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Formoxyboranes as hydroborane surrogates for the catalytic reduction of carbonyls through transfer hydroboration†‡

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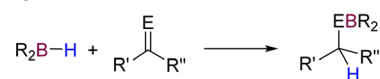
A new class of Lewis base stabilized formoxyboranes demonstrates the feasibility of catalytic transfer hydroboration. In the presence of a ruthenium catalyst, they have shown broad applicability for reducing carbonyl compounds. Various borylated alcohols are obtained in high selectivity and yields up to 99%, tolerating several functional groups. Computational studies enabled to propose a mechanism for this transformation, revealing the role of the ruthenium catalyst and the absence of hydroborane intermediates.

Introduction

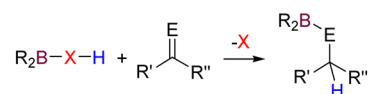
Hydroboranes are highly efficient reductants towards unsaturated C=C and C=O bonds and are widely used to reduce functional groups such as aldehydes, ketones, esters, or amides (Scheme 1).¹ However, they are still considered disposable hydrides and are produced by an energy-intensive process known as the Schlesinger or Bayer process.² Surrogates of hydroboranes that could be recycled are therefore of particular interest for improving these hydroboration procedures. Hydroelementation reactions traditionally require the presence of a well-defined E–H bond in the reagent. In related silicon chemistry, recent investigations have shown the possibility of performing transfer hydrosilylation reactions circumventing the use of genuine hydrosilanes.³ The potential of formates and their derivatives in reduction chemistry has attracted high interest due to their availability and renewable nature.⁴ Indeed, formates can be efficiently and selectively produced by hydrogenation or electroreduction of CO₂.⁵ Nevertheless, the concept of transfer hydroboration chemistry has not been investigated so far. Previously, we have shown that bisformoxyboranes could yield methoxyboranes upon thermal decomposition, suggesting the implication of borohydride intermediates, which in turn could be trapped by adding

aldehydes.⁶ Similarly, alkyl boranes decompose thermally at high temperatures (>150 °C) to produce well-defined B–H intermediates for hydroboration reactions (Scheme 1),⁷ with some exceptions that can proceed at lower temperatures through a 6-member ring transition state.⁸

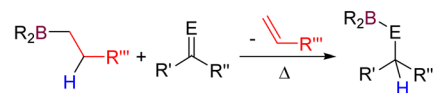
Hydroboration

R'/R'' = H, alkyl, aryl
E = O, NR, CR₂

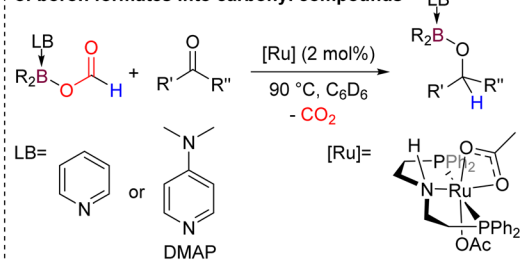
Concept: Transfer hydroboration



Transfer hydroboration via thermal activation of alkylboranes



This work: catalyzed transfer hydroboration of boron formates into carbonyl compounds



Scheme 1 Examples of hydroboration and transfer hydroboration of unsaturated functional groups.

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To our knowledge, a catalytic strategy that allows the use of a hydroborane surrogate has yet to be demonstrated. In this communication, we report the synthesis of Lewis base-stabilized formoxyboranes and their reactivity for catalytic transfer hydroboration of aldehydes and ketones without the formation of intermediates containing B–H bonds. This methodology gives access to a variety of borylated alcohols with high yields and selectivities.

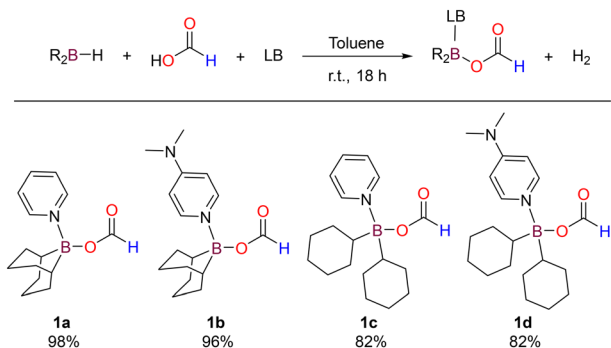
Results and discussion

Formoxyboranes are scarce in the literature, being only observed as products or intermediates in the hydroboration of CO₂,⁹ and their reactivity remains elusive. To probe the feasibility of using formoxyboranes as hydroborane surrogates, we decided to synthesize such compounds and explore their reactivity in the reduction of aldehydes and ketones as model substrates. Two possible synthetic routes can be envisaged for the formation of formoxyboranes: (i) the dehydrogenative coupling of a hydroborane with formic acid or (ii) the addition of a formate salt to the corresponding chloroborane. When Cy₂BH is placed in the presence of formic acid in THF at room temperature for 16 h, we were pleased to observe that a reaction did take place, but that instead of the targeted bis-alkylformoxyborane Cy₂BOCHO, an oligomer was obtained: a crystalline cyclic hexamer was observed, formed through Lewis adduct formation between the terminal oxygen atom of the formate group and the borane (see ESI,† Section S2). It is reminiscent of the tetramer reported by Hazari *et al.* as a product of CO₂ hydroboration with 9-BBN.⁹ To avoid this oligomerization, we considered using an additional Lewis base, which could also help modulate the reactivity of the formoxyborane.¹⁰ Thus, we considered adding pyridine to synthesize formoxyboranes to lead to monomeric formate species. We were pleased to see that a solution of 9-BBN (9-borabicyclo[3.3.1]nonane), pyridine, and formic acid in toluene led, after 18 h at room temperature, to the desired formoxyborane (**1a**) in 96% yield and H₂ as the only by-product (Scheme 2). This method is very efficient and enables the isolation of four different Lewis-base stabilized formoxyboranes **1a–d** in good to high

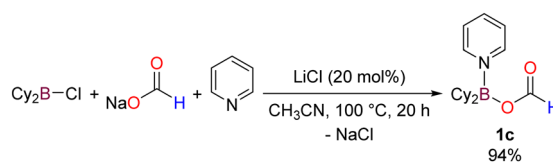
yield (82 to 98%), with varying substituents at boron (BBN *vs.* Cy₂B) and Lewis bases (pyridine *vs.* DMAP). To our knowledge, they are the first monomeric formoxyboranes and were fully characterized by NMR spectroscopy and X-ray diffraction. In contrast, poor yields were obtained for the synthesis of quinoline analogs, and, despite our efforts, we could not purify such compounds (see ESI,† Section S3).

Instead of dehydrogenating formic acid with hydroboranes, an alternative synthesis involves a salt metathesis starting from chloroboranes and sodium formate (Scheme 3). Interestingly, chloroboranes can be directly generated from the reaction between BCl₃ and boronic anhydrides,² the latter being typical byproducts of hydroboration reactions, allowing a route towards circular boron usage. The reaction between Cy₂BCl and NaOCHO in the presence of pyridine in acetonitrile has been first investigated. Under these conditions, no reaction occurred even at an increased temperature of 130 °C for 48 h. However, using LiCl as a phase transfer catalyst (20 mol%) improved the efficiency of the reaction, and Cy₂-BOCHO-pyridine (**1c**) was obtained in 94% yield after 20 h at 100 °C.

The reactivity of formoxyboranes was then probed in the reduction of carbonyl groups to demonstrate their ability to mimic the behavior of hydroboranes. Acetophenone was chosen as a model substrate. A mixture of **1a** and acetophenone (**3a**) heated at 130 °C in C₆D₆ did not lead to any reaction (Table 1, entry 1). Since Cy₂BH readily reacts with ketones,¹¹ this reaction suggests that **1a** does not generate a B–H intermediate by direct decarboxylation at 130 °C. [(PN(H)P)Ru(OAc)₂] (**2a**) (PN(H)P = HN-(CH₂CH₂P(Ph)₂)₂) was introduced as a catalyst due to its ability to promote the decarboxylation of formates and the subsequent C=O bond reduction by a Ru–H intermediate.¹² The use of 2 mol% of **2a** with a mixture of BBNOCHO-pyridine (**1a**) and acetophenone (**3a**) at 90 °C led to the desired borylated alcohol product **4aa** in 99% yield after 4 h (Table 1, entry 2). Lowering the temperature from 90 to 70 °C (Table 1, entry 3) decreased the catalytic performance to 71% after 40 h, and no conversion was observed at room temperature (Table 1, entry 4). Switching the Lewis base from pyridine to DMAP gave similar results (Table 1, entry 5). A change of substituents on boron, *e.g.*, using **1c** instead of **1a**, has no significant influence on this reaction, obtaining a similar yield of *ca.* 98% of borylated alcohol **4ac** (Table 1, entry 6). However, **1d** was less effective (**4ad** was obtained in 63% yield, Table 1, entry 7).

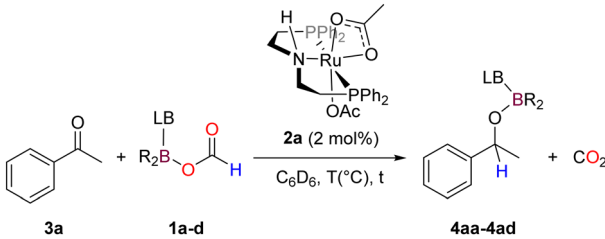


Scheme 2 Synthesis of formoxyboranes from hydroboranes and formic acid.



Scheme 3 Synthesis of formoxyboranes from chloroborane and sodium formate.



Table 1 Optimization of the catalytic transfer hydroboration of **3a**^a


Entry	Formoxyborane	T (°C)	t (h)	Yield ^b (%)
1 ^c	1a	130	48	0
2	1a	90	4	99
			2	49
3	1a	70	40	71
4	1a	r.t.	40	0
5	1b	90	3	96
			2	93
6	1c	90	3	98
			2	95
7	1d	90	3	63

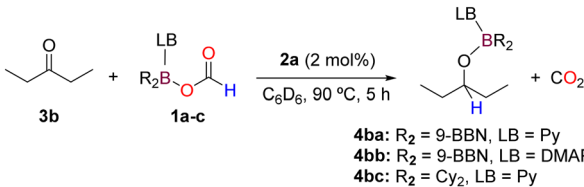
^a 0.1 mmol scale. ^b Yields are determined by ¹H NMR with 1,3,5-trimethoxybenzene as the internal standard. See ESI† for more details. ^c This reaction was run without any catalyst.

As the performances of formates **1a**, **1b**, and **1c** were very similar (>95% yield within a few hours), their reactivity in the catalytic transfer hydroboration of pentan-3-one was tested (Table 2). After 5 h at 90 °C, the borylated alcohol products **4ba**, **4bb**, and **4bc** were obtained in 50, 92, and 27% yield, respectively (Table 2, entries 1 to 3). The most reactive 9-BBN-based formoxyboranes **1b** was chosen for the rest of the study.

The transfer hydroboration could be extended to a wide variety of ketones and aldehydes (Scheme 4). Electron-donating (**4c–e**) and electron-withdrawing groups (**4f–i**) were tolerated with different substitution patterns, giving a quantitative yield in a short reaction time (<3 h) in most cases. We noted a drop in the yield when a nitro group (**4g**) was present, presumably due to its interaction with the boron or its reduction. The presence of heterocycles, such as pyridine or furane, was perfectly

tolerated by the system obtaining the hydroborylated products **4j–l** quantitatively. The same behavior was observed for ketones bearing a longer alkyl chain (**4m**) or diarylketones (**4n**). Aliphatic ketones also reacted in excellent yields (**4o**). More challenging α,β -unsaturated ketones were also tested, and the formal 1,2-addition of the hydroborane was observed in moderate to excellent yields for **4p–r** (62–93%). In all these cases, the unsaturation remained untouched, and no 1,4-addition product or enol ether was observed. Finally, aldehydes were easily reduced into their corresponding borylated alcohols (**4s**, **4t**) within 30 minutes.

All the related free alcohols were obtained upon aqueous workup, except for **4k**. This particular case can be explained by the chelating effect of the nearby nitrogen of the pyridine moiety, which stabilizes the borylated product. To highlight the potential applicability of the method, the free alcohol

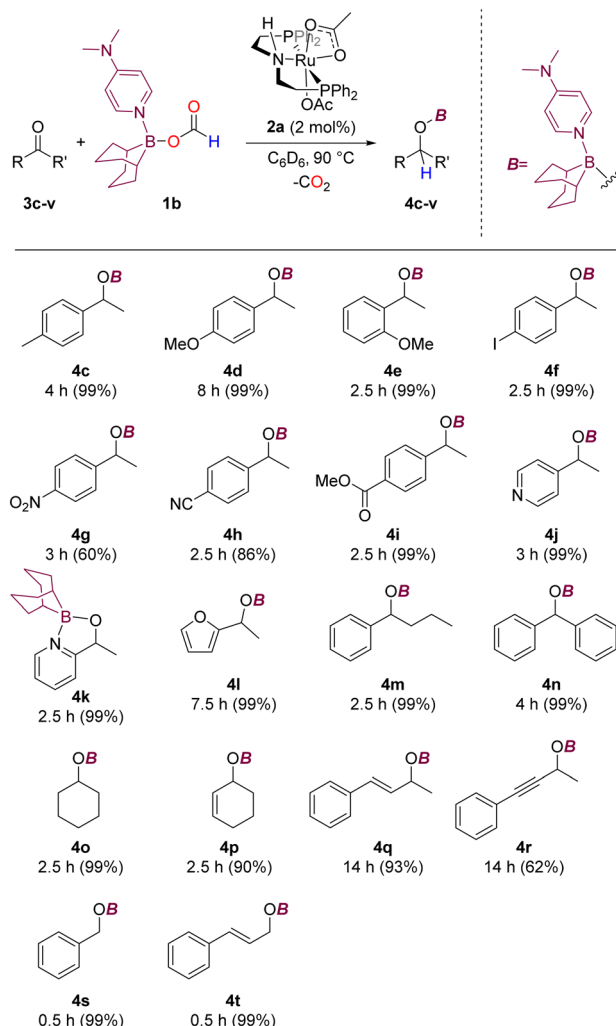
Table 2 Catalytic transfer hydroboration of pentanone (**3b**)^a


Entry	Formoxyborane	R ₂	LB	Yield ^b (%)
1	1a	9-BBN	Pyridine	50
2	1b	9-BBN	DMAP	92
3	1c	Cy ₂	Pyridine	27

4ba: R₂ = 9-BBN, LB = Py
4bb: R₂ = 9-BBN, LB = DMAP
4bc: R₂ = Cy₂, LB = Py

^a General conditions: 0.1 mmol of substrate, 0.15 mmol of formoxyborane, 2 μ mol of catalyst, 0.5 mL of C₆D₆. ^b NMR yields were determined by ¹H NMR integration of the –CH signals versus an internal standard (1,3,5-trimethylbenzene).

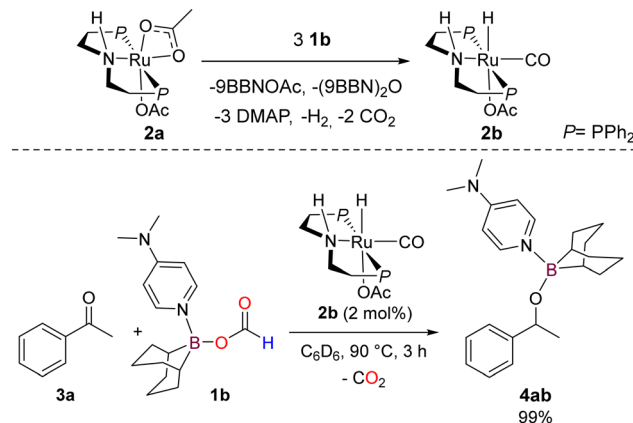




Scheme 4 Scope of the catalytic transfer hydroboration of carbonyl compounds.

resulting from the hydrolysis of **4i** was isolated upon purification in 97% yield (see ESI,† Section S10).

To gain insights into the mechanism of the reaction, we searched for the active species involved in the catalytic transfer of hydroboration. First, the formation of CO_2 as a by-product of the reaction was confirmed by GC analysis of the gas phase of the reaction (see ESI,† Section S12). Then, we observed that the recorded 1H NMR spectrum shows a main ruthenium hydride species at -16.7 ppm during catalysis. This signal is closely related to the previously reported carbonyl complex $[(PN(H)P)RuH(CO)(OAc)]$ (**2b**) ($\delta = -16.6$ ppm).¹³ This species **2b** was identified as a ruthenium complex generated from the reaction with silyl formates. Therefore, it is plausible that the same pathway exists in the presence of formoxyboranes. In addition, the presence of a ruthenium carbonyl complex was also confirmed by IR spectroscopy, showing a ν_{CO} frequency of 1923 cm^{-1} (see ESI,† Section S13). To prove this hypothesis, **2b** was synthesized and used as a precatalyst (Scheme 5). A similar catalytic activity was obtained for the borylated product **3a**

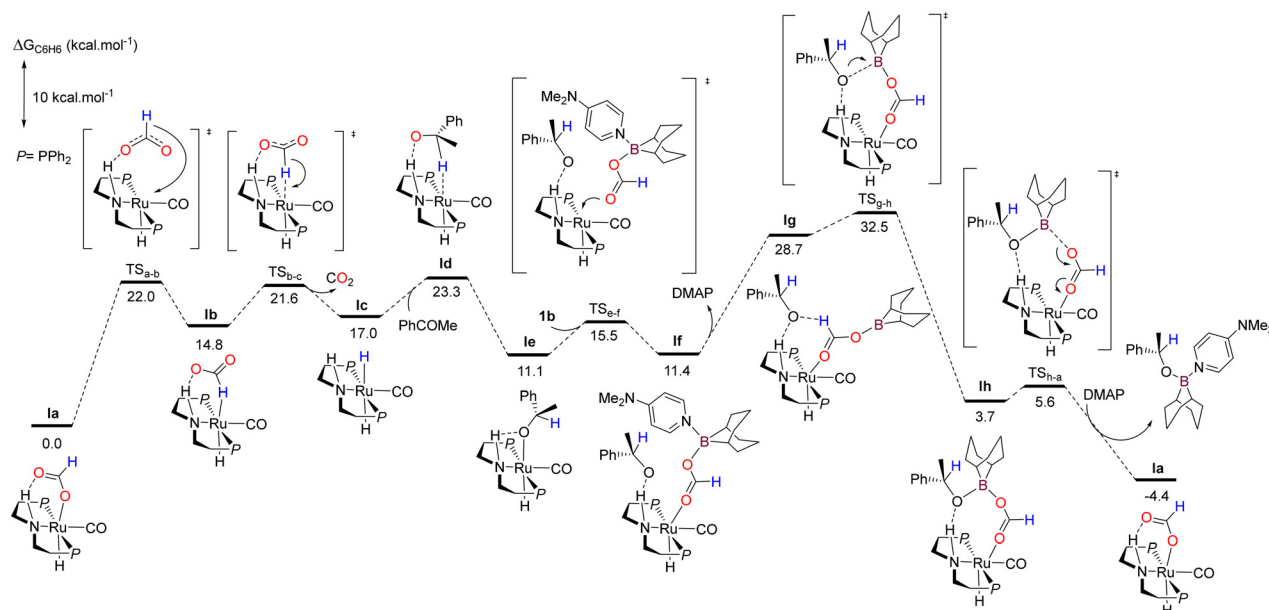


Scheme 5 Plausible precatalyst pathway from **2a** to **2b** (top) and precatalyst test with **2b** (bottom).

(99%) after 3 h, supporting the conversion of **2a** to **2b** under catalytic conditions. Finally, the replacement of $[(PN(H)P)Ru(OAc)_2]$ by the methylated derivative $[(PN(Me)P)Ru(OAc)_2]$ as the catalyst suppressed almost completely the reaction, showing the critical role of the N-H moiety in the ligand for this reaction (see ESI,† Sections S13–S15).

Density functional theory (DFT) calculations were performed to understand better the mechanism of the reaction (Scheme 6). A multi-step initiation pathway can be proposed as described in Scheme 5, starting from **2a** to generate **2b**. A ligand exchange from acetate to formate is needed to enter the catalytic cycle from $[(PN(H)P)RuH(CO)OCHO]$ (**1a**) species. The formate ligand in **1a** first switches from η^1-O to η^1-H coordination, leading to **1b** ($\Delta G = +14.8\text{ kcal mol}^{-1}$) through TS_{a-b} at $22.0\text{ kcal mol}^{-1}$, with H-bonding between one oxygen atom in the formate and the N-H moiety in the ligand. Decarboxylation can then occur via TS_{b-c} ($\Delta\Delta G^\ddagger = +6.8\text{ kcal mol}^{-1}$) to form ruthenium bis-hydride complex **1c**, lying $17.0\text{ kcal mol}^{-1}$ above the starting reactants. The latter complex is reminiscent of intermediates found in the mechanisms of formic acid dehydrogenation, as described by the groups of Schneider and Hazari for iron complexes,¹⁴ or ourselves in the case of cobalt.¹⁵ Hydrogen bonding between the N-H ligand and the ketone favors the barrierless hydride transfer of $[Ru]-H$ to form the η^1-H ruthenium alkoxide complex **1d** ($\Delta G = 23.3\text{ kcal mol}^{-1}$). The reorganization of this complex from η^1-H to η^1-O ruthenium alkoxide **1e** ($\Delta G = 7.2\text{ kcal mol}^{-1}$) is also barrierless. Formoxyborane **1b** can be coordinated through TS_{e-f} ($\Delta G^\ddagger = +15.5\text{ kcal mol}^{-1}$), leading to **1f**, $11.4\text{ kcal mol}^{-1}$ higher in energy than **1a**. Complex **1f** features a formate ligand bridging between ruthenium and boron, and the alkoxy moiety is H-bonded to the N-H moiety of the PNP ligand. The decoordination of DMAP from boron is barrierless and leads to high-energy intermediate **1g** ($\Delta G = 28.7\text{ kcal mol}^{-1}$). A nucleophilic attack of the alkoxide on the boron atom can occur through TS_{g-h} ($\Delta G^\ddagger = +32.5\text{ kcal mol}^{-1}$), leading to **1h** ($\Delta G = +3.7\text{ kcal mol}^{-1}$). Complex **1h** features a formate bridging between Ru and B and an alkoxide bridging between B and the N-H moiety of the PNP





Scheme 6 Computed mechanism for the catalytic transfer of hydroboration of acetophenone **3a** with **1b** catalyzed by **1a** at B3LYP-D3/Def2SVP level of theory and SMD model to account for solvent effect (C_6D_6).

ligand on Ru. The release of the product through transition state TS_{h-a} ($\Delta G^\ddagger = +5.6$ kcal mol $^{-1}$) followed by the coordination of DMAP regenerates **1a**, thereby closing the catalytic cycle. The total energetic span of the catalytic cycle, 32.5 kcal mol $^{-1}$, is slightly higher than expected compared to the reaction conditions (4 h at 90 °C) but consistent within the expected uncertainty range of 3 kcal mol $^{-1}$.¹⁶ It is defined by **1a** and the transition state for the transmetalation TS_{g-h} , which is the rate-determining transition state of the reaction.

Other mechanistic pathways were also considered but discarded because of their high energy demand (see ESI,† Section S15). In particular, forming the B–H bond is not thermodynamically possible under the reaction conditions (BBNOCHO-DMAP \rightarrow BBNH + CO $_2$ + DMAP: $\Delta G = +30.7$ kcal mol $^{-1}$). It is interesting to note that compared to silyl formates, formoxyboranes are thermodynamically more difficult to decarboxylate (Et $_3$ SiOCHO \rightarrow Et $_3$ SiH + CO $_2$: $\Delta G = +5.8$ kcal mol $^{-1}$; BBNOCHO \rightarrow BBNH + CO $_2$: $\Delta G = +15.2$ kcal mol $^{-1}$; BBNOCHO-DMAP \rightarrow BBNH-DMAP + CO $_2$: $\Delta G = +13.9$ kcal mol $^{-1}$).

Conclusions

In summary, the synthesis of Lewis base-stabilized formoxyboranes is reported. The combination of formoxyboranes with a suitable ruthenium catalyst enables mimicking the reactivity of hydroboranes, as demonstrated with the formal hydroboration of ketones and aldehydes. Mechanistic studies have highlighted the crucial role of the ligand during the catalytic process and indicated that the rate-determining transition state is the transmetalation of a formate ligand from boron to ruthenium. This work

demonstrates the potential of hydroborane surrogates as hydroborating reagents in challenging transformations.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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