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Synthesis of hydrosilylboronates *via* the monoborylation of a dihydrosilane Si–H bond and their application for the generation of dialkylhydrosilyl anions†

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The synthesis of a series of hydrosilylboronates *via* the selective iridium- or nickel-catalyzed monoborylation of dihydrosilane Si–H bonds is described. The synthesized silylboronates, which bear a single Si–H bond, can be used as novel silicon nucleophiles in the presence of transition-metal catalysts or bases. The first ²⁹Si(¹H) NMR spectroscopic evidence for the formation of (t-Bu)₂HSiLi, generated by the reaction of (t-Bu)₂HSi–B(pin) with MeLi, is reported as the first example of a dialkylhydrosilyl lithium species.

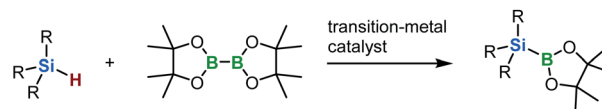
Introduction

Silicon-based compounds have many applications in catalyst design, drug discovery, materials science, and polymer chemistry.¹ The development of new reagents for the synthesis of organosilicon compounds is therefore of considerable interest in a broad range of scientific fields.¹ Since the pioneering study of Suginome and Ito in 1996, silylboronates have become indispensable silylation reagents on account of their reactivity and the ease with which they can be handled.^{1–3} In the presence of a transition-metal catalyst or a base, silylboronates can be activated and used as silicon nucleophiles for reactions with a wide variety of electrophiles.^{1–3} Given their high synthetic utility, the development of efficient methods for the preparation of new silicon-based boron nucleophiles would expand the range of silicon-based compounds that are synthetically accessible.

The typical synthetic route to silylboronates involves a stoichiometric reaction between a silyl anion and a boron electrophile.² As silyl anions are in most cases produced by the reduction of chlorosilanes with alkali metals, the variety of substituents tolerated on the silicon atom is quite limited; moreover, at least one aromatic group is required at the silicon center in order to reduce chlorosilanes and disilane intermediates.^{4,5} Additionally, due to the harsh reduction conditions, this method suffers from low functional-group compatibility. Therefore, only a limited range of silylboronates can be prepared using this approach.

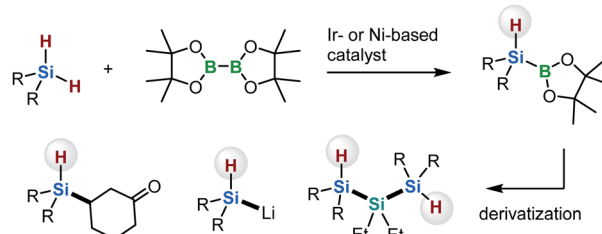
Instead, the direct borylation of Si–H bonds has emerged as a valuable complementary method for the synthesis of silylboronates (Scheme 1a).^{6,7} In 2008, Hartwig and co-workers reported a ground-breaking study on the borylation of trialkylhydrosilanes with bis(pinacolato)diboron [B₂(pin)₂] in the presence of an iridium-based catalyst. This reaction forms trialkylsilylboronates, which cannot be synthesized using the conventional reduction based on alkali metals.⁶ In 2020, our group reported that rhodium- and platinum-based catalysts can promote the borylation of trialkylhydrosilanes with B₂(pin)₂. Our method enables the synthesis of bulky and functionalized trialkylsilylboronates that are difficult to access *via* either the iridium-catalyzed borylation or the conventional reduction method (Scheme 1a).⁷

(a) Transition-metal-catalyzed Si–H borylation of hydrosilanes



- Ir catalyst (Hartwig, 2008) • Rh and Pt catalysts (Ito, Kubota, 2020)

(b) This work: Si–H monoborylation of dihydrosilanes



- Hydrosilylboronates: novel silicon nucleophiles in organic synthesis

Scheme 1 Transition-metal-catalyzed Si–H bond borylation of hydrosilanes.

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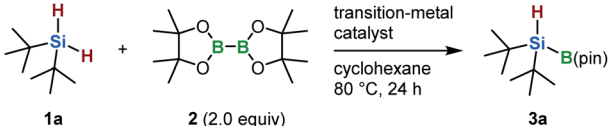
In the present study, we discovered that the monoborylation of a dihydrosilane Si–H bond can be achieved in the presence of iridium- or nickel-based catalysts, yielding hydrosilyboronates that bear a hydrogen atom at the silicon center (Scheme 1b). In 2004, Tokitoh and co-workers reported the first synthesis of diarylhydrosilylboronates *via* the insertion of a silylene into a H–B bond.⁸ Although this pioneering study is remarkable, the substituents on the silicon atom are limited to extremely bulky aryl moieties, such as mesityl and 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl groups, due to the highly reactive silylene species involved in the reaction.⁸ The monoborylation approach reported here is applicable to the synthesis of dialkylhydrosilylboronates and alkylarylhydrosilylboronates from easily accessible dihydrosilanes. These hydrosilylboronates are difficult to access by any other means. Furthermore, we demonstrate that these hydrosilylboronates can be used as novel silicon nucleophiles in the presence of a transition-metal catalyst or base. Moreover, we report the first ²⁹Si{¹H} NMR spectroscopic evidence for the formation of (*t*-Bu)₂HSiLi, generated *via* the reaction of (*t*-Bu)₂HSi–B(pin) with MeLi. Although the synthesis of disilylhydrosilyl lithium compounds has already been reported by Iwamoto, Kira and co-workers,⁹ this is the first example of the formation of dialkylhydrosilyl lithium species.

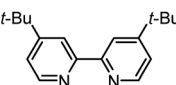
Results and discussion

We started by optimizing the reaction conditions for the borylation of di-*tert*-butylsilane (**1a**) with B₂(pin)₂ (**2**) in the presence of a variety of transition-metal catalysts (Table 1). Initially,

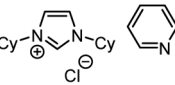
we focused on an iridium-based catalytic system, as originally reported by Hartwig and co-workers (entry 1).⁶ The reaction using [Ir(cod)Cl]₂/4,4'-di-*tert*-butyl-2,2'-dipyridyl (L1) as the catalyst in cyclohexane at 80 °C proceeded smoothly to give the desired monoborylated product (**3a**) in 68% yield (entry 1). Notably, the di-borylated product was not detected. We also attempted the reaction with known Si–H bond borylation catalysts, such as [Rh(cod)Cl]₂/1,3-dicyclohexylimidazolium chloride (ICy·HCl) (L2) and Pt/C.⁷ However, the rhodium-based catalyst generated a complex product mixture (**3a**: <1%; entry 2), and the platinum-based catalyst produced **3a** in 36% yield (entry 3). In an effort to improve the iridium-based catalytic system, we decided to use *N*-heterocyclic carbene (NHC) ligands instead of dtbpy (L1).⁷ The use of ICy·HCl (L2) resulted in 43% yield of **3a** (entry 4), whereas the use of L3, *i.e.*, an NHC ligand that contains a pyridine moiety, provided a slightly higher yield than when dtbpy (L1) was employed (73%, entry 5).⁹ We found that **3a** could be obtained in 71% yield (entry 6) even at a lower catalyst loading (0.5 mol%). Although there aren't any reports in the literature on the borylation of Si–H bonds using a nickel catalyst,¹⁰ we discovered that nickel-based catalysts are also effective for the monoborylation of **1a**. While the formation of **3a** was not observed when Ni(cod)₂/1,3-dimesitylimidazolium chloride (IMes·HCl) (L4) was employed (**3a**: <1%; entry 7), the use of L2 instead of L4 afforded **3a** in 50% yield (entry 8). However, the reproducibility of the reaction was unsatisfactory under these conditions (for details, see the ESI†). After an extensive screening of the reaction conditions, we found that when the reaction was carried out in *n*-octane at 120 °C, **3a** was

Table 1 Optimization of the reaction conditions^a

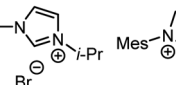
				
Entry	Catalyst (mol%)	Ligand (mol%)	Base (mol%)	Yield (%) of 3a ^b
1	[Ir(cod)Cl] ₂ (2.5)	L1 (5)	None	68
2 ^c	[Rh(cod)Cl] ₂ (2.5)	L2 (10)	K(O- <i>t</i> -Bu) (20)	<1
3	Pt/C (5 wt%) (5)	None	None	36
4	[Ir(cod)Cl] ₂ (2.5)	L2 (10)	K(O- <i>t</i> -Bu) (15)	43
5	[Ir(cod)Cl] ₂ (2.5)	L3 (5)	K(O- <i>t</i> -Bu) (10)	73
6 ^d	[Ir(cod)Cl] ₂ (0.5)	L3 (1)	K(O- <i>t</i> -Bu) (2)	71 (63)
7	Ni(cod) ₂ (5)	L4 (10)	K(O- <i>t</i> -Bu) (10)	<1
8	Ni(cod) ₂ (5)	L2 (10)	K(O- <i>t</i> -Bu) (10)	50 ^e
9 ^f	Ni(cod) ₂ (5)	L2 (10)	K(O- <i>t</i> -Bu) (10)	54 ^e




L1
dtbpy



L2
ICy·HCl

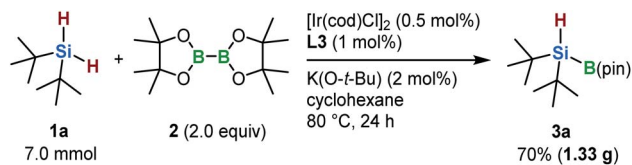


L3



L4
IMes·HCl

^a Conditions: **1a** (0.50 mmol), **2** (1.0 mmol), catalyst, ligand, and base in cyclohexane (1.0 mL) at 80 °C. ^b Determined by GC analysis of the reaction mixture using *n*-C₁₃H₂₈ as the internal standard. The isolated yield is shown in parentheses. ^c *N,N*-Dimethylformamide (DMF) was used as the solvent. ^d The reaction was carried out at the 1.0 mmol scale. ^e Average of four runs. ^f *n*-Octane was used as the solvent and the reaction was carried out at 120 °C.

Scheme 2 Gram-scale synthesis of **3a**.

obtained in 54% yield with excellent reproducibility (entry 9; for details, see the ESI†). We also demonstrated that **3a** can be isolated in 63% yield using column chromatography on silica gel (entry 6).

To highlight the practical utility of this borylation protocol, a gram-scale synthesis of **3a** was carried out (Scheme 2). In the presence of the newly developed iridium-based catalyst, **3a** was obtained in 70% yield (1.33 g) even when a lower catalyst loading was employed (0.5 mol%).

The molecular structure of **3a** was confirmed by single-crystal X-ray diffraction analysis (for details, see the ESI†). Although several conformers of **3a** were observed in the disordered structure, the presence of a silicon–boron bond was confirmed unambiguously.

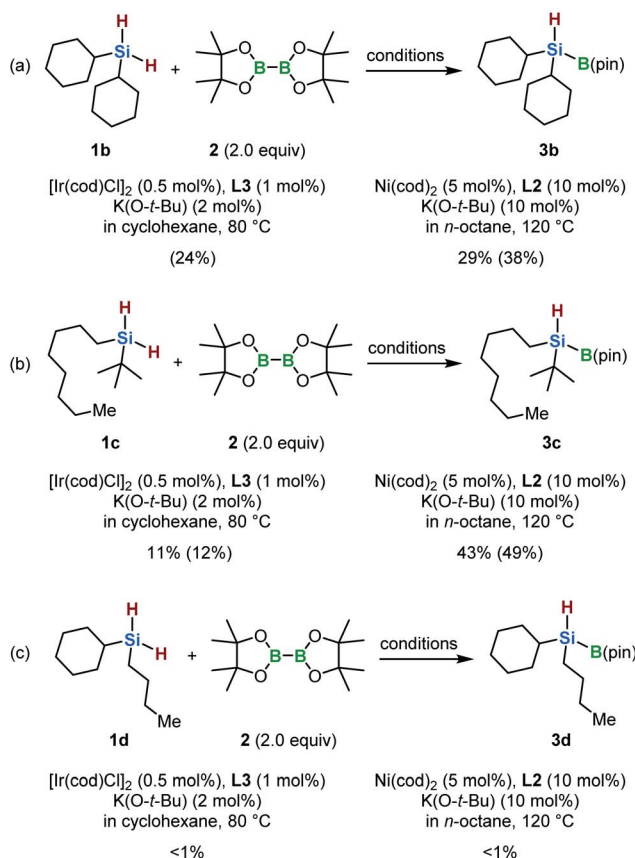
With the optimized conditions in hand, the synthesis of various dialkylhydrosilylboronates was investigated (Scheme 3). The dialkylhydrosilylboronate that bears two cyclohexyl groups

(**3b**) was produced *via* both of the iridium- and nickel-catalyzed borylation reactions of the corresponding dihydrosilane (**1b**) (24% and 38% GC yields, respectively). In the case of nickel-catalyzed borylation, **3b** was isolated by silica-gel column chromatography without significant decomposition (29% isolated yield). Next, the monoborylation of a dihydrosilane bearing a tertiary and a primary alkyl group (**1c**) was investigated. The desired dialkylhydrosilylboronate (**3c**) was obtained in low yield using the iridium-based catalyst (11% isolated yield,

Table 2 Monoborylation of alkylaryldihydrosilanes^a

Entry	Silane (1)	Product (3)	Isolated yield (%)
1			[Ir]: 57% [Ni]: 31%
2			[Ir]: <1% [Ni]: <1%
3			[Ir]: <1% [Ni]: <1%
4			[Ir]: 61% [Ni]: 29%
5			[Ir]: 58% [Ni]: 31%
6			[Ir]: <1% [Ni]: 59%
7			[Ir]: 71% [Ni]: 29%

^a [Ir] conditions: **1e–i** (0.50 mmol), **2** (1.0 mmol), $[\text{Ir}(\text{cod})\text{Cl}]_2$ (0.50 mol%), and **L1** (1.0 mol%) in cyclohexane (1.0 mL) at 80 °C for 24 h. [Ni] conditions: **1e–i** (0.50 mmol), **2** (1.0 mmol), $\text{Ni}(\text{cod})_2$ (5.0 mol%), **L2** (10 mol%), and $\text{K}(\text{O}-t\text{-Bu})$ (10 mol%) in *n*-octane (1.0 mL) at 120 °C for 24 h.

Scheme 3 Si–H monoborylation of dihydrosilanes **1b–1d**. Isolated yields are shown. GC yields are shown in parentheses.

Scheme 3b). The nickel-based catalyst was more effective for the borylation of **1c**, generating **3c** in 43% isolated yield (Scheme 3b). We found that the sterically less hindered dialkyldihydrosilane **1d** did not provide **3d** under either set of conditions (Scheme 3c). We speculated that less hindered dihydrosilanes could potentially undergo fast dehydrogenative coupling with another dihydrosilane molecule, facilitated by the metal catalyst, to form silicon-based oligomers,¹¹ thus impeding the desired borylation reaction.

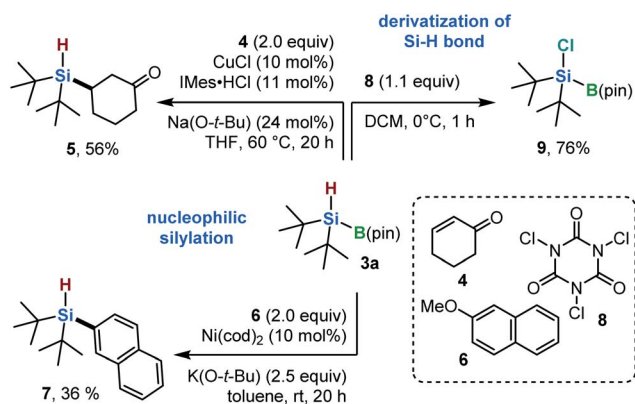
Furthermore, aryl-substituted dihydrosilanes were employed for the present monoborylation reaction (Table 2). Pleasingly, *t*-BuPhHSi-B(pin) (**3e**) was obtained from both the iridium- and nickel-based catalytic systems in 57% and 31% yield, respectively (entry 1). Unfortunately, sterically less hindered CyPhSiH₂ (**1f**) and *n*-BuPhSiH₂ (**1g**) did not produce the corresponding hydrosilylboronates (**3f** and **3g**; entries 2 and 3). In these cases, the formation of oligosilanes produced by dehydrogenative homo-coupling was observed,¹¹ suggesting that the presence of a bulky *t*-Bu group on the silicon atom is necessary for efficient Si-H monoborylation. Next, the steric effect of the aryl group was investigated (entries 4–6). *para*-Tolyl- and *meta*-tolyl-substituted hydrosilylboronates **3h** and **3i** were obtained in yields comparable to that of **3e** (entries 4 and 5). However, *ortho*-tolyl-substituted hydrosilylboronate **3j** was not obtained by the Si-H monoborylation using the iridium-based catalyst; this is probably due to a competing benzylic C-H borylation (entry 6).¹² In contrast, the nickel-based catalyst afforded **3j** in good yield (59% isolated yield; entry 6). Hydrosilylboronate **3k**, which bears a 4-MeOC₆H₄ group, was also obtained in a yield comparable to that of **3e** (entry 7). Notably, these hydrosilylboronates (**3e** and **3h–3k**) show high stability toward air and moisture and can be isolated by flash column chromatography on silica gel. Although the monoborylation of diarylsilanes was also attempted, the desired silylboronates were not obtained (for details, see the ESI†).

To demonstrate the synthetic utility of the newly synthesized hydrosilylboronates, a preliminary study of the activity of **3a** in nucleophilic silylation reactions was conducted (Scheme 4). A copper(i)-catalyzed conjugated silylation of cyclohexenone (**4**) with **3a** proceeded to form the desired β -silylated ketone (**5**) in 56% yield (Scheme 4).¹³ Furthermore, a nickel-catalyzed

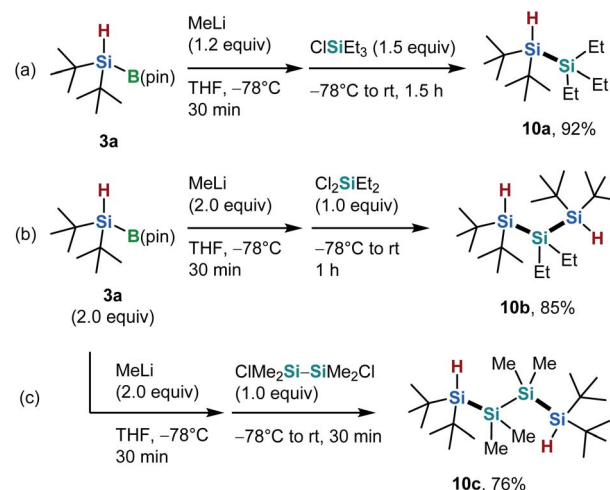
silylation of 2-methoxynaphthalene **6** with **3a** produced the corresponding aryl silane (**7**) in 36% yield (Scheme 4).¹⁴ In addition to nucleophilic silylations, **3a** could also be applied to a Si-H bond-functionalization reaction. For example, the chlorination of a Si-H bond in **3a**, when treated with trichloroisocyanuric acid (**8**), furnished chlorosilylborane **9** in 76% yield (Scheme 4).¹⁵

Oligosilanes are currently of interest due to their unique optical, electronic, and photoreactive properties, which originate from their silicon-silicon bonds.¹⁶ Thus, we carried out silicon-silicon cross-coupling reactions between newly synthesized silylboronate **3a** and various silyl chlorides, in the presence of an activating nucleophile (Scheme 5).^{7,17} The silicon-silicon coupling between **3a** and triethylsilyl chloride in the presence of methyl lithium (MeLi) afforded the corresponding Si-H bond-bearing disilane (**10a**) in excellent yield (92%, Scheme 5a). Furthermore, the nucleophilic disilylation of both dichlorodiethylsilane and 1,2-dichlorotetramethyldisilane proceeded smoothly to form the desired trisilane (**10b**) and tetrasilane (**10c**) in 85% and 76% yield, respectively (Scheme 5b and c). The silicon-silicon coupling products can be used as building blocks for the construction of novel silicon-based compounds *via* further derivatizations based on Si-H bond functionalizations.

Finally, we conducted *in situ* ²⁹Si{¹H} NMR experiments to confirm the formation of a dialkylhydrosilyl anion in the reaction of **3a** with MeLi. Kawachi and Tamao have reported the formation of Ph₃SiLi during the reaction of Ph₃Si-B(pin) with MeLi.¹⁷ More recently, we have reported the formation of *i*-Pr₃SiLi during the reaction of *i*-Pr₃Si-B(pin) with MeLi.⁷ Although Iwamoto, Kira and co-workers have already reported the generation of disilylhydrosilyllithium compounds in the reaction between disilyldihydrosilanes and alkylolithiums,^{5f} to the best of our knowledge, the generation of a dialkylhydrosilyllithium species has not been reported so far.^{5f} In the present study, we attempted to produce the dialkylhydrosilyl anion of **3a** *via* treatment with MeLi in THF-*d*₈ (Fig. 1). We observed a new ²⁹Si signal (σ 14.2 ppm), which was attributed to



Scheme 4 Selective transformations with **3a**.



Scheme 5 Silicon-silicon coupling reactions with **3a**.



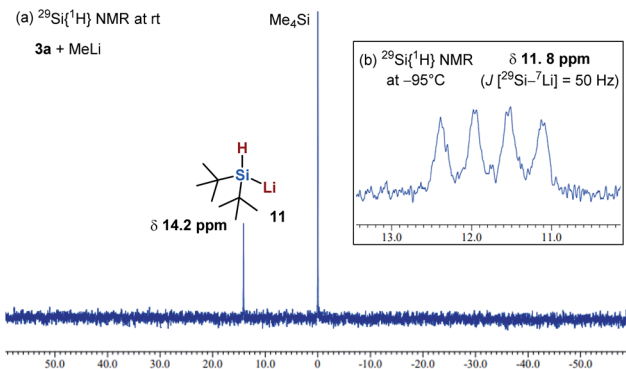


Fig. 1 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of $(t\text{-Bu})_2\text{HSi-Li}$ (**11**) obtained from the reaction of **3a** with MeLi: (a) **3a** (0.1 mmol) with MeLi (0.15 mmol) in THF- d_8 (0.2 M) after stirring for 1 h at -78°C and further 1 h at rt. The $^{29}\text{Si}\{^1\text{H}\}$ NMR analysis was conducted at room temperature. Me $_4$ Si was used as an external standard to calibrate the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra. (b) The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the mixture of **3a** (0.1 mmol) and MeLi (0.15 mmol) in THF- d_8 (0.2 M) analyzed at -95°C .

silyllithium **11**, in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum at room temperature (Fig. 1a). Furthermore, the $^{29}\text{Si}\text{-}^7\text{Li}$ coupling of **11** was observed at -95°C (σ 11.8 ppm, quartet, $J[^{29}\text{Si}\text{-}^7\text{Li}] = 50$ Hz) (Fig. 1b). These results indicate that $(t\text{-Bu})_2\text{HSiLi}$ (**11**) is generated *in situ*. This is in agreement with the reports from Kawachi and our group on the heterolytic cleavage and the formation of silyl anion species Ph_3SiLi and $i\text{-Pr}_3\text{SiLi}$.^{7,17} To the best of our knowledge, this is the first $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopic evidence for the formation of a dialkylhydrosilyllithium species.

Conclusions

In conclusion, we have developed iridium- and nickel-catalyzed monoborylations of dihydrosilane Si-H bonds with bis(pinacolato)diboron to produce hydrosilylboronates. Notably, these molecules bear a hydrogen atom at the silicon center. Importantly, the newly synthesized silylboronates can be used in the presence of activating transition-metal catalysts or bases as novel silicon nucleophiles. Furthermore, the first $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopic evidence for the formation of a $(t\text{-Bu})_2\text{HSiLi}$ species was reported.

Author contributions

K. K. and H. I. conceived and designed the study. T. T., K. K. and H. I. co-wrote the paper. T. T. performed the chemical experiments and analyzed the data. R. S. performed the preliminary experimental studies. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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