

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

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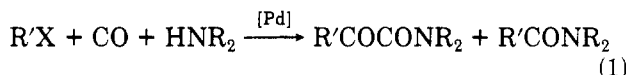
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trans-Pt(COPh)Cl(PPh₃)₂ (1) reacts with secondary amines under CO pressure (10 atm) at room temperature to give *cis*-Pt(COPh)(CONR₂)(PPh₃)₂ complexes (NR₂ = NMe₂ (5a), N(CH₂)₄CH₂ (5b), N(CH₂)₃CH₂ (5c), NEt₂ (5d)) exclusively, while the same amines react with *trans*-[Pt(COPh)(CO)(PPh₃)₂]BF₄ (7) under a nitrogen atmosphere to afford *trans*-Pt(COPh)(CONR₂)(PPh₃)₂ complexes (NR₂ = NMe₂ = NMe₂ (6a), N(CH₂)₄CH₂ (6b), N(CH₂)₃CH₂ (6c), NEt₂ (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 PMe₃ ligands, *trans*-Pt(COPh)Cl(PMe₃)₂ (2) and *trans*-[Pt(COPh)(acetone)(PMe₃)₂]BF₄ (4), give *trans*-Pt(COPh)(CONR₂)(PMe₃)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

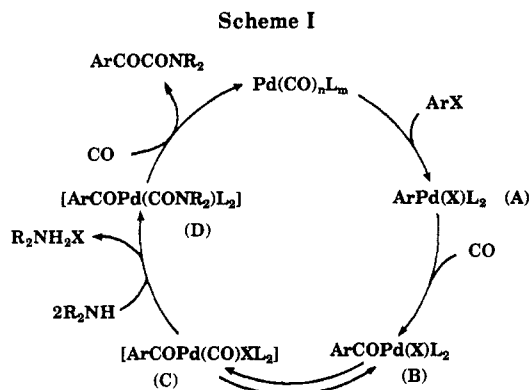
The palladium-catalyzed double carbonylations of organic halides and secondary amines provide convenient synthetic means for preparing α -keto amides.^{1,2}



R' = 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 PMe₃-coordinated benzoylpalladium complexes *trans*-[Pd(COPh)(acetone)(PMe₃)₂]X (X = BF₄, PF₆) and *trans*-Pd(COPh)Cl(PMe₃)₂ with secondary amines and CO give the isolable benzoyl(carbamoyl)palladium complexes *trans*-Pd(COPh)(CONR₂)(PMe₃)₂.⁵ The PMe₃-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-PtR₂L₂ 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



*L = tertiary phosphine.

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

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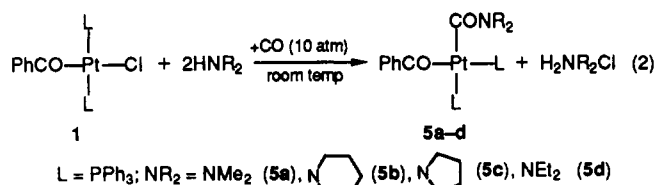
proper choice of the starting benzoylplatinum complexes and the reaction conditions.^{7,8} Detailed studies on the formation pathways of *trans*- and *cis*-benzoyl(carbamoyl)platinum complexes as well as the *trans* to *cis* isomerization process have provided further insight into the mechanistic details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

Results

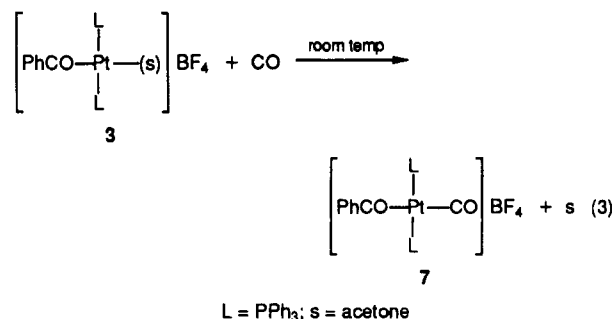
Selective Synthesis of *trans*- and *cis*-Benzoyl-(carbamoyl)platinum Complexes by the Reactions of Benzoylplatinum Complexes with CO and Secondary Amines. The previous study regarding solvent effects on the reaction of *trans*-Pd(COPh)X(PMePh₂)₂ (X = Cl, Br, I) with CO and secondary amine to give an α -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)(PMePh₂)] generated by ligand exchange of the PMePh₂ ligand with CO. When the bromide and iodide complexes were used, on the other hand, the reactions were indicated to involve ionization of these halide ligands to give ionic *trans*-[Pd(COPh)(CO)L₂]⁺X⁻ intermediates. Therefore, we started the present study by examining reactivities toward CO and amines of neutral benzoylplatinum complexes, *trans*-Pt(COPh)Cl(PPh₃)₂ (1) and *trans*-Pt(COPh)Cl(PMe₃)₂ (2), and of ionic benzoylplatinum complexes, *trans*-[Pt(COPh)(acetone)(PPh₃)₂]BF₄ (3) and *trans*-[Pt(COPh)(acetone)(PMe₃)₂]BF₄ (4).

1. Reactions of PPh₃-Coordinated Benzoylplatinum Complexes (1 and 3). The neutral and ionic PPh₃-coordinated complexes (1 and 3, respectively) exhibit reaction behavior considerably different from each other.

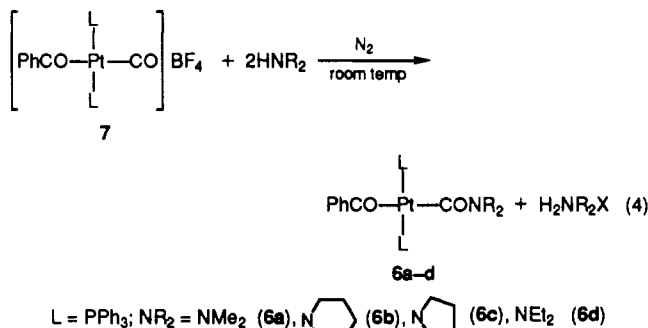
The neutral benzoyl chloride complex 1 reacts smoothly with secondary amines under CO pressure at room temperature to give the *cis* complexes *cis*-Pt(COPh)(CONR₂)(PPh₃)₂ (5a-d), selectively, which have been isolated as bright yellow crystals by recrystallization from benzene-Et₂O mixtures.



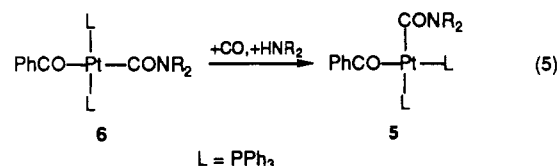
The ionic benzoylplatinum complex 3, on the other hand, forms benzoyl-carbamoyl complexes with different geometries (*trans* and *cis*) depending upon the reaction conditions. Selective synthesis of *trans*-benzoyl-carbamoyl complexes (6) can be achieved by the following sequence of reactions. Treatment 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



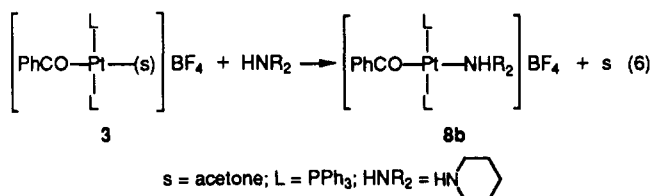
crystals by recrystallization from CH₂Cl₂-Et₂O mixtures.



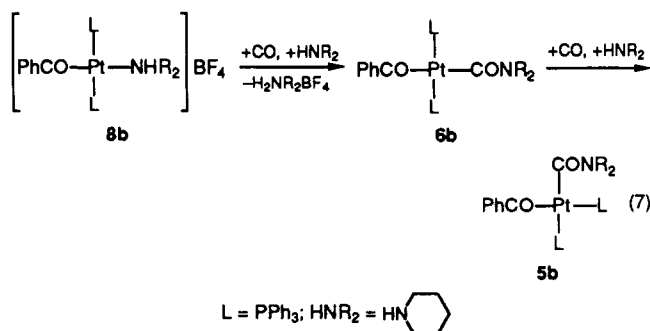
Reaction 4 was performed *in the absence of free CO*. In contrast, when the reaction of 7 and secondary amine was carried out *under a CO atmosphere* (1 atm), the reaction gave a mixture of *cis*- and *trans*-benzoyl-carbamoyl complexes, with the *cis*:*trans* ratio increasing with time. As described 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 AgBF₄ under CO.⁸

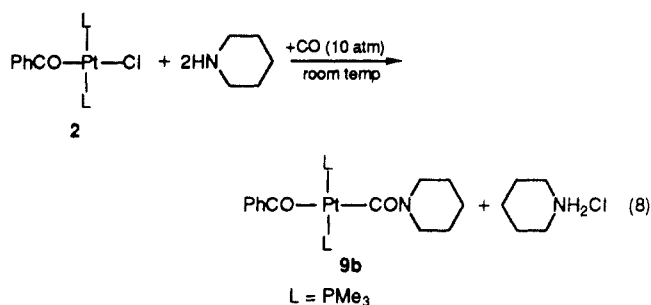
Table I. Characteristic NMR and IR Data for *trans*-Pt(COPh)(CONR₂)L₂ Complexes^a

complex	¹³ C{ ¹ H} NMR ^b		³¹ P{ ¹ H} NMR ^c		IR, ^d cm ⁻¹
	δ	² J _{P-C} , Hz	δ	¹ J _{Pt-P} , Hz	
6a	259.4 (t)	10	21.7 (s)	3258	1567
	203.6 (t) ^e	13			1525/
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 ^f				

^a¹H NMR data are reported in the Experimental Section.

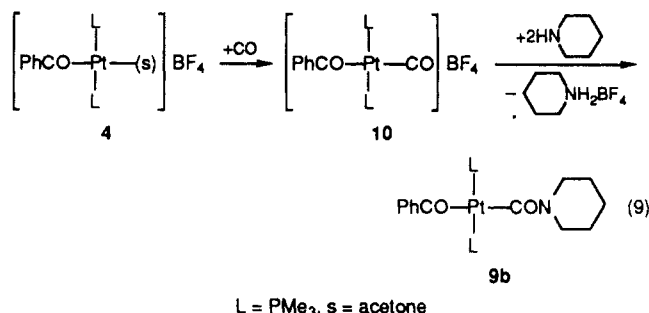
^bSignals due to the carbonyl carbons; at 125 MHz except for 6b (67.8 MHz), in CD₂Cl₂, at room temperature. ^c40 MHz, in CD₂Cl₂, at -20 °C. Chemical shifts are referred to PPh₃ as an external standard. ^dν(CO) bands; in KBr disks. ^e¹J_{Pt-C} = 1190 Hz, determined by using *trans*-Pt(COPh)(¹³CONMe₂)(PMe₃)₂. ^fν(¹³CO) = 1495 cm⁻¹. ^gSignal due to the PMe₃ carbons; virtual triplet, *J* = 19 Hz.

2. Reactions of PMe₃-Coordinated Benzoyl-platinum Complexes (2 and 4). Reactions of the PMe₃-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(CH₂)₄CH₂)(PMe₃)₂ (9b), selectively. The same complex 9b can be



prepared by starting from the ionic benzoylplatinum complex 4 as illustrated in eq 9. In contrast to the *trans*-benzoyl-carbamoyl complexes coordinated with PPh₃ ligands (6a-d), the PMe₃ 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 ν(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 ν(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 ¹³CO (see Experimental Section).

The geometry at the platinum center has been determined by NMR spectroscopy. In the ¹³C{¹H} NMR spectra, the *trans*-benzoyl-carbamoyl complexes show two sets of triplets around δ 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 δ 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')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 ¹³CO. For example, *trans*-Pt(COPh)(¹³CONMe₂)(PPh₃)₂ (6a-¹³CO) with the ¹³CO label at the carbamoyl group exhibits a strong triplet signal at δ 203.6 with ¹⁹⁵Pt satellites (*J*_{Pt-C} = 701 Hz) in the ¹³C NMR spectrum.

In the ³¹P{¹H} NMR spectra, the phosphorus nuclei in the *trans* complexes are observed as a singlet with ¹⁹⁵Pt satellites, while those in the *cis* isomers appear as an AB quartet with ¹⁹⁵Pt 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*-PtR₂(PR')₂ type complexes having R groups with *trans* influence greater than that of the PR'₃ ligands. As shown in Figure 1, the ³¹P{¹H} NMR spectrum of the ¹³CO-enriched *cis*-Pt(¹²COPh)(¹³CONMe₂)(PPh₃)₂ (6a-¹³CO) exhibits two sets of doublets of doublets with ¹⁹⁵Pt 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 ¹³C 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)(CONR₂)(PPh₃)₂ Complexes^a

complex	¹³ C{ ¹ H} NMR ^b		³¹ P{ ¹ H} NMR ^c		IR, ^d cm ⁻¹
	δ	² J _{P-C} , Hz	δ	¹ J _{Pt-P} , Hz	
5a	237.1 (dd)	110, 10	20.6 (d)	1584	1600
	188.5 (dd) ^e	120, 13		1907	1550/
5b	236.9 (dd)	110, 10	20.7 (d)	1602	1608
	186.4 (dd)	120, 13		1874	1550
5c	238.7 (dd)	110, 10	22.0 (d)	1629	1600
	187.5 (dd)	120, 13		1803	1540
5d	236.4 (dd)	110, 10	19.6 (d)	1587	1600
	187.6 (dd)	120, 13		1879	1545

^a¹H NMR data are reported in the Experimental Section. ^bSignals due to the carbonyl carbons; at 125 MHz, in CD₂Cl₂, at room temperature. ^c40 MHz, in CD₂Cl₂, at -20 °C. Chemical shifts are referred to PPh₃ as an external standard. ^dν(CO) bands; in KBr disks. ^e¹J_{Pt-C} = 701 Hz, determined by using *trans*-Pt(COPh)(¹³CONMe₂)(PPh₃)₂. ^fν(¹³CO) = 1515 cm⁻¹.

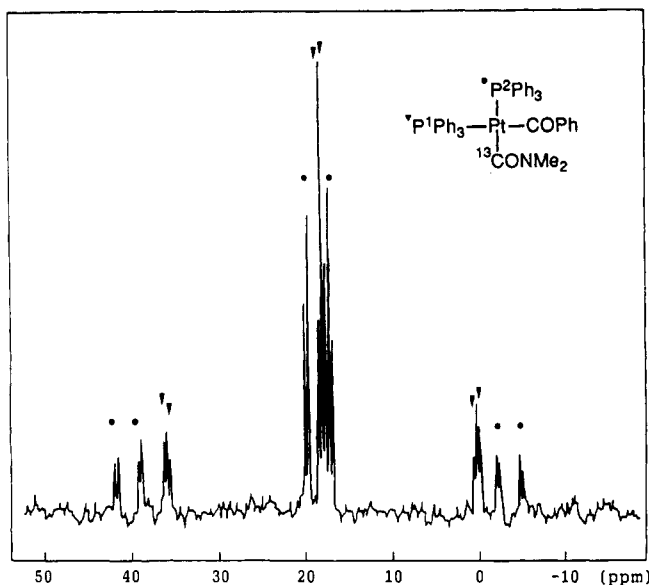


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of *cis*-Pt-($^{12}\text{COPh}$)($^{13}\text{CONMe}_2$)(PPh_3) $_2$ in CD_2Cl_2 at room temperature (40 MHz; chemical shifts are referred to external PPh_3). The filled triangles ($\blacktriangledown$) denote signals due to the phosphorus nucleus cis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

is assigned to the phosphorus trans to the carbamoyl group and the signal (b) with the smaller $^2J_{\text{P-C}}$ value (13 Hz) to the phosphorus trans to the benzoyl group. The former signal (a) has a larger $^1J_{\text{Pt-P}}$ 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 $^{31}\text{P}\{^1\text{H}\}$ 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/eq 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 $\text{S}=\text{PPh}_3$ (94%/equiv of Pt) and three kinds of PPh_3 -coordinated platinum species, probably assignable to three geometrical isomers of $[\text{Pt}(\text{COPh})(\text{CO})(\text{PPh}_3)\text{Cl}]$ (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/eq 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

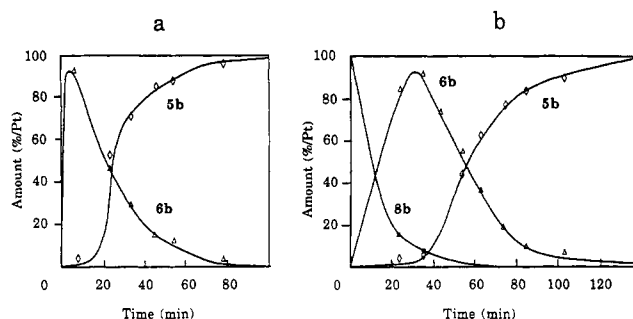
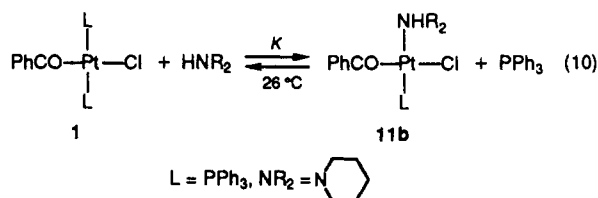


Figure 2. (a) Change of the platinum complexes with time in the reaction of *trans*-[Pt(COPh)(CO)(PPh_3) $_2$] BF_4 (8) and piperidine (4 equiv/eq of Pt) in CD_2Cl_2 under an atmospheric pressure of CO at room temperature to give *trans*-Pt(COPh)-(CON(CH $_2$) $_4$ CH $_2$)(PPh_3) $_2$ (6b) and *cis*-Pt(COPh)-(CH $_2$) $_4$ CH $_2$)(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/eq of Pt) and CO at atmospheric pressure in CD_2Cl_2 at room temperature to give *trans*-Pt(COPh)-(CON(CH $_2$) $_4$ CH $_2$)(PPh_3) $_2$ (6b) and *cis*-Pt(COPh)-(CON(CH $_2$) $_4$ CH $_2$)(PPh_3) $_2$ (5b).

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



piperidine-coordinated benzoylplatinum chloride complex 11b, which was observed as a singlet with ^{195}Pt satellites at 15.6 ppm ($^1J_{\text{Pt-P}} = 4387$ Hz). Liberation of PPh_3 from 1 into the solution was evidenced by observation of a broad ^{31}P NMR signal around 0 ppm¹¹ 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 $\text{Pt}(\text{COPh})(\text{pyridine})\text{Cl}(\text{PPh}_3)$.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 $(2.1 \pm 0.2) \times 10^{-3}$ 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/eq 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 $\delta = -5.9$ 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.

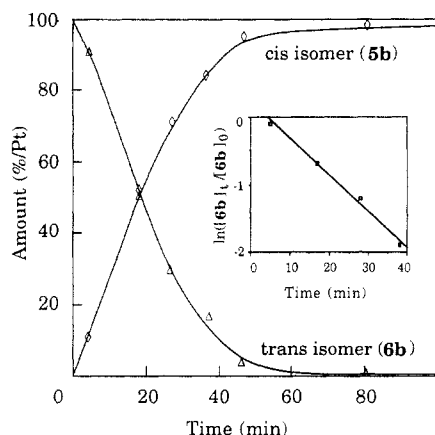


Figure 3. Change of platinum complexes with time in the isomerization of *trans*-Pt(COPh)(CON(CH₂)₄CH₂)(PPh₃)₂ (**6b**) to the *cis* isomer **5b** in CD₂Cl₂ containing piperidine (3 equiv/equiv of Pt) under an atmospheric pressure of CO at room temperature. The first-order plot is shown in the inset.

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 PPh₃ ligands in **1** with amine, a process making the coordination site *cis* to the benzoyl group available for conversion into the carbamoyl group.

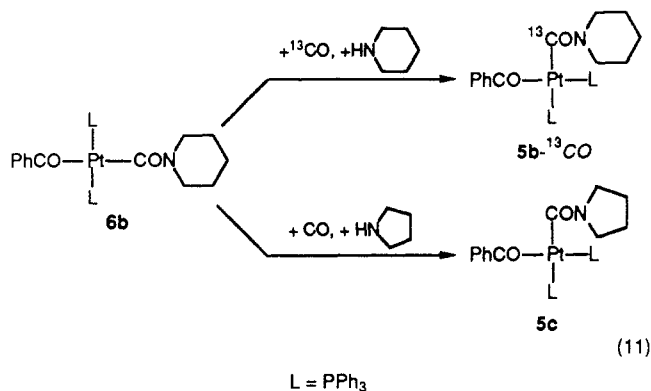
NMR Studies on the Reactions of Ionic Benzoylplatinum Complexes with CO and Amines. Figure 2a illustrates the change of the ionic PPh₃-coordinated benzoyl-carbonyl complex **7** with time on treatment with piperidine in CD₂Cl₂ under a CO atmosphere as followed by ³¹P NMR spectroscopy. For the first NMR 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-(CH₂)₄CH₂}(PPh₃)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 CD₂Cl₂ in the absence of CO and amine at room temperature was also examined by ³¹P 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 CD₂Cl₂ 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 (³¹P NMR). The *trans*-*cis* isomerization obeys first-order kinetics regarding the concentration of **6b** (*k*_{obsd} = 8.9 × 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.

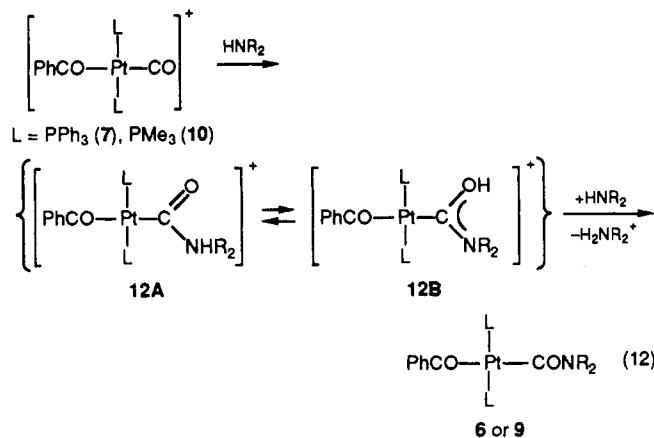
When the isomerization reaction of **6b** with piperidine and ¹³CO is carried out, the ¹³CO-labeled complex *cis*-Pt(COPh){¹³CON(CH₂)₄CH₂}(PPh₃)₂ is formed. Furthermore, the reaction of **6b** with pyrrolidine (4 equiv/equiv of Pt) under a CO atmosphere gives the *cis*-benzoyl-carbamoyl complex with the pyrrolidino group (**5c**) instead of **5b** having the piperidino group in the carbamoyl ligand.



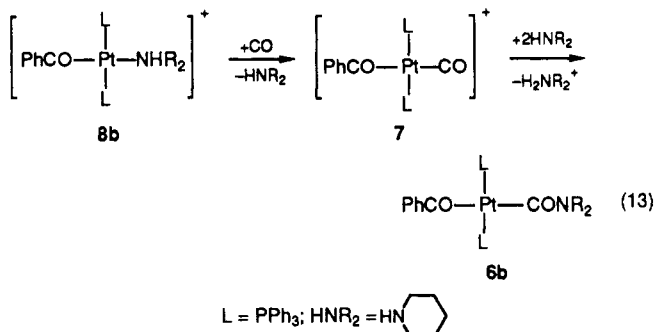
The ³¹P{¹H} NMR spectra of the *trans*-benzoyl-carbamoyl complex **6b** under CO pressure (10 atm) in CD₂Cl₂ at room temperature showed no sign for direct interaction of **6b** with CO. In contrast, liberation of a small amount of PPh₃ was observed in a solution containing **6b** and 4 equiv of piperidine at room temperature as evidenced by the appearance of a very broad signal arising from free PPh₃ 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 PPh₃ was observed throughout the reaction and disappeared at the final stage of the reaction. The behavior of these PPh₃-coordinated benzoylplatinum complexes is in sharp contrast with that of the PMe₃-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

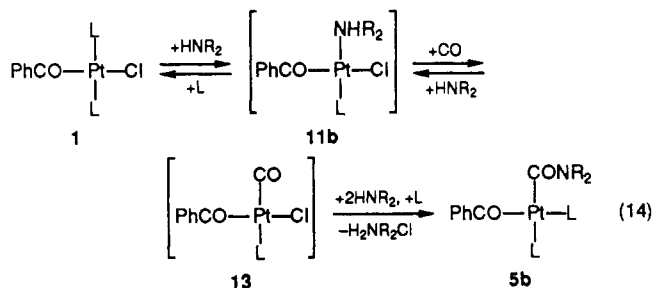


The PPh_3 -coordinated *trans*-benzoyl-carbamoyl complex **6b** is formed also by the reaction of the amine-coordinated ionic complex *trans*-[Pt(COPh){N(H)-(CH₂)₄CH₂}(PPh₃)₂]BF₄ (**8b**) with CO and piperidine. As judged by comparison of the reaction curves in Figure 2, the reaction of the piperidine-coordinated 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



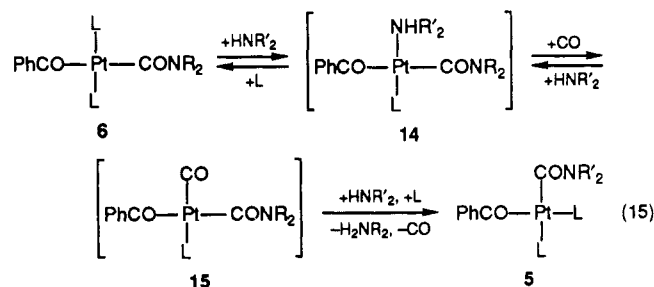
In contrast to the processes giving the *trans*-benzoyl-carbamoyl type complexes, the processes to give the *cis* complexes require dissociation of the tertiary phosphine ligand. The NMR examination of the reaction of the PPh_3 -coordinated benzoylpalladium chloride **1** with CO and piperidine to afford 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(PPh₃)(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)(CONR₂)(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 ¹³CO 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 displacement 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(PMePh₂)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)(PMePh₂)₂]I,³⁶ it is likely that the first product of the reaction of *trans*-Pd(COPh)I(PMePh₂)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 α -keto amide is suggested.

Experimental Section

All manipulations were carried out under an atmosphere of argon, nitrogen, or carbon monoxide or in vacuo. ¹H, ¹³C, and ³¹P NMR spectra were measured on JEOL GX-500, GX-270, and FX-100 spectrometers by Dr. Y. Nakamura, Ms. R. Ito, and Ms. A. Kajiware in our laboratory. ¹H and ¹³C signals are referred to Me₄Si as an internal standard and ³¹P 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 at-

mosphere. Carbon monoxide was used as purchased (Nippon Sanso) without further purification. ¹³CO (99% isotopic purity) was purchased from CEA.

The complex *trans*-Pt(COPh)Cl(PPh₃)₂ (1) was prepared by oxidative addition of PhCOCl to Pt(PPh₃)₄.¹⁵ The complex *trans*-Pt(COPh)Cl(PMe₃)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) δ 1.34 (t, $J = 3.8$ Hz, 18 H, PMe_3); ¹³C{¹H} NMR (CD_2Cl_2) δ 213.8 (t, $^2J_{\text{P-C}} = 7$ Hz, $^1J_{\text{Pt-C}} = 1044$ Hz, COPh), 13.5 (t, $J = 18$ Hz, PMe_3); ³¹P{¹H} NMR (CD_2Cl_2) -9.5 ppm (s, $^1J_{\text{Pt-P}} = 2934$ Hz); IR (KBr) 1612 cm^{-1} (COPh). Anal. Calcd for $\text{C}_{13}\text{H}_{23}\text{OP}_2\text{ClPt}$: C, 32.0; H, 4.8; Cl, 7.3. Found: C, 31.8; H, 4.8; Cl, 7.4.

Preparation of *cis*-Pt(COPh)(CONMe₂)(PPh₃)₂ (5a). To a 100-mL glass pressure bottle containing *trans*-Pt(COPh)Cl(PPh₃)₂ (1.10 g, 1.28 mmol) was added an acetone solution (2 mL) of Me₂NH (850 μL , 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 $\times$ 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 Et₂O and cooled to 5 $^\circ\text{C}$ to give yellow crystals of 5a (0.97 g, 85%): ¹H NMR (CD_2Cl_2 , -20 $^\circ\text{C}$) δ 2.05 (s, 3 H, NMe), 3.17 (s, 3 H, NMe'). Anal. Calcd for $\text{C}_{46}\text{H}_{41}\text{NO}_2\text{P}_2\text{Pt}$: 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 ¹³CO-labeled complex *cis*-Pt(COPh)(¹³CONMe₂)(PPh₃)₂ (5a-¹³CO) was similarly prepared by using ¹³CO 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 (COPh), 1515 cm^{-1} (¹³CONMe₂). The ¹³C{¹H} NMR spectrum of 5b-¹³CO (CD_2Cl_2) exhibited a strong signal (dd) arising from the carbonyl carbon in the carbamoyl group at δ 188.5. The ³¹P{¹H} NMR spectrum is illustrated in Figure 1.

Similarly prepared are complexes 5b (77%), 5c (50%), and 5d (80%) by using piperidine, pyrrolidine, and Et₂NH in place of Me₂NH, respectively. These complexes were isolated as yellow crystals by recrystallization from a benzene-Et₂O mixture. 5b: ¹H NMR (CD_2Cl_2 , -20 $^\circ\text{C}$) δ 0.6-1.8 (br, 7 H, NCH₂(CH₂)₃ and NCH), 2.4-2.7 (br, 1 H, NCH), 3.3-3.6 (br, 1 H, NCH), 4.8-5.1 (br, 1 H, NCH). Anal. Calcd for $\text{C}_{48}\text{H}_{45}\text{NO}_2\text{P}_2\text{Pt}$: 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 $^\circ\text{C}$) δ 1.44 (br, 4 H, NCH₂(CH₂)₂), 2.34 (br, 1 H, NCH), 2.74 (br, 1 H, NCH), 3.42 (br, 1 H, NCH), 4.18 (br, 1 H, NCH). Anal. Calcd for $\text{C}_{48}\text{H}_{43}\text{NO}_2\text{P}_2\text{Pt}$: 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 $^\circ\text{C}$) δ 0.34 (t, $^3J_{\text{H-H}} = 7$ Hz, 3 H, NCH₂CH₃), 0.93 (t, $^3J_{\text{H-H}} = 7$ Hz, 3 H, NCH₂CH₃), 2.36 (m, 1 H, NCH), 2.76 (m, 1 H, NCH), 3.05 (m, 1 H, NCH), 4.65 (m, 1 H, NCH). Anal. Calcd for $\text{C}_{48}\text{H}_{45}\text{NO}_2\text{P}_2\text{Pt}$: 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)(CONMe₂)(PPh₃)₂ (6a). To a Schlenk tube containing *trans*-[Pt(COPh)(CO)(PPh₃)₂]BF₄ (7; 2.74 g, 2.92 mmol) in acetone (6 mL) was added HNMe₂ (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 $\times$ 2 mL), and dried under vacuum. The crude product was recrystallized from a CH_2Cl_2 -Et₂O mixture to give orange crystals of complex 6a (1.97 g, 80.5%): ¹H NMR (CD_2Cl_2 , -20 $^\circ\text{C}$) δ 1.88 (s, 3 H, NMe), 2.73 (s, 3 H, NMe'). Anal. Calcd for $\text{C}_{46}\text{H}_{41}\text{NO}_2\text{P}_2\text{Pt}$: 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 ¹³CO-labeled complex *trans*-Pt(COPh)(¹³CONMe₂)(PPh₃)₂ (6a-¹³CO) was similarly prepared by using *trans*-[Pt(COPh)(¹³CO)(PPh₃)₂]BF₄ in place of complex 7 (72%): IR (KBr)

1567 (COPh), 1495 cm^{-1} ($^{13}\text{CONMe}_2$). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **6a**- ^{13}CO exhibited a strong triplet signal due to the carbonyl carbon in the carbamoyl group at δ 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) δ 0.88–1.16 (br, 6 H, $\text{NCH}_2(\text{CH}_2)_3$), 2.72 (br, 2 H, NCH_2), 3.67 (br, 2 H, NCH_2). Anal. Calcd for $\text{C}_{48}\text{H}_{45}\text{NO}_2\text{P}_2\text{Pt}\cdot\text{CH}_2\text{Cl}_2$: 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) δ 1.10 (br, 4 H, $\text{NCH}_2(\text{CH}_2)_2$), 2.45 (br, 2 H, NCH_2), 3.27 (br, 2 H, NCH_2). Anal. Calcd for $\text{C}_{48}\text{H}_{43}\text{NO}_2\text{P}_2\text{Pt}$: 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) δ 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 $\text{C}_{48}\text{H}_{45}\text{NO}_2\text{P}_2\text{Pt}$: 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)(PPh₃)₂]BF₄ (8b**).** To a dichloromethane solution (5 mL) of trans-[Pt(COPh)(acetone)(PPh₃)₂]BF₄ (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 $\times$ 5 mL) and dried under vacuum (0.743 g, 90%): ^1H NMR (CD_2Cl_2 , -20°C) δ 1.0–1.2 (br, 2 H, $\text{N}(\text{CH}_2)_2\text{CH}_2$), 1.3–1.5 (br, 4 H, $\text{N}(\text{CH}_2)_2\text{CH}_2$), 2.4–2.6 (br, 4 H, NCH_2), 2.8 (br, 1 H, NH); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 207.5 (br, COPh); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) 24.0 ppm (s, $^1J_{\text{Pt-P}} = 3418$ Hz); IR (KBr) 3244 (NH), 1632 cm^{-1} (COPh).

Preparation of trans-[Pt(COPh)(CO)(PMe₃)₂]BF₄ (10**).** The complex trans-Pt(COPh)Cl(PMe₃)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 $\times$ 5 mL), and dried under vacuum (0.669 g, 82%): ^1H NMR (CD_2Cl_2) δ 1.60 (t, $J = 4.3$ Hz, PMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 227.0 (t, $^2J_{\text{P-C}} = 10$ Hz, $^1J_{\text{Pt-C}} = 814$ Hz, COPh), 178.2 (t, $^2J_{\text{P-C}} = 10$ Hz, $^1J_{\text{Pt-C}} = 877$ Hz, PtCO), 15.1 (t, $J = 20$ Hz, PMe_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ -13.1 ppm (s, $^1J_{\text{Pt-P}} = 2602$ Hz), IR (KBr) 2110 (PtCO), 1624 cm^{-1} (COPh). Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{BF}_4\text{O}_2\text{P}_2\text{Pt}$: C, 29.6; H, 4.1. Found: C, 28.8; H, 4.2.

Preparation of trans-Pt(COPh)(CON(CH₂)₄CH₂)(PMe₃)₂ (9b**).** To a dichloromethane solution (2 mL) of trans-[Pt(COPh)(CO)(PMe₃)₂]BF₄ (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) δ 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, $\text{NCH}_2(\text{CH}_2)_3$). The other spectroscopic data are listed in Table I. Anal. Calcd for $\text{C}_{19}\text{H}_{33}\text{NO}_2\text{P}_2\text{Pt}$: 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(PMe₃)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 μL , 0.92 mmol) was added, and then CO gas (10 atm) was introduced at room temperature. $^{31}\text{P}\{^1\text{H}\}$ 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 ($^1J_{\text{Pt-P}} = 2934$ Hz), which was gradually replaced by a new singlet at -15.3 ppm ($^1J_{\text{Pt-P}} = 2887$ 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

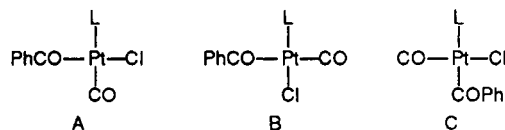
the only reaction product. Also noted was precipitation of white crystals of the piperidinium salt in the solution. After the CO gas was purged, the white crystals were removed by filtration and the filtrate was connected to dryness under reduced pressure to give an orange solid of **9b**, which was 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 μL) 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 $^{31}\text{P}\{^1\text{H}\}$ 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)(PPh₃)₂ (11b**).** To a Schlenk tube containing $\text{Pt}_2(\text{COPh})_2(\mu\text{-Cl})_2(\text{PPh}_3)_2$ (1.48 g, 1.22 mmol) was added a benzene solution (5 mL) of piperidine (133 μL , 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) δ 1.2–1.6 (br, 6 H, $\text{NCH}_2(\text{CH}_2)_3$), 2.64 (br, 2 H, NCH_2), 3.42 (br, 2 H, NCH_2), 3.67 (br, 1 H, NH); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 212.4 (d, $^2J_{\text{P-C}} = 7$ Hz, COPh); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) 15.6 ppm (s, $^1J_{\text{Pt-P}} = 4387$ Hz); IR (KBr) 3174 (NH), 1613 cm^{-1} (COPh). Anal. Calcd for $\text{C}_{30}\text{H}_{32}\text{NOPClPt}\cdot\text{C}_6\text{H}_6$: 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(PPh₃)₂ (1**) with CO and Piperidine. 1. Reaction of **1** and CO under Pressure in the Presence of S₈.** 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. When the system was allowed to stand at room temperature, a singlet at 48.4 ppm arising from $\text{S}=\text{PPh}_3$ and three singlets with ^{195}Pt satellites at 21.3 ppm ($^1J_{\text{Pt-P}} = 2385$ Hz, signal a), 15.5 ppm ($^1J_{\text{Pt-P}} = 3037$ Hz, signal b), and 22.0 ppm ($^1J_{\text{Pt-P}} = 1340$ Hz, signal c) gradually increased at the expense of the peaks due to **1** at 26.1 ppm (s, $^1J_{\text{Pt-P}} = 3406$ Hz). The peak integration for $\text{S}=\text{PPh}_3$ 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** ($k_{\text{obsd}} = 1.7 \times 10^{-6} \text{ s}^{-1}$). In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum after 10 days, where 98% of **1** was consumed and 94% of $\text{S}=\text{PPh}_3$ 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).

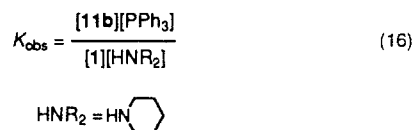
These observations indicate the occurrence of a ligand-exchange reaction of **1** and CO to give the three benzoyl-carbonyl geometrical isomers A–C, which correspond to the signals a–c in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, respectively. This reaction also forms



free PPh_3 , which may rapidly react with sulfur to give $\text{S}=\text{PPh}_3$. The NMR assignments of these three isomers were determined on the basis of the $^1J_{\text{Pt-P}}$ values, which are in fair agreement with the reported values for three geometrical isomers of $\text{PtPh}(\text{CO})\text{Cl}(\text{PPh}_3)$.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

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction solution showed two singlets with ^{195}Pt satellites at 26.0 ppm ($J_{\text{Pt-P}} = 3412$ Hz) and 15.6 ppm ($J_{\text{Pt-P}} = 4387$ Hz) due to complex 1 and a piperidine-coordinated complex, $\text{Pt}(\text{COPh})(\text{Cl})(\text{piperidine})(\text{PPh}_3)$ (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.



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) 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this solution showed two singlets with ^{195}Pt satellites due to 1 and 11b at 26.0 ppm ($^1J_{\text{Pt-P}} = 3412$ Hz) and 15.6 ppm ($^1J_{\text{Pt-P}} = 4381$ 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 $^{31}\text{P}\{^1\text{H}\}$ 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, $^1J_{\text{Pt-P}} = 1578$ Hz; 19.8 ppm, $^1J_{\text{Pt-P}} = 1834$ Hz; $^2J_{\text{P-P}} = 18$ 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)(CONR₂)(PPh₃)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 $^{31}\text{P}\{^1\text{H}\}$ 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 ($^1J_{\text{Pt-P}} = 3296$ Hz) was replaced by an AB quartet with ^{195}Pt satellites at 19.4 ppm ($^1J_{\text{Pt-P}} = 1565$ Hz, $^2J_{\text{P-P}} = 18$ Hz) and 20.2 ppm ($^1J_{\text{Pt-P}} = 1898$ 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 $3.2 \times 10^{-6} \text{ s}^{-1}$. The resulting *cis* isomer 5a was found to react subsequently with the solvent to give complex 1 (26.1 ppm, $^1J_{\text{Pt-P}}$

$= 3398$ 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 3.8×10^{-6} , 8.8×10^{-6} , and $1.9 \times 10^{-5} \text{ s}^{-1}$, respectively.

2. Isomerization of 6b in the Presence of Piperidine and CO. The $^{31}\text{P}\{^1\text{H}\}$ 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, $^1J_{\text{Pt-P}} = 3342$ Hz). After piperidine (0.015 mL, 0.15 mmol) was added to the solution, the change of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum with time was followed. The signal of the *cis* isomer 5b (19.4 ppm, $^1J_{\text{Pt-P}} = 1861$ Hz; 19.9 ppm, $^1J_{\text{Pt-P}} = 1588$ Hz; $^2J_{\text{P-P}} = 18$ 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 $k_{\text{obsd}} = 8.9 \times 10^{-4} \text{ s}^{-1}$. 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 $^{31}\text{P}\{^1\text{H}\}$ 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 (P¹ (*trans* to the carbamoyl group) 19.4 ppm, $^1J_{\text{Pt-P}} = 1861$ Hz, $^2J_{\text{P-C}} = 117$ Hz; P² (*cis* to the carbamoyl group) 19.9 ppm, $^1J_{\text{Pt-P}} = 1588$ Hz, $^2J_{\text{P-C}} = 13$ Hz; $^2J_{\text{P-P}} = 18$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction solution after 2 h shows one AB quartet with ^{195}Pt satellites (P¹ (*trans* to carbamoyl group) 18.7 ppm, $^1J_{\text{Pt-P}} = 1814$ Hz; P² (*cis* to carbamoyl group) 20.7 ppm, $^1J_{\text{Pt-P}} = 1648$ Hz; $^2J_{\text{P-P}} = 18$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum with time was examined. The main signal of the *trans*-benzoyl-carbamoyl complex 6b (s, 19.3 ppm, $J_{\text{Pt-P}} = 3341$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the solution was examined with time. The signal of the starting complex 8b at 24.0 ppm ($^1J_{\text{Pt-P}} = 3418$ 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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