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Efficient electrocatalysis for the preparation of (hetero)aryl chlorides and vinyl chloride with 1,2-dichloroethane

Yujie Liang, Fengguirong Lin, Yeerlan Adeli, Rui Jin, and Ning Jiao*

Abstract: Although the application of DCE as a chlorinating reagent in organic synthesis concomitant with release of vinyl chloride as a useful byproduct is a fantastic idea, it is still a big challenge and is hardly achieved because of the harsh dehydrochlorination conditions and the inert C-H chlorination process. Here we report a bifunctional electrocatalysis strategy for catalytic dehydrochlorination of DCE at cathode simultaneously with the anodic oxidative aromatic chlorination using the released HCl as chlorosource for the efficient synthesis of value-added (hetero)aryl chlorides. The mildness and practicality of the protocol was further demonstrated by the efficient late stage chlorination of bioactive molecules.

1,2-Dichloroethane (DCE), an inexpensive colorless liquid, has been widely used as a common solvent in various organic transformations. In industry, DCE was used predominantly for vinyl chloride monomer manufacture via pyrolysis, which is typically run at 500-550 °C and 25-35 bar.^[1] Alternative process such as using heterogeneous catalysts to catalyzed dehydrochlorination of DCE has also been explored (usually performed at > 240 °C) with the formation of HCl byproduct which could be reused in the oxychlorination process, but fast deactivation is observed on all the catalysts due to the coke formation that blocks the active sites of the catalysts (Scheme 1a).^[2]

Inspired by the tremendous chlorinated natural products and approved drugs,^[3] the C-H chlorination of (hetero)arenes and bioactive molecules has been an attractive procedure for drug discovery and development. Recently, although a special 7-azaindole group directed C-H chlorination was developed using DCE as the chlorinating reagent,^[4] that protocol is restricted by the expensive Rhodium-catalyst as well as 2.0 equivalent copper-oxidants, and the very limited substrate scope. Ideally, if the C-H chlorinating reagent, it may produce vinyl chloride and H₂ as useful byproducts. This transformation looks wonderful with high atom efficiency. However, this one-stone-two-birds approach to (hetero)aryl chlorides and vinyl chloride from DCE is generally too difficult to be practical because of the harsh dehydrochlorination conditions and the tandem inert C-H chlorination process.

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The incorporation of a chlorine atom has been demonstrated to have a profound effect on enhancing biological properties of small molecules.^[5] In addition, chlorinated arenes and heterocycles are frequently utilized as valuable intermediates in cross-coupling reactions.^[6] Therefore, the development of highly efficient and atom-economic chlorination under mild conditions has been a long-term goal of synthetic scientists. The traditional electrophilic aromatic chlorination with Cl₂, SO₂Cl₂, and *t*-BuOCl as chlorinating reagents is a straightforward method for aryl chlorination. However, their toxic and aggressive nature has plagued their wide applications in organic synthesis.^[7] In the past decades, some classical solid chlorinating reagents (e.g. NCS, DCDMH, TCCA, CBMG) are developed.^[8] Despite their high efficiency and wide applications, the atom-economy is low by using these chlorinating reagents leaving the extra part as the wastes.

Alternatively, the *in situ* generation of electrophilic Cl⁺ species by the oxidation of chloride ion has been widely utilized as an oxidative strategy normally using stoichiometric amounts of K₂S₂O₈, PhI(OAc)₂, DDQ or some metal salts as oxidants, which would generate unwanted wastes.^[9] In contrast, electrochemical oxidation has been recognized as an environmentally friendly strategy in organic synthesis, since generally no sacrificial oxidants are required only with the electricity consumption.^[10] However, the electrochemical chlorination was particularly more difficult than the iodination and bromination due to the difficulty to oxidize Clthrough anodic oxidation. The rarely reported electrochemical chlorination required the assistance of palladium catalysis with a directing group in an divided reaction cell.^[10t] Inspired by these fantastic work^[10] and our oxidative halogenation protocols,^[11] we envisage that, if the dehydrochlorination of DCE could occur under the electrochemical conditions by controlling the current intensity producing vinyl chloride with the incidental formation of HCl, which provides a chance for anodic oxidative C-H chlorination (Scheme 1b). The in situ HCl generation and consumption would avoid the usage of strong acidic condition and therefore enable the selective chlorination with broad substrate scope including inactive electron-deficient (hetero)arenes.

The challenging issue of this hypothesis is how the dehydrochlorination process of DCE could be executed by electrochemistry. The thermal cracking dehydrochlorination of DCE for vinyl chloride manufacture is known via chloroethyl radical intermediate, which is produced from the pyrolysis of 1,2-DCE itself.^[12] Gas phase DCE, like many other halocarbons, has been reported to have an extensive electron attachment chemistry.^[13] It has a large electron capture cross section for electron hunting to form an excited negative ion DCE^{*}, which can decompose promptly on metal surface to lead to the chloroethyl radical and chemisorbed chlorine.^[14] The generation of chloroethyl radical supports our hypothesis that an electrochemical strategy could enable the dehydrochlorination process of DCE, where the DCE would be absorbed and dissociated on the surface of the electrode. The electrons may be released from the surface of electrode and enter into the antibonding C-C1 σ^* orbital of DCE, thus triggering the cleavage of C-Cl bond to produce vinyl chloride and HCl at mild conditions. Furthermore, it may also be possible to enable the anodic oxidative C-H chlorination with the in situ generated HCl,[10t] and therefore complete the electrochemical circle (Scheme 1b). Herein, we report a bifunctional electrocatalysis for catalytic

dehydrochlorination of DCE and direct C-H chlorination of (hetero)arenes at mild conditions (Scheme 1c). This chemistry provides a practical and high atom-efficient protocol for the preparation of various high-valued (hetero)aryl chlorides with the formation of vinyl chlorides and H₂ as the byproducts. To the best of our knowledge, this represents the first example that DCE is activated and utilized as an efficient chlorinating reagent for aromatic chlorination by electrolysis.



Scheme 1. Bifunctional electrocatalysis for dehydrochlorination of DCE and the anodic oxidative C-H chlorination.

Based on our mechanistic design (Scheme 1b), we first tested the viability of dehydrochlorination of DCE under electrochemical conditions. Intriguingly, when the reaction was conducted in an undivided cell filled with liquid DCE (15 mL, ~192 mmol) and n-Bu4NBF4 (1 mmol) as electrolyte using graphite anode and Pt-plate cathode at 60 °C under constant-current electrolysis I = 100 mA, notable gas bubble was observed in the reaction vessel. After electrolysis overnight, a gas chromatographical examination of the outlet volatile organic compounds indicated that vinyl chloride was indeed produced as the major component with 45% selectivity, but a notable amount of ethylene (53%) and small amount of other components (2%) were also observed in this case using this electrolyte. Furthermore, when the readily available and inexpensive n-Bu₄NOH (1 mmol, 37% MeOH solution) was used as electrolyte instead of *n*-Bu₄NBF₄, the desired vinyl chloride was produced in 48% selectivity along with generation of ethylene (46%), a small amount of 1,1-dichloroethylene (5%) and other components (1%) (Scheme 2). A notable amount of HCl was also produced, which was observed in both the outlet flow as well as the reaction solution, and was detected by GC-MS (Scheme 2, and see Supporting Information). It should be noted that, the ethylene and HCl could be efficiently reused to generate DCE via ethylene oxychlorination for further vinyl chloride preparation.^[2, 15] Therefore, this protocol should be very useful, since after reusing the ethylene and HCl to produce DCE, the vinyl chloride would almost be the sole product. Thus, the atom efficiency of this protocol should be very high, which holds great potential for the further application in large-scale vinyl chloride manufacture. The generation of ethylene also supports the formation of a DCE⁻ ion transition state by electron capture from the Pt surface, which follows a similar process depicted in Scheme 1b to furnish the chloroethyl radical. This radical would finally lead to the ethylene formation by stripping of a Cl atom, or like in the thermal cracking dehydrochlorination process of DCE to produce vinyl chloride. The results are consistent with our mechanistic hypothesis.



Scheme 2. Electrolysis enabled dehydrochlorination of DCE.

Encouraged by these promising results, we further tested the possibility of direct aromatic chlorination in one pot. Initially, we investigated the chlorination of N-(4-chlorophenyl)acetamide 1a with DCE under electrochemical conditions (Table S1). After extensive attempts, we found the chlorination of 1a proceeded efficiently under constant-current electrolysis at 10 mA for 10 h, using graphite anode, Pt-plate cathode, and *n*-Bu₄NOH as electrolyte in an undivided cell (Table S1, entry 1). Replacing the Pt-plate cathode with Ni-plate would lead to the efficiency decrease (Table S1, entry 2). Surprisingly, when replaced the Pt-plate cathode with Cu-plate, no desired chlorination product was formed (Table S1, entry 3). This is probably due to the instability of Cu-plate under the electrochemical condition, since the destruction of Cu-plate was observed after electrolysis 10 h. Other electrolytes were also tested, but lower yields were obtained (Table S1, entries 4-8). The reaction became sluggish when performed at room temperature (Table S1, entry 9). Decreasing the electric current to 5 mA proved also viable, albeit prolonged reaction time is required for full consumption of starting material (Table S1, entry 10). Control experiment showed that the reaction did not occur without electricity (Table S1, entry 11).

With the optimized conditions in hand, the substrate scope was then investigated (Table 1). Notably, various *para*-substituted anilides even with strong electron-withdrawing groups, could all be smoothly chlorinated with good to excellent yields (**2a-2i**). When the *para* position of acetanilides was not occupied, the bis chlorination products were produced (**2a**, **2j-2k**). Additionally, chlorination of *N*-(naphthalen-2-yl)acetamide and *N*-(naphthalen-1yl)pivalamide were also facile (**2m**, **2n**). In addition, anisole was chlorinated in excellent yield with 16:1 *para/ortho* selectivity (**2o**). In some cases, the loading of Cu(OAc)₂ (5 mol%) could increase the yields.

Significantly, the protocol can also be extended to the selective chlorination of some druglike molecules. The sensitive benzylic C-H of naproxen methyl ester (**3a**), the reactive imide N-H bond of aminoglutethimide derivative (**3b**), the fragile isoxazole group of leflunomide (**3c**), and even the subtle hydroxyl group of paracetamol (**3d**), were also compatible in this protocol. These results demonstrate the mildness and practicality of the chlorination protocol.

Encouraged by the efficient chlorination of arenes, the substrate scope with regard to heterocycles were then examined (Table 1). To our delight, reactions of thiophenes (4a, 4b), pyrazole (4c), imidazole (4d), indoles (4e-4g), and some pyridine and quinolone anilides (4h-4l) could all lead to clean chlorination with high regioselectivity, affording mono-chlorination products in most cases even for substrates with multiple potential chlorination sites. It is

noteworthy that some inactivated chemicals which are not accepted by NCS, reacted smoothly under the current electrochemical conditions (2h, 2i, 3c, 4i, 4j, 4l) (see Figure S8, Supporting Information).

Table 1. Scope of the electrochemical aromatic C-H chlorination with DCE.



[a] Reaction conditions: 1 (0.5 mmol), n-Bu4NOH (1 mmol, used as 37% MeOH solution), graphite anode, Pt-plate cathode, I = 10 mA $(j_{anode} \approx 4.4 \text{ mA cm}^{-2})$, DCE, 60 °C, undivided cell. Isolated yields. [b] Constant current = 20 mA ($j_{anode} \approx 8.9$ mA cm⁻²). [c] Reaction conditions: 1 (0.5 mmol), 2,4,6-trimethylaniline (10 mol%), NCS (0.6 mmol), DCM (0.25 M) at r.t. for 12 h (see ref 8c). [d] Reaction conditions: 1 (0.5 mmol), n-Bu4NBF4 (1 mmol), Cu(OAc)2 (0.05 equiv), DCE, 60 °C, I = 10 mA ($j_{anode} \approx 4.4 \text{ mA cm}^{-2}$), graphite anode, Pt-plate cathode, undivided cell. [e] n-Bu₄NOH (1 mmol) without MeOH was used. [f] Trace amount of bis chlorination product was observed.

The scalability of this electrochemical aromatic C-H chlorination was further evaluated. To our delight, this reaction can be easily scaled up to 15 mmol scale using a simple and readily made device, which shows great potential of this method for industrial synthesis (Scheme 3).



To get more insights into the mechanism, some experiments were performed. Firstly, we test the constancy of the assembled undivided cell for aromatic chlorination. Delightedly, after the first round chlorination of **1a** (0.5 mmol), another 1 mmol of **1a** was simply added into the same vessel, which sequentially proceed smoothly without extra addition of electrolyte or using new electrode. We repeated this same process 2 times, the efficiency was not affected by the continual substrate addition producing the desired chlorinated product 2a in 85% yield based on the total 3 mmol consumption of 1a (Scheme 4a). This result suggests that the reaction did not rely on

the stoichiometric amount of base and the HCl that produced from DCE dehydrochlorination would serve as chloride source.^[16] In addition, when performed the reaction in the absence of substrate under constant current electrolysis overnight, the reaction mixture clearly became acidic by pH measurement. Moreover, the outlet gas was also collected in a balloon among them the HCl was proved by GC-MS (Scheme 4b, and see in the Supporting Information). It is noteworthy that, without electricity, the reaction mixture remains basic after stirring overnight. Furthermore, the employment of stoichiometric amount of TEMPO significantly inhibited the chlorination reaction, probably due to the suppression of the radical process (see Figure S6, Supporting Information).



Furthermore, we conducted cyclic voltammetry experiment (Figure 1). Based on preliminary measurements, we chose the 0-1.5

V potential window for cyclovoltammetry in DCE. As it can be seen in this potential window, one oxidation wave appeared on the forward potential sweep (1.06 V) and one reduction wave (0.94 V) exhibited on the backward potential sweep at a Pt disc electrode at 100 mV s⁻¹ in 0.1 M *n*-Bu₄NOH in DCE (Figure 1a). This redox couple is probably due to the oxidation of Cl⁻ by the forward sweep and the reduction of DCE to DCE⁻ by the backward sweep. This assumption is supported by the cyclic voltammetry of the *n*-Bu₄NCl (3 mM) with n-Bu₄NBF₄ (0.1 M) in DCE, which exhibited also one oxidation wave (1.11 V) and one reduction wave (0.70 V) (Figure 1b). Furthermore, with substrate 1a (3 mM) and n-Bu₄NBF₄ (0.1 M) in DCE, an oxidation occurred at 1.03 V was observed (Figure 1c). This is probably due to the oxidation of **1a** or the oxidation of Cl⁻ (Figure 1c). Moreover, the oxidative potential of 1a is further decreased to 0.81 V under basic condition and the oxidation of Clwas also observed at 1.10 V at this condition (Figure 1d). This is consistent with the cyclic voltammetry of 0.1 M n-Bu4NOH in DCE (Figure 1a) where the oxidation of Cl⁻ occurred at 1.06 V. Based on these results, we assume that anodic oxidation of 1a would form a cationic intermediate,^[17] which then interact with the chloride anion to generate the chlorinated product. It should be noted that the exact reaction pathway depends highly on the oxidative potential of the substrate.^[18] If the oxidative potential of a substrate is higher than the Cl-, the anodic oxidation of Cl- is preferential, thus, an electrophilic aromatic chlorination mechanism would be favored. Based on the above results, a plausible mechanism for the chlorination of arenes and the formation of vinyl chloride and ethylene was proposed (see Figure S7, Supporting Information).



Figure 1. Cyclic voltammetry experiment. Recorded on a Pt disc electrode at 100 mVs⁻¹ in (a) 0.1 M *n*-Bu₄NOH in DCE; (b) 3 mM *n*-Bu₄NOI and 0.1 M *n*-Bu₄NBF₄ in DCE; (c) 3 mM **1a** and 0.1 M *n*-Bu₄NBF₄ and 0.05 M *n*-Bu₄NOH in DCE.

In conclusion, we have developed an ideal bifunctional electrocatalysis strategy for catalytic dehydrochlorination of DCE simultaneously with the aromatic chlorination using the released HCl. The common solvent DCE is ideally employed as a reactant producing vinyl chloride and as a chlorinating reagent for efficient aromatic chlorination. Notably, this external oxidant free electrocatalysis can also be easily scaled up and is demonstrated very green and sustainable with the tolerance of inactive chemicals. Considering the benign process for DCE dehydrochlorination, and the broad substrate scope of aromatic chlorination, this method would open new avenue for vinyl chloride and (hetero)aryl chlorides preparation in an efficient and environmentally benign manner. The present bifunctional electrocatalysis strategy is expected to be of high interest to scientists from both academia and industry.

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- a) I. Mochida, T. Tsunawaki, C. Sotowa, Y. Korai, K. Higuchi, *Ind. Eng. Chem. Res.* **1996**, *35*, 3803; b) C. Li, G. Hu, W. Zhong, W. He, W. Du, F. Qian, *Ind. Eng. Chem. Res.* **2013**, **52**, 17501.
- [2] R. Lin, A. P. Amrute, J. Pérez-Ramírez, *Chem. Rev.* **2017**, *117*, 4182.
- [3] G. W. Gribble, J. Chem. Educ. 2004, 81, 1441.
- [4] G. Qian, X. Hong, B. Liu, H. Mao, B. Xu, Org. Lett. 2014, 16, 5294.
- [5] a) J. Latham, E. Brandenburger, S. A. Shepherd, B. R. K. Menon, J. Micklefield, *Chem. Rev.* 2018, *118*, 232; b) Z. Xu, Z. Yang, Y. Liu, Y. Lu, K. Chen, W. Zhu, *J. Chem. Inf. Model.* 2014, *54*, 69.

- a) P. Ruiz-Castillo, S. L. Buchwald, *Chem. Rev.* **2016**, *116*, 12564; b) A. F. Littke, G. C. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 4176; *Angew. Chem.* **2002**, *114*, 4350.
- [7] a) W. D. Watson, J. Org. Chem. 1985, 50, 2145; b) V. Stimson, Aust. J. Chem. 1965, 18, 126.

[6]

- [8] a) G. K. S. Prakash, T. Mathew, D. Hoole, P. M. Esteves, Q. Wang, G. Rasul, G. A. Olah, J. Am. Chem. Soc. 2004, 126, 15770; b) R. B. Bedford, M. F. Haddow, C. J. Mitchell, R. L. Webster, Angew. Chem. Int. Ed. 2011, 50, 5524; Angew. Chem. 2011, 123, 5638; c) R. C. Samanta, H. Yamamoto, Chem. Eur. J. 2015, 21, 11976; d) X. Xiong, Y.-Y. Yeung, Angew. Chem. Int. Ed. 2016, 55, 16101; Angew. Chem. 2016, 128, 16335; e) D. R. Motati, D. Uredi, E. B. Watkins, Chem. Sci. 2018, 9, 1782; f) R. A. Rodriguez, C. M. Pan, Y. Yabe, Y. Kawamata, M. D. Eastgate, P. S. Baran, J. Am. Chem. Soc. 2014, 136, 6908.
- [9] a) S. C. Fosu, C. M. Hambira, A. D. Chen, J. R. Fuchs, D. A. Nagib, *Chem* 2018, DOI: 10.1016/j.chempr.2018.11.007; b) L. Gu, T. Lu, M. Zhang, L. Tou, Y. Zhang, *Adv. Synth. Catal.* 2013, *355*, 1077; c) K. Ohkubo, A. Fujimoto, S. Fukuzumi, *Chem. Asian J.* 2016, *11*, 996; d) X. Wan, Z. Ma, B. Li, K. Zhang, S. Cao, S. Zhang, Z.-J. Shi, *J. Am. Chem. Soc.* 2006, *128*, 7416.
- [10] a) For some recent reviews, see: a) M. Yan, Y. Kawamata, P. S. Baran, Chem. Rev. 2017, 117, 13230; b) K. D. Moeller, Chem. Rev. 2018, 118, 4817; c) Y. Jiang, K. Xu, C. Zeng, Chem. Rev. 2018, 118, 4485; d) S. Tang, Y. Liu, A. Lei, Chem 2018, 4, 27; e) J.-I. Yoshida, A. Shimizu, R. Hayashi, Chem. Rev. 2018, 118, 4702; For some recent examples, see: f) A. Badalyan, S. S. Stahl, Nature 2016, 535, 406; g) N. Fu, G. S. Sauer, A. Saha, A. Loo, S. Lin, Science 2017, 357, 575; h) E. J. Horn, B. R. Rosen, Y. Chen, J. Tang, K. Chen, M. D. Eastgate, P. S. Baran, Nature 2016, 533, 77; i) X. Huang, Q. Zhang, J. Lin, K. Harms, E. Meggers, Nat. Catal. 2018, DOI:10.1038/S41929-018-0198-y; j) L. Schulz, M. Enders, B. Elsler, D. Schollmeyer, K. M. Dyballa, R. Franke, S. R. Waldvogel, Angew. Chem. Int. Ed. 2017, 56, 4877; Angew. Chem. 2017, 129, 4955; k) N. Sauermann, T. H. Meter, C. Tian, L. Ackermann, J. Am. Chem. Soc. 2017, 139, 18452; 1) T. Morofuji, A. Shimizu, J.-I. Yoshida, J. Am. Chem. Soc. 2013, 135, 5000; m) Q.-L. Yang, Y.-Q. Li, C. Ma, P. Fang, X.-J. Zhang, T.-S. Mei, J. Am. Chem. Soc. 2017, 139, 3293; n) X. Gao, P. Wang, L. Zeng, S. Tang, A. Lei, J. Am. Chem. Soc. 2018, 140, 4195; o) N. Fu, G. S. Sauer, S. Lin, J. Am. Chem. Soc. 2017, 139, 15548; p) J. Li, W. Huang, J. Chen, L. He, X. Chang, G. Li, Angew. Chem. Int. Ed. 2018, 57, 5695; Angew. Chem. 2018, 130, 5797; q) L. Sun, X. Zhang, Z. Li, J. Ma, Z. Zeng, H. Jiang, Eur. J. Org. Chem. 2018, 4949; r) C.-Y. Cai, H.-C. Xu, Nat. Commun. 2018, 9, 3511; s) P. Xiong, H.-H. Xu, H.-C. Xu, J. Am. Chem. Soc. 2017, 139, 2956; t) F. Kakiuchi, T. Kochi, H. Mutsutani, N. Kobayashi, S. Urano, M. Sato, S. Nishiyama, T. Tanabe, J. Am. Chem. Soc. 2009, 131, 11310; u) M. Konishi, K. Tsuchida, K. Sano, T. Kochi, F. Kakiuchi, J. Org. Chem. 2017, 82, 8716; v) B. V. Lyalin, V. A. Petrosyan, Chem. Heterocycl. Compd. 2014, 49, 1599.
- [11] S. Song, X. Sun, X. Li, Y. Yuan, N. Jiao, Org. Lett. 2015, 17, 2886.
- [12] W. Zhao, M. Sun, H. Zhang, Y. Dong, X. Li, W. Li, J. Zhang, RSC Adv. 2015, 5, 104071.
- [13] a) J. P. Johnson, L. G. Christophorou, J. G. Carter, J. Chem. Phys. 1977, 67, 2196; b) D. L. McCorkle, I. Szamrej, L. G. Christophorou, J. Chem. Phys. 1982, 77, 5542.
- [14] a) W. K. Walter, R. B. Jones, *Catal. Lett.* **1994**, *24*, 333; b) R. B. Jones, S. Turton, R. Ithnin, *Surf. Sci.* **1997**, *377-379*, 705.
- [15] M. Scharfe, P. A. Lira-Parada, V. Paunović, M. Moser, A. P. Amrute, J. Pérez-Ramírez, Angew. Chem. Int. Ed. 2016, 55, 3068; Angew. Chem. 2016, 128, 3120.
- [16] X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, J. Am. Chem. Soc. 2006, 128, 6790.
- [17] T. Gieshoff, A. Kehl, D. Schollmeyer, K. D. Moeller, S. R. Waldvogel, J. Am. Chem. Soc. 2017, 139, 12317.
- [18] a) E. M. Ungureanu, A. C. Razus, L. Birzan, G. Buica, M. Cretu, E. Cristian, *Electrochimica Acta* 2006, 52, 794; b) D. Stevanović, I. Damljanović, M. Vukićević, N. Manojlović, N. S. Radulović, R. D. Vukićević, *Helv. Chim. Acta* 2011, 94, 1406; c) B. V. Lyalin, V. A. Petrosyan, *Russ. J. Electrochem.* 2013, 49, 497.

Entry for the Table of Contents

C-H Functionalization

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A bifunctional electrocatalysis strategy for catalytic dehydrochlorination of DCE at cathode simultaneously with the anodic oxidative aromatic chlorination using the released HCl as chloro-source for the efficient synthesis of value-added (hetero)aryl chlorides is demonstrated.