Conclusions

OPLS parameters have been developed for the nucleotide bases and DAP. Interaction energies were obtained using these parameters for 31 base pair geometries that are consistent with the limited, related experimental data.

Relative association constants between the G–C and A–U base pairs and between G–C and U–DAP in chloroform were then calculated via Monte Carlo simulations. The results are qualitatively consistent with experimental data, although the calculated preferences for G–C are larger than the experimentally based estimates. Comparison of the two results, however, leads to similar association constants for A–U and U–DAP, a result in agreement with experiment.

The much stronger association of G–C relative to the similarly triply hydrogen-bonded U–DAP is explained by consideration of secondary electrostatic interactions. The arrangement of hydrogen-bond donor and acceptor sites in the two molecules forming a complex can lead to a substantial attractive or repulsive secondary interactions. Such considerations have general applicability in understanding variations in hydrogen-bonding complexation in many contexts.

Acknowledgment. Gratitude is expressed to the National Institutes of Health and the National Science Foundation for support of this work.

Registry No. DAP, 141-86-6; 9-methylguanine, 5502-78-3; 1-methylcytosine, 1122-47-0; 9-methyladenine, 700-00-5; 1-methyluracil, 615-77-0; uracil, 66-22-8; cytosine, 71-30-7; 4-aminopyrimidine, 591-54-8; 2-aminopyrimidin-4-one, 71-30-7; imidazole, 288-32-4; water, 7732-18-5; 1-methylthymine, 4160-72-9.

Supplementary Material Available: Optimized geometries and interaction energies for the 31 complexes of the DNA base pairs and tables showing the incremental free energy changes for the perturbation calculations (13 pages). Ordering information is given on any current masthead page.

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Activation of Carbon Dioxide by Electron Transfer and Transition Metals. Mechanism of Nickel-Catalyzed Electrocarboxylation of Aromatic Halides

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Abstract: In the presence of stoichiometric amounts of carbon dioxide, and catalytic amounts of $Ni^{II}(dppe)Cl_2$, electrolysis of bromobenzene results in the nearly quantitative formation of benzoic acid with negligible production of benzene or biphenyl. The mechanism of the nickel-catalyzed electrocarboxylation is shown to proceed through a chain reaction involving Ni(0), Ni(I), Ni(II), and Ni(III) intermediates, very reminiscent of that previously established for the nickel-catalyzed coupling of bromobenzene. Based on a detailed kinetic analysis of the propagation of this catalytic chain and of its competition with the biphenyl chain, all the key steps of the catalytic chain are identified and their rate constants determined.

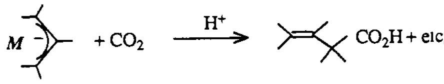
Introduction

A large amount of work has been devoted to reductive activation of carbon dioxide,[1] because of the possibility of energy storage or of using this ubiquitous molecule as a C_1 building block in organic chemistry.[2] Direct electrochemical reduction of CO_2 occurs at rather negative potentials (more negative than −2 versus SCE in most solvents). Depending on the exact experimental conditions, CO_2 reduction affords oxalate, formate, or equimolar amounts of carbon monoxide and carbonate.[1r,s] Therefore, the search for catalysts able to decrease the relatively high overpotential and to increase the selectivity of the reductive process has become an important challenge. Several groups have demonstrated that transition metal catalysts can be used advantageously in this search.[3] Indeed, carbon dioxide can bind to transition metal complexes in a variety of ways[4-8] that may allow its selective activation at rather low potentials.

In the inorganic or organometallic fields the importance of carbon dioxide coordination by metal complexes has been well recognized,[4] with a special emphasis on the creation of carbon–carbon bonds.[4,9,10] For example, CO_2 insertion into carbon–metal bonds:[10]

$$M\text{–}R + CO_2 \rightarrow M\text{–}O\text{–}C(O)\text{–}R \qquad (1)$$

or CO_2 addition to unsaturated hydrocarbons coordinated to a metal center,[4,9,11,12] as, e.g., to η^3-allyl complexes:[11]



(2)

or to η^2 complexes:[12]

$$\{M, CH_2{=}CHC_nH_{2n+1}\} + CO_2 \xrightarrow{H_2} C_{n+2}H_{2n+5}\text{–}CO_2H \qquad (3)$$

result in the overall formation of carboxylic acids or their de-

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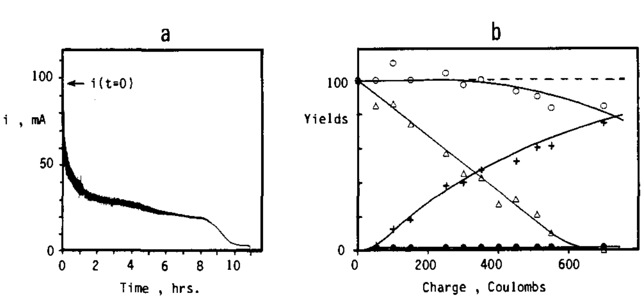

Figure 1. Preparative electrolysis ($E = -2$ V versus SCE at a mercury pool electrode) of PhBr (2.5 mmol in 65 mL) in the presence of CO_2 (saturated: 0.08 M) and of $Ni^{II}(dppe)Cl_2$ (0.25 mmol) in THF/HMPA (2:1 v/v) + 0.1 M n-Bu_4NBF_4 at 25 °C. (a) Variations of the electrolysis current with time. (b) Variations of the solution composition normalized to the initial bromobenzene, as a function of the charge consumed: (△) unreacted PhBr, (+) benzoic acid, (●) biphenyl, (○) mass balance including phenylnickel derivatives.

rivatives, in a way reminiscent of the reaction of Grignard reagents with carbon dioxide.[13]

In these reactions the reducing agent may consist of the metal itself, the anionic organic ligand (e.g., eq 1 or 2), or possibly another reagent such as hydrogen in eq 3. In an attempt to activate simpler organic reagents in the presence of catalytic amounts of readily available transition metal complexes, several authors have successfully investigated the transposition of such reactions to electrochemical conditions;[14]

$$\mathrm{R{-}X} + \mathrm{CO_2} + 2\mathrm{e} \xrightarrow{[\mathrm{M}^{n}]} \mathrm{R{-}CO_2^-} + \mathrm{X^-} \qquad (4)$$

Interestingly, the optimum experimental conditions (medium, reactant, and catalyst concentrations, electrolysis potential, electrode materials, etc.) found for reaction 4 are generally identical with or very close to those used for transition-metal-catalyzed electrochemical coupling of organic halides:[15,16]

$$2\mathrm{R{-}X} + 2\mathrm{e} \xrightarrow{[\mathrm{M}^{n}]} \mathrm{R{-}R} + 2\mathrm{X^-} \qquad (5)$$

This is a puzzling observation. Indeed, it has been shown that the metal-catalyzed dimerization in eq 5 proceeds through an efficient chain reaction without any significant termination step.[16] However, only negligible yields of dimer are usually obtained when stoichiometric amounts of CO_2 are present in the medium.[14] Moreover, the turnover numbers corresponding to the carboxylate (in the presence of CO_2) or to the dimer (in the absence of CO_2) formation are comparable. We therefore decided to investigate the mechanism of this reaction. Owing to our previous studies[16] of the mechanism of biphenyl electrosynthesis from bromobenzene catalyzed by $Ni^{II}(dppe)Cl_2$, where dppe = 1,2-bis(diphenylphosphino)ethane, we choose to develop this study using the same substrate and catalyst.

Results

As shown in Figure 1, preparative scale electrolysis (−2 V versus SCE at the mercury pool) of a solution of bromobenzene (2.5 mmol, i.e., 0.038 M in 65 mL of THF/HMPA (2:1 v/v) + 0.1 M n-Bu_4NBF_4) and carbon dioxide (0.08 M, constant concen-

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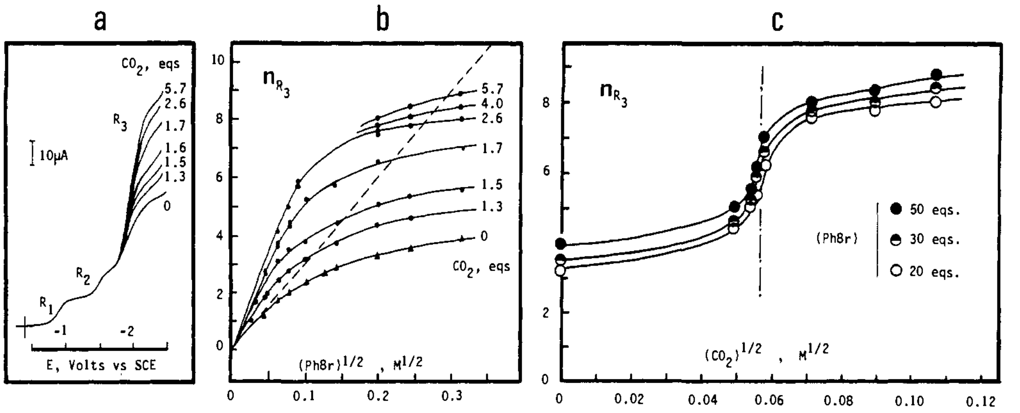


Figure 2. Steady-state voltammetry of $Ni^{II}(dppe)Cl_2$, 2 mM in THF/HMPA (2:1 v/v) + 0.1 M n-Bu_4NBF_4 at 25 °C at a gold disk rotating electrode (ϕ 2 mm, w = 105 rad s^{-1}, v = 20 mV s^{-1}). (a) Steady-state voltammogram in the presence of 10 equiv of PhBr and various amounts of carbon dioxide (numbers on the curves indicate the equivalents per nickel). (b,c) Variations of the number of electrons consumed at wave R_3 as a function of the bromobenzene and carbon dioxide concentrations.

tration imposed by continuous saturation) in the presence of $Ni^{II}(dppe)Cl_2$ (0.25 mmol) affords benzoic acid in good yields. As already observed in the absence of carbon dioxide,[16] the electrolysis current drops rapidly to a nearly constant value at which it remains poised up to the end of electrolysis (Figure 1a). The initial current drop corresponds roughly to what is observed when the electrolysis of the nickel(II) complex is performed in the absence of bromobenzene. This is in agreement with the fact that the charge consumed during this early stage of the electrolysis corresponds to almost no formation of benzoic acid although ca. 1 equiv of bromobenzene per nickel has been consumed (see Figure 1b). In a second stage, i.e., when the current is almost constant, bromobenzene disappears at a nearly steady rate[17] corresponding to 2 faradays per mole, with the concomitant formation of benzoic acid in a one-to-one stoichiometry (Figure 1b):

$$PhBr + CO_2 + 2e \xrightarrow{Ni^{II}(dppe)Cl_2,\ 10\%} Ph\text{-}CO_2^- + Br^- \tag{6}$$

Noteworthy biphenyl, formed in an overall negligible yield (<0.2%), is produced only during the earliest stages of electrolysis after the fast initial current drop.

The similarities between the biphenyl[16a] and benzoic acid electrosynthesis are further confirmed by the steady-state voltammograms presented in Figure 2a. Indeed it is seen that as in the absence of carbon dioxide, the electrochemistry of $Ni^{II}(dppe)Cl_2$ consists of two one-electron waves,[18] R_1 and R_2, and of a third wave R_3 observed only in the presence of bromobenzene. Wave R_3 features[16] the one-electron reduction of the phenylnickel(II) intermediate formed by oxidative addition of bromobenzene to the low-ligated zerovalent nickel complex formed at wave R_2:

Wave R_1

$$Ni^{II}(dppe)Cl_2 + e \rightarrow Ni^{I}(dppe)Cl + Cl^- \tag{7}$$

Wave R_2

$$Ni^{I}(dppe)Cl + e \rightarrow Ni^{0}(dppe) + Cl^- \tag{8}$$

$$Ni^{0}(dppe) + PhBr \xrightarrow{k_0} Ph\text{-}Ni^{II}(dppe)Br \tag{9}$$

Wave R_3

$$Ph\text{-}Ni^{II}(dppe)Br + e \rightarrow Ph\text{-}Ni^{I}(dppe) + Br^-, \text{etc} \tag{10}$$

It is further noted that the limiting current (of catalytic origin related to bromobenzene[16]) of wave R_3 increases by a factor of ca. 2 to 3 in the presence of CO_2, as evidenced by Figure 2, b and c. Moreover, the plots shown in this figure indicate a saturation of this trend when the concentrations of PhBr or CO_2 increase.

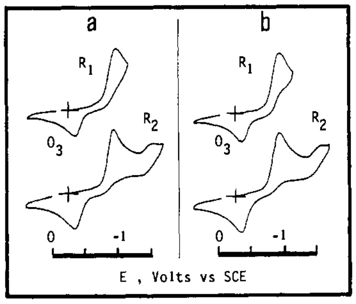
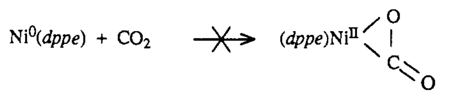


Figure 3. Cyclic voltammetry of $Ni^{II}(dppe)Cl_2$, 2 mM in THF/HMPA (2:1 v/v) + 0.1 M n-Bu_4NBF_4 at 25 °C in the absence (a) or in the presence (b) of saturated CO_2 (0.08 M). Stationary gold disk electrode (ϕ 0.5 mm, v = 0.2 V s^{-1}). Inversion potential: −1.1 (top voltammograms of a or b) or −1.65 V versus SCE (bottom voltammograms of a or b).

Since zerovalent[6b,e] or monovalent[3t] nickel complexes are reported to coordinate carbon dioxide (via insertion in one carbon–oxygen π bond), we investigated this possibility by cyclic voltammetry. Figure 3 reports the voltammograms of $Ni^{II}(dppe)Cl_2$ in the presence and in the absence of CO_2. The fact that the two sets of voltammograms are identical demonstrates that neither $Ni^{I}(dppe)Cl$ nor $Ni^{0}(dppe)$ reacts with carbon dioxide within the time scale of cyclic voltammetry.



$$Ni^{0}(dppe) + CO_2 \not\longrightarrow (dppe)Ni^{II}(\eta^2\text{-}CO_2) \tag{11}$$

Discussion

Identification of the Intermediate Reacting with CO_2. From the voltammograms in Figure 3 it is seen that the efficient catalytic electrosynthesis of benzoic acid occurring when the electrode potential is set on wave R_3 does not involve any coordination of $Ni^{I}(dppe)Cl$ or $Ni^{0}(dppe)$ by carbon dioxide. Moreover, $Ni^{II}(dppe)Cl_2$ remains untouched in the presence of CO_2, as shown by the invariance of its current peak (wave R_1) in Figure 3, a and b. On the other hand, we know that in the absence of CO_2 a fast chain leading to biphenyl[16] is initiated by the fast reaction of $Ni^{0}(dppe)$ with bromobenzene (eq 9) to afford the phenylnickel(II) complex reduced at wave R_3 (eq 10). This intermediate is also formed in the presence of CO_2 as shown by the persistence of wave R_3 in Figure 2a. Therefore, one is led to the conclusion that the fast biphenyl chain should also develop in the presence of CO_2, unless one of its transient intermediates reacts with CO_2 faster than it propagates the biphenyl chain, with the result of deactivating it. In a preceding study,[16] these intermediates have been identified as $Ni^{0}(dppe)$, $Ph\text{-}Ni^{II}(dppe)Br$, $Ph\text{-}Ni^{I}(dppe)$,

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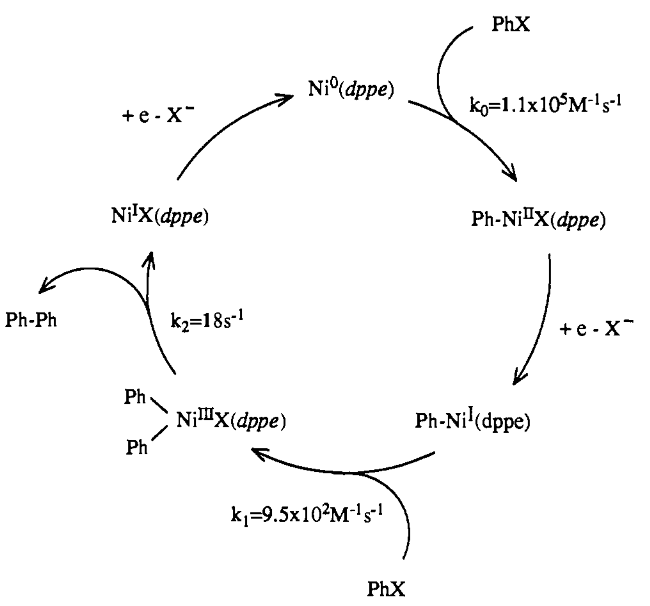
[17] Note that the value of the rate of bromobenzene consumption is comparable to that observed[16a] in the absence of carbon dioxide for identical electrolysis conditions.

[18] Amatore, C.; Azzabi, M.; Calas, P.; Jutand, A.; Lefrou, C.; Rollin, Y. *J. Electroanal. Chem.* **1990**, *288*, 45.

Scheme I (X = Br)



$(Ph)_2Ni^{III}$(dppe)Br, and Ni^I(dppe)Br (see Scheme I). Among these we know from the above results that Ni^0(dppe), $Ph{-}Ni^{II}$(dppe)Br, and Ni^I(dppe)Br are unreactive with CO_2 within a time scale compatible with the deactivation of the fast biphenyl chain. We are thus forced to conclude that this deactivation may only occur at the level of $Ph{-}Ni^I$(dppe) or at that of $(Ph)_2Ni^{III}$(dppe)Br. Noteworthy, this conclusion is in agreement with the fact that the electrode potential must be set on the plateau of wave R_3 in order to obtain benzoic acid. This is evidence that the carboxylation chain reaction requires $Ph{-}Ni^I$(dppe) and/or $(Ph)_2Ni^{III}$(dppe)Br to be formed in the medium in order to proceed. Let us then examine successively each of these two possible situations.

If $(Ph)_2Ni^{III}$(dppe)Br were the intermediate reacting with CO_2, the rate of propagation of the carboxylation chain could not exceed the rate of oxidative addition of bromobenzene to the phenylnickel(I) species electrogenerated in reaction 10:

$$\mathrm{Ph{-}Ni^{I}(dppe) + PhBr \xrightarrow{k_1} (Ph)_2Ni^{III}(dppe)Br} \qquad (12)$$

This implies that n_{R3}, the apparent number of electrons consumed at wave R_3, should be less than its limiting value imposed by eq 12:[16b]

$$n_{R3} = 2(k_1\delta^2/D)[\mathrm{PhBr}]^{1/2} - 1 \qquad (13)$$

This limit, represented by the dashed line in Figure 2b, is evidently not respected by the experimental values of n_{R3}. This suffices to demonstrate that CO_2 intercepts the biphenyl chain before reaction 12 can take place. One is then forced to conclude that the intermediate reacting with CO_2 is $Ph{-}Ni^I$(dppe).

Mechanism of the Chain Reaction Leading to Benzoic Acid. At this point we have established that the deactivation of the biphenyl chain occurs by reaction of $Ph{-}Ni^I$(dppe) with CO_2. Yet it is not known whether this reaction occurs via insertion of CO_2 into the phenyl–nickel bond to afford nickel(I) carboxylate in a single step:[19]

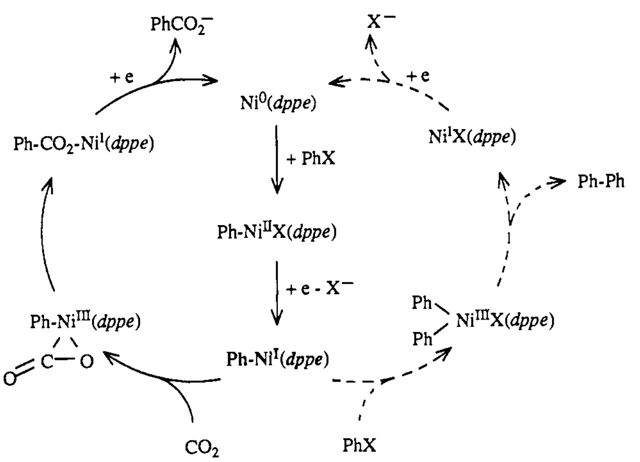
$$\mathrm{Ph{-}Ni^{I}(dppe) + CO_2 \xrightarrow{k_3} Ph{-}CO_2{-}Ni^{I}(dppe)} \qquad (14)$$

or occurs via a more complex sequence.

Independent cyclic voltammetry of $Ph{-}CO_2{-}Ni^I$(dppe) (see Experimental Section) shows that the latter is reducible (E^p −1.28 V versus SCE at 0.2 V s^{-1}) to afford Ni^0(dppe) and benzoate:

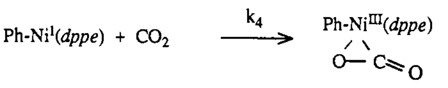
$$\mathrm{Ph{-}CO_2{-}Ni^{I}(dppe) + e \rightarrow Ni^{0}(dppe) + Ph{-}CO_2^{-}} \qquad (15)$$

Scheme II



Therefore, this intermediate must be exergonically reduced at any potential on the plateau of wave R_3. Oxidative addition (eq 9) of bromobenzene to Ni^0(dppe) thus formed, followed by a one-electron reduction (eq 10) of the phenylnickel(II), closes the catalytic cycle by regeneration of $Ph{-}Ni^I$(dppe). Were reaction 14 consisting of a single elemental step, the rate of propagation of the chain reaction should then increase when the concentration of CO_2 is increased, reflecting its acceleration. This trend should continue up to the point where eq 9 becomes the rate-determining step (rds). Then the rate of propagation of the chain should depend on the concentration of bromobenzene only, and should increase when the concentration of PhBr is increased. From this qualitative analysis of the factors controlling the rate of propagation of the chain, one does not expect to observe a simultaneous saturating effect when increasing both CO_2 and PhBr concentrations. Such a conclusion, which can be confirmed on quantitative grounds (vide infra), is then in contradiction with the trends observed in Figure 2, b and c, n_{R3} becoming independent of $[CO_2]$ or [PhBr] for large values of these concentrations.

As already discussed in the similar situation encountered for the biphenyl chain,[16] the saturating effects observed in Figure 2, b and c, prove that, when $[CO_2]$ and [PhBr] increase, the carboxylation rate is controlled by a step which has to be zero order in CO_2 or in PhBr.[20] Moreover, since n_{R3} is independent of $Ni(dppe)Cl_2$ concentration, this step must be first order in a nickel-centered species.[20] The only way to conciliate this fact with the above conclusions is to consider that eq 14 is not a true elemental reaction but occurs through a succession of at least two steps:[19] (i) reaction of CO_2 with $Ph{-}Ni^I$(dppe) to afford an intermediate adduct, followed by (ii) the first-order decay of this intermediate which affords the nickel(I) benzoate already considered in eq 14. By analogy with the reported structures of nickel(II) complexes (compare eq 11), the intermediate adduct can be tentatively described as follows:[21]

 (16)

$$\mathrm{Ph{-}Ni^{I}}(dppe) + \mathrm{CO_2} \xrightarrow{k_4} \mathrm{Ph{-}Ni^{III}}(dppe)(\mathrm{O{-}C{=}O}) \qquad (16)$$

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[19] For a discussion, in the context of Rh(I), of the concerted or nonconcerted nature of insertion of CO_2 into M–R bond, see ref 10i.

[20] (a) Amatore, C. In *Organic Electrochemistry*, 3rd ed.; Baizer, M., Lund, H., Eds.; Marcel Dekker: New York, 1991; Chapter 2, pp 11–119. (b) Amatore, C.; Savéant, J.-M. *J. Electroanal. Chem.* **1983**, *144*, 59. (c) Andrieux, C. P.; Savéant, J.-M. In *Investigation of Rates and Mechanisms of Reactions*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. 6, 4/E, Part 2, pp 305–390.

[21] By analogy with the reaction[6b,e] of $Ni^0(PR_3)_2$ with CO_2, where nickel–carbon and nickel–oxygen bonds are created, with the result of an increase in the oxidation state of the nickel center (from 0 to +II), we favor a description of the adduct in eq 16 as a nickel(III). On purely formal grounds, this reaction may then be viewed as an oxidative addition of a phenylnickel(I) center into a C–O π bond. For oxidative addition to electron-rich Ni(I) species (eq 16) see ref 16 and: (a) Gosden, C.; Healy, K. P.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1978**, 972. (b) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547. (c) Tsou, T. T.; Kochi, J. K. *J. Org. Chem.* **1980**, *45*, 1930. (d) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627.

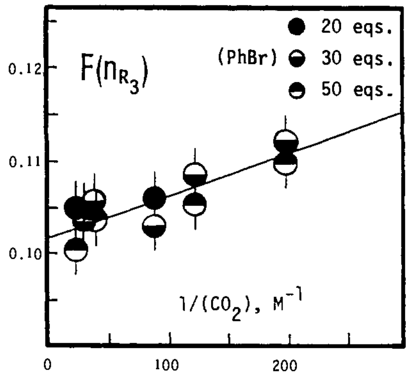
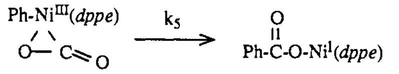


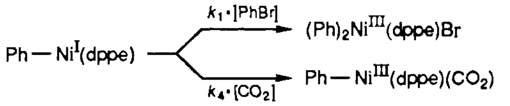
Figure 4. Variations of $F(n_{R3}) = \{(2\delta/D^{1/2})/(n_{R3}+1)-(k_0[PhBr])^{-1/2}\}$ as a function of $[CO_2]^{-1}$. See text and eq 21 and 22 for definition of the variables used in $F(n_{R3})$.

Insertion[22] of CO_2 affords the nickel(I) benzoate previously considered in eq 14:

 (17)

As already explained in the discussion related to eq 14, reduction of the nickel(I) benzoate (eq 15) followed by eq 9 and 10 closes the catalytic cycle. When the electrode potential is set on the plateau of wave R_3, each of the electron transfers involved in the propagation of the chain (see Scheme II) are diffusion controlled. The only steps which may then control the rate of propagation of the chain are its three homogeneous steps.

Determination of the Rate Constants of Addition of CO_2 (k_4 in Eq 16) and Insertion of CO_2 (k_5 in Eq 17). Examination of the variations of n_{R3} versus $[CO_2]^{1/2}$ in Figure 2c shows that a sharp transition occurs around ca. 1 equiv of CO_2 per nickel. Within the accuracy of the measurements the location of this transition point is independent of the concentration of PhBr. This establishes that the origin of the transition is not a competition between the additions of PhBr and CO_2 on Ph–Ni^I(dppe):



$$\text{Ph—Ni}^{I}\text{(dppe)} \xrightarrow{k_1\cdot[\text{PhBr}]} (\text{Ph})_2\text{Ni}^{III}(\text{dppe})\text{Br} \quad (18)$$

$$\text{Ph—Ni}^{I}\text{(dppe)} \xrightarrow[k_4\cdot[\text{CO}_2]]{} \text{Ph—Ni}^{III}(\text{dppe})(\text{CO}_2) \quad (19)$$

If this were the case, the transition between the two mechanisms would occur at constant values of $[CO_2]/[PhBr]$.[23,24] The fact that the transition is observed around $[CO_2] \approx [Ni^{II}(dppe)Cl_2]$ appears more consistent with a nearly total depletion of CO_2 in the diffusion layer, for small excesses. Indeed, considering $k_4 \gg k_1$ (vide infra and footnote 24 for a confirmation of this hypothesis), reaction 19 overcomes reaction 18 provided that CO_2 is not depleted in the diffusion layer. When this condition is fulfilled, the solution of the pertinent diffusion-reaction equations describing the kinetics of the carboxylation chain shows that at the rotating disk electrode (RDE) the apparent number of electrons consumed on the plateau of wave R_3 is given by:[23,25]

$$n_{R3} + 1 = 2(\delta/D^{1/2})/\{(k_0[PhBr])^{-1/2} + (k_4[CO_2])^{-1/2} + (k_4[CO_2]/k_5)^{1/2}/[(k_4[CO_2])^{1/2} + k_5^{1/2}]\} \quad (20)$$

where k_0, k_4, and k_5 are respectively the rate constants of the reactions in eq 9, 16, and 17; δ is the thickness of the diffusion layer at the RDE[20,26] and D the average diffusion coefficient of the nickel-centered species.

Figure 2c shows also that, provided that a few equivalents of CO_2 are present in the solution, n_{R3} is almost independent of $[CO_2]$. Besides supporting the above conclusion, this also demonstrates that eq 16 is not the rds of the chain propagation. One is then forced to the conclusion that reaction 16 is considerably faster than the insertion in eq 17. Under these conditions, i.e., for $k_5 \ll (k_4[CO_2])$, a series expansion of eq 20 allows one to predict that[23]

$$F(n_{R3}) = \{(2\delta/D^{1/2})/(n_{R3} + 1) - (k_0[PhBr])^{-1/2}\} \quad (21)$$

is a linear function of $(1/[CO_2])$:

$$F(n_{R3}) = k_5^{-1/2} + (k_5^{1/2}/k_4)[CO_2]^{-1} \quad (22)$$

Replotting of the data already presented in Figure 2, b and c, under the form of eq 21 and 22 (where[16] $k_0 = 1.1 \times 10^5$ M^{-1} s^{-1} and $(2\delta/D^{1/2}) = 1.09$ s$^{1/2}$) affords Figure 4. Since the system behaves under conditions where reaction 16 affects only marginally the kinetics of the chain, the effect of the CO_2-dependent term in eq 22 is small (compare Figure 2c). The variations in Figure 4 are therefore small, being close to the experimental uncertainties. Thus, the plot in Figure 4 does not ascertain the validity of eq 22 (linear dependence of $F(n_{R3})$ on $[CO_2]^{-1}$), but merely shows that our data are consistent with the kinetic formulation in eq 22. From the intercept of the correlation line, one can determine k_5

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[22] (a) Within the formalism considered in footnote 21, reaction 17 may be viewed as a reductive elimination, involving the creation of a carbon–phenyl bond, the oxygen atom remaining coordinated to the nickel center. For fast reductive eliminations from nickel(III) intermediates, see, e.g., ref 21b–d and: (i) Morrell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 7262. (ii) Almemark, M.; Akermark, B. *J. Chem. Soc., Chem. Commun.* **1978**, 66. (b) We consider that the nickel(III) intermediate formed in eq 16 is not reducible under our experimental conditions. Otherwise, an alternative mechanism consisting of a one-electron reduction of the nickel(III) intermediate formed in eq 16, necessarily followed by elimination of Ph-CO_2^- from the nickel(II) formed must be considered,[23] since the cycle is operative. Yet treatment of our data within this second mechanistic frame results in severe inconsistencies (negative rate constants are obtained)[23] in the evaluation of the rate constant of elimination of benzoate from the electrogenerated nickel(II) intermediate. On this basis we are enclined to favor the mechanism given in the text. Compare ref 16b for a similar situation in the case of biphenyl.

[23] Amatore, C.; Jutand, A. *J. Electroanal. Chem.* **1991**, in press.

[24] When the competition with biphenyl chain is considered, one must consider the following sequence[16] (compare Scheme I):

$$\text{PhNi}^{I}(\text{dppe}) + \text{PhBr} \rightarrow (\text{Ph})_2\text{Ni}^{III}(\text{dppe})\text{Br} \quad (k_1)$$

$$(\text{Ph})_2\text{Ni}^{III}(\text{dppe})\text{Br} \rightarrow \text{Ph-Ph} + \text{Ni}^{I}(\text{dppe})\text{Br} \quad (k_2)$$

$$\text{Ni}^{I}(\text{dppe})\text{Br} + e \rightarrow \text{Ni}^{0}(\text{dppe}) + \text{Br}^-$$

in addition to the reaction sequence in eqs 9, 10, 16, 17, and 15. Resolution of the corresponding kinetic equations[23] shows that the competition between the two chains depends on the magnitude of the parameter:

$$p = (k_4/k_1)([CO_2]/[PhBr])$$

The biphenyl chain is outrun for $p \gg 1$, whereas $p \ll 1$ corresponds to the converse situation. Introducing $k_4 \approx 1.5 \times 10^5$ M^{-1} s^{-1} as determined here (vide infra), and $k_1 \approx 10^3$ M^{-1} s^{-1} as determined previously,[16] shows that, provided PhBr and CO_2 are present in stoichiometric amounts in the solution, p is of the order of 100 to 200. Such a value is sufficient for the carboxylation chain to account for more than 99% of the conversion of bromobenzene. Note that for the preparative experiment presented in Figure 1, $[CO_2] = 0.08$ M was initially ca. twice $[PhBr] = 0.038$ M, which favors even more the formation of benzoate. Moreover, since $[CO_2]$ was kept constant by saturation during electrolysis, while PhBr decreased, this also explains why biphenyl is produced (yield <0.2%) only during the early stages of electrolysis.

[25] Note that if reactions 16 and 17 were a single elemental step[19] with a rate constant k_3 (compare eq 14), eq 20 would be replaced by:[23]

$$n_{R3} + 1 = 2(k_3[CO_2]k_0[PhBr][\delta^2/D])^{1/2}/\{k_3[CO_2]^{1/2} + k_0[PhBr]^{1/2}\}$$

where δ is the diffusion layer thickness and D the average diffusion coefficient of the nickel-centered species. Indeed, kinetically, this is equivalent to making k_5 infinite and replacing k_4 by k_3 in eq 20. Such an expression predicts that $(n_{R3} + 1) \propto [CO_2]^{1/2}$ when $k_0[PhBr] \gg k_3[CO_2]$, i.e., at large bromobenzene concentrations, whereas $(n_{R3} + 1) \propto [PhBr]^{1/2}$ when $k_3[CO_2] \gg k_0[PhBr]$, i.e., at large CO_2 concentrations. Therefore, under these conditions it is expected that n_{R3} should increase as either $[CO_2]^{1/2}$ or $[PhBr]^{1/2}$, in contradiction with the observations in Figure 2, b and c. Oppositely, when $[CO_2]$ and $[PhBr]$ are increasingly large, eq 20 predicts that n_{R3} is limited by:[23]

$$(n_{R3})_{max} = -1 + 2(k_5\delta^2/D)^{1/2}$$

which corresponds to a kinetic control of the chain by the insertion step in eq 17 (with a rate constant k_5). This limit is independent of either $[CO_2]$ or $[PhBr]$, a result in qualitative agreement with the trend of the experimental data in Figure 2, b and c.

[26] (a) Levich, V. G. *Physicochemical Hydrodynamics*; Prentice-Hall: Englewood Cliffs, NJ, 1962. (b) Bard, A. J.; Faulkner, L. R. In *Electrochemical Methods*; Wiley: New York, 1980.

$\approx 10^2$ s^{-1} for the rate constant of insertion in eq 17. From its slope, one can estimate the rate constant k_4 of CO_2 addition to Ph–Ni^{I}(dppe) in eq 16; $k_4 = (1.5 \pm 0.5) \times 10^5$ M^{-1} s^{-1}.

Conclusion

The fact that the addition of CO_2 to Ph–Ni^{I}(dppe) in eq 16 is ca. 100 to 200 times faster than that of PhBr to the same intermediate explains why the biphenyl chain is totally annihilated when carbon dioxide is present in stoichiometric amounts in the reaction medium.[24] Yet this does not mean that the carboxylation chain is considerably faster than the biphenyl one. Indeed, the rate of propagation of the carboxylation chain, i.e., the value of the apparent number of electron exchanged at wave R_3, is limited by its slowest step, i.e., the insertion of CO_2 in eq 17. Then:[23]

$$(n_{R3})_{\text{carbox}} \leq -1 + 2(k_5\delta^2/D)^{1/2} \qquad (23)$$

Similarly, in the absence of CO_2, the rate of biphenyl formation is limited by the rate of the reductive elimination of biphenyl from the $(Ph)_2$Ni^{III}(dppe)Br intermediate:[16]

$$(n_{R3})_{\text{biphen}} \leq -1 + 2(k_2\delta^2/D)^{1/2} \qquad (24)$$

The rate constants, $k_5 \approx 10^2$ s^{-1} and $k_2 \approx 20$ s^{-1},[16] of these two reactions being of comparable magnitude, the rates of propagation of the two chains are comparable:

$$(n_{R3})_{\text{carbox}}/(n_{R3})_{\text{biphen}} \approx (k_5/k_2)^{1/2} \approx 2.5 \qquad (25)$$

in agreement with the experimental observations (see, e.g., Figure 2a).

The biphenyl chain involves two oxidative addition steps of bromobenzene,[16] one with Ni^0(dppe), the second with Ph–Ni^{I}(dppe). In agreement with chemical expectations,[21a–d] it was found that the reaction with Ni^0(dppe) is considerably faster than that with Ph–Ni^{I}(dppe):

$$\text{Ni}^0(\text{dppe}) + \text{PhBr} \rightarrow \text{Ph–Ni}^{II}(\text{dppe})\text{Br}$$

$$k_0 = 1.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$$

$$\text{Ph–Ni}^{I}(\text{dppe}) + \text{PhBr} \rightarrow (\text{Ph})_2\text{Ni}^{III}(\text{dppe})\text{Br}$$

$$k_1 = 9.6 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$$

Similarly the carboxylation chain also involves two addition steps, but now they differ in nature. Ni^0(dppe) still reacts with PhBr, but is unreactive with CO_2. Conversely Ph–Ni^{I}(dppe) reacts ca. 100 to 200 times faster with CO_2 than with PhBr. This is evidence that the chemical nature of these two steps is intrinsically different.[27] This difference may be related to the fact that Ni^0(dppe) is a diamagnetic species, whereas Ph–Ni^{I}(dppe) is paramagnetic. On the other hand, owing to its π bonds, CO_2 is prone to radical additions at the carbon center.[1r] A tentative explanation for the observed inversion of reactivity may then be that the reaction of Ph–Ni^{I}(dppe) with CO_2 is of radical nature, a pathway impossible to achieve for the reaction between Ni^0(dppe) and CO_2 and obviously difficult for Ph–Ni^{I}(dppe) and PhBr.

Experimental Section

Chemicals. THF (Janssen) was dried and distilled from sodium benzophenone. HMPA (Merck) was distilled from CaH_2. Bromobenzene (Janssen) was distilled prior use. CO_2 was purchased from l'Air Liquide and dried over $CaCl_2$ before use. Ni^{II}(dppe)Cl_2 was prepared according to a published procedure.[28] Ph-Ni^{II}(dppe)Br was synthesized according to a previously reported procedure.[16a] Ph–CO_2–Ni^{I}(dppe) was generated in situ by cyclic voltammetry, from one-electron reduction of Ni^{II}(Ph-CO_2)$_2$(dppe) in THF/HMPA (2:1 v/v) + 0.1 M n-Bu_4NBF_4 (vide infra). Ni^{II}(Ph-CO_2)$_2$(dppe) was obtained by reaction of Ni$^{II}Cl_2$(dppe) with 2 equiv of sodium benzoate in the same medium.[29]

Instruments. Preparative electrosynthesis were carried out with a Solea-Tacussel PRT 4Q-1X potentiostat connected in series with a Tacussel IG5-LN coulometer. The same potentiostat was used for RDE experiments. Cyclic voltammetry was performed with a homemade ultrafast potentiostat equipped with positive feedback ohmic drop compensation.[30] The signal generator was an EG&G PARC Model 175.

Chemical analysis and product identifications were performed using the following instrumentation: Brucker WH 80 for ^{1}H NMR, and LKB 2152 equipped with a reverse-phase column (RP 18, 5 μm, 250 × 4 mm) and a UV detector (254 nm) for HPLC analyses.

Electrochemical Experiments. Voltammetric experiments were performed under argon/CO_2 mixtures in an air-tight cell connected to a vacuum line and used according to classical vacuum line techniques. The cell was double jacketted to ensure a proper temperature control (usually at 25 °C) using a Lauda RC20 cryostat/thermostat. For cyclic voltammetry, the working electrode consisted of a gold[31] disk (ϕ 0.5 mm) obtained by cross section of a gold wire sealed into Pyrex. Rotating disk electrode (RDE) experiments were performed with a RDE Tacussel EDI 65109 equipped with a gold[31] disk (ϕ 2 mm) electrode and controlled by a Tacussel Controvit. In both cases, the reference electrode was a SCE (Tacussel C10) equipped with a bridge (3 mL) of composition identical with that of the cell. All potentials given in the text refer to this reference electrode. The counter electrode was a platinum spiral of ca. 1 cm^2 apparent surface area, located at ca. 1 cm from the working electrode, facing to it. The voltammetric cell was filled with 14 mL of THF/HMPA (2:1 v/v) + 0.1 M n-Bu_4NBF_4.

Preparative electrosyntheses were performed at room temperature under a stream of CO_2, in a two-compartment air-tight three-electrode cell. The two compartments (ca. 80 mL) were separated by a sintered glass disk (ϕ 4 cm, porosity 4). The working electrode was a mercury pool[31] of ca. 25 cm^2 surface area. A lithium rod was used as the anode. The reference electrode was a SCE (Tacussel C10) equipped with a bridge (3 mL) of composition identical with that of the cell. Each of the cathodic and anodic compartments were filled with 65 mL of THF/HMPA (2:1 v/v) + 0.1 M n-Bu_4NBF_4. The electrolysis described in Figure 1 was conducted at a constant potential of –2 V versus SCE. Every 50 C, 100-μL samples were withdrawn from the solution and analyzed by HPLC after addition of a known amount of anisole as an internal standard. Eluant was a mixture of acetonitrile and water (1:1 v/v) containing 2% by weight of acetic acid. After 50 C an aliquot of the electrolyzed solution was transferred with a cannula to an NMR tube previously filled with argon. In addition to the signals pertaining to free PhBr, the ^{1}H NMR (80 MHz, versus TMS) spectrum of the sample showed the presence of a phenylnickel species[16a] [7.55 ppm, multiplet (8 H: PPh_2 coordinated to Ni); 7.28 ppm, multiplet (12 H: PPh_2 coordinated to Ni); 6.85–7.05 ppm, multiplet (5 H: Ph coordinated to Ni); 2.52 ppm (4 H: CH_2 from dppe coordinated to Ni)], at a concentration close to that of the initial Ni^{II}(dppe)Cl_2. No evidence for free benzene in the solution could be obtained from the NMR spectrum. Yet, after acidic hydrolysis, benzene was detected by HPLC at a concentration similar to that of the initial Ni^{II}(dppe)Cl_2. This was accounted for considering that benzene results from hydrolysis of the phenylnickel intermediates under acidic conditions.[16a] In the last stages of electrolysis, benzene was produced in higher amounts (compare Figure 1b for conversions > 60%, i.e., for $Q > 500$ C).

Cyclic Voltammetry of $(PhCO_2)_2$Ni^{II}(dppe). Cyclic voltammetry of $(PhCO_2)_2$Ni^{II}(dppe), 2 mM in THF/HMPA (2:1 v/v) + 0.1 M n-Bu_4NBF_4, is almost identical with that represented on Figure 3 for Ni$^{II}Cl_2$(dppe). Thus two reduction peaks, R'_1 or R'_2 ($E^p = -0.98_5$ and -1.28_0 V versus SCE at 0.2 V s^{-1}, respectively; compare R_1 and R_2 in Figure 3), of unequal sizes are followed upon scan inversion by an anodic peak ($E^p = -0.41_0$ V versus SCE at 0.2 V s^{-1}) featuring the reoxidation of Ni^0(dppe).[16a] Peak R'_1 corresponds to a one-electron reduction of $(PhCO_2)_2$Ni^{II}(dppe), as determined by the procedure in ref 18, which then affords $PhCO_2$Ni^{I}(dppe), reduced at wave R'_2. The latter undergoes a partial dimerization while the potential is scanned between waves R'_1 and R'_2. This decreases the concentration of $PhCO_2$Ni^{I}(dppe) to be reduced at R'_2, with the result of wave R'_2 being smaller than wave R'_1,

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[27] (a) For a discussion on the nature of oxidative addition (concerted, via electron transfer, via radical transfer, etc.), see, e.g., ref 21b,c and: Amatore, C.; Pflüger, F. *Organometallics* **1990**, *9*, 2276. (b) Note that in THF/HMPA (2:1 v/v) CO_2 and PhBr are reduced in the same potential range (at 0.2 V s^{-1}, E^p = –2.75 and –2.85 V versus SCE, respectively).

[28] Chatt, J.; Booth, G. *J. Chem. Soc.* **1965**, 3238.

[29] Compare: Soyenkoff, B. C. *J. Phys. Chem.* **1930**, *34*, 2519.

[30] Amatore, C.; Lefrou, C.; Pflüger, F. *J. Electroanal. Chem.* **1989**, *270*, 43.

[31] Preparative scale electrocarboxylations, mediated by transition metal complexes, are independent of the nature of the cathode material (compare, e.g., ref 14d and 14f). In transient electrochemistry, we found that gold electrodes gave a better resolution of the waves than other cathode material. This may be due to apparent variations of the rate of heterogeneous electron transfers, due to inhomogeneities at electrode surfaces.[32]

[32] Amatore, C.; Tessier, D.; Savéant, J.-M. *J. Electroanal. Chem.* (a) **1983**, *146*, 37; (b) **1983**, *147*, 39.

in a similar fashion as was already observed in the electrochemistries of $Ni^{II}Cl_2$(dppe) and $Ni^{II}Br_2$(dppe)[16a] (compare, e.g., the respective sizes of waves R_1 and R_2 in Figure 3). However in steady-state voltammetry, provided that the electrode potential is maintained at a potential on the plateau of wave R'_2, the effect of the partial dimerization of $PhCO_2Ni^I$(dppe) is negligible on the rate of propagation of the carboxylation chain.[16,33]

Determination of Carbon Dioxide Concentration. One of the main experimental difficulties in this work consists in the determination of the concentration of carbon dioxide in the reaction medium, with an accuracy sufficient for kinetic studies to be conducted. For this purpose the solution was first saturated by bubbling with a known mixture of CO_2 and argon, adjusted with two floating ball flowmeters (OSI). After saturation, the cell was kept under a continuous stream of the same argon/CO_2 mixture. After each series of voltammetric experiments corresponding to a given concentration of CO_2, $[CO_2]$ was determined for this series of experiments according to the following procedure.[34] $BaCl_2$ (1 g) was added to the cell. A known volume of 0.01 M NaOH was then added to the solution up to the point of color change of *o*-cresolphthaleine. The excess of $Ba(OH)_2$ was then determined by titration with 0.01 M HCl.

For preparative electrolysis the solutions were saturated by continuous bubbling of pure CO_2. For a cell maintained at 25 °C, $[CO_2]_{sat} = 0.08$ M was obtained in THF/HMPA (2:1 v/v) + 0.1 M *n*-Bu_4NBF_4.

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[33] Amatore, C.; Savēant, J.-M. *J. Electroanal. Chem.* **1981**, *125*, 23.

[34] Pieters, H. A. J. *Anal. Chim. Acta* **1948**, *2*, 263.