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Communication

Cu-Electrocatalytic Diazidation of Alkenes at ppm Catalyst Loading

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ABSTRACT: The 1,2-diamine motif is prevalent in natural products, small-molecule pharmaceuticals, and catalysts for asymmetric synthesis. Transition metal catalyzed alkene diazidation has evolved to be an attractive strategy to access vicinal primary diamines but remains challenging, especially for practical applications, due to the restriction to a certain type of olefins, the frequent use of chemical oxidants, and the requirement for high loadings of metal catalysts (1 mol % or above). Herein we report a scalable Cu-electrocatalytic alkene diazidation reaction with 0.02 mol % (200 ppm) of copper(II) acetylacetonate as the precatalyst without exogenous ligands. In addition to its use of low catalyst loading, the electrocatalytic method is scalable, compatible with a broad range of functional groups, and applicable to the diazidation of α,β-unsaturated carbonyl compounds and mono-, di-, tri-, and tetrasubstituted unactivated alkenes.

The 1,2-diamine moiety is featured in numerous natural products, pharmaceutical compounds, and molecular catalysts.[1−4] While numerous efforts have been devoted to the development of efficient and practical alkene diamination methods, it remains challenging to directly install two amino groups across the alkene system to provide 1,2-diamines, especially free primary 1,2-diamines.[1,5,6] Alkene 1,2-diazidation reactions provide an attractive alternative strategy for 1,2-diamine synthesis because the vicinal diazide can be easily reduced to free primary 1,2-diamines. Significant progress has been achieved over the past decade in alkene 1,2-diazidation reactions,[7,8] mainly through Pd-,[9] Fe-,[10−13] and Cu-catalyzed[14−16] radical azidation (Figure 1A, top). Unfortunately, these methods still suffer from drawbacks such as the use of relatively high metal catalyst loading (1−10 mol %) and stoichiometric amounts of chemical oxidants (e.g., iodine(III) reagents[10,11,14,15] and organic peroxides[12,13,16]) and limited compatibility of electron-deficient alkenes. Electron-deficient alkenes without aryl substituents are known to be more difficult than more electron-rich ones in reaction with the electrophilic azide radical.[12,17,18] The relatively slow azidation of the electron-deficient olefins allows catalyst-promoted decomposition of the oxidant and azido source, leading to low diazidation efficiency.[12]

Organic electrochemistry, which drives redox processes with electric current, is increasingly pursued as a sustainable synthetic method.[19−33] The integration of electrochemistry with transition metal catalysis has significantly expanded the scope of organic electrosynthesis.[34−41] In this context, Lin and co-workers have recently developed an electrocatalytic olefin 1,2-diazidiation reaction employing $MnBr_2$ (5 mol %) as the catalyst under acidic conditions.[42,43] This method displays exceptional substrate scope with unactivated alkenes and aryl alkenes and broad functional group compatibility (Figure 1A, middle). The same research group has also disclosed an organocatalyzed reaction employing an aminoxyl catalyst to avoid acidic conditions and metal catalysts (Figure 1A, middle).[44] However, the organocatalyst requires a four-step synthesis from commercial materials and the scope is inferior to metal electrocatalysis.

While transition metal catalyzed alkene 1,2-diazidation remains the most efficient method for the preparation of vicinal diazides, the cumulation of hazardous metal azides at high catalyst loading causes significant safety concerns.[45−47] Hence, it is highly desirable to reduce the metal catalyst loading and address the limited efficiency of the diazidation of electron-deficient alkenes. Like many transition metal catalyzed radical reactions, a key step in the diazidation involves ligand transfer from the metal catalyst to a transient alkyl radical (Figure 1B),[48−50] which exists at very low concentration. An also low concentration of the metal catalyst would significantly reduce the rate of its bimolecular reaction with the alkyl radical. Hence, a fundamental question is whether it is possible to significantly reduce the metal catalyst loading to the ppm level in transition metal catalyzed radical azidation and in the meanwhile expand the substrate scope.

Herein, we report Cu-electrocatalytic diazidation of alkenes with 0.02 mol % (200 ppm) of a simple copper salt as the precatalyst without any exogenous ligands (Figure 1A, bottom). The electrocatalytic method is scalable, compatible with numerous functional groups, and applicable to alkenes of diverse electronic properties and substitution patterns including α,β-unsaturated carbonyl compounds and mono-, di-, tri-, and tetrasubstituted unactivated alkenes.

Considering the challenges with diazidation of electron-deficient alkenes, acrylamide **1** was chosen as a model substrate for reaction development (Table 1). The electrolysis was conducted with an undivided cell (a Schlenk tube) with a simple

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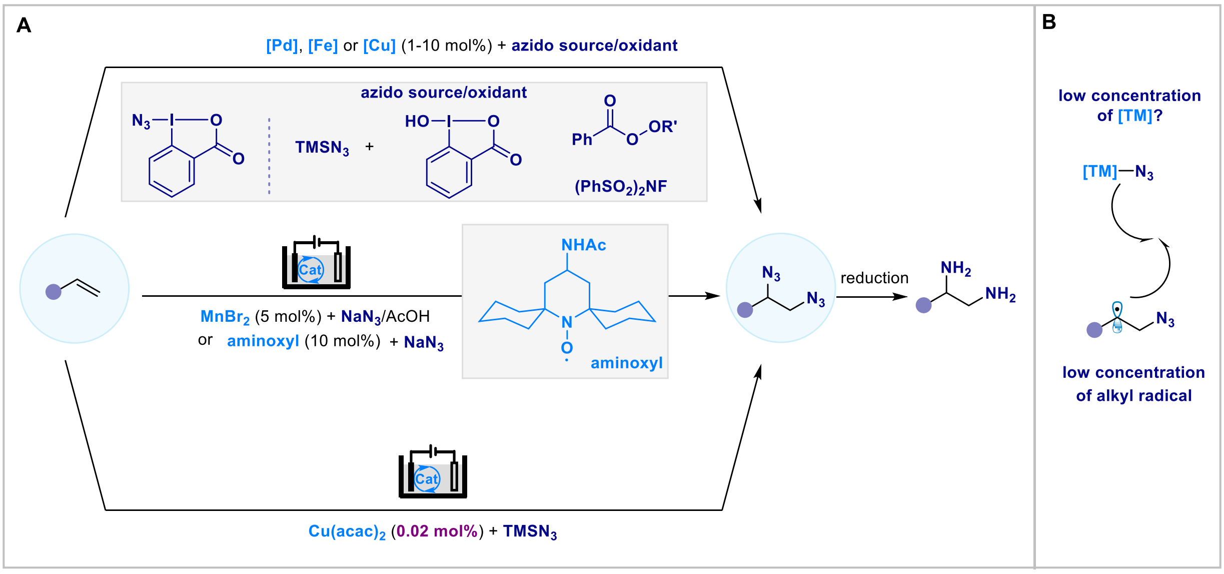
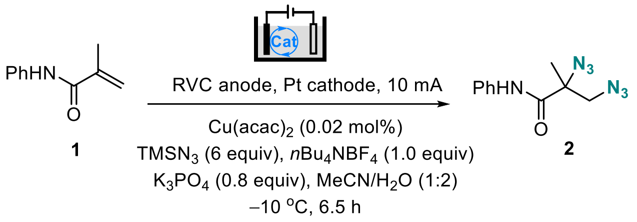


Figure 1. Diazidation of alkenes. (A) Top, transition metal catalyzed alkene diazidation employing chemical oxidants. Middle, established electrocatalytic alkene diazidation employing a Mn salt or an aminoxyl catalyst. Bottom, copper-catalyzed electrochemical diazidation of alkenes at 0.02 mol % (200 ppm) catalyst loading (this work). (B) Key step for the transition metal catalyzed alkene diazidation involves azide transfer from the metal catalyst to a transient alkyl radical at very low concentration. $TMSN_3$, trimethylsilyl azide. TM, transition metal.

Table 1. Optimization of Reaction Conditions[b]



entry	deviation from standard conditions	yield, %[b]
1	none	73 (69)[c]
2	$Cu(acac)_2$ (0.1 mol %)	70
3	$Cu(acac)_2$ (0.01 mol %)	58
4	no $Cu(acac)_2$	30
5	$CuSO_4$ instead of $Cu(acac)_2$	70
6	$CuCl_2$ instead of $Cu(acac)_2$	65
7	$MnBr_2 \cdot 4H_2O$ instead of $Cu(acac)_2$	40
8	$Fe(acac)_3$ instead of $Cu(acac)_2$	40
9	no K_3PO_4	33
10	rt	37
11	$MeCN/H_2O$ (2:1)	38
12	$MeCN/H_2O$ (9:1)	31
13	Ni plate as cathode	70
14	stainless steel plate as cathode	70

[a] Standard reaction conditions: **1** (0.4 mmol), 6.1 F mol^{-1}. [b] Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. [c] Isolated yield. RVC, reticulated vitreous carbon. $Cu(acac)_2$, copper(II) acetylacetonate.

two-electrode configuration. The optimal conditions for the electrocatalytic diazidation of **1** were identified to involve constant current electrolysis in $MeCN/H_2O$ (1:2) at −10 °C in the presence of $Cu(acac)_2$ (0.02 mol %) as the catalyst, $TMSN_3$ as the azido donor, and K_3PO_4 as the base. Under these conditions, the desired alkene diazidation product **2** was isolated in 69% yield (entry 1). Increasing the amount of copper catalyst to 0.1 mol % failed to further increase the yield (entry 2). The reaction with a lower catalyst loading of 0.01 mol % or no copper catalyst resulted in a decreased yield of 58% (entry 3) and 30% (entry 4), respectively. While the replacement of $Cu(acac)_2$ with copper salts such as $CuSO_4$ (entry 5) and $CuCl_2$ (entry 6) did not affect much of the reaction efficiency, $MnBr_2$ and $Fe(acac)_3$ were not effective catalysts for the electrochemical diazidation reaction (entries 7 and 8). Yield reduction to 31−38% was observed when the electrocatalytic reaction was conducted in the absence of K_3PO_4 (entry 9), at rt (entry 10), or increasing the ratio of $MeCN/H_2O$ to 2:1 (entry 11) or 9:1 (entry 12). Pleasingly, Ni (entry 13) and stainless steel (entry 14) were also suitable cathode materials for the electrocatalytic diazidation reaction.

Subsequent substrate scope studies found our electrocatalytic alkene diazidation reaction to be compatible with various alkene substitution patterns (Figure 2). First, α,β-unsaturated amide (**3**), esters (**4−8**), and ketones (**9−12**) were suitable substrates. In the case of **6**, the reaction occurred selectively at the trisubstituted alkene without touching the internal alkyne. On the other hand, steric effects were responsible for the selective reaction of the less hindered trisubstituted (**7**) or disubstituted (**10**) alkene in the presence of an extra tetrasubstituted alkene moiety. In addition, nonactivated mono-, di-, tri-, and tetrasubstituted alkenes (**13−36**) all reacted successfully.

Notably, the electrocatalytic method tolerated many functional groups such as coordinating heteroarenes (pyridine (**5**), imidazole (**20**), and pyrazole (**21**)), carboxylic acid (**9** and **13**), alcohol (**14**), silyl ether (**16**), electrophilic tosylate (**17**), alkyl bromide (**18**), epoxide (**19**, **30**, and **32**), acid-sensitive ketal (**22** and **27**), Boc-protected amine (**28**), dipeptide (**29**), oxidation-labile anilide (**3**), sulfonamide (**15** and **36**), and thioether (**23**). The method was also applied to the diazidation of natural products and drug molecules such as ethacrynic acid (**9**), (+)-nootkatone (**31**), (−)-caryophylle oxide (**32**), and exemestane (**33**).

A gram-scale diazidation of acrylamide **1** was conducted to give 9.4 g of **2** in 55% yield (Figure 2, bottom). The diazide **2** could participate in a copper-catalyzed click reaction[51] with phenylacetylene to give triazole **37**, complete reduction to give

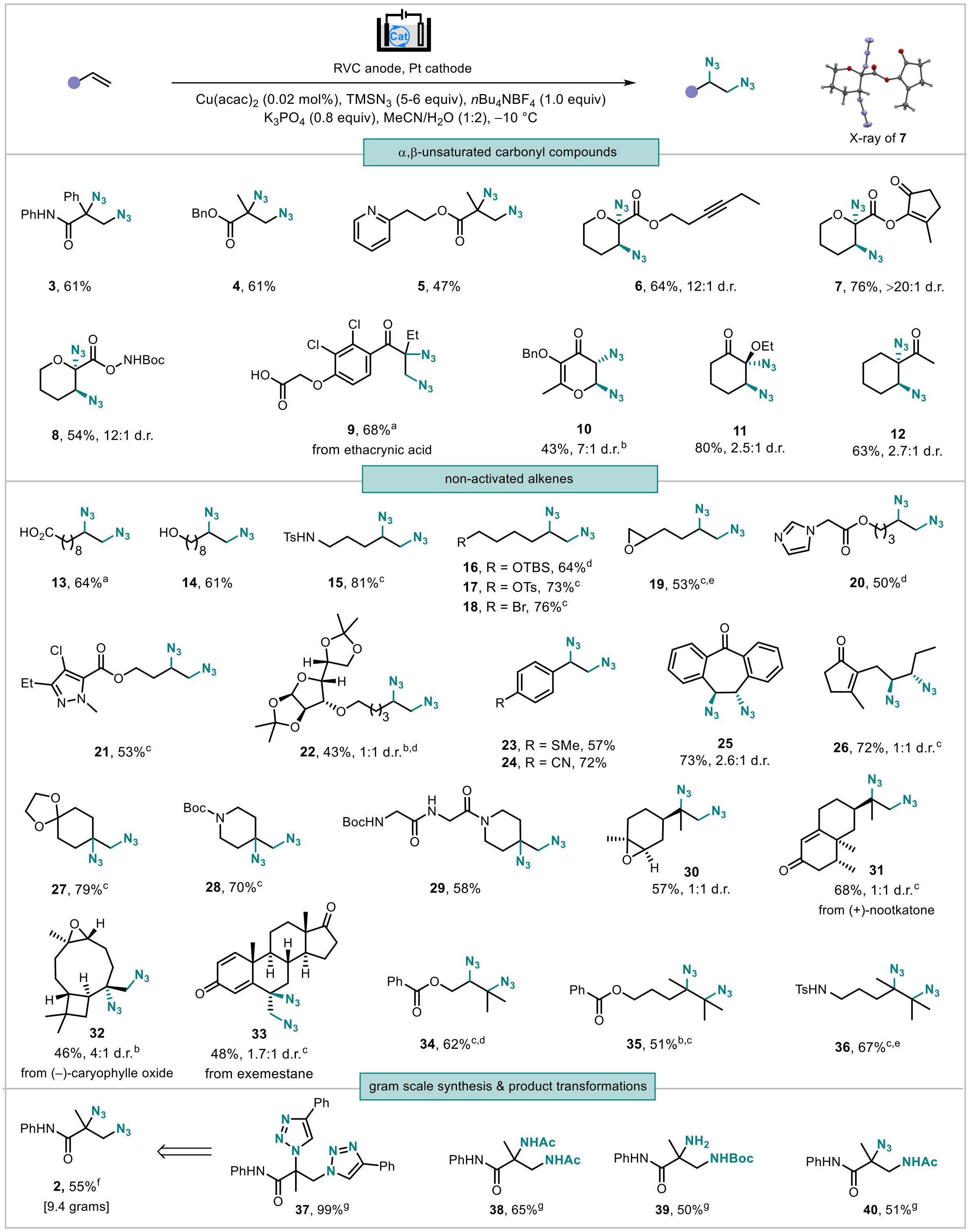


Figure 2. Scope of Cu-electrocatalytic diazidation of alkenes. Reaction conditions: alkene (0.4 mmol), TMSN$_3$ (6 equiv), MeCN (2 mL), H$_2$O (4 mL), 10 mA, 5.0−7.0 h. The yield represents purified product. [a]Reaction with 1 equiv of K$_3$PO$_4$ at 0 °C. [b]Reaction with 0.04 mmol % of Cu(acac)$_2$. [c]Reaction with 5 equiv of TMSN$_3$ at 12.5 mA. [d]Reaction with nBu$_4$PBF$_4$ instead of nBu$_4$NBF$_4$. [e]Reaction with 0.8 mmol of alkene. [f]Reaction on a 70 mmol scale of alkene **1**. [g]See the Supporting Information for detailed reaction conditions. Bn, benzyl. Boc, *tert*-butoxy carbonyl. TBS, *tert*-butyldimethylsilyl. Ts, tosyl. Ac, acetyl.

vicinal diamines (**38**, **39**), or selective reduction of the less hindered azido group to afford α-azido-β-amino amide **40**.

The investigations by cyclic voltammetry indicated that the copper azide species formed from Cu(acac)$_2$ and TMSN$_3$ in the presence of K$_3$PO$_4$ were oxidized at lower potential than N$_3^-$, TMSN$_3$, and Cu(acac)$_2$ (Figure 3A). The voltammogram of the copper azide complex showed a reversible Cu$^{I/II}$ redox couple and an irreversible Cu$^{II/III}$ redox couple (Figure 3A, trace c), revealing the much higher reactivity of copper(III) azide species. In addition, the peak current for Cu$^{II/III}$ did not change much in

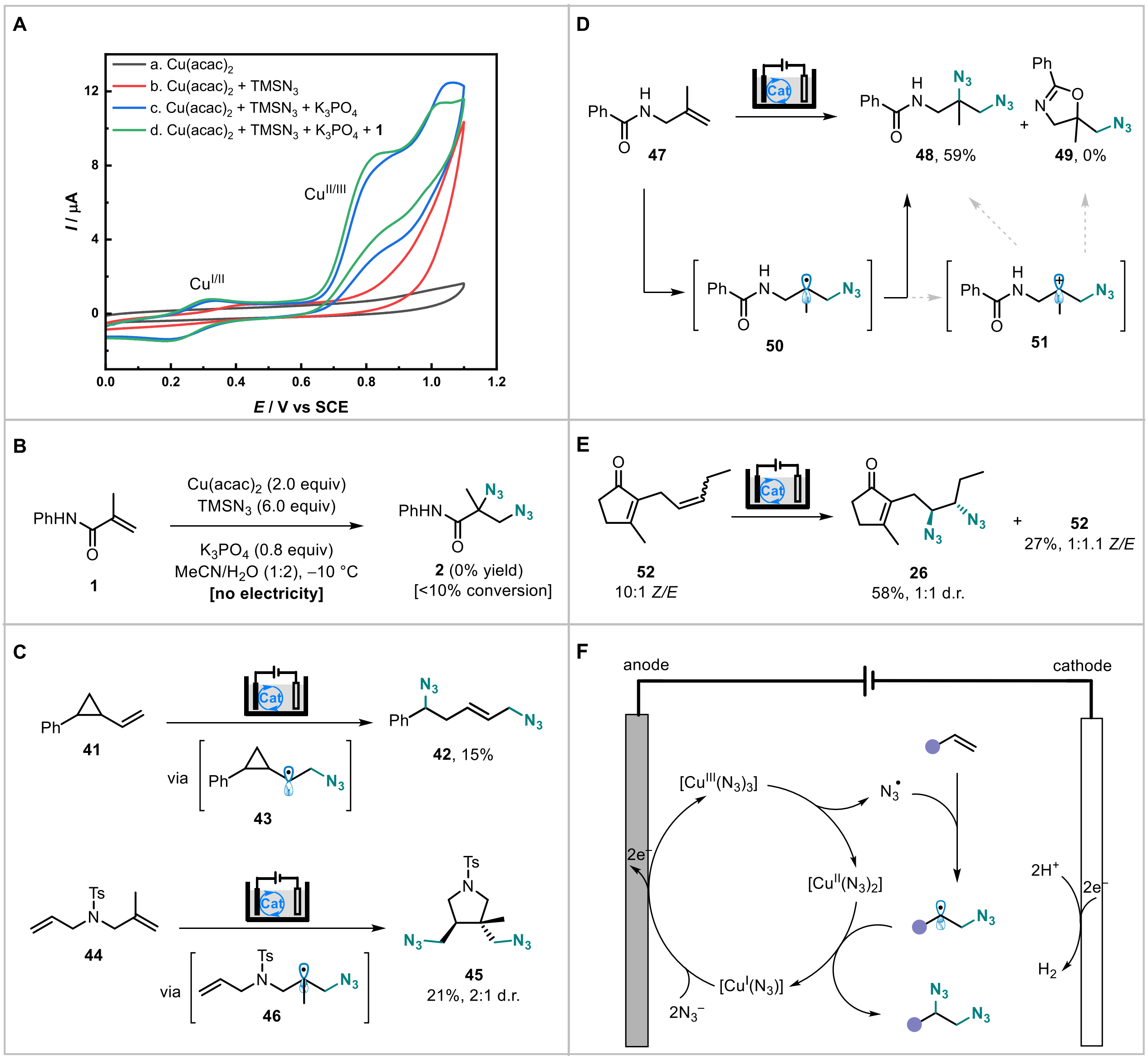


Figure 3. Mechanistic studies and proposal. (A) Cyclic voltammograms obtained at a scan rate of 100 mV s^{-1}. (B) Reaction with stoichiometric Cu(acac)$_2$ without electricity. (C) Probing the radical mechanism. (D) Probing carbocation intermediates. (E) Probing the reversibility of azido addition. (F) Proposed mechanism.

the presence of alkene **1** (Figure 3A, trace d). These results suggested that the alkene did not reduce Cu^{III} on the time scale of the CV scan and argued against a direct ligand transfer from Cu(III) azide species to the alkene. Otherwise, the peak current for Cu$^{II/III}$ would increase if the alkene reduced Cu^{III} to Cu^{II} efficiently through direct ligand transfer. Consistent with the voltammetric results, the reaction of alkene **1** in the presence of a stoichiometric amount of Cu(acac)$_2$ but without electricity afforded no diazidation product **2** with more than 90% of **1** left unreacted (Figure 3B). It was evident from these results that Cu(II) azide species were not responsible for initiating the electrochemical diazidation reaction and a higher valent copper species such as Cu^{III} was involved in the electrocatalytic process. Under the Cu-electrocatalytic conditions, the reactions of cyclopropane-containing alkene **41** and the diene **44** afforded ring-opening product **42** and cyclization-derived pyrrolidine **45** (Figure 3C), respectively, providing strong support for the involvement of alkyl radical intermediates such as **43** and **46**. The reaction of alkene **47**, bearing an amide group, furnished the diazide **48** in 59% yield without observation of cyclization product **49**, suggesting that carbocation intermediates such as **51** were not formed during the electrocatalytic diazidation of alkyl alkenes (Figure 3D). The reaction of aryl alkenes might involve carbocation intermediates due to the ease of oxidation of benzylic radicals.[52] To probe the reversibility of the azido addition to the alkene, jasmone (**52**) with an *E*/*Z* ratio of 1:10 was subjected to the electrocatalytic diazidation and stopped at 73% conversion (Figure 3E). Analysis of the leftover **52** revealed that the *E*/*Z* ratio of the disubstituted alkene increased to 1:1.1, suggesting reversible addition of the azide radical.[42]

A possible mechanism is proposed and shown in Figure 3F. The anodically produced Cu^{III}(N$_3$)$_3$ releases an azide radical and generates cuprous azide [Cu^{II}(N$_3$)$_2$]. The azide radical reacts with the alkene to produce an alkyl radical, which reacts with [Cu^{II}(N$_3$)$_2$] through ligand transfer to give cupric azide [Cu^{I}(N$_3$)] and the final diazide.[53] We do not rule out the possibility that a minor portion of the azide radical is produced through direct anodic oxidation of azide.[54] Cu^{I}(N$_3$) is oxidized to $Cu^{III}(N_3)_3$ on the anode in the presence of N_3^- to complete the catalytic cycle. A key role of K_3PO_4 is to promote the hydrolysis of $TMSN_3$ to N_3^-, as indicated by additional voltammetric studies (Figure S3). Note that the copper azide species $Cu^{III}(N_3)_3$, $Cu^{II}(N_3)_2$, and $Cu^{I}(N_3)$ are simplified formulas for the purpose of presentation but likely to exist as more complex polymeric species.[46,55] Our hypothesis on the success of the electrochemical diazidation with low catalyst loading is that the diazidation process occurs near the electrode surface instead of in the bulk solution. In this scenario, the reactive copper species and the intermediate alkyl radical concentrate in a small space with relatively high concentration, allowing the use of a low catalyst loading.

In conclusion, we have successfully developed a Cu-electrocatalytic alkene diazidation reaction with a ppm catalyst loading. The low catalyst loading, coupled with its broad compatibility with alkene substitution patterns and functional groups, makes the electrocatalytic method highly attractive for the preparation of vicinal diamines. The ability to use a ppm loading of transition metal catalyst for electrocatalytic radical reactions will stimulate wider adaption of organic electrochemistry in radical chemistry research and as a synthetic tool in general.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c05126.

Additional experimental details, materials, and methods, including photographs of the experimental setup, compound characterization data, and NMR spectra (PDF)

Accession Codes

CCDC 2165968 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

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