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A *trans*-Selective Hydroboration of Internal Alkynes**

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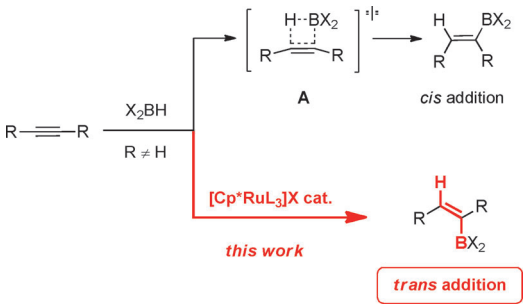
The discovery of the hydroboration of olefins and alkynes heralded a new era of synthetic chemistry with profound implications for industrial practice.[1–3] The resulting organoborane derivatives are rather stable and hence easier to handle than many of the traditional organometallic reagents; yet, they are readily engaged in an overwhelming number of synthetically useful transformations, most notably as nucleophiles in various types of transition-metal-catalyzed C–C bond-forming reactions, including the venerable Suzuki–Miyaura coupling.[1–5] The reigning stereochemical principle of hydroboration is the suprafacial delivery of hydrogen and boron to the same π-face of a given starting material, which results from stringent frontier-orbital control via a four-membered transition state **A** (*cis* addition; Scheme 1). We



Scheme 1. Conventional *cis*-selective hydroboration of alkynes versus the ruthenium-catalyzed *trans* addition described herein. Cp* = η^5-C_5Me_5, L = generic labile ligand.

now report that simple ruthenium catalysts, most notably the cationic complex $[Cp^*Ru(MeCN)_3]PF_6$ ($Cp^* = \eta^5$-C_5Me_5), which is commercially available, allow this fundamental and largely unchallenged rule to be broken for internal alkynes as the substrates. The ensuing *trans*-selective hydroboration opens a practical new entry into *E*-configured alkenylboron derivatives, which could previously only be made by indirect routes (Scheme 1). Therefore, we expect this stereo-complementary method to add another dimension to the prolific field of organoboron chemistry.

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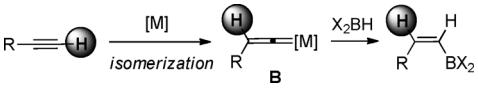
The *syn*-addition mode is also strictly obeyed when transition metals are used to catalyze such hydroboration reactions.[6,7] In fact, only very few exceptions are documented where this rule is formally violated. Thus, terminal alkynes were recently shown to lead to a net *anti* addition when reacted with catecholborane (cat-BH) or pinacolborane (pin-BH) in the presence of certain rhodium, iridium, or ruthenium complexes as the catalysts (Scheme 2).[8,9] This

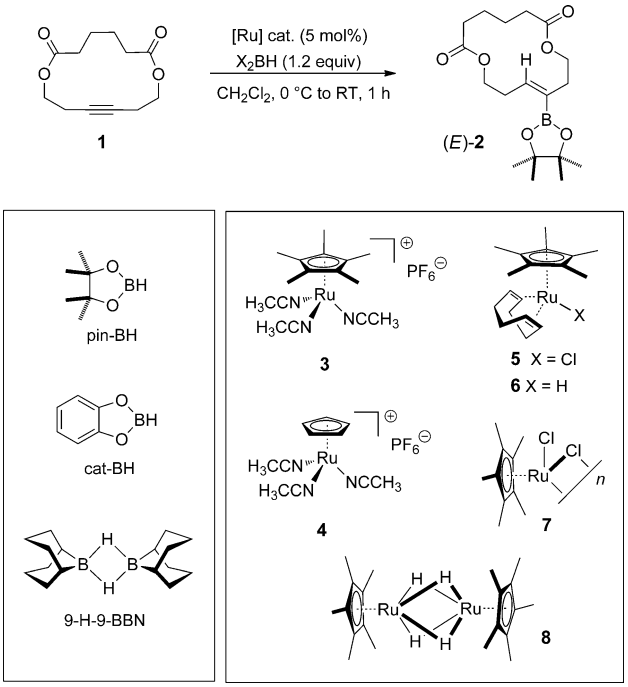


Scheme 2. Literature-known formal *trans* hydroboration of terminal alkynes that proceeds via metal vinylidene intermediates; as a consequence, it is the alkyne proton that ends up *trans* to the boron moiety.[8–10]

unusual outcome results from an initial rearrangement with formation of metal vinylidene complexes **B** as reactive intermediates. As a consequence, it is the alkyne proton itself, rather than the hydrogen from the borane reagent, that ends up *anti* to the boron moiety in the product, as unequivocally shown by labeling studies.[8–10] For this very reason, the method does not work with internal alkynes, for which *trans* hydroborations remain basically unknown. The only exception is an *indirect* method employing (pin)B–B(pin) (pin = 4,4,5,5-tetramethyl-[1,3,2]dioxaborolanyl) in combination with NaO*t*Bu, CuCl, and a phosphine ligand in MeOH.[11] When applied to bulky alkynes of the type ArC≡C*t*Bu (Ar = aryl), the corresponding *E*-configured alkenylboronates are formed; upon the smallest decrease in size, however, the system relaxes and returns to the usual *syn*-addition pathway.

Herein, we outline the first broadly applicable, functional-group-tolerant, and highly stereoselective *trans* hydroboration of internal alkynes. Inspiration was provided by pioneering studies on *trans*-selective hydrosilylations (and -germylations)[12–14] and by a recent report on a *trans*-selective hydrogenation,[15] which rely on the use of cationic ruthenium complexes as precatalysts. First attempts to extend this chemistry to hydroboration, however, were largely unsuccessful (Scheme 3, Table 1). Thus, the reaction of cycloalkyne **1**[16,17] with the 9-H-BBN dimer[2,3] in the presence of $[Cp^*Ru(MeCN)_3]PF_6$ (**3**; 5 mol%) gave a rather complex product mixture (Table 1, entry 1). The use of catecholborane (cat-BH), despite the excellent track record of this reagent in metal-catalyzed hydroborations,[6] resulted in an unacceptably low conversion (< 20%, determined by GC) and a poor isomer ratio (*E*/*Z* = 1.2:1; entry 2).

Although catecholborane[18] and pinacolborane[19] exhibit comparable reactivity in uncatalyzed hydroboration reac-



Scheme 3. Model reaction for the study of the *trans* hydroboration of internal alkynes.

Table 1: Optimization of the *trans*-selective hydroboration shown in Scheme 3.[a]

Entry	Borane	[Ru]	E/Z[b]	Yield[c] [%]
1	9-H-BBN	**3**	–	–[d]
2	cat-BH	**3**	1.2:1	< 20 (GC)[e]
3	pin-BH	**4**	75:25	84
4	pin-BH	**3**	≥ 98:2	95
5	pin-BH	**3**	≥ 98:2	88[f]
6	pin-BD[g]	**3**	≥ 98:2	88[g]
7	pin-BH	**5**[h]	≥ 98:2	71
8	pin-BH	**5**	≥ 98:2	44 (GC)[e]
9	pin-BH	**7**	≥ 98:2	67
10	pin-BH	**6**	95:5	15 (GC)[e]
11	pin-BH	**8**	98:2	24 (GC)[e]

[a] The reactions were carried out in CH_2Cl_2 (1 M) under Ar atmosphere; [b] determined by GC analysis; [c] yields refer to isolated material; [d] complex mixture; [e] conversion by GC analysis rather than yield; [f] the reaction was performed in the dark; [g] the deuterium content in the reagent was ca. 95%, in the product ca. 93% (by NMR spectroscopy); [h] complex **5** was ionized with AgOTf (5 mol%) prior to addition of the borane and the substrate. pin = 4,4,5,5-tetramethyl-[1,3,2]dioxaborolanyl.

tions, we were pleased to find that they perform markedly different in the presence of $[Cp^*Ru(MeCN)_3]PF_6$ (**3**). Thus, addition of 5 mol% of this complex to a solution of **1** and pin-BH in CH_2Cl_2 resulted in a fast (< 10 min), clean, and exquisitely *trans*-selective hydroboration ($E/Z = \geq 98:2$, GC; entry 4); this result is particularly gratifying as pinacolboranes are the most robust and hence the most popular boron reagents. On a 5 mmol scale, product (*E*)-**2** was isolated in 91% yield using only 3 mol% of the ruthenium catalyst. When the catalyst loading was further reduced to 1 mol%, the reaction still proceeded smoothly, reaching ≥ 95% conversion within 3 h at ambient temperature. Importantly, monitoring by GC analysis showed that the E/Z ratio was consistently high throughout the entire course of the reaction. The same excellent *E* selectivity was recorded when the hydroboration was performed in the dark, which excludes that the *trans*-alkenylborane product is formed by a secondary photochemcial $Z \rightarrow E$ isomerization (entry 5).[20] Likewise, authentic (*Z*)-**2** remained unchanged when exposed to catalytic amounts of complex **3** in CH_2Cl_2. As an additional control experiment, deuterated pinacolborane (pin-D, ca. 95% D) was used to rule out that the hydrogen atom residing *trans* to the boronate unit in the product derives from any other hydrogen source than the chosen borane reagent (ca. 93% deuterium incorporation in the product by NMR spectroscopy; entry 6). Collectively, these data suggest that the observed *trans* addition is an inherent feature of the new method, and that the reaction is a true *trans* hydroboration rather than an isomerization process.

As all other metal-catalyzed hydroborations of internal alkynes follow the traditional *syn*-addition mode,[6,7,11,22,23] utmost care was taken to confirm the unusual stereochemical outcome of the new procedure. The *trans* configuration of product (*E*)-**2** is evident from its spectroscopic data and was confirmed by comparison (GC, NMR) with an authentic sample of (*Z*)-**2**, which was made by conventional hydroboration of **1**.[24] Furthermore, single crystals suitable for X-ray diffraction analysis could be grown; the structure of (*E*)-**2** in the solid state unambiguously confirms the constitution and configuration of this product (Figure 1).

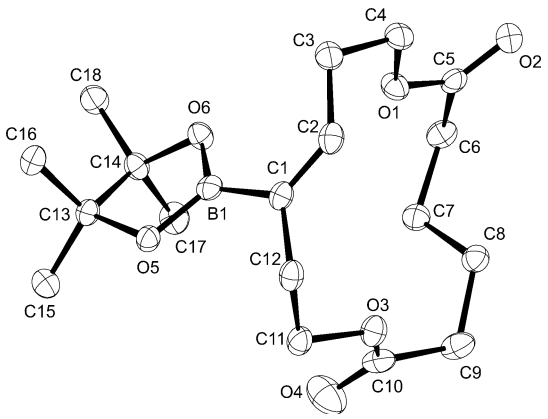


Figure 1. Structure of (*E*)-**2** in the solid state.[21] Ellipsoids set at the 50% probability level.

A brief survey showed that the use of the complex $[Cp^*Ru(MeCN)_3]PF_6$ (**3**) in CH_2Cl_2 is optimal at the present stage of development. Full conversion could also be reached in THF, whereas 1,4-dioxane caused a dramatic rate deceleration, and toluene basically halted the conversion (< 10%, GC). This result likely reflects the affinity of $[LRu]^+$ (L = Cp, Cp*) towards arenes (and other conjugated π systems),[25] which leads to the formation of kinetically robust adducts of the type $[LRu(\eta^6\text{-arene})]^+$.[26,27] This interpretation is supported by a control experiment that showed that the use of $[Cp^*Ru(\eta^6\text{-}C_6H_5Et)]Cl$[15] as the catalyst did not engender any *trans* hydroboration of our model substrate **1** under standard

conditions. A similar interaction likely explains why catecholborane with its electron-rich arene ring is largely inferior to the purely aliphatic pinacolborane as the reagent in the present *trans* addition, although these reagents show only gradually different reactivity with alkynes otherwise.

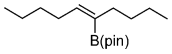
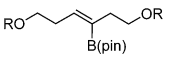
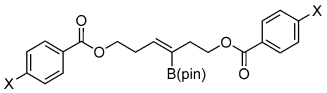
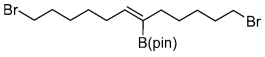
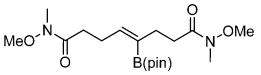
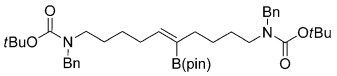
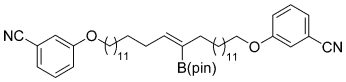
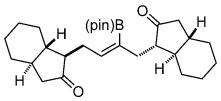
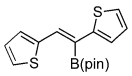
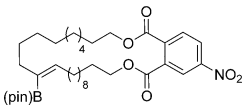
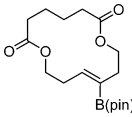
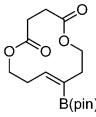
Formal replacement of the labile MeCN ligands on the cationic $[Cp^*Ru]^+$ template by a kinetically more tightly bound cyclooctadiene (cod) moiety allows the reaction to proceed, but makes it somewhat less productive. Whereas cationic [Cp*Ru(cod)]OTf gave a respectable yield of 71% (Table 1, entry 7), the neutral variant [Cp*Ru(cod)Cl] (**5**) furnished no more than 44% conversion (GC) after 1 h (entry 8). In this case, the borane reagent itself may help the release of a cationic species in solution by slow abstraction of the chloride from the ruthenium precatalyst.[28] A similar process is thought to account for the activation of the chloride-bridged complex **7** (entry 9). Although the tested precatalysts greatly differ in efficiency, the *E*/*Z* ratio was impeccably high in all cases, which may indicate the formation of a (largely) common active species. Moreover, it is unlikely that the actual catalyst is an ordinary ruthenium hydride, because complexes **6** and **8**, which comprise a preformed Ru–H bond, gave rather poor results (entries 10, 11).

Of high mechanistic significance is the observation that the exquisite *trans* selectivity is compromised upon formal replacement of the Cp* unit by the parent cyclopentadienyl (Cp) ring in **4** (entries 3/4). Therefore, we conclude that the stereodetermining step of the catalytic cycle must have a large steric component. A possible rationale is outlined below.

Next, the optimized reaction conditions were applied to a set of representative alkyne derivatives to explore the scope of the new procedure. As can be seen from the results compiled in Tables 2 and 3, good to outstanding *trans* selectivity was observed for a variety of substrates. In close analogy to the uncatalyzed hydroboration,[1–3] unsymmetric alkynes lead to the formation of regioisomers, with a slight preference for placing the boronate residue away from the bulkier substituent (Table 3); careful NMR analysis confirmed that either regioisomer comprises an *E*-olefin subunit. Importantly, a variety of functional groups were tolerated, including ethers, esters, carbamates, acetals, nitriles, aryl and alkyl halides, and a primary alkyl tosylate. Even readily reducible sites, such as a ketone, a nitro group, or the N–O bond of a Weinreb amide, remained intact. Equally remarkable is the fact that an internal acetylene could be selectively hydroborated in the presence of a terminal olefin; the obvious "alkynophilicity" of the catalyst has mechanistic implications, too.

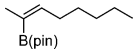
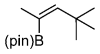
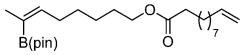
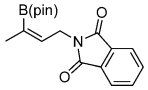
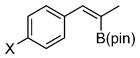
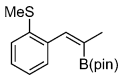
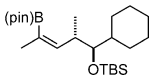
The known affinity of [Cp*Ru] to arenes explains why tolane failed to react under the standard conditions (Figure 2). We conjectured, however, that electron-withdrawing substituents on the aromatic ring should destabilize sandwich complexes of the general type $[Cp^*Ru(\eta^6\text{-arene})]^+$.[26,27] In fact, arylalkynes bearing electron-withdrawing groups (CF_3, COOMe) on the aromatic ring reacted well,

Table 2: *trans*-Selective hydroboration of symmetric internal alkynes.[a]

Entry	Major Product	*t* [h]	*E*/*Z*[b]	Yield[c] [%]
1		1	97:3	89
2		2.5	>98:2	83 (R = Bn)
3		2.5	>98:2	73 (R = Ts)
4		2	>84:16	61 (R = THP)
5		2.3	>98:2	94 (X = Cl)
6		1	>98:2	75 (R = OMe)
7		4	95:5	85
8		5	>96:4	75
9		23	>92:8	82
10		4	91:9	87
11		20	95:5	75
12		72	84:16	59
13		4	>98:2[d]	77
14		4	>98:2	91[e]
15		0.3	75:25	54

[a] Unless stated otherwise, all reactions were performed at ambient temperature in CH_2Cl_2 (1 M) under Ar atmosphere using **3** (5 mol%) as the catalyst; [b] determined by GC and/or ^1H NMR analysis; [c] isolated material comprising both isomers; [d] although the presence of the nitro group makes the product unsymmetric, only one dataset could be resolved by NMR; [e] **3** (3 mol%); the reaction was performed on a 5 mmol scale, see the Supporting Information. Bn = benzyl, THP = tetrahydropyranyl, Ts = 4-toluenesulfonyl.

Table 3: *trans*-Selective hydroboration of unsymmetric internal alkynes.[a]

Entry	Major Isomer	*t* [h]	Isomer ratio[b]	Yield [%][c]
1		3	80:11:5:1	68
2		1	63:37:<1	67
3		3	55:45	60
4		2	56:44	88
5		3	58:38:4	70 (X = COOMe)
6		1.3	60:40	64 (X = CF_3)
7		2.7	85:15	91
8		2	47:53	94

[a] All reactions were performed at ambient temperature in CH_2Cl_2 (1 M) under Ar atmosphere using **3** (5 mol%) as the catalyst; [b] isomer ratio in the crude material as determined by GC analysis; NMR analysis showed that the major isomers are *trans*-configured; [c] yield of isolated material; TBS = *tert*-butyldimethylsilyl.

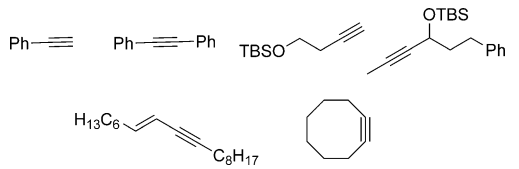


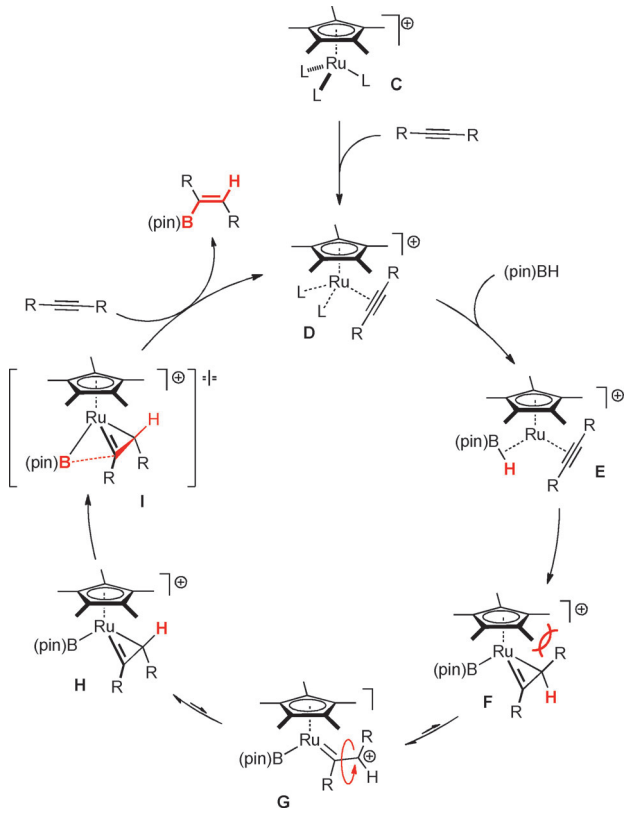
Figure 2. Unreactive or problematic substrates.

although they took longer to reach full conversion (Table 3, entries 5, 6). Particularly noteworthy is the *trans* hydroboration of sulfur-containing substrates. Although they are electron-rich, the thiophilicity of ruthenium seems to outweigh π-complex formation and directs the catalyst towards the triple bond. In any case, the compatibility of a thiophene (Table 2, entry 12) or an unhindered thioether (Table 3, entry 7) with a reaction catalyzed by a soft transition-metal species is quite remarkable.

Despite this significant scope and functional group tolerance, a few limitations also need to be noted. Whereas the 14-membered cycloalkyne **1** reacted with exquisite *E* selectivity (Table 2, entry 14), its 12-membered homologue gave a 3:1 isomeric mixture (Table 2, entry 15), and cyclooctyne was merely polymerized (Figure 2). This trend is ascribed to ring strain, which strongly disfavors *E*-configured cycloalkenes over the corresponding *Z* isomers as the ring size decreases, and is very high for an eight-membered cycle; the current method is obviously incapable of overriding this intrinsic adverse effect. Another limitation was encountered with terminal alkynes, which failed to react under standard conditions. Although regrettable, this gap in coverage is of no major consequence, because effective formal *trans* hydroboration is possible by the vinylidene mechanism mentioned above (Scheme 2).[8,9] In analogy to the ruthenium-catalyzed *trans* hydrogenation,[15] problems were also encountered with substrates containing a conjugated enyne motif or a bulky propargylic substituent (Figure 2).

Although it is premature at this stage to draw a conclusive mechanistic picture, the basic features of the *trans*-selective hydroboration can be rationalized as follows. NMR analysis of a 1:1 mixture of pinacolborane and $[Cp^*Ru(MeCN)_3]PF_6$ (**3**) in CD_2Cl_2 in the absence of an alkyne substrate showed no signs of chemical reaction or strong interaction of the partners; in any case, distinct metal boryl[29] or metal hydride complexes could not be observed even at low temperature. This result is in line with the screening data that had shown that preformed ruthenium hydride complexes perform poorly in the present reaction. On the other hand, alkynes are known to readily engage with complexes of the general type $[LRu]^+$ (L = Cp, Cp*), leading to the coupling of two substrates via ruthenacyclic intermediates.[30] This smooth C–C bond formation is obviously outperformed by the *trans* hydroboration presented herein.

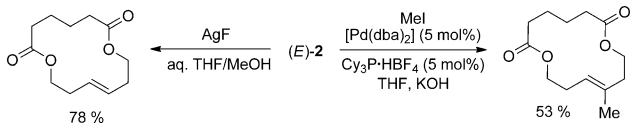
In consideration of this situation and in a certain analogy to the computed pathway of the *trans* hydrosilylation,[31] we assume that binding of an alkyne to the electrophilic metal center of a cationic precatalyst of type **C** favors coordination of the borane rather than of a second alkyne on electronic grounds (Scheme 4). In the resulting loaded complex **E**, the acetylene moiety is supposed to function as a four-electron donor, which explains why alkenes do not react under the chosen conditions. This bonding situation in turn facilitates an inner-sphere delivery of the hydride[32] with formation of a metallacyclopropene **F** (η^2-vinyl complex)[33] without prior



Scheme 4. Possible mechanism of the *trans* hydroboration.

generation of a discrete Ru–H species. It is well precedented that the substituents at the β-carbon atom of such complexes are configurationally labile and can swap places through a $\eta^2 \rightarrow \eta^1 \rightarrow \eta^2$ hapticity change.[33] As they are approximately orthogonal to the plane of the metallacyclopropene, the sheer size of the Cp* ring will exert a massive influence on the stereochemical outcome. As a result, isomer **H**, in which the hydrogen rather than the R group is oriented towards the bulky lid, will be largely favored over **F**. This decisive steric factor loses weight if the lateral methyl groups of the Cp* ring are removed, and [CpRu]-based catalysts are used. The trajectory of the ensuing reductive elimination places the boron entity *anti* to the hydrogen atom, and hence leads to an *E*-configured alkenylboronate product. Although this scenario accounts for all of the preliminary information of mechanistic relevance, it is emphasized that further investigations are necessary to confirm or disprove it.

Of the countless possible derivatizations of *E*-alkenylboronates made available by this convenient new procedure, we explored only the protodeborylation of (*E*)-**2** with AgF,[13] as well as an equally stereo-retentive Suzuki–Miyaura coupling with methyl iodide (Scheme 5).[5] Both reactions led, without



Scheme 5. Preparation of a di- and trisubstituted *E*-cycloalkene by derivatization of (*E*)-**2**. Cy = cyclohexyl, dba = dibenzylidene acetone.

any detectable loss of stereochemical integrity, to *E*-configured cycloalkenes that cannot be made by olefin metathesis in a predictable manner, as inherently *E*-selective alkene-metathesis catalysts are currently unknown.[34] The new method is therefore expected to be highly enabling for target-oriented synthesis where stereochemical integrity and catalyst control are of key strategic importance.

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