Preparation and Reactions of *trans*-Pd(COPh)($CONR_2$)(PMe_3)$_2$ and *trans*-PdPh($CONR_2$)(PMe_3)$_2$ Complexes as Models for Intermediates Involved in the Palladium-Catalyzed Double- and Single-Carbonylation Reactions of Phenyl Halides

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Received December 15, 1989

The reaction of *trans*-Pd(COPh)Cl(PMe_3)$_2$ (1) with secondary amines (R_2NH) and CO under pressure at room temperature gives *trans*-Pd(COPh)($CONR_2$)(PMe_3)$_2$ complexes (R_2N = Me_2N (**3a**), $\overline{CH_2(CH_2)_4N}$ (**3b**), $\overline{CH_2(CH_2)_3N}$ (**3**)) quantitatively, together with the ammonium salts R_2NH_2Cl. Complexes **3a-c** are prepared also by treating the cationic benzoylpalladium complex *trans*-[Pd(COPh)(acetone)(PMe_3)$_2$]X (**2**, X = BF_4 or PF_6) with the secondary amines and CO at atmospheric pressure. The reactions of **2** with amines and CO affording the benzoyl-carbamoyl complexes proceed rapidly at -20 °C, while the same systems at room temperature yield α-keto amides ($PhCOCONR_2$) quantitatively. The isolated benzoyl-carbamoyl complexes **3a-c** are fairly stable toward direct reductive elimination to afford α-keto amides in solutions containing secondary amines under a CO atmosphere at room temperature. In the presence of an ammonium salt ($R_2NH_2BF_4$), on the other hand, these complexes readily afford α-keto amides under the otherwise same conditions. Treatment of *trans*-[PdPh(acetone)(PMe_3)$_2$]PF_6 (**7**) instead of the benzoyl complex **2** with secondary amines and CO at -20 °C forms *trans*-PdPh($CONR_2$)(PMe_3)$_2$ complexes (R_2N = Me_2N (**8a**), $\overline{CH_2(CH_2)_4N}$ (**8b**), $\overline{CH_2(CH_2)_3N}$ (**8c**)), while the same systems give α-keto amides and amides at room temperature. Mechanisms of formation of the benzoyl- and phenyl-carbamoyl complexes and of α-keto amide and amide have been studied in detail in conjunction with proposed mechanisms for the catalytic double- and single-carbonylation reactions.

Introduction

Previously, Tanaka's and our groups independently reported a novel double-carbonylation reaction of aryl halides (ArX) and secondary amines (R_2NH) catalyzed by palladium complexes to give α-keto amides. This reaction also affords amides as the single-carbonylation byproducts:[1,2]

$$ArX + CO + 2HNR_2 \xrightarrow{[Pd]} ArCOCONR_2\ (+ArCONR_2) + R_2NH_2X \quad (1)$$

For the α-keto amide and amide forming reactions, we proposed the mechanism represented in Scheme I.[3,4] The mechanism is comprised of two catalytic cycles. Cycle I gives an α-keto amide, whereas cycle II produces an amide. Both cycles involve the Pd(0) species A and the aryl-palladium(II) species B as common intermediates. For α-keto amide formation, complex B undergoes CO insertion into the Ar-Pd bond to give the aroylpalladium complex C. Coordination of CO to C followed by nucleophilic attack of secondary amine on the resulting CO ligand in D affords the aroyl(carbamoyl)palladium species E. Reductive elimination of the aroyl and carbamoyl groups from E gives the α-keto amide. On the other hand, for the amide formation, the aryl complex B undergoes CO coordination to give the aryl-carbonyl species F. Attack of amine on the CO ligand in F gives the aryl(carbamoyl)-palladium intermediate G, which reductively eliminates amide.

Of the palladium species assumed in Scheme I, A-C have been observed in actual catalytic systems by NMR spectroscopy.[3a,e] The intermediacy of B and C has been supported also by studies on reactivities of isolated phenyl- and benzoylpalladium complexes toward amines and CO.[3,4] The other species D-G, on the other hand, have yet to be characterized. Since in the actual catalytic reactions the processes occurring after the rate-determining reactions of the aroylpalladium (step D → E for cycle I) and the arylpalladium species (step F → G for cycle II) with amine and CO proceed rapidly, direct observation of the later catalytic processes and intermediates is not feasible. Although IR and NMR spectroscopic studies have suggested that *trans*-Pd(COPh)(X)L_2 complexes (X = I and ClO_4, L = tertiary phosphine ligands) in solution under CO pressure are in rapid equilibrium with the corresponding *trans*-[Pd(COPh)(CO)L_2]X species,[3a,e] the intermediacy of the *trans*-benzoyl-carbonyl complexes in the α-keto

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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. A related double carbonylation of a secondary amine was also reported recently: Alper, H.; Vasapollo, G.; Hartstock, F. W.; Mlekuz, M. *Organometallics* **1987**, *6*, 2391.

(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 for the double carbonylation has been reported: (a) Chen, J.; Sen, A. *J. Am. Chem. Soc.* **1984**, *106*, 1506. (b) Sen, A.; Chen, J.; Vetter, E. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 148.

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Scheme I. Proposed Mechanism for the Catalytic Double and Single Carbonylation of Aryl Halides and Secondary Amines to Give α-Keto Amides and Amides

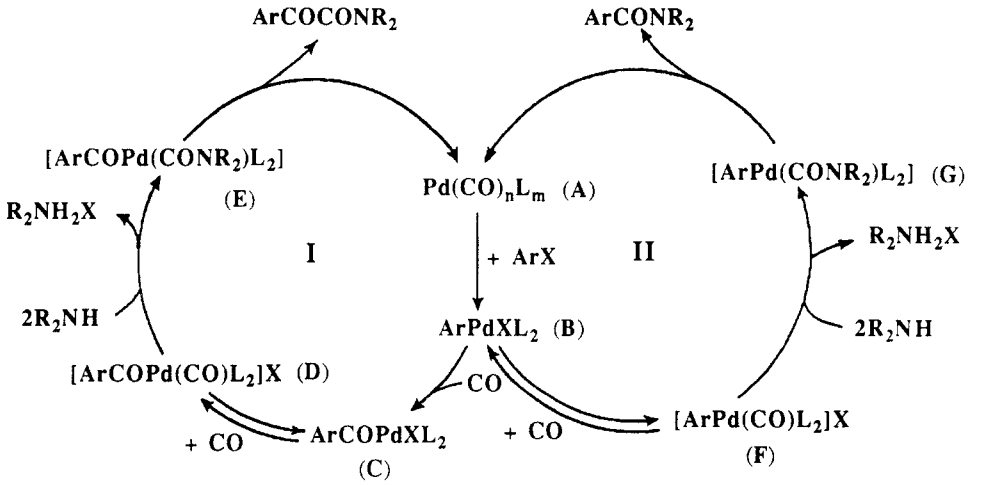


Table I. NMR and IR Data for the Benzoyl- and Phenyl(carbamoyl)palladium Complexes

	$^{13}C\{^1H\}$ NMR[a]		^1H NMR[b]				IR, cm^{-1} [d]
complex	δ	J_{P-C}, Hz	δ	J_{P-H}, Hz	assignt	$^{31}P\{^1H\}$ NMR,[c] ppm	ν(CO)
3a	15.7 (t)[f]	15	1.11 (t)[f]	3.5	P*Me*	−11.4	1564 (benzoyl)
	31.3 (s)		2.76 (s)		N*Me*		
	38.4 (s)		3.29 (s)		N*Me′*		1526 (carbamoyl)
	212.5 (t)	15			$CONMe_2$		
	275.3 (t)	10			COPh		
3b	15.6 (t)[f]	15	1.13 (t)[f]	3.5	P*Me*	−12.0	1565 (benzoyl)
	26.4 (s)		1.5 (b)		$NCH_2(CH_2)_3$		
	26.5 (s)				$NCH_2(CH_2)_3$		1528 (carbamoyl)
	27.6 (s)				$NCH_2(CH_2)_3$		
	40.5 (s)		3.4 (b)		NCH_2		
	48.6 (s)		3.8 (b)		NCH_2'		
	210.4 (t)	13			$CONR_2$		
	275.0 (t)	10			COPh		
3c	15.8 (t)[f]	15	1.14 (t)[f]	3.5	P*Me*	−11.7	1561 (benzoyl)
	24.8 (s)		1.8 (b)		$NCH_2(CH_2)_2$		
	25.8 (s)				$NCH_2(CH_2)_3$		1518 (carbamoyl)
	43.5 (s)		3.3 (br)		NCH_2		
	47.8 (s)		3.8 (br)		NCH_2'		
	211.9 (t)	14			$CONR_2$		
	276.1 (t)	10			COPh		
8a	13.9 (t)[f]	15	1.08 (t)[f]	3.4	P*Me*	−10.4	1505 (carbamoyl)
	30.1 (s)		2.79 (s)		N*Me*		
	37.2 (s)		3.32 (s)		N*Me′*		
	211.4 (t)	9			$CONMe_2$		
8b[e]	14.9 (t)[f]	15	*g*		P*Me*	−11.5	*g*
	211.8 (t)	9			$CONR_2$		
8c[e]	14.6 (t)[f]	15	*g*		P*Me*	−10.7	*g*
	213.5 (t)	10			$CONR_2$		

[a] At 67.8 MHz, in CD_2Cl_2 (**3a–c** and **8a**) or acetone-d_6 (**8b,c**), at 0 °C (**3a–c**) or −20 °C (**8a–c**). [b] At 100 MHz, in CD_2Cl_2, at 26 °C (**3a–c**) or −20 °C (**8a**). [c] At 40 MHz, in CD_2Cl_2 (**3a–c** and **8c**) or acetone-d_6 (**8b,c**), at −50 °C (**3a–c**) or −20 °C (**8a–c**); chemical shifts are relative to PPh_3 as an external standard. [d] In KBr disks. [e] The complex was examined without isolation. [f] Virtual triplet. [g] Not measured.

amide formation has not been confirmed.

In order to obtain further information on the double- and single-carbonylation mechanisms, particularly on the mechanisms for the α-keto amide and amide formation from the aroyl- and arylpalladium species, we attempted in this study to prepare models for the aroyl(carbamoyl)- and aryl(carbamoyl)palladium species E and G. In previous studies steric repulsion between the tertiary phosphine ligands in D and secondary amine has been suggested to be a main factor controlling the reaction rate of D and amine.[2c,3a] Furthermore, a bulky and less basic tertiary phosphine ligand is considered to favor dissociation of the ligand with a subsequent promotion effect on the reduction elimination of the aroyl and carbamoyl groups from E. Thus, we reasoned that use of a small and basic tertiary phosphine ligand such as PMe_3 would make the attack of amine on the CO-coordinated complex more facile and would render the resulting PMe_3-coordinated aroyl–carbamoyl complex stable enough against reductive elimination to allow its isolation. This assumption led to the successful isolation of a *trans*-benzoyl(carbamoyl)-palladium complex with the PMe_3 ligands as preliminarily reported.[5,6] Employment of the trimethylphosphine ligand also enabled isolation of a *trans*-phenyl(carbamoyl)palladium complex. Properties of the isolated *trans*-phenyl-

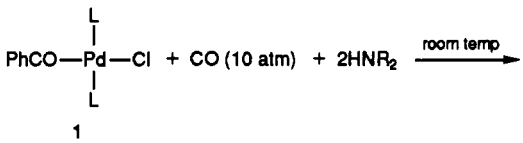
(5) Ozawa, F.; Huang, L.; Yamamoto, A. *J. Organomet. Chem.* **1987**, *334*, C9.

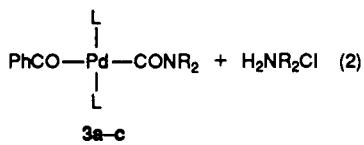
(6) Isolation of related benzoyl(methoxycarbonyl)platinum(II) complexes has been reported.[4b]

palladium complex lend strong support for the validity of cycle II. Cycle II comprises a reaction pathway that has not been previously considered, involving the amine attack on the CO-coordinated phenylpalladium complex (F). The proposed mechanism differs from the generally considered assumption involving attack of the benzoylpalladium complex (C) by amine to liberate amide.

Results

1. Preparation and Reactions of *trans*-Benzoyl(carbamoyl)palladium(II) Complexes. Preparation of *trans*-Pd(COPh)(CONR$_2$)(PMe$_3$)$_2$ (3). Reactions of *trans*-Pd(COPh)(Cl)(PMe$_3$)$_2$ (1) with secondary amines (10 equiv/equiv of 1, R$_2$NH = Me$_2$NH, piperidine, and pyrrolidine) in CD_2Cl_2 under CO pressure (10 atm) give *trans*-benzoyl(carbamoyl)palladium complexes (**3a–c**) in



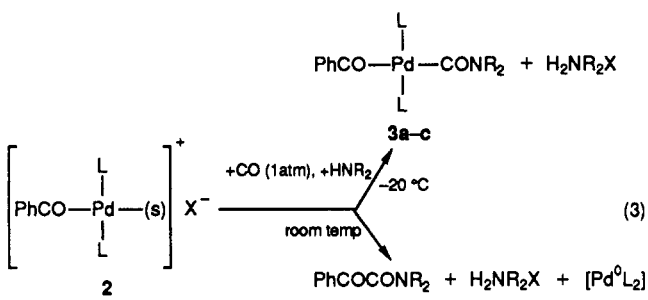


L = PMe$_3$; NR$_2$ = NMe$_2$ (**3a**), N⬡ (**3b**), N⬠ (**3c**)

quantitative yields as confirmed by NMR spectroscopy. The reactions need several days for their completion at room temperature. No α-keto amide formation has been observed under these reaction conditions.

The reactivity of the benzoylpalladium complex toward CO and amine can be increased by treating **1** with silver salts to convert **1** into the cationic benzoylpalladium complex *trans*-[Pd(COPh)(acetone)(PMe$_3$)$_2$]X (**2**, X = BF$_4$, PF$_6$), which has a coordination site occupied by a weakly bonding solvent molecule.

The reactions of **2** with secondary amines and CO (1 atm) in acetone proceed rapidly at −20 °C to give the *trans*-benzoyl–carbamoyl complexes **3a–c** in good yields.



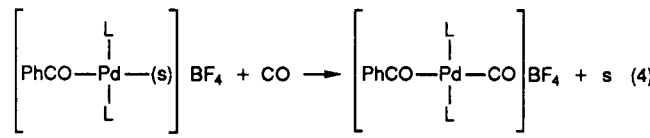
L = PMe$_3$; s = acetone; X = BF$_4$, PF$_6$

Complexes **3a** and **3b** are sparingly soluble in the solvent acetone under the reaction conditions and readily separated out as red crystalline solids from the reaction systems. For the isolation of **3c**, on the other hand, addition of a large excess of pyrrolidine or Et$_3$N was required. The same reactions carried out at room temperature, on the other hand, afford the corresponding α-keto amides, quantitatively.

The benzoyl–carbamoyl complexes **3a–c** thus prepared were characterized by means of IR and NMR spectroscopy (Table I) and elemental analysis. The IR spectra show two ν(CO) bands at about 1560 cm^{-1} (for the benzoyl group) and 1520 cm^{-1} (for the carbamoyl group). $^{13}C\{^1H\}$ NMR spectra of the complexes exhibit two sets of triplets around δ 210 and 275, which are assigned to the carbonyl carbons in the benzoyl and carbamoyl groups, respectively. These assignments have been confirmed by using the ^{13}CO-labeled complexes *trans*-Pd(COPh)(^{13}CONR$_2$)(PMe$_3$)$_2$.

NMR Examination of the Reaction of the Cationic Benzoylpalladium Complex 2 with CO and Amine. Reactions of the acetone-coordinated benzoylpalladium complex **2** with CO and pyrrolidine have been examined separately by NMR spectroscopy.

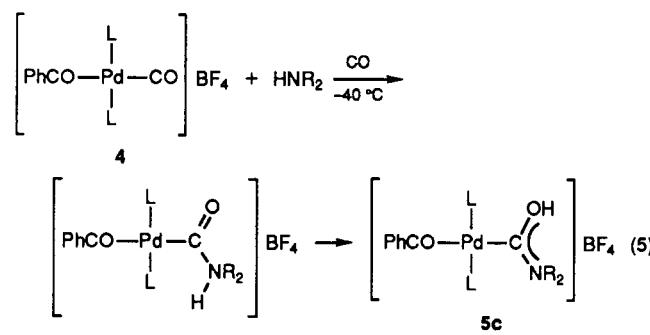
Complex **2** (X = BF$_4$) was dissolved in CD_2Cl_2 under a CO atmosphere. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the solution revealed the formation of *trans*-[Pd(COPh)(CO)(PMe$_3$)$_2$]BF$_4$ (**4**). The ^{13}C NMR spectrum of **4**



s = acetone; L = PMe$_3$

measured at −80 °C exhibits a triplet assignable to the terminal CO carbon at δ 180.8 (J_{P-C} = 18 Hz). The triplet changes to a broad signal at −30 °C and to a sharp singlet at −10 °C. Since the Me carbon in the PMe$_3$ ligands was observed as a virtual triplet with the P–C coupling (J = 16 Hz) even at −10 °C, the disappearance of the P–C coupling on the terminal carbonyl carbon at elevated temperatures is attributable to the occurrence of a rapid exchange of the CO lilgand with a free CO molecule. Complex **4** could be isolated as an off-white precipitate on evaporation of the solvent by passing CO gas through the solution at room temperature. The IR spectrum of **4** shows a sharp ν(CO) band due to the terminal CO group at 2138 cm^{-1}.

Two equivalents of pyrrolidine was added to a CD_2Cl_2 solution of **4** (0.10 M) prepared from **2** (X = BF$_4$) and CO (1 atm). The color of the solution instantly changed from pale yellow to bright orange. The NMR spectra of the solution measured at −40 °C revealed the absence of **4** and the formation of the new cationic benzoylpalladium species **5c**. As demonstrated in our recent paper,[7] the NMR data



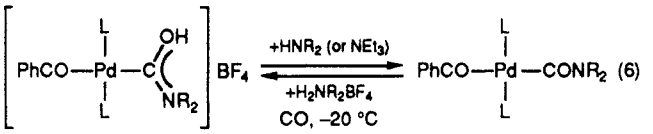
L = PMe$_3$, HNR$_2$ = pyrrolidine

indicate that complex **5c** is a cationic benzoylpalladium complex coordinated with an *O*-protonated carbamoyl ligand, which may be formed by nucleophilic addition of pyrrolidine to the terminal CO ligand in **4** followed by proton rearrangement in the resulting pyrrolidine-coordinated carbonyl group.

Further addition of pyrrolidine to the NMR sample solution of **5c** results in a rapid conversion of **5c** into the

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

benzoyl(carbamoyl)palladium complex **3c**. In the presence of 20 equiv of pyrrolidine/equiv of Pd, **3c** and **5c** were observed in a 1:1 ratio in the ^{31}P NMR spectrum. The relative ratio of **3c** to **5c** increases with an increase in the concentration of pyrrolidine in the system. The conversion of **5c** into **3c** is performed also by addition of Et_3N to the system. Addition of $\overline{CH_2(CH_2)_3NH_2}BF_4$ to the system, on the other hand, increases the amount of **5c**. These results clearly indicate the following deprotonation–protonation equilibrium between **5c** and **3c** with the aid of pyrrolidine and the pyrrolidinium salt:

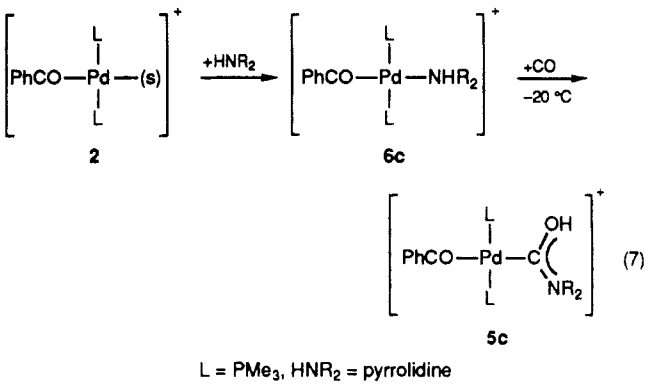


5c **3c**

L = PMe_3, HNR_2 = pyrrolidine

Reaction 6 is a rapid process on the NMR time scale. In the $^{31}P\{^1H\}$ NMR spectrum (200 MHz) of a 1:1 mixture of **3c** and **5c** with 20 equiv of pyrrolidine measured at −50 °C, **3c** and **5c** exhibit well-separated singlet peaks at −11.7 and −12.0 ppm, respectively. These peaks broaden on keeping the approximately 1:1 ratio at elevated temperatures and coalesce into a broad sinlet at about −15 °C.[7]

Treatment of **2** (X = BF_4) with pyrrolidine in CH_2Cl_2 affords the pyrrolidine-coordinated benzoylpalladium complex *trans*-[Pd(COPh)(pyrrolidine)$(PMe_3)_2$]BF_4 (**6c**).



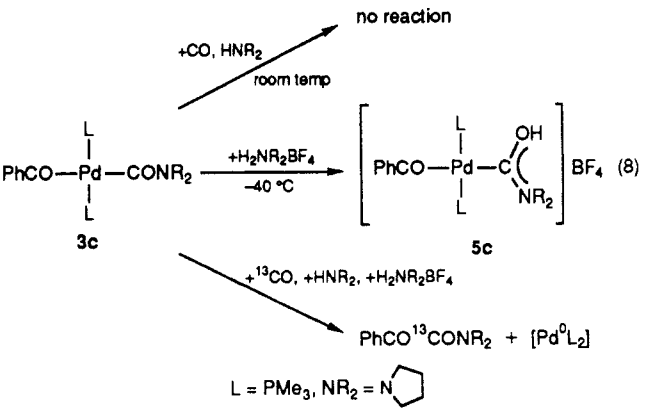
2 **6c** **5c**

L = PMe_3, HNR_2 = pyrrolidine

Complex **6c** has been isolated as a yellow precipitate and characterized by means of IR and NMR spectroscopy and elemental analysis. Reaction of **6c** and CO in CD_2Cl_2 affords a mixture of **5c** and **6c** together with some unidentified palladium species.

Reactions of *trans*-Benzoyl(carbamoyl)palladium Complexes 3a–c Related to the α-Keto Amide Formation. As described above, the reactions of **2**, secondary amines, and carbon monoxide in acetone at −20 °C cleanly give the *trans*-benzoyl–carbamoyl complexes **3a–c**. The reactions carried out at room temperature, on the other hand, liberate the corresponding α-keto amides quantitatively. To test the possibility that the *trans*-benzoyl–carbamoyl complexes serve as intermediates in the α-keto amide formation, reactions of complexes **3a–c** have been examined.

The isolated complex **3c** is fairly stable in neat solvents such as acetone and dichloromethane. No reaction takes place when **3c** is allowed to stand at room temperature for 1 day under a CO atmosphere in solution containing an excess amount of pyrrolidine. On the other hand, **3c** readily gives the α-keto amide $PhCOCO\overline{N(CH_2)_3CH_2}$ in solution containing the pyrrolidinium salt $\overline{CH_2(CH_2)_3NH_2}BF_4$ (1 equiv/equiv of Pd) and an excess amount of pyrrolidine under a CO atmosphere at room temperature. Similar results were obtained with **3a** and **3b**.

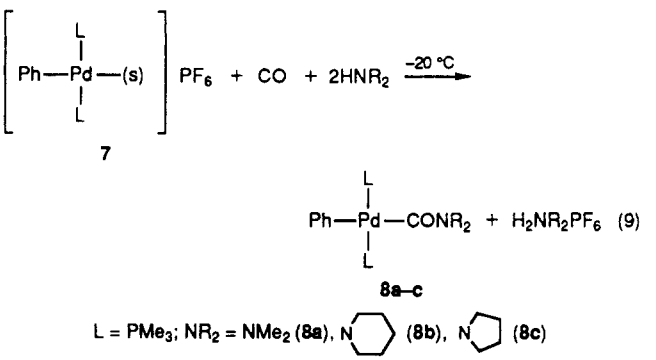


3c **5c**

L = PMe_3, NR_2 = N⬠

Treatment of **3c** with 1 equiv of the pyrrolidinium salt in CD_2Cl_2 at −40 °C under a CO atmosphere gives the cationic O-protonated carbamoyl complex **5c** by the reverse process of eq 6, as confirmed by NMR spectroscopy. The same reaction system decomposes readily at room temperature to give ca. 40%/equiv of Pd of α-keto amide. The yield of α-keto amide increases to 100%/equiv of **3c** by addition of pyrrolidine (5 equiv/equiv of **3c**) to the system. The presence of free CO in the system is of particular importance to obtain α-keto amide. Thus, treatment of **3c** with the pyrrolidinium salt under an N_2 atmosphere in CD_2Cl_2 containing an excess amount of pyrrolidine at room temperature affords the pyrrolidine-coordinated complex **6c**, quantitatively. When the reaction is carried out under a ^{13}CO atmosphere, the ^{13}CO-labeled α-keto amide $PhCO^{13}CO\overline{N(CH_2)_3CH_2}$ is formed almost selectively. These results also suggest participation of free CO in the α-keto amide forming reaction.

2. Reactions of Phenylpalladium Complexes. Preparation of *trans*-PdPh(CONR$_2$)(PMe$_3$)$_2$ (8). Treatment of *trans*-[PdPh(acetone)$(PMe_3)_2$]PF_6 (**7**) with dimethylamine under an atmospheric pressure of CO in acetone at −20 °C readily gives *trans*-PdPh$(CONMe_2)$-$(PMe_3)_2$ (**8a**), which has been isolated as a white crystalline



7 **8a–c**

L = PMe_3; NR_2 = NMe_2 (**8a**), N⬠ (**8b**), N⬠ (**8c**)

solid and identified by means of IR and NMR spectroscopy and elemental analysis. Similar reactions of **7** with piperidine and pyrrolidine under a CO atmosphere afford the corresponding phenyl–carbamoyl complexes **8b** and **8c**, respectively.[8]

Reactions of the Cationic Phenylpalladium Complex 7 with Amines and CO at Room Temperature. At room temperature, instead of −20 °C, the reactions of **7**

(8) Complexes **8b** and **8c** have been identified by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy without isolation.

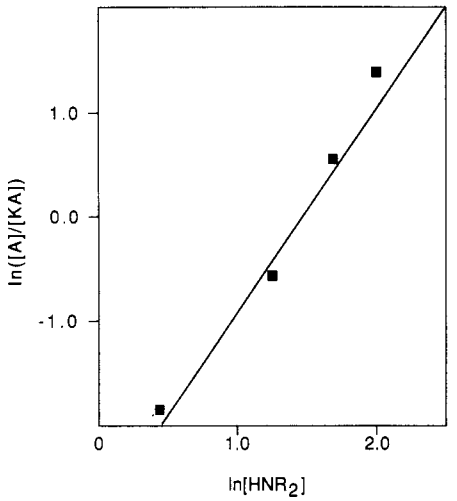
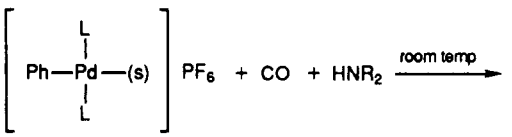


Figure 1. Plot of ln ([A]/[KA]) vs ln [HNR_2] for the reaction of *trans*-[PdPh(acetone)(PMe_3)$_2$]BF_4 (**7**) with piperidine in acetone under a CO atmosphere at room temperature. [A] and [KA] stand for the amounts of amide and α-keto amide formed in the reaction at 100% conversion of **7**, whereas [HNR_2] stands for the initial concentration of piperidine. The linear correlation has a slope of 2.0 with a correlation coefficient of 0.99.

with secondary amines and CO at atmospheric pressure afford the corresponding amides and α-keto amides:



7

$$PhCONR_2 + PhCOCONR_2 + R_2NH_2PF_6 \quad (10)$$

s = acetone; L = PMe_3; HNR_2 = $HNMe_2$, piperidine, pyrrolidine

The relative ratio of amide to α-keto amide in reaction 10 depends on the concentration of amine employed in the reaction. Thus, the higher concentration of amine results in lower selectivity for the α-keto amide formation. A plot of logarithms of the relative ratio of amide and α-keto amide (ln ([A]/[KA])) versus those of the concentration of amine (ln [HNR_2]) gives a straight line with a slope of 2.0 (Figure 1).

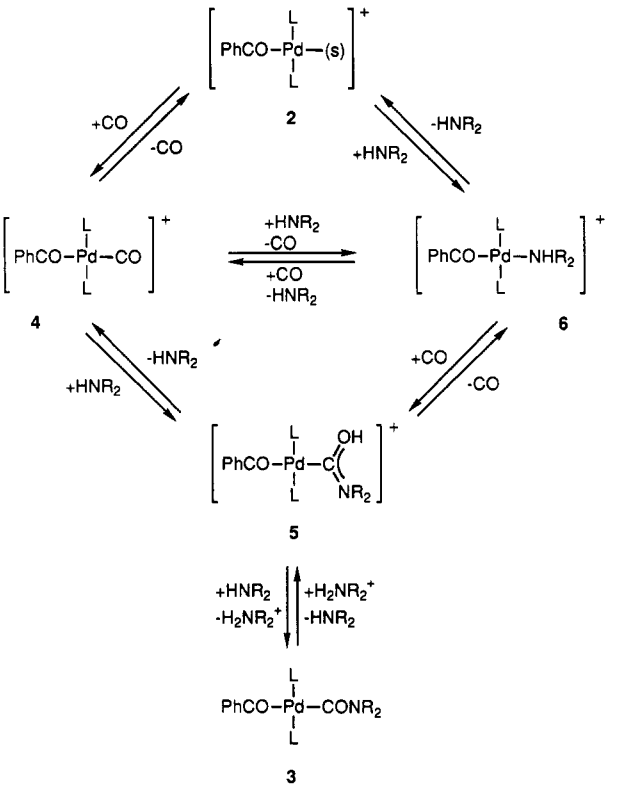
The reaction of **7** with piperidine (10 equiv/equiv of Pd) in acetone under a CO atmosphere at room temperature was followed by means of GLC. At the early stage of the reaction, rapid formation of amide accompanied by production of a small amount of α-keto amide was observed. The amide formation stopped within 10 min, and the selective formation of α-keto amiie at a slower reaction rate was observed over 1 h. Finally, the reaction yielded 75% of amide/equiv of Pd and 17% of α-keto amide.

Reactions of *trans*-Phenyl(carbamoyl)palladium Complexes 8a–c Related to the Amide Formation. The reactivity of the isolated phenyl–carbamoyl complexes in the amide-forming reaction is quite similar to that of the benzoyl–carbamoyl complexes in the α-keto amide formation. For example, *trans*-PdPh($CONMe_2$)(PMe_3)$_2$ (**8a**) is quite stable against reductive elimination to form amide *in the absence of* $Me_2NH_2BF_4$ even at elevated temperatures. In the presence of the ammonium salt, on the other hand, **8a** rapidly forms amide at room temperature. Under ^{13}CO gas the reaction selectively gives the ^{13}CO-labeled amide $Ph^{13}CONMe_2$.

Discussion

Mechanisms of Formation of the *trans*-Benzoyl(carbamoyl)palladium and *trans*-Phenyl(carbamoyl)palladium Complexes. The reaction processes represented in Scheme II are suggested for formation of the *trans*-benzoyl(carbamoyl)palladium complexes (**3a–c**) in the reactions of the cationic benzoylpalladium complex **2** with CO and amines. Ligand-exchange reactions of the coordinated acetone in **2** with CO and amine form the CO-coordinated and the amine-coordinated complexes **4** and **6**, respectively. Complex **4** subsequently undergoes nucleophilic addition of amine on the CO ligand to give the O-protonated carbamoyl complex **5**.[9] Complex **5** is formed also by the interaction of **6** and CO.[10] The equilibrium between **4** and **5** or between **6** and **5** lies far to the side of **5**.[7] In the presence of an excess amount of amine, complex **5** undergoes deprotonation to give the benzoyl(carbamoyl)palladium complex **3**, while complex **3** thus formed regenerates **5** on its interaction with the ammonium salt in the system. The protonation–deprotonation equilibrium between **3** and **5** is a rapid process on the NMR time scale.

Scheme II[a]



[a] Abbreviations: L = PMe_3; s = acetone.

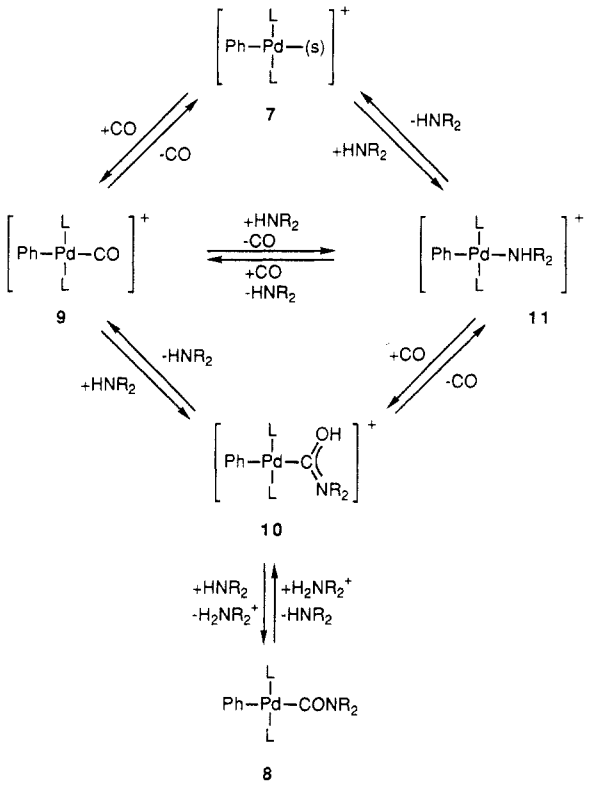
A reaction pattern quite analogous to Scheme II is operative in the reactions of the cationic phenylpalladium complex **7** with CO and amines to give *trans*-phenyl(carbamoyl)palladium complexes (**8a–c**) as shown in Scheme III. Coordination of CO to **7** gives the cationic phenylcarbonyl complex **9**, which undergoes nucleophilic addition of amine to give a benzoyl complex coordinated with an O-protonated carbamoyl ligand (**10**).[11] Complex **10** may

(9) Complex **5** has been characterized by spectroscopic means and also by establishment of the X-ray molecular structure of its related complex in which the oxygen-bound proton is replaced by an ethyl group.[7]

(10) It is plausible that, in the formation of **5** from **6** and CO, complex **6** initially undergoes a ligand-exchange reaction with CO to give the CO-coordinated complex **4**, which subsequently reacts with amine to give the O-protonated carbamoyl complex **5**.

(11) Complex **10** has not been characterized, but its involvement is considered quite probable by formation of complex **8** and in view of the quite analogous behavior of its corresponding benzoyl complex.

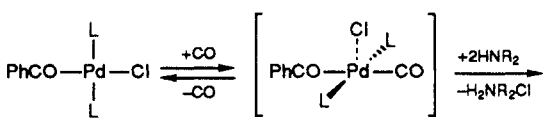
Scheme III[a]



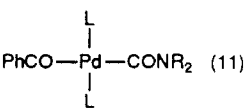
[a] Abbreviations: L = PMe_3; s = acetone.

be formed also by the reaction of the amine-coordinated complex **11** with CO. Complex **10** thus formed interacts with amine to undergo a deprotonation reaction, affording the phenyl–carbamoyl complex **8** and ammonium salt. Among the intermediates assumed in Scheme III, the carbonyl complex **9** could be isolated in the reaction of **7** and CO and characterized by means of IR and NMR spectroscopy and elemental analysis (see Experimental Section).

In contrast to the cationic complex **2** having a coordination site occupied by a weakly coordinating acetone, the neutral benzoylpalladium complex **1** may be less prone to undergo CO coordination to form the benzoyl–carbonyl intermediate.[4a] The reaction of **1**, therefore, requires a higher CO pressure and a longer reaction time than that of **2**. Formation of the benzoyl–carbamoyl complexes in the reactions of benzoylpalladium chloride (**1**) with CO and amines may be accounted for by assuming the following reaction sequence involving the benzoyl–carbonyl intermediate **12**:



1 **12**



3 (11)

L = PMe_3

Mechanism of α-Keto Amide Formation from the *trans*-Benzoyl(carbamoyl)palladium Complexes. The isolated benzoyl–carbamoyl complex **3c** has proved to be fairly stable toward reductive elimination to give an α-keto amide. This result is in accord with the general observation that a diorganopalladium(II) complex having a trans geometry is not suitable for direct reductive elimination, and a prior trans–cis isomerization should be involved for reductive elimination to occur.[12] On the other hand, complex **3c** readily undergoes protonation by $\overline{CH_2(CH_2)_3NH_2BF_4}$ to give the cationic species **5c**. When the reaction is carried out at room temperature in the presence of amine and CO, the α-keto amide can be liberated (eq 8). The presence of free CO is essential to obtain the α-keto amide. Thus, in the presence of pyrrolidine and the pyrrolidinium salt without CO, the system forms the amine-coordinated species **6**, exclusively. Furthermore, the reaction of **3c** and $\overline{CH_2(CH_2)_3NH_2BF_4}$ under a ^{13}CO atmosphere in the presence of an excess amount of pyrrolidine gives the ^{13}CO-labeled α-keto amide $PhCO^{13}CON\overline{(CH_2)_3CH_2}$. These results strongly suggest that the isolated *trans*-benzoyl–carbamoyl complex is not the direct precursor to produce an α-keto amide but another species, presumably a *cis*-benzoyl–carbamoyl complex, serves as the direct precursor to reductively eliminate α-keto amide.

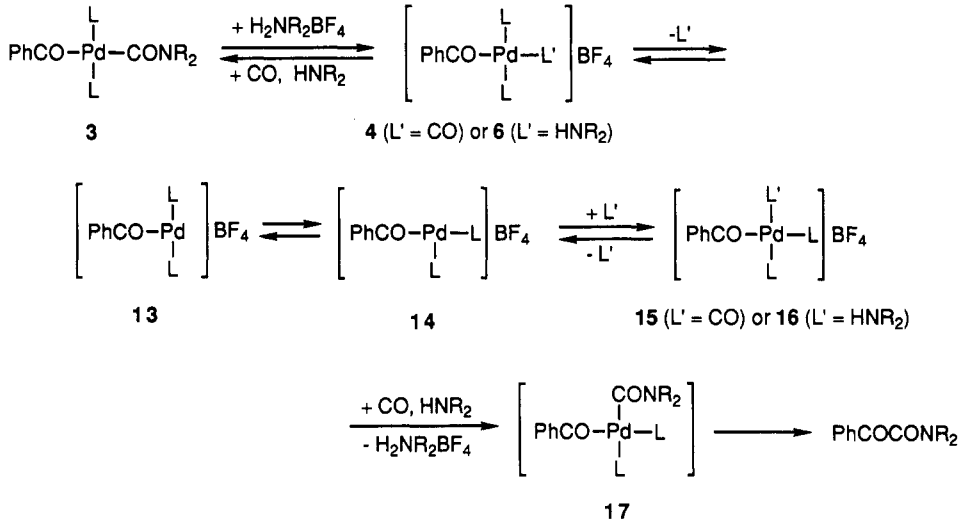
Scheme IV shows a possible sequence of processes consistent with the experimental results to liberate α-keto amide from the *trans*-benzoyl–carbamoyl complex **3** having PMe_3 ligands. Protonation of the *trans*-benzoyl–carbamoyl complex by the ammonium salt affords the CO-coordinated and the amine-coordinated cationic benzoyl complexes **4** and **6**, respectively. Dissociation of the CO or the amine liigand (L′) from **4** or **6** gives the T-shaped three-coordinated species **13**, which may isomerize to its geometrical isomer **14**. Coordination of CO or amine to **14** gives the *cis*-benzoyl–carbonyl or *cis*-benzoyl–amine complex **15** or **16**, respectively. Further reaction of **15** with amine or of **16** with CO and amine forms the *cis*-benzoyl–carbamoyl complex **17**, which has the appropriate geometry for reductive elimination to afford the α-keto amide. The processes affording the carbamoyl group by the reactions of the carbonyl complex with amine, or of the amine-coordinated species with CO and amine, must be similar to those depicted in eqs 5 and 6 and eq 7, respectively. The trans–cis isomerization of the three-coordinated cationic acyl complex with two tertiary phosphine ligands has been proposed for platinum analogues.[4b]

In contrast to the rapid formation of α-keto amide from the cationic benzoyl complex **2** at room temperature, no α-keto amide formation has been observed in the reactions of the neutral benzoylpalladium chloride **1** with CO (10 atm) and amines. As assumed in Scheme IV, formation of the three-coordinated $[Pd(COPh)(PMe_3)_2]^+$ species **13** and **14** will be of particular importance for the formation of α-keto amide from the cationic benzoyl complexes, since the three-coordinate complex **13** can be isomerized to **14** and further converted into the *cis*-benzoyl(carbamoyl)-palladium complex **17**, which liberates the α-keto amide. On the other hand, the chloride ligand in **1**, in contrast to the BF_4 anion in **2**, is less prone to be ionized to form a three-coordinated benzoylpalladium species.

Next we consider the reaction of phenylpalladium complex **7** with CO and amine at room temperature to give the amide and α-keto amide. The relative ratio of amide to α-keto amide in the reaction of **7** increases as the con-

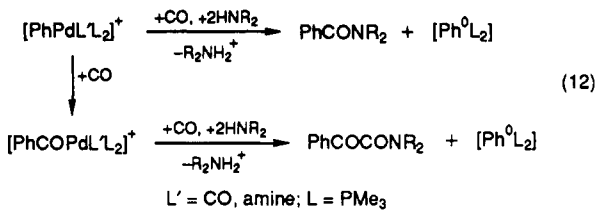
(12) (a) Yamamoto, A.; Yamamoto, T.; Komiya, S.; Ozawa, F. *Pure Appl. Chem.* **1984**, *56*, 1621. (b) Stille, J. K. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2, p 652. (c) Ozawa, F.; Kurihara, K.; Fujimori, M.; Hidaka, T.; Toyoshima, T.; Yamamoto, A. *Organometallics* **1989**, *8*, 180.

Scheme IV[a]



[a] Abbreviations: L = PMe_3; L' = CO, R_2NH.

centration of amine increases (Figure 1). This result can be understood by assuming the mechanism given in eq 12.



(12)

In this mechanism we assume that (i) amide is formed by the reaction of the phenyl complex with amine and CO without participation of the benzoylpalladium complex,[13] (ii) CO insertion to give the benzoyl species is an irreversible process, and (iii) the reaction of the benzoyl complex with CO and amine gives the α-keto amide, exclusively. Thus, the phenyl complex **7** in solution containing amine and CO undergoes two types of reactions, the amide formation and the CO insertion, both processes competing with each other. The rate for the amide formation depends on the concentration of amine, while the CO insertion may proceed without participation of amine. The linear relationship between ln ([A]/[KA]) and ln [HNR_2] values in Figure 1 with the slope of 2.0 supports this mechanism, where the amide formation reaction consumes 2 equiv of amine/equiv of phenylpalladium. As in the formation of α-keto amide from the benzoyl complex (Scheme IV), a similar trans–cis isomerization process to give *cis*-phenyl(carbamoyl)palladium may be involved to produce the amide from **7**.

Relevance of the Present Results to the Catalytic Double- and Single-Carbonylation Reactions. Finally, we consider the relation of the present results with the actual catalytic double- and single-carbonylation reactions of aryl halides and secondary amines to give α-keto amides and amides. The isolation of *trans*-[Pd(Ph)(CO)-(PMe_3)$_2$]PF_6 (**9**), *trans*-PdPh($CONR_2$)(PMe_3)$_2$ (**8**), *trans*-[Pd(COPh)(CO)(PMe_3)$_2$]BF_4 (**4**), and *trans*-Pd-(COPh)($CONR_2$)(PMe_3)$_2$ (**3**) provides direct evidence for nucleophilic attack of amine on a coordinated CO to form the carbamoyl species as assumed in Scheme I. Furthermore, an amine-coordinated complex, *trans*-[Pd-(COPh)(amine)(PMe_3)$_2$]BF_4 (**6**), was isolated. Due to the strong basicity of amines used in the reactions, complex **6** is stable toward deprotonation to give benzoyl(amido)-palladium species from which carboxylic amide might be formed on coupling of the amido ligand with the benzoyl group. The results obtained in this study lend further support to our previously proposed mechanisms for the catalytic double and single carbonylations of aryl halides and amines.[3a] For the single carbonylation it has been often implicitly assumed that a benzoylpalladium complex as a key intermediate undergoes the direct or indirect attack of amine as a potent nucleophile to produce carboxylic amide. The present results clearly exclude the route involving the benzoylpalladium complex as an intermediate for the single carbonylation to give carboxylic amide when highly basic secondary amine was used as nucleophile. The bulk of evidence derived in the present study supports the alternative route involving nucleophilic attack of amine on the CO ligand in the phenylpalladium intermediate to give a phenyl(carbamoyl)palladium intermediate. The similar pattern of the nucleophilic attack of amine on the CO-coordinated benzoyl intermediate to give the benzoyl(carbamoyl)palladium intermediate (E in Scheme I) is quite consistent with the previously proposed mechanisms of the catalytic double carbonylation.

We believe that the present results provide a rather rare example where almost *all* of the putative intermediates and their closely related analogues in the proposed multistep, double-cycle catalytic processes (Scheme I) have been successfully isolated and unambiguously characterized. These results lend strong support to the overall validity of Scheme I. Problems still remaining are the mechanisms to produce α-keto amide and amide from benzoyl and phenyl intermediates having tertiary phos-

(13) Note that, in contrast to the amide formation reaction, the reaction of the benzoyl complex with alcohols is responsible for the ester formation in the palladium-catalyzed carbonylation of aryl halides and alcohols.[3e,14,16] See ref 3e for further discussion on the difference in the single-carbonylation mechanisms giving amide and ester.

(14) (a) Hidai, M.; Hikita, T.; Wada, Y.; Fujikura, Y.; Uchida, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2075. (b) Kudo, K.; Sato, M.; Hidai, M.; Uchida, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2820. (c) Hidai, M.; Kokura, M.; Uchida, Y. *J. Organomet. Chem.* **1973**, *52*, 431. (d) Kudo, K.; Hidai, M.; Uchida, Y. *J. Organomet. Chem.* **1971**, *33*, 393. (e) Schoenberg, A.; Bartoletti, I.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 3318. (f) Milstein, D. *J. Chem. Soc., Chem. Commun.* **1986**, 817. (g) Sugita, M.; Minkiewicz, J. V.; Heck, R. F. *Inorg. Chem.* **1978**, *17*, 2809. (h) Stille, J. Kk.; Wong, P. K. *J. Org. Chem.* **1975**, *40*, 532. (i) Anderson, G. K.; Cross, R. J. *Acc. Chem. Res.* **1984**, *17*, 67. (j) Anderson, G. K. *Organometallics* **1983**, *2*, 665. (k) Moser, W. R.; Wang, A. W.; Kildahl, N. K. *J. Am. Chem. Soc.* **1988**, *110*, 2816.

phine ligands that have higher dissociation tendencies from palladium and provide higher catalytic activities to the palladium center than the less dissociating trimethylphosphine. The subsequent paper deals with the chemistry of platinum analogues having triphenylphosphine and trimethylphosphine ligands, systems studied with the hope of clarifying the remaining problems.[15]

Experimental Section

All manipulations were carried out under an atmosphere of argon or nitrogen or in vacuo. ^1H, ^{13}C, and ^{31}P NMR spectra were measured on JEOL FX-100 and GX-270 spectrometers by Dr. Y. Nakamura and Ms. A. Kajiwara in our laboratory. ^1H and ^{13}C signals were referred to Me_4Si as an internal standard and ^{31}P NMR signals to PPh_3 as an external reference. IR spectra were recorded on a JASCO IR-810 spectrometer. Elemental analysis was carried out by Dr. M. Tanaka and Mr. T. Saito of our laboratory by 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*-Pd(COPh)Cl(PMe_3)$_2$ (**1**) was prepared by the ligand-exchange reaction of *trans*-Pd(COPh)Cl(PPh_3)$_2$[16] with PMe_3 in Et_2O and characterized by means of NMR and IR spectroscopy and elemental analysis.

Preparation of *trans*-[Pd(COPh)(acetone)(PMe_3)$_2$]PF_6 (2). To an acetone solution (10 mL) of *trans*-Pd(COPh)Cl(PMe_3)$_2$ (1.94 g, 4.86 mmol) was added a white powder of $AgPF_6$ (1.23 g, 4.86 mmol) at −50 °C. The system was stirred at the same temperature for 1 h to give a pale yellow solution containing a white precipitate of AgCl, which was removed by filtration. Then, Et_2O (10 mL) was added slowly to the resulting pale yellow solution to give a pale yellow crystalline solid of **2**, which was filtered and dried under vacuum at −10 °C (2.23 g, 81%): ^1H NMR (CD_2Cl_2, −40 °C) δ 1.08 (t, J = 3.7 Hz, 18 H, P*Me*$_3$), 2.43 (s, 6 H, Me_2CO); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ 12.7 (t, J = 15 Hz, P*Me*$_3$), 32.4 (br, *Me*$_2$CO), 219.4 (br, PhCO), 220.9 (br, Me_2CO); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C) −13.3 ppm (s); IR (KBr) 1640 (PhCO), 1650 cm^{-1} (Me_2CO). Anal. Calcd for $C_{16}H_{29}F_6O_2P_3Pd$: C, 33.9; H, 5.2. Found: C, 34.0; H, 5.3.

The acetone-coordinated benzoyl complex having a BF_4 anion was similarly prepared by using $AgBF_4$ in place of $AgPF_6$ (78%). Anal. Calcd for $C_{16}H_{29}BF_4O_2P_2Pd$: C, 37.8; H, 5.7. Found: C, 37.6; H, 5.8. The IR and NMR data were in agreement with those for the PF_6 complex.

Preparation of *trans*-Benzoyl(carbamoyl)palladium Complexes (3a–c). The complex *trans*-[Pd(COPh)(acetone)(PMe_3)$_2$]PF_6 (0.29 g, 0.51 mmol) was placed in a Schlenk tube, and acetone (5 mL) was added under an atmospheric pressure of CO. The system was cooled to −20 °C, and $HNMe_2$ (430 μL, 6.5 mmol) was added by means of a syringe. The pale yellow solution quickly turned to a red homogeneous solution, from which a red precipitate of **3a** was gradually formed. This precipitate was collected by filtration, washed with acetone at −30 °C, and dried under vacuum. The crude product thus obtained was recrystallized from CH_2Cl_2–Et_2O to give red crystals of *trans*-Pd(COPh)(CONMe$_2$)(PMe_3)$_2$ (**3a**; 0.18 g, 81%). Anal. Calcd for $C_{16}H_{29}NO_2P_2Pd$: C, 44.1; H, 6.7; N, 3.2. Found: C, 44.4; H, 7.1; N, 3.1. The IR and NMR data are listed in Table I.

The ^{13}CO-labeled complex *trans*-Pd(COPh)(^{13}CONMe$_2$)(PMe_3)$_2$ was similarly prepared by using ^{13}CO in place of CO in natural abundance. IR (KBr): 1565 (benzoyl), 1495 cm^{-1} (carbamoyl).

Complex **3b** was prepared also by a procedure similar to that for **3a**, with use of piperidine in place of dimethylamine in a yield of 41%. Anal. Calcd for $C_{19}H_{33}NO_2P_2Pd$: C, 48.0; H, 6.9; N, 2.9. Found: C, 48.1; H, 7.4; N, 2.9.

The preparation of **3c** was performed as follows. To a solution of *trans*-[Pd(COPh)(acetone)(PMe_3)$_2$]BF_4 (0.16 g, 0.31 mmol) in acetone (0.5 mL) was added pyrrolidine (3.5 mL, 42 mmol) at −20 °C under a CO atmosphere. When the system was stirred at the same temperature, the white suspension gradually turned to a red homogeneous solution. Then, Et_3N (2 mL) was added and the system was allowed to stand at −20 °C for 3 days to form red crystals of **3c**, which was filtered, washed with acetone, and dried under vacuum (0.083 g, 58%). Anal. Calcd for $C_{18}H_{31}NO_2P_2Pd$: C, 46.8; H, 6.8; N, 3.0. Found: C, 46.7; H, 7.1; N, 3.1.

Preparation of *trans*-[Pd(COPh)(CO)(PMe_3)$_2$]BF_4 (4). The acetone-coordinated complex *trans*-[Pd(COPh)(acetone)(PMe_3)$_2$]BF_4 (0.56 g, 1.1 mmol) was dissolved in CH_2Cl_2 (2 mL) at −20 °C. The solvent was evaporated by bubbling CO gas into the solution at room temperature for 30 min to give an off-white powder of **4** (0.52 g, 99%). Since complex **4** is unstable in the solid state as well as in solution in the absence of free CO, analytically pure complex **4** could not be isolated. Under a CO atmosphere, on the other hand, complex **4** is fairly stable in solution and could be characterized by NMR spectroscopy: ^1H NMR (CD_2Cl_2, −40 °C) δ 1.31 (t, J = 3.9 Hz, 18 H, P*Me*$_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ 14.8 (t, J = 16 Hz, P*Me*$_3$), 180.2 (t, J = 18 Hz, terminal CO), 231.2 (br, *C*OPh); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C) −11.9 ppm (s); IR (KBr) 1638 (Ph*CO*), 2138 cm^{-1} (terminal CO).

Preparation of *trans*-[Pd(COPh)(pyrrolidine)(PMe_3)$_2$]BF_4 (6c). To a solution of the acetone-coordinated complex **2** (0.21 g, 0.41 mmol) in CH_2Cl_2 (3 mL) was added pyrrolidine (0.5 mL, 6 mmol) under an argon atmosphere at room temperature. The color of the solution quickly turned from pale yellow to bright yellow. The system was cooled to −20 °C, and Et_2O (5 mL) was slowly added to the solution to give a yellow precipitate of **6c**, which was filtered, washed with Et_2O, and dried under vacuum (0.21 g, 100%): ^1H NMR (CD_2Cl_2) δ 1.29 (t, J = 3.5 Hz, 18 H, P*Me*$_3$), 1.9 (br, 4 H, NCH$_2$(*CH*$_2$)$_2$), 3.2 (br, 4 H, NC*H*$_2$), 4.0 (br, 1 H, N*H*); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ 13.8 (t, J = 14 Hz, P*Me*$_3$), 24.6 (s, NCH$_2$*C*H$_2$), 51.1 (s, N*C*H$_2$), 231.5 (br, Ph*C*O); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −50 °C) −15.8 ppm (s); IR (CH_2Cl_2) 3292 (*NH*), 1641 cm^{-1} (Ph*CO*). Anal. Calcd for $C_{17}H_{32}NOP_2PdBF_4$: C, 39.1; H, 6.2; N, 2.7. Found: C, 39.2; H, 6.4; N, 2.6.

Preparation of *trans*-[PdPh(acetone)(PMe_3)$_2$]PF_6 (7). To a solution of *trans*-PdPh(I)(PMe_3)$_2$[17] (1.0 g, 2.2 mmol) in acetone (5 mL) was added a white solid of $AgPF_6$ (0.55 g, 2.2 mmol) at −50 °C. The pale yellow solution instantly turned to a colorless solution, from which a white precipitate of AgI gradually formed. After removal of the precipitate by filtration, Et_2O (10 mL) was added slowly to the solution to give colorless crystals of **7** (1.0 g, 87%): ^1H NMR (CD_2Cl_2, −40 °C) δ 1.10 (t, J = 3.6 Hz, 18 H, P*Me*$_3$), 2.4 (br, 6 H, COMe$_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ 12.5 (t, J = 15 Hz, P*Me*$_3$), 32.2 (s, *Me*$_2$CO), 217.0 (br, Me$_2$*C*O); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C) −10.5 ppm (s); IR (KBr) 1650 cm^{-1} (Me$_2$*CO*). Anal. Calcd for $C_{15}H_{29}F_6OP_3Pd$: C, 33.4; H, 5.4. Found: C, 34.1; H, 5.8.

Preparation of *trans*-PdPh(CONMe$_2$)(PMe_3)$_2$ (8a). The complex *trans*-[PdPh(acetone)(PMe_3)$_2$]PF_6 (0.52 g, 0.97 mmol) was dissolved in acetone (5 mL) at −40 °C under a CO atmosphere. Then, Me_2NH (1.3 mL, 19.6 mmol) was added to the solution to give a pale yellow solution, from which a white crystalline precipitate of **8a** gradually formed. The product was filtered, washed with acetone, and dried under vacuum (0.29 g, 73%). Anal. Calcd for $C_{15}H_{29}NOP_2Pd$: C, 44.2; H, 7.2; N, 3.4. Found: C, 43.6; H, 6.9; N, 3.2. The NMR and IR data are listed in Table I.

Complexes **8b** and **8c** were prepared in acetone-d_6 and characterized by NMR spectroscopy without isolation. The acetone-coordinated complex **7** (ca. 20 mg) was placed in a Schlenk tube and dissolved in acetone-d_6 (0.4 mL) under a CO atmosphere. The amine (piperidine for **8b** and pyrrolidine for **8c**; 20 equiv/equiv of **7**) was added at −40 °C by means of a syringe. The resulting pale yellow solution was transferred into an NMR sample tube under a CO atmosphere at the same temperature by means of a cannula and examined by NMR spectroscopy. The ^{31}P NMR

(15) Huang, L.; Ozawa, F.; Yamamoto, A. *Organometallics*, following paper in this issue.

(16) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.

(17) The complex *trans*-Pd(Ph)I(PMe_3)$_2$ was prepared by treatment of *trans*-PdEt$_2$(PMe_3)$_2$ with PhI without solvent at 40 °C for 1 h, and colorless crystals of *trans*-Pd(Ph)I(PMe_3)$_2$ were obtained by addition of hexane to the resulting yellow solution. The complex was characterized by elemental analysis and NMR and IR spectroscopy: ^1H NMR (CD_2Cl_2, −20 °C) δ 1.23 (t, J = 3.5 Hz, P*Me*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C) −12.6 ppm; IR (KBr) 1560 cm^{-1} (skeletal vibration of the Ph group). Anal. Calcd for $C_{12}H_{23}P_2IPd$: C, 31.1; H, 5.0; I, 27.5. Found: C, 31.2; H, 4.9; I, 27.4.

spectrum revealed the absence of the starting complex **7** and formation of a single product. The NMR data for complexes **8b** and **8c** are listed in Table I.

Preparation of *trans*-[PdPh(CO)(PMe_3)$_2$]PF_6 (9). The complex *trans*-[PdPh(acetone)(PMe_3)$_2$]PF_6 (0.27 g, 0.50 mmol) was dissolved in CH_2Cl_2 (3 mL) at −30 °C under a CO atmosphere. After the system was stirred for 20 min, Et_2O (5 mL) was slowly added to the solution to form a white precipitate of **9**, which was filtered, washed with cold Et_2O, and dried under vacuum below 0 °C: ^1H NMR (CD_2Cl_2, −40 °C) δ 1.24 (t, J = 4.0 Hz, 18 H, P*Me*$_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C) δ 14.3 (t, J = 16 Hz, P*Me*$_3$), 183.1 (t, J = 14 Hz, *C*O); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −50 °C) −8.7 ppm (s).

Reaction of *trans*-[PdPh(acetone)(PMe_3)$_2$]PF_6 (7) with Piperidine and CO at Room Temperature. The acetone-coordinated complex **7** (ca. 0.06 g) was placed in a Schlenk tube and dissolved in acetone (1 mL) at room temperature under an atmospheric pressure of CO. Piperidine (4–20 equiv/equiv of **7**) was added by means of a syringe. The pale yellow solution quickly changed to dark red. After the system was stirred for 2 h at room temperature, the organic products formed in the system were examined by means of GLC to determine the relative amounts of amide (PhCO$\overline{N(CH_2)_4CH_2}$) and α-keto amide (PhCOCO$\overline{N(CH_2)_4CH_2}$) that were produced in the combined yield of over 95%. The relationship between the amount of piperidine employed in the reaction and the relative ratio of the amide and α-keto amide formed is given in Figure 1.

Reactions of *trans*-[Pd(COPh)(acetone)(PMe_3)$_2$]PF_6 (2) with Secondary Amines under CO. The acetone-coordinated complex **2** (0.083 g, 0.15 mmol) was dissolved in acetone (1 mL) at room temperature under a CO atmosphere. Pyrrolidine (0.13 mL, 1.5 mmol) was added into the yellow solution. The color of the solution quickly turned dark red, and PhCOCO$\overline{N(CH_2)_3CH_2}$ was formed as confirmed by GLC (yield 52 and 97% after 2 and 20 h). The reactions of **2** with piperidine and dimethylamine were carried out similarly, and PhCOCO$\overline{N(CH_2)_4CH_2}$ and PhCOCONMe_2 were formed respectively in the yields of 96 and 81% after 2 h.

Reactivities of *trans*-Pd(COPh)(CO$\overline{N(CH_2)_3CH_2}$)(PMe_3)$_2$ (3c). 1. Reaction of 3c with Pyrrolidine under CO. To a Schlenk tube containing complex **3c** (0.025 g, 0.054 mmol) were added CH_2Cl_2 (1 mL) and pyrrolidine (0.045 mL, 0.54 mmol) at room temperature under an atmospheric pressure of CO. The solution was examined by GLC after 1 day, and only a small amount of PhCOCO$\overline{N(CH_2)_3CH_2}$ (ca. 5%) was observed.

2. Reaction of 3c with the Ammonium Salt $\overline{CH_2(CH_2)_3NH_2}BF_4$ under CO at −40 °C. Complex **3c** (0.030 g, 0.066 mmol) was placed in a pressurizable NMR sample tube and dissolved in CD_2Cl_2 (0.3 mL) at room temperature under N_2. The ammonium salt $\overline{CH_2(CH_2)_3NH_2}BF_4$ (0.016 g, 0.1 mmo6) was added to the solution of **3c** at −40 °C, and CO (1 atm) was introduced into the system after the NMR tube was evacuated by pumping. The solution changed color from red to orange quickly. The reaction solution was examined by $^{13}C\{^1H\}$ NMR spectroscopy at −40 °C, and the signals due to the carbonyl carbons in benzoyl and hydroxy(amino)carbene groups of the *trans*-[Pd(COPh){C(OH)($\overline{N(CH_2)_3CH_2}$)}(PMe_3)$_2$]BF_4 complex (**5c**) were observed at δ 278.1 and 215.4 together with two small signals arising from the carbonyl carbons in the benzoyl and carbamoyl groups of the starting complex **3c** at δ 275 and 212. At −50 °C, the $^{31}P\{^1H\}$ NMR spectrum of the solution showed two singlets in a ratio of 4:1 at −12.0 and −11.7 ppm due to the complexes **5c** and **3c**.

3. Reaction of Complex 3c with the Ammonium Salt $\overline{CH_2(CH_2)_3NH_2}BF_4$ under ^{13}CO at Room Temperature. To a Schlenk tube containing complex **3c** (0.041 g, 0.089 mmol) were added acetone (1 mL) and $\overline{CH_2(CH_2)_3NH_2}BF_4$ (0.030 g, 0.19 mmol) at −20 °C. After the system was evacuated, ^{13}C-labeled CO was introduced into the Schlenk tube. The reaction solution was then stirred for 20 h at room temperature. The resulting dark red solution was examined by GC–MS. The α-keto amide was found to be formed selectively in a yield of 51% and the ratio of PhCO^{13}CO$\overline{N(CH_2)_3CH_2}$ and PhCO^{12}CO$\overline{N(CH_2)_3CH_2}$ was determined to be 0.92:0.08.

Reactivities of *trans*-Pd(Ph)($CONMe_2$)(PMe_3)$_2$ (8a). 1. Thermal Stability of Complex 8a. The complex **8a** (0.020 g, 0.049 mmol) was dissolved in acetone (1 mL), and the solution stood at room temperature for 3 days. The GLC examination of the acetone solution revealed that no amide was formed. On heating the solution at 40 °C for 5 h the color of the solution changed to pink. Only 2%/Pd of $PhCONMe_2$ was found to be formed.

2. Reaction of Complex 8a with the Ammonium Salt $Me_2NH_2BF_4$ under CO. To a Schlenk tube containing complex **8a** (0.027 g, 0.067 mmol) were added acetone (1 mL) and $Me_2NH_2BF_4$ (0.018 g, 0.14 mmol) under N_2 at room temperature. After the system was evacuated, CO (1 atm) was introduced. The colorless solution quickly turned to dark red. The GLC examination of the solution that was stirred for 2 h at room temperature indicated formation of $PhCONMe_2$ in a yield of 31%.

3. Reaction of Complex 8a with the Ammonium Salt $Me_2NH_2BF_4$ under ^{13}CO. To a colorless acetone solution (1 mL) containing complex **8a** (0.038 g, 0.092 mmol) was added $Me_2NH_2BF_4$ (0.025 g, 0.19 mmol) under N_2. After the system was evacuated, ^{13}C-labeled CO (1 atm) was introduced. The solution turned dark red quickly. The reaction solution was examined by GC–MS after the system was stirred for 15 h at room temperature. *N,N*-Dimethylbenzamide containing Ph$^{13}CONMe_2$ and Ph$^{12}CONMe_2$ in a ratio of 89:11 was obtained in a 60% yield.

Acknowledgment. This work was supported by a Grant-in-Aid from the Ministry of Education, Science and Culture of Japan. Financial support from the Toray Science Foundation is gratefully acknowledged.