

THE DIRECT ELECTROCHEMICAL SYNTHESIS OF 2,2'-BIPYRIDINE ADDUCTS OF ORGANOMAGNESIUM HALIDES, AND OF SALTS OF ORGANODIHALOGENOMAGNESIUM(II) ANIONS

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Summary

The electrochemical oxidation of magnesium into acetonitrile solutions containing alkyl or aryl halides (RX) and 2,2'-bipyridine (bipy) yields the neutral adducts $\text{RMgX} \cdot \text{bipy}$. With α, ω -dihalides $\text{XR}'\text{X}$, the products are the corresponding $\text{R}'\text{Mg}_2\text{X}_2 \cdot 2\text{bipy}$ compounds. The preparation proceeds equally well with either aryl or alkyl compounds, and with chlorides, bromides, or iodides, but the resultant adducts show none of the typical reactions of Grignard reagents other than alkane elimination with mineral acids. With solutions containing RX and $\text{R}'_4\text{NX}$, the products of electrochemical oxidation are the salts $\text{R}'_4\text{N}[\text{RMgX}_2 \cdot \text{CH}_3\text{CN}]$, which also lack typical Grignard reagent chemistry.

Introduction

A number of recent publications from this laboratory have reported the direct electrochemical synthesis of a variety of inorganic and organometallic compounds [1]. The method is based on the one-step electrochemical oxidation of a metal anode into a non-aqueous solution of the ligand, or ligand precursor, and its advantages include the simplicity and cheapness of the apparatus, and high product yields. Of particular relevance to the present work are syntheses of the organometallic halides of a number of Main Group and transition element metals, where the products were conveniently stabilized in situ as adducts with neutral donors, or as the tetraalkylammonium salts of the corresponding anionic complexes [2–5].

We now report the direct electrochemical synthesis of neutral organometallic halides of magnesium, which were stabilized as the 2,2'-bipyridine adducts for convenience in isolation and characterization, and of salts of $\text{R}'\text{MgX}_2^-$ anions. The electrochemical method is equally well suited to the preparation of compounds of all three types for X = Cl, Br, or I, and can be used with alkyl, aryl, perfluoroalkyl, or perfluoroaryl halides, and alkyl or aryl dihalides. The products resist chemical

attack, so that the present work does nothing to extend the range of application of organomagnesium reagents in synthesis.

Experimental

General

Magnesium metal (M4N) was used as supplied, in the form of a rod (4.5 cm long, 1.5 cm diam.). Solvents were thoroughly dried and stored over sodium, and all experimental work was carried out in an atmosphere of dry nitrogen.

Analysis for magnesium was by atomic absorption spectrophotometry, and for halogen by Volhard titration. Spectroscopic techniques were as described in previous publications [2–5], except that mass spectra were run on a Finnegan 4000 GC/MS quadrupole instrument.

Electrochemical synthesis

As in previous work, the cell consisted of a 100 ml tall-form beaker closed with a tightly fitting rubber bung through which electrical leads and gas inlet and outlet tubes were introduced. The anode consisted of a magnesium rod attached to a platinum wire, while a second platinum wire formed the cathode. The solution composition, electrical parameters, time of electrolysis, and quantity of metal dissolved are shown in Tables 1–3. In the case of RXX compounds, we found that the best results were obtained when the temperature of the solution was kept between -10 and -20°C ; for the preparation of salts of RMgX_2^- , temperatures of -20 to -30°C were used.

The final solution from the cell was filtered to remove the fine particles of magnesium which usually fell from the anode during the electrolysis. Small quantities of the main product also precipitated during the electrolysis, especially for RMgXL , and were also removed at this point. In the case of the neutral adducts, diethyl ether was then added dropwise to the filtrate, causing the precipitation of an off-white (RMgXL) or orange ($\text{R'Mg}_2\text{X}_2 \cdot 2\text{L}$) solid, which was collected and dried

TABLE 1

REACTION CONDITIONS FOR THE DIRECT ELECTROCHEMICAL SYNTHESIS OF 2,2'-BI-PYRIDINE ADDUCTS OF ORGANOMAGNESIUM HALIDES

| Product ^a | Solution composition ^b | | Initial voltage (V) | Initial current (mA) | Time of electrolysis (h) | Magnesium dissolved (mg) |
|--|-----------------------------------|-------------------------|---------------------|----------------------|--------------------------|--------------------------|
| | RX (ml) | CH ₃ CN (ml) | | | | |
| C ₂ H ₅ MgBr·L | 5 | 50 | 40 | 30 | 5 | 83 |
| C ₂ H ₅ MgI·L | 5 | 50 | 30 | 25 | 2 | 50 |
| n-C ₄ H ₉ MgCl·L | 5 | 50 | 40 | 30 | 8 | 81 |
| n-C ₄ H ₉ MgBr·L | 5 | 50 | 40 | 25 | 8 | 76 |
| C ₆ H ₅ MgCl·L | 5 | 50 | 45 | 30 | 12 | 81 |
| C ₆ H ₅ MgBr·L | 5 | 50 | 30 | 30 | 12 | 79 |
| C ₆ H ₅ MgI·L | 5 | 50 | 30 | 30 | 12 | 85 |
| C ₃ F ₇ MgI·L | 2 | 20 ^c | 20 | 15 | 8 | 108 |

^a L = 2,2'-bipyridine. ^b Plus 0.8–1.0 g of L and 20–30 mg of (C₂H₅)₄NX in each case. ^c Plus 8 ml benzene; experiment run at 0°C.

TABLE 2

REACTION CONDITIONS FOR THE DIRECT ELECTROCHEMICAL SYNTHESIS OF 2,2'-BI-PYRIDINE ADDUCTS OF $\text{XMg}(\text{CH}_2)_n\text{MgX}$ COMPOUNDS

| Product ^a | Solution composition ^b | | Initial voltage (V) | Initial current (mA) | Time of electrolysis (h) | Magnesium dissolved (mg) |
|--|-----------------------------------|--|---------------------|----------------------|--------------------------|--------------------------|
| | XRX (ml) | $\text{CH}_3\text{CN} + \text{C}_6\text{H}_6$ (3/1) (ml) | | | | |
| $(\text{CH}_2)_2\text{Mg}_2\text{Br}_2 \cdot 2\text{L}$ | 5 | 40 | 8 | 20 | 5 | 81 |
| $(\text{CH}_2)_4\text{Mg}_2\text{Br}_2 \cdot 2\text{L}$ | 2.5 | 50 | 8 | 20 | 6 | 101 |
| $(\text{CH}_2)_5\text{Mg}_2\text{Br}_2 \cdot 2\text{L}$ | 3.0 | 40 | 10 | 20 | 6 | 115 |
| $p\text{-C}_6\text{H}_4\text{Mg}_2\text{Cl}_2 \cdot 2\text{L}$ | 1.5 (g) | 40 | 25 | 25 | 3 | 55 |
| $p\text{-C}_6\text{H}_4\text{Mg}_2\text{Br}_2 \cdot 2\text{L}$ | 2.0(g) | 40 | 15 | 30 | 8 | 109 |
| $p\text{-C}_6\text{H}_4\text{Mg}_2\text{I}_2 \cdot 2\text{L}$ | 1.5(g) | 40 | 20 | 40 | 6 | 106 |

^a L = 2,2'-bipyridine. ^b Plus 1.2 g of L and 25 mg of $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ in each case.

in vacuo. With salts of RMgX_2^- , the volume of the filtrate was reduced in vacuo before adding diethyl ether; the precipitated solid was washed several times with cold acetonitrile or dichloromethane to remove any $\text{R}'_4\text{NX}$, and then dried in vacuo. The yields, based on the mass of magnesium dissolved, were typically 50–60% for the RMgX compounds, 60–80% for the adducts of $\text{R}'\text{Mg}_2\text{X}_2$ and 60–70% for RMgX_2^- salts.

The characterization of the neutral adducts was based on metal and halogen analysis; in some cases of RMgXL , the volume of alkane released on decomposition with acetic acid was also measured (see Table 4). The presence of 2,2'-bipyridine was confirmed by infrared spectroscopy. Despite the initial solubility of these products in the $\text{CH}_3\text{CN}/\text{RX}$ reaction mixture, the solid precipitated by addition of ether (see above) is essentially insoluble in either CH_3CN or $\text{CH}_3\text{CN}/\text{RX}$. A slight solubility in dimethylsulphoxide allowed the presence of 2,2'-bipyridine and the group R to be confirmed by NMR spectroscopy, but meaningful integration of the peaks was not possible. The solids darken on standing under dry nitrogen for a few days, and

TABLE 3

REACTION CONDITIONS FOR THE DIRECT ELECTROCHEMICAL SYNTHESIS OF SALTS OF RMgX_2^-

| Anion ^a | Solution composition | | | | Initial voltage (V) | Initial current (mA) | Time of electrolysis (h) | Mg dissolved (mg) | Colour of product |
|---|----------------------|-----------------------------|-----------------------------|---------------------------|---------------------|----------------------|--------------------------|-------------------|-------------------|
| | RX (mL) | CH_3CN (ml) | C_6H_6 (ml) | R_4NX (g) | | | | | |
| $[\text{C}_2\text{H}_5\text{MgBr}_2\text{S}]^-$ | 5 | 40 | 15 | 1.6 ^b | 10 | 25 | 8 | 112 | yellow |
| $[\text{C}_2\text{H}_5\text{MgI}_2\text{S}]^-$ | 5 | 40 | 15 | 2.0 ^c | 15 | 30 | 10 | 110 | yellow |
| $[\text{n-C}_4\text{H}_9\text{MgCl}_2\text{S}]^-$ | 5 | 30 | 10 | 1.5 ^b | 25 | 25 | 6 | 89 | white |
| $[\text{n-C}_4\text{H}_9\text{MgBr}_2\text{S}]^-$ | 8 | 40 | 15 | 1.6 ^b | 15 | 25 | 12 | 130 | off-white |
| $[\text{C}_3\text{F}_7\text{MgI}_3\text{S}]^-$ | 4 | 30 | 10 | 1.5 ^c | 20 | 30 | 6 | 76 | dark brown |
| $[\text{C}_6\text{H}_5\text{MgCl}_2\text{S}]^-$ | 5 | 30 | 10 | 1.5 ^c | 25 | 25 | 8 | 105 | white |
| $[\text{C}_6\text{H}_5\text{MgBr}_2\text{S}]^-$ | 5 | 30 | 10 | 1.5 ^b | 20 | 30 | 10 | 108 | orange-yellow |
| $[\text{C}_6\text{H}_5\text{MgI}_2\text{S}]^-$ | 5 | 30 | 10 | 1.5 ^c | 15 | 25 | 8 | 110 | yellow |
| $[\text{C}_6\text{F}_5\text{MgBr}_2\text{S}]^-$ | 5 | 30 | 10 | 1.5 ^b | 25 | 30 | 12 | 117 | dark brown |

^a S = CH_3CN . ^b R = C_2H_5 . ^c R = $\text{n-C}_3\text{H}_7$.

TABLE 4
ANALYTICAL RESULTS FOR RMgXL COMPOUNDS (L = 2,2'-bipyridine)

| Compound | Found (calcd.) (%) | |
|---|--------------------|----------------|
| | Mg | halogen |
| C ₂ H ₅ MgBr·L | 8.6 (8.4) | 27.8 (27.6) |
| C ₂ H ₅ MgI·L ^a | 7.7 (7.2) | 37.2 (37.8) |
| n-C ₄ H ₉ MgCl·L ^b | 9.1 (8.9) | 12.3 (12.9) |
| n-C ₄ H ₉ MgBr·L ^c | 7.8 (7.7) | 25.1 (25.2) |
| C ₆ H ₅ MgCl·L | 8.8 (8.3) | 11.3 (12.0) |
| C ₆ H ₅ MgBr·L | 7.4 (7.2) | 23.5 (23.7) |
| C ₆ H ₅ MgI·L | 6.4 (6.3) | 33.4 (33.0) |
| C ₃ F ₇ MgI·L | 5.2 (5.1) | 26.6 (26.6) |

^a Acid decomposition of 0.102 g gave 5.1 ml gas at STP (calcd. 5.6 ml). ^b Acid decomposition of 0.037 g gave 2.9 ml gas at STP (calcd. 3.2 ml). ^c Acid decomposition of 0.041 g gave 2.7 ml gas at STP (calcd. 2.9 ml).

microanalysis results were generally unsatisfactory, presumably because of decomposition of the solid.

For the salts of RMgX₂⁻, analysis (Mg, X) (Table 6) and infrared spectroscopy provided the primary characterization. The salts are soluble in dimethylsulphoxide.

TABLE 5
ANALYTICAL RESULTS FOR RMg₂X₂L₂ COMPOUNDS (L = 2,2'-bipyridine)

| Compound | Colour | Found (calcd.) | |
|--|-----------------|----------------|----------------|
| | | Mg | halogen |
| (CH ₂) ₂ Mg ₂ Br ₂ ·2L | orange | 8.9 (8.9) | 29.3 (29.1) |
| (CH ₂) ₄ Mg ₂ Br ₂ ·2L ^a | orange | 8.5 (8.4) | 27.8 (27.7) |
| (CH ₂) ₅ Mg ₂ Br ₂ ·2L | orange | 8.4 (8.2) | 27.0 (27.0) |
| <i>p</i> -C ₆ H ₄ Mg ₂ Cl ₂ ·2L | pale- orange | 9.5 (9.6) | 31.6 (31.4) |
| <i>p</i> -C ₆ H ₄ Mg ₂ Br ₂ ·2L | light- brown | 8.2 (8.1) | 26.8 (26.8) |
| <i>p</i> -C ₆ H ₄ Mg ₂ I ₂ ·2L | light- brown | 7.2 (7.0) | 23.2 (23.1) |

^a Found: C, 29.20; H, 2.80; N, 4.92; calcd.: C, 29.12; H, 2.77; N, 4.85%.

TABLE 6
ANALYTICAL RESULTS FOR $R_4N[R'MgX_2 \cdot CH_3CN]$ SALTS

| Compound ^a | Found (calcd.) (%) | |
|--|--------------------|----------------|
| | Mg | halogen |
| $(C_2H_5)_4N[C_2H_5MgBr_2S]$ | 6.2 (6.3) | 41.7 (41.6) |
| $(C_3H_7)_4N[C_2H_5MgI_2S]$ ^b | 4.5 (4.6) | 47.6 (47.5) |
| $(C_2H_5)_4N[C_4H_9MgCl_2S]$ | 7.8 (7.5) | 22.2 (21.9) |
| $(C_2H_5)_4N[C_4H_9MgBr_2S]$ | 6.1 (5.9) | 37.6 (37.8) |
| $(C_3H_7)_4N[C_3F_7MgI_2S]$ | 4.4 (4.4) | 46.5 (46.4) |
| $(C_3H_7)_4N[C_6H_5MgCl_2S]$ | 5.9 (6.1) | 18.0 (17.7) |
| $(C_2H_5)_4N[C_6H_5MgBr_2S]$ | 5.5 (5.6) | 37.2 (37.0) |
| $(C_3H_7)_4N[C_6H_5MgI_2S]$ | 4.2 (4.2) | 43.7 (43.6) |
| $(C_2H_5)_4N[C_6F_5MgBr_2S]$ | 5.6 (5.5) | 36.3 (36.2) |

^a S = CH₃CN. ^b Acid decomposition of 0.172 g gave 6.8 ml gas at STP (calcd. 7.2 ml). ^c Acid decomposition of 0.149 g gave 8.5 ml gas at STP (calcd. 8.6 ml).

but an immediate reaction occurs and the solution forms a gel within a few minutes, thus preventing integration of the NMR spectra. Decomposition with acid to release alkane was also used in two cases (Table 6). The formulation as salts was confirmed by conductivity measurements in acetonitrile at mM concentration. These compounds are extremely hygroscopic.

Results and discussion

Synthesis of RMgX · bipy and R'Mg₂X₂ · 2bipy

The electrochemical oxidation of metallic magnesium is apparently a general route for the preparation of the 2,2'-bipyridine adducts at RMgX in good yield, irrespective of the nature of R and X, and R'Mg₂X₂ · 2bipy derivatives of both α,ω -dihaloalkanes and 1,4-dihalobenzenes were also obtained in this way. Given the ease of preparation, it is unfortunate that the chemical properties of the compounds are so unrewarding (see below).

We also investigated the direct preparation of adducts with other neutral donors, with limited success. With 1,4-dioxane and C₆H₅Br, the final filtrate yielded a white precipitate on the addition of diethyl ether, but the analytical results (Mg, 9.0; Br, 2.2%) suggest that this material is predominantly (C₆H₅)₂Mg · diox (Mg, 9.0%) with some bromide-containing impurity; the presence of 1,4-dioxane was confirmed by NMR spectroscopy. With this same ligand and C₆H₅I, the product contained Mg, 9.9; I, 27.9% (i.e. Mg/I = 2.7), but neither in this system, nor with C₂H₅Br and 1,4-dioxane (Mg, 12.3; Br, 7.6%), did the analytical results correspond to any reasonable formula. With triethylamine and C₆H₅I, the NMR of the isolated

product showed an almost complete absence of aliphatic protons. With *N,N,N',N'*-tetramethylethanediamine (TMED) and C_6H_5Br , we obtained a stable 1/1 adduct (Found: Mg, 7.8; Br, 26.6, $C_6H_5MgBr \cdot TMED$ (calcd.: Mg, 8.2; Br, 26.8%), whose properties do not appear to be significantly different from those of the 2,2'-bipyridine adduct. We therefore conclude that bidentate nitrogen ligands are favoured as stabilizing ligands in the electrochemical method of preparation.

Solvents other than acetonitrile were also tested. The choice is clearly restricted to liquids of reasonably high dielectric constant in order that ionic species may be generated in and transported through the medium. With either diethyl ether or tetrahydrofuran solutions of alkyl halides, little or no dissolution of untreated magnesium took place over a period of several hours at approximately 40 V potential. Magnesium metal which had been treated with hydrochloric acid reacted spontaneously with such mixtures, in keeping with known experience.

The overall conclusion then is that while electrochemical oxidation in acetonitrile in the presence of 2,2'-bipyridine leads to the neutral adducts, none of the obvious variations of solvents or basic ligand produce products of comparable stability, or enhanced reactivity. In the absence of basic ligands, a reaction occurs with acetonitrile (see below), but the replacement of this solvent by others is not conducive to the successful electrochemical synthesis of $RMgX$ adducts.

Chemical reactivity of $RMgX \cdot bipy$ compounds

The products of the electrochemical synthesis are formally the adducts of Grignard reagents, and we therefore investigated the reaction of selected compounds with some of the electrophiles typically used in organic syntheses involving such reagents. We note immediately that such reactions are hindered by the almost complete insolubility of the 2,2'-bipyridine adducts of $RMgX$ in common organic solvents. The treatment of a suspension of $EtMgBr \cdot bipy$ with benzaldehyde or ethyl benzoate in boiling THF under nitrogen over periods of several hours resulted only in the recovery of unreacted carbonyl and 2,2'-bipyridine, but no alcoholic products were detected after hydrolysis of the final reaction mixture. Similar findings were recorded when boiling xylene was the reaction solvent. The treatment of $PhMgBr \cdot bipy$ with solid carbon dioxide produced no evidence of benzoic acid in the final products after conventional work-up. Finally, we note that the substances isolated from the electrochemical synthesis are slow to react with aqueous acids, although the release of alkane was shown to be essentially quantitative in those cases where the volume of gas was measured (Table 4). The identity of the alkane was confirmed in some cases by infrared spectroscopy.

The results of these experiments, together with the insolubility of the substance precipitated from the reaction solution, suggest that the 2,2'-bipyridine adducts of $RMgX$ obtained in the present work are homopolymers of $RMgX \cdot bipy$. The structural information on crystalline adducts of $RMgX$ has been recently reviewed by Lindsell [6]; oligomeric structures involving four-, five-, and six-coordinate magnesium are known, but there is apparently no information which relates to the chemical reactivity in terms of solid state structure, although much has been published on solution phase structure and chemical behaviour [6]. In the present case, it appears that $RMgX$ is formed by attack at the anode (see below), and remains in solution coordinated by 2,2'-bipyridine and/or acetonitrile, but on precipitation goes to a cross-linked product which then resists chemical attack unless

the coordinated 2,2'-bipyridine can be removed, as is the case in acid attack. This solid homopolymer could involve either five- or six-coordination at the magnesium.

In an attempt to overcome these difficulties in the synthetic use of electrochemically generated RMgX , we briefly investigated the reactions of the solution of RMgX in the electrolyte phase. Magnesium metal was dissolved electrochemically in acetonitrile containing EtBr and Et_4NClO_4 (cf. Table 1) but the subsequent addition of ethyl benzoate led to an incompletely characterized product (mol. wt. 186, by field desorption mass spectrometry). The ^1H NMR spectrum of this unstable yellow oil revealed the presence of a benzoyl group and at least three vinyl methyl groups ($\delta \sim 2.1$ ppm). A band in the infrared spectrum at 2200 cm^{-1} suggested the presence of a conjugated nitrile, and the molecular weight corresponded to the addition of two CH_3CN molecules to ethyl benzoate, so that a tentative explanation of this result is that the treatment of ethyl benzoate with an acetonitrile solvate of EtMgBr results in a reaction between substrate and solvate. In any case, such procedures do not offer any prospect of using an electrochemically generated solution of RMgX in organic synthesis.

Derivatives of organic dihalides

Derivatives of XRX in which two atoms of magnesium are inserted into C-X bonds have been reported for both aliphatic and aromatic systems [7]. The results in Tables 2 and 4 show that electrochemical oxidation provides a convenient route to the adducts $\text{RMg}_2\text{X}_2 \cdot 2\text{bipy}$. The only chemical investigation carried out involved the decomposition of $(\text{CH}_2)_5\text{Mg}_2\text{Br}_2 \cdot 2\text{bipy}$ (ca. 150 mg) with aqueous hydrochloric acid (2 ml, 10% v/v). A sample of the gaseous phase above the reaction mixture was injected directly into a GC/mass spectrometer. The mass spectrum of the main product was almost identical to that of n-pentane, showing that acid attack follows the same course here as with the alkyl $\text{RMgX} \cdot \text{bipy}$ adducts, and that no significant rearrangement of the C_5 chain occurs during the reaction.

Salts of RMgX_2^- anions

Anionic organometallic derivatives of magnesium do not appear to have been reported previously (cf. ref. 6). Following earlier electrochemical syntheses of salts of RZnX_2^- [3], RCdX_2^- [8], and RInX_3^- [4], we have successfully prepared a series of salts of RMgX_2^- , in which R may be alkyl, perfluoroalkyl, aryl or perfluoroaryl, and X = Cl, Br or I (not all combinations). As noted earlier, the NMR spectra provide qualitative evidence of the presence of the appropriate R_4N^+ group, and of a phenyl group for aromatic derivatives. The infrared spectra, in addition to confirming the NMR spectra, also show in each case an intense peak at $\sim 2150\text{ cm}^{-1}$, indicating the presence of coordinated CH_3CN . Conductivity measurements gave molar conductivities of $145\text{ ohm}^{-1}\text{ cm}^2$ for $(\text{C}_2\text{H}_5)_4\text{N}[\text{C}_6\text{H}_5\text{MgBr}_2 \cdot \text{CH}_3\text{CN}]$ and $152\text{ ohm}^{-1}\text{ cm}^2$ for $(\text{C}_3\text{H}_7)_4\text{N}[\text{C}_2\text{H}_5\text{MgI}_2 \cdot \text{CH}_3\text{CN}]$, showing that the compounds are 1/1 electrolytes in dilute solution.

All attempts to use anionic RMgX_2^- as Grignard reagents with benzophenone failed to yield any tertiary alcohol, and the unreacted ketone was recovered. There is clearly a reaction with dimethylsulphoxide, as evidenced by gel formation, but this was not investigated further. The structure of the anion is presumed to be based on four-coordinate magnesium, with a $\text{MgX}_2(\text{C})(\text{N})$ core, although the formation of higher coordinate species by halogen bridging cannot be excluded at this point.

Electrochemical efficiencies

The electrochemical efficiency, defined as mol Mg dissolved per Faraday of electricity, was found to be 0.5 ± 0.05 mol F^{-1} for two typical $RMgX$ systems ($n-C_4H_9Br$, C_6H_5I), while for the dihalide system $Mg/1,5-C_5H_{10}Br_2$, E_F 0.97 mol F^{-1} . In systems yielding $RMgX_2$ anions, with solutions containing gram quantities of X^- , the values for $(C_2H_5)_4NBr + C_2H_5Br$, and $(C_2H_5)_4NI + C_6H_5I$ were 0.52 and 0.56 mol F^{-1} respectively. The interpretation of these results must await further study, especially since previous work on R/MX systems gave E_F values which are higher (and sometimes substantially higher) than those required for Faradaic behaviour [1].

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