Title:

Merging shuttle reactions and paired electrolysis: *e*-shuttle unlocks reversible halogenations

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Abstract

Polyhalogenated molecules have found widespread applications as flame retardants, pest-control agents, polymers and pharmaceuticals[1,2]. They also serve as versatile synthetic intermediates in organic chemistry due to the inherent reactivity of carbon-halogen bonds[3,4]. Despite these attractive features, the preparation of polyhalogenated molecules still mainly relies on the use of highly toxic and corrosive halogenating reagents, such as Cl_2 and Br_2, which are hazardous compounds to transport, store, and handle[4,5]. Moreover, the use of such highly reactive reagents inherently makes the development of the reverse reactions, *retro*-dihalogenations, highly challenging, despite their potential for the recycling of persistent halogenated pollutants. Here, we introduce an electrochemically-assisted shuttle *(e-shuttle)* paradigm for the facile and scalable interconversion of alkenes and vicinal dihalides, a class of reactions which can be used both to synthesize useful polyhalogenated molecules from simple alkenes and to recycle waste material through *retro*-dihalogenation. The power of this reaction is best highlighted by an example, in which different soils contaminated with a persistent environmental pollutant (Lindane), could be directly used as Cl_2-donors for the transfer dichlorination of simple feedstock alkenes, merging a recycling process with a synthetically relevant dichlorination reaction. We further demonstrate that this paired electrolysis-enabled shuttle protocol, which uses a simple setup and inexpensive electrodes, is applicable to four different, synthetically useful transfer halogenation reactions, and can be readily scaled-up to a decagram scale. In a broader context, the symbiotic merging of shuttle reactions and electrochemistry introduced in this work opens new horizons for safer transfer functionalization reactions that will address important challenges across the molecular sciences.

Main text:

Transfer hydrofunctionalization proceeding through a shuttle catalysis[6] paradigm has emerged as a powerful and versatile strategy to reversibly functionalize and defunctionalize organic molecules without employing or releasing highly toxic reagents[7,8,9,10,11,12], such as HCN[7]. However, catalytic and reversible transfer reactions have so far been limited to alkene *monofunctionalization*[13] reactions which usually involve the transfer of an HX molecule[6,12]. In contrast, the synthetically appealing, simultaneous transfer of two functional groups, in a catalytic reversible transfer *difunctionalization* process, has so far remained elusive, despite the vast synthetic potential of these reactions in organic synthesis. In particular, reactions involving the formal transfer of extremely hazardous molecules, such as Cl_2[14,15] or Br_2, from easy-to-handle and less toxic bulk chemicals, such as inexpensive dichloro- and dibromoethane, would be highly desirable because of the widespread synthetic applications of polyhalogenated molecules in flame retardants, pesticides, materials and natural products[1,2,16] (Fig. 1A). The inherent reversibility of such a shuttle reaction would further unlock the facile *retro*-dihalogenations of end-of-life halogenated products, providing a new entry into a circular economy approach to these products.

The challenge in developing transfer difunctionalizations such as transfer dihalogenations originates from the catalytic approach generally employed in shuttle catalysis. Transfer hydrofunctionalizations, such as hydrocyanation[7], rely on the intermediacy of an alkyl-metal complex which readily undergoes fast and reversible β-hydride elimination, thus triggering the transfer of an hydrogen atom alongside the desired functional group[12] (Fig. 1B). Unfortunately, the ease of β-hydride elimination makes the selective, competitive elimination of other synthetically useful groups extremely challenging[17]. Furthermore, while β-hydride elimination is a fast and reversible process, the subsequent migratory re-insertion of an alkene into a metal−halogen bond is often kinetically and thermodynamically disfavored due to the high stability of metal-halogen bonds[18]. Thus, a mechanistically distinct approach to favor halogen transfer over hydrogen transfer is crucial to unlock this important class of transfer difunctionalization reactions.

Electrosynthesis has recently experienced a renaissance in organic chemistry, as it utilizes inexpensive and readily available electrical current from renewable resources as a sustainable and inherently safe redox reagent[19,20,21,22]. Notable advances have been made in halogenation reactions, as illustrated by an elegant example of dichlorination reaction from Lin and coworkers[23]. However, this reaction, as well as the vast majority of other electrochemical reactions, have to be coupled to another sacrificial half reaction, for example proton reduction to form hydrogen, at the counter-electrode. Besides this limitation, current protocols can often be further limited by the use of complex reaction setups including expensive metal electrodes, or the generation of by-products implying safety issues (e.g. hydrogen)[24].

We envisaged that consecutive paired electrolysis involving a domino reduction-oxidation cascade[25,26], a class of ideal yet extremely rare electrochemical reactions wherein electrons at both electrodes are employed in the desired transformation, could provide a totally unexplored path to reversible electrochemically-mediated shuttle reactions (*e*-shuttle). We surmised that the reversible cleavage of two strong carbon─halogen bonds through a controlled electron transfer process initiated by a simultaneous, simple reduction and oxidation of key intermediates at the anode and cathode, respectively, would unlock this new class of transformations (Fig. 1C/D). In our hypothesis, the single-electron reduction of the dihalide at the cathode releases the Y^- anion and generates the carbon radical **1**, which is almost instantly reduced again to generate a carbanion[27]. As a central design, the subsequent selective loss of X^- instead of a hydride breaks the C─X bond, releasing the alkene compound. Considering that a halide anion is a much better leaving group than a hydride, the competing undesired β–H elimination, which is often the preferred pathway when alkyl-transition metal complexes are involved as intermediates, can be effectively suppressed by this electrochemical approach. The subsequent oxidation of X^- at the anode followed by reaction with the alkene delivers the desired product, which closes the cycle by reestablishing the C─X and C─Y bonds in a fully isodesmic process. Highly precise control of the potential applied on the electrodes and the highly tunable cell voltage would make this strategy outstandingly modular and versatile with regard to the group transferred, opening new horizons for further shuttle reaction development. This is a great advantage over the organometallic strategy, where each shuttle reaction relies on a completely different combination of metal and catalyst requiring tedious optimization campaigns[12].

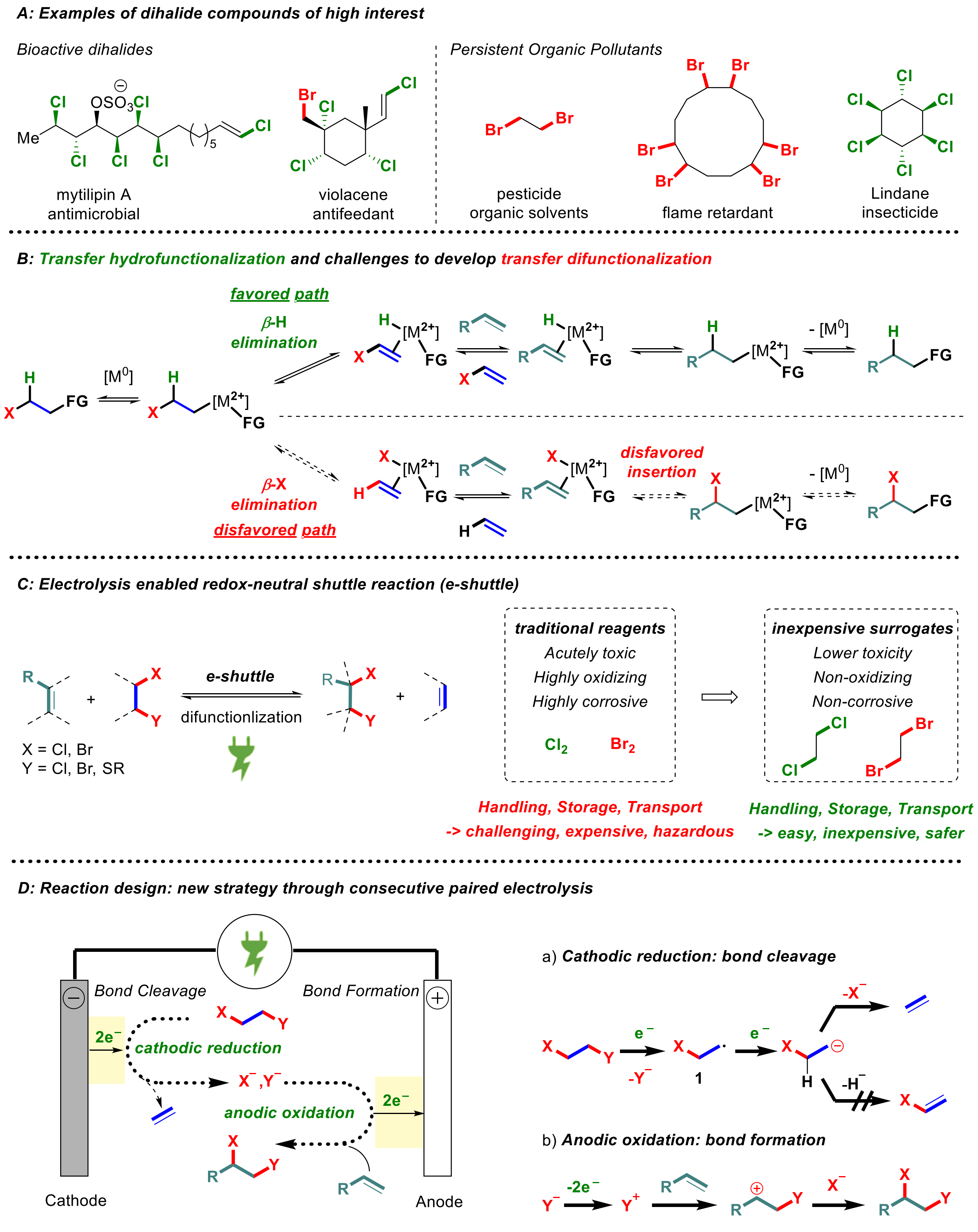


Fig. 1 │ Reaction design and challenges of transfer difunctionalization.

At the outset of our investigations, a transfer dibromination was uniformly optimized in an undivided cell using inexpensive isostatic graphite as the electrode material under constant current conditions at room temperature, a reaction setup easily accessible to non-specialized laboratories. 1,2-Dibromoethane (DBE) was selected as a formal Br_2 donor because it is an inexpensive reagent, produced on a bulk scale, that would solely release benign ethylene, a naturally occurring phytohormone, as a by-product. It is also notable that most commercial suppliers offer this reagent at an even lower price (per mol of Br_2-equivalents) than Br_2 itself, presumably reflecting the challenges and costs inherent to transporting and storing toxic and volatile Br_2[28]. Optimal results were obtained with 5 equiv. of 1,2-dibromoethane as the Br_2 donor, 1 vol% HFIP as the key additive[29], and 2 equiv. of Et_4NBF_4 as electrolyte, providing the targeted 1,2-dibromide **2** in 84% NMR yield when 3 F of electricity with respect to 1-dodecene was applied (Fig. 2). As indicated by cyclic voltammetry (CV) studies, the HFIP additive plays a key role in facilitating the reduction of the DBE donor and suppressing the undesired and unproductive reductive oligo/polymerization of alkene acceptors at the cathode (see Fig. 2A and Supplementary Fig. 5 and 6 for more details). It is noteworthy, that the supporting electrolyte can be easily crystallized from the reaction mixture to be recycled.

Using this protocol, a broad range of unactivated terminal alkenes (**2**−**11**) were readily converted to the corresponding dibromide product in good to excellent yields, in which a large variety of functional groups such as amide (**3**), ester (**4**), free carboxylic acid (**5**), primary alcohol (**6**), tosyl (**7**) and bromide (**8**) were well tolerated. Activated alkenes, such as styrene (**12**–**15**) and vinyl silane (**16** and **17**), proved to be suitable substrates as well, albeit giving slightly lower yields. While hexa-1,5-diene underwent two-fold 1,2-dibromination to yield the tetra brominated product **18** in decent yield, selective mono 1,2-dibromination was observed for several other unconjugated dienes (**19** and **20**). To demonstrate the scalability and robustness of this *e*-shuttle process, the transfer bromination of 1-dodecene was readily scaled-up to a 250 mL beaker cell from a 10 mL reaction vial to give 7.58 g of product **2** under otherwise identical reaction conditions (Fig. 2C).

Taking advantage of the reversible elimination of a ─SR group[30], we could next also develop a transfer bromothiolation of alkenes to make 1,2-bromothioether derivatives which are valuable synthetic intermediates usually accessed through multistep synthesis involving toxic and highly reactive R─SBr reagents[31,32]. Several terminal alkenes were successfully converted to the targeted bromothio-ether product, under otherwise identical conditions, taking 2-bromoethyl phenyl sulfide (10 equiv.) as the PhS─Br donor (Fig. 2D). The high regioselectivity obtained clearly highlights the possibility to transfer two different functionalities with high efficiency. The carboxylic acid (**22**) and ester (**23**) functional groups were well tolerated. Interestingly, an interrupted shuttle reaction took place when pent-4-en-1-ol and pent-4-enoic acid were employed as the substrates, delivering the cyclic ether (**24**) or lactone derivatives (**25**) via subsequent intramolecular nucleophilic attack, demonstrating the method´s potential for the development of new cascade reactions.

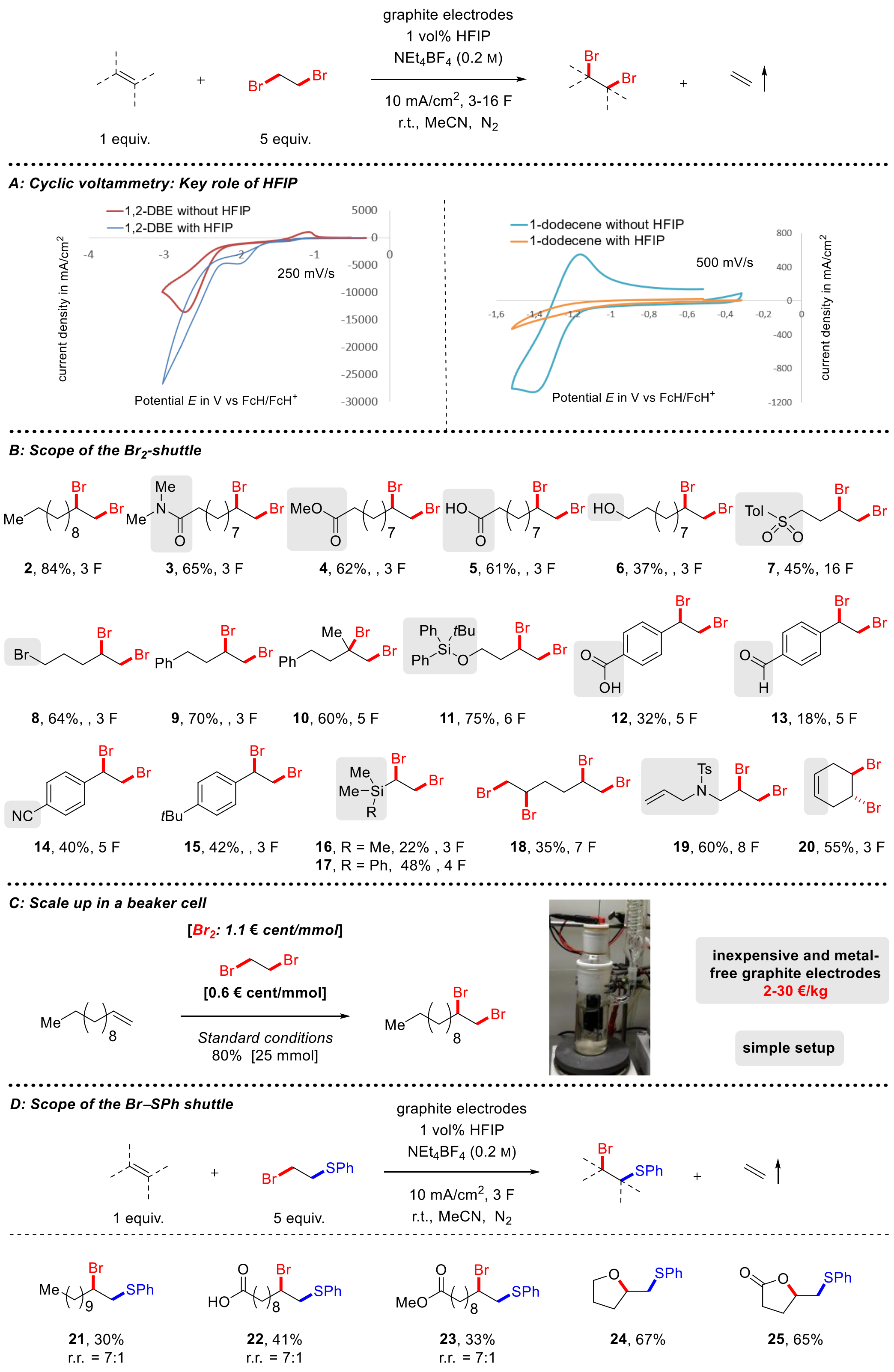


Fig. 2 │ Scope of the Br_2 and Br–SPh-shuttle reactions. CV studies: A 5 mM solution of 1,2-DBE and 1-dodecene in MeCN using NEt_4BF_4 (0.2M) at a graphite electrode with and without 1 vol% HFIP as the additive.

In order to further demonstrate the modularity of this conceptually new approach to reversible transfer reactions, we next developed a transfer dichlorination reaction (Fig. 3). 1,2-Dichloroethane (DCE) was selected as the donor, because it is an inexpensive bulk chemical (20 million ton/year), which is produced as a central intermediate in polyvinylchloride (PVC) production using the excess of Cl_2 gas generated during the Chlor-alkali electrolysis process[33]. The desired dichloride **28** was obtained in 39% yield when 5 mol% of a Mn(II) salt (e.g., $MnCl_2 \cdot 4H_2O$) was introduced as a mediator[23] using an otherwise identical electrochemical setup to the dibromination protocol. The yield was further increased to 70% when DCE (ca. 125 equiv.) was used as the solvent[34]. While this procedure was efficient for a wide set of terminal alkenes (**28**–**34**, Fig. 3B), it failed for more challenging 1,1,2-trisubstituted alkene **26** (Fig. 3A), a feature largely attributed to the undesired 1,2-dechlorinative decomposition of the product **27** and alkene oligomerization of the starting material via cathodic reduction. We reasoned that these two challenges could be smoothly addressed by choosing a more suitable dichloride donor. Based on the known redox potentials of a large set of simple chlorinated compounds[35] , we hypothesized that polychlorinated C2-donors, which are more readily reduced, should lead to a more favorable reaction outcome. Experimentally, an excellent correlation between the redox potentials of a series of donors was indeed observed, leading to the identification of 1,1,1,2-tetrachloroethane as the reagent of choice, affording the desired dichloride product **27** in 90% NMR yield (Fig. 3A). Using this procedure, a series of mono-substituted, di-substituted and tri-substituted alkenes participated smoothly in the 1,2-transfer dichlorination reaction, with free alcohol (**29**, **35**, and **37**), ester (**30**), imide (**32**), phosphonate (**33**), sulfone (**34**), internal alkyne (**37**), and Ts and Boc protected amine moieties (**38** and **39**) well tolerated. Various styrene-derived alkenes were converted to the corresponding 1,2-dichlorides in good to excellent yield (**42–52**), leaving the Br, Cl, CN, CF_3, CHO, and COOH functional groups untouched. Indene was diastereoselectively transformed into *trans*-1,2-dichloride **50** (d.r. > 19:1). Interestingly, both (*E*)- and (*Z*)-1-phenylpropene were converted to the *anti*-dichloride **51** in similarly high diastereoselectivity. The 1,2-dichloride compound **52**, bearing a reactive benzylic tertiary C─Cl bond, was prepared in good yield from *α*–methylstyrene. Several other activated alkenes, such as the silyl and ester attached alkenes, also proved to be viable substrates (**53–56**), in particular, methyl cinnamate was converted to the 1,2-dichloride **56** in an excellent d.r. ratio (> 19:1). To our delight, preliminary experiments show that this protocol can be readily extended to the 1,2-chlorothiolation transfer reaction using the commercially available 2-chloroethyl phenyl sulfide (10 equiv.) as the donor (Fig. 3C).

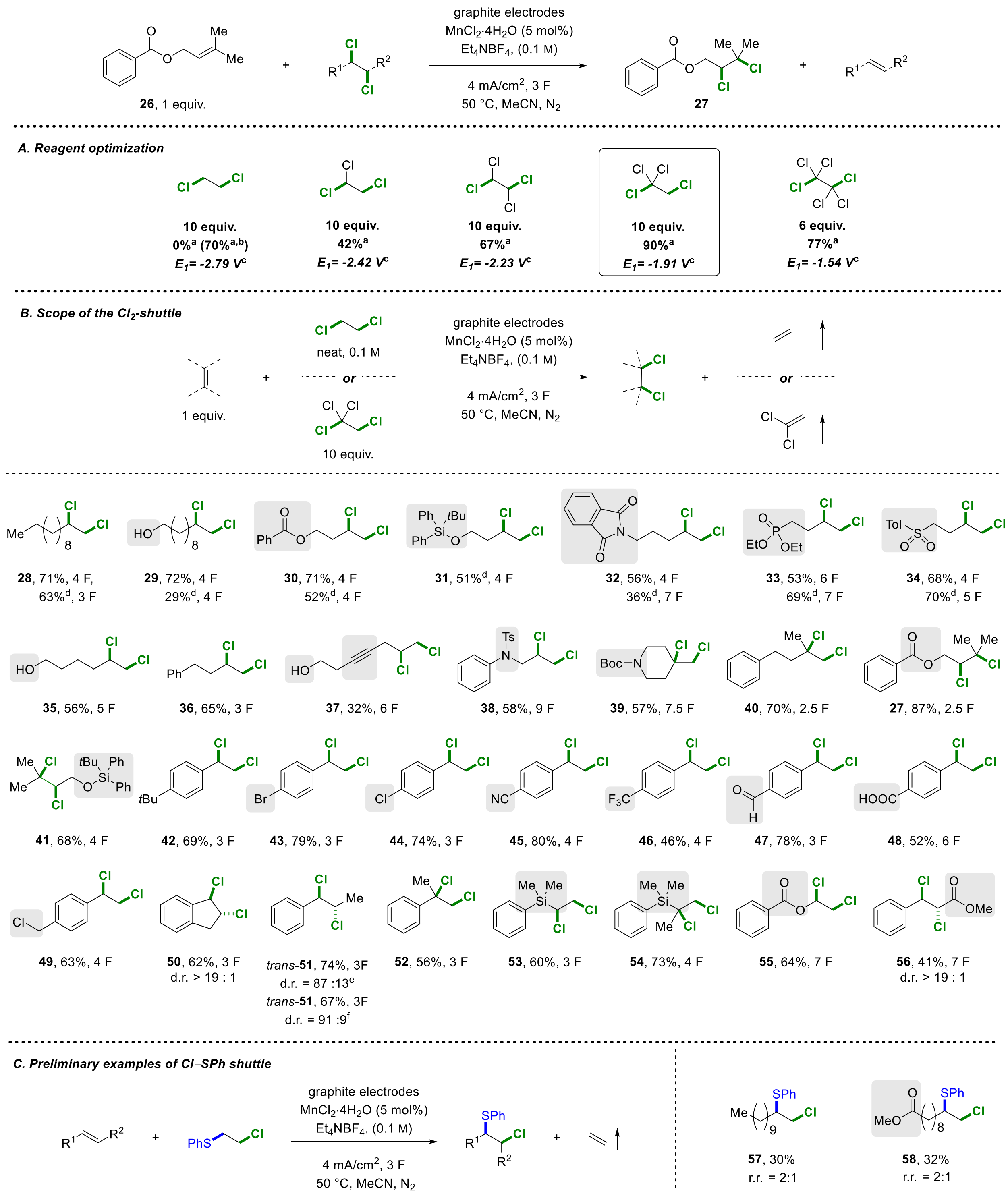
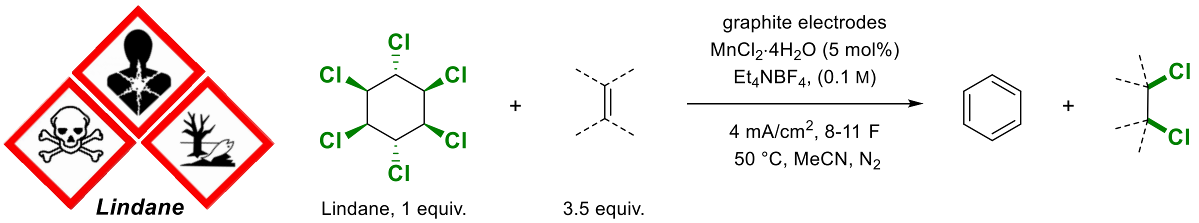


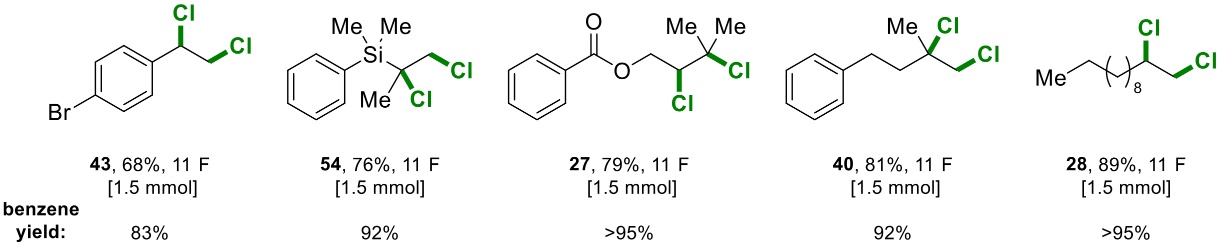
Fig. 3 | Scope of the Cl_2 and Cl−SPh-shuttle reactions. a: NMR yield. b: Neat DCE (0.1 M) as the donor, 1-dodecene (1 equiv.) as the acceptor. c: Redox potential (V vs SCE) measured for the first reduction peak at 0.2 Vs^{-1}, polychlororethanes (2 mM) in DMF + 0.1 M $(C_3H_7)_4NBF_4$ at a glassy carbon electrode acc. to lit.[35] d: Neat DCE (0.1 M) as the donor. e: (*E*)-prop-1-en-1-ylbenzene as the acceptor. f: (*Z*)-prop-1-en-1-ylbenzene as the acceptor.

Lindane, which was once widely used as an effective insecticide in crop protection, is classified as a persistent organic pollutant due to its high toxicity and high persistency in the environment[36,37]. We thus questioned whether this waste material, which, among other chemical and biological approaches,[36] can only be inefficiently degraded through normal electrochemical recycling methods[38,39,40], could instead be repurposed as an efficient Cl_2 donor in a synthetically useful transfer dichlorination (Fig. 4A). Indeed, lindane served, through three successive *retro*-dichlorination events, as an excellent donor in this reaction generating the desired dichlorinated products alongside benzene, the fully dechlorinated by-product of lindane. We were able to show the broad applicability of this reaction by performing the reaction with five illustrative examples in excellent yields up to 93% (with respect to 3 equiv. of alkene at >95% GC yield of benzene, Fig. 4B), as well as by scaling the reaction to 75 mmol of alkene (Fig. 4C). The exceptional functional group tolerance of our *e*-shuttle strategy made us question whether we could directly use lindane-contaminated soils as reagents for our transfer dichlorination reaction (Fig. 4D). To mimic the composition of soils contaminated by high concentration of hexachlorocyclohexane (HCH), which is mainly caused by leachates of improper disposal at landfilling or dump sites[36], three soil samples from different locations near our university campus, i.e., roadside, flower field, and farmland, were collected and homogeneously mixed with commercially available lindane. Remarkably, the 50 w% lindane contaminated soil could be used directly in the reaction without any pre-extraction or filtration, delivering both the benzene and dichloride product in excellent yields, a result comparable to the experiments using pure lindane (Fig. 4D). This result shows that our degradation process is compatible with the biological and mineral impurities present in three different soil types. A much lower lindane-soil ratio of 1 w%, where lindane was extracted with the reaction solvent prior to the degradation, also afforded good yields for both benzene (76%) and dichloride (76%). Collectively, these results show that *e*-shuttle provides a powerful new avenue to not only recycle toxic wastes, but also to valorize them through coupling with a synthetically relevant reaction. These results further provide a conceptual blueprint for the development of ideal shuttle reactions, in which the synthetically relevant functionalization of a substrate is directly coupled with the recycling of a persistent environmental pollutant.

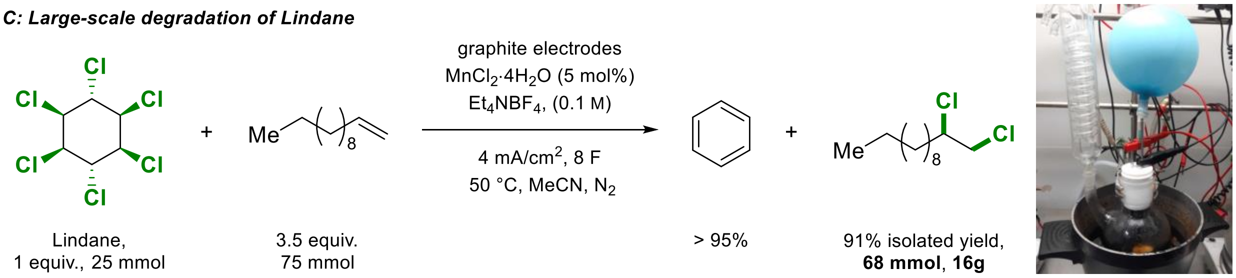
A: Persistent polychlorinated waste degradation



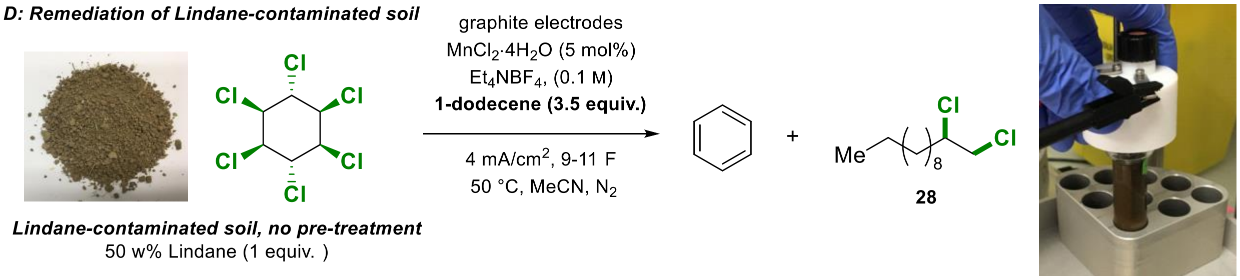
B: Scope for Lindane waste degradation



C: Large-scale degradation of Lindane



D: Remediation of Lindane-contaminated soil



Entry	Soil sample	benzene yield	**28**, isolated yield
1	Roadside soil, 50 w% Lindane	>95%	84%
2	Flower field soil, 50 w% Lindane	>95%	84%
3	Farmland soil, 50 w% Lindane	92%	83%
4	Farmland soil, 1 w% Lindane[a]	76%	76%
5	Pure Lindane	>95%	89%

Fig. 4 | Application of *e*-shuttle reactions. a: Lindane was extracted by MeCN before degradation.

Summary

In conclusion, we have reported a scalable *e*-shuttle strategy to unlock previously elusive transfer difunctionalization reactions. Using an easily accessible electrochemical setup involving consecutive paired electrolysis in a domino reduction-oxidation cascade, we have been able to take advantage of single electron transfer processes to develop four distinct, synthetically relevant transfer reactions using this unified strategy. The utility of the reaction's reversibility is demonstrated in the concomitant degradation of a waste molecule to functionalize simple feedstocks. In a broader context, we believe that these results lay the groundwork for the development of countless new reversible reactions which take advantage of the merger between shuttle reactions and electrochemistry.

Acknowledgements:

This project received funding from the European Research Council under the European Union's Horizon 2020 research and innovation program (Shuttle Cat, Project ID: 757608) and the ETH Zurich. X.D. acknowledges the Marie Skłodowska-Curie Action (HaloCat, Project ID: 886102) for a postdoctoral fellowship. J.L.R. is a recipient of a DFG fellowship through the Excellence Initiative by the Graduate School Materials Science in Mainz (GSC 266). We thank M. Zesiger, the NMR service, the Molecular and Biomolecular Analysis Service (MoBiAS) and ETH Zürich for technical assistance. Support by SusInnoScience (JGU Mainz) is highly acknowledged. We thank S. Makai for assistance with GC-MS headspace analysis and helpful discussions, and E. Falk for reproducing one of the Lindane-soil experiments. S. Makai, E. Falk, B. Bhawal, and T. Delcaillau are acknowledged for generous sharing of chemicals. We thank the whole Morandi group for critical proof-reading of this manuscript.

Author contributions: B.M. and X.D. conceived the project. X.D. and J.L.R. designed and performed all the synthetic studies. S.W. and B.M. supervised the research. All authors contributed to the writing and editing of the manuscript.

References:

1. Kirk, K. L. Persistent Polyhalogenated Compounds: Biochemistry, Toxicology, Medical Applications,and Associated Environmental Issues. in *Biochemistry of the Elemental Halogens and Inorganic Halides* 191–238 (Springer, 1991).
2. Häggblom, M. M. & Bossert, I. D. Halogenated organic compounds—a global perspective. in *Dehalogenation Microbial Processes and Environmental Applications* (eds. Häggblom, M. M.) 3–29 (Springer, 2004).
3. Patai, S. *The Chemistry of the Carbon-Halogen Bond: Part 1*, (John Wiley & Sons, Ltd, 1973).
4. Saikia, I., Borah, A. J. & Phukan, P. Use of bromine and bromo-organic compounds in organic synthesis. *Chem. Rev.* **116**, 6837–7042 (2016).
5. Denmark, S. E., Kuester, W. E. & Burk, M. T. Catalytic, asymmetric halofunctionalization of alkenes—a critical perspective. *Angew. Chem. Int. Ed.* **51**, 10938–10953 (2012).
6. Bhawal, B. N. & Morandi, B. Catalytic transfer functionalization through shuttle catalysis. *ACS Catal.* **6**, 7528–7535 (2016).
7. Fang, X., Yu, P. & Morandi, B. Catalytic reversible alkene-nitrile interconversion through controllable transfer hydrocyanation. *Science* **351**, 832–836 (2016).
8. Fang, X., Cacherat, B. & Morandi, B. CO-and HCl-free synthesis of acid chlorides from unsaturated hydrocarbons via shuttle catalysis. *Nat. Chem.* **9**, 1105–1109 (2017).
9. Murphy, S. K., Park, J.-W., Cruz, F. A. & Dong, V. M. Rh-catalyzed C─C bond cleavage by transfer hydroformylation. *Science* **347**, 56–60 (2015).
10. Petrone, D. A., Franzoni, I., Ye, J., Rodriguez, J. F., Poblador-Bahamonde, A. I. & Lautens, M. Palladium-catalyzed hydrohalogenation of 1, 6-enynes: hydrogen halide salts and alkyl halides as convenient HX Surrogates. *J. Am. Chem. Soc.* **139**, 3546–3557 (2017).
11. Chen, W., Walker, J. C. & Oestreich, M. Metal-free transfer hydroiodination of C–C multiple bonds. *J. Am. Chem. Soc.* **141**, 1135–1140 (2018).
12. Bhawal, B. N. & Morandi, B. Catalytic isofunctional reactions—expanding the repertoire of shuttle and metathesis reactions. *Angew. Chem. Int. Ed.* **58**, 10074–10103 (2019).
13. Beller, M., Seayad, J., Tillack, A., & Jiao, H. Catalytic Markovnikov and anti-Markovnikov functionalization of alkenes and alkynes: recent developments and trends. *Angew. Chem. Int. Ed.* **43**, 3368–3398 (2004).
14. Sakai, K., Sugimoto, K., Shigeizumi, S. & Kondo, K. A new selective dichlorination of C−C double bonds. *Tetrahedron lett.* **35**, 737–740 (1994).
15. Ho, M. L., Flynn, A. B. & Ogilvie, W. W. Single-isomer iodochlorination of alkynes and chlorination of alkenes using tetrabutylammonium iodide and dichloroethane. *J. Org. Chem.* **72**, 977–983 (2007).
16. Gribble, G. W. Naturally occurring organohalogen compounds. *Acc. Chem. Res.* **31**, 141–152 (1998).
17. Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, *5th Edition*. (John Wiley & Sons, 2009).
18. Cresswell, A. J., Eey, S. T.-C. & Denmark, S. E. Catalytic, stereoselective dihalogenation of alkenes: challenges and opportunities. *Angew. Chem. Int. Ed.* **54**, 15642–15682 (2015).
19. Yan, M., Kawamata, Y. & Baran, P. S. Synthetic organic electrochemical methods since 2000: on the verge of a renaissance. *Chem. Rev.* **117**, 13230–13319 (2017).
20. Siu, J. C., Fu, N. & Lin, S. Catalyzing electrosynthesis: a homogeneous electrocatalytic approach to reaction discovery. *Acc. Chem. Res.* **53**, 547–560 (2020).
21. Wiebe, A., Gieshoff, T., Möhle, S., Rodrigo, E., Zirbes, M. & Waldvogel, S. R. Electrifying organic synthesis. *Angew. Chem. Int. Ed.* **57**, 5594–5619 (2018).
22. Röckl, J. L., Pollok, D., Franke, R. & Waldvogel, S. R. A decade of electrochemical dehydrogenative C, C-coupling of aryls. *Acc. Chem. Res.* **53**, 45–61 (2020).
23. Fu, N., Sauer, G. S. & Lin, S. Electrocatalytic radical dichlorination of alkenes with nucleophilic chlorine sources. *J. Am. Chem. Soc.* **139**, 15548–15553 (2017).
24. Yuan, Y. et al. Electrochemical oxidative clean halogenation using HX/NaX with hydrogen evolution. *iScience* **12**, 293–303 (2019).

25. Pollok, D. & Waldvogel, S. R. Electro-organic synthesis–a 21st century technique. *Chem. Sci.* DOI: 10.1039/d0sc01848a (2020).
26. Hartmer, M. F. & Waldvogel, S. R. Electroorganic synthesis of nitriles via a halogen-free domino oxidation-reduction sequence*. Chem. Commun.* **51**, 16346–16348, (2015).
27. Casanova, J. & Eberson, L. Electrochemistry of the Carbon–Halogen Bond. in *The Chemistry of The Carbon-Halogen Bond* (eds. Patai, S.) 979–1047 (John Wiley & Sons, Ltd., 1973).
28. Hill, D. M. *Safety review of bromine-based electrolytes for energy storage applications*, Report 1 http://energystorageicl.com/wp-content/uploads/2018/04/DNV-GL-Safety-Review-of-Bromine-Based-Electrolytes-for-Energy-Storage-Applications.pdf (2018).
29. Schulz, L. & Waldvogel, S. R. Solvent control in electro-organic synthesis*, Synlett* **30**, 275–286 (2019).
30. Denmark, S. E., Collins, W. R. & Cullen, M. D. Observation of direct sulfenium and selenenium group transfer from thiiranium and seleniranium ions to alkenes. *J. Am. Chem. Soc.* **131**, 3490–3492 (2009).
31. Schneider, E. Darstellung und Eigenschaften von Alkylschwefelhalogeniden, *Chem. Ber.* **84**, 911–916 (1951).
32. Drabowicz, J., Kiełbasiński, P. & Mikołajczyk, M. Synthesis of sulphenyl halides and sulphenamides. in *Sulfenic Acids and Derivatives* (eds. Patai, S.) 221–292 (John Wiley & Sons, Ltd., 1990).
33. Hoffmann, C., Weigert, J., Esche, E. & Repke, J. U. Towards demand-side management of the chlor-alkali electrolysis: Dynamic, pressure-driven modeling and model validation of the 1, 2-dichloroethane synthesis. *Chem. Eng. Sci.* **214**, 115358 (2020).
34. Liang, Y., Lin, F., Adeli, Y., Jin, R. & Jiao, N. Efficient electrocatalysis for the preparation of (hetero)aryl chlorides and vinyl chlorides with 1,2-dichloroethane. *Angew. Chem. Int. Ed.* **58**, 4566–4570 (2019).
35. Huang, B., Isse, A. A., Durante, C., Wie, C. & Gennaro, A. Electrocatalytic properties of transition metals toward dichlorination of polychloroethanes. *Electrochim. Acta* **70**, 50–61 (2012).
36. Bhatt, P., Kumar, M. S. & Chakrabarti, T. Fate and degradation of POP-hexachlorocyclohexane. *Crit. Rev. Environ. Sci. Technol.* **39**, 655–695 (2009).
37. Walker, K., Vallero, D. A. & Lewis, R. G. Factors influencing the distribution of lindane and other hexachlorocyclohexanes in the environment. *Environ. Sci. Technol.* **33**, 4373–4378 (1999).
38. Rondinini, S. & Vertova, A. Electroreduction of Halogenated Organic Compounds. in *Electrochemistry for the Environment* (eds. Comninellis, C. & Chen, G.) 279–306 (Springer, 2010).
39. Merz, J. P., Gamoke, B. C., Foley, M. P., Raghavachari, K. & Peters, D. G. Electrochemical reduction of (1*R*,2*r*,3*S*,4*R*,5*r*,6*S*)-hexachlorocyclohexane (Lindane) at carbon cathodes in dimethylformamide. *J. Electroanal. Chem.* **660**, 121–126 (2011).
40. Martin, E. T., McGuire, C. M., Mubarak, M. S. & Peters, D. G. Electroreductive remediation of halogenated environmental pollutants. *Chem. Rev.* **116**, 15198–15234 (2016).