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H_2 and carbon-heteroatom bond activation mediated by polarized heterobimetallic complexes

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Abstract

The field of heterobimetallic chemistry has rapidly expanded over the last decade. In addition to their interesting structural features, heterobimetallic structures have been found to facilitate a range of stoichiometric bond activations and catalytic processes. The accompanying review summarizes advances in this area since January of 2010. The review encompasses well-characterized heterobimetallic complexes, with a particular focus on mechanistic details surrounding their reactivity applications.

Keywords

Heterobimetallic; Metalloligand; Bond activation; Catalysis

1. Introduction

Over the past several decades there has been explosion of research into the synthesis, structure, and reactivity of heterobimetallic complexes. While heterobimetallic architectures can, in theory, involve any two metals from the periodic table, the primary focus has been on systems in which there are potentially advantageous differences between the two metal centers [1–36]. Though originally investigated as a way to model surface attachment sites for supported catalysts [37–54], this motif has seen a recent resurgence in interest because electronically differentiated metals can be exploited synergistically to activate chemical bonds [8,55–59].

In general, bimetallic systems react in one of two ways. In the first, the metal centers work in a concerted fashion to activate the bond of interest. In the second, bond activation is facilitated by a single metal that is electronically influenced by the ancillary metal (Fig. 1).

In systems of this type, pseudo-tandem reactions can occur in which each metal center serves as the site of an isolated elementary reaction in a multi-step cascade. In either

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case, understanding the interplay between the two metal centers is vitally important to understanding the observed reactivity.

Understanding the interplay between two metal centers is also foundational to the investigation of homobimetallic systems. Homobimetallic chemistry has been an active area of study for decades and is still a thriving field of study. Advances in synthesis, bond activation and other areas are reported frequently [59–93]. A broad field, homobimetallic chemistry is deserving of a separate review. In this article, we choose to focus our attention on the synthetically more challenging field of heterobimetallic chemistry.

As the field of heterobimetallic chemistry continues to grow, structure-reactivity relationships will allow researchers to target their complex design to target reactivity with specific classes of molecules. The review below details advances in understanding the reactivity of heterobimetallic systems over the last ten years. Heterobimetallic complexes consisting of one early transition metal (ETM, groups 3–7) and one late transition metal (LTM, groups 8–12) constitute a significant portion of recent heterobimetallic chemistry research [1,4,11,13,16,18,19,25,26,31,94–129]. They have been shown to activate H_2 [12,32,130] and a multitude of carbon-heteroatom bonds, most commonly carbon–halogen [103,131,132] and carbon–oxygen bonds [102,108,133–135]. In addition, heterobimetallics comprised of one LTM and one main group metal, though less studied in comparison to their early/late counterparts, have seen a marked uptick in exploration over the past decade, yielding exciting results [8,9,17,22,23,56,130,136–209]. The final category of heterobimetallic complexes frequently encountered are those comprising two late transition metals. Research into late-late systems covers a wide array of topics including synthesis [15,129,210–212] and catalysis [213–219]. Examples relevant to C-X and H-H bond activation are discussed below, though it should be noted that there are applications not covered in this article. Systems containing two early transition metals, or an early transition metal and a main group metal are relatively rare [220–224]. They are most commonly employed for polymerization applications which are beyond the scope of this review.

In an effort to reinforce connections between complex structure and observed reactivity we have broken down the review, discussing each unique class of chemical bond individually (H-H, C-H, C-O, C-R [R = other heteroatom], and C-X [X = halogen]), and separated each section into portions discussing advances in early/late heterobimetallic and late/main group heterobimetallic systems. Late/late systems are discussed when relevant. In an effort to focus on recent advances, this report will summarize reports published from January 2010 to June 2020. For brevity, we have limited our discussion to well-defined, well-characterized heterobimetallic systems. While Lewis acid (LA) additives are commonly invoked as accelerants in organic reactions, and many potential bimetallic intermediates have been postulated in catalytic systems, we have chosen to include only systems which are structurally characterized as we believe these will be most instructive for the design of future molecular catalysts [6,8,32,55,56,108,133–135,225–236]. Additionally, neither metalloboron complexes, a rich field of study which has been reviewed extensively elsewhere [237–244], nor heterobimetallic polymerization complexes [245–256], another important, blossoming field of study which merits an independent review, will be discussed in depth herein. We also have omitted discussion of intermolecular frustrated Lewis pair (FLP) chemistry. Though proposed intermediates in FLP reactions can involve heterodinuclear p-block/p-block [257–259] and d-block/p-block [260,261] complexes, the bimolecular nature of the reactions make them a poor fit for a discussion of well-defined heterobimetallic species [262–267]. Additionally, FLP chemistry is a massive field itself and has been reviewed multiple times elsewhere [264,265,268–270]. Finally, we have chosen to limit our discussion to synthetic, small-molecule bimetallics. Though interesting avenues for study, enzymatic systems, metal-organic frameworks, and multimetallic systems are beyond the scope of this review.

2. H–H activation

Hydrogen activation is an essential elementary step in any catalytic hydrogenation system. The prevalence of small-molecule catalysts for industrial hydrogenations and the potential of using hydrogenation catalysis as a means of chemical hydrogen storage for alternative energy production make the study of hydrogen activation extremely important. Though most homogeneous hydrogenation systems feature precious metals as catalysts, highly polarized, early/late heterobimetallic systems have recently been found to interact productively with the polarizable H_2. Natural hydrogenase enzymes, similarly, often include a bimetallic active site [271]. Indeed, these hydrogenases and other enzymes have inspired myriad biomimetic catalysis investigations, and we would be remiss not to acknowledge the important and insightful work from the groups of Darensbourg, Rauchfuss, Fontecave and others [272–294]. However, because the field of biomimetic catalysis has already been recently, extensively, reviewed elsewhere [295–298], these complexes are not discussed herein in detail. Further development of synthetic bimetallic, base-metal systems is of great interest. The following H_2 section of this work is organized based on the class of heterobimetallic mediating the bond activation (i.e., early/late or late/main group). When necessary, a delineation between stoichiometric and catalytic bond activation will also be included.

2.1. Early/Late

Early/late heterobimetallic systems for activation of dihydrogen have been known for several decades [132,299]. Experimental work on Ta-Ir bimetallic systems was performed by Bergman and coworkers in the early 1990s [300,301]. In an effort to better understand these systems, Ess and coworkers used density functional theory (DFT) to investigate the reactivity and mechanism of alkene hydrogenation catalyzed by the Ta-Ir heterobimetallic complex $Cp_2Ta(CH_2)_2Ir(CO)(PPh_3)$ (**1**) [32]. Their calculations supported the catalytic cycle originally proposed by Bergman (Fig. 2) [301]. Interestingly though, the authors also found that, upon formation of intermediate **D**, the possibility exists for a short circuit catalytic loop back to **B** without going back to **1** (blue arrows, Fig. 2). In fact, a comparison of the activation enthalpy and activation free energy for the full cycle to the short circuit cycle resulted in the authors belief that the short circuit loop is responsible for most of the alkene hydrogenation.

A new catalyst family featuring a bimetallic species containing solely cheap, first-row transition metals has recently emerged. In 2019, the Thomas lab reported the demonstrated ability of the Co-Zr heterobimetallic (THF)(I)Zr(XylNP^{i}Pr$_2$)$_2$CoPR$_3$ (PR$_3$ = PMe$_3$, **2a**; PR$_3$ = PMePh$_2$, **2b**) to activate molecular hydrogen (Fig. 3) [12].

Hydrogen activation was found to occur readily in<5 min at room temperature to generate **3a-b**. Subsequently, both **2a** and **2b** were shown to catalytically hydrogenate alkenes such as styrene and internal alkynes such as diphenylacetylene. **2b** proved to be significantly more active than **2a** for both alkene and internal alkyne hydrogenation. Interestingly, upon complete conversion of styrene leading to product **3b**, the addition of additional styrene was found to regenerate **2b'**. Subsequent exposure to H_2 resumed hydrogenation (Fig. 4). This report represents the first isolated and structurally characterized early/late heterobimetallic H_2 activation products that are themselves active for further catalytic or stoichiometric reactivity. Moreover, **2** and **3** use two base metals working in concert to catalyze the two-electron transformations required for H_2 activation and hydrogenation.

2.2. Late/Late

In a couple of highly related investigations, Mankad et al. demonstrated the ability of a Ru-Ag heterobimetallic complex to activate molecular hydrogen, resulting in *E*-selective semi-hydrogenation of alkynes as well alkane/alkene elimination reactions (Fig. 5) [34,302].

The authors found that the catalyst tolerates both electron-rich and electron-poor alkynes as well as terminal alkynes, and that sterics are key in promoting *E*-selective alkene elimination instead of *Z*-alkene or alkane generation.

2.3. Late/Main group

Beyond early/late and late/late heterobimetallic systems, the vast electronegativity difference between late transition metals and main group cations has made them attractive targets for cooperative activation of the polarizable H_2 molecule.

In an effort to exploit weak, Z-type, metal–metal bonds as Lewis pairs for bond activation, Bourissou and coworkers synthesized platinum-aluminum heterobimetallic complex **4** (Fig. 6). The authors subsequently demonstrated its ability to activate molecular hydrogen (H_2) stoichiometrically via oxidative addition of H–H bonds at elevated temperature (80 °C) and pressure (3 bar) (Fig. 7) [56]. DFT calculations, performed to illuminate the role of the Lewis acidic Al moiety in H_2 activation, revealed that each step in the reaction is facilitated by stabilizing interactions with the Al moiety; thus, cooperative interaction between the two metal centers is required for successful H_2 activation.

More recently, the Brewster lab reported hydrogen activation by heterobimetallic iridium-aluminum and rhodium-aluminum complexes (Fig. 8) [8]. A series of mechanistic experiments were undertaken to distinguish between several possible, plausible reaction mechanisms (Fig. 9). The authors determined, based on derivation of a second-order rate law (first order in bimetallic and first order in hydrogen) and observation of a stable intermediate resulting from oxidative addition of hydrogen to the transition metal, that proposed mechanism 1 is most likely to be in operation. This is noteworthy in light of the Bourissou results discussed above. While the Bourissou system involves a cooperative, concerted activation of H_2 across the two metal centers, the Brewster system is, instead, reminiscent of tandem catalysis. The transition metal facilitates a classical oxidative addition reaction and subsequently transfers hydride to a proximal acceptor. In development of future catalytic systems, it will be important to distinguish between these two mechanistic possibilities.

In 2014, the Miller group reported the ability of a heterobimetallic Ir-crown ether complex, in which the crown either moiety contains either Li^+ or Na^+, to catalyze H_2 activation and facilitate H/D exchange (Fig. 10) [303]. The main group cation is thought to sequester the crown ether and prevent an oxygen atom from competing with H_2 for an open site at the iridium center.

Interestingly, the authors elucidated the rate of H_2 activation can be controlled by choice of cation. It turns out that Li^+-containing reactions occur roughly 10 times faster than Na^+-containing reactions. In addition, the H/D exchange reaction rate can be enhanced up to 250-fold when catalytic quantities of Li^+ are added. Thus, the identity and concentration of the main-group cation can be modified to influence the reaction.

In 2015, the Lu lab described a Ni-In (**5**) and a Ni-Ga complex (**6**) complex, both of which catalyzed olefin hydrogenation (Fig. 11) [159]. Complex **6** was shown to be a highly active catalyst for hydrogenation of styrene, while **5** was much less active. Ni-Al analogue **7** was also investigated, but it demonstrated negligible, if any, catalytic activity (Table 1). The authors performed an expanded substrate scope study using complex **6** that revealed it hydrogenates fairly unhindered olefins. Moreover, terminal alkynes were hydrogenated more efficiently than internal alkenes (Table 2). The observed selectivity was attributed the steric bulk of the isopropyl groups of the ligand impeding the binding ability of hindered substrates.

The authors also addressed the observed reactivity difference between the chosen Group 13 cations. An in-depth study on the thermodynamics and kinetics of H_2 binding in these compounds was published by the Lu group in 2019 [304]. While larger group 13 ions withdraw more electron density from the nickel metal center, making nickel more amenable to binding small molecules, catalytic hydrogenation activity was shown to not rigorously increase with larger group 13 metals.

As a follow-up to their work on Group 13 cations, in 2019 Lu and coworkers reported a trio of Ni-Lu heterobimetallics (**8**, **9**, **10**; Fig. 12) that are active for activation of H_2 [305]. The electronic similarity between tricationic Group 13 metals and lanthanide ions made these complexes attractive synthetic targets. Notably, the ligand structure about the Lu center has been modified from **5** to **7** to accommodate the larger Lu center (van der Waals radii: Lu: 227 pm; Al: 184 pm; Ga: 187 pm; In: 193 pm). Complexes **8**–**10** exhibited the ability to catalyze styrene hydrogenation, with **8** found to be the most efficient. As would be expected from the structure of complex **9**, increased equivalents of THF (favoring accumulation of **9**) was found to decrease the rate of catalysis when employing **8** (Table 3).

The authors then expanded their investigation of the substrate scope. They found that **8** was competent for the hydrogenation of unhindered alkenes (>99%), including cyclic as well as terminal olefins. Linear internal olefins either experienced reduced hydrogenation rates or were found to be unreactive (Table 4).

This work introduced the first two examples of heterobimetallics with Lu-Ni bonding interactions, the first reported non-classical H_2 adducts for any d-f heterobimetallics, and the first example of using Ln supports to induce H_2 binding at a single Ni center.

Finally, in 2020, the Lu group reported a Ni-Ga heterobimetallic (**11**) and a series of Ni-Ln complexes (Ln = La, **12**; Ln = Y, **13**) using the bridging ligands present in champion Lu complex **8**. This new suite of heterobimetallics were found to be competent catalysts for the semihydrogenation of alkynes [229]. The authors used two different synthetic routes to prepare their heterobimetallic complexes; in the case of Ni-Ga, the gallium metalloligand is synthesized first and in the case of Ni-Ln, the metalation sequence is flipped (Fig. 13). Comparison of ^{31}P NMR shifts for THF binding in **11–13** to those for previously reported complexes [305], led the authors to conclude that THF binding to a $NiML_3$ heterobimetallic can be regulated by the size of M. Sufficiently large M (La, Lu, and Y) allow for solvent binding, whereas smaller M (Ga and Sc) do not.

The authors proposed a mechanism for the selective hydrogenation of diphenylacetylene (DPA) to (*E*)-stilbene. Importantly, **11** and **12–13** were found to have different catalyst resting states – their mechanisms are shown independently in Fig. 14. Ni-Ga **11** first binds H_2, resulting in the observed resting state **11a**. H_2 activation, subsequent phosphine dissociation and then DPA binding results in intermediate **I**. Migratory alkyne insertion into the Ni-hydride bond generates Ni vinyl intermediate **II**. Reductive elimination of (*Z*)-stilbene and H_2 binding to regenerate **11a** constitutes the end of the first catalytic cycle (*syn* hydrogenation). The second catalytic cycle (*cis to trans* isomerization) then begins in the same fashion, with hydrogen activation and phosphine dissociation, giving intermediate **III**, which is the alkene equivalent to **I**. Migratory alkene insertion into the Ni-hydride results in intermediate **IV**. Finally, rotation of the ethyl C–C bond followed by β-hydride elimination yields (*E*)-stilbene.

While proposed to operate through similar intermediates, the mechanism of Ni-Ln catalysts **12–13** diverges in a few critical ways. First, **12–13** operate via the Ni(η^2-PhC≡CPh) resting state, in which the dissociated phosphine binds to Ln (**I’**). Secondly, due to the favorability of the alkyne adduct, (*Z*)-stilbene is unable to enter the *cis*-to-*trans* isomerization cycle until almost all the DPA is exhausted, and Ni(η^2-PhC≡CPh) is no longer the default resting state. The *cis to trans* isomerization cycle is also similar to that for **11**, save for the “naked” $NiLnL_3$ species in the new resting state. The proposed mechanism for **12–13** is, thus, directly analogous to that proposed above for complex **8**. Moreover, dihydrogen binding is proposed to take place prior to alkene binding because the Ni-Ln heterobimetallics all exhibit weak H_2 binding, whereas alkene binding was not detected for any of those catalysts. The authors observed that less Lewis acidic rare-earth ions yield faster initial rates in the *syn*-hydrogenation of DPA while the opposite was observed for initial rates of alkene isomerization. This led to the suggestion that dihydrogen binding and activation are reliant on the Lewis acidity of the support and are the crucial step in alkene isomerization for their catalysts.

3. C–H activation

Selective C–H functionalization is one of the “Holy Grails” of organic synthesis [306,307]. Implicit in C–H functionalization reactions is the ability to activate a C–H bond. Extensive efforts toward the development of catalytic C–H bond functionalization protocols using a range of transition metals, most notably Pd, Pt, and Ni, have been undertaken and thoroughly reviewed elsewhere [308–311]. Only recently have bimetallic systems been employed for C–H activation. In this section we will highlight the recent advances in this burgeoning area.

3.1. Early/Late

C–H activation by early/late bimetallic constructs is currently limited to highly activated C–H bonds. In 2020, the Thomas lab reported C–H activation by the Zr-Co heterobimetallic (THF)Zr $(MesNP^{i}Pr_2)_3CoN_2$ (**14**) [312]. **14** was shown to activate the weak, acidic C–H bond of terminal alkynes, such as phenylacetylene and trimethylsilylacetylene (Fig. 15). Reaction of **14** with phenylacetylene results in near complete conversion of alkyne to a mixture of products (**14b**–**14d**). In an attempt to elucidate the mechanism of alkyne dimerization, the authors exchanged the N_2 ligand in **14** for $CN^{t}Bu$ (**15**). The isonitrile ligand effectively blocks the Co coordination site. Treatment of **15** with trimethylsilylacetylene resulted in **16** (Fig. 16). Isolation of **16** indicates that C–H activation constitutes the first step in the alkyne dimerization process promoted by **3**. Further efforts are currently being undertaken by the Thomas lab to induce catalytic turnover and explore potential applications in alkyne cross-dimerization reactions.

In the process of investigating surface organometallic chemistry, the Camp group briefly highlighted the demonstrated ability of a Ta-Ir complex to activate C–H bonds in the electon-deficient substrate fluorobenzene [313]. The heterobimetallic complex [{Ta $(CH_2{}^{t}Bu)_3\}\{IrH_2(Cp^*)\}]$ (**17**) was shown to catalyze H/D exchange between C_6D_6 and fluorobenzene over the course of 24 h at elevated temperature (Fig. 17).

3.2. Late/Late

Analogous to their H_2 work [34,302], Mankad and coworkers also demonstrated the arene C–H borylation ability of an analogous heterobimetallic iron-copper catalyst (Fig. 18) [314,315]. A variety of arenes were well-tolerated including anisole, benzene, and xylene. The authors noted selectivity of these borylations to be influenced by sterics, similar to iridium-catalyzed borylations [316], while attributing the effectiveness of their catalyst to its photochemical stability relative to other related systems [315].

3.3. Late/Main group

As with H_2, significantly more work has been done over the last decade on LTM/main group bimetallics with respect to C–H activation. Aluminum, in particular, has been exploited in several systems as a directing group for regioselective activation of sp^2 C–H bonds.

In mid-2010, Ong and coworkers described a Ni-Al heterobimetallic that catalyzed *para*-selective alkenylation of pyridine [317]. In their report, the authors offered a possible mechanism for catalysis (Fig. 19). The addition of pyridine and (NHC)AlMe_3 (NHC = N-heterocyclic carbene) to (NHC)Ni (**I**) leads to heterobimetallic **II**. Oxidative addition of the alkyne gives Ni-H intermediate **III**. Subsequent alkyne insertion into the Ni-H bond affords **IV**, which then reductively eliminates alkenylated product and regenerates **I**. Significantly, the authors were able to isolate and structurally characterize proposed Ni-Al intermediate **II** prior to the C–H activation step. This serves as the first structurally isolated example of C–H activation through a synergistic effect caused by a Ni-Al interaction.

Around the same time in 2010, Hiyama and coworkers reported direct C-4-selective pyridine alkylation catalyzed by a nickel-aluminum heterobimetallic complex [318]. Further, the authors proposed a plausible catalytic cycle for the selective alkylation reaction (Fig. 20) that closely resembles that proposed by Ong. In both systems the aluminum center is found to activate the pyridine ring and to sterically enforce reactivity at the electronically activated *para* position (over *ortho*). Oxidative addition of the pyridine C(4)-H bond of **A** yields **B**. This is followed by alkene coordination to give **C**, which undergoes subsequent migratory alkene insertion into the Ni-H bond to generate **D**. Finally, reductive elimination affords C-4-alkylated pyridine and regenerates **A**.

In this system, the authors determined the use of bulky *N*-heterocyclic carbene (NHC) ligands and (2,6-*t*-Bu_2-4-Me-$C_6H_2O)_2$AlMe (MAD) to be essential to promoting C-4 selectivity in both the oxidative addition and reductive elimination steps. This represents the first example of direct C-4-selective alkylation of pyridines by a Ni-Al catalyst.

Continuing with their Ni-Al work, a year later the Hiyama group demonstrated the capacity for a Ni-Al heterobimetallic to catalyze dehydrogenative [4 + 2] cycloaddition of formamides with alkynes [319]. The reaction is believed to take place beginning with η^2 coordination of Al-bound formamide to Ni, giving **A**, which then undergoes oxidative addition of the formyl C–H bond to produce **B**. Alkyne coordination and subsequent migratory insertion results in **C** and **D**, respectively. A second C–H activation via a concerted cyclometalation then generates **E**. A second migratory insertion of a coordinating alkyne then occurs to yield **F**, which reductively eliminates the AlMe_3-containing cycloadduct. Lastly, decomplexation of AlMe_3 from the cycloadduct generated product and recomplexation of AlMe_3 with another formamide molecule allows for regeneration of **A** via η^2 coordination (Fig. 21).

In 2012, Ong et al. discovered the ability of a Ni-Al heterobimetallic catalyst to promote regioselective C–H activation of benzimidazole [320]. Use of the heterobimetallic structure generates a steric constraint for achieving the linear insertion product of benzimidazole into styrene, whereas utilizing monometallic Ni $(COD)_2$ as the catalyst results in a change towards the branched product.

The Cramer group demonstrated the ability of a heterobimetallic Ni-Al complex (**18**) to catalyze the asymmetric hydrocarbamoylation of alkenes [55]. Interestingly, the Ni and Al moieties of **18** are added independently to a solution containing the substrate and they come together in solution to bind and catalyze enantioselective hydrocarbamoylation of the alkene substrate (Fig. 22).

The authors evaluated the substrate scope of the reaction and found that reaction selectivity is mainly independent of substitution at nitrogen. Additionally, a mechanism for catalysis was proposed (Fig. 23). The highly Lewis acidic Al center of **18** activates the substrate carbonyl of **A** to give **18a**. Then, the Ni center oxidatively inserts into the activated C–H bond intramolecularly, forming **18b**. Subsequent migratory insertion results in **18c**, which reductively eliminates product **B**, regenerating **18**.

In 2016, Nakao and coworkers expanded upon the prior Hiyama et al. work by reporting a cooperative Ni/Al catalytic system that promotes *para*-selective alkylation of aromatic ketones as well as benzamides (Fig. 24) [321].

The authors tested the scope of their system towards various ketone and benzamide substrates. In both cases, a wide variety of functionalities were tolerated. Neither steric bulk nor the addition of fluorine substituents to the *ortho*- or *meta*- positions of the benzamide or ketone inhibited alkylation. Potentially reactive silyl-functionalized alkenes were also well-tolerated.

The next year, Nakao et al. followed up this work by demonstrating the successful extension of their system to sulfonylarenes (Fig. 25) [322].

As before, the authors then turned towards probing the scope of their system towards sulfonylarenes and *N*,*N*-diethylbenzenesulfonamide. They found results similar to their previous investigation—fluoro-substituted sulfonylarenes, bulky alkenes, and silyl-functionalized olefins were all tolerated well. Additionally, in agreement with DFT calculations performed on the analogous previously reported reaction [321], the authors proposed a plausible catalytic cycle (Fig. 26).

Ni complex **I** undergoes ligand exchange with a MAD/sulfonylarene adduct to form **II**. Subsequent C–H activation and hydrogen transfer yields **III**, which then isomerizes to **IV**. Finally, **IV** reductively eliminates alkylated sulfonylarene product. This report represents the first *para*-selective alkylation of aromatic sulfones and benzenesulfonamides using a cooperative catalytic approach based on Ni and Al.

More recently, Nakao et al. described an Ir-Al heterobimetallic that catalyzes *meta*-selective C–H borylation of pyridines and benzamides [323]. The catalyst exhibited good functional group tolerance without experiencing a drop-off in selectivity—N-containing, O-containing, amine, ether, and carbonyl functionalities were all tolerated, yielding the respective functionalized pyridylborates. Importantly, this investigation highlights the potential of Lewis acid-base interactions as potent instruments for controlling site-selectivities of catalytic C–H functionalization reactions at remote positions (Fig. 27).

Early in 2020, Wang and Yoshikai detailed the ability of a cobalt-aluminum heterobimetallic complex to catalyze the hydrocarbofunctionalization of alkynes (Fig. 28) [324].

Their Co-Al catalyst was very effective with electron-deficient and Lewis basic substrates including pyridines and associated azines, pyridones, formamides, azole derivatives, and imidazo[1,2-*a*] pyridines via site-selective cooperative C–H activation. This system is likely superior to Ni-LA systems for analogous transformations due to the use of an inexpensive, bench-stable precatalyst and ligand as well as facile setup. This system represents the first example of *completely* C-4-selective alkenylation of pyridine. DFT calculations on the addition of formamide to alkyne suggest the carbamoyl C–H cleavage to be the rate-determining step, occurring via a ligand-to-ligand hydrogen transfer (LLHT) mechanism. This is quite significant because this mechanistic insight may indicate that the parallelism between low-valent Co and Ni is, in fact, not superficial, but based on fundamental common reactivity shared by 3d transition metals, which would warrant further synthetic and mechanistic explorations [325].

4. C–O activation

The most widespread application of polarized heterobimetallic complexes over the last decade has been in the activation of C-O bonds. Particular focus has been placed on the activation of carbon dioxide, a potentially useful C_1 feedstock. The large disparity in electronegativity between the two metal centers makes a polarized heterobimetallic construct ideal for this application.

4.1. Early/Late

Thomas and coworkers demonstrated activation of CO_2 at room temperature using the early/late heterobimetallic complex $Co(^{i}Pr_2\text{-}PNMes)_3Zr(THF)$ (**19**) (Fig. 29) [102]. The complex was found to oxidatively add CO_2, yielding $(CO)Co(^{i}Pr_2PNMes)_2Zr(^{i}Pr_2PNMes)$ (**20**), which can then be reduced to produce either the Zr-oxoanion or Zr-carbonate, depending on the reduction conditions. It was determined that the hemilabile nature of the phosphinoamide ligand scaffold is critical to reactivity, for it is through dissociation of a phosphine from cobalt that substrate access to the metal–metal bond is provided. Also noteworthy, the bridging oxo ligand was found to be functionalizable via silane addition, yielding a heterobimetallic complex consisting of a Zr-siloxide and a terminal Co-hydride moiety (**21**, Fig. 30).

The closely related cobalt-zirconium heterobimetallic complex $(THF)Zr(MesNP^{i}Pr_2)_3CoN_2$ (**14**) was also found to facilitate the catalytic hydrosilylation of ketones using $PhSiH_3$ [108]. Stoichiometrically, **14** was unreactive towards $PhSiH_3$, yet it reacted readily with ketones (Fig. 31) suggesting that the heterobimetallic complex is involved in the crucial C-O bond activation step. Isolation of a radical coupling product from the hydrosilylation of benzophenone $[(Ph_2CO)Zr(MesNP^{i}Pr_2)_3CoN_2]_2$ (**22**, Fig. 31) led to the proposal of a radical-based mechanism for this transformation (Fig. 32).

A wide variety of both aliphatic and aryl ketone substrates were tolerated in this catalytic system. Significantly, as substrate steric bulk increased and the substrate became more electron-rich, the reaction rate decreased dramatically. The bulkiest, electron-rich ketones, such as 2-acetylnaphthalene and 1,3-diphenylacetone, required much longer reaction times at elevated temperature to reach completion. Comparative screening against analogous monometallic complexes led the authors to determine that both the zirconium and cobalt metal centers of **14** were actively participating in catalysis.

As a follow-up to this catalytic study, the Thomas group conducted a thorough mechanistic investigation which revealed thermolysis of the previously discovered radical coupling product **22**. Thermolysis led to cleavage of the C–O bond, generating an oxo-bridged Zr-Co heterobimetallic species containing a terminal C = CPh_2 carbene, (η^2-MesNP^{i}Pr2)Zr(μ-O)(MesNM^{i}Pr$_2$)$_2$Co = CPh_2 (2**3**) [133]. Complex **23** represents a rare example of a structurally characterized non-heteroatom-stabilized Co-carbene complex. Originally intending to probe for an equilibrium between **22** and a monomeric ketyl radical, a solution of complex **22** in benzene was thermolyzed under nitrogen yielding a mixture of **23** and its structural isomer **24** (Fig. 33).

The failure of multiple attempts to generate **23** exclusively (including thermolysis under higher N_2 pressure) led the authors to propose that dissociation of N_2 is a prerequisite for the formation of both **23** and **24**. Additionally, seemingly irreversible C–O bond cleavage upon direct reaction of **23** with phenylsilane (Fig. 34) allowed for the conclusion that **23** does not play an active role in the previously reported catalytic hydrosilylation of benzophenone [108].

Interestingly, though not a hydrosilylation intermediate, it was found that when **23** is treated with styrene at elevated temperature (110 °C), cyclopropanation occurs. Generation of a mixture of diphenylmethane, tetraphenylethane, and tetraphenylethylene via decomposition of **23** in the absence of styrene under the same conditions suggested the diphenylcarbene moiety is expelled at increased temperatures. The authors, therefore, postulate that cyclopropanation occurs via trapping of the free: CPh_2 by styrene.

A year later, the Thomas lab successfully synthesized the monomeric ketyl radical complexes which had previously proven elusive. Upon reaction of heterobimetallic complex **14** with fluorenone, the monomeric ketyl radical complex **25** was generated and isolated (Fig. 35) [134].

Further experimentation revealed that the electronic parameters of the diaryl ketone substrates determine whether a ketone adduct or a ketyl radical is formed; the more electron-rich the ketone, the more disfavored the single-electron transfer to generate the ketyl radical (i.e. more electron-rich ketones favor adduct formation, while more electron-poor ketones favor ketyl radical formation) [134].

In 2015, the Thomas lab switched the identity of the Group IV metal from Zr to Ti. This led to the isolation of a low coordinate Ti-Co heterobimetallic, ClTi(XylNP^{i}Pr$_2$)$_2$CoPMe$_3$ (**30**) (Fig. 36) [135].

The authors subsequently demonstrated that **30** promotes reductive coupling of aryl ketones into alkenes. Reaction of **30** with benzophenone in benzene at ambient temperature led to formation of 30′ through loss of PMe_3. Multiple attempts at crystallization of **30′** failed due to thermal instability. Subsequent addition of NaI to **30′** generated [Ti(μ_3-O)(XylNP^{i}Pr$_2$)$_2$CoI]$_2$ (**31**) and tetraphenylethylene (Fig. 37).

Typically, reductive coupling of ketones to alkenes (McMurry reaction) [326] requires stoichiometric reagents and increased temperatures, and there are often selectivity and reproducibility challenges [327,328]. In contrast, **30** was found to be reactive towards a variety of ketones at ambient temperature with short reaction times, in the presence of stoichiometric NaI, resulting in moderate-to-high yield of alkenes. Significantly, control reactions were performed that indicate both Ti and Co are active essential participants in the reaction. Based on their study of the mechanism the authors propose a possible pathway for the McMurry reaction mediated by **30** (Fig. 38).

In an effort to obtain additional mechanistic information regarding CO bond activation processes, the Thomas lab then investigated the reactivity of Zr-Co and Ti-Co heterobimetallics $(THF)Zr(MesNP^{i}Pr_2)_3CoN_2$ (**14**) and $(THF)Ti(XylNP^{i}Pr_2)_3CoN_2$ (**32**) towards diaryl ketones [329]. Zirconium-bound ketyl radical formation (via single electron transfer) takes place for all save extremely electron-rich diaryl ketones. In the absence of N_2, this initial product transforms into a cobalt carbene product as a result of C = O cleavage. In contrast, the authors found no ketone reduction in the case of the titanium-cobalt heterobimetallic analogues, with structural data indicating that interaction between the group IV metal and the ketone oxygen is a necessity for subsequent C = O activation.

In addition to hydrosilylation of C-O bonds, strides have been made toward hydroboration using heterobimetallic catalysts. In 2015, Mankad and coworkers discovered a tunable bimetallic effect on selectivity of catalytic CO_2 reduction products via Cu-NHC (*N*-heterocyclic carbene) complexes [225]. The authors showed that, while the monometallic, copper-only, system catalyzes CO_2 hydroboration with HBpin (pinacolborane) to generate formate as the sole product, a bimetallic effect is introduced upon addition of a second metal (W, Mo, and Fe) into the catalyst framework. Moreover, this bimetallic effect is tunable by changing the Cu-bound second metal, with the second metal being necessary for CO_2 deoxygenation by HBpin (Fig. 39).

The authors, via multiple experimental observations, proposed a hypothetical mechanism (Fig. 40).

It was found that, consistent with their proposed mechanism, the rate of decarbonylation is related to the lability of [M]-Bpin. This lability follows the $[M]^-$ leaving group ability of $[Mp]^- > [Wp]^- > [Fp]^-$ which, notably, correlates with their relative pK_a values.

4.2. Late/Main group

The late/main group heterobimetallic $Cp^*(CO)(H)Ru = Si(H)\{C(SiMe_3)_3\}$ (**33**) was found to selectively hydrosilylate heterocumulene C = O bonds at room temperature by Tobita and coworkers (Fig. 41) [230].

Hydrosilylation results in a five-membered arene-containing metallacycle including both Ru and Si, in which the arene ring corresponds to the arene in the original heterocumulene ArNCO. Further, the authors discuss a possible reaction mechanism (Fig. 42) for the reaction of **33** with ArNCO involving oxygen atom coordination to the electron-deficient silylene Si atom to form complex **33a**. This is followed by hydride migration from Ru to carbon, yielding complex **33b**, with subsequent rotation of the CO bond in **33b** and nitrogen coordination to Ru, resulting in the product **34**. Thus, this mechanistic similarity to C-O bond activations in early/late heterobimetallic systems merits its inclusion in this review despite the fact that many transition metal silanes and transition metal silylenes are known [184,330–338], but not often considered to be heterobimetallic species.

Heterobimetallic complexes $[(N_2)CoM(\textit{o}\text{-}(NCH_2P^{i}Pr_2)C_6H_4)_3N]^-$ (**35**), where M is aluminum (**35a**) or gallium (**35b**), have recently been reported by the Lu group to catalytically hydrogenate CO_2 via a Co(−I)/Co(I) redox cycle (Fig. 43) [231]. The catalytically active species for CO_2 hydrogenation, as proposed from DFT calculations, and turnover frequencies as a function of main group metal can both be seen in Fig. 43. The full calculated mechanism can be found in Fig. 44.

When M is indium, the catalyst is inactive, and the authors' determined that the increased catalytic efficiency of the gallium analogue relative to the aluminum analogue can be explained by a 5 kcal/mol increase in thermodynamic hydricity when Al is changed to Ga, a slightly more exergonic binding equilibrium (ΔG^{o}_{bind}) at 1 atm H_2 for the HCoGaL intermediate than the HCoAlL, and a lower pK_a of $H(H_2)CoGaL$ compared to $H(H_2)CoAlL$. In addition, the rate law for the optimized Co-Ga catalyst was approximated to be zeroth order with respect to H_2 pressure and first order with respect to CO_2 pressure, consistent with the proposed mechanism.

Following up on this work, the Lu group discovered the analogous nickel-containing late/main group heterobimetallic complex $NiGa(N(\textit{o}\text{-}(NCH_2P^{i}Pr_2)C_6H_4)_3)$ (**36**) catalyzes the hydrogenation of CO_2 to formate at ambient temperature with a turnover frequency of 9700 h^{-1} [232]. Evidence supports the Ga(III) ion being crucial to the stabilization of a rare, and highly reactive, anionic d^{10} nickel hydride catalytic intermediate which the authors were able to structurally and spectroscopically characterize (Fig. 45).

The authors determined that a strong base is required for catalysis by conducting catalytic trials with bases of decreasing strength, resulting in lower yields and decreased maximum rates. Triethylamine (weak base) resulted in no formate generation at all. The authors attribute diminished yields to incomplete deprotonation of dihydrogen complex **36a**, preventing formation of the catalytically active **36b** (Fig. 45). In other words, Ni facilitates formation of dihydrogen complex **36a**, but it is the strong base that leads to deprotonation, and subsequently, the oxidatively added Ni monohydride **36b**.

A follow-up computational/experimental study was undertaken to further elucidate mechanistic information regarding CO_2 hydrogenation by their catalyst (**36**) [158]. The authors found that the most energetically favorable reaction mechanism for CO_2 hydrogenation involves dihydrogen binding to Ni (**36a**) followed by deprotonation (**36b**), then outer-sphere hydride transfer to CO_2 (**36c**), and finally formate release (Fig. 46). This conclusion is highly consistent with that proposed from their experimental work described above.

The authors found that the activation barrier for H_2 deprotonation is dependent on both the pK_b of the base and, moreso, on the steric bulk of the base; the stronger and less bulky the base, the lower the activation barrier. Interestingly, formate was also found to play a cocatalytic role in the H_2 deprotonation step, in which it behaves as a proton shuttle between

36a and Verkade's base (Vkd), resulting in a dramatic decrease in the activation barrier relative to using Verkade's base alone. [NOTE: Verkade's base is the name given to a family of superbases, and the two specific Verkade's bases utilized by Lu and coworkers herein are Vkd_Me and Vkd_iPr (Fig. 47)]

With formate assistance, the rate-determining step is projected to switch to hydride transfer to CO_2 from H_2 deprotonation. In addition, the stronger binding of formate versus H_2 indicates the formate release step also likely impedes catalysis.

The Iwasawa group recently synthesized and characterized a palladium-aluminum heterobimetallic complex (**37**) that hydrosilylates carbon dioxide (Fig. 48) [233].

Though not discussed in detail in their communication, it is reasonable to suggest that activation of CO_2 by the aluminum center facilitates hydride attack. The thermodynamically strong Si-O bond formed in the product then provides driving force for product release from aluminum. This complex represents the most efficient CO_2 hydrosilylation catalyst to date, with a turnover frequency of 19,300 h^{-1} at ambient temperature under only 1 atm of CO_2.

C-O bond activation at late metal/main group bimetallics is not limited to functionalization of CO_2. The heterobimetallic dimer $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ (**38**) has been shown to exhibit interesting catalytic properties when it comes to the nucleophilic substitution of propargylic alcohol [234]. The authors demonstrate what they refer to as "preactivation of the propargylic alcohol" by **38**, in which the −OH group coordinates to the Sn metal center before the nucleophile attacks the propargylic −OH carbon (Fig. 49).

Interestingly, the "monometallic" $[Ir(COD)(\mu\text{-}Cl)]_2$ dimer was inactive and $SnCl_4$ was weakly active; this "preactivation" is clearly significant and the heterobimetallic complex is likely involved. The authors attribute the increased efficiency of the heterobimetallic catalyst to the enhanced Lewis acidity of the iridium-tin bond versus tin on its own. Also noteworthy, this same catalyst also functions similarly in certain alkylation, allylation, and allyl disproportionation reactions (Fig. 50) [339,340].

5. C–R activation [R = N, S]

Much less explored is the ability of heterobimetallic species to activate other polar carbon-heteroatom bonds. The lack of focus in this area makes it ripe for further development as the field of heterobimetallic chemistry continues to grow. This section will briefly discuss recent advances in C-N and C-S activation. Heavier congeners (P, Te, etc.) are not commonly encountered.

5.1. C-N activation

Yin and coworkers, in 2017, discovered that the addition of scandium ions into the reaction mixture for palladium-catalyzed hydration of nitriles to amines dramatically accelerates the reaction [226]. This represents the first reported example of addition of non-redox metal ions resulting in the considerable acceleration of nitrile hydration to amides at ambient temperature. The authors proposed the formation of a Pd-Sc heterobimetallic complex demonstrating a synergistic effect as the crucial species for the nitrile hydration (Fig. 51).

This system accommodated both a wide substrate scope and functional group tolerance (Table 5); benzonitriles bearing both electron-donating (EDG) and electron-withdrawing groups (EWG) in the *meta* or *para* position yielded the corresponding amides. EWG-containing substrates displayed enhanced reactivity relative to those containing EDG. This was explained (and supported by corresponding Hammett plot analysis) to be a consequence of the presence of the EWG increasing the susceptibility of the nitrile carbon to nucleophilic attack by an activated water molecule. Both *ortho*-substituted nitriles, due to partial steric congestion between the cyano group and metal center, as well as those containing a fused ring exhibited decreased reactivity relative to monocyclic nitriles. Interestingly, the authors reported hydration of heteroaromatic nitriles to the corresponding amides in good yields. Aliphatic nitriles were able to be hydrated to amides as well. This system was also shown to yield comparable results when extended to hydration of dinitriles.

The dimeric heterobimetallic complex $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ (**38**) has also been shown to catalyze the aza-Friedel–Crafts reaction (AFCR) of substituted indoles and 1,3,5-trimethoxybenzene with *N*-sulfonyl aldimines, generating diarylamines as well as triarylmethanes (Fig. 52) [341].

At elevated temperature (80 °C), the heterobimetallic Ir-Sn complex activates the sp^3 carbon–nitrogen bond of the isolated diarylamine in the presence of a suitable nucleophile to generate the corresponding triarylmethane (Fig. 52). This is interesting because it means **38** catalyzes the synthesis of diarylmethanes and the subsequent synthesis of triarylmethanes (TRAMs) from those exact diarylmethanes it just aided in forming; **38** catalyzes two independent reactions via a *consecutive* Friedel–Crafts reaction pathway.

5.2. C-S activation

The Thomas group demonstrated that the aforementioned $(THF)Zr(MesNP^{i}Pr_2)_3CoN_2$ (**14**) heterobimetallic complex reacts with thiones differently than ketones. Reaction of **14** with diphenylthione produced a new complex with thione bound η^2 to cobalt instead of undergoing single-electron transfer (**39**, Fig. 53) [134]. This interaction is further stabilized by a long-distance interaction between sulfur and zirconium and a C–H agostic interaction with the cobalt center. Addition of CO then leads to substitution of the agostic interaction and formation of a thione-carbonyl complex (**40**).

When the cobalt-bound N_2 ligand is replaced with a carbonyl prior to addition of diphenylthione, a dimeric thioketyl radical-containing heterobimetallic complex (**41**) similar to radical coupling product **22** is generated instead. This reveals that formation of a thioketyl radical complex via one-electron transfer is indeed possible; however, without the CO ligand the favored site of reactivity is at Co rather than Zr. The authors attribute this difference to the increased strength of the Co-CO bond relative to the weaker Co-N_2 bond.

Previously discussed heterobimetallic complex **33** also exhibited the ability to activate heterocumulene C = S bonds [230]. Contrary to the observed hydrosilylation reaction discussed before, reaction of the Ru-Sicomplex with MesNCS leads to complete cleavage of the carbon–sulfur double bond at ambient temperature. The authors describe two possible mechanistic pathways, though they do not preclude additional possibilities (Fig. 54). Route

I begins with coordination of the sulfur atom of ArNCS to the silylene Si atom, resulting in **33c**. [2 + 2] cycloaddition between the C = S and Ru = Si bonds then leads to **33d** which generates **33f** following coordination of sulfur to the metal after reductive elimination of the Si–H bond. Then, facile cleavage of the weak C–S bond of **33f** gives **42**. Alternatively, Route II proceeds via ArNCS to Ru of the unsaturated silyl complex (generated by 1,2-H migration from Ru to Si), giving **33e**. This is followed by silyl migration to sulfur to yield **33f**, which then produces **42** after C–S cleavage. Importantly, this represents the first example of a silylene complex facilitating C = S bond cleavage.

6. C–X activation [X = Halogen]

The final portion of this review will detail recent advances in the activation of carbon-halogen bonds by heterobimetallic species. Oxidative addition of C-X bonds is a common elementary step in many late-metal catalyzed processes. Classic methods for oxidative addition observed in these systems (concerted, S_N2) are foundational to the study of organometallic chemistry [342–347]. The presence of a second metal center opens many more mechanistic possibilities for C-X cleavage. Additionally, inclusion of a hard, Lewis acidic metal center allows for access to processes for C-F cleavage, a reaction that is difficult to achieve with a single, late transition metal. We focus our attention below on C-X activations in which *both* metal centers play a well-defined role.

6.1. Early/Late

Reaction of the sulfido-bridged heterobimetallic complex $\left[\mathrm{Cp}_2^{\mathrm{tt}}-\mathrm{Zr}(\mu_3-\mathrm{S})_2\{\mathrm{Rh}(\mathrm{CO})\}_2(\mu-\mathrm{dppm})\right]$ (**43**) with iodomethane results in formation of $\left[\mathrm{Cp}_2^{\mathrm{tt}}\mathrm{Zr}(\mu_3-\mathrm{S})_2\mathrm{Rh}_2(\mu-\mathrm{CO})(\mu-\mathrm{dppm})(\mathrm{I})(\mathrm{COCH}_3)\right]$ (**44**) [227]. The resultant heterobimetallic product is thought to form via an initial oxidative addition of methyl iodide to the rhodium center followed by insertion of a carbonyl into the resultant rhodiummethyl. The authors attributed the formation of this unusual oxidative addition product to steric and electronic effects imparted by the early $\mathrm{Cp}_2^{\mathrm{tt}}\mathrm{Zr}$ moiety; particularly, the bulkiness of the $\mathrm{Cp}_2^{\mathrm{tt}}\mathrm{Zr}$ moiety plays a pivotal part in promoting the CO oxidative isomerization process following coordination of I^- to the second Rh (Fig. 55).

In contrast, the early/late heterobimetallic (THF)Zr(MesNP^i-Pr$_2$)$_3$CoN$_2$ (**14**) was found to oxidatively add iodomethane *across* the Zr-Co bond, generating (η^2-MesNP^{i}Pr$_2$)Zr(MesNP^{i}Pr$_2$)$_2$-(μ-CH$_3$)CoI (**45**) [132]. One of the phosphinoamide ligands dissociates from Co to bind η^2 to Zr to integrate the methyl ligand that bridges the two metal centers. The methyl ligand forms a traditional, X-type interaction with zirconium and an agostic interaction to cobalt (Fig. 56). Unsurprisingly, the soft iodide ligand is found bound to cobalt.

It is noteworthy that the observed product is likely kinetic. DFT calculations indicated that an unobserved, hypothetical, terminal heterobimetallic complex MeZr(MesNP^{i}Pr$_2$)$_3$CoI (**46**) should be more thermodynamically stable than the observed heterobimetallic. Changing the halogenated reagent from iodomethane to chlorocyclohexane resulted in similar activation of the C–Cl bond.

During their initial study of the heterobimetallic complex **14**, the Thomas lab discovered its ability to function as a catalyst for Kumada coupling of primary and secondary alkyl halides, including alkyl chlorides, with *n*-octylmagnesium bromide [103]. Their 2011 report represented the first example of cobalt catalysts demonstrating activity towards alkyl chlorides, ordinarily a challenge due to the strength of the carbon-chloride σ-bond. Much more recently, DFT calculations were performed on truncated derivatives of **14** (**14-trunc**) to elucidate mechanistic information regarding this reaction [228]. A catalytic cycle was proposed and compared to that of the monometallic Co-tris (phosphinoamide) complex **47**, so as to demonstrate the superiority of the heterobimetallic Co-Zr Kumada coupling catalyst over the monometallic cobalt-tris(phosphinoamide) catalyst (Fig. 57).

6.2. Late/Main group

Recently, Collins et al. discovered novel heterobimetallic rhodium-bismuth paddlewheel complexes of the type MRh(R)$_4$ (M = Bi, **48**; M = Rh, **48′**; Fig. 58) that catalyze carbene insertion into a C–Cl bond of the CH_2Cl_2 solvent (Fig. 59) [348]. By performing a comparative study of isosteric complexes, the authors were able to clearly highlight the importance of the distal metal center to the reactivity of their catalyst. Notably, the distal metal is shown to be critical to the modulation of π-back-donation and, consequently, to the manipulation of the reactivity and stability of the carbene. Replacement of the distal Rh by Bi results in a significant increase in electrophilicity of the bound carbene, leading to new reactivity. By screening a series of dirhodium and Bi-Rh catalysts, the authors were able to demonstrate that only heterobimetallic complexes catalyze the C–Cl insertion (Fig. 60). This represents the first example of a rhodium-catalyzed carbene insertion into a C–Cl bond.

More recently, the Nakao lab reported a Rh-Al heterobimetallic complex (**49**), which they generated *in situ* via the reduction of a previously reported Rh-Al complex [151], that activates C–F bonds under nitrogen to produce **49a** as shown in Fig. 61 [235].

Interestingly, C–F activation was demonstrated to proceed at temperatures as low as −30 °C, making these the mildest conditions reported thus far for inactivated C–F bond activation facilitated by a homogeneous metal complex. DFT calculations revealed the Gibbs energy of activation ($\Delta G^{o\ddagger}$) for cooperative C–F activation to be very small compared to the much larger $\Delta G^{o\ddagger}$ for C–F bond activation by just Rh. The small $\Delta G^{o\ddagger}$ value for cooperative activation better matched the experimentally observed reaction that proceeds even at low temperature. The authors proposed a catalytic cycle in which the aryl fluoride first binds to the bimetallic (**50**) and is then cooperatively activated by both the Al and Rh metal centers, affording **51**. The oxidatively added complex can be finally reduced with Mg to regenerate the starting complex (Fig. 62). When taken together these steps provide the basis for a catalytic magnesiation of aryl fluorides.

Applying this methodology, the authors then tested the substrate scope. They determined that substrates with EDGs at the *meta*- or *para*-position of fluorobenzene were tolerated, and sterically bulky substrates such as 2,6-dimethylfluorobenzene were tolerated. Also worth noting, B(O*i*-Pr)$_3$, *N*-methoxy-*N*-methylbenzamide, and D_2O can serve as quenching electrophiles as well, to generate the corresponding borylated, acylated, and deuterated products (Table 6). The versatility of this magnesiation system is remarkable, as aryl fluorides are not often considered as synthons for arene elaboration; they are generally viewed as inert under standard coupling conditions due to the strength of C–F bonds [349,350].

In another striking example of C-F activation, the Lu lab recently described the synthesis of the Rh-In heterobimetallic complex Cl–RhInL (**52**; L = $N(o\text{-}(NHCH_2P^iPr_2)C_6H_4)_3$) that was found to catalyze the hydrodefluorination of aryl C–F bonds with 1 atm H_2 and NaO*t*-Bu (Fig. 63) [236].

Over the course of an extensive investigation of reaction scope (Table 7), they determined alkyl C–F bonds were unreactive and sterics can regulate selectivity. Furthermore, and perhaps unsurprisingly, reactions with *p*-dihaloarenes *p*-F-XC_6H_4 (X = I, Cl) demonstrated preferential cleavage of the weaker C–X bond over the C–F bond.

In contrast to *o*-difluorobenzene (DFB), which reacts quite readily under the chosen conditions [351], neither *m*-DFB nor *p*-DFB experienced significant conversion. Longer reaction times at elevated temperatures led to minimal conversion. In contrast, PhF was hydrodefluorinated to benzene with almost full conversion after heating to 90 °C for five days.

The authors went on to propose a catalytic cycle. Each proposed intermediate was identified through isolation or *in situ* characterization (Fig. 64).

First, hydride **53** is formed from **52** on addition of H_2 and *tert*-butoxide, presumably via the intermediacy of an acidic dihydrogen complex. This is followed by reversible H_2 binding, resulting in the Rh(I) hydride/H_2-adduct, **54**. Deprotonation facilitated by *t*-butoxide generates a transient Rh(I) dihydride that undergoes reductive coupling to form the Rh(−I) H_2-adduct, **55**. Then, an unsaturated Rh(−I) active species **56** is formed by the reversible loss of H_2. This *highly* reactive species oxidatively cleaves the C–F bond, yielding the Rh(I) phenyl complex **57** and NaF. In the final step, **57** reacts with H_2 to generate benzene and **52** which reenters the catalytic cycle. Taken together, their results demonstrated that leveraging direct interactions between a transition metal and Lewis acid is a feasible method for C–F activation under mild conditions.

It is instructive to consider the mechanistic difference between the C-F activations observed by Nakao and Lu. In the Nakao system, the aluminum center serves as an active participant in the C-F cleavage step. The thermodynamic benefit of formation of an Al-F bond is undoubtedly responsible for reaction efficacy. In the case of complex **52**, the indium center serves only to stabilize the Rh (−I) intermediate that is responsible for C-F cleavage. Indium is sterically prevented from having a direct, meaningful interaction with the C-F bond. This fact, in combination with the weak thermodynamic stability of an In-F bond, relative to an Al-F bond, likely accounts for the drastic mechanistic deviation.

As a final example of C-F activation, Braun and coworkers reported a Rh-Si heterobimetallic complex $[Rh\{Si(OR)_3\}(PEt_3)_3]$ (R = Et, **58a**; R = Me, **58b**) that was found to activate aryl C–H bonds (Fig. 65) [352]. Interestingly, the authors found that **58a**-**b** activate the C–H bond when pentafluorobenzene is used as substrate (Fig. 66). This stands in stark contrast to earlier work from the Milstein group in which selective C–F activation of pentafluorobenzene at [Rh(SiMe$_2$Ph)(PMe$_3$)$_3$] (analogous to **58a-b**) in the position *para* to the hydrogen was observed at elevated temperatures [353]. This interesting reactivity divergence compared to earlier work merits the inclusion of this Rh-Si complex in this review despite the fact that transition metal-silicon complexes are not often considered to be heterobimetallic. The authors attributed the difference in observed selectivity to the electronic difference between an alkyl silane and an alkoxysilane. The authors were also delighted to find that C–F activation extended to 2,3,5,6-tetrafluoropyridine and pentafluoropyridine to form **59** and **60** respectively (Fig. 67). The formation of **59**, specifically, was noted by the authors to be quite astonishing, due to the fact that C–H activation occurs in comparable reactions [354–356].

7. Conclusion

The renaissance of heterobimetallic and heteromultimetallic chemistry over the last decade has primed the field for a dramatic leap. As has been illustrated in the work highlighted above, whether the two metal centers function cooperatively, independently, or the second metal serves as a simple electronic modifier to the active site metal, incorporation of two *electronically distinct* metal centers within a single complex can dramatically increase activity and selectivity for a desired process.

Though significant progress has been made over the last decade, much remains to be done. Regioselective C–H activations which direct reactivity to specific sp^3 carbon centers remain unrealized using bimetallic structures. Within the area of C-O activation, polarized heterobimetallic structures seem ideally suited for cleavage of ethereal C-O bonds or deoxygenation reactions that would be critical for efficient utilization of overfunctionalized feedstocks (i.e., biomass). Finally, carbon-heteroatom activations beyond C-O have not been extensively explored to date. Continued efforts in this area, particularly those building on the recent reports of selective C-F cleavage would be of great use to the synthetic community. For these particularly difficult transformations, two (or more) metal centers may be better than one. In short, the past decade has seen significant growth in the field of heterobimetallic chemistry, yet there is still plenty of avenues still ripe for additional study. As such, the next ten years of heterobimetallic investigation are primed to yield even more exciting discoveries than the previous ten.

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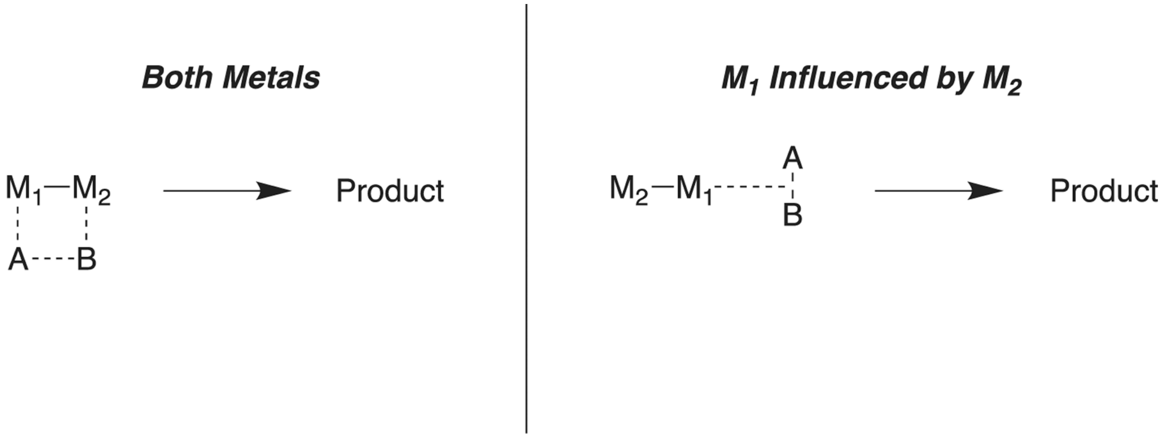


Fig. 1.

Two general methods of bimetallic bond activation.

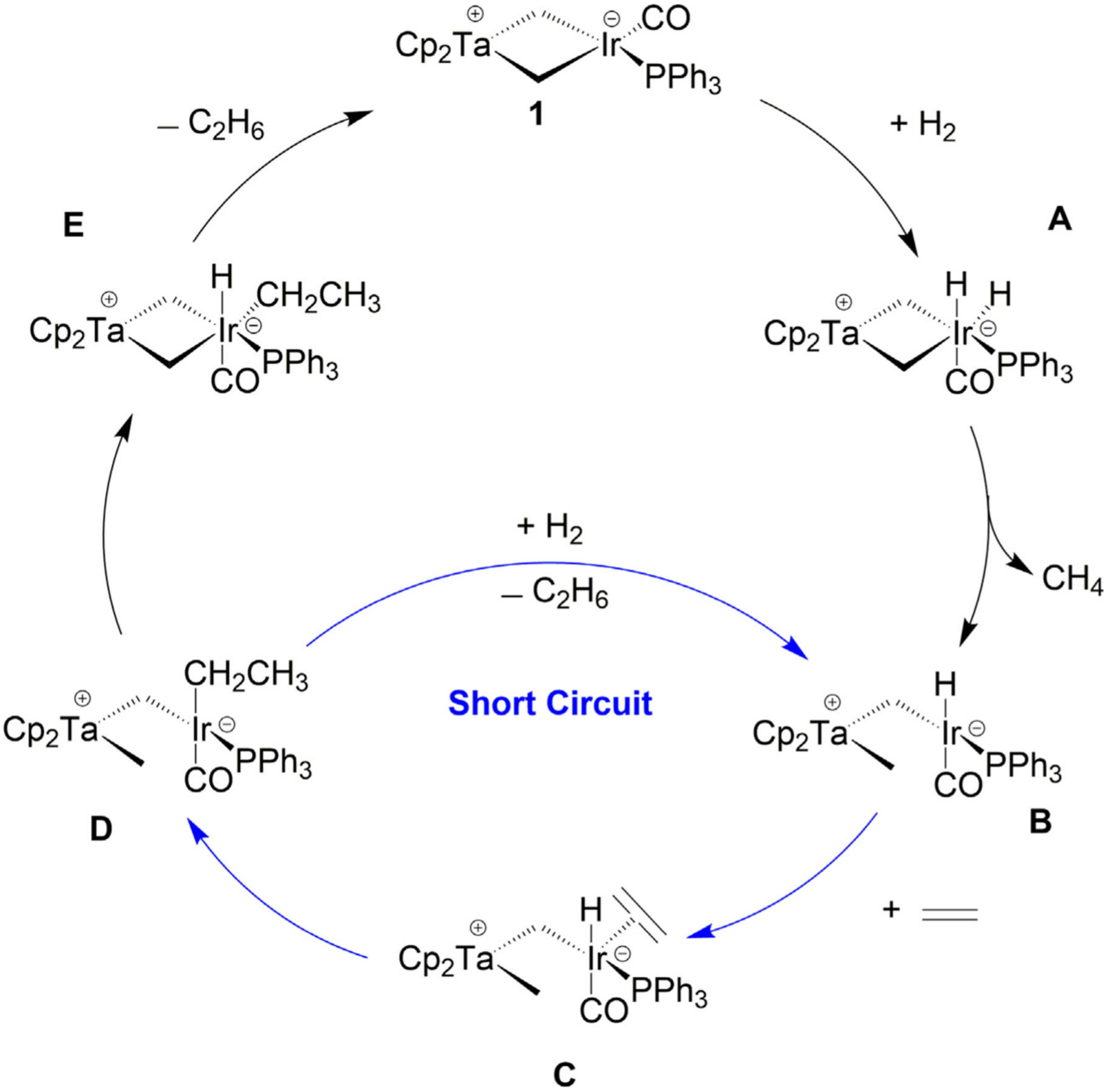


Fig. 2.

Computationally supported proposed catalytic cycle for alkene hydrogenation by **1** with plausible short circuit loop shown in blue.

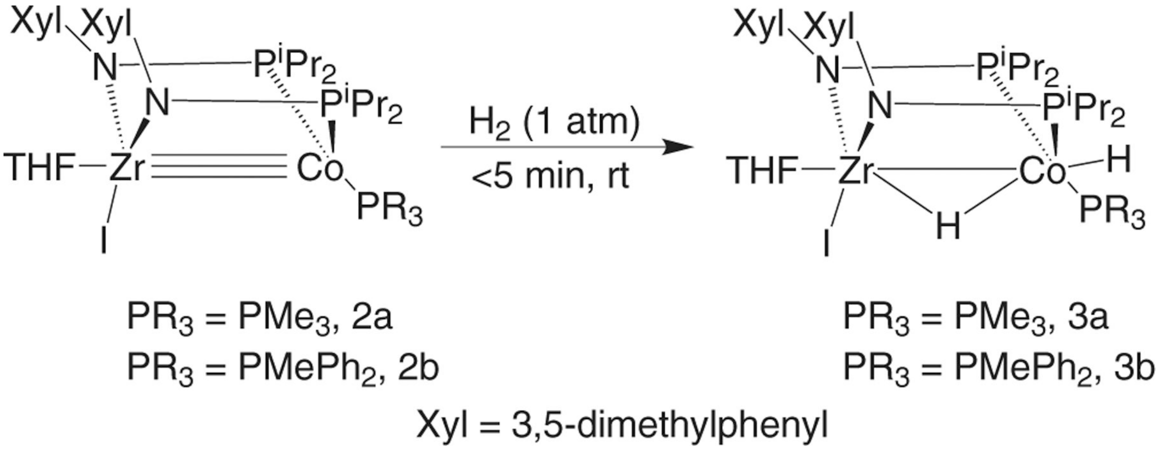


Fig. 3.

Activation of H_2 by **2a-b**.

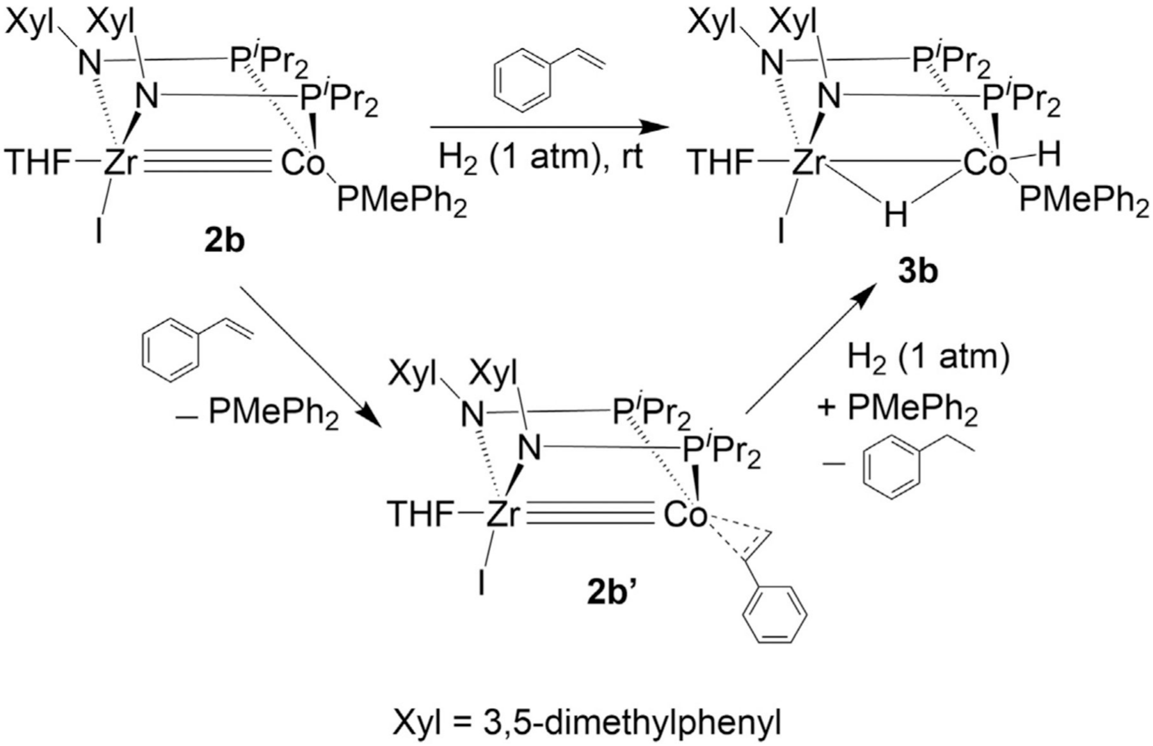


Fig. 4.

Hydrogenation of styrene by **2b**.

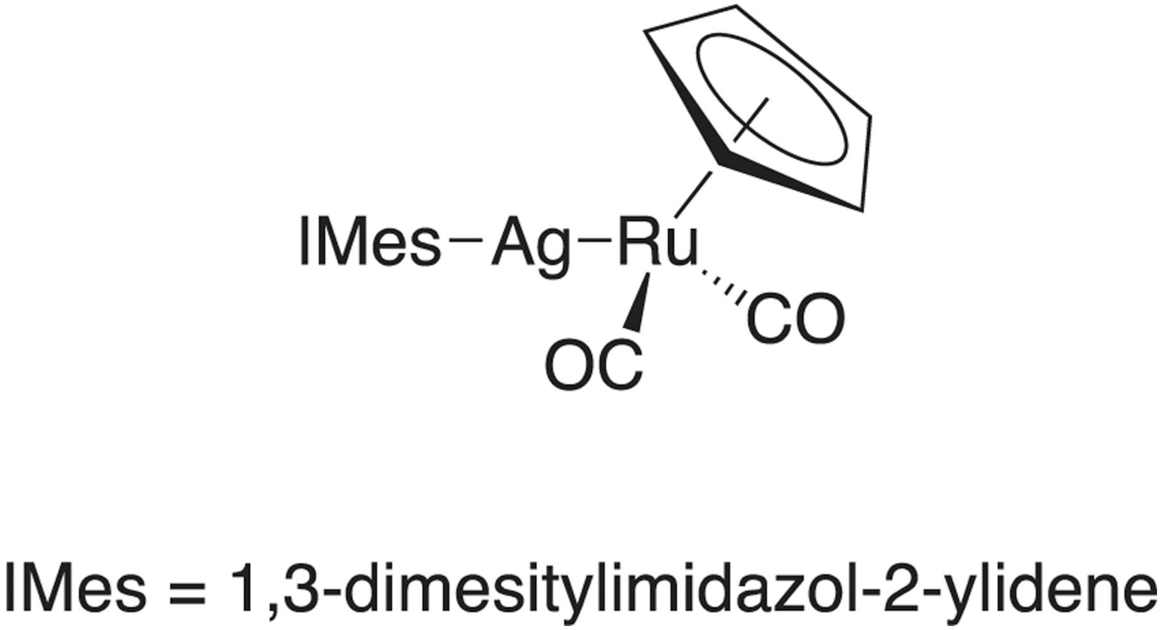
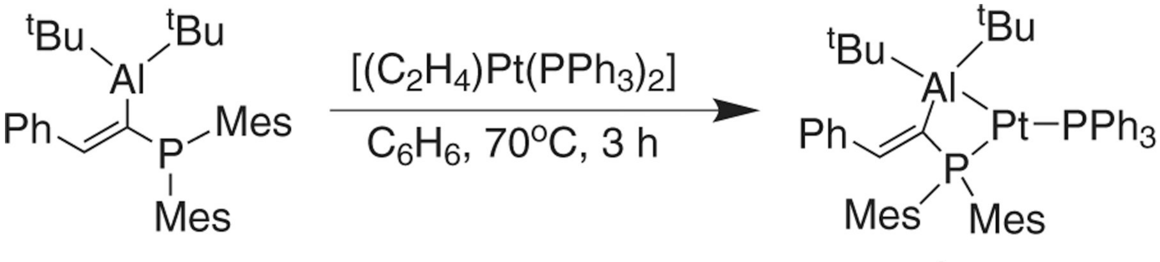


Fig. 5.
Ru-Ag heterobimetallic complex.



4

Fig. 6.

Synthesis of Pt-Al heterobimetallic complex **4**.

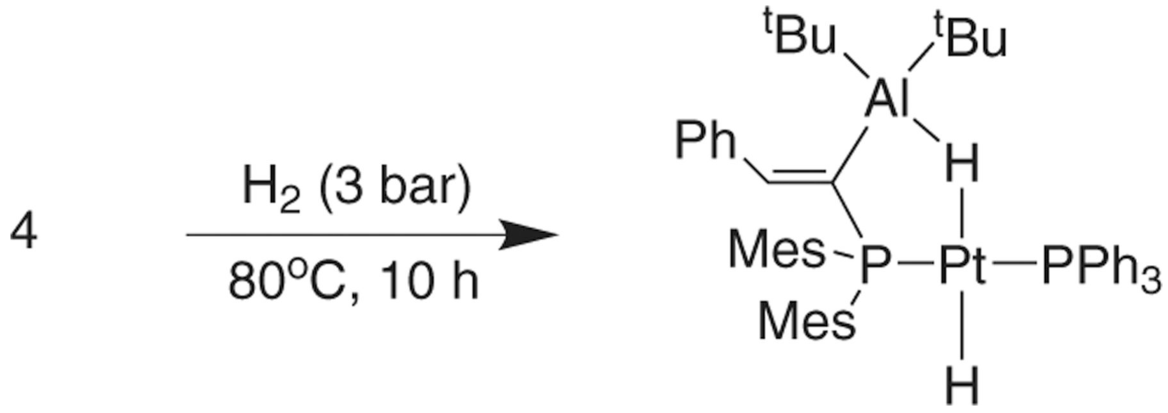


Fig. 7.

Activation of H_2 by **4**.

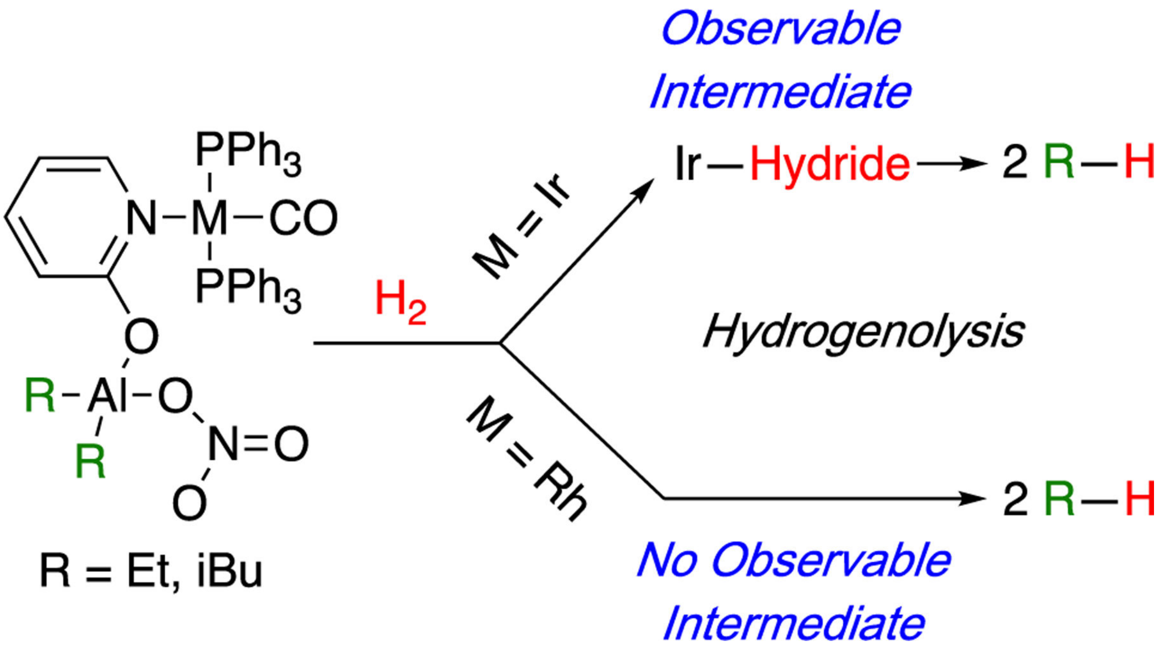


Fig. 8.

General hydrogen activation and hydrogenolysis reaction.

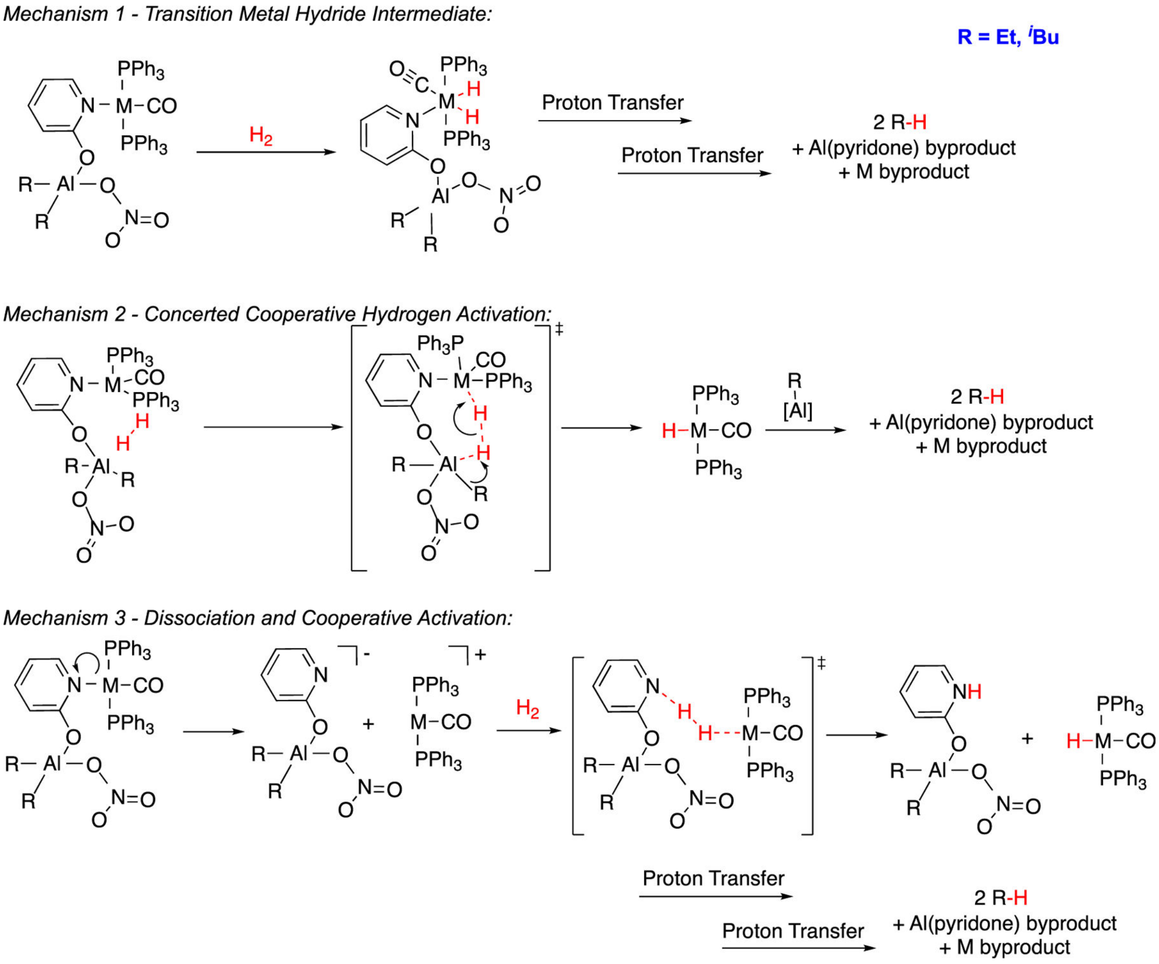


Fig. 9.

Considered mechanisms for reaction of Ir-Al and Rh-Al heterobimetallics with H_2.

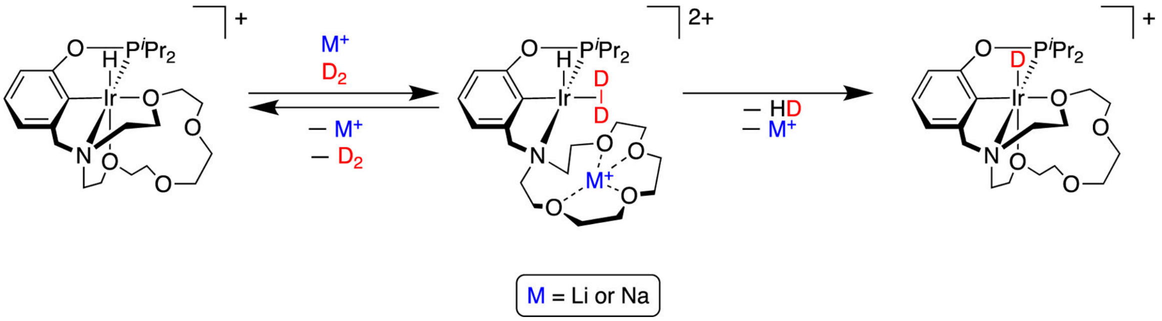


Fig. 10.

General H_2 activation and H/D exchange reaction.

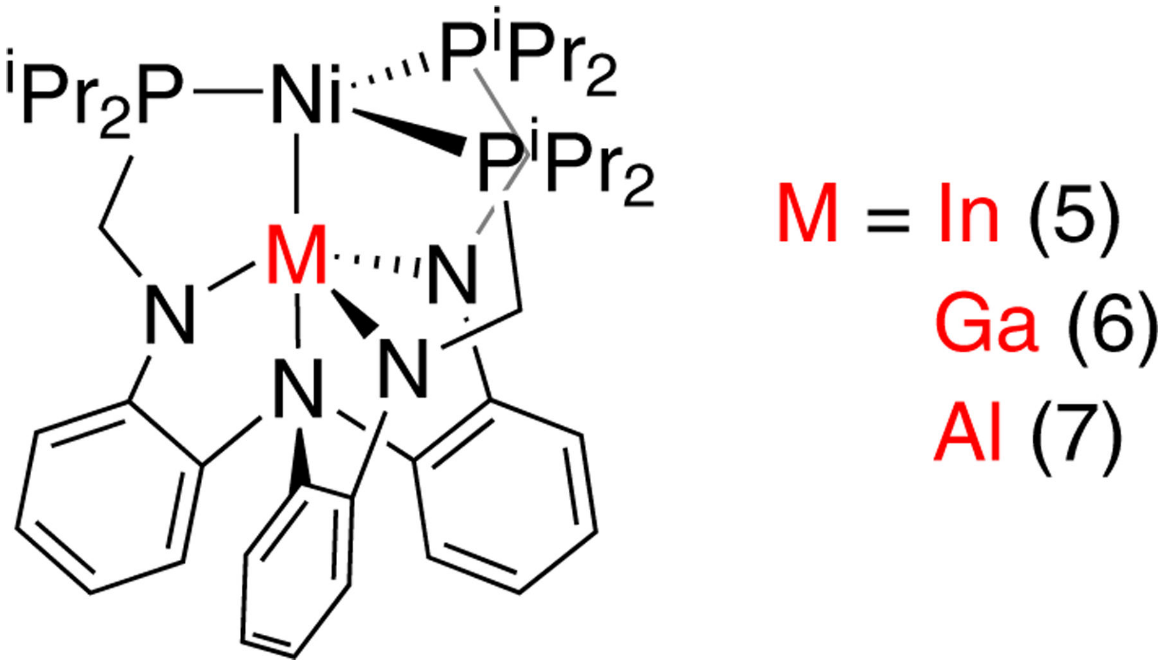
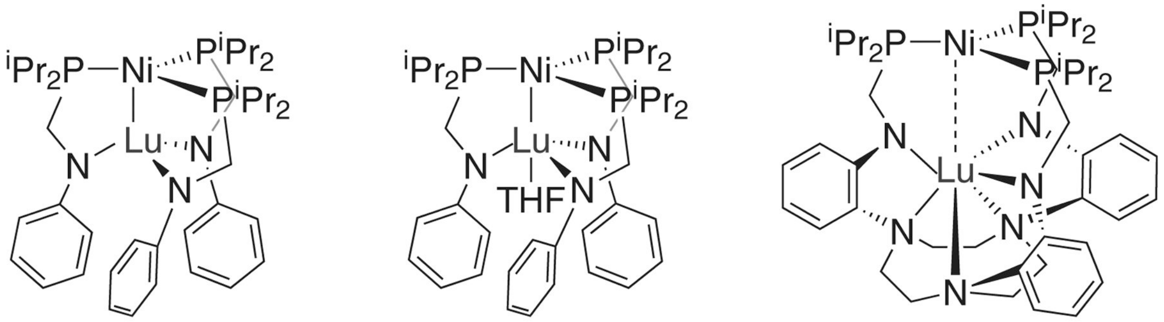


Fig. 11.

Ni-Group 13 olefin hydrogenation catalysts.



8 9 10

Fig. 12.

Heterobimetallic Ni-Lu catalysts **8**, **9**, **10**.

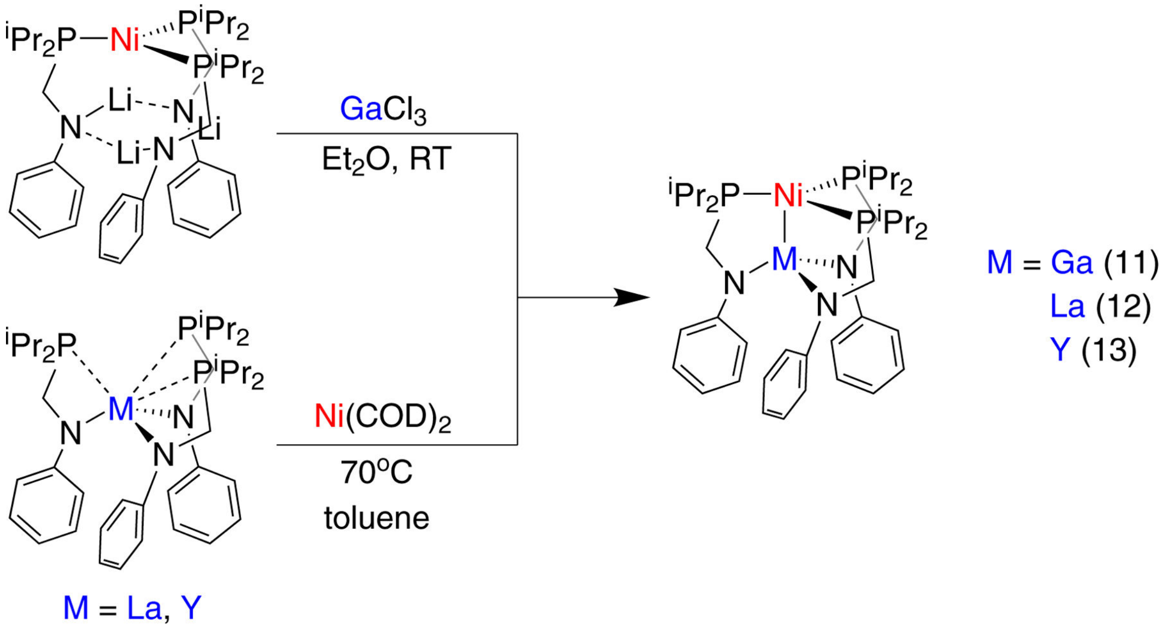


Fig. 13.

Synthetic routes for preparation of heterobimetallics **11–13**.

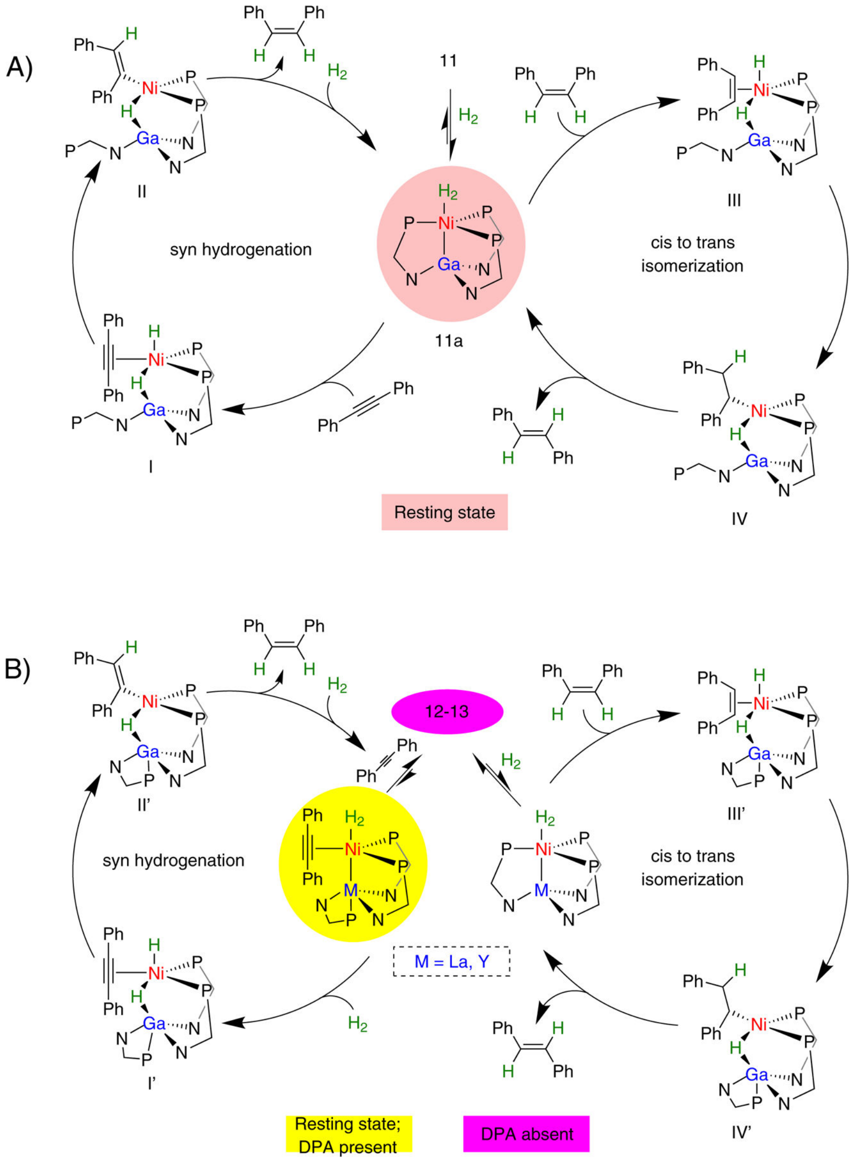


Fig. 14.

Proposed catalytic cycles for (E)-selective semihydrogenation of DPA catalyzed by **11** (A) and **12–13** (B).

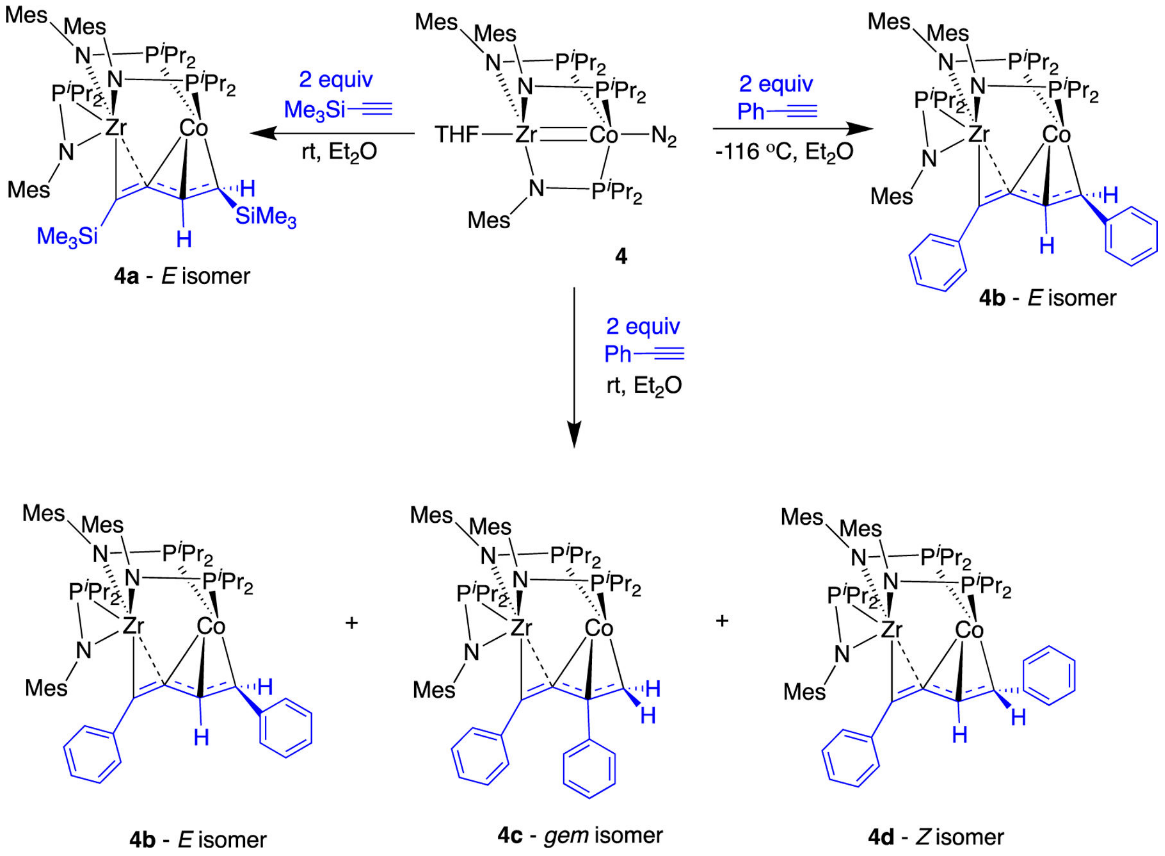


Fig. 15.

Reaction of terminal alkynes with **14**.

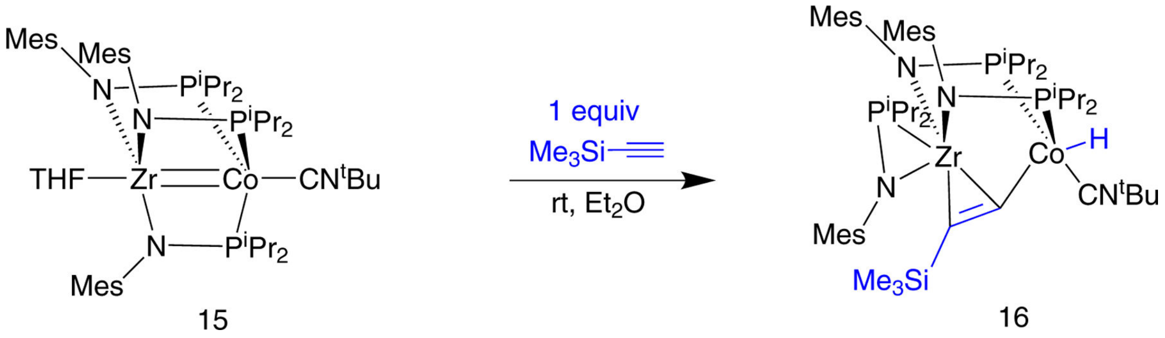


Fig. 16.

Reaction of trimethylsilylacetylene with **15**.

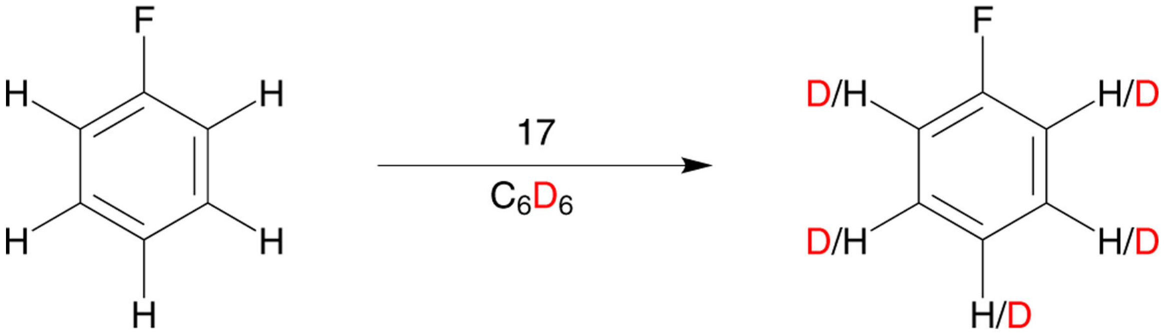


Fig. 17.

H/D exchange of fluorobenzene catalyzed by **17**.

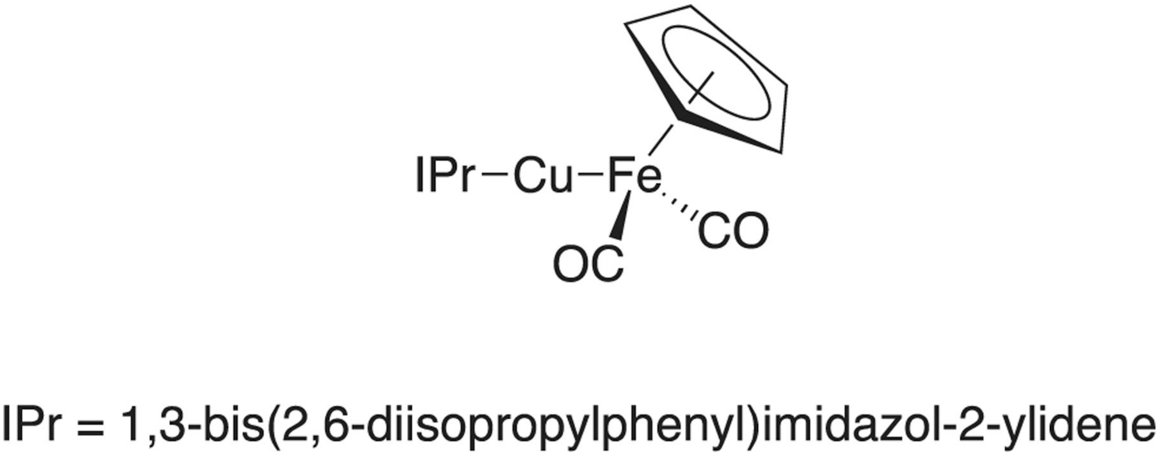


Fig. 18.

Fe-Cu arene C–H borylation catalyst.

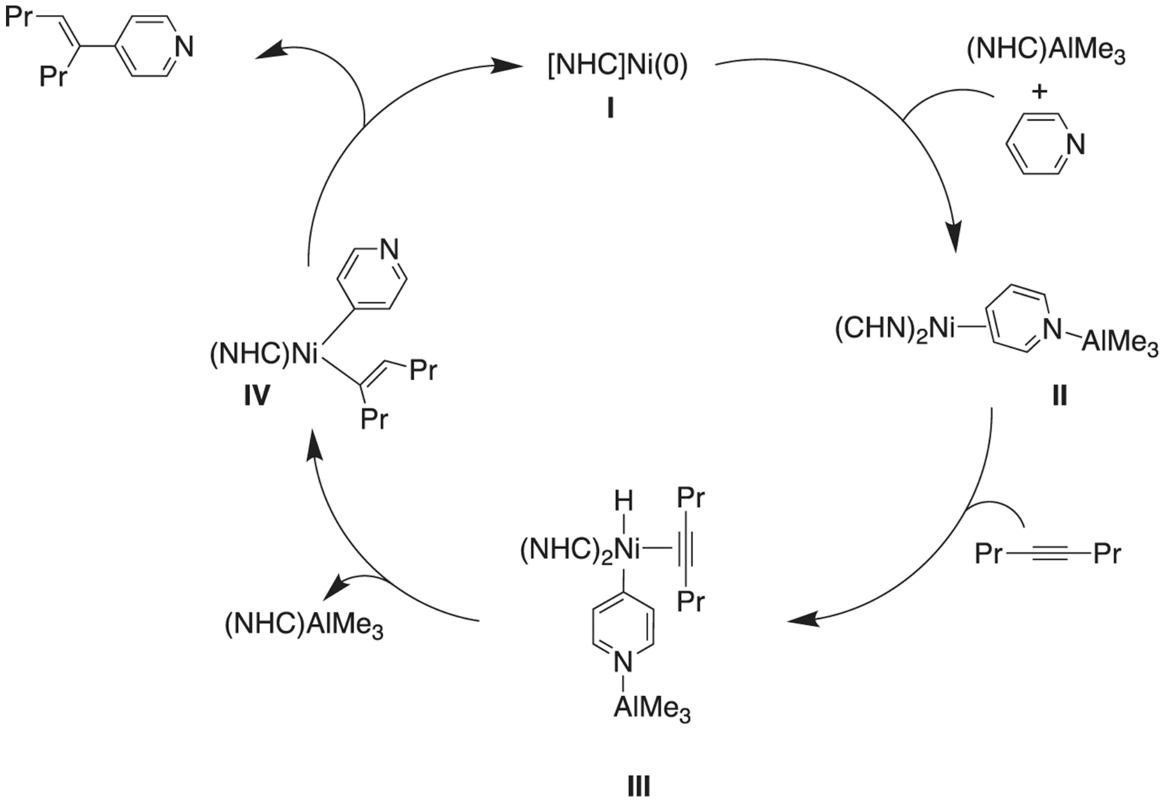


Fig. 19.

Proposed catalytic cycle for *para*-selective pyridine alkenylation.

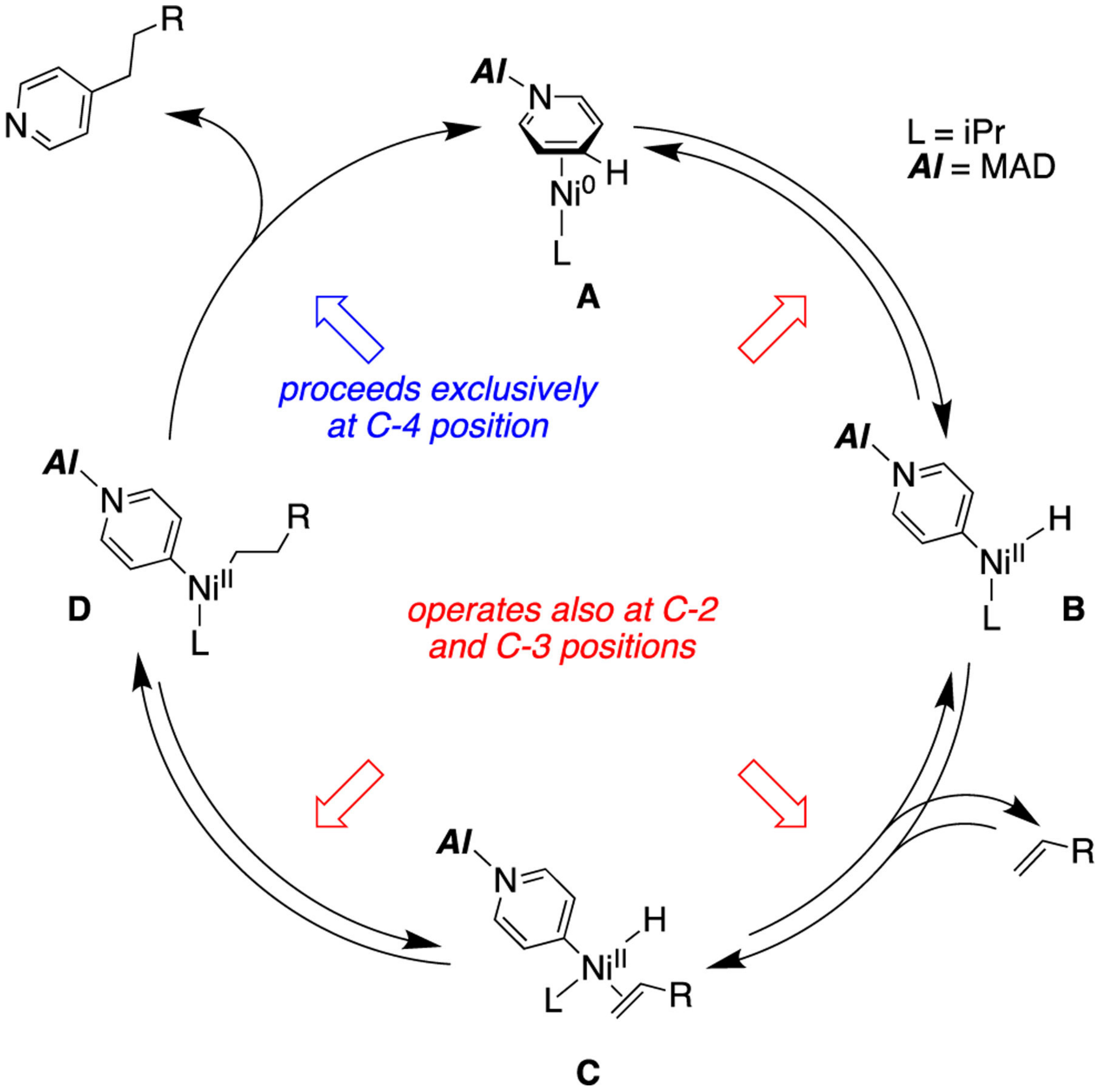


Fig. 20.

Proposed catalytic cycle for C-4-selective alkylation of pyridine.

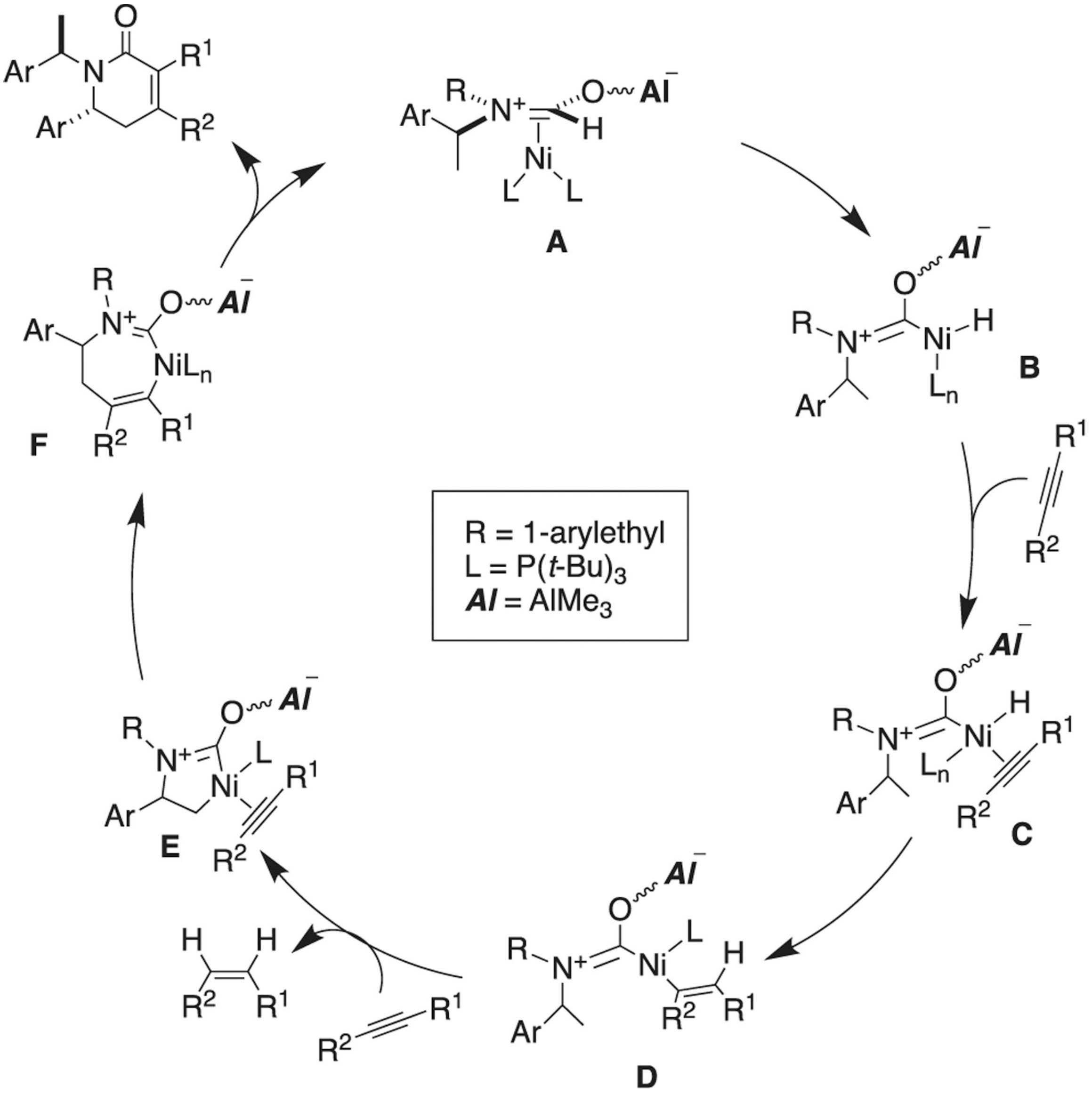


Fig. 21.

Plausible catalytic cycle for dehydrogenative [4 + 2] cycloaddition of formamides with alkynes.

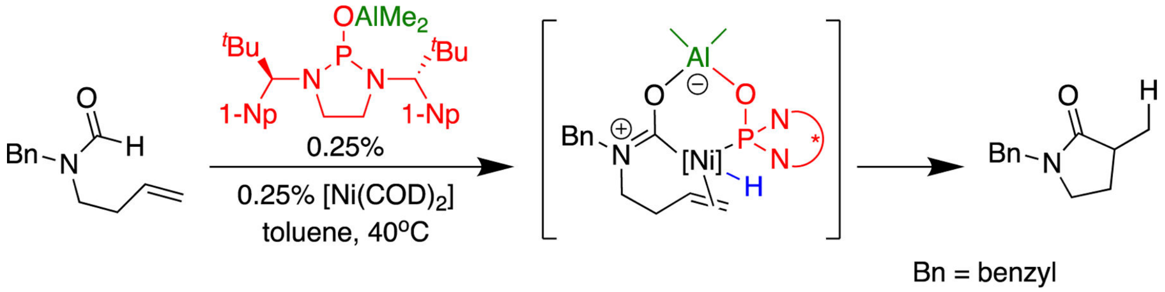


Fig. 22.

Asymmetric hydrocarbamoylation reaction catalyzed by **18**; note, **18** assembled from Ni and Al in solution.

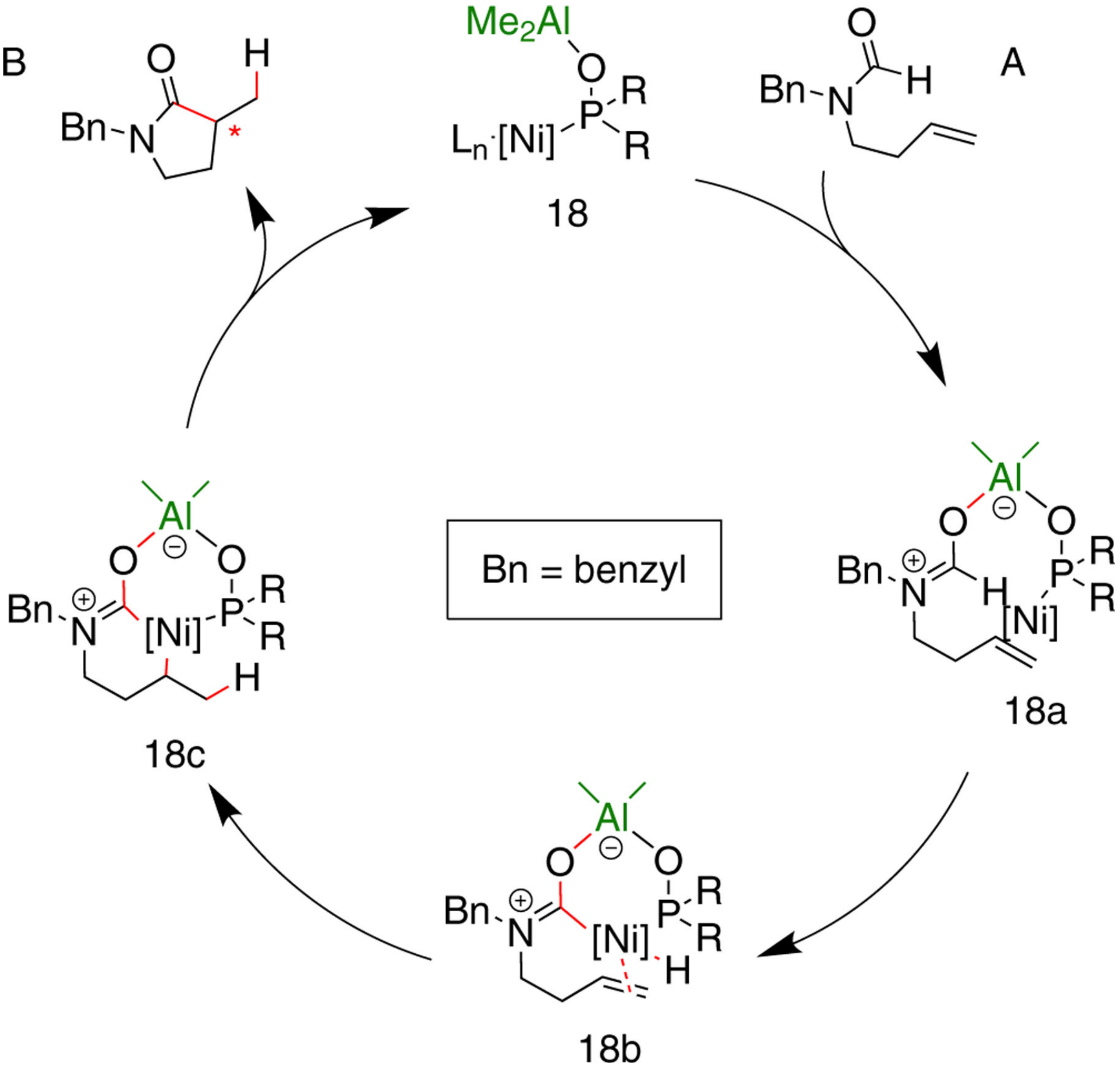


Fig. 23.

Proposed catalytic cycle for asymmetric hydrocarbamoylation of alkenes catalyzed by **18**.

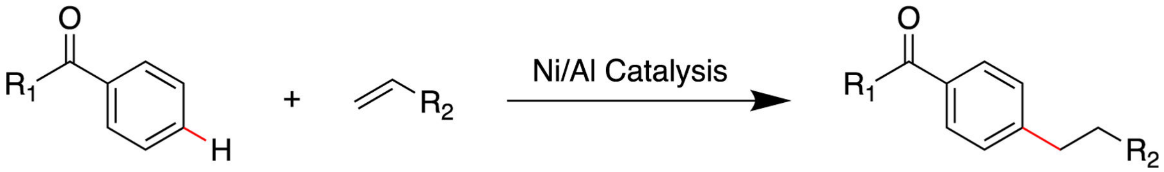


Fig. 24.
Overall *para*-selective alkylation reaction mediated by Ni/Al catalysis.

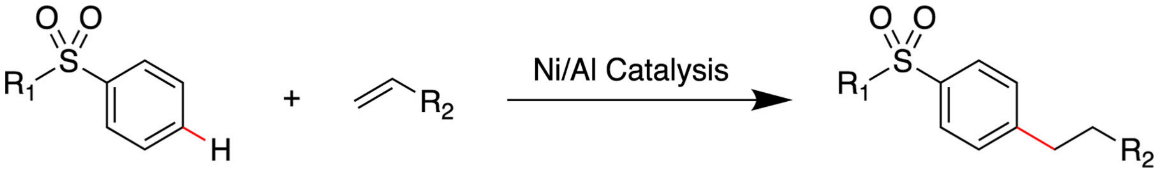


Fig. 25.

Overall *para*-selective alkylation reaction mediated by Ni/Al catalysis.

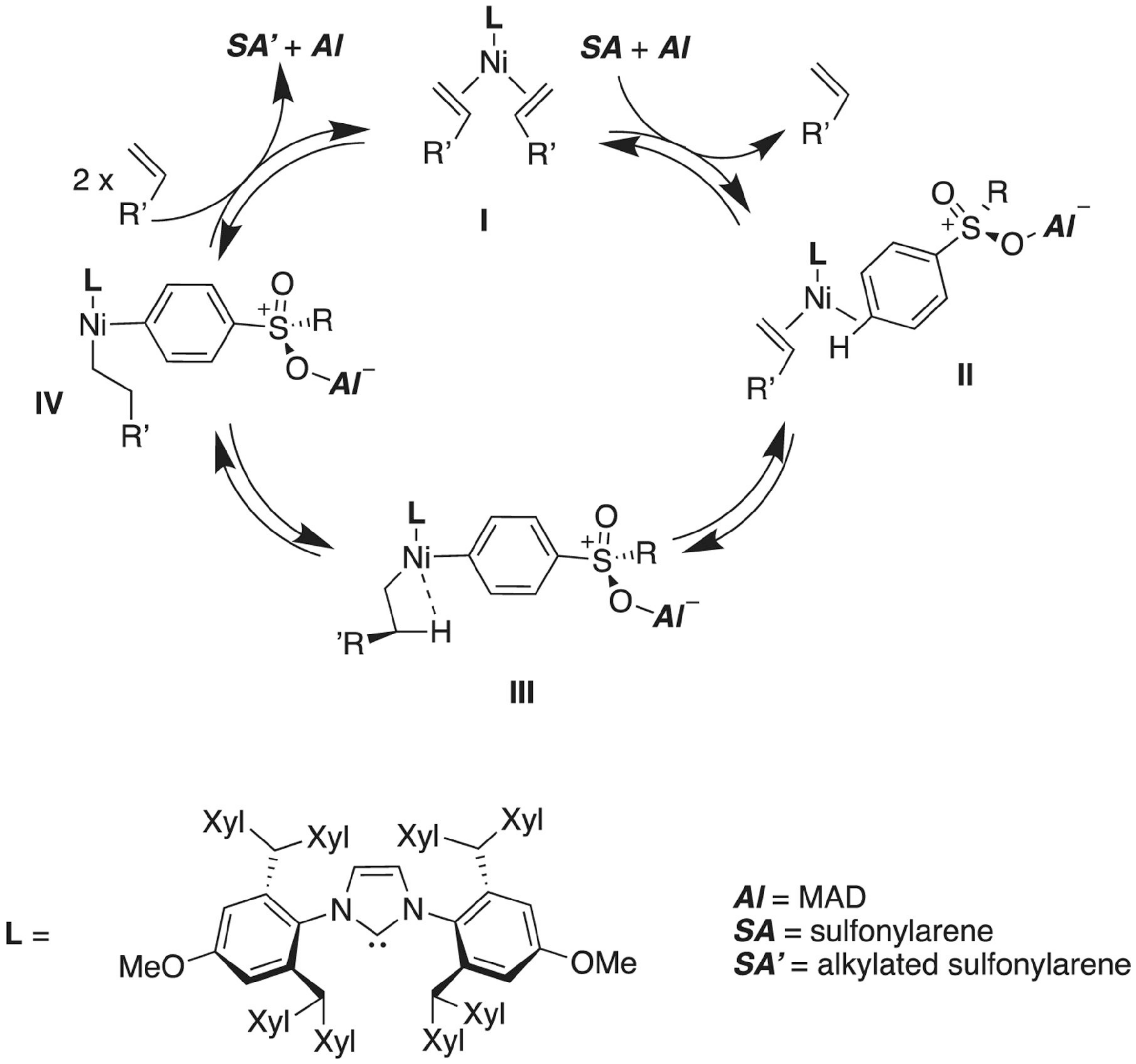


Fig. 26.

Plausible mechanism for *para*-selective alkylation of sulfonylarenes.

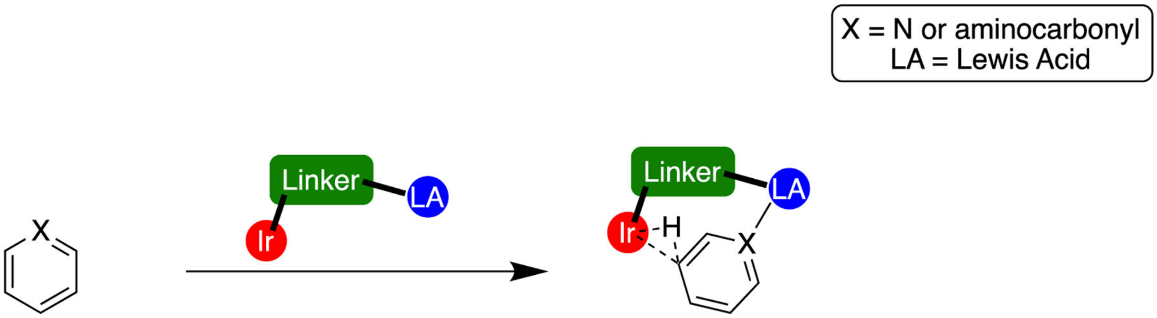


Fig. 27.

General reaction for *meta*-selective C–H borylation of pyridines and benzamides.

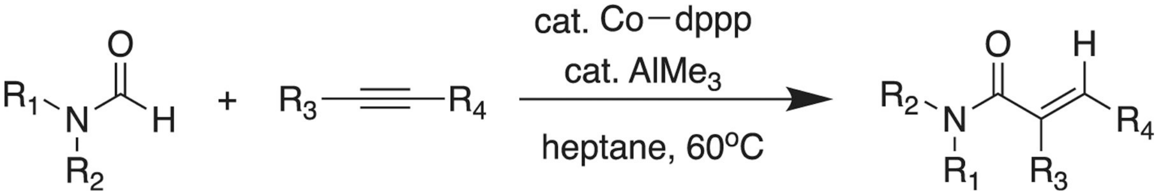
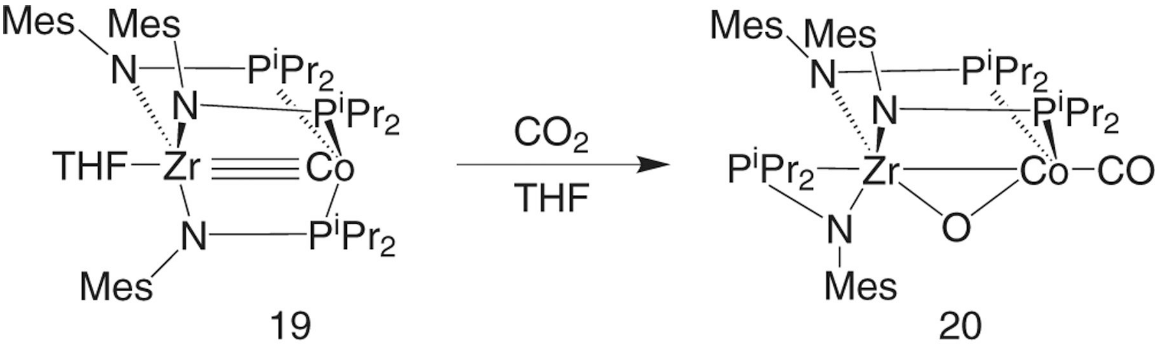


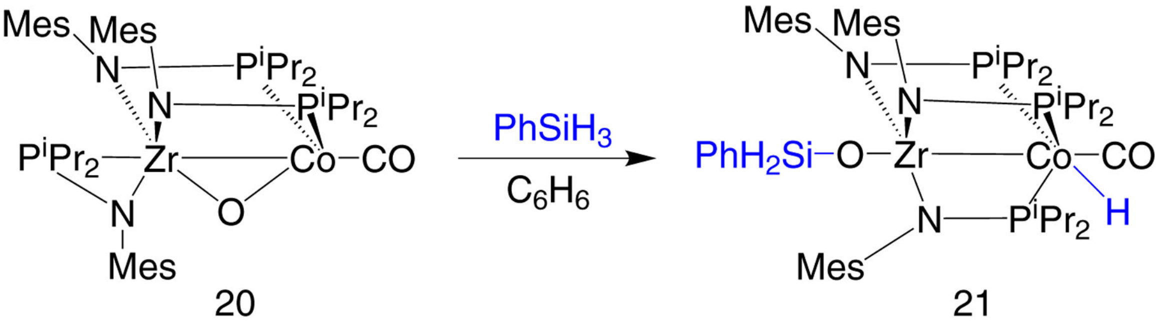
Fig. 28.

General alkyne hydrocarbofunctionalization reaction.



Mes = mesityl

Fig. 29.
Oxidative addition of CO_2 by Zr-Co heterobimetallic complex **19**.



Mes = mesityl

Fig. 30.
Functionalization of oxo bridging ligand.

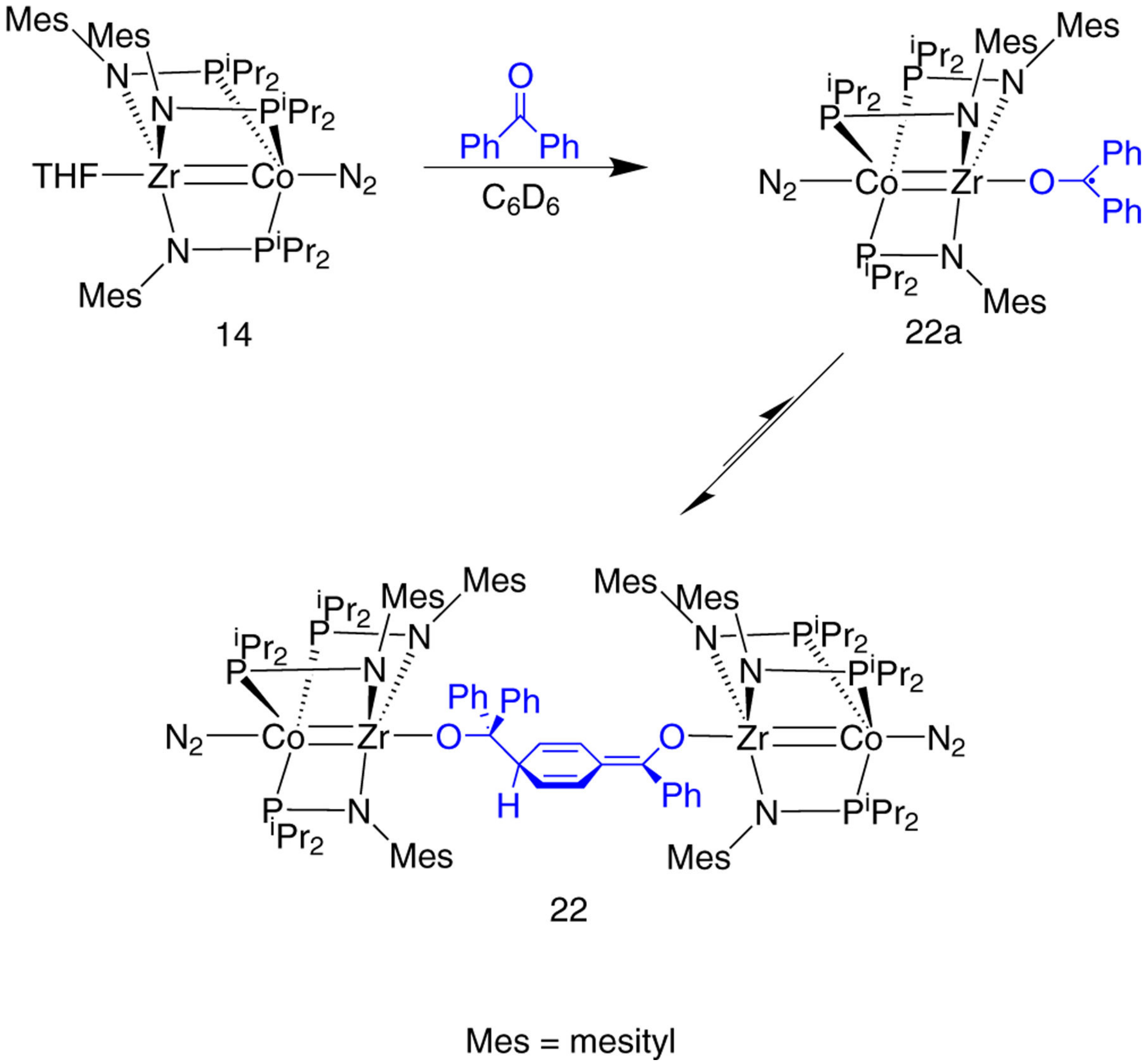


Fig. 31.

Stoichiometric reactions of **14**.

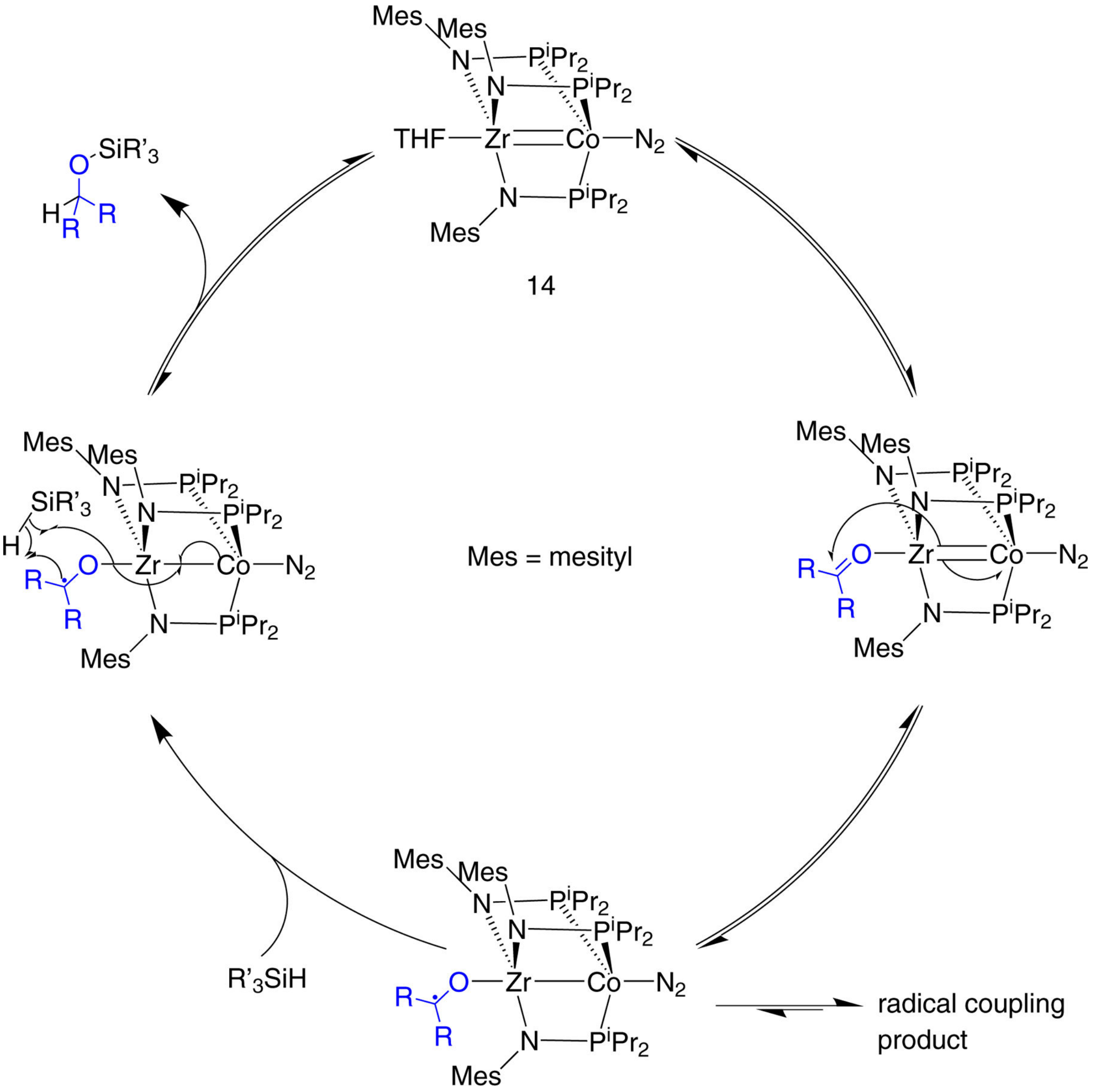


Fig. 32.

Proposed catalytic cycle for hydrosilylation of ketones using heterobimetallic Zr/Co complex **14**.

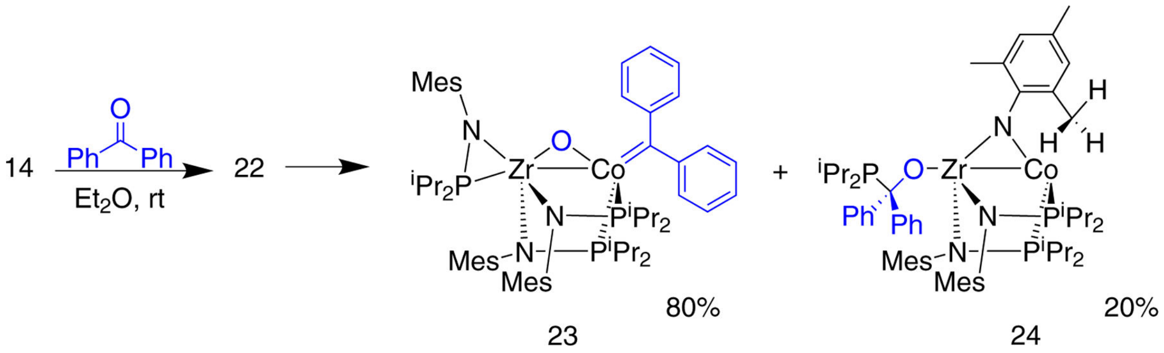


Fig. 33.

Generation of **23** and **24** via thermolysis of **22**.

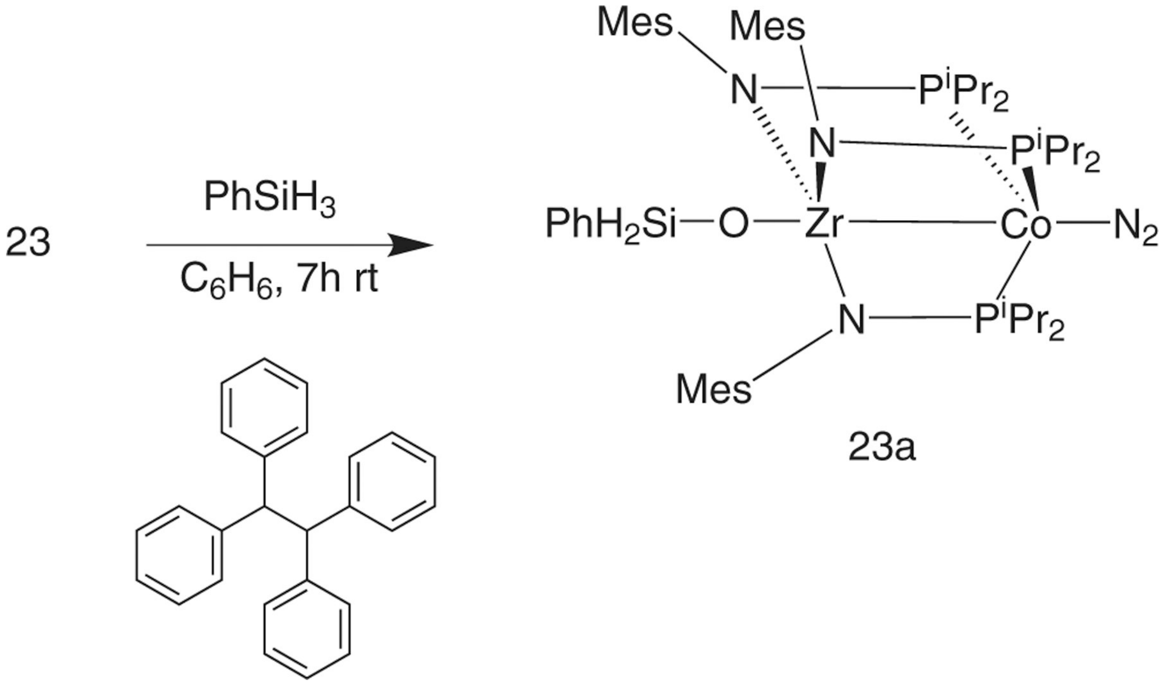


Fig. 34.
Reaction of **23** with phenylsilane.

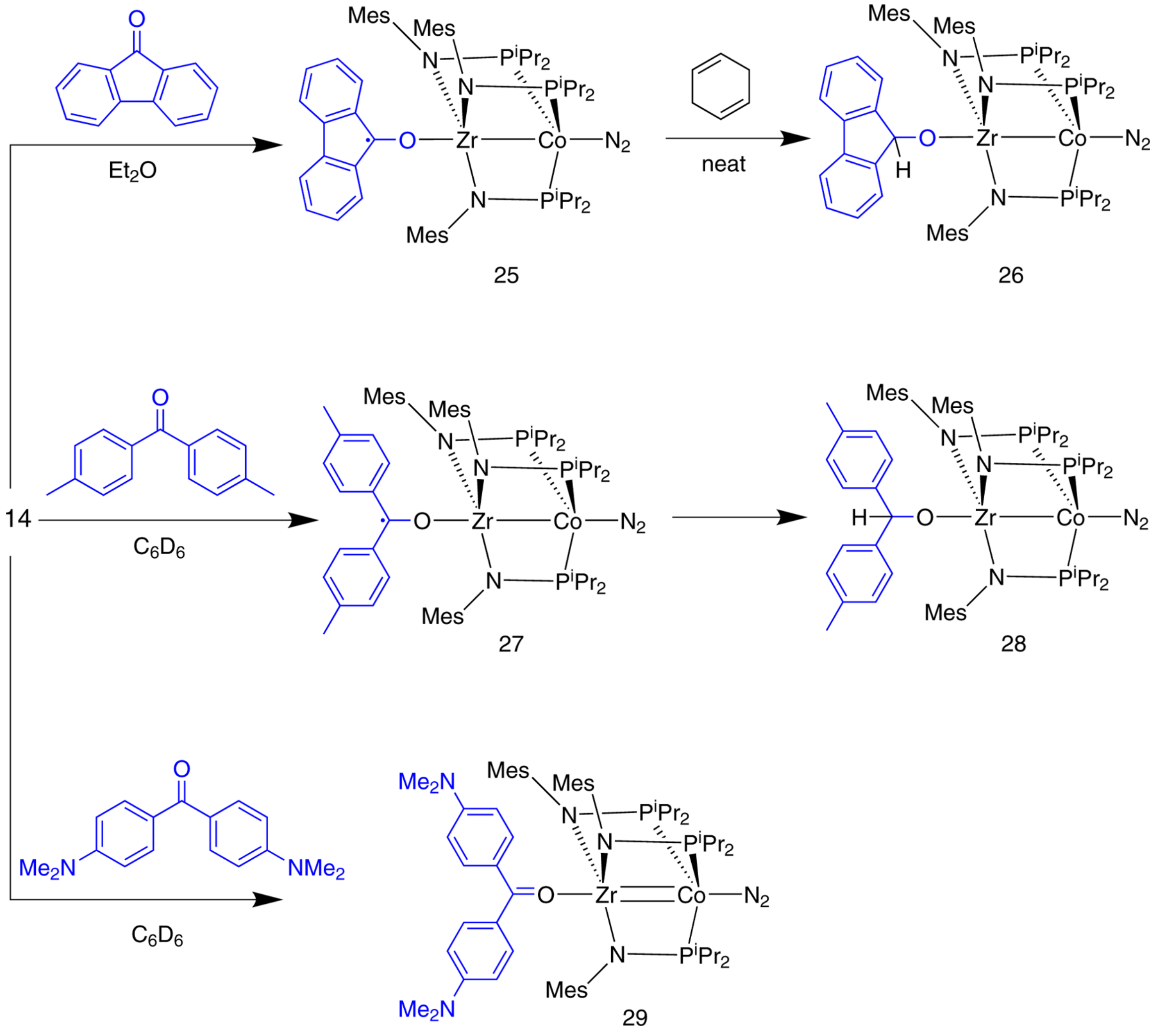


Fig. 35.

Synthesis of heterobimetallic complexes **25–29** from **14**.

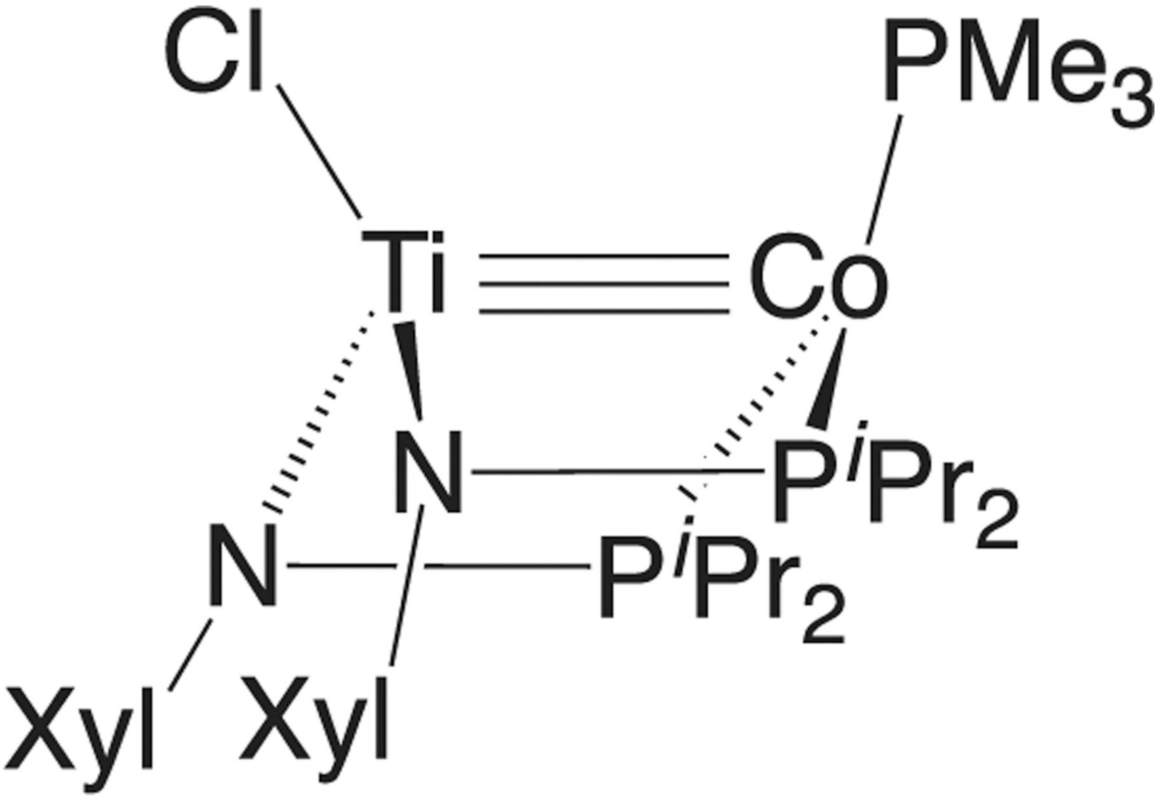


Fig. 36.
Ti-Co heterobimetallic **30**.

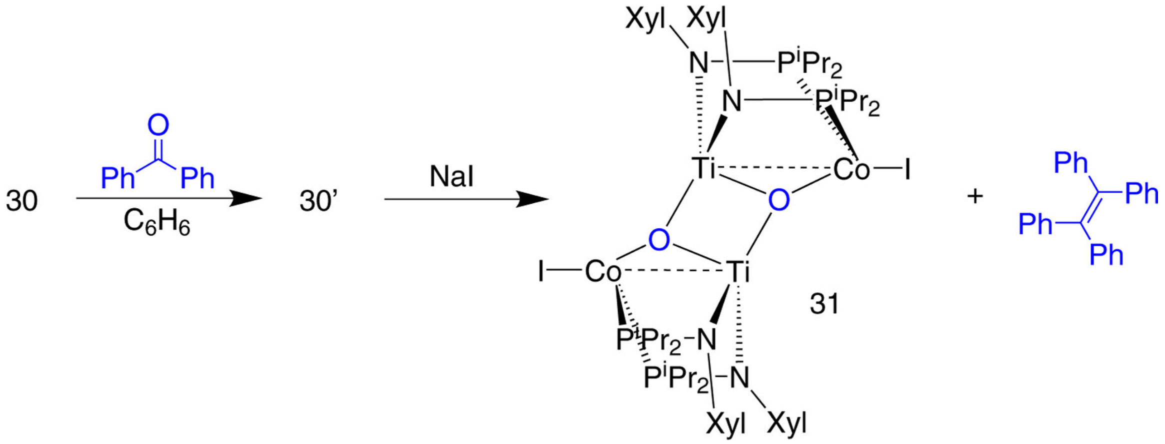


Fig. 37.

Reaction of **30** with benzophenone.

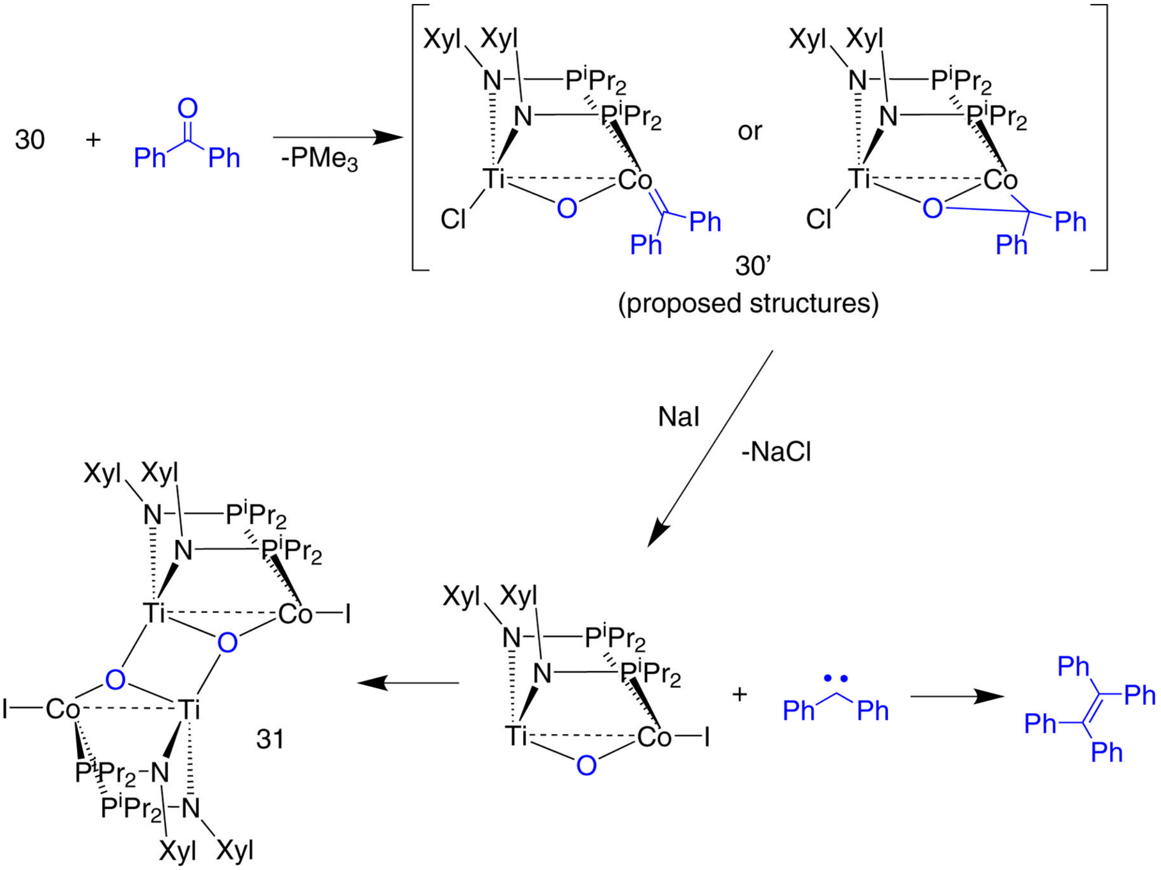


Fig. 38.

Proposed reaction pathway of McMurry reaction mediated by **30**.

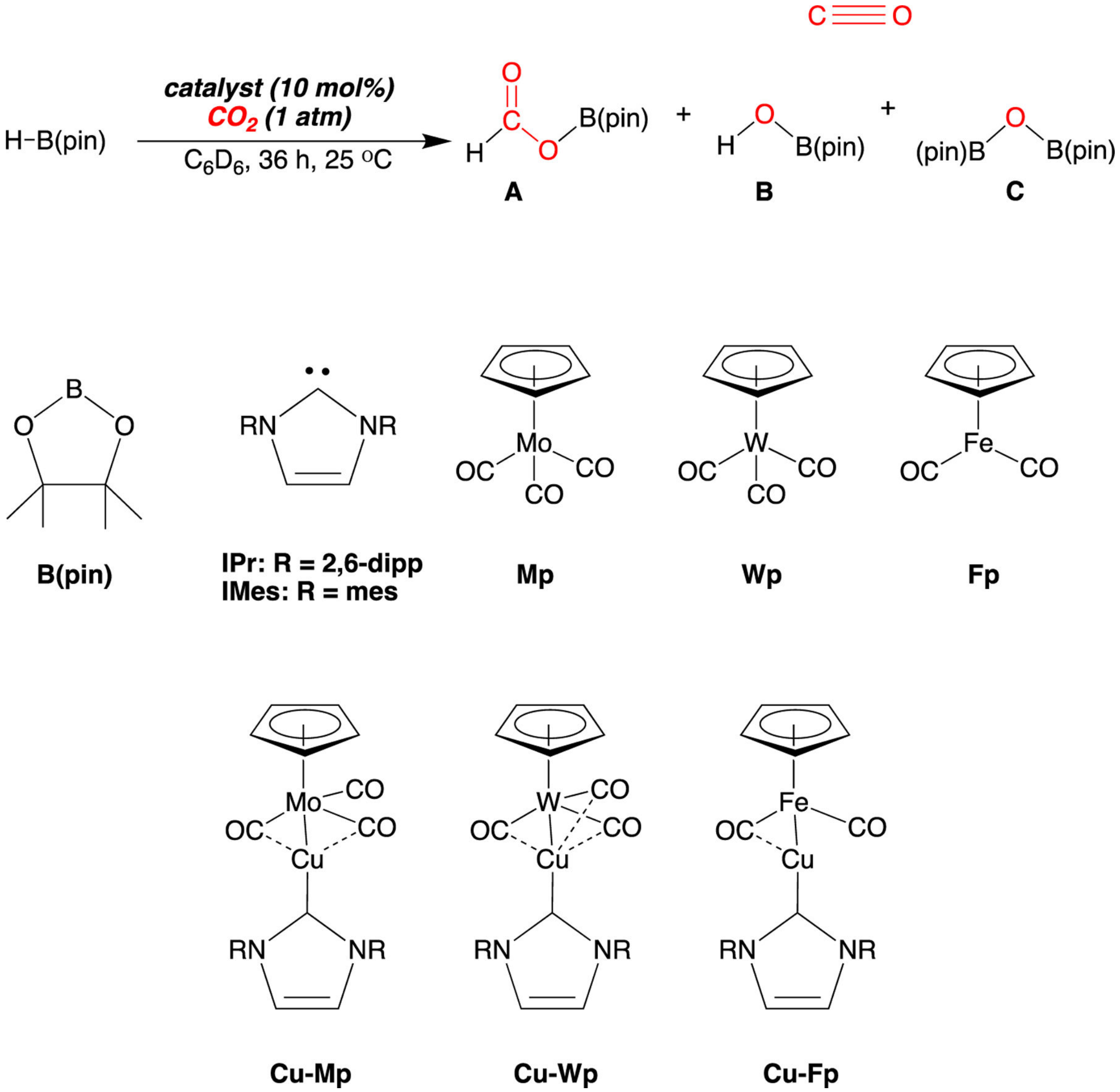


Fig. 39.

Heterobimetallic Cu-M catalysts. L = IPr or IMes, [M] = W, Mo, or Fe.

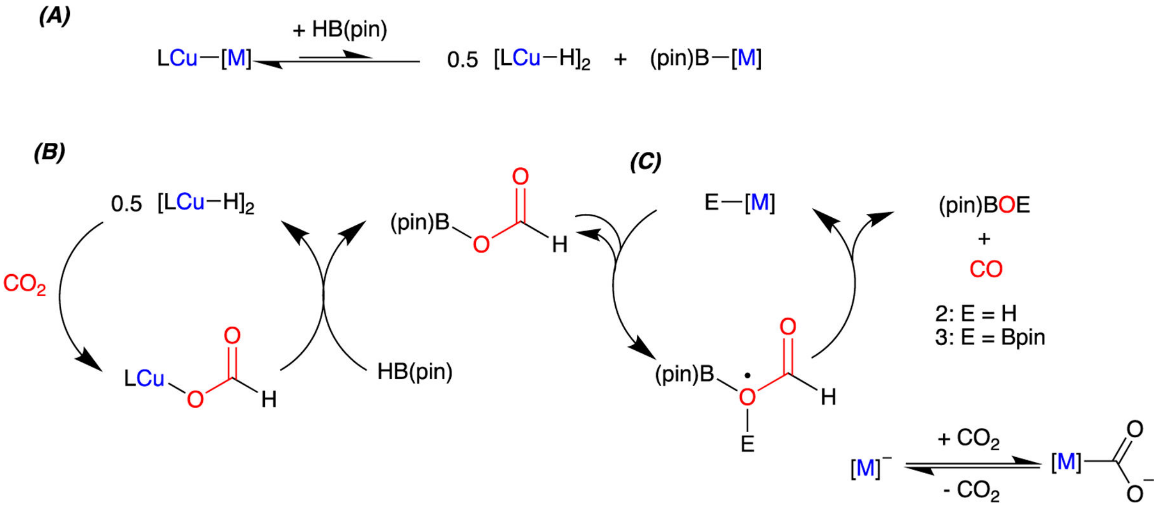


Fig. 40.

Proposed mechanism for Cu-M catalyzed hydroboration: (a) catalyst activation, followed by autotandem (b) CO_2 hydroboration, and (c) CO_2-assisted formate decarbonylation. E = B(pin) for the first turnover and then H throughout. L = IPr or IMes, [M] = Fp, Wp, or Mp, pin = pinacolate.

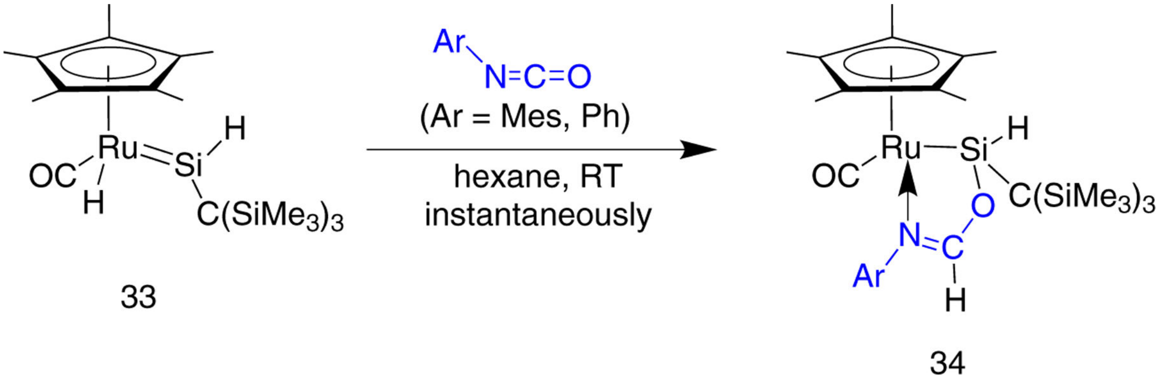


Fig. 41.

Reaction of **33** with ArNCO.

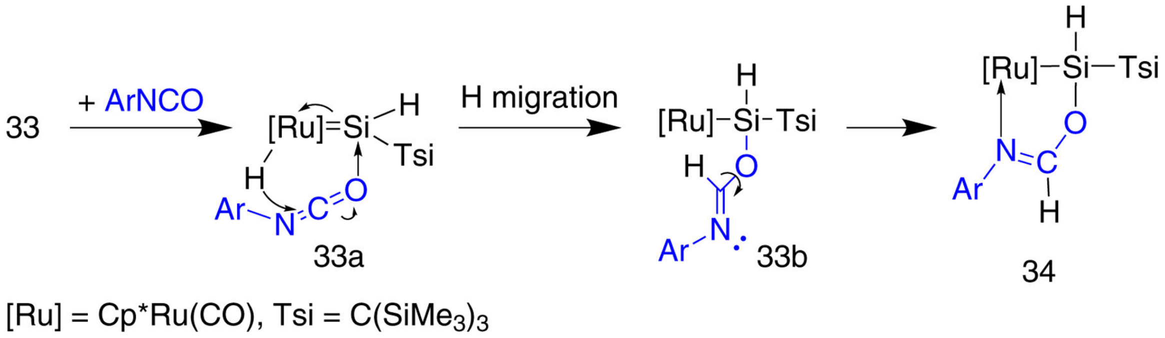


Fig. 42.

Possible mechanism for reaction of **33** with ArNCO.

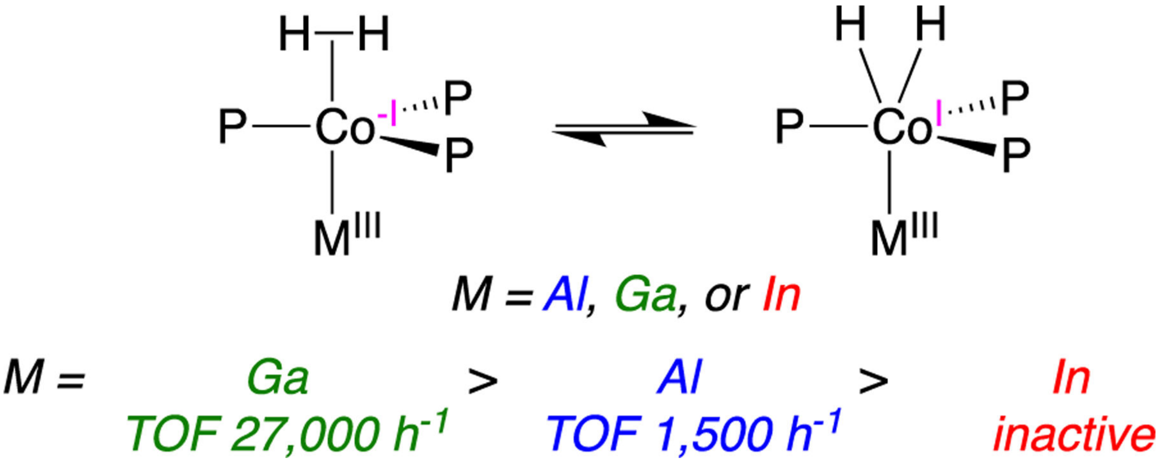


Fig. 43.

Catalytically active species for **35**.

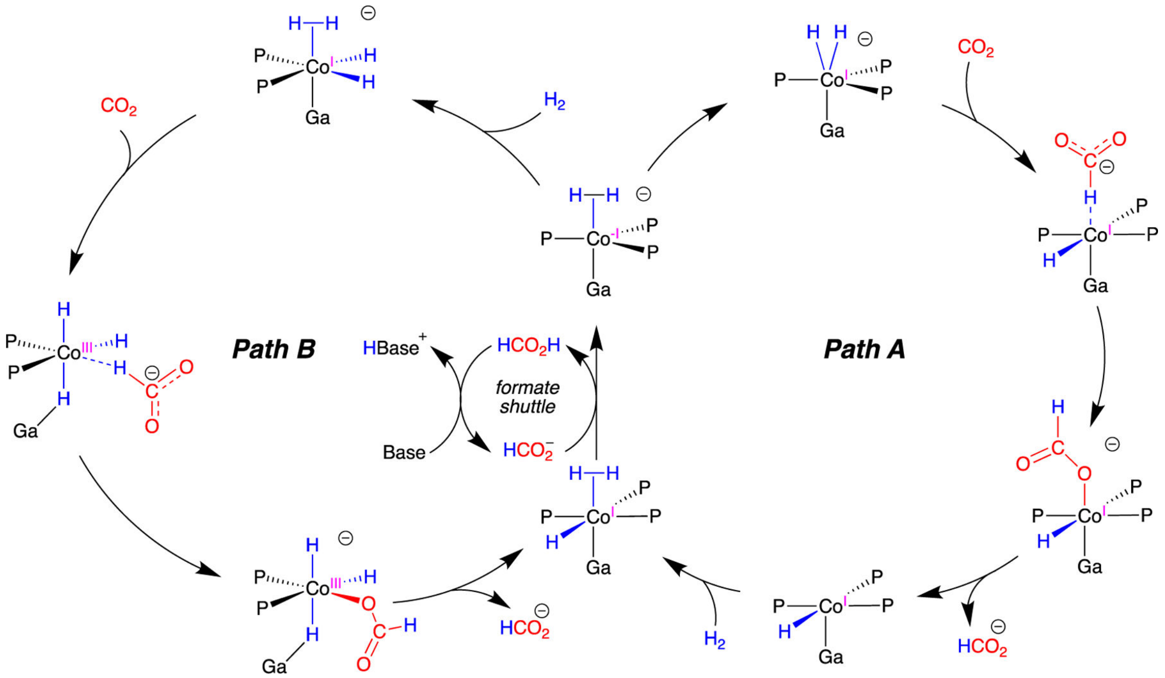


Fig. 44.

DFT-calculated mechanism for CO_2 hydrogenation to formate by the Co-Ga catalyst, [**35b**-H_2].

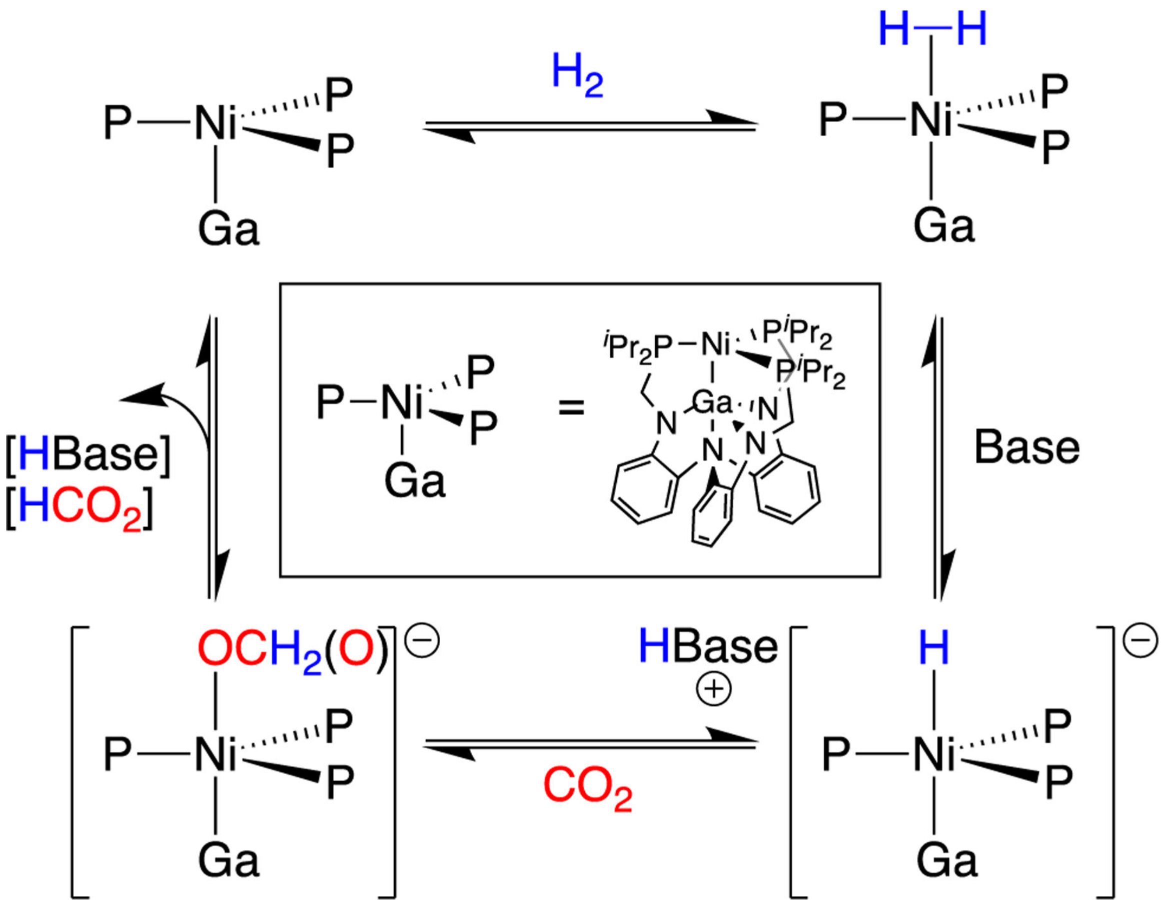


Fig. 45.

Catalytic scheme for CO_2 hydrogenation to formate by NiGaL (**36**).

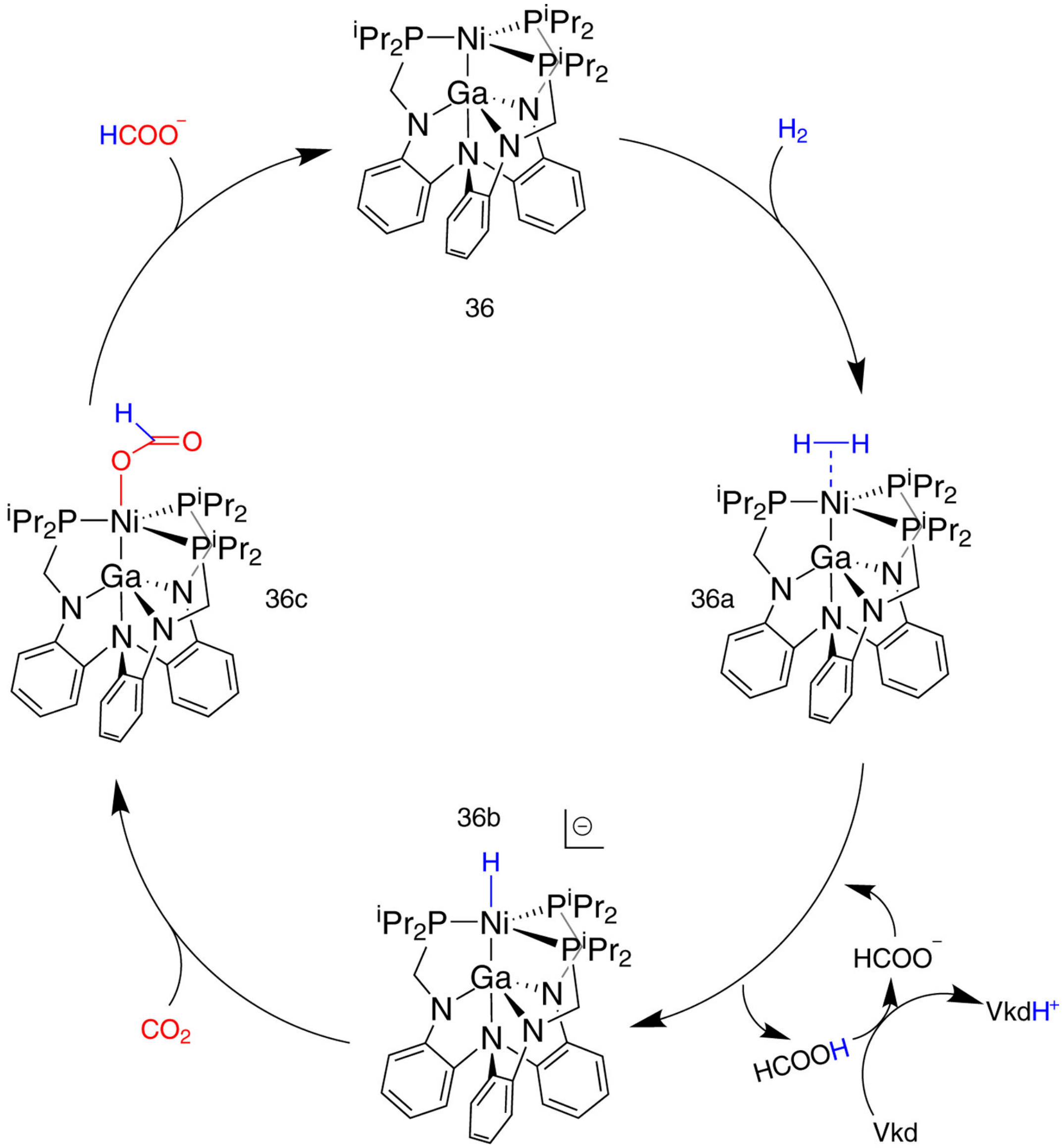


Fig. 46.

Most energetically favorable catalytic cycle for CO_2 hydrogenation catalyzed by **36**.

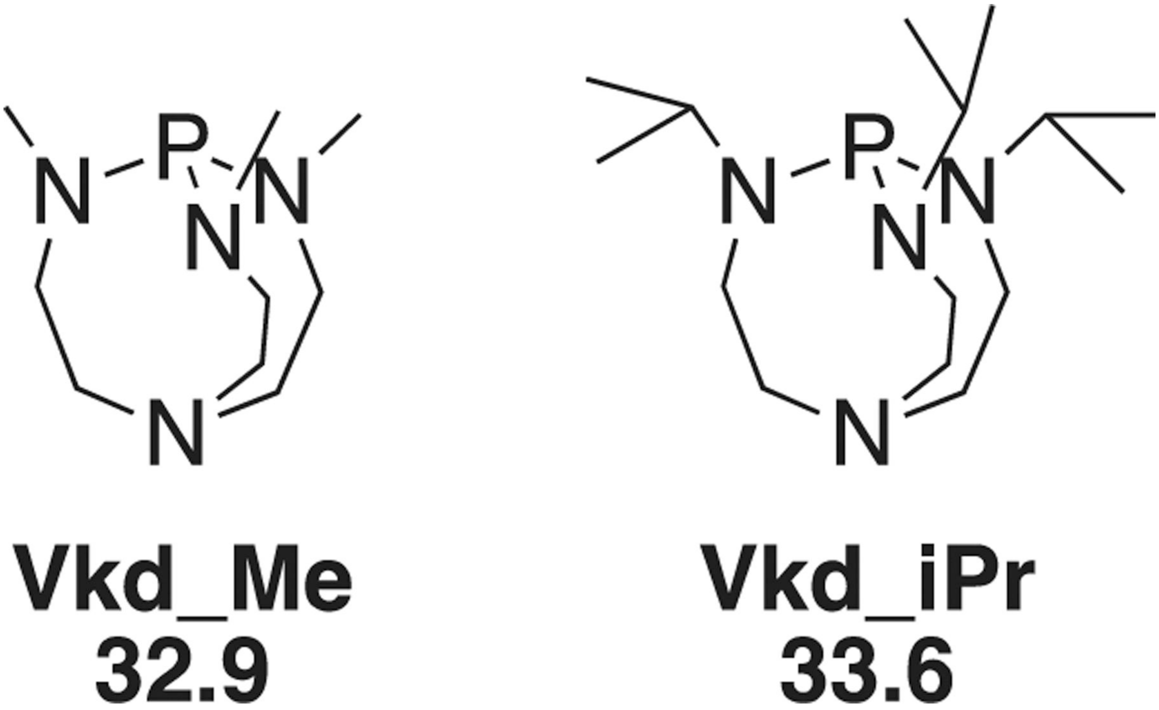


Fig. 47.

Two Verkade's bases (Vkd_Me and Vkd_iPr) and the pK_a values of their conjugate acids in CH_3CN.

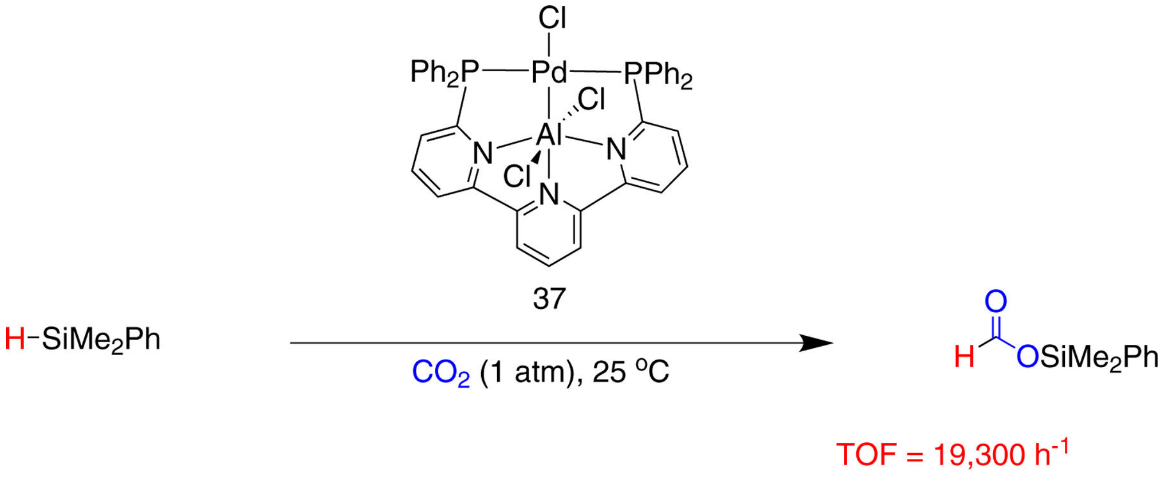


Fig. 48.
Hydrosilylation of CO_2 catalyzed by **37**.

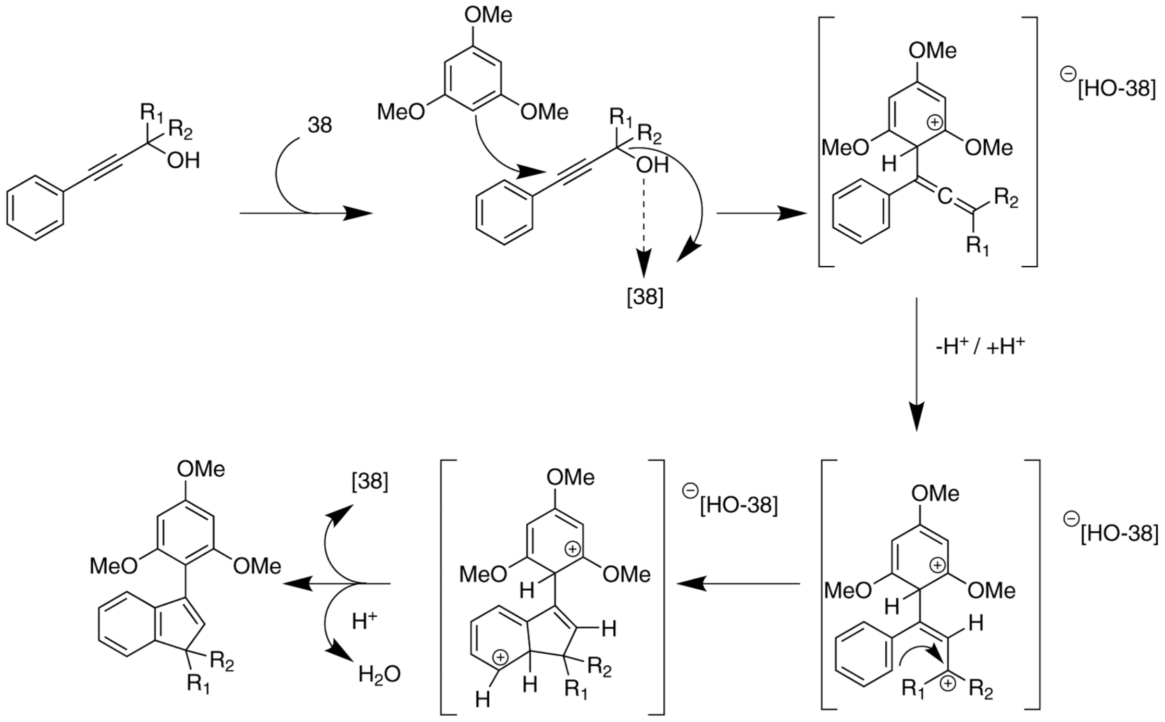


Fig. 49.

Plausible mechanism of indene formation reaction catalyzed by **38**.

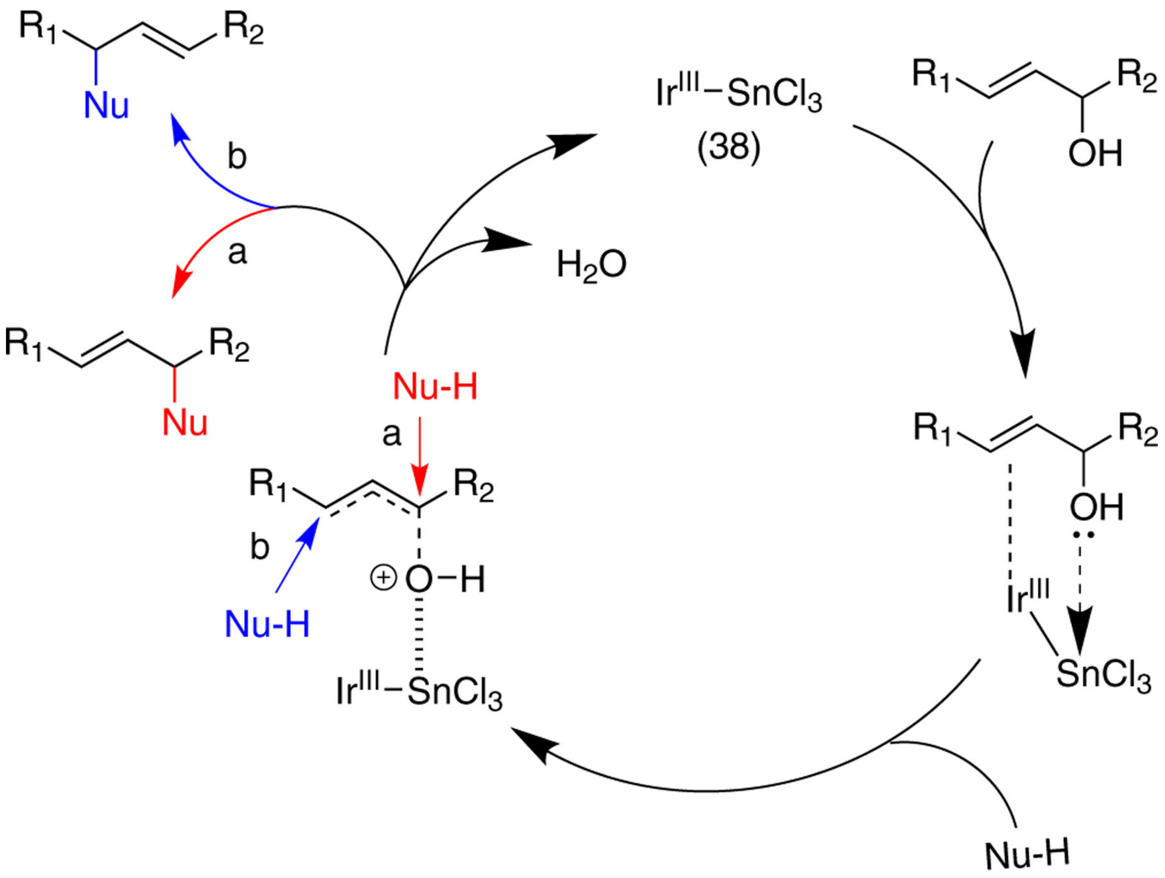


Fig. 50.

Plausible mechanism of the nucleophilic substitution of allylic alcohols catalyzed by **38**.

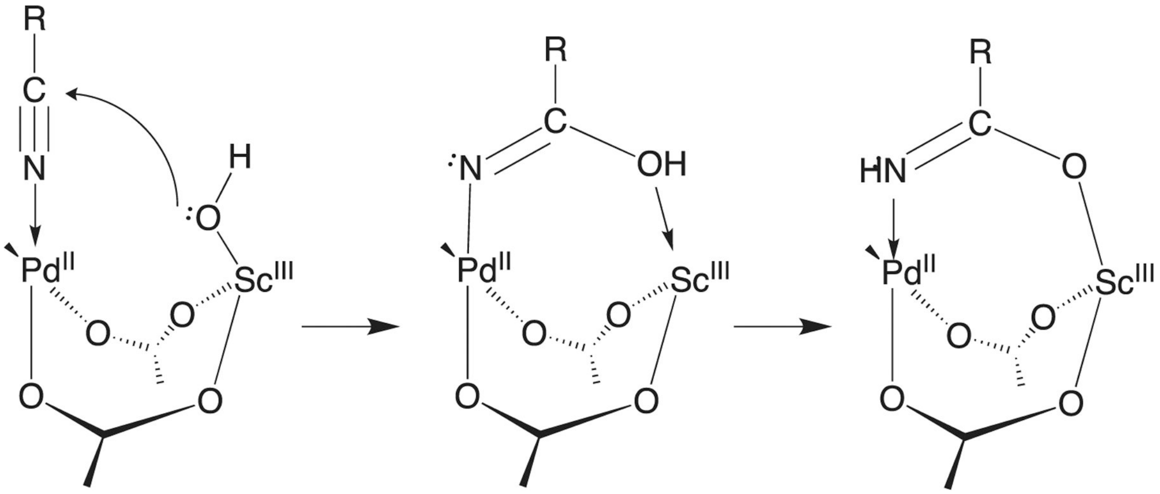


Fig. 51.
Proposed Pd-Sc heterobimetallic complex for nitrile hydration.

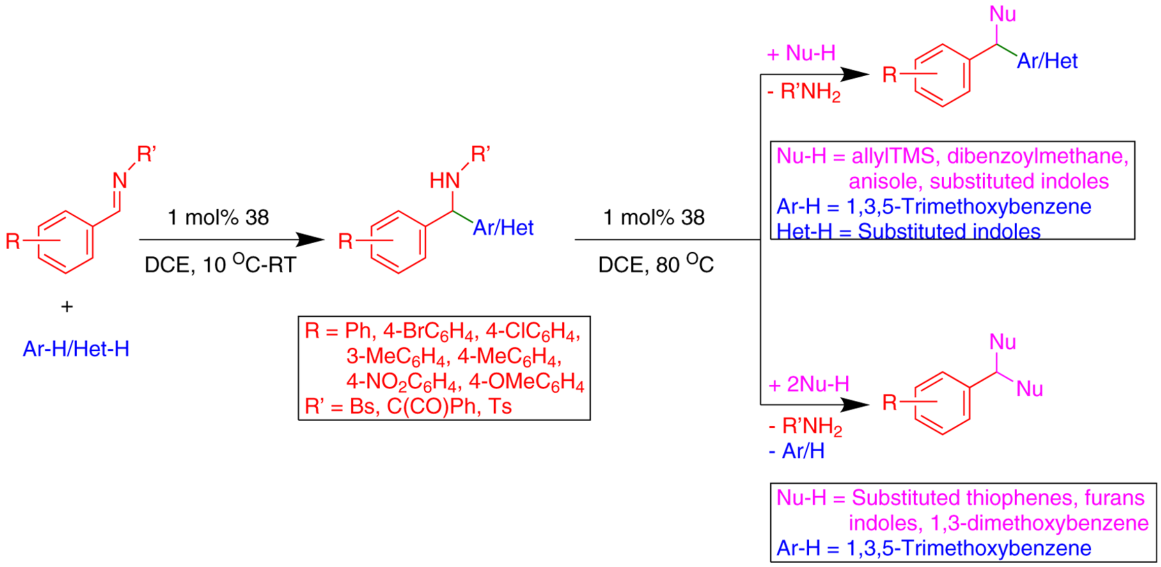
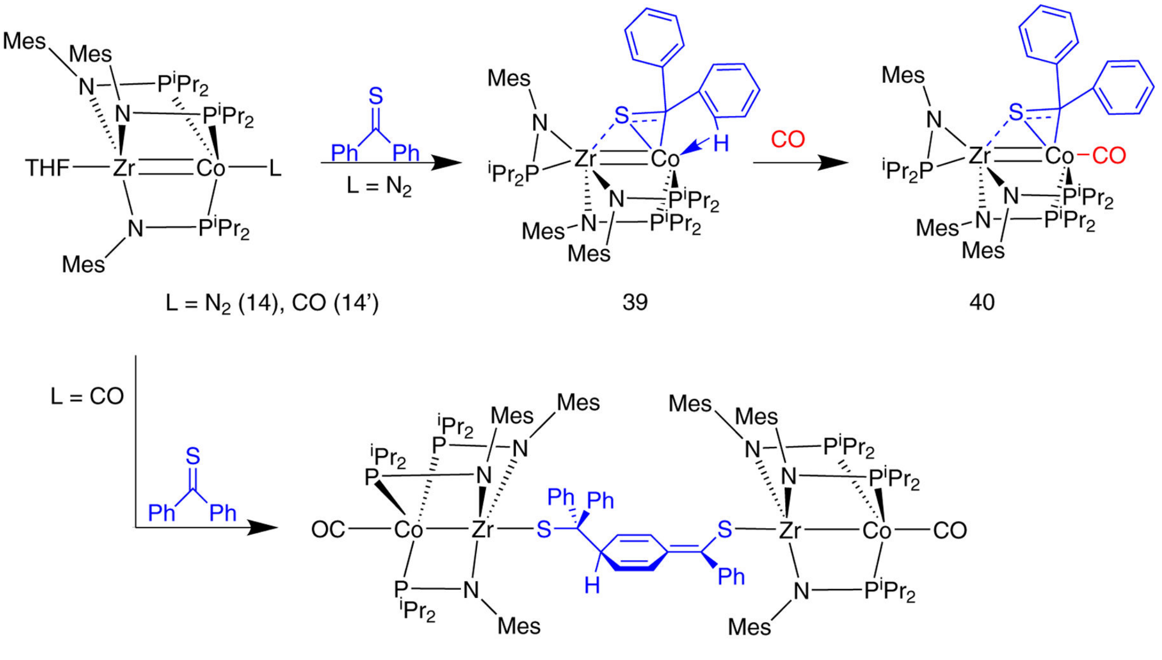


Fig. 52.

AFCR of indoles and 1,3,5-trimethyoxybenzene with N-sulfonyl aldimines catalyzed by **38**.



41

Fig. 53.

Reaction of **4** with thiobenzophenone compared to ketone.

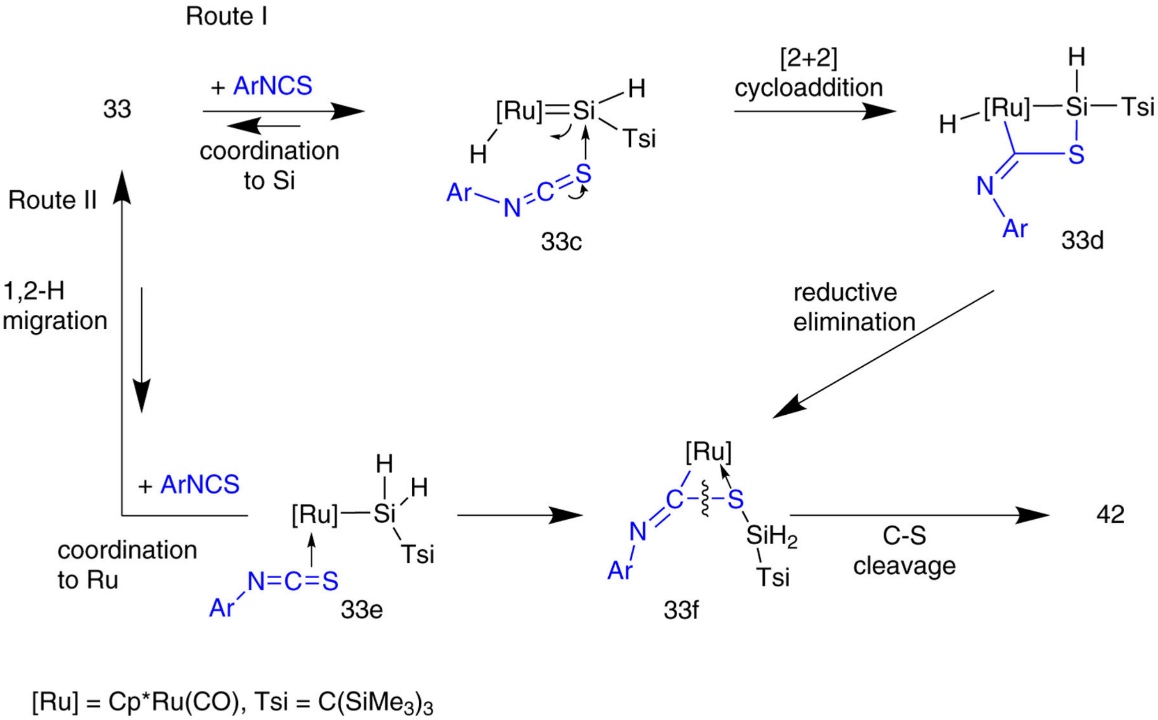


Fig. 54.

Two possible mechanisms for reaction of **33** with ArNCS.

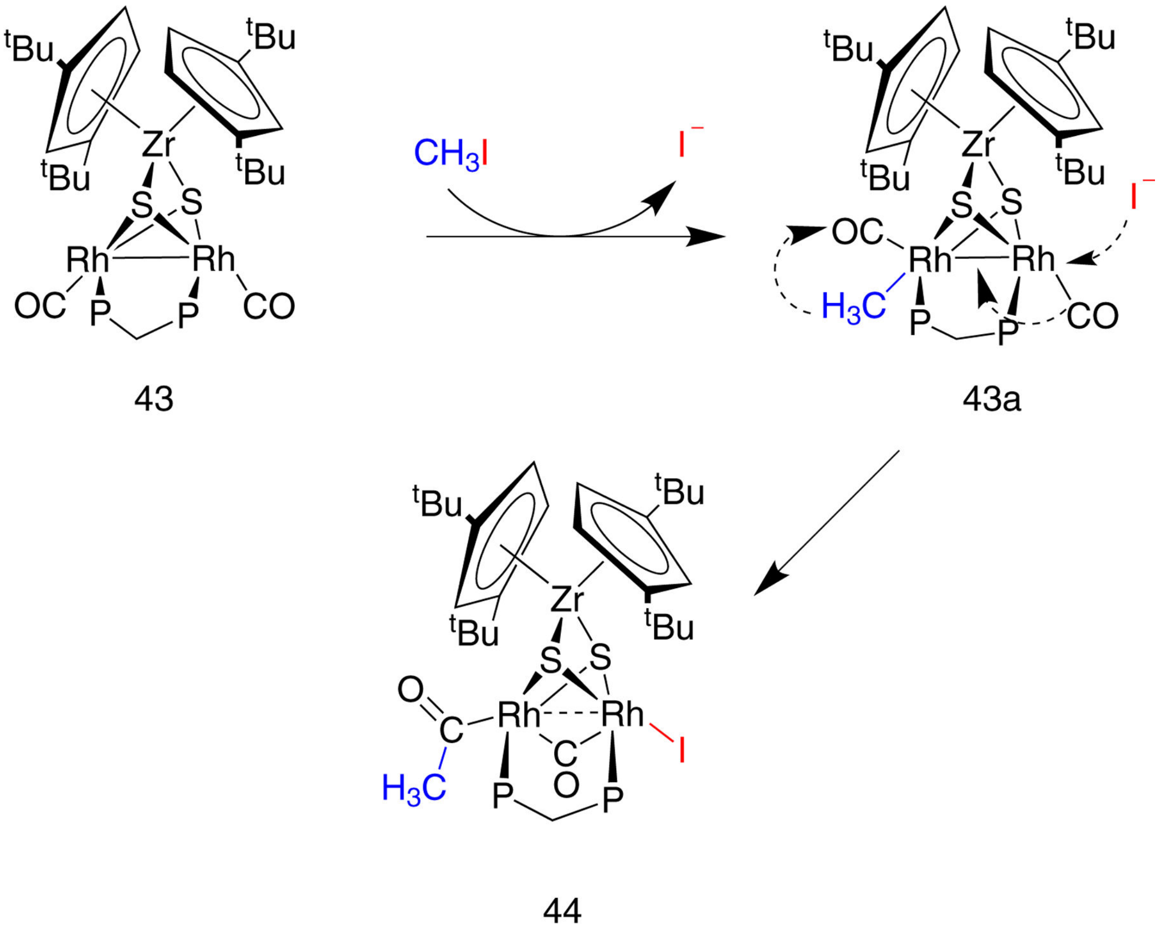
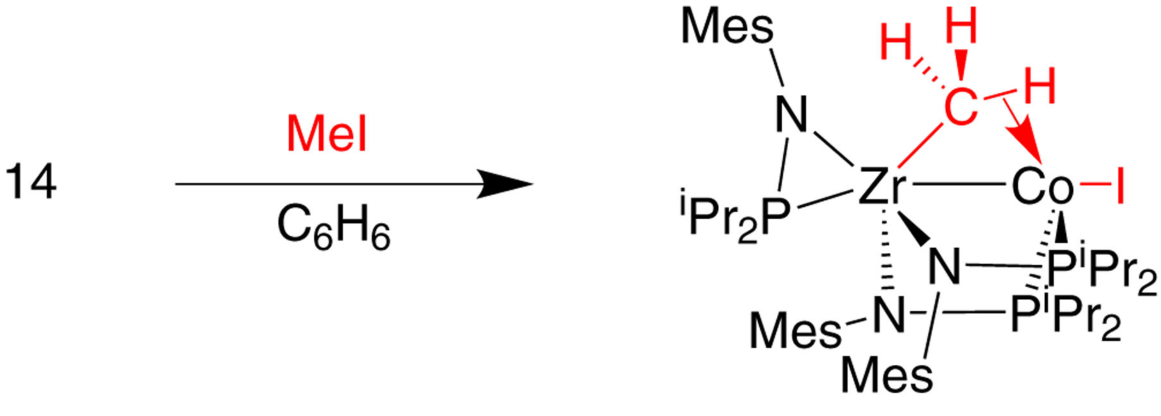


Fig. 55.
Proposed mechanism for synthesis of **44** via oxidative addition of MeI to **43**.



45

Fig. 56.
Oxidative addition of CH_3I by **14**.

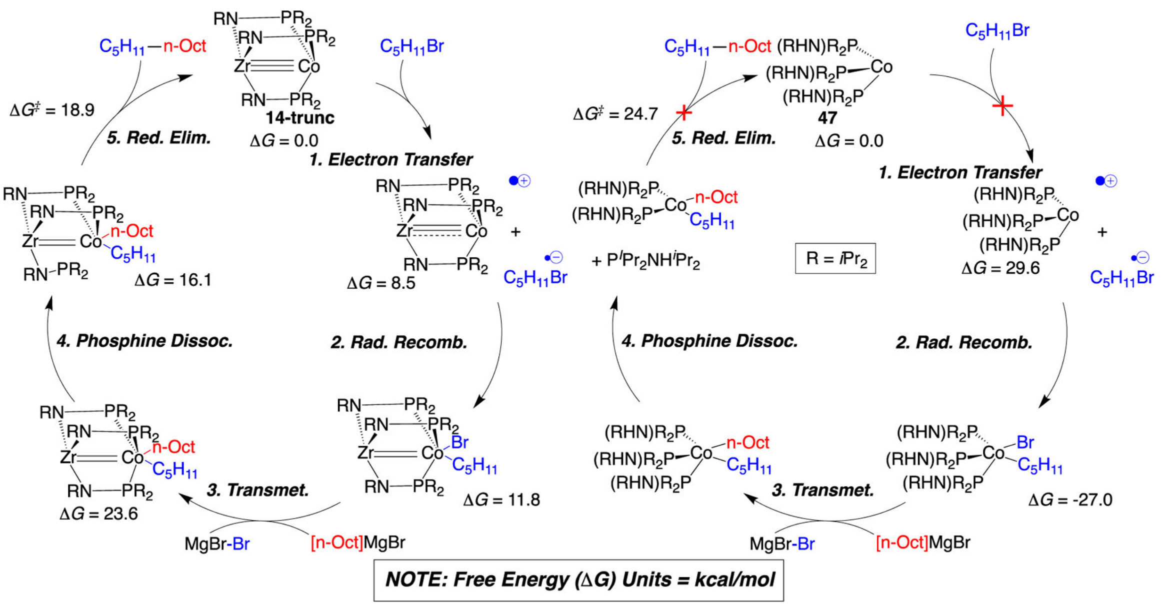
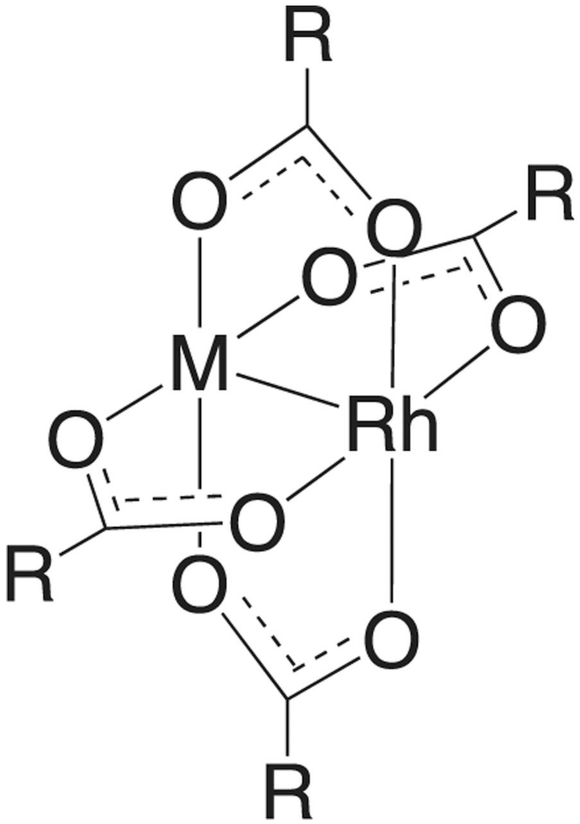


Fig. 57.

Proposed catalytic cycle of Kumada coupling reaction via **14-trunc** (left) compared to monometallic complex **47** (right); note that **14** was truncated in authors' calculations.



M = Bi (**48**)
Rh (**48’**)

Fig. 58.
Metal-Rh paddlewheel complexes **48** and **48′**.

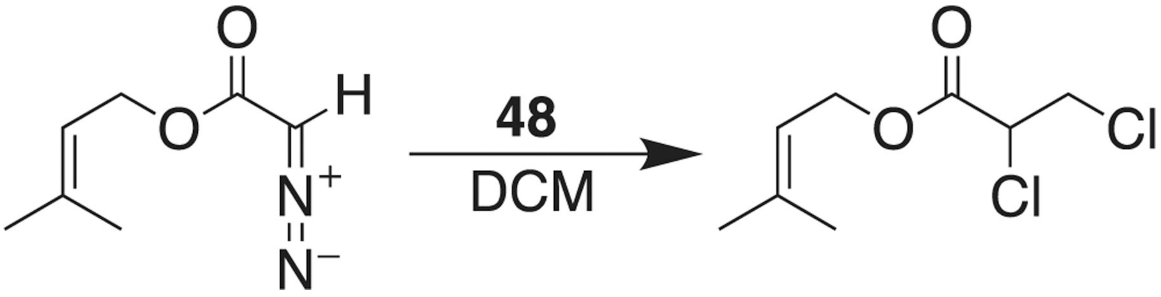


Fig. 59.

Carbene insertion into C–Cl bond catalyzed by **48**.

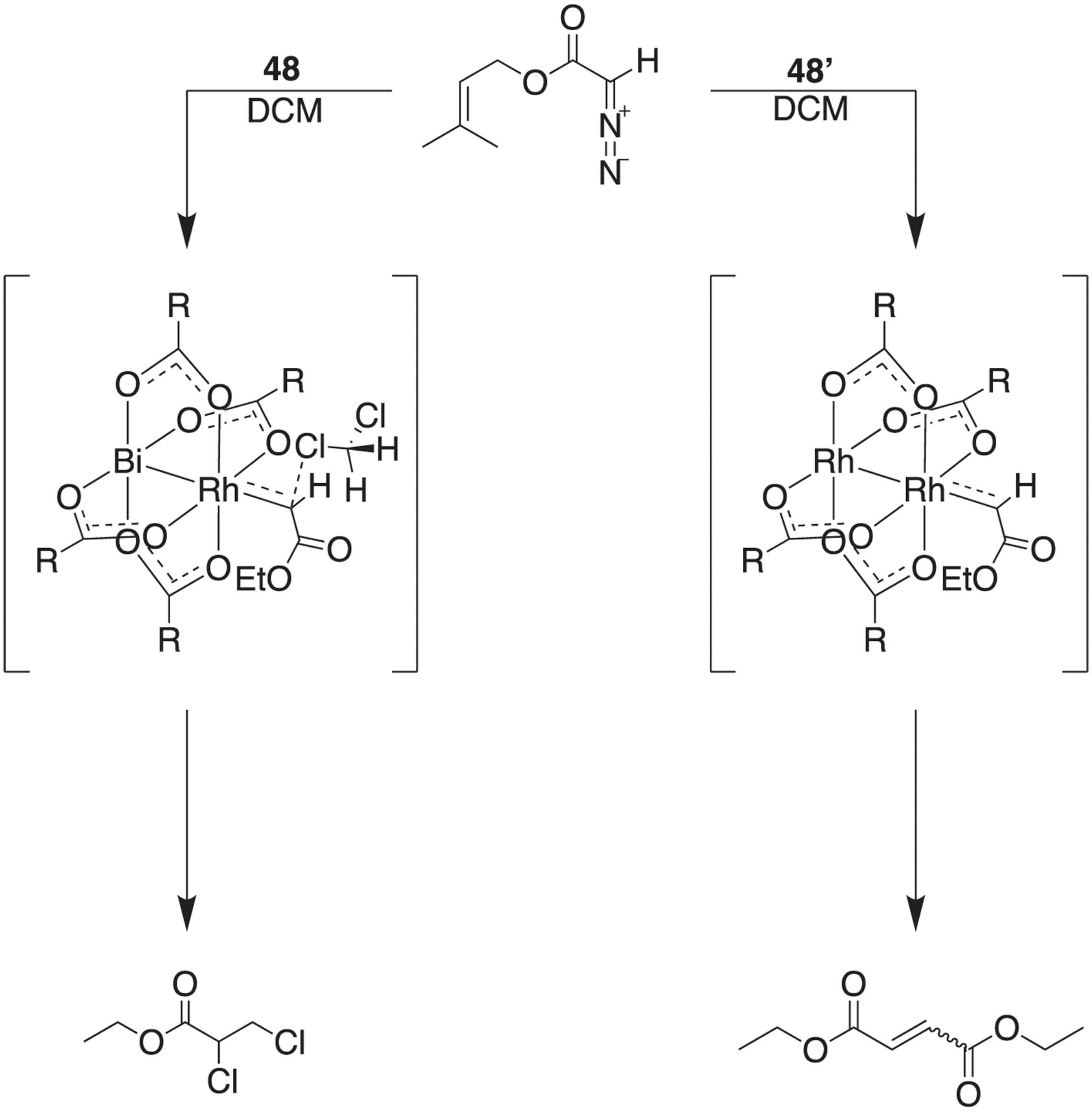


Fig. 60.

Decomposition of ethyl diazoacetate by **48** and **48′**.

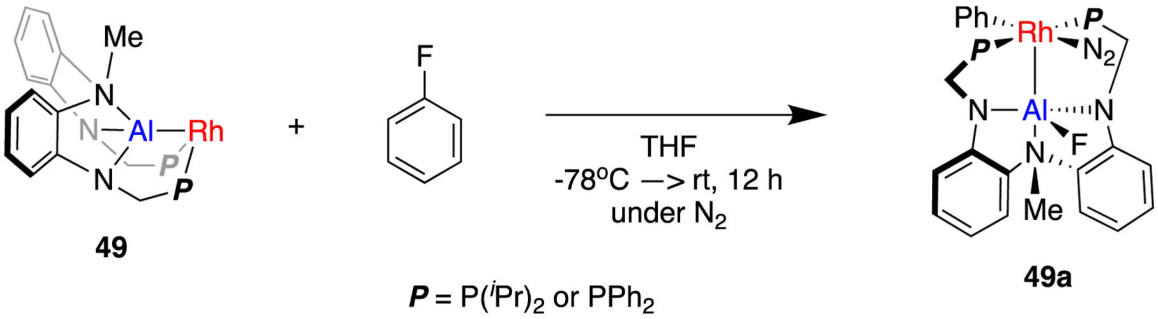


Fig. 61.

C–F bond activation by **49**.

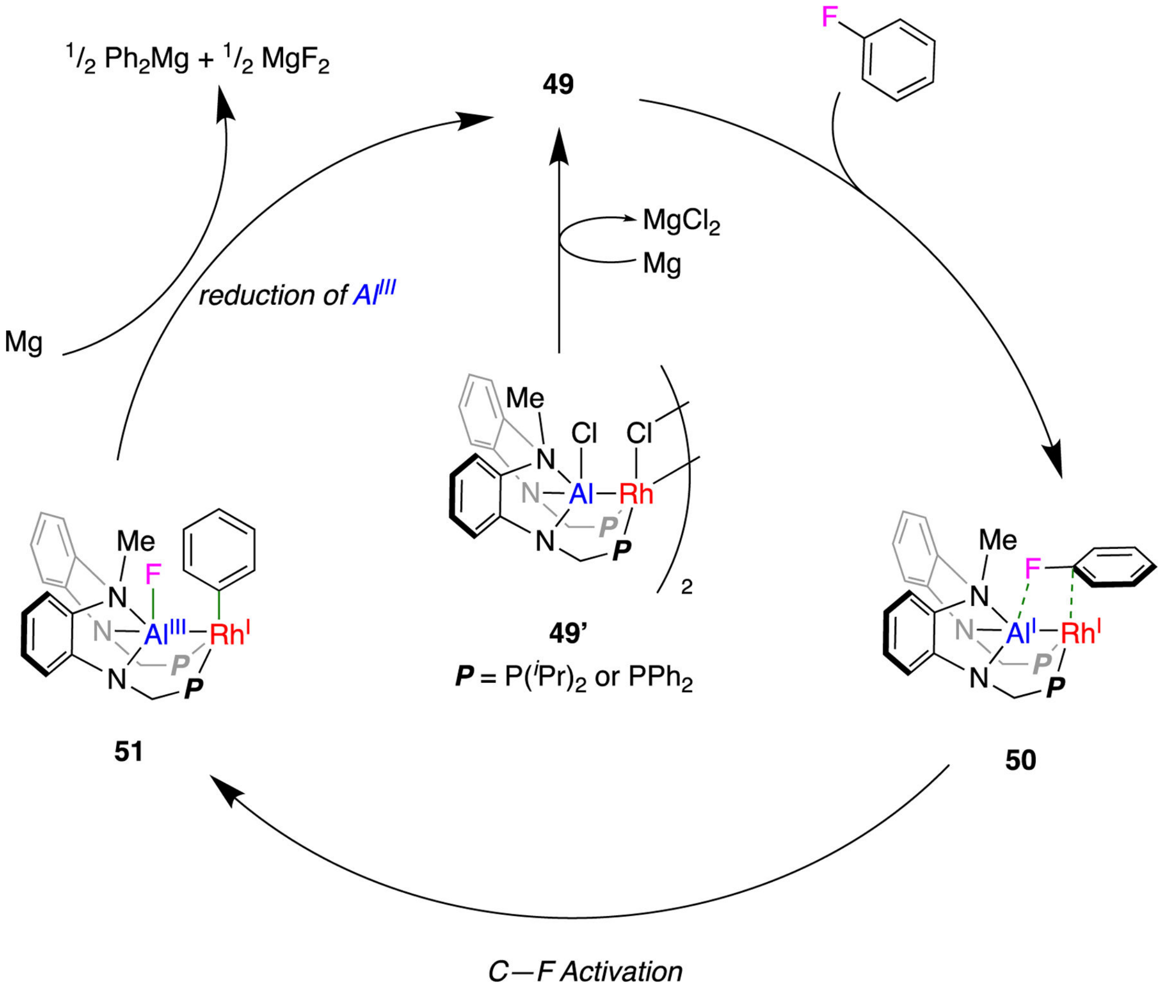


Fig. 62.

Proposed catalytic cycle for magnesiation of aryl fluorides by **49**.

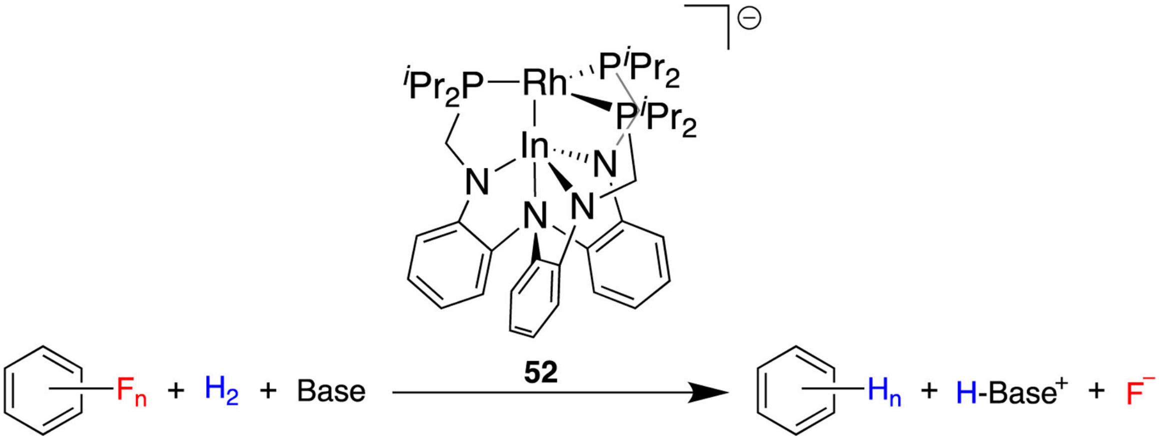


Fig. 63.

Overall hydrodefluorination reaction catalyzed by **52**.

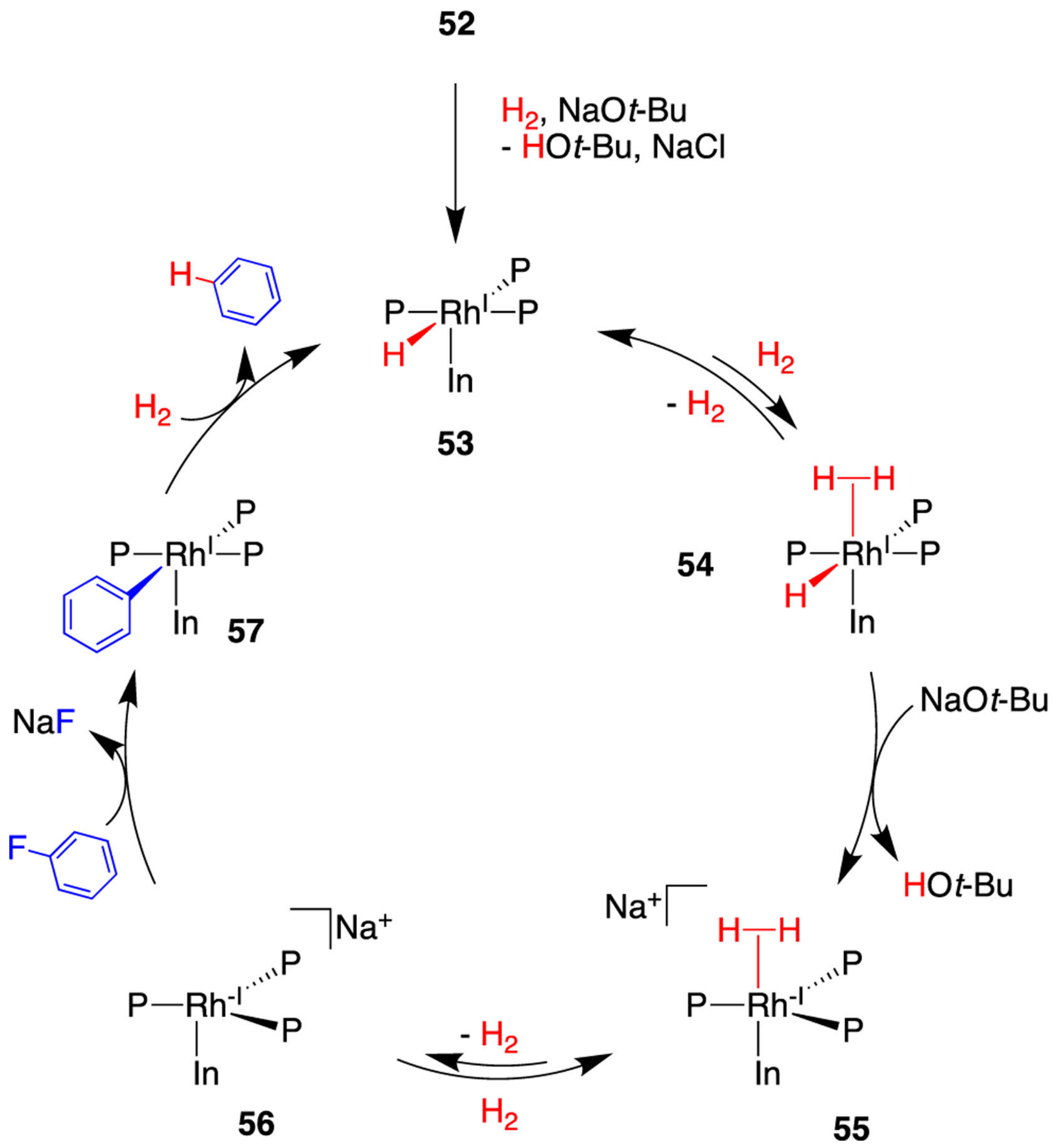
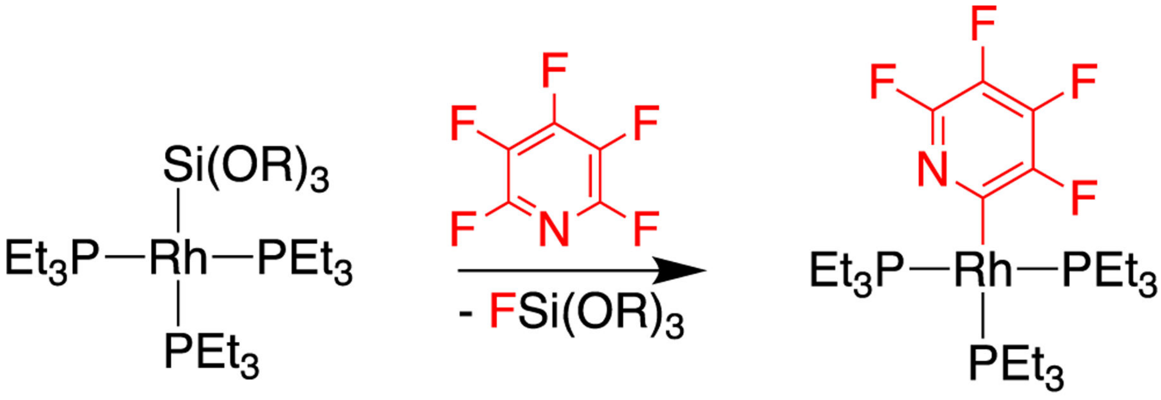


Fig. 64.

Proposed cycle for hydrodefluorination catalyzed by **52**; note, **52** is truncated in the cycle for clarity.



58a: R = Et
58b: R = Me

Fig. 65.

Overall C–F activation reaction of pentafluoropyridine facilitated by **58a**-**b**.

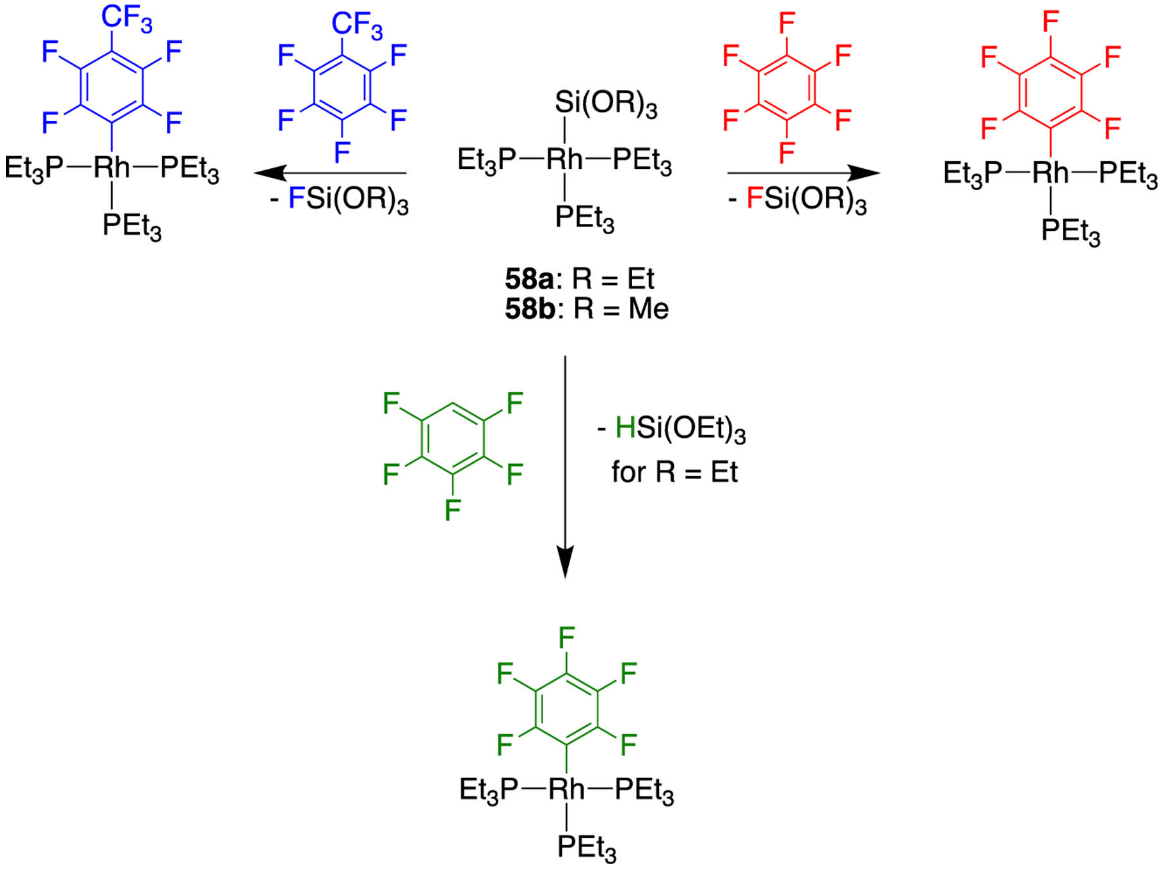


Fig. 66.

C–H and C–F activation of fluorinated aromatics facilitated by **58a**-**b**.

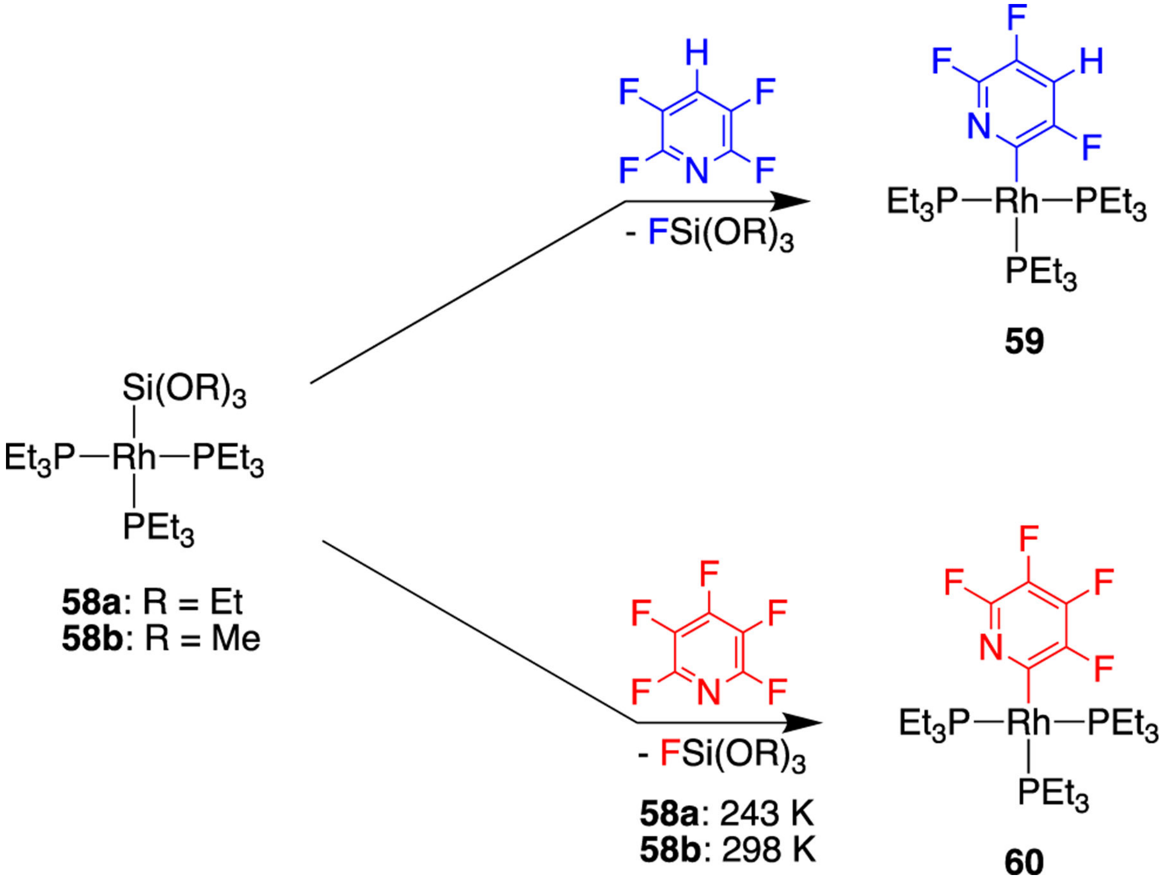


Fig. 67.
C–F activation of 2,3,5,6-tetrafluoropyridine and pentafluoropyridine facilitated by **58a**-**b**.

Table 1

Hydrogenation of styrene to ethylbenzene by **5**–**7**.[a]

Catalyst	**Yield (%)**[b]	**TOF (h^{-1})**[c]
5	12(5)[d]	0.10(4)
6	>99	2.4(1)
7	<1	0

[a] Catalytic conditions: 5 mol % precatalyst, 0.087 M olefin in ca. 700 μL of C_6D_6, 1 atm H_2, room temperature.

[b] Yields at 24 h for triplicate runs based on ^{1}H NMR or GC–MS analysis.

[c] Turnover frequencies obtained by ^{1}H NMR analysis at >90% product or after 24 h.

[d] Five runs.

Table 2

Substrate scope for olefin hydrogenation catalyzed by **6**.[a]

Substrate	**Yield (%)**[b]	**Time to > 90% Yield (h)**[b]
1-octene	>99	<1.5
1-hexene	>99	<2.75
styrene	>99	8
4-phenyl-1-butene	>99	10
cis-cyclooctene	93(3)	18
allyl butyl ether	68(16)	>116
trans-2-octene	10(2)	–
allylbenzene	3(2)	–

[a] Catalytic conditions: 5 mol % precatalyst, 0.087 M olefin in ca. 700 μL of C_6D_6, 1 atm H_2, room temperature.

[b] Yields at 24 h for triplicate runs based on ^1H NMR analysis. Hydrogenated product was exclusively formed.

Table 3

Hydrogenation of styrene to ethylbenzene mediated by **8–10.**[a]

Entry	Catalyst	T (°C)	% Conversion	Overall rate (h^{-1})
1	**8**	100	94(4)[c]	18.8(9)
2	**10**	100	24(3)[c]	4.7(2)
3	**8**	63	>99[d]	4.1(1)
4[b]	**9**	63	35(2)[d]	1.4(1)

[a] Catalytic conditions: 2.5 mol % catalyst, 0.37 M olefin in ca. 600 μL of d_8-toluene, 4 atm H_2. Conversion are based on triplicate runs using ^1H NMR integration.

[b] In ca. 600 μL of d_8-THF.

[c] t = 2 h.

[d] t = 10 h.

Table 4

Substrate scope for olefin hydrogenation for **8**.[a]

Entry	Substrate	% Conversion[b]	Time to > 90% Conversion (h)[b]
1	styrene	>99	2
2	1-octene	>99	<1
3	*cis*-cyclooctene	>99	1.5
4	allylbenzene	>99	2
5	*trans*-2-octene	68[c]	–
6	*trans*-4-octene	<1	–
7	*cis*-stilbene	>99 (93:7 *trans*:bibenzyl)	6
8	*trans*-stilbene	2 (bibenzyl product only)	–

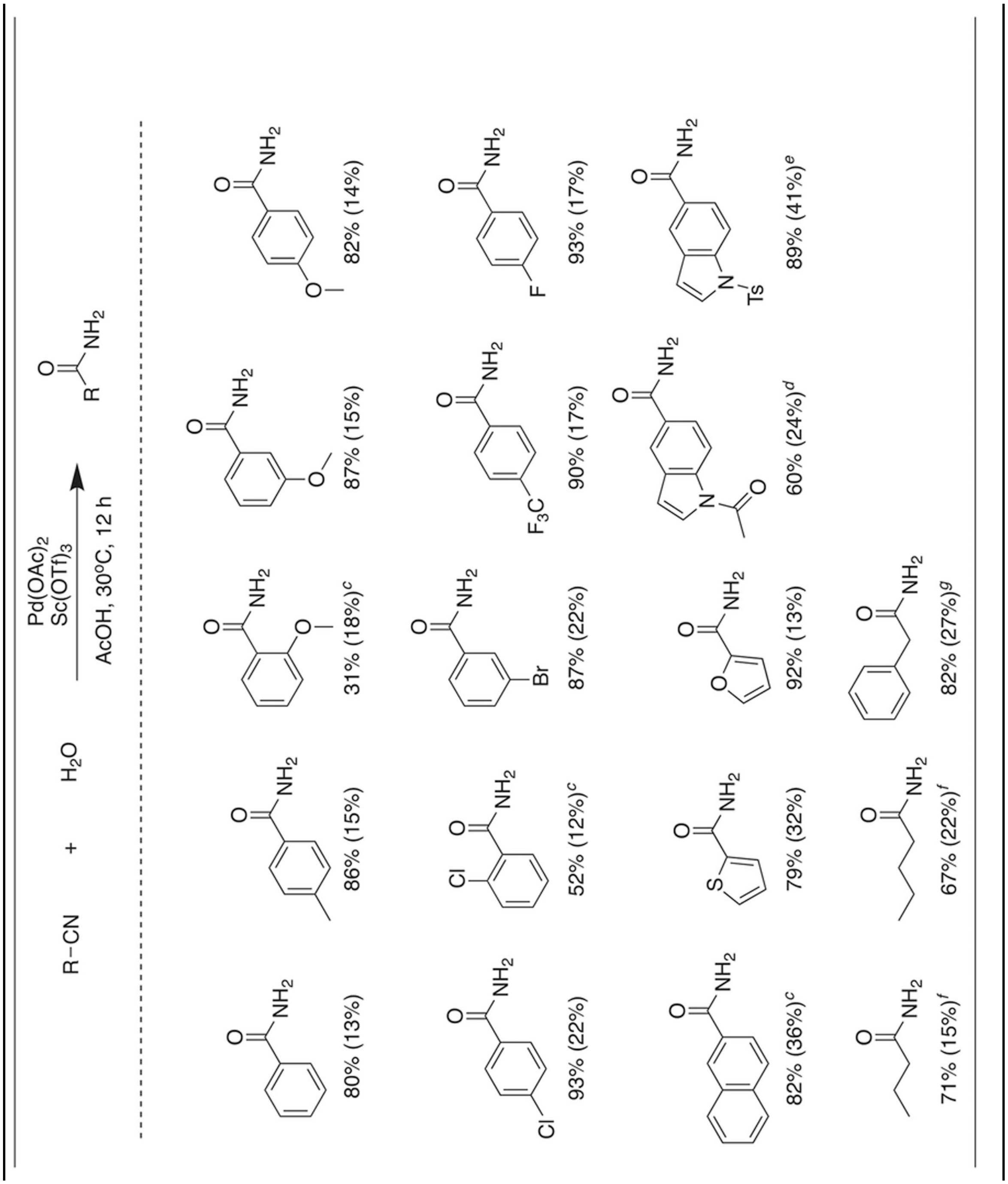
[a] See Table 3 for catalytic conditions.

[b] If > 90% conversion not reached reaction was stopped at 24 h.

[c] Trace isomerization products were observed.

Table 5

Substrate scope of Pd/Sc-catalyzed nitrile hydration reactions.[a,b]



[a] Reagents and conditions: R-CN (0.2 mmol), H_2O (0.4 mmol), $Pd(OAc)_2$ (1.5 mol%), $Sc(OTf)_3$ (3 mol%), AcOH (2 mL), 30 °C, 12 h.

[b] Isolated yields; values in parentheses were obtained in the absence of $Sc(OTf)_3$.

[c] At 50 °C for 36 h.

[d] 10 mol% $Pd(OAc)_2$ and 20 mol% $Sc(OTf)_3$ were used, 36 h.

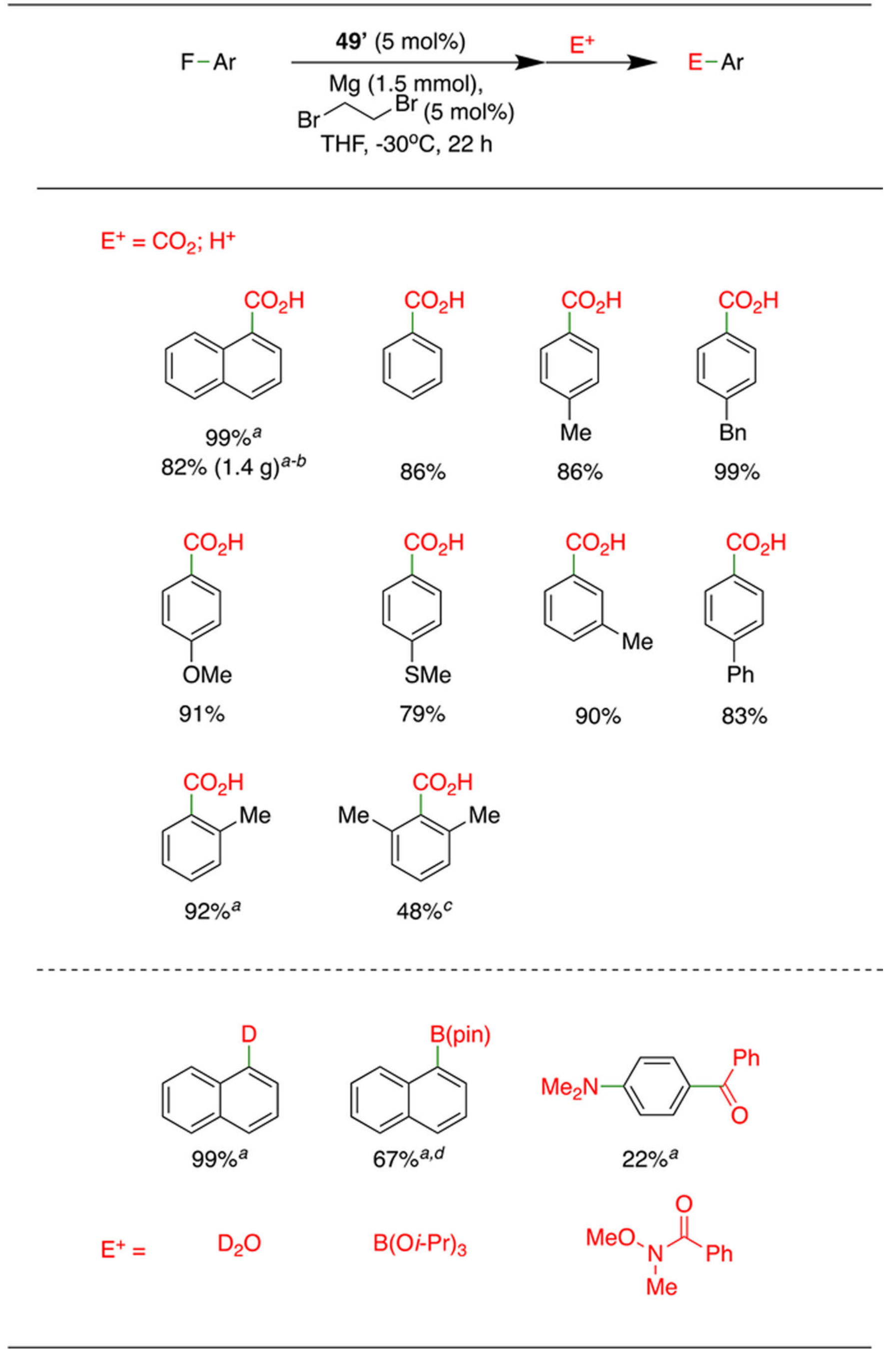
[e] 10 mol% $Pd(OAc)_2$ and 20 mol% $Sc(OTf)_3$ were used, 12 h.

[f] 5 mol% $Pd(OAc)_2$ and 10 mol% $Sc(OTf)_3$ were used in 3 mL of AcOH/H_2O (v/v, 2:1) at 70 °C, 12 h.

[g] 3 mol% $Pd(OAc)_2$ and 6 mol% $Sc(OTf)_3$ were used in 3 mL of AcOH/H_2O, (v/v, 2:1), 24 h.

Table 6

Substrate scope of Rh/Al-catalyzed aryl fluoride magnesiation reaction.



[a] Reaction was carried out at room temperature.

[b] Reaction was run on a 10 mmol scale.

[c] Reaction was carried out at 50 °C.

[d] The pinacol ester was isolated after reacting with pinacol; pin = pinacolato.

Table 7

Substrate scope for catalyst **52**[a].

Substrate	Mol % Cat.	Yield (%)[b]	Completion Time (h)
p-Cl,F-C_6H_4	1.78	**PhF**, 54.2 [97(1)] PhH, 1.9 [3(1)]	68
p-F,I-C_6H_4	6.30	**PhF**, 15.3 [91(1)] PhH, 1.6 [9(1)]	19
2,5-F_2-tolyl	3.13	***o*-F-C_6H_3Me**, 25.3 [75 (12)] *m*-F-C_6H_3Me, 0.6 [<1][e]	80
m-DFB[c]	7.93	PhF, 3.6 [29(6)] **PhH**, 9.0 [71(6)]	84
p-DFB[c]	3.90	**PhF**, 15.3 [65(5)] PhH, 2.3 [9(5)][e]	80
PhF[c,d]	7.74	PhH, 12.6 [98(1)]	114
p-F,I-CF_3-C_6H_4[d]	3.14	PhCF_3, 31.5 [99.2(3)]	43

[a] Catalytic conditions (unless otherwise specified): 1 atm H_2, 70 °C, 2.5 equiv NaOt-Bu, THF.

[b] Yields are based on averages of triplicate runs using ^{1}H NMR integration.

[c] 90 °C.

[d] 1.25 equiv NaOt-Bu.

[e] Remainder is unreacted substrate.

[f] Unidentified byproducts account for 2.7% (from ^{19}F NMR), and unreacted substrate accounts for remainder. Note, when multiple products form, the major product is in bold.