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Review

Recent advances in organic electrosynthesis employing transition metal complexes as electrocatalysts

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ABSTRACT

Organic electrosynthesis has been widely used as an environmentally conscious alternative to conventional methods for redox reactions because it utilizes electric current as a traceless redox agent instead of chemical redox agents. Indirect electrolysis employing a redox catalyst has received tremendous attention, since it provides various advantages compared to direct electrolysis. With indirect electrolysis, overpotential of electron transfer can be avoided, which is inherently milder, thus wide functional group tolerance can be achieved. Additionally, chemoselectivity, regioselectivity, and stereoselectivity can be tuned by the redox catalysts used in indirect electrolysis. Furthermore, electrode passivation can be avoided by preventing the formation of polymer films on the electrode surface. Common redox catalysts include *N*-oxyl radicals, hypervalent iodine species, halides, amines, benzoquinones (such as DDQ and tetrachlorobenzoquinone), and transition metals. In recent years, great progress has been made in the field of indirect organic electrosynthesis using transition metals as redox catalysts for reaction classes including C–H functionalization, radical cyclization, and cross-coupling of aryl halides-each owing to the diverse reactivity and accessible oxidation states of transition metals. Although various reviews of organic electrosynthesis are available, there is a lack of articles that focus on recent research progress in the area of indirect electrolysis using transition metals, which is the impetus for this review.

1. Introduction

Owing to the limited supply of fossil fuel resources and strict cutbacks in carbon dioxide emission allowances, the development of efficient, economical, safe, and sustainable synthetic practices is increasingly important for the field of organic synthesis. Recently, organic electrosynthesis has received significant research attention since inexpensive, safe, sustainable, and readily accessible electrical current is used as the “traceless” redox agent, replacing chemical oxidants or reductants associated with conventional approaches to redox transformations [1,2]. Organic electrosynthesis, therefore, provides economical and sustainable synthetic approaches and can limit side reactions and catalyst deactivation promoted by chemical redox reagents [3]. In addition, the ability to regulate electrical current and potential is a unique handle for organic electrosynthesis, since chemists can tame redox transformations with a precision seldom seen using conventional approaches [4]. Various electrochemical transformations have been well developed and utilized for industrial commodity chemical synthesis, such as the Kolbe reaction [5,6], the Simons fluorination process [7], and the Monsanto adiponitrile process [8], to name a few. Combined with the standardization of electrolysis devices [9,10], burgeoning mechanistic insights [11], and the development of new redox catalysts [12–14], organic electrosynthesis has become a powerful field wherein to showcase and promote sustainable practices and innovative strategies (Fig. 1a) [15–20].

Organic electrosynthesis methods can be classified based on whether they involve direct or indirect electrolysis [21]. In direct

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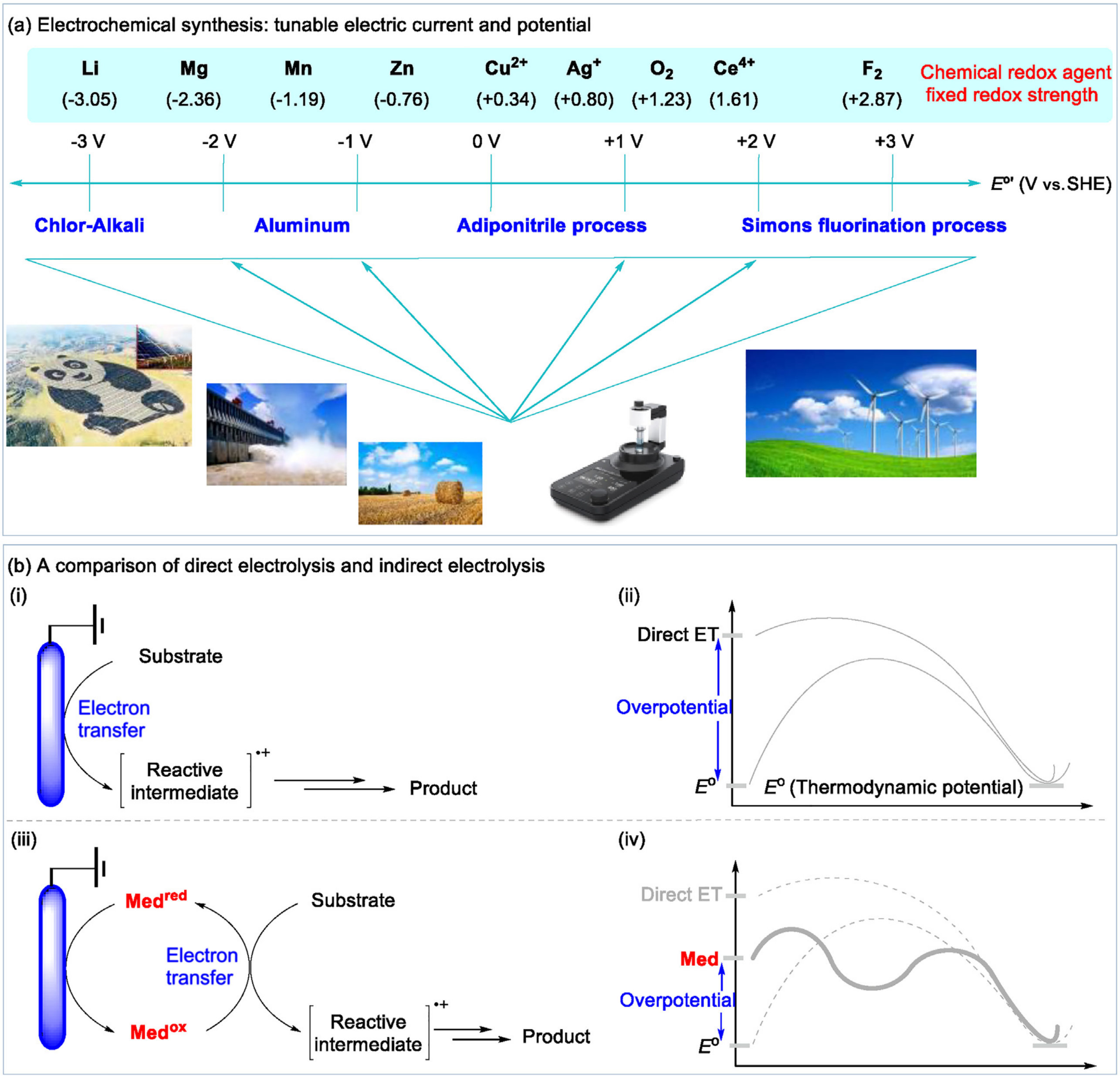


Fig. 1. (Color online) (a) Electrochemical synthesis: tunable electric current and potential; (b) a comparison of direct electrolysis and indirect electrolysis.

electrolysis, in the case of oxidation at an anode, electricity-rather than a chemical oxidant-drives electron transfer by shuttling electrons between the surface of the electrode and the organic substrates (Fig. 1bi). Electron transfer (ET) from and to an electrode is a heterogeneous process that can be kinetically hindered resulting in over-potentials on the electrode surface. In addition, organic compounds can be adsorbed on the electrode surface and thereby reduce conductivity; in some cases, conductive polymer films can be formed. If an insulating film is formed on an electrode surface, the terminal voltage reaches the limit of a galvanostat and no current can flow. Similarly, no electrical current will flow through an electrochemical cell being run in galvanostatic (constant current) mode. Indirect electrolysis can be helpful in circumventing the aforementioned undesired processes [14]. Taking anodic oxidation as an example again, in an indirect electrolysis, a redox catalyst is used to shuttle electrons between the surface of the anode and the organic substrates via outer-sphere or inner-sphere electron transfer (Fig. 1biii), hence the aforementioned limitations of direct electrolysis can be avoided. The use of redox catalysts as homogeneous electron transfer mediators (ETMs) frequently allows reactions to occur at potentials that are substantially less positive (oxidations) or less negative (reductions) than those required for direct electron transfer at the electrode, thereby reducing energy consumption and improving the energy efficiency of a reaction and complementing the enhanced atom economy generated by avoiding the use of a chemical oxidant or reductant. Overpotential of electron transfer can be reduced, which equates to mild reaction conditions and broader functional group tolerance. In addition, chemo-, regio-, and stereo-selectivity outcomes can be manipulated by the catalysts used in indirect electrolysis. Various homogeneous ETM's have been developed including *N*-oxyl radicals, hypervalent iodine species, halides, amines, benzoquinones (DDQs), and transition metals. Compared to other catalysts, transition metals are attractive because: (1) transition metal-catalyzed reactions are versatile and, in many cases, well understood; (2) the redox potentials of transition metal catalysts may be tuned via ligand modification; and (3) chemo-, regio-, and stereo-selectivity can be dictated by the transition metal catalysts. Although various reviews on organic electrosynthesis are available [21–26], this article will highlight recent progress in indirect electrolysis using transition metal catalysts.

2. Iron complex as an electrocatalyst

Iron is a naturally abundant transition metal and relatively non-toxic. Ferrocene (Fc), an organometallic compound, is an inexpensive single electron transfer catalyst. It was synthesized by accident and was first reported by Kealy and Pauson [27] in 1951. Later on, Wilkinson, Woodward [28] and Fischer [29] suggested that it had a "sandwich" structure, and officially named it ferrocene. The development, understanding, and utility of ferrocene inspired the development of organometallic chemistry and organometallic electrochemistry [30–32]. Ferrocene can be used as an ET-type catalyst in electrochemical reactions due to its unique single ET redox properties. In recent years, many groups reported ferrocene-catalyzed electrochemical transformations, in which intermediates were mainly free radicals such as nitrogen-centered radicals [33–40], carbon-centered radicals [41–45], and some other radical ions [46–49].

Electrochemical oxidation provides a useful strategy to generate N-centered radicals directly from amines and amides [50–52]. In the past few years, Xu and co-workers [53] have carried out extensive studies with ferrocene as a catalyst to access amidyl radicals, which can react with olefins or alkynes by intramolecular addition. For instance, they have reported an interesting example of intramolecular hydroamidation of olefins with 1,4-cyclohexadiene (1,4-CHD) as a hydrogen atom donor, employing Fc as the redox catalyst to generate amidyl radicals from N-aryl amides (Fig. 2a) [33]. Owing to the relatively low oxidation potential of Fc, the electrochemical system exhibits broad functional group compatibility. Mechanistically, the anode is proposed to oxidize Fc to Fc^+ while MeOH is reduced to H_2 and MeO^- at the cathode. The latter deprotonates **1a** to give the corresponding anion **1b**, which is readily oxidized by Fc^+ via single electron transfer (SET) to form the amidyl radical **3** and regenerate Fc. Upon cyclization of **3** with the tethered olefin and H-atom abstraction of the resulting carbon radical **4** from 1,4-CHD or a solvent molecule, the final product **2a** is formed as shown in Fig. 2a. The use of a relatively nonpolar solvent, such as THF, is crucial to reduce the gap of oxidation potential between ferrocene and **1b**. In MeOH the difference in oxidation potential between ferrocene and **1b** was measured to be 460 mV but in THF/MeOH (5:1) the difference decreases to 60 mV, which prevents hydroamidation due to the lack of effective SET between **1b** and Fc^+. Xu and co-workers [34] subsequently developed a dehydrogenative annulation of **5** to afford a series of functionalized indole and azaindole compounds (Fig. 2b). The use of a Fc redox catalyst instead of direct electrolysis is crucial since the annulation products have similar or lower oxidation potentials than the starting materials. As a showcase of the methodology, indole derivative **7e** can be transformed into isocryptolepine **8** in one step. This strategy using Fc as a redox catalyst also provides an effective method to produce carbon-centered radicals. For instance, Xu and co-workers [41] also reported a highly chemoselective electrochemical cross dehydrogenative coupling to afford C3 fluorinated oxindoles (Fig. 2c). This method avoids decomposition of the heat and base-sensitive oxindole products. Iron has also been explored as an electrochemical catalyst. For instance, in 2019, Ackermann and co-workers [54] reported an electrochemical C–H arylation using iron as a catalyst (Fig. 2d).

3. Late transition metals as electrocatalysts

Over the past several decades, organic electrosynthesis employing late transition metal complexes as electrocatalysts has received tremendous attention [13,55,56]. Late transition metal complexed also transfer electrons to and from an electrode, but unlike conventional redox catalysts such as Fc, they can catalyze reactions by the formation of catalyst–substrate adducts. Because of the variability of the valence state of late transition metals, they not only undergo anodic oxidation but also cathodic reduction. Moreover, chemo-, regio- and stereo-selectivities of the reactions they catalyze can be tuned via modification of the organic ligand, thus providing numerous possibilities for chemical transformations.

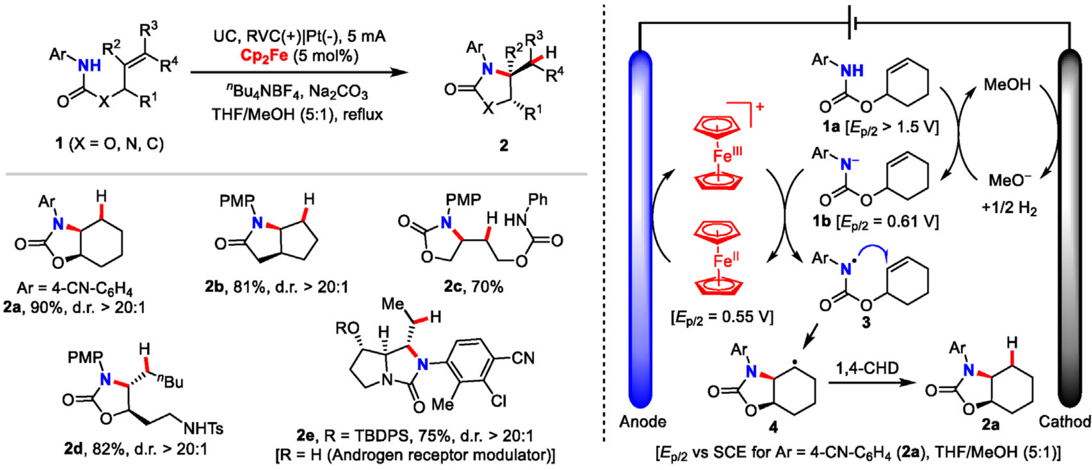
3.1. Palladium complexes

Electrochemical C–H functionalization is an appealing method for the construction of C–C and C–Z (carbon-heteroatom) bonds because it avoids prefunctionalization of the substrate [57]. However, direct electrochemical functionalization of C–H bonds is challenging from a chemoselectivity standpoint due to the high redox potential of C–H bonds compared to common functional groups and organic solvents [58,59]. In the past decade, palladium-catalyzed selective functionalizations of primary C–H bonds proximal to a suitable directing group has been extensively developed [60–64]. However, stoichiometric chemical oxidants like $Cu(OAc)_2$, Ag_2CO_3, and hypervalent iodine reagents are typically required. The use of these stoichiometric additives could be avoided by integrating anodic oxidation [20,65,66]. Anodic oxidation can be employed to oxidize Pd(0) to Pd(II) or to generate high valent Pd(III) or Pd(IV) species from Pd(II), depending on the catalyst.

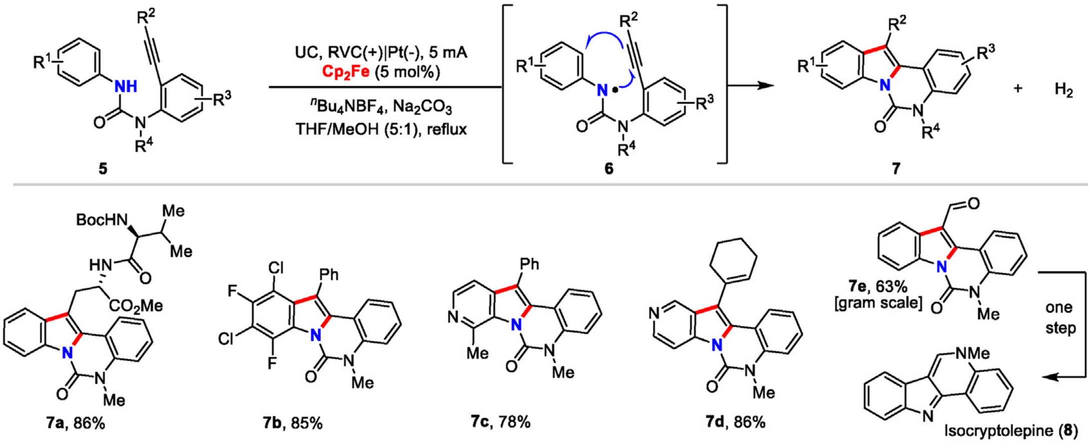
Some early investigations on Pd-catalyzed electrochemical arene C–H functionalization have been reported by the groups of Amatore [67], Kakiuchi [68–71], and Budnikova [72–75]. Recently, Mei and co-workers [76] developed a Pd-catalyzed electrochemical $C(sp^3)$–H acetoxylation reaction (Fig. 3a). Therein, direct anodic oxidation of Pd(II) complexes putatively produces a Pd(IV) intermediate that is prone to reductive elimination to give the C–H acetoxylation products while regenerating Pd(II) catalysts. Direct comparison to chemical oxidation (specifically $NaNO_3/O_2$) [77] demonstrated the superiority of anodic oxidation for this transformation. Sanford and co-workers [78] independently reported a similar $C(sp^3)$–H acetoxylation around the same time. Subsequently, Mei and co-workers demonstrated $C(sp^2)$–H acetoxylation [79], alkylation [80], acylation [80], and halogenation (Fig. 3b) [81,82]. A divided cell is typically needed in these electrochemical systems because high valent Pd species are prone to cathodic reduction, which leads to catalyst deactivation or decomposition. Electrochemical C–H alkylation of 2-phenylpyridine derivatives could conducted in an undivided cell when a mixture of trifluoroethanol (TFE), acetic acid, and water is used as the solvent system (Fig. 3b) [83]. In 2020, Lei and co-workers [84] reported a Pd-catalyzed electrochemical intramolecular C–H/N–H annulation reaction in an undivided cell (UC), affording a series of pyrido[1,2-*a*]benzimidazoles. Mechanistic studies indicate that Pd(0) could be recycled through via anodic oxidation (Fig. 3c). Recently, Ackermann and co-workers [85] demonstrated the first palladium-catalyzed electrochemical asymmetric synthesis of axially chiral biaryls via C–H olefinations in an undivided cell using a catalytic amount of a transient directing group (TDG) (Fig. 3d). Other interesting protocols that merge anodic oxidation and Pd catalysis have also been reported [86–89].

Cathodic reduction can generate low-valent metal species that are typically inaccessible using chemical reductants.

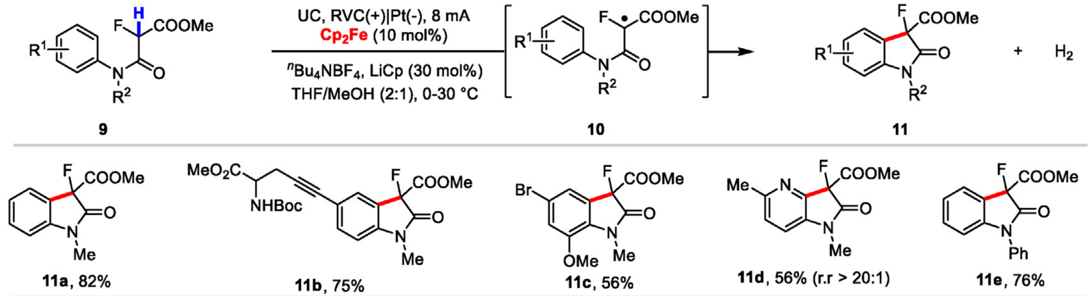
(a) Ferrocene-catalyzed electrochemical hydroamination of di-and tri-substituted olefins via N-centered radicals (Ref. [33])



(b) Ferrocene-catalyzed electrochemical synthesis of (aza)indoles via amidyl radicals (Ref. [34])



(c) Ferrocene-catalyzed electrochemical synthesis of C3-fluorinated oxindoles via C-centered radicals (Ref. [41])



(d) Iron-catalyzed electrochemical C–H arylations (Ref. [54])

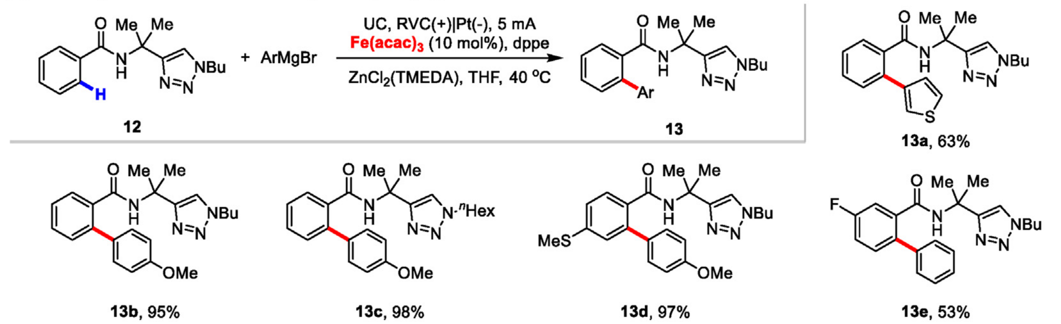


Fig. 2. (Color online) Iron-catalyzed electrochemical synthesis of heterocycles via N- or C-centered radicals. (a) Ferrocene-catalyzed electrochemical hydroamination of di- and tri-substituted olefins via N-centered radicals [33]; (b) ferrocene-catalyzed electrochemical synthesis of (aza)indoles via amidyl radicals [34]; (c) ferrocene-catalyzed electrochemical synthesis of C3-fuorinated oxindoles via C-centered radicals [41]; (d) iron-catalyzed electrochemical C–H arylations [54].

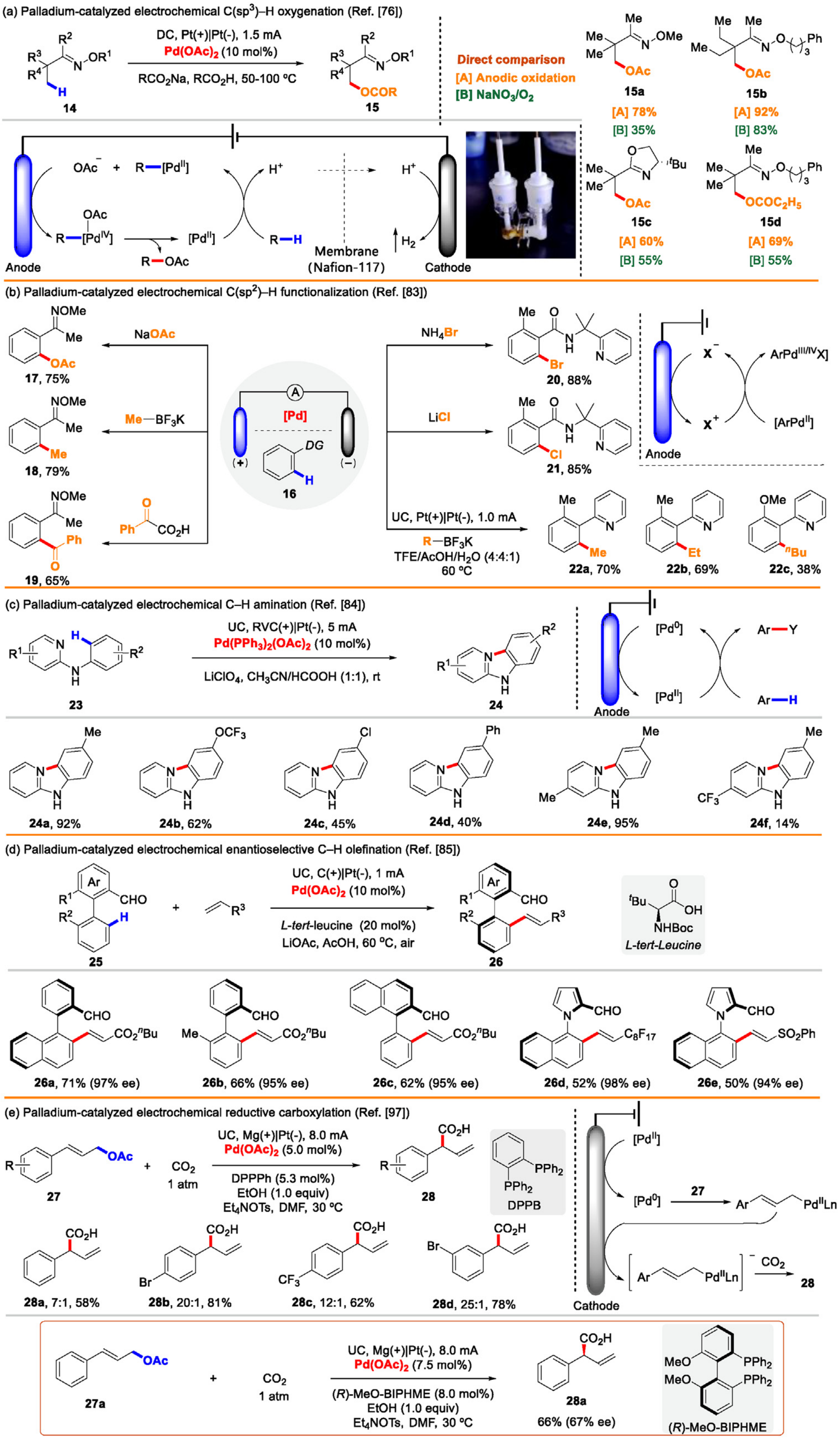


Fig. 3. (Color online) Palladium-catalyzed electrochemical C–H functionalization and carboxylation. Palladium-catalyzed electrochemical (a) $C(sp^3)$–H oxygenation [76], (b) $C(sp^2)$–H functionalization [83], (c) C–H amination [84], (d) enantioselective C–H olefination [85], and (e) reductive carboxylation [97].

The combination of cathodic reduction with transition metal catalysis could therefore not only improve existing chemical reactions, but also allow the discovery of new reactions. In such a process, the active transition metal species can be generated and recycled continually by cathodic reduction while the electrons are consumed stoichiometrically by the substrates. In 1985, Torii and co-workers [90] reported an early example of Pd-catalyzed electroreductive coupling of aryl halides to form biaryls in divided cells, wherein biaryl formation occurs in the cathodic cell. In 2017, Huang and co-workers [91] developed a Pd-catalyzed electrochemical cross-coupling of alkyl and allyl halides in aqueous media. The use of a Zn cathode is important for this reaction, which suggests that Zn particles generated *in situ* might participate in the coupling reactions.

Catalytic C–C bond-forming reactions that utilize CO_2 to directly access carboxylic acids are attractive transformations because CO_2 is an ideal C1 synthon [92–95]. In 1986, Torii and co-workers [96] reported an early example of Pd-catalyzed carboxylation of allyl acetates with CO_2 in divided cells, affording a mixture of branched and linear carboxylic acids. In 2018, Mei and co-workers [97] developed a regioselective Pd-catalyzed electrocarboxylation of homostyrenyl acetates with CO_2 using 1,2-bis(diphenylphosphino)benzene (DPPB) as the ligand and a Mg sacrificial anode, affording α-aryl carboxylic acids in good selectivity in an undivided cell (Fig. 3e). Of critical importance, the metal reductant (Mn or Zn powder) does not give significant amounts of desired products in the absence of electric current under otherwise identical conditions, which underscores the unique reactivity offered by the merger of Pd catalysis and electrochemistry. Mechanistically, $Pd(OAc)_2$ undergoes cathodic reduction to give a Pd(0) species, which reacts with the substrate via oxidative addition to give an η^1-allylpalladium(II) intermediates. Then the η^1-allylpalladium(II) species is reduced at the cathode to give a nucleophilic η^1-allylpalladium(0) complex which reacts with CO_2 to deliver the carboxylic acids. In addition, chiral bidentate triarylphosphine ligands are suitable for modestly enantioselective carboxylations (67% enantiomeric excess) (Fig. 3e).

3.2. Nickel complexes

Numerous nickel-catalyzed C–H functionalization methods have been developed in recent decades. Ackermann and co-workers [98] demonstrated the first example of carboxylate-enabled Ni-catalyzed electrochemical C–H amination of benzamides with cyclic or acyclic amines in an undivided cell. More electron-deficient arenes react faster in this electrochemical system, suggestive of a concerted metalation deprotonation (CMD) mechanism [99]. Anodic oxidation is responsible for recycling the nickel catalyst and producing a Ni(IV) intermediate that undergoes reductive elimination (Fig. 4a) [98]. The same group later demonstrated electrochemical C–H alkoxylation with secondary alcohols via a similar putative mechanism to the one shown in Fig. 4a [100]. In addition, Ackermann and co-workers [101] also reported an intriguing example of Ni-catalyzed C–H alkylations of unactivated 8-aminoquinoline amides with primary or secondary alkyl iodides at room temperature via cathodic reduction (Fig. 4b). Detailed mechanistic studies suggest that the reaction involves a Ni(II/III/I) catalytic cycle involving two SET steps. The groups of Xu, Zeng and co-workers [102] also reported a Ni-catalyzed electrochemical Minisci acylation of electron-deficient aromatic heterocycles with α-keto acids. Cyclic voltammetric analysis suggested that the generation of the key acyl radicals may involve a ligand-to-metal charge electron transfer (LMCT) process.

Ni-catalyzed electrochemical reductive coupling reactions have been developed as powerful tools to join two electrophiles, including reductive homo-coupling of aryl bromides [103], reductive cross-couplings of aryl and alkyl bromides [104–106], reductive relay cross-couplings of aryl bromides (or chlorides) and aryl-substituted alkyl bromides [107,108], and other transformations [109–111]. Recently, Reisman and co-workers [112] reported the first example of catalytic enantioselective reductive cross-couplings of benzyl chlorides and alkenyl bromides using a chiral Box ligand via cathodic reduction (Fig. 4c). Subsequently, Mei and co-workers [113] demonstrated electrochemical Ni-catalyzed enantioselective reductive homo-coupling of aryl bromides to afford axially chiral BINOL derivatives in good yield and enantiomeric excess (ee) (Fig. 4d). It is worth noting that, for comparison, Mn or Zn powder gives significantly lower yields without electric current under otherwise identical conditions. The plausible catalytic cycle of these Ni-catalyzed electrochemical reductive coupling reactions is shown in Fig. 4d.

The combination of nickel catalysis and paired electrolysis is another powerful strategy for organic electrosynthesis. Baran and co-workers [114,115] reported an elegant example of Ni-catalyzed couplings of aryl (pseudo) halides and aliphatic amines via paired electrolysis under mild conditions in an undivided cell. Inspired by this seminal work, various electrochemical reductive cross-couplings of aryl halides have been developed including C–C [116,117], C–P [118–121], C–S [122–124], C–O [125–127], and other bond-forming variants [128,129]. Most recently, Mei and co-workers [130] employed a similar strategy for the Ni-catalyzed N-arylation of NH-sulfoximines with aryl halides in an undivided cell (Fig. 4e). Mechanistic studies indicate that the anodic oxidation of a Ni(II) species is needed to promote reductive elimination from a Ni(III) intermediate at room temperature and thereby form the key C–N bond.

3.3. Cobalt complexes

In recent years, cobalt-catalyzed C—H functionalizations have witnessed tremendous progress [131–133]. In 2017, Ackermann and co-workers [134] reported one of the earliest examples of an electrochemical cobalt-catalyzed C–H oxygenation of pyridine-N-oxide-functionalized benzamides or alkenes **40** with various alcohols in divided cells under mild reaction conditions, wherein reductive elimination is likely taking place from Co(IV) species afforded by anodic oxidation (Fig. 5a). Excitingly, biomass-derived γ-valerolactone (GVL) proved to be the optimal solvent. Subsequently, Ackermann and co-workers [135] demonstrated Co-catalyzed electrochemical C–H amination of pyridine-N-oxide-functionalized benzamides **42** with secondary amines under similar reaction conditions (Fig. 5b). Around the same time, Lei and co-workers [136] independently developed a similar transformation of benzamides **44** (Fig. 5c). Lei and co-workers [137] further reported an elegant example of cobalt-catalyzed electrochemical oxidative C–H/N–H carbonylation involving H_2 release at the cathode in an undivided cell (Fig. 5d). Various substituted benzamides, acrylamides, and heterocyclic amides are well tolerated. Based on X-ray absorption near edge structure (XANES) and cyclic voltammetry studies, a plausible Co(II/III/I) catalytic cycle was proposed (Fig. 5d). Inspired by these works, various cobalt-catalyzed electrochemical C–H functionalization reactions have been developed including acyloxylations [138], allylations [139], annulations [140–145], and other transformations [146–148]. Besides the anodic oxidation, the combination of cathodic reduction with cobalt catalysis can also be applied to discovery new reactions [149–151]. Very recently, Ackermann and co-workers [152] reported a cobalt-catalyzed electroreductive carboxylation of allylic chlorides with CO_2 (Fig. 5e). According to IR spectroscopy and cyclic voltammetry studies, allyl-Co(III) complexes undergo cathodic reduction to generate low-valent allyl-Co(I) complexes which then react with CO_2 to give the final carboxylation product.

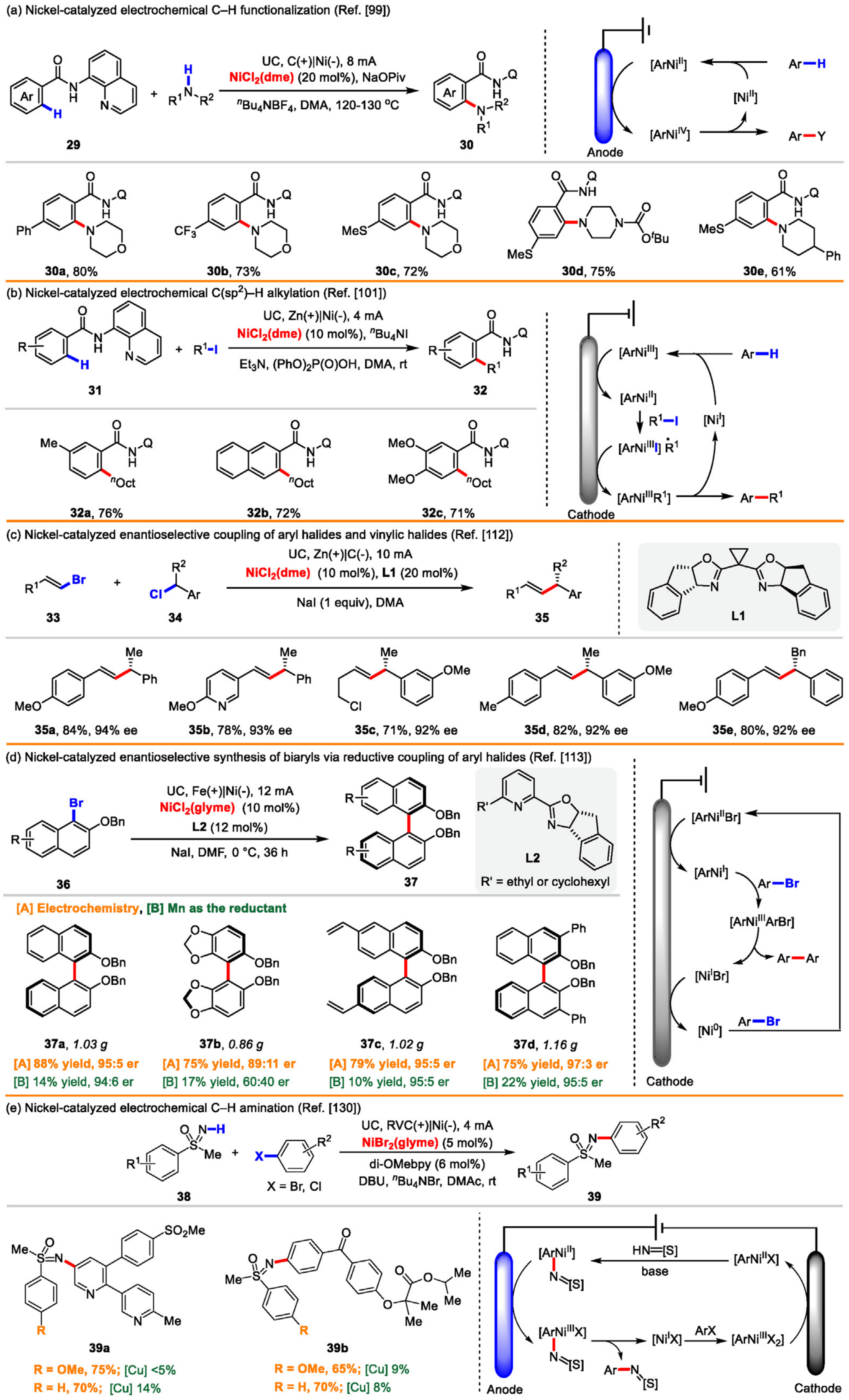
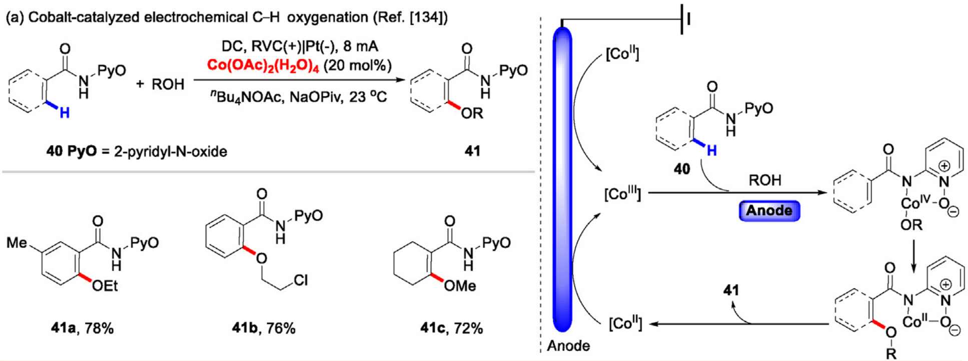
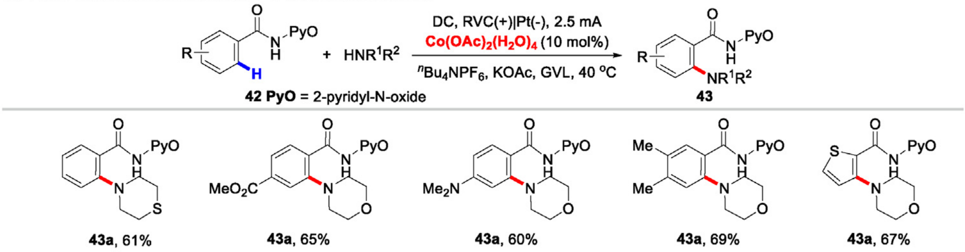


Fig. 4. (Color online) Nickel-catalyzed electrochemical reactions. (a) Nickel-catalyzed electrochemical C–H functionalization [99]; (b) nickel-catalyzed electrochemical C(sp^2)–H alkylation [101]; (c) nickel-catalyzed enantioselective coupling of aryl halides and vinylic halides [112]; (d) nickel-catalyzed enantioselective synthesis of biaryls via reductive coupling of aryl halides [113]; (e) nickel-catalyzed electrochemical C–H amination [130].

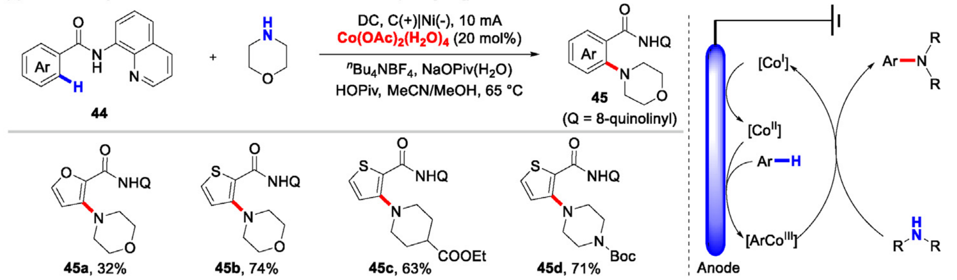
(a) Cobalt-catalyzed electrochemical C–H oxygenation (Ref. [134])



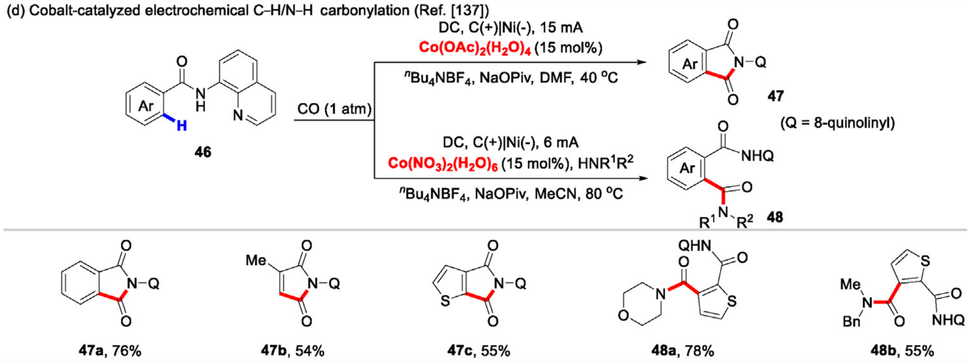
(b) Cobalt-catalyzed electrochemical C–H amination (Ref. [135])



(c) Cobalt-catalyzed electrochemical C–H functionalization (Ref. [136])



(d) Cobalt-catalyzed electrochemical C-H/N-H carbonylation (Ref. [137])



(e) Cobalt-catalyzed electrochemical carboxylation (Ref. [152])

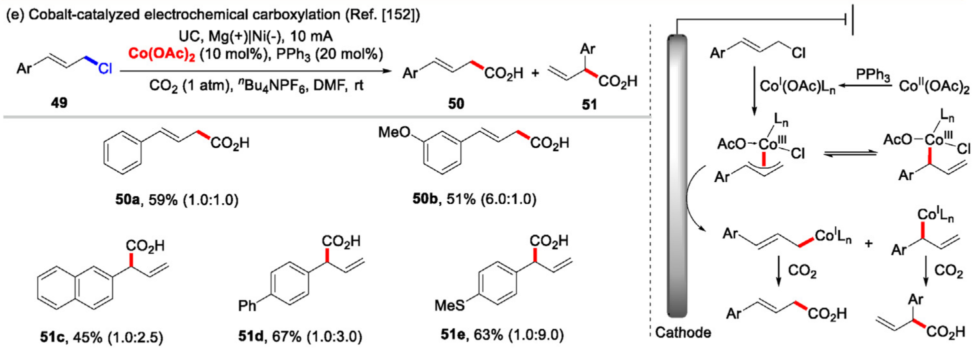
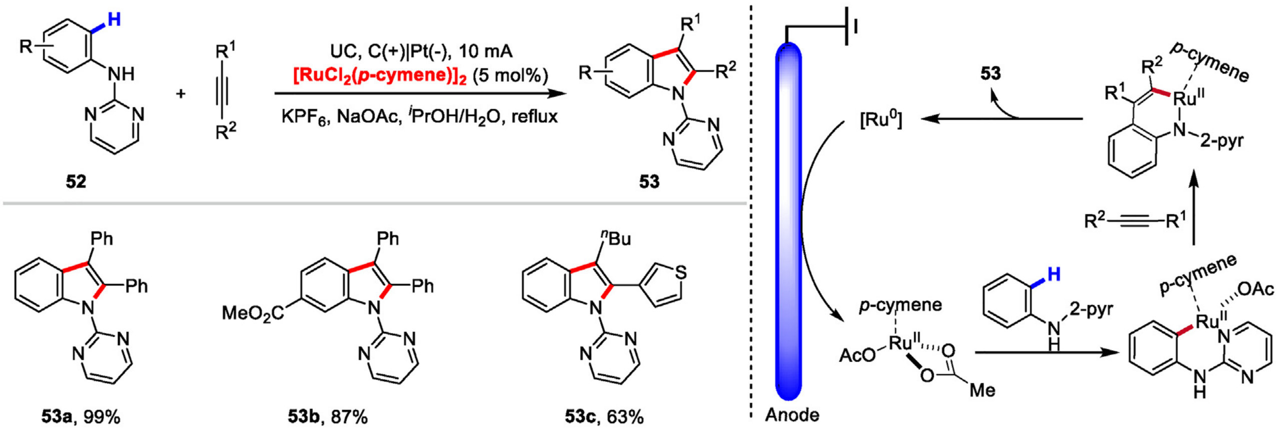


Fig. 5. (Color online) Cobalt-catalyzed electrochemical (a) C–H oxygenation [134], (b) C–H amination [135], (c) C–H functionalization [136], (d) C–H/N–H carbonylation [137], and (e) carboxylation [152].

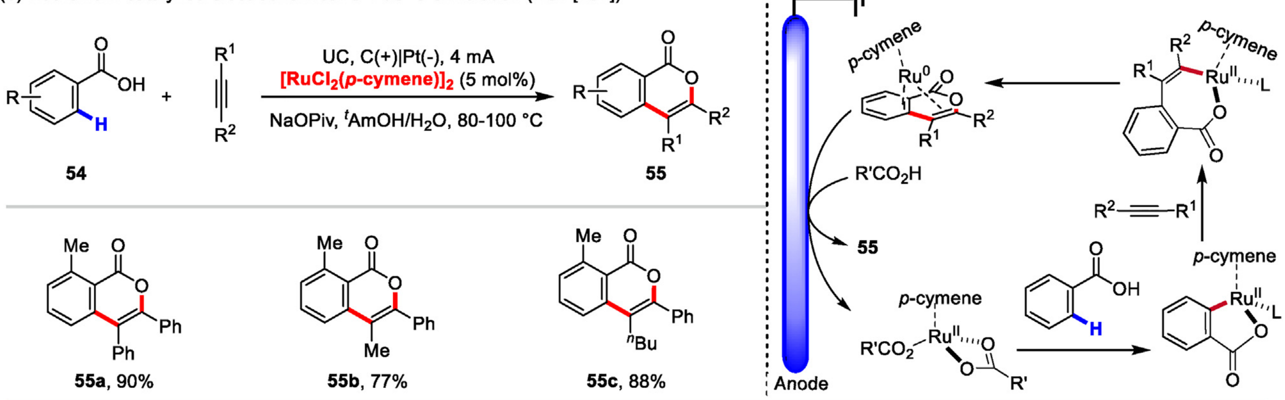
3.4. Ruthenium complexes

Like the aforementioned methods, in the absence of electricity, ruthenium-catalyzed oxidative C–H functionalization reactions typically require stoichiometric amount of oxidants, such as Cu^{II} or Ag^{I} [153–155]. Xu and co-workers [156] demonstrated the first example of a Ru-catalyzed electrochemical C–H annulation of anilines and alkynes to afford various indoles under mild reaction conditions in undivided cells (Fig. 6a). Anodic oxidation is used to recycle the active Ru catalyst and the cathode is used to promote H_2 evolution. Concurrently, Ackermann and co-workers [157] reported an electrochemical Ru-catalyzed C–H annulation of benzoic acids **54** with alkynes (Fig. 6b). The carboxyl group not only directs the Ru-catalyzed C–H activation, but also annulates to

(a) Ruthenium-catalyzed electrochemical dehydrogenative alkyne annulation (Ref. [156])



(b) Ruthenium-catalyzed electrochemical C–H/C–O annulation (Ref. [157])



(c) Ruthenium-catalyzed electrochemical alkyne annulations (Ref. [158])

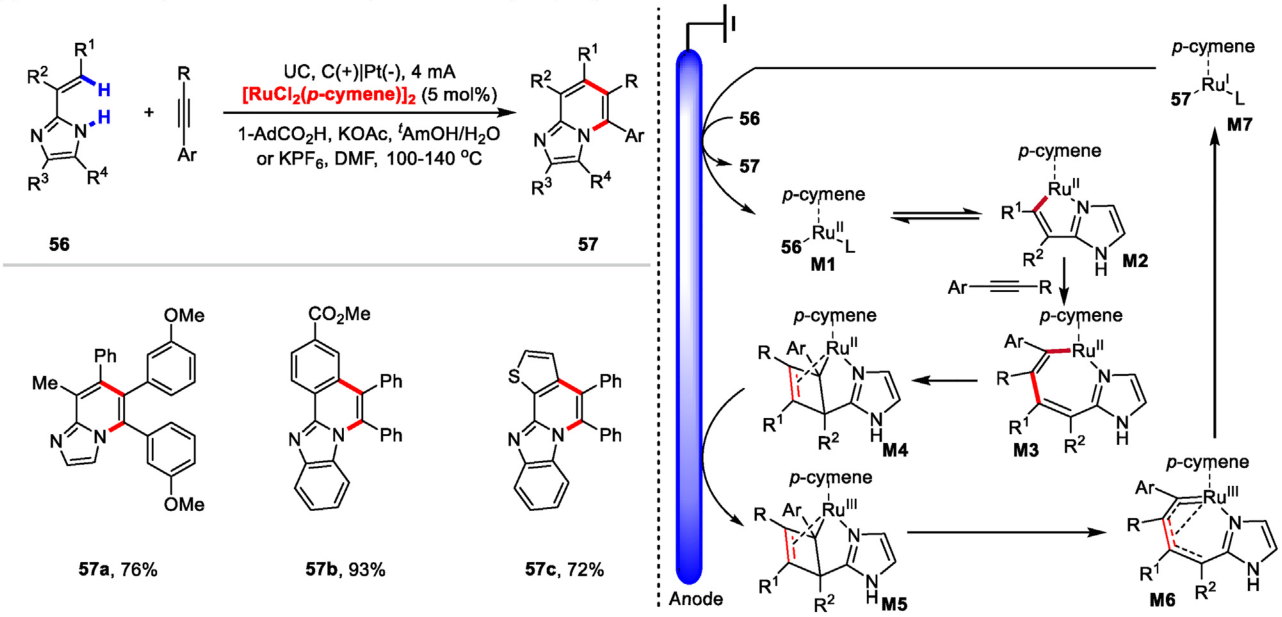


Fig. 6. (Color online) Ruthenium-catalyzed electrochemical (a) dehydrogenative alkyne annulation [156], (b) C–H/C–O annulation [157], and (c) alkyne annulations [158].

alkynes, ultimately affording derivatives of 1*H*-isochromen-1-one. Based on their mechanistic studies, the key step of the catalyst recycle appears to be the reoxidation of the ruthenium(0) complex via anodic oxidation. Later, the same group [158] employed imidazoles as substrates in a ruthenium-catalyzed electrochemical annulation with alkynes, wherein several azaruthena(II)-bicyclo[3.2.0]heptadienes were prepared, isolated, and characterized. Based on their mechanistic studies, anodic oxidation induced reductive elimination was proposed (Fig. 6c). Zhong and co-workers [159] applied a similar strategy to achieve the Ru-catalyzed dehydrogenative [3 + 2] annulation to synthesize various indulines.

3.5. Rhodium complexes

Rhodium-catalyzed C–H functionalization has emerged as a powerful method for construction of carbon–carbon (C–C) or carbon–heteroatom (C–Y) bonds [160–164]. However, chemical oxidants are typically required for Rh catalyst turnover. In 2018, Ackermann and co-workers [165] reported an early example of rhodium-electrocatalyzed C–H activation with benzoic acids and acrylates as the weakly coordinating groups, affording derivatives of 2-benzofuran-1(3*H*)-one as products (Fig. 7a). In addition to benzoic acids, benzamides and N-pyrimidyl (pym) indoles are also suitable substrates for this transformation. The catalytically active pentamethylcyclopentadienyl rhodium(III) is regenerated via anodic oxidation. Subsequently, the same group [166] developed an elegant C–C activation for alkenylations, which demonstrates a preference for C–C cleavage over C–H cleavage. With this C–C activation strategy, 1,2,3-substituted arenes that are not easy to access with known C–H functionalization methods are efficiently produced (Fig. 7b). Transition metal-catalyzed C–H functionalizations are also useful method for the construction of C–P bonds. In 2019, Xu and co-workers [167] realized a Rh-catalyzed electrochemical phosphorylation of aryl C–H bonds (Fig. 7c). Anodic oxidation is used to generate the oxidized Rh-complex from which reductive elimination readily forges the C–P bond. This transformation is highly efficient and overcomes several disadvantages of previously reported non-electrochemical methods. Very recently, Mei, Hong, and co-workers [168] developed electrochemical Rh(III)-catalyzed vinylic C–H annulation of acrylamides with alkynes. Varying the N-substitution of acrylamides enables divergent syntheses of α-pyridones and cyclic imidates. Excellent regioselectivities are achieved with unsymmetrical alkynes, including terminal alkynes (Fig. 7d). The origins of the substituent-controlled chemoselectivity were probed by DFT calculations. A seven-membered vinyl-rhodium intermediate is formed after C–H activation and alkyne insertion. The seven-membered vinyl-rhodium intermediate then undergoes either a classic neutral concerted reductive elimination to give α-pyridones or an ionic stepwise pathway to give cyclic imidates. Gooßen and co-workers [169] developed an interesting protocol for Rh-catalyzed dehydrogenative coupling of benzoic acids to prepare 2,2′-biaryldicarboxylate derivatives.

3.6. Copper complexes

Cu-catalyzed intermolecular C–H amination of arenes has been widely investigated since Yu and Chatani groups [170,171] independently developed aerobic Cu-catalyzed C–H aminations in 2006. However, these transformations typically require chemical oxidants. In 2018, Mei and co-workers [172] demonstrated an early example of a Cu-catalyzed electrochemical C–H amination of aniline derivatives with secondary amines under mild reaction conditions in an undivided cell (Fig. 8a). *n*-Bu_4NI is essential for this transformation. The process is an operationally simple and robust method for the construction of arylamines. Subsequently, Ackermann and co-workers [173] developed an elegant example of an electrooxidative Cu-catalyzed annulative C–H alkynylation cascade reaction (Fig. 8b). Electron deficient and electron-rich benzamides are both suitable for this transformation, and the process is also successful when alkynyl carboxylic acids are used instead of terminal alkynes. An anodic oxidation for Cu(I/II/III) recycling was proposed. Recently, Xie and co-workers [174] demonstrated an elegant protocol for Cu-catalyzed electrochemical B–H oxygenation of *ortho*-carboranes (Fig. 8c). B(4,5)-diphenolated *o*-carboranes could be afforded with lithium phenolates, whereas B(4)-monooxygenated *o*-carboranes could be produced with lithium *tert*-butoxide. These reactions putatively require that an active Cu(III) species be generated via anodic oxidation. Lin and co-workers [175] developed a novel dual electrocatalysis for enantioselective hydrocyanation of conjugated alkenes, which merges two radical reactions: a cobalt-catalyzed hydrogen atom transfer (HAT) and a copper-promoted radical cyanation (Fig. 8d). Anodic oxidation is required for recycling both cobalt and copper. Notably, a chiral copper catalyst enables an enantioselective variant of the reaction. Lin and Hu group [176,177] have also developed other interesting electrochemical Cu-catalyzed works via anodic oxidation, involving radical process in the absence of chemical oxidants.

3.7. Iridium and gold complexes

In 2019, Mei and co-workers [178] reported the first example of an Ir-catalyzed vinylic C–H annulation of acrylic acids with alkynes (Fig. 9a). Preliminary mechanistic experiments revealed that anodic oxidation is essential for the reoxidation of the diene-Ir(I) complex to an Ir(III) species with concomitant release of the product. Recently Guo, Mei and co-workers [179] further extended this system to regioselective annulations of benzoic acids with internal alkynes. Shi and co-workers [180] applied this combined electrochemistry and Ir catalysis strategy to realize the alkynylation of $C(sp^2)$–H bonds. The high oxidation potential between Au(I) and Au(III) makes gold redox catalysis require strong oxidants such as Selectfluor or (diacetoxyiodo)benzene, which results in low functional group compatibility. A more sustainable, economical, and practical protocol to promote Au(I)/Au(III) redox catalysis is thus in high demand. In 2019, Shi and co-workers [181] reported the first example of a gold-catalyzed electrochemical oxidative coupling of terminal alkynes that affords symmetrical or unsymmetrical 1,3-diynes with high functional group compatibility (Fig. 9b). This reaction is proposed to involve Au(I)/Au(III) redox catalysis wherein oxidation of Au(I) to Au(III) by the anode is key.

4. Manganese complexes as electrocatalysts

In 2017, Lin and co-workers [182] realized an electrochemical diazidation of olefins using a redox-active manganese catalyst to give various 1,2-diazides, which can be easily converted to vicinal diamines in a single step (Fig. 10a). Following this study, the Lin group and other groups developed various of electrochemical manganese-catalyzed radical cascade difunctionalizations of alkenes, including dichlorination [183], chlorotrifluoromethylation [184], chloroalkylation [185], oxychlorination [186], trifluoromethylation [187], Wacker oxidation [188] and other transformations [189,190]. In 2020, Lei and co-workers [191] developed manganese-catalyzed electrochemical cascade cyclization reactions of N-substituted 2-arylbenzoimidazoles with alkylboronic acids, affording various benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one derivatives (Fig. 10b). Associated mechanistic studies indicate that alkyl radicals are generated from alkylboronic acids via anodic oxidation. Recently, the same group [192] developed a manganese-catalyzed electrochemical azidation of $C(sp^3)$–H bonds using an electrophotocatalytic strategy (Fig. 10c). This transforma-

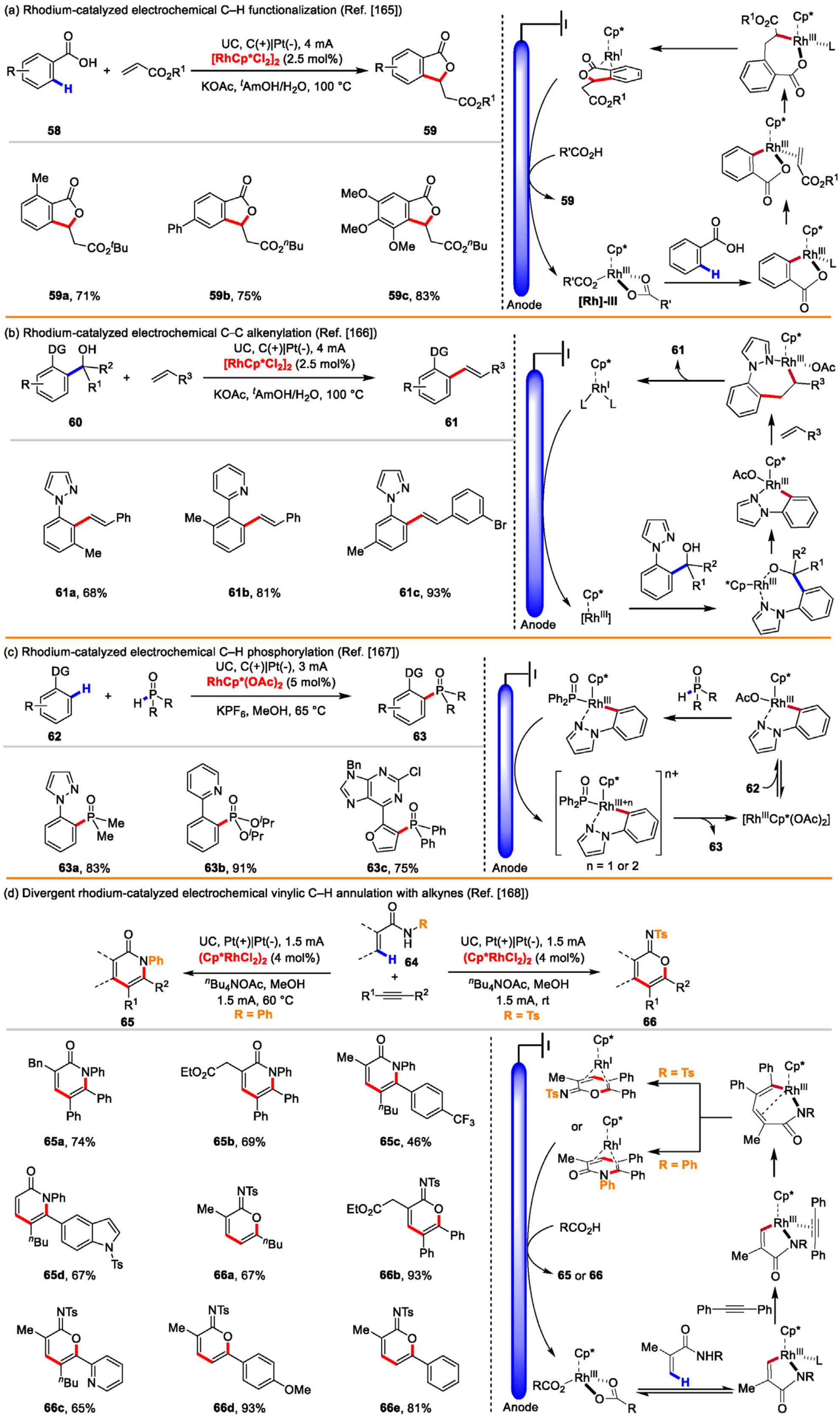


Fig. 7. (Color online) (a) Rhodium-catalyzed electrochemical C–H functionalization [165], (b) C–C alkenylation [166], and (c) C–H phosphorylation [167]. (d) Divergent rhodium-catalyzed electrochemical vinylic C–H annulation with alkynes [168].

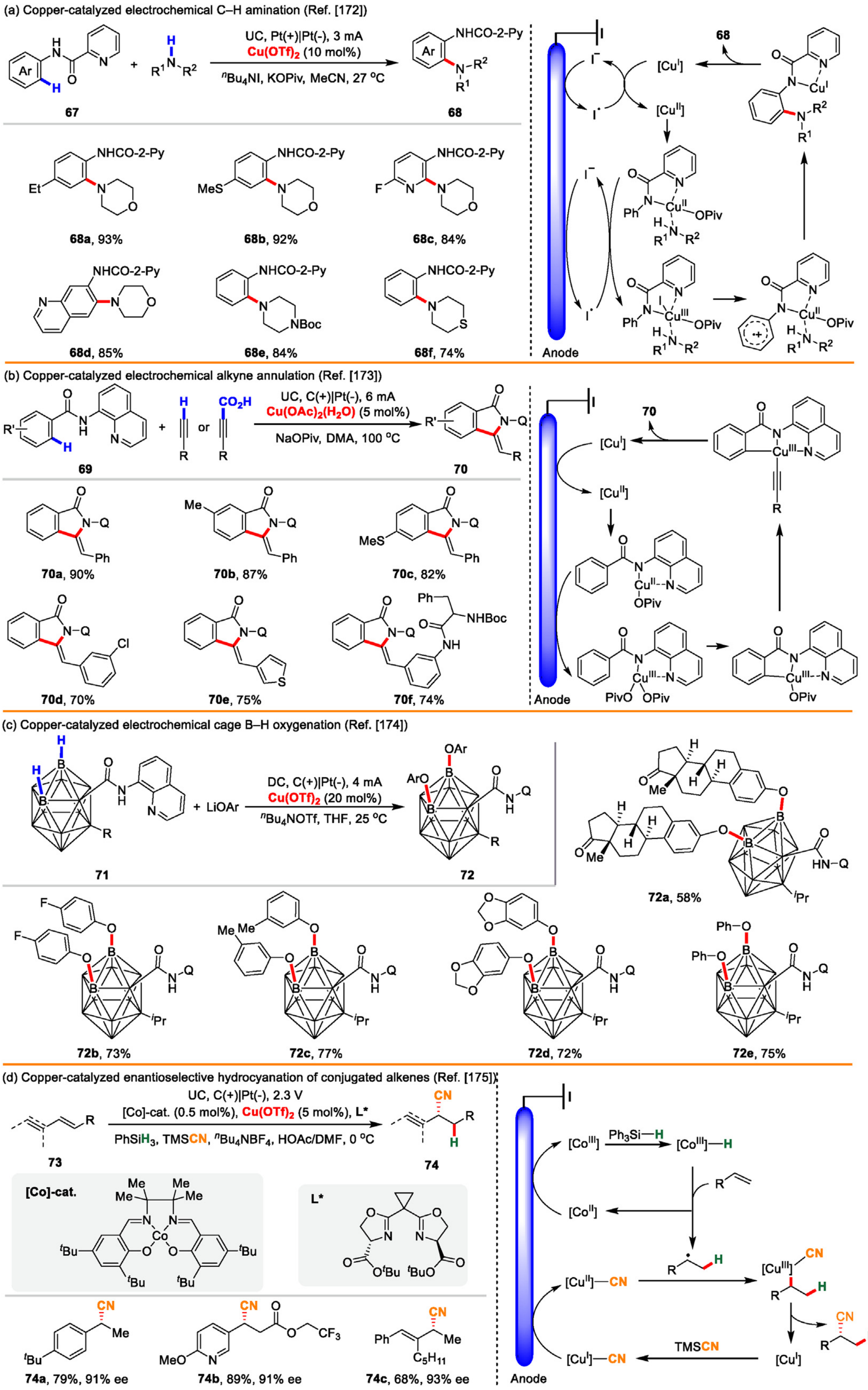
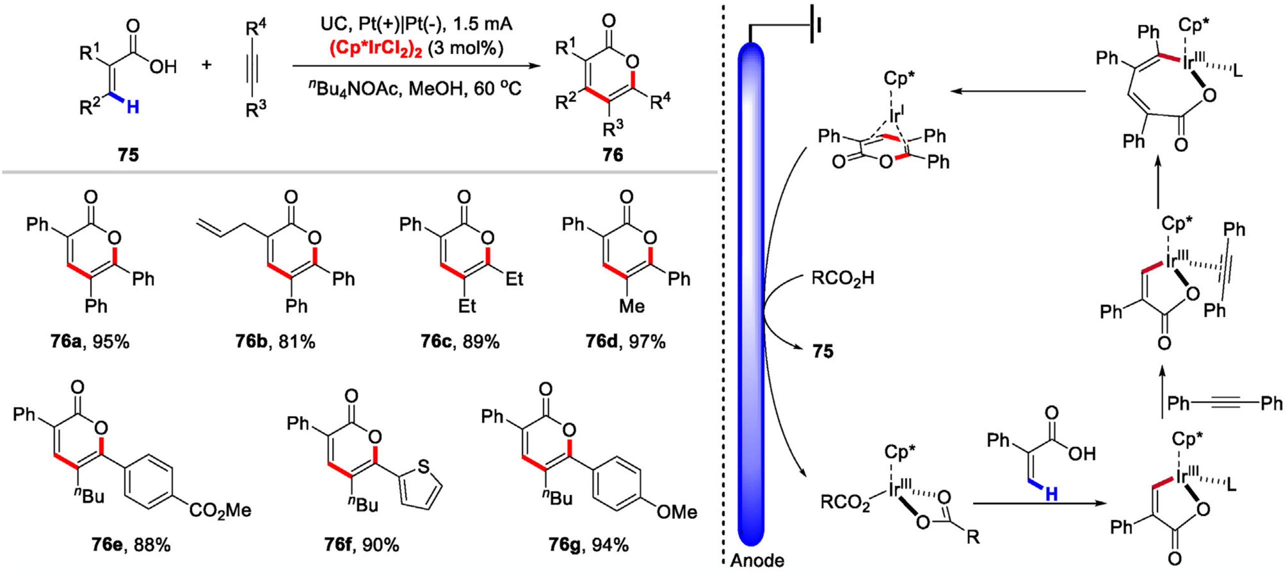


Fig. 8. (Color online) Copper-catalyzed electrochemical (a) C–H amination [172], (b) alkyne annulation [173], and (c) cage B–H oxygenation [174]. (d) Copper-catalyzed enantioselective hydrocyanation of conjugated alkenes [175].

(a) Iridium-catalyzed electrochemical vinylic C–H annulation (Ref. [178])



(b) Gold-catalyzed electrochemical oxidative coupling of terminal alkynes (Ref. [181])

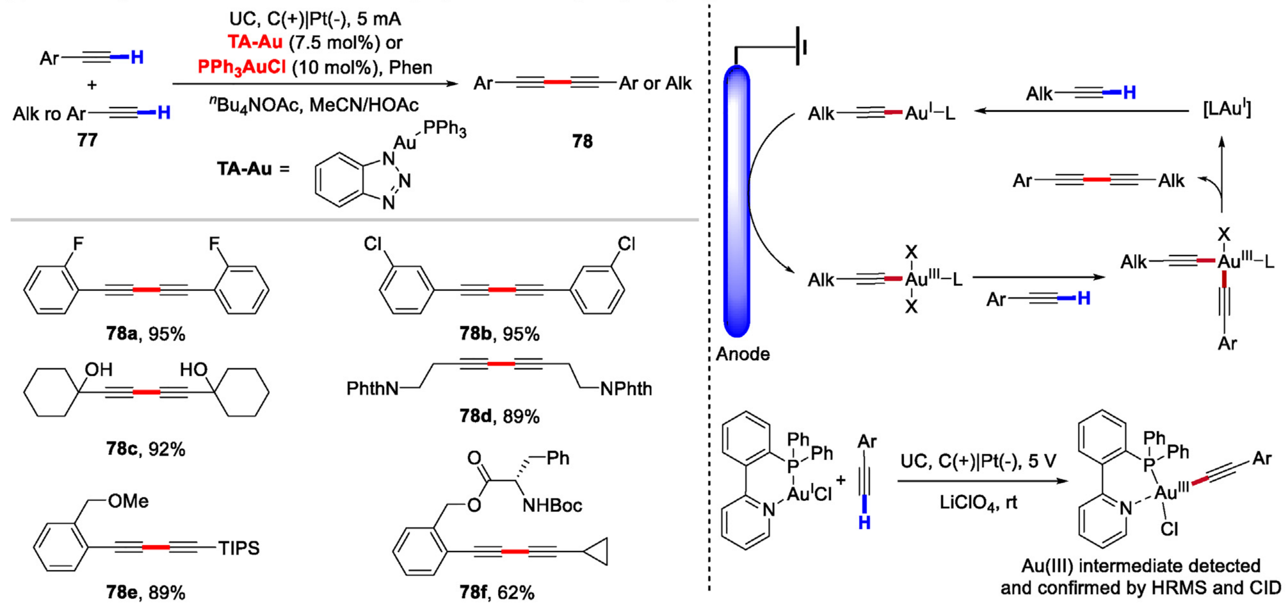


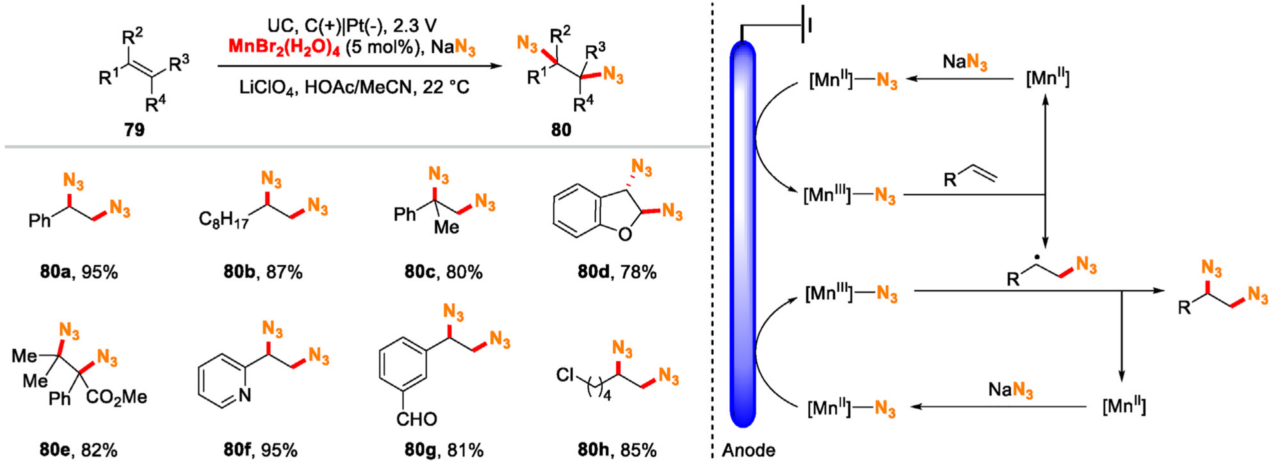
Fig. 9. (Color online) (a) Iridium-catalyzed electrochemical vinylic C–H annulation [178]; (b) gold-catalyzed electrochemical oxidative coupling of terminal alkynes [181].

tion provides an efficient method for azidation of tertiary and secondary benzylic C(sp^3)–H bonds, aliphatic C(sp^3)–H bonds, and drug-molecule-based C(sp^3)–H bonds. An alkyl azide could be formed from the transfer of an azide from Mn(III)/L-N$_3$ to an alkyl radical, which itself could be generated from photo-catalytic HAT or abstraction of an C(sp^3)–H bond by an azide radical (Fig. 10c). More recently, the same group [193] developed a Mn-catalyzed C–H/P–H cross coupling reaction. Ackermann and co-workers [194] reported a similar protocol for Mn-catalyzed electrochemical C(sp^3)–H azidation without light irradiation.

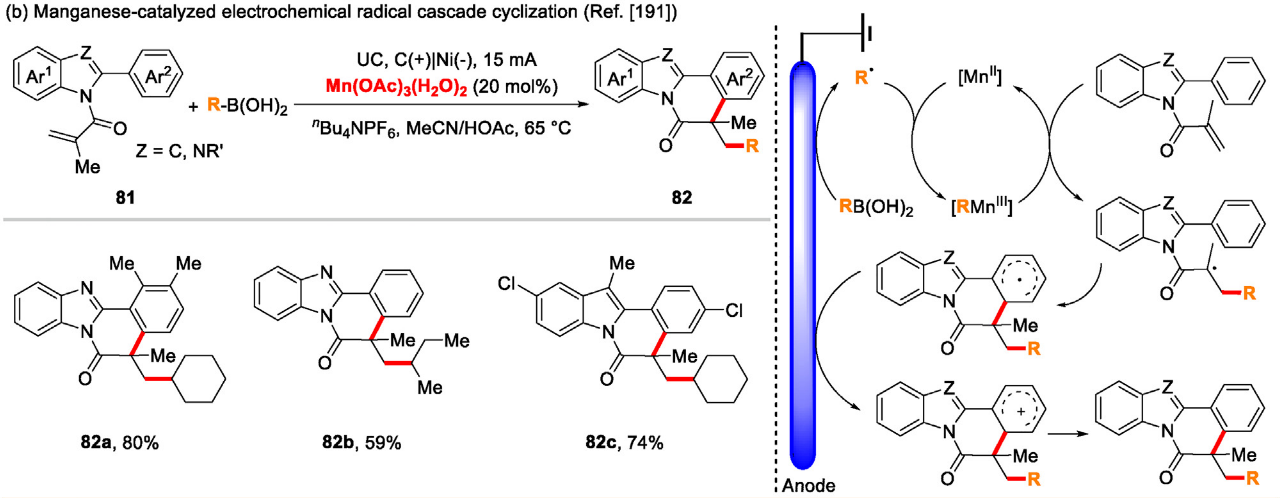
5. Conclusion and outlook

In this review, recent advances in transition metal-catalyzed electroorganic synthesis are summarized. The combination of electrocatalysts and electrosynthesis allows the generation of novel intermediates that can modulate and better control chemical reactivity. In addition, electrochemistry with electrocatalysts provides the basis for much broader functional group combability and synthetic scope. As shown, significant progress has been made in this area in recent years, but some issues remain to be resolved. For example, the development of more efficient electrocatalysts is highly needed since catalytic efficiency is still relatively low (in most of the reported examples, 5 mol%–20 mol% of the electrocatalyst is often required). Improvement will require the discovery and development of electrochemically competent ligands that could tune catalytic activity. Another issue requiring resolution is the development of electrode materials which are modified with immobilized transition metal electrocatalysts. The modified electrode would ostensibly provide a recyclable electrocatalyst, thus improving resource utilization. Thirdly, asymmetric electrochemistry with transition metal complexes has been sparingly developed. The discovery of novel chiral electrocatalysts to enable enantioselective transformations is at the forefront of organic elec-

(a) Manganese-catalyzed diazidation of alkenes (Ref. [182])



(b) Manganese-catalyzed electrochemical radical cascade cyclization (Ref. [191])



[c] Manganese-electrophotocatalytic oxidative azidation of C(sp3)–H Bonds (Ref. [192])

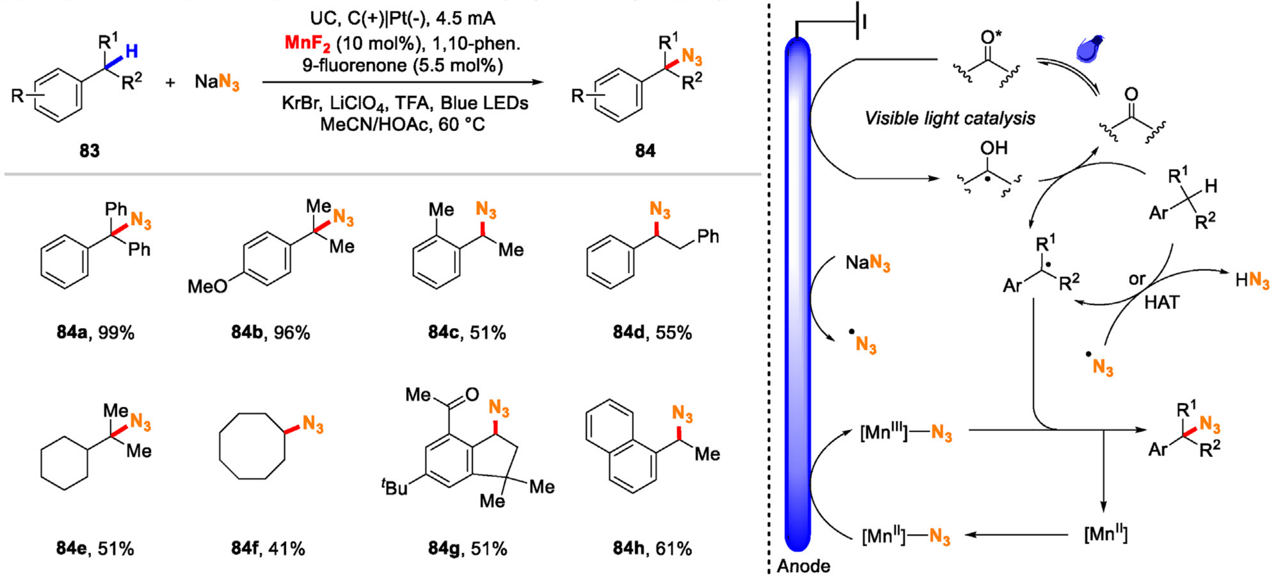


Fig. 10. (Color online) (a) Manganese-catalyzed diazidation of alkenes [182]; (b) manganese-catalyzed electrochemical radical cascade cyclization [191]; [c] manganese-electrophotocatalytic oxidative azidation of C(sp^3)–H Bonds [192].

trochemistry. Lastly, functionalization of simple unactivated alkyl C–H bonds needs to be developed. Through the control of electrochemical oxidation potential, transition metal electrocatalysts could be maintained at a high oxidation state, which would be conducive for the activation such bonds. Electrocatalytic methods should be well suited to tackle this problem, but unfortunately there is scant research in this area to date. We hope that this review provides a helpful overview of the current state of indirect electrocatalytic organic reactions. We hope that remaining issues mentioned above will be solved by novel electrocatalysis methods developed in near future.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Kun Xu, Xu Cheng, Aiwen Lei, Hai-Chao Xu, Chengchu Zeng, and Tian-Sheng Mei conceived the idea and organised the manuscript. Cong Ma, Ping Fang, Zhao-Ran Liu, and Shi-Shuo Xu carried out concept, design, literature search and manuscript preparation. Cong Ma and Tian-Sheng Mei supported and supervised the manuscript revision. All authors contributed to discussion.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2021.07.011.

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