# Selective Synthesis and Formation Mechanisms of *trans*- and *cis*-Benzoyl(carbamoyl)platinum(II) Complexes Coordinated with Tertiary Phosphine Ligands

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*trans*-Pt(COPh)Cl($PPh_3$)$_2$ (**1**) reacts with secondary amines under CO pressure (10 atm) at room temperature to give *cis*-Pt(COPh)($CONR_2$)($PPh_3$)$_2$ complexes ($NR_2$ = $NMe_2$ (**5a**), $N(CH_2)_4CH_2$ (**5b**), $N(CH_2)_3CH_2$ (**5c**), $NEt_2$ (**5d**)) exclusively, while the same amines react with *trans*-[Pt(COPh)(CO)($PPh_3$)$_2$]$BF_4$ (**7**) under a nitrogen atmosphere to afford *trans*-Pt(COPh)($CONR_2$)($PPh_3$)$_2$ complexes ($NR_2$ = $NMe_2$ (**6a**), $N(CH_2)_4CH_2$ (**6b**), $N(CH_2)_3CH_2$ (**6c**), $NEt_2$ (**6d**)). The isomerization of the *trans*-benzoyl-carbamoyl complexes (**6a-d**) to their cis isomers (**5a-d**) in a neat solvent is a slow process, but the isomerization is significantly accelerated by addition of amine and CO. On the other hand, benzoylplatinum complexes coordinated with compact and basic $PMe_3$ ligands, *trans*-Pt(COPh)Cl($PMe_3$)$_2$ (**2**) and *trans*-[Pt(COPh)(acetone)($PMe_3$)$_2$]$BF_4$ (**4**), give *trans*-Pt(COPh)($CONR_2$)($PMe_3$)$_2$ (**9**) exclusively on treatment with CO and the secondary amines. Complex **9** is inert to isomerization to its cis isomer. Formation pathways of *trans*- and *cis*-benzoyl(carbamoyl)platinum complexes and their trans-cis isomerization process are examined in detail, and a new type of isomerization pathway involving participation of added CO and amine is proposed.

## Introduction

The palladium-catalyzed double carbonylations of organic halides and secondary amines provide convenient synthetic means for preparing α-keto amides:[1,2]

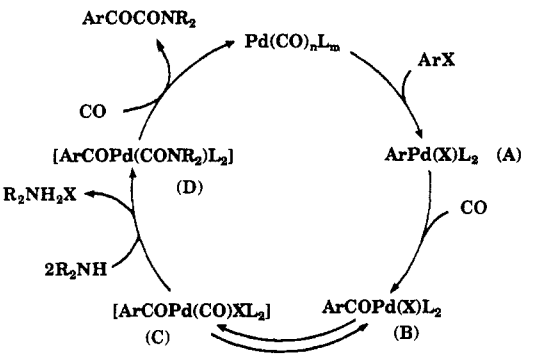
$$R'X + CO + HNR_2 \xrightarrow{[Pd]} R'COCONR_2 + R'CONR_2 \quad (1)$$

R′ = aryl, alkenyl; X = Br, I; R = alkyl

In previous studies we proposed the mechanism given by Scheme I involving an aroylpalladium intermediate and its subsequent reactions to account for the formation of α-keto amide.[3-5] Coordination of CO to the aroyl complex B in Scheme I gives the CO-coordinated aroyl complex C. The subsequent attack of amine on the CO ligand affords the aroyl(carbamoyl)palladium species D, which reductively eliminates α-keto amide. Recently, we found that the reactions of the $PMe_3$-coordinated benzoylpalladium complexes *trans*-[Pd(COPh)(acetone)($PMe_3$)$_2$]X (X = $BF_4$, $PF_6$) and *trans*-Pd(COPh)Cl($PMe_3$)$_2$ with secondary amines and CO give the isolable benzoyl(carbamoyl)palladium complexes *trans*-Pd(COPh)($CONR_2$)($PMe_3$)$_2$.[5] The $PMe_3$-coordinated *trans*-benzoyl-carbamoyl complexes thus prepared, however, proved to be quite stable toward reductive elimination to give α-keto amide. For the α-keto amide formation to proceed from the intermediate D in Scheme I, the aroyl-carbamoyl species should have a cis configuration suitable for the reductive elimination. However, we could not find a preparative route to a *cis*-aroyl(carbamoyl)palladium complex, and no direct information was obtained concerning the mechanism to convert the trans complex into the cis isomer.

*cis*-$PtR_2L_2$ type complexes are known to be inert to reductive elimination as compared with their palladium analogues.[6] Thus, pertinent information regarding the formation process of *cis*-aroyl(carbamoyl)palladium was expected to be derived by studying reactions of analogous benzoylplatinum complexes with CO and secondary amines in place of the benzoylpalladium complexes themselves. We describe here that *trans*- and *cis*-benzoyl(carbamoyl)platinum complexes can be separately prepared by a

**Scheme I**




[a] L = tertiary phosphine.

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(1) (a) Kobayashi, T.; Tanaka, M. *J. Organomet. Chem.* **1982**, *233*, C64. (b) Yamashita, H.; Kobayashi, T.; Sakakura, T.; Tanaka, M. *J. Mol. Catal.* **1987**, *40*, 333.

(2) (a) Ozawa, F.; Soyama, T.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett.* **1982**, *23*, 3383. (b) Ozawa, F.; Yanagihara, H.; Yamamoto, A. *J. Org. Chem.* **1986**, *51*, 415. (c) Yamamoto, A.; Yamamoto, T.; Ozawa, F. *Pure Appl. Chem.* **1985**, *57*, 1799. (d) Son, T.; Yanagihara, H.; Ozawa, F.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1251. (e) Ozawa, F.; Nakano, M.; Aoyama, I.; Yamamoto, T.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1986**, 382. (f) Ozawa, F.; Yamagami, I.; Nakano, M.; Fujisawa, F.; Yamamoto, A. *Chem. Lett.* **1989**, 125.

(3) (a) Ozawa, F.; Soyama, H.; Yanagihara, H.; Aoyama, I.; Takino, H.; Izawa, K.; Yamamoto, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1985**, *107*, 3235. (b) Ozawa, F.; Yamamoto, A. *Chem. Lett.* **1982**, 865. (c) Ozawa, F.; Sugimoto, T.; Yuasa, Y.; Santra, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 683. (d) Ozawa, F.; Sugimoto, T.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 692. (e) Ozawa, F.; Kawasaki, N.; Okamoto, H.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1987**, *6*, 1640.

(4) A similar mechanism was independently proposed: Chen, J.; Sen, A. *J. Am. Chem. Soc.* **1984**, *106*, 1506.

(5) (a) Ozawa, F.; Huang, L.; Yamamoto, A. *J. Organomet. Chem.* **1987**, *334*, C9. (b) Huang, L.; Ozawa, F.; Yamamoto, A. *Organometallics* preceding paper in this issue.

(6) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115; *Organometallics* **1986**, *5*, 609 and references cited therein.

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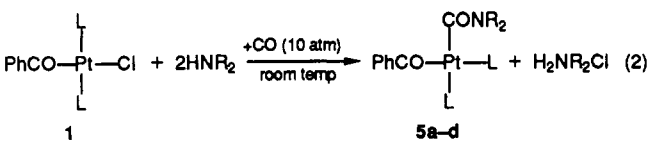
proper choice of the starting benzoylplatinum complexes and the reaction conditions.[7,8] Detailed studies on the formation pathways of *trans*- and *cis*-benzoyl(carbamoyl)platinum complexes as well as the trans to cis isomerization process have provided further insight into the mechanistic details of the catalytic double-carbonylation reaction.

## Results

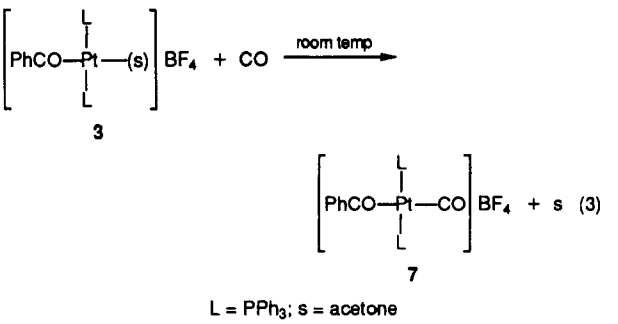
**Selective Synthesis of *trans*- and *cis*-Benzoyl(carbamoyl)platinum Complexes by the Reactions of Benzoylplatinum Complexes with CO and Secondary Amines.** The previous study regarding solvent effects on the reaction of *trans*-$Pd(COPh)X(PMePh_2)_2$ (X = Cl, Br, I) with CO and secondary amine to give an $\alpha$-keto amide suggested that the reaction involves two types of CO-coordinated benzoylpalladium species depending upon the nature of the halide ligand (X).[3c] The reaction of the chloride complex involves probable formation of the neutral intermediate $[Pd(COPh)CO(Cl)(PMePh_2)]$ generated by ligand exchange of the $PMePh_2$ ligand with CO. When the bromide and iodide complexes were used, on the other hand, the reactions were indicated to invole ionization of these halide ligands to give ionic *trans*-$[Pd(COPh)(CO)L_2]^+X^-$ intermediates. Therefore, we started the present study by examining reactivities toward CO and amines of neutral benzoylplatinum complexes, *trans*-$Pt(COPh)Cl(PPh_3)_2$ (**1**) and *trans*-$Pt(COPh)Cl(PMe_3)_2$ (**2**), and of ionic benzoylplatinum complexes, *trans*-$[Pt(COPh)(acetone)(PPh_3)_2]BF_4$ (**3**) and *trans*-$[Pt(COPh)(acetone)(PMe_3)_2]BF_4$ (**4**).

**1. Reactions of $PPh_3$-Coordinated Benzoylplatinum Complexes (1 and 3).** The neutral and ionic $PPh_3$-coordinated complexes (**1** and **3**, respectively) exhibit reaction behavior considerably different from each other.

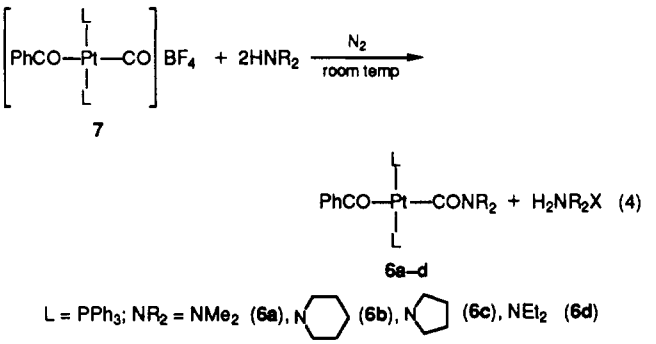
The neutral benzoyl chloride complex **1** reacts smoothly with secondary amines under CO pressure at room temperature to give the cis complexes *cis*-$Pt(COPh)(CONR_2)(PPh_3)_2$ (**5a–d**), selectively, which have been isolated as bright yellow crystals by recrystallization from benzene–$Et_2O$ mixtures.



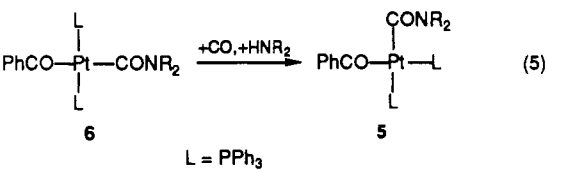

The ionic benzoylplatinum complex **3**, on the other hand, forms benzoyl–carbamoyl complexes with different geometries (trans and cis) depending upon the reaction conditions. Selective synthesis of *trans*-benzoyl–carbamoyl complexes (**6**) can be achieved by the following sequence of reactions. Treatment of **3** with an atmospheric pressure of CO in acetone gives a CO-coordinated benzoyl complex with trans geometry (**7**).[9] The isolated benzoyl–carbonyl complex **7** readily undergoes nucleophilic attack of amines on its carbonyl ligand at room temperature to give selectively the *trans*-benzoyl(carbamoyl)platinum complexes **6a–d**, which have been isolated as orange



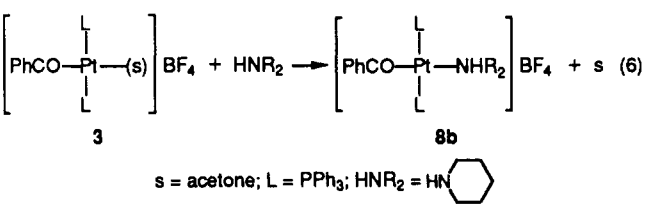

crystals by recrystallization from $CH_2Cl_2$–$Et_2O$ mixtures.



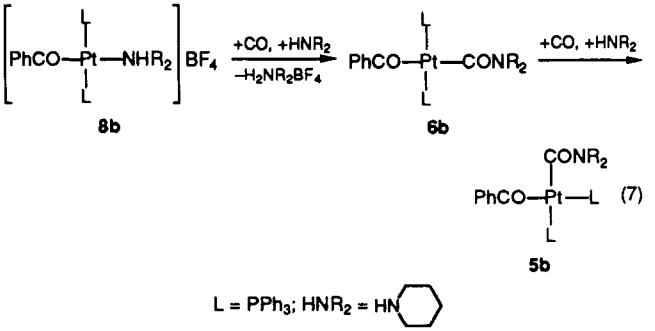

Reaction 4 was performed *in the absence of free CO*. In contrast, when the reaction of **7** and secondary amine was carried out *under a CO atmosphere* (1 atm), the reaction gave a mixture of *cis*- and *trans*-benzoyl–carbamoyl complexes, with the cis:trans ratio increasing with time. As described in eq 5, the reaction involves trans–cis isomerization of **6** to **5**, proceeding in the presence of amine and CO.




The ionic benzoylplatinum complex **3** readily binds piperidine to give a piperidine-coordinated complex (**8b**), which can be isolated as white crystals. Complex **8b** reacts




with CO in acetone containing an excess amount of piperidine to give initially the *trans*-benzoyl–carbamoyl complex **6b**, which is subsequently isomerized to its cis isomer **5b** according to eq 7, as confirmed by NMR spectroscopy (vide infra).




(7) A part of the results has been reported: Ozawa, F.; Huang, L.; Yamamoto, T.; Yamamoto, A. Abstract, *5th International Symposium on Homogeneous Catalysis*, Kobe, Japan, 1986; p 173.

(8) Related *trans*- and *cis*-acyl(alkoxycarbonyl)platinum complexes have been already reported: Sen, A.; Chen, J.; Vetter, E. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 148. See also: Bennett, M. A. *Organometallics* **1985**, *4*, 180.

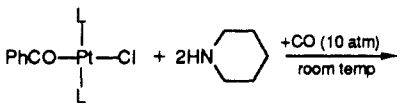
(9) Sen previously prepared the CO-coordinated benzoylplatinum complex **7** by treating **1** with $AgBF_4$ under CO.[8]

**Table I. Characteristic NMR and IR Data for *trans*-Pt(COPh)(CONR$_2$)L$_2$ Complexes[a]**

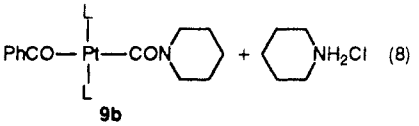
| | $^{13}C\{^1H\}$ NMR[b] | | $^{31}P\{^1H\}$ NMR[c] | | |
|---|---|---|---|---|---|
| complex | $\delta$ | $^2J_{P-C}$, Hz | $\delta$ | $^1J_{Pt-P}$, Hz | IR,[d] cm$^{-1}$ |
| **6a** | 259.4 (t) | 10 | 21.7 (s) | 3258 | 1567 |
| | 203.6 (t)[e] | 13 | | | 1525[f] |
| **6b** | 258.3 (t) | 10 | 21.0 (s) | 3309 | 1565 |
| | 202.4 (t) | 13 | | | 1528 |
| **6c** | 260.0 (t) | 10 | 21.8 (s) | 3287 | 1560 |
| | 203.2 (t) | 13 | | | 1515 |
| **6d** | 257.5 (t) | 9 | 24.6 (s) | 3262 | 1565 |
| | 203.5 (t) | 12 | | | 1520 |
| **9b** | 260.8 (t) | 10 | -15.3 (s) | 2889 | 1557 |
| | 203.8 (t) | 13 | | | 1519 |
| | 15.6[g] | | | | |

[a] $^1H$ NMR data are reported in the Experimental Section. [b] Signals due to the carbonyl carbons; at 125 MHz except for **6b** (67.8 MHz), in $CD_2Cl_2$, at room temperature. [c] 40 MHz, in $CD_2Cl_2$, at -20 °C. Chemical shifts are referred to $PPh_3$ as an external standard. [d] $\nu$(CO) bands; in KBr disks. [e] $^1J_{Pt-C}$ = 1190 Hz, determined by using *trans*-Pt(COPh)($^{13}CONMe_2$)($PMe_3$)$_2$. [f] $\nu(^{13}CO)$ = 1495 cm$^{-1}$. [g] Signal due to the $PMe_3$ carbons; virtual triplet, $J$ = 19 Hz.

**2. Reactions of PMe$_3$-Coordinated Benzoylplatinum Complexes (2 and 4).** Reactions of the $PMe_3$-coordinated benzoyl complexes **2** and **4** with CO and amines give *trans*-benzoyl(carbamoyl)platinum complexes exclusively, independent of the starting benzoyl complex, if it is neutral (**2**) or ionic (**4**), and regardless of the reaction conditions. Thus, treatment of **2** with pyrrolidine under CO pressure affords *trans*-Pt(COPh){CON(CH$_2$)$_4$CH$_2$}($PMe_3$)$_2$ (**9b**), selectively. The same complex **9b** can be




**2**



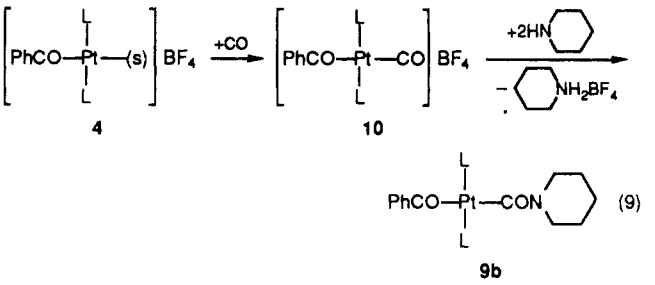

(8)

**9b**

L = $PMe_3$

prepared by starting from the ionic benzoylplatinum complex **4** as illustrated in eq 9. In contrast to the *trans*-benzoyl-carbamoyl complexes coordinated with $PPh_3$ ligands (**6a–d**), the $PMe_3$ complex **9b** thus prepared is totally stable toward trans–cis isomerization in solution containing an excess amount of pyrrolidine under CO pressure at room temperature.

**Characterization of the Benzoyl(carbamoyl)platinum Complexes.** The benzoyl–carbamoyl complexes have been characterized by means of IR and NMR spectroscopy and elemental analysis.[8] Tables I and II list the characteristic IR and NMR data. IR spectra of the trans complexes show two $\nu$(CO) absorptions around 1560 and 1520 cm$^{-1}$, which are assigned to the C=O stretching bands of the benzoyl and carbamoyl groups, respectively. On the other hand, the cis isomers exhibit two $\nu$(CO) bands at about 1600 cm$^{-1}$ (for the benzoyl group) and 1545 cm$^{-1}$ (for the carbamoyl group). The assignments are based on labeling experiments with $^{13}CO$ (see Experimental Section).




The geometry at the platinum center has been determined by NMR spectroscopy. In the $^{13}C\{^1H\}$ NMR spectra, the *trans*-benzoyl–carbamoyl complexes show two sets of triplets around $\delta$ 260 and 203 with relatively small $^2J_{C-P}$ values (ca. 10 Hz). In contrast, the signals due to the carbonyl carbons in the cis isomers split into doublets of doublets around $\delta$ 237 and 187 with large (110–120 Hz) and small (10–13 Hz) $^2J_{P-C}$ values, consistent with their square-planar *cis*-PtRR'(PR''$_3$)$_2$ type structures. Of the two sets of signals arising from the carbonyl carbons in each complex, the signal at higher magnetic field is assigned to the carbamoyl group and the other at lower field to the benzoyl group on the basis of labeling experiments with $^{13}CO$. For example, *trans*-Pt(COPh)($^{13}CONMe_2$)($PPh_3$)$_2$ (**6a**-$^{13}CO$) with the $^{13}CO$ label at the carbamoyl group exhibits a strong triplet signal at $\delta$ 203.6 with $^{195}Pt$ satellites ($J_{Pt-C}$ = 701 Hz) in the $^{13}C$ NMR spectrum.

In the $^{31}P\{^1H\}$ NMR spectra, the phosphorus nuclei in the trans complexes are observed as a singlet with $^{195}Pt$ satellites, while those in the cis isomers appear as an AB quartet with $^{195}Pt$ satellites. The $J_{Pt-P}$ values for the trans complexes (ca. 3000 Hz) and for the cis isomers (ca. 1600 and 1800–1900 Hz) are typical of *trans*- and *cis*-PtR$_2$(PR'$_3$)$_2$ type complexes having R groups with trans influence greater than that of the PR'$_3$ ligands. As shown in Figure 1, the $^{31}P\{^1H\}$ NMR spectrum of the $^{13}CO$-enriched *cis*-Pt($^{12}$COPh)($^{13}CONMe_2$)($PPh_3$)$_2$ (**6a**-$^{13}CO$) exhibits two sets of doublets of doublets with $^{195}Pt$ satellites (one set is observed as an apparent triplet in Figure 1). On the basis of the magnitude of the P–C coupling constants of the phosphorus nuclei to the $^{13}C$ atom in the carbamoyl group, the signal (a) with the larger $^2J_{P-C}$ value (120 Hz)

**Table II. Characteristic NMR and IR Data for *cis*-Pt(COPh)(CONR$_2$)(PPh$_3$)$_2$ Complexes[a]**

| | $^{13}C\{^1H\}$ NMR[b] | | $^{31}P\{^1H\}$ NMR[c] | | | |
|---|---|---|---|---|---|---|
| complex | $\delta$ | $^2J_{P-C}$, Hz | $\delta$ | $^1J_{Pt-P}$, Hz | $^2J_{P-P}$, Hz | IR,[d] cm$^{-1}$ |
| **5a** | 237.1 (dd) | 110, 10 | 20.6 (d) | 1584 | 19 | 1600 |
| | 188.5 (dd)[e] | 120, 13 | 20.6 (d) | 1907 | | 1550[f] |
| **5b** | 236.9 (dd) | 110, 10 | 20.7 (d) | 1602 | 19 | 1608 |
| | 186.4 (dd) | 120, 13 | 20.0 (d) | 1874 | | 1550 |
| **5c** | 238.7 (dd) | 110, 10 | 22.0 (d) | 1629 | 19 | 1600 |
| | 187.5 (dd) | 120, 13 | 18.8 (d) | 1803 | | 1540 |
| **5d** | 236.4 (dd) | 110, 10 | 19.6 (d) | 1587 | 19 | 1600 |
| | 187.6 (dd) | 120, 13 | 20.6 (d) | 1879 | | 1545 |

[a] $^1H$ NMR data are reported in the Experimental Section. [b] Signals due to the carbonyl carbons; at 125 MHz, in $CD_2Cl_2$, at room temperature. [c] 40 MHz, in $CD_2Cl_2$, at -20 °C. Chemical shifts are referred to $PPh_3$ as an external standard. [d] $\nu$(CO) bands; in KBr disks. [e] $^1J_{Pt-C}$ = 701 Hz, determined by using *trans*-Pt(COPh)($^{13}CONMe_2$)($PPh_3$)$_2$. [f] $\nu(^{13}CO)$ = 1515 cm$^{-1}$.

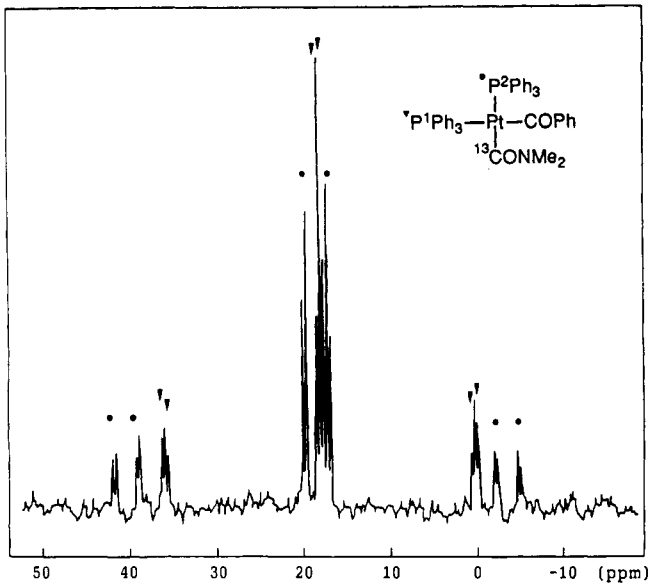



**Figure 1.** $^{31}P\{^1H\}$ NMR spectrum of *cis*-Pt($^{12}$COPh)($^{13}$CONMe$_2$)(PPh$_3$)$_2$ in $CD_2Cl_2$ at room temperature (40 MHz; chemical shifts are referred to external $PPh_3$). The filled triangles (▼) denote signals due to the phosphorus nucleus cis to the $^{13}CONMe_2$ group ($P^1$, 19.5 ppm, referred to external $PPh_3$, $^1J_{Pt-P^1}$ = 1570 Hz, $^1J_{P^1-^{13}C}$ = 13 Hz, $^2J_{P^1-P^2}$ = 19 Hz), and the filled circles (●) indicate those arising from the phosphorus nucleus trans to the $^{13}CONMe_2$ group ($P^2$, 19.9 ppm, $^1J_{Pt-P^2}$ = 1920 Hz, $^2J_{P^2-^{13}C}$ = 120 Hz, $^2J_{P^1-P^2}$ = 19 Hz).

is assigned to the phosphorus trans to the carbamoyl group and the signal (b) with the smaller $^2J_{P-C}$ value (13 Hz) to the phosphorus trans to the benzoyl group. The former signal (a) has a larger $^1J_{Pt-P}$ value (~1900 Hz) than the latter (b) (~1600 Hz), indicating that the benzoyl group has a greater trans influence than the carbamoyl group.

**NMR Examination of Reaction 2.** The reaction of the $PPh_3$-coordinated benzoylplatinum chloride complex 1 with piperidine and CO to give the *cis*-benzoyl–carbamoyl complex **5b** was examined by NMR spectroscopy.

When a chlorobenzene solution of 1 under CO pressure (10 atm) was monitored by $^{31}P\{^1H\}$ NMR spectroscopy at room temperature, no species other than 1 was observed and no broadening of the signals due to 1 occurred. Next, reaction of 1 and CO was examined in the presence of 10 equiv of sulfur/equiv of Pt, which is known to trap free $PPh_3$ released from platinum by ligand exchange with carbon monoxide.[10] The $^{31}P$ NMR spectrum of the reaction solution containing 1 and sulfur under CO pressure (10 atm) after 10 days at room temperature revealed the formation of S=$PPh_3$ (94%/equiv of Pt) and three kinds of $PPh_3$-coordinated platinum species, probably assignable to three geometrical isomers of [Pt(COPh)(CO)($PPh_3$)Cl] (see Experimental Section). These results indicate that the direct reaction of 1 with CO to displace the coordinated $PPh_3$ ligand to give a CO-coordinated benzoylplatinum complex is a slow process, whereas the reactions of 1 with CO in the presence of amine, affording the *cis*-benzoyl(carbamoyl)platinum complexes, are completed in 1–2 h at room temperature.

In contrast to the slow reaction of 1 toward CO, its reaction with piperidine proceeds at a much higher rate. When piperidine (40 equiv/equiv of Pt) was added to a chlorobenzene solution of 1 (0.053 mmol) at room temperature, the pale yellow solution of 1 quickly turned to

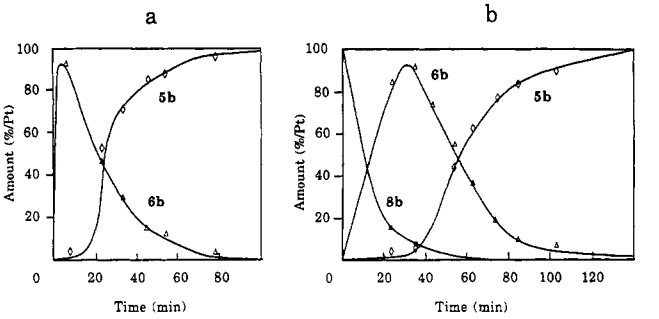
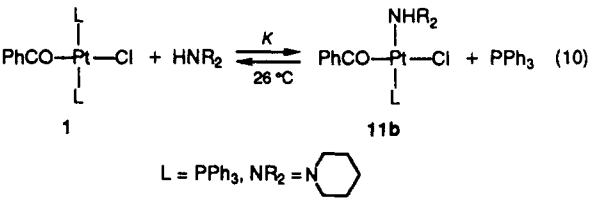



**Figure 2.** (a) Change of the platinum complexes with time in the reaction of *trans*-[Pt(COPh)(CO)($PPh_3$)$_2$]$BF_4$ (**8**) and piperidine (4 equiv/equiv of Pt) in $CD_2Cl_2$ under an atmospheric pressure of CO at room temperature to give *trans*-Pt(COPh)(CON$\overline{(CH_2)_4CH_2}$)($PPh_3$)$_2$ (**6b**) and *cis*-Pt(COPh)(CON$\overline{(CH_2)_4CH_2}$)($PPh_3$)$_2$ (**5b**). (b) Change of the platinum complexes with time in the reaction of *trans*-[Pt(COPh)(piperidine)($PPh_3$)$_2$]$BF_4$ (**8b**) with piperidine (3 equiv/equiv of Pt) and CO at atmospheric pressure in $CD_2Cl_2$ at room temperature to give *trans*-Pt(COPh)(CON$\overline{(CH_2)_4CH_2}$)($PPh_3$)$_2$ (**6b**) and *cis*-Pt(COPh)(CON$\overline{(CH_2)_4CH_2}$)($PPh_3$)$_2$ (**5b**).

bright yellow. $^{31}P$ NMR examination of the solution revealed the equilibrium given in eq 10 between 1 and the




(10)

piperidine-coordinated benzoylplatinum chloride complex **11b**, which was observed as a singlet with $^{195}Pt$ satellites at 15.6 ppm ($^1J_{Pt-P}$ = 4387 Hz). Liberation of $PPh_3$ from 1 into the solution was evidenced by observation of a broad $^{31}P$ NMR signal around 0 ppm[11] at room temperature, which became a sharp singlet at −50 °C. Identification of **11b** was performed by comparison of its $^{31}P$ NMR chemical shift with that of the authentic sample separately prepared in a manner similar to that for Pt(COPh)(pyridine)Cl($PPh_3$).[12] The relative ratio of **11b** to 1 increased with an increasing amount of piperidine in the system, while the ratio decreased by addition of free $PPh_3$ to the system. The equilibrium constant $K$ for reaction 10 was determined by $^{31}P$ NMR spectroscopy to be (2.1 ± 0.2) × $10^{-3}$ at 26 °C with varying concentrations of piperidine (20–60 equiv) and added $PPh_3$ (0–0.6 equiv).

An equilibrium mixture of **11b** and 1 prepared from 1 and piperidine (15 equiv/equiv of 1) in chlorobenzene was treated with CO (10 atm), and the system was observed with time by $^{31}P$ NMR spectroscopy. In the absence of CO, the system contained **11b** and 1 in a 1:5 ratio. After CO gas was introduced, the amount of the piperidine-coordinated complex (**11b**) relative to that of 1 rapidly decreased to ca. 1:30, while the signal of free $PPh_3$ became sharp and remained without noticeable change in its intensity. Following this change at the initial stage, the *cis*-benzoyl–carbamoyl complex **5b** was formed at the expense of 1 in 2 h. At the end of the reaction, the signals arising from 1, **11b**, and free $PPh_3$ completely disappeared

(10) Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1434.

(11) All the chemical shifts in $^{31}P$ NMR spectroscopy are indicated in δ (ppm) from an external $PPh_3$ standard, which appeared at δ −5.9 when the spectrum was observed with an 85% $H_3PO_4$ standard.

(12) Clark, H. C.; Goel, A. B.; Jain, V. K.; Tyers, K. G. *J. Organomet. Chem.* **1987**, *321*, 123.

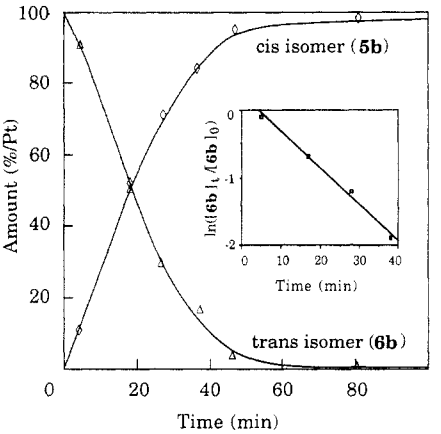



**Figure 3.** Change of platinum complexes with time in the isomerization of *trans*-Pt(COPh)(CON$\overline{(CH_2)_4CH_2}$)$(PPh_3)_2$ (**6b**) to the cis isomer **5b** in $CD_2Cl_2$ containing piperidine (3 equiv/equiv of Pt) under an atmospheric pressure of CO at room temperature. The first-order plot is shown in the inset.

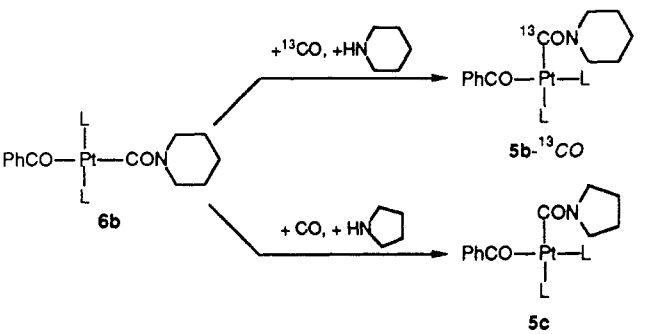
and the signals of **5b** were observed with 95% selectivity together with some unidentified small peaks. No trace of signals arising from the *trans*-benzoyl–carbamoyl complex **6b** has been observed throughout the reaction. The results described here strongly suggest that the conversion of the *trans*-benzoylplatinum chloride complex **1** into the *cis*-benzoyl–carbamoyl complex **5** is associated with replacement of one of the $PPh_3$ ligands in **1** with amine, a process making the coordination site cis to the benzoyl group available for conversion into the carbamoyl group.

**NMR Studies on the Reactions of Ionic Benzoylplatinum Complexes with CO and Amines.** Figure 2a illustrates the change of the ionic $PPh_3$-coordinated benzoyl–carbonyl complex **7** with time on treatment with piperidine in $CD_2Cl_2$ under a CO atmosphere as followed by $^{31}P$ NMR spectroscopy. For the first NMR run 10 min after piperidine (4 equiv/equiv of Pd) was added to the system, the starting benzoyl–carbonyl complex **7** could no longer be detected, while *trans*-Pt(COPh)$\{$CON$\overline{(CH_2)_4CH_2}\}(PPh_3)_2$ (**6b**) was observed exclusively. As the reaction progressed, complex **6b** thus formed was gradually consumed, to be replaced by the *cis*-benzoyl(carbamoyl)-platinum complex **5b**, formed by isomerization of **6b**. In the reaction of the piperidine-coordinated benzoylplatinum complex **8b** with CO and piperidine, conversion of **8b** into the *trans*-benzoyl–carbamoyl complex **6b** was slower than the conversion of the CO-coordinated complex **7** to **6b** but the rest of the reaction proceeded similarly to that of **7** with piperidine and CO (Figure 2b). These observations are consistent with the reaction pathways where the *trans*-benzoyl(carbamoyl)platinum complexes **6a–d** initially formed in the systems undergo subsequent isomerization to their cis isomers.

Trans to cis isomerization of **6a–d** in neat $CD_2Cl_2$ in the absence of CO and amine at room temperature was also examined by $^{31}P$ NMR spectroscopy. The isomerization reactions are significantly slower than those taking place in the presence of CO and amine, and they take several days for completion. Addition of secondary amine does not accelerate the reaction. The reactions under a CO atmosphere in the absence of secondary amine are also slow processes. However, simultaneous introduction of CO and secondary amines to the systems results in rapid trans–cis isomerization reactions.

**Trans to Cis Isomerization of Isolated Benzoyl(carbamoyl)platinum Complexes.** Complex **6b** dissolved in $CD_2Cl_2$ containing 3 equiv of piperidine under an atmospheric pressure of CO is isomerized readily at room temperature to the corresponding cis isomer **5b**. Figure 3 shows the time course of the reaction ($^{31}P$ NMR). The trans–cis isomerization obeys first-order kinetics regarding the concentration of **6b** ($k_{obsd} = 8.9 \times 10^{-4}$ $s^{-1}$ at 26 °C). It is noted that the reaction rate derived from Figure 3 is comparable to those for the isomerization in Figure 2 as judged from the reaction curves.

When the isomerization reaction of **6b** with piperidine and $^{13}CO$ is carried out, the $^{13}CO$-labeled complex *cis*-Pt(COPh)$\{^{13}$CON$\overline{(CH_2)_4CH_2}\}(PPh_3)_2$ is formed. Furthermore, the reaction of **6b** with pyrrolidine (4 equiv/equiv of Pt) under a CO atmosphere gives the *cis*-benzoyl–carbamoyl complex with the pyrrolidino group (**5c**) instead of **5b** having the piperidino group in the carbamoyl ligand.



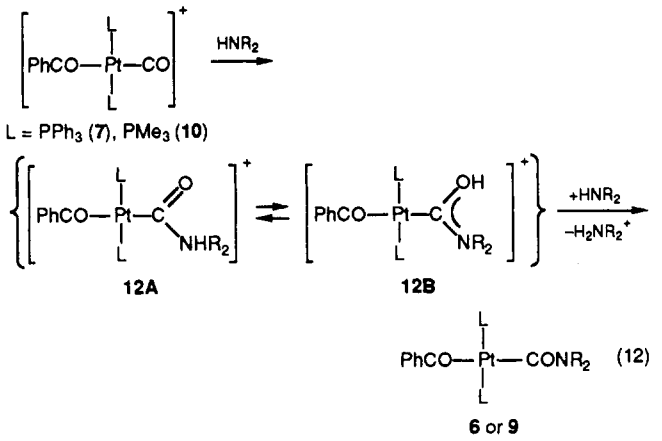

(11)

L = $PPh_3$

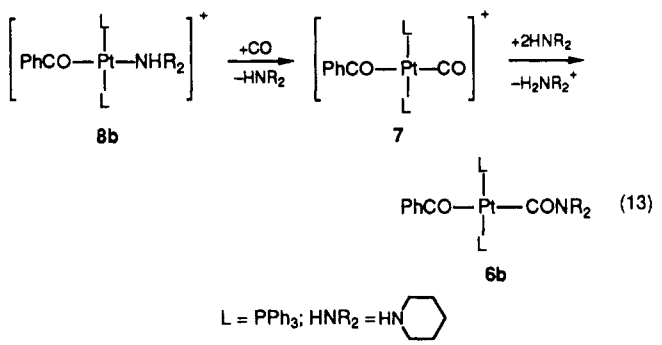
The $^{31}P\{^1H\}$ NMR spectra of the *trans*-benzoyl–carbamoyl complex **6b** under CO pressure (10 atm) in $CD_2Cl_2$ at room temperature showed no sign for direct interaction of **6b** with CO. In contrast, liberation of a small amount of $PPh_3$ was observed in a solution containing **6b** and 4 equiv of piperidine at room temperature as evidenced by the appearance of a very broad signal arising from free $PPh_3$ together with the signals due to **6b**. No other signal has been detected. Introduction of CO into the same system resulted in conversion of **6b** into the cis complex (**5b**). The broad signal of free $PPh_3$ was observed throughout the reaction and disappeared at the final stage of the reaction. The behavior of these $PPh_3$-coordinated benzoylplatinum complexes is in sharp contrast with that of the $PMe_3$-coordinated complexes, which are quite inert to trans–cis isomerization.

## Discussion

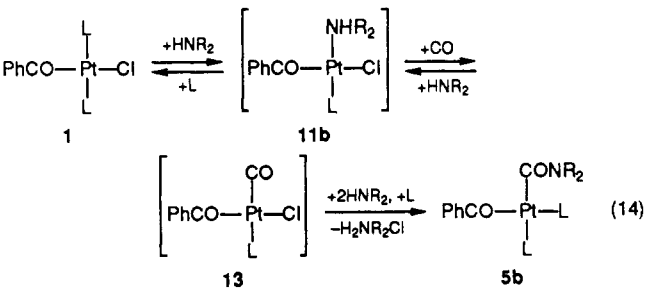
**Formation Processes of the *trans*- and *cis*-Benzoyl(carbamoyl)platinum Complexes.** Since the ionic benzoyl complexes **3** and **4** have a coordination site trans to the benzoyl ligand available for reactions with CO and amine, no dissociation of the tertiary phosphine ligand is required for their conversion into the *trans*-benzoyl–carbamoyl complexes. The selective formation of the *trans*-benzoyl–carbamoyl complex on the reaction of the ionic *trans*-benzoyl–carbonyl **7** or **10** with amine may be simply accounted for by nucleophilic attack of amine on the coordinated CO ligand as illustrated in eq 12. The external attack of amine on the CO ligand in **7** (or **10**) forms cationic benzoyl complexes with an amine-coordinated carbonyl group (**12A**) and/or an *O*-protonated carbamoyl group (**12B**). These complexes undergo deprotonation with the aid of another amine to give the *trans*-benzoyl–carbamoyl complex **6** or **9** with liberation of the ammonium salt. The sequence of reactions is analogous to what we have proposed for the corresponding benzoylpalladium complex.[13]




The $PPh_3$-coordinated *trans*-benzoyl–carbamoyl complex **6b** is formed also by the reaction of the amine-coordinated ionic complex *trans*-$[Pt(COPh)\{N(H)(CH_2)_4CH_2\}(PPh_3)_2]BF_4$ (**8b**) with CO and piperidine. As judged by comparison of the reaction curves in Figure 2, the reaction of the piperidine-coordinated complex **8b** to give **6b** and then **5b** as observed in Figure 2b is slower than that of the CO-coordinated complex **7** in Figure 2a. Thus, the reaction curve for formation of the *trans*-benzoyl–carbamoyl complex **6b** from **7** has a peak after 5 min, whereas the reaction curve for the piperidine complex **8b** shows a maximum point of **6b** after 30 min. This observation is consistent with the following sequence of processes involving the initial substitution of the ligated piperidine in **8b** with CO to give the benzoyl–carbonyl complex **7**, which subsequently reacts rapidly with amine to give the *trans*-benzoyl–carbamoyl complex **6b**:[14]

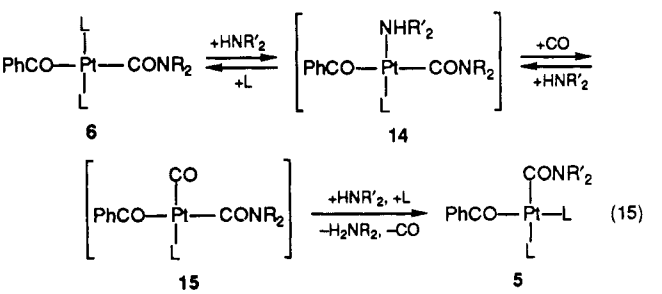



In contrast to the processes giving the *trans*-benzoyl–carbamoyl type complexes, the processes to give the cis complexes require dissociation of the tertiary phosphine ligand. The NMR examination of the reaction of the $PPh_3$-coordinated benzoylpalladium chloride **1** with CO and piperidine to afford the *cis*-benzoyl–carbamoyl complex **5b** has indicated that the reaction involves prior substitution of the $PPh_3$ ligand with piperidine to give the piperidine-coordinated benzoyl chloride complex [Pt(COPh)Cl($PPh_3$)(piperidine)] (**11b**), whereas the $PPh_3$ ligand in **1** is difficult to replace by CO in the absence of piperidine. After the replacement of the $PPh_3$ ligand with piperidine, the piperidine ligand in **11b** may then be replaced with CO to give the CO-coordinated complex **13**, which has the benzoyl and carbonyl ligands in mutually cis positions. The subsequent attack of piperidine on the CO ligand in **13** is accompanied by removal of the chloride ligand as the piperidinium chloride salt with the aid of another piperidine and is followed by recoordination of the liberated $PPh_3$ to form the *cis*-benzoyl(carbamoyl)platinum complex **5b** (eq 14).




For the $PMe_3$-coordinated complexes, this type of ligand dissociation and the subsequent route to trans–cis isomerization is hindered because of the strongly coordinating ability of the $PMe_3$ ligand arising from its very basic and stereochemically less demanding nature. In the absence of $PMe_3$ replacement, the reaction of *trans*-Pt(COPh)Cl($PMe_3$)$_2$ (**2**) with CO and amine to give *trans*-Pt(COPh)($CONR_2$)($PMe_3$)$_2$ (**9**) may involve the replacement of the chloride ligand either by ionization, which may take place with difficulty, or by stereo-retaining substitution of the chloride ligand in **2** by the incoming CO through a pentacoordinate intermediate (see eq 11 of the preceding paper for the palladium analogue). We cannot determine which process is operative from the presently available data.

**Process of Trans to Cis Isomerization of the $PPh_3$-Coordinated Benzoyl(carbamoyl)platinum Complex.** The trans to cis isomerization of the pure benzoyl–carbamoyl complexes **6a–d** in neat solvents is a rather slow process. In contrast, the isomerization proceeds rapidly in solution containing free amine and CO (Figures 2 and 3). This reaction probably involves prior ligand exchange of the $PPh_3$ ligand with amine as shown in eq 15 to give the amine-coordinated benzoyl–carbamoyl




complex **14**, as suggested by NMR spectroscopy. The labeling experiment as shown in eq 11 revealed that a $^{13}CO$ molecule added to the solution containing the trans complex and amine was incorporated into the carbamoyl ligand in the isomerized cis complex. The results in eq 11 also showed that the isomerization reaction involves exchange of the amino group between the starting trans-carbamoyl complex and the amine added to the system. These observations may be accounted for by the processes in eq 15, which are analogous to those in eq 14. This isomerization process is initiated by the replacement of one of the $PPh_3$ ligands in **6** with amine. The amine-coordinated complex **14** thus formed subsequently reacts with external CO to

(13) Huang, L.; Ozawa, F.; Osakada, K.; Yamamoto, A. *Organometallics* **1989**, *8*, 2065; *J. Organomet. Chem.* **1990**, *383*, 587.

(14) An implication of the mechanism shown in eq 13 is that a conceivable reaction pathway through coordination of CO to the amine-coordinated complex **8**, followed by internal attack of the coordinated amine at the bound CO and subsequent deprotonation to directly give the carbamoyl complex **6**, is a high-energy process compared with the "detour" process involving the first displacment of the coordinated amine by CO to give the CO-coordinated complex **7**, whose coordinated CO is *externally* attacked by amine.

give the carbonyl complex **15**. This two-step displacement of the $PPh_3$ ligand with amine is required because CO itself cannot displace the $PPh_3$ ligand in **6** to form **15**. Nucleophilic attack of amine on the CO ligand in **15** gives the *cis*-benzoyl(carbamoyl)platinum complex **5** accompanied by liberation of CO and amine originating from the carbamoyl group in the starting complex **6**.

**Relevance of the Behavior of the Platinum Complexes to the Catalytic Double Carbonylation Promoted by Palladium Complexes.** The observation obtained in the present study that employment of a tertiary phosphine such as $PPh_3$ having less coordinating ability than $PMe_3$ allows the formation of *cis*-benzoyl(carbamoyl)platinum complexes through a trans to cis isomerization is associated with the experimental results regarding the catalytic system; i.e., bulkier and less basic tertiary phosphines serve as more effective ligands in the catalytic systems than a basic and compact phosphine such as $PMe_3$. The present results indicate two possible routes for the formation of the *cis*-benzoyl–carbamoyl complexes involving substitution of the tertiary phosphine ligand L. The first is replacement of L without halide ionization (eq 14), and the other is transformation of the already formed *trans*-benzoyl–carbamoyl complexes into their cis isomers (eq 15). Although it is difficult to decide which process is operative in the actual catalytic systems, the inapplicability of the usual aryl chlorides to the double carbonylation due to the difficulty of their oxidative addition to the Pd(0) species to give the arylpalladium chloride (A in Scheme I) relieves us from the need to consider a process such as eq 14. Since *trans*-$Pd(COPh)I(PMePh_2)_2$ was previously observed to exchange rapidly with CO, retaining the two mutually trans phosphine ligands under CO pressure to give *trans*-$[Pd(COPh)(CO)(PMePh_2)_2]I$,[3e] it is likely that the first product of the reaction of *trans*-$Pd(COPh)I(PMePh_2)_2$ with CO and amine is the *trans*-benzoyl–carbamoyl complex, which was in fact isolated with the $PMe_3$ ligands. Establishment of the isomerization route from the already formed *trans*-benzoyl–carbamoyl complex to its cis isomer (eq 15) is deemed to have clarified the important unsolved problem regarding the route to the *cis*-benzoyl–carbamoyl complex to lend further support for the validity of the mechanism represented by Scheme I.

## Conclusion

The present study revealed that the nature of the tertiary phosphine has a strong influence on the selective formation of the *trans*- and *cis*-benzoyl(carbamoyl)platinum complexes and on their isomerization behavior. A previously unknown mechanism for converting the *trans*-benzoyl(carbamoyl)platinum complexes to their cis isomers through multistep ligand displacement reactions and nucleophilic attack of amine on the coordinated CO ligands has been found. The likelihood of involvement of such a trans to cis isomerization in the palladium-catalyzed double carbonylation to give $\alpha$-keto amide is suggested.

## Experimental Section

All manipulations were carried out under an atmosphere of argon, nitrogen, or carbon monoxide or in vacuo. $^1H$, $^{13}C$, and $^{31}P$ NMR spectra were measured on JEOL GX-500, GX-270, and FX-100 spectrometers by Dr. Y. Nakamura, Ms. R. Ito, and Ms. A. Kajiwara in our laboratory. $^1H$ and $^{13}C$ signals are referred to $Me_4Si$ as an internal standard and $^{31}P$ NMR signals to an external $PPh_3$ standard. IR spectra were recorded on a JASCO IR-810 spectrometer. Elemental analysis was carried out by Dr. M. Takana and Mr. T. Saito of our laboratory using a Yanagimoto Type MT-2 CHN autocorder. Solvents and amines were dried in the usual manners, distilled, and stored under an argon atmosphere. Carbon monoxide was used as purchased (Nippon Sanso) without further purification. $^{13}CO$ (99% isotopic purity) was purchased from CEA.

The complex *trans*-$Pt(COPh)Cl(PPh_3)_2$ (**1**) was prepared by oxidative addition of PhCOCl to $Pt(PPh_3)_4$.[15] The complex *trans*-$Pt(COPh)Cl(PMe_3)_2$ (**2**) was prepared by the ligand-exchange reaction of **1** and $PMe_3$ in $CH_2Cl_2$ and characterized by means of elemental analysis and NMR and IR spectroscopy: $^1H$ NMR ($CD_2Cl_2$) $\delta$ 1.34 (t, $J$ = 3.8 Hz, 18 H, P*Me*$_3$); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 213.8 (t, $^2J_{P-C}$ = 7 Hz, $^1J_{Pt-C}$ = 1044 Hz, *C*OPh), 13.5 (t, $J$ = 18 Hz, P*Me*$_3$); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) −9.5 ppm (s, $^1J_{Pt-P}$ = 2934 Hz); IR (KBr) 1612 $cm^{-1}$ (*C*OPh). Anal. Calcd for $C_{13}H_{23}OP_2ClPt$: C, 32.0; H, 4.8; Cl, 7.3. Found: C, 31.8; H, 4.8; Cl, 7.4.

**Preparation of *cis*-$Pt(COPh)(CONMe_2)(PPh_3)_2$ (5a).** To a 100-mL glass pressure bottle containing *trans*-$Pt(COPh)Cl(PPh_3)_2$ (1.10 g, 1.28 mmol) was added an acetone solution (2 mL) of $Me_2NH$ (850 $\mu$L, 12.8 mmol) under a nitrogen atmosphere. Carbon monoxide gas (20 atm) was introduced at room temperature, and the white heterogeneous mixture was stirred for 20 h at the same temperature to give a yellow heterogeneous mixture. After the CO gas was purged, the yellow precipitate thus formed was collected by filtration, washed with acetone (3 × 2 mL), and dried under vacuum. The crude product was dissolved in a minimum amount of benzene at room temperature. The resulting yellow solution was diluted with the same volume of $Et_2O$ and cooled to 5 °C to give yellow crystals of **5a** (0.97 g, 85%): $^1H$ NMR ($CD_2Cl_2$, −20 °C) $\delta$ 2.05 (s, 3 H, N*Me*), 3.17 (s, 3 H, N*Me'*). Anal. Calcd for $C_{46}H_{41}NO_2P_2Pt$: C, 61.6; H, 4.6; N, 1.6. Found: C, 61.6; H, 4.7; N, 1.6. The other characteristic data in NMR and IR analyses are listed in Table II.

The $^{13}CO$-labeled complex *cis*-$Pt(COPh)(^{13}CONMe_2)(PPh_3)_2$ (**5a**-$^{13}CO$) was similarly prepared by using $^{13}CO$ gas (1 atm) in place of CO in natural abundance. Since this reaction was carried out at normal pressure, the reaction took 3 days for its completion (55%): IR (KBr) 1600 (*C*OPh), 1515 $cm^{-1}$ ($^{13}C$ONMe$_2$). The $^{13}C\{^1H\}$ NMR spectrum of **5b**-$^{13}CO$ ($CD_2Cl_2$) exhibited a strong signal (dd) arising from the carbonyl carbon in the carbamoyl group at $\delta$ 188.5. The $^{31}P\{^1H\}$ NMR spectrum is illustrated in Figure 1.

Similarly prepared are complexes **5b** (77%), **5c** (50%), and **5d** (80%) by using piperidine, pyrrolidine, and $Et_2NH$ in place of $Me_2NH$, respectively. These complexes were isolated as yellow crystals by recrystallization from a benzene–$Et_2O$ mixture. **5b**: $^1H$ NMR ($CD_2Cl_2$, −20 °C) $\delta$ 0.6–1.8 (br, 7 H, $NCH_2(CH_2)_3$ and NC*H*), 2.4–2.7 (br, 1 H, NC*H*), 3.3–3.6 (br, 1 H, NC*H*), 4.8–5.1 (br, 1 H, NC*H*). Anal. Calcd for $C_{49}H_{45}NO_2P_2Pt$: C, 62.8; H, 4.8; N, 1.5. Found: C, 63.1; H, 5.1; N, 1.5. **5c**: $^1H$ NMR ($CD_2Cl_2$, −20 °C) $\delta$ 1.44 (br, 4 H, $NCH_2(CH_2)_2$), 2.34 (br, 1 H, NC*H*), 2.74 (br, 1 H, NC*H*), 3.42 (br, 1 H, NC*H*), 4.18 (br, 1 H, NC*H*). Anal. Calcd for $C_{48}H_{43}NO_2P_2Pt$: C, 62.5; H, 4.7; N, 1.5. Found: C, 62.5; H, 4.7; N, 1.5. **5d**: $^1H$ NMR ($CD_2Cl_2$, −20 °C) $\delta$ 0.34 (t, $^3J_{H-H}$ = 7 Hz, 3 H, $NCH_2CH_3$), 0.93 (t, $^3J_{H-H}$ = 7 Hz, 3 H, $NCH_2CH_3$), 2.36 (m, 1 H, NC*H*), 2.76 (m, 1 H, NC*H*), 3.05 (m, 1 H, NC*H*), 4.65 (m, 1 H, NC*H*). Anal. Calcd for $C_{48}H_{45}NO_2P_2Pt$: C, 62.3; H, 4.9; N, 1.5. Found: C, 62.2; H, 5.0; N, 1.5. The other NMR data for **5b–d** are summarized in Table II together with IR data.

**Preparation of *trans*-$Pt(COPh)(CONMe_2)(PPh_3)_2$ (6a).** To a Schlenk tube containing *trans*-$[Pt(COPh)(CO)(PPh_3)_2]BF_4$ (**7**; 2.74 g, 2.92 mmol) in acetone (6 mL) was added $HNMe_2$ (1.94 mL, 29.2 mmol) under a nitrogen atmosphere at room temperature. The yellow suspension quickly turned to an orange solution, from which an orange precipitate gradually formed. The resulting precipitate was filtered, washed with acetone (3 × 2 mL), and dried under vacuum. The crude product was recrystallized from a $CH_2Cl_2$–$Et_2O$ mixture to give orange crystals of complex **6a** (1.97 g, 80.5%): $^1H$ NMR ($CD_2Cl_2$, −20 °C) $\delta$ 1.88 (s, 3 H, N*Me*), 2.73 (s, 3 H, N*Me'*). Anal. Calcd for $C_{46}H_{41}NO_2P_2Pt$: C, 61.6; H, 4.6; N, 1.6. Found: C, 62.2; H, 4.8; N, 1.7. The other spectroscopic data are listed in Table I.

The $^{13}CO$-labeled complex *trans*-$Pt(COPh)(^{13}CONMe_2)(PPh_3)_2$ (**6a**-$^{13}CO$) was similarly prepared by using *trans*-$[Pt(COPh)(^{13}CO)(PPh_3)_2]BF_4$ in place of complex **7** (72%): IR (KBr)

(15) Ugo, R.; Caliati, F.; La Monica, G. *Inorg. Synth.* **1968**, *11*, 105.

1567 (*CO*Ph), 1495 $cm^{-1}$ ($^{13}CONMe_2$). The $^{13}C\{^1H\}$ NMR spectrum of complex **6a**-$^{13}CO$ exhibited a strong triplet signal due to the carbonyl carbon in the carbamoyl group at $\delta$ 203.6.

The trans complexes **6b** (63%), **6c** (75%), and **6d** (45%) were prepared by similar procedures with piperidine, pyrrolidine, and $Et_2NH$ in place of $Me_2NH$, respectively, and isolated as reddish orange crystals by recrystallization from a $CH_2Cl_2$–$Et_2O$ mixture (+25 to −20 °C). Complex **6b** was isolated as orange crystals containing 1 equiv of $CH_2Cl_2$. **6b**: $^1H$ NMR ($CD_2Cl_2$, −20 °C) $\delta$ 0.88–1.16 (br, 6 H, $NCH_2(CH_2)_3$), 2.72 (br, 2 H, $NCH_2$), 3.67 (br, 2 H, $NCH_2$). Anal. Calcd for $C_{49}H_{45}NO_2P_2Pt{\cdot}CH_2Cl_2$: C, 58.8; H, 4.6; N, 1.5; Cl, 6.9. Found: C, 58.7; H, 4.8; N, 1.2; Cl, 7.2. **6c**: $^1H$ NMR ($CD_2Cl_2$, −20 °C) $\delta$ 1.10 (br, 4 H, $NCH_2(CH_2)_2$), 2.45 (br, 2 H, $NCH_2$), 3.27 (br, 2 H, $NCH_2$). Anal. Calcd for $C_{48}H_{43}NO_2P_2Pt$: C, 62.5; H, 4.7; N, 1.5. Found: C, 62.8; H, 4.7; N, 1.2. **6d**: $^1H$ NMR ($CD_2Cl_2$, −60 °C) $\delta$ 0.26 (br, 6 H, $NCH_2CH_3$), 2.53 (br, 2 H, $NCH_2$), 3.90 (br, 2 H, $NCH_2$). Anal. Calcd for $C_{48}H_{45}NO_2P_2Pt$: C, 62.3; H, 4.9; N, 1.5. Found: C, 62.6; H, 4.8; N, 1.5. The other spectroscopic data for **6b–d** are summarized in Table I.

**Preparation of *trans*-[Pt(COPh)(piperidine)($PPh_3$)$_2$]$BF_4$ (8b).** To a dichloromethane solution (5 mL) of *trans*-[Pt(COPh)(acetone)($PPh_3$)$_2$]$BF_4$ (0.803 g, 0.828 mmol) was added piperidine (0.82 mL, 8.3 mmol) under a nitrogen atmosphere at −30 °C. The resulting pale yellow solution was stirred for 20 min at the same temperature, and then $Et_2O$ (10 mL) was added to the solution to give a pale yellow precipitate of **8b**, which was filtered, washed with $Et_2O$ (3 × 5 mL) and dried under vacuum (0.743 g, 90%): $^1H$ NMR ($CD_2Cl_2$, −20 °C) $\delta$ 1.0–1.2 (br, 2 H, $N(CH_2)_2CH_2$, 1.3–1.5 (br, 4 H, $N(CH_2)CH_2$), 2.4–2.6 (br, 4 H, $NCH_2$), 2.8 (br, 1 H, NH); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 207.5 (br, *CO*Ph); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) 24.0 ppm (s, $^1J_{Pt-P}$ = 3418 Hz); IR (KBr) 3244 (NH), 1632 $cm^{-1}$ (*CO*Ph).

**Preparation of *trans*-[Pt(COPh)(CO)($PMe_3$)$_2$]$BF_4$ (10).** The complex *trans*-Pt(COPh)Cl($PMe_3$)$_2$ (0.702 g, 1.44 mmol) and $AgBF_4$ (0.280 g, 1.44 mmol) were placed in a 50-mL Schlenk tube equipped with a rubber septum cap, and the system was purged with CO gas. Dichloromethane (2 mL) was added to the system by means of a syringe at −20 °C to give a colorless solution containing a white precipitate of AgCl. After the mixture was stirred while CO gas was passed through the solution for 1 h at room temperature, the precipitate of AgCl was removed by filtration, and then $Et_2O$ (5 mL) was slowly added to the filtrate at −20 °C to give a white crystalline precipitate of **10**. The product was filtered washed with $Et_2O$ (3 × 5 mL), and dried under vacuum (0.669 g, 82%): $^1H$ NMR ($CD_2Cl_2$) $\delta$ 1.60 (t, $J$ = 4.3 Hz, P*Me*$_3$); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 227.0 (t, $^2J_{P-C}$ = 10 Hz, $^1J_{Pt-C}$ = 814 Hz, *C*OPh), 178.2 (t, $^2J_{P-C}$ = 10 Hz, $^1J_{Pt-C}$ = 877 Hz, Pt*C*O), 15.1 (t, $J$ = 20 Hz, P*Me*$_3$); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) −13.1 ppm (s, $^1J_{Pt-P}$ = 2602 Hz), IR (KBr) 2110 (Pt*CO*), 1624 $cm^{-1}$ (*CO*Ph). Anal. Calcd for $C_{14}H_{23}BF_4O_2P_2Tp$: C, 29.6; H, 4.1. Found: C, 28.8; H, 4.2.

**Preparation of *trans*-Pt(COPh)(CON$\overline{(CH_2)_4CH_2}$)($PMe_3$)$_2$ (9b).** To a dichloromethane solution (2 mL) of *trans*-[Pt(COPh)(CO)($PMe_3$)$_2$]$BF_4$ (0.39 g, 0.69 mmol) was added piperidine (0.68 mL, 6.9 mmol) at room temperature. The colorless solution quickly turned orange. After the system was stirred for 30 min, $Et_2O$ (10 mL) was added to the solution to give an orange powder of **9b**, which was filtered, washed with $Et_2O$, and dried under vacuum (0.27 g, 69%): $^1H$ NMR ($CD_2Cl_2$) $\delta$ 3.97 (br, 2 H, $NCH_2$), 3.47 (br, 2 H, $NCH_2$), 1.65, 1.56, and 1.45 (br, 2 H each, $NCH_2(CH_2)_3$). The other spectroscopic data are listed in Table I. Anal. Calcd for $C_{19}H_{33}NO_2P_2Pt$: C, 40.4; H, 5.9; N, 2.5. Found: C, 40.0; H, 5.9; N, 2.5.

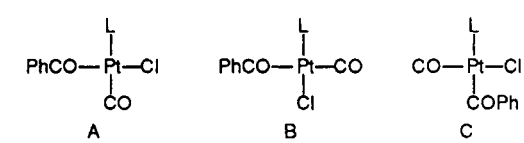
The complex *trans*-Pt(COPh)Cl($PMe_3$)$_2$ (0.030 g, 0.062 mmol) was placed in a pressurizable NMR sample tube and dissolved in $CD_2Cl_2$ (0.8 mL) under an argon atmosphere. Piperidine (90 $\mu$L, 0.92 mmol) was added, and then CO gas (10 atm) was introduced at room temperature. $^{31}P\{^1H\}$ NMR spectra of the solution were observed at intervals. Initially, the NMR spectrum exhibited a singlet due to the benzoyl chloride complex at −9.5 ppm ($^1J_{Pt-P}$ = 2934 Hz), which was gradually replaced by a new singlet at −15.3 ppm ($^1J_{Pt-P}$ = 2887 Hz) assignable to the benzoyl–carbamoyl complex **9b**. After 2 h the signal due to the starting complex disappeared and complex **9b** was observed as the only reaction product. Also noted was precipitation of white crystals of the piperidinium salt in the solution. After the CO gas was purged, the white crystals were removed by filtration and the filtrate was connected to dryness under reduced pressure to give an orange solid of **9b**, which was identified by means of IR spectroscopy.

The isolated complex **9b** (0.032 g, 0.056 mmol) was placed in a pressurizable NMR sample tube and dissolved in $CD_2Cl_2$ (0.8 mL) and piperidine (50 $\mu$L) under an argon atmosphere. After CO gas (10 atm) was introduced, the system was allowed to stand at room temperature and monitored by means of $^{31}P\{^1H\}$ NMR spectroscopy. After 4 days no reaction took place, complex **9b** being observed as the only platinum–phosphine species.

**Preparation of Pt(COPh)Cl(piperidine)($PPh_3$) (11b).** To a Schlenk tube containing $Pt_2(COPh)_2(\mu\text{-}Cl)_2(PPh_3)_2$ (1.48 g, 1.22 mmol) was added a benzene solution (5 mL) of piperidine (133 $\mu$L, 1.34 mmol). After the system was stirred for 30 min at room temperature, pentane (10 mL) was slowly added to the pale yellow solution to give pale yellow crystals of **11b**, which were filtered and dried under vacuum (1.63 g, 88%). This crystalline product contains 1 equiv/equiv of **11b** of benzene as confirmed by $^1H$ NMR spectroscopy: $^1H$ NMR ($CD_2Cl_2$) $\delta$ 1.2–1.6 (br, 6 H, $NCH_2(CH_2)_3$), 2.64 (br, 2 H, $NCH_2$), 3.42 (br, 2 H, $NCH_2$), 3.67 (br, 1 H, NH); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 212.4 (d, $^2J_{P-C}$ = 7 Hz, *C*OPh); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 15.6 ppm (s, $^1J_{Pt-P}$ = 4387 Hz); IR (KBr) 3174 (NH), 1613 $cm^{-1}$ (*CO*Ph). Anal. Calcd for $C_{30}H_{32}NOPClPt{\cdot}C_6H_6$: C, 56.8; H, 4.9; N, 1.8; Cl, 4.7. Found: C, 57.2; H, 5.1; N, 1.9; Cl, 4.7.

**NMR Examination of the Reaction of *trans*-Pt(COPh)Cl($PPh_3$)$_2$ (1) with CO and Piperidine. 1. Reaction of 1 and CO under Pressure in the Presence of $S_8$.** To a pressurizable NMR sample tube containing complex **1** (60 mg, 0.070 mmol) and a yellow solid of sulfur (11 mg) were added chlorobenzene (0.9 L) and $C_6H_6$ (0.1 mL) at room temperature under an argon atmosphere. After CO gas (10 atm) was introduced, the resulting mixture was examined with time by $^{31}P\{^1H\}$ NMR spectroscopy. When the system was allowed to stand at room temperature, a singlet at 48.4 ppm arising from S=$PPh_3$ and three singlets with $^{195}Pt$ satellites at 21.3 ppm ($^1J_{Pt-P}$ = 2385 Hz, signal a), 15.5 ppm ($^1J_{Pt-P}$ = 3037 Hz, signal b), and 22.0 ppm ($^1J_{Pt-P}$ = 1340 Hz, signal c) gradually increased at the expense of the peaks due to **1** at 26.1 ppm (s, $^1J_{Pt-P}$ = 3406 Hz). The peak integration for S=$PPh_3$ agreed very closely with the total integration for signals a–c in every NMR run. Furthermore, the decrease of **1** has been found to obey first-order kinetics regarding the concentration of **1** ($k_{obsd}$ = 1.7 × $10^{-6}$ $s^{-1}$). In the $^{31}P\{^1H\}$ NMR spectrum after 10 days, where 98% of **1** was consumed and 94% of S=$PPh_3$ was formed, signals a–c were observed in a ratio of 60:27:13. After the CO gas was purged, the NMR sample solution was concentrated to dryness under reduced pressure to give a yellow precipitate. This solid exhibited two strong absorptions due to terminal carbonyl groups at 2100 and 2065 $cm^{-1}$ in its IR spectrum (KBr).

These observations indicate the occurrence of a ligand-exchange reaction of **1** and CO to give the three benzoyl–carbonyl geometrical isomers A–C, which correspond to the signals a–c in the $^{31}P\{^1H\}$ NMR spectrum, respectively. This reaction also forms




free $PPh_3$, which may rapidly react with sulfur to give S=$PPh_3$. The NMR assignments of these three isomers were determined on the basis of the $^1J_{Pt-P}$ values, which are in fair agreement with the reported values for three geometrical isomers of PtPh(CO)Cl($PPh_3$).[16]

**2. Reaction of 1 and Piperidine.** To an NMR sample tube containing complex **1** (0.045 g, 0.053 mmol) were added chlorobenzene (0.36 mL), $C_6D_6$ (0.04 mL), and piperidine (0.1 mL, 1.0 mmol) at room temperature under $N_2$. The color of the resulting solution changed from pale yellow to yellow immediately. The

(16) Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* **1980**, 712.

$^{31}P\{^1H\}$ NMR spectrum of the reaction solution showed two singlets with $^{195}Pt$ satellites at 26.0 ppm ($J_{Pt-P}$ = 3412 Hz) and 15.6 ppm ($J_{Pt-P}$ = 4387 Hz) due to complex **1** and a piperidine-coordinated complex, Pt(COPh)(Cl)(piperidine)($PPh_3$) (**11b**), in a ratio of 4.74:1. In addition to these signals, a very broad peak at about −0.1 ppm due to free $PPh_3$ was also observed. When the temperature was decreased to −50 °C, the broad signal of free $PPh_3$ became a sharp singlet. Adding piperidine and free $PPh_3$ to the reaction solution altered the ratio of **1** and **11b** according to eq 16.

$$K_{obs} = \frac{[\mathbf{11b}][PPh_3]}{[\mathbf{1}][HNR_2]} \qquad (16)$$

$HNR_2$ = 

When the concentrations of piperidine (19 and 38 equiv/equiv of Pt; no $PPh_3$ was added) and added $PPh_3$ (0.20 and 0.58 equiv/equiv of Pt; the concentration of piperidine was 38 equiv/equiv of Pt) in the solution were varied, the ratios of complexes **1** and **11b** were observed as 4.74, 3.00, 4.85, and 8.33, respectively. When the ratios of **11b** and **1** were plotted versus the ratios of amounts of piperidine and $PPh_3$, the equilibrium constant in eq 16 was determined as $(2.1 \pm 0.2) \times 10^{-3}$.

**3. Reaction of 1 and Piperidine under CO.** To a Schlenk tube containing complex **1** (0.065 g, 0.076 mmol) were added PhCl (0.63 mL), $C_6D_6$ (0.07 mL), and piperidine (0.11 mL, 1.1 mmol) under $N_2$ at room temperature. The resulting yellow solution was immediately transferred to a pressurizable NMR sample tube by means of a syringe. The $^{31}P\{^1H\}$ NMR spectrum of this solution showed two singlets with $^{195}Pt$ satellites due to **1** and **11b** at 26.0 ppm ($^1J_{Pt-P}$ = 3412 Hz) and 15.6 ppm ($^1J_{Pt-P}$ = 4381 Hz) in a ratio of 5.0:1 accompanied by a broad peak at −0.1 ppm due to free $PPh_3$. After the reaction system was evacuated, CO (10 atm) was introduced into the NMR sample tube and the reaction solution was examined by $^{31}P\{^1H\}$ NMR spectroscopy immediately. In the first NMR run after 5 min, the ratio of complexes **11b** and **1** rapidly decreased to ca. 1:30, while the signal of free $PPh_3$ changed to a sharp singlet and no *cis*-benzoyl–carbamoyl complex **5b** was observed. The AB quartet of complex **5b** (20.8 ppm, $^1J_{Pt-P}$ = 1578 Hz; 19.8 ppm, $^1J_{Pt-P}$ = 1834 Hz; $^2J_{P-P}$ = 18 Hz) was observed to be formed smoothly after 11 min. At the end of the reaction after ca. 2 h, the signals arising from **1**, **11b**, and free $PPh_3$ completely disappeared and the signal of **5b** was observed in 99% selectivity together with some unidentified small peaks. In the process of formation of the cis complex **5b**, the signal of its trans isomer **6b** has never been observed.

**NMR Examination of the Trans–Cis Isomerization of *trans*-Pt(COPh)($CONR_2$)($PPh_3$)$_2$ (6). 1. Trans–Cis Isomerization of 6 in the Absence of Amine and CO.** As a typical example, complex **6a** (0.027 g, 0.03 mmol) was introduced into an NMR sample tube and dissolved in $CD_2Cl_2$ (0.4 mL) at room temperature under $N_2$. The NMR sample tube was then evacuated and sealed. The resulting orange solution was examined with time by $^{31}P\{^1H\}$ NMR spectroscopy at 26 °C. The color of the solution slowly turned to bright yellow, and the signal of the starting complex **6a** at 20.2 ppm with $^{195}Pt$ satellites ($^1J_{Pt-P}$ = 3296 Hz) was replaced by an AB quartet with $^{195}Pt$ satellites at 19.4 ppm ($^1J_{Pt-P}$ = 1565 Hz, $^2J_{P-P}$ = 18 Hz) and 20.2 ppm ($^1J_{Pt-P}$ = 1898 Hz) arising from the cis isomer **5a**. The reaction was complete within 1 week. From the pseudo-first-order plot for the conversion of the trans isomer, the rate constant $k_{obsd}$ was obtained as $3.2 \times 10^{-6}$ s$^{-1}$. The resulting cis isomer **5a** was found to react subsequently with the solvent to give complex **1** (26.1 ppm, $^1J_{Pt-P}$ = 3398 Hz) in about 10% yield at the end of the isomerization. In a similar way, the rate constants for the trans–cis isomerization of complexes **6b–d** in the absence of amine and CO were determined as $3.8 \times 10^{-6}$, $8.8 \times 10^{-6}$, and $1.9 \times 10^{-5}$ s$^{-1}$, respectively.

**2. Isomerization of 6b in the Presence of Piperidine and CO.** The $^{31}P\{^1H\}$ NMR spectrum of a $CD_2Cl_2$ solution (1 mL) of complex **6b** (0.046 g, 0.05 mmol) under CO (1 atm) showed a singlet with $^{195}Pt$ satellites (19.9 ppm, $^1J_{Pt-P}$ = 3342 Hz). After piperidine (0.015 mL, 0.15 mmol) was added to the solution, the change of the $^{31}P\{^1H\}$ NMR spectrum with time was followed. The signal of the cis isomer **5b** (19.4 ppm, $^1J_{Pt-P}$ = 1861 Hz; 19.9 ppm, $^1J_{Pt-P}$ = 1588 Hz; $^2J_{P-P}$ = 18 Hz) was found to increase smoothly at the expense of **6b** accompanied by a small, sharp peak at −0.1 ppm due to free $PPh_3$. The decrease in **6b** obeys first-order kinetics (90, 50, 30, and 15% of **6b** were observed to remain after 5, 17, 28, and 38 min) with $k_{obsd} = 8.9 \times 10^{-4}$ s$^{-1}$. The reaction was complete within 2 h with selective formation of the cis isomer **5b**.

**3. Reaction of 6b with Piperidine and $^{13}CO$.** To a $CD_2Cl_2$ (0.4 mL) solution of **6b** (0.03 g, 0.032 mmol) was added piperidine (0.033 mL, 0.33 mmol) under $^{13}CO$ at room temperature. After 2 h, the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution showed two sets of doublets of doublets with $^{195}Pt$ satellites due to the $^{13}C$-labeled complex **5b**-$^{13}CO$ ($P^1$ (trans to the carbamoyl group) 19.4 ppm, $^1J_{Pt-P}$ = 1861 Hz, $^2J_{P-C}$ = 117 Hz; $P^2$ (cis to the carbamoyl group) 19.9 ppm, $^1J_{Pt-P}$ = 1588 Hz, $^2J_{P-C}$ = 13 Hz; $^2J_{P-P}$ = 18 Hz). No signal for **5b**-$^{12}CO$ was observed.

**4. Reaction of 6b with Pyrrolidine and CO.** Complex **6b** (0.045 g, 0.048 mmol) was dissolved in $CD_2Cl_2$ (0.4 mL), and pyrrolidine (0.016 mL, 0.20 mmol) was added to the orange solution under CO (1 atm) at room temperature. The $^{31}P\{^1H\}$ NMR spectrum of the reaction solution after 2 h shows one AB quartet with $^{195}Pt$ satellites ($P^1$ (trans to carbamoyl group) 18.7 ppm, $^1J_{Pt-P}$ = 1814 Hz; $P^2$ (cis to carbamoyl group) 20.7 ppm, $^1J_{Pt-P}$ = 1648 Hz; $^2J_{P-P}$ = 18 Hz). The spectrum was in agreement with that of **5c** prepared by reaction 2.

**5. Reaction of 7 with Piperidine under CO.** To a $CD_2Cl_2$ solution (1 mL) of complex **6b** (0.054 g, 0.055 mmol) was added piperidine (0.015 mL, 0.15 mmol) under CO (1 atm). The change of the $^{31}P\{^1H\}$ NMR spectrum with time was examined. The main signal of the *trans*-benzoyl–carbamoyl complex **6b** (s, 19.3 ppm, $J_{Pt-P}$ = 3341 Hz, 95% yield) was formed in the first NMR run after 10 min, while the signal of the starting complex **7** completely disappeared. After 10 min, the AB quartet of the cis isomer **5b** increased smoothly at the cost of the singlet of the complex **6b**. A small singlet at −0.1 ppm due to free $PPh_3$ was observed accompanying the formation of **5b** while the $PPh_3$ peak disappeared at the end of the reaction.

**6. Reaction of 8b with Piperidine under CO.** The piperidine-coordinated complex **8b** (0.131 g, 0.131 mmol) was dissolved in $CD_2Cl_2$ (1 mL), and piperidine (0.04 mL, 0.40 mmol) was added under CO (1 atm). The $^{31}P\{^1H\}$ NMR spectrum of the solution was examined with time. The signal of the starting complex **8b** at 24.0 ppm ($^1J_{Pt-P}$ = 3418 Hz) decreased smoothly to about 10% of its original amount and the signal of the *trans*-benzoyl–carbamoyl complex **6b** increased to 90% yield after 35 min. The AB quartet of the cis isomer **5b** began to be observed after 45 min, and it increased smoothly at the expense of the signal of the trans isomer **6b**.

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