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Preliminary communication

Ligand-directed reaction products in the nickel-catalyzed electrochemical carboxylation of terminal alkynes

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Abstract

The influence of a series of N and P ligands in the nickel-catalyzed electrochemical carboxylation of 1-octyne has been studied. Different carboxylic acids are obtained depending on the nature of the ancillary ligand, and results afford an example of high ligand-directed product specificity.

The course of most homogeneous organometallic reactions is influenced by the changes in the nature and the number of ligands coordinated to the metal centre [1]. The use of appropriate ligands may lead to regio- en stereo-control of reaction products, a change in the reaction rate, and a significant improvement in the overall yield. The construction of suitable ligands plays an important role in achieving highly selective catalytic reactions.

Relatively few systematic studies have been carried out on the influence of the ligands on the catalytic activity of transition metal catalysts [2]. A few cases are known in which small changes in the nature of the ligands determine not only the regio- or stereo-selectivity but the nature of the products formed [3].

We report here, for the nickel-catalyzed electrochemical carboxylation of 1-octyne, a case in which the choice of the ligand very strongly affects the course of the reaction.

The reaction of carbon dioxide with unsaturated substrates at transition metal centers has found attractive application in the field of homogeneous catalytic reactions in recent years [4–7]. Effects of changing ligands in the phosphine series have been observed for the activation of alkenes and alkynes with CO_2 at nickel centers.

The reaction of $Ni(COD)_2$ with disubstituted alkynes under CO_2 pressure yields to pyrone derivatives and oligomer mixtures without much selectivity when diphosphine ligands are used [5], but high selectivity towards pyrone synthesis has been recently achieved by use of basic monodentate phosphines [6].

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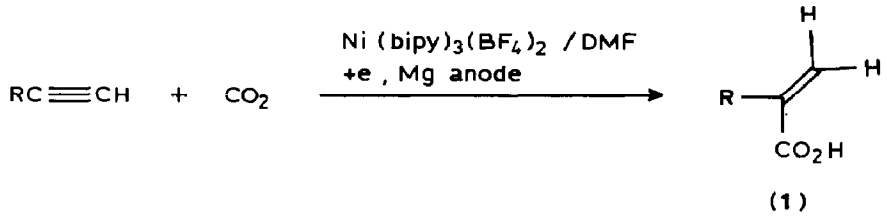
We recently reported [8] the nickel catalyzed electrochemical carboxylation of alkynes with $Ni(bipy)_3(BF_4)_2$ in DMF, and showed that 'in situ' electrogenerated Ni^0 complexes were the active catalysts for the functionalization of the 2-position of terminal alkynes (Scheme 1):

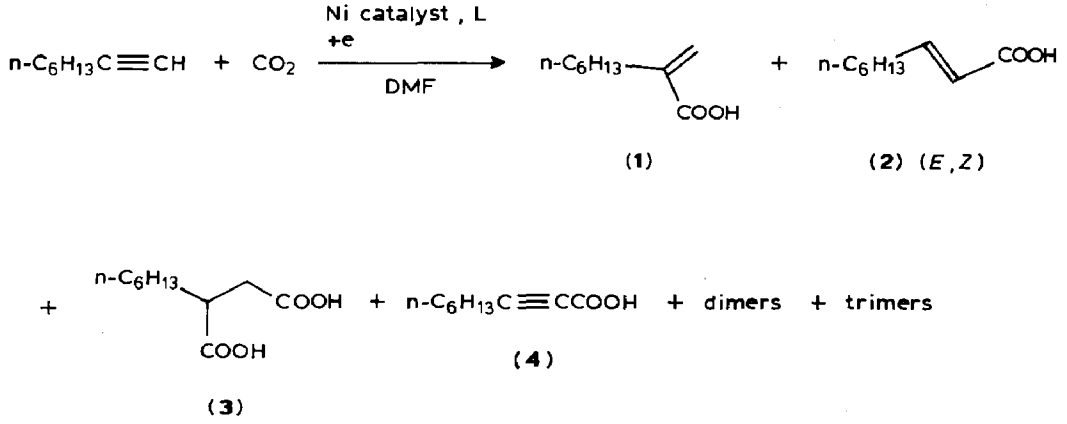


Scheme 1

A series of α-monosubstituted acrylic acids of type **1** was obtained, with selectivities in the range of 60–90% and yields of 40–80%. The carboxylation was carried out in an electrolytical cell (single compartment, magnesium anode) at atmospheric pressure of CO_2 in the presence of a catalytic amount of a Ni^{II} catalyst precursor [8]. In the absence of carbon dioxide, oligomerization of the alkyne to dimers and trimers was observed.

In a study of the influence of the ligand in this reaction with 1-octyne as the model substrate, we observed that the choice of the ligand drastically influences the type of carboxylic acid or oligomerization product obtained (Scheme 2). Carboxylated products **1**–**4** could be obtained selectively by appropriate choice of ligand (see Table 1).

The carboxylation reaction was carried out in a single-compartment electrolytical cell fitted with a sacrificial anode of magnesium and a carbon fibre cathode. The carboxylations were performed at 70 °C in DMF under one atmosphere pressure of CO_2 at constant current intensities. Supporting electrolytes were Bu_4NBF_4 (or Bu_4NBr), and a 10% molar Ni^{II} catalyst precursor was generally used.



Scheme 2

The reactions at the electrodes can be represented schematically as follows:

Anode: $Mg \rightarrow Mg^{2+} + 2e$

Cathode: $NiX_2L_n + 2e \rightarrow L_mNi^0 + 2X^-$

Details of the reaction products obtained with various ligands are presented in Table 1, in which only the major product is shown for each reaction.

With $Ni(bipy)_3(BF_4)_2$ as catalyst precursor (entry 1), 2-hexyl acrylic acid **1** was isolated in 75% with a regioselectivity **1/2** of 88%. Under the same reaction conditions, use of the complex Ni(phenanthroline)Cl_2 (entry 2) mainly gave cyclic trimers of 1-octyne [9*]. For 3,4,7,8-tetramethylphenanthroline (entry 4) cyclic trimers of 1-octyne were again obtained (together with 30% of dimers), and only very small amounts of carboxylated adducts were observed.

For 2,9-dimethylphenanthroline (entry 3) the steric effect of the two *ortho*-methyl groups facilitates the activation of carbon dioxide and inhibits oligomerization; acid **1** is obtained regioselectively, with a **1/2** ratio of 98/2. Within the series of phenanthroline-type ligands (entries 2–4) the enhancement of the rate of reaction of 1-octyne increases with the ligand basicity. Upon increase in the basicity in the absence of steric congestion about the metal center the rate of trimerization increases, but change in the steric demands of the ligand associated with the presence of a CH_3 group in α to nitrogen promotes selective carboxylation. It has previously been noticed (for $Rh-CO_2$ and $Ni-CO_2$ complexes) that increase in the electron density at the metal center enhances the rate of carboxylation [10].

Same saturated bidentate tertiary amine ligands were also examined. With TMEDA (entry 5), the nickel complex gave a 90% yield of carboxylated products, with 1,2-dicarboxylation of 1-octyne taking place preferentially to yield saturated 1,4-dicarboxylic acid (**3**). Upon replacement of TMEDA by the more rigid DABCO (1,4-diazabicyclo[2.2.2]octane, entry 6), monocarboxylation takes place at the 1-position, and the 2-substituted acrylic acid **3** is isolated regioselectively (**2/1** = 92/8) as a mixture of *cis/trans* isomers. With the more bulky tetra(n-propyl) ethylene diamine reactions rates are lower and dimers of 1-octyne became predominant. Similar results are observed with tetramethyl-1,4-butanediamine.

The results obtained with aliphatic diamines confirm that once again the difference in behaviour is associated with apparently small changes in the steric or electronic nature of the ligand.

The cyclic tetraamine cyclam (1,4,8,11-tetraazacyclotetradecane, entry 7) was found to be a very selective ligand for formation of a different carboxylated adduct, use of the complex Ni(cyclam)Br_2 [11] leading to stoichiometric monocarboxylation of 1-octyne to yield 2-nonynoic acid **4** with 96% selectivity.

Among the 1,4-diazadiene-type ligands, neither the *N,N'*-bis(*p*-methoxyphenyl) ethylenediimine (entry 8) nor dimethylglyoxime (entry 9) showed any catalytic activity towards carboxylation nor oligomerization, and in both cases 1-octyne was almost completely recovered.

Similar differences in reactivity and in product distribution were found for phosphine-type ligands. With PPh_3, and with 3 equivalents of ligand per equivalent of nickel (entry 10), and with bis(diphenylphosphino)butane (entry 12), dicarboxyla-

* Reference number with asterisk indicates a note in the list of references.

Table 1. Ligand influence in the electrochemical carboxylation of 1-octyne

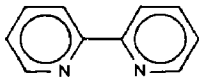
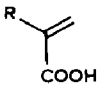
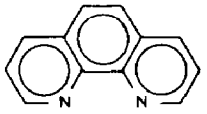
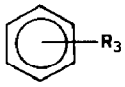
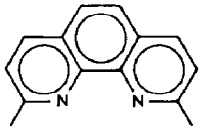
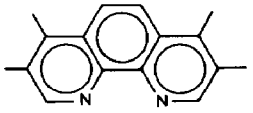
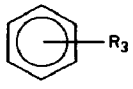
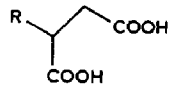
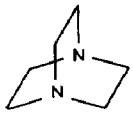
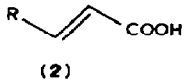
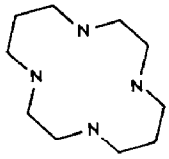
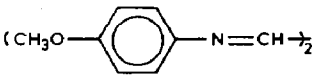
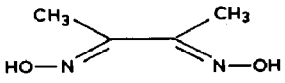
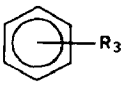
Entry	Ligand (L)	Complex	Trans formed 1-octyne (%)	Reaction product [a]	Yield (%) [b]
1		$Ni(bipy)_3(BF_4)_2$	80	 (1)	75 [e]
2		$NiCl_2$(phen)	50		50
3		$NiBr_2$·dme [c]	100	(1)	50 [e]
4		$NiBr_2$·dme +2L	100		58
5	$(CH_3)_2N(CH_2)_2N(CH_3)_2$	$NiBr_2$·dme +2L	50	 (3)	45
6		$NiBr_2$·dme [d] +2L	90	 (2)	50 [e]
7		Ni(cyclam)Br_2	10	R–≡–COOH (4)	96
8		$NiBr_2$·dme +2L	<1	–	
9		$NiBr_2$·dme +2L	1		
10	PPh_3	$Ni(PPh_3)_2Br_2$ +PPh_3	50	3	50

Table 1 (continued)

Entry	Ligand (L)	Complex	Trans formed 1-octyne (%)	Reaction product [a]	Yield (%) [b]
11	$Ph_2P(CH_2)_2PPh_2$	$Ni(dppe)Cl_2$	80		45
12	$Ph_2P(CH_2)_4PPh_2$	$Ni(dppb)Cl_2$	50	3	45

[a] Major reaction product, R = n-C_6H_{13}. General procedure: DMF, 40 ml; Ni complex, 0.6 mmol; 1-octyne, 6 mmol (added in 4 h); n-Bu_4NBF_4, 0.6 mmol; CO_2 bubbling at atm. pressure; at 70 °C, 50 mA applied between a magnesium anode and a carbon fibre cathode, for 15 h. [b] Yields are expressed as isolated products/reacted 1-octyne. Carboxylic acids were esterified and isolated as methyl esters [8] after column chromatography. [c] dme = dimethoxyethane. [d] Solvent, CH_3CN; electrolyte, n-Bu_4NBr. [e] Selectivity **1**/**2** entry 1; 88/12; entry 3; 98/2; entry 6; 8/92 $E/Z = 2/1$.

tion of the terminal alkyne takes place, and diacid **3** is the main product. However, with bis(diphenylphosphino)ethane (entry 11) cyclic trimers of 1-octyne are obtained (45%), the carboxylated product in this case being the acetylenic acid **4** (30%). No reaction of 1-octyne was observed with the less basic triphenylphosphite ligand.

Under the electrolysis conditions we use, the polarity of the solvent (DMF) and the presence of Mg^{2+} ions (from anodic oxidation) may also contribute to the determination of the course of the reaction.

The results clearly demonstrate the determining influence of the ligand in the nickel-catalyzed electrochemical carboxylation of 1-octyne. Some features worthy of note are: (a) the rates of transformation of 1-octyne increase with increase in the electron density at the metal center caused by the more basic ligands; (b) π-ligands are not essential for the carboxylation: secondary or tertiary aliphatic amines can also be used; (c) a certain degree of steric hindrance seems favourable for a selective carboxylation (entries 3, 5), but too bulky substituents lower the reaction rate and selectivity; (d) the length of the carbon chain between the two donor atoms strongly influences the products, as can be seen in entry 5, showing dimers obtained with tetramethyl-1,4-butane diamine, and entries 11, 12; and (e) the ligand rigidity has similar effects as can be seen from entries 1, 2 and 5, 6.

With appropriate ligands, all the reactions were catalytic except for the nickel-cyclam system (entry 7). In this case only, a high yield, very selective stoichiometric carboxylation was observed. The cyclam ligand is known to stabilize the Ni^{I} oxidation state [12].

Although some generalizations can be made, the factors affecting the competition between insertion of CO_2 and oligomerization of the alkyne are subtle, and predictions concerning the products remain difficult. The strong ligand effect not only influences the relative rates of oligomerization of the alkyne and its carboxylation, but also controls the regio-, the stereo-, and the chemo-selectivity of the carboxylation, affording an example of high product specificity.

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