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.

Acknowledgment. We are grateful for support of this work by a Grant-in-Aid for scientific research from the Ministry of Education, Japan, and by Kawakami Memorial Foundation for Engineering Research.

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-

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

(1) Ozawa, F.; Soyama, H.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett.* **1982**, *23*, 3383.
(2) Kobayashi, T.; Tanaka, M. *J. Organomet. Chem.* **1982**, *233*, C64.
(3) Ozawa, F.; Sugimoto, T.; Yuasa, Y.; Santra, M.; Yamamoto, T.; Yamamoto, A. *Organometallics*, preceding paper in this issue.

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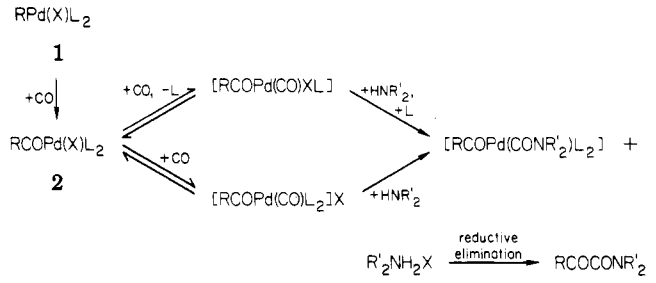
Scheme I



dative addition of organic halides to zerovalent palladium species; step 2, CO insertion into the Pd–C bond in the resultant organopalladium halide complex (**1**) to give an acylpalladium halide complex (**2**); step 3, attack of complex **2** by CO and the amine to produce the α-keto amide together with a minor amount of amide.

Study of the reaction mechanism by using model organopalladium complexes established the feasibility of step 1 and step 2 relevant to the catalytic processes. For the elementary step 3 the following two possible reaction pathways were considered. One involves the coordination of the second CO molecule to the acylpalladium complex, followed by external attack of the coordinated CO by the amine to give a carbamoyl group. The carbamoyl group is then reductively eliminated together with the acyl group to release the α-keto amide (Scheme I). The feasibility of this reaction pathway was established on the basis of stoichiometric reactions of acylpalladium complexes with the amine and CO in the preceding paper.[3] The alternative reaction pathway involves the consecutive CO insertion into the organopalladium compounds to give alkyl- (or aryl-) glyoxyl species, RCOCOPdXL$_2$ (**3**), which may be attacked by the amine to produce the α-keto amide (eq 2). Although the equilibrium between **2** and **3** seems to

$$\underset{\mathbf{1}}{\mathrm{RPd(X)L_2}} \overset{+CO}{\rightleftharpoons} \underset{\mathbf{2}}{\mathrm{RCOPd(X)L_2}} \overset{+CO}{\rightleftharpoons} \underset{\mathbf{3}}{\mathrm{RCOCOPd(X)L_2}} \xrightarrow{HNR'_2} \mathrm{RCOCONR'_2} \quad (2)$$

be unfavorable for the formation of **3**,[4] this pathway still may be possible if the alkylglyoxyl species should be highly reactive so as to be quickly intercepted by amine to release the α-keto amide. Since the precedents of transition-metal complexes having the alkylglyoxyl groups are quite limited, and none is reported concerning the palladium complex, we set out to prepare pyruvoyl- and (phenylglyoxyl)palladium complexes and examine their reactivities for probing the alternative possibility of consecutive CO insertion as the elementary step for the double carbonylation.

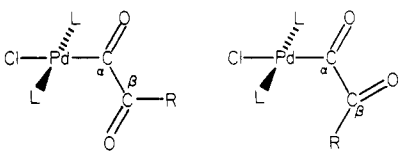
Results

Preparation of *trans*-Pd(COCOR)Cl(PMePh$_2$)$_2$ (R = Me and Ph). The pyruvoylpalladium and (phenylglyoxyl)palladium complexes **3a** and **3b** were prepared in good yield by the reactions of Pd(styrene)(PMePh$_2$)$_2$[5] with excess amounts of RCOCOCl (eq 3). The styrene-coordinated zerovalent palladium complex used for reaction 3 was prepared in situ by the reaction of *trans*-PdEt$_2$(PMePh$_2$)$_2$ in toluene with styrene. The reactions of the styrene–palladium complex with RCOCOCl were carried

$$\mathrm{Pd(styrene)(PMePh_2)_2} + \mathrm{RCOCOCl} \xrightarrow{-\text{styrene}} \underset{\mathbf{3a},\mathrm{R}=\mathrm{Me}\quad \mathbf{3b},\mathrm{R}=\mathrm{Ph}}{\textit{trans}\text{-Pd(COCOR)Cl(PMePh}_2)_2} \quad (3)$$

out below –30 °C in order to avoid decarbonylation of **3** to the corresponding acyl complexes, *trans*-Pd(COR)Cl(PMePh$_2$)$_2$ (R = Me, **2a**; R = Ph, **2b**). Attempts to prepare the corresponding (phenylglyoxyl)palladium bromide complexes using RCOCOBr gave only *trans*-Pd(COPh)Br(PMePh$_2$)$_2$ with evolution of 1 equiv of CO even at –70 °C.

Complexes **3a** and **3b** are slightly red, diamagnetic solids and considerably soluble in CH_2Cl_2 but poorly soluble in toluene and ether. Their characterization was made by means of IR and NMR spectroscopy as well as by elemental analysis. The spectroscopic data are given in Table I together with those of the corresponding acyl complexes **2a** and **2b**. The IR spectra of complexes **3a** and **3b** show three (for **3a**) and four (for **3b**) ν(CO) bands. Similar absorption patterns have been reported for the spectra of *trans*-M(COCO$_2$R)(Cl)L$_2$ (M = Pd, Pt; R = Me, Et; L = tertiary phsphine) and were attributed to ν(CO) bands arising from two kinds of rotamers, s-trans and s-cis.[4a] The resemblance of the IR absorption patterns of **3a** and **3b** in the ν(CO) region to those of the alkoxoglyoxyl complexes suggest the presence of two rotamers for **3a** and **3b**:



Assignments of the ν(CO) bands of **3a** and **3b** in Table I have been made by comparison with the reported IR data of RCOCOML$_n$ (M = Mn[4c] and Ir[4e]), *trans*-M(COCO$_2$R)(Cl)L$_2$ (M = Pd, Pt),[4a,b] α-keto acid esters, and amides. The absorption bands in the higher frequency region of 1710–1690 cm^{-1} are assignable to the β-carbonyl groups, whereas those below 1650 cm^{-1} are attributable to the α-carbonyl groups bonded to palladium. By taking into account the assignments of IR bands of s-trans and s-cis *trans*-Pt(COCO$_2$Me)(Cl)L$_2$, for which the s-trans structure in the solid state has been established by X-ray analysis, the higher frequency band of the β-carbonyl group is ascribed to the s-cis isomer and the lower frequency band to the s-trans isomer, whereas the higher frequency band of the α-carbonyl group may be attributed to the s-trans and the lower frequency band to the s-cis isomer.

The trans configuration of **3a** and **3b** is supported by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopic data recorded at –30 °C in CD_2Cl_2 as presented in Table I. Each of the ^{1}H and ^{13}C{^{1}H} NMR spectra of **3a** and **3b** shows the P–Me signal as a triplet due to a virtual coupling and ^{31}P{^{1}H} NMR spectra a singlet at 12.4 (for **3a**) and 12.1 (for **3b**) ppm, suggesting the trans configuration around Pd.

The singlets at 233.2 (**3a**) and 236.2 (**3b**) ppm in the ^{31}C{^{1}H} NMR spectra are ascribable to the α-carbonyl carbons bonded to palladium by comparison with the ^{13}C{^{1}H} NMR spectra of the corresponding acyl complexes **2a** and **2b**. The β-carbonyl carbons in **3a** and **3b** give rise to three peaks in the ^{13}C{^{1}H} NMR spectra in about 1:2:1 intensity ratio for **3a** and four peaks of almost equal intensity for **3b**. The presence of rotamers may be associated with the observation of the three or four peaks, but the cause for the ^{13}C{^{1}H} NMR spectral pattern was not pursued further.

(4) (a) Dobrzynski, E. D.; Angelici, R. J. *Inorg. Chem.* **1975**, *14*, 59. (b) Fayous, J.; Dobrzynski, E. D.; Angelici, R. J.; Clardy, J. *J. Organomet. Chem.* **1973**, *59*, C33. (c) Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1166. (d) Cawse, J. N.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405. (e) Blake, D. M.; Vinson, A.; Dye, R. *Ibid.* **1981**, *204*, 257.

(5) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *J. Organomet. Chem.* **1979**, *168*, 375.

Table I. IR and NMR Data of Pyruvoyl- and (Phenylglyoxyl)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] β_{CO}	^{13}C{^{1}H} NMR[b,d] α_{CO}	^{13}C{^{1}H} NMR[b,d] others	^{31}P{^{1}H} NMR[b,e,g]
trans-Pd(COCOMe)Cl(PMePh$_2$)$_2$ (**3a**)	1710[h]	2.13 (3.5)	0.89 (-CO*Me*)[g]	12.1 (14.7)	193.8[h]	233.2	22.3 (-CO*Me*)[g]	12.4
	1690				194.3			
	1640				194.8			
trans-Pd(COCOPh)Cl(PMePh$_2$)$_2$ (**3b**)	1695[h]	2.11 (3.4)		13.0 (15.6)	185.4[h]	236.2		12.1
	1690				185.9			
	1650				187.8			
	1645				188.3			
trans-Pd(COMe)Cl(PMePh$_2$)$_2$ (**2a**)	1665	2.07 (3.4)	1.46 (-CO*Me*)[i]	13.2 (13.7)		235.4	19.6 (-CO*Me*)[i]	8.9
trans-Pd(COPh)Cl(PMePh$_2$)$_2$ (**2b**)	1640	1.87 (3.5)		13.1 (14.7)		231.4		8.8

[a] In cm^{-1}, KBr disk. [b] In CD_2Cl_2, at −30 °C (**3a**, **3b**) or at room temperature (**2a**, **2b**). [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] See text. [i] Triplet, J_{H-P} = 1.3 Hz. [j] Triplet, J_{C-P} = 20.1 Hz.

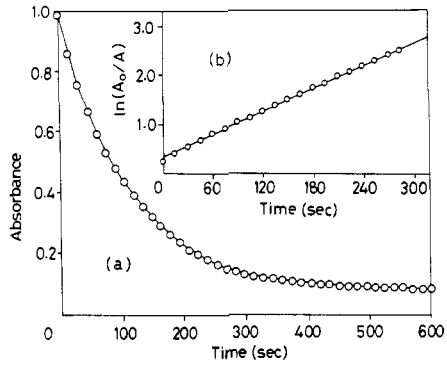


Figure 1. Time–decay curve of the electronic absorption band at 474 nm (a) and pseudo-first-order plot (b) for the decarbonylation of *trans*-Pd(COCOPh)Cl(PMePh$_2$)$_2$ (**3b**) in CH_2Cl_2 at 11.0 °C; A_0, initial absorbance calculated from the initial concentration of **3b** and the molar absorption coefficient of **3b** at 474 nm; A, absorbance at time t.

Reactions of *trans*-Pd(COCOR)Cl(PMePh$_2$)$_2$. Decarbonylation. Heating of complex **3b** in the solid state causes the decarbonylation at 105–108 °C to yield the benzoyl complex **2b**, which is decomposed at its decomposition point of 181–185 °C. On the other hand, the pyruvoyl complex **3a** was decomposed at 144–146 °C without undergoing the two-step decarbonylation because the decomposition point of the decarbonylated acetyl complex (133–134 °C) is lower than that of the pyruvoyl complex.

The decarbonylation of the pyruvoyl- and (phenylglyoxyl)palladium complexes **3a** and **3b** takes place readily in CH_2Cl_2 solution at room temperature, yielding the *trans*-acylpalladium complexes **2a** and **2b**, which were characterized by means of IR and ^{31}P NMR spectroscopy (eq 4). Conversely, treatment of the CH_2Cl_2 solution of

$$\underset{\mathbf{3}}{\textit{trans}\text{-Pd(COCOR)Cl(PMePh}_2)_2} \xrightarrow{-CO} \underset{\mathbf{2}}{\textit{trans}\text{-Pd(COR)Cl(PMePh}_2)_2} \quad (4)$$

the benzoylpalladium complex **2b** with CO (~9 atm) showed no sign of formation of **3b** as confirmed by ^{31}P NMR spectroscopy.

The decarbonylation reactions of **3a** and **3b** in CH_2Cl_2 solution were followed by observing the decay of the electronic absorption bands at 464 nm (ϵ = 86 cm^{-1} M^{-1}) of **3a** and at 474 nm (ϵ = 174 cm^{-1} M^{-1}) of **3b**. These bands in the visible region are characteristic for the RCOCOM-type complexes[4c] and are absent in the spectra of the corresponding acyl complexes. The spectral change showed clear isosbestic points. The decay curve of **3b** in CH_2Cl_2 in vacuo is shown in Figure 1, which shows the first-order kinetics with the rate constant of 7.59 × 10^{-3} s^{-1} at 11.0 °C (the initial concentration of **3b** was 7.1 × 10^{-3} M). The decarbonylation is not affected by the presence of an atmospheric pressure of CO but is severely hindered by addition of small amounts of free $PMePh_2$ to the system. Addition of an equimolar amount of $PMePh_2$ to the solution of **3b** completely blocked the decarbonylation at 11.0 °C, and at a higher temperature of 27.0 °C a very slow decarbonylation with the first-order rate constant of 4.1 × 10^{-5} s^{-1} was observed. The results strongly suggest a decarbonylation mechanism with a rate-determining dissociation of the $PMePh_2$ ligand from **3b**.

From the first-order rate constants of the decarbonylation reaction of **3b** at 11.0 °C (k = 7.59 × 10^{-3} s^{-1}), 12.9 °C (8.30), 15.3 °C (10.1), and 17.7 °C (12.1), the following activation paramenters at 12.9 °C for the decarbonylation

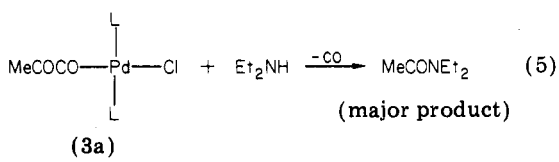
Table II. Reactions of *trans*-Pd(COCOR)Cl(PMePh$_2$)$_2$ (R = Me, 3a; Ph, 3b) and *trans*-Pd(COR)Cl(PMePh$_2$)$_2$ (R = Me, 2a; Ph, 2b) with HNEt$_2$[a]

run	complex	CO, atm	solvent	yield, % RCOCONEt$_2$	yield, % RCONEt$_2$
1	3a	0	CH_2Cl_2	2	81
2		1	CH_2Cl_2	3	89
3		1	toluene	2	98
4	2a	1	CH_2Cl_2	14	0
5		1	toluene	22	4
6		10	CH_2Cl_2	56	0
7	3b	0	CH_2Cl_2	0	0
8[b]		0	CH_2Cl_2	15	7
9		0	toluene	0	trace
10		1	CH_2Cl_2	7	5
11	2b	1	CH_2Cl_2	4	4
12[b]		10	CH_2Cl_2	trace	16

[a] Reactions were carried out on a 0.1-mmol scale (complex/HNEt$_2$ = 1:10) at room temperature for 1 day. [b] PMePh$_2$ (× 10/Pd) was added to the system.

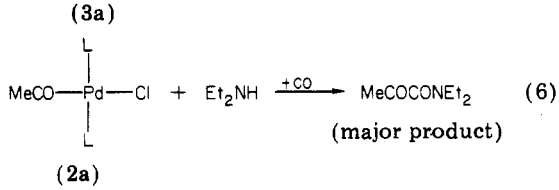
were estimated: $\Delta H^{\ddagger}$ = 13.0 ± 1.0 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −22.6 ± 1.0 eu; $\Delta G^{\ddagger}$ = 19.4 ± 1.0 kcal mol^{-1}. The relatively large negative value of the entropy of activation is in the reported range of −15 to −30 eu for the ligand displacement reactions of square-planar complexes through an associative mechanism[6] and is compatible with the ligand-dissociation process assisted by solvent. The decarbonylation of the pyruvoyl complex **3a** proceeds at a much slower rate ($t_{1/2} \simeq$ 30 min at 14.0 °C) than that of **3b** ($t_{1/2}$ = 91 s at 11.0 °C). The strong retardation effect of added PMePh$_2$ was observed also for decarbonylation of **3a**.

Reactions of *trans*-Pd(COCOR)Cl(PMePh$_2$)$_2$ with Et$_2$NH. Complexes **3a** and **3b** were treated with an excess of Et$_2$NH in the presence or absence of CO at room temperature for a day. Table II summarizes the yields of α-keto amides and amides in comparison with those of the corresponding acylpalladium complexes **2a** and **2b**. These results reveal an interesting dichotomy in the behavior of the pyruvoyl and acetylpalladium complexes. Treatment of **3a** with Et$_2$NH (eq 5) afforded almost quantitative yields of acetamide and minor yields of pyruvamide regardless of the presence or absence of CO (runs 1–3), whereas the reactions of the acetyl complex **2a** with Et$_2$NH (eq 6) in the presence of CO gave pyruvamide predominantly (runs 4–6).



(5)

(3a)



(6)

(2a)

Examination of the reaction system of **3a** with diethylamine (eq 5) by means of ^{31}P NMR indicated the complete disappearance of **3a** and formation of a small amount of *trans*-Pd(COMe)Cl(PMePh$_2$)$_2$ (**2a**) and an unidentified product, presumably a zerovalent palladium carbonyl complex containing PMePh$_2$ ligands.

In comparison with the pyruvoyl complex **3a**, treatment of the phenylglyoxyl complex **3b** with Et$_2$NH in the absence of CO (runs 7 and 9) caused mainly decarbonylation and gave negligible amounts of phenylglyoxylamide and benzamide. The yields of PhCOCONEt$_2$ and PhCONEt$_2$ obtained on treatment of **3b** with Et$_2$NH under 1 atm of CO in CH_2Cl_2 (run 10) were comparable to those produced on treatment of **2b** with Et$_2$NH and CO under similar conditions (run 11). In the reactions of **3b** with Et$_2$NH and CO in the presence of a 10-molar excess of PMePh$_2$ the decarbonylation was retarded, and a moderate amount of PhCOCONEt$_2$ and a small amount of PhCONEt$_2$ were produced (run 8), whereas the reaction of the benzoyl complex **2b** with Et$_2$NH and CO in the presence of added PMePh$_2$ (run 12) gave a moderate yield of PhCONEt$_2$.

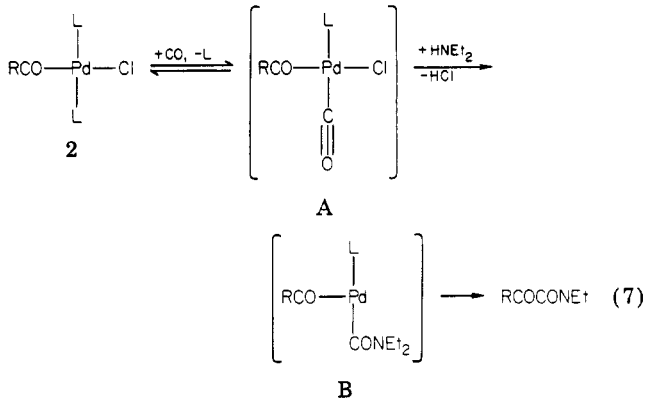
Discussion

The low reactivities of *trans*-Pd(COCOR)Cl(PMePh$_2$)$_2$ type complexes toward attack of Et$_2$NH to produce α-keto amide revealed in the present study provide evidence *against* the mechanism presuming the rapid trapping of the RCOCO moiety bonded to palladium by amine (eq 2) as the step in the catalytic double carbonylation of organic halides. The (phenylglyoxyl)palladium complex **3b** which would act as the supposed intermediate in this mechanism is quite susceptible to decarbonylation and unreactive toward the attack of the amine in the absence of added phosphine ligand.[7] The results of treatment of the pyruvoyl complex **3a** and the acetyl complex **2a** with amine revealed the strikingly different behavior of **2a** and **3a** (eq 5 and 6). These contrasting results again make the RCOCOPd moiety highly unlikely as the species to give α-keto amide.

The strikingly different behavior of **2a** and **3a** toward the amine can be accounted for consistently by assuming two types of CO-coordinated acylpalladium intermediates of different configurations. As the mechanism giving the α-keto amide from **2** the following pathway (eq 7) is proposed as the most reasonable one.[3] In this reaction, coordination of CO probably causes a displacement of the tertiary phosphine ligand to give the intermediate A, which has the acyl and the CO ligands in mutually cis positions. If the nucleophilic attack of the amine takes place on the CO ligand in the intermediate A, the carbamoyl intermediate B thus formed would possess the acyl and the carbamoyl groups in mutually cis positions which are favorable for reductive elimination to produce α-keto amide.

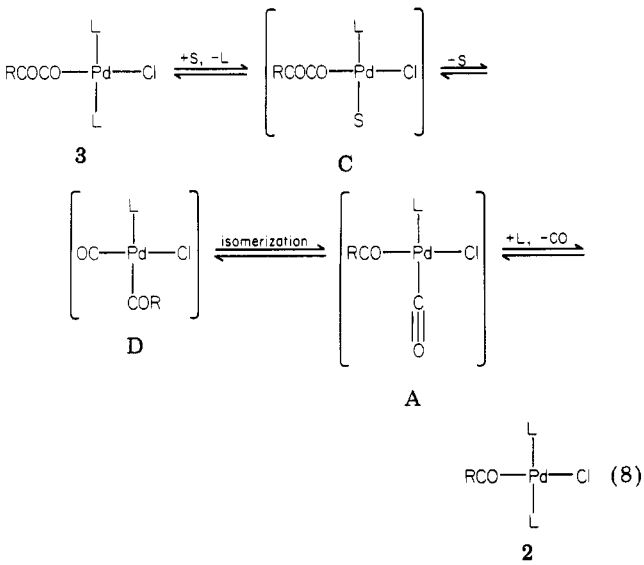
(6) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967.

(7) It should be added that in the presence of the phosphine the decarbonylation is prevented, and the α-keto amide may be formed on the direct trapping of the phenylglyoxyl group by the amine.



2 A B

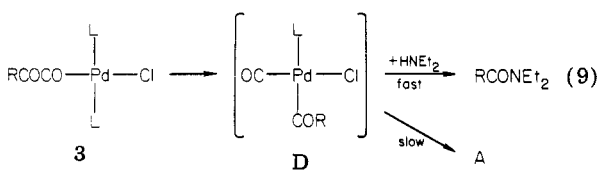
Kinetic studies on the decarbonylation of the alkylglyoxyl complex 3 in the absence of amine suggest a solvent-assisted decarbonylation mechanism involving the rate-determining phosphine ligand dissociation. If we assume an acyl group migration from the (alkylglyoxyl)palladium chloride (C) as the reverse process of CO insertion, which is known to proceed by an alkyl group migration mechanism in most cases,[8] the product will possess the configuration D having the acyl and the chloro ligands in mutually cis positions (eq 8). Since the final



3 C D A 2

decarbonylation product from the pyruvoyl as well as the phenylglyoxyl complexes has trans configuration, the isomerization of D to A may ensue to give the end product of *trans*-Pd(COR)ClL$_2$. A possible mechanism for the isomerization from D to A, such as that proposed for isomerization of PtPh(X)(CO)(PR$_3$), may be operative.[9]

In the presence of amine, if the nucleophilic attack of amine takes place on RCO group (not on CO ligand) in intermediate D and this reaction is much faster than the isomerization of D to A, amide will be predominantly formed from alkylglyoxyl complex 3 and Et$_2$NH.

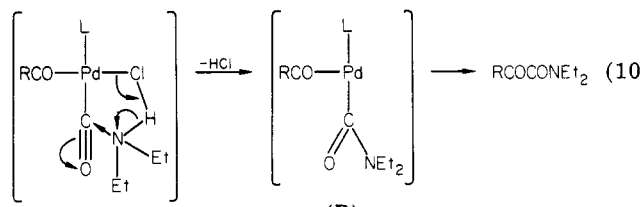


3 D

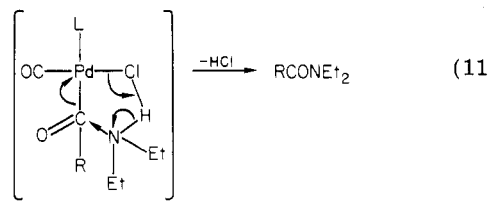
(8) For review: (a) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (b) Flood, T. C. In "Topics in Stereochemistry"; Geoffroy, G. L., Ed.; Wiley: New York, 1981; Vol. 12, p 37.

(9) Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1246; **1980**, 1434, 712.

In these mechanisms, several assumptions based on the configurational constraints of the square-planar palladium complexes have been made. These are (i) stereochemical retention in the displacement of the tertiary phosphine ligand by CO, (ii) the acyl group migration in the decarbonylation of RCOCO ligand, (iii) slow isomerization process between the CO-coordinated acyl intermediates D and A, and (iv) difference in the reactivity of D and A toward the attack of the amine. Assumption i is in agreement with our previous observation concerning the reactions of *cis*- and *trans*-PdR$_2$L$_2$ with CO.[10] Assumptions ii and iii have not been proved but seem to be probable. Assumption iv is convenient to explain the experimental results in a consistent manner, but the exact reason to account for the product difference from D and A and why the acyl group in D is attacked by the amine to give amide whereas the CO ligand in A is attacked to give the α-keto amide is difficult to provide. One possible explanation for the different reactivities of the intermediates D and A is the difference of the effect of the tertiary phosphine on the CO or acyl ligand trans or cis to it. Although the steric and electronic effect of the tertiary phosphine ligand would exert certain influences on the reactivity of the carbonyl or acyl ligand, the effect may not suffice to cause such a clear-cut dichotomy in the reactivity toward the attack of amine. Another possible mechanism is the concerted reaction mechanism depicted below in which the nucleophilic attack of the amine on the acyl or CO ligand trans to L is assisted by interaction with the neighboring chloro ligand to promote the removal of HCl.



(A′) (B)



(D′)

Although the results obtained here concerning the chloro complex are not directly applicable to the discussions of the catalytic double-carbonylation reactions that proceed with the organic bromides and iodides, the contrasting behavior of the acetyl- and pyruvoylpalladium chloride complexes toward the attack of the amine makes the double CO insertion mechanism quite unlikely and gives strong support for the alternative mechanism as represented by Scheme I.

Experimental Section

General procedure was as described in the preceding paper.[3]

Preparation of *trans*-Pd(COCOMe)Cl(PMePh$_2$)$_2$ (3a). To a Schlenk tube containing *trans*-PdEt$_2$(PMePh$_2$)$_2$ (0.82 g, 1.5

(10) Ozawa, F.; Yamamoto, A. *Chem. Lett.* **1981**, 289. We recently confirmed that the displacement of the phosphine ligand of *cis*-PdMe$_2$(PMePh$_2$)$_2$ and *cis*-PtMe$_2$(PPh$_3$)$_2$ with CO afforded *cis*-PdMe$_2$(CO)(PMePh$_2$) and *cis*-PtMe$_2$(CO)(PPh$_3$), respectively, with retention of the cis configuration. The latter complex was isolated and characterized by means of IR and NMR spectroscopy and elemental analysis: Ozawa, F.; Lu, X.; Yamamoto, A., unpublished results.

mmol) were added toluene (10 mL) and styrene (0.34 mL, 2.9 mmol) by means of a syringe. The system was stirred at room temperature to yield a pale yellow, homogeneous solution. The solution was cooled to −55 °C and MeCOCOCl[11] (0.78 g, 7.3 mmol) was then added. After stirring of the system at −30 °C for 1.5 h, 30 mL of hexane was added to yield a slightly red pecipitate of **3a**, which was washed with Et_2O (20 mL × 4) at the same temperature and dried in vacuo (0.86 g, 97%). The product was analytically pure without further purification. *trans*-Pd(COCOPh)Cl($PMePh_2$)$_2$ (**3b**) was similarly obtained using PhCOCOCl[11] instead of MeCOCOCl. Anal. (**3a**) Calcd for $C_{29}H_{29}ClO_2P_2Pd$: C, 56.8; H, 4.8; Cl, 5.8. Found: C, 57.3; H, 5.0; Cl, 5.7. (**3b**) Calcd for $C_{34}H_{31}ClO_2P_2Pd$: C, 60.5; H, 4.6; Cl, 5.3. Found: C, 60.6; H, 4.8; Cl, 5.4.

(11) Ottenhijm, H. C. J.; de Man, J. H. M. *Synthesis* **1975**, 163.

Acknowledgment. We are grateful for support of this work by a Grant-in-Aid for scientific research from the Ministry of Education, Japan, and by Kawakami Memorial Foundation for Engineering Research.

Registry No. 2a, 89177-93-5; **2b**, 84624-62-4; **3a**, 89177-94-6; **3b**, 89177-95-7; Pd($PMePh_2$)$_2$B (B = Styrene), 70316-76-6; *trans*-Pd(COPh)Br($PMePh_2$)$_2$, 89177-97-9; MeCOCOCl, 5704-66-5; PhCOCOCl, 25726-04-9; MeCOCOBr, 74100-44-0; PhCOCOBr, 89177-96-8; Et_2NH, 109-89-7.

Syntheses of Some Methyldiplatinum(I) Complexes by Oxidative Addition or Reductive Elimination Reactions of Binuclear Complexes

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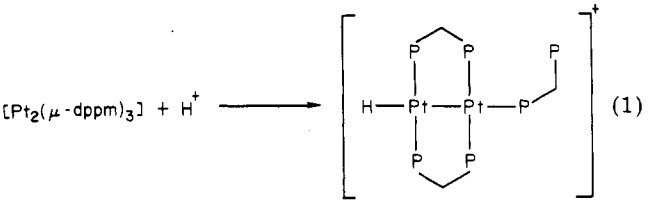
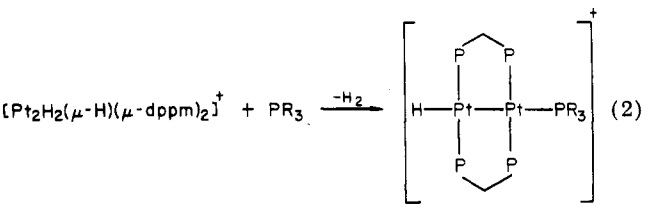
Oxidative addition of MeI to [Pt_2(dppm)$_3$] in benzene followed by anion exchange with K[PF_6] led to isolation of the first methyldiplatinum(I) complex [$Pt_2Me(\eta^1$-dppm)(μ-dppm)$_2$][PF_6], and further reaction with MeI in CH_2Cl_2 solution gave [$Pt_2Me_2(\mu$-I)(μ-dppm)$_2$][PF_6]. Methyldiplatinum(I) complexes were also formed by reaction of tertiary phosphines (L = dppm, PPh_3, PMe_2Ph) with [$Pt_2H(\mu$-H)Me(μ-dppm)$_2$][SbF_6] to give [$Pt_2MeL(\mu$-dppm)$_2$][SbF_6] and H_2. The reductive elimination followed second-order kinetics, and an intermediate, [H(Ph_3P)Pt(μ-H)(μ-dppm)$_2$PtMe][SbF_6], was detected by low-temperature NMR spectroscopy in the case with L = PPh_3.

Introduction

Syntheses of hydridoplatinum(I) complexes by oxidative addition to diplatinum(0) complexes[2–4] or reductive elimination from diplatinum(II) complexes,[5–10] stabilized by bridging bis(diphenylphosphino)methane (dppm or P⁀P) ligands, have been reported as shown, for example, in eq 1 and 2.



(1)



(2)

The mechanism of the binuclear reductive elimination reaction of eq 2 has been studied.[11]

In this paper the synthesis of methyldiplatinum(I) complexes by similar methods is described, together with

(1) (a) University of Western Ontario. (b) University of Liverpool. This is contribution 304 from the photochemistry unit, University of Western Ontario.
(2) Grossel, M. C.; Brown, M. P.; Nelson, C. D.; Yavari, A.; Kallas, E.; Moulding, R. P.; Seddon, K. R. *J. Organomet. Chem.* **1982**, *232*, C13.
(3) Manojlović-Muir, Lj.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1155.
(4) Chin, C.-S.; Sennett, M. S.; Wier, P. J.; Vaska, L. *Inorg. Chim. Acta* **1978**, *31*, L443.
(5) Brown, M. P.; Fisher, J. R.; Hill, R. H.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1981**, *20*, 3516.
(6) Manojlović-Muir, Lj.; Muir, K. W. *J. Organomet. Chem.* **1981**, *219*, 129.
(7) Foley, H. C.; Morris, R. H.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 7337.
(8) Hill, R. H.; de Mayo, P.; Puddephatt, R. J. *Inorg. Chem.* **1982**, *21*, 3642.
(9) Fisher, J. R.; Mills, A. J.; Sumner, S.; Brown, M. P.; Thomson, M. A.; Puddephatt, R. J.; Frew, A. A.; Manojlović-Muir, Lj.; Muir, K. W. *Organometallics* **1982**, *1*, 1421.
(10) Minghetti, G.; Bandini, A. L.; Banditelli, G.; Bonati, F.; Szostak, R.; Strouse, C. E.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1983**, *22*, 2332.

(11) Hill, R. H.; Puddephatt, R. J. *Inorg. Chim. Acta* **1981**, *54*, L277, *J. Am. Chem. Soc.* **1983**, *105*, 5797. The evidence for the structure of the adduct being as shown in eq 7 is discussed in detail in ref 11. Similar reasoning suggests the structure A, but the precise stereochemistry at the five-coordinate platinum center could be different.[11] We cannot eliminate the possibility of a low concentration of B, which might still exchange at −90 °C and hence give broad weak resonances which would not be detected.

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