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Reaction of Olefin-Palladium(II) Chloride Complexes with *n*-Butylamine

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Olefin-palladium(II) chloride complexes reacted with *n*-butylamine to form Schiff's bases. *N*-Ethylidene-*n*-butylamine was obtained by the reaction of the ethylene complex with *n*-butylamine, accompanied by reduction of palladium(II) to the metal. A tris(*n*-butylamine)palladium chloride complex was formed simultaneously by ligand substitution reaction. The yield of *N*-ethylidene-*n*-butylamine was 15—19 mol% (calcd on palladium) in 2.5 hr at 25°C, and decreased at temperatures higher than 60°C with increasing reduction of palladium(II), owing to conversion of *N*-ethylidene-*n*-butylamine into either *N*-crotylidene-*n*-butylamine or a tarry polymeric substance by aldol type condensation reaction. The *n*-butylamine-palladium(II) chloride complex did not react with ethylene at 25°C, but reacted with ethylene at 150°C to form a large amount of tarry polymer and a small amounts of *N*-ethylidene-*n*-butylamine and *N*-crotylidene-*n*-butylamine. The propylene complex and the cyclohexene complex reacted with *n*-butylamine to yield both 2- and 1-*N*-propylidene-*n*-butylamine, and *N*-cyclohexylidene-*n*-butylamine respectively. The yield of Schiff's bases from olefin complex decreased in the order, ethylene>propylene≫cyclohexene.

The reaction of olefin-palladium(II) chloride complexes with nucleophilic reagents have been studied by many workers[1,2] in recent years. Aldehydes,[3] ketones,[3] vinyl ethers[4,5] and vinyl acetates[4,5] were sythesized by the reaction of the olefin complex, or by the reaction of olefin in the presence of palladium(II) salt as catalyst, with nucleophilic reagents such as water, alcohols and acetic acid. These reagents containing nucleophilic oxygen atoms attack on a positively charged carbon atom of the olefin to give the product containing a C–O bond. Olefin-palladium(II) complexes were also reported to react with benzene,[6] cyanide,[7] ethylmalonate[8] and carbon monoxide[9] to yield styrene derivatives, unsaturated nitriles, malonate derivatives and carbonyl compounds, respectively. In these cases the nucleophiles attack with their negatively charged carbon atoms to form C–C bond.

Reaction of olefin-palladium(II) complexes with nucleophiles containing nitrogen, however, has been very scantily reported. Stern and Spector reported briefly the formation of *n*-butylisopropylamine by the reaction of propylene and palladium chloride with *n*-butylamine in the presence of disodium hydrogen phosphate with subsquent hydrogenation.[5] There has been, however, very little information on the reaction of olefin complexes with the compounds containing nitrogen on account of the complicatedness of the reaction. The nucleophilic reagents containing nitrogen such as amines and amides make stable complexes with metal satls. This is a great difference from the case of the reagents containing oxygen such as water or alcohols. Further, both the nucleophiles and the reaction products would form the stable complexes with palladium chloride, which prevent the occurrence of the expected reaction making the analysis of the products complicated. On the other hand, these complex formations can be expected, in view of coordination chemistry, to be useful for elucidation of the mechanism of the reaction where palladium(II) complexes play an important role. Paiaro, Renzi and Polumbo reported the reaction of diene-palladium(II) chloride complex with primary amines, in which a new amine-palladium(II) complex containing a Pd–C bond was formed quantitavely at room temperature.[10] Independently,

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[1] C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Logos Press, London (1966), pp. 88—112.

[2] A. Guilo, "Advances in Organometallic Chemistry," Vol. 5, ed. by F. G. A. Stone and R. West, Academic Press, New York (1967), p. 321.

[3] J. Smidt, W. Hafner, R. Jira, J. Seldmeier, R. Sieber, R. Ruttinger and H. Kojer, *Angew. Chem.*, **71**, 176 (1959).

[4] I. I. Moiseev, M. N. Vergaftik and Y. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **133**, 377 (1960).

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

[6] I. Moritani and Y. Fujiwara, *Tetrahedron Lett.*, **1967**, 1119.

[7] Y. Odaira, T. Oishi, T. Yukawa and S. Tsutsumi, *J. Amer. Chem. Soc.*, **88**, 4105 (1966).

[8] J. Tsuji and H. Takahashi, *ibid.*, **87**, 3275 (1965).

[9] J. Tsuji, M. Morikawa and J. Kiji, *ibid.*, **86**, 4581 (1964).

[10] G. Paiaro, A. D. Renzi and R. Palumbo, *Chem. Commun.*, **1967**, 1150; R. Palumbo, A. D. Renzi, A. Panunzi and G. Paiaro, *J. Amer. Chem. Soc.*, **91**, 3874 (1969).

we have found the formation of Schiff's bases on the reaction of olefin - palladium(II) chloride complexes with *n*-butylamine.[11] In the present paper, the formation of the Schiff's bases will be described under various temperature, pressure and amount of *n*-butylamine. The reaction mechanism will be discussed on the basis of the results.

Results and Discussion

Reaction of Ethylene - Palladium(II) Chloride Complex with *n*-Butylamine. Ethylene - palladium(II) chloride complex reacted with *n*-butylamine at 25°C for 2.5 hr under 5 atm of ethylene pressure. *N*-Ethylidene-*n*-butylamine (**1**) was obtained in 16 mol% yield based on palladium(II) chloride, accompanying the formation of palladium metal. The reddish brown solution of reaction mixture turned white-yellow forming tris(*n*-butylamine)palladium(II) chloride complex (**2**), the structure of which was confirmed by elemental analysis. These facts indicate two types of reaction, a Schiff's base formation and a ligand substitution.

$$\tfrac{1}{2}\,[PdCl_2(C_2H_4)]_2 + n\text{-}C_4H_9NH_2 \rightarrow \underset{\mathbf{1}}{CH_3CH{=}NC_4H_9} + Pd + 2HCl \qquad (1)$$

$$\tfrac{1}{2}\,[PdCl_2(C_2H_4)]_2 + 3\ n\text{-}C_4H_9NH_2 \rightarrow [PdCl(n\text{-}C_4H_9NH_2)_3]Cl + C_2H_4 \qquad (2)$$

Hydrochloric acid formed by reaction(1) was mostly caught by an excess of *n*-butylamine as *n*-butylamine hydrochloride.

The effect of the reaction temperature on the yield of the reaction products is shown in Table 1. Compound **1** was obtained at 25°C in a yield nearly equal to that of palladium metal. The formation of the palladium metal increased at temperatures higher than 60°C, and palladium(II) was reduced almost completely to metal at 150°C. The yield of **1**, however, decreased with increasing temperature and only a trace amount was obtained at 150°C, while *N*-crotylidene-*n*-butylamine (**3**) and a tarry reddish substance were obtained in fairly good yields. The infrared spectrum of the tarry substance was essentially the same as that of the tarry substance which was prepared by heating **1**. The molar amount of **2** decreased with the elevation of temperature and was in good agreement with the moles of palladium(II) which was not reduced.

Table 1. Effect of temperature on the reaction of ethylene - palladium(II) chloride complex with *n*-butylamine

Temp. °C	Yield mol% CH_3–CH=NBu	 CH_3CH=CHCH=NBu	 Pd (metal)	 [PdCl(*n*-BuNH$_2$)$_3$]Cl	Tarry substance[b) mg
25	16	0	14	86	0
65	16	4	19	81	trace
85	13	5	35		
100	15	15	59	44	190
150	1	42	99	0	510

a) Molar conversion based on palladium chloride.
b) Crude substance.
Conditions: Initial pressure of ethylene, 5 atm; Reaction time, 2.5 hr; Palladium chloride, 0.005 mol; *n*-Butylamine, 0.02 mol.

Formation of amine complex by ligand substitution seems to be favored, and a *n*-butylamine-palladium(II) chloride complex was too stable to react with ethylene at room temperature. Thus, the extent of the Schiff's base formation (1) at 25°C was not very high. Formation of **3** and tarry substance at elevated temperature can be explained by the reaction.

$$\underset{\mathbf{1}}{CH_3CH{=}NC_4H_9} \xrightarrow{\Delta} \underset{\mathbf{3}}{CH_3CH{=}CHCH{=}NC_4H_9}$$

$$\xrightarrow{\Delta} CH_3CH({=}CH\text{-}CH)_n{=}NC_4H_9$$

Elevation of temperature promoted not only the formation of **1** by reaction (1), but also the conversion of **1** either into **3** or into tarry substance through aldol type condensation reaction. Aliphatic Schiff's bases containing α-methylene group have been reported to undergo aldol type condensation easily at elevated temperature.[12] The formation of palladium metal indicates the extent of the Schiff's base formation reaction (1). Thus, the difference between the yield of palladium metal and that of **1** means the extent of the aldol type condensation. The condensation reaction was not observed at 25°C in 2.5 hr. However, it increased with elevating temperature becoming predominant at 150°C.

Table 2 shows the effect of molar ratio of *n*-butylamine to palladium(II) chloride on the yield of **1** and on the species of *n*-butylamine - palladium(II) chloride complex. The yield of **1** determined by g.l.p.c. increased with the molar ratio and saturated at a ratio of four. In the range of ratios smaller than four, the yield of **1** increased by addition of pyridine to the mixture of reaction products, bacause a part of **1** which had formed a complex with palladium(II) could be made free by pyridine.

The composition of *n*-butylamine - palladium(II) complex changed with the amount of *n*-butylamine as shown in Table 2. Bis(*n*-butylamine)palladium(II) chloride (**4**) was produced at the molar ratio of two, while the complex **2** was obtained at that of more than four. The formation of **2** and **4**

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

[12] R. W. Rayer, *Chem. Rev.*, **13**, 489 (1963).

Table 2. Effect of amount of *n*-butylamine

$[n\text{-BuNH}_2]/[\text{PdCl}_2]$[a)]	Yield of CH_3–CH=NBu, mol%[b)] free[c)]	free+complexed[d)]	*n*-Buthylamine complex
1	3	6	$(n\text{-}C_4H_9NH_3)_2^+(PdCl_4)$
2	5	7	$PdCl_2(n\text{-}C_4H_9NH_2)_2$
4	16	16	$[PdCl(n\text{-}C_4H_9NH_2)_3]Cl$
10	15	15	$[PdCl(n\text{-}C_4H_9NH_2)_3]Cl$
40	16	16	$[PdCl(n\text{-}C_4H_9NH_2)_3]Cl$

a) Molar ratio.
b) Based on palladium chloride.
c) Yield of $CH_3CH{=}NBu$ analyzed by gaschromatography on reaction mixture.
d) Yield of $CH_3CH{=}NBu$ analyzed by gaschromatography on reaction mixture after addition of pyridine.
Conditions: Initial pressure of ethylene, 5 atm; Reaction time, 2.5 hr; Reaction temperature, 25°C; Palladium chloride, 0.005 mol.

respectively is nearly equal to the remaining amount of palladium(II). At the molar ratio of one, *n*-butylammonium tetrachloropalladate(II) (**5**) was obtained in a yield approximately equal to that of **1**. Palladium(II) chloride reacted with both *n*-butylamine and hydrochloric acid to form **5**.

The ethylene-palladium(II) chloride complex was prepared either by the reaction of palladium(II) chloride with ethylene under 50 atm in 6 hr, or by the reaction of bis(benzonitrile)palladium(II) chloride complex with ethylene under 10 atm in 1 hr. These two methods were approximately equal in yields of **1** on reaction with *n*-butylamine at 25°C under 5 atm of ethylene pressure. Table 3 shows that the ethylene complex was prepared completely from palladium(II) chloride in 6 hr under 50 atm, but incompletely in 1 hr under 10 atm. The yield of **1** increased with increasing pressure of ethylene on reaction with *n*-butylamine up to 50 atm as shown in Table 3. The promotion of the yield of **1** can be explained by assuming that the pressure of ethylene not only promoted the coordination of ethylene but also suppressed the ligand substitution reaction resulting in a small acceleration of Schiff's base formation.

Table 3. Effect of pessure of ethylene on the yield of *N*-ethylidene-*n*-butylamine

Pressure atm[a)]	Time[a)] hr	Reaction pressure[b)] atm	Yield mol%
50	6	1	15
50	6	5	16
50	6	10	18
50	6	25	19
50	6	50	19
10	1	1	4
10	2	25	10
10	1	5	16[c)]

a) Pressure of ethylene and reaction time for preparation of the ethylene complex from palladium chloride with ethylene.
b) Pressure of ethylene for the reaction of ethylene complex with *n*-butylamine.
c) Bis(benzonitrile) palladium chloride complex was used instead of palladium chloride.
Conditions:Temperature, 25°C ; Reaction time, 2.5 hr; Palladium chloride, 0.005 mol; *n*-Butylamine, 0.02 mol.

Reaction of Tris(*n*-butylamine)palladium(II) Chloride Complex with Ethylene. *n*-Butylamine-palladium(II) chloride complex **2** was very stable and did not react with ethylene at room temperature. This complex, however, was found to react easily with ethylene at a higher temperature; for example, 95% of palladium (II) in the complex was reduced to the metal at 150°C, yielding **1**, **3** and tarry polymeric substance, as shown in Table 4. These products were consistent with those obtained by the reaction of the ethylene-palladium(II) chloride complex with *n*-butylamine.

Table 4. Reaction of tris (*n*- butylamine)-palladium chloride complex with ethylene

Temp. °C	Yield, mol%[a)] $CH_3CH{=}$NBu	$CH_3CH{=}CH{=}$CH=NBu	Pd (metal)	Tarry substance[b)] mg
25	0	0	0	0
150	1	11	95	500

a) Based on palladium chloride.
b) Crude substance.
Conditions: Tris(*n*-butylamine)palladium chloride, 0.005 mol; Pressure of ethylene, 50 atm; Reaction time, 2.5 hr.

Reaction of Other Olefin-Palladium(II) Chloride Complexes with *n*-Butylamine. The reaction of propylene-palladium(II) chloride complex with *n*-butylamine gave 2- and 1-*N*-propylidene-*n*-butylamine as shown in Table 5. The yield of 2- and 1-*N*-propylidene-*n*-butylamine were in the ratio of the yield of 6 : 1 approximately, which is in fair agreement with the ratio of the yield of acetone to that of propionaldehyde obtained by reaction of palladium(II) chloride with propylene and water.[3)]

$$\tfrac{1}{2}\,[PdCl_2(C_3H_6)]_2 + n\text{-}C_4H_9NH_2$$

$$\swarrow \qquad\qquad \searrow$$

$CH_3CH_2CH{=}NC_4H_9$	$(CH_3)_2C{=}NC_4H_9$
(1-*N*-proylidene-*n*-butylamine)	(2-*N*-propylidene-*n*-butylamine)

Cyclohexene-palladium(II) chloride complex yielded a small amount of *N*-cyclohexylidene-*n*-butylamine. Schiff's base formation proceeded to remarkably smaller extent in the case of higher olefins than in that of ethylene. This tendency is greater than that of aldehydes or ketones obtained by the reaction of palladium(II) chloride with higher olefins and water.[3)]

TABLE 5. REACTION OF OLEFIN-PALLADIUM(II) CHLORIDE COMPLEXES WITH *n*-BUTYLAMINE AT 25°C

Olefin	Reaction time hr	$[n\text{-BuNH}_2]/[\text{PdCl}_2]$	Product	Yield mol%
C_2H_4[a)]	2.5	4	$CH_3CH{=}NBu$	16
C_3H_6[a)]	5	5	$CH_3CH_2CH{=}NBu$	1.3
			$(CH_3)_2C{=}NBu$	7.6
C_6H_{10}	5	5	$\underbrace{-(CH_2)_5-C}{=}NBu$	trace[b)]

[a)] Pressure, 5 atm.
[b)] Less than 1 mol%.

Effect of Small Amount of Water on the Reaction. Schiff's bases are usually obtained from aldehydes and primary amines. Acetaldehyde can be formed from ethylene-palladium(II) chloride complex with water,[3)] which remains in a very small amount in the reaction system in spite of careful treatment to prevent contamination with water. Consequently, **1** could be formed by reaction of the acetaldehyde with *n*-butylamine as follows.

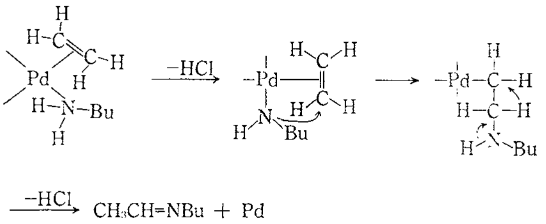
$$1/2[PdCl_2(C_2H_4)]_2 + H_2O \longrightarrow CH_3CHO + Pd + 2HCl \qquad (3)$$

$$CH_3CHO + n\text{-}C_4H_9NH_2 \longrightarrow CH_3CH{=}NC_4H_9 + H_2O \qquad (4)$$

For examination of this possibility, the formation of acetaldehyde was determined by g.l.p.c. before addition of *n*-butylamine. The result shows that the amount of acetaldehyde is less than 0.8 mol% based on palladium(II) chloride. If **1** were formed by reactions (3) and (4), water should be used twenty times repeatedly to obtain **1** in 16 mol% yield at 25°C, and the yield of **1** could be expected to increase on addition of a small amount of water with *n*-butylamine. The yield, however, decreased from 16 mol% to 9 mol% by the use of *n*-butylamine which contained water in equimolar amount to palladium(II) chloride, instead of dried *n*-butylamine. The fact that the added water played a role of inhibitor indicates that the most of **1** was not formed by reactions (3) and (4), but formed by the direct reaction of *n*-butylamine with ethylene complex. This is consistent with the fact that the ethylene-palladium(II) chloride complex yields *N*-vinylpyrrolidone on reaction with pyrrolidone, which attacks coordinated ethylene with its >NH group to form C–N bond.[13),14)] Pyrrolidone cannot react with acetaldehyde under such mild conditions as used in this study.

Reaction Mechanism. The reaction mechanism of direct attack of *n*-butylamine on ethylene-palladium(II) chloride complex will be discussed. The ethylene-palladium(II) chloride complex with equimolar *n*-butylamine was a homogeneous solution under ethylene pressure, and evolved a gas of ethylene with precipitation of complex **5** on standing for several minutes under ordinary pressure of air. Addition of methanol to the homogeneous solution produced palladium metal and methyl vinyl ether. The results indicate the presence of some ethylene-palladium(II) complex in the homogeneous solution. On the other hand, an amine has a stronger coordinating affinity to palladium(II) than ethylene. It is reasonable to suppose that both *n*-butylamine and ethylene coordinate palladium (II) under ethylene pressure to form a complex such as $PdCl_2$(olefin)(amine), which is so unstable as to evolve ethylene under ordinary pressure of air. A platinum complex such as $PtCl_2$(olefin)-(amine) is well known,[15)] while a corresponding palladium(II) has never been isolated. The fact that the *n*-butylamine-palladium(II) complex can react with ethylene to give **1** at 150°C indicates the coordination of ethylene to *n*-butylamine-palladium(II) complex. The complex coordinating both ethylene and *n*-butylamine can be considered to be a reaction intermediate of Schiff's base formation. That the formation of this intermediate is essential for the reaction has been supported also by the results of the allylamine-palladium(II) chloride complexes in dry tetrahydrofuran.[16)] The 1 : 1 allylamine-palladium(II) complex which can coordinate olefinic double bond besides amino group could react at 50°C to form palladium metal and Schiff's base, while the 3 : 1 allylamine-palladium(II) chloride complex, which coordinates only amino group, could not.

The following reaction scheme can be proposed



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

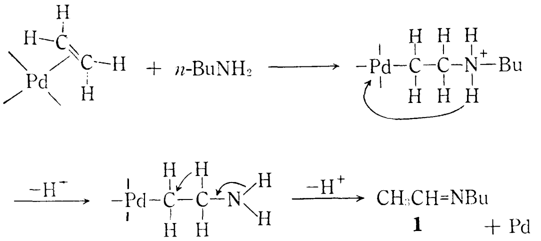
[14)] H. Hirai, H. Sawai and S. Makishima, Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

[15)] G. E. Coates and F. Glockling, "Organometallic Chemistry," ed. by H. Zeiss, Reinhold Publishing Co., New York, (1960), p. 456.

[16)] H. Sawai and H. Hirai, Presented at the 19th Annual Meeting of Coordination Chemistry, Sendai, Sept., 1969.

involving an ethylene-*n*-butylamine-palladium(II) complex as the intermediate. The proton of coordinated *n*-butylamine would be withdrawn by palladium(II) to form amido-palladium(II) complex. Then the coordinated ethylene would enter the Pd–N bond to form Schiff's base **1**. The withdrawal of proton of coordinated amine has been proposed by Tsuji and Iwamoto for the carbonylation reaction of amine catalyzed by palladium(II) chloride.[17]

The following reaction scheme can be also considered.



In this case uncoordinated *n*-butylamine attacks coordinated ethylene to form an intermediate complex which is an alkyl palladium derivative containing a quaternary ammonium group. Palladium(II) withdraws two protons from the ammonium group to form Schiff's base. The metal alkyl derivative containing a quaternary ammonium group was isolated in the case of platinum complex prepared from dichloro(olefin)(*t*-phosphine)platinum complex with amine.[18]

The facts that amines have strong coordinating affinity to palladium(II) chloride, and that *n*-butylamine-palladium(II) chloride complex reacts with ethylene at 150°C, suggest that the former scheme is preferable. In either scheme, the elevation of reaction temperature is expected to make the *n*-butylamine complex so labile that the coordination of ethylene becomes possible, and to promote both the withdrawal of proton of *n*-butylamine and the formation of Schiff's base **1** with the subsequent aldol type condensation. These tendencies are supported by the fact that total yield of Schiff's base including the products of condensation increased extensively at higher temperatures and that *n*-butylamine-palladium(II) chloride complex which could not react with ethylene at room temperature reacted at 150°C in a high yield.

Experimental

Materials. Bis(benzonitrile)palladium chloride complex was prepared as described by Kharasch.[19] Ethylene and propylene were from Nihon Petrochemical Co. and used without further purification. Cyclohexene and *n*-butylamine were obtained commercially, dried over calcium hydride and distilled. Tetrahydrofuran used as solvent was dried over calcium hydride and distilled over sodium immediately before use.

Reaction of Ethylene-Palladium(II) Chloride Complex with *n*-Butylamine. Palladium chloride (0.9 g, 0.005 mol) and tetrahydrofuran (20 m*l*) were put into in a magnetically stirred 100 m*l* autoclave in a slow stream of nitrogen. A glass reaction tube containing the reaction mixture was used in the autoclave. The stirrer was gilded with gold to prevent palladium(II) chloride from reacting with steel. Ethylene-palladium(II) chloride complex was prepared under 50 atm of ethylene pressure for 6 hr. The autoclave was then opened and *n*-butylamine (2 m*l*, 0.02 mol) was added. The reaction was carried out at a given pressure of ethylene (1—50 atm) and temperature (25—150°C) by stirring for 2.5 hr. The formation of the ethylene-palladium(II) chloride complex depended on pressure of ethylene and reaction time. To confirm the complete formation of the ethylene complex, bis(benzonitrile)palladium chloride complex was used instead of palladium chloride. In this case the ethylene complex was prepared completely.[19]

The reaction products were analyzed by gaschromatography; 3 m Carbowax 1500 on Diasolid A column at 65°C and a nitrogen flow rate of 60 m*l*/min; 2 m Apiezon Grease L on Diasolid A column at 50°C and a nitrogen flow rate of 50 m*l*/min. Identification of product **1** was carried out by comparison of gas chromatogram and infrared spectrum with that of the authentic sample prepared according to Campbell.[20] Yield data were obtained by gas chromatography using cyclohexane as an internal standard. White crystalline insoluble in tetrahydrofuran was obtained remarkably at elevated temperature. Recrystallization from methanol gave purified *n*-butylamine hydrochloride (mp 195—197°C). Infrared spectrum and melting point of this crystals were identical with those of the authentic sample prepared from *n*-butylamine and hydrochloric acid. The soluble reaction mixture was evaporated to dryness and recrystallization from methanol gave cream yellow crystals, which was **2**, $[\mathrm{PdCl}(n\text{-}\mathrm{C_4H_9NH_2})_3]\mathrm{Cl}$; mp 149.5—150.5°C.

Found: C, 36.30; H, 8.56; N, 10.16%. Calcd for $\mathrm{PdCl_2C_{12}H_{33}N_3}$: C, 36.38; H, 8.38; N, 10.60%.

Analysis of Reaction Products at Elevated Temperature. Product **3** was analyzed by gaschromatography under the same conditions as in **1**. Tarry substance was obtained as follows. The reaction mixture was evaporated and **2** was removed by crystallization from methanol. The black red filtrate was evaporated to dryness under reduced pressure at 60°C for 8 hr and weighed without further purification. Identification of **3** and the tarry substance was made by comparison of gaschromatogram and infrared spectra with those of authentic sample prepared from **1** by heating.[12] The infrared spectrum of the tarry substance showed a broad absorption at 1600—1650 cm^{-1} referred to $\nu_{\mathrm{C=C}}$ and $\nu_{\mathrm{C=N}}$, but no clear absorption at 3200—3300 cm^{-1} referred to $\nu_{\mathrm{N-H}}$.

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[17] J. Tsuji and N. Iwamoto, *Chem. Commun.*, **1966**, 828.

[18] A. Panunzi, A. D. Renzi, R. Palumbo and G. Paiaro, *J. Amer. Chem. Soc.*, **91**, 3879 (1969).

[19] M. S. Kharasch, R. C. Seyler and F. R. Mayo, *ibid.*, **60**, 882 (1938).

[20] K. N. Campbell, A. H. Sommers and B. K. Campbell, *ibid.*, **66**, 82 (1944).

Analysis of Reaction Products with a Small Amount of *n*-Butylamine. Analysis of **1** was carried out by gas chromatography before and after the addition of pyridine. *n*-Butylamine-palladium(II) chloride complexes which were obtained at molar ratios of *n*-butylamine to palladium chloride of 1 and 2 were different from **2**. When the molar ratio of *n*-butylamine to palladium chloride was 1, *i. e.* $[n\text{-}C_4H_9NH_2]/[PdCl_2]=1$, the reaction mixture was reddish orange and homogeneous immediately after the reaction. In a few minutes copper-red crystals precipitated evolving gas of ethylene. Recrystallization from methanol gave **5**: $(PdCl_4)(n\text{-}C_4H_9NH_3)^+{}_2$; mp (decomp.) 240—260°C.

Found: C, 24.14; H, 6.07; N, 9.06%. Calcd for $PdCl_4C_8H_{24}N_2$: C, 24.14; H, 6.05; N, 9.05%.

The infrared spectrum was similar to that of *n*-butylamine hydrochloride. Isolation of other complexes was unsuccessful.

At the molar ratio of 2, *i. e.* $[n\text{-}C_4H_9NH_2]/[PdCl_2]=2$, the reaction mixture was yellow and homogeneous. Orange yellow crystals was obtained by the same method as **2**. Recrystallization from methanol gave **4**; $PdCl_2(n\text{-}C_4H_9NH_2)_2$: mp 146—147°C.

Found: C, 29.74; H, 6.66; N, 8.60%. Calcd for $PdCl_2C_8H_{22}N_2$: C, 29.72; H, 6.81; N, 8.67%.

Complex **3** was obtained at the ratio of more than **4**.

Reaction of Tris(*n*-butylamine)palladium(II) Chloride Complex 2 with Ethylene. Both 1.834 g of **2** and 20 m*l* of dry tetrahydrofuran were placed in the autoclave. Ethylene was compressed to 50 atm and stirred for 2.5 hr at 25°C or 150°C. Analysis of the products was carried out by the same method as described in the reaction of ethylene complex.

Reaction of Propylene-Palladium(II) Chloride Complex with *n*-Butylamine. Bis(benzonitrile)palladium chloride complex (1.9 g) and dry tetrahydrofuran (20 m*l*) were put into the autoclave. Propylene was compressed to 10 atm and stirred for 30 min to prepare the propylene complex. The autoclave was opened and *n*-butylamine (2 m*l*) was added. The reaction was carried out under 5 atm of propylene pressure by stirring for 5 hr at 25°C. Analysis of the reaction products was carried out by gas chromatography; 2 m Apiezon Grease L on Diasolid A column at 74°C and a nitrogen flow rate of 50 m*l*/min. Identification of the products was carried out by comparison of gaschromatogram with an authentic sample prepared according to Campbell.[20] Yield data were obtained by gaschromatography using toluene as an internal standard.

Reaction of Cyclohexene-Palladium(II) Chloride Complex with *n*-Butylamine. In a 30-m*l* conical beaker, 0.394 g of bis(benzonitrile)palladium chloride complex, 10 m*l* of dry tetrahydrofuran and 1 m*l* of cyclohexene were stirred by magnetic stirrer for 10 min to prepare the cyclohexene complex. To this reaction mixture 0.4 m*l* of *n*-butylamine was added gradually with stirring. Reaction was carried out at 25°C by stirring for 5 hr. The reaction product was analyzed by gaschromatography; 2 m Apiezon Grease L on Diasolid A column at 144°C and a nitrogen flow rate of 50 m*l*/min. Identification of the product was carried out by comparison of gas chromatogram with an autnentic sample prepared from cyclohexanone and *n*-butylamine.