Arylboronic Acid Synthesis

International Edition: DOI: 10.1002/anie.201611974
German Edition: DOI: 10.1002/ange.201611974

Rhodium-Catalyzed Decarbonylative Borylation of Aromatic Thioesters for Facile Diversification of Aromatic Carboxylic Acids

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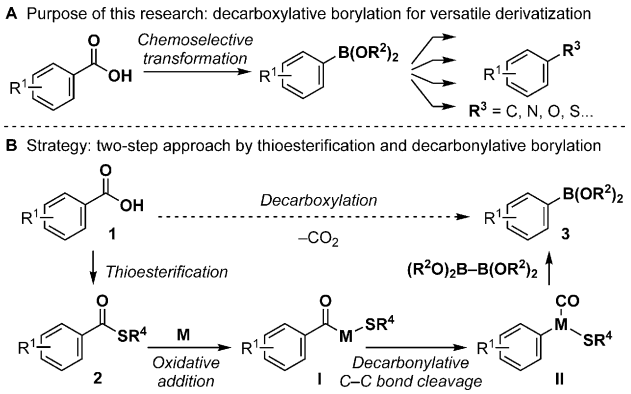
Abstract: *Transformation of aromatic thioesters into arylboronic esters was achieved efficiently using a rhodium catalyst. The broad functional-group tolerance and mild conditions of the method have allowed for the two-step decarboxylative borylation of a wide range of aromatic carboxylic acids, including commercially available drugs.*

The carboxylic acid is a fundamental functional group often found in a broad range of organic molecules, including natural products, pharmaceuticals, agrochemicals, and functional materials. The availability of carboxylic acids has been further increased by recent advances in carboxylation reactions.[1] In line with the increasing availability of carboxylic acids, their direct decarboxylative functionalization, which significantly expands the diversity of synthesizable molecules, has also been attracting considerable interest.[2] One of the most straightforward approaches for facile diversification is to transform carboxylic acids into multitransformable intermediates such as organoboron compounds, which serve as versatile synthetic intermediates demonstrating a wide spectrum of reactivities (Scheme 1 A).[3] Indeed, recent studies,[4–10] including ours,[9b,10a] on catalytic borylative transformations by cleavage of stable bonds, such as C–H,[5] C–O,[6] C–N,[7] C–CN,[8] C–F,[9] and C–S[10] bonds, have confirmed the validity of this approach. Herein, we report a decarbonylative borylation of aromatic thioesters that enabled two-step decarboxylative borylation of aromatic carboxylic acids.

The challenge of this transformation was to cleave a stable C(aromatic)–C(carbonyl) bond while forming an easily transformable C–B bond. Although various transition-metal-catalyzed decarboxylative transformations of aromatic carboxylic acids have been reported,[2] these transformations were achieved at elevated temperature (typically $>150\,^{\circ}C$), which greatly limits the scope of applicable substrates.[11] This is probably because a large amount of energy is required to cleave the stable C–C bond. To achieve the C–C bond cleavage under milder conditions, we focused on transition-metal-mediated decarbonylation by acylmetal species **I** (Scheme 1 B).[12] We anticipated that reverse insertion of a carbonyl group in **I** could smoothly occur by the cleavage of the C–C bond under mild conditions to afford arylmetal species **II**,[2a,13] which could react with a diboron compound to furnish the borylated product **3**.[10a] Recently, Shi et al. and Rueping et al. independently reported nickel-catalyzed decarbonylative borylations based on this approach using esters and amides as precursors for the acylmetal species. However, these reactions still required high temperature ($>150\,^{\circ}C$) with moderate substrate scope.[14] We envisioned that thioester **2**, which is a stable carboxylic acid derivative,[15] would be a better precursor of the acylmetal species **I** because highly chemoselective cleavage of a C(carbonyl)–S bond in thioester **2** by oxidative addition to a low-valent transition metal was anticipated to proceed under mild conditions.[16]



Scheme 1. Proposed strategy.

After extensive screening of the reaction conditions using *S*-ethyl 4-phenylbenzothioate (**2a**, 0.200 mmol), we found that a rhodium complex in the presence of a phosphine ligand and a base efficiently catalyzed the desired decarbonylative borylation under mild conditions (Table 1). Heating a mixture of **2a**, bis(pinacolato)diboron (**4a**, $(Bpin)_2$, 2 equiv), $[Rh(OH)(cod)]_2$ (5 mol%; cod = 1,5-cyclooctadiene), $P(n\mathrm{Bu})_3$ (50 mol%), and KOAc (20 mol%) in cyclopentyl methyl ether (CPME) at 80 °C for 24 h afforded the desired arylboronate **3a** in high yield (Table 1, entry 1). Reactions using a ligand other than $P(n\mathrm{Bu})_3$ and PEt_3, as well as the ligandless reaction, provided poor results with recovery of **2a** (Table 1, entries 2–5; Supporting Information, Table S1). Whereas the amount of $P(n\mathrm{Bu})_3$ could be reduced to 10 mol% (Rh:P = 1:1) to afford **3a** in a reasonable yield (Supporting Information, Table S2) and highly reproducible

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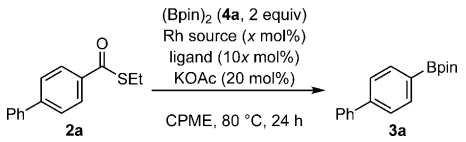
Table 1: Optimization of reaction conditions.



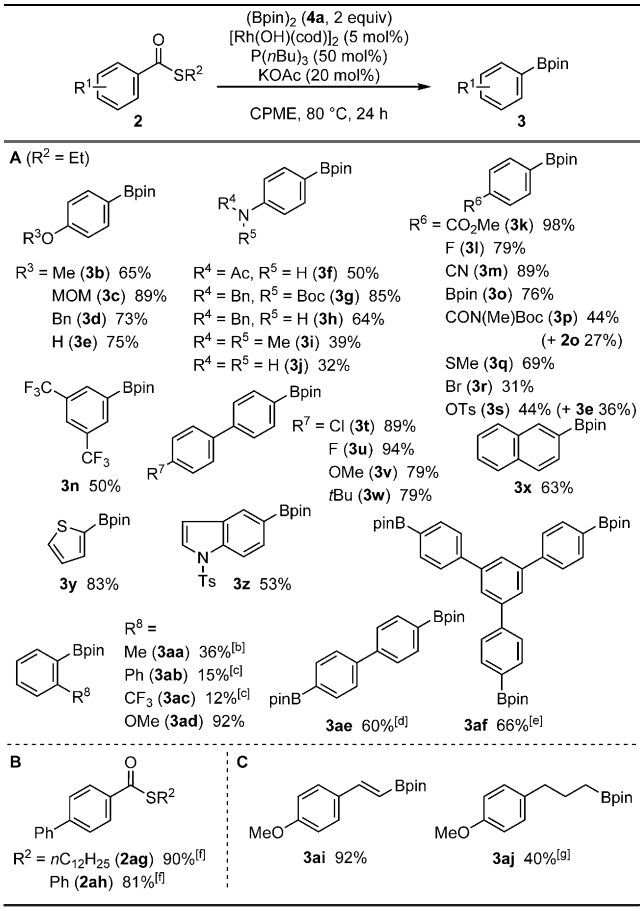
Entry	Rh source (*x* mol %)	Ligand	Yield **3a** [%][a]
1	$[Rh(OH)(cod)]_2$ (5)	$P(nBu)_3$	95 (83)[b]
2	$[Rh(OH)(cod)]_2$ (5)	PCy_3	1
3	$[Rh(OH)(cod)]_2$ (5)	PPh_3	48
4	$[Rh(OH)(cod)]_2$ (5)	dcpe	0
5	$[Rh(OH)(cod)]_2$ (5)	–	17
6	$[RhCl(cod)]_2$ (5)	$P(nBu)_3$	27 [>99][c]
7	$[RhCl(CO)_2]_2$ (5)	$P(nBu)_3$	22 [>99][c]
8[d]	$[Rh(OH)(cod)]_2$ (5)	$P(nBu)_3$	25 [29][c]
9	$[Rh(OH)(cod)]_2$ (0.05)	$P(nBu)_3$	[72][c]
10[e]	$[Rh(OH)(cod)]_2$ (0.5)	$P(nBu)_3$	89 (89)[b]

[a] Yields were determined by GC analysis, unless otherwise noted. [b] Isolated yields are shown in parentheses. [c] Yields for the reactions conducted for 120 h in brackets. [d] Reaction was conducted without KOAc. [e] Reaction was conducted for 120 h using 1.21 g (5 mmol) of **2a**. Key: dcpe = 1,2-bis(dicyclohexylphosphino)ethane.

result was obtained using 50 mol % of the ligand.[17] The complexes $[RhCl(cod)]_2$ and $[RhCl(CO)_2]_2$ also catalyzed this reaction, although prolongation of the reaction time from 24 h to 120 h was needed to achieve efficient transformation (Table 1, entries 6 and 7; Supporting Information, Table S3). At the very least, a catalytic amount of KOAc (Supporting Information, Table S4) was essential to achieve efficient transformation (Table 1, entry 8; Supporting Information, Table S5). Although KOAc gave the best result among the bases examined, several other bases were also employable (Supporting Information, Table S6). Even when the amount of the rhodium source was reduced to 0.05 mol %, **3a** was obtained in a reasonable yield by extending the reaction time to 120 h (Table 1, entry 9; Supporting Information, Table S7). The reaction proceeded smoothly in low-polarity solvents, especially in ethereal solvents such as CPME, THF (tetrahydrofuran), and 1,4-dioxane (Supporting Information, Table S8). The scalability of the reaction was demonstrated in a gram-scale synthesis of **3a** using a reduced amount (0.5 mol %) of $[Rh(OH)(cod)]_2$ (Table 1, entry 10). Using bis(neopentyl glycolato)diboron (**4b**, $(Bnep)_2$) instead of $(Bpin)_2$ (**4a**) gave the corresponding borylarene in 43 % yield (Supporting Information, Scheme S2).

The optimal conditions (Table 1, entry 1) were applicable to a broad range of aromatic thioesters (Table 2). Borylation of substituted *S*-ethyl benzothioates bearing an electron-donating group, such as **2b–j**, or an electron-withdrawing group, such as **2k–p,** afforded arylboronic esters **3b–p** in good to excellent yields (Table 2 A). Notably, substrates with a protic hydroxy or amino group, such as **2e**, **2f**, **2h**, and **2j**, were applicable, showing the excellent functional-group tolerance of the method. The reaction of **2q** bearing a methylthio group afforded **3q** uneventfully. During this reaction, neither rhodium-catalyzed *ortho*-borylation of the sulfanyl group[10a,18] nor borylative cleavage of the C(aryl)–S bond[10a] was observed, demonstrating the high chemoselectivity of the method. Furthermore, borylation of thioester **2p**, bearing an imide moiety, afforded the desired borylarene **3p** and borylated thioester **2o** in 44 % and 27 % yield, respectively, suggesting that decarbonylative borylation of the imide group also proceeded.[14a,19] Substrates having a functional group that is sensitive to low-valent transition metals, such as **2r** (C–Br bond), **2s** (C–OTs bond), or **2t** (C–Cl bond),[20] also participated in this reaction, although unidentified byproducts or a considerable amount of desulfonylated product **3e** were also obtained from the reaction of **2r** or **2s**, respectively. Borylation of thioesters with other aromatic systems, including biphenyl, naphthalene, thiophene, and indole, proceeded efficiently to afford **3t–z**. While this method showed a broad substrate scope, significant retardation was observed for the reaction of thioesters with an *ortho*-substituent. For example, borylation of *S*-ethyl 2-methylbenzothioate (**2aa**) remained incomplete even after heating for 72 h, and the reactions of substrates with a bulkier *ortho*-substituent, such as **2ab** or **2ac**, did not proceed. In these cases, using two times the amounts of the reagents and elevating the reaction temperature afforded the borylated products **3ab** or **3ac**, albeit in

Table 2: Decarbonylative borylation of thioesters.[a]

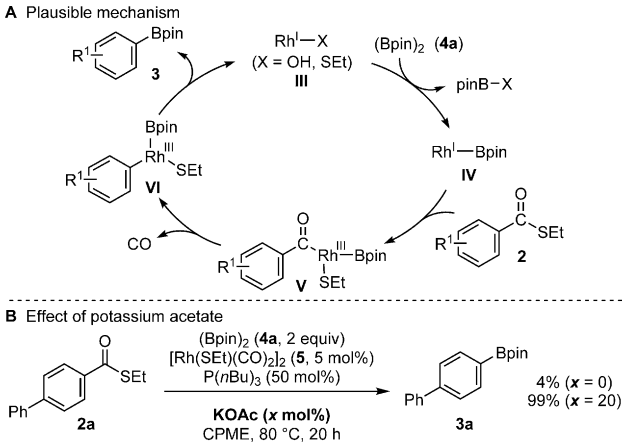


[a] Yields of isolated products are shown, unless otherwise noted. [b] Reaction was performed for 72 h. [c] Yields for the reactions conducted at 110 °C using two times the amounts of the reagents. [d] Two times the amounts of the reagents were used. [e] Three times the amounts of the reagents were used. [f] Yields of **3a** determined by GC analysis. [g] CsF (3 equiv) was used instead of KOAc.

low yields. In contrast, the borylation of *ortho*-methoxy substrate **2ad** proceeded smoothly under the standard conditions, indicating the involvement of a directing effect. Multiple decarbonylative borylations also took place simultaneously; di- and triborylated arenes such as **3ae** and **3af**, which are useful building blocks for covalent organic frameworks,[21] were efficiently obtained from di- and trithioesters **2ae** and **2af**, respectively. Moreover, this transformation was not limited to *S*-ethyl thioesters; *S*-dodecyl and *S*-phenyl thioesters **2ag** and **2ah** were also borylated smoothly under the same conditions to give **3a** in high yields (Table 2B).

The method was also applicable to the decarbonylative borylation of alkenyl and alkyl thioesters, expanding the range of available compounds (Table 2C).[22] While soft nucleophiles such as thiols easily react with α,β-unsaturated thioesters to form 1,4-adducts, 4-methoxycinnamic acid *S*-ethyl ester (**2ai**) was transformed to alkenylboronic ester **3ai** in high yield under the same conditions. Furthermore, although not fully optimized, the borylative cleavage of a C(sp^3)–C bond in **2aj** also proceeded to afford alkylboronic ester **3aj** by the use of cesium fluoride as a base instead of KOAc.[11]

We currently anticipate that the borylative C–C bond cleavage of thioester **2** proceeds by the decarbonylation of acyl(boryl)rhodium(III) species **V**, as we initially envisioned (Scheme 2A). This mechanism begins with transmetalation



Scheme 2. Mechanistic considerations.

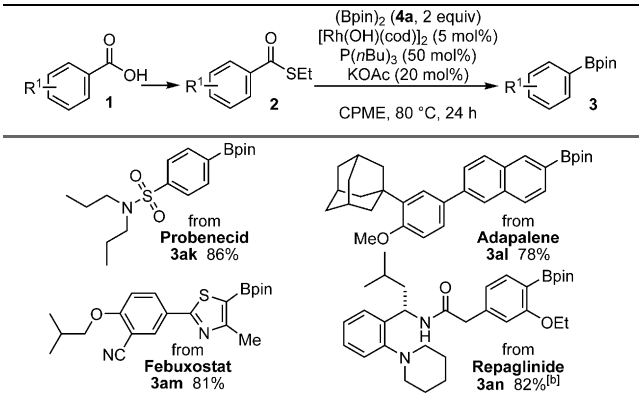
between a rhodium(I) species **III** and diboron **4a** to afford borylrhodium(I) **IV**,[23] which then generates **V** by oxidative addition of thioester **2**. Subsequent reverse insertion of the carbonyl group in **V** gives arylrhodium(III) species **VI** with the liberation of carbon monoxide.[24] Finally, reductive elimination of **3** from **VI** completes the catalytic cycle. The decarbonylative borylation of **2a** proceeded efficiently to afford **3a** even in the presence of a radical scavenger such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT; Supporting Information, Table S9), indicating that a one-electron transfer process is not involved in this reaction. Additionally, a competitive reaction between **2b** and **2k** showed that electron-deficient thioesters are more favored substrates for this reaction (Supporting Information, Scheme S5). This result suggested that oxidative addition (**IV** to **V**) or decarbonylation (**V** to **VI**) is the rate-determining step.[25]

Interestingly, under the optimal conditions, deactivation of the rhodium catalyst, which is potentially caused by coordination of carbon monoxide to the metal center, was not observed.[26] To gain more mechanistic insight into this reaction, we focused on the result obtained from the borylation of **2a** performed without adding KOAc (Table 1, entry 8). As described above, in this case the yield of **3a** did not reach 30% even when the reaction time was prolonged to 120 h, which indicated that the catalyst was deactivated in the absence of KOAc. This speculation was supported by the results obtained from the reactions using di(carbonyl)rhodium dimer $[Rh(SEt)(CO)_2]_2$ (**5**; Scheme 2B). Whereas only a trace amount of **3a** was obtained when the reaction was performed without KOAc, almost quantitative transformation was achieved using 20 mol% of KOAc.[27] These results suggested that KOAc contributed to the regeneration of an active species from the deactivated rhodium complex.[28]

The practicality of this method was demonstrated by the two-step decarboxylative borylation of carboxylic acid-containing drugs such as probenecid, adapalene, febuxostat, and repaglinide, which have various functional groups (Table 3). After thioesterification of these acids by conventional methods,[15] thioesters **2ak**–**an** were smoothly converted to the corresponding boronates **3ak**–**an** in high yields.

In summary, we have developed an efficient synthetic method for borylarenes from a wide range of aromatic carboxylic acids by a simple two-step procedure. The key to success was the use of thioesters and the rhodium catalyst, which enabled the promotion of the desired decarbonylative borylation at significantly lower temperature (80 °C) than that (> 150 °C) required for previously reported nickel-catalyzed methods using ester or amide derivatives.[14] In combination with versatile and reliable organoboron chemistries, as well as recent progress on carboxyl group-directed C–H bond

Table 3: Two-step borylation of carboxylic acid-containing drugs.[a]



[a] Isolated yields of **3** from *S*-ethyl thioesters **2** are shown. For the preparation of **2** from acids **1**, see the Supporting Information.
[b] Reaction was performed for 72 h using two times the amounts of the reagents.

functionalizations,[29] this method would allow for facile derivatization of readily available carboxylic acids to a diverse range of compounds. Applications of this method to the synthesis of densely functionalized molecules, including molecular probes, and further mechanistic studies, particularly on the regeneration step of the catalyst mediated by KOAc, are currently underway in our laboratory.

Acknowledgements

This research was supported by JSPS KAKENHI Grant Number 15K05509 (C; T.N.) and Special Postdoctoral Researcher Program from RIKEN (H.O.).

Conflict of interest

The authors declare no conflict of interest.

Keywords: borylation · carboxylic acids · decarbonylation · rhodium catalysts · thioesters

How to cite: *Angew. Chem. Int. Ed.* **2017**, *56*, 2482–2486
Angew. Chem. **2017**, *129*, 2522–2526

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[17] A highly reproducible result was also obtained using a preheated (80 °C, 1 h) mixture of $[Rh(OH)(cod)]_2$ (5 mol %), $P(n\text{Bu})_3$ (10 mol %), and KOAc (20 mol %) in CPME, indicating that using an excessive amount of the ligand is avoidable (Supporting Information, Scheme S1).

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[19] Borylation of thioester **2ao** bearing a phenyl ester moiety did not afford **3ao**, and instead, *S*-ethyl 4-borylbenzoate **2o** (27 %) and diborylbenzene **3o** (34 %) were obtained (Supporting Information, Scheme S3), indicating that the phenyl ester moiety is more reactive than the thioester moiety under these conditions.

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[24] We have detected carbon monoxide in the gas phase of the reaction vial using a gas detector tube. See the Supporting Information for details.

[25] At this stage, we cannot exclude the possibility that the reaction begins with oxidative addition of thioester **2** to the rhodium center, followed by transmetalation with diboron **4a** to afford **V**. For preliminary mechanistic studies, see the Supporting Information (Scheme S4 and Figure S1).

[26] Decarbonylation of carbonyl compounds such as aldehydes typically requires more than equimolar amounts of rhodium complex because of deactivation of the complex by coordination of carbon monoxide to the rhodium center. The reaction at a temperature higher than 180 °C enabled decarbonylation with a catalytic amount of the rhodium complex. See: Refs [13b] and [13c].

[27] The borylation of **2a** using $[Rh(OAc)(cod)]_2$ instead of $[Rh(OH)(cod)]_2$ without KOAc gave **3a** in 24% yield (Supporting Information, Table S3, entry 5). This result implies that the acetate bound to the rhodium center was trapped as pinB-OAc after the transmetalation step (Scheme 2 A III, (X = OAc) + **4a** to **IV**), and thus, the acetate could no longer participate in the reaction. Therefore, we believe that the transmetalation occurs not from rhodium(I) acetate but from rhodium(I) thiolate, and additional KOAc does not participate in transmetalation as a base.

[28] ^{31}P NMR analysis of the reaction mixture for the borylation of **2a** without addition of KOAc (Table 1, entry 8) after heating for 24 h at 80 °C showed a major doublet signal at $\delta = 8.3$ ppm ($J_{P,Rh} = 108$ Hz) as a single Rh-phosphine complex. Further study to characterize this species is currently underway.

[29] For selected reviews, see: a) T. Satoh, M. Miura, *Synthesis* **2010**, 3395; b) K. M. Engle, T.-S. Mei, M. Wasa, J.-Q. Yu, *Acc. Chem. Res.* **2012**, *45*, 788; c) G. Shi, Y. Zhang, *Adv. Synth. Catal.* **2014**, *356*, 1419; d) M. P. Drapeau, L. J. Gooßen, *Chem. Eur. J.* **2016**, *22*, 18654.

Manuscript received: December 9, 2016
Final Article published: January 26, 2017

