Vanadium-Catalyzed Stereo- and Regioselective Hydroboration of Alkynes to Vinyl Boronates

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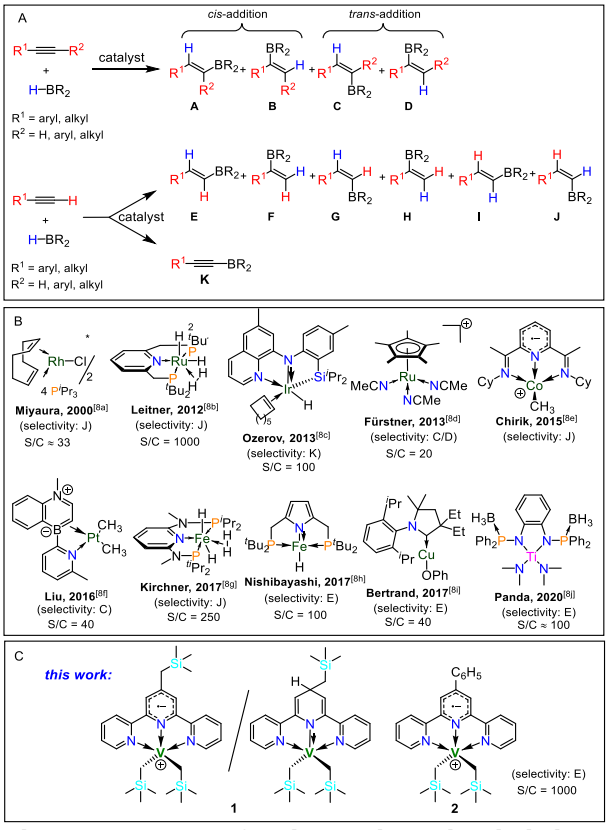
ABSTRACT: Molecular complexes of vanadium catalyze *cis*-selective *anti*-Markovnikov hydroboration of alkynes to generate vinyl boronate esters with appreciable turnover numbers of up to 4,000 at room temperature. This represents the first example of the use of vanadium in homogeneous catalytic hydroboration of alkynes. The method is tolerant to various functional groups, including C=C double bonds. Accordingly, 1-hexen-5-yne can be quantitatively and selectively reduced at the triple bond, leaving the double bond unaffected. Preliminary computational analysis of the catalytic cycle reveals both two-state reactivity and previously unknown complexity associated with the redox-active ligand. Specifically, it was found that the ligand can shuttle up to two electrons back-and-forth to and from the metal, which thus adapts three different oxidation states on the catalytic reaction coordinate.

KEYWORDS: Vanadium; Redox non-innocent ligand; Terpyridine; Hydroboration; Alkyne; Regioselectivity

Vinyl boronic esters (vinyl boronates) are versatile building blocks in organic synthesis.[1] Selected examples of their use include Suzuki–Miyaura couplings,[2] Chan–Lam couplings,[3] Petasis-borono Mannich reactions,[4] and Hayashi–Miyaura conjugate additions.[5] Multiple strategies have been developed for the synthesis of vinyl boronates.[1b] Among these methods, hydroboration of alkynes with mild and dry air-stable dialkoxyborane compounds such as Brown's catecholborane and the more robust Knochel's pinacolborane (HBpin) is of special importance.[6] Over the past decades, various uncatalyzed, base- and acid-catalyzed, and metal-catalyzed reactions have been reported for the stereo- and/or regioselective hydroboration of alkynes to vinyl boronates with these reagents.[6-7] The demands placed by the need to access boronate esters of many differing substitution patterns, stereochemistries and functional groups triggered the development of well-defined transition metal catalysts, selected examples of which are shown in Scheme 1A-B.[8] Here we report an example of stereo- and regioselective hydroboration of terminal and internal alkynes with HBpin leading to pinacol vinyl boronate esters catalyzed by well-defined vanadium (V) molecular complexes **1**–**2**,[9] illustrated in Scheme 1C (selectivity: E).

Vanadium is the 20th most abundant element in the Earth's crust and sixth most abundant among the transition metals.[10] Catalysis is the second largest application for V after its use as an additive to improve steel production. Vanadium has found several uses in catalytic homogeneous transformations, most often in oxidations.[11] In contrast, the applications of vanadium in catalytic reductions are extremely sparse. To the best of our knowledge, only four examples, with three involving H_2 as the reductant,[12] and one involving HBpin[9] have been reported



Scheme 1. A. Diversity of products in the catalytic hydroboration of internal and terminal alkynes. B. Selected examples of well-defined transition metal molecular catalysts for this reaction

(selectivity signifies preferential formation, S/C = substrate/catalyst ratio). *Structure of a possible active species is [RhH(Cl)(BR$_2$)(P^{i}Pr$_3$)$_2$].[14i] C. V catalysts in this work for stereo- and regioselective hydroboration of alkynes to vinyl boronates.[13]

Table 1. Reactivity Test for V-Catalyzed Hydroboration of Phenylacetylene with Pinacolborane to Afford 3a.[a]

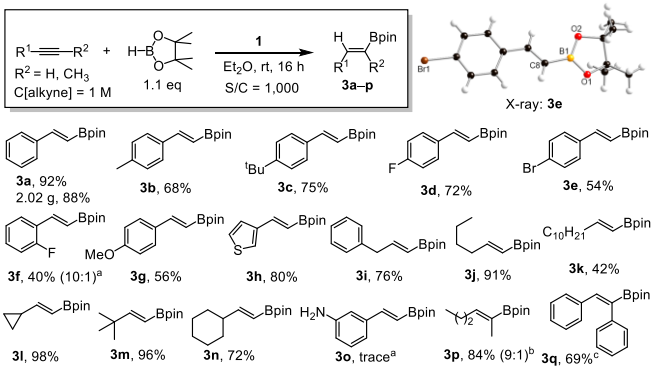
Entry	Catalyst	S/C	Solvent	Yield (%)[b]
1	None	-	Et_2O	trace
2	VCl_3/tpy	100	Et_2O	trace
3	**1**	100	Et_2O	94
4	**2**	100	Et_2O	88
5	**1**	100	THF	76
6	**1**	100	toluene	72
7	**1**	100	benzene	65
8	**1**	100	pentane	78
9	**1**	100	neat	80
10	**1**	200	Et_2O	94
11	**1**	1,000	Et_2O	92
12	**1**	10,000	Et_2O	35

[a]Conditions: phenylacetylene (1.0 mmol), pinacolborane (1.1 mmol) and solvent (1 mL), 25 °C, 16 h, N_2. [b]Determined by GC analysis with hexamethylbenzene as an internal standard. S/C: substrate-to-catalyst ratio.

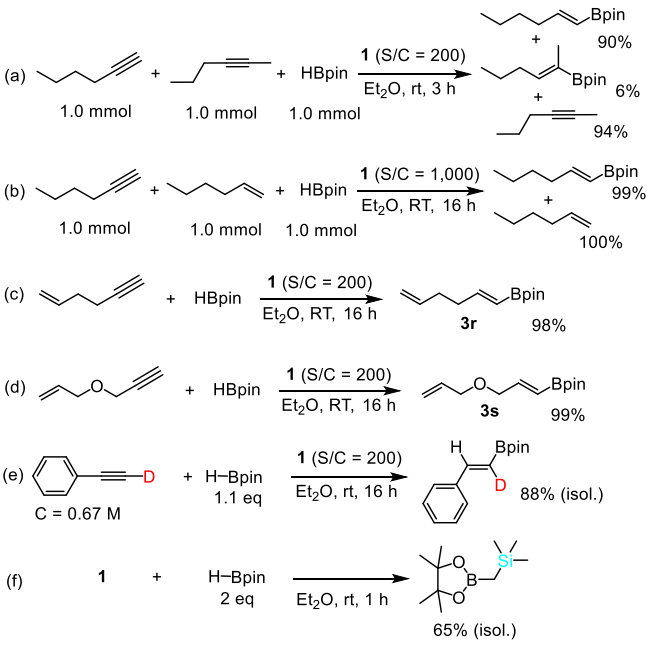
under homogeneous conditions. Developed at our laboratories, complexes **1–2**[9] are notable in the fact that they are supported by redox and/or chemically non-innocent ligands.[13] Molecular catalysis based on such ligands is an active field of study: such ligands might temporarily store electrons and/or participate in a catalytic reaction through bond cleavage/formation events, and both these properties might affect a catalytic reaction in several ways.[14]

Table 1 compares the catalytic efficiency of VCl_3/tpy (tpy = terpyridine) and complexes **1** and **2**, as well as complex **1** in some different solvents and under different substrate-to-catalyst ratios (S/C), in phenylacetylene hydroboration with HBpin. While the reaction barely occurs in the absence of a catalyst[7b] or with a VCl_3/tpy combination (entries 1–2, Table 1), both **1** and **2** catalyze the hydroboration of phenylacetylene with pinacolborane to give the corresponding *anti*-Markovnikov product **3a** (selectivity E as in Scheme 1A), with **1** producing slightly higher GC yields (S/C = 100, entries 3–4, Table 1). Solvent effect tests (entries 3, 5–9, Table 1) indicate that diethyl ether is the solvent of choice; additionally, this transformation has been achieved under neat conditions. The reaction can also proceed under higher S/C ratios of 200 and even 1,000, providing the product in >92% yield (entries 10 and 11, Table 1). Increasing the S/C ratio to 10,000 affords **3a** in 35% yield (entry 12), which increases to 40% after 45 h, after which remains unchanged (41% at 62 h). Thus, a turnover number (TON)[15] of ~4,000 (TON = S/C × (yield, %)/100) is achieved for this catalytic system prior to catalyst deactivation.

Scheme 2 provides further information on the substrate scope using precatalyst **1** under the optimized conditions (diethyl ether, rt, S/C = 1,000), including isolated yields and the X-ray structure of one of the products. Terminal aryl alkynes bearing electron-withdrawing or donating substituents are hydroborated with pinacolborane and **1**, affording the corresponding *anti*-Markovnikov *E*-vinylboronates **3b–g** in moderate to good isolated yields (54–75%), except for **3f**, which is obtained in 40% yield and is also



Scheme 2. The substrate scope of 1-catalyzed alkyne hydroboration with pinacolborane. Conditions: alkyne (1.0 mmol), pinacolborane (1.1 mmol), catalyst 1 (S/C = 1,000) and Et$_2$O (1 mL), room temperature, N$_2$, 16 h. Yields of isolated products. S/C: substrate-to-catalyst ratio. [a]Reaction run with S/C = 20. [b]Ratio of two *E*-regioisomers. [c]GC yield using hexamethylbenzene as an internal standard.

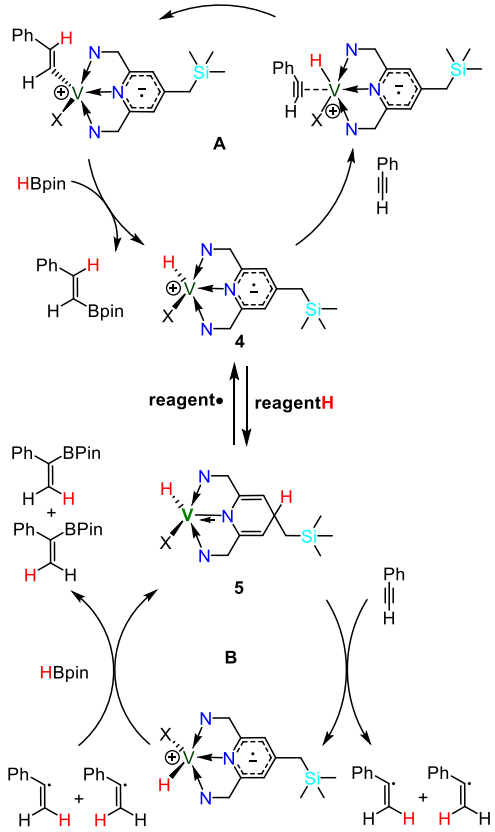


Scheme 3. (a) The competing hydroboration of 1-hexyne vs 2-hexyne, GC analysis against internal standard; (b) the competing hydroboration of 1-hexyne vs 1-hexene (issue of C≡C *vs.* C=C chemoselectivity), GC analysis against internal standard; (c–d) hydroboration of substrates containing both a double and triple bond (issue of intramolecular C≡C *vs.* C=C chemoselectivity), isolated yields are shown; (e) Deuterium-labeling experiment; (f) Isolation of pinBCH$_2$Si(CH$_3$)$_3$ from the stoichiometric reactions between 1 and 2 equiv. of HBpin.

contaminated by 10% of a regioisomer. Product **3e** was additionally characterized by X-ray diffraction, and the solid-state structure confirmed the identity of the product. Heterocyclic 3-ethynylthiophene and terminal aliphatic alkynes were hydroborated in the same stereo- and regioselective fashion, affording **3h** and **3i–3n** in better isolated yields of 80% and 72–98%, respectively, except for **3k**, which was obtained from 1-dodecyne in 42% yield. Alkynes containing an NH$_2$, NHR or OH groups were not suitable substrates for hydroboration, possibly because of the competing dehydrocoupling reaction or catalyst deactivation,[16] *e.g.* only traces of *anti*-Markovnikov *E*-vinylboronate **3o** were observed in the hydroboration of 3-ethynylaniline. Finally, internal alkynes, 2-hexyne and diphe-

nylacetylene, were hydroborated to give **3p** and **3q** in 84% isolated and 69% GC yields, respectively. In the former case, the product contains ~10% of the regioisomer. As a last point, gram-scale hydroboration of terminal alkynes was demonstrated with the example of phenylacetylene. Thus ~2g of the product **3a** was isolated in 88% yield from ~1g of the starting material (Scheme S1).

In the next step, we performed a series of catalytic and stoichiometric studies useful for analysis of the reaction selectivity and mechanism with precatalyst **1**, as shown in Scheme 3. The competing hydroboration of 1-hexyne *vs* 2-hexyne shows preferential hydroboration of the terminal alkyne (Scheme 3a), suggesting the importance of sterics in the rate-determining transition structure. The competing hydroboration of terminal C≡C *vs* C=C shows excellent (>99%) chemoselectivity in favor of the C≡C bond, in agreement with its higher



Scheme 4. Plausible catalytic cycles for the phenylacetylene hydroboration with pinacolborane catalyzed by vanadium molecular complexes supported by redox non-innocent (A) and chemically non-innocent (B) ligands. X = H or $CH_2Si(CH_3)_3$. The drawings for the 4′-$CH_2Si(CH_3)_3$-substituted terpyridine ligand are simplified for clarity. The operation of cycle A seems to be more probable, see discussion in the main text.

nucleophilicity (Scheme 3b–d). For example, products **3r** and **3s** were isolated in >98% yield from commercially available 1-hexen-5-yne and 3-(allyloxy)-1-propyne, respectively. The competitive hydroborations of terminal C≡C *vs* keto, ester, carboxamide and imine groups[9] were also performed, see Scheme S2. The following activity trend has been established: C=N (imino) << C(NHR)=O (amido) < C(OR)=O (ester) ~ C≡C << C=O (keto). Thus, reacting *N*-benzylideneaniline, phenylacetylene and HBpin in a 1:1:1 ratio affords **3a** in 88% GC yield. On the contrary, substituting the imine in this reaction with acetophenone affords **3a** in only 4% GC yield. A deuterium-labeling experiment, shown in Scheme 3e, confirms the *cis*-addition of pinacolborane to alkynes. The stoichiometric reactions between **1** and 5 equiv. of HBpin and/or phenylacetylene were not informative: NMR spectra were silent as expected from the open-shell nature of **1**,[9] while attempts to crystallize the reaction product are not currently successful in our hands. Reacting **1** and 2 equiv. of HBpin (diethyl ether, 1 h) afforded $pinBCH_2Si(CH_3)_3$ in ~65% isolated yield,[9] as shown in Scheme 3f. Isolation of $pinBCH_2Si(CH_3)_3$ in the reaction between **1** and HBpin suggests that vanadium monohydride and/or dihydride compounds could be relevant catalytic species, Scheme 4, complexes **4**–**5**.[7a]

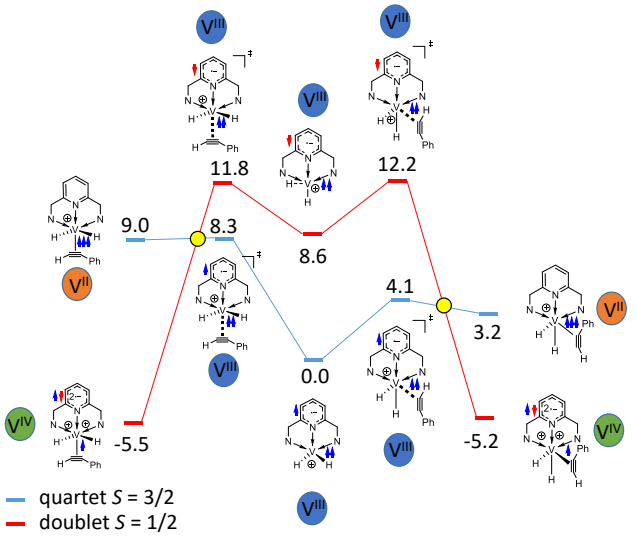


Figure 1. Computed by density functional theory free energy profiles in kcal·mol^{-1} for the first step of the catalytic cycle A (Scheme 4) taking place on quartet and doublet surfaces. Three different oxidation states for V are depicted in circles. The drawings for the 4′-$CH_2Si(CH_3)_3$-substituted terpyridine ligand are further simplified for clarity. Red arrows: α-spin electron. Blue arrows: β-spin electron. Yellow circles represent MECPs.

Catalyzed hydroboration may occur by an array of mechanisms.[7a] With respect to the unique nature of **1**,[13] two plausible catalytic cycles can be envisoned based on intermediary complexes **4** and **5** (Scheme 4). Catalytic cycle A is based on a redox non-innocent ligand, consistent with the observed *cis*-stereoselectivity and regioselectivity of the major final product (Scheme 4). On the contrary, plausible catalytic cycle B based on a chemically non-innocent ligand and radical character of the reaction could be arguably excluded based on predicted *trans*-stereoselectivity and/or opposite regioselectivity (Scheme 4).[17] The operation of cycle **A** is also consistent with the identity of **2**, a V complex supported by a redox non-innocent ligand.

As the last point, catalytic cycle **A**, if operative, might involve two-state reactivity.[18] Indeed, based on the electronic structure of catalyst precursors **1**–**2**,[9] one could imagine involvement of two spin surfaces with the total spin *S* of 3/2 and 1/2. Figure 1 shows free energy profiles computed by unrestricted and broken-symmetry density functional theory (DFT) for the first step of the catalytic cycle **A**, taking place on quartet and doublet surfaces (see SI for more details). Three important conclusions can be made from these calculations: 1) the reaction coordinate for phenylacetylene coordination on the metal starts on the quartet surface but ends on the doublet surface; 2) the minimum energy crossing point (MECP)[18d] for this hopping occurs after the transition state

region of triple bond coordination; 3) on each surface the oxidation state of the metal changes from +3 to +2 (quartet surface) or from +3 to +4 (doublet surface). Such a change in the oxidation state of the metal is possible due to additional one-electron oxidation or reduction (the ligand and metal can shuttle up to two electrons). Although hopping from one surface to another is the core phenomena in the context of two-state reactivity,[18] we note here that the ability to reversibly shuttle up to two electrons between the ligand and the metal as well as the possibility for ferro- or antiferromagnetic coupling between unpaired electrons localized in these domains to conserve total spin is a notable advance in undertstanding molecular catalysis based on redox non-innocent ligands. A detailed investigation of this effect as well as overall sophisticated catalytic reaction described here is warranted in the future.

In summary, this paper reports the first example of vanadium-catalyzed alkyne hydroboration to generate alkenylboronates in a *cis*-selective and *anti*-Markovnikov fashion, representing a rare application of well-defined low-valent vanadium complexes for reductive catalysis. Turnover numbers of up to 4,000 place this vanadium(III) catalyst among the most effective molecular catalysts for this reaction (up to 98% isolated yield under S/C = 1,000). Preliminary computational analysis of the catalytic cycle reveals both two-state reactivity and signifigantly underappreciated complexity associated with the redox-active ligand, which might accept up to two electrons or be completely regenerated to its initial form, leading to the change of of the oxidation state of the metal from +3 to +2 or +4, respectively.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interests.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.xxx. Detailed experimental procedures, characterization data, X-ray crystallographic data (CIF) and computational details (PDF).

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REFERENCES

1. (a) Armstrong, R. J.; Sandford, C.; García-Ruiz, C.; Aggarwal, V. K., Conjunctive functionalization of vinyl boronate complexes with electrophiles: a diastereoselective three-component coupling. *Chem. Commun.* **2017,** *53* (36), 4922-4925; (b) Carreras, J.; Caballero, A.; Pérez, P. J., Alkenyl Boronates: Synthesis and Applications. *Chem. Asian J.* **2019,** *14* (3), 329-343.

2. (a) Lennox, A. J. J.; Lloyd-Jones, G. C., Selection of boron reagents for Suzuki–Miyaura coupling. *Chem. Soc. Rev.* **2014,** *43* (1), 412-443; (b) Beletskaya, I. P.; Alonso, F.; Tyurin, V., The Suzuki-Miyaura reaction after the Nobel prize. *Coord. Chem. Rev.* **2019,** *385*, 137-173.

3. (a) Shade, R. E.; Hyde, A. M.; Olsen, J.-C.; Merlic, C. A., Copper-Promoted Coupling of Vinyl Boronates and Alcohols: A Mild Synthesis of Allyl Vinyl Ethers. *J. Am. Chem. Soc.* **2010,** *132* (4), 1202-1203; (b) Winternheimer, D. J.; Merlic, C. A., Alkoxydienes via Copper-Promoted Couplings: Utilizing an Alkyne Effect. *Org. Lett.* **2010,** *12* (11), 2508-2510.

4. Candeias, N. R.; Montalbano, F.; Cal, P. M. S. D.; Gois, P. M. P., Boronic Acids and Esters in the Petasis-Borono Mannich Multicomponent Reaction. *Chem. Rev.* **2010,** *110* (10), 6169-6193.

5. (a) Takaya, Y.; Ogasawara, M.; Hayashi, T., Rhodium-catalyzed asymmetric 1,4-addition of 2-alkenyl-1,3,2-benzodioxaboroles to α,β-unsaturated ketones. *Tetrahedron Lett.* **1998,** *39* (46), 8479-8482; (b) Takaya, Y.; Senda, T.; Kurushima, H.; Ogasawara, M.; Hayashi, T., Rhodium-catalyzed asymmetric 1,4-addition of arylboron reagents to α, β-unsaturated esters. *Tetrahedron: Asymmetry* **1999,** *10* (20), 4047-4056.

6. Rej, S.; Das, A.; Panda, T. K., Overview of Regioselective and Stereoselective Catalytic Hydroboration of Alkynes. *Adv. Synth. Catal.* **2021,** *363* (21), 4818-4840.

7. (a) Trost, B. M.; Ball, Z. T., Addition of Metalloid Hydrides to Alkynes: Hydrometallation with Boron, Silicon, and Tin. *Synthesis* **2005,** *2005* (06), 853-887; (b) Barbeyron, R.; Benedetti, E.; Cossy, J.; Vasseur, J.-J.; Arseniyadis, S.; Smietana, M., Recent developments in alkyne borylations. *Tetrahedron* **2014,** *70* (45), 8431-8452; (c) Stockland, R. A. J., Synthesis of Organoboronic Acids, Organoboronates, and Related Compounds. In *Practical Functional Group Synthesis*, John Wiley & Sons, Inc.: 2016.

8. (a) Ohmura, T.; Yamamoto, Y.; Miyaura, N., Rhodium- or Iridium-Catalyzed trans-Hydroboration of Terminal Alkynes, Giving (Z)-1-Alkenylboron Compounds. *J. Am. Chem. Soc.* **2000,** *122* (20), 4990-4991; (b) Gunanathan, C.; Hölscher, M.; Pan, F.; Leitner, W., Ruthenium Catalyzed Hydroboration of Terminal Alkynes to Z-Vinylboronates. *J. Am. Chem. Soc.* **2012,** *134* (35), 14349-14352; (c) Lee, C.-I.; Zhou, J.; Ozerov, O. V., Catalytic Dehydrogenative Borylation of Terminal Alkynes by a SiNN Pincer Complex of Iridium. *J. Am. Chem. Soc.* **2013,** *135* (9), 3560-3566; (d) Sundararaju, B.; Fürstner, A., A trans-Selective Hydroboration of Internal Alkynes. *Angew. Chem. Int. Ed.* **2013,** *52* (52), 14050-14054; (e) Obligacion, J. V.; Neely, J. M.; Yazdani, A. N.; Pappas, I.; Chirik, P. J., Cobalt Catalyzed Z-Selective Hydroboration of Terminal Alkynes and Elucidation of the Origin of Selectivity. *J. Am. Chem. Soc.* **2015,** *137* (18), 5855-5858; (f) Xu, S.; Zhang, Y.; Li, B.; Liu, S.-Y., Site-Selective and Stereoselective trans-Hydroboration of 1,3-Enynes Catalyzed by 1,4-Azaborine-Based Phosphine–Pd Complex. *J. Am. Chem. Soc.* **2016,** *138* (44), 14566-14569; (g) Gorgas, N.; Alves, L. G.; Stöger, B.; Martins, A. M.; Veiros, L. F.; Kirchner, K., Stable, Yet Highly Reactive Nonclassical Iron(II) Polyhydride Pincer Complexes: Z-Selective Dimerization and Hydroboration of Terminal Alkynes. *J. Am. Chem. Soc.* **2017,** *139* (24), 8130-8133; (h) Nakajima, K.; Kato, T.; Nishibayashi, Y., Hydroboration of Alkynes Catalyzed by Pyrrolide-Based PNP Pincer–Iron Complexes. *Org. Lett.* **2017,** *19* (16), 4323-4326; (i) Romero, E. A.; Jazzar, R.; Bertrand, G., (CAAC)CuX-catalyzed hydroboration of terminal alkynes with pinacolborane directed by the X-ligand. *J. Organomet. Chem* **2017,** *829*, 11-13; (j) Bhattacharjee, J.; Harinath, A.; Bano, K.; Panda, T. K., Highly Chemoselective Hydroboration of Alkynes and Nitriles Catalyzed by Group 4 Metal Amidophosphine–Borane Complexes. *ACS Omega* **2020,** *5* (3), 1595-1606.

9. Zhang, G.; Wu, J.; Zheng, S.; Neary, M. C.; Mao, J.; Flores, M.; Trovitch, R. J.; Dub, P. A., Redox-Noninnocent Ligand-Supported Vanadium Catalysts for the Chemoselective Reduction of C═X (X = O, N) Functionalities. *J. Am. Chem. Soc.* **2019,** *141* (38), 15230-15239.

10. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. Advanced Inorganic Chemistry, 6th ed.; John Wiley & Sons: New York, 1999.

11. (a) Langeslay, R. R.; Kaphan, D. M.; Marshall, C. L.; Stair, P. C.; Sattelberger, A. P.; Delferro, M., Catalytic Applications of Vanadium:

A Mechanistic Perspective. *Chem. Rev.* **2019,** *119* (4), 2128-2191; (b) Sutradhar, M.; Martins, L. M. D. R. S.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L., Vanadium complexes: Recent progress in oxidation catalysis. *Coord. Chem. Rev.* **2015,** *301-302*, 200-239; (c) Nomura, K.; Zhang, S., Design of Vanadium Complex Catalysts for Precise Olefin Polymerization. *Chem. Rev.* **2011,** *111* (3), 2342-2362.

12. (a) Pierre;, H. S. L.; Arnold;, J.; Toste, D. F., Z‐Selective Semihydrogenation of Alkynes Catalyzed by a Cationic Vanadium Bisimido Complex. *Angew. Chem. Int. Ed.* **2011,** *50* (17), 3900-3903; (b) Aharonian, G.; Gambarotta, S.; Yap, G. P. A., Oxidative Addition of a Dinuclear and Divalent Vanadium Hydride to an Olefin C−H Bond, Leading to Catalytic Hydrogenation. *Organometallics* **2001,** *20* (24), 5008-5010; (c) Sobota, P.; Jeżowska-Trzebiatowska, B.; Utko, J., Catalytic hydrogenation of olefins with the VCl_4–Mg–H_2 system in tetrahydrofuran. *React. Kinet. Catal L.* **1976,** *4* (1), 113-119.

13. Crystalline catalyst **1** represents a combination of two molecular species in a ~1:1 ratio, see Ref. [9].

14. (a) Dub, P. A.; Gordon, J. C., The role of the metal-bound N‐H functionality in Noyori-type molecular catalysts. *Nat. Rev. Chem.* **2018,** *2*, 396-408; (b) Dub, P. A.; Gordon, J. C., Metal‐Ligand Bifunctional Catalysis: The "Accepted" Mechanism, the Issue of Concertedness, and the Function of the Ligand in Catalytic Cycles Involving Hydrogen Atoms. *ACS Catal.* **2017,** *7* (10), 6635-6655; (c) de Bruin, B.; Gualco, P.; Paul, N. D., Redox Non-innocent Ligands. In *Ligand Design in Metal Chemistry*, Stradiotto, M.; Lundgren, R. J., Eds. John Wiley & Sons, Ltd: 2016; pp 176-204; (d) van der Vlugt, J. I., Chapter 28 - Advances in the Design and Application of Redox-Active and Reactive Pincer Ligands for Substrate Activation and Homogeneous Catalysis A2 - Morales-Morales, David. In *Pincer Compounds*, Morales-Morales, D., Ed. Elsevier: 2018; pp 599-621; (e) Berben, L. A.; de Bruin, B.; Heyduk, A. F., Non-innocent ligands. *Chem. Commun.* **2015,** *51* (9), 1553-1554; (f) Luca, O. R.; Crabtree, R. H., Redox-active ligands in catalysis. *Chem. Soc. Rev.* **2013,** *42* (4), 1440-1459; (g) Lyaskovskyy, V.; de Bruin, B., Redox Non-Innocent Ligands: Versatile New Tools to Control Catalytic Reactions. *ACS Catal.* **2012,** *2* (2), 270-279; (h) Caulton, K. G., Systematics and Future Projections Concerning Redox-Noninnocent Amide/Imine Ligands. *Eur. J. Inorg. Chem.* **2012,** *2012* (3), 435-443; (i) Hindson, K.; de Bruin, B., Cooperative & Redox Non-Innocent Ligands in Directing Organometallic Reactivity (Eur. J. Inorg. Chem. 3/2012). *Eur. J. Inorg. Chem.* **2012,** *2012* (3), 340-342; (j) Chirik, P. J., Preface: Forum on Redox-Active Ligands. *Inorg. Chem.* **2011,** *50* (20), 9737-9740; (k) Chirik, P. J.; Wieghardt, K., Radical Ligands Confer Nobility on Base-Metal Catalysts. *Science* **2010,** *327* (5967), 794-795; (l) Butin, K. P.; Beloglazkina, E., K.; Zyk, N., V., Metal complexes with non-innocent ligands. *Russian Chemical Reviews* **2005,** *74* (6), 531.

15. Kozuch, S.; Martin, J. M. L., "Turning Over" Definitions in Catalytic Cycles. *ACS Catal.* **2012,** *2* (12), 2787-2794.

16. Romero, E. A.; Peltier, J. L.; Jazzar, R.; Bertrand, G., Catalyst-free dehydrocoupling of amines, alcohols, and thiols with pinacol borane and 9-borabicyclononane (9-BBN). *Chem. Commun.* **2016,** *52* (69), 10563-10565.

17. Shimoi, M.; Watanabe, T.; Maeda, K.; Curran, D. P.; Taniguchi, T., Radical trans-Hydroboration of Alkynes with N-Heterocyclic Carbene Boranes. *Angew. Chem. Int. Ed.* **2018,** *57* (30), 9485-9490.

18. (a) Schröder, D.; Shaik, S.; Schwarz, H., Two-State Reactivity as a New Concept in Organometallic Chemistry. *Acc. Chem. Res.* **2000,** *33* (3), 139-145; (b) Shaik, S., Two-State Reactivity: Personal Recounting of its Conception and Future Prospects. *Isr. J. Chem.* **2020,** *60* (10-11), 938-956; (c) Dzik, W. I.; Böhmer, W.; de Bruin, B., Multiple Spin-State Scenarios in Organometallic Reactivity. In *Spin States in Biochemistry and Inorganic Chemistry*, 2015; pp 103-129; (d) Poli, R.; Harvey, J. N., Spin forbidden chemical reactions of transition metal compounds. New ideas and new computational challenges. *Chem. Soc. Rev.* **2003,** *32* (1), 1-8; (e) Poli, R., The elucidation of mechanisms in homogeneous catalysis. *Comments Inorg. Chem.* **2009,** *30* (5-6), 177-228; (f) Poli, R., 9.19 - Spin Crossover Reactivity. In *Comprehensive Inorganic Chemistry II (Second Edition)*, Reedijk, J.; Poeppelmeier, K., Eds. Elsevier: Amsterdam, 2013; pp 481-500.