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Electroreduction of Organic Compounds 32.[1] Indirect Electrodehalogenation of Chloroarenes in Methanol Mediated by Nickel Complexes

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Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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The indirect electroreduction of chlorinated benzenes and dibenzofurans in methanol has been investigated. (2,2′-Bipyridyl)nickel(II) chloride (**1**) and (1,4,8,11-tetraazacyclotetradecane)nickel(II) chloride (**2**) were used as mediators for the electron transfer. The electrolyses were carried out potentiostatically at −1.4 V vs. Ag/AgBr in a divided batch cell. Indirect reduction of more highly chlorinated benzenes lead to chlorobenzene as the main product. In case of the chlorodibenzofurans, reduction to unsubstituted dibenzofuran was achieved. Much higher selectivity in the mediated electroreduction as compared with the direct cathodic reduction is observed. In particular the formation of hydrogenated products is completely suppressed.

Over recent decades the problematic nature of organohalogen compounds has become obvious. These compounds are used in many commercial products because of their low costs and widespread applicability, e.g. as technical solvents, transformer oils or for wood-protection. Furthermore, they are unavoidably formed as by-products during industrial processes and waste incineration.[2] However, polyhalogenated compounds have proved to be especially dangerous xenobiotics. They are both resistant to biodegradation and – in certain cases extremely – toxic. There is, therefore, a demand for improved methods of degradation and decontamination because existing methods, such as high-temperature incineration, have significant disadvantages, e.g. the risk of uncontrolled formation and emission of chlorinated dioxins.[3]

In principle, electroreduction of halogenated compounds is possible. It works smoothly at ambient temperature and has frequently been described in the literature.[3,4] However, DMF or DMSO are commonly used as solvents and mercury as cathode material, which are less suitable for practical purposes. The target of our investigations presented here was, therefore, to develop a useful procedure which might offer the possibility of technical application.

Results and discussion

In our experiments we used technical grade methanol as the solvent. Water is unfavourable because of the low solubility of organic substances. In earlier publications we have described the cathodic dechlorination of several classes of compound such as chloro-benzenes,[5] -biphenyls,[5] -naphthalenes,[6] -phenols,[7] -anisoles,[7] -dibenzofurans[8] and -dioxins[8] as well as oligochlorocycloalkanes[9] by direct electrolysis. The reductions were performed at a lead cathode. The disadvantage of these electroreductions is their lack of selectivity. Furthermore in some cases the reaction leads to hydrogenated products, which is unfavourable because these compounds are toxic to micro-organisms.[10] In addition, the use of lead – a very toxic metal – as the cathode material is not the best choice. Moreover, Kulikov *et al.*[11] described the corrosive decomposition of a lead cathode and formation of unidentified organometallic products.

To overcome these difficulties we examined the indirect electrolysis method. We chose the nickel complexes **1** and **2** as mediators (Scheme 1), which have been introduced by Pletcher *et al.* (**2**)[12] and widely applied by Périchon *et al.* (**1**)[13] and Duñach *et al.* (**2**).[14] We began our investigations with the dichlorobenzenes as model compounds and for the present used a batch cell without recycling of the electrolyte and mediator.

The mediator **1** is probably first transformed into another Ni^{II} complex **1a** by excess 2,2′-bipyridyl, which is added to the electrolyte and subsequently reduced to a Ni^{0} complex **1b** at the cathode. The redox cycle should thus work as shown in Fig. 1.

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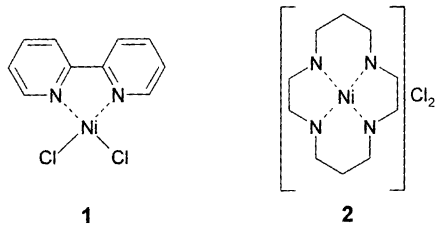


Scheme 1.

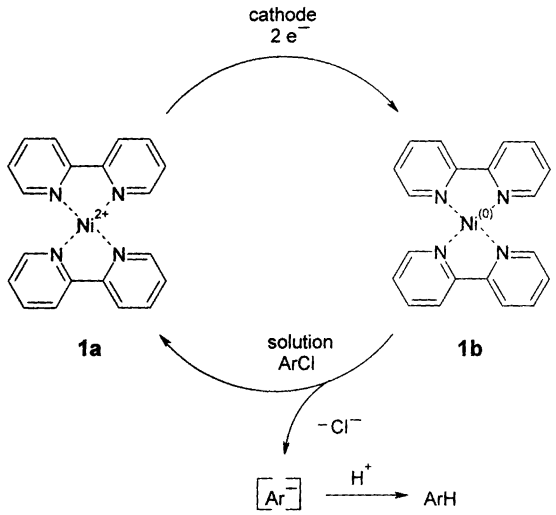


Fig. 1. Electrocatalytic cycle for the reduction of ArCl in the presence of **1**.

The two-electron reduction step of **1** ($Ni^{II} \rightarrow Ni^{0}$) at −0.92 V vs. Ag/AgBr (in methanol) is reversible as shown by cyclic voltammetry. It is, however, not significantly influenced by addition of dichlorobenzene although electrodehalogenation can be achieved on a preparative scale by use of **1** (see below).

The mediator cycle of **2**, on the other hand, involves a Ni^{I} complex as the active species according to the literature.[15] In this case we were able to confirm the electrocatalytic mechanism by cyclic voltammetry. The reversible one-electron reduction step of **2** becomes irreversible upon addition of dichlorobenzene and the peak current is significantly increased as expected. The effect is most pronounced for 1,2-dichlorobenzene whereas 1,4-dichlorobenzene exhibits virtually no peak current enhancement (cf. Fig. 2).

The nickel(II) complexes **1** and **2** proved to be suitable mediators for the preparative electrochemical dehalogenation of dichlorobenzenes in methanolic media. Figure 3 demonstrates the reduction of an equimolar mixture of 1,2-, 1,3- and 1,4-dichlorobenzene with **1** and **2**. With both mediators the electrolysis leads to chlorobenzene (**3**) as the main product. The efficiencies of **1** and **2** are, however, considerably different. Evidently **2** is more suitable for the electroreduction of 1,2-dichloro- and 1,3-dichloro-benzene (cf. Fig. 3 but note the different charge scales). The dehalogenation of 1,4-dichlorobenzene is slow with both **1** and **2**. However, on prolonged electrolysis at −1.4 V vs. Ag/AgBr this isomer is also transformed into **3**, whereas no electroreduction of any of the isomers occurs at this potential in methanol in the absence of a mediator.

Remarkably, 1,3-dichlorobenzene is faster reduced than 1,2-dichlorobenzene if **1** is used, but the reverse is true for **2**, which very smoothly converts 1,2-dichlorobenzene into **3** (cf. Fig. 3). This observation is not easy to explain. It is possible that the steric requirements for suitable coordination of the two isomers in the activated complex are different for **1** and **2**, perhaps because of their different flexibility.

When the reduction was performed in non-protic solvents such as *N*-methylpyrrolidone or DMF instead of methanol virtually no substitution of chlorine by

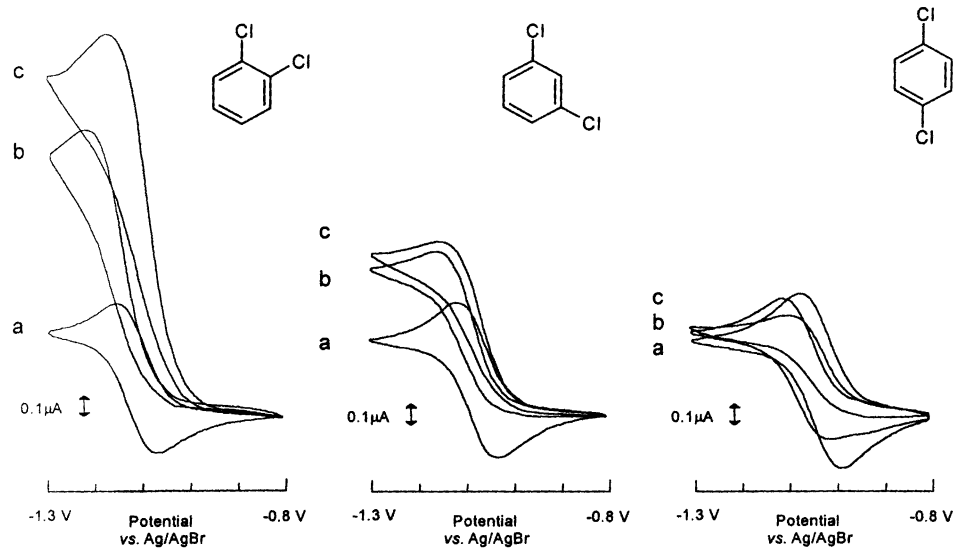
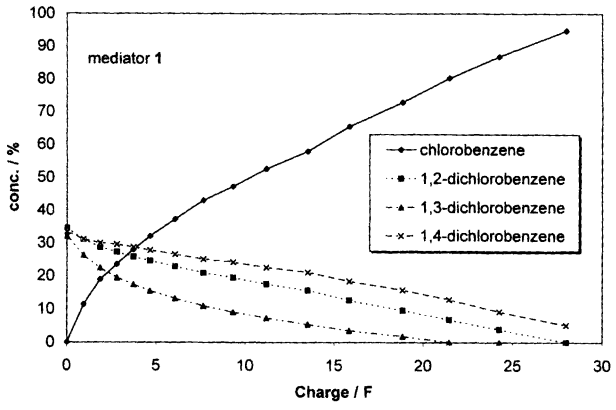


Fig. 2. Cyclovoltammetric behavior of **2** (0.03 mmol dm^{-3} TEAB in methanol) without (a) and in the presence of 0.1 mmol dm^{-3} (b) and 1.0 mmol dm^{-3} (c) dichlorobenzene.



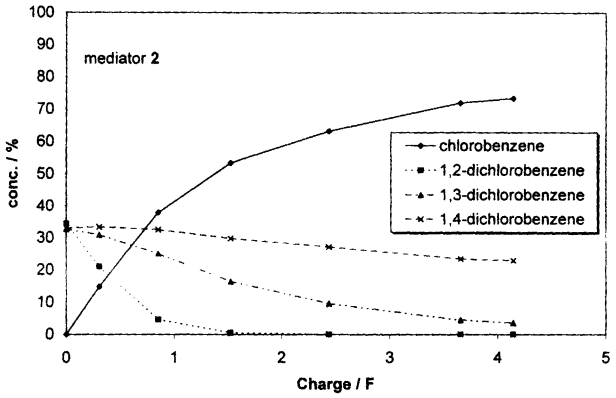
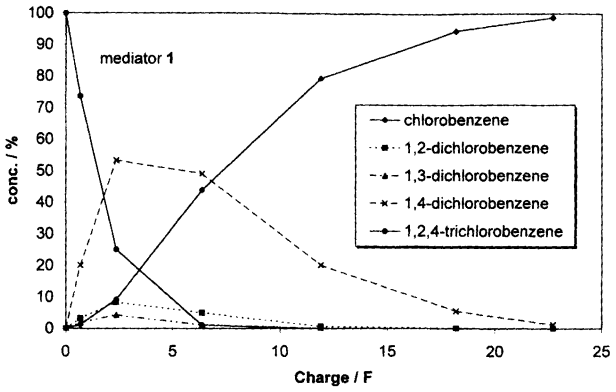


Fig. 3. Comparison of the electrochemical reduction of equimolar mixtures of 1,2-, 1,3- and 1,4-dichlorobenzene with $Ni(bipy)Cl_2$ (**1**), top, and $Ni(cyclam)Cl_2$ (**2**), bottom, as mediators, at −1.4 V vs. Ag/AgBr.



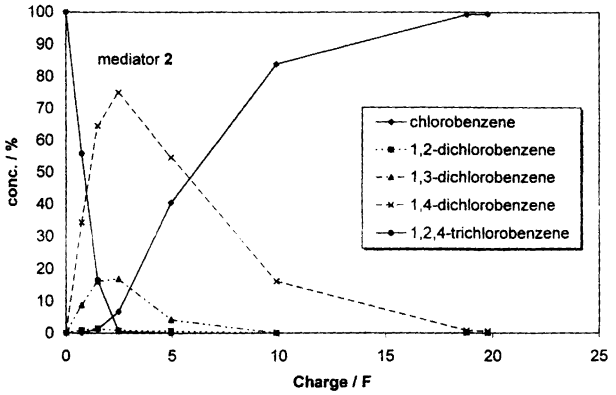
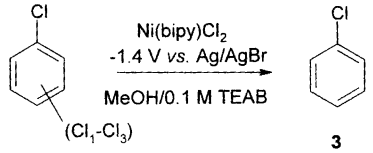


Fig. 4. Comparison of the electrochemical reduction of 1,2,4-trichlorobenzene with $Ni(bipy)Cl_2$ (**1**), top, and $Ni(cyclam)Cl_2$ (**2**), bottom, as mediators, at −1.4 V vs. Ag/AgBr.

hydrogen took place. Instead, in accordance with the literature[16] a coupling reaction was favoured. In methanol any anionic intermediates are protonated and carbon–carbon coupling occurs only as a negligible side reaction with yields of less than 1%.

Next we took a look on the electroreduction of 1,2,4-trichlorobenzene (Scheme 2).[17] With both mediators (Fig. 4) 1,4-dichlorobenzene was formed primarily, which underwent further reduction to chlorobenzene (**3**) on prolonged electrolysis.



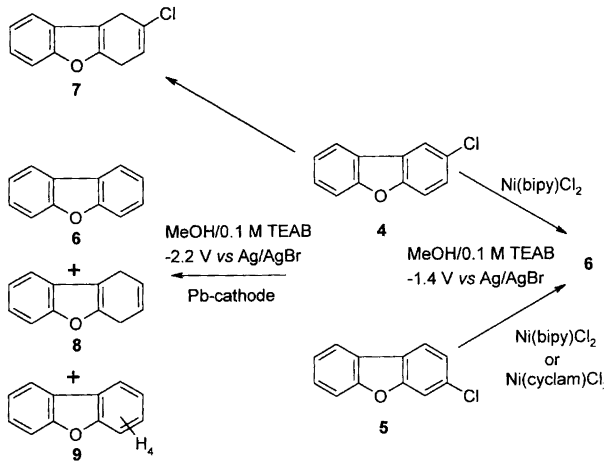
Scheme 2.

The mediated electrochemical reduction procedure seems to be more efficient, compared with conventional chemical methods reported in the literature. Stiles[18] used a nickel complex for catalytic dehalogenation of chlorinated benzenes with sodium borohydride and hydrazine as reducing agents instead of electrolysis. No complete reduction to chlorobenzene (**3**) was achieved. For 1,2-dichlorobenzene a conversion of only 73% was reached and the other congeners yielded only traces of **3**. Lassova *et al.*[19] described a Pd complex which was able to degrade polychlorinated benzenes to monochlorobenzene. In this case an 18% conversion of 1,3-dichlorobenzene to **3** – as best example – was observed after 200 h of reaction time.

After the efficacy of the mediators **1** and **2** had been proved for chlorinated benzenes we extended our investigations to the dehalogenation of 2- and 3-chlorodibenzofuran (**4**) and (**5**), which is more interesting and important from the environmental point of view mentioned in the introduction. Earlier experiments had shown[1] that the direct reductive dehalogenation of **4** and **5** at lead cathodes competes with a Birch-type hydrogenation. Even for 2-chlorodibenzofuran (**4**), which is not easy to reduce, hydrogenation was favoured over dehalogenation and 2-chloro-1,4-dihydrodibenzofuran (**7**) was mainly formed, with only a small amount of the desired dibenzofuran (**6**), i.e. the direct reduction is unspecific and results in a product mixture.

Using the mediator **1** we could avoid all side reactions and were able to obtain selectively dibenzofuran (**6**) from both **4** and **5** with no hydrogenated products. Mediator **2** was able to reduce only 3-chlorodibenzofuran (**5**); no reaction took place between **2** and **4**. The reason for this observation seems to be that **4** is, in general, more

difficult to reduce ($E_{red} = -1.61$ V vs. Ag/AgBr), compared with **5** ($E_{red} = -1.49$ V vs. Ag/AgBr). However, this difficulty is obviously overcome by a specific, e.g. steric, effect associated with mediator **1**.



Scheme 3.

For practical reasons the working potential during the electrolyses with both mediators was set at -1.4 V vs. Ag/AgBr in order to achieve reasonable currents and, on the other hand, to remain below the decomposition potential of methanol (-1.5 vs. Ag/AgBr).

In Table 1 the product distributions of the direct and the indirect electroreduction of 2- and 3-chlorodibenzofuran (**4**) and (**5**) are compared.

Conclusions. The nickel complexes **1** and **2** have proved to be suitable mediators for the electrochemical dehalogenation of chlorinated arenes. The mediated electrolysis exhibits substantial advantages over direct electrolysis. The cathodic potentials and thus the necessary cell voltage are lower. The selectivity is improved. All chlorinated benzenes studied yield virtually a single product, monochlorobenzene (**3**). Both 2-chloro- (**4**) and 3-chloro-dibenzofuran (**5**) are cleanly dehalogenated with **1** as mediator. Mediator **2** is also suitable for the reduction of **5**. No hydrogenation of the aromatic ring occurs, which is an important result with respect to further degradation of the electrolysis products by micro-organisms[10,20] in a two-step route for the decontamination of chlorinated xenobiotics.

Experimental

General. Melting points are corrected (Electrothermal). Infrared spectra were recorded on a ATI-Mattson Genesis Series instrument. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM 400 spectrometer using tetramethylsilane as an internal standard. Electrochemical measurements were recorded with a Metrohm polarography stand VA 663 connected to a Polarecord 626. Gas chromatography (GC) was performed on a Fisons GC 8000 equipped with a fused silica gel column (30 m, DB-1701). GC–MS coupling spectra were recorded on a VG/70–250S from VG Analytical. Methanol was of technical grade and used as received from Merck, Darmstadt. 2,2′-Bipyridyl (bipy) was purchased from Fluka and 1,4,8,11-tetraazacyclotetradecane (cyclam) from Aldrich.

Syntheses. The Ni complexes **1**[21] and **2**[22] were prepared by mixing a solution of the free ligand (bipy or cyclam) in ethanol with an equimolar solution of $NiCl_2 \cdot 6H_2O$ in hot ethanol. The mixtures were stirred for 1 h under reflux. In the case of **1** the solvent was distilled off and in the case of **2** violet crystals formed on cooling, which were filtered off, yielding 64%. 2-Chlorodibenzofuran (**4**) and 3-chlorodibenzofuran (**5**) were prepared as described earlier.[1]

Electrolysis. Electrolyses were carried out in a divided glass cell (2×100 ml). The compartements were separated by an anion-exchange membrane (12H02R-CT7, Reichelt, Chemietechnik Heidelberg, Germany). A graphite disk electrode (15 cm^2) served as cathode, a platinum net as counter electrode and a silver wire as reference electrode. The potential was controlled with a potentioscan POS 88 from Bank Elektronik, Göttingen, Germany.

General procedure. The cell was constructed and the cathodic compartment was filled with 100 ml methanol containing 0.1 M tetraethylammonium bromide (TEAB) as supporting electrolyte. The anolyte consisted of a 0.1 M TEAB solution in methanol or a 0.1 M aqueous NaOH solution. After addition of the substrate and the mediator to the catholyte, nitrogen was bubbled through the solution to avoid any oxidation of the reduced mediator by oxygen. In order to achieve sufficient turnover rates the potential was adjusted to -1.4 V vs.

Table 1. Comparison of the product distribution after direct[1] and mediated electrolyses of **4** and **5**.

Electrolysis conditions	2-Chlorodibenzofuran (**4**)					3-Chlorodibenzofuran (**5**)			
	4[a]	**6**	**7**	**8**	**9**	**5**[a]	**6**	**8**	**9**
Lit[1]	16	1	56	14	13	6	16	74	4
1	>99	—	—	—	—	2	97	—	—
2	–	>99	—	—	—	—	>99	—	—

[a]Recovered starting compound after electrolysis.

Ag/AgBr. The progress of the electrolysis was monitored by GC. For work-up the catholyte was poured into 100 ml water, acidified with 18% aqueous hydrochloric acid and extracted twice with pentane (2 × 150 ml). The organic layers were dried with magnesium sulfate. The proportions of benzene derivatives present were determined by GC after addition of a known amount of mesitylene as an internal standard. In the case of **4** and **5** the solvent was evaporated off *in vacuo* and the products were weighed. If the electrolyses were carried out with **1** as the mediator, double the amount of 2,2′-bipyridyl was added.

Electrolysis of a mixture of 1,2-, 1,3- and 1,4-dichlorobenzene in the presence of **1**. Starting products, 1,2-dichlorobenzene (99 mg, 0.67 mmol), 1,3-dichlorobenzene (99 mg, 0.67 mmol) and 1,4-dichlorobenzene (99 mg, 0.67 mmol); mediator, **1** (100 mg, 0.35 mmol) and 2,2′-bipyridyl (100 mg); coulombs consumed, 5760 A s (28.0 F mol^{-1}); current, 200–240 mA; current densities, 133–160 A m^{-2}; current efficiency, 6.7%; catholyte, methanol–0.1 M TEAB; anolyte, methanol–0.1 M TEAB; products (GC), **3** 96% (1.31 mmol), 1,4-dichlorobenzene 3% (0.04 mmol), and 1,2-dichlorobenzene 1% (0.01 mmol); chemical yield (GC), 67%.

Electrolysis of a mixture of 1,2-, 1,3- and 1,4-dichlorobenzene in the presence of **2**. Starting products, 1,2-dichlorobenzene (150 mg, 1.01 mmol), 1,3-dichlorobenzene (150 mg, 1.01 mmol) and 1,4-dichlorobenzene (150 mg, 1.01 mmol); mediator, **2** (51 mg, 0.15 mmol); coulombs consumed, 1224 A s (4.2 F mol^{-1}); current, 24–70 mA; current densities, 16–47 A m^{-2}; current efficiency, 47.0%; catholyte, methanol–0.1 M TEAB, anolyte, methanol–0.1 M TEAB; products (GC), **3** 73% (1.48 mmol), 1,4-dichlorobenzene 23% (0.44 mmol), and 1,3-dichlorobenzene 4% (0.07 mmol); chemical yield (GC), 65%.

Electrolysis of 1,2,4-trichlorobenzene in the presence of **1**. Starting product, 1,2,4-trichlorobenzene (149 mg, 0.82 mmol); mediator, **1** (100 mg, 0.35 mmol) and 2,2′-bipyridyl (100 mg); coulombs consumed, 1800 A s (22.8 F mol^{-1}); current, 40–160 mA; current densities, 27–107 A m^{-2}; current efficiency, 17.6%; catholyte, methanol–0.1 M TEAB, anolyte, H_2O–0.1 M NaOH; products (GC), **3** 98% (0.45 mmol), 1,4-dichlorobenzene 1.3% (0.01 mmol); chemical yield (GC), 56%.

Electrolysis of 1,2,4-trichlorobenzene in the presence of **2**. Starting product, 1,2,4-trichlorobenzene (137 mg, 0.76 mmol); mediator, **2** (100 mg, 0.3 mmol); coulombs consumed, 1440 A s (19.6 F mol^{-1}); current, 40–140 mA; current densities, 27–93 A m^{-2}; current efficiency, 20.3%; catholyte, methanol–0.1 M TEAB, anolyte, methanol–0.1 M TEAB; products (GC), **3** 99% (0.35 mmol), 1,4-dichlorobenzene 0.8% (0.01 mmol); chemical yield (GC), 46%.

Electrolysis of 2-chlorodibenzofuran (**4**) *in the presence of* **1**. Starting product, **4** (200 mg, 1.0 mmol); mediator, **1** (100 mg, 0.35 mmol) and 2,2′-bipyridyl (100 mg); coulombs consumed, 5400 A s (56.0 F mol^{-1}); current, 55–380 mA; current densities, 37–253 A m^{-2}; current efficiency, 3.6%; catholyte, methanol–0.1 M TEAB, anolyte, H_2O–0.1 M NaOH; products (GC), **6** >99% (0.79 mmol); chemical yield, 133 mg (80%).

Dibenzofuran (**6**): IR (KBr): 3047, 2925, 2854, 1597, 1472, 1445, 1322, 1241, 1198, 1153, 1100, 928, 848, 841, 747, 722, 423 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (ddd, $J_{H2,H1}$ 7.7 Hz, $J_{H2,H3}$ 7.3 Hz, $J_{H2,H4}$ 1.0 Hz, H2), 7.46 (ddd, $J_{H3,H4}$ 8.3 Hz, $J_{H3,H2}$ 7.3 Hz, $J_{H3,H1}$ 1.3 Hz, H3), 7.58 (ddd, $J_{H4,H3}$ 8.3 Hz, $J_{H4,H2}$ 1.0 Hz, $J_{H4,H1}$ 0.6 Hz, H4), 7.96 (ddd, $J_{H1,H2}$ 7.7 Hz, $J_{H1,H3}$ 1.3 Hz, $J_{H1,H4}$ 0.6 Hz, H1). ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.2 (C-4), 120.2 (C-1), 122.3 (C-2), 123.8 (C-9a/9b), 126.7 (C-3), 155.7 (C-4a/C-5a). MS *m/z* (rel. int.): 170 (1), 169 (12), 168 (100) [M^+], 141 (1), 140 (8), 139 (34), 138 (2), 137 (1) 114 (6), 113 (6), 89 (6), 87 (4), 84 (10), 75 (2), 69 (4), 63 (6).

Electrolysis of 2-chlorodibenzofuran (**4**) *in the presence of* **2**. Under the same conditions as described above, except using mediator **2** (100 mg, 0.15 mmol) instead of **1**, no reaction occurred. Only **4** was recovered.

Electrolysis of 3-chlorodibenzofuran (**5**) *in the presence of* **1**. Starting product, **5** (203 mg, 1.0 mmol); mediator, **1** (100 mg, 0.35 mmol) and 2,2′-bipyridyl (100 mg); coulombs consumed, 1800 A s (18.7 F mol^{-1}); current, 20–250 mA; current densities, 13–167 A m^{-2}; current efficiency, 10.7%; catholyte, methanol–0.1 M TEAB, anolyte, methanol–0.1 M TEAB; products (GC), **6** 97.7% (0.96 mmol), **5** 2.3% (0.02 mmol); chemical yield, 167 mg (99%).

Electrolysis of 3-chlorodibenzofuran (**5**) *in the presence of* **2**. Starting product, **5** (303 mg, 1.5 mmol); mediator, **2** (33 mg, 0.1 mmol); coulombs consumed, 1728 A s (11.9 F mol^{-1}); current, 36–150 mA; current densities, 24–100 A m^{-2}; current efficiency, 16.8%; catholyte, methanol–0.1 M TEAB, anolyte, H_2O–0.1 M NaOH; products (GC), **6** >99% (1.35 mmol); chemical yield, 227 mg (90%).

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