Journal of Organometallic Chemistry, 385 (1990) C43–C46
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20724PC

Preliminary communication

Electrogenerated nickel(0) catalyzed carbon dioxide incorporation into α,ω-diynes

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(Received December 7th, 1989)

Abstract

Electrogenerated low-valent nickel complexes are active catalysts for carbon dioxide incorporation into α,ω-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 α-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 α-pyrones have been reported by Tsuda [4] to undergo the Ni-catalyzed cycloaddition of non-conjugated diynes with CO_2 under 50 atm pressure.

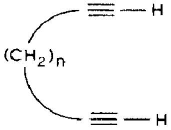
We recently described the carboxylation of terminal alkynes catalyzed by electrogenerated nickel(0) complexes [5]. The electrochemical method enables us to synthesise α-substituted acrylic acids in reasonable yields under mild conditions. Electrocarboxylation of organic substrates by CO_2 is a currently 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 α,ω-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

0022-328X/90/$03.50

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.



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

(**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 α-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 α-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.

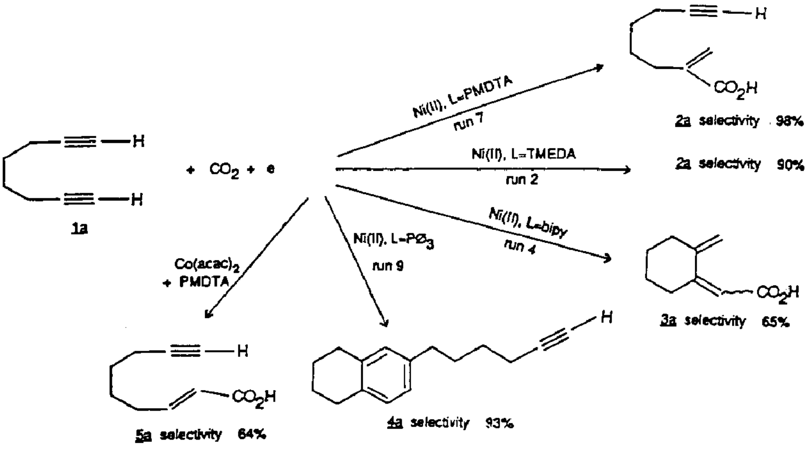
Dimethylformamide proved to be a better solvent than acetonitrile. In CH_3CN a low yield of carboxylated adducts was obtained, and bicyclic pyridine 3-methyl-5,6,7,8-tetrahydroisoquinoline was isolated as a by-product (11% yield, run 2). This

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 $Cp_2TiCl_2/PMePh_2$ 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 α,ω-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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