Synthesis and Solid State and Solution Characterization of Mono- and Di-(η^1-C) Carbamoyl−Palladium Complexes. New Efficient Palladium-Catalyzed Routes to Carbamoyl Chlorides: Key Intermediates to Isocyanates, Carbamic Esters, and Ureas

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Pd complexes have been used in catalytic conversion of primary and secondary amines into isocyanates or carbamoyl chlorides, respectively. The latter have been used as intermediates for the synthesis of carbamates and ureas. The palladium-based catalytic system is very active and operates in two steps, avoiding the synthesis of phosgene ($COCl_2$), but making use of CO and Cl_2 as in phosgene chemistry. In the first step the palladium(II) complex $PdCl_2L_2$ [L_2 = 2,2′ dipyridine (dipy) or 1,10-phenantroline (phen); L = triphenylphosphine (PPh_3)] reacts with the amine [NH_2R, R = *n*-C_3H_7 (**a**), *n*-C_4H_9 (**b**), *n*-C_5H_{11} (**c**); NHRR′, NRR′ = $\overline{CH_2(CH_2)_4N}$ (**d**), $\overline{CH_2(CH_2OCH_2)CH_2N}$ (**e**)] and CO to produce the carbamoyl complexes $PdCl(CONHR)L_2$ and $PdCl_{(2-x)}(CONRR')_xL_2$ (x = 1, 2). When primary amines NH_2R, (**a**, **b**, and **c**) are used, only monocarbamoyl complexes [PdCl(CONHR)(dipy) (**1a**−**c**), PdCl(CONHR)(phen) (**2a**−**c**), and $PdCl(CONHR)(PPh_3)_2$ (**3a**,**b**)] are isolated. Secondary amines NHRR′ (**d** and **e**) afford both monocarbamoyl PdCl(CONRR′)(dipy) (**4d**,**e**) and PdCl(CONRR′)(phen) (**5d**,**e**) and dicarbamoyl complexes, $Pd(CONRR')_2$(dipy) (**6d**,**e**) and $Pd(CONRR')_2$(phen) (**7d**). **4d** and **6d** have been structurally characterized: they are the first example of mono- and dicarbamoyl complexes, respectively, of the same metal system for which the solid state structure is reported.The carbamoyl complexes are subsequently reacted with halogen donors ($CuCl_2$, *N*-chlorosuccinimide, Cl_2, I_2) with elimination of the carbamoyl ligand as isocyanate (primary amines complexes **1**−**3**) or carbamoyl chloride (secondary amines complexes **4**−**7**) and quantitative formation of the starting Pd(II) complex. Cl_2 and I_2 are most effective and selective. They do not generate byproducts and allow an easy and quantitative recovery of the catalyst, making the reaction of potential utility.

Introduction

The chemistry of transition metal systems [mainly Ni(II), Pd(II), Pt(II), Cu(I), Cu(II)] bearing the alkoxocarbonyl (−COOR)[1] or carbamoyl (−CONHR)[2a,b] moiety has attracted much attention. Such interest is justified by the fact that the metallorganic species are intermediates in innovative syntheses of compounds such as carbonates, carbamates, ureas, and isocyanates, which play an important role in the chemical industry.

The existing attitude to develop ecoefficient syntheses gives a new role to "nonphosgene-based routes"[3,4] to the mentioned compounds and justifies the new interest in the chemistry of the metallorganic species mentioned above.[2c,e]

The chemistry of M−COOR moieties is well documented in the literature, and Cu(II)−COOR and Pd(II)−COOR are likely intermediates in the synthesis of dimethyl carbonates in processes recently developed by ENIChem[4] and Ube,[5] respectively. We have shown[6] that compounds of formula $LnM(COOR)_xCl_{2-x}$ (x = 1, 2; M = Ni, Pd) react under mild conditions with $CuCl_2$ or halogens to afford chloroformates (ClCOOR), the precursors of carbonates, carbamates, or isocyanates.

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Conversely, the chemistry of carbamoylmetal systems $M-(CONRR')_xCl_{2-x}$ ($x = 1, 2$; M = Ni, Pd, Pt) is scarcely documented, despite their being known for a long time[2a,b] and their potential as generators of ClCONRR′, chlorocarbamoyl moieties that are precursors of carbamates, ureas, and isocyanates. To date, several monocarbamoyl [η^1-C (W,[7] Mn,[8] Re,[9] Fe,[10] Ni),[11] η^2-C−O (Re,[9] Th),[12] η-C−O (Fe)][13] and a few dicarbamoyl complexes [η^1-C (Hg,[14] Ru)[15] and η^2-C−O (U[12])] have been structurally characterized together with two acyl−carbamoyl complexes [a cationic Pd−(II)[16] and a neutral Pt(II)][17] and an α-chetoacyl carbamoyl [Pt(II)][18] complex.

However, in no cases was the structure of both mono- and dicarbamoyl complexes of the same metal system reported. Moreover, the reactivity of M−C bonds in "M−CONRR′" systems, for example, as precursors of carbamoyl−chlorides or isocyanates is scarcely documented, and the potential in innovative syntheses is not at all discussed.

Experimental Section

General Comments. All reactions were carried out in deaerated solvents and in an atmosphere of the proper gas (dinitrogen or carbon monoxide) using standard vacuum-line techniques. NMR spectra were measured at 298 K in $CDCl_3$ using a AM 500 MHz Bruker spectrometer. GC−MS analyses were performed with a Hewlett-Packard 5995 instrument.

Carbamoyl halides were detected by IR spectroscopy and GC−MS analysis of the reaction solution. Because of partial decomposition of carbamoyl halides in the GC column, they were converted into the relevant methylcarbamate (by reaction with CH_3OH/Et_3N mixtures or with CH_3ONa), which was determined by GC analysis with a Varian Vista 6000 gas chromatograph using a SP-2100/01% Carbowax column and toluene as internal standard.

Mixtures of Cl− and I−carbamoyl were analyzed by titrating the chloride and iodide produced by reaction with CH_3ONa (see later).

Among the isocyanates, only n-C_4H_9NCO was stable enough to allow a direct determination by GC−MS. All others required a conversion in situ into *N*,*N*′-ureas by reaction with the proper amine. Ureas were determined via GC−MS analysis with a HP 1050 HPLC instrument using a Supelcosil LC-8, 15 cm × 4.6 mm i.d. column.

Monocarbamoyl Complexes of Primary Amines. Preparation of PdCl(CONHC$_3$H$_7$)(dipy) (1a). To a suspension of freshly prepared $PdCl_2$(dipy) (0.370 g, 1.12 mmol) in CH_3CN (8 mL) was added *n*-propylamine (0.4 mL, 4 mmol; amine/Pd = 3.5), and the suspension was allowed to react at room temperature under nitrogen atmosphere. The reaction mixture turned white in about 15 min, nitrogen was pumped off, and carbon monoxide was admitted (0.1 MPa). The system was kept under stirring at room temperature for 6 h. The suspension gradually gave a green solution, from which, by cooling to 250 K, black-green crystals of pure carbamoyl complex precipitated (0.331 g, yield 65%). More product was isolated from the mother liquor. The overall yield was close to 99%. Anal. Calcd for $C_{14}H_{16}ClN_3OPd$: C, 43.78; H, 4.20; N, 10.93; Cl, 9.23; Pd, 27.70. Found: C, 43.91; H, 4.15; N, 10.85; Cl, 9.20; Pd, 27.37. IR (Nujol-KBr, cm^{-1}): ν(NH) 3360 (m), ν(CO) 1590 (vs).

Compounds PdCl(CONHC$_4$H$_9$)(dipy) (**1b**) and PdCl(CONHC$_5$H$_{11}$)(dipy) (**1c**) were prepared according to the above procedure (**1b** yield 53%, **1c** yield 58% as pure crystals) by addition of n-$C_4H_9NH_2$ and n-$C_5H_{11}NH_2$, respectively.

PdCl(CONHC$_4$H$_9$)(dipy) (1b). Anal. Calcd for $C_{15}H_{18}ClN_3OPd$: C, 45.25; H, 4.56; N, 10.55; Cl, 8.90; Pd, 26.72. Found: C, 45.52; H, 4.41; N, 10.42; Cl, 9.03; Pd, 26.53. IR (Nujol-KBr, cm^{-1}): ν(NH) 3360 (m), ν(CO) 1590 (vs).

PdCl(CONHC$_5$H$_{11}$)(dipy) (1c). Anal. Calcd for $C_{16}H_{20}ClN_3OPd$: C, 46.62; H, 4.89; N, 10.19; Cl, 8.60; Pd, 25.81. Found: C, 46.74; H, 4.69; N, 10.24; Cl, 8.75; Pd, 25.79. IR (Nujol-KBr, cm^{-1}): ν(NH) 3360 (m), ν(CO) 1590 (vs).

Preparation of PdCl(CONHC$_3$H$_7$)(phen) (2a), PdCl(CONHC$_4$H$_9$)(phen) (2b), and PdCl(CONHC$_5$H$_{11}$)(phen) (2c). The pure crystalline compounds **2a, 2b**, and **2c** were prepared (**2a** in 68% yield, **2b** in 70% yield, and **2c** in 65% yield) following a procedure similar to the synthesis of **1a** starting from $PdCl_2$(phen) and n-$C_3H_7NH_2$, n-$C_4H_9NH_2$, and n-$C_5H_{11}NH_2$, respectively.

PdCl(CONHC$_3$H$_7$)(phen) (2a). Anal. Calcd for $C_{16}H_{16}ClN_3OPd$: C, 47.08; H, 3.95; N, 10.29; Cl, 8.68; Pd, 26.07. Found: C, 47.22; H, 4.03; N, 10.32; Cl, 8.75; Pd, 26.13. IR (Nujol-KBr, cm^{-1}): ν(NH) 3320 (m), ν(CO) 1610 (vs).

PdCl(CONHC$_4$H$_9$)(phen) (2b). Anal. Calcd for $C_{17}H_{18}ClN_3OPd$: C, 48.36; H, 4.30; N, 9.95; Cl, 8.40; Pd, 25.20. Found: C, 47.90; H, 4.12; N, 9.89; Cl, 8.60; Pd, 25.33. IR (Nujol-KBr, cm^{-1}): ν(NH) 3350 (m), ν(CO) 1610 (vs).

PdCl(CONHC$_5$H$_{11}$)(phen) (2c). Anal. Calcd for $C_{18}H_{20}ClN_3OPd$: C, 49.56; H, 4.62; N, 9.63; Cl, 8.13; Pd, 24.39. Found: C, 49.62; H, 4.57; N, 9.58; Cl, 8.20; Pd, 24.29. IR (Nujol-KBr, cm^{-1}): ν(NH) 3350 (m), ν(CO) 1610 (vs).

Preparation of PdCl(CONHC$_4$H$_9$)(PPh$_3$)$_2$ (3b). A yellow suspension of $PdCl_2(PPh_3)_2$ (0.300 g, 0.43 mmol) and n-butylamine (0.6 mL, 6.07 mmol; amine/Pd = 14) in CH_3CN (15 mL) was stirred under dinitrogen atmosphere until a pale-cream solution was obtained. Nitrogen was pumped off, carbon monoxide (0.1 MPa) was admitted, and the system was stirred at room temperature until a pale-yellow precipitate was formed. The product was filtered, washed twice with cold ethanol (5 mL), and dried in vacuo (0.275, yield 83% as pure crystals). More product was isolated from the mother solution with an overall yield > 98%. Anal. Calcd for $C_{41}H_{40}ClNOP_2Pd$: C, 64.24; H, 5.26; N, 1.83; Cl, 4.63; P, 8.09; Pd, 13.88. Found: C, 64.08; H, 5.24; N, 1.79; Cl, 4.68; P, 8.10; Pd, 13.6. IR (Nujol-KBr, cm^{-1}): ν(NH) 3380 (m), ν(CO) 1605 (vs).

Compound **PdCl(CONHC$_3$H$_7$)(PPh$_3$)$_2$ (3a)** was prepared according to the above procedure by using n-$C_3H_7NH_2$ (yield 78%). Anal. Calcd for $C_{40}H_{38}ClNOP_2Pd$: C, 63.44; H, 5.09; N, 1.86; Cl, 4.71; P, 8.24; Pd, 14.14. Found: C, 63.50; H, 4.98; N, 1.89; Cl, 4.83; P, 8.21; Pd, 14.09. IR (Nujol-KBr, cm^{-1}): ν(NH) 3378 (m), ν(CO) 1605 (vs).

Monocarbamoyl Complexes of Secondary Amines. Preparation of PdCl[CON(CH$_2$)$_4$CH$_2$](dipy) (4d). To a suspension of freshly prepared $PdCl_2$(dipy) (0.865 g, 2.59 mmol) in CH_3CN (15 mL) was added piperidine (0.443 g, 5.18 mmol; amine/Pd = 2), and the yellow suspension was allowed to react under stirring with CO (0.1 MPa) at room temperature for 3 h. The suspension gradually turned to olive green. The product was filtered off (yield close to 99%), washed with a mixture of

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CH_3CN/CH_3OH (10:1) to dissolve impurities of piperidinium chloride, and dried in vacuo (0.826 g, yield 78%). Anal. Calcd for $C_{16}H_{18}ClN_3OPd$: C, 46.85; H, 4.24; N, 10.24; Cl, 8.64; Pd, 25.94. Found: C, 46.58; H, 4.09; N, 10.18; Cl, 8.66; Pd, 25.69. IR (Nujol-KBr, cm^{-1}): ν(CO) 1590 (vs). ^1H NMR ($CDCl_3$, carbamoyl moiety): 1.3 (b, 1 H), 1.4 (b, 1 H), 1.5 (b, 1 H), 1.6 (q, 2 H), 1.7 (b, 1 H), 3.5 (m, 2 H), and 4.2 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, carbamoyl moiety): 174 (s), 25.0 (s), 26.3 (s), 26.5 (s), 44.5 (s), 48.8 (s) ppm.

Preparation of PdCl[CON(CH₂)₄CH₂](phen) (5d). The pure crystalline olive green product was prepared (in 80% yield) according to the procedure reported above starting from $PdCl_2$(phen) and piperidine at 313 K. Anal. Calcd for $C_{18}H_{18}ClN_3OPd$: C, 49.79; H, 4.18; N, 9.67; Cl, 8.15; Pd, 24.51. Found: C, 49.80; H, 4.12; N, 9.61; Cl, 8.22; Pd, 24.50. IR (Nujol-KBr, cm^{-1}): ν(CO) 1585 (vs).

Preparation of PdCl[CONCH₂(CH₂OCH₂)CH₂](dipy) (4e). To a suspension of freshly prepared $PdCl_2$(dipy) (0.50 g, 1.50 mmol) in CH_3OH (12 mL) was added morpholine (0.45 g, 5.17 mmol; amine/Pd = 3.5), and the mixture was allowed to react with CO at 313 K at ambient pressure for 6 h. The resulting green solution was concentrated under reduced pressure to one-third its volume, Et_2O (5 mL) was added, and the solution was left overnight at 273 K. Yellow crystals of pure monocarbamoyl complex were obtained (0.400 g, yield 65%). Anal. Calcd for $C_{15}H_{16}ClN_3O_2Pd$: C, 43.71; H, 3.91; N, 10.19; Cl, 8.60; Pd, 25.82. Found: C, 43.68; H, 3.80; N, 10.15; Cl, 8.65; Pd, 25.67. IR (Nujol-KBr cm^{-1}): ν(CO) 1595 (sh) and 1575 (vs). The complex is moisture sensitive. By exposure to air, the CO bands shift to 1550 cm^{-1} and a new broad band centered at 3520 cm^{-1} appears. By heating in vacuo the original complex is regenerated without CO loss.

Preparation of PdCl[CONCH₂(CH₂OCH₂)CH₂](phen) (5e). To a suspension of freshly prepared $PdCl_2$(phen) (0.270 g, 0.80 mmol) in CH_3CN (10 mL) was added morpholine (0.25 g, 2.87 mmol; amine/Pd = 3.6), and the suspension was allowed to react at 313 K with CO at atmospheric pressure for 6 h. The resulting suspension was filtered, and the solid was washed with CH_3OH and dried in vacuo (0.296 g, yield 85%). Anal. Calcd for $C_{17}H_{16}ClN_3O_2Pd$: C, 46.81; H, 3.70; N, 9.63; Cl, 8.13; Pd, 24.39. Found: C, 46.58; H, 3.68; N, 9.57; Cl, 8.10; Pd, 24.29. IR (Nujol-KBr, cm^{-1}): ν(CO) 1570 (vs).

Dicarbamoyl Complexes of Secondary Amines. Preparation of Pd[CON(CH₂)₄CH₂]₂(dipy) (6d). To a suspension of freshly prepared $PdCl_2$(dipy) (0.531 g, 1.59 mmol) in CH_3CN (12 mL) was added piperidine (1.36 g, 15.9 mmol; amine/Pd = 10), and the resulting mixture was reacted with CO (0.1 MPa) at room temperature for about 2 h. The initial yellow color gradually converted into orange. From the solution ca. 0.2 g of piperidine hydrochloride was isolated by filtration, and the mother solution was concentrated to half volume under reduced pressure. The salt that eventually precipitated was eliminated again by filtration. The solution was kept overnight at 278 K to afford impure red crystals of the dicarbamoyl complex (0.74 g). Further purification for eliminating the piperidinium hydrochloride was necessary. The crude product (containing about 3.3% in weight of chlorine) was suspended in 10 mL of CH_3CN containing piperidine (1 mL), and 2.5 mL of a 0.3 N solution of CH_3ONa in ethanol was added dropwise under stirring at 273 K. The resulting orange suspension was filtered and concentrared to half its volume and kept at 278 K overnight. Red crystals of pure dicarbamoyl complex precipitated and were collected by filtration (0.556 g, yield 72% with respect to initial Pd). Anal. Calcd for $C_{22}H_{28}N_4O_2Pd$: C, 54.32; H, 5.80; N, 11.50; Pd, 21.85. Found: C, 54.19; H, 5.78; N, 11.47; Pd, 21.77. IR (Nujol-KBr, cm^{-1}): ν(C=O) 1545 (vs). ^1H NMR ($CDCl_3$, carbamoyl moiety): 1.4 (8H, pseudo quintet, $J \approx 5.8$ Hz), 1.5 (4 H, pseudo quintet, $J \approx 5.4$ Hz), 3.5 (4 H, broad multiplet) and 4.2 (4 H, broad multiplet) ppm. ^{13}C NMR ($CDCl_3$, carbamoyl moiety): 196.2 (s), 25.6 (s), 26.9 (s), 27.3 (s), 41.8 (s), and 49.1 (s) ppm.

Table 1. Characterization of Mono- and Dicarbamoyl Complexes through Reaction with HCl

compound	amount (g) (mmol)	*V* CO(mL) (mmol)	CO/Pd
1a	0.096 (0.25)	5.4 (0.24)	0.96
2b	0.316 (0.75)	16.0 (0.71)	0.95
3b	0.234 (0.31)	6.5 (0.29)	0.94
5d	0.195 (0.45)	9.7 (0.43)	0.96
6d	0.136 (0.28)	11.4 (0.49)	1.75
7d	0.150 (0.29)	11.2 (0.50)	1.72

Preparation of Pd[CONCH₂(CH₂OCH₂)CH₂]₂(dipy) (6e). To a suspension of $PdCl_2$(dipy) (0.500 g, 1.5 mmol), in CH_3CN (15 mL), was added morpholine (1.17 g, 13.45 mmol; amine/Pd = 9), and the mixture was allowed to react with CO at atmospheric pressure and room temperature for 4−5 h. The resulting brown-orange solid mixture (dicarbamoyl complex and morpholinium salt) was filtered and purified using a solution of CH_3ONa as described above. Yield: 0.477 g, 65%. Anal. Calcd for $C_{20}H_{24}N_4O_4Pd$: C, 48.94; H, 4.93; N, 11.41; Pd, 21.68. Found: C, 48.69; H, 4.88; N, 11.37; Pd, 21.49. IR (Nujol-KBr, cm^{-1}): ν(CO) 1512 (vs).

Preparation of Pd[CON(CH₂)₄CH₂]₂(phen) (7d). To a suspension of a freshly prepared $PdCl_2$(phen) (0.700 g, 1.96 mmol) in CH_3CN (17 mL) was added piperidine (1.67 g, 19.6 mmol; amine/Pd = 10), and the resulting mixture was reacted with CO (0.1 MPa) at room temperature for about 4 h. The initial yellow mixture gradually turned to orange. The resulting solid mixture of Pd[(CON(CH₂)₄CH₂]₂(phen) and HN(CH₂)₄CH₂·HCl was filtered off (1.35 g). Red crystals of pure dicarbamoyl complex (0.698 g, yied 70%) were obtained after elimination of the ammonium salt following the methodology reported above. Anal. Calcd for $C_{24}H_{28}N_4O_2Pd$: C, 56.42; H, 5.52; N, 10.98; Pd, 20.83. Found: C, 56.27; H, 5.47; N, 10.95; Pd, 20.68. IR (Nujol-KBr, cm^{-1}): ν(CO) 1540 (vs).

Reaction of Dicarbamoyl Complexes with Amonium Salts: Back-Conversion into Monocarbamoyl Complexes. To an orange solution of **7d** (0.250 g, 0.49 mmol) in ethanol (6 mL) was added 0.60 g (0.49 mmol) of HCl·HN(CH₂)₄CH₂ at room temperature under dinitrogen. After mixing, the color turned to yellow-green. The solution was filtered and concentrated to one-third its volume, and diethyl ether (5 mL) was added. By cooling to 273 K yellow-green crystals of monocarbamoyl **5d** (0.18 g, 85%) were obtained and identified by comparison with an authentic sample.

Characterization of the Carbamoyl Complexes by Reaction with HCl. The CO quantitative analysis was carried out by decomposing a weighted amount of a carbamoyl complex with an excess of HCl (10^{-2} M dry HCl in toluene). The reaction was carried out in an inverted Y-shaped reactor connected to a gas buret. The gas evolved was also analyzed by GC, and only trace amounts of CO_2 were found. Table 1 shows analytical data for some complexes.

Reaction of Carbamoyl Complexes of Secondary Amines with $CuCl_2$: Synthesis of Carbamoyl Chlorides. In a typical reaction, the carbamoyl complex **4d** (0.320 g, 0.78 mmol) in 4 mL of THF and $CuCl_2$ (0.210 g, 1.56 mmol) in 3 mL of THF were charged separately into two branches of an inverted Y-shaped glass reactor. After mixing, the resulting liquid and solid were analyzed. The IR spectrum of the supernatant liquor shows a band at 1735 cm^{-1} ascribed to the carbamoyl chloride ClCON(CH₂)₄CH₂. The GC−MS spectrum shows the presence of chlorocarbamoyl by comparison with an authentic sample synthesized by an independent route. *m*/*z* (relative intensity %): 147 (M^+, 68), 112 (100), 106 (19), 84 (19), 69 (38), 56 (37), 55 (21), 42 (30), 41 (5), 39 (38). After

reaction with CH_3ONa or NEt_3-CH_3OH the peak of the Cl−carbamoyl species disappeared and that of the relevant methylcarbamate appeared, which was identified by comparison with the fragmentation spectrum of an authentic sample. The conversion of the Cl−carbamoyl into methylcarbamate allowed the quantitative determination of the Cl−carbamoyl formed.

The solid revealed to be a mixture of $PdCl_2$(dipy) and CuCl, which were separated and identified as previously reported.[6]

Other mono- and dicarbamoylpiperidine or mono- and dicarbamoylmorpholine complexes were reacted according to the above procedure.

$ClCON\overline{CH_2(CH_2OCH_2)}CH_2$ obtained from compounds **4e** and **5e** was characterized by IR and GC−MS. IR (THF solution): ν(CO) 1735 cm^{-1}. EI-MS (% intensity): *m*/*z*, 149 (M^+, 30), 134 (38), 114 (57), 106 (5), 86 (30), 70 (36), 56 (100), 42 (72).

Its carbamate derivative, obtained by reaction with CH_3OH/Et_3N, was also characterized (see below) and quantitatively determined by GC. This analysis showed the quantitative conversion (>99%) of the metal-bound carbamoyl moiety into the Cl−carbamoyl product.

Reaction of Carbamoyl Complexes of Primary Amines with $CuCl_2$: Synthesis of Isocyanates. The reaction of monocarbamoyl complexes **1a**−**c**, **2a**−**c**, **and 3a**,**b** with $CuCl_2$ (which was performed according to the procedure described for carbamoyl complexes of secondary amines) afforded quantitatively the isocyanates *n*-C_3H_7NCO, *n*-C_4H_9NCO, and *n*-C_5H_{11}-NCO, which were analyzed as methylcarbamate derivatives (after reaction with CH_3OH) or as ureas (after reaction with amines, see below). A quantitative conversion (>99%) of the metal-bound carbamoyl moiety into isocyanate was obtained.

Reaction of Carbamoyl Complexes of Primary and Secondary Amines with *N*-Chlorosuccinimide: Synthesis of Isocyanates and Carbamoyl Chlorides, Respectively. Reaction of 3b with *N*-Chlorosuccinimide: Synthesis of *n*-Butylisocyanate. 3b (0.213 g, 0.27 mmol) in THF (2 mL) and *N*-chlorosuccinimide (0.035 g, 0.26 mmol) in THF (1 mL) were charged into the inverted Y-shaped reactor (see above). The reactants were mixed and allowed to react for 10 min. From the reaction mixture a yellow solid, which analyzed for $(PPh_3)_2PdCl_2$, was separated by filtration. The IR spectrum of the liquid phase showed bands at 2272 (m) and 1720 (s) cm^{-1}, assigned respectively to *n*-C_4H_9NCO and succinimide. The presence of these species was confirmed by GC−MS. *n*-C_4H_9NCO was formed quantitatively with respect to the starting carbamoyl complex as shown by GC analysis of the methylcarbamate derivative (see later). EI-MS: *m*/*z* (% intensity) for $NH(COCH_2)_2$, 100 (M^+, 5), 99 (100), 56 (64). Analysis of the solid residue. Calcd for $C_{36}H_{30}Cl_2P_2Pd$: Cl, 10.10; P, 8.82; Pd, 15.16. Found: Cl, 10.25; P, 8.87; Pd, 14.95.

Compounds **1a**−**c**, **2a**−**c**, and **3a** were reacted in a similar way with halosuccinimide, affording the relevant isocyanate (*n*-C_3H_7NCO, *n*-C_4H_9NCO, and *n*-$C_5H_{11}NCO$) in almost quantitative yield (>98%) with respect to the starting carbamoyl complex.

Reaction of 5d with *N*-Chlorosuccinimide. The reaction of **5d** (0.180 g, 0.41 mmol) in C_6H_6 (3 mL) with *N*-chlorosuccinimide (0.055 g, 0.41 mmol) was carried out as described above. The reaction mixture was filtered, and the yellow residue and the solution were analyzed. Carbamoyl chloride (IR band at 1735 cm^{-1}) was formed in very high yield (>98%), as shown by the GC quantitative determination of its methylcarbamate $CH_3OC(O)\overline{N(CH_2)_4}CH_2$ (obtained by reaction with CH_3ONa). The yellow residue analyzed for $PdCl[N(COCH_2)_2]$-(phen). Anal. Calcd for $C_{16}H_{12}ClN_3O_2Pd$: Pd, 25.33; Cl, 8.44. Found: Pd, 25.39; Cl, 8.60. IR (Nujol/KBr, cm^{-1}): ν(CO) 1750 (vs).

This compound reacts in methanol with HCl to produce $PdCl_2$(phen) and succinimide. It reacts also with Cl_2 to afford $PdCl_2$(phen) and *N*-Cl−succinimide.

Compounds **4d**,**e** and **5e** were reacted in a similar procedure with halosuccinimide, affording $ClC(O)\overline{N(CH_2)_4}CH_2$ and $ClC(O)\overline{NCH_2(CH_2OCH_2)}CH_2$, which respectively were quantitatively determined by GC as their carbamate derivatives formed quantitatively with respect to the starting Pd−carbamoyl complex.

Reaction of Carbamoyl Complexes of Primary and Secondary Amines with Halogens (Cl_2 and I_2): Synthesis of Isocyanates and Carbamoyl Chlorides, Respectively. Reaction of 2b with I_2: Synthesis of *n*-Butyl Isocyanate. A suspension of **2b** (0.105 g, 0.25 mmol) in 3 mL of hexane and a solution of I_2 (0.63 g, 0.25 mmol) in hexane (5 mL) were charged separately into the two branches of an inverted Y-shaped glass reactor under dinitrogen atmosphere. The reactor was closed, and the iodine solution was added to the carbamoyl suspension. A rapid reaction occurred. The IR spectrum of the solution displayed the *n*-butylisocyanate band at 2278 cm^{-1}. The suspension was filtered, and the isocyanate was determined by GC−MS. EI-MS: *m*/*z* (% intensity) 98 (M^+, 20), 70 (13), 56 (34), 43 (100) 41 (96). The formation of $CH_3OC(O)NHC_4H_7$ (obtained after reaction of *n*-C_4H_7NCO with CH_3OH) was quantitative with respect to the Pd−carbamoyl starting species. The residual solid analyzed for PdClI(phen). Analysis of the solid. Calcd for $C_{12}H_8ClIN_2Pd$: Cl, 7.90; I, 28.27; Pd 23.70. Found: Cl 7.77; I, 30.80; Pd, 23.59.

Other monocarbamoyl complexes (**1a**−**c**, **2a**, **2c**, **3a**,**b**) were reacted with I_2 according to the same procedure. Isocyanates of the *n*-propyl- and *n*-pentylamine, which completely decompose in the GC column, were detected by IR. [$C_3H_7N{=}C{=}O$: IR (hexane), ν(CO) 2262 cm^{-1}; $C_5H_{11}N{=}C{=}O$: IR (hexane) ν(CO) 2268 cm^{-1}] and quantitatively determined by reaction with CH_3OH or an amine as the corresponding methylcarbamate or urea derivatives (see later).

Reaction of 7d with Cl_2. The orange suspension of **7d** (0.300 g, 0.59 mmol) in C_6H_6 (6 mL) was reacted with a stream of Cl_2 at room temperature. It rapidly turned yellow.

The IR spectrum of the liquid phase shows the presence of a band at 1735 cm^{-1} assigned to the ν(CO) of $ClC(O)\overline{N(CH_2)_4}CH_2$, which was qualitatively analyzed by GC−MS and quantitatively determined as its carbamate derivative. The solid yellow reaction product was filtered and identified as $PdCl_2$(phen) by elemental analysis and comparison of the IR spectrum with that of an authentic sample. The Pd catalyst was quantitatively recovered.

Other carbamoyl compounds (**4d**,**e**, **5d**,**e**, **6d**,**e**) were reacted with Cl_2 according to the same procedure. The GC−MS analysis of the in situ reaction solution with a NEt_3/CH_3OH mixture showed the formation of the carbamate derivative of the carbamoyl chlorides in a quantitative yield with respect to Pd−carbamoyl species.

Reaction of 7d with I_2. The orange suspension of **7d** (0.105 g, 0.21 mmol) in 4 mL of hexane and the solution of I_2 (0.107 g, 0.42 mmol) in hexane (5 mL) were separately charged into the two arms of an inverted Y-shaped reactor under dinitrogen atmosphere. The reactor was closed, and the iodine solution was added to the carbamoyl suspension at room temperature. A rapid reaction occurred. The IR spectrum of the solution displayed a band at 1742 cm^{-1} assigned to the C=O stretching of $IC(O)\overline{N(CH_2)_4}CH_2$, which was analyzed as its carbamate derivative (see below).The hexane solution of the carbamoyl iodide was filtrated and reacted with CH_3ONa 0.5 N (1 mL in CH_3OH). NaI was extracted with H_2O and titrated. Found: 0.40 mol of I^-, with a 95% yield with respect to the amount expected to be generated in the following reactions:

$$(phen)Pd[C(O)\overline{N(CH_2)_4}CH_2]_2 + 2\ I_2 \rightarrow (phen)PdI_2 + 2\ IC(O)\overline{N(CH_2)_4}CH_2 \quad (1)$$

$$2\ \mathrm{IC(O)N(CH_2)_4CH_2} + 2\ \mathrm{CH_3ONa} \rightarrow 2\ \mathrm{CH_3O{-}C(O)N(CH_2)_4CH_2} + 2\ \mathrm{NaI} \quad (2)$$

The brown solid residue of the filtration was identified as PdI_2(phen) by elemental analysis and by comparison of its IR spectrum with that of an authentic sample prepared by reaction of Pd−acetate, KI, and phen. (see below). Anal. Calcd for $C_{12}H_8N_2I_2Pd$: Pd, 19.69; I, 46.97. Found: Pd, 19.73; I, 46.88.

The reaction of **6d**,**e** and **6e** with I_2 according to the same procedure afforded quantitatively $IC(O)N(CH_4)_4CH_2$ and $IC(O)NCH_2(CH_2OCH_2)CH_2$, which were detected in solution by IR spectroscopy (IR, ν(CO) 1742 cm^{-1}) and determined by GC as their methylcarbamate derivatives (see below).

Synthesis of PdI_2(phen). To 0.111 g (0.50 mmol) of $Pd(OAc)_2$ dissolved in EtOH (10 mL) were added KI (0.2 g, 1.2 mmol; I/Pd = 2.4, dissolved in 10 mL of EtOH) and phenantroline (0.10 g, 0.5 mmol, dissolved in 10 mL of EtOH). After 30 min the resulting precipitated pink-brown product was filtered, washed with an H_2O/EtOH mixture (1:1, v/v), and dried in vacuo. Anal. Calcd for $C_{12}H_8N_2I_2Pd$: Pd, 19.69; I, 46.97. Found: Pd, 19.70; I, 46.90.

Reaction of 5d with I_2: Quantitative Determination of Chloro- and Iodocarbamoyl Species. A suspension of **5d** (0.120 g, 0.28 mmol) in 3 mL of hexane and a solution of I_2 (0.071 g, 0.28 mmol) in hexane (5 mL) were allowed to react as described above, and the reactor was heated for 15 min at 323 K. The reaction mixture was filtered, and the solution and the residue were analyzed. The solution displayed IR bands at 1742 (m) and 1735 (sh) cm^{-1}, which shifted to 1718 (s) cm^{-1} by adding CH_3OH/NEt_3. The GC−MS spectrum showed only the presence of $ClC(O)N(CH_2)_4CH_2$, as $IC(O)N(CH_2)_4CH_2$ decomposed in the GC column.

Halogens were quantitatively determined by titration as reported above.

As an example, when **4d** (0.130 g, 0.30 mmol) and I_2 (0.076 g, 0.30 mmol) were reacted, the filtered hexane solution after reaction with 0.55 mL of 0.6 N CH_3ONa in methanol and extraction with H_2O gave 0.08 mol of Cl^- and 0.19 mol of I^-, corresponding to 30% $ClC(O)N(CH_2)_4CH_2$ and 70% $IC(O)N(CH_2)_4CH_2$ (conversion yield: 90% with respect to the initial **4d** compound). The elemental analyses of the solid residue showed that it is a mixture of PdCl(I)(dipy) and PdI_2(dipy).

Similar reactivity was observed by reacting compounds **4e** and **5e** with I_2.

Conversion of Carbamoyl Chlorides and Isocyanates into Carbamates and *N*,*N*′-Ureas. $ClC(O)N(CH_2)_4CH_2$, $IC(O)N(CH_2)_4CH_2$, $ClC(O)NCH_2(CH_2OCH_2)CH_2$, and $IC(O)NCH_2(CH_2OCH_2)CH_2$ obtained as reported above were reacted with a 5:2 methanol−NEt_3 mixture (1 mL) or with the proper amine. The filtered solution was warmed to 313 K. The reaction took place during the warming-up process. The formed isocyanates RNCO (R = *n*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11}) were reacted with CH_3OH or amines.

Piperidinecarbamates, morpholinecarbamates, *N*-alkylcarbamates, or *N*,*N*′-ureas were isolated and identified by means of IR and mass spectra. *N*,*N*-Ureas were also isolated in the solid state as crystalline pure products in quantitative yield.

Characterization of Carbamates. Carbamates were obtained in quantitative yield by reacting either the relevant carbamoyl chloride with CH_3OH/NEt_3 or the isocyanate with CH_3OH. They were identified by their GC−MS spectrum.

$(CH_3O)C(O)N(CH_2)_4CH_2$. IR (hexane/CH_3OH/NEt_3): ν(CO), 1718 cm^{-1}. EI-MS: *m*/*z*, (% intensity) 143 (M^+, 35), 142 (28), 128 (100), 112 (9), 84 (29), 59 (5), 56 (21), 55 (12), 42 (38).

$(CH_3O)C(O)NCH_2(CH_2OCH_2)CH_2$. IR (hexane/$CH_3OH$/$NEt_3$): ν(CO), 1718 cm^{-1}. EI-MS: *m*/*z* (% intensity) 145 (M^+, 27), 130 (57), 114 (11), 100 (19), 70 (16), 56 (36), 42 (100).

(*n*-$C_3H_7NHCOOCH_3$): IR (hexane/CH_3OH), ν(CO), 1731 cm^{-1}. EI-MS: *m*/*z* (% intensity), 117 (M^+, 20), 102 (4), 89 (4), 88 (100), 59 (20), 44 (45).

(*n*-$C_4H_9NHCOOCH_3$). IR (hexane/CH_3OH): ν(CO), 1731 cm^{-1}. EI-MS: *m*/*z* (% intensity), 131 (M^+, 9), 88 (100), 59 (15); 57 (12), 44 (51).

(*n*-$C_5H_{11}NHCOOCH_3$). IR (hexane/CH_3OH): ν(CO), 1738 cm^{-1}. EI-MS: *m*/*z* (% intensity), 145 (M^+, 5), 130 (1), 102 (2), 88 (100), 76 (11), 59 (13), 44 (40).

Characterization of *N*,*N*′-Ureas. These compounds were obtained by reaction (molar ratio 1:1) of the relevant carbamoyl chloride or isocyanate with an amine ($HN(CH_2)_4CH_2$, $HNCH_2(CH_2OCH_2)CH_2$, *n*-$C_3H_7NH_2$, *n*-$C_4H_9NH_2$, *n*-$C_5H_{11}NH_2$) in hexane. The reaction took place in a few minutes at room temperature. Heating to 323 K brought the reaction to completion. The resulting mixture was concentrated under vacuum almost to dryness and the residue extracted with CH_3CN (5 mL). Cooling to 268 K allowed the urea to separate as pure solid.

***N*,*N*′-Dipiperidineurea $CO[N(CH_2)_4CH_2]_2$.** EI-MS: *m*/*z* (% intensity), 196 (M^+, 11), 112 (16), 84 (100), 69 (33), 56 (19), 41 (40).

***N*,*N*′-Dimorpholineurea $CO[NCH_2(CH_2OCH_2)CH_2]_2$.** EI-MS: *m*/*z* (% intensity), 200(M^+, 9), 169(45), 143(15), 114-(75), 86(36), 70(100), 42(48).

***N*,*N*′- Dipropylurea $CO(n\text{-}C_3H_7NH)_2$.** IR (CH_3CN): ν(CO), 1670 cm^{-1}. EI-MS: *m*/*z* (% intensity), 145 (9), 144 (M^+, 92), 116 (5), 115 (22), 87 (20), 86 (10), 58 (55), 43 (100).

***N*,*N*′-Dibutylurea $CO(n\text{-}C_4H_9NH)_2$.** IR (CH_3CN): ν(CO), 1670 cm^{-1}. EI-MS: *m*/*z* (% intensity), 172 (M^+, 34), 101 (18), 100 (17), 74 (35), 44 (100).

***N*,*N*′-Dipentylurea $CO(n\text{-}C_5H_{11}NH)_2$.** IR ($CH_3CN$), ν(CO), 1670 cm^{-1}. IR (Nujol mull): ν(N−H) 3350 cm^{-1}, ν(CO), 1630 and 1580 cm^{-1}. EI-MS: *m*/*z* (% intensity), 200 (M^+, 35), 171 (32), 144 (13), 114 (24), 88 (21), 87 (20), 44 (100), 43 (74), 41 (51).

Crystal Structure Determination of 4d and 6d. Single crystals of ca. 0.2 × 0.3 × 0.4 (**4d**) and 0.3 × 0.3 × 0.5 (**6d**) mm suitable for X-ray analyses were mounted on glass rods without protection from the air. The crystal data and the most relevant experimental parameters used in the X-ray measurements and in the crystal structure analyses are reported in Table 2.

The X-ray experiments were carried out on a Philips PW100 (**4d**) and on a Siemends AED (**6d**) diffractometer using graphite-monocromated Mo Kα radiation (λ = 0.71073 Å). For both compounds the intensities were calculated from profile analysis according to the Lehmann and Larsen method.[19] During the two data collections of **4d** and **6d**, one standard reflection for each compound, collected every 100, showed no significant fluctuation. The intensities were corrected for Lorentz and polarization but not for absorption effects. The two structures were solved by the Patterson method using SHELX86[20] and direct methods using SIR92[21] and then completed by a Fourier ΔF map and refined by full-matrix least-squares methods on *F* using SHELX96.[22] For both complexes the parameters refined were the following: the

(19) Lehmann, M. S.; Larsen, F. K *Acta Crystallogr., Sect, A* **1974**, *30*, 580.

(20) Sheldrick, G. *SHELX86*, *Program for Crystal Structure Solutions*; University of Göttingen: Germany, 1986.

(21) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. SIR92. *J. App. Crystallogr.* **1994**, *27*, 435.

(22) Sheldrick, G. M. *SHELX96*, *Program for the refinement of crystal structures*; University of Göttingen: Germany, 1996.

Table 2. Experimental Data for the X-ray Diffraction Studies

	4d	6d
formula	$C_{16}H_{18}ClN_3OPd$	$C_{22}H_{28}N_4O_4Pd$
cryst syst	orthorhombic	orthorhombic
space group	*Pbca*	*Pna*2_1
cell params at 295 K[a]		
a, Å	17.880(5)	16.089(5)
b, Å	11.301(5)	16.576(5)
c, Å	16.378(5)	8.216(5)
V, Å^3	3309(2)	2191(2)
Z	8	4
D_{calcd}, g cm^{-3}	1.647	1.476
F(000)	1648	1000
mol wt	410.191	486.889
linear abs coeff, cm^{-1}	12.87	8.71
scan type	$\omega/2\theta$	$\omega/2\theta$
scan speed, deg/min	≤0.16	≤0.08
2θ range, deg	6−50	6−48
index ranges	$0 \le h \le 21$	$0 \le h \le 18$
	$0 \le k \le 13$	$0 \le k \le 19$
	$0 \le l \le 19$	$0 \le l \le 9$
no. of reflns measd	3304	2007
no. of unique data	2916 (R_{int} = 0.03)	1826 (R_{int} = 0.05)
no. of params, restraints	202, 0	265, 1
wR2 (all data)[b]	0.125	0.180
a,*b*[23]	0.078, 0	0.128, 0
R1 [I>4σ(*I*)][b]	0.044	0.066
no. of obsd reflns	1798	858
criterion for obsd	$F_o \ge 4\sigma(F_o)$	$F_o \ge 4\sigma(F_o)$
goodness-of-fit on F^2 (all data)[b]	0.896	0.85
maximum shift/σ	0.208	0.91
peak, hole in final difference map, e Å^{-3}	0.99, −1.21	1.68, −1.32
extinction coeff	0.0	0.0002

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 30 reflections found in a random search on the reciprocal space. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$. Goodness-of-fit = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* the number of parameters.

overall scale factor, the atomic coordinates, and anisotropic temperature factors for all the non-hydrogen atoms. The hydrogen atoms were placed at their calculated positions and refined "riding" on their corresponding carbon atoms with the geometrical constraint C−H 1.0 Å. The geometrical calculations were obtained by PARST.[23]All the calculations were carried out on the GOULD ENCORE91 of the Centro di Studio per la Strutturistica Diffrattometrica of C.N.R., Parma.

Results and Discussion.

Synthesis of Carbamoyl Complexes of Primary and Secondary Amines: Role of the Solvent. Only one *trans*-acyl−carbamoyl Pd(II) complex, of formula *trans*-{$(Me_3P)_2$Pd(COPh){C(OEt)[N$(CH_2)_4$CH$_2$]}}BF_4, has been structurally characterized to date,[16] and it appears to be a cationic complex with an O-ethylated carbamoyl ligand. Neutral Pd−carbamoyl complexes have not been isolated and characterized, as they are usually reported to be quite reactive and undergo an easy Pd−C cleavage by several agents that may act intra- or intermolecularly. They have been postulated as intermediates in catalytic double carbonylation of aryl halides and secondary amines to afford α-keto-amides.[24]

In our case, both mono- and dicarbamoyl Pd complexes have been isolated and characterized and their reactivity has been studied under controlled conditions.

Palladium monocarbamoyl complexes PdCl(CONHR)(dipy) (**1a**−**c**), PdCl(CONHR)(phen) (**2a**−**c**), and PdCl(CONHR)$(PPh_3)_2$ (**3a**,**b**) [(dipy = 2,2′-dipyridine; phen = 1,10-phenantroline; PPh_3= triphenylphosphine; R= *n*-C_3H_7 (**a**), *n*-C_4H_9 (**b**), *n*-C_5H_{11} (**c**)] have been prepared in CH_3CN according to eq 3.

$$PdCl_2L_2 + 2\ NH_2R + CO \rightarrow PdCl(CONHR)L_2 + NH_2R{\cdot}HCl \quad (3)$$

An excess of amine (RNH_2/Pd = 3−4) was used. The reaction proceeds via the formation of a white Pd(II) complex whose elemental analyses are consistent with an amine complex of composition $PdCl_2(NH_2R)L_2$.[25]

Mono- and dicarbamoyl complexes of formula PdCl(CONRR′)(dipy) (**4d**,**e**), PdCl(CONRR′)(phen) (**5d**,**e**), Pd(CONRR′)$_2$(dipy) (**6d**,**e**), and Pd(CONRR′)$_2$(phen) (**7d**) [NRR′ = N$(CH_2)_4$CH$_2$ (**d**), NCH$_2$$(CH_2OCH_2)CH_2$ (**e**)] have been prepared following the two-step procedure reported in eqs 4 and 5.

$$PdCl_2L_2 + 2\ NHRR' + CO \rightleftharpoons PdCl(CONRR')L_2 + NHRR'{\cdot}HCl \quad (4)$$

$$PdCl(CONRR')L_2 + CO + 2\ NHRR' \rightleftharpoons Pd(CONRR')_2L_2 + NHRR'{\cdot}HCl \quad (5)$$

The solvent can play an important role in this reaction. In fact, when the reaction is carried out in ethanol, the amine carbonylation process stops at the first step (eq 4) and only monocarbamoyl complexes can be isolated, also in the presence of an excess of amine.

In CH_3CN, the carbonylation proceeds further and dicarbamoyl complexes are obtained (eq 5). The influence of the solvent on the extent of the amine carbonylation can be rationalized taking into account that reactions 4 and 5 are reversible and the equilibrium position depends on the solution acidity.

Therefore, in CH_3CN, in which the ammonium salt NHRR′·HCl is not soluble, the excess of amine shifts to the right of the equilibrium. On the contrary, in ethanol, which is a good solvent for the ammonium salt, the increase of acidity shifts to the left the second step.

This hypothesis is supported by the behavior of a 1:1 mixture of the dicarbamoyl complexes (**6** or **7**) and NHRR′·HCl. The suspension of **6** or **7** in CH_3CN is stable for hours; by adding ethanol, the dicarbamoyl complex converts into the corresponding monocarbamoyl according to eq 6.

$$Pd[CON(CH_2)_4CH_2]_2L_2 + CH_2(CH_2)_4NH{\cdot}HCl \rightarrow PdCl[CON(CH_2)_4CH_2]L_2 + CO + 2\ CH_2(CH_2)_4NH \quad (6)$$

However, the poor solubility of ammonium salts in CH_3CN makes difficult the isolation of pure dicarbamoyl complexes. The latter have been isolated in a pure form by reacting the crude reaction mixture of dicarbamoyl complex and ammonium salt with an ethanol solution

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(24) Huang, L.; Ozawa, F.; Yamamoto, A. *Organometallics* **1990**, *9*, 2603.
(25) Studies are in progress in order to elucidate the exact nature and the geometry of the intermediate $PdCl_2(NH_2R)L_2$.

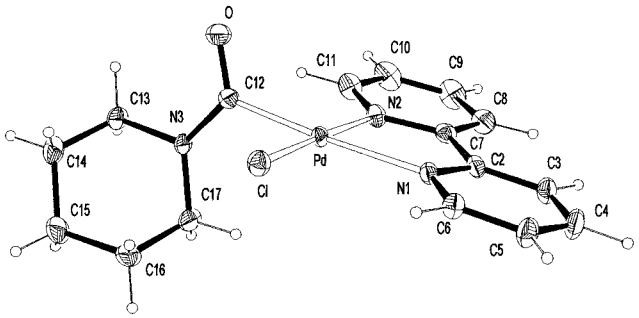


Figure 1. ORTEP drawing of complex **4d** showing thermal ellipsoids drawn at 30% probability.

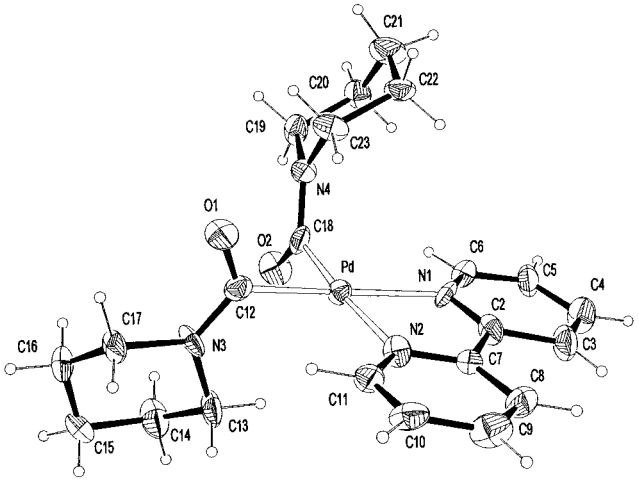


Figure 2. ORTEP drawing of complex **6d** showing thermal ellipsoids drawn at 30% probability.

of CH_3ONa, which converts the ammonium salt into the corresponding amine (eq 7):

$$\overbrace{Pd[CON(CH_2)_4CH_2]_2L_2} + \overbrace{CH_2(CH_2)_4NH}\cdot HCl + CH_3ONa \rightarrow Pd[CON(CH_2)_4CH_2]_2L_2 + \overbrace{CH_2(CH_2)_4NH} + CH_3OH + NaCl \quad (7)$$

This procedure slightly affects the yield of pure carbamoyl complexes.

Characterization of the Compounds 1−7 by Reaction with HCl. All carbamoyl compounds have been characterized in solution by measurement of CO evolved upon reaction with dry HCl (see Table 1).

This is a fast method for distinguishing mono- and dicarbamoyl complexes (eqs 8 and 9, see Experimental Section).

$$PdCl(CONRR')L_2 + 2\ HCl \rightarrow PdCl_2L_2 + NHRR'\cdot HCl + CO \quad (8)$$

$$Pd(CONRR')_2L_2 + 4\ HCl \rightarrow PdCl_2L_2 + 2\ NHRR'\cdot HCl + 2\ CO \quad (9)$$

X-ray Single-Crystal Structure of 4d and 6d. Both complexes **4d** and **6d** (Figures 1 and 2) are characterized by an almost square-planar coordination around the metal center.

Two *cis* positions are occupied by the dipy nitrogen atoms and the remaining two by one piperidinecarbamoyl-C group and one chloride anion in **4d** and by two piperidinecarbamoyl-C groups in **6d**. The displacements of the palladium atoms from the N1 N2 C12 Cl and N1 N2 C12 C13 donor least-squares planes are 0.0311(5) and −0.029(2) Å in **4d** and **6d**, respectively. The Pd−Cl bond length in **4d** and the Pd−N bond distances in **4d** and **6d** are consistent with those observed in palladium(II) square-planar complexes previously reported (see Tables 3 and 4).[26]

Table 3. Selected Bond Distances (Å) and Angles (deg) of Complex 4d

Pd−Cl	2.3201(18)	O−C12	1.212(8)
Pd−N1	2.151(5)	N3−C12	1.354(8)
Pd−N2	2.054(5)	N3−C13	1.467(8)
Pd−C12	1.979(6)	N3−C17	1.453(9)
Cl−Pd−N1	96.90(13)	C12−N3−C13	119.9(5)
Cl−Pd−N2	175.38(15)	C12−N3−C17	125.1(5)
Cl−Pd−C12	89.41(17)	C13−N3−C17	114.4(5)
N1−Pd−N2	78.72(18)	Pd−C12−O	119.8(5)
N1−Pd−C12	173.4(2)	Pd−C12−N3	118.4(4)
N2−Pd−C12	94.9(2)	O−C12−N3	121.6(6)

Table 4. Selected Bond Distances (Å) and Angles (deg) of Complex 6d

Pd−N1	2.155(17)	N3−C12	1.29(3)
Pd−N2	2.098(17)	N3−C13	1.47(3)
Pd−C12	2.01(2)	N3−C17	1.49(3)
Pd−C18	1.97(2)	N4−C18	1.33(3)
O1−C12	1.26(3)	N4−C19	1.51(2)
O2−C18	1.22(3)	N4−C23	1.44(4)
N1−Pd−N2	78.8(6)	Pd−C18−O2	122.6(17)
N1−Pd−C12	176.5(7)	Pd−C18−N4	120.3(14)
N1−Pd−C18	94.9(7)	O2−C18−N4	117(2)
N2−Pd−C12	98.7(7)	C12−N3−C13	123.6(18)
N2−Pd−C18	173.6(8)	C12−N3−C17	124.0(17)
C12−Pd−C18	87.6(8)	C13−N3−C17	111.3(15)
Pd−C12−O1	118.1(14)	C18−N4−C19	127.0(16)
Pd−C12−N3	121.2(15)	C18−N4−C23	122(2)
O1−C12−N3	121(2)	C19−N4−C2	110.2(17)

The Pd−C(sp^2) bond distances [1.979(6) Å in **4d** and 1.97(2)−2.01(2) Å in **6d**] suggest a back-π-bonding character from the metal to the ligand for the Pd−C(O) bond in both complexes, as the sum of covalent radii of Pd(II) and sp^2 carbon is 2.05 Å.[16]

In the carbamoyl moieties of both compounds the C−O and C−N bond lengths and bond angles at the C and N carbamoyl atoms also indicate delocalization of π-electrons in the Pd−C(O)−N− moiety (the Pd−C(O)−NCC moieties are almost planar), with a non-negligible double-bond character of the C(O)−N bond. Such extended π-bond character that involves Pd−C−N atoms prevents the rotation of the carbamoyl group around the Pd−C bond and the rotation of the piperidine group around the C−N bond. The nonfluxional character of the carbamoyl group in **4d** is conserved also in solution, as demonstrated by the ^{1}H NMR spectrum (Figure 3, see discussion below). In both mono- and dicarbamoyl complexes, the carbamoyl carbonyl groups of the Pd−C(O)−NCC moieties are almost perpendicular to the coordination plane. In **4d** the dihedral angle between the N1 N2 C12 Cl and C12 O1 N3 planes is 82.7(1)°. In **6d** the dihedral angles between the coordination plane N1 N2 C12 C18 and the C12 O1 N3 and C18 O2 N4 planes are 89.4(6)° and 87.2(7)°, respectively. In **6d** the two C═O groups show an

(26) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1979**, S1−S83.

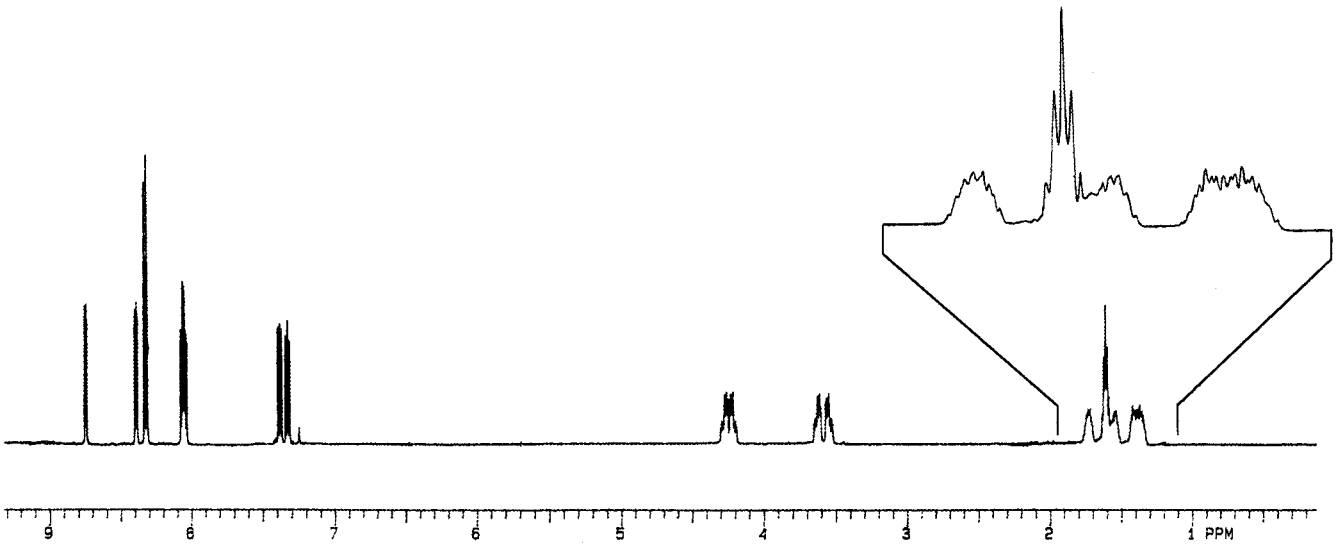


Figure 3. ^{1}H NMR spectrum ($CDCl_3$, 278 K) of complex 4d.

s-trans orientation, being arranged in a head-to-tail fashion with the torsional angle O1−C12−C18−O2 being 135(2)°.

The structures of the two complexes show long-range interactions of the hydrogen atoms from the piperidine methylene groups (adjacent to nitrogen atoms) with the metal centers. One hydrogen atom from one methylene group in **4b** [H(17a)−Pd = 2.572(1) Å] and two H atoms from two *trans*-methylene groups in **6d** [H(13b)−Pd = 2.600(3) Å and H(23a)−Pd = 2.489(2) Å] complete the distorted tetragonal pyramidal and the distorted octahedral environment of the metal center in **4d** and **6d,** respectively, even if in **6d** the Pd···H(23a) contact is significantly shorter than the Pd···H(13b).

In both complexes the dipy C−H groups play a significant role in determining the crystal packing being involved in intermolecular hydrogen bonds with oxygen and chlorine atoms in **4d** and with oxygen atoms only in **6d**. In complex **6d** the piperidine ring, involved in the smaller Pd···H contact, is more strained [torsion angles ranging from −47(3)° to −56(3)° and from 50-(3)° to 54(3)°] than the second one, which shows an almost unstrained *chair* conformation [from (−57(3)° to −62(3)° and from 58(3)° to 62(3)°]. In **4d** the analogous six-membered system shows the less distorted conformation [from −53.5(7)° to −55.8(7)° and from 53.5(7)° to 55.0(7)°].

To the best of our knowledge, **4b** and **6d** are the first examples of mono- and dicarbamoyl complexes structurally characterized for the same metal system. Moreover, complex **6d** is the first Pd *cis*-dicarbamoyl complex and one of the rare η^1-C bound dicarbamoyl complexes structurally characterized, together with Ru(dppe)$(CO)_2$[C(O)NHCH$(CH_3)_2]_2$,[15] Ru(dppe)$(CO)_2$[C-(O)NHCH$(CH_3)_2]_2$,[15] and Hg[C(O)N$Et_2]_2$ complexes. The only example of a Pd− or Pt−carbamoyl complex similar to **6d** is the *cis* neutral acyl−carbamoyl complex of Pt(II), Pt(COPh)(CONEt_2)$(PPh_3)_2$.[17] To complete the list of known structures of acyl−carbamoyl complexes, we mention the *trans* cationic[16] acyl−carbamoyl complex of Pd and the neutral[18] α-ketoacyl−carbamoyl complex of Pt. When compared with the structure of the neutral *cis*-Pt(COPh)(CONEt_2)$(PPh_3)_2$ compound (in which both the benzoyl and carbamoyl carbonyls lie in planes nearly orthogonal to the coordination plane), complex **6d** presents a significant increase of the C−Pd−C bond angle [87.6(8)° vs 79.6(5)°]. The lengthening of one of the two M−C bonds has been observed also for the dicarbamoyl complex Ru(dppe)$(CO)_2$[C(O)NHCH-$(CH_3)_2]_2$,[15] in which a *trans* influence of the phosphine and carbonyl ligands has been invoked. The absence of such differential *trans* influence in compound **6d** suggests that other factors (steric hindrance of the ancillary ligands or molecular packing) may also play a role.

Spectroscopic Characterization of the Complexes. Complexes **1**−**7** have been characterized by means of IR spectra, elemental analyses, and reactivity (see Experimental Section). Complexes **4d** and **6d** were additionally characterized by ^{1}H and ^{13}C NMR spectroscopy. All the dicarbamoyl complexes display in the IR spectrum strong absorptions in the 1600−1550 cm^{-1} region, which is typical for the carboxyamido ligands. The comparison of the CO-stretching of carbamoyl complexes of both primary and secondary amines allows us to unequivocally distinguish the ν(CO) from δ(NH).[27] Such assignment may not be straightforward if only primary amines are used.[2a,b]

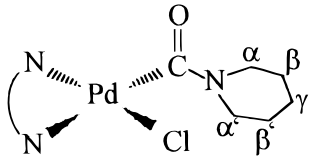
The monocarbamoyl complexes of primary amines display the N−H stretching between 3450 and 3300 cm^{-1}.

NMR Data of Complex 4d. ^{13}C NMR data show that the carbonyl-carbon resonance of monocarbamoyl complex **4d** is found at higher field (174 ppm) with respect to the carbonyl-carbon absorption of the dicarbamoyl complex **6d** (196 ppm).

At higher field, five different carbon signals are observed [25.0(s), 26.3(s), 26.5(s), 44.5(s), 48.8(s) ppm] that can be assigned to the carbon atoms of the piperidine ring. They demonstrate a hindered rotation around the C−N bond of the carbamoyl moiety due to its partial double-bond character (see above), which causes the nonequivalence of the piperidine *ortho*- and *meta*-carbon atoms. Such rigid character of the C−N bond in the carbamoyl complexes has been reported also for other carbamoyl complexes.[2a,b]

(27) Pouchert, C. J. *The Aldrich Library of IR Spectra*; Aldrich Chemical Co.: 1970.

Scheme 1. Synthesis and Solid State and Solution Characterization of Mono- and Di-(η^1-C) Carbamoyl−Pd Complexes



In the high-field region of the ^{1}H NMR spectrum of **4d** seven signals (Figure 3) due to the piperidine protons are observed [1.3 (b, 1 H), 1.4 (b, 1 H), 1.5(b, 1 H), 1.6 (q, 2 H), 1.7 (b, 1 H), 3.5 (m, 2 H) and 4.2 (m, 2 H) ppm].

The piperidine α- and α′-protons (with respect to N, see Scheme 1) appear as two second-order multiplets at 4.2 (2 H) and 3.5 (2 H) ppm.

Selective irradiation of one multiplet by a homonuclear decoupling experiment does not affect the other. This allows us to conclude that the two multiplet signals originate from proton nuclei not magnetically interacting.

In agreement with data reported in the literature[28] the multiplet centered at 4.2 ppm is assigned to the α-CH_2-protons pseudo-*cis* to the C═O group and the multiplet centered at 3.5 to the α′-CH_2-protons pseudo-*trans* to the C═O group in the piperidine moiety.

Interestingly, the spectrum of complex **4b** shows a pseudo-quintet at 1.6 ppm (2 H) assigned to the γ-protons of the piperidine moiety. This pseudo-quintet originates from two isochronous γ-protons coupled with four β- and β′-protons with an almost similar coupling constant ($J \approx 5.6$ Hz). The four β- and β′-protons appear as broad multiplets at 1.3 (1 H), 1.4 (1 H) (these two multiplets partially overlap, Figure 3), 1.5 (1 H) and 1.7 (1 H) ppm.

In the absence of free rotation around the Pd−C bond (as shown by the ^{13}C NMR spectrum), the features of the ^{1}H NMR spectrum of compound **4d** indicate hindered rotation also around the Pd−C bond. In fact, a free rotation around the Pd−C bond would cause the equivalence of the CH_2 protons (axial and equatorials) attached to each piperidinic carbon and the appearance of five signals. The presence of more than five signals indicates that the rigid structure of the Pd−C(O)−N moiety observed in the solid state is retained also in solution.

NMR Data of Complex 6d. ^{13}C NMR data show that the carbonyl-carbon resonances of dicarbamoyl complex **6d** is found at 196.2 (s) ppm. Five signals observed in the high-field region are attributed to the piperidine carbons, indicating that also in this case there is a hindered rotation around the C−N bond because of its partial double-bond character.

^{1}H NMR data (see Experimental Section) are not supportive, at first sight, of a hindered rotation around the Pd−C bonds. In fact, four groups of signals are found in the ^{1}H NMR spectrum, while 10 signals (or, eventually, more that five, as for **4d**) are expected for piperidinic protons in a rigid Pd−C(O)−N moiety. The rigid structure shown to exist in the solid state is the effect of the partial double-bond character (see above) of both the Pd−C and C−N bonds; the mutual steric hindrance of the two carbamoyl groups should further contribute to prevent the rotation around the Pd−C bond.

A molecular modeling analysis of compound **6d**, carried out with the program WebLab Viewer, shows that the rotation around the Pd−C bond would bring the piperidinic carbons to a very short distance (<1.3 Å) from the dipyridinic carbons. Therefore, compound **6d**, as **4d**, is expected not to show a free rotation around the Pd−C and C−N bonds in solution. The presence of only four signals in the ^{1}H spectrum of the piperidine moiety can be, thus, explained considering incidentally coincident chemical shifts of the protons.

Reactivity of Compounds 1−7 toward $CuCl_2$. The Pd−(CONHR) moiety is quite stable at room temperature in the solid state and does not undergo a reductive elimination to afford a Pd(0) complex in solution. Conversely, the Pd−C bond is easily cleaved by Broensted acids (see above) and oxidants. For example, as expected on the basis of our previous studies,[2a] both mono- (**1**−**5**) and dicarbamoyl complexes (**6**, **7**) react with $CuCl_2$ at room temperature under dinitrogen atmosphere to afford isocyanates or carbamoyl chlorides according to reactions 10−12.

$$\underset{\mathbf{1-3}}{PdCl(CONHR)L_2} + 2\ CuCl2 \rightarrow PdCl_2L_2 + RNCO + 2\ CuCl + HCl \quad (10)$$

$$\underset{\mathbf{4,\ 5}}{PdCl(CONRR')L_2} + 2\ CuCl2 \rightarrow PdCl_2L_2 + ClCONRR' + 2\ CuCl \quad (11)$$

$$\underset{\mathbf{6,\ 7}}{Pd(CONRR')_2L_2} + 4\ CuCl_2 \rightarrow PdCl_2L_2 + 2\ ClCONRR' + 4\ CuCl \quad (12)$$

Two moles of copper(II) chloride per each carbamoyl ligand are required; so, when reaction 12 is carried out with a molar ratio $CuCl_2/Pd = 2$, only one amide Pd−C bond is cleaved (eq 13) producing monocarbamoyl complexes.

$$Pd(CONRR')_2L_2 + 2\ CuCl_2 \rightarrow PdCl(CONRR')L_2 + ClCONRR' + 2\ CuCl \quad (13)$$

These results, coupled with the analogous reactivity demonstrated by dimethoxycarbonyl complexes ($L_2Pd[C(O)OCH_3]_2$),[6] enabled us to say that the cleavage of the palladium−carbon bond by copper(II) chloride can be considered quite a general reaction for complexes of formula $Pd(CONu)_xCl_{(2-x)}L_2$ (where Nu = OR, NHR, NRR′).

Therefore, the reactions described here can be considered as a potential alternative route to the use of phosgene for the synthesis of either chloroformates or carbamoyl chlorides, which are key intermediate to carbonates, carbamates, and ureas.

It is worth emphasizing that Pd and Cu complexes can be quantitatively recovered and recycled, which makes more acceptable the hypothesis of application.

We have also developed a technique for the recovery of pure Cu and Pd complexes. In fact, the solid mixture ($PdCl_2L_2$ + CuCl), from reactions 10−12, can be treated with an ethanol solution of dipy (stoichiometric amount

(28) Lynch, D. M.; Cole, W. *J. Chem. Soc., Dalton Trans.* **1966**, 3337.

with respect to Cu), which allows CuCl to be extracted in solution as CuCl(dipy) while $PdCl_2L_2$ is left as a solid residue.

On the other hand, the recycling of the Pd-catalyst can be more conveniently carried out by reacting the solid mixture of Pd/Cu with a hydro-alcoholic HCl solution under O_2, which converts the insoluble CuCl into soluble $CuCl_2$ (eq 14), which can be reused.

$$2\ CuCl + 2\ HCl + 1/2\ O_2 \rightarrow 2\ CuCl_2 + H_2O \quad (14)$$

It is worth noting that reaction 14 makes the overall process of the amine conversion catalytic in both palladium and $CuCl_2$. When primary amines are used, the net reaction is (eq 15)

$$RNH_2 + CO + 1/2\ O_2 \rightarrow RNCO + H_2O \quad (15)$$

With secondary amines the net reaction is the production of carbamoyl chlorides (eq 16):

$$RR'NH + CO + HCl + 1/2\ O_2 \rightarrow ClCONRR' + H_2O \quad (16)$$

Analogously, the chloroformates synthesis can be depicted as a reaction involving only alcohol, CO, HCl, and O_2 (eq 17):

$$ROH + CO + HCl + 1/2\ O_2 \rightarrow ClCOOR + H_2O \quad (17)$$

Reaction of the Carbamoyl Complexes with Halosuccinimide. With the aim of having a complete view of the reactivity of carbamoyl complexes, we have explored other reagents able to react with the Pd−C bond. We found that halosuccinimides $X-N(COCH_2)_2$ (X = Cl, Br) are effective agents for the selective cleavage of the Pd−C bond with halogenation of carbamoyl ligands (eq 18).

$$PdCl(CONRR')L_2 + X-N(COCH_2)_2 \rightarrow XCONRR' + PdCl[N(COCH_2)_2]L_2 \quad (18)$$

(X = Cl, Br)

Also in this case, carbamoyl complexes of primary amines (eq 19) directly afford isocyanates.

$$PdCl(CONHR)L_2 + X-N(COCH_2)_2 \rightarrow PdClXL_2 + RNCO + HN(COCH_2)_2 \quad (19)$$

However, the catalyst recovery procedure, in the case of secondary amines, requires an additional step to regenerate the starting palladium catalyst (eq 20) by using HCl.

$$PdCl[N(COCH_2)_2]L_2 + HCl \rightarrow PdCl_2L_2 + HN(COCH_2)_2 \quad (20)$$

In the case of monocarbamoyl complexes of primary amines, HCl is not required, as eq 19 proceeds in two steps (eqs 21 and 22).

$$PdCl(CONHR)L_2 + X-N(COCH_2)_2 \rightarrow PdCl[N(COCH_2)_2]L_2 + RNCO + HX \quad (21)$$

$$PdCl[N(COCH_2)_2]L_2 + HX \rightarrow PdClXL_2 + HN(COCH_2)_2 \quad (22)$$

The acid produced in reaction 21 is enough to cleave the Pd−N bond in the Pd-intermediate complex (eq 22) and to regenerate the catalyst. Although halosuccinimides afford a quantitative cleavage of the Pd−C bond, they have no value from the application point of view, due to their cost and the fact that succinimide is formed, which accumulates in the catalytic cycle. If Cl_2 is used instead of HCl, in eq 20, halosuccinimide is re-formed in addition to $PdCl_2L_2$, with a total regeneration of the reagents.

Reaction of the Carbamoyl Complexes with Halogens: Direct Synthesis of Isocyanates and Carbamoyl−Halides. The reaction of Cl_2 and I_2 with carbamoyl complexes is the most effective way to synthesize isocyanates and carbamoyl−halides from mono- and dicarbamoyl complexes, respectively. The halogens react in a selective way and regenerate the active starting palladium catalyst without side products. The yield is quantitative.

Both chlorine and iodine are very good reagents: the latter may be safer to use. (eqs 23 and 24).

$$PdCl(CONHR)L_2 + X_2 \xrightarrow{\textbf{1-3}} PdClXL_2 + RNCO + HX \quad (23)$$

$$PdCl_{(2-x)}(CONRR')_xL_2 + x\ X_2 \xrightarrow{\textbf{4-7}} PdCl_{(2-x)}X_xL_2 + x\ XCONRR' \quad (24)$$

$X_2 = Cl_2, I_2;\ x = 1, 2$

With these reagents the overall process of amine conversion is represented by eqs 25 and 26.

$$RNH2 + CO + X_2 \rightarrow RNCO + 2\ HX \quad (25)$$

$$RR'NH + CO + X_2 \rightarrow XCONRR' + HX \quad (26)$$

(X = Cl, I)

These reactions represent a substantial simplification of the process for obtaining isocyanates and carbamoyl chlorides. In a catalytic cycle (that does not require the isolation of the pure carbamoylmetal complex) the Pd(II) complex is formed in a quantitative yield and can be reused several times, giving a two-step reaction of potential interest from the application point of view.

Reaction Mechanism. The reaction mechanism of Pd−methoxycarbonyl or carbamoyl species with $CuCl_2$ and halogens presents several interesting aspects, some of which we have highlighted.[2a,6] The use of $CuCl_2$ opens the question about the molecularity of the reaction, as two molecules of $CuCl_2$ per mol of Pd complex are used for the cleavage of a single Pd−C bond (eqs 10−13).

In our previous papers,[2a] we suggested that isocyanate, chloroformate, or carbamoyl chloride formation could occur either through ligand exchange between the palladium carbamoyl complex and copper chloride or by

oxidative addition of copper chloride, leading to the formation of unstable Pd(IV)−carbamoyl complexes.

The oxidation may take place to **4d** or **6d** to afford $PdCl_3(CONRR')L_2$ or $PdCl_2(CONRR')_2L_2$, which then decay to Pd(II) complexes with elimination of 1 mol of ClCONRR′.

While the elucidation of the reaction mechanism of carbamoyl complexes with $CuCl_2$ deserves further investigation in order to exclude possibilities, the reaction of monocarbamoyl Pd−Cl complexes with I_2 is a useful tool for getting information about the reaction mechanism when Cl_2, I_2, or halosuccinimide is used. In fact, starting from $PdCl(CONRR')L_2$ and I_2, the reaction affords both ClCONRR′ and ICONRR′ (see Experimental Section).

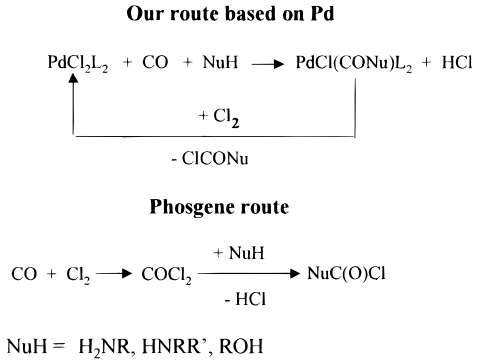
This result can be explained if one assumes that I_2 behaves as a two-electron acceptor and the reaction occurs through an oxidative addition of I_2 to $PdCl(CONRR')L_2$ to afford a palladium(IV) carbamoyl complex $[PdClI_2(CONRR')L_2]$, which can, by reductive elimination, afford either the carbamoyl-chloride or -iodide species.

Support for this hypothesis comes also from the observation that, as already reported for the case of $Pd(COOMe)_2L_2$, when **6d** is reacted with Cl_2, some features of the reaction mixture are observed that are characteristic of a Pd(IV) complex[6] (transient red color) that is then readily reduced to Pd(II). The initial formation of a radical (either X• or •CONRR′) might also account for the observed features. Nevertheless, the experimental evidence available to date (no effect of radical scavengers) do not support such a mechanism.

Conclusions

Stable Pd−carbamoyl complexes of formula $PdCl_{(2-x)}(CONRR')_xL_2$ (x = 1,2; L = dipy, phen, PPh_3) can be isolated, characterized in the solid state, and easily reacted with $CuCl_2$, halosuccinimides, or halogens to afford isocyanates or carbamoyl chlorides, which are the precursors of carbamates or ureas. This result, coupled with our previous observations on the reactivity of Pd−methoxy carbonyl complexes $PdCl_{2-x}(COOMe)_{(2-x)}L$ (x = 1,2; L = dipy, phen),[6] brings to a general conclusion that Pd(II) complexes with bidentate N-ligands are catalysts for developing new synthetic processes that use the same reagents used in phosgene chemistry, but avoid the synthesis of phosgene (Scheme 2).

Scheme 2. Synthesis and Solid State and Solution Characterization of Mono- and Di-(η^1-C) Carbamoyl−Pd Complexes



The Pd mediation allows the use of an alternative reaction sequence. In fact, Pd makes possible the direct reaction of CO with the nucleophile (ROH or the amine) to afford the methoxy carbonyl or carbamoyl, respectively, which are then reacted with halogen donors.

The very mild conditions used in the synthesis and the easy and quantitative recovery of Pd emphasize that it is possible to avoid the use of toxic molecules and shift to environmentally benign syntheses by slightly modifying the processes and choosing the proper catalyst.

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Supporting Information Available: List of the atomic fractional coordinates of the non-hydrogen atoms (Table 5 (**4d**)), Table 6 (**6d**)), list of the anisotropic temperature factors (Table 7 (**4d**), Table 8 (**6d**)), list of the atomic fractional coordinates of the hydrogen atoms (Table 9 (**4d**), Table 10 (**6d**)), and a full list of the bond distances and angles (Table 11 (**4d**), Table 12 (**6d**)). This material is available free of charge via the Internet at http://pubs.acs.org.

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