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High-Activity Cobalt Catalysts for Alkene Hydroboration with Electronically Responsive Terpyridine and α-Diimine Ligands

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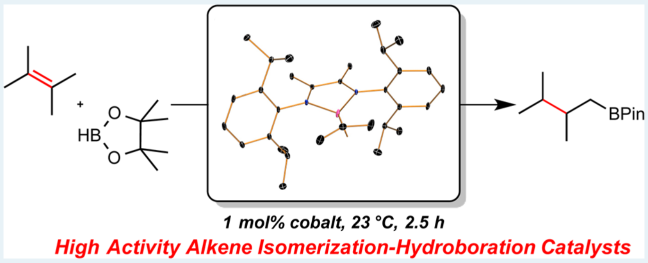
Supporting Information

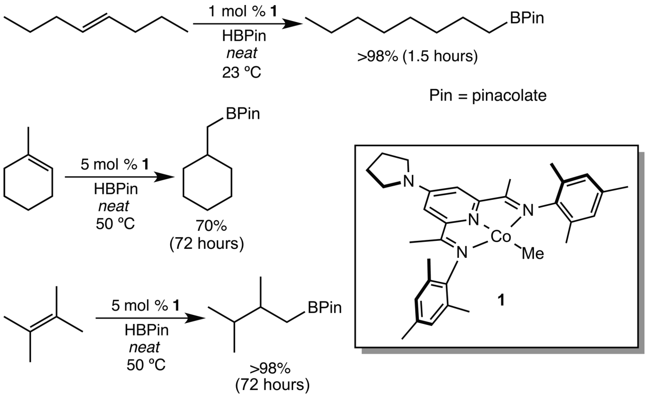
ABSTRACT: Cobalt alkyl complexes bearing readily available and redox-active 2,2′:6′,2″-terpyridine and α-diimine ligands have been synthesized, and their electronic structures have been elucidated. In each case, the supporting chelate is reduced to the monoanionic, radical form that is engaged in antiferromagnetic coupling with the cobalt(II) center. Both classes of cobalt alkyls proved to be effective for the isomerization−hydroboration of sterically hindered alkenes. An α-diimine-substituted cobalt allyl complex proved exceptionally active for the reduction of hindered tri-, tetra-, and geminally substituted alkenes, representing one of the most active homogeneous catalysts known for hydroboration. With limonene, formation of an η^3-allyl complex with a C−H agostic interaction was identified and accounts for the sluggish reactivity observed with diene substrates. For the terpyridine derivative, unique Markovnikov selectivity with styrene was also observed with HBPin.



KEYWORDS: *cobalt, hydroboration, catalysis, redox-active ligands, boronates*

Organoboronates are a valuable class of reagents owing to their stability, ease of handling, and versatility in various carbon−carbon and carbon−heteroatom bond-forming reactions.[1] Metal-catalyzed alkene hydroboration has proven to be an effective route to alkyl boronates with precious metal catalysts using rhodium and iridium being the most common.[2] Interest has recently shifted to catalysts that employ more earth-abundant transition metals such as iron and cobalt.[3,4] In addition to their potential economic and environmental benefits, catalysts based on first row transition metals, by virtue of the smaller atomic radii and unique electronic structures, offer the ability to promote new chemistry or expand substrate scope not encountered with traditional precious metal catalysts.[5]

Scheme 1. Examples of Bis(imino)pyridine-Cobalt-Catalyzed Alkene Isomerization−hydroboration



Bis(imino)pyridine cobalt alkyl complexes have proven to be highly active and selective catalysts for the hydroboration of alkenes.[6] Modification of C_1 symmetric variants of these ligands used in cobalt-catalyzed alkene hydrogenation[7] has recently been extended to the enantioselective hydroboration of certain 1,1-disubstituted aryl alkenes.[8] Introduction of a pyrrolidinyl substituent into the 4-position of the chelate, (4-pyrr-^{Mes}PDI)-$CoCH_3$ (**1**), resulted in improved performance and enabled tandem isomerization−hydroboration of hindered alkenes, a method pioneered by Crudden and co-workers in rhodium catalysis.[9] With *trans*-4-octene, methyl-cyclohexene and 2,3-dimethyl-2-butene, cobalt-catalyzed hydroboration exclusively furnished the terminal-substituted boronate ester arising from remote hydrofunctionalization of the methyl positions (Scheme 1).[6] Recently, the tandem isomerization−hydroboration was replicated for 4-octene with *N*-phosphinoamidinate-supported cobalt catalysts, but activity with more substituted internal alkenes was not reported.[10] Given the utility of this transformation for the introduction of versatile boron functionality at remote, saturated C−H bonds, more active catalysts with broader substrate scope are of interest. For the most hindered substrates, catalytic reactions with **1** required neat conditions and elevated temperatures (Scheme 1). Here we describe the synthesis and electronic structure determination of new cobalt alkyl complexes with readily available

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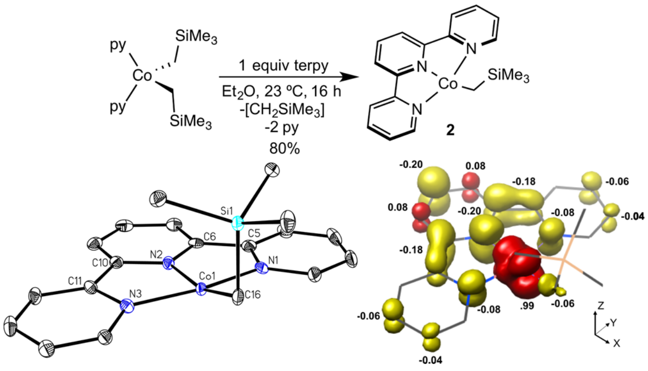
2,2′:6′,2″-terpyridine (terpy) and α-diimine ligands and their exceptional activity for alkene isomerization−hydroboration. The two different precatalyst classes also offer complementary performance among different substrate types.

Given the success of redox-active bis(imino)pyridine ligands in promoting base metal-catalyzed hydrofunctionalization reactions,[5] terpy was explored due to its commercial availability, open steric environment, and established redox activity.[11] Our laboratory previously demonstrated the utility and electronic participation of a terpy chelate in the iron-catalyzed hydrosilylation of vinyl cyclohexane oxide.[12] The synthesis of (terpy)CoCH$_2$SiMe$_3$ (**2**) was accomplished by straightforward addition of the free ligand to a diethyl ether solution of (py)$_2$Co(CH$_2$SiMe$_3$)$_2$.[13] Ejection of one of the alkyl ligands accompanied displacement of the pyridine ligands and **2** was isolated as a purple diamagnetic solid in 80% yield (Scheme 2).

Scheme 2. Synthesis, Solid-State Structure (30% Probability Ellipsoids, Hydrogens Omitted) and DFT-Computed[14] Mulliken Spin Density Plot of 2

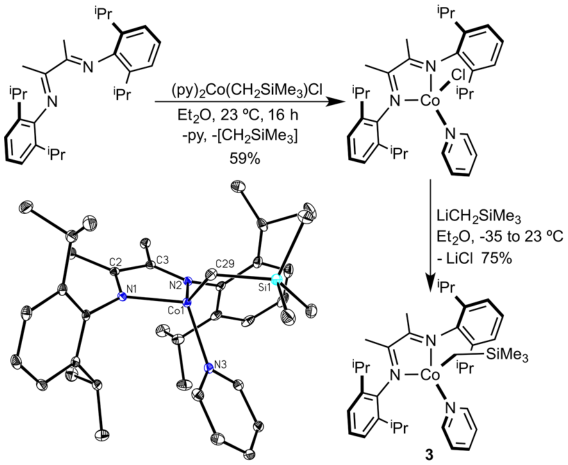


The X-ray structure established an idealized planar geometry, expected for an $S = 0$ ground state. The N(1)−C(5), C(5)−C(6) and N(2)−C(6) distances of 1.373(7), 1.447(8), and 1.366(7) Å, respectively, are consistent with one electron reduction of the terpyridine chelate.[11] DFT calculations[14] converged to a broken symmetry (1,1) solution corresponding to a low-spin cobalt(II) center engaged in antiferromagnetic coupling to a terpyridine radical anion.

Cobalt alkyl complexes of aryl-substituted α-diimine (DI) ligands were also targeted due to the ease of synthesis and modularity of the chelate and its established redox-activity with first row transition metal complexes.[15] Iron dialkyl, diene, and alkyne complexes of this ligand class have previously been reported for alkene hydrogenation, although performance was limited by deactivation due to formation of bis(chelate) or iron arene compounds.[16,17] Despite the ubiquity of this ligand class, especially in the context of alkene polymerization,[18] α-diimine cobalt complexes have only been preliminarily investigated, and reduced compounds include monohalide and η^6-arene derivatives.[19,20]

Pyridine displacement coupled with alkyl ejection was again utilized as a synthetic entry point to monoalkyl cobalt chemistry. Addition of 1 equivalent of ^{iPr}DI (^{iPr}DI = [2,6-^{i}Pr$_2$−C$_6$H$_3$N=C(CH$_3$)]$_2$) to a diethyl ether solution of (py)$_2$CoCl(CH$_2$SiMe$_3$) furnished (^{iPr}DI)Co(py)Cl as a paramagnetic green solid in 59% yield (Scheme 3). Subsequent alkylation with 1 equivalent of LiCH$_2$SiMe$_3$ in diethyl ether followed by recrystallization from pentane furnished red crystals identified as (^{iPr}DI)Co(py)CH$_2$SiMe$_3$ (**3**) in 70% yield (Scheme 3). The solid-state structure of **3** was determined by X-ray diffraction and established a near tetrahedral geometry.

Scheme 3. Synthesis and Molecular Structure (30% Probability Ellipsoids, Hydrogens Omitted) of 3



The C(2)−C(3) distance of 1.417(2) Å in combination with other α-diimine bond distortions are consistent with a ligand-centered radical and hence an overall Co(II) oxidation state.[15] The observed $S = 1$ magnetic ground state arises from antiferromagnetic coupling of the α-diimine radical with the high spin, $S = 3/2$ Co(II) center. Computational studies corroborate this view of the electronic structure where a broken symmetry (3,1) solution corresponding to a high-spin Co(II) complex with an α-diimine radical anion was preferred. The substitutional lability of the pyridine ligand was established by addition of excess pyridine to a benzene-d_6 solution of the independently synthesized pyridine-d_5 isotopologue (**3-*d*$_5$**). Over the course of 90 min at 23 °C, the paramagnetically shifted resonances began to appear in the ^{1}H NMR spectrum at 9.27, 20.72, and 79.61 ppm corresponding to coordinated pyridine, signaling chemical exchange between the isotopologues.

A pyridine-free α-diimine cobalt alkyl complex was also targeted to avoid complications from pyridine inhibition during catalysis (vide infra). The cobalt allyl complex, (^{iPr}DI)Co(η^3-C$_3$H$_5$) (**4**) was isolated in 73% yield as diamagnetic green crystals following allylation of [(^{iPr}DI)CoCl]$_2$[18] with CH$_2$=CHCH$_2$MgCl in diethyl ether (Scheme 4). The toluene-d_8 ^{1}H NMR spectrum of **4** recorded at 22 °C exhibits the number of resonances consistent with a C_{2v} symmetric α-diimine environment with the imine methyl groups located at −5.60 ppm, diagnostic of participation of the chelate in the electronic structure of the compound.[21−23] The resonances for the allyl ligand were located at −0.21 (*anti*), 10.28 (*syn*) and 11.19 (*meso*) ppm, consistent with η^3 coordination and either rapid rotation or facile η^3, η^1 interconversion. An EXSY experiment at 22 °C revealed no crosspeaks between the *syn* and *anti* proton resonances, suggesting no chemical exchange is occurring, as would be expected for η^3, η^1 interconversion. The distinguishability and observation of coupling in these resonances further indicates lack of exchange and support a rapid η^3-rotation mechanism.[24] The solid-state structure was determined by single crystal X-ray diffraction and established η^3 coordination of the allyl ligand in the solid state (Scheme 4). The methine hydrogen is directed above the metal−chelate plane between

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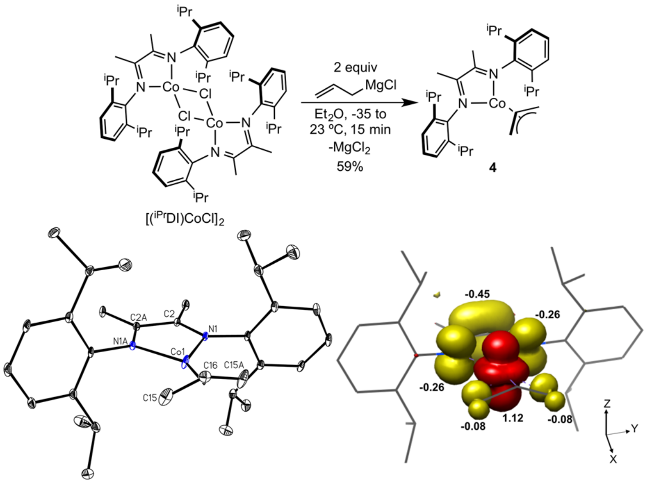
Scheme 4. Synthesis, Molecular Structure (30% Probability Ellipsoids, Hydrogens Omitted) and DFT-Computed Mulliken Spin Density Plot of 4



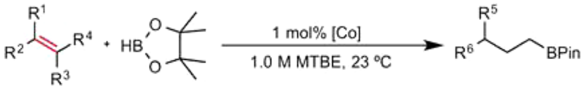
the large 2,6-diaryl imine substituents. The C(2)–C(2A) and N(1)–C(2) distances of 1.427(4) and 1.329(3) Å are consistent with one-electron reduction of the diimine chelate[15] and establish a Co(II) oxidation state.

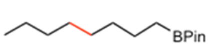
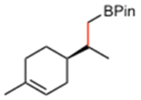
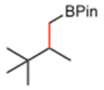
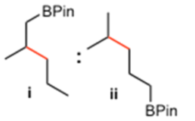
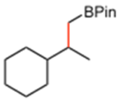
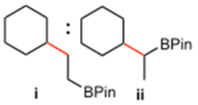
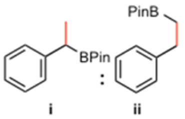
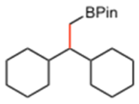
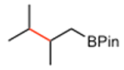
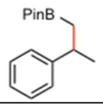
With new cobalt alkyl complexes bearing redox-active ligands in hand, the performance of **2**–**4** in catalytic alkene hydroboration was evaluated. Standard conditions employed 1% of the desired cobalt alkyl precatalyst with 1.0 M solution of the substrate in methyl *tert*-butyl ether (MTBE) and 1.05 equiv of HBPin (Pin = pinacolate) at 23 °C (Table 1). Included in Table 1 are the selected examples of analogous reactions promoted by the previously reported bis(imino)pyridine cobalt methyl complex, **1**.[6] Each of the cobalt alkyl complexes new to this study proved to be active for the isomerization–hydroboration of *trans*-4-octene (entry **A**). Both the terpyridine derivative, **2**, and the base-free allyl complex, **4**, proved to be more active than **1** reaching complete conversion in 8 and 1.5 h, respectively. Using **2** as a precatalyst, a mixture of hydroborated products was obtained and composed predominantly of the 1-substituted (55%) and the 2-substituted (38%) octylboronate esters. With **4**, the *n*-octyl boronate product was obtained exclusively in high isolated yield following removal of the cobalt catalyst by exposure to air and subsequent filtration through silica.

The pyridine stabilized cobalt alkyl complex, **3**, was the slowest in the series for the catalytic isomerization–hydroboration of *trans*-4-octene, requiring 32 h to reach complete conversion to the terminal alkylboronate ester product. Suspecting pyridine dissociation was required to generate the active catalyst, the effect of added pyridine on catalytic performance was determined using **4**. A more readily reduced substrate, 1-octene was used for these studies. In the absence of added pyridine, >98% conversion to *n*-octyl boronate ester was observed in less than 5 min at 22 °C with 1 mol % of catalyst. Addition of 5 mol % pyridine significantly slowed the reaction, as 6 h was required for complete conversion. Saturation behavior was achieved at 25 mol % pyridine as 18 h was required for complete conversion. The same amount of time was required with 50 mol % of added pyridine.

Solvent effects were also explored with cyclohexyl methyl ethylene (entry **J**) using **3** as the precatalyst. This substrate was selected for these studies because it is relatively challenging and could delineate relative rates. In toluene, only 47% conversion

Table 1. Room-Temperature Catalytic Alkene Hydroboration with Pinacolborane Using Precatalysts 1–4



Product	Conversion[a]	Product	Conversion[a]	Product	Conversion[a]
A 	**1:** >98% (18 h, 85%) **2:** >98% (8 h, 87%)[b] **3:** >98% (32 h, 77%) **4:** >98% (1.5 h, 85%)	**E** 	**2:** >98% (9 h, 81%) **3:** <5% (>48 h) **4:** <5% (>48 h)	**I** 	**1:** 51% (66 h, 23%) **2:** <5% (>48 h) **3:** >98% (9 h, 78%) **4:** >98% (<10 min, 79%)
B 	**1:** >98% (18 h, 46%, 1.0:1.9) **2:** >98% (9 h, 43%, 3.1:1.0)[c] **3:** >98% (36 h, 65%, 1.0:1.8) **4:** >98% (2 h, 74%, 1.0:3.7)	**F** 	**2:** >98% (18 h, 85%, *dr* 4.3:1.0) **3:** 57% isomerized (<48 h)[f] **4:** 22% isomerized (>48 h)[f]	**J** 	**2:** >98% (9 h, 79%) **3:** >98% (24 h, 79%) **4:** >98% (<5 min, 89%)
C 	**1:** 95% (78 h, 64%, 23:1.0)[d] **2:** >98% (36 h, 85%, 7.1:1.0) **3:** 74% (144 h, 58%, >98:1.0)[e] **4:** >98% (2 h, 89%, >98:1.0)	**G** 	**2:** >98% (<20 min, 83%, 25:1.0) **3:** 87% (>48 h, 62%, 13:1.0)[g] **4:** 42% (>48 h)[h]	**K** 	**2:** <5% (>48 h) **3:** >98% (12 h, 86%) **4:** >98% (1 h, 97%)
D 	**1:** 73% (66 h, 33%) **2:** <5% (>48 h) **3:** >98% (96 h, 55%) **4:** >98% (2.5 h, 79%)	**H** 	**2:** >98% (18 h, 72%) **3:** <5% (>48 h) **4:** <5% (>48 h)	**L** 	**2:** 68% (144 h, 66%, 1.7:1.0 dr)[i] **3:** >98% (14 h, 93%, 1.3:1.0 dr) **4:** >98% (1 h, 95%, 1.3:1.0 dr)[j]

[a] Percent conversions based on GC-FID. Reaction times, isolated yields, and product ratios shown in parentheses. Ratios determined by ^{1}H NMR, quantitative ^{13}C NMR, or GC-FID. [b] Isolated as a mixtureof products: 55% 1-octylboronate ester, 38% 2-octylboronate ester, and 7% unidentified hydroborated products. [c] 14% of product mixture composed of a third unidentified hydroboration product. [d] 7% ethylcyclohexane observed in product mixture prior to isolation of hydroboration products. [e] 10% ethylcyclohexane observed in product mixture prior to isolation of hydroboration products. [f] Isomerized to α-pinene. Only trace hydroborated product detected. [g] 5% ethylbenzene observed in product mixture prior to isolation of hydroboration products. [h] Exclusively reduced to ethylbenzene. No hydroboration product detected. [i] 6% of isolated mixture composed of two additional unidentified products. [j] Major diastereomer determined by oxidation to the corresponding alcohol and analysis by quantitative ^{13}C NMR.

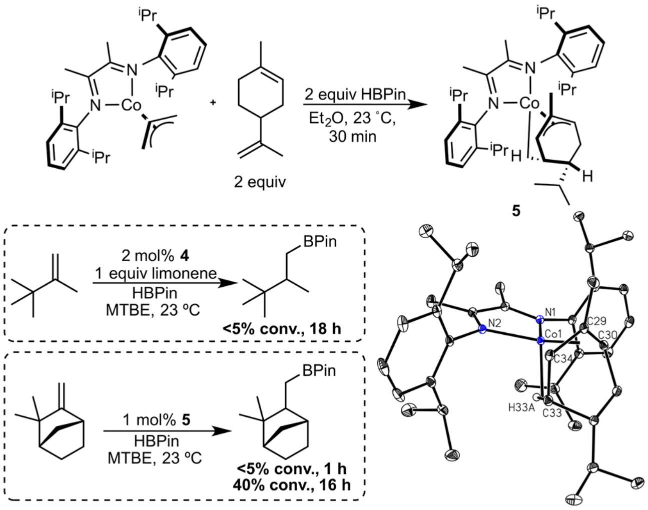
was obtained in 1 h, reaching a maximum of 58% after 12 h. It is likely that the η^6-arene complex, $(^{iPr}DI)Co(\eta^6-C_7H_8)$[20] is formed under these conditions. Control experiments with isolated compound demonstrated that it is inactive for hydroboration. This deactivating effect was not seen in nonaromatic solvents such as pentane, hexane, diethyl ether and MTBE. As a consequence, all catalytic reactions reported in this study were conducted in MTBE.

The cobalt-catalyzed isomerization−hydroboration of more hindered tri- and tetrasubstituted alkenes was also explored as few catalysts, either precious or base metal, are known to reduce these substrates.[6] With 2-methyl-2-pentene (entry **B**), mixtures of the chain walking products, **B-i** and **B-ii** were obtained. In all cases, except for **2**, **B-ii** was favored. The cyclohexyl-substituted trisubstituted alkene (entry **C**) also underwent isomerization−hydroboration with **1**−**4**. The α-diimine-substituted precatalysts, **3** and **4**, gave exclusive selectivity, whereas with **1** and **2**, small amounts of the secondary alkyl boronate were observed. With a more challenging tetrasubstituted alkene such as entry **D**, cobalt precatalysts with tridentate ligands either required long reaction times (**1**) or were inactive (**2**). By contrast, complete conversion was observed with both **3** and **4** with the base-free example exhibiting extremely high activity.

In the case of hindered, geminally substituted alkenes (entries **I**−**L**), the α-diimine precatalysts again proved superior and the base-free example, **4**, was exceptionally active. Complete conversion with the most hindered substrates was achieved over the course of minutes at ambient temperature, representing one of the most active alkene hydroboration catalysts known. Hydroboration of 2,3,3-trimethyl-1-butene (entry **I**) was conducted with 0.1 mol % of **4** over the course of 3 h at 23 °C; lowering the loading to 0.05% resulted in irreproducible results likely due to the sensitivity of the catalyst. The terpyridine precatalyst, **2** offered unique anti-Markovnikov selectivity for the hydroboration of styrene with HBPin, a rare feature among base metal catalysts.[4d,e,i,6]

Precatalyst **4** proved sluggish with diene substrates such as limonene (entry **E**) and β-pinene (entry **F**), whereas the terpy derivative, **2**, proved more effective reaching complete conversion in 9 and 18 h, respectively. To elucidate the origin of the catalytic inhibition, a diethyl ether solution of **4** was treated with HBPin and a slight excess of limonene and yielded orange crystals in 41% yield following recrystallization from pentane at −35 °C (Scheme 5). A combination of NMR spectroscopy and X-ray diffraction established the identity of the product as a cobalt allyl complex, **5**, where the gem−alkene has been reduced to an isopropyl group. The allyl formed from the six-membered ring likely arises from isomerization of the gem−alkene to an endocyclic position followed by reduction by a putative Co−H. Both the NMR and X-ray data support an agostic interaction with the C−H bond in the 3-position of the ring with Co(1)−H(33A) bond length of 1.8861(44) Å, and a Co(1)-H(33A)-C(33) bond angle of 102.7(10)°. A doublet for this proton was located at 5.00 ppm in the benzene-d_6 ^1H NMR spectrum. Importantly, attempted hydroboration of 2,3,3-trimethyl-1-butene in the presence of limonene with 1 mol % of **4** resulted in <5% conversion of the substrate after 18 h. Similar results were obtained using camphene with isolated **5** as the precatalyst. The diminished catalytic activity when **5** was used instead of **4** under identical conditions suggest slower activation of the precatalyst and further establish the inhibitory effect of the diene on cobalt catalyzed hydroboration.

Scheme 5. Synthesis, Molecular Structure (30% Probability Ellipsoids, Hydrogens Omitted Except for C−H Agostic Interaction), and Diminished Catalytic Activity of 5



In summary, new cobalt alkyl complexes bearing readily available and redox-active 2,2′:6′,2″-terpyridine and aryl-substituted α-diimine ligands have been synthesized, and their catalytic performance has been proven to be complementary. The lower electron count α-diimine-substituted cobalt catalyst was exceptionally active for the reduction of hindered tri-, tetra-, and geminally substituted alkenes. In substrates containing dienes or arene groups, the terpyridine derivative was more effective, likely a result of being more resistant to competitive deactivation pathways or inhibition due to a more open coordination environment. These results establish the potential reactivity advantages available in base metal catalysts and serve to highlight the importance of having a versatile compound library to overcome the limitations with individual members.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The following files are available free of charge on the ACS Publications website at DOI: 10.1021/cs501639r.

Complete experimental procedures, characterization data for all new compounds, and computational results (PDF)
Crystallographic data: CCDC 1025114−1025117, 1038682 (CIF)
For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b000000x/.

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Notes

The authors declare no competing financial interest.

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