

Journal of Organometallic Chemistry, 419 (1991) 251–258
Elsevier Sequoia S.A., Lausanne
JOM 22052

Oxidative carbonylation of aliphatic amines catalysed by nickel-complexes

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(Received March 21st, 1991)

Abstract

The catalytic activity of some nickel-complexes in the dioxygen-induced oxidative carbonylation of amines has been studied. *N,N'*-substituted ureas were obtained in fairly low yields (maximum 55%), instead of *N,N'*-oxamides expected on the basis of a previous report. The study of the reaction mechanism shows that amines are carbonylated in a reductive step, during which either ureas or oxamides can be obtained depending on the amount of water present. When dioxygen is used as the oxidant the oxidative step produces water, which promotes the urea formation. The oxygen is also responsible for the low yields owing to a side reaction involving amine oxidation.

These conclusions were confirmed when the carbonylations were carried out under pseudo-catalysis conditions, or when oxidants which do not produce water in the oxidative step were used.

Introduction

N,N'-Substituted ureas and carbamates have recently been obtained, by ourselves [1] and others [2], by oxidative carbonylation of amines, mostly with palladium-based catalysts.

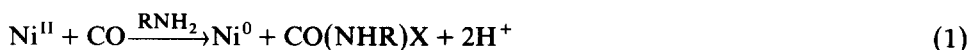
We have now examined the catalytic activities of the less expensive nickel complexes. The ability of Ni-complexes to promote the carbonylation [3] and to give stable carbamoyl complexes [4], considered to be key intermediates in the catalysed synthesis of ureas and carbamates, prompted this choice of catalyst.

Results and discussion

It has been reported that some amine complexes of nickel react stoichiometrically under carbon monoxide pressure to give oxamides [3] (*vide infra* eq. 5). In an attempt to carry out this process catalytically we allowed a primary amine RNH_2 ($\text{R} = \text{butyl, cyclohexyl, benzyl}$) to react at 70°C with a mixture of CO and O_2 (P_{O_2} from 5 to 10 atm; $P_{\text{tot}} = 40\text{--}50$ atm) in the presence of catalytic amounts of nickel

complex $(\text{NiX}_2(\text{RNH}_2)_4)$; $\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{alkyl}$). Instead of oxamides, expected on the basis of a previous report [3], N,N' -dialkylureas were obtained. Yields, in the best cases, were never $> 55\%$ (Table 1).

In order to account for these results we carried out a study of the mechanism of the process, and found that the catalysis takes place through the following redox process (reactions 1 and 2).



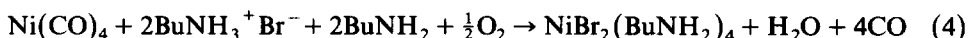
While reaction 2 occurs at room temperature under one atmosphere pressure of O_2 , use of higher temperatures and pressures ($T > 50^\circ\text{C}$, $P_{\text{CO}} > 10 \text{ atm}$) are required for reaction 1. This two-step process was confirmed by first allowing the nickel complex to react with CO and then exposing the reaction mixture to dioxygen.

The reactions were also confirmed by oxidizing with dioxygen a CH_3CN solution of $\text{Ni}(\text{CO})_4$ containing RNH_2 and $\text{RNH}_3^+\text{Br}^-$, and monitoring the change in IR and UV-Vis spectra. The initial solution displays bands at 2044 and 1970 cm^{-1} , which are ascribed to the CO stretching vibrations of $\text{Ni}(\text{CO})_4$ [5] and $\text{Ni}(\text{CO})_3(\text{RNH}_2)$, respectively. The latter is formed according to equilibrium 3.



The second band of $\text{Ni}(\text{CO})_3\text{L}$, expected on the basis of a C_{3v} symmetry [6], is probably masked by the very strong $\text{Ni}(\text{CO})_4$ absorption.

When O_2 was introduced into the solution at room temperature, the carbonyl bands in the IR spectrum disappeared while a new band appeared in the UV-Vis spectrum. This is consistent with a fast oxidation of Ni^0 to Ni^{II} . Ni^{II} can be isolated as $\text{NiBr}_2(\text{BuNH}_2)_4$, in accord with the stoichiometry of reaction 4, by carrying out the oxidation in *n*-butylamine.



When the oxidized reaction mixture were subjected to a CO pressure ($P_{\text{CO}} > 10 \text{ atm}$) at 70°C , reduction of Ni^{II} to Ni^0 took place, as evidenced by the reappearance in the IR spectrum of the 2044 and 1970 cm^{-1} bands.

Moreover, we found that in the reductive step, in which the amine carbonylation occurs, either N,N' -oxamide (reaction 5), or N,N' -dialkylurea (reaction 6) can be obtained, depending on the amount of water present (see experimental section) in the reaction medium. N,N' -dialkylurea is formed in the presence of trace amounts of water, whereas N,N' -dialkylloxamide is formed in anhydrous conditions.

The Ni^0 -carbonyl compounds obtained are present as an equilibrium mixture, as represented in equation 3.

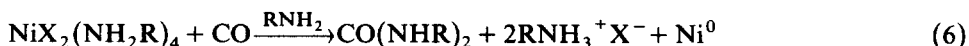
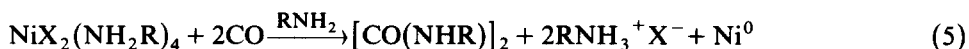
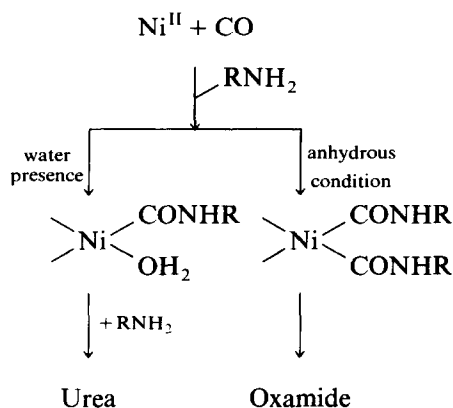


Table 1
Oxidative carbonylations of amines. Yields of *N,N'*-dialkylurea ^a

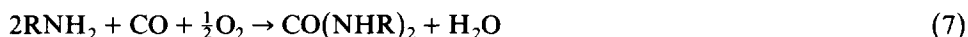
Entry	Catalyst	<i>T</i> (°C)	Time (h)	<i>P</i> _{O₂} (atm)	<i>P</i> _{CO} (atm)	Amine	Solvent	Yields ^b (%)	Reacted amine
1	Ni(BuNH ₂) ₄ Cl ₂	70	6	10	30	Butylamine	Acetonitrile	34	72
2	Ni(BuNH ₂) ₄ Br ₂	70	6	10	30	Butylamine	Acetonitrile	42	73
3	Ni(BuNH ₂) ₄ I ₂	70	6	10	30	Butylamine	Acetonitrile	47	73
4	Ni(BuNH ₂) ₆ (ClO ₄) ₂	70	6	10	30	Butylamine	Acetonitrile	47	74
5	Ni(BuNH ₂) ₄ Br ₂ ^c	70	6	10	50	Butylamine	Acetonitrile	41	70
6	Ni(PPh ₃) ₂ I ₂	70	6	10	30	Butylamine	Acetonitrile	39	69
7	Ni(BuNH ₂) ₄ Br ₂	70	6	10	30	Butylamine	Benzene	10	50
8	Ni(BuNH ₂) ₄ Br ₂	70	6	10	30	Butylamine	THF/Et ₂ O (1:1)	15	55
9	Ni(BuNH ₂) ₄ Br ₂	70	6	10	30	Butylamine	Butanol	30	60
10	Ni(BuNH ₂) ₄ Br ₂	70	7	10	30	Butylamine	Methanol	8	58
11	Ni(BuNH ₂) ₄ Br ₂	50	8	5	30	Butylamine	Acetonitrile	55	60
12	Ni(BuNH ₂) ₄ Br ₂	70	6	5	30	Butylamine	Acetonitrile	42	71
13	Ni(BuNH ₂) ₄ Br ₂	70	6	10	50	Butylamine	Acetonitrile	41	73
14	Ni(BuNH ₂) ₄ Br ₂	70	6	10	60	Butylamine	Acetonitrile	45	72
15	Ni(BzNH ₂) ₄ Br ₂	130	6	10	30	Benzylamine	Acetonitrile	48	65
16	NiCl ₂	130	6	10	30	Cyclohexylamine	Acetonitrile	45	65

^a All reactions were carried out with 0.20 mmol of catalyst and 2 ml of amine. ^b Yields based on the amount of amine consumed. ^c 0.20 mmol of 2,2'-bipyridyl was added.



Scheme 1

These observations account for our results since when amines are carbonylated in the presence of catalytic amounts of a nickel complex, (even if the initial reaction mixture is dry) the water produced in the system by reaction 2 directs the reductive step to reaction 6. The over-all process is therefore the catalytic conversion of amine into ureas (reaction 7).



The effect of water on the course of the reaction has been observed previously in the palladium-catalyzed synthesis of oxalate [7]. We cannot say with certainty what the precise effect of water is. It is possible that a water molecule coordinates to the nickel atom, thereby allowing the formation of only one carbamoyl group. This species could then decay to produce a urea and not an oxamide, whose formation requires the presence of two carbamoyl groups (Scheme 1).

However, we cannot rule out the possibility that water is involved in nucleophilic attack on the carbamoyl intermediate giving the monoamide of carbonic acid, which is transformed into urea.

An alternative route could conceivably have involved formation of *N,N'*-dialkyl-oxamide and its subsequent conversion into *N,N'*-dialkylurea by reaction with free amine catalyzed by Ni^0 or Ni^{II} species. However, this possibility has to be excluded on the basis of the absence of both H_2 and urea when $\text{Ni}(\text{CO})_4$ or Ni^{II} compounds were allowed to react with preformed oxamide in the presence of free amine.

The most significant results are shown in Table 1. The maximum yield of the urea was 55%, and only slight differences were observed when the neutral and/or charged ligand coordinated to the nickel were changed.

The reason for this weak ligand effect could be that reaction 8 between the nickel complex and the free amine, which under the catalysis conditions used (with massive amounts of the amine present) takes place to convert the various initial nickel compounds into the same nickel-complex.



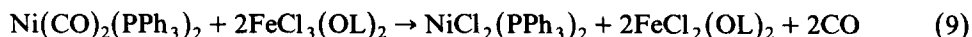
A significant solvent effect was observed, and the CH_3CN was found to give the best results. The low yields of N,N' -ureas were due to the fact that at temperatures higher than 50°C a side reaction occurred involving amine oxidation, (see Experimental section). Unfortunately, the catalysed process did not take place at lower temperatures because the reductive step does not occur (see above). The best yields were obtained at 50°C and 5 atm of O_2 (entry 11). An increase in the CO pressure had no significant effect (entry 14).

On the basis of these findings, we formed the view that in order to increase the yields the process should be carried out either under pseudocatalytic conditions, or in the presence of oxidants which do not bring about amine oxidation. To verify this both procedures were investigated.

Pseudo-catalytic conditions were realized by submitting the reactants to an alternate succession of carbonylation and oxidation reactions, under various temperature and pressures. Carbonylations were carried out under carbon monoxide pressure ($P_{\text{CO}} = 30$ atm) at 100°C , and oxidations were performed at room temperature under one atmosphere of O_2 . HPLC analyses of the mixture during reaction showed that in the first two or three catalytic cycles N,N' -oxamide is the main product. Its formation is then inhibited and N,N' -urea is formed in increasing amounts until it becomes the main product. This provides further evidence for the effect of water on the reaction progress. We confirmed that *n*-butylamine was carbonylated in almost quantitative yield and converted into N,N' -dibutylurea with a selectivity up to 85%.

Fe^{III} and Cu^{II} salts or their amine- or pyridine-complexes, able to oxidize Ni^0 to Ni^{II} , were used as substitutes for dioxygen. Alkyl formamides were the main products obtained when catalysis was achieved with large amounts of one of these reagents. Control experiments showed that formamides were also formed when the reaction took place in the absence of nickel.

Finally, when the triphenylphosphine oxide complex $\text{FeCl}_3(\text{OPPh}_3)_2$ was used as oxidant, *n*-butylamine was converted into a mixture of N,N' -dibutylloxamide and N,N' -dibutylurea in good yields. This is in keeping with the above findings, since in this case, the oxidative step does not produce water. Equation 9 shows the stoichiometry of the reaction between the Ni^0 -complex $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$, and $\text{FeCl}_3(\text{OPPh}_3)_2$.



Conclusions

This study has revealed the effect of water on the selectivity of nickel complexes in the oxidative carbonylation of amines. In rigorously dried solvents amines are converted into oxamides whereas in non-anhydrous conditions N,N' -substituted ureas are formed.

Experimental section

Solvents were dried by standard methods, distilled under a stream of nitrogen, and stored under nitrogen. $\text{Ni}(\text{CO})_4$ was purchased from Strem Chemicals and used as received. The amines were obtained from Aldrich and were distilled from CaO

before use. $\text{NiX}_2(\text{NH}_2\text{R})_4$, $[\text{Ni}(\text{BuNH}_2)_6](\text{ClO}_4)_2$ [8], $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ [9], $\text{FeCl}_3(\text{OPPh}_3)_2$ [10] were prepared by published methods. IR and UV-Vis spectra were recorded on a Perkin Elmer 883 and a Varian Cary 219 spectrophotometer, respectively. Ureas and oxamides were either isolated as solids and identified by IR and MS spectra, or detected by a Varian HPLC Gas Chromatograph using a Si-10 packing. Yields were based either on the amounts of isolated products or on HPLC analysis of reaction solutions. Quantitative analysis for amines and their products was carried out with a Varian Vista 6000 Gas Chromatograph using a Carbowpack 20 $M/0.8\%$ KOH 1.8 m glass column.

Reactions under pressure were performed in a 55.6 stainless steel autoclave mounted in an electrical oven having a magnetic stirrer in its base.

N,N'-dibutylurea synthesis

A glass test-tube containing $\text{NiBr}_2(\text{NH}_2\text{Bu})_4$ (0.20 mmol), butylamine (2 ml, 20.27 mmol), CH_3CN (8 ml) and a Teflon-coated magnetic stirring bar, was placed in the autoclave, which was charged with oxygen (10 atm) and carbon monoxide (30 atm) and then kept at 70°C for 6 h. It was then cooled to room temperature, the gas was purged, and the mixture was analyzed. GLC analysis showed the presence of unreacted amine (5.47 mmol) and of two amine oxidation products, which were identified as $\text{C}_4\text{H}_9\text{N}=\text{CHC}_3\text{H}_7$ and the corresponding N-oxide by comparison of their MS spectra with those of authentic samples. HPLC analysis showed the presence of *N,N'*-dibutylurea and trace amounts of dibutyloxamide. The reaction mixture was cooled to -5°C and the colorless crystalline *N,N'*-dibutylurea that separated, was filtered off, washed with cold hexane (4 ml), dried *in vacuo* and weighed (0.540 g, 42% of reacted amine). Mass spectrum m/e , 44 (relative intensity 100, CONH_2), 57 (33, C_4H_9), 74 (32, $\text{NH}_3\text{C}_4\text{H}_9^+$), 100 (15, CONHC_4H_9), 101 (20, $\text{CONH}_2\text{C}_4\text{H}_9^+$), 172 (37, M^+).

Reactions with other catalysts, amines and solvents were carried out by the above procedure. Conditions and yields were as shown in Table 1.

Carbonylations under suitable conditions

(a) *Pseudo catalysis conditions*

A test-tube containing $\text{NiBr}_2(\text{NH}_2\text{Bu})_4$ (0.20 mmol), butylamine (20.27 mmol), CH_3CN (8 ml) and a Teflon-coated magnetic stirring bar, was placed in the autoclave which was charged with CO (30 atm) and then kept 100°C for 1 hour. The autoclave was then cooled to room temperature, purged of carbon monoxide, recharged with one atm of oxygen, and reaction under these conditions allowed to proceed for 0.5 h. After this first cycle, the carbonylation and oxidation steps were repeated in succession for five days (ca. 25 cycles). HPLC analysis of reaction mixture gave the following results: after three cycles *N,N'*-butyloxamide 0.078 g and *N,N'*-dibutylurea 0.016 g, (relative selectivity, 80 and 20%); after seven cycles respectively 0.10 g and 0.12 g (selectivity 42 and 58%); at the end of the reaction, oxamide 0.13 g, urea 0.57 g (relative selectivity 16 and 84%), unreacted butylamine (11.1 mmol; GLC analysis), and trace amounts of amine oxidation products.

(b) *With $\text{FeCl}_3(\text{OPPh}_3)_2$ as oxidant*

$\text{NiBr}_2(\text{NH}_2\text{Bu})_4$ (0.20 mmol), n-butylamine (20.27 mmol), CH_3CN (8 ml) and $\text{FeCl}_3(\text{OPPh}_3)_2$ (2 mmol) were placed in a glass test-tube, which was placed in the

autoclave which was charged with CO (30 atm) and kept for 6 h. The autoclave was then cooled, the gas purged, and the mixture analyzed. GLC analysis showed the presence of large amounts of butylamine and traces of n-butylformamide. HPLC analysis revealed the presence of oxamide (0.24 g) and dibutylurea (0.12 g) (relative selectivity 63 and 37%).

Reactions with other oxidants were carried out by the same procedure.

Catalysis steps and water effect

1. Reductive step

(a) *Under anhydrous conditions.* A glass test tube containing $\text{NiB}_2(\text{NH}_2\text{Bu})_4$ (2.8 mmol), n-butylamine (20.27 mmol) and dried CH_3CN (10 ml), was introduced in the autoclave which was charged with carbon monoxide (30 atm) and kept at 70°C with stirring of the mixture for 10 h. After cooling of the autoclave the gas was vented and the mixture was analyzed (IR, HPLC). IR (solution): bands at 2044 cm^{-1} ($\text{Ni}(\text{CO})_4$), at 1970 cm^{-1} ($\text{Ni}(\text{CO})_3(\text{BuNH}_2)$) and at 1660 cm^{-1} (N,N' -dibutylloxamide). HPLC analysis showed the presence of dibutylloxamide as the main product (0.39 g, 69% based on the nickel complex) and some N,N' -dibutylurea (0.024 g). The mixture was cooled at -5°C and the crystalline N,N' -dibutylloxamide that separated was filtered off, washed with cold hexane, dried and weighed (0.350 g). Mass spectrum m/e , 41 (relative intensity 55, C_3H_5), 57 (100, C_4H_9), 72 (16, NHC_4H_9), 100 (77, $\frac{1}{2}M^+$), 172 (5, $M^+ - \text{CO}$), 200 (5, M^+).

(b) *Under non-anhydrous conditions.* When the reaction described above was performed in the presence of added H_2O (0.1 ml), a lower yield of carbonylated amine was obtained. HPLC analysis showed the presence of oxamide (0.145 g) and urea (0.188 g), relative selectivity 40 and 60%, respectively. A smaller amount of oxamide was obtained when the reactants were kept for 1 h at 70°C under nitrogen before introduction of the CO.

2. Oxidative step

A stream of a pure $\text{Ni}(\text{CO})_4$ was bubbled in a glass reactor containing BuNH_2 (5 ml). The solution showed IR bands at 2044 cm^{-1} ($\text{Ni}(\text{CO})_4$) and 1970 cm^{-1} ($\text{Ni}(\text{CO})_3(\text{BuNH}_2)$). After addition of $\text{BuNH}_3^+\text{Br}^-$ (3.2 mmol), the mixture was kept at room temperature under one atmosphere of O_2 . The solution turned from green to blue, and cooling gave blue crystals of $\text{NiBr}_2(\text{BuNH}_2)_4$, which was identified from the IR spectrum and elemental analysis. Found: C, 37.8; H, 8.5; N, 11.1; Br, 31.0; Ni, 11.4. $\text{C}_{16}\text{H}_{44}\text{Br}_2\text{N}_4\text{Ni}$ calcd.: C, 37.57; H, 8.68; N, 10.96; Br, 31.27; Ni, 11.49%.

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