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CARBAMOYL AND ALKOXYCARBONYL COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

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Summary

Carbamoyl and alkoxycarbonyl complexes of palladium(II) and platinum(II) of the type M(pnp)(CONHR)Cl (pnp = 2,6-bis(diphenylphosphinomethyl)pyridine; M = Pd, R = C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, C_6H_{11}, t-Bu; M = Pt, R = C_6H_5), Pd(pnp)[CON(Pr)$_2$]Cl (Pr = propyl), M(pnp)(COOR)Cl (M = Pd, R = C_6H_5, CH_3; M = Pt, R = CH_3), Pd(pnp)(COOCH$_3$)$_2$ result from reaction of M(pnp)Cl$_2$ with carbon monoxide and amines or alkoxides at room temperature and atmospheric pressure.

The carbamoyl complexes react with bases to give urethane or diphenylurea depending upon the experimental conditions.

Introduction

The synthesis of carbamoyl and alkoxycarbonyl complexes of transition metals has received considerable attention in recent years owing to their recognition as intermediates in several important catalytic process such as carbonylation of amines or alcohols [1]. These compounds have usually been prepared by reaction of a variety of metal carbonyl complexes with primary and secondary amines and alkoxides [2], or by reaction of metal complexes and amines in presence of carbon monoxide [3]. Nucleophilic attack at the carbon atom of a coordinated carbon monoxide molecule has been suggested to occur in all cases [4], and a variety of carbamoyl and alkoxycarbonyl complexes of nickel [5], palladium [1a,3a,5c,6,7a,12], platinum [7], manganese [8], iron [2], ruthenium [9], molybdenum and tungsten [10] have been prepared.

As Angelici, Blacik, and other authors [2] have reported, the tendency of the CO ligand to react with amines, or with others nucleophiles depends upon the electronic density on the carbon atom, which is related to its C–O bond force constant. In particular, it has been observed that only carbonyl complexes with a bond stretching absorption value higher than 2000 cm^{-1} yield alkoxycarbonyl or carbamoyl complexes.

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In a recent report [11] we described some new routes to carbamoyl- and alkoxycarbonyl-nickel(II) complexes which involve the intermediate formation of a labile carbonyl species, which however was not detected by IR spectroscopy. In this paper we describe alkoxycarbonyl and carbamoyl complexes of palladium(II) and platinum(II) of formula M(pnp)(COOR)Cl (pnp = 2,6-bis(diphenylphosphinomethyl)pyridine; M = Pd, R = C_6H_5, CH_3; M = Pt, R = CH_3); Pd(pnp)($COOCH_3$)$_2$; Pd(pnp)(CONHR)Cl (R = C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, C_6H_{11}, t-butyl; M = Pt, R = C_6H_5) and Pd(pnp)[$CON(Pr)_2$]Cl obtained from M(pnp)Cl_2, carbon monoxide and alkoxydes or amines in methanol or acetonitrile at room temperature and atmospheric pressure, and give an account of their reactions with bases.

Results and discussion

The reaction of M(pnp)Cl_2 (M = Pd, Pt) with methoxide or phenoxide ion in a molar ratio 1/1 in dry methanol under a carbon monoxide atmosphere proceeds rapidly at ambient temperature and atmospheric pressure to produce the corresponding alkoxycarbonyl complexes of formula [M(pnp)(COOR)]Cl (R = CH_3, C_6H_5) in good yields. The reaction is usually complete within a few minutes after the addition of the alkoxide. The compounds obtained were characterized by their elemental analysis (Table 1) and IR spectra; the latter show characteristic absorption bands in the region 1670–1598 and 1065–1028 cm^{-1}, assignable to the C=O and C–O–C stretchings (Table 2). The ready formation of these complexes strongly supports the view that, as in the case of similar complexes of nickel(II) [11] previously described, an ionic carbonyl complex $[M(pnp)(CO)Cl]^+$ is formed at low carbon monoxide pressures and room temperature, although we were not able to detect such an intermediate by IR spectroscopy. If the reaction of Pd(pnp)Cl_2 with methoxyde is carried out in 1/2 molar ratio in methanol the dialkoxycarbonyl complex Pd(pnp)($COOCH_3$)$_2$ is obtained.

The carbamoyl complexes of palladium(II) and platinum(II) can also be readily prepared in good yields by treating an excess of the amine with M(pnp)Cl_2 in dry methanol under carbon monoxide at room temperature. With very basic amines, such as n-butylamine, t-butylamine, n-propylamine, an aprotic solvent, such as acetonitrile, is needed in order to suppress the formation of the alkoxycarbonyl according to eq. 1.

$$Pd(pnp)Cl_2 + ROH + CO + RNH_2 \rightarrow [Pd(pnp)(COOR)]Cl + RNH_3Cl \qquad (1)$$

The metal in the carbamoyl complexes, as well in the corresponding alkoxycarbonyl complexes, is tetracoordinated, as shown by the molar conductivity of the compounds in acetonitrile.

The infrared spectra of the complexes (Table 2) show absorption bands in the region 3200–3300 and 1620–1580 cm^{-1} assignable, respectively, to the N–H and C=O stretchings. The absorption in the 1620–1580 cm^{-1} region is characteristic of carbamoyl complexes and corresponds to a combination of the carboxamido C–O stretching mode and an N–H bending mode [1].

The proton NMR spectra (Table 3) of all but one of the carbamoyl complexes obtained, show, in addition to the phenyl protons, a triplet in the region 4.6–4.8 ppm with J(P–H) of ca. 4.5 Hz, due to the equivalent methylene protons of the pnp

TABLE 1

ANALYTICAL DATA FOR CARBAMOYL AND ALKOXYCARBONYL COMPLEXES

Compound	Λ_M [a]	Colour	Dec. point (°C)	Analysis (Found (calcd.) (%))			
				C	H	Cl	P
Pd(pnp)($CONHC_6H_5$)Cl		yellow	188–189	62 (61.9)	5 (4.51)	5.08 (4.81)	8.25 (8.4)
Pt(pnp)($CONHC_6H_5$)Cl		white	190	55.8 (55.2)	4.1 (4.03)	4.2 (4.29)	7.5 (7.5)
Pd(pnp)(CONH-*p*-$CH_3C_6H_5$)Cl		yellow	220	61.9 (62.3)	4.58 (4.82)	4.7 (4.71)	8.96 (8.23)
Pd(pnp)(CONH-*p*-$CH_3OC_6H_5$)Cl		yellow	174	60.9 (61.0)	5.0 (4.72)	4.88 (4.61)	7.84 (8.06)
Pd(pnp)($CONHC_6H_{11}$)Cl		yellow	185–188	61.00 (61.38)	5.1 (5.29)	4.6 (4.77)	8.2 (8.33)
Pd(pnp)(CONH-t-Bu)Cl	89	white-brown	208	59.7 (60.26)	5.3 (5.20)	5.1 (4.94)	8.7 (8.63)
Pd(pnp)[$CON(n\text{-}Pr)_2$]Cl		yellow-white		59.0 (61.2)	5.8 (5.54)	4.9 (4.76)	8.1 (8.31)
Pd(pnp)($COOCH_3$)Cl	109	white	182	59.0 (58.6)	4.9 (4.47)	4.98 (5.24)	8.88 (9.2)
Pd(pnp)($COOC_6H_5$)Cl		yellow	185	60.99 (61.8)	4.6 (4.37)	5.0 (4.80)	8.6 (8.39)
Pt(pnp)($COOCH_3$)Cl		orange	238	50.9 (51.8)	3.7 (3.95)	4.98 (4.63)	8.49 (8.10)
Pd(pnp)($COOCH_3$)$_2$		red	196	59.9 (60.05)	4.6 (4.75)	– –	9.1 (8.85)

[a] In CH_3CN, $ohm^{-1}\ cm^2\ mol^{-1}$.

ligand (Fig. 1a). This triplet is probably due to the virtual coupling to two equivalent ^{31}P nuclei, and the magnitude of J(P–H) is similar to that found for other complexes with *trans* phosphine ligands in which there is a strong phosphorus coupling, such as $Pd(PMe_2Ph)_2Br_2$ [13] and $Pd_2(dpm)_2Cl_2$ [14] (dpm = bis(diphenylphosphino)methane). The equivalence of the two phosphorus nuclei is confirmed by the ^{31}P NMR spectra of the carbamoyl complexes, which display a characteristic singlet (Table 4).

TABLE 2

IR DATA FOR CARBAMOYL AND ALKOXYCARBONYL COMPLEXES (cm^{-1})

Compound	ν(N–H)	ν(C–O)	ν(C–O–C)
Pd(pnp)($CONHC_6H_5$)Cl	3210(w)	1640(vs)	
Pt(pnp)($CONHC_6H_5$)Cl	3330(w)	1662(vs)	
Pd(pnp)CONH-*p*-$CH_3C_6H_4$)Cl	3360(w)	1628(vs)	
Pd(pnp)(CONH-*p*-$CH_3OC_6H_4$)Cl	3200(w)	1630(vs)	
Pd(pnp)($CONHC_6H_{11}$)Cl	3280(w)	1621(vs)	
Pd(pnp)(CONH-t-Bu)Cl	3400(w)	1612(vs)	
Pd(pnp)[$CON(n\text{-}Pr)_2$]Cl	3400(w)	1580(vs)	
Pd(pnp)($COOCH_3$)Cl		1670(vs)	1065(s)
Pd(pnp)($COOC_6H_5$)Cl		1620(vs)	1065(s)
Pt(pnp)($COOCH_3$)Cl		1620(vs)	1028(s)
Pd(pnp)($COOCH_3$)$_2$		1648, 1610(vs)	1050(s)

TABLE 3

^{1}H NMR DATA (ppm) FOR Pd(pnp)(CONHR)Cl [a] AND Pd(pnp)(COOR)Cl

Compound	pnp		NH	R	
	Ph	CH_2			
pnp	7.5–6.9(m)	3.25(s)			
$Pd(pnp)Cl_2$	8.0–7.3(m)	4.48(t) J(PH) 4.6			
Pd(pnp)(CONH-p-$CH_3C_6H_4$)Cl	8.0–7.26(m)	4.63(t) J(PH) 4.6		1.9(s)	
Pd(pnp)(CONH-t-But)Cl	8.0–7.26(m)	4.47(t) J(PH) 4.1	1.4(s)	0.56(t)	
Pd(pnp)[CON(Pr)$_2$]Cl	8.0–7.26(m)	4.7 (doublet of quartet) J(AB) 18		1.76 (sextet)	0.7(t) 0.2(t)
Pd(pnp)(CONHCy)Cl	8.0–7.26(m)	4.6(t) J(PH) 4.6	3.6(m)	0.9–1.8(m)	
Pd(pnp)(COOCH$_3$)Cl [b]	7.8–7.5(m)	4.6(t) J(PH) 4.6		3.55(s)	

[a] Chemical shifts in ppm relative to Me_4Si, coupling constants in Hz, solvent $CDCl_3$ unless otherwise indicated. [b] In CD_2Cl_2.

A square planar structure of the complexes in solution, with the phosphorus atoms in *trans* position as shown in Fig. 2, is also supported by the proton NMR spectrum of the [Pd(pnp)(CON(Pr)$_2$]Cl complex, which exhibits two N-propyl resonances and an AB quartet split into triplets, assignable to the methylene protons

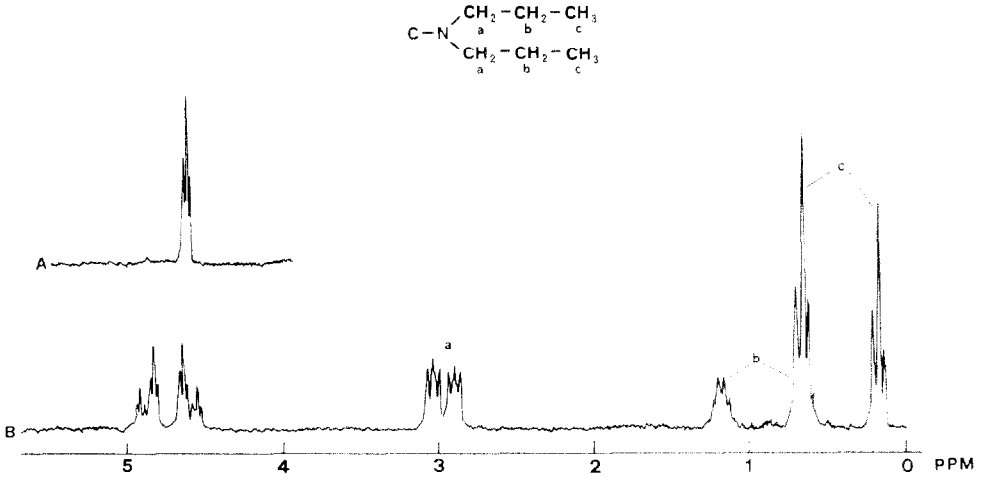

Fig. 1. ^{1}H NMR spectra showing the pnp methylene region of (A) $Pd(pnp)Cl_2$ and Pd(pnp)(CONHR)Cl, (B) Pd(pnp)[CON(Pr)$_2$]Cl in $CDCl_3$.

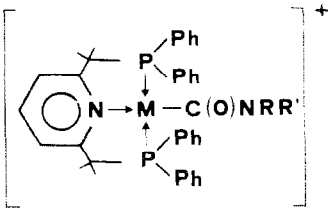

Fig. 2.

TABLE 4

^{31}P NMR PARAMETERS FOR PALLADIUM COMPOUNDS

Compound	$^{31}P\{^1H\}$ NMR [a]
pnp	−11.13
$Pd(pnp)Cl_2$	24.35 [b]
Pd(pnp)(CONH-t-But)Cl	10.24
$Pd(pnp)[CON(Pr)_2]Cl$	14.68

[a] In $CDCl_3$ unless otherwise indicated; chemical shifts in ppm relative to 85% H_3PO_4. [b] CD_2Cl_2.

of the pnp ligand (see Fig. 1b). The double resonance of the N-propyl protons is attributable to the restricted rotation around the Pd–C and the C–N bonds, previously observed in other carbamoyl complexes [15].

The AB quartet, centered at 4.7 ppm (J_{AB} 18 Hz) assignable to the methylene protons of the pnp ligand, also arises from the non-equivalence of the two groups of methylene protons, each of which is coupled to the equivalent phosphorus nucleus. A similar behaviour has been observed in many other complexes [16] containing *trans* tertiary-phosphine ligands in which there is no plane of symmetry through the two *trans* phosphorus atoms.

Reactions of carbamoyl complexes

The carbamoyl complexes of palladium readily react at room temperature with bases (such as sodium carbonate or triethylamine) to give isocyanates, urethanes or substituted ureas, depending on the experimental conditions.

Experimental

All preparations were carried out in deoxygenated solvents, and all operations were performed under dinitrogen or carbon monoxide, using standard Schlenk tecniques. Infrared spectra were recorded on a Perkin–Elmer 577 instrument. ^1H NMR spectra (at 200 MHz) and ^{31}P NMR spectra (at 81 MHz) were recorded with a Varian XL 200 pulsed Fourier transformer spectrometer. For ^{31}P NMR spectra external 85% phosphoric acid was used as reference.

The complexes $Pd(C_6H_5CN)_2Cl_2$ [17] and $Pt(C_6H_5CN)_2Cl_2$ [18] were prepared by literature methods.

The pnp ligand was made as described by Nelson et al. [19].

Preparation of $Pd(pnp)Cl_2$ and $Pt(pnp)Cl_2$

Only the preparation of $Pd(pnp)Cl_2$ is reported: the Pt complex was prepared in a similar manner.

A solution of pnp (0.5 mmol) in 10 ml of dichloromethane was added to 0.200 g (0.5 mmol) of $Pd(C_6H_5CN)_2Cl_2$ in 10 ml of dichloromethane. The solution was stirred at room temperature for 1 h then concentrated to 10 ml. The yellow crystals precipitated were washed with ether and dried in vacuo. Yield ≈ 70%. Anal. Found.: C, 57; H, 4.0; Cl, 10.5; P, 9.35. $C_{31}H_{27}NCl_2P_2Pd$ calcd.: C, 57.0; H, 4.17; Cl, 10.86; P, 9.5%.

Preparation of the alkoxycarbonyl complexes

M(pnp)(COOR)Cl (M = Pd; R = C_6H_5, CH_3; M = Pt; R = CH_3). A solution of sodium alkoxide (CH_3ONa or C_6H_5ONa) (0.41 mmol in 8 ml of methanol) was added to a stirred solution of M(pnp)Cl_2 (0.4 mmol) in 10 ml of methanol under carbon monoxide. The solution was stirred for 2 h (overnight for the platinum complex) at room temperature. After filtration the solution was evaporated in vacuo and the residue extracted with benzene. Addition of hexane and cooling at −30°C produced a crystalline product, which was filtered off, washed with hexane, and dried in vacuo. Yield 55–65%.

Pd(pnp)($COOCH_3$)$_2$. A solution of sodium methoxide (0.82 mmol) in 10 ml of methanol was added to a stirred solution of Pd(pnp)Cl_2 (0.4 mmol) in 10 ml of methanol under carbon monoxide. The solution was stirred for 2 h at room temperature. After filtration the solution was evaporated in vacuo and the residue extracted with benzene. Addition of hexane and cooling at −30°C produced a crystalline product, which was filtered, washed with hexane, and dried in vacuo. Yield 75%.

Preparation of the carbamoyl complexes

M(pnp)(CONHAr)Cl (M = Pd; Ar = C_6H_5, p-$CH_3C_6H_4$; p-$CH_3OC_6H_4$; M = Pt, R = C_6H_5). A solution of the amine (1.6 mmol) in 10 ml of methanol was added to a stirred solution of M(pnp)Cl_2 (0.4 mmol) in 10 ml of anhydrous methanol under carbon monoxide. The mixture was stirred for 1 h at room temperature. After filtration, the yellow solution was concentrated and addition of ether followed by cooling at −30°C gave a crystalline product which was filtered off, washed with ether, and dried in vacuo. Yield 40–65%.

Pd(pnp)(CONHAlk)Cl (Alk = Cy, t-Bu). A solution of the amine (1.6 mmol in 10 ml of CH_3CN) was added to a stirred suspension of Pd(pnp)Cl_2 in 10 ml of CH_3CN under carbon monoxide. After 1 h the solution was filtered and the filtrate, concentrated in vacuo to give a crystalline product, which was filtered off, washed with ether, and dried in vacuo. Yield 42–55%.

Pd(pnp)[CON(Pr)$_2$]Cl. A solution of dipropylamine (1.6 mmol in 10 ml of CH_3CN) was added to a stirred suspension of Pd(pnp)Cl_2 in 10 ml of CH_3CN under carbon monoxide. After 0.5 h the solution was filtered and the filtrate concentrated in vacuo to produce a crystalline product, which was filtered off, washed with ether and dried in vacuo. Yield 56%.

Reaction of Pd(pnp)Cl_2 with carbon monoxide in methanol in the presence of a primary amine

A solution of cyclohexylamine (3 mmol) (or t-butylamine) in 10 ml of methanol, was added to a stirred solution of Pd(pnp)Cl_2 (0.4 mmol) in 10 ml of methanol under carbon monoxide. The mixture was stirred for 10 h at room temperature. After filtration the solution was concentrated in vacuo to give white crystals of Pd(pnp)($COOCH_3$)Cl, which were filtered off, washed with ether and dried in vacuo. Yield 61–70%.

Reactivity of the carbamoyl complexes

(a) A mixture of Pd(pnp)($CONHC_6H_5$)Cl (0.250 mg, 0.33 mmol) and Na_2CO_3(200 mg, 1.88 mmol) in 8 ml of anhydrous ethanol was stirred at 70°C for 1

h. GLC analysis of the solution showed the formation of ethyl carboxylate. Yield ≃ 70%.

(b) A mixture of Pd(pnp)($CONHC_6H_5$)Cl (0.250 mg, 0.33 mmol), aniline (1.65 mmol) and Na_2CO_3 (200 mg, 1.88 mmol) in 10 ml of dichloromethane was stirred at room temperature under carbon monoxide for 24 h. GLC analysis of the solution showed the formation of diphenylurea. Yield ≃ 73%.

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