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Carbamoyl and Alkoxycarbonyl Complexes of Nickel(II)

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The preparation is described of carbamoyl complexes of nickel(II), of formula Ni(pnp)(CONHR)Cl (pnp = 2,6-bis(diphenylphosphinomethyl)pyridine, R = C_6H_5, o-$CH_3C_6H_4$, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-ClC_6H_4, p-$NO_2C_6H_4$, n-Bu, $C_6H_5CH_2$), obtained from Ni(pnp)Cl_2 and aromatic or aliphatic amines under CO at room temperature and atmospheric pressure in anhydrous solvents. The complexes react with bases to give, depending upon the experimental conditions, aryl- and alkyl-isocyanates, urethanes or substituted ureas in very good yields. The preparation and properties of the methoxycarbonyl complex, Ni(pnp)(CO_2Me)Cl, are also described.

Introduction

The reaction between amines and metal carbonyl complexes represents the most general method of preparing carbamoyl complexes [1].

Although primary and secondary alkylamines react readily with metal carbonyls having force constant higher than 17.2 mdyn/Å [1, 2], aromatic amines have not yet been found to undergo a similar reaction.

We have recently found that the 2,6-bis(diphenylphosphinomethyl)pyridine complexes of nickel(II), which do not show any evidence of formation of carbonyl complexes by treatment with carbon monoxide in anhydrous ethanol or in methylene chloride, readily react with carbon monoxide in water–ethanol solutions at room temperature and atmospheric pressure to give carbon dioxide and nickel(0) carbonyl complexes [3].

This behaviour, suggesting a nucleophilic water attack on a very labile carbonyl complex intermediate of nickel(II), prompted us to undertake a study of the reaction between carbon monoxide and the 2,6-bis(diphenylphosphinomethyl)pyridine complexes of nickel(II) in the presence of nucleophiles such as amines and alkoxides.

Results and Discussion

Although several pentacoordinated [4] and a few cationic tetracoordinated [5, 6] carbonyl complexes of nickel(II) have been reported, the reactions between these carbonyls and amines or alkoxides have not been investigated, except that of $[C_6Cl_5Ni(PPhMe_2)_2CO]ClO_4$ with methanol or ethanol in the presence of triethylamine to give alkoxycarbonylnickel(II) complexes [6].

The carbamoyl complexes of the type Ni(pnp)(CONHR)Cl (R = primary alkyl- or aryl-amines, Table I), obtained by us from Ni(pnp)Cl_2 and amines in anhydrous ethanol or acetonitrile solution under carbon monoxide at room temperature and atmospheric pressure, therefore represent the first examples of stable and well-characterised carbamoyl complexes obtained from aromatic amines and transition metal complexes.

Preparation of Complexes

The primary aryl-amines RNH_2 (R = C_6H_5, p-$CH_3C_6H_4$, o-$CH_3C_6H_4$, p-ClC_6H_4, p-$CH_3OC_6H_4$) react promptly with Ni(pnp)Cl_2 under a carbon monoxide atmosphere to give the carbamoyl complexes Ni(pnp)(CONHR)Cl according to eqn. 1:

$$\mathrm{Ni(pnp)Cl_2 + CO + 2RNH_2 = Ni(pnp)(CONHR)Cl + RNH_3Cl} \quad (1)$$

This behaviour confirms the previous suggestion [3] that an ionic nickel carbonyl complex, $[\mathrm{Ni(pnp)(CO)Cl}]^+$, must also form in solution at low carbon monoxide pressure and at room temperature, albeit in very low concentration.

The basicity of the nucleophile is strong enough to displace the equilibrium of reaction (1) completely to the right when the pK_α of the amine is higher than 4. Using the much less basic p-nitroaniline (pK_α = 1), the carbamoyl complex is formed in good yield only in the presence of a base such as sodium or potassium carbonate or triethylamine. On the contrary, a strict control of the stoichiometry is necessary when more basic amines, like benzylamine or n-butylamine (pK_α = 9–10) are used, since the formed carbamoyl complex reacts further with the amine in excess.

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TABLE I. Analytical Data of Ni(pnp)(CONHR)Cl and of Ni(pnp)(CO_2R')Cl.

R	Found % (Calc %)					
	C	H	N	P	Cl	Ni
C_6H_5	65.8	5.0	4.1	8.9	5.4	8.4
	(66.2)	(4.82)	(4.06)	(8.98)	(5.14)	(8.51)
p-$CH_3C_6H_4$	66.0	5.3	3.9	8.7	5.1	8.1
	(66.5)	(5.01)	(3.98)	(8.80)	(5.04)	(8.34)
o-$CH_3C_6H_4$				8.8	5.2	8.2
				(8.80)	(5.04)	(8.34)
p-ClC_6H_4				8.3	10.1	7.9
				(8.55)	(9.79)	(8.11)
p-$CH_3OC_6H_4$				8.4	5.2	7.9
				(8.61)	(4.93)	(8.15)
p-$NO_2C_6H_4$				8.5	5.1	8.0
				(8.43)	(4.82)	(7.99)
n-C_4H_9				9.4	5.4	8.8
				(9.25)	(5.29)	(8.76)
$C_6H_5CH_2$				8.6	5.1	8.5
				(8.80)	(5.04)	(8.34)
R'						
CH_3				9.8	5.6	9.4
				(9.85)	(5.64)	(9.34)

TABLE II. I.r. Data of Ni(pnp)(CONHR)Cl, cm^{-1}.

R	νN–H	νCO
C_6H_5	3220 (w)	1605 (vs)
p-$CH_3C_6H_4$	3210 (w)	1600 (vs)
o-$CH_3C_6H_4$	3210 (w)	1600 (vs)
p-ClC_6H_4	3240 (w)	1610 (vs)
p-$CH_3OC_6H_4$	3240 (w)	1605 (vs)
p-$NO_2C_6H_4$	3210 (w)	1600 (vs)
n-C_4H_9	3310 (w)	1590 (vs)
$C_6H_5CH_2$	3310 (w)	1585 (vs)

TABLE III. Spectral Data of Ni(pnp)(CO_2Me)Cl.

I.r., cm^{-1} [a]		N.m.r., τ [b]		
νCO	νC–O–C	Ph	CH_2	CH_3
1618 (vs)	1063 (s)	2.2–2.6 (m)	5.69 (t)	6.93 (s)

[a] Nujol mull. [b] In CD_2Cl_2. TMS as internal reference. Multiplicity is indicated in parentheses.

The compounds resulting from reaction (1) are characterized by a very strong carbonyl stretching vibration at about 1600 cm^{-1} (Table II), which is attributed to the carbamoyl carbonyl group [1].

The methoxycarbonyl complex Ni(pnp)(CO_2Me)-Cl has been prepared by treating a methanolic solution of Ni(pnp)Cl_2 under a carbon monoxide atmosphere with the stoichiometric amount of sodium methoxide. The compound is characterized by strong i.r. absorption bands at 1618 and 1063 cm^{-1} (Table III), which are attributed to the methoxycarbonyl group [7].

Reactions of Carbamoyl Complexes

It is well known that the carbamoyl complexes can react easily with triethylamine to give isocyanates according to eqn. 2, and that the equilibrium reaction can be displaced to the right or left depending upon the experimental conditions [1]:

$$L_nM(CONHR) + Et_3N = L_nM^- + RNCO + Et_3NH^+ \quad (2)$$

Indeed, we have found that the carbamoyl complex Ni(pnp)(CONHPh)Cl reacts at room temperature in methylene chloride with triethylamine or with potassium carbonate to give phenylisocyanate. Actually, most of the formed isocyanate remains bound to the nickel to give a compound which we were not able to purify completely, but which can be confidently formulated as Ni(pnp)(PhNCO). In fact, the compound is characterized by a strong i.r. absorption band at 1725 cm^{-1}, a value very near to that of 1763 cm^{-1} shown by Ni(PPh_3)$_2$(PhNCO) [8]. Moreover, the compound gives ethyl carbanilate in very good yield on treating with ethanol.

The aryl urethanes have been obtained more easily and with better yields by treating the carbamoyl complexes in ethanol with anhydrous bases, such as triethylamine, sodium or potassium carbonate, and calcium oxide.

The intermediate isocyanate formed according to eqn. (2) reacts easily with primary amines to give substituted ureas. With the aromatic primary amines characterized by a pK ranging from 4 to 6 the overall reaction occurs according to eqn. 3:

$$\mathrm{Ni(pnp)Cl_2 + 2ArNH_2 + 2K_2CO_3 + 3CO = (ArNH)_2CO + Ni(pnp)(CO)_2 + 2KHCO_3 + 2KCl} \quad (3)$$

The basicity of the primary alkyl amines is strong enough to displace to the right the equilibrium of reaction (2), and therefore with amines like n-butyl- or benzyl-amine the overall reaction occurs according to eqn. 4:

$$\mathrm{Ni(pnp)Cl_2 + 4AlkNH_2 + 3CO = (AlkNH)_2CO + Ni(pnp)(CO)_2 + 2AlkNH_3Cl} \quad (4)$$

Experimental

All preparations were carried out in deoxygenated solvents and all operations were routinely performed in an atmosphere of reagent grade dinitrogen or carbon monoxide using standard Schlenk techniques. Infrared spectra were recorded on a Perkin-Elmer 577 instrument and the n.m.r. spectra were recorded on a Varian XL 200 spectrometer. Gas chromatographic determinations were carried out on EGSSX and Porapack Q columns using a Hewlett-Packard 5750 apparatus. Typical examples of each reaction type are given below.

Preparation of the Carbamoyl Complexes

Ni(pnp)(CONHAr)Cl (Ar = Ph, o-$CH_3C_6H_4$, p-$CH_3C_6H_4$, p-ClC_6H_4, p-$CH_3OC_6H_4$)

A solution of the amine (6 mmol in 20 ml of ethanol) was added to a stirred solution of Ni(pnp)-Cl_2 (0.60 g, 1 mmol) in 20 ml of anhydrous ethanol under a carbon monoxide atmosphere. The mixture was stirred for 1 hr. at room temperature to produce a deep yellow precipitate which was filtered, washed with ethanol, and dried *in vacuo.* Yield 70–80%.

Ni(pnp)(CONH$C_6H_4NO_2$)Cl

A mixture of p-nitroaniline (300 mg, 2.4 mmol), Ni(pnp)Cl_2 (0.60 g, 1 mmol) and potassium carbonate (500 mg, 3.6 mmol) in anhydrous ethanol was stirred at room temperature under a carbon monoxide atmosphere for 2 hr. The carbamoyl complex was extracted with methylene chloride from the filtered solid residue, and crystallized by adding benzene to the solution concentrated *in vacuo.* Yield 75%.

Ni(pnp)(CONHAlk)Cl (Alk = n-Bu, $C_6H_5CH_2$)

A solution of the amine (1.94 mmol in 1 ml of MeCN) was added to a stirred solution of Ni(pnp)Cl_2 (0.60 g, 1 mmol) in 20 ml of MeCN under a carbon monoxide atmosphere at room temperature. After 0.5 hr. the red solution obtained was filtered and the filtrate was concentrated *in vacuo* to produce deep red crystals, which were washed with diethyl ether and dried *in vacuo*. Yield 70%.

Preparation of the Methoxycarbonyl Complex Ni(pnp)(CO_2Me)Cl

A solution of sodium methoxide (1.50 mmol in 8 ml of methanol) was slowly added to a stirred solution of Ni(pnp)Cl_2 (0.90 g, 1.49 mmol) in 25 ml of methanol under a carbon monoxide atmosphere. The mixture was stirred for 1 hr at room temperature to produce a brown-red solution, which was evaporated *in vacuo.* The solid residue was washed with benzene and then recrystallized from warm acetone to produce pink crystals (0.70 g, yield 62%). Molar conductivity in nitromethane (10^{-3} *M*): 56 ohm^{-1} cm^2 M^{-1}.

Reactivity of the Carbamoyl Complexes

Formation of ethyl carbanilate

A mixture of Ni(pnp)(CONHPh)Cl (300 mg, 0.43 mmol) and potassium carbonate (500 mg, 3.6 mmol) in 5 ml of anhydrous ethanol was stirred at 70 °C for 3 hr. under a carbon monoxide atmosphere. The glpc analysis of the filtered solution showed the formation of ethyl carbanilate (61 mg, yield 85%). From the solution, concentrated *in vacuo,* the dicarbonyl Ni(pnp)$(CO)_2$, identified by its i.r. spectrum [3], was obtained as white crystals. The same results were obtained by using CaO or triethylamine instead of the potassium carbonate.

Formation of diphenylurea

A mixture of Ni(pnp)(CONHPh)Cl (1.0 g, 1.45 mmol), aniline (0.60 g, 6.5 mmol) and potassium carbonate (2.0 g) in 15 ml of methylene chloride was stirred at room temperature for 40 hr. under a carbon monoxide atmosphere. The solution was then evaporated *in vacuo* and the solid residue washed with benzene until complete extraction of the dicarbonyl complex Ni(pnp)$(CO)_2$. The solid residue was then washed with water, dried, and treated with diethyl ether to extract the diphenylurea, which was identified by elemental and spectral analysis (260 mg, yield 85%).

Formation of di-n-butylurea

A solution of n-butylamine (0.50 ml in 2 ml of MeCN) was added at room temperature to a stirred solution of Ni(pnp)(CONHBu)Cl (500 mg, 0.75 mmol) in 10 ml of MeCN, under a carbon monoxide atmosphere. As soon as the pink solution became colourless, the solvent was evaporated *in vacuo* and the di-n-butylurea, which was identified by elemental and spectral analysis, was extracted with diethyl ether from the residue (yield 84%). The same results were obtained by treating directly Ni(pnp)Cl_2 with an excess of n-butylamine in MeCN under a carbon monoxide atmosphere.

Formation of phenylisocyanate

A mixture of Ni(pnp)(CONHPh)Cl (0.40 g) and potassium carbonate (3.0 g) in 15 ml of methylene chloride was stirred at room temperature under a dinitrogen atmosphere for 6 days. The color of the solution slowly changed from red-brown to light yellow. The glpc analysis of the filtered solution showed the presence of some free phenylisocyanate and its i.r. spectrum showed, beside a very weak absorption band at 1608 cm^{-1}, ascribable to the free phenylisocyanate, an absorption band at 1725 cm^{-1}. The evaporation of the solvent *in vacuo* yielded an oily residue, showing in its i.r. spectrum, beside the absorption bands characteristic of the pnp ligand, a strong absorption band at 1725 cm^{-1}. By treating this oily residue with ethanol, the ethyl carbanilate was produced in good yield.

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