metal–ligand complex in a ratio of 1:1 (Figure 1). Preliminary NMR spectroscopic analysis of this complex was hampered by its low solubility. Unexpectedly, and contrary to our earlier study,[7b] NMR spectroscopic analysis of allyl boronate **2** in [D_8]toluene/MeOH (16:1) at room temperature revealed that **2** is stable in the presence of the preformed chiral In^I–L* **3d** complex (50 mol%); no B-to-In transmetalation was observed even after an extended reaction time. However, upon addition of hydrazone **1a** (0.67 equiv) asymmetric C–C bond formation occurred smoothly. This observation suggests that, at least in the first cycle, **1a** may act as a Lewis base to activate **2** (B-to-In transmetalation; Scheme 2). The chiral allyl In^I-ate complex formed in situ may then undergo C–C bond formation with **1a** via a cyclic transition state to provide (*R*)-**4a**.[15,17,27]



Scheme 2. Assumed catalytic B-to-In transmetalation.

To the best of our knowledge, the reactions described in this report represent the first example of asymmetric In^I catalysis, which are of fundamental importance. We have uncovered enantioselective allylation, crotylation, and α-chloroallylation of hydrazones with boronates by employing an in situ generated chiral indium(I)–semicorrin catalyst. Rare regioselectivity and high configurational selectivities were observed with α-substituted allyl boronates; the present In^I protocol is therefore clearly distinct from previous catalytic use of allyl boronates.[12,28] Various compounds bearing reactive aliphatic C–Cl and aromatic O–H bonds were shown to be compatible. At this stage, we assume that the in situ generation of reactive chiral allyl In^I-ate species takes place through B-to-In transmetalation. Further mechanistic studies and the extension of this concept to new reactions involving boronates are currently underway.

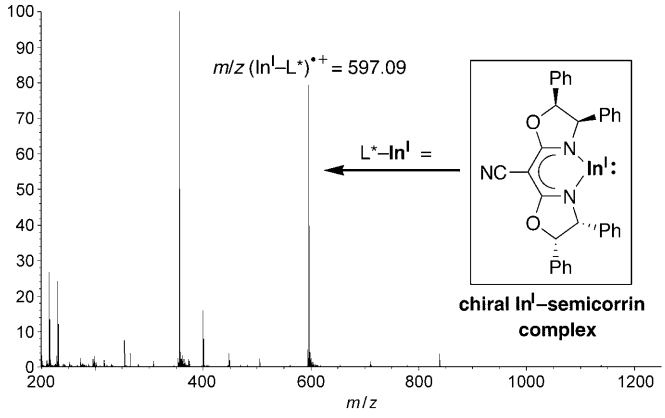


Figure 1. MALDI-TOF MS analysis of the postulated chiral indium(I)–semicorrin complex, generated in situ from InI and L* **3d** (the matrix used was pyrene).

Received: November 9, 2009
Revised: January 9, 2010
Published online: February 4, 2010

Keywords: asymmetric catalysis · boron · C–C coupling · indium · semicorrin

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[24] Regioselectivity: $\alpha/\gamma => 99{:}1$ (this report) vs. 6.7:1 (Ref. [13b]); configurational selectivity: *anti*-**6a**/*syn*-**6a** = 19:1 (this report) vs. 1.6:1 (Ref. [13b]); the same level of asymmetric induction (e.r.) was observed in both cases.

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[26] Recent examples of the formation of stereogenic centers bearing chlorine atoms in total syntheses: a) asymmetric: S. A. Snyder, Z.-Y. Tang, R. Gupta, *J. Am. Chem. Soc.* **2009**, *131*, 5744; b) racemic: C. Nilewski, R. W. Geisser, E. M. Carreira, *Nature* **2009**, *457*, 573.

[27] So far, there is no direct evidence to support this transmetalation mechanism even after several trials. A referee suggested the possibility that the equilibrium might lie to allyl boronate **2**, and that the addition of hydrazone **1a** might drain the unobserved allyl In^{I}-ate complex and the equilibrium might be rapidly reestablished.

[28] Acid-catalyzed allyl boration of carbonyl compounds: D. G. Hall, *Synlett* **2007**, 1644.

