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Atom-Economical Regioselective Ni-Catalyzed Hydroborylative Cyclization of Enynes: Development and Mechanism

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We report a full study on the novel regioselective Ni-catalyzed hydroborylative cyclization of enynes using HBpin as the borylation agent. Alkyl and alkenyl boronates can be obtained depending on the substituent on the alkyne. The reaction takes place in smooth conditions with an inexpensive catalytic Ni-based system, constituting a fully atom-economic eco-friendly method. This process shows a broad scope, allowing the formation of carbo- and heterocycles in moderate to good yields. The utility of the resulting boronates is also illustrated. We have studied the reaction mechanism both experimentally and computationally. The process involves initial oxidative cyclometalation to Ni(0)(xantphos) species followed by the key C-B bond formation through σ-bond metathesis, and reductive elimination.

Introduction

Transition metal-catalyzed reactions of polyunsaturated structures allow the preparation of cyclic compounds, which are important scaffolds in synthetic organic chemistry. In this context, enynes are versatile starting materials for the construction of a wide range of carbocycles and heterocycles.[1] Nowadays, novel synthetic strategies have to take into account environmental and economic aspects.[2] The use of first-row transition-metals is an interesting approach to the development of inexpensive and environmentally friendly synthetic methods.[3] This is especially important when the use of such catalysts is combined with readily available substrates that permit the presence of functional groups and that can be prepared and reacted under smooth conditions, avoiding the use of highly basic reagents (such as organomagnesium or organilithium reagents). On the other hand, boronates are relatively stable synthons with low toxicities for a wide variety of applications due to their synthetic versatility and broad functional group compatibility. Thus, carboboration,[4,5] and borylative cyclization reactions,[6] constitute powerful methods for the synthesis of boron derivatives since they provide one C-C and one C-B bonds in a single operation. Interestingly, first-row transition metal reactions may involve different activation mechanisms compared to Pd or other transition metals classically employed as catalysts and, therefore, the discovery of new reactions is also attractive from a mechanistic point of view.

During last years, our group has developed Pd-catalyzed borylative cyclization reactions of several polyunsaturated compounds such as enynes, enallenes, allenynes and enediynes.[7] A related oxidative reaction has been described by Bäckvall on allene derivatives.[8] Our methodology has allowed to access allylic, homoallylic and alkenylic boronates in smooth ligandless conditions and stereoselectively. However, it shows some drawbacks, such as the use of diboron derivative B_2pin_2 (losing one boryl unit) and the impossibility to tune the catalyst properties, since the reaction takes place in the absence of added ligands. Very recently, we have developed the first iron-catalyzed hydroborylative cyclization reaction of 1,6-enynes.[9,10] This method constitutes a more convenient alternative due to the use of an inexpensive catalytic system, the atom-economy of the reaction (using HBpin instead of B_2pin_2) and the wider substrate scope compared to the Pd-catalyzed reaction. Lu and co-workers had previously developed the Co-catalyzed hydroborylative cyclization of 1,6-enynes. Formation of both alkyl and alkenylboronates can be achieved by suitable choice of catalyst.[11] Shortly after Ge reported an enantioselective version of this reaction, that affords high enantiomeric excess in the formation of cyclic alkylboronates from 1,6-enynes adn HBpin, using Co salts and chiral diphosphines.[12]

We were interested in the use of a Ni catalyst in this context, since this metal has been shown to catalyze hydroboration,[13] and diboration,[14] of carbon-carbon double bonds. To the best of our knowledge, there is only one example of Ni-catalyzed borylative cyclization of enynes. Thus, Hsieh and Cheng have developed a regioselective borylative cyclization of 1,6-enynes to alkyl and alkenylboronates using B_2pin_2 as the borylation reagent.[15] However, this reaction is not atom-economical and shows a more restricted scope (Scheme 1).

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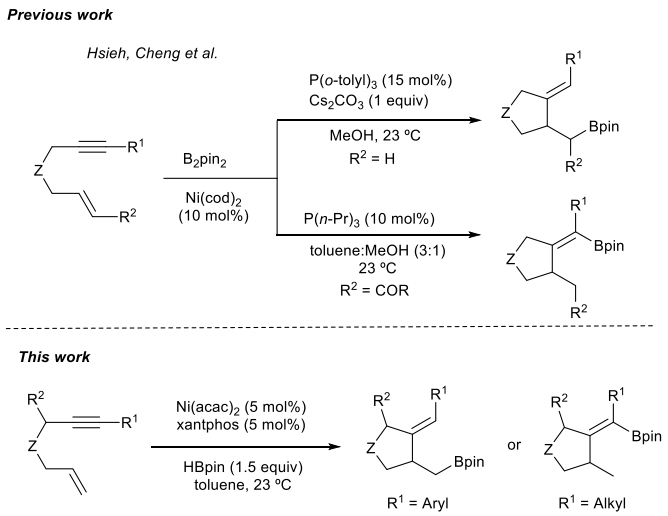


Scheme 1. Ni-catalyzed borylative cyclization of enynes

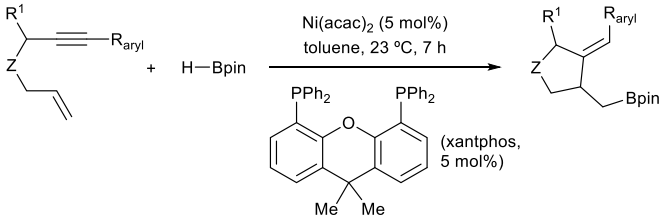
In this work, we report a novel Ni-catalyzed hydroborylation reaction that shows a broad scope, and provides cyclic alkyl- or alkenylboronates that are useful synthetic intermediates. We also illustrate the utility of these derivatives for synthetic purposes. Finally, a mechanistic study performed both experimental and computationally has led us to propose a detailed reaction pathway in which oxidative cyclometalation and σ–bond metathesis are the key steps, and that accounts for the observed regioselectivity.

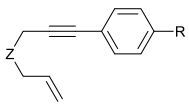
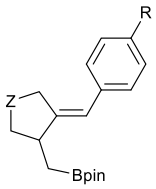
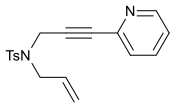
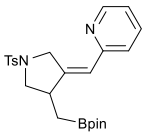
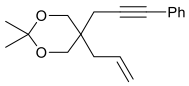
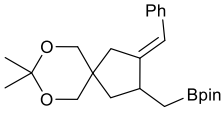
Results and Discussion

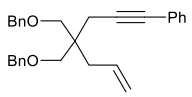
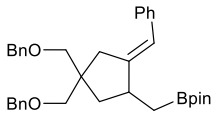
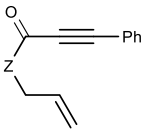
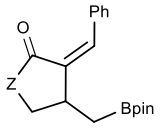
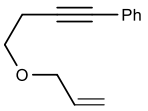
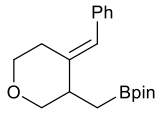
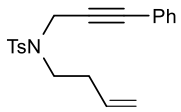
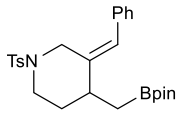
Reaction conditions, outcome and scope

We began our study by evaluating the reaction between 1,6-enyne **1a** and HBpin in the presence of $Ni(cod)_2$ and several ligands. The use of xantphos afforded the corresponding alkylboronate **2a** as the major reaction product, although in low yield (25% yield). After extensive experimentation, we found that the best reaction conditions comprise the use of $Ni(acac)_2$ (5 mol%) and xantphos (5 mol%) in toluene at room temperature. In other conditions, some by-products could be identified (see ESI for details). Nevertheless, alkylboronate **2a** was isolated in just 38% yield (see ESI for details). However, when we extended the reaction to a wide variety of different substrates containing an aryl ring on the alkyne, much better yields were obtained. The reaction shows a broad scope (Table 1), tolerating different tethering groups between the alkene and the alkyne, as well as a wide variety of substituents on the aromatic ring. Thus, for ether derivatives, electron donating (Me, OMe) and electron withdrawing (CN, CF_3) groups on the aryl ring gave the corresponding alkylboronates (**2b-e**, entries 2-6). Better yields were observed for the sulfonamide derivatives (**2f-j**, entries 7-11), for the malonate compounds (**2l-p**, entries 13-17), and for quaternary carbon-containing precursor species (**2s,t**, entries 20 and 21).

Table 1 Ni-catalyzed hydroborylative cyclization of 1,6-enynes containing an aryl-substituted alkyne.[a]



	Substrate	Product	Yield[b]
			
1	**1a**	**2a** : Z = O, R = H	38
2	**1b**	**2b** : Z = O, R = Me	51
3	**1c**	**2c** : Z = O, R = OMe	44
5	**1d**	**2d** : Z = O, R = CF_3	52
6	**1e**	**2e** : Z = O, R = CN	24
7	**1f**	**2f** : Z = NTs, R = H	63
8	**1g**	**2g** : Z = NTs, R = OMe	63
9	**1h**	**2h** : Z = NTs, R= CF_3	43
10	**1i**	**2i** : Z = NTs, R = CN	61
11	**1j**	**2j** : Z = NTs, R = COMe	68
12	 **1k**	 **2k**	41
13	**1l**	**2l** : Z = $C(CO_2Me)_2$, R = H	58
14	**1m**	**2m** : Z = $C(CO_2Me)_2$, R = 3-OMe	67
15	**1n**	**2n** : Z = $C(CO_2Me)_2$, R = 4-OMe	70
16	**1o**	**2o** : Z = $C(CO_2Me)_2$, R = CF_3	37
17	**1p**	**2p** : Z = $C(CO_2Me)_2$, R = CN	74
18	**1q**	**2q** : Z = CH_2, R = H	37
19	**1r**	**2r** : Z = CH_2, R = Me	22
20	 **1s**	 **2s**	64

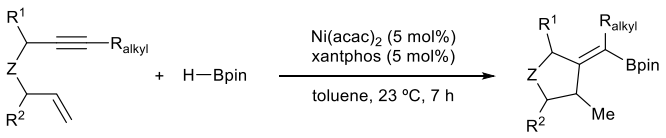
21	 **1t**	 **2t**	58
			
22	**1u**	**2u** : Z = O	66
23	**1v**	**2v** : Z = NPh	77
24	 **1w**	 **2w**	9
25	 **1x**	 **2x**	25

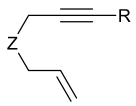
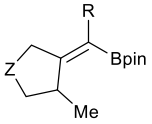
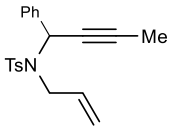
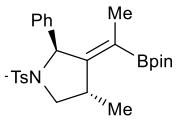
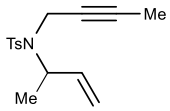
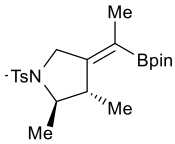
[a] Conditions: enyne **1** (0.4 mmol), HBpin (0.6 mmol), Ni(acac)$_2$ (5 mol%), xantphos (5 mol%) and toluene (2 mL) at rt for 7 h. [b] Isolated yield.

The presence of a ketone group conjugated to the alkyne effectively afforded borylated cyclopentanones (**2u,v**, entries 22 and 23). 1,7-enynes gave the corresponding six-membered ring derivatives albeit in low yields (**2w,x**, entries 25 and 26), probably due to entropic reasons. This may also be the case for CH_2–connected compounds (**2q,r**, entries 18 and 19) that lack a potential Thorpe-Ingold effect. There does not seem to be a correlation between the yields and the electron richness of the ring. The reaction also takes place with pyridine derivative **1k** (entry 12). The configuration of the C-C double bond in products **2** is in accordance with the occurrence of a cis-selective carbometalation involving an intermediate complex with, at least, coordinated alkyne. The smooth reactions conditions render this process compatible with haloarene, acetal, ester, sulfonamide, nitrile, and ketone groups.

Interestingly, the regioselectivity of the reaction changes completely when alkyl-substituted alkynes are subjected to the reaction conditions. In this case, the boryl group incorporates into the external alkyne carbon affording cyclic alkenylboronates (Table 2). Configuration of the new C-C double bond was confirmed by nOe measurements and X-ray diffraction (see below). The highest yields were observed for the formation of pyrrolidine compounds. In contrast, ether and malonate derivatives furnished poor yields (entries 7 and 8). The presence of a stereogenic center on the propargylic or allylic positions resulted in fully diastereoselective reactions (entries 9, 10; Table 2). The relative configuration of the new stereogenic centers in **4i** could be determined by single crystal X-ray diffraction, revealing a trans arrangements for Ph and Me groups (Figure 1).[16] The presence of Me substituent on the allylic carbon (**3j**) afforded a vicinal dimethyl product with both methyl groups in trans configuration (**4j**), as determined on the basis of NMR analysis.

Table 2 Ni-catalyzed hydroborylative cyclization of 1,6-enynes containing alkyl-substituted alkyne.[a]



	Substrate	Product	Yield[b] (%)
			
1	**3a**	**4a** : Z = NTs, R = Me	77
2	**3b**	**4b** : Z = NTs, R = Et	61
3	**3c**	**4c** : Z = NTs, R = *n*-Pr	59
4	**3d**	**4d** : Z = NTs, R = *n*-Oct	45
5	**3e**	**4e** : Z = NPh, R = Me	65
6	**3f**	**4f** : Z = NBz, R = Me	75
7	**3g**	**4g** : Z = O, R = Me	15
8	**3h**	**4h** : Z = C(CO$_2$Me)$_2$, R = Me	18
9	 **3i** (*rac*)	 **4i**	72[c]
10	 **3j** (*rac*)	 **4j**	54[c]

[a] Conditions: enyne **3** (0.4 mmol), HBpin (0.6 mmol), Ni(acac)$_2$ (5 mol%), xantphos (5 mol%) and toluene (2 mL) at rt for 7 h. [b] Isolated yield. [c] Only one diastereoisomer is observed (NMR)

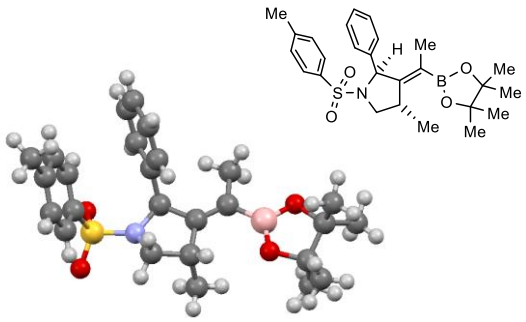
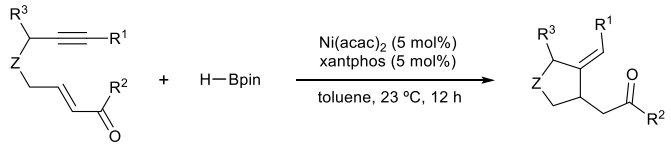


Fig. 1 Crystal structure of compound **4i**.

In contrast to the above mentioned results, we were not able to find the desired cyclized alkyl- or alkenylboronates for substrates containing the alkene conjugated to ketone. Noticeably, the reaction of enones **5** under the same conditions led to the formation of reductive cyclization derivatives, in moderate yields, without incorporation of the boryl fragment (HBpin acts as a reducing agent). In this case, the same kind of products are obtained for both aryl- and alkyl-substituted alkynes. NTs and methylene could be used as tethering groups (Table 3).

Table 3 Ni-catalyzed reductive cyclization of enynones with HBpin.[a]

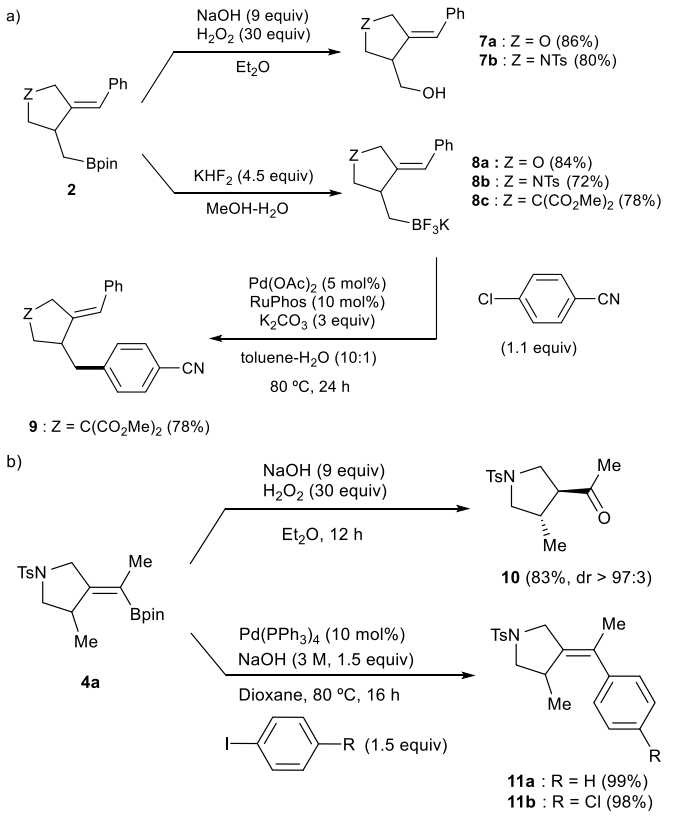


	Substrate	Product	Yield[b] (%)
1	**5a**	**6a** : Z = NTs, R^1 = Ph, R^2 = Me	57
2	**5b**	**6b** : Z = NTs, R^1 = Me, R^2 = Me	60
3	**5c**	**6c** : Z = NTs, R^1 = Me, R^2 = Ph	69
4	**5d**	**6d** : Z = CH_2, R^1 = Ph, R^2 = Me	24

[a] Conditions: enynone **5** (0.4 mmol), HBpin (0.6 mmol), $Ni(acac)_2$ (5 mol%), xantphos (5 mol%) and toluene (2 mL) at rt for 7 h. [b] Isolated yield.

Formation of compounds **6** probably involves the generation of a boron enolate that is hydrolyzed during the reaction work-up, rather than incorporation of a second hydride, since the reaction requires less than 2 equiv of HBpin.

We performed derivatization reactions on the alkyl- and alkenylboronates to illustrate the synthetic utility of our method. Thus, alkylboronates can be oxidized to the corresponding alcohols (**7a,b**) in good yields (Scheme 2, a).



Scheme 2. Functionalisation of boronates.

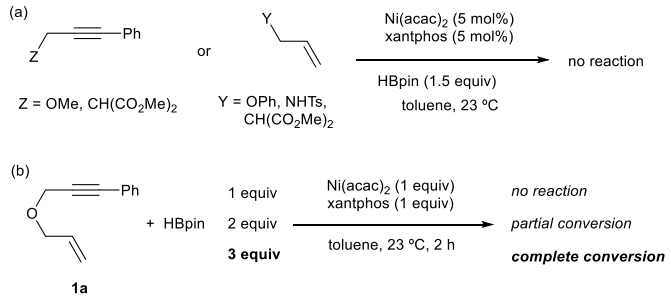
On the other hand, treatment with potassium bifluoride gave rise to the corresponding potassium trifluoroborate salts (**8a-c**), which are usually the more convenient nucleophiles for Suzuki coupling reactions of alkyl nucleophiles.[17] As an example, we performed the reaction of **8c** with *p*-chlorobenzonitrile to obtain the corresponding coupling compound **9** in high yield. Alkenylboronate **4a** can be oxidized as well to give the expected ketone **10**. Finally, direct Suzuki coupling reaction with two iodoarenes allowed the preparation of the expected stereodefined aryl-alkenyl derivatives **11a,b** in quantitative yields (Scheme 2, b).

The above-mentioned reactions show the usefulness of the boron compounds in the context of the preparation of unsymmetrical exocyclic ketones and in the preparation of stereo-defined tetrasubstituted alkenes.

Mechanistic investigation

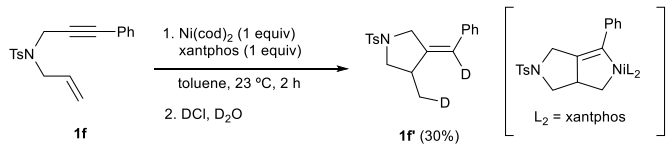
We were interested in the determination of the reaction pathway of this reaction, which can be considered as a formal 1,7-hydroborylative cyclization. In contrast to the previously reported Ni-catalyzed borylative cyclization, involving B_2pin_2, no transmetalation reaction is expected in this case. Both computation and experimental mechanistic study was undertaken in order to determine the actual activation mechanism of HBpin and the enyne by the catalyst, to derive a feasible complete reaction pathway, and to explain the observed regioselectivity.

We firstly examined the reactivity of simple alkenes or alkynes to the optimized reaction conditions. No product was observed, which suggests that the presence of both alkene and alkyne is necessary for the reaction to start (Scheme 3, a).



Scheme 3. Reactions with simple substrates (a), and with stoichiometric Ni(II) (b).

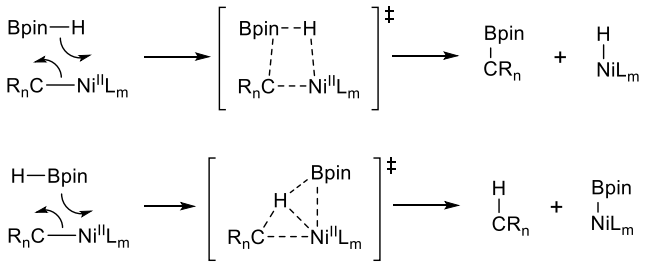
With the aim of determining the oxidation state of the catalytically active species, we carried out some experiments with stoichiometric amounts of nickel precursor. Thus, the reaction of enyne **1a** with 1 equiv of HBpin in the presence of 100 mol% of $Ni(acac)_2$/xantphos does not take place. We need to add two additional equivalents of HBpin in order to get complete conversion. This result suggests that reduction of the Ni(II) precatalyst to Ni(0) is necessary for the reaction to proceed (Scheme 3, b). In fact, we observed complete consumption of the enyne when using 1 equiv of $Ni(cod)_2$/xantphos in the presence of just 1 equiv of HBpin (see ESI for details). This result further supports that the catalytically active species is a Ni(0) complex, and that HBpin acts as the reducing agent when using a Ni(II) source. Moreover, reaction of $Ni(acac)_2$ and xantphos with 2 equiv of HBpin in toluene takes place at room temperature with H_2 evolution to give a brick-red precipitate of previously described complex $Ni(xantphos)_2$.[18] Finally, reaction of **1f** with 100 mol% of $Ni(cod)_2$/xantphos, followed by quenching with DCl in D_2O afforded dideuterated product **1f'** in 30% yield. (Scheme 4). Therefore, a nickelacyclopentene formed by oxidative cyclometalation seems to be a reaction intermediate.



Scheme 4. Stoichiometric reaction of enyne **1f** and Ni(0).

With these results in hand, we performed a detailed computational study at DFT level to derive a complete reaction pathway. The full structure of xantphos ligand, without any simplification, was used for the calculations. Optimizations were performed in toluene with PCM model. Although the experiments clearly pointed to an initial formation of a nickelacycle, we explored the feasibility of the oxidative addition of HBpin to Ni(xantphos) (**I**). This process resulted to be endoergic (14.2 kcal mol^{-1}, see ESI) and therefore, we centered our efforts in the study of the activation of the enyne to give the putative metalacycle, as well as its evolution to the final products (Scheme 6).

Initial coordination of enyne to Ni(xantphos) (**I**) would afford intermediate **II**, which would evolve through oxidative cyclometalation to Ni(II) metalacycle **III**. Then, we considered the reaction of this key intermediate with HBpin by oxidative addition of the B-H bond to Ni(II). However, we were not able to locate any structure corresponding to a Ni(IV) complex (Scheme 6, bottom center). Alternatively, activation of the boron hydride may take place through σ–bond metathesis, with participation of H-B and Ni-C bonds. Subsequent reductive elimination would account for the formation of the final products. It is important to note that, in principle, σ-metathesis may involve either the alkenyl-Ni or the alkyl-Ni bonds. Additionally, this process could proceed in two different fashions to afford either Ni-H and C-B bonds, or Ni-B and C-H bonds (Scheme 5). Therefore, there are two possible pathways for the formation of both the alkylboronate **VIII** and the alkenylboronate **IX**, depending firstly on the kind of Ni-C bond involved in the metathesis, and on the chemoselectivity of this reaction. We have calculated all the possible intermediates and transition states for model enynes containing methyl and phenyl groups as substituents on the alkyne, in order to determine the most favorable pathways and get insight into the origin of the observed regioselectivity.



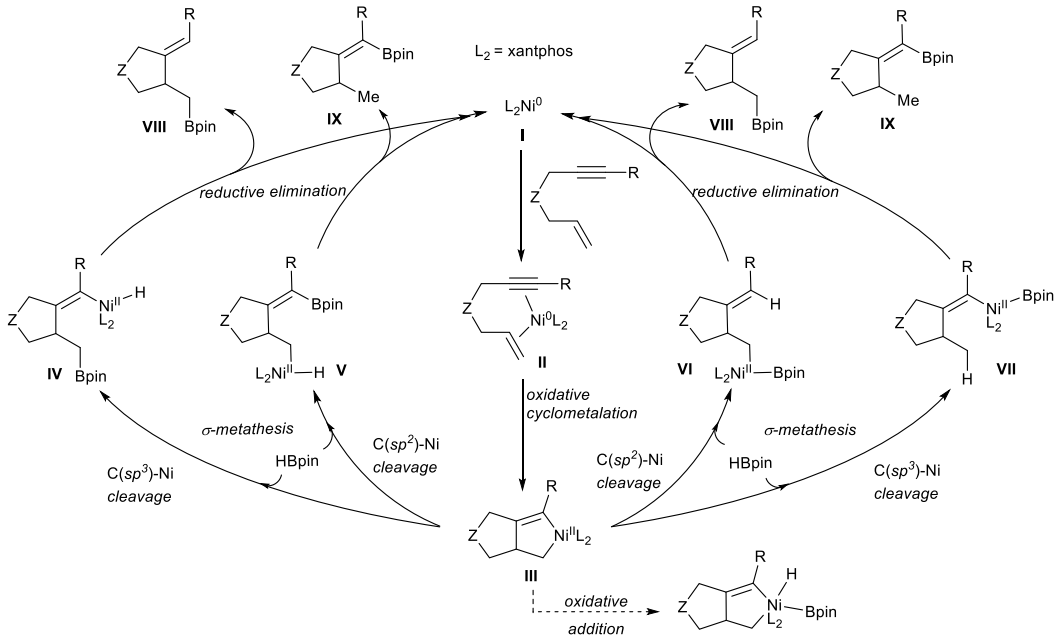
Scheme 5. Possible σ-bond metathesis involving Ni-C and B-H bonds.

We considered methylamine derivatives **Ia** and **Ib** as the model enynes for the computational study (Schemes 7 and 8). Coordination of both enynes to Ni(xantphos) to give **IIa** and **IIb** is strongly favored in spite of the entropy loss, and results especially exoergic for the aryl-substituted derivative **I** (-25.1 and -33.5 kcal mol^{-1}, respectively). Subsequent formation of metalacycle **IIIa** by oxidative cyclometalation from **IIa** is practically thermoneutral, and proceeds through a low barrier (E_a =14.5 kcal mol^{-1}). The analogous reaction involving the phenyl-substituted derivative that gives rise to **IIIb** shows a similar barrier (15.9 kcal mol^{-1}). In this case, the reaction is slightly endergonic (+3.4 kcal mol^{-1}). These two-step processes are thermodynamically very favorable. Therefore, the Ni catalyst seems to activate the enynes prior to the reaction with HBpin.

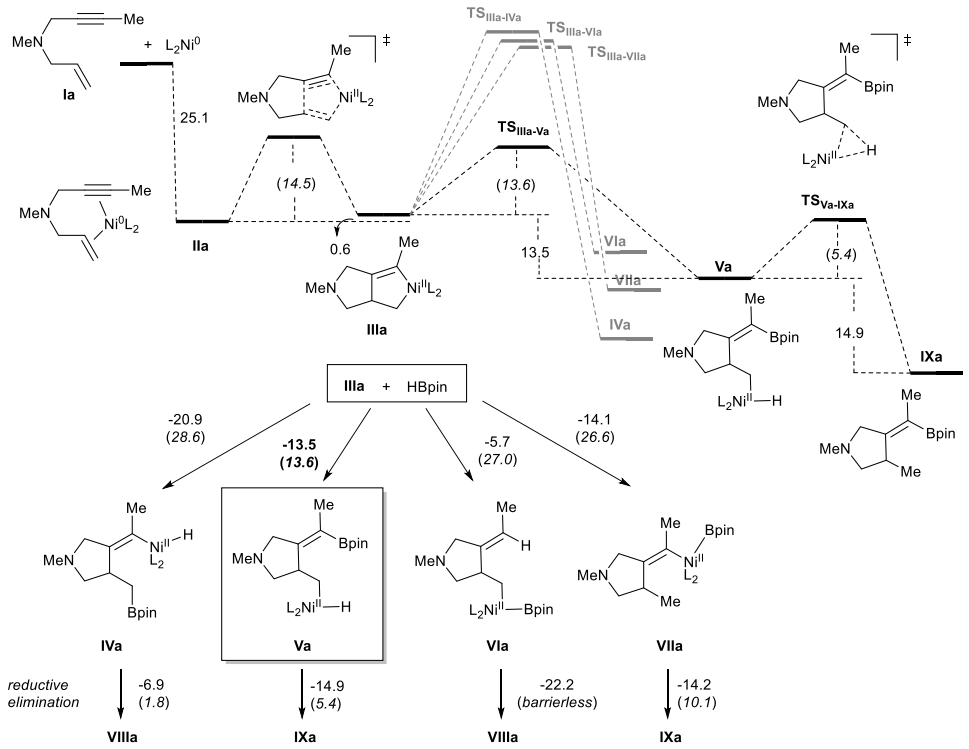
Then, we explored the feasibility of the oxidative addition of HBpin to the Ni(II) metalacycles **III**. The expected octahedral Ni(IV) complexes that would be formed in this reaction were not

located. Instead, we found species resulting from C-B or C-H bond formation. Evolution of complexes **III** does not seem to involve B-H bond oxidative addition to give a Ni(IV) intermediate.

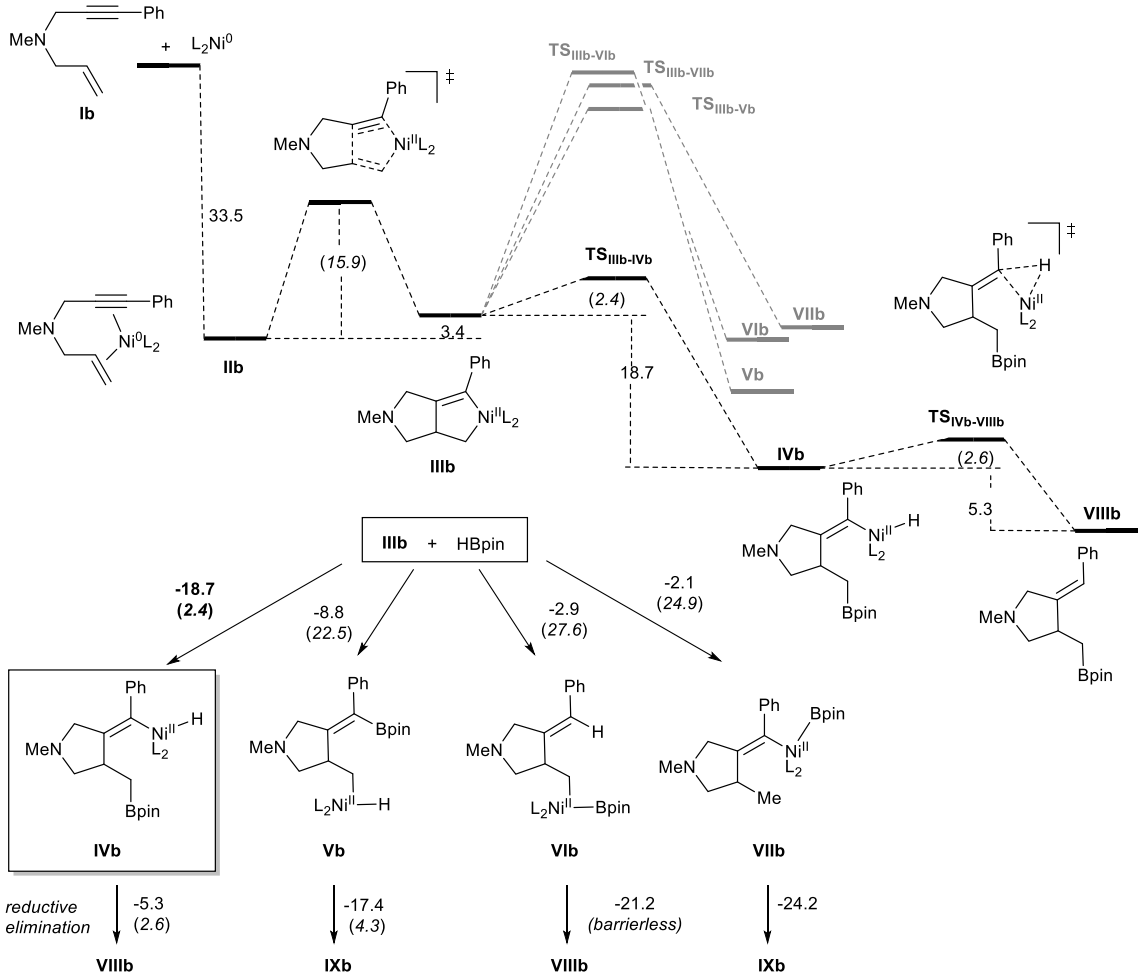
Consequently, we explored the different kinds of σ–bond metathesis involving HBpin and **IIIa** and **IIIb** than can be proposed in principle (Scheme 6). These processes involve a Ni-C bond and the H-B bond. Taking into account that both Ni-C(sp^2) or Ni-C(sp^3) bonds can participate in the reaction, and that either of them may evolve in two different ways, to give Ni-B or Ni-H bonds along with the boronate, there are four possible reaction pathways from every metalacycle (Scheme 6).



Scheme 6. Possible reaction pathways for the formation of the observed alkyl- and alkenylboronates.



Scheme 7: Computed reaction profile for the methyl-substituted alkyne. ΔG (kcal mol^{-1}) are calculated in toluene (PCM) at 6-31G(d) (C,H,N,P,O,B), LANL2DZ (Ni) level. Calculated activation energies in toluene are shown in brackets. L_2=Xantphos.



Scheme 8: Computed reaction profile for the phenyl-substituted alkyne. ΔG (kcal mol^{-1}) are calculated in toluene (PCM) at 6-31G(d) (C,H,N,P,O,B), LANL2DZ (Ni) level. Calculated activation energies in toluene are shown in brackets. L_2=Xantphos

We were able to obtain the structures of the corresponding transition states for all the possible metathesis reactions from **IIIa** (Scheme 7) and **IIIb** (Scheme 8). The activation energies for the reactions of **IIIa** with HBpin are high (E_a > 25 kcal mol^{-1}) and would not take place at room temperature, except for the reaction involving the *cleavage of the alkenyl-Ni bond* to give the corresponding complex containing an alkyl-Ni hydride and an alkenylboronate (**Va**). This complex is formed exoergically (-13.5 kcal mol^{-1}) with a low activation energy (13.6 kcal mol^{-1}). Subsequent Ni-H reductive elimination from this compound is highly exothermal (and kinetically irrelevant, E_a = 5.4 kcal mol^{-1}) and leads to the observed product **IXa**. Therefore, computational data perfectly match the regioselectivity observed for the reaction of the methyl-substituted alkyne. Moreover, calculations for the σ–metathesis from the Ph-substituted metalacycle **IIIb**, are also in agreement with the formation of the experimentally observed product, the alkylboronate. In this case, the most favorable process corresponds to the *cleavage of the alkyl-Ni* bond, with the same regioselectivity previously found: the formation of an intermediate Ni-H complex. Activation energy is even lower for this reaction (2.4 kcal mol^{-1}), whereas the alternative processes are far much slower (E_a > 22 kcal mol^{-1}). Reductive elimination of either C-H or C-B bonds to give Ni(0) are fast and exothermic reactions, and do not affect the reaction kinetics. According to the computed reaction profile, oxidative cyclometalation is the rate-limiting step for this reaction for the substrates bearing aryl-substituted alkynes. For the methyl-substituted

derivatives, this cannot be definitively stated, due to the similar activation energy found for the σ–bond metathesis. Transition states corresponding to the two possible metathesis reactions leading to Ni-H complexes **IV** and **V** show the expected four-membered geometry. As an example, the transition state from **IIIa** to **Va** is depicted in Figure 2 (top). Noteworthy, the transition states for the alternative processes, leading to boryl-Ni complexes **VIa** and **VIIa**, show a nearly linear C-H-B arrangement in the H atom transfer from B to C, with short Ni-H distances, suggesting metal-hydride interaction along the reaction coordinate (Figure 2, bottom shows the transition state that would lead to **VIa**). It is important to note the activation energy for this different kind of σ–metathesis reaction is similar to that found for the non-preferred pathways involving the formation of C-B and Ni-H bonds. Therefore, although the formation of Ni-boryl complexes is not competitive in this case, it constitutes a feasible pathway that could operate in other Ni-catalyzed reactions.

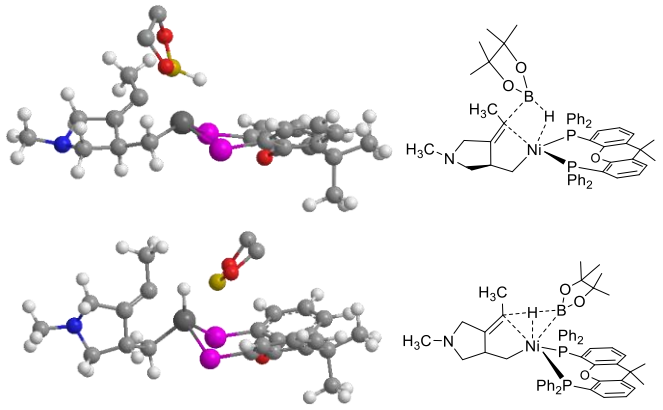


Figure 2. Top: Structure of the calculated transition state leading from **IIIa** to model Ni-hydride **Va**. Bottom: Transition state leading from **IIIa** to **VIa** (Phenyl groups of xantphos and methyls of Bpin have been omitted for clarity in the 3D representations).

Careful inspection of the structure of all the transition states calculated for the different metathesis reactions point to the steric hindrance as the reason for the observed regioselectivity. Frontier orbitals do not show important differences (see ESI). The special structure of xantphos, along with the steric encumbrance exerted by the methyl groups of the pinacol fragment and the aryl on the alkyne, condition the approach of HBpin to the nickelacycle. The common feature of the preferred transition states is that they show comparatively shorter Ni-H distances and a longer Ni-P distance with respect to the P atom cis to the carbon involved in the metathesis (Table 4). This fact suggests that the accessibility of the lowest energy transition states requires an effective Ni-H interaction.

Table 4 Relevant bond distances (Å) for the transition states leading to Ni hydrides through σ–metathesis reaction of **IIIa** and **IIIb** with HBpin.[a]

	Ni-P[b]	Ni-P	Ni-C[c]	Ni-H	B-C[c]	B-H
IIIa-IVa	2.493	2.532	2.174	1.993	2.133	1.237
IIIa-Va	*2.317*	*2.723*	*2.184*	*1.895*	*2.033*	*1.256*
IIIb-IVb	*2.434*	*2.985*	*2.050*	*1.693*	*2.397*	*1.233*
IIIb-Vb	2.344	2.725	2.261	1.912	2.095	1.243

[a] Data corresponding to the lowest energy transition states in italics. [b] P atom trans to the C involved in the C-B formation. [c] Distances to the C atom involved in the metathesis.

Conclusions

We have developed a Ni-catalyzed hydroborylative cyclization reaction that affords one C-C and one C-B bond in a single operation, and have proposed a reasonable reaction mechanism. The reaction provides either homoallyl- or alkenylboronates, the regioselectivity depending on the substitution of the alkyne. The reaction shows a wide scope and allows the formation of carbo- and heterocycles in a single step, smooth conditions, with an inexpensive catalytic system and full atom economy. Experimental and computational results suggest that the reaction involves a Ni(0)-Ni(II) catalytic cycle, implying an initial oxidative cyclometalation on the enyne coordinated to Ni(xantphos). A subsequent feasible σ–metathesis reaction, followed by reductive elimination explain the formation of the final boronates. Compared with the previously reported Pd-catalyzed reaction, this process has advantages regarding economic and environmental issues. In addition, the kind of active ligands opens the possibility to develop enantioselective versions of this process.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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