Mechanistic and synthetic aspects of a novel route to poly-*p*-xylylene (PPX) *via* nickel complex catalysed electropolymerisation of 1,4-bis(chloromethyl)benzene

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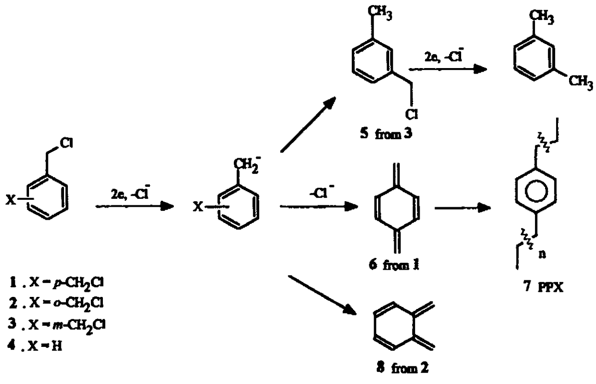
It is shown that in the presence of catalytic amounts of $Ni^{II}Cl_2L_2$ (L_2 = dppe or dppp) 1,4-bis(chloromethyl)benzene is electrochemically reduced to poly-*p*-xylylene (PPX). Cyclic voltammetric examination of this reaction, and of the analogous conversion of benzyl chloride into bibenzyl, is combined with the construction of reactant/product *vs.* charge profiles to develop a detailed mechanistic description. There is compelling evidence that, in contrast with the established cathodic formation of PPX from 1,4-bis(halomethyl)benzene *via* electrogenerated quinodimethane (xylylene), the Ni complex catalysed route involves oxidative addition of the halide derivative to Ni^0L_2.

Introduction

Versatile and efficient electrochemical routes to poly(*p*-xylylene) (PPX) and poly(phenylenevinylene) (PPV) polymers have recently been reported.[1,2] The method involves cathodic elimination of halides from 1,4-bis(halomethyl)arenes (**1**) to give *p*-quinodimethane intermediates (*p*-xylylenes) (**6**); the corresponding 1,2-bis(halomethyl)arenes give *o*-quinodimethanes (*o*-xylylenes) (**8**) (Scheme 1). The polymers so produced (**7**) are linear and highly regular and a considerable variety of functionality is tolerated. Because a liquid electrode is used (mercury) the reactions are not stopped by electrode fouling and proceed to completion and may be carried out on a useful scale.

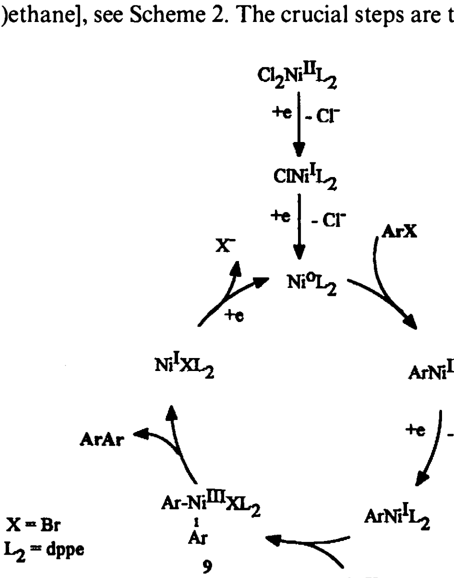


Scheme 1

A limitation of this method, however, is that with few exceptions bis(bromomethyl) derivatives must be used. The cheaper and less lachrymatory chloride derivatives reduce at potentials more negative than do the bromides and, crucially, at potentials where the quinodimethanes are further reduced, thus precluding polymerisation.

We have therefore sought a catalysed route whereby the initial electron transfer is at less negative potentials and which would allow effective conversion of the chloride precursors without losing the advantages of the direct reduction (see above). The redox catalysed formation of *o*-quinodimethanes from 1,2-bis(bromomethyl)benzenes has been realised,[3] and there are many encouraging reports of the use of nickel complexes to effect coupling of aryl halides[4] and to polymerise[5] 1,4-dihalobenzenes to poly(*p*-phenylene). The coupling of benzal dichloride ($PhCHCl_2$) to stilbene (PhCH:CHPh) by electroreduction[6] in the presence of Ni^{II}(salen) [salen = bis(salicylidene)ethylenediamine] is further support for the proposed coupling reactions. In addition, carbon–carbon bond-forming reactions have been shown to result from a variety of other electroreductions of aryl and alkyl halides in the presence of complexes of transition metals other than nickel, notably palladium[7] and cobalt.[8]

A complete mechanistic description has been established[4c,9] for the conversion of bromobenzene into biphenyl by reduction in the presence of $NI^{II}Cl_2$(dppe) [dppe = 1,2-bis(diphenylphosphino)ethane], see Scheme 2. The crucial steps are the oxidative addition of PhBr to an electrogenerated Ni^0 species with subsequent steps to incorporate two phenyl groups into an intermediate (**9**) from which biphenyl is eliminated. It is relevant that, although not in the context of a coupling reaction, benzyl halides have been shown[10] to undergo oxidative addition to Ni^0 complexes and, in a separate study, bibenzyl is formed in high



Scheme 2

yield by reduction of benzyl chloride (**4**) in the presence of $NiBr_2bipy$ (bipy = 2,2′-bipyridine)[11] or $NiCl_2(PPh_3)_2$.[12]

Thus two important questions arise. Can nickel complexes be used catalytically to effect not only coupling of benzylic halides but also to polymerise 1,4-bis(halomethyl)benzenes? If so, is 'classical' redox catalysis[13] the reason, with a low-valent nickel complex acting as an electron-transfer redox mediator to generate quinodimethanes (Scheme 1) or will the halides add successively and oxidatively to a reduced nickel complex from which coupled or polymeric products will eliminate in a stepwise fashion by a route similar to that in Scheme 2?

We have addressed this issue using 1,4-bis(chloromethyl)benzene (**1**) and benzyl chloride (**4**) as representative substrates in a detailed examination of both products and mechanism. We report here experiments which: (*i*) show that 1,4-bis(chloromethyl)benzene (**1**) is cathodically polymerised to PPX (**7**) in high yield *via* generation of $Ni^0(dppe)$; and (*ii*) develop a detailed profile, as a function of charge, of the reactants and products of the comparable coupling of benzyl chloride (**4**), which leads to a complete mechanistic description. Furthermore, the results have implications for the improvement of preparative routes to important polymers.

Results and discussion

The electrochemical behaviour of 1,4-bis(chloromethyl)benzene (1) in the presence of nickel(II) complexes

Cyclic voltammograms of the separate components were first obtained using substrates, 2 mM, in a mixture of DMF and THF (4:1 v/v) containing Bu_4NBF_4 (0.3 M). That of 1,4-bis(chloromethyl)benzene (**1**), exhibited a single, irreversible, reduction peak at $E_{pc}(R_0) = -2.30$ V *vs.* SCE (Fig. 1). Preparative reduction at this potential gave only *p*-xylene with the consumption of 4 F mol^{-1}.

The cyclic voltammogram of $Ni^{II}Cl_2(dppe)$ exhibited two successive irreversible reduction peaks at $E_{pc}(R_1) = -0.88$ V and $E_{pc}(R_2) = -1.41$ V (Fig. 1) which is known to be due to the reduction of the bivalent nickel complex to a zero-valent nickel complex in two one-electron steps.[4c,9]

$$Ni^{II}Cl_2(dppe) + 1e \longrightarrow Ni^{I}Cl(dppe) + Cl^- \quad E_{pc}(R_1) \quad (1)$$

$$Ni^{I}Cl(dppe) + 1e \longrightarrow Ni^{0}(dppe) + Cl^- \quad E_{pc}(R_2) \quad (2)$$

When the complex $Ni^{II}Cl_2(dppe)$ was reduced in the presence of one equivalent of 1,4-bis(chloromethyl)benzene (**1**) the reduction peak for **1** diminished and a new reduction peak developed at $E_{pc}(R_3) = -2.12$ V, *i.e.*, at a less negative potential than $E_{pc}(R_0)$ for 1,4-bis(chloromethyl)benzene (Fig. 1). This is consistent with reduction to nickel(0) which activates one C–Cl bond of 1,4-bis(chloromethyl)benzene *via* an oxidative addition to form a benzylnickel(II) complex which, in turn, is reduced at $E_{pc}(R_3)$, see eqn. (4).

$$Ni^0(dppe) + Ar\text{–}CH_2\text{–}Cl \longrightarrow Ar\text{–}CH_2\text{–}Ni^{II}\text{–}Cl(dppe) \quad (3)$$

$$(Ar = p\text{-}Cl\text{–}CH_2\text{–}C_6H_4)$$

$$Ar\text{–}CH_2\text{–}Ni^{II}\text{–}Cl(dppe) + 1e \longrightarrow \qquad E_{pc}(R_3) \quad (4)$$

As the concentration of 1,4-bis(chloromethyl)benzene was increased the reduction peak $E_{pc}(R_3)$ grew. This demonstrates the catalytic nature of the process whereby product(s) are formed with regeneration of the nickel(0) complex which can again undergo oxidative addition with 1,4-bis(chloromethyl)benzene to give the species responsible for $E_{pc}(R_3)$, see eqn. (5).

$$Ar\text{–}CH_2\text{–}Ni^{II}\text{–}Cl(dppe) + 1e + Ar\text{–}CH_2\text{–}Cl \longrightarrow$$
$$\text{product(s)} + Ni^0(dppe) \quad E_{pc}(R_3) \quad (5)$$

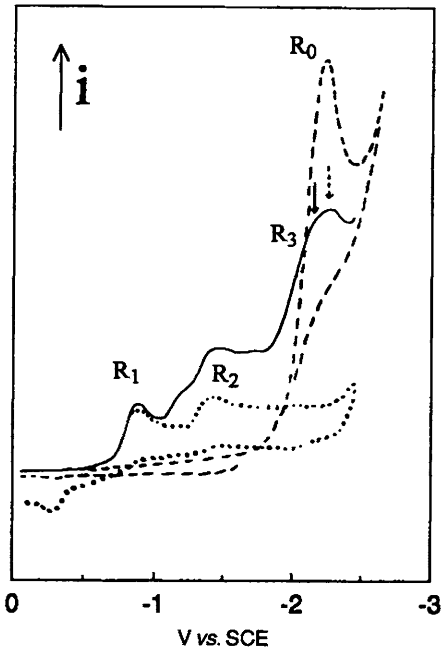


Fig. 1 (----) Cyclic voltammetry of compound **1** (2 mmol dm^{-3}) in 12 cm^3 of THF–DMF (4:1 v/v) containing ($Bu^n_4NBF_4$, 0.3 mol dm^{-3}) at a stationary gold disk electrode ($\phi = 0.5$ mm) with a scan rate of 0.2 V s^{-1}; (····) cyclic voltammetry of $NiCl_2(dppe)$ (2 mmol dm^{-3}) performed under the same conditions as above; (—) cyclic voltammetry of $NiCl_2(dppe)$ (2 mmol dm^{-3}) performed in the presence of **1** (2 mmol dm^{-3})

The same behaviour was observed using an alternative complex $Ni^{II}Cl_2(dppp)$ [dppp = 1,3-bis(diphenylphosphino)propane]. The corresponding reduction peak potentials are collected in Table 1 which also contains data pertaining to other isomers of bis(chloromethyl)benzene (**2** and **3**) and the *o*- and *p*-quinodimethanes (the xylylenes **6** and **8**).

This analysis of the voltammetric data from reductions of 1,4-bis(chloromethyl)benzene (**1**) in the presence of the nickel complexes indicates that catalytic conversion into products should take place at the potential $E_{pc}(R_3)$.

The results in Table 1 do not, however, unequivocally rule out the quinodimethanes (xylylenes **6** and **8**) as intermediates. The *o*- and *p*-bis(bromomethyl)benzenes reduce at much less negative potentials than the corresponding chlorides; the products of direct reduction from the bromides [the quinodimethanes, *p*-xylylene (**6**) and *o*-xylylene (**8**)] are sufficiently long-lived to allow their characterisation[14] by cyclic voltammetry. They give irreversible reduction peaks at up to 100 V s^{-1} and the relevant potentials are listed in Table 1. *p*-Xylylene **6** reduces at a potential which is comparable to $E_{pc}(R_3)$ so the possibility of redox-mediated formation of this quinodimethane must remain under consideration at this stage although, because electrolyses are carried out at or close to their reduction potential, it is probable that, if formed, they would reduce further, eventually to the corresponding xylenes. This is what happens when the bis(chloromethyl)benzenes are directly reduced at the cathode. Furthermore, it is unlikely that the *p*-xylylene is formed by the Ni^0 species acting as a redox mediator because the difference in peak potentials (0.92 V) between its formation (at −1.19 V, at Hg) and reduction of 1,4-bis(chloromethyl)benzene (at −2.11 V) is too great to permit normal redox catalysis,[13] even allowing for the fact that potentials for irreversible reduction are being compared.

The products of electrolysis catalysed by the nickel complexes

Larger scale electrolyses were typically carried out potentiostatically on a 4 mmol scale with an 0.1 mol equivalent of catalyst using a divided cell with a mercury pool cathode. The results are summarised in Table 2 and the footnotes give details

Table 1 Reduction peak potentials[a] (E_{pc}) of starting materials and intermediate nickel complexes

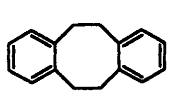
Species	$-E_{pc}(R_1)$/V *vs.* SCE	$-E_{pc}(R_2)$/V *vs.* SCE	$-E_{pc}(R_3)$/V *vs.* SCE	$-E_{pc}(R_0)$/V *vs.* SCE
$Ni^{II}Cl_2$(dppe)	0.88 (0.64)[d]	1.41 (1.19)[d]		
$Ni^{II}Cl_2$(dppp)	0.57	1.47		
p-$ClCH_2C_6H_4CH_2Cl$ (**1**)				2.30 (2.11)[b]
p-$ClCH_2C_6H_4CH_2Ni^{II}Cl$(dppe)			2.12 (1.87)[b]	
p-$ClCH_2C_6H_4CH_2Ni^{II}Cl$(dppp)			2.19	
p-Xylylene (**6**)				(1.93,[b] 2.01[c])
p-$BrCH_2C_6H_4CH_2Br$				(1.27)[b]
m-$ClCH_2C_6H_4CH_2Cl$ (**3**)				2.36
m-$ClCH_2C_6H_4CH_2Ni^{II}Cl$(dppe)			2.20	
m-$ClCH_2C_6H_4CH_2Ni^{II}Cl$(dppp)			2.28	
o-$ClCH_2C_6H_4CH_2Cl$ (**2**)				2.09 (2.08)[b]
o-$BrCH_2C_6H_4CH_2Br$				(1.16)[b]
o-Xylylene (**8**)				(1.74,[b] 1.73[c])
o-$ClCH_2C_6H_4CH_2Ni^{II}Cl$(dppe)			1.74	
o-$ClCH_2C_6H_4CH_2Ni^{II}Cl$(dppp)			1.80	
$C_6H_5CH_2Cl$ (**4**)				2.38
$C_6H_5CH_2Ni^{II}Cl$(dppe)				2.15

[a] Au disk cathode, 0.2 V s^{-1}, DMF–THF (1 : 1 v/v), $Bu^n_4NBF_4$ (0.3 mol dm^{-3}), 20 °C. [b] See ref. 14, Hg bead cathode, 1 V s^{-1}, DMF, $Bu^n_4NPF_6$ (0.1 mol dm^{-3}). [c] As for *b* but at 100 V s^{-1}. [d] As for *a* but with an Hg-plated Au cathode.

Table 2 Products of electrolysis[a] in the presence of $Ni^{II}Cl_2L_2$

Substrate	Ligand, L_2[b]	$-E_{red}$[c]/ V *vs.* SCE	Charge/ F mol^{-1}	Product (%)
1	dppe	1.9	1.65	**7** (81)
	dppp	2.0	1.63	**7** (98)
2	dppe	1.8	1.48	**10** (20)[d]
3	dppp	2.0	1.83	**11** (43)[d] **12** (12) **5** (1)
4	dppe	2.3	*ca.* 0.8	**13** (*ca.* 75)[e]

[a] Divided cell, Hg pool cathode, THF–DMF (4 : 1 v/v), $Bu^n_4NBF_4$ (0.1 mol dm^{-3}), catalyst present in 0.1 mol equiv. [b] dppe = $Ph_2PCH_2CH_2PPh_2$, dppp = $Ph_2PCH_2CH_2CH_2PPh_2$. [c] Corresponds to the reduction peak R_3 of the complex resulting from the oxidative addition as determined by cyclic voltammetry. [d] Determined by ^1H NMR spectroscopy on crude product. [e] Determined by HPLC analysis, see Fig. 4.



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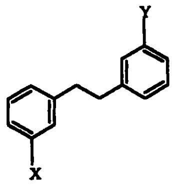


11 X = Y = CH_3

12 X = CH_3, Y = CH_2Cl

13 X = Y = H

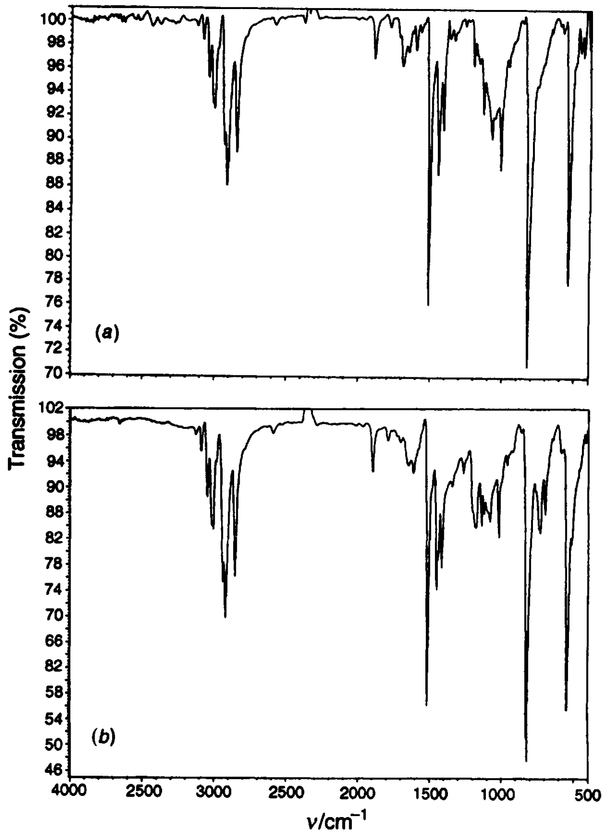


Fig. 2 (*a*) IR spectrum of PPX (**7**) resulting from the direct electroreduction of *p*-$BrCH_2C_6H_4CH_2Br$;[1] (*b*) IR spectrum of PPX (**7**) resulting from the $NiCl_2$(dppe)-catalysed electropolymerisation of *p*-$ClCH_2C_6H_4CH_2Cl$ (**1**)

of the conditions used. The most significant result is that reduction of 1,4-bis(chloromethyl)benzene (**1**) in the presence of either of the nickel catalysts gives poly(*p*-xylylene) (**7**) in high yield. Electrogenerated PPXs have been thoroughly examined and characterised[1] by solid-state ^{13}C spectroscopy, direct pyrolysis mass spectrometry, thermal analysis and infrared spectroscopy. Because of insolubility the molecular weight of the parent PPX has not been measured in this or in the earlier work. However, those formed by polymerisation of electrogenerated quinodimethanes were found[1] to be linear and highly regular, with high softening points (>400 °C). Furthermore, their FTIR spectra are quite distinctive with several sharp and strong absorptions which allow matching by 'fingerprinting'. According to the FTIR spectra, the PPXs formed electrocatalytically from 1,4-bis(chloromethyl)benzene (**1**) in the presence of the nickel complexes are identical with those well characterised polymers formed by direct reduction of 1,4-bis(bromomethyl)benzene. The spectra of samples of PPX from both routes are displayed in Fig. 2. The softening points of the PPXs formed by direct reduction[1] and by the nickel-catalysed route are 425–431 °C and >285 °C, respectively. Those lower melting and soluble PPXs whose molecular weight could be measured[1] had degrees of polymerisation (*n*) of the order of 20. The polymers formed by the nickel-catalysed route were insoluble and *n* could not be measured—but see the later discussion.

The products of nickel-complex-catalysed reduction of the 1,2- and 1,3-bis(chloromethyl)benzenes (**2** and **3**) suggest that a route other than generation of quinodimethanes is operative.

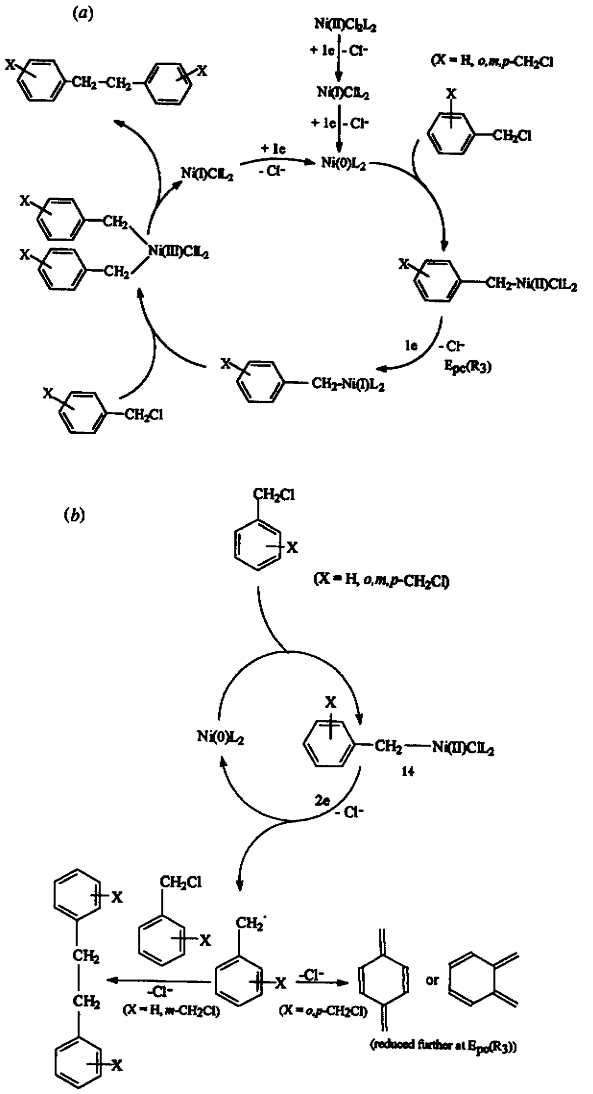
The direct route[1] from 1,2-bis(bromomethyl)arenes does give a significant amount of the corresponding PPXs, albeit in modest yields (30–55%), and co-electrolysis to *ortho*- and *para*-quinodimethanes gives[1] a good yield of a copolymer (64%). Electrolysis of 1,3-bis(bromomethyl)benzene gives *m*-xylene only, consistent with the impossibility of it eliminating to a quinodimethane. In contrast, the nickel-complex-catalysed route described herein gives no polymer from either 1,2- or 1,3-bis(chloromethyl)benzene (**2** and **3**) but modest yields of dimeric products with C–C coupling (**10**–**12**) are observed in both cases. Benzyl chloride **4** is smoothly converted in high yield into bibenzyl; an analogous reaction has been reported.[11,12]

Thus, the intermediacy of a nickel complex analogous to **9** is supported by: (*i*) the analysis of the voltammetric results; (*ii*) the fact that 1,3-bis(chloromethyl)benzene gives products of C–C coupling (**11** and **12**), to the extent of 55%; and, (*iii*) the analogy with the nickel-complex-catalysed coupling of aryl halides. The requirement for the formation of an 'inner sphere' nickel complex can also explain the different reactivities of the *o*- and *m*-isomers of bis(chloromethyl)benzene *vis à vis* the *p*-isomer because, as coupling proceeds, the dimers formed from the *o*- and *m*-isomers will be bulkier than the linear dimer formed from the *p*-isomer and therefore less reactive in a second oxidative addition.

However, although the voltammetry strongly suggests an oxidative addition step there are at least two plausible ways in which conversion into the observed products might follow. These are set out in Schemes 3; one route [Scheme 3(*a*)] involves a second oxidative addition, hereafter called the 'double oxidative addition route'. This is analogous to the mechanism for conversion of aryl halides (Scheme 2). The alternative route [Scheme 3(*b*)] involves reductive cleavage of the benzyl Ni^{II} complex **14** arising from the first oxidative addition to give a benzylic anion, hereafter called the 'anionic cleavage route'. This is depicted as a concerted reduction and cleavage by analogy with the widely held view[15] that for benzylic systems with good leaving groups electron transfer and cleavage are usually concerted. This could also be considered as the expulsion of a benzylic radical which would be rapidly reduced at the reduction potential of the Ni^{II} intermediate **14**. For the benzylic anions derived from *o*- and *p*-bis(chloromethyl)benzene further loss of chloride anion will be rapid (if not concerted with the initial cleavage) to give the *o*- and *p*-xylylenes **6** and **8** (quinodimethanes). In principle, polymers or the dimer **10** could result, but because the electrolysis is being driven at a potential at which it is known that the xylylenes (quinodimethanes) would be further reduced, it is unlikely that polymers arise *via* route 3(*b*). We have attempted to make a clearer distinction by exploring the precise sequence of events through the construction of reaction profiles in which the concentrations of starting material and products were monitored as a function of charge passed.

Reaction profiles: the cathodic reduction of 1,4-bis(chloromethyl)benzene (1) and of benzyl chloride (4) in the presence of $NiCl_2$(dppe)

The substrates, 1,4-bis(chloromethyl)benzene (**1**) and benzyl chloride (**4**) were electrolysed in the presence of $Ni^{II}Cl_2$(dppe) (0.1 mol equiv.) using the conditions of preparative electrolysis (Table 2). Samples of the electrolyte were taken at known charge intervals and analysed by HPLC with quantification of the starting materials by comparison with authentic samples. The concentration–charge profiles thus obtained are displayed in Figs. 3 and 4. Fig. 3 is the profile for consumption of 1,4-bis(chloromethyl)benzene **1** [known to give the polymer, PPX (**7**)] and Fig. 4 relates to the consumption of benzyl chloride **4** to give bibenzyl **13** as the major product. The slopes expected for one-electron and two-electron reduction are superimposed. Only that part of the reaction in which the starting material disappears was followed. In preparative runs the reaction was continued past that point, until the residual current was low (0.5 mA cm^{-2}). It should be noted that in Scheme 3(*a*), it is assumed, for the 'double oxidative addition route', that polymerisation is stepwise, *i.e.*, the monomer is converted into the dimer (1 F mol^{-1}) which is then converted into the tetramer (total of 1.5 F mol^{-1}) and thence to the octomer (total of 1.75 F mol^{-1}) and so on. Complete polymerisation would need the passage of 2 F mol^{-1}, whichever pathway is followed. For the stepwise 'double oxidative addition' process this may not be achieved because at quite modest chain lengths ($n < 20$)[1] the polymer will precipitate from the electrolyte. Also, in practice, the growing concentration of dimer (which CH_2Cl end groups) might allow its participation in oxidative addition before the monomer is exhausted, *e.g.*, the dimer could re-enter the cycle to react with a monomer. However the reactant–charge profiles do not suggest that this is significant because of the complete disappearance of the monomer in a 1 F mol^{-1} process (Fig. 3). Although degrees of polymerisation (*n*) could not be measured the high yields of PPX at *ca.* 1.65 F (Table 2) indicates *n* values of *ca.* 6 using the above model.



Scheme 3 (*a*) Double oxidative addition route; (*b*) anionic cleavage route following oxidative addition

The first experiment (Fig. 3) shows that 1,4-bis(chloromethyl)-benzene is consumed initially by a 2e process which becomes a steady 1e decay. The expectation for the 'double oxidative addition route' [Scheme 3(*a*)] is that until the catalytic cycle is fully established, by formation and regeneration of Ni^0(dppe), the substrate is consumed at the rate of 2 F mol^{-1} which becomes 1 F mol^{-1} in the steady state (*i.e.*, in the cycle from and back to Ni^0L_2 where 2 mol of the starting material are consumed with

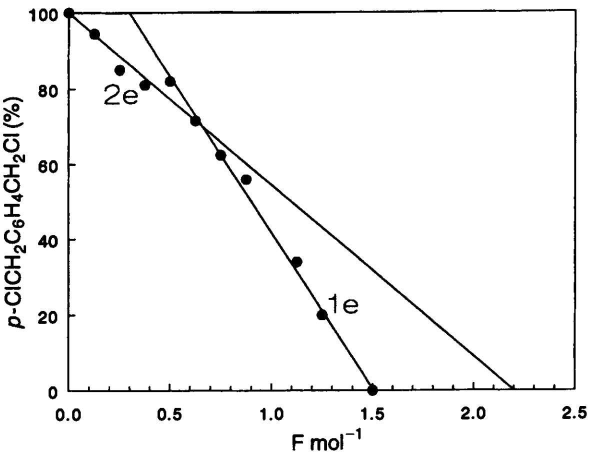


Fig. 3 Reaction profiles of p-ClCH$_2$C$_6$H$_4$CH$_2$Cl (**1**) as a function of the charge passed through the cell during the NiCl$_2$(dppe)-catalysed electrosynthesis of PPX (**7**) from **1** at 25 °C. The concentration of **1** was monitored by HPLC.

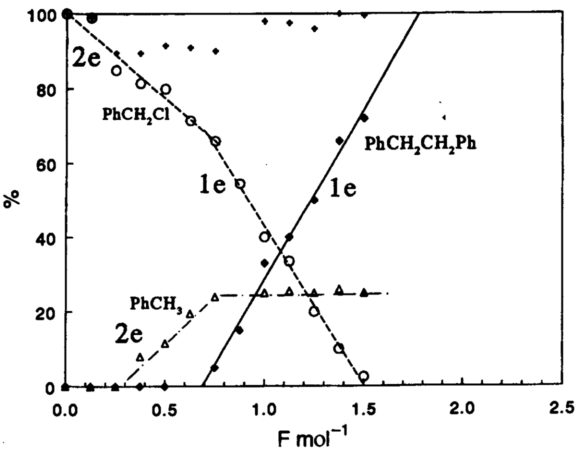


Fig. 4 Reaction profiles as a function of charge passed through the cell during the NiCl$_2$(dppe)-catalysed electrosynthesis of bibenzyl from C$_6$H$_5$CH$_2$Cl (**4**) at 25 °C. The concentrations were monitored by HPLC. (○) C$_6$H$_5$CH$_2$Cl; (◆) C$_6$H$_5$CH$_2$CH$_2$C$_6$H$_5$; (△) C$_6$H$_5$CH$_3$; (+) sum.

the passage of 2 F mol^{-1}). However, the catalyst is present in only 0.1 mol equiv. so the 2 F mol^{-1} period associated with the reduction from Ni^{II} to Ni^0 should not be so prolonged as is observed (Fig. 3). Initially, therefore, there is a competing process whereby the organic starting material is consumed in a 2 F mol^{-1} process, but *ca.* 65% of the 1,4-bis(chloromethyl)benzene is consumed as predicted by the 'double oxidative addition hypothesis' in a 1 F mol^{-1} process. In contrast the 'anionic cleavage route' [Scheme 3(*b*)] would lead from the 1,4-bis(chloromethyl)benzene to polymer *via* the p-xylylene **6** and this is a 2e process. Furthermore, for the reasons given above, it is unlikely that the xylylene **6** or **8** will survive under the conditions of electrolysis.

The situation is clarified by examination of the reaction profile (Fig. 4) for the catalytic conversion of benzyl chloride **4** where it is possible to monitor the concomitant formation of the two major products, bibenzyl (1e) and toluene (2e). As for Fig. 3 a similarly prolonged initial 2 F mol^{-1} process is observed for the decay of the benzyl chloride which becomes a 1 F mol^{-1} reaction. However, in this case, it is shown that the 2e process results in cleavage of the C–Cl bond (to give toluene) and that after a period this reaction ceases and the 1e formation of the coupling product (bibenzyl) begins. Furthermore, for much of the reaction, the sum of reactant and products is 90% of the expected amount which is consistent with 10% of the reactant being incorporated into the nickel species (and not detected by HPLC) and as such it is further evidence in favour of oxidative addition to the Ni^0 species *vis à vis* redox catalysis by a low-valent Ni complex.

The origin of the toluene is not clear. The 2 F mol^{-1} cleavage could be direct reduction of benzyl chloride (the potential used is only a few hundred millivolts less negative than the measured reduction potentials) or cleavage of C$_6$H$_5$CH$_2$Ni^{II}Cl(dppe) (**14**) and further reduction as proposed for the 'anionic cleavage route'. Alternatively the toluene could arise from hydrolysis by adventitious water of the nickel complex intermediate C$_6$H$_5$CH$_2$Ni^{II}Cl(dppe) or of C$_6$H$_5$CH$_2$Ni^{I}(dppe) which is the only complex able to undergo oxidative addition with water. No special precautions were taken to ensure the complete dryness of the electrolyte solution. Whereas the first two explanations do not account for the switch to a 1e reduction, the third and fourth, which invoke hydrolysis of intermediate nickel complexes, are more attractive because they rely on the presence of adventitious water which, when it has been consumed in the hydrolysis, will leave conditions for the reaction to switch to the expected 1e process with C–C coupling. This hypothesis concerning the presence of adventitious water is supported by the fact that when the electropolymerisation of 1,4-bis(chloromethyl)benzene **1** was performed in dry solvents (Table 2) only the polymer was formed and no p-CH$_3$C$_6$H$_4$CH$_2$Cl was detected.

Conclusions

Cathodic polymerisation of 1,4-bis(chloromethyl)benzene is catalysed by Ni^{II}Cl$_2$L$_2$ (L$_2$ = dppe or dppp). The intermediacy of p-xylylene **6** has been ruled out although such intermediates are the key species in both direct reduction and redox-mediated reduction of bis(bromomethyl)benzenes[1,14] The results of cyclic voltammetric experiments and reactant–charge profiles, which show that the monomer is mainly consumed in a 1 F mol^{-1} process, are evidence in favour of the 'double oxidative addition mechanism' outlined in Scheme 3(*a*) in which, starting from a Ni^0 species, successive oxidative additions of the halides (ArCH$_2$Cl) leads to the (ArCH$_2$)$_2$Ni^{III}ClL$_2$ which is the key intermediate.

Experimental

^{31}P NMR spectra were recorded for samples dissolved in CDCl$_3$ and referenced to TMS, on a Bruker spectrometer (200 MHz). IR spectra were recorded on a Nicolet Impact 400 spectrometer for KBr pellets. Mass spectroscopy was performed on a Nermag R1010C spectrometer. HPLC analyses were performed on an LKB-Pharmacia 2152 apparatus equipped with a reversed phase column (RP 18, 5 µm, 250 × 4 mm) and a UV detector (254 nm).

Chemicals

DMF was distilled from calcium hydride. Compounds **1**–**4** were commercial (Aldrich) and used as received. NiCl$_2$(dppe)[16a] and NiCl$_2$(dppp)[16b] were synthesised according to published procedures. Bu$^n_4$NBF$_4$ was synthesised as previously reported.[17]

Electrochemical set-up and electrochemical procedure for cyclic voltammetry

All the experiments were performed at 25 °C under argon. Cyclic voltammetry was performed with a home-made potentiostat and a wave-form generator, PAR Model 175. The cyclic voltammograms were recorded with a Nicolet 3091 digital oscilloscope. Experiments were carried out in a three-electrode cell connected to a Schlenk line. The cyclic voltammetry was performed at a stationary disk electrode [a gold disk made from the cross-section of a wire (ϕ = 0.5 mm) sealed into glass] with a scan rate of 0.2 V s^{-1}. The counter electrode was a platinum wire of *ca.* 1 cm^2 apparent surface area; the reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge (3 cm^3) filled with a 0.3 mol dm^{-3} Bu$^n_4$NBF$_4$ solution in THF–DMF (4:1 v/v). 12 cm^3 of THF–DMF (4:1 v/v) containing 0.3 mol dm^{-3} Bu$^n_4$NBF$_4$, were poured into the cell.

General procedure for cyclic voltammetry

A 4.2 mg amount of **1** (0.024 mmol, 2×10^{-3} mol dm^{-3}) was added to the cell and the cyclic voltammogram recorded. NiCl$_2$(dppe) (12.6 mg) (0.024 mmol, 2×10^{-3} mol dm^{-3}) was then added and cyclic voltammogram recorded.

Preparative electrolysis and reaction profiles

General procedure. Preparative electrolyses were carried out at room temperature in a two-compartment air-tight three electrode cell. The two compartments were separated by a sintered glass disk (porosity 4). The cathode was a mercury pool (*ca.* 25 cm^2 surface area). A lithium rod was used as the anode. The reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge (3 cm^3) filled with a 0.1 mol dm^{-3} Bu$^n_4$NBF$_4$ solution in THF–DMF (4:1 v/v). The cathodic and anodic compartments were filled, respectively, with 65 and 5 cm^3 of THF–DMF (4:1 v/v) containing Bu$^n_4$NBF$_4$ (0.1 mol dm^{-3}). 0.7 g (4 mmol) of **1** were added to the cell followed by 0.2 g (0.4 mmol) of NiCl$_2$(dppe). The electrolysis was conducted at the controlled potential of -1.90 V. The initial orange colour turned progressively brown and a precipitate appeared after the consumption of 1 F mol^{-1}. The electrolysis was stopped when the current was about 5% of its initial value. After being filtered, the solid was washed twice with water and twice with diethyl ether. It was then dried under vacuum (0.33 g) and characterised as polymer **7** by IR spectroscopy, by comparison with an authentic sample (see Fig. 2). The filtrate was hydrolysed with aqueous HCl (1 mol dm^{-3}), extracted with diethyl ether and analysed by ^{1}H NMR spectroscopy in order to identify unchanged starting material or by-products. In the present case no organic material was recovered.

From another electrolysis, 50 µl aliquots were taken from the cell after every 50 C and analysed by HPLC, after addition of a known amount of isobutylbenzene as an internal standard: eluent, acetonitrile–water (9:1 v/v); flow, 1 cm^3 min^{-1}. The corresponding reaction profile is reported in Fig. 3.

Product characterisation and analysis

Compound **5** was not isolated but detected in the crude product mixture and characterized: δ_H(200 MHz) 2.41 (3 H, s), 4.59 (2 H, s) and 7.07 (4 H, m); *m/z* 142, 140 (M$^+$), 105. Compound **10**: δ_H(200 MHz) 2.80 (8 H, m) and 7.07 (8 H, m); *m/z* 208 (M$^+$). Compound **11**: δ_H(200 MHz) 2.36 (6 H, s), 2.86 (4 H, m) and 7.07 (8 H, s); *m/z* 210 (M$^+$). Compound **12**: δ_H(200 MHz) 2.24 (3 H, s), 2.91 (4 H, m), 4.55 (2 H, s) and 7.14 (8 H, s); *m/z* 246, 244 (M$^+$), 209. Compound **13**: characterized by HPLC by comparison with an authentic sample.

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