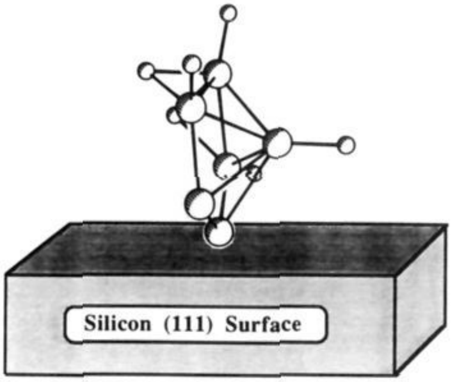

Figure 3. Schematic representation showing the orientation of the adsorbed carborane molecule on the Si(111) surface.

toemission binding energies with the MNDO derived bonding energies. The differences between the calculated energies for the parent *nido*-2,3-$C_2B_4H_8$ cage and the binding energies observed for the adsorbed molecular species at low coverage is about 7.3 ± 0.2 eV except for the photoemission bands at 8.6, 14.6, and 17.2 eV. By applying the assignments shown in Figure 1 and Table I, the photoemission features which have binding energies smaller than expected (the 8.6 eV band) can be assigned to molecular orbitals with substantial C(2) or C(3) atomic contributions. If the carbons are bound to the Si(111) surface via lone pair p-electrons, then these carborane molecular orbitals would be either nonbonding or only very weakly bonding. The photoemission feature at 14.6 eV has a binding energy much greater than expected based on a comparison of the MNDO calculated molecular orbital energies and the photoemission features. This feature can be assigned to a molecular orbital with large C(2) and C(3) 2s components and would strongly bond with the silicon surface with the orientation of carbon atoms toward the silicon surface.

With increasing exposure, further carborane molecular species are adsorbed. The increase in the intensity and width of the 6.5 eV feature relative to the other photoemission features, as seen in Figure 2, is indicative of the adsorption of molecular species *with* ethyl groups intact. This is confirmed by the existence of two molecular orbital features at 12.6 and 13.3 eV which cannot be reconciled with the calculated *nido*-2,3-$C_2B_4H_8$ molecular orbitals (Figure 1). Thus, with increasing molecular coverage, molecular adsorption results in no loss (or at least a smaller loss) of ethyl groups and a decreasing amount of molecular fragmentation. Similar results have been observed for highly reactive molecular diatomic species.[3,4]

On the basis of the photoemission results, it is apparent that with increasing molecular coverage the molecular species adsorb with increasingly random orientations. This may be a consequence of the presence of the relatively bulky exopolyhedral ethyl groups in the adsorbed molecular species. These ethyl species would effectively provide a significant steric blocking of the C(2) and C(3) atoms with respect to the surface. In addition, the ethyl groups are not as rigidly oriented as the *nido*-2,3-$C_2B_4H_6$ cage framework and would therefore make adsorption in one specific orientation difficult.

Conclusion

In summary, on the basis of angle-resolved photoemission results and MNDO theoretical calculations, it appears that the initial adsorption of diethylcarborane on Si(111) at 90 K results in the loss of ethyl units. The adsorption of the parent *nido*-2,3-$C_2B_4H_8$ fragment is otherwise molecular. This molecular fragment bonds to the surface with the basal plane of the carborane molecule essentially parallel with the surface normal. Subsequent molecular adsorption results in little or no fragmentation, but the molecules adsorb with increasingly random orientations with respect to the surface normal.

Acknowledgment. We thank the National Science Foundation (Grants No. DMR-8820779 and MSS-89-09793), the Wisconsin Alumni Research Foundation, and the Wright-Patterson Laboratory (Award No. F33615-90-C-5291) for support of this work. The authors thank Mr. John A. Glass, Jr. and Prof. T. Whelan (S.U.N.Y. Potsdam) for their technical assistance with the MNDO calculations and the staff of the Synchrotron Radiation Center in Stoughton, WI. The Synchrotron Radiation Center is supported by the National Science Foundation.

From Stoichiometry to Catalysis: Electroreductive Coupling of Alkynes and Carbon Dioxide with Nickel–Bipyridine Complexes. Magnesium Ions as the Key for Catalysis

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Abstract: The incorporation of carbon dioxide into nonactivated alkynes catalyzed by electrogenerated nickel–bipyridine complexes affords α,β-unsaturated acids in moderate to good yields. The electrocarboxylation reaction was undertaken on a preparative scale in the presence of a sacrificial magnesium anode: the formation of acids from alkynes is stoichiometric with respect to the nickel complex if performed in a two-compartment cell but can be made catalytic in a single-compartment cell. An intermediate nickelacycle was isolated from the reaction with 4-octyne. The cleavage of this metallacycle by magnesium ions is the key step to explain catalysis.

Introduction

The vast natural abundance of carbon dioxide in the world makes it an attractive raw material for the synthesis of organic compounds. The development of catalytic reactions that form C–C bonds from CO_2 has the potential to provide short, economical routes to functionalized products.

The coordination chemistry of carbon dioxide and its biological, chemical, photochemical, and electrochemical activity have been recently reviewed.[1-3] Although CO_2 binding to metal complexes

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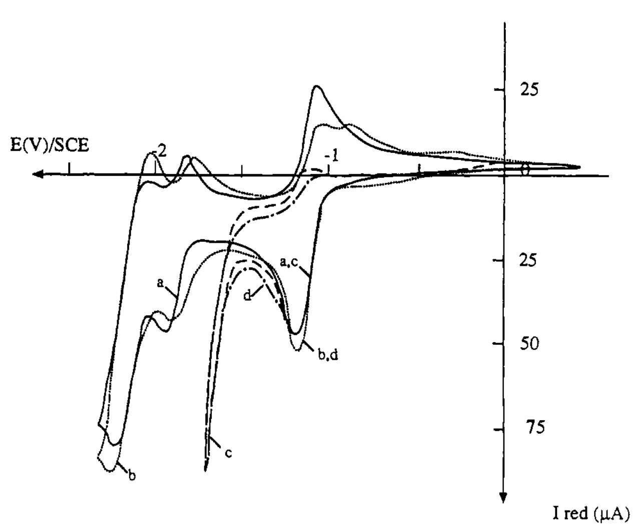


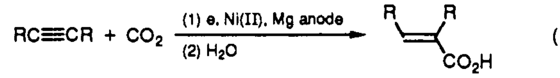
Figure 1. Cyclic voltammograms obtained with a freshly polished vitreous carbon microelectrode (3 mm^2) at 20 °C at a scan rate of 100 mV·s^{-1} for a solution of **1** (0.3 mmol) in DMF (30 mL) containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte: (a) solution under argon; (b) solution after addition of 4-octyne (**2a**) (0.3 mmol); (c) solution a saturated with CO_2; (d) solution b saturated with CO_2.

has received much attention,[4,5] relatively little information is available on the transition-metal-catalyzed carbon–carbon bond formation involving CO_2.[6,7]

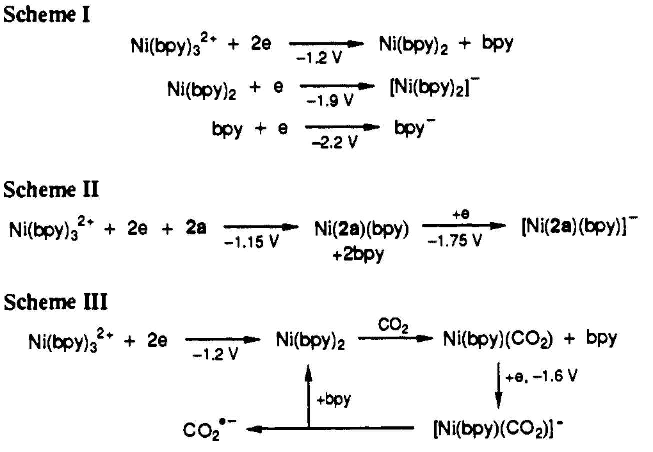
In these reactions, the role of the transition metal is to activate both the carbon dioxide and the unsaturated organic molecule toward C–C bond formation.

Hoberg and co-workers developed a method for alkyne carboxylation,[8] using stoichiometric amounts of zerovalent nickel reagents,[9] such as $Ni(COD)_2$ (COD = 1,5-cyclooctadiene). The Ni(0)-catalyzed synthesis of pyrones from alkynes[10] (or diynes[11]) and CO_2 (at a pressure higher than 50 kg·cm^{-2}) has also been described.

We were interested in the reactivity of electrogenerated low-valent nickel species, and we have already reported a new method of electrosynthesis of unsaturated carboxylic acids from acetylenic derivatives and CO_2, which utilizes a catalytic amount of a Ni(II) salt as the starting complex[12] (eq 1).



(1)



Scheme I

$$Ni(bpy)_3^{2+} + 2e \xrightarrow[-1.2\ V]{} Ni(bpy)_2 + bpy$$

$$Ni(bpy)_2 + e \xrightarrow[-1.9\ V]{} [Ni(bpy)_2]^-$$

$$bpy + e \xrightarrow[-2.2\ V]{} bpy^-$$

Scheme II

$$Ni(bpy)_3^{2+} + 2e + \mathbf{2a} \xrightarrow[-1.15\ V]{} \underset{+2bpy}{Ni(\mathbf{2a})(bpy)} \xrightarrow[-1.75\ V]{+e} [Ni(\mathbf{2a})(bpy)]^-$$

Scheme III

There is considerable interest in electrochemical methodology as applied to organic[13] and organometallic chemistry.[14] Recent advances in some electrochemical reactions have been associated with the use of sacrificial anodes.[15]

The present study is devoted to the electrochemical, mechanistic, and synthetic aspects of the nickel-catalyzed electroreductive carboxylation of both terminal and internal alkynes with CO_2 under mild conditions. The octahedral complex $Ni(bpy)_3(BF_4)_2$ (**1**) (bpy = 2,2′-bipyridine) has been used as the catalyst[12] throughout this work. We first present the results of our electrochemical study on the interaction of **1** with CO_2 and alkynes and of the related preparative-scale electrolyses. The latter experiments led us to isolate, from the electrolysis medium, a nickel complex which we show to be an intermediate in the coupling reaction. In the second part of this paper, we report the use of magnesium metal as a consumable anodic material and demonstrate the importance of the Mg^{2+} ions produced for the nickel catalysis. Finally, the electrosynthesis of a series of substituted carboxylic acids was carried out in a single-compartment cell fitted with a central magnesium anode surrounded by a carbon-fiber cathode. Several mono- and disubstituted alkynes were carboxylated. The CO_2 fixation resulted in a reductive hydrocarboxylation reaction of the carbon–carbon triple bond.

Results and Discussion

Electrochemical Studies. Cyclic Voltammetry of 1. These studies were initiated by examining the electrochemical behavior of **1** in the absence and presence of alkynes and CO_2. The cyclic voltammetric curves of **1** in dimethylformamide (DMF) containing tetrabutylammonium tetrafluoroborate ($(TBA)BF_4$) as supporting electrolyte are presented in Figure 1. The reversible two-electron reducing process at −1.2 V vs SCE (curve a) results in $Ni(bpy)_2$, as clearly supported by coulometry. The second wave corresponds to a one-electron reduction of the $Ni(bpy)_2$ species at −1.9 V and, finally, the reduction of the free bpy ligand at −2.2 V. These processes are summarized in Scheme I. The voltammogram of **1** is analogous to those found in the electrochemical reduction of $Ni(bpy)Br_2$ in CH_3CN,[16] *N*-methylpyrrolidone (NMP),[17] or HMPT[18] solutions containing excess ligand.

Addition of Alkynes to 1. Nonactivated internal and terminal alkynes, i.e. 4-octyne (**2a**) and 1-octyne (**2b**), were chosen as model compounds. Reduction of **2a** or **2b** occurs at less than −2.8 V vs SCE, at which potential we observe the reduction of the solvent,

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DMF. The cyclic voltammetric behavior of **1** is modified upon addition of **2a**, as shown in Figure 1, curve b. The two-electron reducing wave of **1** is slightly advanced to −1.15 V and becomes less reversible, indicative of a fast chemical reaction between electrogenerated $Ni(bpy)_2$ and the alkyne. The interaction of the Ni(0) with the alkyne is also evidenced by the presence of several Ni(0) to Ni(II) reoxidation waves from −1.2 to −0.3 V. These different oxidation waves are indicative of the formation of several Ni^0(alkyne) complexes.[19] The further reduction of the Ni(0) complex occurs reversibly at −1.75 V. This potential change from −1.9 V in **1** to −1.75 V in the presence of the alkyne can be explained via ligand exchange between the alkyne and bpy (Scheme II). The $Ni(bpy)_2$ is known to be unreactive due to the strong bonding of bpy with tetracoordinated Ni(0),[18] but the cyclic voltammetry curves show that it is reactive toward alkyne ligand substitution under the electrochemical conditions.

Addition of Carbon Dioxide to 1. The direct reduction of carbon dioxide occurs at potentials more negative than −2.2 V, in agreement with literature data.[20a] The solubility of CO_2 in DMF at 25 °C was estimated to be about 2×10^{-1} M. Bubbling CO_2 into a solution of **1** results in the modified cyclic voltammograms, as illustrated in Figure 1, curve c. The first two-electron reducing wave remains at −1.2 V and becomes less reversible, whereas a catalytic wave appears at −1.6 V. Earlier work has shown that the catalytic process observed is characteristic of the reduction of coordinated CO_2 to its radical anion[16,17] (Scheme III).

Addition of Alkyne and Carbon Dioxide to 1. In the presence of both the alkyne **2a** and CO_2, the voltammogram of a solution of **1** (curve d, Figure 1) exhibits a nonreversible Ni(II)/Ni(0) transition at −1.15 V and an irreversible catalytic current at −1.6 V. Analogous with curve c in Figure 1, the catalytic wave at −1.6 V corresponds to an electron transfer to a CO_2 group coordinated to nickel in a $Ni(bpy)(\mathbf{2a})(CO_2)$ type complex.

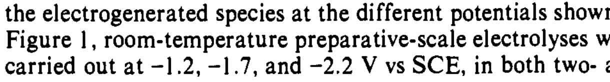
Preparative-Scale Electrolyses. To compare the reactivity of the electrogenerated species at the different potentials shown in Figure 1, room-temperature preparative-scale electrolyses were carried out at −1.2, −1.7, and −2.2 V vs SCE, in both two- and one-compartment cells.

(1) Controlled-Potential Experiments in a Two-Compartment Cell. At −1.2 V. The controlled-potential coulometry of **1** (in a $DMF-(TBA)BF_4$ solution in the cathodic compartment) in the presence of the alkyne (**2a** or **2b**) and CO_2 (bubbling at atmospheric pressure) at −1.2 to −1.4 V vs SCE proceeds with the consumption of 2 mol of electrons/mol of nickel complex. The overall electronic balance of the reaction is independent of the alkyne concentration (up to a 10-fold excess). Electrolysis of **1** followed by the simultaneous addition of the alkyne and CO_2 to the nickel(0) species gave identical results.

When the reaction is performed in a two-compartment cell, the alkyne consumption corresponds to a 1/1 reaction with the electrogenerated Ni(0) complex.

After electrolysis of **1** (at −1.2 V, 2 faradays/mol of nickel) in the presence of 4-octyne (**2a**/**1** ratio of 1) and CO_2, **2a** was entirely consumed. However, almost no organic product could be isolated through the standard workup procedure (0.1 N HCl hydrolysis followed by diethyl ether extraction). A prolonged and stronger hydrolysis of the reaction mixture (2 N H_2SO_4, 50 °C, 48 h) afforded (*E*)-2-propyl-2-hexenoic acid (**3a**) (eq 2) isolated as a methyl ester in 70% yield with respect to the alkyne. This result is consistent with the formation of an intermediate nickel complex resistant to hydrolysis, containing both the alkyne and the CO_2 moieties (for its isolation, v.i.).

$Ni(bpy)_3(BF_4)_2$ + $n\text{-}C_3H_7C{\equiv}C\text{-}n\text{-}C_3H_7$ +
1 **2a**

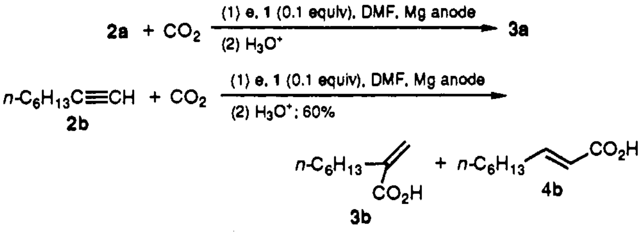


(2)

3a (70%)

At −1.7 V. When the above experiment was run at −1.7 V (at a higher intensity), the consumption rose to 2 faradays/mol of nickel. The intensity dropped to zero when only about 50% of the alkyne was reacted, and **3a** was isolated in 35% yield with respect to the initial alkyne. At −1.7 V, the nickel-mediated carbon dioxide–alkyne coupling is competitive with a second process that corresponds to the reduction of carbon dioxide at −1.6 V in the presence of $Ni(bpy)_2$, in agreement with curve c in Figure 1.

Scheme IV



(2) Controlled-Potential Experiments in a Single-Compartment Cell. At −1.2 V. Interestingly, when a simple one-compartment cell fitted with a consumable magnesium anode was used, with an alkyne/nickel ratio of 10 (**2a** was slowly added to a solution of **1** in DMF), the electrolysis proceeded up to the consumption of 2 faradays/mol of **2a** (i.e. 20 faradays/mol of **1**). The reaction was carried out at −1.2 to −1.4 V, at the reduction potential of the Ni(II)/Ni(0) transition, with the progressive disappearance of the alkyne (followed by GC analysis). Carboxylic acid **3a** (isolated and characterized as its methyl ester derivative) was obtained in 80% yield with respect to the alkyne after a standard workup procedure. Under these conditions, **2a** was efficiently carboxylated in 90% faradaic yield by utilizing a catalytic amount of **1**, thus with a recycling of the active Ni(0) complexes. It should be noted that no carboxylation of **2a** or **2b** occurred in the absence of complex **1** in any of the experimental conditions (one- or two-compartment cell), and neither carboxylation occurred in the absence of current. The reaction requires a continuous electrochemical generation and regeneration of the Ni(0) promoters and consumes 2 faradays/mol of alkyne.

The same behavior was observed in reactions utilizing 1-octyne (**2b**). At −1.2 V in a single-compartment cell, carboxylic acids **3b** and **4b** were formed in 60% yields and a 90/10 regioselectivity of **3b**/**4b** (Scheme IV).

At −1.7 V. An identical experiment with the electrolysis conducted at −1.7 to −1.8 V needed 3.5–4.5 faradays/mol of **2** to reach a 90% alkyne conversion. A 70% yield of **3a** was isolated from exhaustive carboxylation of **2a** at this potential. The carboxylation is in competition with the electroreduction of CO_2 (see Figure 1, curves c and d).

At −2.2 V. Performing the reduction at −2.2 V gave results concerning conversion and selectivity analogous to those obtained at −1.7 V, although a lower faradaic yield was observed.

(3) Electrolysis of 1 and CO_2 in the Absence of Alkyne in a Single-Compartment Cell. The electrochemical reduction of carbon dioxide has been the subject of numerous investigations.[20] Its reduction yields a variety of products highly dependent on the nature of the cathodic material, the catalyst, and the electrolytic conditions. In the presence of nickel–bipyridine complexes in CH_3CN[16] or NMP,[17] reduction and disproportionation of carbon dioxide to CO and CO_3^{2-} utilizing platinum or gold cathodes have been described.

In a single-compartment cell (DMF, Mg/carbon-fiber or gold electrode), the CO_2 reduction at −1.6 to −1.7 V vs SCE (see Figure 1, curve c) was catalyzed by **1** to give a mixture of magnesium oxalate, carbon monoxide, and magnesium carbonate. These products are a result of two competitive reactions of the radical anion of carbon dioxide (see Scheme V).

The reduction of CO_2 at −1.7 V in the presence of alkyne and electrogenerated $Ni(bpy)_2$ is in competition with alkyne carbox-

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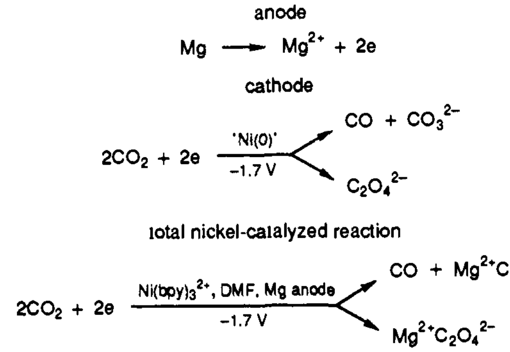
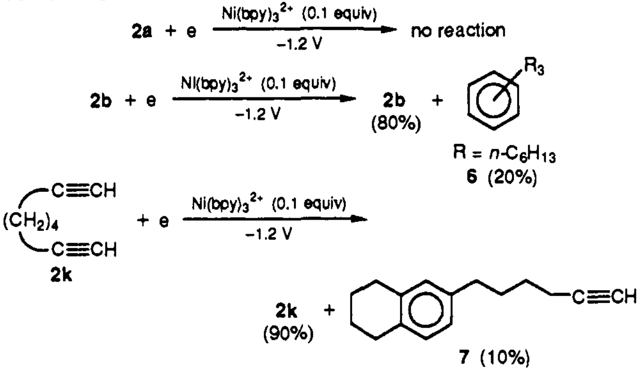
Scheme V



Scheme VI



ylation that occurs at the same potential (see Figure 1, curve d). These competing processes cause a decrease in the current efficiency for the alkyne carboxylation, 40–60% faradaic yield.

(4) Electrolysis of 1 and Alkynes in the Absence of CO_2 in a Single-Compartment Cell. Numerous Ni(0) reagents[21] are active catalysts for the oligomerization of alkynes, giving trimers or tetramers as the major products, depending upon the ligands attached to Ni.

To our surprise, when electrolyses of **1** and **2a** were run at −1.2 to −1.4 V in the absence of CO_2 under argon, the alkyne was relatively inert and could be quantitatively recovered at the end of the reaction. With use of the more reactive terminal alkyne **2b** (in a 10/1 molar ratio of **2b**/$Ni(bpy)_3^{2+}$), less than 20% of the alkyne was converted into trimers **6**. With 1,7-octadiyne (**2k**), dimer **7** was isolated in less than 10% yield (Scheme VI).

Under these conditions, the electrogenerated $Ni(bpy)_2$ complex in DMF is not a suitable catalyst for alkyne oligomerization, although an alkyne coordination to Ni(0) takes place according to cyclic voltammetry (see Figure 1, curve b).

However, it should be noted that the presence of CO_2 enhanced the catalytic activity of $Ni(bpy)_2$ toward alkyne oligomerization. When excess alkyne is used (particularly for terminal alkynes such as **2b**) in electrolysis of **1** under CO_2 at −1.2 V (one-compartment cell), dimers and trimers may be obtained in up to 70% yields. The fact that CO_2 can enhance the oligomerization rate suggests that it interacts with the metal center, changing the catalytic properties. An enhanced oligomerization of butadiene by CO_2 has already been reported for Pd complexes.[22]

Due to the competitive oligomerization of alkynes by complex **1** under CO_2, a slow syringe-pump addition of the substrate during electrolysis allowed a substantial increase in the yield of the carboxylation.

(5) Intensiostatic Conditions for Carboxylations in a Single-Compartment Cell. On the preparative scale also, the results obtained in the electrolysis of **2a** or **2b** catalyzed by **1** (2/1 ratio of 10/1) run in DMF/$(TBA)BF_4$ solutions at imposed constant current intensity (50 mA, apparent cathodic current density of 0.2–0.3 A·dm^{-2}) in a one-compartment cell with a Mg anode were similar to those obtained under controlled potential at −1.2 V. Thus, carboxylation of **2a** at imposed constant intensity yielded **3a** in 80% yield. **2b** afforded 60% of carboxylated compounds, from which **3b** was the predominant isomer (**3b**/**4b** ratio of 90/10) (Scheme IV).

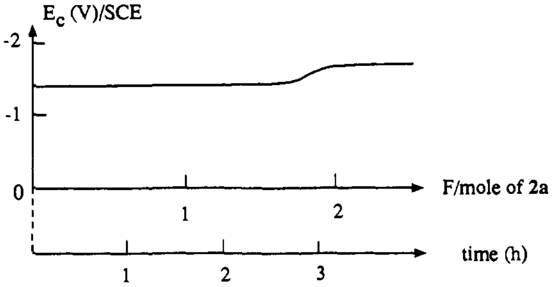


Figure 2. Cathode potential (V vs SCE) versus electricity consumed or versus time measured during electrocarboxylation of **2a** (3 mmol) in a DMF solution (40 mL) containing **1** (0.3 mmol) and $(TBA)BF_4$ (0.3 mmol) at a constant intensity of 50 mA, in a one-compartment cell with Mg/carbon-fiber electrodes.

From both a preparative and an electrochemical setup point of view (the simplicity and the cost of the equipment), the possibility of carrying out the electrocarboxylations at constant intensity is very advantageous.[15] A simple and inexpensive current supply connected to both electrodes of the cell can be utilized for preparative purposes. The carboxylations were carried out under the intensiostatic conditions, and the disappearance of the starting alkyne was followed by GC.

A plot of the cathode potential versus time (or electricity consumed) during the electrocarboxylation of **2a** is shown in Figure 2. The cathode potential stays constant at −1.4 V up to a consumption of 1.8 faradays/mol of alkyne (with 90% alkyne conversion) and then shifts to −1.6 V.

These results are in agreement with the experiments run under controlled potential; i.e., the carboxylation involves the Ni(II)/Ni(0) transition at −1.2 to −1.4 V with 2 faradays/mol of alkyne. Only toward the end of the reaction (low alkyne concentration) does the cathode potential shift to −1.6 V. At this potential, we observe a slower alkyne consumption and a loss of faradaic yield due to the competitive CO_2 reduction process (see Figure 1 and Scheme V).

The intensiostatic conditions were applied to the carboxylation of a series of alkynes after optimization of several parameters, such as CO_2 pressure, reaction temperature, solvent, supporting electrolyte, and nature of the electrodes. It should be noted that the reaction can give rise to a large variety of products, including chemio-, regio-, and stereoselective CO_2 incorporation, polycarboxylation, oligomerization, and/or reduction. We were interested in the optimal conditions for a highly regioselective CO_2 insertion into terminal alkynes such as **2b** (see Scheme IV). Apart from our work,[12a] no transition-metal-mediated or -catalyzed insertion of CO_2 into terminal alkynes has been described nor has the functionalization of the 2-position of terminal alkynes by CO_2.

Under the standard intensiostatic reaction conditions (see Experimental Section), a Mg/carbon-fiber combination was found to be the best anode/cathode couple with relation to the yield of **3b**, the regioselectivity, and the CO_2 incorporation (**3b**/**4b** ratio of 90/10). A Zn/carbon-fiber couple did carboxylate **2b** at −1.2 V in 80% yield but resulted in an inversion of regioselectivity with a **3b**/**4b** ratio of 30/70. This result is indicative of the large influence that metal cations, e.g. Mg^{2+} or Zn^{2+}, exert on the reactivity of transition-metal complexes toward CO_2.[23] Elec-

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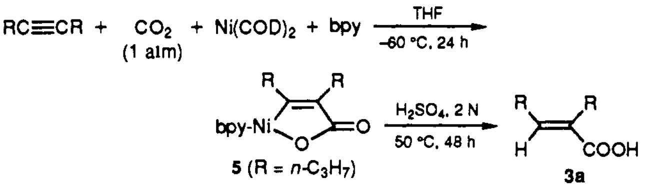
[21] See, for example: (a) Wilke, G. *Pure Appl. Chem.* **1978**, *50*, 677. (b) Rosenthal, U.; Schulz, W. *J. Organomet. Chem.* **1987**, *321*, 103. (c) Eisch, J. J.; Galle, J. E.; Aradi, A. A.; Boleslawski, M. P. *J. Organomet. Chem.* **1986**, *312*, 399. (d) Alphose, P.; Moyen, F.; Mazeroles, P. *J. Organomet. Chem.* **1988**, *345*, 209.

[22] Kohnle, J. F.; Slaugh, L. H.; Nakamaye, K. L. *J. Am. Chem. Soc.* **1969**, *91*, 5904.

[23] (a) Fischer, K.; Jonas, K.; Misbach, P.; Stabba, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 943. (b) See ref 1, pp 100 and 110; see also ref 14a. (c) Eisch, J. J.; Sexsmith, S. R.; Fichter, K. C. *J. Organomet. Chem.* **1990**, *382*, 273. (d) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5092.

Scheme VII



trocarboxylations with either a stainless steel or a nickel cathode were ineffective. Increasing the CO_2 pressure from 1 to 5 atm did not enhance the selectivity or the rate of the reaction of **2a** or **2b** but afforded better yields in the case of 1,7-octadiyne (**2k**).[12c] The increase of the reaction temperature from 20 to 70 °C favored carboxylation versus oligomerization of **2b** despite the decrease in the CO_2 solubility. Finally, the DMF—$(TBA)BF_4$ combination afforded the best results, when compared to the use of CH_3CN or NMP as solvents and KI or n-$Bu_4N^+Br^-$ as supporting electrolytes. It is noteworthy that only a low concentration of supporting electrolyte is required for this reaction (less than 10^{-2} M) in contrast to standard electrolysis. This is due to the presence of Mg^{2+} ions (from anodic oxidation), which ensure conductivity. An alkyne/**1** molar ratio of 10/1 (10% catalyst) was generally used. A turnover of 35 (3% catalyst) was reached in the electrocarboxylation of **2a** conducted at −1.4 V (**3a** was isolated in 80% yield). However, the reaction of **2b** at constant current intensity with a **2b**/**1** molar ratio of 100/1 (1% catalyst) afforded less conversion and loss of regioselectivity. Under our experimental conditions, the catalyst remains active for 8–10 h. It progressively loses its activity when a high ratio of $[Mg^{2+}]/[Ni^{2+}]$ is attained.

When **1** was first electrolyzed under intensiostatic conditions (up to 2 faradays/mol of nickel) followed by the addition of **2a** and CO_2, the electrolysis proceeded normally and **3a** was obtained in 70% yield. Thus, the presence of Mg^{2+} in solution during the preparation of $Ni(bpy)_2$ did not prevent CO_2 and alkyne addition to the electrogenerated Ni complex.

Mechanistic Outline. Isolation of Nickelacycle 5. In order to understand the factors that determine the stoichiometry or catalysis in the nickel carboxylation reactions and to make predictions of other transformations required some insight into the mechanism of this reaction.

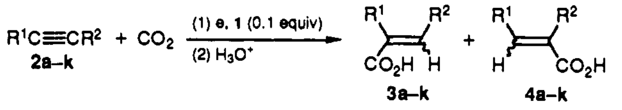
As indicated in (1), the preparative-scale electrolysis of complex **1** in the presence of **2a** and CO_2 in a two-compartment cell at −1.2 V (stoichiometric reaction with 2 faradays/mol of nickel) afforded carboxylic acid **3a** (70% yield) only after a prolonged hydrolysis (eq 2). When an identical experiment was carried out with the hydrolysis step being avoided, a nickel complex was isolated from the reaction mixture by precipitation with Et_2O. Its structure was tentatively assigned to 1-oxa-2-nickelacyclopentenone derivative **5**.

The isolation of this complex by electrosynthesis is closely related to the $Ni(COD)_2$-mediated carboxylation of disubstituted alkynes described by Hoberg.[8] Following the stoichiometric chemical procedure, we isolated a complex from **2a**, and its structure was assigned to **5** (Scheme VII).

Both complexes, isolated from the chemical and electrochemical syntheses, have identical spectroscopic properties (IR, MS) and correct elemental analyses. These metallacycles are not electroactive. They are stable complexes, although they react with MeI or CO.[8] Strong hydrolysis conditions were necessary to open the metallacycles (H_2SO_4, Δ, 48 h, 70%) to yield **3a**, in agreement with the above observations on electrocarboxylations in two-compartment cells.

The role of a Ni(0) reagent is implicated in the formation of intermediate **5** by oxidative addition of CO_2 and C≡C. Our results demonstrate that the electrochemical reduction of **1** generates in situ an active Ni(0) species under mild conditions (DMF, 20 °C, 2 h). The Ni(0) species generated is more active toward alkyne carboxylation than $Ni(COD)_2$ + bpy (THF, −60 °C, 48 h). There is a strong solvent effect that accelerates the rate of the Ni(0) reaction in DMF by increasing the coordinating power of the solvent.

Table I. Electrochemical Carboxylation of Alkynes in the Presence of **1** (10%)[a]



entry	starting alkyne	R^1	R^2	T, °C	% carboxylation	3:4
1	**2a**	n-C_3H_7	n-C_3H_7	20	93	
2	**2b**	n-C_6H_{13}	H	20	65	90:10
3	**2c**	n-$C_{12}H_{25}$	H	20	60	88:12
4	**2d**	c-C_5H_9	H	50	50	91:9
5	**2e**	Ph	H	20	55	71:29
6	**2f**	Ph	CH_3	20	72	38:62
7	**2g**	Ph	Ph	80	70	
8	**2h**	Ph	CO_2Et	5	75[b]	
9	**2i**	$AcO(CH_2)_3$	H	70	65	50:50
10	**2j**	$AcO(CH_2)_2$	CH_3	50	45	47:53
11	**2k**	$CH{\equiv}C(CH_2)_4$	H	65	60	25:50[c]

[a] For general electrosynthesis procedure, see Experimental Section (catalytic method, one-compartment cell). Carboxylic acids were esterified and analyzed as methyl esters after column chromatography. Yields are expressed in terms of the isolated methyl esters relative to the amount of alkyne that has reacted. [b] A 74/26 ratio of di- versus monocarboxylation was obtained. [c] Isomer **4** is (2-methylenecyclohexylidene)acetic acid.[36]

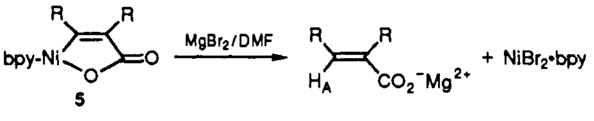
In order to prepare a nickelacycle with a monosubstituted acetylene, an analogous preparative-scale stoichiometric electrocarboxylation was carried out with the terminal alkyne **2b**. No metallacycle such as **8** or **9** (see Scheme X) could be isolated in pure form. By use of the chemical procedure for **2b** (as in Scheme VII), a powder with a high carbonate content was obtained. Analysis of the solution in both cases revealed the presence of dimers and trimers of **2b**, e.g. **6**. Although a metallacycle from 1-octyne could not be isolated, its electrochemical carboxylation (as well as those for other monosubstituted alkynes) was carried out successfully (see Table I).

Nickelacycle 5 as a Reaction Intermediate. To test if **5** was an intermediate in the electrochemical carboxylation, the complex was added as the sole source of nickel to an electrolytic solution containing **2a** (**2a**/**5** ratio of 10/1) and CO_2 in a two-compartment cell (absence of Mg^{2+} ions). No current passed through the solution at −1.2 V nor at −1.7 V. The starting compound **2a** was quantitatively recovered after the standard workup procedure. However, when anhydrous $MgBr_2$ (prepared by electrolysis of a dibromoethane solution in DMF with the presence of a magnesium anode) was added to the cathodic compartment containing **5** ($MgBr_2$/**5** ratio of 1), up to 2 faradays/mol of nickel could be electrolyzed at −1.4 V. After a standard workup, **3a** was obtained in 90% yield with respect to **5**, corresponding to 10% of the total alkyne added. If additional $MgBr_2$ was introduced into the cathodic compartment, the electrolysis could be continued with further carboxylation of the alkyne.

A stoichiometric carboxylation reaction occurs with nickelacycle **5** in the presence of 1 molar equiv of $MgBr_2$. The isolated complex **5** is a likely reaction intermediate.

When the carboxylation of **5** with excess **2a** was run under intensiostatic conditions in a one-compartment cell (**2a**/**5** ratio of 10/1, Mg anode, i = 50 mA), the electrolysis proceeded until 2 faradays/mol of **2a** was consumed. Continuous monitoring of the cathode potential during electrolysis, as in Figure 2, showed an initial value of −1.6 V for 30 min followed by a shift to −1.4 V for the rest of the reaction. Moreover, a constant cathodic potential of −1.4 V was measured for an identical electrolysis (up to 80% alkyne consumption) when anhydrous $MgBr_2$ was added before electrolysis ($MgBr_2$/**5** ratio of 1). In both cases, carboxylic acid **3a** was obtained in 80% yield with respect to **2a** after the standard workup. We conclude that, under these conditions, complex **5** acts as a catalyst in the alkyne electrocarboxylation reaction. This represents one of the first examples with an organonickel reagent as the catalyst for a coupling reaction.

Scheme VIII



5

Influence of Mg^{2+} Ions. The above results show, on one hand, that complex **5** acts as an intermediate in the electrochemical carboxylation. On the other hand, **5** (or **1**) catalyzes the reactions only in the presence of Mg^{2+} ions. This suggests that free Ni(II) (eventually Ni(0)) complexes are formed from metallacycle **5** by reaction with Mg^{2+}. We proved that metallacycle **5** was opened in the presence of Mg^{2+} ions and that the Mg^{2+}/Ni^{2+} exchange is a chemical (and not electrochemical) reaction. When **5** was added to an anhydrous $MgBr_2$ solution in DMF and the mixture stirred at 40 °C for 5 min and then directly esterified or quickly hydrolyzed, the ester of **3a** or the acid **3a** was quantitatively recovered (Scheme VIII). The same procedure in the absence of $MgBr_2$ yielded less than 15% of the organic products.

The recovery of a free $Ni(bpy)^{2+}$ complex from **5** in the presence of Mg^{2+} was further demonstrated by voltamperometry. We measured the height of the Ni(II)/Ni(0) wave at −1.2 V as a function of the Mg^{2+} concentration. The Ni^{2+}/Mg^{2+} exchange is a 1/1 molar reaction. This novel reactivity of oxanickelacyclopentenone derivatives with Mg^{2+} is not limited to this ion; experiments with the addition of 1 or 2 molar equiv of $AlBr_3$ or $ZnBr_2$ to DMF solutions of **5** generalized the reactivity of the metallacycles in the presence of Lewis acids.

For the opening of the nickelacycle, we propose a coordination of the Mg^{2+} to the carboxylate group of **5**, followed by a Ni–O cleavage with scission (protonation) of the nickel–vinyl bond (Scheme VIII). This leads to a magnesium carboxylate and a Ni(II) complex and also opens the question of the hydrogen source (H_A) at the 3-position of the acrylic acid derivatives.

The cleavage of the Ni–O bond of **5** by Mg^{2+} ions is the key to the success of the nickel catalysis. The strong Ni–O bond makes difficult the transformation of bonded CO_2 in analogous complexes.[8] In the presence of Mg^{2+} ions, we can overcome this problem. The Lewis acid promoted synthesis of acrylate derivatives from alkynes and CO_2, including the Ni–O cleavage, utilizes a binary Ni–Mg system. The magnesium carboxylates formed are accumulated as a stable species during electrolysis, with the further advantage that no bimetallic complexes need to be prepared.[22]

Sources of H_A. The attempts to introduce a deuterium atom or a methyl group at the 3-position of carboxylic acid derivatives **3** by quenching the electrolysis mixture (one-compartment cell, Mg anode, catalytic or stoichiometric conditions) with D_2O or MeI failed. Exclusively 3-protonated (H_A) coupling products were isolated. The same negative results were obtained when several electrophiles (D_2O, MeI, PhCHO, PhCOCl) were added to DMF solutions of metallacycle **5** containing $MgBr_2$. However, when D_2O or MeI was added to a freshly prepared solution of **5** in a two-compartment cell (absence of Mg^{2+}) followed by the addition of anhydrous $MgBr_2$, the 3-deuterio or 3-methyl derivatives could be respectively obtained. Under nonanhydrous conditions, protonated **3a** was formed. This set of experiments points out that the 3-position of derivatives **3** should be protonated during electrolysis at the stage of metallacycle cleavage.

In order to identify the origin of H_A in the electrolytic medium (no specific proton source is added in the electrocarboxylation procedure), the residual water, the supporting electrolyte, and the solvent itself (DMF) were examined as possible proton sources. Several experiments were carried out:

(a) The electrocarboxylation of **2a** under intensiostatic conditions with 1 mL of D_2O added to the DMF solution (1.4 M) yielded 3-deuterated **3a**. Yet, the high concentration of water (or D_2O) affected negatively the electrosynthesis, involving high overpotential and low turnover. Thus, the protons arising from water (or D_2O) are effectively a source of H_A in the final product. However, under the standard electrolysis conditions (freshly distilled DMF), only traces of water might be present. Thus, the residual water is only a partial source of H_A.

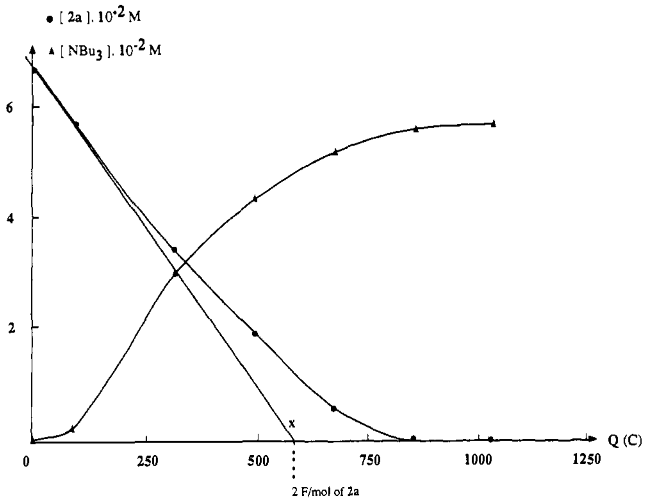


Figure 3. NBu_3 formation and alkyne consumption versus electricity passed (coulombs) in the carboxylation (CO_2, 1 atm) of **2a** (3 mmol) in a DMF solution (45 mL) containing $(TBA)BF_4$ (3 mmol) at 50 mA: (x) theoretical consumption of **2a** at 2 faradays/mol; (●) experimental concentration of **2a** during electrolysis, followed by GC; (▲) concentration of NBu_3 during electrolysis, followed by GC.

(b) When a proton source such as methanol was added to a DMF solution (DMF/MeOH = 97/3) of **2b**, no electrocarboxylation took place, instead, the reduction of 1-octyne to 1-octene occurred in 40% yield.

(c) In electrolysis carried out in the presence of excess $(TBA)BF_4$ as supporting electrolyte (under the intensiostatic conditions) with a **2a**/**1**/$(TBA)BF_4$ molar ratio of $1/10^{-1}/1$, aliquots were analyzed throughout the reaction. A plot of the NBu_3 concentration as a function of the faradaic consumption is presented in Figure 3. After a short induction period (possibly due to the traces of water as the proton source), NBu_3 was formed progressively while the alkyne concentration decreased. Carboxylated adduct **3a** was isolated in 70% yield. The supporting electrolyte is therefore a contributing source of H_A in the final product, via its decomposition following a Hoffman-type, nonthermal degradation:

$$n\text{-}Bu_4N^+ \rightarrow n\text{-}Bu_3N + H^+ + C_4H_8$$

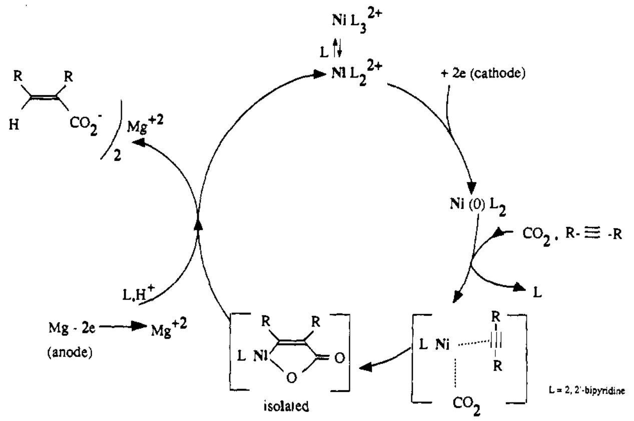
It should be noted that in the standard carboxylation procedure only a low supporting electrolyte concentration is used (**2**/**1**/$(TBA)BF_4$ molar ratio of $1/10^{-1}/10^{-1}$) and the contribution of the ammonium salt decomposition to H_A in the final product can only partially explain the proton source.

(d) The solvent, DMF, is also a proton donor in this reaction. When **5** was dissolved in DMF-d_7 followed by the addition of anhydrous $MgBr_2$, 3-D-**3a** was obtained.

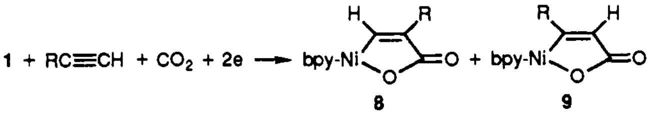
We therefore conclude that there are three different sources for H_A in the electrochemical carboxylation of alkynes which intervene in the order residual water, ammonium salt, and DMF solvent.

Mechanistic Cycle. A mechanistic cycle is presented in Scheme IX. The starting Ni(II) complex **1** is initially reduced at −1.2 V vs SCE in a two-electron process to a $Ni^0(bpy)_2$ species. This Ni(0) complex undergoes a fast ligand exchange to take up the alkyne and CO_2 and to form a nickel–oxacyclopentenone intermediate **5**, followed by a chemical reaction between **5** and Mg^{2+}. A key feature is that the Mg^{2+} ions in solution are formed progressively in the anodic process and at the same rate as the reduction of Ni(II) to Ni(0). The metallacycle cleavage occurs in the presence of $(TBA)BF_4$ or DMF as proton donors to afford the unsaturated magnesium carboxylate. A $Ni^{II}(bpy)$ species is liberated. The cycle is closed via a two-electron reduction of Ni(II), which regenerates the starting zerovalent nickel. The Mg^{2+} carboxylate, the species that accumulates during electrolysis, is hydrolyzed (or directly esterified) at the end of the reaction. The

Scheme IX



Scheme X



attractiveness of the single-compartment-cell procedure, apart from its simplicity, lies in the fact that both anodic and cathodic processes yield essential components for the reaction.

In the case of the electrolysis run in a two-compartment cell in the absence of magnesium ions, the reaction stops at the stage of the metallacycle formation. The nickel species is not recycled, and the reaction is therefore stoichiometric.

Synthetic Applications. Stereo- and Regioselectivity. The incorporation of CO_2 and H_A across the triple bond occurs with cis addition. When **3a** or its methyl ester was obtained from **5**, a single *E* isomer was isolated. However, in the Ni-catalyzed electrocarboxylation of **2a** (intensiostatic conditions), an 85/15 mixture of cis/trans addition products was formed. The cis/trans isomerization takes place under the electrolysis conditions, due to the presence of Ni(0) species in solution. Ni(0) is known to catalyze such double-bond isomerization.[24]

The carboxylation of unsymmetrically substituted alkynes, $R^1 \neq R^2$, can give rise to two possible regioisomers: **3** and **4**. Table I presents some selected examples, which show that mono- as well as disubstituted alkynes or diynes are carboxylated.

In some cases, the electrochemical carboxylation was very selective. For example, if we examine the reactivity of **2b** ($R^1 = n\text{-}C_6H_{13}$; R^2 = H), the CO_2 was regioselectively incorporated into the 2-position of the alkyne, yielding a 90/10 mixture of **3**/**4**. The regiochemical outcome is controlled at the stage of the metallacycle formation. For terminal alkynes, an intermediate such as **8**, in which the metal occupies the less hindered site of the metallacycle, would be favored (Scheme X).

High regiocontrol was also obtained for other terminal alkynes (R^1 = Ph, cyclopentyl, *n*-alkyl, ...; R^2 = H). For alkyl substituents, approximately a 90/10 ratio of **3**/**4** was generally obtained. For phenylacetylene (entry 5), the regioselective outcome is less remarkable than with an alkyl group (compare entries 2–5) and isomers **3e** and **4e** were formed in a 71/29 ratio. This result accounts for the electronic effect of the phenyl substituent, which tends to favor an intermediate of type **9**.

The carboxylation of a difunctional α,ω-diyne such as 1,7-octadiyne (**2k**) (entry 11) resulted in the incorporation of a single CO_2 molecule in 60% yield, together with 30% of dimer **7** (see Scheme VI). Several carboxylic acids can be formed in the reaction with an α,ω-diyne, including cyclic and noncyclic adducts. In the case of **2k**, the main reaction product obtained with 50% selectivity was the cyclic (2-methylenecyclohexylidene)acetic acid.[12c] The second main carboxylation product was acyclic 2-methylene-7-octynoic acid (**3k**), corresponding to the incorporation of one molecule of CO_2 at the 2-position of one of the triple bonds of the diyne.

The carboxylation of disubstituted acetylene derivatives occurred more slowly than that of terminal alkynes, particularly when two bulky substituents were present (e.g. Ph). The tendency to form cyclic trimers from terminal alkynes (e.g. **6**, Scheme VI) was suppressed with disubstituted derivatives. With symmetrical alkynes ($R^1 = R^2$), the monocarboxylic acids (**3** = **4**) were obtained in high yields. In the case of diphenylacetylene (**2g**), acid **3g** was obtained together with its saturated analogue. The addition of CO_2 to disubstituted alkynes with $R^1 \neq R^2$ occurred with low regioselectivity. It is difficult to assess the relative importance of steric and electronic effects in the CO_2 incorporation. Steric factors likely play an important role, as can be inferred by comparing the results of entries 5 and 6. Phenylacetylene is carboxylated preferentially in the position α to the phenyl group, whereas in phenylpropyne (entry 6) the β position is preferred. In the case of phenylacetylene, an intermediate such as **8** is favored because of steric reasons, although the electronic effect of the phenyl increases the ratio of **9** produced. For phenylpropyne, a closer competition exists between the steric hindrances of phenyl and methyl groups, in addition to the electronic effect that preferentially places the phenyl substituent in a position α to the nickel in the intermediate metallacycle. This results in a 38/62 ratio of products **3f**/**4f**.

A regiocontrol derived from the effect of a remote binding group is observed for entries 9 and 10, in which an acetate group is present on the side chain. Scheme X suggests that, for entry 9, the nickel in complex **9** could additionally bind to the remote site of unsaturation located on the alkyl chain, favoring isomer **4**. Indeed, a 1/1 mixture of acrylate derivatives **3i** and **4i** was isolated. Identical results were found in the case of internal alkyne **2j**.

Electronic effects play an important role as well, not only in controlling regioselectivity but also in some cases determining the reactivity of the alkyne toward oligomerization or polycarboxylation. Thus, a bisinsertion of CO_2 was the major product with electron-deficient alkynes such as phenyl propiolate (entry 8). A carboxylative oligomerization occurred with methyl propiolate ($R^1 = CO_2Et$; R^2 = H).

Conclusions

A simple and general procedure for the electrocarboxylation of alkynes under mild conditions has been developed. With use of **1** as the catalyst precursor, one molecule of CO_2 is incorporated into both terminal and internal alkynes to afford substituted acrylic acids in moderate to good yields. Before our work, no example of CO_2 fixation into monosubstituted alkynes had been reported.

When the in situ electrochemical preparation of active Ni(0) species and a magnesium anode are used rather than the chemical method, the reaction proceeds catalytically with respect to **1**. Complex **1** is reduced to a $Ni^0(bpy)_2$ species able to form a nickelacycle intermediate, which was isolated from the reaction mixture in the case of 4-octyne. Ni(II) is recycled in the presence of Mg^{2+} ions and an appropriate proton source such as $(TBA)BF_4$ or DMF. The nickel–magnesium exchange reaction is the key step to explain nickel catalysis.

The advantages of the method can be summarized as follows: (1) a stable, easily available Ni(II) starting complex instead of air-sensitive $Ni(COD)_2$; (2) catalytic use of the nickel complex **1**; (3) use of CO_2 as the carbon source for organic chemicals; (4) easy electrochemical setup (electrosynthesis in a single-compartment cell connected to a constant current supply under intensiostatic conditions); (5) mild conditions (CO_2 pressure of 1 atm, T = 20–80 °C; to be compared to CO_2 pressures higher than 50 atm in pyrone synthesis[11]); (6) use of readily available Mg anodes, with the versatile role of (a) noninterference of the anode in the reduction process, (b) supply of Mg^{2+} ions in solution for the nickelacycle cleavage, and (c) carboxylate counterion accumulated as nonreducible species during electrolysis; (7) carboxylation of mono- and disubstituted alkynes; (8) generally, incorporation of one molecule of CO_2 into a hydrocarboxylation-type reaction; (9) high regioselectivity in the carbon dioxide incorpo-

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[24] Kanai, H.; Choe, S. B.; Klabunde, K. J. *J. Am. Chem. Soc.* **1986**, *108*, 2019.

ration into the 2-position of terminal alkynes.

The electrochemical method offers an alternative for bringing about transition-metal-catalyzed CO_2 insertion into acetylenic derivatives under mild conditions.

Experimental Section

Reagents and Chemicals. All the chemicals employed were of reagent grade quality. Dimethylformamide (Prolabo) was distilled under argon from calcium hydride and copper sulfate under reduced pressure and was dried over 4-Å molecular sieves. Tetrabutylammonium tetrafluoroborate ($(TBA)BF_4$, Fluka) was dried by heating overnight at 70 °C in vacuo. $Ni(bpy)_3(BF_4)_2$ (**1**) was prepared according to ref 12a. Metals used as the anode were of high purity: magnesium rod (99.8%, diameter 1 cm, Prolabo) zinc rod and Ni wire (Alfa). The cathode was of carbon fiber. Anhydrous magnesium bromide solution was prepared by electrolysis of a 1,2-dibromoethane (5–10 mmol) solution in DMF (40 mL) in a one-compartment cell fitted with a magnesium anode until consumption of 2 faradays/mol of $C_2H_4Br_2$. Other reagents were obtained commercially and used as supplied. Carbon dioxide was N45 (Alphagaz). The electrolyses in the absence of CO_2 were run under argon atmosphere.

Cells and Instrumentation. The electrochemical one-compartment cell is a cylindrical glass vessel of ~40-mL volume, such as that described in ref 15, equipped with a carbon-fiber cathode (20 cm^2) and a magnesium-rod (immersed to 3 cm) anode. The two-compartment cell is described in ref 17. The two compartments are separated by sintered glass (No. 4); the anodic compartment has a nickel wire as the anode, and the cathodic compartment is equipped with a gold or a carbon-fiber cathode and a SCE electrode. Cyclic voltammetric experiments and controlled-potential electrolyses were performed with the aid of Solea-Tacussel conventional equipment and were carried out at 25 °C by utilizing gold or glassy-carbon microelectrodes (Tacussel). All potentials were quoted with respect to a saturated calomel electrode (SCE). Intensiostatic electrolyses were carried out by using a stabilized constant current supply (Sodilec, EDL 36.07).

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 E spectrometer. Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer, and FT-IR spectra, on a Perkin-Elmer-1760 spectrophotometer. Mass spectra were obtained on a Nermag R-10-10 (Orsay, France) or a Finnigan ITD 800 spectrometer coupled to a Varian 300 chromatograph with a DB-1 capillary column, either by electron impact or with CH_4 or NH_3 as the ionizing agent. Gas chromatography was performed on either an Intersmat IGC 120 chromatograph with an SE-30 stainless steel ($^1/_8$ in. × 13 ft) column or a Delsi DI 200 chromatograph equipped with a 25-m DB-1 capillary column. Products were isolated by flash silica gel (230–240 mesh) column chromatography. Elemental analyses were performed by the Service de Microanalyse du CNRS, Lyon, France.

Electrocarboxylation of Alkynes in a Single-Compartment Cell. General Catalytic Procedure. A DMF (40 mL) solution containing **1** (420 mg, 0.6 mmol) and $(TBA)BF_4$ (100 mg, 0.3 mmol) was placed in the cell under 1 atm of CO_2 and stirred at the desired temperature (20–80 °C). The alkyne **2** (6 mmol) was slowly introduced by a syringe-pump addition over 4 h. A current of 50 mA was applied between the electrodes connected to a DC power supply (apparent cathodic current density of 0.25 $A{\cdot}dm^{-2}$, applied voltage ca. 3–15 V). The alkyne consumption was followed by GC analysis of aliquots withdrawn from the reaction mixture, and the electrolysis was continued until the starting material was almost depleted, e.g. about 7 h. Generally, 2–3 faradays/mol of **2** was necessary to achieve a 95% alkyne consumption. The reaction mixture was esterified directly in DMF by adding anhydrous K_2CO_3 (8 mmol) and methyl iodide (10–15 mmol) and stirring the mixture at 50 °C for 5 h. The solution was hydrolyzed with 50 mL of 0.1 N HCl solution and extracted with Et_2O, and the organic layer was washed with H_2O, dried over $MgSO_4$, and evaporated. The methyl esters corresponding to carboxylic acid **3** and **4** were isolated by flash chromatography on silica gel with pentane/Et_2O mixtures as eluent. The products were analyzed by NMR and IR spectrometry, mass spectroscopy, and GLC. The following compounds were identified by comparison of their physical and spectral data with those given in the cited references: **3a**,[25] **3b**,[26] **4b**,[27] **3c**,[36] **4c**,[28] **3d**,[12a] **4d**,[29] **3e**,[30] **4e**,[31] **3f**,[32] **4f**,[33] **3g**,[34] **4h**,[35] **3i**,[22a] **4i**,[12a] **3j**,[12b] **4j**,[12b] **3k**,[12c] **4k**,[36] **6**,[37] **7**.[38]

Electrocarboxylation of Alkynes in a Two-Compartment Cell. General Stoichiometric Procedure. Both compartments were filled with a DMF solution (30 mL each) of $(TBA)BF_4$ (1.0 g, 3 mmol) under 1 atm of CO_2. Complex **1** (700 mg, 1 mmol) and alkyne **2a** (110 mg, 1 mmol), were added to the cathodic compartment. The electrolyses were run at 20 °C at the desired cathode potential and were stopped after 2 faradays/mol of **1** was consumed or when the current was negligible. An anhydrous $MgBr_2$ (1.2 mmol) solution in DMF was added to the cathodic compartment and the mixture stirred for 15 min. The esterification and further workup were the same as described above, unless stated otherwise. The methyl ester of **3a** (120 mg) was isolated in 70% yield.

Preparation of Oxanickelacyclopentenone (5). According to the general stoichiometric procedure in a two-compartment cell, **1** (700 mg, 1 mmol) and **2a** (110 mg, 1 mmol) were added to the cathodic compartment under 1 atm of CO_2. The electrolysis was run at 20 °C at −1.2 to −1.3 V vs SCE until 2 faradays/mol of **1** was consumed. The reaction mixture was then stirred for 2 h under CO_2. A light green complex separated when dry diethyl ether (50 mL) was added to the cathodic solution and was filtered off, washed with diethyl ether, and dried under vacuum (0.1 mmHg) at 50 °C overnight. Complex **5** (260 mg) was isolated in 70% yield. FT-IR (KBr): 3106, 3072, 3032, 2958, 2930, 2870, 1639, 1620, 1600, 1575, 1567, 1505, 1493 cm^{-1}. Mass spectrum (70 eV, *m/e*): 369 (M^+), 214 (M^+ − bpy + 1), 156 (bpy), 154 (M^+ − Ni(bpy)). Anal. Calcd for $C_{19}H_{18}N_2O_2$: C, 61.83; H, 6.01; N, 7.59; Ni, 15.90. Found: C, 61.89; H, 5.99; N, 7.62; Ni, 15.79.

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