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Carbamoyl complexes as a source of isocyanates or carbamyl chlorides

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Abstract

Isocyanates or carbamyl chlorides have been prepared by reaction of carbamoyl complexes of nickel and palladium with $CuCl_2$. Isocyanates are selectively produced from the carbamoyl complexes of primary amines, [LNiCl(CONHR)], (L = 2,6- bis(diphenylphosphinomethyl) pyridine; R = C_6H_5, *p*-$CH_3C_6H_4$, or *p*-ClC_6H_4)) and $[Pd(PPh_3)_2Cl(CONHCH_2COOCH_3)]$, whereas carbamoyl complexes of secondary amines, such as $[Pd(PPh_3)_2Cl(CON(CH_2)_4CH_2)]$, afford carbamyl chloride. As expected, the reaction of the resulting isocyanates or carbamyl chlorides *in situ* with alcohols or amines produces carbamates or *N,N'*-substituted ureas, respectively.

Key words: Carbamyl chloride; Carbamate; Carboxamide; Chloroformamide; Complex; Isocyanates; Palladium; Phosphine; Synthesis

1. Introduction

The study of the reactivity of transition alkoxycarbonyl and carbamoyl complexes (**a** and **b**) is a subject of current interest because they are a potential source of carbamates, oxamates, ureas, *etc.*, and because of their role as intermediates in the catalyzed carbonylation of amines and alcohols [1].

[LM-COOR] [LM-CONHR]
(**a**) (**b**)

Their conversions are believed to proceed according to one of the following reaction sequences;

i) nucleophilic attack by an alcohol or amine at the CO of the alkoxycarbonyl or carbamoyl ligand;

ii) coordination of an alcohol or amine followed by reductive elimination to afford the organic product.

Recently we discovered that copper(II) chloride reacts with alkoxycarbonyl complexes of palladium(II) and promotes the elimination of the alkoxycarbonyl –COOR as chloroformate (eqn. 1) [2].

$$[LPd^{II}\text{-}COOR] + 2CuCl_2 \longrightarrow [LPd^{II}Cl] + ClCOOR + 2CuCl \quad (1)$$

As the chloroformates react *in situ* to give the corresponding carbamates, we also suggested [3] that this route might be involved in the oxidative carbonylation of amines catalyzed by palladium-copper systems [4].

In order to determine whether the metal–carbon bond of a carbamoyl complex (M–CONHR, **b**) reacts analogously upon addition of $CuCl_2$ to afford the corresponding carbamyl chloride (eqn. 2), we have investigated the reactivity of nickel(II) and palladium(II) carbamoyl complexes towards $CuCl_2$.

$$[LMCONRR'] + 2CuCl_2 \longrightarrow LMCl + ClCONRR' + 2CuCl \quad (2)$$

However, very few nickel and palladium carbamoyl complexes have been prepared under mild conditions by reaction of the corresponding dichloro-complexes with an amine and CO (reaction 3) [1a,5], although the analogous reaction giving alkoxycarbonyl complexes by alkoxycarbonylation is very common (eqn. 4) [1c,6].

$$[LMX_2] + CO + NH_2R \longrightarrow [LMXCONHR] + HX \quad (3)$$

$$[LMX_2] + CO + ROH \longrightarrow [LMXCOOR] + HX \quad (4)$$

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In this paper we discuss the synthesis of palladium and nickel carbamoyl complexes and their reactivity towards $CuCl_2$ to afford chloroformamides or isocyanates.

2. Results and discussion

2.1. Carbamoyl complexes

Two new palladium carbamoyl complexes $[Pd(PPh_3)_2Cl(CON\overline{(CH_2)_4CH_2})]$ (**1**) and $[Pd(PPh_3)_2Cl(CONHCH_2COOCH_3)]$ (**2**), have been prepared by reaction of $[PdCl_2(PPh_3)_2]$ with piperidine or glycine methyl ester, respectively (reactions (5 and 6)).

$$[PdCl_2(PPh_3)_2] + 2\overline{CH_2(CH_2)_4NH} + CO \longrightarrow \underset{\mathbf{1}}{[Pd(PPh_3)_2Cl(CON\overline{(CH_2)_4CH_2})]} + [\overline{CH_2(CH_2)_4NH_2}]Cl \quad (5)$$

$$[PdCl_2(PPh_3)_2] + 2NH_2CH_2COOCH_3 + CO \longrightarrow \underset{\mathbf{2}}{[Pd(PPh_3)_2Cl(CONHCH_2COOCH_3)]} + [NH_3CH_2COOCH_3]Cl \quad (6)$$

The IR spectrum of **1** shows ν(C=O) bands at 1589vs and 1582sh cm^{-1}. The ^{13}C NMR spectrum shows a triplet at 180.9 ppm (^2J(c–p) = 9.5 Hz) due to the amide carbon coupling with the phosphines. Compound **2** shows bands at 3415 m, ν(NH) at 1723vs, ν(C=O) ester; and at 1614vs cm^{-1}, ν(C=O) amid in the IR spectrum.

The volume of CO produced upon decomposition with HCl (reaction 7, see Experimental section) supports their formulations.

$$[Pd(PPh_3)_2ClCONHR] + 2HCl \longrightarrow [PdCl_2(PPh_3)_2] + CO + NH_2R \cdot HCl \quad (7)$$

2.2. Reaction with $CuCl_2$: Syntheses of carbamyl chlorides or isocyanates

The reaction of $CuCl_2$ at room temperature and under dinitrogen with $[Pd(PPh_3)_2Cl(CON\overline{(CH_2)_4CH_2})]$ which contains a carboxy amide derived from a secondary amine, affords the carbamyl chloride $ClCON\overline{(CH_2)_4CH_2}$ (**3**) (reaction 8).

$$[Pd(PPh_3)_2Cl(CON\overline{(CH_2)_4CH_2})] + 2CuCl_2 \longrightarrow 2CuCl + [PdCl_2(PPh_3)_2] + \underset{\mathbf{3}}{ClCON\overline{(CH_2)_4CH_2}} \quad (8)$$

The IR spectrum of the reaction solution shows a band at 1735 cm^{-1} ascribed to ν(C=O) of (**3**). This was confirmed by the mass spectrum. The reaction *in situ* with methanol produces the related carbamate $CH_3OCON\overline{(CH_2)_4CH_2}$ (see Experimental section).

Similarly $[Pd(PPh_3)_2Cl(CONHCH_2COOCH_3)]$ (**2**), reacts with $CuCl_2$ under analogous conditions to afford the isocyanate $OCNCH_2COOCH_3$ (**4**) (reaction 9), that is formed upon dehydrohalogenation of the unstable carbamyl chloride "$ClCONHCH_2COOCH_3$".

$$[Pd(PPh_3)_2Cl(CONHCH_2COOCH_3)] + 2CuCl_2 \longrightarrow 2CuCl + [PdCl_2(PPh_3)_2] + HCl + \underset{\mathbf{4}}{OCNCH_2COOCH_3} \quad (9)$$

The nickel carbamoyl complexes [LNiClCONHR] (L = 2,6-bis(diphenylphosphinemethyl)pyridine; R = C_6H_5, p-$CH_3C_6H_4$, or p-ClC_6H_4) [5b], similarly react with $CuCl_2$ at room temperature under dinitrogen to afford isocyanates (**5a–d**) in good yield (eqn. 10).

$$[LNiClCONHR] + 2CuCl_2 \longrightarrow [ClCONHR] + [LNiCl_2] + 2CuCl \quad (10)$$

$$[ClCONHR] \xrightarrow{HCl} RNCO\ (\mathbf{5})$$

(R = Ph (**a**); $CH_3C_6H_4$ (**b**); ClC_6H_4 (**c**); ^nBu (**d**))

The formation of isocyanates **4** and **5a–d** is supported by the IR spectrum and reactivity of the reaction solutions. The IR spectra support these formulations.

The overall stoichiometry in eqns. (8–10) was established by carrying out the reactions with a molar ratio Cu/complex > 2 and titrating the unreacted Cu^{II} (see Experimental section). Formation of isocyanate was confirmed by the GC and MS-spectrum and the products were quantitatively analyzed using their reaction products with methanol and/or 1-butylamine.

The solid residue that separates from the reaction solutions is CuCl and $[PdCl_2(PPh_3)_2]$ in reactions 8 and 9 (see Experimental section), whereas in the reactions of the nickel complexes the residue is a mixture of free copper(I) chloride and [CuClL], as ligand exchange occurs according to reaction (11).

$$[LNiCl_2] + CuCl \rightleftharpoons NiCl_2 + [CuClL] \quad (11)$$

Reactions (8–10) are of practical interest as they provide a phosgene-free route to isocyanates and carbamyl chlorides or their carbamate derivatives.

The synthesis of isocyanate promoted by transition metal complexes, has been carried out either stoichiometrically, as when nitrene compounds are carbonylated [7], or catalytically by carbonylation of nitro,

compounds [8,9]. Several patents [10] concern the latter process. As the conversion of nitro compounds into isocyanates has been proposed to proceed through the formation of nitrenes [9,11], it follows that these species may be the real intermediates in the synthesis of isocyanates.

The addition of an amine or an alcohol to a carbamoyl complex in the presence of additional base has been reported to generate *N,N'*-ureas or carbamates, respectively. This seems to suggest that carbamoyl complexes can generate isocyanates even if only indirect evidence for the formation of the last compounds has yet been reported. However, a few years ago [5b], we reported that a solution of [LNiCONHPh] and Na_2CO_3 give a compound in solution which showed a strong band at 1725 cm^{-1}. We assigned that band to the isocyanate complex [LNi(PhNCO)] which has not been isolated.

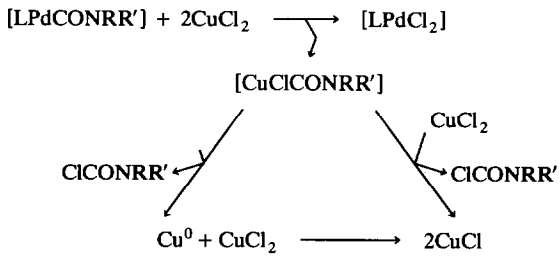
Carbamoyl species have been also proposed as intermediates when amines are converted stoichiometrically to isocyanates [1b,12].

The isolation of isocyanates and carbamyl chloride reported here is, therefore, the first firm evidence of the formation of these compounds from a carbamoyl complex.

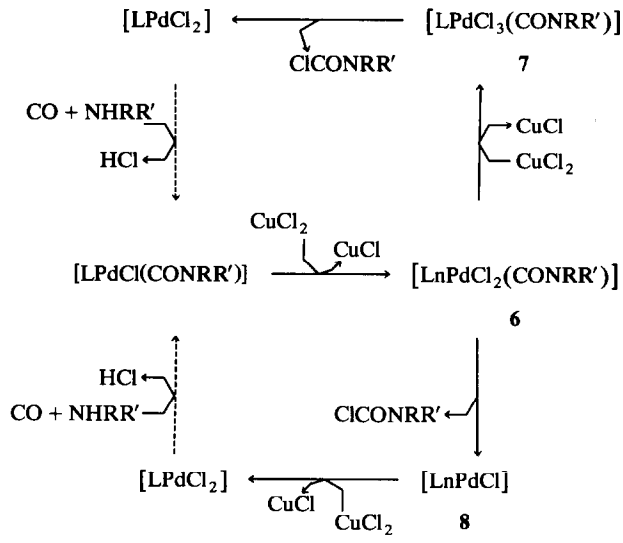
2.3. Reaction mechanism

It seems likely that reactions (9–10) proceed through the *N*-carbamylchloride that, in the case of primary amines changes to isocyanate and hydrogen chloride (see eqn. 10). In the case of reaction (8) the chlorocarbamyl derivative $ClCON\overline{(CH_2)_4CH_2}$ (**3**) is isolated, as HCl elimination is precluded. As far as the role played by $CuCl_2$ in the Pd–C bond cleavage is concerned, we proposed a mechanism for the synthesis of methyl chloroformate from methoxycarbonylpalladium complexes and $CuCl_2$ [2]. *N*-alkylcarbamylchloride formation may occur through one of the following pathways:

a) ligand-exchange between [LPdCl(CONHR)] and $CuCl_2$ with formation of [CuCl(CONRR')], which can either further react with $CuCl_2$ to afford *N*-alkylcarbamoylchloride (ClCONRR'), or undergo a reductive elimination to afford ClCONRR' and Cu^0 which then reacts with $CuCl_2$ to form the same products (Scheme 1).



Scheme 1.



Scheme 2.

A similar mechanism has been also proposed for the reaction of alkylpalladium complexes with $CuCl_2$ (eqn. 12) [13]

$$[LPd^{II}R] + 2CuCl_2 \longrightarrow [LPd^{II}Cl] + RCl + 2CuCl \quad (12)$$

b) oxidation of the initial carbamoylpalladium(II) complex by $CuCl_2$ to form an unstable Pd^{III}- or Pd^{IV}-intermediate (**6–7**) which then undergoes easy reductive elimination of carbamyl chloride (Scheme 2).

Although Pd^{III} (**6**) and Pd^{IV} (**7**) carbamoyl complexes have not been reported, their formation cannot be excluded. For example, we have found that the oxidation of $[Pd(PPh_3)_2Cl(CON\overline{(CH_2)_4CH_2})]$ with chlorine affords $[PdCl_2(PPh_3)_2]$ and carbamyl chloride (reaction 13).

$$[Pd(PPh_3)_2Cl(CONRR') + Cl_2 \longrightarrow [PdCl_2(PPh_3)_2] + ClCONRR' \quad (13)$$

The unstable carbamoyl palladium(IV) complex **7** is a likely product in this case.

2.4. Conversion of isocyanates and carbamyl chloride

Isocyanates **4** and **5a–d** and carbamyl chloride **3** have been transformed into carbamates or *N,N'*-ureas by reaction *in situ* with the appropriate alcohol or amine. Methanol, in the presence of a base such as NEt_3, converts $ClCON\overline{(CH_2)_4CH_2}$ into the methylcarbamate. The reaction is very selective (100%) as demonstrated by the GC and IR spectra of the reaction solutions.

When the reaction of [LNiClCONH^{n}Bu] with $CuCl_2$ is carried out under carbon monoxide, in the presence of free amine, with a molar ratio of $CuCl_2$ to nickel complex > 2, *N,N'*-dibutylurea is obtained with a yield greater than 100%. This suggests that a catalytic cycle is operating (Scheme 1). The same results can be obtained by carrying out the reaction under a 2:1 $CO:O_2$ mixture using a molar ratio Cu/Pd < 2. Under the latter conditions the dioxygen is a reoxidant of copper(I), simulating the Wacker process, and our system resembles the well known system for the catalytic conversion of amines into ureas and carbamates [4].

3. Conclusions

The formation of isocyanates and carbamylchloride from a transition metal carboxamido-complex is unprecedented. Besides the potential synthetic application, this reaction provides direct evidence of the role of intermediate carbamoyl complexes in the catalytic conversion of amines into ureas and carbamates. The role of copper chloride as promoter of the conversion of the carbamoyl into isocyanate or carbamyl chloride has been well attested. These last species react *in situ* with alcohols or amines to afford carbamates or ureas, respectively. Copper chloride not only reoxidizes Pd^0, simulating the Wacker process, but also promotes the conversion of carbamoyl complexes into isocyanates or carbamyl chlorides, that are the precursors of carbamates and ureas.

4. Experimental section

All preparations were carried out in deoxygenated solvents, and all operations were performed under dinitrogen or carbon monoxide using standard Schlenk techniques. Amines and dry $CuCl_2$ were from Aldrich and were used as purchased. Complexes [LNiCONHR] (L = 2,6-bis(diphenylphosphinomethyl)pyridine) were prepared by published methods [5b]. The yields of isocyanates and carbamyl chlorides were calculated by evaluating the amount of methyl carbamates produced by the reaction with methanol *in situ*. GLC quantitative analyses of carbamates were carried out with a Varian Vista 6000 gas chromatograph using a SP-2100/01% Carbowax column and toluene as internal standard. The quantitative analysis of *N,N'*-dibutylurea was carried out with a Varian HPLC instrument using a LC-8.5 μm, 15 cm × 4.6 mm column. IR spectra were recorded on a Perkin Elmer 883 spectrophotometer, GC-MS analyses were performed using a Hewlett Packard 5995 instrument. The ^{13}C NMR spectra were obtained using a 500 mHz Bruker apparatus.

4.1. Carbamoyl complexes preparation

4.1.1. Preparation of $[Pd(PPh_3)_2Cl(CO\overline{N(CH_2)_4CH_2})]$

To a suspension of $[PdCl_2(PPh_3)_2]$ (0.500 g, 0.71 mmol) in 10 ml of CH_3CN, piperidine (0.6 ml, 6.1 mmol) was added. The resulting yellow mixture was allowed to react with carbon monoxide (0.1 MPa) at room temperature. The suspension gradually turned pale yellow and finally became cream (about 2 h). The product was filtered, washed with ethanol and dried *in vacuo* (0.463 g, yield 84%). Anal. Found (%): C, 65.2; H, 4.9; Cl, 4.7; N, 1.9; P, 7.8; Calcd. for $C_{42}H_{40}ClNOP_2Pd$: C, 64.85; H, 5.19; Cl, 4.56; N, 1.80; P, 7.96%.

4.1.2. Preparation of $[PdCl(CONHCH_2COOCH_3)(PPh_3)_2]$

To a suspension of glycine methyl ester hydrochloride (0.560 g, 4.4 mmol) in 15 ml of acetone, 0.180 g (4.5 mmol) of NaOH was added. After 0.5 h of stirring, 0.560 g (0.76 mmol) of $PdCl_2(PPh_3)_2$ were added and the resulting reaction mixture was allowed to react with one atmosphere of carbon monoxide at room temperature. The suspension turned white-cream and the product was filtered, washed with acetone-ethanol mixture (2:1) and dried *in vacuo* (0.380 g, yield 64%). ^{13}C NMR 180.9 (t) ppm (CO amide), $^2J(C-P) = 9.5$ Hz. Anal. Found: Cl, 4.6; P, 7.8; Pd, 13.8. Calcd for $C_{40}H_{36}ClNO_3P_2Pd$: Cl, 4.53; P, 7.93; Pd, 13.61%.

4.2. Characterization of complexes: HCl decomposition and CO analyses

In a typical analysis, a weighed quantity of carbamoyl complex in CH_3CN (3 ml) and an ethanol solution of HCl 1 N (4 ml) were separately charged into the two branches of an inverted Y-shaped glass reactor. The reactor was connected to a gas burette, the contents were mixed and the CO developed was measured at 20°C and 0.1 MPa.

$[Pd(PPh_3)_2Cl(CO\overline{N(CH_2)_4CH_2})]$ (0.185 g, 0.24 mmol) yielded 5.1 ml of CO (about 88% of the theoretical value). $[Pd(PPh_3)_2Cl(CONHCH_2COOCH_3)]$ (0.195 g, 0.25 mmol) yielded 5.0 ml of CO (about 83%).

4.3. Reaction of carbamoyl complexes with $CuCl_2$

4.3.1. Synthesis of isocyanates

General procedure: a suspension of [LNiCl-CONHPh] (0.270 g, 0.39 mmol) in 5 ml of THF and $CuCl_2$ (0.105 g, 0.78 mmol) in 3 ml of THF were separately charged into the two branches of a Y-shaped reactor. The reactor was closed under dinitrogen, and the contents mixed and allowed to react with stirring

for 0.5 h. The initial brown suspension gave a brown semi-solid product that finally turned to pale-yellow. The IR spectrum of the resulting supernatant liquor showed bands at 2278 sh and 2262 m cm^{-1} due to phenyl isocyanate [14] the presence of which was confirmed by the GC-MS spectrum. *m/z* (relative intensity %), 119 (100%), 91 (65), 65 (10), 64 (45), 63 (21), 51 (12), 50 (12), 39 (19), 38 (21).

The reaction of the other complexes was carried out using a similar procedure. Isocyanates **5b–d** and **4** were analyzed by IR and mass spectra and GC methods.

p-$CH_3C_6H_4NCO$: IR (νC=O), 2274m cm^{-1}; *m/z*: 133 (100%), 132 (56), 105 (20), 104 (48), 91 (14), 78 (18), 77 (15), 51 (16).

p-ClC_6H_4NCO: IR (νC=O), 2273m cm^{-1}; *m/z*: 155 (35%), 154 (11), 153 (100), 127 (20), 125 (62), 90 (39), 63 (22), 62 (16).

^{n}Bu NCO: IR (νC=O), 2272m cm^{-1}. *m/z*: 98 (18), 70 (12), 56 (37), 43 (100), 41 (98).

CH_3OCOCH_2NCO: IR (νC=O), 2273m, 1723s cm^{-1}; *m/z*: 115 (12), 71 (5), 59 (20), 56 (100).

4.3.2. Synthesis of carbamyl chloride

$[Pd(PPh_3)_2Cl(CO\overline{N(CH_2)_4CH_2})]$ (0.350 g, 0.45 mmol) in THF (4 ml) and $CuCl_2$ (0.121 g, 0.90 mmol) in THF (3 ml) were charged in the Y-shaped reactor described above. The reactants were mixed and allowed to react for 0.5 h under dinitrogen. The solid reaction mixture was separated by filtration. The IR spectrum of the solution showed a band at 1735w cm^{-1} assigned to the carbamyl chloride whose formation was also confirmed by GC-MS *m/z*: 149 (23%), 147 (68), 112 (100), 106 (19), 84 (19), 69 (38), 56 (37), 55 (21), 42 (30), 41 (54), 39 (18).

4.4. Reaction of carbamoyl complexes with chlorine

Chlorine was bubbled into a suspension of $[Pd(PPh_3)_2Cl(CO\overline{N(CH_2)_4CH_2})]$ (0.350 g) in THF (5 ml) at room temperature. Solid yellow $[PdCl_2(PPh_3)_2]$, recognized by its IR spectrum and elemental analyses, was rapidly formed. The IR spectrum of the reaction solution shows a band at 1735w cm^{-1} assigned to the carbamyl chloride that was also confirmed by MS.

4.5. Reactions stoichiometry

The reaction stoichiometry (Cu/Pd = 2) was determined by carrying out the reaction with an excess of $CuCl_2$ and titrating the unreacted $CuCl_2$ by iodometry.

The following procedure is typical [LNiClCONHPh] (0.150 g, 0.22 mmol) and $CuCl_2$ (0.104 g, 0.77 mmol, Cu/Ni = 3,5) were allowed to react under dinitrogen as described above. The reaction mixture was evaporated *in vacuo* and the resulting solid residue was extracted with 15 ml de-aerated water. Acetic acid and KI were added to the resulting aqueous solution and the liberated iodine was titrated with 3.0 ml of a $Na_2S_2O_3$ 0.1 N solution corresponding to 0.29 mmol of unreacted Cu^{II}.

4.6. Conversion of isocyanates and carbamyl chloride: synthesis of carbamates and N,N'-ureas synthesis

4.6.1. N-phenylmethylcarbamate

[LNiClCONHPh] (0.250 g, 0.36 mmol) and $CuCl_2$ (0.097 g, 0.72 mmol) were allowed to react as described above. To the resulting reaction mixture containing PhNCO, 1 ml of methanol was added and the reactor was warmed up to 50°C for 0.5 h. The liquid phase was analyzed for *N*-phenylmethylcarbamate.

IR: ν(C=O) 1710 cm^{-1}; Mass spectrum: *m/z* 151 (M^+, 68%), 120 (13), 119 (65), 106 (100), 92 (46), 77 (39), 65 (89), 59 (37), 39 (74).

GLC quantitative analyses gave 0.046 g of PhNH-$COOCH_3$ corresponding to a 85% yield.

4.6.2. N-butylmethylcarbamate

Butylisocyanate was synthesized by reaction of [LNiClCONHBu] (0.200 g, 0.30 mmol) with $CuCl_2$ (0.081 g, 0.60 mmol). Methanol (1 ml) was added and the resulting reaction mixture was analyzed for *N*-butylmethylcarbamate. IR: ν(C=O) 1725 cm^{-1}. *m/z*: 131 (9%), 88 (100), 59 (17), 57 (12), 44 (52).

GLC quantitative analyses gave 0.031 g (0.24 mmol) of compound, 80% yield.

The methylcarbamates of *p*-ClC_6H_4NCO and *p*-$CH_3C_6H_4NCO$ were prepared in a similar way.

4.6.3. N-piperidinemethylcarbamate

The carbamyl chloride $ClCO\overline{N(CH_2)_4CH_2}$ was prepared according to the procedure described above using $[Pd(PPh_3)_2Cl(CO\overline{N(CH_2)_4CH_2})]$ (0.250 g, 0.32 mmol) in THF (3 ml) and $CuCl_2$ (0.086 g 0.064 mmol) in THF (3 ml). Methanol-NEt_3 5:2 mixture (1 ml) was added to the filtered reaction solution which was warmed to 40°C and analyzed by IR and GC-MS. The IR spectrum had a band due to (νC=O) 1623 cm^{-1}, from *N*-piperidinemethylcarbamate, whose formation was confirmed by mass spectrum *m/z*: 143 (35%), 142 (28), 128 (100), 112 (9), 84 (29), 59 (15), 56 (21), 55 (12), 42 (38), 41 (19).

4.6.4. N,N'-dibutylurea

Butylisocyanate was synthesized by reaction of [LNiClCONHBu] (0.200 g, 0.30 mmol) with $CuCl_2$ (0.081 g, 0.60 mmol). $^nBuNH_2$ (1 ml) was added and the resulting reaction mixture was analyzed for *N,N'*-dibutylurea. IR: ν(C=O) 1670 cm^{-1}; Mass spectrum:

m/z: 172 (37%), 101 (20), 100 (15), 74 (32), 44 (100). GLC quantitative analyses gave 0.041 g (0.24 mmol) of compound, 80% yield.

4.7. Catalytic cycles for the synthesis of ureas

4.7.1. Use of copper chloride as reoxidant

To [NiLClCONHBu] (0.250 g, 0.37 mmol) in CH_3CN (6 ml), $CuCl_2$ (0.100 g, 0.74 mmol) was added under dinitrogen. After reaction, to the resulting mixture that contained ^nBuNCO, $^nBuNH_2$ (0.5 ml) and $CuCl_2$ (0.530 g, 3.94 mmol) were added and the system was allowed to react with one atmosphere of CO at room temperature. After 3 h, the liquid phase was analyzed for *N,N'*-dibutylurea (IR and MS). The HPLC quantitative analyses gave 0.146 g of *N,N'*-dibutylurea (yield 230%, based on the initial complex) that was isolated as colourless crystals by cooling the filtered solution (concentrated *in vacuo* to dryness and treated with diethyl ether) at −8°C.

4.7.2. Use of O_2 as reoxidant

^nBuNCO was prepared in a 100 ml glass reactor by adding $CuCl_2$ (0.075 g, 0.55 mmol) to a suspension of [NiLClCONHBu] (0.250 g 0.37 mmol) in CH_3CN (6 ml). $^nBuNH_2$ (0.5 ml) was added to the resulting mixture and the system was allowed to react with a 2:1 CO/O_2 mixture. After 5 h, *N,N'*-dibutylurea was detected in solution (IR, MS). The HPLC quantitative analyses gave 0.178 g (1.04 mmol) of *N,N'*-dibutylurea (yield 292%). The GC analysis of the gas phase revealed the presence of CO_2 that may come from the Ni-catalyzed oxidation of CO with O_2.

References

1 (a) R.J. Angelici, *Acc. Chem. Res., 5* (1972) 335 and references therein; (b) E.W. Stern and M.L. Spector, *J. Org. Chem., 31* (1966) 596; (c) F. Rivetti and U. Romano, *La Chimica e L'Industria, 62* (1980) 7 and refs. therein; (d) D. Belli Dell'amico, F. Calderazzo and G. Pelizzi, *Inorg. Chem., 18* (1979) 1165; F. Rivetti and U. Romano, *J. Organomet. Chem., 174* (1979) 221; W.E. Martin and M.F. Faraona *J. Organomet. Chem.*, 206 (1981) 393; F. Calderazzo, *Inorg. Chem., 4* (1965) 293; T. Saegusa, S. Kobayashi, K. Hirota and Y. Ito, *Bull. Chem. Soc. Jap., 42* (1969) 2610; D. Fenton and P.J. Steinwand, *J. Org. Chem., 5* (1974) 701; Ph. Bréchot, Y. Chauvin, D. Commerceu and L. Saussine, *Organometallics, 9* (1990) 26; P. Giannoccaro, C.F. Nobile and M. Latronico, *Inorg. Chim. Acta, 175* (1990) 133 and refs. therein.

2 P. Giannoccaro, N. Ravasio and M. Aresta, *J. Organomet. Chem., 451* (1993) 243.

3 P. Giannoccaro, *J. Organomet. Chem.*, in press.

4 P. Giannoccaro, *J. Organomet. Chem., 336* (1987) 271; P. Giannoccaro, *Inorg. Chim. Acta, 142* (1988) 81; H. Alper and F.W. Harstock, *J. Chem. Soc., Chem. Commun.*, (1985) 1141; H. Alper, G. Vasapollo, F.W. Hartstok and M. Mlekuz, *Organometallics, 6* (1987) 2391; S. Fukuoka, M. Chono and M. Kohno, *J. Organomet. Chem., 83* (1884) 99.

5 (a) C.R. Green and R.J. Angelici, *Inorg. Chem., 11* (1972) 2095; G. Vasapollo, C.F. Nobile and A. Sacco, *J. Organomet. Chem., 296* (1985) 435; (b) A. Sacco, P. Giannoccaro and G. Vasapollo, *Inorg. Chim. Acta, 83* (1984) 125; (c) W. Beck and B. Purucker, *J. Organomet. Chem., 112* (1976) 361.

6 See for example: (a) D.J. Darensbourg and M.Y. Darensbourg, *Inorg. Chem., 9* (1970) 1691; K.G. Coulton and R.F. Fenske, *Inorg. Chem., 7* (1968) 1273. b) G. Vasapollo, C.F. Nobile and A. Sacco, *J. Organomet. Chem., 296* (1985) 435 and references therein.

7 A. Basu, S. Bhaduri and H. Khwaya, *J. Organomet. Chem., 319* (1987) C28 and references therein; S.H. Han and G.L. Geoffroy, *Polyhedron 7* (1988) 2331 and references therein; M. Pizzotti, F. Porta, S. Cenini and F. Demartin, *J. Organomet. Chem., 356* (1988) 105.

8 See for example: S. Cenini, M. Pizzotti and C. Crotti in R. Ugo (ed.), *Aspects of Homogeneous Catalysis*, Vol. 6, D. Reidel, Dordrecht, 1988, p. 97, and pp. 153–157 and references therein; S. Cenini, F. Ragaini, M. Pizzotti, F. Porta, G. Mestroni and E. Alessio, *J. Mol. Catal., 64* (1991) 179; R. Ugo, M. Pizzotti, P. Nardi, C. Dossi, A. Andreetta and G. Capparella, *J. Organomet. Chem., 417* (1991) 221; W.B. Hardy and R.P. Bennet, *Tetrahedron Lett., 961* (1967); B.K. Nefedov and V.I. Manov-Yuvenskii, *Bull. Acad. Sci. USSR., 28* (1979) 540.

9 S.P. Gupte and R.V. Chaudhari, *J Mol. Catal., 24* (1984) 1979; S.B. Alligudi, R.V. Chaudhari and L.K. Doraiswamy, *Ind. Eng. Chem. Proc. Des. Dev., 23* (1979) 80.

10 W.W. Prichard, US Patent 3, 576, 836 (1971) to Du Pont; British Patent 1,025,436(1966); G.F. Ottman and E.H. Kober, US Patent 3,523,962(1970) to Olin Corp.; E. Smith and W. Schnabel, US Patent 3,576,835 to Olin Corp.

11 F.J. Veigert, *J. Organomet. Chem., 38* (1973) 1316; G.W. Parshal, *Homogeneous catalysis*, Wiley, New York, 1980, p. 73; A.F.M. Iqbal, *ChemTech*, September (1974) 566.

12 J. TsuJi and N. Iwamoto, *J. Chem. Soc., Chem. Commun.*, (1966) 828.

13 P.M. Henry *J. Org. Chem., 39* (1974) 3871 and references therein.

14 C.J. Pouchert, *The Aldrich Library of IR spectra*, Aldrich Chemical Company, 1970.