Palladium-Promoted Double-Carbonylation Reactions. Reactions of Organopalladium Compounds with Carbon Monoxide and Amines To Give α-Keto Amides

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A variety of mono- and diorganopalladium complexes, *trans*-$PdR(X)L_2$ (R = Me, Et, and Ph; X = Cl, Br, I, and aryloxo; L = teritary phosphine ligand) and *cis*-$PdMe_2L_2$, react with carbon monoxide and secondary amines under mild conditions to give α-keto amides as double-carbonylation products. A series of acylpalladium complexes, *trans*-$Pd(COR)X(PMePh_2)_2$ (R = Ph, X = Cl, Br, and I; R = Me, X = Cl), the presumed reaction intermediates, were prepared, and their reactions with carbon monoxide and amines were investigated. The reaction of benzoylpalladium having bromo and iodo ligands with CO and amines proceeds more smoothly in a solvent of higher polarity than in nonpolar solvents, whereas the reaction with benzoyl(chloro)palladium complex takes place more readily in nonpolar solvents. On the basis of the effect of the solvent polarity on the reactions, two types of reaction pathways have been proposed: one involves an ionic acyl(carbonyl)palladium intermediate $[PhCOPd(CO)L_2]^+X^-$ attacked by amine to give acyl–carbamoyl species, from which α-keto amide is reductively eliminated, while the other mechanism proceeds through a neutral acyl–carbonyl intermediate [Pd(COR)(CO)XL]. Evidence to support the former mechanism has been obtained from the experiments using *trans*-$[Pd(COPh)(CO)(PMePh_2)_2]ClO_4$, which is prepared by the treatment of *trans*-$Pd(COPh)Cl(PMePh_2)_2$ with $AgClO_4$ and CO.

Introduction

Carbonylation reactions of organic compounds promoted by transition-metal complexes are widely utilized in organic synthesis to produce carbonyl compounds such as esters, amides, aldehydes, carboxylic acids, and ketones.[1] These reactions generally consist of monocarbonylation processes in which one CO molecule can be introduced into organic compounds in one step. For example, alkoxycarbonylation[2] and amidation[3] of aryl or vinyl halides catalyzed by palladium compounds give esters and amides, respectively (eq 1).

$$RX + CO + HY \xrightarrow{\text{Pd catalyst}} RCOY + HX \quad (1)$$

(RX = organic halides; HY = alcohol or amine)

If two CO molecules can be introduced into organic compounds successively, the products containing the two reactive carbonyl groups in adjacent positions can be utilized as convenient starting materials in organic syntheses. The precedents of such double-carbonylation reactions are extremely limited.[4,5a,b] Except for the processes producing oxalic acid derivatives,[4d,e] the double carbonylation of benzyl halides using a phase-transfer technique with a cobalt carbonyl anion constitutes the sole example until recently.[4a-c] This process, for which a consecutive CO insertion into the benzyl–cobalt bond was postulated, appears to involve the participation of an enolized form of the benzylic protons for driving the second CO insertion.[4c] Thus the scope of application of this type of double-carbonylation process is restricted to benzyl halides and their derivatives.

Recently we found that organopalladium complexes *trans*-$PdR(X)(PMePh_2)_2$ (R = Me, X = I; R = Ph, X = Br) reacted with CO in the presence of secondary amines (R'_2NH) to afford α-keto amides (eq 2) ($RCOCONR'_2$)

$$trans\text{-}PdR(X)(PMePh_2)_2 + 2CO + R'_2NH \rightarrow RCOCONR'_2 \quad (2)$$

under mild conditions.[6] On the basis of this finding a catalytic process (eq 3) of converting various organic halides (RX) into α-keto amides in the presence of CO and amines has been developed.[7] A similar process was also

$$RX + 2CO + 2R'_2NH \xrightarrow{\text{Pd catalyst}} RCOCONR'_2 + R'_2NH_2X \quad (3)$$

developed by Kobayashi and Tanaka independently.[8] Since a variety of organic halides can be utilized in this type of double-carbonylation process, the scope of application is much wider than that of the previously reported benzyl halide double carbonylation, and the α-keto acid derivatives obtained can be utilized for synthesizing various compounds.[9]

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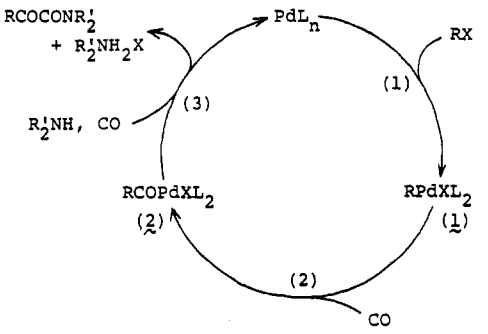

Figure 1. A possible scheme of catalytic double carbonylation of organic halides (RX) with secondary amines (R'_2NH) involving elementary steps 1–3.

The essence of this reaction probably consists of several elementary processes as shown in Figure 1: (i) oxidative addition of organic halides to zerovalent palladium complex to give organopalladium halide species (**1**), (ii) insertion of CO into the palladium–carbon bond to give acylpalladium halide species (**2**), and (iii) further reaction of the CO molecule with complex **2** to release the α-keto amides on interaction with amine, regenerating the palladium(0) species, which further carries the catalytic cycle as shown in Figure 1. The oxidative addition of organic halide to Pd(0) complexes (step 1)[10] and CO insertion into the Pd–C bond (step 2)[11] are known processes, but no detailed study has been made regarding the exact course of step 3, which involves the reaction of acylpalladium complexes (**2**) with a secondary amine in the presence of carbon monoxide.

Two pathways are conceivable for the process. One is the consecutive insertion of the second CO molecule into the acyl–palladium bond to give an (organoglyoxyl)palladium species (A), which is attacked by the amine to liberate the α-keto amide (eq 4). The other is the coordi-

$$\underset{\mathbf{2}}{RCOPd(X)L_2} + CO \rightleftharpoons \underset{\mathbf{A}}{RCOCOPd(X)L_2} \xrightarrow{2R'_2NH} RCOCONR'_2 + R'_2NH_2X + PdL_n \quad (4)$$

nation of a second CO to acylpalladium species to give an acyl(carbonyl)palladium species (B), which is attacked by the amine to generate an acylcarbamoylpalladium complex (C). The α-keto amide is then reductively eliminated from C (eq 5).

$$\underset{\mathbf{2}}{RCOPd(X)L_2} + CO \rightarrow \underset{\mathbf{B}}{RCOPd(CO)XL_n} \xrightarrow[-R'_2NH_2X]{2R'_2NH} \underset{\mathbf{C}}{L_nPd(CONR'_2)(COR)} \xrightarrow{CO} L_nPd(CO)_m + RCOCONR'_2 \quad (5)$$

Limited studies have been made so far concerning the equilibrium between the acyl and alkylglyoxyl transition-metal complexes, and the forward reaction is considered thermodynamically unfavorable.[12] However, if the (organoglyoxyl)palladium complex (A) should be very reactive toward the attack of amine to liberate the α-keto amide (eq 4), the catalytic reaction involving double CO insertion still may be possible. As for the other possibility, if the (organoglyoxyl)palladium species should have an η^2-coordination mode, the equilibrium might be favorable for the double CO insertion.[5]

On the other hand, attack of amines on the coordinated CO ligand to generate the carbamoyl transition-metal complexes is well-documented,[13] although the succeeding reductive elimination of α-keto amide from the acyl–carbamoyl intermediate (C in eq 5) has no precedent.

It is the primary objective of the present and accompanying papers to examine factors influencing the selectivity in the formation of α-keto amides by studying the basic reactions of the organopalladium complexes with CO and amines and to shed light on the mechanism of the double-carbonylation reactions. The present paper is mainly concerned with the reactions of alkyl(or aryl)palladium and acyl(or aroyl)palladium complexes with CO and amines. The succeeding paper[14] deals with the reactions of the (alkyl- and arylglyoxyl)palladium complexes with amines.

Results

The following types of organopalladium complexes were prepared and subjected to reactions with CO and amines: (i) *trans*-alkyl- and -aryl(halo)bis(tertiary phosphine)palladium(II), *trans*-$PdR(X)L_2$, (ii) alkyl(aryloxo)bis(tertiary phosphine)palladium(II), *trans*-$PdR(OAr)L_2$, (iii) *cis*-dialkylbis(tertiary phosphine)palladium(II), *cis*-PdR_2L_2, (iv) acyl(including aroyl)(halo)bis(tertiary phosphine)palladium(II), *trans*-$Pd(COR)(X)L_2$, and (v) acylbis(tertiary phosphine)palladium(II) perchlorate.

(i) Reactions of *trans*-$PdR(X)L_2$. The alkyl- and arylpalladium halides having two tertiary phosphine ligands were prepared by oxidative-addition reactions of zerovalent palladium complexes with alkyl or aryl halides or by treatment of dialkylpalladium complexes with HCl. All of these complexes were established to have trans configurations by means of ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

Reactions of these complexes (eq 6) with amines (10

$$trans\text{-}PdR(X)L_2 + R'_2NH + CO \rightarrow RCOCONR'_2 + R'_2NH_2X + Pd(CO)_nL_m \quad (6)$$

(R = Me, Et, and Ph; X = Cl, Br, and I; L = $PMePh_2$, PMe_2Ph, PEt_2Ph, and PPh_3)

mol/mol of Pd) under a pressure of CO (10 atm) proceeded smoothly at room temperature to yield α-keto amides and amides as summarized in Table I.

Among the tertiary-phosphine-coordinated complexes examined, only $PdPh(Br)(PEt_3)_2$ produced neither amide nor α-keto amide (run 24) and gave only a small amount of *trans*-$Pd(COPh)Br(PEt_3)_2$. For driving reaction 6 to proceed, it was necessary to carry out the reactions under pressurized CO; at 1 atm of CO the reaction stopped at the step to give the acylpalladium species and no amides were formed (run 7). In other runs where the alkyl- or arylpalladium complexes were transformed to α-keto amides and amides, formation of palladium(0) carbonyl complexes containing the tertiary phosphine ligands was confirmed by examination of the IR spectra of substances recovered from the reaction systems after removal of

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Table I. Carbonylation of *trans*-PdR(X)L_2 Complexes in the Presence of Amines (R'_2NH)[a]

run	complex R	complex X	complex L	amine	solvent (mL)	yield, %/Pd RCOCONR'$_2$	yield, %/Pd $RCONR'_2$	selectivity of RCOCONR'$_2$, %
1				Et_2NH	THF (1)	88	7	93
2				piperidine	THF (1)	63	14	82
3	Me	I	$PMePh_2$	morpholine	toluene (1)	75	5	94
4				morpholine	THF (1)	52	41	56
5				morpholine	CH_2Cl_2 (1)	27	40	40
6				Et_2NH	toluene (1)	39	4	91
7[b]	Me	Cl	PEt_2Ph	Et_2NH	toluene (1)	0	trace	0
8				Et_2NH	THF (1)	30	1	97
9				Et_2NH	acetone (1)	27	0	100
10	Me	Cl	PMe_2Ph	Et_2NH	toluene (1)	14	13	52
11				Et_2NH	acetone (1)	6	19	24
12	Et	Cl	PMe_2Ph	Et_2NH	toluene (1)	34	7	83
13				Et_2NH	acetone (1)	18	6	75
14	Ph	Br	PPh_3	Et_2NH	THF (1)	31	69	31
15				Et_2NH	THF (2)	62	1	98
16	Ph	Br	$PMePh_2$	Et_2NH	CH_2Cl_2 (2)	64	0	100
17				Et_2NH	acetone (2)	92	4	96
18				Me_2NH	acetone (3)	96	4	96
19				piperidine	acetone (3)	94	6	94
20	Ph	I	$PMePh_2$	Et_2NH	toluene (3)	30	0	100
21				Et_2NH	THF (1)	48	1	98
22				Et_2NH	acetone (3)	64	0	100
23				Pr_2NH	acetone (3)	58	1	98
24	Ph	Br	PEt_3	Et_2NH	THF (1)	0	0	-

[a] Reaction conditions: complex (~0.1 mmol), amine (~1 mmol), at room temperature for 1 day, $p(CO) = 10$ atm except for run 7. [b] $p(CO) = 1$ atm.

Table II. Carbonylation of *trans*-PdR(OAr)L_2 Complexes in the Presence of Et_2NH[a]

run	complex R	complex ArO	complex L	solvent	yield, %/Pd RCOCONEt$_2$	yield, %/Pd $RCONEt_2$	yield, %/Pd ROOAr	selectivity of RCOCONEt$_2$, %
1	Me	PhO	PMe_2Ph	toluene	3	17	5	12
2	Me	PhO	PEt_2Ph	acetone	25	15	4	57
3				toluene	13	19	13	29
4	Et	*p*-MeC_6H_4O	PMe_2Ph	acetone	12	5	20	32
5				toluene	10	5	24	26
6	Et	PhO	PMe_2Ph	acetone	44	12	17	60
7				THF	31	6	45	38
8				toluene	7	6	59	10
9	Et	*p*-NCC_6H_4O	PMe_2Ph	acetone	67	20	*b*	77
10				toluene	70	12	*b*	85

[a] Reaction conditions: complex (~0.1 mmol), Et_2NH (~1 mmol), solvent (1 mL), $p(CO) = 10$ atm at room temperature for 1 day. [b] Not measured.

solvents. The rest of the alkyl- or arylpalladium complexes other than those transformed into α-keto amides and amides with the concomitant formation of the Pd(0) carbonyl complexes were recovered as the corresponding acylpalladium complexes. Whether dialkylammonium halide was in fact produced in the reaction systems was not confirmed.[15]

Distinct influences of solvents on the formation of α-keto amides are noted. For alkylpalladium (R = Me and Et), employment of nonpolar solvents such as toluene is more suitable for selective formation of α-keto amides (runs 3–6 and 8–13), whereas reactions of phenyl complexes, *trans*-$Pd(Ph)X(PMePh_2)_2$ (X = Br and I), proceed more readily in polar ones to give $PhCOCONR'_2$ in higher yields (runs 15–23). It is also noted in the reactions of *trans*-$PdMe(I)(PMePh_2)_2$ with various amines that more basic amines such as Et_2NH and piperidine gave higher selectivity of α-keto amides than the less basic morpholine. Aniline, the least basic amine examined, gave only acetanilide in a poor yield without giving any double-carbonylation product. Reaction of methanol in place of amines with *trans*-$PdMe(I)(PMePh_2)_2$ and CO afforded methyl acetate as the only reaction product.

When a primary amine was used instead of the secondary amines, Schiff bases of the α-keto amides were obtained. For example, the reaction of *trans*-$PdMe(I)(PMePh_2)_2$ with butylamine and CO (eq 7) gave a quantitative yield of MeC(=NBu)CONHBu, which may be formed by the dehydration reaction of $BuNH_2$ with MeCOCONHBu.[16]

trans-$PdMe(I)(PMePh_2)_2 + BuNH_2 +$ CO (10 atm) $\xrightarrow[\text{toluene}]{\text{room temperature}}$ [MeCOCONHBu] $\xrightarrow{+BuNH_2}$ MeC(=NBu)CONHBu (100%/Pd) (7)

(ii) Reactions of *trans*-PdR(OAr)L_2. Monoalkylpalladium complexes containing aryloxo ligands instead of the halide ligands also give α-keto amides (eq 8) together

trans-$PdR(OAr)L_2 + CO + Et_2NH \rightarrow RCOCONEt_2 +$ $RCONEt_2 + ROOAr + ArOH + Pd(CO)_nL_m$ (8)

(15) Formation of dialkylammonium halides was confirmed in the catalytic system.[7]

(16) Formation of Schiff bases of α-keto amides was also noted in the catalytic double-carbonylation system.[8]

Table III. Carbonylation of *cis*-$PdMe_2L_2$ Complexes in the Presence of Amines (R'_2NH)[a]

run	L	amine	yield, %/Pd				selectivity of $MeCOCONR'_2$, %
			$MeCOCONR'_2$	$MeCONR'_2$	MeCOMe	MeCOCOMe	
1	$PMePh_2$	Et_2NH	30	13	56	0	30
2		piperidine	17	60	17	0	18
3		morpholine	50	36	14	0	50
4		aniline	0	49	28	23	0
5	PEt_2Ph	Et_2NH	41	8	49	0	42
6	$PEtPh_2$	Et_2NH	20	4	57	0	25

[a] Reaction conditions: complex (~0.1 mmol), amine (~1 mmol) under 1 atm of CO in toluene (1 mL) at room temperature for 1 day.

Table IV. Reactions of Benzoylpalladium Complexes with CO in the Presence of Various Amines[a]

run	complex	amine	pK_b	yield, %/Pd		selectivity of $PhCOCONR'_2$, %
				$PhCOCONR'_2$	$PhCONR'_2$	
1	*trans*-$Pd(COPh)Cl(PMePh_2)_2$ (2a)	Me_2NH	3.28	77	trace	100
2		piperidine	2.88	71	trace	100
3		Et_2NH	2.90	35	2	95
4		$^nPr_2NH$	3.02	17	2	90
5		$^iPr_2NH$	2.95	0	0	
6		aniline	9.34	0	0	
7	*trans*-$Pd(COPh)Br(PMePh_2)_2$ (2b)	Me_2NH		64	trace	100
8		piperidine		76	trace	100
9		Et_2NH		68	0	100
10		$^nPr_2NH$		3	trace	100
11		$^iPr_2NH$		0	0	
12		aniline		0	0	

[a] The reactions were carried out on a 0.1-mmol scale in CH_2Cl_2 (3 mL) at room temperature for 1 day (complex/amine ≃ 1:10); $p(CO) = 10$ atm.

with amides and esters in the reactions with diethylamine under 10 atm of CO at room temperature as shown in Table II. Formation of phenol was also confirmed. The alkyl(aryloxo)palladium complexes used for reaction 8 were prepared by treatment of dialkylbis(tertiary phosphine)-palladium(II) with various substituted and unsubstituted phenols (see Experimental Section). Formation of aryl carboxylate in reaction 8 is accounted for by CO insertion into the alkyl–palladium bond in *trans*-$PdR(OAr)L_2$ followed by reductive elimination of the acyl and aryloxo ligands as observed in the reactions of *trans*-$PdR(OAr)L_2$ with CO carried out in the absence of the amines.[17]

The solvent effect on the selectivity of the $RCOCONEt_2$ formation is also noted in reaction 8. As observed in the reactions of arylpalladium bromide and iodide with CO and the secondary amines, employment of more polar solvents appears to favor the formation of α-keto amides. The substituent at the para position on the phenoxo ligand influences the selectivity in the α-keto amides; the electron-releasing substituent such as the methyl group causes the decrease in the yield of α-keto amide.

(iii) Reactions of *cis*-$PdMe_2L_2$. Previously we reported that *trans*-PdR_2L_2 (R = Me, Et) gave RCOR on interaction with 1 atm of CO at room temperature, whereas the reactions of *cis*-$PdMe_2L_2$ and *cis*-$PdEt_2L_2$ with CO under similar conditions gave acetone and biacetyl from the *cis*-dimethyl complex and ethylene and EtCHO from the *cis*-diethyl complex, respectively.[18] Addition of amines to the systems containing *trans*-PdR_2L_2 and CO did not alter the reaction course, and no α-keto amides were formed, whereas addition of secondary amines to the systems containing *cis*-$PdMe_2L_2$ and CO yielded α-keto amides and amides in addition to acetone as shown in Table III. The reaction with aniline did not afford $MeCOCONEt_2$, whereas a considerable amount of biacetyl was formed together with acetone and acetanilide (run 4, Table III). The reaction of *cis*-$PdEt_2(PMePh_2)_2$ with CO and Et_2NH did not give any α-keto amide.

(iv) Reactions of Acylpalladium Complexes. The results described in section i above indicate that the reactions of $RPd(X)L_2$ with pressurized CO proceed to give $RCOPd(X)L_2$ but that the further reactions with CO and amines are slower processes.

For studying the reactivities of the presumed acylpalladium intermediates, the acyl complexes were prepared separately and subjected to the reactions with CO and the amines. The acyl complexes were prepared by oxidative-addition reactions of acetyl or benzoyl halides with zerovalent palladium complexes or by treatment of phenylpalladium halide complexes with 1 atm of CO, and they were characterized by means of IR and NMR spectroscopy as well as elemental analysis (see Experimental Section).

The results of the reactions of the isolated acylpalladium halides with amine and CO summarized in Tables IV–VI indicate that the isolated acylpalladium halide complexes in fact react with amines in the presence of CO to product α-keto amides as the major products together with minor amounts of amides (eq 9).

$$\textit{trans}\text{-}Pd(COR)X(PMePh_2)_2 + CO + R'_2NH \rightarrow RCOCONR'_2 + RCONR'_2 + R'_2NH_2X + Pd(CO)_nL_m \quad (9)$$

(R = Ph, X = Cl (**2a**), Br (**2b**), I (**2c**); R = Me, X = Cl (**2d**))

Table IV shows the influence of the amines employed for the reactions of benzoylpalladium chloride and bromide complexes. In these reactions, part of the initial benzoylpalladium complexes was recovered, and the combined yields of the α-keto amides and amides corresponded to the amounts of the acylpalladium complexes consumed. For example, the reaction of *trans*-$Pd(COPh)Cl(PMePh_2)_2$

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Table V. Effects of CO Pressure and Added Phosphine on the Reactions of Benzoylpalladium Complexes with CO in the Presence of Et_2NH[a]

run	complex	CO, atm	yield, %/Pd		selectivity of $PhCOCONEt_2$, %
			$PhCOCONEt_2$	$PhCONEt_2$	
1	*trans*-Pd(COPh)Cl($PMePh_2$)$_2$ (**2a**)	0	0	5	0
2		1	4	4	50
3		10	35	2	95
4		40	79	2	98
5[b]		10	trace	16	0
6	*trans*-Pd(COPh)Br($PMePh_2$)$_2$ (**2b**)	0	0	4	0
7		1	16	6	73
8		10	68	0	100
9		40	90	0	100
10[b]		10	0	5	0

[a] The reactions were carried out on a 0.1-mmol scale (complex/amine ≃ 1:10) in CH_2Cl_2 (3 mL) at room temperature for 1 day. [b] 10-molar excess amount of $PMePh_2$ was added.

Table VI. Effect of Solvent on the Reactions of Acylpalladium Complexes with Et_2NH[a]

run	complex	solvent (dielectric const)	yield, %/Pd		selectivity of $RCOCONEt_2$, %
			$RCOCONEt_2$	$RCONEt_2$	
1	*trans*-Pd(COPh)Cl($PMePh_2$)$_2$ (**2a**)	acetone (20.70)	18	1	95
2		CH_2Cl_2 (8.93)	35	2	95
3		THF (7.58)	72	0	100
4		toluene (2.38)	90	10	90
5	*trans*-Pd(COPh)Br($PMePh_2$)$_2$ (**2b**)	acetone	88	3	97
6		CH_2Cl_2	68	0	100
7		THF	55	2	96
8		toluene	29	trace	100
9	*trans*-Pd(COPh)I($PMePh_2$)$_2$ (**2c**)	acetone	53	trace	100
10		CH_2Cl_2	33	1	97
11		THF	26	5	84
12		toluene	24	trace	100
13	*trans*-Pd(COMe)Cl($PMePh_2$)$_2$ (**2d**)	acetone	47	0	100
14		CH_2Cl_2	51	0	100
15		toluene	56	0	100

[a] The reactions were carried out on a 0.1-mmol scale (complex/Et_2NH ≃ 1:10) in solution (3 mL) at room temperature for 1 day.

(**2a**) with Et_2NH and CO (10 atm) gave α-keto amide and amide in a combined yield of 37% (run 3 in Table IV). The examination of the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution after 1 day revealed that about 60% of **2a** was remaining. Extension of the reaction time to 3 days at room temperature led to the almost complete conversion of **2a** into $PhCOCNEt_2$ and $PhCONEt_2$. Thus, the combined yields of α-keto amides and amides in Table IV reflect the relative rates of the reactions at room temperature.

The results in Table IV indicate the pronounced steric effect of the kind of amines. In the reactions of **2a**, the combined yield of α-keto amide and amide decreases in the order of Me_2NH > piperidine > Et_2NH > *n*-Pr_2NH > *i*-Pr_2NH ≃ aniline. Since the five secondary amines have almost the same basicities, the decreasing order in yields may reflect the effect of increasing steric bulkiness of the amines. The poor reactivity of aniline may be partly due to its weaker base strength. The *trans*-benzoylbromopalladium complex **2b** shows almost the same trend in yields as **2a**, depending on the amines.

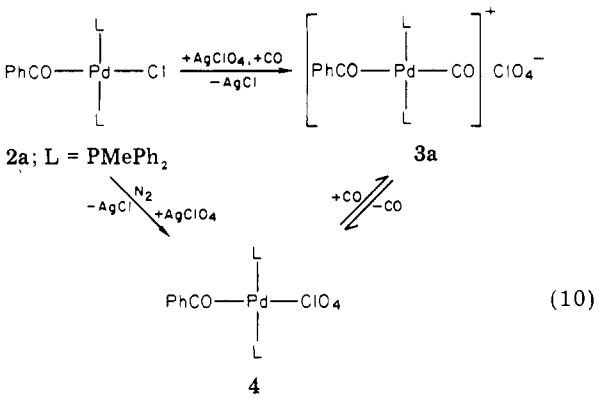
Increase in the CO pressure causes enhancement in yields and selectivity of α-keto amides as shown in Table V. Addition of free $PMePh_2$ completely blocks the formation of α-keto amide, whereas the amide formation is not hindered or even slightly increased by addition of the tertiary phosphine (runs 5 and 10).

Table VI demonstrates the marked solvent effect on the yields of α-keto amide in the reactions of the benzoylpalladium complexes (**2a–2c**) having chloro, bromo, and iodo ligands in four solvents with different dielectric constants. The striking feature is the complete reversal in the trends of yields depending on solvent in the reactions of the chloro complex **2a** on the one side and of the bromo and iodo complexes, **2b** and **2c**, on the other. Toluene, the solvent of the smallest dielectric constant, served as the most favorable solvent for α-keto amide formation, whereas acetone, having the highest dielectric constant, proved to be the least favorable solvent when the chloro complex was used. The trend was in exactly the reverse order with the bromo and iodo complexes. The results with the acetyl(chloro)palladium complex **2d** are also included in Table VI. The yields of $MeCOCONEt_2$ are almost independent of the solvent polarity in these systems.

The opposite trends of the solvent effects depending on the dielectric constant of the solvent in the systems with benzoyl complexes suggest the presence of two reaction pathways, one involving a nonionic species (for the reaction of **2a**) and the other involving an ionic species (for the reactions of **2b** and **2c**) as the key intermediates. Since the catalytic double-carbonylation reactions proceed only with bromides and iodides, studies on the reactivities of the assumed ionic complexes are expected to provide important information regarding the mechanism of the catalytic double carbonylation of organic halides. Hence, the cationic acylpalladium complexes were prepared and their reactivities were studied.

(v) Preparation and Reactions of Cationic Benzoyl(carbonyl)palladium(II) Complexes. A cationic benzoylpalladium complex (**3a**) containing $PMePh_2$ and CO ligands was prepared in situ by treatment of *trans*-

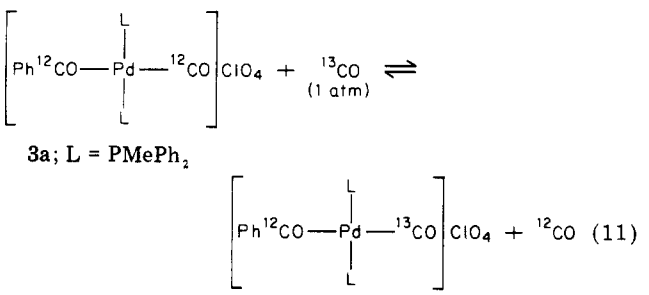
$Pd(COPh)Cl(PMePh_2)_2$ (**2a**) with an equimolar amount of $AgClO_4$ at room temperature under a CO atmosphere. The same complex was also obtained in two steps. The reaction of **2a** with $AgClO_4$ under N_2 first gave *trans*-$Pd(COPh)(ClO_4)(PMePh_2)_2$ (**4**), and further reaction of **4** with CO produced **3a** (eq 10).



(10)

Complex **4** is isolable from the reaction mixture, but attempts to isolate **3a** have been unsuccessful since **3a** easily loses CO. Identity of **3a** formed in situ, however, was available from NMR spectroscopy (see Experimental Section).

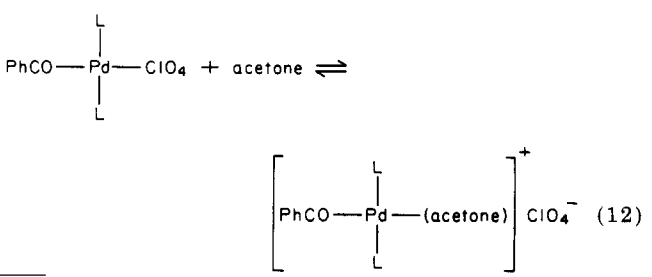
The CO ligand in **3a** can be readily exchanged with incoming CO molecule as observed in the reaction of *trans*-$[Pd(^{12}COPh)(^{12}CO)(PMePh_2)_2]ClO_4$ with 1 atm of ^{13}CO (eq 11). After introduction of the ^{13}CO gas into the



(11)

CD_2Cl_2 solution of **3a**, the intensity of the signal of coordinated CO in ^{13}C NMR was rapidly enhanced. The ^{13}C signal lacked in coupling to the tertiary phosphine ligands in agreement of the rapid exchange reaction. The ^{13}CO added to the system, however, was not incorporated into the benzoyl moiety, indicating that the benzoyl group is not susceptible to rapid decarbonylation and CO-reinsertion processes under ambient conditions.

The electric conductivity of **4** (0.5 mmol/L) measured in acetone showed the value of 43×10^{-6} S/cm, suggesting the formation of an ionic species in the solvent of high dielectric constant. Thus complex **4** is considered to be dissociated in acetone as shown below.



(12)

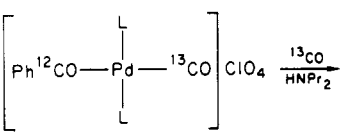
No precedent of this type for an ionic benzoylpalladium complex has been reported, but its platinum analogues are known.[19]

Table VII. Reactions of *trans*-$[Pd(COPh)(CO)(PMePh_2)_2]ClO_4$ (**3a**) with Amines[a]

run	amine	yield, % PhCOCONR′$_2$	yield, % PhCONR′$_2$	selectivity of PhCOCONR′$_2$, %
1	Me_2NH	86	5	95
2	piperidine	83	4	95
3	Et_2NH	69	8	89
4	$^nPr_2NH$	35	21	63

[a] Reactions were carried out on a 0.1-mmol scale in CH_2Cl_2 (2.5 mL) at room temperature for 22 h under 1 atm of CO (complex/amine ≃ 1:10).

Reactions of the ionic benzoylpalladium complex **3a** with a series of secondary amines and 1 atm of CO proceed more readily than those of the neutral benzoylpalladium bromide or iodide complexes descried above. For example, treatment of **2b** (X = Br) with Et_2NH under 1 atm of CO at room temperature in CH_2Cl_2 gave only 16% of $PhCOCONEt_2$ with a 73% selectivity in 1 day (run 7, Table V), whereas the reaction of **3a** with Et_2NH under the almost same conditions produced 69% of $PhCOCONEt_2$ in a selectivity of 89% (run 3, Table VII). The yield and selectivity of α-keto amide decrease with increasing steric bulkiness of the amine employed in the order of Me_2NH > piperidine > Et_2NH > *n*-Pr_2NH. Among the three homologous secondary amines, the selectivity of α-keto amide was the lowest for dipropylamine. Furthermore, highly sterically demanding diisopropylamine gave no carbonylation products at all. Aniline gave only benzamide in a poor yield (10%/Pd). The reaction of *trans*-$[Pd(^{12}COPh)(^{13}CO)(PMePh_2)_2]ClO_4$ prepared from **4** and ^{13}CO (isotopic purity 90%) at 1 atm with *n*-Pr_2NH at room temperature gave $Ph^{12}CONPr_2$ (free of $Ph^{13}CONPr_2$ over natural abundance) and $Ph^{12}CO^{13}CONPr_2$, which contained the 90% of the ^{13}CO label (eq 13). The result



(13)

confirmed that the CO entity in the $-CONR'_2$ group of the α-keto amide is derived from gaseous CO and that the α-keto CO group originates from the benzoyl group without involvement of any decarbonylation and its reverse CO-insertion processes.

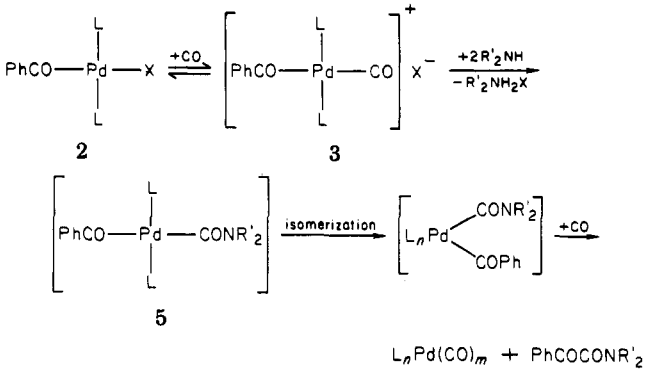
Discussion

Several lines of evidence favoring the process proceeding through the acyl–carbamoyl intermediate followed by reductive elimination of α-keto amide were obtained in the present study. In the succeeding paper we present the evidence disfavoring the alternative mechanism involving consecutive CO insertion into the Pd–C bond.

In this discussion we focus our attention on the mechanism of the reactions of acylpalladium halide complexes with CO and amines to produce α-keto amides and amides. The marked opposite trends of the solvent effect on the reactions of the benzoylpalladium chloride complex on the one hand and of the benzoylpalladium bromide or iodide on the other with CO and amines suggest that two reaction pathways are involved in these reactions. One is the

(19) (a) Kubota, M.; Rothrock, R. K.; Geibel, J. *J. Chem. Soc., Dalton Trans.* **1973**, 1267. (b) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1981**, *20*, 1636.

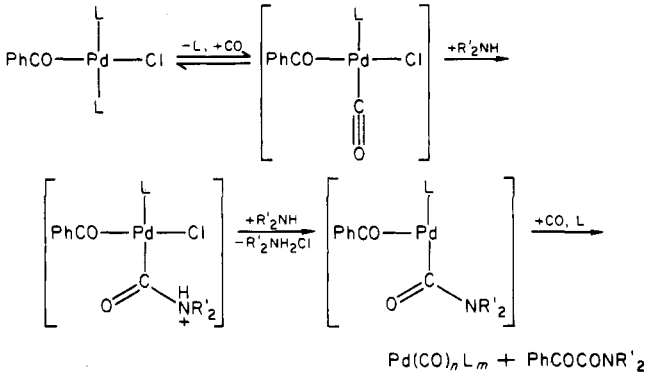
Scheme I. Possible Pathways to Produce α-Keto Amides in Reactions of *trans*-Pd(COPh)(X)L_2 with Amine and CO Involving a Cationic Intermediate



pathway that favors the formation of α-keto amides in nonpolar solvents, while the other favors the α-keto amides formation in polar solvents. For the latter pathway we assume the involvement of a cationic intermediate to which the CO ligand coordinates and undergoes the nucleophilic attack of amine to be followed by reductive elimination of the benzoyl and carbamoyl ligands as in Scheme I. Involvement of the cationic intermediate *trans*-[Pd(COPh)(CO)L_2]$^+X^-$ is supported by the more facile formation of α-keto amide in the reactions of CO and amines when the cationic benzoylpalladium complex having a perchlorate anion (**3a**) was used. The nucleophilic attack of amine on **3** appears to be a slow process that is not favorable for bulkier amines. Whether the amine directly attacks the coordinated CO or first attacks the cationic palladium center followed by migration of the NR'_2 entity to the coordinated CO ligand has not been determined. By either route, an intermediate benzoyl–carbamoyl complex (**5**) with a trans configuration would be formed. Since the trans configuration is not suitable for direct reductive elimination of the benzoyl and carbamoyl groups, an isomerization process to bring the both ligands into cis positions would be intervened. In the studies on reductive elimination of ethane from *trans*-$PdMe_2L_2$, the existence of an energy barrier was observed for the trans isomer to isomerize to *cis*-$PdMe_2L_2$, from which ethane can be reductively eliminated.[20] A theoretical work on the behavior of square-planar diorganopalladium complexes predicts that the energy barrier for the trans to cis polytopal rearrangement is smaller when the ligand to undergo the rearrangement is more electron withdrawing.[21] Thus there would not be too great a barrier for the rearrangement of the acyl and carbamoyl ligands from the mutually trans to the mutually cis positions. Furthermore, the problem of isomerization would not exist at all when a chelating ditertiary phosphine ligand is employed in the actual catalyst systems as a suitable ligand.[8]

The strong inhibition effect of the added tertiary phosphine ligand on the formation of α-keto amide in the reactions of the benzoylpalladium bromide complex **2b** with CO and Et_2NH also is accounted for by assuming the occupation of the coordination site for CO by the added phosphine ligand. On the other hand, the fact that the formation of the amide is not hindered by the added phosphine is consistent with the direct attack of the amine on the benzoyl group attached to palladium or by prior

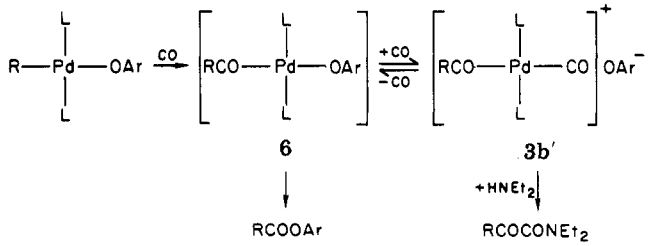
Scheme II. A Possible Mechanism of α-Keto Amide Formation in the Reaction of a Neutral Benzoylpalladium Chloride Complex with Secondary Amines Involving the Replacement of the Tertiary Phosphine Ligand by CO



coordination of the amine on palladium atom followed by the migratory attack on the benzoyl group.

The trend that the reactivity of *trans*-Pd(COPh)Cl-$(PMePh_2)_2$ is greater in solvents of lower dielectric constants is not compatible with the ionic intermediate. A mechanism involving the neutral intermediate should be invoked. If the chloride ligand is reluctant to be dissociated from the palladium atom, the phosphine ligand is a likely candidate to dissociate in the solution. A possible mechanism is shown in Scheme II in which the incoming CO replaces the phosphine ligand cis to the acyl group. Displacement of the tertiary phosphine ligand by CO in a nonpolar solvent is a quite likely process as shown in the previous studies.[11a,18a] The ensuing attack of the amine on the coordinated CO ligand would give the *cis*-benzoylcarbamoylpalladium intermediate which is subject to direct reductive elimination of α-keto amide.

The mechanisms of formation of α-keto amides and amides together with esters in the reactions of *trans*-$PdR(OAr)L_2$ with CO and Et_2NH can be explained similarly by assuming two pathways. The reactions most probably proceed by CO insertion into palladium–alkyl bonds to give acylpalladium intermediates. The polar solvents are generally more suitable for α-keto amide formation (runs 2–8, Table II). It is also noticeable that the complex containing the aryloxo ligand having the electron-withdrawing cyano group gives the higher yields of α-keto amide. These results are compatible with the involvement of an ionic intermediate having the coordinated CO ligand, since the formation of ionic species **3b'** would be more favorable in polar solvents and for complexes having the more electron-withdrawing aryloxo ligand (eq 14). It has been also established that the reductive



(14)

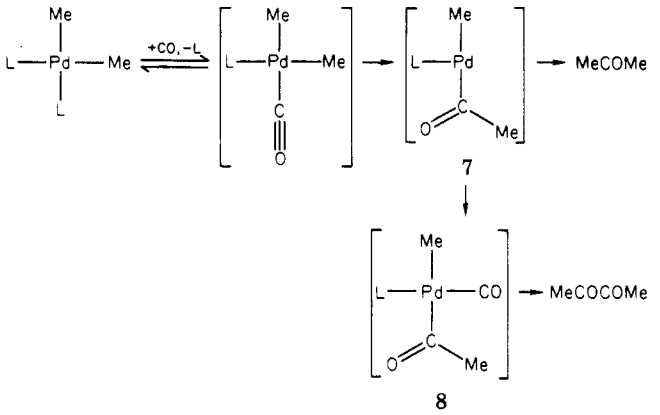
elimination of the ester from **6** is slower with the acyl–aryloxo complexes having the electron-withdrawing substituent at the aryloxo group.[17] This effect would also contribute to decrease the ester formation in polar solvents.

For the reactions of *cis*-$PdMe_2L_2$ with CO and amines a mechanism such as given in Scheme I involving the ionic intermediate is not reasonable. As we have reported

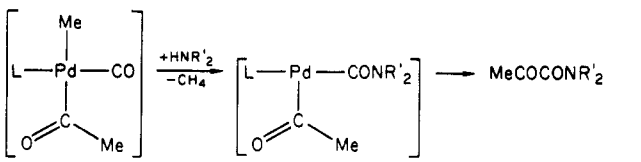
(20) (a) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. (b) Gille, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.

(21) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

Scheme III



previously,[18a] a mechanism involving the displacement of the tertiary phosphine by CO followed by alkyl migration on the coordinate CO to give an acyl–alkyl intermediate seems to be operative. The mechanism showing the formation of acetone and biacetyl from *cis*-$PdMe_2L_2$ is shown in Scheme III. The acetyl–methyl intermediate **7** in Scheme III seems to have a moderate kinetic stability against the reductive elimination of acetone at low temperature because of the trans T-shape configuration. Thus, it is subject to further coordination by CO. In the absence of amine, the coordinated CO would be inserted into the other Pd–Me bond to give a diacetyl species which liberates biacetyl (2,3-butanedione). In the presence of the amine, the nucleophilic attack of R'_2NH on the coordinated CO ligand in **8** would give an acetylcarbamoylpalladium intermediate (**9**) with liberation of methane. Reductive elimination of the acetyl and carbamoyl groups from **9** would give pyruvamide, $MeCOCONR'_2$ (eq 15).



(15)

Experimental Section

All manipulations were carried out under an atmosphere of nitrogen, argon, or carbon monoxide or in vacuo. Solvents and amines were dried in the usual manner, distilled, and stored under a nitrogen atmosphere.

Infrared spectra were recorded on a Hitachi 295 spectrometer using KBr pellets. ^1H, ^{31}P, and ^{13}C NMR spectra were measured on JEOL PS-100 and FX-100 spectrometers. ^1H and ^{13}C NMR signals are referred to Me_4Si as an internal or external standard. ^{31}P NMR signals are referred to PPh_3 as an external standard. Microanalyses (C, H, and halogen) were carried out by T. Saito of our laboratory, using a Yanagimoto CHN Autocorder Type MT-2 and a Yazawa halogen analyzer.

trans- and *cis*-dialkylbis(tertiary phosphine)palladium(II) complexes were prepared according to the methods described previously.[18b,20a]

Preparation of *trans*-PdPh(Br)($PMePh_2$)$_2$. $Pd(PMePh_2)_4$ (0.35 g, 0.39 mmol) prepared from *trans*-$PdEt_2(PMePh_2)_2$[18b] and 2 equiv of $PMePh_2$ were dissolved in 1.0 mL of phenyl bromide to give a homogeneous, light orange solution. After the solution was heated at 60–80 °C for several hours, 10 mL of hexane was added to the system at room temperature to yield a white precipitate, which was filtered, washed with hexane, and dried in vacuo. The product was recrystallized from THF–Et_2O to give a white powder of *trans*-$PdPh(Br)(PMePh_2)_2$ (0.21 g, 83%): mp 164–166 °C dec; ^1H NMR (δ, in acetone-d_6 at room temperature) 1.62 (t, P–CH_3, 3 H, J = 4 Hz), 6.4–6.7 and 6.7–7.1 (m, Pd–Ph, 5 H), and 7.1–7.8 (m, P–Ph, 20 H); $^{31}P\{^1H\}$ NMR (in CD_2Cl_2 at room temperature) 12.4 ppm (s). Anal. Calcd for $C_{32}H_{31}BrP_2Pd$: C, 57.9; H, 4.7; Br, 12.0. Found: C, 57.6; H, 4.6; Br, 11.2. Similarly prepared were *trans*-$PdPh(Br)(PEt_3)_2$[22] and *trans*-$PdPh(Br)(PPh_3)_3$[10a] by using the corresponding tetrakis(tertiary phosphine)palladium complexes in place of $Pd(PMePh_2)_4$.

Preparation of *trans*-PdPh(I)($PMePh_2$)$_2$. To a homogeneous, pale yellow, toluene solution (10 mL) of $Pd(C_6H_5CH{=}CH_2)(PMePh_2)_2$ generated from *trans*-$PdEt_2(PMePh_2)_2$ (2.16 g, 3.8 mmol) and styrene (0.88 mL, 7.6 mmol) in situ[23] was added phenyl iodide (2.1 mL, 19 mmol) at 0 °C. The reaction system was stirred at room temperature to give a white precipitate. After addition of hexane to the system the precipitate formed was filtered, washed with Et_2O (10 mL × 3), and dried in vacuo. The product was recrystallized from THF–Et_2O to yield a white powder of *trans*-$PdPh(I)(PMePh_2)_2$ (2.1 g, 76%): ^1H NMR (δ, in CD_2Cl_2 at room temperature) 1.64 (t, P–CH_3, 6 H, J = 3.4 Hz), 6.6 and 6.7 (m, Pd–Ph, 5 H), and 7.3 and 7.5 (m, P–Ph, 20 H); $^{31}P\{^1H\}$ NMR (in CD_2Cl_2 at room temperature) 11.3 ppm (s). Anal. Calcd for $C_{32}H_{31}IP_2Pd$: C, 54.1; H, 4.4; I, 17.9. Found: C, 54.0; H, 4.3; I, 18.2.

Similarly obtained was *trans*-$PdMe(I)(PMePh_2)_2$[20b] by using methyl iodide instead of PhI. Anal. Calcd for $C_{27}H_{29}IP_2Pd$: C, 50.0; H, 4.5; I, 19.6. Found: C, 49.7; H, 4.6; I, 21.0.

Preparation of *trans*-PdMe(Cl)(PEt_2Ph)$_2$. To a heterogeneous white mixture of *trans*-$PdMe_2(PEt_2Ph)_2$[20a] (0.84 g, 1.7 mmol) and Et_2O (5 mL) cooled to −20 °C was added an Et_2O solution of dry HCl (0.32 N, 5.3 mL). The reaction mixture was stirred at the same temperature to allow it to turn instantly into a colorless homogeneous solution, from which a white precipitate was gradually formed. The precipitate was filtered and recrystallized from acetone to yield white crystals of *trans*-$PdMe(Cl)(PEt_2Ph)_2$ (0.33 g, 74%): ^1H NMR (δ, in CD_2Cl_2 at room temperature) 0.02 (t, Pd–CH_3, 3 H, J = 6 Hz), 1.17 (quintet, P–C–CH_3, 12 H, J = 8 Hz), 1.9–2.3 (m, P–CH_2–, 8 H), and 7.3–7.9 (m, Pd–Ph, 10 H). Anal. Calcd for $C_{21}H_{33}ClP_2Pd$: C, 51.6; H, 6.8; Cl, 7.3. Found: C, 51.8; H, 7.1; Cl, 7.4.

Similarly prepared were *trans*-$PdMe(Cl)(PMe_2Ph)_2$ and *trans*-$PdEt(Cl)(PMe_2Ph)_2$ by using the corresponding dialkyl complexes[20a] in place of *trans*-$PdMe_2(PEt_2Ph)_2$. Anal. (*trans*-$PdMe(Cl)(PMe_2Ph)_2$) Calcd for $C_{17}H_{25}ClP_2Pd$: C, 47.1; H, 5.8; Cl, 8.2. Found: C, 47.5; H, 5.0; Cl, 8.8. (*trans*-$PdEt(Cl)(PMe_2Ph)_2$) Calcd for $C_{18}H_{27}ClP_2Pd$: C, 48.3; H, 6.1. Found: C, 47.9; H, 6.3.

Preparation of *trans*-PdEt(OPh)(PMe_2Ph)$_2$. To a heterogeneous mixture of *trans*-$PdEt_2(PMe_2Ph)_2$ (1.25 g, 2.8 mmol) and Et_2O (15 mL) cooled to −50 °C was added an Et_2O solution (5 mL) of PhOH (2.8 mmol). When the temperature of the mixture was raised gradually, the mixture turned to a pale yellow homogeneous solution at −10 °C and gradually yielded a white precipitate. The product thus formed was filtered, dried in vacuo, and recrystallized from acetone to yield white crystals of *trans*-$PdEt(OPh)(PMe_2Ph)_2$ (0.76 g, 53%): ^1H NMR (δ, in CD_2Cl_2 at −40 °C) 0.64 (m, Pd–C–CH_3, 3 H), 0.88 (m, Pd–CH_2–, 2 H), 6.34 (t, O–Ph(*p*), 1 H, J = 7 Hz), 6.76 (d, O–Ph(*o*), 2 H, J = 7 Hz), 7.00 (t, O–Ph(*m*), 2 H, J = 7 Hz), 7.46 (m, P–Ph(*m,p*), 6 H), and 7.66 (m, P–Ph(*o*), 4 H). Anal. Calcd for $C_{24}H_{32}OP_2Pd$: C, 57.1; H, 6.4; Pd, 21.1. Found: C, 57.0; H, 6.6; Pd, 21.4.

A series of alkyl(aryloxo)palladium complexes listed in Table II was similarly prepared from the corresponding dialkylpalladium complexes and phenols. Anal. (*trans*-$PdMe(OPh)(PMe_2Ph)_2$) Calcd for $C_{23}H_{30}OP_2Pd$: C, 56.3; H, 6.2. Found: C, 57.0; H, 6.4. (*trans*-$PdMe(OPh)(PEt_2Ph)_2$) Calcd for $C_{27}H_{38}OP_2Pd$: C, 59.3; H, 7.0. Found: C, 59.2; H, 7.1. (*trans*-$PdEt(OC_6H_4Me(p))(PMe_2Ph)_2$) Calcd for $C_{25}H_{34}OP_2Pd$: Pd, 20.5. Found: Pd, 20.0. (*trans*-$PdEt(OC_6H_4CN(p))(PMe_2Ph)_2$) Calcd for $C_{25}H_{31}NOP_2Pd$: Pd, 20.1. Found: Pd, 20.4.

Preparation of *trans*-Pd(COPh)Cl($PMePh_2$)$_2$ (2a). *trans*-$Pd(COPh)Cl(PMePh_2)_2$ (**2a**) was prepared by the reaction of benzoyl chloride with $Pd(C_6H_5CH{=}CH_2)(PMePh_2)_2$ generated from *trans*-$PdEt_2(PMePh_2)_2$ and styrene in situ.[23] Typical procedure is as follows.

To a Schlenk tube containing *trans*-$PdEt_2(PMePh_2)_2$ (0.54 g, 0.96 mmol) cooled to −30 °C were added styrene (0.22 mL, 1.9

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Table VIII. IR and NMR Data of Acyl(halo)palladium Complexes

complex	IR[a] ν(CO)	^{1}H NMR[b,c] P-*Me* (J_{H-P}, Hz)[f]	^{1}H NMR[b,c] others	^{13}C{^{1}H} NMR[b,d] P-*Me* (J_{C-P}, Hz)[f]	^{13}C{^{1}H} NMR[b,d] Pd-*CO*[g]	^{13}C{^{1}H} NMR[b,d] others	^{31}P{^{1}H} NMR[b,e,g]
trans-Pd(COPh)Cl($PMePh_2$)$_2$ (**2a**)	1640	1.87 (3.5)		13.1 (14.7)	231.4		8.8
trans-Pd(COPh)Br($PMePh_2$)$_2$ (**2b**)	1645	1.96 (3.4)		14.6 (14.7)	*h*		8.1
trans-Pd(COPh)I($PMePh_2$)$_2$ (**2c**)	1640	2.10 (3.4)		16.1 (13.7)	233.0		7.0
trans-Pd(COMe)Cl($PMePh_2$)$_2$ (**2d**)	1665	2.07 (3.4)	1.46[i]	13.2 (13.7)	235.4	39.6[j]	8.9

[a] In cm^{-1}, KBr disk. [b] In CD_2Cl_2 at room temperature. [c] 100 MHz, chemical shifts are in δ referred to Me_4Si as an internal standard. [d] 25 MHz, chemical shifts are in δ referred to Me_4Si as an internal standard. [e] 40 MHz, chemical shifts are in ppm referred to PPh_3 as an external standard (downfield positive). [f] Triplet. [g] Singlet. [h] Chemical shift is obscured due to its weak intensity. [i] -CO*Me*, t, J_{H-P} = 1.3 Hz. [j] -CO*Me*, t, J_{C-P} = 20.1 Hz.

Table IX. IR and NMR Data of Benzoylpalladium Perchlorate Complexes

complex	IR[a] ν(CO)	^{1}H NMR[b,c] P-*Me* (J_{H-P}, Hz)[f]	^{13}C{^{1}H} NMR[b,d] P-*Me* (J_{C-P}, Hz)[f]	^{13}C{^{1}H} NMR[b,d] $(CO)_{acyl}$[g]	^{13}C{^{1}H} NMR[b,d] $(CO)_{terminal}$[g]	^{31}P{^{1}H} NMR[b,e,g]
trans-Pd(COPh)(ClO_4)($PMePh_2$)$_2$ (**4**)	1680	1.94 (3.3)	12.3 (13.7)	216.9		10.4
trans-[Pd(COPh)(CO)($PMePh_2$)$_2$]ClO_4 (**3a**)	*h*	2.04 (*i*)	13.7 (16.5)	224.6	180.0	9.1

[a] In cm^{-1}, KBr disk. [b] In CD_2Cl_2 at -30 °C in vacuo (for **4**) or under CO atmosphere (for **3a**). [c] 100 MHz, chemical shifts are in δ referred to Me_4Si as an internal standard. [d] 25 MHz, chemical shifts are in δ referred to Me_4Si as an internal standard. [e] 40 MHz, chemical shifts are in ppm referred to PPh_3 as an external standard (downfield positive). [f] Triplet. [g] Singlet. [h] Not measured. [i] Broad triplet.

mmol) and toluene (5 mL). When the system was stirred at room temperature, the white heterogeneous mixture turned into a homogeneous pale yellow solution after 2 h. Then benzoyl chloride (1.1 mL, 9.6 mmol) was added to the system to yield a pale yellow precipitate, which was filtered, washed with Et_2O, and dried in vacuo. The product was recrystallized from CH_2Cl_2–hexane to yield a pale yellow powder of **2a** (96% yield). Similarly prepared were *trans*-Pd(COPh)Br($PMePh_2$)$_2$ (**2b**) and *trans*-Pd(COMe)-Cl($PMePh_2$)$_2$ (**2d**) by using benzoyl bromide and acetyl chloride, respectively, in place of benzoyl chloride. Anal. (**2a**) Calcd for $C_{33}H_{31}ClOP_2Pd$: C, 61.2; H, 4.8; Cl, 5.5. Found: C, 61.0; H, 4.0; Cl, 5.4. (**2b**) Calcd for $C_{33}H_{31}BrOP_2Pd$: C, 57.3; H, 4.5; Br, 11.6. Found: C, 57.4; H, 4.4; Br, 12.2. (**2d**) Calcd for $C_{28}H_{29}ClOP_2Pd$: C, 57.5; H, 5.0; Cl, 6.1. Found: C, 57.3; H, 5.1; Cl, 6.2. Mp **2a**, 182–185 °C dec; **2b**, 158–162 °C dec; **2d**, 133–134 °C dec. The characteristic IR and NMR data of the complexes **2a–d** are given in Table VIII.

Preparation of *trans*-Pd(COPh)I($PMePh_2$)$_2$ (2c). *trans*-Pd(COPh)I($PMePh_2$)$_2$ (**2c**) was prepared by the treatment of *trans*-PdPh(I)($PMePh_2$)$_2$ with CO as follows. To a Schlenk tube containing *trans*-PdPh(I)($PMePh_2$)$_2$ (0.95 g, 1.3 mmol) was added 5 mL of CH_2Cl_2 at -30 °C. After evacuation of the system, 1 atm of CO was introduced. When the system was stirred at room temperature, the color quickly changed from colorless to yellow. After stirring for 3 h the system was concentrated and then 30 mL of hexane was added. The resulting yellow precipitate was filtered, dried in vacuo, and recrystallized from CH_2Cl_2–hexane to yield a yellow powder of *trans*-Pd(COPh)I($PMePh_2$)$_2$ (96% yield): mp 142–145 °C dec. Anal. Calcd for $C_{33}H_{31}IOP_2Pd$: C, 53.6; H, 4.2; I, 17.2. Found: C, 53.6; H, 4.3; I, 16.4.

Preparation of *trans*-[Pd(COPh)(ClO_4)($PMePh_2$)$_2$] (4). To a Schlenk tube containing *trans*-Pd(COPh)Cl($PMePh_2$)$_2$ (**2a**) (1.1 g, 1.7 mmol) and $AgClO_4$ (0.36 g, 1.7 mmol) cooled to -50 °C was added acetone (6 mL) under a nitrogen atmosphere. When the mixture was stirred at room temperature, the system turned into a pale yellow solution with a white precipitate of AgCl. The solution was collected by filtration at -30 °C. Addition of 40 mL of Et_2O to the filtrate yielded a white precipitate, which was filtered, washed with Et_2O (20 mL × 3), and dried in vacuo. The product was recrystallized from CH_2Cl_2 to yield white crystals of **4** (0.78 g, 63%): mp 118–120 °C dec. Anal. Calcd for $C_{33}H_{31}ClO_5P_2Pd$: C, 55.7; H, 4.4; Cl, 5.0. Found: C, 55.4; H, 4.4; Cl, 5.2%.

Further characterization of **4** was made by means of IR and NMR spectroscopy. The characteristic IR and NMR data are given in Table IX. Complex **4** shows a strong ν(C=O) band at 1680 cm^{-1}, which is considerably higher than the ν(C=O) bands of **2a–c** (Table VII). The ^{1}H NMR spectrum of **4** shows a triplet at δ 1.94 arising from the methyl protons of $PMePh_2$ ligands. This triplet pattern shows that **4** has a trans configuration. The trans geometry of **4** is further supported by the appearance of a triplet signal at 12.3 ppm due to the methyl carbon of $PMePh_2$ in the ^{13}C{^{1}H} NMR spectrum.

Preparation and Characterization of *trans*-[Pd(COPh)(CO)($PMePh_2$)$_2$]ClO_4 (3a). To a Schlenk tube containing *trans*-Pd(COPh)Cl($PMePh_2$)$_2$ (**2a**) (0.070 g, 1.1 mmol) and $AgClO_4$ (0.22 g, 1.1 mmol) was added CD_2Cl_2 (2.5 mL) by means of syringe at -30 °C. After evacuation of the system, 1 atm of carbon monoxide was introduced. Stirring the solution at room temperature for 1 h yielded a bright yellow solution with precipitation of AgCl. The solution was collected by filtration under CO atmosphere at -30 °C. A part of the filtrate (~1 mL) was transferred into an NMR sample tube under CO atmosphere at the same temperature, and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were measured. NMR spectra of the solution indicated the presence of *trans*-[Pd(COPh)(CO)($PMePh_2$)$_2$]ClO_4 (**3a**). Addition of Et_2O (40 mL) to the other part of the filtrate yielded a white precipitate, which was washed with Et_2O (20 mL × 2) under CO atmosphere and dried in vacuo. An IR spectrum of the white precipitate showed an identical absorption pattern with that of **4** and no sign of formation of the carbonyl complex was observed.

The characteristic NMR data of the filtrate are given in Table IX. The ^{31}P{^{1}H} NMR spectrum shows only one singlet at δ 9.1 (downfield from PPh_3 external standard) beyond the absorption region of **4** (10.4 ppm). The ^{31}C{^{1}H} NMR spectrum exhibits the two singlet signals corresponding to the terminal and the acyl carbonyl carbons at 180.0 and 224.6, respectively.[19] The intensity of the former signal increases on allowing the solution to stand under ^{13}CO atmosphere, indicating the occurrence of a rapid exchange of the coordinated CO ligand with the free CO molecule. Furthermore, the coupling patterns (triplet) of the methyl groups of the $PMePh_2$ ligands in the ^{13}C{^{1}H} and ^{1}H NMR spectra support the trans geometry of **3a**.

Reactions of Organopalladium Complexes with CO and Amines. General Procedure. To a Schlenk tube containing an organopalladium complex (~0.1 mmol) cooled at -50 °C were added solvent (1–3 mL) and amine (~1 mmol) and/or additive by means of a syringe. After stirring for a few minutes, the solution was quickly transferred into a stainless steel autoclave (50 mL) under an atmosphere of argon. Carbon monoxide was then introduced into the system and the mixture was magnetically stirred at room temperature. After 1 day, the resulting red solution was

again transferred into a Schlenk tube and analyzed by means of GLC (Shimadzu GC-3BT; column, PEG-HT 1 m). Identification of carbonylation products, α-keto amides and amides, was carried out by means of GC–mass spectrometry (Hitachi M-80; column, Silicone OV-1 1 m) and comparison with authentic samples prepared from the corresponding carboxylic acid chloride and amine or by the catalytic double carbonylation.[7] Furthermore, the characterization of the palladium(0) carbonyl complexes as well as the acylpalladium complexes produced in the reaction was made by comparison of IR and/or $^{31}P\{^1H\}$ NMR spectra with those of authentic samples. Authentic samples of carbonyl complexes were prepared by the reactions of dialkylpalladium complexes with CO[18] and used in a crude state since these complexes were too unstable to isolate in a pure state. Pure acyl(halo)palladium complexes were prepared by the treatment of the corresponding alkyl or aryl complexes with CO in solution and used as the authentic samples.

Carbonylation of *trans*-[Pd(COPh)(CO)($PMePh_2$)$_2$]ClO_4 (3a). A solution of **3a** was prepared by the reaction of **2a** with $AgClO_4$ under CO atmosphere or by the treatment of isolated **4** with CO in solution. Typical procedure is as follows.

To a Schlenk tube containing *trans*-Pd(COPh)Cl($PMePh_2$)$_2$ (**2a**) (0.062 g, 0.096 mmol) and $AgClO_4$ (0.020 g, 0.096 mmol) was added CH_2Cl_2 (2.5 mL) under CO atmosphere. After the system was stirred at room temperature for 1 h, the produced white precipitate of AgCl was removed by filtration at −30 °C. Dipropylamine (0.96 mmol) was then added to the system by means of a syringe at −60 °C. When the solution was stirred at room temperature under CO, the color of the system readily turned to red, indicating the formation of Pd(0)–carbonyl species. After 22 h the solution was analyzed by means of GLC, using Ph_2O as an internal standard for determining the yields of α-keto amides and amides. The results are given in Table VII.

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Registry No. **2a**, 84624-62-4; **2b**, 89177-97-9; **2c**, 68391-88-8; **2d**, 89177-93-5; **3a**, 89232-45-1; **4**, 89232-46-2; *trans*-PdMe(I)($PMePh_2$)$_2$, 42582-53-6; *trans*-PdMe(Cl)(PEt_2Ph)$_2$, 89232-47-3; *trans*-PdMe(Cl)(PMe_2Ph)$_2$, 30179-98-7; *trans*-PdEt(Cl)(PMe_2Ph)$_2$, 89232-48-4; *trans*-PdPh(Br)(PPh_3)$_2$, 33381-14-5; *trans*-PdPh(Br)($PMePh_2$)$_2$, 89300-28-7; *trans*-PdPh(I)($PMePh_2$)$_2$, 68391-86-6; *trans*-PdPh(Br)(PEt_3)$_2$, 52230-30-5; *trans*-PdMe(PhO)(PMe_2Ph)$_2$, 89232-49-5; *trans*-PdMe(PhO)(PEt_2Ph)$_2$, 89232-50-8; *trans*-PdEt(*p*-MeC_6H_4O)(PMe_2Ph)$_2$, 89232-51-9; *trans*-PdEt(PhO)(PMe_2Ph)$_2$, 89232-52-0; *trans*-PdEt(*p*-NCC_6H_4O)(PMe_2Ph)$_2$, 89232-53-1; *cis*-$PdMe_2$($PMePh_2$)$_2$, 60885-30-5; *cis*-$PdMe_2$(PEt_2Ph)$_2$, 77881-04-0; *cis*-$PdMe_2$($PEtPh_2$)$_2$, 77881-05-1; *trans*-$PdEt_2$($PMePh_2$)$_2$, 75172-21-3; *trans*-$PdMe_2$(PEt_2Ph)$_2$, 77831-30-2; *trans*-$PdMe_2$(PMe_2Ph)$_2$, 82916-00-5; *trans*-$PdEt_2$(PMe_2Ph)$_2$, 75108-70-2; Pd($PMePh_2$)$_4$, 24981-80-4; Pd(PEt_3)$_4$, 52230-29-2; Pd(PPh_3)$_4$, 14221-01-3; Pd($C_6H_5CH{=}CH_2$)($PMePh_2$)$_2$, 70316-76-6; $MeCOCONEt_2$, 22381-21-1; $MeCOCON(CH_2)_5$, 22381-22-2; $MeCOCON(CH_2CH_2OCH_2CH_2)$, 38382-92-2; $EtCOCONEt_2$, 69016-02-0; $PhCOCONEt_2$, 34906-86-0; $PhCOCONMe_2$, 51579-87-4; $PhCOCON(CH_2)_5$, 14377-63-0; $PhCOCONPr_2$, 84017-26-5; Et_2NH, 109-89-7; Me_2NH, 124-40-3; *n*-Pr_2NH, 142-84-7; *i*-Pr_2NH, 108-18-9; $PMePh_2$, 1486-28-8; CO, 630-08-0; piperidine, 110-89-4; morpholine, 110-91-8; aniline, 62-53-3; phenyl bromide, 108-86-1; styrene, 100-42-5; phenyl iodide, 591-50-4; benzoyl chloride, 98-88-4; benzoyl bromide, 618-32-6; acetyl chloride, 75-36-5.

Preparation of *trans*-Pd(COCOR)Cl($PMePh_2$)$_2$ Complexes (R = Ph and Me) and Their Reactivities Related to Double Carbonylation Promoted by Palladium

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In order to examine the feasibility of the reaction mechanism involving double insertion of CO into the Pd–C bond in the double carbonylation of organic halides catalyzed by palladium complexes giving α-keto amides, *trans*-Pd(COCOR)Cl($PMePh_2$)$_2$ complexes (R = Me, **3a**; Ph, **3b**) were prepared, and their reactivities with Et_2NH were investigated. Complexes **3a** and **3b** were prepared by the reactions of Pd(styrene)($PMePh_2$)$_2$ with the corresponding RCOCOCl and were characterized by means of IR and NMR spectroscopy and elemental analysis. Complexes **3a** and **3b** undergo a facile decarbonylation in solution obeying the first-order rate law with respect to the concentration of the palladium complexes to give quantitative yields of acyl complexes, *trans*-Pd(COR)Cl($PMePh_2$)$_2$. The decarbonylation reactions are effectively retarded by the addition of free $PMePh_2$, suggesting a reaction mechanism involving a rate-determining dissociation of tertiary phosphine ligand. Treatment of **3a** with Et_2NH gives $MeCONEt_2$ as the major product. This result is in sharp contrast with the reaction of the corresponding acyl complex, *trans*-Pd(COMe)Cl($PMePh_2$)$_2$, with Et_2NH under CO atmosphere, where $MeCOCONEt_2$ was obtained as the major product. These observations provide the evidence *against* the mechanism involving consecutive insertion of CO into the Pd–C bond.

Introduction

A novel palladium-catalyzed process (eq 1) converting organic halides, amines, and CO into α-keto amides (double carbonylation) has been recently reported from two groups independently.[1,2] In the preceding paper possible reaction mechanisms for the double-carbonylation process were presented (cf. Figure 1 of the paper[3]). The catalytic cycle proposed consists of three elementary steps: step 1, oxi-

$$RX + 2HNR'_2 + 2CO \xrightarrow{[Pd]} RCOCONR'_2 + R'_2NH_2X \quad (1)$$

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