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Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
*J. Serb. Chem. Soc.***00(0)** 1-28 (2024)
JSCS–12848
Review
Published DD MM, 2024

Cobalt catalyzed defunctionalization reactions

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(Received 15 March 2023; revised 8 April; accepted 9 April 2024)

Abstract: Catalytic defunctionalization of complex molecules has attracted significant attention in organic synthesis. This reaction enables common functional groups to serve as "traceless handles" for the new bond construction. In this mini-review, we have summarized the latest advances, methodologies and mechanistic insights into the selective cleavage of C-C and C-X bonds catalyzed by cobalt complexes, shedding light on their increasing importance in modern chemical synthesis. The content of this review is categorized according to the type of functional group being removed from molecules.

Keywords: decarbonylation; decarboxylation; dehalogenation; desulfurization; deoxygenation.

INTRODUCTION

Transition metal-mediated defunctionalization through cleavage of C–C or C-X bonds is an essential synthetic approach.[1] Moreover, defunctionalization reactions exert a direct influence on synthetic organic chemistry by enabling the temporary utilization of functional groups in synthetic transformations.[2] In various contexts, defunctionalized substrates are deemed more advantageous than their functionalized form. For example, dehalogenation of polychlorinated aromatic pesticides yields less environmentally hazardous compounds. Deoxygenation of aldehydes, acids, and similar molecules derived from natural sources produces compounds suitable for use as biofuels.[3] While highly effective, the typical utilization of expensive palladium,[4,5] rhodium[6,7] and ruthenium[8,9] complexes might impede the development of this field. On the other hand, cobalt is earth-abundant, inexpensive and less toxic compared to second row transition metals. Over the last two decades, cobalt has garnered significant attention for its applications as a catalyst in bond formation[10] and bond cleavage[11] processes. In this mini-review, we highlight the development of cobalt-catalyzed defunctionalization reactions and their applications in synthetic organic chemistry.

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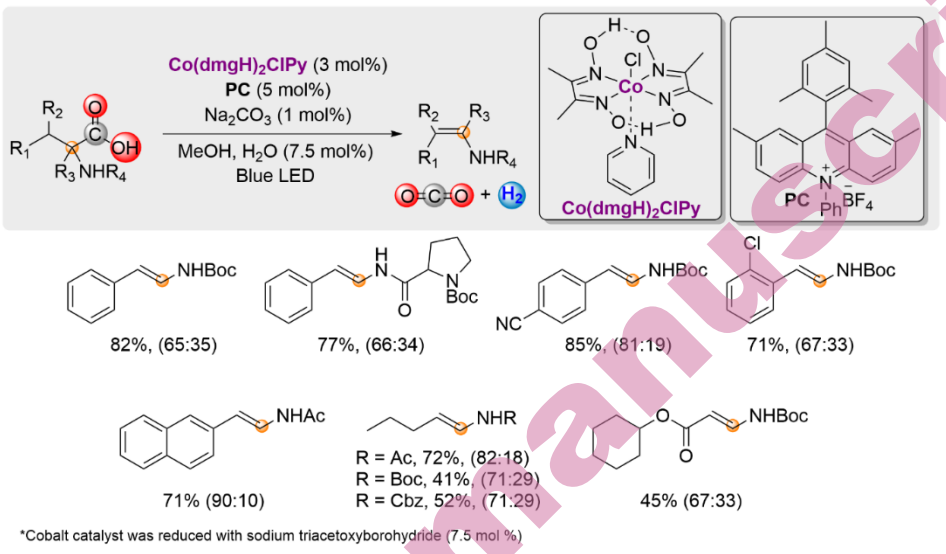
https://doi.org/10.2298/JSC240315045K

DEHYDRODECARBOXYLATION

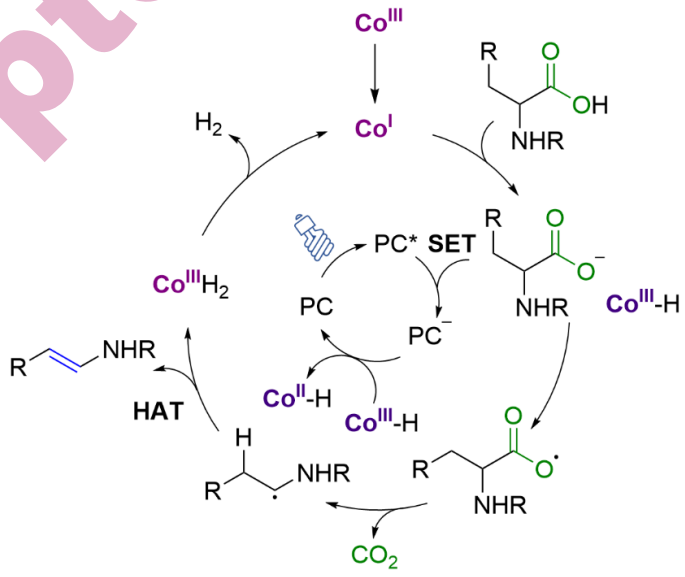
Obtaining terminal alkenes from carboxylic acids is a significant pursuit in organic chemistry with far-reaching implications in both academic research and industrial applications. Terminal alkenes are versatile building blocks used in the synthesis of various compounds, including pharmaceuticals, agrochemicals, and materials.[12] The practicability of accessing terminal alkenes from carboxylic acids lies in the abundance and accessibility of carboxylic acids as starting material. Carboxylic acids are prevalent in nature, and can be derived from renewable sources such as biomass or waste streams, offering a sustainable alternative to petroleum-derived feedstocks.[13] Moreover, carboxylic acids are relatively inexpensive and can be synthesized through various routes, making them attractive precursors for alkene synthesis.[14] Traditional methods for alkene synthesis often involve multi-step low atom economy processes with the use of toxic and expensive reagents.[15] In contrast, direct conversion of carboxylic acids to terminal alkenes offers a more atom-efficient and environmentally benign route. In recent years, significant advancements have been made in the development of catalytic systems and reaction methodologies for the selective conversion of carboxylic acids to terminal alkenes. Transition metal catalysis, particularly involving palladium,[16] nickel,[17,18] or iron catalysts,[19] has emerged as a powerful tool for this transformation.

Tunge and Cartwright have successfully developed a two-catalyst approach to produce enamides and enecarbamates directly from readily available and affordable *N*-protected amino acids using a photoredox catalyst under blue LED irradiation and a cobaloxime catalyst $Co(dmgH)_2ClPy$.[20] The protocol, despite its success with diverse amino acids, exhibits low selectivity, resulting in the production of significant quantities of both olefin isomers (*E*/*Z*) (Scheme 1). Maintaining a slight excess of photocatalyst relative to cobaloxime is essential for the reaction to succeed.



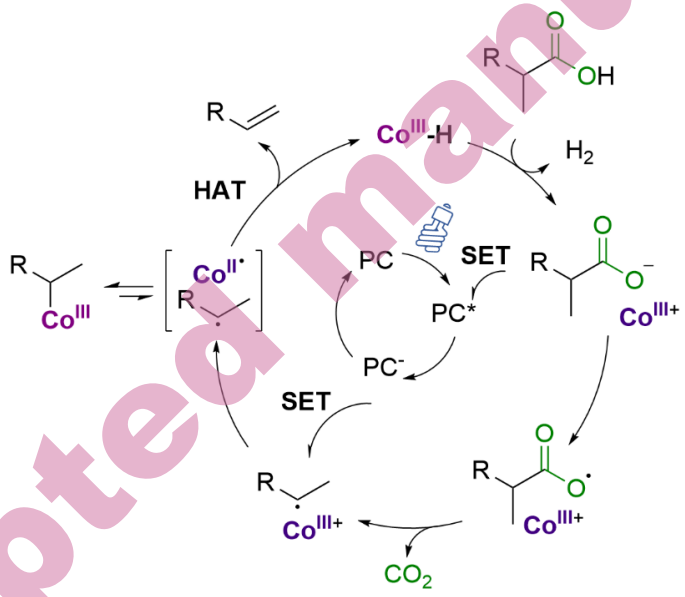
Scheme 1. Scope of *N*-acyl amino acids.

In the reaction mechanism, olefin formation was initially proposed to occur through oxidative decarboxylation, generating a radical intermediate followed by a Hydrogen Atom Transfer (HAT) reaction (Scheme 2). This process ultimately produces only CO_2 and H_2 as the stoichiometric byproducts.



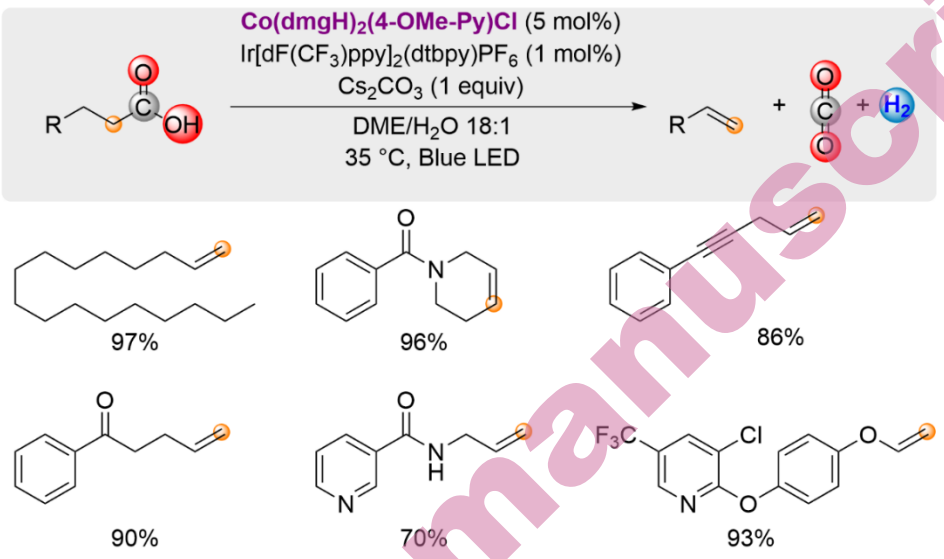
Scheme 2. Proposed mechanism for photoredox/cobalt dual-catalyzed decarboxylative elimination.

Two years later, the same research group reported novel insights into the underlying reaction mechanism. Their experimental studies suggest that the primary catalytic cycle involves Co(II) and Co(III) intermediates rather than an anionic Co(I) species.[21] This proposal is based on thorough experimentation and analysis, providing valuable insights into the mechanistic pathways of the reaction. Based on their research, it was proposed that a PCET (Proton-coupled electron transfer) pathway is the preferred route for HAT, and HE by protonation of the Co(III) hydride is the most probable pathway (Scheme 3).



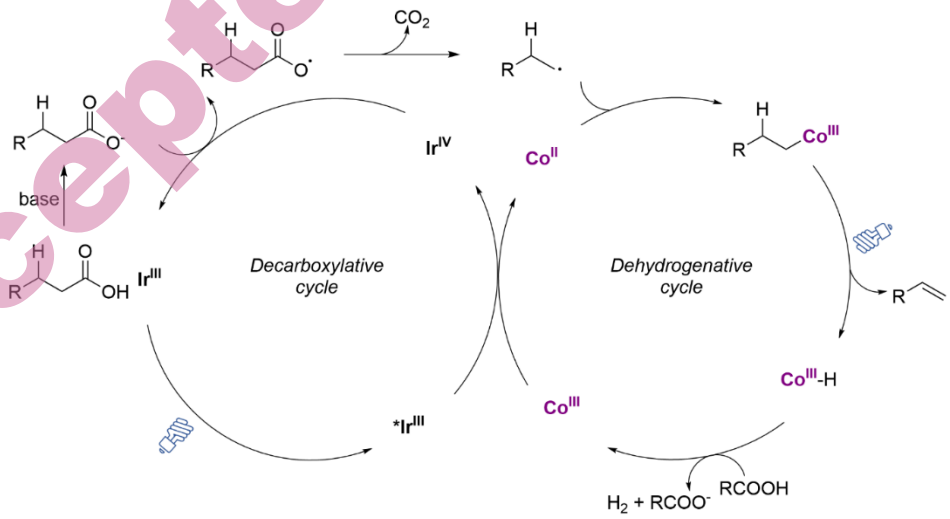
Scheme 3. Hypothetical mechanism for photoredox/cobalt dual-catalyzed decarboxylative elimination.

Under photochemical conditions, Ritter and coworkers achieved the catalytic dehydrogenative decarboxyolefination of both fatty acids, and structurally complex carboxylic acids, into olefins.[22] They identified the cobaloxime Co(dmgH)$_2$(4-OMe-py)Cl as a proton reduction catalyst and the photoredox catalyst Ir[dF(CF$_3$)ppy]$_2$(dtbpy)PF$_6$, which mediates oxidative decarboxylation, as optimal catalytic system that enables high reaction yields requirement for stoichiometric additives. From their substrate scope study, it is evident that the decarboxyolefination of a large variety of structurally and functionally complex carboxylic acids had been successful (Scheme 4).



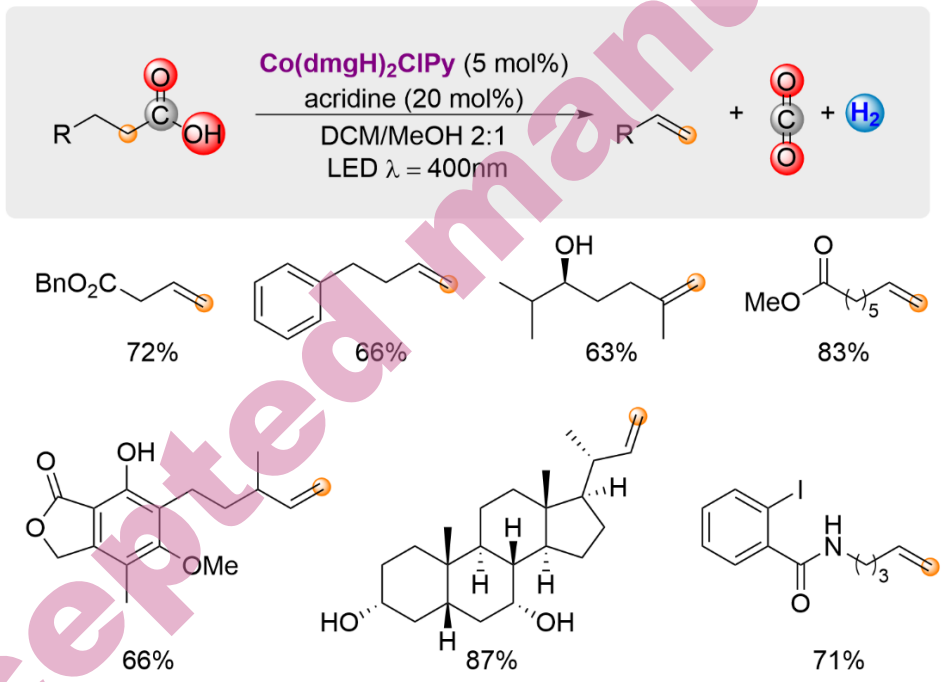
Scheme 4. Substrate scope for dehydrogenative decarboxyolefination.

In this method, the presence of a base is significantly important as it increases the concentration of carboxylate, facilitating efficient one-electron oxidation to form the neutral carboxyl radical by the iridium catalyst (Scheme 5).



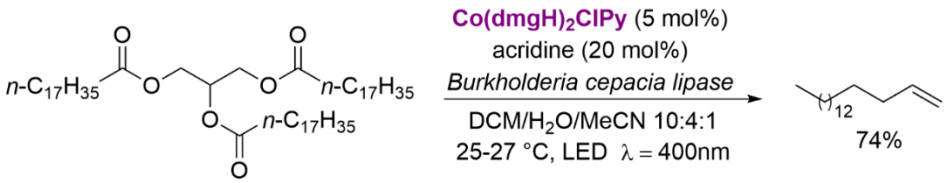
Scheme 5. Proposed mechanism for catalytic dehydrogenative decarboxyolefination of carboxylic acid.

Larionov and coworkers also apllied a photoinduced dual catalytic dehydrodecarboxylation strategy to carboxylic acids using acridine as a photocatalyst and cobaloxime in a mixture of dichloromethane and methanol under Blue LED irradiation to obtain alkenes.[23] From their comprehensive substrate scope study, it was observed that the developed method exhibits a broad substrate scope, encompassing various carboxylic acids, and demonstrated high tolerance towards diverse functional groups, thereby showcasing its versatility and potential applicability (Scheme 6).



Scheme 6. Substrate scope of photoinduced dehydrodecarboxylation.

They also discovered an efficient chemoenzymatic synthesis (LACo, lipase-acridine-cobaloxime method) of long-chain alkenes from triglycerides and unrefined biomass. Amano lipase PS from *Burkholderia cepacia* was utilized to achieve enhanced conversion in the hydrolysis of triglycerides (Scheme 7).

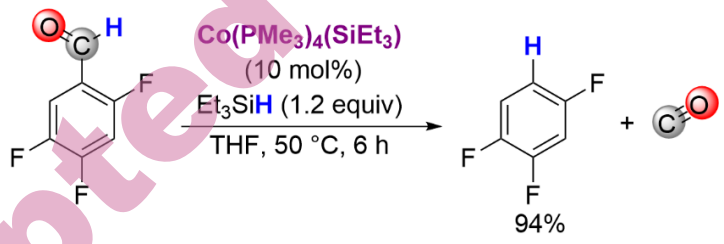


Scheme 7. Cooperative chemoenzymatic LACo process.

DECARBONYLATION

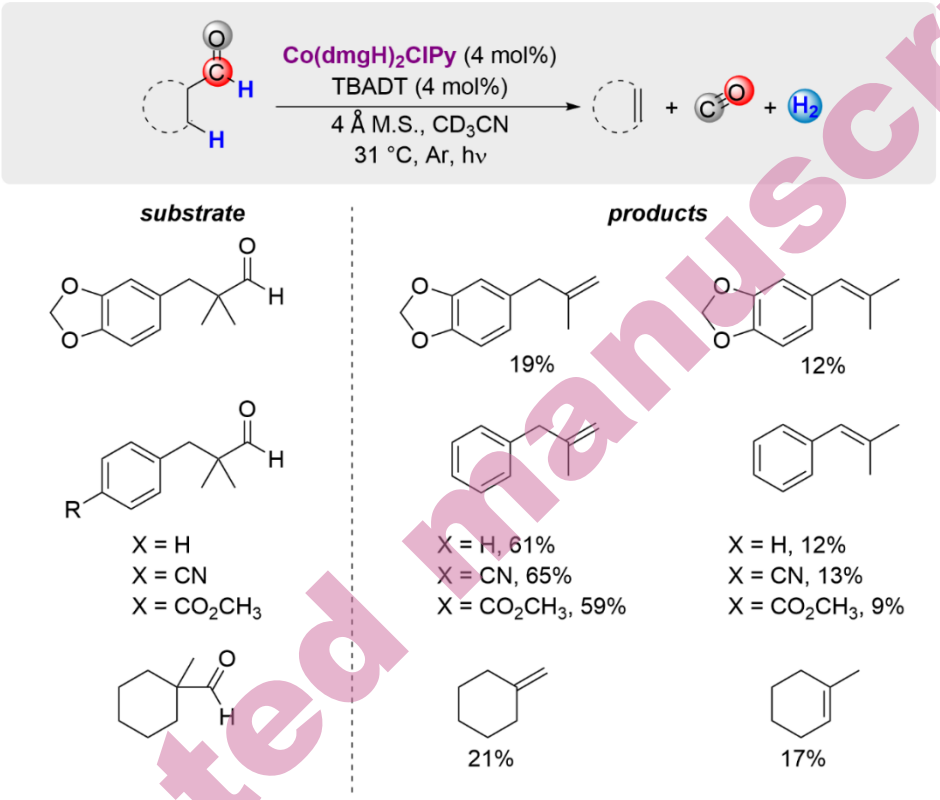
The aldehyde decarbonylation reaction is among the most important transformations both in biological systems and in a synthetic laboratory. Various organisms possess the ability to convert long-chain aldehydes into alkanes or alkenes via a group of enzymes known as aldehyde decarbonylases.[24] This process is accomplished by the release of small molecules such as formic acid, carbon dioxide and carbon monoxide. Numerous methods have been identified for the decarbonylation of aldehydes catalyzed by transition metals and their complexes.[25,26] Given the ubiquity of the aldehyde group, selective decarbonylation can serve as an important synthetic strategy, utilizing the aldehyde groups as "traceless handles" in various transformations such as the Diels–Alder (DA) reaction, C-H activation, and others.[2]

Li and coworkers in 2016 reported the first example of the Co-catalyzed decarbonylation.[27] It was exemplified only on one substrate, 2,4,5-trifluorobenzaldehyde. They demonstrated catalytic decarbonylation reaction of 2,4,5-trifluorobenzaldehyde to afford 1,2,4-trifluorobenzene with $CoMe(PMe_3)_4$ as a catalyst, and with 1.2 equiv of triethylsilane as a hydrogen source (Scheme 8).



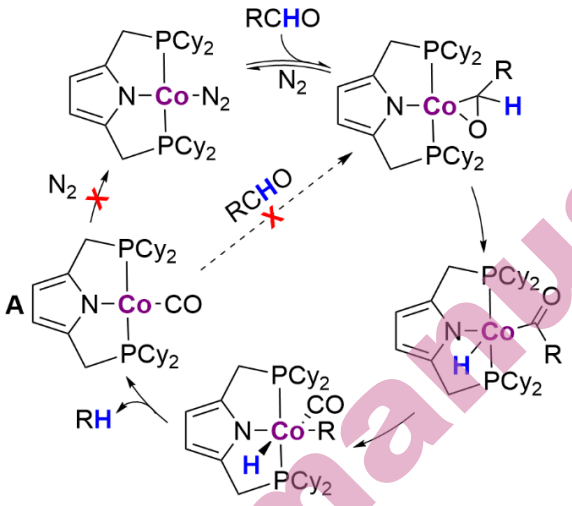
Scheme 8. Decarbonylation of 2,4,5-trifluorobenzaldehyde catalyzed by $CoMe(PMe_3)_4$.

Dehydroformylation of α-quaternary aldehydes that involves a decarbonylation step was achieved by Sorensen and coworkers using dual catalytic system (Scheme 9).[28] Tetrabutylammonium decatungstate (TBADT) and cobaloxime pyridine chloride (COPC) were used as catalysts and upon UV irradiation at room temperature olefinic products were obtained as regioisomeric mixtures in low yields (Scheme 9).



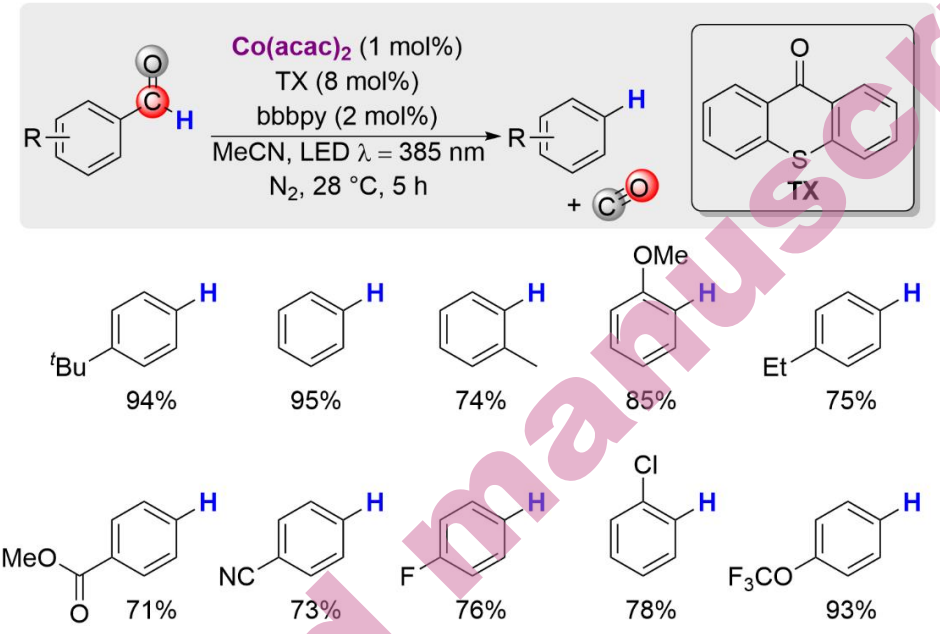
Scheme 9. Dehydroformylation of α-quaternary aldehydes.

Next year, Tonzetich and colleagues successfully conducted the decarbonylation of aromatic and aliphatic aldehydes using cobalt(I) pincer complexes as catalyst.[29] However, a drawback of this method is necessity for a stoichiometric amount of the catalyst. As depicted in the reaction mechanism illustrated in Scheme 10, following the formation of the product, cobalt carbonyl complex **A** is unable to undergo further substitution to complete the catalytic cycle.



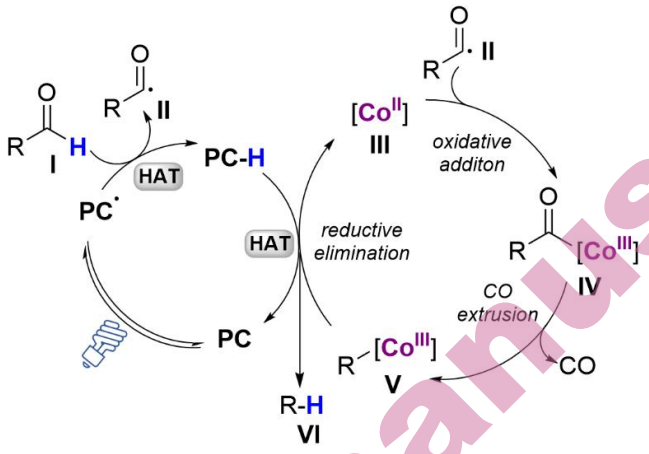
Scheme 10. Proposed mechanism for aldehyde decarbonylation.

Based on the previous observations of Sorensen and colleagues, König *et al*. reported a photocatalytic method for the decarbonylation of benzaldehydes in short reaction time.[30] Their method utilizes thioxanthone (TX) as an inexpensive hydrogen atom transfer (HAT) agent, cobalt(II) acetylacetonate ($Co(acac)_2$) as the cobalt source, and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (bbbpy) as the ligand (Scheme 11). The limitations of this methodology include the unreactivity of substrates bearing hydroxy, thioether, nitro, and carboxylic acid groups, degradation of amino and bromo substituted derivatives, and limited success with aliphatic aldehydes.

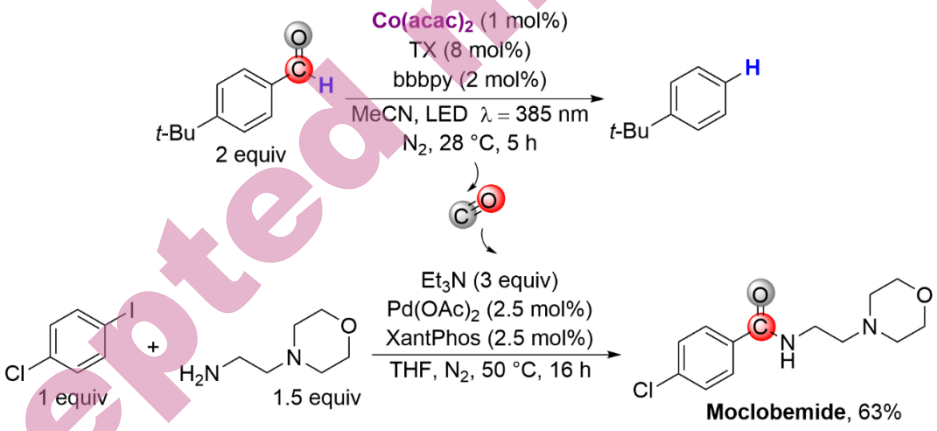


Scheme 11. Decarbonylation of benzaldehydes.

Initially, when the photocatalyst (PC) is excited to its triplet state (PC*), a hydrogen atom transfer (HAT) occurs with benzaldehyde (**I**), resulting in the formation of an acyl radical (**II**). This intermediate can then combine with the cobalt(II) complex (**III**) to produce a cobalt(III) complex (**IV**). This acyl complex (**IV**) is likely to undergo decarbonylation, releasing carbon monoxide and forming organocobalt complex **V** which can interact with the reduced form of the photocatalyst (PC–H), restoring it to its ground state (PC) through HAT. Concomitantly, the final product, decarbonylated arene (**VI**), is formed in this last step, and active cobalt species is regenerated (Scheme 12). To confirm the evolution of carbon monoxide, CO produced from the decarbonylation of 4-*t*-butylbenzaldehyde is utilized in the palladium-catalyzed aminocarbonylation reaction, resulting in the synthesis of the anxiolytic drug moclobemide in good yield (Scheme 13).

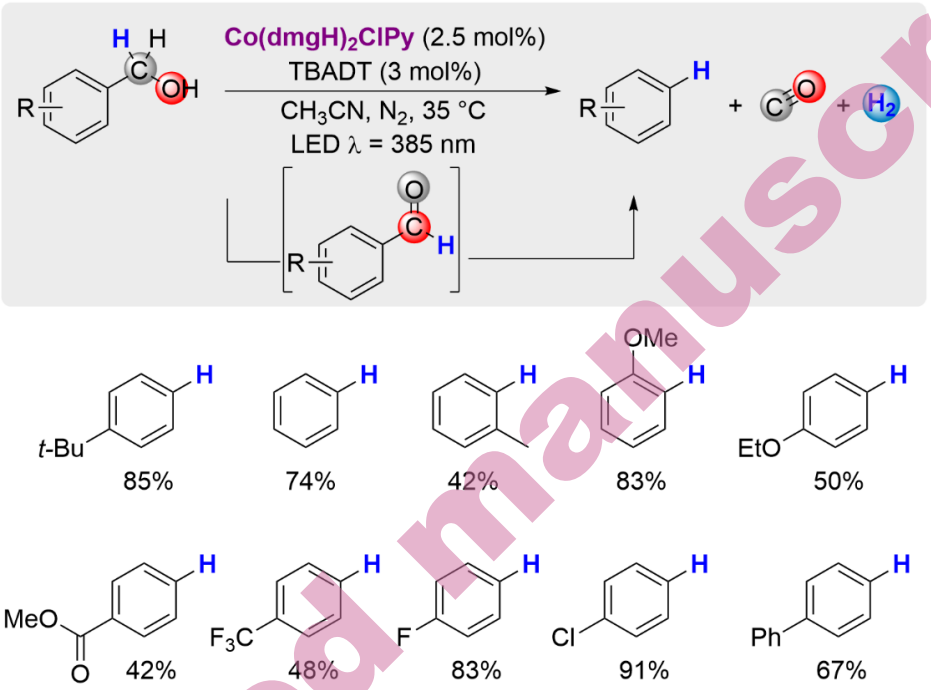


Scheme 12. Proposed reaction mechanism.



Scheme 13. Test reaction for confirming CO evolution.

Following their research on the photocatalytic method for the decarbonylation of benzaldehydes, König *et al*. reported a photocatalytic dehydroformylation.[31] This process integrates the dehydrogenation of benzyl alcohols into benzaldehydes, followed by decarbonylation to produce arenes in a one-pot two-step protocol. It enables the efficient conversion of diverse benzyl alcohols under mild photocatalytic conditions. The combination of tetrabutylammonium decatungstate as photoexcitable HAT-agent and cobaloxime pyridine chloride as co-catalyst was found to be highly effective (Scheme 14).



Scheme 14. Substrate scope for benzylalcohols.

DEHALOGENATION

Utilization of halides as blocking/protecting groups is an intriguing concept. For this purpose, it is essential to develop efficient dehalogenation strategies.[32,33] Additionally, dehalogenation processes are crucial for eliminating toxic halogenated compounds, like chlorinated arenes, which persist in the environment and resist natural degradation a few examples are depicted in Figure 1.[34] Efficient reductive dehalogenation methods, often involving transition metals and hydride sources, have been explored extensively.[35]

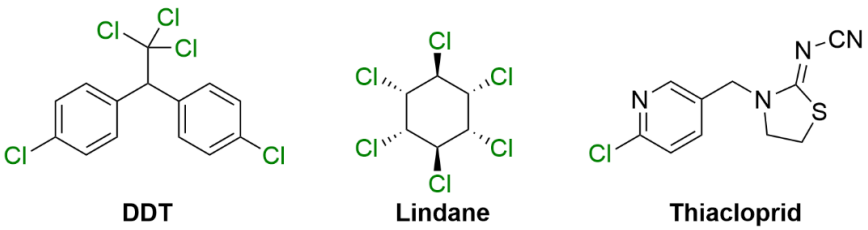
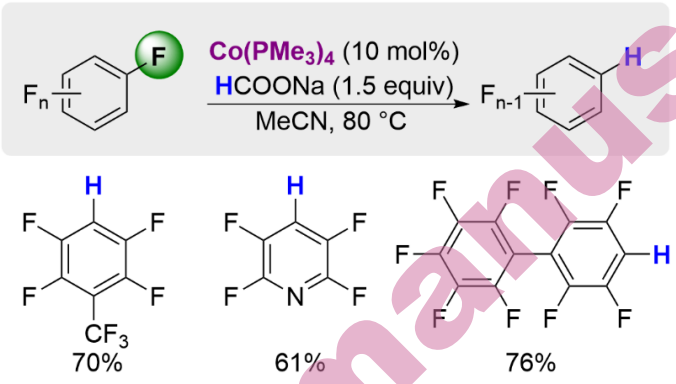


Fig. 1. Halogen-containing pesticides.

Based on their previous research related to selective C–F/C–H bond activation of fluoroarenes by cobalt complexes, Li *et al.* reported selective

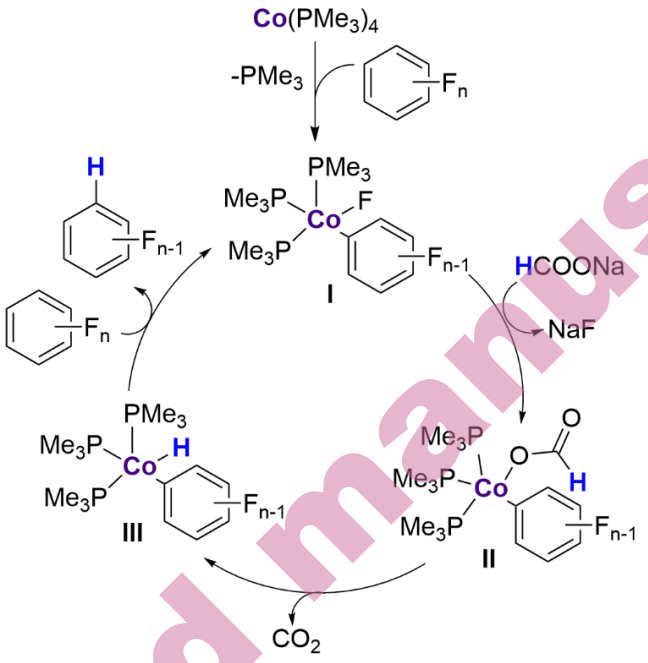
hydrodefluorination of aryl fluorides catalyzed by $Co(PMe_3)_4$.[36] In this method, sodium formate was utilized as a reducing agent, and the reaction can be conducted in either acetonitrile or DMSO (Scheme 15).



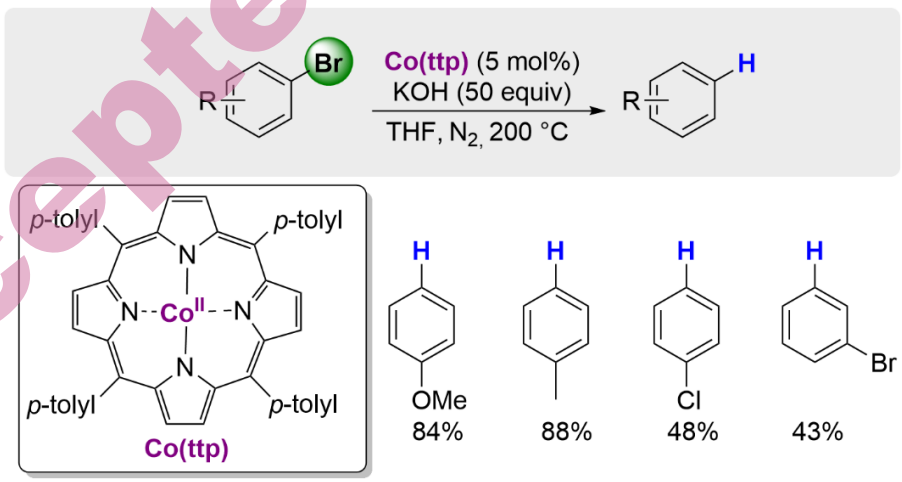
Scheme 15. Cobalt-catalyzed hydrodefluorination of polyfluoroarenes.

Based on the proposed mechanism, the process begins with the oxidative addition of the C–F bond of the aryl fluoride to the cobalt(0) center, forming intermediate **I**, followed by substitution of fluoride ligand by a formate anion to yield complex **II**. Decarboxylation of **II** generates the hydrido cobalt(II) intermediate, **III**. Subsequent ligand exchange between the hydrido H atom and the F atom of the perfluoroarenes produces the hydrodefluorination product, regenerating the starting Co(II) fluoride (Scheme 16).

Hydrodehalogenation of aryl bromides in the presence of cobalt porphyrin catalyst was achieved by Chan and coworkers.[37] The optimized reaction conditions, encompassing cobalt porphyrin catalyst and 50 equiv of KOH, at 200 °C in THF under nitrogen, were applied for hydrodehalogenation of few electron-rich and electron-poor aryl bromides (Scheme 17). Although yields were moderately good, substrate scope was mainly limited. Conducting the reaction in air using 2-propanol as the solvent and 4-bromoanisole as the model substrate resulted in the formation of anisole, only slightly lower yield than that obtained under a nitrogen atmosphere.



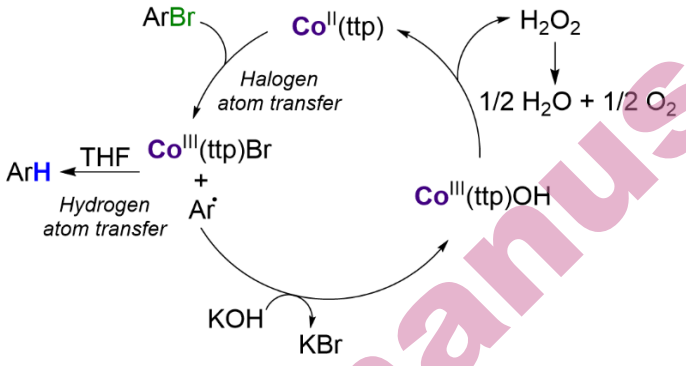
Scheme 16. Proposed mechanism of the catalytic hydrodefluorination.



Scheme 17. Substrate scope of aryl-bromides.

The reaction starts with Co^{II}(ttp) abstracting a bromine atom from ArBr, leading to the formation of aryl radical and Co^{III}(ttp)Br. Subsequently, the aryl radical abstracts a hydrogen atom from the solvent to produce ArH and Co^{III}(ttp)Br intermediate undergoes ligand substitution with KOH, yielding KBr and

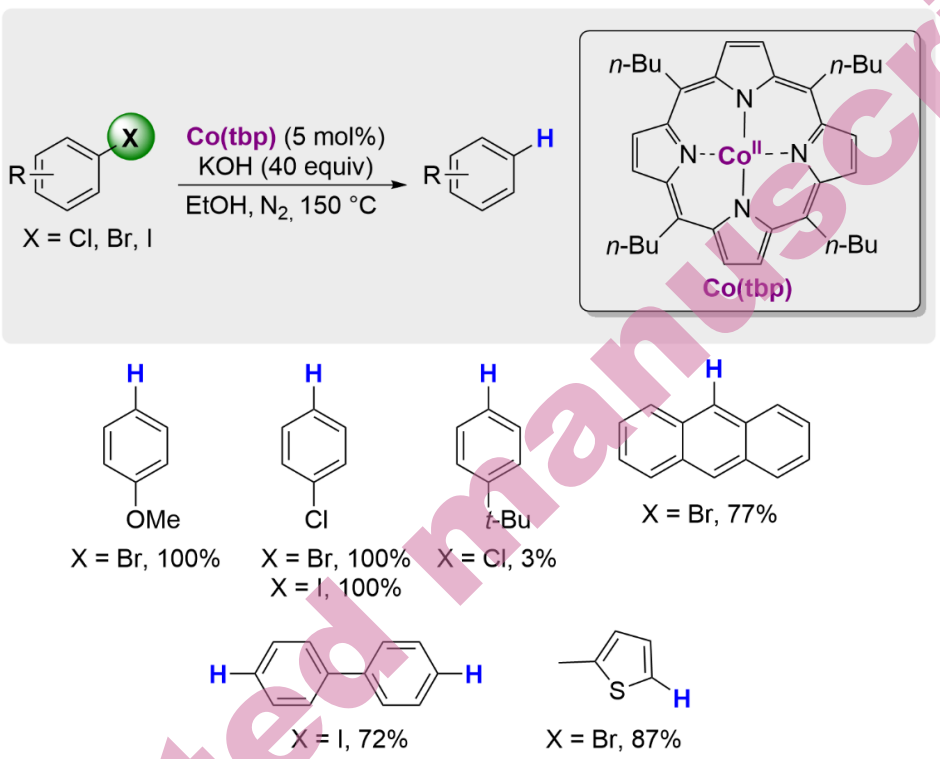
Co^{III}(ttp)OH. The Co^{III}(ttp)OH species then generates H_2O_2 and regenerate Co^{II}(ttp) via reductive elimination (Scheme 18).



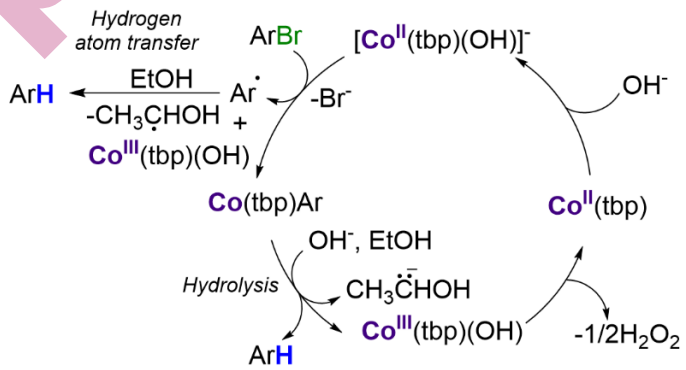
Scheme 18. Proposed reaction mechanism.

A few years later, the same group improved their method for the catalytic hydrodebromination reaction of aryl bromides in the presence of a cobalt porphyrin catalyst.[38] Replacing Co^{II}(ttp) with more electron rich Co^{II}(tbp) at lower temperature, in the less reactive hydrogen donating solvent (EtOH) resulted in a higher yield and broader scope. The limited reactivity is observed for the C-Cl bond suggests that aryl chlorides exhibit inertness towards hydrodechlorination under the optimized reaction conditions (Scheme 19).

They have also proposed a revised mechanism, that is based on single electron transfer. In strongly basic conditions, Co^{II}(tbp) coordinates with OH^- to form $[Co^{II}(tbp)(OH)]^-$, which transferes one electron to an aryl bromide, generating an aryl bromide radical anion. This radical anion undergoes rapid carbon-bromide bond cleavage to produce an aryl radical and a bromide anion. The aryl radical can abstract a hydrogen atom from EtOH, yielding the corresponding arene as the final product. Alternatively, the Co(tbp)aryl intermediate can undergo hydrolysis to yield the corresponding arene and Co^{III}(tbp)OH. The resullting Co^{III}(tbp)OH then undergoes reductive dimerization to regenerate Co^{II}(tbp) (Scheme 20).



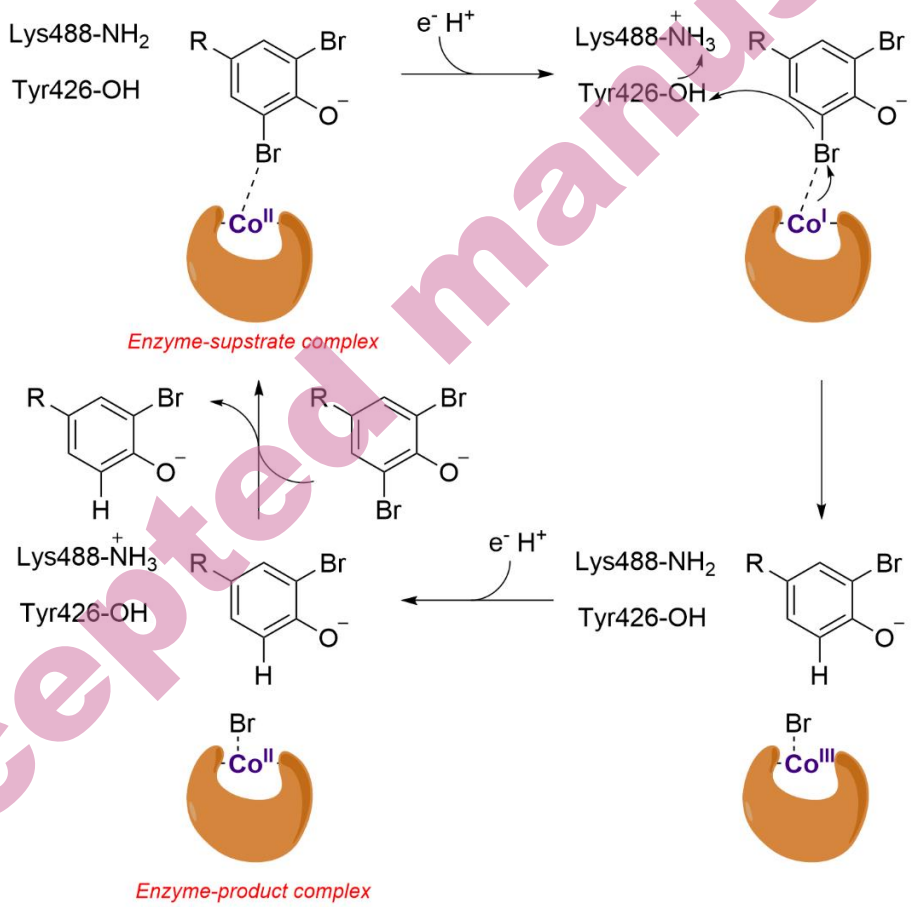
Scheme 19. Substrate scope of Co(tbp) catalyzed hydrodehalogenation.



Scheme 20. Catalytic cycle for Co^{II}(tbp) catalyzed hydrodebromination.

In 2015, Liao and coworkers proposed the reaction mechanism of debromination, catalyzed by the B_{12}-dependent reductive dehalogenase (NpRdhA), elucidated using the quantum chemical cluster approach with 2,6-

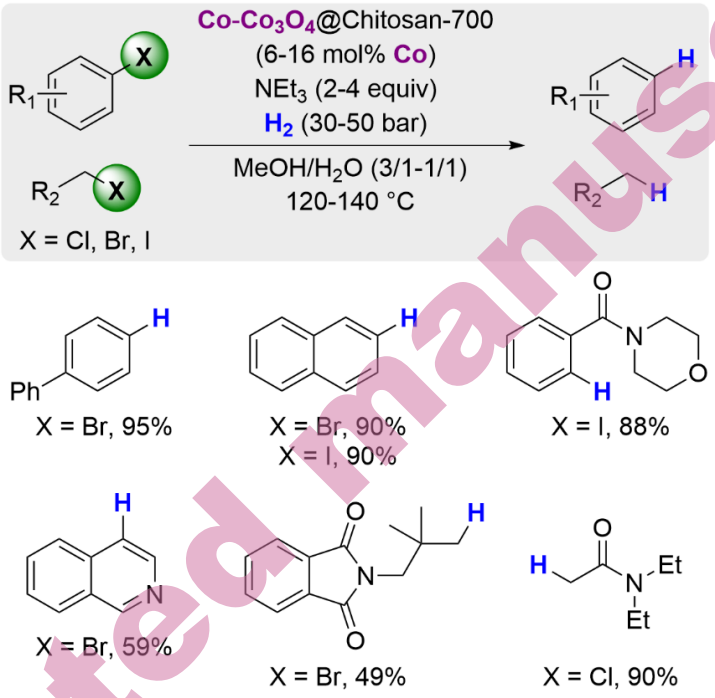
dibromophenolate as a model substrate (Scheme 21).[39] According to the proposed mechanism, the reaction proceeds through Co^{I}-initiated concerted dehalogenation for the reductive dehalogenase NpRdhA. They also demonstrated that reactivity in the dehalogenation reaction changes with various halogen substitutions (F, Cl, Br, I) and indicated the enzyme's inability to catalyze the defluorination of 2,6-difluorophenolate.



Scheme 21. Suggested reductive debromination mechanisms for NpRdhA.

Using molecular hydrogen as a green reducing agent, Beller and coworkers reported a method for hydrodehalogenation of alkyl and (hetero)aryl-halides in the presence of heterogeneous cobalt catalyst.[40] Synthesis of novel sustainable catalyst was based on the complexation of cobalt salt $Co(OAc)_2$ by chitosan (a polymer of D-glucosamine) followed by pyrolysis. The substrate scope was very broad; a range of alkyl, aryl, heteroaryl halides successfully underwent

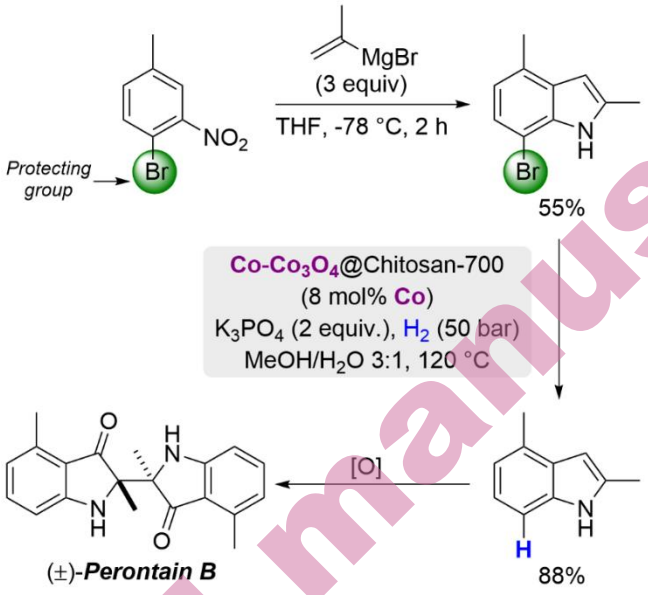
hydrodehalogenation in the presence of this new cobalt catalyst from cheap and readily available biowaste with good chemoselectivity (Scheme 22).



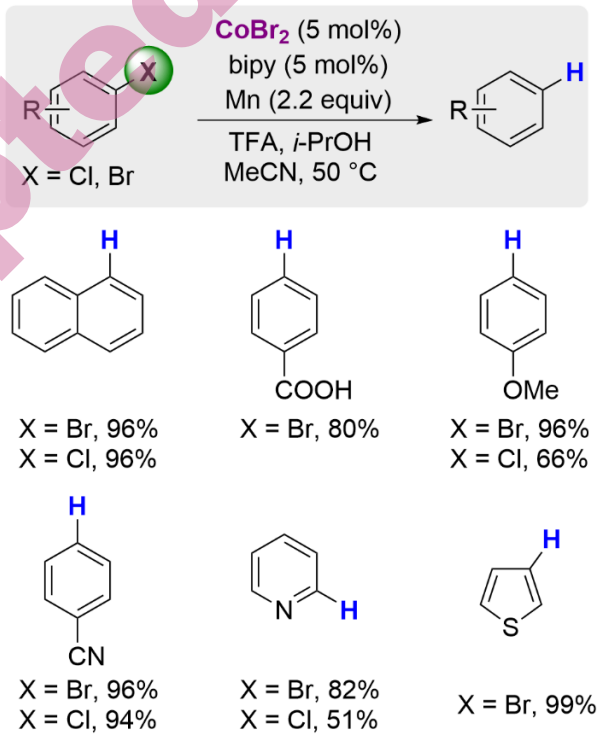
Scheme 22. Hydrodehalogenationof alkyl and aryl halides.

They demonstrated the utility of this method in the multistep synthesis of (±)-peronatin B alkaloid (Scheme 23) and in degradation of halogen containing pesticides (Metazachlor, Benodanil).

Dehalogenation of bromo- and chloro-aryl and -alkyl derivatives in the presence of $CoBr_2$, manganese as reductant, and bipyridine ligand, in acetonitrile at 50°C, and isopropanol as hydrogen donor, was explored by Gosmini and coworkers in 2021.[41] A range of aryl halides featuring both electron-withdrawing and electron-donating functional groups underwent successful dehalogenation (Scheme 24).



Scheme 23. Application in (±)-peronatin B alkaloid synthesis.



Scheme 24. Reactivity of aryl electrophiles.

In addition to the classic methods described previously, there have also been developments in the utilization of vitamin B_{12} and related bioinspired complexes as efficient catalysts for dehalogenation reactions. These compounds undergo chemical,[42] photochemical,[43] or electrochemical[44] reduction to form supernucleophilic cobalt species, which then reacts with alkyl and aryl halides to produce alkyl/aryl complexes, by the cleavage of C-X bond (Fig. 2.).[45]

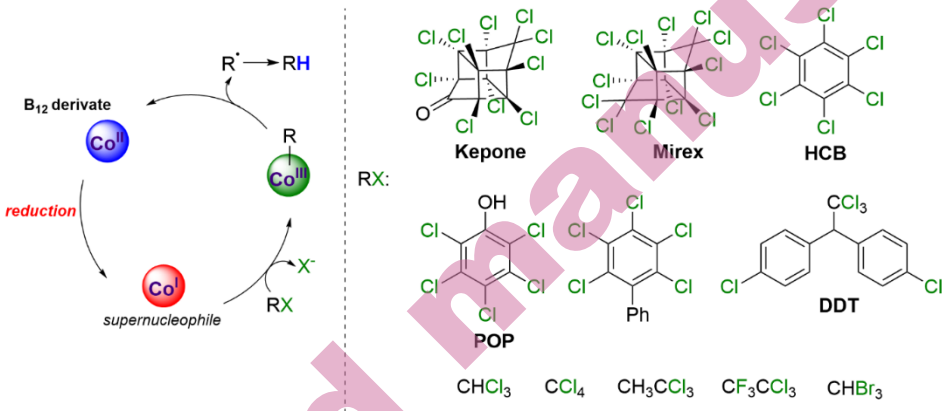


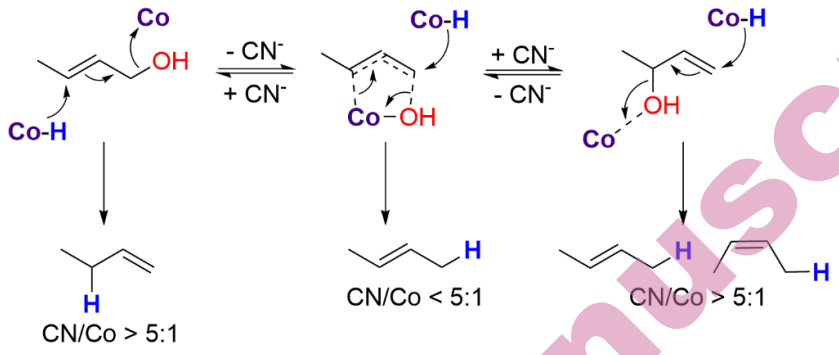
Fig. 2. Vitamin B_{12} derivatives as efficient catalysts for dehalogenation

DEOXYGENATION

Over the past few decades, the increasing costs associated with petroleum and other fossil fuels, both in financial, environmental, and societal terms, have underscored the need to turn to renewable resources for fuel and chemicals production. Biomass-derived materials have emerged as prime contenders for renewable chemical sources due to their abundance and ease of handling.[3] However, these materials are typically rich in oxygen, necessitating efficient deoxygenation processes. Therefore, it is necessary to continually develop new methodologies and catalytic systems for removing oxygen-containing functional groups (hydroxy[46], alkoxy[47], etc.).

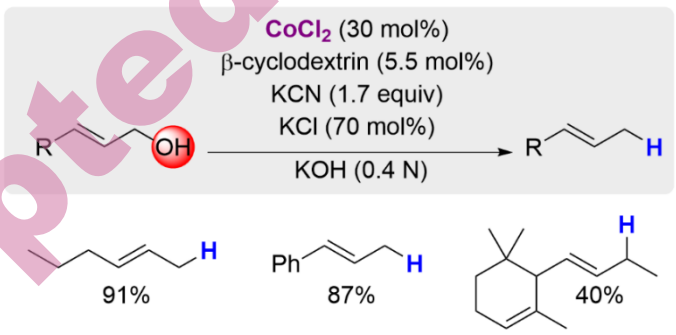
Dehydroxylation

In 1978, Funabiki and coworkers reported the use of the cobalt complex $HCo(CN)_5^{-3}$, formed *in situ* from cobalt(II) chloride and potassium cyanide under hydrogen atmosphere, as a catalyst for the deoxygenation of allylic alcohols.[48] According to the proposed concerted reaction mechanism, hydrogenation of the C=C bond was followed by elimination of the hydroxy group. However, the occurrence of double bond transposition is contingent upon the ratio of cyanide to cobalt, leading to the formation of a mixture of products (Scheme 25).



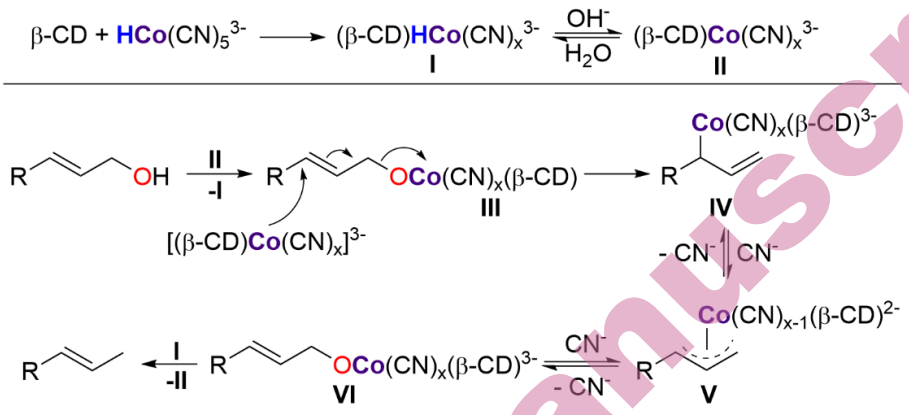
Scheme 25. Direct deoxygenation of allylic alcohols with *in situ* formed $HCo(CN)_5^{-3}$.

Later, in 1990 Jong-Tae Lee and Howard Alper demonstrated the deoxygenation of allylic alcohols using β-cyclodextrin as a phase transfer catalyst and hydridopentacyanocobaltate anion as a catalyst.[49] Catalytic deoxygenation of primary and secondary allylic alcohols was achieved in good yields affording olefins, however tertiary allylic alcohols did not undergo the reaction under these reaction conditions (Scheme 26).



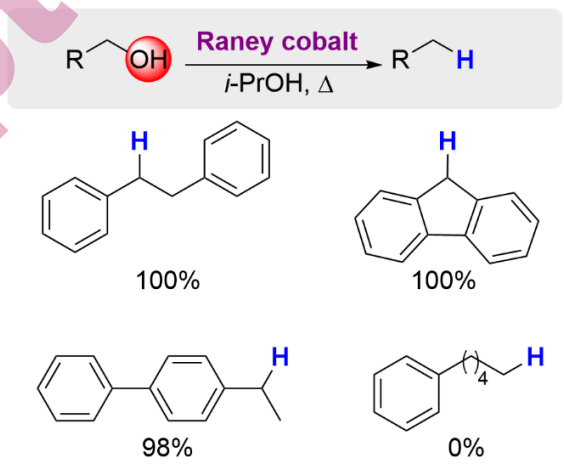
Scheme 26. Hydrogenolysis of allylic alcohols using $HCo(CN)_5^{-3}$ and β-cyclodextrin.

The advantage of this method is evident as no hydrogenation or shift of the double bond was observed. According to the proposed mechanism, the reaction of the adduct of β-cyclodextrin (β-CD) and $HCo(CN)_5^{-3}$ with the σ-allyl complex **VI** would yield the product and regenerate **II** (Scheme 27).



Scheme 27. Proposed reaction mechanism.

Mebane and coworkers in 2001 reported a novel method for deoxygenation of aromatic alcohols using Raney catalysts.[50] Raney cobalt was first utilized in this kind of transformation and demonstrates its effectiveness exclusively in catalyzing the deoxygenation of α-substituted alcohol (Scheme 28). Compared to Raney nickel, Raney cobalt is less reactive in transfer hydrogenolysis reactions. However, its advantage is reflected in the absence of ring reduction encountered during the deoxygenation of α-substituted alcohols containing two or more aromatic rings, which can occur with Raney nickel.

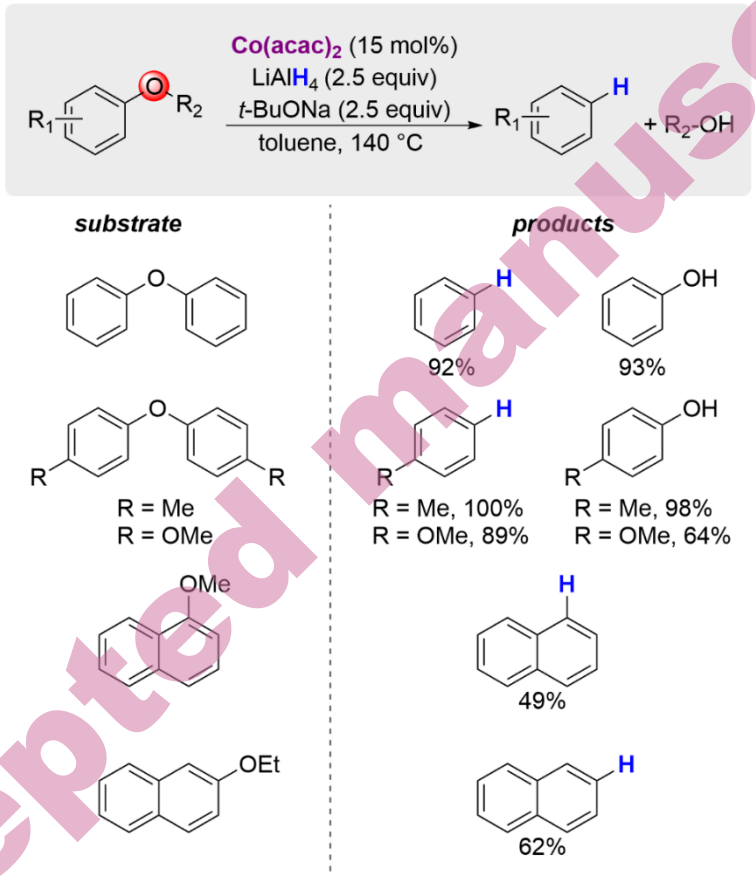


Scheme 28. Deoxygenation of α-substituted alcohols.

Deoxygenation of phenol ether

In 2014, Wang and coworkers demonstrated an efficient cobalt-catalyzed method for the reductive cleavage of inert aromatic C-O bonds with high

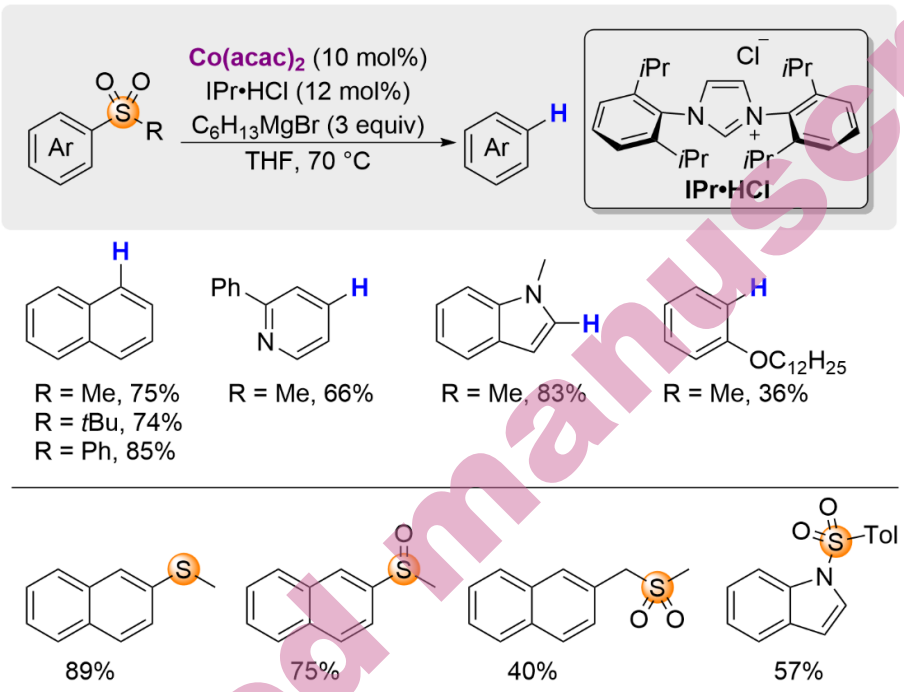
selectivity.[51] The desired products were obtained in good to moderate yields using airstable $Co(acac)_2$ as a catalyst (Scheme 29).



Scheme 29. Co-catalyzed reductive cleavage of various aromatic C-O bonds.

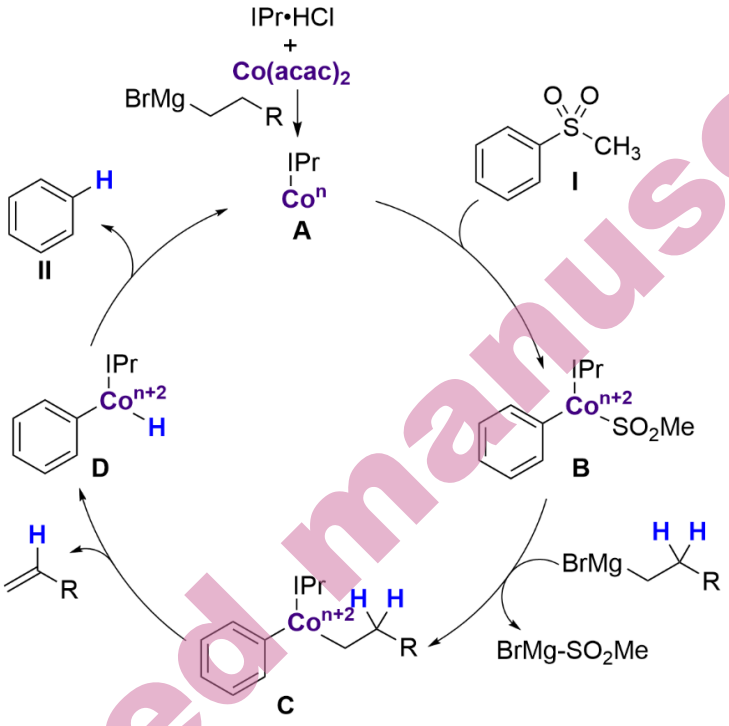
REDUCTIVE DESULFURIZATION

In 2018, Yorimitsu and colleagues developed a method for the reduction of aryl sulfones to produce the corresponding arenes using cobalt–NHC as a cataylst, and primary alkylmagnesium reagent as a hydride source.[52] Additionally, they demonstrated versatility by extending their methodology to a variety of organosulfur compounds, including alkenyl and benzyl sulfones, *N*-tosylindole, as well as aryl sulfide and sulfoxide derivatives (Scheme 30).



Scheme 30. Cobalt-calatyzed reduction of aryl sulfones and other sulfonyl compounds

The proposed reaction mechanism for the reduction of aryl methyl sulfones is presented in Scheme 32. In the presence of alkylmagnesium reagent, a low-valent Co-NHC complex **A** is formed. The oxidative addition of aryl methyl sulfone **I** leads to the formation of arylcobalt methanesulfinate **B**. Intermediate **B** then undergoes transmetalation with an alkylmagnesium reagent to produce alkylarylcobalt **C**, followed by subsequent *β*-hydride elimination and reductive elimination to yield arene **II**. The methanesulfinate anion generated as the leaving group might undergo reduction under the present highly reductive conditions, hence requiring an excess amount of alkylmagnesium reagent (Scheme 31).



Scheme 31. Plausible reaction mechanism.

CONCLUSION

Cobalt-catalyzed defunctionalization has emerged as a powerful tool in the field of organic synthesis, offering chemists efficiency and selectivity in the modification of complex molecules. Emerging defunctionalization strategies are poised to become integral to various energy production methods, such as the conversion of biomass into biofuels. Additionally, defunctionalization holds great importance in drug synthesis, converting environmentally hazardous molecules (such as pesticides) into less harmful forms and obtaining precursors for the polymer industry.

Acknowledgements: This research was financially supported by the Ministry of Science, Technological Development and Innovation of Republic of Serbia. Contract number: 451-03-66/2024-03/200288

И З В О Д

РЕАКЦИЈЕ ДЕФУНКЦИОНАЛИЗАЦИЈЕ КАТАЛИЗОВАНЕ КОБАЛТОМ

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Реакције дефункционализације од великог су значаја у модерној органској хемији. Често, функционална група може бити привремено присутна у молекулу као блокирајућа или заштитна група која се селективно може уклонити из једињења. У овом прегледном чланку хронолошки су описане методе за дефункционализацију органских молекула катализоване кобалтом и његовим комплексним једињењима. Такође, детаљно су приказани реакциони механизми ових трансформација као и примена у органској синтези.

(Примљено 15. марта; ревидирано 8. априла; прихваћено 9. априла 2024.)

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