Selected Paper

Selective Oxidative Carbonylation of Amines to Oxamides and Ureas Catalyzed by Palladium Complexes

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A new process for converting secondary amines into *N*,*N*,*N*′,*N*′-tetraalkyloxamides under CO pressure, catalyzed by homogeneous palladium complexes in the presence of 1,4-dichloro-2-butene (DCB) as an oxidant, has been developed. The mechanism of the oxidative double-carbonylation process, consisting of the oxidation of Pd(0) to Pd(II) with DCB through a β-chloride elimination of the η^3-(chloromethyl)allylpalladium(II) intermediate, the formation of mono- and bis(carbamoyl)palladium species, and a reductive elimination of the two carbamoyl ligands, is proposed based on studies of the behavior of carbamoylpalladium complexes. When primary amines are employed with DCB as the oxidant, *N*,*N*′-dialkyloxamide is catalytically produced, whereas urea is exclusively produced when iodine is used as the oxidant. The reaction of an *N*-monopropylcarbamoylpalladium complex with propylamine under CO gave *N*,*N*′-dipropylurea, whereas a treatment with diethylamine yielded unsymmetrical *N*,*N*-diethyl-*N*′-propylurea, implying the intermediate formation of propyl isocyanate that is converted into the urea upon a reaction with the added amine. A kinetic study on the reaction of chloro-*N*-propylcarbamoylpalladium with triethylamine suggested a process proceeding through a base-promoted deprotonation of the *N*-monoalkylcarbamoyl ligand to form propyl isocyanate.

Palladium catalysts have been extensively utilized for quite a range of important laboratory and industrial processes.[1,2] Among various palladium-catalyzed synthetic methods, the catalytic oxidative carbonylation of alcohols to produce carbonates and oxalates (e.g., Ube process)[3] constitutes an important class of industrial process for realizing phosgene-free processes for introducing CO groups.[4] When the oxidative carbonylation is applied to amines, the development of catalytic single and double carbonylation of amines to produce ureas and oxamides can be expected.

The palladium-catalyzed synthesis of urea and oxamide has attracted intermittent attention. Tsuji converted primary amines into mixtures of oxamides and ureas under 100 atm of CO using $PdCl_2$ as a catalyst without any oxidants added at 180 °C.[5] Murahashi and co-workers noted the formation of oxamide as a byproduct in the palladium(II)-catalyzed oxidative carbonylation of a secondary amine to give oxamate, carbamate, and urea in a process carried out in the presence of O_2 as an oxidant and a copper salt as a cocatalyst.[6] The use of I_2 or KI promotes oxidative carbonylation in the absence of copper salts. Alper and Pri-Bar have reported that ureas were formed exclusively from primary amines using iodine as an oxidant, whereas oxamides were obtained as the main products when secondary amines were carbonylated by palladium(II) acetate in the presence of O_2, K_2CO_3, and KI.[7] It has also been demonstrated that the combination of O_2 with halide anion for the oxidative carbonylation was applicable to the selective formation of *N*,*N*′-diphenylurea from aniline[8] and unsymmetrically substituted ureas from a mixture of primary and secondary amines.[9]

For designing selective carbonylation processes, understanding the mechanism of the carbonylation of amine nucleophiles is essential. In these palladium-catalyzed oxidative processes, the re-oxidation of a Pd(0) species formed in the principal catalytic cycle to an electrophilic Pd(II) species is also crucial for accomplishing the catalytic processes.

We found that 1,4-dichloro-2-butene (DCB) serves as a convenient oxidizing agent in combination with Pd catalysts in the double carbonylation of primary and secondary amines to give oxamide derivatives with high selectivities. In order to clarify the courses of the catalytic formation of oxamides and ureas and the mechanism of oxidation of Pd(0) into Pd(II) species by DCB, we also carried out basic studies concerning the properties of carbamoylpalladium complexes as models for key intermediates formed by nucleophilic attacks of amines on CO coordinated to palladium(II) species.[10] The present paper summarizes the scope of the catalytic processes using DCB or I_2 as the oxidizing agent, and the results of fundamental studies focusing on the mechanistic aspects for selectively producing oxamides and ureas from amines and carbon monoxide.

Results

Oxidation of a Pd(0) to Pd(II) Complex with Dichlorobutenes. We first examined the reaction course in the conversion of a Pd(0) into a Pd(II) complex with DCB in the presence of diethylamine. The triphenylphosphine-coordinated Pd(0)

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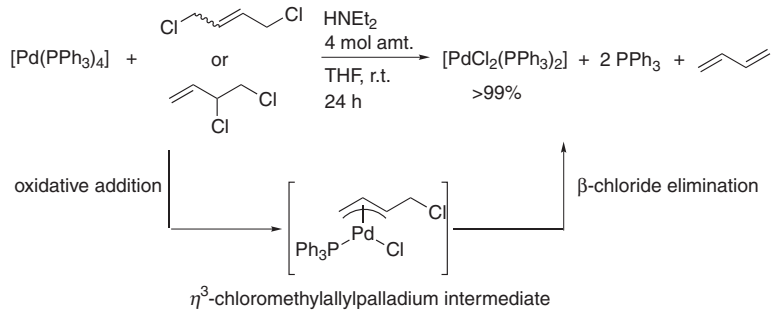


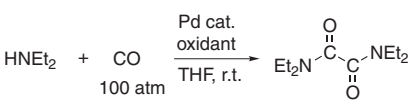
Scheme 1. Oxidation of $[Pd(PPh_3)_4]$ to *trans*-$[PdCl_2(PPh_3)_2]$ by cleavage of the two carbon–chloride bonds in dichlorobutenes.

complex, $[Pd(PPh_3)_4]$, was found to be smoothly converted into *trans*-$[PdCl_2(PPh_3)_2]$ in high yields upon reactions with 1,4-dichloro-2-butene or 1,2-dichloro-3-butene along with the release of 1,3-butadiene and PPh_3 in THF at room temperature. In the presence of the diethylamine, the yield of *trans*-$[PdCl_2(PPh_3)_2]$ was almost quantitative. We also found that the oxidation proceeded smoothly in the absence of the amine as well.

The facile oxidation of the Pd(0) complex to give *trans*-$[PdCl_2(PPh_3)_2]$ with two dichlorobutenes suggests that the two carbon–chloride bonds in the dichlorobutenes were cleaved through a common allylic palladium intermediate, η^3-(chloromethyl)allylpalladium(II) chloride, which undergoes further abstraction of the chlorine at the β position to produce *trans*-$[PdCl_2(PPh_3)_2]$ with the liberation of 1,3-butadiene (Scheme 1).[11]

The result suggested the utility of DCB as a convenient oxidizing agent to cleanly convert Pd(0) species into Pd(II) with the liberation of 1,3-butadiene as the only volatile matter, readily removable from the reaction system. Other disubstituted 2-butenes with an OH or OAc group at the 1,4-positions did not show a similar oxidation behavior of Pd(0) through β-heteroatom elimination.[12]

Catalytic Oxidative Carbonylation of Amines to Oxamides. In the presence of DCB, the selective formation of *N*,*N*,*N*′,*N*′-tetraethyloxamide was achieved by the Pd(II)-catalyzed oxidative carbonylation of diethylamine (Eq. 1). Table 1 compares the effectiveness of various oxidizing agents under the catalytic conditions.



(1)

The results given in Table 1 show that DCB in combination with PPh_3-coordinated palladium dichloride gave an excellent yield of the oxamide when the reaction was performed under a CO pressure of 50 atm at room temperature (run 1). Other palladium catalysts, such as $PdCl_2$ and Pd/C, without the PPh_3 ligands showed less activity, whereas $[PdCl_2(PPh_3)_2]$ with $CuCl_2$ as the oxidizing agent showed medium activity (runs 2–4). The combination of $Pd(OAc)_2$ with other oxidizing agents, shown in runs 5 and 6, showed much less activity.

Table 2 gives the effects of the ligands employed in combination with palladium catalysts in carbonylation of diethylamine.

The results showed the effectiveness of a dichloropalladium complex bearing PPh_3 ligands in achieving the carbonylation of diethylamine. The addition of an excess of the PPh_3 ligand caused some decrease in the activity of the catalyst (runs 1 to 3). Bidentate diphosphine ligands, such as 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP), and 1,4-bis(diphenylphosphino)butane (DPPB), having two, three, and four methylene units, were less effective,

Table 1. Palladium-Catalyzed Oxidative Carbonylation of Diethylamine into Oxamide with Various Oxidants

Run	Oxidant[a)]	Catalyst (mol amt.)	Yield[b)]/% $(CONEt_2)_2$
1[c)]	DCB	$PdCl_2(PPh_3)_2$ (0.005)	96
2[c)]	DCB	$PdCl_2$ (0.01)	27
3[c)]	DCB	Pd/C (0.01)	32
4[d)]	$CuCl_2$	$PdCl_2(PPh_3)_2$ (0.01)	63
5	O_2 (5 atm)	$Pd(OAc)_2$, PPh_3, $CuCl_2$, 1,4-benzoquinone[e)]	11
6	1,4-benzoquinone	$Pd(OAc)_2$ (0.01), PPh_3 (0.03)	6.2

a) Oxidizing agent:diethylamine = 1:4. b) Based on diethylamine, determined by GLC. c) $p(CO) = 50$ atm. d) DMF was used as a solvent. e) $HNEt_2$:$Pd(OAc)_2$:PPh_3:$CuCl_2$:benzoquinone = 400:1:3:4:5.

Table 2. Ligand Effects in Palladium-Catalyzed Oxidative Carbonylation of Diethylamine

Run	Catalyst (mol amt./DCB)	P/Pd ratio	Yield[a)]/% $(CONEt_2)_2$
1	$[PdCl_2(PPh_3)_2]$ (0.005)	2	95
2	$[PdCl_2(PPh_3)_2]$ (0.005) + $2PPh_3$	4	84
3	$[PdCl_2(PPh_3)_2]$ (0.005) + $4PPh_3$	6	78
4	$[PdCl_2(dppe)]$ (0.005)	2	15
5	$[PdCl_2(dppp)]$ (0.005)	2	14
6	$PdCl_2(dppb)$ (0.005)	2	41
7	$PdCl_2(dppf)$[b)] (0.005)	2	62
8	$PdCl_2$(tm-phen)[c)] (0.005)	—	0
9	$[Pd(dba)_2]$ (0.01)	—	10
10	$[Pd(dba)_2]$ (0.01) + $2PPh_3$	2	72

Conditions: $HNEt_2$/DCB = 4, CO = 50 atm, stirred at r.t. for 17 h. a) Based on DCB, determined by GLC. No urea derivatives were formed. b) $p(CO) = 100$ atm. c) tm-phen = 3,4,7,8-tetramethyl-1,10-phenanthroline.

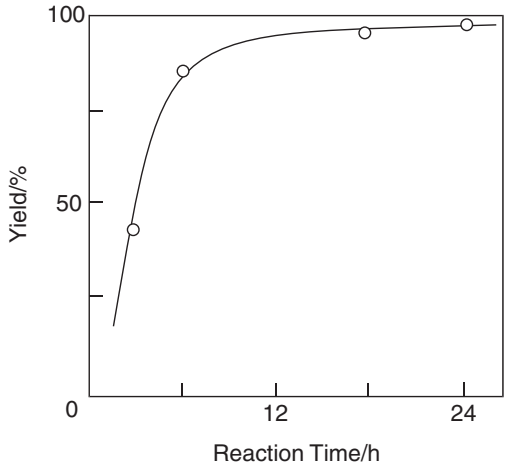


Fig. 1. Time course of the palladium-catalyzed oxidative carbonylation of diethylamine into *N*,*N*,*N*′,*N*′-tetraethyloxamide. Reaction conditions: Pd catalyst = *trans*-[$PdCl_2(PPh_3)_2$], $HNEt_2$:DCB:Pd cat = 800:200:1, CO 100 atm, at r.t. in THF.

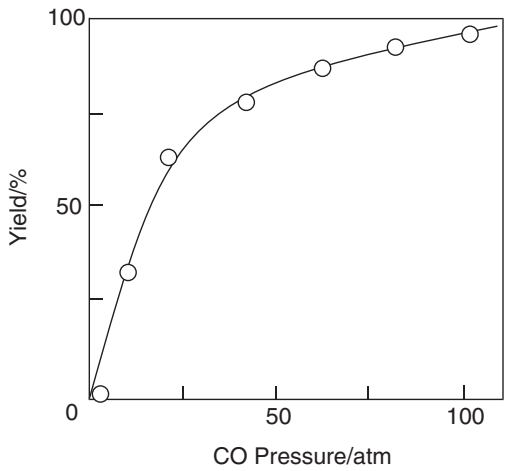


Fig. 2. Effect of the CO pressure on formation of oxamide in palladium-catalyzed carbonylation of diethylamine. Reaction conditions: Pd catalyst = *trans*-[$PdCl_2(PPh_3)_2$], $HNEt_2$:DCB:Pd cat = 800:200:1, for 17 h, at r.t. in THF.

whereas 1,1′-bis(diphenylphosphino)ferrocene ligand (DPPF) gave the oxamide in medium yield (runs 4–7). A phenanthroline ligand having nitrogen donors proved to be ineffective (run 8). [$Pd(dba)_2$], itself, showed a meager catalytic activity, which was enhanced by adding PPh_3 ligands (runs 9 and 10).

The time course of the carbonylation of diethylamine into oxamide, catalyzed by *trans*-[$PdCl_2(PPh_3)_2$] in the presence of DCB, and the effect of CO pressure on the oxamide yield have been examined, as shown in Figs. 1 and 2.

The formation of oxamide is a slow process when the reaction is performed at room temperature, taking about 18 h for completion (Fig. 1). The application of CO pressure over 50 atm was required for the complete conversion of diethylamine into the corresponding oxamide in THF at room temperature (Fig. 2). In any of the experiments listed in Table 2, no formation of the monocarbonylated product, *N*,*N*,*N*′,*N*′-tetraethylurea was observed.

Table 3. Palladium-Catalyzed Oxidative Carbonylation of Secondary and Primary Amines into Oxamides

Run	Amine	Pd cat./DCB	Time/h	Yield[a)]/%
1	Et_2NH	0.005	17	96
2	piperidine	0.05	24	72
3	pyrrolidine	0.005	17	92
4	$^{i}Pr_2NH$	0.005	17	8.2
5[b)]	$^{i}Pr_2NH$	0.005	17	10
6	$^{i}Pr_2NH$	0.05	24	30
7	Ph_2NH	0.05	24	0
8	$^{n}PrNH_2$	0.05	6	89
9	aniline	0.05	17	0
10[c)]	NH_3 (10 atm)	0.05	20	75[d)]
11[c)]	$CyNH_2$	0.05	17	80[d)]

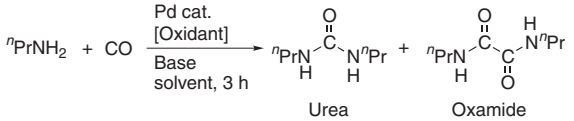
Conditions: Amine/DCB = 4, CO = 100 atm, stirred at r.t. in THF. a) Based on DCB, determined by GLC. No urea derivatives were formed. b) Triethylamine (10 mol amt./DCB) was added. c) $p(CO) = 50$ atm. d) Isolated yield.

Aliphatic secondary amines other than diethylamine can be used to produce oxamides, as shown in Table 3.

Cyclic secondary amines, such as piperidine and pyrrolidine, can be converted into oxamides in good-to-excellent yields (runs 2 and 3). The ratio of the palladium catalyst per mol of DCB could be reduced to 0.005. The oxamide yield from diisopropylamine, a bulkier secondary amine, was lower, presumably due to a steric effect (runs 4–6). An increase in the catalyst amount and of reaction time in the oxidative carbonylation of the diisopropylamine caused an increase in the yields, whereas the addition of triethylamine had no effect. Less-basic diphenylamine was not carbonylated (run 7).

Primary amines, such as propylamine and cyclohexylamine, could also be double-carbonylated into oxamides with DCB as the oxidant, as included in Table 3 (runs 8 and 11). In the case of primary amines, the effect of a steric hindrance on the yields of oxamide was less pronounced, as can be seen from the production of oxamides in similarly high yields from propylamine and cyclohexylamine. Aniline, being a less-basic primary amine, was not carbonylated (run 9), whereas ammonia was carbonylated into oxamide in a good yield without producing any urea under pressurized CO and ammonia (run 10).

Effect of Oxidizing Agent in Carbonylation of Primary Amines. In contrast to the above results of oxidative carbonylation with DCB, which gave only oxamides, the catalytic course of carbonylation of primary amines was influenced most strongly by the nature of the oxidant. Table 4 summarizes the relative yields of urea and oxamide from propylamine (Eq. 2).



(2)

It was observed that use of I_2 as an oxidant gave *N*,*N*′-dipropylurea as the principal carbonylation product (run 2), whereas DCB favored oxamide formation (run 1).

The choice of the base also affected the product selectivity,

Table 4. Effect of Oxidants and Bases in Palladium-Catalyzed Oxidative Carbonylation of Propylamine

Run	Catalyst	Oxidant	Base	Temp/°C	Yield[a]/%	
					Urea	Oxamide
1[b]	$PdCl_2(PPh_3)_2$	DCB	$^nPrNH_2$	r.t.	0	87
2[b]	$PdCl_2(PPh_3)_2$	I_2	$^nPrNH_2$	r.t.	75	0
3[b]	$PdCl_2(PPh_3)_2$	DCB	K_2CO_3	r.t.	10	88
4[c]	$Pd(OAc)_2$	DCB	K_2CO_3	95	67	33

a) Based on propylamine, determined by ^{1}H NMR. b) Propylamine (2.0 mmol), oxidant (1.0 mmol), base (2.0 mmol), catalyst (0.05 mmol), $p(CO) = 50$ atm, in THF (5 mL) for 3 h. c) Propylamine (1.5 mmol), oxidant (0.8 mmol), base (1.6 mmol), catalyst (0.1 mmol), $p(CO) = 50$ atm, in CH_3CN (10 mL) for 3 h.

Table 5. Palladium-Catalyzed Oxidative Carbonylation of Propylamine into Urea in the Presence of I_2 as an Oxidant[a]

Run	Catalyst	Base	Temp/°C	$p(CO)$/atm	Yield[b]/%	
					Urea	Oxamide
1	$Pd(OAc)_2$	K_2CO_3	95	5	99	0
2	$PdCl_2(PPh_3)_2$	K_2CO_3	95	5	98	0
3	$Pd(OAc)_2 + 2PPh_3$	K_2CO_3	95	5	93	3
4	$Pd(OAc)_2$	$^nPrNH_2$	95	5	60	0
5	$Pd(OAc)_2$	K_2CO_3	r.t.	5	87	13
6	$Pd(OAc)_2$	K_2CO_3	95	50	87	9

a) Reaction conditions: Propylamine (1.5 mmol), iodine (0.8 mmol), base (1.6 mmol), and catalyst (0.1 mmol) were stirred in CH_3CN (10 mL) for 3 h. b) Based on propylamine, determined by ^{1}H NMR.

even in the presence of DCB. The use of K_2CO_3 instead of propylamine, itself, as a base caused some increase of the urea (run 3). When K_2CO_3 was used as the base with DCB as the oxidant, as in run 4 with $Pd(OAc)_2$ as the catalyst without addition of PPh_3, urea was produced as the major carbonylation product.

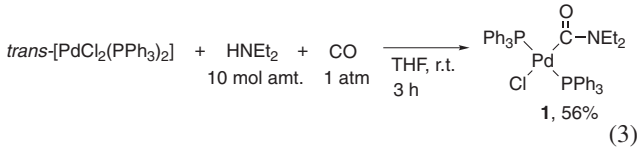
The preferential formation of urea using the Pd–I_2 catalyst system was observed under various experimental conditions with a variation of the catalyst precursors, the nature of the base, the reaction temperature, and the CO pressure, as compared in Table 5.

The carbonylation of propylamine catalyzed by $Pd(OAc)_2$ with I_2 as the oxidant in combination with K_2CO_3 at 95 °C under a CO pressure of 5 atm yielded urea as the sole product in an excellent yield (run 1 in Table 5), in agreement with a previous report by Alper.[7] Similarly, urea was produced as the only carbonylation product in experiments catalyzed by *trans*-$[PdCl_2(PPh_3)_2]$ with I_2 as the oxidant and K_2CO_3 as a base (run 2). The reaction at room temperature, or under high pressure of CO, afforded oxamide as a minor product (runs 5 and 6).

These results show that iodine is most suitable for the preparation of ureas, particularly from primary amines, whereas DCB serves as an excellent oxidant for the production of oxamide in combination with PPh_3-coordinated palladium chloride complexes, without using an alkali base. Another advantage of the system using I_2 as the oxidant is that the addition of a tertiary phosphine is not required for accomplishing the carbonylation processes.

Behavior of Carbamoylpalladium Complexes as Models of Intermediates in Catalytic Cycles. The effectiveness of DCB as the oxidant to convert Pd(0) into the Pd(II) complex and the ability of the *trans*-$[PdCl_2(PPh_3)_2]$ as a catalyst for the production of oxamides suggest the involvement of the reaction of the chloropalladium(II) species with amine, and CO giving an intermediate carbamoylpalladium(II) species.[13] Thus, we have synthesized various carbamoylpalladium complexes and examined their reactivities for obtaining information concerning the mechanisms of the carbonylation processes.

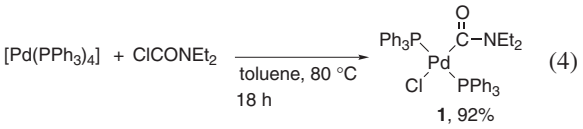
1. Preparation of Carbamoylpalladium Complexes Derived from Secondary Amines: There have been reports concerning the preparation of carbamoyl complexes, but studies associated with the catalytic carbonylation processes are limited.[6,14] We have prepared carbamoylpalladium complexes bearing phosphine ligands, such as PPh_3, PMe_3, and DPPE, by various routes, and compared their reactivities in relation to the oxidative carbonylation of amines. The treatment of *trans*-$[PdCl_2(PPh_3)_2]$ with an atmospheric pressure of CO and diethylamine (10 mol amt.) in THF at room temperature for 3 h yielded the *trans*-[chloro(*N*,*N*-diethylcarbamoyl)bis(triphenylphosphine)palladium(II)] (**1**) (Eq. 3).



(3)

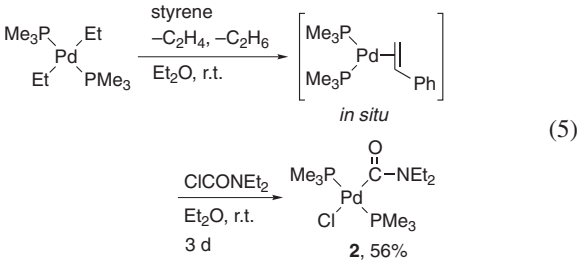
The PPh_3-coordinated carbamoylpalladium complex **1** was characterized by a comparison with a complex prepared from

$[Pd(PPh_3)_4]$ via the oxidative addition of *N*,*N*-diethylcarbamoyl chloride (Eq. 4).



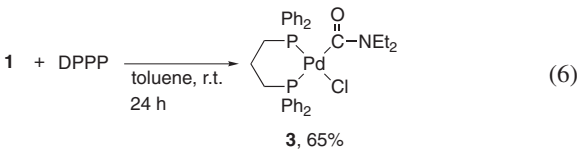
(4)

A similar carbamoylpalladium complex (**2**) having PMe_3 ligands was also prepared by oxidative addition of the *N*,*N*-diethylcarbamoyl chloride to a Pd(0)–styrene complex[15] formed by thermolysis of *trans*-$[PdEt_2(PMe_3)_2]$ in the presence of styrene (Eq. 5).



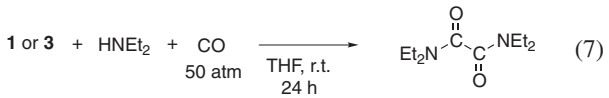
(5)

A ligand-exchange reaction of the PPh_3 ligands in **1** with DPPP provided the *cis*-carbamoyl complex (**3**) with the chelating ligand in a yield of 65% (Eq. 6).



(6)

The treatment of the carbamoylpalladium complexes, **1** and **3**, with carbon monoxide (50 atm) in the presence of diethylamine gave *N*,*N*,*N*′,*N*′-tetraethyloxamide (Eq. 7). The results are summarized in Table 6.



(7)

In base-assisted carbonylation reactions of the PPh_3-coordinated carbamoylpalladium complex **1** with diethylamine, the oxamide was produced almost quantitatively when more than 4 mol amounts of diethylamine were employed under a CO pressure of 50 atm at room temperature for 1 day (run 3).

Table 6. Conversion of the Carbamoylpalladium Complexes into Oxamide with Diethylamine and CO[a)]

Run	Complex	$HNEt_2$ mol amt./Pd	NEt_3 mol amt./Pd	Yield[b)]/%
1	**1**	1	—	17
2	**1**	2	—	60
3	**1**	4	—	97
4	**1**	2	10	97
5	**3**	4	—	94
6	**2**	4	—	0

a) Reaction conditions: Pd complex = 0.1 mmol, at r.t. in THF (10 mL) for 24 h, $p(CO) = 50$ atm. b) Determined by GLC. No urea derivatives were formed.

The use of the amine in molar amounts of less than two caused a decrease in the yield of the oxamide (runs 1 and 2). An improvement in the yield of the oxamide was achieved, however, by treating a mixture of **1** and 2 molar amounts of diethylamine with an excess of triethylamine. The result indicates the secondary role of the amines as a base in addition to the role as a nucleophile to attack the Pd-coordinated CO ligand (run 4).

No oxamide formation was observed when the PMe_3-coordinated complex **2** was used (run 6). The result suggests that an increase in the electron density in the carbamoylpalladium complex causes a decrease in the reactivity of the Pd(II) complex, either by hindering the dissociation of the chloride or tertiary phosphine ligand to provide the coordination site for the incoming CO or amine molecules, or by suppressing the nucleophilic attack of diethylamine on the coordinated CO by reducing its electrophilicity. The smooth reaction of the DPPP-coordinated carbamoylpalladium(II) complex **3** (run 5) as readily as complex **1** bearing the two monodentate PPh_3 ligands suggests that the dissociation of a tertiary phosphine ligand from the carbamoylpalladium complex may not be a prerequisite for generating the oxamide.

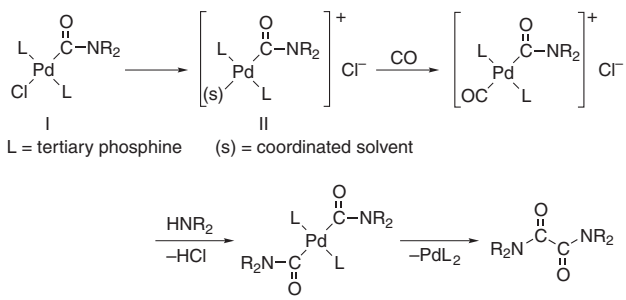
Scheme 2 represents a plausible mechanism for the oxamide formation from carbamoyl-chloropalladium complexes through cationic palladium intermediates.

The reactivity of the carbamoylchloropalladium complex **I** in Scheme 2 may be enhanced by a partial dissociation of the chloro ligand, generating a more electrophilic cationic carbamoylpalladium intermediate[16] **II**. The cationic carbamoylpalladium species produced would have a higher affinity toward CO, facilitating the attack of a secondary amine to help generate a bis-carbamoyl complex. The bis(carbamoyl)palladium complex may reductively eliminate the oxamide, presumably after *trans* to *cis* isomerization, to bring the two carbamoyl ligands into adjacent positions.

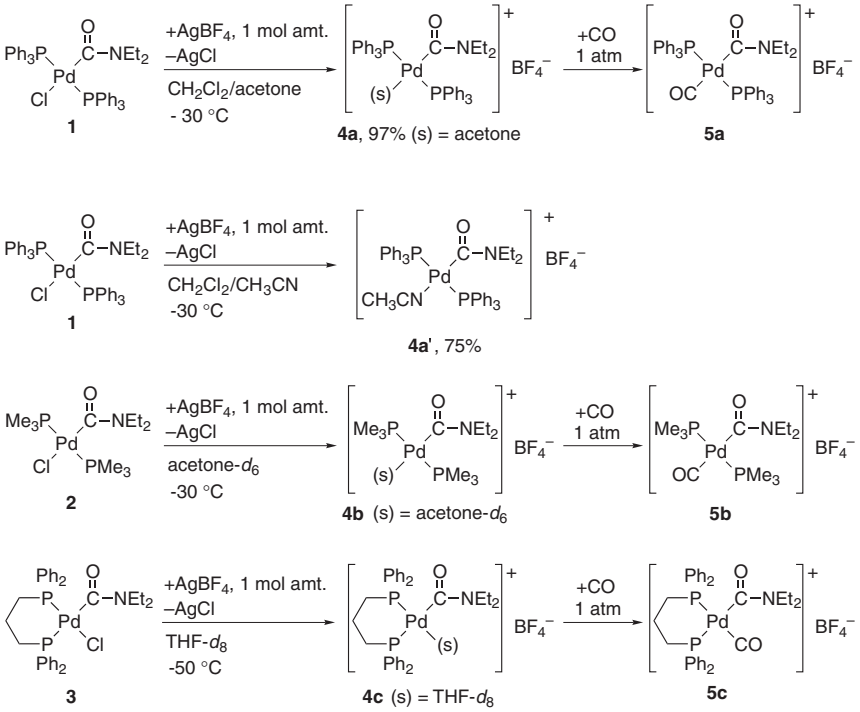
For further gaining insight into the carbonylation mechanism involving cationic species, we attempted to prepare cationic carbamoylpalladium complexes as model intermediates. Removal of the chloride ion in **1** with an equimolar amount of $AgBF_4$ in acetone and CH_2Cl_2 at −30 °C gave a novel acetone-coordinated cationic carbamoyl complex **4a**, accompanied by formation of AgCl (Scheme 3).

The structure of the isolated cationic complex **4a** was established by NMR as well as by single-crystal X-ray analysis.

Figure 3 shows the aliphatic region of the ^1H NMR spec-



Scheme 2. Assumed reaction course to give oxamide through cationic carbamoylpalladium complexes.



Scheme 3. Formation of cationic carbamoylpalladium complexes **4** and **5**.

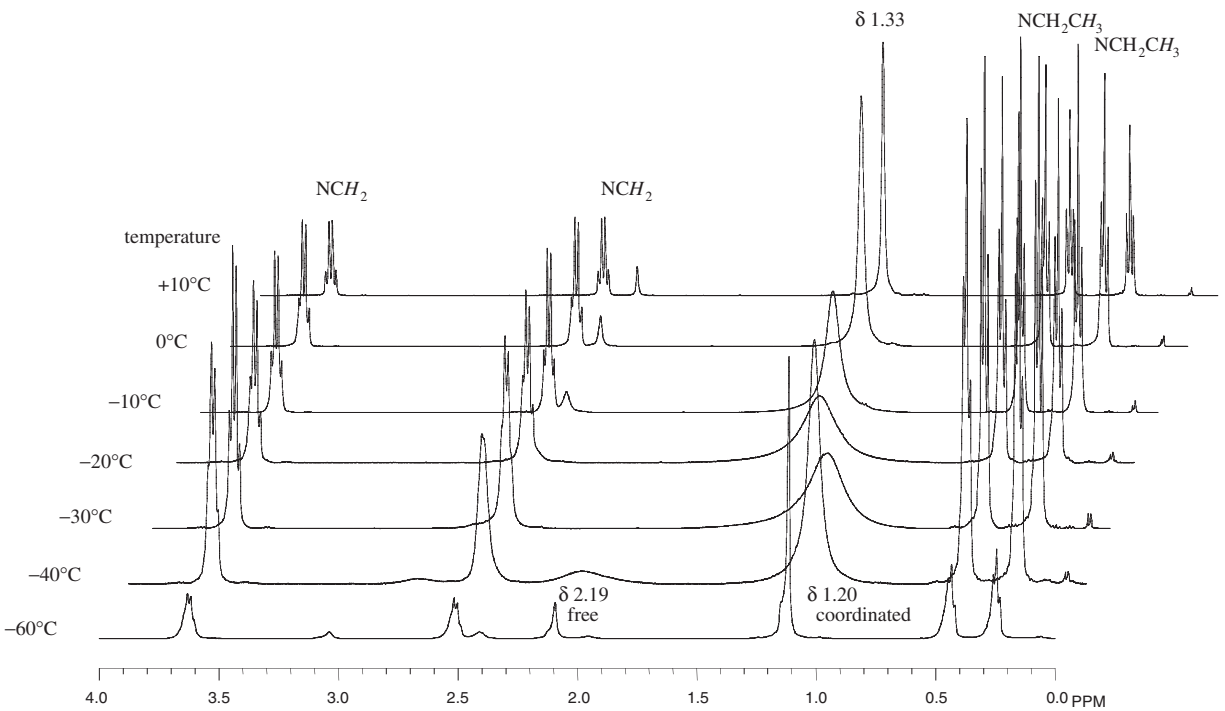


Fig. 3. ^{1}H NMR spectra of cationic acetone-coordinated carbamoylpalladium **4a** at various temperatures.

trum of **4a** in CD_2Cl_2 observed at various temperatures. The CH_2 and CH_3 signals of the *N*,*N*-diethylcarbamoyl ligand are observed as two inequivalent quartets and triplets, respectively, in support of the C–N double bond character of the carbamoyl entity. In addition to these resonances, the ^{1}H NMR spectrum of **4a** in CD_2Cl_2 at -60 °C showed two acetone resonances at δ 2.19 and 1.20 ppm in a ratio of 1:5, the former being ascribable to the free acetone and the latter to the coordinated acetone. These two resonances broadened upon warming the solution to -40 °C, and coalesced into a singlet at temperatures above -20 °C, indicating the presence of an equilibrium between the acetone-coordinated and non-coordi-

nated species. An analysis of the dynamic equilibrium with NMR afforded an activation energy of $\Delta G^{\ddagger} =$ ca. 11.2 kcal·mol^{-1} for the exchange process.

In contrast to the weak bonding of solvent molecules, such as acetone and dichloromethane, with the palladium center, acetonitrile was found to bind the cationic carbamoylpalladium complex more firmly. The CH_3CN-coordinated complex **4a′**, prepared from **1** with an equimolar amount of $AgBF_4$ in CH_2Cl_2–CH_3CN solution, showed no sign of dissociation.

Similarly, PMe_3- and DPPP-coordinated carbamoylpalladium complexes, **4b** and **4c**, could be generated by the treatment of **2** and **3** with $AgBF_4$, respectively, in an NMR tube (Scheme 3).

2. Molecular Structure of the Acetone-Coordinated Cationic Carbamoylpalladium Complex 4a: An ORTEP diagram of the acetone-coordinated carbamoylpalladium complex **4a** is shown in Fig. 4, and the relevant bond distances and bond angles are given in Table 7.

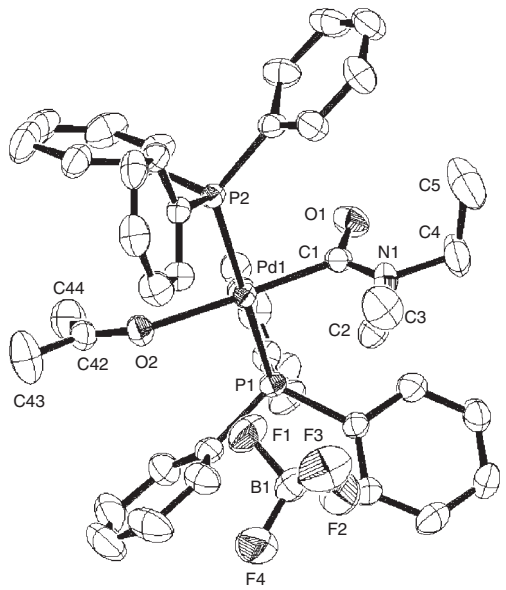


Fig. 4. ORTEP drawing of the acetone-coordinated carbamoylpalladium complex **4a** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for *trans*-[Pd{O=C(CH_3)$_2$}{CON(CH_2CH_3)$_2$}{P(C_6H_5)$_3$}$_2$]-BF_4, **4a**

Bond lengths			
Pd(1)–P(1)	2.3370(10)	Pd(1)–P(2)	2.3440(10)
Pd(1)–C(1)	1.981(2)	Pd(1)–O(2)	2.195(2)
O(1)–C(1)	1.214(3)	N(1)–C(1)	1.350(3)
O(2)–C(42)	1.220(3)	C(42)–C(43)	1.467(4)
C(42)–C(44)	1.491(4)		
Bond angles			
P(1)–Pd(1)–C(1)	88.76(8)	P(1)–Pd(1)–O(2)	95.08(6)
P(2)–Pd(1)–C(1)	90.30(7)	P(2)–Pd(1)–O(2)	86.17(5)
Pd(1)–O(2)–C(42)	144.6(2)	Pd(1)–C(1)–O(1)	119.0(2)
C(1)–N(1)–C(2)	123.6(2)	C(1)–N(1)–C(4)	117.8(2)
C(2)–N(1)–C(4)	117.7(2)		

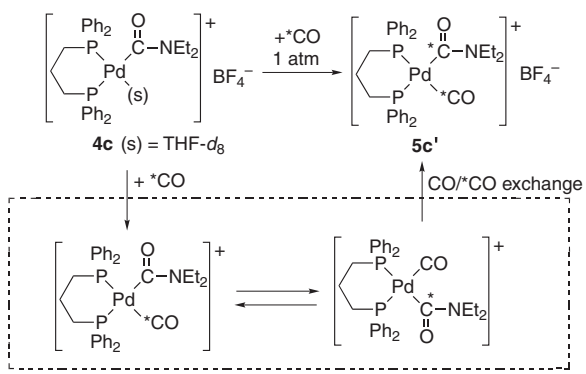
The molecular structure of **4a** shows a square-planar geometry of the complex having a trans configuration. The C–N bond (1.350 Å) in the carbamoyl moiety in **4a** shows a double-bond character, in agreement with the ^{1}H and ^{13}C NMR spectra, indicating the existence of two inequivalent ethyl groups bound to the carbamoyl nitrogen atom (Fig. 3). The coordinated acetone molecule is not enolized and bonded with the palladium center through a lone pair of the acetone carbonyl group, with a Pd–O–C bond angle of 144.6 deg. The BF_4 anion is situated apart from the central palladium cation without any interaction with it, keeping the tetrahedral configuration.

3. Reactivity of Cationic Carbamoylpalladium Complexes: The introduction of CO at −30 °C into an acetone-d_6 or THF-d_8 solution of **4a**–**4c**, prepared by removal of the chloro ligand in neutral complexes **1**–**3** with an equimolar amount of $AgBF_4$, respectively, afforded CO-coordinated carbamoylpalladium complexes **5a**–**5c** in situ (Scheme 3).

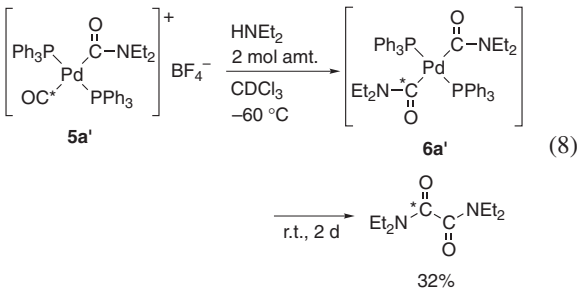
When a carbon monoxide labeled with ^{13}C (>99 atom % ^{13}C) was employed for the reaction with **4a**, the intensity of the triplet signal of the labeled complex **5a′** at δ 177.8 ppm ($^2J_{PC} = 18.2$ Hz) in the ^{13}C{^{1}H} NMR spectrum was markedly enhanced in support of the assignment of the signal to the coordinated CO. Interestingly, the reaction of the DPPP-coordinated cationic carbamoylpalladium complex **4c** with ^{13}C-labeled CO provided the carbamoyl(carbonyl)palladium complex **5c′**, in which the ^{13}C-label was found both in the coordinated CO ligand as well as on the carbamoyl ligand, indicating the occurrence of an exchange process, as depicted in Scheme 4.

The exchange process may have occurred through an equilibrium process, as shown in the lower part of Scheme 4 in the dotted square, proceeding through a facile transfer of the NEt_2 group from the *N*,*N*-diethylcarbamoyl ligand to the adjacent CO ligand.

The addition of 2 molar amounts of diethylamine to **5a′** at −60 °C in $CDCl_3$ caused an immediate decomposition of the solution along with the precipitation of a black solid. A gas chromatographic analysis of the reaction solution revealed the formation of 32% of *N*,*N*,*N′*,*N′*-tetraethyloxamide from **5a′**. A mass spectrometric examination of the oxamide derived from **5a′** containing the ^{13}CO ligand indicated the formation of the oxamide labeled *at one carbonyl entity*, as shown in Eq. 8.



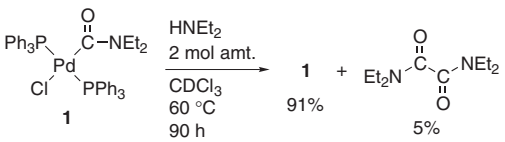
Scheme 4. Treatment of cationic carbamoyl complex **4c** with ^{13}CO.



(8)

The result is consistent with a nucleophilic attack of diethylamine at the coordinated ^{13}CO ligand in the PPh_3-coordinated complex **5a′** to give a singly ^{13}C-labeled bis(carbamoyl)palladium intermediate **6a′**, which liberated the singly ^{13}CO-labeled oxamide upon reductive elimination. The absence of oxamide without the ^{13}C label excludes a possible disproportionation of the cationic mono-carbamoylpalladium species **5a′** into the oxamide.

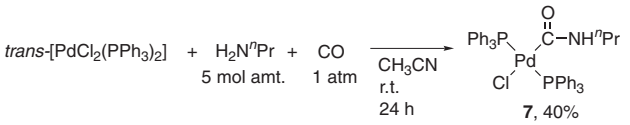
In contrast to the behavior of the cationic CO-coordinated carbamoylpalladium complex **5a**, which reacted immediately at low temperature with diethylamine, the neutral carbamoylchloropalladium complex **1** is thermally stable and much less reactive toward diethylamine. It liberated 5% of the *N*,*N*,*N*′,*N*′-tetraethyloxamide upon heating at 60 °C for 90 h in the presence of diethylamine, leaving 91% of **1** unreacted (Eq. 9). The small amount of oxamide detected may have been produced by disproportionation of the mono-carbamoyl group, followed by reductive elimination from the bis(carbamoyl)palladium intermediate.



(9)

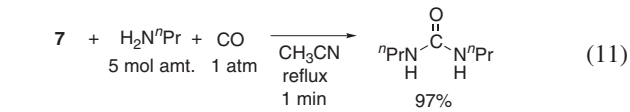
4. Examination of the Reaction Route to Give Ureas from Primary Amines: We now address the remaining problem of urea formation by the palladium-catalyzed carbonylation of *primary amines*. As a possible reaction route to urea, one can conceive the attack of an amine on the carbamoylpalladium complex in the presence of a base (including the added primary amine itself). As described above (Eq. 9), the neutral *N*,*N*-diethylcarbamoylpalladium complex **1** proved to be thermally stable and unreactive toward an attack of diethylamine, whereas the cationic carbamoylpalladium complex **4a** reacted smoothly with diethylamine under CO, producing oxamide. Attempts to isolate an amine-coordinated cationic carbamoylpalladium yielded only an oily product without giving the expected amine-coordinated cationic intermediate. Evidence suggesting the formation of an amido(carbamoyl)palladium complex that might be derived from the amine-coordinated carbamoyl complex by deprotonation of the Pd-coordinated amine by a base was not obtained. In none of these attempts was the formation of urea from the carbamoylpalladium complex derived from diethylamine detected in the systems containing PPh_3.

For obtaining further information on the effect of primary amines in the selective catalytic synthesis of ureas and oxamides, we prepared *N*-monopropylcarbamoylpalladium complex (**7**) from *trans*-$[PdCl_2(PPh_3)_2]$ by its treatment with propylamine under atmospheric CO (Eq. 10).



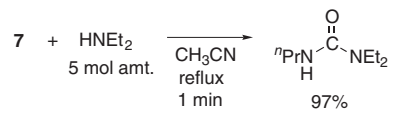
(10)

The *N*-monopropylcarbamoylpalladium complex **7** was characterized by elemental analysis and NMR. A treatment of the *N*-monopropylcarbamoylpalladium complex **7** with 5 molar amounts of propylamine in acetonitrile under refluxing conditions afforded the *N*,*N*′-dipropylurea in 97% yield (Eq. 11).



(11)

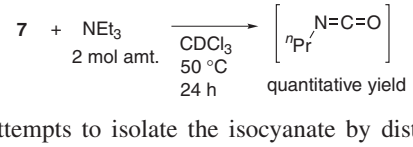
A treatment of **7** with diethylamine in acetonitrile produced unsymmetrically substituted urea, *N*,*N*-diethyl-*N*′-propylurea, in an almost quantitative yield (Eq. 12).



(12)

These results clearly indicate that an *N*-monoalkylcarbamoyl complex **7** behaves differently from the *N*,*N*-dialkylcarbamoylpalladium complexes, and suggest that intermediates having the *N*-monoalkylcarbamoyl group derived from primary amines are required for the production of urea, whereas the second amine to attack the carbamoylpalladium complex can be either a secondary or primary amine.

We next examined the reaction of the *N*-monopropylcarbamoyl complex **7** with triethylamine to see if the tertiary amine as a Lewis base can abstract the proton from **7**. An examination of the reaction product after one day at 50 °C indicated the quantitative formation of propyl isocyanate by means of ^1H NMR (Eq. 13).



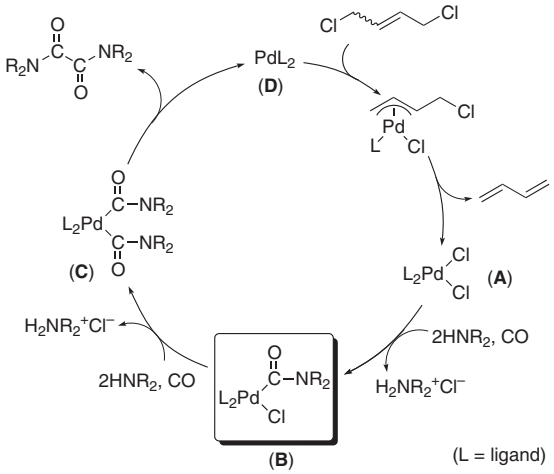
(13)

Attempts to isolate the isocyanate by distillation from the reaction mixture were unsuccessful, probably due to strong binding of the isocyanate with the Pd(0) species.[17] Similar strong binding of isocyanates with the Ni(0) complex was observed by Hoberg.[18]

Discussion

1. The Mechanism of Catalytic Oxamide Formation. Based on the experimental results on the catalytic conversion of secondary amines into oxamides, and of fundamental studies on the properties of model carbamoylpalladium complexes, we propose Scheme 5 as a mechanism to account for the catalytic oxamide formation by carbonylation of secondary amines.

In the presence of DCB, the oxidation of the Pd(0) species



Scheme 5. Proposed mechanism for the catalytic carbonylation of a secondary amine into oxamide with DCB as oxidant.

takes place readily to give a dichloropalladium(II) complex (**A** in Scheme 5) through a β-chloride elimination of the η^3-(chloromethyl)allylpalladium(II) intermediate as shown in Scheme 1. Recently, Szabó discussed the effect of a chlorine substituent at the β-position of η^3-allylpalladium(II) complexes on the stability of the complexes based on a theoretical calculation.[19] The characteristic features derived in the study are a partial coordination of the β-carbon on the η^3-(chloromethyl)allyl ligand to palladium(II) and an elongation of the carbon–chlorine bond, facilitating a possible chloride dissociation to form the dichloropalladium(II) species in the process shown in Scheme 1.

The ready conversion of the PPh_3-coordinated palladium dichloride into the chloro-*N*,*N*-diethylcarbamoylpalladium complex **1** upon a treatment with CO and diethylamine (Eq. 3) is in support of the assumed formation of the carbamoylpalladium intermediate **B** in Scheme 5 from **A**.

An examination of the subsequent course from **B** to give the oxamide has further indicated the probable involvement of a cationic carbamoyl species, as shown in Scheme 2. Since examples of the partial dissociation of a halide or carboxylate anion from neutral organopalladium complexes having a halo or carboxylato ligand to provide a coordination site are known,[16d] the spontaneous dissociation of the chloro ligand in **I** to give **II**, as shown in Scheme 2, may be involved in a process to give an oxamide. We have studied the properties of such cationic carbamoylpalladium complexes prepared by removing the chloro ligand from the neutral complex **1** by a treatment with $AgBF_4$, as shown in Scheme 3. The isolation and unequivocal characterization of an acetone-coordinated carbamoylpalladium complex **4a** by single-crystal X-ray analysis further support the intermediacy of the cationic carbamoyl intermediate having a vacant coordination site.

The reaction of CO with **4a** was found to give a CO-coordinated complex **5a** (Scheme 3), as established by a study using ^{13}C-labeled CO. Although the assumed bis(carbamoyl)palladium complex **C** in Scheme 5 could not be isolated, possibly because of the intrinsic lability of the intermediate, liberation of oxamide by a treatment of the CO-coordinated carbamoyl complex **5a** with secondary amine supports the route through a reductive elimination from the intermediate **C** in Scheme 5.

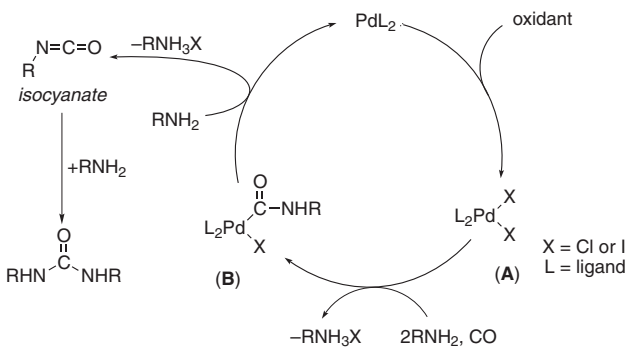
In a recent study, Aresta and co-workers, who have been working on the catalytic conversion of amines into isocyanates or carbamoyl chlorides by carbonylation of amines, isolated and characterized bis(carbamoyl)palladium complexes coordinated with a bipyridine ligand.[14f] Their results provide indirect support for the intermediacy of the bis(carbamoyl)palladium complexes **C** in the catalytic conversion of amines into oxamide, as shown in Scheme 5.

As another possible route to give the bis(carbamoyl)palladium species **C** from the monocarbamoylpalladium species **B** in Scheme 5, partial dissociation of the tertiary phosphine ligand L from **B** to provide a vacant site for the CO coordination, followed by a subsequent nucleophilic attack by amine for yielding the bis-carbamoyl species is conceivable. However, the results given in Table 2, that the oxamide was produced with the catalyst systems having bidentate phosphines (runs 4–7), and the result that the DPPP-coordinated complex **3** also gave oxamide (Eqs. 6 and 7), suggest that the dissociation of L is not the principal course to produce oxamide.

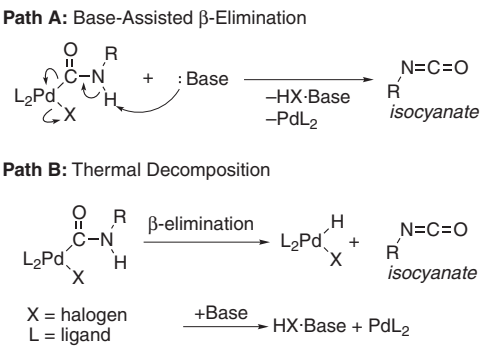
2. Mechanism of Catalytic Production of Ureas from Primary Amines. In contrast to the clean carbonylation of secondary amines to oxamides, the use of primary amines in a similar system produces ureas as well as oxamides, depending on experimental conditions. To account for the production of ureas from primary amines in the palladium-catalyzed carbonylation assisted by a base, two possible mechanisms are conceivable.

One is the route to proceed through the formation of an intermediate with the carbamoyl and amido ligands, to be followed by reductive elimination to liberate urea, as proposed by Alper.[7] The other route consists of an intermediate formation of alkyl isocyanate from the *N*-monoalkylcarbamoylpalladium species, followed by a subsequent capture of the alkyl isocyanate by a primary or secondary amine to release symmetrically or unsymmetrically substituted urea, as represented by Scheme 6. A similar mechanism was proposed by Gabriele on the basis of their studies of catalytic reactions.[9]

The production of *N*,*N*′-dipropylurea, observed in the reaction of the *N*-monopropylcarbamoylpalladium complex **7** with propylamine (Eq. 11), and the generation of *N*,*N*-diethyl-*N*′-propylurea by a treatment of **7** with diethylamine (Eq. 12) are compatible with the carbamoyl-amido reductive elimina-



Scheme 6. Proposed mechanism for production of urea through an *N*-monoalkylcarbamoyl intermediate.



Scheme 7. Two possible courses of hydrogen abstraction from *N*-monoalkylcarbamoylpalladium species.

tion mechanism. However, this mechanism can not offer a rational explanation for the absence of any *N*,*N*,*N*′*N*′-tetraethylurea in the reaction of the *N*,*N*-diethylcarbamoylpalladium complexes **1** and **3** with diethylamine, as demonstrated in Table 6.

An alternative route involving isocyanate formation by deprotonation of the *N*-monoalkylcarbamoylpalladium complex derived from primary amine,[20] on the other hand, accounts for the differences in the reactivity between the primary and secondary amines toward oxidative carbonylation.

For obtaining information regarding the possible course of the deprotonation of the *N*-monoalkylcarbamoylpalladium complex by amine, we carried out kinetic studies on the reaction of the *N*-monoalkylcarbamoyl complex **7** with triethylamine. The use of the tertiary amine was expected to allow us to examine the effect of deprotonation without any complication of the succeeding reaction of the isocyanate produced with a primary or secondary amine.

There are two conceivable routes for production of isocyanate from the *N*-monoalkylcarbamoyl complex, as shown in Scheme 7.

Path A involves direct proton abstraction from the *N*-monoalkylcarbamoyl complex by a base. On the other hand, path B proceeds in two steps, the first step involving the liberation of a chloride ion from the neutral complex, followed by spontaneous β-H abstraction from the carbamoyl ligand by the Pd(II) cation to give a chloro(hydrido)palladium complex that is trapped by a base.

We have followed the rates of decrease of the starting carbamoylpalladium complex **7** with ^{1}H NMR spectroscopy at 50 °C in $CDCl_3$ in the presence of NEt_3. The measurements were performed using [NEt_3] in a sufficient excess over complex **7**, the initial concentration ranges being 2.53×10^{-2} mol/L for **7**, and 3.19×10^{-1} to 8.18×10^{-1} mol/L for NEt_3. In each run the pseudo-first-order rate constant k_{obsd} (Table 8) was obtained over 80% conversion by plotting $\ln([\mathbf{7}]/[\mathbf{7}]_0)$ vs time. Figure 5 indicates the linear dependence of k_{obsd} on [NEt_3].

These results give the following kinetic equation:

$$-\mathrm{d}[\mathbf{7}]/\mathrm{d}t = 1.36 \times 10^{-3}[\mathbf{7}][\mathrm{NEt_3}]. \quad (14)$$

The observation of the first-order dependence of the rate of disappearance of [**7**] on [NEt_3] is consistent with Path A in Scheme 7, suggesting that the isocyanate production proceeds with the proton abstraction by a base from the carbamoyl group attached to the nitrogen in the monoalkylcarbamoyl entity.

Table 8. Kinetic Results of the Reaction of **7** with NEt_3[a)]

Run	[NEt_3]/mol L^{-1}	k_{obsd}[b)]/10^4 s^{-1}
1	0.319	2.73
2	0.408	4.40
3	0.569	5.23
4	0.818	8.18

a) Reaction conditions: $[\mathbf{7}]_0 = 0.1$ mmol, at 50 °C in $CDCl_3$. b) Rate constants for the consumption of **7**, estimated by least-squares treatment of first-order plots at the conversion over 80%.

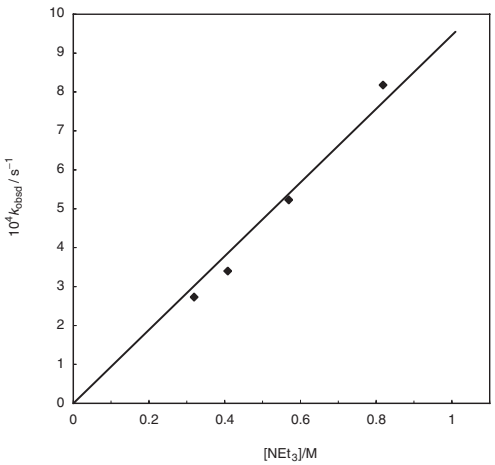


Fig. 5. Plot of the pseudo-first-order rate constants of the decrease rate of complex **7** versus concentrations of NEt_3 added.

As shown in Table 4, the relative yield of the *N*,*N*′-dipropylurea and *N*,*N*′-dipropyloxamide in the carbonylation of propylamine varies, depending on experimental conditions, the effect of the oxidizing agent being most important. The reason for the differences in the effect of the oxidizing agents, such as DCB and I_2, has not yet been fully clarified. Since it has been reported that I_2 can react directly with carbamoylchloropalladium(II) complexes bearing bidentate nitrogen ligands to give a mixture of the corresponding isocyanates, chloro(iodo)palladium(II) complexes and HI,[14f] a direct route from the intermediate **B** to **A** in Scheme 6 without the formation of Pd(0) and bis-carbamoyl complexes is conceivable in the presence of I_2 as an oxidant. Another possible explanation is that the halide ion derived from the oxidants may have some effect in controlling the reaction course from *N*-monoalkylcarbamoyl intermediates to ureas or oxamides, but we have not addressed this issue further.

Conclusion

Fundamental studies on the properties of the carbamoylpalladium complexes led to proposals concerning the mechanisms to account for the palladium-catalyzed oxidative carbonylation of primary and secondary amines into ureas and oxamides. The urea formation can be accounted for by a two-step mechanism involving the initial formation of an *N*-monoalkylcarbamoyl-

palladium intermediate, and a subsequent deprotonation by a base to produce isocyanate that is trapped by amine forming the urea. On the other hand, the *N*,*N*-dialkylcarbamoylpalladium species further undergoes a reaction with CO and amine to produce a bis(carbamoyl)palladium species that reductively eliminates the oxamide.

The availability of the two types of oxidants, iodine and DCB, provides us with a wider choice in performing the carbonylation of amines to selectively produce ureas or oxamides. Although the use of DCB has an intrinsic problem from the viewpoint of atom economy, the high selectivity for the oxamide production with DCB from NH_3, primary and secondary amines, offers an attractive choice for preparing various oxamides. The ease of its handling in laboratory procedures with the liberation of only butadiene as a volatile by-product, provides us with a wider selection in performing carbonylation with a clean oxidant.

Experimental

General Procedures. All manipulations were carried out under an argon atmosphere using Schlenk tube techniques. Solvents were purified by the usual methods under argon. NMR spectra were recorded on a JEOL EX-270, JMN-AL300, or JEOL Lambda 500 spectrometer for ^{1}H (referenced to $SiMe_4$ via residual solvent protons), $^{13}C\{^1H\}$ (referenced to $SiMe_4$ via the solvent resonance), and $^{31}P\{^1H\}$ (referenced to 85% H_3PO_4 as an external standard) NMR. In the measurement of the ^{19}F NMR, CF_3COOH (in $CDCl_3$ solution) was used as an external standard. The coupling constants (*J* values) are given in hertz (Hz), and the spin multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), vt (virtual triplet), and br (broad). Infrared spectra were measured on a Perkin Elmer Paragon 1000. Gas chromatographic analyses (GC) were carried out on a Hitachi 263-30 equipped with a TC1 column (0.25 mm I.D. × 30 m), using N_2 as a carrier gas. Mass spectra were obtained with a JEOL JMS-Automass 150 that was coupled with a gas chromatograph. Elemental analyses were performed with a Yanako MT-3 by the Materials Characterization Central Laboratory of Waseda University.

Reagents. Solvents and amines were used after drying and distillation, and stored under argon. Other reagents were commercial products, and were used without further purification. $[Pd(PPh_3)_4]$,[21] $[Pd(dba)_2]$,[22] *trans*-$[PdCl_2(PPh_3)_2]$,[23] and *trans*-$[PdEt_2(PMe_3)_2]$[22] were prepared according to the reported preparative methods. $Pd(OAc)_2$ (Aldrich), 10% Pd/C (Kojima Chemicals Co.), and $PdCl_2$ (Tanaka Kikinzoku) were used as received from commercial suppliers. All tertiary phosphines were commercial products, and were used without further purification.

Reaction of $[Pd\{P(C_6H_5)_3\}_4]$ with 1,4-Dichloro-2-butene. To a THF (5 mL) suspension in a 50 mL Schlenk tube containing $[Pd(PPh_3)_4]$ (146 mg, 0.126 mmol) was added diethylamine (0.0528 mL, 0.505 mmol) and 1,4-dichloro-2-butene (0.0136 mL, 0.126 mmol). The reaction mixture was stirred for 24 h at room temperature. The formation of 1,3-butadiene was confirmed by means of GC. After evaporation of the volatile matter, the formed yellow powder was washed with acetone (5 mL × 2). After removal of the solvent, a yellow powder of *trans*-$[PdCl_2(PPh_3)_2]$ (0.088 g, 0.125 mmol, >99% yield), as confirmed by ^{1}H and $^{31}P\{^1H\}$ NMR, was obtained.

A similar experiment treating $[Pd(PPh_3)_4]$ with 1 mol amount of 1,2-dichloro-3-butene gave *trans*-$[PdCl_2(PPh_3)_2]$ in a yield of over 99%.

Typical Experimental Procedures for Catalytic Carbonylation of Amines. For the catalytic carbonylation of amines, a 100 mL stainless-steel autoclave was used, which could be pressurized and heated. The catalytic carbonylation of diethylamine is described below as a typical example. To the stainless-steel autoclave was placed *trans*-$[PdCl_2(PPh_3)_2]$ (17.5 mg, 0.0250 mmol), which was dissolved in THF (3 mL). Diethylamine (2.07 mL, 20.0 mmol) and 1,4-dichloro-2-butene (0.540 mL, 5.00 mmol) were added in that order. After carbon monoxide (1 to 100 atm) was introduced at room temperature, the autoclave was stirred at room temperature for 3 to 17 h. After the release of CO, the reaction mixture was recovered and analyzed by GC with *n*-$C_{12}H_{26}$ as an internal standard. The oxamide of diethylamine (*N*,*N*,*N*′,*N*′-tetraethyloxamide) was identified by a comparison with a standard sample prepared from oxalyl chloride and diethylamine. The effects of the catalyst and amines, CO pressure, and of the absence or addition of O_2 were examined in a similar manner along with a variation of the substrates, and the reaction conditions.

Synthesis of Carbamoylpalladium Complexes. 1. Synthesis of *trans*-$[PdCl\{CON(CH_2CH_3)_2\}\{P(C_6H_5)_3\}_2]$ (1): To a yellow THF suspension (1 mL) of *trans*-$[PdCl_2(PPh_3)_2]$ (70.2 mg, 0.010 mmol) in a 25 mL Schlenk tube was added $HNEt_2$ (0.103 mL, 1.00 mmol); the reaction mixture was stirred under a balloon pressure of CO at room temperature for 3 h. A yellow precipitate was separated by filtration and washed with water (5 mL × 3) and diethyl ether (2 mL × 3), and dried in vacuo to give a light-yellow powder in 53% yield (43 mg).

The same complex was prepared by the reaction of $[Pd(PPh_3)_4]$ with $ClCONEt_2$. In a 100 mL Schlenk tube was prepared a brown toluene solution (50 mL) of $[Pd(PPh_3)_4]$ (1.26 g. 1.09 mmol). After the addition of $ClCONEt_2$ (0.138 mL, 1.09 mmol) to the solution and stirring it for 20 h at 80 °C, toluene was removed by evaporation in vacuo at room temperature, and the residue was extracted with CH_2Cl_2 (20 mL × 2 and 10 mL × 1). The CH_2Cl_2 extract was evaporated in vacuo and the residue was washed with ether (20 mL × 3) to give a light yellow powder of **1** (0.769 g, 1.00 mmol) in 86% yield. ^{1}H NMR (270.0 MHz, $CDCl_3$, 25 °C) δ 7.41–7.80 (30H, C_6H_5), 3.78 (2H, CH_2CH_3, q, $^3J_{HH} = 7.2$ Hz), 2.36 (2H, CH_2CH_3, q, $^3J_{HH} = 7.2$ Hz), 0.68 (3H, CH_2CH_3, t, $^3J_{HH} = 7.2$ Hz), 0.22 (3H, CH_2CH_3, t, $^3J_{HH} = 7.2$ Hz); $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 181.1 ($CONEt_2$, s), 135–127 (C_6H_5), 43.3 (CH_2CH_3, s), 41.1 (CH_2CH_3, s), 14.2 (CH_2CH_3, s), 13.3 (CH_2CH_3, s); $^{31}P\{^1H\}$ NMR (109.4 MHz, $CDCl_3$, 25 °C) δ 20.2. Found: C, 63.63; H, 5.07; N, 1.75%. Calcd for $C_{41}H_{40}ClNOP_2Pd$: C, 64.24; H, 5.26; N; 1.83%.

2. Synthesis of *trans*-$[PdCl\{CON(CH_2CH_3)_2\}\{P(CH_3)_3\}_2]$ (2): To a 50 mL Schlenk tube cooled at −30 °C were added ether (9 mL) and *trans*-$[PdEt_2(PMe_3)_2]$ (492 mg, 1.55 mmol) and the mixture was stirred at −30 °C for 5 min. Styrene (0.266 mL, 2.32 mmol) was added to the mixture, and the system was stirred at room temperature for 20 h to give a yellow solution. Carbamoyl chloride, $ClCONEt_2$ (196 mL, 1.55 mmol) was added to the solution, and the mixture was stirred at room temperature for 3 d. The addition of pentane to the reaction product caused the formation of a yellow precipitate. The precipitate was collected by filtration and dissolved in CH_2Cl_2 (5 mL). Upon reprecipitation of the solid using ether, a white precipitate was obtained, which was filtered and washed with pentane (10 mL and 5 mL) and dried in vacuo to give a white powder (344 mg, 0.873 mmol), yield 56%. ^{1}H NMR (500.2 MHz, $CDCl_3$, 25 °C) δ 3.96 (2H, CH_2CH_3, q, $^3J_{HH} = 7.1$ Hz), 3.33 (2H, CH_2CH_3, q, $^3J_{HH} = 7.1$ Hz), 1.41

(18H, P(CH_3)$_3$, vt, $^2J_{PH}$ = 3.7 Hz), 1.23 (3H, CH$_2$CH_3, t, $^2J_{HH}$ = 7.1 Hz), 1.06 (3H, CH$_2$CH_3, t, $^2J_{HH}$ = 7.1 Hz); ^{13}C{^{1}H} NMR (67.9 MHz, CD_2Cl_2, 25 °C) δ 184.1 (*C*ONEt$_2$, t, $^2J_{PC}$ = 4.9 Hz), 43.1 (*C*H$_2$CH$_3$, s), 39.5 (*C*H$_2$CH$_3$, s), 14.1 (P(*C*H$_3$)$_3$, vt, J_{PC} = 14.2 Hz), 13.9 (CH$_2$*C*H$_3$, s); ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 25 °C) δ −17.6 (s). IR (KBr disc) 1574 cm^{-1} ($\nu_{C=O}$). Found: C, 33.53; H, 7.14; N, 3.40%. Calcd for $C_{11}H_{28}ClNOP_2Pd$: C, 33.52; H, 7.16; N, 3.55%.

3. Synthesis of [PdCl{CON(CH$_2$CH$_3$)$_2$}{(C$_6$H$_5$)$_2$P(CH$_2$)$_3$P-(C$_6$H$_5$)$_2$}] (3): To a toluene (18 mL) solution of **2** (46.0 mg, 0.60 mmol) in a 50 mL Schlenk tube was added DPPP (248 mg, 0.60 mmol) in toluene (5 mL), and the reaction mixture was stirred for 24 h at room temperature. Toluene was removed under reduced pressure at room temperature, and the residue was purified by recrystallization from CH_2Cl_2 (2 mL) and ether (10 mL) at −70 °C. After removing the solvent by filtration, the obtained pale-yellow blocks of crystals were washed with ether (5 mL × 3) and dried in vacuo at room temperature, yield, 65% (254 mg, 0.388 mmol). ^{1}H NMR (500.2 MHz, $CDCl_3$, 25 °C) δ 7.8–7.2 (20H, C$_6H_5$, m), 3.97 (1H, CH_2CH$_3$, dq, $^3J_{HH}$ = 7.1 Hz, $^2J_{HH}$ = 14.1 Hz), 2.77 (1H, CH_2CH$_3$, dq, $^3J_{HH}$ = 7.2 Hz, $^2J_{HH}$ = 14.4 Hz), 2.73 (1H, CH_2CH$_3$, dq, $^3J_{HH}$ = 7.2 Hz, $^2J_{HH}$ = 14.4 Hz), 2.63 (1H, CH_2CH$_3$, dq, $^3J_{HH}$ = 7.0 Hz, $^2J_{HH}$ = 14.0 Hz), 2.55–0.87 (2H, CH$_2$CH_3 of dppp, dd,), 2.18–1.79 (2H, CH_2 of dppp, m), 1.44–1.32 (2H, CH_2 of dppp, m), 0.87 (3H, CH$_2$CH_3, dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 7.1 Hz), 0.48 (3H, CH$_2$CH_3, dd, $^3J_{HH}$ = 7.1 Hz, $^2J_{HH}$ = 7.1 Hz); ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, 25 °C) δ 186.0 (*C*ONEt$_2$, dd, $^2J_{PC}$ = 24.3, 160.7 Hz), 136–128 (*C*$_6$H$_5$, m), 43.4 (*C*H$_2$CH$_3$, d, $^3J_{PC}$ = 2.5 Hz), 40.1 (*C*H$_2$CH$_3$, d, $^3J_{PC}$ = 3.7 Hz), 28.2 (*C*H$_2$PPh$_2$, dd, $^1J_{PC}$ = 28.6 Hz, $^3J_{PC}$ = 6.2 Hz), 27.0 (*C*H$_2$PPh$_2$, d, $^1J_{PC}$ = 18.1 Hz), 19.1 (Ph$_2$PCH$_2$*C*H$_2$CH$_2$PPh$_2$, d, $^3J_{PC}$ = 5.0 Hz), 13.5 (CH$_2$*C*H$_3$, s), 13.2 (CH$_2$*C*H$_3$, s); ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2, 25 °C) δ 9.0 (d, $^2J_{PP}$ = 69.2 Hz), −8.8 (d, $^2J_{PP}$ = 69.2 Hz); IR (KBr disc) 1584 cm^{-1} ($\nu_{C=O}$). Found: C, 58.21; H, 5.48; N, 2.21%. Calcd for $C_{32}H_{36}ClNOP_2Pd$: C, 58.73; H, 5.54; N, 2.14%.

4. Synthesis of *trans*-[PdCl{CONH(CH$_2$CH$_2$CH$_3$)}{P-(C$_6$H$_5$)$_3$}$_2$][14f] (7): To an acetonitrile suspension (20 mL) of *trans*-[$PdCl_2(PPh_3)_2$] (510 mg, 0.726 mmol) in a 100 mL Schlenk tube was added $PrNH_2$ (0.298 mL, 3.63 mmol), and the reaction mixture was stirred under a balloon pressure of CO at room temperature. After the reaction for 24 h, a pale-yellow suspension was obtained. The solvent was removed by filtration, and the residue was purified by recrystallization from CH_2Cl_2 (10 mL) and ether (40 mL) at −30 °C. After removing the solvent by filtration, the obtained crystals were washed with pentane (2 mL × 3) and dried in vacuo. The pale-yellow blocks (220 mg, yield 40%) obtained were identified as **7** by comparing the spectroscopic data.

^{1}H NMR (500.2 MHz, $CDCl_3$, 25 °C) δ 7.3–7.8 (30H, C$_6H_5$), 4.58 (1H, N*H*, t, $^3J_{HH}$ = 4.9 Hz), 1.94 (2H, NHCH_2, dt, $^3J_{HH}$ = 4.9 Hz, $^3J_{HH}$ = 7.4 Hz), 0.57 (2H, CH$_2$CH_2CH$_3$, tq, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.4 Hz), 0.38 (3H, CH_3, t, $^3J_{HH}$ = 7.4 Hz); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 25 °C) δ 180.8 (*C*ON, t, $^2J_{PC}$ = 5.7 Hz), 135–128 (*C*$_6$H$_5$), 43.5 (NH*C*H$_2$, s), 21.8 (CH$_2$*C*H$_2$CH$_3$, s), 11.0 (*C*H$_3$, s); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 25 °C) δ 20.1 (s).

Preparation of Cationic Carbamoylpalladium Complexes. The cationic carbamoylpalladium complexes **4** were prepared by treating the corresponding carbamoylchloropalladium complexes **1**–**3** with an acetone solution of $AgBF_4$ at low temperature. Representative examples of preparation of the cationic complexes are described below. Most of the cationic complexes were prepared in situ, and their structures were confirmed in solutions by NMR, except for the acetone-coordinated carbamoylpalladium complex **4a**.

Preparation of *trans*-[Pd(s){CON(CH$_2$CH$_3$)$_2$}{P(CH$_3$)$_3$}$_2$]-BF$_4$ (s = Acetone-*d*$_6$) (4b). In an NMR tube filled with argon was placed *trans*-[PdCl(CONEt$_2$)(PMe$_3$)$_2$] (30.2 mg, 76.6 μmol) and acetone-d_6 (ca. 0.3 mL) was added at room temperature to dissolve the complex, giving a light-brown solution. Upon cooling the solution at −30 °C, an acetone-d_6 solution of $AgBF_4$ (0.218 mL, 0.352 M, 76.6 μmol) was added to cause an immediate precipitation of a white precipitate of AgCl. The NMR tube was shaken and allowed to cause the precipitation of a white solid. An NMR investigation of the supernatant showed the formation of a cationic carbamoylpalladium complex **4b**. ^{1}H NMR (270.5 MHz, acetone-d_6, −30 °C) δ 3.96 (2H, CH_2CH$_3$, q, $^3J_{HH}$ = 7.1 Hz), 3.32 (2H, CH_2CH$_3$, q, $^3J_{HH}$ = 7.1 Hz), 1.39 (18H, P(CH_3)$_3$, vt, J_{PH} = 3.8 Hz), 1.22 (3H, CH$_2$CH_3, t, $^3J_{HH}$ = 7.1 Hz), 1.02 (3H, CH$_2$CH_3, t, $^3J_{HH}$ = 7.1 Hz); ^{13}C{^{1}H} NMR (67.9 MHz, acetone-d_6, −30 °C) δ 175.6 (*C*ONEt$_2$, t, $^2J_{PC}$ = 8.7 Hz), 43.2 (*C*H$_2$CH$_3$, s), 40.5 (*C*H$_2$CH$_3$, s), 14.5 (CH$_2$*C*H$_3$, s), 13.6 (CH$_2$*C*H$_3$, s), 13.3 (P(*C*H$_3$)$_3$, vt, J_{PC} = 14.1 Hz); ^{31}P{^{1}H} NMR (109.4 MHz, acetone-d_6, −30 °C) δ −17.6 (vt, J_{PC} = 14.1 Hz); ^{19}F NMR (254.0 MHz, acetone-d_6, −30 °C) δ −144.8 (s).

NMR Data for [Pd(s){CON(CH$_2$CH$_3$)$_2$}{(C$_6$H$_5$)$_2$P(CH$_2$)$_3$P-(C$_6$H$_5$)$_2$}]BF$_4$ (s = THF-*d*$_8$) (4c): ^{31}P{^{1}H} NMR (109.4 MHz, THF-d_8, −20 °C) δ 16.1 (d, $^2J_{PP}$ = 59.4 Hz), −3.9 (d, $^2J_{PP}$ = 59.4 Hz).

Synthesis of [Pd(acetone){CON(CH$_2$CH$_3$)$_2$}{P(C$_6$H$_5$)$_3$}$_2$]-BF$_4$ (4a). In a 25 mL Schlenk tube was placed *trans*-[PdCl(CONEt$_2$)(PPh$_3$)$_2$] (204 mg, 0.266 mmol) dissolved in a mixture of CH_2Cl_2 (5 mL) and acetone (1 mL). After cooling the solution to 0 °C, an acetone solution of $AgBF_4$ (0.266 mL, 1.00 M, 0.266 mmol) was added to cause the immediate precipitation of AgCl. After removing the precipitate by filtration, pentane (15 mL) was slowly added, and the system was allowed to stand for 3 d to cause the deposition of colorless blocks of crystals. After removing the solvent by filtration, the crystals were washed with 5 mL of pentane three times and dried at −30 °C to give the acetone-coordinated **4a** in 97% yield. Since the crystals are prone to lose the solvent molecules, they were kept at a low temperature in the mother liquor before subjecting to X ray analysis.

^{1}H NMR (500.2 MHz, $CDCl_3$, 0 °C) δ 7.6–7.2 (30H, C$_6H_5$), 3.71 (2H, CH_2CH$_3$, q, $^3J_{HH}$ = 7.0 Hz), 2.45 (2H, CH_2CH$_3$, q, $^3J_{HH}$ = 7.0 Hz), 1.33 (6H, CO(CH_3)$_2$, br) 0.58 (2H, CH$_2$CH_3, t, $^3J_{HH}$ = 7.0 Hz), 0.22 (2H, CH$_2$CH_3, t, $^3J_{HH}$ = 7.0 Hz); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 0 °C) δ 220.7 (*C*O(CH$_3$)$_2$, s), 168.4 (*C*ON, t, $^2J_{PC}$ = 6.5 Hz), 135–128 (*C*$_6$H$_5$), 43.3 (*C*H$_2$CH$_3$, s), 42.5 (*C*H$_2$CH$_3$, s), 30.8 (CO(*C*H$_3$)$_2$, s), 12.31 (CH$_2$*C*H$_3$, s), 12.27 (CH$_2$*C*H$_3$, s); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 0 °C) δ 18.0 (s); ^{19}F NMR (470.5 MHz, $CDCl_3$, 0 °C) δ −151.1 (s); IR (KBr disc) $\nu_{C=O}$ = 1681 (acetone), $\nu_{C=O}$ = 1613 cm^{-1} (*C*ONEt$_2$). Found: C, 60.23; H, 5.06; N, 1.65%. Calcd for $C_{44}H_{46}BF_4NO_2P_2Pd$: C, 60.33; H, 5.29; N, 1.60%.

Synthesis of [Pd(CH$_3$CN){CON(CH$_2$CH$_3$)$_2$}{P(C$_6$H$_5$)$_3$}$_2$]-BF$_4$ (4a′). In a 25 mL Schlenk tube was placed complex **1** (200 mg, 0.261 mmol) dissolved in a mixture of CH_2Cl_2 (4 mL) and acetonitrile (1 mL). After cooling the solution to −30 °C, an acetone solution of $AgBF_4$ (0.261 mL, 1.00 M, 0.261 mmol) was added to cause the immediate precipitation of AgCl. After removing the precipitate by filtration, pentane (10 mL) was slowly added, and the system was allowed to stand for 2 d at −30 °C to give colorless blocks of crystals. After removing the solvent by filtration, the crystals were washed with 3 mL of pentane four

times and dried at −30 °C to give acetonitrile-coordinated **4a′** in 75% yield. ^{1}H NMR (500.2 MHz, $CDCl_3$, 0 °C) δ 7.6–7.2 (30H, C_6H_5), 3.51 (2H, CH_2CH_3, q, $^3J_{HH} = 7.2$ Hz), 2.42 (2H, CH_2CH_3, q, $^3J_{HH} = 7.2$ Hz), 1.34 (3H, CH_3CN, s) 0.54 (3H, CH_2CH_3, t, $^3J_{HH} = 7.2$ Hz), 0.24 (3H, CH_2CH_3, t, $^3J_{HH} = 7.2$ Hz); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 0 °C) δ 173.6 (*C*ON, t, $^2J_{PC} = 9.1$ Hz), 135–128 (C_6H_5), 124.5 (CH_3CN), 43.2 (CH_2CH_3), 41.9 (CH_2CH_3), 13.3 (CH_2CH_3), 12.9 (CH_2CH_3), 1.6 (CH_3CN); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 0 °C) δ 20.8 (s); ^{19}F NMR (470.5 MHz, $CDCl_3$, 0 °C) δ −150.8 (s). Found: C, 59.94; H, 5.31; N, 3.37%. Calcd for $C_{43}H_{43}BF_4NO_2P_2Pd$: C, 60.12; H, 5.05; N, 3.26%.

Preparation of [Pd(13CO){CON(CH2CH3)2}{P(C6H5)3}2]-BF4 (5a′). Carbon monoxide labeled with ^{13}C was added to a $CDCl_3$ solution of *trans*-[Pd(s)(CONEt$_2$)(PPh$_3$)$_2$]BF_4 (26.4 μmol) prepared in a high-pressure NMR tube so as to make the pressure 10 atm at −30 °C. The NMR tube was shaken several times. An observation of the NMR spectra of the colorless solution indicated coordination of the ^{13}CO to palladium. ^{1}H NMR (500.2 MHz, $CDCl_3$, −20 °C) δ 7.7–7.2 (C_6H_5), 3.39 (2H, CH_2CH_3, q, $^3J_{HH} = 7.0$ Hz), 2.34 (2H, CH_2CH_3, q, $^3J_{HH} = 7.0$ Hz), 0.50 (3H, CH_2CH_3, t, $^3J_{HH} = 7.0$ Hz), 0.13 (3H, CH_2CH_3, t, $^3J_{HH} = 7.0$ Hz); ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$, −20 °C) δ 177.8 (^{13}*C*O, t, $^2J_{PC} = 18.2$ Hz), 134–124 (C_6H_5), 43.3 (CH_2CH_3, s), 42.4 (CH_2CH_3, s), 12.9 (CH_2CH_3, s), 12.5 (CH_2CH_3, s); ^{31}P{^{1}H} NMR (109.4 MHz, $CDCl_3$, −20 °C) δ 17.6 (s); ^{19}F NMR (254.0 MHz, $CDCl_3$, −30 °C) δ −151.3 (s). The ^{13}CO of the free carbon monoxide was observed at δ 184.1 (br) in the ^{13}C{^{1}H} NMR.

NMR Data for *trans*-[Pd(CO){CON(CH2CH3)2}{P-(CH3)3}2]BF4 (5b): ^{1}H NMR (270.0 MHz, acetone-d_6, −30 °C) δ 3.72 (2H, CH_2CH_3, q, $^3J_{HH} = 6.8$ Hz), 3.33 (2H, CH_2CH_3, q, $^3J_{HH} = 7.2$ Hz), 1.62 (18H, P(CH_3)$_3$, vt, $J_{PH} = 3.7$ Hz), 1.19 (3H, CH_2CH_3, t, $^3J_{HH} = 7.1$ Hz), 1.05 (3H, CH_2CH_3, t, $^3J_{HH} = 7.0$ Hz); ^{13}C{^{1}H} NMR (67.9 MHz, acetone-d_6, −30 °C) δ 183.1 (*C*ONEt$_2$, t, $^2J_{PC} = 7.4$ Hz), 181.5 (Pd*C*O, t, $^2J_{PC} = 18.2$ Hz), 42.9 (CH_2CH_3, s), 40.2 (CH_2CH_3, s), 14.7 (P(CH_3)$_3$, vt, $J_{PC} = 16.1$ Hz), 14.2 (CH_2CH_3, s), 13.6 (CH_2CH_3, s); ^{31}P{^{1}H} NMR (109.4 MHz, acetone-d_6, −30 °C) δ −15.3 (s); ^{19}F NMR (254.0 MHz, acetone-d_6, −30 °C) δ −149.3 (s).

NMR Data for *trans*-[Pd(CO){CON(CH2CH3)2}{(C6H5)2P-(CH2)3P(C6H5)2}]BF4 (5c): ^{13}C{^{1}H} NMR (67.9 MHz, THF-d_8, −30 °C) δ 179.4 (*C*ONEt$_2$, dd, $^2J_{PC} = 18.6$, 93.1 Hz), 163.1 (Pd*C*O, d, $^2J_{PC} = 30$ Hz), 135–125 (m, C_6H_5), 23.4 (CH_2PPh_2), 22.6 (CH_2PPh_2), 19.0 ($Ph_2PCH_2CH_2CH_2PPh_2$), 14.2 (CH_2CH_3, s), 13.3 (CH_2CH_3, s); ^{31}P{^{1}H} NMR (109.4 MHz, THF-d_8, −20 °C) δ −2.1 (d, $^2J_{PP} = 77.8$ Hz), −5.9 (d, $^2J_{PP} = 77.8$ Hz).

Reaction of Diethylamine with *trans*-[Pd(13CO){CON-(CH2CH3)2}{P(C6H5)3}2]BF4. A $CDCl_3$ solution containing complex **5′** (26.4 μmol) in an NMR tube was cooled down to −60 °C, and diethylamine (5.46 μL, 52.8 μmol) was added to the solution. A black precipitate was gradually deposited, as indicated by an NMR observation of the decomposition of the complex. After leaving the system for 24 h at room temperature, the mass spectrum and GC analysis of the supernatant revealed the formation of the singly ^{13}CO-labeled *N*,*N*,*N*′,*N*′-tetraethyloxamide, $Et_2N^{13}COCONEt_2$, in 32% yield; GC–MS *m*/*z* (rel. intensity) 201 (4), 101 (92), 100 (100), 72 (86).

Kinetic Study. To a mixture of complex **7** (11.4 mg, 15.2 μmol) and 1,1,2,2-tetrachloroethane (1.6 μL, 15.2 μmol) as an internal standard in $CDCl_3$ (0.6 mL) in an NMR tube equipped with a rubber septum was added NEt_3 (21.1 μL, 15.2 mmol) at room temperature. The sample tube was placed in an NMR sample probe controlled at 50 ± 0.1 °C, and examined at intervals by ^{1}H NMR spectroscopy. The rates of the reactions were measured by following the disappearance of the signals ascribed to **7**.

Table 9. Crystal Data and Structure Refinement for Complex **4a**

Formula	$C_{44}H_{46}BF_4NO_2P_2Pd$
Formula weight	876.00
Crystal color, habit	Colorless block
Crystal size/mm	0.20 × 0.15 × 0.30
Cryst system	Monoclinic
Space group	$P2_1/n$ (# 14)
Temp/K	193
a/Å	12.309(4)
b/Å	18.595(5)
c/Å	19.211(6)
β/deg	107.868(4)
V/Å^3	4185.1(21)
Z	4
d_{calcd}/g cm^{-3}	1.390
No. of reflections collected	33020
No. of unique reflections	15549 ($R_{int} = 0.043$)
No. of obsd reflections	15549
No. of variables	542
$R1$ (based on F)	0.040
$wR2$ (based on F^2)	0.117
GOF	0.83
Max shift/error in final cycle	0.006
Max/min residuals/e Å^{-3}	1.31/−0.97

X-ray Structure Determination of Complex 4a. Colorless prismatic crystals of **4a** of an adequate quality for X-ray measurements were grown from a CH_2Cl_2/pentane solution of the crude complex at −30 °C. A single crystal of approximate dimensions of 0.20 × 0.15 × 0.30 mm was mounted on a glass fiber. Crystallographic details for all structure determinations are provided in Table 9.

Data Collection. All measurements were made on a Rigaku Saturn CCD area detector with a graphite-monochromatized Mo Kα source ($\lambda = 0.71070$ Å). Indexing was performed from 7 images that were exposed for 3 seconds. The crystal-to-detector distance was 45.07 mm. The data were collected at a temperature of −80 ± 1 °C to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. A sweep of data was carried out using ω scans from −110.0 to 70.0° in 0.5° steps, at $\chi = 45.0°$ and $\phi = 0.0°$. A second sweep was performed using scans from −110.0 to 70.0° in 0.5° steps, at $\chi = 45.0°$ and $\phi = 90.0°$. The exposure rate was 6.0 s/°, and the detector swing angle was −19.87°. Readout was performed in the 0.070 mm pixel mode. Of the 33020 reflections collected, 15549 were unique ($R_{int} = 0.043$); equivalent reflections were merged. The data were collected for Lorentz and polarization effects as well as absorption.

Structure Solution and Refinement. Structure solution and refinements were carried out by using the CrystalStructure crystallographic software package provided by Rigaku Corporation. The heavy atom positions were determined by a direct program method (SIR92), and the remaining non-hydrogen atoms were found by subsequent Fourier techniques (DIRDIF94). All of the non-hydrogen atoms were refined anisotropically. In the final cycles of refinement, hydrogen atoms were located at idealized positions (d(C–H) = 0.95 Å) with isotropic thermal parameters, and were

included in calculations without refinement of their parameters. The function minimized in least-squares was $\Sigma w(F_o^2 - F_c^2)^2$ ($w = 1/[\sigma^2(F_o^2)]$). The final $R1$ and $wR2$ ($R1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$) values were 0.040 and 0.117, respectively.

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