CHEMICAL REVIEWS

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Selective Decarbonylation via Transition-Metal-Catalyzed Carbon–Carbon Bond Cleavage

Hong Lu,[§] Tian-Yang Yu,[§] Peng-Fei Xu, and Hao Wei*

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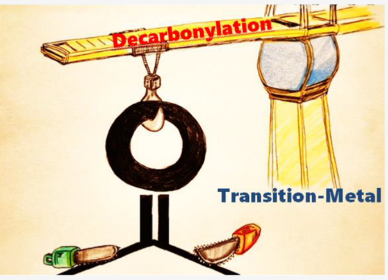
ABSTRACT: Transition-metal-catalyzed decarbonylation via carbon–carbon bond cleavage is an essential synthetic methodology. Given the ubiquity of carbonyl compounds, the selective decarbonylative process offers a distinct synthetic strategy using carbonyl groups as “traceless handles”. This reaction has been significantly developed in recent years in many respects, including catalytic system development, mechanistic understanding, substrate scope, and application in the synthesis of complex functional molecules. Therefore, this review aims to summarize the recent progress on transition-metal-catalyzed decarbonylative process, from the discovery of new transformations to the understanding of reaction mechanisms, to reveal the great achievements and potentials in this field. The contents of this review are categorized by the type of chemical bond cleavage in the decarbonylative process. The main challenges and opportunities of the decarbonylative process are also examined with the goal of expanding the application range of decarbonylation reactions.



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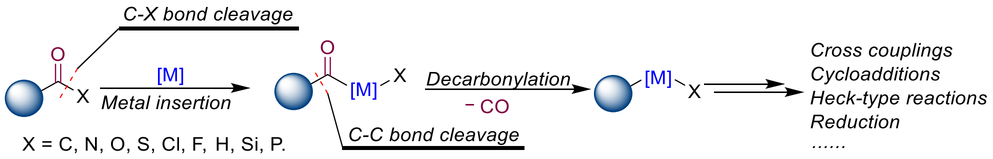
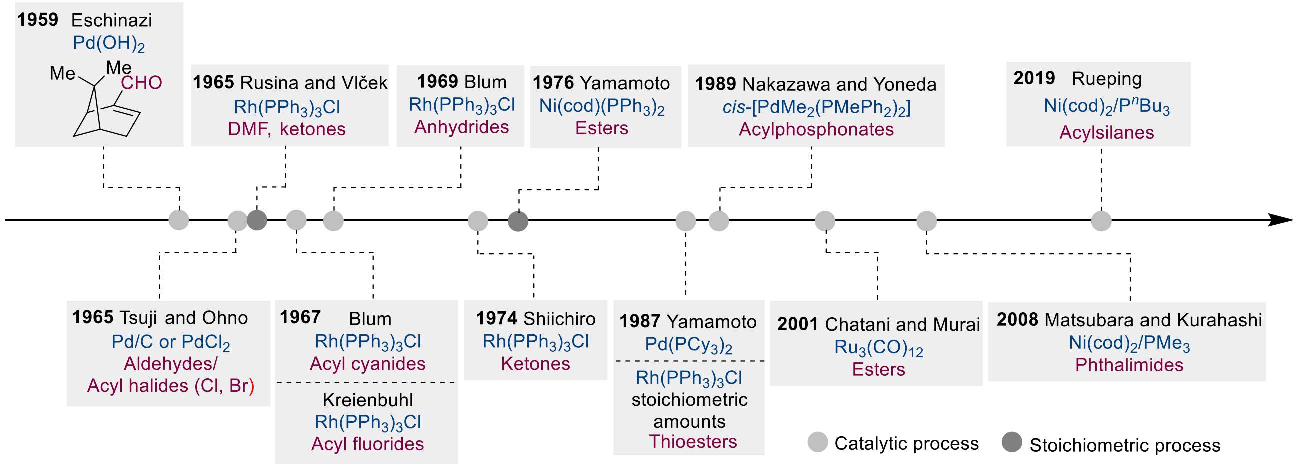
Scheme 1. General Procedure of Transition-Metal-Catalyzed Decarbonylation



Scheme 2. Chronological Evolution of Transition-Metal-Mediated/Catalyzed Decarbonylation



1. INTRODUCTION

Carbonyl functionalities (e.g., acyl chlorides, anhydrides, esters, amides, aldehydes, and ketones) comprise one of the most widespread and fundamental functional groups in organic compounds. Thus, these groups are found in different functional molecules in, among others, pharmaceuticals, organic materials, and polymers. Moreover, the C−C (O) bond can be easily cleaved because of its weaker C−C bond energy [the bond dissociation energies (BDEs) of $C_6H_5{-}CH_3$, $C_6H_5{-}CH_2CH_3$, $C_6H_5{-}C(O)H$, $C_6H_5{-}C(O)CH_3$, and $C_6H_5{-}C(O)OCH_3$ are approximately 102, 115, 97, 94, and 102 kcal/mol, respectively],[1] which make the transformation of carbonyl groups one of the central topics in organic chemistry.[2−10]

Modern chemical research has witnessed the development of acyl C−C[11−20] and C−heteroatom[21−40] bond activation mediated by transition metals. From the resulting acyl−metal intermediate, the reaction can diverge into two reaction pathways: a decarbonylative and a nondecarbonylative process. In particular, a decarbonylative process via C−C bond cleavage has recently emerged as a particularly efficient and powerful approach for chemical bond formation. The aryl- and alkyl-metal intermediates formed in the decarbonylation step can participate in numerous subsequent transformations (Scheme 1).[41−47] These prospects, together with the formation of less harmful waste products (CO is the major side product) and the ubiquity of carbonyl compounds, make decarbonylation a highly promising new manifold in organic chemistry.

Historically, the extrusion of CO from aldehyde was the pioneering approach for decarbonylation.[48] This approach was reported by Eschinazi in 1959 by using 5% $Pd(OH)_2$ on $BaSO_4$.[49,50] Substrate scope and kinetic studies were then explored independently by Hawthorne[51] and Hoffman.[52,53] In 1965, Tsuji and Ohno et al. also reported the use of palladium and rhodium complex for the decarbonylation of aldehydes as well as acyl halides.[54,55] In the same year, the stoichiometric decarbonylation of DMF and ketones using the Wilkinson's catalyst was reported by Rusina and Vlček.[56] The decarbonylation of acyl halides with palladium was limited to acyl chlorides and bromides; however, in 1967, Olah and Kreienbuhl demonstrated that acyl fluorides could be decarbonylated using the Wilkinson's complex.[57] Although less extensively studied than acyl halides, some other carbonyl compounds have also been decarbonylated by transition metals. A Rh-catalyzed decarbonylative process for acyl cyanides was reported by Blum et al. in 1967.[58] In 1969, a Rh-catalyzed decarbonylative conversion of benzoic anhydrides to fluorenones was also reported by the same group.[59] A few years later, Yamamoto et al. observed that stoichiometric amounts of nickel complex $Ni(cod)(PPh_3)_2$ can be inserted into the C(acyl)−O bond to promote decarbonylation of the ester.[60] In 1987, Pd-catalyzed decarbonylation of thiol esters was disclosed by Yamamoto et al.;[61] they also found that stoichiometric amounts of the Wilkinson's catalyst were capable of promoting this process. Nakazawa et al. reported a decarbonylative reaction for acylphosphonates in 1989:[62] *α*-ketophosphonates were activated with Pd and proceeded with decarbonylation. Following the seminal work described above, much effort has been focused on transition-metal-catalyzed decarbonylative transformations. A breakthrough was achieved by Murakami et al., who, motivated by their Rh-promoted decarbonylative process in 1994,[63] reported the catalytic decarbonylation of cyclobutanone.[64] In 2001, Chatani et al. realized the Ru-catalyzed decarbonylative conversion of esters with the assistance of a directing group.[65] In 2008, a Ni-catalyzed decarbonylative addition of phthalimides was first reported by Matsubara and Kurahashi et al.,[66] and advances in the catalytic decarbonylative transformations of acyl fluorides and acylsilanes have also been achieved by Schoenebeck and Rueping, respectively, in recent years (Scheme 2).[67,68]

At present, transition-metal-catalyzed decarbonylation has become a hot topic since 2010 because it provides a new and creative synthetic strategy using carbonyl groups as "traceless handles".[69] Although significant progress has been made over the past few decades, some pending issues, such as the reactivity, selectivity, and transformation efficiency, still need to be resolved urgently. Nowadays, research on the development of decarbonylation mainly focuses on four directions: (a) development of new types of reactions including the decarbonylative process; (b) application of "inert" substrates in decarbonylation reactions, such as decarbonylation of unstrained ketones and alkyl esters; (c) development of regio-, chemo-, and stereoselective decarbonylation reactions with high selectivity; and (d) development of new, cheap, and mild catalyst systems for high efficiencies.

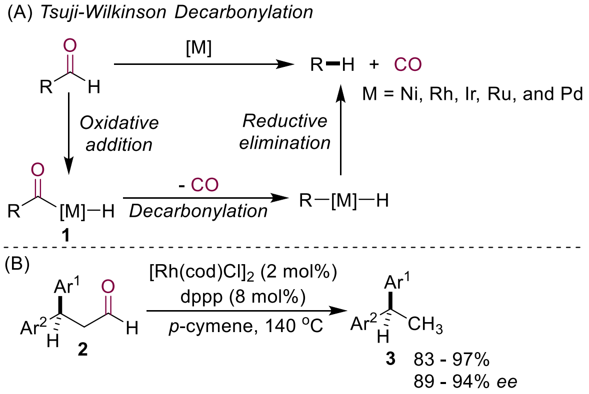
In this review, we mainly focus on recent advances in transition-metal-catalyzed selective decarbonylation reactions, from the discovery of new transformations to the understanding of reaction mechanisms, to reveal the great achievements and potentials in this field. Additionally, as background, a brief history on the seminal work is also presented. Transformations proceeding via radical-initiated[70,71] and photoinduced[72−76] decarbonylation have been covered before and fall out of the scope of this review. For a better discussion and understanding, this review is organized according to six major chemical bond cleavage types in the decarbonylative process: (1) C−H/C−C, (2) C−halide (Cl, F)/C−C, (3) C−O/C−C, (4) C−S/C−C, (5) C−N/C−C, and (6) two C−C bonds cleavages.

2. DECARBONYLATION WITH CLEAVAGE OF C(ACYL)−H/C(ACYL)−C BONDS

2.1. Tsuji−Wilkinson Decarbonylation

The decarbonylation of an aldehyde to its parent alkane is known as the Tsuji−Wilkinson decarbonylative process.[77,78] In such transformations, the oxidative addition of a transition metal (M) to an aldehyde C−H bond generates acyl-metal intermediate **1**; subsequent decarbonylation through C−C bond cleavage followed by reductive elimination leads to the corresponding products (Scheme 3A). In 1965, Tsuji and Ohno reported the first example of the Pd-catalyzed decarbonylation of aldehydes with Pd/C or $PdCl_2$ as the catalyst.[54] Since then, the decarbonylation of aldehydes has been accomplished by catalysts containing Rh,[78] Ni,[79] Rh,[80−83] Ir,[84−87] Ru,[88,89] and Pd.[90−93] This reaction allows for an aldehyde group to be used as a removable functional group and has consequently been widely used in organic syntheses. For example, Carreira et al. developed a strategy to form 1,1-diarylethane compounds in high yield and optical purity (Scheme 3B).[94] Aldehydes **2** were used as removable steering groups for the preparation of optically active building blocks. After decarbonylation, the optical purity of the afforded products **3** was unchanged from that of the starting aldehydes.

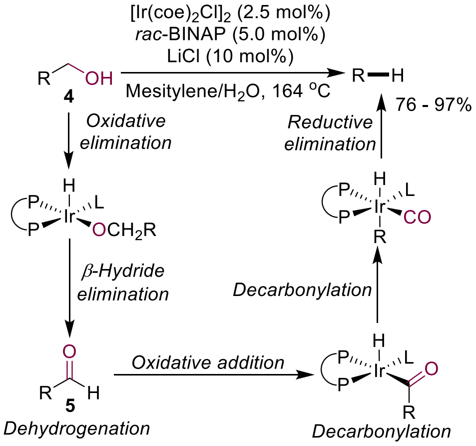
Scheme 3. Transition-Metal Catalyzed Tsuji−Wilkinson Decarbonylation



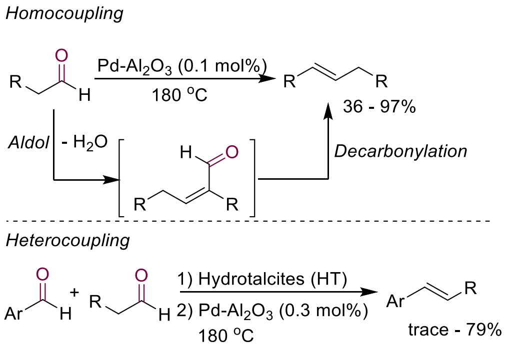
Madsen et al. reported a sequence of consecutive dehydrogenation and decarbonylative processes of primary alcohols.[95] They proposed a mechanism comprising two catalytic processes (Scheme 4): the first catalytic process was the Ir-catalyzed dehydrogenation of alcohols **4** to the corresponding aldehydes **5**, while the second process was the Ir-catalyzed decarbonylation reaction. Subsequently, related processes using a Pd catalyst were reported by Maiti et al.,[96] which allowed the dehydroxymethylation of aryl substrates as well as the extension of this protocol to heteroaromatic and aliphatic moieties.

On the basis of the observation that *α*,*β*-unsaturated aldehydes decarbonylate faster than aromatic and saturated aliphatic aldehydes, Voutchkova-Kosta et al. achieved the olefination of carbonyls via tandem aldol condensation−decarbonylation of aldehydes using recyclable supported Pd catalysts (Scheme 5).[97] The process was most effectively facilitated by multifunctional Pd catalysts, such as $Pd-Al_2O_3$, Pd−HT (hydrotalcites), and Pd−MgO, where the relative rates of the two steps was dependent on the catalytic support. The process could be used to obtain olefins from both

Scheme 4. Ir-Catalyzed the Consecutive Dehydrogenation and Decarbonylation of Primary Alcohols



Scheme 5. Pd-Catalyzed Aldol-Decarbonylative Coupling of Aldehydes

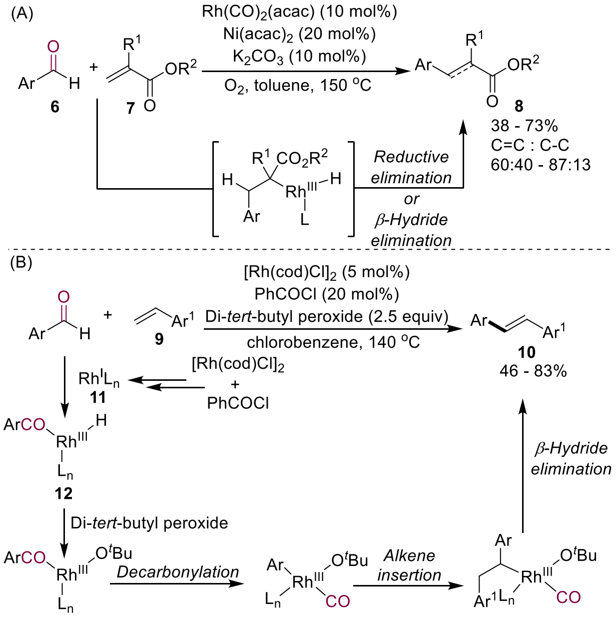


homocoupling of aliphatic aldehydes and heterocoupling of aliphatic and aromatic aldehydes.

2.2. Decarbonylative Insertion and Addition Reactions

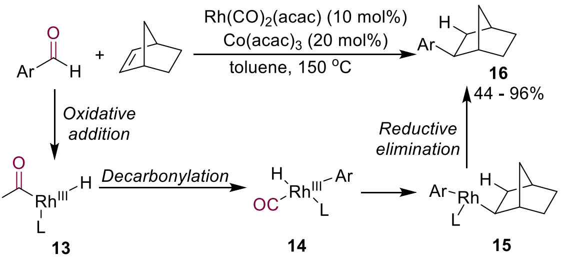
The Mizoroki–Heck reaction is a general and convenient method for arylation of olefinic compounds. Since the pioneering report in 1999,[98] Li et al. extensively studied decarbonylative Mizoroki–Heck coupling of aldehydes. In 2009, they revealed that treatment of aromatic aldehydes **6** with unsaturated carbonyl compounds **7** together with catalytic amounts of $(CO)_2Rh(acac)$ leads to the arylated product **8**. Furthermore, a small amount of $Ni(acac)_2$ was found to increase the reaction yield (Scheme 6A).[99] Here, moderate selectivity for the Mizoroki–Heck and conjugate addition products were observed. This was attributed to the competition between the reductive and β-hydride elimination of the catalyst. Related improvements to Rh-catalyzed decarbonylative coupling was reported by Yang et al. (Scheme 6B).[100] With the replacement of carbonyl compounds with aryl olefins **9**, a variety of 1,2-disubstituted alkenes **10** could be obtained in moderate to good yield with good regio- and *E*-selectivity. Mechanistic investigations revealed that the catalyst precursor $[Rh(cod)Cl]_2$ first reacted with PhCOCl and aryl olefins **9** to generate the activated rhodium catalyst, **11**, which underwent oxidative addition with an aldehyde to yield aroyl rhodium hydride **12**. Then, the hydride was oxidized by di-*tert*-butyl peroxide and subjected to subsequent decarbonylation. Alkene insertion and β-hydride elimination yielded the Heck-type coupling product **10**.

Scheme 6. Rh-Catalyzed Decarbonylative Mizoroki–Heck Reactions



In 2010, Li et al. also reported the successful decarbonylative coupling of aldehydes and norbornene analogues (Scheme 7).[101] In this process, β-hydride elimination of intermediate **15** was suppressed, because of the lack of coplanarity upon catalyst elimination. The proposed mechanism comprised rapid oxidative addition of Rh with the aldehyde C–H bond to produce acylrhodium hydride **13**, which then underwent decarbonylation to afford arylrhodium hydride **14**. Insertion of norbornene was followed by reductive elimination to deliver product **16**.

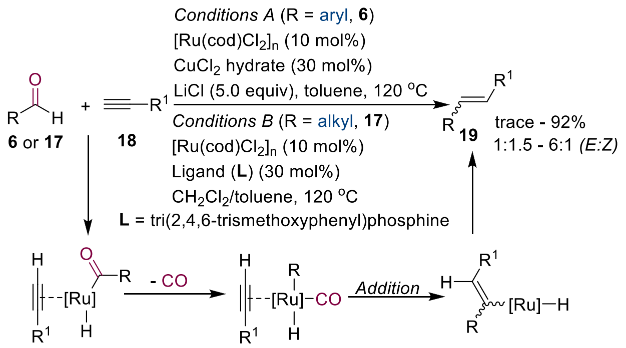
Scheme 7. Rh-Catalyzed Decarbonylative Coupling of Aldehydes and Alkenes



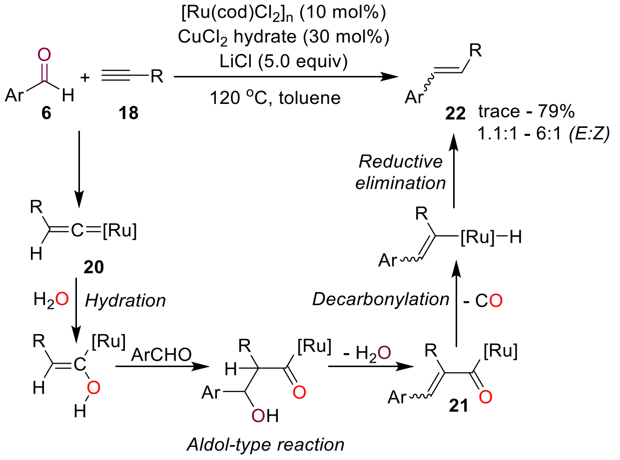
Alkynes represent another type of unsaturated moieties for use in decarbonylative alkenylation reactions. In 2009, Li et al. reported a Ru-catalyzed decarbonylative addition between aromatic aldehydes **6** and terminal alkynes **18** to produce 1,2-disubstituted alkenes **19** (Scheme 8, conditions A).[102] This work was further extended to aliphatic aldehydes **17** by using tri(2,4,6-trismethoxyphenyl)phosphine as the ligand (Scheme 8, conditions B).[103] A decarbonylative addition mechanism was proposed for both processes.

Notably, a revised mechanism was proposed recently by Li and Moitessier, via a combination of computational investigations and isotope-labeling experiments (Scheme 9).[104] On the basis of detailed mechanistic studies, instead of the insertion of the C(acyl)–H bond of aldehyde **6**, the Ru catalyst

Scheme 8. Ru-Catalyzed Decarbonylative Addition of Aldehydes to Terminal Alkynes



Scheme 9. Decarbonylative Addition of Aldehydes to Terminal Alkynes

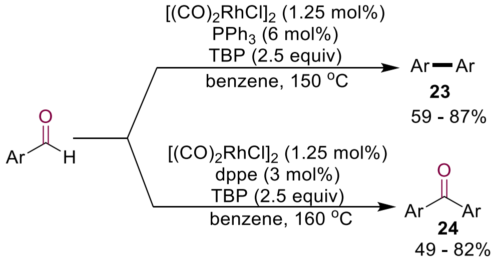


was considered to first react with alkyne **18** to generate ruthenium−vinylidene intermediate **20**. Subsequent hydration of **20** followed by aldol-type reaction with aldehyde **6** produced intermediate **21**, which underwent decarbonylation and reductive elimination to release product **22**. Notably, the aldehyde carbonyl was released by the formation of water in the process of the aldol-type reaction.

2.3. Decarbonylative Coupling Reactions

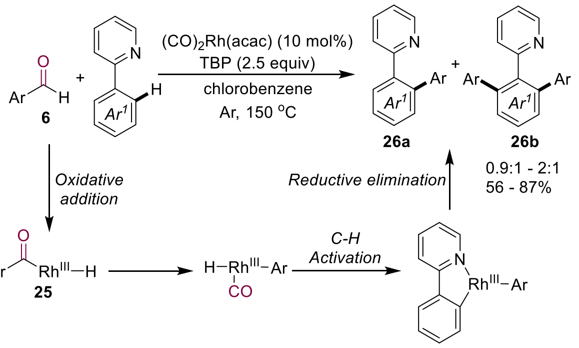
Aldehydes have also been used as arylating agents via a decarbonylative coupling strategy. An interesting homocoupling of aromatic aldehydes under Rh-catalyzed conditions was reported by Li et al. (Scheme 10).[105] Notably, the decarbonylative process could be controlled by the nature of the ligands. Thus, when PPh$_3$ was employed, the reaction formed biaryl product **23** in good yield. On the other hand, under similar reaction conditions, the bidentate ligand 1,2-bis(diphenylphosphino)ethane (dppe) afforded biaryl ketone **24** as the major product.

Scheme 10. Rh-Catalyzed Decarbonylative Homocoupling of Aromatic Aldehydes



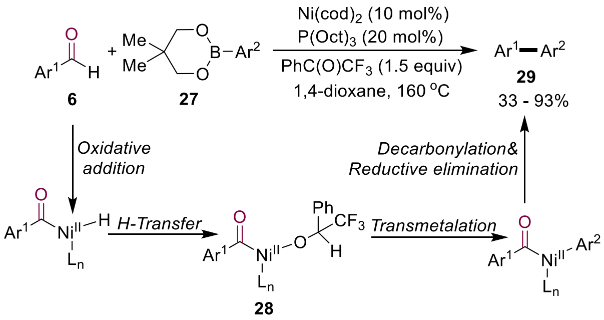
Li et al. also discovered that aromatic aldehydes could undergo decarbonylation when used as coupling partners in Rh-catalyzed C−H functionalization (Scheme 11).[106] Here, exposure of aldehyde **6** to a Rh(I) system led to species **25** via oxidative addition. Extrusion of CO was then followed by directing-group-assisted C−H bond activation and reductive elimination to afford the arylated and biarylated products (**26a** and **b,** respectively).

Scheme 11. Rh-Catalyzed C−H Functionalization via Decarbonylative Coupling of Aldehydes



The decarbonylative Suzuki−Miyaura coupling of aldehydes has also been realized. Very recently, Rueping et al. reported the decarbonylative coupling between aldehydes **6** and aryl boronic esters **27** catalyzed by nickel (Scheme 12).[107]

Scheme 12. Ni-Catalyzed Decarbonylative Suzuki−Miyaura Coupling of Aldehydes

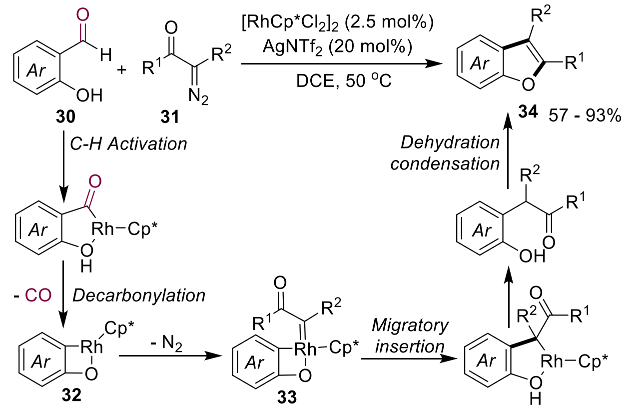


Trifluoroacetophenone could be used as a suitable H-acceptor to enable the transmetalation with the aryl boronic ester while suppressing the decarbonylation reductive coupling pathway. Density functional theory (DFT) calculations combined with experimental data suggested that the catalytic cycle involved the oxidative addition of the aldehyde C(acyl)−H bond. Subsequent hydrogen transfer led to **28**. Finally, transmetalation with aryl boronic ester **27** followed by decarbonylation and reductive elimination afforded product **29**.

2.4. Decarbonylative Cyclization Reactions

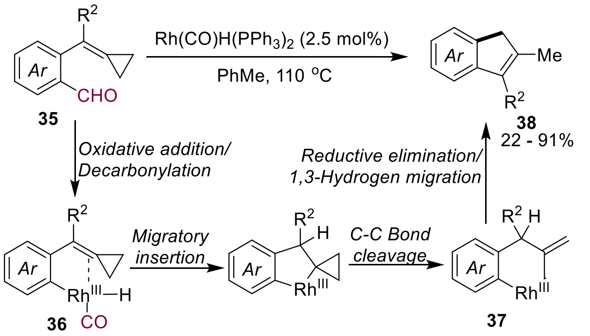
The application of the aldehyde decarbonylation strategy in cyclization reactions has been further explored in recent years. The prominent advantage of such cyclization reactions is that they can be used in annulation at specific sites via selective decarbonylation. In 2016, Yao and Lin reported the Rh-catalyzed decarbonylative annulation of salicylaldehydes **30** with diazo compounds **31**.[108] As illustrated in Scheme 13, a sequential C−H activation and decarbonylative process of the salicylaldehydes generated oxa-metallacycles **32**. These were then trapped by diazo compounds to form Rh−carbene complex **33**. Subsequent migratory insertion and intramolecular dehydration condensation yielded benzofuran **34**. Notably, complementary regioselectivity was obtained as a result of the *in situ* decarbonylation orientation effect.

Scheme 13. Rh-Catalyzed Annulation between Salicylaldehydes and Diazo Compounds



Shi et al. have demonstrated the intramolecular decarbonylative cyclization reaction of *ortho*-formyl group-tethered alkylidene cyclopropanes **35** (Scheme 14).[109] The mechanism commenced with the conversion of an aldehyde to Rh−H species **36** via decarbonylative oxidative addition. Migratory insertion was followed by C−C bond cleavage to provide allylic rhodium **37**. Subsequently, reductive elimination and 1,3-hydrogen migration provided the corresponding 2-methylindene **38**. The proposed mechanism was supported by the control and deuterium labeling experiments on a related substrate.

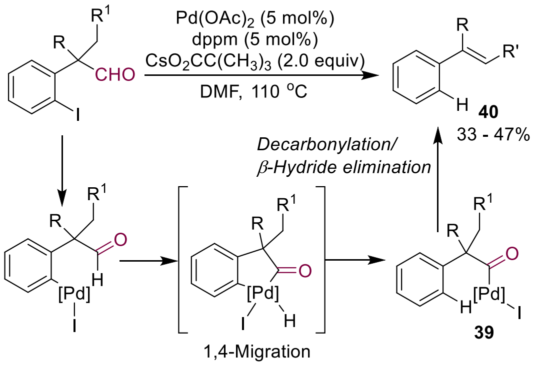
Scheme 14. Intramolecular Decarbonylative Cyclization Reaction



2.5. Retro-Hydroformylation-Type Reactions

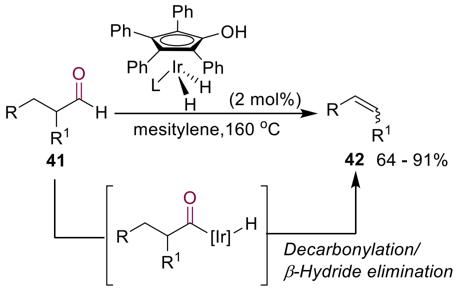
Hydroformylation, a reaction comprising the addition of carbon monoxide and dihydrogen to compounds with unsaturated moieties, is a well-established process.[110] The reverse process, retro-hydroformylation, can also prove useful in modifying complex molecules for pharmaceutical research.[111] In 2009, Larock et al. reported the distinct activation process of an aldehyde (Scheme 15).[112] Unlike in the direct insertion of a transition metal into a C−H bond of an aldehyde, acylpalladium intermediate **39** could be formed as a result of 1,4-migration of palladium from the aryl to acyl position. Subsequent decarbonylation and *β*-hydride elimination afforded the corresponding olefin **40**. Recently, Martin et al. reported that the scope of substrates in this transformation could be significantly expanded by using aryl bromides as the substrates and 1,3-dicyclohexylphosphinepropane bis(tetrafluoroborate) as the ligand, with low palladium catalyst loadings.[113]

Scheme 15. Pd-Catalyzed Retro-Hydroformylation Type Reactions



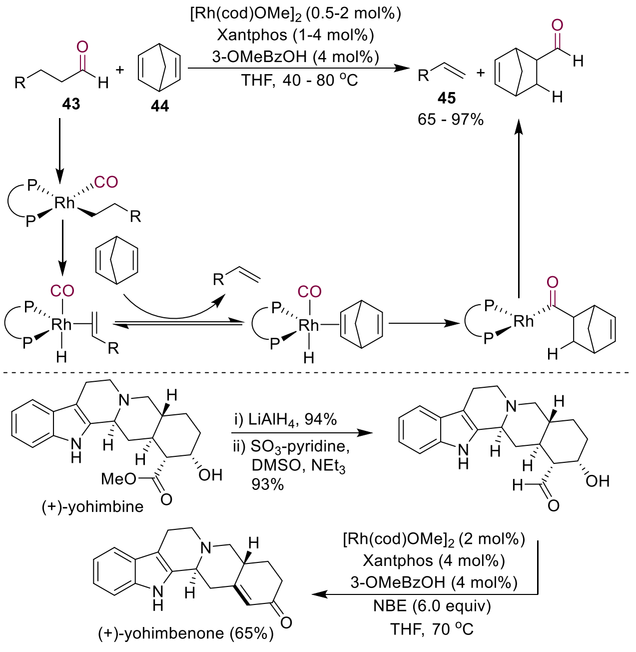
The retro-hydroformylation reaction triggered by directed insertion into an aldehyde C−H bond has been realized by Nozaki et al. (Scheme 16).[114] In 2015, they reported an Ir-catalyzed retro-hydroformylation process for the degradation of aliphatic aldehydes **41** into the corresponding alkenes **42** in moderate yield with good chemo- and stereoselectivities. The deuterium-labeling and control experiments suggested that the probable mechanism involved oxidative addition of the aldehyde C−H bond to the iridium catalyst followed by decarbonylation and *β*-hydride elimination.

Scheme 16. Ir-Caralyzed Retro-Hydroformylation Reaction



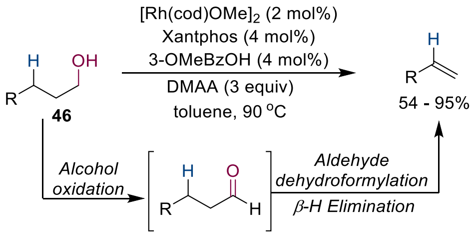
In 2015, Dong et al. developed a transfer hydroformylation reaction for the conversion of aliphatic aldehydes into the corresponding alkenes by transferring a hydrogen atom and a formyl group to a strained alkene (Scheme 17).[115] In this process, the key for the reaction to proceed was proposed to be the use of strained alkenes, such as norbornadiene **44**, as an effective hydrogen and formyl-group acceptor. The use of a Rh/Xantphos catalytic system allowed the activation of aldehyde **43** C−H bonds to trigger C−C bond cleavage and generate products **45** at low loadings (0.3−2 mmol %) and temperatures (22−80 °C). The chemistry was also applied to the synthesis of (+)-yohimbenone. Recently, this group expanded the scope of the process to primary alcohols **46** by

Scheme 17. Rh-Catalyzed Dehydroformylation of Aldehydes by Transfer Hydroformylation



the combination of alcohol oxidation and aldehyde dehydroformylation (Scheme 18).[116] With the use of *N*,*N*-dimethylacrylamide (DMAA) as an efficient acceptor for transfer hydrogenation, excellent efficiencies and selectivities were achieved for a broad range of alcohols. These reactions present a high proven synthetic potential exemplified by their applications to the two-step semisynthesis of (+)-yohimbenone.

Scheme 18. Rh-Catalyzed Oxidative Dehydroxymethylation



3. DECARBONYLATION WITH CLEAVAGE OF THE C(ACYL)−CL/C(ACYL)−C BONDS

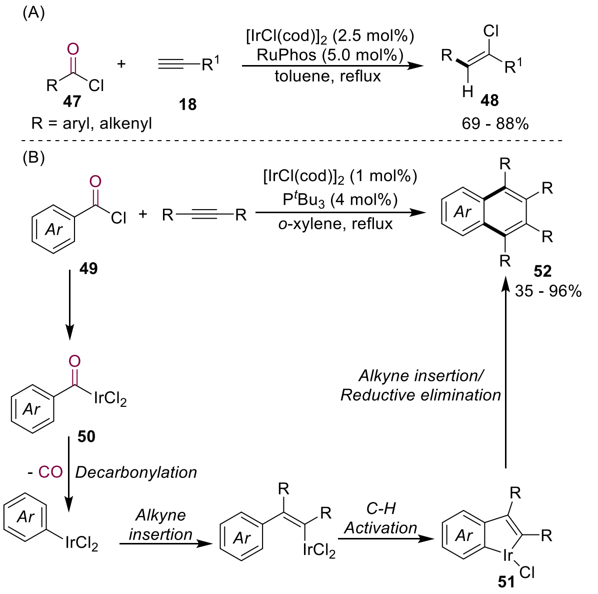
Because of their facile oxidative addition to metal centers, acyl chlorides have a long history in the decarbonylative process. In this approach, metal insertion into the active C(acyl)−Cl bond results in the acyl−M−Cl intermediate, which undergoes decarbonylation for subsequent functionalization. As early as 1966, it was shown that acyl chlorides could react with chlorotris(triphenylphosphine)rhodium (Wilkinson's catalyst), whereby the generated complex smoothly undergoes decarbonylation to form the corresponding olefin, alkyl, or aryl chloride product.[117] Subsequent mechanistic and kinetic studies by Stille and Regan confirmed the catalytic cycle through the isolation of the corresponding acyl and alkyl intermediates.[118] Acyl chlorides have become the most commonly used reagents for transition-metal-mediated C−C bond coupling, since their first reported use by Chiusoli et al. in 1977, wherein the decarbonylated monomer was isolated as the side product under Ni-catalyzed conditions.[119] Following these seminal works, many other historical studies have been summarized,[14,43] with the focus herein on a selection of recent methodologies.

3.1. Decarbonylative Addition and Coupling Reactions

3.1.1. Alkenylation and Alkynylation.

Building on earlier work of the Rh-catalyzed decarbonylative addition of aroyl chlorides,[120] Tusji et al. presented the Ir-catalyzed decarbonylative addition of acyl chlorides **47** with alkynes **18** for the synthesis of (*Z*)-vinyl chlorides **48** with high regio-and stereoselectivities (Scheme 19A).[121] Although no catalytic cycle was proposed, stoichiometric experiments indicated that oxidative addition followed by decarbonylation and insertion of the alkyne might be a plausible mechanism. Later, Miura et al. reported the decarbonylative cyclization of acyl chlorides **49** to produce the naphthalene and anthracene derivatives **52** (Scheme 19B).[122] At the initial generation stage of acyl−Ir−Cl intermediate **50**, decarbonylation and alkyne insertion combined with C−H activation afforded intermediates **51**. Subsequent alkyne insertion to **51** and reductive elimination afforded products **52**.

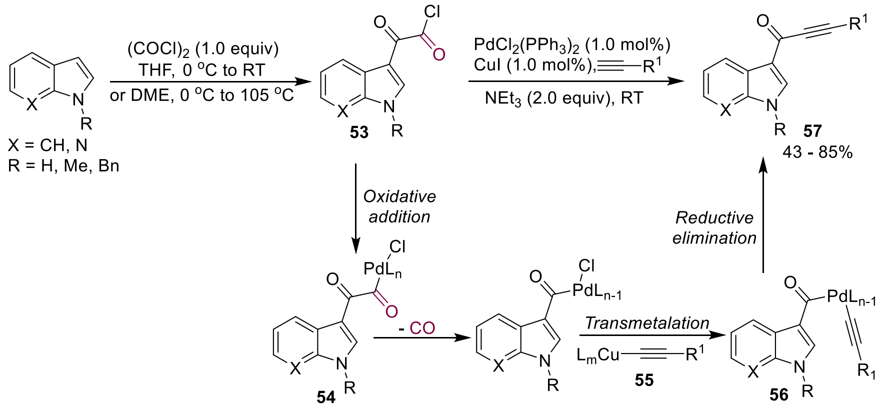
Scheme 19. Ir-Catalyzed Decabonylative Addition of Aroyl Chlorides to Alkynes



An alternative alkynyl coupling using α-dicarbonyl chlorides was achieved by Müller et al., where indole-3-glyoxylyl chlorides **53** were coupled with terminal alkynes to produce alkynones, using Pd(OAc)$_2$ and CuI as cocatalysts (Scheme 20).[123,124] The proposed mechanism involved the initial oxidative addition of Pd to the C(acyl)−Cl bond of **53** to form adduct **54**, which underwent decarbonylation and transmetalation with copper acetylide **55** to form acyl-alkynyl-Pd complex **56**; subsequent reductive elimination afforded product **57**. A one-pot strategy with the *in situ* formation of indole-3-glyoxylyl chlorides was also achieved.[123,124]

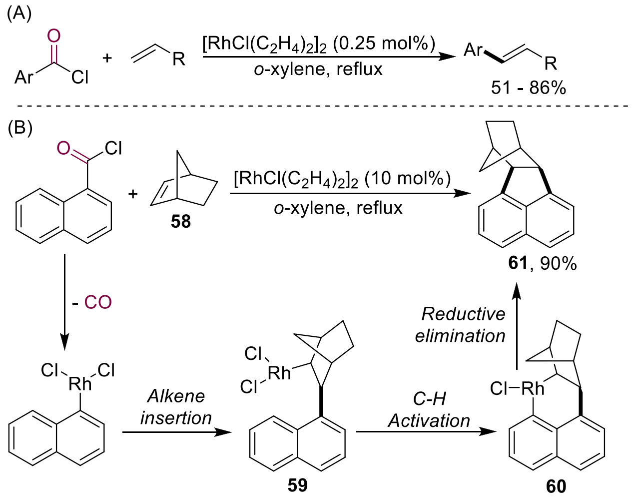
In terms of C−C bond forming reactions using the decarbonylative strategy, alkenes have also proved to be practicable coupling partners. The first decarbonylative Heck reaction of acyl chlorides was discovered by Blaser and

Scheme 20. Pd-Catalyzed Decarbonylative Sonogashira Coupling of α-Dicarbonyl Chlorides and Alkynes



Spencer.[125] In 2003, Miura et al. carried out a Rh-catalyzed Mizoroki−Heck reaction of acyl chlorides under base- and ligand-free conditions (Scheme 21A).[126] Interestingly, when bicycloalkenes **58** were used as the coupling partners, intermediated **59** underwent C−H activation instead of β-hydride elimination to form intermediate **60**, which in turn underwent reductive elimination to afford the fluoranthene derivatives **61** (Scheme 21B).[127] Pd-catalytic systems were later proven to be available for the Mizoroki−Heck reaction for acyclic alkenes.[128]

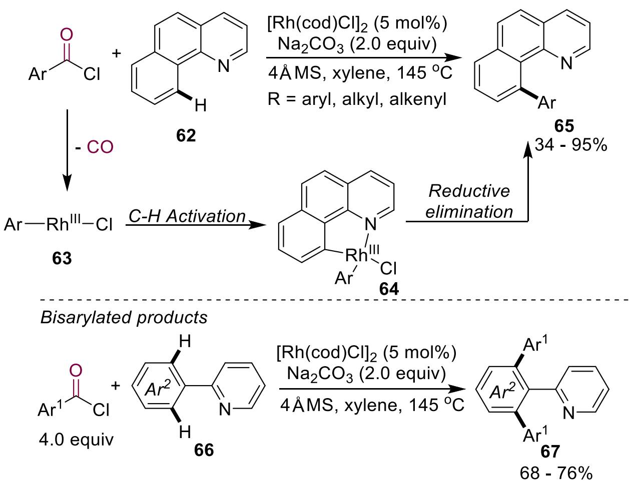
Scheme 21. Rh-Catalyzed Decarbonylative Mizoroki−Heck Reaction



3.1.2. C−H Functionalization.

By combining the decarbonylation of acyl chlorides with C−H bond activation, Yu et al. reported a Rh-catalyzed chelation-assisted C−H functionalization strategy using acyl chlorides as the coupling partners (Scheme 22).[129] In this process, aryl-chlororhodium(III) intermediate **63** reacted with arene **62** to afford intermediate **64** with assistance of pyridyl directing-groups. Subsequently, reductive elimination of **64** released the desired arylated product **65**. The bisarylated products **67** could also be obtained using *N*-heteroaromatic biaryls **66** as the substrates. Subsequently, Yu et al. reported that cinnamoyl chlorides could be used for C−H alkenylation.[130] Notably, cinnamic anhydrides are also compatible under the same conditions.

Scheme 22. Rh-Catalyzed Decarbonylative C−H Functionalization

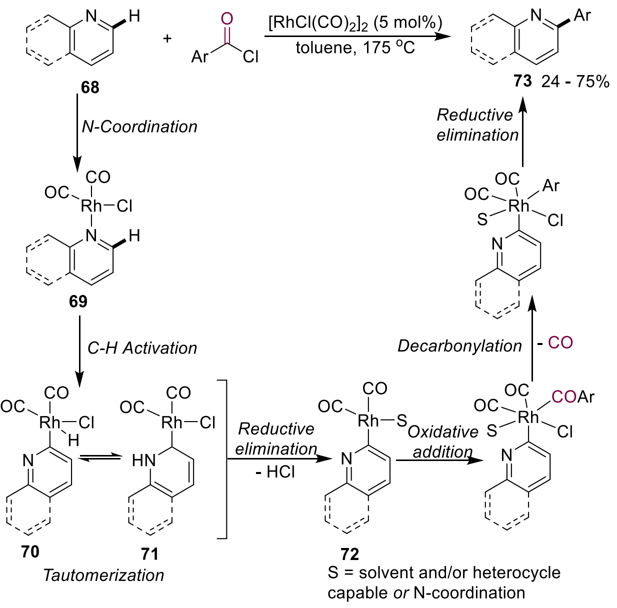


A distinctive decarbonylative C−H functionalization of aroyl chlorides via a nondirecting group strategy was reported by Bergman and Ellman (Scheme 23).[131] The proposed mechanism involved the nitrogen coordination of 2-substituted pyridine **68** to the Rh catalyst. The generated intermediate **69** then underwent *ortho*-C−H activation, tautomerization, and reductive elimination to form intermediate **72**. Subsequent oxidative addition and decarbonylation followed by reductive elimination generated the desired product **73**. Notably, ortho-substitution was necessary for the success of the arylation. This was attributed to the unfavorable steric interactions of the *N*-bound complex of the ortho-substituted pyridines, which accelerated the equilibrium ratio of complexes **70** and **71** relative to that of complex **69**.

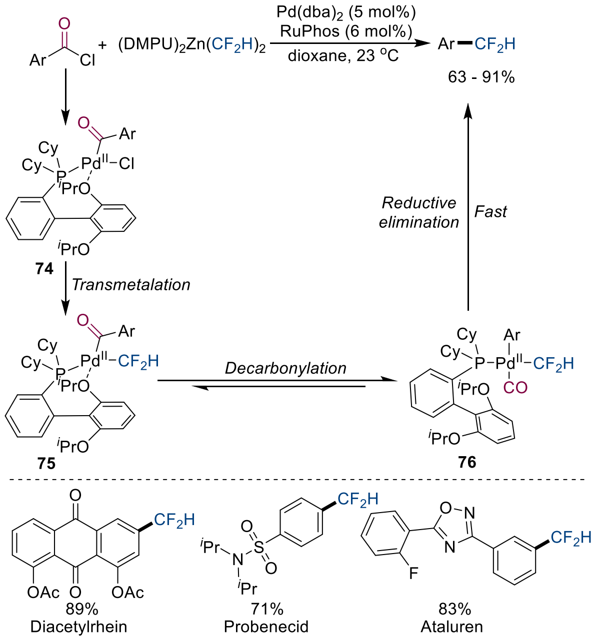
3.1.3. Decarbonylative Difluoromethylation and Cyanation.

Recently, a new method for the direct synthesis of difluoromethylated arenes has been achieved from the decarbonylation of acyl chlorides (Scheme 24).[132] This synthesis provides a facile decarbonylative coupling at room temperature. The mechanistic studies revealed that an open coordination site of RuPhos-ligated complex **74** was curial for transmetalation under mild conditions, while fast reductive elimination of difluoromethyl−Pd(II) intermediate **76** facilitated reversible decarbonylation of **75** to generate intermediate **76**. The significance of this report is the modification of acid-

Scheme 23. Rh-Catalyzed Decarbonylative Arylation of Azines



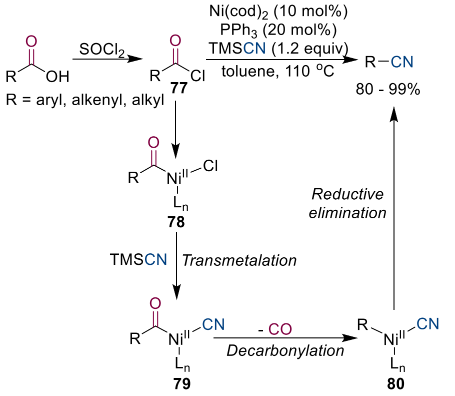
Scheme 24. Pd-Catalyzed Decarbonylative Difluoromethylation of Acyl Chlorides



containing drugs with broad functional group tolerance, such as diacetylrhein, probenecid, and ataluren.

Acyl chloride coupling with trimethylsilyl cyanide is also active under Ni-catalyzed conditions. An interesting decarbonylative cyanation example was recently reported by Nishihara et al. (Scheme 25),[133] whereby the *in situ* preparation of acyl chlorides **77** from carboxylic acids further expanded the practicability of this reaction. Detailed mechanistic studies clarified the occurrence of the transmetalation of acyl(chloro)-nickel(II) **78** to produce complex **79**, which underwent decarbonylation to form intermediate **80** for subsequent reductive elimination. Here, the weaker coordinating PPh_3 ligand was considered to facilitate both decarbonylation and reductive elimination.

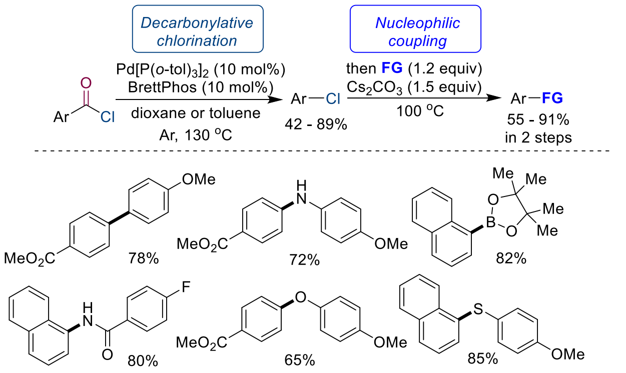
Scheme 25. Ni-Catalyzed Decarbonylative Cyanation of Acyl Chlorides



3.2. Decarbonylative Sequential Reactions

As well as to direct the decarbonylative coupling reaction discussed thus far, intramolecular decarbonylative chlorination[58,134−136] could also be used as a valuable strategy for various C−X (X = N, O, S, and B) bond constructions. A Pd-catalyzed sequential decarbonylative chlorination and nucleophilic coupling was developed by Sanford et al. (Scheme 26),[137] where the catalytic system used for decarbonylation was also competent for subsequent coupling reactions. The reaction exhibited an impressive substrate scope, enabling the conversion of acyl chlorides to various C−X bonds, such as C−C, C−N, C−O, C−S, C−B, and C−CF_3 bonds. At the decarbonylative chlorination stage, the electron-rich and sterically bulky monophosphine ligand Brettphos was necessary to promote decarbonylation and C−Cl bond-forming reductive elimination.

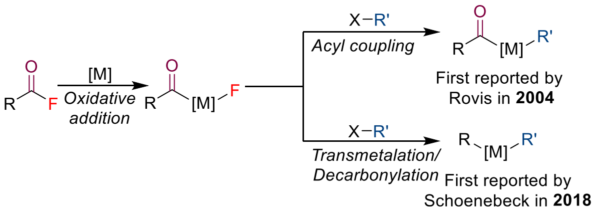
Scheme 26. Pd-Catalyzed Coupling Reactions via Decarbonylative Chlorination



4. DECARBONYLATION WITH CLEAVAGE OF THE C(ACYL)−F/C(ACYL)−C BONDS

Acyl fluorides, although less reactive than the corresponding acyl chlorides, are still susceptible to C−F oxidative addition. Indeed, because of the electrostatic stability of the C−F bond,[138] acyl fluorides exhibited a better stability than that of commonly employed acyl chlorides under nucleophilic conditions but higher reactivity than that of the corresponding (thio)esters, amides, and carboxylic acids. The potential nucleophilicity of fluorine on metal-fluoride species is capable of activating the coupling partner, thereby allowing base-free cross-coupling in some cases. Traditionally, acyl fluorides have been used as acylating reagents for nucleophilic molecules. Moreover, the number of reports on transition-metal-catalyzed acyl coupling reactions has rapidly increased in recent years since the seminal work of Rovis et al. in 2004.[67,139] The decarbonylative coupling of acyl fluorides was not discovered until 2018,[140,141] although the decarbonylative process of acyl fluorides was observed as early as 1967 (Scheme 27).[57]

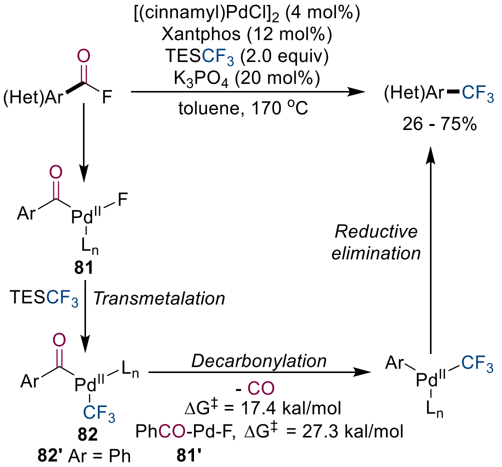
Scheme 27. Development of Acyl Fluorides in Metal-Catalyzed Coupling Reactions



4.1. Decarbonylative Coupling Reactions

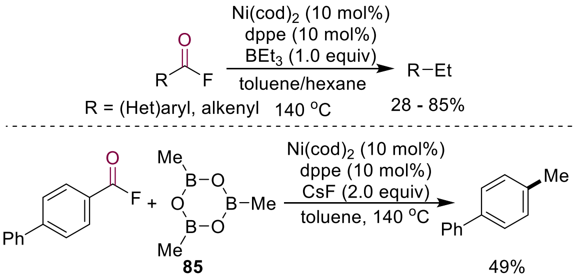
4.1.1. Trifluoromethylation. The first catalytic decarbonylative coupling of acyl fluorides was showcased by Schoenebeck et al. (Scheme 28).[67] A Pd/Xantphos catalytic system was used to achieve decarbonylative trifluoromethylation. Here, an intramolecular supply of fluoride for Pd(II)−F intermediate **81** avoided the need for exogenous fluoride additives and eliminated the detrimental propensity of the "CF_3 anions" to displace these weaker coordinating ligands of intermediate **81**. Computational and experimental data revealed that decarbonylation from PhCO−Pd−CF_3 **82′** was more favorable than that from PhCO−Pd−F **81′**, supporting the supposition that transmetalation occurred prior to decarbonylation. A two-step conversion of the carboxylic acids to $ArCF_3$ further demonstrated its practical value.

Scheme 28. Pd-Catalyzed Decarbonylative Trifluoromethylation of Acyl Fluorides

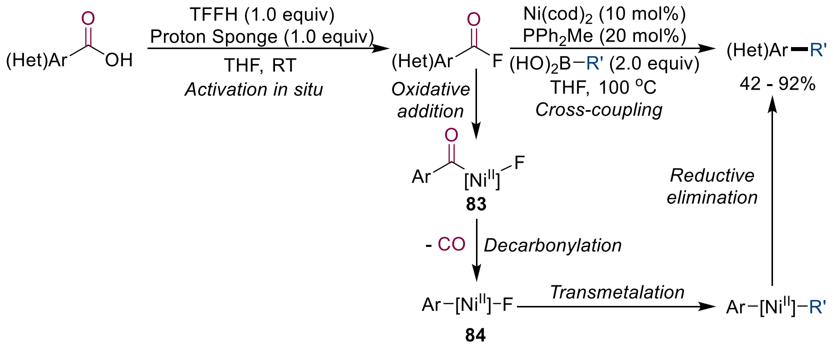


4.1.2. Arylation and Alkylation. Sanford et al. developed a base-free nickel-catalyzed decarbonylative Suzuki−Miyaura coupling process with acyl fluorides as the electrophiles (Scheme 29).[142] The authors proposed that the directly formed "transmetalation-active" intermediate Ar−Ni−F **84**, which was generated from oxidative addition and decarbonylation of intermediate **83**, smoothly underwent transmetalation under base-free conditions, averting the competitive decomposition of the base-sensitive organoboron substrates. Stoichiometric studies have also proven that Ar−Ni−F intermediates **84** are more reactive than the analogous phenyl nickel chlorides and bromides. These reactions have a high proven compatibility and synthetic potential. This was exemplified by the modification of carboxylic acid-containing bioactive molecules (e.g., probenecid, bexarotene, and tamibarotene) with the one-pot generation of acyl fluorides and decarbonylative coupling. The decarbonylative ethylation of aromatic and vinylic acyl fluorides was subsequently reported by Nishihara et al. (Scheme 30).[143] This reaction proceeded according to a mechanism similar to that described above. Notably, the excess base required for the methylation

Scheme 30. Ni-Catalyzed Decarbonylative Alkylation of Acyl Fluorides



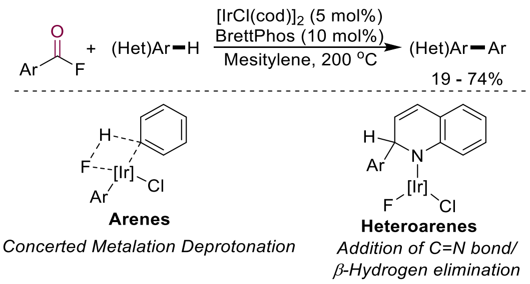
Scheme 29. Base-Free Ni-Catalyzed One-Pot Decarbonylative Suzuki−Miyaura Coupling



reaction was achieved using trimethylboroxine **85** as the alkylation reagent.

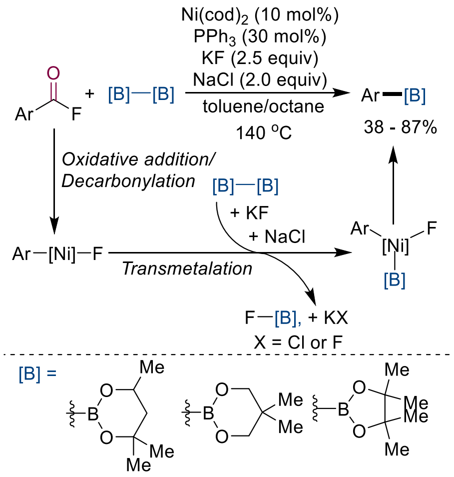
4.1.3. C−H Functionalization. Tobisu et al. reported the Ir-catalyzed decarbonylative arylation of acyl fluorides combined with C−H activation (Scheme 31).[144] The kinetic isotope effect indicated that a concerted metalation deprotonation (CMD) mechanism was involved in the case of arenes. On the other hand, for quinoline substrates, the addition of aryliridium fluoride to the C═N moiety of quinoline was proposed with subsequent *β*-hydrogen elimination to afford the desired product.

Scheme 31. Ir-Catalyzed Decarbonylative Coupling of Acyl Fluorides with Arenes and Heteroarenes



4.1.4. Borylation Reactions. The synthetic utility of the decarbonylative reactivity of acyl fluorides was also demonstrated for selective borylation. In 2018, Nishihara et al. reported a Ni-catalyzed protocol for the decarbonylative borylation of acyl fluorides (Scheme 32).[145] The combination of Ni(cod)$_2$ and PPh$_3$ was established as being the optimal catalyst. Additives such as NaCl and KF were necessary for the reaction to proceed, presumably to promote transmetalation with the diboron reagent.

Scheme 32. Ni-Catalyzed Decarbonylative Borylation of Aroyl Fluorides



More recently, Sanford et al. expanded their base-free decarbonylative coupling strategy[142] to the borylation of carboxylic acid fluorides **86** to generate aryl boronate esters **89** (Scheme 33).[146] The acid fluorides were generated *in situ* directly from the carboxylic acids. Detailed mechanism studies indicated that the diboron reagents underwent transmetalation with this Ni(aryl)(fluoride) intermediate **87** at rates significantly faster than those of their aryl boronate ester **88** congeners, and this has provided a rationale for preventing competing overcoupling of the aryl-Bpin product.

4.1.5. Silylation and Stannylation. Building on their decarbonylative coupling studies, Nishihara et al. further developed the Ni/Cu-*co*-catalyzed decarbonylative silylation of acylfluorides (Scheme 34A).[147] Here, the fluoride ion activated the silylborane to generate silylcopper intermediate **90**, which underwent transmetalation with aryl(fluoro)nickel(II) complex **91** to form intermediate **92**. Subsequent reductive elimination of **92** afforded the desired arylsilane. Related processes using silylstannanes as the coupling reagent were also reported, which provided various arylstannanes **93** under ligand-free conditions (Scheme 34B).[148]

4.2. Decarbonylative Reduction

The examples discussed thus far highlight recent progress in the development of the decarbonylative function of acyl fluorides. However, significant interest in decarbonylative defunctionalization has also been seen in recent years.[149] In 2018, Ogiwara and Sakai demonstrated the controllable palladium-catalyzed reductive conversion of acyl fluorides using a Pd(OAc)$_2$/Et$_3$SiH combination (Scheme 35).[150] They reported that the ligand properties, particularly those of bidentate phosphines such as Cy$_2$P(CH$_2$)$_2$PCy$_2$ (DCPE), determined the decarbonylative selectivity. Further, DFT calculations revealed that transmetalation involving decarbonylation and C−H reductive elimination of intermediate **94** would result in reductive product **95**.[151] Unfavorable decarbonylation for PCy$_3$ was illustrated by the repulsive interactions between the ligand and substrates revealed by distortion/interaction analysis (Scheme 35).

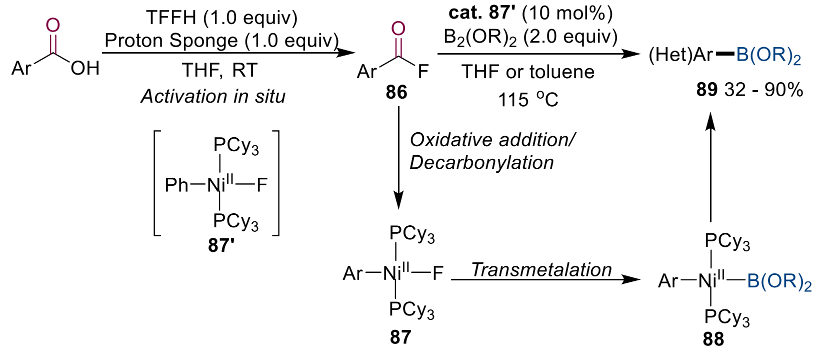
5. DECARBONYLATION WITH CLEAVAGE OF THE C(ACYL)−O/C(ACYL)−C BONDS

The carboxylic acid derivatives discussed thus far involve cleavage of the C(acyl)−halogen (X = Cl and F) bond. The use of esters and anhydrides as alternatives may eliminate some of the difficulties observed in the preparation and handling of acyl halide, thereby making them extensively explored substrates in decarbonylative reactions.[152,153] Generally, decarbonylation is triggered by the oxidative addition of a C(acyl)−O bond (Scheme 36, path A). The plausible decarbonylative route triggered by C(acyl)−C bond cleavage, which will also be discussed in this section, was also proposed (Scheme 36, path B).[153]

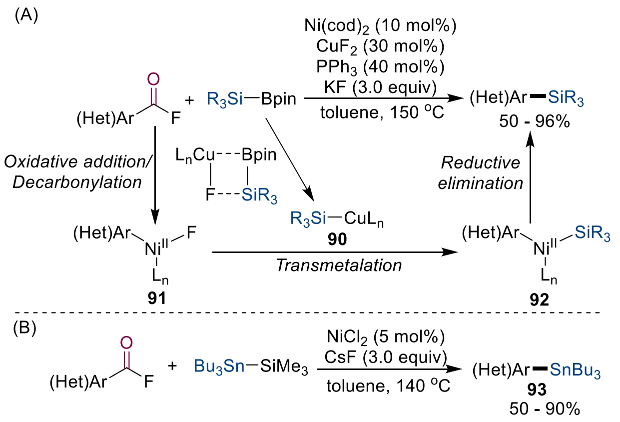
5.1. Decarbonylation of Esters

5.1.1. Decarbonylative Insertion Reactions. Pioneering work by Yamamoto et al. demonstrated that stoichiometric amounts of nickel complex **96** could be inserted into the C(acyl)−O bond of an ester, where decarbonylation was supported by the isolation and characterization of Ni(CO)(PPh$_3$)$_3$ complexes **97** (Scheme 37).[60,154] This was the first observation of oxidative addition of a generally inert C(acyl)−O bond to transition metals as well as a decarbonylation event from an ester. In 2002, Gooßen et al. first reported the interconversion of a Pd-catalyzed ester to an alkene via the decarbonylative Mizoroki−Heck reaction (Scheme 38A).[155] By employing electron-deficient esters **98** such as nitrophenolic esters as the arylating source, the palladium catalyst could be smoothly inserted into the C(acyl)−O bond, thereby ensuring subsequent decarbonylative olefination. Further, they reported that in this process, the enol esters **99** could be used as arylating precursors by utilizing the tetraalkylammonium salt

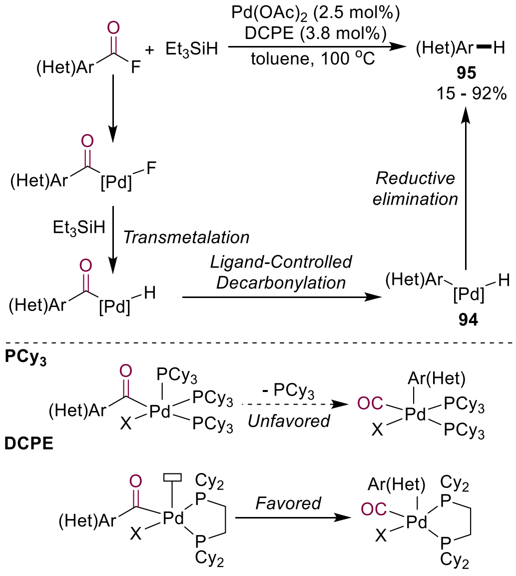
Scheme 33. Ni-Catalyzed Decarbonylative Borylation of Carboxylic Acid Fluorides



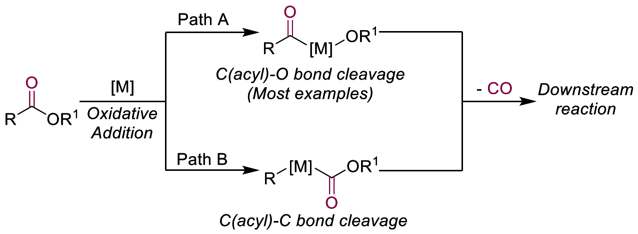
Scheme 34. Ni-Catalyzed Decarbonylative Silylation and Stannylation of Acyl Fluorides



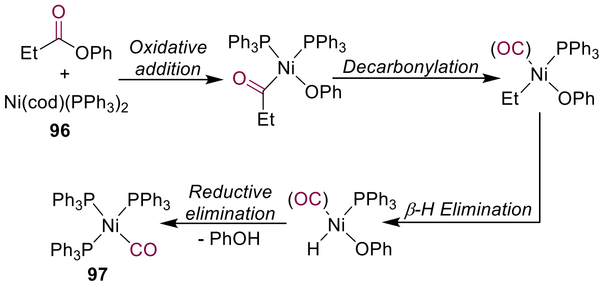
Scheme 35. Pd-Catalyzed Reductive Conversion of Acyl Fluorides



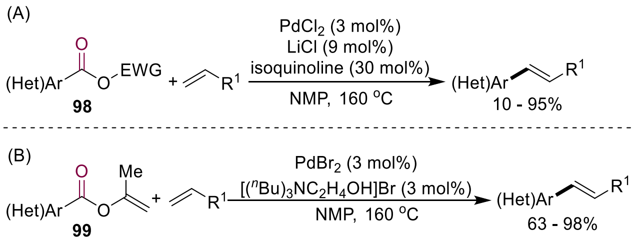
Scheme 36. Different Pathways of Decarbonylation of Ester



Scheme 37. Oxidative Addition of Aryl Carboxylates to Ni Involving Cleavage of the C(acyl)−O Bond



Scheme 38. Pd-Catalyzed Decarbonylative Mizoroki−Heck Olefination of Aryl and Enol Esters

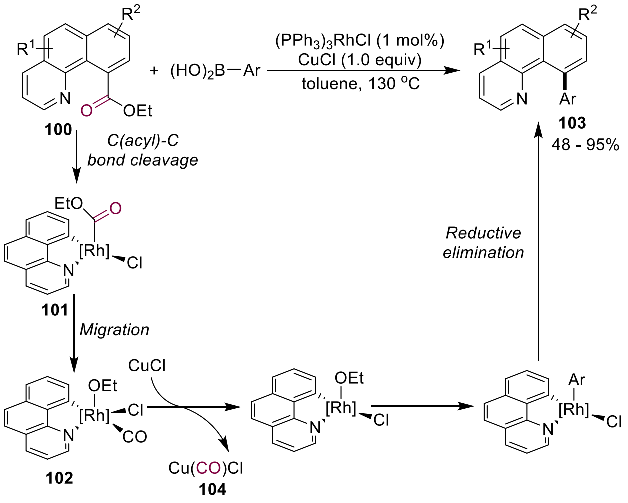


$[(n\text{-Bu})_3NC_2H_4OH]Br$ as an additive (Scheme 38B).[156] The formation of a stabilized leaving group (acetone) was considered to facilitate C(acyl)−O bond cleavage.

5.1.2. Decarbonylative Coupling Reactions.

5.1.2.1. Arylation and Alkylation. The catalytic conversion of C(acyl)−C bond to other types of C−C bond is one of the most challenging topics in organic syntheses. Transition-metal-catalyzed coupling reactions of organic halides with boron compounds (Suzuki−Miyaura coupling) are general and quite useful tools for the synthesis of a wide repertoire of organic compounds. In fact, esters were previously considered to be inert to coupling reactions. Thus, the method by which the ester C−C and C−O bonds are activated is strategically important. Analogously, it was supposed that esters could be used in Suzuki−Miyaura coupling. In 2012, Wang et al. developed the Rh-catalyzed Suzuki−Miyaura coupling of ethyl benzo[*h*]quinoline-10-carboxylates **100** with arylboronic acids through chelation-assisted C−C bond activation (Scheme 39).[157] Instead of the typical C(acyl)−O bond activation, a selective C(acyl)−C bond cleavage occurred to form Rh

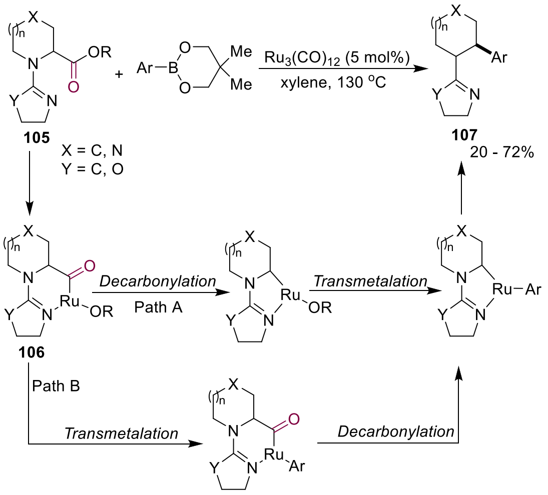
Scheme 39. Rh-Catalyzed Decarbonylated Coupling of Ethyl Benzo[*h*]quinoline-10-carboxylates and Organoborons



complex **101**. Subsequent migration of the ethoxyl group and elimination of the PPh_3 moiety generated intermediate **102**, which underwent decarbonylation, transmetalation, and reductive elimination to produce arylated products **103**. DFT calculations indicated that the role of CuCl in this process was to reduce the CO−metal dissociation energy by the formation of the thermodynamically stable copper carbonyl complex **104**.

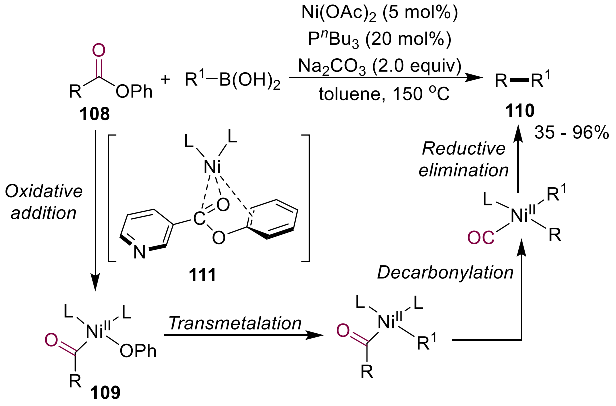
Sames et al. also adapted chelation-assisted strategy to the Ru-catalyzed Suzuki−Miyaura coupling reaction of cyclic 2-amino esters **105** (Scheme 40).[158] The catalytic process was initiated by insertion of ruthenium into the C(acyl)−O bond to form the six-membered cyclic ruthenium complex **106**. Subsequent decarbonylation, transmetalation, and reductive elimination (Scheme 40, path A or B) furnished arylated products **107**. The use of the directing group was found to be critical to facilitate both the insertion into the C(acyl)−O bond and the decarbonylation steps, thus ensuring the formation of the decarbonylative coupling products instead of the ketone.

Scheme 40. Ru-Catalyzed Decarbonylative Arylation

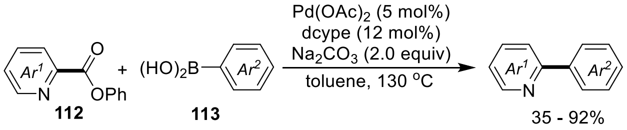


In 2015, Yamaguchi, Musaev, Itami et al. reported a Ni-catalyzed decarbonylative Suzuki−Miyaura coupling employing phenolic ester **108** (Scheme 41).[159] Aromatic groups as well as aliphatic substituents could be successfully employed in this coupling. The proposed mechanism involved the addition of Ni to the ester C(acyl)−O bond, leading to the formation of an acylnickel(II) intermediate **109**. This in turn underwent transmetalation, decarbonylation, and reductive elimination, offering diverse coupling products **110**. Computational studies indicated that the interaction between the metal and π-bonds of the phenyl and carbonyl groups rendered the C(acyl)−O bond reactive intermediate **111**. A similar reaction was reported by Love et al.[160] They reported the decarbonylative coupling of phenyl benzoic esters **112** and arylboronic acids **113** using a Ni/PCy_3 catalyst. Later, a palladium version of this transformation was developed using a $Pd(OAc)_2$/dcype catalyst (Scheme 42).[161]

Scheme 41. Ni-Catalyzed "Ester-Based" Suzuki−Miyaura Coupling



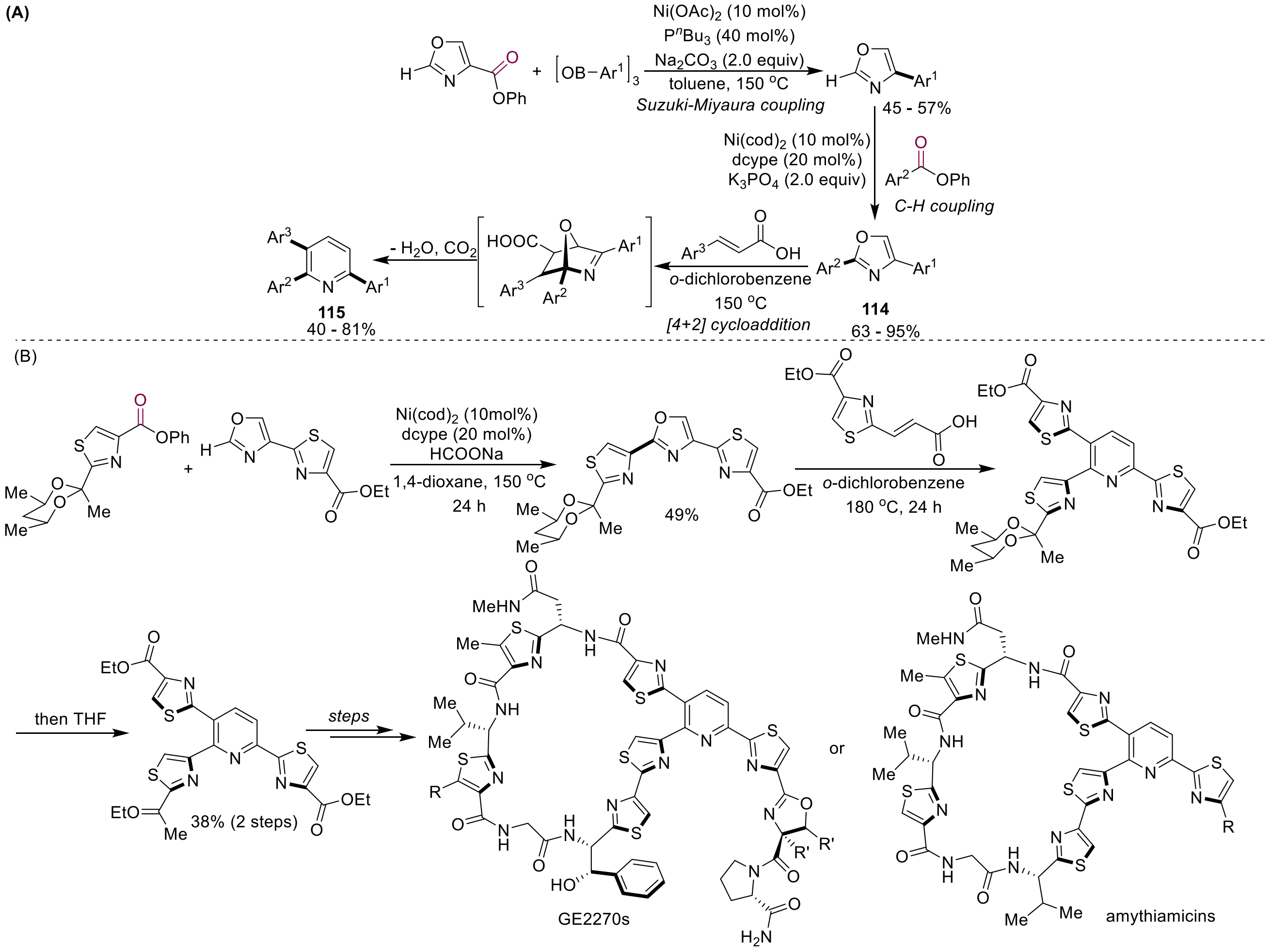
Scheme 42. Pd-Catalyzed Suzuki−Miyaura Coupling of Azinecarboxylates



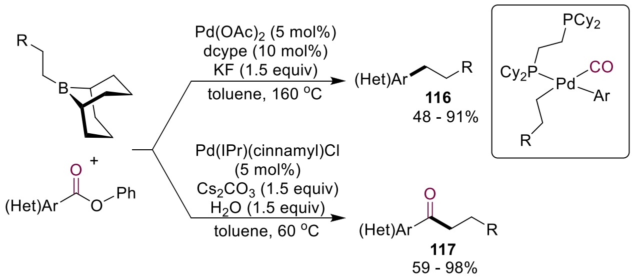
With their consecutive interest in decarbonylative reactions, Yamaguchi et al. further applied this decarbonylative Suzuki−Miyaura coupling for the regioselective synthesis of triarylpyridine derivatives **115** (Scheme 43A).[162] This strategy included nickel-catalyzed decarbonylative Suzuki−Miyaura coupling and decarbonylative C−H coupling for the synthesis of 2,4-diaryloxazoles **114** and [4 + 2] cycloaddition of **114** with (hetero)arylacrylic acids. By using this strategy, the formal syntheses of thiopeptide antibiotics GE2270s and amythiamicins were achieved (Scheme 43B).

Recently, the Pd-catalyzed ligand-controlled chemoselective alkylation of phenolic esters with alkyl boranes was reported by Newman et al. (Scheme 44).[163] By using a NHC ligand, alkyl ketones **117** could be prepared via a nondecarbonylative Suzuki−Miyaura reaction because of their steric bulk. In contrast, the Pd/dcype catalyst favored decarbonylative coupling to afford alkylated arenes **116** in good yield. It is supported that the dissociation of one of the dcype phosphine

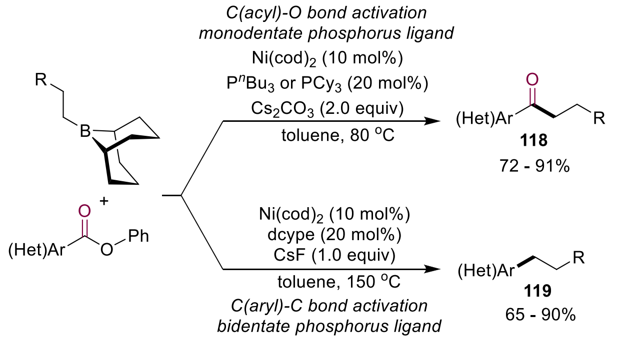
Scheme 43. Synthesis of Triarylpyridines with C−H Arylation/Ring-Transformation Strategy



Scheme 44. Pd-Catalyzed Decarbonylative Coupling of Pd and Alkyl Boranes



Scheme 45. Ni-Catalyzed Ligand-Controlled Suzuki−Miyaura Coupling with Aromatic Esters and Alkyl Organoboron Reagent

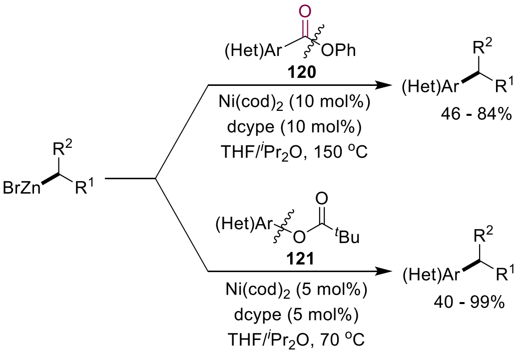


arms opened a coordination site for the subsequent decarbonylative process.

A similar ligand influence on the Suzuki−Miyaura coupling of aromatic esters and alkyl organoboron reagents was also observed by Rueping, Cavallo et al. under Ni-catalyzed conditions (Scheme 45).[164] When monodentate phosphorus ligands, such as P^nBu_3 and PCy_3, were used, alkyl ketones **118** could be prepared in good yield *via* a Suzuki−Miyaura coupling, proceeding by activation of the C(acyl)−O bond. On the other hand, use of a Ni−dcype catalyst favored decarbonylative coupling, leading to alkylated products **119** *via* C(aryl)−C bond cleavage. Computational studies also revealed the origin of the chemoselectivity in this transformation. Notably, amides were also compatible in the decarbonylative process, affording the alkylated products in moderate yield.

Apart from Suzuki−Miyaura coupling, esters are also applicable to decarbonylative Negishi coupling reactions. In 2017, Rueping et al. reported an efficient $Ni(cod)_2$/dcype catalytic system for the decarbonylative alkylation of esters (Scheme 46).[165] In this process, the choice of ester significantly influenced the selectivity for the oxidative addition of nickel. Phenolic esters **120** were particularly active in the

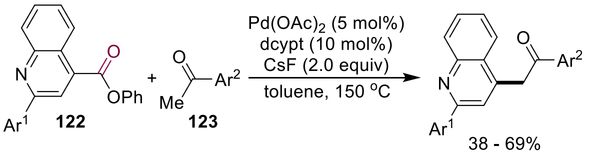
Scheme 46. Ni-Catalyzed Selective C—O Bond-Cleaving Alkylation of Esters



addition of C(acyl)—O bonds and decarbonylation, introducing alkyl groups to the carboxylic acid component. On the other hand, C(aryl)—O bond cleaving alkylation was observed when pivaloyl esters **121** were used as substrates.

Yamaguchi et al. disclosed that esters could also be used as arylating reagents in the α-arylation of ketones **123** (Scheme 47).[166] In this study, 2-phenyl-4-quinoline carboxylates **122** were reported to be a specific arylating source for this reaction, with other (hetero)aromatic alternatives resulting in inferior results.

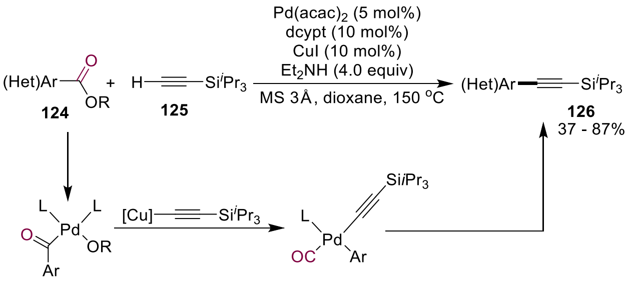
Scheme 47. Pd-Catalyzed Decarbonylative α-Arylation of Esters



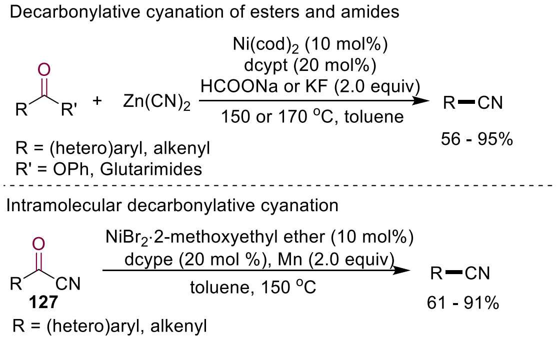
5.1.2.2. Alkynylation and Cyanation. In addition to the various classes of arylation and alkylation reactions described above, Yamaguchi and Itami reported Sonogashira-type coupling for the alkynylation of aromatic esters **124** with silylacetylene **125** using a palladium/copper cocatalytic system (Scheme 48).[167] The process tolerated a range of transferable groups such as alkenyls, alkyls, aryls, and heteroaryls, affording various alkynylated arenes **126** in moderate to good yield.

A Ni-catalyzed decarbonylative cyanation protocol of aromatic esters was reported by Rueping et al., using zinc cyanide as a CN source (Scheme 49).[168] Additionally, in this process, intramolecular decarbonylative cyanation of acyl cyanide **127**,[58,169] which could be directly prepared from acyl chlorides, was also observed. Notably, the amide derivatives, glutarimides, were also compatible under these conditions.

Scheme 48. Pd-Catalyzed Decarbonylative Alkynylation of Esters

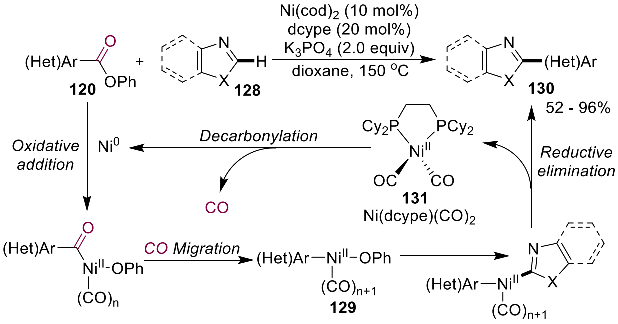


Scheme 49. Ni-Catalyzed C—CN Bond Formation via Decarbonylative Cyanation



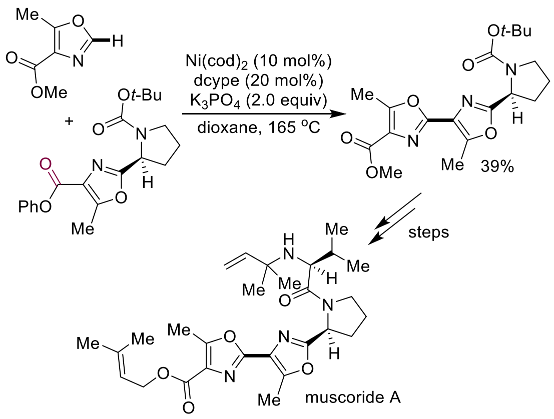
5.1.2.3. C—H Functionalization. Because of the high selectivity of ester decarbonylation, this tactic has also been explored for directed C—H bond activation. Itami and Yamaguchi first described a nickel-based catalytic system for decarbonylative C—H functionalization of azoles **128** using ester **120** as the arylating reagent (Scheme 50).[170,171] Here, oxidative addition of Ni to the C(acyl)—O bond followed by CO migration generated intermediate **129**, which underwent azole C—H nickelation, reductive elimination, and decarbonylation to afford the desired arylated products **130** and regenerate the catalyst. The intermediate Ni(dcype)(CO)$_2$ **131** was considered as a precatalyst in this process, which was also supported by experimental studies. The synthetic utility of this protocol was also demonstrated for the formal synthesis of muscoride A (Scheme 51). The substrate scope was further extended to unsaturated substrate **132**, whereby related decarbonylative alkenylation was achieved by the same group (Scheme 52). The process was most aptly exemplified by its application to the synthesis of siphonazole B.[172] Later, Gade et al. reported a new Ni catalyst that exhibited a similar reactivity for the decarbonylative C—H coupling of a benzoxazole and phenyl ester.[173]

Scheme 50. Ni-Catalyzed Decarbonylative C—H Diaryl Coupling

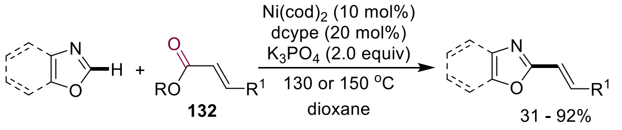


5.1.2.4. Borylation and Silylation. Apart from the C—C bond formation discussed thus far, decarbonylative borylation and silylation represent another appealing field for the decarbonylative coupling of esters. In 2016, Shi et al. established an efficient Ni-catalyzed system for the direct decarbonylative borylation and silylation of phenolic esters **133** (Scheme 53).[174] This distinct C—O bond borylative and

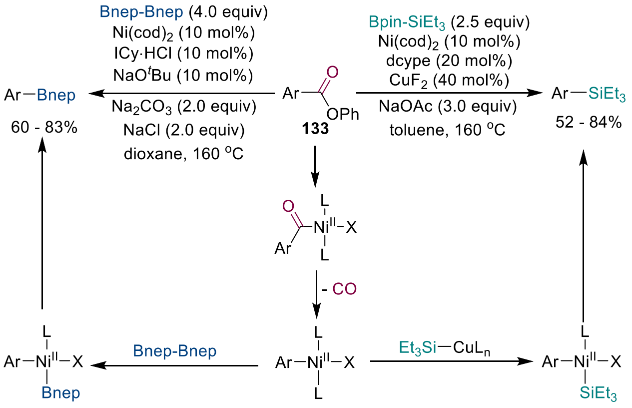
Scheme 51. Application of Ni-Catalyzed Selective Decarbonylative C−H Diaryl Coupling to Synthesis of Muscoride A



Scheme 52. Ni-Catalyzed Decarbonylative C−H Alkenylation of Azoles



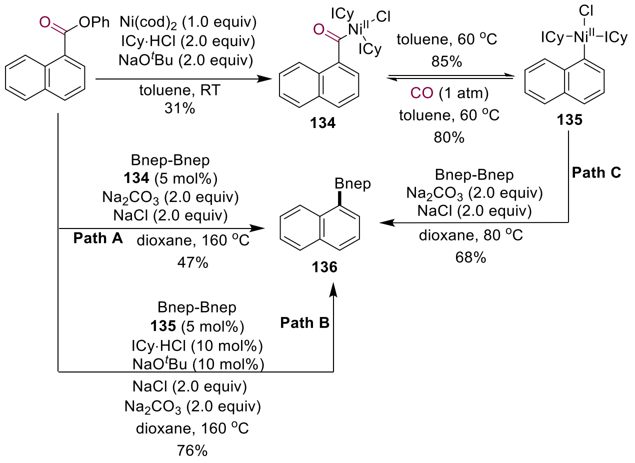
Scheme 53. Ni-Catalyzed Decarbonylative Borylation and Silylation of Esters



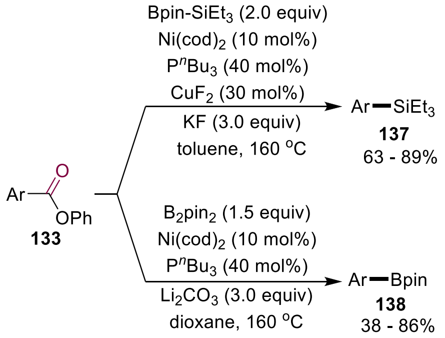
silylative cleavage is controlled by the appropriate choice of ligands and additives. The proposed mechanism is supported by the isolation and characterization of acylnickel(II) species **134** and arylnickel intermediate **135** (Scheme 54). By employing these reversible intermediates as the catalyst and starting point, respectively (Scheme 54, paths A, B, and C), borylated product **136** was produced in good yield. According to these experiments, a silylation process involving similar decarbonylation and transmetalation with *in situ* generated copper silane was also proposed. Concurrently, the decarbonylative interconversion of esters **133** to silanes[175] **137** and organoboronates[176] **138** was developed by Rueping et al. (Scheme 55). These processes are distinct from the outline presented in Scheme 53, as it was proposed that transmetalation occurs prior to CO extrusion.

5.1.2.5. Amination. Rueping et al. subsequently disclosed a decarbonylative interconversion strategy toward the synthesis of aryl amine derivatives **141** from esters **120** (Scheme 56A).[177] In the proposed mechanism, acyl nickel(II) intermediate **139**, generated from oxidative addition of the Ni complex into the C(acyl)−O bond, underwent CO migration and ligand exchange to deliver arylimine nickel(II) intermediate **140**. Subsequent reductive elimination and extrusion of CO produced aryl amine **141** and the regeneration of the catalyst. Notably, the use of imines as nucleophiles prevented the undesired amide-bond formation; thus, other

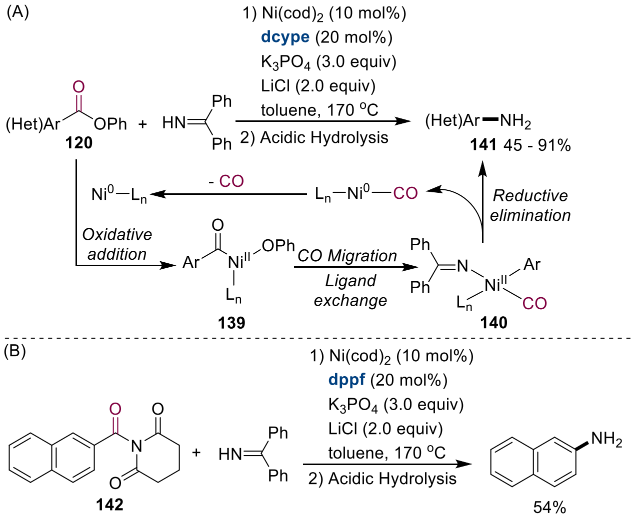
Scheme 54. Mechanistic Investigation of Ni-Catalyzed Decarbonylative Borylation



Scheme 55. Ni-Catalyzed Functional Group Interconversion of Esters



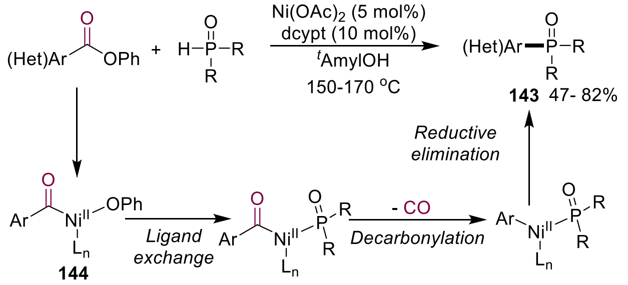
Scheme 56. Ni-Catalyzed Decarbonylative Amination of Esters and Amides



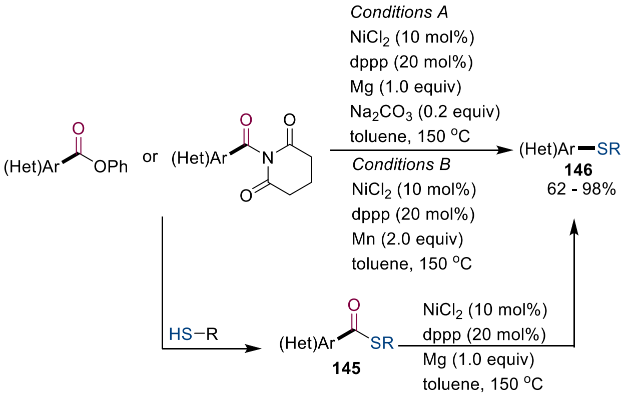
nitrogen sources such as morpholine and pyrazole were not suitable for this reaction. By changing the ligand from dcype to dppf, this protocol was also applied to the decarbonylative amination of naphthyl amide **142** (Scheme 56B).

5.1.2.6. Phosphorylation, Thioesterification, and Stannylation. Recently, decarbonylative C−P bond formation has also been realized, suggesting a potentially wider application of decarbonylative bond formation. Yamaguchi et al. demonstrated decarbonylative coupling between aromatic esters and organophosphorus compounds in the presence of Ni(OAc)$_2$/dcypt (Scheme 57).[178] The mechanism likely involved a ligand exchange from intermediate **144**, decarbonylation, and C−P reductive elimination sequence to form the desired products **143**. The Ni-catalyzed decarbonylative thioesterification of the C(acyl)−O or C(acyl)−N bond, with subsequent decarbonylation of thioester **145** followed by reductive elimination to afford thioether **146** (Scheme 58).[179] Notably, the intramolecular protocol for the direct decarbonylation of thioesters has also been proven.

Scheme 57. Ni-Catalyzed Decarbonylative Phosphorylation of Esters



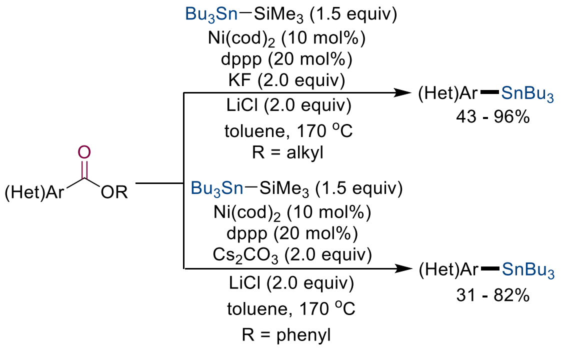
Scheme 58. Ni-Catalyzed Decarbonylative Thioetherification



Conditions A for aryl esters; *Conditions B* for aryl amides

Although the decarbonylative functionalization of phenolic esters displayed great advantages in coupling reactions, the substrate scope was mainly limited to the phenyl substituents. The conversion of methyl esters to stannanes via decarbonylative stannylation reaction was reported by Rueping et al. (Scheme 59).[180] By using Ni(cod)$_2$/dppp as catalysts, methyl esters as well as other common esters, such as ethyls, cyclohexyls, and benzyls, were all compatible in this system. The reaction is notable because it is the first decarbonylative reaction of simple methyl esters. In this process, phenyl substituents are also compatible with slight modification of reaction conditions.

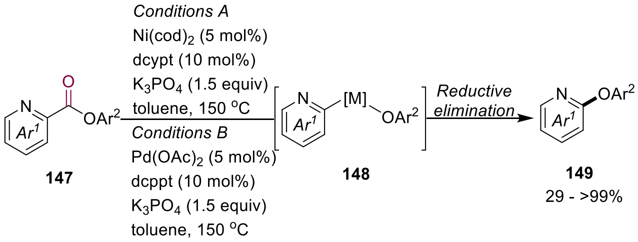
Scheme 59. Ni-Catalyzed Ester to Stannane Functional Group Interconversion



5.1.3. Intramolecular Decarbonylative Reactions.

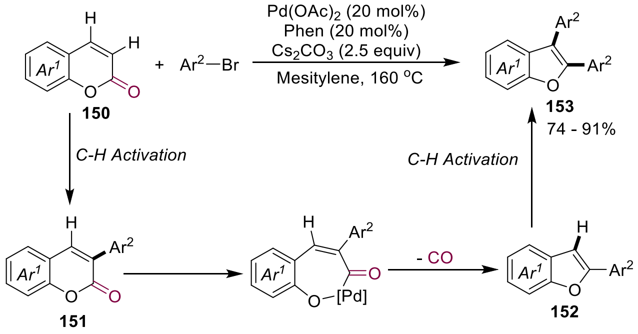
5.1.3.1. Etherification. The intramolecular decarbonylation of esters is also an extensively studied area for C−O bond formation. In 2017, Yamaguchi and Itami demonstrated that a decarbonylative functionalization of aryl azinecarboxylates **147** could proceed smoothly under nickel- or palladium-catalyzed conditions to afford the corresponding diaryl ethers **149** (Scheme 60).[181] The limitation of 2-azinecarboxylates **147** in this process was attributed to the electron-withdrawing nature of the 2-azinyl group, which destabilized the metal center to promote the reductive elimination of intermediate **148**.

Scheme 60. Ni-Catalyzed Decarbonylative Etherification of Aromatic Esters



An interesting extension of this chemistry involved its application to the synthesis of diaryl benzo[*b*]-furans **153** from coumarins **150** through a one-pot process (Scheme 61).[182] The first step of this process was C−H activation of coumarin **150** to form **151**. Subsequent Pd insertion to the C(acyl)−O bond followed by decarbonylation generated 2-aryl benzofuran

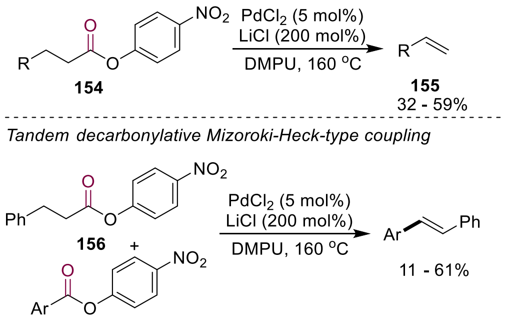
Scheme 61. Pd-Catalyzed Domino Arylation/Decarbonylation/Arylation of Coumarins



152, which underwent another C−H activation process to produce desired products **153**.

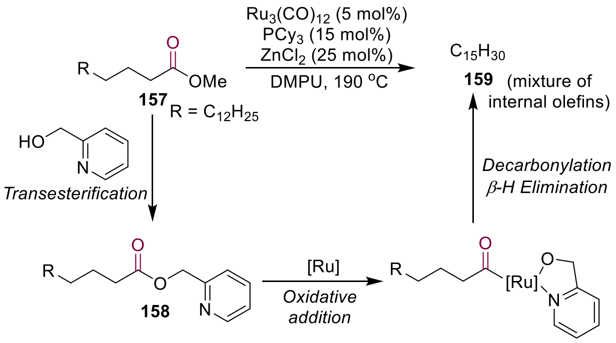
5.1.3.2. Alkenylation. Hillmyer, Tolman, et al. reported the Pd-catalyzed conversion of *p*-nitrophenylesters **154** of aliphatic carboxylic acids to the corresponding olefins **155** (Scheme 62).[183] Although no catalytic cycle was proposed, the authors state that decarbonylation of *p*-nitrophenylesters **154** was involved in this process. By using this strategy, hydrocinnamic acid ester **156** was considered as a "masked olefin" in tandem decarbonylative Mizoroki−Heck coupling, providing a new route to (*E*)-stilbenes.

Scheme 62. Pd-Catalyzed Esters Decarbonylation and Tandem Mizoroki−Heck Coupling



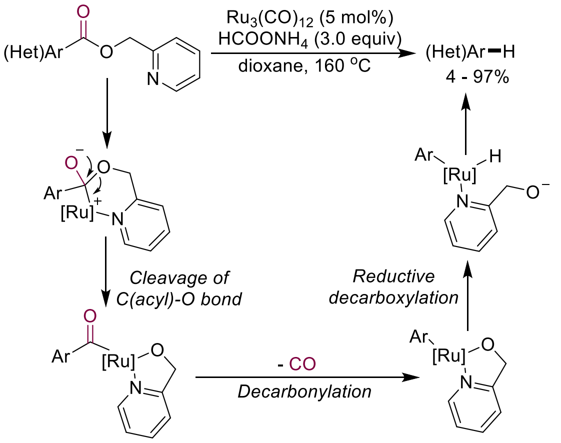
In subsequent studies, a dual-catalytic directing group strategy for dehydrative decarbonylation of fatty acid methyl esters **157** (FAMEs) was reported by LaPointe, Tolman, et al. (Scheme 63).[184] In this process, a Lewis acid ($ZnCl_2$) was used to catalyze transesterification to produce the corresponding esters **158**, comprising a pyridine-2-methylene directing group. These were then bound to the Ru catalyst to facilitate the oxidative addition of the acyl C−O bond, while subsequent decarbonylation and *β*-H elimination resulted in a mixture of olefin products **159**.

Scheme 63. Dual-Catalytic Decarbonylation of Fatty Acid Methyl Esters

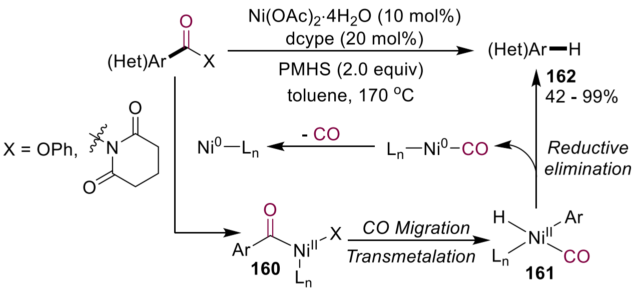


5.1.4. Decarbonylative Reduction. The paramount importance of the reductive transformation of esters has attracted much attention across a wide range field of research because of its application to practical organic syntheses. In the initial studies of Murai and Chatani,[65,185] heteroatom-directed C(acyl)−O bond cleavage followed by decarbonylation and reductive decarboxylation was established under Ru-catalyzed conditions (Scheme 64). Following these studies, the Ni-catalyzed selective reductive removal of both the ester and amide was achieved by Rueping et al. (Scheme 65).[186] In this process the hydrogen source employed was the inexpensive and stable polymethylhydrosiloxane (PMHS). The authors proposed that acyl nickel(II) intermediate **160** underwent CO migration and transmetalation with the hydrosilane to produce aryl hydride nickel(II) intermediate **161**. Subsequent reductive elimination provided hydrocarbon **162** and regenerated the nickel catalyst.

Scheme 64. Ru-Catalyzed Decarbonylative Reduction of Esters

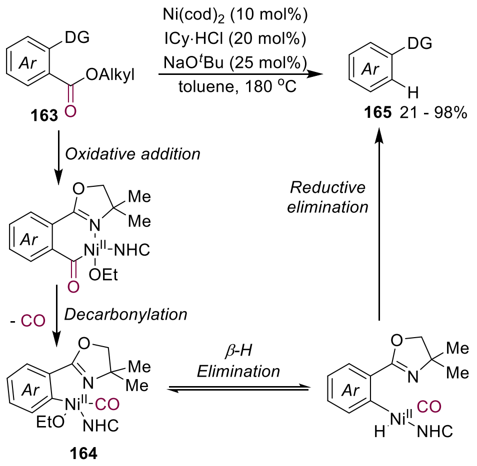


Scheme 65. Ni-Catalyzed Selective Reductive Defunctionalization of Esters and Amides



Most recently, Chatani et al. described the Ni-catalyzed selective reductive defunctionalization of esters in the absence of an external reductant (Scheme 66).[187] Various groups, such as *N*-containing heterocycles, esters, amides, and even weaker

Scheme 66. Ni-Catalyzed Reductive Defunctionalization of Alkyl Esters in the Absence of External Reductant

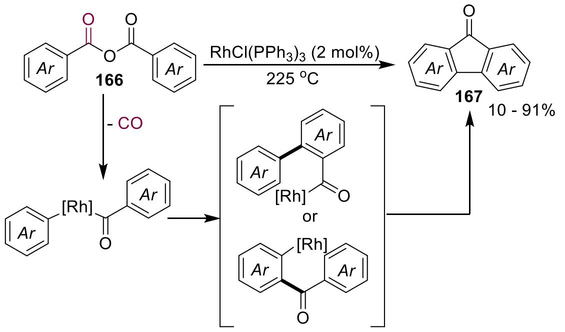


arene rings could all function as directing groups. The first step of this decarbonylative defunctionalization was thought to be the oxidative addition of the C(acyl)−O bond of **163** to the nickel complex through the assistance of a directing group. Upon decarbonylation, the five-membered nickelacycle **164** was formed, which underwent reversible β-H elimination and reductive elimination to release products **165**. The mechanism was supported by deuterium labeling studies on related substrates.

5.2. Decarbonylation of Anhydrides

Driven by their electron deficiency, acid anhydrides, as "activated ester derivatives" in the reaction, are also an important class of building blocks for use in the decarbonylative reaction via C(acyl)−O/C−C bond cleavage. Pioneering work on the transition-metal-catalyzed decarbonylation of benzoic anhydrides **166** was reported by Blum (Scheme 67).[59] The reactivity comprised the synthesis of fluorenones **167** via the Rh-catalyzed decarbonylation of benzoic anhydrides.

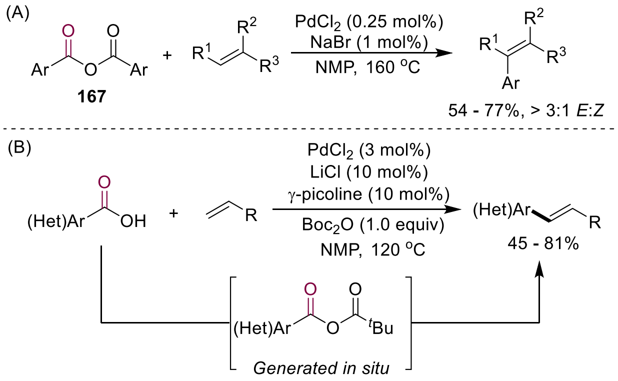
Scheme 67. Rh-Catalyzed Synthesis of Fluorenones via Decarbonylation of Benzoic Anhydrides



5.2.1. Decarbonylative Insertion and Annulation.

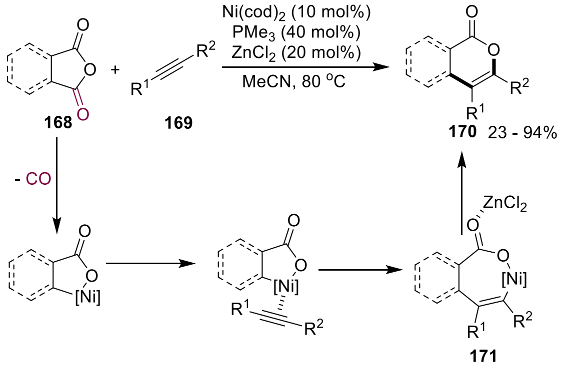
Inspired by the synthetic importance of Mizoroki−Heck reactions, in 1998, Stephan, de Vries, et al. reported early significant examples of the Pd-catalyzed decarbonylative insertion of alkenes using aromatic acid anhydrides **167** as coupling partners (Scheme 68A).[188] Over the past decade, carboxylic acids have been representative of advantageous coupling reagents in transition-metal-catalyzed decarboxylative coupling ($-CO_2$).[46,47,189] Recently, significant progress has been made in the development of carboxylic acid coupling reactions via redox-neutral decarbonylative pathways (−CO). In this approach, the carboxylic acid is first converted *in situ* into an activated acyl carboxylic acid derivative anhydride for decarbonylative reactions. Gooßen et al. disclosed that a strategy comprising *in situ* generation of anhydrides is also compatible in the decarbonylative Mizoroki−Heck reaction (Scheme 68B).[190]

Scheme 68. Aromatic Carboxylic Anhydrides as Arylating Agents in Mizoroki−Heck Reactions

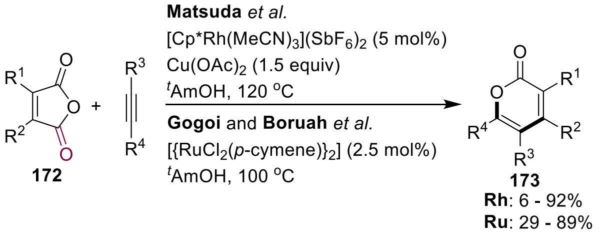


Given the importance of the synthetic application of annulation reactions, Matsubara and Kurahashi achieved the decarbonylative cycloaddition of phthalic anhydride **168** with internal alkyne **169** to afford isocoumarin **170**, using a Ni catalyst together with a Lewis acid as the cocatalyst (Scheme 69).[191] Lewis acids such as zinc salts were critical to ensure high reactivity, presumably by increasing the electrophilicity of the carbonyl moiety of intermediate **171**. Terminal alkynes failed to participate in the reaction because of their rapid oligomerization. By taking advantage of the high selectivity of this decarbonylative protocol, Matsuda et al. reported the Rh-catalyzed formal decarbonylative [5 − 1 + 2] annulation of maleic anhydrides **172** for the preparation of substituted α-pyrones **173** (Scheme 70).[192] Gogoi and Boruah subsequently reported similar processes using a Ru catalyst (Scheme 70).[193]

Scheme 69. Ni-Catalyzed Decarbonylative Addition of Anhydrides to Alkynes

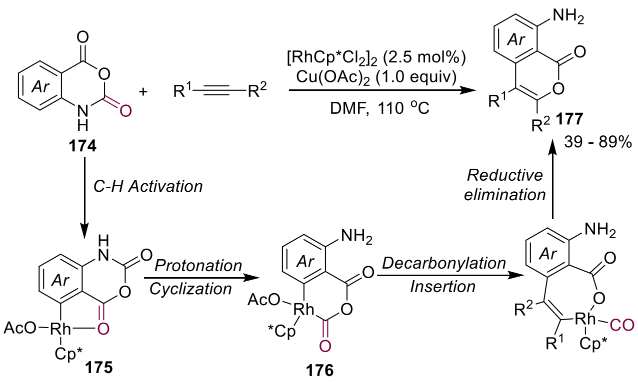


Scheme 70. Decarbonylative Addition Reaction of Anhydrides with Alkynes



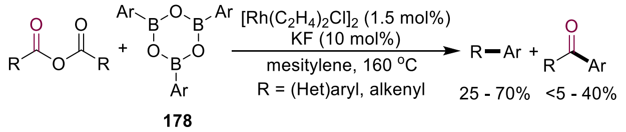
Recently, Uma Maheswari, Perumal, et al. reported the Rh-catalyzed decarbonylative annulation of the less-strained isatoic anhydrides **174** with alkynes for the synthesis of amino-isocoumarins **177** (Scheme 71).[194] In this process, the weakly coordinating anhydrides facilitated the C−H activation to deliver the five-membered rhodacyclic intermediate **175**. Subsequent protonation and cyclization led to C−N bond cleavage and the formation of intermediate **176**, which underwent decarbonylation, insertion of the alkyne, and reductive elimination to afford the desired products **177**. Competitive reactions between electron-rich and -poor anhydrides further elucidated this mechanism.

Scheme 71. Rh-Catalyzed Decarbonylative Annulation of Isatoic Anhydrides



5.2.2. Decarbonylative Coupling Reactions. In subsequent studies, the use of other coupling partners such as haloalkanes, organozinc reagents, boroxines, and boric acids were reported. Previous works by Echavarren et al. showed that the decarbonylation of aspartic acid could easily lead to the formation of C(sp^3)−C(sp^3)-coupled products in the presence of haloalkanes under Ni-catalyzed conditions.[195−197] In 2003, Rovis et al. disclosed a stereoselective reaction in which cyclic meso-anhydrides were reacted with diarylzinc compounds using stoichiometric amounts of Ni(0) complexes.[198] In 2004, Gooßen, Paetzold, et al. realized the decarbonylative Suzuki−Miyaura coupling of anhydrides catalyzed by $[Rh(C_2H_4)_2Cl]_2$ without the addition of a base and ligand (Scheme 72).[199] A broad range of anhydrides, such as aromatic, heteroaromatic, and vinylic carboxylic anhydrides, smoothly coupled with boroxines **178**. Notably, nondecarbonylated selectivity was also achieved, particularly when electron-rich boroxines were used, whereby the rate of transmetalation was faster than that of the competing decarbonylation.

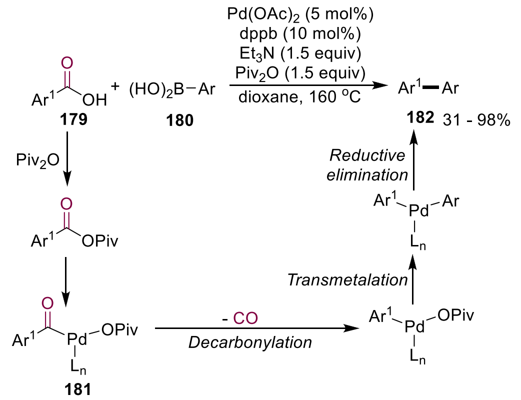
Scheme 72. Rh-Catalyzed Suzuki−Miyaura Coupling of Anhydrides and Boroxines



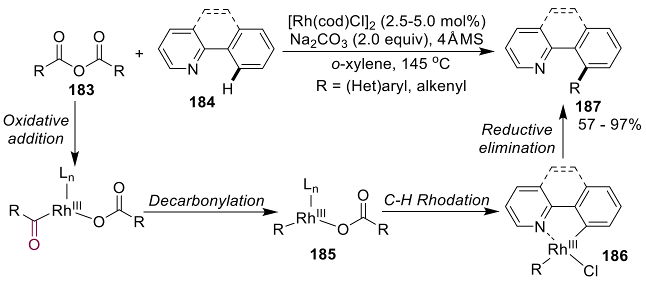
Hong, Szostak, et al. also reported the Pd-catalyzed decarbonylative Suzuki−Miyaura coupling of carboxylic acids **179** and arylboronic acids **180** using *in situ* generated anhydrides (Scheme 73).[200] In this process, a sterically hindered *O*-acyl group and the bidentate ligand dppb facilitated the decarbonylation of intermediate **181**, with subsequent transmetalation and reductive elimination affording biaryls **182**. Computational studies also demonstrated that the ligand denticity determined the chemoselectivity, whereby a bidentate ligand favored the decarbonylation pathway for intermediate **187**.

5.2.2.1. C−H Functionalization. One of the more extensively studied decarbonylative reactions of anhydrides involves the combination of C−H functionalization strategies. In 2009, Yu et al. reported on Rh-catalyzed aromatic C−H activation, with aromatic carboxylic and cinnamic anhydrides as the coupling partners, under chelation assistance (Scheme 74).[201] In the mechanism suggested by the authors, anhydride **183** underwent oxidative addition followed by decarbonylation to produce Rh complex **185**. Subsequent base-promoted C−H rhodation of **184** and reductive elimination from the resulting complex **186** afforded coupling products **187** and regenerated the Rh(I) catalyst.

Scheme 73. Pd-Catalyzed Decarbonylative Suzuki−Miyaura Coupling of Carboxylic Acids



Scheme 74. Rh-Catalyzed Suzuki−Miyaura Coupling

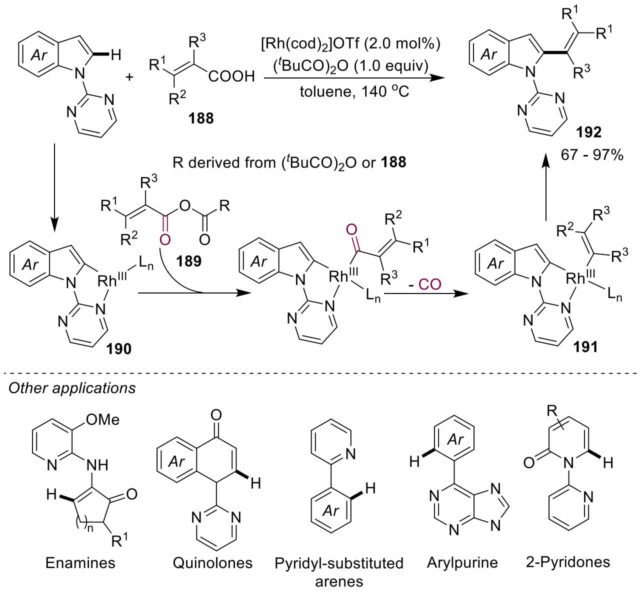


In 2014, Li, Xu, et al. reported the Rh-catalyzed decarbonylative direct C2-olefination of indoles with vinyl carboxylic acids **188** via an *in situ* activation strategy (Scheme 75).[202] Experimental studies suggested that the reaction proceeded via the initial formation of acid anhydride **189**, with subsequent oxidative addition of Rh complex **190** and decarbonylation to produce intermediate **191**. This in turn underwent reductive elimination to produce the olefination products **192**. Later, new transformations using the same strategy were gradually developed and expanded to alkenylation and arylation of cyclic enamines,[203] quinolones,[204] pyridyl-substituted arenes,[205,206] arylpurine,[206,207] and 2-pyridones.[208]

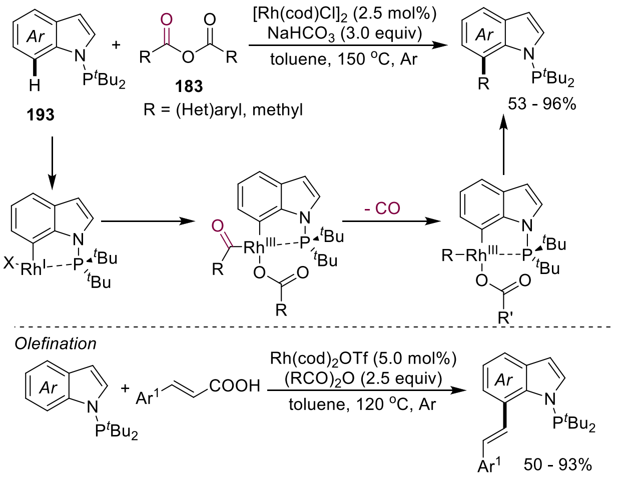
Recently, Shi et al. further reported the Rh-catalyzed C7−H functionalization of indoles **193** with anhydrides **183** as the coupling reagent (Scheme 76).[209] An indole *N*-P^tBu_2 chelation-assisted group was highly crucial for the regioselectivity of this transformation. Apart from arylation and olefination, the methylation of indoles was also realized using acetic anhydride. This group further applied this methodology to the C7-selective trideuteromethylation of indoles with commercially available Ac_2O-d_6 **194** (Scheme 77).[210]

The intramolecular version of C−H functionalization involving decarbonylation of *in situ* generated anhydrides also works well for the construction of five-membered heterocyclic rings (Scheme 78).[211] In the presence of Rh(acac)(cod) as the catalyst, intramolecular C−H activation

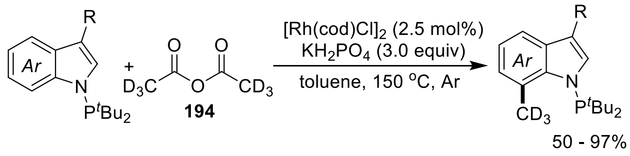
Scheme 75. Direct Arylation and Alkenylation of Arene C–H Bonds via Decarbonylation of Anhydrides



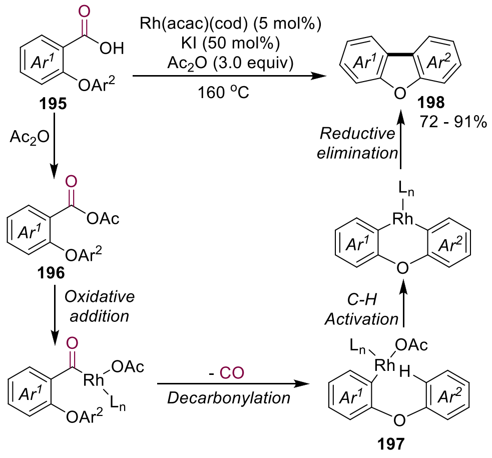
Scheme 76. Rh-Catalyzed C7–H Functionalization of Indole with Anhydrides as Coupling Reagent



Scheme 77. Rh-Catalyzed Selective C–H Trideuteromethylation of Indoles



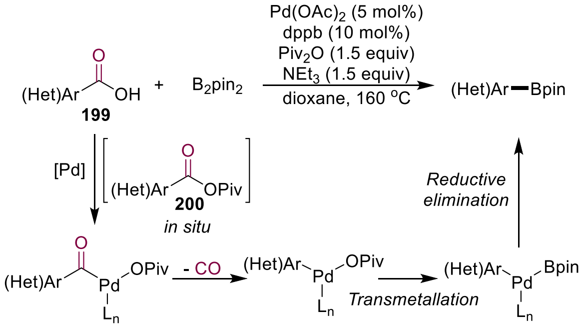
Scheme 78. Rh-Catalyzed Intramolecular C–H Arylation Accompanied by Decarbonylation



proceeded smoothly via an acylrhodium species **197**, which originated from 2-aryloxybenzoic acids **195** by oxidative addition and decarbonylation of anhydride **196**. Finally, reductive elimination provided facile access to benzofuran derivatives **198**.

5.2.2.2. Borylation, Phosphorylation, and Etherification. Other classes of coupling reactions, apart from C–C bond formation reactions, have also been developed. Szostak and Hong first demonstrated the decarbonylative borylation of carboxylic acids **199** via decarbonylative palladium catalysis (Scheme 79).[212] The decarbonylation proceeded with *in situ*-formed mixed anhydride **200**, with subsequent oxidative addition, decarbonylation, transmetalation, and reductive elimination accounting for C–B bond formation. Computations revealed the mechanistic details of the chemoselectivities of the C–O bond activation of carboxylic acids.

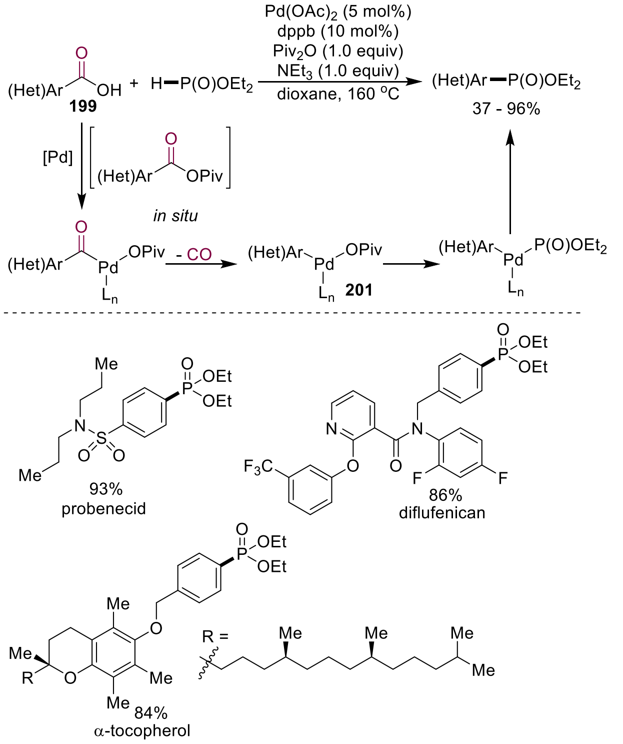
Scheme 79. Pd-Catalyzed Decarbonylative Borylation of Carboxylic Acids



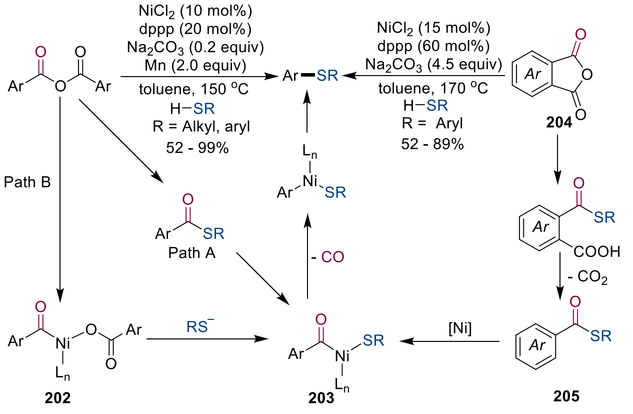
Later, a Pd-catalyzed decarbonylative phosphorylation of aryl and vinyl carboxylic acids **199** was also reported by Szostak and Hong et al. (Scheme 80).[213] In this process, phosphorylation of decarbonylative intermediate **201** followed by reductive elimination affording desired organophosphorus compounds. DFT calculations provide rationalization of the reactivity and selectivity of this transformation. This group further applied this methodology to the direct derivatization of drugs and natural products such as probenecid, diflufenican, and α-tocopherol.

Most recently, Zhu et al. demonstrated a Ni-catalyzed decarbonylation coupling reaction of aryl anhydrides with thiophenols as the coupling partners (Scheme 81).[214] In this process, interconversion of the anhydrides to the corresponding thioester (Scheme 81, path A) or addition of a phenyl sulfide anion to intermediate **202** (Scheme 81, path B) were all possible routes for the generation of acyl nickel(II) intermediate **203**. Phthalic anhydride **204** could also be used as an aryl source through decarboxylation to afford thioester **205**, while subsequent decarbonylation produced the corresponding thioether in moderate to good yield.

Scheme 80. Pd-Catalyzed Decarbonylative Phosphorylation of Mixed Anhydrides

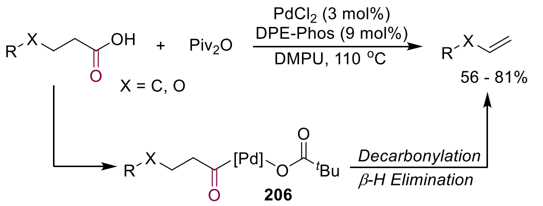


Scheme 81. Forging C−S Bonds through Ni-Catalyzed Decarbonylative Coupling of Aryl Anhydrides and Thiophenols



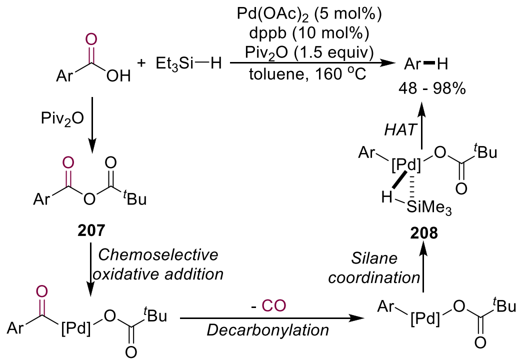
5.2.2.3. Decarbonylative Defunctionalization. In addition to the coupling reactions discussed thus for, anhydrides have also become commonly used reagents for synthesizing of alkenes.[215] Building on the preliminary work of Trost[216] and Miller et al.,[217] Gooßen et al. reported the palladium-DPEPhos-catalyzed decarbonylative conversion of carboxylic acids to 1-alkenes (Scheme 82).[218] At low temperatures, smooth decarbonylation and β-hydride elimination of acyl Pd-complexes **206** delivered the corresponding 1-alkene products with high selectivity. Later, much attention focused on improving the efficiency of this strategy, which indicated that low catalyst loadings and high regioselectivity were all accessible under diverse Pd-catalytic conditions.[219−224] The synthetic potential of this chemistry was proven by applications in the total synthesis of (−)-aspewentins A, B, and C.[225] Apart from the Pd catalytic system, a related investigation by Fukuyama, Ryu, and Hapiot revealed that Ir,[226,227] Fe,[226] and Ni[228] were also competent catalysts.

Scheme 82. Pd-Catalyzed Conversion of Carboxylic Acids to Olefins



More recently, the direct reduction of carboxylic acids to aromatic hydrocarbons was realized by Hong, Szostak, et al. (Scheme 83).[229] The authors proposed that the initial step of the catalytic cycle involved oxidative addition of the acyl C−O bond of the *in situ* generated anhydrides **207**. Subsequent decarbonylation and silane coordination afforded intermediate **208**, which underwent hydrogen atom transfer (HAT) to produce the reduced arene. Detailed DFT studies revealed that the acyl C−O bond insertion was determined by the substituent of the anhydride, whereby steric repulsions between the bulky ^{t}Bu group and dppb ligand leading to C−O bond activation only occurred on the benzoic acid.

Scheme 83. Pd-Catalyzed Reduction of Carboxylic Acids to Aromatic Hydrocarbons

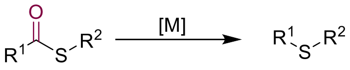


6. DECARBONYLATION WITH CLEAVAGE OF C(ACYL)−S/C(ACYL)−C BONDS

6.1. Intramolecular Decarbonylative Coupling

Thioesters are intriguing structural motifs that are frequently utilized in pharmaceutically relevant compounds. Metal-catalyzed intramolecular decarbonylative coupling of thioesters for thioether synthesis was first reported by Yamamoto et al. in 1987, using Pd(PCy$_3$)$_2$ as the catalyst (Scheme 84).[61] Since then, other catalysis systems have been reported to be effective for this reaction. For example, Wenkert and co-workers reported a Ni-mediated decarbonylation of aryl thioesters to generate thioether products.[230] Kambe, Kuniyasu, et al. showed that appropriately placed lone pair electrons in unsaturated thioesters could facilitate the oxidative addition of Pd(PPh$_3$)$_4$ and decarbonylation to yield vinyl sulfides.[231] Sanford et al. reported Pd- and Ni-catalyzed decarbonylative C−S coupling to convert thioesters to thioethers.[232] The substrate scope was very broad, as a range of aryl, heteroaryl,

Scheme 84. Intramolecular Decarbonylative Coupling of Thioesters

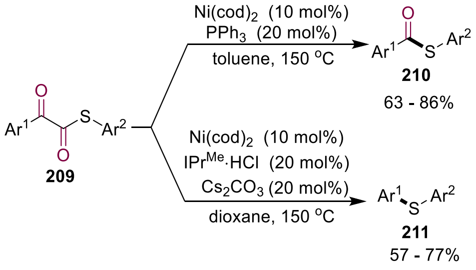


1987, Yamamoto, $Pd(PCy_3)_2$
1991, Wenkert, $NiCl_2/PPh_3$
2006, Kambe and Kuniyasu, $Pd(PPh_3)_4$
2018, Sanford, $Pd[P(o\text{-tol})_3]_2/PAd_2Bn$ or $Ni(cod)_2/PCy_3$
2018, Szostak, $Ni(dppp)Cl_2$ or $Ni(PCy_3)_2Cl_2$
2018, Rueping, $NiCl_2$/dppp
2018, Yamaguchi, $Ni(OAc)_2$/dppb or P^nBu

and even alkyl thioesters successfully underwent intramolecular decarbonylative C−S bond formation. However, the use of an air-sensitive Ni(0) species in the catalysis system was required. Szostak,[233] Rueping,[179] and Yamaguchi[234] independently demonstrated the decarbonylation of thioesters using an air- and moisture-stable nickel(II) catalyst (Scheme 84). The method generated widely useful thioethers, thereby representing an excellent alternative to the Ni(0)-catalyzed decarbonylation of thioesters.

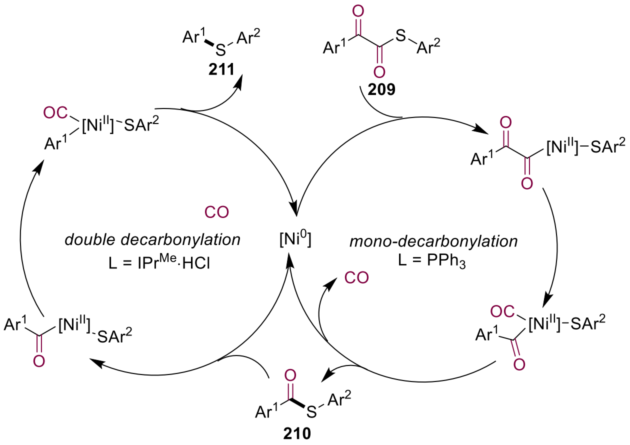
In a related report, Wei et al. reported the controllable nickel-catalyzed intramolecular decarbonylation of *α*-ketothioesters **209** (Scheme 85).[235] The electronic properties of the ligand played an essential role in the selectivity of the decarbonylative process. Thus, when a phosphine ligand such as PPh_3 was used, the monodecarbonylated products **210** were obtained in good yields. In contrast, when using the *N*-heterocyclic carbene (NHC) as an alternative, further decarbonylation of thioester **210** was observed, resulting in the exclusive formation of the doubly decarbonylated products **211** (Scheme 86).

Scheme 85. Ni-Catalyzed Controlled Intramolecular Decarbonylation of *α*-Ketothioesters

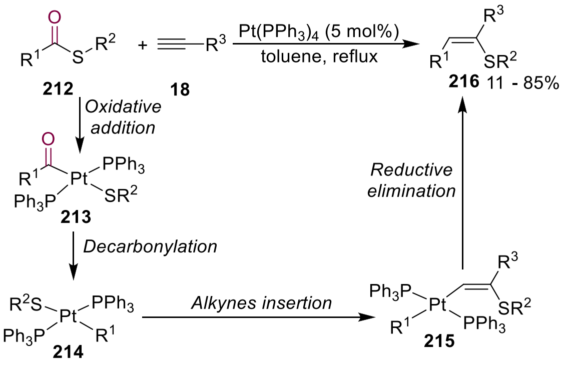


6.2. Decarbonylative Coupling and Addition

Scheme 86. Proposed Mechanism of Ni-Catalyzed Decarbonylations of *α*-Ketothioesters

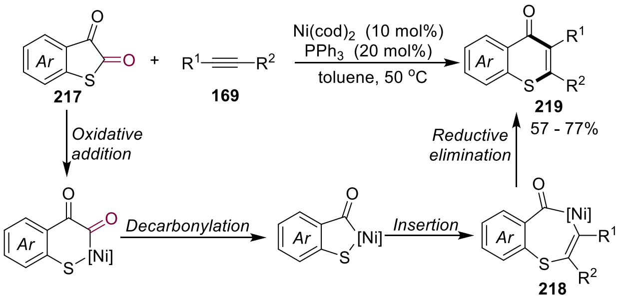


Scheme 87. Pt-Catalyzed Arylthiolation of Alkynes



Decarbonylative coupling of a thioester was initially reported by Lee et al., in which potassium thioacetate was used as the sulfide source to obtain unsymmetrical diaryl sulfides from aryl bromides and iodides with $Pd(dba)_2$.[236] An interesting extension of decarbonylation of thioester involves its application to the decarbonylative addition between thioesters and alkynes. Under Pt-catalyzed conditions, Kuniyasu, Kambe, and Kurosawa achieved the regio- and diastereoselective decarbonylative arylthiolation of aryl thioesters **212** and terminal alkynes **18** (Scheme 87).[237] The proposed mechanism involved oxidative addition by a Pt catalyst followed by decarbonylation to provide aryl platinum **214**. The thermodynamical disadvantage of S−C(sp^2) bond formation for the reductive elimination of the Pt catalyst facilitated the insertion of aryl platinum **214** into the alkyne **18**, converting the S−Pt−C unit to the C−Pt−C of intermediate **215**. Subsequent facile reductive elimination for C−C bond formation delivered alkenyl sulfides **216**. Stoichiometric reactions with isolation of intermediates **213** and **214** further supported this mechanism. The substrate scope was also extended to internal alkynes.[238] In this case, introduction of the oxygen-containing group in the alkynes at the proper position was key to the success of this transformation. Extension of the reaction mode to formal cycloadditions has also been achieved. Matsubara and Kurahashi demonstrated the nickel-catalyzed decarbonylation cycloaddition reaction of thioisatins **217** with alkynes **169** to generate thiochromones **219** (Scheme 88).[239] The C−S bond easily underwent insertion of the Ni species, which in turn underwent decarbonylation and intermolecular addition to the

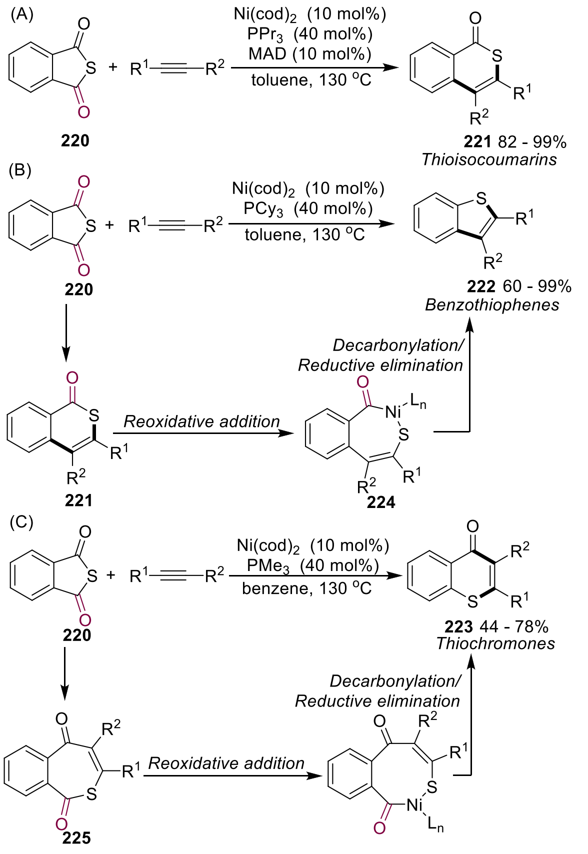
Scheme 88. Ni-Catalyzed Cycloadditions of Thioisatins with Alkynes



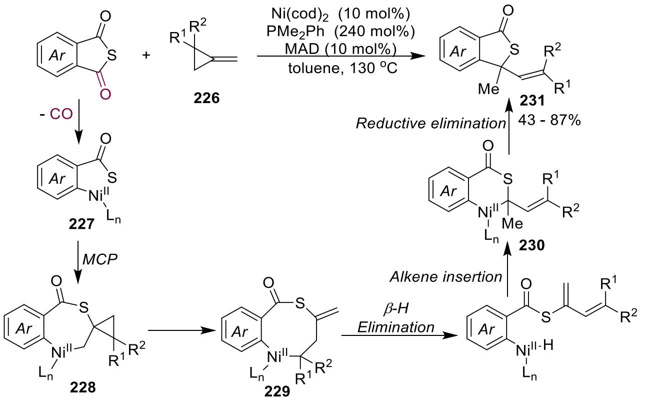
alkynes. Subsequently, the seven-membered nickelacycle **218** underwent reductive elimination to form the products and regenerate the Ni(0) catalyst. Notably, both internal and terminal alkynes could be tolerated in this process.

Having a continuous interest in decarbonylative reactions, this group also demonstrated the ability to control the regioselectivity as well as decarbonylation of thiophthalic anhydrides **220** by adjusting the reaction conditions (Scheme 89).[240] Three types of cycloaddition products, namely thioisocoumarins **221**, benzothiophenes **222**, and thiochromone **223**, were selectively obtained. In this process, methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) was considered to increase the electrophilicity of the carbonyl moiety of thiophthalic anhydride **220** to promote the formation of thioisocoumarin **221** (Scheme 89A). When the bulky ligand PCy_3 was used, reoxidative addition of thioisocoumarin **221** resulted in intermediate **224**, which underwent further decarbonylation and reductive elimination to afford benzothiophene **222** (Scheme 89B). Interestingly, the authors reported that the less sterically hindered PMe_3 allowed carbonickelation of the alkyne prior to decarbonylation in the presence of benzene as solvent. Finally, reoxidative addition of intermediate **225** with decarbonylation and reductive elimination were proposed to furnish thiochromone **223** (Scheme 89C). The replacement of alkyne moieties with methylenecyclopropane (MCP) **226** was later realized by Matsubara and Kurahashi (Scheme 90)[241] to afford the corresponding [4 + 1] adduct in moderate to good yield and high regioselectivity. In the proposed mechanism based on deuterated experiments, nickelacycle **228**, generated from insertion of decarbonylative intermediate **227** to MCP **226**, underwent cyclopropylmethyl−homoallyl metal-type rearrangement to afford nickelacycle **229**. Subsequent β-hydride elimination and insertion provided the thermally more stable complex **230**, while reductive elimination of **230** produced the [4 + 1] adduct **231**.

Scheme 89. Ni-Catalyzed Cycloadditions of Thiophthalic Anhydrides with Alkynes



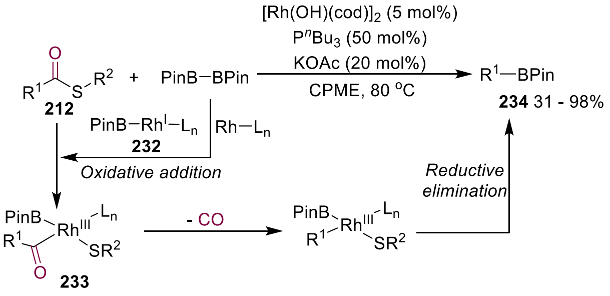
Scheme 90. Ni-Catalyzed [4 + 1] Cycloadditions of Thiophthalic Anhydrides



6.3. Decarbonylative Borylation

Aromatic thioesters can also serve as the precursors of arylboronate esters in the decarbonylative process. Niwa and Hosoya demonstrated the efficient Rh-catalyzed conversion of aromatic thioesters **212** to arylboronicesters **234** (Scheme 91).[242] The reaction was supposed to involve the oxidative addition of borylrhodium **232** to the thioester to afford **233**. Subsequent decarbonylation and reductive elimination released products **234**. A feasible synthetic application of this strategy was exhibited in the two-step borylation of carboxylic acid-containing drugs.

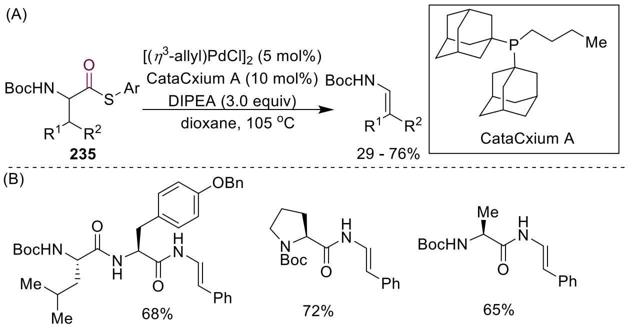
Scheme 91. Rh-Catalyzed Decarbonylative Borylation of Aromatic Thioesters



6.4. Retro-Hydroamidocarbonylation

Retro-hydroamidocarbonylation represents another type of decarbonylative reaction for use in enamide synthesis. On the basis of the previous observations of Liebeskind et al.,[243] Skrydstrup et al. reported a method for the synthesis of various enamides from aminothioesters **235** via Pd-catalyzed decarbonylation and β-hydride elimination processes (Scheme 92A).[244] Both the amino acid thioesters and peptides with an aminothioester were competent in this tactic, forming enamides without epimerization at the stereogenic centers (Scheme 92B).

Scheme 92. Synthesis of Enamides from Aminothioesters via a Pd-Catalyzed Decarbonylation



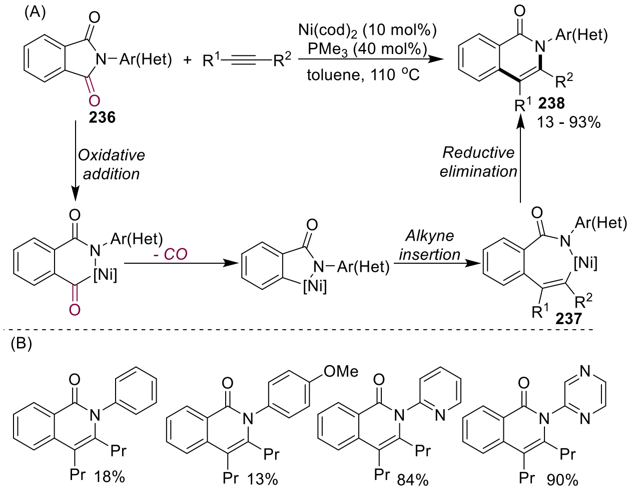
7. DECARBONYLATION WITH CLEAVAGE OF C(ACYL)−N/C(ACYL)−C BONDS

The introduction of the amide as a candidate for decarbonylative reactions via the direct oxidative addition to transition metals into the C(acyl)−N bond has attracted significant interest in recent years. Historically, activation of the amide C(acyl)−N bond by transition metals has been largely unexplored[56] because of strong $n_N \rightarrow \pi^*_{C=O}$ conjugation. However, recent structural studies have demonstrated that with electronical activation and steric distortion,[41,245,246] such as electron deficiency, weak π−π interaction, amide bond twist, and chelation assistance,[41] C(acyl)−N bond activation is, in contrast to conventional strategies, quite straightforward. This opens the way for the utilization of amide components as electrophiles in the synthesis of valuable molecules by previously unknown catalytic modes.[42,247−249] To date, two general types of amides have been often used for the decarbonylation process: (1) cyclic amides with specialized amide bonds, such as phthalimides and saccharins, wherein the cleavage of amide bonds was mainly driven by electron deficiency and (2) acyclic amides, such as *N*-acyl-glutarimides, tosyl amides, Boc amides, which have a C(acyl)−N bond that can be cleaved by disruption of the amide resonance energy.[41]

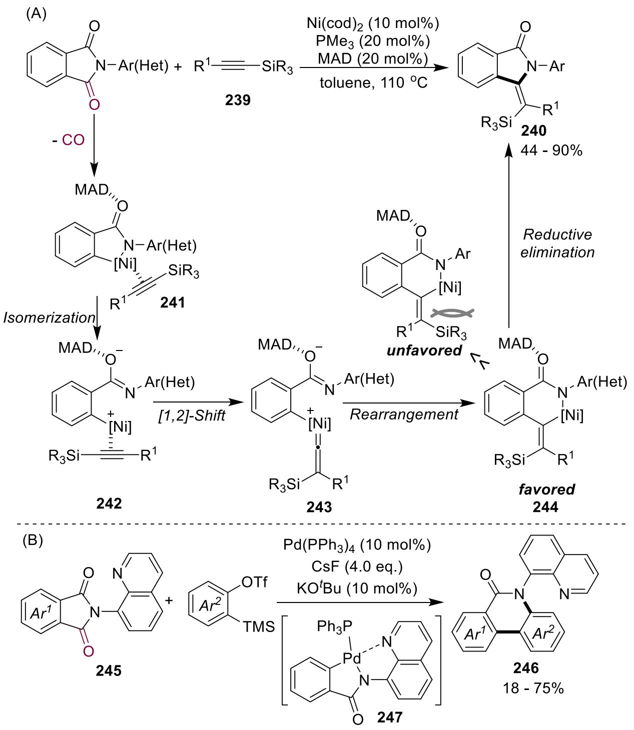
7.1. Decarbonylation of Cyclic Amide Derivatives

7.1.1. Decarbonylative Insertion Reactions. Phthalimides are cyclic amides with electron deficiency on their nitrogen atoms, thus rendering them appealing substrates for decarbonylative processes.[41] In 2008, Kurahashi and Matsubara reported the Ni-catalyzed selective decarbonylative addition of phthalimides **236** onto internal alkynes (Scheme 93A).[66] As shown in Scheme 91B, various isoquinolines **238** were synthesized with catalytic amounts of Ni/PMe$_3$ in the presence of alkynes. The results revealed that the electron-withdrawing arenes on the phthalimide nitrogen atom afforded better yields. The proposed mechanism involved the oxidative addition of nickel to the amide C(acyl)−N bond, followed by decarbonylation and insertion of an alkyne to form the seven-membered nickelacycle **237** (Scheme 93A). This then underwent reductive elimination to produce the desired products **238**. DFT studies by Poater et al. substantially confirmed this proposed mechanism.[250]

Scheme 93. Ni-Catalyzed Decarbonylative Addition of Phthalimides to Alkynes



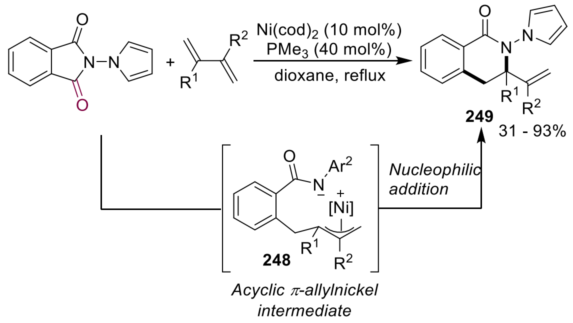
Scheme 94. Ni-Catalyzed Decarbonylative Cycloaddition of Phthalimides



In subsequent studies, a distinct reaction pattern was reported by Kurahashi and Matsubara which, in the presence of a Ni-catalyst and MAD-co-catalyst, provided the five-membered isoindolinones **240** from phthalimides and trimethylsilyl-substituted alkynes **239** (Scheme 94A).[251] In the presence of a Lewis acid, the Ni in intermediate **241** was thought to be electron deficient and could strongly coordinate to the alkyne. Upon isomerization, intermediate **242** afforded the cationic nickel vinylidene complex **243** via the [1,2]-shift of the silyl group. Rearrangement of vinylidene complex **243** generated the six-membered azanickelacycle **244**, which underwent reductive elimination to furnish isoindolinone. The high stereoselectivity of this reaction was attributed to the directed insertion of the vinylidene moiety in intermediate **243**, in which the steric repulsive interaction between the trimethylsilyl group and phosphine ligand on the nickel was minimal. Recently, Xu et al. further extended the scope of the decarbonylative annulation of phthalimides **245** by replacing the alkyne with arynes, thereby leading to phenanthridinones **246** (Scheme 94B).[252] In this case, the quinoline substituents on the N atoms of phthalimides **245** might have been crucial to stabilize the active Pd species **247**.

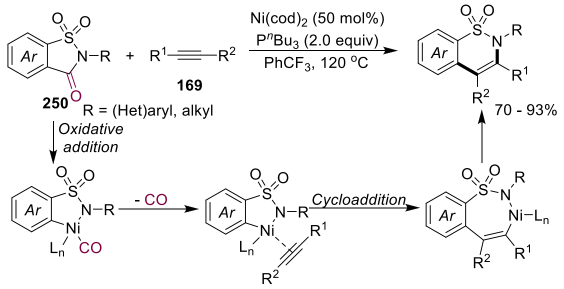
Similar to the decarbonylative cycloaddition of alkynes, the use of 1,3-dienes in decarbonylative annulation of phthalimides has also been explored by Kurahashi and Matsubara (Scheme 95).[253] This protocol proposed that acyclic π-allylnickel intermediate **248** was formed with the insertion of a bidentate diene to activate the C−Ni bond, with subsequent nucleophilic addition affording isoquinolones **249**.

Scheme 95. Ni-Catalyzed Decarbonylative Cycloaddition of Phthalimides with 1,3-Dienes



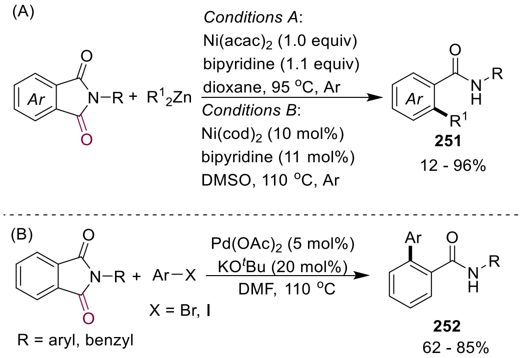
In addition to phthalimides, decarbonylative cycloaddition has also been achieved by using saccharins as the substrate. In 2015, Bi et al. reported the Ni-catalyzed decarbonylative cycloaddition between saccharins **250** and alkynes **169** (Scheme 96);[254] decarbonylative homocoupling was also developed in this work. Mechanistically, the oxidative addition of Ni and extrusion of CO were key steps for both procedures.

Scheme 96. Decarbonylative Cycloaddition of Saccharins by Ni Catalysis

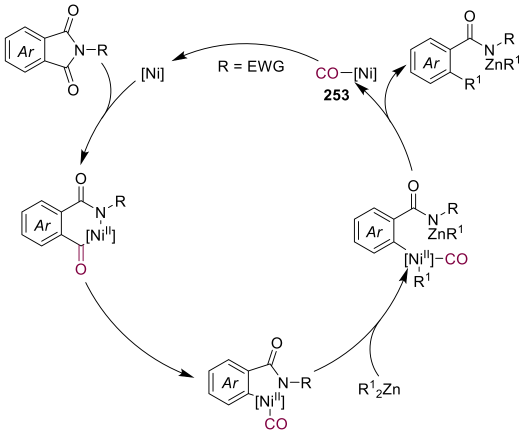


7.1.2. Decarbonylative Coupling Reactions. Given the importance of the construction of C−C bonds through decarbonylative reactions, Johnson et al. demonstrated a Ni-mediated decarbonylative coupling of phthalimides and diorganozinc reagents, producing ortho-substituted benzamides **251** in high yield. Although good functional group tolerance was observed, the reaction required a stoichiometric amount of nickel catalyst (Scheme 97A, Condition A).[255] According to the postulated mechanism (Scheme 98), Ni−CO complex **253** was generated during the reaction, which made turnover problematic. Subsequently, a catalytic version was reported by the same group (Scheme 97A, condition B).[256] They discovered that Ni-catalytic coupling of phthalimides and organozinc could be achieved just by introducing an electron-withdrawing group onto the phthalimide nitrogen atom. These results indicated that electron-deficient substituents could weaken the Ni−CO bond in intermediate **253** (Scheme 98). Very recently, Biswas et al. developed coupling reactions of phthalimides with aryl halides in the presence of Pd(OAc)$_2$ via a decarbonylative process to produce ortho-substituted benzamides **252** (Scheme 97B).[257]

Scheme 97. Decarbonylative Coupling of Phthalimides

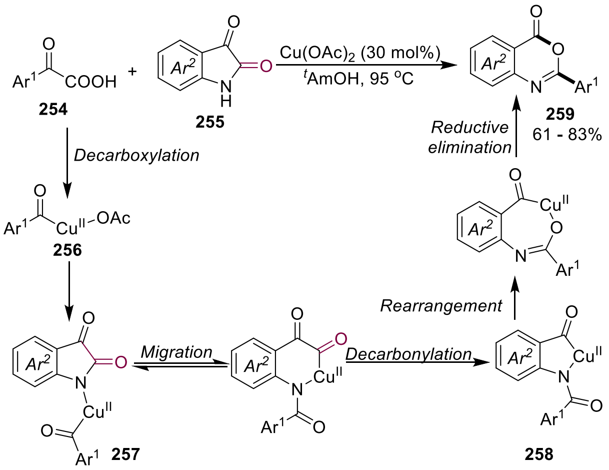


Scheme 98. Proposed Mechanism of Decarbonylative Coupling of Phthalimides and Diorganozinc Reagents



In 2016, Gogoi et al. reported a Cu-catalyzed isatin decarbonylative coupling reaction with α-oxocarboxylic acid **254** (Scheme 99).[258] The Cu(II) species **256**, generated from decarboxylation of α-oxocarboxylic, was proposed to react with

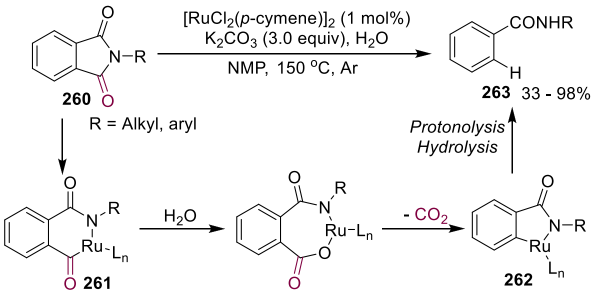
Scheme 99. Cu-Catalyzed Sequential Decarboxylative and Decarbonylative Coupling Reaction



isatin **255** to afford intermediate **257**. Subsequent migration of Cu, followed by decarbonylation led to intermediate **258**, which underwent rearrangement and reductive elimination to produce products **259**. Control experiments indicated that the presence of the free isatin N−H group was a crucial factor for this reaction, and no products were observed with N−H-protected isatin as the substrate.

7.1.3. Hydrogenation. Hydrogenation represents another type of decarbonylative reaction of phthalimide. In 2013, García et al. reported a Ni catalyst that could hydrogenate phthalimide to benzamide in 82% selectivity under 50 bar H_2.[259] Later, Gramage-Doria et al. reported the ruthenium-catalyzed protodecarbonylation of phthalimide derivatives **260** to form secondary amides **263** (Scheme 100).[260] Under Ru-catalyzed conditions, intermediates **261** underwent hydroxylation and decarboxylation to form ruthenacycles **262**, while subsequent protonolysis and hydrolysis afforded the products. Recent DFT calculations combined with experimental data unraveled the whole reaction mechanism and revealed that the base plays multiple roles in the reaction.[261]

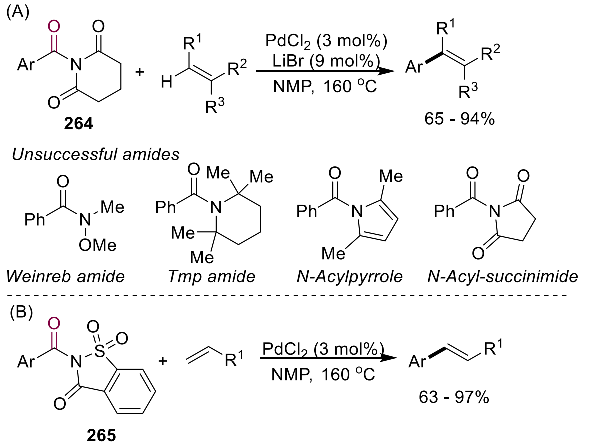
Scheme 100. Ru-Catalyzed Protodecarbonylation of Phthalimides



7.2. Decarbonylation of *N*-Acyl-Glutarimides

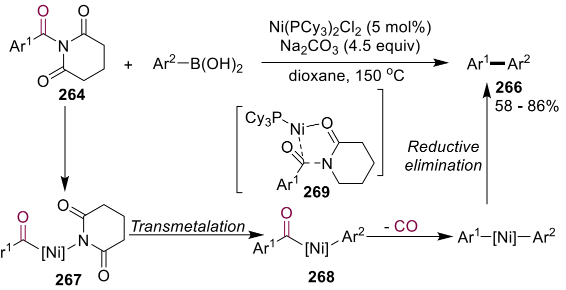
7.2.1. Decarbonylative Insertion Reactions. The other extensively studied approach for decarbonylation that involves cyclic amides is the selective activation at the exocyclic C(acyl)−N bond. Steric activation of amides by disruption of the amide bond resonance provides a new amide reactivity platform for N−C scission.[262] Amide ground-state distortion, a characteristic property of nonplanar amides, can be used to facilitate metal insertion into the C(acyl)−N amide bond, while the selective decarbonylation of the acyl-metal intermediate provides a valuable aryl/alkyl-metal intermediate capable of participating in various catalytic coupling reactions.[245,248] A seminal study by Szostak et al. reported a decarbonylative Mizoroki−Heck reaction of aromatic glutarimide amides **264** (Scheme 101A).[263] The twisted amides **264** exhibited a unique reactivity in the transformation reaction. Other amides such as Weinreb and tmp amides, *N*-acylpyrrole, and *N*-acyl-succinimide were all unreactive (Scheme 101A). The reaction was amenable to a wide range of functional groups and underwent high coupling selectivity to afford single olefin isomers (*E*/*Z* > 98:2). Later, Szostak et al. reported that *N*-acylsaccharins **265** could also be used as arylating reagents in decarbonylative Mizoroki−Heck reactions (Scheme 101B).[264] Competition experiments revealed that *N*-acylsaccharins **265** displayed a higher reactivity than *N*-acyl-glutarimides **264**.

Scheme 101. Pd-Catalyzed Decarbonylative Mizoroki−Heck Reaction of Amides



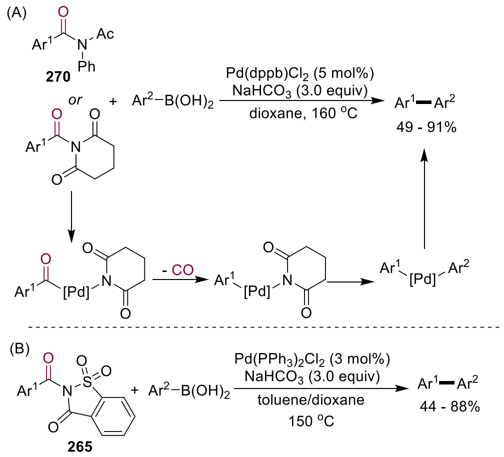
7.2.2. Decarbonylative Coupling Reactions. *7.2.2.1. Arylation and Alkynylation.* Amides can also be regarded as aryl pseudo halides in coupling reactions. For instance, Szostak et al. demonstrated that the Ni-catalyzed Suzuki−Miyaura coupling reaction of *N*-acyl-glutarimides **264** with arylboronic acids yielded biaryls **266** in high yield (Scheme 102).[265] The authors proposed that decarbonylation did not occur directly from acyl intermediate **267**, which instead underwent transmetalation to generate intermediate **268**; subsequent decarbonylation and reductive elimination afforded products **266**. Having interest in this report, Hong et al. performed a computational study, with the results suggesting that interaction of nickel and the *N*-glutarimide amide carbonyl provided a crucial directing effect for C(acyl)−N bond cleavage (Scheme 102, intermediate **269**).[266] The geometric twisting weakened the resonance stability by removing the acyl-nitrogen conjugation, which lowered the energy penalty for C−N bond stretching during oxidative addition. Having a continuous interest in decarbonylative coupling, Szostak, Hong, et al. reported a palladium-catalyzed decarbonylative Suzuki−Miyaura reaction of glutarimide amides (Scheme 103A).[267] Compared to the Ni-catalyzed conditions,[265] decarbonylation was considered prior to transmetalation. Notably, acyclic *N*-acetyl (*N*−Ac) amides **270** were also applicable in this process. More recently, Zeng et al. also demonstrated that *N*-acylsaccharins **265** are compatible substrates in Pd-catalyzed decarbonylative Suzuki−Miyaura coupling (Scheme 103B).[268]

Scheme 102. Ni-Catalyzed Suzuki−Miyaura Decarbonylative Coupling of Amides



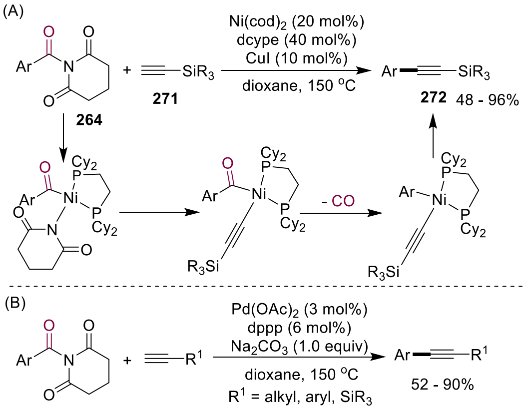
The Sonogashira coupling is an exceptionally versatile method for the synthesis of aryl alkynes. In 2017, Rueping et

Scheme 103. Pd-Catalyzed Decarbonylative Suzuki–Miyaura Coupling of Amides



al. developed the Sonogashira-type coupling reaction of *N*-acylglutarimides **264** with terminal alkynes (Scheme 104A).[269] In the presence of Ni(cod)$_2$ and CuI catalysts and a dcype ligand, the amides **264** underwent selective decarbonylation to couple with a terminal alkyne **271**, affording various aryl and heteroaryl internal alkynes **272** in good to excellent yield. Notably, this reaction was only applicable to silylacetylenes **271** because of facile polymerization of the aryl and alkyl terminal acetylenes. Later, Chen et al. disclosed a Pd catalysis version of this transformation (Scheme 104B).[270] Except for silylacetylenes, this transformation was also applicable to both aromatic and aliphatic terminal alkynes.

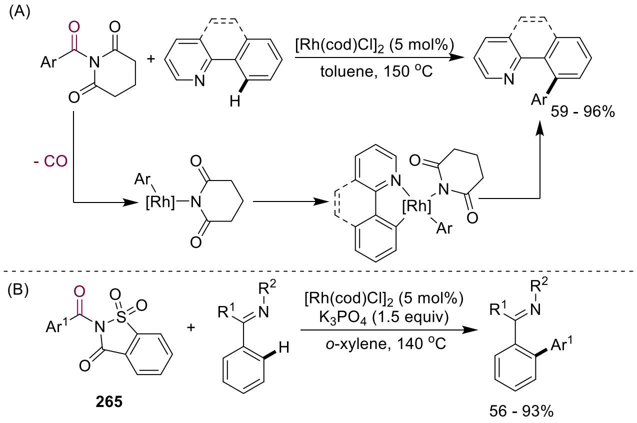
Scheme 104. Decarbonylative Alkynylation of Amides



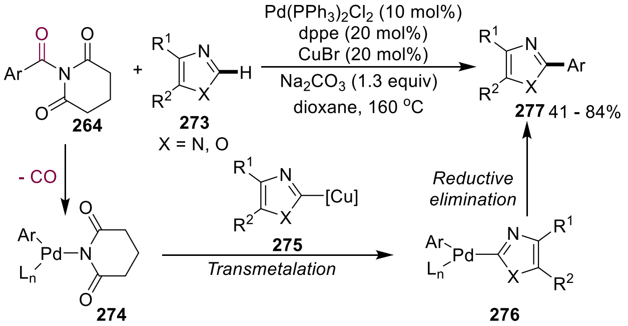
7.2.2.2. C–H Functionalization. Because of the beneficial character of the direct functionalization of arenes, C–H bond activation methods have been extensively investigated with the combination of the decarbonylation of amides. In 2016, by utilizing a nitrogen-containing directing group strategy, Szostak et al. achieved Rh-catalyzed direct C–H arylation and alkenylation reactions via the decarbonylation of twisted amides (Scheme 105A).[271] This is the first reported example of Rh-catalyzed decarbonylation of amides. Later, Zeng et al. also demonstrated that *N*-acylsaccharin amides **265** could be applied to decarbonylate C–H bond activation (Scheme 105B).[272]

Recently, Zhou, Ge, et al. developed a palladium/copper-catalyzed decarbonylative C–H arylation of 1,3-azoles **273** with twisted amides **264** (Scheme 106).[273] In this process, the Pd catalyst was inserted into the C–N bond of the amides to provide decarbonylative intermediate **274**. Possible subsequent mechanistic pathways involved transmetalation between intermediate **274** and Cu species **275** to provide Pd-aryl intermediates **276**, which underwent reductive elimination to release the 2-arylated oxazole derivatives **277**.

Scheme 105. Rh-Catalyzed Decarbonylative Coupling and C–H Functionalization

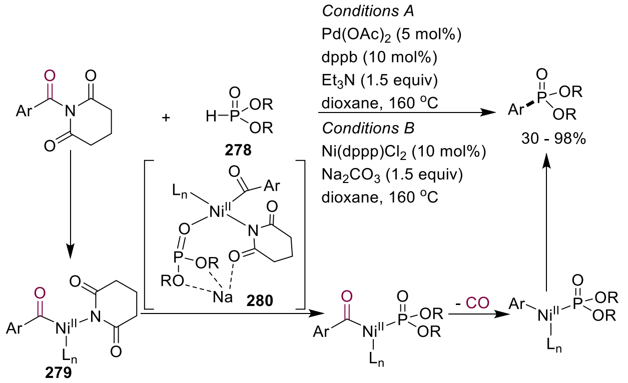


Scheme 106. Decarbonylative C–H Functionalization of Amides



7.2.3. Phosphorylation. Decarbonylative phosphorylation of *N*-acyl-glutarimides was realized by the Szostak laboratory (Scheme 107).[274] This reaction provided an alternative to the classic Hirao reaction using amide derivatives as electrophiles.[275] They demonstrated that both the Pd and Ni

Scheme 107. Decarbonylative Phosphorylation of Amides by Pd and Ni Catalysis

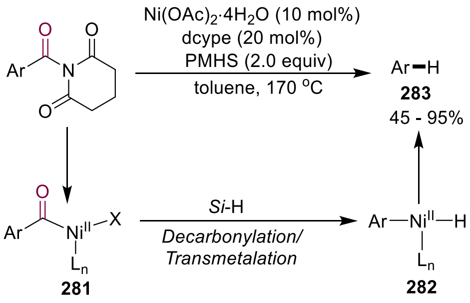


complexes were competent catalysts for this transformation. Recent computational calculations revealed oxidative addition as the rate-determining step and supported that for intermediate **279**, phosphorylation proceeds prior to decarbonylation.[276] In this process, Na_2CO_3 not only emerges as an alkali to mediate the H-transfer of phosphate **278**, but also coordinates with the adjacent carbonyl to activate the Ni−N bond in **280**. The coupling pattern described above can be extended to other nucleophilic reagents to broaden the range of the coupling reactions. For instance, amination,[277,278] cyanation,[168,279] silylation,[278] borylation,[278,280] and thioetherification[179] were further realized.

7.2.4. Defunctionalization.

In addition to coupling reactions, reductive decarbonylation of amides with commercially available hydrosilanes was realized by Rueping et al. (Scheme 108).[281] Here, acyl nickel(II) intermediate **281** underwent CO deinsertion/transmetalation with the hydrosilane to afford aryl hydride nickel(II) **282**, which delivered the products **283** by reductive elimination. A variety of aryl and heteroaryl amides as well as heteroaryl esters were suitable substrates for this transformation.

Scheme 108. Decarbonylative Reductive Defunctionalization of Amides



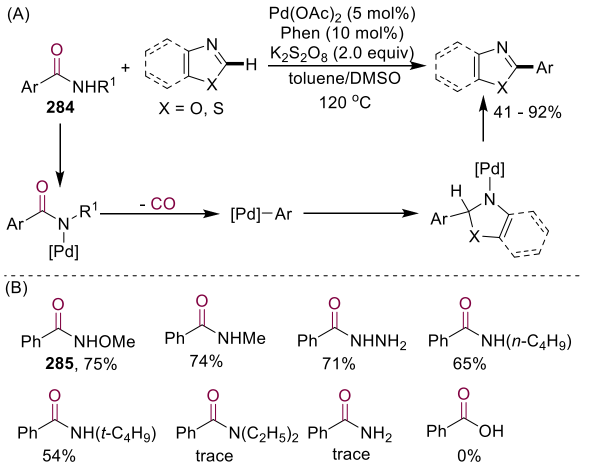
7.3. Decarbonylation of Other Acyclic Amides

7.3.1. C−H Functionalization.

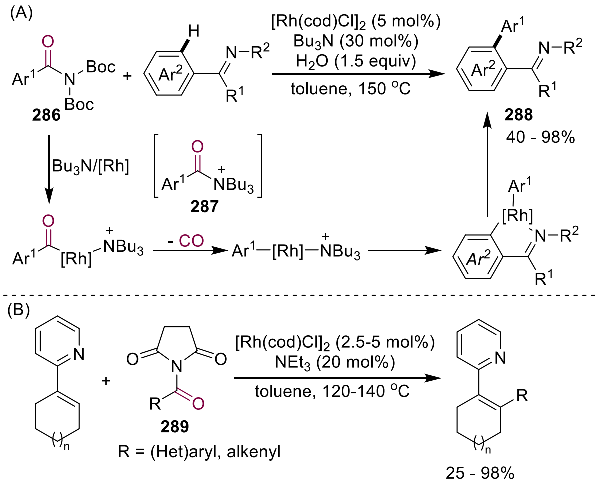
Decarbonylative reactions of acyclic amides, in which the steric and electronic properties are remodeled, have also attracted significant interest. In a pioneering report from 2002, Miura et al. used *N*-(2-thenoyl)aniline for the decarbanoylative coupling of bromobenzene.[282] Later, the Pd-catalyzed decarbonylative C−H arylation of aromatic amides was reported by Wang et al. (Scheme 109A).[283] A variety of *N*-substituted benzamides were examined to investigate the scope of benzamides **284**. Particularly, *N*-methoxybenzamide **285** displayed the highest reactivity in this transformation (Scheme 109B).

Recently, Szostak et al. reported a Rh-catalyzed decarbonylative C−H arylation using primary amides as the arylating reagents (Scheme 110A).[284] With the combination of a Lewis base, the inert C(acyl)−N bonds in primary amides **286** were converted to weak acylammonium bonds (Scheme 110, intermediate **287**). Selective insertion of the acylammonium bonds was then followed by decarbonylation, C−H arylation, and reductive elimination to afford biaryl products **288**. A variety of heterocycle substrates, such as benzo[*h*]quinolone, pyrimidine, pyrrole, indole, and benzothiophene, were all successfully coupled with amides to afford the biaryl products in good to excellent yield. Notably, the activation of *N*-Boc was particularly useful because its twisted character allowed it to engage common primary and secondary amides in decarbonylative transformations.[285] In this process, the protonation of the *N*-carbamate carbonyl group also increased the propensity of metal insertion. More recently, Wang et al. expanded C−H functionalization to alkenyl C−H bond using aroyl- and acrylamides **289** as the arylating and alkenylating agents, respectively (Scheme 110B).[286]

Scheme 109. Pd-Catalyzed Tandem Decarbonylation/C−H Functionalization



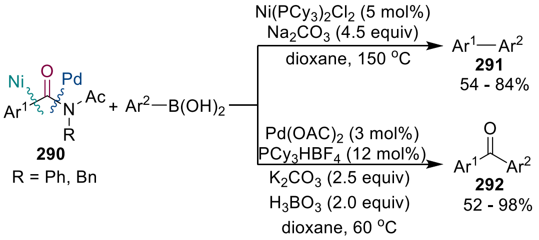
Scheme 110. Site-Selective C−H/C−N/C−C Activation by Cooperative Catalysis



7.3.2. Arylation.

One main obstacle in Pd- and Ni-catalyzed amide C(acyl)−N coupling is the undesired cleavage of the N−X (X = Ts, Boc) bond. To solve this issue, Szostak et al. presented *N*-Ac-amides **290** as an alternative (Scheme 111),[287] producing diverse biaryls derivatives **291** in fair to high yield. Structural and computational studies revealed that

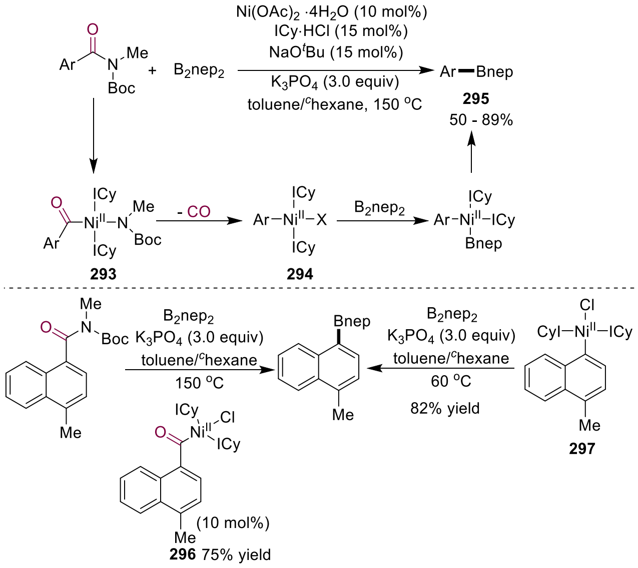
Scheme 111. Acyl and Decarbonylative Suzuki−Miyaura Coupling of N-Acetyl Amides



amide twist, electronic destabilization, and high resonance energy (RE) of the *N*-Ac group are all determining features for the high reactivity of the C(acyl)−N bond. Intriguingly, the replacement of nickel with palladium led to the non-decarbonylative Suzuki−Miyaura coupling products **292** under lower temperature conditions.

7.3.3. Borylation and Phosphorylation. In 2016, Shi et al. developed a decarbonylative borylation of amides using a Ni/*N*-heterocyclic carbene catalytic system (Scheme 112).[288]

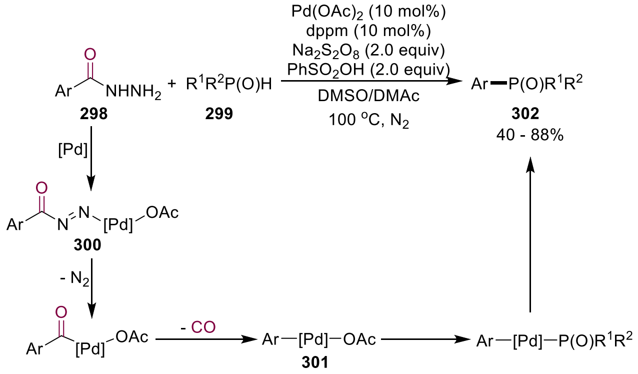
Scheme 112. Ni-Catalyzed Decarbonylative Borylation of Amides



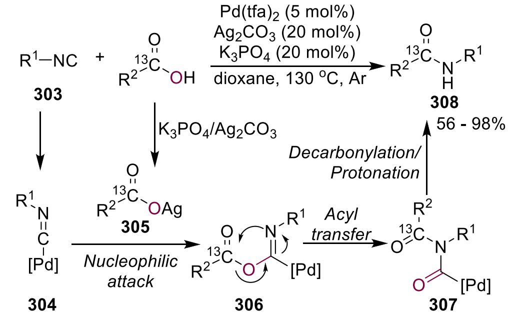
Unlike the above-mentioned Pd-catalyzed decarbonylative process of amides, *N*-acyl-glutarimides and *N*-methoxybenzamide were not suitable substrates. A Boc group was necessary for the oxidative addition of Ni to the C(acyl)−N bond. As shown in Scheme 112, acyl−nickel(II) intermediate **293** underwent decarbonylation to produce aryl nickel intermediate **294** under high reaction temperature conditions. Subsequent reductive elimination afforded the desired products **295**. The X-ray analysis of the structures of both acyl−nickel(II) **296** and aryl−nickel(II) **297** complexes further conformed the proposed mechanism.

Zhou et al. also developed the Pd-catalyzed decarbonylative coupling of aroylhydrazides **298** with P(O)H compounds **299** (Scheme 113).[289] The proposed mechanism began with the oxidative dehydrogenation of aroyl hydrazide **298**, with subsequent extrusion of molecular nitrogen and decarbonylation of intermediate **300** to afford the Ar−PdOAc intermediate **301**. This underwent ligand exchange and reductive elimination to produce aryl phosphorus compounds **302**. Notably, in the presence of a Brønsted acid and bidentate phosphine ligand, the cooperative reaction system suppressed the undesired oxidation and coordination of the P(O)−H compounds and activated the C(acyl)−C bonds selectively.

Scheme 113. Pd-Catalyzed Decarbonylative Coupling of Aroylhydrazides with P(O)H Compounds



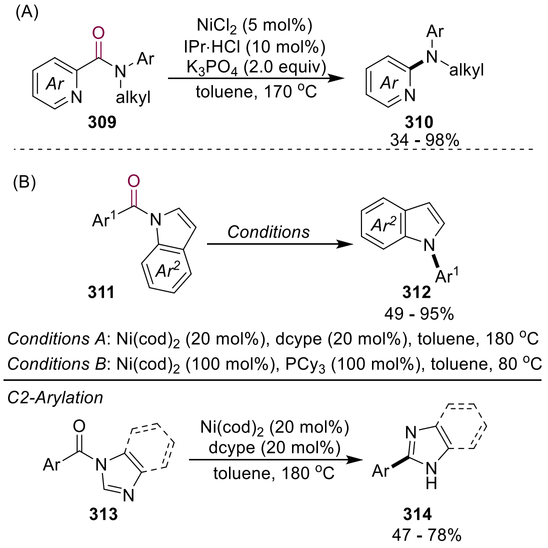
Scheme 114. Pd-Catalyzed Decarbonylative Coupling of Carboxylic Acids with Isocyanides



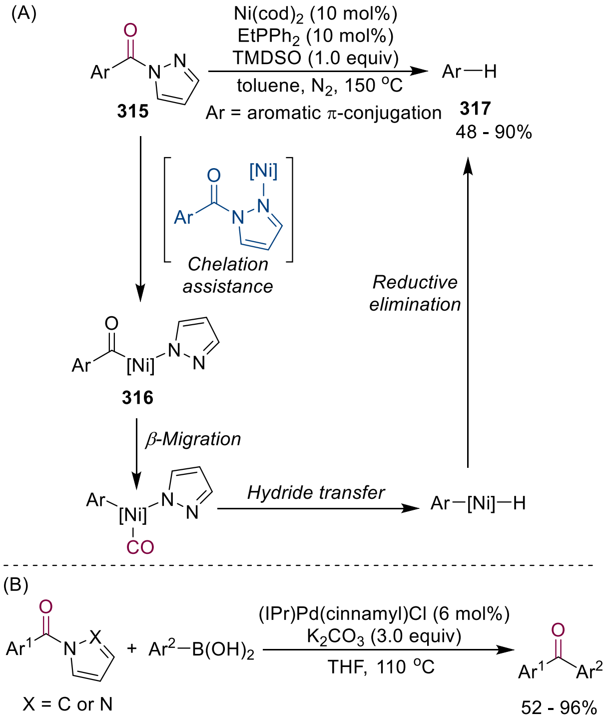
7.3.4. Amidation. Except for the preformed amide substrates, an unprecedented decarbonylation coupling between carboxylic acids and isocyanides was achieved by Xie et al. via an *in situ* generated amidate−metal intermediate, selectively affording various amidated products in high yield (Scheme 114).[290] In this process, initial oxidative addition of Pd to C(acyl)−O did not occur and the authors proposed that coordination of isocyanide **303** with Pd to form intermediate **304** occurred instead. Subsequently, direct nucleophilic attack of silver carboxylate **305** to **304** produced imidoyl−Pd intermediate **306**, which underwent intramolecular acyl transfer to form amidate−Pd intermediate **307**. Subsequent decarbonylation and protonation afforded the amidated products **308**. A ^{13}C-labeled reaction further supported this mechanism by proving that the carbon atom of the extruded CO group originated from isocyanide. Various carboxylic acids and aryl isocyanides are compatible with this reaction, while alkyls, except for benzyl isocyanides, are not.

In addition to the intermolecular processes, intramolecular decarbonylative recombination has also been developed. Pioneering work by Reuping et al. revealed that under Ni-catalyzed conditions, various 2-azinecarboxamides **309** could be converted to amidines **310** through CO extrusion and recombination (Scheme 115A).[291] Subsequent studies by Chatani and Tobisu further applied decarbonylative recombination of *N*-acylated *N*-heteroarenes **311** to produce *N*-aryl heteroarenes **312** (Scheme 115B).[292] Here, the pK_a value of the parent amine of amide **311** had a significant impact on the reactivity, whereby a stronger C(acyl)−N bond was observed as the parent amine became more basic. This led to lower reactivity under catalytic conditions (Scheme 115B, conditions A) and, thus, equivalent Ni with PCy$_3$ was used for these substrates as an alternative (Scheme 115B, conditions B). Interestingly, when *N*-acylated benzimidazoles **313** were used as substrates, decarbonylation accompanied by 1,2-migration delivered 2-arylated benzimidazoles **314**. Preliminary mechanistic studies revealed that a distinct intermolecular pathway is likely to be involved.

Scheme 115. Ni-Catalyzed Decarbonylative Amination through Intramolecular Recombination



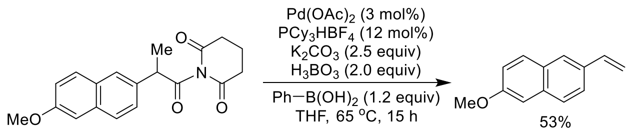
Scheme 116. Ni-Catalyzed Deamidative Reduction of Amides



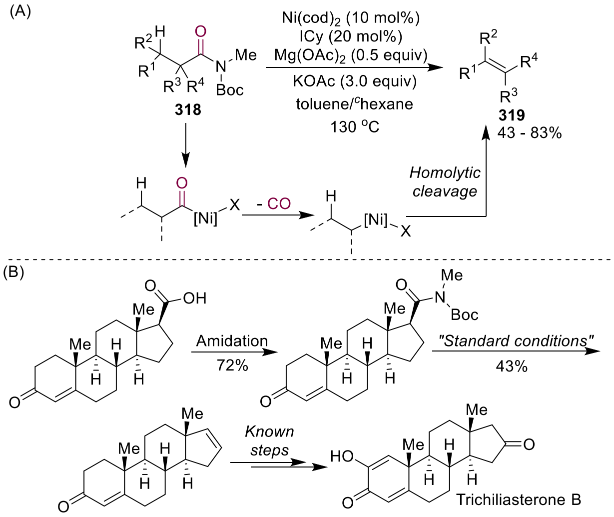
7.3.5. Defunctionalization. While all of the examples discussed thus far have focused on amides comprising a distorted constitutional framework, a Ni-catalyzed reduction of planar/nontwisted amides was recently explored by Maiti and Lahiri (Scheme 116A).[293] The stable C(acyl)−N bond was activated with electronic conjugation as well as chelation assistance of nitrogen on the pyrazole of amide **315**. The generated acyl−Ni intermediate **316** underwent β-migration of CO and hydride transfer, while subsequent C−H reductive elimination afforded the deamidative products **317**. The proposed mechanism was supported by isotope-labeling experiments and ESI-MS analysis. Additionally, the divergent reactivity of these planar and electronically activated amides was further disclosed by Szostak et al. (Scheme 116B).[294] They also reported nondecarbonylative Suzuki−Miyaura coupling products synthesized under Pd-catalyzed conditions. Computational studies revealed that the electronic destabilization of $n_N \rightarrow \pi^*_{C=O}$ conjugation enabled selective N−C activation in *N*-acylpyrroles and pyrazoles.

By taking advantage of the β-H elimination propensity of alkyl-metal intermediates, amides bearing activated β-hydrogens can also be used as viable precursors for the generation of alkenes. In 2016, Szostak and Meng first observed the decarbonylation and β-hydride elimination process instead of the Suzuki−Miyaura coupling of an aliphatic amide using a Pd/PCy$_3$ catalyst (Scheme 117).[295] Subsequently, Shi et al. discovered that aliphatic amides **318** could also be involved in the Ni-catalyzed decarbonylative process, affording thermodynamically more stable internal *E*-2-alkene isomers **319** as the major products (Scheme 118A).[296,297] In this process, substituents at the γ position of the amide displayed significant influence on olefin isomerization. Thus, aryl groups favored olefin monoisomerization to form internal alkenes, while alkyl groups inhibited the process to afford terminal products. Preliminary mechanistic studies suggested that a distinct homolytic cleavage might be involved in the elimination process. Synthetic applications revealed that this approach can be used for the formal synthesis of Trichiliasterone B (Scheme 118B).

Scheme 117. Pd-Catalyzed Decarbonylation/β-Hydride Elimination of Aliphatic Amides



Scheme 118. Ni-Catalyzed Retro-Hydroamidocarbonylation of Aliphatic Amides



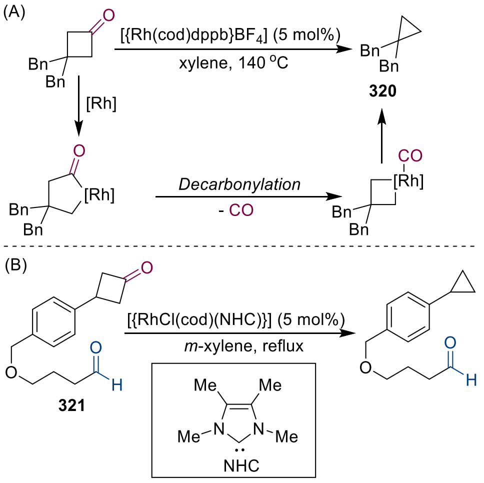
8. DECARBONYLATION WITH CLEAVAGE OF TWO C(ACYL)–C BONDS

Ketones are very common and abundant in many organic molecules. The development of transition-metal-catalyzed decarbonylation of ketones is crucial for organic synthesis. Notably, all the methods presented thus far have involved metal-catalyzed cleavage of carbon–heteroatom bonds prior to decarbonylation. However, the decarbonylation of ketones is rather special as it first requires C–C bond cleavage. Since both the thermodynamic and kinetic barriers contribute to the overall lack of reactivity of the C–C bond, several methods have been employed to overcome such barriers by using transition metal catalysts, such as Rh, Ru, Pd, and Ni. Among these strategies is the direct decarbonylation of ketones of high reactivity. Strained molecules with a C–C bond adjacent to the carbonyl of ketones can be easily cleaved due to the weaker C–C bond and lesser steric hindrance of the planar structure of the carbonyl motif. The increased entropy of this system is an essential driving force for this process.[11] For the reaction of less reactive ketones, chelation assistance is considered as one of the most effective means for decarbonylation. Appropriate directing groups perform two major roles: (1) bringing the metal center closer to the targeted C–C bond and (2) generating the resulting metal species through the formation of a relatively stable five- or six-membered metallacycle, which is beneficial for decarbonylation and subsequent reactions.[11]

8.1. Strain-Driven Decarbonylation

8.1.1. Decarbonylation of Cyclobutenones. Pioneering work by Murakami and Ito established that a stoichiometric amount of Wilkinson's catalyst could promote the decarbonylation of cyclobutenone to provide cyclopropanes.[63] In 1996, catalytic processes of this transformation were developed by changing the catalyst system to [Rh(cod)dppb]BF_4 to deliver cyclopropane **320** in quantitative yield (Scheme 119A).[64]

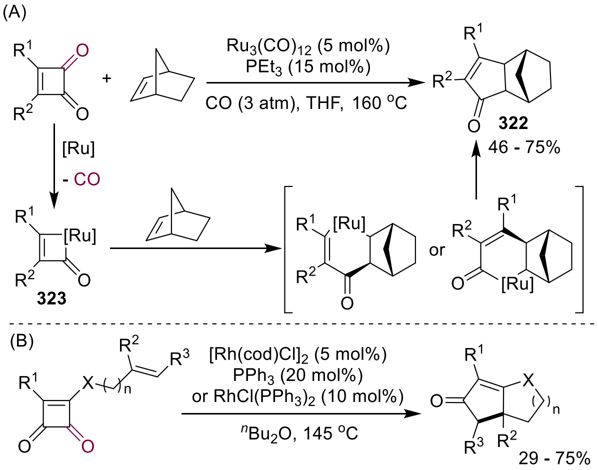
Scheme 119. Rh-Catalyzed Decarbonylation of Cyclobutanone



Murakami et al. later demonstrated a chemoselective Rh-catalyzed decarbonylation of cyclobutanone (Scheme 119B).[298] When RhCl(cod)(NHC) was used as the catalyst, cyclobutanone **321** could be selectively decarbonylated and the aldehyde group remained intact. Interestingly, Wilkinson's catalyst exhibited the opposite chemoselectivity and only the aldehyde group was removed. These seminal examples paved the way for the development of decarbonylation chemistry with cyclobutanones.

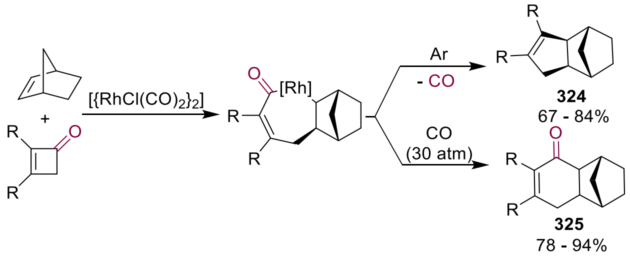
From a synthetic viewpoint, perhaps the most attractive processes are those that involve the decarbonylation-triggered insertion of C-based units into cyclobutanones. Mitsudo et al. demonstrated the Ru-catalyzed insertion of norbornene to provide cyclopentenones **322** (Scheme 120A).[299] In this reaction, the formation of ruthenium intermediates **323** was followed by the insertion of the norbornene and reductive elimination to afford cyclopentenones **322**. Yamamoto et al. later developed a related intramolecular coupling between cyclobutenediones and tethered olefins.[300] The proposed mechanism was similar to the aforementioned intermolecular olefin insertion into cyclobutenones (Scheme 120B).

Scheme 120. Decarbonylative Cycloadditions of Cyclobutenediones



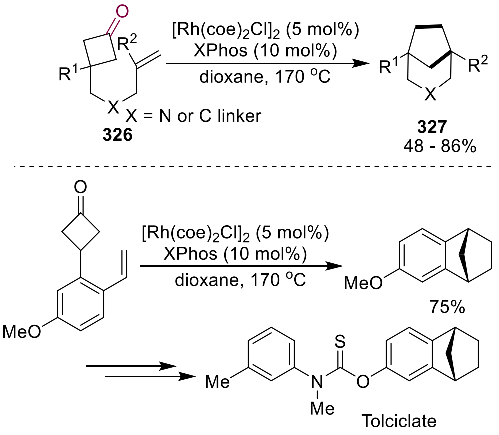
In 2004, Kondo, Mitsudo, et al. expanded their approach to cyclobutenones (Scheme 121).[301] The selectivity of the reactions could be controlled by adjusting the carbon monoxide pressure. Under argon atmosphere, these substrates underwent decarbonylative alkene insertion to exclusively provide cyclopentane **324**. In contrast, a higher carbon monoxide pressure afforded cyclohexenone **325** as the major products.

Scheme 121. Intermolecular Decarbonylative Cycloadditions of Cyclobutenones



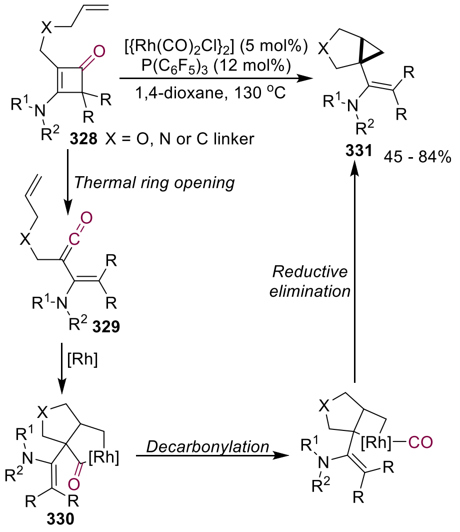
Intramolecular variants are particularly powerful for the construction of carbocycles. Dong et al. showcased this in the construction of challenging saturated bridged cyclopentane derivatives **326**, where initiation occurred by oxidative addition into cyclobutenones **327** (Scheme 122).[302] The chemistry was later applied to the synthesis of the antifungal drug tolciclate.

Scheme 122. Intramolecular Decarbonylative Cycloadditions



An alternative approach by this group generated vinylketene intermediate **329** by thermal ring opening of 3-amino-4,4-disubstituted cyclobutenones **328** (Scheme 123).[303] Oxidative capture of **329** by a Rh(I) catalyst generated rhodacycles **330**, which underwent subsequent decarbonylative reductive elimination to form [3.1.0]bicyclic products **331**.

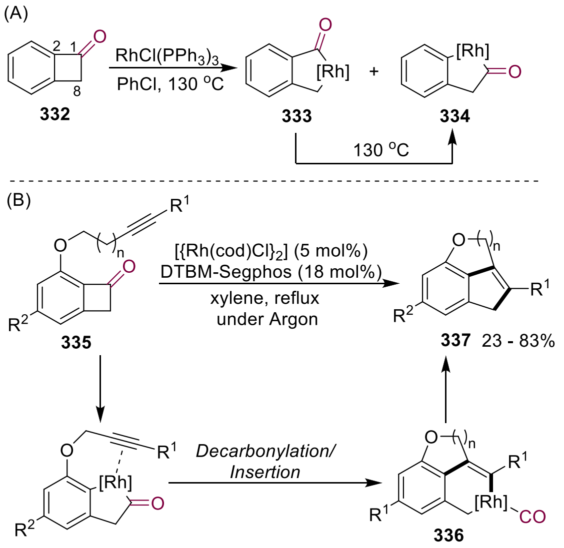
Scheme 123. Rh-Catalyzed Intramolecular Decarbonylative Coupling of 3-Aminocyclobutenones and Alkenes



8.1.2. Decarbonylation of Benzocyclobutenones.

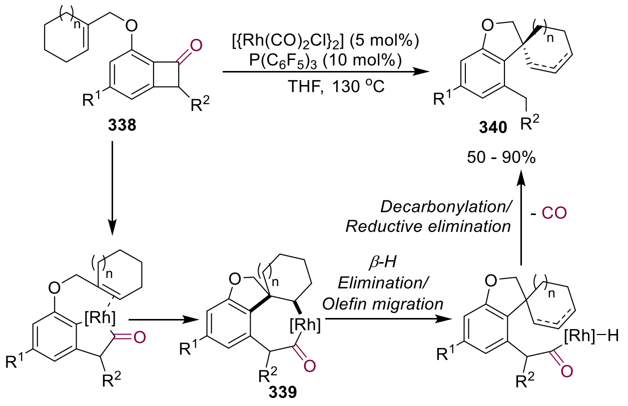
Pioneering work by Liebeskind et al. in 1992 demonstrated that a Rh catalyst could be inserted into the C1−C8 bond of benzocyclobutenone **332** to form rhodaindanone **333** (Scheme 124A).[304] However, thermodynamically favored regioisomer **334** could be obtained via thermal isomerization. Dong et al. exploited this activation mode to provide a wide range of benzocyclobutenone methodologies. The related decarbonylative processes have also been achieved. For example, this group reported the ligand-controlled selectivity of the Rh-catalyzed intramolecular coupling reaction of alkyne-benzocyclobutenone **335** (Scheme 124B).[305] When the chiral ligand DTBM-segphos was used, decarbonylation of intermediate **336** afforded tricyclic indenes **337** as the products.

Scheme 124. Intramolecular Cycloadditions of Benzocyclobutenones and Alkynes



In addition to forming fused rings, spirocyclic systems can also be constructed from olefin-tethered benzocyclobutenones **338** through Rh-catalytic decarbonylative cycloadditions (Scheme 125).[306] On the basis of the DFT studies by Fu and Yu,[307] β-hydride elimination occurred at the rhodaindanone **339** stage, which subsequently underwent decarbonylation and C−H reductive elimination to afford the spirocyclic products **340**. It is worth noting that an olefin migration process is also possible after the β-hydride elimination of intermediate **339** to afford the isomerized olefin product.

Scheme 125. Decarbonylative Cycloadditions of Benzocyclobutenones and Alkenes



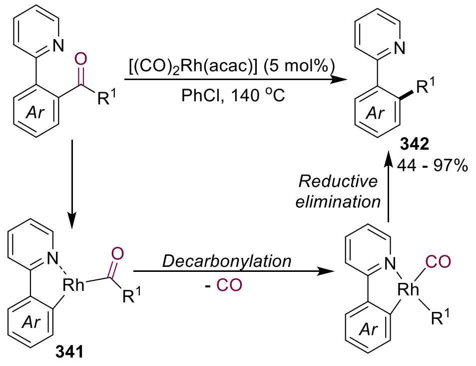
8.2. Decarbonylation of Unstrained Ketones

8.2.1. Decarbonylation Assisted by Chelation.

The examples provided thus far in this section involved strained ring systems; however, there have also been significant developments with unstrained substrates.[308−311] In this respect, the formation of a stable chelate is a commonly used strategy for the catalyzed decarbonylative process of unstrained ketones. This subject was pioneered by Murai et al., who reported an oxazoline-directed decarbonylation reaction via activation of unstrained C−C bonds.[312]

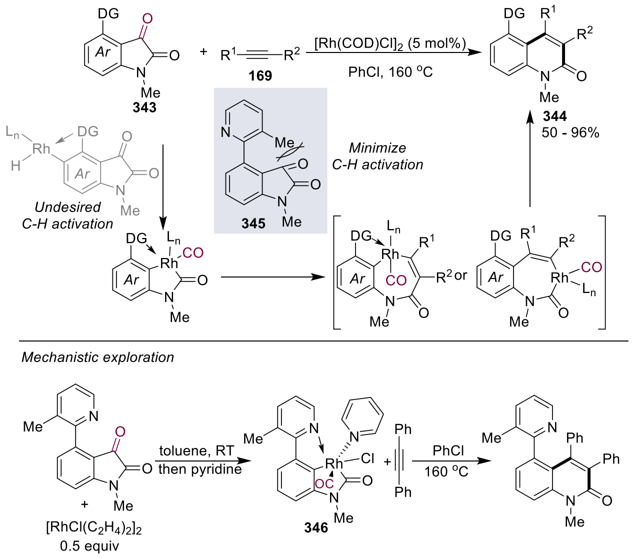
In 2012, Shi et al. developed a Rh-catalyzed decarbonylative process of unstrained ketones using a pyridyl group as an auxiliary directing group (Scheme 126).[313] The process tolerated a range of groups such as alkenyls, alkyls, aryls, and heteroaryls, affording the decarbonylative products in moderate to excellent yield. Mechanistic studies revealed that the reaction proceeded through the pyridine-assisted oxidative addition of the C−C bond to form a five-membered rhodacycle **341**. Subsequent decarbonylation and reductive elimination delivered the final decarbonylative products **342**.

Scheme 126. Rh-Catalyzed Decarbonylative Coupling of Unstrained Ketones

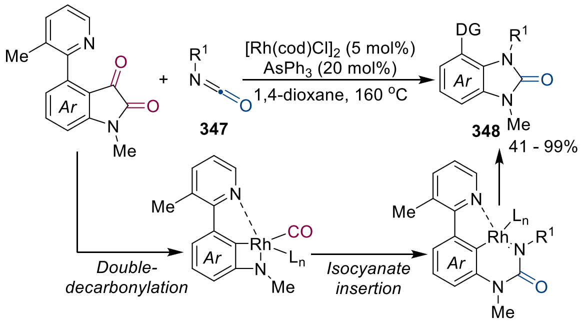


Extension of the activation mode to less strained cyclopentanones has also been achieved. Dong et al. realized the decarbonylative annulation between isatins **343** and alkynes **169** through catalytic C−C activation of isatins to form 2-quinolinone derivatives **344** (Scheme 127).[314] Notably, the addition of aryl C−H bonds across alkynes is a major inefficiency associated with isatin activation processes. To address this, Dong adapted 3-methyl-2-pyridyl as the directing group because the steric hindrance of the methyl group on the "back" site of the directing group minimized the conformation of **345** that led to C−H activation. Mechanistic exploration revealed that C−C bond cleavage occurred smoothly at room temperature; however, alkyne insertion was not observed with intermediate **346** when the temperature was <130 °C. Other classes of π-unsaturates can also be exploited. Indeed, this group later demonstrated insertion of isocyanates **347** to form benzimidazolidinone products **348** (Scheme 128).[315] The reaction is notable because double-decarbonylative cycloaddition was observed.

Scheme 127. Rh-Catalyzed Decarbonylative Coupling with Isatins

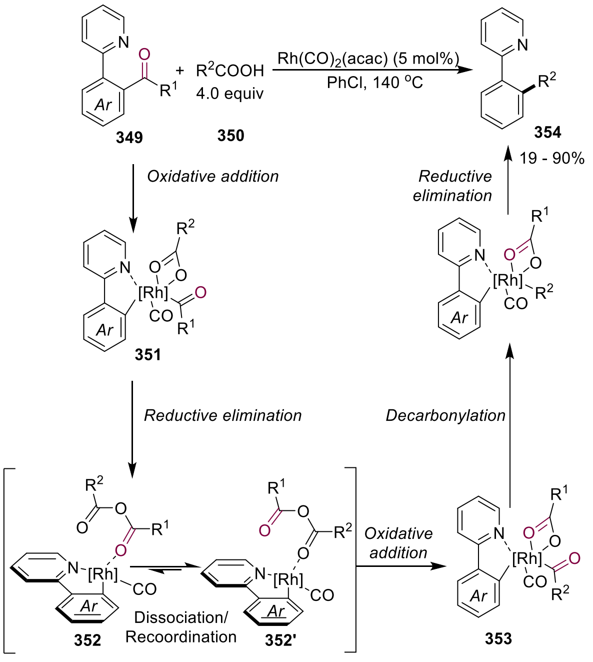


Scheme 128. Rh-Catalyzed Double-Decarbonylative Coupling with Isatins



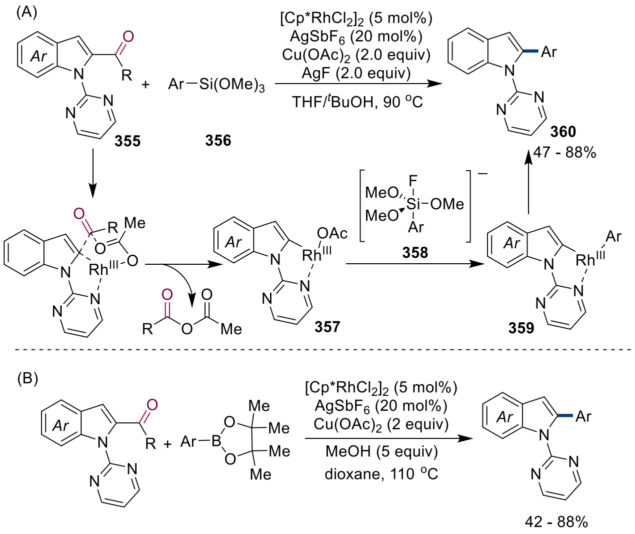
An interesting extension to this area was reported by Shi et al., who developed a Rh-catalyzed simple group exchange transformation between unstrained ketones **349** and carboxylic acids **350** via decarbonylation (Scheme 129).[316] The competing decarbonylation could be inhibited by increasing the size of the ketone α-substituents. Oxidative addition of ketone **349** to the $Rh(CO)_2(O_2CR^2)$ species, formed from $Rh(CO)_2(acac)$ and carboxylic acids **350**, afforded Rh(III)-acyl complex **351**. Subsequent reductive elimination provided the tightly coordinated anhydride complex **352**. Dissociation and recoordination of **352** and second oxidative addition formed intermediate **353**, while subsequent decarbonylation and reductive elimination generated the group-exchanged products **354**. The proposed mechanism was supported by DFT calculation and isotope-tracing studies.

Scheme 129. Rh-Catalyzed Group-Transfer Reaction between Ketones and Carboxylic Acids



In 2019, Wei et al. reported the Rh(III)-catalyzed Hiyama coupling reaction between unstrained ketones **355** and arylsiloxanes **356** via decarbonylation (Scheme 130A).[317]

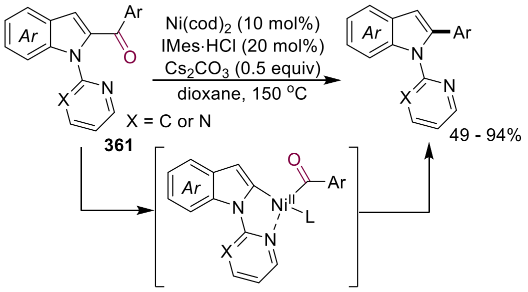
Scheme 130. Rh-Catalyzed Coupling of Unstrained Ketones



Essentially, these processes represent interrupted variants of those outlined in Scheme 130A. Rather than the second oxidative addition of the anhydride at the **357** stage, transmetalation with *in situ* generated siliconate complex **358** afforded the new rhodacycle **359**, which then underwent reductive elimination to generate products **360**. Moreover, this group also described the Suzuki−Miyaura coupling of unstrained ketones (Scheme 130B).[318]

The examples given thus far in this section involve Rh-based catalysts; however, there have also been significant developments in Ni systems. Tobisu and Chatani have recently demonstrated that nickel complexes can promote the activation of simple diaryl ketone decarbonylation.[319] Although good functional group tolerance was observed, the proposed reaction system required a stoichiometric amount of nickel catalyst. The absence of turnover under catalytic conditions suggested a high barrier to dissociate CO from the $[\mathrm{Ni(0)L(CO)}_n]$ complex, making the regeneration of the active species challenging. To address this, Wei et al. adapted the directing group to promote the release of carbon monoxide from the nickel coordination sphere (Scheme 131).[320] The decarbonylation of bi(hetero)aryl ketones **361** was realized using Ni(cod)$_2$ as the catalyst. Control experiments revealed that the use of 2-pyrimidinyl/pyridyl as the directing group was crucial. A decarbonylation mechanism similar to that previously reported for rhodium was proposed according to the DFT calculations.

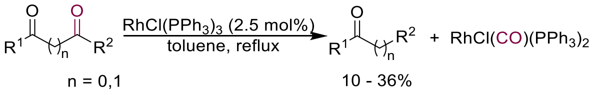
Scheme 131. Ni-Catalyzed Decarbonylation of Bi(hetero)aryl Ketones



8.2.2. Chelation-Free Decarbonylation of Unstrained Ketones.

In addition to directed chelation, transition-metal-catalyzed decarbonylation reactions in the absence of a directing group were also reported. In 1969, Müller, Stegnitz, et al. first reported the use of Wilkinson's complex to decarbonylate conjugated diynones to generate diynes.[321,322] The decarbonylation reactions of 1,2- and 1,3-diketones were then studied by Tehanishi et al. in 1974, albeit with low efficiency and a limited substrate scope (Scheme 132).[323]

Scheme 132. Rh-Catalyzed Decarbonylation of 1,2- and 1,3-Diketones

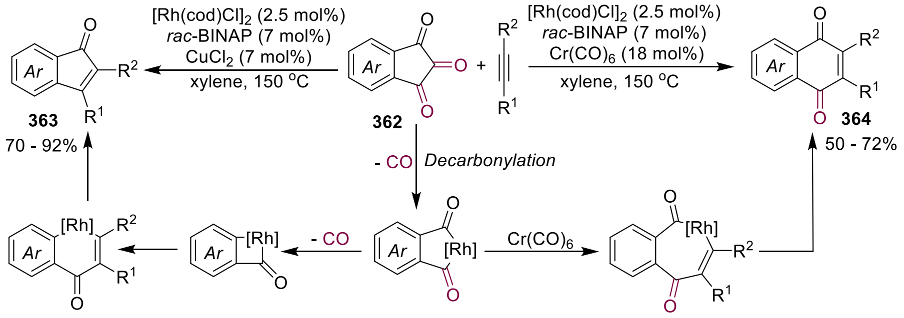


Alkynes are one of the most commonly used coupling partners for annulation and cycloaddition reactions for the decarbonylation of ketones. In 2018, Yu, Wang, et al. developed selective decarbonylation cycloadditions of 1*H*-indene-1,2,3-triones **362** and alkynes using [Rh(COD)Cl]$_2$/*rac*-BINAP as the catalytic system (Scheme 133).[324] When using CuCl$_2$ as the additive, double-decarbonylation was favored to afford indanone derivatives **363** as the products. On the other hand, when Cr(CO)$_6$ was used as an additive, second decarbonylation was suppressed and quinone derivatives **364** were afforded.

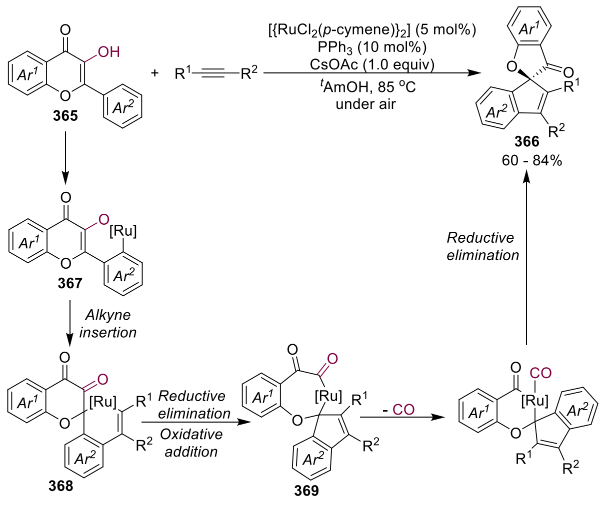
Gogoi et al. reported the Ru-catalyzed decarbonylative insertion of 3-hydroxy-2-phenylchromones **365** with alkynes to generate spiroindenebenzofuranones **366** (Scheme 134).[325] The mechanism commenced with the conversion of **365** to Ru(II) complex **367** by elimination of two molecules of acetic acid. Subsequent insertion of the alkyne into the C−Ru bond afforded complex **368**. Reductive elimination followed by carbonyl-group-assisted oxidative addition into the C−C(acyl) bond generated complex **369**. Decarbonylation and subsequent reductive elimination afforded spiroindenebenzofuranones **366**. Mechanistic studies such as isotopically labeled experiments and kinetic isotope effects were conducted. The afforded results indicated that the Ru−C bond formation might be the rate-determining step of this reaction. Recently, this group also developed a Pd(II)-catalyzed decarbonylative C−H/C−C activation and annulation reaction (Scheme 135).[326] This process is distinct from that outlined in Scheme 134 and is thought to proceed via intramolecular cyclization from an alkyne insertion intermediate **370** rather than from reductive elimination.

Additionally, Oh et al. reported the decarbonylation of 1,2-diketones **371** by including an additional molecular oxygen (Scheme 136).[327] After selective decarbonylation of intermediate **372**, possible subsequent mechanistic pathways involved capture by molecular oxygen to provide rhodacycle intermediates **373**, which upon reductive elimination would afford isocoumarins **374** as the products. The Dong laboratory has extended the range of catalytic decarbonylation to ynones. They reported the Rh-catalyzed decarbonylation of diynones **375** and monoyones **377** to produce 1,3-diynes **376** (Scheme 137A)[328] and disubstituted alkynes **378** (Scheme 137B),[329] respectively. The use of bidentate phosphine ligands with

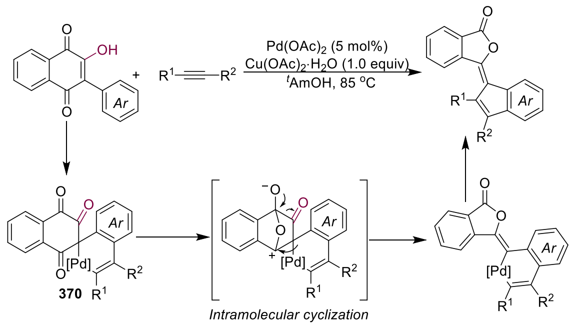
Scheme 133. Rh-Catalyzed Decarbonylative Cycloadditions of 1*H*-Indene-1,2,3-Triones and Alkynes



Scheme 134. Ru-Catalyzed Decarbonylative Annulation Reactions of Cyclic α-Diketones



Scheme 135. Pd-Catalyzed Decarbonylative Annulation Reactions

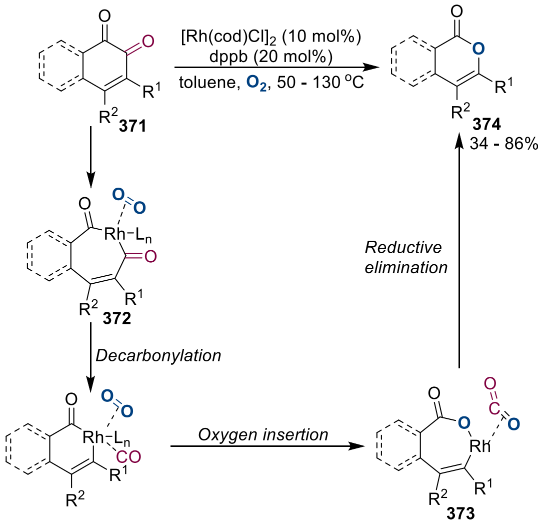


relatively large bite angles was key in achieving catalyst turnover. Computational studies were used to support the initial cleavage of the alkynyl acyl bond and decarbonylation for these transformations. Later, this group also developed the Rh-catalyzed controlled decarbonylation of alkynyl α-diones **379** (Scheme 138).[330] By using different ligand and solvent combinations, mono- and double-decarbonylations were selectively achieved to afford conjugated ynones **380** and disubstituted alkynes **381**, respectively.

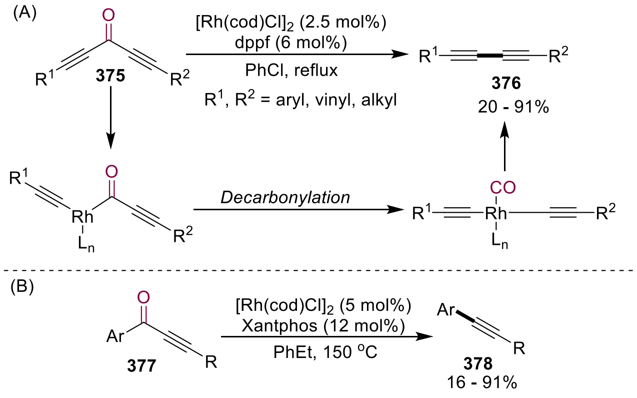
9. MISCELLANEOUS

The transition-metal-catalyzed decarbonylative reactions of aldehydes, ketones, and naturally abundant carboxylic acid derivatives such as acyl halides, (thio)esters, anhydrides, and

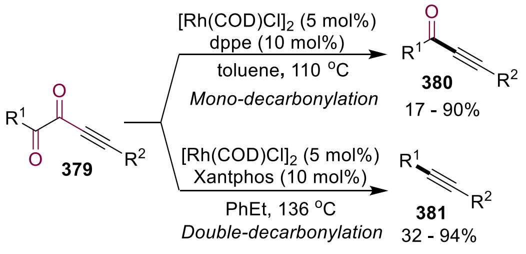
Scheme 136. Rh-Catalyzed Decarbonylative Aerobic Oxidation of Cyclic α-Diketones



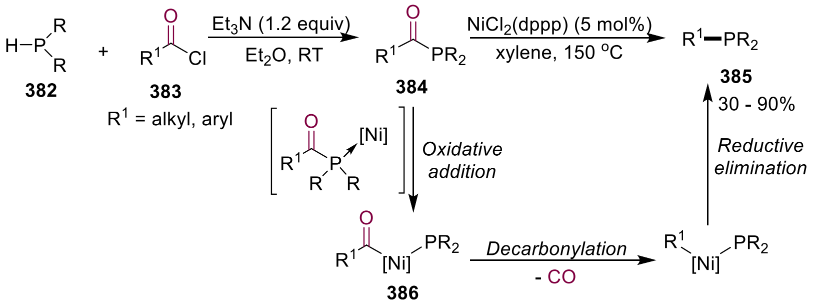
Scheme 137. Rh-Catalyzed Decarbonylation of Ynones



Scheme 138. Rh-Catalyzed Mono- and Double-Decarbonylation of Alkynyl α-Diones



Scheme 139. Ni-Catalyzed Decarbonylation of Acylphosphines

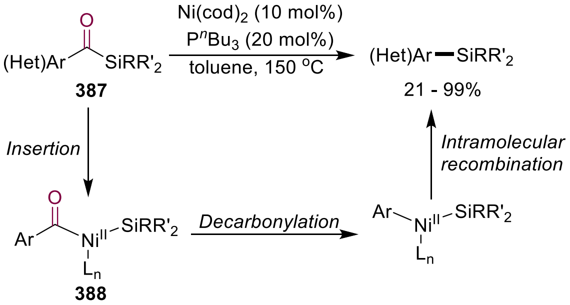


amides have been extensively studied under various conditions. We now discuss examples in which other undeveloped substrates, such as acylphosphines and acylsilanes, were involved in the decarbonylative process.

Although activation of the C(acyl)−P bond has been known since 1989 and the Pd-catalyzed decarbonylation of acylphosphonates was reported by Nakazawa et al.,[62] decarbonylative processes involving the C(acyl)−P bond are still rare.[331−333] Recently, Wang et al. explored a "pre-join and transform" strategy for the decarbonylation of acylphosphines **384**, giving a facile pathway for the synthesis of trivalent phosphines **385** (Scheme 139).[334] Here, disubstituted phosphine **382** was first coupled with acid chloride **383** to form acylphosphine **384**, which underwent coordination and oxidative addition to generate intermediate **386**. Subsequent decarbonylation and reductive elimination afforded the desired products **385**. The practicability of this method has been exemplified by construction of novel triaryl phosphines and bis-phosphorus derivatives.

Given the synthetic importance of organosilicons, Rueping et al. reported the Ni-catalyzed intramolecular decarbonylative version of acylsilanes **387** (Scheme 140).[68] The proposed mechanism involved insertion of Ni into the C−Si bond to generate intermediate **388**, while subsequent CO extrusion with intramolecular recombination fragment coupling produced the arylsilane. Silicon-residue-bearing bulky substituents displayed a lower reaction rate, which was attributed to the weak coordinating ability to the nickel complex.

Scheme 140. Ni-Catalyzed Decarbonylative Silylation of Silyl Ketones



10. SUMMARY

As demonstrated by the reactions summarized in this review, transition-metal-catalyzed decarbonylative reactions exhibit unique and diverse chemical reactivity. This allows common carbonyl groups to become a handle for the construction of carbon−carbon and carbon−heteroatom bonds. Because of the unique advantages of carbonyl functionalities, this synthetic approach is desirable to offer new opportunities for organic syntheses.

Initially aldehyde precursors were employed for decarbonylation; however, this was later expanded to acyl halides and thioesters. In recent years, other types of carbonyl functionalities, including esters, amides, acyl fluorides, and ketones, were employed as precursors to participate in the decarbonylative reactions. On the other hand, transition metal catalysts are not limited to Pd and Rh, and other transition metal catalysts, including Cu, Ni, Ir, Pt, and Ru, can also catalyze the decarbonylative process. Furthermore, a series of transition-metal-catalyzed processes, including transmetalation, C−H activation, migratory insertion, and β-hydride elimination, can be merged with the decarbonylative process, leading to a diversity of decarbonylative reactions. A variety of cascade processes are also possible in decarbonylative reactions, resulting in the development of creative designs and enabling the interconversion of carbonyl groups by the decarbonylation reactions.

Few works in this area were reported prior to 2010. However, notably, the >200 papers described in this review have appeared over the past 10 years, clearly indicating the rapid evolvement of this field. Despite this remarkable progress, several challenges still need to be addressed. In view of the widespread occurrence of carbonyl groups in chemicals, it is highly desirable to develop a chemoselective decarbonylative process that only reacts with a specific carbonyl group when there are multiple reactive carbonyl functional groups in one molecule. On the other hand, most of the cases described herein require relatively harsh conditions (>130 °C) for the completion of the reaction and this is usually incompatible in multistep syntheses. Although, various previous attempts, such as the generation of an unstable acyl-metal intermediate,[123,124,239] the exploration of novel ligand and additives, or the modulation of the rate of reductive elimation by tuning the electronic synergy of the substrates,[132,242] provided new insights into the decarbonylative step under mild conditions. The design of more efficient catalyst systems (e.g., catalysts with high TONs and TOFs) and milder reaction conditions still continues to be an important issue in this area. Additionally, the development of an enantioselective decarbonylative process, which would lead to new types of asymmetric transformations, is also highly desirable. Finally, recent trends have focused on the use of DFT calculations to understand the decarbonylative process,[250,335−337] especially for the decarbonylation and transmetalation sequence in cross-coupling. Elegant computational studies on esters,[157] amides,[159,266,276] acyl fluorides,[151,338] and *in situ* anhydrides[200,213,229] have been reported. However, because of the great influence of the structure of the substrate and the properties of the catalytic system, detailed mechanisms of distinctive decarbonylation reactions should be investigated. Such investigations would be useful for the refinement and further improvement in the field of catalysis. It is envisioned that more synthetically useful transformations with respect to the decarbonylation reaction might become an interesting research direction in the near future.

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Notes

The authors declare no competing financial interest.

Biographies

Hong Lu was born in Gansu, China, in 1987. He received his Ph.D. degrees from Lanzhou University in 2015, under the supervision of Professor Peng-Fei Xu, and conducted postdoctoral studies at Lanzhou University (Prof. Hong-Yu Li's group) for 2 years. Since 2019, he has been a lecturer at Northwest University, where he is involved in new synthetic methods of metal-catalyzed reactions.

Tian-Yang Yu received his Ph.D. degree (2015) from Lanzhou University with Prof. Peng-Fei Xu. He then moved to the College of Chemistry and Materials Science at Northwest University as a lecturer. His research interests include the development of new synthetic methods based on transition-metal-catalyzed activation of inert bonds.

Peng-Fei Xu received his Ph.D. degree from Lanzhou University in 1998 and conducted postdoctoral studies at National Chung-Hsing University (hosted by Prof. Ta-Jung Lu). In 2002, he became a full professor at Lanzhou University. In 2003−2004, he worked as a visiting professor at Nagoya University (hosted by Prof. Kazuyuki Tatsumi) for 18 months. His research interests focus on the design, development, and application of new strategies in asymmetric catalysis, photocatalysis, and total synthesis of natural products.

Hao Wei received his Ph.D. degree (2011, with Prof. Peng-Fei Xu) at Lanzhou University. He was a postdoctoral associate at Peking University from 2011 to 2013 (with Prof. Zhen Yang and Chuang−Chuang Li) and the University of Idaho from 2013 to 2015 (with Prof. Jean'ne M. Shreeve). He began his independent academic career at Northwest University in 2015 as a lecturer and was promoted to full professor in 2016. His current research efforts are focused on new synthetic methodology based on transition-metal-catalysis and application to the synthesis of biologically active molecules.

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ABBREVIATIONS

Ag	silver
BINAP	bis(diphenylphosphino)-1,1′-binaphthalene
acac	acetylacetonate
Co	cobalt
coe	cyclooctene
cod	1,5-cyclooctadiene
Cp*	1,2,3,4,5-pentamethylcyclopentadiene
Cy	cyclohexyl
dcppt	3,4-bis(dicyclopentylphosphino)thiophene
dcype	1,2-bis(dicyclohexylphosphino)ethane
dcypt	3,4-bis(dicyclohexylphosphino) thiophene
DCE	dichloroethane
DEC	diethyl carbonate
DIPEA	*N*,*N*-diisopropylethylamine
DMAA	*N*,*N*-dimethylacrylamide
DMAc	dimethylacetamide
DME	dimethyl ether
DMPU	1,3-dimethyl-tetrahydropyrimidin-2(1*H*)-one
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino) propane
Ir	iridium
Mg	magnesium
MS	molecular sieve
NBE	norbornene
Ni	nickel
NTf	(trifluoromethane)sulfonimide
Oct	octyl
Pd	palladium
Phen	1,10-phenanthroline
B_2pin_2	bis(pinacolato)diboron
Piv_2O	pivalic anhydride
Rh	rhodium
Ru	ruthenium
TFA	trifluoroacetic acid
TBP	tri-*n*-butyl phosphate
TES	triethylsilane
TFFH	fluoro-*N*,*N*,*N*′,*N*′-tetramethylformamidinium hexafluorophosphate
TMDSO	1,1,3,3-tetramethyldisiloxane
TONs	turnover numbers
TOFs	turnover frequencies

Zn	zinc

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