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# ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS XLI*. REACTION OF ISOCYANIDE WITH π-ALLYLPALLADIUM CHLORIDE

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## SUMMARY

The treatment of cyclohexyl isocyanide with π-allylpalladium chloride in benzene at room temperature gave di-μ-chloro-bis[1-(cyclohexylimino)-3-butenyl]-bis(cyclohexyl isocyanide)dipalladium by the insertion reaction. The progress of the insertion reaction was followed by NMR spectroscopy. The ethanolysis of the complex gave ethyl *N*-cyclohexyl-3-butenimidate.

## INTRODUCTION

The insertion reaction is one of the most essential reactions in organometallic chemistry and several simple molecules are known to undergo the insertion reaction into a metal–carbon sigma bond. Among them, the carbon monoxide insertion is the most well studied and established reaction. In view of the fact that an isocyanide is isoelectronic with carbon monoxide, a reaction similar to that of carbon monoxide is expected. In addition, isocyanides could be interesting starting materials for organic synthesis if they can be brought into reaction with olefinic compounds. Isocyanides are strongly coordinated to transition metal compounds, but their reactions have received little attention from the standpoint of organic synthesis. In order to explore the usefulness of isocyanides, studies of their insertion reaction into a metal–carbon sigma bond were undertaken. Undoubtedly, the insertion reaction is an important intermediate step in organic syntheses catalyzed by transition metal complexes. Hagihara *et al.*[2] isolated π-cyclopentadienyl(cyclohexyl isocyanide)[1-(cyclohexylimino)ethyl] nickel by the reaction of π-cyclopentadienylmethyl(triphenylphosphine)-nickel with cyclohexyl isocyanide.

The insertion reaction of carbon monoxide into π-allylpalladium chloride is assumed in the carbonylation reaction of the complex, but the intermediate acyl-palladium complex has not been isolated. Thus π-allylpalladium chloride was selected for the studies of the isocyanide insertion. In this paper, the facile insertion of cyclohexyl isocyanide into π-allylpalladium chloride is described. Dynamic π-allyl spectra of several π-allylic palladium complexes have been reported in the presence of

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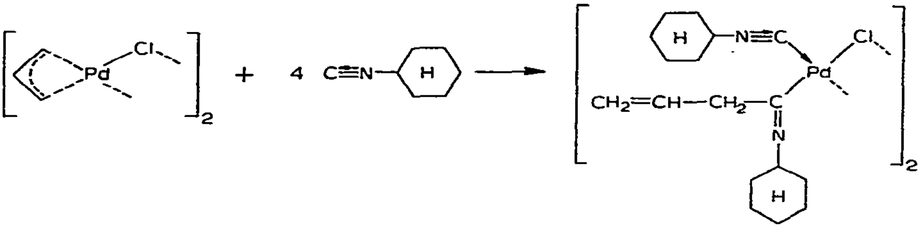
* For Part XL see ref. 1.

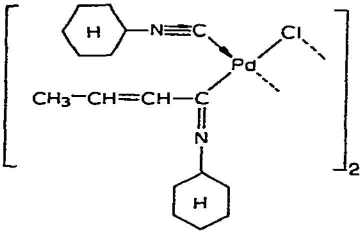
ligands such as $R_3P$, $R_3As$ and dimethyl sulfoxide[3]. By careful addition of cyclohexyl isocyanide into a solution of π-allylpalladium chloride, dynamic π-allyl spectra were observed.

## RESULTS AND DISCUSSION

Cyclohexyl isocyanide was added dropwise to a benzene solution of π-allylpalladium chloride; the yellow solution turned colorless when an equivalent amount of the isocyanide was added. A pale yellow color appeared again when two equivalents were added. Benzene was distilled off and ether was added to the residue. A colorless complex was obtained which had a molecular formula $Pd(C_3H_5)(CNC_6H_{11})_2Cl$ (I). Based on IR and NMR spectra, the following structure, di-μ-chloro-bis[1-(cyclohexylimino)-3-butenyl] bis(cyclohexyl isocyanide)dipalladium, was assigned to the complex. The IR spectrum showed characteristic bands at 2240 $cm^{-1}$ for N≡C and 1580 $cm^{-1}$ for C=N. The presence of a terminal double bond was shown by bands at 3080, 1635, 970 and 915 $cm^{-1}$. When the above ether solution was allowed to stand overnight, another complex (II) was isolated. The IR spectrum of this complex showed a band of a trans double bond at 960 $cm^{-1}$, and the C=N absorption shifted to 1550 $cm^{-1}$ suggesting the conjugation with the double bond. Thus the following structure, di-μ-chloro-bis[1-(cyclohexylimino)-2-butenyl]bis(cyclohexyl isocyanide)-dipalladium, can be assigned for the complex (II), in which the allylic double bond has migrated to the 1-propenyl position. This complex was contaminated by a small amount of the complex (I) and could not be freed from it completely.



(I)



(II)

Apparently the complex (I) was formed by the insertion of cyclohexyl isocyanide. In order to study the mechanism of the insertion reaction, the stepwise addition of cyclohexyl isocyanide, followed by the measurement of NMR spectra, was carried out. The spectra observed are shown in Fig. 1.

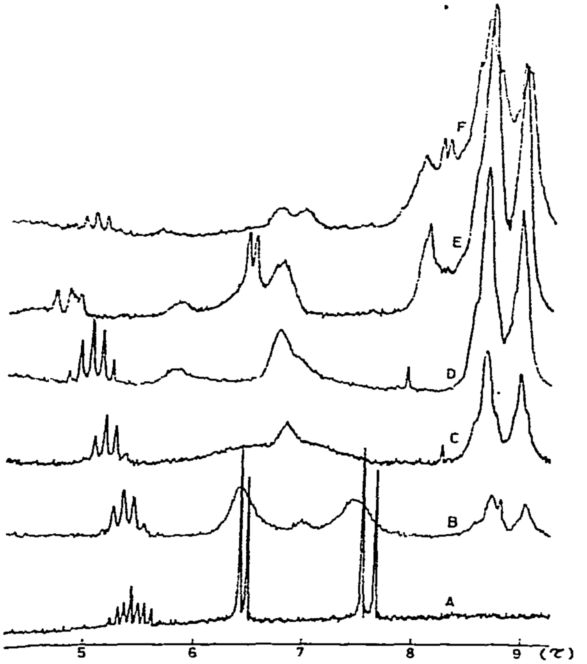
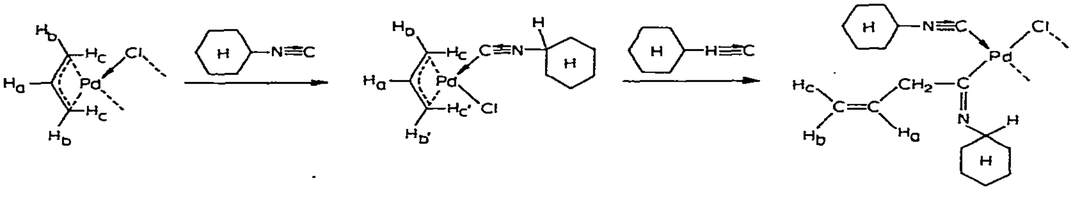


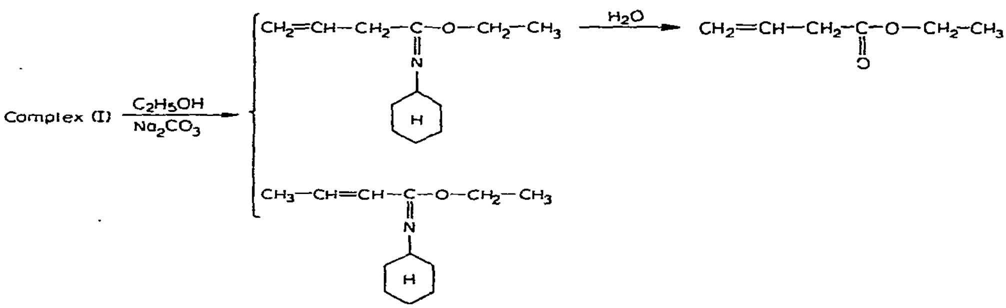
Fig. 1. Changes of NMR spectra during the reaction of $\pi$-allylpalladium chloride with cyclohexyl isocyanide. A: original $\pi$-allylpalladium chloride; B: 0.18 part of the isocyanide added; C: 0.5 part of the isocyanide added; D: one equivalent of the isocyanide added; E: two equivalents of the isocyanide added; F: the solution of E heated up to 40–50°.

In the spectrum B observed after the addition of 0.18 part of the isocyanide, peaks due to $H_b$ and $H_c$ became broader and $H_a$ became a quintet. These changes can be explained in terms of the transformation into the dynamic $\pi$-allyl system proposed by Wilke[4] for the nickel complex. Observations of the dynamic $\pi$-allyl spectra with palladium complexes have been reported in the presence of ligands such as $R_3P$, $R_3As$, $R_3Sb$ and dimethyl sulfoxide[3]. By the addition of 0.5 part of the isocyanide, the peaks due to $H_b$ and $H_c$ were brought close together as shown in the spectrum C. A new peak at $\tau$ 6.68 can be assigned to the $\alpha$-hydrogen of cyclohexyl isocyanide. The spectrum D was observed when one equivalent of the isocyanide was added.

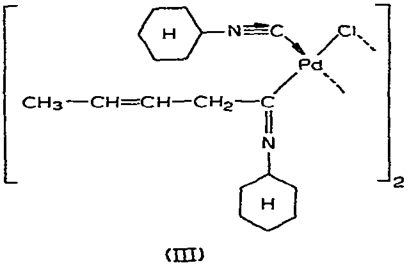


A new peak at $\tau$ 5.84 may be assigned to $H_{b'}$, and the shift of the peak due to $H_a$ to a lower field is noteworthy. The peaks due to $H_b$, $H_c$, and $H_{c'}$ are overlapped with that of the $\alpha$-hydrogen of cyclohexyl isocyanide. When two equivalents of the isocyanide were added, the spectrum E was observed. The $\pi$-allyl system disappeared and a new complex by the isocyanide insertion was formed. A new peak due to the α-hydrogen of the cyclohexylimino group was observed at τ 8.15 and a doublet due to the methylene protons of the allyl group at τ 6.45. The vinyl hydrogens were observed at τ 4.8–5.0. The spectrum of the intermediate complex of the insertion reaction might be contaminated with that of the complex (I). The spectrum F was observed when the above solution was heated to 40–50°. A new doublet at τ 8.3 might be assigned to the methyl protons of the complex (II), though the presence of contaminants interfered with precise analysis.

In order to confirm the structures of the complexes by chemical reaction, ethanolysis of the complex (I) was carried out. The complex was stirred in ethanol in the presence of sodium carbonate at room temperature for one day, during which period black palladium precipitated. From the reaction mixture, a 1/1 mixture of ethyl *N*-cyclohexyl-3-butenimidate and ethyl *N*-cyclohexyl-2-butenimidate was isolated by distillation. This reaction is similar to the ester formation by the reaction of an acyl complex with alcohol, and supports the cyclohexylimine structure. The 2-butenimidate was formed presumably by the ethanolysis of the complex (II), formed by the isomerization of the complex (I). Mild acid hydrolysis of the above mixture gave ethyl 3-butenoate and left the 2-butenimidate intact. Resistance of the latter to the hydrolysis is reasonable. From these results the carbon–carbon bond formation by the isocyanide insertion was definitely proved.



Similarly di-μ-chloro-di-2-butenyldipalladium was treated with the isocyanide and the complex obtained was di-μ-chloro-bis[1-(cyclohexylimino)-3-pentenyl]bis(cyclohexyl isocyanide)dipalladium (III). In this reaction, the isocyanide was inserted into the less substituted side of the π-allyl system. The IR spectrum of the complex (III) showed a strong N=C stretching absorption at 1580 $cm^{-1}$ indicating no conjugation with a double bond and a C–H out-of-plane deformation band of a double bond at 965 $cm^{-1}$ suggesting the absence of a terminal double bond.



(III)

## EXPERIMENTAL

### *NMR spectra*

The 100-MHz spectra were recorded with a Varian HA-100 spectrometer.

### *Reaction of π-allylpalladium chloride with cyclohexyl isocyanide*

π-Allyl complex (0.914 g, 0.0025 mol) was dissolved in benzene (50 ml) and cyclohexyl isocyanide (1.90 g, 0.01 ml) was added with stirring. After 30 min benzene was evaporated and viscous yellow liquid was obtained, which was triturated with ether to give colorless solid. Recrystallization from benzene gave colorless crystals (I) (0.55 g), m.p. 126°. (Found: C, 50.95; H, 6.81; Cl, 8.88; N, 7.04; ash, 26.4. $C_{17}H_{27}ClN_2Pd$ calcd.: C, 50.89; H, 6.78; Cl, 8.84; N, 6.98; ash, 26.52%.) IR (KBr); 2950 s, 2870 s, 2240 s, 1635 w, 1580 s, 1450 m, 1420 m, 1365 w, 1320 w, 1260 w, 1210 w, 1150 w, 1120 w, 1070 w, 1040 w, 1025 w, 1000 w, 970 m, 915 m, 890 w, 845 w, and 800 w.

The ether solution was concentrated to 5 ml and left overnight. Colorless precipitate (0.8 g) was obtained, which was found to be a mixture of the complex (II) and a small amount of the complex (I). (Found: C, 50.83; H, 6.69; Cl, 8.96; N, 7.13; ash, 26.3. $C_{17}H_{27}ClN_2Pd$ calcd.: C, 50.89; H, 6.78; Cl, 8.84; N, 6.98; ash, 26.52%.) IR (KBr): 1550 s, and 960 m.

### *Ethanolysis of the complex (I)*

The complex (2.0 g), sodium carbonate (5.0 g) and ethanol (20 ml) were mixed in a 50 ml flask and stirred magnetically for one day. After filtration, the filtrate was distilled to give a 1/1 mixture (0.7 g) of ethyl *N*-cyclohexyl-3-butenimidate and ethyl *N*-cyclohexyl-2-butenimidate at 60–65°/1 mm. The above mixture was warmed with dil. HCl for a short time and then neutralized with ammonia. The gas chromatography showed the presence of ethyl 3-butenoate and the 2-butenimidate was recovered from the mixture. The NMR spectrum ($CDCl_3$, 100 Mc) of the 2-butenimidate showed a triplet at $\tau$ 8.73 (3 H, $CH_3{-}CH_2{-}$, $J$ 6.6 Hz), a multiplet at $\tau$ 8.15 (3 H, $CH_3{-}CH{=}$), broad multiplets at $\tau$ 8.1–8.7 (10 H, methylene protons of cyclohexyl group), a broad singlet at $\tau$ 6.67 (1 H, N–CH–), a quartet at $\tau$ 5.94 (2 H, $-CH_2{-}CH_3$, $J$ 7.4 Hz), a doublet at $\tau$ 3.91 (1 H, $CH_3{-}CH{-}$, $J$ 15.3 Hz) and a multiplet at $\tau$ 3.44 (1 H, $CH_3{-}CH{=}$). The mass spectrum showed *m/e* 195 (calcd. 195.3). The NMR spectrum of the 3-butenimidate showed a triplet at $\tau$ 8.78 (3 H, $CH_3{-}$, $J$ 6.6 Hz), broad multiplets, at $\tau$ 8.1–8.7 (10 H, methylene protons of cyclohexyl group), multiplet at $\tau$ 7.02 (2 H, $CH_2{-}C{=}N$), a broad singlet at $\tau$ 6.8 (1 H, N–CH), a quartet at $\tau$ 5.97 (2 H, $-CH_2{-}CH_3$), a pair of doublets at $\tau$ 4.96 and 4.92 (2 H, terminal protons of a double bond, $|J_{cis}|$ 11 Hz, $|J_{trans}|$ 16 Hz) and a multiplet (1 H, $CH_2{=}CH{-}$) at $\tau$ 6.56.

### *Reaction of di-μ-chloro-di-2-butenyldipalladium and cyclohexyl isocyanide*

The complex (0.7 g) was treated with the isocyanide (0.73 g) as above and an air stable complex was isolated (0.8 g). (Found: C, 52.09; H, 6.96; Cl, 8.58; ash, 25.8. $C_{18}H_{29}ClN_2Pd$ calcd.: C, 52.06; H, 7.04; Cl, 8.54; N, 6.75; ash, 25.62%.) IR (KBr): 2950 s, 2870s, 2240s, 1580 s, 1450 m, 1370 w, 1320 w, 1260 w, 1195 w, 1160 w, 1115 w, 1070 w, 1040 w, 1025 w, 965 m, 930 w, 895 w, 865 w, 845 w, and 805 w.

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