Bis(cyclohexyl isocyanide)palladium(II) Halides and Their Benzene Complexes

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Bis(cyclohexyl isocyanide)palladium(II) chloride, $PdCl_2(C_6H_{11}NC)_2$ (**1**) was prepared from $PdCl_2$. The configuration of the complex **1** is cis with respect to the isocyanides. The isocyano group in one cyclohexyl isocyanide takes axial conformation to chair form cyclohexyl group, while another takes equatorial conformation. By recrystallization of **1** from benzene bis(cyclohexyl isocyanide)palladium(II) chloride–benzene, $PdCl_2(C_6H_{11}NC)_2(C_6H_6)_2$ (**2**) was prepared. IR spectrum of **2** shows a characteristic absorption at 700 cm^{-1} which is due to the benzene incorporated in the complex. Similar benzene complex was also prepared from $PdBr_2$.

Many benzenoid complexes are known with various transition metals, but a few with palladium.[1] Synthesis of a unique benzene–palladium(II) complex with the formula of $[PdAl_2Cl_7(C_6H_6)]_2$ was reported and its X-ray structural analysis showed that the Pd–Pd system is sandwitched between two benzene rings with each palladium essentially associated with three carbon atoms of each benzene.[2] Formation of an unstable benzene–palladium(I) complex was also reported.[3] In the preceeding paper we reported an insertion reaction of cyclohexyl isocyanide to π-allylpalladium chloride.[4] Palladium halides have been reported to react readily with aryl isocyanides yielding stable complexes, $PdX_2(RNC)_2$.[5] These complexes had been treated with benzene, but benzene complex was not reported to be formed. We obtained bis(cyclohexyl isocyanide)palladium(II) chloride, $PdCl_2(C_6H_{11}NC)_2$(**1**) by the use of cyclohexyl isocyanide in place of aryl isocyanide and found that the complex **1** has a unique structure and gives a new benzene complex, bis(cyclohexyl isocyanide)palladium(II) chloride–benzene, $PdCl_2(C_6H_{11}NC)_2(C_6H_6)$(**2**) by recrystallization from benzene. Similar benzene complex was also prepared from palladium bromide. Details of the reaction and IR spectroscopic analyses of the complexes are presented in this paper.

Results and Discussion

The complex **1** was obtained as white precipitates by the reaction of two molar equivalents of cyclohexyl isocyanide with palladium(II) chloride in benzene, successive concentration and dilution with ethyl ether. Recrystallization of **1** from hot benzene gave a yellow complex **2**, the analysis of which suggested the molecular formula, $PdCl_2(C_6H_{11}NC)_2(C_6H_6)$. On the other hand, recrystallization of **1** from *p*-xylene or toluene gave no complex containing xylene or toluene and the complex **1** was recovered. IR spectra of **1** and **2** are shown in Fig. 1.

$$PdCl_2 + 2C_6H_{11}NC \longrightarrow \underset{\textbf{1}}{cis\text{-}PdCl_2(C_6H_{11}NC)_2} \underset{Et_2O}{\overset{C_6H_6}{\rightleftharpoons}} \underset{\textbf{2}}{PdCl_2(C_6H_{11}NC)_2(C_6H_6)}$$

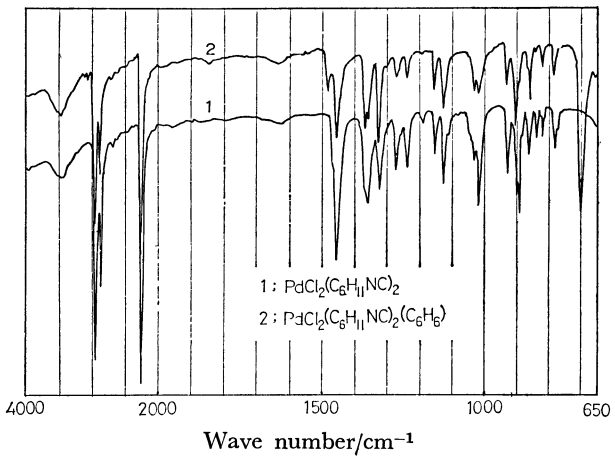

Fig. 1. IR spectra of $PdCl_2(C_6H_{11}NC)_2$ and $PdCl_2(C_6H_{11}NC)_2(C_6H_6)$.

By heating at 95 °C for 15 min, **2** was transformed into **1**, but **2** is fairly stable in air at room temperature and decomposes slowly with liberation of benzene. The complex **2** was also transformed into **1** by treating with ethyl ether. This result was ascertained by IR spectrum and elemental analysis of the complex obtained. The presence of benzene in the ether after contacting with **2** was confirmed by UV spectrum.

The IR spectrum of **2** shows several characteristic absorptions at 700, 1480, 1840, 1985, 3030, and 3075 cm^{-1} which are thought to be originated from the benzene incorporated in the complex. Especially the strong absorption at 700 cm^{-1} is worth noticing. It is well-known that the absorption of out of plane deformation band of benzene proton(ν_{11}) is observed at 672 cm^{-1} in vapor or liquid state, and at 687 cm^{-1} in solid state with free benzene as a stronger and broader absorption.[6] Shifting of the absorption to higher wave length suggests some probable interaction of benzene with palladium in the complex.

Crystallographic analyses of these complexes have been carried out and the crystal data are shown in Table 1. It is noteworthy that the extent of symmetry of **2** is higher than that of **1**. This result also suggests an interaction of benzene with palladium in complex **2**. We could not succeed in obtaining precise X-ray structural analysis of **2** because of its de-

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Table 1. Crystal data of $PdCl_2(C_6H_{11}NC)_2$ and $PdCl_2(C_6H_{11}NC)_2(C_6H_6)$

	$PdCl_2(C_6H_{11}NC)_2$	$PdCl_2(C_6H_{11}NC)_2(C_6H_6)$
Molecular weight	395.7	471.4
Crystal system	Monoclinic	Tetragonal
Cell parameters	a; 12.299 Å, b; 9.604 Å, c; 17.383 Å, β; 127.59°	a; 17.95 Å, c; 14.12 Å
Unit cell volume	1627.0 Å^3	4549.5 Å^3
Dencity obsd(calcd)	1.605(1.615)	1.3—1.5(1.376)
Z	4	8
Space group	C_{2h}^5-$P2_1/c$(No. 14)	D_{4h}^{12}-$P4_2/nnm$(No. 134)

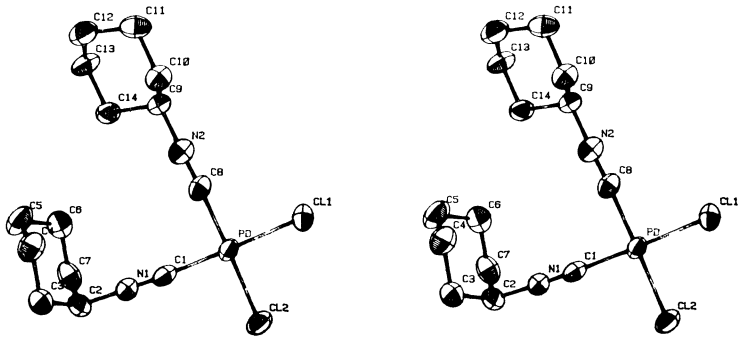

Fig. 2. Stereographic schematic drawing of $PdCl_2(C_6H_{11}NC)_2$.

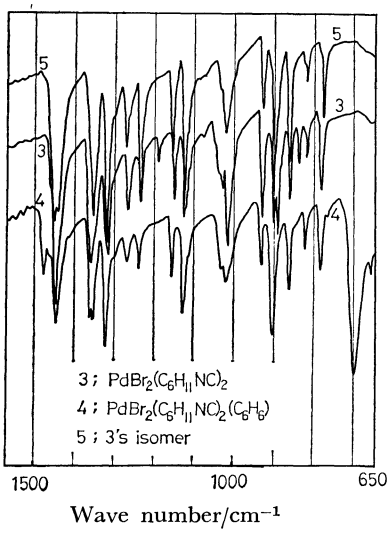

Fig. 3. IR spectra of $PdBr_2(C_6H_{11}NC)_2$, its isomer and $PdBr_2(C_6H_{11}NC)_2(C_6H_6)$.

composition during the diffraction analysis. It is suspected that **2** is five-co-ordinate with a π-bond of benzene, two chlorines and two isocyanides. X-ray structural analysis showed that the complex **1** has the structure shown in Fig. 2. Details of the analysis will be given in a forthcoming paper, but it should be noticed that the configuration of **1** is cis with respect to the isocyanides. Furthermore it is quite interesting that one isocyano group takes equatorial conformation and another isocyano group takes axial conformation to chair form cyclohexyl group.

The reaction of palladium(II) bromide with cyclohexyl isocyanide gave bis(cyclohexyl isocyanide)palladium(II) bromide, $PdBr_2(C_6H_{11}NC)_2$(**3**). By recrystallization of **3** from hot benzene, another benzene complex, bis(cyclohexyl isocyanide)palladium(II) bromide–benzene, $PdBr_2(C_6H_{11}NC)_2(C_6H_6)$(**4**) was obtained. Two kinds of complexes having the same molecular formula; $PdBr_2(C_6H_{11}NC)_2$ and different IR absorptions were obtained from the complex **4**. By washing with ethyl ether, **4** was transformed into **3**, but by heating at 100 °C for 1 h, **4** was transformed into another complex **5**. Recrystallization of **3** from hot *p*-xylene gave the complex **5** too. The complexes **3** and **5** are thought to be stereoisomers, but it is not clear why the two distinct IR absorptions at 860 and 1180 cm^{-1} observed with **3** are not in the spectrum of **5** as shown in Fig. 3.

$$PdBr_2 + 2C_6H_{11}NC \longrightarrow PdBr_2(C_6H_{11}NC)_2 \quad (\mathbf{3})$$

$$\mathbf{3} \xrightarrow{p\text{-Xylene}} \mathbf{5}$$

$$\mathbf{3} \underset{Et_2O}{\overset{C_6H_6}{\rightleftharpoons}} PdBr_2(C_6H_{11}NC)_2(C_6H_6) \quad (\mathbf{4})$$

$$\mathbf{4} \xrightarrow{100\,^\circ C} \mathbf{5}$$

As a related reaction, it was reported that $RuCl_2(C_6H_{11}NC)_2(C_6H_6)$ was formed by the reaction of $[RuCl_2(C_6H_6)]_2$ with cyclohexyl isocyanide, while only $RuCl_2(C_6H_5NC)_4$ was formed with phenyl isocyanide.[7] Formation of benzene complex from $PdCl_2(C_6H_5NC)_2$ is not known as described in the introduction. On the other hand, the benzene complexes were obtained from the cyclohexyl isocyanide complexes. According to these facts cyclohexyl isocyanide rather than phenyl isocyanide is essential as the ligand in order to obtain benzene complexes from palladium halides and ruthenium halides.

Experimental

*Preparation of $PdCl_2(C_6H_{11}NC)_2$ (**1**).* To a benzene solution (100 cm^3) containing palladium chloride (4.5 mmol, 0.80 g) was added cyclohexyl isocyanide (9 mmol, 1.1 cm^3)

with continuous stirring by a magnetic stirrer and the mixture was heated at temperatures between 70 °C and 80 °C to give a yellow solution. After filtration the hot solution to remove the remaining palladium chloride (0.08 g), the filtrate was concentrated under reduced pressure and ethyl ether (100 cm^3) was added to give white precipitates (1.43 g); mp 123 °C.

Found: C, 42.52; H, 5.58; N, 7.14; Cl, 18.17; ash, 27.2%. Calcd for $C_{14}H_{22}N_2Cl_2Pd$: C, 42.51; H, 5.58; N, 7.09; Cl, 17.93; ash, 26.90%.

Preparation of $PdCl_2(C_6H_{11}NC)_2(C_6H_6)$ ***(2)***. $PdCl_2(C_6H_{11}NC)_2$ (0.5 g) was recrystallized from hot benzene (20 cm^3) to give yellow crystals (0.52 g); mp 127—128 °C.

Found: C, 50.67; H, 5.98; N, 6.04; Cl, 15.28; ash, 22.6%. Calcd for $C_{20}H_{28}N_2Cl_2Pd$: C, 50.70; H, 5.97; N, 5.91; Cl, 14.97; ash, 22.47%.

Preparation of $PdBr_2(C_6H_{11}NC)_2$ ***(3)***. To a benzene solution (125 cm^3) containing palladium bromide (5 mmol, 1.33 g) was added cyclohexyl isocyanide (10 mmol, 1.2 cm^3) with stirring and the mixture was heated at temperatures between 70 °C and 80 °C to give a yellow solution. After filtration of the hot solution to remove the remaining palladium bromide, the filtrate was concentrated under reduced pressure and ethyl ether (150 cm^3) was added to give pale yellow crystals (1.81 g); mp 152 °C.

Found: C, 34.71; H, 4.58; N, 5.86; ash, 22.1%. Calcd for $C_{14}H_{22}N_2Br_2Pd$: C, 34.70; H, 4.58; N, 5.78; ash, 21.96%.

Preparation of $PdBr_2(C_6H_{11}NC)_2(C_6H_6)$ ***(4)***. The complex **3** was recrystallized from hot benzene to give yellow crystals; mp 155—160 °C.

Found: C, 42.44; H, 5.02; N, 5.10; Br, 28.52; ash, 19.2%. Calcd for $C_{20}H_{28}N_2Br_2Pd$: C, 42.70; H, 5.01; N, 4.98; Br, 28.42; ash, 18.90%.

Preparation of $PdBr_2(C_6H_{11}NC)_2$ ***(5)***. The complex **4** was treated with ethyl ether and dried under reduced pressure to give pale yellow powder; mp 152 °C.

Found: C, 34.80; H, 4.59; N, 5.86; ash, 22.1%. Calcd for $C_{14}H_{22}N_2Br_2Pd$: C, 34.70; H, 4.58; N, 5.78; ash, 21.96%.

Apparatus. IR spectra were obtained on a Perkin-Elmer 125 spectrometer and Hitachi EPI-S spectrometer in KBr disks, UV spectra on a Varian Cary 14 spectrometer. X-ray spectra were obtained on a Rigakudenki AFC-6A diffractometer.

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