# ORGANOPALLADIUM(II) COMPLEXES CONTAINING CARBON-BONDED PYRIDINE AND PICOLINE AS A LIGAND: PREPARATION, STRUCTURES, AND REACTIONS

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Oxidative addition reactions of monohalopyridines, 2,6-dichloropyridine, 2-chloropyrazine, and 2-chlorobenzothiazole as well as 2- and 3-chloromethylpyridines with tetrakis(triphenylphosphine)palladium(0) gave $[PdX(R)(PPh_3)]_2$ or $[PdX(R)(PPh_3)_2]$ depending on the nature of the carbon-bonded heterocycles R. Most of these novel organopalladium(II) complexes were characterized by the analytical, molecular-weight, and IR data together with the $^1H$ and $^{13}C$ NMR spectroscopy. The molecular structures of some pyridyl and picolyl complexes were determined by X-ray analysis to reveal the novel C,N-bridging modes of the 2-pyridyl and 2-picolyl ligands. Reactions of these complexes with carbon monoxide and other reagents were examined. The pyridyl complexes catalyze the cross coupling reactions between halopyridines and methylmagnesium bromide.

Palladium complexes are frequently used as catalysts for producing carbon-carbon bonds.[1] In these reactions organopalladium(II) species must be involved as important intermediates. In fact a number of organopalladium compounds containing σ-carbon-bonded alkyl, aryl, aralkyl, and vinyl ligands have been prepared[2] and their reactions with carbon monoxide,[3] carbon dioxide,[4] olefins,[1d] acetylenes,[5] and isocyanides[6] have been investigated. Furthermore, trans-iodo(phenyl)bis(triphenylphosphine)palladium(II)[7] was found to catalyze cross coupling between aryl halides and Grignard reagents[8] and cyanation of aryl iodides with potassium cyanide.[9] However, no organopalladium(II) complexes containing σ-carbon-bonded heterocycles as a ligand have been prepared as yet, although some complexes of the carbon-bonded pyridyl ligands with cobalt,[10] gold,[11] titanium,[12] nickel,[13] and a few other metals[14] and some picolyl complexes of Cr,[15] Co,[16] and other metals such as Mn, Fe, Mo, and W[17] have been reported. This article describes preparation, characterization, and reactions of some palladium(II) complexes containing carbon-bonded pyridine and picoline. The carbon-bonded complexes of pyrazine and benzothiazole are also mentioned.

*Preparation and Characterization of the 2-Pyridyl, 2-Pyrazinyl, and 2-Benzothiazolyl Complexes*. The reactions of tetrakis(triphenylphosphine)palladium(0), [Pd-$(PPh_3)_4$] (1), with excess 2-halopyridines and 2-chloropyrazine in toluene at 90 °C gave $[PdCl(C_5H_4N\text{-}\underline{C}^2)PPh_3]_2$ (2a), $[PdBr(C_5H_4N\text{-}\underline{C}^2)PPh_3]_2$ (2b), and $[PdCl(C_4H_3N_2\text{-}\underline{C}^2)\text{-}PPh_3]_2$ (5) in 65, 55, and 79% yields, respectively. On the other hand, similar reactions of 1 with 2,6-dichloropyridine and 2-chlorobenzothiazole afforded trans-$[PdCl(C_5H_3(6\text{-}Cl)N\text{-}\underline{C}^2)(PPh_3)_2]$ (2e) and trans-$[PdCl(C_7H_4SN\text{-}\underline{C}^2)(PPh_3)_2]$ (6) in 95 and 80% yields, respectively. Elemental analysis and molecular-weight data determined by the vapor pressure osmometry in dichloromethane at 25 °C indicate that complexes 2a, 2b, and 5 are dinuclear, while 2e and 6 are mononuclear.

The dinuclear structure with bridging halide anions is quite common among palladium(II) complexes[18] and is usually subject to cleavage by donor ligands to give mononuclear species. However, complexes 2a and 2b are very stable and do not react with excess bases such as triphenylphosphine, pyridine, and thiourea. X-ray analysis of 2b disclosed that the 2-pyridyl ligand is bridging two palladium atoms.[19] Important bond lengths (in Å) and angles (in degree) are shown in Fig.1. The Pd-$(C_5H_4N)_2$-Pd part is folded along the Pd---Pd line to give a six-membered boat-form ring. The dihedral angle between the pyridyl planes is 82° and that between the coordination planes is 79°. This is the first example of the pyridyl-bridged dinuclear complex fully characterized by X-ray analysis, although a similar bridged trinuclear structure was presumed for 2-pyridylgold(I)[11] merely to accord with the coordination number 2 of gold(I). Complex 2a and $[PdI(C_5H_4N\text{-}\underline{C}^2)\text{-}PPh_3]_2$ (2c) derived from 2a by halide replacement seem to have the same structure

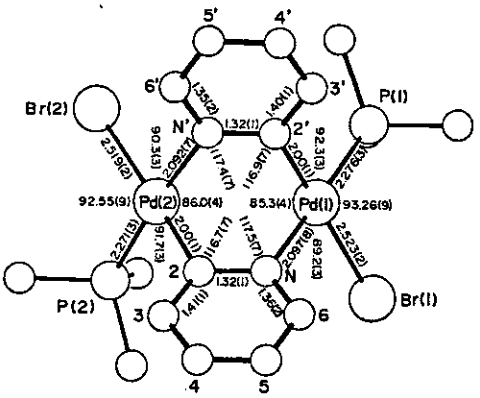


Fig. 1. Molecular structure of trans-(P,N)-$[PdBr(C_5H_4N\text{-}\underline{C}^2)PPh_3]_2$ (2b) viewed perpendicularly to the plane C(2), N, C(2'), and N'.

as 2b, since their IR and $^1$H NMR spectra are very similar to each other except the characteristic ν(Pd-X) bands, the ν(Pd-Cl) : ν(Pd-Br) : ν(Pd-I) ratio giving a reasonable value of 1:0.75:0.55. Exact molecular structure of 5 has not been determined, but the 2-pyrazinyl ligand might also be bridging palladium atoms.

Ligand Substitution Reactions of the 2-Pyridyl Complexes. Complex 2e seems to liberate a minute amount of triphenylphosphine in dichloromethane to give rise to the dinuclear complex 2f.

$$\underset{\textstyle 2e}{2[\mathrm{PdCl(C_5H_3(6\text{-}Cl)N\text{-}\underline{C}^2)(PPh_3)_2}]} \rightleftharpoons \underset{\textstyle 2f}{[\mathrm{PdCl(C_5H_3(6\text{-}Cl)N\text{-}\underline{C}^2)PPh_3}]_2} + 2\mathrm{PPh_3} \qquad (1)$$

The equilibrium is favorable for 2e, but is completely shifted to right by oxidation of the freed phosphine to afford 2f conveniently. Reaction 1 is readily reversed by addition of $PPh_3$. Replacement of $PPh_3$ with more basic $PEt_3$ and $PMe_2Ph$ gave trans-[$\mathrm{PdCl(C_5H_3(6\text{-}Cl)N\text{-}\underline{C}^2)L_2}$] (L = $PEt_3$ and $PMe_2Ph$), respectively, of which the trans structure was confirmed by $^1$H NMR spectroscopy. The chloride ligand in 2a, 2e, and 2f was easily replaced by pseudohalides, $N_3^-$, $NCO^-$, $NCS^-$, and $NCSe^-$ as well as other weak ligands such as $ClO_4^-$, $BF_4^-$, and $PF_6^-$.

Comparative Studies of the 2-, 3-, and 4-Pyridyl Complexes. Although the 2-pyridylnickel(II) complexes [$\mathrm{NiX(C_5H_4N\text{-}\underline{C}^2)PPh_3}$]$_2$ (X = halide and pseudohalide ligands) are quite stable, the corresponding 3-pyridyl complex (X = Cl) is less stable and the 4-pyridyl complex has not been prepared.[13] On the contrary, the reactions of 1 with 3- and 4-bromopyridines in toluene at 90 °C gave trans-[$\mathrm{PdBr(C_5H_4N\text{-}\underline{C}^3)(PPh_3)_2}$] (3b) and trans-[$\mathrm{PdBr(C_5H_4N\text{-}\underline{C}^4)(PPh_3)_2}$] (4b) in 90 and 73% yields, respectively. The corresponding chloro- (3a and 4a) and iodo- (3c and 4c) complexes were also prepared by substitution reactions of 3b and 4b with sodium chloride and iodide, respectively, in a mixture of dichloromethane and methanol. The reactions of 2b, 3b, and 4b with excess triethylphosphine in diethyl ether at room temperature gave a set of linkage isomers, trans-[$\mathrm{PdBr(C_5H_4N\text{-}\underline{C}^2}$, -$\underline{C}^3$, and -$\mathrm{\underline{C}^4)(PEt_3)_2}$] (2d, 3d, and 4d) in 30, 65, and 75% yields, respectively.

Analytical and molecular-weight data together with $^1$H NMR spectra indicate that complexes 2d-4d are mononuclear and have the trans structure, the thermal stability decreasing in the sequence 2d > 4d > 3d. Table 1 lists the $^{13}$C NMR data from these complexes together with those from free pyridine[20] for comparison. The methyl and methylene carbons of triethylphosphine resonate at about 8 and 15 ppm, respectively, and the latter $^{13}C\{^1H\}$ signal from each complex appears as a 1:2:1 triplet in accordance with the proposed trans structure. Compared with the $^{13}$C

Table 1. $^{13}C$ Chemical Shifts δ (ppm from External $Me_4Si$) and Coupling Constants J (Hz) in $CDCl_3$

| Complex | | Pyridine ring carbons | | | | | $CH_2$ | $CH_3$ |
|---|---|---|---|---|---|---|---|---|
| | | $C^2$ | $C^3$ | $C^4$ | $C^5$ | $C^6$ | | |
| <u>1d</u> | δ | 179.7 | 133.3 | 132.5 | 117.5 | 149.1 | 14.9 | 8.1 |
| | $^1J$(C-H) | | 163.2 | 161.8 | 163.2 | 176.5 | 129.4 | 129.4 |
| | J(C-P) | 6.0 | 7.3 | | | | 13.0 | |
| <u>2d</u> | δ | 155.3 | 150.8 | 144.0 | 123.9 | 143.7 | 15.0 | 8.1 |
| | $^1J$(C-H) | 177.2 | | 160.3 | 161.0 | 179.4 | 133.8 | 128.0 |
| | J(C-P) | 3.7 | 6.1 | 2.4 | | | 13.4 | |
| <u>3d</u> | δ | 146.8 | 133.8 | 170.8 | 133.8 | 146.8 | 14.8 | 8.0 |
| | $^1J$(C-H) | 175.0 | 160.3 | | 160.3 | 175.0 | 133.8 | 128.0 |
| | J(C-P) | | 3.7 | 5.9 | 3.7 | | 13.5 | |
| py[a)] | δ | 149.7 | 123.6 | 135.5 | 123.6 | 149.7 | | |
| | $^1J$(C-H) | 170.0 | 163.0 | 152.0 | 163.0 | 170.0 | | |

a) Data for uncoordinated pyridine from ref. 20.

shieldings for uncoordinated pyridine carbons,[20] ring carbons in <u>2d</u>, <u>3d</u>, and <u>4d</u> show the following tendency. (i) The carbon atom bonded to palladium shows a very large downfield shift of ca. 30 ppm. (ii) Carbon atoms adjacent to the quaternary carbon also show downfield shifts by 6-10 ppm, appearing as triplets due to coupling to $^{31}P$ as does the metal-bonded carbon. (iii) Carbons at the meta position of the quaternary carbon suffer the least effect on coordination, showing upfield shift by less than 3 ppm. (iv) Carbons at the para position of the quaternary carbon also experience upfield shift by ca. 6 ppm.

In order to investigate the nature of the Pd-C bonds in these complexes and charge densities at the pyridine-ring carbons which are to be related with $^{13}C$ shieldings, the MO calculations of the model compounds trans-[PdCl($C_5H_4N$-$\underline{C}^2$, -$\underline{C}^3$, and -$\underline{C}^4$)$(PH_3)_2$] were carried out based on the CNDO/2 method.[21] As is seen in Fig. 2, the plot of observed $^{13}C$ shieldings for ring carbons of <u>2d</u>-<u>4d</u> and pyridine against the calculated charge densities gave two straight lines, one for the carbon atoms bonded to palladium and the other for other carbons. The specific behavior of the quaternary carbons might be caused by the contribution of dσ orbitals to the Pd-C bond. The calculated bond orders associated with the Pd-C bonds indicate that the contribution of σ-donation to the Pd-C bond is in the order 2d > 3d ∿ 4d, while that of π-back donation lies in the sequence 2d ∿ 4d > 3d. Therefore the overall strength of the Pd-C bond is expected to be in the order 2d > 4d > 3d in accordance with the sequence of thermal stability.

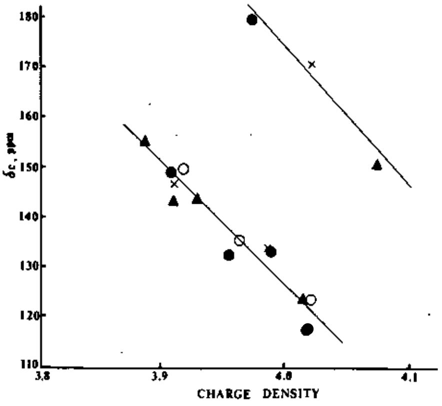


Fig. 2. Observed $^{13}$C shieldings for uncoordinated pyridine (○), complexes 2d (●), 3d (▲), and 4d (×) vs. the calculated charge densities, the upper straight line referring to the quaternary carbons bonded to palladium and the lower one to the other ring carbons.

Basicities of complexes 2d-4d were determined by titration with perchloric acid in dioxane-water (1:1 by volume) at 25 °C and $\mu = 0.1(NaClO_4)$, and the $pK_a$ values for the conjugate acids of 2d and 3d were determined to be 8.04 and 5.47, respectively. Basicity of 2d is astonishingly stronger than that of uncoordinated pyridine ($pK_a = 4.47$). Solubility of 4d is not sufficient in the presence of added sodium perchlorate to give an accurate $pK_a$ value. For the sake of comparison, acid titration was carried out in the same solvent in the absence of sodium perchlorate and the $pK_a$ values obtained were 7.44, 5.01, and 5.38 for 2d, 3d, and 4d, respectively. The order of basicity, 2d > 4d > 3d, coincides with that of the Pd-C bond strength. The remarkably enhanced basicity of the 2-pyridyl ligand must be the cause of stabilizing the dinuclear complexes.

X-Ray crystallographic studies performed with the aim of comparing the molecular structures of 2d-4d showed no serious difference among them.[21] Table 2 lists bond distances and bond angles around palladium. The only significant difference in the bond lengths appears as the longer Pd-Br distance in 4d than those in 2d and 3d, although a reasonable rationalization is difficult. The substituents of the phosphorus atoms are staggered about the P-Pd-P sequence in 2d, whereas they are almost eclipsed in 3d and 4d.

Preparation and Characterization of the Picolyl Complexes. As an extension of our studies on the pyridylpalladium(II) complexes, the reactions of 2-, 3-, and 4-chloromethylpyridines with $[Pd(PPh_3)_4]$ were examined in toluene at 100 °C. The

Table 2. Some Results of Structure Analyses Including Bond Distances (Å) and Bond Angles (degree) around Pd with Esd's in Parentheses

| | 2d | 3d | 4d |
|---|---|---|---|
| Crystal system | triclinic | monoclinic | orthorhombic |
| Space group | $P\bar{1}$ | $P2_1/c$ | $Pn2_1a$ |
| Bond distances | | | |
| Pd-C | 1.993(6) | 1.998(6) | 2.030(17) |
| Pd-Br | 2.524(1) | 2.522(1) | 2.563(3) |
| Pd-P | 2.313(3) | 2.322(2) | 2.328(5) |
| | 2.314(2) | 2.323(2) | 2.325(4) |
| Bond angles | | | |
| P-Pd-P | 175.88(8) | 176.71(7) | 171.1(2) |
| Br-Pd-C | 178.2(2) | 178.2(2) | 178.1(5) |
| P-Pd-Br | 88.36(6) | 89.77(5) | 89.0(2) |
| | 95.55(6) | 90.37(5) | 92.8(1) |
| P-Pd-C | 89.9(2) | 90.1(1) | 89.8(5) |
| | 86.2(2) | 89.8(2) | 88.6(5) |

2- and 3-picolyl complexes were obtained in 73 and 15% yields, respectively, but insufficient stability and solubility prevented full characterization of the latter complex. The 4-picolyl complex was not even isolated. Thus stability of the picolylpalladium(II) complexes varies remarkably with the site of substitution on the ring.

The analytical and molecular-weight data indicate that $[PdCl(C_5H_4N\text{-}2\text{-}CH_2)PPh_3]_2$ (7) and $[PdX(C_5H_4N\text{-}2\text{-}CH_2)L]_2$ (X = Br and I for L = $PPh_3$; X = Cl for L = $PMePh_2$ and $PMe_2Ph$) derived from 7 by ligand substitution reactions are all dinuclear, whereas trans-$[PdCl(C_5H_4N\text{-}2\text{-}CH_2)L_2]$ (L = $PMe_2Ph$ and $PEt_3$) which were obtained by bridge cleavage of 7 with excess L are mononuclear. The molecular structure of 7 shown in Fig. 3 was determined by X-ray analysis.[22] The picolyl ligands span the two palladium atoms to form a boat-like eight-membered ring with dihedral angles of 34° between the pyridine-ring planes, 63° between the coordination planes, and 85° between the pyridine-ring and the coordination plane.

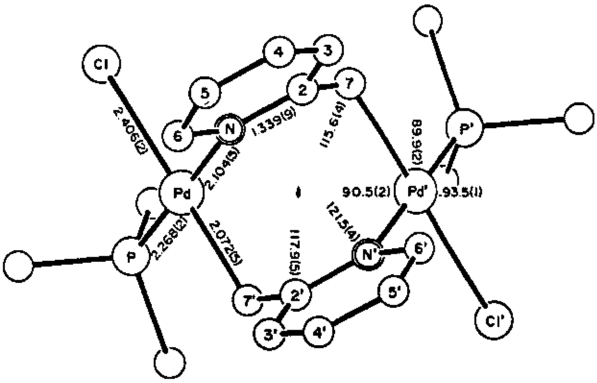
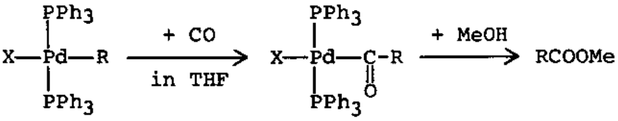


Fig. 3. Stereochemistry of trans(P,N)-[$PdCl(C_5H_4N\text{-}2\text{-}CH_2)PPh_3]_2$ (7) viewed along the crystallographic two-fold axis. The atoms with and without a prime are related to each other by the axis.

The methylene protons of the picolyl ligand in 7 are not magnetically equivalent, but exhibit two separate signals at 2.44 and 3.81 ppm as a triplet and a doublet, respectively. Double irradiation experiments indicated that these protons couple to each other with the geminal coupling constant of 9 Hz. The $^{31}P$ NMR spectroscopy confirmed the coupling of one of the methylene protons to $^{31}P$, $^{3}J(P\text{-}H)$ being 9 Hz, accidentally equal to the $J_{gem}$ value. The methylene carbon resonates at 28.47 ppm, appearing as a triplet of doublets under the off-resonance conditions. The small value of $^{2}J(P\text{-}C)$ as ca. 7 Hz conforms with the mutually cis arrangement of the methylene and phosphine ligands.

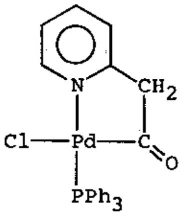
Reactions of the Pyridyl and Picolyl Ligands Coordinated to Palladium. Mononuclear complexes 2e, 3b, and 4b readily reacted with bubbling carbon monoxide in THF at room temperature to afford the pyridinecarbonyl complexes in 73, 80, and 81% yields, respectively, which are presumed to maintain the trans structure since single sharp ν(Pd-P) bands are observed at 312, 312, and 322 $cm^{-1}$, respectively. The acyl complexes reacted with methanol easily in the absence of a base to liberate methyl pyridinecarboxylates.



$$X\text{—}\underset{PPh_3}{\overset{PPh_3}{Pd}}\text{—}R \xrightarrow[\text{in THF}]{+\ CO} X\text{—}\underset{PPh_3}{\overset{PPh_3}{Pd}}\text{—}\underset{O}{\overset{}{\underset{\|}{C}}}\text{-}R \xrightarrow{+\ MeOH} RCOOMe$$

where R = $C_5H_3(6\text{-}Cl)N\text{-}\underline{C}^2$, $C_5H_4N\text{-}\underline{C}^3$, and $C_5H_4N\text{-}\underline{C}^4$

For example, methyl 6-chloropicolinate was obtained in a 60% yield by methanolysis of the CO-insertion product of 2e. These reactions may be useful in organic synthesis, since one carbon unit can be easily added to any carbon of pyridine. It should be noted that only the mononuclear pyridyl complexes containing triphenylphosphine as ancillary ligands react with carbon monoxide, and the dinuclear complexes do not. The palladium-carbon bond in the latter complexes may be strengthened synergically by bridging of the pyridyl ligand to another metal atom through nitrogen. Mononuclear bis(triethylphosphine) complexes do not react with carbon monoxide either. Triethylphosphine is a better $\sigma$ donor than triphenylphosphine, strengthening the Pd-C bond to prevent CO insertion.



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2-Picolyl complex 7 also reacted with carbon monoxide in THF at room temperature to afford $PdCl(C_5H_4(2\text{-}CH_2CO)N\text{-}C,N)PPh_3$ (8) in a 47% yield, which gives satisfactory analysis and molecular weight as a mononuclear complex. Now the methylene protons resonate at 4.11 ppm as a sharp singlet in accordance with the proposed structure in which the pyridine ring lies on the coordination plane and the methylene protons experience equal magnetic environment. The $\nu$(Pd-Cl) frequency of 8 (292 $cm^{-1}$) is as low as that observed for 7 (284 $cm^{-1}$), indicating that the chloride lies on the position trans to a strong ligand. Similarly the $\nu$(Pd-P) frequency (427 $cm^{-1}$) is comparable to that for 7 (420 $cm^{-1}$) and is much higher than those observed for complexes which contain mutually trans phosphines ($\sim$310 $cm^{-1}$), showing that $PPh_3$ in 8 occupies the site trans to a weak ligand. The above structure is well reconciled with these IR data. Complex 8 reacts with sodium methoxide in methanol to afford methyl pyridine-2-acetate, of which an isomer, 2-picolyl acetate was obtained by the reaction of 7 with silver acetate in benzene.

*Cross Coupling Reactions*. Although $[NiCl(C_5H_4N\text{-}C^2)PPh_3]_2$ selectively catalyzes the cross coupling of 2-chloropyridine with methylmagnesium bromide in THF at room temperature,[13] refluxing temperature is needed for the palladium(II) complex (2a) to act as a catalyst in THF, and the yield of 2-methylpyridine was as low as 13% when 1/100 molar amount of 2a was added to 2-chloropyridine. Complex 2f is more effective as a catalyst for the reaction of 2,6-dichloropyridine with methylmagnesium bromide in refluxing THF to give 2-methyl-6-chloropyridine in a 58% yield, reflecting lability of 2f compared with 2a. In the presence of excess triphenylphosphine to prevent transformation of 2e to 2f, the mononuclear complex 2e similarly attains a 53% yield of the same product. On the other hand, the yield of 2,6-dimethylpyridine from 2,6-dichloropyridine was only 4% in the case of 2f and was negligibly small when 2e was employed, although the nickel(II) catalyst was reported to promote the Grignard coupling of organo dihalides at both the reaction sites.[23] It is worth noting that the palladium(II) catalysts are less active but more selective than the nickel(II) complexes for the synthesis of 2-methyl-6-chloropyridine.

Acknowledgment. This work was performed as a part of the Special Research Project, "Chemical Research in Development and Utilization of Nitrogen-Organic Resources." The authors are grateful to the Ministry of Education, Science, and Culture for the financial support and also to Professor Yoshio Ban of the Hokkaido University, organizer of the Project.

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Received, 1st May, 1981