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**Preliminary communication**

# Electrogenerated nickel(0) catalyzed carbon dioxide incorporation into $\alpha,\omega$-diynes

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## Abstract

Electrogenerated low-valent nickel complexes are active catalysts for carbon dioxide incorporation into $\alpha,\omega$-diynes. A strong influence of the nature of the ligand on the selectivity of this carboxylation has been observed.

Carbon dioxide incorporation into organic molecules is being actively investigated [1]. Despite the considerable number of studies of $CO_2$ chemistry, there are only a few homogeneous and catalytic reactions which lead to the incorporation of $CO_2$ into an organic compound [2].

Transition-metal catalyzed reactions of unsaturated hydrocarbons such as dienes and acetylenes with $CO_2$ have been reported [2]. With alkyne substrates, nickel(0) complexes have shown catalytic activity for the $CO_2$ fixation. Thus, disubstituted alkynes yield $\alpha$-pyrones under high $CO_2$ pressure when $Ni(COD)_2/PR_3$ is used as the catalytic system in a cycloaddition reaction [3]. Recently bicyclic $\alpha$-pyrones have been reported by Tsuda [4] to undergo the Ni-catalyzed cycloaddition of non-conjugated diynes with $CO_2$ under 50 atm pressure.

We recently described the carboxylation of terminal alkynes catalyzed by electrogenerated nickel(0) complexes [5]. The electrochemical method enables us to synthesise $\alpha$-substituted acrylic acids in reasonable yields under mild conditions. Electrocarboxylation of organic substrates by $CO_2$ is a currently expanding field; thus, organic halides may be converted into the corresponding carboxylates [6], and mono- and di-carboxylation reactions of styrene and butadiene have recently been reported [7].

We present here our observations on the nickel-catalyzed electrocarboxylation of unsubstituted $\alpha,\omega$-diynes **1**. The electrochemical method allows the use of a catalytic amount of a stable readily-available nickel(II) compound as the precursor, e.g. the commercially available $NiBr_2$/dimethoxyethane. When appropriate the relevant ligand is simply added to the nickel(II) solution, without the necessity to isolate the

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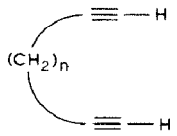
complex. The carboxylation is performed in a single-compartment electrolytical cell [8], fitted with a central anode of magnesium and a carbon fiber cathode, at constant current density and low $CO_2$ pressure (1 to 5 atm), in DMF as solvent. At the anode the magnesium is oxidized to $Mg^{2+}$ species. At the cathode, nickel(II) complex is reduced to nickel(0). The nickel(0) generated in solution coordinates the diyne as well as $CO_2$, to give, after hydrolysis, the carboxylation products and nickel(II), which is recycled and again reduced (eq. 1). We suggest a similar mechanism to that suggested by Hoberg [9] for stoichiometric alkyne carboxylations by $Ni(COD)_2$.

The magnesium anode is consumed and the $Mg^{2+}$ ions are trapped as the carboxylate.




$$+ CO_2 \xrightarrow[(2)\ H_3O^+]{\text{(1) e, Ni}^{II}\text{ (0.1 equiv.) + L, Mg anode, DMF, n-Bu}_4\text{N}^+\ \text{BF}_4^-} \mathbf{2} + \mathbf{3} + \mathbf{4} \qquad (1)$$

(**1a**, $n = 4$;
**1b**, $n = 3$)

Unsaturated monocarboxylic acids **2** and **3** are the major products, and are accompanied by the diyne dimers **4** and to a lesser extent, some dicarboxylated species. No bicyclic $\alpha$-pyrone formation has been observed. In a study of the selectivity of the carbon dioxide fixation several factors were examined. Table 1 summarizes the observations on the influence of the nature of the ligand as well as that of the reaction conditions (solvent, temperature, $CO_2$ pressure) in electrocarboxylation of 1,7-octadiyne (**1a**, $n = 4$) and 1,6-heptadiyne (**1b**, $n = 3$).

The products are highly dependent on the structure of the ligand, as previously noted for simple alkynes [10]. The nature of the ligand strongly influences both the rate of carboxylation relative to that of oligomerization, and the selectivity towards the various carboxylated compounds (Scheme 1). Acyclic $\alpha$-methylene carboxylic acid **2** is preferentially formed when nickel(0) is associated with basic polyamines such as TMEDA (tetramethylethylene diamine) (runs 1, 2) or PMDTA (*N,N,N′,N″,N″*-pentamethyldiethylene triamine) (runs 6–8). In the last case, the carboxylation is very selective at $P(CO_2)$ 5 atm (run 7).

In the formation of carboxylic acid **2** the diyne reacts as a monofunctionalized compound, in accord with the reactivity behaviour observed for the $Ni(bipy)_3(BF_4)_2$ (bipy = 2,2′-bipyridine) catalyzed electrocarboxylation of terminal monoalkynes [5], e.g. the selective $CO_2$ fixation at position 2 of the terminal triple bond. Use of the same nickel-bipy catalytic system in the carboxylation of **1a** or **1b** (runs 3–5) leads preferentially to carbon dioxide fixation with concomitant diyne cyclization, to give preferentially **3a** or **3b**.

With $PPh_3$ as ligand (runs 9, 10) almost no carboxylated products were formed and the bicyclic dimer **4** was obtained in good yield. Both **4a** and its olefin reduced analogue were the only products under the conditions of run 6 in the absence of $CO_2$.

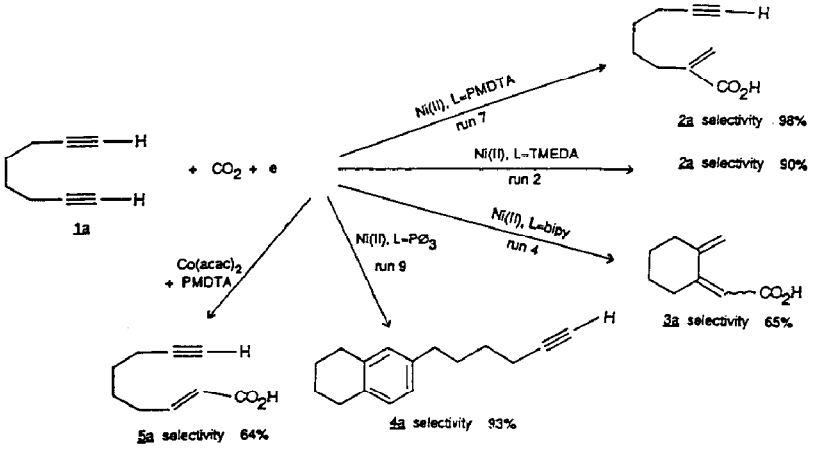
Dimethylformamide proved to be a better solvent than acetonitrile. In $CH_3CN$ a low yield of carboxylated adducts was obtained, and bicyclic pyridine 3-methyl-5,6,7,8-tetrahydroisoquinoline was isolated as a by-product (11% yield, run 2). This

Table 1

Nickel-catalyzed electrocarboxylation of **1** [a]

| Run | *n* | Complex | Ligand L | Reactions conditions | Diyne conversion (%) | Yield of monocarboxylic acids (%) | Product selectivity [b] **2 3** | Yield of **4** (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | 4 | $NiBr_2$-DME [c] + 2L | TMEDA | DMF 65 °C, 1 atm | 88 | 40 | 50 15 | 20 |
| 2 | 4 | $NiBr_2$-DME + 2L | TMEDA | $CH_3CN$ 65 °C, 1 atm | 65 | 10 | 90 5 | 55 |
| 3 | 4 | $NiL_3(BF_4)_2$ | bipy | DMF, 65 °C, 1 atm | 100 | 60 | 25 50 | 30 |
| 4 | 4 | $NiL_3(BF_4)_2$ | bipy | DMF, 20 °C, 5 atm | 90 | 50 | 25 65 | 15 |
| 5 | 3 | $NiL_3(BF_4)_2$ | bipy | DMF, 65 °C, 1 atm | 35 | 65 | 5 90 [d] | 10 |
| 6 | 4 | $NiBr_2$-DME + 2L | PMDTA | DMF 65 °C, 1 atm | 80 | 30 | 80 20 | 20 |
| 7 | 4 | $NiBr_2$-DME + 2L | PMDTA | DMF, 20 °C, 5 atm | 50 | 60 | 98 2 | 6 |
| 8 | 3 | $NiBr_2$-DME + 2L | PMDTA | DMF, 20 °C, 5 atm | 30 | 60 | 75 15 | 3 |
| 9 | 4 | $NiBr_2L_2$ + L | $PPh_3$ | DMF, 65 °C, 1 atm | 50 | 5 | | 70 |
| 10 | 4 | $NiBr_2L_2$ + L | $PPh_3$ | DMF-$CH_3CN$ (1/2) 20 °C, 5 atm | 80 | – | | 61 [e] |

[a] General electrolysis procedure: solvent, 40 ml; Ni complex, 0.6 mmol; **1**, 6 mmol; n-$Bu_4NBF_4$, 0.2 mmol; $CO_2$ bubbling at atm pressure or at 5 atm in a closed-cell; 50 mA applied between a Mg anode and a carbon fiber cathode (20 $cm^2$) for 10 h. Carboxylic acids were esterified and isolated as methyl esters [5] after column chromatography. [b] Calculated as percentage of **2** or **3** per total amount of monocarboxylic acids. [c] DME = dimethoxyethane. [d] The methylene bond of **3b** was partially reduced. [e] In addition, 20% trimers of **1a** were also obtained.




Scheme 1. Reaction selectivity as a function of the catalytic system.

compound arises from a [2 + 2 + 2] type cycloaddition between the diyne and acetonitrile, and this reaction has been performed previously with cobalt complexes [11].

The reaction temperature has a marked effect on the diyne conversion. Under the conditions of run 7, at 0 °C the conversion of diyne **1a** was only 5%; at 20 °C, 50% was converted, and at 50 °C there was almost quantitative diyne consumption, but at the expense of the selectivity.

In order to minimize the formation of **4**, carboxylations of **1a** and **1b** were carried out at $P(CO_2)$ 5 atm; the yields of dimers were significantly reduced (compare runs 3, 4; 6, 7 and 9, 10).

The Ni-PMDTA catalyzed carboxylation became more selective towards **2** when the $P(CO_2)$ was 5 atm, but increasing $CO_2$ pressure from 1 to 5 atm, caused no significant increase of dicarboxylated products in the yield.

Other electrogenerated low-valent transition-metal complexes were examined. Noteworthy is that carboxylation of **1a** catalyzed by $Co(acac)_2$ associated with PMDTA (under the conditions of run 5), yielded the linear carboxylic acid **5a** in 45% yield with 64% selectivity. However, $PdCl_2(PPh_3)_2$, $Cp_2Fe$ or $Cp_2TiCl_2$/PMe-$Ph_2$ were ineffective catalysts, giving rise to only low $CO_2$ incorporation.

In conclusion, we note that by appropiate choice of the catalytic system, the carboxylation can be directed towards the separate products **2**, **3**, **4** or **5** with good selectivity, as shown in Scheme 1. The electrochemical method makes possible the nickel-catalyzed carboxylation of unsubstituted $\alpha,\omega$-diynes to yield unsaturated carboxylic acids. The structure of the resulting carboxylic acid is highly dependent on the ancillary ligand. The reaction offers a new method for bringing about of transition-metal catalyzed $CO_2$ incorporation into unsaturated hydrocarbons under mild conditions.

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