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Cobalt–N-Heterocyclic Carbene Complexes in Catalysis

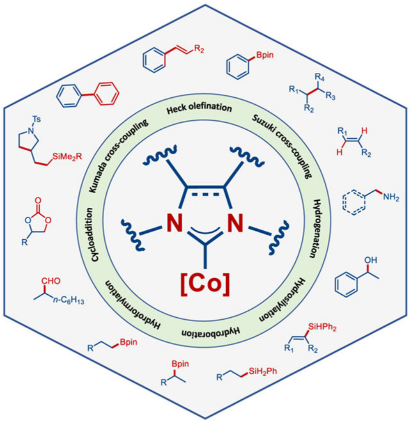
Sourav Sekhar Bera[†], **Michal Szostak**[†]

[†]Department of Chemistry, Rutgers University, 73 Warren Street, Newark, New Jersey 07102, United States

Abstract

Cobalt–NHC complexes have emerged as an attractive class of 3d transition metal catalysts for a broad range of chemical processes, including cross-coupling, hydrogenation, hydrofunctionalization and cycloaddition reactions. Herein, we present a comprehensive review of catalytic methods utilizing cobalt–NHC complexes with a focus on catalyst structure, the role of the NHC ligand, properties of the catalytic system, mechanism and synthetic utility. The survey clearly suggests that the recent emergence of well-defined cobalt–NHC catalysts may have a tremendous utility in the design and application of catalytic reactions using more abundant 3d transition metals.

Graphical Abstract



Keywords

cobalt; Co–NHCs; N-heterocyclic carbenes; NHCs; cross-coupling; hydrogenation; hydrofunctionalization

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Corresponding Author michal.szostak@rutgers.edu.

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1. Introduction

N-Heterocyclic carbenes (NHCs) represent a tremendously attractive class of ancillary ligands for transition metal catalysis.[1] Since the first isolation of a stable free N-heterocyclic carbene, 1,3-di(adamantyl)imidazol-2-ylidene, by Arduengo in 1991,[2] and the first application of metal–NHC complexes in catalysis by Herrmann in 1995,[3] an increasingly large toolbox of NHC ligands, NHC–metal complexes, and their derivatives have been developed. The overwhelming significance of NHC ligands, including their key role in Ru-metathesis[4,5] and Pd-cross-coupling reactions,[6] hinges upon their favorable properties as compared to phosphine ligands, including stronger σ-donation, differential umbrella-type ligand shape (cf. cone-shape), facile synthesis from readily accessible starting materials, and straightforward variation of steric and electronic properties by N-wingtip substitution.[7–17] These features have rendered NHCs as one of the most important class of ligands used in metal coordination chemistry and catalysis.[4–17]

In the last 20 years, major advances have been made in the use of inexpensive and more abundant, less toxic, environmentally more sustainable first-row transition metals, such as Fe, Co, Ni in organic synthesis and catalysis.[18–28] The unique *d*-electron configuration compared to their 4d and 5d congeners unveils many interesting reactivities and properties. Meanwhile, among the 3d transition metals, in the last decade, cobalt has especially undergone explosive growth in the field of catalysis.[29,30] Because of flexible coordination geometries (e.g., tetrahedral, square-planar, octahedral, triangular or bipyramidal), multiple spin states, and high density of states, cobalt complexes have opened up numerous possibilities of tuning the electronic structure, which is an integral part of catalyst design.[31,32] The substitutional lability of cobalt, compared to the homologous group 9 elements, surges the chances of broader functional group compatibility, particularly with unprotected heterocycles and heteroatoms, which often bind the metal strongly as catalyst poisons. The reduced electronegativity and small size of cobalt, compared to its 4d or 5d homologues, offer more nucleophilic organometallic cobalt intermediates, which could switch many traditional reaction pathways as well as change regio- and chemoselectivity. All these characteristics make cobalt a potential catalyst for a broad range of C–C and C–heteroatom bond forming reactions.

Cobalt is an important dietary component present in many metalloenzymes, such as vitamin B_{12}, nitrile hydratase and methionine aminopeptidase.[33a] It is the first and lightest element among the group 9 transition metals, while in terms of abundance, the reserve is over 10^3 times larger than the total content of platinum group metals in the geosphere.[33b] Cobalt complexes have been applied in a broad range of small molecule activation chemistry and catalytic reactions, such as cross-coupling reactions, hydrogenation reactions, hydrofunctionalizations, C–H activation and cycloaddition reactions. In this context, cobalt complexes show great potential for applications in catalysis.[16,30,34–36] Despite that cobalt has been established as an efficient catalyst in synthetic chemistry and transition-metal-catalysis, most of the present cobalt catalytic systems still rely on air-sensitive, toxic, and expensive phosphine ligands (**L1-L17**)[37–52] or less σ-donating amine ligands (**L18-L27**)[53–61] (Figure 1).

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In the historical context, the first cobalt-NHC complexes were reported by Lappert and co-workers in 1977,[62] however, the research on their reactivity did not begin until almost thirty years later. Cobalt complexes can exist in several oxidation states ranging from −2 to 4. N-Heterocyclic carbenes can stabilize metals in different oxidation states and support coordinatively unsaturated catalytically active intermediates.[4–17] With the perfect combination of cobalt and N-heterocyclic carbenes, a larger number of cobalt-NHC complexes have been reported,[63–71] and gradually applied in various transformations. Despite major achievements in this field, there is still no comprehensive review on Co–NHC-catalyzed organic reactions.

In this article, we present a comprehensive review of catalytic methods utilizing cobalt–NHC complexes with a focus on catalyst structure, the role of the NHC ligand, properties of the catalytic system, mechanism and synthetic utility. The review covers the literature until November 2021. The review is organized by the class of reactions, including cross-coupling (Section 2), hydrogenation (Section 3), hydrofunctionalization (Section 4), cycloaddition (Section 5) and miscellaneous reactions (Section 6). Co–NHC-catalyzed C–H functionalizations are not covered because this topic has been recently reviewed.[16] Figure 2 presents structures of the most common NHC ligands used in Co–NHC catalysis. We hope that the review will stimulate an even greater interest in this important field.

2. Cobalt–NHC Catalyzed Cross-Coupling Reactions

NHC ligands show excellent reactivity in transition-metal-catalyzed cross-coupling reactions.[6] In contrast to the rapid development of Pd–NHC or Ni–NHC systems, co-balt–NHC-catalyzed cross-coupling reactions have been slower to emerge.

2.1. Kumada Cross-Coupling.

In 2007, the Oshima group reported the first example of cobalt-catalyzed sequential cyclization/cross-coupling reactions of 6-halo-1-hexene derivatives with Grignard reagents using NHC pro-ligands (Scheme 1).[72–73] The cross-coupling reactions required the use of NHC ligands to give the corresponding 3-(silylethyl)pyrrolidine or tetrahydrofuran derivatives in good yields. Among various imidazolium salts, SIEt·HCl was identified as the best pro-ligand. The use of phosphines (PPh_3, $PtBu_3$, dppp) and diamines (TMEDA, N,N,N’,N’-tetramethyl-1,2-cyclohexanediamine) as ligands was much less productive (<10%). Furthermore, when changing the NHC pro-ligand to IMes·HCl, the reaction was found to be compatible with 1-alkynyl Grignard reagents (Scheme 2).[72–73]

Interestingly, in this case, other NHC pro-ligands, such as SIEt·HCl, SIMes·HCl, and IPr·HCl did not give coupling product. The corresponding cyclization/cross-coupling products could be easily transformed into 1,3-diol units.

Subsequently, the same group disclosed a cobalt–NHC catalyst system for the highly regioselective dehydrohalo-genation of alkyl halides (Scheme 3).[74] This reaction proceeds in the presence of cobalt(II) chloride, IMes·HCl and $Me_2PhSiCH_2MgCl$ in dioxane at 25 °C. Furthermore, other bulky NHC pro-ligand precursors, such as IPr·HCl, were screened, however, lower reaction efficiency and selectivity was observed. NHC ligands were superior

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to phosphine ligands with respect to both reactivity and selectivity. The proposed mechanism involves (1) single-electron transfer from Co-catalyst **A**; (2) capture of the radical by Co-complex **C**; (3) β-hydride elimination. The *syn*-β-hydride elimination depends on the conformation in minimizing the steric repulsion. This protocol nicely exemplifies the advantage of the regioselective alkene formation. In light of the isomerization of terminal alkenes, the same group reported cobalt–NHC-catalyzed isomerization of 1-alkenes to (*E*)-2-alkenes.[75]

In 2008, the Oshima group reported cobalt–NHC catalyzed cross-coupling reactions of aryl bromides with alkyl Grignard reagents (Scheme 4).[76] They found that catalytic amounts of cobalt(II) chloride and the combination of N-heterocyclic carbene, IMes·HCl, as pro-ligand precursor and N,N,N',N'-tetramethyl-1,3-propanediamine (TMPDA) as an additive enabled mild cross-coupling.

Comparison with other NHC pro-ligands showed that more sterically-demanding NHC precursor, IPr·HCl, was less effective, while phosphines (PPh_3, PCy_3, $Pt\text{-}Bu_3$) and heteroatom substituted phosphine oxides (Mes·HASPO) did not promote the cross-coupling. It is essential to use TMPDA to promote the reaction by coordination to magnesium. A wide range of aryl bromides were successfully coupled in good to excellent yields. Furthermore, the reaction is completely selective for the cross-coupling of Ar–Br, while Ar–Cl are unreactive. However, the method is not compatible with simple alkyl magnesium halides, such as MeMgI, EtMgCl, ^{i}PrMgCl, while aryl magnesium bromides give low yields under the reaction conditions. The authors proposed that lower reactivity might be a result of slow transmetallation, while reactive Grignard reagents, such as allylMgBr, could decompose the NHC ligand.

In 2009, Chen and co-workers reported the first trivalent cobalt NHC complexes **1** for the Kumada–Corriu cross-coupling reactions of aryl halides with Grignard reagents at room temperature (Scheme 5).[77] The method is characterized by high catalytic activity and compatibility with various aryl and heteroaryl halide substrates. The proposed mechanism involves the following steps: (1) reduction of Co(III)-species to low-valent cobalt-complex in the presence of Grignard reagent; (2) oxidative addition of aryl halide; (3) reductive elimination to form the biaryl product. The authors proposed that NHC ligands stabilize the low-valent cobalt species and facilitate oxidative addition. The use of bulkier NHC ligands was less effective, which was proposed to result from steric inhibition of the oxidative addition step.

In 2009, Nakamura and co-workers reported Kumada biaryl cross-coupling reactions catalyzed by cobalt(II)-fluoride/NHC systems (Scheme 6).[78] Unlike previous reports on Co-catalyzed Kumada cross-coupling, this reaction was performed using $CoF_2 \cdot 4H_2O$ as a catalyst. The method relies on the synergistic role of fluoride counterion and NHC ligand, permitting high selectivity for the cross-coupling vs. homocoupling. Strong coordination of fluoride to the divalent cobalt center leads to slower reduction of the metal and results in the formation of high-valent heteroleptic $[ArCoF_2]MgBr$ complexes. The reactivity of cobalt was compared with other iron-group metals (Fe, Ni), where CoF_2/IPr system was found to be preferred for the crosscoupling of heteroaromatic substrates.

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In 2018, the Duong group reported another catalytic system for cobalt-catalyzed Kumada biaryl cross-coupling reactions of arylmagnesium reagents and aryl halides (Scheme 7).[79a] These reactions are promoted by a fluoride-free combination of $CoCl_2$, IPr and NaO*t*Bu as a base. Various aryl bromides and chlorides could be cross-coupled at mild room temperature conditions. Interestingly, the formation of homocoupling products was minimized by the choice of NHC pro-ligand with less bulky and *N*-aliphatic NHCs leading to lower cross-coupling selectivity, while the counterion had a minor effect on the cross-coupling/homocoupling selectivity. Furthermore, LiCl and $ZnCl_2$ additives which are advantageous in select Kumada cross-couplings,[79b] were detrimental in this case.

In 2012, Matsubara reported new cobalt(II)-complexes **2** and **3** bearing bulky NHC backbones that were tested in the Kumada cross-coupling of aryl halides (Scheme 8).[80] This method represented the first example of well-defined cobalt(II)-NHC complexes that catalyze cross-coupling of aryl halides. It is noteworthy that pyridine-coordinated complex **3a** that is analogous to Pd–PEPPSI systems[6] as well as **2** that is analogous to Pd(II)-chloro dimer systems, $[Pd(IPr)(\mu\text{-}Cl)Cl]_2$,[81] afforded the product in similar yields. The yields were further dependent on the halogen atoms in dimers **3a**-**3c**, with (X = I) affording the highest reactivity.

In contrast to aryl halides, the reaction of *n*-octyl bromide with phenyl magnesium chloride gave the cross-coupling product in very low yield (<20%).[80] Interestingly, replacement of IPr with IMes in catalyst **3a** delivered 1-and 2-octenes, suggesting that β-elimination of the octylcobalt species outperformed reductive elimination of the octyl(phenyl)cobalt species. The authors proposed that β-hydride elimination is promoted by the strong σ-donor ability of NHC ligands.

In 2013, the Tonzetich group reported a new well-defined cobalt(II)-complex, $[CoCl_2(IMes)_2]$ **4**, having pseudotetrahedral geometry and tested catalytic activity in Kumada cross-coupling reactions (Scheme 9).[82] Three different combinations of coupling partners were tested, namely aryl/alkyl, aryl/aryl, and alkyl/aryl. Their results showed that aryl/aryl cross-coupling was most successful. In contrast, aryl/alkyl cross-coupling resulted in low yields, while no reaction was observed for the alkyl/aryl combination. These results mirror the findings established for the $[Co(IPr)(\mu\text{-}I)I]_2$ dimer by Matsubara[80] and further demonstrate that aryl electrophiles are preferred coupling partners for Co(II)–NHC systems.

In the context of biaryl Kumada cross-coupling, in 2011, the Deng group reported a new square-planar cobalt(I)-complex, $[Co(IEt)_4][BPh_4]$ **5**, which was tested in oxidative homocoupling of aryl Grignard reagents (Scheme 10).[83] The homocoupling proceeded efficiently at only 1 mol% catalyst loading using 2-methyl-1,2-dichloropropane as the oxidant. This method permits for the synthesis of functionalized (Cl, OMe) as well as extremely sterically-hindered ortho-tetrasubstituted biaryls. The authors proposed a radical mechanism involving a $[Co(NHC)_4]^+/[Co(NHC)_4)^{2+}]$ redox shuttle.

In 2021, our group reported the first Co-catalyzed cross-coupling of aryl tosylates as bench-stable C–O electrophiles (Scheme 11).[84] This versatile method utilizes a catalytic system based on Co(III)-fluoride (10 mol%), IPr·HCl (20 mol%), Grignard reagent (1.5

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equiv) in THF at 80 °C. Screening of various NHC ligand precursors demonstrated IPr·HCl as the most effective pro-ligand for this reaction. The excellent reactivity of the cobalt fluoride was associated with the low potential for reduction by Grignard reagents and the subsequent formation of low-valent cobalt species, in agreement with studies by Nakamura.[78] Stoichiometric experiments were supported by the amount of biaryl formation ($Co(acac)_3$ (22%), $CoCl_2$ (18%), CoF_2: <5%; CoF_3: <5%). Control experiments with radical trapping reagent (TEMPO) excluded radical process. The orthogonal nature of phenolic C–O electrophiles was highlighted through the sequential orthogonal cross-coupling via Pd-catalyzed biaryl Suzuki cross-coupling and Co–NHC catalyzed C–O alkyl Kumada cross-coupling.

2.2. Suzuki Cross-Coupling.

In 2017, Bedford and co-workers reported Suzuki cross-coupling of aryl chlorides and bromides with aryl–Bpin esters activated by alkyllithium catalyzed by $CoCl_2$/SIPr·HCl system (Scheme 12).[85] Several phosphine ligands (PPh_3, dppp, Xantphos) resulted in negligible product formation (<10%). Imidazolinylidene SIPr is the preferred NHC ligand for this cross-coupling, however, several other NHCs gave high conversions (IMes, SIMes, IPr). This reaction tolerates a remarkable variety of functional groups, including esters, amides, amines, and heterocycles. Interestingly, 4-chlorotoluene showed higher reactivity compared to its bromo counterpart. This reactivity is opposite to the classical palladium-catalyzed cross-couplings, where the weaker Ar–Br bonds are coupled more readily. The authors isolated Co(0)–SIPr complex supported by norbornene ligands and demonstrated its catalytic activity. A mechanism involving radical-centered oxidative addition was proposed.

In 2019, Duong and co-workers reported similar cross-coupling of aryl triflates with lithium arylborates catalyzed by $CoCl_2$/IAd·HBF_4 (Scheme 13).[86] One of the key features of this study is the correlation between steric bulk of NHC ligands (expressed as percent buried volume, $\%V_{bur}$) and reactivity in the cross-coupling in that more sterically-demanding NHC ligands resulted in more efficient coupling. Furthermore, *N*-alkyl NHC ligands (IAd, I*t*Bu, ICy) performed better than their *N*-Ar counterparts (IPr, SIPr, IMes, SIMes). Similar to the method by Bedford,[85] the scope of the reaction is very broad, while the method advanced the Co–NHC cross-coupling manifold to C–O electrophiles using organoboronates activated by *n*-butyllithium.

In 2021, Bedford and co-workers reported another approach to cobalt–NHC catalyzed Suzuki cross-coupling of aryl chlorides with aryl boronic esters to access biaryl motifs, where the organoboron nucleophile is activated by alkoxides (Scheme 14).[87] This reaction employs catalytic amount of $CoCl_2$ (5 mol %), IPr·HCl (5 mol%) and 1.5 equiv of KO^{t}Bu in THF as a solvent at 60 °C. The comparison between different alkoxide bases in this reaction showed that KO^{t}Bu was superior to its counterparts (K > Na > Li). The authors proposed that increasing oxophilicity of the counterions of the boronate salt facilitates the transmetallation step. The loading of KO^{t}Bu was also highly significant as small deviation from the optimized conditions abruptly decreased the performance. Interestingly, in this finely-tuned protocol, increasing the KO^{t}Bu loading from 1.5 to 1.8 equiv with respect to aryl chloride led to a nearly complete halt of the reaction. The scope of the reaction is

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more limited than with lithium arylborates; however, the *in situ* activation of aryl boronic esters with alkoxide bases might find application in facilitating transmetallation in Co–NHC catalysis.

2.3. Heck Olefination.

In 2013, Matsubara and co-workers reported a new less bulky PEPPSI-type cobalt(II)-complex **6**, [Co(NHC)(py)I_2], bearing IMes imidazolylidene ligand, which was found to promote catalytic Heck olefination of alkyl halides (Scheme 15 cf. Scheme 8).[88] The cobalt center in [Co(NHC)(py)I_2] has a d^7-tetrahedral geometry. The complex is synthesized from the corresponding [Co(IPr)(μ-I)I]$_2$ dimer. [Co(IMes)(py)I_2] was found to mediate trans-selective Heck reaction of 1° alkyl bromides in the presence of Grignard reagents as reductants; however the yields were modest (up to 50%) due to competing dehydrohalogenation. Nevertheless, the results showcased the importance of steric tuning of the carbene ligand in that Co(II) complexes bearing less bulky IMes were more reactive than with IPr in activation of alkyl halides.

In 2016, Hajipour and co-workers reported another approach to Heck olefination using Co–NHC complexes supported by multi-walled carbon nanotubes, Co–NHC@MWCNTs **7** (Scheme 16).[89a] The Co(II)–NHC complex was immobilized on multi-walled carbon nanotubes by the grafting amination approach. In contrast to [Co(NHC)(py)I_2], complex **7** was found to be air-stable.

The complex was found to be catalytically active in the Heck reaction of aryl iodides and bromides with acrylates and styrene. In addition, the catalyst could be reused 6 times without loss of catalytic activity, while cobalt was determined not to be leaching from the catalyst. In 2019, Hajipour and co-workers reported the same cobalt-catalyst **7** for three-component A^3 coupling of aldehydes, amines and alkynes for the synthesis of propargylamines and Sonogashira cross-coupling of aryl halides (not shown).[89b]

2.4. Miyaura Borylation.

In 2018, Geetharani and co-workers reported an efficient catalytic system for borylation of aryl chlorides and bromides using Co(IMes)$_2$Cl$_2$ (Scheme 17).[90] The catalyst system appears to be general, tolerating a wide range of functional groups and heterocycles (thiophene, pyridine, quinoline, pyrrole, indole). The reaction shows very good chemoselectivity in that borylation of C(sp^2)–Cl is possible in the presence of benzylic C(sp^3)–Cl as well as C(sp^2)–Br borylation is feasible in the presence of C(sp^2)–Cl bond. Mechanistic studies indicated that the reaction does not involve a radical process. Co(I)/Co(III) cycle was proposed for this reaction. To confirm the participation of Co(I) species as the active catalyst, [Co(IMes)$_2$Cl] was synthesized and when used as a catalyst, it gave the reaction product in 92% yield. The involvement of Co(I) species in the borylation reaction was further elucidated in a series of NMR monitoring experiments, showing the formation of [Co(IMes)$_2$Cl] under the reaction conditions. The mechanism was proposed to involve the following steps: (1) generation of the active catalyst **A**; (2) ligand exchange to produce complex **B**; (3) reaction with B$_2$pin$_2$; (4) oxidative addition with aryl halide to form **D**; (5) reductive elimination to give the final product.

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In 2020, Geetharani and co-workers reported anther efficient Co–NHC-catalyzed method for borylation of alkyl chlorides and bromides using bis(pinacolato)diboron (Scheme 18).[91] This reaction proceeds in presence of catalytic amount [Co(PPh_3)$_3$Cl] (2 mol%), ICy (4 mol%), NaOEt (1.3 equiv) in MTBE (*tert*-butylmethyl ether) as a solvent at 50 °C. This method offers access to a wide range of alkyl boronic esters from unactivated 1°, 2° and 3° alkyl halides. Impressively, this methodology is also successful to activate simple alkyl chlorides, a class of substrates that is challenging in direct borylation reactions. Synthetically difficult tertiary halides are also competent substrates, furnishing tertiary boronate esters. Mechanistically, the authors proposed that a radical intermediate might be involved in the oxidative addition step.

3. Hydrogenation Reactions Catalyzed by Cobalt–NHC Complexes

Catalytic hydrogenation is among the most important reactions in organic synthesis and catalysis. Although Co–NHC catalyzed hydrogenation is far from fully exploited, notable advances have been recently reported.

3.1. Hydrogenation of Alkynes and Alkenes

In 2013, Chirik and co-workers established a highly efficient protocol for hydrogenation of challenging, sterically hindered, unactivated tri- and tetrasubstituted alkenes, utilising bis(arylimidazol-2-ylidene)pyridine CNC cobalt(I) methyl pincer complex **8** as a catalyst under H_2 (4 atm) in benzene at 22 °C (Scheme 19).[92a] All tested tri-substituted alkenes responded well to the catalytic conditions giving excellent yields of the alkane products (>95%). Hydrogenation of a tetrasubstituted olefin, 2,3-dimethyl-2-butene, was also possible at slightly elevated temperature (50 °C), illustrating the high reactivity of precatalyst **8**, as compared with the corresponding iron counterpart.[92b] Based on extensive structural, spectroscopic, and computational studies, CNC ligand has been proposed to act as a redox-active ligand[25,45,50,59] that participates in one-electron reduction chemistry. Interestingly, the spin density calculations showed that radicals are mostly localized on the pyridine ring with little influence from the NHC ligands. The hydride and alkyl group migration onto the C4 position of the pyridine backbone of the bis(arylimidazol-2-ylidene)pyridine chelate was observed and further supported the localization of the radical on the pyridine ring.

Three years later, Fout and co-workers reported hydrogenation of olefins catalyzed by Co(I)–NHC CCC pincer complex, (^{Mes}CCC)-CoN_2PPh_3 **9** (^{Mes}CCC = bis(mesityl-benzimidazol-2-ylidene)phenyl) under 4 atm of H_2 in benzene-d_6 at room temperature (Scheme 20).[93] Impressively, reactive functional groups, such as aldehyde, ketone, hydroxyl and anhydride, were well tolerated under the reaction conditions. Interestingly, the catalyst was selective for hydrogenation of terminal alkenes as demonstrated by isoprene and 4-vinylcyclohexene, where the disubstituted olefin remained untouched. Hydrogenation of internal olefins required elevated temperature (60 °C). The addition of stoichiometric HCl·Et_2O to **9** in THF afforded the corresponding Co(III)HCl complex through oxidative addition. This Co(III)HCl complex was converted back to **9** by the addition of hydride transfer reagent, Cp_2ZrHCl, emphasizing the Co(I)/(III) redox pathway. Mechanistic studies revealed that Co(I)–(N_2) precursor **9** can exchange N_2 for H_2 and can also facilitate

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the scrambling of H_2/D_2. The para-hydrogen induced polarization (PHIP) transfer NMR studies showed that Co(I) dihydrogen complex **A** is the key reaction intermediate and that olefin coordination is reversible. The reaction mechanism involves the following steps: (1) generation of dihydrogen complex **A** by displacing the N_2 ligand from **9**; (2) olefin coordination to form intermediate **B**; (3) oxidative addition of H_2; (4) migratory insertion to give dihydrogen hydride **D**; (5) reductive elimination, and re-coordination of PPh_3. Complexes **D** and **E** can regenerate **C** via β-hydride elimination.

In the same year, Fout and co-workers reported a method for semihydrogenation of internal alkynes using the same Co(I)–(N_2) CCC precatalyst **9** in the presence of H_2 (4 atm) in THF at 30 °C (Scheme 21).[94a] This method is particularly notable for a wide variety of functional groups, such as amino, hydroxyl, silyl, furanyl, thienyl, imidazolyl, boronates that can be tolerated in the semihydrogenation conditions to give internal olefins in good to excellent yields (59%–96%) and with excellent *E/Z* ratios. Interestingly, terminal alkynes are unreactive in this catalytic system. Extensive mechanistic studies revealed the initial formation of cis-olefin, followed by Co-mediated alkene isomerization to afford the trans-olefin product. Similar to the previous report, the reaction involves the following steps: (1) formation of the dihydrogen complex **A** under H_2 atmosphere from **9**; (2) phosphine displacement by alkyne coordination; (3) oxidative addition of H_2 onto the cobalt center; (4) migratory insertion of alkyne to give Co(III)–(η^{1-}vinyl) hydride/dihydrogen species; (5) generation of cis-alkene by reductive elimination, and coordination of PPh_3 to regenerate the active species **A**. The key difference with the alkene hydrogenation (cf. Scheme 20) is that the cis-trans isomerization process is initiated by a reversible coordination of cis-olefin to **A**. Oxidative addition of H_2 to cobalt, followed by migratory insertion of olefin gives Co(III)–alkyl dihydrogen/hydride species **G** and **H**. Finally, β-hydride elimination affords trans-alkene products, while reductive elimination pathway gives alkanes.

The synthesis of dialkyl three-coordinate Co(II)–NHC complex $[(\mathrm{I}t\mathrm{Bu})\mathrm{Co}(\mathrm{CH_2SiMe_3})_2]$ **10** was reported by Walter and co-workers in 2018 (Scheme 22).[95a] The catalytic activity of complex **10** was evaluated in homogeneous alkene and alkyne hydrogenation. Cyclic ring systems, such as cyclooctadiene and 1-methyl-1-cyclohexene, were fully hydrogenated at low catalyst loading (0.5 mol%) using this catalyst system. In stark contrast, the same substrates were significantly less reactive in the hydrogenation using related four-coordinate Co(II)–phosphine complexes $[(\mathrm{P–P})\mathrm{Co}(\mathrm{CH_2SiMe_3})_2]$ (P–P = dppe, 1,2-bis(diphenylphosphino)ethane).[95b] Challenging tetrasubstituted olefins, such as 2,3-dimethyl-2-butene, were also tested; however, gave low yield under the reaction conditions. The authors synthesized Co(0)–NHC bis(alkyne) complex $[(\mathrm{I}t\mathrm{Bu})\mathrm{Co}(\eta^2\text{-PhCCPh})_2]$ using diphenyl acetylene in presence of H_2; however, the complex was unreactive in hydrogenation reactions. The proposed mechanism involves the following steps: (1) generation of the reactive $[(\mathrm{NHC})\mathrm{CoH_2}]$ species **A**; (2) olefin insertion; (3) reductive elimination to give the alkane and [(NHC)Co] species **C**; (4) H_2 addition to regenerate **A**.

In 2020, Liu and co-workers devised a powerful semihydrogenation strategy for the synthesis of *Z*-alkenes, terminal alkenes and aryl conjugated *E*-alkenes utilising Co–NHC catalysis (Scheme 23).[96] This protocol involves $CoCl_2$ (2 mol%), tridentate ligand precursor

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11 (2 mol%) and ^{t}BuOK (16 mol%) under H_2 (5–10 atm) in THF at room temperature. Among many ligands tested, a lutidine-based CNC pincer bearing a Dipp-substituent was most effective in this reaction. The authors showed that the increase of steric bulk of the NHC ligand largely amplified the reactivity and *Z*:*E* selectivity. Interestingly, the choice and utilisation of base play a crucial role in this reaction; under the base-catalyzed conditions, terminal alkynes first isomerize through chain-walking to form internal alkynes. Further, the base serves to activate the ligand precursor in the reaction, which enables to use imidazolium salt. ^{t}BuOK as a base is required for this reaction. The use of other bases, including NaH, ^{t}BuONa, LiHMDS, MeONa, KOH, Cs_2CO_3, KOAc did not show any reactivity (conversion <5%). Depending upon the sequence of addition of base, different alkene products were obtained. Excellent functional group tolerance was observed (halides, ester, ether, methoxy, siloxy, thioether, alkenyl, heterocycles) to give the corresponding (*Z*)-2-alkenes in good to excellent yields (74%–99%) with high *Z*:*E* selectivity. In addition, internal alkynes could also be hydrogenated to give (*Z*)-alkenes. By increasing the amount of base and temperature, thermodynamically stable aryl-conjugated (*E*)-alkenes were obtained via isomerization/semihydrogenation of terminal alkynes. Deuterium labelling suggested that hydrogenation was accomplished from 2-alkyne intermediate (cf. allene).

In 2018, hydrogenation of alkenes using cobalt(I)–NHC complex, $[(^{Me}IMe)_4Co][BPh_4]$ (^{Me}IMe = 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene) **12**, as a catalyst and diphenylsilane (Ph_2SiH_2) was reported by Deng and co-workers (Scheme 24).[97] One of the highlights is the use of one of the smallest NHC ligands available, ^{Me}IMe (IMe_2Me_2, ITMe). This catalytic system involves Co–NHC complex **12** (5 mol%), Ph_2SiH_2 (1.5 equiv) in THF at 70 °C. The scope of this reaction successfully included different alkyl and arylalkenes as substrates. The authors noted that alkene hydrosilylation by-products are formed in low amounts (1–13%). This reaction is chemoselective for terminal alkenes, while disubstituted alkenes, such as 1,1-diphenylethylene, (*E*)-3-octene and (*Z*)-2-octene, are unreactive due to steric reasons. Diphenylsilane is required in that the use of other hydride sources, such as Et_3SiH, Ph_3SiH, $(EtO)_3SiH$ and $PhSiH_3$, failed to give hydrogenation products. The proposed mechanism involves the following steps: (1) formation of cobalt hydride species **A** as the active catalyst; (2) reaction with an alkene to form the alkyl intermediate **B**; (3) formation of cobalt silyl intermediate **C**, which further reacts with Ph_2SiH_2 to regenerate the active species **A**.

In 2020, the Liu group reported another strategy for hydrogenation of hindered alkenes using Co–NHC catalytic systems (Scheme 25).[98] This reaction involves $CoCl_2$ (0.5–20 mol%), bidentate NHC pro-ligand **13** (1–20 mol%) and $NaHBEt_3$ (3–60 mol%) under H_2 (10–50 bar) in THF solvent. Among several pro-ligands tested, including tridentate pincer ligands, simple bidentate pro-ligands, such as **13** were found to be significantly more reactive under the reaction conditions. Both NHMe and NMe_2 substitution of the ethylene tether of the catalyst gives similar reactivity. The reaction is compatible with various mono, di-, tri- and even the most challenging tetrasubstituted alkenes. The functional group tolerance is also broad, including esters, amides, bromides, amines and heterocycles. The limit of this method is in hydrogenation of nonactivated tetrasubstituted alkenes, such as pentamethylcyclopentadiene or 2,3-dimethyl-2-norbornene, which are recovered unchanged

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from the reaction conditions. Importantly, the method is readily scalable; a gram scale hydrogenation of an ethyl acrylate was efficiently performed under the reaction conditions.

3.2. Hydrogenation of Arenes

In 2019, an intriguing Co–NHC catalyzed regioselective hydrogenation of polycyclic aromatic hydrocarbons was reported by Zeng and co-workers (Scheme 26).[99] The catalytic system employs Co(acac)$_2$ (22 mol%) and IPr·HCl (22 mol%) in combination with MeMgBr (1.5 equiv) under H_2 (8 MPa). The reaction is selective for the formation of terminal carbocycle-reduced products in moderate to good yields (34%–89%). The authors showed that cyclic (alkyl)(amino)carbenes (CAACs) are less effective than classical imidazolylidenes, such as IPr, for this reaction. In terms of scope, sterically-hindered 9,10-dimethyl- or 9,10-diphenyl substituted anthracenes were efficiently converted to the corresponding octahydroanthracenes at slightly elevated temperature (60 °C). Pentacene underwent reduction of the three carbocycles (A, B, C), while the reduction of perylene proceeded with the reduction of two carbocycles. This hydrogenation method is scalable and can be achieved on 10 mmol scale. Theoretical mechanistic studies suggested the participation of a low-valent cobalt monohydride, most likely in a zerovalent state, facilitating the hydrogenation of fused aromatic hydrocarbons.

3.3 Hydrogenation of Nitriles

A well-defined bench-stable cobalt(III) CCC pincer complex ($^{\text{Mes}}$CCC)-CoCl$_2$py **14** was introduced by Fout and co-workers for the hydrogenation of nitriles to amines with the assistance of Lewis acid (Scheme 27).[100a] The reaction takes place using **14** (2 mol%), KO^{t}Bu (6 mol%) and NaHBEt$_3$ (4 mol%) in toluene under H_2 (4 atm) at 115 °C. Other cobalt catalysts, including [(PPh$_3$)$_3$CoCl] and Co(acac)$_3$ were tested and found inactive in this reaction. NaHBEt$_3$ plays a dual role in this method: (1) to reduce complex **14** to Co(I) active catalyst; (2) the resulting BEt$_3$ acts as Lewis acid and assists the hydrogenation. The scope of this method is very broad, including aromatic and aliphatic nitriles containing electron-donating groups (methyl, methoxy, naphthyl, amine) and electron-withdrawing groups (ester, fluoro, chloro, trifluoromethyl). Substrate scope studies further revealed that electron-deficient nitriles give slightly lower yield. Although 4-acetyl benzonitrile was unreactive under the standard reaction conditions, the use of stoichiometric Lewis acid (BEt$_3$, 1.04 equiv) furnished the desired primary amine in the presence of the acetyl group. This chemoselectivity is in a stark contrast between cobalt and other metals (iron, ruthenium, palladium), which are unselective.[100b,c] Mechanistically, the possible intermediate is cobalt(I) complex ($^{\text{Mes}}$CCC)-Co-py, and pyridine is not essential for catalysis. PHIP transfer NMR studies indicated a pairwise hydrogen transfer via Co(I)/Co(III) redox process. Lewis acid is crucial in the reaction through enabling side-on coordination of the nitrile **π** orbital to the cobalt center.

Similar well-defined cobalt(I) CCC pincer complex ($^{\text{Mes}}$CCC)-Co-py was synthesized by the same group and efficiently used as a catalyst for ammonia-borane dehydrogenation to form borazine, polyborazylene and (poly(aminoborane) (not shown).[101]

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3.4. Hydrogenation of Ketones and Aldehydes

In 2019, hydrogenation of ketones and aldehydes was reported by Liu and co-workers utilizing Co–NHCs with flexible CNC pincer ligands bearing N–H substitution (Scheme 28).[102] The method involves *in situ* formed cobalt(II)-catalyst **15** or precatalyst **16** (0.5–4 mol%), ^{t}BuOK or KOH as a base (5–20 mol%) under H_2 (10–30 bar) in THF at 60 °C. ^{t}BuOK as a base works best for *in situ* catalytic system **15**, whereas KOH was identified for preformed catalytic system **16**. Screening of different NHC pro-ligands showed that the bulkier N-mesityl wingtip was most effective. A wide variety of acetophenones, linear and cyclic aliphatic ketones, including pharmaceutically important molecules, such as pentoxifylline, progesterone, and testosterone were chemoselectively reduced to the corresponding alcohol products. Aldehyde substrates were also equally effective for hydrogenation under the same conditions. Notably, the authors showed the practicality of this method through gram-scale hydrogenation of acetophenone obtaining 87% yield with high turnover number (TON = 2610) at room temperature. Furthermore, stereoselective reduction of substituted cyclohexanones was achieved by tuning the steric bulk of the pincer NHC pro-ligands; thus, reduction of *t*-butyl-cyclohexanal in the presence of bulky CNC NHC pincer with N-Dipp wingtips delivered the kinetically controlled cis-4-*t*-butyl-cyclohexanol (98%, *cis*:*trans* >99:1), whereas the use of small NHC pro-ligand with N-Me wingtips furnished the thermodynamically controlled trans-isomer (95%, *trans*:*cis* = 89:11). This synthetically useful divergence is attributed to the bulky Co–H species experiencing more repulsion from the axial side and preference to attack from the less sterically hindered equatorial C=O face.

In 2020, the Bala group reported new air-stable six-coordinate Co(III)–NHC complexes **17a-c** and tested their reactivity in transfer hydrogenation of ketones (Scheme 29).[103a] The reactions were carried out in presence of cobalt complex **17** (0.4 mol%), KOH as a base (20 mol%) and 2-propanol as both the solvent and the hydrogen donor under reflux conditions. N-Me-substituted complex **17a** proved to be more efficient than more sterically demanding **17b** or **17c**, hence implying that relatively smaller substituents on the N-wingtip result in more active catalysts than bulkier *N*-substituents for this transfer hydrogenation. Mechanistically, the reaction is proposed to involve single-electron transfer. The catalyst stability throughout the reduction was studied by cyclic voltammetry, mass spectrometry, UV and IR techniques. The authors also found that at higher complex concentrations, agglomeration of active species in solution decreases catalytic activity of the catalysts. The same group reported C–N coupling using (^{Me}CCC)-Co(I)Cl-complex.[103b]

3.5. Hydrogenation of Esters

In 2020, the Liu group reported hydrogenation of nonactivated esters to alcohols catalyzed by Co–NHC complex **15** (Scheme 30 cf. Scheme 28).[104] The catalyst system involves $CoCl_2$ (2 mol%), pro-ligand **15** (2 mol%), ^{t}BuOK (10 mol%) under H_2 (30 bar) in THF at 100 °C. This reaction features a broad scope of esters, including aromatic esters, aliphatic esters, lactones and polyesters as well as pharmaceuticals, all of which were successfully reduced in good to excellent yields. Interestingly, when the N-Mes wingtip group of the NHC pro-ligand was replaced by other substituents, including Me, Ph, Dipp, no reactivity was observed. This steric effect indicates a major impact of the ligand structure on the

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catalytic activity. Notably, gram-scale hydrogenation was achieved at low catalyst loading with impressive turnover number (TON = 2,391), indicating high efficiency and stability of this Co–NHC catalytic system.

4. Hydrofunctionalization Reactions Catalyzed by Cobalt–NHC Complexes

Hydrofunctionalization reactions are among the most powerful tools for the direct access to C–Si and C–B bonds. Owing to the importance of this mode of catalysis, several reviews on the use of Earth abundant metals for catalytic hydrofunctionalization reactions have been published.[105–111] In this section, our focus is on hydrosilylation and hydroboration reactions catalyzed by cobalt–NHC complexes.

4.1. Hydrosilylation Reactions

In 2013, the Deng group reported well-defined, strongly electron-donating, silyl-donor-functionalized Co(II)–NHC complexes **18**, which efficiently catalyzed the anti-Markovnikov hydrosilylation of 1-octene in presence of $PhSiH_3$ (Scheme 31).[112] Single-crystal X-ray diffraction studies of these air- and moisture-sensitive complexes showed that all the complexes have a distorted square-planar cobalt(II) center. The longer Co–C(benzyl) bonds in the [(IMes’)Co] moiety in **18** are consistent with the strong trans effect of the silyl moieties. Complexes **18a-c** showed very high reactivity in hydrosilylation. Less-sterically hindered complex **18a** was the most reactive. Notably, the desired anti-Markovnikov product could be formed in 75% yield at very low catalyst loading of **18a** (0.005 mol %) at room temperature with high turnover number (TON = 15,000) in 24 h. In comparison to catalyst **18a**, cobalt carbonyl $[Co_2(CO)_8]$ and monodentate Co(II)–NHC, trans-$[(IPr_2Me_2)_2CoPh_2]$, were less effective, highlighting the role of the strongly electron-donating silyl ligand for the success of this hydrosilylation reaction.

Subsequently, in 2014, the Deng group reported three-coordinated cobalt(I)-alkyl and silyl complex **19** for the regio- and stereoselective hydrosilylation of alkynes (Scheme 32).[113] These reactions were catalyzed by **19** (2 mol %) in the presence of H_2SiPh_2 to deliver *β*-(*E*)-hydrosilylation products at room temperature or 70 °C in excellent yields. In stark contrast, the use of other well-known alkyne hydrosilylation catalysts, including $Co(IMes)(IMes)(N_2)$, $Co_2(CO)_8$, $Rh(PPh_3)_3Cl$, and $Pt_2(dvtms)_3$, afforded mixtures of *β*-(*E*), *β*-(*Z*) and α-vinylhydrosilanes. Interestingly, the three-coordinate Co(II)–NHC complex, $(IPr)Co(CH_2TMS)_2$, was also much less effective under the same conditions.

Various phenyl or alkyl substituted terminal alkynes are suitable substrates for this reaction, offering selective access to (*E*)-vinylsilanes. Notably, 1,6-diynes can be selectively reacted to furnish 1,2-dialkylidenecyclopentanes. In addition, at elevated temperatures (70 °C), selective *syn*-hydrosilylation of internal alkynes could also be accomplished. Alkynes bearing a trimethylsilyl group selectively afforded (*Z*)-α,α-disilylalkenes, where the Si-atom is adjacent to the smaller substituent. Mechanistically, the steric bulk of N-Ad wingtip directs the reaction selectivity. This reaction proceeds through a modified Chalk–Harrod-type mechanism. The proposed mechanism involves the following steps: (1) cobalt(I) complex **19** reacts with H_2SiPh_2 to give the silyl intermediate **A**; (2) alkyne coordinates to the intermediate **B** by replacing the phosphine ligand; (3) migratory insertion takes place

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to give the alkenyl metal species **C**; (4) Ph_2SiH_2 reacts with the intermediate **C** to deliver the desired hydrosilylation product along with the regeneration of the active catalyst **A**.

In 2016, Fout and co-workers reported highly selective anti-Markovnikov hydrosilylation of terminal alkenes using well-defined Co(II)–NHC CCC pincer complex (^{DIPP}CCC)CoN_2 (^{DIPP}CCC = bis(diisopropylphenyl-imidazol-2-ylidene)-phenyl) **20** as a catalyst (Scheme 33).[114] This method proceeds in presence of **20** (5 mol%) using tertiary silanes or hydrosiloxanes in benzene at room temperature. The method is notable for functional group tolerance to wide variety of substrates, including challenging functional groups, such as amines, nitriles, aldehydes, ketones, and esters, to give the corresponding hydrosilylated products in good to excellent yields. Furthermore, the method is exceedingly mild, permitting the successful use of unprotected alcohols and epoxides without ring opening, which is superior over other base metal catalysts. Cyclic alkenes and 1,1-disubstitued olefins, such as cyclohexene and limonene, are not reactive, presumably due to steric hindrance of the Dipp substituents. The proposed mechanism follows a Chalk-Harrod-type mechanism and involves the following steps: (1) oxidative addition of silane with complex **20** to afford the silyl hydride complex **A**; (2) coordination of the alkene forms species **B**; (3) migratory insertion; (4) reductive elimination to provide the hydrosilylation product and regenerate catalyst **20**.

Along the same lines, in 2017, Deng and co-workers reported hydrosilylation of alkenes catalyzed by unsymmetrical cobalt(II) amide complex $[(IMes/Me)Co(N(SiMe_3)_2)_2]$ **21** (Scheme 34).[115] This hydrosilylation reaction is promoted by **21** (1 mol%) in the presence of $HSi(OEt)_3$ (1.2 equiv) as the silane source at room temperature. Interestingly, other bulky Co(II)–NHC catalysts, such as $[(IPr)Co(N(SiMe_3)_2)_2]$, $[(IMes)Co(N(SiMe_3)_2)_2]$ and $[(IMes/Pr)Co(N(SiMe_3)_2)_2]$, were also active under the same conditions; however, showed lower reactivity than **21**. Similar to the previous reports, the functional group tolerance of this Co–NHC catalyzed hydrosilylation is broad, including compatibility with esters, epoxides and amines. Furthermore, hydrosilylation of 4-vinyl-cyclohexene occurred chemoselectively at the exocyclic vinyl group, demonstrating the capacity of **21** and related Co–NHC catalysts to differentiate steric bulk in alkenes. Sterically-demanding hydrosilanes, such as $HSiEt_3$ and 1,1,1,3,5,5,5-heptamethyltrisiloxane, were incompatible with this reaction. Mechanistically, complex **21** reacts with hydrosilane to provide the low-coordinated cobalt(I)-amide and cobalt(I)-hydride species, which may act as catalysts for the hydrosilylation.

In 2018, the Deng group reported two different cobalt(I)–NHC complexes, $[(IAd)(PPh_3)CoCl]$ **22** and $[(IMes)_2CoCl]$ **23**, for selective 2,1-hydrosilylation and 1,2-hydrosilylation of alkenes (Scheme 35).[97] The reaction was carried out in presence of **22** or **23** (2–5 mol%) and Ph_2SiH_2 (1.2 equiv) as the silane source in toluene at 70 °C. The most intriguing feature of this protocol is that the use of mono(NHC)cobalt complex $[(IAd)(PPh_3)CoCl]$ **22** (2 mol %) selectively provided the *anti*-Markovnikov hydrosilylation products, while bis(NHC)cobalt complex $[(IMes)_2CoCl]$ (5 mol %) **23** furnished the highly regioselective Markovnikov hydrosilylation. Notably, both alkyl- and aryl-substituted alkenes were smoothly transformed in good yields in the *anti*-Markovnikov hydrosilylation. Interestingly, in the Markovnikov hydrosilylation, although aryl-substituted alkenes were well-compatible, the alkyl-substituted alkenes gave relatively lower yields

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and regioselectivity. More sterically-demanding ortho-substituted styrenes and di-substituted alkenes were unreactive in both of the hydrosilylation methods. Mechanistically, the (NHC)cobalt(I) silyl species and bis(NHC)cobalt(I) hydride species might be the key intermediates in the reactions. The selectivity between *anti*-Markovnikov and Markovnikov hydrosilylation might be a result of different steric nature of *N*-alkyl imidazolylidene, IAd, vs. its *N*-aryl counterpart, IMes, and the potential of IMes to promote $\pi\cdots\pi$ interactions with aryl-substituted alkenes.

Recently, the same group established a novel synthetic route for the selective Markovnikov hydrosilylation of terminal alkynes with tertiary silanes using dicobalt(0)–NHC carbonyl complex $[(IPr)_2Co_2(CO)_6]$ **24** (Scheme 36).[116] This reaction provides an efficient way to synthesize α-vinylsilanes with excellent selectivity. Apart from the broad hydrosilylation scope of various alkyl- and aryl-substituted terminal alkynes, hydrosilylative polymerization of terminal alkynes to produce silicon polymers makes this protocol stand out among other Co–NHC catalyzed methods. Importantly, NHC ligand is required in this system as the phosphine ligand replacement did not offer desired selectivity of α:β vinylsilanes (observed selectivity 1:2 to 1:1).

Mechanistic studies revealed that among possible cobalt intermediates, the mono-(NHC)-dicobalt alkyne complex, $[(IPr)(CO)_2Co(\mu\text{-}\eta^2\text{:}\eta^2\text{-HCCR})Co(CO)_3]$, showed catalytic activity at both 60 °C and room temperature. The authors proposed that the mono(IPr)-dicobalt species is the active catalyst for the Markovnikov hydrosilylation reaction. α-Selectivity in the product formation was attributed to the unique binding pattern of $\mu\text{-}\eta^2\text{:}\eta^2$-HCCPh coordination of alkyne in dicobalt complex **25a** and the steric hindrance engendered by the NHC ligand. The proposed mechanism involves the following steps: (1) first, the precatalyst **24** reacts with the alkyne to form cobalt-alkyne complexes **A** and **A'** followed by dissociation of CO or IPr ligand to provide **B**; (2) hydrosilane interacts with species **B** in a sterically-accessible fashion to give intermediate **C**, which takes part in σ-bond metathesis; (3) new Si–C bond is formed upon reductive elimination from **D** and **D'**; (4) the desired alkene product leaves from the intermediate **E**, keeping the coordinatively unsaturated dicobalt complex **F** ready for the next catalytic cycle.

4.2. Hydroboration Reactions

In 2016, Hollis and co-workers reported a well-defined, distorted octahedral, CCC pincer Co(III)–NHC complex **26** and its application in hydroboration of styrene (Scheme 37).[117] This air-stable Co–NHC pincer was synthesized from an isolated Zr–NHC pincer by transmetallation with $Co(acac)_3$. The hydroboration reaction was promoted by complex **26** (0.3 mol%) as precatalyst in the presence of HBpin (1 equiv) and $LiHBEt_3$ (1 mol%) as the hydride additive in THF at 22 °C. Markovnikov hydrosilylation product was obtained with high selectivity (20:1) in this method.

In 2017, selective anti-Markovnikov hydroboration of alkenes and nitriles was established by Fout and co-workers using Co(I)–NHC pincer complex $(^{DIPP}CCC)CoN_2$ **20** (Scheme 38),[118] which was previously applied in alkene hydrosilylation by the same group (cf. Scheme 33).[114] This transformation shows broad scope and functional group compatibility,

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including tolerance to many useful functional groups, such as ketones, esters, amines, allyl ethers, epoxides. The reaction is sensitive to sterics in that sterically-hindered substrates, such as limonene and cyclohexene, did not afford hydroboration products. In contrast, 4-vinylcylohexene and isoprene underwent selective hydroboration at the less-substituted olefinic bond. Interestingly, at higher temperature, the same method could be applied to various aromatic and aliphatic nitriles, which afforded the corresponding N,N-bis(borylated) amines in good yields. Deuterium labelling studies indicated that both 2,1- and 1,2-insertions pathways were involved in this process; however, the 2,1-insertion was unproductive and reversibly underwent β-hydride elimination. The proposed mechanism involves the following steps: (1) oxidative addition of borane with **20** first generates a Co(III)-hydrido boryl species **A**; (2) the alkene or nitrile substrate coordinates with **A** to form the intermediate **B**, which furnishes both possible insertion pathways to form Co(III)-alkyl intermediates **C** and **D**; (3) reversible β-hydride elimination pathway in secondary alkyl cobalt species **D** reverts back to **B**, which follows the facile product forming pathway to **C** because of steric shielding; (4) reductive elimination furnishes the selective *anti*-Markovnikov product along with regeneration of Co(I)-catalyst **20**.

In 2018, Geetharani and co-workers developed the Markovnikov hydroboration of alkenes using cobalt(I)–NHC complex, $Co(IMes)_2Cl$ **23** (Scheme 39, cf. Scheme 35).[119] The reaction is promoted by **23** (3 mol%) in the presence of HBpin (1.1 equiv) in THF at 50 °C. This protocol is effective for a wide variety of alkenes, including challenging multisubstituted internal alkenes, such as 1,1-disubstituted and 1,1,2-trisubstituted vinylarenes that furnish valuable branched alkylboronic esters. The reaction gives higher selectivity for vinylarenes bearing electron-donating substituents than with electron-withdrawing substituents. Interestingly, no hydroborated product was observed when the analogous cobalt(II)–NHC complex, $Co(IMes)_2Cl_2$, was used as a catalyst. The authors proposed that the Markovnikov regioselectivity is due to η^3-benzylic coordination of the styryl moiety, which was previously observed in Ni-catalysis. This assumption was further supported by the observation that aliphatic alkenes selectively produced anti-Markovnikov products.

5. Cobalt–NHC Catalyzed Cycloaddition Reactions

Only few examples of Co–NHC systems in cycloaddition reactions have been reported to date,[120–122] despite advantages of NHC ligands over phosphines in this mode of catalysis. In 2003, Gibson and co-workers reported the synthesis of NHC–dicobalt(0) complexes **27**–**29** and their catalytic application in the intramolecular Pauson-Khand reaction (Scheme 40).[120] The authors proposed that phosphine-free (NHC)carbonyl–cobalt(0) species, $[(NHC)Co_2(CO)_6]$, is initially formed from **27**–**29** and promotes the catalysis.

In 2005, Okamoto and co-workers developed the intramolecular cyclotrimerization of triynes using NHC–$CoCl_2$ as a catalyst in the presence of Zn as a reductant (Scheme 41).[121] Optimization studies indicated that the bulky IPr was significantly more effective than IMes in this reaction. Comparison between metal precursors showed that $CoCl_2$ showed higher activity than $NiCl_2$ or $PdCl_2$. $[(IPr)Co(II)Cl_2]$ complex was separately synthesized from IPr/$CoCl_2$ in 2:1 ratio and used for the cyclotrimerization reaction. A variety of triynes can

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be used in this cyclotrimerization reaction in high yields; however, as observed in other Co–NHC-catalyzed reactions, sterically-hindered substrates were less efficient. The authors proposed that the *in situ* generated Co(II)–NHC complex is reduced by Zn to give a low valent cobalt complex which acts as an active catalyst in the reaction.

In 2009, Gandon and co-workers reported a practical approach to [2+2+2] cycloaddition of enediynes using Co(II)–NHC system (Scheme 42).[122] This reaction proceeds in the presence of CoI_2 (1 equiv), Mn (1 equiv), IPr (6 mol%) in THF at reflux. Interestingly, the use of PPh_3 ligand instead of IPr made this cycloisomerization less effective. Furthermore, the use of other cobalt salts, such as $CoCl_2$, $CoBr_2$, $Co(acac)_2$ and $Co(acac)_3$, was unsuccessful. This cyclization was highly efficient compared to the previous related protocols where a stoichiometric amount of cobalt source was required along with the large excess of PPh_3 and Mn. Meanwhile, Mn is important as a reductant in this method as the use of Zn did not give any products. Enediynes containing several functional groups and heteroatoms were well tolerated and provided tricyclic products in generally high yields. Notably, sterically demanding enediynes can also be tolerated to give the desired cyclization products.

6. Miscellaneous Reactions

In 2006, Llewellyn and co-workers reported hydroformylation of 1-octene catalyzed by cobalt(I)–hydride complex, $[Co(IMes)(CO)_3(H)]$, **31** under mild conditions (Scheme 43).[123] Complex **31** could be efficiently synthesised from the corresponding acyl complex, $[Co(IMes)(CO)_3(COMe)]$, **30** under hydrogen atmosphere. The reaction selectively affords 2-methyloctanal with branched selectivity (cf. linear nonanal selectivity). The authors proposed that isomerisation of terminal alkene to internal alkene occurs prior to the hydroformylation step, and is the reason for the unusual branched selectivity in product formation. The use of relatively low temperature in this method prevents the reduction to alcohol by-product. The implementation of mild reaction conditions enabled by Co–NHC represents a significant advantage of this method over the existing Co–phosphine complex, $[Co(PR_3)(CO)_3(H)]$, in hydroformylation catalysis.

In 2018, Yorimitsu and co-workers reported Co–NHC-catalyzed reduction of aryl sulfones using primary alkyl Grignard reagents as a hydride source (Scheme 44).[124] The reaction is efficiently promoted by $Co(acac)_2$ (10 m0l%), $C_6H_{13}MgBr$ (3 equiv) and IPr·HCl (12 m0l %) in THF at 75 °C. Several other NHC ligand precursors can be used in this transformation, including ICy·HCl, I(2-Ad)·HBF_4, SIPr·HCl, however, IPr·HCl is the most effective. This reaction features broad substrate scope, showing tolerance to pyridyl, alkenyl and benzylic sulfones. Furthermore, N-tosylindole was smoothly converted to indole by N–S cleavage.

The Grignard reagent must be capable of β-hydride elimination as methyl and arylmagnesium reagents were unsuccessful. The proposed mechanism involves the following steps: (1) generation of low-valent Co–NHC complex **A**; (2) oxidative addition with sulfone to form arylcobalt methanesulfinate **B**; (3) transmetalation with alkylmagnesium reagent to afford alkylarylcobalt **C**; (4) β-hydride elimination; (5) reductive elimination to deliver the desired product along with regeneration of the active species **A**.

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In 2018, the Deng group reported the synthesis of low-coordinate Co–NHC complexes **34**, **35**, **37**, which feature Co coordination to primary aryl phosphines. Their reactivity was compared with Co–NHC complexes **32**, **33**, **36** in dehydrocoupling of primary aryl phosphines to give diphosphines (Scheme 45).[125] These reactions were carried out in presence of Co–NHC (10 mol%), H_2PAr (2 equiv) in D_6-benzene at 80 °C. The excellent activity of **32**–**36** in dehydrocoupling was proposed to arise from the use of strongly σ-donating and sterically demanding NHC ligands.

Subsequently, the Deng group reported a series of NHC– cobalt–N_2 complexes **38**–**40**, and their application in dinitrogen reduction (Scheme 46).[126] The authors showed that all of the prepared NHC–cobalt complexes, Co(0)–NHC **38**, Co(−1)–NHC **39**, and Co(II)–NHC $[(ICy)_2Co(\eta^2\text{-}R_3SiNNSiR_3)]$ **40** or $(ICy)_2CoCl_2$ **41**, have the capacity to catalyze the reduction of N_2 with R_3SiCl/KC_8 to give $N(SiMe_3)_3$. These NHC–Co catalysts show comparable turnover numbers (TON = 120) and surpass the efficiency of the known 3d-metal catalysts.

In 2018, Maleczka and co-workers reported mono- or diborylation of benzylic C(*sp*^{3})–H bonds using Co(II)–NHC precatalyst, $[(IPr)_2Co(O\textit{t}Bu)_2]$ **42** (Scheme 47).[127] This method was extended to C(*sp*^{2})–H borylation of electron-rich heterocycles, such as indoles, pyrroles, and pyrazoles. Borylation of indoline derivatives occurred at the C(*sp*^{3})–H bond adjacent to the nitrogen atom. Competition studies between toluene and N-methyl pyrazole suggested that precatalyst **42** favors C–H borylation of C(*sp*^{2})–H bonds of heteroarenes over C(*sp*^{3})–H of benzylic alkyl groups. This cobalt complex **42** is the first 3d transition metal precatalyst that promotes selective borylation of primary and secondary benzylic C(*sp*^{3})–H bonds.

In 2020, Wei and co-workers reported an intramolecular decarbonylative coupling catalyzed by Co–NHCs (Scheme 48).[128] This reaction relies on pyrimidine-directed C–C bond cleavage of 2-acylindoles and pyridine nitrogen-directed C–C bond cleavage of diarylketones to afford synthetically useful biaryl derivatives. The catalytic system involves $Co_2(CO)_8$ (10 mol%), IMes·HCl (20 mol%) and $CsCO_3$ (40 mol %) in dioxane at 150 °C. The driving force is the affinity of cobalt to carbonyl groups. Interestingly, the reaction was unsuccessful under Ni-catalysis. The scope of the reaction is broad, and as expected, decarbonylation requires high temperature. The method was further exemplified in the total synthesis of pharmaceuticals.

In 2020, Liu and co-workers reported a series of cobalt complexes for the synthesis of cyclic carbonates from epoxides and carbon dioxide (Scheme 49).[129] Among the complexes synthesized, complex **43** was the most reactive. The method allows for achieving high turnover number (TON = 22,500). There is a strong counteranion effect in the order of $Br^- > Cl^- > I^-$. This method was successfully applied to challenging internal epoxides and fatty acid-derived epoxides with good to excellent yields (50%–94%). Tetrabutyl ammonium bromide (TBAB) has a crucial role in this reaction, acting as a nucleophilic catalyst. The high activity of complex **43** relies on the trans effect between NHCs and acetylacetone ligand, which the authors established through spectroscopic methods and DFT calculations. DFT studies indicated an electron transfer process during elimination of the acetylacetone group, which leaves a vacant coordination site at the cobalt centre and changes the valence

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state of cobalt from Co(III) to Co(II). The proposed mechanism involves the following steps: (1) coordination of epoxide to intermediate **A** to form **B**; (2) nucleophilic bromide attack with TBAB to give **C**; (3) negatively charged oxygen in **C** reacts with carbon dioxide to form an open-chain intermediate **D**; (4) nucleophilic attack of oxygen at the C–Br bond gives intermediate **E**; (5) release of epoxide from **E** regenerates the active catalyst **A**.

In 2015, Sarkar and co-workers reported the mesoionic pyridylcarbene cobalt(III) complex **44** in electrocatalytic H_2 production, employing acetic acid as a proton source (Figure 3A).[130] Interestingly, the analogous pyridyltriazole complex **45** and (bis)triazole complex **46** showed no activity in the reaction. This mesoionic carbene Co(III) complex showed very high turnover number (650,000) during 30 min of electrocatalysis in the reaction-diffusion layer. Furthermore, a TOF of 4×10^2 s^{-1} was achieved at very low overpotential of 0.13 V. The authors proposed that the remarkable activity of **44** results from a strong $C_{(carbene)}$–Co bond in mesoionic carbene ligand. Previously, Sakai reported a photochemical hydrogen evolution from water employing Co(III)–NHC complex **47**.[131]

In 2019, Jurss and co-workers reported a series of stable cobalt(II)–NHC complexes **48**–**50** for electrocatalytic CO_2 reduction (Figure 3B).[132] The catalytic activity was found to increase with rigidity of the ligand: **50** > **49** > **48**. Localized orbital bonding analysis and DFT calculations suggested that the first reduction is ligand-based to form $[Co(II)(L^{\bullet-})]^+$ species. Kinetic studies indicated that the catalysis is firstorder with respect to catalyst and CO_2, and second-order with respect to H_2O at low concentrations.

7. Conclusions and Outlook

As demonstrated in this review, it is evident that Co–NHC catalysis is a burgeoning area of research with a plethora of highly active complexes that promote valuable synthetic reactions.

Transformations, such as cross-cross-coupling, hydrogenations, hydrofunctionalizations and cycloadditions, exploit diverse oxidation states of cobalt–NHC catalysts available from −1 to +3 in their mechanisms. Many of the developed methods, such as Suzuki cross-coupling, Kumada cross-coupling, hydrogenation of olefins, Markovnikov hydrosilylation of alkynes, showed that NHC ligands are the stand-out choice over the more ubiquitous phosphine ligands. Moreover, the unique reactivity of cobalt–NHC catalysts often outshines the more common 3d transition metals, such as iron or nickel, in many cases. One-electron reduction chemistry of Co–NHCs enabled by redox-active CNC ligands also brings a new aspect to this field. An eye-catching development is the regiocontrolled hydrogenation and selective hydrosilylation of alkenes catalyzed by different Co–NHC complexes. Electrochemical transformations under cobalt–NHC catalysis are yet another important development in this area. All of these recent discoveries impart knowledge about the unique reactivity and selectivity of cobalt–NHC catalytic systems.

In general, various well-defined Co–NHC catalysts having tetrahedral, trigonal-planar, square planner, trigonal bipyramidal, octahedral and two-legged piano stool geometry have been employed in catalysis. In many cases, these catalysts show distortion from standard

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geometry. Catalytic pathways include redox-neutral, one-electron redox and two-electron redox pathways. In many cases, a low-valent cobalt species is generated *in situ* by the reducing agent present under the reaction conditions. Co–NHC complexes change their spin states depending on the associated ligands, geometry and oxidation states. For example, $[CoCl_2(IMes)_2]$ characterized by a pseudo-tetrahedral geometry stays in high spin state (S = 3/2) at ground state; however, the corresponding alkyl complex $[Co(Me)_2(IMes)_2]$ with a square-planar geometry is in low spin state (S = 1/2). In contrast, $[Co(CH_2SiMe_3)_2(IPr)]$ characterized by a trigonal-planar geometry is in high spin state (S = 3/2). Tuning of NHC ligands has a comparatively larger effect on changes in bond angles of the Co–NHC complexes rather than Co–carbene bond lengths with the exception of pincer ligands, where Co–$C_{(NHC)}$ bond is significantly longer in CCC–NHC pincer ligands compared to CNC–NHC ligands.

This rapidly evolving field also has numerous challenges that should be addressed. (1) First, the synthesis of stable and active cobalt catalysts is one of the most important criteria in catalysis for practical applications by a broad range of researchers, including in academia and industry. Many of the complexes that have been discussed in this review are air- and moisture-sensitive, hence, needing a strict inert atmosphere for their synthesis and handling. (2) The limited diversity in substrates scope is also an issue in several established methods. The execution of new cobalt catalytic systems with rational ligand design could address these limitations. (3) Until now, many C–C cross-coupling reactions have been reported; however, few reports on C–X bond forming cross-coupling reactions were perceived. Thus, the development of new cross-couplings should be more rigorously explored. (4) Furthermore, there are no studies to date that have addressed the difference between *in situ* generated catalysts and well-defined cobalt catalysts. (5) Enantioselective transformations, including asymmetric hydrogenations and hydrofunctionalizations is another important direction using suitable chiral NHC ligands for Co–NHC catalysis. (6) Apart from that, cobalt–NHC catalysts should become useful in olefin polymerizations, which require specific electronic and steric tuning. Thus far, cobalt-catalyzed olefin polymerization reactions are mainly based on sterically hindered bis(imino)pyridine derivatives, which could be replaced with bidentate NHC ligands. (7) In another direction, the use of well-defined, stable and rapidly-activating Co–NHC complexes is still rare and requires more attention. (8) Finally, more extensive mechanistic studies need to be routinely conducted to further develop the Co–NHC chemistry. A comprehensive understanding of the mechanisms would result in new avenues for the design and discovery of improved catalyst systems, which could have widespread applications in various areas of organic synthesis and catalysis.

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REFERENCES

(1). (a)Hopkinson MN; Richter C; Schedler M; Glorius F An overview of N-heterocyclic carbenes. Nature 2014, 510, 485–496. [PubMed: 24965649] (b)Nolan SP N-Heterocyclic Carbenes: Effective Tools for Organometallic Synthesis, Ed.; Wiley: Weinheim, 2014, pp. 1–568.(c)Cazin CSJ N-Heterocyclic Carbenes in Transition Metal Catalysis, Ed.; Springer: New York, 2011, pp. 1–336.(d)Diez-Gonzalez S N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools, Ed.; RSC: Cambridge, 2016, pp. 1–442.(e)Huynh HV The Organometallic Chemistry of N-Heterocyclic Guerret O; Gabbai FP; Bertrand G Stable Carbenes. Chem. Carbenes, Wiley: Hoboken, 2017, pp. 1–368.(f)Bourissou D; Rev. 2000, 100, 39–92.(g)Hermann WA N-Heterocyclic Carbenes: A New Concept in Organometallic Catalysis. Angew. Chem., Int. Ed 2002, 41, 1290–1309.(h)Peris E Routes to N-Heterocyclic Carbene Complexes. Top. Organomet. Chem 2007, 23, 83–116.(i)Peris E Smart N-Heterocyclic Carbene Ligands in Catalysis. Chem. Rev 2018, 118, 9988–10031. [PubMed: 28151645] (j)Iglesias M; Oro LA A leap forward in iridium–NHC catalysis: new horizons and mechanistic insights. Chem. Soc. Rev 2018, 47, 2772–2808. [PubMed: 29557434]

(2). Arduengo AJ III; Harlow RL; Kline M A Stable Crystalline Carbene. J. Am. Chem. Soc 1991, 113, 361–363.

(3). Herrmann WA; Elison M; Fischer J; Köcher C; Artus GRJ Metal Complexes of N-Heterocyclic Carbenes—A New Structural Principle for Catalysts in Homogeneous Catalysis. Angew. Chem., Int. Ed. Engl 1995, 34, 2371–2374.

(4). Vougioukalakis GC; Grubbs RH Ruthenium-Based Heterocyclic Carbene-Coordinated Olefin Metathesis Catalysts. Chem. Rev 2010, 110, 1746–1787. [PubMed: 20000700]

(5). Ogba OM; Warner NC; O'Leary DJ; Grubbs RH Recent advances in ruthenium-based olefin metathesis. Chem. Soc. Rev 2018, 47, 4510–4544. [PubMed: 29714397]

(6). Fortman GC; Nolan SP N-Heterocyclic Carbene (NHC) Ligands and Palladium in Homogeneous Cross-Coupling Catalysis: A Perfect Union. Chem. Soc. Rev 2011, 40, 5151–5169. [PubMed: 21731956]

(7). Cesar V; Bellemin-Laponnaz S; Gade LH Chiral N-Heterocyclic Carbenes as Stereodirecting Ligands in Asymmetric Catalysis. Chem. Soc. Rev 2004, 33, 619–636. [PubMed: 15592627]

(8). Enders D; Niemeier O; Henseler A Organocatalysis by N-Heterocyclic Carbenes. Chem. Rev 2007, 107, 5606–5655. [PubMed: 17956132]

(9). Nair V; Vellalath S; Babu BP Recent Advances in Carbon-Carbon Bond-Forming Reactions Involving Homoenolates Generated by NHC Catalysis. Chem. Soc. Rev 2008, 37, 2691–2698. [PubMed: 19020682]

(10). Nair V; Menon RS; Biju AT; Sinu CR; Paul RR; Jose A; Sreekumar V Employing Homoenolates Generated by NHC Catalysis in Carbon-Carbon Bond-Forming Reactions: State of the Art. Chem. Soc. Rev 2011, 40, 5336–5346. [PubMed: 21776483]

(11). Wang FJ; Liu LJ; Wang WF; Li SK; Shi M Chiral NHC-Metal-Based Asymmetric Catalysis. Coord. Chem. Rev 2012, 256, 804–853.

(12). Bugaut X; Glorius F Organocatalytic Umpolung: N-Heterocyclic Carbenes and Beyond. Chem. Soc. Rev 2012, 41, 3511–3522. [PubMed: 22377957]

(13). Fevre M; Pinaud J; Gnanou Y; Vignolle J; Taton D N-Heterocyclic Carbenes (NHCs) as Organocatalysts and Structural Components in Metal-Free Polymer Synthesis. Chem. Soc. Rev 2013, 42, 2142–2172. [PubMed: 23288304]

(14). Crabtree RH Abnormal, Mesoionic and Remote N-Heterocyclic Carbene Complexes. Coord. Chem. Rev 2013, 257, 755–766.

(15). Soleilhavoup M; Bertrand G Cyclic (Alkyl)(Amino) Carbenes (Caacs): Stable Carbenes on the Rise. Acc. Chem. Res 2015, 48, 256–266 [PubMed: 25515548]

(16). Zhao Q; Meng GR; Nolan SP; Szostak M N-Heterocyclic Carbene Complexes in C–H Activation Reactions. Chem. Rev 2020, 120, 1981–2048. [PubMed: 31967451]

(17). Bellotti P; Koy M; Hopkinson MN; Glorius F Recent advances in the chemistry and applications of N- heterocyclic carbenes. Nat. Rev. Chem 2021, 5, 711–725.

Author Manuscript Author Manuscript Author Manuscript Author Manuscript

(18). Kovuru G Chiral Iron Catalysts for Asymmetric Synthesis. Chem. Rev 2013, 113, 3248–3296. [PubMed: 23461563]

(19). Riener K; Haslinger S; Raba A; Högerl MP; Cokoja M; Herrmann WA; Kühn FE Chemistry of Iron N- Heterocyclic Carbene Complexes: Syntheses, Structures, Reactivities, and Catalytic Applications. Chem. Rev 2014, 114, 5215–5272. [PubMed: 24655079]

(20). For selected reviews on Co-catalysis in C-H functionalization, see: (a)Gao K; Yoshikai N Low-Valent Cobalt Catalysis: New Opportunities for C-H Functionalization. Acc. Chem. Res 2014, 47, 1208–1219. [PubMed: 24576170] (b)Moselage M; Li J; Ackermann L Cobalt-Catalyzed C-H Activation. ACS Catal. 2016, 6, 498–525.(c)Sk MR; Bera SS; Basuli S; Metya A; Maji MS Recent Progress in the C–N Bond Formation via High-Valent Group 9 Cp*M(III)-Catalyzed Directed sp^2 C–H Activation. Asian J. Org. Chem 2020, 9, 1701–1717. For selected examples, see: (d)Li J; Ackermann L Cobalt-Catalyzed C-H Arylations with Weakly-Coordinating Amides and Tetrazoles: Expedient Route to Angiotensin-II-Receptor Blockers. Chem. Eur. J 2015, 21, 5718–5722. [PubMed: 25728566] (e)Oliveira JCA; Dhawa U; Ackermann L Insights into the Mechanism of Low-Valent Cobalt-Catalyzed C-H Activation. ACS Catal. 2021, 1505–1515.

(21). Guérinot A; Cossy J Cobalt-Catalyzed Cross-Couplings between Alkyl Halides and Grignard Reagents. Acc. Chem. Res 2020, 53, 1351–1363. [PubMed: 32649826]

(22). Tasker SZ; Standley EA; Jamison TF Recent Advances in Homogeneous Nickel Catalysis. Nature 2014, 509, 299–309. [PubMed: 24828188]

(23). Su B; Cao ZC; Shi Z-J Exploration of Earth-Abundant Transition Metals (Fe, Co, and Ni) as Catalysts in Unreactive Chemical Bond Activations. Acc. Chem. Res 2015, 48, 886–896. [PubMed: 25679917]

(24). Gandeepan P; Müller T; Zell D; Cera G; Warratz S; Ackermann L 3d Transition Metals for C-H Activation. Chem. Rev 2019, 119, 2192–2452. [PubMed: 30480438]

(25). Chirik PJ Iron- and Cobalt-Catalyzed Alkene Hydrogenation: Catalysis with Both Redox-Active and Strong Field Ligands. Acc. Chem. Res 2015, 48, 1687–1695. [PubMed: 26042837]

(26). Li Y-Y; Yu S-L; Shen W-Y; Gao J-X Iron-, Cobalt-, and Nickel-Catalyzed Asymmetric Transfer Hydrogenation and Asymmetric Hydrogenation of Ketone. Acc. Chem. Res 2015, 48, 2587–2598. [PubMed: 26301426]

(27). Liu Y; Cheng J; Deng L Three-Coordinate Formal Cobalt(0), Iron(0), and Manganese(0) Complexes with Persistent Carbene and Alkene Ligation. Acc. Chem. Res 2020, 53, 244–254. [PubMed: 31880150]

(28). Alig L; Fritz M; Schneider S First-Row Transition Metal (De)Hydrogenation Catalysis Based On Functional Pincer Ligands Chem. Rev 2019, 119, 2681–2751. [PubMed: 30596420]

(29). Hapke M; Hilt G Cobalt Catalysis in Organic Synthesis: Methods and Reactions; Wiley-VCH: Weinheim, 2020, pp 1–462.

(30). Gandeepan P; Cheng C-H Cobalt Catalysis involving π Component in Organic Synthesis. Acc. Chem. Res 2015, 48, 1194–1206. [PubMed: 25854540]

(31). Cotton FA, Wilkinson G, Murillo CA, Bochmann M Advanced Inorganic Chemistry, 6th Edition; Eds.; John Wiley & Sons: New York, 1999; pp 877–878.

(32). Frazier BA; Wolczanski PT; Lobkovsky EB Aryl-Containing Chelates and Amine Debenzylation to Afford 1,3-Di-2-pyridyl-2-azaallyl (smif): Structures of {K-C,N,Npy_2-(2-pyridylmethyl)$_2$N(CH_2(4-t Bu-phenyl-2-yl))}FeBr and (smif)CrN$(TMS)_2$. Inorg. Chem 2009, 48, 11576–11585. [PubMed: 19769380]

(33). (a)Yamada K Cobalt: Its Role in Health and Disease. In: Sigel A, Sigel H, Sigel R. (eds.). Interrelations between Essential Metal Ions and Human Diseases. Metal Ions in Life Sciences. 13. Springer. pp. 295–320. [PubMed: 24470095] (b)Jefferson Lab. It’s Elemental: The Periodic Table of Elements”. https://education.jlab.org/itselemental/(accessed Dec 20, 2021).

(34). Cahiez G; Moyeux A Cobalt-Catalyzed Cross-Coupling Reactions. Chem. Rev 2010, 110, 1435–1462. [PubMed: 20148539]

(35). Gao K; Yoshikai N Regioselectivity-Switchable Hydroarylation of Styrenes. J. Am. Chem. Soc 2011, 133, 400–402. [PubMed: 21158461]

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Author Manuscript

(36). Lukasevics L; Cizikovs A; Grigorjeva L C–H Bond Functionalization by High-Valent Cobalt Catalysis: Current Progress, Challenges and Future Perspectives. Chem. Commun 2021, 57, 10827–10841.

(37). Shirakawa E; Imazaki Y; Hayashi T Cobalt-Catalyzed Coupling of Alkenyl Triflates with Aryl and Alkenyl Grignard Reagents. Chem. Lett 2008, 37, 654–655.

(38). Chen Q-A; Kim DK; Dong VM Regioselective Hydroacylation of 1,3-Dienes by Cobalt Catalysis. J. Am. Chem. Soc 2014, 136, 3772–3775. [PubMed: 24588202]

(39). Hilt G; du Mesnil F-X; Lüers S An Efficient Cobalt(I) Catalyst System for the Selective 1,4-Hydrovinylation of 1,3-Dienes. Angew. Chem., Int. Ed 2001, 40, 387–389.

(40). Santhoshkumar R; Mannathan S; Cheng C-H Ligand-Controlled Divergent C-H Functionalization of Aldehydes with Enynes by Cobalt Catalysts. J. Am. Chem. Soc 2015, 137, 16116–16120. [PubMed: 26645104]

(41). (a)Korstanje TJ; van der Vlugt JI; Elsevier CJ; de Bruin B Hydrogenation of Carboxylic Acids with a Homogeneous Cobalt Catalyst. Science 2015, 350, 298–302. [PubMed: 26472903] (b)Cabrero-Antonino JR; Adam R; Junge K; Beller M Cobalt-Catalysed Reductive C–H Alkylation of Indoles Using Carboxylic Acids and Molecular Hydrogen. Chem. Sci 2017, 8, 6439–6450. [PubMed: 29163930]

(42). (a)Federsel C; Ziebart C; Jackstell R; Baumann W; Beller M Catalytic Hydrogenation of Carbon Dioxide and Bicarbonates with a Well-Defined Cobalt Dihydrogen Complex. Chem.-Eur. J 2012, 18, 72–75. [PubMed: 22147509] (b)Adam R; Bheeter CB; Cabrero-Antonino JR; Junge K; Jackstell R; Beller M Selective Hydrogenation of Nitriles to Primary Amines by using a Cobalt Phosphine Catalyst. ChemSusChem 2017, 10, 842–846. [PubMed: 28066996]

(43). Adam R; Cabrero-Antonino JR; Spannenberg A; Junge K; Jackstell R; Beller M A General and Highly Selective Cobalt-Catalyzed Hydrogenation of N-Heteroarenes under Mild Reaction Conditions. Angew. Chem., Int. Ed 2017, 56, 3216–3220.

(44). Yang J; Seto YW; Yoshikai N Cobalt-Catalyzed Intermolecular Hydroacylation of Olefins through Chelation-Assisted Imidoyl C–H Activation. ACS Catal. 2015, 5, 3054–3057.

(45). Obligacion JV; Semproni SP; Pappas I; Chirik PJ Cobalt-Catalyzed C(sp^2)-H Borylation: Mechanistic Insights Inspire Catalyst Design. J. Am. Chem. Soc 2016, 138, 10645–10653. [PubMed: 27476954]

(46). Wu CZ; Teo WJ; Ge SZ Cobalt-Catalyzed (*E*)-Selective anti-Markovnikov Hydrosilylation of Terminal Alkynes. ACS Catal. 2018, 8, 5896–5900.

(47). Jin M-Y; Yoshikai N Cobalt–Xantphos-Catalyzed, LiClMediated Preparation of Arylzinc Reagents from Aryl Iodides, Bromides, and Chlorides. J. Org. Chem 2011, 76, 1972–1978. [PubMed: 21384804]

(48). Gibson SE; Kaufmann KAC; Haycock PR; White AJP; Hardick DJ; Tozer MJ Pendant Alkenes Promote Cobalt–Cobalt Bond Cleavage in (Alkyne)(binap)tetracarbon-yldicobalt(0) Complexes. Organometallics 2007, 26, 1578–1580.

(49). Kim DK; Riedel J; Kim RS; Dong VM Cobalt Catalysis for Enantioselective Cyclobutanone Construction. J. Am. Chem. Soc 2017, 139, 10208–10211. [PubMed: 28704053]

(50). Friedfeld MR; Zhong HY; Ruck RT; Shevlin M; Chirik PJ Cobalt-Catalyzed Asymmetric Hydrogenation of Enamides Enabled by Single-Electron Reduction. Science 2018, 360, 888–893. [PubMed: 29798879]

(51). (a)Spentzos AZ; Barnes CL; Bernskoetter WH Effective Pincer Cobalt Precatalysts for Lewis Acid Assisted CO_2 Hydrogenation. Inorg. Chem 2016, 55, 8225–8233. [PubMed: 27454669] (b)Mills MR; Barnes CL; Bernskoetter WH Influences of Bifunctional PNPPincer Ligands on Low Valent Cobalt Complexes Relevant to CO_2 Hydrogenation. Inorg. Chem 2018, 57, 1590–1597. [PubMed: 29350924] (c)Zhang G; Scott BL; Hanson SK Mild and Homogeneous Cobalt-Catalyzed Hydrogenation of C–C, C–O, and C–N Bonds. Angew. Chem., Int. Ed 2012, 51, 12102–12106.

(52). Gomes P; Gosmini C; Périchon J Cobalt-Catalyzed Cross-Coupling Reactions of Arylboronic Esters and Aryl Halides. Tetrahedron 2003, 59, 2999–3002.

(53). Adak L; Yoshikai N Cobalt-Catalyzed Preparation of Arylindium Reagents from Aryl and Heteroaryl Bromides. J. Org. Chem 2011, 76, 7563–7568. [PubMed: 21838263]

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Author Manuscript

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(54). Mao JY; Liu FP; Wang M; Wu L; Zheng B; Liu SZ; Zhong JC; Bian QH; Walsh PJ Cobalt–Bisoxazoline-Catalyzed Asymmetric Kumada Cross-Coupling of Racemic α-Bromo Esters with Aryl Grignard Reagents. J. Am. Chem. Soc 2014, 136, 17662–17668. [PubMed: 25479180]

(55). Chen C; Dugan TR; Brennessel WW; Weix DJ; Holland PL Z-Selective Alkene Isomerization by High-Spin Cobalt(II) Complexes. J. Am. Chem. Soc 2014, 136, 945–955. [PubMed: 24386941]

(56). Raya B; Biswas S; RajanBabu TV Selective Cobalt-Catalyzed Reduction of Terminal Alkenes and Alkynes Using (EtO)2Si(Me)H as a Stoichiometric Reductant. ACS Catal. 2016, 6, 6318–6323. [PubMed: 28078166]

(57). (a)Zhang L; Zuo Z; Wan X; Huang Z Cobalt-Catalyzed Enantioselective Hydroboration of 1,1-Disubstituted Aryl Alkenes. J. Am. Chem. Soc 2014, 136, 15501–15504. [PubMed: 25325782] (b)Chen J; Xi T; Ren X; Cheng B; Guo J; Lu Z Asymmetric Cobalt Catalysts for Hydroboration of 1,1-Disubstituted Alkenes. Org. Chem. Front 2014, 1, 1306–1309.

(58). Zuo Z; Yang J; Huang Z Cobalt-Catalyzed Alkyne Hydrosilylation and Sequential Vinylsilane Hydroboration with Markovnikov Selectivity. Angew. Chem., Int. Ed 2016, 55, 10839–10843.

(59). Palmer WN; Diao T; Pappas I; Chirik PJ High-Activity Cobalt Catalysts for Alkene Hydroboration with Electronically Responsive Terpyridine and α-Diimine Ligands. ACS Catal. 2015, 5, 622–626.

(60). Duong HA; Wu WQ; Teo Y-Y Cobalt-Catalyzed Cross-Coupling Reactions of Arylboronic Esters and Aryl Halides. Organometallics 2017, 36, 4363–4366.

(61). Shao Z; Fu S; Wei M; Zhou S; Liu Q Mild and Selective Cobalt-Catalyzed Chemodivergent Transfer Hydrogen-ation of Nitriles. Angew. Chem., Int. Ed 2016, 55, 14653–14657.

(62). Lappert MF; Pye PL Carbene Complexes. Part 12. Electron-rich Olefin-Derived Neutral Mono- and Bis-(Carbene) Complexes of Low-Oxidation-State Manganese, Iron, Cobalt, Nickel, and Ruthenium. J. Chem. Soc., Dalton Trans 1977, 2172–2180.

(63). Andjaba J; Tye JW; Yu P; Pappas I; Bradley CA Cp*Co(IPr): Synthesis and Reactivity of an Unsaturated Co(I) Complex. Chem. Commun 2016, 52, 2469–2472.

(64). Danopoulos AA; Braunstein P Mono-N-Heterocyclic Carbene Amido and Alkyl Complexes. Cobalt-Mediated C–H Activation and C–C Coupling Reactions Involving Benzyl Ligands on a Putative 3-Coordinate Intermediate. Dalton Trans. 2013, 42, 7276–7280. [PubMed: 23508380]

(65). Danopoulos AA; Simler T; Braunstein P N-Heterocyclic Carbene Complexes of Copper, Nickel, and Cobalt. Chem. Rev 2019, 119, 3730–3961. [PubMed: 30843688]

(66). Day BM; Pal K; Pugh T; Tuck J; Layfield RA Carbene Rearrangements in Three-Coordinate N-Heterocyclic Carbene Complexes of Cobalt(II) Bis(trimethylsilyl)amide. Inorg. Chem 2014, 53, 10578–10584. [PubMed: 25203858]

(67). Du JZ; Wang LB; Xie MH; Deng L A Two-Coordinate Cobalt(II) Imido Complex with NHC Ligation: Synthesis, Structure, and Reactivity. Angew. Chem., Int. Ed 2015, 54, 12640–12644.

(68). Hansen CB; Jordan RF; Hillhouse GL Protonolysis and Amide Exchange Reactions of a Three-Coordinate Cobalt Amide Complex Supported by an N-Heterocyclic Carbene Ligand. Inorg. Chem 2015, 54, 4603–4610. [PubMed: 25938547]

(69). Hering F; Berthel JHJ; Lubitz K; Paul USD; Schneider H; Harterich M; Radius U Synthesis and Thermal Properties of Novel NHC-Stabilized Cobalt Carbonyl Nitrosyl Complexes. Organometallics 2016, 35, 2806–2821.

(70). Simler T; Braunstein P; Danopoulos AA Cobalt PNP^{NHC}'Pincers': Ligand Dearomatisation, Formation of Dinuclear and N_2 Complexes and Promotion of C-H Activation. Chem. Commun 2016, 52, 2717–2720.

(71). Simler T; Choua S; Danopoulos AA; Braunstein P Reactivity of A Dearomatised Pincer CoIIBr Complex with PNC^{NHC} Donors: Alkylation and Si-H Bond Activation via Metal-Ligand Cooperation. Dalton Trans. 2018, 47, 7888–7895. [PubMed: 29774906]

(72). Someya H; Ohmiya H; Yorimitsu H; Oshima K N-Heterocyclic Carbene Ligands in Cobalt-Catalyzed Sequential Cyclization/Cross-Coupling Reactions of 6-Halo-1-hexene Derivatives with Grignard Reagents. Org. Lett 2007, 9, 1565–1567. [PubMed: 17362026]

(73). Someya H; Ohmiya H; Yorimitsu H; Oshima K Cobalt-Catalyzed Sequential Cyclization/Cross-Coupling Reac-tions of 6-Halo-1-hexene Derivatives with Grignard Reagents and their Application to the Synthesis of 1,3-Diols. Tetrahedron 2007, 63, 8609–8618.

(74). Kobayashi T; Ohmiya H; Yorimitsu H; Oshima K Cobalt-Catalyzed Regioselective Dehydrohalogenation of Alkyl Halides with Dimethylphenylsilylmethylmagnesium Chloride. J. Am. Chem. Soc 2008, 130, 11276–11277. [PubMed: 18671349]

(75). Kobayashi T; Yorimitsu H; Oshima K Cobalt-Catalyzed Isomerization of 1-Alkenes to (*E*)-2-Alkenes with Dimethylphenylsilylmethylmagnesium Chloride and Its Application to the Stereoselective Synthesis of (*E*)-Alkenylsilanes. Chem. Asian. J 2009, 4, 1078–1083. [PubMed: 19479930]

(76). Hamaguchi H; Uemura M; Yasui H; Yorimitsu H; Oshima K Cobalt-Catalyzed Cross-Coupling Reactions of Aryl Bromides with Alkyl Grignard Reagents. Chem. Lett 2008, 37, 1178–1179.

(77). Xi ZX; Liu B; Lu CX; Chen WZ Cobalt(III) Complexes Bearing Bidentate, Tridentate, and Tetradentate N-Heterocyclic Carbenes: Synthesis, X-ray Structures and Catalytic Activities. Dalton Trans. 2009, 7008–7014. [PubMed: 20449143]

(78). Hatakeyama T; Hashimoto S; Ishizuka K; Nakamura M Highly Selective Biaryl Cross-Coupling Reactions between Aryl Halides and Aryl Grignard Reagents: A New Catalyst Combination of *N*-Heterocyclic Carbenes and Iron, Cobalt, and Nickel Fluorides. J. Am. Chem. Soc 2009, 131, 11949–11963. [PubMed: 19639999]

(79). (a)Wu WQ; Duong HA A Highly Active Cobalt Catalyst System for Kumada Biaryl CrossCoupling. Synlett 2018, 29, 1199–1202.(b)Liu N; Wang Z-X Kumada Coupling of Aryl, Heteroaryl, and Vinyl Chlorides Catalyzed by Amido Pincer Nickel Complexes. J. Org. Chem 2011, 76, 10031. [PubMed: 22077596]

(80). Matsubara K; Sueyasu T; Esaki M; Kumamoto A; Nagao S; Yamamoto H; Koga Y; Kawata S; Matsumoto T Cobalt(II) Complexes Bearing a Bulky N-Heterocyclic Carbene for Catalysis of Kumada–Tamao–Corriu Cross-Coupling Reactions of Aryl Halides. Eur. J. Inorg. Chem 2012, 2012, 3079–3086.

(81). Zhou T; Ma S; Nahra F; Obled AMC; Poater A; Cavallo L; Cazin CSJ; Nolan SP; Szostak M $[Pd(NHC)(\mu\text{-}Cl)Cl]_2$: Versatile and Highly Reactive Complexes for Cross-Coupling Reactions that Avoid Formation of Inactive Pd(I) Off-Cycle Products. iScience 2020, 23, no. 101377. [PubMed: 32759055]

(82). Przyojski JA; Arman HD; Tonzetich ZJ NHC Complexes of Cobalt(II) Relevant to Catalytic C-C Coupling Reactions. Organometallics 2013, 32, 723–732.

(83). For homocoupling of Grignard reagents, see: Mo ZB; Li YX; Lee HK; Deng L Square-Planar Cobalt Complexes with Monodentate N-Heterocyclic Carbene Ligation: Synthesis, Structure, and Catalytic Application. Organometallics 2011, 30, 4687–4694.

(84). Piontek A; Ochędzan-Siodłak W; Bisz E; Szostak M Cobalt–NHC Catalyzed C(sp^2)–C(sp^3) and C(sp^2)–C(sp^2) Kumada Cross-Coupling of Aryl Tosylates with Alkyl and Aryl Grignard Reagents. ChemCatChem 2021, 13, 202–206.

(85). Asghar S; Tailor SB; Elorriaga D; Bedford RB Cobalt-Catalyzed Suzuki Biaryl Coupling of Aryl Halides. Angew. Chem., Int. Ed 2017, 56, 16367–16370.

(86). Duong HA; Yeow Z-H; Tiong Y-L; Kamal M NHB; Wu WQ Cobalt-Catalyzed Cross-Coupling Reactions of Aryl Triflates and Lithium Arylborates. J. Org. Chem 2019, 84, 12686–12691. [PubMed: 31496246]

(87). Tailor SB; Manzotti M; Smith GJ; Davis SA; Bedford RB Cobalt-Catalyzed Coupling of Aryl Chlorides with Aryl Boron Esters Activated by Alkoxides. ACS Catal. 2021, 11, 3856–3866.

(88). Matsubara K; Kumamoto A; Yamamoto H; Koga Y; Kawata S Synthesis and Structure of Cobalt(II) Iodide Bearing a Bulky N-Heterocyclic Carbene Ligand, and Catalytic Activation of Bromoalkanes. J. Organomet. Chem 2013, 727, 44–49.

(89). (a)Hajipour AR; Khorsandi Z Multi Walled Carbon Nanotubes Supported N-Heterocyclic Carbene Cobalt(II) as a Novel, Efficient and Inexpensive Catalyst for the Mizoroki–Heck. Catal. Commun 2016, 77, 1–4.(b)Hajipour AR; Khorsandi Z; Mohammadi B Cobalt-Catalyzed Three-Component Synthesis of Propargylamine Derivatives and Sonogashira Reaction: A Comparative Study between Co-NPs and Co-NHC@MWCNTs. ChemistrySelect 2019, 4, 4598–4603. For an example of Co–NHCs in amination of aryl bromides, see: (c)Ibrahim H; Bala MD Earth abundant metal complexes of donor functionalised N-heterocyclic carbene ligands: synthesis, characterisation and application as amination catalysts. New J. Chem 2016, 40, 6986–6997.

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(90). Verma PK; Mandal S; Geetharani K Efficient Synthesis of Aryl Boronates *via* Cobalt-Catalyzed Borylation of Aryl Chlorides and Bromides. ACS Catal. 2018, 8, 4049–4054.

(91). Verma PK; Prasad KS; Varghese D; Geetharani K Cobalt(I)-Catalyzed Borylation of Unactivated Alkyl Bromides and Chlorides. Org. Lett 2020, 22, 1431–1436. [PubMed: 32037844]

(92). (a)Yu RP; Darmon JM; Milsmann C; Margulieux GW; Stieber SCE; DeBeer S; Chirik PJ 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. [PubMed: 23968297] (b)Yu RP; Darmon JM; Hoyt JM; Margulieux GW; Turner Z; Chirik PJ High-Activity Iron Catalysts for the Hydrogenation of Hindered, Unfunctionalized Alkenes. ACS Catal. 2012, 2, 1760–1764. [PubMed: 26229734]

(93). Tokmic K; Markus CR; Zhu LY; Fout AR Well-Defined Cobalt(I) Dihydrogen Catalyst: Experimental Evidence for a Co(I)/Co(III) Redox Process in Olefin Hydrogenation. J. Am. Chem. Soc 2016, 138, 11907–11913. [PubMed: 27569420]

(94). (a)Tokmic K; Fout AR Alkyne Semihydrogenation with a Well-Defined Nonclassical Co-H_2 Catalyst: A H_2 Spin on Isomerization and E-Selectivity. J. Am. Chem. Soc 2016, 138, 13700–13705. [PubMed: 27709917] (b)Muhammad SR; Nugent JW; Tokmic K; Zhu L; Mahmoud J; Fout AR Electronic Ligand Modifications on Cobalt Complexes and Their Application toward the Semi-Hydrogenation of Alkynes and Para-Hydrogenation of Alkenes. Organometallics 2019, 38, 3132–3138.

(95). (a)Enachi A; Baabe D; Zaretzke M-K; Schweyen P; Freytag M; Raeder J; Walter MD [(NHC)CoR_2]: Pre-Catalysts for Homogeneous Olefin and Alkyne Hydrogenation. Chem. Commun 2018, 54, 13798–13801.(b)Friedfeld MR; Margulieux GW; Schaefer BA; Chirik PJ Bis(phosphine)cobalt Dialkyl Complexes for Directed Catalytic Alkene Hydrogenation. J. Am. Chem. Soc 2014, 136, 13178–13181. [PubMed: 25166760]

(96). Liu XF; Liu BX; Liu Q Migratory Hydrogenation of Terminal Alkynes by Base/Cobalt Relay Catalysis. Angew. Chem., Int. Ed 2020, 59, 6750–6755.

(97). Gao YF; Wang LJ; Deng L Distinct Catalytic Performance of Cobalt(I)-NHC Complexes in Promoting the Reaction of Alkene with Diphenylsilane: Selective 2,1 Hydrosilylation, 1,2-Hydrosilylation, and Hydrogenation of Alkene. ACS Catal. 2018, 8, 9637–9646.

(98). For hydrogenation of hindered alkenes, see: Wei Z; Wang Y; Li Y; Ferraccioli R; Liu Q Bidentate NHC-Cobalt Catalysts for the Hydrogenation of Hindered Alkenes. Organometallics 2020, 39, 3082–3087.

(99). Han B; Ma PC; Cong XF; Chen H; Zeng XM Chromium- and Cobalt-Catalyzed, Regiocontrolled Hydrogenation of Polycyclic Aromatic Hydrocarbons: A Combined Experimental and Theoretical Study. J. Am. Chem. Soc 2019, 141, 9018–9026. [PubMed: 31074625]

(100). (a)Tokmic K; Jackson BJ; Salazar A; Woods TJ; Fout AR Cobalt-Catalyzed and Lewis Acid-Assisted Nitrile Hydrogenation to Primary Amines: A Combined Effort. J. Am. Chem. Soc 2017, 139, 13554–13561. [PubMed: 28906106] (b)Lange S; Elangovan S; Cordes C; Spannenberg A; Jiao H; Junge H; Bachmann S; Scalone M; Topf C; Junge K; Beller M Selective Catalytic Hydrogenation of Nitriles to Primary Amines Using Iron Pincer Complexes. Catal. Sci. Technol 2016, 6, 4768–4772.(c)Lu Z; Williams TJ A Dual Site Catalyst for Mild, Selective Nitrile Reduction. Chem. Commun 2014, 50, 5391–5393.

(101). (a)Nugent JW; García-Melchor M; Fout AR Cobalt-Catalyzed Ammonia Borane Dehydrogenation: Mechanistic Insight and Isolation of a Cobalt Hydride-Amidoborane Complex. Organometallics 2020, 39, 2917–2927.(b)Tokmic K; Greer RB; Zhu LY; Fout AR ^{13}C NMR Signal Enhancement Using Parahydrogen-Induced Polarization Mediated by a Cobalt Hydrogenation Catalyst. J. Am. Chem. Soc 2018, 140, 14844–14850. [PubMed: 30358390]

(102). Zhong R; Wei ZY; Zhang W; Liu S; Liu Q A Practical and Stereoselective *In Situ* NHC-Cobalt Catalytic System for Hydrogenation of Ketones and Aldehydes. Chem 2019, 5, 1552–1566.

(103). (a)Abubakar S; Bala MD Transfer Hydrogenation of Ketones Catalyzed by Symmetric IminoN-heterocyclic Carbene Co(III) Complexes. ACS Omega 2020, 5, 2670–2679. [PubMed: 32095690] (b)Ibrahim H; Bala MD Air stable pincer (CNC) N-heterocyclic carbene–cobalt complexes and their application as catalysts for C–N coupling reactions. J. Organomet. Chem 2015, 794, 301–310. For another example of transfer hydrogenation of ketones, see: (c)Ibrahim JJ; Reddy CB;

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Fang XL; Yang Y Efficient Transfer Hydrogenation of Ketones Catalyzed by a Phosphine-Free CobaltNHC Complex. Eur. J. Org. Chem 2020, 4429–4432.

(104). Shao ZH; Zhong R; Ferraccioli R; Li YB; Liu Q General and Phosphine-Free Cobalt-Catalyzed Hydrogenation of Esters to Alcohols. Chin. J. Chem 2019, 37, 1125–1130.

(105). Sun J; Deng L Cobalt Complex-Catalyzed Hydrosilylation of Alkenes and Alkynes. ACS Catal. 2016, 6, 290–300.

(106). Du X; Huang Z Advances in Base-Metal-Catalyzed Alkene Hydrosilylation. ACS Catal. 2017, 7, 1227–1243.

(107). Zuo Z; Wen H; Liu G; Huang Z Cobalt-Catalyzed Hydroboration and Borylation of Alkenes and Alkynes. Synlett 2018, 29, 1421–1429.

(108). Chen J; Lu Z Asymmetric Hydrofunctionalization of Minimally Functionalized Alkenes via Earth Abundant Transition Metal Catalysis. Org. Chem. Front 2018, 5, 260–272.

(109). Obligacion JV; Chirik PJ Earth-Abundant Transition Metal Catalysts for Alkene Hydrosilylation and Hydroboration. Nat. Rev. Chem 2018, 2, 15–34. [PubMed: 30740530]

(110). Ai WY; Zhong R; Liu XF; Liu Q Hydride Transfer Reactions Catalyzed by Cobalt Complexes. Chem. Rev 2019, 119, 2876–2953. [PubMed: 30565455]

(111). Fan WW; Li L; Zhang GQ Branched-Selective Alkene Hydroboration Catalyzed by Earth-Abundant Metals. J. Org. Chem 2019, 84, 5987–5996. [PubMed: 31017441]

(112). Mo ZB; Liu Y; Deng L Anchoring of Silyl Donors on a N-Heterocyclic Carbene Through the Cobalt-Mediated Silylation of Benzylic C–H Bonds. Angew. Chem., Int. Ed 2013, 52, 10845–10849.

(113). Mo ZB; Xiao J; Gao YF; Deng L Regio- and Stereoselective Hydrosilylation of Alkynes Catalyzed by Three-Coordinate Cobalt(I) Alkyl and Silyl Complexes. J. Am. Chem. Soc 2014, 136, 17414–17417. [PubMed: 25426965]

(114). Ibrahim AD; Entsminger SW; Zhu LY; Fout AR A Highly Chemoselective Cobalt Catalyst for the Hydrosilylation of Alkenes using Tertiary Silanes and Hydrosiloxanes. ACS Catal. 2016, 6, 3589–3593.

(115). Liu Y; Deng L Mode of Activation of Cobalt(II) Amides for Catalytic Hydrosilylation of Alkenes with Tertiary Silanes. J. Am. Chem. Soc 2017, 139, 1798–1801. [PubMed: 28121434]

(116). Wang D; Lai Y; Wang P; Leng X; Xiao J; Deng L Markovnikov Hydrosilylation of Alkynes with Tertiary Silanes Catalyzed by Dinuclear Cobalt Carbonyl Complexes with NHC Ligation. J. Am. Chem. Soc 2021, 143, 12847–12856. [PubMed: 34347477]

(117). Reilly SW; Webster CE; Hollis TK; Valle HU Transmetallation from CCC-NHC Pincer Zr Complexes in the Synthesis of Air-Stable CCC-NHC Pincer Co(III) Complexes and Initial Hydroboration Trials. Dalton Trans. 2016, 45, 2823–2828. [PubMed: 26814468]

(118). Ibrahim AD; Entsminger SW; Fout AR Insights into a Chemoselective Cobalt Catalyst for the Hydroboration of Alkenes and Nitriles. ACS Catal. 2017, 7, 3730–3734.

(119). Verma PK; Sethulekshmi AS; Geetharani K Markovnikov-Selective Co(I)-Catalyzed Hydroboration of Viny-larenes and Carbonyl Compounds. Org. Lett 2018, 20, 7840–7845. [PubMed: 30525691]

(120). Gibson SE; Johnstone C; Loch JA; Steed JW; Stevenazzi A Novel Structures and Pauson-Khand Activities of N-Heterocyclic Carbene Dicobalt Complexes. Organometallics 2003, 22, 5374–5377.

(121). Saino N; Kogure D; Okamoto S Intramolecular Cyclotrimerization of Triynes Catalyzed by N-Heterocyclic Carbene-$CoCl_2$/Zn or -$FeCl_3$/Zn. Org. Lett 2005, 7, 3065–3067. [PubMed: 15987206]

(122). Geny A; Gaudrel S; Slowinski F; Amatore M; Chouraqui G; Malacria M; Aubert C; Gandon V A Straightforward Procedure for the [2+2+2]Cycloaddition of Enediynes. Adv. Synth. Catal 2009, 351, 271–275.

(123). (a)Llewellyn SA; Green MLH; Cowley AR Cobalt N-Heterocyclic Carbene Alkyl and Acyl Compounds: Synthesis, Molecular Structure and Reactivity. Dalton Trans. 2006, 4164–4168. [PubMed: 16924294] For the first cobalt carbonyl–NHC dimer, $Co_2(CO)_6(IMes)_2$, see:$_{262}$ (b)Rensburg H. v.; Tooze RP; Foster DF; Slawin AMZ The Synthesis and X-ray Structure of the First Cobalt Carbonyl-NHC Dimer. Implications for the Use of NHCs in Hydroformylation

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Catalysis. Inorg. Chem 2004, 43, 2468–2470. [PubMed: 15074962] For a study using ring-expanded NHC, see: (c)Takebayashi S; Fayzullin RR [Co(NHC)$(CO)_3$]: Isolation and Reactivity Study of a Model 17-Electron Species in the Oxo Process. Organometallics 2021, 40, 500–507.

(124). Fukuda J-I; Nogi K; Yorimitsu H Cobalt-Catalyzed Reduction of Aryl Sulfones to Arenes by Means of Alkylmagnesium Reagents. Asian J. Org. Chem 2018, 7, 2049–2052.

(125). Wang DY; Chen Q; Leng XB; Deng L Reactions of Low-Coordinate Cobalt(0)-N-Heterocyclic Carbene Complexes with Primary Aryl Phosphines. Inorg. Chem 2018, 57, 15600–15609. [PubMed: 30507168]

(126). Gao YF; Li GY; Deng L Bis(dinitrogen)cobalt(−1) Complexes with NHC Ligation: Synthesis, Characterization, and Their Dinitrogen Functionalization Reactions Affording Side-on Bound Diazene Complexes. J. Am. Chem. Soc 2018, 140, 2239–2250. [PubMed: 29328668]

(127). Jayasundara CRK; Sabasovs D; Staples RJ; Oppenheimer J; Smith MR III; Maleczka RE Jr. Cobalt-Catalyzed C–H Borylation of Alkyl Arenes and Heteroarenes Including the First Selective Borylations of Secondary Benzylic C–H Bonds. Organometallics 2018, 37, 1567–1574.

(128). Yu T-Y; Xu W-H; Lu H; Wei H Cobalt-Catalyzed Intramolecular Decarbonylative Coupling of Acylindoles and Diarylketones Through the Cleavage of C–C Bonds. Chem. Sci 2020, 11, 12336–12340. [PubMed: 34094442]

(129). Song W-Y; Liu Q; Bu Q; Wei D; Dai B; Liu N Rational Design of Cobalt Complexes Based on the trans Effect of Hybrid Ligands and Evaluation of their Catalytic Activity in the Cycloaddition of Carbon Dioxide with Epoxide. Organometallics 2020, 39, 3546–3561.

(130). van der Meer M; Glais E; Siewert I; Sarkar B Electrocatalytic Dihydrogen Production with a Robust Mesoionic Pyridylcarbene Cobalt Catalyst. Angew. Chem., Int. Ed 2015, 54, 13792–13795.

(131). Kawano K; Yamauchi K; Sakai K A cobalt–NHC Complex as an Improved Catalyst for Photochemical Hydrogen Evolution from Water. Chem. Commun 2014, 50, 9872–9875.

(132). Su XJ; McCardle KM; Chen LZ; Panetier JA; Jurss JW Robust and Selective Cobalt Catalysts Bearing Redox-Active Bipyridyl-N-heterocyclic Carbene Frameworks for Electrochemical CO_2 Reduction in Aqueous Solutions. ACS Catal. 2019, 9, 7398–7408.

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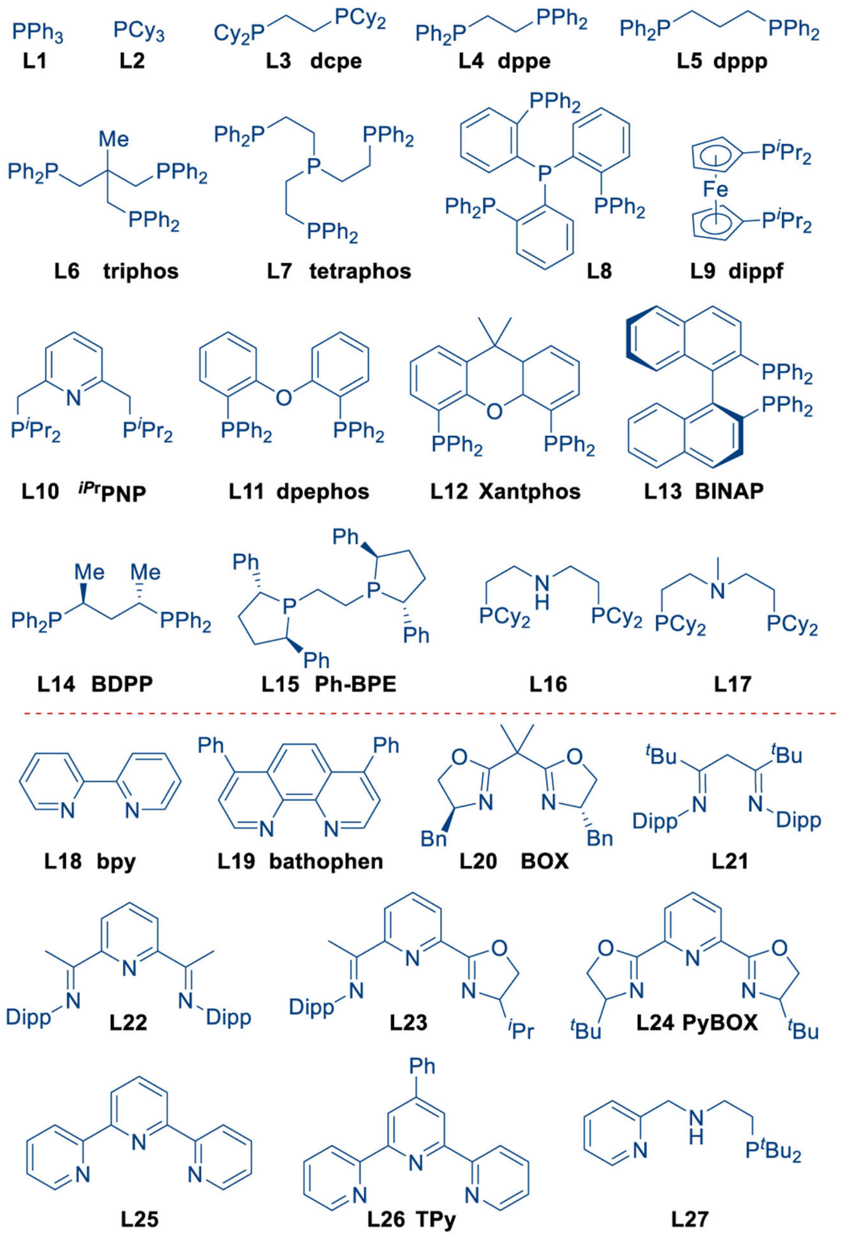

Figure 1.

Structures of the most common phosphine and amine ligands used in cobalt catalysis.

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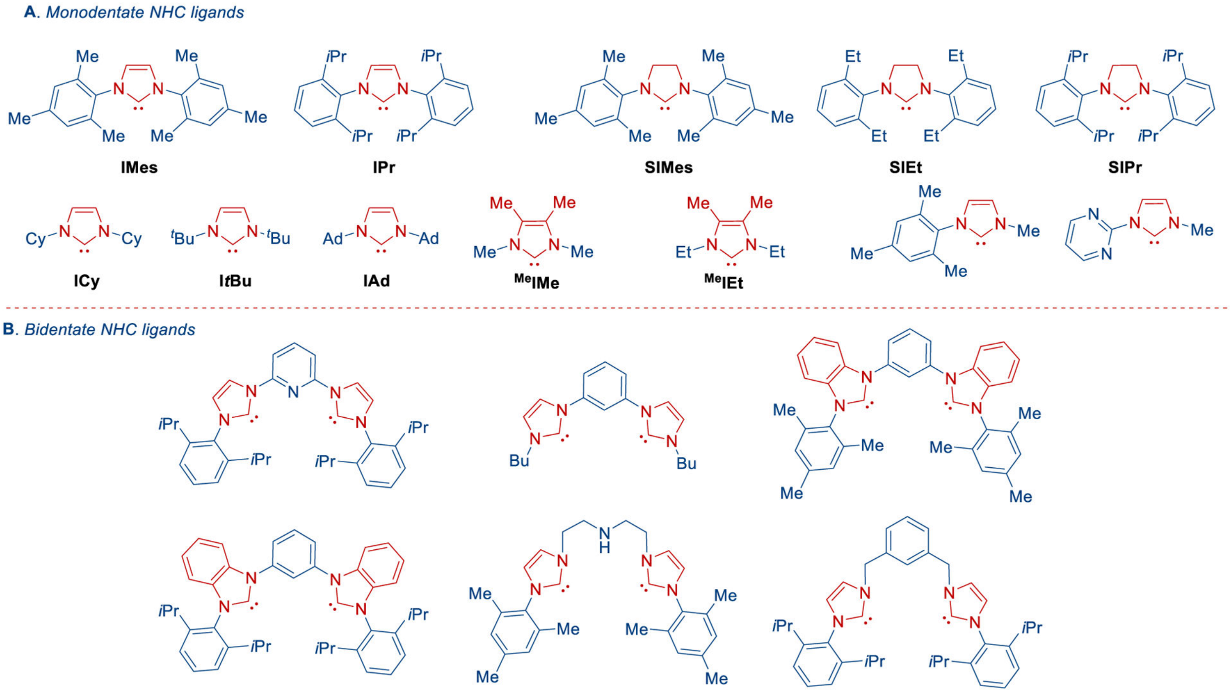

Figure 2.

Structures of the most common NHC ligands used in cobalt catalysis.

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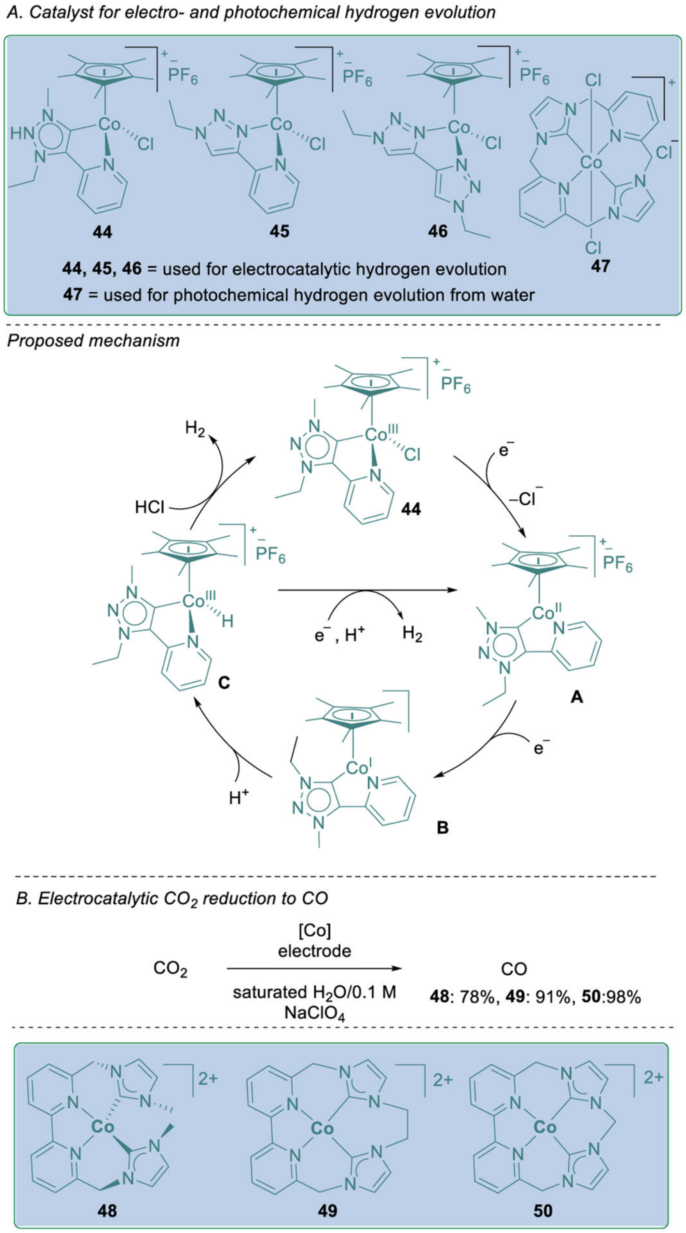

Figure 3.

(A) Co–NHC Catalyzed Electro- and Photocatalytic Hydrogen Evolution Reported by Sarkar and Sakai. (B) Co–NHC Catalyzed Electrocatalytic CO_2 Reduction Reported by Jurss.

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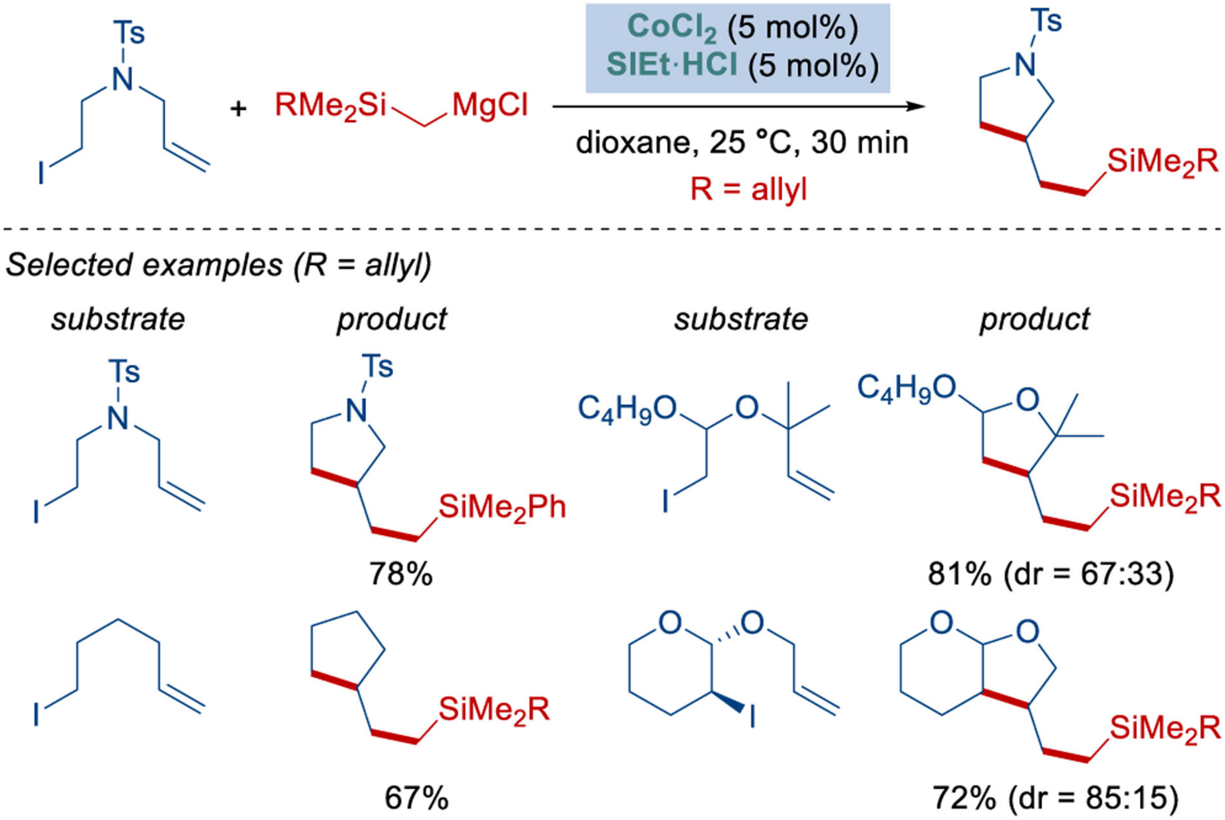

Scheme 1.

Co–NHC Catalyzed Sequential Cyclization/Cross-Coupling of 6-Halo-1-Hexene Derivatives with Grignard Reagents Reported by Oshima.

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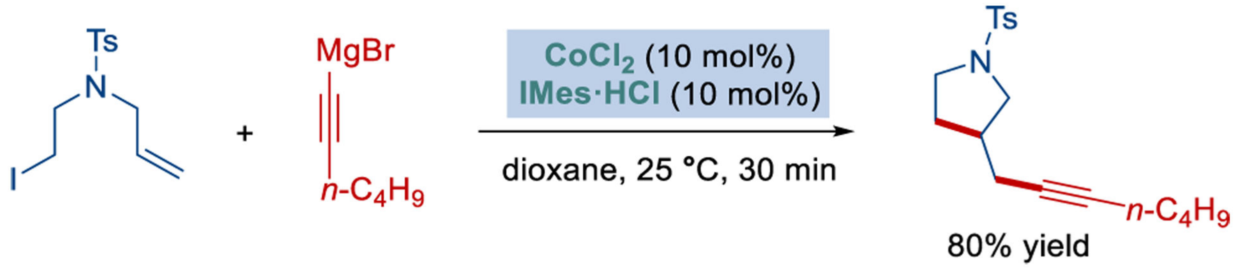

Scheme 2.

Co–NHC Catalyzed Sequential Cyclization/Cross-Coupling of 6-Halo-1-Hexene Derivatives with Alkynyl Grignard Reagents Reported by Oshima.

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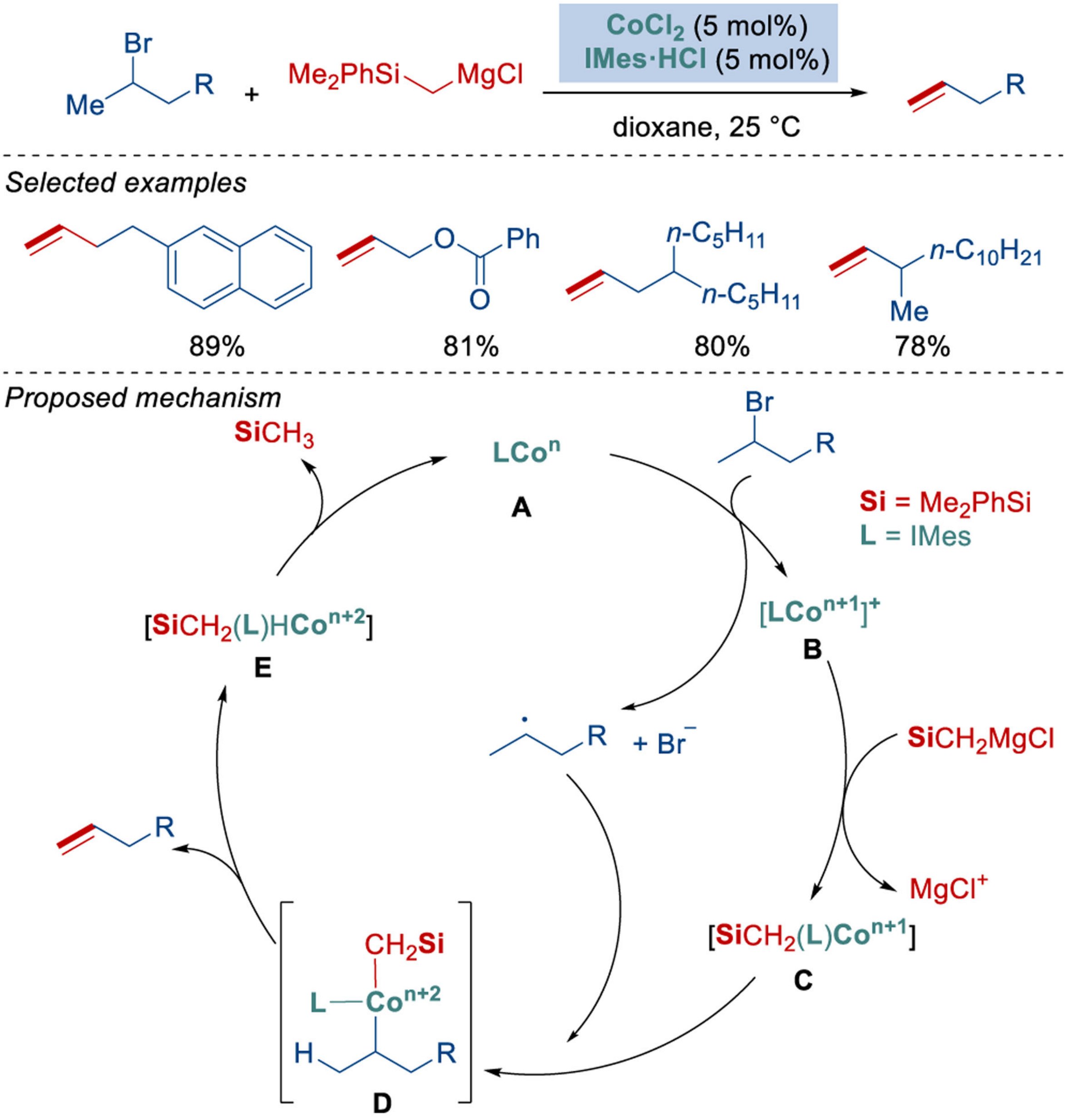

Scheme 3.

Co–NHC Catalyzed Regioselective Dehydrohalogenation of Alkyl Halides Reported by Oshima.

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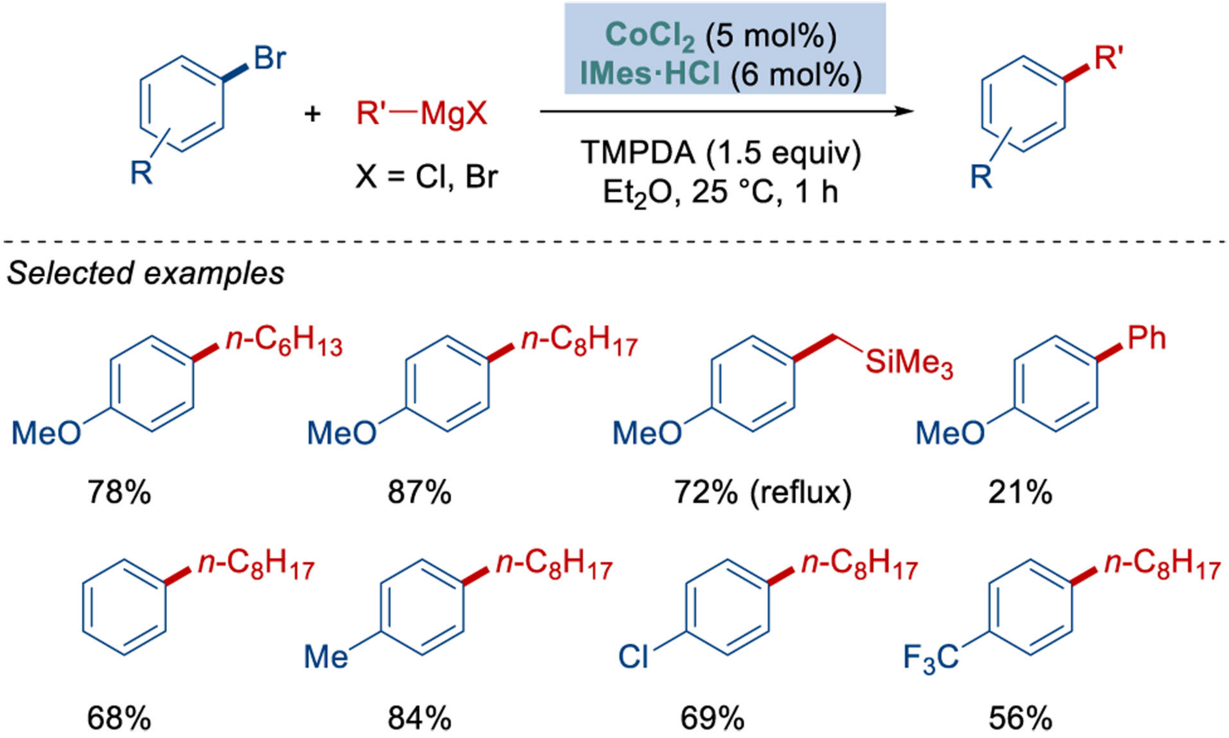

Scheme 4.

Co–NHC Catalyzed Cross-Coupling of Aryl Bromides with Grignard Reagents Reported by Oshima.

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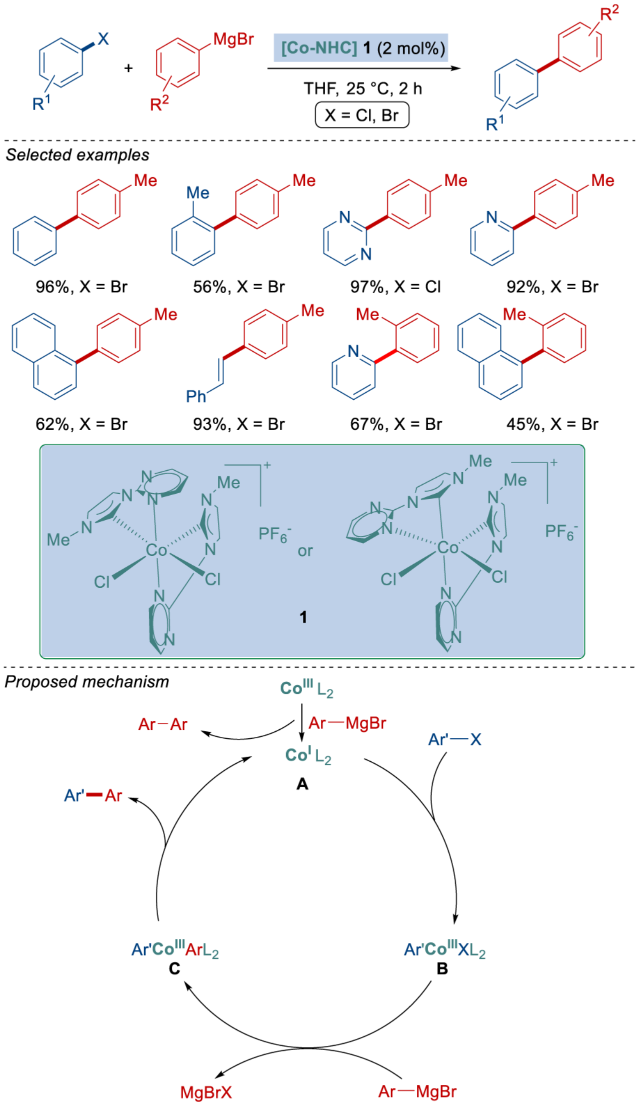

Scheme 5.

Co–NHC Catalyzed Cross-Coupling of Aryl Halides with Grignard Reagents Reported by Chen.

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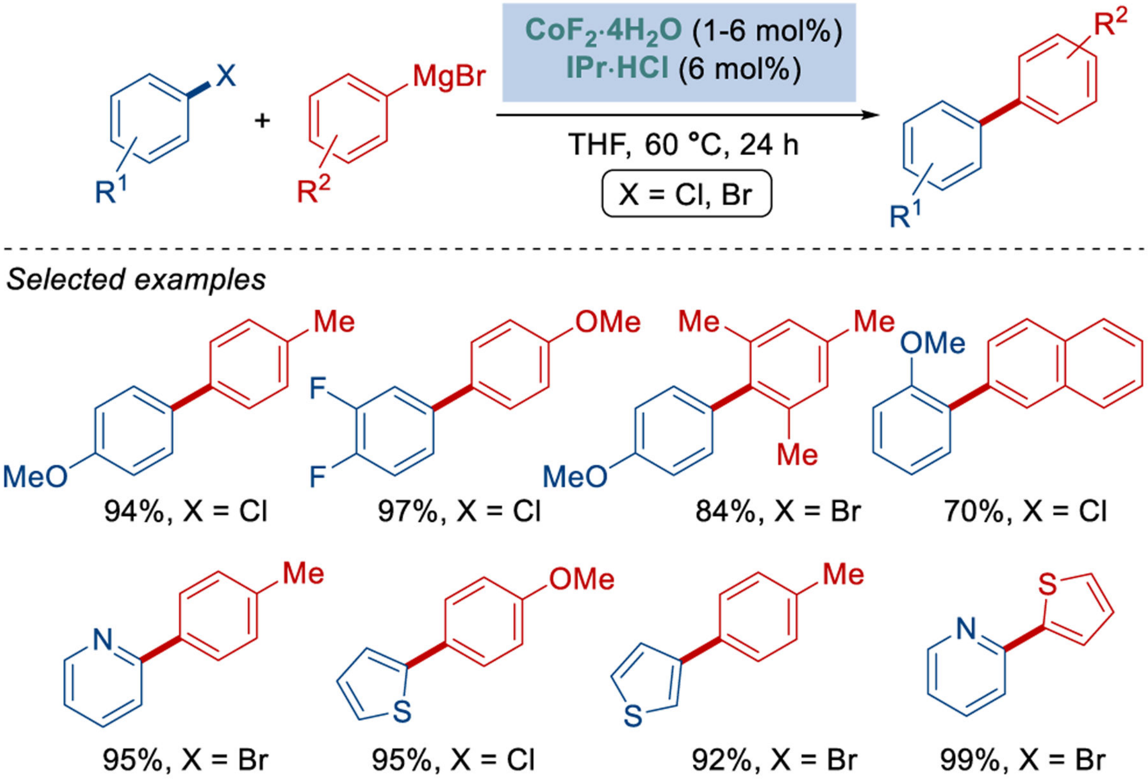

Scheme 6.

Co–NHC Catalyzed Cross-Coupling of Aryl Halides with Aryl Grignard Reagents Reported by Nakamura.

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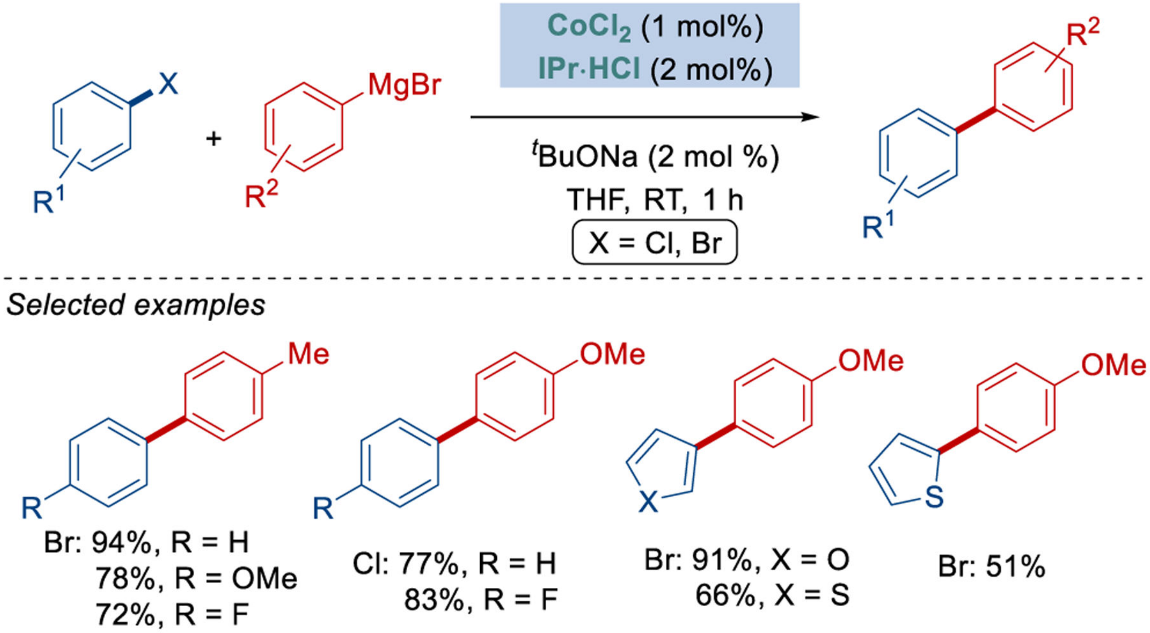

Scheme 7.
Co–NHC Catalyzed Cross-Coupling of Aryl Halides with Aryl Grignard Reagents Reported by Duong.

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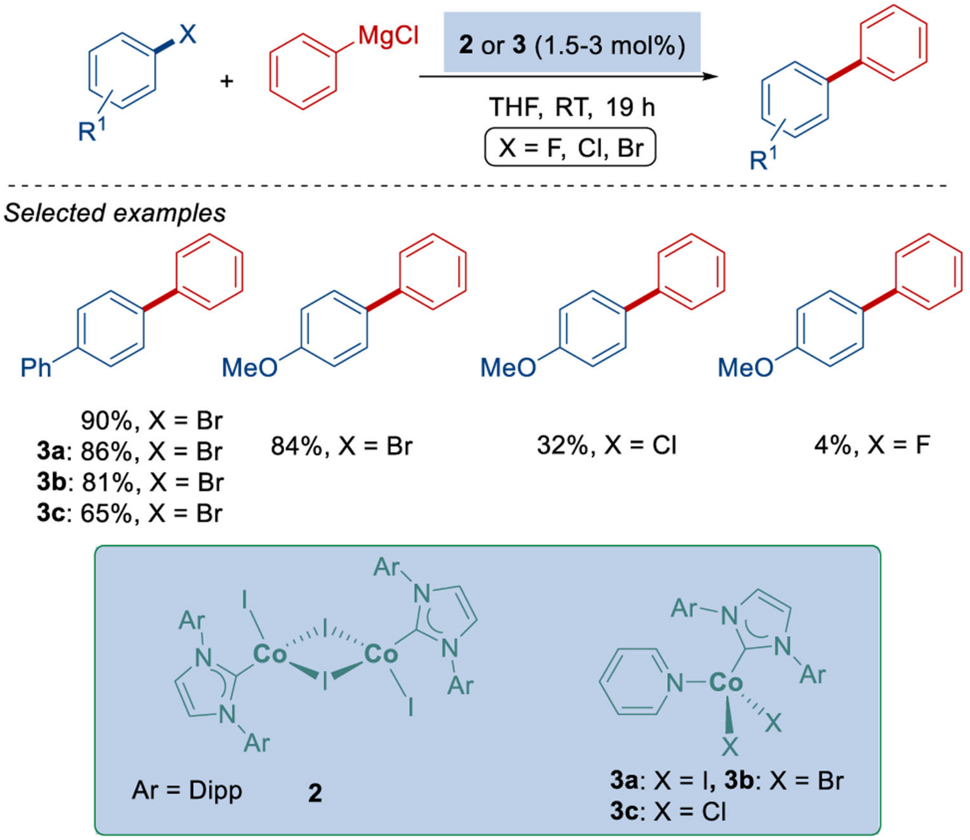

Scheme 8.

Co–NHC Catalyzed Cross-Coupling of Aryl Halides with Aryl Grignard Reagents Reported by Matsubara.

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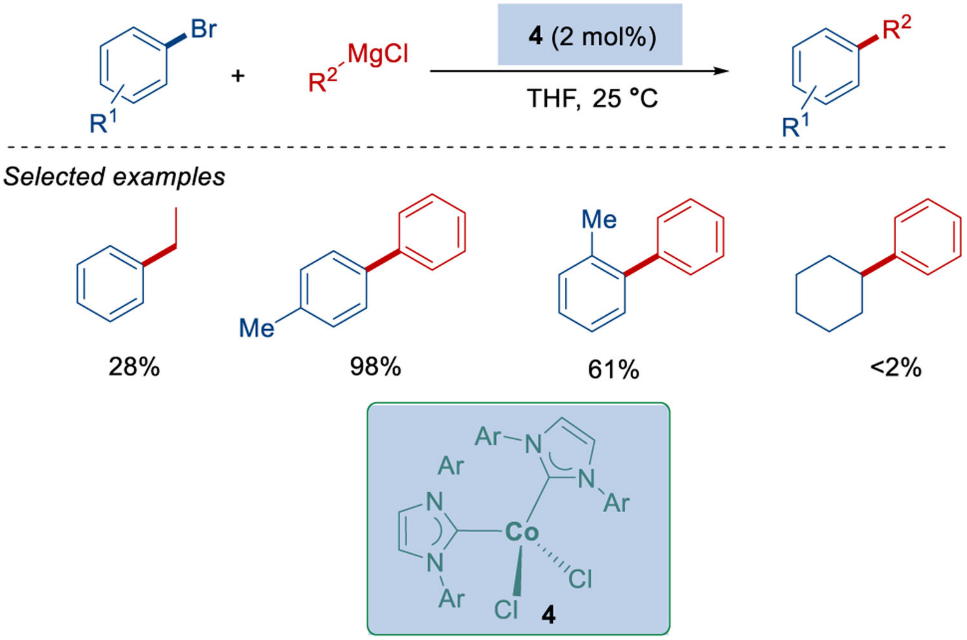

Scheme 9.
Co–NHC Catalyzed Cross-Coupling of Aryl Halides with Grignard Reagents Reported by Tonzetich.

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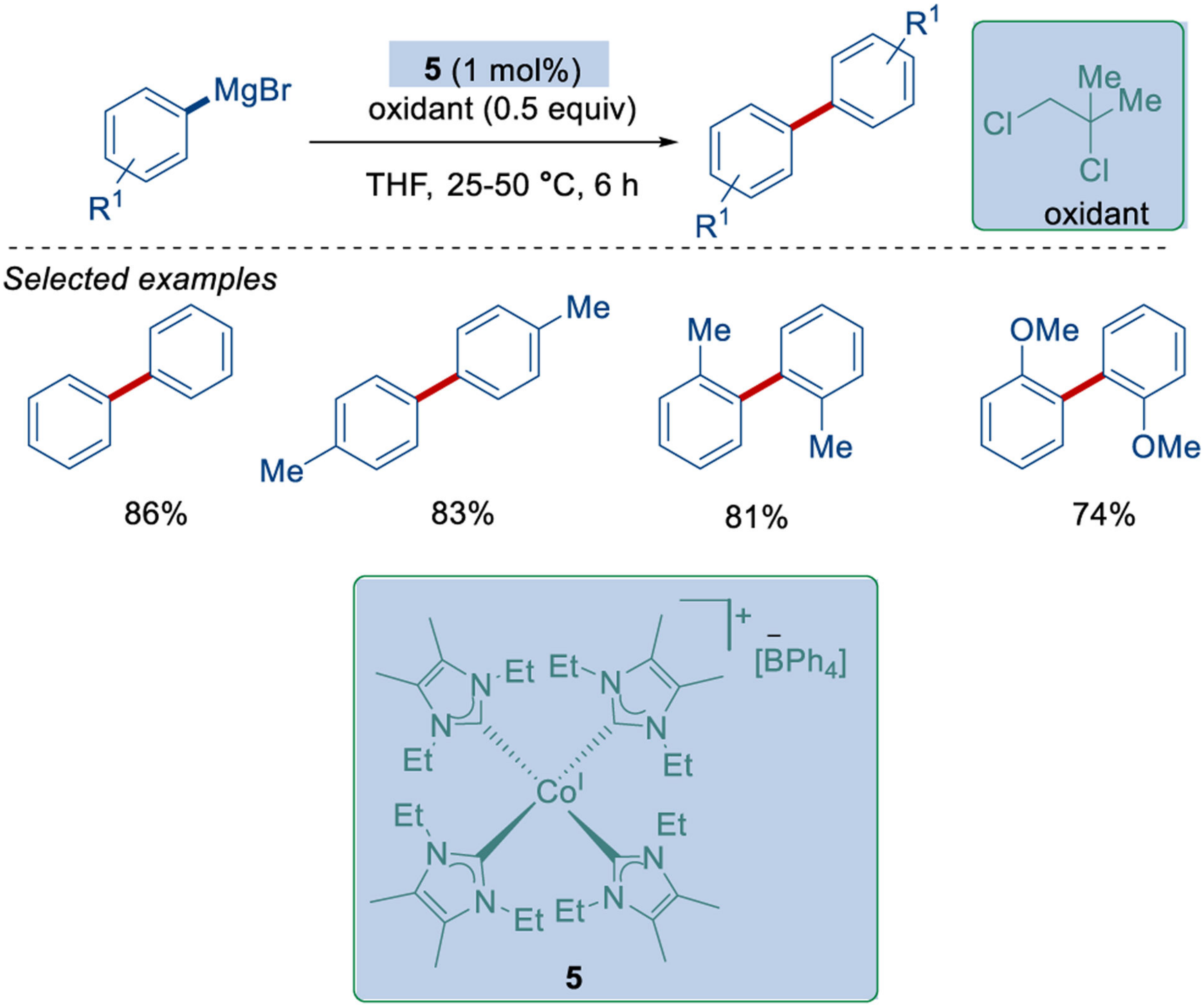
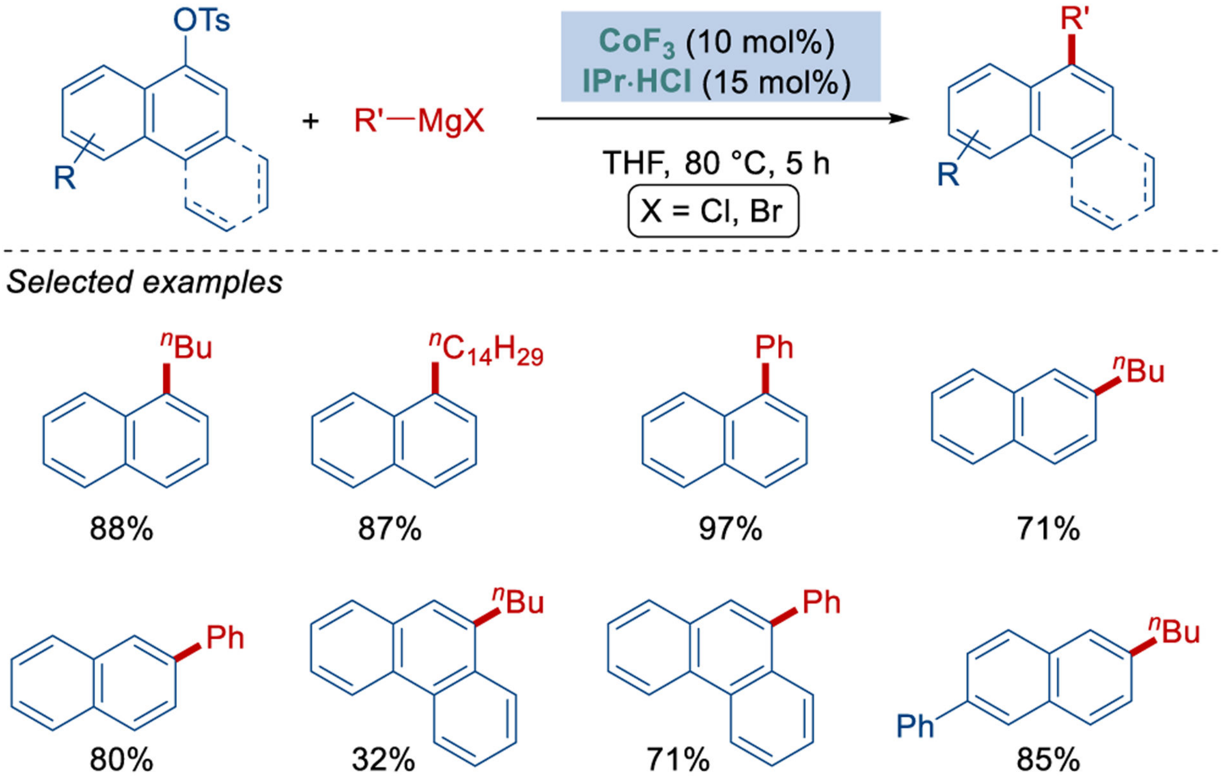


Scheme 10.

[Co(IEt)$_4$][BPh$_4$] Catalyzed Oxidative Homocoupling of Aryl Grignard Reagents Reported by Deng.



Scheme 11.

Cobalt–NHC Catalyzed Kumada Cross-Coupling of Aryl Tosylates with Alkyl and Aryl Grignard Reagents Reported by Szostak.

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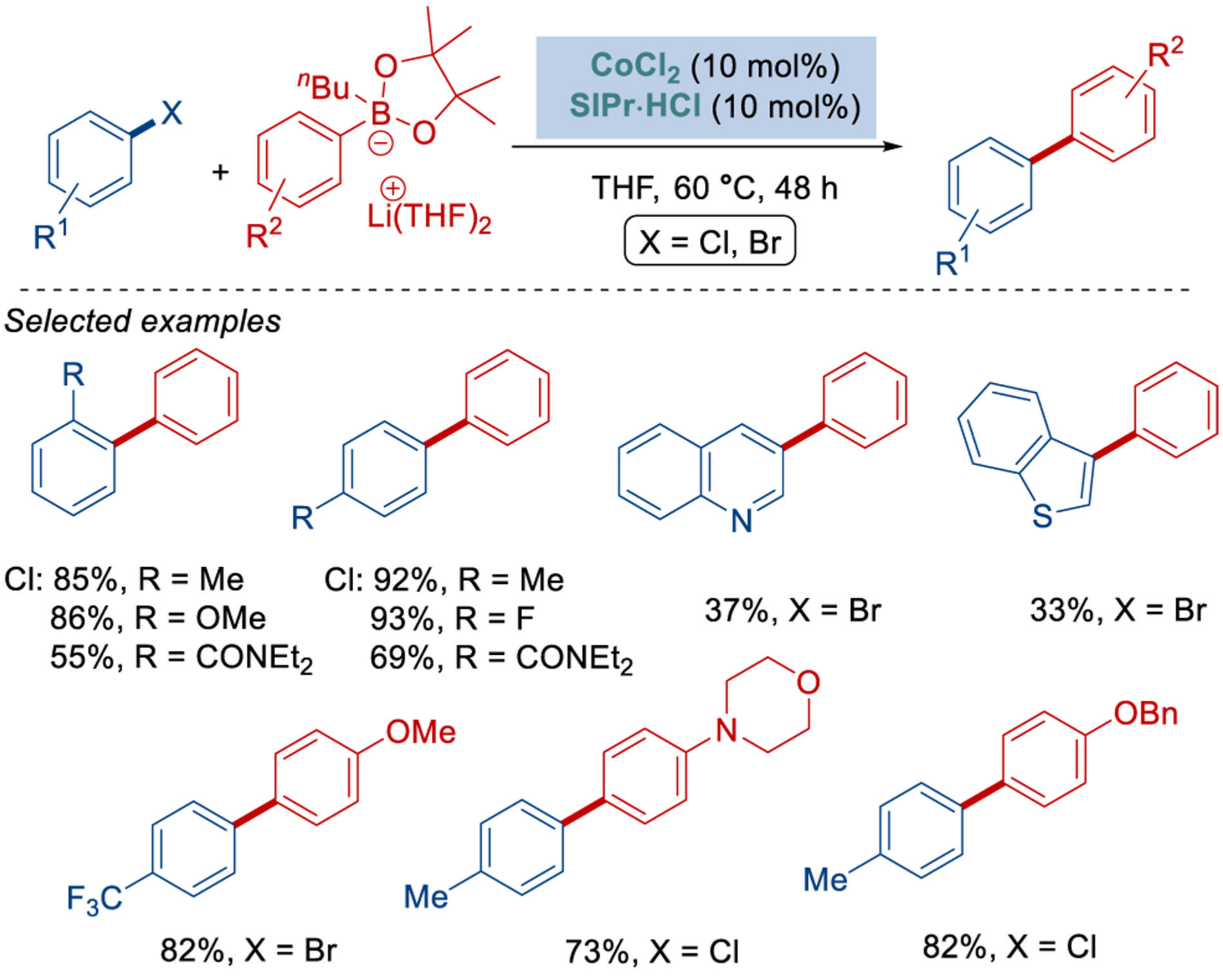

Scheme 12.

Co–NHC Catalyzed Suzuki Cross-Coupling of Aryl Halides with Lithium Arylborates Reported by Bedford.

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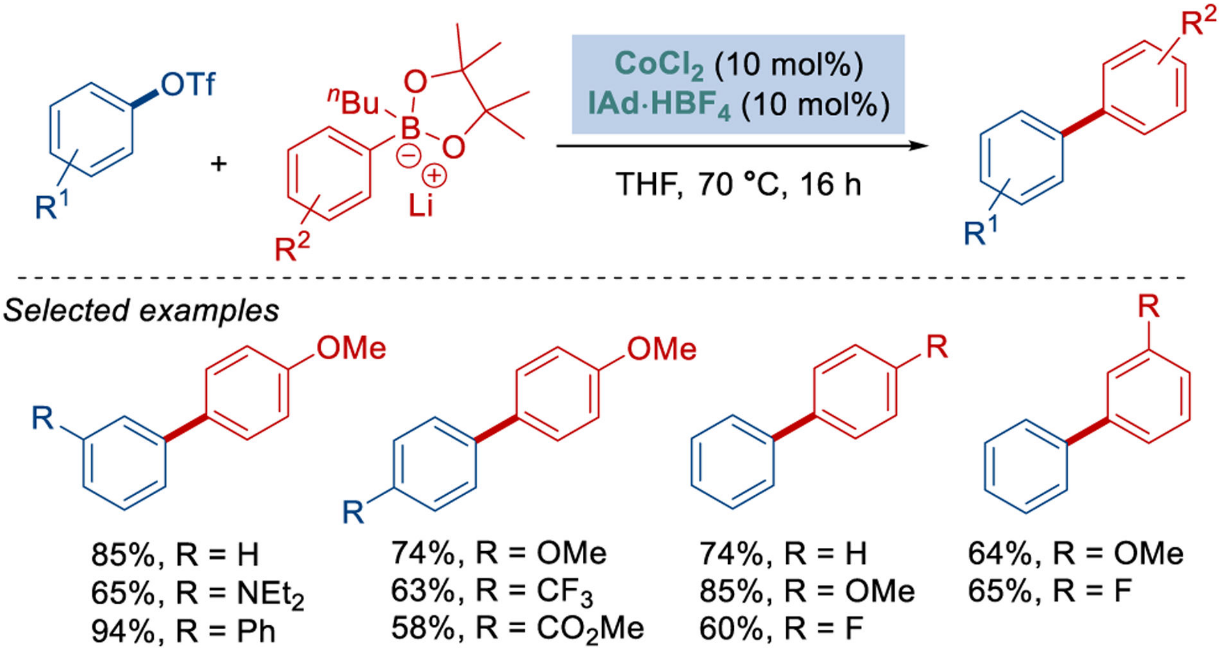

Scheme 13.

Co–NHC Catalyzed Suzuki Cross-Coupling of Aryl Triflates with Lithium Arylborates Reported by Duong.

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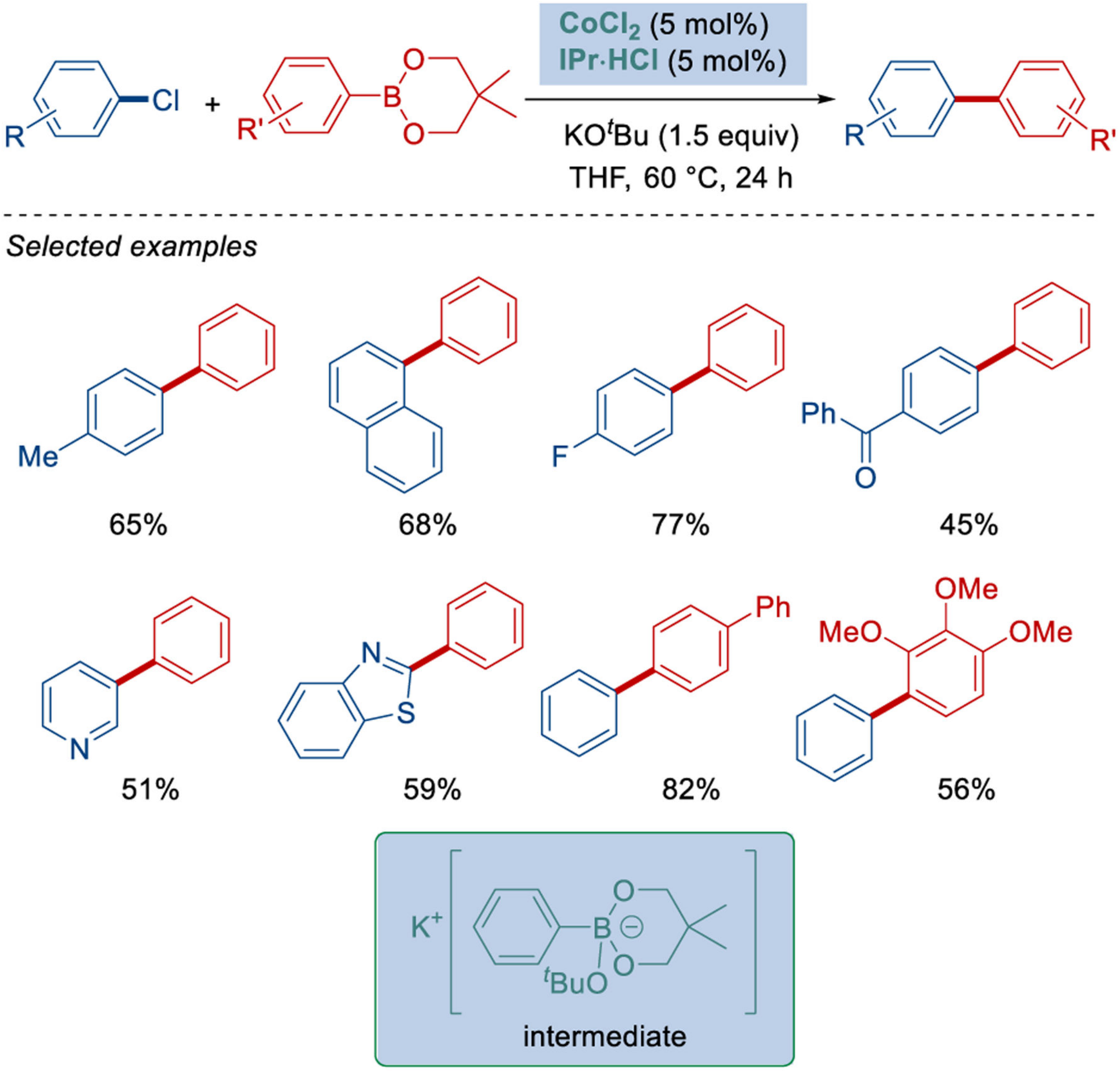

Scheme 14.

Co–NHC Catalyzed Suzuki Cross-Coupling of Aryl Chlorides with Aryl Boronic Esters Through Alkoxide Activation Reported by Bedford.

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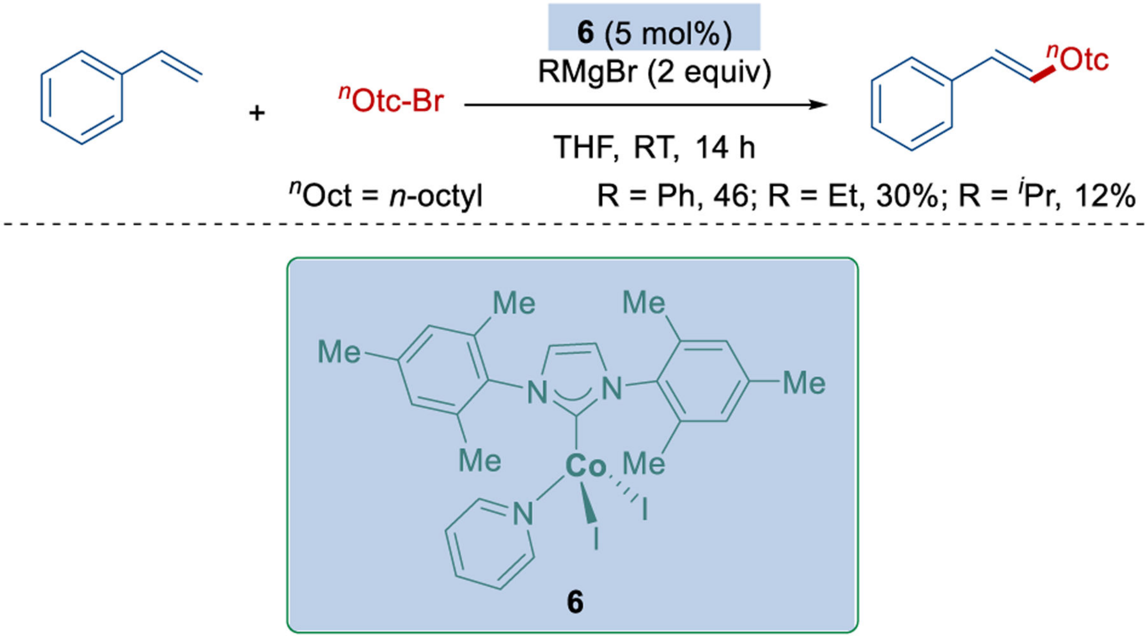

Scheme 15.

Co–NHC Catalyzed Heck Reaction of Alkyl Bromides Reported by Matsubara.

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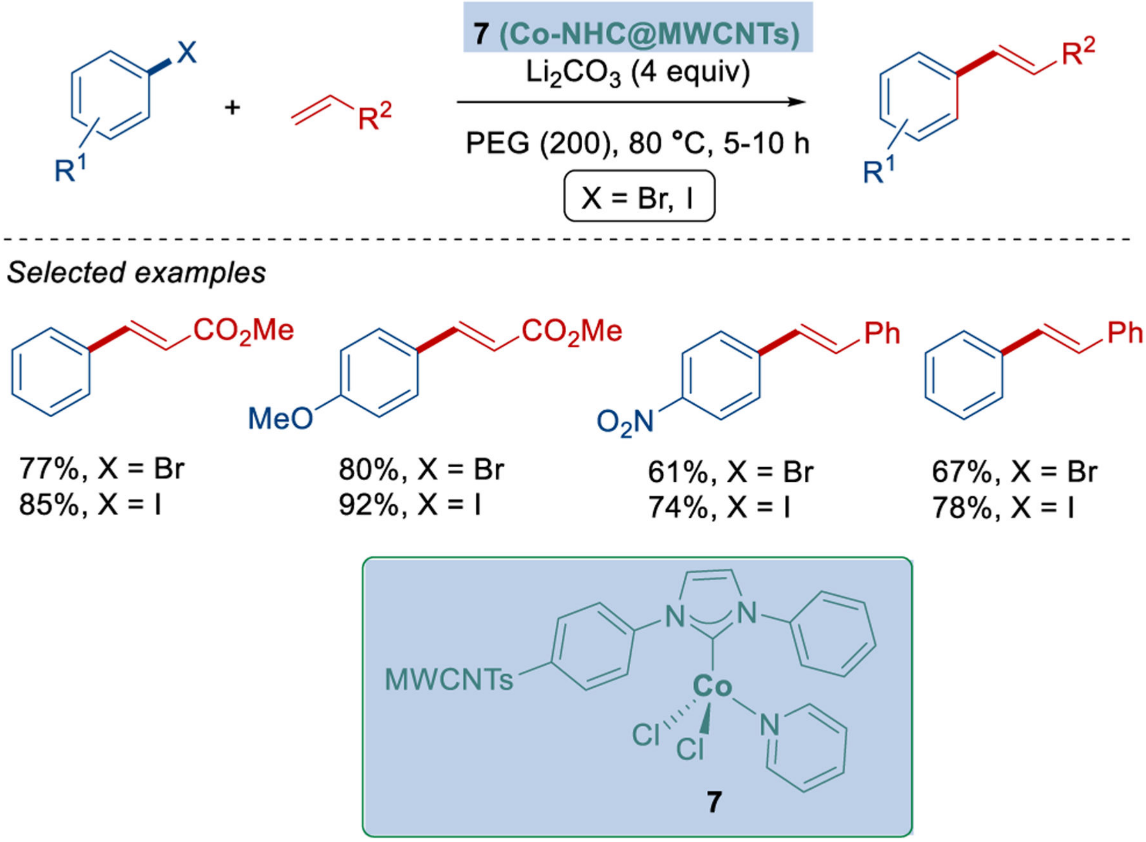

Scheme 16.

Co–NHC Catalyzed Heck Reaction of Aryl Halides Reported by Hajipour.

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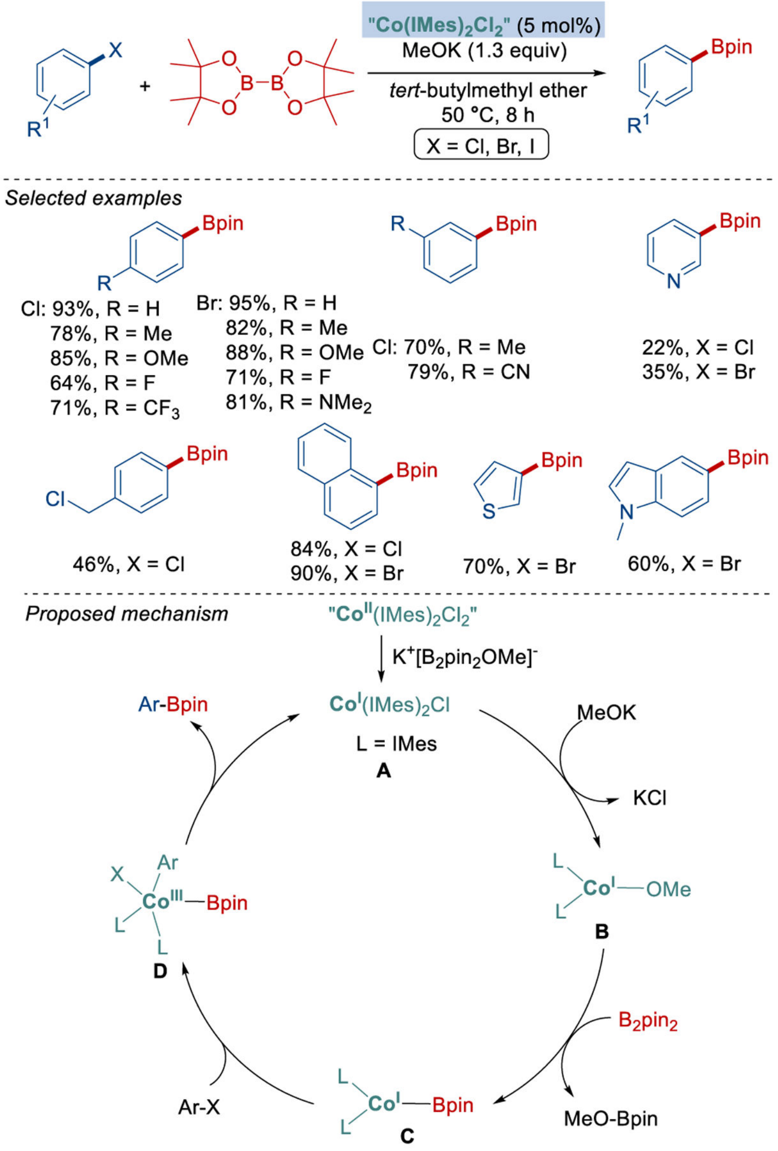

Scheme 17.

Co–NHC Catalyzed Borylation of Aryl Chlorides and Bromides Reported by Geetharani.

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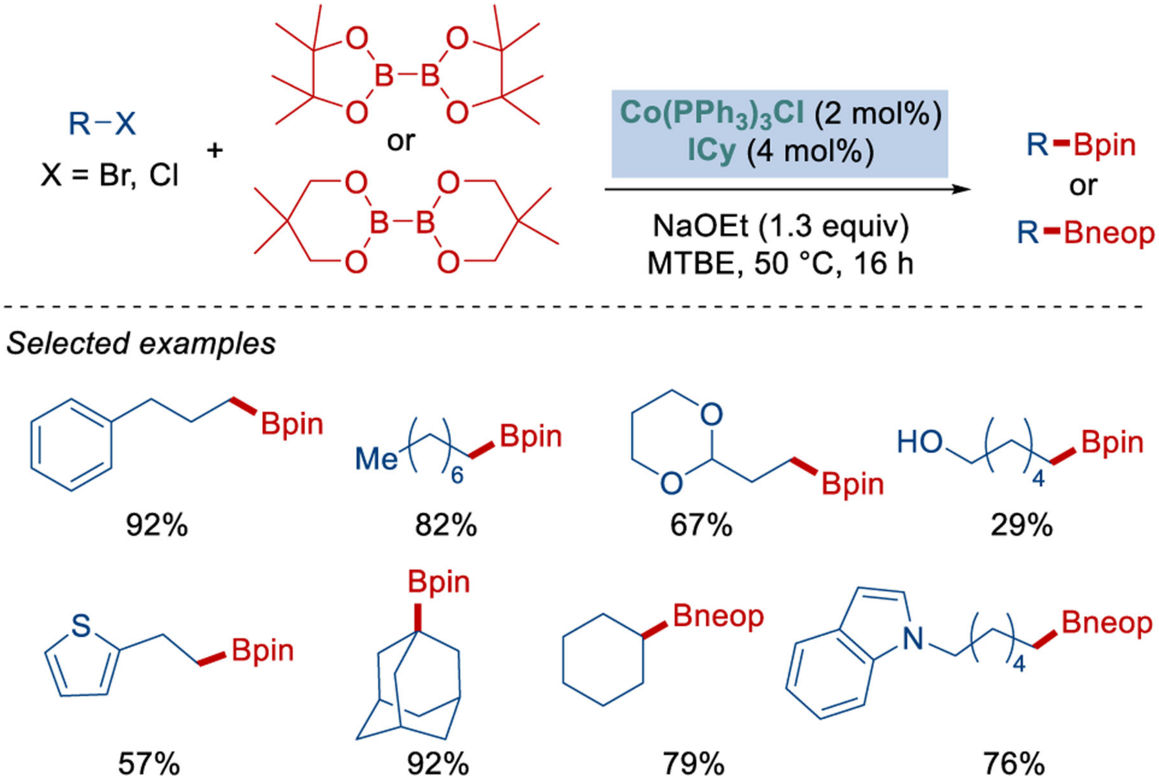

Scheme 18.

Co–NHC Catalyzed Borylation of Alkyl Chlorides and Bromides Reported by Geetharani.

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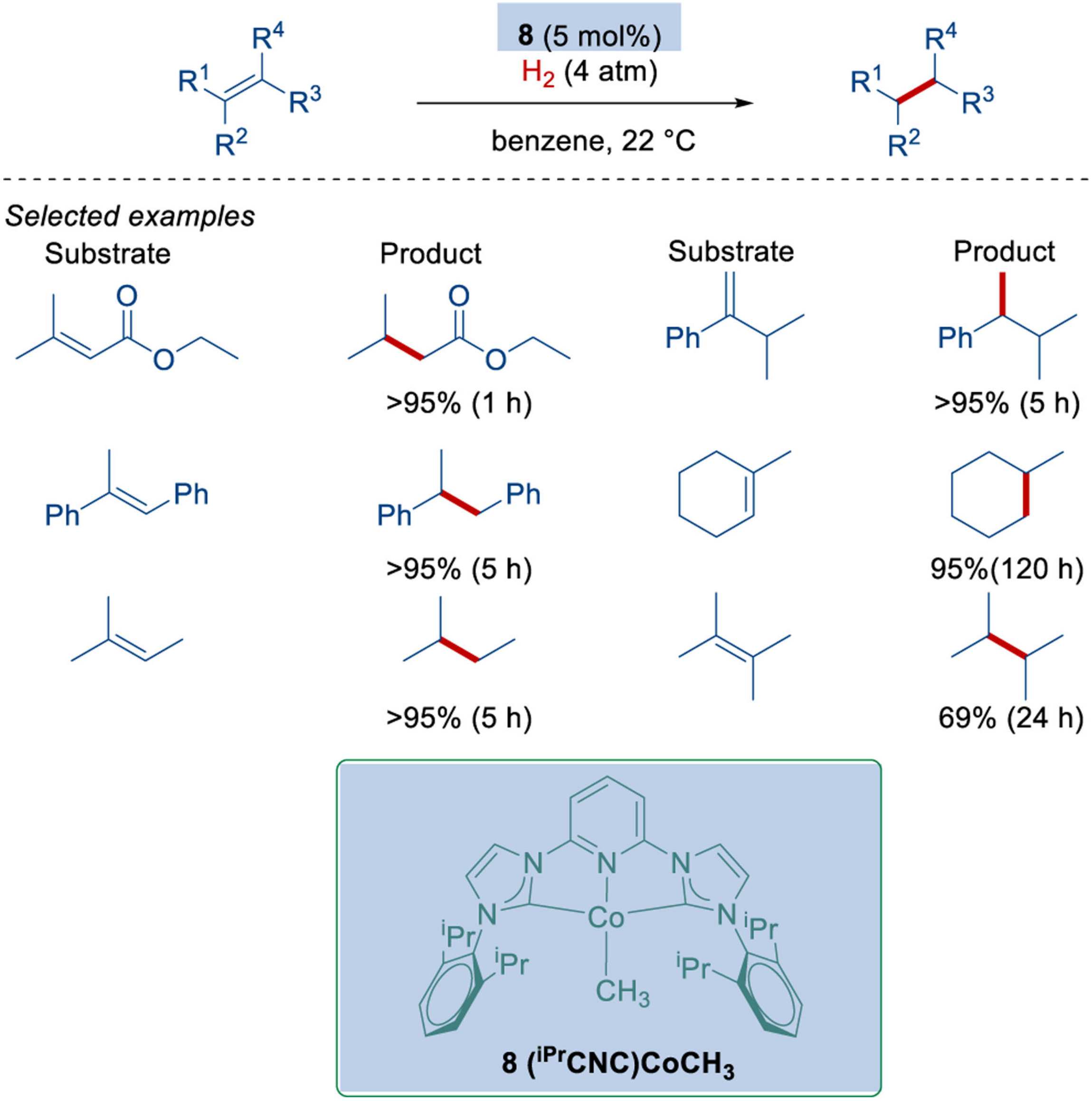

Scheme 19.

Catalytic Hydrogenation of Alkenes using Co–NHC CNC Precatalysts Reported by Chirik.

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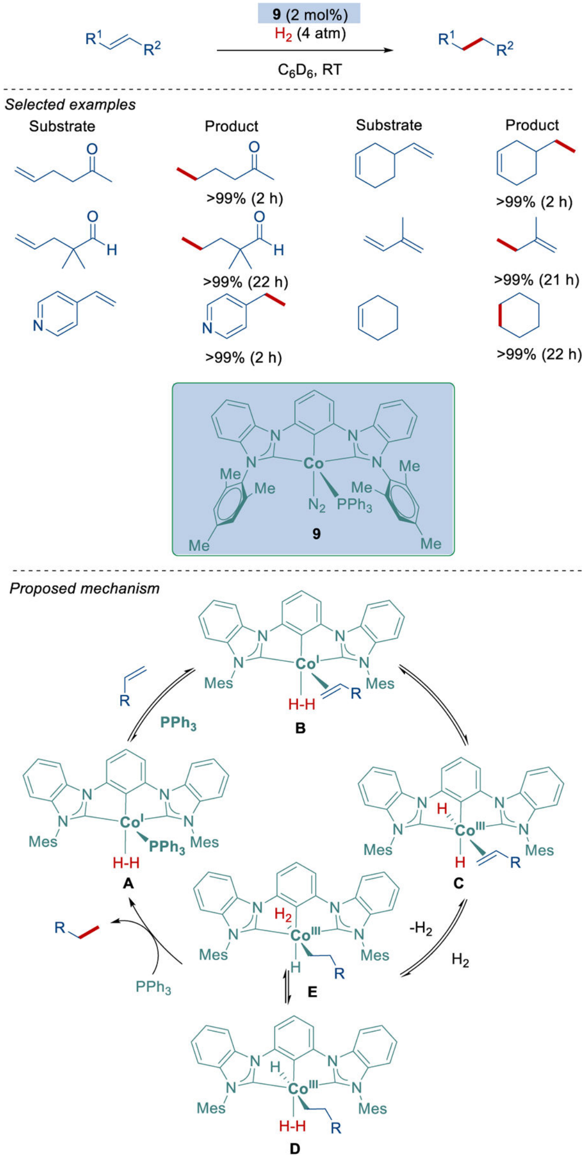

Scheme 20.

Catalytic Hydrogenation of Alkenes using Co–NHC CCC Precatalysts Reported by Fout.

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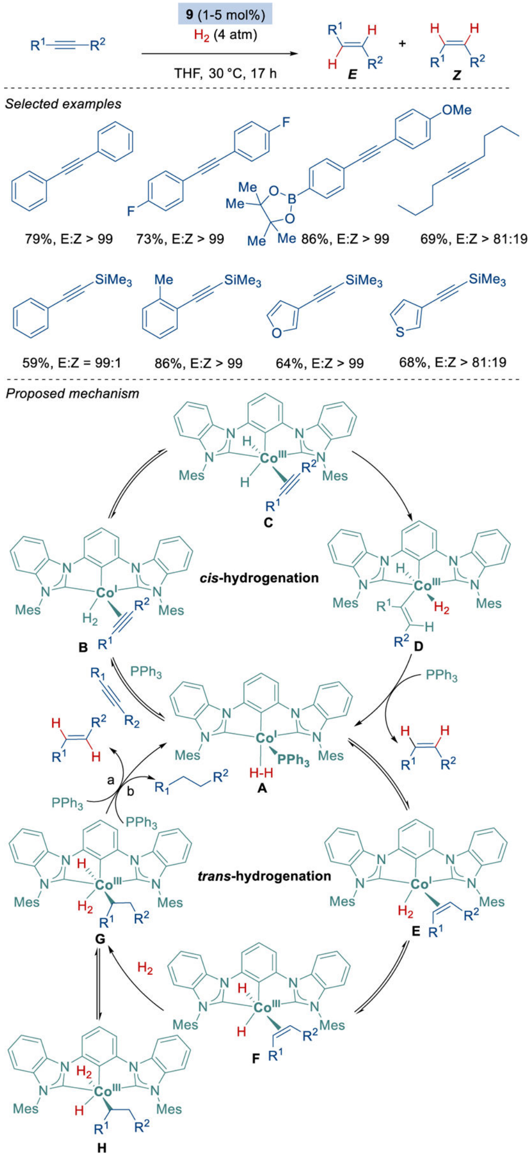

Scheme 21.

Catalytic Semihydrogenation of Alkynes using Co–NHC CCC Precatalysts Reported by Fout.

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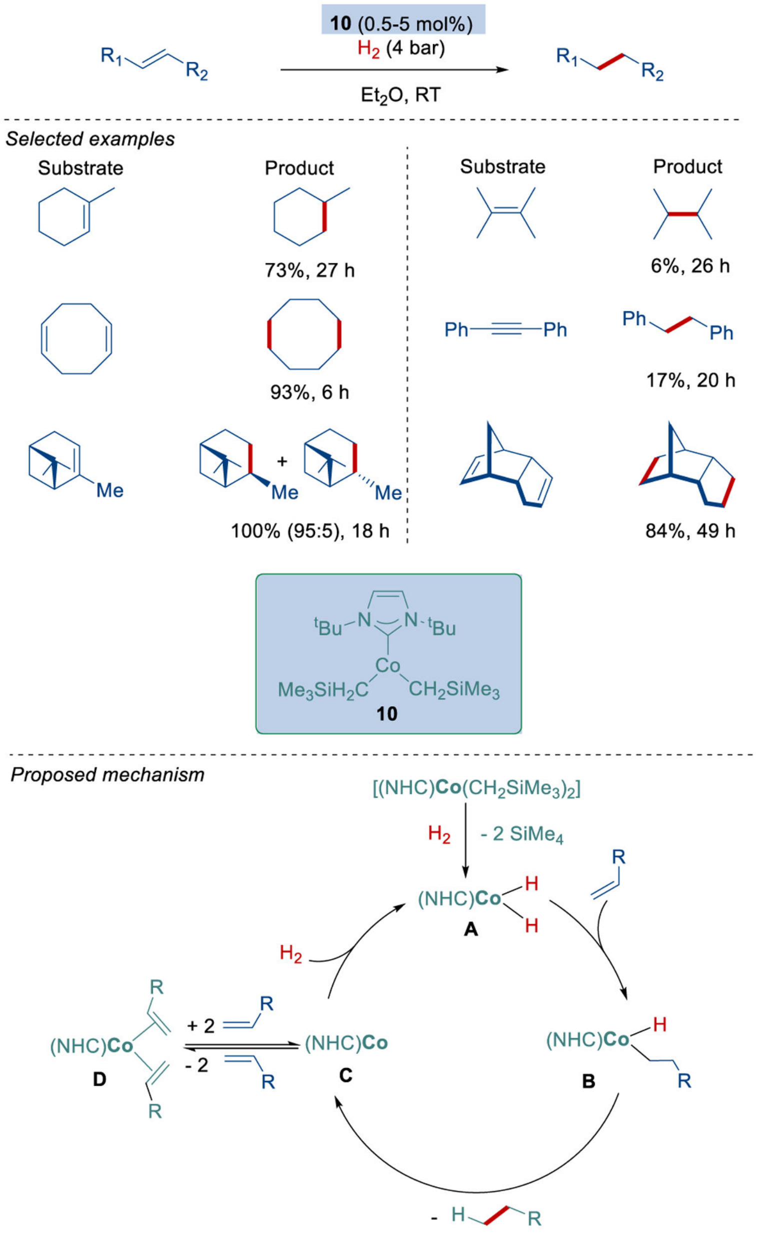

Scheme 22.

Co–NHC Catalyzed Hydrogenation of Alkenes and Alkynes Reported by Walter.

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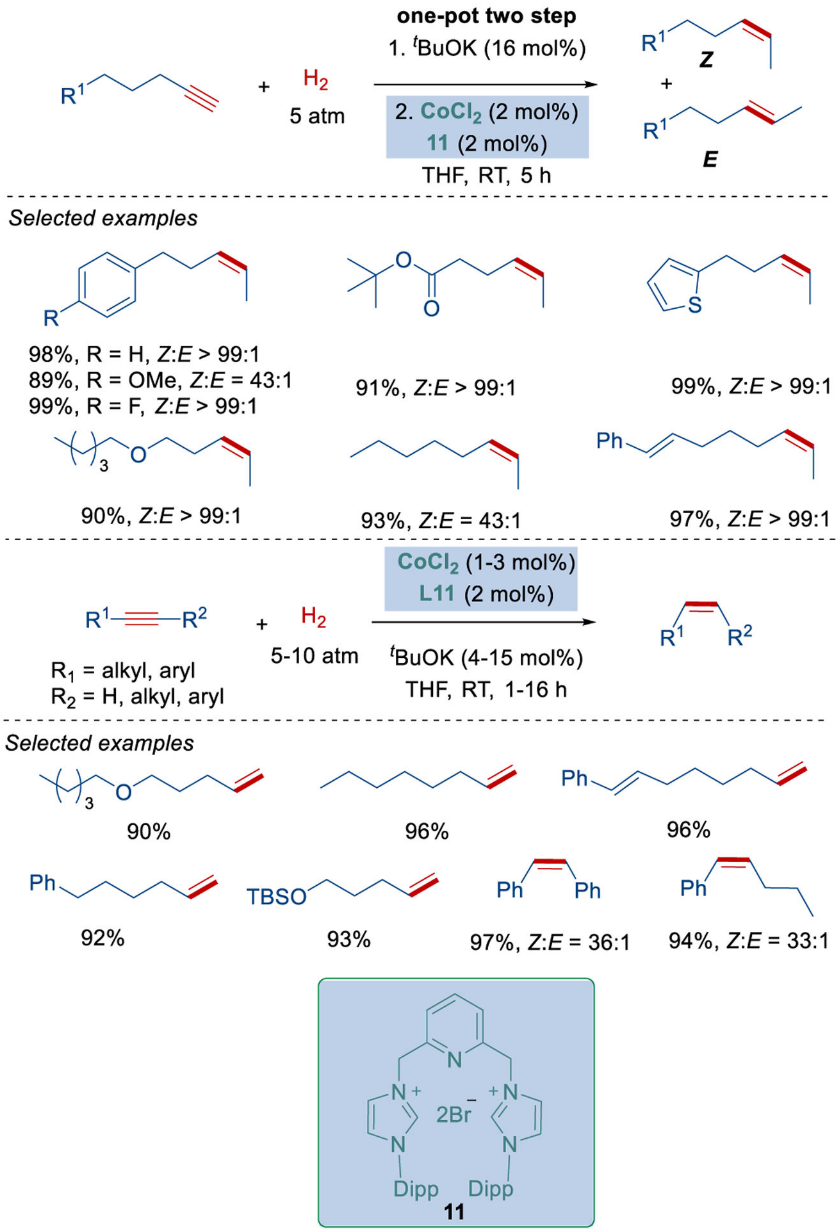

Scheme 23.

Co–NHC Catalyzed Hydrogenation of Terminal Alkynes Reported by Liu.

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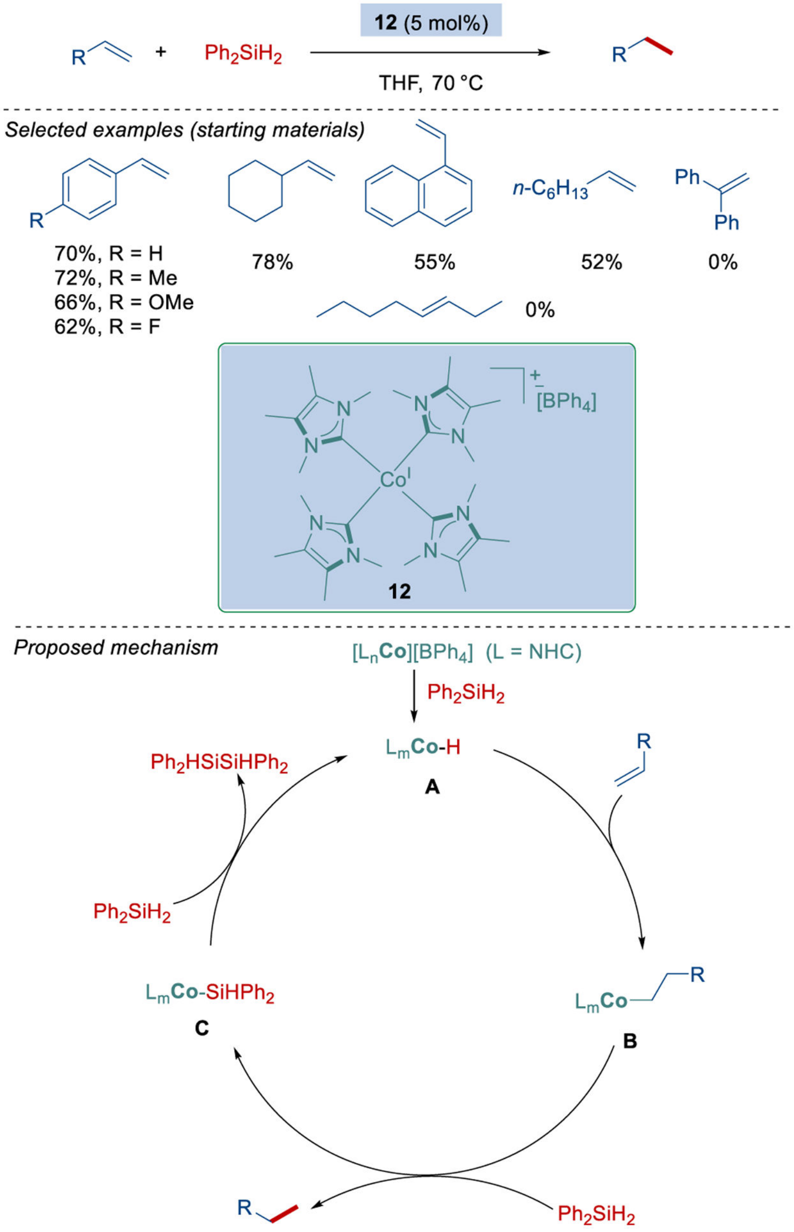

Scheme 24.

Hydrogenation of Alkenes Catalyzed by $[(^{Me}IMe)_4Co][BPh_4]$ Reported by Deng.

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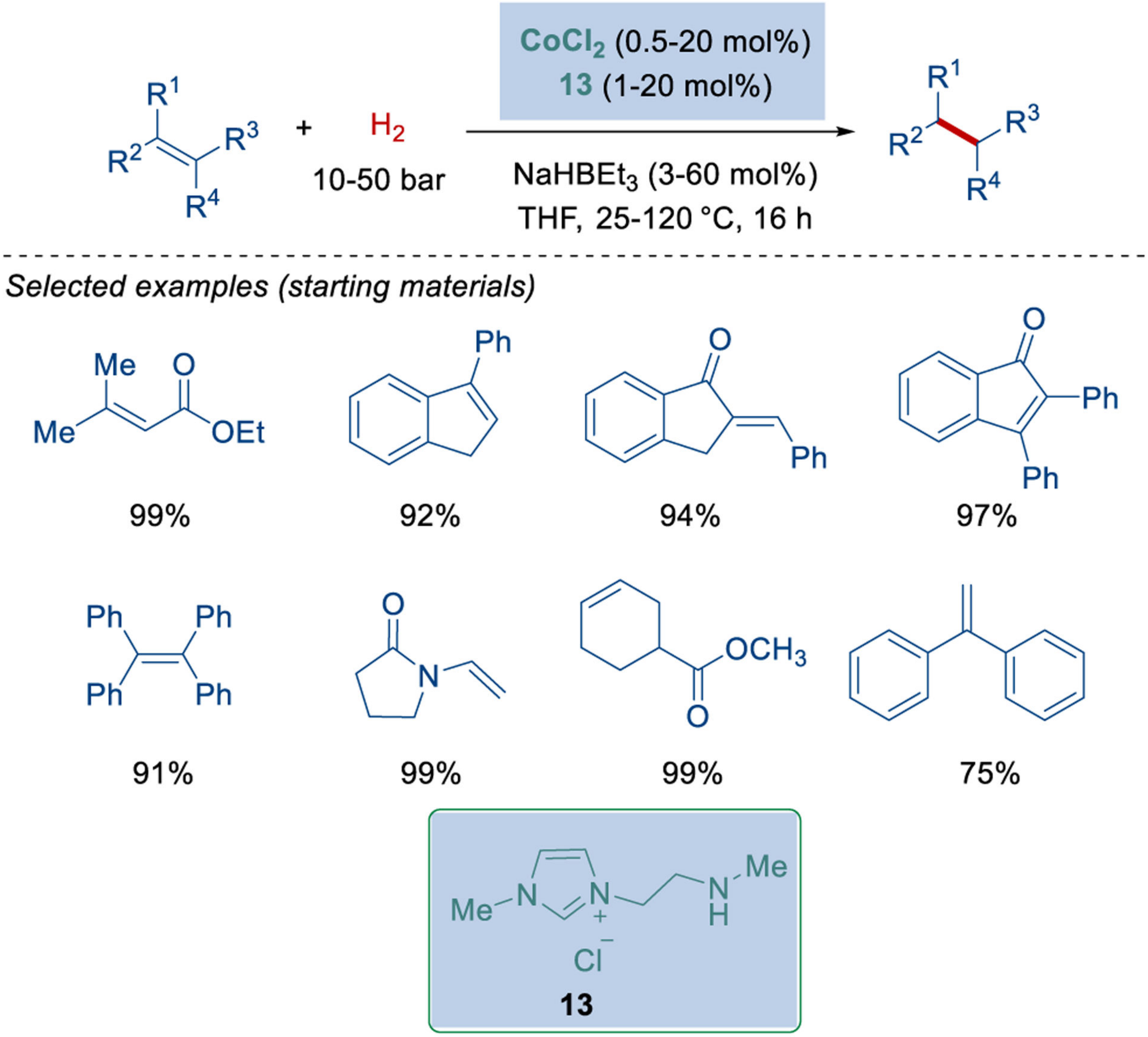

Scheme 25.

Co–NHC Catalyzed Hydrogenation of Hindered Alkenes using Bidentate NHC Reported by Liu.

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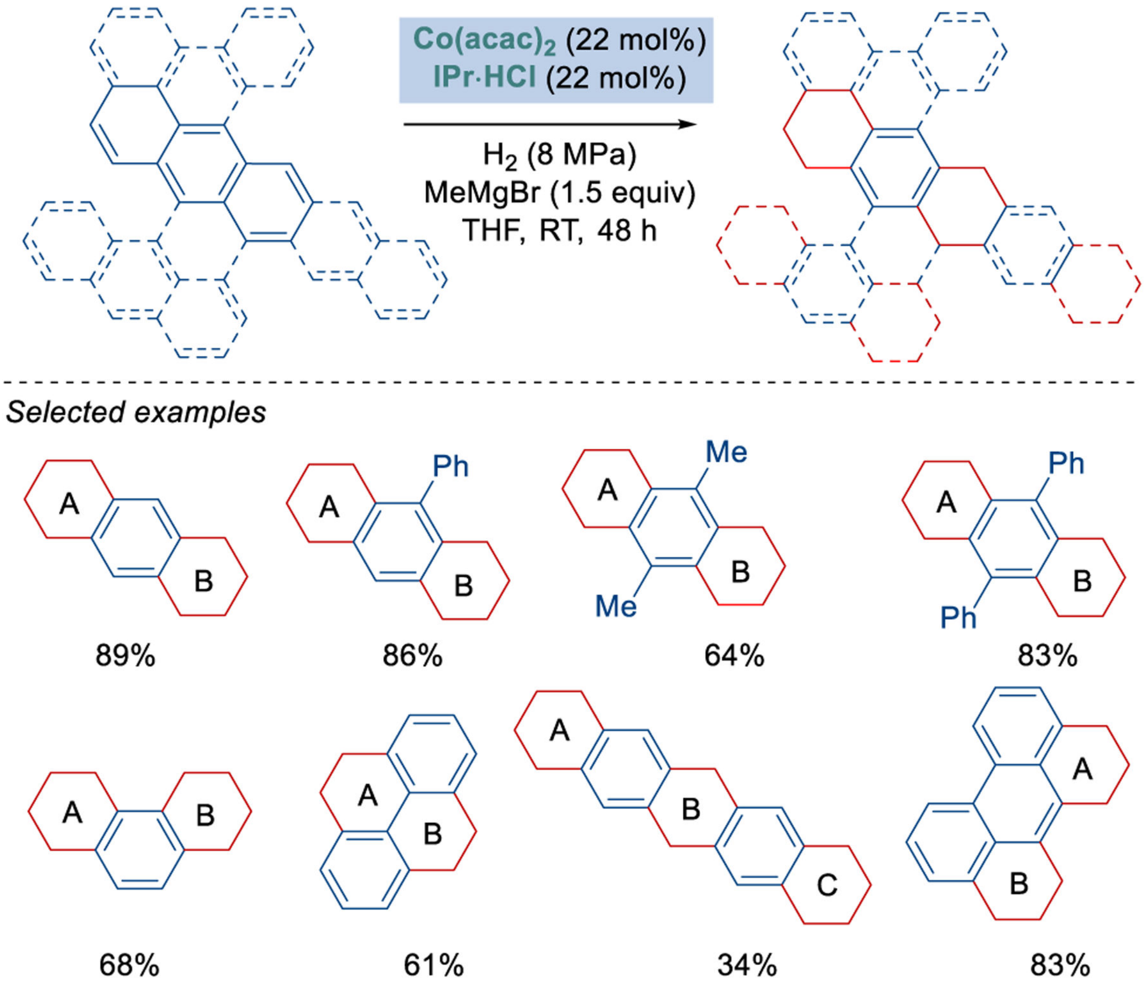

Scheme 26.

Co–NHC Catalyzed Regioselective Hydrogenation of Polycyclic Aromatic Hydrocarbons Reported by Zeng.

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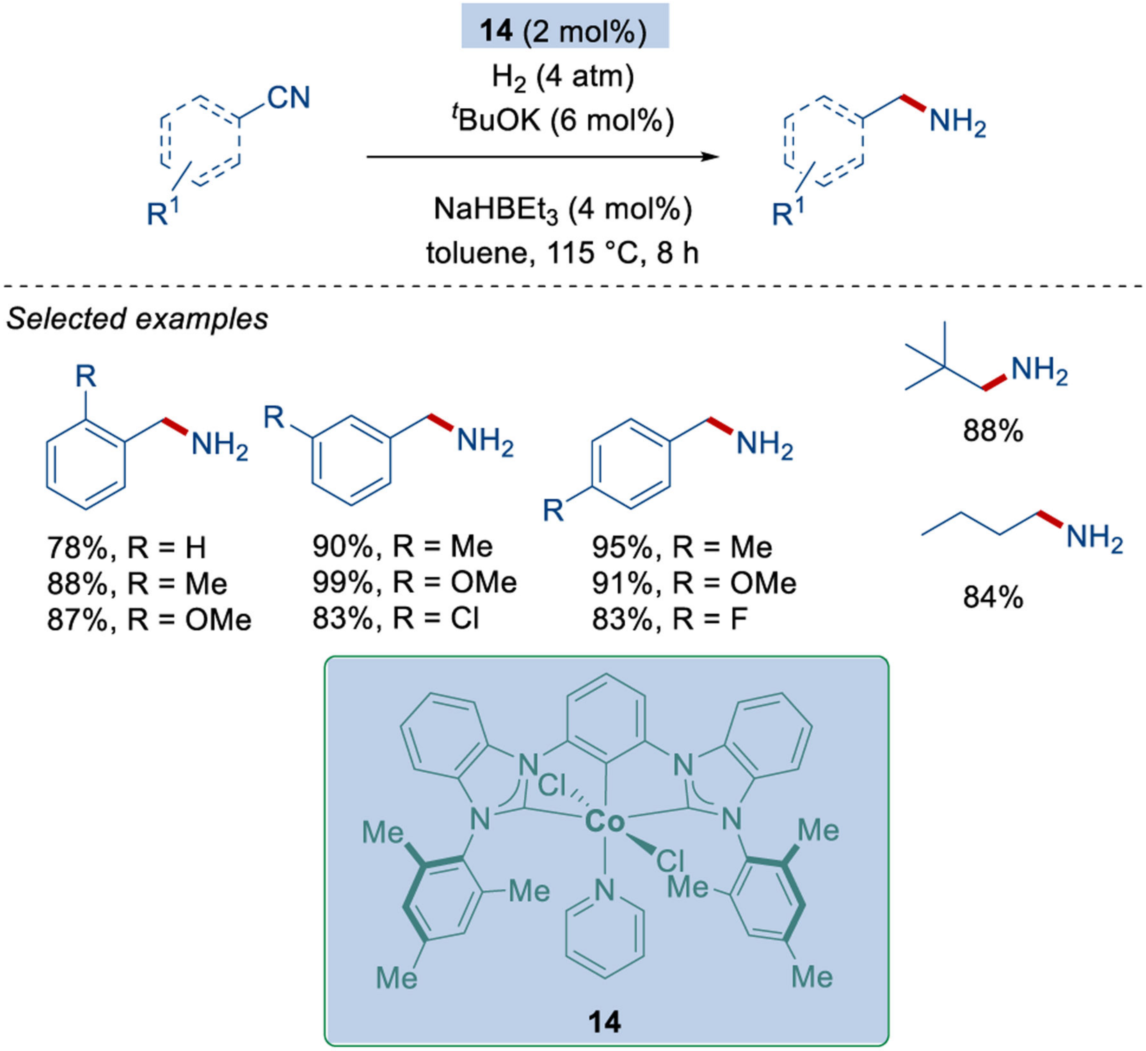

Scheme 27.

Co–NHC Catalyzed, Lewis Acid Assisted Hydrogenation of Nitriles Reported by Fout.

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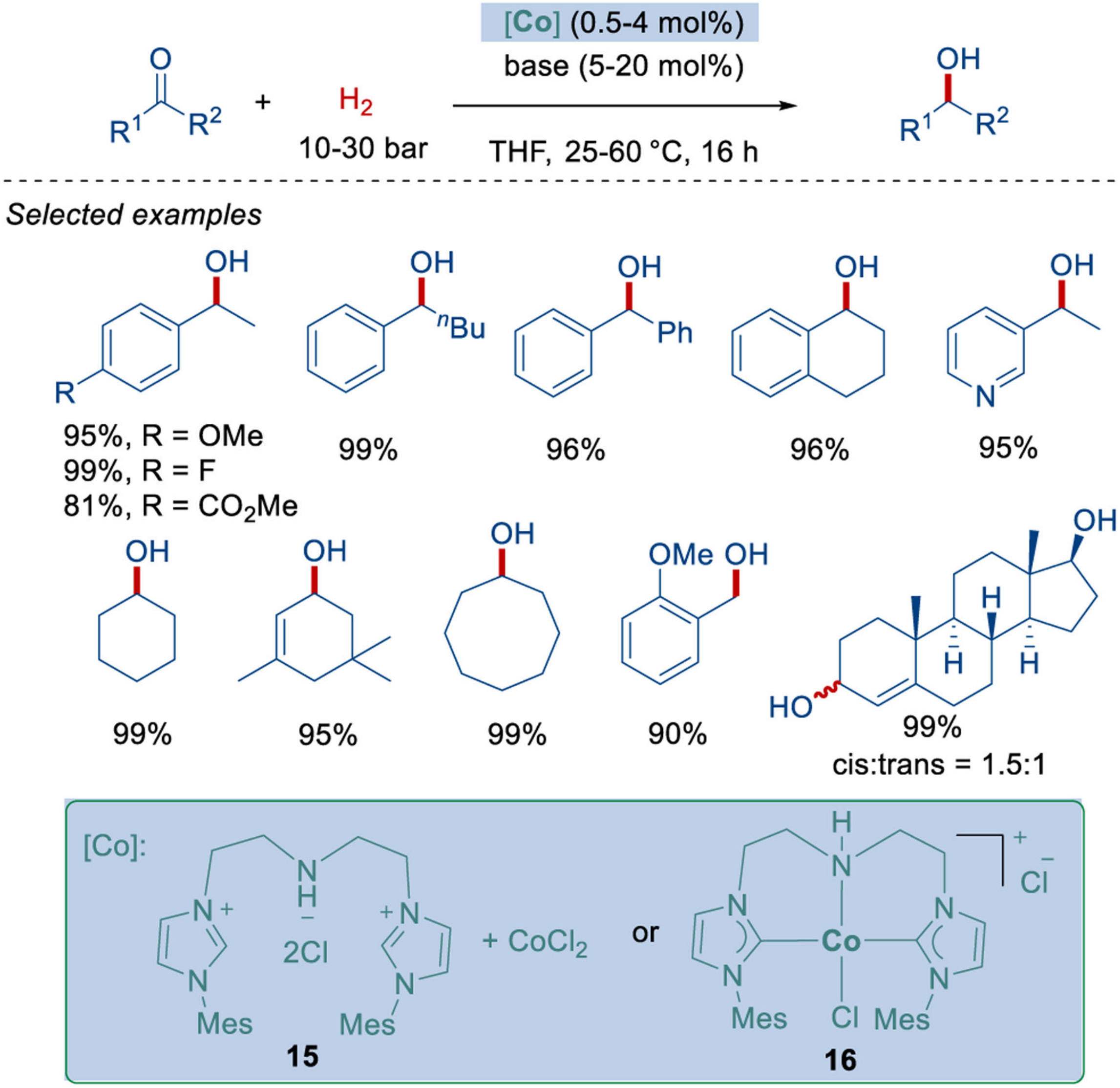

Scheme 28.

Co–NHC Catalyzed Hydrogenation of Ketones and Aldehydes Reported by Liu.

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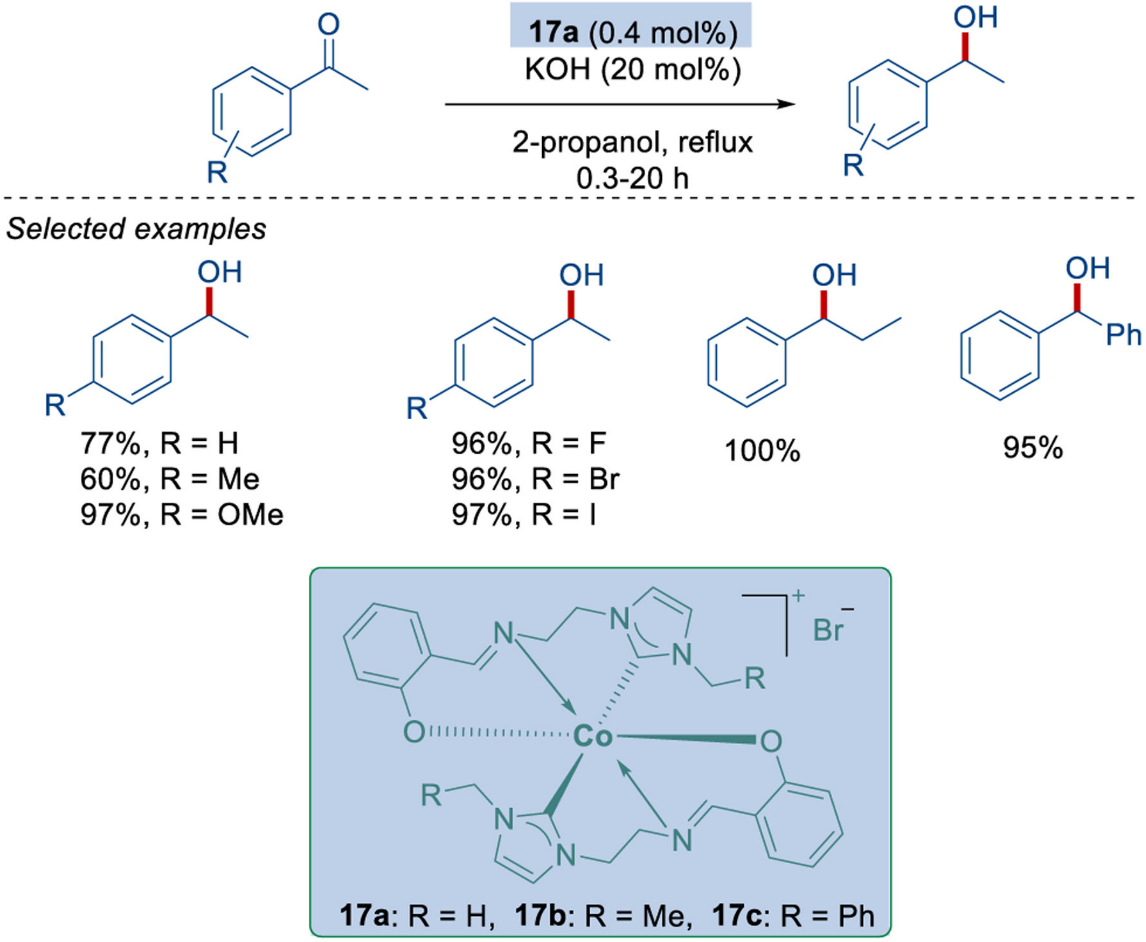

Scheme 29.

Co–NHC Catalyzed Transfer Hydrogenation of Ketones Reported by Bala.

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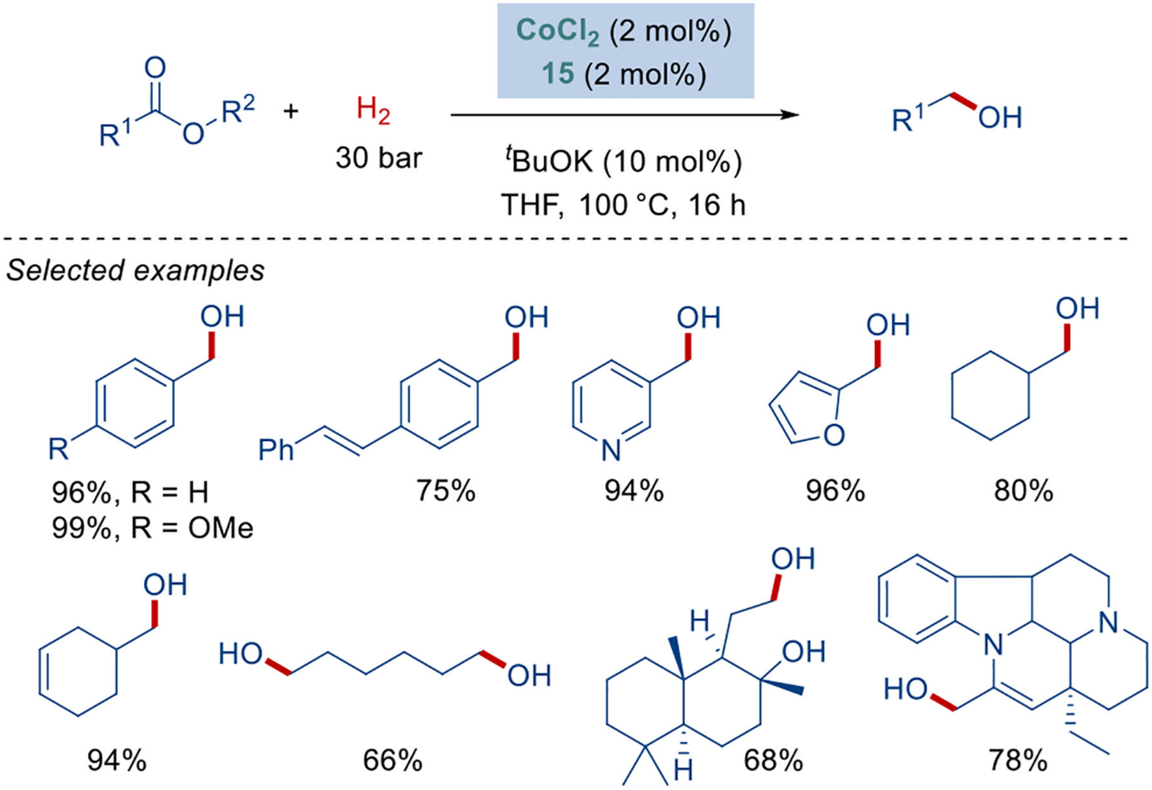

Scheme 30.

Co–NHC Catalyzed Hydrogenation of Esters Reported by Liu.

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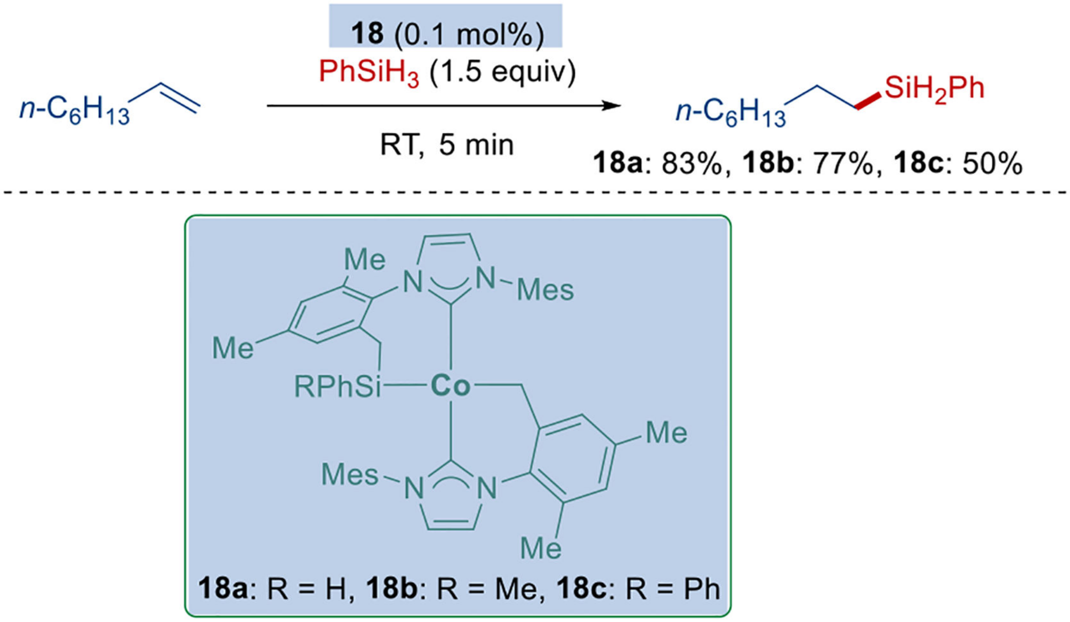

Scheme 31.

Co–NHC Catalyzed Hydrosilylation of 1-Octene using PhSiH$_3$ Reported by Deng.

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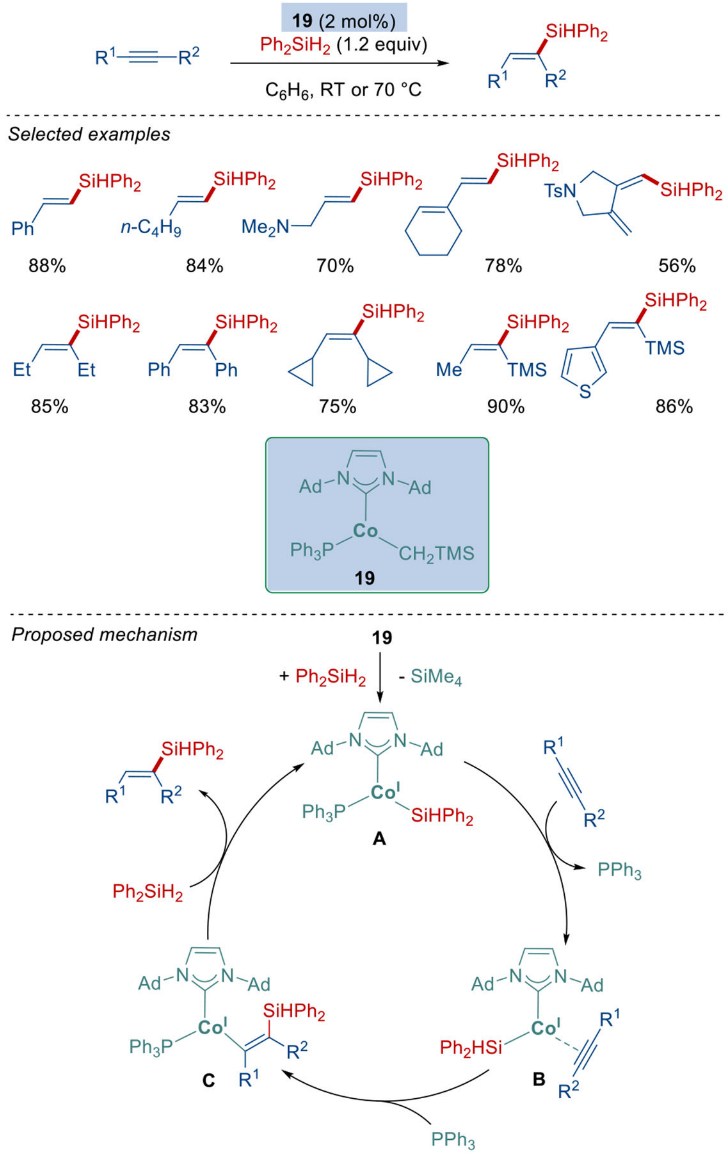

Scheme 32.

Co–NHC Catalyzed Regio- and Stereoselective Hydrosilylation of Alkynes Reported by Deng.

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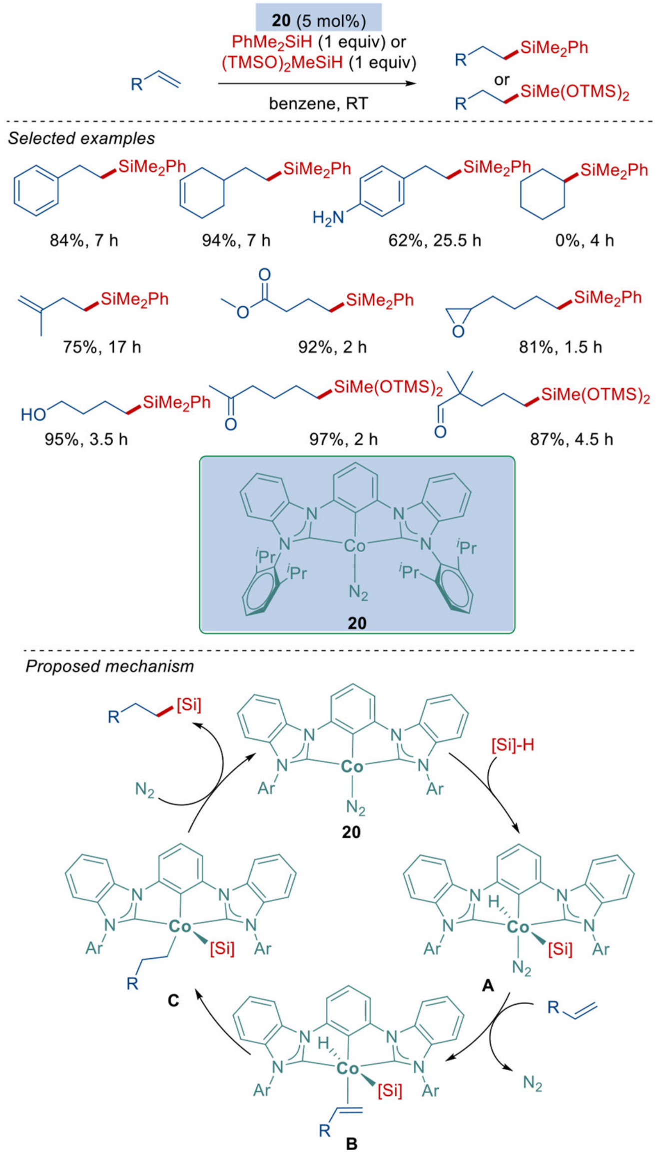

Scheme 33.

Co–NHC Catalyzed Hydrosilylation of Alkenes Reported by Fout.

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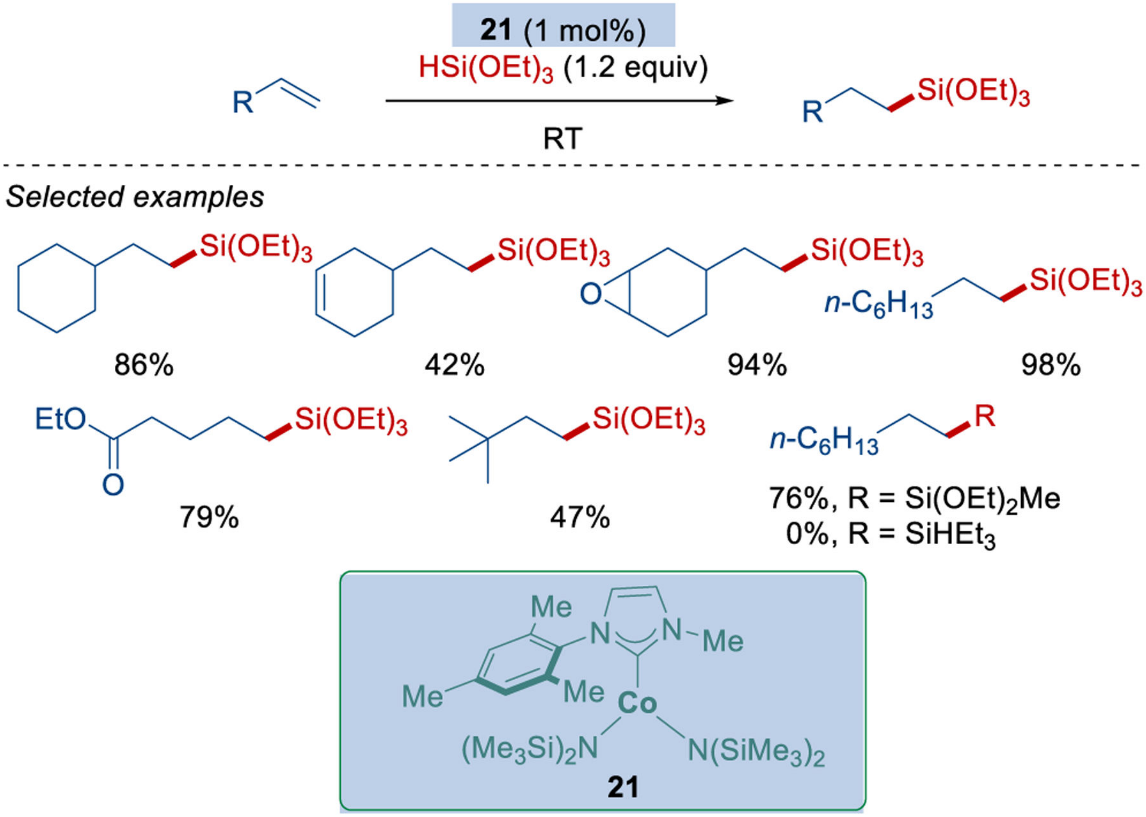

Scheme 34.

Co–NHC Catalyzed Hydrosilylation of Alkenes with Tertiary Silanes Reported by Deng.

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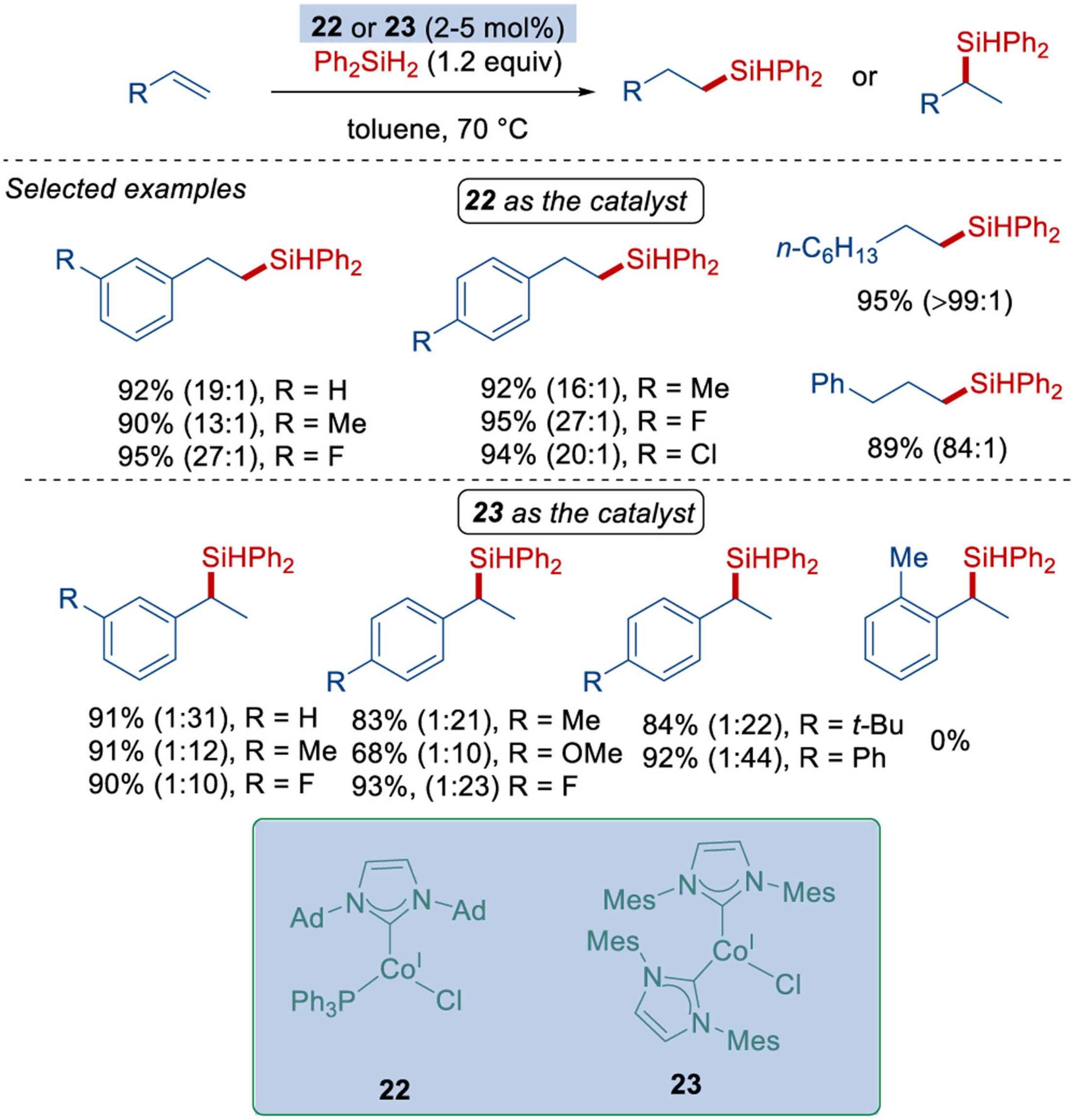

Scheme 35.

Co–NHC Catalyzed Hydrosilylation of Alkenes Reported by Deng.

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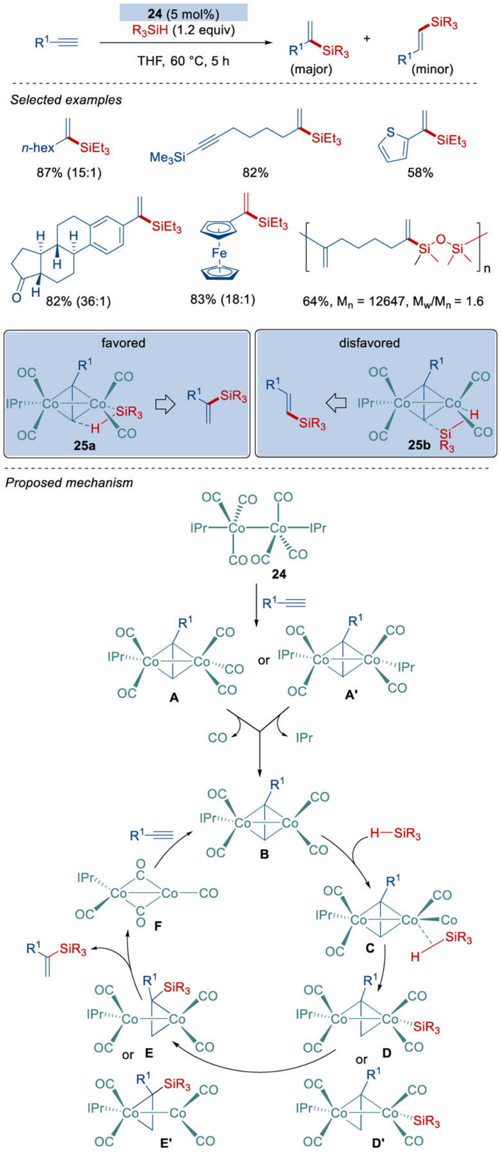

Scheme 36.

Co–NHC Catalyzed Markovnikov Hydrosilylation of Alkynes Reported by Deng.

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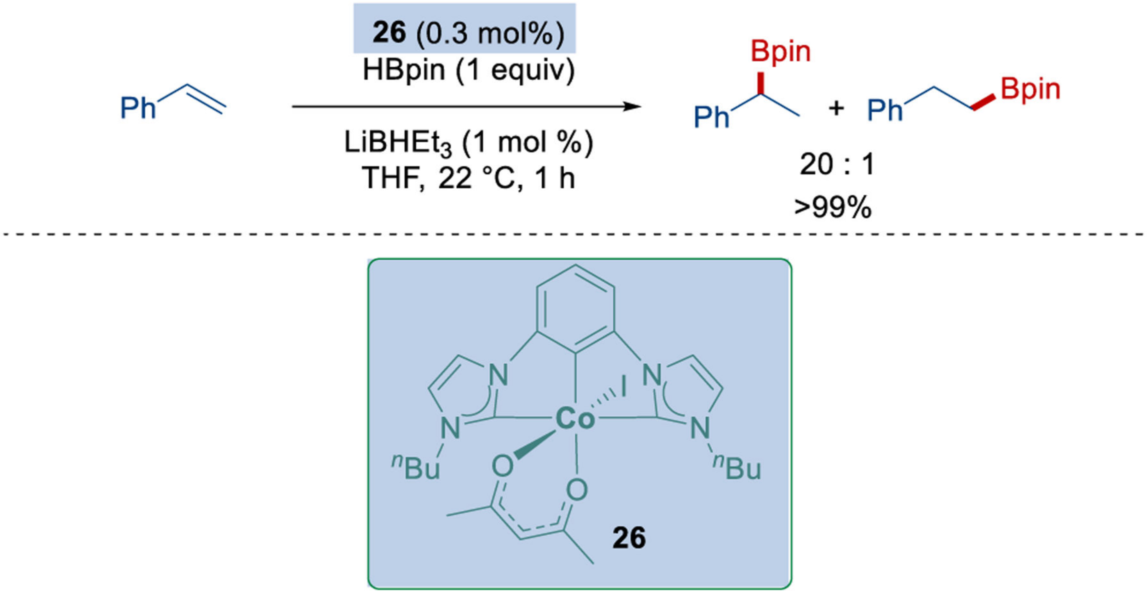

Scheme 37.

Co–NHC Catalyzed Alkene Hydroboration Reported by Hollis.

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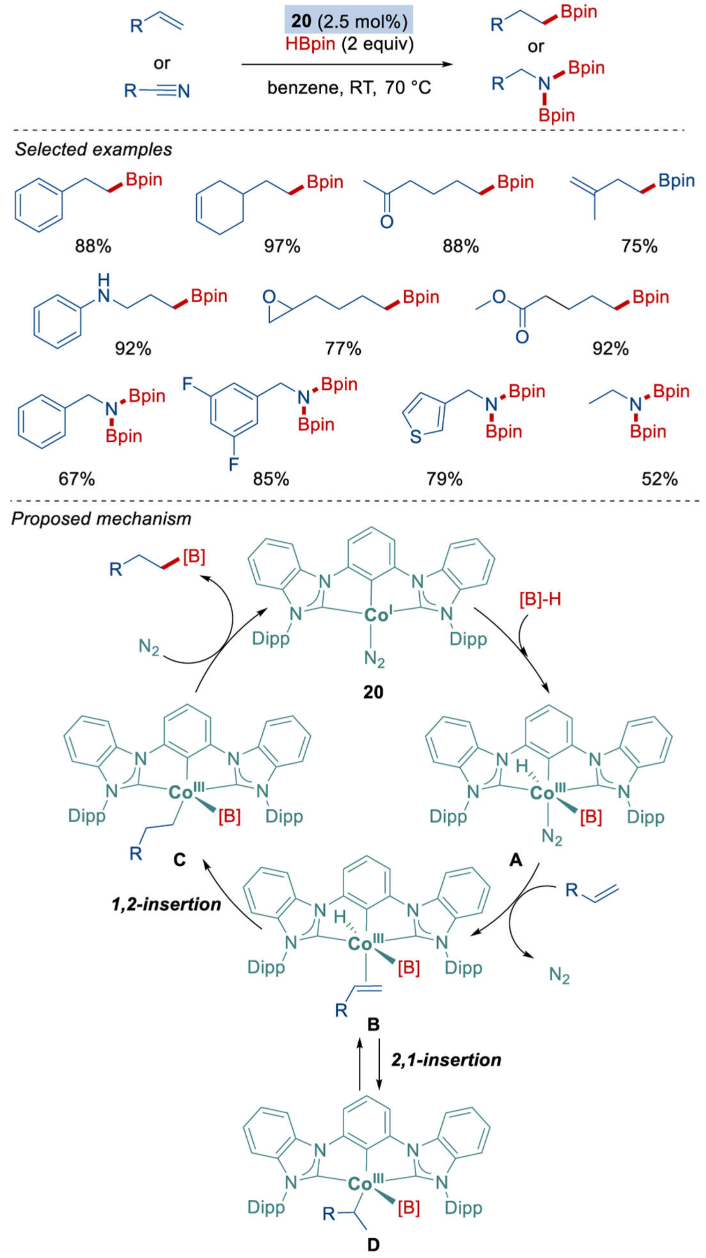

Scheme 38.

Co–NHC Catalyzed Hydroboration of Alkenes and Nitriles Reported by Fout.

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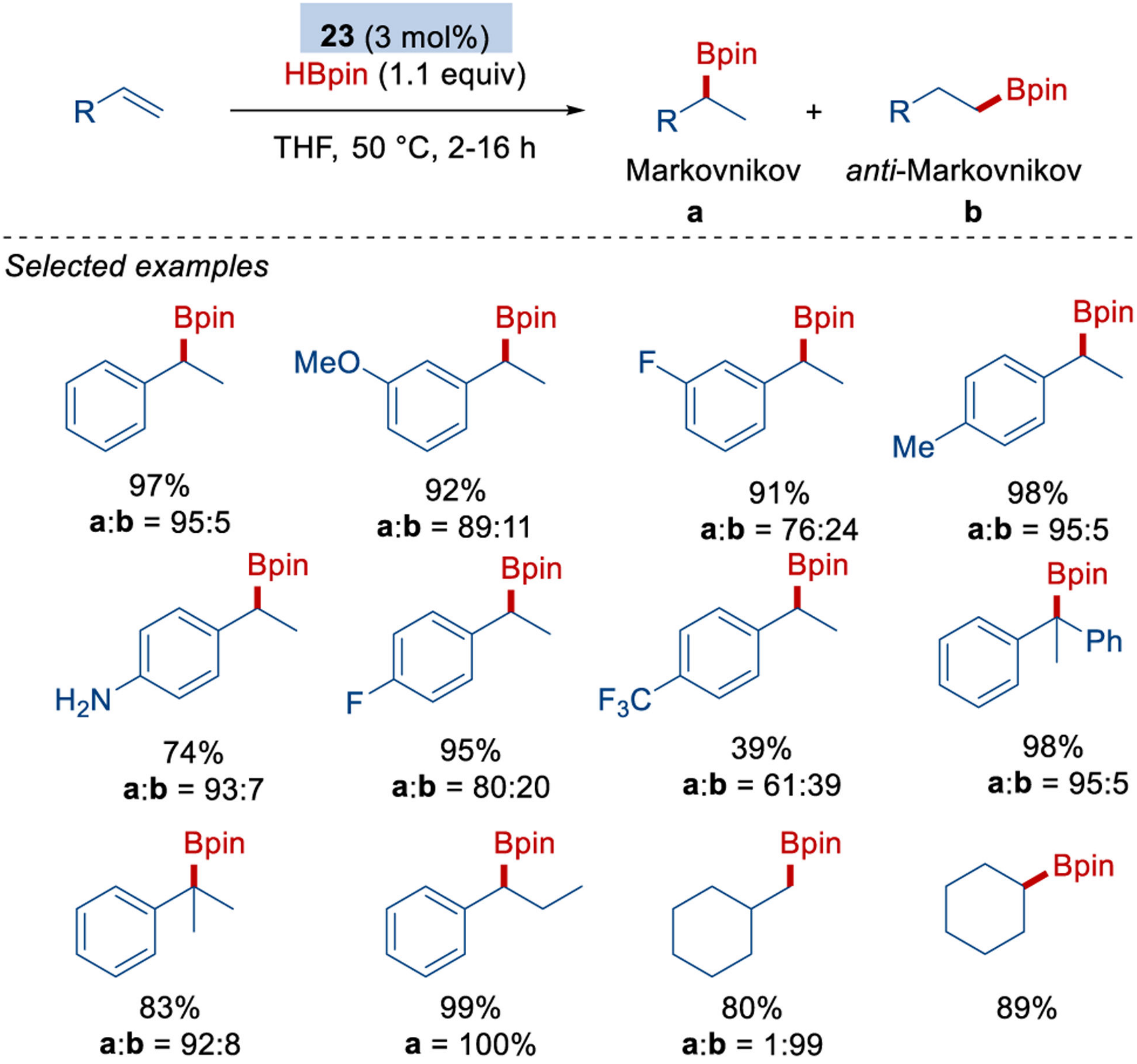

Scheme 39.

Co–NHC Catalyzed Hydroboration of Alkenes Reported by Geetharani.

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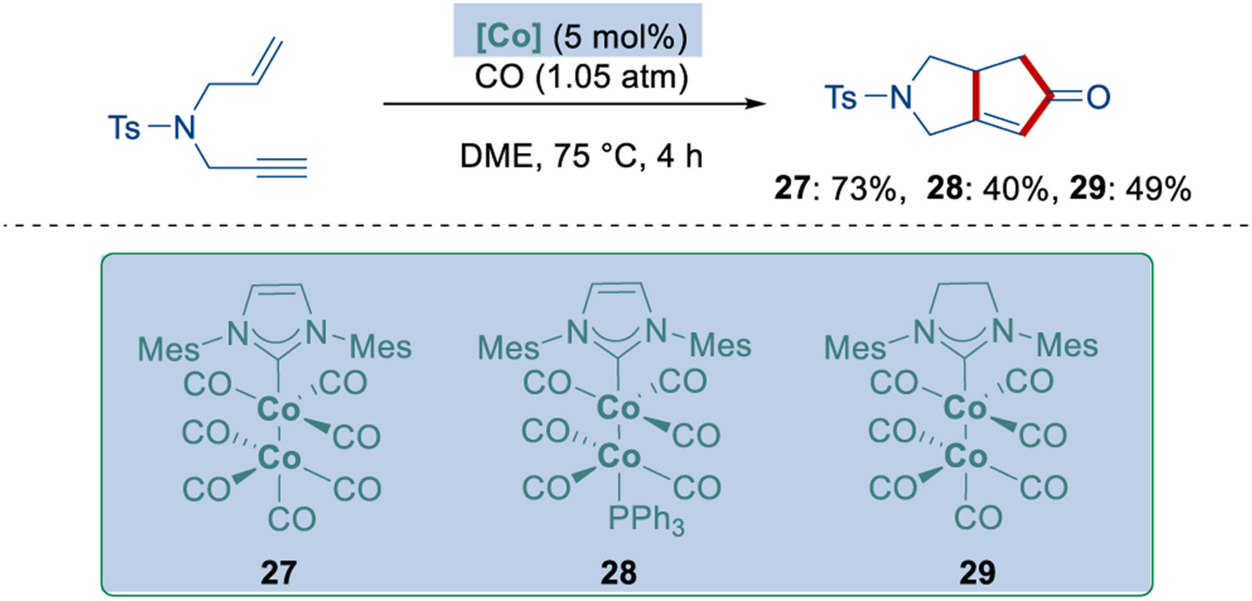

Scheme 40.

Co–NHC Catalyzed Pauson-Khand Cycloaddition Reported by Gibson.

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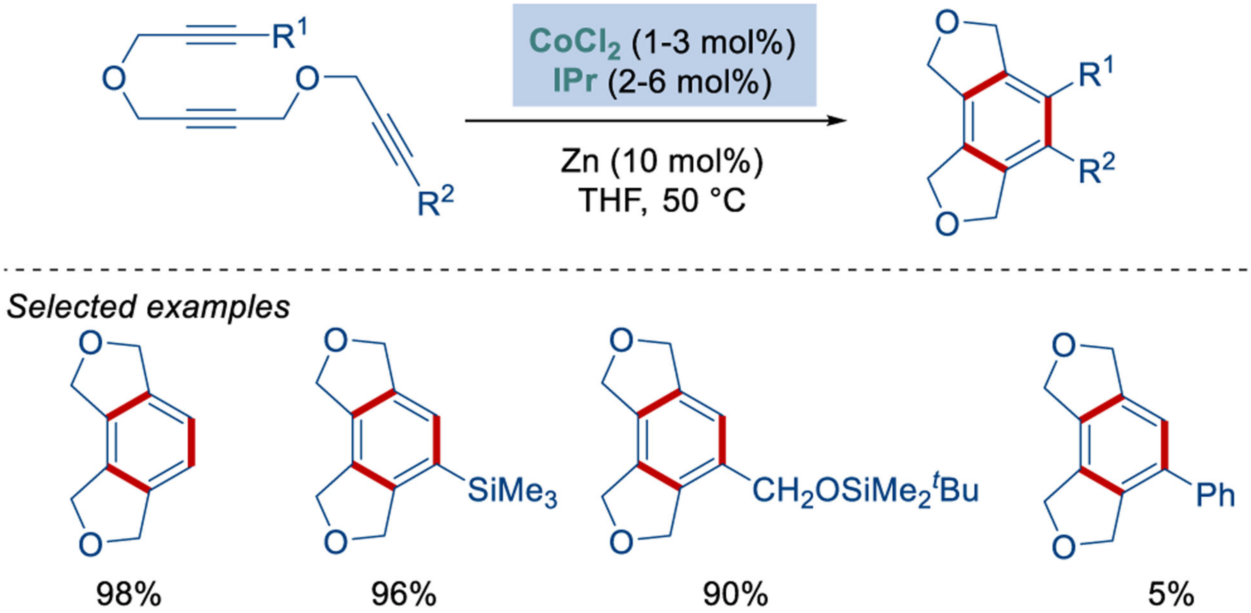

Scheme 41.
Co–NHC Catalyzed Intramolecular Cyclotrimerization of Triynes Reported by Okamoto.

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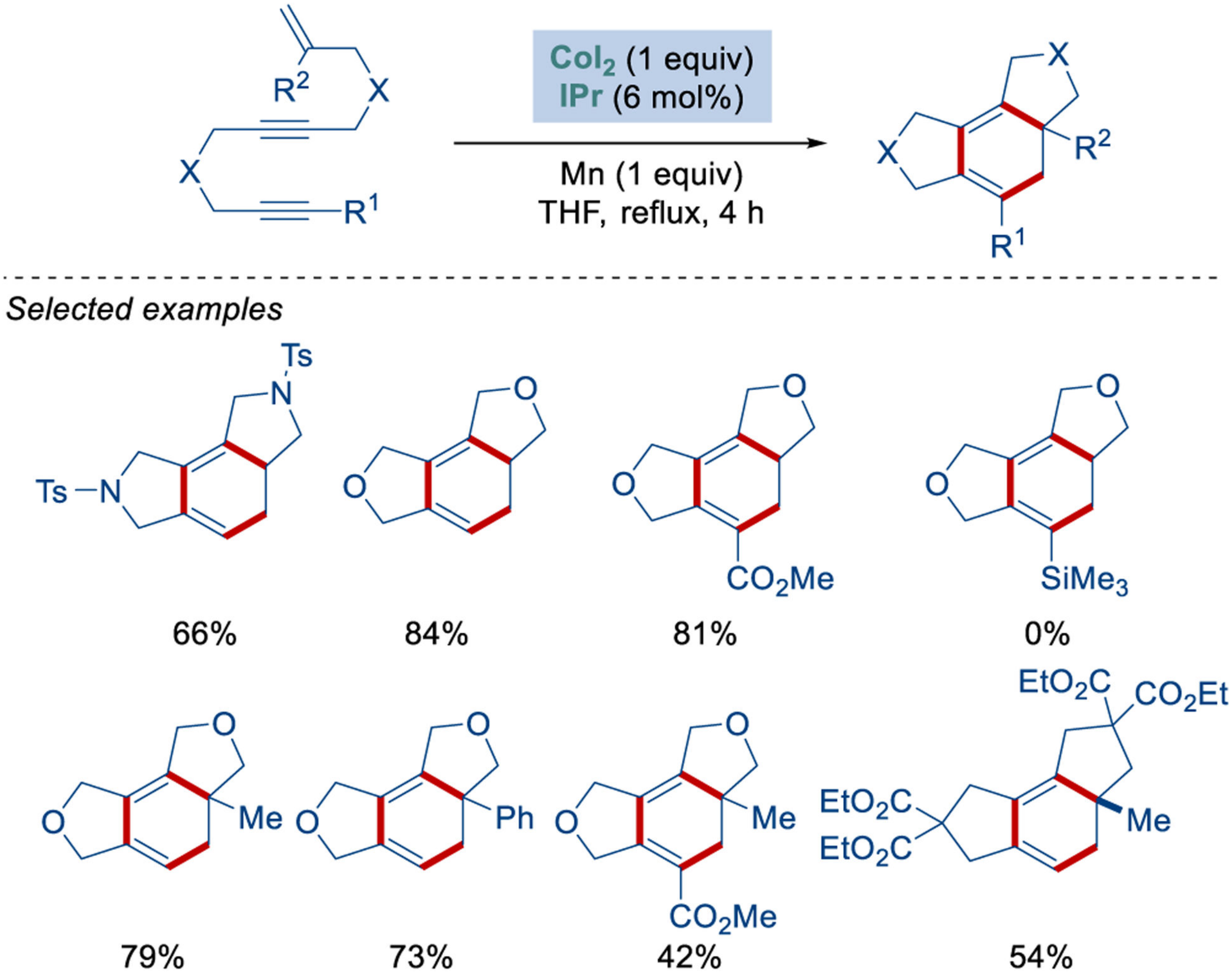

Scheme 42.

Co–NHC Catalyzed Cycloaddition of Enediynes Reported by Gandon.

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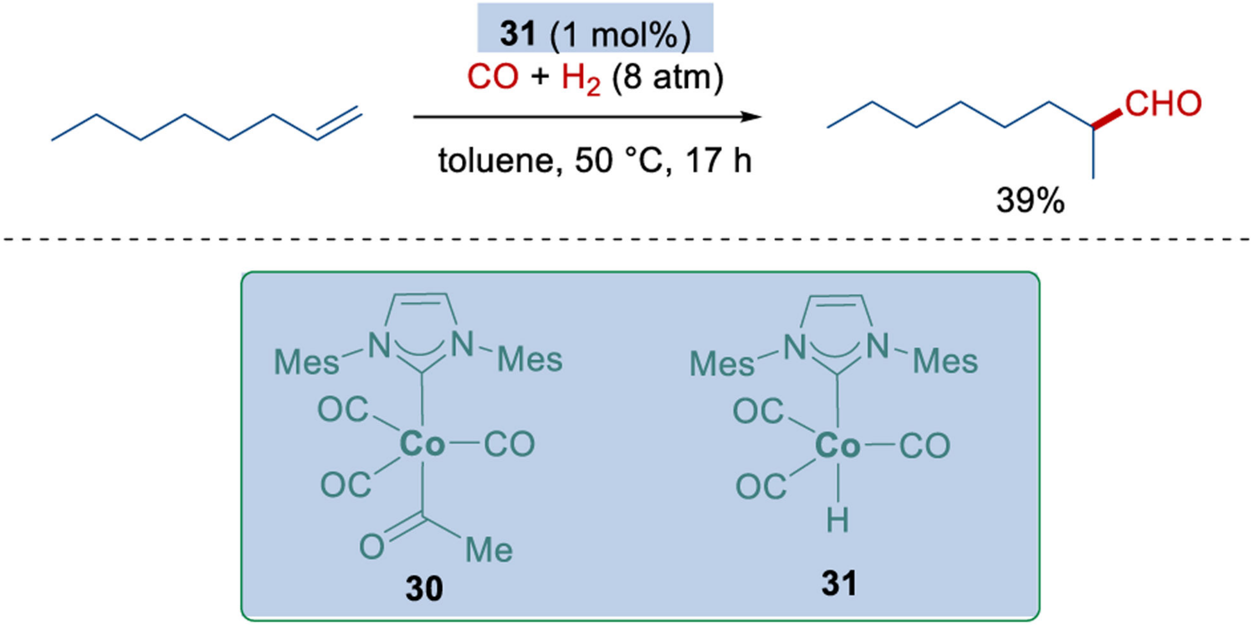

Scheme 43.
Co–NHC Catalyzed Hydroformylation of 1-Octene Reported by Llewellyn.

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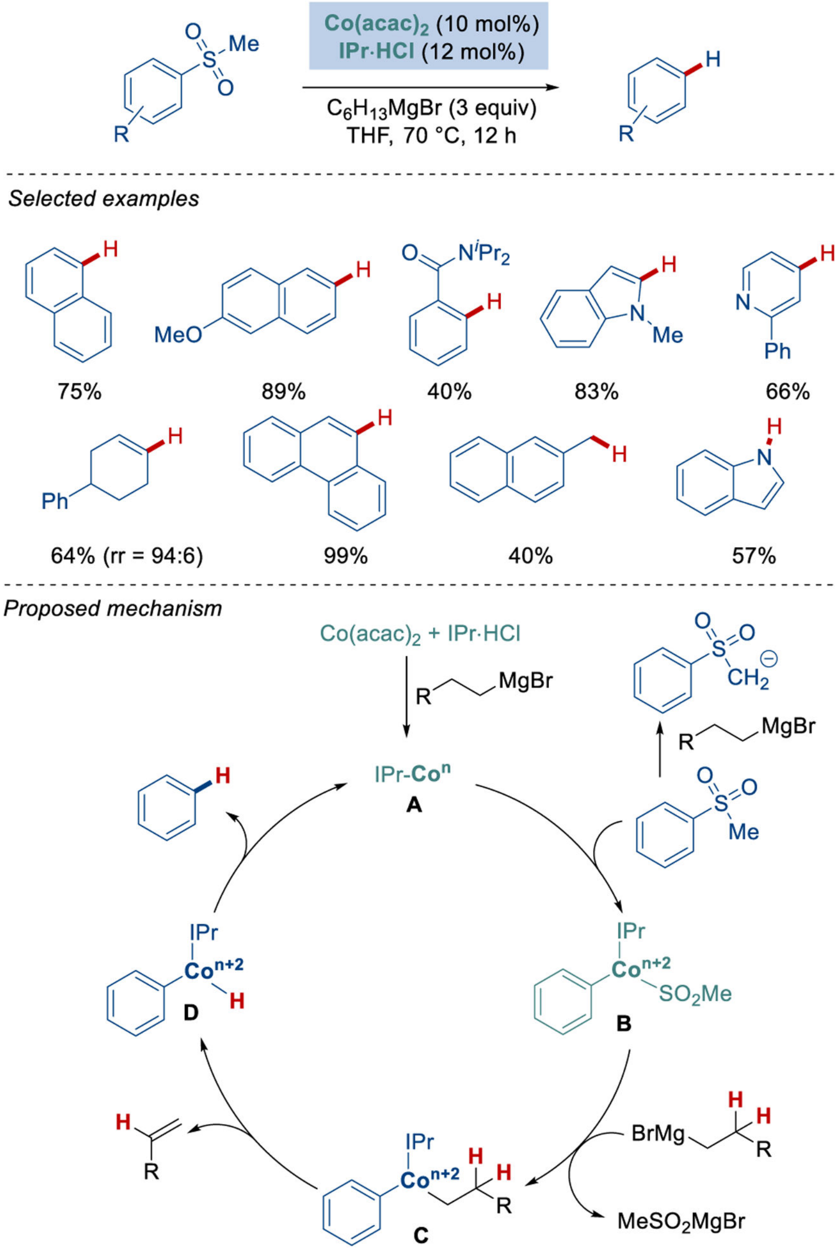

Scheme 44.

Co–NHC Catalyzed Reduction of Aryl Sulfones Reported by Yorimitsu.

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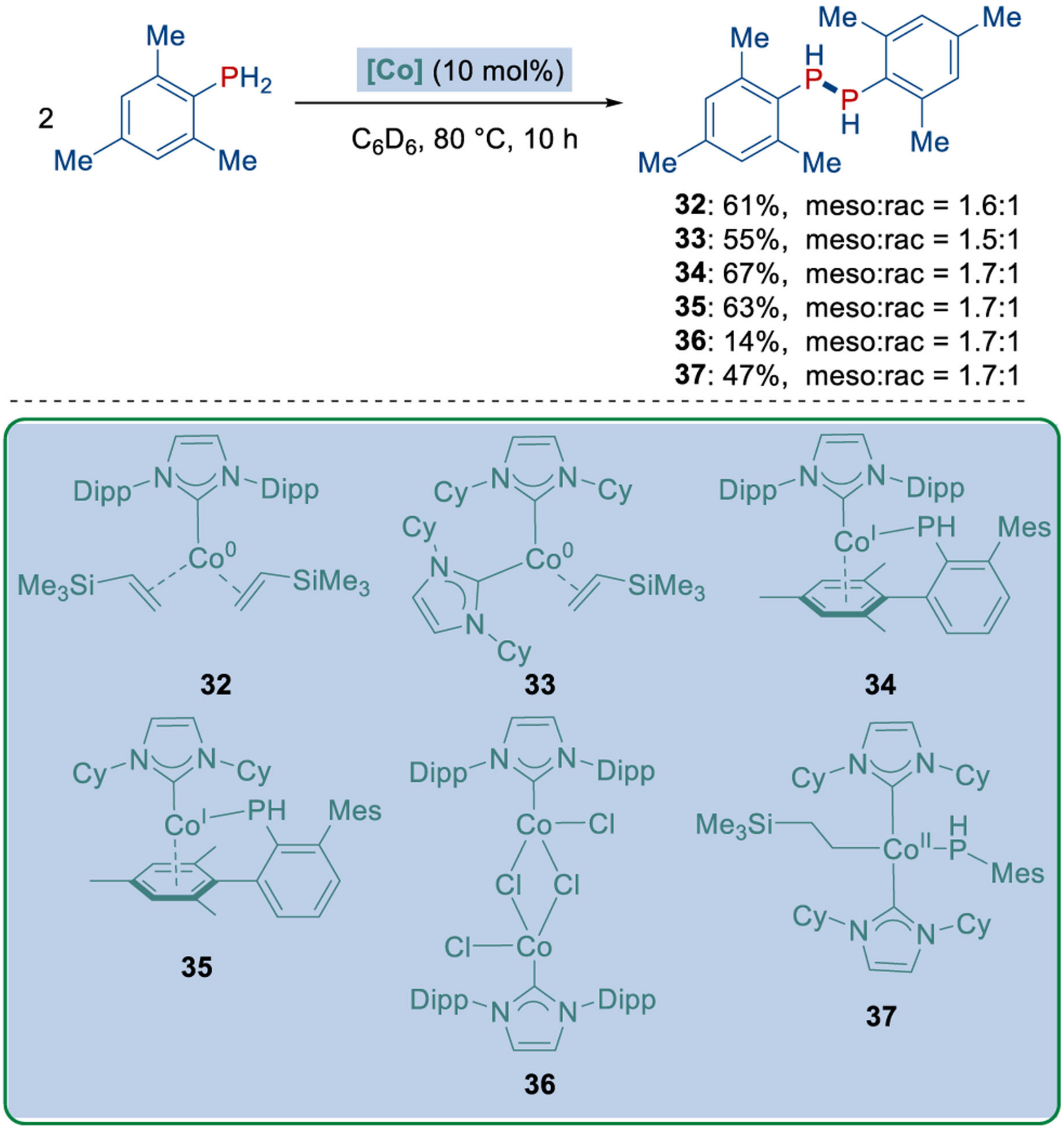

Scheme 45.

Co–NHC Catalyzed Dehydrocoupling of Hydrophosphines Reported by Deng.

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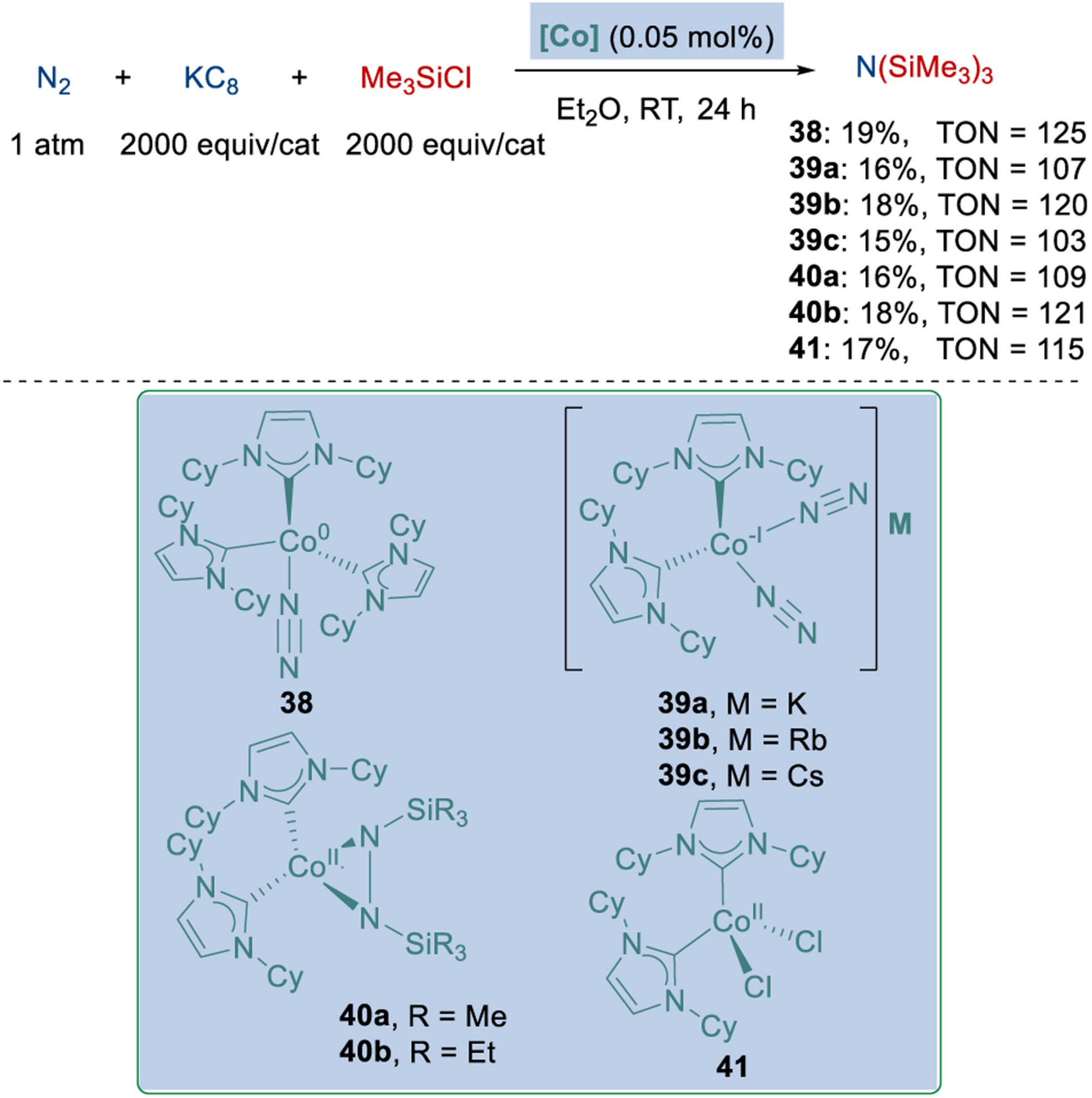

Scheme 46.

Co–NHC Catalyzed Dinitrogen Reduction Reported by Deng.

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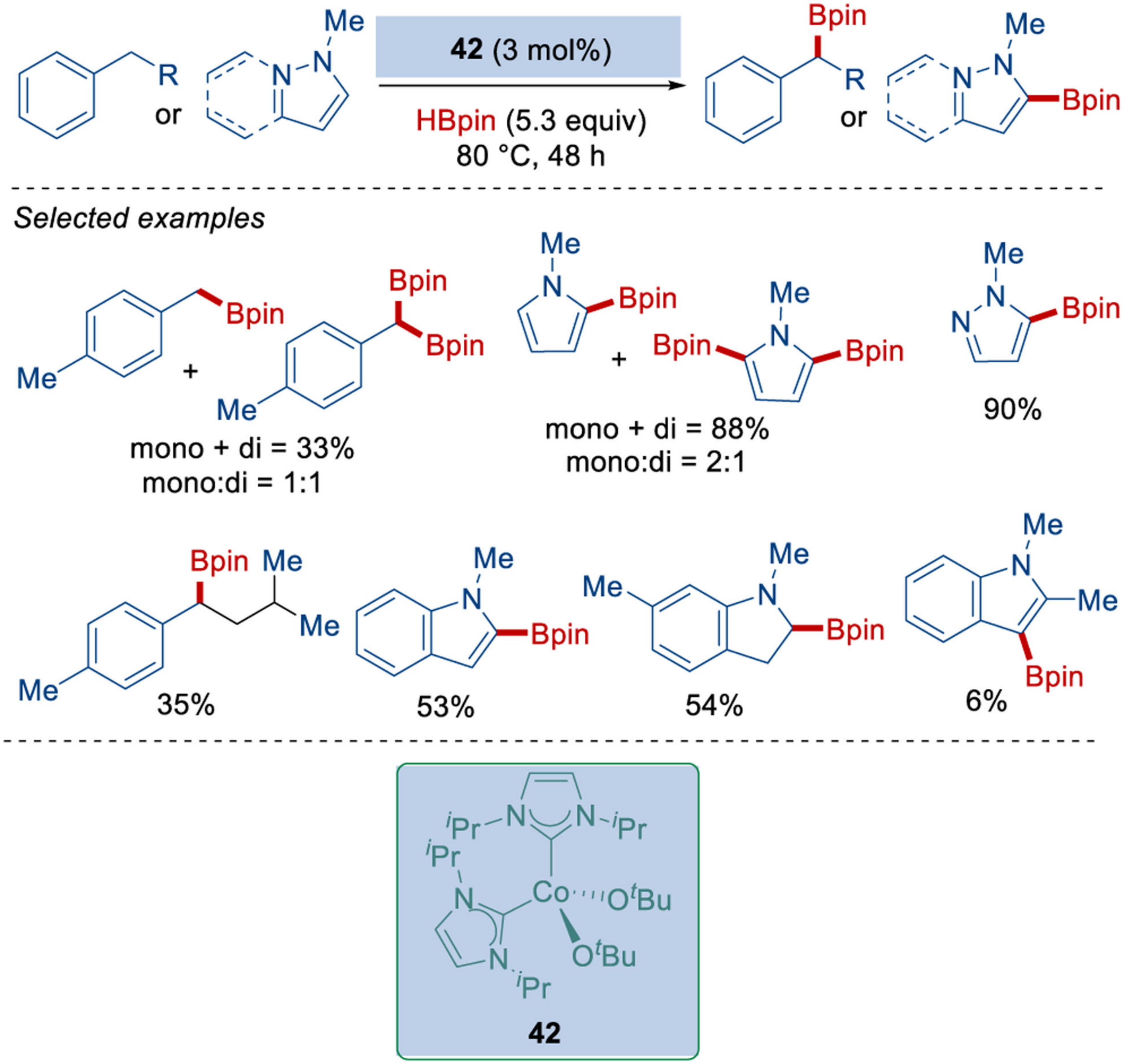

Scheme 47.

Co–NHC Catalyzed C–H Borylation of Alkyl Arenes and Heteroarenes Reported by Maleczka.

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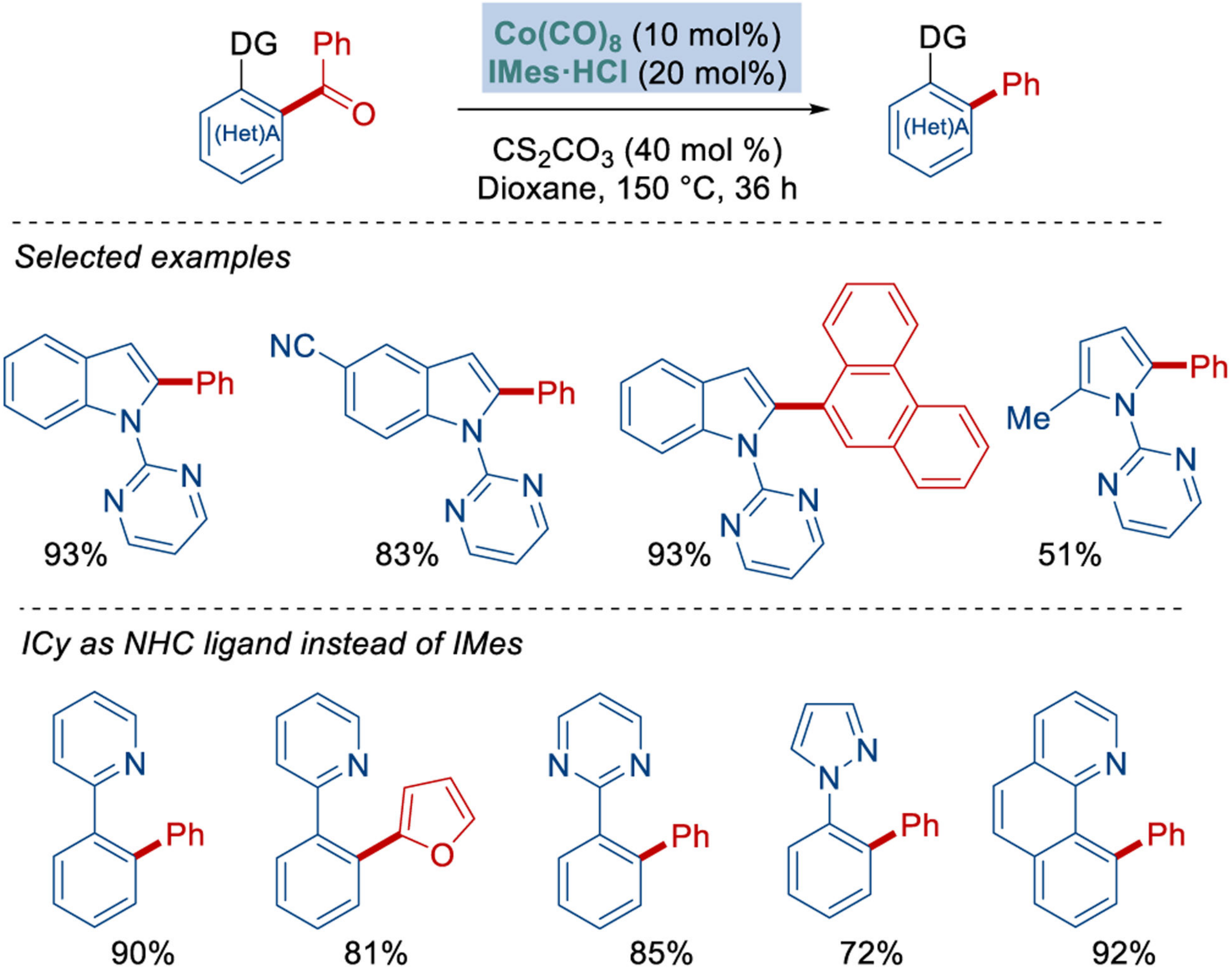

Scheme 48.

Co–NHC Catalyzed Intramolecular Decarbonylative Coupling Reported by Wei.

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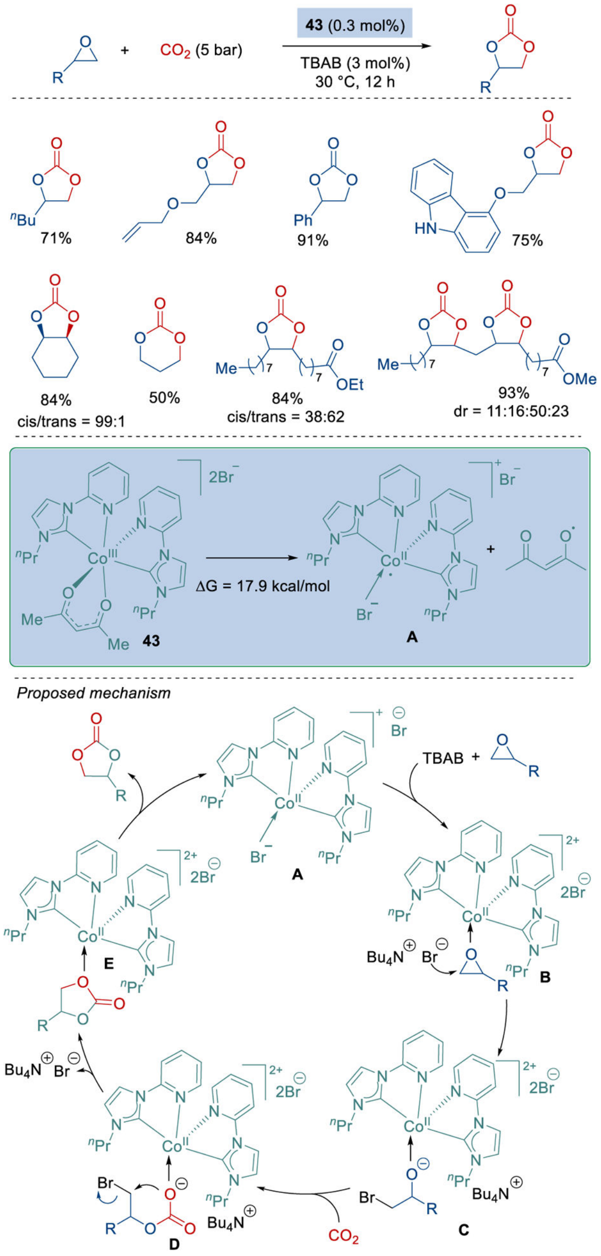

Scheme 49.

Co–NHC Catalyzed Carboxylation of Epoxides Reported by Liu.