ORGANOMETALLICS

Article

Cite This: *Organometallics* XXXX, XXX, XXX−XXX

pubs.acs.org/Organometallics

Sequential Transformation of Terminal Alkynes to 1,3-Dienes by a Cooperative Cobalt Pyridonate Catalyst

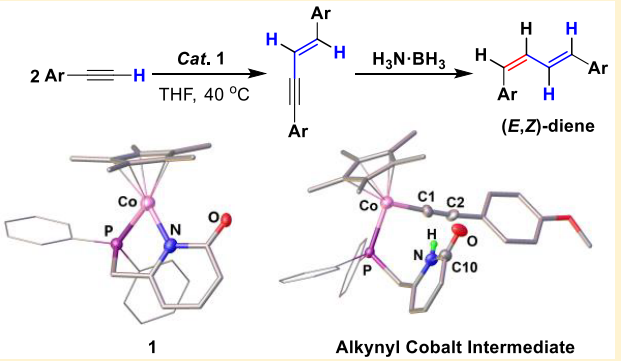
Xuewen Zhuang,[†] Jia-Yi Chen,[‡] Zhuoyi Yang,[†] Mengjing Jia,[†] Chengjuan Wu,[†] Rong-Zhen Liao,*[,‡] Chen-Ho Tung,[†] and Wenguang Wang*[,†]

[†]Key Lab of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, No. 27 South Shanda Road, Jinan 250100, People's Republic of China

[‡]School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, People's Republic of China

Supporting Information

ABSTRACT: We describe the cobalt(II) catalyst **1** bearing a phosphinopyridonate ligand for sequential transformation of aryl terminal alkynes to (*E*,*Z*)-1,3-dienes with excellent stereoselectivity. By cooperative metal−ligand reactivity, **1** reacts readily with the terminal alkynes to afford the alkynyl cobalt intermediate for dimerization, producing (*E*)-1,3-enynes, and then to smoothly catalyze reduction of the acetylene unit to the olefin by $H_3N{\cdot}BH_3$. A plausible catalytic cycle for both dimerization and transfer hydrogenation was proposed on the basis of stoichiometric reactions and DFT calculations, which suggest the ability of the cobalt catalyst to activate the amine−borane as well as the terminal alkyne through cobalt pyridonate cooperation.

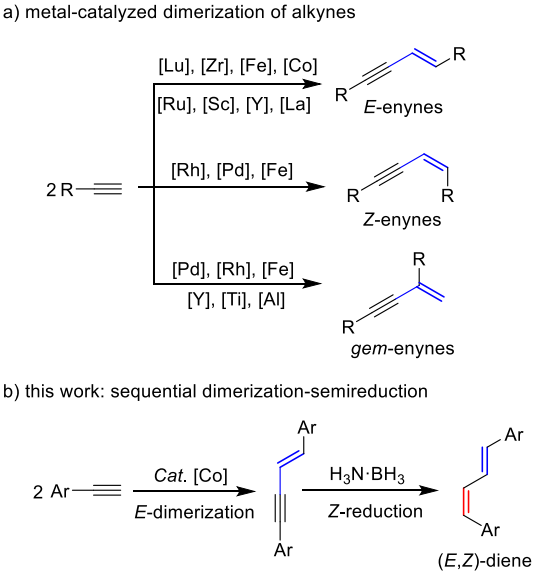


INTRODUCTION

Sequential catalysis combining two or multiple reactions in a single reaction vessel can generate the desired targets efficiently, obviating the need for purification at each step and meeting the demand for highly atom-economical and sustainable synthesis.[1] The research of sequential catalysis by a single catalyst is therefore important and of interest. Representative examples are Grubbs catalysts, which process sequential olefin metathesis and hydrogenation,[2] ring-closing metathesis and olefin isomerization,[3] and sequential alkene isomerization and oxidation.[4] Although interest has extended to base-metal catalysis,[5] sequential reactions performed by a single metal catalyst are sparse.[6,7]

1,3-Enynes are practically useful precursors in the synthesis of conjugated dienes by metal-catalyzed reductive coupling with various electrophiles.[8,9] The produced dienes also find widespread applications in organic synthesis such as Diels−Alder reactions,[10] and they are important structural motifs in many biologically active entities[11] and polymer materials.[12] Dimerization of two terminal alkynes is one of the most convenient methods to synthesize conjugated enynes.[13] Studies of this reaction were originally focused on the regioselective dimerization catalyzed by d-block and f-block metals to produce specific *Z*,[14] *E*,[15] or *gem* stereoisomers[16] (Scheme 1a). In particular, the related regioselective catalysis has been established for abundant metals, represented by the pincer iron(II) hydrides for *Z* dimerization,[17] a cyclic (alkyl)amino carbene iron catalyst for *E* dimerization,[18] and the piano-stool iron(II) catalysts featuring NHC ligands for the *gem* dimerization.[19] Sequential dimerization of terminal

Scheme 1. Metal-Catalyzed Formation of Enynes and Their Reduction to Dienes



Received: July 18, 2019

DOI: 10.1021/acs.organomet.9b00486
Organometallics XXXX, XXX, XXX−XXX

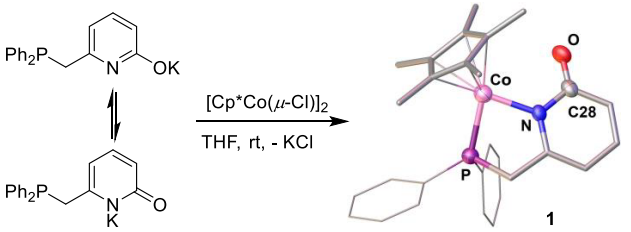
alkynes and partial reduction of the resultant 1,3-enynes could offer a new and straightforward synthetic route to access conjugated dienes (Scheme 1b). However, the challenge is to combine the regioselective dimerization with the chemoselective reduction of the acetylene unit in tandem using a *single* metal catalyst.[20]

Our group has been particularly interested in incorporating ligand reactivity in inexpensive metal catalysis for organic transformations.[21,22] With flexible binding modes of either an O or a N coordination,[23] the tautomeric 2-hydroxypyridine/2-pyridone[24] is rich with opportunities to design efficient metal catalysts for a proton-transfer reaction, hydrogenation, and transfer hydrogenation.[25] Here, we describe a phosphinopyridonate cobalt complex (**1**), which can activate aryl terminal alkynes for dimerization and, subsequently, catalytic reduction of 1,3-enyne to the (*E*,*Z*)-1,3-diene.

RESULTS AND DISCUSSION

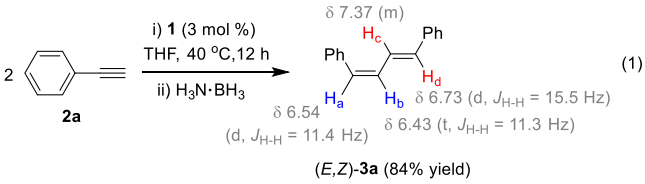
Synthesis and Characterization of Half-Sandwich Cobalt Complexes. Complex **1** was synthesized by the reaction of potassium diphenylphosphinopyridonate[26] with 0.5 equiv of $[Cp^*CoCl]_2$[27] in THF at room temperature (Scheme 2). The product isolated as a brown solid has a measured

Scheme 2. Synthesis and Solid-State Structure of 1



magnetic moment of 2.24 μ_B in benzene, consistent with a low-spin d^7 configuration.[28] A crystallographic analysis of **1** reveals that both P and N are coordinated to the metal center, forming a five-membered ring. The C−O distance of 1.248(3) Å in **1** is consistent with the reported values for phosphinopyridonate metal complexes.[26]

Transformation of Terminal Alkynes to Conjugated Dienes. Our studies began with the evaluation of activity of **1** in promotion of the dimerization of the simplest terminal aryl alkyne, phenylacetylene (**2a**), and subsequent reduction of the resulting 1,3-enyne to 1,4-diphenyl-1,3-dibutadiene (**3a**) by $H_3N{\cdot}BH_3$, which behaves as a convenient dihydrogen source for transfer hydrogenations.[29] A solution in THF of **2a** with 3 mol % of **1** was stirred at 40 °C to conduct the dimerization, which was followed by addition of solid $H_3N{\cdot}BH_3$ into the system. The progress of the reactions was monitored by GC-MS, which revealed full conversion of the substrate after 12 h. Analysis of the isolated product by ^1H NMR and ^1H−^1H COSY spectroscopy established the formation of **3a** in an (*E*,*Z*) configuration (eq 1). Synthesizing conjugated dienes

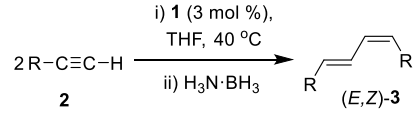


(1)

containing *cis* double bonds is challenging, because (*E*,*E*)-dienes are generally more thermodynamically favored than the (*E*,*Z*)-dienes.[30] For example, in the case of Ir-catalyzed dehydrogenative couplings of aryl olefin, (*E*,*Z*)-**3a** is formed as a minor product.[31] In contrast, our sequential catalysis with a single cobalt(II) catalyst produces the (*E*,*Z*)-product exclusively. Conversion of (*E*,*Z*)-**3a** to its stereoisomers was not observed in the reaction.

A series of conjugated (*E*,*Z*)-dienes were obtained by this sequential protocol (Table 1). Aryl alkenes with electron-

Table 1. Cobalt-Catalyzed Sequential Transformation of Aryl Alkynes to (*E*,*Z*)-1,3-Dienes[a]



R	conversion (%)[a]	product	yield (%)[b]
Ph (**2a**)	>99	**3a**	84
o-MeC_6H_4 (**2b**)	>99	**3b**	86
o-FC_6H_4 (**2c**)	>99	**3c**	80
m-MeC_6H_4 (**2d**)	>99	**3d**	84
m-FC_6H_4 (**2e**)	95	**3e**	73
m-ClC_6H_4 (**2f**)	95	**3f**	50
p-MeC_6H_4 (**2g**)	>99	**3g**	88
p-FC_6H_4 (**2h**)	>99	**3h**	84
p-$MeOC_6H_4$ (**2i**)	>99	**3i**	89
p-$F_3CC_6H_4$ (**2j**)	>99	**3j**	81[c]
p-^{t}BuC_6H_4 (**2k**)	>99	**3k**	87
3,5-$(CF_3)_2C_6H_4$ (**2l**)	90	**3l**	83[d]
2-naphthyl (**2m**)	>99	**3m**	91
3-thienyl (**2n**)	80	**3n**	63

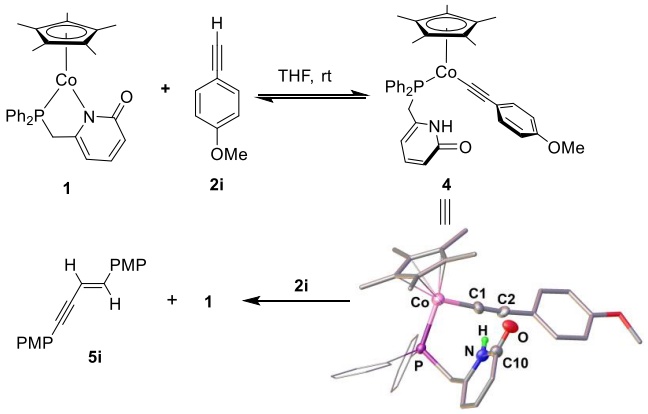
[a]Conditions unless specified otherwise: substrate (0.8 mmol), catalyst (3 mol %) in THF (1 mL) at 40 °C for 12 h, then $H_3N{\cdot}BH_3$ (0.8 mmol, 2 equiv) was added for 4 h. [b]Isolated yields are provided. [c]9% yields of *Z*,*Z* isomers were also isolated. [d]With 1 equiv of $H_3N{\cdot}BH_3$ at 0 °C.

donating or electron-withdrawing substituents such as a methyl (**2b**, **2d**, **2g**) or fluoro group (**2c**, **2e**, **2d**) on the phenyl ring, are compatible with the transformation and gave the corresponding (*E*,*Z*)-dienes with good yields. Synthesis of chloro-substituted diarylbutadienes was found to be somewhat difficult. The sequential transformation of **2f** led to formation of **3f** in 50% yield. Although the acidity of terminal alkynes is sensitive to the electronic nature of the substituent, both electron-rich and electron-deficient aromatic groups allow the alkyne to undergo dimerization−reduction under the present catalytic conditions, providing conjugated dienes such as **3g**−**k**. Interestingly, the reaction of *p*-trifluoromethylacetylene (**2j**) not only provides (*E*,*Z*)-product but also produces the (*Z*,*Z*)-isomer (9% yield) as a minor product. Further studies indicate that the production of the (*Z*,*Z*)-isomer arises from the hydrogenation of the (*Z*)-enyne product generated at the dimerization step, as is described below. Increasing the acidity of the alkyne appears to accelerate the reduction process. In the reaction of **2l**, the reduction can proceed to completion within 2 h at 0 °C to produce exclusively the (*E*,*Z*)-diene (**3l**) in 83% yield. This catalyst also displays excellent activity in transformation of alkynes with other aromatic groups such as thienyl and naphthyl groups (**2m**, **2n**), providing the corresponding (*E*,*Z*)-products in reasonable yields.

DOI: 10.1021/acs.organomet.9b00486
Organometallics XXXX, XXX, XXX−XXX

Dimerization of Aryl Alkynes. To gain mechanistic insight into the catalysis, we investigated the stoichiometric reaction of **1** with alkynes in the first step of the dimerization. By cooperative Co−N reactivity, **1** reacts readily with aryl alkynes to afford the alkynyl cobalt species. For instance, reaction of **1** with an equimolar quantity of **2i** ((PMP)C≡CH, in Scheme 3) was indicated by an instant color change from

Scheme 3. Dimerization of 2i by 1 Proceeding through an Alkynyl Cobalt Intermediate

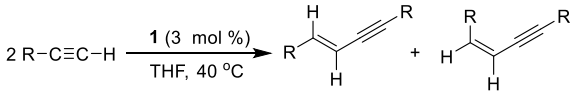


brown to deep green. Production of the alkynyl cobalt intermediate (**4**) was initially recognized from ESI-MS studies of the reaction solution. When (PMP)C≡CD was used, a peak at m/z 619.202 appeared, in comparison to m/z = 618.195 for **2i** with **1**.

Crystallographic analysis confirms that **4** is a 17-electron alkynyl cobalt(II) complex. The RC≡CH group in the structure is activated by the Co−N site, resulting in formation of the Co^{II}−C≡CR moiety with a detached pyridone group. The Co−C distance is 1.88(1) Å, about 0.08 Å shorter than that in Tp^{iPr2}Co−C≡C−R.[32] Since the C≡C length is not sensitive to the electronic effect of the substituents, the bond length of 1.19(1) Å in **4** is thought to be in accord with the mean value (ca. 1.20 Å) of alkynes.[33] In comparison to **1**, the C−O distance of 1.230(1) Å is slightly decreased, by 0.01 Å. In comparison to the ν_{CO} band at 1624 cm^{-1} observed for **1**, the IR spectrum of **4** appears as two bands for ν_{CO} in THF, one at 1624 cm^{-1} and the other at 1606 cm^{-1}, suggesting tautomerism of the detached pyridone group.[34] The C≡C stretching vibration for alkynyl cobalt(II) complexes is weak,[32] but the band at 2106 cm^{-1} is displayed.

As expected, the further reaction of **4** with **2i** provided a mixture of **4** with (PMP)C≡CD, suggesting that the organocobalt product is **1**. The isolated (*E*)-enyne product was identified by NMR spectroscopy and GC-MS analysis. On the basis of the ^{2}H NMR spectrum, the alkene protons at the enyne moiety were found to be partially labeled (Figure S9), indicating intermolecular H/D exchange between the pyridinone site of **4** and *d*-**2i** during the dimerization.

Table 2. Dimerization of Terminal Alkynes[a]

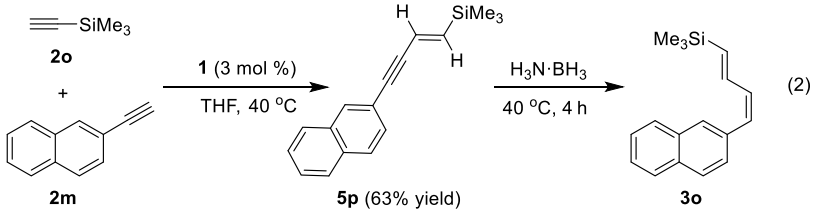


R	conversion (%)[a]	product	yield (%)[b] (*E*:*Z*)
Ph (**2a**)	>99	**5a**	96:0
o-MeC_6H_4 (**2b**)	>99	**5b**	93:0
o-FC_6H_4 (**2c**)	>99	**5c**	96:0
m-MeC_6H_4 (**2d**)	>99	**5d**	95:0
m-FC_6H_4 (**2e**)	93	**5e**	96:0
m-ClC_6H_4 (**2f**)	95	**5f**	88:5
p-MeC_6H_4 (**2g**)	>99	**5g**	95:0
p-FC_6H_4 (**2h**)	>99	**5h**	96:0
p-$MeOC_6H_4$ (**2i**)	>99	**5i**	98:0
p-$F_3CC_6H_4$ (**2j**)	>99	**5j**	86:11
p-^{t}BuC_6H_4 (**2k**)	>99	**5k**	93:0
3,5-$(CF_3)_2C_6H_4$ (**2l**)	87	**5l**	87:0
2-naphthyl (**2m**)	>99	**5m**	95:0
3-thienyl (**2n**)	73	**5n**	70:0
triethylsilyl (**2o**)	80	**5o**[c]	57:19

[a]Conditions unless specified otherwise: substrate (0.4 mmol), catalyst (3 mol %), in 0.5 mL of THF at 40 °C for 12 h. [b]The conversions and yields were determined by ^{1}H NMR analysis using tetraethylsilane as internal standard. [c]The reaction was carried out at 60 °C.

Indeed, the cobalt complex is capable of catalyzing the dimerization of alkynes without addition of an external base (Table 2). With 3 mol % of **1** in THF at 40 °C, **2a** dimerized to (*E*)-**5a** with an excellent yield. All of the alkyne substrates subjected to the sequential transformation were converted to the corresponding (*E*)-enynes in similar yields. Although the reaction for **2l** is comparably slower and delivered 87% conversion, only the (*E*)-enyne was formed. A larger scale preparation (510 mg, 92% yield) was conducted for **5m**, whose structure was confirmed crystallographically (Figure S31). In the dimerization of **2j**, both *E* and *Z* isomers of **5j** were detected with yields of 86% and 11%, respectively. A small amount of the *Z* isomer was also observed in the reaction of **2f**.

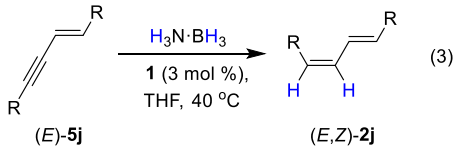
Although the catalytic dimerization performed by **1** has not been observed for common alkyl alkynes such as 1-hexyne and 1-butyne, the reaction of trimethylsilylacetylene (**2o**) at 60 °C for 48 h resulted in a 80% conversion, providing a mixture of dimerized products (*E*)-**5o** and (*Z*)-**5o** in a ratio of 57:19. Interestingly, the cobalt catalyst can perform selective cross-dimerization of **2o** with aryl terminal alkynes. For an instance, the reaction of **2m** with excess of **2o** (5 equiv) at 40 °C achieved cross-coupling to provide the desired enyne **5p** with 63% isolated yield (eq 2). Besides the cross-dimerized product, the 2-ethynylnaphthalene homodimerized product **5m** was isolated in 18% yield, whereas the formation of **5o** arisen from homocoupling of **2o** was not observed. With 3 mol % catalyst loading, further transformation of **5p** to the

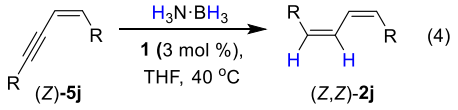


DOI: 10.1021/acs.organomet.9b00486
Organometallics XXXX, XXX, XXX−XXX

(*E*,*Z*)-diene by $H_3N{\cdot}BH_3$ underwent smoothly, giving **3o** nearly quantatively. Note that selective cross-dimerization is more challenging than the homodimerization.[17a,19] The present sequential dimerization-semireduction strategy provide a potential alternative approach to synthesize the conjugated vinylsilanes, which are valuable synthetic intermediates and found versatile applications in organic chemistry and material science.[35]

The stereochemical relationship between the 1,3-enyne and the corresponding 1,3-diene product provides mechanistic insight into this semireduction process. In the sequential transformation of **2j**, both (*E*,*Z*)- and (*Z*,*Z*)-dienes were obtained, and *Z* dimerization as well as *E* dimerization was observed in the initial homocoupling process. Examinations of the kinetics show that the interconversion of the *E* and *Z* isomers of **5j** is not possible and the ratio of (*E*,*Z*)- and (*Z*,*Z*)-**2j** is almost retained, at 86:11 during the reduction. The stereoisomers (*E*)-**5j** and (*Z*)-**5j** were isolated, and the subsequent reductions by $H_3N{\cdot}BH_3$ were conducted separately (eqs 3 and 4). It was found that the (*E*)-enyne was essentially





converted to (*E*,*Z*)-**2j** and the (*Z*)-enyne precursor was transformed only to the (*Z*,*Z*)-isomer. These results unambiguously show that the cobalt-catalyzed reduction of the acetylene unit proceeds through *cis* addition.

Mechanistic Insights. DFT calculations[36] were performed in an attempt to elucidate the mechanism of the entire reaction. Complex **1** is a 17-electron complex, and it was calculated to be agreeing with the established magnetic moment. The dimerization reaction is initiated by the formation of a catalyst−alkyne complex. The calculations showed that the triplet bond of the alkyne does not favor side-on coordination to Co, which would generate a 19-electron complex (Figure S17). Instead, the alkyne forms a hydrogen bond with the pyridonate oxygen atom (O−H distance of 1.97 Å at **Int1**). This is followed by a concerted metalation−deprotonation[37] reaction through **TS1**, generating a Co−alkyl intermediate (**Int2**, Figure 1), with the proton delivered to the pyridonate oxygen atom. This step has a barrier of 9.3 kcal/mol in the quartet state (21.2 kcal/mol in the doublet). Spin crossing from doublet to quartet is thus required during the reaction. During the formation of the Co−C bond, the pyridonate nitrogen atom dissociates from the Co center; therefore, **Int2** retains a 17-electron configuration. Tautomeric proton transfer from the pyridonate oxygen atom to the pyridonate nitrogen atom is almost barrierless (Figure S18). This results in the formation of **Int3**, which is 6.9 kcal/mol more stable than **Int2** and in line with the crystal structure of the alkynyl cobalt intermediate.

From **Int3**, the binding of the second alkyne molecule to form a 19-electron side-on coordinated Co−alkyne complex is not favorable. Instead, the alkynide migratory 1,2-insertion[38] into a second molecule of alkyne takes place from the van der Waals either to the terminal carbon of alkyne ($\mathbf{TS2_{B1}}$) or to the α-carbon of alkyne ($\mathbf{TS2_{B2}}$). The barriers for $\mathbf{TS2_{B1}}$ and $\mathbf{TS2_{B2}}$ were calculated to be 26.8 and 30.3 kcal/mol relative to **Int3** plus an alkyne molecule, suggesting that migratory insertion to the α-carbon is energetically less favorable. Finally, proton transfer from the NH to the alkene anion leads to the

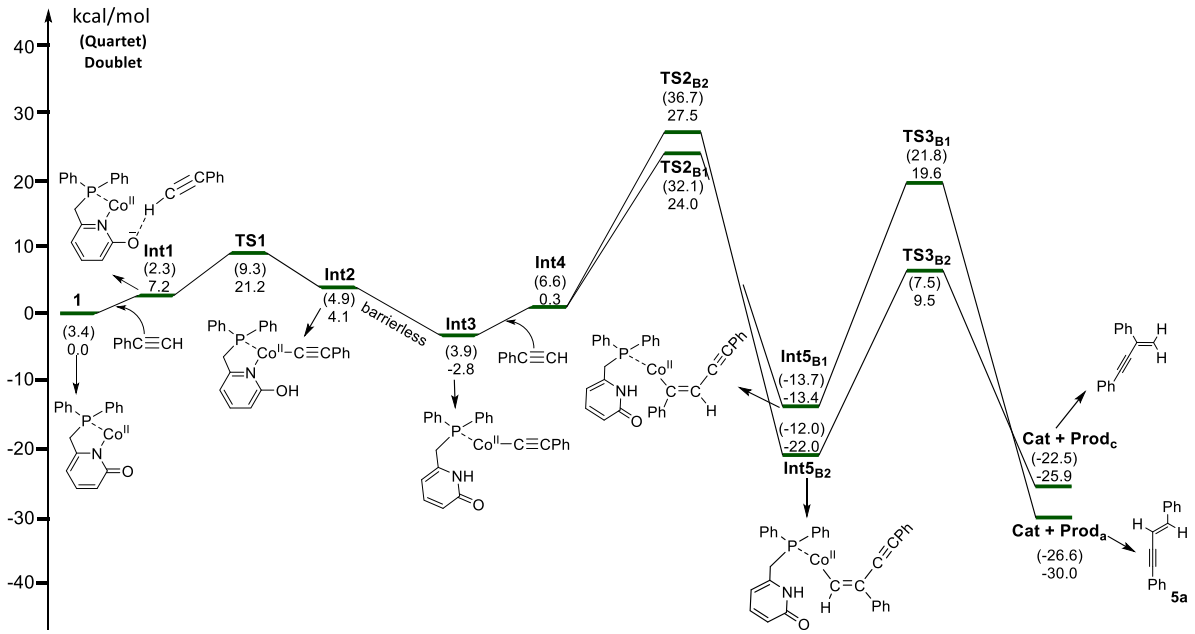


Figure 1. Gibbs free energy diagram at the M06-D3/SDD-6-311+G(2df,2p)//B3LYP-D3/SDD-6-31G(d,p) level (in kcal/mol) for the dimerization of phenylacetylene catalyzed by **1**. Schematic representations of all intermediates are shown. Energies in the quartet states are given in parentheses. Cp* is omitted for clarity. For optimized structures, see the Supporting Information.

DOI: 10.1021/acs.organomet.9b00486
Organometallics XXXX, XXX, XXX−XXX

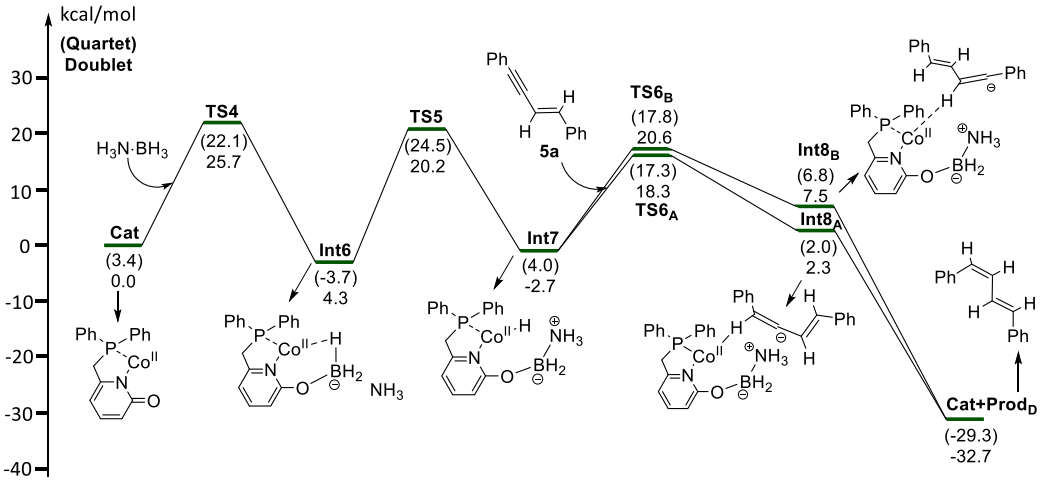


Figure 2. Gibbs free energy diagram at the M06-D3/SDD-6-311+G(2df,2p)//B3LYP-D3/SDD-6-31G(d,p) level (in kcal/mol) for the semireduction of 5a by $H_3N{\cdot}BH_3$ catalyzed by **1**. Schematic representations of all intermediates are shown. Energies in the quartet states are given in parentheses. Cp* is omitted for clarity. For optimized structures, see the Supporting Information.

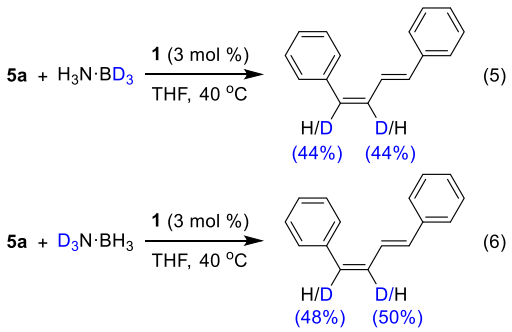
formation of the product and regeneration of the catalyst. **TS2** was calculated to be the turnover-limiting step with a total barrier of 26.8 kcal/mol using the M06-D3[39] functional, which can be considered as being in excellent agreement with the experimental condition. For steric reasons, the corresponding Markovnikov product is 5.1 kcal/mol higher in energy. Importantly, the total barrier for the formation of the Markovnikov product is 3.5 kcal/mol higher.

Catalyst **1** thus preferentially mediates the anti-Markovnikov addition of the alkynide to the alkyne. It should be pointed out that the B3LYP*-D3[40] functional (energy diagram shown in Figure S18) gave a total barrier of 29.8 kcal/mol, which is somewhat overestimated. Importantly, B3LYP*-D3 also favors the anti-Markovnikov addition pathway (29.8 kcal/mol vs 31.0 kcal/mol). Therefore, both reproduce the regioselectivity well. Other plausible pathways from **Int2** (alkynide migratory 1,2-insertion) and **Int4** (converted metalation and hydrogen atom transfer) have been considered (see Figure S19), but both were associated with higher barriers, ruling out their possibilities.

The reduction process was also calculated to involve four key steps (Figure 2). At the outset, **1** reacts with $H_3N{\cdot}BH_3$ via a nucleophilic attack of the pyridonate oxygen on the boron moiety (**TS4**), which is coupled with the coordination of one of the boron hydrides to the metal center. The barrier for this step was calculated to be 22.1 kcal/mol in the quartet state, and the resulting intermediate **Int6** lies at −3.7 kcal/mol relative to **1** plus $H_3N{\cdot}BH_3$. In the next step, the NH_3 molecule that is released performs a nucleophilic attack (**TS5**) on the boron moiety of **Int6**, leading to the formation of a critical Co−H intermediate (**Int7**). **TS5** was calculated to be 23.9 kcal/mol relative to **Int6**. Then, the substrate alkyne carbon could react with the Co−H moiety of **Int7** though a hydride transfer reaction.

The calculations showed that the hydride transfer to the α-C adjacent to the phenyl group ($\mathbf{TS6_A}$) is slightly more favorable than that to the β-C ($\mathbf{TS6_B}$), with a barrier difference of only 0.5 kcal/mol. The barriers for these two transition states are 21.0 and 21.5 kcal/mol, respectively, relative to **Int6** plus substrate. Owing to the small difference in the energy barrier, both pathways could compete with each other. This hydride transfer generates a transit ionic pair intermediate (**Int8**). Finally, the proton is delivered from the amino group to the substrate almost without a barrier, producing **3a**. The second step is calculated to be turnover limiting, with an energy barrier of 23.9 kcal/mol.

To verify the *Z*-reduction route, transfer hydrogenations of 1,3-enyne with deuterated amine boranes were performed. For instance, reduction of **5a** either by $H_3N{\cdot}BD_3$ or $D_3N{\cdot}BH_3$ produces deuterated-**3a** (eqs 5 and 6). ^2H NMR spectrum



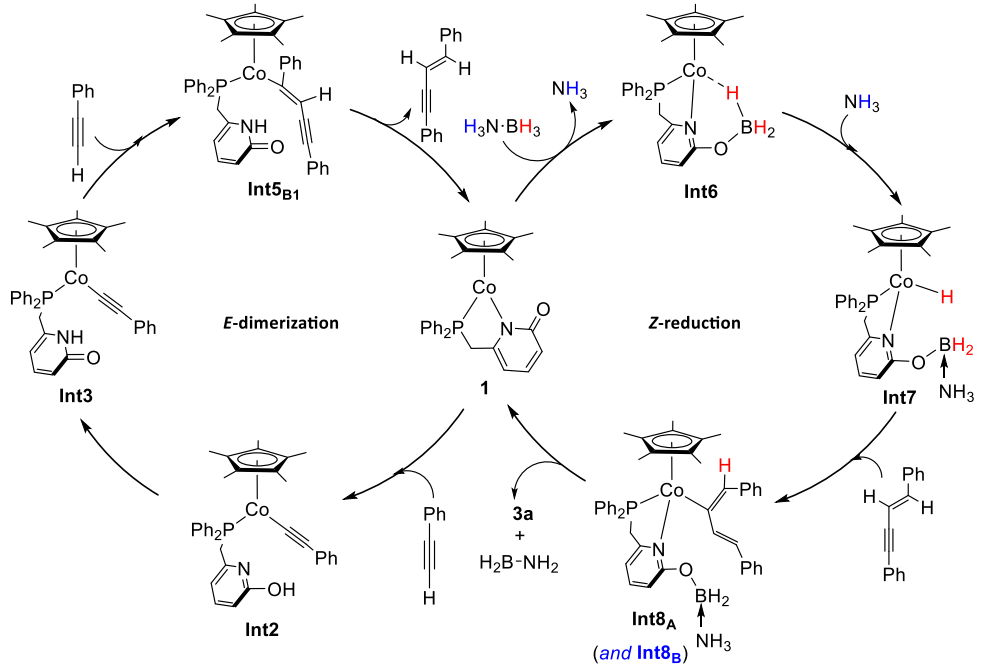
studies indicate that the D atom was added to both the α-carbon and β-carbon of the alkyne moiety for the reaction of **5a** with either $H_3N{\cdot}BD_3$ or $D_3N{\cdot}BH_3$. These results support the DFT predictions that the two pathways involving $\mathbf{Int8_A}$ and $\mathbf{Int8_B}$ compete with each other.

CONCLUSIONS

On the basis of experimental and calculated results, a catalytic cycle is proposed for the sequential dimerization−reduction of **2a** (Scheme 4). Complemented by the pyridonate site, our cobalt(II) complex is able to activate the terminal alkyne, affording the isolable alkynyl cobalt intermediate (**Int3**). The alkynide insertion into a second molecule of alkyne gives $\mathbf{Int5_{B1}}$. Subsequently, proton transfer from the NH to the alkene anion leads to the formation of the (*E*)-enyne product (**5a**) and regeneration of the catalyst. It was predicted that the cobalt catalyst reacts with $H_3N{\cdot}BH_3$ through cobalt−pyridonate cooperation (**Int6**), and the formation of the cobalt hydride intermediate (**Int7**) is thermodynamically favorable. The insertion of **5a** to the cobalt hydride **Int7** generates the intermediates $\mathbf{Int8_A}$ and $\mathbf{Int8_B}$, which are two

DOI: 10.1021/acs.organomet.9b00486
Organometallics XXXX, XXX, XXX−XXX

Scheme 4. Proposed Cycle for the Sequential Transformation of 2a to the (*E,Z*)-1,3-Diene on the Basis of Calculated Full Energy Diagrams



competing pathways. Finally, the proton delivery from the amino group to the substrate is essentially exergonic.

Through metal−ligand cooperation, the cobalt complex not only can activate the terminal alkyne for dimerization but also reacts with amine−borane for the subsequent transfer hydrogenation. Using a single cobalt catalyst, we realized the two distinct transformations in tandem to harvest 1,3-butadienes with excellent stereoselectivity. Such a sequential strategy portends the potential utility of inexpensive metals for these significant organic transformations.[41]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00486.

Experimental details, characterization of the products, crystallographic data, and computational details (PDF)

Accession Codes

CCDC 1893491−1893493 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, or 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 for R.-Z.L.: rongzhen@hust.edu.cn.
*E-mail for W.W.: wwg@sdu.edu.cn.

ORCID

Chengjuan Wu: 0000-0002-8552-2654
Rong-Zhen Liao: 0000-0002-8989-6928
Chen-Ho Tung: 0000-0001-9999-9755
Wenguang Wang: 0000-0002-4108-7865

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the National Natural Science Foundation of China (21871166, 21873031, and 91427303).

■ REFERENCES

(1) (a) Ajamian, A.; Gleason, J. L. Two Birds with One Metallic Stone: Single-Pot Catalysis of Fundamentally Different Transformations. *Angew. Chem., Int. Ed.* **2004**, *43*, 3754−3760. (b) Beligny, S.; Eibauer, S.; Maechling, S.; Blechert, S. Sequential catalysis: A Metathesis/Dihydroxylation Sequence. *Angew. Chem., Int. Ed.* **2006**, *45*, 1900−1903. (c) Zeng, X. Recent Advances in Catalytic Sequential Reactions Involving Hydroelement Addition to Carbon-Carbon Multiple Bonds. *Chem. Rev.* **2013**, *113*, 6864−6900. (d) Cai, Q.; Zhao, Z.-A.; You, S.-L. Asymmetric Construction of Polycyclic Indoles through Olefin Cross-Metathesis/Intramolecular Friedel-Crafts Alkylation under Sequential Catalysis. *Angew. Chem., Int. Ed.* **2009**, *48*, 7428−7431.

(2) Louie, J.; Bielawski, C. W.; Grubbs, R. H. Tandem Catalysis: The Sequential Mediation of Olefin Metathesis, Hydrogenation, and Hydrogen Transfer with Single-Component Ru Complexes. *J. Am. Chem. Soc.* **2001**, *123*, 11312−11313.

(3) Sutton, A. E.; Seigal, B. A.; Finnegan, D. F.; Snapper, M. L. New Tandem Catalysis: Preparation of Cyclic Enol Ethers through a Ruthenium-Catalyzed Ring-Closing Metathesis-Olefin Isomerization Sequence. *J. Am. Chem. Soc.* **2002**, *124*, 13390−13391.

(4) Liniger, M.; Liu, Y.; Stoltz, B. M. Sequential Ruthenium Catalysis for Olefin Isomerization and Oxidation: Application to the Synthesis of Unusual Amino Acids. *J. Am. Chem. Soc.* **2017**, *139*, 13944−13949.

(5) (a) Sonehara, T.; Murakami, S.; Yamazaki, S.; Kawatsura, M. Iron-Catalyzed Intermolecular Hydrothiolation of Internal Alkynes with Thiosalicylic Acids, and Sequential Intramolecular Cyclization Reaction. *Org. Lett.* **2017**, *19*, 4299−4302. (b) Lecomte, V.; Bolm, C. Iron (III)-Catalyzed Tandem Sequential Methanol Oxidation/Aldol Coupling. *Adv. Synth. Catal.* **2005**, *347*, 1666−1672.

DOI: 10.1021/acs.organomet.9b00486
Organometallics XXXX, XXX, XXX−XXX

(6) Guo, J.; Cheng, B.; Shen, X.; Lu, Z. Cobalt-Catalyzed Asymmetric Sequential Hydroboration/Hydrogenation of Internal Alkynes. *J. Am. Chem. Soc.* **2017**, *139*, 15316−15319.
(7) Guo, J.; Shen, X.; Lu, Z. Regio- and Enantioselective Cobalt-Catalyzed Sequential Hydrosilylation/Hydrogenation of Terminal Alkynes. *Angew. Chem., Int. Ed.* **2017**, *56*, 615−618.
(8) (a) Wessig, P.; Müller, G. The Dehydro-Diels-Alder Reaction. *Chem. Rev.* **2008**, *108*, 2051−2063. (b) Trost, B. M. Atom Economy-A Challenge for Organic Synthesis: Homogeneous Catalysis Leads the Way. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259−281.
(9) Shang, X.; Liu, Z.-Q. Transition Metal-Catalyzed C Vinyl-C Vinyl Bond Formation via Double C Vinyl-H Bond Activation. *Chem. Soc. Rev.* **2013**, *42*, 3253−3260.
(10) (a) Fringuelli, F.; Taticchi, A. *Dienes in the Diels-Alder Reaction*; Wiley: New York, 1990. (b) Winkler, J. D. Tandem Diels-Alder Cycloadditions in Organic Synthesis. *Chem. Rev.* **1996**, *96*, 167−176.
(11) Negishi, E.-i.; Wang, G. In *Science of Synthesis*; Jacobsen, E. N., Meijere, A. D., Eds.; Thieme: Stuttgart, Germany, 2010; Vol. *47*, pp 909−1016.
(12) Rappoport, Z. *The Chemistry of Dienes and Polyenes*; Wiley: Chichester, U.K., 1997 and 2001; Vols. *1* and *2*.
(13) Trost, B. M. The Atom Economy-A Search for Synthetic Efficiency. *Science* **1991**, *254*, 1471−1477.
(14) (a) Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. Novel Z-Selective Head-to-Head Dimerization of Terminal Alkynes Catalyzed by Lanthanide Half-Metallocene Complexes. *J. Am. Chem. Soc.* **2003**, *125*, 1184−1185. (b) Ge, S.; Meetsma, A.; Hessen, B. Scandium, Yttrium, and Lanthanum Benzyl and Alkynyl Complexes with the *N*-(2-pyrrolidin-1-ylethyl)-1, 4-diazepan-6-amido Ligand: Synthesis, Characterization, and Z-Selective Catalytic Linear Dimerization of Phenylacetylenes. *Organometallics* **2009**, *28*, 719−726. (c) Platel, R. H.; Schafer, L. L. Zirconium Catalyzed Alkyne Dimerization for Selective Z-enyne Synthesis. *Chem. Commun.* **2012**, *48*, 10609−10611. (d) Gorgas, N.; Stöger, B.; Veiros, L. F.; Kirchner, K. Complexes as Key Intermediates in the Catalytic Hydrofunctionalization of Terminal Alkynes. *ACS Catal.* **2018**, *8*, 7973−7982.
(15) (a) Rubina, M.; Gevorgyan, V. Can Agostic Interaction Affect Regiochemistry of Carbopalladation? Reverse Regioselectivity in the Palladium-Catalyzed Dimerization of Aryl Acetylenes. *J. Am. Chem. Soc.* **2001**, *123*, 11107−11108. (b) Lauer, M. G.; Headford, B. R.; Gobble, O. M.; Weyhaupt, M. B.; Gerlach, D. L.; Zeller, M.; Shaughnessy, K. H. A Trialkylphosphine-Derived Palladacycle as a Catalyst in the Selective Cross-Dimerization of Terminal Arylacetylenes with Terminal Propargyl Alcohols and Amides. *ACS Catal.* **2016**, *6*, 5834−5842. (c) Storey, C. M.; Gyton, M. R.; Andrew, R. E.; Chaplin, A. B. Terminal Alkyne Coupling Reactions Through a Ring: Mechanistic Insights and Regiochemical Switching. *Angew. Chem., Int. Ed.* **2018**, *57*, 12003−12006. (d) Xu, D.; Sun, Q.; Quan, Z.; Wang, X.; Sun, W. Cobalt-Catalyzed Dimerization and Homocoupling of Terminal Alkynes. *Asian J. Org. Chem.* **2018**, *7*, 155−159. (e) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. Ruthenium-Catalyzed Dimerization of Terminal Alkynes Initiated by a Neutral Vinylidene Complex. *Organometallics* **1996**, *15*, 5275−5277.
(16) (a) Trost, B. M.; Masters, J. T. Transition Metal-Catalyzed Couplings of Alkynes to 1, 3-enynes: Modern Methods and Synthetic Applications. *Chem. Soc. Rev.* **2016**, *45*, 2212−2238. (b) Korolev, A. V.; Guzei, I. A.; Jordan, R. F. Reactivity of Cationic Organoaluminum Aminotroponiminate Compounds with Unsaturated Substrates Formation of Dinuclear Dicationic Aluminum Complexes. *J. Am. Chem. Soc.* **1999**, *121*, 11605−11606. (c) Dash, A. K.; Eisen, M. S. Chemo-and Regioselective Dimerization of Terminal Alkynes Promoted by Methylaluminoxane. *Org. Lett.* **2000**, *2*, 737−740.
(17) (a) Rivada-Wheelaghan, O.; Chakraborty, S.; Shimon, L. J.; Ben-David, Y.; Milstein, D. *Z*-Selective (Cross-) Dimerization of Terminal Alkynes Catalyzed by an Iron Complex. *Angew. Chem., Int. Ed.* **2016**, *55*, 6942−6945. (b) 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*, 8130−8133.
(18) (a) Bhunia, M.; Sahoo, S. R.; Vijaykumar, G.; Adhikari, D.; Mandal, S. K. Cyclic (Alkyl) amino Carbene Based Iron Catalyst for Regioselective Dimerization of Terminal Arylalkynes. *Organometallics* **2016**, *35*, 3775−3780. (b) Grenier-Petel, J.; Collins, S. K. Photochemical Cobalt-Catalyzed Hydroalkynylation To Form 1,3-Enynes. *ACS Catal.* **2019**, *9*, 3213−3218.
(19) (a) Liang, Q.; Osten, K. M.; Song, D. Iron-Catalyzed gem-Specific Dimerization of Terminal Alkynes. *Angew. Chem., Int. Ed.* **2017**, *56*, 6317−6320. (b) Liang, Q.; Sheng, K.; Salmon, A.; Zhou, V. Y.; Song, D. Active Iron(II) Catalysts toward *gem*-Specific Dimerization of Terminal Alkynes. *ACS Catal.* **2019**, *9*, 810−818.
(20) Guthertz, A.; Leutzsch, M.; Wolf, L. M.; Gupta, P.; Rummelt, S. M.; Goddard, R.; Fares, C.; Thiel, W.; Fuerstner, A. Half-Sandwich Ruthenium Carbene Complexes Link trans-Hydrogenation and gem-Hydrogenation of Internal Alkynes. *J. Am. Chem. Soc.* **2018**, *140*, 3156−3169.
(21) (a) Liu, J.; Chen, J.; Jia, M.; Ming, B.; Jia, J.; Liao, R.-Z.; Tung, C.-H.; Wang, W. Ni-O Cooperation versus Nickel(II) Hydride in Catalytic Hydroboration of N-Heteroarenes. *ACS Catal.* **2019**, *9*, 3849−3857. (b) Yu, X.; Pang, M.; Zhang, S.; Hu, X.; Tung, C.-H.; Wang, W. Terminal Thiolate-Dominated H/D Exchanges and H_2 Release: Diiron Thiol−Hydride. *J. Am. Chem. Soc.* **2018**, *140*, 11454−11463. (c) Song, H.; Ye, K.; Geng, P.; Han, X.; Liao, R.; Tung, C. H.; Wang, W. Activation of Epoxides by a Cooperative Iron Thiolate Catalyst: Intermediacy of Ferrous Alkoxides in Catalytic Hydroboration. *ACS Catal.* **2017**, *7*, 7709−7717. (d) Zhang, F.; Song, H.; Zhuang, X.; Tung, C. H.; Wang, W. Iron-Catalyzed 1,2-Selective Hydroboration of N-Heteroarenes. *J. Am. Chem. Soc.* **2017**, *139*, 17775−17778.
(22) (a) Omann, L.; Königs, C. D. F.; Klare, H. F.; Oestreich, M. Cooperative Catalysis at Metal-Sulfur Bonds. *Acc. Chem. Res.* **2017**, *50*, 1258−1269. (b) Friedfeld, M. R.; Shevlin, M.; Margulieux, G. W.; Campeau, L.-C.; Chirik, P. J. Cobalt Precursors for High-Throughput Discovery of Base Metal Asymmetric Alkene Hydrogenation Catalysts. *Science* **2013**, *342*, 1076−1080. (c) Friedfeld, M. R.; Shevlin, M.; Margulieux, G. W.; Campeau; Chirik, P. J. Cobalt-Catalyzed Enantioselective Hydrogenation of Minimally Functionalized Alkenes: Isotopic Labeling Provides Insight into the Origin of Stereoselectivity and Alkene Insertion Preferences. *J. Am. Chem. Soc.* **2016**, *138*, 3314−3324. (d) Chakraborty, A.; Kinney, R. G.; Krause, J. A.; Guan, H. Cooperative Iron-Oxygen-Copper Catalysis in the Reduction of Benzaldehyde under Water-Gas Shift Reaction Conditions. *ACS Catal.* **2016**, *6*, 7855−7864. (e) Ryken, S. A.; Schafer, L. L. N,O-Chelating Four-Membered Metallacyclic Titanium(IV) Complexes for Atom-Economic Catalytic Reactions. *Acc. Chem. Res.* **2015**, *48*, 2576−2586.
(23) Drover, M. W.; Love, J. A.; Schafer, L. L. 1,3-N, O-Complexes of Late Transition Metals. Ligands with Flexible Bonding Modes and Reaction Profiles. *Chem. Soc. Rev.* **2017**, *46*, 2913−2940.
(24) Rawson, J. M.; Winpenny, R. E. P. The Coordination Chemistry of 2-Pyridone and Its Derivatives. *Coord. Chem. Rev.* **1995**, *139*, 313−374.
(25) (a) Royer, A. M.; Rauchfuss, T. B.; Gray, D. L. Organoiridium Pyridonates and Their Role in the Dehydrogenation of Alcohols. *Organometallics* **2010**, *29*, 6763−6768.
(26) (a) Sahoo, A. R.; Jiang, F.; Bruneau, C.; Sharma, G. V. M.; Suresh, S.; Roisnel, T.; Dorcet, V.; Achard, M. Phosphine-pyridonate Ligands Containing Octahedral Ruthenium Complexes: Access to Esters and Formic Acid. *Catal. Sci. Technol.* **2017**, *7*, 3492−3498. (b) Breit, B.; Seiche, W. Hydrogen Bonding as a Construction Element for Bidentate Donor Ligands in Homogeneous Catalysis: Regioselective Hydroformylation of Terminal Alkenes. *J. Am. Chem. Soc.* **2003**, *125*, 6608−6609. (c) Waloch, C.; Wieland, J.; Keller, M.; Breit, B. Self-assembly of Bidentate Ligands for Combinatorial Homogeneous Catalysis: Methanol-Stable Platforms Analogous to the Adenine-Thymine Base Pair. *Angew. Chem., Int. Ed.* **2007**, *46*, 3037−3039.

DOI: 10.1021/acs.organomet.9b00486
Organometallics XXXX, XXX, XXX−XXX

(27) Pang, M.; Wu, C.; Zhuang, X.; Zhang, F.; Su, M.; Tong, Q.; Tung, C.-H.; Wang, W. Addition of a B-H Bond across an Amido-Cobalt Bond: Co^{II}-H-Catalyzed Hydroboration of Olefins. *Organometallics* **2018**, *37*, 1462−1467.
(28) Fryzuk, M. D.; Leznoff, D. B.; Thompson, R. C.; Rettig, S. J. One-Electron Transformations of Paramagnetic Cobalt Complexes. Synthesis and Structure of Cobalt(II) Amidodiphosphine Halide and Alkyl Complexes and Their Reaction with Alkyl Halides. *J. Am. Chem. Soc.* **1998**, *120*, 10126−10135.
(29) (a) Brzozowska, A.; Azofra, L. M.; Zubar, V.; Atodiresei, I.; Cavallo, L.; Rueping, M.; El-Sepelgy, O. Highly Chemo- and Stereoselective Transfer Semihydrogenation of Alkynes Catalyzed by a Stable, Well-Defined Manganese(II) Complex. *ACS Catal.* **2018**, *8*, 4103−4109. (b) Ai, W.; Zhong, R.; Liu, X.; Liu, Q. Hydride Transfer Reactions Catalyzed by Cobalt Complexes. *Chem. Rev.* **2019**, *119*, 2876−2953.
(30) (a) Mcalpine, N. J.; Wang, L.; Carrow, B. P. A Diverted Aerobic Heck Reaction Enables Selective 1,3-Diene and 1,3,5-Triene Synthesis through C-C Bond Scission. *J. Am. Chem. Soc.* **2018**, *140*, 13634−13639. (b) Sun, Q.; Cai, L.; Ding, Y.; Xie, L.; Zhang, C.; Tan, Q.; Xu, W. Dehydrogenative Homocoupling of Terminal Alkenes on Copper Surfaces: A Route to Dienes. *Angew. Chem., Int. Ed.* **2015**, *54*, 4549−4552.
(31) Wilklow-Marnell, M.; Li, B.; Zhou, T.; Krogh-Jespersen, K.; Brennessel, W. W.; Emge, T. J.; Jones, W. D. Catalytic Dehydrogenative C-C Coupling by a Pincer-Ligated Iridium Complex. *J. Am. Chem. Soc.* **2017**, *139*, 8977−8989.
(32) Yoshimitsu, S. I.; Hikichi, S.; Akita, M. Synthesis and Characterization of Coordinatively Unsaturated Alkynyl-and Aryl-Cobalt Complexes with 15 Valence Electrons, Tp^{iPr2}Co-R, Bearing the Hydrotris(3,5-diisopropylpyrazolyl) borato Ligand (Tp^{iPr2}). *Organometallics* **2002**, *21*, 3762−3773.
(33) Smith, M. B. *March's Advanced Organic Chemistry*, 7th ed.; Wiley: Hoboken, NJ, 2013; Vol. *12*, p 823.
(34) Gellrich, U. Reversible Hydrogen Activation by a Pyridonate Borane Complex: Combining Frustrated Lewis Pair Reactivity with Boron-Ligand Cooperation. *Angew. Chem., Int. Ed.* **2018**, *57*, 4779−4782.
(35) (a) Langkopf, E.; Schinzer, D. Uses of Silicon-Containing Compounds in the Synthesis of Natural Products. *Chem. Rev.* **1995**, *95*, 1375−1408. (b) Fleming, I.; Barbero, A.; Walter, D. Stereochemical Control in Organic Synthesis Using Silicon-Containing Compounds. *Chem. Rev.* **1997**, *97*, 2063−2192.
(36) For computational details, see the Supporting Information.
(37) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. Analysis of the Concerted Metalation-Deprotonation Mechanism in Palladium-Catalyzed Direct Arylation Across a Broad Range of Aromatic Substrates. *J. Am. Chem. Soc.* **2008**, *130*, 10848−10849.
(38) (a) Yu, R. P.; Darmon, J. M.; Milsmann, C.; Margulieux, G. W.; Stieber, S. C. E.; DeBeer, S.; Chirik, P. J. Catalytic Hydrogenation Activity and Electronic Structure Determination of Bis(arylimidazol-2-ylidene)pyridine Cobalt Alkyl and Hydride Complexes. *J. Am. Chem. Soc.* **2013**, *135*, 13168−13184. (b) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. Catalytic Markovnikov and anti-Markovnikov Functionalization of Alkenes and Alkynes: Recent Developments and Trends. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368−3398.
(39) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215−241.
(40) (a) Reiher, M.; Salomon, O.; Hess, B. A. Reparameterization of hybrid functionals based on energy differences of states of different multiplicity. *Theor. Chem. Acc.* **2001**, *107*, 48−55. (b) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
(41) (a) Docherty, J. H.; Peng, J.; Dominey, A. P.; Thomas, S. P. Activation and Discovery of Earth-Abundant Metal Catalysts Using Sodium *tert*-Butoxide. *Nat. Chem.* **2017**, *9*, 595−600. (b) Ruddy, A. J.; Sydora, O. L.; Small, B. L.; Stradiotto, M.; Turculet, L. (N-Phosphinoamidinate) Cobalt-Catalyzed Hydroboration: Alkene Isomerization Affords Terminal Selectivity. *Chem. - Eur. J.* **2014**, *20*, 13918−13922. (c) Greenhalgh, M. D.; Thomas, S. P. Chemo-, Regio-, and Stereoselective Iron-Catalysed Hydroboration of Alkenes and Alkynes. *Chem. Commun.* **2013**, *49*, 11230−11232. (d) Ogawa, T.; Ruddy, A. J.; Sydora, O.; Stradiotto, L. M.; Turculet, L. Cobalt-and Iron-Catalyzed Isomerization−Hydroboration of Branched Alkenes: Terminal Hydroboration with Pinacolborane and 1,3,2-Diazaborolanes. *Organometallics* **2017**, *36*, 417−423.

DOI: 10.1021/acs.organomet.9b00486
Organometallics XXXX, XXX, XXX−XXX