Intercepting Hydrogen Evolution with Hydrogen-Atom Transfer: Electron-Initiated Hydrofunctionalization of Alkenes

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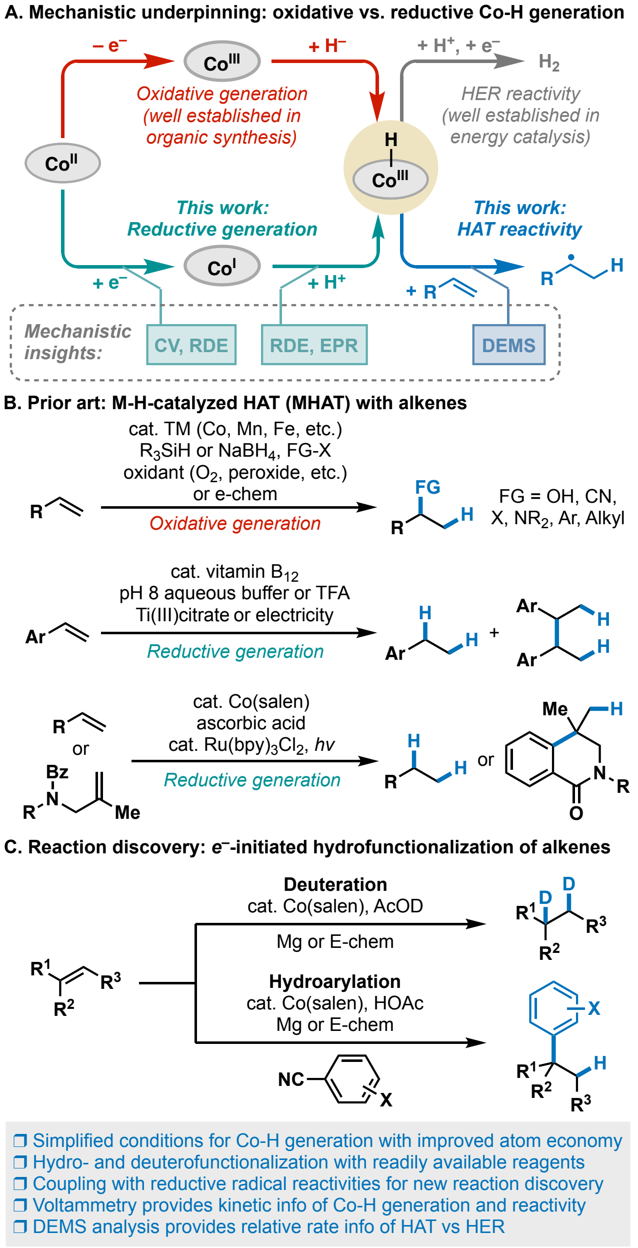
ABSTRACT: Hydrogen-atom transfer mediated by earth-abundant transition-metal hydrides (M-Hs) has emerged as a powerful tool in organic synthesis. Current methods to generate M-Hs most frequently rely on oxidatively initiated hydride transfer. Herein, we report a reductive approach to generate Co-H, which allows for canonical hydrogen evolution reactions to be intercepted by hydrogen-atom transfer to an alkene. Electroanalytical and spectroscopic studies provided mechanistic insights into the formation and reactivity of Co-H, which enabled the development of two new alkene hydrofunctionalization reactions.

Transition-metal hydrides (M-Hs) are a class of versatile organometallic intermediates that have found broad applications in energy storage,[1] materials chemistry,[2] and enzymatic catalysis.[3,4] In recent years, M-Hs have also seen increasing use in organic synthesis and catalysis, offering new bond disconnection strategies for accessing complex targets.[5,6] In particular, M-Hs based on earth-abundant first-row transition metals benefit from the relatively weak M-H bond and often display high reactivities with organic functional groups.[7] For example, transition metals such as Fe,[8] Mn,[9] and Co[10] have been shown to form M-Hs with predominantly acidic characters, which can engage in a variety of hydrogen atom transfer (HAT) reactions with alkenes. Importantly, the radical nature of the HAT mechanism renders such transformations compatible with a broad scope of functional groups, further augmenting their synthetic utility.[11]

In contrast to the increasing volume of reactions enabled by M-Hs, methods to generate them remain limited. Using Co^{III}-H as an example, its formation generally relies on the use of a pair of a stoichiometric single-electron oxidant and a hydride-donor reductant. The former oxidizes a precatalyst (typically Co^{II}) to a high valent Co^{III} species whereas the latter delivers a H^- (e.g., via transmetallation) to generate the active Co^{III}-H (Scheme 1A). Common oxidants include dioxygen, peroxides, and *N*-fluoropyridinium salts,[12] and common hydride sources include hydrosilanes, borohydrides, and isopropanol.[13] Having both oxidants and reductants could potentially complicate the reaction systems and hamper their adoption in process-scale applications. As a complementary approach, Norton showed that Co-H can be generated from cobaloximes in the context of radical cyclizations under a high pressure of H_2.[14] In the context of overall redox-neutral isomerization or polymerization reactions, the generation of Co-H has been achieved via HAT from an in-situ generated alkyl radical to Co^{II};[15] this mechanism however is not amenable to alkene difunctionalizations that are net-oxidative or net-reductive.

In searching for an alternative means for generating Co-H intermediates, we were inspired by the large body of work in the field of energy catalysis on hydrogen evolution reactions (HERs).[16] It has been well established that Co^{III}-H intermediates can form via a sequence of cathodic reduction and protonation in an acidic medium.[17] The incipient Co^{III}-H can then undergo either a heterolytic pathway (via sequential reduction and protonation of Co-H) or a homolytic pathway (via dimerization of Co-H) to evolve H_2 (Scheme 2A).[18] We reasoned that this electrochemically generated Co^{III}-H could be intercepted by a HAT pathway, reacting with an alkene to achieve hydrofunctionalization instead of hydrogen evolution. This reaction design would circumvent the use of traditional oxidants and hydride donors, leading to a potentially more practical methodology that employs electrons and protons as the redox equivalent and hydrogen source, respectively. Related to this strategy, Fischli,[19] van der Donk,[20] and Hisaeda[21] independently reported the hydrogenation and hydrodimerization of electron-deficient alkenes and styrenes using vitamin B_{12} by means of chemical or electrochemical reduction. Shenvi developed a simplified system for the hydrogenation of monosubstituted alkenes using catalytic $Co(OAc)_2$ and HCl.[22] Recently, Kojima and Matsunaga reported a dual cobalt-photoredox approach for the hydrogenation and intramolecular hydroarylation of alkenes (Scheme 1B).[23] Baran demonstrated electroreductive generation of Co^{III}-H in the context of alkyne hydrogenation, alkene isomerization, and related transformations.[24] Nevertheless, the exploration of such strategies in synthetic contexts remains rare beyond these examples.[25] In this work, we employed analytical and synthetic tools to study a family of electronically distinct Co(salen) complexes and obtained qualitative and quantitative insights into the electroreductive generation of Co^{III}-H and its reaction with alkenes (Scheme 1A). This information allowed us to establish reductive M-Hs formation as a general strategy for the hydrofunctionalization of alkenes (Scheme 1C).

Scheme 1. Background and introduction



❐ Simplified conditions for Co-H generation with improved atom economy
❐ Hydro- and deuterofunctionalization with readily available reagents
❐ Coupling with reductive radical reactivities for new reaction discovery
❐ Voltammetry provides kinetic info of Co-H generation and reactivity
❐ DEMS analysis provides relative rate info of HAT vs HER

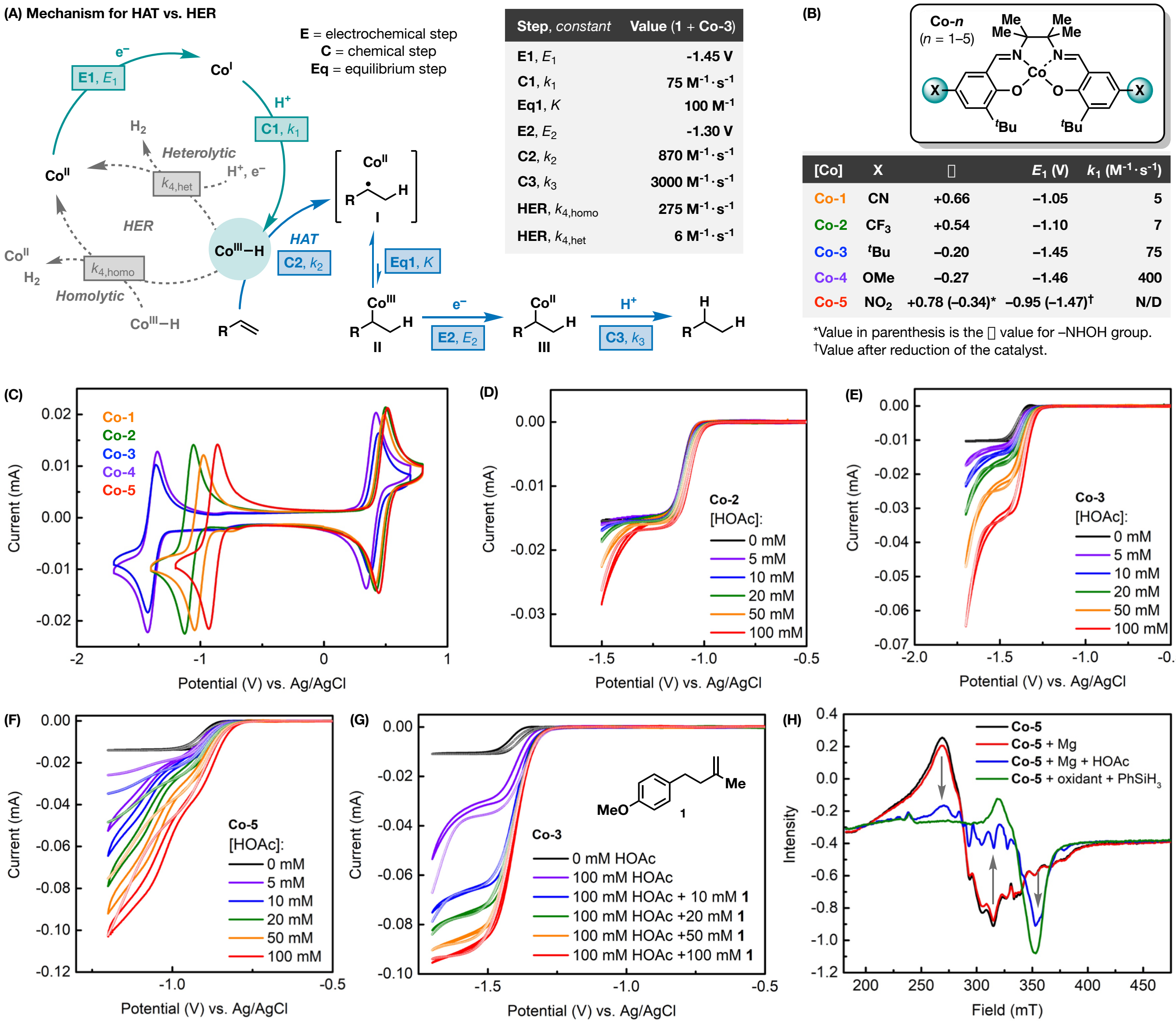
We began our study by characterizing five Co(salen) complexes using cyclic voltammetry (CV) and rotating disk electrode (RDE) voltammetry techniques,[26] which revealed a strong dependence of the HER reactivity on the electronic properties of the ligand (Scheme 2B–F). Cobalt complexes bearing electron-withdrawing groups (CF$_3$, CN) displayed sluggish HER in the presence of HOAc, whereas substantially faster rates were observed for catalysts with electron-donating groups (^{t}Bu, OMe), showing pronounced catalytic currents upon addition of HOAc. However, an electron-deficient nitro complex, **Co-5**, broke the trend, displaying the largest current enhancement. CV suggested that, in this case, the nitro group was preferentially reduced to an electron-rich substituent (likely hydroxylamino). Indeed, upon electrolysis of **Co-5** with HOAc, a new reduction feature appeared at –1.47 V (vs Ag/AgCl) while the original peak disappeared (see SI).

Quantitative kinetic data were obtained by simulation of the RDE data with DigiElch, taking into consideration both homolytic and heterolytic mechanisms for the generation of H_2 from Co-H (Scheme 2A).[19] Excellent fits were obtained, which yielded rate constants of Co$^{\text{III}}$-H formation of k_1 = 5 M^{-1}·s^{-1} and 7 M^{-1}·s^{-1} for **Co-1** and **Co-2**. In contrast, their electron-rich counterparts **Co-3** and **Co-4** yielded values of k_1 = 75 M^{-1}·s^{-1} and 400 M^{-1}·s^{-1}, respectively. In general, catalysts bearing electron-donating substituents (^{t}Bu, OMe) preferred the homolytic pathway for HER, whereas those bearing electron-withdrawing substituents (CN, CF$_3$) predominantly underwent heterolytic protonation. Curiously, fitting the data from **Co-5** to the general HER mechanisms proved challenging, which is consistent with the proposed -NO$_2$ reduction.

To compare Co-H generation via reductive and oxidative pathways, we conducted electron paramagnetic resonance (EPR) studies. The addition of Mg as a chemical reductant[27] to **Co-5** did not lead to any noticeable change to the characteristic EPR signals (Scheme 2H). Subsequent introduction of HOAc resulted in disappearance of Co$^{\text{II}}$ signals[28] and formation of new features over a 15-minute period. A similar set of features were also observed when **Co-5** was treated with 1-fluoro-2,4,6-trimethylpyridinium triflate as the oxidant along with PhSiH$_3$; conditions that are frequently employed to generate Co$^{\text{III}}$-H complexes for alkene hydrofunctionalization. While we cannot unambiguously assign these new features to specific intermediates, these results showed that similar Co species are generated from the reductive and oxidative pathways.

With mechanistic insights into the electroreductive Co-H generation, we began to test the hypothesis that the HER can be intercepted by an HAT toward alkene hydrofunctionalization. Thus, a series of RDE and differential electrochemical mass spectrometry (DEMS) experiments were carried out. The addition of alkene **1** to a solution of catalyst **Co-3** and HOAc led to a current enhancement, the magnitude of which increased with higher concentrations of **1** (Scheme 2G). Simulations of the voltammetry data showed excellent agreement with the proposed reaction mechanism (Scheme 2A) wherein the reductively generated Co$^{\text{III}}$-H (via **E1**, **C1** steps) reacts with the alkene via HAT to afford radical **I** and Co$^{\text{II}}$ (**C2** step). This radical cage pair is in equilibrium with cage-collapsed species **II** favoring the former (**Eq1** step).[29] In the absence of a radical trapping agent, **I** is further reduced to generate putative intermediate **III** (**E2** step),[30] and this latent carbanion undergoes final protonolysis to give the hydrogenated product (**C3** step). The rate constant of the HAT step (k_2 = 870 M^{-1}·s^{-1}) is 3 times that of the homolytic HER ($k_{4,\text{homo}}$= 275 M^{-1}·s^{-1}). We also simulated an alternative mechanism wherein radical **I** undergoes HAT with another equivalent of Co$^{\text{III}}$-H to complete hydrogenation but this scenario exhibited poor consistency with the RDE data (see SI). The kinetic preference of Co$^{\text{III}}$-H for HAT over HER provides a foundation for developing a silane-free alkene hydrofunctionalization.

Scheme 2. (A) Mechanism for HAT vs. HER and simulated reaction constants. (B) Key properties of Co catalysts. (C) CVs of Co catalysts. (D-F) RDE studies of **Co-2**, **Co-3**, and **Co-5** with HOAc. (G) RDE studies of **Co-3** with HOAc and alkene **1**. (H) EPR analysis of **Co-5**.



Step, *constant*	Value (1 + Co-3)
E1, E_1	-1.45 V
C1, k_1	75 $M^{-1}\cdot s^{-1}$
Eq1, K	100 M^{-1}
E2, E_2	-1.30 V
C2, k_2	870 $M^{-1}\cdot s^{-1}$
C3, k_3	3000 $M^{-1}\cdot s^{-1}$
HER, $k_{4,homo}$	275 $M^{-1}\cdot s^{-1}$
HER, $k_{4,het}$	6 $M^{-1}\cdot s^{-1}$

[Co]	X	▯	E_1 (V)	k_1 ($M^{-1}\cdot s^{-1}$)
Co-1	CN	+0.66	–1.05	5
Co-2	CF_3	+0.54	–1.10	7
Co-3	^{t}Bu	–0.20	–1.45	75
Co-4	OMe	–0.27	–1.46	400
Co-5	NO_2	+0.78 (–0.34)*	–0.95 (–1.47)†	N/D

*Value in parenthesis is the ▯ value for –NHOH group.
†Value after reduction of the catalyst.

The HAT activity of reductively generated Co-H was further studied using DEMS, which provides operando measurements of electrogenerated volatile products.[31] We measured the Faradaic current while monitoring H_2 formation in real time during electrolysis. When a solution of HOAc in DMA was electrolyzed, H_2 production was observed, and as expected, the rate of HER was further augmented when **Co-3** was present. Interestingly, when alkene **1** was added, the Faradaic current increased but the HER was nearly completely suppressed (Figure 1A). This result again shows that electrochemically generated Co^{III}-H preferentially reacts with the alkene.[32] Notably, alkanes were detected by mass spectrometer when volatile alkenes were used, providing direct evidence for alkene hydrogenation. We observed a dependence of the HAT vs. HER selectivity on the degree of substitution of the alkene (see SI), which is consistent with reported sensitivity of Co^{III}-H to steric profile of the substrate.[14c, 12b]

We employed DEMS to further evaluate the suitability of various Co catalysts in hydrofunctionalization reactions (Figure 1B-C). At a constant cell voltage of 1.0 V, **Co-3**, **Co-4**, and **Co-5** showed the highest steady state Faradaic current (i.e., HAT + HER current) and minimal HER current, and are thus predicted to be efficient catalysts. Notably, we observed a spike of high current in the first 10 s of electrolysis of **Co-5**, which likely corresponds to initial nitro reduction before reaching a steady current. In contrast, electron-deficient **Co-1** and **Co-2** displayed lower Faradaic current and poorer HAT vs. HER selectivity. We carried out additional DEMS experiments by sweeping the working electrode potential at 10 mV/s and obtained consistent results (Figure 1D-F).

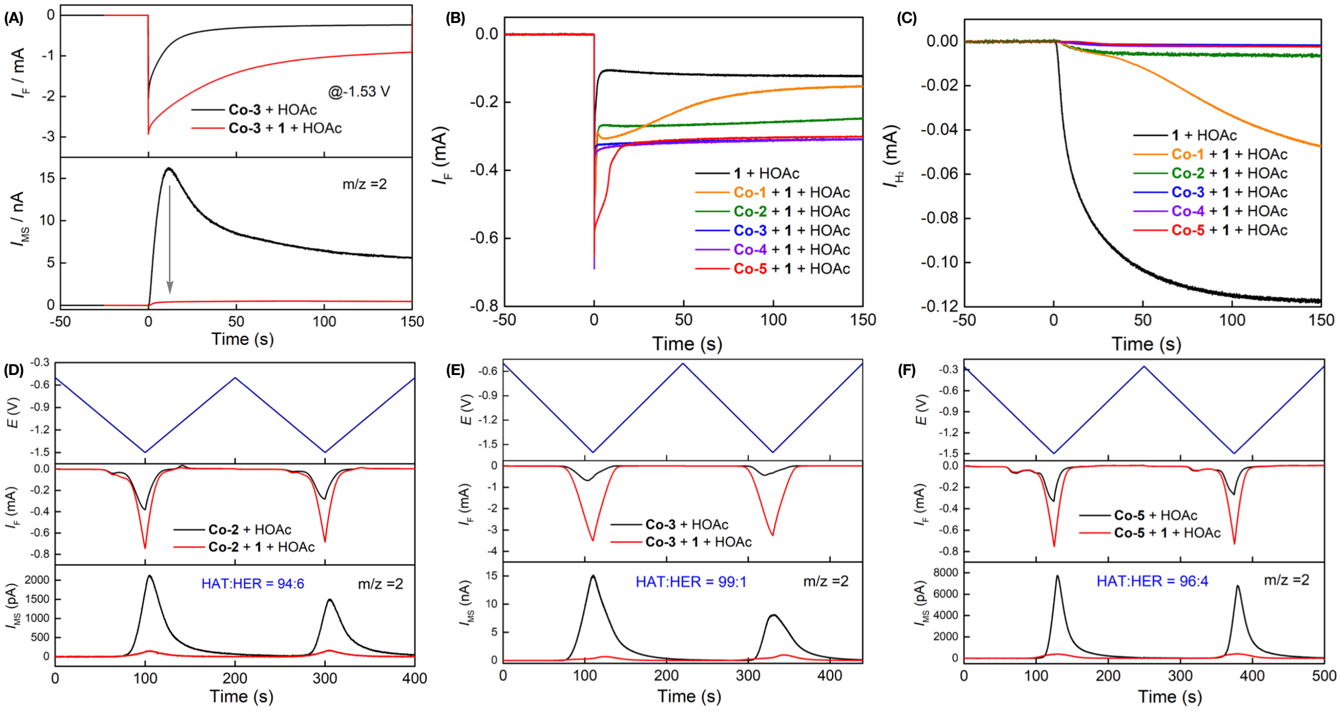
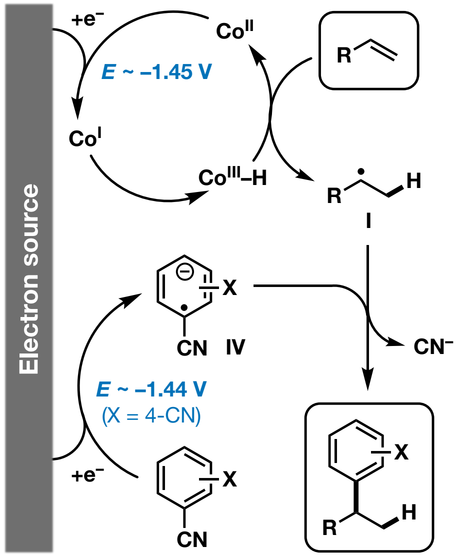


Figure 1. (A) DEMS studies of **Co-3** under controlled potential of -1.53 V vs Ag/AgCl. Comparison of Faradaic current (B) and hydrogen current (C) for various Co catalysts under constant cell voltage = 1.0 V. Comparison of HER and HAT selectivity for **Co-2** (D), **Co-3** (E) and **Co-5** (F) under sweeping potential.

The suite of analytical data provided the foundation for the development of alkene hydrofunctionalization via the reductive generation of Co-H. We first developed the deuteration of alkenes with readily available acetic acid-*d*$_4$ as the deuterium source and Mg as the terminal reductant (Table 1). Consistent with RDE and DEMS data, electron-rich catalysts gave superior efficiency with **Co-5** (presumably its reduced form) being the optimal. A series of unactivated and electronically activated alkenes were converted to corresponding products in generally good yields with high deuterium incorporation. As predicted by DEMS analysis, internal olefins are challenging substrates due to steric congestion. This procedure is more practical than canonical oxidatively initiated methods that would require elusive deuterosilanes or other deuterides.

This initial success prompted us to develop a new reaction with higher complexity. The ability to reductively generate Co^{III}-H in a synthetic context allows us to couple it with radical reactivities that are either unique to reductive chemistry or incompatible with previous hydride-based methods, thereby further expanding the scope of Co HAT chemistry. For example, we hypothesized that C-centered radical (**I**) formed upon HAT can be intercepted by a persistent radical such as reductively generated dicyanobenzene (DCB) radical anion (**IV**, X = CN; Scheme 3). The resultant anionic intermediate will undergo cyanide elimination to give an overall hydroarylation product. We note that alkene hydroarylation has previously been achieved using a dual Co-H/Ni catalytic strategy,[33] but that our reaction provides a distinct bond disconnection using cyanoarenes as coupling partners without needing a second catalyst.

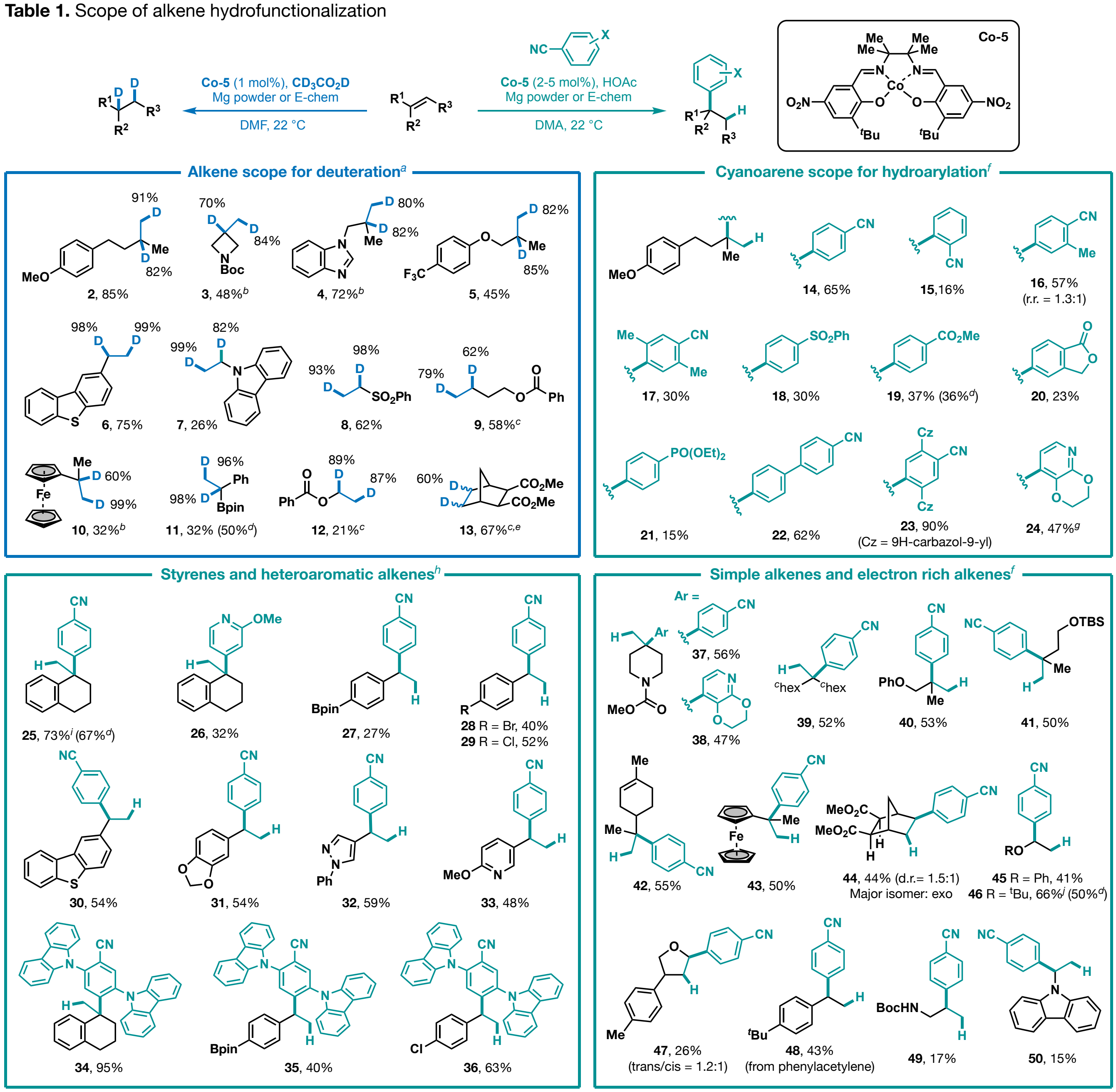
Scheme 3. Reaction design for hydroarylation of alkenes



Electron source = Mg powder or C cathode

Various cyanoarenes bearing sulfone, ester, lactone, and phosphonate groups were transformed into the corresponding products in moderate to good yields. Carbazole-substituted dicyanobenzene afforded desired products (**23**, **34**–**36**) in excellent yield, which provides a new way to functionalize this class of photoactive molecules.[34] Importantly, cyanopyridines can also participate in the hydroarylation with different types of alkenes (**24**, **26**, **38**).[35]

Table 1. Scope of alkene hydrofunctionalization



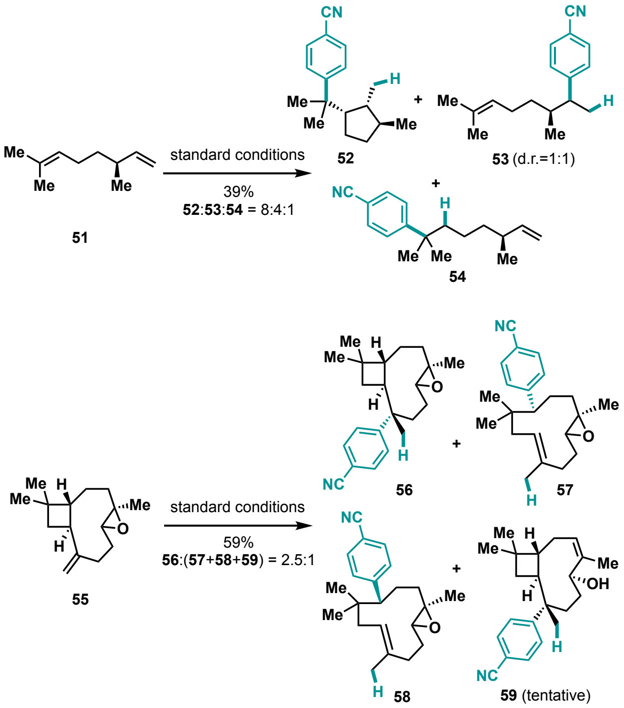
[a] Alkene (0.2 mmol,1 equiv), Mg powder (5 equiv), acetic acid-*d4* (8.8 equiv), **Co-5** (1 mol%), DMF (0.1 M in respect to alkene). The deuterium incorporation was determined by ^{1}H NMR and ^{2}H NMR. [b] Mg powder (10 equiv), acetic acid-*d4* (8.8 equiv), **Co-5** (2 mol%). [c] Mg powder (10 equiv), acetic acid-*d4* (8.8 equiv), **Co-5** (5 mol%). [d] Using electrochemical condition, see SI for details. [e] Two different types of D were observed, see SI for stereochemistry assignment. [f] Alkene (0.5 mmol, 1 equiv), cyanoarene (2 equiv), Mg powder (5 equiv), HOAc (22.0 equiv), **Co-5** (5 mol%), DMA (0.1 M in respect to alkene). [g] Structrually similar **s39** was used as alkene, see SI. [h] Alkene (0.5 mmol, 1 equiv), 1,4-dicyanoarene (1.5 equiv), Mg powder (5 equiv), HOAc (8.8 equiv), **Co-5** (2 mol%), DMA (0.1 M in respect to alkene). [i] Using DMF:MeCN (9:1) instead of DMA. [j] 1,4-Dicyanobenzene was used as the limiting reagent.

Various substituted styrenes (**25–29**, **34–36**) and heteroaromatic alkenes (**30–33**) proved to be viable substrates. Notably, functional groups such as aryl halides (**28**, **29**, **36**) and Bpin (**27**, **35**) were compatible in the reaction, which may cause catalyst promiscuity in transition-metal-catalyzed systems. 1,1-disubstituted alkenes (**37–43**) were successfully transformed to hydroarylated products featuring quaternary carbon centers. Limonene (**42**) was exclusively functionalized at the terminal alkene over the internal C=C. A norbornene analogue (**44**), vinyl ether derivatives (**45–47**) and phenylacetylene (**48**) were all converted to corresponding products, the latter of which underwent hydrogenation-hydroarylation to provide a saturated product. Finally, *N*-Boc allylamine (**49**) and vinylcarbazole (**50**) were also suitable substrates albeit giving diminished yields.

Finally, we demonstrated both deuteration and hydroarylation reactions using electrochemistry, providing comparable and sometimes higher efficiency (e.g., **11**, **19**, **25**, **46**, see SI for details). Further study of this electrochemical system will lead to improved procedures that are amenable to practical synthesis at scale.[24] We then surveyed substrates that provided additional mechanistic insights (Scheme 4).

With citronellene (**51**), the overall selectivity between the trisubstituted alkene and terminal alkene is about 1:12, which is consistent with sensitivity of Co-H to the sterics of the alkene. Radical cyclization (**52**) was observed as the major product as a single diastereomer, which indicates that the rate of arylation via radical-radical anion cross-coupling is smaller than but comparable to that of the 5-*exo*-trig radical clock ($k \sim 3 \times 10^{4}\ \mathrm{s}^{-1}$ to $10^{5}\ \mathrm{s}^{-1}$).[36a] In the case of (−)-caryophyllene oxide (**55**), direct hydroarylated product (**56**) and ring-opened products (**57** and **58**)[37] were obtained in a ratio of 2.5:1, which shows that the arylation is faster than radical-triggered ring opening of cyclobutane ($k \sim 4 \times 10^{3}\ \mathrm{s}^{-1}$).[29c,36a] These results are consistent with a proposed radical mechanism and provide an estimation of the rate constant for C–C bond formation to be $k_{\mathrm{obs}} = k[\mathrm{DCB}^{\bullet -}] \sim 10^{4}\ \mathrm{M}^{-1}\cdot\mathrm{s}^{-1}$.[36b,c]

Scheme 4. Mechanistic probe substrates



In conclusion, we developed a reductive strategy for the generation of Co-H species from readily available acetic acid and demonstrated its application in the deuteration and hydroarylation of alkenes. The reaction development was guided by systematic spectroscopic and electroanalytical investigations, which provided qualitative and quantitative information about the formation, identity, and reactivity of Co-H. We will continue to explore this catalytic strategy in other synthetically useful reaction systems.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.
Experimental procedures and characterization data

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Notes

Any additional relevant notes should be placed here.

ACKNOWLEDGMENT

This work was supported by the NSF (CHE-2055451 to S.L. and CHE-2002158 to H.D.A.). This study made use of the Cornell University NMR facility supported by the National Science Foundation (CHE-1531632). We thank Dr. Ivan Keresztes for NMR data collection and analysis. We thank Dr. Alex L. Lai for EPR data collection and analysis.

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37. The relative stereochemistry of **57** and **58** were assigned based on computed conformer of the 11-membered ring and ROESY NMR. Due to low concentration of **59**, the absolute stereochemistry was speculative.

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