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## Carbonylation with 3d metal hydrides: expanding the potential for industrial applications

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Metal-hydride-mediated carbonylation toward value-added products has found broad applications in synthetic chemistry, materials science, pharmaceuticals, and industrial catalysis, exemplified by hydroformylation and Reppe-type carbonylation. However, most of these applications rely on highly active but precious metal catalysts. Therefore, the development of novel, practically useful, and inexpensive catalytic systems based on earth-abundant metals is highly desirable. On the other hand, olefin isomerization-carbonylation tandem processes can assist in converting mixed olefins into single products, which is of relevance to chemical industry applications. In this review, we summarize and discuss recent advances in abundant metal-hydride-mediated carbonylation and its isomerization-carbonylation tandem process (chain-walking carbonylation), with the aim of providing insights to researchers in both organic chemistry and industrial catalysis for future reaction design.

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### Broader context

Carbon monoxide based C1 chemistry has a significant influence on economics based on its origin and consumption. Over 80% of global acetic acid production was achieved by methanol carbonylation. And of course, hydroformylation is mediated by metal hydride. The produced products have found broad applications in synthetic chemistry, materials science, pharmaceuticals, and industrial catalysis. However, most of these applications rely on highly active but precious metal catalysts. Therefore, the development of novel, practically useful, and inexpensive catalytic systems based on earth-abundant metals is highly desirable. On the other hand, olefin isomerization-carbonylation tandem processes can assist in converting mixed olefins into single products, which is of relevance to chemical industry applications. In this review, we summarize and discuss recent advances in abundant metal-hydride-mediated carbonylation and its isomerization-carbonylation tandem process (chain-walking carbonylation), with the aim of providing insights to researchers in both organic chemistry and industrial catalysis for future reaction design.

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# 1. Introduction

Carbon monoxide, a cost-effective and accessible C1 source, has been central to industrial and energy chemistry for nearly a hundred years of continuous development.<sup>1–3</sup> The development of carbonylation chemistry has been closely intertwined with the evolution of industrial catalysis. As early as 1925, the Fischer–Tropsch process was established, enabling the conversion of coal or natural gas into synthesis gas (CO and H<sub>2</sub>) through the water–gas shift reaction. Employing transition-metal catalysts such as Fe, Co, Ni, and Ru, synthesis gas could be transformed into fuels and lubricants, representing one of the most important routes toward energy transition and clean fuel production.<sup>4</sup> In 1938, German chemist Otto Roelen discovered the formation of *n*-propionaldehyde during the Fischer–Tropsch reaction of ethylene over cobalt catalysts – marking the birth of the hydroformylation reaction.<sup>5</sup> Subsequently, in 1941, Walter Reppe developed the carbonylation of methanol, which proceeded under extremely harsh conditions (500–700 bar, 250–270 °C). After significant improvement by BASF, the cobalt-catalyzed methanol carbonylation was commercialized in 1960, representing the first industrial application of carbonylation chemistry.<sup>6</sup> A breakthrough came in 1967, when Monsanto developed a rhodium-catalyzed process for methanol carbonylation to acetic acid, operating under much milder conditions (180–220 °C, 30–40 bar) with excellent selectivity.<sup>7</sup> Building on Roelen's work, Geoffrey Wilkinson reported a rhodium-catalyzed hydroformylation process with remarkable activity and regioselectivity in 1968, firmly establishing the industrial significance of hydroformylation.<sup>8</sup> In 1996, BP Chemicals introduced the Cativa process, employing an iridium-based catalyst [Ir(CO)<sub>2</sub>I<sub>2</sub>]<sup>–</sup>, which surpassed the Monsanto process in both efficiency and environmental performance.<sup>9</sup> Later, in 2008, Mitsubishi Chemical developed a two-step process for methyl methacrylate (MMA) production

via ethylene carbonylation and subsequent condensation. This new route offered competitive economics and a significantly reduced environmental impact compared with the conventional acetone cyanohydrin (ACH) and isobutylene (C<sub>4</sub>) processes.<sup>10</sup> More recently, in 2019, the Beller group achieved the double carbonylation of 1,3-butadiene to directly produce dimethyl adipate, a key nylon-6,6 precursor, in a one-step, highly active, and selective catalytic system with strong potential for industrial application.<sup>11</sup> In 2023, the Liu group realized the industrial production of ethanol *via* dimethyl ether carbonylation, marking another milestone in the evolution of carbonylation chemistry (Scheme 1A).<sup>12</sup>

Among the diverse industrial applications of carbonylation chemistry, metal-hydride-mediated carbonylation reactions hold a particularly important position. A notable example is the rhodium-catalyzed hydroformylation reaction. The Oxo Alcohol Process, developed and commercialized by Johnson Matthey plc, utilizes a rhodium-based catalytic system to take hydroformylation efficiently of long-chain alkenes, representing a milestone in the large-scale application of carbonylation technology.<sup>13</sup> The ExxonMobil Oxo process employs rhodium-catalyzed hydroformylation to produce highly branched long-chain alcohols.<sup>14</sup> Ding and co-workers achieved a rhodium-catalyzed heterogeneous hydroformylation process through the utilization of porous organic ligands (POLs), providing an efficient and recyclable system for industrially relevant carbonylation reactions.<sup>15</sup> Cobalt-catalyzed systems, owing to their low cost and catalyst stability, continue to offer advantages in the production of high-carbon alcohols, as exemplified by industrial processes at BASF, Sasol, and Shell. Pd–H intermediates are employed in processes such as the Lucite Alpha process and the conversion of 1,3-butadiene toward Nylon 66. Notably, the Lucite Alpha process has achieved an annual production capacity of approximately 250 000 tons of MMA per year.<sup>10</sup> Another notable example of metal-hydride chemistry in industrial applications is isomerization–hydroformylation tandem reactions (known as chain-walking carbonylation). In industrial production, chemists and engineers aim to avoid generating mixtures of isomeric products. To achieve this, hydroformylation of mixed alkenes under appropriate reaction conditions can yield a single, well-defined product while suppressing isomer formation. This is particularly important because most industrial feedstocks or by-products contain internal alkenes; utilizing such mixed alkenes as starting materials, obtaining a single product is a highly desirable goal. The process is accomplished *via* isomerization of the double bond to a terminal alkenyl unit prior to hydroformylation, and the overall methodology is referred to as isomerization–hydroformylation (Scheme 1B2). The relevant industrial applications operate on a 10 000–100 000-ton scale.<sup>16</sup>

Although impressive progress has been achieved with noble metal catalysts in hydrocarbonylation, their high cost together with the even more expensive combined phosphine ligands making alternative, cheaper catalytic systems attractive. Among the candidates, 3d metals are meaningful due to their abundance and low toxicity. This idea has also been recognized by



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*(DICP) and established a group on light carbon transformation and practical synthesis. Xiao-Feng has authored >700 publications, edited >10 books and filed many patents. Xiao-Feng received several awards and was selected as a Fellow of the Royal Society of Chemistry (FRSC) in 2024.*

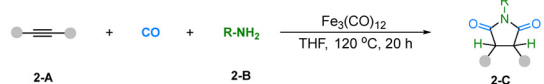




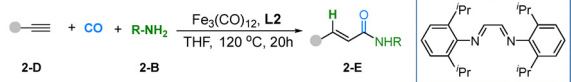
## 2. Carbonylation involving Fe–H species

metal with very low safety risks, allowing residual levels of iron in pharmaceuticals as high as 1300 ppm.<sup>22</sup> In recent years, iron-catalyzed carbonylation reactions have been actively developed, including the carbonylation of halides,<sup>23,24</sup> unsaturated compounds,<sup>25</sup> inert gases,<sup>26</sup> Suzuki-type carbonylative coupling,<sup>27</sup> and so on. Among these, Fe-H-mediated carbonylation transformations have been developed by the Beller group. For instance, in 2009, the Beller group reported the first example of an iron-catalyzed double carbonylation of alkynes with amines to afford succinimides with good functional-group tolerance, both aryl-, alkyl-, and internal alkynes reacted efficiently.<sup>28</sup> In 2011, Beller and co-workers further achieved the selective carbonylation of terminal alkynes to give linear  $\alpha,\beta$ -unsaturated amides.<sup>29</sup> The corresponding mechanism is illustrated in Scheme 2. Initially,  $\text{Fe}_3(\text{CO})_{12}$  reacts with amines to generate Fe-H species **2a**. Hydride species **2a** undergoes hydroironation of the alkyne to afford intermediate **2b**, which subsequently captures carbon monoxide to form the acyl intermediate **2c**. Upon nucleophilic attack by the amine, the mono-carbonylated product **2-e** is obtained. A second Fe-H addition to the alkyne furnishes intermediate **2d**, which then undergoes intramolecular cyclization to form **2e**. Following CO coordination and migratory insertion, the acyl intermediate **2f** is generated. Finally, reductive elimination from **2f** delivers the double carbonylation product **2-C**.

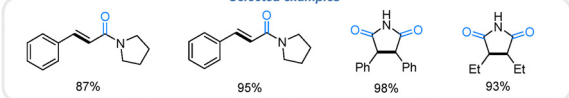
2009, Beller



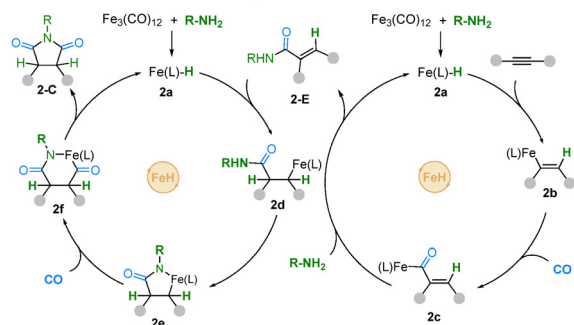
2011, Beller



Selected examples



Proposed Mechanism



Scheme 2 Iron-catalyzed carbonylation of alkynes and amines.

### 3. Carbonylation involving Co–H species

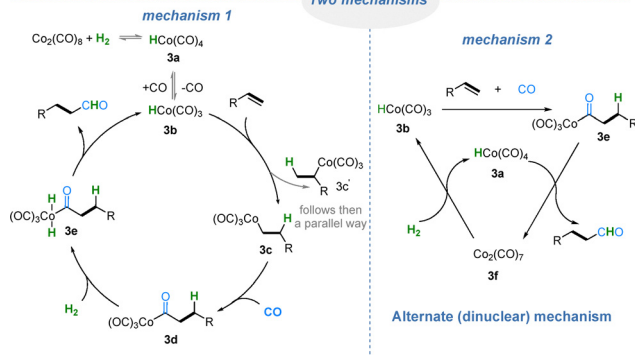
CoH-mediated carbonylation was first exemplified in hydroformylation reactions.<sup>30</sup> In this process, molecular hydrogen serves as the hydrogen source. Cobalt-catalyzed hydroformylation typically affords a mixture of linear and branched aldehydes, and compared to rhodium-catalyzed systems, selectivity control is more challenging, primarily because cobalt catalysts exhibit lower sensitivity toward ligand modification.<sup>31</sup> As illustrated in Scheme 3, the cobalt hydride species  $[\text{Co}(\text{H})(\text{CO})_4]$  and  $[\text{Co}(\text{H})(\text{CO})_3]$  are recognized as key reactive intermediates. Two main mechanistic pathways have been proposed. In the first mechanism,  $\text{Co}_2(\text{CO})_8$  reacts with  $\text{H}_2$  to generate intermediate **3a**, which can lose one ligand of CO to form **3b**. Subsequent olefin coordination and insertion afford **3c**, followed by CO migratory insertion to generate **3d**. Addition of hydrogen to **3d** yields **3e**, which then undergoes reductive elimination to produce the corresponding aldehyde. The second mechanism involves an alternating (binuclear) pathway, in which, under stoichiometric cobalt conditions,  $[\text{Co}(\text{H})(\text{CO})_4]$  (**3a**) directly reacts with the acyl intermediate **3e** to form the aldehyde product and  $[\text{Co}_2(\text{CO})_7]$ . The latter unsaturated dimer can coordinate with  $\text{H}_2$ , regenerating the two cobalt hydride species  $[\text{Co}(\text{H})(\text{CO})_4]$  and  $[\text{Co}(\text{H})(\text{CO})_3]$ . However, this binuclear pathway is generally operative only at high cobalt concentrations in the catalytic solution.<sup>31</sup>

In 2017, the Alexanian group reported a cobalt-catalyzed silylcarbonylation of secondary alkyl tosylates under mild

Hydroformylation by Co-catalysis



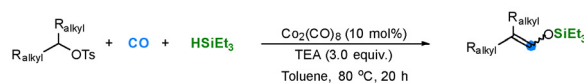
Two mechanisms



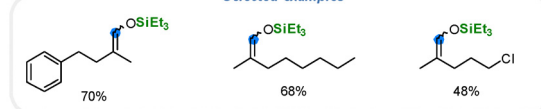
Scheme 3 Cobalt-catalyzed hydroformylation of alkenes.

conditions (Scheme 4).<sup>32</sup> As illustrated in Scheme 4, the reaction begins with a nucleophilic substitution of the alkyl tosylate by the tetracarbonylcobalt anion,  $\text{Co}(\text{CO})_4^-$  (intermediate **4a**), to generate an alkyl-cobalt species. Insertion of carbon monoxide then furnishes the acyl cobalt intermediate **4b**. Subsequently, oxidative addition of triethylsilane ( $\text{Et}_3\text{SiH}$ ) to **4b** produces intermediate **4c**, which undergoes 1,3-silyl migration to form the cobalt-carbene intermediate **4d**. A following 1,2-hydride shift yields intermediate **4e**, and finally,  $\beta$ -hydride

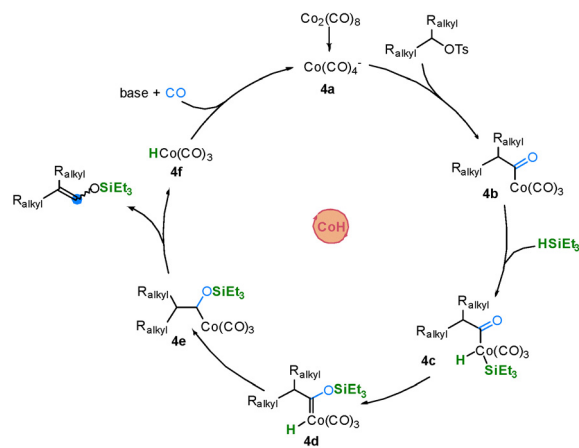
2017, Alexanian



Selected examples



Proposed Mechanism



Scheme 4 Diverse types of single-electron reduction processes of organic halides.



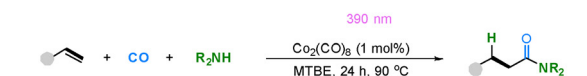
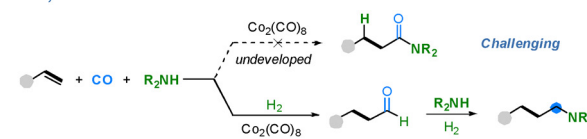


elimination affords the silyl enol ether product along with regeneration of the cobalt species **4f**. The reaction performs poorly with primary alkyl tosylates, likely because less substituted alkyl-cobalt intermediates undergo  $\beta$ -hydride elimination at a significantly slower rate, thus reducing the overall efficiency of the transformation.

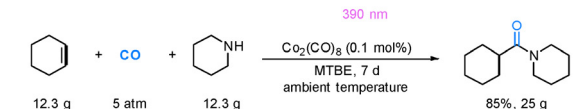
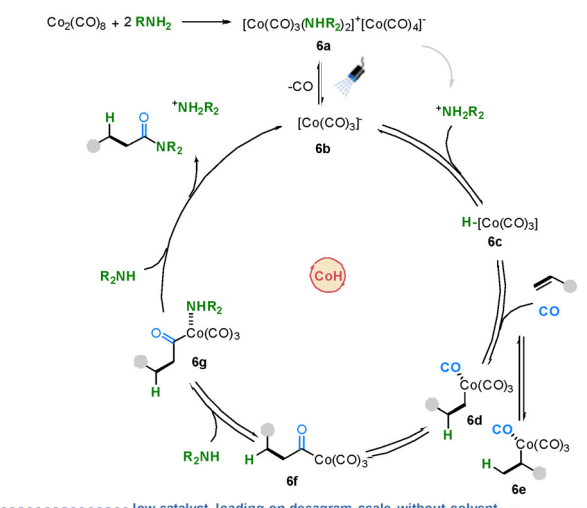
In 2023, Wu and co-workers reported the cobalt-catalyzed hydroxymethylation of alkyl halides by using PMHS as the H source.<sup>33</sup> The proposed reaction mechanism is depicted in Scheme 5. Initially, cobalt(i) species **5a** undergoes single-electron transfer (SET) to the alkyl iodide, generating an alkyl radical and the cobalt(II) intermediate **5b**. In the presence of  $\text{Et}_3\text{SiH}$  and CO, the alkyl radical is trapped by CO to afford an acyl radical, which then associates with the cobalt center to form intermediate **5c**. Subsequent radical recombination produces the acyl-cobalt intermediate **5d**, which undergoes reductive elimination to deliver the corresponding aldehyde and regenerate the active Co(i) catalyst (**5a**). Finally, the aldehyde is reduced by the Cu-H species to furnish the alcohol product bearing one additional  $-\text{CH}_2$  moiety.

In 2024, the Alexanian group reported the light-promoted cobalt-catalyzed carbonylation of alkenes and amines toward amides, representing a significant breakthrough in the field.<sup>34</sup> Since the discovery of the cobalt-catalyzed hydroformylation reaction in 1938 and Otto Reppe's development of  $\text{Ni}(\text{CO})_4$ -mediated acetylene carbonylation (Reppe carbonylation) in the 1930s, Pd-H-mediated carbonylation has been extensively explored and well-established.<sup>35</sup> However, CoH-mediated Reppe-type carbonylation had not been realized due to several intrinsic challenges: the relatively low activity of cobalt catalysts, the difficulty in controlling alkene selectivity through ligands, and the strong influence of Lewis-basic amines on the catalyst's reactivity. To address these challenges, Alexanian and co-workers developed a Reppe-type carbonylation with the

2024, Alexanian

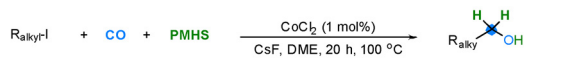


Proposed Mechanism

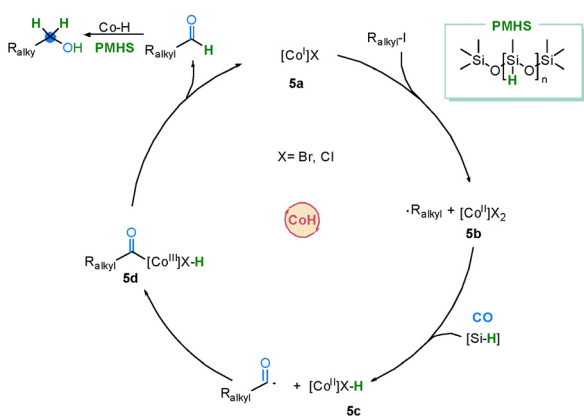


Scheme 6 Cobalt-catalyzed Reppe-type carbonylation of amines promoted by light.

2023, Wu



Proposed Mechanism



Scheme 5 Cobalt-catalyzed carbonylation of alkyl halides.

combination of photochemistry, and thus the long-standing limitations of Co-H-mediated systems were effectively overcome. As illustrated in Scheme 6, complex **6a** is formed by the reaction of  $\text{Co}_2(\text{CO})_8$  with an amine. Under irradiation with 390 nm LED light, one CO ligand dissociates to generate the active cobalt species **6b**,  $[\text{Co}(\text{CO})_3]^-$ . Subsequent protonation of **6b** affords intermediate **6c**  $\text{HCo}(\text{CO})_3$ , which undergoes hydrocobaltation with the alkene to form linear and branched intermediates (**6d** and **6e**, respectively; **6d** being the major species). Coordination and migratory insertion of CO then lead to intermediate **6f**. Nucleophilic coordination of the amine to the cobalt center produces **6g**, which undergoes concerted addition and reductive elimination to afford the amide product along with regeneration of **6b**,  $[\text{Co}(\text{CO})_3]^-$ , thereby completing the catalytic cycle.

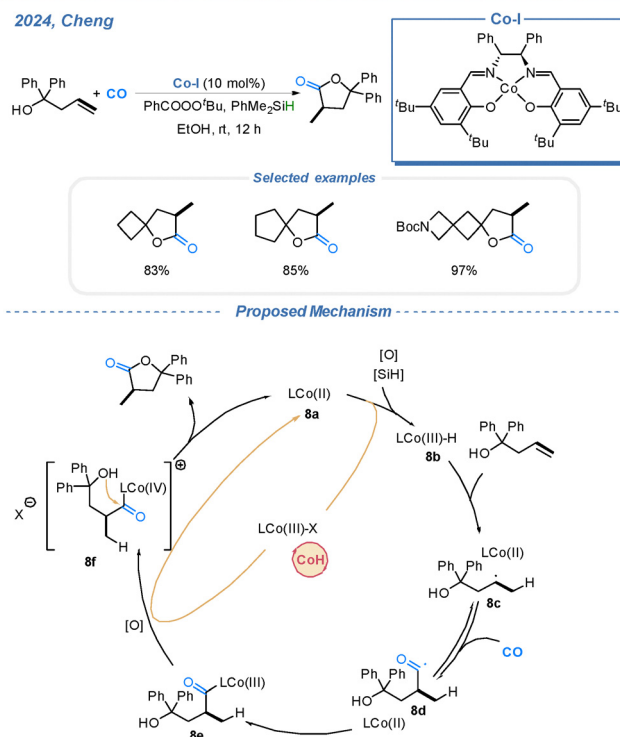
In this hydroaminocarbonylation reaction, a high quantum yield ( $\Phi = 15.7$ ) was observed, indicating that after the initial photolytic CO dissociation, the catalytic cycle can proceed through multiple turnovers without the need for further photoexcitation. This efficient catalytic turnover is likely attributed to



the rapid protonation of  $[\text{Co}(\text{CO})_3]^-$  under low CO pressure, which outcompetes CO re-coordination and thereby facilitates the formation of the stable cobalt hydride intermediate **6c**  $\text{HCo}(\text{CO})_3$ . Notably, this hydride species **6c** exhibits remarkable tolerance toward Lewis-basic amines and remains catalytically competent for alkene coordination and activation, enabling the reaction to proceed efficiently under mild conditions.

In 2025, the Alexanian group further extended their cobalt hydride catalytic system to achieve a hydroesterification reaction, representing the Reppe-type carbonylation of alcohols.<sup>36</sup> As illustrated in Scheme 7, intermediate **7a** is generated from the reaction of  $\text{Co}_2(\text{CO})_8$  with a nucleophile under irradiation with 390 nm LED light. In the presence of triethylamine sulfonate, the cobalt hydride species **7b** is formed. Subsequently, **7b** coordinates to the alkene, producing intermediate **7c**, which can evolve into either the linear or branched cobalt intermediates (**7d** or **7c'**), with the linear intermediate **7d** being predominant. Under the promotion of DMAP, **7d** is converted into an acyl-DMAP salt intermediate **7e**. Finally, nucleophilic attack by an alcohol affords the desired ester product, while regenerating **7a** to complete the catalytic cycle.

In 2024, the Cheng group developed the cobalt-catalyzed intramolecular Markovnikov hydrocarbonylation of unactivated alkenes.<sup>37</sup> In this reaction, mechanistic investigations revealed that the transformation proceeds *via* a CO-mediated hydrogen atom transfer (HAT) and radical-polar crossover (RPC) process, in which an acyl-Co(IV) complex serves as the key intermediate. As illustrated in Scheme 8, the reaction begins with the formation of cobalt hydride species **8b** from Co(II) precursor **8a** in the presence of an oxidant and a silane. The Co-H species then adds to the alkene, generating radical intermediate **8c**

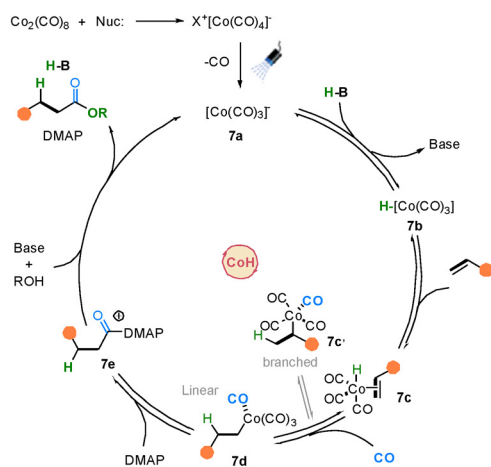
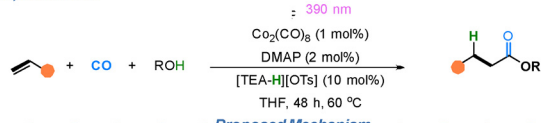


Scheme 8 Cobalt-catalyzed intramolecular Markovnikov hydrocarbonylation of alkenes.

along with a Co(II) species. Under a CO atmosphere, the resulting radical captures CO to form acyl radical **8d**. Subsequent radical-polar crossover process between the acyl radical and Co(II) affords the acyl-Co(III) intermediate **8e**. Intermediate **8e** undergoes oxidation or disproportionation to yield the crucial acyl-Co(IV) species **8f**, which then undergoes reductive elimination to furnish the desired lactone products while regenerating the Co(II) catalyst, thereby completing the catalytic cycle (Scheme 8).

In 2025, the Cheng group developed a Co-H-mediated hydroaryloxy carbonylation of unactivated alkenes, enabling remote aryl migration.<sup>38</sup> Mechanistic studies revealed that the acyl radical species is generated under a CO atmosphere *via* a hydrogen atom transfer (HAT) process. The driving force for the aryl migration arises from the formation of a thermodynamically favourable five-membered cyclic transition state. The detailed reaction mechanism is illustrated in Scheme 9. Initially, Co(II) species **9a** reacts with an oxidant and a silane to generate the Co(III)-H species **9b** and a Co(III) complex. The Co(III)-H species then undergoes a hydrogen atom transfer process to the alkene, producing the alkyl radical intermediate **9c**. Under a CO atmosphere, this alkyl radical is readily trapped by CO to form the acyl radical **9d**. Owing to the thermodynamic stability of the five-membered cyclic transition state, **9d** readily undergoes intramolecular cyclization to afford intermediate **9e**. Subsequently, aryl migration occurs *via* homolytic C-C bond cleavage, generating a more stable hydroxyalkyl radical intermediate, **9f**. This radical then reacts with Co(II) species to form

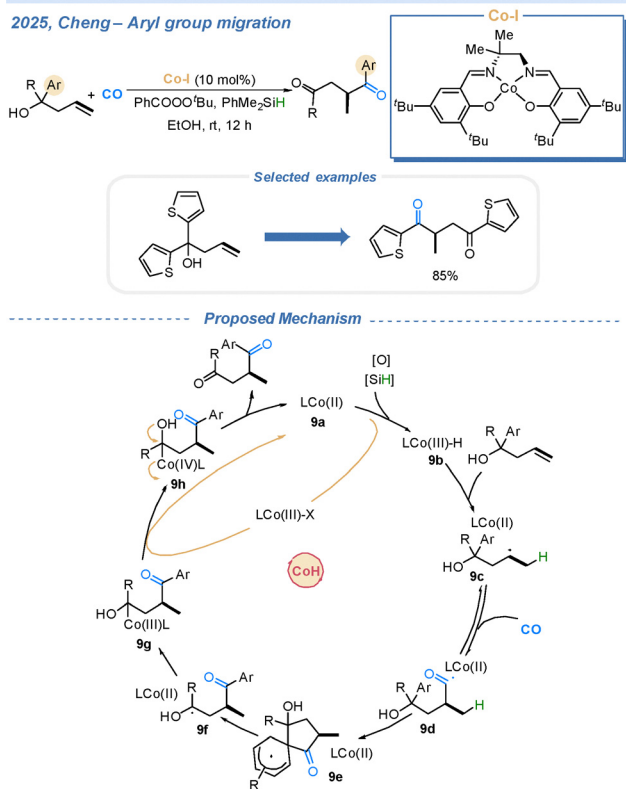
2025, Alexanian



Scheme 7 Cobalt-catalyzed anti-Markovnikov carbonylation of alcohols promoted by light.



## 2025, Cheng – Aryl group migration



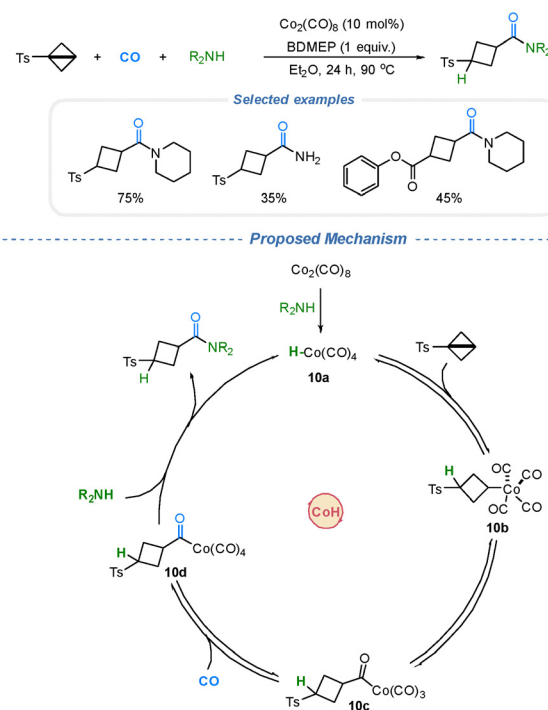
Scheme 9 Cobalt-catalyzed Markovnikov hydroarylcobonylation of alkenes via distal aryl migration.

a Co(III) complex **9g**. Finally, **9g** is oxidized by either the Co(III) complex or an external oxidant to yield a highly electrophilic Co(IV) intermediate **9h**, which undergoes reductive elimination to deliver the aryl migration product while regenerating Co(II) **9a**, completing the catalytic cycle. Alternatively, the hydroxyalkyl radical **9f** may be directly oxidized by the Co(III) complex or oxidant, followed by deprotonation to furnish the product and regenerate Co(II) catalyst **9a**.

In 2025, the Wu group reported the Co–H-mediated hydroamination of bicyclo[1.1.0]butanes (BCBs) with aliphatic amines.<sup>39</sup> As illustrated in Scheme 10, the HCo(CO)<sub>4</sub> intermediate is first generated *via* a disproportionation reaction between Co<sub>2</sub>(CO)<sub>8</sub> and the amine. The HCo(CO)<sub>4</sub> species then inserts into the C–C bond of the BCB, forming intermediate **10b**. Subsequently, migratory insertion of a CO ligand occurs to produce intermediate **10c**. This step is reversible, and applying higher CO pressure drives the equilibrium toward the formation of **10c**. Under a CO atmosphere, **10c** coordinates an additional CO molecule to regenerate the tetracarbonyl cobalt complex **10d**. Finally, nucleophilic attack by the amine on the carbonyl group affords the desired product, while regenerating the HCo(CO)<sub>4</sub> species **10a**, thereby completing the catalytic cycle.

In 2025, the Wu group developed the photoredox-cobalt co-catalyzed Markovnikov-selective hydrocarboxylation of unactivated alkenes under blue-light irradiation.<sup>40</sup> As illustrated in Scheme 11, upon exposure to blue light, the photocatalyst (PC)

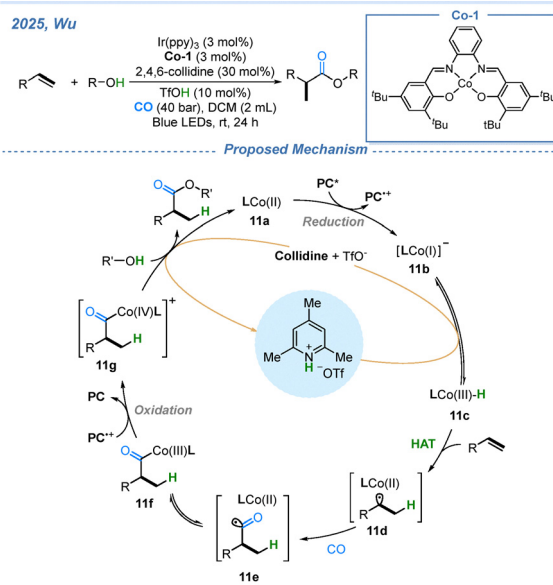
## 2025, Wu



Scheme 10 Cobalt-catalyzed carbonylation of BCBs and amines.

is excited to its active state (PC<sup>\*</sup>). The excited PC<sup>\*</sup> then reduces the Co(II) intermediate **11a** to generate Co(I) species **11b** and the oxidized PC<sup>+</sup>. Subsequently, protonation of Co(I) **11b** by a Brønsted acid affords the Co(III)–H intermediate **11c**. This Co(III)–H species undergoes a hydrogen atom transfer (HAT) process with the alkene substrate, forming a metal–alkyl radical

## 2025, Wu



Scheme 11 Photoredox-cobalt co-catalyzed Markovnikov-selective hydrocarboxylation of alkenes.



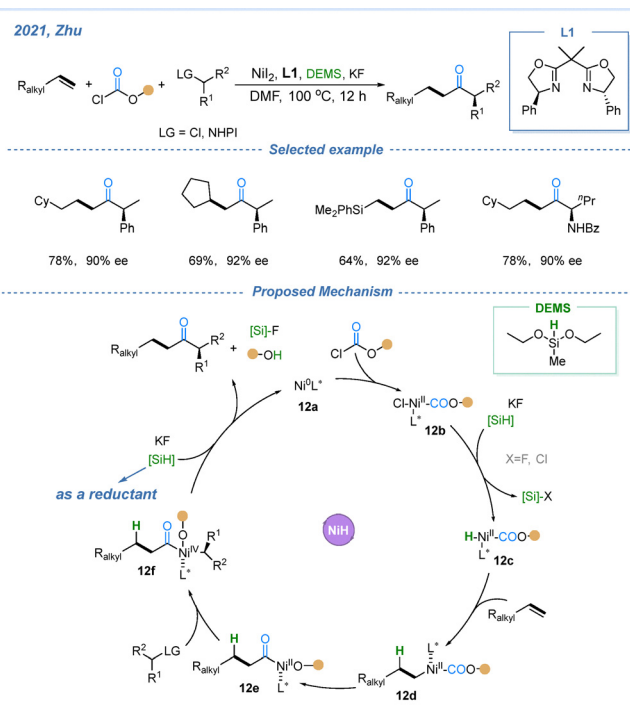
pair **11d**. Under a CO atmosphere, the alkyl radical captures a molecule of CO to generate the metal-acyl radical pair **11e**, which exists in reversible equilibrium with the acyl-Co(III) intermediate **11f**. The acyl-Co(III) species **11f** is then oxidized by  $PC^{+}$  via a single-electron transfer (SET) process to produce the high-valent cationic acyl-Co(IV) intermediate **11g**. Finally, in the presence of a base, the Co(IV) intermediate **11g** undergoes nucleophilic substitution with an alcohol, yielding the ester product while regenerating the Co(II) catalyst, thereby completing the catalytic cycle.

## 4. Carbonylation involving Ni–H species

Nickel is an earth-abundant and inexpensive metal that exhibits similar catalytic properties to palladium in coupling reactions.<sup>41</sup> Due to its smaller atomic radius, nickel demonstrates strong oxidative insertion ability but weaker reductive elimination capability. In recent years, there has been growing interest in developing nickel-catalyzed carbonylation reactions, driven by the need for more sustainable and cost-effective catalytic systems.<sup>42</sup> Carbon monoxide binds strongly to nickel, and this property is exploited industrially in the Mond process.<sup>43</sup> In this process, impure nickel reacts with CO at 50–60 °C to form the volatile compound nickel tetracarbonyl,  $Ni(CO)_4$ . The gaseous  $Ni(CO)_4$  is then decomposed at 180–200 °C, yielding high-purity nickel metal. Therefore, when employing nickel catalysts in CO-involved carbonylation reactions, catalyst poisoning often occurs due to the strong coordination between CO and nickel.<sup>44,45</sup> As a result, the development of nickel-catalyzed carbonylation reactions has been relatively slow. In recent years, however, several research groups have focused on using CO surrogates or designing pincer-type  $NN_2$  nickel catalysts to effectively avoid the formation of  $Ni(CO)_4$  and thus overcome this challenge.<sup>46–48</sup> This review primarily focuses on the recent advances in Ni–H-mediated carbonylation reactions employing CO surrogates.

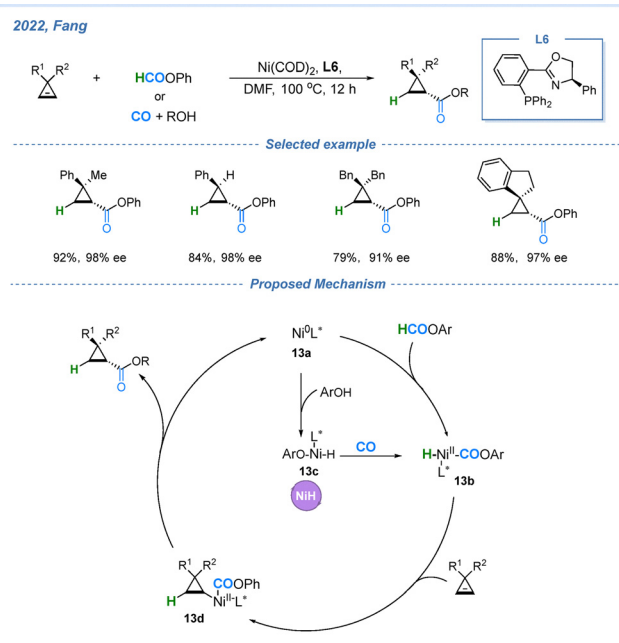
In 2021, the Zhu group reported a nickel-catalyzed multi-component regio- and enantioselective hydrocarbonylative coupling reaction.<sup>49</sup> This method features a broad substrate scope and excellent enantioselectivity. The proposed reaction mechanism is shown in Scheme 12: first, the nickel catalyst **12a** undergoes oxidative addition to the chloroformate reagent, generating the Ni(II) intermediate **12b**. In the presence of a silane and a base, **12b** is converted into the Ni–H species **12c**, which then adds across the alkene to form **12d**. Subsequent migratory insertion of the CO ligand affords intermediate **12e**. At this stage, nickel remains in the +2 oxidation state. Oxidative addition of the electrophile then produces the possible Ni(IV) intermediate **12f**. Finally, reduction by the silane yields the desired product and regenerates catalyst **12a**, completing the catalytic cycle.

In 2022, the Fang group developed the first nickel-catalyzed asymmetric Reppe-type carbonylation of cyclopropenes.<sup>50</sup> This method enables the synthesis of a variety of highly substituted



Scheme 12 Nickel-catalyzed Reppe-type carbonylation of alcohols.

$\alpha$ -chiral cyclopropanecarboxylates and bicyclic lactones under CO-free conditions or using only a CO balloon, delivering excellent diastereo- and enantioselectivities, respectively. The proposed reaction mechanism, shown in Scheme 13, proceeds as follows: The nickel catalyst **13a** undergoes oxidative addition to a formate ester to produce intermediate **13b**, or alternatively,



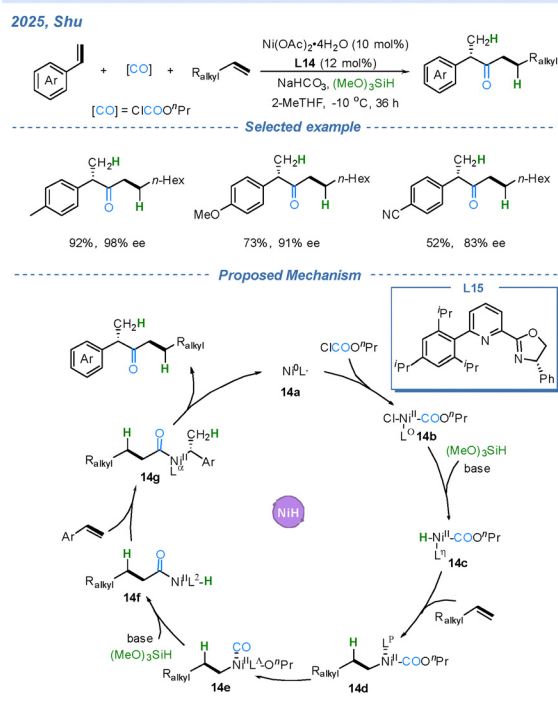
Scheme 13 Nickel-catalyzed Reppe-type carbonylation of alcohols.



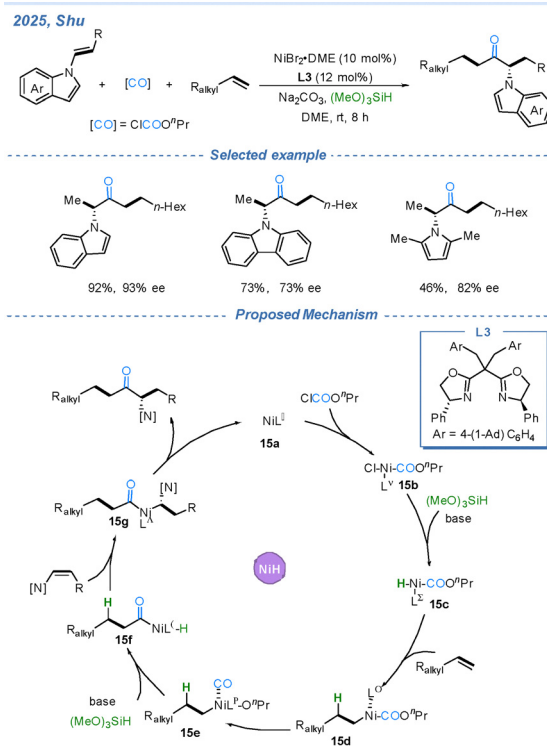


under CO atmosphere, oxidative addition to phenol occurs to give intermediate **13c**, which then undergoes migratory insertion of CO to furnish **13b**. Intermediate **13b** adds to the cyclopropene derivative, generating **13d**. Finally, reductive elimination affords the desired product and regenerates the Ni(0) species **13a**, thereby completing the catalytic cycle.

In 2025, the Shu group developed nickel-catalyzed asymmetric cross-hydrocarbonylation between aryl olefins and alkyl olefins.<sup>51</sup> A key feature of this reaction is that two different alkenes undergo Ni-catalyzed hydrocarbonylation with distinct regioselectivities. This method shows excellent chemoselectivity and regioselectivity, providing an efficient synthetic pathway to asymmetric dialkyl ketones from simple and readily available starting materials. As shown in Scheme 14, the reaction mechanism proceeds as follows: first, Ni(0) species **14a** undergoes oxidative addition to chloroformate, generating **14b**. In the presence of a silane and base, a metal exchange process affords the Ni(II)–H intermediate **14c**. Intermediate **14c** then selectively undergoes migratory insertion with the alkyl olefin, forming the alkyl–Ni(II) species **14d**. Subsequent ligand dissociation and migratory CO insertion generate the acyl–Ni(II) intermediate **14e**. Next, **14e** undergoes another metal exchange process with a silane and base to form a second Ni(II)–H species, **14f**. This Ni–H intermediate selectively inserts into the aryl olefin through a hydrometallation step to afford **14g**. Reductive elimination from **14g** delivers the final product and regenerates the Ni(0) catalyst **14a** to complete the catalytic cycle. A possible side pathway involves homolytic cleavage of the Ni–C bond in **14g**, forming a Ni(I)/benzyl-radical pair.



**Scheme 14** Nickel-catalyzed carbonylation of aryl alkenes and alkyl alkenes.



**Scheme 15** Nickel-catalyzed carbonylation of *N*-alkenyl heteroarenes and alkyl alkenes.

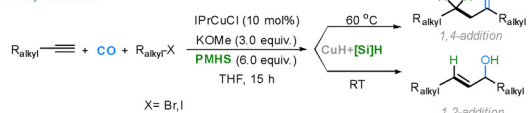
In 2025, the Shu group developed another nickel-catalyzed reductive carbonylation that couples two different olefins – an unactivated alkene and an *N*-alkenyl heteroarene – to afford chiral  $\alpha$ -*N*-heteroaryl ketones (Scheme 15).<sup>52</sup> The reaction proceeds with a similar mechanism and starts with Ni(0) species **15a**. After the acyl–Ni(II)–H species **15f** as the key intermediate was generated, a regio- and enantioselective migratory hydrometallation of the *N*-alkenyl heteroarene with **15f** furnishes the acyl–Ni(II)–alkyl intermediate **15g**, which then delivers the desired product after reductive elimination and regenerates the Ni(0) species **15a** for the next catalytic cycle.

## 5. Carbonylation involving Cu–H species

Copper-catalyzed carbonylative transformations have developed rapidly over the past decade, largely due to the versatile reactivity of Cu–H, Cu–B, and Cu–Si species in both hydrofunctionalization of unsaturated bonds and single-electron reduction of alkyl halides.<sup>53,54</sup> In 2017 and 2018, Mankad and co-workers reported the copper-catalyzed hydrocarbonylation of terminal alkynes for the construction of dialkyl ketones and allylic alcohol derivatives.<sup>55,56</sup> By controlling the temperature of this reaction, they further achieved either 1,4- or 1,2-addition of Cu–H species to the resulting enone intermediate, leading to two types of products. As described in Scheme 16, IPrCuCl first reacts with a base to form IPrCuOMe, which then undergoes

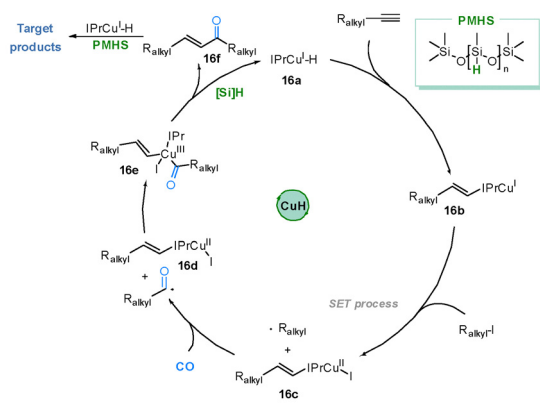


2017, Mankad



X = Br, I

Proposed Mechanism

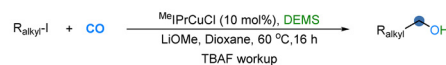


Scheme 16 CuH-mediated carbonylation of alkynes and alkyl halides.

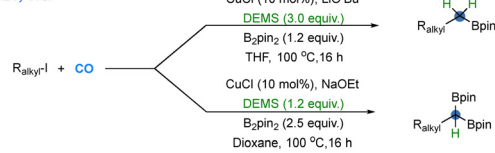
transmetalation with a silane to yield the active Cu-H species **16a**. This species adds across the terminal alkyne to give intermediate **16b**. Subsequently, **16b** engages in a single-electron process of the alkyl iodide, giving intermediate **16c** and an alkyl radical. The alkyl radical rapidly adds CO to produce an acyl radical, which then combines with **16c** to yield the Cu(III) intermediate **16d**. Reductive elimination from **16d** affords the unsaturated ketone **16e** and reproduces the Cu(I) salts, which re-enter the next catalytic cycle *via* conversion with a base and silane to get IPrCuH. Then **16e** undergoes further functionalization. It undergoes 1,4-addition with Cu-H at 60 °C, followed by quenching of [Si]-H compounds to obtain dialkyl ketones. In another pathway, **16e** intermediate undergoes 1,2-addition with Cu-H at room temperature, and subsequent quenching with [Si]-H compounds to obtain allylic alcohols.

In 2018, the Mankad group reported the copper-catalyzed hydroxymethylation of unactivated alkyl iodides.<sup>57</sup> This transformation represents an intriguing homologation strategy: alkyl iodides, readily prepared from the corresponding alcohols, are converted into alcohols extended by one carbon. The newly formed alcohols can be further transformed back into alkyl iodides, enabling iterative chain elongation to access progressively longer alkyl iodides and alcohols. Later in 2021, Wu and co-workers developed a borylative methylation that simultaneously engages both Cu-Bpin and Cu-H intermediates (Scheme 17).<sup>58</sup> In this catalytic system, the reaction of Cu-H with alkyl iodides is significantly faster than that of Cu-Bpin. The proposed mechanism is outlined as follows: in the presence of a silane, the copper catalyst **17a** is converted into the Cu-H species **17b**, which reduces the alkyl iodide *via* a single-electron process to form a carbon-centered radical and copper intermediate **17c**. Under a CO atmosphere, the carbon radical rapidly captures CO to generate an acyl radical that then

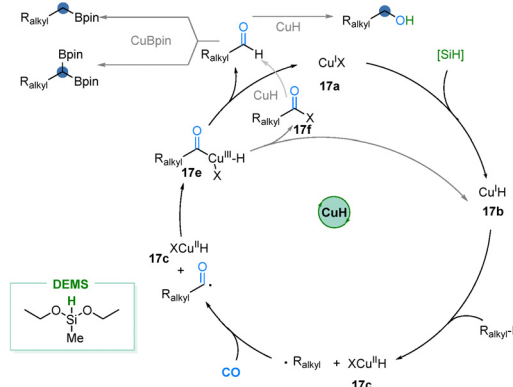
2018, Mankad



2021, Wu



Proposed Mechanism



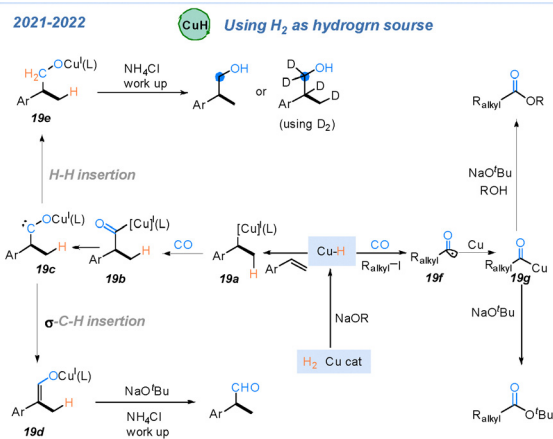
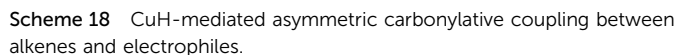
Scheme 17 CuH-mediated carbonylation of alkyl halides.

couples with **17c**, producing the acyl-copper intermediate **17d**. Reductive elimination from **17d** affords either an acyl halide or an aldehyde, while regenerating the active copper species (**17a** or **17b**). The acyl halide can be further reduced by Cu-H to the corresponding aldehyde, which may then undergo subsequent transformations, including reduction to one-carbon-extended alcohols, borylmethylation to give boronates, or diborylmethylation to yield diboron-containing products.

In copper-catalyzed carbonylation chemistry, particularly over the past five years, CuH-mediated asymmetric carbonylation has emerged as one of the most efficient strategies for constructing chiral carbonyl compounds. In 2020, Wu and co-workers developed the first Cu-catalyzed carbonylative hydroamidation of aryl alkenes and its related asymmetric variants, enabling the synthesis of chiral amides in good yields and excellent enantioselectivities (up to 99% ee).<sup>59</sup> In 2023, Wu and co-workers reported the Cu-catalyzed carbonylative hydroamidation of unactivated alkenes.<sup>60</sup> A key to this transformation was the use of the highly sterically demanding bidentate phosphine ligand (*R*)-DTBM-Segphos, which significantly enhanced the hydrometallation capability of the Cu-H species toward unactivated C=C bonds. β-Chiral amides were obtained when 1,1-disubstituted alkenes were employed. In 2024, while existing methods for synthesizing chiral amides primarily focused on accessing α- and β-substituted amides, controlling remote stereocenters in γ-chiral amides typically required harsh reaction conditions. To address this challenge, the Wu group developed a general Cu-catalyzed strategy for the enantioselective synthesis of γ-chiral amides through a reductive relay hydroamidation process.<sup>61</sup> This method exhibited a

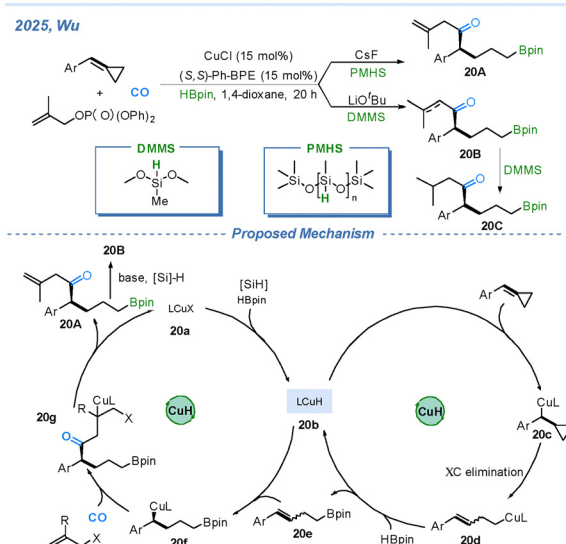


Hydrogen gas, as an inexpensive and readily available hydrogen source, is widely favoured in metal-hydride chemistry.<sup>64</sup> As described in Scheme 19, the Cu-H species can add to alkenes to form intermediate **19a**, which can then capture CO to afford the acyl-copper intermediate **19b**. Intermediate **19b** undergoes isomerization to form carbene species **19c**. Hydrogenation of **19c** gives **19e**, after quenching with ammonium chloride, yields the corresponding alcohols. Alternatively,  $\alpha$ -C-H insertion of **19c** forms intermediate **19d**, which, after quenching with a base and ammonium chloride, provides the corresponding aldehydes. When D<sub>2</sub> is used instead of H<sub>2</sub>, various deuterated compounds can be obtained. In addition, the Cu-H intermediate can reduce alkyl iodides *via* a single-electron process to generate alkyl radicals, which capture CO to form acyl radicals. Trapping of these radicals by copper gives acyl-copper intermediates **19g**, which deliver esters upon nucleophilic quenching.<sup>65–67</sup>



**Scheme 19** Cu–H mediated divergent carbonylative transformations using H<sub>2</sub> as a hydrogen source.

In 2025, the Wu group developed the highly selective copper-catalyzed carbonylation of methylenecyclopropanes, enabling the construction of chiral  $\delta$ -boryl ketones.<sup>68</sup> This methodology allows three structurally distinct chiral organoboron ketones to be selectively synthesized from a common set of starting materials, and diverse downstream derivatizations further enrich the chemical space of chiral ketones. As illustrated in Scheme 20, the reaction begins with the formation of the active LCuH species **20b** through the reaction of the copper catalyst with a silane. Hydrometalation of the methylenecyclopropane affords intermediate **20c**, followed by  $\beta$ -C scission to generate **20d**. Trapping of **20d** by a boron reagent yields the key homoallyl boronate intermediate **20e** while regenerating LCuH. Subsequently, intermediate **20e** undergoes hydrometalation with LCuH to form the chiral copper species **20f**. Coordination of an allyl phosphate and CO to **20f** gives intermediate **20g**, which



**Scheme 20** CuH-mediated asymmetric carbonylative coupling between strained alkenes and electrophiles.

then undergoes  $\beta$ -halogen elimination to deliver product **20A**. In the presence of an appropriate base, product **20A** can be further isomerized or reduced to give product **20B**.

## 6. Isomerization–carbonylation tandem reactions

In metal-hydride-mediated hydroformylation reactions, isomerization–carbonylation tandem reactions have long been among the most intriguing and valuable transformations. Their greatest advantage is the ability to convert a mixture of starting olefins into a single carbonylated product. This is particularly important in the chemical industry, where mixtures of olefins that are difficult to separate can be further transformed *via* this tandem process. The isomerization–carbonylation sequence can convert such mixed olefins into terminal esters, which can serve as valuable single-component products, for example, as plasticizers.<sup>69</sup>

### 6.1 Isomerization–hydroformylation tandem reactions

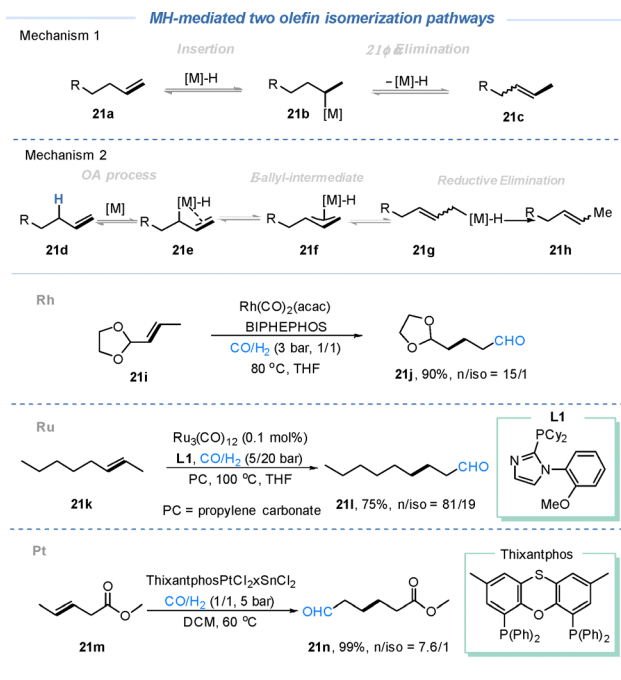
In isomerization–carbonylation tandem reactions, isomerization–hydroformylation tandem processes have already been applied in the chemical industry on a 10 000–100 000-ton scale.<sup>16</sup> The isomerization–carbonylation tandem reactions generally proceed *via* two mechanistic pathways, as illustrated in Scheme 21. In the first pathway, **21a** undergoes M–H addition to form **21b**, followed by  $\beta$ -hydride elimination to yield **21c**. The second pathway involves oxidative addition of an allylic C–H bond to generate **21e**, which then forms the  $\pi$ -allyl intermediate **21f**. Subsequent isomerization affords **21g**, and finally reductive elimination gives **21h**. Moreover, comparisons of catalysts based on different metals (Rh, Ru, and Pt) in isomerization–carbonylation tandem reactions reveal that rhodium, as a noble metal catalyst, generally provides superior selectivity.

### 6.2 PdH-mediated isomerization–carbonylation tandem reactions

In isomerization–carbonylation tandem reactions, palladium-catalyzed migratory hydrocarbonylation is the most fully developed case. As shown in Scheme 22, the HeMaRaphos ligand developed by the Beller group enables terminal-selective migratory carbonylation with high selectivity.<sup>11</sup> In addition, the commercially available 1,2-DTBPMB also provides excellent selectivity. Using mixed allenes and 1,3-butadiene in this migratory carbonylation process affords the single diester product **22d** (Nylon-66 monomer) in high yield.<sup>70</sup> Moreover, when phenyl formate is employed as an alternative carbonyl source, the terminally migrated carbonylation product **22f** can also be obtained.<sup>71</sup>

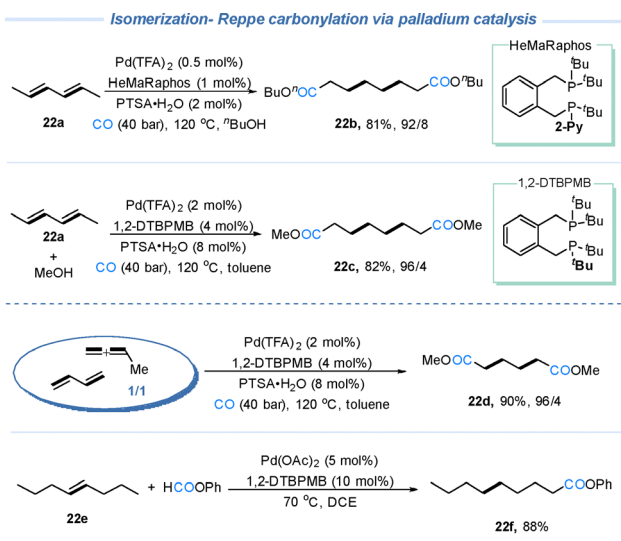
### 6.3 Earth abundant metal–hydride-mediated isomerization–carbonylation tandem reactions

In the cobalt-catalyzed hydroamidation reported by the Alexanian group in 2024, the reaction can be applied to isomerization–carbonylation, achieving a linear-to-branched selectivity of



Scheme 21 Precious metal–hydride-mediated isomerization–hydroformylation tandem reactions.

up to 19:1. The corresponding mechanism is illustrated in Scheme 23. First, **23a** reacts with the ammonium salt to generate the cobalt–hydride intermediate **23b**, which can subsequently add to the mixed olefins to form **23c** and **23d**. These intermediates then undergo chain-walking to reach the terminal position, giving **23f**. Coordination of CO and the amine leads to intermediate **23g**, which finally delivers the amide product under the action of the amine, along with regeneration of the ammonium salt and **23a**, thereby completing an isomerization–carbonylation catalytic cycle.<sup>34</sup>

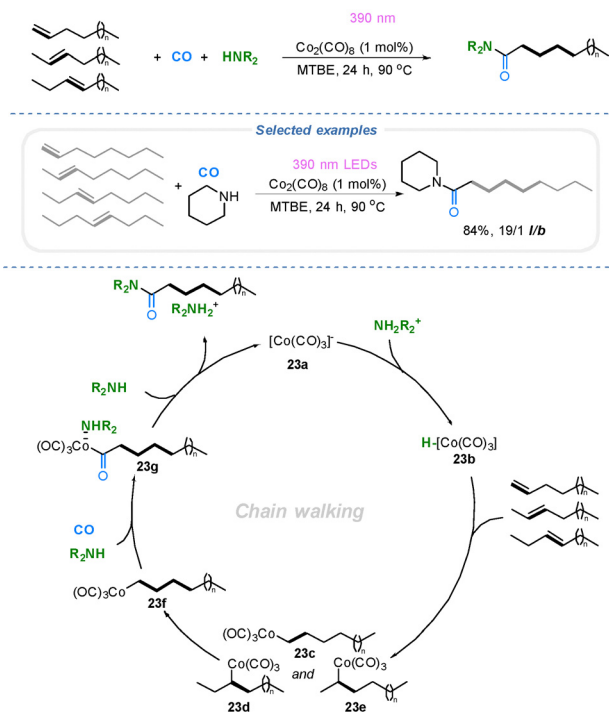


Scheme 22 PdH-mediated isomerization–hydroformylation tandem reactions.





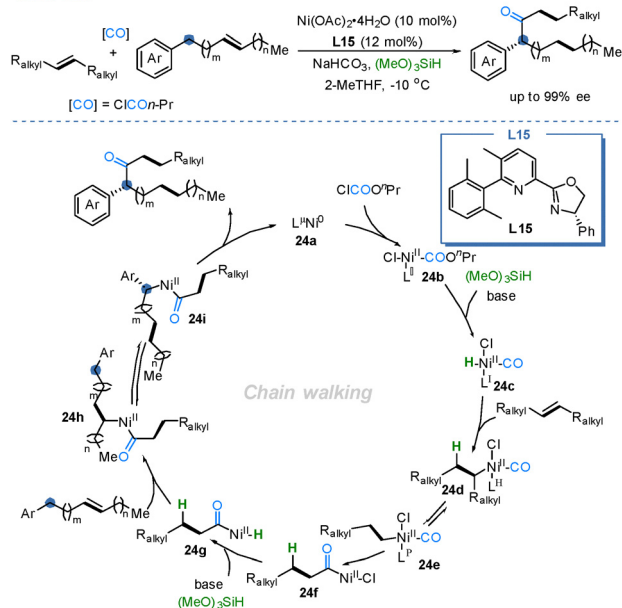
2024, Alexanian



Scheme 23 CoH-mediated isomerization-carbonylation tandem reaction.

In 2025, Shu and co-workers reported a nickel-catalyzed migratory carbonylation reaction involving two different alkenes. The substrates included two alkyl-substituted alkenes and a chloroformate derivative, with one of the alkenes bearing a terminal aryl group. This migratory carbonylation enabled the

2025, Shu



Scheme 24 NiH-mediated isomerization-carbonylation tandem reaction.

synthesis of benzyl-position chiral ketones. Unlike previous examples, in this reaction, one alkene undergoes migration toward the internal position (benzyl site), while the other alkene migrates to the terminal position of the alkyl-substituted alkene. The mechanism is illustrated in Scheme 24. First, Ni(0) species **24a** undergoes oxidative addition with the chloroformate derivatives to form **24b**, which, in the presence of a silane and base, is converted to **24c**. Intermediate **24c** adds across the alkene to give **24d**. Under the influence of ligand L15, it undergoes migration to form the terminal organonickel intermediate **24e**. Subsequent CO migratory insertion yields the acyl-nickel intermediate **24f**. Treatment with a silane and base regenerates the Ni-H species **24g**, which adds to the aryl-substituted alkene to form **24h**. Ligand-controlled migration then affords the chiral intermediate **24i**, which undergoes reductive elimination to give the target product and regenerates Ni(0) intermediate **24a**, completing the catalytic cycle.<sup>72</sup>

## 7. Conclusions and outlook

In summary, carbonylation has become a powerful strategy for constructing value-added chemicals across organic synthesis, materials science, pharmaceuticals, and industrial processes.<sup>73–78</sup> Hydrocarbonylation, exemplified by hydroformylation and Reppe-type carbonylation, plays an especially prominent role. While traditional carbonylation technologies rely heavily on noble-metal catalysts, growing attention is now being directed toward developing efficient, practical, and cost-effective catalytic systems based on earth-abundant metals. In this review, we have summarized recent advances in Fe-, Co-, Ni-, and Cu-catalyzed hydroesterification and hydroamidation reactions, and we anticipate that these transformations will find increasing relevance in industrial applications.

Furthermore, olefin isomerization-carbonylation tandem processes (chain-walking carbonylation) provide a valuable approach for converting complex or mixed olefin feedstocks into single products, an aspect of particular interest to the chemical industry. This review also highlights recent progress in earth-abundant-metal-hydride-mediated carbonylation and isomerization-carbonylation tandem processes. Looking forward, we expect that even more economical metal catalysts, such as iron or copper, will continue to expand the scope of migratory hydrocarbonylation chemistry.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.



## Acknowledgements

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