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Reaction of Olefin-Palladium(II) Chloride Complexes with Amides[*1]

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Ethylene-palladium(II) chloride complex reacts with pyrrolidone and ε-caprolactam to produce *N*-vinylpyrrolidone and *N*-vinyl-ε-caprolactam, respectively. The yield of *N*-vinylpyrrolidone increases with increasing reaction temperature up to 120°C and decreases above 120°C owing to conversion of *N*-vinylpyrrolidone to an oily polymer through thermal polymerization. By addition of quinone, the yield increases remarkably at 25°C and 90°C. Pyrrolidone - palladium(II) chloride complex, which is too stable to react with ethylene at 25°C, reacts at 120°C to give *N*-vinylpyrrolidone. Open chain amides such as *N*-ethylacetamide, acetanilide and acetamide also react with ethylene - palladium(II) chloride complex, though the corresponding *N*-vinylamides cannot be obtained. The reaction of a styrene - palladium(II) chloride complex with pyrrolidone was also investigated.

Olefin-palladium(II) chloride complexes react with various nucleophilic reagents to form carbonyl compounds or substituted olefins.[1] Little is known about the reaction with nitrogen compounds such as amines or amides. Amine or amide forms a very stable complex with palladium(II) chloride, which would prevent or complicate the reaction. Stern and Spector reported very briefly the reaction of acetamide with propylene in the presence of palladium(II) chloride and that with ethylene-palladium(II) chloride complex.[2] Destruction of the resulting stable complexes by hydrogenation yielded *N*-isopropylacetamide and *N*-ethylacetamide, respectively.

Shortly after we had shown the formation of *N*-vinylpyrrolidone by the reaction of ethylene-palladium(II) chloride complex with pyrrolidone,[3] the process for production of ethylenylated lactams

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[*1] The major part of this paper was presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

[1] C. W. Bird, "Transitional Metal Intermediates in Organic Synthesis," Logos Press, London (1966), p. 88—112; A. Guilo, "Advances in Organometallic Chemistry," Vol 5, ed. by F. G. A. Stone and R. West, Academic Press, New York (1967), p. 321; E. W. Stern, "Catalysis Review," Vol. 1, ed. by H. Heinemann, Marcel Dekker, Inc., New York (1968), p. 74.

[2] E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, **1961**, 370.

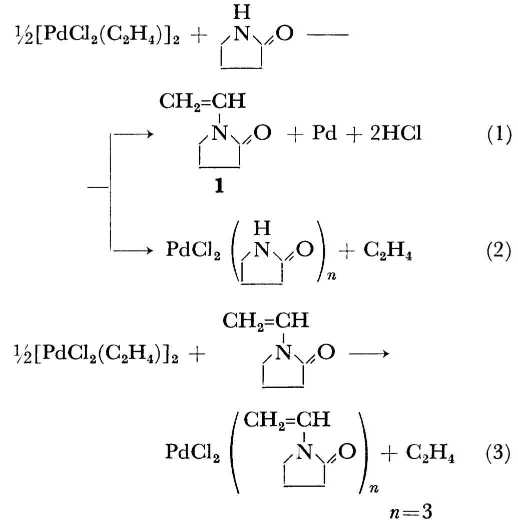
[3] H. Hirai, H. Sawai and S. Makishima, Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

from olefins and lactams in the presence of palladium(II) chloride and cupric ion was patented.[4] This patent covered cyclic lactams such as pyrrolidone, ε-caprolactam and 2-ketopiperidone as a nucleophilic reagent, but little information on the reaction was given.

The present paper deals with the formation of *N*-vinylamides under various reaction conditions in detail to propose a reaction mechanism. The reaction of styrene-palladium(II) chloride complex with pyrrolidone is also described.

Results and Discussion

Reaction of Ethylene-Palladium(II) Chloride Complex with Pyrrolidone. Ethylene-palladium(II) chloride complex reacted with pyrrolidone at 25°C for 2.5 hr under 10 atm of ethylene pressure to give *N*-vinylpyrrolidone (**1**) in 42 mol% yield based on palladium(II), accompanying the reduction of palladium(II) ion to the metal, as shown in Table 1. Simultaneously, a ligand substitution of the ethylene-palladium(II) chloride complex occurred to form pyrrolidone-palladium(II) chloride complex and *N*-vinylpyrrolidone-palladium(II)chloride complex. These reactions are schematically shown by the following equations.



Addition of pyridine makes **1** free from the coordination state in the reaction mixture by ligand substitution, which was confirmed by the change of color of the reaction mixture. The total yield of **1** could be determined by glpc after the addition of pyridine. As shown in Table 1, the yield of **1** increased from 24 to 42 mol% by addition of pyridine to the reaction mixture at 25°C. This means that 43% of **1** formed by reaction (1) was coordinated to palladium(II) chloride.

TABLE 1. EFFECT OF TEMPERATURE ON THE REACTION OF ETHYLENE-PALLADIUM(II) CHLORIDE COMPLEX WITH PYRROLIDONE[a]

Temp. °C	Yield (mol%)[b] *N*-Vinylpyrrolidone free	Yield (mol%)[b] *N*-Vinylpyrrolidone free+coordinated	Yield (mol%)[b] Pd (metal)	Polymer[c] mg	Complex[d] mg
25	24	42	41	0	660(670)
60	32	51	49	0	570(590)
90	37	66	68	0	444(400)
120	65	72	77	100	240(260)
150	57	61	84	315	140(180)
180	13	13	88	500	50(150)

a) Reaction conditions: initial pressure of ethylene, 10 atm; time, 2.5 hr; [Pyrrolidone]/[Pd(II)]=4.
b) Based on palladium(II).
c) Crude substance.
d) Calculated amounts of the sum of pyrrolidone- and *N*-vinylpyrrolidone-palladium(II) chloride complexes are shown in parentheses.

Table 1 shows the effect of reaction temperature on the yields of reaction products. The yield of **1** increased with temperature and was nearly equal to that of palladium metal up to 90°C. Above 120°C, the yield of **1** decreased, while that of palladium metal increased and an oily resin of light greenish brown color resulted. The IR spectrum of this resin was identical with that of poly-*N*-vinylpyrrolidone. Elevation of temperature above 120°C promoted not only the extent of reaction (1) but also the polymerization of **1** by heat. The sum of the amount of pyrrolidone-palladium(II) chloride complex and that of *N*-vinylpyrrolidone-palladium(II) chloride complex in the reaction, decreased with the rise of temperature and was in fairly good agreement with the amount of these complexes calculated from unreduced palladium(II) ion.

The effects of the addition of quinone and diphenylpicrylhydrazyl on the yield of the products are shown in Table 2. Quinone is expected to regenerate palladium(II) ion in this system, forming a redox system and inhibiting thermal polymerization of **1**. Diphenylpicrylhydrazyl is known to be an inhibitor for the polymerization. Addition of quinone increased the yield of **1** remarkably at 25°C or 90°C, but depressed the formation of palladium metal less than 38 mol%. The yield of **1** became more than 100 mol% based on the initial amount of palladium(II). It is evident that quinone acted as an oxidant for the resulting palladium(0) at these temperatures. Above 150°C, however, the yield of **1** decreased remarkably, accompanying a definite increment of the yield of palladium metal, *e.g.*, about 50 mol%. The greater the amount of quinone added, the less the yield of

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[4] J. E. Mckeon and P. S. Stracher, U. S. 3318906; *Chem. Abstr.*, **68**, 39466k (1968).

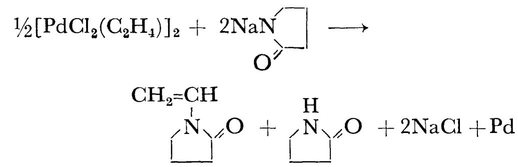
1. It can be concluded that quinone cannot inhibit the thermal polymerization of **1**. The added diphenylpicrylhydrazyl behaved in the reaction at 160°C just as quinone, as shown in Table 2.

Table 2. Effect of quinone on the reaction of ethylene palladium(II) chloride complex with pyrrolidone[a]

Temp. °C	[Quinone]/[Pd(II)] molar ratio	Yield (mol%)[b]			Polymer
		N-Vinylpyrrolidone		Pd (metal)	
		free	free+ coordinated		
25	2	94	173	28	—
25	4	93	174	37	—
90	2	114		38	—
90	4	114	204	38	—
150	2	15	16	87	+
150	4	4	4	93	+
160	2[c]	17	17	85	+

a) Reaction conditions: initial pressure of ethylene, 10 atm; time, 2.5 hr; [Pyrrolidone]/[Pd(II)] = 4.
b) Based on palladium(II).
c) Diphenylpicrylhydrazyl was used instead of quinone.

Ethylene-palladium(II) chloride complex reacted also with sodium pyrrolidone at 25°C for 2.5 hr under 10 atm of ethylene pressure. *N*-Vinylpyrrolidone was obtained in 6 mol% yield, accompanying the formation of pyrrolidone, which was detected by glpc in the reaction mixture. This reaction can be expressed by the following equation.



The depression of the yield is attributable to the lower solubility of sodium pyrrolidone in tetrahydrofuran.

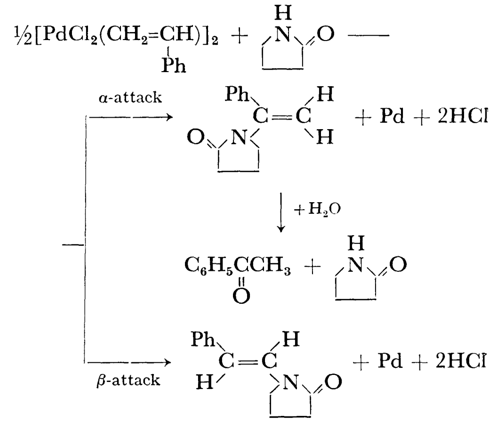
Reaction of Tris(pyrrolidone)palladium(II) Chloride Complex with Ethylene. Tris(pyrrolidone)palladium(II) chloride complex was too stable to react with ethylene at 25°C. This complex, however, was found to react with ethylene in a good yield at 120°C as shown in Table 3.

Table 3. Reaction of tris(pyrrolidone)palladium(II) chloride complex with ethylene[a]

Temp. °C	Yield (mol%)[b]			Polymer
	N-Vinylpyrrolidone		Pd (metal)	
	free	free+ coordinated		
25	0	0	0	—
120	62	70	69	—

a) Reaction conditions: initial pressure of ethylene, 20 atm; time, 2.5 hr.
b) Based on palladium(II).

Reaction of Styrene-Palladium(II) Chloride Complex with Pyrrolidone. Styrene-palladium(II) chloride complex reacted with pyrrolidone at 120°C for 2.5 hr, accompanied by precipitation of palladium metal in 38 mol%. Reaction products isolated by column chromatography were *trans-β*-styrilpyrrolidone, 1,4-diphenylbutadiene and acetophenone in 20, 5 and 5 mol% yield based on palladium(II), respectively. Acetophenone can be considered to be derived from α-styrilpyrrolidone by hydrolysis in the silica gel column of chromatography. The sterical unstability of α-styrylpyrrolidone would give rise to a low yield and a high susceptibility for hydrolysis. The possibility that acetophenone is formed by the reaction of styrene-palladium(II) chloride complex with water is excluded for the following reasons. No phenylacetaldehyde was formed in the present reaction, although the styrene complex is reported to react with water to yield phenylacetaldehyde and acetophenone in a molar ratio of about 1 : 2.[5] The reaction system was prevented from water contamination, and acetophenone was formed in a yield less than 1.5 mol% in a blank test.



1,4-Diphenylbutadiene has been reported to be obtained from styrene in the presence of palladium(II) ion and acetate anion.[6] Pyrrolidone probably becomes pyrrolidonium anion which can play the same role of acetate anion for the formation of 1,4-diphenylbutadiene

Reaction of Ethylene-Palladium(II) Chloride Complex with Other Amides. ε-Caprolactam, *N*-ethylacetamide, acetanilide and acetamide were allowed to react with ethylene-palladium(II) chloride complex. Table 4 shows the results of glpc

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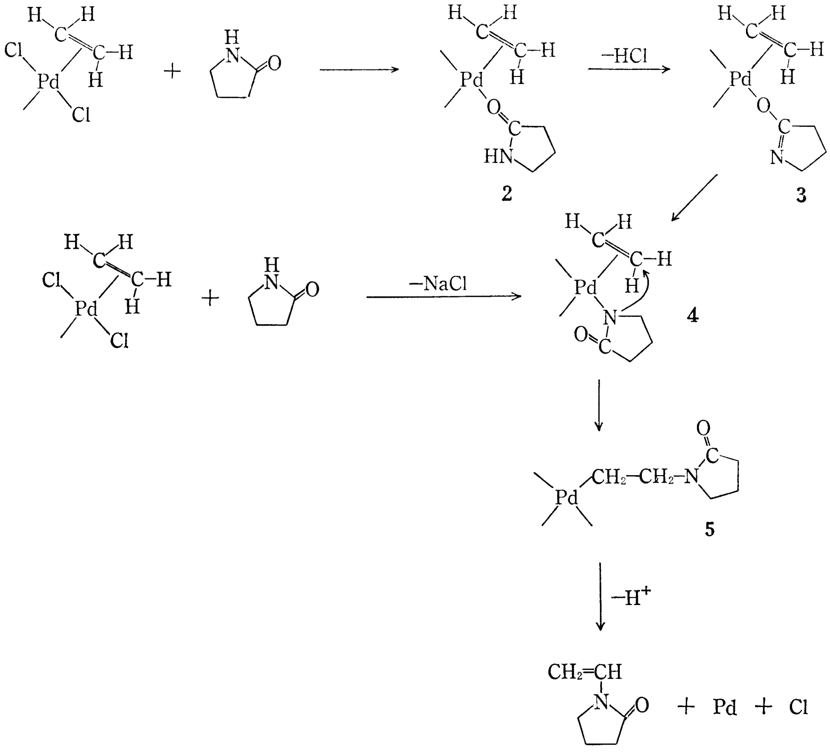
5) H. Okada and H. Hashimoto, *Kogyo Kagaku Zasshi*, **69**, 2137 (1966).

6) Y. Fujiwara, I. Moritani, M. Matsuda and S. Teranishi, *Tetrahedron Lett.*, **1968**, 3863.

TABLE 4. REACTION OF ETHYLENE-PALLADIUM(II) CHLORIDE COMPLEX WITH AMIDES[a]

Amide	Temp. °C	Yield (mol%)[b]			
		N-Vinylamide		Pd (metal)	Polymer
		free	free+coordinated		
ε-Caprolactam	25	8	20	21	—
	120	10	10	80	+
N-Ethylacetamide	25	0	0	6	—
	120	0.5	0.5	74	+
Acetanilide	28	0	0	20	—
	110	0	0	56	+
Acetamide	25	19[c]		38	

a) Reaction conditions: initial pressure of ethylene, 10 atm; time, 2.5 hr; [Amide]/[Pd(II)] = 4.
b) Based on palladium(II).
c) After hydrogenation, *N*-ethylacetamide was analyzed.



Scheme 1

analysis of the reaction products. *N*-Vinyl-ε-caprolactam was obtained in 20 mol% yield at 25°C, and the yield decreased at 120°C accompanying the formation of a large amount of polymer. *N*-Vinyl-ε-caprolactam seems to polymerize thermally more easily than *N*-vinylpyrrolidone. Cyclic amides gave *N*-vinylamides in fairly good yields, while open chain secondary amides such as *N*-ethylacetamide and acetanilide could not produce the corresponding *N*-vinylamides at room temperature. The formation of palladium metal was small in these cases. At a higher reaction temperature, the corresponding oily poly-*N*-vinylamide was obtained. In the case of open chain amides, *N*-vinylamide seems to undergo hydrolysis or polymerization easily. *N*-Vinylacetanilide is reported to undergo hydrolysis very easily in the presence of acid.[7]

In the case of acetamide, the product was analyzed by glpc after hydrogenation to *N*-ethylacetamide, because no gas chromatogram of *N*-vinylacetamide could be obtained by addition of pyridine and the

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[7] S. Murahashi, S. Nozakura, A. Umehara and F. Nagoshi, *Kobunshi Kagaku*, **22**, 451 (1965).

authentic sample could not be prepared with the thermal decomposition of ethylidenediacetamide.[8] In the reaction mixture, only acetamide was detected by glpc. The product probably decomposed in the column of glpc. Two types of reaction products can be considered; $CH_3CH{=}NCOCH_3$ and $CH_2{=}CHNHCOCH_3$. However, further characterization was unsuccessful.

Reaction Scheme. A scheme for ethylene-palladium(II) chloride complex with pyrrolidone is proposed (Scheme 1.)

At first pyrrolidone reacts with the ethylene complex to form ethylene-pyrrolidone-palladium(II) complex (**2**). In this complex, pyrrolidone is considered to coordinate to palladium(II) ion with the carbonyl group, because the coordination of the carbonyl group of pyrrolidone in tris(pyrrolidone)palladium(II) chloride complex has been confirmed by the shift of the IR stretching band: $\Delta\ \nu_{CO}=45\ \text{cm}^{-1}$. The proton of coordinated pyrrolidone is withdrawn to form complex (**3**) which tautomerize to complex (**4**) on account of the stronger affinity of amide nitrogen anion for palladium(II) than that of alkoxy type anion. Coordinated ethylene is then inserted into the resulting Pd–N bond to give complex (**5**) which decomposes to yield **1**. Sodium pyrrolidone reacts with ethylene complex to form complex (**4**) by the exchange reaction of chloride ion with pyrrolidonium anion. Sodium pyrrolidone cannot coordinate to palladium(II) ion by the steric and the ionic effect of sodium ion. The fact that pyrrolidone-palladium(II) chloride complex could not react with ethylene at 25°C, but could at 120°C means that the elevation of temperature makes the stable pyrrolidone complex so labile as to enable ethylene to coordinate palladium(II) ion. The high temperature also activates the withdrawal of hydrogen of coordinated pyrrolidone and promotes the extent of the reaction.

The proposed scheme is essentially the same as that for the reaction of ethylene-palladium(II) chloride complex with *n*-butylamine.[9] Usually, amine or amide in a free state cannot dissociate its *N*-proton easily, while its proton in the coordination state can be withdrawn by palladium(II) ion to its strong affinity for hydrogen to result in the reaction with ethylene[9] or carbon monoxide.[10]

Experimental

Materials. Bis(benzonitrile)dichloro palladium(II) and styrene-palladium(II) chloride complex were prepared according to Kharasch.[11] *N*-Ethylacetamide was prepared from ethylamine and acetic anhydride. ε-Caprolactam, acetanilide and acetamide were of reagent grade and dried under reduced pressure. Sodium pyrrolidone was prepared from pyrrolidone and sodium hydroxide by heating on a sand bath. Tris(pyrrolidone)-palladium(II) chloride complex was prepared from bis-(benzonitrile)dichloro palladium(II) with pyrrolidone in tetrahydrofuran in a quantitative yield, and recrystallized from methanol. Tetrahydrofuran used as a solvent was dried over lithium aluminum hydride and distilled before use.

Reaction of Ethylene-Palladium(II) Chloride Complex with Pyrrolidone. Bis(benzonitrile)dichloro-palladium(II) (0.96 g, 0.0025 mol) and dry tetrahydrofuran (20 m*l*) were charged in a magnetically stirred 100 m*l*-autoclave in a slow stream of nitrogen. In the autoclave, a glass tube was used as a reactive vessel and the stirrer was made of Teflon to prevent palladium-(II) ion from reacting with steel. Ethylene-palladium-(II) chloride complex was prepared under 10 atm of ethylene pressure for half an hour with stirring. The autoclave was then opened for addition of pyrrolidone (1 m*l*, 0.01 mol) and the reaction was carried out under 10 atm of initial ethylene pressure at 25—150°C for 2.5 hr. A similar procedure was applied for the reaction with quinone or diphenylpicrylhydrazyl.

Reaction of Ethylene-Palladium(II) Chloride Complex with Sodium Pyrrolidone. Bis(benzonitrile)dichloro palladium(II) (0.96 g, 0.0025 mol), sodium pyrrolidone (1.3 g, 0.0125 mol) and dry tetrahydrofuran were placed in the autoclave. The reaction was carried out under 10 atm of ethylene pressure at 25°C for 2.5 hr.

Reaction of Tris(pyrrolidone)palladium(II) Chloride Complex with Ethylene. Tris(pyrrolidone)-palladium(II) chloride complex (1.08 g, 0.0025 mol) and dry tetrahydrofuran were charged in the autoclave. The reaction was carried out under 20 atm of initial ethylene pressure at 25 or 120°C for 2.5 hr.

Products Analysis. *N*-Vinylpyrrolidone was analyzed by glpc (a 2 m Carbowax 20 M on Diasolid A column at 160°C and a nitrogen flow rate of 55 m*l*/min) and IR. The yield data were obtained by glpc with benzonitrile as an internal standard. Glpc analysis was carried out both before and after addition of pyridine to the reaction mixture to make the product free from coordination. Other reaction products were examined as follows. The reaction mixture was filtered through a glass filter and the residue was washed with tetrahydrofuran (Filtrate I), then with methanol (Filtrate II) and finally with dimethylformamide (Filtrate III). The resulting precipitate was palladium metal and was weighed after drying. Filtrate I was concentrated under reduced pressure to a few mililiter in order to crystallize a small amount of reddish brown complex. After removal of the crystals, a large amount of ether was added to the solution to separate an oily residue which was dried under reduced pressure and weighed. The IR spectrum of this substance was essentially the same as that of poly-*N*-vinylpyrrolidone obtained commercially.

Concentration of Filtrate II gave reddish brown

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[8] D. Ben-Ishai and R. Giger, *Tetrahedron Lett.*, **1965**, 4523.

[9] H. Hirai, H. Sawai and S. Makishima, This Bulletin, **43**, 1143 (1970).

[10] E. W. Stern and M. L. Spector, *J. Org. Chem.*, **31**, 596 (1966); J. Tsuji and N. Iwamoto, *Chem. Commun.*, **1966**, 380.

[11] M. S. Kharasch, R. C. Seyler and F. R. Mayo, *J. Amer. Chem. Soc.*, **60**, 882 (1938).

crystals, which were confirmed to be a mixture of pyrrolidone-palladium(II) chloride complex and *N*-vinylpyrrolidone-palladium(II) chloride complex by IR spectrum; (3200(ν_{NH}), 2930, 2850, 1670(ν_{CO}), 1640(ν_{CO} or $\nu_{C=C}$), 1625 (ν_{CO} or $\nu_{C=C}$), 1290).

In the presence of quinone, a dark reddish brown precipitate was obtained from Filtrate III after concentration. This precipitate seems to be quinone-palladium(II) complex, but further characterization was unsuccessful.

Reaction of Styrene-Palladium(II) Chloride Complex with Pyrrolidone. Styrene-palladium(II) chloride complex (3.172 g, 0.0113 mol), styrene (2 m*l*), pyrrolidone (4.5 ml, 0.0045 mol) and dry tetrahydrofuran were charged in the autoclave. Reaction was carried out at 120°C for 2.5 hr. After the reaction, 2 m*l* of pyridine was added to the reaction mixture to make the product free from the coordination state. Then the reaction mixture was filtered through a glass filter, and the precipitate was washed with tetrahydrofuran. The filtrate was concentrated by evaporation and chromatographed on silica gel.

From the first fraction white crystals were obtained by using cyclohexane as an eluent. Recrystallization from *n*-hexane gave pure 1,4-diphenylbutadiene; mp 152—153°C (lit,[6]) 149.5°C).

From the second fraction colorless liquid was obtained, which was confirmed to be acetophenone by IR and glpc.

Finally white crystals were obtained by using benzene as an eluent. Recrystallization from cyclohexane-ether gave purified *trans-β*-styrylpyrrolidone; mp 128°C (lit,[12]) 129°C).

Reaction of Ethylene-Palladium(II) Chloride Complex with ε-Caprolactam, *N*-Ethylacetamide and Acetanilide. The procedure was similar to that used for the reaction of ethylene complex with pyrrolidone. Analysis of the products was carried out by glpc; A 2 m Carbowax 20 M on Diasolid A column, and a nitrogen flow rate of 60 m*l*/min, at 170°C for ε-caprolactam and acetanilide, at 122°C for *N*-ethylacetamide. The yield data were obtained by glpc with benzonitrile as an internal standard. The products were identified by comparison of gas chormatograms and IR spectra with those of authentic sample prepared according to Reppe.[13])

Reaction of Ethylene-Palladium(II) Chloride Complex with Acetamide. The reaction method was similar to that for the case of pyrrolidone. The product was analyzed by glpc; A 2 m Carbowax 20 M on Diasolid A column at 122°C and a nitrogen flow rate of 60 m*l*/min. The reaction product could not be detected by glpc, but *N*-ethylacetamide was obtained after hydrogenation of the reaction mixture catalyzed by palladium metal under 80 atm of hydrogen, as described by Stern.[2]) The yield data were obtained by glpc with benzonitrile as an internal standard. The preparation of *N*-vinylacetamide as an authentic sample, reported by Ben-Ishai and Giger,[8]) was unsuccessful.

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12) W. Ziegenbein and W. Franks, *Chem. Ber.*, **90,** 2291 (1957).

13) W. Reppe and Mitarbeiter, *Ann.*, **601**, 81 (1956).