OL Organic Letters
Letter
Cite This: Org. Lett. XXXX, XXX, XXX−XXX
pubs.acs.org/OrgLett

Atom-Economical Ni-Catalyzed Diborylative Cyclization of Enynes: Preparation of Unsymmetrical Diboronates

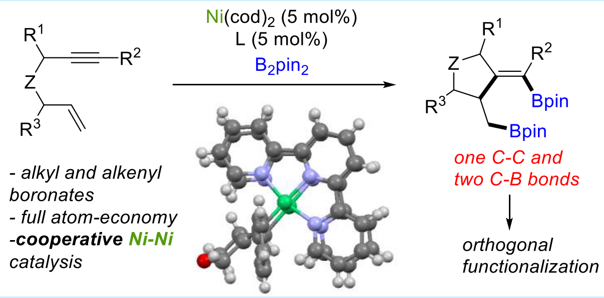
Natalia Cabrera-Lobera,[†] M. Teresa Quirós,[†] William W. Brennessel,[‡] Michael L. Neidig,[‡] Elena Buñuel,*,[†] and Diego J. Cárdenas*,[†]

[†]Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, Institute for Advanced Research in Chemical Sciences (IAdChem), Av. Francisco Tomás y Valiente 7, Cantoblanco 28049, Madrid, Spain

[‡]Department of Chemistry, University of Rochester, Rochester, New York 14627, United States

Supporting Information

ABSTRACT: We report a Ni-catalyzed diborylative cyclization of enynes that affords carbo- and heterocycles containing both alkyl- and alkenylboronates. The reaction is fully atom-economical, shows a broad scope, and employs a powerful and inexpensive catalytic Ni-based system. The reaction mechanism seems to involve activation of the enyne by Ni(0) through oxidative cyclometalation of the enyne prior to diboron reagent activation. An unprecedented dinuclear bis(organometallic) Ni(I) intermediate complex was isolated.



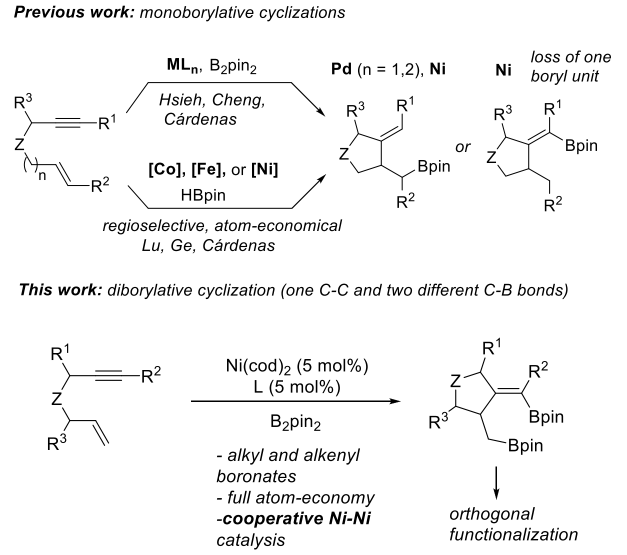
The development novel efficient synthetic methodology cannot ignore environmental and economic aspects. This is one of the reasons for the renaissance of the Earth-abundant first-row transition metals as catalysts during the last few years. Recently, Ni derivatives have demonstrated their utility in a wide variety of synthetically useful reactions.[1] The ability of Ni to access a variety of oxidation states is related to the rich reactivity of Ni derivatives and the discovery of unprecedented activation pathways.[2] In addition, cooperative catalysis or a combination of metal-catalyzed and photoredox reactions constitute novel promising approaches to solve synthetic problems.[3] On the other hand, boronates are especially relevant synthons due to their stability, functional group tolerance, low toxicity, versatility, and wide applicability.[4] Preparation of boronates from alkenes, alkynes, and other unsaturated compounds by diboration reactions has been performed with a variety of heavy metals.[5] More recently, Fe,[6] Co,[7] Ni,[8] and Cu[9] have demonstrated to be useful for these purposes as well. Carboboration[10,11] and borylative cyclization reactions[12] of polyunsaturated compounds constitute powerful methods for the formation of complex boron-containing carbo- and heterocycles by formation of C−C and C−B bonds in cascade reactions. These products are useful synthetic intermediates. Pd-catalyzed borylative cyclizations have proven to be valuable for the preparation of cyclic boronates from di- and polyunsaturated substrates (enynes, enediynes, allenynes, enallenes, etc.) and diboron derivatives,[13,14] but have some drawbacks related to the loss of one boryl unit and the difficult catalyst tuning in the necessary ligandless conditions. On the other hand, recently reported Co-,[15] Fe-,[16] and Ni-catalyzed[17] hydroborylative cyclizations of enynes with HBpin are far more convenient for their high atom economy, use of inexpensive catalysts, and possibility of developing enantioselective transformations.

Herein we wish to report a full atom-economical, versatile, widely applicable synthetic method for the preparation of cyclic compounds containing two different kinds of boronate units, starting from an ample variety of simple enynes by cooperative homometallic catalysis involving Ni complexes. We report the structure of the first unsymmetrical bis[organonickel(I)] complex, which we propose as the key intermediate for this transformation (Scheme 1).

Our aim was to develop diborylative cyclizations that led to diboronates containing two different boryl units that could be sequentially functionalized. To the best of our knowledge, this process has not been achieved yet. Enynes are especially interesting in this respect because they may provide diboronates containing to different boryl units. We began our study by searching reaction conditions for the diboration of enyne **1a**. After much experimentation, the desired product **2a** could be obtained using B_2pin_2 (1.05 equiv), $Ni(cod)_2$ (5 mol %), and 5,5′′-dimethylterpyridine (**L1**, 5 mol %) in diisopropylether at 60 °C (see Supporting Information for more details on the optimization of the reaction conditions). Ni(II) salts were ineffective and led to recovery of the unaltered starting enyne. Although the yield obtained for the model reaction was moderate, the process is very general and proceeds with excellent yields for a wide variety of substrates, providing boron-functionalized carbo- and heterocycles (Scheme 2).

Received: July 18, 2019

Scheme 1. Metal-Catalyzed Mono- and Diborylative Cyclizations



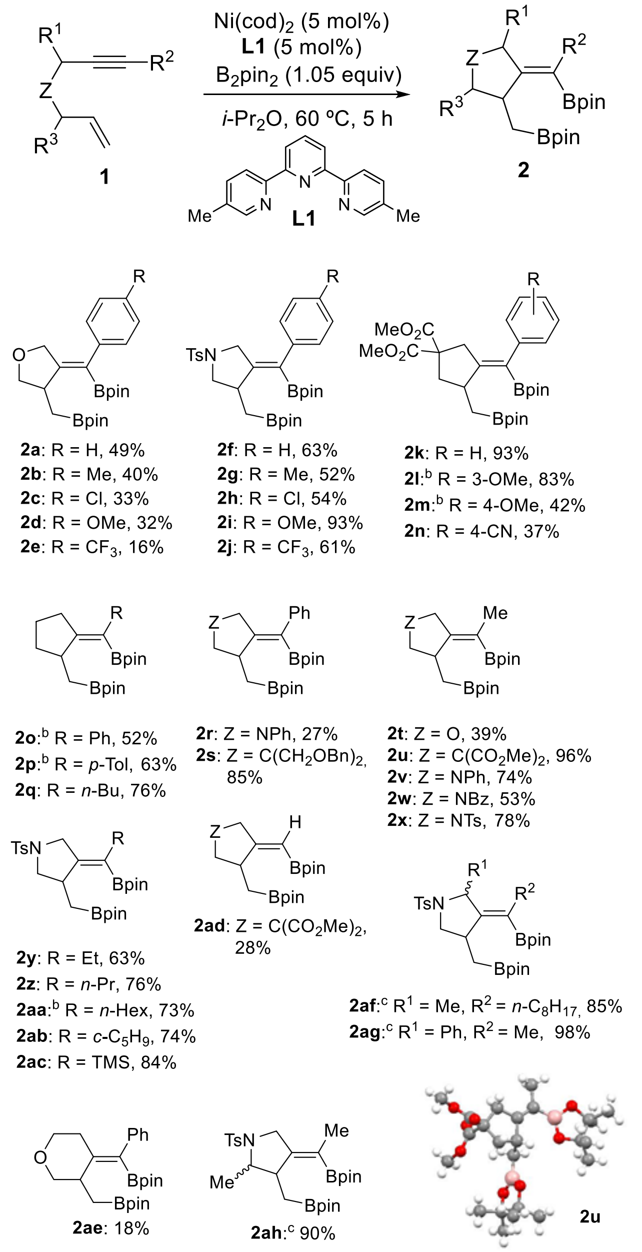
Thus, enynes containing arylalkynes afforded the corresponding products in moderate to good yields for oxygen- (**2a–e**), nitrogen- (**2f–j**, **2r**), or malonate-derived (**2k–n**) derivatives within the tethering chains. The reaction tolerates a variety of functional groups with different electronic properties on the aromatic ring (Me, Cl, MeO, CN, and CF_3 in *meta*- and *para*- positions). Simple carbocycles are also accessible in good yields for substrates containing both aryl and alkyl substituents on the alkyne (**2o–q**, **2s**). Substrates containing methyl-substituted alkynes were also effective and provided high to excellent yields, regardless of the kind of the tethering chain (**2t–x**). The presence of other primary or secondary alkyl chains was also possible to give diboronates **2y–ab**. TMS derivative **1ac** gave rise to the corresponding-1-silylalkenylboronates **2ac** in high yield. The process also tolerates substitution on the propargyl and allyl carbon atoms, affording the expected products in excellent to quantitative yields (**2af–ah**). However, no stereocontrol on the formation of the new stereogenic center was observed. The poorest results were obtained for the reactions of enynes **1ad**, containing a terminal alkyne, and for 1,7-enyne **1ae**, which afforded the six-membered ring product in just 18%.

With the aim of illustrating the synthetic utility of the obtained diboronates, we performed some functionalization reactions. Thus, oxidation of both boronate groups gave the corresponding hydroxy-ketone **3** in high yield (Scheme 3).

More interestingly, we succeeded at performing an orthogonal derivatization of diboronates **2u** and **2k** by selective Suzuki cross-coupling reactions. First, we coupled the alkenylboronate moiety with iodobenzene to obtain **4**. Then, the remaining alkylboronate group was converted into the trifluoroborate salts **5**, which were used in subsequent Suzuki cross-couplings to give compounds **6** (Scheme 3). There is no need to have different boronates such as Bpin and Bdan[5g,7b]

To get insight into the reaction mechanism, we performed some experiments. Thus, when simple alkenes or alkynes were subjected to the optimized conditions, we did not observe borylation of any of the substrates. On the other hand, the stoichiometric reaction of enynes **1f** or **1k** with $Ni(cod)_2$ and **L1** in the absence of boron reagent followed by hydrolysis with

Scheme 2. Ni-Catalyzed Diborylative Cyclization of Enynes[a]

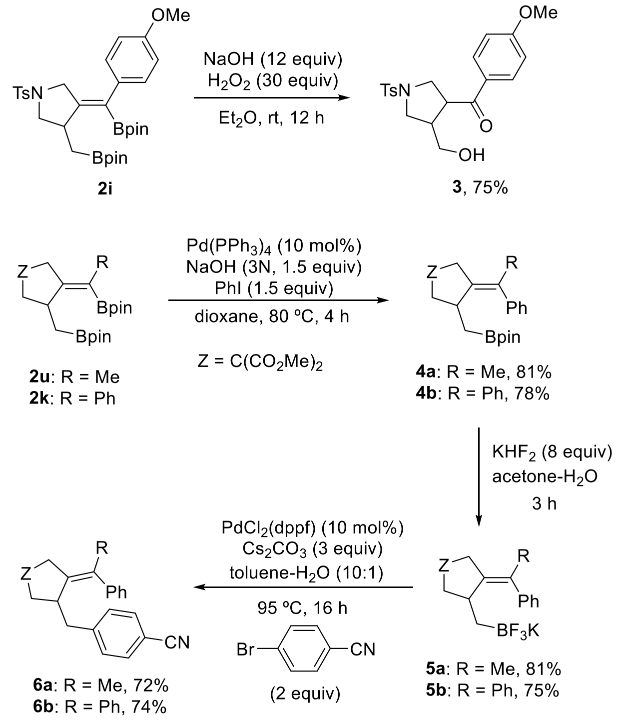


[a] Conditions: enyne **1** (0.2 mmol), B_2pin_2 (0.21 mmol), $Ni(cod)_2$ (5 mol %), **L1** (5 mol %), and i-Pr_2O (1 mL) at 60 °C for 5 h. Isolated yields by column chromatography. [b] Toluene was used instead of i-Pr_2O. [c] A mixture of two diastereoisomers was obtained d.r. = 1:1.7 (**2af**), d.r. = 1:3.7 (**2ag**), d.r. = 1:1.2 (**2ah**).

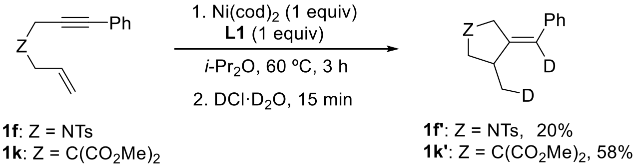
DCl in D_2O led to the corresponding dideuterated cyclic derivatives **1f′** and **1k′** (Scheme 4). These results suggest the formation of an intermediate complex containing both alkyl- and alkenyl-Ni bonds. In fact, we obtained dark red single crystals resulting from the stoichiometric reaction of **1a** and $Ni(cod)_2$-tpy.

X-ray diffraction analysis revealed the structure of a fascinating bimetallic complex containing a carbocycle and two Ni(I)-tpy units bound to alkyl and alkenyl carbon ligands (**7**, Figure 1).

Scheme 3. Functionalization of Diboronates



Scheme 4. Experiments To Probe the Reaction Pathway



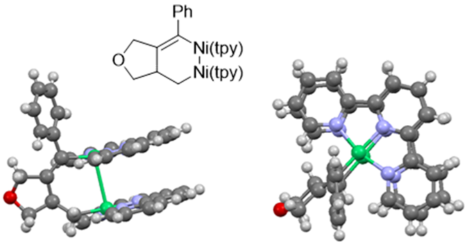


Figure 1. Two different views of the crystal structure of dinuclear Ni complex **7** derived from **1a**.

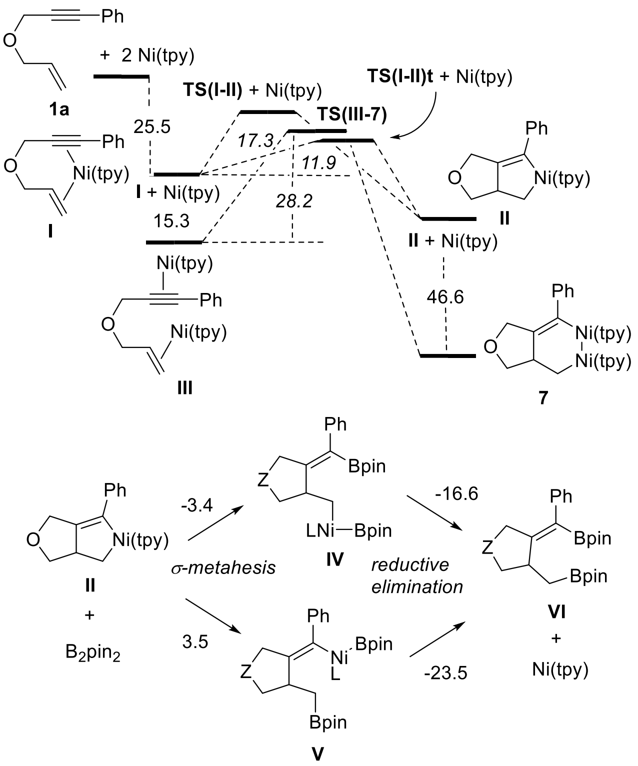
The short Ni–Ni distance (2.97 Å) indicates a strong interaction among both metals (van der Waals radius for Ni is 1.63 Å). This is reminiscent of the structure of MeNi(tpy), in which a weaker intermolecular interaction between the Ni atom was observed in the solid state (3.18 Å).[18] Both metal atoms are formally Ni(I), and therefore, the structure of the complex corresponds to an oxidative cyclometalation with each metal increasing its oxidation state by one unit.

We envisioned two possible mechanisms for the formation of **7**, and calculations at the DFT level were performed on **1a** as a model to probe their feasibility (Scheme 5, see Supporting Information for details).

Thus, the process could involve the cyclization of a bimetallic precursor containing two Ni(tpy) units coordinated to each unsaturation (**III**). Formation of **III** is exoergic, and its evolution to **7** would take place with a moderate activation energy (28.2 kcal mol^{-1}) compatible with a process taking place at 60 °C. Alternatively, oxidative cyclometalation could occur from a mononuclear Ni species with both the alkyne and the alkene coordinated to the metal (**I**). Activation energy for the formation of metallacycle **II** from this complex is lower (17.3 kcal mol^{-1}), albeit the corresponding transition state lies above the above-mentioned one. On the other hand, a triplet transition state, **TS(I–I)t**, lying 1.1 kcal mol^{-1} below **TS(III-7)**, would lead to the formation of **II**. Subsequent comproportionation with N(tpy) would afford species **7** as well. Complex **7** shows a triplet ground state according to its EPR spectrum (μ_{eff} = 3.1, see Supporting Information). The calculated triplet state for **7** is only 3.1 kcal mol^{-1} more stable compared to the singlet. When we subjected complex **7** to reaction with an excess of B_2pin_2, simulating the reaction relative concentrations, bis(boronate) **2a** was formed, but in moderate yield (41% NMR yield, Scheme 6).

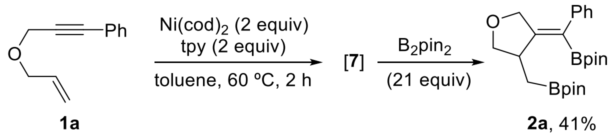
Computational and experimental results are not conclusive to decide whether the reaction takes place through monometallic intermediate **II** or by direct formation of **7**

Scheme 5. (Top) Calculated Possible Reaction Pathways for the Formation of 7 and (Bottom) Reaction Energies for the Reaction of II with Diboron Reagent[a]



[a] ΔG (kcal mol^{-1}) values were calculated with the M06-2x functional using 6-31G(d) (C, H, N, O), LANL2DZ (Ni) basis set, in diisopropylehter (PCM) (activation energies are in italics).

Scheme 6. Formation of Complex 7 with a Stoichiometric Amount of Catalyst and Subsequent Reaction with B_2pin_2



because DFT methods overestimate the stability of high-spin states, and therefore, the computed energy for **TS(I−II)t** is not fully reliable.[19] In addition, the low energy of dinuclear complex **7** suggests that it could be a resting state rather than a reaction intermediate. Moreover, inspection of the structure of **7** makes it difficult to guess how this complex could react with B_2pin_2. We studied the interaction of **II** with the boron reagent (Scheme 5, bottom). Exploration of the potential energy surface strongly suggests that oxidative addition of the B−B bond to give a Ni(IV) intermediate does not take place. Instead, we propose a σ-bond metathesis, which may involve both Ni−C bonds to give either intermediate **IV** or **V**. Reaction involving cleavage of the alkenyl−Ni bond to provide **IV** seems more feasible because it is exoergic (−3.4 kcal mol^{-1}), whereas formation of **V** is endoergic (+3.5 kcal mol^{-1}). Finally, downhill C−B reductive elimination would give the final diboronate and would regenerate the Ni(0) catalyst.

In conclusion, synthetically useful carbo- and heterocycles containing and alkyl- and alkenylboronate units can be efficiently synthesized from enynes with inexpensive catalyst. Activation of the organic substrate takes place prior to reaction with the borylation reagent. Further studies to ascertain the reaction mechanism, especially regarding the activation of diboron derivatives with novel dinuclear Ni(I)−Ni(I) complexes, are underway.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02485.

> Experimental procedures and analytical data for all compounds; X-ray diffraction details; and computational methods, energies, and coordinates (PDF)

Accession Codes

CCDC 1834503 and 1891623 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: diego.cardenas@uam.es; Tel.: +34 914974358
*E-mail: elena.bunnel@uam.es; Tel.: 914973879

ORCID

William W. Brennessel: 0000-0001-5461-1825
Michael L. Neidig: 0000-0002-2300-3867
Diego J. Cárdenas: 0000-0002-1707-6445

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Spanish MINECO for funding (Grant CTQ2016-79826-R) and a Juan de la Cierva fellowship to M.T.Q., the MECD for a FPU fellowship to N.C.-L., the Centro de Computación Científica-UAM, and the U.S. National Institutes of Health (Grant R01GM111480 to M.L.N.).

REFERENCES

(1) (a) Juliá-Hernández, F.; Moragas, T.; Cornella, J.; Martin, R. Remote carboxylation of halogenated aliphatic hydrocarbons with carbon dioxide. *Nature* **2017**, *545*, 84−88. (b) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. Recent advances in homogeneous nickel catalysis. *Nature* **2014**, *509*, 299−309.

(2) (a) Hu, X. Nickel-catalyzed cross coupling of non-activated alkyl halides: a mechanistic perspective. *Chem. Sci.* **2011**, *2*, 1867−1886. (b) Phapale, V. B.; Cárdenas, D. J. Nickel-catalysed Negishi cross-coupling reactions: scope and mechanisms. *Chem. Soc. Rev.* **2009**, *38*, 1598−1607.

(3) (a) Tellis, J. C.; Primer, D. N.; Molander, G. A. Dual catalysis. Single-electron transmetalation in organoboron cross-coupling by photoredox/nickel dual catalysis. *Science* **2014**, *345*, 433−436. (b) Zuo, Z.; Ahneman, D. T.; Chu, L.; Terrett, J. A.; Doyle, A. G.; MacMillan, D. W. Dual catalysis. Merging photoredox with nickel catalysis: coupling of α-carboxyl sp^3-carbons with aryl halides. *Science* **2014**, *345*, 437−440.

(4) (a) Neeve, E. C.; Geier, S. J.; Mkhalid, I. A. I.; Westcott, S. A.; Marder, T. B. Diboron(4) Compounds: From Structural Curiosity to Synthetic Workhorse. *Chem. Rev.* **2016**, *116*, 9091−9161. (b) Xu, X.; Zhang, S.; Li, P. Boron-selective reactions as powerful tools for modular synthesis of diverse complex molecules. *Chem. Soc. Rev.* **2015**, *44*, 8848−8858. (c) Fernández, E., Whiting, A., Eds. Synthesis and Application of Organoboron Compounds. *Top Organomet. Chem.*; Springer: Switzerland, 2015; Vol *49*, pp 1−331.

(5) (a) Morgan, J. B.; Miller, S. P.; Morken, J. P. Rhodium-Catalyzed Enantioselective Diboration of Simple Alkenes. *J. Am. Chem. Soc.* **2003**, *125*, 8702−8703. (b) Miller, S. P.; Morgan, J. B.; Nepveux, F. J.; Morken, J. P. Catalytic Asymmetric Carbohydroxylation of Alkenes by a Tandem Diboration/Suzuki Cross-Coupling/Oxidation Reaction. *Org. Lett.* **2004**, *6*, 131−133. (c) Trudeau, S.; Morgan, J. B.; Shrestha, M.; Morken, J. P. Rh-Catalyzed Enantioselective Diboration of Simple Alkenes: Reaction Development and Substrate Scope. *J. Org. Chem.* **2005**, *70*, 9538−9544. (d) Kliman, L. T.; Mlynarski, S. N.; Morken, J. P. Pt-Catalyzed Enantioselective Diboration of Terminal Alkenes with $B_2(pin)_2$. *J. Am. Chem. Soc.* **2009**, *131*, 13210−13211. (e) Iwadate, N.; Suginome, M. Differentially Protected Diboron for Regioselective Diboration of Alkynes: Internal-Selective Cross-Coupling of 1-Alkene-1,2-diboronic Acid Derivatives. *J. Am. Chem. Soc.* **2010**, *132*, 2548−2549. (f) Coombs, J. R.; Haeffner, F.; Kliman, L. T.; Morken, J. P. Asymmetric 1,4-Dihydroxylation of 1,3-Dienes by Catalytic Enantioselective Diboration. *J. Am. Chem. Soc.* **2013**, *135*, 11222−11231. (g) Lee, C.-I.; Shih, W.-C.; Zhou, J.; Reibenspies, J. H.; Ozerov, O. V. Synthesis of Triborylalkenes from Terminal Alkynes by Iridium-Catalyzed Tandem C-H Borylation and Diboration. *Angew. Chem., Int. Ed.* **2015**, *54*, 14003−14007. (h) Liu, J.; Nie, M.; Zhou, Q.; Gao, S.; Jiang, W.; Chung, L. W.; Tang, W.; Ding, K. Enantioselective palladium-catalyzed diboration of 1,1-disubstituted allenes. *Chem. Sci.* **2017**, *8*, 5161−5165. (i) Takaya, J.; Iwasawa, N. Catalytic, Direct Synthesis of Bis(boronate) Compounds. *ACS Catal.* **2012**, *2*, 1993−2006. (j) Zhao, F.; Jia, X.; Li, P.; Zhao, J.; Zhou, Y.; Wang, J.; Liu, H. Catalytic and catalyst-free diboration of alkynes. *Org. Chem. Front.* **2017**, *4*, 2235−2255. (k) Royes, J.; Cuenca, A. B.; Fernández, E. Access to 1,1-Diborylalkenes and Concomitant Stereoselective Reactivity. *Eur. J. Org. Chem.* **2018**, *2018*, 2728−2739.

(6) Nakagawa, N.; Hatakeyama, T.; Nakamura, M. Iron-Catalyzed Diboration and Carboboration of Alkynes. *Chem. - Eur. J.* **2015**, *21*, 4257−4261.

(7) (a) Zhang, L.; Huang, Z. Synthesis of 1,1,1-Tris(boronates) from Vinylarenes by Co-Catalyzed Dehydrogenative Borylations−Hydroboration. *J. Am. Chem. Soc.* **2015**, *137*, 15600−15603. (b) Krautwald, S.; Bezdek, M. J.; Chirik, P. J. Cobalt-Catalyzed 1,1-Diboration of Terminal Alkynes: Scope, Mechanism, and Synthetic Applications. *J. Am. Chem. Soc.* **2017**, *139*, 3868−3875. (c) Wen, H.; Zhang, L.; Zhu, S.; Liu, G.; Huang, Z. Stereoselective Synthesis of Trisubstituted Alkenes via Cobalt-Catalyzed Double Dehydrogenative Borylations of 1-Alkenes. *ACS Catal.* **2017**, *7*, 6419−6425. (d) Teo, W. J.; Ge, S.

Cobalt-Catalyzed Diborylation of 1,1-disubstituted Vinylarenes: A Practical Route to Branched gem-Bis(boryl)alkanes. *Angew. Chem., Int. Ed.* **2018**, *57*, 1654−1658.

(8) (a) Cho, H. Y.; Morken, J. P. Diastereoselective Construction of Functionalized Homoallylic Alcohols by Ni-Catalyzed Diboron-Promoted Coupling of Dienes and Aldehydes. *J. Am. Chem. Soc.* **2008**, *130*, 16140−16141. (b) Cho, H. Y.; Morken, J. P. Ni-Catalyzed Borylative Diene−Aldehyde Coupling: The Remarkable Effect of P(SiMe3)3. *J. Am. Chem. Soc.* **2010**, *132*, 7576−7577. (c) Ely, R. J.; Morken, J. P. Ni(0)-Catalyzed 1,4-Selective Diboration of Conjugated Dienes. *Org. Lett.* **2010**, *12*, 4348−4351. (d) Li, L.; Gong, T.; Lu, X.; Xiao, B.; Fu, Y. Nickel-catalyzed synthesis of 1,1-diborylalkanes from terminal alkenes. *Nat. Commun.* **2017**, *8*, 1−7.

(9) (a) Lillo, V.; Fructos, M. R.; Ramírez, J.; Braga, A. A. C.; Maseras, F.; Díaz-Requejo, M. M.; Pérez, P. J.; Fernández, E. A Valuable, Inexpensive CuI/N-Heterocyclic Carbene Catalyst for the Selective Diboration of Styrene. *Chem. - Eur. J.* **2007**, *13*, 2614−2621. (b) Lee, Y.; Jang, H.; Hoveyda, A. H. Vicinal Diboronates in High Enantiomeric Purity through Tandem Site-Selective NHC−Cu-Catalyzed Boron−Copper Additions to Terminal Alkynes. *J. Am. Chem. Soc.* **2009**, *131*, 18234−18235. (c) Moore, C. M.; Medina, C. R.; Cannamela, P. C.; McIntosh, M. L.; Ferber, C. J.; Roering, A. J.; Clark, T. B. Facile Formation of β-Hydroxyboronate Esters by a Cu-Catalyzed Diboration/Matteson Homologation Sequence. *Org. Lett.* **2014**, *16*, 6056−6059. (d) Yoshida, H.; Kawashima, S.; Takemoto, Y.; Okada, K.; Ohshita, J.; Takaki, K. Copper-Catalyzed Borylation Reactions of Alkynes and Arynes. *Angew. Chem., Int. Ed.* **2012**, *51*, 235−238.

(10) Ni and Fe-catalyzed carboboration reactions: (a) Nakagawa, N.; Hatakeyama, T.; Nakamura, M. Iron-Catalyzed Diboration and Carboboration of Alkynes. *Chem. - Eur. J.* **2015**, *21*, 4257−4261. (b) Daini, M.; Yamamoto, A.; Suginome, M. Nickel-Catalyzed Cyclizative trans-Carboboration of Alkynes through Activation of Boron−Chlorine Bonds by Using Organometallic Reagents as Donors of Organic Groups. *Asian J. Org. Chem.* **2013**, *2*, 968−976. (c) Suginome, M.; Shirakura, M.; Yamamoto, A. Nickel-Catalyzed Addition of Alkynylboranes to Alkynes. *J. Am. Chem. Soc.* **2006**, *128*, 14438−14439.

(11) (a) Kageyuki, I.; Osaka, I.; Takaki, K.; Yoshida, H. Copper-Catalyzed B(dan)-Installing Carboboration of Alkenes. *Org. Lett.* **2017**, *19*, 830−833. (b) Logan, K. M.; Smith, K. B.; Brown, M. K. Copper/Palladium Synergistic Catalysis for the syn- and anti-Selective Carboboration of Alkenes. *Angew. Chem., Int. Ed.* **2015**, *54*, 5228−5231. (c) Kageyuki, I.; Yoshida, H.; Takaki, K. Three-Component Carboboration of Alkenes under Copper Catalysis. *Synthesis* **2014**, *46*, 1924−1932. (d) Smith, K. B.; Logan, K. M.; You, W.; Brown, M. K. Alkene Carboboration Enabled by Synergistic Catalysis. *Chem. - Eur. J.* **2014**, *20*, 12032−12036. (e) Yoshida, H.; Kageyuki, I.; Takaki, K. Copper-Catalyzed Three-Component Carboboration of Alkynes and Alkenes. *Org. Lett.* **2013**, *15*, 952−955. (f) Alfaro, R.; Parra, A.; Alemán, J.; García-Ruano, J. L.; Tortosa, M. Copper(I)-Catalyzed Formal Carboboration of Alkynes: Synthesis of Tri- and Tetrasubstituted Vinylboronates. *J. Am. Chem. Soc.* **2012**, *134*, 15165−15168. (g) Daini, M.; Suginome, M. Palladium-catalyzed carboboration of alkynes using chloroborane and organozirconium reagents. *Chem. Commun.* **2008**, 5224−5226.

(12) A review: Buñuel, E.; Cárdenas, D. J. Borylative Cyclization Reactions. *Eur. J. Org. Chem.* **2016**, *2016*, 5446−5464.

(13) (a) Marco-Martínez, J.; López-Carrillo, V.; Buñuel, E.; Simancas, R.; Cárdenas, D. J. Pd-Catalyzed Borylative Cyclization of 1,6-Enynes. *J. Am. Chem. Soc.* **2007**, *129*, 1874−1875. (b) Pardo-Rodríguez, V.; Marco-Martínez, J.; Buñuel, E.; Cárdenas, D. J. Pd-Catalyzed Borylative Polycyclization of Enediynes to Allylboronates. *Org. Lett.* **2009**, *11*, 4548−4551. (c) Marco-Martínez, J.; Buñuel, E.; López-Duran, R.; Cárdenas, D. J. Pd-Catalyzed Borylative Polycyclization of Enediynes to Alkylboronates. *Chem. - Eur. J.* **2011**, *17*, 2734−2741. (d) Pardo-Rodríguez, V.; Buñuel, E.; Collado-Sanz, D.; Cárdenas, D. J. Pd-catalyzed borylative cyclisation of 1,7-enynes. *Chem. Commun.* **2012**, *48*, 10517−10519. (e) Marco-Martínez, J.; Buñuel, E.; Muñoz-Rodríguez, R.; Cárdenas, D. J. Pd-Catalyzed Borylative Polycyclization of Enediynes to Allylboronates. *Org. Lett.* **2008**, *10*, 3619−3621. (f) López-Durán, R.; Martos-Redruejo, A.; Buñuel, E.; Pardo-Rodríguez, V.; Cárdenas, D. J. Preparation of allylboronates by Pd-catalysed borylative cyclisation of dienynes. *Chem. Commun.* **2013**, *49*, 10691−10693.

(14) (a) Naidu, V. R.; Posevins, D.; Volla, C. M. R.; Bäckvall, J. E. Selective Cascade Reaction of Bisallenes via Palladium-Catalyzed Aerobic Oxidative Carbocyclization−Borylation and Aldehyde Trapping. *Angew. Chem., Int. Ed.* **2017**, *56*, 1590−1594. (b) Jiang, T.; Bartholomeyzik, T.; Mazuela, J.; Willersinn, J.; Bäckvall, J. E. Palladium(II)/Brønsted Acid-Catalyzed Enantioselective Oxidative Carbocyclization−Borylation of E.nallenes. *Angew. Chem., Int. Ed.* **2015**, *54*, 6024−6027. (c) Deng, Y.; Bartholomeyzik, T.; Bäckvall, J. E. Control of Selectivity in Palladium-Catalyzed Oxidative Carbocyclization/Borylation of Allenynes. *Angew. Chem., Int. Ed.* **2013**, *52*, 6283−6287. (d) Persson, A. K. Å.; Jiang, T.; Johnson, M. T.; Bäckvall, J. E. Palladium-Catalyzed Oxidative Borylative Carbocyclization of Enallenes. *Angew. Chem., Int. Ed.* **2011**, *50*, 6155−6159.

(15) (a) Xi, T.; Lu, Z. Cobalt-Catalyzed Ligand-Controlled Regioselective Hydroboration/Cyclization of 1,6-Enynes. *ACS Catal.* **2017**, *7*, 1181−1185. (b) Yu, S.; Wu, C.; Ge, S. Cobalt-Catalyzed Asymmetric Hydroboration/Cyclization of 1,6-Enynes with Pinacolborane. *J. Am. Chem. Soc.* **2017**, *139*, 6526−6529.

(16) (a) Cabrera-Lobera, N.; Rodríguez-Salamanca, P.; Nieto-Carmona, J. C.; Buñuel, E.; Cárdenas, D. J. Iron-Catalyzed Hydroborylative Cyclization of 1,6-Enynes. *Chem. - Eur. J.* **2018**, *24*, 784−788. (b) Buñuel, E.; Cárdenas, D. J. Towards Useful Boronates through Atom-Economical Catalyzed Cascade Reactions. *Chem. - Eur. J.* **2018**, *24*, 11239−11244.

(17) Cabrera-Lobera, N.; Quirós, M. T.; Buñuel, E.; Cárdenas, D. J. Novel Atom-Economical Regioselective Ni-Catalyzed Hydroborylative Cyclization of Enynes: Development and Mechanism. *Catal. Sci. Technol.* **2019**, *9*, 1021−1029.

(18) (a) Anderson, T. J.; Jones, G. D.; Vicic, D. A. Evidence for a NiI Active Species in the Catalytic Cross-Coupling of Alkyl Electrophiles. *J. Am. Chem. Soc.* **2004**, *126*, 8100−8101. Dinuclear Ni complexes: (b) Somerville, R. J.; Hale, L. V. A.; Gómez-Bengoa, E.; Burés, J.; Martín, R. Intermediacy of Ni−Ni Species in sp^2 C−O Bond Cleavage of Aryl Esters: Relevance in Catalytic C−Si Bond Formation. *J. Am. Chem. Soc.* **2018**, *140*, 8771−8780.

(19) (a) Radon, M. Revisiting the role of exact exchange in DFT spin-state energetics of transition metal complexes. *Phys. Chem. Chem. Phys.* **2014**, *16*, 14479−14488. (b) Coskun, D.; Jerome, S. V.; Friesner, R. A. Evaluation of the Performance of the B3LYP, PBE0, and M06 DFT Functionals, and DBLOC-Corrected Versions, in the Calculation of Redox Potentials and Spin Splittings for Transition Metal Containing Systems. *J. Chem. Theory Comput.* **2016**, *12*, 1121−1128.

DOI: 10.1021/acs.orglett.9b02485